SYNTHESIS OF HIGH TECHNOLOGY COLORANTS

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BY
MUHAMMAD SHAHID

RESEARCH SUPERVISOR
PROF. DR. MUNAWAR ALI MUNWAR

INSTITUTE OF CHEMISTRY
UNIVERSITY OF THE PUNJAB LAHORE PAKISTAN

January 2012
to my beloved mom& dad…
for supporting me throughout my life
especially during this study
and a special thank to my wife…
for waiting all this while.
DECLARATION

I declare that this thesis entitled “SYNTHESIS OF HIGH TECHNOLOGY COLORANTS” is the result of my own research work except as cited in references. The thesis has not been accepted for any degree and is not currently submitted in the candidature of any other degree.

MUHAMMAD SHAHID
CERTIFICATE

This is to certify that research work described in this thesis entitled "SYNTHESIS OF HIGH TECHNOLOGY COLORANTS" is the original work of Muhammad Shahid. We have personally gone through all the data/results/materials reported in this manuscript and certify to their correctness/authenticity. We further certify that the material included in this thesis has not been used in part or full for any manuscript already submitted or in process of submission in partial/complete fulfillment of the award of any other degree from any other institution. We also certify that Mr Muhammad Shahid has fulfill all the conditions and is qualify to submit the thesis in regard to the degree of philosophy in chemistry.

In our opinion this thesis is sufficient in terms of scope and quality for the award of degree of philosophy in chemistry.

Signature: ……………………………………………
Name of Supervisor: Dr. Munawar Ali Munawar
: Professor of Organic Chemistry
Date: ……………………………………………

Signature: ……………………………………………
Name of Co-Supervisor: Prof. Dr. Jamil Anwar Ch.
Date: ……………………………………………
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ABSTRACT

Phthalocynines and perylenes constitute an important group of industrial dyes with broad ranging activities. The research work reported in the thesis comprises three parts. First part comprised of the synthesis of various substituted phthalocyanines and in the second part perylene based dyes were synthesized. In part three, the potential of the selected synthesized compounds for applications in organic electronics was demonstrated.

In order to synthesize phthalocynine dyes various precursors including 4-[[6-hydroxyhexylamino)methyl]phthalonitrile,(130) 4-[[2-dioxo-9,10-dihydroanthracen-2-ylamino)methyl]phthalonitrile,(131) 4-[[1-[(4-nitrophenyl)diazenyl]naphthalen-2-yl oxy)methyl]phthalonitrile,(132) 4-[[4-[(4-nitrophenyl)diazenyl]naphthalen-1-yl oxy)methyl]phthalonitrile,(133) 4-(pyrrolidin-1-yl)phthalonitrile, (126) 4-(piperidin-1-yl)phthalonitrile (127) and 4-(azepan-1-yl)phthalonitrile (128) were prepared. These precursors were then cyclotetramerized by refluxing in the presence of metal chlorides (where required) in nitrobenzene to obtain substituted metallated and non metallated phthalocyanines (152-169, 189-196) (Scheme-I).
2(3),9(10),16(17),23(24)-Tetra(chlorosulfonyl)phthalocyanines (170) were prepared from the chlorosulfonylation of unsubstituted phthalocyanines. The tetra(chlorosulfonyl)phthalocyanines (170) were then hydrolyzed to obtain 2(3),9(10),16(17),23(24)-tetrasulfophthalocyanines (146-151). 2(3),9(10),16(17),23(24)-Tetra(octylaminosulfonyl)-, (171-182) 2(3),9(10),16(17),23(24)-tetra(6-hydroxyhexylaminosulfonyl)- (183-188) and 2(3),9(10),16(17),23(24)-tetra(p-sulfophenylaminosulfonyl)phthalocyanines (171-176) (metallated and metal free) were prepared by reacting the tetrachlorosulfonylphthalocyanines with aminooctane, 6-aminohexanol and 4-amniobenzenesulfonic acid respectively (Scheme-II).
Scheme II

In the second phase few alkylated perylene diimides were synthesized from perylene-3,4,9,10-tetracarboxylic acid dianhydride (Scheme-III) to study their applications in organic electronics. Aggregational behavior of non-alkylated and alkylated perylene dyes.
All precursors (Phthalonitriles) were characterized by IR, NMR, Mass and elemental analysis while structure final products were established by UV/Vis, IR, Mass and elemental analysis.

In phase three of this research, investigation of the selected synthesized organic semiconducting materials for potential applications in organic electronics was undertaken. In this thesis, fabrication and characterization of Au/K₄NiPTS/Ag, Au/K₄NiPTS/Au and N-BuPMIMA/p-Si surface type Schottky barrier diode, surface type capacitive humidity sensor and heterojunction, respectively, is reported.

Current-voltage (I-V) characteristics of the Au/K₄NiPTS/Ag Schottky diode are studied. The device has shown rectification behavior. Interpretation of the charge transportation in K₄NiPTS is provided. From the I-V curves the diode parameters are extracted. This has successfully demonstrated the potential of the synthesized organic semiconductor reported in this thesis for a wide range of Schottky diode based electronic and photonic devices of current industrial importance. Effect of relative humidity on the capacitance of the surface-type Au/K₄NiPTS/Au sensor is investigated. It is observed that the capacitance of the
sensor increases with the rise in humidity level. Humidity dependent capacitance properties of this sensor make it attractive for use in humidity sensors. Current-voltage (I-V) characteristics of the N-BuPMIMA/p-Si heterojunction are studied. The device has shown rectification behavior. Interpretation of the charge transport through N-BuPMIMA is provided.

Further work on the fabrication of a number of organic electronic devices including Schottky diodes, heterojunctions, sensors and organic field effect transistors using the synthesized organic semiconducting materials reported in this thesis, is in progress.
### List of Selected Symbols / Abbreviations / Notation / Terminology

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>degrees Celcius</td>
</tr>
<tr>
<td>BASF</td>
<td>Baden Aniline and Soda Factory</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-Diazabicyclo[5.4.0]undec-7-ene</td>
</tr>
<tr>
<td>DMAE</td>
<td>Dimethylethanolamine</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethoxyethane</td>
</tr>
<tr>
<td>DMF</td>
<td><em>N</em>,<em>N</em>-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide-\textit{d6}</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye sensitized solar cell</td>
</tr>
<tr>
<td>DTMP</td>
<td>Deuterated tetramethylpiperidine</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transformed infra red</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared (Spectroscopy)</td>
</tr>
<tr>
<td>LiTMP</td>
<td>Lithium tetramethylpiperidine</td>
</tr>
<tr>
<td>mmol</td>
<td>milli moles (10^{-3} moles)</td>
</tr>
<tr>
<td>MP</td>
<td>melting point</td>
</tr>
<tr>
<td>MPLC</td>
<td>Medium-Performance Liquid Chromatography</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>OFETs</td>
<td>Organic field-effect transistor</td>
</tr>
<tr>
<td>PC</td>
<td>Phthalocyanine</td>
</tr>
<tr>
<td>PCT</td>
<td>Photoinduced charge transfer</td>
</tr>
<tr>
<td>PDI</td>
<td>perylenediimide</td>
</tr>
<tr>
<td>PDT</td>
<td>Photodynamic therapy</td>
</tr>
<tr>
<td>PET</td>
<td>Photoinduced electron transfer</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million (NMR)</td>
</tr>
<tr>
<td>PTCDA</td>
<td>Perylene tetracarboxylic acid dianhydride</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimmetric Analysis</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS

1- Introduction: ................................................................................................................. 1

1.1 High Technology Colorants ...................................................................................... 1

1.1.1 Dyes for Solar Cells: ......................................................................................... 1

1.1.2 Dyes for optical data storage: ............................................................................. 6

1.1.3 Dyes for PDT: ................................................................................................... 8

1.1.4 Dyes for Fluorescent Sensors: ........................................................................... 12

1.2 Phthalocyanines ....................................................................................................... 16

1.2.1 Alkylated and arylated phthalocyanines .......................................................... 19

1.2.1.1 Tetrasubstituted phthalocyanines .............................................................. 19

1.2.1.2 Octa-substituted Phthalocyanines ............................................................ 23

1.2.1.3 Hexadecasubstituted phthalocyanines ...................................................... 28

1.2.2 Alkenyl and alkynyl substituted phthalocyanine ............................................ 29

1.2.3 Silylated phthalocyanines ................................................................................. 31

1.2.4 Heteromethyl substituted Phthalocyanines .................................................... 32

1.2.5 Halogen substituted phthalocyanines ............................................................. 34

1.2.5.1 Chlorinated phthalocyanines ..................................................................... 35

1.2.5.2 Brominated phthalocyanines ..................................................................... 36

1.2.5.3 Iodinated phthalocyanines ........................................................................ 36

1.2.6 Haloalkylated Phthalocyanines ........................................................................ 37

1.2.6.1 Trifluoromethylsulfanyl and trifluoromethylsulfonyl substituted phthalocyanines ................................................................................................................. 38

1.2.6.2 Fluoroalkoxyphthalocyanines .................................................................... 38

1.2.7 Nitrophthalocyanines ......................................................................................... 40

1.2.8 Sulfophthalocyanines and their derivatives .................................................... 42

1.2.8.1 Alkyl- and Arylsulfonyl and -sulfinylphthalocyanines ......................... 44

1.2.9 Carboxyphthalocyanines and their derivatives .............................................. 45

1.2.10 Phosphophthalocyanines and their derivatives ............................................ 49

1.2.11 Aminophthalocyanines ................................................................................... 50

1.2.12 Hydroxy, alkoxy and aryloxyphthalocyanines ............................................ 52
1.2.13 Alkylsulfanyl- and Arylsulfanylphthalocyanines ...................................... 54
1.3 Perylene-3,4,9,10-tetracarboxylic dianhydride ........................................ 54
1.3.1 Redox properties ......................................................................................... 67
1.3.2 Solid State Structure and Self –Assembly .................................................. 68
1.3.3 Photo-Induced Electron Transfer ................................................................. 68
1.3.4 PDIs in Organic Electronics ........................................................................ 71
2- MATERIALS AND METHODS ..................................................................... 73
  2.1 Chemicals and Instruments ........................................................................... 73
  2.2 Synthetic Work ............................................................................................... 73
    2.2.1 General method for the preparation of substituted phthalodinitrile: ........ 73
    2.2.1.1 4-(Pyrrolidin-1-yl)phthalonitrile (126): ............................................. 74
    2.2.1.2 4-(Piperidin-1-yl)phthalonitrile (127): ............................................. 74
    2.2.1.3 4-(Azepan-1-yl)phthalonitrile (128): ............................................. 75
    2.2.2 4-(Bromomethyl)phthalonitrile (129): .................................................. 76
    2.2.3 4-((6-Hydroxyhexylamino)methyl)phthalonitrile (130) ....................... 77
    2.2.4: 4-((9,10-Dioxo-9,10-dihydroanthracen-2-ylamino)methyl)phthalonitrile (131) .................................................. 78
    2.2.5: 4-({1-[{(4-Nitrophenyl)diazenyl]}naphthalen-2-loxy}methyl)phthalonitrile (132) .................................................. 79
    2.2.6: 4-{(4-{(4-Nitrophenyl)diazenyl}naphthalen-1-yloxy)methyl)phthalonitrile (133) .................................................. 80
  2.3 Synthesis of phthalocyanines: ..................................................................... 81
    2.3.1 Tetramethylphthalocyanines: ................................................................. 81
    2.3.1.1 [2(3),9(10),16(17),23(24)-Tetramethylphthalocyanine (134) ......... 81
    2.3.2 M(II) Tetramethylphthalocyanines ............................................................ 82
    2.3.2.1 Copper(II) [2(3),9(10),16(17),23(24)-tetramethylphthalocyanine] (135): ........................................................................ 82
    2.3.2.2 Nickel(II) [2(3),9(10),16(17),23(24)-tetramethylphthalocyanine] (136): ........................................................................ 83
    2.3.2.3 Zinc(II) [2(3),9(10),16(17),23(24)-Tetramethylphthalocyanine] (137): ........................................................................ 83
2.3.2.4 Cobalt(II) [2(3),9(10),16(17),23(24)-tetramethylphthalocyanine] (138): ................................................................. 84

2.3.2.5: Plumbum(II) [2(3),9(10),16(17),23(24)-tetramethylphthalocyanine] (139): ......................................................... 85

2.3.3  Tetranitrophthalocyanines: ......................................................................................................................... 85

2.3.3.1 [2(3),9(10),16(17),23(24)-tetranitrophthalocyanine (140) .......... 85

2.3.4  M(II) Tetranitrophthalocyanines: .................................................................................................................. 86

2.3.4.1 Copper(II) [2(3),9(10),16(17),23(24)-tetranitrophthalocyanine] (141): ................................................................. 87

2.3.4.2: Nickel(II) [2(3),9(10),16(17),23(24)-tetrakis(nitro)phthalocyanine] (142): ................................................................. 88

2.3.4.3 Zinc(II) [2(3),9(10),16(17),23(24)-tetranitrophthalocyanine] (143): ................................................................. 88

2.3.4.4 Cobalt(II) [2(3),9(10),16(17),23(24)-tetranitrophthalocyanine] (144): ................................................................. 89

2.3.4.5 Plumbum(II) [2(3),9(10),16(17),23(24)-tetranitrophthalocyaninato] (145): ................................................................. 90

2.3.5  Tetrasulfophthalocyanine: ............................................................................................................................... 90

2.3.5.1 2(3),9(10),16(17),23(24)-tetrosulfophthalocyanine (146): ........ 91

2.3.5.2 Copper(II) [2(3),9(10),16(17),23(24)-tetrasulfophthalocyanine] (147): ................................................................. 91

2.3.5.3 Nickel(II) [2(3),9(10),16(17),23(24)-tetrasulfophthalocyanine] (148): ................................................................. 92

2.3.5.4: Zinc(II) [2(3),9(10),16(17),23(24)-tetrasulfophthalocyanine] (149): ................................................................. 93

2.3.5.5 Cobalt(II) [2(3),9(10),16(17),23(24)-tetrasulfophthalocyanine] (150): ................................................................. 93

2.3.5.6 Plumbum(II) [2(3),9(10),16(17),23(24)-tetrasulfophthalocyanine] (151): ................................................................. 94

2.3.6  Tetrapyrrrolidine substituted phthalocyanine: ................................................................................................. 95
2.3.6.1 [2(3),9(10),16(17),23(24)-Tetra(pyrrolidin-1-yl)phthalocyanine]
(152) ...................................................................................................................... 95
2.3.6.2 Metallated tetra-pyrrolidine substituted phthalocyanines .......... 96
2.3.6.2.1: Copper(II) [2(3),9(10),16(17),23(24)-tetra(pyrrolidin-1-
yl)phthalocyanine] (153) .................................................................................. 96
2.3.6.2.2: Nickel(II) [2(3),9(10),16(17),23(24)-tetra(pyrrolidin-1-
yl)phthalocyanine] (154) .................................................................................. 97
2.3.6.2.3: Zinc(II) [2(3),9(10),16(17),23(24)-tetra(pyrrolidin-1-
yl)phthalocyanine] (155) .................................................................................. 98
2.3.6.2.4: Cobalt(II) [2(3),9(10),16(17),23(24)-tetra(pyrrolidin-1-
yl)phthalocyanine] (156) .................................................................................. 99
2.3.6.2.5: Plumbum(II) [2(3),9(10),16(17),23(24)-tetra(pyrrolidin-1-
yl)phthalocyanine] (157) ................................................................................ 100
2.3.7 Tetra(piperidin-1-yl)substituted phthalocyanines: ....................... 100
2.3.7.1: 2(3),9(10),16(17),23(24)-Tetra(piperidin-1-yl)phthalocyanine
(158): .................................................................................................................. 100
2.3.7.2 M(II) 2(3),9(10),16(17),23(24)-tetra(piperidin-1-yl)phthaloylanles
............................................................................................................................... 101
   2.3.7.2.1 Copper(II) [2(3),9(10),16(17),23(24)-tetra(piperidin-1-
yl)phthalocyanine] (159): .................................................................................. 102
   2.3.7.2.2 Nickel(II) [2(3),9(10),16(17),23(24)-tetra(piperidin-1-
yl)phthalocyanine] (160): .................................................................................. 103
   2.3.7.2.3 Zinc(II) [2(3),9(10),16(17),23(24)-tetra(piperidin-1-
yl)phthalocyanine] (161): .................................................................................. 104
   2.3.7.2.4 Cobalt(II) [2(3),9(10),16(17),23(24)-tetra(piperidin-1-
yl)phthalocyanine] (162): .................................................................................. 105
   2.3.7.2.5 Zinc(II) [2(3),9(10),16(17),23(24)-tetra(piperidin-1-
yl)phthalocyanine] (163): ................................................................................ 106
2.3.8 Tetra(azepan-1-yl)substituted phthalocyanines: ....................... 106
2.3.8.1: 2(3),9(10),16(17),23(24)-Tetra(azepan-1-yl)phthalocyanine
(164): .................................................................................................................. 106
### 2.3.8.2 M(II) 2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthaloyalnes

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Compound Name (Number)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.8.2.1</td>
<td>Copper(II) [2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanine] (165)</td>
<td>108</td>
</tr>
<tr>
<td>2.3.8.2.2</td>
<td>Nickel(II) [2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanine] (166)</td>
<td>109</td>
</tr>
<tr>
<td>2.3.8.2.3</td>
<td>Zinc(II) [2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanine] (167)</td>
<td>110</td>
</tr>
<tr>
<td>2.3.8.2.4</td>
<td>Cobalt(II) [2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanine] (168)</td>
<td>111</td>
</tr>
<tr>
<td>2.3.8.2.5</td>
<td>Plumbum(II) [2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanine] (169)</td>
<td>112</td>
</tr>
</tbody>
</table>

### 2.3.9 Chlorosulfonylphthalocyanines:

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Compound Name (Number)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.9.1</td>
<td>2(3),9(10),16(17),23(24)-Tetra(chlorosulfonyl)phthalocyanine (170)</td>
<td>113</td>
</tr>
<tr>
<td>2.3.9.2</td>
<td>2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylaminosulfonyl)phthalocyanines</td>
<td>113</td>
</tr>
<tr>
<td>2.3.9.2.1</td>
<td>2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylaminosulfonyl)phthalocyanine (171)</td>
<td>114</td>
</tr>
<tr>
<td>2.3.9.2.2</td>
<td>2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylaminosulfonyl)phthalocyanine (172)</td>
<td>115</td>
</tr>
<tr>
<td>2.3.9.2.3</td>
<td>2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylaminosulfonyl)phthalocyanine (173)</td>
<td>116</td>
</tr>
<tr>
<td>2.3.9.2.4</td>
<td>2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylaminosulfonyl)phthalocyanine (174)</td>
<td>117</td>
</tr>
<tr>
<td>2.3.9.2.5</td>
<td>2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylaminosulfonyl)phthalocyanine (175)</td>
<td>118</td>
</tr>
<tr>
<td>2.3.9.2.6</td>
<td>2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylaminosulfonyl)phthalocyanine (176)</td>
<td>119</td>
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### 2.3.10 2(3),9(10),16(17),23(24)-Tetra(octylaminosulfonyl)phthalocyanines:

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</tr>
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<tr>
<td>2.3.10</td>
<td>2(3),9(10),16(17),23(24)-Tetra(octylaminosulfonyl)phthalocyanines</td>
<td>120</td>
</tr>
</tbody>
</table>
2.3.10.1 2(3),9(10),16(17),23(24)-Tetrakis(octylaminosulfonyl)phthalocyanine] (177) ............... 120
2.3.10.2 Copper(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl)phthalocyanine] (178) ............... 121
2.3.10.3 Nickel(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl)phthalocyanine] (179) ............... 122
2.3.10.4 Zinc(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl)phthalocyanine] (180) ............... 123
2.3.10.5 Cobalt(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl)phthalocyanine] (181) ............... 124
2.3.10.6 Plumbum(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl)phthalocyanine] (182) ............... 125

2.3.11 [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine] ................. 126
2.3.11.1 [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (183) ............... 127
2.3.11.2 Copper(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (184) ............... 128
2.3.11.3 Nickel(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (185) ............... 129
2.3.11.4 Zinc(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (186) ............... 130
2.3.11.5 Cobalt(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (187) ............... 131
2.3.11.6 Plumbum(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (188) ............... 132

2.3.12 2(3),9(10),16(17),23(24)-Tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines] ................. 133
2.3.12.1 Copper(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189) ............... 133
2.3.12.2 Nickel(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (190) ................. 134
2.3.12.3 Zinc(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (191): .................. 135
2.3.12.4 Cobalt(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (192) ............... 136
2.3.12.5 Plumbum(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (193) ............. 137
2.3.13 2(3),9(10),16(17),23(24)-Tetrakis-[(9,10-dioxo-9,10-dihydroanthracen-2-yl)amino]methyl]phthalocyanines .......... 138
   2.3.13.1 Copper(II) 2(3),9(10),16(17),23(24)-tetrakis-[(9,10-dioxo-9,10-dihydroanthracen-2-yl)amino]methyl]phthalocyanines (194): 138
   2.3.13.2 Cobalt(II) 2(3),9(10),16(17),23(24)-tetrakis-[(9,10-dioxo-9,10-dihydroanthracen-2-yl)amino]methyl]phthalocyanines (195): 139
   2.3.13.3 Nickel(II) 2(3),9(10),16(17),23(24)-tetrakis-[(9,10-dioxo-9,10-dihydroanthracen-2-yl)amino]methyl]phthalocyanines (196): 140
2.3.14 2(3),9(10),16(17),23(24)-Tetrakis-([1-[(4-nitrophenyl)diazenyl]naphthalen-2-yl]oxymethyl)phthalocyanines (197) .................................................................................. 140
2.4 Perylenetetracarboxylic acid Derivatives ........................................ 141
   2.4.1 Synthesis of mono potassium salt of PTCDA .......................... 141
   2.4.2 N-Butylperylene-3,4,9,10-tetracarboxylic acid monoanhydride monoimide (199) ................................................................. 141
   2.4.3 N-Octylperylene-3,4,9,10-tetracarboxylic acid monoanhydride monoimide (200) ................................................................. 142
   2.4.4 N-Butyl-N’-(6-aminohexyl)perylene-3,4,9,10-tetracarboxylic diimide (201): ................................................................. 143
   2.4.5 N-Butyl-N’-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (202): ................................................................. 144
   2.4.6 N,N’-Bis(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (203): ................................................................. 145
Table of Contents

3- RESULT AND DISCUSSION ........................................................................................................ 146

3.1 Phthalocyanines .......................................................................................................................... 146

3.2 2,9(10),16(17),23(24)-Tetramethylphthalocyanines ............................................................... 149

3.3 2,9(10),16(17),23(24)-Tetranitrophthalocyanine ................................................................. 150

3.4 2(3),9(10),16(17),23(24)-tetryl(pyrrrolidin-1-yl)phthalocyanines (152-157) .................... 154

3.5 2(3),9(10),16(17),23(24)-tetra(piperidine-1-yl)phthalocyanines (158-163) ......................... 158

3.6 2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanines (164-169). 162

3.7 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193) ......... 166

3.8 2(3),9(10),16(17),23(24)-tetrakis-{{1-[(4-nitrophenyl)diazenyl]naphthalen-2-yl}oxymethyl}phthalocyanines & 2(3),9(10),16(17),23(24)-Tetrakis-[(4-[(4-nitrophenyl)diazenyl]naphthalen-2-yl)oxymethyl]phthalocyanines ............................................................... 170

3.9 2(3),9(10),16(17),23(24)-tetrakis-[(9,10-dioxo-9,10-dihydroanthracen-2-yl)amino]methyl]phthalocyanines (194-196) ................................................................. 172

3.10 Tetrasulfophthalocyanines ......................................................................................................... 175

3.11 Perylenetetracarboxylic acid diimides (PDIs) ......................................................................... 185

3.12 N-Alkyl perylenetetracarboxylic acid monoanhydride monoimides .... 186

3.13 N-Butyl-N’(6-aminohexyl)perylene-3,4,9,10-tetracarboxylic acid diimide and N-Butyl-N’(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide (201,202) .................................................................................................................................................. 187

3.14 N,N’-Bis(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide (202) ................. 188

4- Studies on the Applications of selected phthalocyanine and perylene dyes. ...................... 190

4.1 Nickel (II) 4,4’,4’’,4’’’ potassium-tetrasulfophthalocyanine (Tetrapotassium salt of Ni 2,9(10),16(17),23(24)-tetrasulfophthalocyanine). (206) .......... 190

4.1.1 Application in Organic Electronics ...................................................................................... 190

4.1.2 Application in humidity Sensors .......................................................................................... 198
4.2 N-Buty-N’-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide (N-BuHHPDI) (202) .......................................................... 204

4.2.1 Potential Application in Organic Electronics .................................. 204

CONCLUSION ................................................................................. 215

REFERENCES: ........................................................................... 222
LIST OF FIGURES

Fig.1: Structures with ring open and Closed form................................. 8
Fig.2: Switches for Different Cations .............................................. 15
Fig.3: Switches Working on PCT ..................................................... 16
Fig.3a UV-vis absorption (solid line) and emission (dashed line) spectra of a typical PDI in toluene. ................................. 65
Fig. 4: Cross sectional view of the Au/K4NiPTS/Ag surface type Schottky diode............................................................. 193
Fig.5: Current voltage (I-V) characteristics of Au/K4NiPTS/Ag device ............................................................. 194
Fig.6: Semilogarithmic current voltage characteristics (ln I-V) of Au/K4NiPTS/Ag diode ............................................................. 195
Fig.7: Double logarithmic current voltage characteristics (log I-log V) of Au/K4NiPTS/Ag diode ............................................................. 196
Fig.8: F(V) vs. V plot of Al/methyl-red/Ag Schottky diode ......................... 197
Fig.10: Cross sectional view of the Au/K4NiPTS/Au surface type sensor ............................................................. 200
Fig.11: Capacitance-humidity relationship for the Au/K4NiPTS/Au sensor ............................................................. 202
Fig.12: Cross-sectional view of N-BuHHPDI/p-Si device .......................... 205
Fig.13: Current-voltage (I-V) characteristics of N-BuHHPDI/p-Si heterojunction diode ............................................................. 206
Fig.14: Semi-logarithmic (I-V) characteristics of N-BuHHPDI/p-Si heterojunction diode ............................................................. 207
Fig.15: Junction resistance vs. voltage graph of N-BuHHPDI/p-Si diode under different temperatures ............................................................. 208
Fig.16: dV/d(ln I) vs I characteristics of N-BuHHPDI/p-Si heterojunction diode 209
Fig.17: H(I) vs. I characteristics of N-BuHHPDI/p-Si heterojunction diode ............................................................. 210
Fig.18: F(V)–V plot of N-BuHHPDI/p-Si heterojunction diode .................. 212
Fig.19: Current-voltage curves of N-BuHHPDI/p-Si diode at temperature room ............................................................. 213
LIST OF SCHEMES

Scheme 1: Synthesis of phthalocyanines by different precursors. .............. 18
Scheme 2: Synthetic route for phthalocyanines with tert butyl substituent................................. 21
Scheme-3: Synthesis of substituted phthalocyanines. ......................... 25
Scheme-4: Synthesis of octasubstituted phthalocyanines..................... 26
Scheme-5: Alkynyl substituted phthalocyanines.................................. 31
Scheme-6: Synthesis of phosphinylmethylphthalocyanines. ................. 33
Scheme-7: Synthesis of fluoroalkoxy phthalocyanines........................... 39
Scheme-8: Synthesis of fluoroalkoxy sulfonylphthalocyanines.................. 40
Scheme-9: Synthesis of nitrophthalocyanines................................. 41
Scheme-10: Synthesis of chlorosulfonylphthalocyanines...................... 43
Scheme-11: Synthesis of carboxyphthalocyanines by route 1. ............... 46
Scheme-12: Synthesis of carboxyphthalocyanines by route 2. ............... 47
Scheme-13: Synthesis of carboxamidophthalocyanines rout 1................. 48
Scheme-14: Synthesis of carboxyphthalocyanines by rout 2................... 48
Scheme-15: Synthesis of phosphothalocyanines.................................. 50
Scheme-16: Synthesis of aminophthalocyanines................................. 51
Scheme-17: Synthesis of symmetric perylene-3,4,9,10-tetracarboxylic diimide. .............................................................................. 56
Scheme-18: Synthesis of unsymmetric perylene-3,4,9,10-tetracarboxylic diimide by route 1............................................................... 57
Scheme-19: Synthesis of unsymmetric perylene-3,4,9,10-tetracarboxylic diimide by route 2............................................................... 58
Scheme-20: Synthesis of benzimidazole based perylene derivatives........ 59
Scheme-21: Synthesis of tetrachloroperylene-3,4,9,10-tetracarboxylic diimide .......................................................... 60
Scheme-22: Synthesis of tetrafluoroperylene-3,4,9,10-tetracarboxylic diimide. .......................................................... 60
Scheme-23: Coupling of PDIs with phenols, amines, cyanides, fluorides etc. ................................................................. 62

Scheme-24: Synthesis of aryl and alkyl substituted PDIs ................................................. 63

Scheme-25: Coupling of PDIs with different amines. ................................................ 64

Scheme-26: Proposed scheme of phthalocyanines and derivatives by route 1. .................. 147

Scheme-27: Proposed scheme of phthalocyanines and derivatives by route 2. .................. 148

Scheme-28: Synthesis of tetramethylphthalocyanines (134-139) .................................. 149

Scheme-29: Synthesis of tetranitrophthalocyanines (140-145) .................................. 150

Scheme 30: Synthesis of 4-(pyrrolidin-1-yl)phthalonitrile ....................................... 155

Scheme 31: Synthesis of Tetra(pyrrolidin-1-yl)phthalocyanines (152-157) ...................... 156

Scheme 32: Synthesis of 4-(piperidin-1-yl)phthalonitrile ........................................ 158

Scheme 33: Synthesis of tetra(piperidine-1-yl)phthalocyanines (158-163) ................. 160

Scheme 34: Synthesis of 4-(azepan-1-yl)phthalonitrile ........................................ 163

Scheme 35: Synthesis of tetra(azepan-1-yl)phthalocyanines (164-169) .......................... 164

Scheme 36: Synthesis of 4-(bromomethyl)phthalonitrile ......................................... 167

Scheme 37: 4-((6-hydroxyhexylamino)methyl)phthalonitrile (130) ............................. 167

Scheme 38: Synthesis of tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193) .... 168


Scheme 41: Synthesis of 4-{{9,10-Dioxo-9,10-dihydroanthracen-2- ylaminomethyl]phthalonitrile (131) ...................................................... 173
<table>
<thead>
<tr>
<th>Scheme 42:</th>
<th>Synthesis of tetrakis-{[(9,10-dioxo-9,10-dihydroanthracen-2-yl) amino]methyl}phthalocyanines (194-196)</th>
<th>173</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme 43:</td>
<td>Synthesis of Tetrasulfophthalocyanines</td>
<td>176</td>
</tr>
<tr>
<td>Scheme 44:</td>
<td>Proposed Synthesis of the PC–PDI Complexes</td>
<td>186</td>
</tr>
<tr>
<td>Scheme 45:</td>
<td>Synthesis of N-Alkyl perylenetetracarboxylic acid monoanhydride monoimides</td>
<td>187</td>
</tr>
<tr>
<td>Scheme 46:</td>
<td>Synthesis of PDI’s</td>
<td>188</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table-1: Effect of the position of substituent and coplanarity on Q absorption bands ................................................................. 23
Table-2: IR Spectra of tetramethylphthalocynines (134-139) ............. 151
Table-3: Elemental Analysis and Mass Data of tetramethylphthalocynines (134-139) ................................................................. 152
Table-4: IR Spectra tetrinitrophthalocynines (140-145) .................... 153
Table-5: Elemental analysis and mass data of tetrinitrophthalocynines (140-145) 154
Table-6: IR Spectra of tetra(pyrrolidin-1-yl)phthalocyanines (152-157) .... 157
Table-7: Elemental Analysis and Mass Data of tetra(pyrrolidin-1-yl) phthalocyanines (152-157) .......................................................... 158
Table-8: IR Spectra of tetra(piperidine-1-yl)phthalocyanines (158-163) .... 161
Table-9: Elemental Analysis and Mass Data tetra(piperidine-1-yl) phthalocyanines (158-163) .............................................................. 162
Table-10: IR Spectra of tetra(azepan-1-yl)phthalocyanines (164-169) ..... 165
Table-11: Elemental Analysis and Mass Data of tetra(azepan-1-yl) phthalocyanines (164-169) .............................................................. 166
Table-12: IR Spectra tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193) ......................................................... 169
Table-13: Elemental Analysis and Mass Data of tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193) .............................. 170
Table-14: IR Spectra of tetrakis-[[9,10-dioxo-9,10-dihydroanthracen-2-yl] amino]methyl]phthalocyanines (194-196) .............................. 174
Table-15: IR Spectra of tetrakis-[[9,10-dioxo-9,10-dihydroanthracen-2-yl] amino]methyl]phthalocyanines (194-196) .............................. 175
Table-16: IR Spectra of Tetrasulfophthalocyanines (146-151) .............. 177
Table-17: Elemental Analysis and Mass Data of Tetrasulfophthalocyanines (146-151) .............................................................. 178
Table-18: IR Spectra of sulfonamide phthalocyanines (171-176) ............ 179
Table-19: IR Spectra of sulfonamide phthalocyanines (177-182) ............ 180
List of Tables

Table 20: IR Spectra of sulfonamide phthalocyanines (183-188) .................. 181
Table 21: Elemental Analysis and Mass Data of sulfonamide phthalocyanines (171-176) ......................................................... 182
Table 22: Elemental Analysis and Mass Data of sulfonamide phthalocyanines (177-182) ................................................................. 183
Table 23: Elemental Analysis and Mass Data of sulfonamide phthalocyanines (183-188) ................................................................. 184
Chapter – 1

INTRODUCTION
1- INTRODUCTION:

1.1 High Technology Colorants

The colorants (Dyes and pigments) which have applications other than just dyeing can be termed as high technology colorants. The term functional dyes were coined for such colorants by Japanese researchers in 1981. These colorants are usually used in electronics and opto-electronics for example they are used in optical data storage devices, reprographics, dye-sensitized solar cells (DSSCs), photodynamic therapy in cancer treatment (PDT), biomedical probes, photoconductors, photosensitizers, photo-catalysts, photocopying, laser printing, etc.

1.1.1 Dyes for Solar Cells:

Dye sensitized solar cells are photovoltaic cells known as Gratzel’s cell\(^1\). In the dye-sensitized solar cells a semiconductor is used for charge transport and the photoelectrons are provided by photosensitive dye. In these cells the charge separation takes place at the surfaces between the dye, semiconductor and the electrolyte. It is made up of porous layer of nanoparticles of titanium dioxide covered with a molecular dye which captures sunlight just like chlorophyll does in plants.

Both organic and inorganic dyes are used in DSSC. Organic dyes include both natural and synthetic organic dyes and pigments while inorganic dyes include ruthenium (\(e.g.1-3\))\(^2\) and osmium complexes of poly pyridyl, metal porphyrins, inorganic quantum dots and phthalocyanines.
High cost and limited resources have forced the researchers to develop cheaper photosensitive dyes. It has been reported that metal free organic dyes have superior molar extinction co-efficients coupled with low cost and diverse molecular structures. Recently cyanine (e.g. 3)\textsuperscript{3} (e.g. 4), hemicyanine (e.g. 5)\textsuperscript{4}, coumarins (e.g. 6, 7)\textsuperscript{5}, indoline (e.g. 8)\textsuperscript{6}, triphenylamine (e.g. 9)\textsuperscript{7}, dialkylaniline (e.g. 10)\textsuperscript{8}, phenothiazine (e.g. 11)\textsuperscript{9}, carbazole (e.g. 12)\textsuperscript{10}, tetrahydroquinoline (e.g. 13)\textsuperscript{11}, bis(dimethylflourenyl)aminophenyl dyes (e.g. 14)\textsuperscript{12,13} have been developed and employed in DSSC. These dyes have 5% - 9% solar to electrical power conversion efficiencies as compared to black ruthenium dye which have 11.2% conversion efficiency.
Chapter – 1

Introduction

(4)

(5)

(6)

(7)

(8)

R₁ = CH₂COOH. R₂ = CH₂CH₃, CH₃COOH. R₃ = S.

(9)

X = S, Se.
A photosensitive dye has three components (a) one or two electron donating groups to increase the electron donating capability of dye (b) a conjugated bridge or polyene to adjust the absorption spectra by changing the degree of conjugation, and (c) a cyanoacrylic acid moiety which fix the dye with the semiconductor film.

A major concern of organic dyes is their photo stability in comparison with the inorganic dyes which possess high stability. The instability of the organic dyes is attributed to their reactive nature and tendency to form excited triplet
states. Another factor contributing to the decreased efficiency is the pi-pi stacking, however this effect can be reduced by the presence of bulky groups as in 15 which results in the loss of planarity of the molecule leading to reduction of pi-pi stacking. Naturally occurring dyes on the other hand are less toxic, low cost, environmental friendly and 100% biodegradeable. Cyanine dye 16 dye is one of the naturally occurring dyes which possess proper structure to be used in DSSCs. It has two hydroxyl groups at ortho position to be anchored with TiO$_2$ nano particles (17).^{14,15}
1.1.2 Dyes for optical data storage:

The reversible photo-transformation of a chemical compound having different absorption spectra is known as photochromism.\(^{16}\) Optical data recording on photochromic multi-layer optical discs has ensured a high density of data recorded on the pico- or fermi to second scale. Therefore the photonic devices containing photochromic molecules are the future of digital optical storage. The most prominent organic photochromic switches are based on the photoinduced ring opening/closure reactions. Spiropyrans (18) and spiroxazines (19) represent an important class of compounds possessing photochromic property. The irradiation of the colorless compound with ultraviolet light results in the opening of pyran or oxazine ring by the cleavage of C-O bond (20 & 21). This results in the formation of intensely colored merocyanines (22 & 23) which possess high degree of conjugation and quasiplanar conformations.

![Diagram of photochromic compounds](image)

Flavylium salts, the benzopyrylium derivatives (e.g. 25) also belong to the family of compounds which show phochochromism.\(^{17}\) They have structure similarity with anthocyanins (Glycosides of anthocyanidins). Flavylium systems results from the photo-induced cis-trans isomerization of ortho-hydroxy chalcones (e.g. 24) to produce cis form which finally undergoes ring closure to yield cyclic
flavylium salt (25). The chromophore 7-(N,N-diethylamino)-4-hydroxyflavylium switches from its yellow chalcone form to the red flavylium cation upon irradiation and reverts back to the chalcone form in the dark. They are pH sensitive and show different colors at different pH of the medium, they are also used in probes for accessing any change in the microenvironment of polymers like micelles and gels.

Dihydroazulenes (e.g. 26), diarylethenes (e.g. 27), spiropyans (e.g. 28), spiroxazines (e.g. 29), naphthopyrans (e.g. 30), dihydropyrenes (e.g. 31), fulgides (e.g. 32) and other similar compounds can be utilized as organic photochromic switches, they exhibit ring opening and closure when subjected to photoinduced electrolytic reactions (Fig 1).
Chapter – 1

1.1.3 Dyes for PDT:

Photodynamic therapy refers to the treatment employing light, is used to destroy diseased organs. This involves the use of harmless photosensitive...
dye coupled with controlled supply of light to cure bacterial infections in living tissues.\textsuperscript{23}

The extent to which light penetrates into the tissue varies with the wavelength of light used and the optical properties of the tissue. Wavelengths shorter than 700 nm are scattered by macromolecules and those having wavelength longer than 900 nm are absorbed by the water molecules while wavelengths less than 650 nm are absorbed by the cell chromophores. The drug is regarded as ideal if it absorbs in the near infrared region known as Therapeutic Window, which ranges from 700-950 nm. Biological tissues show minimum absorbance in the region from 700-950 nm\textsuperscript{24} Photofrin (33) and verteporfin (34) (Porphrin based photosensitizers used in PDT) absorbs at 630 & 690 nm respectively.\textsuperscript{25} The first clinically applied PDT agent was Photofrin and is recommended for the treatment of cervical, esophageal, endobroncheal, lungs, stomach, bladder and skin cancer\textsuperscript{22} but still it is not considered as an ideal drug.\textsuperscript{26} Porphyrin ring system is under extensive study for the development of effective PDT agents. Novel hydrophilic conjugated dimmers of porphyrin have been reported with $\lambda_{\text{max}}$ in the range from 700-800 nm.\textsuperscript{27}
Poor quantum yield of singlet oxygen generation, weak absorption by the photosensitizers in the therapeutic window and incompatibility with patient cells are the major concern areas in the use of photosensitizers as PDT agents. Strong absorption by cyanine dyes in the therapeutic window (near infrared region) has made them a suitable choice as PDT drugs. Cyanine dyes possess two nitrogen containing heterocyclic rings connected through methine linkages. The resonance in cyanine dyes occurs between the tertiary and quaternary nitrogen atoms through conjugated system. The use of merocyanines (e.g. 35) and ketocyanines (e.g. 36) for solid tumor treatment as radiation sensitizers and photodynamic therapeutic agents is under extensive study. The studies of merocyanine dyes (e.g. 35) have shown that substitution of oxygen atom with sulphur results in much higher yields of singlet oxygen. The substitution of oxygen with heavier atom also stabilized the polymethine moiety to photoisomerization, which is one of the major deactivation pathways. Several modifications like N-alkylation and lengthening of methine chain produced hopeful results such as, increase in the lipophilicity of the dye and significant bathochromic shifts. Indocyanine Green also shows long wavelength absorption in the therapeutic window (e.g. 37).
The studies have shown that the substitution of one of the oxygen atom of central four membered ring of squarylium cyanine dyes (e.g. 38) based on benzothiazol, benzoselenazole and quinoline dyes with benzylamine, 3-iodoaniline, aniline, N,N-dimethylhydrazine and 2-aminosulfonic acid resulted in the derivatives which have strong absorption bands in the region of interest with enhanced singlet oxygen production.\textsuperscript{32,33}
1.1.4 Dyes for Fluorescent Sensors:

The application of functional dyes in optical sensor is another area which has received great attention in the recent years. These sensors can be applied for visualizing specific molecular targets in vitro and in vivo\cite{34} For this purpose there is a need to develop fluorescent sensors in variety of colors.\cite{35} Fluorescent sensors are nondestructive in nature and possess high sensitivity in addition to specificity. In chemosensors change in electrical and optical properties takes place due to the interaction of dyes with small cations, anions or neutral species.

Molecular switches operated chemically comprises of three main components which are: receptor, linker or spacer, and finally reporter. Receptors are the binding sites which should trigger the ions or molecules with desirable selectivity and specificity. Linkers serve as the electronic communicators between the receptor and reported moieties.

Electronic communication can be established by three different ways: (a) bridge that should overlap the pi electron system of two moieties, (b) small linker that should enable photoinduced transfer of electrons and (c) arrangement of receptor and reporter moieties. The photophysical phenomena involved in
chemical switches with optical read out are photo-induced electron transfer (PET) and photo-induced charge transfer (PCT).

The switches that work on the principle of PET are triggered by stimuli like protons, metal cations, organic molecules and nanoparticles. In order to induce desired spectral properties and life time of switches various organic compounds like pyrene (e.g. 39), anthracene (e.g. 40), fluoresceins (e.g. 41), pyromellitimide, (e.g. 42), coumarins (e.g. 43) are employed. Among the inorganic compounds like polypyridine Ru(II) complexes and lanthanide complexes can also serve the same purpose. The large diversity of organic ligands has enabled the designing of chemical switches having desired properties much easier.
Figure 2: Switches for Different Cations

Figure 2 shows a variety of switches (44-50) specific for different cations.\(^ {37,38,39,40}\) There is another class of chemical switches that work on photoinduced charge transfer (PCT) system. PCT switches are composed of receptor (fluorophore) in a donor-π-acceptor system, as depicted in Fig 3. As a result of color change upon cation sensing different wavelengths can be used in photo-induced charge transfer switches which are one of the main advantages of PCT switches over PET switches. PCT-based switches can be derived from well-known pH colorimetric indicators.\(^ {41}\) Molecular switches driven by Hg\(^ {2+}\) ion have been reported\(^ {42,43}\) based on donor-acceptor-donor systems. These switches possess central acceptor moieties: 1,8-naphthyridine (e.g. 51) or squaraine coupled with two identical donor fragments: 1,4-dioxo-7,13-dithia-10 azacyclopentadecane (52). The naphthyridine-based (e.g. 51) shows a strong absorption band at 450 nm. Binding of one mercury equivalent reduces the symmetry of electron distribution within the molecule, which results in the bathochromic shift of the lowest energy absorption band. Binding of the second
mercury ion results in turn in a hypsochromic shift of the low-energy band due to interaction of bound cations with photoinduced dipole moments. This switch possess low binding constant and thus requires high concentrations of triggering cation.\textsuperscript{44} Due to considerably high affinity of Dithiazacrown receptors for mercury ions, even very small amount of Hg\textsuperscript{2+} ions are sufficient to induce optical changes of the squaraine-based switch (e.g. 52). A huge hypsochromic shift from 650 to 285 nm results on binding of Hg\textsuperscript{2+} ions with the switch\textsuperscript{43}.

![image](51)

(51)

![image](52)

(52)

**Figure 3: Switches Working on PCT**

In addition to above cited applications organic colorants including phthalocyanines, perylenes etc are being used in photoconductor, photosensitizer, photocopying and laser printing. As most of our work is associated with the synthesis of phthalocyanine and perylene derivatives, so in the following two sections phthalocyanines and perylenes have been reviewed with respect to their synthesis and applications.

### 1.2 Phthalocyanines

Linstead\textsuperscript{45} and his coworkers in 1930s carried out extensive study on phthalocyanines. For the first three decades phthalocyanines were mainly
employed in paper and textile industry as blue and green colorants with light resistant properties. Phthalocyanines possess high thermal, chemical and photochemical stabilities. Unsubstituted phthalocyanines possess low solubility even in high boiling solvents like 1-chloronaphthalene and 1-bromonaphthalene, however they show good solubility in sulfuric acid.

Nature of the central metal atom and its axial coordination, nature of meso-atoms and substituents attached at the peripheral positions greatly effects the properties of these macromolecule. Nature of substituents has pronounced effect on the solubility of the phthalocyanines. The positions 1, 4, 8, 11, 15, 18, 22 and 25 located at the phthalocyanine ring (53) are referred as α-positions and substituents present at these positions are called α-substituents while positions 2, 3, 9, 10, 16, 17, 3 and 24 (54) are named as β- positions and substituent attached at these positions are referred as β-substituents.

Introduction of substituents at peripheral positions not only increases the solubility of phthalocyanines in common solvents like water, chloroform, ethyl acetate, dichloromethane, N,N-dimethylformamide etc. but also provides positions for bridging groups for the formation of supramolecular assemblies and other similar applications. Substituted phthalocyanines are now extensively used as pigments and dyes, industrial catalysts, photosensitizers for photodynamic cancer therapy; Materials for ink jet printing, electro-
photography, electrochemical devices, semiconductors, chemical sensors; liquid crystals and functional polymers; nanotechnology; and non-linear optics. Most of these applications are attributed to the optical (low-energy Q-band) and redox properties of these macromolecules which can be tuned by changing the peripheral substituents.

Two methodologies are applied for the introduction of peripheral substituents to 55. First is the utilization of already substituted benzene-1,2-dicarboxylic acid derivatives like anhydrides, amides, imides and nitriles (Scheme-1) as precursors for cyclotetramerization and second involves the addition of substituent to the phthalocyanine core by electrophilic substitution or cycloaddition reactions.

![Scheme 1: Synthesis of phthalocyanines by different precursors.](image-url)
1.2.1 Alkylated and arylated phthalocyanines

1.2.1.1 Tetrasubstituted phthalocyanines

Literature has shown that only few alkyl and aryl substituted phthalocyanines have been synthesized. The most commonly employed starting materials for the synthesis of 1,8(11),15(18),22(25)-tetra-substituted phthalocyanines are 3-substituted derivatives of phthalic acid. During tetramerization process all the four possible positional isomers \( C_{4h} \) (56), \( C_{2v} \) (57), \( C_s \) (58) and \( D_{2h} \) (59) can be formed but the nature of the substituent on the precursor controls the formation of the dominant isomer. Isomer with \( C_{4h} \) symmetry (56) is usually dominant because it is least sterically crowded. Brewis et al.\(^{54}\) have reported that tetramerization adopting mild reaction conditions i.e. the use of alkoxides resulted in the formation of least sterically hindered isomer (\( C_{4h} \) isomer which in the metal free state has \( C_{2h} \) symmetry) while under drastic reaction conditions all the four isomers were formed. Mikhalenko and coworkers\(^{16}\) have enumerated that vanadyl-1,8(11),15(18),22(25)-tetraphenylphthalocyanine could be prepared in 90% yield from 3-phenylphthalonitrile at 180 °C while this yield reduces to 55% when 3-phenylphthalonitrile along with urea was heated at 250 °C.

![Diagram](C4h_56.png)  ![Diagram](C2v_57.png)
2,9(10),16(17),23(24)-tetraalkyl- and tetraaryl- phthalocyanines are the most studied and explored tetramers. Tetramethyl\textsuperscript{55}, tetraethyl\textsuperscript{56,57,58} and tetra(cyclopropyl) phthalocynines\textsuperscript{59} possess low solubility in common organic solvents and thus are of limited scientific interest.

Prbably metallated and metal free 2,9(10),16(17),23(24)-tetra-\textit{tert}-butylphthalocyanines\textsuperscript{60} are the most commonly studied alkylated phthalocyanines. These were first synthesized in 1960 and a number of complexes containing main group elements, lanthanides and transition metals has so far been synthesized.\textsuperscript{61} The \textit{tert}-butyl substituents at β-positions although do not affect the electronic spectroscopic and redox properties but at the same time dramatically enhance the solubility in common organic solvents without disturbing Q and B absorption bands of the phthalocyanines\textsuperscript{62}. These complexes also occur in four positional isomers. Presence of \textit{tert}-butyl group at peripheral position also inhibits aggregation which is one of the most encountered problems in phthalocyanine chemistry.

The starting material for the preparation of 4-\textit{tert}-butylphathalonitrile is o-xylene which is converted into 4-\textit{tert}-butyl-o-xylene\textsuperscript{60} and then oxidized to 4-\textit{tert}-butylphthalic acid which through acidic route (sub-phthalic acid---phthalic anhydride—imide—amide--phthalonitrile) produces substituted phthalonitrile in low yield (25%). For the large laboratory synthesis this method was modified to
two step procedure involving bromination of tert-butyl benzene followed by Rosenmund-von Braun (or palladium-catalyzed) reaction of dibromo compound with CuCN or Zn(CN)$_2$ (Scheme 2).$^{63,64}$ This method is quite efficient and more sterically hindered phthalocyanines like 2,9(10),16(17),23(24)-tetraadamantyl- and 2,9(10),16(17),23(24)-tetra(trimethy-ladamantyl)-phthalocyanines (60) has been reported by employing this synthetic route.$^{65}$ Introduction of more bulky substituents like triphenylmethyl$^{41}$ and (1,1,3,3-tetramethyl)butyl$^{56}$ markedly increases the solubility of phthalocyanines in common non polar solvents probably by reducing the aggregation of the macromolecules.

![Scheme 2: Synthetic route for phthalocyanines with tert butyl substituent.](image)

As compared to 3-substituted phthalic acid derivatives 4-substituted phthalic acid analogues provide less steric hindrance during cyclization reaction$^{66}$. The statistically calculated values of different isomers of substituted values are $C_s = 50\%$, $C_{2v} = 25\%$, $C_{4h} = 12.5\%$ and $D_{2h} = 12.5\%$ respectively. Hanack and his coworkers$^{67}$ in 1993 reported the successful separation of two isomers of nickel 2,9(10),16(17),23(24)-tetra-tert-butyl phthalocyanine i.e $C_s$ and
C\textsubscript{2v} by employing direct phase HPLC and MPLC techniques. In 2001 they again attempted to test the isomeric distribution of metal free 2,9(10),16(17),23(24)-tetraethyl- and In(C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3}-p) 2,9(10),16(17),23(24)-tetra-tert-butylphthalocyanines. The results obtained showed that peak area for 'C\textsubscript{4h}' (C\textsubscript{4}) and 'D\textsubscript{2h}' were in agreement with the statistical predictions for 'cyclo-tetramerization reaction' whereas the aggregate of the remaining isomers was expected to 75% (C\textsubscript{s} = 50%, C\textsubscript{2v} = 25%,). These new findings were contrary to their earlier observations\textsuperscript{68} where they claimed the formation of pure C\textsubscript{2v} isomer of zinc 2,9(10),16(17),23(24)-tetra-tert-butylphthalocyanines from tert-butylphthalonitrile and zinc.

It has been shown that ortho-substituted tetraphenylphthalocyanines showed enhanced solubility as compared to the para substituted phenyl macrocycles probably due to steric hindrance of conjugation between phenyl ring and phthalocyanine macrocycle. The aggregational behavior further reduced with the induction of more bulky groups like (pentaphenyl)phenyl in the phthalocyanines because of the out of plane orientation of bulky (pentaphenyl)phenyl moieties with the phthalocynine tetramer.\textsuperscript{69}

Q bands of phthalocynines are also affected by the change in the coplanarity of the tetramers. Mikhalenko et al\textsuperscript{70} reported that the presence of chloro at the ortho position of phenyl ring break π conjugation, and the resulting Q bands becomes indistinguishable from the unsubstituted tetramer. Appreciable (Prominent) red shift in the Q band occurs in case of partial overlapping of π orbital of Pc and that of aromatic ring. Effect of phenyl group at β-position is insignificant as compared to the α-substituted analogues (table-1).
Table No. 1: Effect of the position of substituent and coplanarity on Q absorption bands.

<table>
<thead>
<tr>
<th></th>
<th>R₁</th>
<th>R₂</th>
<th>Q-bands (nm)</th>
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</thead>
<tbody>
<tr>
<td>H</td>
<td>C₆H₅</td>
<td></td>
<td>715</td>
</tr>
<tr>
<td>H</td>
<td>p-ClC₆H₄</td>
<td></td>
<td>716</td>
</tr>
<tr>
<td>H</td>
<td>o-ClC₆H₄</td>
<td></td>
<td>707</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td></td>
<td>723</td>
</tr>
<tr>
<td>p-ClC₆H₄</td>
<td>H</td>
<td></td>
<td>731</td>
</tr>
<tr>
<td>o-ClC₆H₄</td>
<td>H</td>
<td></td>
<td>704</td>
</tr>
</tbody>
</table>

It has been reported that non planar substituted PC show absorption bands quite similar to the unsubstituted tetramers. In both octa-phenylsubstituted (2,3,9,10,16,17,23,24-octaphenylphthalocyanine) and tetra-phenylsubstituted (2,9,10,16,17,23,24-tetraphenylphthalocyanines), phenyl rings are not coplanar with the phthalocyanine ring which results in the diminished conjugation between the phenyl moiety and Pc core and therefore show absorption bands at 691 nm and 698 nm respectively.

1.2.1.2 Octa-substituted Phthalocyanines

Few examples of octa substituted Pc have been reported in literature.⁷¹,⁷² During the last decade, the synthesis of 1,3,8,10(9,11),15,17(16,18),22,24(23,25)octa-methylphthalocyanine and 1,3,8,10(9,11),15,17(16,18),22,24(23,25)octa-tert-butylyphthalocyanine have been described. Kalashnikova and many others⁷³ have discussed the synthesis of double decker metallated (lanthanum) and metal free 1,3,8,10(9,11),15,17(16,18),22,24(23,25)octa-methylphthalocyanines from 3,5-dimethylphthalonitrile but they possess poor solubility as compared to phthalocyanines containing tert-butyl moieties.⁷⁴
The isomeric symmetry of 1,4,8,11,15,18,22,25-octasubstituted tetrarers exclusively followed $D_{4h}$ or $C_{4v}$ symmetry due to their symmetrical nature with the central metal occupying place just above or inside the cavity. Phthalocyanines containing long chain alkyl or bulky groups not only make them soluble in common organic solvents but also make them liquid crystals.

Tetramerization of 3,6-dialkylphthalonitrile (61) can be achieved in alcohol, initiated by alkoxide, to afford metal and metal free 1,4,8,11,15,18,22,25-octaalkylphthalocyanines.\textsuperscript{75} Another methodology used to synthesize 1,4,8,11,15,18,22,25-octaalkylphthalocyanines is the metallation of metal free tetrarers by using standard methods.\textsuperscript{76} As expected the yield of 3,6-dialkylatedphthalocyanines is quite low as compared to the Pcs obtained from 4,5-dialkylphthalonitrile due to the steric hindrance of bulky alky moieties. For instance the yield of metal free 1,4,8,11,15,18,22,25-octabutylphthalocyanines obtained by heating 3,6-dibutylphthalonitrile in butanol/BuOLi mixture was 20% while 4,5-dibutylphthalonitrile under similar reaction conditions afforded 38% tetramer probably due to less steric hindrance of alkyl chains. The synthesis of 1,4,8,11,15,18,22,25-octabutylphthalocyanines is also influenced by the order of added reagents. When lithium was added to the mixture of 3,6-dihexylphthalonitrile and pentanol, an additional porphyrin (1,4,8,1,15,18,22,25-octahexyl-29H31H-tetrabenzo[b,g,l,q]-[5,10,15]triazaporphyrin) was also observed along with 1,4,8,11,15,18,22,25-octahexylphthalocyanines (Scheme 3). The nature of alcohol and amount of lithium dictated the yield of phthalocyanine (62) and porphyrin (63). When 2.1 equivalents of lithium was used the tetrabenzoazaporphyrin:phthalocyanine were obtained in 5:95 but when 19 equivalents of lithium was employed slight shifting of the ratio in favor of porphyrin was observed (23:77).
1,4,8,11,15,18,22,25-octaarylphthalocyanines offers greater steric hindrance as compared to 1,4,8,11,15,18,22,25-octaalkylphthalocyanines. Kobayashi and his coworkers\textsuperscript{77} in 1997 synthesized numerous transition metal complexes of 1,4,8,11,15,18,22,25-octaarylphthalocyanines and studied their crystal structures. These studies revealed distorted structures of these complexes lead to huge red shift in Q bands in the UV-Vis spectra. Due to the steric hindrance, the yields of the products were also very low. Metal free unsubstituted phthalocyanines can be selectively lithiated and afterwards deuterated at α positions at very low temperatures.\textsuperscript{78} Similarly metal free Pc react with Lithium 2,2,6,6-tetramethylpiperidine (LiTMP) in the presence of deuterated tetramethylpipridine (D-TMP) at -23 °C to yield 1,4,8,11,15,18,22,25-octadeuterophthalocyanines. 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines \textit{e.g.} 1,4,8,11,15,18,22,25-octasubstitutedphthalocyanines
exclusively occur as single isomer. One of the most effective methods for the synthesis of 2,3,9,10,16,17,23,24-octaalkyl-substituted phthalocyanines (e.g. 66) is from 1,2-dialkyl benzene (64) as shown in the scheme 4. But 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines (e.g. 66) are of little synthetic interest due to their poor solubility.

\[ R = \text{Alkyl.} \]

\[ \text{(64)} \]

\[ \text{Scheme-4: Synthesis of octasubstituted phthalocyanines} \]

In late 1980s, alicyclic alkyl substitutents were introduced onto phthalocynine core. 6,7-Dicyano-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene was prepared and cyclotetramerized to metal free and metellated phthalocynines (e.g. 67) which were found to possess good solubility in common organic solvents without affecting their optical properties just like tetra-tert-butylphthalocyanines. Metal free phthalocynine was claimed to be useful as luminescence sensors for laser-singlet oxygen generation in solution.\textsuperscript{79}
Gal'pern and his coworkers\textsuperscript{80} have reported the synthesis of sterically hindered concave shaped moieties containing phthalocynines (68) from 2,3-dibromotriptycene and its derivatives. Interestingly optical properties of this complex were not altered as compare to the unsubstituted phthalocynines.

\textbf{(68)}

\textbf{(67)}
Another concave analogue ($69$)\textsuperscript{81,82,83} was synthesized from 2,3-dicyano-(4,5-dibenzobarelleno)naphthalene.

1.2.1.3 Hexadecasubstituted phthalocyanines

Only few examples of 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecaalkyl- or aryl substituted phthalocyanines are reported in literature. Hanack \textit{et al.}\textsuperscript{84} have reported the synthesis of hexadecaalkyl substituted zinc phthalocyanines by the ‘template condensation’ of various teraalkylphthalonitriles in octanol under refluxing conditions for seven days. Surprisingly with tetra(n-hexyl)phthalonitrile, the yield of resulting complex was less than 1\% but when 3,6-diheptyl-4,5-dimethylphthalonitrile was tetramerized the yield of the product raised to 10\%. All the attempts to cyclize tetraphenylphthalonitrile proved futile however tetraipyrazolylphthalonitrile on teramerization in hydroquinone (180 °C) amazingly produced hexadecapyrazolylphthalocyanine in yields around 70\%.\textsuperscript{85}
1.2.2 Alkenyl and alkynyl substituted phthalocyanine

Hanack\textsuperscript{86} in 1993 reported the synthesis of metal free 2,9(10),16(17),23(24)-tetravinylphthalocyanine from 1,3-dihydro-1,3-diimino-5-vinyl-isoindole in DME and characterized the tetramer using various spectroscopic techniques. Kimura et al\textsuperscript{87} in 2002 reported stilbenoid phthalocyanines with extended conjugation due to oligo(p-phenylenevinylene). 4-Alkynylphthalonitriles can be tetramerized to yield 2,9(10),16(17),23(24)-tetraalkynylphthalocyanines, however sensitive alkynyl groups under severe reaction conditions undergo partial degradation and produce oligomeric materials. Some interesting porphyrin-phthalocyanine assemblies have been reported by Lindsey and his group where phthalocyanines and porphyrin rings are joined through $\text{C}=$. In these assemblies each phthalocyanine is connected via $\text{C}=$ with four or eight porphyrin ring systems which results in quite interesting redox properties in addition to photophysical properties. Leznoff and his group\textsuperscript{48} have enumerated the synthesis of a series of 1,2,8,9,15,16,22,23-octakis substituted phthalocyanines. The 1,2,8,9,15,16,22,23-octakis(3,3-dimethyl-1-butynyl)phthalocynine (70) was obtained from the cyclotetramerization of 3,4-bis(tert-butylethynyl)phthalonitrile using lithium 1-pentanolate.
They have claimed that 4,5-disubstituted phthalonitriles with silyl or alkyl moieties linked to acetylene can be directly cyclotetramerized to generate 2,3,9,10,16,17,23,24-octaalkynyl substituted phthalocyanines by heating in dimethylaminoethanol (DMAE) in the presence of metal salt and ammonia. Removal of silyl group using tetrabutylammonium fluoride led to the formation of 2,3,9,10,16,17,23,24-octaalkynyl substituted phthalocyanines with terminal acetylenic group (e.g. 71) (Scheme 5). These phthalocyanines were further reacted with alkylazides in the presence of Cu (I) to yield octa triazole containing phthalocyanines (e.g. 72) which can be used to obtain well defined
supramolecules.

\[
\begin{align*}
R = H & \quad \text{(71)} \\
R = \text{SiMe}_2\text{But} / \text{H}_2\text{O} & \quad \text{(72)}
\end{align*}
\]

Scheme-5: Alkynyl substituted phthalocyanines.

1.2.3 Silylated phthalocynines

Chen et al.\textsuperscript{88} reported the synthesis of 1,8(11),15(18),22(25)-tetrakis(trimethylsilyl)phthalocyanines (metal free) from 3-trimethylsilylphthalonitrile which was synthesized from unsubstituted phthalonitrile by direct silylation reaction. The resulting phthalocyanines possess
good solubility in chlorinated hydrocarbon and exhibited a singlet at -2.336 ppm (relative to TMS). The authors enumerated that direct lithiation of unsubstituted phthalonitrile predominantly takes place at alpha position. Treatment of metal free phthalocyanine with 2,2,6,6 tetramethylpiperidine and chlorotrimethylsilane produces a mixture of trimethyl silyl-substituted phthalocyanines (H\textsubscript{2}Pc(SiMe\textsubscript{3})\textsubscript{n}, where n=2-4). The yield of different isomers depends upon the phthalocyanines and base ratio. The Si NMR suggested\textsuperscript{55} that in spite of the bulkiness of the trimethylsilyl groups all the four isomers exist in the product mixture. In the same manner polysilated zinc phthalocyanines was synthesized by treating zinc phthalocyanines with Me\textsubscript{3}SiCl after lithiation of phthalocyanines.\textsuperscript{89} Manganese and zinc 2,3,9,10,16,17,23,24-octakis(trimethylsilyl)phthalocyanines have been synthesized from 1-imino-5,6-bis(trimethylsilyl)-1H-isindol-3-amine by heating in a mixture of appropriate metal salts and DBU in pentanol.\textsuperscript{90}

### 1.2.4 Heteromethyl substituted Phthalocyanines

Phthalocyanine with substituents attached to phthalocyanine core via methylene group constitutes another important class of phthalocyanines. Two different synthetic methodologies can be adopted for the synthesis of such complexes. First involves the tetramerization of appropriately substituted phthalonitriles and secondly by carrying out various substitution reactions on already prepared phthalocyanines.

In first method the appropriately substituted phthalonitriles are prepared from bromomethylatedphthalonitriles prepared by free radical bromination of methylated phthalonitrile or by Rosenmund-von Braun reaction of bromomethylated 1,2-dibromobenzene (scheme-4). In final nucleophilic substitution step, the use of alcohols, thiol, amines and trialkylphosphites has been reported in literature.\textsuperscript{91,92}

Second route for the preparation of phthalocyanine with substituents attached to phthalocyanine core via methylene group involves chloromethylation
of phthalocyanine. This reaction produces tetra- and octa-
chloromethylphthalocyanines as a mixture of positional isomers. These
chloromethylated PCs (e.g. 73) can be used to obtain a variety of functionalized
phthalocyanines. A number of phosphinylmethylphthalocyanines (e.g. 74) have
been prepared from the corresponding chloromethylated phthalocyanines and
trialkylphosphites employing Arbuzov-Michaelis reaction (scheme-6).\textsuperscript{93} These
complexes were found to be highly soluble in water and did aggregate in
aqueous solutions.

\begin{equation}
\begin{array}{c}
\begin{array}{c}
\text{Cl}_2\text{C} & \text{N} & \text{N}
\end{array}
\begin{array}{c}
\text{N} & \text{N}
\end{array}
\begin{array}{c}
\text{N} & \text{N}
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\begin{array}{c}
\text{N} & \text{N}
\end{array}
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\text{M}
\end{array}
\begin{array}{c}
\text{Cl}_2\text{C}
\end{array}
\begin{array}{c}
\text{N} & \text{N}
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\text{Cl}_2\text{C}
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\begin{array}{c}
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\text{CH}_2\text{Cl}
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\text{Cl}_2\text{C}
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\end{array}
\end{equation}

\textbf{Scheme-6: Synthesis of phosphinylmethylphthalocyanines.}

As compared to the corresponding sulfo derivatives they absorb at longer
wavelength and therefore can be utilized as more efficient photosensitizers for
PDT of the deeply located tumors. For example aluminium
octakis(diethylphosphinylmethyl)phthalocyanine have strong absorption at 698 nm
($\varepsilon > 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).\textsuperscript{94}

Water soluble cationic phthalocyanines (75a-e) have been synthesized
from octa chloromethylphthalocyanine precursor and their efficiency in singlet
oxygen photosensitization has been determined.\textsuperscript{95} The authors have claimed that
zinc (octakis(pyridinomethyl)phthalocyanines (75a) and zinc [octakis-(2-
hydroxyethyl)-N,N-dimethylammoniomethyl]phthalocyanines (75b) are the best
photosensitizers with excellent photodynamic applications.
Carborane cages can also be introduced to phthalocyanine core using tetra and octa-chloromethylphthalocyanines as precursor. The carborane cages containing phthalocyanines can be useful in boron neutron capture therapy. The sodium salts of tetrakis and octakis(undecahydroclosododecacarboranylaminomethyl)phthalocyanines have been prepared by the treatment of tetrakis and octakis(chloromethyl)phthalocyanines with Na$_2$B$_{12}$H$_{11}$NH$_2$. The complexes were found to be water soluble due to the presence of anionic boranyl moieties.$^{96}$

1.2.5 Halogen substituted phthalocyanines

One of the remarkable property of fluorine substituted phthalocyanines is their semiconducting properties.$^{97,98}$ Mayer et al.$^{99}$ synthesized copper and zinc complexes of 1,8(11),15(18),22(25)-tetrafluorophthalocyanine from 3-fluorophthalonitrile and studied as molecular semiconductor thin films and as prospective material for solar energy conversion.$^{99a}$ 4-Fluorophthalonitrile has also been converted to 2,9(10),16(17),23(24)-tetrafluorophthalocyanines under normal reaction conditions.$^{99c}$ Three types of octafluorophthalocyanines have been reported in literature. Transition-metal 1,3,8,10(11,9),15,17(18,16),22,24(25,23)-octafluorophthalocyanines have been synthesized from the diazonium salts of corresponding octaaminophthalocyanines by treating with NaBF$_4$ at 50°C.$^{100}$ Mayer et al$^{99a}$
investigated zinc 1,4,8,11,15,18,22,25-octafluorophthalocyanine as a potentially useful compound for the conversion of solar energy. Many other transition metal 2,3,9,10,16,17,23,24-octafluorophthalocynines have been prepared and investigated for their optical and redox properties.\textsuperscript{99a,101} 3,4,5,6-tetrafluorophthalonitrile was cyclotetramerized to obtain metallated and metal free 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluorophthalocyanines and examined for their potential application as ‘low voltage thin film transistors’.\textsuperscript{102} These compounds were found to be soluble to some extent in common organic solvents such as chlorobenzene, chloroform, acetone and DMF.

**1.2.5.1 Chlorinated phthalocynines**

A variety of copper complexes of 1,8(11),15(18),22(25)-tetrachloro, 2,9(10),16(17),23(24)-tetrachloro, 1,4,8,11,15,18,22,25-octachloro-, 1,2,8,9,(10,11),15,16(17,18)22,23(24,25-octachloro-, 2,3,9,10,16,17,23,24-octachloro-, 1,2(3),4,8,9(10),11,15,16(17),18,22,23(24),25-dodecachloro-, 1,2,3,8(11),9,10,15(18),16,17,22(25),23,24-dodecachloro-, and hexadecachlorophthalocyanines have been synthesized from substituted phthalic anhydrides, copper salt and urea in excellent yields. It was observed that less sterically hindered polychloro phthalocyanines were obtained in higher yields as compared to the Pcs substituted at $\alpha$-positions. Cyclotetramerization of tetrachlorophthalic anhydride led to partial dechlorination of macrocycle core, however cyclotetramerization of tetrachlorophthalonitrile in the absence of urea and other nucleophiles afforded pure hexadecachlorophthalocyanine.\textsuperscript{103,104} Using chlorinated phthalonitriles a large number chlorinated phthalocyanines have been prepared and reported in literature. It has been recently observed that the yields of chlorinated phthalocyanines from chlorinated phthalic anhydrides can be enhanced by employing ionic liquids as the reaction media.\textsuperscript{105} Introduction of chlorine moieties into phthalocyanine core usually enhances the first oxidation potential of the respective phthalocynine\textsuperscript{106} and changes the colour from blue to green.\textsuperscript{107} The position and and number of chlorine atom effect the Q absorption
band in UV-Vis spectra of the chlorinated phthalocyanines–Q band is red shifted if chloro groups are substituted at α-position of phthalocyanines.

1.2.5.2 Brominated phthalocyanines

Brominated phthalocyanines have also been reported in literature. Transition metal based 1,8(11),15(18),22(25)-tetrabromophthalocyanines have been synthesized by the tetramerization of 3-bromophthalonitrile in the presence of metal salt at 220-240 ºC.\textsuperscript{108} A similar reaction scheme have been used for the synthesis of metal complexes of 2,9(10),16(17),23(24)-tetrabromophthalocyanines.\textsuperscript{108,109} Tetrahalogenated phthalocyanines complexes of copper and nickel (doped and undoped) possess electrical conductivity 100 times higher than unsubstituted Pcs.\textsuperscript{110} These complexes have also potential to be used for NO\textsubscript{2} gas sensors.\textsuperscript{111} Copper 2,9(10),16(17),23(24)-tetrabromophthalocyanine have been used as catalyst in the cumene autoxidation.\textsuperscript{112} Only one copper complex of 1,4,8,11,15,18,22,25-octabromophthalocyanine has been reported by Mikhalenko et al.\textsuperscript{113} Numerous researchers\textsuperscript{114} have described the synthesis and characterization of 2,3,9,10,16,17,23,24-octabromophthalocyanine complexes of copper and silicon obtained from substituted phthalonitriles, cuprous chloride or silicon tetrachloride. Hexadecabromosubstituted Pcs have attained less attention due to lesser stability as compared to their fluoro and chloro derivatives.\textsuperscript{115}

1.2.5.3 Iodinated phthalocyanines

The preparation of several 1,8(11),15(18),22(25)-tetrachlorophthalocyanines from 3-iodophthalonitrile or by modification of phthalocyanine core have been described by many research workers.\textsuperscript{116,108,117} In the latter case, copper 1,8(11),15(18),22(25)-tetrachlorophthalocyanine was prepared from 1,8(11),15(18),22(25)-tetranitrophthalocyanine through a sequence of reactions which involves reduction of nitro groups, diazotization of the resultant amino group and finally treatment with sodium iodide.\textsuperscript{118} Bazanov and others\textsuperscript{116,108,119} have reported the synthesis of several transition metals based
2,9(10),13(14),23(24)-tetradiodophthalocynine from 4-iodophthalonitrile. Copper
1,4,8,11,15,18,22,25-octaiodo- and 2,3,10,11,16,17,23,24-octaiodo-
phthalocynines have been prepared from corresponding iodophthalic anhydrides
by heating with urea, cupric chloride and catalytic amount of titanium chloride,
however attempted synthesis of hexadecaiodophthalocyanine under similar
conditions in trichlorobenzene resulted in partial loss of iodine atoms from the
macrocycle.

One of the problems with the halogenated phthalocyanines is their
solubility, this solubility can be enhanced by introducing substituents (e.g. tert-
butyl) at peripheral positions. Metallated and metal free 1,8(11),15(18),22(25)-
tetrahalo-3,10(9),17(16),24(23)-tetra-tert-butylphthalocyanines obtained from 3-
halo-5-tert-butylphthalonitriles, are highly soluble in saturated hydrocarbons,
chlorinated solvents and aromatic compounds.\textsuperscript{120,121} Another method for
the synthesis of such compounds involves the diazotization of 1,8(11),15(18),22(25)-
tetraamino-3,10(9),17(16),24(23)-tetra-tert-butylphthalocyanines\textsuperscript{118} followed by
replacement of diazo group with halogens.

Shishkina et al\textsuperscript{122} have reported the synthesis of metallated
3,10(9),17(16),24(23)-tetrachloro/bromo-3,10(9),17(16),24(23)-
tetranitrophthalocyanines from 4-chloro/bromophthalimides. The nitro moieties in
octasubstituted phthalocyanines with halo group at ortho position are not planar
and thus not greatly affect the absorption spectra.

1.2.6 Haloalkylated Phthalocyanines

Another important class of halogenated phthalocyanines comprises of chain
halogenated substituted phthalocyanines. Yagupol’skii et al were the first to
report the synthesis of variously substituted trifluoromethylphthalocyanines in
1970s.\textsuperscript{99c,123} Induction of trifluoromethyl moieties increased their solubility in
chlorobenzene, nitrobenzene and DMF, however the solubility of these
complexes remained very low in other organic solvents. Phthalocyanines
possessing two trifluoromethyl moieties at α-positions were found to have better solubility as compared to 2,3,9,10,16,17,23,24-octakis(trifluoromethyl) analogues.

Zinc, cobalt and iron complexes of 2,3,9,10,16,17,23,24-octakis(perfluoroisopropyl)-1,4,8,11,15,18,22,25-octafluorophthalocyanines have with higher stabilities towards self-oxidation have been synthesized from 4,5-bis(perfluoroisopropyl)-3,6-difluorophthalonitrile. Cobalt complex has been found to be a potential catalyst for carbon-phosphorus oxidative bonds formation reactions by using air.

1.2.6.1 Trifluoromethylsulfanyl and trifluoromethylsulfonyl substituted phthalocyanines

Trifluoromethylsulfanyl and trifluoromethylsulfonyl substituted phthalocyanines have been synthesized from 4-trifluoromethylsulfanyl-, 4-trifluoromethylsulfonyl and 4,5-di(trifluoromethylsulfanyl)phthalonitriles. The complexes were found to be slightly soluble organic solvents and introduction of fluorinated substituent into the phthaocyanine core did not showed pronounced effect on the Q absorption band in the UV-visible spectra of these phthalocyanines.

1.2.6.2 Fluoroalkoxyphthalocyanines

Kondratenko et al. have reported that the introduction of fluoroalkoxy (e.g. 76) group in place of trifluoromethyl moiety markedly increase the solubility of phthalocyanines. Phthalocanines obtained by the methods described in the scheme-7 were found to be soluble many common organic solvents with optical properties similar to that of tetra-tert-butylphthalocyanines. The first oxidation potential values of phthalocyanines substituted with fluoroalkoxy groups were found to be higher than tetra-tert-butylphthalocyanines.
4-Chlorosulfonylphthalonitrile was esterified by treating it with fluoro-substituted alcohols to afford polyfluoroalkoxysulfonylethanolamines which were then transformed into 2,9(10),16(17),23(24)-tetrakis(fluroalkoxysulfonyl)phthalocyanines (e.g. 77)\(^{129}\) (Scheme-8). High solubility of these phthalocyanines in common organic solvents have made them potential candidates to be used in 'homogenous catalytic reactions.'

**Scheme-7: Synthesis of fluoroalkoxy phthalocyanines.**
Scheme-8: Synthesis of fluoroalkoxy sulfonylphthalocyanines

1.2.7 Nitrophthalocyanines

Nitro moiety can be introduced both at α and β position to obtain phthalocyanines containing four nitro groups.\textsuperscript{49,112,130} Lunardi and others\textsuperscript{108,131} have reported the synthesis of both 1,8(11),15(18),22(25)- and 2,9(10),16(17),23(24)-tetranitrophthalocyanine (\textit{e.g.} 78) from 3-, 4-nitrophthalonitriles respectively (scheme-9).

Negrimovsky and his coworkers in 1991 prepared transition metal based 1,3,8(11),10(9),15(18),17(16),22(25),24(23)-octanitrophthalocyanines from 3,5-dinitrophthalonitrile.\textsuperscript{132} Unusual redox properties were observed in phthalocyanines substituted with eight nitro groups at α and β positions resulted. These compounds showed reduction potential nearly equal to 1 V more positive as compared to those phthalocyanines with alkyl substitutions.\textsuperscript{133} Transition metal octa-nitrophthalocyanines were found to be very labile towards reduction. Cobalt (II) complex of octanitrophthalocyanine can be easily reduced in DMF containing traces of dimethylamine to Co (I) complex.
Scheme-9: Synthesis of nitrophthalocyanines.

The lack of oxidative tendency of 1,3,8(11),10(9),15(18),17(16),22(25),24(23)-octanitrophthalocyanine complexes make them as the most appropriate choice in oxidative catalytic reactions. However low solubility of 1,8(11),15(18),22(25)- and 2,9(10),16(17),23(24)-tetranitro-, and 1,3,8(11),10(9),15(18),17(16),22(25),24(23)-octanitrophthalocyanines in organic solvents is one of the major issue confronted in the use of these complexes. This problem has stimulated many workers to synthesize nitro substituted phthalocyanines with greater solubility in organic solvents. These efforts has resulted in the synthesis of 1,8(11),15(18),22(25)-tetranitro-3,10(9),17(16),24(23)-tetra-tert-butylphthalocyanines. Cyclotetramerization of 5-tert-butyl-3-nitro-phthalonitrile afforded the desired complex with high solubility in organic solvents.
1.2.8 Sulfophthalocyanines and their derivatives

Sulfo, alkoxy sulfo, aminosulfonyl, chlorosulfonyl etc. substituted phthalocyanines represent an important class of phthalocyanines dyes. They are mostly used in textile, printing, photodynamic therapy and as catalysts. General synthetic route for the synthesis sulfoacid based phthalocyanines is described in scheme-10. Sulfonation of phthalocyanines core can be conveniently carried achieved in trichlorobenzene using chlorosulfonic acid as sulfonating agent. Metal free sulfonated phthalocyanines or their alkali salts can be metallated by treating them with suitable metallating agent containing metal.\(^\text{136}\)

Water soluble phthalocyanines are very useful in photodynamic cancer therapy.\(^\text{20,137}\) The sodium salt of hydroxyaluminium trisulfophthalocyanine is being used in Russia for the treatment of various cancers for almost fourteen years. Sodium salt of non-metallated trisulfophthalocyanine is under preclinical studies.\(^\text{138}\) The \(\text{SO}_2\text{NR}^1\text{R}^2\) moieties render high solubility to the phthalocyanines without affecting the absorption spectra to any appreciable extent.\(^\text{139}\) Dicyanobenzenesulfonamides (79) are the starting materials for the synthesis of these aminosulfonylatedphthalocyanines (80). Another route is the direct condensation of chlorosulphonyl substituted phthalocyanine with amines (Scheme-10). The condensation of chlorosulfonylphthalocyanine with amino functionalities on polymeric species may lead to the heterogenization of transition metal based phthalocyanines.\(^\text{140}\) These heterogenous phthalocyanines have found wide range applications as heterogenous catalyst. They are being used in the oxidation of organic thiols to disulfides (Merox Process).\(^\text{141}\)
Scheme-10: Synthesis of chlorosulfonylphthalocyanines.

Phthalocyanines substituted with specially designed substituents at peripheral positions can also be used in pH sensors and photovoltaic cells. Derkachera and Kozentsova, working separately, have synthesized rhodamine-phthalocyanine conjugates (e.g. 81) and have claimed that the conjugates exhibit different optical and electron transfer properties at different pH values. Rhodamine moiety in these conjugates exists in lactam form in neutral
and alkaline medium and the absorption spectra (Q and B absorption bands) followed the same typical pattern of unsubstituted phthalocyanines showing no influence of rhodamine in close form. However in acidic media an additional absorption band around 530 nm may be observed due to conversion of lactam ring into open ionic form.

\[ R = \begin{array}{c}
\text{(open form)} \\
\text{(closed form)} 
\end{array} \]

**1.2.8.1 Alkyl- and Arylsulfonyl and -sulfinylphthalocyanines**

Alkyl and Arylsulfonyl and sulfinyl substituted phthalocyanines can be generated by cyclotetramerization of appropriate phthalonitriles and aminoisoinoisoidolenines, or by the oxidation of alkylsulfanyl and arylsulfanyl groups linked to phthalocyanines. Alkyl- and arylsulfanyl substituted phthalocyanines can be easily generated by treating nitro or chloro substituted phthalonitrile with alkyl or arylthiols in DMSO under basic conditions followed by cyclotetramerization of the resultant alkylsulfanyl or arylsulfanyl substituted phthalonitriles. Octakis(alkylsulfonyl)phthalocyanines have been prepared generated by oxidation of 2,3,9,10,16,17,23,24-
octakis(alkylsulfanyl)phthalocyanines (82) with \( m \)-chloroperoxybenzoic acid in dichloromethane.\(^{147}\)

\[
\begin{align*}
\text{RO}_2\text{S} & \quad \text{SO}_2\text{R} \\
\text{RO}_2\text{S} & \quad \text{SO}_2\text{R} \\
\text{RO}_2\text{S} & \quad \text{SO}_2\text{R} \\
\text{RO}_2\text{S} & \quad \text{SO}_2\text{R}
\end{align*}
\]

(82)

1.2.9 **Carboxyphthalocyanines and their derivatives**

Phthalocyanines with carboxylic group or derived functionalities constitute another group of phthalocyanines. 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines (84) can be synthesized by heating pyrometric imide (82) or anhydride (83) with urea and metal salts at high temperature followed by basic hydrolysis of the resultant products (Scheme 10) along with some polymeric by-products.\(^{148}\) The same carboxyphthalocyanine can also be obtained by hydrolysis of the 2,3,9,10,16,17,23,24-octacyanophthalocynine a templated cycloteramer of 1,2,4,5-tetracyanobenzene.\(^{149}\) The octacarboxyphthalocyanines can be converted to corresponding phthalocyanines anhydrides on heating in vacuum. **Scheme-11**
Opris and his coworkers\textsuperscript{150} have introduced another methodology for the synthesis of the octacarboxyphthalocynines. Diamyl 4,5-dicyanophthalate\textsuperscript{85} was prepared and tetramerized into phthalocynine octaesters \textsuperscript{86} in the presence of metal salts and then hydrolysed to 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines \textsuperscript{84}\textsuperscript{149} (Scheme 12).
Scheme-12: Synthesis of carboxyphthalocyanines by route 2.

Solov, eva and his coworkers\textsuperscript{150} have also reported the synthesis of phthalocyanine \textit{2,3,9,10,16,17,23,24,-octacarboxylate} using the similar methodology.

Sodium salt of cobalt complex of \textit{2,3,9,10,16,17,23,24-}octacarboxyphthalocyanine \textbf{(84)} is currently under clinical trial to be used in the catalytic therapy of cancer.\textsuperscript{151} Phthalocyanine carboxylic esters can be generated from esters of carboxyphthalonitriles\textsuperscript{152,153} or by the Esterification of carboxyphthalocyanines\textsuperscript{154,155} Some of the long chain alkoxy carbonyl moieties containing phthalocyanines have shown discotic liquid crystal properties.\textsuperscript{153}

Phthalocyanines containing tetra- and octacarboxamides have been reported to be prepared by the direct tetramerization of proper phthalic anhydride with metal salts (\textbf{scheme-13}).\textsuperscript{152,156} However \textit{N}-substituted \textit{2,3,9,10,6,17,23,24-}imides of octacarboxyphthalocyanines can be synthesized by two different
strategies (scheme-14). The first involves the reactions of primary amino functionality with phthalocynineoctacarboxylic tetraanhydride (83) (Scheme-12).\textsuperscript{143,144,157} Using this route α, β and γ-amino acids, di- and tripeptide etc. were made to react with 2,3,9,10,6,17,23,24-octacarboxyphthalocyanines (84) in N-methylpyrrolidone to yield water soluble anionic conjugates.\textsuperscript{158} The second involves the N-alkylation of N-unsubstituted phthalocyanines imides (82) in the presence of strong base (e.g. NaH) (Scheme-13).\textsuperscript{159}

\textbf{Scheme-13: Synthesis of carboxamidophthalocyanines rout 1.}

\textbf{Scheme-14: Synthesis of carboxyphthalocyanines by rout 2.}

Phthalocyanine-2,3,9,10,16,17,23,24-octacarboxamide can be synthesized by treating \textit{N}-unsubstituted phthalocyanines tetraimide with aqueous
ammonia.\textsuperscript{160} Phthalocynine-2,9(10),16(17),23(24)-teta and 2,3,9,10,16,17,23,24-octacarbboxamide can also be prepared directly by tetramerization of aminocarbonyl substituted phthalonitriles in the presence of metal salts.\textsuperscript{152,158a,161}

Cyclotetramerization of 1,2,4-tricyanobenzene and 1,2,4,5-tetracyanobenzene is good method for the synthesis of cyano substituted phthalocyanines. Many transition metal based phthalocyanines has been reported by this method.\textsuperscript{162,163} However oligomeric and polymeric phthalocyanines are also obtained. Nemykin et al\textsuperscript{164} have reported an efficient method for the synthesis of metal free cyano substituted phthalocyanines by reacting 1,2,4,5-tetracyanobenzene and sodium methoxide at room temperature with negligible hydrolysis of cyano moiety.

1.2.10 Phosphophthalocyanines and their derivatives

Only a few examples of this class are known. Protected phosphoric acid bearing phthalonitriles can be prepared from 4-halophthalonitrile as shown in the scheme-15.\textsuperscript{165}
Diethyl (3,4-dicyanophenyl)phosphonate on templated cyclotetramerization yield metallated and nonmetallated 2,9(10),16(17),23(24)-tetrakis-(diethoxyphosphonyl)phathalocyanines (88) which can be further hydrolysis to phosphophthalocynines (89) (Scheme-15).\(^{166}\) Direct phosphorylation of phthalocyanines can be achieved by heating the phthalocyanines with tert-butyl peroxide and dialkylphosphite.\(^{167,168}\)

### 1.2.11 Aminophthalocyanines

Tetraminophthalocyanines are found to be useful in the preparation of electrodes for electroanalytical reactions and as reagents for immobilization on chemically modified surfaces.\(^{169,170,171,172}\) Tetraaminophthalocyanines can be synthesized either by the hydrolysis of acylamino groups or by the reduction of nitro groups in appropriate tetra substituted phthalocyanines.\(^{173}\) Direct attempted
synthesis of tetraaminophthalocyanines from 4-aminophthalonitrile resulted in the formation of uncharacterized black polymer, however in the presence of urea 2,9(10),16(17),23(24)-tetraureidophthalocyanine (Scheme-16). It was observed that 3-aminophthalonitrile and metal salt on cyclotetramerization produced the desired complex (both in the presence or absence of urea). This difference in reactivity can be attributed to steric hindrance in 3-aminophthalonitrile due to which it cannot freely take part in the intermolecular nucleophilic attack on cyano moiety.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{CN} \\
\text{CN} & \quad \text{CN} \\
\text{H}_2\text{N} & \quad \text{CN} \\
\text{CN} & \quad \text{M} \\
\text{H}_2\text{NOCHN} & \quad \text{NHCONH}_2 \\
\text{NHCONH}_2 & \quad \text{H}_2\text{NOCHN} \\
\end{align*}
\]

(90)

**Scheme-16: Synthesis of aminophthalocyanines.**

Similar to tetra-amino substituted phthalocyanines, octasubstituted aminophthalocyanines can be prepared either by the reduction of octanitrophthalocyanines. Ahsen et al have reported the synthesis of nickel 2,3,9,10,16,17,23,24-octaaminophthalocyanine by the hydrolysis of octatosylamido phthalocyanine in concentrated sulfuric acid at 100 °C. Macrocyclization of 4,5-dicyano-N,N-ditosyl-o-phenylenediamine have generated metal free, zinc and nickel complexes of 2,3,9,10,16,17,23,24-octakis(tosylamido)phthalocyanines.

Derivitization of peripheral amino groups in aminophthalocynines is very rare. Quite a number of transition metal complexes like 1,8,15,22-tetrakis(3-phenylprop-2-enylideneamino)- and 1,8,15,22-tertrak...
anisylimino)phthalocyanines have been prepared by the condensation of $1,8(11),15(18),22(25)$-tetraaminophthalocyanines with cinnamaldehyde and p-anisaldehyde respectively. Yukse et al. have reported the synthesis of $2,3,9,10,16,17,23,24$-octahexanoyl- and octalauroylamidophthalocyanines by treating the tetraaminophthalocyanine with hexanoyl chloride and lauroyl chloride respectively.

Alkyl- or dialkylamino substituted phthalocyanines can be prepared by the cyclotetramerization of alkyl- or dialkylamino substituted phthalonitriles or phthalamides obtained from the reaction of nitro or bromo phthalonitriles or phthalamides respectively with amines. Celenk et al. have reported the synthesis of $2,3,9,10,16,17,23,24$-tetrakis(tetraaza)phthalocyanines in good yields from 4,5-tetraazamacrocyclic substituted precursors which were obtained from the substitution reaction between tosyl protected tetraaza macrocyclic compounds and 4,5-dichlorophthalonitrile.

1.2.12 Hydroxy, alkoxy and aryloxyphthalocyanines

Alkoxyc- and aryloxyphthalocyanines can be prepared by the template cyclotetramerization of respective phthalonitriles. A huge number of alkoxy- and
aryloxyphthalocyanines are reported in literature.\textsuperscript{182,183,184,185,186,187,162c} 1,8(11),15(18),22(25)-Tetra-, 2,9(10),16(17),23(24)-tetra-, and 2,3,9,10,16,17,23,24-octa substituted phthalocyanines are more common while 1,4,8,11,15,18,22,25-octa, dodeca- and hexadeca substituted phthalocyanines are rare. An important characteristic of phthalocyanines with alkoxy substituents is the basicity of meso-nitrogen which can be easily protonated even in water as compared with the unsubstituted Pcs.\textsuperscript{188} The protonation of alkoxy substituted phthalocyanines in organic solvent is accompanied by change in colour from green to brown.

2,9,(10),15(16),23(24)-Tetrahydroxyphthalocyanines (92) can be prepared either by metallation of free tetrahydroxyphthalocyanine with metal salt in DMF/Toluene mixture\textsuperscript{189} or by tetramerization of hydroxyphthalonitriles in the presence of metal salt at high temperature.\textsuperscript{190} Hydroxyl group into the phthalocyanine core can also be introduced by the diazotization of aminophthalocyanines followed by hydrolysis\textsuperscript{108a,163} Dealkylation of alkoxyphthalocyanines\textsuperscript{191,192,189,193} and by the desilylation of silylatedphthalocyanines.\textsuperscript{192d} Pierpont\textsuperscript{192d} and Kobayashi\textsuperscript{192e} have reported that hydroxyl group of 2,3,9,1016,17,23,24-octahydroxyphthalocyanines (93) can form chelation with metal atoms and thus have tendency to form stable assemblies of supramolecules.
1.2.13 Alkylsulfanyl- and Arylsulfanylphthalocyanines

The same synthetic methodology has been reported in the literature for the preparation of alkylsulfanyl and arylsulfanyl as is employed for the synthesis of alkyloxy and aryloxy substituted phthalocyanines. Alkylsulfanyl- and arylsulfanyl (mono, di, tri, tetra) substituted phthalonitriles can be prepared by the reaction of respective nitrophthalonitriles and halophthalonitriles by nucleophilic substitution with alkyl and aryl thiols. The alkylsulfanyl and arylsulfanylphthalonitriles have been converted to the respective alkylsulfanyl and arylsulfanyl substituted phthalocyanines. Due to greater electron donating tendency Q band of sulfanyl substituted phthalocyanines is observed at longer wavelength as compared to their phenoxy analogues. The Q bands of 1,8(11),15(18),22(25)-tetraphenylthiophthalocyanines occur in the near infra red region and are thus potential candidate for PDT applications.

In addition to the phthalocyanines described above a huge number of diad, triad, etc. with other dyes, and oligomer and polymer with phthalocyanine moieties have been prepared, characterized and studied for their potential applications.

The present study involves the synthesis of a variety of novel phthalocyanines and their potential applications in various fields.

1.3 Perylene-3,4,9,10-tetracarboxylic dianhydride

Perylene-3,4,9,10-tetracarboxylic dianhydride (93) is the parent compound of perylene-3,4,9,10-tetracarboxylic diimide derivatives which are abbreviated as PDIs and constitute a class of colorants both as dye and pigments. This nucleus [N,N'-dimethylperylene-3,4,9,10-tetratetracarboxylic diimide (94) was first introduced by Kardos in 1913 as industrial pigment. Since then a large variety of perylene derivatives ranging from red to black shades have been developed. Derivatization of perylene at imide N, N' positions 1, 6, 7 and 12 positions (bay
positions) induce different properties in the perylene pigments. These pigments possess high chemical, thermal and weather stability\textsuperscript{202,203} and therefore can be conveniently used in weather resistant paints. In addition PDI based paints show good migration stability after coating on plastic material, and can be over-coated onto the already painted surfaces. Perylene-3,4,9,10-tetracarboxylic acid diimide (PDI) based pigments are used where cost is outweighed by quality and durability of the colours\textsuperscript{202,203}. They are usually used in dyeing carpet fibers and in high-grade industrial paints. PDIs also possess other interesting properties including high fluorescence quantum yields, excellent photochemical stability and high degree of electron accepting potential which made them a very suitable choice in number of optical and electronic applications\textsuperscript{203,204,205,206,207,208,209,210,211,212,213} like fluorescent solar collectors\textsuperscript{14}, organic field-effect transistors\textsuperscript{213,214,215,216,217,218,219,220}, dye lasers\textsuperscript{209,210}, electrophotographic devices\textsuperscript{220}, organic photovoltaic cells\textsuperscript{214-219}, electric power limiters\textsuperscript{221,222} etc.. The remarkable reversible reduction ability, easily identifiable excited state, and anion and dianion absorption spectra of PDIs have played an important role for their extensive use these applications\textsuperscript{203,205,223,224,225,226,227}.

The starting raw material, perylene-3,4,9,10-tetracarboxylic acid can be prepared from 1,2-dihydrocenaphthalene\textsuperscript{202,203} (95) as described in Scheme-17. The oxidation of acenaphthalene (95) to 1,8-naphthalene dicarboxylic acid anhydride (96) followed by the reaction with ammonia yields 1,8-naphthalene dicarboxylic acid imide (97). The oxidative coupling of naphthalene-1,8-
dicarboxylic imide produce perylene-3,4,9,10-tetracarboxylic acid diimide (98) which is then hydrolyzed in the presence of sulfuric acid at 220 °C to obtain perylene-3,4,9,10-tetracarboxylic acid anhydride (93). A large number of perylene diimide (PDIs) with different aggregational behavior, solubility and shades have been synthesized by introducing different substituents at N, N', 1, 2, 5, 6, 7, 8, 11 and 12 positions of perylene-3,4,9,10-tetracarboxylic diimide. The introduction of different aryl and alkyl amines at N and N' positions affect the solubility of the molecule and the substitution of aromatic protons by different groups affects the optical and electronic properties.

![Scheme-17: Synthesis of symmetric perylene-3,4,9,10-tetracarboxylic diimide.](image)

Langhals et al.228, have reported that the introduction of certain alkyl and aryl substituents at the imide positions of PDI resulted in the increase solubility of the perylene based dyes in common halogenated organic solvents such as dichloromethane, chloroform and chlorobenzene. The introduction of N-aryl groups (with substitution at ortho positions) and amines having symmetrical long alkyl chains also enhances the solubility of these pigments229,230. This probably is
due to the limited π-π stacking because of the bulky groups. Other groups which render the perylene pigments water soluble are Newkome type carboxylates\textsuperscript{231}, phosphatic surfactants\textsuperscript{232}, polyglycerol dendrons\textsuperscript{233}, and cyclodextrin.\textsuperscript{234}

The successful synthesis of unsymmetrical PDIs is a complex process and involves number of steps. Iverson and Tam-Chang\textsuperscript{235} were the first to report the synthesis of unsymmetrical perylene pigments (103) involving partial hydrolysis of PTCDA (93) into anhydride-dicarboxylate salt (101) subsequently followed by successive imidization (Scheme-18). It has been reported that synthesis of perylene monoimide directly from PTCDA (93) is not possible. This can be attributed to the greater solubility of monoimide as compared to PTCDA in the reaction media with increased chance to react further to diimide (103).

\textbf{Scheme-18: Synthesis of unsymmetric perylene-3,4,9,10-tetracarboxylic diimide by route 1.}
Linder\textsuperscript{236} and others\textsuperscript{237,238,239,240}, have reported a convenient method for the synthesis of unsymmetrical perylene pigments (Scheme-19). This method involves the partial hydrolysis of symmetrical perylenetetracarboxylic diimide (100) to perylenedicarboxylic monoimide dicarboxylic monoanhydrides (102) followed by reaction with a second amine such as aniline to obtain desired unsymmetrical PDIs (103). This methodology is widely employed as it produces product in higher yield and requires easy purification technique.

![Scheme-19: Synthesis of unsymmetric perylene-3,4,9,10-tetracarboxylic diimide by route 2.](image)

Maki and coworkers\textsuperscript{241} have reported the synthesis of benzimidazole based perylene derivatives (104 & 105) by heating substituted and unsubstituted \textit{o}-phenylene diammunes with PTCDA in quinoline. It has been described in literature that this method produces a mixture of two inseparable regioisomers 104 & 105 (Scheme-20).\textsuperscript{242,243}
Scheme-20: Synthesis of benzimidazole based perylene derivatives.

The incorporation of substituent in the bay position of PDIs increases the solubility by disturbing the face to face \(\pi-\pi\) stacking due to the twisting of naphthalene half units and forcing out of the substituent from PDI plain. Rogovic\textsuperscript{244} was the first to report the successful synthesis of 1,6,7,12-chloro PDI. Chlorination of PTCDA at bay position was achieved by using \(\text{Cl}_2\) and sulfuric acid as shown in Scheme-21. Seybold and coworkers\textsuperscript{211} working at BASF synthesized water soluble PDIs (Scheme 22) by heating tetrachloro-PDIs with substituted or unsubstituted phenols in \(N\)-methylpyrrolidone as solvent in the presence of potassium carbonate.\textsuperscript{245} The preparation of 1,6,7,12-tetraflouro PDIs (107) have been reported by heating 1,6,7,12-tetrachloro PDIs (106) with potassium fluoride in sulfolane employing \(N,N\)-dimethylimidazolidinodi(tetramethyl guanidinium chloride or 18-crown-6 as catalyst. These fluoro derivatives (107) have found their application in OFETS as electron transport materials.\textsuperscript{246,247}
Scheme-21: Synthesis of tetrachloroperylene-3,4,9,10-tetracarboxylic diimide

Scheme-22: Synthesis of tetrafluoroperylene-3,4,9,10-tetracarboxylic diimide.

Bohm et al.\textsuperscript{248}, have developed the reaction conditions to brominate PDIs. Usually a mixture of mono, di and tri brominated products is obtained. Mono and tri bromo products can be separated by chromatography but 1,6 and 1,7 dibrominated PDIs are very difficult to separate and can only be recognized by using greater than 400 MHz NMR spectrometers.\textsuperscript{249} It has been described in literature that pure dibromo PDIs can be isolated by repeated crystallization. Recent studies have shown that dibromo contaminated with mono- and tribromo PDIs can be synthesized at room temperature by mixing bromine with perylenetetracarboxylic diimides in common organic solvents \textit{i.e} dichloromethane. With proper control of reaction condition and the bromine quantity mono bromo- PDIs can be isolated in good yields, however under
forcing conditions *i.e.* heating at 50 °C dibromo PDIs can be obtained in good yield (79%).250 Synthesis of 1,6,7,12-tetrabromo PDIs have also been described in literature. The synthesis involves the tetrabromination of PTCDA under aggressive conditions followed by amidation.251,252 The substitution of these bay bromines by other nucleophiles is very easy. Nucleophiles like phenols228, amines253, cyanides213 and fluorides246 can be easily coupled with brominated PDIs (Scheme 23). In addition metal catalyzed C-C couplings like Suzuki254,255, Sonogashira and Stile coupling250,256 has also been reported (Scheme 23). This substitution or coupling at bay positions enhances the solubility by reducing the π-π stacking of PDIs as the presence of long chain or bulky groups forces the PDIs out of plane with respect to each other and thus reduces their aggregation.
Scheme-23: Coupling of PDIs with phenols, amines, cyanides, fluorides etc.

Nakazono et al.\textsuperscript{257,258} have reported the synthesis of aryl and alkyl substituted PDIs (117) at 2,5,8 and 11 positions by the activation of C-H bond
using ruthenium metal as catalyst (Scheme-24). They have reported that alkyl substituted PDIs showed better quantum yields, good solubility and lesser degree of distortion from planarity as compared to PDIs substituted at bay positions.

\[
\begin{align*}
\text{Scheme-24: Synthesis of aryl and alkyl substituted PDIs.}
\end{align*}
\]

Pasaogullari and coworkers\(^{259}\) synthesized a series of symmetrical and unsymmetrical novel PDIs by coupling perylene-3,4,9,10-tetracarboxylic acid dianhydride with dodecylamine, octadecylamine, 1,12-diaminododecane, p-phenylenediamine, p-chloroaniline, p-aminophenol (Scheme-25) and studied their physical properties. The structures of synthesized compounds were confirmed by Vis-UV, IR, MS techniques and their thermal stability was determined using TGA and DSC techniques. Although perylene derivatives in general are characterized by poor solubility but studies indicated that symmetrical derivatives possess slightly better solubility as compared to the unsymmetrical ones. All the perylene derivatives have shown almost same fluorescent life times, other physical characteristics like colour, thermal stability
and aggregational behavior with slight variation depending on the nature of the substituents.

\[
\begin{align*}
\text{(93)} & \\
\text{(100)} & \\
\text{(102)} & \\
\text{(118)} & \\
\text{(103)} & 
\end{align*}
\]

\[
R = (\text{CH}_2)_n\text{CH}_3, \ (\text{CH}_2)_m\text{NH}_2, \ (\text{CH}_2)_n\text{CH}_m, \ p\text{-Aminophenyl, } p\text{-Chlorophenyl, } p\text{-Hydroxyphenyl.}
\]

\[
R_1 = \text{H, } p\text{-Hydroxyphenyl.}
\]

\[
R_2 = (\text{CH}_2)_n\text{CH}_3, \ (\text{CH}_2)_m\text{NH}_2, \ (\text{CH}_2)_n\text{CH}_m, \ p\text{-Aminophenyl, } p\text{-Chlorophenyl, } p\text{-Hydroxyphenyl.}
\]

**Scheme-25: Coupling of PDIs with different amines.**

Perylene core containing \(N,N\)-dialky (e.g. 119) or diaryl substituents shows absorption maxima at 525 nm with maximum absorptivities in the range of \(10^5 \text{ M}^{-1} \text{ cm}^{-1}\). Example of the typical absorption and emission spectra is shown in the **figure-3a** which shows small Stokes shift and appear as mirror image of
each other in solvents like chloroform and toluene. In most of the cases the fluorescence quantum yields approach unity and life times of singlet excited state are approximately 4 ns. Due to the long excited state life times they have found utility in photon-induced optical limiting applications.

\[
\begin{align*}
&\text{C}_{11}\text{H}_{23} - \text{N} - \text{C} - \text{O} \\
&\text{C}_{11}\text{H}_{23} - \text{C} - \text{N} - \text{C} - \text{O} \\
&\text{C}_{11}\text{H}_{23} - \text{C} - \text{N} - \text{C} - \text{O} \\
&\text{C}_{11}\text{H}_{23} - \text{C} - \text{N} - \text{C} - \text{O} \\
\end{align*}
\]

\((119)\)

**Figure-3a** UV-vis absorption (solid line) and emission (dashed line) spectra of a typical PDI in toluene.

This \(S_0 \rightarrow S_1\) transition is attributed to HOMO \(\rightarrow\) LUMO excitation of simple PDI based on DFT calculations is quite similar to that suggested by computational methods. The orbital symmetries suggested that optical transition is polarized along the N-N molecular axis. The orbitals suggested that the nitrogen atoms are positioned on the nodal plane of both the HOMO and LUMO that is why the effects of imide substitution on frontier orbital energies are predicted to be inductive leading to slight change in optical
properties. The variation in absorption and emission spectra in case of \( N,N' \) aryl or alkyl substituted PDIs is just 5 nm. However significant bathochromic shift was observed in the spectra of benzimidazole annulated derivatives of perylene due to extensive delocalization of HOMO onto the terminal arylene groups as suggested by MO caculations\(^{263,262}\). Both the absorption and emission spectra is significantly affected in case of substitution on the perylene core. suggests significant coefficients, in both HOMO and LUMO, on the bay positions as well as 2, 5, 8 and 11 positions. It is expected that HOMO is destabilized by \( \pi \)-donor while LUMO is stabilized by \( \pi \)-acceptor substituents resulting in the bathochromic shift of the spectra in both cases. It has been shown that steric factors due to the bay position substituents can result in the twisting of the core which leads to hypsochromic shift. PDIs substituted with 1,7-diphenoxy \( \pi \)-donor substituents show vibronic structure almost similar to PDIs without bay substitution but show bathochromic shift of 20-40 nm, accompanied by the change of fluorescence colour from yellow or yellow green to orange. More significant shifts are observed in case of stronger \( \pi \)-donor groups for example 1,7-dipyrrolidino substitute PDIs shows dark green colour in both solid state and in solution. It shows bathochromic shift of more than 150 nm as compared to unsubstituted analogues. These compounds develop amino-to-PDI quadrupolar charge transfer and consequently these compounds are solvatochromic and their fluorescence quantum yields are much decreased.\(^{260,264,253}\) Due to weak \( \pi \)-donor character fluoro, chloro and bromo compounds show no significant change in bathochromic shift (only few nm) and charge transfer.\(^{260,246,265,213}\) Substitution by cyano group also have no significant effect on fluorescence quantum yields inspite of their \( \pi \)-donor ability, this is probably due to the mismatch in the energy of PDI and CN-localized orbitals resulting in difference in stabilization of LUMO relative to HOMO. Addition of groups at bay position with extended conjugation results in bathochromic shift. No change in vibronic spectra was observed in case aryl and arylethynyl groups with para substituents ranging from moderately \( \pi \)-donating to \( \pi \)-acceptor groups.\(^{225,226,266}\)
Strong pi-donor groups like p-aminophenyl, (p-aminophenyl)ethynyl, oligothiophene-based moieties, etc produce spectra with a band in the range 460-530 nm and broad structureless band in the range of 600-720 nm. Calculations based on molecular orbital treatment have shown that HOMOs of these molecules are localized on the donor substituent while the LUMOs are similar to simple PDIs. Thus strong donor to PDI charge transfer develops in low energy bands. PDIs bearing oligothiophene at bay position also exhibit similar type of spectra.\textsuperscript{214,218,267,268,269,270} Such compounds have low fluorescence quantum yields.\textsuperscript{266,271,272} in addition to short excited state lifetimes.\textsuperscript{225,271,272}

Optical properties are greatly influenced by the electronic nature of aryl substituents at 2,5,8 and 11 position of PDIs\textsuperscript{257,76}. For instance $p$-($N,N$-dimethylamino)phenyl moieties at 2,5,8 and 11 positions show abroad band in the range of 600-700 nm with fluorescence quantum yields approaching almost zero. (e.g. tetrakis($p$-(n,n-dimethylamino)phenyl)-substituted PDIs).\textsuperscript{257} Annulation affects the optical properties of PDI core in a variety of ways e.g. the spectra of coronene diimides shows hypsochromic shift while spectra pyridine fused PDIs remain unaffected.\textsuperscript{273}

Aggregation affects the vibronic structure of absorption and fluorescence spectra. As a result the optical properties of bay-substituted and unsubstituted PDIs are greatly affected by concentration, solvent polarity and temperature.

1.3.1 Redox properties

It has been shown that $N,N'$-dialkyl or aryl PDIs having no core substitution shows two reversible reduction waves (at 1.0 and -1.2 V vs FeCp$_2$ $^{+0}$) and only one reversible oxidation wave (at +1.2 V) in suitable solvent.\textsuperscript{260,213,253,274,275} Introduction of $N,N'$-di-pentafluorophenyl groups in place of diphenyl or diaryl enhances the reduction by only 0.11 V.\textsuperscript{203,276} Imide nitrogen resides on the nodal plane in the LUMO (and HOMO) and change in orbital energies is relayed through nitrogen atom. In contrary the core substitution in
PDIs with strong electron withdrawing groups like cyano and fluoro increase their reduction potential by 0.3-0.4 volts\textsuperscript{260,213} and decrease their oxidation potential by the same value. These changes can be attributed to the inductive effect of the cyano and fluoro on the frontier orbitals and thus both have significant coefficient on carbon atoms to which they are attached. On the other hand substituents with pi-donating ability at bay positions like pyrrolidino moiety decrease the reduction potential of PDIs by 0.3 V and enhance the oxidation potential by 1.0 volts than bay-unsubstituted analogues.\textsuperscript{203,277,274}

Nature of the substitution at 2,5,8,11 position also alter the redox properties significantly.\textsuperscript{257} The presence of electron donor groups cause cathodic shift and the induction of electron withdrawing group results in the anodic shift of reduction potential of PDIs.

### 1.3.2 Solid State Structure and Self –Assembly

Another important aspect which has been studied comprehensively is the molecular packing of perylene diimides. Crystal studies have shown that planar diimides form π stacking with interplanar distance almost similar to that in graphite (3.4 Å).\textsuperscript{260,236,278,279} The π stacking is greatly influenced by the nature of the substituents at imide positions resulting in the alteration of intermolecular interactions of the π system of the crystal lattice which leads to the change in colour of the PDIs in the solid state from red to nearly black.\textsuperscript{260,280} Substitution at bay position often results in the loss of planarity which disturbs the pi stacking in the solid state.\textsuperscript{211,281,282}

### 1.3.3 Photo-Induced Electron Transfer

Wasielewski and Lindsey carried out extensive study on the electron transfer in molecules having porphyrins linked with perylene diimides (e.g. 120).\textsuperscript{223,224,274,283,284} Wasielewski\textsuperscript{225} reported that photoexcitation of diporphin perylenediimide at 585 nm results in the formation of D^+ - A^- - D (Donor-Acceptor-
Donor) with rate constant $1.1 \times 10^{11} \text{ s}^{-1}$ followed by charge recombination of $9.1 \times 10^9 \text{ s}^{-1}$. In case of excitation at 580 nm double charge separation occurs with the formation of $D^+ - A^{-2} - D^+$ with charge separation rate constant of $5.6 \times 10^9 \text{ s}^{-1}$ and charge recombination rate constant of $2.2 \times 10^8 \text{ s}^{-1}$, which is quite lower than single charge separated states. As radical anion and dianion show different absorption behavior, therefore they can be used as light-intensity dependent optical switches in photovoltaic systems.

![Diagram of 120]

It has been reported in literature that zinc tetraphenylporphyrin$^{283}$ having four PDI substituent has four time greater rate of charge separation and 1.4 times slower charge recombination rate than 121. Compound 121 self assembles into nano particles in solution with twelve molecules in each nano particle.$^{283}$

![Diagram of 121]
The absorption spectra of photogenerated PDI anion suggested the delocalization of negative charge from PDI\(^1\) on the PDI. However the the optical and redox properties suggested that having a spacer (phenylene) between porphyrin and PDI donot show strong electronic coupling probably due to the twisting of PDI. Perylene with ethylene linked porphyrin at two bay positions show strong donor acceptor interaction.\(^{223,284}\) Photoinduced electron transfer has also been reported in dyads made up of zinc phthalocyanines-PDI system (122)\(^{227}\). Photoexcitation in 122 provided triplet excited state (ZnPc-\(^3\)PDI*) whereas the photoexcitation of 122 in the presence of Mg\(^{+2}\) produced state which have lifetime as long as 240 micro seconds. This long life time is attributed to the complex formation between PDI anion and Mg\(^{+2}\) having lower energy than ZnPc-\(^3\)PDI*. The lifetime of the excited states in case of Pc-PDI-Pc is just 0.5 ns with no substantiation of PDI triplet states. Wasielewski et al have recently described the light induced solvent dependent charge transfer of dyad.\(^{285,286}\)

![Image](image.png)

122

Literature has shown that PDIs coupled with weak donor systems generate charge separated states having longer life time with absorption spectra indicating strong absorption bands at 720 and/or 550 nm respectively.\(^{210,223}\) PDIs without substitution at bay positions show no absorption in near infra red region, therefore these photo-generated ions can be applied in ‘optical limiting application’ at those wavelength where radical anions show stronger absorption.\(^{287,288}\)
1.3.4 PDIs in Organic Electronics

**OFETs:** Due to high electron affinity values PDIs (e.g. 123) can be used as active layer of n-channel field effect transistors. Horowitz was the first to report the use of PDIs employing vacuum deposited 123 with electron mobilities $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Horowitz et al. reported that OFET devices with fluoro substituted PDIs show high electron mobilities in the vacuum and air (e.g. 124).

![Image of PDIs 123 and 124]

Chen et al. described that $N,N'$-bis(fluorophenyl)-substituted perylene diimides (e.g. 124) proved to be air stable materials in n-channel OFETs. Fluoro substituted PDIs showed higher air stability as compared to unsubstituted PDIs due to better molecular packing thus the effectively prevent the penetration of water and oxygen.

Bay substituted dicyano PDIs (e.g. 125) have also been studied as active materials in n-channel OFETs. These PDIs showed much higher electron affinity in addition to good solubility.

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*Chapter – 1*  
*Introduction*  

71
Chapter – 1

Introduction

125
Chapter – 1

MATERIALS & METHODS
Chapter – 2  
Materials & Methods

2- MATERIALS AND METHODS

2.1 Chemicals and Instruments

All the chemicals were purchased from Sigma Aldrich and Merck and used without further purification. All the organic solvents are of research grade and distilled prior to use.

$^1$H NMR spectra were taken in DMSO-$d_6$ and recorded at 300 and 400 MHz on a Brucker/XWIN-NMR instrument. Chemical shifts are given in ppm relative to $(\text{Me})_4\text{Si}$ or deuterated solvents as internal standard. Mass spectra were recorded on Jeol MS Route and IR spectra were measured on Perkin Elmer FTIR Spectrometer Spectrum RX 1 as KBr pellets. UV absorption spectra were recorded in sulfuric acid from Perkin-Elmer spectrophotometer. Elemental analyses were performed in H.E.J. Research Institute, Karachi University, Karachi. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

2.2 Synthetic Work

2.2.1 General method for the preparation of substituted phthalodinitrile:

Dihaloalkane (178 mmol) was added to the suspension of 4-aminophthalonitrile (5.0 gm, 35 mmol) in anhydrous DMF (20ml) containing $\text{K}_2\text{CO}_3$ (4.83 gm, 35 mmol). The resulting mixture was heated at 100 °C for 5 hours. The reaction mixture was diluted with cold water and the precipitates were filtered, washed with excess of water and dried in vacuum desiccator.
2.2.1.1 4-(Pyrrolidin-1-yl)phthalonitrile (126):

![Chemical Structure of 4-(Pyrrolidin-1-yl)phthalonitrile (126)]

The 4-(pyrrolidin-1-yl)phthalonitrile (126) was prepared from 1,4-dibromoalkane (25.4g, 178 mmol) using a procedure as described in general method 2.2.1.

Yield: 63%
m.p: 132 °C.
Colour: Light green.
FT-IR (KBr) ν (cm⁻¹): 3083(Ar CH), 2956(CH₂), 2860, 2232(CN), 1605, 1507.
¹H NMR (300 MHz, DMSO-d₆): δ = 7.73 (d, J = 8.8 Hz, 1H, ArH-5) 7.12 (d, J = 2.4 Hz, 1H, ArH-3), 6.84 (dd, J = 8.8 Hz, 2.4 Hz, 1H, ArH-6), 3.3 (t, J = 6.5 Hz, 4H, 2CH₂), 1.97-1.93 (m, 4H, 2CH₂).
¹³C NMR: 24.6 (2C), 47.2 (2C), 108 (C), 113 (2C), 116 (C), 117 (C), 118 (C), 123 (C), 158 (C).
ES-MS m/z: 197 (M⁺, 29.5%), 183 (6.9), 169.0 (25.0), 156 (100), 155 (9.5), 141 (11.0), 127 (17.1).
CHN: C₁₂H₁₁N₃ Calculated: C, 73.07; H, 5.62; N, 21.30. Found: C, 72.95; H, 5.57; N, 21.18.

2.2.1.2 4-(Piperidin-1-yl)phthalonitrile (127):

![Chemical Structure of 4-(Piperidin-1-yl)phthalonitrile (127)]

The 4-(piperidin-1-yl)phthalonitrile (127) was synthesized from 1,5-dibromoalkane using a general procedure described above.
Yield: 67%

m.p: 141 °C.

Colour: Light green.

FT-IR (KBr) v (cm⁻¹): 3071 (Ar CH), 2951(CH₂), 2855, 2234(CN), 1634, 1501.

¹H NMR (300 MHz, DMSO-d₆): δ = 7.72 (d, J = 8.7 Hz, 1H, ArH-5) 7.11 (d, J = 2.4 Hz, 1H, ArH-3), 6.72 (dd, J = 8.7 Hz, 2.4 Hz, 1H, ArH-6), 3.4 (t, J = 6.7 Hz, 4H, 2CH₂), 1.76-1.71 (m, 6H, 3CH₂).

¹³C NMR: 24.4 (C), 24.8 (2C), 47.3 (2C), 108 (C), 115.6 (2C), 116 (C), 117 (C), 118 (C), 125 (C), 163 (C).

ES-MS m/z: 211 (M⁺, 22.5%), 197 (4.3), 183 (4.1), 169.0 (27.4), 156 (100), 155 (10.5), 141 (8.2), 127 (12.2).

CHN: C₁₃H₁₃N₃ Calculated: C, 73.91; H, 6.20; N, 19.89. Found: C, 73.74; H, 6.10; N, 19.78.

2.2.1.3 4-(Azepan-1-yl)phthalonitrile (128):

![Chemical Structure](image)

4-(Azepan-1-yl)phthalonitrile (128) was prepared from 1,6-dibromoalkane using a general procedure as above.

Yield: 61%

m.p: 153 °C.

Colour: Light green.

FT-IR (KBr) v (cm⁻¹): 3081( Ar-H), 2953 (CH₂), 2856, 2233 (CN), 1601, 1507.

¹H NMR (300 MHz, DMSO-d₆): δ = 7.68 (d, J = 8.7 Hz, 1H, ArH-5) 7.10 (d, J = 2.5 Hz, 1H, ArH-3), 6.65 (dd, J = 8.7 Hz, 2.5 Hz, 1H, ArH-6), 3.2 (t, J = 6.7 Hz, 4H, 2CH₂), 1.76-1.64 (m, 8H, 4CH₂).
13C NMR: 26 (2C), 29 (2C), 48 (2C), 110 (C), 116 (2C), 117 (C), 118 (C), 119 (C), 126 (C), 161 (C).

ES-MS m/z: 225 (M⁺, 23.0%), 211 (17.0), 197 (7.6), 183 (4.7), 169.0 (31.1), 156 (100), 155 (21.1), 141 (9.9), 127 (7.3).

CHN: C₁₄H₁₅N₃ Calculated: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.56; H, 6.61; N, 18.60.

2.2.2  4-(Bromomethyl)phthalonitrile (129):

\[
\text{Br} \quad \text{CN} \quad \text{CN}
\]

A solution of 4-methylphthalonitrile (1.42 gm, 10 mmol), N-bromosuccinimide (2.04 gm, 11.5 mmol) and catalytic amount of benzoyl peroxide (0.03 mmol) in carbon tetrachloride (10 mL) was heated at 50 °C and stirred in the presence of bright sunshine for two hours until the all NBS was converted to succinimide and start floating on the top. Then Succinimide was removed by filtration and the residue was washed with CCl₄. The solvent was removed under reduced pressure to obtain red oil residue which was purified by chromatography on silca column using dichloromethane as eluent to get pure 4-(bromomethyl)phthalonitrile as reddish liquid which solidify on standing.

Yield. 50 %
m.p.62 °C.

FT-IR (KBr) δ (cm⁻¹): 3081, 2831, 2230, 1606, 1503

¹H NMR (300 MHz, CHCl₃-d): δ = 7.85 (d, J = 1.6 Hz, 1H, ArH₃), 7.79 (d, J = 8.1 Hz, 1H, ArH₅), 7.72 (dd, J = 8.1 Hz, J = 1.6 Hz, 1H, ArH₅), 4.46 (s, 2H, Ar CH₂ Br).

ES-MS m/z: 220 (M⁺, 50%), 222 (48), 141 (20), 127 (15).

CHN: C₉H₇BrN₂. Calculated: C, 48.90; H, 2.28; N, 12.67. Found: C, 48.60; H, 2.58; N, 12.69.
2.2.3 4-((6-Hydroxyhexylamino)methyl)phthalonitrile (130)

6-Aminohexan-1-ol (2.34 gm, 20 mmol) was added to the ice cold solution of 4-(bromomethyl)phthalonitrile (3.0 gm, 13.57 mmol) containing K$_2$CO$_3$ (3.58 gm, 20 mmol) in DMF (10ml) and the reaction mixture was stirred at room temperature for twelve hours and then diluted with cold water. The precipitates were filtered and washed with excess of water. The residue was dried in vacuum desiccator and used as such without further purification.

Yield: 61%.
m.p: 149 °C.

FT-IR (KBr) ν (cm$^{-1}$): 3433 (OH), 3395 (NH), 3083 (Ar-H), 2957 (N(CH$_2$)), 2235 (C≡N), 1607, 1499.

Colour: White solid.

$^1$H NMR (400 MHz, DMSO-d$_6$): δ = 7.81 (d, $J = 1.4$ Hz, 1H, ArH), 7.75 (d, $J = 7.9$ Hz, 1H, ArH), 7.69 (dd, $J = 7.9$, 1.4 Hz, 1H, ArH), 3.99 (s, 2H, NCH$_2$), 3.65 (t, $J = 7.1$ Hz, 2H, HOCH$_2$) 2.65 (t, $J = 6.8$ Hz, 2H, NCH$_2$), 1.80-1.75 (br.s, 2H, OH & NH), 1.52-1.47 (m, 4H, 2CH$_2$), 1.40-1.35 (m, 4H, 2CH$_2$).

ES-MS m/z: 257.1 (M$^+$, 10%), 239.1 (21), 212 (18), 141 (16).

CHN: C$_{15}$H$_{19}$N$_3$O. Calculated: C, 70.01; H, 7.44; N, 16.33. Found: C, 70.31; H, 7.14; N, 16.23.
2.2.4: 4-((9,10-Dioxo-9,10-dihydroanthracen-2-ylamino)methyl)phthalonitrile (131)

![Chemical Structure](image)

4-(Bromomethyl)phthalonitrile (1.5 gm, 6.7 mmol) was added to the ice cold suspension of 2-amino-anthraquinone (13.5 mmole, 3.0g) and K$_2$CO$_3$ (1.8 gm, 10 mmol) in DMF (25 mL) and was first stirred at room temperature for two hours and then at 80 °C for twenty four hours. After the completion of reaction, the mixture was diluted with cold water and precipitates were filtered and washed with excess of water. The precipitates were then dried in vacuum dessicator.

Yield: 59 %.

m.p: 163 °C.

Colour: Dark Red.

FT-IR (KBr) $\nu$ (cm$^{-1}$): 3394 (NH), 3086 (Ar-H), 2952 (CH$_2$), 2233 (C≡N), 1671 (C=O), 1612, 1504.

$^1$H NMR (400 MHz, DMSO-d$_6$): $\delta = 8.2$ (m, 2H, Ar-H), 8.17 (d, $J = 6.3$ Hz, 1H, ArH), 7.95 (m, 1H, ArH), 7.89 (m, 1H, ArH), 7.80 (m, 1H, ArH), 7.52-7.46 (m, 2H, ArH), d 7.36 (m, 1H, ArH), 6.91 (s, 1H, ArH), 6.71 (t, $J = 6.1$ Hz, 1H, NH), 4.34 (d, $J = 6.3$, 2H, NHCH$_2$).

ES-MS m/z: 363 (M$^+$, 12%), 222 (8), 156 (13), 337 (9).

Elemental Analysis: C$_{23}$H$_{13}$N$_3$O$_2$. Calculated: C, 76.02; H, 3.61; N, 11.56. Found: C, 75.81; H, 3.67; N, 11.27.
2.2.5: 4-\{1-[(4-Nitrophenyl)diazenyl]\}naphthalen-2-loxy\}methyl\)phthalonitrile (132)

1-[(4-Nitrophenyl)diazenyl]naphthalen-2-ol was added to the ice cold suspension of 4-(bromomethyl)phthalonitrile (3.0 gm, 13.57 mmol) and K$_2$CO$_3$ (3.58 gm, 20 mmol) in dry DMF(20 ml) and the mixture was stirred at 100 °C for ten hours. Then the reaction mixture was diluted with cold water and precipitates were filtered and washed with water. The residue was dried in vacuum dessicator to obtain dyes.

Yield: 49 %.
m.p: 165 °C.
Colour. Red
FT-IR (KBr) ν (cm$^{-1}$): 3081 (Ar-H), 2227 (C≡N), 1629 (N=N),1607, 1490, 1520 (NO$_2$), 1335 (NO$_2$).
$^1$H NMR (400 MHz, DMSO-d$_6$): δ = 8.31-8.18 (m, 4H, Ar-H), 7.80-7.60 (m, 5H, ArH), 7.3-7.2 (m, 2H, ArH), 7.98(d, 1H, ArH, j=7.7Hz), 7.51-7.48 (m, 1H, Ar-H), 5.37 (s, 2H, CH$_2$).
ES-MS m/z: 433 (M$^+$, 7%), 283 (11), 276 (15), 141 (15).
2.2.6: 4-({4-[(4-Nitrophenyl)diazenyl]naphthalen-1-yloxy}methyl)phthalonitrile (133)

![Chemical Structure](image)

4-({4-[(4-Nitrophenyl)diazenyl]naphthalen-1-yloxy}methyl)phthalonitrile (133) was synthesized by the same method as described for 132.

Yield: 53 %.
m.p: 161°C
Colour: Orange

FT-IR (KBr) ν (cm⁻¹): 3083 (Ar-H), 2233 (C≡N), 1625 (N=N), 1601, 1490, 1517 (NO₂), 1337 (NO₂).

¹HNMR (400 MHz, DMSO): δ =8.50 (d, 1H, Ar-H, J =7.6Hz), 8.40-8.25(m, 5H, ArH), 7.80-7.60 (m, 6H, ArH), 6.9(d, 1H, J=7.6Hz), 5.35 (s, 2H, CH₂),
ES-MS m/z: 433 (M⁺, 8%) 311 (15), 283 (12), 126 (27).

2.3 Synthesis of phthalocyanines:

2.3.1 Tetramethylphthalocyanines:

2.3.1.1 [2(3),9(10),16(17),23(24)-Tetramethylphthalocyanine (134)]

4-Methylphthalonitrile (5.68 gm, 0.04 mole) and sodium sulphide (0.012 g) in nitrobenzene (30 mL) was heated under reflux for 6 hours. After the completion of the reaction the resulting phthalocyanine was filtered under reduced pressure and the residue obtained was washed with methanol (100 mL), hot water and then dried in oven at 100 °C.

\[
\begin{align*}
\text{Yield: } & 58 \% . \\
\text{mp: } & > 300 ^\circ C \\
\text{Colour: } & \text{Blue.} \\
\text{FT-IR (KBr) } & \nu (\text{cm}^{-1}): 3403 (\text{NH}), 3081 (\text{Ar-CH}), 3050, 2959 (\text{CH}_3), 1690 (\text{C=N}), 1601, 1523, 1487, 1470, 1435, 1396, 1326, 1295, 1283, 1245, 1185, 1157, 1119, 1087, 995, 866, 755, 730, 683. \\
\text{UV/Vis (} & \lambda_{\text{max}}, \text{nm, H}_2\text{SO}_4): 233(0.30), 342,(0.33), 674 (0.40). \\
\text{ES-MS m/z: } & 571.2 [\text{M} + \text{H}]^+. \\
\text{CHN: } & C_{36}H_{26}N_{8}. \text{ Calculated C, 75.77; H, 4.59; N, 19.64. Found C, 75.62; H, 4.48; N, 19.55.}
\end{align*}
\]
2.3.2 M(II) Tetramethylphthalocyanines

General Method

Metal halide (0.01 mole) was added to the suspension of 4-methylphthalonitrile (5.68 gm, 0.04 mole) in nitrobenzene (20ml) and the resulting mixture was heated at reflux temperature for 6 hours. The complex formed was filtered under reduced pressure and washed with methanol (100 mL), hot water and dried in oven at 100 °C.

2.3.2.1 Copper(II) [2(3),9(10),16(17),23(24)-tetramethylphthalocyanine] (135):

Yield: 56 %.
mp: > 300 °C
Colour: Blue.
FT-IR (KBr) ν (cm⁻¹): 3089 (Ar-CH), 2961 (CH₃), 1698 (C=N), 1602, 1500, 1457, 1415, 1328, 1282, 1166, 1085, 1067, 897, 871, 799, 775, 752, 726.
UV/Vis (λ_max, nm, H₂SO₄): 340 (0.1.92), 665 (1.54).
ES-MS m/z: 632.1 [M + H]^+.
CHN: C₃₆H₂₄CuN₈. Calculated C, 68.40; H, 3.83; N, 17.73. Found C, 68.21; H, 3.75; N, 17.51.
2.3.2.2 Nickel(II) [2(3),9(10),16(17),23(24)-
tetramethylphthalocyanine] (136):

Yield: 53 %.
mp: > 300 °C.
Colour: Green.
FT-IR (KBr) ν (cm\(^{-1}\)): 3084 (Ar-H), 2965 (CH\(_3\)), 1695 (C=N), 1611, 1507, 1455, 1421, 1327, 1287, 1158, 1114, 1086, 911, 886, 770, 758, 723.
UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 342 (2.05), 663 (1.20).
ES-MS m/z: 627.1 [M+H]+.
CHN: C\(_{36}\)H\(_{24}\)NiN\(_8\). Calculated C, 68.93; H, 3.86; N, 17.86; Found C, 68.79; H, 3.75; N, 17.72.

2.3.2.3 Zinc(II) [2(3),9(10),16(17),23(24)-
Tetramethylphthalocyanine] (137):
Chapter – 2

Materials & Methods

Yield: 58 %.
mp: > 300 °C.
Colour: Blue.

FT-IR (KBr) v (cm\(^{-1}\)): 3085 (Ar-H), 2970 (CH\(_3\)), 1698(C=N), 1600, 1500 (C=C), 1460, 1415, 1325, 1285, 1158, 1112, 1065, 948, 864, 775, 751, 726.

UV/Vis (\(\lambda_{max}\), nm, H\(_2\)SO\(_4\)): 340 (3.74), 665 (3.23).

ES-MS m/z: 633.1 [M + H].

CHN: C\(_{36}\)H\(_{24}\)ZnN\(_8\). Calculated C, 68.20; H, 3.82; N, 17.67; Found C, 68.03; H, 3.69; N, 17.51.

2.3.2.4 Cobalt(II) [2(3),9(10),16(17),23(24)-tetramethylphthalocyanine] (138):

Yield: 55 %.
mp: > 300 °C
Colour: Violet.

FT-IR (KBr) v (cm\(^{-1}\)): 3079 (Ar-H), 2966 (CH\(_3\)), 1690 (C=N), 1604, 1517, 1484, 1420, 1326, 1284, 1153, 1115, 1024, 1085, 946, 911, 871, 778, 756.

UV/Vis (\(\lambda_{max}\), nm, H\(_2\)SO\(_4\)): 338 (1.74), 663 (3.18)

ES-MS m/z: 628.1 [M + H].

CHN: C\(_{36}\)H\(_{24}\)CoN\(_8\). Calculated C, 68.90; H, 3.85; N, 17.86. Found C, 68.59; H, 3.53; N, 17.50.
2.3.2.5: Plumbum(II) [2(3),9(10),16(17),23(24)-
tetramethylphthalocyanine] (139):

\[
\begin{array}{c}
\text{H}_3\text{C} - \text{N} - \text{N} - \text{N} - \text{Pb} - \text{N} - \text{N} - \text{N} - \text{N} - \text{CH}_3 \\
\text{H}_3\text{C} \\
\end{array}
\]

Yield: 51 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm\(^{-1}\)): 3082 (Ar-H), 2964 (CH\(_3\)), 1688 (C=N), 1602, 1500, 1457,
1415, 1324, 1292, 1166, 1085, 1067, 897, 877, 799, 775, 752, 724, 591.
UV/Vis (λ\(_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 330 (0.45), 668 (0.39).
ES-MS m/z: 777.1 [M + H]\(^+\).
CHN: C\(_{36}\)H\(_{24}\)PbN\(_8\). Calculated C, 55.73; H, 3.12; N, 14.44; Found C, 55.35; H,
2.90; N, 14.11.

2.3.3 Tetranitrophthalocyanines:

2.3.3.1 [2(3),9(10),16(17),23(24)-tetranitrophthalocyanine
(140)

Ammonium molybdate (0.012 g) and urea (7.2 gm, 0.12 mole) was added
to the suspension of 4-nitrophthalic anhydride (7.72 gm, 0.04 mole) in
nitrobenzene and the resulting mixture was heated at reflux temperature for 6
hours. The resulting metal free phthalocyanine was filtered under reduced
pressure and the residue was washed with methanol (100 mL), hot water and
dried in an oven at 100 °C.
Yield: 65 %.
mp: > 300 °C
Colour: Blue.
FT-IR (KBr) ν (cm\(^{-1}\)): 3401 (NH), 3090 (Ar-H), 3047, 1693 (C=N), 1530 (NO\(_2\)), 1503, 1487, 1470, 1435, 1396, 1326 (NO\(_2\)), 1295, 1283, 1245, 1185, 1157, 1119, 1087, 995, 866, 755, 730, 595.
UV/Vis (λ\(_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 376(0.45), 658 (0.42).
ES-MS m/z: 695.1 [M + H]\(^+\)
CHN: C\(_{32}\)H\(_{14}\)N\(_{12}\)O\(_8\). Calculated C, 55.34; H, 2.03; N, 24.20; Found C, 55.17; H, 1.81; N, 24.04.

2.3.4 M(II) Tetranitrophthalocyanines:

General Method
Metal halide (0.01 mole), ammonium molybedate (0.012 gm) and urea (7.2 gm, 0.12 mole) was added to the suspension of 4-nitrophthalicanhydride (7.72 gm, 0.04 mole) in nitrobenzene and the resulting mixture was heated at reflux temperature for 6 hours. The complex formed after completion of reaction was filtered under reduced pressure and washed with methanol (100 mL), followed by hot water and dried in an oven at 100 °C.
2.3.4.1 Copper(II) [2(3),9(10),16(17),23(24)-
tetranitrophthalocyanine] (141):

![Chemical structure of Copper(II) [2(3),9(10),16(17),23(24)-tetranitrophthalocyanine] (141)]

Yield: 53 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm⁻¹): 3084 (Ar-H), 1698 (C=N), 1604, 1520 (NO₂), 1507, 1453 (C=N), 1415, 1345, 1282, 1166, 1085, 1067, 897, 871, 799, 775, 752, 724, 584.
UV/Vis (λmax, nm, H₂SO₄): 277 (0.45), 380 (0.83), 663 (0.92).
ES-MS m/z: 756.0 [M + H]⁺.
CHN: C₃₂H₁₂CuN₁₂O₈. Calculated C, 50.83; H, 1.60; N, 22.23; Found C, 50.60; H, 1.45; N, 22.02.
2.3.4.2: Nickel(II) [2(3),9(10),16(17),23(24)-tetrakis(nitro)phthalocyanine] (142):

Yield: 49 %.
mp: > 300 °C.
Colour: Dirty green.
FT-IR (KBr) ν (cm⁻¹): 3087 (Ar-H), 2908, 1695 (C=N), 1601, 1526 (NO₂), 1511, 1455, 1351 (NO₂), 1287, 1158, 1114, 1086, 911, 886, 770, 758, 724, 590.
UV/Vis (λ_max, nm, H₂SO₄): 270 (0.14), 667 (0.39).
ES-MS m/z: 751.0 [M + H]⁺.
CHN: C₃₂H₁₂Ni₁₂N₁₂O₈. Calculated C, 51.16; H, 1.61; N, 22.37; Found C, 50.98; H, 1.42; N, 22.21.

2.3.4.3 Zinc(II) [2(3),9(10),16(17),23(24)-tetratinophthalocyanine] (143):
Chapter – 2   Materials & Methods

Yield: 61 %.
mp: > 300 °C
Colour: Blue.
FT-IR (KBr) ν (cm$^{-1}$): 3081 (Ar-CH), 1695 (C=N), 1605, 1525 (NO$_2$), 1499, 1462, 1417, 1334 (NO$_2$), 1282, 1155, 1109, 1066, 953, 867, 778, 754, 720, 591.
UV/Vis ($\lambda_{max}$, nm, H$_2$SO$_4$): 345 (0.47), 684 (0.32).
ES-MS m/z: 757.0 [M + H]$^+$. 
CHN: C$_{32}$H$_{12}$ZnN$_{12}$O$_8$. Calculated C, 50.71; H, 1.60; N, 22.18; Found C, 50.51; H, 1.44; N, 22.13.

2.3.4.4 Cobalt(II) [2(3),9(10),16(17),23(24)-
tetranitrophthalocyanine] (144):

Yield: 51 %.
mp: > 300 °C
Colour Blue.
FT-IR (KBr) ν (cm$^{-1}$): 3079 (Ar-H), 1699 (C=N), 1607, 1527 (NO$_2$), 1501, 1480, 1416, 1350 (NO$_2$), 1280, 1155, 1119, 1087, 1027, 948, 915, 877, 791, 761, 723.
UV/Vis ($\lambda_{max}$, nm, H$_2$SO$_4$): 273 (0.36), 668 (0.12).
ES-MS m/z: 752.0 [M + H]$^+$. 
CHN: C$_{32}$H$_{12}$CoN$_{12}$O$_8$. Calculated C, 51.15; H, 1.61; N, 22.37; Found C, 51.01; H, 1.49; N, 22.20.
2.3.4.5 Plumbum(II) [2(3),9(10),16(17),23(24)-tetranitrophthalocyaninato] (145):

\[
\begin{align*}
\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} \\
\text{Pb} & \quad \text{O}_2 & \quad \text{N} \\
& \quad \text{NO}_2 & \quad \text{NO}_2 & \quad \text{O}_2 \\
(145)
\end{align*}
\]

Yield: 47 %.

mp: > 300 °C

Colour: Blue.

FT-IR (KBr) \(\nu (\text{cm}^{-1})\): 3096 (Ar-H), 1698 (C=N), 1607, 1525 (NO\(_2\)), 1509, 1453, 1419, 1341 (NO\(_2\)), 1282, 1161, 1082, 1063, 899, 871, 804, 779, 748, 719, 596.

UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 278 (0.31), 663 (0.33).

ES-MS m/z: 901.0 [M + H]\(^+\).

CHN: C\(_{32}\)H\(_{12}\)PbN\(_{12}\)O\(_8\). Calculated C, 42.72; H, 1.34; N, 18.68; Found C, 42.62; H, 1.22; N, 18.70.

2.3.5 Tetrasulfophthalocyanine:

General Method

Phthalocyanine (2.0 gm) (metallated or metal free) was added to the ice cold solution of chlorosulfonic acid (10 mL) over a period of 10 minutes and the mixture was then refluxed for ten hours. After the completion of reaction the contents were poured into ice cold water, the precipitates formed were filtered and washed with excess water before drying in high vacuum dessicator.
2.3.5.1 2(3),9(10),16(17),23(24)-tetrosulfophthalocyanine (146):

Yield: 65%.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) \( v \) (cm\(^{-1}\)): 3421 (OH), 3401 (NH), 3094 (Ar-H), 1702 (C=N), 1595, 1505, 1449, 1388, 1365, 1326, 1292, 1277, 1193 (S=O), 1102, 1067, 981, 865, 740, 726, 693, 592.
UV/Vis (\( \lambda_{\text{max}} \), nm, H\( _2 \)SO\(_4 \)): 315 (1.30), 670 (0.495).
ES-MS m/z: 834.9 [M + H].

CHN: C\(_{32}\)H\(_{18}\)N\(_8\)O\(_{12}\)S\(_4\). Calculated C, 46.04; H, 2.17; N, 13.42; Found C, 46.34; H, 2.41; N, 13.09.

2.3.5.2 Copper(II) [2(3),9(10),16(17),23(24)-tetrosulfophthalocyanine] (147):
Yield: 69 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm⁻¹): 3427(OH), 3096 (Ar-H), 1698 (C=N), 1594, 1573, 1486, 1414, 1375, 1299, 1230, 1191 (S=O), 1129, 969, 931, 845, 778, 661, 585, 530, 480.
UV/Vis (λ_max, nm, DMF): 350 (1.763), 680 (3.77)
ES-MS m/z: 895.9 [M + H]^+.
CHN: C_{32}H_{16}CuN_{8}O_{12}S_{4}. Calculated C, 42.88; H, 1.80; N, 12.50; Found C, 42.60; H, 1.94; N, 12.67.

### 2.3.5.3 Nickle(II) [2(3),9(10),16(17),23(24)-tetrasulfophthalocyanine] (148):

![Image of the compound](image)

Yield: 57 %.
mp: > 300 °C.
Colour: Green.
FT-IR (KBr) ν (cm⁻¹): 3421(OH), 3096 (Ar-H), 1701 (C=N), 1601, 1504, 1470, 1426, 1371, 1290, 1195 (S=O), 915, 870, 811, 775, 726, 589, 523, 468.
UV/Vis (λ_max, nm, DMF): 290 (0.812), 340 (0.631), 660 (1.55).
ES-MS m/z: 890.9 [M + H]^+.
CHN: C_{32}H_{16}NiN_{8}O_{12}S_{4}. Calculated C, 43.11; H, 1.81; N, 12.57; Found C, 43.41; H, 1.75; N, 12.39.
2.3.5.4: **Zinc(II) [2(3),9(10),16(17),23(24)-tetrosulfoporphthalocyanine] (149):**

![Zinc(II) complex](image)

Yield: 53%.

mp: > 300 °C.

Colour: Blue.

FT-IR (KBr) $\nu$ (cm$^{-1}$): 3425 (OH), 3097 (Ar-H), 1694 (C=N), 1604, 1499, 1457, 1374, 1291, 1221, 1215, 1190 (S=O), 963, 915, 881, 758, 711, 671, 586, 517, 478.

UV/Vis ($\lambda_{max}$, nm, DMF): 264 (0.456), 352 (0.157), 674 (0.394).

ES-MS m/z: 896.9 [M + H]$^+$.  

CHN: C$_{32}$H$_{16}$ZnN$_8$O$_{12}$S$_4$. Calculated C, 42.79; H, 1.80; N, 12.48; Found C, 42.54; H, 1.91; N, 12.63.

2.3.5.5 **Cobalt(II) [2(3),9(10),16(17),23(24)-tetrosulfoporphthalocyanine] (150):**

![Cobalt(II) complex](image)

(150)
Yield: 41 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBR) ν (cm\(^{-1}\)): 3431 (OH), 3095 (Ar-H), 1698 (C=N), 1598, 1496, 1464, 1366, 1284, 1240, 1194 (S=O), 1121, 1069, 967, 875, 796, 781, 717, 584, 521, 464.
UV/Vis (\(\lambda_{\text{max}}, \text{nm}, \text{DMF}\)): 340 (1.25), 665 (2.05).
ES-MS m/z: 891.9 [M + H]\(^+\).
CHN: \(\text{C}_{32}\text{H}_{16}\text{CoN}_8\text{O}_{12}\text{S}_4\). Calculated C, 43.10; H, 1.81; N, 12.57; Found C, 43.41; H, 1.61; N, 12.45.

2.3.5.6 **Plumbum(II) [2(3),9(10),16(17),23(24)-tetrasulfophthalocyanine] (151):**

Yield: 51 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm\(^{-1}\)): 3426 (OH), 3095 (Ar-H), 1699 (C=N), 1595, 1551, 1499, 1361, 1344, 1291, 1228, 1211, 1199 (S=O), 1121, 1063, 967, 911, 809, 771, 707, 685, 593(A, 531, 475.
UV/Vis (\(\lambda_{\text{max}}, \text{nm}, \text{DMF}\)): 230 (1.96), 285 (0.591), 670 (0.439).
ES-MS m/z: 1040.9 [M + H]\(^+\).
2.3.6 Tetrpyrrolidine substituted phthalocyanine

2.3.6.1 [2(3),9(10),16(17),23(24)-Tetra(pyrrolidin-1-yl)phthalocyanine] (152)

A mixture of 4-(pyrrolidin-1-yl)phthalonitrile (7.88 gm, 0.04 mole) and sodium sulfide (0.15 g, 0.002 mole), metal halide (0.01 mole) in nitrobenzene was heated at reflux for 6 hours. After the completion of the reaction the complex was filtered and washed with methanol (100 mL) and hot water and dried in oven at 100 °C.

Yield: 43%.
mp: > 300 °C.
Colour: Blue.
IR (KBr, ν cm⁻¹): \(3396 \text{ (NH)}, 3084 \text{ (Ar-H)}, 2851 \text{ (CH}_2\text{)}, 1704 \text{ (C=N),1603, 1499, 1461, 1411, 1325, 1286, 1172, 1081, 1063, 894.}\)
UV/Vis (\(\lambda_{\text{max}}\), nm, H₂SO₄): 265 (0.66), 670 (0.12).
ES-MS m/z: 791.3 [M + H]⁺.
CHN: Chemical Formula: C\(_{48}H_{46}N_{12}\). Calculated C, 72.89; H, 5.86;; N, 21.25. Found C, 72.71; H, 5.89; N, 21.03.

### 2.3.6.2 Metallated tetra-pyrrolidine substituted phthalocyanine

A mixture of 4-(pyrrolidin-1-yl)phthalonitrile (0.04 mole) and metal halide (0.01 mole) in nitrobenzene was heated at reflux for 6 hours. After the completion of the reaction the complex was filtered and the residue was washed with methanol (100 mL), and hot water and dried in oven at 100 °C.

#### 2.3.6.2.1: Copper(II) \[2(3),9(10),16(17),23(24)-\text{tetra(pyrrolidin-1-yl)phthalocyanine}\] (153)

![Chemical structure of Copper(II) phthalocyanine](image_url)

Yield: 46%.

mp: > 300 °C.

Colour: Blue.

IR (KBr, \(\nu\) cm\(^{-1}\)): 3079 (Ar-H), 2858 (CH\(_2\)), 1701 (C=N), 1605, 1507, 1463, 1419, 1324, 1287, 1170, 1089, 1061, 893, 865, 809, 784, 744, 729, 591.

UV/Vis (\(\lambda_{\text{max}},\) nm, H\(_2\)SO\(_4\)): 277(0.0.38), 286(0.34), 667 (0.41).

ES-MS m/z: 852.3 [M + H]\(^+\).
CHN: Chemical Formula: C\textsubscript{48}H\textsubscript{44}CuN\textsubscript{12}. Calculated C, 67.63; H, 5.20; N, 19.72. Found C, 67.45; H, 5.03; N, 9.52.

2.3.6.2.2: Nickel(II) [2(3),9(10),16(17),23(24)-tetra(pyrrolidin-1-yl)phthalocyanine] (154)

Yield: 63%.

mp: > 300 °C.

Colour: Bluish green.

IR (KBr, ν cm\textsuperscript{-1}): 3078 (Ar-H), 2854 (CH\textsubscript{2}), 1707 (C=N), 1607, 1541, 1498, 1425, 1333, 1281, 1155, 1121, 1090, 917, 893, 779, 762, 735, 590.

UV/Vis (λ\textsubscript{max}, nm, H\textsubscript{2}SO\textsubscript{4}): 270(1.30), 286(0.80), 670(0.23).

ES-MS m/z: 847.3 [M + H]\textsuperscript{+}.

CHN: C\textsubscript{48}H\textsubscript{44}Ni\textsubscript{12}. Calculated C, 68.01; H, 5.23; N, 19.83; Found C, 67.77; H, 5.03; N, 19.61.
2.3.6.2.3: Zinc(II) [2(3),9(10),16(17),23(24)- tetra(pyrrolidin-1-yl)phthalocyanine] (155)

Yield: 51%
m.p >300 °C
Colour: blue.
IR (KBr, ν cm⁻¹): 3082 (Ar-H), 2855 (CH₂), 1705 (C=N), 1601, 1504, 1462, 1423, 1318, 1202, 1161, 1117, 1071, 954, 870, 771, 761, 731, 591.
UV/Vis (λ_max, nm, H₂SO₄): 284(0.25), 374(1.21), 681(0.45).
ES-MS m/z: 853.3 [M + H]⁺.
CHN: C₄₈H₄₄N₁₂Zn. Calculated C, 67.48; H, 5.19; N, 19.67; Found C, 67.26; H, 5.00; N, 19.57.
2.3.6.2.4: Cobalt(II) [2(3),9(10),16(17),23(24)-tetra(pyrrrolidin-1-yl)phthalocyanine] (156)

Yield: 45%
m.p>300°C
Colour: Violet.
IR (KBr, \nu, cm^{-1}): 3079 (Ar-H), 2853 (CH\textsubscript{2}), 1698 (C=N), 1609, 1511, 1489, 1420, 1319, 1278, 1145, 1109, 1071, 1012, 948, 907, 861, 774, 763, 598.
UV/Vis (\lambda\textsubscript{max}, nm, H\textsubscript{2}SO\textsubscript{4}): 340 (1.20), 665 (0.81).
ES-MS m/z: 848.3 [M + H]\textsuperscript{+}.
CHN: C\textsubscript{48}H\textsubscript{44}CoN\textsubscript{12}. Calculated C, 67.99; H, 5.23; N, 19.82. Found C, 67.79; H, 5.01; N, 19.61.
2.3.6.2.5: Plumbum(II) [2(3),9(10),16(17),23(24)-tetra(pyrrolidin-1-yl)phthalocyanine] (157)

Yield: 47%
m.p.>300°C
Colour: Blue
IR (KBr, v,cm⁻¹): 3080 (Ar-H), 2857 (CH₂), 1697 (C=N), 1599, 1494, 1954, 1411, 1328, 1282, 1164, 1174, 1071, 891, 868, 795, 781, 747, 587.
UV/Vis (λ_max, nm, H₂SO₄): 264 (0.45), 674 (0.39).
ES-MS m/z: 997.3 [M + H]⁺.
CHN: C₄₈H₄₄N₁₂Pb. Calculated C, 57.87; H, 4.45; N, 16.87; Found C, 57.69; H, 4.27; N, 16.68.

2.3.7 Tetra(piperidin-1-yl)substituted phthalocyanines:

2.3.7.1: 2(3),9(10),16(17),23(24)-Tetra(piperidin-1-yl)phthalocyanine (158):

A mixture of 4-(piperidin-1-yl)phthalonitrile (8.44 gm, 0.04 mole), and sodium sulfide (0.15 g, 0.002 mole), metal halide (0.01 mole) in nitrobenzene was heated at reflux for 6 hours. After the completion of the reaction the complex was filtered and washed with hot water and dried in oven at 100 °C.
Yield: 45%.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) $\nu$ (cm$^{-1}$): 3400 (NH), 3079 (Ar-H), 2859 (CH$_2$), 1694 (C=N), 1611, 1517, 1467, 1411, 1329, 1288, 1161, 1083, 1077, 899.
UV/Vis ($\lambda_{\text{max}}$, nm, H$_2$SO$_4$): 296 (1.8), 342 (1.3), 668 (2.6).
ES-MS m/z: 847.3 [M + H]$^+$. 
CHN: C$_{52}$H$_{54}$N$_{12}$. Calculated C, 73.73; H, 6.43; N, 19.84. Found C, 73.52; H, 6.41; N, 19.61.

2.3.7.2 M(II) 2(3),9(10),16(17),23(24)-tetra(piperidin-1-yl)phthaloylanes

General Method
A mixture of 4-(piperidin-1-yl)phthalonitrile (9.0 gm, 0.04 mole) and metal halide (0.01 mole) in nitrobenzene was heated at reflux for 6 hours. After the completion of the reaction the complex was filtered and the residue was washed with methanol (100 mL), with hot water and dried in oven at 100 °C.
2.3.7.2.1 Copper(II) [2(3),9(10),16(17),23(24)- tetra(piperidin-1-yl)phthalocyanine] (159):

Yield: 47%.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm$^{-1}$): 3079 (Ar-H), 2857 (CH$_2$), 1695 (C=N), 1609, 1501, 1461, 1417, 1323, 1282, 1166, 1081, 1067, 897, 871, 799, 775, 753, 587.
UV/Vis ($\lambda_{\text{max}}$, nm, H$_2$SO$_4$): 278(0.98), 385(1.11), 667(0.32).
ES-MS m/z: 908.3 [M + H]$^+$.
CHN: C$_{52}$H$_{52}$CuN$_{12}$. Calculated C, 68.74; H, 5.77; N, 18.50. Found C, 68.55; H, 5.62; N, 18.37.
2.3.7.2.2 Nickel(II) [2(3),9(10),16(17),23(24)- tetra(piperidin-1-yl)phthalocyanine] (160):

Yield: 44%.
mp: > 300 °C.
Colour: Bluish green.
IR (KBr, $\nu$, cm$^{-1}$): 3078 (Ar-H), 2855 (CH$_2$), 1698 (C=N), 1599, 1501, 1459, 1424, 1321, 1287, 1170, 1110, 1080, 917, 887, 773, 757, 591.
UV/Vis ($\lambda_{\text{max}}$, nm, H$_2$SO$_4$): 295 (0.99), 660 (0.23).
ES-MS m/z: 903.3 [M + H]$^+$. 
CHN: C$_{52}$H$_{52}$N$_{12}$Ni. Calculated C, 69.11; H, 5.80; N, 18.60; Found C, 69.31; H, 5.63; N, 18.45.
2.3.7.2.3 Zinc(II) [2(3),9(10),16(17),23(24)- tetra(piperidin-1-yl)phthalocyanine] (161):

Yield: 53%

mp: >300 °C.

Colour: Blue.

IR (KBr, \( \nu, \text{cm}^{-1} \)): 3080 (Ar-H), 2858 (CH\(_2\)), 1697 (C=N), 1610, 1506, 1465, 1415, 1329, 1277, 1163, 1108, 1060, 954, 864, 770, 751, 585.

UV/Vis (\( \lambda_{\text{max}}, \text{nm}, \text{H}_2\text{SO}_4 \)): 340(0.12), 665(0.12).

ES-MS m/z: 909.3 [M + H]\(^+\).

CHN: C\(_{52}\)H\(_{52}\)N\(_{12}\)Zn. Calculated C, 68.60; H, 5.76; N, 18.46; Found C, 68.41; H, 5.64; N, 18.33.
2.3.7.2.4 Cobalt(II) [2(3),9(10),16(17),23(24)- tetra(piperidin-1-yl)phthalocyanine] (162):

![Chemical Structure](image)

Yield: 45%.
mp: > 300 °C.
Colour: Violet.
FT-IR (KBr) ν (cm\(^{-1}\)): 3083 (Ar-H), 2860 (CH\(_2\)), 1703 (C=N), 1611, 1518, 1480, 1421, 1325, 1280, 1155, 1078, 1023, 946, 870, 589.
UV/Vis (\(\lambda_{\text{max}}, \text{nm, } \text{H}_2\text{SO}_4\)): 285 (0.81), 670 (0.33).
ES-MS m/z: 904.3 [M + H]\(^+\).
CHN: C\(_{52}\)H\(_{52}\)CoN\(_{12}\). Calculated C, 69.09; H, 5.80; N, 18.59. Found C, 68.93; H, 5.65; N, 18.47.
2.3.7.2.5 Zinc(II) [2(3),9(10),16(17),23(24)- tetra(piperidin-1-yl)phthalocyanine] (163):

Yield: 47%
mp: > 300 °C.
Colour: Blue.
IR (KBr, ν, cm⁻¹): 3080 (Ar-H), 2857 (CH₂), 1691 (C=N), 1604, 1503, 1456, 1411, 1337, 1274, 1144, 1081, 1063, 896, 873, 796, 786, 745, 592.
UV/Vis (λ_max, nm, H₂SO₄): 383(0.41), 669(0.26).
ES-MS m/z: 1051.4 [M + H]⁺.
CHN: C₅₂H₅₂N₁₂Pb. Calculated C, 59.35; H, 4.98; N, 15.97; Found C, 59.23; H, 4.85; N, 15.79.

2.3.8 Tetra(azepan-1-yl)substituted phthalocyanines:

2.3.8.1: 2(3),9(10),16(17),23(24)-Tetra(azepan-1-yl)phthalocyanine (164):

4-(Azepan-1-yl)phthalonitrile (9.0 gm, 0.04 mole) and sodium sulfide (0.15 g, 0.002 mole) in nitrobenzene was heated at 100 °C for 6 hours. After the
completion of the reaction the complex was filtered and washed with hot water and dried in oven at 100 °C.

Yield: 49 %.
Colour: Blue.
mp: > 300 °C.
FT-IR (KBr) ν (cm⁻¹): 3403 (NH), 3095 (Ar-H), 2861 (CH₂), 1696 (C=N), 1602, 1501, 1457, 1415, 1326, 1283, 1168, 1089, 1063, 891, 875.
UV/Vis (λ_max, nm, H₂SO₄): 255 (0.60), 670 (0.16).
ES-MS m/z: 903.4 [M + H]⁺.

2.3.8.2 M(II) 2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthaloylanes
General Method
4-(Azepan-1-yl)phthalonitrile (9.0 gm, 0.04 mole) and metal halide (0.01 mole) in nitrobenzene was heated at 100 °C for 6 hours. After the completion of the reaction the complex was filtered and washed with methanol (100 mL), with hot water and dried in oven at 100 °C.
2.3.8.2.1 Copper(II) [2(3),9(10),16(17),23(24)- tetra(azepan -1-yl)phthalocyanine] (165):

![Chemical Structure](image)

Yield: 48 %.
mp: > 300 °C.
Colour: Blue.
IR (KBr, ν, cm⁻¹): 3092 (Ar-H), 2859 (CH₂), 1698 (C=N), 1602, 1500, 1457, 1415, 1328, 1282, 1166, 1085, 1067, 897, 871, 799, 775, 752, 594.
UV/Vis (λₘₐₓ, nm, H₂SO₄): 264 (0.60), 672 (0.16).
ES-MS m/z: 964.4 [M + H]⁺.
CHN: C₅₆H₆₀CuN₁₂. Calculated C, 69.72; H, 6.27; N, 17.42. Found C, 69.55; H, 6.10; N, 17.25.
2.3.8.2.2 Nickel(II) [2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanine] (166)

Yield: 41%.

mp: > 300 °C.

Colour: Blue.

IR (KBr) \(\nu\) (cm\(^{-1}\)): 3092 (Ar-H), 2863 (CH\(_2\)), 1705 (C=N), 1604, 1508, 1455, 1421, 1327, 1287, 1158, 1114, 1086, 911, 886, 770, 758, 581.

UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 382 (0.43), 664 (0.21).

ES-MS m/z: 959.4 [M + H]\(^+\).

CHN: C\(_{56}\)H\(_{60}\)N\(_{12}\)Ni. Calculated C, 70.07; H, 6.30; N, 17.51; Found C, 69.89; H, 6.17; N, 17.34.
2.3.8.2.3 Zinc(II) [2(3),9(10),16(17),23(24)- tetra(azepan -1-yl)phthalocyanine] (167):

Yield: 53 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) v (cm$^{-1}$): 3097 (Ar-H), 2862 (CH$_2$), 1696 (C=N), 1606, 1502, 1462, 1415, 1325, 1282, 1158, 1112, 1065, 948, 864, 775, 751, 586.
UV/Vis ($\lambda_{\text{max}}$, nm, H$_2$SO$_4$): 287(0.21), 375(0.33), 667(0.49).
ES-MS m/z: 965.4 [M + H]$^+$.  
CHN: C$_{56}$H$_{60}$N$_{12}$Zn. Calculated C, 69.59; H, 6.26; N, 17.39; Found C, 69.41; H, 6.11; N, 17.18.
2.3.8.2.4 Cobalt(II) [2(3),9(10),16(17),23(24)- tetra(azepan-1-yl)phthalocyanine] (168):

Yield: 52 %.

mp: > 300 °C.

Colour: Violet.

FT-IR (KBr) ν (cm\(^{-1}\)): 3093 (Ar-H), 2857 (CH\(_2\)), 1699 (C=N), 1613, 1507, 1478, 1434, 1341, 1298, 1167, 1102, 1039, 1099, 961, 902, 857, 761, 742, 591.

UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 383(0.39), 665(0.24).

ES-MS m/z: 960.4 [M + H]\(^+\).

CHN: C\(_{56}\)H\(_{60}\)CoN\(_{12}\). Calculated C, 70.06; H, 6.30; N, 17.51. Found C, 69.91; H, 6.21; N, 17.37.
2.3.8.2.5 Plumbim(II) [2(3),9(10),16(17),23(24)- tetra(azepan -1-yl)phthalocyanine] (169):

Yield: 54 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm⁻¹): 3088 (Ar-H), 2860 (CH₂), 1698 (C=N), 1599, 1500, 1494, 1415, 1328, 1282, 1166, 1085, 1067, 897, 871, 799, 775, 752, 587.
UV/Vis (λmax, nm, H₂SO₄): 380 (0.83), 662 (0.46).
ES-MS m/z: 1109.4 [M + H]⁺.
CHN: C₅₆H₆₀N₁₂Pb. Calculated C, 60.68; H, 5.46; N, 15.16; Found C, 60.51; H, 5.29; N, 14.83.

2.3.9 Chlorosulfonylphthalocyanines:

Phthalocyanine (metallated or metal free) (2.0 gm) was added to the ice cold solution of chlorosulfonic acid (10 mL) over a period of 10 minutes and the mixture was refluxed for ten hours. After the completion of reaction the contents were poured into ice cold water, the precipitates formed were filtered and washed with ice cold water before drying in high vacuum dessicator.
2.3.9.1 2(3),9(10),16(17),23(24)-Tetra(chlorosulfonyl)phthalocyanine (170):

![Chemical structure of 170](image)

2.3.9.2 2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylaminosulfonyl) phthalocyanines

**General method:**

Metallated or metal free chloro sulfonyl substituted phthalocyanine (2.0 gm) was added in dry DMF containing 4-aminobenzenesulfonic acid (0.5 gm) and sodium bicarbonate (0.48 gm, 0.006 moles) and the solution was stirred for 24 hours. After the completion of reaction the contents were poured into ice cold water and the resulting precipitates were filtered, washed with cold water and recrystallized in methanol to afford methyl substituted phenylsulfonyl phthalocyanines.
2.3.9.2.1 2(3),9(10),16(17),23(24)-Tetrakis(p-sulfophenylamino sulfonyl)phthalo cyanine (171)

Yield: 70 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm⁻¹): 3433 (OH), 3405 (NH), 3087 (Ar-H), 3040, 1692 (C=N), 1612, 1558, 1490, 1451, 1372, 1301, 1237, 1185 (S=O), 1115, 1061, 945, 896, 859, 817, 753, 715, 686, 545, 519, 472.
UV/Vis (λ_max, nm, H₂SO₄): 294, 343, 667.
ES-MS m/z: 1455.0 [M + H]^+.
CHN: C₅₆H₃₈N₁₂O₂₀S₈. Calculated C, 46.21; H, 2.63; N, 11.55; Found C, 46.04; H, 2.48; N, 11.38.
2.3.9.2.2 2(3),9(10),16(17),23(24)-Copper(II)[tetraakis(p-sulfophenylaminosulfonyl)phthalocyanine] (172)

Yield: 67 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm⁻¹): 3436 (OH), 3401 (NH), 3142, 3087 (Ar-H), 3049, 1698 (C=N), 1612, 1490, 1429, 1363, 1207, 1185 (S=O), 1087, 965, 781, 705, 671, 527, 474.
UV/Vis (λ_max, nm, H₂SO₄): 294, 341, 669.
ES-MS m/z: 1515.9 [M + H]⁺.
CHN: C₅₆H₃₆CuN₁₂O₂₀S₈. Calculated C, 44.34; H, 2.39; N, 11.08; Found C, 44.22; H, 2.29; N, 10.90.
2.3.9.2.3 2(3),9(10),16(17),23(24)-Nickel(II)[tetrakis(p-sulfophenylamino sulfonyl)phthalocyanine] (173)

Yield: 65%.
mp: > 300 °C
Colour: Blue.
FT-IR (KBr) ν (cm⁻¹): 3433 (OH), 3399 (NH), 3142, 3080 (Ar-H), 3042, 1692 (C=N), 1606, 1576, 1484, 1428, 1367, 1228, 1206, 1183 (S=O), 1088, 966, 780, 706, 670, 526, 473.
UV/Vis (λ_max, nm, H_2SO_4): 297, 345, 670.
ES-MS m/z: 1513.0 [M + H]^+.
CHN: C_{56}H_{36}Ni_{12}O_{20}S_8. Calculated C, 44.48; H, 2.40; N, 11.12; Found C, 44.26; H, 2.19; N, 11.00.
2.3.9.2.4 2(3),9(10),16(17),23(24)-Zinc(II) [tetrakis(p-sulfophenylaminosulfonyl)phthalocyanine] (174)

Yield: 67 %.

mp: > 300 °C.

Colour: Blue.

FT-IR (KBr) ν (cm⁻¹): 3432 (OH), 3397 (NH), 3106, 3089 (Ar-H), 3041, 1694 (C=N), 1610, 1560, 1489, 1361, 1264, 1216, 1186 (S=O), 1121, 1097, 952, 932, 738, 667, 651, 512, 468.

UV/Vis (λmax, nm, H2SO4): 295, 346, 671.

ES-MS m/z: 1516.9 [M + H]+.

CHN: C56H36ZnN12O20S8. Calculated C, 44.28; H, 2.39; N, 11.07; Found C, 44.10; H, 2.23; N, 10.85.
2.3.9.2.5 2(3),9(10),16(17),23(24)-Cobalt(II) [tetrakis(p-
  sulfophenylaminosulfonyl)phthalocyanine] (175)

Yield: 68 %.

mp: > 300 °C.

Colour: Purple.

FT-IR (KBr) ν (cm\(^{-1}\)): 3435 (OH), 3404 (NH), 3140, 3089 (Ar-H), 3035, 1691
(C=N), 1611, 1496, 1391, 1363, 1276, 1212, 1275, 1191 (S=O), 1114, 1092, 949,
923, 815, 661, 623, 595, 515.

UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 293, 340, 668.

ES-MS m/z: 1511.9 [M + H]\(^+\).

CHN: C\(_{56}\)H\(_{36}\)CoN\(_{12}\)O\(_{20}\)S\(_8\). Calculated C, 44.47; H, 2.40; N, 11.11; Found C,
44.31; H, 2.25; N, 10.84.
2.3.9.2.6 2(3),9(10),16(17),23(24)-Plumbum(II) [tetrakis(p-sulfophenylamin osulfonyl)phthalocyanine] (176)

Yield: 63 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr) ν (cm⁻¹): 3437 (OH), 3402 (NH) 3105, 3096, 3035, 1689 (C=N), 1592, 1574, 1491, 1442, 1373, 1283, 1231, 1184 (S=O), 1105, 1067, 1011, 963, 912, 895, 857, 779, 574, 531, 479.
UV/Vis (λ_max, nm, H_2SO_4): 293, 343, 674.
ES-MS m/z: 1660.9 [M + H]^+.
CHN: C_{56}H_{36}PbN_{12}O_{20}S_{8}. Calculated C, 40.50; H, 2.19; N, 12.12; Found C, 40.29; H, 2.04; N, 12.15.
2.3.10 2(3),9(10),16(17),23(24) -
Tetra(octylaminosulfonyl)phthalocyanines:

General method:

Octyl amine (0.004 mole) was added to the solution of metallated and
metal free chloro sulfonyl substituted phthalocyanine (0.001 mole) was added in
dry DMF containing and sodium bicarbonate (0.48 gm, 0.006 moles) and the
solution was stirred for 24 hours. After the completion of reaction the contents
were poured into ice cold water and the resulting precipitates were filtered,
washed with cold water and recrystallized in methanol to afford alkyl substituted
sulfonyl phthalocyanines.

2.3.10.1 2(3),9(10),16(17),23(24) -
Tetrakis(octylaminosulfonyl)phthalocyanine] (177)
Yield: 45 %.

mp: > 300 °C.

Colour: Blue.

FT-IR (KBr) ν (cm\(^{-1}\)): 3392 (NH), 3094 (Ar-H), 3031, 2927 (CH\(_2\)), 1695 (C=N), 1641, 1595, 1490, 1444, 1377, 1283, 1231, 1182 (S=O), 1103, 1061, 1013, 963, 914, 896.

UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 294, 330, 672.

ES-MS m/z: 1279.6 [M + H]\(^+\).

CHN: C\(_{64}\)H\(_{86}\)N\(_{12}\)O\(_8\)S\(_4\). Calculated C, 60.06; H, 6.77; N, 13.13; Found C, 59.89 H, 6.81; N, 12.91.

2.3.10.2 Copper(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl)phthalo cyanine (178)
Yield: 71 \%.

mp: > 300 °C.

Colour: Blue.

FT-IR (KBr) \( \nu \) (cm\(^{-1}\)): 3395 (NH), 3145, 3091 (Ar-H), 3044, 2930 (CH\(_2\)), 1696 (C=N), 1597, 1570, 1488, 1423, 1369, 1211, 1185 (S=O), 1081, 964, 775, 701, 679, 521, 476.

UV/Vis (\( \lambda_{\text{max}} \), nm, H\(_2\)SO\(_4\)): 295, 340, 660

ES-MS m/z: 1340.4 [M + H]\(^{+}\).

CHN: C\(_{64}\)H\(_{84}\)CuN\(_{12}\)O\(_8\)S\(_4\). Calculated C, 57.31; H, 6.31; N, 12.53; Found C, 57.06; H, 6.33; N, 12.31.

2.3.10.3 Nickel(II) 2(3),9(10),16(17),23(24)-tetrakis (octylaminosulfonyl)phthalocyanine] (179)

Yield: 69 \%.

mp: > 300 °C

Colour: Blue.
FT-IR (KBr) ν (cm$^{-1}$): 3394 (NH), 3096 (Ar-H), 3037, 2925 (CH$_2$), 1706 (C=N), 1591, 1485, 1421, 1360, 1235, 1187 (S=O), 1124, 1093, 969, 787, 706, 673, 531, 469.

UV/Vis ($\lambda_{max}$, nm, H$_2$SO$_4$): 296, 342, 668.

ES-MS m/z: 1335.4 [M + H]$^+$. 

CHN: C$_{64}$H$_{84}$Ni$_{12}$O$_8$S$_4$. Calculated C, 57.52; H, 6.34; N, 12.58; Found C, 57.24; H, 6.37; N, 12.35.

2.3.10.4 Zinc(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl)phthalocyanine] (180)

Yield: 67 %.

mp: > 300 °C.

Colour: Blue.
FT-IR (KBr, ν, cm⁻¹): 3396 (NH), 3097 (Ar-H), 3037, 2933 (CH₂), 1700 (C=N), 1601, 1558, 1484, 1374, 1262, 1226, 1189 (S=O), 1127, 1094, 957, 933, 738, 661, 649, 510, 468.

UV/Vis (λ_{max}, nm, H₂SO₄): 290, 335, 661.

ES-MS m/z: 1341.5 [M + H]^+.

CHN: C₆₄H₈₄Zn₁₂O₈S₄. Calculated C, 57.23; H, 6.30; N, 12.51; Found C, 57.02; H, 6.23; N, 12.29.

### 2.3.10.5 Cobalt(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl)phthalocyanine] (181)

Yield: 67%.

mp: > 300 °C.

Colour: Purple.
FT-IR (KBr, \(\nu\), cm\(^{-1}\)): 3393 (NH), 3079 (Ar-H), 3035, 2931 (CH\(_2\)), 1701 (C=N), 1599, 1486, 1391, 1369, 1276, 1212, 1275, 1185 (S=O), 1126, 1092, 949, 923, 815, 661.

UV/Vis (\(\lambda_{\text{max}}, \text{nm}, \text{H}_2\text{SO}_4\)): 295, 340, 665.

ES-MS m/z: 1336.4 [M + H]\(^+\).

CHN: \(\text{C}_{64}\text{H}_{84}\text{CoN}_{12}\text{O}_{8}\text{S}_{4}\). Calculated C, 57.51; H, 6.33; N, 12.58; Found C, 57.30; H, 6.21; N, 12.34.

2.3.10.6 Plumbum(II) 2(3),9(10),16(17),23(24)-tetrakis(octylaminosulfonyl) phloocyamine] (182)

\[
\text{H}_3\text{C} \\
(\text{H}_2\text{C})_7 \\
\text{NH} \\
\text{O=S=O} \\
\text{H}_3\text{C} \\
(\text{H}_2\text{C})_7 \\
\text{NH} \\
\text{O=S=O} \\
\text{CH}_3 \\
(\text{CH}_2)_7 \\
\text{HN} \\
\text{O=S=O} \\
\text{HN} \\
(\text{CH}_2)_7 \\
\text{CH}_3
\]

Yield: 63 %.

mp: > 300 °C.

Colour: Blue.
Chapter – 2

Materials & Methods

FT-IR (KBr, ν, cm\(^{-1}\)): 3396 (NH), 3096 (Ar-H), 3035, 2932 (CH\(_2\)), 1706 (C=N), 1641, 1592, 1491, 1442, 1371, 1283, 1231, 1183 (S=O), 1122, 1105, 1067, 1011, 963, 912, 895, 857, 779, 574, 531, 479.

UV/Vis (λ\(_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 297, 332, 667.

ES-MS m/z: 1485.7 [M + H]\(^+\)

CHN: C\(_{64}\)H\(_{84}\)PbN\(_{12}\)O\(_8\)S\(_4\). Calculated C, 51.77; H, 5.70; N, 11.32; Found C, 51.49; H, 5.73; N, 11.06.

2.3.11 [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine:

6-amino-1-ol (0.04 mole) was added to the mixture of metallated 2(3),9(10),16(17),23(24)-tetrakisulfonylexalaminosulfonylphthalocyanine (0.01 mole) and sodium bicarbonate (0.48 gm, 0.06 moles) in dry DMF and the solution was stirred for 24 hours. After the completion of reaction the contents were poured into ice cold water and the resulting precipitates were filtered, washed with cold water and recrystallized in methanol to afford tetra-hydroxyalkylaminosulfonylphthalocyanine.
2.3.11.1 [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (183)

Yield: 63 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr, ν, cm\(^{-1}\)): 3431 (OH), 3393 (NH isoindole) 3107, 3094 (Ar-H), 3035, 2928 (CH\(_2\)), 1699 (C=N), 1592, 1574, 1491, 1442, 1370, 1285, 1231, 1184 (S=O), 1069, 1011, 965, 912, .
UV/Vis (λ\(_{max}\), nm, H\(_2\)SO\(_4\)):335, 670.
ES-MS m/z: 1231.4 [M + H]\(^+\).
CHN: C\(_{56}\)H\(_{70}\)N\(_{12}\)O\(_{12}\)S\(_{4}\). Calculated C, 54.62; H, 5.73; N, 13.65; Found C, 54.41; H, 5.71; N, 13.40.
2.3.11.2 Copper(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (184)

Yield: 71 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr, ν, cm⁻¹): 3430(OH), 3391 (NH) 3145, 3091(ArH), 3044, 2930(CH₂), 1704 (C=N), 1570, 1486, 1423, 1369, 1185 (S=O), 1081, 964, 775, 701, 679, 521, 476.
UV/Vis (λ_max, nm, H₂SO₄): 295, 340, 660.
ES-MS m/z: 1292.3 [M + H]^+.
CHN: C₅₆H₆₈CuN₁₂O₁₂S₄. Calculated C, 52.02; H, 5.30; N, 13.0; Found C, 51.80; H, 5.33; N, 12.83.
2.3.11.3 Nickel(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (185)

Yield: 69 %.
mp: > 300 °C
Colour: Blue.
FT-IR (KBr, ν, cm\(^{-1}\)): 3432(OH), 3394(NH), 3151, 3086 (Ar-H), 3037, 2925 (\(\text{CH}_2\)), 1706 (C=N), 1570, 1475, 1421, 1360, 1235, 1201, 1187 (S=O), 1093, 969, 787, 706, 673, 531, 469.
UV/Vis (\(\lambda_{\text{max}}\), nm, \(\text{H}_2\text{SO}_4\)): 296, 342, 668.
ES-MS m/z: 1287.3 [M + H]\(^+\).
CHN: C\(_{56}\)H\(_{68}\)NiN\(_{12}\)O\(_{12}\)S\(_{4}\). Calculated C, 52.21; H, 5.32; N, 13.05; Found C, 52.03; H, 5.34; N, 12.86.
2.3.11.4 Zinc(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (186)

Yield: 67 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr, ν, cm⁻¹): 3433 (OH), 3396 (NH), 3131, 3087 (ArH), 3037, 2933 (CH₂), 1700 (C=N), 1669, 1620, 1558, 1494, 1374, 1262, 1226, 1191, 1188 (S=O), 1094, 957, 933, 738, 661, 649, 510, 468.
UV/Vis (λ_max, nm, H₂SO₄): 296, 342, 670.
ES-MS m/z: 1293.3 [M + H]^+.
CHN: C₅₆H₆₈ZnN₁₂O₁₂S₄. Calculated C, 51.94; H, 5.29; N, 12.98; Found C, 51.69; H, 5.23; N, 12.79.
2.3.11.5cobalt(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-
hydroxyhexyl)aminosulfonyl]phthalocyanine (187)

Yield: 67 %.

mp: > 300 °C.

Colour: Purple.

FT-IR (KBr, v, cm⁻¹): 3435 (OH), 3393 (NH), 3140, 3089 (ArH), 3035, 2934 (CH₂),
1701 (C=N), 1611, 1496, 1391, 1369, 1276, 1275, 1196, 1185 (C=O),
1092, 949, 923, 815, 661, 623, 595, 515.

UV/Vis (λmax, nm, H₂SO₄): 295, 340, 660.

ES-MS m/z: 1288.3 [M + H]⁺.

CHN: C₅₆H₆₈CoN₁₂O₁₂S₄. Calculated C, 52.20; H, 5.32; N, 13.05; Found C,
52.01; H, 5.33; N, 12.89.
2.3.11.6 Plumbum(II) [2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexyl)aminosulfonyl]phthalocyanine (188)

Yield: 63 %.
mp: > 300 °C.
Colour: Blue.

FT-IR (KBr, ν, cm⁻¹): 3437 (OH), 3396 (NH), 3105, 3096 (Ar-H), 3035, 2931 (CH₂), 1706 (C=N), 1641, 1592, 1574, 1491, 1442, 1371, 1283, 1231, 1188 (S=O), 1105, 1067, 1011, 963, 912, 895, 857, 779, 574, 531, 479.

UV/Vis (λ_max, nm, H₂SO₄): 295, 340, 665.

ES-MS m/z: 1437.3.4 [M + H]⁺.

CHN: C₅₆H₆₈PbN₁₂O₁₂S₄. Calculated C, 46.82; H, 4.77; N, 11.70; Found C, 46.57; H, 4.74; N, 11.48.
2.3.12 2(3),9(10),16(17),23(24)-Tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines:

General Method:

4-[(6-Hydroxyhexylamino)methyl]phthalonitrile (0.04 mole), metal halide (0.01 mole) in nitrobenzene was heated at reflux temperature for 6 hours. After the completion of the reaction the complex was filtered under reduced pressure and the residue was first washed with methanol (100 mL) and then with hot water and dried in oven at 100 °C.

2.3.12.1 Copper(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189)

Yield: 63 %.
mp: > 300 °C.
Colour: Blue.
F FT-IR (KBr, ν, cm\(^{-1}\)): 3433 (OH), 3391 (NH), 3081 (Ar-H), 3045, 2867 (CH\(_2\)), 1699 (C=N), 1650, 1596, 1580, 1501, 1488, 1451, 1296, 1206, 961, 901, 770, 709, 535.

UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 290, 667.

ES-MS m/z: 1092.5 [M + H]\(^+\).

CHN: C\(_{60}\)H\(_{76}\)CuN\(_{12}\)O\(_4\). Calculated C, 65.94; H, 7.01; N, 15.38; Found C, 65.68; H, 6.99; N, 15.12.

### 2.3.12.2 Nickel(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (190)

![Chemical Structure](image)

Yield: 45 %.

mp: > 300 °C.

Colour: Green.
FT-IR (KBr, v, cm\(^{-1}\)): 3437 (OH), 3394 (NH), 3088 (Ar-H), 3042, 2864 (CH\(_2\)), 1701 (C=N), 1656, 1594, 1572, 1526, 1499, 1446, 1288, 1118, 1055, 964, 806, 711, 526.

UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 284, 671.

ES-MS m/z: 1087.5 [M + H]\(^+\).

CHN: C\(_{60}\)H\(_{76}\)NiN\(_{12}\)O\(_4\). Calculated C, 66.23; H, 7.04; N, 15.45; Found C, 66.06; H, 6.81; N, 15.31.

2.3.12.3 Zinc(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (191):

Yield: 45 %.

mp: > 300 °C.

Colour: Blue.

FT-IR (KBr, v, cm\(^{-1}\)): 3432 (OH), 3392 (NH), 3082 (Ar-H), 3049, 3048, 2865 (CH\(_2\)), 1701 (C=N), 1652, 1598, 1497, 1449, 1333, 1291, 1215, 1018, 770, 526.
UV/Vis ($\lambda_{\text{max}}, \text{nm, H}_2\text{SO}_4$): 296, 668.
ES-MS m/z: 1093.5 [M + H]$^+$.  
CHN: C$_{60}$H$_{76}$ZnN$_{12}$O$_{4}$. Calculated C, 65.83; H, 7.00; N, 15.35; Found C, 65.60; H, 6.77; N, 15.14.

2.3.12.4 Cobalt(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (192)

Yield: 46 %.  
mp: > 300 °C.  
Colour: Blue.  
FT-IR (KBr, $\nu$, cm$^{-1}$): 3438 (OH), 3391 (NH), 3090 (Ar-H), 2863 (CH$_2$), 1707 (C=N), 1642, 1601, 1503, 1476, 1409, 1281, 1124, 1083, 1075, 1022, 975, 909, 899, 851, 789, 729, 570.  
UV/Vis ($\lambda_{\text{max}}, \text{nm, H}_2\text{SO}_4$): 340, 670.  
ES-MS m/z: 1088.5 [M + H]$^+$.  

(192)
2.3.12.5 Plumbum(II) 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (193)

Yield: 41 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr, v, cm⁻¹): 3431 (OH), 3395 (NH), 3088 (Ar-H), 3043, 2868 (CH₂), 1699 (C=Н), 1599, 1502, 1411, 1296, 1231, 1127, 1029, 967, 908, 862, 776, 721, 663, 476.
UV/Vis (λₘₐₓ, nm, H₂SO₄): 296, 342, 668.
ES-MS m/z: 1237.6 [M + H]⁺.
2.3.13 2(3),9(10),16(17),23(24)-Tetrakis-{{{(9,10-dioxo-9,10-dihydroanthracen-2-yl)amino}methyl}phthalocyanines

4-((9,10-Dioxo-9,10-dihydroanthracen-2-ylamino)methyl)phthalonitrile (0.04 mole), metal halide (0.01 mole) was added in nitrobenzene and the resulting mixture was heated at reflux temperature for 6 hours. After the completion of the reaction the complex was filtered under reduced pressure and the residue was washed with hot water and then dried in oven at 100 °C.

2.3.13.1 Copper(II) 2(3),9(10),16(17),23(24)-tetrakis-{{{(9,10-dioxo-9,10-dihydroanthracen-2-yl)amino}methyl}phthalocyanines (194):

\[ R = \text{HN-} \]

Yield: 55 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr, ν, cm\(^{-1}\)): 3385, 3080 (Ar-H), 3043, 2850, 1688 (C=N), 1670 (C=O), 1595, 1571, 1489, 1446, 1291, 1251, 1233, 1207, 977, 901, 772, 701, 665, 526, 473.
UV/Vis (λ\(_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 296, 345, 670.
ES-MS m/z: 1516.33 [M + H]\(^+\).
Elemental Analysis: C\textsubscript{92}H\textsubscript{52}CuN\textsubscript{12}O\textsubscript{8}. Calculated C, 72.84; H, 3.45; N, 11.08; Found C, 72.51; H, 3.34; N, 10.79.

2.3.13.2 Cobalt(II) 2(3),9(10),16(17),23(24)-tetrakis-[[9,10-dioxo-9,10-dihydroanthracen-2-yl]amino]methyl]phthalocyanines (195):

\[
\begin{array}{c}
\text{Co} \\
\text{N} \quad \text{N} \\
\text{R} \\
\text{O} \\
\text{O} \\
\text{HN} \\
\text{R} \\
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\]

\( \text{(195)} \)

Yield: 49 %.

mp: > 300 °C.

Colour: Blue.

FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3390 (NH), 3088 (Ar-H), 2858, 1691 (C=N), 1673 (C=O), 1601, 1562, 1488, 1414, 1278, 1134, 1035, 917, 889, 867, 760, 734, 586, 516, 464.

UV/Vis (\( \lambda_{\text{max}}, \text{nm, H}_2\text{SO}_4 \)): 296, 345, 668.

ES-MS m/z: 1512.34 [M+H]\(^+\)

Elemental Analysis: C\textsubscript{92}H\textsubscript{52}CoN\textsubscript{12}O\textsubscript{8}. Calculated C, 73.06; H, 3.47; N, 11.11; Found C, 72.81; H, 3.20; N, 10.89.
2.3.13.3 Nickel(II) 2(3),9(10),16(17),23(24)-tetrakis-[[[9,10-dioxo-9,10-dihydroanthracen-2-yl]amino]methyl]phthalocyanines (196):

\[ \text{Ni} \]

Yield: 46 %.
mp: > 300 °C.
Colour: Blue.
FT-IR (KBr, ν, cm\(^{-1}\)): 3393 (NH), 3078 (Ar-H), 2824 (CH\(_2\)), 1693 (C=N), 1671 (C=O), 1598, 1580, 1492, 1440, 1299, 1228, 1216, 1112, 1072, 1008, 972, 897, 777, 732, 654, 578, 534, 480.
UV/Vis (\(\lambda_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 292, 673.
mp: > 300 °C.
ES-MS m/z: 1511.34 [M+H]\(^+\)
Elemental Analysis: C\(_{92}\)H\(_{52}\)N\(_{12}\)NiO\(_8\). Calculated C, 73.07; H, 3.47; N, 11.12; Found C, 72.87; H, 3.51; N, 11.01.

2.3.14 2(3),9(10),16(17),23(24)-Tetrakis-\{1-[(4-nitrophenyl)diazenyl]naphthalen-2-yl\}oxymethylphthalocyanines (197)

A mixture of \{1-[(4-nitrophenyl)diazenyl]naphthalen-2-yl\}oxymethylhthalonitrile (0.04 mole), K\(_2\)CO\(_3\) (0.06 mole) and metal halide (0.01 mole) was refluxed in nitrobenzene for 6 hours. After the completion of the
reaction mixture was filtered under reduced pressure and the residue was washed with hot water followed by methanol and then dried in oven at 100 °C. A mixture of products was obtained which were inseparable.

2.4 Perylenetetracarboxyllic acid Derivatives

2.4.1 Synthesis of mono potassium salt of PTCDA

Synthesis of mono potassium salt of Perylene-3,4,9,10-tetracarboxyllic acid monoanhydride (198):

![Chemical Structure 198]

Perylene-3,4,9,10-tetracarboxylic acid dianhydride (19.6 gm) and potassium hydroxide (8.3 gm of 100%) were dissolved in water (250 mL) at 80 °C, the pH of the solution was adjusted to 4.5 by the dropwise addition of hydrochloric acid (10%) at this temperature over a period of two hours. The reaction mixture was stirred for two hours at 80 °C. After cooling the product was filtered and washed with water to make it chloride-free and dried. The product thus obtained was used further without further purification.

2.4.2 N-Butylperylene-3,4,9,10-tetracarboxylic acid monoanhydride monoimide (199)

![Chemical Structure 199]
Mono potassium salt of perylene-3,4,9,10-tetracarboxylic acid monoanhydride (22.4 gm) was added into the solution of n-butylamine (14.6 gm, 0.2 moles) in 250 mL water and the mixture was stirred at room temperature for one hour and then at 90 °C for one hour. The product was precipitated by acidification and filtered. In order to remove diimide and perylene tetracarboxylic acid, the product was dissolved in 350 mL of 5% KOH solution at 90-95 °C and the di-potassium salt was precipitated by adding 30 gm KCl. The resulting dipotassium salt was filtered and washed with 14% KCl and then with 1% KOH. The residue was dissolved in boiling water and acidified to afford 19.4 gm (86.8%) of N-butylperylenetetracarboxylic acid monoanhydride monoimide on filteration.

Yield: 86.8%.
mp: > 300 °C.
Colour: Black powder.
FT-IR (KBr, ν, cm\(^{-1}\)): 2930, 2860, 1765, 1721, 1693, 1656, 1592, 1504, 1454, 1405, 1322, 1240, 1151, 1126, 1087, 1016, 864, 800, 793, 737.
UV/Vis (λ\(_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 360, 620.
ES-MS m/z: 447.0 (M\(^+\), 100%), 448 (29.5) 430 (30.7), 405 (31.2), 391 (88.5), 374 (14.1), 361 (7.3), 347 (24.8), 333 (6.0), 320 (10.5), 319 (22.6), 274 (10.6).
CHN: C\(_{28}\)H\(_{17}\)NO\(_5\). Calculated C, 75.16; H, 3.83; N, 3.13; Found C, 75.02; H, 3.67; N, 3.01.

2.4.3 N-Octylperylene-3,4,9,10-tetracarboxylic acid monoanhydride monoimide (200)
Mono potassium salt of perylene-3,4,9,10-tetracarboxylic acid monoanhydride (22.4 gm) was added into the solution n-octylamine (25.8 gm, 0.2 moles) in 250 mL water and the mixture was stirred at room temperature for one hour and then at 90 °C for one hour. The product was precipitated by acidification and filtered. In order to remove diimide and perylene tetracarboxylic acid the product was dissolved in 350 mL of 5% KOH solution at 90-95 °C and the di-
potassium salt was precipitated by adding 30 gm KCl. The resulting dipotassium salt was filtered and washed with 14% KCl and then with 1% KOH. The residue was dissolved in boiling water and acidified to afford 19.4 gm (85.8%) of perylenetetracarboxylic acid monoanhydride monobutylimide on filtration.

![Diagram](200)

Yield: 85.8%.
mp: > 300 °C.
Colour: Black powder.
FT-IR (KBr, ν, cm⁻¹): 2923, 2855, 1767, 1721, 1693, 1656, 1592, 1504, 1454, 1405, 1322. 1240, 1151, 1126, 1087, 1016, 864, 800, 793, 737.
UV/Vis (λ_max, nm, H₂SO₄): 553, 603, 795.
ES-MS m/z: 503.0 (M⁺).
CHN: C₃₂H₂₅NO₅. Calculated C, 76.33; H, 5.00; N, 2.78; Found C, 76.17; H, 4.87; N, 2.61.

2.4.4 N-Butyl-N’-(6-aminohexyl)perylene-3,4,9,10-tetracarboxylic diimide (201):

A mixture of N-butylperylene-3,4,9,10-tetracarboxylic acid monoanhydride monoimide 199 (20 gm, 44.7 mmol) and hexane-1,6-diamine (6.48 gm, 55.9 mmol) in ethylene glycol was heated at 175 °C for two hours. The mixture was cooled to 80 °C and then diluted with methanol (30 mL) and filtered. The precipitates were washed with excess methanol (20 mL) and water and dried in oven at 110 °C to afford N-Butyl-N’-(6-aminohexyl)perylene-3,4,9,10-tetracarboxylic diimide (201) as a black powder.
Chapter – 2   Materials & Methods

Yield: 71%.
mp: > 300 °C.
Colour: Black powder.
FT-IR (KBr, ν, cm\(^{-1}\)): 3624 & 3582 (NH\(_2\)), 2920, 2840, 1766, 1693, 1681, 1659, 1650, 1632, 1592, 1555, 1503, 1562, 1454, 1377, 1084, 882, 722.
UV/Vis (λ\(_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 556, 601, 794.
ES-MS m/z: 545.0 (M\(^+\)).

CHN: C\(_{34}\)H\(_{31}\)N\(_3\)O\(_4\). Calculated C, 74.84; H, 5.73; N, 7.70; Found C, 74.70; H, 5.60; N, 7.53.

2.4.5 N-Butyl-N’-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (202):
A mixture of N-butylperylene-3,4,9,10-tetracarboxylic acid monoanhydride monoimide 199 (20 gm, 44.7 mmol) and 6-hydroxyhexylamine (6.54 gm, 55.9 mmol) in ethylene glycol was heated at 175 °C for two hours. The mixture was cooled to 80 °C and then diluted with methanol (30 mL) and filtered. The precipitates were washed with excess methanol (20 mL) and water and dried in oven at 110 °C to afford N-Butyl-N’-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (202) as a black powder (17 gm).
Yield: 74%.
mp: > 300 °C.
Colour: Black powder.
FT-IR (KBr, ν, cm\(^{-1}\)): (KBr, ν, cm\(^{-1}\)), 2919, 2845, 1766, 1693, 1645, 1632, 1592, 1555, 1503, 1562, 1450, 1375, 1084, 722.
UV/Vis (λ\(_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 553, 603, 795.
ES-MS m/z: 532.0 (M\(^+\)).
CHN: C\(_{33}\)H\(_{28}\)N\(_2\)O\(_5\). Calculated C, 74.42; H, 5.30; N, 5.26; Found C, 74.25; H, 5.13; N, 5.10.

2.4.6 **N,N’-Bis(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (203):**

N,N’-Bis(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (203) was synthesized from mono potassium salt of perylene-3,4,9,10-tetracarboxylic acid monoanhydride as described in the previous section for compounds 201 and 202.

\[ \text{(203)} \]

Yield: 70%.
mp: > 300 °C.
Colour: Black powder.
FT-IR (KBr, ν, cm\(^{-1}\)): 2926, 2840, 1766, 1690, 1655, 1631, 1590, 1551, 1503, 1560, 1459, 1376, 1084, 721.
UV/Vis (λ\(_{\text{max}}\), nm, H\(_2\)SO\(_4\)): 400, 555, 600, 795.
ES-MS m/z: 590.3 (M\(^+\)).
CHN: C\(_{36}\)H\(_{34}\)N\(_2\)O\(_6\). Calculated C, 73.20; H, 5.80; N, 4.74; Found C, 72.99; H, 5.83; N, 4.46.
Chapter – 3

RESULTS & DISCUSSION
3- RESULT AND DISCUSSION

3.1 Phthalocyanines

Phthalocyanines are important macrocyclic compounds for instance approximately 25% of all artificial organic pigments are phthalocyanine derivatives. Metal phthalocyanines have long been examined as catalysts for redox reactions. Phthalocyanine compounds have been investigated as donor materials in molecular electronics, e.g. organic field-effect transistors. Keeping in view the importance of phthalocyanines, synthesis of peripheral substituted phthalocyanines as potential high technology colorants was the main objective of this work. Two major routes for the synthesis of targeted phthalocyanines were considered. The first route involved the synthesis of tetramethyl related phthalocyanines using methyl phthalonitride followed by Bromination of methyl to form bromo methyleted phthalocyanines which could be subsequently coupled with suitable nucleophiles like amines or alcohols (Scheme 26). But after number of attempts we were unable to optimize the yield of targeted compounds. Therefore we shifted our synthesis via tetranitrophthalocyanine which was subsequently reduced to tetraminophthalocyanines for their coupling with appropriate alkyl halides. But once again coupling resulted in mixture of products (Scheme 27). This situation diverted us towards the synthesis of these phthalocyanines by cyclotetramerization of substituted methyl phthalonitriles. Thus for this purpose substituted phthalonitriles were synthesized and converted to the respective phthalocyanines using the known methodologies.
Scheme-26: Proposed scheme of phthalocyanines and derivatives by route 1.
Ammonium molybdate, Urea
Nitrobenzene, Reflux 6 hrs

M = 2H, Cu, Ni, Zn, Co, Pb.

Scheme-27: Proposed scheme of phthalocyanines and derivatives by route 2.
3.2 2,9(10),16(17),23(24)-Tetramethylphthalocyanines

2,9(10),16(17),23(24)-Tetramethylphthalocyanines (134-139) were synthesized from 4-methylphthalonitrile (prepared from p-toluidine using bromination-diazotization-cyanation sequence). Tetr amers obtained were characterized by using IR, Mass and elemental analysis.

Scheme-28: Synthesis of tetramethylphthalocyanines (134-139).

The disappearance of absorption band near 2230 cm\(^{-1}\) and the appearance of bands near 1690 cm\(^{-1}\) provided ample evidence for the conversion of C≡N to isoindole ring. All the Metal free phthalocyanines showed absorption near 3400 cm\(^{-1}\) due to the NH of isoindole whereas no such absorptions were seen for metallated phthalocyanines due to the deprotonation of nitrogen and its involvement in chelation with the central metal. Methyl moiety in methyl substituted phthalocyanines showed absorption in the range of 2960 cm\(^{-1}\) (Table-2). Mass and elemental analysis results also confirm the formation of target complexes (Table-3). The Q band of these phthalocynines observed around 670 nm and the soret bands in the region of 230-330 nm.
2,9(10),16(17),23(24)-Tetranitrophthalocyanine (140-145) were synthesized from 4-nitrophthalic anhydride using literature method. Metal free and metal chelated tetramers obtained were characterized by using IR, Mass and elemental analysis.

\[
\begin{array}{c}
\text{Ammonium molybdate} \\
\text{MX}_2 \quad \text{Urea,} \\
\text{Nitrobenzene 6hrs reflux}
\end{array}
\]

\[
\begin{array}{c}
\begin{array}{c}
\text{O}_2\text{N} \\
\text{O}_2\text{N}
\end{array} \\
\begin{array}{c}
\text{NO}_2 \\
\text{NO}_2 \\
\text{NO}_2 \\
\text{NO}_2
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{O}_2\text{N} \\
\text{O}_2\text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{M = Cu, Ni, Zn, Co, Pb}
\end{array}
\]

Scheme-29: Synthesis of tetranitrophthalocyanines (140-145).

The disappearance of absorption band near 2230 cm\(^{-1}\) and the appearance of bands near 1690 cm\(^{-1}\) provided ample evidence for the disappearance of C≡N and formation of isoindole ring. All the Metal free phthalocyanines showed absorption near 3400 cm\(^{-1}\) due to the NH of isoindole whereas no such absorption was seen for metallated phthalocyanines due to the deprotonation of nitrogen and its involvement in chelation with the central metal. Stretching vibrations typical for NO\(_2\) were observed near 1530 and 1345 cm\(^{-1}\). Mass spectral and elemental analysis results also confirmed the formation of target complexes.

Soret band appears between 230-350 nm in uv/visible spectras of phthalocynine. Similarly the Q –band appeared around 650-670 nm.
Table-2: IR Spectra of tetramethylphthalocyanines (134-139)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Formula</th>
<th>NH (cm(^{-1}))</th>
<th>C=N (cm(^{-1}))</th>
<th>C=C (Ar) (cm(^{-1}))</th>
<th>C-H (Ar) (cm(^{-1}))</th>
<th>CH(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>134</td>
<td>C(<em>{36})H(</em>{26})N(_8)</td>
<td>3403</td>
<td>1690</td>
<td>1523, 1601</td>
<td>3050</td>
<td>2959</td>
</tr>
<tr>
<td>135</td>
<td>C(<em>{36})H(</em>{24})N(_8)Cu</td>
<td>-</td>
<td>1698</td>
<td>1500,1602</td>
<td>3089</td>
<td>2961</td>
</tr>
<tr>
<td>136</td>
<td>C(<em>{36})H(</em>{24})N(_8)Ni</td>
<td>-</td>
<td>1695</td>
<td>1507,1611</td>
<td>3084</td>
<td>2965</td>
</tr>
<tr>
<td>137</td>
<td>C(<em>{36})H(</em>{24})N(_8)Zn</td>
<td>-</td>
<td>1698</td>
<td>1500,1600</td>
<td>3085</td>
<td>2970</td>
</tr>
<tr>
<td>138</td>
<td>C(<em>{36})H(</em>{24})N(_8)Co</td>
<td>-</td>
<td>1690</td>
<td>1517,1604</td>
<td>3079</td>
<td>2966</td>
</tr>
<tr>
<td>139</td>
<td>C(<em>{36})H(</em>{24})N(_8)Pb</td>
<td>-</td>
<td>1688</td>
<td>1500,1602</td>
<td>3082</td>
<td>2964</td>
</tr>
</tbody>
</table>
### Table-3: Elemental Analysis and Mass Data of tetramethylphthalocynines (134-139)

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>MS [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C  H  N  C  H  N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>C\textsubscript{36}H\textsubscript{26}N\textsubscript{8}</td>
<td>75.77 4.59 19.64</td>
<td>75.62 4.48 119.55</td>
<td>571.2</td>
</tr>
<tr>
<td>135</td>
<td>C\textsubscript{36}H\textsubscript{24}N\textsubscript{8}Cu</td>
<td>68.40 3.83 17.73</td>
<td>68.21 3.59 17.51</td>
<td>632.1</td>
</tr>
<tr>
<td>136</td>
<td>C\textsubscript{36}H\textsubscript{24}N\textsubscript{8}Ni</td>
<td>68.93 3.86 17.86</td>
<td>68.79 3.75 17.72</td>
<td>627.1</td>
</tr>
<tr>
<td>137</td>
<td>C\textsubscript{36}H\textsubscript{24}N\textsubscript{8}Zn</td>
<td>68.20 3.82 17.67</td>
<td>68.03 3.69 17.51</td>
<td>633.1</td>
</tr>
<tr>
<td>138</td>
<td>C\textsubscript{36}H\textsubscript{24}N\textsubscript{8}Co</td>
<td>68.90 3.85 17.86</td>
<td>68.59 3.53 17.50</td>
<td>628.1</td>
</tr>
<tr>
<td>139</td>
<td>C\textsubscript{36}H\textsubscript{24}N\textsubscript{8}Pb</td>
<td>55.73 3.12 14.44</td>
<td>55.35 2.90 14.11</td>
<td>777.1</td>
</tr>
</tbody>
</table>
Table 4: IR Spectra tetranitrophthalocycnines (140-145)

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>NH (cm(^{-1}))</th>
<th>C=N (cm(^{-1}))</th>
<th>C=C (Ar) (cm(^{-1}))</th>
<th>C-H (Ar) (cm(^{-1}))</th>
<th>NO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>C(<em>{32})H(</em>{14})N(_{12})O(_8)</td>
<td>3401</td>
<td>1693</td>
<td>1523</td>
<td>3090</td>
<td>1530,1326</td>
</tr>
<tr>
<td>141</td>
<td>C(<em>{32})H(</em>{12})N(_{12})O(_8)Cu</td>
<td>-</td>
<td>1698</td>
<td>1507,1604</td>
<td>3084</td>
<td>1525,1345</td>
</tr>
<tr>
<td>142</td>
<td>C(<em>{32})H(</em>{12})N(_{12})O(_8)Ni</td>
<td>-</td>
<td>1695</td>
<td>1511,1601</td>
<td>3087</td>
<td>1526,1351</td>
</tr>
<tr>
<td>143</td>
<td>C(<em>{32})H(</em>{12})N(_{12})O(_8)Zn</td>
<td>-</td>
<td>1695</td>
<td>1499,1605</td>
<td>3081</td>
<td>1525,1344</td>
</tr>
<tr>
<td>144</td>
<td>C(<em>{32})H(</em>{12})N(_{12})O(_8)Co</td>
<td>-</td>
<td>1699</td>
<td>1501,1607</td>
<td>3079</td>
<td>1527,1350</td>
</tr>
<tr>
<td>145</td>
<td>C(<em>{32})H(</em>{12})N(_{12})O(_8)Pb</td>
<td>-</td>
<td>1698</td>
<td>1509,1607</td>
<td>3096</td>
<td>1525,1341</td>
</tr>
</tbody>
</table>
Table-5: Elemental analysis and mass data of tetranitrophthalocyanines (140-145)

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>MS [M+H](^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>140</td>
<td>C(<em>{32})H(</em>{14})N(<em>{12})O(</em>{8})</td>
<td>55.34</td>
<td>2.03</td>
<td>24.20</td>
</tr>
<tr>
<td>141</td>
<td>C(<em>{32})H(</em>{12})N(<em>{12})O(</em>{8})Cu</td>
<td>50.83</td>
<td>1.60</td>
<td>22.23</td>
</tr>
<tr>
<td>142</td>
<td>C(<em>{32})H(</em>{12})N(<em>{12})O(</em>{8})Ni</td>
<td>51.16</td>
<td>1.61</td>
<td>22.37</td>
</tr>
<tr>
<td>143</td>
<td>C(<em>{32})H(</em>{12})N(<em>{12})O(</em>{8})Zn</td>
<td>50.71</td>
<td>1.60</td>
<td>22.18</td>
</tr>
<tr>
<td>144</td>
<td>C(<em>{32})H(</em>{12})N(<em>{12})O(</em>{8})Co</td>
<td>51.15</td>
<td>1.61</td>
<td>22.37</td>
</tr>
<tr>
<td>145</td>
<td>C(<em>{32})H(</em>{12})N(<em>{12})O(</em>{8})Pb</td>
<td>42.72</td>
<td>1.34</td>
<td>18.68</td>
</tr>
</tbody>
</table>

3.4 2(3),9(10),16(17),23(24)-tetra(pyrroolidin-1-yl)phthalocyanines (152-157)

In order to synthesize variously substituted phthalocyanines we planned to prepare 4-(4-bromobutylamino)phthalonitrile from 4-aminophthalonitrile and 1,4-dibromobutane. The isolated product was found to be 4-(pyrroolidin-1-yl)phthalonitrile instead of 4-(4-bromobutylamino)phthalonitrile (Scheme 30). Purity of the product was checked by TLC employing \(n\)-hexane and ethyl acetate.
mixture (1:4). The structure of the product was confirmed by IR, NMR, CNMR and elemental analysis. Disappearance of band due to NH$_2$ in the range of 3100-3300 cm$^{-1}$ and appearance of absorption band at 2860 cm$^{-1}$ due to methylene in the IR spectra established the formation of 4-(pyrrolidin-1-yl)phthalonitrile while CN stretching was visible at 2232 cm$^{-1}$ and the bands due to aromatic ring (C=C) showed stretching at 1605 & 1507 cm$^{-1}$.

![Scheme 30: Synthesis of 4-(pyrrolidin-1-yl)phthalonitrile](image)

In the $^1$H NMR spectra absence of peaks due to two amino protons indicated the formation of pyrrolidine ring. In $^1$H NMR a doublet at 7.73 ppm with coupling constant 8.8 Hz was assigned to aryl-H$_5$ and another doublet at 7.12 ppm with J = 2.4 Hz was assigned to aryl H$_3$. While a doublet of doublets around 6.84 ppm was assigned to aryl H$_6$ on the basis of coupling constant. The four methylene protons of NCH$_2$ appeared as triplet at 3.3 $\delta$ while a multiplet corresponding to four protons of two methylene groups appeared in range of 1.97-1.93 $\delta$. The molecular ion peak in the mass spectra and elemental analysis data was also found in good agreement with the expected result.

2(3),9(10),16(17),23(24)-tetra(pyrrolidin-1-yl)phthalocyanines (152-157) were synthesized by refluxing the mixture of 4-(pyrrolidin-1-yl)phthalonitrile (0.04 mole) with or without metal halides (0.01 mole) in nitrobenzene for 6 hours (Scheme 31). The precipitates formed were washed with hot water and dried in oven. All the synthesized compounds were characterized with the help of IR, Mass and Elemental analysis.
Disappearance of nitrile stretching band around 2230 cm$^{-1}$ in the IR spectra of metal free phthalocyanines provided remarkable evidence for the formation of macrocycles. IR spectra of Metal free phthalocyanines showed NH (isoindole ring) stretching at 3400 cm$^{-1}$ however this band was absent in the IR spectra of metallated 2(3),9(10),16(17),23(24)-tetrakis(pyrrolidin-1-yl)phthalocyanines (152-157), methylene protons of pyrrolidine moiety showed absorption bands around 2858 cm$^{-1}$. Absorption bands in the range of 1700 cm$^{-1}$ was attributed to C=N of isoindole ring while the aromatic stretching bands where observed around 1500 cm$^{-1}$ and 1600 cm$^{-1}$ respectively (Table-6).

Molecular ion peak in the mass spectrum and elemental analysis data also confirm the structure of the respective 2(3),9(10),16(17),23(24)-tetrakis(pyrrolidin-1-yl)phthalocyanines (152-157) (Table-7). The UV/visible spectrum showed Q band maxima at 681 nm and soret bands found in the range of 280-340 nm.
Table-6: IR Spectra of tetra(pyrrolidin-1-yl)phthalocyanines (152-157)

Table:

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH (Isoindole) (cm⁻¹)</th>
<th>C=N (cm⁻¹)</th>
<th>C=C Aromatic (cm⁻¹)</th>
<th>C-H (Aromatic) (cm⁻¹)</th>
<th>CH₂ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>152</td>
<td>3396</td>
<td>1704</td>
<td>1499, 1603</td>
<td>3084</td>
<td>2851</td>
</tr>
<tr>
<td>153</td>
<td>-</td>
<td>1701</td>
<td>1507, 1605</td>
<td>3079</td>
<td>2858</td>
</tr>
<tr>
<td>154</td>
<td>-</td>
<td>1707</td>
<td>1498, 1607</td>
<td>3078</td>
<td>2854</td>
</tr>
<tr>
<td>155</td>
<td>-</td>
<td>1705</td>
<td>1504, 1601</td>
<td>3082</td>
<td>2855</td>
</tr>
<tr>
<td>156</td>
<td>-</td>
<td>1698</td>
<td>1511, 1609</td>
<td>3079</td>
<td>2853</td>
</tr>
<tr>
<td>157</td>
<td>-</td>
<td>1697</td>
<td>1494, 1599</td>
<td>3080</td>
<td>2857</td>
</tr>
</tbody>
</table>
Table-7: Elemental Analysis and Mass Data of tetra(pyrrolidin-1-yl)phthalocyanines (152-157)

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>Mass [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_{48}H_{46}N_{12}</td>
<td>72.89</td>
<td>5.86</td>
<td>21.25</td>
</tr>
<tr>
<td>152</td>
<td>C_{48}H_{44}N_{12}Cu</td>
<td>67.63</td>
<td>5.12</td>
<td>19.72</td>
</tr>
<tr>
<td>153</td>
<td>C_{48}H_{44}N_{12}Ni</td>
<td>68.01</td>
<td>5.23</td>
<td>19.83</td>
</tr>
<tr>
<td>154</td>
<td>C_{48}H_{44}N_{12}Zn</td>
<td>67.48</td>
<td>5.19</td>
<td>19.67</td>
</tr>
<tr>
<td>155</td>
<td>C_{48}H_{44}N_{12}Co</td>
<td>67.99</td>
<td>5.23</td>
<td>19.82</td>
</tr>
<tr>
<td>156</td>
<td>C_{48}H_{44}N_{12}Pb</td>
<td>57.87</td>
<td>4.45</td>
<td>16.87</td>
</tr>
</tbody>
</table>

3.5 2(3),9(10),16(17),23(24)-tetra(piperidine-1-yl)phthalocyanines (158-163)

For the synthesis of title compounds 4-(piperidin-1-yl)phthalonitrile was prepared from 4-aminophthalonitrile coupling with 1,5-dibromopentane in DMF using Potassium carbonate base (Scheme 32).

\[ \text{Scheme 32: Synthesis of 4-(piperidin-1-yl)phthalonitrile} \]
The structure of 4-(piperidin-1-yl)phthalonitrile was verified by IR, $^1$H NMR, $^{13}$C bNMR and elemental analysis. In the IR spectra absence of characteristic absorption band of NH$_2$ in the range of 3100-3300 cm$^{-1}$ confirmed the formation of piperidine ring on aminophthalonitrile. The (C-H) bond stretching band appeared at 2855 cm$^{-1}$ and characteristic bands of (C=C) aromatic ring appeared at 1501 and 1634 cm$^{-1}$ while cyano group showed strong stretching at 2234 cm$^{-1}$.

The $^1$H NMR spectra of 4-(piperidin-1-yl)phthalonitrile did not show peaks due to resonance of the protons attached to nitrogen confirming the formation of product. The three aromatic protons resonated from 6.72 to 7.72 as three doublets each peak corresponding to one proton each. Four methylene protons attached to nitrogen of piperidine ring resonated as triplet at 3.4 δ integrating to four protons while remaining three methylene appeared as multiplet from 1.76 to 1.71 δ integrating to six protons. Data obtained from $^{13}$C NMR mass spectra also confirmed the synthesis of 4-(piperidin-1-yl)phthalonitrile.

Cycloctetramerization of 4-(piperidin-1-yl)phthalonitrile with or without metal halides using nitrobenzene as solvent under refluxing conditions generated metallated and metal free 2(3),9(10),16(17),23(24)-tetra(piperidine-1-yl)phthalocyanines (158-163) (Scheme 33). All the synthesized complexes were characterized with the help of IR, Mass and Elemental analysis.
Scheme 33: Synthesis of tetra(piperidine-1-yl)phthalocyanines (158-163)

IR spectra provided ample evidence for the formation of 2,9(10),16(17),23(24)-tetrakis(4-(piperidin-1-yl))phthalocyanines (158-163). No absorption bands due to nitrile group around 2230 cm\(^{-1}\) observed confirming the formation of isoindole ring. Stretching band around 3400 cm\(^{-1}\) in metal free phthalocyanine was attributed to the NH (isoindole) while metallated phthalocyanines did not show this band. Aromatic C-H stretching bands appeared from 3078-3081 cm\(^{-1}\). Absorption bands in the range of 1696 cm\(^{-1}\) was attributed to C=N of ring while the aromatic stretching bands where observed around 1500 cm\(^{-1}\) and 1600 cm\(^{-1}\) respectively (Table-8). Elemental analysis data and molecular ion peak were also corresponded to the expected structure of the synthesized phthalocyanines (Table-9). The Q band in UV/visible spectra of these complexes observed around 665 nm while soret bands observed in the range 260-385 nm.
Table-8: IR Spectra of tetra(piperidine-1-yl)phthalocyanines (158-163)

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH (Isoindole) (cm(^{-1}))</th>
<th>C=N (cm(^{-1}))</th>
<th>C=C Aromatic (cm(^{-1}))</th>
<th>C-H (Aromatic) (cm(^{-1}))</th>
<th>CH(_2) (cm(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>158</td>
<td>3400</td>
<td>1694</td>
<td>1611, 1511</td>
<td>3079</td>
<td>2820</td>
</tr>
<tr>
<td>159</td>
<td>-</td>
<td>1695</td>
<td>1511, 1609</td>
<td>3079</td>
<td>2858</td>
</tr>
<tr>
<td>160</td>
<td>-</td>
<td>1698</td>
<td>1501, 1599</td>
<td>3078</td>
<td>2824</td>
</tr>
<tr>
<td>161</td>
<td>-</td>
<td>1697</td>
<td>1610, 1506</td>
<td>3082</td>
<td>2819</td>
</tr>
<tr>
<td>162</td>
<td>-</td>
<td>1703</td>
<td>1611, 1518</td>
<td>3079</td>
<td>2835</td>
</tr>
<tr>
<td>163</td>
<td>-</td>
<td>1691</td>
<td>1503, 1604</td>
<td>3081/3080</td>
<td>2868</td>
</tr>
</tbody>
</table>
Table-9: Elemental Analysis and Mass Data tetra(piperidine-1-yl) phthalocyanines (158-163).

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>Mass [M+H]+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>158</td>
<td>C_{52}H_{54}N_{12}</td>
<td>73.73</td>
<td>6.43</td>
<td>19.84</td>
</tr>
<tr>
<td>159</td>
<td>C_{52}H_{52}N_{12}Cu</td>
<td>68.74</td>
<td>5.77</td>
<td>18.5</td>
</tr>
<tr>
<td>160</td>
<td>C_{52}H_{52}N_{12}Ni</td>
<td>69.11</td>
<td>5.80</td>
<td>18.6</td>
</tr>
<tr>
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<td>C_{52}H_{52}N_{12}Zn</td>
<td>68.60</td>
<td>5.76</td>
<td>18.46</td>
</tr>
<tr>
<td>162</td>
<td>C_{52}H_{52}N_{12}Co</td>
<td>69.09</td>
<td>5.80</td>
<td>18.59</td>
</tr>
<tr>
<td>163</td>
<td>C_{52}H_{52}N_{12}Pb</td>
<td>59.35</td>
<td>4.98</td>
<td>15.97</td>
</tr>
</tbody>
</table>

3.6 2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanines (164-169)

4-(Azepan-1-yl)phthalonitrile was obtained when 1,6-dibromohexane was treated with 4-aminophthalonitrile (Scheme 34) for the synthesis of phthalocyanines (164-169). The structure of 4-(azepan-1-yl)phthalonitrile was also verified by IR, NMR {sup 13}CNMR and elemental analysis. An IR spectrum was found devoid of any absorption band in the region from 3100 to 3300 cm⁻¹
indicating the conversion of amino group into azepane ring. Absorption band due to C-H stretching of CH$_2$ group appeared at 2930 cm$^{-1}$ and the cyano group showed stretching absorption band at 2233 cm$^{-1}$.

![Scheme 34: Synthesis of 4-(azepan-1-yl)phthalonitrile](image)

The $^1$H NMR spectra of 4-(azepan-1-yl)phthalonitrile showed three peaks located at 7.68, 7.10 and 6.65 $\delta$ corresponding to three aromatic protons. The four protons of two methylene groups attached to nitrogen resonated as triplet at 3.2 $\delta$ integrating to four protons, while eight methylene protons of azepane ring appeared as multiplet from 1.64-1.76 $\delta$. CNMR, mass spectral and elemental analysis data also supported the formation of 4-(azepan-1-yl)phthalonitrile.

Tetramerization of 4-(azepan-1-yl)phthalonitrile in nitrobenzene with or without metal halide generated the metallated and metal free complexes of 2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanines (164-169) (Scheme 35). Structures of all the synthesized dyes were established with the help of IR, mass and elemental data. The phthalocyanines gave their Q and Soret bands in the range of 670 nm and 300 nm respectively.


Scheme 35: Synthesis of tetra(azepan-1-yl)phthalocyanines (164-169)

Disappearance of C≡N (nitrile) stretching band around 2230 cm⁻¹ in the IR spectra of metal free phthalocyanines provided reliable evidence for the formation of macrocycles. IR spectra of metal free phthalocyanines showed NH (isoindole ring) stretching at 3400 cm⁻¹ however this band was absent in the IR spectra of metallated 2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanines (164-169), methylene protons of azepan ring showed absorption bands around 2860 cm⁻¹. Absorption bands in the range of 1696 cm⁻¹ was attributed to C=N of isoindole ring while the aromatic stretching bands were observed around 1500 cm⁻¹ and 1600 cm⁻¹ respectively (Table-10).

Molecular ion peak in the mass spectrum and elemental analysis data also established the structure of the respective metallated and metal free 2(3),9(10),16(17),23(24)-tetra(azepan-1-yl)phthalocyanines (Table-11).
Table-10: IR Spectra of tetra(azepan-1-yl)phthalocyanines (164-169).

M = 2H, Cu, Ni, Zn, Co, Pb.

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH (Isoindole) (cm⁻¹)</th>
<th>C=N (cm⁻¹)</th>
<th>C=C Aromatic (cm⁻¹)</th>
<th>C-H (Aromatic) (cm⁻¹)</th>
<th>CH₂ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>164</td>
<td>3403</td>
<td>1696</td>
<td>1500,1602</td>
<td>3095</td>
<td>2861</td>
</tr>
<tr>
<td>165</td>
<td>-</td>
<td>1698</td>
<td>1500, 1602</td>
<td>3092</td>
<td>2859</td>
</tr>
<tr>
<td>166</td>
<td>-</td>
<td>1705</td>
<td>1508, 1604</td>
<td>3092</td>
<td>2863</td>
</tr>
<tr>
<td>167</td>
<td>-</td>
<td>1696</td>
<td>1502, 1606</td>
<td>3097</td>
<td>2862</td>
</tr>
<tr>
<td>168</td>
<td>-</td>
<td>1699</td>
<td>1507, 1613</td>
<td>3093</td>
<td>2857</td>
</tr>
<tr>
<td>169</td>
<td>-</td>
<td>1698</td>
<td>1494, 1599</td>
<td>3088</td>
<td>2860</td>
</tr>
</tbody>
</table>
Table-11: Elemental Analysis and Mass Data of tetra(azepan-1-yl)phthalocyanines (164-169).

![Diagram of tetra(azepan-1-yl)phthalocyanines]

M = 2H, Cu, Ni, Zn, Co, Pb.

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Mass [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>164</td>
<td>C(<em>{56})H(</em>{62})N(_{12})</td>
<td>74.47</td>
<td>6.92</td>
</tr>
<tr>
<td>165</td>
<td>C(<em>{56})H(</em>{60})N(_{12})Cu</td>
<td>69.72</td>
<td>6.27</td>
</tr>
<tr>
<td>166</td>
<td>C(<em>{56})H(</em>{60})N(_{12})Ni</td>
<td>70.07</td>
<td>6.30</td>
</tr>
<tr>
<td>167</td>
<td>C(<em>{56})H(</em>{60})N(_{12})Zn</td>
<td>69.59</td>
<td>6.26</td>
</tr>
<tr>
<td>168</td>
<td>C(<em>{56})H(</em>{60})N(_{12})Co</td>
<td>70.06</td>
<td>6.30</td>
</tr>
<tr>
<td>169</td>
<td>C(<em>{56})H(</em>{60})N(_{12})Pb</td>
<td>60.68</td>
<td>5.46</td>
</tr>
</tbody>
</table>

3.7 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193)

In the first step 4-(bromomethyl)phthalonitrile (129) was synthesized by heating 4-methylphthaonitrile with N-bromosuccinimide in carbon tetrachloride in bright sunlight (Scheme 36). The compound 129 was characterized with IR spectra which showed absorption band due to methylene protons stretching...
around 2831 cm\(^{-1}\) and characteristic band for aryl group around 1503 and 1606 cm\(^{-1}\).

![Scheme 36: Synthesis of 4-(bromomethyl)phthalonitrile](image)

The synthesis 4-(bromomethyl)phthalonitrile (129) was confirmed by \(^1\)H NMR data. The aryl protons were appeared down field as two doublets around 7.85 and 7.79 ppm while doublet of doublets at 7.72 ppm each integrating to single proton were assigned to aryl-H\(_3\), aryl-H\(_6\) and aryl-H\(_5\). A singlet at 4.46 ppm integrating to two protons was assigned to methylene group. Mass spectra showed two peaks corresponding to M\(^+\) and M+2 in almost 50:50 ratios due to the presence of two isotopes of bromine. Elemental analysis also confirmed the formation of 4-(bromomethyl)phthalonitrile (129). Then 4-((6-hydroxyhexylamino)methyl)phthalonitrile (130) was synthesized by stirring 4-(bromomethyl)phthalonitrile (129) with 6-aminohexanol in DMF using Potassium carbonate (Scheme 37). Reaction was monitored by TLC and the product obtained was characterized by IR, \(^1\)H NMR, mass and elemental analysis.

![Scheme 37: 4-((6-hydroxyhexylamino)methyl)phthalonitrile (130)](image)

IR spectra showed band due to the absorption of OH was observed at 3433 cm\(^{-1}\) while amino group absorbed at 3395 cm\(^{-1}\) and CN absorbed at 2235 cm\(^{-1}\).
NMR spectra aromatic protons resonated in the usual range from 7.69-7.81 δ as three peaks integrating to three protons while OH and NH protons appeared as broad peak at 1.80-1.75 δ. The methylene protons attached to hydroxyl group resonated as triplet 3.65 ppm while a singlet at 3.99 ppm was assigned to aryl-CH₂ protons and a triplet at 2.65 ppm was assigned to -N CH₂. Mass spectra and elemental analysis also confirmed the formation of target compound.

2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193) were obtained by the cyclo-tetramerization of 4-((6-hydroxyhexylamino)-methyl)phthalonitrile and different metal halides (130) using standard conditions for the synthesis of phthalocyanines (Scheme 38). The structures of all synthesized macrocycles were established on the basis of data obtained from IR, Mass and elemental analysis. The Q and Soret bands for these complexes were found in the range of 650-675 nm and 260-350 nm respectively.

![Scheme 38: Synthesis of tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193)](image)

M = 2H, Cu, Ni, Zn, Co, Pb.
Chapter – 3  Results & Discussion

No absorption band in the range of 2235 cm$^{-1}$ due to -C≡N (nitrile) stretching was observed in the IR spectra of 2(3),9(10),16(17),23(24)-tetrakis[(6-hydroxyhexylamino)-methyl]phthalocyanines (189-193) which indicated the formation of macrocycles, other evidence in the IR spectra that indicate the formation of product included absorption band near 1690-1700 cm$^{-1}$ due to C=N. While bands near 3390-3400 cm$^{-1}$ and 2920 cm$^{-1}$ were attributed to NH stretching and aliphatic chain respectively. Finger print region showed characteristic pattern of phthalocyanines (Table 12).

Molecular ion peak (M+H) in the mass spectrum and combustion analysis also supported the formation of macrocycles (Table 13).

**Table 12: IR Spectra tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>OH cm$^{-1}$</th>
<th>NH (Isoindole)/ S-Amide (cm$^{-1}$)</th>
<th>C=N (cm$^{-1}$)</th>
<th>C=C Aromatic (cm$^{-1}$)</th>
<th>C-H (Aromatic) (cm$^{-1}$)</th>
<th>CH$_2$, (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>189</td>
<td>3433</td>
<td>3391</td>
<td>1699</td>
<td>1501, 1596</td>
<td>3081</td>
<td>2867</td>
</tr>
<tr>
<td>190</td>
<td>3437</td>
<td>3394</td>
<td>1701</td>
<td>1594, 1499</td>
<td>3088</td>
<td>2864</td>
</tr>
<tr>
<td>191</td>
<td>3432</td>
<td>3392</td>
<td>1701</td>
<td>1497, 1503</td>
<td>3082</td>
<td>2865</td>
</tr>
</tbody>
</table>
Table 13: Elemental Analysis and Mass Data of tetrakis[(6-hydroxyhexylamino)methyl]phthalocyanines (189-193)

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>Mass [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_60H_76N_12M,O_4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>189</td>
<td>C_60H_76N_12CuO_4</td>
<td>65.94 7.01 15.38</td>
<td>65.68 6.99 15.12</td>
<td>1092.5</td>
</tr>
<tr>
<td>190</td>
<td>C_60H_76N_12NiO_4</td>
<td>66.23 7.04 15.45</td>
<td>66.06 6.81 15.31</td>
<td>1087.5</td>
</tr>
<tr>
<td>191</td>
<td>C_60H_76N_12ZnO_4</td>
<td>65.83 7.00 15.35</td>
<td>65.60 6.77 15.14</td>
<td>1093.5</td>
</tr>
<tr>
<td>192</td>
<td>C_60H_76N_12CoO_4</td>
<td>66.22 7.04 15.44</td>
<td>66.09 7.07 15.29</td>
<td>1088.5</td>
</tr>
<tr>
<td>193</td>
<td>C_60H_76N_12PbO_4</td>
<td>58.28 6.20 13.59</td>
<td>58.09 6.22 13.43</td>
<td>1237.6</td>
</tr>
</tbody>
</table>

3.8 2(3),9(10),16(17),23(24)-tetrakis-{{1-[(4-nitrophenyl)diazenyl]naphthalen-2-yl}oxymethyl}phthalocyanines & 2(3),9(10),16(17),23(24)-Tetrakis-{{4-[(4-
nitrophenyl)diazenyl] naphthalen-2-yl]oxymethyl)phthalocyanines:

Compound (132) and (133) were synthesized by heating bromomethyl phthalonitrile with 1-[(4-nitrophenyl)diazenyl]naphthalen-2-ol and 4-[(4-nitrophenyl)diazenyl]naphthalen-1-ol in acetone at refluxing temperature in the presence of Potassium carbonate (Scheme 39). These structures were confirmed by IR, $^1$H NMR, Mass spectroscopy and elemental analysis.

Scheme 39: Synthesis of 4-{1-[(4-Nitrophenyl)diazenyl])naphthalen-2-loxy}methyl)phthalonitrile (132) 4-{4-[(4-Nitrophenyl)diazenyl]naphthalen-1-yloxy}methyl)phthalonitrile (133)

The IR spectra of both compound 132 & 133 showed absorption bands for -CN group stretching 2227 and 2233 cm$^{-1}$ while N=N stretchings were observed around 1629 and 1625 cm$^{-1}$. Absorption bands of nitro group were observed in the range of 1518 and 1335 cm$^{-1}$. In $^1$H NMR spectra a group of multiplets were observed around 6.9 – 8.50 $\delta$ which corresponded to aromatic protons. The singlets for methylene moiety were observed around 5.37 and 5.35 $\delta$ each integrated to two protons. Mass spectra and elemental analysis results were also agreement with the structures.
The final step of cyclotetramerization of compounds (132) & (133) using standard protocol (Scheme 40) resulted in inseparable mixture of products. An effort was in progress to optimize their synthesis.

![Scheme 40: Synthesis of tetrakis-({1-[(4-nitrophenyl)diazenyl]naphthalen-2-yl}oxymethyl)phthalocyanines & Tetrakis-({4-[(4-nitrophenyl)diazenyl]naphthalen-2-yl}oxymethyl)phthalocyanines](image)

\[
\begin{align*}
R &= \text{NO}_2 \text{N} \equiv \text{N}, \\
M &= \text{2H, Cu, Ni, Zn, Co, Pb.}
\end{align*}
\]

197

Scheme 40: Synthesis of tetrakis-({1-[(4-nitrophenyl)diazenyl]naphthalen-2-yl}oxymethyl)phthalocyanines & Tetrakis-({4-[(4-nitrophenyl)diazenyl]naphthalen-2-yl}oxymethyl)phthalocyanines

3.9 2(3),9(10),16(17),23(24)-tetrakis-[[9,10-dioxo-9,10-dihydroanthracen-2-yl]amino]methyl]phthalocyanines (194-196)

4-((9,10-Dioxo-9,10-dihydroanthracen-2-ylamino)methyl)phthalonitrile (131) was prepared by reacting 4-bromomethylphthalonitrile with 2-aminoanthraquinone in DMF at 80 °C (Scheme 41). The product separated was characterized by IR, \(^1\)H NMR, Mass and elemental analysis. IR spectra showed absorption bands due to NH and C≡N at 3394 and 2233 cm\(^{-1}\) while C=O was observed at 1671 cm\(^{-1}\). In the NMR spectra multiplets ranging from 8.9-6.9 δ integrating to ten protons were attributed to aromatic hydrogen while amino proton resonated at 6.71 δ as triplet and methylene protons appeared as doublet.
at 4.34 δ corresponding to two protons. Mass and elemental analysis also confirmed the formation of the 4-((9,10-Dioxo-9,10-dihydroanthracen-2-ylamino)methyl)phthalonitrile (131).

\[
\begin{align*}
\text{Scheme 41: Synthesis of 4-((9,10-Dioxo-9,10-dihydroanthracen-2-ylamino)methyl)phthalonitrile (131)}
\end{align*}
\]

Metallated 2(3),9(10),16(17),23(24)-tetrakis-[(9,10-dioxo-9,10-dihydroanthracen-2-yl) amino] methyl]phthalocyanines 194-196 were synthesized by refluxing 4-[(9,10-Dioxo-9,10-dihydroanthracen-2-ylamino)methyl]phthalonitrile 131 and metal halides in nitrobenzene for 6 hours (Scheme 42). The product was characterized by IR, Mass and elemental analysis.

\[
\begin{align*}
\text{Scheme 42: Synthesis of tetrakis-[(9,10-dioxo-9,10-dihydroanthracen-2-yl) amino]methyl]phthalocyanines (194-196)}
\end{align*}
\]

Due to the formation of isoindole ring by the nitrile the absorption band at 2220 cm\(^{-1}\) disappeared in the IR spectra. The C=N group showed its presence by absorption band near 1690 cm\(^{-1}\).while ketonic C=O of anthraquinone moiety
absorbed around 1670 cm\(^{-1}\) and aromatic C-H stretching bands absorbed in the range of 3090 cm\(^{-1}\). Molecular ion peak and elemental analysis also seconded the formation of proposed structures (194-196).

**Table 14:** IR Spectra of tetrakis-\{[(9,10-dioxo-9,10-dihydroanthracen-2-yl) amino]methyl\}phthalocyanines (194-196)

![Diagram of compound structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH (Isoindole) (cm(^{-1}))</th>
<th>C=N (cm(^{-1}))</th>
<th>C=O (cm(^{-1}))</th>
<th>C=C Aromatic (cm(^{-1}))</th>
<th>C-H Aromatic (cm(^{-1}))</th>
<th>CH(_2) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
<td>3385</td>
<td>1688</td>
<td>1670</td>
<td>1595, 1489</td>
<td>3080</td>
<td>2850</td>
</tr>
<tr>
<td>195</td>
<td>3390</td>
<td>1691</td>
<td>1673</td>
<td>1488, 1601</td>
<td>3088</td>
<td>2858</td>
</tr>
<tr>
<td>196</td>
<td>3393</td>
<td>1693</td>
<td>1671</td>
<td>1492, 1598</td>
<td>3078</td>
<td>2824</td>
</tr>
</tbody>
</table>
Table 15: IR Spectra of tetrakis-{{[9,10-dioxo-9,10-dihydroanthracen-2-yl]amino)methyl}phthalocyanines (194-196)

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>Mass [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>194</td>
<td>C_{92}H_{52}CuN_{12}O_{8}</td>
<td>72.84</td>
<td>3.45</td>
<td>11.08</td>
</tr>
<tr>
<td>195</td>
<td>C_{52}H_{52}CoN_{12}O_{8}</td>
<td>73.06</td>
<td>3.47</td>
<td>11.11</td>
</tr>
<tr>
<td>196</td>
<td>C_{92}H_{52}NiN_{12}O_{8}</td>
<td>73.07</td>
<td>3.47</td>
<td>11.12</td>
</tr>
</tbody>
</table>

3.10 Tetrasulfophthalocyanines

Tetrachlorosulfonlyphthalocyanines were prepared by chlorosulfonation of metal and metal free unsubstituted phthalocyanines (prepared from phthalonitrile). Chlorosulfonation was accomplished by refluxing the phthalocyanines in chlorosulfonic acid for twelve hours. Hydrolysis of tetrachlorosulfonlyphthalocyanines gave tetrasulfophthalocyanine (146-151). These were subsequently converted to tetra-potassium salts (206) with potassium hydroxide. The tetrachlorosulfonlyphthalocyanines were also condensed with alkyl or aryl amines to obtain a series of sulfonamide phthalocyanines.
Scheme 43: Synthesis of Tetrasulfophthalocyanines

Appearance of absorption band in the range of 3400, 1360 and 1185 cm\(^{-1}\) in the IR spectra provided the evidence for the induction SO\(_3\)H group in tetrasulfophthalocyanines (146-151). For phthalocyanines (171-188) the absorption bands around 3400 cm\(^{-1}\) in the IR spectra could be assigned to the N-H of sulfonamide moieties. (Table 19-21). Other characterization techniques including mass spectral and elemental analysis also confirmed the formation of target compounds (Table 22-24). The characteristic Q and Soret bands to these complexes were observed around 660-680 nm and 250-350 nm.
Table 16: IR Spectra of Tetrasulfophthalocyanines (146-151)

![Diagram of Tetrasulfophthalocyanine]

<table>
<thead>
<tr>
<th>Comp.</th>
<th>OH/NH (cm(^{-1}))</th>
<th>C=N (cm(^{-1}))</th>
<th>C=C (Ar) (cm(^{-1}))</th>
<th>C-H (Ar) (cm(^{-1}))</th>
<th>SO(_2) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>146</td>
<td>3421, 3401</td>
<td>1702</td>
<td>1595, 1505</td>
<td>3094</td>
<td>1365, 1193</td>
</tr>
<tr>
<td>147</td>
<td>3427</td>
<td>1698</td>
<td>1594, 1486</td>
<td>3096</td>
<td>1375, 1191</td>
</tr>
<tr>
<td>148</td>
<td>3421</td>
<td>1701</td>
<td>1601, 1504</td>
<td>3096</td>
<td>1371, 1195</td>
</tr>
<tr>
<td>149</td>
<td>3425</td>
<td>1694</td>
<td>1604, 1499</td>
<td>3097</td>
<td>1374, 1190</td>
</tr>
<tr>
<td>150</td>
<td>3431</td>
<td>1698</td>
<td>1496, 1598</td>
<td>3095</td>
<td>1366, 1194</td>
</tr>
<tr>
<td>151</td>
<td>3426</td>
<td>1699</td>
<td>1595, 1499</td>
<td>3095</td>
<td>1361, 1199</td>
</tr>
</tbody>
</table>
Table 17: Elemental Analysis and Mass Data of Tetrasulfophthalocyanines (146-151)

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>Mass [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>146</td>
<td>C_{32}H_{16}N_{8}O_{12}S_{4}</td>
<td>46.04</td>
<td>2.17</td>
<td>13.42</td>
</tr>
<tr>
<td>147</td>
<td>C_{32}H_{16}N_{8}CuO_{12}S_{4}</td>
<td>42.88</td>
<td>1.80</td>
<td>12.50</td>
</tr>
<tr>
<td>148</td>
<td>C_{32}H_{16}N_{8}NiO_{12}S_{4}</td>
<td>43.11</td>
<td>1.81</td>
<td>12.57</td>
</tr>
<tr>
<td>149</td>
<td>C_{32}H_{16}N_{8}ZnO_{12}S_{4}</td>
<td>42.79</td>
<td>1.80</td>
<td>12.48</td>
</tr>
<tr>
<td>150</td>
<td>C_{32}H_{16}N_{8}CoO_{12}S_{4}</td>
<td>43.10</td>
<td>1.81</td>
<td>12.57</td>
</tr>
<tr>
<td>151</td>
<td>C_{32}H_{16}N_{8}PbO_{12}S_{4}</td>
<td>36.96</td>
<td>1.55</td>
<td>10.77</td>
</tr>
</tbody>
</table>
Table 18: IR Spectra of sulfonamide phthalocyanines (171-176)

![M = 2H, Cu, Ni, Zn, Co, Pb. R = NH-SO_2H](image)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>OH / NH (cm(^{-1}))</th>
<th>C=N (cm(^{-1}))</th>
<th>C=C (Ar) (cm(^{-1}))</th>
<th>C-H (Ar) (cm(^{-1}))</th>
<th>SO(_2) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>171</td>
<td>3433/ 3405</td>
<td>1692</td>
<td>1612, 1490</td>
<td>3087</td>
<td>1372, 1185</td>
</tr>
<tr>
<td>172</td>
<td>3436/ 3401</td>
<td>1698</td>
<td>1490, 1612</td>
<td>3087</td>
<td>1363, 1185</td>
</tr>
<tr>
<td>173</td>
<td>3433/ 3339</td>
<td>1692</td>
<td>1484, 1606</td>
<td>3080</td>
<td>1367, 1183</td>
</tr>
<tr>
<td>174</td>
<td>3432/ 3397</td>
<td>1694</td>
<td>1494, 1602</td>
<td>3089</td>
<td>1361, 1186</td>
</tr>
<tr>
<td>175</td>
<td>3435/ 3404</td>
<td>1691</td>
<td>1496, 1611</td>
<td>3089</td>
<td>1361, 1186</td>
</tr>
<tr>
<td>176</td>
<td>3437/ 3402</td>
<td>1689</td>
<td>1592, 1491</td>
<td>3096</td>
<td>1373, 1184</td>
</tr>
</tbody>
</table>
Table 19: IR Spectra of sulfonamide phthalocyanines (177-182)

![Phthalocyanine structure]

R = CH$_3$(CH$_2$)$_7$NH$, \quad$M = 2H, Cu, Ni, Zn, Co, Pb.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>NH (cm$^{-1}$)</th>
<th>C=N (cm$^{-1}$)</th>
<th>C=C (Ar) (cm$^{-1}$)</th>
<th>C-H (Ar) (cm$^{-1}$)</th>
<th>CH$_2$, CH$_3$ (cm$^{-1}$)</th>
<th>SO$_2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>177</td>
<td>3392, 3345</td>
<td>1695</td>
<td>1595, 1490</td>
<td>3094</td>
<td>2927</td>
<td>1377, 1182</td>
</tr>
<tr>
<td>178</td>
<td>3395</td>
<td>1696</td>
<td>1570, 1488</td>
<td>3091</td>
<td>2930</td>
<td>1369, 1185</td>
</tr>
<tr>
<td>179</td>
<td>3394</td>
<td>1706</td>
<td>1591, 1485</td>
<td>3096</td>
<td>2925</td>
<td>1360, 1187</td>
</tr>
<tr>
<td>180</td>
<td>3396</td>
<td>1700</td>
<td>1484, 1601</td>
<td>3097</td>
<td>2933</td>
<td>1374, 1189</td>
</tr>
<tr>
<td>181</td>
<td>3393</td>
<td>1701</td>
<td>1496, 1599</td>
<td>3079</td>
<td>2931</td>
<td>1369, 1185</td>
</tr>
<tr>
<td>182</td>
<td>3396</td>
<td>1706</td>
<td>1592, 1491</td>
<td>3096</td>
<td>2932</td>
<td>1371, 1183</td>
</tr>
</tbody>
</table>
Table 20: IR Spectra of sulfonamide phthalocyanines (183-188)

\[ R = \text{HO(}CH_2\text{)}_6\text{NH}^-; \quad M = \text{2H, Cu, Ni, Zn, Co, Pb}. \]

<table>
<thead>
<tr>
<th>Comp.</th>
<th>OH (cm(^{-1}))</th>
<th>NH (cm(^{-1}))</th>
<th>C=N (cm(^{-1}))</th>
<th>C=C (Ar) (cm(^{-1}))</th>
<th>C-H (Ar) (cm(^{-1}))</th>
<th>CH(_2) (cm(^{-1}))</th>
<th>SO(_2) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>183</td>
<td>3431</td>
<td>3393</td>
<td>1699</td>
<td>1592, 1491</td>
<td>3094</td>
<td>2928</td>
<td>1370, 1184</td>
</tr>
<tr>
<td>184</td>
<td>3430</td>
<td>3391</td>
<td>1704</td>
<td>1570, 1486</td>
<td>3091</td>
<td>2930</td>
<td>1369, 1184</td>
</tr>
<tr>
<td>185</td>
<td>3432</td>
<td>3394</td>
<td>1706</td>
<td>1570, 1475</td>
<td>3086</td>
<td>2925</td>
<td>1360, 1187</td>
</tr>
<tr>
<td>186</td>
<td>3433</td>
<td>3396</td>
<td>1700</td>
<td>1494, 1620</td>
<td>3087</td>
<td>2933</td>
<td>1374, 1188</td>
</tr>
<tr>
<td>187</td>
<td>3435</td>
<td>3393</td>
<td>1701</td>
<td>1496, 1611</td>
<td>3089</td>
<td>2934</td>
<td>1369, 1185</td>
</tr>
<tr>
<td>188</td>
<td>3437</td>
<td>3396</td>
<td>1706</td>
<td>1592, 1491</td>
<td>3096</td>
<td>2931</td>
<td>1371, 1188</td>
</tr>
</tbody>
</table>
Table 21: Elemental Analysis and Mass Data of sulfonamide phthalocyanines (171-176)

M = 2H, Cu, Ni, Zn, Co, Pb.  
\[
R = \begin{array}{c}
\text{NH} \\
\text{SO}_{3}\text{H}
\end{array}
\]

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>Mass [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>171</td>
<td>C_{56}H_{36}N_{12}O_{20}S_{8}</td>
<td>46.21</td>
<td>2.63</td>
<td>11.55</td>
</tr>
<tr>
<td>172</td>
<td>C_{56}H_{36}N_{12}CuO_{20}S_{8}</td>
<td>44.34</td>
<td>2.39</td>
<td>11.08</td>
</tr>
<tr>
<td>173</td>
<td>C_{56}H_{36}N_{12}NiO_{20}S_{8}</td>
<td>44.48</td>
<td>2.40</td>
<td>11.12</td>
</tr>
<tr>
<td>174</td>
<td>C_{56}H_{36}N_{12}ZnO_{20}S_{8}</td>
<td>44.28</td>
<td>2.39</td>
<td>11.07</td>
</tr>
<tr>
<td>175</td>
<td>C_{56}H_{36}N_{12}CoO_{20}S_{8}</td>
<td>44.47</td>
<td>2.40</td>
<td>11.11</td>
</tr>
<tr>
<td>176</td>
<td>C_{56}H_{36}N_{12}PbO_{20}S_{8}</td>
<td>40.50</td>
<td>2.19</td>
<td>12.12</td>
</tr>
</tbody>
</table>
Table 22: Elemental Analysis and Mass Data of sulfonamide phthalocyanines (177-182)

![Diagram of sulfonamide phthalocyanines]

\[
\text{R} = \text{CH}_3(\text{CH}_2)_7\text{NH}, \quad \text{M} = 2\text{H}, \text{Cu}, \text{Ni}, \text{Zn}, \text{Co}, \text{Pb}
\]

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>Mass [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>177</td>
<td>(\text{C}<em>6\text{H}</em>{88}\text{N}_{12}\text{O}_8\text{S}_4)</td>
<td>60.07</td>
<td>6.77</td>
<td>13.13</td>
</tr>
<tr>
<td>178</td>
<td>(\text{C}<em>6\text{H}</em>{84}\text{N}_{12}\text{CuO}_8\text{S}_4)</td>
<td>57.31</td>
<td>6.31</td>
<td>12.53</td>
</tr>
<tr>
<td>179</td>
<td>(\text{C}<em>6\text{H}</em>{84}\text{N}_{12}\text{NiO}_8\text{S}_4)</td>
<td>57.52</td>
<td>6.34</td>
<td>12.58</td>
</tr>
<tr>
<td>180</td>
<td>(\text{C}<em>6\text{H}</em>{84}\text{N}_{12}\text{ZnO}_8\text{S}_4)</td>
<td>57.23</td>
<td>6.30</td>
<td>12.51</td>
</tr>
<tr>
<td>181</td>
<td>(\text{C}<em>6\text{H}</em>{84}\text{N}_{12}\text{CoO}_8\text{S}_4)</td>
<td>57.51</td>
<td>6.33</td>
<td>12.58</td>
</tr>
<tr>
<td>182</td>
<td>(\text{C}<em>6\text{H}</em>{84}\text{N}_{12}\text{PbO}_8\text{S}_4)</td>
<td>51.77</td>
<td>5.70</td>
<td>11.32</td>
</tr>
</tbody>
</table>
### Table 23: Elemental Analysis and Mass Data of sulfonamide phthalocyanines (183-188)

![Diagram of sulfonamide phthalocyanine](image)

\[ R = \text{HO(} \text{CH}_2\text{)}_6\text{NH}^- \quad \text{M} = 2\text{H, Cu, Ni, Zn, Co, Pb.} \]

<table>
<thead>
<tr>
<th>Comp</th>
<th>Formula</th>
<th>Calculated %</th>
<th>Found %</th>
<th>Mass [M+H]^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>183</td>
<td>( \text{C}<em>{56}\text{H}</em>{76}\text{N}<em>{12}\text{O}</em>{12}\text{S}_4 )</td>
<td>54.62 5.73 13.65</td>
<td>54.41 5.71 13.40</td>
<td>1231.4</td>
</tr>
<tr>
<td>184</td>
<td>( \text{C}<em>{56}\text{H}</em>{68}\text{N}<em>{12}\text{CuO}</em>{12}\text{S}_4 )</td>
<td>52.02 5.30 13.00</td>
<td>51.80 5.33 12.83</td>
<td>1292.3</td>
</tr>
<tr>
<td>185</td>
<td>( \text{C}<em>{56}\text{H}</em>{68}\text{N}<em>{12}\text{NiO}</em>{12}\text{S}_4 )</td>
<td>52.21 5.32 13.05</td>
<td>52.03 5.34 12.86</td>
<td>1287.3</td>
</tr>
<tr>
<td>186</td>
<td>( \text{C}<em>{56}\text{H}</em>{68}\text{N}<em>{12}\text{ZnO}</em>{12}\text{S}_4 )</td>
<td>51.94 5.29 12.98</td>
<td>51.59 5.23 12.79</td>
<td>1293.3</td>
</tr>
<tr>
<td>187</td>
<td>( \text{C}<em>{56}\text{H}</em>{68}\text{N}<em>{12}\text{CoO}</em>{12}\text{S}_4 )</td>
<td>52.20 5.32 13.05</td>
<td>52.01 5.33 13.89</td>
<td>1288.3</td>
</tr>
<tr>
<td>188</td>
<td>( \text{C}<em>{56}\text{H}</em>{68}\text{N}<em>{12}\text{PbO}</em>{12}\text{S}_4 )</td>
<td>46.82 4.77 11.70</td>
<td>46.57 4.74 11.48</td>
<td>1437.3</td>
</tr>
</tbody>
</table>
3.11 Perylenetetracarboxylic acid diimides (PDIs)

Due to high fluorescent quantum yields, good molar absorptivities, electron accepting abilities, excellent thermal and photostability, and inertness towards most of the chemicals, perylene tetracarboxylic diimides (PDIs) have attracted the academic and industrial scientists. This class of n-type molecular materials has shown excellent environmental stability in OFETs. PDIs are being used in a variety of applications in the field of organic electronics such as field effect transistors, photovoltaics, biosensors, light emitting diodes (OLED), molecular wires and optical switches. The use of PDIs in artificial photosynthetic systems is also a burning topic of today’s research.\textsuperscript{299}

One of the objectives of our research was to combine the p-type materials (such as PCs) with n-type materials (such as PDIs) through a spacer without conjugation. The Following scheme (scheme-44) was designed to achieve the objective;
3.12 N-Alkyl perylenetetracarboxylic acid monoanhydride monoimides

N-Butyl and n-octyl perylenetetracarboxylic acid monohydrate monoimides (199,200) were prepared by heating mono potassium salt of perylene-3,4,9,10-tetracarboxylic acid monoanhydride with n-butyl and n-octyl amine respectively in water for one hour.
Scheme 45: Synthesis of N-Alkyl perylenetetracarboxylic acid monoanhydride monoimides

IR spectra of the mono imides (199,200) showed absorption bands around 2920 and 2850 cm\(^{-1}\) due to C-H stretching of methylene and methyl group. Carbonyl group of monoanhydride absorbed at 1721 cm\(^{-1}\) while that of imide C=O showed absorption band around 1690 cm\(^{-1}\). C=C absorption bands were seen in the vicinity of 1650 cm\(^{-1}\). Molecular ion peaks and elemental analysis were also in full agreement with the target structure.

3.13 N-Butyl-N’(6-aminohexyl)perlenetetracarboxylic acid diimide and N-Butyl-N’(6-hydroxyhexyl)perlenetetracarboxylic acid diimide (201,202)

N-Butyl-N’(6-aminohexyl)perlenetetracarboxylic acid diimide and N-Butyl-N’(6-hydroxyhexyl)perlenetetracarboxylic acid diimide were synthesized by heating N-butylperlenetetracarboxylic acid mono anhydride monoimide (199) with hexane-1,6-diamine and 1-amino-6-hexanol respectively in ethylene glycol at 175 °C for two hours.
In the IR spectra of the compounds (201,202) no absorption bands corresponding to anhydride carbonyl moieties were observed which supported the formation of the target compound. Absorption bands due to symmetric and asymmetric stretching of NH$_2$ were observed at 3375 and 3306 cm$^{-1}$ respectively in the IR spectrum of (amino hexyl 2 compounds). Absorption band at 3600 cm$^{-1}$ in the IR spectrum of (202) may be assigned to OH of hydroxylhexyl group. The carbonyl moieties of the imide functionalities showed absorption bands in the region of 1680 cm$^{-1}$. The mass spectra and CHN also confirmed the formation of target molecules.

The compounds (201,202) were treated with 4-(bromomethyl)phthalonitrile in DMF. We tried our best efforts to get the target molecules (204) as a precursor of the desired phthalocyanine-PDI complex (205) but no fruitful results were obtained. However further work is in progress to get the target molecules. The prepared PDIs are being studied for their high tech applications.

3.14 N,N’-Bis(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (202)

6-hydroxyhexyl perylene-3,4,9,10-tetracarboxylic acid monohydrde monoimide was prepared by heating mono potassium salt of perylene-3,4,9,10-tetracarboxylic acid monoanhydride with 6-aminohexanol in water for one hour, the product thus obtained was the heated at 175 C with 6-aminohexanol in glycol for two hours to yield N,N’-Bis(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (202). The product obtained was characterized by IR, Mass, UV and elemental analysis.
The disappearance of the anhydride absorption band around 1750 cm\(^{-1}\) provided evidence for the formation diimide. The appearance of absorption band near 2920 cm\(^{-1}\) was attributed to methylene chain. Mass spectra and elemental analysis also confirmed the formation of N,N'-Bis(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic diimide (202)
Chapter – 4

HI TECH APPLICATIONS
OF SELECTED DYES
4- STUDIES ON THE APPLICATIONS OF SELECTED PHTHALOXYANINE AND PERYLENE DYSES.

Studies on the application of selected phthalocyanine and perylene dyes were carried out in collaboration with the organic electronics research group of Prof. Dr. Muhammad Hassan Sayyad, Faculty of Engineering Sciences, Ghulam Ishaq Khan (GIK) Institute of Engineering Sciences and Technology, Topi, KPK, Pakistan.

4.1 Nickel (II) $4,4',4'',4'''$ potassium-tetrasulfophthalocyanine (Tetrapotassium salt of Ni $2,9(10),16(17),23(24)$-tetrasulfophthalocyanine). (206)

4.1.1 Application in Organic Electronics

There is growing interest in the synthesis and characterization of organic semiconductors because of their potential applications for a wide range of electronic and photonic devices, such as, junction diodes, OFETs, OLEDs, LDs, memories, optical power limiting, optical amplifiers, sensors, etc. Also, these conjugated materials are the candidates for the mass production of low cost, large area, flexible, disposable devices, etc., but some issues regarding the processing of these materials and the performance of the organic devices need attention. For example, some organic semiconductors, such as, metal phthalocyanines (MPcs), possess excellent properties are easily available and can be used as active materials in the fabrication of almost every organic electronic and photonic device. But expensive equipment is needed for the
fabrication of the devices due to their poor solubility in organic solvents. Solution processable organic semiconductors have proven viable materials for the fabrication of electronics devices. Using these conjugated organic materials electronic devices can be fabricated using low cost fabrication techniques, such as, spin coating, printing, etc.

Among the electronic devices, Schottky diodes have simplest structure but these junctions are very helpful in order to determine the electronic parameters of the materials and are also the base of a large number of electronic devices, such as, photosensors, light emitting diodes, memories, solar cells. \(^{300,301}\). There are many factors that can affect the properties of the junction. These factors include the effects of series resistance \(R_s\), formation of barrier height, insulating layer between metal and semiconductor, and interface states.\(^{302}\).

Very recently, some authors\(^{303,304}\) investigated Schottky diodes fabricated using p-type organic semiconductors and reported that the p-type organic materials are very suitable for electronic devices mainly due to their stability.\(^{304,305,306}\) The electrical properties of a non-polymeric p-type semiconductor methyl-red based surface-type Schottky diode has been reported by Zubair and Sayyad.\(^{302}\) The electrical properties of surface-type Schottky diodes prepared by a thermal evaporator have been studied.\(^{306,307}\) and various electrical parameters of metal/nickel phthalocyanine (NiPc) junctions from current–voltage \((I–V)\), capacitance–voltage \((C–V)\) and capacitance–frequency \((C–F)\) characteristics have been determined. NiPc is one of the metal phthalocyanines which appears to be a more promising material for application in active devices due to its relative high mobility.\(^{308,309}\)

In this work, surface-type Au/K\(_4\)NiPTS/Ag Schottky diode is fabricated and its electrical characteristics are studied. The potential of the water soluble nickel (II) \(4,4',4''\) potassium-tetrasulphophthalocyanine (206) for electronic applications is determined. The device has shown rectification behavior.
Interpretation of the charge transportation in K₄NiPTS is provided. From the I-V curves the diode parameters are extracted.

Nickel (II) 4,4',4",4"' potassium-tetrasulfophthalocyanine (K₄NiPTS) \( \text{(206)} \) was synthesized from nickel tetrasulfophthalocyanine \( \text{(148)} \) by a modification of the method of Webar and Busch.

The surface-type Au/ K₄NiPTS/Ag Schottky diode was fabricated on a glass slide by vacuum thermal evaporation and drop casting. A 1 wt% solution of the K₄NiPTS \( \text{(206)} \) was prepared in distilled water in a test tube at room temperature. With a little shaking a homogeneous solution was obtained. The substrate was cleaned for 10 min. using distilled water in ultrasonic cleaner and after drying, the substrate was plasma cleaned for 5 min. followed by the thermal deposition of Au and Ag electrodes by using mask. During thermal deposition the chamber pressure was \( 5.5 \times 10^{-5} \) mbar while the deposition rate was kept at 0.1 nm/s. The thickness of the electrodes was 100 nm and gap between the electrodes was 50 µm. The length of the gap was 3 mm. After that the thin film of K₄NiPTS was deposited by drop casting. The fabricated device was left at room temperature for 24 hours to let the moisture in the film evaporate. Cross-sectional view of the fabricated Au/K₄NiPTS/Ag surface type Schottky diode is shown in Fig. 4. The current-voltage (I-V) characteristics of the diode were measured at room temperature.
The $I–V$ characteristics of the Au/K$_4$NiPTS/Ag diode are exhibited in Fig. 5. In forward bias the gold (Au) and silver (Ag) electrodes were connected to positive and negative of the voltage source, respectively. The $I–V$ graph of the Schottky barrier diode showed asymmetric nonlinear rectification behavior. The rectification ratio is found 1.98 at $±1.4$ V. Rectification ratio is the ratio of forward current to reverse current at certain voltage. It is subject to the applied voltage. It is assumed that the $I$-$V$ characteristics of the diode follow the thermionic emission. The thermionic emission can be expressed by the equation given as $^{310}$

$$I = I_o \left[ \exp \left( \frac{q(V - IR_s)}{nkT} \right) - 1 \right]$$  

(1)

Where $I_o$ is the saturation current given as:

$$I_o = A^* A T^2 \exp \left( \frac{-q\phi_b}{kT} \right)$$  

(2)

Where $V$ is the applied voltage, $A$ is the effective diode area, $A^*$ is the effective Richardson constant, $\phi_b$ is the effective barrier height at zero-bias, $k$ is the Boltzmann constant. $T$ is the temperature in Kelvin and $n$ is the ideality factor. The value of reverse saturation current obtained from forward bias semi-log $I$-$V$ (figure 6) curve was $1.83 \times 10^{-7}$ A. The value of ideality factor $n$ can be calculated, from the slope of the linear region of the forward bias $\text{ln}I$–$V$ plot by using the following relation:
By using above equation the value of ideality factor was calculated to be 11. The ideality factor shows that how much the quality of diode is comparable to an ideal diode. For ideal diode the value \( n \) is equal to one. However, usually \( n \) has a value higher than unity. High values of ideality factor can be attributed to the presence of native oxide layer on electrodes and non-homogenious barrier.\(^{302}\) The high values of ideality factor may also be due to possibly other effects, such as non-homogeneous thickness of organic film, organic layer effect, etc. The value of zero bias barrier height was found to be 0.27 eV, which was calculated by using Eq. (2).

![Fig.5: Current voltage (I-V) characteristics of Au/K\(_4\)NiPTS/Ag device.](image)

Using the value of reverse saturation current \( I_0 \), the effective barrier height \( \Phi_b \) of the junction is calculated to be 0.69 eV using equation 4.
To study the conduction mechanism of the diode, current was plotted against voltage on logarithmic scale i.e. log I-log V as shown in figure 7. The graph has three distinct regions according to power law (I~V^m). The first region has slope ~1.0 which represents the Ohmic region, where current is directly proportional to voltage. The second region has slope 2.1 which is the space charge limited current (SCLC) region. The third region has slope 4.8 which is proof of existence of the deep traps and is called trapped charge limited (TCLC) region.
An alternate method for the determination of the junction's parameters was proposed by Norde and known as Norde's Method. The modified Norde's function can be expressed by the following equations.\(^{311,312}\)

\[
F(V) = \frac{V}{\gamma} - \frac{kT}{q} \ln \left[ \frac{I(V)}{AA'T^2} \right]
\]

(8)

Where \(\gamma\) has value larger than \(n\). In this case, its value is taken as 12. The \(I(V)\) is value of current taken from the \(I-V\) curve. If the minimum of the \(F(V)\) vs. \(V\) plot is found then the barrier height can be calculated by using the following eq:

\[
\phi_b = F(V_0) + \frac{V_0}{\gamma} - \frac{kT}{q}
\]

(9)

\(F(V_0)\) is the minimum value of \(F(V)\), and \(V_0\) is the corresponding voltage. The value of the series resistance can be calculated by using the following relation:
\[ R_s = \frac{kT(\gamma - n)}{qI} \]  

(10)

The Norde plot for the Schottky diode is shown in Fig. 8. From the graph the values of \( \Phi_b \) and \( R_s \) were calculated to be 0.73 eV and 47 k\( \Omega \), respectively using the above equations. We can see parameters obtained from the two different methods are in good agreement.

![Fig. 8: F(V) vs. V plot of Al/methyl-red/Ag Schottky diode](image)

In conclusion, we have fabricated surface-type Au/K\textsubscript{4}NiPTS/Ag Schottky barrier diode. The electronic parameters such as ideality factor, barrier height and series resistance of the diode were extracted. The parameters obtained by using different methods were in good agreement. The electronic parameters of the water soluble nickel (II) \( 4,4^{\prime},4^{\prime\prime},4^{\prime\prime\prime} \) potassium-tetrasulphophthalocyanine show that this organic compound has great potential for different electronic applications. It is expected that the work reported can be helpful for the fabrication of future organic electronic devices using solution processable metal phthalocyanines.
### 4.1.2 Application in humidity Sensors

A sensor is a device that measures a physical quantity and converts it into an electrical signal. The demand for the low-cost, reliable, highly sensitive and robust sensors is ever increasing. Environmental monitoring food safety, industrial process control, medical diagnostics, military and security are all areas that would benefit from the deployment of sensors. Improvements in sensor technology are required on multiple fronts, including sensitivity and specificity, power consumption, portability, and cost. Conjugated organic materials offer many advantages in comparison with their inorganic counterparts, which make them particularly attractive for sensor applications.\(^{313}\)

First, the films of organic semiconductors can be deposited at or near room temperature on large area surfaces and are compatible with mechanically flexible supports such as paper and plastic. This enables their use in roll-to-roll fabrication techniques, which can dramatically decrease manufacturing costs, an important attribute for disposable sensors. Second, their properties can be tailored by means of chemical synthesis. This includes electronic properties (such as energy gap and electron affinity) but also properties such as surface energy, solubility. Of particular interest for sensors is the ability to covalently attach biologically relevant moieties to organic semiconductor molecules. Such hybrid materials have the potential to lead to the fabrication of sensors with high sensitivity and specificity.

The electrical properties of organic semiconductors change with the interaction of biological, chemical, electromagnetic waves, temperature, humidity, pressure, gasses, light, mechanical displacement, radioactive radiation, etc. Recently, the characterization of organic semiconductors for potential sensor applications has been reported in a number of publications by Sayyad and Co-workers.\(^{314,315,316}\) Organic conjugated materials have unique physical properties, which offer many advantages to inorganic semiconductors. They have exhibited large changes in their electrical and optical properties towards humidity, light, temperature, gases and toxic species. Therefore, these are potential candidates for the sensors required in environmental monitoring, sensing of hazard species,
etc. A comprehensive and up-to-date account of the theory (physical principles), design, and practical implementations of various (especially, the newest) sensors for scientific, industrial, and consumer applications is given by Jacob Fraden.\textsuperscript{317}

The water content in surrounding air is an important factor for the well-being of humans and animals. The level of comfort is determined by a combination of two factors: relative humidity and ambient temperature. Humidity is an important factor for operating certain equipments, for instance, high impedance electronic circuits, electrostatic sensitive components, high voltage devices, fine mechanisms, etc. A rule of thumb is to assure a relative humidity near 50\% at normal room temperature (20–25 °C). This may vary from as low as 38\% for the Class-10 clean rooms to 60\% in hospital operating rooms. Moisture is the ingredient common to most manufactured goods and processed materials.

Humidity sensors are classified on the basis of their measuring principles and are of capacitive, resistive, hydrometric, gravimetric, optical reflection, optical absorption and waveguide type. Capacitive-type humidity sensors have advantages such as low power consumption and large output signals. Organic materials are being extensively studied for the fabrication of capacitive-type sensors.\textsuperscript{318} Most of these sensors are fabricated in a sandwich configuration, and this structure requires the deposition of organic thin film onto a suitable substrate and a top metallic electrode. This often damages the active material and causes device failure due to shortening.\textsuperscript{314} Surface-type devices offer low cost and simple technology for investigating different properties of organic materials, such as charge transport,\textsuperscript{319} electroluminescence\textsuperscript{320}, light sensitivity, effect of temperature and effect of humidity.\textsuperscript{321,322,323,324}

In this work, surface-type Au/K\textsubscript{4}NiPTS/Au capacitive humidity sensor is fabricated and variation of its capacitance as a function of relative humidity (RH) is investigated. The potential of the water soluble nickel (II) \textit{4,4′,4″,4‴} potassium-tetrasulfophthalocyanine (206) for sensor applications is determined.
Increase in capacitance of the sensor is observed with the increase in relative humidity. Interpretation of this humidity dependant capacitance is provided and potential water soluble nickel (II) $4_4,4_7,4_1$ potassium-tetrasulfophthalocyanine (206) for sensor applications is demonstrated.

The surface-type Au/K₄NiPTS/Au Schottky diode was fabricated on a glass slide by casting a drop of the K₄NiPTS (206) solution prepared in distilled water on the gap between preliminary deposited gold electrodes. The thickness of the electrodes was 100 nm and gap between the electrodes was 50 µm. Cleaning of the substrate, preparation of the K₄NiPTS solution and deposition of the gold electrodes is described in section 5.1.1. Cross-sectional view of the fabricated Ag/K₄NiPTS/Ag surface type sensor is shown in Fig. 10.

The humidity response of the sensor was investigated under dynamic conditions in a home-made chamber equipped with a commercial humidity sensor, and the capacitance measurements were made using LCR meter at the frequency of 10 kHz and voltage of 1 V at room temperature ($25\pm0.5 ^\circ C$).

![Cross-sectional view of the Au/K₄NiPTS/Au surface type sensor.](image)

Humidity is used to represent the amount of water vapor in air and is defined in terms of relative humidity, specific humidity and absolute humidity.
Absolute humidity measures the water vapor content in absolute terms, i.e., how much there is, without any concern about the maximum amount the air could carry. Relative humidity (RH) is the type mostly used in conventional humidity meters. The RH is the ratio of partial water vapor pressure ($p_w$) in an air-water mixture at any temperature, to the saturated vapor pressure ($p_s$) of water at the same temperature. Relative humidity in percents is defined as:

$$RH = 100 \times \frac{p_w}{p_s}$$

The effect of relative humidity on the capacitances of Au/K4NiPTS/Au sensor is shown in figure 11. The measurements were made at room temperature and under dark conditions. It is observed that in the range 0-55% RH the capacitance of the sensor does not change but above 55% RH it increases significantly with the corresponding increase in humidity. Similar behaviour has been reported in the case of polypyrrole based sensor and porphyrin based sensors.

This increase in the sensor capacitance with the increase in relative humidity can be explained on the basis of water adsorption and dielectric physics theory. According to adsorption theory, adsorption of water molecules in the sensing material occurs in the two stages of chemisorption and physisorption. When the sensor is exposed to humidity, the formation of chemisorbed layer starts. The capacitance of the sensor does not change until the complete chemisorbed layer is not formed. The threshold RH at which the chemisorbed layer is completed has been observed dependent upon material type, film surface morphology and film thickness. When the chemisorbed layer is completed with the increase in further humidity many more physisorbed layers are formed and due to the formation of these additional layers on the surface of a sensitive material, capacitance of the sensor increases.
According to the dielectric physics theory, the capacitance of an ideal capacitor is independent of the frequency and is given by:

\[ C_0 = \varepsilon_r \varepsilon_0 \frac{A}{d} \]  \hspace{1cm} (2)

Where \( C_0 \) is the sensor capacity, \( \varepsilon_r \) the dielectric constant, \( \varepsilon_0 \) the vacuum dielectric constant, \( A \) the electrode surface area and \( d \) the thickness of dielectric organic layer.

At low RH, the capacitor exhibits ideal behavior. This shows that the amount of water vapor adsorbed by the sensing material is not large enough. At higher RH as more water molecules are adsorbed, the leak conduction appears in the sensing material, therefore, the expression of the capacitance of the sensor could be written as:
$C = \varepsilon^* C_0 = \left( \varepsilon \frac{\gamma}{\omega s_0} \right) C_0$  \hfill (3)

Where $C_0$ the capacitance of the ideal capacitor, $\varepsilon^*$ is the complex dielectric constant, $\varepsilon_r$ the relative dielectric constant of the ideal capacitor, $\varepsilon_0$ the vacuum capacitance constant, $\omega$ is the frequency and $\gamma$ the leak conductance. Using this equation the increase in capacitance of the sensor with the increase in relative humidity can be explained. The leak conductance $\gamma$ is directly proportional to the RH, so, the capacitance of the sensor is directly proportional to RH. Thus capacitance of the sensor increases with increase in humidity. We also see from the expression that the capacitance is inversely proportional to $\omega$. Therefore, the sensor is expected to show better performance at low frequencies. At low frequencies, the carriers have enough time to respond and the capacitance is affected greatly. At higher frequencies, the change of electric field becomes too fast for the carriers to follow and the capacitance is not affected significantly by RH.

Response and recovery times are the most important parameters for all humidity sensors. Response/recovery time is defined as the time taken by a capacitive sensor to attain 90% of the total capacitance change. Response time of the sensor was measured by quickly moving the sensor from a RH level of 30% to 90% and the recovery time was measured by moving very quickly from a humidity level of 90% RH, maintained in a closed chamber, to open atmosphere at a humidity level of 30% RH. Both the response and recovery times for the Au/K4NiPTS/Au sensor were observed approximately less than 10 s which are much less than the times reported for the capacitive humidity sensors based on other nanostructured materials\textsuperscript{327,328} and many commercially available humidity meters. Therefore, this sensor can be used for the fabrication of a fast hygrometer for the measurement of high RH where the commercially available humidity sensors are either too slow or incapable of working.\textsuperscript{329}
4.2 N-Buty-N`-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide (N-BuHHPDI) (202)

4.2.1 Potential Application in Organic Electronics

Most organic semiconductors are p-type which have highly mobile hole transport carriers, such as pentacene and thiophene derivatives. However, there are few reports that n-type organic semiconductors have been synthesized that have distinct properties in organic devices. In the present work we have undertaken synthesis and investigation an n-type organic semiconductor N-Buty-N´-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide (N-BuHHPDI) (202) for potential applications in organic electronics. The N-BuHHPDI (202) is a polycyclic aromatic organic compound and consists of five fused benzene rings, yielding an extended $\pi$-conjugated planar structure. Due to the large $\pi$-conjugated electrons, it has high field-effect electron mobility and strong electron affinity. In order to investigate its potential for applications in organic electronics, we have fabricated and studied the electronic properties of N-BuHHPDI/p-Si heterojunction diode. The current-voltage ($I$-$V$) characteristics of the diode showed good rectifying behavior. The values of ideality factor $n$, barrier height $\Phi_b$, and series resistance $R_s$ of N-BuHHPDI/p-Si diode were extracted from the conventional $I$-$V$ characterization method, Cheung functions and Norde’s function.

Molecular structure of N-Buty-N´-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide (N-BuHHPDI) (202).
The p-Si with orientation (100) was used as a substrate and it was treated with HF:H₂O with a solution strength of 1:10. Afterward, it was cleaned in acetone using ultrasonic bath followed by drying with nitrogen gas for 5 minutes. Then N-BuHHPDI (202) was thermally deposited at a pressure of 10⁻⁵ mbar on the p-Si at a deposition rate of 0.1 nm/sec. The thickness of the film was 150 nm and monitored by FTM5 Quartz Crystal Oscillator. The schematic diagram of the fabricated device N-BuHHPDI/p-Si is shown in figure 12. The current voltage measurements were made on a Keithley 196 system DMM (µA) and Keithley 228 voltage source.

The current-voltage (I-V) characteristics of the N-BuHHPDI/p-Si heterojunction are shown in figure 13, which exhibits the nonlinear, asymmetric...
and good rectification with RR 51.5 at ± 6.8 V in the forward bias. The energy barrier at the junction interface limits rectification to some extent\textsuperscript{332}.

To understand the behavior of heterojunction diode, we have assumed thermionic emission (TE) theory [Eq. 5.1] and analyzed the I-V characteristics using the Equations 5.1, 5.2, 5.3 and 5.4. Using Eqs. (3) and (4) and from \( \ln I \) versus \( V \) plot, shown in \textbf{figure 14}, the experimental values of the ideality factor \( n \), barrier height \( \Phi_b \) and reverse saturation current \( I_0 \) are 12, 0.83 eV and 1.31 nA respectively. The barrier height also depends on the electric field across the contacts and on the applied bias voltage\textsuperscript{333}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure13.png}
\caption{Current-voltage (I-V) characteristics of N-BuHHPDI/p-Si heterojunction diode.}
\end{figure}
Figure 14: Semi-logarithmic ($I$-$V$) characteristics of N-BuHHPDI/p-Si heterojunction diode.

The ideality factor of N-BuHHPDI/p-Si barrier diode is far from the ideal due to the presence of a thick interfacial oxide layer, series resistance and the interface states. Another important parameter in the electrical characteristics of diode is the series resistance $R_s$ which is significant in the downward curvature (nonlinear region) of the forward bias $I$–$V$ characteristics. In order to extract the values of shunt resistance and series resistance, we plot junction resistance $R_j = \frac{\partial V}{\partial I}$ versus bias voltage as shown in figure 15. In forward bias, the lower region of the $R_j$ vs. $V$ exhibits series resistance $R_s$ having value of 1.6 MΩ at room temperature. Similarly, in reverse bias the highest peak resistance is known as shunt resistance $R_{sh}$ whose value is determined as 30MΩ.
An alternative way to calculate the values of $R_s$, $n$ and $\Phi_b$ is the Cheung and Cheung method\textsuperscript{331,335}. This technique is applied to the N-BuHHPDI/p-Si barrier diode and the values $R_s$, $n$ and $\Phi_b$ are calculated at room temperature. From equation (5.1) the Cheung and Cheung\textsuperscript{335} functions are obtained as:

\[
\frac{dV}{d \ln I} = n \frac{KT}{q} + IR_s
\]  
(7.1)

\[
H(I) = V - n \frac{KT}{q} \ln \left( \frac{I_o}{AA^T} \right)
\]  
(7.2)

Where $H(I)$ is given by

\[
H(I) = IR_s + n\Phi_b
\]  
(7.3)

In Figure 16 and 17, $dV/d(lnI)$ vs $I$ and $H(I)$ vs. $I$ plots for the N-BuHHPDI/p-Si are shown. The $I$–$V$ measurements obtained from Eq. (7.1) give a
straight line for the data of the downward curvature region in the forward bias. Hence, the slope of the plot of \(dV/d(\ln I)\) vs. \(I\) gives the value of \(R_s\) while its y-axis intercept gives \(nkT/q\). The values of \(n\) and \(R_s\), given by Eq. (7.1) and \(dV/d(\ln I)\) vs \(I\), are determined to be 11.8 and 1.62 MΩ respectively.

Using the value of \(n\) calculated from Eq. (7.1) and the data of the downward curvature region in the forward bias \(I-V\) characteristics in Eq. (7.2), the \(H(I)\) vs. \(I\) characteristics also lead to a straight line (as shown in Figure 17) with the y-axis intercept equal to \(\Phi_b\). The slope of this graph measures the magnitude of \(R_s\), which confirms the consistency of this approach with the conventional \(I-V\) method. The values of \(\Phi_b\) and \(R_s\) extracted from Eq. (7.3) and \(H(I)\) vs. \(I\) plot of Figure 17 are determined and 1.11 eV and 1.59 MΩ. Finally, it is observed that the values of \(R_s\) achieved from \(dV/d(\ln I)\) vs \(I\) and \(H(I)\) vs. \(I\) characteristics are in good agreement with each other. This, actually, confirms the nice approach of Cheung’s 336 on N-BuHHPDI/p-Si diode.

![Graph](image)

Figure 16: \(dV/d(\ln I)\) vs \(I\) characteristics of N-BuHHPDI/p-Si heterojunction diode
Furthermore, for the case of high series resistance present in diode, Norde introduced another technique to evaluate the barrier height and series resistance using the following function:

\[ F(V) = \frac{V}{\gamma} - \frac{kT}{q} \ln \left( \frac{I}{AA'T^2} \right) \]  \hspace{1cm} (7.4)

Where \( \gamma \) is an arbitrary integer greater than \( n \) (\( \gamma > n \)). Once the minimum of the \( F(V) \) vs. \( V \) plot is determined the barrier height \( \Phi_b \) can be obtained, where \( F(V_o) \) is the minimum value of \( F(V) \) in the \( F(V) \) vs. \( V \) plot, \( V_o \) is the corresponding voltage and and \( I_o \) is the corresponding current at \( V=V_o \).

The effective barrier height is given by

\[ \phi_b = F(V_o) + \frac{V_o}{\gamma} - \frac{kT}{q} \]  \hspace{1cm} (7.5)
and the $R_s$ value is determined from Norde’s function, as

$$R_s = \frac{kT(\gamma - n)}{qI_o} \quad (7.6)$$

Figure 18 shows the $F(V)–V$ plots of the diodes. The value of the series resistance $R_s$ was obtained from Norde’s method for N-BuHHPDI/p-Si heterojunction diode.

From the $F(V)–V$ plot, the values of $\Phi_b$ and $R_s$ of the N-BuHHPDI/p-Si structure have been determined and are 0.83 eV and 1.4 MΩ for the comparison with other characterization techniques.

The values of $\Phi_b$, $n$ and $R_s$ obtained from the conventional $I–V$ measurements, Cheung functions and Norde functions are in good agreement with each other. Furthermore, the value of series resistance indicates that the series resistance is a current-limiting factor for this structure. At higher forward bias voltage, the high series resistance behavior may be attributed to decrease of the exponentially increasing rate in current because of space-charge injection into the N-BuHHPDI thin film.
In order to realize the conduction mechanisms that control the diode behavior, the \( I-V \) characteristic of N-BuHHPDI/p-Si device is presented in \( \log-\log \) scale in Figure 19. Generally, the charge transport of thin film based organic devices is categorized into two regimes: charge injection at the contacts and transport in the bulk - space-charge limited conduction (SCLC). As from Figure 19, the double logarithmic forward bias \( I-V \) plot shows three distinct regions which obey a power law \( (I\approx V^{m+1}) \) behavior of the current with different exponents \( (m+1) \) and the charge transport is mainly governed by SCLC process.

In region-I, at low voltages, the ohmic conduction is dominant where the slope of the line segment is nearly equal to one. In this region, the low bias voltage limits the injection of charge carriers from the electrodes into the semiconductor material \(^{333}\). It is observed that the traps present in the N-BuHHPDI \(^{(202)}\) play critical role in the transition from the Ohmic current region to SCLC region. Thus, the transport through the N-BuHHPDI \(^{(202)}\) organic film is governed by the trapped- charge-limited current (TCLC) in the band gap of the organic layer \(^{333b}\). Furthermore, when the density of injected free-charge carriers
is much larger than the thermally generated charge carriers, then the SCLC conduction is of great importance.

Figure 19: Current-voltage curves of N-BuHHPDI/p-Si diode at temperature room

At higher voltage level (region-II) the slope is calculated to be greater than 2 which indicates the trapped charge-limited current (TCLC) mechanism is controlled by the presence of traps within the band gap of the N-BuHHPDI (202). In region-III, the slope is measured and observed to be very close to 2, indicates the space charge limited current (SCLC). The SCLC regime occurs when the equilibrium charge concentration is negligible compared to the injected charge concentration. Commonly these traps are not localized at the same energy, but, they are distributed in different energy levels. At lower voltages, the slope, m of the logI–logV plots decreases as the temperature of device increase. This phenomenon suggests the SCLC conduction mechanism in an organic semiconductor with deep trapping centers and thermally generated carriers.

The behavior of N-BuHHPDI/p-Si junction was investigated at room temperature and good rectification ratio was observed. The junction showed a
non ideal behavior with an ideality factor greater than unity. Other diode parameters like barrier height, series resistance and ideality factor have been extracted by conventional $I$-$V$ method, Cheung’s functions and Norde’s technique. The values obtained from different methods showed good agreement with each other. The charge transport mechanisms of through the interface of N-BuHHPDI (202) and p-Si were also studied from $I$-$V$ characteristics on logarithmic scale.
CONCLUSION
CONCLUSION

Phthalocyanine and perylene possess broad range of applications ranging applications such as dyes, pigments, in organic field effect transistors (OFETs), fluorescent solar collectors, organic photovoltaic cells, optical power limiters, photodynamic therapy, etc. Keeping in view such diverse utilities of Pcs and PDIs a project was devised to synthesize some useful macromolecules which may possess useful applications.

In the first phase using known protocols some known phthalocyanines such as 2,9(10),16(17),23(24)-tetramethylphthalocyanines and 2,9(10),16(17),23(24)-tetrinitrophthalocyanines were synthesized from 4-methylphthalonitrile and 4-nitrophthalic anhydride (Scheme A & B). 4-Nitrophthalic anhydride cyclized in the presence of urea and ammonium molybdate as catalyst while 4-methylphthalonitrile cyclized in the absence of urea and catalyst. Copper, cobalt, nickel, zinc and lead chelated tetra methyl and nitro substituted phthalocyanines were synthesized in this way.

\[
\text{H}_3\text{C} \quad \text{CN} \quad \text{CN} \quad \text{H}_3\text{C} \quad \text{CN} \quad \text{CN} \\
\text{Nitrobenzene, Reflux 6 hrs} \quad \text{M} = 2\text{H, Cu, Ni, Zn, Co, Pb.} \\
\]

Scheme A
Scheme B

Pyrrolidine, piperidine and azepan ring containing phthalocyanines (152-169) were synthesized by heating dihaloalkanes with 4-aminophthalonitrile in DMF which were then cyclotetramerized in the presence of various metal salts employing nitrobenzene as solvent to obtain metallated (Cu, Co, Ni, Zn and Pb) and metal free phthalocyanines (Scheme C).
Bromomethylphthalonitrile was produced by the bromination of 4-methylphthalonitrile which was then treated with 6-aminohexanol to obtain substituted phthalonitrile which were than tetramerized to obtain amino substituted phthalocyanines \((189-193)\) (Scheme D)
Sulfonic acid and sulfonamide substituted phthalocyanines were generated by the chlorosulfonation of metal based and metal free unsubstituted phthalocyanines. Sulfophthalocyanines were produced by the hydrolysis of tetrachlorosulfonylphthalocyanines (146-151). Condensation of tetrachlorosulfonylphthalocyanines with aliphatic and aryl amines produced phthalocyanine containing sulfonamide moieties (177-188) (Scheme E).
In the last phase a series of alkylated perylenediimides were synthesized from perylene-3,4,9,10-tetracarboxlic acid anhydride as shown in the scheme F.(199-202)
Conclusion

All the reported and novel macromolecules were characterized using IR, Mass and elemental analysis. The data obtained was found in good agreement with the proposed structures.

In the phthalocyanine series, potassium salt of Ni 2,9(10),16(17),23(24)-tetrasulfophthalocyanine was studied for its potential application in organic electronics and humidity sensors.

Tetrapotassium salt of Ni 2,9(10),16(17),23(24)-tetrasulfophthalocyanine was used in the fabrication surface type Au/K₄NiPTS/Ag Schottky barrier diode. The results obtained suggested that this compound has great potential for various electronic applications. It is expected that this work can be helpful in the fabrication of future organic dyes based electronic devices using solution processable metal phthalocyanines.

Tetrapotassium salt of Ni 2,9(10),16(17),23(24)-tetrasulfophthalocyanine was also studied for their potential in humidity sensors. Both the response and recovery times for Au/K₄NiPTS/Au sensors were observed approximately less than 10 seconds which are quite less than the times reported for capacitive
humidity sensors based on other nanostructured materials and commercially available humidity meters. Therefore this type of sensors can be used in the designing of fast hygrometer for the measurement of high RH where commercially available sensors fail to work properly.

In the perylene series, N-Buty-N’-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide (N-BuHHPDI) was studied for its potential application in organic electronics. The behavior of N-BuHHPDI/p-Si junction was investigated at room temperature and good rectification ratio was observed. The junction showed a non ideal behavior with an ideality factor greater than unity. Other diode parameters like barrier height, series resistance and ideality factor have been extracted by conventional $I$-$V$ method, Cheung’s functions and Norde’s technique. The values obtained from different methods showed good agreement with each other. The charge transport mechanisms of through the interface of N-BuHHPDI and p-Si were also studied from $I$-$V$ characteristics on logarithmic scale.

This thesis mainly encompasses the synthetic aspect of phthalocyanines and perylene diimides and only few applications that were studied are reported. Many other applications are under study at Ghulam Ishaq Khan Institute, Topi and in the Institute of Chemistry University of the Punjab, Lahore, Pakistan.
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