

Synthesis, Photophysical and Aggregation Properties of Novel Phenanthrene and Pyrene Substituted Phthalocyanines

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Abstract – We have explained the synthesis of novel phenanthrene and pyrene substituted phthalocyanines (PC-PHE and PC-PYR) and fully confirmed the structures by its spectral, photo physical and elemental analysis. For these phthalocyanines we checked the UV-Visible absorbance in PGMEA and chloroform and transmittance checked in PGMEA. The transmittance results suggested that these phthalocyanines are showing more than 90% transmittance at the 450-550 nm region. These synthesized molecules are nicely soluble in almost all industrial solvents. We checked the aggregation property of these phthalocyanines in PGMEA, and the results suggested no any aggregation for these molecules in PGMEA. The thermogravimetric analysis results concluded that PC-PHE and PC-PYR had high thermal stability. All studies explain that these new phthalocyanines are more suitable for LCD green color filter application.

Key words: Phenanthrene, Aggregation, LCD, Tetrachlorophthalonitrile, PGMEA

1. Introduction

Phthalocyanines are symmetrical, continuous conjugated, aromatic and macrocyclic molecules with an 18π electron system containing isoindole groups and linked with four nitrogen atoms [1]. Phthalocyanines with or without metal have numerous applications in different areas like press inks, laser technology [2-4], solar cells technology [5,6], liquid crystals [7], chemical sensors [8,9], anti-cancer agents [10,11], biomedical technology [12], nanomaterials [13], liquid crystal displays [14], and molecular electronics [15]. The phthalocyanine also have attractive applications with great diversity, flexibility in redox condition, good stability in any thermal and chemical conditions and always have versatile and intense colors. Although phthalocyanines have tremendous applications, they suffer with lack of solubility issue. The industrial solvent solubility of phthalocyanines increased by the substitution of alkyl and aryl groups at the peripheral and non-peripheral positions [16,17]. The advantage of the aryl substitution is Q-band absorption of the phthalocyanine will shift to bathochromic region with high extinction coefficient values [18,19].

Chloro substitution on phthalocyanine is very interesting topic in recent years because of chloro phthalocyanines always possess good stability towards thermal, light and increased solubility [20]. Chloro-phthalocyanines are play a major role in the LCD industry [21]. With our continuous efforts in phthalocyanine work [22-24], here we designed and prepared new zinc phthalocyanines with phenanthrene

(PC-PHE) and pyrene (PC-PYR) substitution with the concept of the introduction that bulkiness with the phenanthrene and pyrene increases the solubility of the phthalocyanine in all industrial solvents and avoids aggregation (Fig. 1). Both synthesized phthalocyanines were confirmed by its spectral analysis.

2. Experimental Section

2-1. Chemicals and instruments

For all our experiments, we used commercial solvents and analytical reagents purchased from commercial source. The $^1\text{H-NMR}$ spectra were recorded with 600 MHz and $^{13}\text{C-NMR}$ spectra were recorded with 600 MHz with Akishima Japan Company made AVANCE-III spectrometer. Deuterated chloroform and dimethyl sulfoxide were used as solvents and the software was Alice 4.0; δ -chemical shifts were used in parts per million (ppm) with respect to tetra methyl silane as an internal standard. UV-Vis absorption spectroscopy and transmittance spectra were done on a Shimadzu SolidSpec-3700 instrument. ALPHA-P spectrometry was used to record the FT-IR results. MALDI-TOF mass spectra were obtained by using a Bruker AutoFlex III mass spectrometer, molecular elemental analysis was done by thermo Fisher scientific instrument (EA112). ESI-mass spectral experiments were recorded with 4000 Q TRAP mass spectral instrument. Thermogravimetric analyses were executed on a Mettler Toledo instrument with $10\text{ }^\circ\text{C}/\text{min}$ heat rate and with $50\text{ mL}/\text{min}$ flow rate of nitrogen.

2-2. Synthesis

2-2-1. 3,4,6-trichloro-5-(phenanthren-9-yloxy)phthalonitrile (3)

Tetra chlorophthalonitrile (1) (5.3 g, 20 mmol) and phenanthren-9-ol (2) (2.88 g, 20 mmol) were dissolved in 100 mL of DMSO at $25\text{ }^\circ\text{C}$,

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[‡]This article is dedicated to Prof. Yong Kang on the occasion of his retirement from Chungnam National University.

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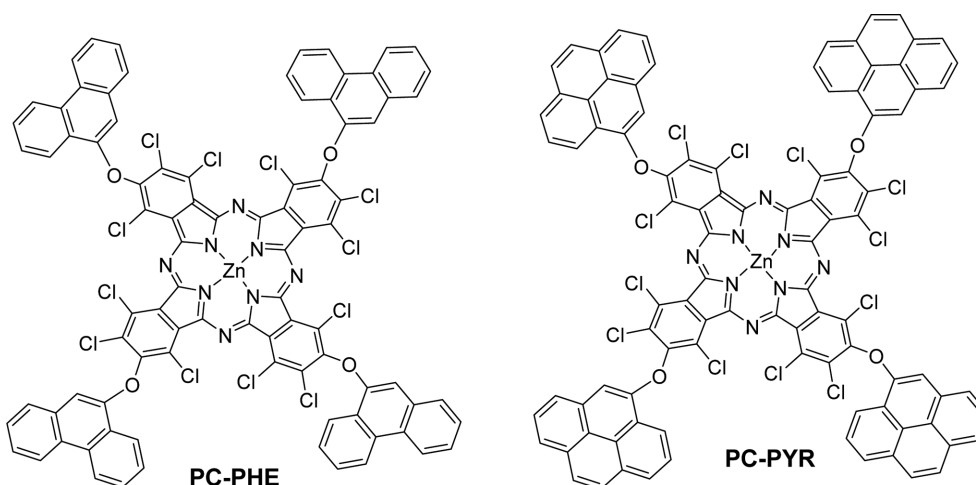


Fig. 1. Structures of new phenanthrene and pyrene substituted phthalocyanines.

followed by lithium hydroxide monohydrate (0.42 g, 10 mmol) slowly added for 1 h. Reaction mixture was stirred for 20 h, and after completion of the reaction the mixture was transferred into 500 mL of distilled water. This solution was extracted with chloroform (2×400 mL) followed by washing with water (200 mL), brine solution (100 mL) and drying with magnesium sulfate (MgSO_4). The solvent was removed with reduced pressure and the crude material was purified by silica-gel column chromatography using hexane:ethyl acetate (7:3) as an eluting solvent to obtain compound 3 as a light yellow solid, yield (6.8 g, 85%). $^1\text{H NMR}$ (600 MHz, CDCl_3 ppm) δ 8.67 (*d*, $J = 8.2$ Hz, 1H), 8.58 (*d*, $J = 8.2$ Hz, 1H), 8.39 (*d*, $J = 7.8$ Hz, 1H), 7.77–7.66 (*m*, 2H), 7.60–7.47 (*m*, 3H), 6.43 (*s*, 1H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , ppm) δ 153.2, 149.4, 137.6, 136.3, 133.1, 132.0, 131.0, 128.2, 128.0, 127.8, 127.5, 127.2, 126.2, 124.6, 123.0, 122.8, 122.2, 117.3, 115.3, 112.0, 111.8, 105.9. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3120, 3011, 2230, 1624, 1540, 1511, 1320, 1207, 1022, 991, 949, 880, 793. ESI-MS: 422 $[\text{M}+\text{H}]^+$.

2-2-2. 3,4,6-trichloro-5-(pyren-1-yloxy)phthalonitrile (5)

Tetra chlorophthalonitrile (1) (5.3 g, 20 mmol) and pyren-4-ol (4) (4.36 g, 20 mmol) were dissolved in 100 mL of DMSO at 25 °C; then lithium hydroxide monohydrate (0.42 g, 10 mmol) was slowly added for 1 h. Reaction mixture was stirred for 20 h, and after completion of the reaction the mixture was transferred into 500 mL of distilled water. This solution was extracted with chloroform (2×400 mL) followed by washing with water (200 mL), brine solution (100 mL) and drying with magnesium sulfate (MgSO_4). The solvent was removed with reduced pressure and the crude material was purified by silica-gel column chromatography using hexane:ethyl acetate (7:3) as an eluting solvent to obtain compound 5 as a light yellow solid, yield (8 g, 90%). $^1\text{H NMR}$ (600 MHz, CDCl_3 ppm) δ 8.50–8.42 (*m*, 1H), 8.21–8.13 (*m*, 3H), 8.04–7.92 (*m*, 4H), 7.05–6.85 (*m*, 1H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , ppm) δ 153.7, 149.2, 147.4, 136.6, 135.3, 132.1, 131.1, 130.8, 130.0, 128.7, 128.4, 128.0, 127.6, 127.2, 127.0, 125.2, 124.6, 123.5, 122.9, 122.2, 116.3, 115.7, 111.2, 110.7, 106.8. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$:

3122, 3011, 2221, 1635, 1555, 1533, 1330, 1305, 1044, 980, 947, 865, 801. ESI-MS: 447 $[\text{M}+\text{H}]^+$.

2-2-3. Zinc 1,2,4,8,9,11,15,16,18,22,23,25-dodecachloro-10-(phenanthren-9-yloxy)-3,17,24-tris(pyren-4-yloxy)phthalocyanine (PC-PHE)

3,4,6-trichloro-5-(phenanthren-9-yloxy)phthalonitrile (3) (842 mg, 2 mmol), zinc acetate dihydrate (132 mg, 0.6 mmol) and diazabicyclo[5.4.0]undec-7-ene (DBU) (152 mg, 1 mmol) were taken in distilled 1-pentanol and stirred at reflux for 24 h in an inert atmosphere. The completion of the reaction was confirmed by thin layer chromatography (TLC) and cooled to room temperature. The crude reaction mixture was concentrated on rotary evaporator and purification was done by using silica-gel column chromatography with $\text{CHCl}_3:\text{CH}_3\text{OH}$ (95:5) as an eluting solvent to get a fine solid. This solid was further recrystallized with dry CH_3OH to give PC-PHE as a bluish-green fine powder. Yield (504 mg, 60%). $\text{C}_{88}\text{H}_{36}\text{Cl}_{12}\text{N}_8\text{O}_4\text{Zn}$; Calculated, %: C 60.05; H 2.06; N 6.37, Found, %: C 60.10; H 2.05; N 6.36; MALDI-TOF-MS: calcd m/z for $\text{C}_{88}\text{H}_{36}\text{Cl}_{12}\text{N}_8\text{O}_4\text{Zn}$, 1757.832; found 1757.837 $[\text{M}]^+$. UV/vis: nm (log ϵ): in CHCl_3 ; 655(92),701(122). IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3021, 1645, 1512, 1427, 1390, 1319, 1192, 1020, 919, 911, 906.

2-2-4. Zinc 1,2,4,8,9,11,15,16,18,22,23,25-dodeca chloro-3,10,17,24-tetrakis (pyren-4-yloxy)phthalocyanine (PC-PYR)

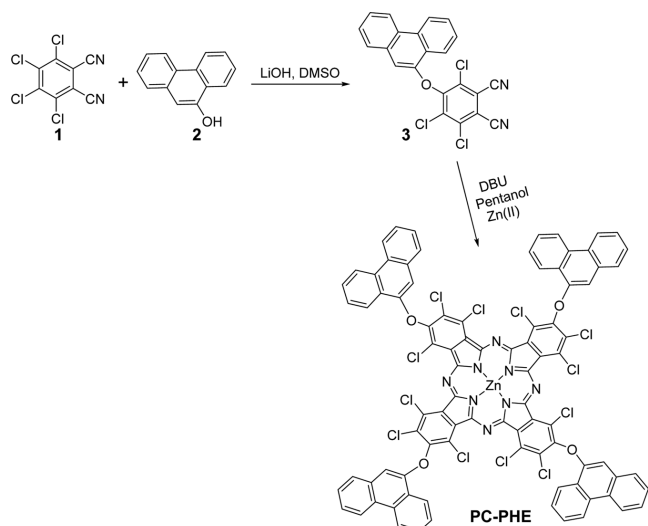
3,4,6-trichloro-5-(pyren-4-yloxy)phthalonitrile (5) (890 mg, 2 mmol), zinc acetate dihydrate (132 mg, 0.6 mmol) and diazabicyclo[5.4.0]undec-7-ene (DBU) (152 mg, 1 mmol) were dissolved in distilled 1-pentanol and stirred at reflux for 24 h in an inert atmosphere. The completion of the reaction was confirmed by thin layer chromatography (TLC) and cooled to room temperature. The crude reaction mixture was concentrated on rotary evaporator and purification was by using silica-gel column chromatography with $\text{CHCl}_3:\text{CH}_3\text{OH}$ (9:1) as an eluting solvent to get a fine solid. This solid was further recrystallized with dry CH_3OH to give PC-PYR as a bluish-green fine powder. Yield (454 mg, 51%). $\text{C}_{96}\text{H}_{36}\text{Cl}_{12}\text{N}_8\text{O}_4\text{Zn}$; Calculated, %: C

62.12; H 1.95; N 6.04, Found, %: C 62.10; H 1.94; N 6.06; UV/vis: nm (log ϵ): in CHCl_3 ; 629(125), 705(199). MALDI-TOF-MS: calcd m/z for $\text{C}_{96}\text{H}_{36}\text{Cl}_{12}\text{N}_8\text{O}_4\text{Zn}$, 1854.835; found 1854.838 $[\text{M}]^+$. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3001, 1615, 1520, 1434, 1329, 1220, 929, 921, 900.

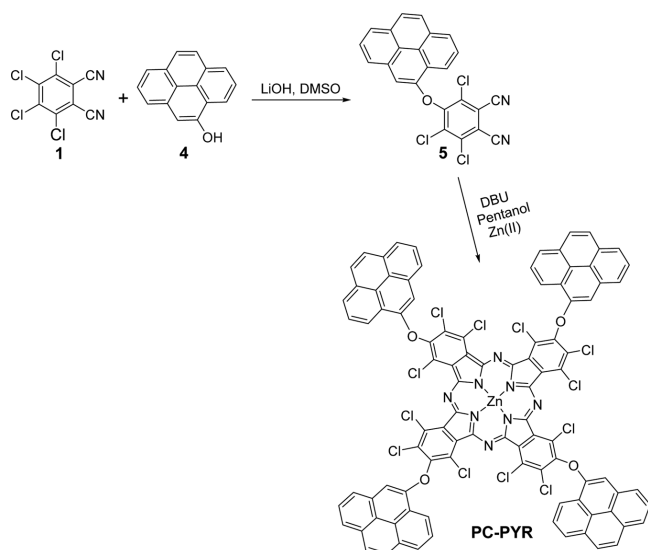
3. Results and Discussion

3-1. Synthesis

We designed and synthesized new phenanthrene and pyrene mono substituted phthalocyanines with trichloro substitution and included the corresponding reaction sequence in Scheme 1 and Scheme 2. For synthesis of phenanthrene substituted phthalocyanine, we started with a reaction between tetrachloro phthalonitrile (1) and hydroxyl phenanthrene (2), and obtained a very good yield (85%) for compound 3. This compound 3 further reacted with DBU and zinc salt to get PC-PHE in good yield (60%). In the same manner for synthesis



Scheme 1. Synthesis of phenanthrene substituted phthalocyanine.



Scheme 2. Synthesis of pyrene substituted phthalocyanine.

of pyrene substituted phthalocyanine, first tetrachloro phthalonitrile (1) was reacted with hydroxyl pyrene (4) and compound 5 was observed in very good yield (90%). Compound 5 further reacted with DBU and zinc salt; we found pyrene substituted phthalocyanine in good yield (51%). Actually, all synthesized phthalocyanines were region isomeric mixtures [25]. To separate these region isomers here we tried different TLC methods and we failed to separate [26,27]. All precursor compounds we confirmed with $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, IR and ESI-Mass spectra. In the case of PC-PHE and PC-PYR, FT-IR, MALDI-TOF mass, UV-Vis absorption and transmittance spectral and elemental analysis methods we followed for confirmation.

Particularly, phthalocyanine formation was a nicely confirmed comparison FT-IR spectra of precursor molecule and phthalocyanine. In the case of precursor phthalonitrile case, we observed IR band in the region of 2220 cm^{-1} to 2230 cm^{-1} which belongs to cyano group stretching. Whereas, in the case of phthalocyanine derivatives (PC-PHE and PC-PYR), there is a disappearance of cyano group stretching band, and this result confirmed the formation of phthalocyanine. Including this band, we observed peaks in the region of $3122\text{--}3010\text{ cm}^{-1}$ belong to aromatic C-H vibrational stretching, and C-O-C vibrational peaks were observed at approximately 1190 cm^{-1} . For these phthalocyanines we observed solubility in almost all industrial solvents.

3-2. UV-Visible absorption spectral results

Generally phthalocyanines have two characteristic peaks in UV-Visible absorption spectra. The peak around $300\text{--}450\text{ nm}$ belongs to B-band or Soret band region and absorption peak at $600\text{--}800\text{ nm}$ with $\pi\text{-}\pi$ transition belongs to Q-band region [28]. The $\pi\text{-}\pi$ transition of the Q-band is always from a_{1u} (HOMO) orbital towards e_g^* (LUMO) orbital, and it on behalf of the Q-band electronic transition of metal phthalocyanine with the D_{4h} symmetrical is displayed as an intense peak in the visible region of the absorption spectrum [29]. For LCD color filter in green part is always fulfilled by phthalocyanine derivatives. Actually, LCD green color filter case Q-band is divided in to Q_1 -band and Q_2 -band. Q_1 -band band always represents the blue region and Q_2 -band denotes the green region. For good LCD property we need to maintain the Q_1 -band also in high intensity [30]. To overcome this problem here we designed and succeeded with the new phthalocyanines. Our synthesized PC-PHE and PC-PYR, both phthalocyanines showed almost equal intensity of Q_1 -band and Q_2 -band. In propylene glycol monomethyl ether acetate (PGMEA), PC-PHE Q_1 -band absorption maxima was observed at 642 nm and Q_2 -band absorption maxima at 701 nm . In the case of PC-PYR we observed Q_1 -band absorption maxima at 652 nm and Q_2 -band absorption maxima at 703 nm (Fig. 2). For both the cases we found sharp absorption peaks and this result hints that PC-PHE and PC-PYR do not have any aggregation in PGMEA.

To further extend our UV-Visible absorption experiments, we checked the absorption in chloroform in $1 \times 10^{-5}\text{ M}$ concentration (Fig. 3). In chloroform PC-PHE, Q_1 -band band absorption maxima were at 651 nm and Q_2 -band at 700 nm . Whereas, in the case of PC-

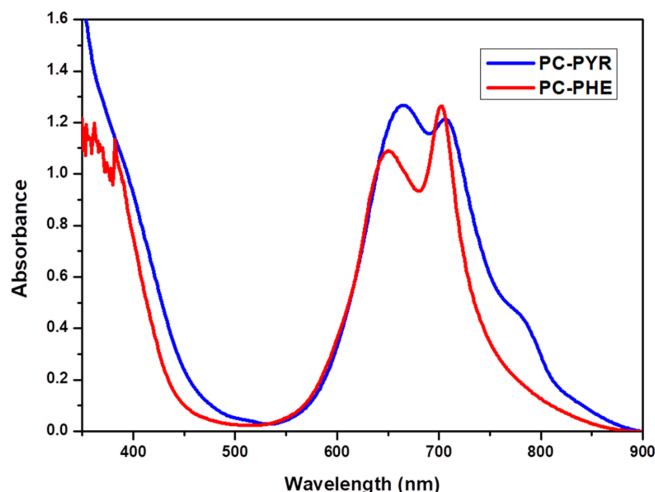


Fig. 2. UV-Visible absorption spectra of PC-PHE and PC-PYR in PGMEA (1×10^{-5} M).

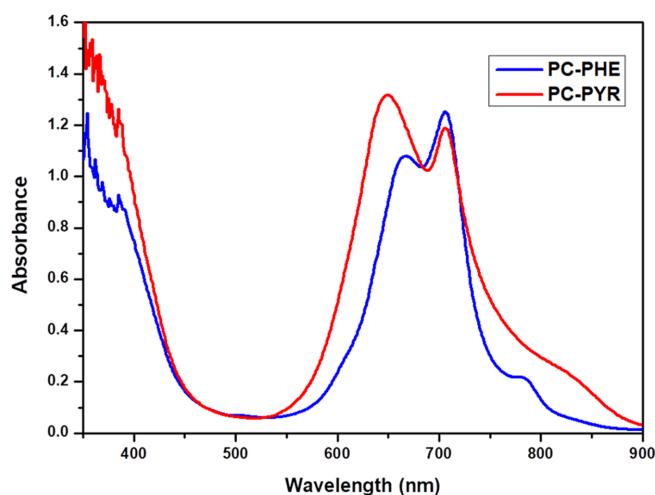


Fig. 3. UV-Visible absorption spectra of PC-PHE and PC-PYR in CHCl_3 (1×10^{-5} M).

PYR, we observed Q_1 -band absorption maxima at 630 nm and Q_2 -band at 700 nm. These results suggested that there is a slight shift in absorption maxima in comparison to PC-PHE and PC-PYR in different solvents. The difference in absorption maxima may be due to polarity difference between PGMEA and Chloroform.

3-3. Transmittance spectra

In a routine conventional system of RGB (red, green, blue) patterned pixels, to get a very high quality displays and to improve the color range, the thickness of the color filters needs to increase. If thickness increases, the brightness will decrease as well as transmittance of the color filter will decrease exponentially. Therefore, the introduction of multi primary color methods in LCD color filters might be a probable solution to overcome this difficult. To develop a green color LCD color filter we need to get a sharp transmittance in the region of 450-550 nm [31]. The dyes also should possess above 90% transmittance and only then will they fulfill the vivid green color LCD requirements [32]. As expected both our prepared

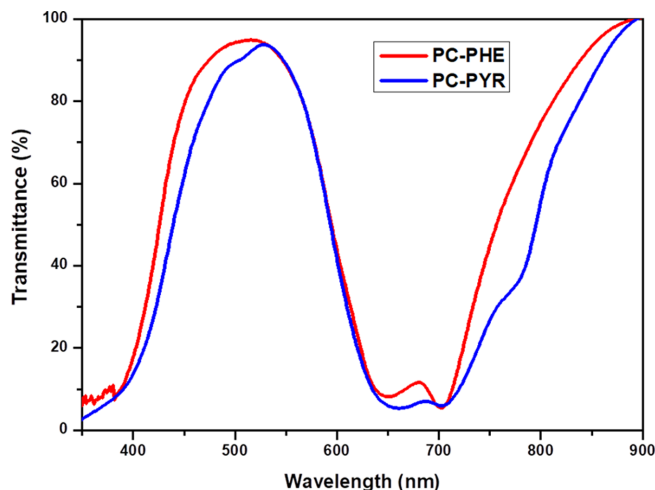


Fig. 4. Transmittance spectra of PC-PHE and PC-PYR in PGMEA (1×10^{-5} M).

phthalocyanine dyes also produced adequate optical spectra for application in vivid green LCD color filters. Fig. 4 represents the corresponding UV-Visible transmittance spectra. The transmittance study in PGMEA solvent will help as preliminary study for LCD color filter application. In PGMEA, PC-PHE and PC-PYR phthalocyanines showed greater than 90% transmittance in the 450-550 nm region. Both phthalocyanines showed sharp transmittance because of bulky phenanthrene and pyrene groups, and with less aggregation had nice solubility. Thus, PC-PHE and PC-PYR should be useful as dye for green colored filters for application in LCD and LED displays (Fig. 4).

3-4. Aggregation experiments

Aggregation is a very big drawback for phthalocyanines; generally, phthalocyanines will associate with each other to form dimers, trimers and oligomers. Always, these aggregates will have different photophysical properties with more decay in comparison with monomeric phthalocyanines. For many applications we need to avoid aggregation of molecules, and at the same time it is very important to study the aggregation. Generally, spectroscopic method is useful to check the nature and degree of aggregation. In metal PCs, the UV-Visible absorption band is conquered by the Q-band arising from π - π^* transitions [33].

Here, we checked the aggregation property of PC-PHE and PC-PYR in PGMEA in the concentration range from 1×10^{-5} M to 1×10^{-6} M (Fig. 5 and Fig. 6). Both the phthalocyanines showed non-aggregative property in PGMEA, and we observed a linear change of absorbance with respect to the concentration change without any distortion. Phthalocyanine molecules have a high aggregation tendency due to the π - π interactions between their molecules, but for the PC-PHE and PC-PYR case the bulky aryl groups make molecules not aggregate, and result in good solubility in PGMEA. By seeing these consequences, we are concluding that our designed and synthesized molecules with phenanthrene and pyrene have high solubility in PGMEA and are suitable for LCD color filter application.

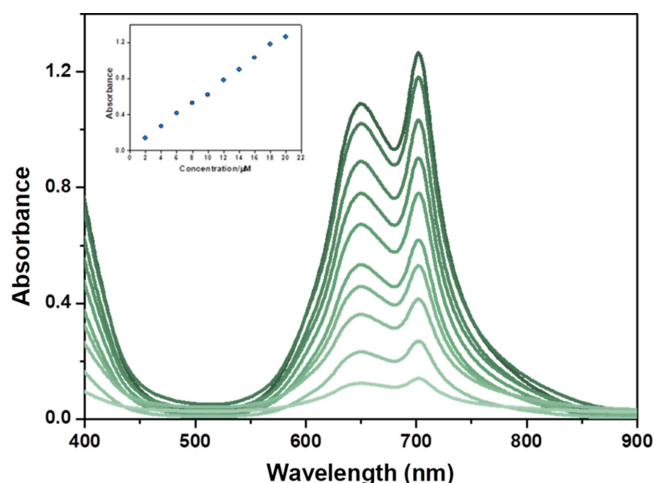


Fig. 5. Aggregation behavior of PC-PHE in PGMEA at different concentrations (1×10^{-6} M to 1×10^{-5} M).

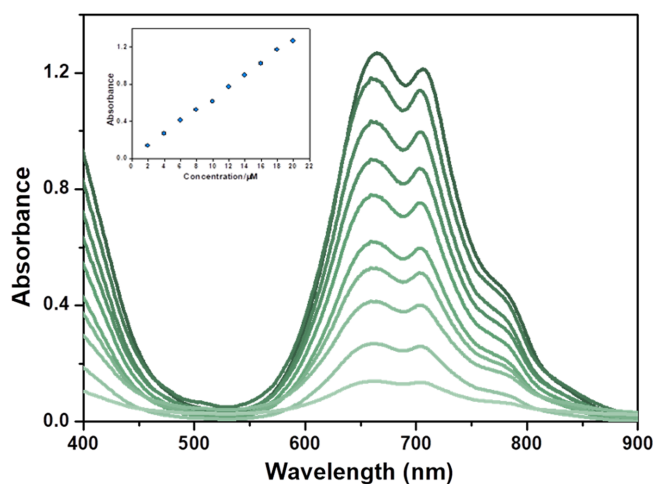


Fig. 6. Aggregation behavior of PC-PYR in PGMEA at different concentrations (1×10^{-6} M to 1×10^{-5} M).

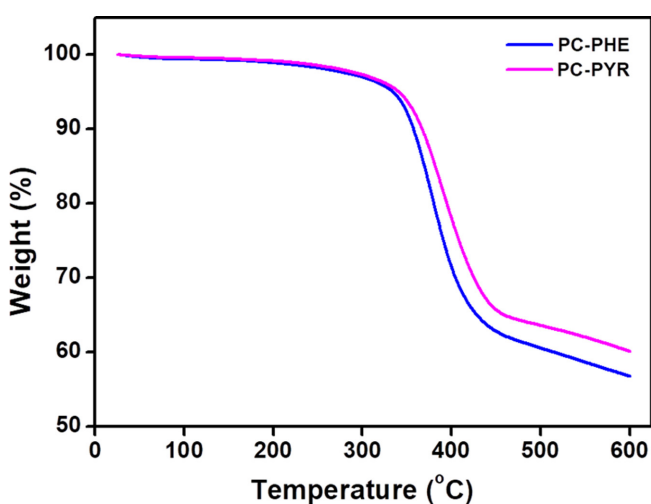


Fig. 7. TGA spectra of PC-PHE and PC-PYR.

3-5. Thermogravimetric analysis (TGA)

TGA studies of both PC-PHE and PC-PYR are depicted in Fig. 7. Generally, phthalocyanines are more resistant towards thermal and

heat [34]. Here the first endothermic peak at 40-200 °C is observed, which belongs to water molecules. The thermal decomposition process follows several steps like oxidation of peripheral groups, macrocycle group break and metal atom oxidation to form higher oxide derivatives. In this analysis for every minute, temperature was increased at a rate of 10 °C under a nitrogen atmosphere (inert) from 35 °C to 600 °C. PC-PHE and PC-PYR showed very good thermal stability, with less than 5% of weight loss up to 300 °C. This thermal stability is more important for LCD color filter molecules. Finally, the char yield of the both phthalocyanines was more than 50% at at 600 °C. This TGA result indicated that PC-PHE and PC-PYR possess high durability.

4. Conclusion

We have synthesized macrocyclic phthalocyanines (PC-PHE and PC-PYR) and confirmed their structure with NMR, FT-IR, Maldi-TOF mass and photo physical properties. Both the synthesized molecules had very good solubility in maximum industrial solvents. In this we have explained about UV-Visible absorption studies in PGMEA and chloroform. In PGMEA, phthalocyanines have more than 90% transmittance, and this property is a must for LCD color filter application. PC-PHE and PC-PYR showed non-aggregative property in PGMEA, and we observed a linear change of absorbance with respect to the concentration change without any distortion. TGA results showed that PC-PHE and PC-PYR were thermally highly stable. By the above results we are concluding that these phthalocyanines are fit for the LCD color filters as green color filters.

Acknowledgments

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