

Synthesis of Blue-green Naphthoxy, Chloro Derivative Zinc-phthalocyanines with LCD Requirements

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Abstract Here we designed and synthesized new zinc phthalocyanines and structures were fully confirmed by spectral and elemental analysis. All phthalocyanines have a very good solubility in industrial solvents like chloroform, dichloromethane, dimethyl sulfoxide, N,N-dimethyl formamide, propylene glycol monomethyl ether acetate (PGMEA), acetone, tetrahydrofuran and acetonitrile. UV-Visible absorption and transmittance in PGMEA showed that these dyes have suitable spectral properties for LCD color filters. By Triton X surfactant study, we confirmed that these dyes are not showing any aggregation in PGMEA. We dissolved the all phthalocyanines in LCD fabricating solvent (PGMEA), and all phthalocyanines showed more than 8 wt% of solubility. Finally, all of these results concluded that PCK1, PCK2 and PCK3 are fit for LCD green color filter.

Keywords *phthalocyanines, synthesis, Triton X, tetrachlorophthalonitrile, zinc*

1. Introduction

Phthalocyanines have tremendous stability and photoelectric properties because of its exclusive chemical structure, and hence have been using in the wide range of areas. Phthalocyanines are one of the largest consumed dyes and pigments in throughout the world market, Phthalocyanine are macrocyclic, stable with 18 π -electron-conjugated and exhibits effective, bright colors like blue, green and bluish green. Phthalocyanines are capable to bonding to the central cavity with metal ions and forms axial ligands. Phthalocyanines, are generally used as dyes and pigments in the textile and paper industries, and have also been useful in many potential applications in many diverse areas like as chemical sensors, textile and paper industries¹⁻³, optics in photovoltaics, molecular electronics⁴, solar cells⁵, electrophotography, optical data storage, energy transfer, laser technology^{6,7}, ionic liquid crystals⁸, different types of catalysis^{9,10}, photo dynamic therapy(PDT)^{11,12}, and LCD color filter applications¹³.

In the area of metal phthalocyanines, copper phthalocyanines are extensively studied. Particularly in the case of LCD color filter application, phthalocyanines have some challenges like solubility, transmittance and to improve these properties, in the continuous phthalocyanine studies of ours¹⁴⁻¹⁷, here we designed and synthesized novel zinc phthalocyanines with mono naphthoxy with different alkyl chain substitution with trichloro derivatives(Figure 1). We designed these schemes with a principle of alkyl chain effect of naphthoxy phthalocyanines solubility and photo physical properties. We have chosen methoxy (PCK1), hexyloxy(PCK2) and decyloxy(PCK3) as alkyl tail chains. These new synthesized products were analyzed by ¹H-NMR, ¹³C-NMR, FT-IR, Maldi-Tof Mass, Elemental analysis and photo physical experiments.

2. Experimental

2.1 Chemicals, reagents and instruments

For all experiments solvents and reagents were pur-

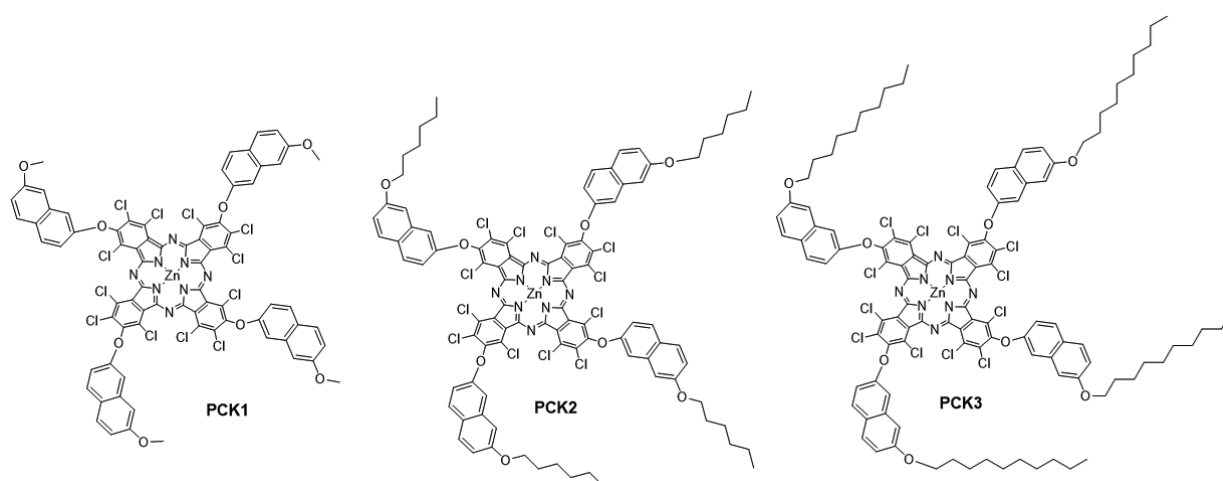


Figure 1. Structures of zinc-phthalocyanine molecules.

chased from commercial source and they are reagent or analytical grade. 600MHz for proton NMR and 150 MHz for carbon NMR spectroscopy with AVANCE III 600-spectrometer(Akishima Japan company) by using duterated chloroform and duterated dimethyl sulfoxide as solvents and the software is Alice 4.0 for spectral analysis, δ values(chemical shifts) were taken in parts per million(ppm) with respect an internal standard by using tetra methyl silane. UV-Vis absorption and transmittance spectra were performed on a Shimadzu SolidSpec-3700 instrument. ALPHA-P spectrometer used for conduct the FT-IR experiments. MALDI-TOF mass spectra were obtained by using a Bruker AutoFlex III mass spectrometer, elemental analysis was performed by EA112-Thermo Fisher Scientific instrument. 4000 Q TRAP mass spectral instrument used for the ESI-mass spectral experiments.

2.2 Synthesis

2.2.1 3,4,6-trichloro-5-((7-methoxynaphthalen-2-yl)oxy)phthalonitrile(3a):

To a mixture of 7-methoxynaphthalen-2-ol(2a)(1.74g, 10mmol) and tetra chlorophthalonitrile(2.65g, 10mmol) in 50mL of DMSO at 30°C, lithium hydroxide monohydrate(0.21g, 5mmol) was added portion wise within 1h. Then this reaction mixture stirred for overnight and the mixture was poured into 300mL of distilled water. After that extracted with dichloro methane

(2×200mL), washed with water(200mL) followed by brine solution(100mL) and dried over MgSO₄. The solvent was removed under rotary evaporator and the crude was purified by silica-gel column chromatography using hexane:ethyl acetate(8:2) as an eluent to obtain compound 3a as a pale yellow solid, yield(3.6g, 90%). ¹H NMR(600MHz, CDCl₃, ppm) δ 7.73(d, J = 8.8Hz, 1H), 7.65(d, J = 8.8Hz, 1H), 7.03(dd, J = 2.6, 8.8Hz, 1H), 7.00(dd, J = 2.6, 8.8Hz, 1H), 6.90(d, J = 2.4Hz, 1H), 6.72(d, J = 2.4Hz, 1H), 3.82(s, 3H). ¹³C NMR(125MHz, CDCl₃, ppm) δ 158.8, 153.8, 153.0, 137.5, 136.3, 135.3, 133.1, 130.5, 129.3, 125.8, 118.3, 117.2, 115.1, 114.1, 111.9, 111.7, 108.8, 105.2, 55.3. IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3120, 3020, 2217, 1605, 1550, 1401, 1370, 1205, 1150, 980, 952, 876, 800. ESI-MS: 402 [M+H]⁺.

2.2.2 3,4,6-trichloro-5-((7-(hexyloxy)naphthalen-2-yl)oxy)phthalonitrile(3b):

To a mixture of 7-(hexyloxy)naphthalen-2-ol(2b) (2.44g, 10mmol) and tetra chlorophthalonitrile(2.65g, 10mmol) in 50mL of DMSO at 30°C, lithium hydroxide monohydrate(0.21g, 5mmol) was added portion wise within 1h. Then this reaction mixture stirred for overnight and the mixture was poured into 300mL of distilled water. After that extracted with dichloro methane(2×200mL), washed with water(200mL) followed by brine solution(100mL) and dried over

MgSO₄. The solvent was removed under rotary evaporator and the crude was purified by silica-gel column chromatography using hexane:ethyl acetate(8.5:1.5) as an eluent to obtain compound 3b as a light yellow solid, yield(3.95g, 83.6%). ¹H NMR(600MHz, CDCl₃, ppm) δ 7.71(d, J = 8.8Hz, 1H), 7.64(d, J = 8.8Hz, 1H), 7.03(dd, J = 2.4, 8.8Hz, 1H), 7.00(dd, J = 2.4, 8.8Hz, 1H), 6.98(dd, J = 2.4, 8.8Hz, 1H), 6.70(d, J = 2.4Hz, 1H), 3.95(t, J = 6.5Hz, 2H), 1.79-1.72(m, 2H), 1.44-1.37(m, 2H), 1.31-1.24(m, 4H), 0.84(t, J = 6.9Hz, 3H). ¹³C NMR (125MHz, CDCl₃, ppm) δ 158.4, 153.8, 153.0, 137.5, 136.4, 135.2, 133.1, 130.5, 129.3, 125.8, 118.7, 117.2, 115.0, 114.0, 111.9, 111.7, 108.7, 105.9, 68.2, 31.5, 29.1, 25.8, 22.6, 14.1. IR(KBr tablet) ν_{max}/cm⁻¹: 3210, 3011, 2237, 1615, 1520, 1500, 1310, 1105, 1050, 990, 952, 885, 801. ESI-MS: 472 [M+H]⁺.

2.2.3 3,4,6-trichloro-5-((7-(decyloxy)naphthalen-2-yl)oxy)phthalonitrile(3c):

To a mixture of 7-(decyloxy)naphthalen-2-ol(2c)(3g, 10mmol) and tetra chlorophthalonitrile(2.65g, 10mmol) in 50mL of DMSO at 30°C, lithium hydroxide monohydrate(0.21g, 5mmol) was added portion wise within 1h. Then this reaction mixture stirred for overnight and the mixture was poured into 300mL of distilled water. After that extracted with dichloromethane (2×200mL), washed with water(200mL) followed by brine solution(100mL) and dried over MgSO₄. The solvent was removed under rotary evaporator and the crude was purified by silica-gel column chromatography using hexane:ethyl acetate(9:1) as an eluent to obtain compound 3c as a light yellow solid, yield (4.49g, 85%). ¹H NMR(600MHz, CDCl₃, ppm) δ 7.71(d, J = 8.8Hz, 1H), 7.64(d, J = 8.8Hz, 1H), 7.03(dd, J = 2.4, 8.8Hz, 1H), 7.00(dd, J = 2.4, 8.8Hz, 1H), 6.88(dd, J = 2.4, 8.8Hz, 1H), 6.70(d, J = 2.4Hz, 1H), 3.95(t, J = 6.6Hz, 2H), 1.79-1.72(m, 2H), 1.44-1.36(m, 2H), 1.34-1.13(m, 12H), 0.81(t, J = 6.9Hz, 3H). ¹³C NMR(125MHz, CDCl₃, ppm) δ 158.4, 153.8, 153.0, 137.5, 136.4, 135.3, 133.1, 130.5, 129.3, 125.7, 118.7, 117.2, 115.1, 113.9, 111.9, 111.8, 108.7, 105.9, 68.1, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 26.0,

22.7, 14.1. IR(KBr tablet) ν_{max}/cm⁻¹: 3110, 3001, 2231, 1625, 1540, 1521, 1220, 1205, 1052, 990, 942, 881, 800. ESI-MS: 529 [M+H]⁺.

2.2.4 General procedure for synthesis of zinc-phthalocyanines(PCK1-PCK3)

Phthalonitrile derivative(1eq.), zinc acetate dihydrate(0.3eq.) and diazabicyclo[5.4.0] undec-7-ene (DBU)(0.5eq.) in analytical grade 1-pentanol were stirred at reflux for overnight in a inert atmosphere. After completion of reaction, allowed to cool to ambient temperature, followed by concentrated on rota evaporator and the crude was purified by silica-gel column chromatography by spending DCM:CH₃OH (9:1) as an eluting solvent to obtain a fine solid and recrystallized from distilled CH₃OH to give zinc phthalocyanines as a bluish-green powder.

2.2.4.1 Zinc 1,2,4,8,9,11,15,16,18,22,23,25-dodecachloro-3,10,17,24-tetrakis((7-methoxy naphthalen-2-yl)oxy)phthalocyanine(PCK1)

For the synthesis of PCK1, we followed the general procedure, by using 3,4,6-trichloro-5-((7-methoxy-naphthalen-2-yl)oxy)phthalonitrile(3a)(800mg, 2mmol), zinc acetate dehydrate(132mg, 0.6mmol), 1-pentanol(10mL), and DBU(152mg, 1mmol). Yield (390mg, 49%) as a bluish green solid. C₇₆H₃₆Cl₁₂N₈O₈Zn; Calculated, %: C 54.34; H 2.16; N 6.67, Found, %: C 54.29; H 2.20; N 6.66. UV/vis: nm(log ε): in propylene glycol monomethyl ether acetate(PGMEA); 647(95), 699(199). IR(KBr tablet) ν_{max}/cm⁻¹: 2925, 1625, 1550, 1434, 1327, 1210, 927, 901. MALDI-TOF-MS: calcd for C₇₆H₃₆Cl₁₂N₈O₈Zn, 1679.952; found 1680.931 [M+H]⁺.

2.2.4.2 Zinc 1,2,4,8,9,11,15,16,18,22,23,25-dodecachloro-3,10,17,24-tetrakis((7-(hexyloxy) naphthalen-2-yl)oxy) phthalocyanine(PCK2)

For the synthesis of PCK2, we followed the general procedure, by using 3,4,6-trichloro-5-((7-(hexyloxy) naphthalen-2-yl)oxy)phthalonitrile(3b)(946mg, 2mmol),

zinc acetate dehydrate(132mg, 0.6mmol), 1-pentanol(10mL), and DBU(152mg, 1mmol). Yield(484mg, 51%) as a bluish green solid. $C_{96}H_{76}Cl_{12}N_8O_8Zn$; Calculated, %: C 58.81; H 3.91; N 5.72, Found, %: C 58.85; H 3.86; N 5.69. UV/vis: nm(log ϵ): in PGMEA; 648(128), 707(125). IR(KBr tablet) ν_{max}/cm^{-1} : 2825, 1605, 1535, 1429, 1307, 1217, 931, 912. MALDI-TOF-MS: calcd for $C_{96}H_{76}Cl_{12}N_8O_8Zn$; 1960.492; found 1961.285 [M+H]⁺.

2.2.4.3 Zinc 1,2,4,8,9,11,15,16,18,22,23,25-dodecachloro-3,10,17,24-tetrakis((7-(decyloxy) naphthalen-2-yl)oxy) phthalocyanine(PCK3)

For the synthesis of PCK3, we followed the general procedure, by using 3,4,6-trichloro-5-((7-(decyloxy) naphthalen-2-yl)oxy) phthalonitrile(3c)(1.06g, 2mmol), zinc acetate dehydrate(132mg, 0.6mmol), 1-pentanol(10mL), and DBU(152mg, 1mmol). Yield(542mg, 52%) as a bluish green solid. $C_{112}H_{108}Cl_{12}N_8O_8Zn$; Calculated, %: C 61.57; H 4.98; N 5.13, Found, %: C 61.51; H 5.02; N 5.09. UV/vis: nm(log ϵ): in PGMEA; 644(131), 704(118). IR(KBr tablet) ν_{max}/cm^{-1} : 2915, 1615, 1555, 1334, 1317, 1240, 977, 907. MALDI-TOF-MS: calcd for $C_{112}H_{108}Cl_{12}N_8O_8Zn$; 2184.924; found 2185.902 [M+H]⁺.

3. Results and discussion

3.1 Synthesis

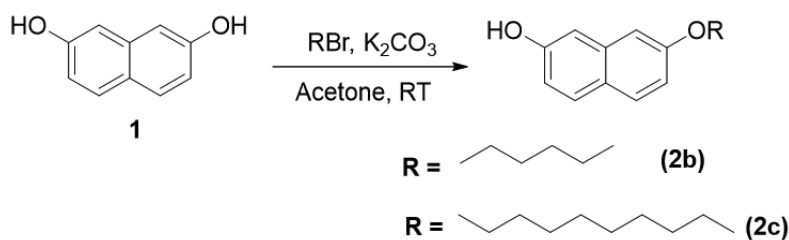
Here we nicely designed and prepared new symmetrical phthalocyanines and for this synthesis we started from alkoxy substituted naphthols(2a-2c) (Scheme 1). These 2a, 2b and 2c we prepared from

previous reported literature¹⁸⁻²⁰. To prepare compounds 3a-3c, corresponding alkoxy naphthols were reacted with tetrachloro phthalonitrile in the presence of lithium hydroxide and we got very good yields(83-90%). These phthalonitrile derivatives further reacted with zinc salt, DBU in pentanol to yield corresponding phthalocyanine(PCK1-PCK3). Here we observed region isomeric phthalocyanines but in for the separation of regioisomers, we used to try different thin layer chromatography(TLC) solvent composition methods, but we are unable to separate these regioisomeric spots²¹⁻²³. Finally all synthesized zinc phthalocyanines were fully analysed by spectroscopic (FT-IR, UV-Vis, MALDI-TOF mass spectral) and elemental analysis(Scheme 2).

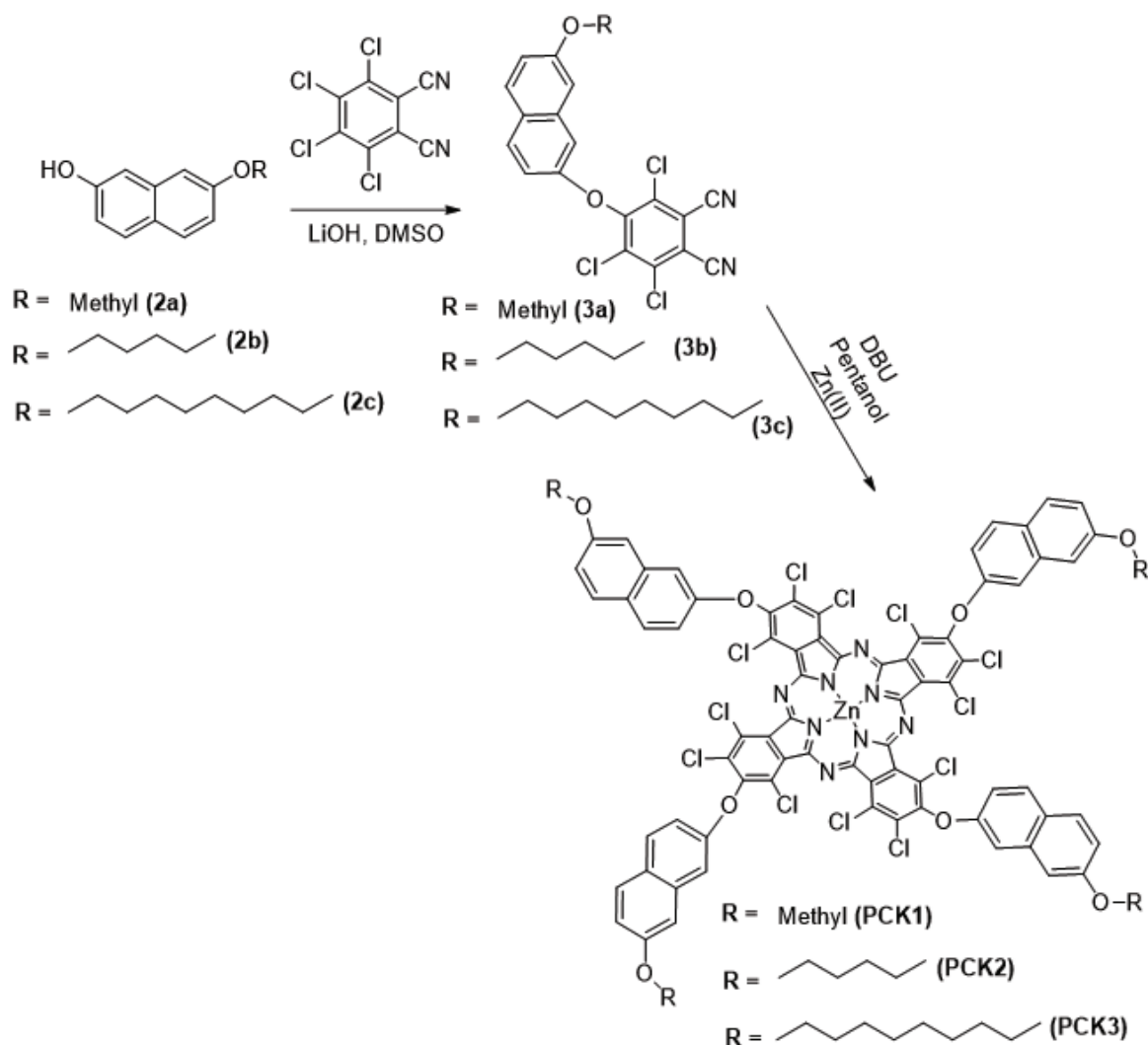
In the comparison of FT-IR spectral absorption peaks among the phthalonitrile derivatives and zinc-phthalocyanine derivatives, there is disappearance of sharp peak characteristic functional group for $C\equiv N$ stretching vibration at the region of 2200-2250 cm^{-1} was observed in all phthalocyanines, whereas which is present in the phthalonitrile, and this is the indicative of phthalocyanine formation. PCK1, PCK2 and PCK3 phthalocyanine compounds had shown almost comparable Infra-Red absorption peaks. Strong absorption peak in the region 2825-2925 cm^{-1} belongs to the vibration band of the aromatic C-H stretching, aliphatic C-H stretching, and C-O-C vibration bands were observed around 1210-1240 cm^{-1} .

3.2 UV-Visible absorption spectra

The zinc-phthalocyanine system can be without difficulty characterized by its UV-Visible absorption spec-



Scheme 1. Synthesis of alkoxy naphthols.



Scheme 2. Synthesis of zinc-phthalocyanines.

trum. Always phthalocyanines show characteristic strong absorption band around 300-400nm, belongs to the B-band, another characteristic band in visible region around 600-800nm, belongs to the Q-band ($\pi-\pi$ transition). These $\pi-\pi$ transition of the Q-band is results since a1u(HOMO) orbital to eg*(LUMO) orbital and the representing the Q-band electronic transition of zinc phthalocyanines with the D4h symmetry is showed as an intense peak in the visible region of the absorption spectrum^{24,25}. For PCK1, PCK2 and PCK3, UV-Visible absorption spectra were taken in PGMEA and shown in Figure 2. For PCK1, we observed B-band absorption maximum at 658nm and Q-band absorption maximum at 699nm. Whereas in PCK2 and PCK3, B-band maxima at 648nm and

637nm, Q-band maxima at 707nm and 704nm, respectively. These very sharp absorption peaks are representing that there was no any aggregation of these phthalocyanine dyes. In the case of extension coefficient values, there is increase in the PCK1 to PCK3, the reason behind in this is increase in the alkyl chain, increases solubility in PEMEA Figure 2. For PCK1, we observed B-band absorption maximum at 658nm and Q-band absorption maximum at 699nm. Whereas in PCK2 and PCK3, B-band maxima at 648nm and 637nm, Q-band maxima at 707nm and 704nm, respectively. These very sharp absorption peaks are representing that there was no any aggregation of these phthalocyanine dyes. In the case of extension coefficient values, there is increase in the PCK1 to PCK3, the

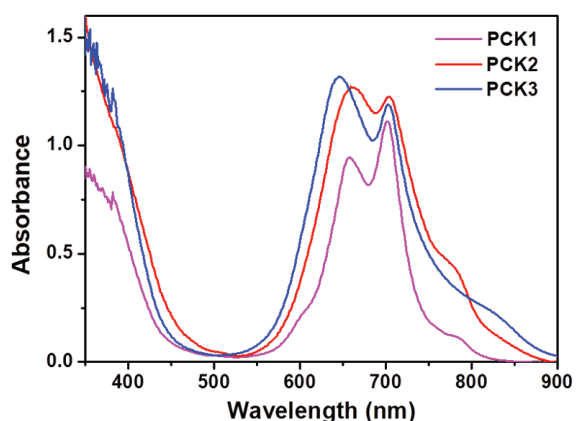


Figure 2. Absorption spectra of PCK1, PCK2 and PCK3 in PGMEA(1.5×10^{-5} M).

reason behind in this is increase in the alkyl chain, increases solubility in PGMEA (Figure 2).

To extent of UV-Visible absorption study, we checked the absorption pattern chloroform in 1.5×10^{-5} M concentration (Figure 3). In comparison with PGMEA, in CHCl_3 , the UV-Visible absorption peaks are slightly shifted and absorption intensity also decreased in some extent. The reason behind this absorption difference may be polarity and solubility difference between PGMEA and CHCl_3 . The lesser extinction coefficient in CHCl_3 is suggesting that, there is present of aggregation in all phthalocyanine dyes.

3.3 Transmittance spectra

The concept has been proved that for green color LCD displays, the transmittance maxima should be in

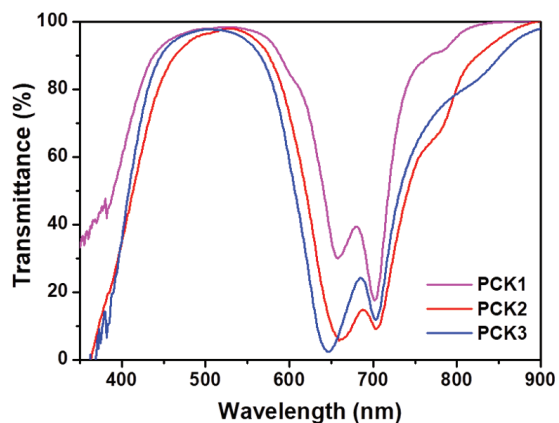


Figure 4. Transmittance spectra of PCK1, PCK2 and PCK3 in PGMEA(1.5×10^{-5} M).

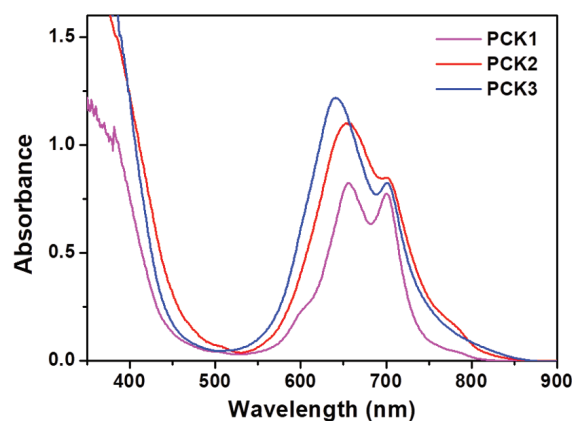


Figure 3. Absorption spectra of PCK1, PCK2 and PCK3 in CHCl_3 (1.5×10^{-5} M).

the region of 500nm to 550nm and sharp²⁶). This transmittance study in PGMEA helps as preliminary study for LCD color filter requirements. In this study all the dyes showed more than 95% of the transmittance. The transmittance of phthalocyanines PCK1-PCK3 is in the following order: PCK3>PCK2>PCK1. Since PCK3 showed sharp transmittance because of nice solubilizing decyl chain, it will results a nice bluish green color. Thus, PCK3 can be useful as perfect phthalocyanine dye for the preparation of green colored filters for LCD and LED displays (Figure 4).

3.4 Aggregation studies

The association of the phthalocyanine individual molecules to yields dimers, trimers and higher oligomers is called aggregation. Because of different

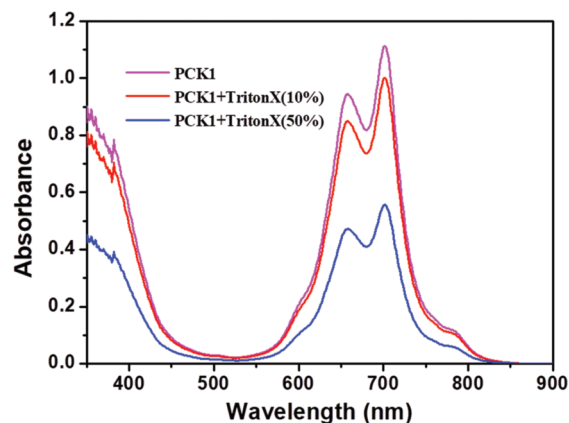


Figure 5. Absorption spectra of PCK1 in PGMEA upon addition of Triton X.

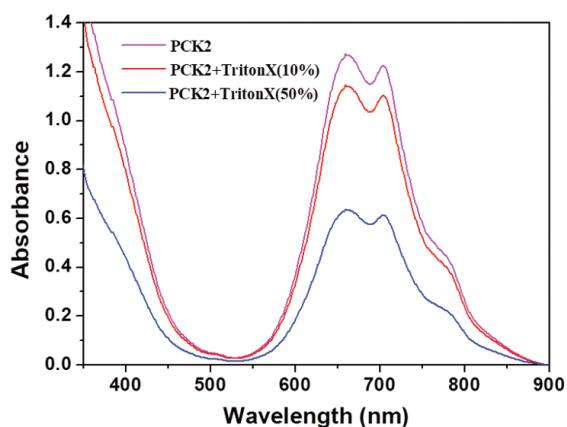


Figure 6. Absorption spectra of PCK2 in PGMEA upon addition of Triton X.

optical properties of these aggregates it is very important to study the aggregation property. There is a general concept that when phthalocyanine molecules have good solubility, there is no any aggregation^{15,27}. Generally by the addition of surfactants there is a breakdown of aggregation in molecules. Here we taken Triton X surfactant, phthalocyanines PGMEA solutions($1.5 \times 10^{-5} \text{M}$)(Figure 5 to Figure 7).

For PCK1, PCK2 and PCK3 10% of the Triton X(V/V) added and we observed almost 10% decrease in absorption peaks. Further added 50% of the Triton X(V/V) and at this stage also we have observed absorption change according to concentration levels only. Finally we not observed any dramatical change in absorption peaks. By considering these results, it has been clearly concluded that PCK1, PCK2 and PCK3 phthalocyanines did not show any aggregation behavior in PGMEA at the concentration range studied. The reason behind this non-aggregation property in PGMEA is the naphthoxy and alkoxy groups made phthalocyanines to highly soluble and which results suitable dyes for LCD color filters.

3.5 Solubility of phthalocyanines in PGMEA

Those phthalocyanines have high solubility in industrial solvents which is most suitable for LCD color filter. PCK1, PCK2 and PCK3 have a very good solubility in almost all industrial solvents like chloroform,

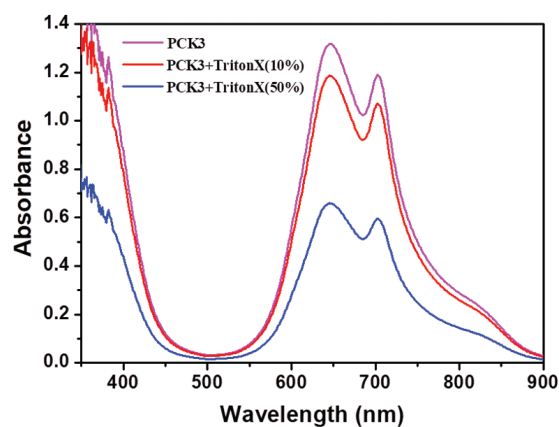


Figure 7. Absorption spectra of PCK3 in PGMEA upon addition of Triton X.

dichloromethane, dimethyl sulfoxide, N,N-dimethyl formamide, PGMEA, acetone, tetrahydrofuran and acetonitrile. PGMEA is very commonly using industrial solvent for the LCD fabrication. In addition to the compatibility with binders, greater than 5 wt% of the phthalocyanine compound should be dissolve in PGMEA. Here for the solubility test PCK1, PCK2 and PCK3 were dissolved in PGMEA and the corresponding results were represented in Table 1.

For this study all phthalocyanines were dissolved by sonication method up to 30min. The results showed that PCK3 have good solubility PCK2 and overall PCK1 have a less solubility. After the addition of the binder also, we have not observed any precipitation. These results suggested that all phthalocyanines were exhibited greater than 8 wt% of solubility in PGMEA. Therefore, PCK1, PCK2 and PCK3 were superior dyes for green color filter in LCD applications.

4. Conclusions

In this study, we have described the synthesis of

Table 1. Solubility of phthalocyanines at 25°C in PGMEA

Sample No.	Phthalocyanine	Solubility(g/100mL)
1	PCK1	8.4
2	PCK2	8.9
3	PCK3	9.3

alkoxy naphthyl phthalocyanine derivatives and the all synthesized compounds were fully confirmed by its spectral analysis. UV-Visible absorption and transmittance results were showed that, these dyes have suitable spectral properties for LCD color filters. In PGMEA to check the aggregation nature, we added Triton X surfactant and all phthalocyanines not showed any aggregation. Solubility test in PGMEA, all phthalocyanines showed more than 8 wt% of solubility. Finally all of these results concluded that PCK1, PCK2 and PCK3 are fulfilled the LCD green color filter requirements.

Acknowledgments

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