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Synthesis and characterization of solubility enhanced metal-free phthalocyanines for liquid crystal display black matrix of low dielectric constant

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ABSTRACT

For the liquid crystal display (LCD) black matrix (BM) with a low dielectric constant and high light absorption property, it is advantageous to employ dyes instead of carbon black or pigments. For this purpose, the dyes should have high solubility in industrial organic solvents. For improved solubility in industrial solvents, three metal-free phthalocyanines (PC), peripherally substituted with bulky groups, were synthesized and dye-based BMs were fabricated. The solubility as well as the spectral and thermal properties of the dyes were examined, and the optical, thermal and dielectric properties of a dye-based black matrix were tested. The greenish phthalocyanine dyes with high molar extinction coefficients and high thermal stability showed enhanced solubility in industrial solvents as a result of the greater steric hindrance among the dye molecules and higher affinity between the dye molecules and solvents. The dye-based BMs had low dielectric constants and exhibited superior optical properties and satisfactory thermal stability.

1. Introduction

The black matrix (BM), a component of LCD color filters, divides the red, green and blue (RGB) pixels of the color filter and blocks light leaking from the areas between the RGB color patterns enhancing contrast ratio of color filters [1]. According to the component materials, BM can be divided into metal oxide, carbon black, titanium black and organic pigment types [2]. Among the various types of BMs, a carbon black BM manufactured by spin-coating is generally employed in industry. The advantage of using carbon black as a BM component arises from its high light absorption property, high thermal stability and low cost [2,3]. On the other hand, malfunctions of the thin film transistor (TFT) of a LCD can occur due to the high dielectric constant of carbon black. To avoid this problem, an organic pigment BM with a low dielectric constant can be used despite its low spectral property due to the lower molar extinction coefficient of organic pigments [4].

If dyes are used for the manufacture of the BM, the high dielectric constant and low light absorption of conventional BMs can be overcome. On the other hand, dyes generally have low thermal stability compared to carbon black and organic pigments. Therefore, the dyes for BM need to be structurally stable [5,6]. They also should have good solubility in industrial solvents, such as propylene glycol methyl ether acetate (PGMEA) and cyclohexanone [6].

In this study, green phthalocyanine (PC) dyes with high thermal stability and high solubility were designed. Three metal-free PC dyes were synthesized by introducing substituents including alkyl or alkoxy groups to the peripheral position of the PC rings, and their spectral properties, solubilities and thermal stabilities were measured. Dye-based BMs were fabricated and their optical and dielectric properties were examined.

2. Experimental

2.1. General

2,5-bis-(1,1-dimethylbutyl)-methoxyphenol, 4-hydroxy-3-tert-butylanisole, 2,4-bis(1,1-dimethylpropyl)phenol were purchased from TCI and, dimethyl sulfoxide (DMSO), potassium carbonate anhydrous, dichloromethane, *m*-xylene anhydrous, ethanol anhydrous and lithium granule purchased from Sigma Aldrich were used as received.

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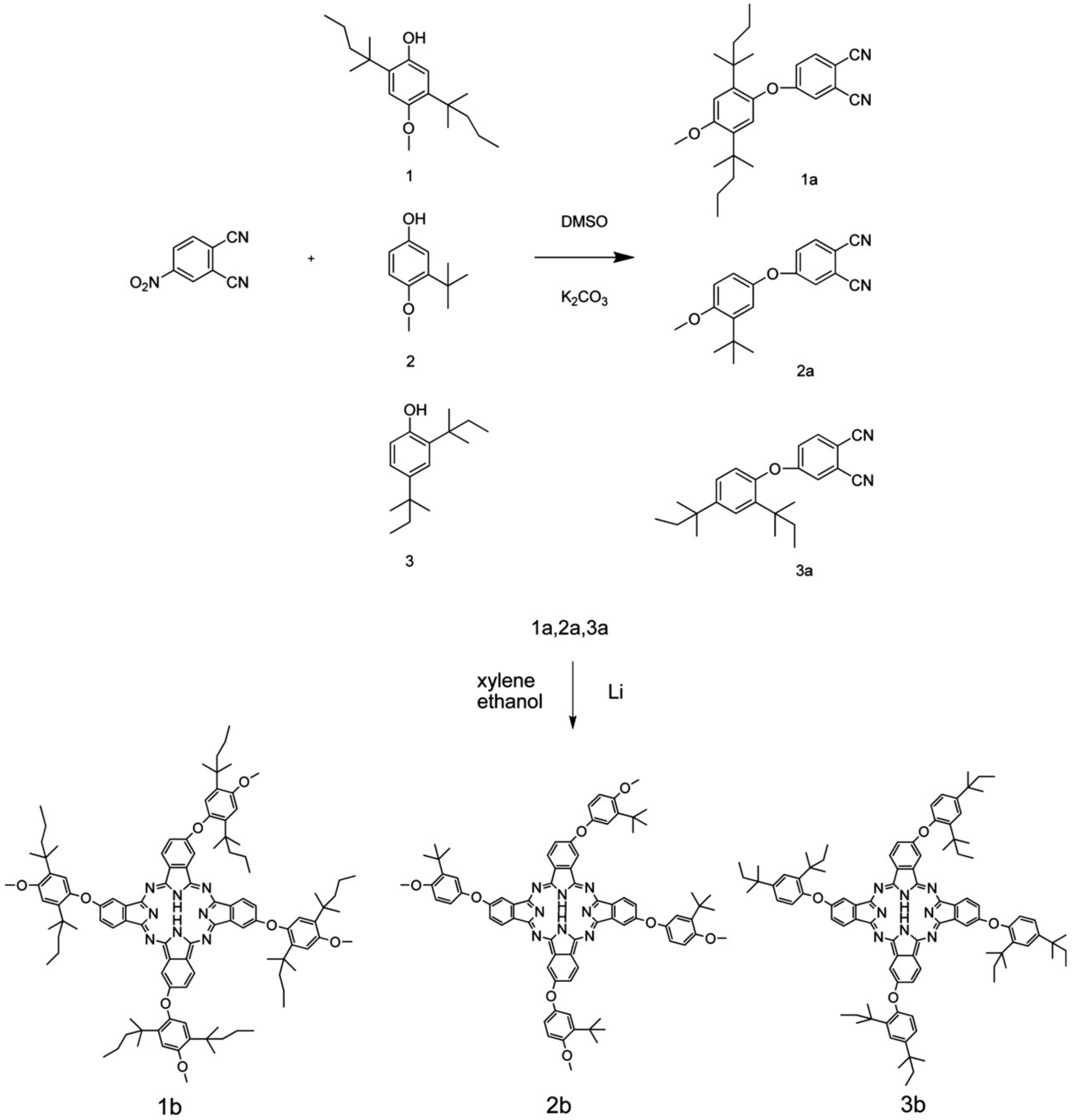
All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. Transparent glass substrates were provided by Paul Marienfeld GmbH & Co. KG and acrylic binder LC20160 were supplied by SAMSUNG Cheil industries Inc.

^{1}H NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz using chloroform-d and tetramethylsilane (TMS), as the solvent and internal standard, respectively. Matrix Assisted Laser Desorption/Ionization Time Of Flight (MALDI-TOF) mass spectra were collected on a Voyager-DE STR Biospectrometry Workstation with α-cyano-4-hydroxy-cynamic acid (CHCA) as the matrix. Fourier transform infrared (FT-IR) spectra were recorded in the form of solid on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Elemental analysis was done on CE Instrument EA1112. Absorption spectra were measured using a HP 8452A spectrophotometer. Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate of 10 °C min^{-1} using a TA Instruments Thermogravimetric Analyzer 2050. Dielectric constants were measured using Edward E306 thermal evaporator and HP 4294A precision impedance analyzer.

2.2. Synthesis

2.2.1. Preparation of 4-(2,5-bis(1,1-dimethylbutyl)-4-methoxyphenoxy)phthalonitrile (1a)

4-Nitrophthalonitrile (1 g, 5.77 mmol) and 2,5-bis-(1,1-dimethylbutyl)-methoxyphenol (1.68 g, 5.77 mmol) were dissolved in dry DMSO (30 ml) and anhydrous K_2CO_3 (1.06 g, 7.66 mmol) was added in portions during 4 h. The mixture was stirred at 40 °C for 24 h under nitrogen atmosphere. After filtering the reaction mixture, the residue was extracted with CH_2Cl_2 and



Scheme 1. Synthesis of the prepared dyes.

dried by rotary evaporation. Pure product (2.19 g, 5.23 mmol) was collected by column chromatography on silica gel using EA/hexane (10:1) mixture as an eluent.

Yield 91%; ^{1}H NMR (CDCl$_3$, ppm): 7.69 (d, 1H), 7.22 (s, 1H), 7.14 (d, 1H), 6.82 (s, 1H), 6.63(s, 1H), 3.08 (s, 3H, $-$O$-$CH$_3$), 1.71 (m, 2H), 1.56 (m, 2H), 1.26(d, 12H), 1.04 (m, 2H), 0.96 (m, 2H), 0.81 (t, 3H), 0.71 (t, 3H).

2.2.2. Preparation of 4-(3-tert-butyl-4-methoxyphenoxy) phthalonitrile (2a)

2a was synthesized following the same procedure for 1a using 2 (1 g, 5.54 mmol), 4-nitrophthalonitrile (0.96 g, 5.54 mmol), DMSO (30 ml), and anhydrous K_2CO_3 (1.06 g, 7.66 mmol).

Yield 85%; ^{1}H NMR (CDCl$_3$, ppm): 7.71 (d, 1H), 7.26 (s, 1H), 7.22 (d, 1H), 7.01 (s, 1H), 6.77 (m, 2H), 3.83 (s, 3H, $-$O$-$CH$_3$), 1.30 (m, 9H).

2.2.3. Preparation of 4-(2,4-bis(1,1-dimethylpropyl)phenoxy) phthalonitrile (3a)

3a was synthesized following the same procedure for 1a using 3 (1.2 g, 5.12 mmol), 4-nitrophthalonitrile (0.89 g, 5.12 mmol), DMSO (30 ml), and anhydrous K_2CO_3 (1.06 g, 7.66 mmol).

Yield 82%; ^{1}H NMR (CDCl$_3$, ppm): 7.71 (d, 1H), 7.35 (s, 1H), 7.27 (s, 1H), 7.22 (d, 1H), 7.18 (d, 1H), 6.75 (d, 1H), 1.66 (m, 4H), 1.30 (d, 12H), 0.70 (t, 3H), 0.63 (t, 3H).

2.2.4. Preparation of tetrakis(2,5-bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-phthalocyanine (1b)

1a (0.9 g, 2.38 mmol) was dissolved in anhydrous xylene (50 ml) and ethanol (10 ml) under nitrogen atmosphere and Li (0.13 g, 18.7 mmol) was added in the solution. The reaction mixture was stirred at 150 °C for 5 h. After cooling the solution, the resulting slurry was extracted with CH_2Cl_2 (100 ml) and washed with saturated NaCl solution. The pure product (0.53 g, 0.31 mmol) was obtained by column chromatography on silica gel using CH_2Cl_2 as an eluent.

Yield 54%; MALDI-TOF MS: *m*/*z* 1675.9 (100%, [M + 2K]+). FT-IR (KBr, cm^{-1}): 3289 (N-H). Calcd for $C_{108}H_{138}N_8O_8$: C, 77.38; H, 8.30; N, 6.68; O, 7.64%. Found: C, 77.36; H, 8.27; N, 6.66; O, 7.69%.

2.2.5. Preparation of tetrakis(3-tert-butyl-4-methoxyphenoxy)-phthalocyanine (2b)

2b was synthesized following the same procedure for 1b using 2a (1 g, 3.26 mmol), Li, ethanol (10 ml), and anhydrous xylene (50 ml).

Yield 41%; MALDI-TOF MS: *m*/*z* 1227.1 (100%, [M + 2K]+). FT-IR (KBr, cm^{-1}): 3289 (N-H). Calcd for $C_{76}H_{74}N_8O_8$: C, 74.37; H, 6.08; N, 9.13; O, 10.43%. Found: C, 74.37; H, 6.08; N, 9.12; O, 10.45%.

2.2.6. Preparation of tetrakis(2,4-bis(1,1-dimethylpropyl)phenoxy)-phthalocyanine(3b)

3b was synthesized following the same procedure for 1b using 3a (1.1 g, 3.05 mmol), Li, ethanol (10 ml), and anhydrous xylene (50 ml).

Yield 41%; MALDI-TOF MS: *m*/*z* 1443.7 (100%, [M + 2K]+). FT-IR (KBr, cm^{-1}): 3293 (N-H). Calcd for $C_{96}H_{114}N_8O_4$: C, 79.85; H, 7.96; N, 7.76; O, 4.43%. Found: C, 79.88; H, 8.75; N, 6.33; O, 4.25%.

2.3. Preparation of dye-based black matrix

The ink for a black matrix was composed of the dye (0.01 g), cyclohexanone (4.0 g), and LC20160 (14 g) as a binder based on acrylate. The prepared dye-based inks were coated on a transparent glass substrate using a MIDAS System SPIN-1200D spin coater. The coating speed was initially 100 rpm for 5 s, which was then increased to 200 rpm and kept constant for 20 s. The wet dye-coated black matrix was then dried at 80 °C for 20 min, prebaked at 150 °C for 10 min, and postbaked at 230 °C for 1 h. After each step, the coordinate values of the black matrix were measured.

Table 1
Solubility of the dyes at 20 °C.

Dye	PGMEA	Cyclohexanone
1b	4 wt%	10 wt%
2b	2.2 wt%	2.8 wt%
3b	Less than 1.0%	Less than 1.0%
PB 16	Insoluble	Insoluble

2.4. Measurement of spectral and chromatic properties

The absorption spectra of the synthesized dyes and the transmittance spectra of the dye-based BM were measured using a UV–vis spectrophotometer. The chromatic values were recorded on a color spectrophotometer (Scinco colormate).

2.5. Measurement of solubility

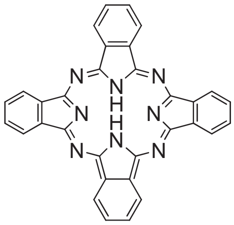
Small amounts of the dyes (0.05 g) were added to the solvents (0.5 g). The solutions were stirred for 20 min and left to stand for 24 h at room temperature. Precipitations were visually checked and additional solvents (0.25 g) were added into the solutions until it made clear solutions. The solubility of the dye was recorded as weight percentage of dyes in the clear solutions.

2.6. Measurement of thermal stability

The thermal stability of the synthesized dyes was evaluated by thermogravimetry (TGA). The prepared dyes were heated to 110 °C and held at that temperature for 10 min to remove the residual water and solvents. The dye was then heated to 230 °C and held at that temperature for 60 min to simulate the processing thermal conditions of color filter manufacturing. The dyes were finally heated to 500 °C to determine their degradation temperature. The heating was carried out at the rate of 10 °C min^{-1} under nitrogen atmosphere. To check the thermal stability of the dyes in black matrix, the fabricated black matrix was heated to 230 °C for 1 h in a forced convection oven (OF-02GW Jeiotech Co., Ltd.). The color difference values (ΔE_{ab}) before and after heating were measured on a color spectrophotometer (Scinco colormate) in CIE L'a'b' mode.

2.7. Geometry optimization of the synthesized dyes

The geometry and electric structure of the studied dyes are optimized by the hybrid density functional theory (DFT) method at the PBE/DNP theory level performed on Materials Studio 5.0 DMol3 program package.



PB 16

Fig. 1. Structure of Pigment Blue 16.

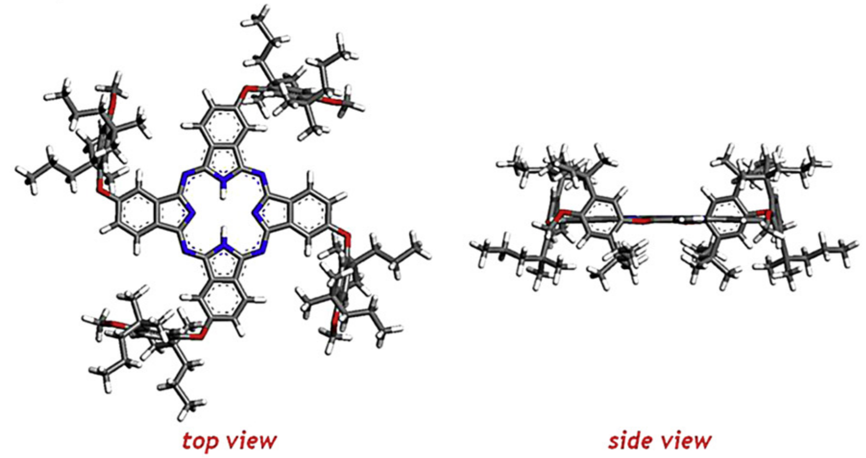
3. Results and discussion

3.1. Synthesis of dyes

Three metal-free PCs with enhanced solubility were designed and synthesized, as shown in Scheme 1. Precursors (1a,2a,3a) were synthesized through a nucleophilic aromatic substitution reaction between nitro phthalonitriles and phenols including functional groups (1,2,3) [7]. Each reaction was conducted under similar conditions and all products were obtained in high yield over 80%. The structures of the synthesized precursors were confirmed by ^{1}H NMR.

The metal-free PCs (1b,2b,3b) were synthesized by a cyclotetramerization reaction of the precursors and purified by column

☐ Optimized structure (1b)



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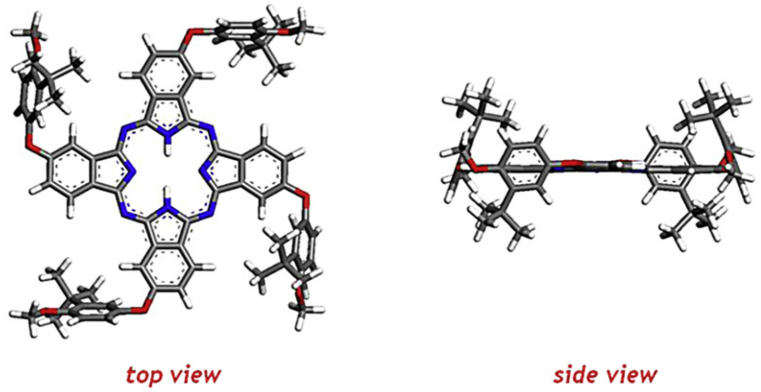

☐ Optimized structure (3b)

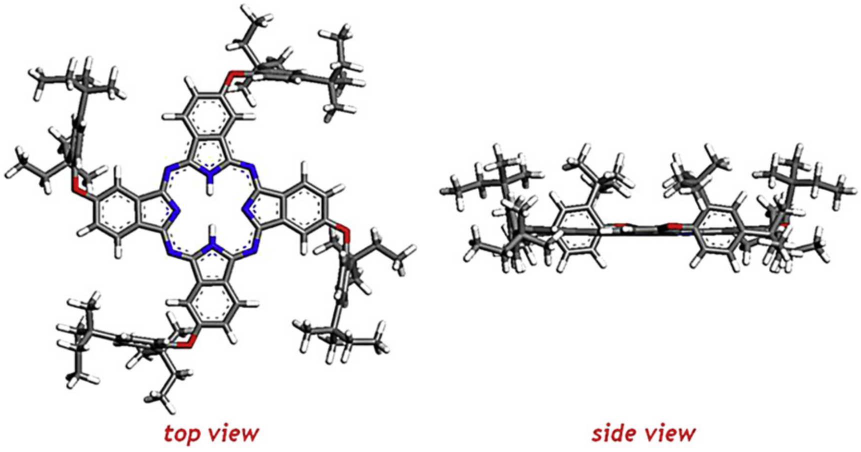

Fig. 2. Geometry-optimized structures of the prepared dyes.

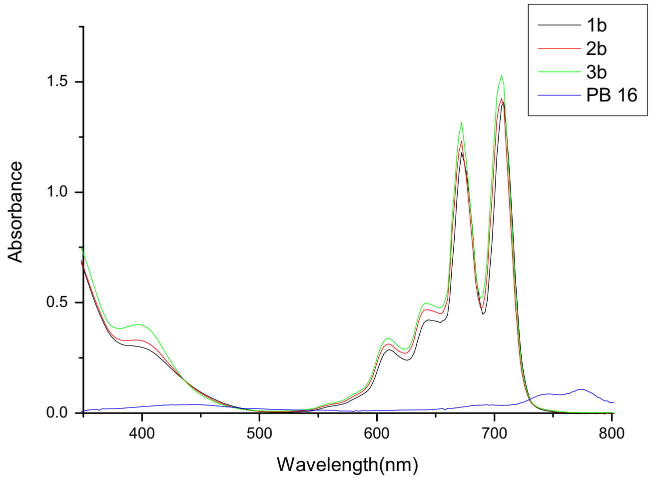

Fig. 3. Absorption spectra of the synthesized dyes in CH_2Cl_2 (10^{-5} mol l^{-1}) and PB 16 in sulfuric acid (10^{-5} mol).

chromatography [8]. Theoretically, metal-free PCs synthesized by monosubstituted phthalonitriles can have 4 constitutional isomers: C_{4h},C_{2v},C_s,D_{2h}. Assuming a statistical distribution, the 4 isomers are expected to be mixed in the ratio of 1:2:4:1 [9]. No attempts to separate these isomers were made and all metal-free PCs were obtained in relatively high yield. The structures of synthesized PCs were confirmed by MALDI-TOF spectroscopy, FT-IR spectroscopy, and elemental analysis.

3.2. Solubility

The dyes need to be dissolved in industrial solvents, such as PGMEA and cyclohexanone, to a concentration of at least 4–5 wt% to be applied for BM [6]. Generally, non-substituted PCs tend to form various crystal structures due to molecular interactions caused by their planar structures. Therefore, non-substituted PCs have low solubility in most organic solvents, which has limited their applications [9].

Substituents including bulky alkyl groups or alkoxy groups were introduced at their peripheral positions to enhance the solubility of PCs. As a result, the solubility of metal-free PCs increased significantly compared to that of non-substituted metal-free PC (PB 16). This is due to the steric hindrance between the planes of the PC molecules caused by the bulky aromatic substituents rotated out of the plane of the molecule. In addition, as previously mentioned, the synthesized dyes would exist in a mixture of 4 isomers, which would increase their solubility due to the unsymmetrical isomers C_s and C_{2v} among them [10]. Table 1 lists the solubility of the PC dyes and PB 16, and Fig. 1 shows the structure of PB 16.

Dyes 1b and 2b, which included alkyl and alkoxy groups at their terminal positions, showed higher solubility than dye 3b, which contained only alkyl groups as substituents. In particular, the solubility of dye 1b in cyclohexanone reached 10 wt% due to the anti-aggregation effects between the PC molecules as well as the affinity between the ether linkages of the dyes and solvent molecules [6]. The solubility of dye 2b was relatively lower than that of dye 1b because of its less bulky alkyl substituents. Dye 3b was barely soluble in industrial solvents due to little affinity between the dyes and solvent molecules.

Table 2
Absorption maxima and extinction coefficients of the prepared dyes in CH_2Cl_2 and PB 16 in sulfuric acid.

Dye	λ_{max} (nm)	ε_{max} (L mol^{-1} cm^{-1})
1b	708	140,875
2b	706	142,473
3b	706	152,855
PB 16	774	10,756

Table 3
Electronic energies of the prepared dyes.

	1b	2b	3b
HOMO + 3	−5.061	−5.086	−5.506
HOMO + 2	−4.972	−5.002	−5.258
HOMO + 1	−4.958	−4.934	−5.233
HOMO	−4.432	−4.445	−4.501
ΔE	1.316	1.318	1.326
LUMO	−3.116	−3.127	−3.175
LUMO − 1	−3.076	−3.093	−3.133
LUMO − 2	−1.722	−1.733	−1.783
LUMO − 3	−1.515	−1.531	−1.573

ΔE means the energy gap difference between HOMO and LUMO.

The solubility of the dyes corresponded to the simulation data optimized by the Materials Studio 5.0 DMol3 program. Fig. 2 shows the optimized structures of the dyes with bulky substituents out of the planar core. The bulky substituents of dyes 1b and 2b were twisted perpendicular to upward and downward directions of the molecular plane, whereas those of dye 3b were twisted toward one side of the molecular plane. Therefore, dyes 1b and 2b were more soluble in industrial solvents than dye 3b.

3.3. *UV–vis absorption spectra*

Fig. 3 and Table 2 show the absorption spectra of dye 1b–3b in CH_2Cl_2 and PB 16 in sulfuric acid, respectively. To apply a dye to a BM, it should have strong and broad absorptions in the visible region. The greenish dyes exhibited absorption maxima in the 706–708 nm range, displaying typical Q-band absorptions in the 600–750 nm range as well as B-band absorptions in the 300–450 nm range [11]. The characteristic Q and B bands were due to π–π^* transitions in the heteroaromatic 18-π electron system [12]. The dyes showed similar spectral properties, indicating that the conjugations of the dyes were not much affected by the change in introduced substituents [11]. The molar extinction coefficients of the dyes were approximately 140,000–150,000, which significantly exceeded those of the pigments. Therefore, the amounts of the dyes needed for BM can be reduced.

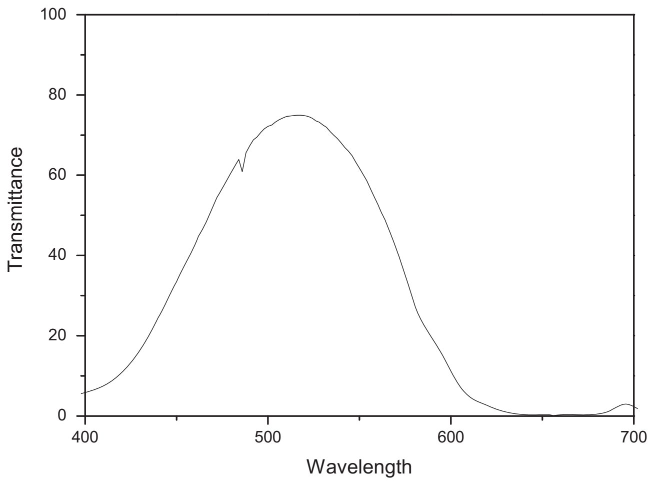

Fig. 4. Transmittance spectra of the spin-coated black matrix with dye 1b.

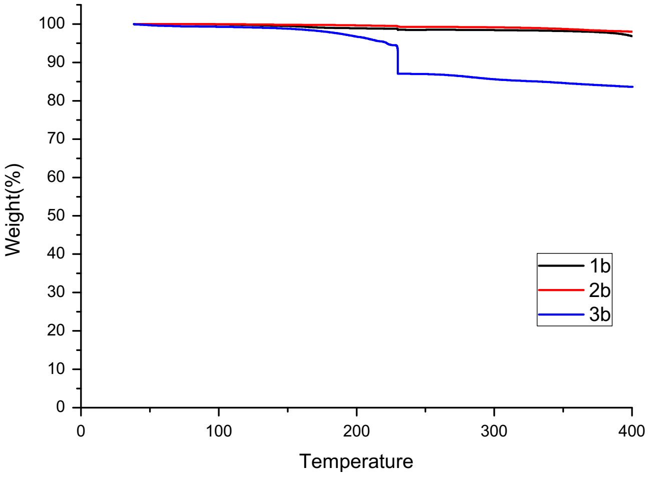

Fig. 5. Thermogravimetric analysis (TGA) of the prepared dyes.

These results corresponded to the simulation data optimized by the Materials Studio 5.0 DMol3 program. As shown in Table 3, the orbital lobes and HOMO-LUMO energy gaps of the dyes were almost identical. Accordingly, the changes in substituents did not affect the absorption maxima of the dyes. Fig. 4 shows the transmittance spectra of the dye-based BM fabricated with the dye 1b. The fabricated BM absorbed light broadly in the 400–450 nm and 600–700 nm ranges. Therefore, compensatory dyes absorbing light in the 450–600 nm range will be needed for complete absorption of light in the visible range.

3.4. *Thermal properties*

Phthalocyanines are highly stable dyes due to the strong π–π stacking interactions from their planar structures [13]. In addition, their high molecular weight is favorable for intermolecular interactions, such as Van der waals forces. On the other hand, phthalocyanines including substituents show reduced stability due to anti-aggregation effects.

For the current LCD manufacturing process, dye molecules need to be stable up to 230 °C [6]. As shown in Fig. 5, dyes 1b and 2b showed $<1\%$ weight loss after 1 h at 230 °C, whereas dye 3b showed approximately 10% weight loss and degraded gradually with increasing temperature. This was attributed to the initial decomposition of phthalocyanines from the terminal groups at 230–250 °C. As PC dyes containing alkoxy groups as substituents were reported to be more stable than those containing terminal alkyl groups, dye 1b and 2b showed higher stability than dye 3b [14].

To measure the thermal stability of BM film, dye 1b was spin coated on a glass and the ΔE_{ab} value of the film was measured. As shown in Table 4, the ΔE_{ab} value of the film was 3.434 after heating for 90 min at 230 °C. This suggests that the original color of the BM was well maintained due to little degradation of the dye [15]. The thermal stability of dye-based BMs would be improved further if a commercial binder, adjusted for the pigments, can be optimized to the dye [16].

Table 4
The coordinate values corresponding to the CIE 1931 chromaticity diagram of the dye-based black matrix.

Black matrix		*L*	*a*	*b*	ΔE_{ab}
1b	Prebake	74.6417	−65.6547	6.851	3.434
	Postbake	77.3913	−66.2442	8.824	

Table 5
Dielectric constants and constitutions of the dye-based black matrix.

Frequency (kHz)	Dielectric constant(ε_r, average)					
	1b-00	1b-20	1b-40	1b-60	1b-80	1b-100
0.1	26.39	20.07	13.94	6.90	6.92	4.96
1	25.47	19.44	13.56	6.78	6.81	4.84
10	20.65	16.10	11.60	6.16	6.25	4.23
100	18.72	14.78	10.89	5.95	6.04	4.12
200	18.22	14.41	12.61	5.87	5.96	4.08
500	17.57	13.94	10.44	5.78	5.86	4.02
700	17.34	13.77	10.35	5.74	5.83	3.99
1000	17.11	13.61	10.25	5.70	5.79	3.99
Thickness	1.2013 μm					
Electrode radius	280, 285, 280 μm					
	1b-00 (wt%)	1b-20 (wt%)	1b-40 (wt%)	1b-60 (wt%)	1b-80 (wt%)	1b-100 (wt%)
Binder	50	50	50	50	50	50
Carbon black	50	40	30	20	10	
Dye 1b		10	20	30	40	50

3.5. *Dielectric properties*

The dielectric constant of BM needs to be <7 for satisfactory industrial applications with a current thickness of BM (1–1.5 μm). On the other hand, carbon black BM has a high dielectric constant >20, which can cause malfunctions of LCD TFTs due to interference of the TFT electric signal with carbon black [4]. Therefore, to reduce the dielectric constant of BM, dye-based BM and carbon black-dye hybrid type BMs were fabricated and their dielectric properties were tested.

Table 5 lists the dielectric constants and constitutions of the prepared BMs. The 6 hybrid type BMs were fabricated with varied compositions of dye 1b and carbon black. The BM 1b-00 prepared with carbon black only had the highest dielectric constant. The dielectric constant of BM decreased significantly with decreasing carbon black and increasing dye concentration due to the low dielectric character of the dye. In particular, BM 1b-100 prepared with the dye only had the lowest dielectric constant of 3.99 at a frequency of 1000 kHz. In addition, the dielectric constants of the samples were a function of the applied electric field frequency. The dielectric constant of BM decreased gradually with increasing frequency from 0.1 kHz to 1000 kHz. This was attributed to the lag in charge transfer inside the dye molecule caused by the rapid change in the external electronic field [17]. Among the 6 BMs prepared, those containing more than 30 wt% of dye had a dielectric constant <7 at the working frequency range (100–300 Hz).

4. Conclusion

Three solubility enhanced phthalocyanine dyes were synthesized, and the dye-based BMs were fabricated with the most soluble dye. The increase in solubility of the prepared dyes was attributed to bulky functional substituents at the peripheral positions of them. Since all dyes had high molar extinction coefficients, dye-based BMs absorbed light in the visible region with the small amounts of the dyes. In addition, the dyes including terminal alkoxy groups showed suitable thermal stability for commercial use due to terminal alkoxy groups are stable at postbaking temperature. The dielectric constants of the BMs containing more than 30 wt% of dyes were significantly lower than that of the BM prepared with carbon black only.

Acknowledgments

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