

Supplementary Material (ESI) for NJC
This journal is (c) The Royal Society of Chemistry 20XX

**Synthesis and Characterization of Thermally Stable Dyes
with Improved Optical Properties for Dye-based LCD Color
Filters**

Supporting information

Jun Choi,^{‡a} Se Hun Kim,^{‡a} Woosung Lee,^a Chun Yoon,^b and Jae Pil Kim*^a

^a Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea. Fax: +82 2 880 7238; Tel: +82 2 880 7238; E-mail: jaepil@snu.ac.kr

^b Department of Chemistry, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 143-747, Korea. Fax: +82 2 3408 3218; Tel: +82 2 3408 3218; E-mail: chuny@sejong.ac.kr

[‡] Both authors contributed equally to the research.

Synthesis

3-(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)phthalonitrile (I).

3-nitrophthalonitrile(1g, 5.77mmol) and 2,5-bis-(1,1-dimethylbutyl)-methoxyphenol(1.68g, 5.77mmol) were dissolved in dry DMF(30ml) and anhydrous K₂CO₃(1.06g, 7.66mmol) was added in portions during 4h. The mixture was stirred at 80 °C for 10h under nitrogen atmosphere. After filtering the reaction mixture, the residue was extracted with CH₂Cl₂ and dried by rotary evaporation. After removal of the solvent, the crude product was purified on a silica gel column (CH₂Cl₂/hexane: 5/1) to afford the target compound as a light brown solid (1.98g, 82.22%). ¹H NMR (500MHz, CDCl₃, 25 °C, TMS): δ = 7.44 (t, 1H), 7.32 (d, 1H), 6.89 (d, 1H), 6.76 (1H, s), 6.60(1H, s), 3.78 (s, 3H, -O-CH₃), 1.64 (m, 2H), 1.54 (m, 2H), 1.20(d, 12H), 1.02 (m, 2H), 0.98 (m, 2H), 0.77 (t, 3H), 0.65 (t, 3H).

1(4)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-phthalocyaninatozinc(II) (Ia).

The solution of **1** (1.26g, 3mmol) in 1-pentanol (50ml) was refluxed under a nitrogen atmosphere and ZnCl₂ (0.41g, 3mmol) was added. After adding DBU (2.25ml, 15mmol), the solution was heated under reflux for 12h. After filtering the reaction mixture, the residue was purified on a silica gel column (CH₂Cl₂/MeOH: 50/1) to afford the target

compound as a bluish green solid (0.76g, 58.35%). MALDI-TOF MS : m/z 1740.07 (100%, $[M+2K]^+$); Found: C, 74.36; H, 7.74; N, 6.37; O, 7.49%. Calc. for $C_{106}H_{132}N_8O_8Zn$: C, 74.38; H, 7.77; N, 6.55; O, 7.48%.

***1(4)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-
phthalocyaninatocopper(II) (1b).***

1b was synthesized following the same procedure for **1a** using **1** (1.26g, 3mmol), 1-pentanol (50ml), $CuCl_2$ (0.40g, 3mmol), and DBU (2.25ml, 15mmol). The crude product was purified on a silica gel column (CH_2Cl_2 /Hexane: 2/3) to afford the target compound as a dark bluish green solid (0.78g, 60.38%). MALDI-TOF MS : m/z 1737.86 (100%, $[M+2K]^+$); Found: C, 74.66; H, 8.18; N, 6.10; O, 7.61%. Calc. for $C_{106}H_{132}N_8O_8Zn$: C, 74.46; H, 7.78; N, 6.55; O, 7.49%.

***1(4)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-
phthalocyaninatocobalt(II) (1c).***

1c was synthesized following the same procedure for **1a** using **1** (1.26g, 3mmol), 1-pentanol (50ml), $CoCl_2$ (0.39g, 3mmol), and DBU (2.25ml, 15mmol). The crude product was purified on a silica gel column (CH_2Cl_2 /Hexane: 1/1) to afford the target compound as a dark bluish green solid (0.68g, 51.71%). MALDI-TOF MS : m/z

1732.87 (100%, $[M+2K]^+$); Found: C, 74.77; H, 7.45; N, 6.55; O, 7.78%. Calc. for $C_{106}H_{132}N_8O_8Zn$: C, 74.66; H, 7.80; N, 6.57; O, 7.51%.

4-(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)phthalonitrile (2).

4-nitrophthalonitrile(1g, 5.77mmol) and 2,5-bis-(1,1-dimethylbutyl)-methoxyphenol(1.68g, 5.77mmol) were dissolved in dry DMF(30ml) and anhydrous K_2CO_3 (1.06g, 7.66mmol) was added in portions during 4h. The mixture was stirred at 80 °C for 8h under nitrogen atmosphere. After filtering the reaction mixture, the residue was extracted with CH_2Cl_2 and dried by rotary evaporation. After removal of the solvent, the crude product was purified on a silica gel column ($CHCl_3$) to afford the target compound as a light brown solid (2.13g, 88.47%). 1H NMR (500MHz, $CDCl_3$, 25 °C, TMS): δ = 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(3)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-phthalocyaninatozinc(II) (2a).

2a was synthesized following the same procedure for **1a** using **2** (1.26g, 3mmol), 1-pentanol (50ml), $ZnCl_2$ (0.41g, 3mmol), and DBU (2.25ml, 15mmol). The crude product

was purified on a silica gel column (CH₂Cl₂) to afford the target compound as a bluish green solid (0.89g, 67.89%). MALDI-TOF MS : m/z 1738.44 (100%, [M+2K]⁺); Found: C, 74.61; H, 8.04; N, 6.59; O, 7.35%. Calc. for C₁₀₆H₁₃₂N₈O₈Zn: C, 74.38; H, 7.77; N, 6.55; O, 7.48%.

***2(3)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-
phthalocyaninatocopper(II) (2b).***

2b was synthesized following the same procedure for **1a** using **2** (1.26g, 3mmol), 1-pentanol (50ml), CuCl₂ (0.40g, 3mmol), and DBU (2.25ml, 15mmol). The crude product was purified on a silica gel column (CH₂Cl₂/Hexane: 1/1) to afford the target compound as a dark bluish green solid (0.85g, 65.57%). MALDI-TOF MS : m/z 1737.54 (100%, [M+2K]⁺); Found: C, 74.50; H, 7.43; N, 6.80; O, 7.19%. Calc. for C₁₀₆H₁₃₂N₈O₈Zn: C, 74.46; H, 7.78; N, 6.55; O, 7.49%.

***2(3)-Tetrakis(2,5-Bis(1,1-dimethylbutyl)-4-methoxyphenoxy)-
phthalocyaninatocobalt(II) (2c).***

2c was synthesized following the same procedure for **1a** using **2** (1.26g, 3mmol), 1-pentanol (50ml), CoCl₂ (0.39g, 3mmol), and DBU (2.25ml, 15mmol). The crude product was purified on a silica gel column (CH₂Cl₂/Hexane: 1/1) to afford the target

compound as a dark bluish green solid (0.62g, 47.56%). MALDI-TOF MS : m/z 1732.52 (100%, [M+2K]⁺); Found: C, 74.63; H, 7.99; N, 6.41; O, 7.46%. Calc. for C₁₀₆H₁₃₂N₈O₈Zn: C, 74.66; H, 7.80; N, 6.57; O, 7.51%.

N,N'-Bis(2,6-diisopropylphenyl)-5-phenylbenzoperylene-2,3,8,9-tetracarboxdiimides 3

A deaerated mixture of EtOH (5.79ml), benzene (33.12ml), H₂O (8.13ml) was added to a solid mixture of **5** (synthesized according to the previously reported procedures,⁹ 1.0 g, 1.27 mmol), 1-phenylvinylboronicacid (0.68 g, 4.6 mmol), Pd(PPh₃)₄ (66.57 mg, 5.0 mol%), and Na₂CO₃ (1.2 g, 11.5 mmol) under nitrogen. The mixture was reacted at 80 °C for 120 h. The reaction was quenched by the addition of water. The mixture was extracted with dichloromethane several times. The combined organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure to provide a crude solid. The crude solid was further purified by column chromatography on silica gel using dichloromethane as the eluent. The band containing a trace of compounds synthesized from tribrominated diimide could be separated firstly. Then, the second band containing yellow compound **3** was collected.

Yield 66.8%; Mp > 300 °C (decomp.). ¹H NMR(500MHz, CDCl₃): δ = 1.21 (d, 24H), 2.84 (septet, 4H), 7.38 (dd, 4H), 7.52 (m, 2H), 7.61 (t, 1H), 7.67 (t, 2H), 7.77 (t, 2H), 8.81 (s, 1H), 9.22 (d, 2H), 9.49 (d, 2H), 9.56 (s, 1H), 9.63 (s, 1H); ¹³C NMR(126MHz,

CDCl_3): $\delta = 24.25, 24.32, 29.55, 29.92, 122.41, 122.60, 123.22, 123.62, 123.71, 124.30,$
 $124.42, 124.49, 124.73, 124.88, 126.08, 128.02, 128.10, 128.93, 129.03, 129.31, 129.72,$
 $129.86, 129.88, 130.00, 130.25, 130.75, 130.92, 130.96, 131.10, 133.50, 133.94, 134.29,$
 $135.21, 138.91, 143.15, 145.91, 145.96, 164.17, 164.26, 164.35$; MALDI-TOF MS: m/z
 811.09 (100%, $[\text{M} + \text{H}^+]$); Found: C, 83.12; H, 5.58; N, 3.42%. Calc. for $\text{C}_{56}\text{H}_{46}\text{N}_2\text{O}_4$: C,
 82.94 ; H, 5.72; N, 3.45%.

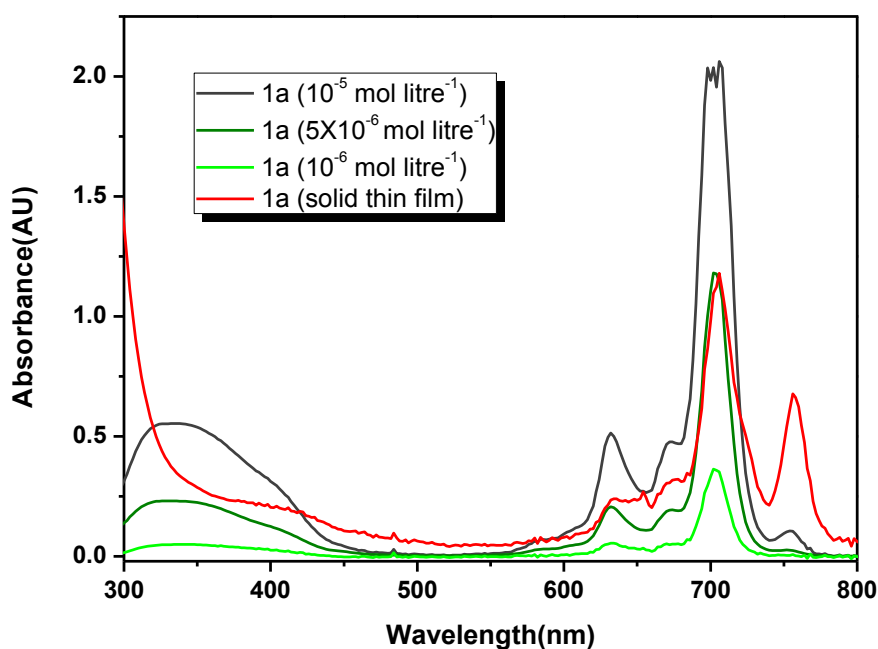


Fig. 1S The UV/Vis absorption spectra of the synthesized dye, **1a**, at different concentrations in PGMEA and in the solid thin films.

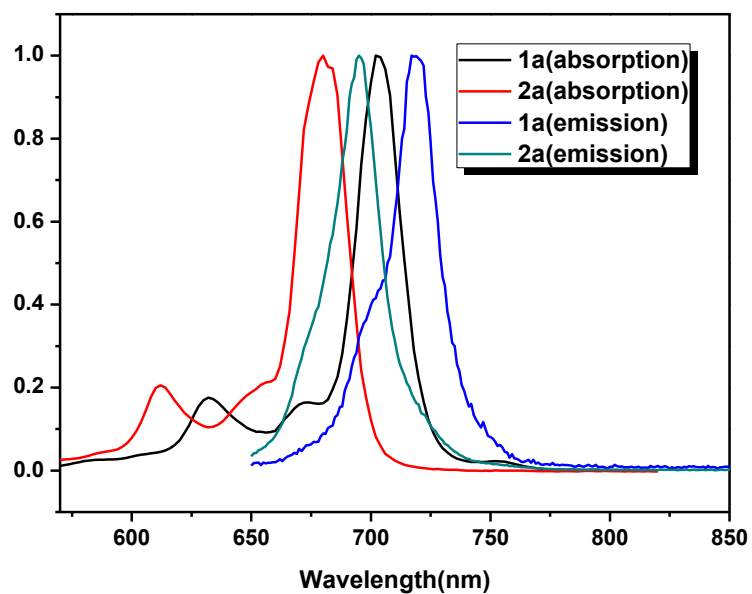


Fig. 2S Normalized absorption and fluorescence spectra of the synthesized dyes, **1a** and **2a**, in PGMEA (5×10^{-6} mol litre⁻¹).

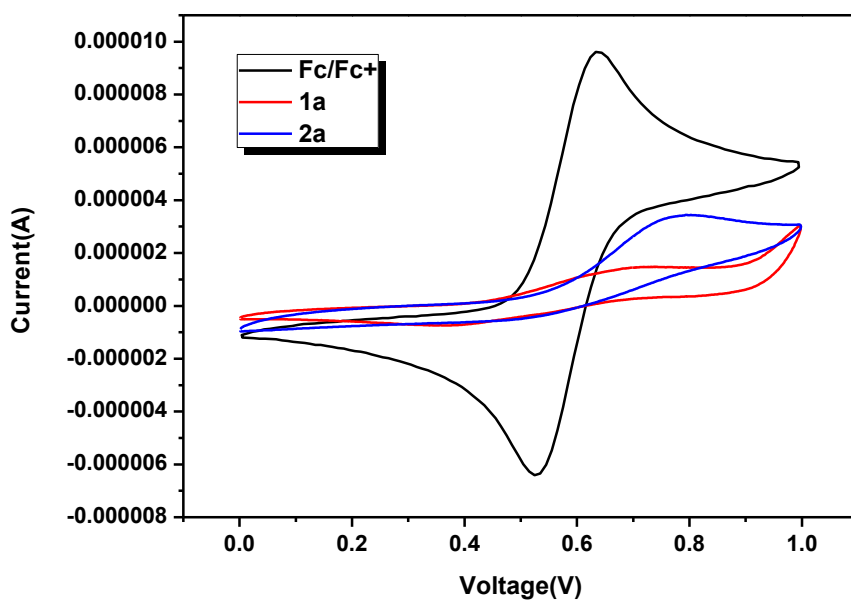


Fig. 3S Cyclic voltammetry curves of ferrocene/ferrocenium (Fc/Fc⁺), **1a** and **2a** in CH₂Cl₂.

dye	absorption ^a	emission ^a	Oxidation potential data ^b		
	λ_{\max}	λ_{\max}	E_{ox} (vs NHE)	E_{0-0} ^c	$E_{\text{ox}}-E_{0-0}$ (vs NHE)
1a	702nm	717nm	0.554V	1.744V	-1.190V
2a	680nm	695nm	0.644V	1.802V	-1.158V

Table 1S Optical and electrochemical properties of the synthesized dyes, **1a** and **2a**

^a Measured in 5×10^{-6} mol litre⁻¹ of PGMEA solutions at room temperature.

^b Measured in CH₂Cl₂ containing 0.1 mol litre⁻¹ of tetrabutylammonium tetrafluoroborate (TBABF₄) electrolyte (working electrode: glassy carbon; counter electrode: Pt; reference electrode: Ag/Ag⁺; calibrated with Fc/Fc⁺ as an internal reference and converted to NHE by addition of 630mV).

^c Estimated from intersection wavelengths between absorption and emission spectra.