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 (1).

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 K$_2$CO$_3$ (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 CH$_2$Cl$_2$ and dried by rotary evaporation. After removal of the solvent, the crude product was purified on a silica gel column (CH$_2$Cl$_2$/hexane: 5/1) to afford the target compound as a light brown solid (1.98g, 82.2%). $^1$H NMR (500MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 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-CH$_3$), 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) (1a).

The solution of 1 (1.26g, 3mmol) in 1-pentanol (50ml) was refluxed under a nitrogen atmosphere and ZnCl$_2$ (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 (CH$_2$Cl$_2$/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_{8}O_{8}Zn: C, 74.38; H, 7.77; N, 6.55; O, 7.48%.

I(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_{2}Cl_{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_{8}O_{8}Zn: C, 74.46; H, 7.78; N, 6.55; O, 7.49%.

I(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_{2}Cl_{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_{8}O_{8}Zn: 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_{2}CO_{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_{2}Cl_{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%). ^{1}H 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 (CH$_2$Cl$_2$) 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 C$_{106}$H$_{132}$N$_8$O$_8$Zn: 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), CuCl$_2$ (0.40g, 3mmol), and DBU (2.25ml, 15mmol). The crude product was purified on a silica gel column (CH$_2$Cl$_2$/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 C$_{106}$H$_{132}$N$_8$O$_8$Zn: 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), CoCl$_2$ (0.39g, 3mmol), and DBU (2.25ml, 15mmol). The crude product was purified on a silica gel column (CH$_2$Cl$_2$/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 C_{106}H_{132}N_8O_8Zn: C, 74.66; H, 7.80; N, 6.57; O, 7.51%.

\textit{N,N'-Bis(2,6-diisoproplyphenyl)-5-phenylbenzoperylene-2,3,8,9-tetracarboxdiimides 3}

A deaerated mixture of EtOH (5.79ml), benzene (33.12ml), H\textsubscript{2}O (8.13ml) was added to a solid mixture of 5 (synthesized according to the previously reported procedures,\textsuperscript{9} 1.0 g, 1.27 mmol), 1-phenylvinylboronic acid (0.68 g, 4.6 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (66.57 mg, 5.0 mol%), and Na\textsubscript{2}CO\textsubscript{3} (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 MgSO\textsubscript{4} 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.). \textsuperscript{1}H NMR(500MHz, CDCl\textsubscript{3}): δ = 1.21 (d, 2H), 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); \textsuperscript{13}C NMR(126MHz,
CDCl$_3$): $\delta = 24.25, 24.32, 29.55, 29.92, 122.41, 122.60, 123.22, 123.62, 123.71, 124.30, 124.42, 124.49, 124.73, 124.88, 126.08, 128.02, 128.10, 128.93, 129.03, 129.31, 129.72, 129.86, 129.88, 130.00, 130.25, 130.75, 130.92, 130.96, 131.10, 133.50, 133.94, 134.29, 135.21, 138.91, 143.15, 145.91, 145.96, 164.17, 164.26, 164.35; MALDI-TOF MS: m/z 811.09 (100%, [M + H$^+$]); Found: C, 83.12; H, 5.58; N, 3.42%. Calc. for C$_{56}$H$_{46}$N$_2$O$_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 (5×10⁶ mol litre⁻¹).
**Fig. 3S**  Cyclic voltammetry curves of ferrocene/ferrocenium (Fc/Fc\(^+\)). 1a and 2a in CH\(_2\)Cl\(_2\).

<table>
<thead>
<tr>
<th>dye</th>
<th>absorption(^a)</th>
<th>emission(^a)</th>
<th>Oxidation potential data(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{\text{max}})</td>
<td>(\lambda_{\text{max}})</td>
<td>(E_{\text{ox}})</td>
</tr>
<tr>
<td></td>
<td>(nm)</td>
<td>(nm)</td>
<td>(Vs NHE)</td>
</tr>
<tr>
<td>1a</td>
<td>702nm</td>
<td>717nm</td>
<td>0.554V</td>
</tr>
<tr>
<td>2a</td>
<td>680nm</td>
<td>695nm</td>
<td>0.644V</td>
</tr>
</tbody>
</table>

**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 CH\(_2\)Cl\(_2\) containing 0.1 mol litre\(^{-1}\) of tetrabutylammonium tetrafluoroborate (TBABF\(_4\)) 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.