Synthesis and very large mechano- and thermo-hypsochromic luminescence of a new-type DPP-based derivative

Zhongwei Liu, Kai Zhang, Qikun Sun, Zhenzhen Zhang, Liangliang Tang, Shanfeng Xue, Dongmei Chen, Haichang Zhang,* and Wenjun Yang*

Key Laboratory of Rubber-plastics of Ministry of Education/Shandong Province (QUST), School of Polymer Science & Engineering, Qingdao University of Science & Technology, 53-Zhengzhou Road, Qingdao, 266042, P. R. China. *E-mail: haichangzhang@hotmail.com, wwjph2004@qust.edu.cn

CONTENTS

S1. Synthesis
S2. Supporting Figures
S3. Supporting Tables

Synthesis of S1 (4-(1,3-dioxolan-2-yl)benzonitrile)

To a solution of 4-cyanobenzaldehyde (15.0 g, 114.4 mmol) in toluene (300 mL) was added ethylene glycol (11.5 mL, 206 mmol) followed by pyridinium-p-toluene-sulfonic acid (1.5 g, 8.7 mmol) and then heated at 130 °C in Dean-Stark apparatus with continuous exclusion of water. After the formation of H\textsubscript{2}O cease. Cooled the reaction solution to room temperature. The solution was washed with saturated aqueous NaHCO\textsubscript{3} (100 mL) and brine (50 mL × 3). The organic layer was dried over anhydrous MgSO\textsubscript{4}, and then concentrated via rotary evaporation. The raw product was purified by column chromatography (silica gel; petroleum/ethyl acetate, 1/4, v/v)
to get 4-(1,3-dioxolan-2-yl)benzonitrile as an off white solid. (Yield: 18.53 g, 92%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.62 (ddt, $J$ = 41.5, 7.4, 3.0 Hz, 4H), 5.89-5.77 (m, 1H), 4.15-3.98 (m, 4H).

S2. Supporting Figure

![Figure S1. FTIR spectra of CODPP solids with different emission colors.](image)

$^1$H NMR and $^{13}$C spectra of the compounds as follows
SI-3. Supporting Tables

Table S1 The solution fluorescence quantum yields (%) and the molar extinction coefficients (M$^{-1}$ cm$^{-1}$) of CODPP in different solvents.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>PhMe</th>
<th>CHCl$_3$</th>
<th>THF</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence quantum yield (%)</td>
<td>74.8</td>
<td>75.1</td>
<td>72.3</td>
<td>67.0</td>
</tr>
<tr>
<td>The molar extinction coefficients</td>
<td>54000</td>
<td>50300</td>
<td>59000</td>
<td>52700</td>
</tr>
</tbody>
</table>

Table S2 The solid fluorescence quantum yields (%) of CODPP in different states.

<table>
<thead>
<tr>
<th>States</th>
<th>Pristine</th>
<th>Ground</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>CODPP</td>
<td>15%</td>
<td>46%</td>
<td>95%</td>
</tr>
</tbody>
</table>