

## **Improving the Electroluminescence Performance of Donor–Acceptor Molecule by Fine Tuning the Torsion Angle and Distance Between Donor and Acceptor Moieties**

Xu Qiu, Shanfeng Xue,\* Yongjin Wu, Mingshuai Chen, Qikun Sun, 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: [sfxue@qust.edu.cn](mailto:sfxue@qust.edu.cn), [ywjph2004@qust.edu.cn](mailto:ywjph2004@qust.edu.cn)

### **CONTENTS**

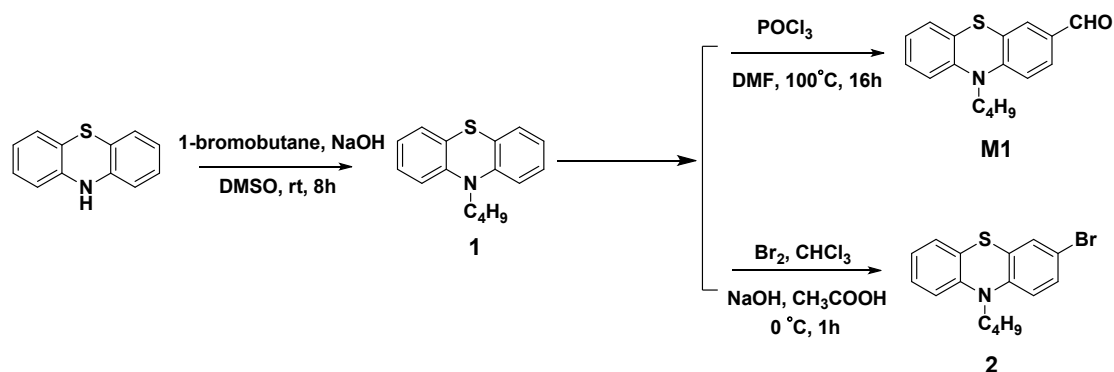
**SI-1. Synthesis**

**SI-2. The UV-vis absorption spectra of the PO and PPO in THF solution.**

**SI-3. SI-3. Lifetime measurement of the PO and PPO in hexane, isopropylether, tetrahydrofuran and acetonitrice solution.**

.

**SI-1. Synthesis**



**Scheme S1** Synthetic route of the reactants **1**, **2** and **M1**.

#### Synthesis of 10-butyl-10H-phenothiazine (**1**):

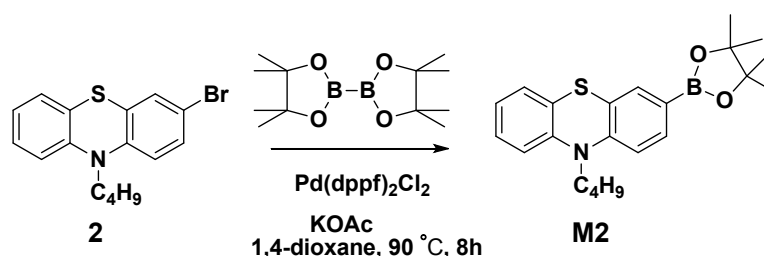
To a phenothiazine (9.96 g, 50 mmol) solution in 150 ml dry DMSO, sodium hydroxide (16 g, 0.4 mol) and 1-bromobutane (10.8 ml, 0.1 mol) were added at room temperature and reacted for 24 h. Then the reaction mixture was poured into water and extracted with dichloromethane. The organic phase was collected and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the residue was purified by silica gel column chromatography using silica gel and petroleum ether- dichloromethane (10:1 ; v/v) as the eluent to give the product as colorless viscous liquid (10.96 g, 86.0 %). <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO, ppm): δ 7.21 (t, 2H), 7.14 (d, 2H), 7.02 (d, 2H), 6.94 (t, 2H), 3.87 (t, 2H), 1.69 (m, 2H), 1.41 (m, 2H), 0.88 (t, 3H); <sup>13</sup>C NMR (500 MHz, d<sub>6</sub>-DMSO, ppm): δ 145.5, 127.6, 127.4, 125.2, 122.5, 115.6, 47.3, 29.3, 20.4, 14.0.

#### Synthesis of 10-Butyl-10H-phenothiazine-3-carbaldehyde (**M1**):

A portion of (1.09 mL, 12 mmol) of POCl<sub>3</sub> was slowly added into 0.4 mL of N,N-dimethylformamide (DMF) at 0 °C. The reaction mixture was stirred for an hour at this temperature. This reaction mixture was slowly added into a solution of (1.02 g, 4 mmol) of **1** in 20 mL of 1,2-dichloroethane at 0 °C. After complete addition of DMF and POCl<sub>3</sub> mixture, the reaction mixture was stirred at 100 °C for 16 hours. After cooling to room temperature, the reaction mixture was neutralized with aqueous K<sub>2</sub>CO<sub>3</sub> and extracted with 100 mL of dichloromethane (DCM) three times. The combined organic layer was washed with 300 mL of water and dried over anhydrous magnesium sulfate and evaporating the organic solvent using a rotary evaporator. The crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (1:10 ; v/v) as the eluent. The light yellow oily product yield was (0.49 g, 43.2 %). <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO, ppm): δ 9.79 (s, 1H), 7.73 (d, 1H), 7.60 (s, 1H), 7.25 (t, 1H), 7.17 (m, 2H), 7.10 (d, 1H), 7.02 (t, 1H), 3.96 (t, 2H), 1.69 (m, 2H), 1.42 (m, 2H), 0.90 (t, 3H).

### Synthesis of 3-Bromo-10-butyl-10H-phenothiazine (2):

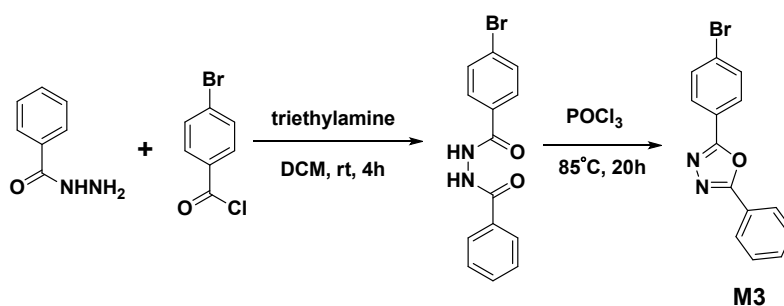
A solution of NaOH (0.46 g, 11.51 mmol) in glacial acetic acid (70 mL) was added to a solution of **1** (2.49 g, 9.75 mmol) in chloroform (15 mL) followed by dropwise addition of a solution of bromine (0.50 mL, 9.75 mmol) in glacial acetic acid (10 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h. The solvents were removed, and, after addition of water (30 mL) and dichloromethane (50 mL), the organic layer was separated and dried with anhydrous MgSO<sub>4</sub>. The solvent was removed, and the residue was purified by column chromatography to give the product as a light-yellow liquid (2.28 g, 70.0 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.17 (d, 2 H), 7.06–7.13 (m, 2 H), 6.86 (t, 1 H), 6.80 (d, 1 H), 6.60 (t, 1 H), 3.75 (t, 2 H), 1.68–1.75 (m, 2 H), 1.35–1.43 (m, 2 H), 0.90 (t, 3 H).



Scheme S2 Synthetic route of the reactant **M2**.

### Synthesis of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-10-*n*-butylphenothiazine (**M2**):

A solution of **2** (2.00 g, 5.98 mmol), bis(pinacolato)diboron (1.82 g, 7.18 mmol), PdCl<sub>2</sub>(dppf) (88 mg, 0.12 mmol) and KOAc (1.76 g, 17.95 mmol) in degassed 1, 4-dioxane (30 mL) was stirred at 90 °C for 8 hours. The reaction was quenched by deionized water, and the resulting mixture was washed with dichloromethane. The organic layers were collected, dried with anhydrous magnesium sulphate, and concentrated in vacuum. It was purified via silica gel chromatography by petroleum ether/dichloromethane (2:1 ; v/v) to give the desired compound as a light green liquid in 78 % yield (1.78 g). <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO, ppm): δ 7.48 (d, 1H), 7.32 (s, 1H), 7.15 (t, 1H), 7.10 (d, 1H), 6.95 (m, 3H), 3.83 (t, 2H), 1.62 (m, 2H), 1.34 (m, 2H), 1.23 (s, 12H), 0.82 (t, 3H).

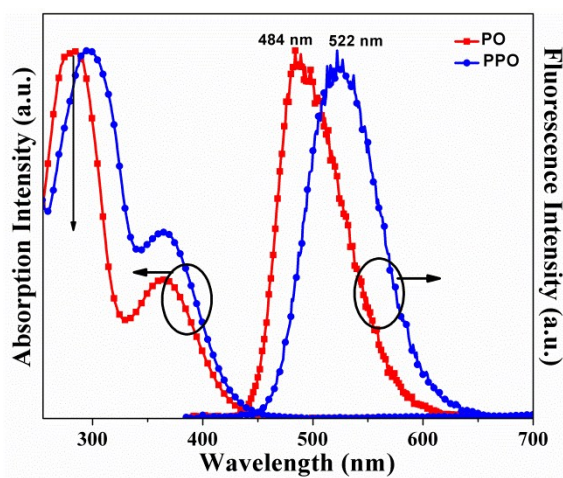


### Scheme S3 Synthetic route of the reactant M3.

#### Synthesis of 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (M3):

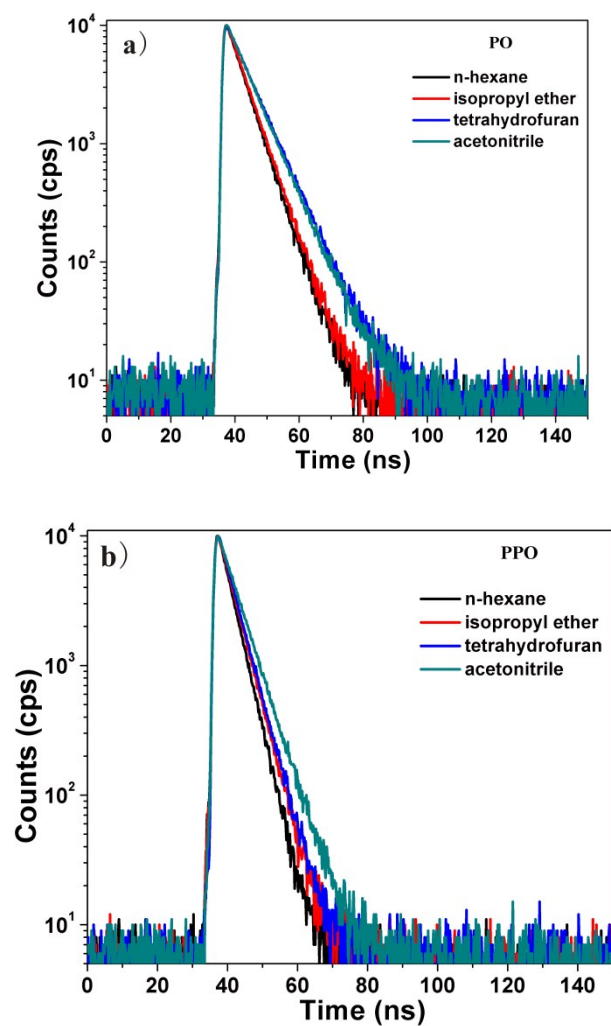
4-Bromo-benzoic chloride (3.63 g, 16.5 mmol) in dichloromethane (25 mL) was added dropwise into a solution of benzoylhydrazine (2.25 g, 16.5 mmol) and triethylamine (3 mL) in dichloromethane (25 mL). The resulting mixture was stirred for 4 h at room temperature and then washed with water. The organic phase separated was evaporated to remove the solvent. Then the solution of the residue in POCl<sub>3</sub> was heated at 85°C for 20 h. After the solvent was removed under reduced pressure, the residue was dissolved into dichloromethane and washed with water. The organic phase separated was dried over MgSO<sub>4</sub> and the solvent was evaporated. The crude product was purified by recrystallization from hexane to afford 4 (4.57 g, 92.0 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.58–7.49 (m, 3H), 7.70 (d, 2H), 8.01 (d, 2H), 8.15–8.09 (m, 2H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 122.8, 123.7, 126.4, 127.0, 128.3, 129.1, 132.0, 132.4, 163.9, 164.8.

**SI-2.** The UV-vis absorption spectra and PL spectra in THF (10<sup>-5</sup> M) solution and in thin film of PO (a) and PPO (b)



**Fig. S1** The UV-vis absorption spectra and PL spectra of PO and PPO in THF solution.

**SI-3. Lifetime measurement of the PO and PPO in hexane, isopropylether, tetrahydrofuran and acetonitrile solution.**



**Fig. S2.** Lifetime measurement of the PO and PPO in hexane, isopropylether, tetrahydrofuran and acetonitrice solution. (The concentrations of the solutions are controlled to less than  $1 \times 10^{-5}$  M to guarantee that the solutions are diluted solutions.)