

## Supporting Information

# All organic double cable polymers of polythiophene donor with rhodanine and perylene diimide acceptors and evaluation of photocurrent generation in photodetector devices

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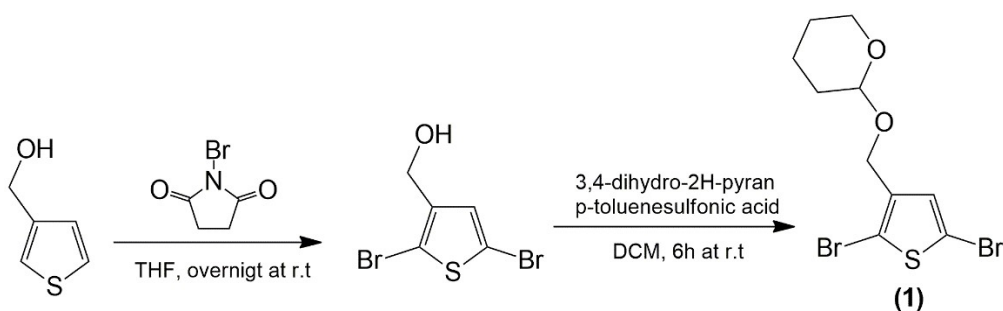
### Synthesis of 2, 5-dibromo-3-thiophenemethanol

This compound was synthesized according to a literature protocol<sup>1</sup>. Two neck (100mL) dried round bottom flask was evacuated and back filled with N<sub>2</sub>(g) through three N<sub>2</sub>(g)/vacuum cycles. 4.5 g (0.04 moles) of 3-thiophene methanol was added to this flask followed by the addition of 40 mL of anhydrous THF. The solution was stirred for 30 minutes under along with N<sub>2</sub>(g) purging. 14.23g (0.08 moles) of NBS was gradually added to the resulting solution over a period of 15 minutes. The solution was allowed to stir at room temperature overnight. As part of reaction work up, unreacted NBS was removed by filtration and THF was removed from the obtained filtrate on a rotary evaporator. The obtained residue was dissolved in diethyl ether and sequentially washed with aq. 1M NaOH solution and DI water. The organic layer was dried over anhydrous MgSO<sub>4</sub>. The MgSO<sub>4</sub> was removed by filtration and filtrate was subjected to rotary evaporation. The crude product obtained was purified by column chromatography using silica gel and hexane:ethyl acetate (80:20) eluent. Fractions containing third UV active spot on TLC (R<sub>f</sub> = 0.45) were collected and combined. The solvent was removed on rotary evaporator to obtain the product as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 1H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.00 (s, 1H), 4.55 (s, 2H), 1.23 (t, J = 1.8 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 140.40, 129.50, 110.43, 108.25, 76.23, 76.02, 75.81, 58.27.

### Synthesis of 2,5-dibromo-3-tetrahydropyranoxymethylthiophene (1)

This compound was synthesized according to a literature protocol.<sup>1</sup> Two neck (100 mL) dried round bottom flask was evacuated and back filled with N<sub>2</sub>(g) through three N<sub>2</sub>(g)/vacuum cycles. 3g (11.03 mmol) of 2,5-dibromo-3-thiophenemethanol was added to this flask followed by the addition of 20 mL of anhydrous DCM. 0.0189g (0.11mmol) of *p*-toluene sulfonic acid was added to the solution and the reaction mixture was stirred along with a dropwise addition of 1.25 ml (13.78 mmol) 3,4-dihydro-2H-pyran protecting agent. The reaction was stirred at room temperature for 6 hours after complete addition of the protecting agent. The progress of

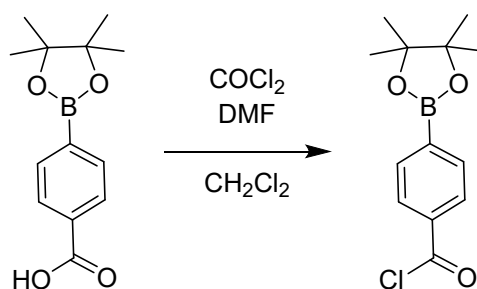
the reaction was monitored with TLC (hexane-ethyl acetate 80:20). The solvent was removed on rotary evaporator and the obtained crude product was purified by column chromatography using silica gel and hexane:ethyl acetate (80:20) eluent. Fractions containing first UV active spot on TLC ( $R_f = 0.786$ ) were collected and combined. The solvent was removed on rotary evaporator to obtain the product as a yellow liquid.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm, Figure S3): 6.97 (s, 1H), 4.66 (t,  $J = 3.5$  Hz, 1H), 4.58 (d,  $J = 12.4$  Hz, 1H), 4.39 (d,  $J = 12.3$  Hz, 1H), 3.87 (ddd,  $J = 11.6, 8.7, 3.0$  Hz, 1H), 3.57 – 3.49 (m, 1H), 1.87 – 1.76 (m, 1H), 1.71 (dddd,  $J = 13.0, 9.9, 4.2, 3.1$  Hz, 1H), 1.66 – 1.48 (m, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ,  $\delta$  ppm): 139.31, 131.01, 111.12, 110.00, 98.00, 62.94, 62.18, 30.42, 25.39, 25.28, 19.25.



**Scheme S1:** Synthesis of 2,5-Dibromo- 3-tetrahydropyranoxymethylthiophene (1) from 3-thiophene methanol.

### Synthesis of TDBC

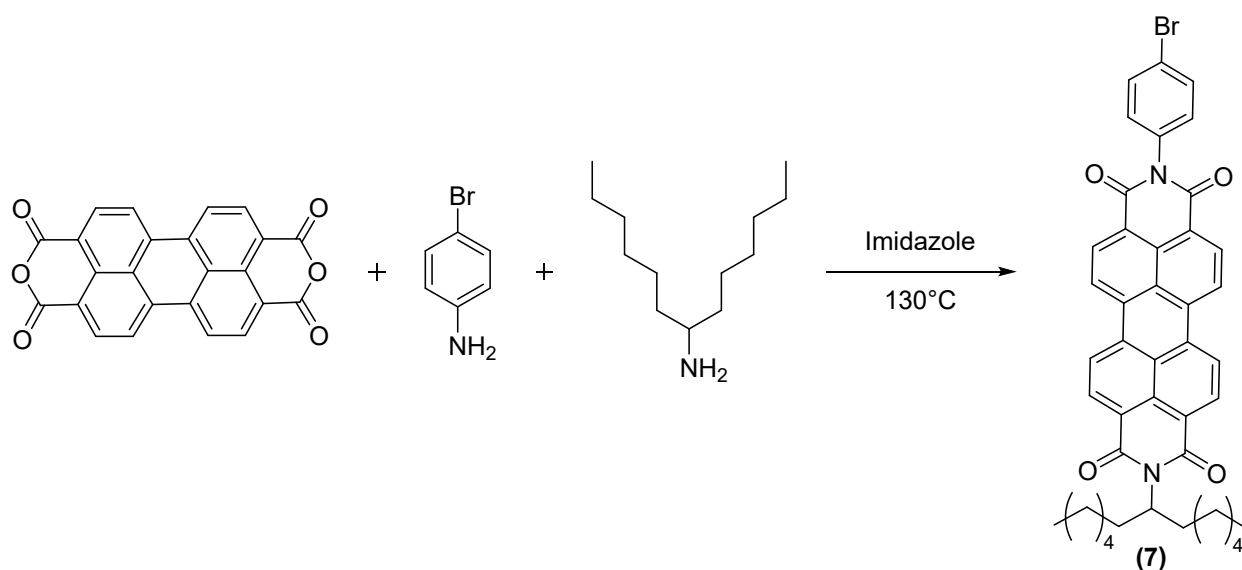
This compound was synthesized according to a literature protocol.<sup>2</sup> 624 mg TDBA was dissolved in 12 mL anhydrous DCM in a 50 mL dry Schlenk flask under inert atmosphere. 38.78  $\mu\text{L}$  (0.503 mmol) DMF) was added to the stirred reaction mixture, followed by placing the reaction flask in an ice-bath for 15 minutes. 0.237 mL (2.76 mmol) oxalyl chloride was added dropwise over the time of 15 minutes. The reaction was then stirred at room temperature overnight and was used as such for the synthesis of copolymer 4.



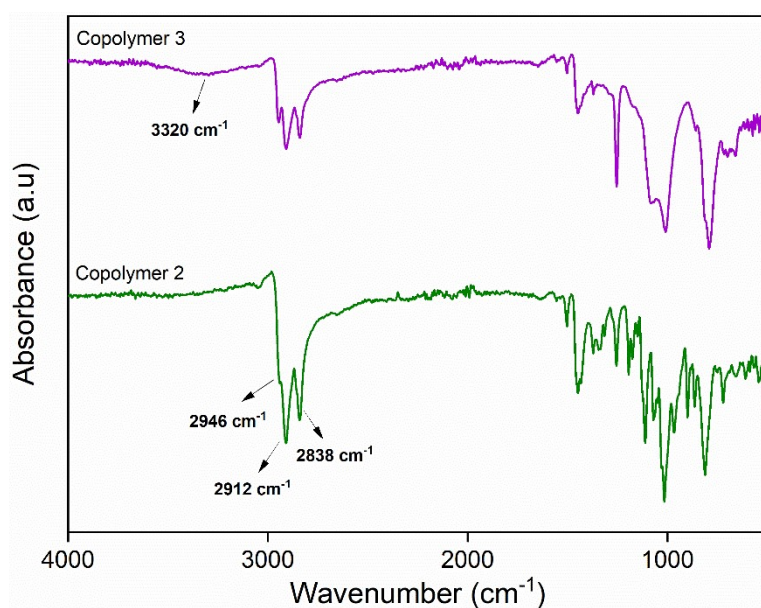
**Scheme S2:** Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl chloride (TDBC) from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (TDBA).

**Synthesis of *N*-(4-bromophenyl)-*N'*-hexylheptyl-3,4,9,10-perylene diimide (9):**

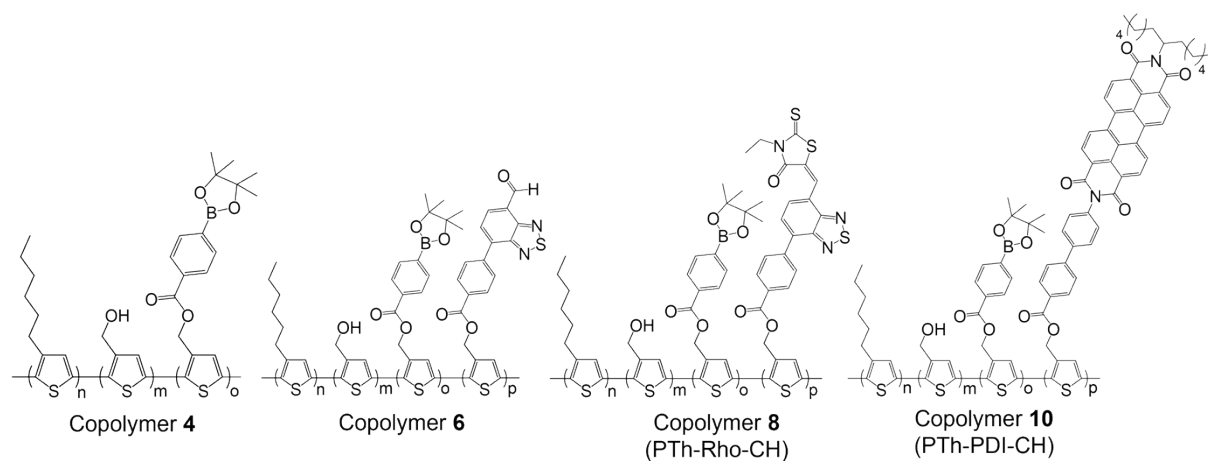
This compound was synthesized according to a literature protocol.<sup>3</sup> 0.71g (1.78 mmol) perylene-3,4,9,10-tetracarboxylic dianhydride, 0.36g (2.08mmol) 4-bromoaniline, 0.43g (2.17mmol) 1-hexylheptylamine and 9.5g imidazole were added into a 100 mL dry round bottom flask. The reaction flask was then purged with nitrogen for 5 minutes and heated at 130 °C for 2 hours under continuous stirring. The flask was then cooled, and the product was extracted in 75 mL chloroform and washed with aq. 2 M HCl solution. The organic layer was dried over anhydrous MgSO<sub>4</sub>. The solid residue was filtered, and filtrate was evaporated on rotary evaporator. The product was purified by column chromatography using silica gel and hexane and DCM (1:2) as eluent. Fractions containing second UV active spot ( $R_f = 0.5$ ) on TLC were collected and combined. The solvent was removed on rotary evaporator to obtain the product as red powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm, Figure S5): 0.79 (6H), 1.1-1.32 (16H), 1.8 (2H), 2.1 (2H), 5.1 (1H), 7.18 (2H), 7.62 (2H), 8.5-8.7 (8H).



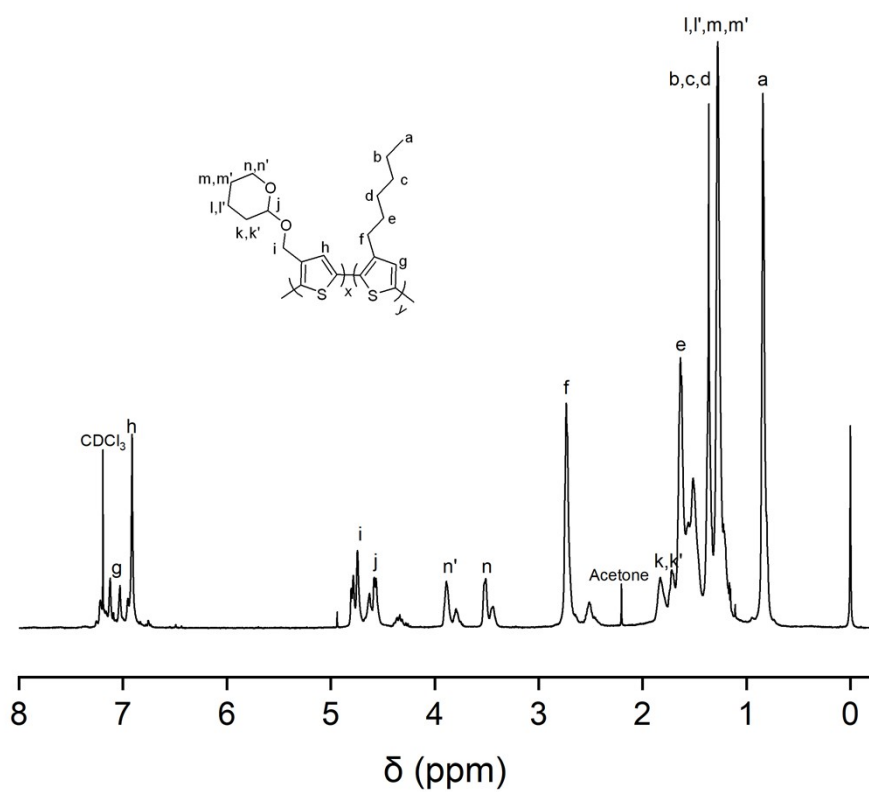
**Scheme S3:** Synthesis of *N*-(4-bromophenyl)-*N'*-hexylheptyl-3,4,9,10-perylene diimide (7) from Perylene-3,4,9,10-tetracarboxylic dianhydride.



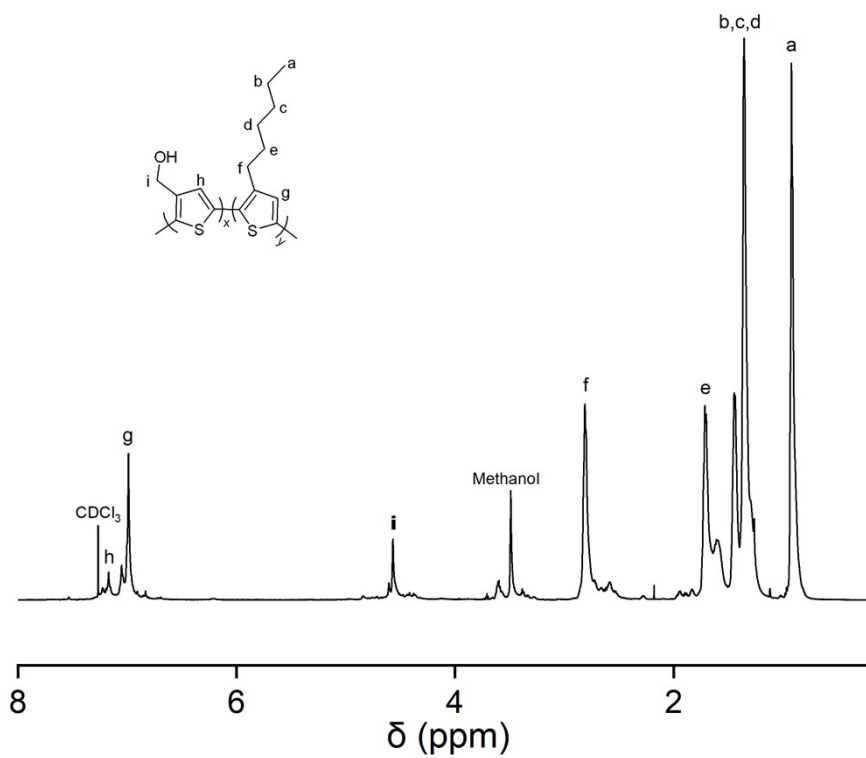
**Figure S1:** FTIR spectra of random copolymer 2 (with pendant tetrahydropyran (THP) ether group) and random copolymer 3 (with pendant OH group).



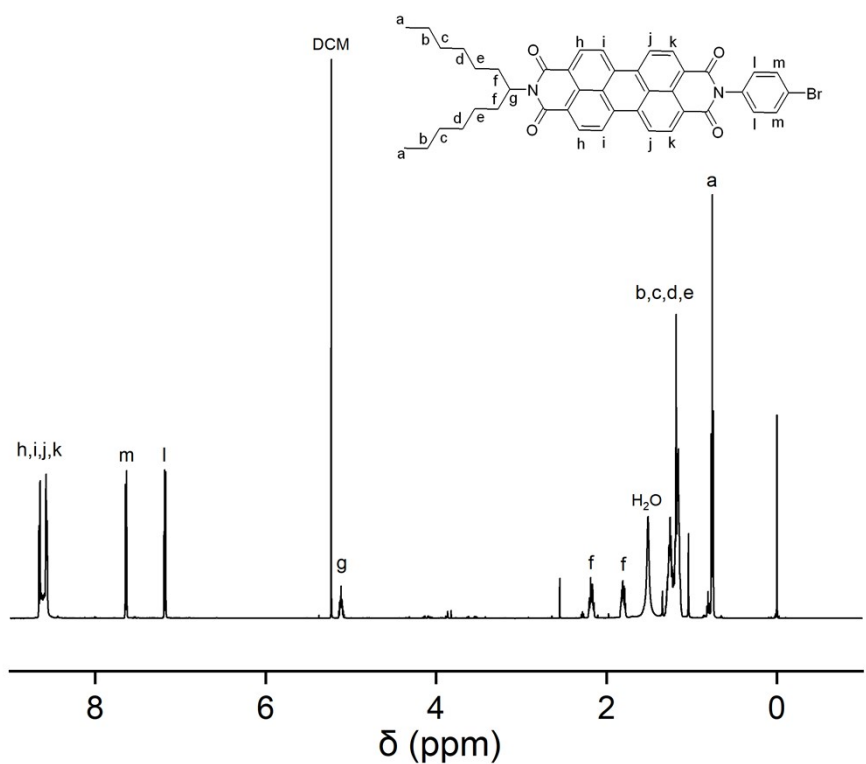
**Figure S2:** Structures and names of the copolymers used in paper.



**Figure S3:** <sup>1</sup>H-NMR of random copolymer 2 with pendant tetrahydropyran (THP) ether group.

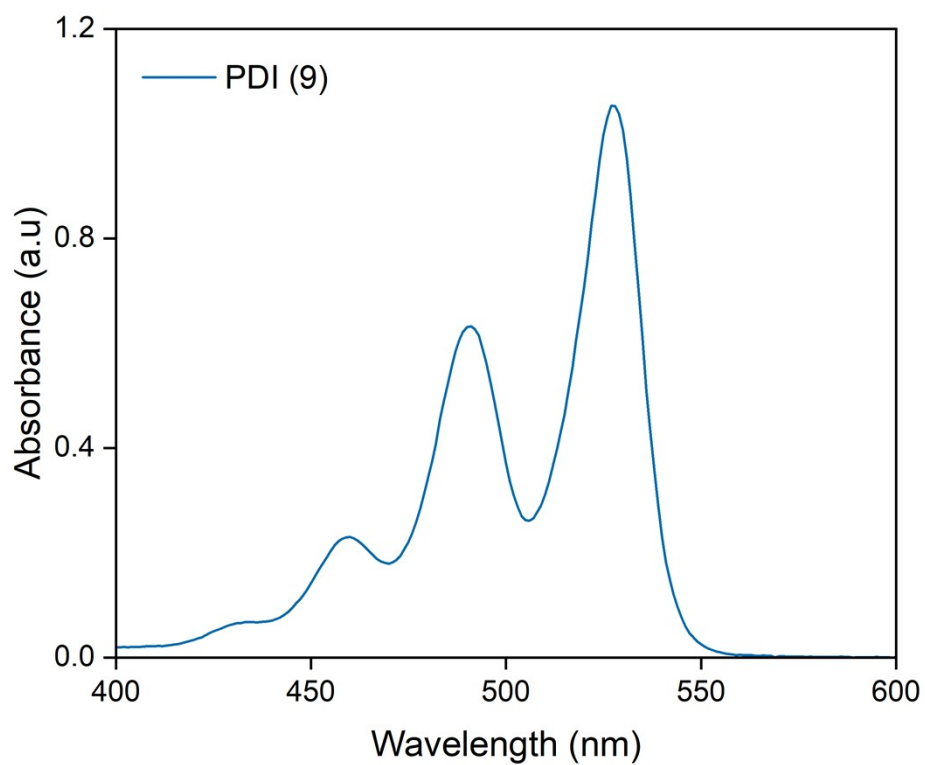


**Figure S4:**  $^1\text{H-NMR}$  of random copolymer 3 (with OH pendant group).

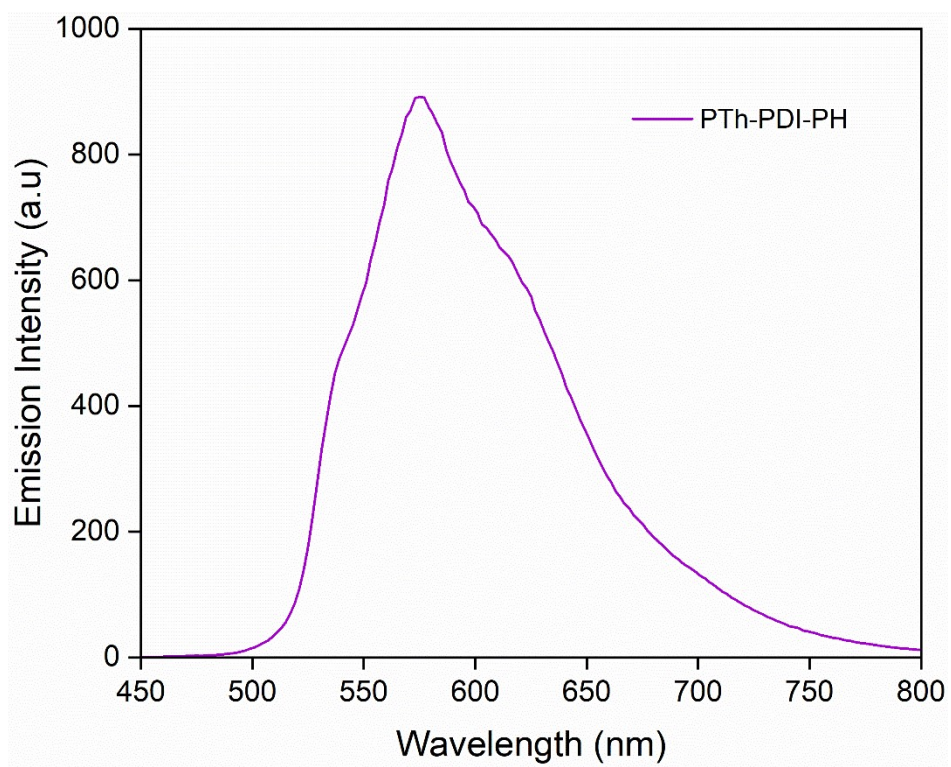


**Figure S5:**  $^1\text{H-NMR}$  of N-(4-bromophenyl)-N'-hexylheptyl-3,4,9,10-perylene diimide (9)





**Figure S6.** UV/Vis spectrum of PDI-9.



**Figure S7.** Fluorescence spectrum of PTh-PDI-PH.

## References

1. B. A. Hammer, F. A. Bokel, R. C. Hayward and T. Emrick, *Chemistry of Materials*, 2011, **23**, 4250-4256.
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