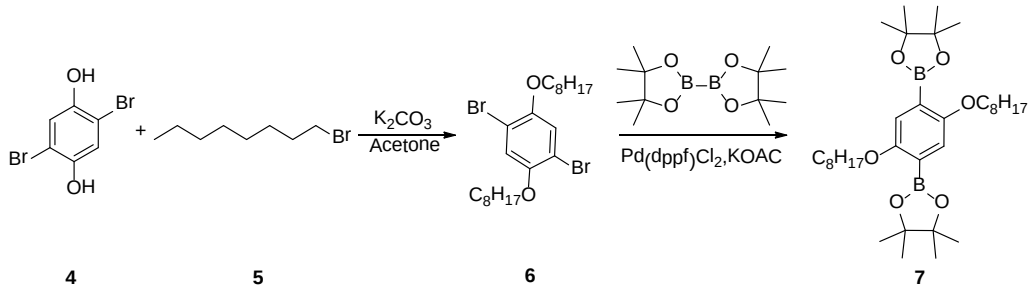
# *Electronic Supplementary Information (ESI)*

## General

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately before to use. The distilled water is bubbled nitrogen prior to use. All other chemicals and solvents are purchased from commercial sources and used as received without further purification. NMR spectra were obtained on a Bruker AV 500 M spectrometer using tetramethylsilane (TMS; $\delta$ = 0) as internal standard. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. The weight-average molecular weights ($M_w$) were measured by a Waters Advanced Polymer Chromatography (APC) system equipped with photo-diode array (PDA) detector. Polystyrene were utilized as standards and THF was used as the eluent in a flow rate of 1.0 mL $min^{-1}$. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449 F3 at a heating rate of 10 $^oC$ $min^{-1}$ in a nitrogen flow. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Particle size of the polymers in THF/water mixtures at high water fractions are measured by malvern ZSE dynamic laser scan (DLS).




**Scheme S1.** Synthetic route of monomer **7**.

## Monomers Synthesis and Characterization

### Synthesis

**1,4-Dibromo-2,5-dioctylbenzene (6).** A mixture of 1.84 g (5 mmol) compound **4**, 2.6 mL

1-bromooctane and 150 mL acetone were added to a 250 mL reaction flask, refluxing for 12 hours. After then the reaction mixture was extracted with chloroform. The organic phases were collected, dried over $Na_2SO_4$, and concentrated in a vacuum. The product was purified by silica gel chromatography to give the desired compound. White solid in 71% yield (1.62 g). $^1$H NMR (500 MHz, $CDCl_3$), $\delta$ (TMS, ppm): 7.01 (s, 2H), 3.88–3.86 (t, $J$ = 6.50 Hz 4H), 1.75–1.69 (m, 4H), 1.43–1.37 (m, 4H), 1.30–1.13 (m, 16H), 0.83–0.80 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$ (ppm):149.1, 117.4, 110.2, 69.3, 30.8, 28.25, 28.19, 24.9, 21.6, 13.1. HRMS ($C_{22}H_{36}Br_2O_2$): *m/z* [M + $Na^+$] 515.0949 (calcd 513.0974).

**2,2'-(2,5-Dioctyl-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (7)**. A mixture of compound **6** (1.47 g, 3.00 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (3.81 g, 15.00 mmol), Pd(dppf)$Cl_2$ (0.07 g, 0.09 mmol) and KOAC (1.29 g, 12.00 mmol) were stirred under $N_2$ atmosphere, after vacuuming and then filling nitrogen for three times, adding 100 mL dioxane, refluxing 8 hours, then the reaction mixture was extracted with chloroform. The organic phases were collected, dried over $Na_2SO_4$, and concentrated in a vacuum. The product was purified by silica gel chromatography to give the desired compound. White solid in 48% yield (0.80 g). $^1$H NMR (500 MHz, $CDCl_3$), $\delta$ (TMS, ppm): 7.01 (s, 2H), 3.88–3.85 (t, $J$ = 6.30 Hz 4H), 1.70–1.65 (m, 4H), 1.44–1.39 (m, 4H), 1.28–1.27 (m, 26H), 1.19 (s, 12H), 0.82–0.80 (m, 8H). $^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$ (ppm): 156.7, 118.9, 82.4, 68.7, 30.9, 28.7, 28.5, 28.3, 24.0, 23.8, 23.5, 21.7, 13.1. HRMS ($C_{34}H_{60}B_2O_6$): *m/z* [M + $Na^+$] 609.4489 (calcd 609.4468).

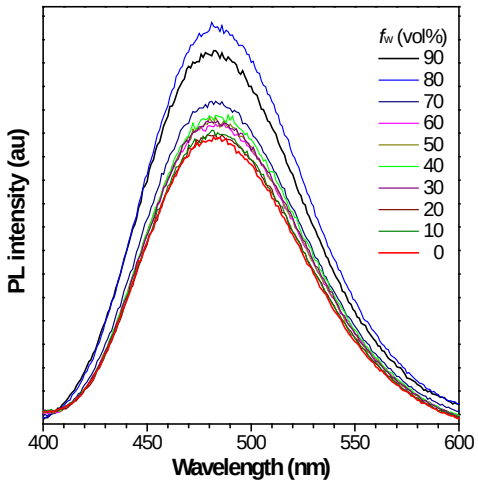



**Fig. S1** PL spectra of (*Z*)-*o*-DBr-BPTPE in THF/water mixture with different water fraction, excitation at 316 nm.

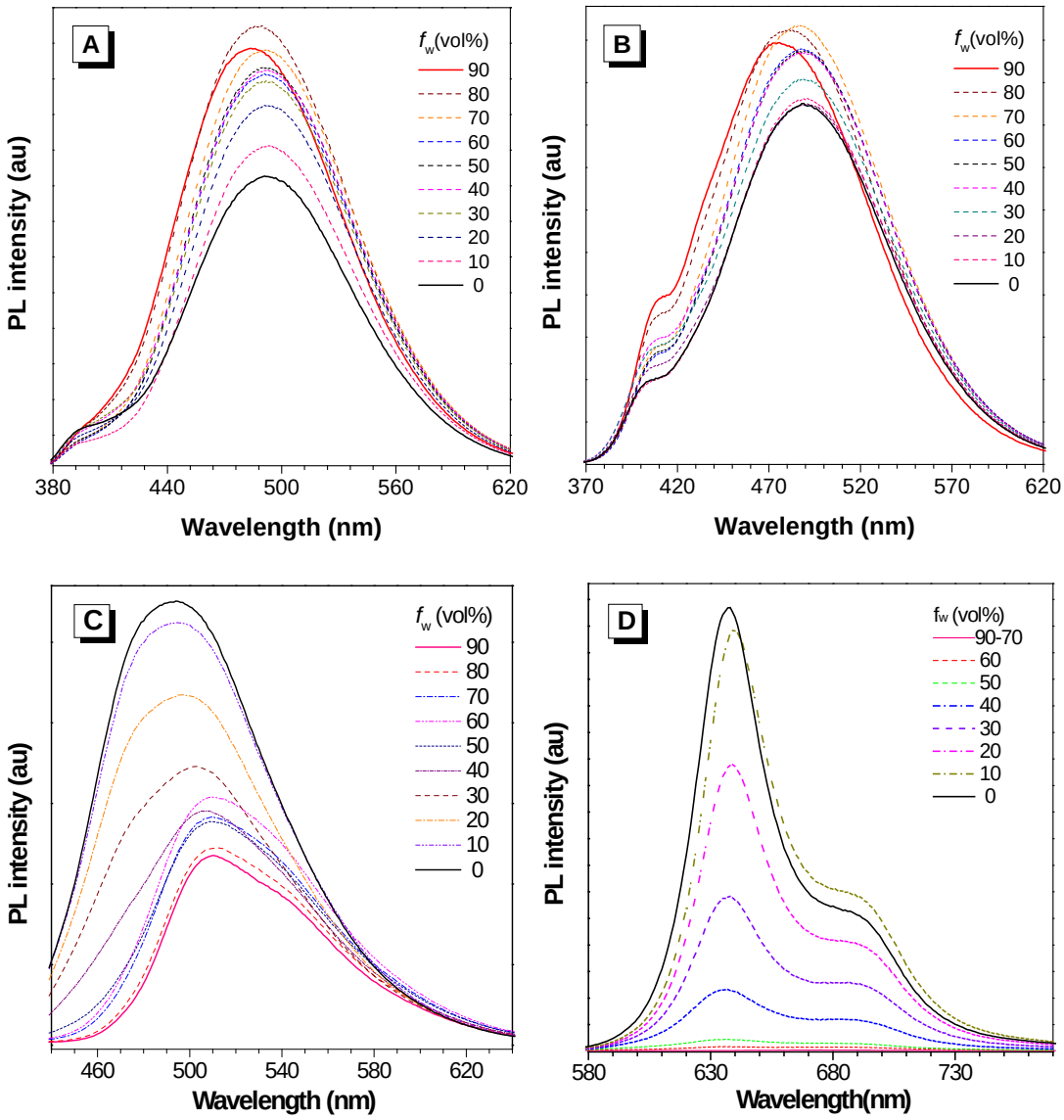



**Fig. S2** PL spectra of (A) P**2**, (B) P**3**, (C) P**4**, (D) P**5** in THF/water mixture with different water fraction (P**2**, P**3** and P**4** excited at their maximum absorption, P**5** excited at 450 nm).

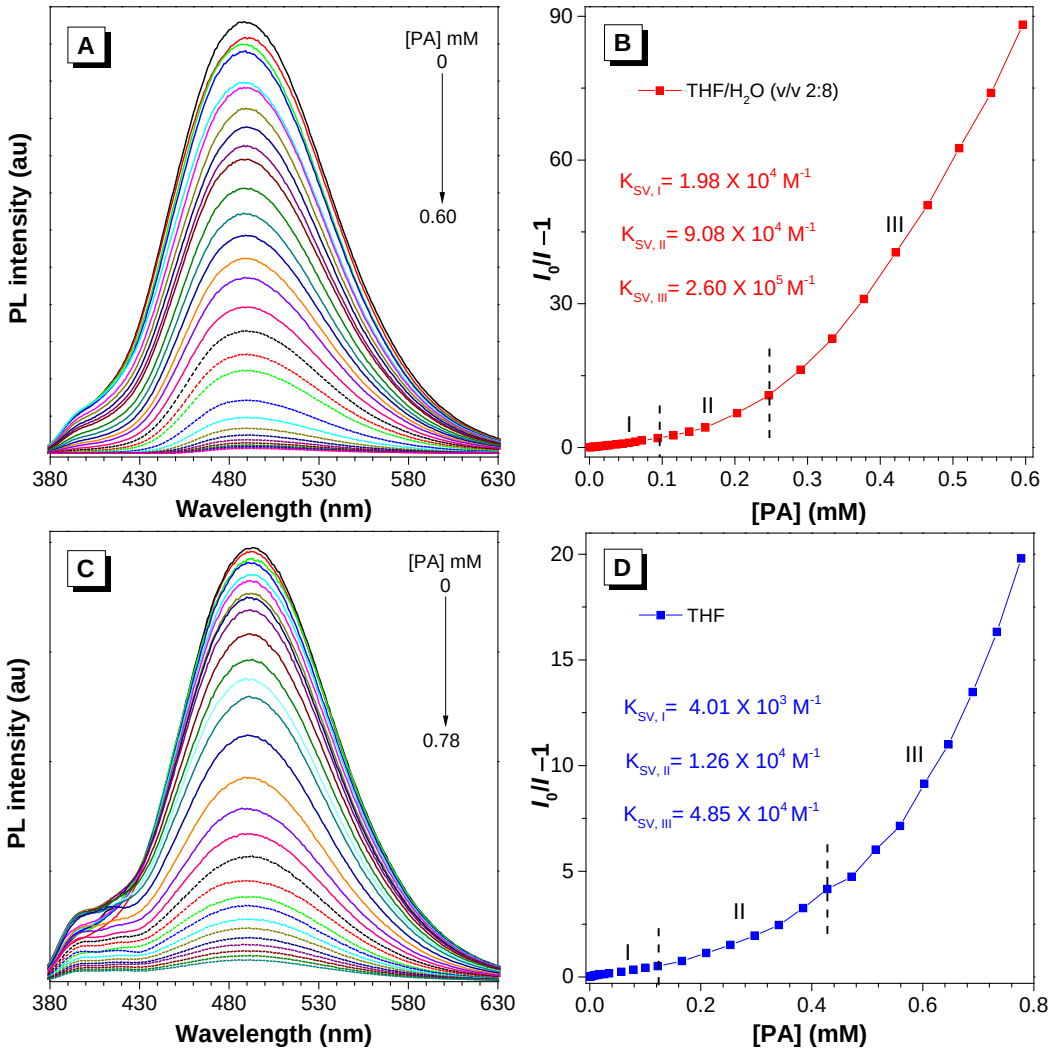



**Fig. S3** (A and C) PL spectra of P**2** in THF/water mixture ($f_w$ = 80%) and THF containing different amounts of PA, respectively. (B and D) Stern−Volmer plots of ($I_0/I$ – 1) versus [PA] concentration in THF/water mixture ($f_w$ = 80%) and THF. Polymer concentration: $10^{-5}$ M.

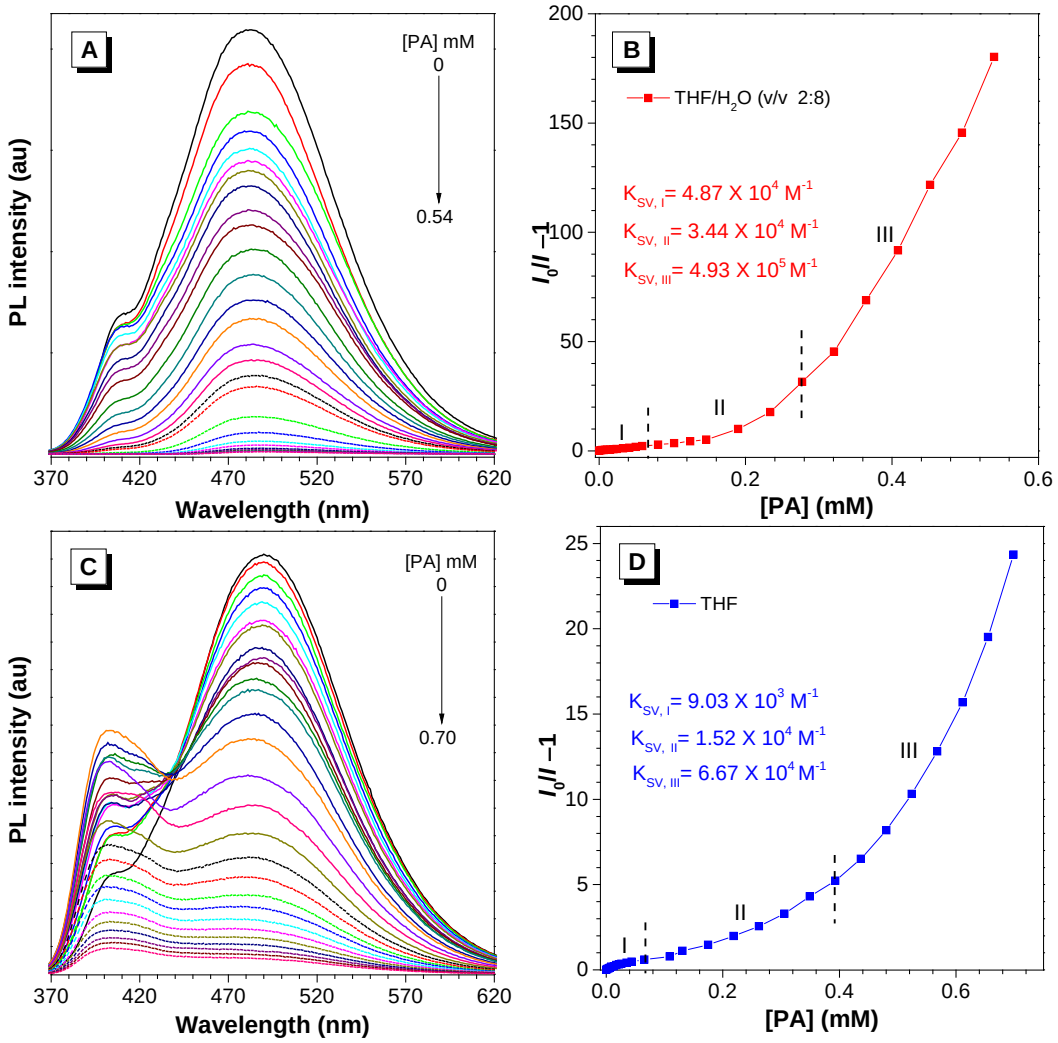



**Fig. S4** (A and C) PL spectra of P**3** in THF/water mixture ($f_w$ = 80%) and THF containing different amounts of PA, respectively. (B and D) Stern−Volmer plots of ($I_0/I$ – 1) versus [PA] concentration in THF/water mixture ($f_w$ = 80%) and THF. Polymer concentration: $10^{-5}$ M.

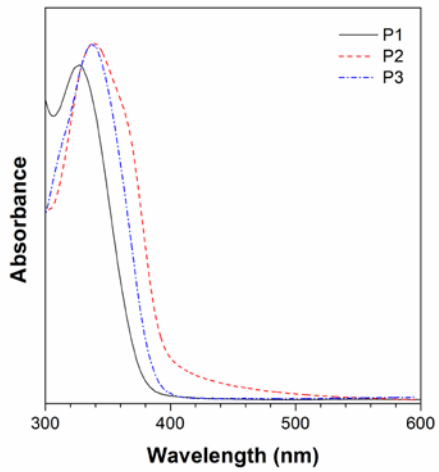



**Fig. S5** Absorbance spectra of P**1**, P**2** and P**3** in THF/$H_2O$ mixture with 90% water fraction.

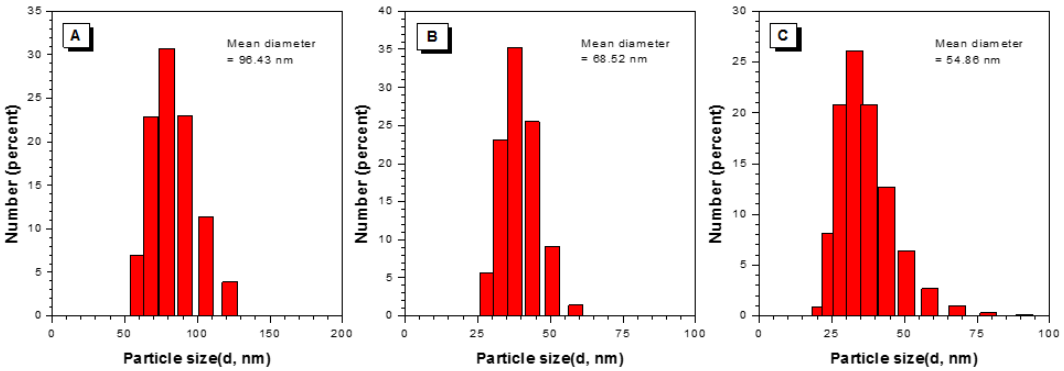



**Fig. S6** Particle sizes of (A) P**1**, (B) P**2** and (C) P**3** in THF/Water mixture with 90% water fraction. Concentration: 10 μM.

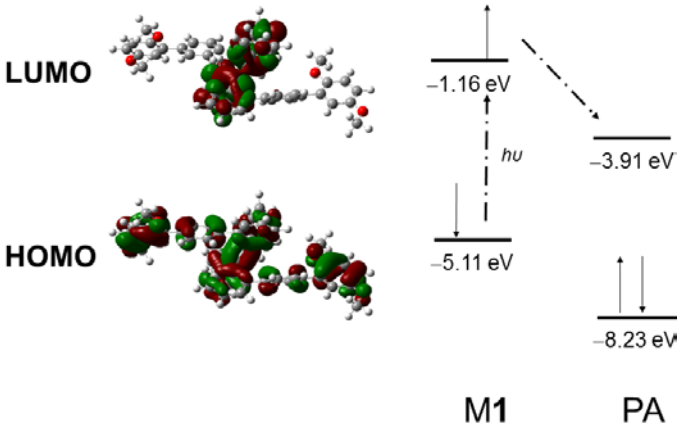



**Fig. S7** Optimized conformation and calculated molecular orbital amplitude plots of HOMO and LUMO for the conjugated fragment M**1** for P**1** (with the shorter alkyl chains) and the calculated energy level diagrams of P**1** and PA.