

Electronic Supporting Information

Structure-dependent emission of polytriazoles

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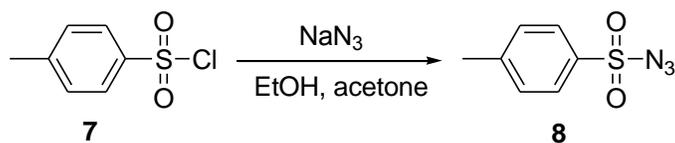
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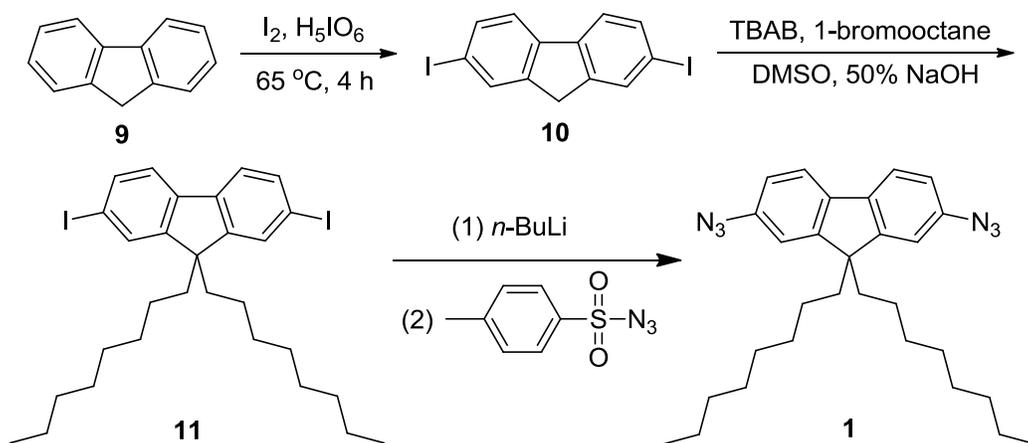
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Monomer Preparation



Scheme S1 Synthetic route to 4-methylbenzenesulfonyl azide **8**.

4-Methylbenzenesulfonyl azide (**8**) Into a 250 mL two-necked round-bottom flask was placed 0.72 g (11 mmol) of sodium azide in ethanol (30 mL). Then 1.91 g (10 mmol) of 4-toluene sulfonyl chloride (**7**) dissolved in 50 mL of acetone was added. The reaction mixture was stirred at room temperature overnight. After removal the solvent with rotatory evaporator, the crude product was dissolved in DCM and washed with water. Light yellow liquid was obtained in 92.1% yield. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.83 (d, 2H), 7.40 (d, 2H), 2.47 (s, 3H).



Scheme S2 Synthetic routes to 2,7-diazido-9,9-dioctyl-9H-fluorene **1**.

2,7-Diiodo-9H-fluorene (**10**)

Into a 250 mL two-necked round-bottom flask was placed 5.07 g (30 mmol) of fluorene (**9**). Then the mixture (100 mL) of acetate acid, water and concentrated sulfate acid (100/20/3, V/V/V) was added. The reaction mixture was heated to reflux (about $140\text{ }^\circ\text{C}$) and the solid was completely dissolved. Then it was cooled down to $65\text{ }^\circ\text{C}$, and 6.38 g (25 mmol) of iodine and 2.91 g (12.5 mmol) of periodic acid were added. The solution was stirred at $65\text{ }^\circ\text{C}$ for 4 h and then cooled to room temperature. The reaction mixture was extracted with DCM, and the collected organic layer was washed with sodium carbonate and sodium thiosulphate solution. After recrystallization from ethyl acetate, slightly yellow powder was obtained. $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.88 (s, 2H), 7.70 (d, 2H), 7.50 (d, 2H), 3.84 (s, 2H).

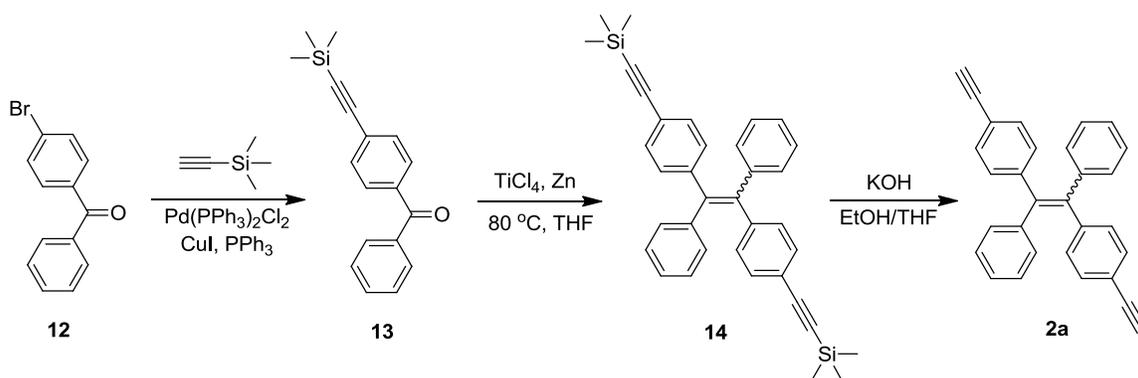
2,7-Diiodo-9,9-dioctyl-9H-fluorene (**11**)

Into a 250 mL two-necked round-bottom flask was added 2.11 g (5 mmol) of 2,7-diiodo-9H-fluorene (**10**) in DMSO (50 mL). 1.44 g (7.5 mmol) of 1-bromooctane were added sequentially. After stirring at room temperature overnight, the reaction mixture was neutralized by hydrochloric acid (1 M) till the solution become light yellow. Then the solution was extracted with diethyl ether. After solvent evaporation, the crude product was purified by silica-gel chromatography column. A slightly yellow solid was obtained

in 56.0% yield (1.80 g). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.65 (d, 4H), 7.40 (d, 2H), 1.88 (m, 4H), 1.27-0.99 (m, 20H), 0.83 (t, 6H), 0.57 (m, 4H).

2,7-Diazido-9,9-dioctyl-9H-fluorene (**1**)

Into a 250 mL two-necked round-bottom flask was added 1.61 g (2.5 mmol) 2,7-diiodo-9,9-dioctyl-9H-fluorene (**11**). The flask was evacuated under vacuum and purged with dry nitrogen three times for 1 h. Then freshly distilled THF (50 mL) was injected to dissolve the solid. The solution was cooled to $-78\text{ }^\circ\text{C}$ and 2.3 mL of *n*-butyllithium (2.5 M in hexane, 5.75 mmol) was added dropwise. After stirring at $-78\text{ }^\circ\text{C}$ for 1.5 h, 1.13 g (5.75 mmol) of 4-Methylbenzenesulfonyl azide (**8**) in 10 mL THF was injected. The reaction mixture was stirred at room temperature overnight. Afterwards, a small amount of water was added to quench the reaction and the solution was extracted with DCM. The organic phase was separated and dried over MgSO_4 . After filtration and solvent evaporation, the crude product was purified by a silica-gel chromatography column to give yellow-brown solid in 47.4 % yield (0.56 g). ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.60 (d, 2H), 7.00 (d, 2H), 6.94 (s, 2H), 1.90 (m, 4H), 1.25-0.99 (m, 20H), 0.82 (t, 6H), 0.57 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 152.47, 138.63, 137.50, 120.44, 117.78, 113.47, 55.35, 40.27, 31.66, 29.78, 29.09, 23.55, 22.49, 13.96. IR (thin film), ν (cm^{-1}): 2925, 2854, 2104, 1608, 1462, 1292, 812, 671. Anal. Calcd for $\text{C}_{29}\text{H}_{40}\text{N}_6$: C, 73.69; H, 8.53; N, 17.78. Found: C, 73.67; H, 8.66; N, 17.73.



Scheme S3 Synthetic routes to 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene **2a**.

4-(2-Trimethylsilylethynyl)benzophenone (**13**)

Into a 250 mL two-necked round-bottom flask equipped with a condenser was placed 5.01 g of (19.2 mmol) of 4-bromobenzophenone (**12**). 670 mg (0.96 mmol) of Pd(PPh₃)₂Cl₂, 370 mg (1.92 mmol) of CuI and 500 mg (1.92 mmol) of PPh₃ were added under nitrogen. 50 mL of THF and 40 mL of triethyl amine were then injected. After the catalysts were completely dissolved, 3.03 mL (23.1 mmol) of trimethylsilyl acetylene was injected and the reaction mixture was stirred at 50 °C for 24 h. An appropriate amount of hydrochloric acid (1 M) was added and the solution was extracted with DCM. The organic layers were collected and dried over anhydrous MgSO₄. After filtration and solvent evaporation, the crude product was purified by a silica gel column. A white solid was obtained in 99.2% yield. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.77 (d, 2H), 7.75 (d, 2H), 7.57 (m, 3H), 7.48 (m, 2H), 0.27 (s, 9H).

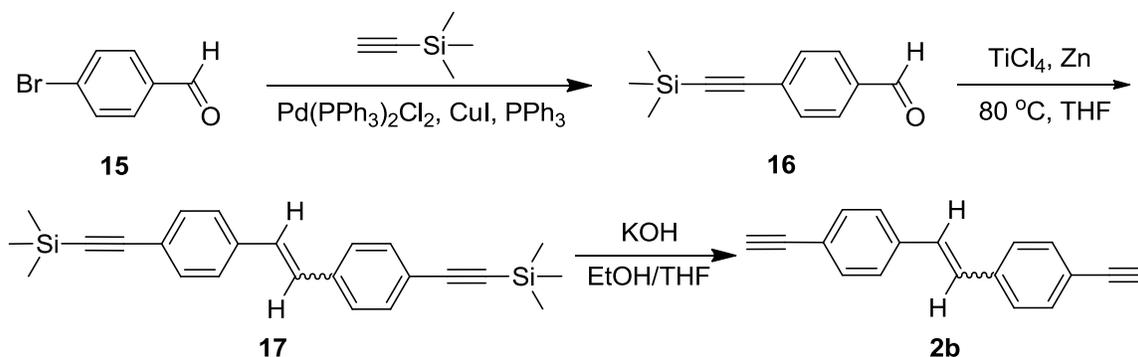
1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene (**14**)

Into a 250 mL two-necked round-bottom flask equipped with a reflux condenser were added 1.41 g (21.6 mmol) of zinc dust and 3.0 g (10.8 mmol) 4-(2-trimethylsilylethynyl)benzophenone (**13**). The flask was evacuated under vacuum and flushed with dry nitrogen three times for 1 h. Freshly distilled THF (100 mL) was then injected. The reaction mixture was cooled to -78 °C and 1.41 mL (10.08 mmol) of titanium tetrachloride was added dropwise. The mixture was allowed to warm to room temperature and then refluxed overnight. The reaction was quenched with 10% aqueous K₂CO₃ solution. After extraction with DCM, combination of the organic phase and removal of the organic solvent with rotary evaporator, the crude product was purified by a silica-gel chromatography column. A white product was obtained in 82.9% yield (2.35 g). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.23-7.17 (m, 4H), 7.13-7.06 (m, 6H), 7.01-6.90 (m, 8H), 0.22 (d, 18H).

1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (**2a**)

Into a 250 mL two-necked round-bottom flask was placed 2.23 g (4.0 mmol) of 1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene (**14**) in THF (50 mL). Then 1.44 g (24.4 mmol) of KOH dissolved in ethanol was added. The mixture was stirred at room temperature overnight and the reaction was quenched by hydrochloric acid (1 M).

The resulting mixture was extracted with DCM. The organic layers were combined and dried over anhydrous MgSO_4 . After filtration and solvent evaporation, the crude product was purified by a silica-gel column. A slightly yellow solid was obtained in 85.9% yield. IR (thin film), ν (cm^{-1}): 3288, 3028, 2104, 1712, 1599, 1496, 1442, 1360, 1223, 1105, 1024, 974, 916, 829, 766, 611, 517. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.27-7.20 (m, 4H), 7.15-7.07 (m, 6H), 7.03-6.94 (m, 8H) 3.03 (d, 2H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 144.10, 143.99, 142.88, 142.79, 140.84, 131.57, 131.43, 131.20, 131.16, 127.88, 127.72, 126.85, 126.74, 120.13, 119.98, 83.63, 77.42. Anal. Calcd for $\text{C}_{30}\text{H}_{20}$: C, 94.70; H, 5.30; Found: C, 94.28; H, 5.43.



Scheme S4 Synthetic routes to 1,2-bis(4-ethynylphenyl)ethane **2b**.

4-[(Trimethylsilyl)ethynyl]benzaldehyde (**16**)

16 was prepared by the similar procedures to those of **13**. Slightly yellow solid; yield 60.2%. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 9.97 (s, 1H), 7.84-7.80 (m, 2H), 7.63-7.58 (m, 2H), 0.26 (s, 9H).

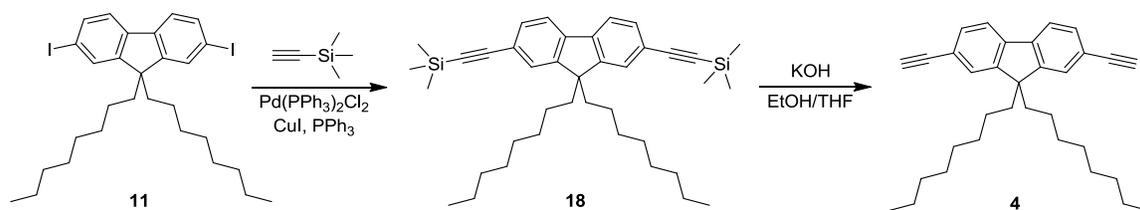
1,2-Bis[4-(trimethylsilyl)ethynyl]phenylethene (**17**)

17 was prepared by the similar procedures to those of **14**. White solid; yield 69.0%. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.51-7.40 (m, 8H), 7.07 (s, 2H), 0.26 (s, 18H).

1,2-Bis(4-ethynylphenyl)ethene (**2b**)

2b was prepared by the similar procedures to those of **2a**. Yellow solid; yield 96.6%. IR (thin film), ν (cm^{-1}): 3269, 3020, 1919, 1504, 1411, 1330, 1298, 1243, 1107, 974, 837, 735, 623, 553, 461. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.50-7.43 (d, 8H), 7.08 (s, 2H), 3.13 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 137.3, 132.4, 128.9,

126.4, 121.3, 83.6, 78.0. Anal. Calcd for C₁₈H₁₂: C, 94.70; H, 5.30. Found: C, 94.33; H, 5.32.



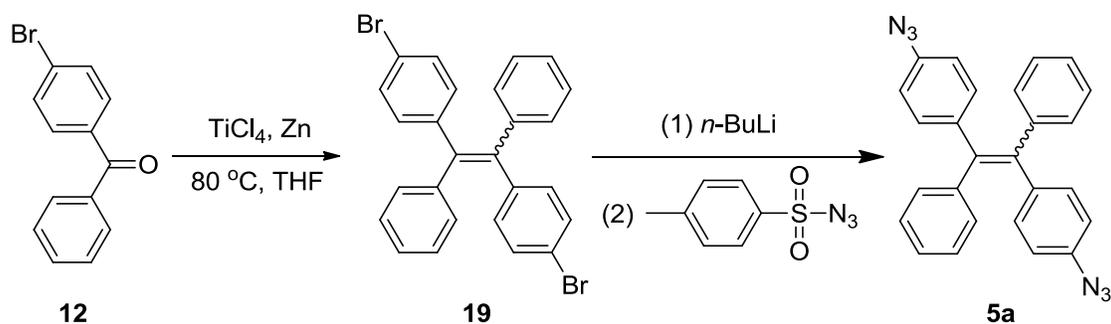
Scheme S5 Synthetic routes to 2,7-diethynyl-9,9-dioctyl-9H-fluorene **4**.

(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(trimethyl-silane) (**18**)

18 was prepared by the similar procedures to those of **13**. Yellow solid; yield 82.3%. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.59 (d, 2H), 7.45 (d, 2H), 7.41(s, 2H), 1.92 (m, 4H), 1.27-0.96 (m, 20H), 0.82 (t, 6H), 0.50 (m, 4H), 0.28(s, 18H).

2,7-Diethynyl-9,9-dioctyl-9H-fluorene (**4**)

Into a 250 mL two-necked round-bottom flask was placed 0.87 g (1.5 mmol) of (9,9-dioctyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(trimethyl-silane) (**18**) in THF (50 ml). Then 0.72g (12 mmol) of KOH dissolved in ethanol was added. After stirring at room temperature overnight, the reaction was quenched by hydrochloric acid (1 M). The resulting mixture was then extracted with DCM. The organic layers were combined and the solvent was removed with rotator evaporator. The crude product was purified by a silica-gel chromatography column. A yellow solid was obtained in 96.6% yield (0.68 g). IR (thin film), ν (cm⁻¹): 3734,3622, 3301, 2925, 2854, 2105, 1741, 1516, 1462, 1399, 1205, 893, 823, 654, 604, 517. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.63 (d, 2H), 7.51-7.44 (t, 4H), 3.15 (s, 2H), 1.94 (m, 4H), 1.25-0.99 (m, 20H), 0.83 (t, 6H), 0.57 (m, 4H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 150.95, 140.86, 131.15, 126.45, 120.75, 119.87, 84.43, 55.11, 40.11, 31.66, 29.83, 29.09, 23.55, 22.48, 13.97. Anal. Calcd for C₃₃H₄₂: C, 90.35; H, 9.65. Found: C, 89.88; H, 9.88.



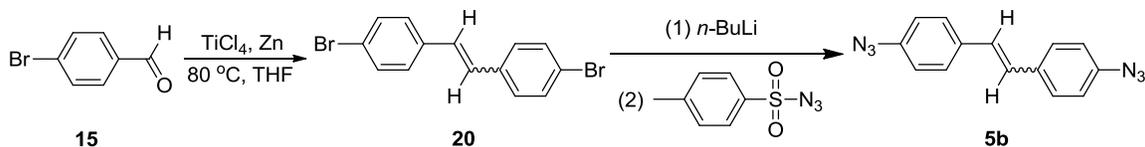
Scheme S6 Synthetic routes to 1,2-bis(4-azidophenyl)-1,2-diphenylethene **5a**.

1,2-Bis(4-bromophenyl)-1,2-diphenylethene (**19**)

19 was prepared by the similar procedures to those of **14**. White solid; yield 91.6% (4.47 g). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.28-7.19 (m, 4H), 7.16-7.08 (m, 6H), 7.02-6.95 (m, 4H), 6.92-6.84 (m, 4H).

1,2-Bis(4-azidophenyl)-1,2-diphenylethene (**5a**)

5a was prepared by the similar procedures to those of **1**. Slightly yellow solid; yield 90.0%. IR (thin film), ν (cm⁻¹): 3853, 3731, 3627, 3028, 1676, 1597, 1500, 1442, 1288, 1180, 1117, 827, 754, 696, 503. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.18-7.08(m, 6H), 7.07-6.97 (m, 8H), 6.83-6.74 (m, 4H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 143.22, 143.18, 140.34, 140.11, 138.09, 137.98, 132.66, 132.65, 131.18, 127.86, 127.75, 126.70, 126.62, 118.44, 118.28. Anal. Calcd for C₂₆H₁₈N₆: C, 75.35; H, 4.38; N, 20.28. Found: C, 75.41; H, 4.52; N, 20.37.



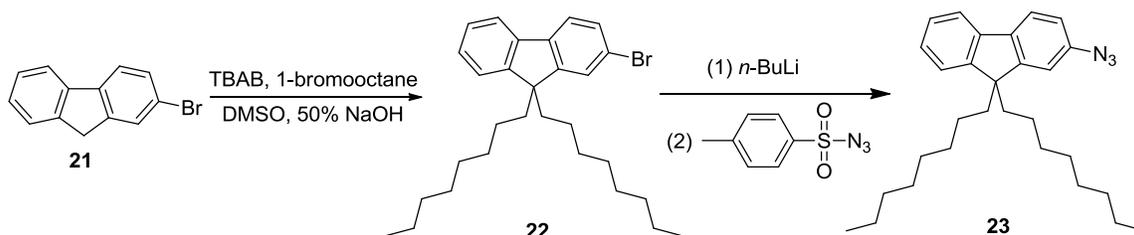
Scheme S7 Synthetic routes to 1,2-bis(4-azidophenyl)ethane **5b**.

1,2-Bis(4-bromophenyl)ethane (**20**)

20 was prepared by the similar procedures to those of **14**. White solid; yield 66.0%. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.48 (d, 4H), 7.36 (d, 4H), 7.02 (s, 2H).

1,2-Bis(4-azidophenyl)ethane (**5b**)

5b was prepared by the similar procedures to those of **1**. Slightly yellow solid; yield 13.4%. IR (thin film), ν (cm^{-1}): 3735, 3622, 2121, 1741, 1599, 1510, 1294, 1222, 1117, 966, 833, 773, 674, 536. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.48 (d, 4H), 7.10-6.95 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 139.1, 134.0, 127.7, 127.3, 119.26. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_6$: C, 64.11; H, 3.84; N, 32.04. Found: C, 63.91; H, 3.86; N, 31.85.



Scheme S8 Synthetic routes to 2-azido-9,9-dioctyl-9H-fluorene **23**.

2-Azide-9,9-dioctyl-9H-fluorene (**22**)

22 was prepared by the similar procedures to those of **11**. Yellow liquid; yield 73.8%. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.65-7.68 (m, 1H), 7.54-7.57 (m, 1H), 7.44-7.47 (m, 2H), 7.32-7.34 (m, 3H), 1.91-1.97 (m, 4H), 1.05-1.31 (m, 16H), 0.81-0.85 (m, 6H), 0.52-0.70 (m, 4H).

2-Azide-9,9-dioctyl-9H-fluorene (**23**)

23 was prepared by the similar procedures to those of **1**. Yellow solid; yield 63.4%. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.62-7.67 (m, 2H), 7.27-7.34 (m, 3H), 6.96-7.02 (m, 2H), 7.02 (s, 2H), 1.86-2.00 (m, 4H), 1.00-1.24 (m, 20H), 0.80-0.84 (t, 6H), 0.53-0.63 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 153.1, 150.6, 140.5, 138.9, 138.6, 127.2, 127.1, 123.0, 120.9, 119.6, 117.9, 113.8, 55.5, 40.6, 32.0, 30.2, 29.4, 23.9, 22.8, 14.3.

1,2-Bis(4-(1-(9,9-dioctyl-fluoren-2-yl)-1,2,3-triazol-4-yl)phenyl)-1,2-diphenylethene (**M1**)

Into a 25 mL Schlenk tube was placed **2a** (38.0 mg, 0.1 mmol). After being evacuated and refilled with dry nitrogen three times, **23** (86.4 mg, 0.2 mmol) dissolved in THF (5

mL) was injected into the tube, followed by ethanol (5 mL) and water (5 mL). When the monomers were completely dissolved, freshly prepared aqueous solutions of sodium ascorbate (1 M, 1 mL, 7.5 equivalent of **2a**) and CuSO₄ (1 M, 150 μL, 1.5 equivalent of **2a**) were added subsequently under vigorous stirring. The reaction mixture was stirred at 70 °C under nitrogen for overnight. After cooled to room temperature, the crude product was extracted with DCM and water. The solvent was then removed with rotatory evaporator. The crude product was purified with silica gel chromatography. Yellow solid in 85.3% isolation yield was obtained. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 8.18 (m, 2H), 7.74-7.83 (m, 2H), 7.67-7.72 (m, 4H), 7.34-7.38 (m, 4H), 7.17-7.21 (m, 2H), 7.13-7.16 (m, 2H), 7.08-7.12 (m, 4H), 1.97-2.04 (m, 8H), 0.99-1.22 (m, 40H), 0.76-0.82 (t, 12), 0.56-0.68 (m, 8H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 152.9, 151.2, 148.4, 144.1, 143.6, 142.0, 141.1, 139.9, 136.2, 132.2, 131.7, 128.7, 128.0, 127.3, 127.1, 125.6, 123.2, 120.8, 120.3, 119.4, 118.0, 115.5, 113.8, 55.8, 40.5, 32.0, 30.2, 29.42, 29.41, 24.0, 22.8, 14.3.

1,2-bis(4-(1-(9,9-dioctyl-fluoren-2-yl)-1,2,3-triazol-4-yl)phenyl)ethene (**M2**)

The synthetic method to **M2** is similar to that of **M1**. **M2** was obtained as pale yellow solid in 76.7% isolation yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 8.29 (m, 2H), 7.79 (d, 4H), 7.83 (d, 2H), 7.81 (d, 2H), 7.72-7.77 (m, 4H), 7.66 (d, 4H), 7.35-7.40 (m, 6H), 7.23 (s, 2H), 2.00-2.07 (m, 8H), 1.00-1.22 (m, 40H), 0.80 (t, 12), 0.59-0.69 (m, 8H). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 152.9, 151.2, 148.3, 142.1, 139.9, 137.5, 136.2, 129.8, 128.7, 128.0, 127.33, 127.29, 126.4, 123.2, 120.8, 120.3, 119.5, 118.0, 115.5, 55.6, 40.6, 32.0, 30.2, 29.43, 29.41, 24.0, 22.8, 14.3.

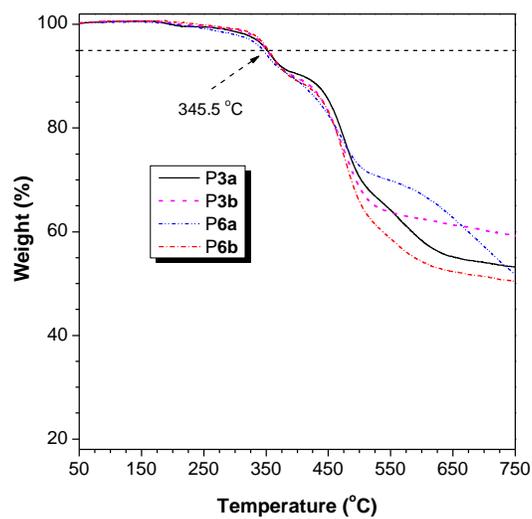


Fig. S1 TGA thermograms of P3a, P3b, P6a and P6b recorded under nitrogen at a heating rate of 20 °C/min.

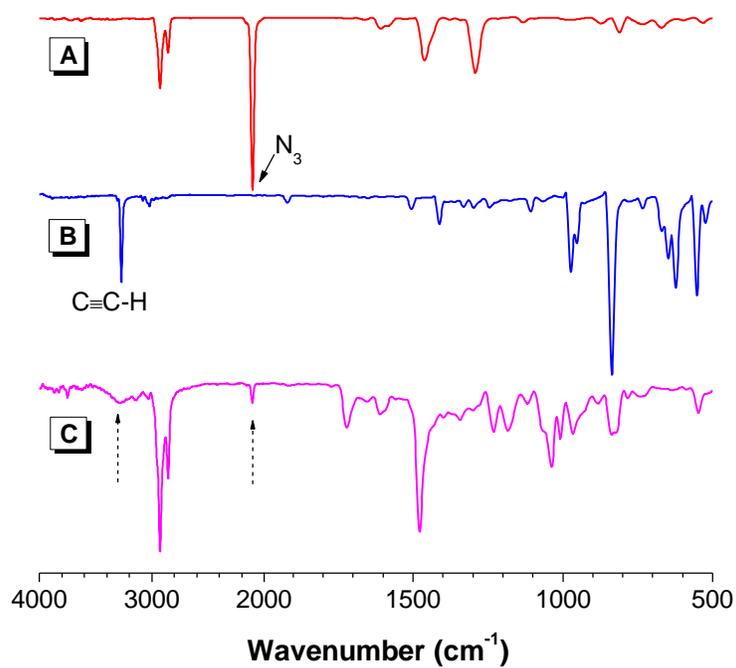


Fig. S2 IR spectra of monomers (A) **1** and (B) **2b** and (C) their polymer P3b.

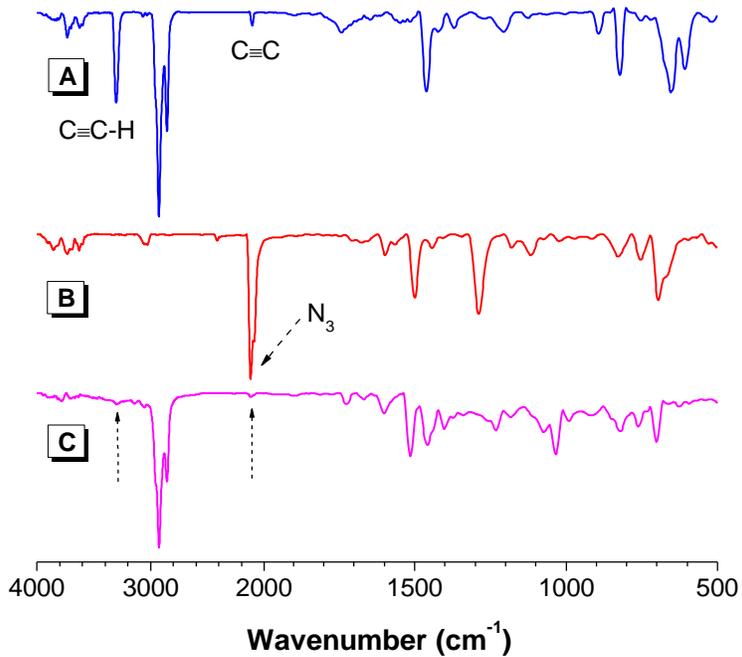


Fig. S3 IR spectra of (A) monomers **4** and (B) **5a** and (C) their polymer **P6a**.

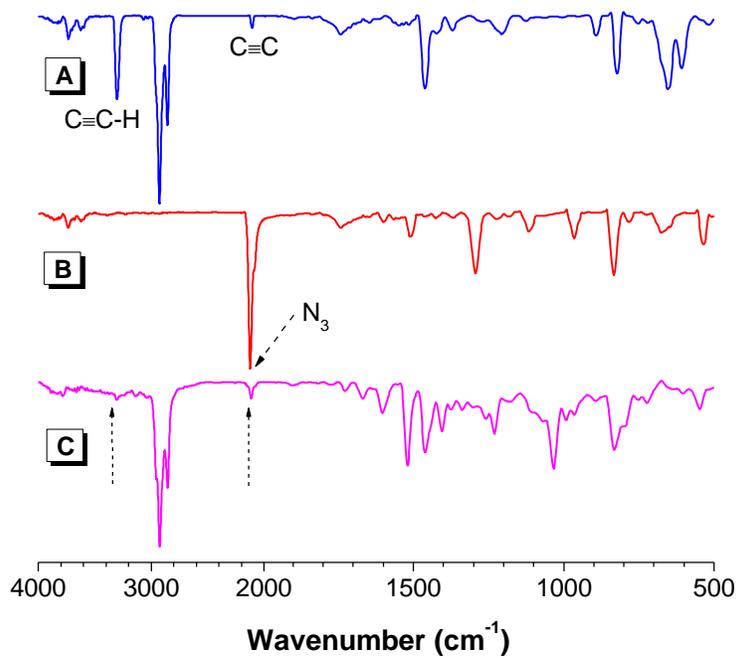


Fig. S4 IR spectra of (A) monomers **4** and (B) **5b** and (C) their polymer **P6b**.

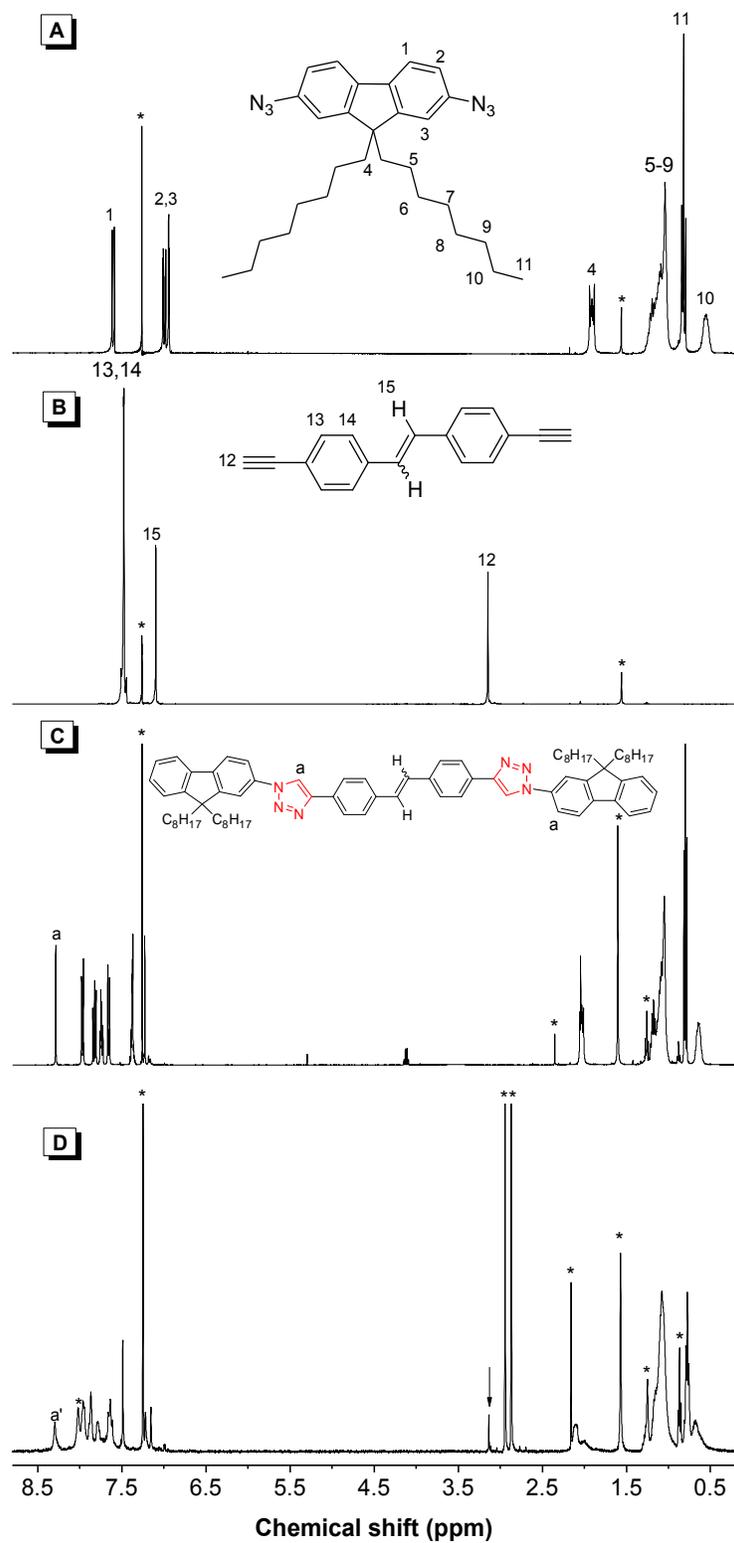


Fig. S5 ^1H NMR spectra of (A) monomer **1**, (B) monomer **2b**, (C) model compound **M2** and (D) polymer **P3b** in CDCl_3 . The solvent and water peaks are marked with asterisks.

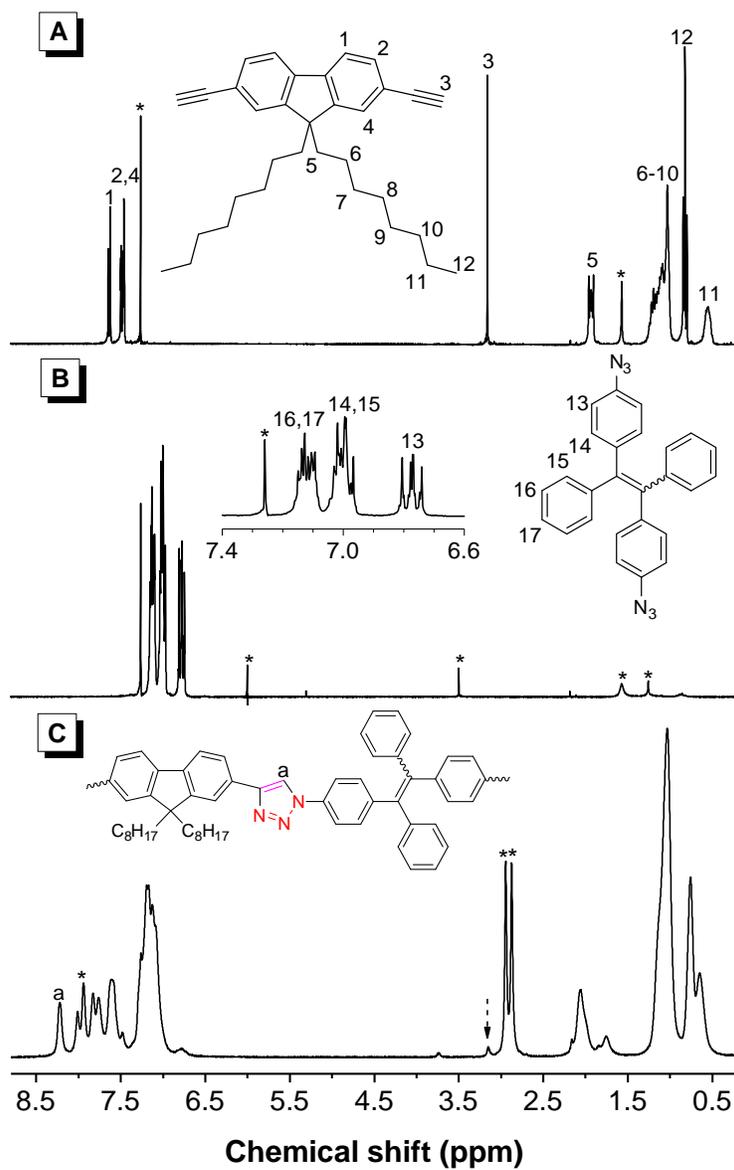


Fig. S6 ^1H NMR spectra of (A) monomer **4**, (B) monomer **5a**, and (C) polymer **P6a** in CDCl_3 . The solvent and water peaks are marked with asterisks.

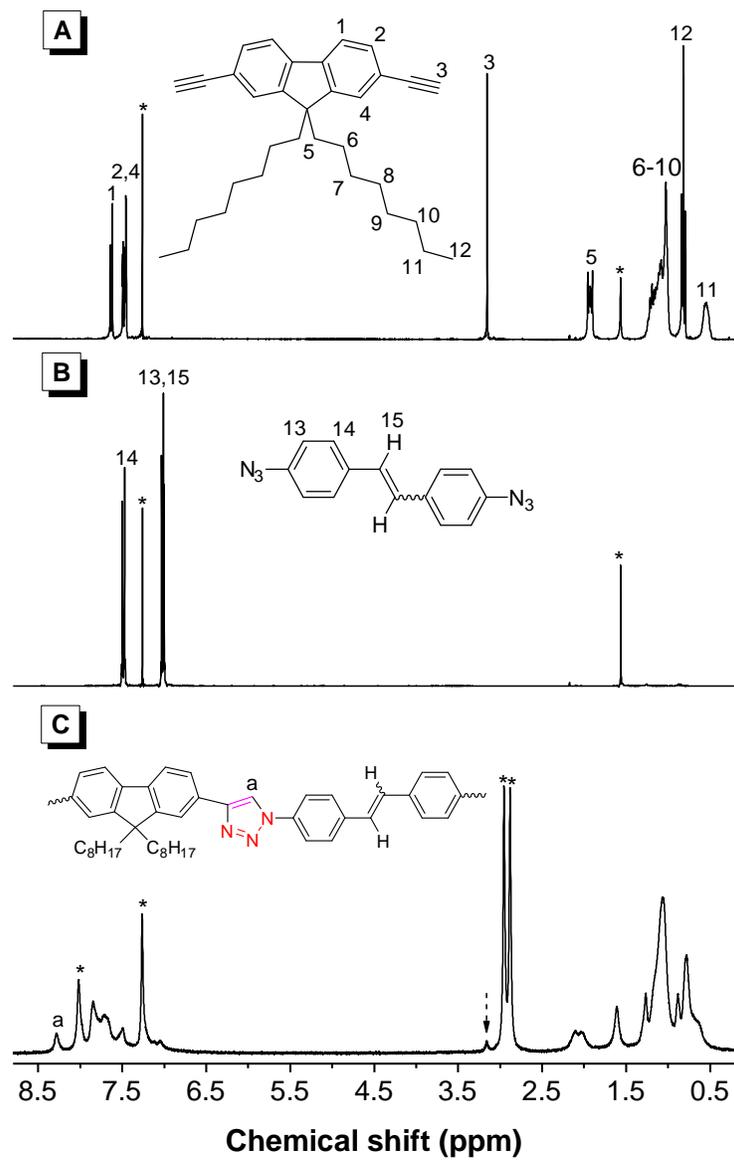


Fig. S7 ¹H NMR spectra of (A) monomer **4**, (B) monomer **5b**, and (C) polymer **P6b** in CDCl₃. The solvent and water peaks are marked with asterisks.

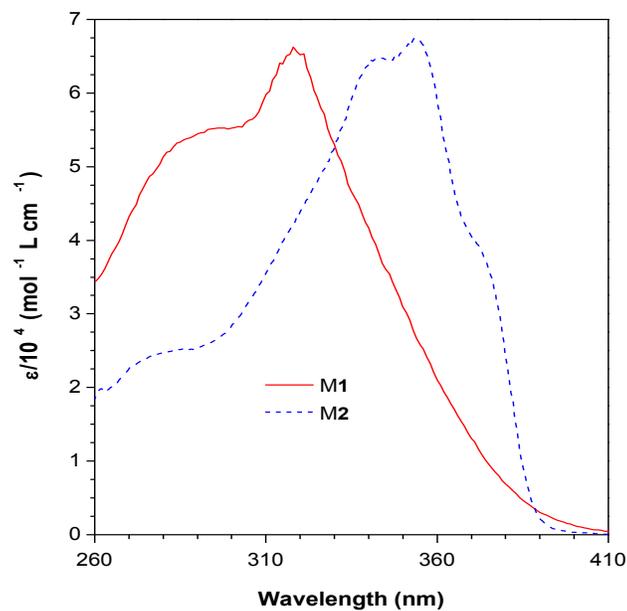


Fig. S8 UV absorption spectra M1 and M2 in THF solutions; concentration: 10 μM .

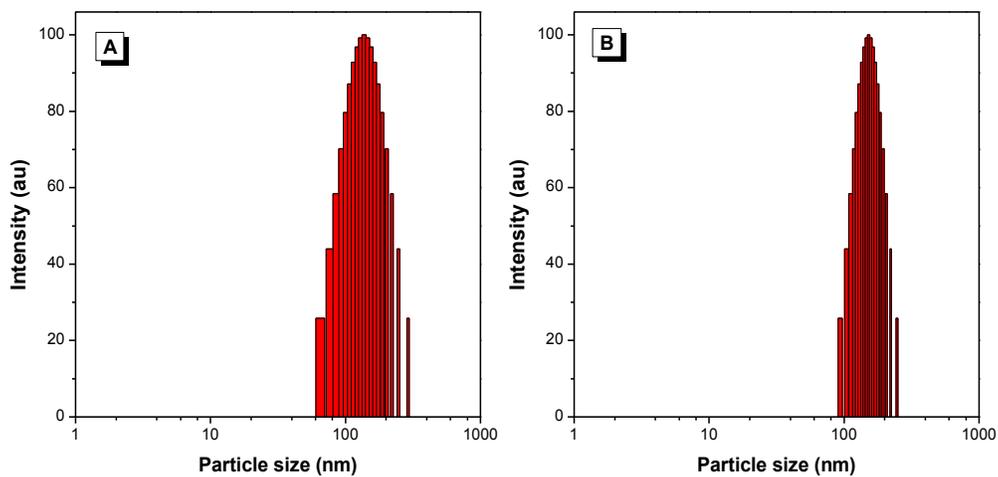


Fig. S9 Particle size analysis of the nano-aggregates of (A) P3a and (B) P3b in THF/water mixtures with water fraction of 90%. Concentration: 10 μM .

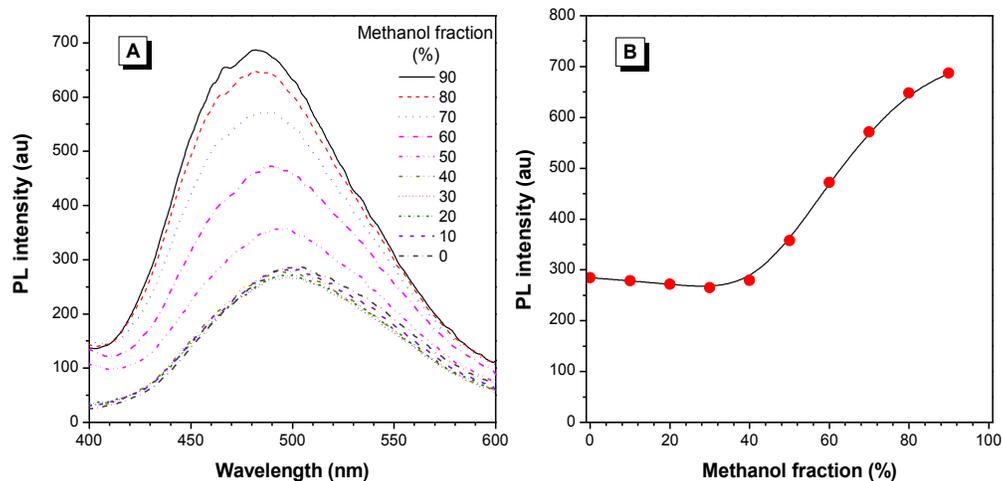


Fig. S10 (A) PL spectra of P3a in THF/methanol mixtures with different methanol fraction; excitation wavelength: 337; polymer concentration: 10 μ M. (B) Plot of relative emission intensity versus methanol fraction in THF/methanol mixtures.

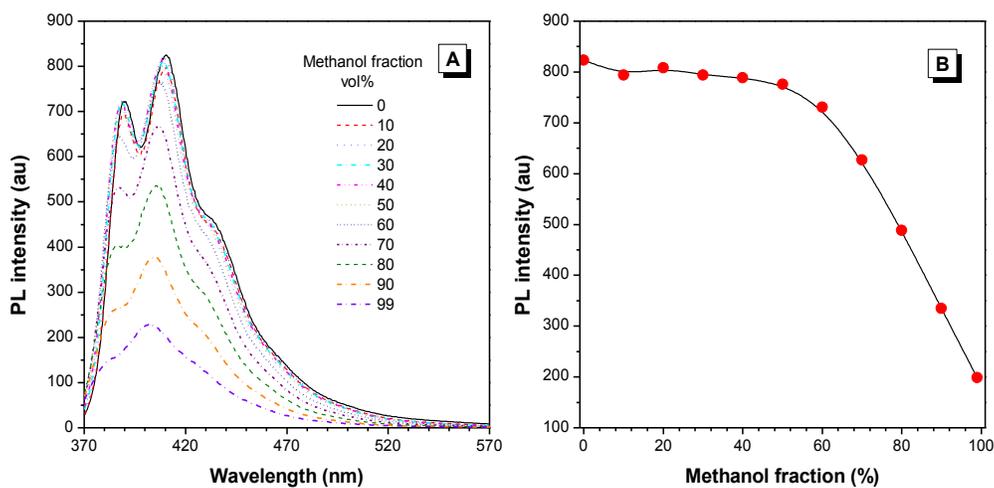


Fig. S11 (A) PL spectra of P3b in THF/methanol mixtures with different methanol fraction; excitation wavelength: 358; polymer concentration: 10 μ M. (B) Plot of relative emission intensity versus methanol fraction in THF/methanol mixtures.

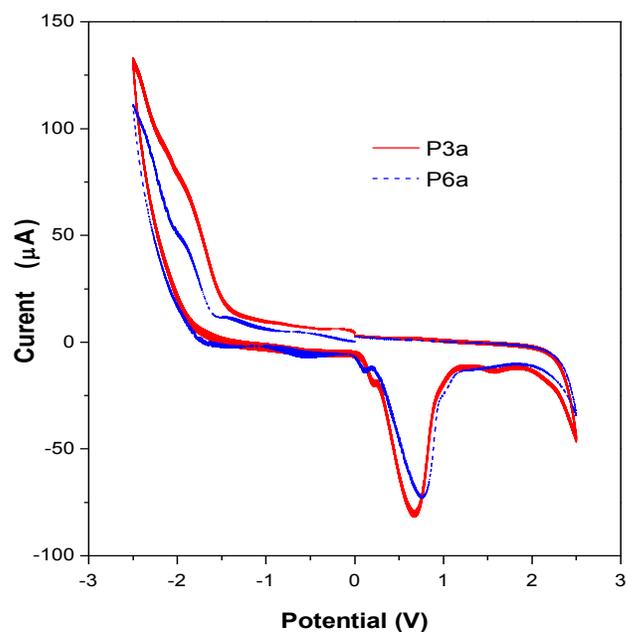


Fig. S12 Cyclic voltammograms of **P3a** and **P6a** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [n\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ at 100 mV/s.

Table S1 The HOMO and LUMO level, and energy gap values of theoretical estimation of **P3a-M** and **P6a-M**, and experimental measurement of **P3a** and **P6a**.

Polymers	Theoretical value (eV)			Experimental value (eV)		
	HOMO	LUMO	Energy gap	HOMO ^a	LUMO ^b	Energy gap
P3a	-5.21	-1.78	3.43	-5.07	-2.06	3.01
P6a	-5.30	-1.83	3.47	-5.16	-2.16	3.00

^a Determined from the onset of UV absorption spectra; ^b calculated from the sum of HOMO and energy gap value; ^c determined from the peak of oxidation wave of the CV spectra, $E_{\text{HOMO}} = -e(E^{\text{ox}} + 4.4)$. E^{ox} of **P3a** and **P6a** are 0.672 V and 0.762 V, respectively.