Electronic Supplementary Information

Synthesis and self-assembly of tetraphenylethene and biphenyl Based AIE-active triazoles

Wang Zhang Yuan,[a,b] Faisal Mahtab,[a] Yongyang Gong,[b] Zhenqiang Yu,[c] Ping Lu,[a,d] Youhong Tang,[a] Jacky W. Y. Lam,[a] Caizhen Zhu,[c] and Ben Zhong Tang*[a]

[a] *Department of Chemistry and State Key Laboratory of Molecular Neuroscience, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.*

[b] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

[c] *School of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, China*

[d] *State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130023, China*

E-mail: tangbenz@ust.hk

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Synthesis and Characterization of 1(*m*) (*m* = 5, 10)

Synthesis of 1,2,2-triphenyl-1-(4-((trimethylsilyl)ethynyl)phenyl)ethanol (**4**). To a solution of diphenylmethane (**2**, 3.03 g, 18 mmol) in dry tetrahydrofuran (30 mL) was added a solution of *n*-butyllithium in hexane (6 mL, 2.5 M, 15 mmol) at 0 °C under nitrogen. After being stirred at 0 °C for 30 min, the solution was added 4-(2-(trimethylsilyl)ethynyl)benzophenone (**3**, 3.76 g, 13.5 mmol). Then the reaction mixture was allowed to warm to room temperature with stirring during a period of 6 h. The reaction was quenched upon addition of an aqueous solution of ammonium chloride, the organic layer was extracted with dichloromethane three times, and the combined organic layers were washed with a saturated brine solution and dried over anhydrous Na_2SO_4. The crude product was condensed and purified on a silica-gel column using a mixture of chloroform/acetone (15:1 by volume) as eluent. A white solid of **4** was isolated in 75.7% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.76, 7.57, 7.49, 7.34, 7.29, 7.20, 7.17, 7.15, 7.10 (aromatic protons), 5.23 (s, 1H, $-CHPh_2$), 2.81 (s, 1H, $-OH$), 0.21 [s, 9H, $-Si(CH_3)_3$]. ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 146.97, 146.08, 140.46, 140.30, 132.54, 131.78, 131.54, 130.42, 130.37, 129.95, 129.90, 128.35, 128.13, 128.06, 127.91, 126.46, 126.37, 126.33, 125.99, 125.88, 120.87 (aromatic carbons), 105.00 ($ArC\equiv$), 93.95 ($\equiv CSi$), 80.41 ($-CHPh_2$), 59.87 (carbon connected to −OH), −0.06 ($-CH_3$). HRMS (MALDI-TOF): Calcd. for $C_{31}H_{30}OSi$: 446.2066. Found: 429.2053 $[(M-OH)]^+$.

Synthesis of trimethyl((4-(1,2,2-triphenylvinyl)phenyl)ethynyl)silane (**5**). **4** (2.01 g, 4.5 mmol) was dissolved in toluene (50 mL) in a 100 mL Schlenk flask fitted with a Dean-Stark trap. *p*-Toluenesulphonic acid (TsOH, 170 mg, 0.9 mmol) was added, and the mixture was refluxed for 3-4 h and cooled to room temperature. The toluene layer was washed with 10% aqueous $NaHCO_3$ solution twice and dried over anhydrous Na_2SO_4. The crude product was condensed and purified on a silica-gel column using hexane as eluent. A white solid of **5** was obtained in 89.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.19, 7.11, 7.10, 7.09, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.94 (aromatic protons), 0.22 (s, 9H, $-[Si(CH_3)_3]$. ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 144.22, 143.45, 143.37, 143.27, 141.62, 140.18, 131.33, 131.26, 131.22, 127.79, 127.69, 127.64, 126.63, 126.57, 120.78 (aromatic carbons), 105.24 (Ar*C*≡), 94.40 (≡*C*Si), −0.06 ($-CH_3$). HRMS (MALDI-TOF): Calcd. for $C_{31}H_{28}Si$: 428.1960. Found: 428.2249 $[M]^+$.

*Synthesis of (2-(4-ethynylphenyl)ethene-1,1,2-triyl)tribenzene (**6**)*. Into a 100 mL round-bottom flask was placed THF (20 mL), **5** (643.0 mg, 1.5 mmol), and TBAF (3 mL, 1 M). After stirring for 45 min, water (60 mL) was added. The mixture was extracted with DCM (200 mL) three times and the DCM solution was washed by brine twice. The mixture was then dried over anhydrous Na_2SO_4 (5 g) for 4 h. The crude product was condensed and purified on a silica-gel column using hexane as eluent. A white solid of **6** was obtained in 95.3% yield. ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 7.22, 7.20, 7.15, 7.13, 7.11, 7.10, 6.96, 6.95, 6.93 (aromatic protons), 4.12 (s, 1H, *H*C≡). ^{13}C NMR (100 MHz, DMSO-d_6), δ (TMS, ppm): 143.71, 142.70, 142.65, 142.51, 141.17, 139.55, 131.01, 130.75, 130.48, 130.45, 130.40, 127.79, 127.76, 127.65, 126.63, 126.55, 119.50 (aromatic carbons), 83.18 (Ar*C*≡), 80.87 (≡*C*H). (HRMS (MALDI-TOF): Calcd. for $C_{28}H_{20}$: 356.1565. Found: 356.1300 $[M]^+$.

*5-Bromopentyl 4,4'-biphenyldicarboxylate [**9**(5)]*. Into a 250 mL round-bottom flask were placed **7**(5) (2.34 g, 12 mmol), **8** (1.12 g, 6 mmol), DCC (3.71 g, 18 mmol), DMAP (293 mg, 2.4 mmol), and TsOH (457 mg, 2.4 mmol) in THF (150 mL). The resultant mixture was stirred at room temperature for 24 h. After filtering the formed urea, the solid was washed with THF and the filtrate was concentrated by a rotary evaporator. The product was purified by a silica gel column using a mixture of chloroform/hexane (1:1 by volume) as eluent. White solid; yield 86.2% (2.79 g). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.54 (d, 4H, aromatic protons meta to OCO–), 7.16 (m, 4H, aromatic protons ortho to OCO–), 3.45 (t, 4H, CH_2Br), 2.61 (t, 4H, $OCOCH_2$), 1.94 (m, 4H, $C\mathit{H}_2CH_2Br$) 1.81 (m, 4H, $OCOCH_2C\mathit{H}_2$), 1.60 (m, 4H, $C\mathit{H}_2CH_2CH_2Br$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 171.94 (C=O), 150.12 (aromatic carbons connected to OCO–), 138.08 (aromatic carbons para to OCO–), 128.12 (aromatic carbons meta to OCO–), 121.86 (aromatic carbons ortho to OCO–), 34.14 (CH_2Br), 33.42 ($OCO\mathit{C}H_2$), 32.34 ($\mathit{C}H_2CH_2Br$), 27.59 ($\mathit{C}H_2CH_2CH_2Br$), 24.04 ($OCOCH_2\mathit{C}H_2$).

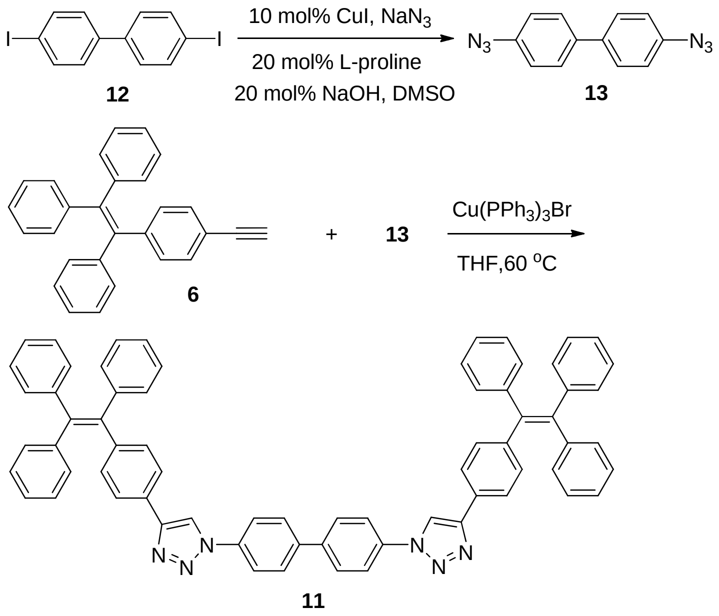
*10-Bromodecyl 4,4'-biphenyldicarboxylate [**9**(10)]*. The synthetic procedures are similar to those of **9**(5) described above. White solid; yield 79.2%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.54 (d, 4H, aromatic protons meta to OCO–), 7.15 (d, 4H, aromatic protons ortho to OCO–), 3.41 (t, 4H, CH_2Br), 2.58 (t, 4H, $OCOCH_2$), 1.84 (m, 4H, $C\mathit{H}_2CH_2Br$), 1.77 (m, 4H, $OCOCH_2C\mathit{H}_2$), 1.32 ~ 1.43 [m, 12H, $CH_2(C\mathit{H}_2)_6CH_2$]. ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 172.45 (C=O), 150.15 (aromatic carbons connected to OCO–), 138.12 (aromatic carbons para to OCO–), 128.11 (aromatic carbons meta to OCO–), 121.89 (aromatic carbons ortho to OCO–), 34.40 (CH_2Br), 34.05 ($OCO\mathit{C}H_2$), 32.82 ($\mathit{C}H_2CH_2Br$), 29.34, 29.31, 29.19, 29.07, 28.72, 28.14 [$(\mathit{C}H_2)_6CH_2CH_2Br$], 24.93 ($OCOCH_2\mathit{C}H_2$).

*5-Azidopentyl 4,4'-biphenyldicarboxylate [**10**(5)]*. Into a 250 mL round-bottom flask were placed **9**(5) (1.62 g, 3 mmol) and NaN_3 (507 mg, 7.8 mmol). Then DMSO (80 mL) was added. After stirring at room temperature for 24 h, water was added. The mixture was extracted by DCM three times. The organic layers were combined, washed with brine, and dried over Na_2SO_4 (5 g) overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using a chloroform/hexane mixture (1:1 by volume). White solid; yield 85.1%. IR (KBr), ν (cm^{-1}): 2096 (N_3 stretching), 1753 (C=O stretching). ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 7.66 (d, 4H, aromatic protons meta to OCO–), 7.20 (d, 4H, aromatic protons ortho to OCO–), 3.33 (t, 4H, CH_2N_3), 2.59 (t, 4H, $OCOCH_2$), 1.66 (m, 4H, $C\mathit{H}_2CH_2N_3$), 1.57 (m, 4H, $OCOCH_2C\mathit{H}_2$), 1.41 (m, 4H, $C\mathit{H}_2CH_2CH_2N_3$). ^{13}C NMR (100 MHz, DMSO-d_6), δ (TMS, ppm): 171.61 (C=O), 149.84 (aromatic carbons connected to OCO–), 136.75 (aromatic carbons para to OCO–), 127.58 (aromatic carbons meta to OCO–), 122.12 (aromatic carbons ortho to OCO–), 50.31 (CH_2N_3), 33.15 ($OCOCH_2$), 27.74 ($CH_2CH_2N_3$), 25.37 ($CH_2CH_2CH_2N_3$), 23.68 ($OCOCH_2CH_2$). HRMS (MALDI-TOF): Calcd. for $C_{24}H_{28}N_6O_4$: 464.2172. Found: 487.2950 $[M+Na]^+$.

*10-Azidodecyl 4,4'-biphenyldicarboxylate [**10**(10)]*. The synthetic procedures are similar to those of **1**(5) described above. However, due to the poor solubility of **9**(10) in DMSO at room temperature, the reaction mixture was carried out at 40 °C. White solid; yield 89.3%. IR (KBr), v (cm^{-1}): 2119 (N_3 stretching), 1747 (C=O stretching). ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.54 (d, 4H, aromatic protons meta to OCO–), 7.15 (d, 4H, aromatic protons ortho to OCO–), 3.26 (t, 4H, CH_2N_3), 2.58 (t, 4H, $OCOCH_2$), 1.77 (m, 4H, $CH_2CH_2N_3$), 1.60 (m, 4H, $OCOCH_2CH_2$), 1.31 [m, 24H, $(CH_2)_6$]. ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 172.34 (C=O), 150.22 (aromatic carbons connected to OCO–), 138.06 (aromatic carbons para to OCO–), 128.10 (aromatic carbons meta to OCO–), 121.89 (aromatic carbons ortho to OCO–), 51.49 (CH_2N_3), 34.41 ($OCOCH_2$), 29.39, 29.32, 29.20, 29.11, 29.08, 29.83 $[(CH_2)_6]$, 26.70 ($CH_2CH_2CH_2N_3$), 24.93 ($OCOCH_2CH_2$). HRMS (MALDI-TOF): Calcd. for $C_{34}H_{48}N_6O_4$ 604.3737. Found: 627.4815 $[M+Na]^+$.

*Synthesis of [1,1'-biphenyl]-4,4'-diyl bis(6-(4-(4-(1,2,2-triphenylvinyl)phenyl)-1H-1,2,3-triazol-1-yl) hexanoate) [**1**(5)]*. In a 15 mL Schlenk tube were placed **10**(5) (46.5 mg, 0.1 mmol), **6** (78.4 mg, 0.2 mmol) and $Cu(PPh_3)_3Br$ (2.8 mg). THF (2 mL) was then injected. The reaction mixture was stirred at 60 °C and found to be gelated 12 h later. The crude product was purified by a silica gel column using a chloroform/actone mixture (15:1 by volume). A white solid of **1**(5) was obtained in 90.1% yield. ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.71 (s, 2H, triazole protons), 7.57 (d, 4H), 7.52 (d, 4H), 7.13, 7.09, 7.07, 7.05, 7.04, 7.02, 4.42 (t, 4H, triaozle-CH_2), 2.59 (t, 4H, $OOCCH_2$), 2.01 (m, 4H, triaozle-CH_2CH_2), 1.82 (m, 4H, $OOCCH_2CH_2$), 1.48 (m, 4H, $OOCCH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 171.83 (C=O), 150.08, 143.73, 143.64, 143.59, 143.53, 141.28, 140.42, 138.08, 131.85, 131.36, 131.31, 128.53, 128.13, 127.76, 127.68, 127.62, 126.52, 126.50, 126.45, 124.98, 121.83, 50.05 (triazole-CH_2), 33.97 (OOCCH_2), 30.01 (triazole-CH_2CH_2), 25.90 ($OOCH_2CH_2$), 24.15 ($OOCH_2CH_2CH_2$). HRMS (MALDI-TOF): Calcd. for $C_{80}H_{68}N_6O_4$: 1176.5302. Found: 1199.4940 $[M+Na]^+$.

*Synthesis of [1,1'-biphenyl]-4,4'-diyl bis(11-(4-(4-(1,2,2-triphenylvinyl)phenyl)-1H-1,2,3-triazol-1-yl) undecanoate) [**1**(10)].* ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.65 (s, 2H, triazole protons), 7.56, 7.53, 7.15, 7.12, 7.11, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 4.36 (t, 4H, triaozle-CH_2), 2.57 (t, 4H, OOCCH_2), 1.92 (m, 4H, triaozle-CH_2CH_2), 1.76 (m, 4H, $OOCCH_2CH_2$), 1.40, 1.34 [m, 24H, $OOCCH_2CH_2(CH_2)_6$]. ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 172.31 (C=O), 150.21, 143.66, 143.61, 143.55, 141.26, 140.46, 138.04, 131.83, 131.37, 131.31, 128.65, 128.10, 127.76, 127.68, 127.63, 126.52, 126.44, 124.98, 121.89, 50.37, 34.39, 30.34, 29.27, 29.15, 29.04, 28.96, 26.45, 24.90. HRMS (MALDI-TOF): Calcd. for $C_{90}H_{88}N_6O_4$: 1316.6867. Found: 1317.7020 $[M+H]^+$.



Scheme S1 Synthetic route to compound **11**.

Synthesis and Characterization of compound 11

*Synthesis of 4,4'-diazidobiphenyl (**13**).* Into a 50 mL round-bottom flask were placed 4,4′-diiodobiphenyl (**12**, 2.0 g, 4.93 mmol), CuI (187.1 mg), NaN_3 (768.7 mg), L-proline (226.8 mg), and NaOH (78.8 mg). Then DMSO (8 mL) was added. After stirring at 60 °C for 20 h, water was added. The mixture was extracted by DCM three times. The organic layers were combined, washed with brine, and dried over Na_2SO_4 (5 g). After filtration and solvent evaporation, the crude product was purified by a silica gel column using hexane as eluent. A white solid (became brown yellow after being dried in vacuum at 40 °C) of **13** was obtained in a yield of 60.5%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.54 (d, 4H, protons meta to $–N_3$), 7.09 (d, 4H, protons ortho to $–N_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 139.24 (carbons connected to $–N_3$), 136.88 (carbons para to $–N_3$), 128.14 (carbons ortho to $–N_3$), 119.48 (carbons meta to $–N_3$). HRMS (MALDI-TOF): Calcd. for $C_{12}H_8N_6$: 236.0810. Found: 236.0816 $[M]^+$.

*Synthesis of 4,4'-bis(4-(4-(1,2,2-triphenylvinyl)phenyl)-1H-1,2,3-triazol-1-yl)biphenyl (**11**).* The synthetic procedures are similar to those of **1**(5). Grey white solid, yield: 75.3%. ^{1}H NMR (400 MHz, DMSO-d_6, 90 °C), δ (TMS, ppm): 9.10 (s, 2H, triazole protons), 8.02 (d, 4H), 7.99 (d, 4H), 7.69 (d, 4H), 7.16, 7.12, 7.11, 7.06, 7.03, 7.01. No ^{13}C NMR signals can be obtained even after 10 000 scans.

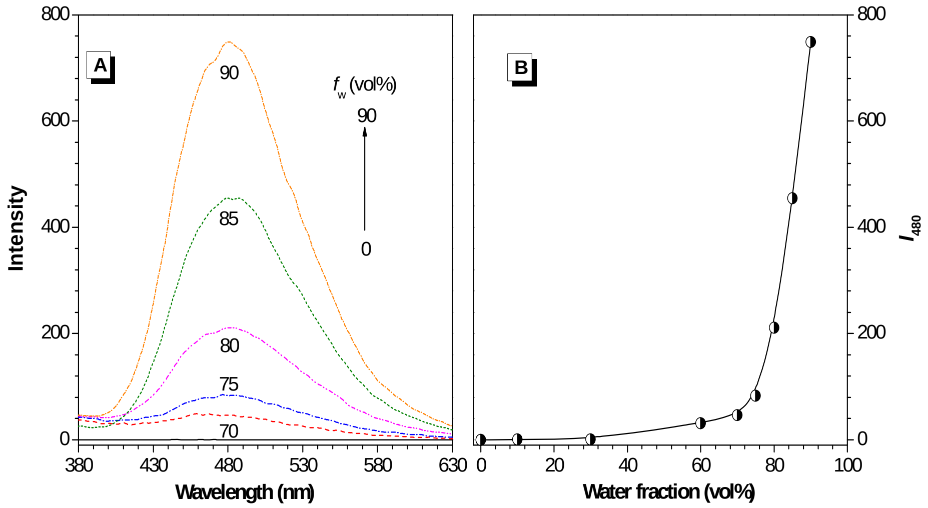


Fig. S1 (A) PL spectra of **1**(10) in THF and THF/water mixtures. (B) Plot of PL peak intensity at 480 nm *vs* water content of the aqueous mixture. Concentration = 20 μM; excitation wavelength = 340 nm.

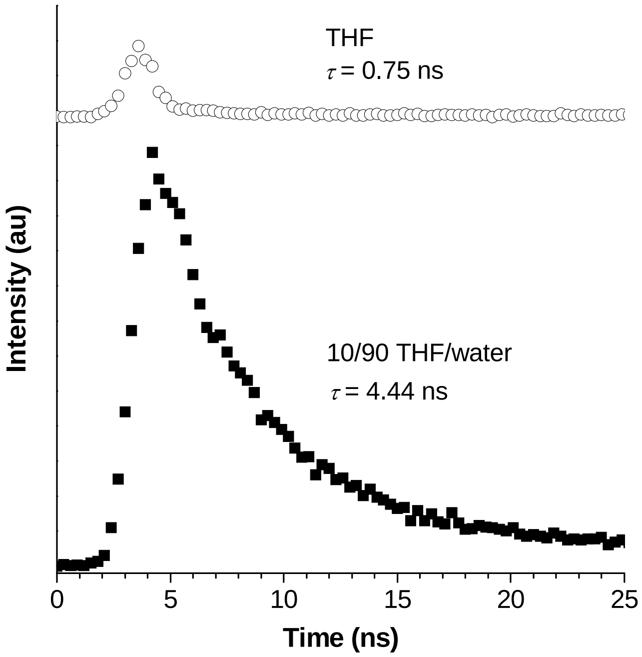


Fig. S2 Time-resolved fluorescence of **1**(5) in THF and 10/90 THF/water mixture. Concentration = 20 μM. Emission intensity was monitored at 480 nm.

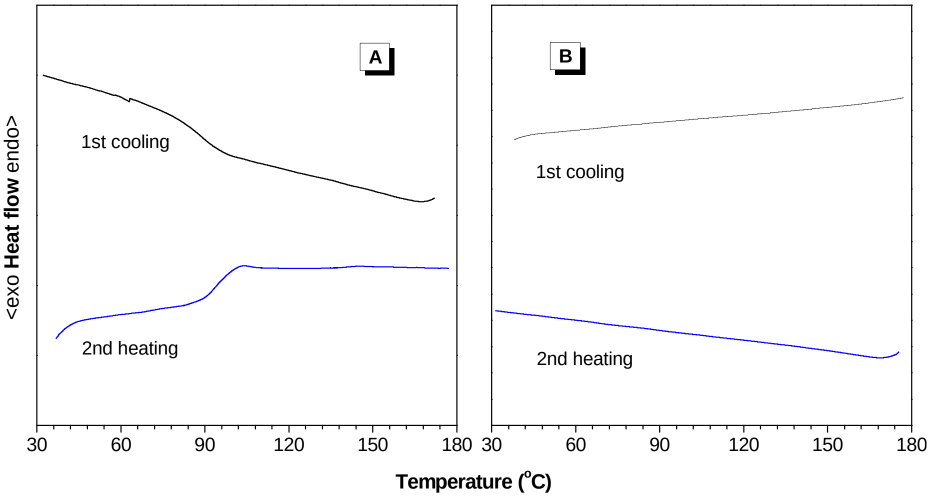


Fig. S3 DSC thermograms of (A) **1**(5) and (B) **1**(10) during the first cooling and second heating cycles at a scan rate of 10 ^{o}C/min.

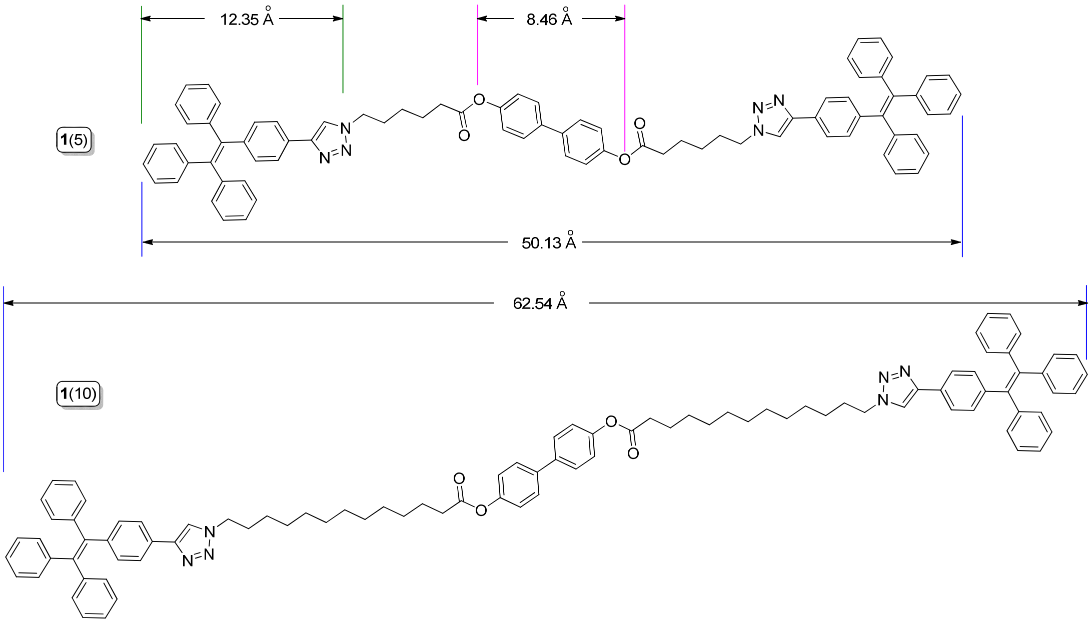


Chart S1 Chemical structure and calculated fully extended molecular lengths of **1**(*m*) (*m* = 5, 10).

Table S1 1D WAXD analysis data of **1**(*m*) (*m* = 5, 10) precipitated in *n*-hexane

1(5)									
2θ (°)	1.73	6.81	9.31	10.55	11.38	16.41	19.10	20.33	21.87
d-spacing (Å)	51.07	12.98	9.50	8.39	7.78	5.40	4.65	4.37	4.06
1(10)									
2θ (°)	1.71	4.27	5.94	9.90	16.33	17.72	19.86	20.98	
d-spacing (Å)	51.67	20.69	14.88	8.93	5.43	5.01	4.47	4.23	

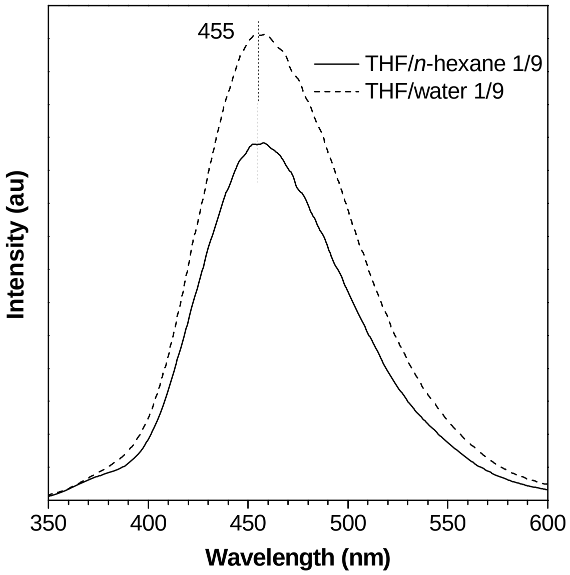


Fig. S4 Emission spectra of the precipitates of **1**(5) formed upon addition of its THF solution (1 mL, 1 mg/mL) into *n*-hexane (9 mL) and water (9 mL). Excitation wavelength = 310 nm.

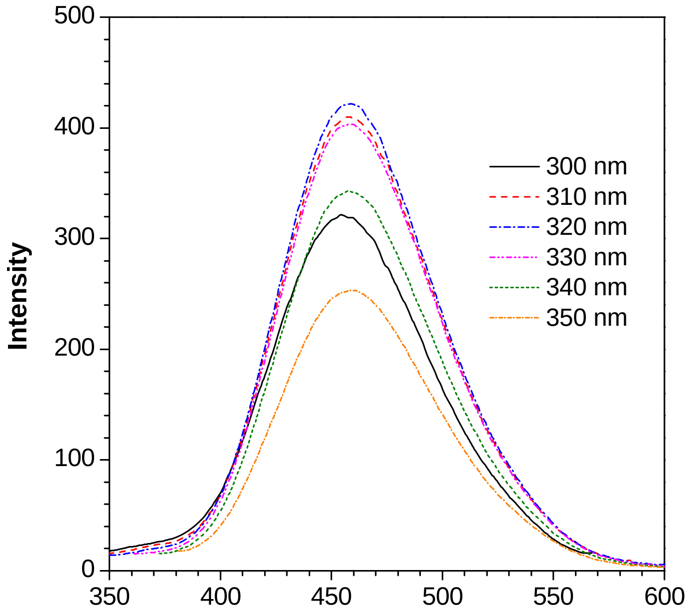


Fig. S5 Emission spectra of **1**(5) in 40/60 THF/water aqueous mixtures (standing for 6 h after being prepared) with different excitation wavelengths as indicated. Concentration = 20 μM.