Electronic Supplementary Information

Organobase-catalyzed Hydroxyl-yne Click Polymerization

Han Si,^a Kaojin Wang,^a Bo Song,^a Anjun Qin,^{*,a} and Ben Zhong Tang^{a,b}

^a State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, Center for Aggregation-Induced Emission, South China University of Technology, Guangzhou 510640, China

^b Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Centre for Tissue Restoration and Reconstruction, Institute for Advanced Study, and Department of Chemical and Biological Engineering, The Hong Kong University of Science & Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong, China

Table of contents

Materials and instruments	S 3
Monomer synthesis	S 4
General polymerization procedure	S7
Click polymerization of diphenols and diynes	S 10
Synthesis of model compound M1	S 11
Figure S1. GPC profiles of P1a2a-P1b2a	S12
Figure S2. FT-IR spectra of polymers P1a2a-P1b2a	S 13
Figure S3. ¹ H spectra of polymers P1a2a-P1b2a	S 14
Figure S4. ¹ H spectra of polymers P1a2l-P1a2k	S15
Figure S5. ¹³ C spectra of polymers P1a2a-P1b2a	S 16
Figure S6. ¹³ C spectra of polymers P1a2l-P1a2k	S 17
Figure S7. ¹ H NMR spectra of P1b2a	S 17
Figure S8. Melting peak temperature and melting enthalpy of polymer P1a2a.	S 18
Figure S9. Melting peak temperature and melting enthalpy of polymer P1a2b.	S 18
Figure S10. Melting peak temperature and melting enthalpy of polymer P1a2c.	S19
Figure S11. Melting peak temperature and melting enthalpy of polymer P1a2d.	S19
Figure S12. Melting peak temperature and melting enthalpy of polymer P1a2e.	S20
Figure S13. Melting peak temperature and melting enthalpy of polymer P1a2g.	S20
Figure S14. Glass transition temperature of polymer P1a2f.	S 21
Figure S15. Glass transition temperature of polymer P1a2h.	S 21
Figure S16. Glass transition temperature of polymer P1b2a.	S22
Figure S17. PL spectra of P1a2h (A) and P1a2j (C) in THF and THF/water mix	xtures
with different water fractions (f_w). Plots of I/I ₀ of P 1a2h (B) and P 1a2j (D) versus	water
fraction	S23
Figure S18. PL spectra of the P1a2h (A) and P1a2j (B) in THF/water mixture	es (f_w :
90%) containing different amounts of picric acid (PA)	S24
Reference	

Materials and instruments

DABCO (bicyclo[2.2.2]-1,4-diazaoctane) and propiolic acid were purchased from TCI. Tetrahydrofuran (THF) was distilled under nitrogen at normal pressure from sodium benzophenone ketyl immediately prior to use. Dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are ultra-dry reagents purchased from Energy. Monomers **2a** to **2g** were purchased from TCI, Energy and other regular reagent companies.

Proton (¹H) and carbon nuclear magnetic resonance (¹³C) spectra were measured on Bruker Advance 400 or 500 MHz NMR spectrometer in CDCl₃ using tetramethylsilane (TMS; $\delta = 0$) as inter reference. Fourier-transform infrared (FT-IR) spectra were performed on a Bruker Vector spectrometer using KBr as matrix. UV-vis transmission spectra were measured on a Shimadzu UV-2600 spectrophotometer with bandwidth of 1 nm, medium scanning rate, and quartz cuvettes of 1 cm path length. Photoluminescence (PL) spectra were investigated on a Horiba Fluoromax-4 spectrofluorometer. The weight-average molecular weight (M_w) and polydispersity indices were tested by Waters Advanced Polymer Chromatography (APC) with a photo-diode array (PDA) detector. Thermal stabilities were measured by thermogravimetric analysis (TGA) thermograms on a Netzsch STA 449 F3 at a heating rate of 20 °C/min in a nitrogen flow. T_g and T_m were measured by Differential scanning calorimetry (DSC) on a TAQ20 under protection of nitrogen.

S3

Monomer synthesis

Synthesis of 1,6-hexanediol dipropiolate (1a)



This monomer was prepared according to our previously published procedure.¹ 1,6-Hexanediol, propiolic acid (5,6 mL, 90 mmol), TsOH (1.03 g, 6 mmol), and 100 mL anhydrous toluene were added (3.54 g, 30 mmol) into a 250 mL round-bottom flask equipped with a Dean–Stark apparatus. The mixture was refluxed for 12 h. The solution was concentrated by a rotary evaporator, and the residue was dissolved in DCM. The organic layer was dried with anhydrous magnesium sulfate (MgSO₄) overnight and then filtered before evaporation. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1, v/v) as eluent. The product (5.24 g) was obtained with the yield of 78.5%.

FT-IR (KBr disk), v (cm⁻¹): 3228, 2946, 2874, 2112, 1698, 1477, 1250, 1077, 965, 904, 773, 713, 606, 424. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 4.19 (t, 4H), 2.88 (s, 2H), 1.70 (m, 4H), 1.42 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 152.92, 74.69, 66.30, 28.31, 25.55.

Synthesis of 4,4'-isopropylidenediphenyl dipropiolate (1b)



This monomer was synthesized according to the previously published literature.^{2,3} Bisphenol A (4.76 g, 20 mmol), DCC (12.38 g, 60 mmol), DMAP (0.98 g, 8 mmol), TsOH (1.38 g, 8 mmol) and DCM (20 mL) were placed into a 500 mL flask equipped with a magnetic stirrer and then immersed into an ice-water bath. Then, DCM solution of propiolic acid (30 mL, 1.47 mol/L) was added dropwise to the reaction system. The reaction was stirred overnight, and filtered and extracted with DCM. The organic layer was dried with anhydrous MgSO₄ overnight and then filtered. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (10:1, v/v) as eluent. The product (1.55 g) was obtained with the yield of 23.3%.

FT-IR (KBr disk), *v* (cm⁻¹): 3271, 2973, 2122, 1715, 1503, 1218, 1014, 918, 849, 816, 742, 702. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.24 (d, 4H), 7.06 (d, 4H), 3.06 (s, 2H), 1.67 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 15.18, 148.69, 147.83, 128.13, 120.81, 76.87, 74.41, 42.37, 31.00.

Synthesis of 4-(6-Hydroxyhexyloxy)benzophenone. (2h)



This monomer was prepared according to the previously published literature.⁴ Zinc powder (4.38 g, 67.0 mmol) and 4-(6-hydroxyhexyloy benzophenone) (5 g, 16.7 mmol) synthesized according to the previous published literature⁵ were added into a 250 mL two-necked round bottom flask equipped with a condenser. After repeating exhausting-refilling process three times, 90 mL THF was added and the reaction mixture was cooled to 0 °C. Afterward, TiCl₄ (2.75 mL, 25.1 mmol) was injected dropwise, and the mixture was refluxed overnight. Afterward, the reaction solution was quenched with 10% aqueous NaHCO₃ solution and insoluble part was filtered. The filtrate was extracted with DCM three times. The organic layer was dried with

anhydrous MgSO₄ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (2:1, v/v) as eluent. A green oil was obtained as product (11.6% yield).

FT-IR (KBr disk), *v* (cm⁻¹): 3446, 2922, 1707, 1624, 1509, 1471, 1327, 1176, 1134, 1030, 825, 736, 700, 605. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.13 – 7.04 (m, 10H), 7.06 – 6.97 (m, 4H), 6.66 – 6.60 (m, 4H), 3.83 (m, 4H), 3.63 (m, 4H), 1.72 (m, 4H), 1.57 (m, 4H), 1.43 (m, 8H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm):157.13, 144.15, 135.83, 129.51, 128.56, 128.19, 125.78, 114.27, 67.74, 63.02, 60.55, 55.78, 32.81, 29.40, 26.01, 25.68.

Synthesis of 1,2-bis(6-hydroxyphenyl)-1,2-diphenylethene (2j).



This monomer was prepared according to the previously published literature.^{6,7} Zinc powder (6.54 g, 100.0 mmol) and 4-hydroxy-benzophenone (4.95 g, 25.0 mmol) were added into a 250 mL two-necked round bottom flask equipped with a condenser. 70 mL THF was added into the flask after exhausting-refilling process for three times. TiCl₄ (4.1 ml, 37.5 mmol) was injected dropwise into the mixture after the system was cooled to 0 °C. The mixture was refluxed overnight. Afterward, the reaction was terminated by adding 10% aqueous NaHCO₃ solution and insoluble part was filtered. The filtrate was extracted three times with DCM and dried with anhydrous MgSO₄ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (3:1, v/v) as eluent. A white powder was obtained as product (yield: 54%).

FT-IR (KBr disk), *v* (cm⁻¹): 3530, 3401, 3024, 1608, 1509, 1438, 1334, 1256, 1170, 823, 701. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.13 – 7.10 (m, 6H), 7.05 – 7.01 (m, 8H), 6.93 – 6.89 (m, 4H), 3.03 (d, 1.79H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 150.82, 148.45, 143.14, 141.94, 140.55, 132.53, 131.42, 128.09, 127.02, 120.55.

General polymerization procedures

A representative procedure of the polymerization of **1a** and **2a** is described below briefly. **1a** (44.8 mg, 0.20 mmol) and **2a** (29.2 mg, 0.20 mmol) were placed into a 10 mL Schlenk tube. THF (0.4 mL) was then injected into the tube to dissolve both monomers, followed by 0.10 mL THF solution of DABCO (0.2 mol/L). After stirring for 1 h at 25 °C, CHCl₃ (4.0 mL) was added into the mixture. The diluted solution was filtered using a cotton and precipitated in 120 mL hexane under stirring. The precipitate was collected by filtration and dried under vacuum at room temperature to a constant weight.

Characteristic data for P1a2a. A white powder was obtained in 96% yield (Table 2, entry 1). M_w : 32 500, D: 2.99. FT-IR (KBr disk), v (cm⁻¹): 2940, 2857, 1704, 1638, 1474, 1403, 1322, 1233, 1128, 1026, 982, 937, 839, 744, 576. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.58 (d, J = 12.0 Hz, 2H), 5.17 (d, J = 12.0 Hz, 2H), 4.09 (t, 4H), 3.82 (t, 4H), 1.69 (m, 4H), 1.67 (m, 4H), 1.39 (m, 8H), 1.34 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 168.15, 162.68, 96.38, 71.12, 63.88, 29.22, 28.95, 28.82, 25.81.

Characteristic data for P1a2b. A white powder was obtained in 99% yield (Table 2, entry 2). M_w : 6 400, D: 2.09 (partially soluble). FT-IR (KBr disk), v (cm⁻¹): 2957,

2863, 1705, 1621, 1459, 1387, 1328, 1135, 1020, 947, 841, 738. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.66 (d, J = 13.0 Hz, 2H), 5.30 (d, J = 13.0 Hz, 2H), 7.36 (m, 4H), 4.90 (s, 4H), 4.10 (t, 4H), 1.65 (m, 4H), 1.39 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 167.79, 161.98, 135.77, 128.11, 97.66, 72.38, 64.04, 28.79, 25.80. *Characteristic data for P1a2c*. A white powder was obtained in 99% yield (Table 2, entry 3). *M*_w: 7 600, *Đ*: 1.71 (partially soluble). FT-IR (KBr disk), ν (cm⁻¹): 2949, 2859, 1703, 1621, 1471, 1326, 1137, 837. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.58 (d, J = 12.0 Hz, 2H), 5.18 (d, J = 12.0 Hz, 2H), 4.10 (t, 4H), 3.84 (t, 4H), 1.72 (m, 4H), 1.65 (m, 4H), 1.43 (m, 4H), 1.40 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 168.11, 162.59, 96.49, 70.91, 63.91, 28.83, 28.95, 25.63.

Characteristic data for P1a2d. A white powder was obtained in 97% yield (Table 2, entry 4). M_w : 32 300, D: 2.27. FT-IR (KBr disk), v (cm⁻¹): 2923, 2853, 1702, 1625, 1470, 1325, 1284, 1211, 1135, 820, 735. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.58 (d, J = 12.0 Hz, 2H), 5.17 (d, J = 12.0 Hz, 2H), 4.09 (t, 4H), 3.82 (t, 4H), 1.67 (m, 8H), 1.39 (m, 8H), 1.29 (m, 8H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 168.18, 162.73, 96.37, 71.21, 63.89, 29.53, 29.34, 28.84, 28.82, 25.89, 25.84.

Characteristic data for P1a2e. A white powder was obtained in 99% yield (Table 2, entry 5). M_w : 33 000, D: 2.38. FT-IR (KBr disk), v (cm⁻¹): 2925, 2854, 1703, 1639, 1474, 1403, 1325, 1232, 1129, 828, 726. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.59 (d, J = 12.0 Hz, 2H), 5.18 (d, J = 12.0 Hz, 2H), 4.10 (t, 4H), 3.83 (t, 4H), 1.67 (m, 8H), 1.40 (m, 8H), 1.27 (m, 12H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 168.19, 162.75, 96.36, 71.25, 63.89, 29.66, 29.63, 28.84, 29.38, 29.02, 28.85, 25.91, 25.85.

Characteristic data for P1a2f. A brown solid was obtained in 94% yield (Table 2, entry 6). M_w : 32 000, D: 2.39. FT-IR (KBr disk), v (cm⁻¹): 2939, 2857, 1709, 1627, 1464, 1431, 1327, 1283, 1200, 1135, 1032, 965, 829, 737. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.55 (d, J = 12.0 Hz, 1.8H), 5.26 (d, J = 12.0 Hz, 1.8H), 6.50 (d, J = 6.8 Hz, 0.2H), 4.90 (d, J = 6.8 Hz, 0.2H), 4.11 (t, 4H), 3.55 (s, 4H), 1.65 (m, 4H), 1.39 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 167.32, 161.15, 98.02, 69.12, 64.16, 43.64, 33.06, 28.77, 25.77.

Characteristic data for P1a2g. A white solid was obtained in 77% yield (Table 2, entry 7). $M_{\rm w}$: 57 600, D: 2.64. FT-IR (KBr disk), v (cm⁻¹): 3360, 2921, 2859, 1706, 1628, 1467, 1326, 1284, 1206, 1133, 828, 737. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.56 (d, J = 13.0 Hz, 2H), 5.21 (d, J = 13.0 Hz, 2H), 4.10 (t, 4H), 4.01 (t, 4H), 2.85 (t, 4H), 1.65 (m, 4H), 2.80 (m, 4H), 1.39 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 167.71, 161.83, 97.30, 70.67, 64.03, 32.86, 31.01, 28.79, 25.79.

Characteristic data for P1a2h. A green solid was obtained in 99% yield (Table 2, entry 8). M_w : 71 000, D: 2.04. FT-IR (KBr disk), v (cm⁻¹): 3358, 2922, 2852, 1707, 1624, 1509, 1471, 1327, 1245, 1210, 1176, 1134, 1030, 825, 736, 700, 605. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.58 (d, J = 12.5 Hz, 2H), 5.17 (d, J = 12.5 Hz, 2H), 7.15 – 7.05 (m, 8H), 7.04 – 6.99 (m, 6H), 6.62 (d, 4H), 4.10 (t, 4H), 3.81 (m, 8H), 1.69 (m, 12H), 1.41 (m, 12H), 2.80 (m, 4H), 1.39 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 168.13, 162.64, 157.56, 157.10, 144.47, 144.17, 136.40, 135.86, 132.66, 131.53, 129.48, 128.57, 128.24, 121.78, 126.27, 125.78, 114.27, 113.74, 71.02, 67.60, 63.89, 55.75, 31.73, 29.02, 26.02, 22.80, 14.27.

Characteristic data for P1b2a. A brown solid was obtained in 99% yield (Table 2, entry 9). M_w : 21 700, D: 1.91. FT-IR (KBr disk), v (cm⁻¹): 2933, 2857, 1727, 1623, 1504, 1466, 1391, 1330, 1200, 1170, 1103, 1016, 987, 930, 828, 730, 552. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.76 (d, J = 12.8 Hz, 1.73H), 5.26 (d, J = 12.8 Hz, 1.73H), 7.95 (d, J = 12.8 Hz, 0.15H), 5.69 (d, J = 12.8 Hz, 0.15H), 7.59(d, J = 6.8 Hz, 0.12H), 5.19 (d, J = 6.8 Hz, 0.12H), 7.22 (d, 4H), 7.00 (d, 4H), 3.92 (t, 3.46H), 4.10 (t, 0.3H), 3.83 (t, 0.24H), 1.74 (m, 4H), 1.66 (s, 6H), 1.38 (m, 8H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 166.54, 164.22, 148.78, 147.71, 127.90, 121.26, 95.89, 71.56, 42.59, 31.86, 29.23, 28.98, 25.83.

Click Polymerization of diphenols and diyne

The reaction conditions of diphenol-diyne click polymerization are similar to those of hydroxyl-diyne one. Briefly, **1a** (44.8 mg, 0.20 mmol) and **2l** (45.6 mg, 0.20 mmol) were placed into a 10 mL Schlenk tube, and THF (1.9 mL) was then injected into the tube to dissolve the monomers, followed by 0.10 mL THF solution of DABCO (1.12 mg, 0.2 mol/L). After stirring at 25 °C for 1 h, the mixture was diluted with 4.0 mL CHCl₃ and added dropwise into 120 mL hexane through a cotton filter under stirring. The precipitate was collected by filtration and dried under vacuum at room temperature to a constant weight.

Characteristic data for P1a21. A white solid was obtained in 91% yield (Table 3, entry 1). M_w : 22 100, D: 2.19. FT-IR (KBr disk), v (cm⁻¹): 2939, 1712, 1624, 1504, 1282, 1227, 1173, 1120, 1014, 951, 835, 735, 556. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.77 (d, J = 12.0 Hz, 1.8H), 5.53 (d, J = 12.0 Hz, 1.8H), 6.86 (d, J = 4.0 Hz, 0.2H),

5.13 (d, J = 4.0 Hz, 0.2H), 7.20 (d, 4H), 6.97 (d, 4H), 4.12 (t, 4H), 1.66 (m, 10H), 1.40 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 167.48, 159.35, 153.98, 147.27, 128.38, 117.75, 102.03, 64.21, 42.49, 31.06, 28.78, 25.80.

Characteristic data for P1a2j. A green powder was obtained in 92% yield (Table 3 entry 2). M_w : 16 900, D: 2.16. FT-IR (KBr disk), v (cm⁻¹): 3054, 2936, 1712, 1649, 1501, 1221, 1168, 1111, 1014, 948, 835, 698. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.73 (m, 2H), 5.52 (m, 2H), 7.13-7.10 (m, 6H), 7.03-6.99 (m, 8H), 6.83-6.78 (m, 4H), 4.12 (t, 4H), 1.66 (m, 4H), 1.40 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 167.45, 158.77, 154.49, 143.30, 140.37, 132.98, 131.36, 128.09, 126.98, 117.37, 102.39, 64.24, 28.77, 25.79.

Characteristic data for P1a2k. A white powder was obtained in 97% yield (Table 3, entry 3). M_w : 6 000, D: 2.66. FT-IR (KBr disk), v (cm⁻¹): 3067, 2943, 1716, 1654, 1595, 1503, 1232, 1165, 1111, 928, 836, 767. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.85 (d, J = 12.0 Hz, 1.8H), 5.70 (d, J = 12.0 Hz, 1.8H), 6.95 (d, J = 4.0 Hz, 0.2H), 5.29 (d, J = 4.0 Hz, 0.2H), 7.82 (d, 4H), 7.17 (d, 4H), 4.16 (t, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 193.83, 166.99, 159.03, 157.20, 134.03, 132.44, 117.47, 104.13, 64.43, 28.73, 25.76.

Synthesis of model compound M1.



Model compound **M1** was synthesized by hydroalkoxylation reaction of methyl propiolate and 1-hexanol. Typically, methyl propiolate (0.447 mL, 5.0 mmol), 1-hexanol (0.753 mL, 6.0 mmol) and 4.9 mL THF were placed into a 25 mL Schlenk

tube equipped with a magnetic stir bar. 0.10 mL THF solution of DABCO (56.08mg, 0.5 mmol) was then injected into the system. The mixture was stirred at 25 °C for 1 h, and then extracted three times with DCM. The organic layer was dried with anhydrous MgSO₄ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (40:1, v/v) as eluent. The product (0.787 g) was obtained in 84.6% yield.

Characteristic data for **M1**. A colorless transparent liquid was obtained in 84% yield. FT-IR (KBr disk), *v* (cm⁻¹): 2953, 2861, 1717 1626, 1466, 1437, 1332, 1287, 1211, 1140, 1050, 973, 825, 752. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 7.59(d, 1H), 5.19 (d, 1H), 3.83 (t, 2H), 3.69 (s, 3H), 1.37 (m, 2H), 1.30 (m, 2H), 0.89 (t, 3H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 168.52, 162.89, 96.06, 71.35, 51.18, 31.52, 28.96, 25.53, 22.64, 14.10.



Figure S1. GPC traces of P1a2a-P1b2a.



Figure S2. FT-IR spectra of (A) P1a2a, (B) P1a2b, (C) P1a2c, (D) P1a2d, (E) P1a2e, (F) P1a2f, (G) P1a2g, (H) P1a2h and (L) P1b2a.



Figure S3. ¹H NMR spectra of (A) P1a2a, (B) P1a2b, (C) P1a2c, (D) P1a2d, (E) P1a2e, (F) P1a2f, (G) P1a2g, (H) P1a2h (L) P1b2a in CDCl₃. The solvent peaks are marked with asterisks.



Figure S4. ¹H NMR spectra of (A) P**1a2l**, (B) P**1a2j** and (C) P**1a2k** in CDCl₃. The solvent peaks are marked with asterisks.



Figure S5. ¹³C NMR spectra of (A) P1a2a, (B) P1a2b, (C) P1a2c, (D) P1a2d, (E) P1a2e, (F) P1a2f, (G) P1a2g, (H) P1a2h (L) P1b2a in CDCl₃. The solvent peaks are marked with asterisks.



Figure S6. ¹³C NMR spectra of (A) P**1a2l**, (B) P**1a2j** and (C) P**1a2k** in CDCl₃. The solvent peaks are marked with asterisks.



Figure S7. ¹H NMR spectra of P**1b2a** in CDCl₃. The solvent peaks are marked with asterisks.



Figure S8. Melting peak temperature and melting enthalpy of polymer P1a2a.



Figure S9. Melting peak temperature and melting enthalpy of polymer P1a2b.



Figure S10. Melting peak temperature and melting enthalpy of polymer P1a2c.



Figure S11. Melting peak temperature and melting enthalpy of polymer P1a2d.



Figure S12. Melting peak temperature and melting enthalpy of polymer P1a2e.



Figure S13. Melting peak temperature and melting enthalpy of polymer P1a2g.



Figure S14. Glass transition temperature of polymer P1a2f.



Figure S15. Glass transition temperature of polymer P1a2h.



Figure S16. Glass transition temperature of polymer P1b2a.



Figure S17. PL spectra of P**1a2h** (A) and P**1a2j** (C) in THF and THF/water mixtures with different water fractions (f_w). Plots of I/I₀ of P**1a2h** (B) and P**1a2j** (D) versus water fraction, where I = peak intensity and I_0 = peak intensity at f_w = 0. Concentrations: 10 μ M; excitation wavelength: 319 nm for P**1a2h** and 314 nm for P**1a2j**. Insert: photograph taken under illumination of hand-held UV lamp.



Figure S18. PL spectra of the P**1a2h** (A) and P**1a2j** (B) in THF/water mixtures (f_w : 90%) containing different amounts of picric acid (PA). Concentration: 10 μ M; excitation wavelength: 319 nm for P**1a2h** and 314 nm for P**1a2j**.

References

- 1. H. Li, J. Wang, J. Z. Sun, R. Hu, A. Qin and B. Z. Tang, Polym. Chem., 2012, 3, 1075-1083.
- J. Liu, L. Zhang, J. W. Y. Lam, C. K. W. Jim, Y. Yue, R. Deng, Y. Hong, A. Qin, H. H. Y. Sung, I. D. Williams, G. Jia and B. Z. Tang, *Macromolecules*, 2009, **42**, 7367-7378.
- C. K. W. Jim, A. Qin, J. W. Y. Lam, M. Häussler, J. Liu, M. M. F. Yuen, J. K. Kim, K. M. Ng and B.
 Z. Tang, *Macromolecules*, 2009, 42, 4099-4109.
- 4.S. S. Liow, Q. Dou, D. Kai, Z. Li, S. Sugiarto, C. Y. Yu, R. T. Kwok, X. Chen, Y. L. Wu, S. T. Ong, A. Kizhakeyil, N. K. Verma, B. Z. Tang and X. J. Loh, Small, 2017, 13, 1603404.
- Y. Park, S. Lee, S.-H. Kim, B. Y. Jang, J. S. Kim, S. M. Oh, J.-Y. Kim, N.-S. Choi, K. T. Lee and B.-S. Kim, *RSC Adv.*, 2013, 3, 12625-12630.
- 6. C. Yu, Y. Wu, F. Zeng, X. Li, J. Shi and S. Wu, Biomacromolecules, 2013, 14, 4507-4514.
- 7. J. Liang, R. T. Kwok, H. Shi, B. Z. Tang and B. Liu, ACS Appl. Mater. Interfaces, 2013, 5, 8784-8789.