

## ***Electronic Supplementary Information (ESI) for***

### **Hyperbranched Polytriazoles with High Molecular Compressibility: Aggregation-Induced Emission and Superamplified Explosive Detection**

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## Experimental Section

### General Information

Unless otherwise stated, all the chemicals used in this study were purchased from Acros or Alfa. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. *N,N*-Dimethylformamide (DMF) was extra-dry grade. Other solvents were purified by standard methods.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker ADVANCE2B/400MHz spectrometer in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  using tetramethylsilane (TMS;  $\delta = 0$ ) as internal reference. FTIR spectra were recorded on a Bruker Vector 22 spectrometer. UV spectra were measured on a Varian VARY 100 Bio UV-visible spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Fluorescence quantum yields ( $\Phi_F$ ) were estimated using quinine sulfate in 0.1 N sulfuric acid ( $\Phi_F = 54.6\%$ ) as standard. The absorbance of the solutions was kept around 0.05 to avoid internal filter effect. The  $\Phi_F$  of spin-coated thin films of the polymers was recorded by a calibrated integrating sphere on a Photon Technology International time-resolved fluorescence spectroscopy, the detailed measuring method referred to reference [1]. Melting points (mp) were measured on Perkin-Elmer DSC-7 under nitrogen at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Elemental analysis was performed on a ThermoFinnigan Flash EA1112. Thermal stabilities were evaluated by measuring thermo-gravimetric analysis (TGA) thermograms on a Perkin-Elmer TGA 7 under dry nitrogen at  $20\text{ }^\circ\text{C}/\text{min}$ . Average molecular weights ( $M_w$  and  $M_n$ ) and polydispersity indices (PDI) of the hyperbranched polymers were estimated by a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with ultraviolet (UV) detector, using a set of monodispersed polystyrenes as calibration standards and THF as the eluent at a flow rate of  $1.0\text{ mL}/\text{min}$ . The nitrogen adsorption porosimetry was done with a Quatachrome Autosorb-1-C, and the surface area of the polymer was determined from the Brunauer-Emmet-Teller (BET) function. The thicknesses of spin-coating films of the polymers were measured by an M-2000DI spectroscopic Ellipsometer from J. A. Woollam. Cyclic voltammetry (CV) measurement of the polymer solution was performed in an electrolyte of  $0.1\text{ M}$  tetrabutylammonium hexafluorophosphate in DCM at a scan rate of  $50\text{ mV}/\text{s}$  at room temperature under the protection of nitrogen. A Pt wire was used as the counter electrode and an  $\text{Ag}/\text{AgNO}_3$  electrode was used as the reference electrode.

### Monomer Preparation

**1,1,1-Tris[4-(6-bromohexyloxy)phenyl]ethane (4a).** Into a 250 mL round-bottom flask was added 1,6-dibromohexane (16.104 g, 66 mmol) and  $\text{K}_2\text{CO}_3$  (20.732 g, 150 mmol) in acetone (60 mL). 1,1,1-

tris(4-hydroxyphenyl)ethane (**3**) (6.128 g, 20 mmol) dissolved in acetone (40 mL) was then added into the flask dropwise within 2 h under reflux. Afterward, the mixture was further refluxed for 24 h and then cooled to room temperature. The inorganic salt was filtered and washed with acetone and chloroform several times. The filtrate was concentrated by a rotary evaporator and the crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate mixture (20:1 by volume) as eluent. A white solid of 1,1,1-tris[4-(6-bromohexyloxy)phenyl]ethane was obtained in 49.9 % yield (7.941 g). mp 55 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (TMS, ppm): 6.96 (d, 6H), 6.75 (d, 6H), 3.91 (t, 6H), 3.40 (t, 6H), 2.10 (s, 3H), 1.86 (m, 6H), 1.76 (m, 6H), 1.47 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 157.5, 142.2, 130.1, 114.0, 68.1, 51.0, 34.3, 33.2, 31.3, 29.6, 28.4, 25.8.

**1,1,1-Tris[4-(6-azidohexyloxy)phenyl]ethane (1a).** Into a 250 mL round-bottom flask was added **4a** (7.870 g, 9.9 mmol) and sodium azide (2.419 g, 37.2 mmol) in DMSO (100 mL). After stirred at room temperature overnight, a small amount of water was added to quench the reaction, during which the solution temperature was increased slightly. After cooled to room temperature, the solution was extracted with 50 mL of diethyl ether five times. The organic phases were combined, washed with brine and water, and then dried over MgSO<sub>4</sub> overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate mixture (20:1 by volume) as eluent. Colorless liquid of 1,1,1-tris[4-(6-azidohexyloxy)phenyl]ethane was obtained in 96.6 % yield (6.516 g). IR (KBr), ν (cm<sup>-1</sup>): 2937, 2094, 1608, 1508, 1248, 1180, 1020, 829, 729, 605. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (TMS, ppm): 6.97 (d, 6H), 6.76 (d, 6H), 3.91 (t, 6H), 3.25 (t, 6H), 2.09 (s, 3H), 1.75 (m, 6H), 1.60 (m, 6H), 1.42 (m, 12H). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>), δ (TMS, ppm): 6.88 (d, 6H), 6.77 (d, 6H), 3.88 (t, 6H), 3.29 (t, 6H), 2.00 (s, 3H), 1.66 (m, 6H), 1.52 (m, 6H), 1.36 (m, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (ppm): 157.2, 142.0, 129.8, 113.8, 67.8, 51.6, 50.8, 31.0, 29.4, 29.0, 26.8, 26.0. Anal. Calcd for C<sub>38</sub>H<sub>51</sub>N<sub>9</sub>O<sub>3</sub>: C, 66.93; H, 7.54; N, 18.49. Found: C, 66.43; H, 7.57; N, 18.30.

**1,1,1-Tris[4-(4-bromobutoxy)phenyl]ethane (4b).** This compound was prepared according to the procedures similar to those of **4a**. 1,4-dibromobutane (14.250 g, 66 mmol) was used and a colorless liquid of 1,1,1-tris[4-(6-bromobutoxy)phenyl]ethane was obtained; yield: 40.4 % (5.748 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (TMS, ppm): 6.98 (d, 6H), 6.76 (d, 6H), 3.96 (t, 6H), 3.46 (d, 6H), 2.10 (s, 3H), 2.03 (m, 6H), 1.92 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>), δ (ppm): 157.1, 142.1, 129.8, 113.8, 66.9, 50.8, 33.8, 31.0, 29.7, 28.2.

**1,1,1-Tris[4-(4-azidobutoxy)phenyl]ethane (1b).** This monomer was prepared according to the procedures similar to those of **1a**. **4b** (5.691 g, 8.0 mmol) and NaN<sub>3</sub> (1.950 g, 30.0 mmol) were used

and a colorless liquid of 1,1,1-tris[4-(4-azidobutoxy)phenyl]ethane was obtained; yield: 95.1 % (4.547 g). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 2929, 2096, 1606, 1508, 1248, 1180, 1032, 829, 729, 605.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 6.97 (d, 6H), 6.76 (d, 6H), 3.94 (t, 6H), 3.33 (t, 6H), 2.10 (s, 3H), 1.82 (m, 6H), 1.76 (m, 6H).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ),  $\delta$  (TMS, ppm): 6.88 (d, 6H), 6.78 (d, 6H), 3.91 (t, 6H), 3.34 (t, 6H), 2.00 (s, 3H), 1.70 (m, 6H), 1.64 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 157.0, 142.0, 129.8, 113.7, 67.2, 51.3, 50.7, 30.9, 26.7, 25.9. Anal. Calcd for  $\text{C}_{32}\text{H}_{39}\text{N}_9\text{O}_3$ : C, 64.30; H, 6.58; N, 21.09. Found: C, 64.38; H, 6.61; N, 21.02.

**1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene (7).** Into a 500 mL two-necked round-bottom equipped with a reflux condenser was placed 4-bromobenzophenone (**5**) (10.444 g, 0.04 mol) and zinc dust (7.848 g, 0.12 mol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. After THF (200 mL) was added, the mixture was cooled down to 0 °C, into which  $\text{TiCl}_4$  (11.38 g, 6.6 mL, 0.06 mol) was added dropwise, then warmed slowly to room temperature and refluxed overnight. Afterward, the reaction mixture was cooled to room temperature, filtered and washed with diethyl ether. After most of the solvent was evaporated, the filtrate was poured into 1 M HCl solution (100 mL), and extracted by DCM three times. The organic layer was combined and washed with brine and water, and then dried over  $\text{MgSO}_4$ . After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether as eluent. A white solid of 1,2-bis(4-bromophenyl)-1,2-diphenylethene (**6**) was obtained in 94.1% yield (9.226 g), mp 159.9 °C.

Into a 500 mL round-bottom flask was added  $\text{PdCl}_2(\text{PPh}_3)_2$  (468.9 mg, 0.668 mmol),  $\text{CuI}$  (254.5 mg, 1.336 mmol),  $\text{PPh}_3$  (525.7 mg, 2.004 mmol), **6** (8.188 g, 16.7 mmol), and a mixture of THF/TEA/piperidine (100:80:20 v/v/v) (200 mL) under nitrogen. After the catalysts were completely dissolved, (trimethylsilyl)acetylene (9.44 mL, 66.8 mmol) was injected into the flask. After stirred at 50 °C for three days, the formed solid was removed by filtration and washed with diethyl ether. The filtrate was concentrated by a rotary evaporator and the crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate mixture (200:1 by volume) as eluent. The obtained product was recrystallized from methanol and THF mixture. White solid of **7** was obtained in 51.5 % yield (4.517 g). mp 175.9 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.19 (m, 4H), 7.08 (m, 6H), 6.93 (m, 8H), 0.21 (d, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 144.4, 143.5, 141.4, 131.9, 131.8, 131.7, 128.2, 127.2, 121.5, 105.6, 94.9, 0.5.

**1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (2).** Into a 500 mL round-bottom flask was placed **7** (4.2 g, 8 mmol) and THF (100 mL). Then KOH (3.59 g, 64 mmol) dissolved in methanol (100 mL)

was added. The mixture was stirred at room temperature overnight. After most of the solvent was evaporated, 1 M HCl solution (70 mL) was added, then extracted by DCM three times. The organic layer was combined and washed with brine and water, and then dried over MgSO<sub>4</sub> for an hour. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether as eluent. Pale yellow solid of 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene was obtained in 85.9 % yield (2.615 g). mp 164.7 °C. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3290, 3058, 2106, 1599, 1498, 1244, 822, 702, 611. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.23 (m, 4H), 7.10 (m, 6H), 6.95 (m, 8H), 3.04 (d, 2H). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 7.23 (m, 4H), 7.12 (m, 6H), 6.95 (m, 8H), 4.15 (d, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 144.3, 143.2, 141.2, 131.9, 131.5, 128.0, 127.1, 120.4, 83.9, 77.7. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (ppm): 144.0, 142.8, 141.0, 131.6, 131.3, 131.1, 128.5, 127.4, 120.3, 83.8, 81.6. Anal. Calcd for C<sub>30</sub>H<sub>20</sub>: C, 94.70; H, 5.30; Found: C, 94.28; H, 5.43.

**1-(6-Bromohexyloxy)benzene (9).** This monomer was prepared according to the procedures similar to those of **4a**. Phenol (2.353 g, 25 mmol) and 1,6-dibromohexane (6.710 g, 27.5 mmol) were used and a colorless liquid of 1-(6-bromohexyloxy)benzene was obtained; yield: 72.3 % (4.650 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.28 (t, 2H), 6.90 (m, 3H), 3.96 (t, 2H), 3.42 (t, 2H), 1.89 (m, 2H), 1.80 (m, 2H), 1.51 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 159.3, 129.6, 120.8, 114.7, 67.8, 34.0, 32.9, 29.4, 28.2, 25.6.

**1-(6-Azidohexyloxy)benzene (10).** This monomer was prepared according to the procedures similar to those of **1a**. **9** (2.572 g, 10 mmol) and NaN<sub>3</sub> (0.780 g, 12 mmol) were used and a pale yellow liquid 1-(6-azidohexyloxy)benzene was obtained; yield: 94.6 % (2.075 g). IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2938, 2094, 1598, 1496, 1245, 1172, 1035, 754, 691. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.27 (t, 2H), 6.90 (m, 3H), 3.95 (t, 2H), 3.27 (t, 2H), 1.79 (m, 2H), 1.63 (m, 2H), 1.46 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 159.4, 129.7, 120.8, 114.7, 67.8, 51.6, 29.4, 29.0, 26.7, 25.9.

**1,2-Bis{4-[1-(6-phenoxyhexyl)-1,2,3-triazol-4-yl]phenyl}-1,2-diphenylethene (11).** Into a 10 mL Schlenk tube were added monomers of **2** (38.0 mg, 0.1 mmol), **10** (65.8 mg, 0.3 mmol) and catalyst of Cu(PPh<sub>3</sub>)<sub>3</sub>Br (3.8 mg, 4 mol% of **2**). After being evacuated and refilled with nitrogen three times, DMF (1.0 mL) was injected into the tube to dissolve the reactants. The mixture was stirred at 60 °C overnight. After cooled to room temperature, the solvent was poured into 1 M HCl solution (50 mL), and extracted by DCM three times. The organic layer was combined and washed with brine and water, and then dried over MgSO<sub>4</sub>. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using hexane/chloroform mixture (1:1 by volume) as eluent. A

light yellow solid of **11** was obtained in 82.8 % yield (67.7 mg). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 2931, 1595, 1491, 1240, 1041, 820, 756, 696.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ),  $\delta$  (TMS, ppm): 8.47 (d, 2H), 7.59 (m, 4H), 7.23 (m, 4H), 7.12 (m, 6H), 7.00 (m, 8H), 6.86 (m, 6H), 4.33 (m, 4H), 3.88 (m, 4H), 1.82 (m, 4H), 1.65 (m, 4H), 1.40 (m, 4H), 1.26 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ),  $\delta$  (ppm): 159.1, 146.5, 143.5, 143.2, 140.9, 131.8, 131.2, 129.9, 129.5, 128.4, 127.2, 125.1, 121.7, 120.8, 114.8, 67.6, 49.9, 30.0, 28.9, 26.0, 25.4.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 159.2, 147.8, 143.9, 143.7, 141.0, 132.1, 131.6, 129.7, 128.9, 128.1, 126.9, 125.2, 120.8, 119.6, 114.7, 67.7, 50.5, 30.5, 29.2, 26.4, 25.8. Anal. Calcd for  $\text{C}_{54}\text{H}_{54}\text{N}_6\text{O}_2$ : C, 79.19; H, 6.65; N, 10.26; Found: C, 78.91; H, 6.78; N, 10.28.

### Polymer Synthesis

Click polymerizations of diyne **2** with triazides **1a** and **1b** were carried out under nitrogen using Schlenk techniques. Typical experimental procedures for the polymerization of **2** with **1a** are given below as an example.

Into a 10 mL Schlenk tube were placed **1a** (68.2 mg, 0.10 mmol), **2** (57.1 mg, 0.15 mmol), and  $\text{Cu}(\text{PPh}_3)_3\text{Br}$  (5.6 mg, 4 mol% of **2**). After being evacuated and refilled with nitrogen three times, DMF (1.0 mL) was injected into the tube to dissolve the reactants. The mixture was stirred at 60 °C for 7 h. Then the reaction was diluted with chloroform (5 mL) and added dropwise into 300 mL of hexane through a cotton filter under stirring. The precipitates were allowed to stand for 2 h, collected by filtration, and dried under vacuum at room temperature to a constant weight.

Characterization Data of *hb*-P**1a**. Yellow powder; yield: 86.6 %.  $M_w$  9800; PDI 4.32. IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3290, 2937, 2094, 1605, 1504, 1244, 1178, 1018, 823, 700.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ),  $\delta$  (TMS, ppm): 8.46, 7.59, 7.23, 7.12, 6.99, 6.86, 6.76, 4.32, 4.13, 3.87, 3.30, 2.00, 1.81, 1.65, 1.52, 1.39, 1.28.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.65, 7.56, 7.47, 7.46, 7.23, 7.10, 6.97, 6.74, 4.34, 3.89, 3.27, 3.03, 2.08, 1.91, 1.74, 1.62, 1.48, 1.39.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 157.2, 147.7, 143.8, 143.6, 141.9, 141.0, 132.1, 131.6, 129.8, 128.9, 128.7, 128.0, 127.9, 126.8, 125.3, 119.6, 113.9, 113.7, 67.7, 51.6, 50.7, 50.4, 31.0, 30.5, 29.3, 29.0, 26.4, 25.8.

*hb*-P**1b**. The polymer was prepared from monomer **1b** (59.8 mg, 0.10 mmol) and **2** (57.1 mg, 0.15 mmol) using  $\text{Cu}(\text{PPh}_3)_3\text{Br}$  (5.6 mg) as catalyst in DMF (1.0 mL) at 60 °C for 5 h. Yellow powder; yield: 88.3 %.  $M_w$  12400; PDI 4.28. IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3289, 2941, 2094, 1604, 1504, 1244, 1180, 1041, 825, 702.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ),  $\delta$  (TMS, ppm): 8.48, 7.59, 7.24, 7.13, 6.99, 6.88, 6.80, 4.39, 4.13, 3.94, 3.36, 1.97, 1.73, 1.66.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.69, 7.55, 7.47, 7.46, 7.23, 7.21, 7.09, 6.96, 6.75, 4.43, 3.95, 3.35, 3.02, 2.08, 1.78.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 156.7, 147.5, 143.6, 143.4, 143.1, 141.9, 141.2, 140.7, 131.8, 131.5, 131.3, 129.6, 128.9,

128.7, 128.4, 127.8, 127.7, 126.7, 125.1, 119.5, 113.5, 83.7, 77.2, 67.0, 66.8, 51.2, 50.6, 50.0, 30.7, 27.3, 26.5, 26.2, 25.7.

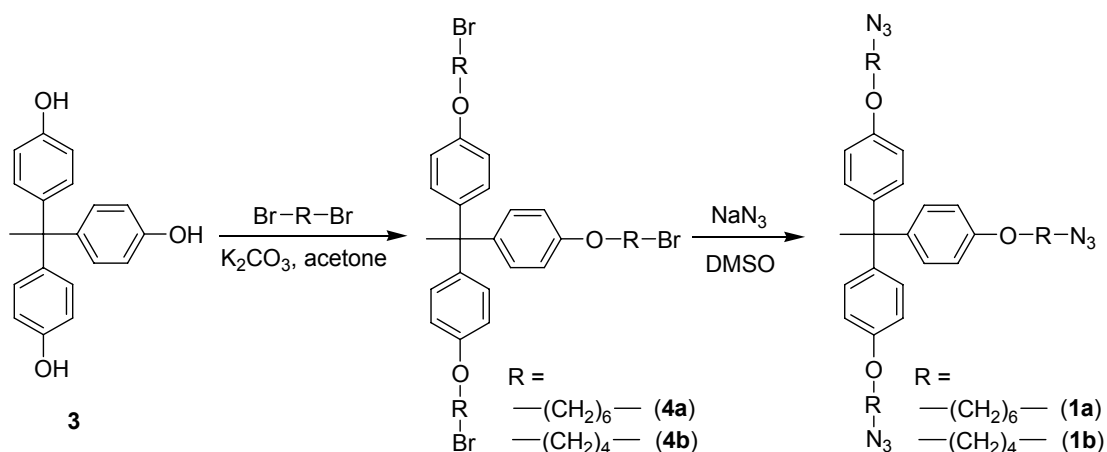
### Preparation of Polymer Aggregates

Stock solutions of *hb-P1a* and *hb-P1b* in THF with concentrations of  $10^{-4}$  M were prepared, respectively. Aliquots of these stock solutions were transferred to 10 mL volumetric flasks, into which appropriate volumes of THF and water were added dropwise under vigorous stirring to furnish  $10^{-5}$  M solutions with different water contents (0–90 vol %). UV and PL spectra were immediately performed once the solutions were prepared.

### References

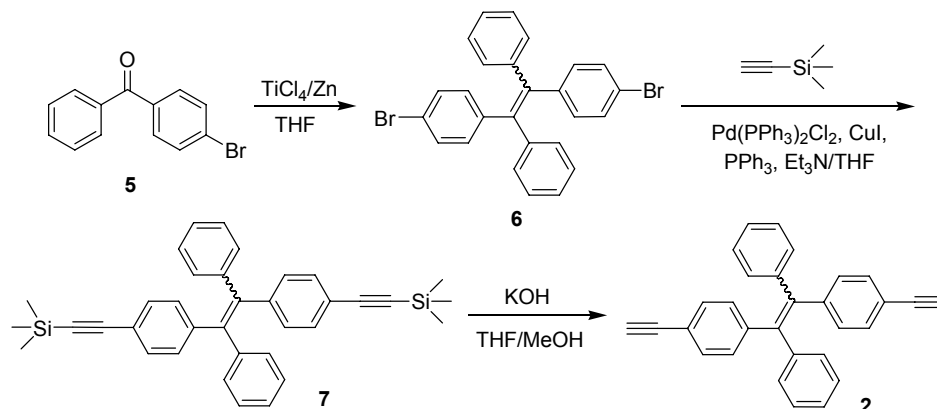
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### Scheme S1 Synthetic Routes to triazide Monomers **1a** and **1b**.

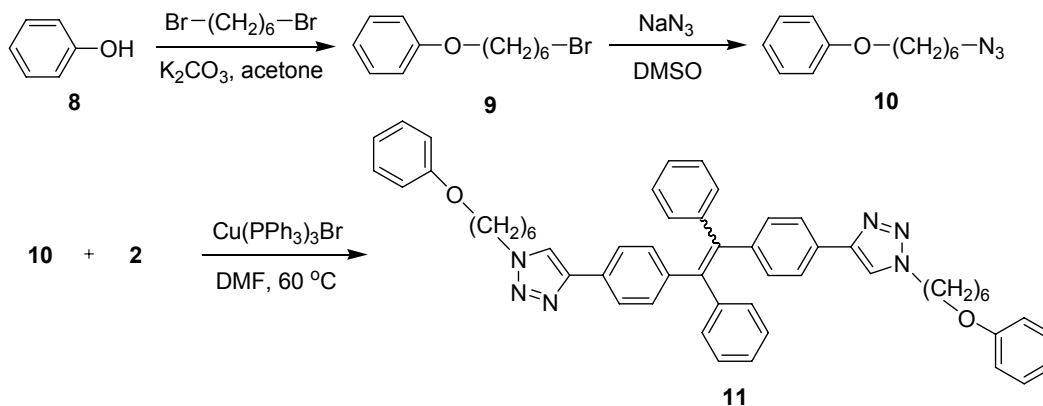




**Scheme S2** Synthetic Routes to diyne Monomer **2**.



**Scheme S3** Synthetic Routes to Model Compound **11**.

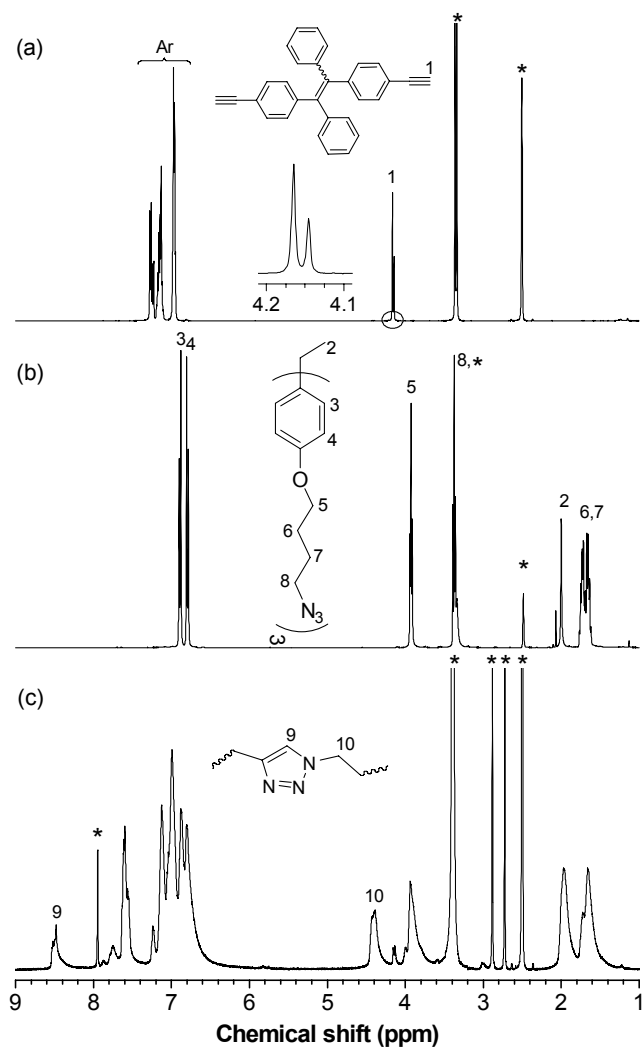


**Table S1** The Condition of Polymerization of **2** and **1**<sup>a</sup>.

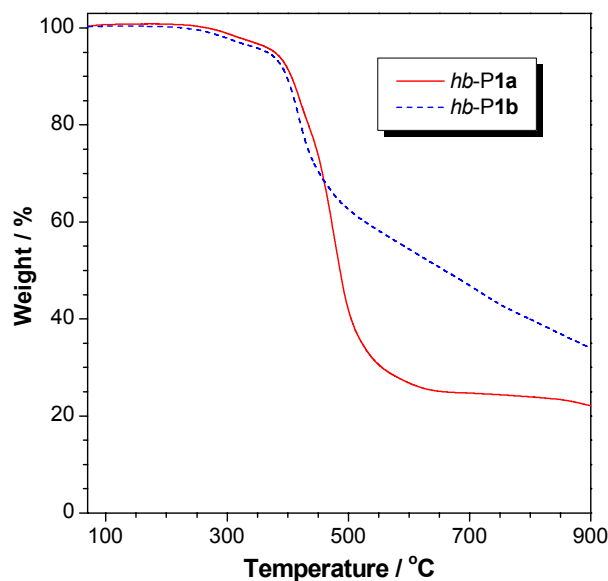
no.	monomers	<i>t</i> (h)	yield (%)	$M_w^b$	PDI <sup>b</sup>	solubility <sup>c</sup>
1	<b>2</b> + <b>1a</b>	7.0	86.6	9800	4.32	√
2	<b>2</b> + <b>1b</b>	5.0	88.3	12400	4.28	√

<sup>a</sup> Polymerization reactions carried out in DMF at  $60^\circ\text{C}$  under nitrogen using  $\text{Cu}(\text{PPh}_3)_3\text{Br}$  as catalyst; [cat.] = 6 mM, [**2**] = 0.15 M, [**2**]:[**1**] = 3:2. <sup>b</sup> Relative (*r*) value estimated by GPC in THF of the basis of a linear polystyrene calibration. <sup>c</sup> Solubility tested in common organic solvents; √ = completely soluble.

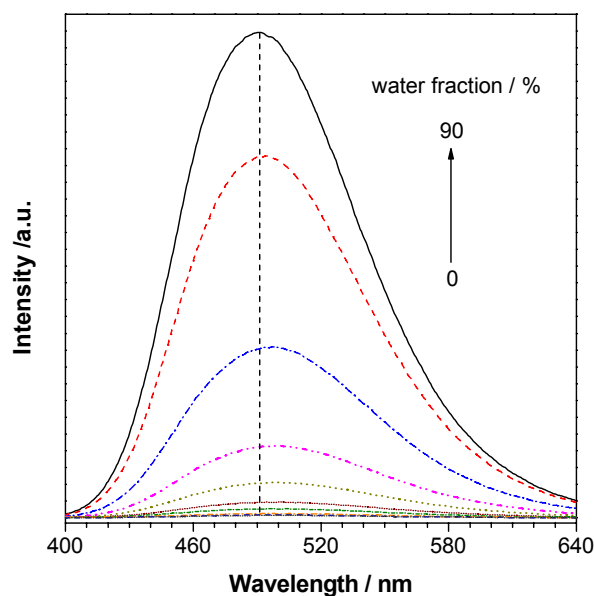




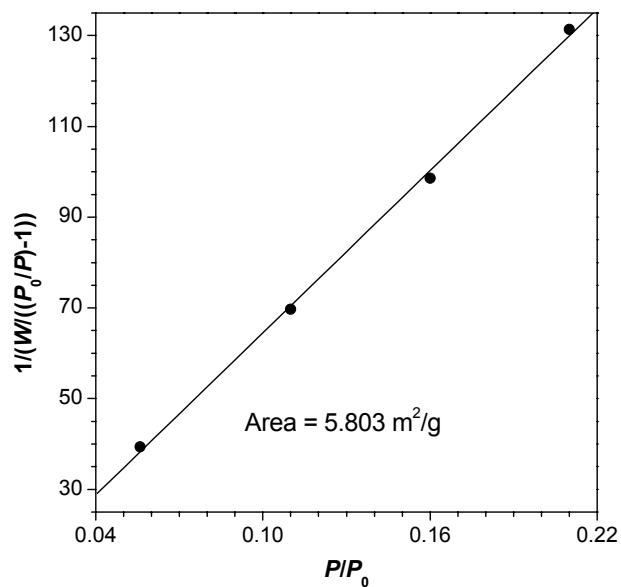
**Fig. S2**  $^1\text{H}$  NMR spectra of (a) **2**, (b) **1b** and (c) **hb-P1b** in  $\text{DMSO-}d_6$ . The solvent peaks are marked with asterisks.



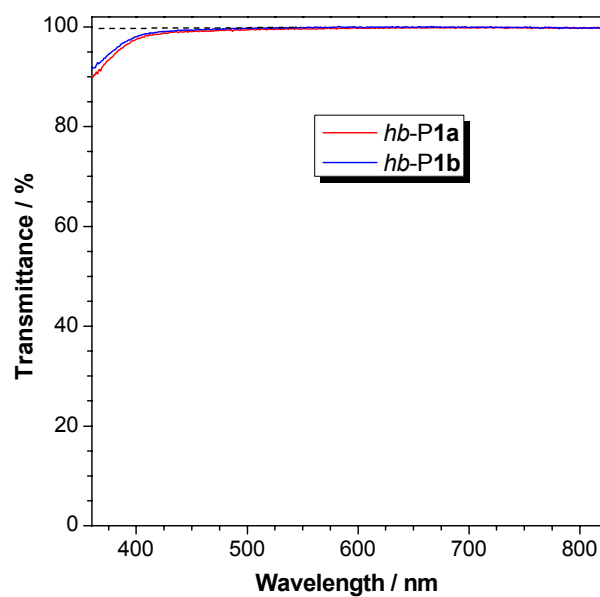
**Fig. S3** TGA thermograms of **hb-P1a** and **hb-P1b** recorded under  $\text{N}_2$  at a heating rate of 20  $^{\circ}\text{C}/\text{min}$ .



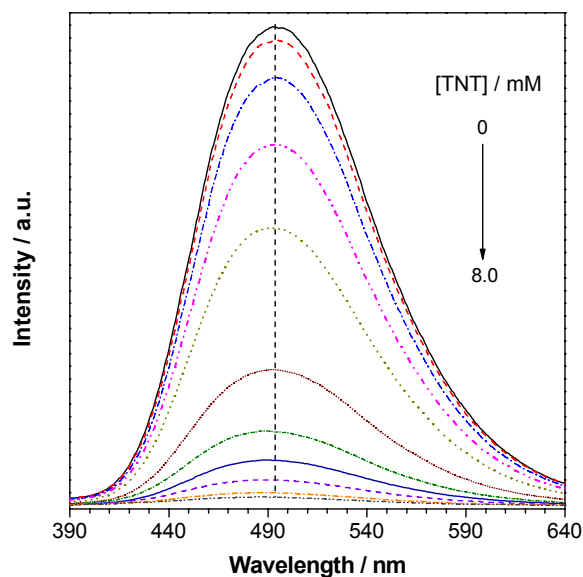
**Fig. S4** PL spectra of *hb-P1b* in THF/water mixtures with different fractions of water.  $\lambda_{\text{ex}} = 332$  nm. Polymer concentration: 10  $\mu\text{M}$ .



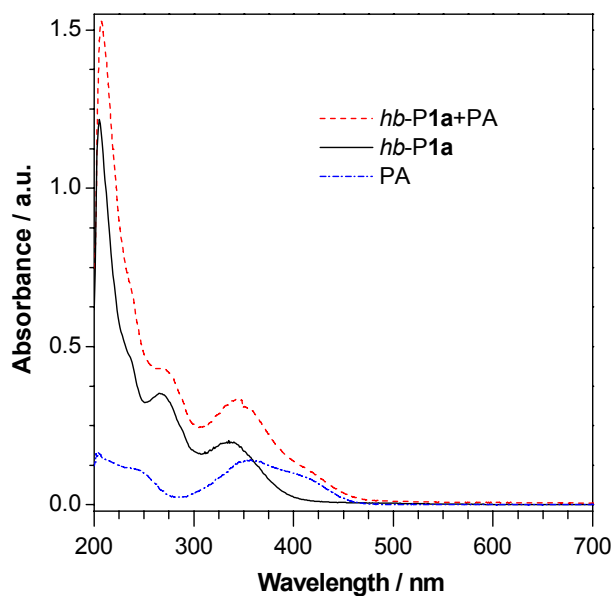
**Fig. S5** The BET plot of *hb-P1a* calculated from  $\text{N}_2$  absorption.



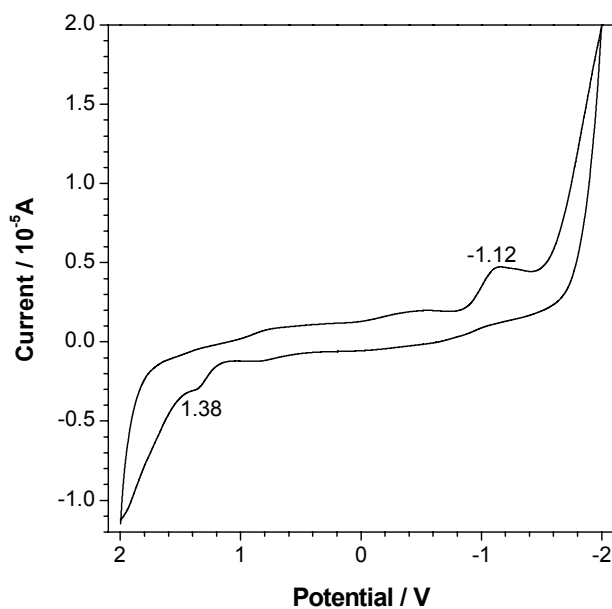
**Fig. S6** Light transmission spectra of spin-coated films of *hb-P1a* and *hb-P1b*. The thicknesses are 24.1 and 20.0 nm, respectively.



**Fig. S7** PL spectra of *hb-P1a* in the THF/ methanol mixture (1:9 v/v) containing different amounts of 2,4,6-trinitrotoluene (TNT). Polymer concentration: 10  $\mu$ M; excitation wavelength: 333 nm.



**Fig. S8** Absorption spectra of PA, *hb-P1a* and their mixture in THF/water ( $f_w = 90\%$ ), [PA]: 9  $\mu\text{M}$ , [*hb-P1a*]: 10  $\mu\text{M}$ .



**Fig. S9** Cyclic voltammograms of *hb-P1a* in  $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$  at 50 mV/s.  $E_{\text{HOMO}} = -e(E^{\text{ox}} + 4.4)$ ,  $E_{\text{LUMO}} = -e(E^{\text{red}} + 4.4)$ .  $E^{\text{ox}}$  and  $E^{\text{red}}$  of *hb-P1a* are 1.38 V and -1.12 V, respectively. And  $E^{\text{red}}$  of TNT is reported to be -0.7 V (S. Zahn, T. M. Swager, *Angew. Chem. Int. Ed.*, 2002, **41**,4225).