Electronic Supporting Information

# HyperbranchedConjugatedPoly(tetraphenylethene):Synthesis,Aggregation-InducedEmission,Photopatterning,Optical Limiting and Explosive Detection

Rongrong Hu,<sup>ab</sup> Jacky W. Y. Lam,<sup>ab</sup> Jianzhao Liu,<sup>ab</sup> Herman H. Y. Sung,<sup>b</sup> Ian D. Williams,<sup>b</sup> Zhounan Yue,<sup>c</sup> Kam Sing Wong,<sup>c</sup> Matthew M. F. Yuen<sup>d</sup> and Ben Zhong Tang\*<sup>abe</sup>

<sup>a</sup>Fok Ying Tung Research Institute, The Hong Kong University of Science &
 Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong, China, <sup>b</sup>Department of Chemistry and State Key Laboratory of Molecular Neuroscience, HKUST,
 <sup>c</sup>Department of Physics, HKUST, <sup>d</sup>Department of Mechanical Engineering, HKUST and <sup>e</sup>Department of Polymer Science and Engineering, Zhejiang University.

## **Table of Contents**

### Synthesis and Characterizations

- Table S1. Crystal Data and Structure Refinement for Compound Z–1.
- Table S2. Crystal Data and Structure Refinement for Compound *E*–1.
- Fig. S1. GPC chromatogram of *hb*–P1.

Fig. S2. Emission spectra of crystals of Z-1 and E-1. Excitation wavelength: 380 nm.

Fig. S3. IR spectra of (A) 3, (B) 1,3,5–2, and (C) 1,2,4–2.

**Fig. S4.** <sup>1</sup>H NMR spectra of (A) **3** and (B) 1,3,5-2 in dichloromethane- $d_2$ .

**Fig. S5.** <sup>13</sup>C NMR spectra of (A) **3** and (B) 1,3,5–**2** in dichloromethane- $d_2$ .

Fig. S6. MS spectrum of 1,3,5–2.

**Fig. S7.** MS spectrum of 1,2,4–2.

**Fig. S8.** (A) Photographs of 1,2,4–2 in THF/water mixtures with different water fractions ( $f_w$ ) taken under 365 nm UV illumination from a hand-held UV lamp. (B) Emission spectra of 1,2,4–2 in THF/water mixtures. (C) Plot of ( $I/I_o$ ) values versus the compositions of the aqueous mixtures. Solution concentration: 10 µM; excitation wavelength: 327 nm.

#### **Experimental Section**

**Synthesis.** The synthetic routes for compound **1** and **3** are shown in Scheme 3 and 4. Detailed experimental procedures are given below.

*4*-(*2*-*Trimethylsilylethynyl)benzophenone* (6). Into a 100 mL two-necked round-bottom flask were added 70.1 mg (0.1 mmol) of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 19 mg (0.1 mmol) of CuI, 13 mg (0.05 mmol) of PPh<sub>3</sub>, 1.3 g (5 mmol) of 4-bromobenzophenone (5), and a solvent mixture of THF/Et<sub>3</sub>N (5 mL/50 mL) in an atmosphere of nitrogen. After the catalysts were completely dissolved, 0.9 mL (6.5 mmol) of (trimethylsiyl)acetylene was injected into the flask and the mixture was stirred at 70 °C for 24 h. The formed solid was removed by filtration and washed with diethyl ether. The solvent was removed and the crude product was purified on a silica-gel column using hexane as eluent. A pale brown solid was obtained in 85.5% yield. IR (KBr), ν (cm<sup>-1</sup>): 2158 (m, C≡C), 1649 (vs, C=O). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), *δ* (TMS, ppm): 7.77 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.57 (m, 3H), 7.48 (m, 2H), 0.27 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), *δ* (TMS, ppm): 195.96 (C=O), 137.34, 136.93, 132.55, 131.76, 129.94, 129.89, 128.34, 127.31, 104.04 (≡ C-Ar), 97.82 (≡C-Si), -0.18 [Si(CH<sub>3</sub>)<sub>3</sub>]. HRMS (MALDI-TOF): *m/z* 278.0110 (M<sup>+</sup>, calcd 278.1127).

 $1-\{[4-(2-Trimethylsilyl)ethynyl]phenyl]-1,2,2-triphenylethene (9).$  To a solution of diphenylmethane (7, 2.02 g, 12 mmol) in dry tetrahydrofuran (20 mL) was added 4 mL of 2.5 M hexane solution of *n*-butyllithium (10 mmol) at 0 °C under an argon atmosphere. The resultant orange-red solution was stirred for 30 min at the same temperature, into which 9 mmol of **6** was added. The reaction mixture was allowed to warm to room temperature and quenched by addition of an aqueous solution of ammonium chloride after 6 h. The organic layer was extracted with 50 mL

dichloromethane three times and the combined organic layers were washed with saturated brine solution and dried over anhydrous MgSO4. The solvent was evaporated and the resultant crude alcohol  $\mathbf{8}$  (containing excess diphenylmethane) was subjected to acid-catalyzed dehydration as follows. Compound 8 was dissolved in about 80 mL of toluene in a 100 mL Schlenk flask fitted with a Dean-Stark trap. A catalytic amount of p-toluenesulfonic acid (342 mg, 1.8 mmol) was added and the mixture was refluxed for 3 h. After cooled to room temperature, the toluene layer was washed with 10% aqueous NaHCO<sub>3</sub> solution ( $2 \times 25$  mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified by silica-gel column chromatography using ethyl acetate/hexane (1:100) mixture to afford pure compound **9** in 95% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.22 (d, J = 8.0 Hz, 2H), 7.11 (m, 9H), 7.02 (m, 6H), 6.98 (d, J = 8.0Hz, 2H), 0.24 (s, 9 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ(TMS, ppm): 143.62, 142.85, 142.77, 142.67, 141.03, 139.58, 130.73, 130.68, 130.67, 130.63, 127.20, 127.10, 127.05, 126.04, 125.98, 125.96, 120.19, 104.66 (=C-Ar), 93.67 (=C-Si), -0.64 [Si(CH<sub>3</sub>)<sub>3</sub>]. HRMS (MALDI-TOF): *m*/*z* 428.2183 (M<sup>+</sup>, calcd 428.1960).

*1-(4-Ethynylphenyl)-1,2,2-triphenylethene (3).* Into a 100 mL round bottom flask were placed 40 mL of THF solution of **9** (1.57 g, 3 mmol) and 12 mL of 1 M THF solution of tetrabutylammonium fluoride. After stirring for 3 h, 40 mL of water was added and the mixture was extracted with 200 mL of dichloromethane three times. The organic layer was washed with brine twice. The mixture was dried over 5 g of anhydrous sodium sulfate for 2 h. The crude product was condensed and purified on a silica-gel column using hexane as eluent. A light yellow solid of **3** was obtained in 93.5% yield. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3364 (≡C–H stretching), 3085, 3025, 2118 (C≡C stretching), 1596, 1492, 1441, 1261, 1072, 1025, 857, 823, 759, 742, 697, 672, 629, 597, 516. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  (TMS, ppm): 7.22 (d, 2H, *J* = 8 Hz), 7.10 (m, 9 H), 7.01 (m, 6H), 6.98 (d, 2H, *J* = 8 Hz), 3.07 (s, 1H, HC≡). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 145.36, 144.53, 144.26, 144.16, 144.04, 142.64, 140.94, 132.14, 132.00, 131.98, 131.91, 128.56, 128.51, 128.42, 128.39, 127.45, 127.36,

127.34, 127.14, 120.62, 84.27 (≡C–Ar), 77.96 (≡C–H). HRMS (MALDI-TOF): *m*/*z* 356.1281 (M<sup>+</sup>, calcd 356.1565).

1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene (10). Into a 250 mL two-necked round-bottom flask with a reflux condenser were placed 12.1 g (18 mmol) of zinc dust and 4.18 g (15 mmol) of 6. The flask was evacuated under vacuum and flushed with dry nitrogen for three times. 100 mL of THF was then added. The mixture was cooled to -78 °C and 1 mL (9 mmol) of TiCl<sub>4</sub> was slowly added. The mixture was slowly warmed to room temperature, stirred for 0.5 h, and then refluxed overnight. The reaction was quenched with 10% aqueous K<sub>2</sub>CO<sub>3</sub> solution and large amount of water was added to the solution until the solid turned to grey or white. The mixture was extracted with dichloromethane three times and the organic layers were combined and washed with brine twice. Solvent was evaporated under reduced pressure and the crude product was purified on a silica-gel column using hexane as eluent. A yellow solid was obtained in 90.2% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.21 (m, 4H), 7.10 (m, 6H), 6.96 (m, 8H), 0.22 and 0.24 [18H, Si(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ(TMS, ppm): 143.94, 143.82, 143.00, 142.95, 140.88, 131.44, 131.34, 131.30, 131.19, 127.88, 127.73, 126.83, 126.74, 121.14, 120.97, 105.16 and 105.11 ( $\equiv$ C-Ar), 94.55 and 94.42 ( $\equiv$ C-Si), -0.06 [-Si(CH<sub>3</sub>)<sub>3</sub>]. HRMS (MALDI-TOF): *m*/*z* 524.2887 (M<sup>+</sup>, calcd 524.2356).

*1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (1).* Into a 100 mL round bottom flask were placed 40 mL of THF solution of **10** (1.57 g, 3 mmol) and 12 mL of 1 M THF solution of tetrabutylammonium fluoride. The mixture was stirred for 3 h and the reaction was terminated by adding 40 mL of water. The mixture was extracted with 200 mL dichloromethane three times. The organic layers were combined and washed with brine twice. The mixture was dried over 5 g of anhydrous sodium sulfate for 2 h. After solvent evaporation, the crude product was purified on a silica-gel column using hexane as eluent. A light yellow solid of **1** was obtained in 92.1% yield. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3339 ( $\equiv$ C–H stretching), 3027, 3025, 2928, 2109 (C $\equiv$ C stretching), 1601, 1497, 1444, 1404, 1247, 1107, 1072, 1019, 862, 818, 698, 627, 601. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$ (TMS, ppm): 7.23 (m, 4H), 7.12 (m, 6H), 6.98 (m, 8H), 3.05 and

3.04 (2H, HC $\equiv$ ). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$ (TMS, ppm): 144.91, 143.76, 141.73, 132.28, 132.14, 131.97, 131.94, 128.66, 128.51, 127.65, 127.52, 120.94, 84.17 ( $\equiv$ C–Ar), 78.13 ( $\equiv$ C–H). HRMS (MALDI-TOF): *m*/*z* 380.1525 (M<sup>+</sup>, calcd 380.1565).

1,3,5-Tri[4-(1,2,2-triphenylethenyl)phenyl]benzene (2). Into a thoroughly baked and carefully evacuated 15 mL Schlenk tube were placed TaCl<sub>5</sub> (74 mg, 0.21 mmol) and Ph<sub>4</sub>Sn (84 mg, 0.20 mmol) under nitrogen in a golvebox. 4 mL of freshly distilled toluene was then injected into the tube using a syringe. After stirring at room temperature under nitrogen for 10 min, a solution of **3** (0.80 g, 2.24 mmol) in 5 mL of anhydrous toluene was injected. The reaction was quenched by the addition of methanol after 16 h. The solvent was removed under reduced pressure and the crude product was purified by silica-gel chromatography using hexane as eluent. 1,2,4-2(yellow solid) and 1,3,5-2 (white solid) were obtained in 27% and 53% yield, respectively. Characterization data: 1,3,5–2: IR (KBr), v (cm<sup>-1</sup>): 3058, 3025, 1598, 1492, 1447, 1074, 1027, 846, 821, 753, 700, 623, 576. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  (TMS, ppm): 7.60 (s, 3H), 7.37 (d, J = 9.3 Hz, 6H), 7.10–7.02 (m, 51 H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>), δ (TMS, ppm): 143.15, 143.09, 142.47, 140.82, 140.61, 139.87, 138.06, 131.02, 130.60, 130.52, 127.11, 127.02, 126.96, 125.87, 125.80, 125.74, 125.65, 123.67. HRMS (MALDI-TOF): m/z 1068.339 (M<sup>+</sup>, calcd 1068.4695). 1,2,4-1: IR (KBr), v (cm<sup>-1</sup>): 3058, 3024, 1598, 1493, 1442, 1075, 1028, 851, 815, 753, 699, 628, 573. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.62 (s, 1H), 7.54 (m, 2H), 7.39 (m, 3H), 7.09 (m, 45H), 6.97, 6.91, and 6.85 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$ (TMS, ppm): 143.76, 143.73, 143.68, 142.98, 142.86, 142.07, 141.98, 141.55, 141.12, 140.87, 140.67, 140.53, 140.47, 139.58, 139.38, 139.03, 139.95, 138.80, 138.20, 131.77, 131.44, 131.40, 131.32, 130.82, 130.60, 129.27, 129.22, 128.74, 127.75, 127.67, 127.62, 126.46, 126.11, 125.66, 124.50. HRMS (MALDI-TOF): *m*/*z* 1068.5785 (M<sup>+</sup>, calcd 1068.4695).

**Polymerization**. The polymerization reaction and manipulation were carried out under nitrogen using Schlenk techniques in a vacuum-line system except for the purification of the resultant polymer, which was done in an open atmosphere. Typical experimental procedures for the polymerization of **1** are given below. Into a thoroughly baked and carefully evacuated 15 mL Schlenk tube was placed TaBr<sub>5</sub> under nitrogen in a golvebox. Freshly distilled toluene was then injected into the tube using a syringe. The mixture was stirred for 10 min, into which a solution of **1** in anhydrous toluene was added. The resultant mixture was stirred at room temperature under nitrogen for 9 h and quenched by the addition of methanol. The resultant mixture was diluted with 2 mL of THF and added dropwise through a cotton filter to 200 mL methanol under stirring. The precipitate was allowed to stand for 24 h and then filtered. The polymer was washed with methanol three times and dried in a vacuum oven at 40 °C to a constant weight. A yellow powder was obtained in 96% yield.  $M_w$  157,800;  $M_w/M_n$  2.65. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3295 ( $\equiv$ C–H stretching), 3057, 3028, 2921, 2857, 2374, 2106 (C $\equiv$ C stretching), 1598, 1505, 1443, 1110, 1073, 1020, 844, 811, 746, 697. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  (TMS, ppm): 7.06 (broad, aromatic protons).

# Table S1. Crystal Data and Structure Refinement for Compound Z–1

# (CCDC 834091)

Empirical formula	C <sub>30</sub> H <sub>20</sub>			
Formula weight	380.46	380.46		
Temperature	173(2) K			
Wavelength	1.54178 Å			
Crystal system	Orthorhombic			
Space group	P2(1)2(1)2(1)			
Unit cell dimensions	a = 9.32330(10) Å	= 90°.		
	b = 14.8844(2) Å	$=90^{\circ}$ .		
	c = 15.9251(2) Å	$=90^{\circ}.$		
Volume	2209.95(5) $\text{\AA}^3$			
Z	4			
Density (calculated)	$1.143 \text{ Mg/m}^3$			
Absorption coefficient	$0.491 \text{ mm}^{-1}$	$0.491 \text{ mm}^{-1}$		
F(000)	800	800		
Crystal size	0.28 x 0.24 x 0.17 mm	0.28 x 0.24 x 0.17 mm <sup>3</sup>		
Theta range for data collection	4.07 to 67.44°.	4.07 to 67.44°.		
Index ranges	-11<=h<=8, -17<=k<=	-11<=h<=8, -17<=k<=16, -19<=l<=19		
Reflections collected	15917	15917		
Independent reflections	2238 [R(int) = 0.0258]	2238 [R(int) = 0.0258]		
Completeness to theta = $66.50^{\circ}$	98.6 %			
Absorption correction	Semi-empirical from e	Semi-empirical from equivalents		
Max. and min. transmission	1.00 and 0.93	1.00 and 0.93		
Refinement method	Full-matrix least-squar	Full-matrix least-squares on $F^2$		
Data / restraints / parameters	2238 / 0 / 271	2238 / 0 / 271		
Goodness-of-fit on $F^2$	1.014	1.014		
Final R indices [I>2sigma(I)]	R1 = 0.0253, wR2 = 0.0253, w	R1 = 0.0253, wR2 = 0.0704		
R indices (all data)	R1 = 0.0276, wR2 = 0.0276, w	R1 = 0.0276, $wR2 = 0.0716$		
Largest diff. peak and hole	$0.083 \text{ and } -0.096 \text{ e.\AA}^{-3}$	$0.083 \text{ and } -0.096 \text{ e.Å}^{-3}$		

# Table S2. Crystal Data and Structure Refinement for Compound *E*-1

# (CCDC 834092)

Empirical formula	$C_{30} H_{20}$	$C_{30} H_{20}$	
Formula weight	380.46	380.46	
Temperature	173(2) K	173(2) K	
Wavelength	1.54178 Å		
Crystal system	Monoclinic		
Space group	C2/c		
Unit cell dimensions	a = 20.918(14)  Å	= 90°.	
	b = 5.5926(18) Å	$= 107.11(7)^{\circ}.$	
	c = 19.778(9) Å	= 90°.	
Volume	2211.4(19) Å <sup>3</sup>		
Z	4		
Density (calculated)	1.143 Mg/m <sup>3</sup>	1.143 Mg/m <sup>3</sup>	
Absorption coefficient	$0.490 \text{ mm}^{-1}$	$0.490 \text{ mm}^{-1}$	
F(000)	800	800	
Crystal size	0.20 x 0.04 x 0.03 mm	0.20 x 0.04 x 0.03 mm <sup>3</sup>	
Theta range for data collection	4.42 to 66.99°.	4.42 to 66.99°.	
Index ranges	-23<=h<=23, -6<=k<	-23<=h<=23, -6<=k<=5, -23<=l<=18	
Reflections collected	4861		
Independent reflections	1790 [R(int) = 0.1206	1790 [R(int) = 0.1206]	
Completeness to theta = $66.50^{\circ}$	91.2 %	91.2 %	
Absorption correction	Semi-empirical from	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.53	1.00 and 0.53	
Refinement method	Full-matrix least-squa	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	1790 / 0 / 136	1790 / 0 / 136	
Goodness-of-fit on $F^2$	1.005	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.0613, w	R1 = 0.0613, wR2 = 0.0864	
R indices (all data)	R1 = 0.1431, wR2 = 0	R1 = 0.1431, wR2 = 0.0995	
Largest diff. peak and hole	0.164 and -0.160 e.Å	$0.164 \text{ and } -0.160 \text{ e.Å}^{-3}$	



Fig. S1. GPC chromatogram of *hb*-P1.



**Fig. S2.** Photoluminescence spectra of crystals of Z-1 and E-1. Excitation wavelength: 380 nm.



Fig. S3. IR spectra of (A) 3, (B) 1,3,5–2 and (C) 1,2,4–2.



**Fig. S4.** <sup>1</sup>H NMR spectra of (A) **3** and (B) 1,3,5-2 in dichloromethane- $d_2$ .



**Fig. S5.** <sup>13</sup>C NMR spectra of (A) **3** and (B) 1,3,5–**2** in dichloromethane- $d_2$ .



Fig. S6. MS spectrum of 1,3,5–2.



Fig. S7. MS spectrum of 1,2,4–2.



**Fig. S8.** (A) Photographs of 1,2,4–2 in THF/water mixtures with different water fractions ( $f_w$ ) taken under 365 nm UV illumination from a hand-held UV lamp. (B) Emission spectra of 1,2,4–2 in THF/water mixtures. (C) Plot of ( $I/I_o$ ) values versus the compositions of the aqueous mixtures. Solution concentration: 10 µM; excitation wavelength: 327 nm.