

**Supporting Information**  
**For**  
**Fluorescent supramolecular polymers based on**  
**Pillar[5]arene for OLED device fabrication**

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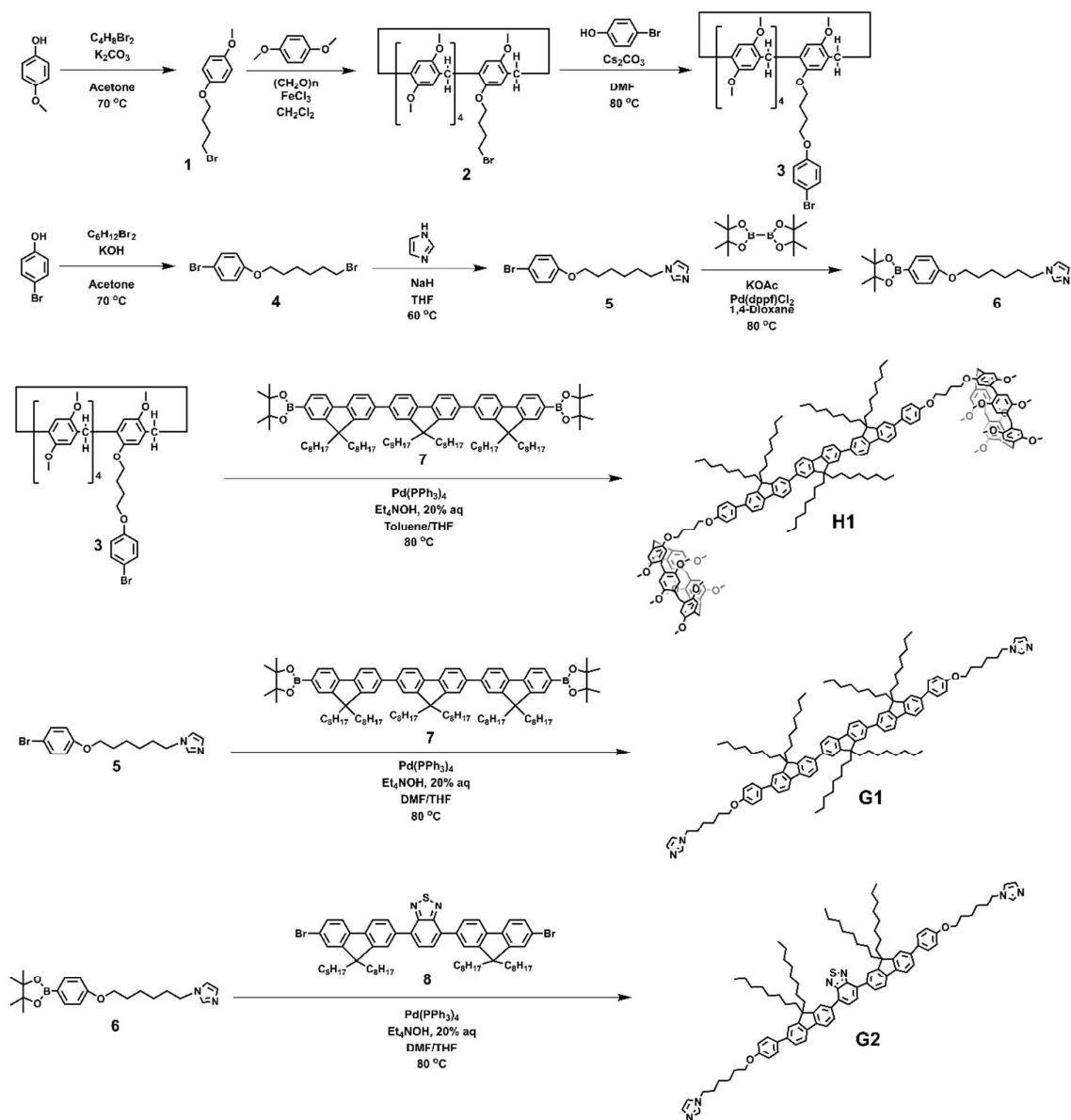
## **1. Measurement and characterization**

$^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded using a Bruker-500 and 600 spectrometers operating at 500 or 600 and 125 MHz at 298K. Chemical shifts are reported as  $\delta$  values (ppm) relative to an internal tetramethylsilane (TMS) standard. 2D DOSY experiments were performed on a Bruker 600 MHz spectrometer. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Melting point of certain compound was measured by Shanghai Precision & Scientific Instrument CO., LTD. WRR melting point detector. MALDI-TOF-MS measurements were carried out on a Waters SYNAPT G2-Si or Bruker Autoflex III Smartbeam. The viscosity was measured with a digital viscometer (model LVDV-I+) from Brookfield Engineering Laboratories, Inc. UV-vis absorption spectra were obtained on a HP 8453 spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescent spectrophotometer. PL quantum efficiency was measured by an absolute PL quantum yield measurement system (C11347-01, Hamamatsu Photonics) under air condition.

## **2. Device fabrication and measurement**

Indium tin oxide (ITO) coated glass with a sheet resistance of  $10\ \Omega$  per square was used as the substrate. The substrates were carefully cleaned with acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol under an ultrasonic bath and treated with  $\text{O}_2$  plasma for 5 min. Then a PEDOT : PSS layer (Clevios P VPCH4083) was spin-coated onto a pre-cleaned ITO glass substrate, dried at  $150\ ^\circ\text{C}$  for 15 min to remove residual water, and then the devices were moved into a glove box under the nitrogen-protected environment. PVK (poly(9-vinylcarbazole)) was later spin-coated from chlorobenzene solution onto the PEDOT : PSS layer. And the emitting layers were spin-coated onto the PVK layer from a filtered o-xylene solution. The samples were transferred into a chamber and kept under vacuum ( $3.0 \times 10^{-4}$  Pa) for 5h. A Ba layer and an Al layer were deposited consecutively on top of the PFN (poly [(9,9-bis(3'-(N, N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]) to form the cathode. EL spectra were measured by an optical analyzer, Photo Research PR705. The current density and luminance versus driving voltage were detected by a Keithley 2420 and a Konica Minolta chromameter CS-200.

### 3. Synthesis route

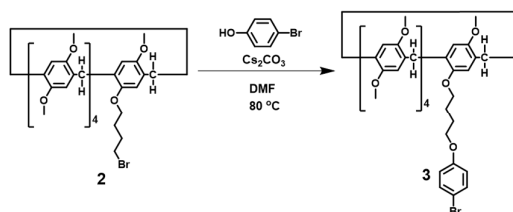


**Scheme S1.** Synthetic routes to monomers

#### 4. Synthesis of monomers.

Compounds **1**,<sup>S1</sup> **2**,<sup>S1</sup> **4**,<sup>S2</sup> **7**<sup>S3</sup> and **8**<sup>S4</sup> were prepared according to previously reported publications and other synthetic procedures are described as follows:

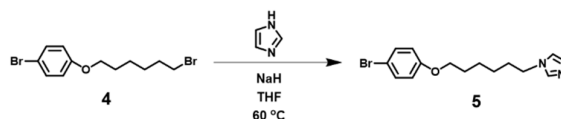
##### Synthesis of Compound 3



A solution of compound **2** (1.74 g, 2 mmol), 4-bromophenol (0.38 g, 2.2 mmol) and cesium carbonate (1.3 g, 4 mmol) in 10 mL DMF was heated and stirred at 80 °C for 12h. After the reaction was completed, 120 mL brine (6 M) was added and then extracted with EtOAc 3 times. The organic phase was dried with  $\text{Na}_2\text{SO}_4$ . The filtrate was collected and concentrated by rotary evaporation. The crude product was isolated by column chromatography (n-hexane : dichloromethane = 1:1) to give a white powder. Yield: 1.72 g, 89%.

M.p. 78~80 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.31 (m, 2H), 6.85 – 6.67 (m, 12H), 3.93 (t,  $J$  = 6 Hz, 2H), 3.89 (t,  $J$  = 6 Hz, 2H), 3.78 (dd,  $J$  = 8, 5 Hz, 10H), 3.68 – 3.59 (m, 27H), 1.93 (qd,  $J$  = 8, 3 Hz, 4H). MALDI-TOF ( $m/z$ ): calcd for  $\text{C}_{54}\text{H}_{59}\text{BrO}_{11}$  962.3220, found  $[\text{M}]^+$  962.2719,  $[\text{M} + \text{Na}]^+$  985.2626.

##### Synthesis of Compound 5

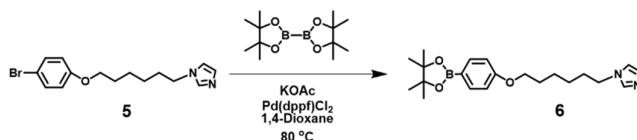


Sodium hydride (60% dispersion in mineral oil, 0.24 g, 6 mmol) was suspended in 10 mL anhydrous THF at 0 °C. Imidazole (0.34 g, 5 mmol) was dissolved in 5 mL anhydrous THF and added dropwise. After gas evolution stopped, compound **4** (1.68 g, 5 mmol) in 5mL dry THF was added dropwise. The resultant mixture was then stirred at room temperature overnight. The reaction was quenched by adding water into the solution by dropwise. Then the organic solvent was removed and diethyl ether (10 mL) was added. This solution was washed 3 times with water, and the combined aqueous layers was re-extracted with diethyl ether (10 mL). The collected organic phase was dried with  $\text{Na}_2\text{SO}_4$ . The filtrate was collected and concentrated by rotary evaporation. The crude product was isolated by column chromatography (n-hexane : dichloromethane : ethyl acetate = 2:2:1) to give a yellow solid. Yield: 1.9 g, 92%.

M.p. 51~53 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (s, 1H), 7.38 – 7.32 (m, 2H), 7.05 (s, 1H), 6.89 (s, 1H), 6.77 – 6.72 (m, 2H), 3.93 (t,  $J$  = 7 Hz, 2H), 3.89 (t,  $J$  = 6 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.75 (dt,  $J$  = 12, 5 Hz, 2H), 1.48 (dt,  $J$  = 15, 7 Hz, 2H), 1.35 (ddd,  $J$  = 18, 9, 6 Hz, 2H).

MALDI-TOF ( $m/z$ ): calcd for  $C_{15}H_{19}BrN_2O$  323.2340, found  $[M]^+$  323.2016.

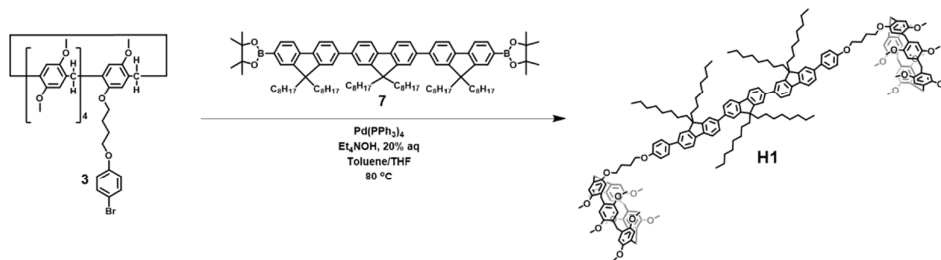
### Synthesis of Compound 6



Compound **5** (3.23 g, 10 mmol), bis(pinacolato)diboron (3.81 g, 15 mmol) and potassium acetate (4 g, 40 mmol) were added to a 100 mL two-necked round bottomed flask and dissolved in 60 mL 1,4-dioxane. Then  $Pd(dppf)Cl_2$  (150 mg) was added. The mixture was heated at reflux and stirred for 36 h under argon. After the mixture was cooled to room temperature, it was poured into brine (6 M) and extracted 3 times with dichloromethane. The collected organic phase was dried with  $Na_2SO_4$ . The filtrate was collected and concentrated by rotary evaporation. The crude product was then isolated by column chromatography (dichloromethane : ethyl acetate = 10:1) to give a yellow solid. Yield: 2.8 g, 76%.

M.p. 62~64 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.72 – 7.68 (m, 2H), 7.46 (s, 1H), 7.09 (s, 1H), 6.87 (s, 1H), 6.85 – 6.81 (m, 2H), 3.95 – 3.88 (m, 4H), 1.82 – 1.70 (m, 4H), 1.63 – 1.55 (m, 2H), 1.44 (t,  $J$  = 7 Hz, 12H), 1.40 – 1.34 (m, 2H). MALDI-TOF ( $m/z$ ): calcd for  $C_{21}H_{31}BN_2O_3$  370.3000, found  $[M]^+$  370.2623.

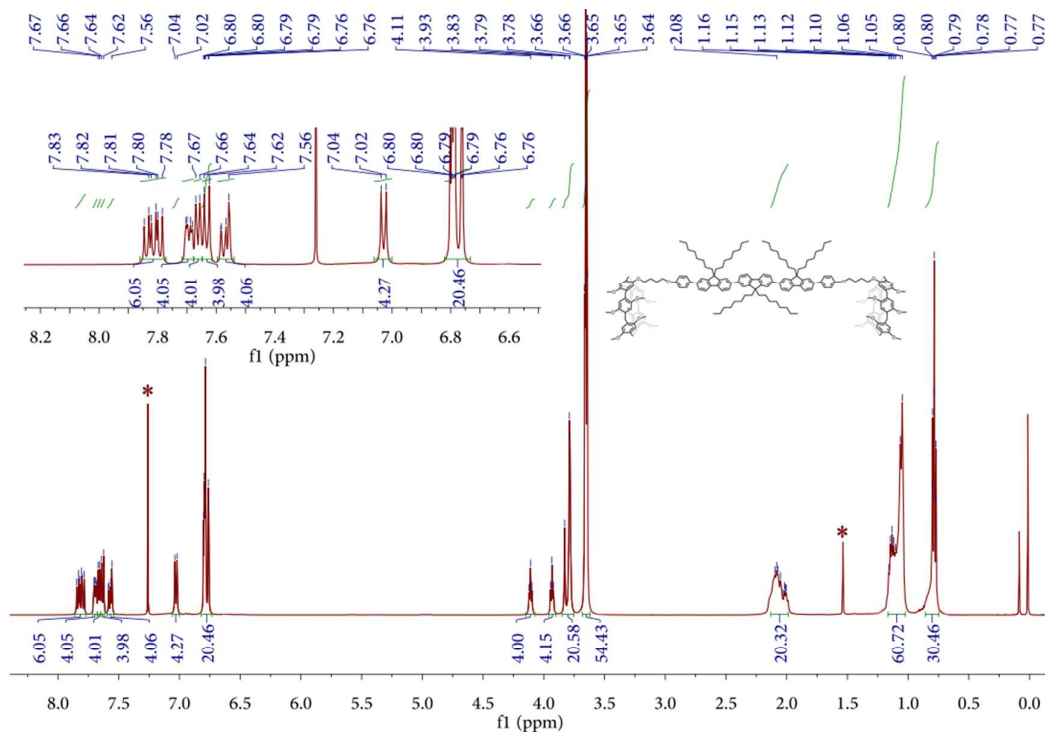
### Synthesis of Monomer H1



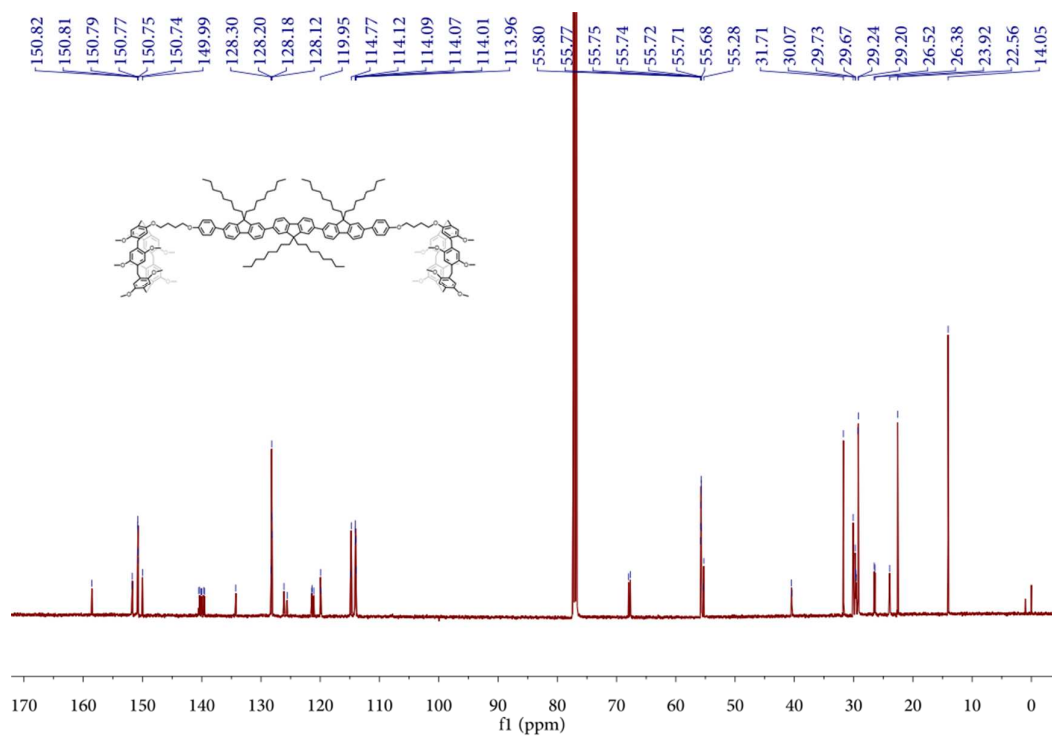
Compound **3** (1.58 g, 1.6 mmol), compound **7** (1.13 g, 0.8 mmol) and tetrakis-(triphenylphosphine) palladium [ $Pd(PPh_3)_4$ ] (45 mg, 0.04 mmol) were added to a 50 mL two-necked round-bottomed flask. Anhydrous toluene (16 mL) and anhydrous THF (8 mL) and 20% aqueous tetraethylammonium hydroxide (2 mL) were added to the flask under argon. The solution was heated at 80 °C and stirred for 48 h under argon. After the mixture was cooled to room temperature, it was poured into brine (6 M) and extracted 3 times with dichloromethane. The collected organic phase was dried with  $Na_2SO_4$ . The filtrate was collected and concentrated by rotary evaporation. The crude product was then isolated by column chromatography (n-hexane : dichloromethane = 1:1) to give a white powder. Monomer H1 was further purified through high-performance liquid chromatography (HPLC) with solvent THF to give a white powder. Yield: 1.46 g, 64%.

M.p. 116~118 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.86 – 7.74 (m, 6H), 7.71 – 7.66 (m, 4H), 7.63 (dd,  $J$  = 15, 7 Hz, 8H), 7.56 (dd,  $J$  = 10, 3 Hz, 4H), 7.02 (t,  $J$  = 7 Hz, 4H), 6.82 – 6.72 (m, 20H),

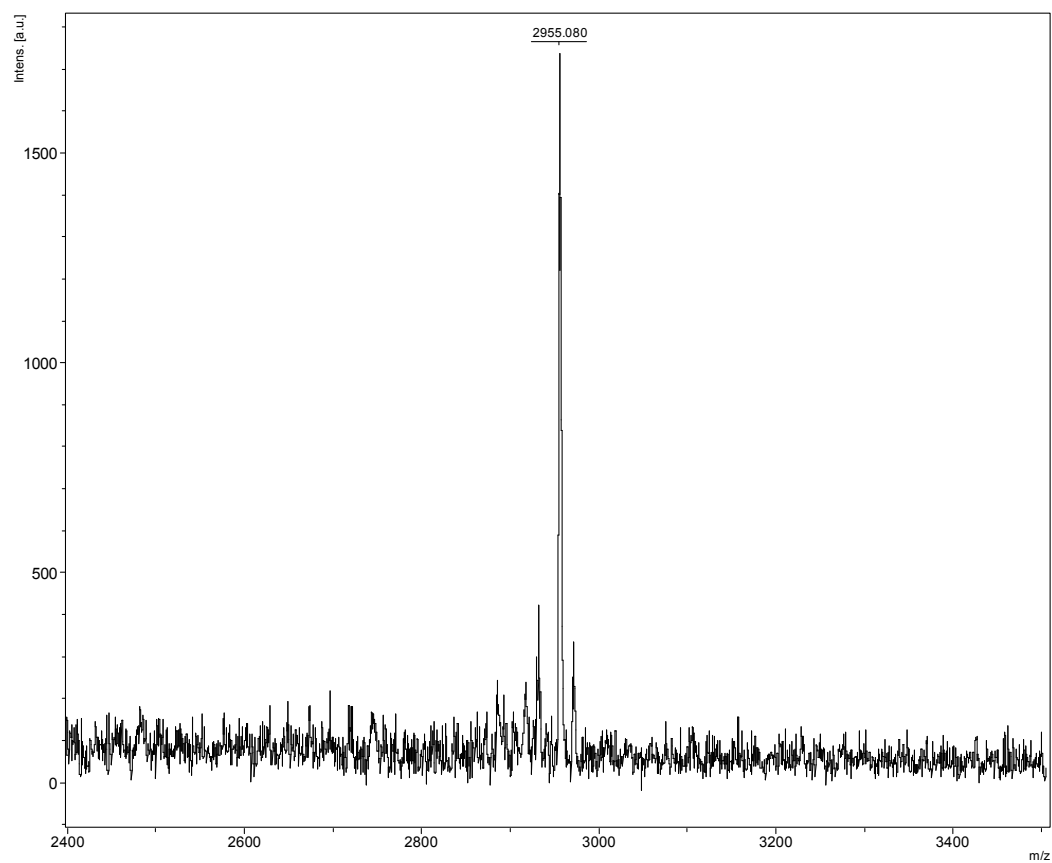
4.12 – 4.07 (m, 4H), 3.92 (t,  $J = 6$  Hz, 4H), 3.84 – 3.73 (m, 20H), 3.68 – 3.60 (m, 54H), 2.16 – 1.95 (m, 20H), 1.18 – 0.98 (m, 60H), 0.86 – 0.70 (m, 30H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 158.54, 151.79, 151.71, 150.82, 150.81, 150.79, 150.77, 150.75, 150.74, 149.99, 140.51, 140.37, 140.09, 140.01, 139.67, 139.54, 134.25, 128.30, 128.20, 128.18, 128.12, 126.12, 125.59, 121.43, 121.39, 121.09, 119.95, 119.87, 114.90, 114.77, 114.12, 114.09, 114.07, 114.01, 113.96, 67.96, 67.68, 55.80, 55.77, 55.75, 55.74, 55.72, 55.71, 55.68, 55.34, 55.28, 40.48, 40.44, 31.71, 30.07, 29.73, 29.67, 29.62, 29.57, 29.24, 29.20, 26.52, 26.38, 23.92, 22.56, 14.05. Anal. calcd for  $\text{C}_{195}\text{H}_{238}\text{O}_{22}$  (%): C, 79.83; H, 8.18; O, 12.00; Found (%): C, 79.57; H, 8.41. MALDI-TOF ( $m/z$ ): calcd for  $\text{C}_{195}\text{H}_{238}\text{O}_{22}$  2934.0270, found  $[\text{M} + \text{Na}]^+$  2955.080.



**Figure S1.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 298 K) of **H1**.

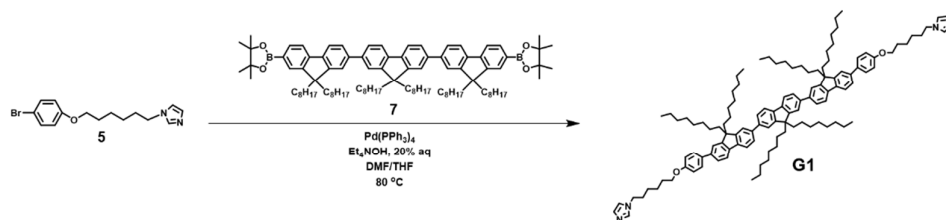


**Figure S2.**  $^{13}\text{C}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ , 298 K) of **H1**.



**Figure S3.** MALDI-TOF MS spectrum of **H1**.

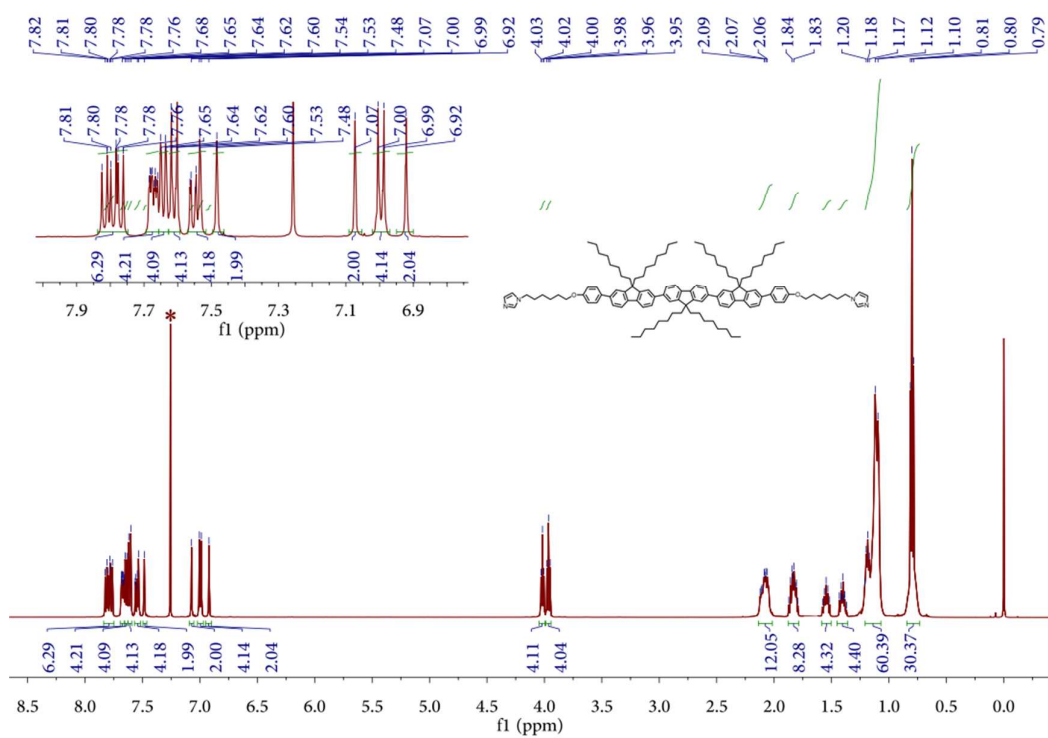
**Synthesis of Monomer G1**



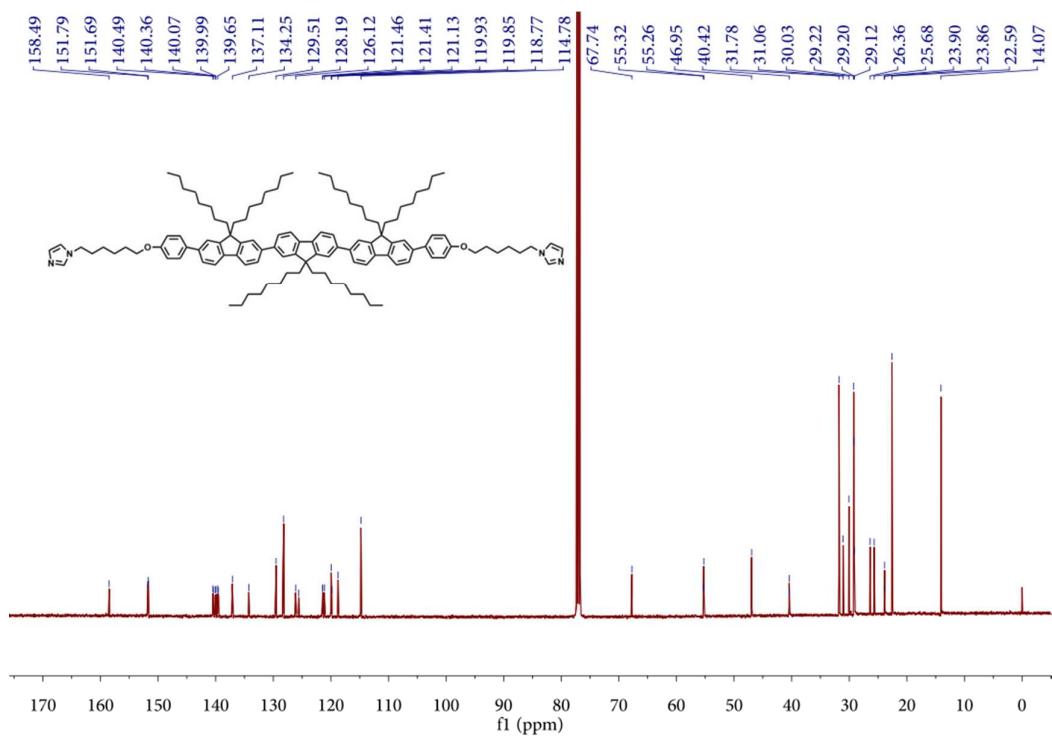
Compound **5** (0.52 g, 1.6 mmol), compound **7** (1.13 g, 0.8 mmol) and tetrakis-(triphenylphosphine) palladium [Pd(PPh<sub>3</sub>)<sub>4</sub>] (45 mg, 0.04 mmol) were added to a 50 mL two-necked round-bottomed flask. Anhydrous toluene (16 mL) and anhydrous THF (8 mL) and 20% aqueous tetraethyl-ammonium hydroxide (2 mL) were added under argon. The solution was heated at 80 °C and stirred for 48h under argon. After the mixture was cooled to room temperature, it was poured into brine (6 M) and extracted 3 times with dichloromethane. The collected organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>. The filtrate was collected and concentrated by rotary evaporation. The crude product was then isolated by column chromatography (n-hexane : dichloromethane = 1:2) to give a yellow powder. Monomer **G1** was further purified through high-performance liquid chromatography (HPLC) with solvent THF to give a yellow powder. Yield: 0.92 g, 71%.

M.p. 52~54 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.84 – 7.74 (m, 6H), 7.71 – 7.59 (m, 12H), 7.57 – 7.52 (m, 4H), 7.48 (s, 2H), 7.07 (s, 2H), 7.02 – 6.98 (m, 4H), 6.92 (t, *J* = 1 Hz, 2H), 4.02 (t, *J* = 6 Hz, 4H), 3.96 (t, *J* = 7 Hz, 4H), 2.16 – 2.00 (m, 12H), 1.89 – 1.78 (m, 8H), 1.59 – 1.50 (m, 4H), 1.40 (ddd, *J* = 15, 9, 6 Hz, 4H), 1.23 – 1.04 (m, 60H), 0.80 (t, *J* = 7 Hz, 30H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm): 158.49, 151.79, 151.69, 140.49, 140.36, 140.07, 139.99, 139.65, 139.52, 137.11, 134.25, 129.51, 128.19, 126.12, 125.58, 121.46, 121.41, 121.13, 119.93, 119.85, 118.77, 114.78, 67.74, 55.32, 55.26, 46.95, 40.42, 40.38, 31.78, 31.06, 30.03, 29.22, 29.20, 29.12, 26.36, 25.68, 23.90, 23.86, 22.59, 14.07. Anal. calcd for C<sub>117</sub>H<sub>158</sub>N<sub>4</sub>O<sub>2</sub> (%): C, 85.04; H, 9.64; N, 3.39; O, 1.94. Found (%): C, 84.79; H, 9.86; N, 3.62. MALDI-TOF (*m/z*): calcd for C<sub>117</sub>H<sub>158</sub>N<sub>4</sub>O<sub>2</sub> 1652.2885, found [M]<sup>+</sup> 1652.017.

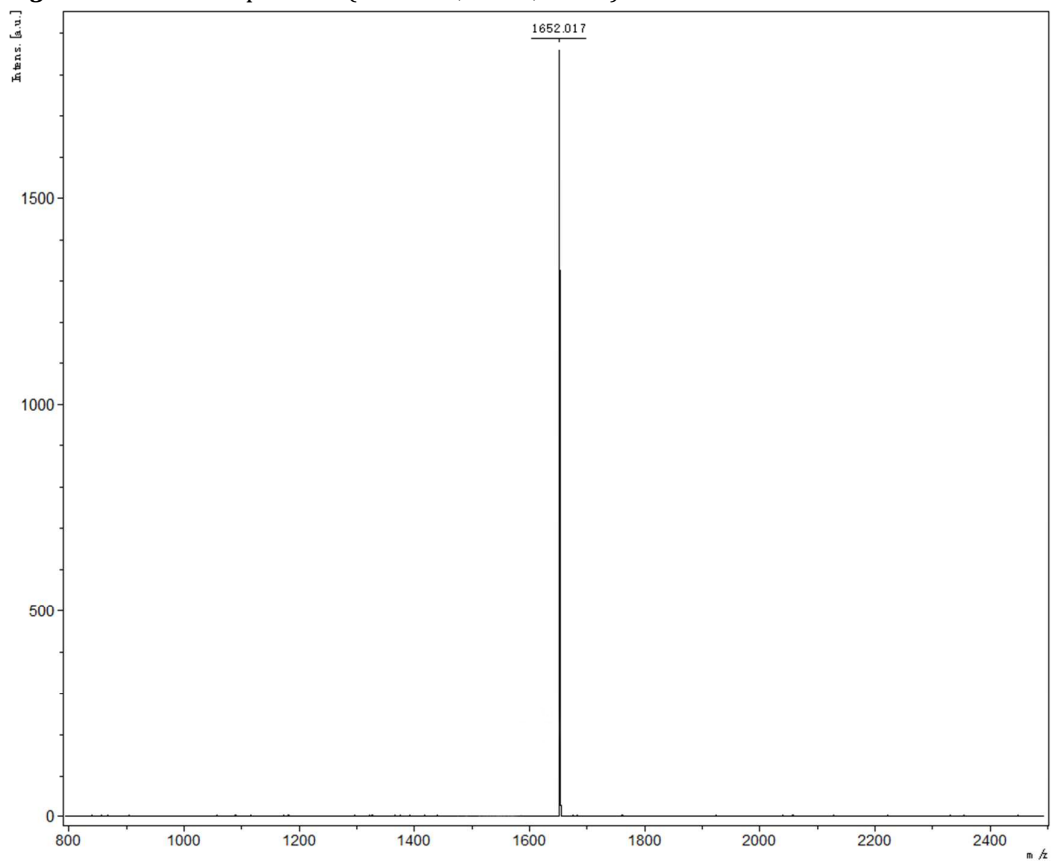




**Figure S4.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 298 K) of **G1**.



**Figure S5.** <sup>13</sup>C NMR spectrum (126 MHz, CDCl<sub>3</sub>, 298 K) of G1.



**Figure S6.** MALDI-TOF MS spectrum of G1.

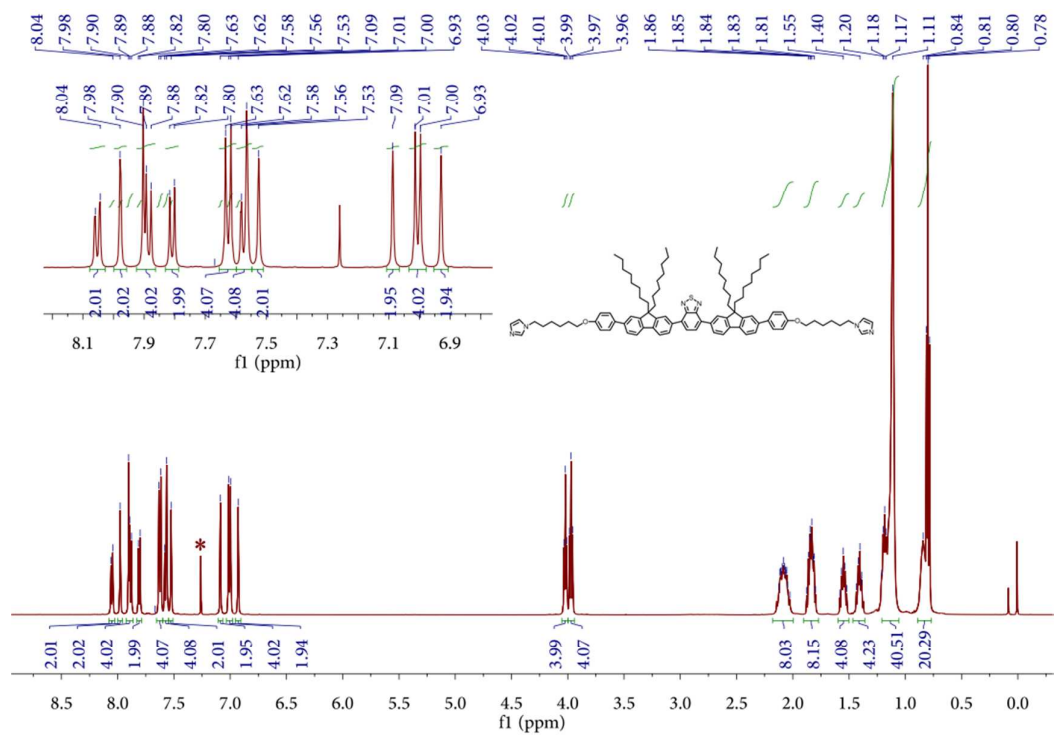
Reaction scheme for the synthesis of G2:

Reactant 6 (a poly(tert-butyl siloxane) with a 4-(6-(1H-imidazol-2-yl)hexyloxy)phenyl end group) reacts with compound 8 (4,4'-bis(bromomethyl)-2,2'-bis(4-(4,5-dithienyl)-1,3,4-thiadiazol-2-yl)benzene) under the following conditions:

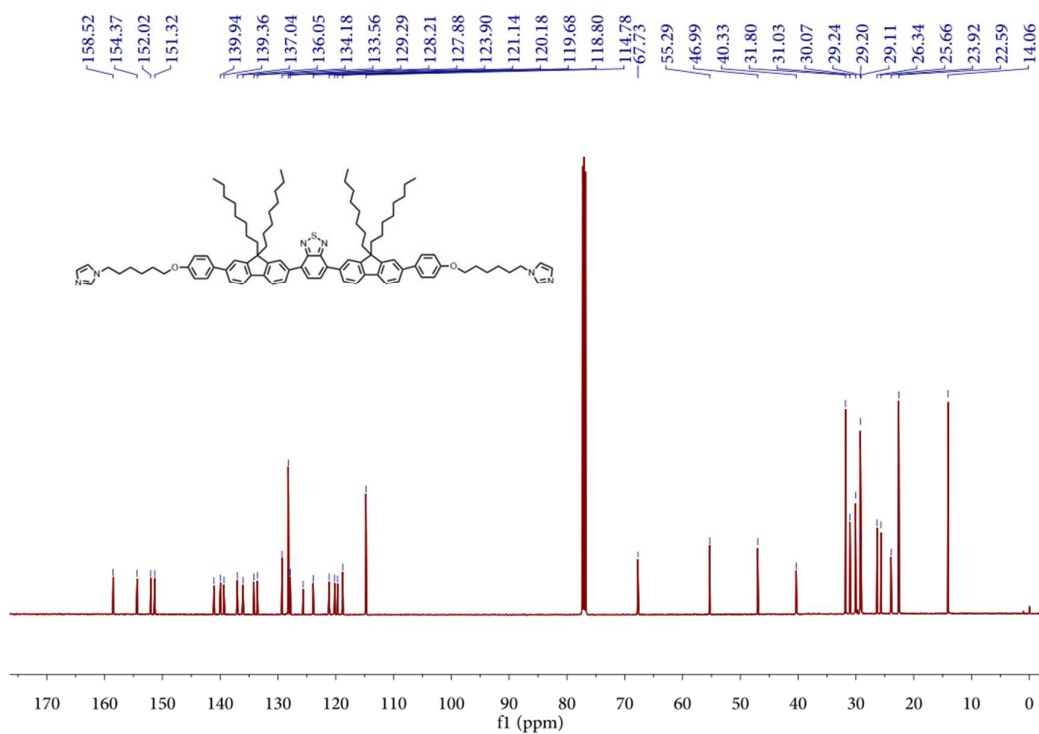
- $\text{Pd(PPh}_3)_4$
- $\text{Et}_3\text{NOH}$ , 20% aq DMF/THF
- 80 °C

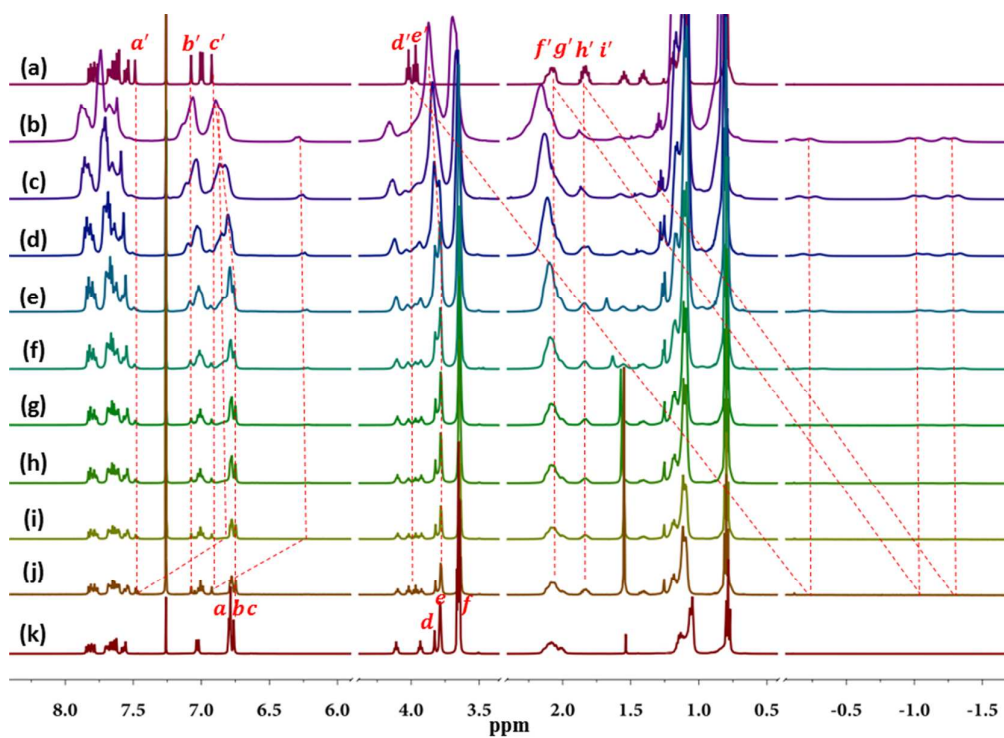
The product is G2, a dendritic molecule with a central 1,3,4-thiadiazole core, four 4,5-dithienyl arms, and four 4-(6-(1H-imidazol-2-yl)hexyloxy)phenyl arms.

M.p. 58~60 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J$  = 7 Hz, 2H), 7.98 (s, 2H), 7.93 – 7.86 (m, 4H), 7.81 (d,  $J$  = 7 Hz, 2H), 7.62 (d,  $J$  = 8 Hz, 4H), 7.57 (d,  $J$  = 8 Hz, 4H), 7.53 (s, 2H), 7.09 (s, 2H), 7.01 (d,  $J$  = 8 Hz, 4H), 6.93 (s, 2H), 4.02 (t,  $J$  = 6 Hz, 4H), 3.97 (t,  $J$  = 7 Hz, 4H), 2.08 (ddt,  $J$  = 19, 16, 6 Hz, 8H), 1.89 – 1.78 (m, 8H), 1.55 (dt,  $J$  = 15, 7 Hz, 4H), 1.44 – 1.36 (m, 4H), 1.21 – 1.06 (m, 40H), 0.81 (dd,  $J$  = 17, 10 Hz, 20H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 158.52, 154.37, 152.02, 151.32, 141.08, 139.94, 139.36, 137.04, 136.05, 134.18, 133.56, 129.29, 128.21, 127.88, 125.64, 123.90, 121.14, 120.18, 119.68, 118.80, 114.78, 67.73, 55.29, 46.99, 40.33, 31.80, 31.03, 30.07, 29.24, 29.20, 29.11, 26.34, 25.66, 23.92, 22.59, 14.06. Anal. calcd for  $\text{C}_{94}\text{H}_{120}\text{N}_6\text{O}_2\text{S}$  (%): C, 80.76; H, 8.65; N, 6.01; O, 2.29; S, 2.29. Found (%): C, 80.40; H, 8.92; N, 5.87; S, 2.07. MALDI-TOF ( $m/z$ ): calcd for  $\text{C}_{94}\text{H}_{120}\text{N}_6\text{O}_2\text{S}$  1398.0940, found  $[\text{M}]^+$  1397.803.

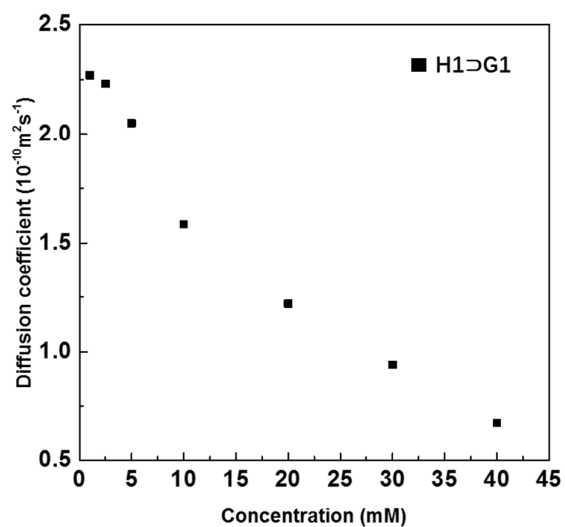


**Figure S7.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 298 K) of **G2**.

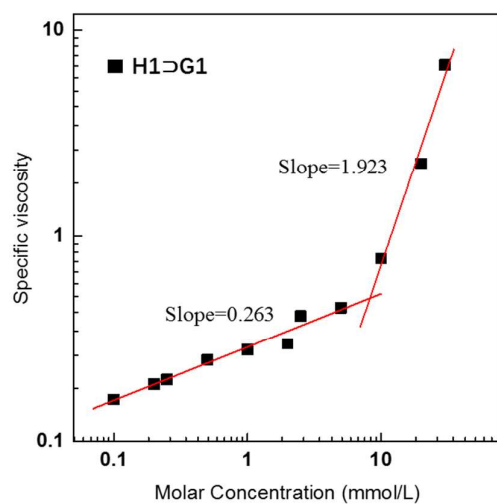




**Figure S10.**  $^1\text{H}$  NMR(500 MHz,  $\text{CDCl}_3$ , 298 K) spectra of (a) 10 mM **G1**, and **H1**⊃**G1** with **H1**:**G1**=1:1 (b) 50 mM, (c) 30 mM, (d) 20 mM, (e) 10 mM, (f) 5 mM, (g) 2.5 mM, (h) 2 mM, (i) 1 mM, (j) 0.5 mM and (k) 10 mM **H1**



**Figure S11.** DOSY (600 MHz, 298 K) plot of solutions in  $\text{CDCl}_3$  of **H1**⊃**G1** with molar ratio **H1**:**G1** =1:1



**Figure S12.** Specific viscosity (298 K) of solutions in  $\text{CHCl}_3$  of **H1⊃G1** (molar ratio at 1:1).

**References:**

- S1. Wang, Y.; Xu, J.-F.; Chen, Y.-Z.; Niu, L.-Y.; Wu, L.-Z.; Tung, C.-H.; Yang, Q.-Z. Photoresponsive supramolecular self-assembly of monofunctionalized pillar[5]arene based on stiff stilbene. *Chem. Commun.* **2014**, 50, 7001-7003.
- S2. Athanasius, J. M.; Patrick, J. M. Dye-sensitized solar cells (DSSCs) based on poly(3-hexylthioacetate thiophene). *Int. J. Phys. Sci.* **2013**, 8, 16-26.
- S3. Zhang, J.; Zhang, K.; Huang, X.; Cai, W.; Zhou, C.; Liu, S.; Huang, F.; Cao, Y. Supramolecular light-emitting polymers for solution-processed optoelectronic devices. *J. Mater. Chem.* **2012**, 22, 12759-12766.
- S4. Scheler, E.; Strohriegel, P. Three Color Random Fluorene-Based Oligomers for Fast Micrometer-Scale Photopatterning. *Chem. Mater.* **2010**, 22, 1410-1419.