

Pyrene-Based Asymmetric Supramolecule: Kinetically Controlled Polymorphic Superstructures by Molecular Self-Assembly

Minwook Park,[†] Won-Jin Yoon,[†] Dae-Yoon Kim,[†] Yu-Jin Choi,[†] Jahyeon Koo,[†] Seok-In Lim,[†] Dong-Gue Kang,[†] Chih-Hao Hsu[‡] and Kwang-Un Jeong^{†*}

1. Experimental details

1.1 Materials: 1-bromooctane (99%, Aldrich), 4,4'-dihydroxybiphenyl (Biphenol, 97%, Aldrich), p-toluenesulfonyl chloride (Tosyl Chloride, 97%, Aldrich), triethylene glycol (Glycol, 99%, Aldrich), triethylamine (TEA, 99%, Aldrich), methyl 3,4,5-trihydroxybenzoate (98%, Aldrich), hydrochloric acid (35%, Showa), dimethyl 5-aminoisophthalate (98%, Aldrich), N,N'-Diisopropylcarbodiimide (DIPC, 99%, Aldrich), 4-(Dimethylamino) pyridinium 4-toluenesulfonate (DPTS, 99%). 1-pyrenemethylamine hydrochloride (95%, Aldrich), 1-hydroxy-7-azabenzotriazole (HOAt, 99%, GL Biochem(shanghai) Ltd), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide (EDC, 98%, TCI), sodium chloride (99%, Aldrich), potassium carbonate (K₂CO₃, 99.5%, Showa), potassium iodide (KI, 99.5%, Showa), sodium hydroxide (NaOH, 93%, Showa) and anhydrous magnesium sulfate (MgSO₄, 99.5%, Showa) were used as received. *N,N*-dimethylformamide (DMF), dimethylene chloride (MC), ethyl acetate (EA), methanol (MeOH), DI-water, and Chloroform (CHCl₃) were purified before use.

1.2 Synthesis

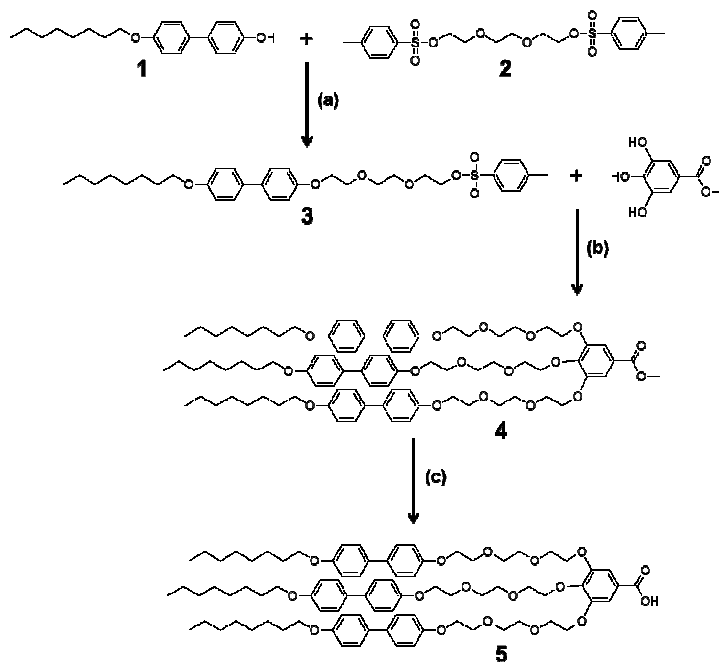


Fig. S1 Schematic illustration; synthetic procedures of reagents, tri-mesogen benzoate derivatives, tri-mesogen benzoic acid derivatives and conditions: (a) K_2CO_3 , DMF, 80 °C for 6 h. (b) K_2CO_3 , DMF, 80 °C for 3 days under N_2 atmosphere, (c) NaOH, THF/MeOH, 60 °C for 2 h.

4-(4'-octyloxy)hydroxybiphenyl (**1**) A solution of 1-bromooctane (11.7 g, 60.58 mmol), 4,4'-dihydroxybiphenyl (13.54 g, 72.71 mmol), K_2CO_3 (8.37 g, 60.56 mmol), and KI (1.01 g, 6.08 mmol) in 80 mL of dried DMF was refluxed for 12 h. After reaction, the resulting mixture was poured in 1000 mL of DI-water and stirring for 8 h to obtain a precipitate. Using a glass filter, the precipitate was filtered and washed with water. The residue dissolved in EA and evaporation, the product was purified by recrystallization from EtOH, reddish product was white crystal (yield = 7.25 g, 40.1 %). ^1H NMR (400 MHz, CDCl_3) : δ 7.46-7.41 (dd, 4H, HF1,F2), 6.95-6.86 (dd, 4H, HE1,E2), 4.73 (s, 1H, HG), 4.00-3.96 (t, 2H, HD), 1.83-1.76 (m, 2H, Hc), 1.48-1.28 (m, 10H, HB1-,B5), 0.90-0.87 (t, 3H, HA).

Triethylene glycol ditosylate (**2**) A solution of p-toluenesulfonyl chloride (40.63 g, 213.11 mmol), triethylen glycol (16 g, 106.54 mmol), and TEA (29.72 mL, 213.08 mmol) in 150 mL of dried MC was stirring at room temperature for 8 h. The precipitation occurs during the reaction. After reaction, MC was poured into mixture, and washed with distilled water several times. The organic layer was dried over MgSO₄. It was purified by column chromatography with silica gel using HEX:EA = 1:1. Resulting product is white solid. (yield = 41 g, 84 %). ¹H NMR (400 MHz, CDCl₃) : δ 7.80-7.78 (d, 4H, HC), 7.35-7.33 (d, 4H, HB), 4.15-4.12 (t, 4H, HD), 3.66-3.64 (t, 4H, HE), 3.52 (s, 4H, HF), 2.44 (s, 6H, HA).

2-(2-(2-(4-(4'-octyloxy)biphenoxy)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**3**) A solution of 1 (4.88 g, 16.35 mmol), 2 (22.50 g, 49.06 mmol) and K₂CO₃ in 150 mL of dried DMF was refluxed for 6 h. After reaction, solvent was removed by evaporation and remaining residue was dissolved in CHCl₃ and washed with distilled water several times. The organic layer was dried over MgSO₄. It was purified by column chromatography with silica gel using HEX:EA = 1:1 and MC:EA = 12:1. Resulting product is white solid (yield = 4.2 g, 44 %). ¹H NMR (400 MHz, CDCl₃) : δ 7.80-7.78 (d, 2H, HJ), 7.46-7.44 (dd, 4H, HF1,F2), 7.32-7.30 (d, 2H, HK), 6.96-6.93 (dd, 4H, HE1,E2), 4.17-4.12 (m, 4H, HG1,G2), 4.00-3.96 (t, 2H, HD), 3.85-3.82 (t, 2H, HH1), 3.71-3.60 (m, 6H, HI1,I2,H2), 2.42 (s, 3H, HL), 1.83-1.76 (m, 2H, HC), 1.50-1.29 (m, 10H, HB1-B5), 0.90-0.87 (t, 3H, HA).

Methyl 3,4,5-tri(2-(2-(2-(4-(4'-octyloxy)biphenoxy)ethoxy)ethoxy)ethoxy) benzoate (**4**) A solution of 3 (4.03 g, 6.89 mmol), methyl 3,4,5-trihydroxybenzoate (0.25 g, 1.36 mmol) and

K_2CO_3 in 40 mL of dried DMF was refluxed for three day. After reaction, solvent was removed by evaporation and remaining residue was dissolved in CHCl_3 and washed with distilled water several times. The organic layer was dried over MgSO_4 . It was purified by column chromatography with silica gel using $\text{CHCl}_3:\text{EA} = 1:1$. Resulting product is white solid (yield = 4.5 g, 46 %). ^1H NMR (400 MHz, CDCl_3) : δ 7.44-7.41 (m, 12H, HF1,F2), 7.29 (s, 2H, HJ), 6.94-6.90 (m, 12H, HE1,E2), 4.25-4.22 (t, 2H, HG2'), 4.20-4.17 (t, 4H, HG2), 4.13-4.09 (m, 6H, HG1), 3.98-3.95 (t, 6H, HD), 3.88-3.80m (m, 12H, HH1,H2), 3.86 (s, 3H, HK), 3.73-3.70 (m, 12H, HI1,I2), 1.82-1.75 (m, 6H, HC), 1.47-1.28 (m, 30H, HB1-B5), 0.90-0.87 (t, 9H, HA).

3,4,5-tri(2-(2-(2-(4-(4'-octyloxy)biphenoxy)ethoxy)ethoxy)ethoxy) benzoic acid (**5**) A solution of **4** (0.5 g, 0.352 mmol), in THF/MeOH (7.6 mL/ 5 mL) was added aqueous NaOH (ca. 10 M, 2.15 mL). The mixture was refluxed for 3 h, and then neutralized with an aqueous hydrochloric acid to obtain a precipitate. The precipitate was filtered off and washed with water. The crude product was purified by reprecipitation with CHCl_3 and EtOH and dried under vacuum to afford **5** as a white waxy solid (yield = 0.47 g, 95 %). ^1H NMR (400 MHz, CDCl_3) : δ 7.44-7.41 (m, 12H, HF1,F2), 7.29 (s, 2H, HJ), 6.94-6.90 (m, 12H, HE1,E2), 4.25-4.22 (t, 2H, HG2'), 4.20-4.17 (t, 4H, HG2), 4.13-4.09 (m, 6H, HG1), 3.98-3.95 (t, 6H, HD), 3.88-3.80m (m, 12H, HH1,H2), 3.73-3.70 (m, 12H, HI1,I2), 1.82-1.75 (m, 6H, HC), 1.47-1.28 (m, 30H, HB1-B5), 0.90-0.87 (t, 9H, HA).

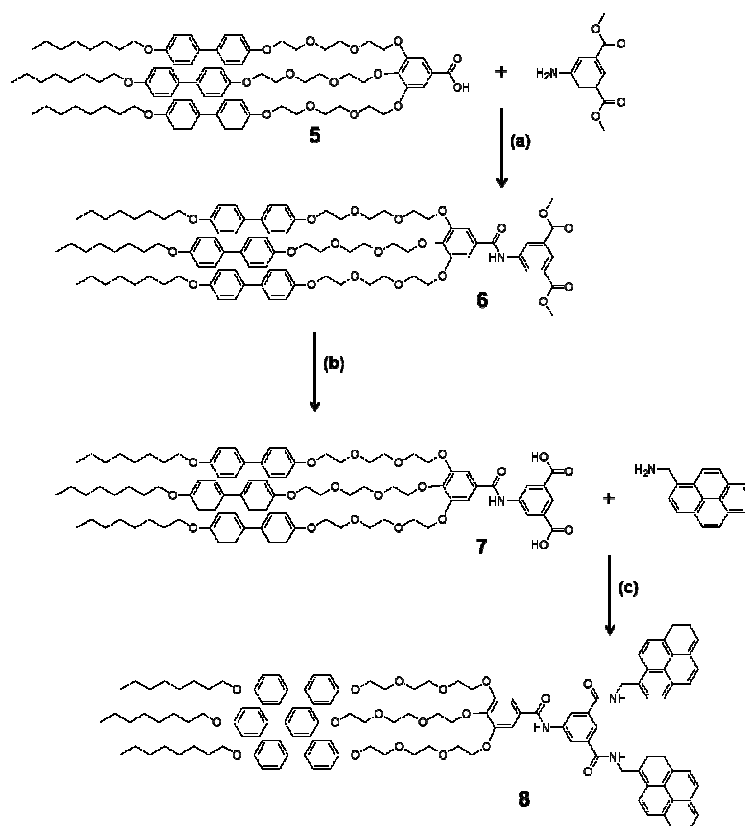


Fig. S2 Schematic illustration; synthetic procedures of reagents, tri-mesogen benzamido isophthalate derivatives, tri-mesogen benzamido isophthalateamide derivatives and conditions: (a) DIPC, DPTS, Chloroform, 25 °C for 1 day. (b) NaOH, THF/MeOH, 60 °C for 2 h. (c) EDC, HOAt, DMF, 25 °C for 1 day.

Dimethyl 5-(3,4,5-tri(2-(2-(2-(4-(4'-octyloxy)biphenoxy)ethoxy)ethoxy)ethoxy)benzamido) isophthalate (**6**) A solution of **5** (0.53 g, 0.376 mmol), dimethyl 5-aminoisophthalate (0.15 g, 0.717 mmol), N,N'-Diisopropylcarbodiimide (0.23 g, 1.823 mmol) and 4-(Dimethylamino) pyridinium 4-toluenesulfonate (0.055 g, 0.257 mmol) in 10 mL of dried chloroform was stirring at room temperature for 1 day. After reaction, CHCl₃ was poured into mixture, and washed with distilled water several times. The organic layer was dried over MgSO₄. It was purified by column chromatography with silica gel using MC:EA = 2:1. Resulting product is white solid (yield = 0.41 g, 68 %). ¹H NMR (400 MHz, CDCl₃) : δ 8.52 (d, 2H, HK), 8.45 (s, 1H, HM), 8.42 (t, 1H, HL), 7.43-7.37 (m, 12H, HF1,F2), 7.25 (s, 2H, HJ), 6.97-6.82 (m, 12H,

HE1,E2), 4.25-4.20 (t, 2H, HG2'), 4.12-4.10 (t, 4H, HG2), 4.07-4.05 (m, 6H, HG1), 3.97-3.94 (t, 6H, HD), 3.90 (s, 6H, HN), 3.85-3.80m (m, 12H, HH1,H2), 3.76-3.71 (m, 12H, HI1,I2), 1.81-1.74 (m, 6H, HC), 1.47-1.20 (m, 30H, HB1-B5), 0.90-0.87 (t, 9H, HA).

5-(3,4,5-tri(2-(2-(2-(4-(4'-octyloxy)biphenoxy)ethoxy)ethoxy)ethoxy)benzamido)isophthalic acid (**7**) A solution of **6** (0.946 g, 0.591 mmol) in THF/MeOH (14.4 mL/ 10.7 mL) was added aqueous NaOH (ca. 10 M, 3.6 mL). The mixture was refluxed for 2.5 h, and then neutralized with an aqueous hydrochloric acid to obtain a precipitate. The precipitate was filtered off and washed with water. The crude product was purified by reprecipitation with CHCl₃ and EtOH and dried under vacuum to afford **7** as a white solid (yield = 0.891 g, 95.9 %). ¹H NMR (400 MHz, CDCl₃) : δ 10.44 (s, 1H, HM), 8.64 (d, 2H, HK), 8.22 (t, 1H, HL), 7.45-7.42 (m, 12H, HF1,F2), 7.40 (s, 2H, HJ), 6.93-6.98 (m, 12H, HE1,E2), 4.23-4.20 (t, 2H, HG2'), 4.15-4.12 (t, 4H, HG2), 4.07-4.05 (m, 6H, HG1), 3.95-3.92 (t, 6H, HD), 3.74-3.69 (m, 12H, HH1,H2), 3.63-3.58 (m, 12H, HI1,I2), 1.72-1.66 (m, 6H, HC), 1.44-1.23 (m, 30H, HB1-B5), 0.87-0.84 (t, 9H, HA).

N1,N3-bis(pyren-1-ylmethyl)-5-(3,4,5-tri(2-(2-(2-(4-(4'-octyloxy)biphenoxy)ethoxy)ethoxy)ethoxy)benzamido)isophthalamide (**8**) A solution of **7** (0.9 g, 0.573 mmol), 1-pyrenemethylamine hydrochloride (0.33 g, 1.23 mmol), 1-hydroxy-7-azabenzotriazole (0.164 g, 1.2 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (0.23 g, 1.2 mmol) in 10 mL of dried DMF was stirring at room temperature for 1 day. After reaction, solvent was removed by evaporation and remaining residue was dissolved in CHCl₃ and washed with saturated sodium chloride solution to remove remaining salts several times. The organic layer was dried over MgSO₄. It was purified by column chromatography with

silica gel using THF:MC:HEX = 1:1:1. Resulting product is white solid (yield = 0.45 g, 39 %). ^1H NMR (400 MHz, CDCl_3) : δ 10.25 (s, 1H, HM), 9.16 (s, 2H, HN), 8.50-8.48 (d, 2H, HP1), 8.45 (d, 2H, HK), 8.27-8.25 (d, 4H, HP7,P3), 8.23-8.19 (m, 4H, HP2,P9), 8.17 (t, 1H, HL), 8.12 (s, 4H, HP4,P8), 8.09-8.03 (m, 4H, HP5,P6), 7.45-7.41 (m, 12H, HF1,F2), 7.34 (s, 2H, HJ), 6.92-6.87 (m, 12H, HE1,E2), 5.23 (d, 4H, HO), 4.18-4.16 (t, 2H, HG2'), 4.13-4.11 (t, 4H, HG2), 4.06-4.04 (m, 6H, HG1), 3.93-3.88 (t, 6H, HD), 3.77-3.70 (m, 12H, HH1,H2), 3.61-3.57 (m, 12H, HI1,I2), 1.65-1.63 (m, 6H, HC), 1.40-1.19 (m, 30H, HB1-B5), 0.84-0.82 (t, 9H, HA).

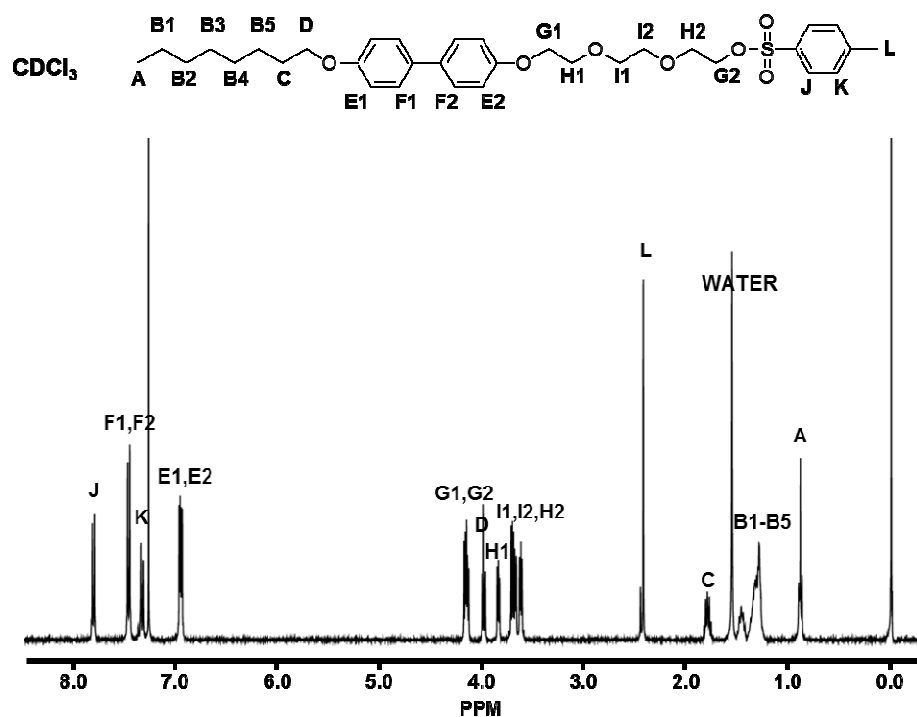


Fig. S5 ¹H NMR spectrum of compound 3

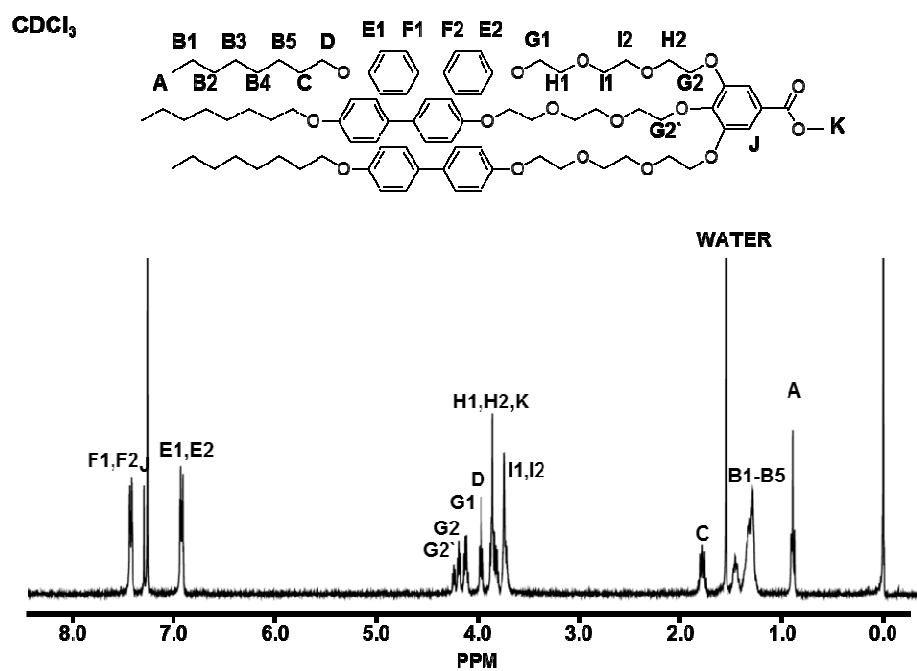


Fig. S6 ¹H NMR spectrum of compound 4

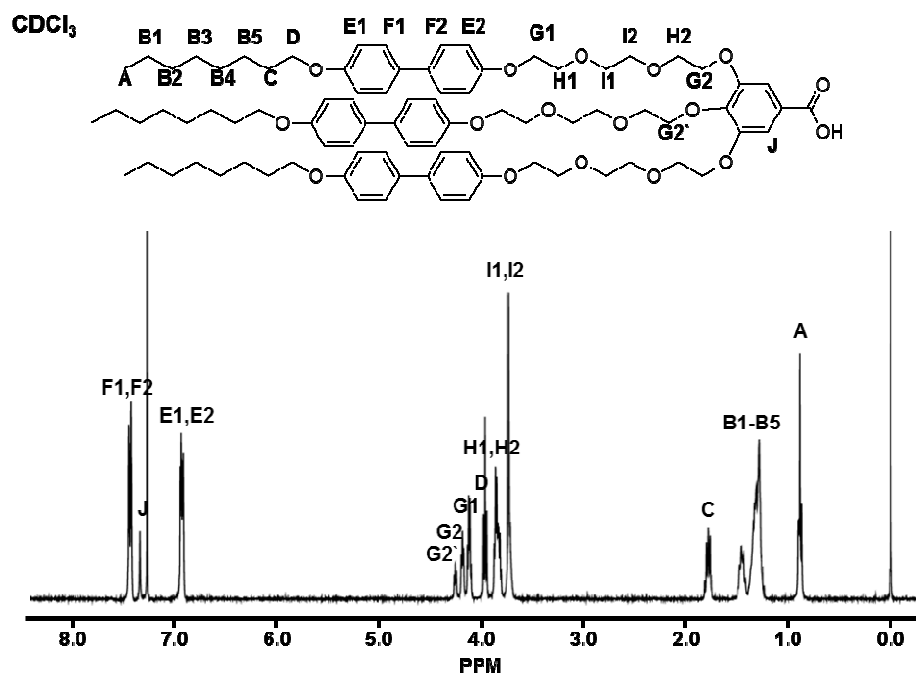


Fig. S7 ¹H NMR spectrum of compound 5

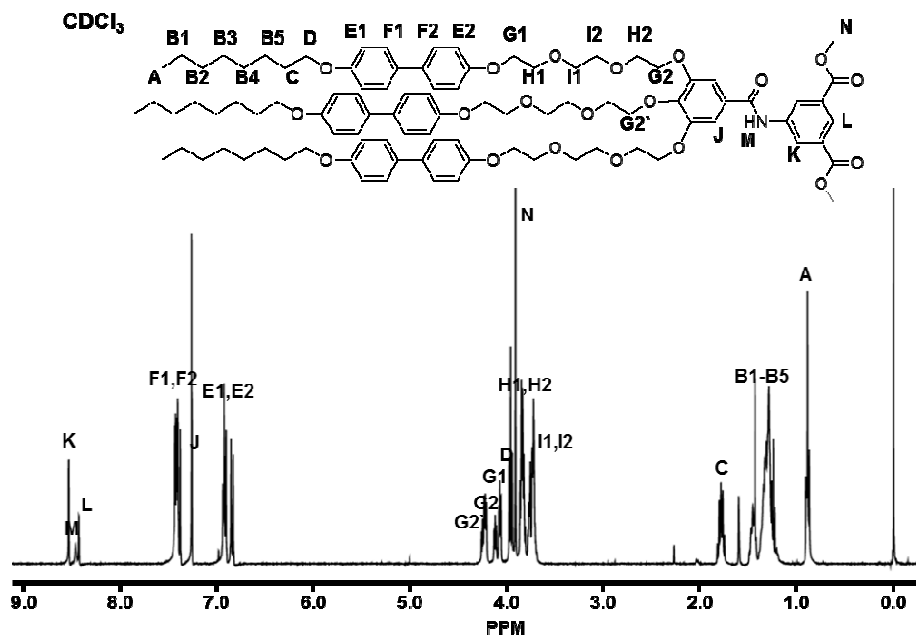


Fig. S8 ¹H NMR spectrum of compound 6

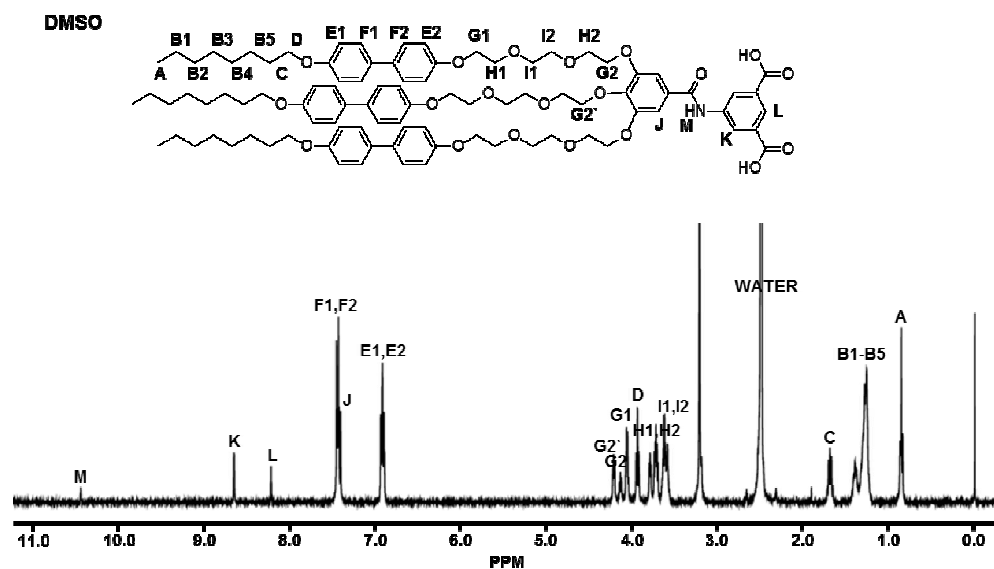


Fig. S9 ^1H NMR spectrum of compound 7

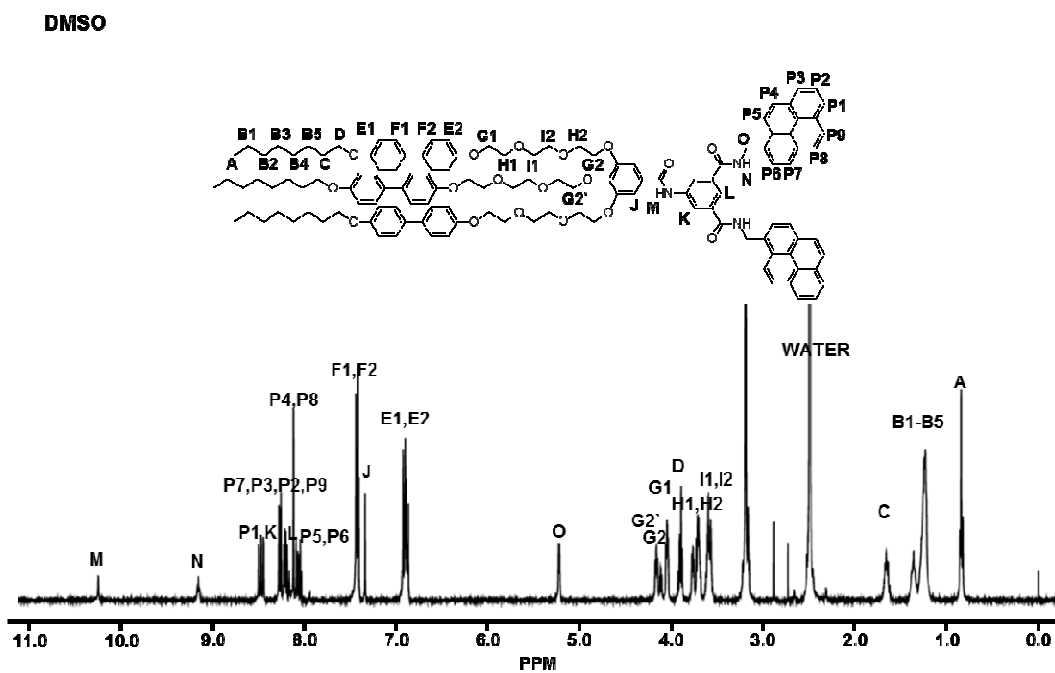


Fig. S10 ^1H NMR spectrum of compound 8

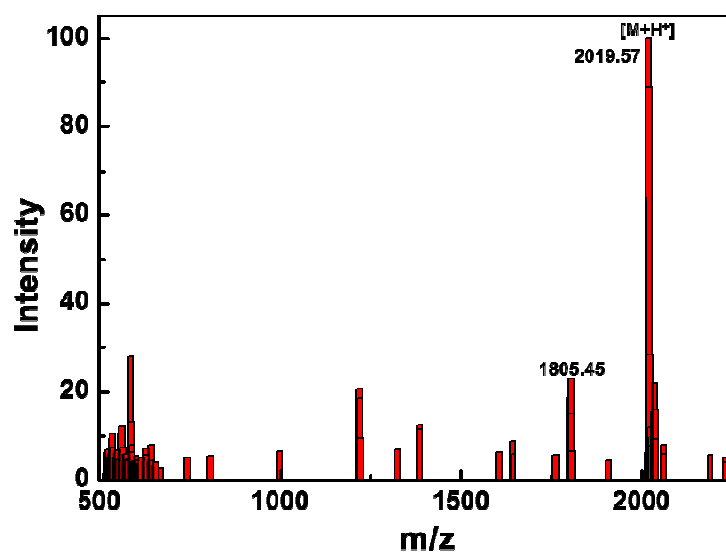


Fig. S11 MALDI-ToF MS spectrum of Py3M.

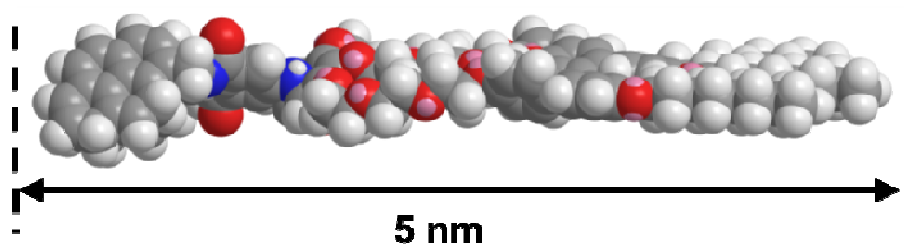


Fig. S12 Computer energy-minimized geometric dimensions of Py3M in the side directions.

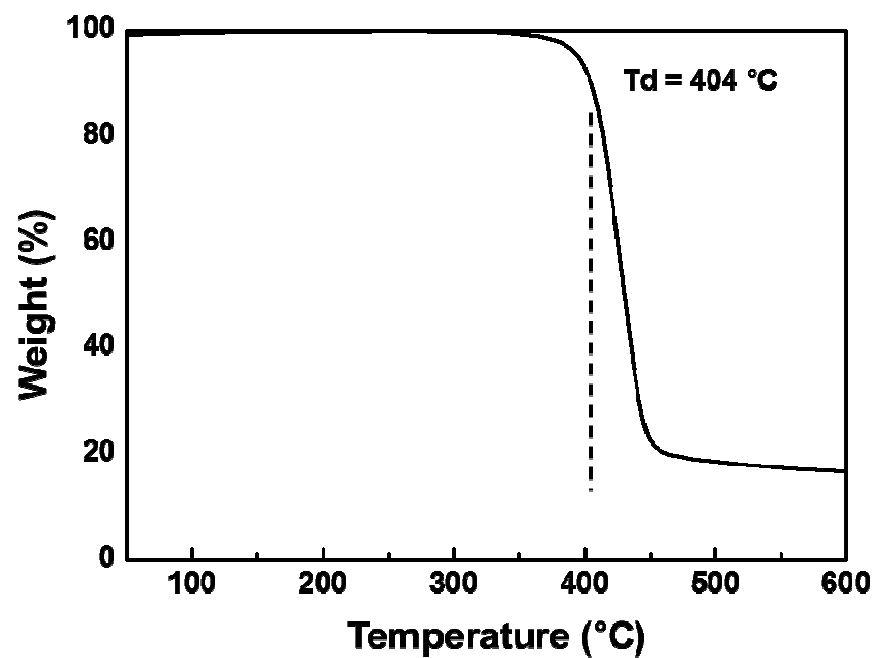


Fig. S13 TGA of Py3M. The 5 wt% weight loss is detected at 404 °C.

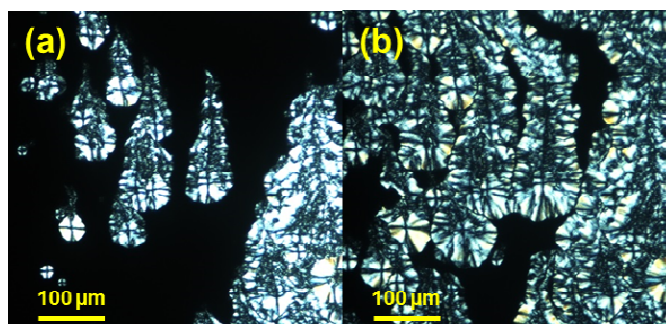


Fig. S14 POM images of Py3M by cooling from 220 °C at -5 °C/min and holding at 178 °C for various times; after (a) 0.5 h and (b) 2 h.

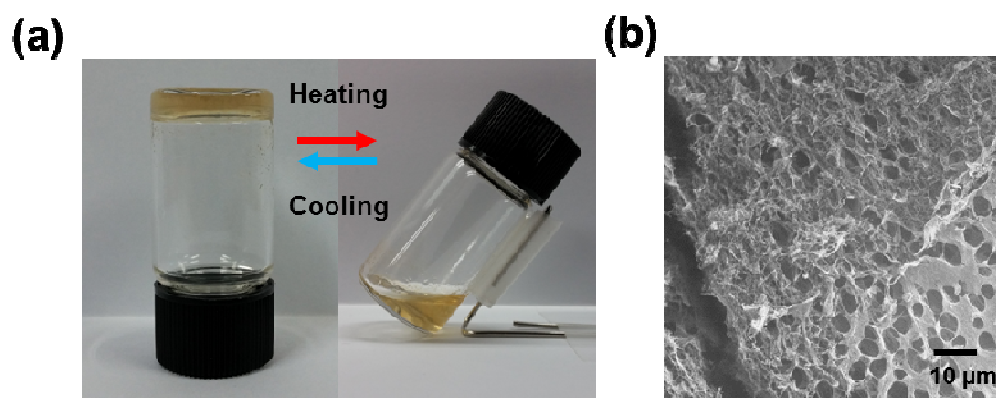


Fig. S15 (a) Photograph of sol-gel transition and (b) SEM image of Py3M multi-network.

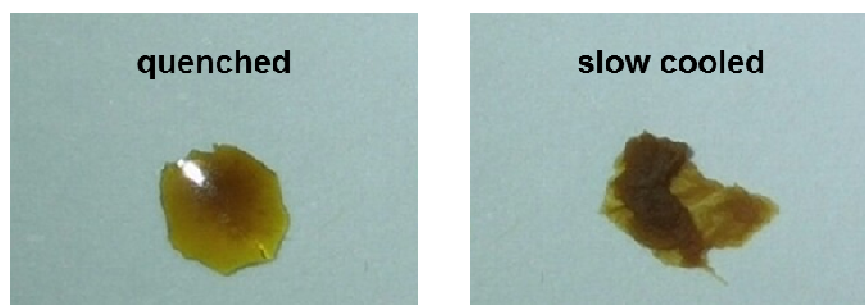


Fig. S16 Photographs of Py3M solids fabricated from two different cooling processes.

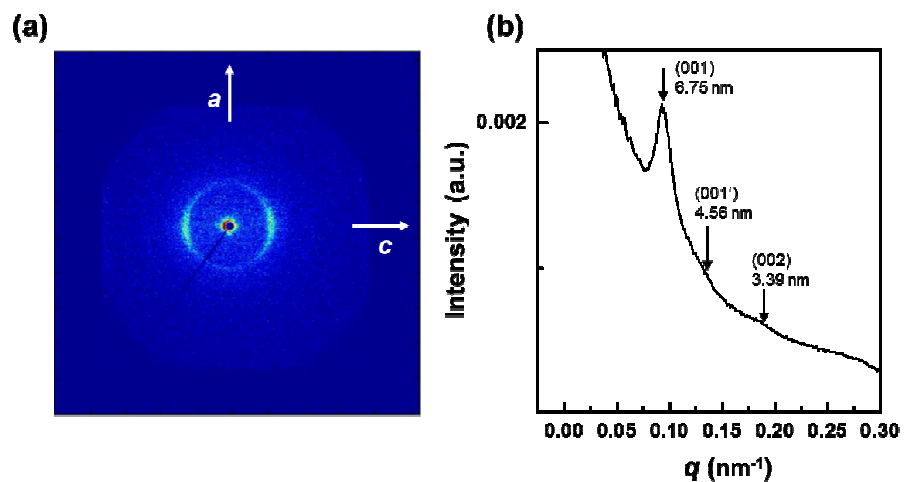


Fig. S17 SAXD pattern of Py3M crystal at room temperature: (a) [010] zone and (b) 1D SAXD pattern.

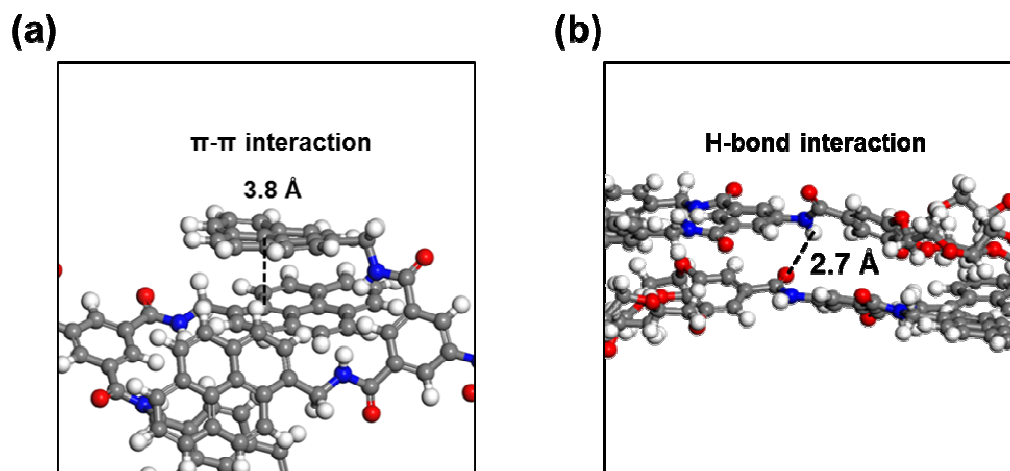


Fig. S18 Computer simulated distance of (a) π - π interaction and (b) H-bond interaction.

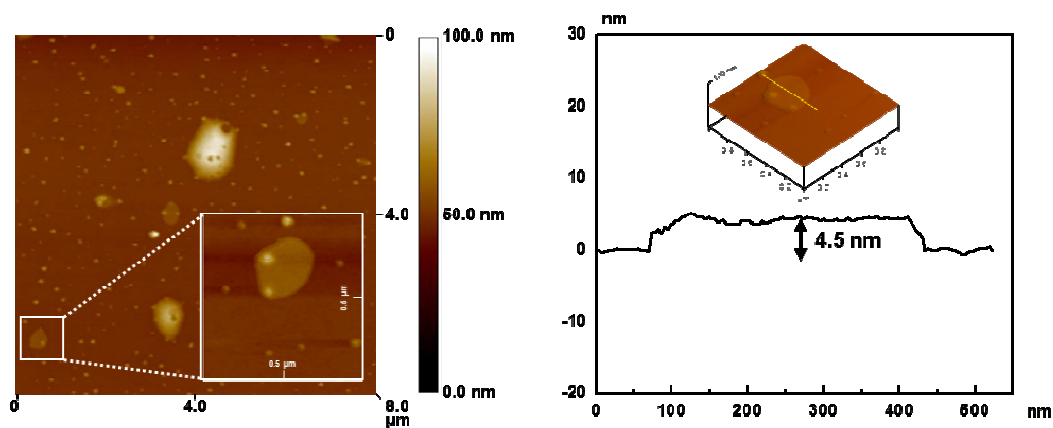


Fig. S19 AFM image and its corresponding height profile of Py3M crystal grown on oxidized glass.

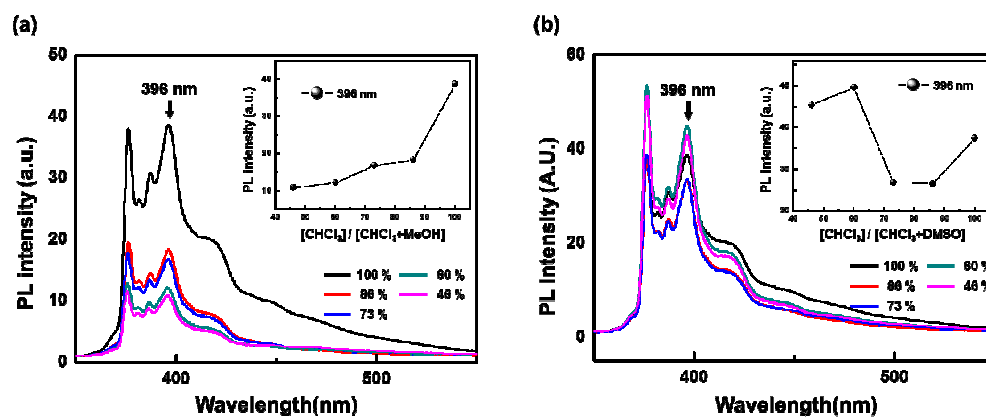


Fig. S20 PL spectra of Py3M with different molecular volumes in (a) MeOH/CDCl₃ and (b) DMSO/CDCl₃.