Supporting Information for

Triangular Arylene Ethynylene Macrocycles: Syntheses, Optical, and Thermotropic Liquid Crystalline Properties

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I. Synthetic Procedures and Characterization Data

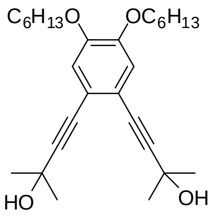
General procedure of Sonogashira coupling reaction A sealed tube containing the aryliodied and aryl acetylene, $Pd(PPh_3)_2Cl_2$ (or $Pd(PPh_3)_4$), and CuI was evacuated and back-filled with N_2 three times. Then degassed Et_3N or mixed solvent of *i*-Pr_2NH and THF (or toluene) was added via a syringe under N_2 atmosphere. The tube was then sealed and the reaction mixture was heated with stirring for 8-24 hours. After cooled to room temperature, the reaction mixture was concentrated in vacuo and then diluted with dichloromethane, washed with saturated aq. NH_4Cl and brine sequentially, and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography to give the product.

General procedure for de-protection of terminal acetylene from 1-hydroxy-1-methylethyl group A reaction mixture of the reactant and KOH in toluene was heated at 100 ^{o}C with stirring under N_2 atmosphere. TLC was taken every 30 min to monitor the reaction until the reactant was transformed to the de-protected product. After cooled to r.t., the reaction mixture was diluted with dichloromethane, washed with 2M HCl and brine sequentially, and then dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chromatography to give the product.

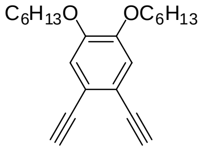
When only one of the two protective groups was to be removed, the following procedures were used: A reaction mixture of the reactant, KOH, and K_2CO_3 in toluene (or THF) was heated at 70 ^{o}C with stirring under N_2 atmosphere. TLC was taken every 5 min to monitor the reaction until the diethynyl product started to appear. After cooled to r.t., the reaction mixture was diluted with dichloromethane, washed with 2M HCl and brine sequentially, and then dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chromatography to separate the product from the reactant and diethynyl byproduct.

General procedure for de-protection of terminal acetylene from trimethylsilyl group A reaction mixture of the reactant, $KF\cdot 2H_2O$, chloroform, and acetonitrile were added into a Schlenk glassware under N_2 atmosphere. After being stirred at 35 °C for 35 hrs, the reaction mixture was cooled, diluted with ethyl acetate, washed with brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography to give the product.

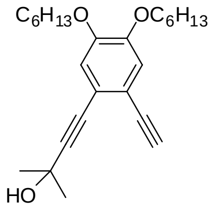
General procedure for preparation of aryliodide from diethyltriazene compound. Under the protection of N_2 atmosphere, the diethyltriazene compound and iodomethane were added into a Schlenk tube. The tube was then sealed and stirred at 145 °C for 2 days. After iodomethane being evaporated and recovered carefully, the reaction mixture was diluted with ethyl acetate, washed with brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography to give the product.



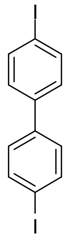
3a



3b

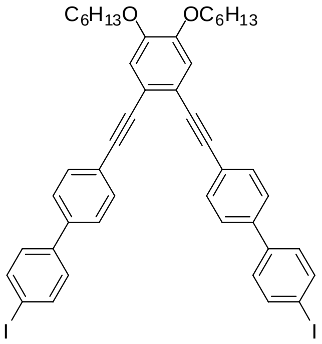


3c



3d

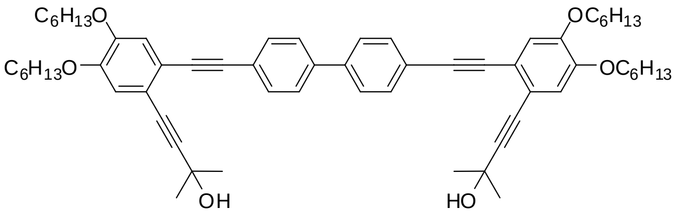
Compounds 3a, 3b, 3c, 3d were synthesized as previously reported in the literature.[1,2]



3e

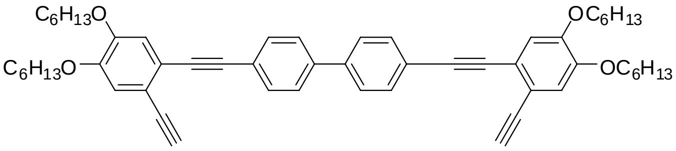
Compound 3e A mixture of **3b** (181.0 mg, 0.55 mmol), **3d** (1.80 g, 4.43 mmol), $Pd(PPh_3)_4$ (19.2 mg, 0.02 mmol), CuI (3.2 mg, 0.02 mmol), *i*-Pr_2NH (20 ml), and toulene (20 ml) was allowed to react according to the general procedure at 45 ^{o}C for 10 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (4/1, v/v) as the eluent to afford the product (198.0 mg, 41%).

TLC (PE/CH_2Cl_2, 3/1) R_f = 0.60. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (4H, d, J = 8.4 Hz), 7.63 (4H, d, J = 8.4 Hz), 7.54 (4H, d, J = 8.4 Hz), 7.34 (4H, d, J = 8.4 Hz), 7.05 (2H, s), 4.05 (4H, t, J = 6.6 Hz), 1.86 (4H, t, J = 7.2 Hz), 1.57-1.34 (12H, m), 0.92 (6H, t, J = 7.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): 149.3, 139.9, 139.6, 138.0, 132.0, 128.8, 126.8, 123.0, 118.7, 116.0, 93.4, 91.9, 89.7, 69.3, 31.6, 29.1, 25.7, 22.6, 14.0.



3f

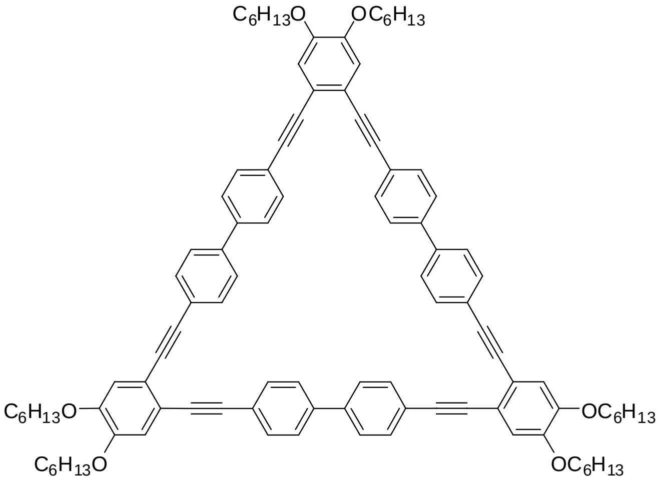
Compound 3f A mixture of **3c** (471.0 mg, 1.22 mmol), **3d** (226.0 mg, 0.56 mmol), $Pd(PPh_3)_4$ (38.6 mg, 0.03 mmol), CuI (6.4 mg, 0.03 mmol), and *i*-Pr_2NH (25 ml) was allowed to react according to the general procedure at 45 °C for 14 hrs. The crude product was further purified by column chromatography on silica gel with PE/EA (5/1, v/v) as the eluent to afford the product (424.0 mg, 83%). TLC (PE/EA, 4/1) R_f = 0.70. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (8H, m), 7.00 (2H, s), 6.92 (2H, s), 4.01 (8H, m), 2.27 (2H, br), 1.85-1.81 (8H, m), 1.73 (12H, s), 1.66-1.26 (24H, m), 0.89 (12H, t, J = 6.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.2, 149.1, 139.8, 131.9, 126.8, 122.8, 118.6, 118.1, 116.1, 116.0, 96.4, 91.5, 89.5, 81.2, 69.2, 65.7, 31.6, 31.5, 29.1, 25.6, 22.6, 14.0.



3g

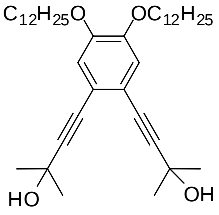
Compound 3g A mixture of **3f** (50.0 mg, 0.05 mmol), KOH (61.0 mg, 1.09 mmol), and toluene (10 ml) was allowed to react according to the general procedure at 100 °C for 1 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (3/1, v/v) as the eluent to afford the product (41.0 mg, 94%). TLC (PE/CH_2Cl_2, 3/1) R_f = 0.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64-7.57 (8H, m), 7.01

(2H, s), 7.00 (2H, s), 4.03 (8H, m), 3.31 (2H, s), 1.86-1.78 (8H, m), 1.50-1.33 (24H, m), 0.92 (12H, t, *J* = 7.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): 149.5, 149.1, 140.0, 132.1, 126.8, 122.7, 119.1, 117.4, 116.7, 115.9, 91.8, 89.2, 82.5, 79.5, 69.2, 31.5, 29.0, 25.6, 22.6, 14.0.

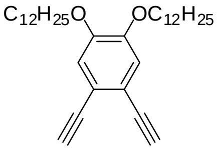


3

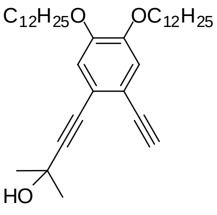
AEM 3 A mixture of **3e** (40.7 mg, 0.05 mmol), **3g** (37.0 mg, 0.05 mmol), $Pd(PPh_3)_4$ (40.0 mg, 0.04 mmol), CuI (8 mg, 0.04 mmol), *i*-Pr_2NH (30 ml) and Tol (30 ml) was allowed to react according to the general procedure at 45 °C for 24 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (2/1, v/v) as the eluent to afford the product (24.0 mg, 46%). TLC (PE/CH_2Cl_2, 2/1) R_f = 0.30.



4a

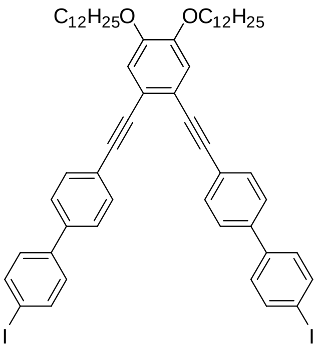


4b



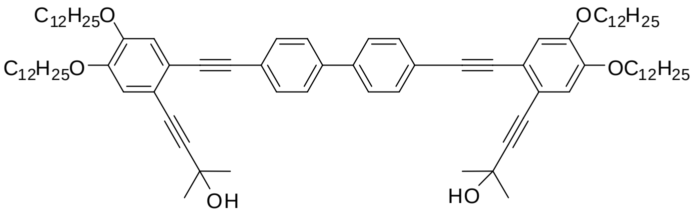
4c

Compounds 4a, 4b, 4c were synthesized as previously reported in the literature.[3]



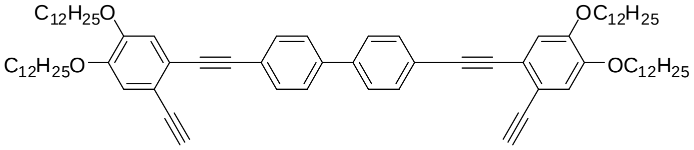
4e

Compound 4e A mixture of **4b** (384.0 mg, 0.78 mmol), **3d** (1.89 g, 4.66 mmol), Pd $(PPh_3)_4$ (33.0 mg, 0.03 mmol), CuI (6.0 mg, 0.03 mmol), *i*-Pr_2NH (5 ml), and toluene (15 ml) was allowed to react according to the general procedure at 45 °C for 10 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (4/1, v/v) as the eluent to afford the product (353.0 mg, 43%). TLC (PE/CH_2Cl_2, 4/1) R_f = 0.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (4H, d, J = 8.4 Hz), 7.63 (4H, d, J = 8.4 Hz), 7.54 (4H, d, J = 8.4 Hz), 7.34 (4H, d, J = 8.4 Hz), 7.05 (2H, s), 4.05 (4H, t, J = 6.6 Hz), 1.88-1.83 (4H, m), 1.55-1.20 (36H, m), 0.88 (6H, t, J = 6.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.3, 139.9, 139.6, 138.0, 132.0, 128.8, 126.8, 123.0, 118.7, 116.0, 93.4, 91.9, 89.7, 69.3, 31.9, 29.7, 29.66, 29.62, 29.4, 29.1, 26.0, 22.7, 14.1.



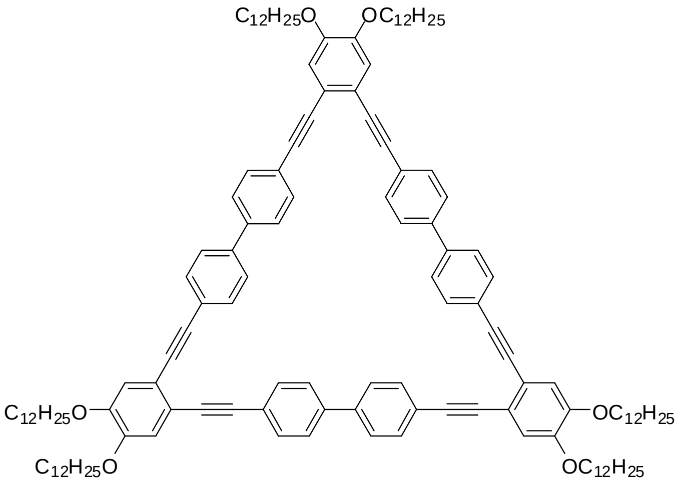
4f

Compound 4f A mixture of **4c** (480.0 mg, 0.87 mmol), **4d** (172.0 mg, 0.43 mmol), Pd $(PPh_3)_4$ (25.0 mg, 0.03 mmol), CuI (5.0 mg, 0.03 mmol), and *i*-Pr_2NH (20 ml) was allowed to react according to the general procedure at 35 °C for 13 hrs. The crude product was further purified by column chromatography on silica gel with PE/EA (6/1, v/v) as the eluent to afford the product (383.4 mg, 71%). TLC (PE/EA, 5/1) R_f = 0.4, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (8H, m), 7.00 (2H, s), 6.93 (2H, s), 4.02 (8H, m), 2.07 (2H, br), 1.83 (8H, m), 1.67 (12H, s), 1.57-1.27 (72H, m), 0.88 (12H, t, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.1, 149.0, 139.7, 131.9, 126.8, 122.7, 118.5, 118.0, 116.0, 115.7, 96.3, 91.4, 89.5, 81.1, 69.1, 65.6, 31.9, 31.6, 31.5, 29.61, 29.58, 29.3, 29.0, 25.9, 22.6, 14.1, 14.0.



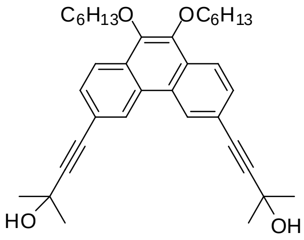
4g

Compound 4g A mixture of **4f** (75.0 mg, 0.06 mmol), KOH (300 mg, 5.35 mmol), and toluene (15ml) was allowed to react according to the general procedure at 100 °C for 2 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (4/1, v/v) as the eluent to afford the product (37.0 mg, 54%). TLC (PE/CH_2Cl_2, 2/1) R_f = 0.8, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64-7.58 (8H, m), 7.007 (2H, s), 6.997 (2H, s), 4.03 (8H, m), 3.31 (2H, s), 1.86-1.82 (8H, m), 1.47-1.27 (72H, m), 0.88 (12H, t, *J* = 6.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.5, 149.1, 140.0, 132.1, 126.8, 122.7, 119.2, 117.4, 116.7, 115.9, 91.8, 89.2, 82.5, 79.5, 69.2, 32.0, 29.68, 29.65, 29.61, 29.4, 29.1, 26.0, 22.7, 14.1.



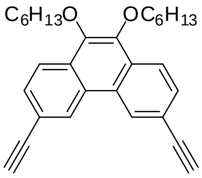
4

AEM 4 A mixture of **4e** (31.4 mg, 0.03 mmol), **4g** (34.0 mg, 0.03 mmol), $Pd(PPh_3)_4$ (10.0 mg, 0.01 mmol), CuI (2.0 mg, 0.01 mmol) and *i*-Pr_2NH (68 ml) was allowed to react according to the general procedure at 45 °C for 24 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (2/1, v/v) as the eluent to afford the product (22.1 mg, 38%). TLC (PE/CH_2Cl_2, 3/2) R_f = 0.50.



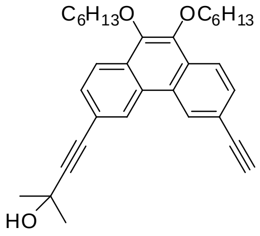
5a

Compound 5a A mixture of 9, 10-bis(hexyloxy)-3,6-diiodophenanthrene (1.00 g, 1.87 mmol), 2-methylbut-3-yn-2-ol (0.8 ml, 7.4 mmol), $Pd(PPh_3)_4$ (63.8 mg, 0.06 mmol), CuI (11.4 mg, 0.06 mmol), Et_3N (10 ml), and toluene (10 ml) were allowed to react according to the general procedure at 70 °C for 24 hrs. The crude product was further purified by column chromatography on silica gel with PE/EA (5/1, v/v) as the eluent to afford the product (953 mg, 94 %). TLC (PE/EA, 4/1) R_f =0.4. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.67 (2H, s), 8.15 (2H, d, J = 8.4 Hz), 7.62 (2H, d, J = 8.4 Hz), 4.19 (4H, t, J = 6.6 Hz), 2.11 (2H, br), 1.97-1.81 (4H, m), 1.70 (12H, s), 1.60-1.31 (12H, m), 0.92 (6H, t, J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 129.4, 129.0, 127.4, 126.1, 122.0, 120.0, 94.5, 82.5, 73.5, 65.5, 31.54, 31.48, 30.2, 25.7, 22.5, 13.9.



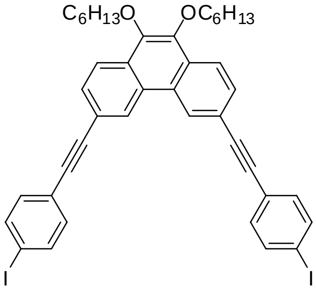
5b

Compound 5b A mixture of **5a** (500 mg, 0.92 mmol), KOH (515 mg, 9.20 mmol), and toluene (20 ml) was allowed to react according to the general procedure at 100 °C for 2.5 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (4/1, v/v) as the eluent to afford the product (334 mg, 85 %). TLC (PE/CH_2Cl_2, 3/1) R_f = 0.7. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.75 (2H, s), 8.18 (2H, d, J = 8.4 Hz), 7.69 (2H, d, J = 8.4 Hz), 4.19 (4H, t, J = 6.6 Hz), 3.20 (2H, s), 1.98-1.83 (4H, m), 1.65-1.31(12H, m), 0.92 (6H, t, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.8, 130.0, 129.8, 127.6, 126.9, 122.4, 119.5, 84.1, 77.7, 73.6, 31.7, 30.4, 25.9, 22.6, 14.0.



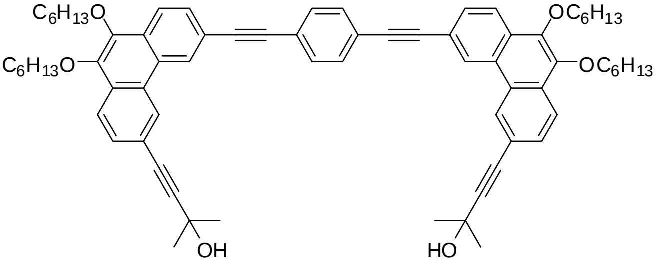
5c

Compound 5c A mixture of **5a** (700.0 mg, 1.29 mmol), KOH (72.2 mg, 1.29 mmol), K_2CO_3 (890.0 mg, 6.45 mmol), and toluene (20 ml) was allowed to react according to the general procedure at 70 °C for 40 min. The crude product was further purified by column chromatography on silica gel with PE/EA (7/1, v/v) as the eluent to afford the product (256.4 mg, 41%). TLC (PE/EA, 5/1) R_f = 0.5. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.73 (1H, s), 8.64 (1H, s), 8.18 (1H, d, *J* = 8.4 Hz), 8.16 (1H, d, *J* = 8.4 Hz), 7.69 (1H, d, *J* = 8.4 Hz), 7.63 (1H, d, *J* = 8.4 Hz), 4.18 (4H, m), 3.21 (1H, s), 2.14 (1H, br), 1.99-1.81 (4H, m), 1.70 (6H, s), 1.63-1.31 (12H, m), 0.89 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.7, 143.3, 129.7, 129.4, 129.0, 127.3, 126.7, 126.0, 122.1, 122.0, 120.0, 119.1, 94.6, 84.1, 82.4, 77.7, 73.4, 65.4, 31.6, 31.5, 30.2, 25.7, 22.5, 14.0.



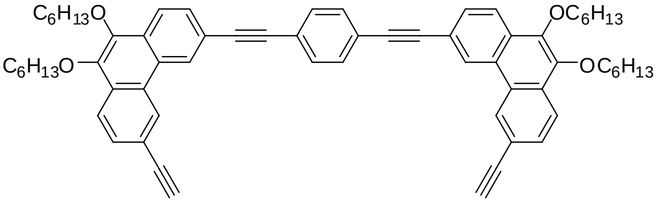
5e

Compound 5e A mixture of **5b** (402.0 mg, 0.94 mmol), 1,4-diiodobenzene (3.106 g, 9.41 mmol), $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol), CuI (2.0 mg, 0.01 mmol), *i*-Pr_2NH (20 ml), and toluene (20 ml) was allowed to react according to the general procedure at 45 °C for 14 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (6/1, v/v) as the eluent to afford product (512 mg, 66%). TLC (PE/CH_2Cl_2, 4/1) $R_f = 0.5$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.78 (2H, s), 8.19 (2H, d, J = 8.4 Hz), 7.71 (6H, m), 7.32 (4H, d, J = 8.4 Hz), 4.20 (4H, t, J = 6.6 Hz), 1.95-1.85 (4H, m), 1.56-1.36 (12H, m), 0.93 (6H, t, J = 7.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.9, 137.6, 133.1, 129.7, 127.8, 126.3, 122.8, 122.6, 120.3, 94.2, 91.4, 89.2, 73.8, 31.7, 30.4, 25.9, 22.6, 14.0.



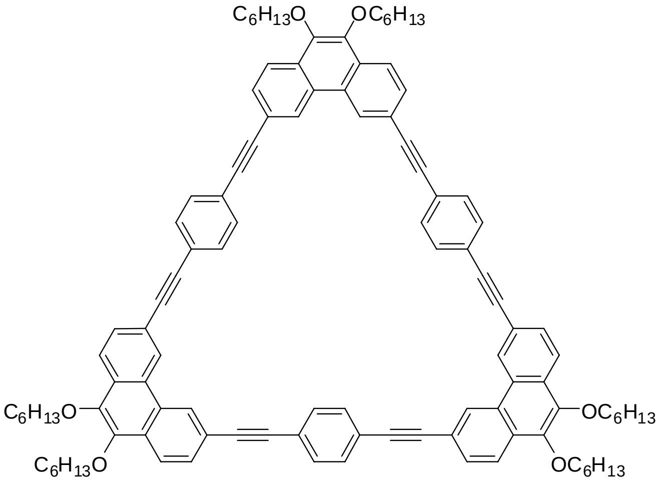
5f

Compound 5f A mixture of **5c** (959.0 mg, 1.98 mmol), 1,4-diiodobenzene (326.0 mg, 0.99 mmol), $Pd(PPh_3)_4$ (23.0 mg, 0.02 mmol), CuI (4.0 mg, 0.02 mmol), and *i*-Pr_2NH (25 ml) was allowed to react according to the general procedure at 40 °C for 10 h. The crude product was further purified by column chromatography on silica gel with PE/EA (4/1, v/v) as the eluent to afford the product (708 mg, 69%). TLC (PE/EA, 3/1) $R_f = 0.6$. ^{1}H NMR (300 MHz, $CDCl_3$): 8.79 (2H, s), 8.71 (2H, s), 8.21 (2H, d, J = 8.7 Hz), 8.16 (2H, d, J = 8.4 Hz), 7.75 (2H, d, J = 8.7 Hz), 7.63 (2H, d, J = 8.4 Hz), 7.64 (4H, s), 4.21 (8H, m), 2.16 (2H, br), 1.96-1.74 (8H, m), 1.71(12H, s), 1.58 -1.39 (24H, m), 0.96-0.91 (12H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.9, 143.7, 131.6, 130.2, 129.8, 129.64, 129.58, 129.5, 127.8, 127.7, 126.3, 123.2, 122.5, 122.4, 120.4, 120.1, 94.4, 92.0, 89.9, 82.7, 73.7, 65.7, 31.7, 31.6, 30.4, 25.9, 22.6, 14.0.



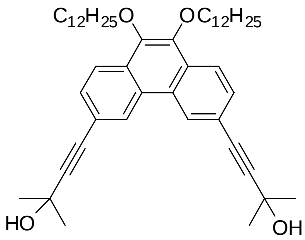
5g

Compound 5g A mixture of **5f** (272.9 mg, 0.26 mmol), KOH (293.5 mg, 5.24 mmol), and toluene (30 ml) was allowed to react according to the general procedure at 100 °C for 70 min. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (6/1, v/v) as the eluent to afford the product (213 mg, 88%). TLC (PE/CH_2Cl_2, 4/1) R_f= 0.40. ^{1}H NMR (300 MHz, $CDCl_3$): 8.79 (4H, s), 8.20 (2H, d, J = 8.7 Hz), 8.18 (2H, d, J = 8.7 Hz),, 7.72 (2H, d, J = 8.7 Hz), 7.70 (2H, d, J = 8.7 Hz), 7.62 (4H, s), 4.19 (8H, m), 3.22 (2H, s), 1.94-1.84 (8H, m), 1.58-1.25 (24H, m), 0.95-0.91 (12H, m) ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.0, 143.8, 131.6, 130.0, 129.9, 129.7, 129.6, 127.8, 127.7, 127.0, 126.3, 123.2, 122.5, 120.5, 119.4, 92.0, 89.9, 84.2, 77.7, 73.7, 31.7, 30.4, 29.7, 25.9, 22.6, 14.0.



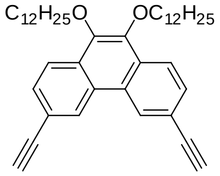
5

AEM 5 A mixture of **5e** (38.0 mg, 0.05 mmol), **5g** (42.0 mg, 0.05 mmol), $Pd(PPh_3)_4$ (26.4 mg, 0.02 mmol), CuI (4.4 mg, 0.02 mmol), *i*-Pr_2NH (40 ml), and toluene (40 ml) was allowed to react according to the general procedure at 50 °C for 1 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (3/1, v/v) as the eluent to afford the product (50.0 mg, 43.5%). TLC (PE/CH_2Cl_2, 1/1) R_f= 0.7.



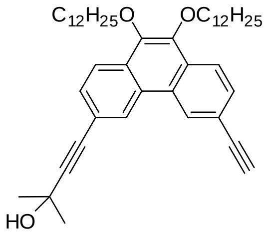
6a

Compound 6a A mixture of 9,10-bis(dodecyloxy)-3,6-diiodophenanthrene (1.15 g, 1.64 mmol), 2-methylbut-3-yn-2-ol (1.0 ml, 9.8 mmol), $Pd(PPh_3)_4$ (128 mg, 0.11 mmol), CuI (20 mg, 0.11 mmol), Et_3N (10 ml), and toluene (10 ml) was allowed to react according to the general procedure at 70 °C for 48 hrs. The crude product was further purified by column chromatography on silica gel with PE/EA (5/1, v/v) as the eluent to afford the product (1.20 g, 95%). TLC (PE/EA, 3/1) R_f = 0.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63 (2H, s), 8.10 (2H, d, J = 8.7 Hz), 7.59 (2H, d, J = 8.7 Hz), 4.15 (4H, t, J = 6.9 Hz), 2.17 (2H, br), 1.94-1.71 (4H, m), 1.82 (6H, s), 1.60-1.00 (36H, m), 0.88 (6H, t, J = 6.9 Hz). ^{13}C NMR (75MHz, $CDCl_3$): δ 143.5, 129.5, 129.1, 127.5, 126.2, 122.1, 119.9, 94.4, 82.6, 73.6, 65.6, 31.9, 31.5, 31.0, 30.4, 29.6, 29.5, 29.3, 26.1, 22.6, 14.1.



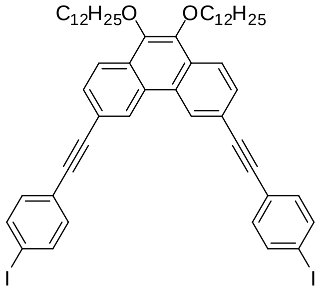
6b

Compound 6b A mixture of **6a** (460 mg, 0.647 mmol), KOH (400 mg, 7.14 mmol) and toluene (20 ml) was allowed to react according to the general procedure at 100 °C for 2 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (4/1, v/v) as the eluent to afford the product (297 mg, 77%). TLC (PE/CH_2Cl_2, 3/1) R_f = 0.7. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.76 (2H, s), 8.19 (2H, d, J = 8.4 Hz), 7.70 (2H, d, J = 8.4 Hz), 4.19 (4H, t, J = 6.6 Hz), 3.21 (2H, s), 1.91-1.76 (4H, m), 1.40-1.27 (36H, m), 0.87 (6H, t, J = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 130.0, 129.8, 127.6, 126.9, 122.5, 119.5, 84.1, 77.7, 73.7, 31.9, 30.4, 29.7, 29.5, 29.4, 26.2, 22.7, 14.1.



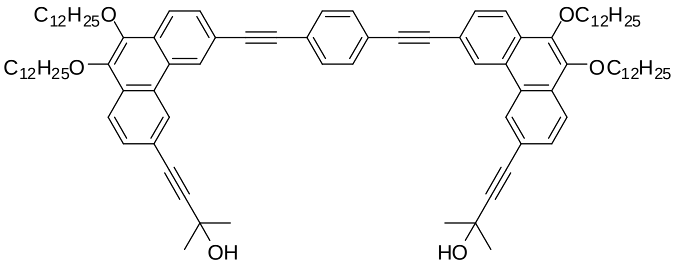
6c

Compound 6c A mixture of **6a** (900.0 mg, 1.26 mmol), KOH (70.5 mg, 1.26 mmol), K_2CO_3 (873.5 mg, 6.33 mmol), and toluene (20 ml) was allowed to react according to the general procedure at 70 °C for 0.5 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (10/1, v/v) as the eluent to afford the product (238 mg, 37%). TLC (PE/EA, 7/1) $R_f = 0.5$. ^1H NMR (300 MHz, $CDCl_3$): δ 8.75 (1H, s), 8.67 (1H, s), 8.18 (1H, d, $J = 8.4$ Hz), 8.16 (1H, d, $J = 8.4$ Hz), 7.69 (1H, d, $J = 8.4$ Hz), 7.63 (1H, d, $J = 8.4$ Hz), 4.18 (4H, m), 3.21 (1H, s), 2.14 (1H, br), 1.91-1.76 (4H, m), 1.70 (6H, s), 1.60-1.27 (36H, m), 0.88 (6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7, 143.4, 129.7, 129.5, 129.0, 127.4, 126.7, 126.0, 122.0, 122.0, 120.1, 119.2, 94.6, 84.2, 82.5, 77.7, 73.5, 65.5, 31.9, 31.6, 30.4, 29.6, 29.3, 26.2, 22.6, 14.0.



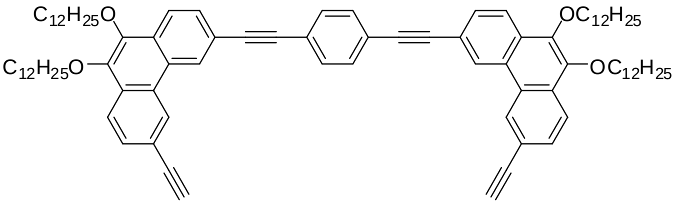
6e

Compound 6e A mixture of **6b** (200.0 mg, 0.34 mmol), 1,4-diiodobenzene (667.0 mg, 2.02 mmol), $Pd(PPh_3)_4$ (8.1 mg, 0.01 mmol), CuI (1.3 mg, 0.01 mmol), Et_3N (10 ml), and toluene (25 ml) was allowed to react according to the general procedure at 40 °C for 13 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (6/1, v/v) as the eluent to afford the product (131 mg, 39%). TLC (PE/CH_2Cl_2, 6/1) $R_f = 0.3$. ^1H NMR (300 MHz, $CDCl_3$): δ 8.80 (2H, s), 8.20 (2H, d, *J* = 8.4 Hz), 7.73 (6H, d, *J* = 8.4 Hz), 7.33 (4H, d, *J* = 8.4 Hz), 4.21 (4H, t, *J* = 6.6 Hz), 1.93-1.88 (4H, m), 1.56-1.27 (36H, m), 0.88 (6H, t, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 137.5, 133.0, 129.6, 129.5, 127.7, 126.2, 122.7, 122.4, 120.2, 94.2, 91.5, 89.1, 73.6, 31.9, 30.5, 29.7, 29.5, 29.4, 26.2, 22.7, 14.1.



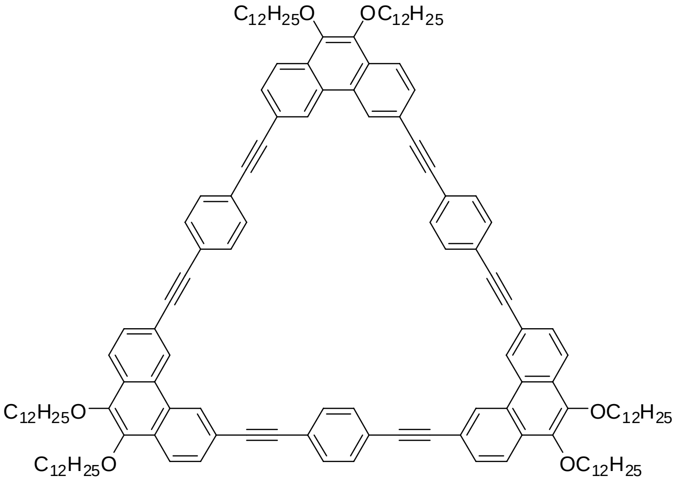
6f

Compound 6f A mixture of **6c** (500.0 mg, 0.77 mmol), 1,4-diiodobenzene (127.0 mg, 0.39 mmol), $Pd(PPh_3)_4$ (23.0 mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (10 ml), and toluene (25 ml) was allowed to react according to the general procedure. The crude product was further purified by column chromatography on silica gel with PE/ EA (5/1, v/v) as the eluent to afford the product (479 mg, 90%). TLC (PE/EA, 5/1) R_f = 0.2. ^{1}H NMR (300 MHz, $CDCl_3$): 8.80 (2H, s), 8.71 (2H, s), 8.20 (2H, d, *J* = 8.4 Hz), 8.16 (2H, d, *J* = 8.7 Hz), 7.75 (2H, d, *J* = 8.7 Hz), 7.64 (4H, s), 7.72 (2H, d, *J* = 8.4 Hz), 4.18 (8H, m), 2.15 (2H, s), 1.92-1.78 (8H, m), 1.71 (12H, s), 1.58-1.23 (72H, m), 0.89-0.83 (12H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 143.6, 131.6, 129.6, 129.5, 129.4, 129.3, 127.7, 127.6, 126.3, 123.1, 122.4, 122.2, 120.3, 120.0, 94.4, 92.0, 89.8, 82.7, 73.6, 65.6, 31.9, 31.6, 30.4, 29.69, 29.66, 29.5, 29.4, 26.2, 22.7, 14.1.



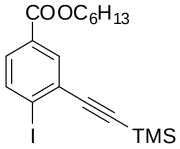
6g

Compound 6g A mixture of **6f** (280.0 mg, 0.20 mmol), KOH (431.0 mg, 7.69 mmol), and toluene (20 ml) was allowed to react according to the general procedure at 100 °C for 2 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (4/1, v/v) as the eluent to afford the product (232.0 mg, 92%). TLC (PE/CH_2Cl_2, 3/1) R_f = 0.7. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 (4H, s), 8.22 (2H, d, J = 8.4 Hz), 8.19 (2H, d, J = 8.7 Hz),, 7.76 (2H, d, J = 8.7 Hz), 7.75 (2H, d, J = 8.4 Hz), 7.63 (4H, s), 4.21 (8H, m), 3.22 (2H, s), 1.92-1.86 (8H, m), 1.54-0.91 (72H, m), 0.89-0.83 (12H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.0, 143.8, 131.7, 130.0, 129.9, 129.7, 129.6, 127.8, 127.7, 127.0, 126.4, 126.3, 123.2, 122.5, 120.5, 119.4, 92.0, 89.9, 84.21, 84.16, 73.8, 31.9, 30.5, 29.7, 29.4, 26.2, 22.7, 14.2.



6

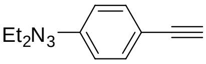
AEM 6 A mixture of **6e** (160.0 mg, 0.16 mmol), **6g** (202.2 mg, 0.16 mmol), $Pd(PPh_3)_4$ (92.5 mg, 0.16mmol), CuI (15.2 mg, 0.16 mmol), Et_3N (120 ml), and THF (140 ml) was allowed to react according to the general procedure at 45 °C for 24 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (3/1, v/v) as the eluent to afford the product (168.0 mg, 53%). TLC (PE/CH_2Cl_2, 3/1) R_f = 0.3.



7a

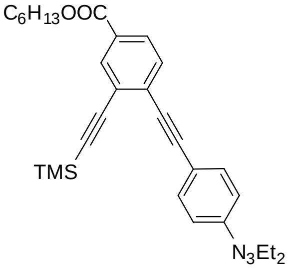
Compound 7a Under the nitrogen atmosphere, a solution hexyl

4-(3,3-diethyltriaz-1-enyl)-3-iodobenzoate (916.0 g, 2.28 mmol) in iodomethane (3 ml) was allowed to react according to the general procedure at 130 °C for 2 days. The product was purified by column chromatography on silica gel with PE/EA (30/1, v/v) as the eluent to afford **7a** (820.0 mg, 84%). TLC (PE/EA, 30/1) R_f= 0.6. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (1H, d, J = 2.1 Hz), 7.93 (1H, d, J = 8.4 Hz), 7.61 (1H, dd, J= 8.1, 2.1 Hz), 4.30 (2H, t, J = 6.8 Hz), 1.73 (2H, m), 1.45-1.31 (6H, m), 0.91 (3H, t, J = 6.9 Hz), 0.26 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0, 138.7, 133.0, 130.1, 129.9, 129.7, 107.0, 105.5, 99.6, 65.3, 31.3, 28.4, 25.5, 22.4, 13.9, -0.1.



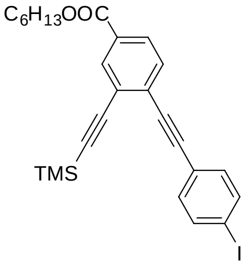
7b

Compound 7b A mixture of 4-(4-(3,3-diethyltriaz-1-enyl)phenyl)-2-methylbut-3-yn-2-ol[6](385.0 mg, 1.48 mmol), potassium hydroxide (584.0 mg, 10.4 mmol), and toluene (10 ml) was allowed to react according to the general procedure at 70 °C for 4 h. The product was purified by column chromatography on silica gel with PE/EA (20/1, v/v) as the eluent to afford **7b** (530.0 mg, 70%). TLC (PE/EA, 20/1) R_f= 0.5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (2H, dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz), 7.37 (2H, dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz), 3.77 (4H, q, J = 7.2 Hz,), 3.07 (1H, s), 1.27 (6H, t, J = 6.6 Hz).



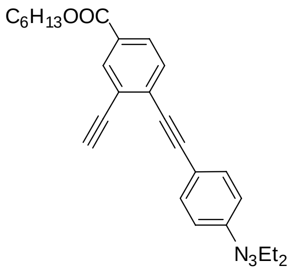
7c

Compound 7c Under the nitrogen atmosphere, a mixture of **7a** (681.0 mg, 1.59 mmol), **7b** (320.0 mg, 1.59 mmol), $Pd(PPh_3)_4$ (37.1mg, 0.003mmol), CuI (6.1 mg, 0.003 mmol), and Et_3N (13 ml) was allowed to react according to the general procedure at 40 °C for 12 hrs. After washed by dilute ammonium chloride and extracted by ethyl acetate, the product was purified by column chromatography on silica gel with PE/EA (40/1, v/v) as the eluent to afford **9c** (780 mg, 97%). TLC (PE/EA, 40/1) R_f= 0.5. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.16 (1H, d, J = 1.8 Hz), 7.94 (1H, dd, J= 8.1, 1.8 Hz), 7.57-7.52 (3H, m), 7.42 (2H, d, J = 8.7 Hz), 4.31 (2H, t, J = 6.6 Hz), 3.80 (4H, q, J = 7.2 Hz), 1.80-1.75 (m, 2H), 1.44-1.28 (12H, m)\, 0.91 (3H, t, J = 7.2 Hz), 0.29 (9H, s). ^{13}C NMR (75 MHz, CDCl$_3$): δ 165.6, 151.5, 133.3, 132.6, 131.4, 130.6, 129.3, 128.9, 125.5, 120.4, 118.8, 102.7, 99.4, 97.4, 87.7, 65.5, 31.4, 28.6, 25.7, 22.5, 14.0, -0.1.



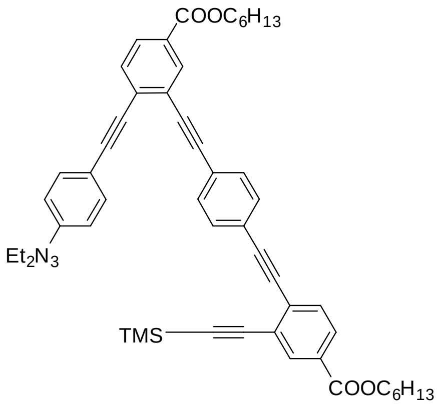
7d

Compound 7d Under the nitrogen atmosphere, a mixture of **7c** (290.0 mg, 0.578 mmol), and iodomethane (5 ml) was allowed to react with stirring at 145 °C for 2 days following the general procedure, and the product was purified by column chromatography on silica gel with PE/EA (50/1, v/v) as the eluent to afford **7d** (259.0 mg, 85%). TLC (PE/EA, 40/1) R_f = 0.5. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.17 (1H, d, J = 1.6 Hz), 7.95 (1H, dd, J= 8.1, 1.6 Hz), 7.73 (2H, d, J = 8.4 Hz), 7.57 (1H, d, J = 8.1 Hz), 7.30 (2H, d, J = 8.4 Hz), 4.32 (2H, t, J = 6.6 Hz), 1.82-1.73 (2H, m), 1.48-1.32 (6H, m), 0.91 (3H, t, J = 6.9 Hz), 0.28 (9H, s). ^{13}C NMR (50 MHz, CDCl$_3$): δ 165.8, 165.3, 141.4, 135.9, 134.9, 133.6, 133.3, 131.7, 130.2, 129.3, 128.9, 125.9, 122.9, 102.3, 99.9, 94.4, 94.0, 89.7, 66.1, 65.6, 31.4, 28.6, 28.5, 25.6, 22.5, 13.9, -0.1.



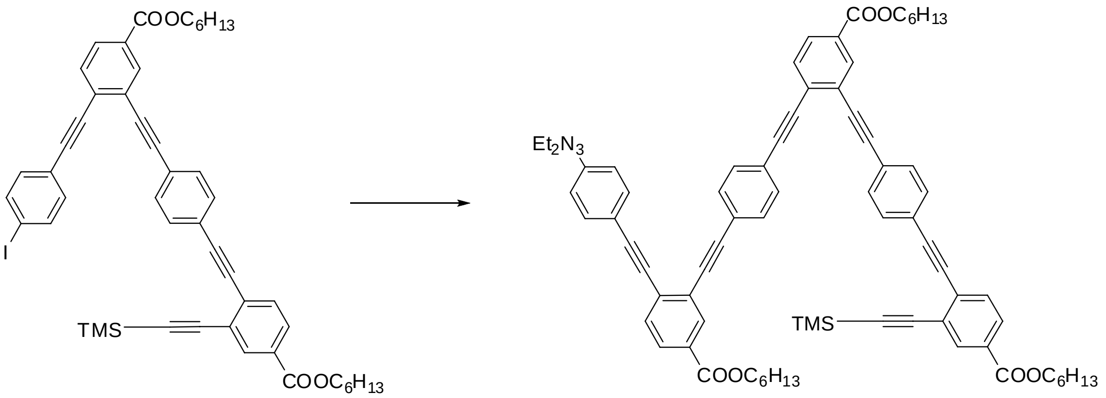
7e

Compound 7e A mixture of **7c** (290.0 mg, 0.578 mmol), $KF{\cdot}2H_2O$ (272.0 mg, 2.89 mmol), chloroform (7.5 ml, degassed), and acetonitrile (7.5 ml, degassed) was allowed to react following the general procedure at 40 °C for 18 hrs. The crude product was purified by column chromatography on silica gel with PE/EA (15/1, v/v) as the eluent to afford **7e** (210.0 mg, 85%). TLC (PE/EA, 15/1) $R_f = 0.3$. ^1H NMR (300 MHz, $CDCl_3$): δ 8.20 (1H, d, $J = 1.6$ Hz), 7.98 (1H, dd, $J = 8.1, 1.6$ Hz), 7.59 (1H, d, $J = 8.1$ Hz), 7.55 (2H, d, $J = 8.6$ Hz), 7.43 (2H, d, $J = 8.6$ Hz), 4.33 (2H, t, $J = 6.9$ Hz), 3.79 (4H, q, $J = 7.2$ Hz), 3.43 (1H, s), 1.82-1.72 (2H, m), 1.46-1.26 (12H, m), 0.91 (3H, t, $J = 6.9$ Hz).



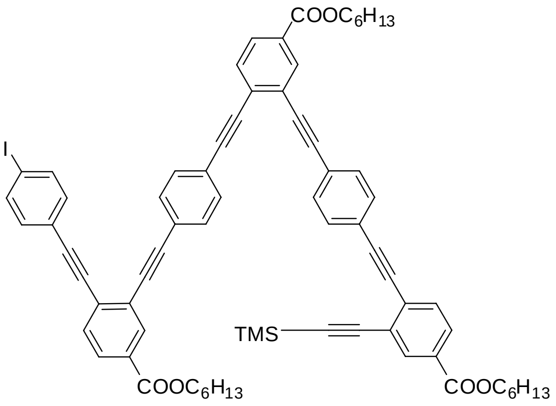
7f

Compound 7f Under the nitrogen atmosphere, a mixture of **7d** (243.0 mg, 460.0 mmol), **7e** (198.0 mg, 0.460 mmol), $Pd(PPh_3)_4$ (10.6 mg, 0.009 mmol), CuI (1.8 mg, 0.009 mmol), and Et_3N (15 ml) was allowed to react at 40 °C for 12 hrs. Following the general procedure of work-up, the crude product was then purified by column chromatography on silica gel with PE/EA (10/1, v/v) as the eluent to afford **7f** (354.0 mg, 93%). TLC (PE/EA, 10/1) $R_f = 0.5$. ^1H NMR (300 MHz, $CDCl_3$): δ 8.22 (1H, d, $J = 1.5$ Hz), 8.17 (1H, d, $J = 1.8$ Hz), 7.99-7.94 (2H, m), 7.63-7.53 (8H, m), 7.42 (2H, d, *J* = 8.7 Hz), 4.36-4.30 (4H, m), 3.80 (4H, q, *J* = 7.2 Hz), 1.85-1.75 (4H, m), 1.45-1.26 (18H, m), 0.98-0.84 (6H, m), 0.29 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.5, 165.4, 151.6, 133.3, 132.7, 132.5, 131.8, 131.6, 130.4, 129.83, 129.79, 129.4, 128.9, 125.9, 125.4, 123.5, 122.9, 120.5, 118.6, 102.5, 99.7, 97.6, 95.8, 93.7, 90.0, 89.7, 87.7, 65.5, 31.4, 28.6, 25.6, 22.5, 14.0, -0.1.



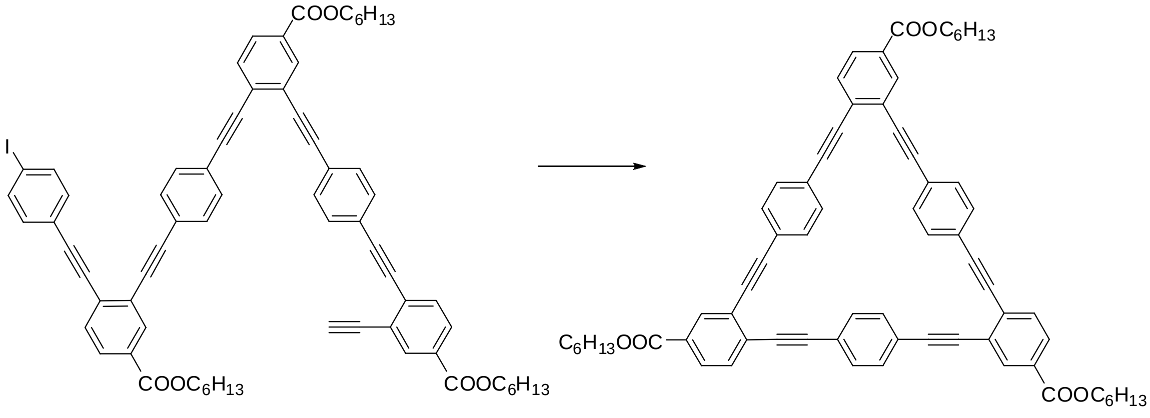
7g **7h**

Compound 7h Under the nitrogen atmosphere, **7f** (280.0 mg, 0.337 mmol) and iodomethane (5 ml) were allowed to react at 150 °C for 2 days. Following the general procedure of work-up, the crude product was purified by column chromatography on silica gel with PE/EA (30/1, v/v) as the eluent to afford **7g** (206.0 mg, 71%). Under the nitrogen atmosphere, a mixture of **7f** (225.0 mg, 0.263 mmol), **7e** (113.0 mg, 0.263 mmol), $Pd(PPh_3)_4$ (6.0 mg, 0.005 mmol), CuI (1.0 mg, 0.005 mmol), and Et_3N (15 ml) was allowed to react overnight at 40 °C. Following the general procedure, the product was purified by column chromatography on silica gel PE/EA (10/1, v/v) as the eluent to afford **7h** (250.0 mg, 90%), TLC (PE/EA, 10/1) $R_f = 0.4$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (1H, s), 8.22 (1H, s), 8.16 (1H, s), 8.01-7.93 (3H, m), 7.66-7.53 (13H, m), 7.41 (2H, d, *J* = 8.1 Hz), 4.37-4.30 (6H, m), 3.76 (4H, q, *J* = 7.2 Hz), 1.82-1.75 (6H, m), 1.46-1.23 (24H, m), 0.95-0.84 (9H, m), 0.27 (9H, s).



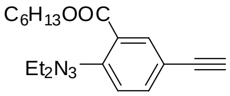
7i

Compound 7i Under the nitrogen atmosphere, a mixture of **7h** (247.0 mg, 0.213 mmol) and iodomethane (5 ml) was allowed to react at 140 °C for 2 days. Following the general procedure, the crude product was purified by column chromatography on silica gel, with PE/CH_2Cl_2 (1.5/1, v/v) as the eluent to afford **7i** (187.0 mg, 74%). TLC (PE/EA, 10/1) $R_f = 0.5$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.24 (1H, d, J = 1.8 Hz), 8.22 (1H, d, J = 1.8 Hz), 8.16 (1H, d, J = 1.2 Hz), 8.02-7.92 (3H, m), 7.72-7.55 (13H, m), 7.28 (2H, d, J = 8.2 Hz), 4.37-4.29 (6H, m), 1.79-1.76 (6H, m), 1.37-1.26 (18H, m), 0.95-0.82 (9H, m), 0.26 (9H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 137.6, 133.2, 133.0, 132.7, 131.8, 131.7, 131.6, 130.0, 129.8, 129.7, 129.5, 128.9, 125.8, 125.7, 125.6, 123.3, 123.2, 123.1, 122.9, 122.1, 102.4, 99.7, 95.9, 95.6, 95.4, 95.1, 93.9, 93.8, 89.9, 89.7, 89.0, 65.5, 31.4, 28.6, 25.6, 22.5, 14.0, -0.1.



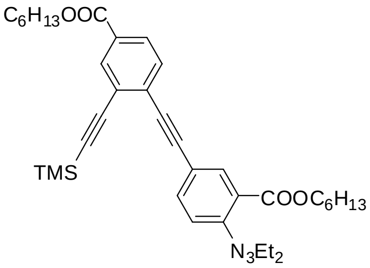
7j **7**

AEM 7 A mixture of **7i** (52.0 mg, 0.044 mmol), KF • $2H_2O$ (21.0 mg, 0.22 mmol), chloroform (10 ml, degassed), and acetonitrile (5 ml, degassed) was allowed to react 40 °C for 10 hrs. Following the general procedure the crude product was purified by column chromatography on silica gel with PE/EA (8/1, v/v) as the eluent to afford **7j** (44.5 mg, 91%). A mixture of **7j** (44.5 mg, 0.04 mmol), $Pd(PPh_3)_4$ (16.0 mg, 0.01 mmol), CuI (2.7 mg, 0.01 mmol), and Et_3N (50 ml) was allowed to react according to the general procedure at 40 ^{o}C for 24 hrs. The crude product was further purified by column chromatography on silica gel with PE/$CHCl_3$ (3/2, v/v) as the eluent and then recrystallized from hexanes and chloroform to afford the product (20.0 mg, 52%). TLC (PE/$CHCl_3$, 3/2) R_f= 0.3.



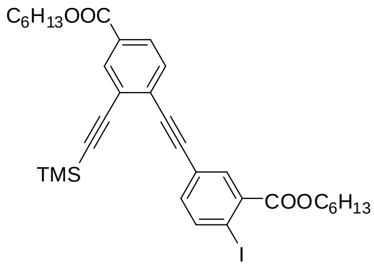
8b

Compound 8b Hexyl 2-(3,3-diethyltriaz-1-enyl)-5-trimethylsilylethynyl-benzoate (156.0 mg, 0.389 mmol), potassium carbonate (11.0 mg, 0.082mmol) and methanol (2 ml) were added into a flask. After being stirred for 65 min, the solution was poured into a saturated ammonium chloride solution. Following the general procedure, the product was purified by column chromatography on silica gel with PE/EA (15/1, v/v) as the eluent to afford **8b** (112.0 mg, 88%). TLC (PE/EA, 10/1) R_f = 0.5. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.72 (1H, d, J = 1.8 Hz), 7.49 (1H, dd, J = 8.4, 1.8 Hz), 7.40 (1H, d, J = 8.4 Hz), 4.26 (2H, t, J = 6.9 Hz), 3.76 (4H, q, J = 6.9 Hz), 3.08 (1H, s), 1.76-1.67 (2H, m), 1.44-1.25 (12H, m), 0.89 (3H, t, J = 6.6 Hz).



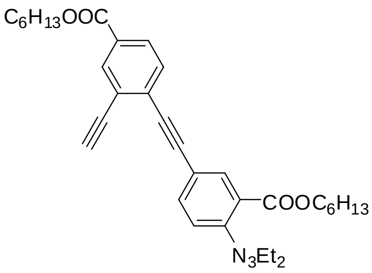
8c

Compound 8c Under the nitrogen atmosphere, **7a** (146.0 mg, 0.340 mmol), **8b** (112.0 mg, 0.340 mmol), Pd(PPh$_3$)$_4$ (7.9 mg, 0.007 mmol), CuI (1.3 mg, 0.007 mmol), and Et$_3$N (5 ml) were allowed to react at 40 °C for 12 hrs. Following the general procedure, the product was purified by column chromatography on silica gel with PE/EA (17/1,v/v) as the eluent to afford **8c** (184.0 mg, 86%). TLC (PE/EA, 17/1) R_f = 0.3. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.16 (1H, d, J = 1.8 Hz), 7.94 (1H, dd, J = 8.0, 1.8 Hz), 7.79 (1H, d, J = 1.8 Hz), 7.60-7.54 (2H, m), 7.45 (1H, d, J = 8.4 Hz), 4.35-4.24 (4H, m), 3.78 (4H, q, J = 7.2 Hz), 1.80-1.70 (4H, m), 1.43-1.22 (18H, m), 0.95-0.86 (6H, m), 0.29 (9H, s). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 165.3, 149.8, 134.2, 133.1, 132.7, 131.4, 130.1, 129.5, 128.8, 127.1, 125.6, 118.9, 118.4, 102.5, 99.5, 96.0, 88.0, 65.4, 65.1, 49.1, 41.7, 29.6, 28.6, 28.5, 25.6, 22.6, 14.0, -0.1.



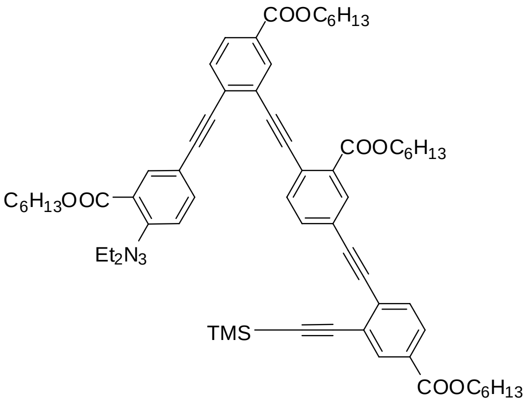
8d

Compound 8d Under the nitrogen atmosphere, **8c** (305.0 mg, 0.484 mmol) and iodomethane (6 ml) were allowed to react at 150 °C for 2 days. Following the general procedure of work-up, the crude product was purified by column chromatography on silica gel with PE/EA (35/1, v/v) as the eluent to afford **8d** (290.0 mg, 91.0%). TLC (PE/EA, 30/1) R_f = 0.30. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.17 (1H, d, J = 1.5 Hz), 8.01 (1H, d, J = 7.5 Hz), 7.98-7.94 (2H, m), 7.58 (1H, d, J = 8.1 Hz), 7.31 (1H, dd, J = 8.1, 2.1 Hz), 4.34 (4H, m), 1.82-1.73 (4H, m), 1.50-1.25 (12H, m), 0.94-0.86 (6H, m), 0.28 (9H, s). ^{13}C NMR (50 MHz, CDCl$_3$): δ 165.8, 165.3, 141.4, 135.9, 134.9, 133.6, 133.3, 131.7, 130.2, 129.3, 128.9, 125.9, 122.9, 102.3, 99.9, 94.4, 94.0, 89.7, 66.1, 65.6, 31.4, 28.6, 28.5, 25.6, 22.5, 14.0, -0.1.



8e

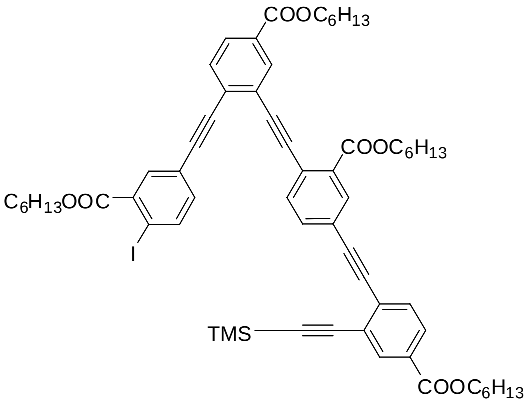
Compound 8e A mixture of **8c** (183.0 mg, 0.291 mmol), potassium carbonate (121.0 mg, 0.873 mmol), methanol (10.5 ml) and dichloromethane (10.5 ml) was allowed to react for ca. 30 min. Following the general procedure, the crude product was purified by column chromatography on silica gel with PE/EA (30/1, v/v) as the eluent to afford **8e** (140.0 mg, 85.0%). TLC (PE/EA, 17/1) R_f = 0.45. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.18 (1H, d, J = 1.8 Hz), 7.97 (1H, dd, J = 8.2, 1.8 Hz), 7.79 (1H, d, J = 1.8 Hz), 7.60-7.55 (2H, m), 7.44 (1H, d, J = 8.8 Hz), 4.36-4.25 (4H, m), 3.77 (4H, q, J = 7.2 Hz), 3.41 (1H, s), 1.80-1.67 (4H, m), 1.48-1.25 (18H, m), 0.95-0.85 (6H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.9, 165.3, 149.9, 134.3, 133.5, 132.8, 131.5, 130.4, 129.6, 129.2, 127.1, 124.6, 119.0, 118.3, 96.2, 87.8, 81.9, 81.3, 65.4, 65.2, 31.40, 31.35, 28.6, 28.5, 25.6, 22.4, 13.9.



8f

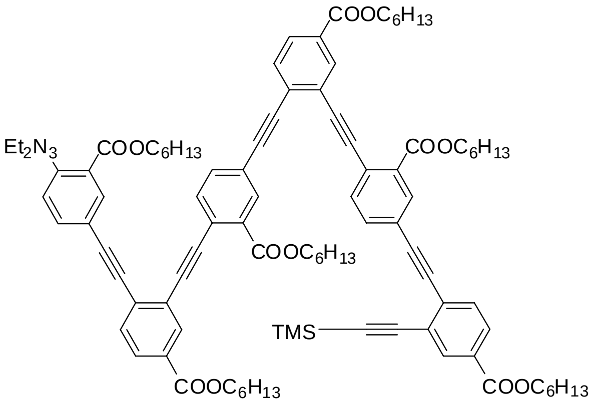
Compound 8f Under the nitrogen atmosphere, **8d** (272.0 mg, 0.414 mmol), **8e** (231.0 mg, 0.414 mmol), $Pd(PPh_3)_4$ (9.0 mg, 0.0083 mmol), CuI (1.6 mg, 0.0083 mmol), and Et_3N (10 ml) were allowed to react overnight at 40 °C. Following the general procedure, the crude product was purified by column chromatography on silica gel with PE/EA (10/1, v/v) as the eluent to afford **8f** (335.0 mg, 75%). TLC (PE/EA, 10/1)

R_f = 0.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (1H, s), 8.20 (1H, s), 8.17 (1H, s), 8.00-7.95 (2H, m), 7.80 (1H, s), 7.76-7.54 (5H, m), 7.42 (1H, d, J = 8.4 Hz), 4.36-4.23 (8H, m), 3.85-3.70 (4H, m), 1.80-1.69 (8H, m), 1.47-1.23 (30H, m), 0.91-0.83 (12H, m), 0.28 (9H, s).



8g

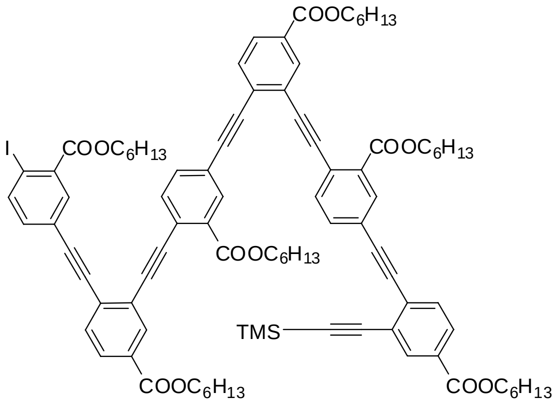
Compound 8g. Under the nitrogen atmosphere, **8f** (336.0 mg, 0.309 mmol) and iodomethane (7 ml) reacted at 140 °C for 2 days. Following the general procedure, the product was purified by column chromatography on silica gel with PE/CH_2Cl_2 (1/1, v/v) as eluent to afford **8g** (280.0 mg, 81%). TLC (PE/CH_2Cl_2, 1/1) R_f = 0.4. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.29 (1H, d, J = 1.8 Hz), 8.19-8.18 (2H, m), 8.04-7.95 (4H, m), 7.73-7.63 (3H, m), 7.60 (1H, d, J = 8.8 Hz), 7.32 (1H, dd, J = 8.2, 2.0 Hz), 4.37-4.24 (8H, m), 1.77-1.66 (8H, m), 1.38-1.26 (24H, m), 0.95-0.85 (12H, m), 0.29 (9H, s).



8h

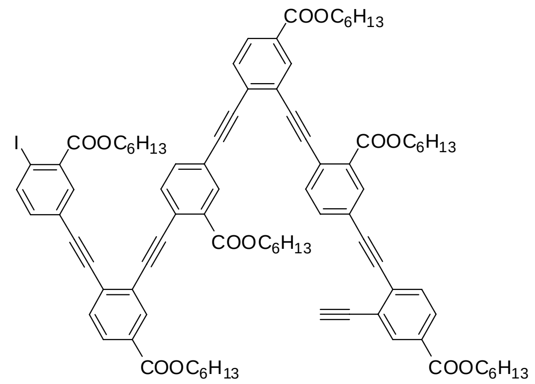
Compound 8h. Under the nitrogen atmosphere, **8g** (280.0 mg, 0.252 mmol), **8e**

(140.0 mg, 0.251 mmol), $Pd(PPh_3)_4$ (6.0 mg, 0.005 mmol), CuI (1.0 mg, 0.005 mmol), and Et_3N (10 ml) were allowed to react at 40 °C for 12 hrs. Following the general procedure, the crude product was purified by column chromatography on silica gel with PE/EA (7/1, v/v) as the eluent to afford **8h** (352.0 mg, 92.0%). TLC (PE/EA, 7/1) R_f = 0.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (1H, d, J = 1.2 Hz), 8.27 (1H, d, J = 1.5 Hz), 8.24 (1H, s), 8.20 (1H, d, J = 1.5 Hz), 8.18 (1H, d, J = 1.5 Hz), 8.04-7.95 (3H, m), 7.80 (1H, d, J = 1.8 Hz), 7.76-7.54 (8H, m), 7.44 (1H, d, J = 8.7 Hz), 4.38-4.22 (12H, m), 3.80-3.76 (4H, m), 1.82-1.65 (12H, m), 1.45-1.16 (42H, m), 0.93-0.76 (18H, m), 0.27 (9H, s).



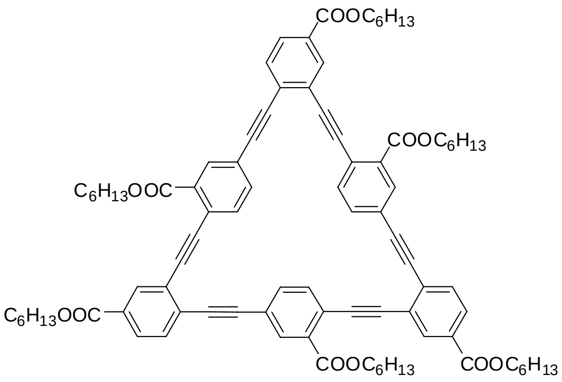
8i

Compound 8i Under the nitrogen atmosphere, **8h** (352.0 mg, 0.232 mmol) and iodomethane (7 ml) were allowed to react at 140 °C for 2 days. Following the general procedure, the crude product was purified by column chromatography on silica gel, with PE/EA (7/1, v/v) as the eluent to afford **8i** (312.0 mg, 87 %). TLC (PE/EA, 7/1) R_f = 0.5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (1H, d, J = 1.5 Hz), 8.27 (1H, d, J = 1.2 Hz,), 8.22-8.21 (2H, m), 8.18 (d, 1H, J = 1.2 Hz), 8.04-7.95 (5H, m), 7.76-7.58 (7H, m), 7.31 (1H, dd, J= 8.1, 1.6 Hz), 4.38-4.23 (12H, m), 1.83-1.61 (12H, m), 1.45-1.18 (36H, m), 0.96-0.78 (18H, m), 0.27 (9H, s).



8j

Compound 8j A mixture of **8i** (10.0 mg, 0.007 mmol), KF • $2H_2O$ (3.1 mg, 0.032 mmol), chloroform (3.5 ml), and acetonitrile (3.5 ml) was allowed to react at 35 °C for 35 hrs. Following the general procedure, the crude product was purified by column chromatography on silica gel with PE/EA (10/1, v/v) as the eluent to afford **8j** (7.6 mg, 80%). TLC (PE/EA, 7/1) R_f= 0.5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (1H, d, J = 1.2 Hz), 8.27 (1H, d, J = 1.2 Hz,), 8.22-8.20 (3H, m), 8.04-7.94 (5H, m), 7.75-7.60 (7H, m), 7.32 (1H, dd, J= 8.0, 2.0 Hz), 4.38-4.22 (12H, m), 3.46 (1H, s), 1.82-1.63 (12H, m), 1.45-1.17 (36H, m), 0.92-0.77 (18H, m).

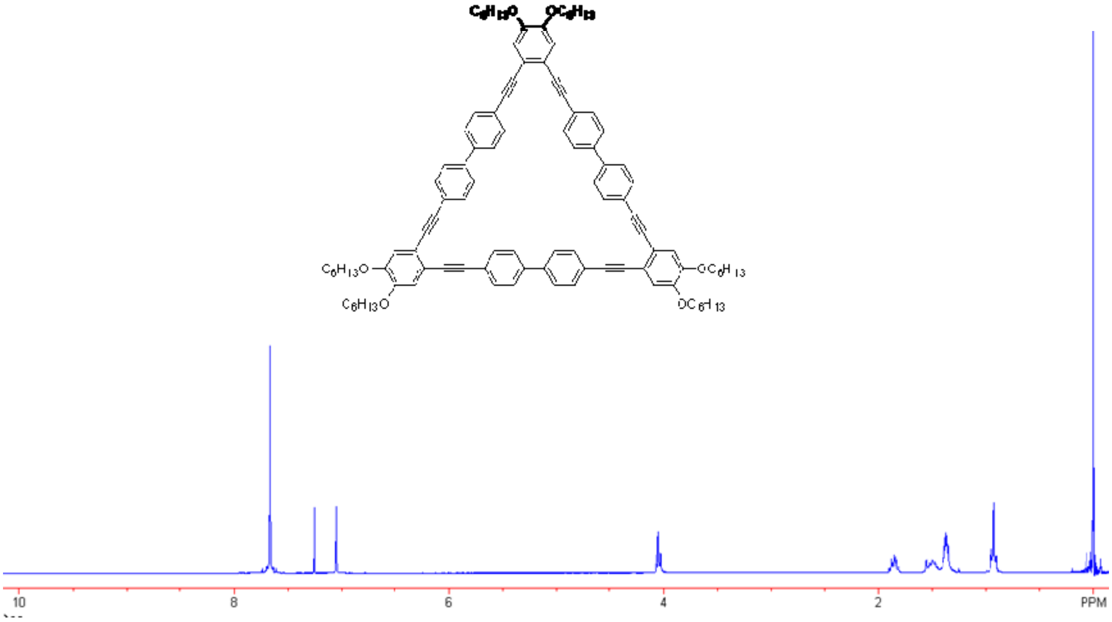


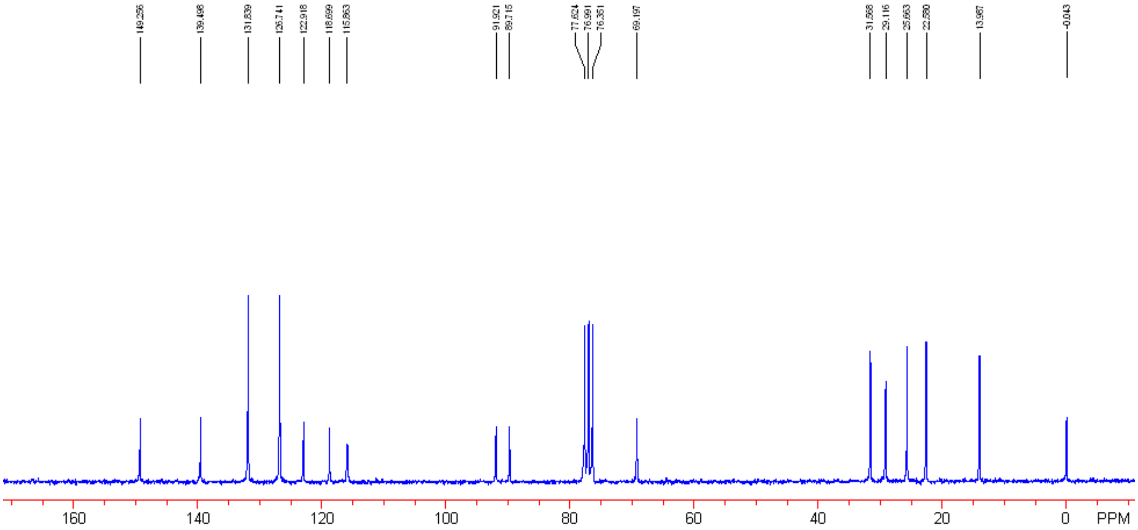
8

AEM 8 A mixture of **8j** (156.0 mg, 0.11 mmol), $Pd(PPh_3)_4$ (61.3 mg, 0.05 mmol), CuI (0.01 mg, 0.05 mmol), and Et_3N (150 ml) was allowed to react according to the general procedure at 40 ^{o}C for 24 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH_2Cl_2 (1/2, v/v) as eluent and recrystallized from hexanes to afford AEM **8** (77.0 mg, 58%). TLC (PE/CH_2Cl_2, 1/2) R_f = 0.5.

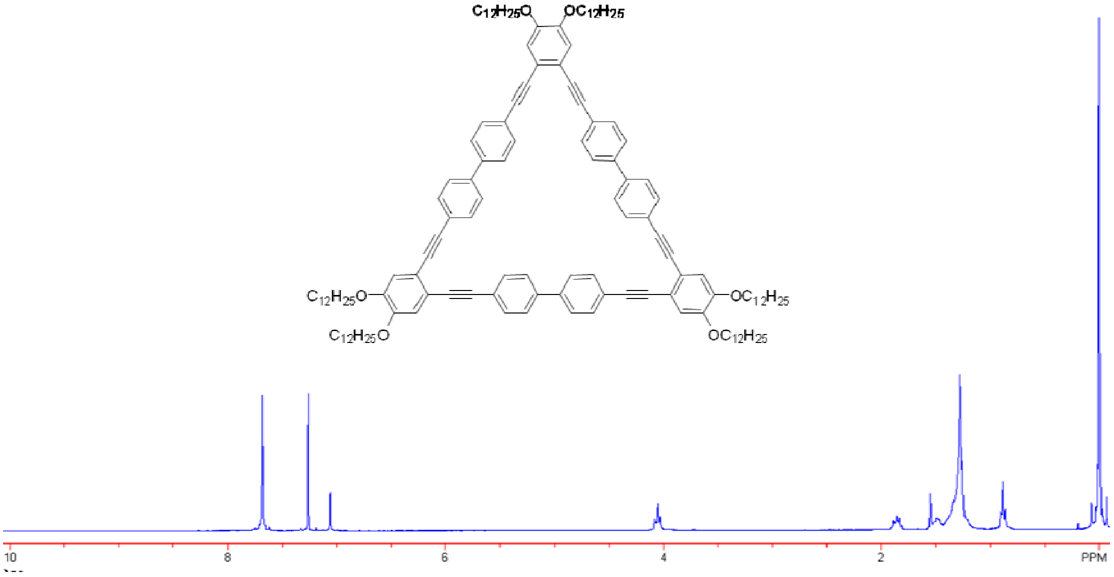
II. Copies of ^{1}H and ^{13}C NMR Spectra of AEMs 3-8

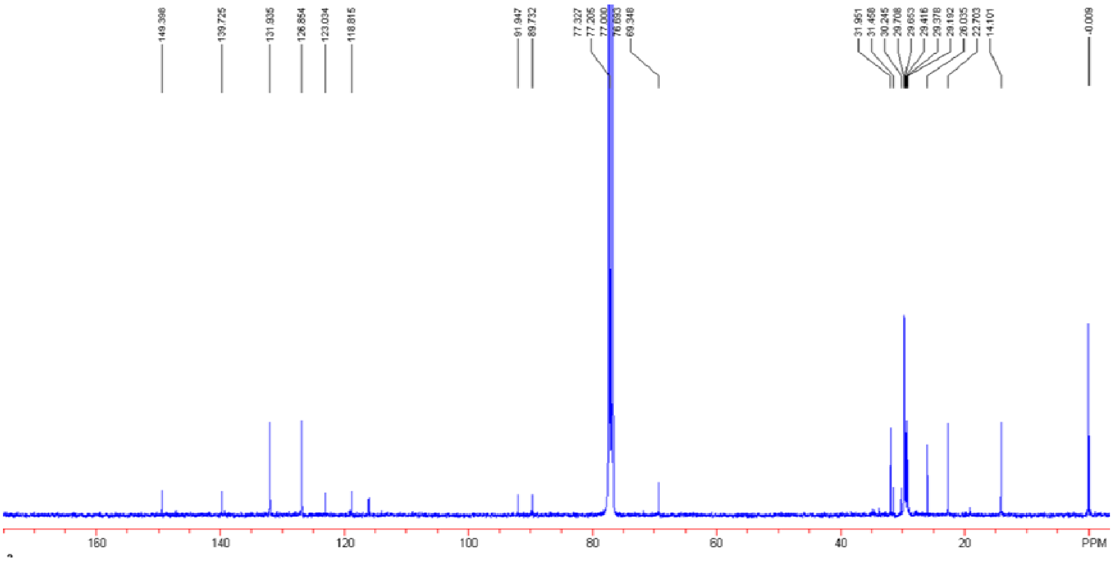
^{1}H and ^{13}C NMR spectra of AEM **3**



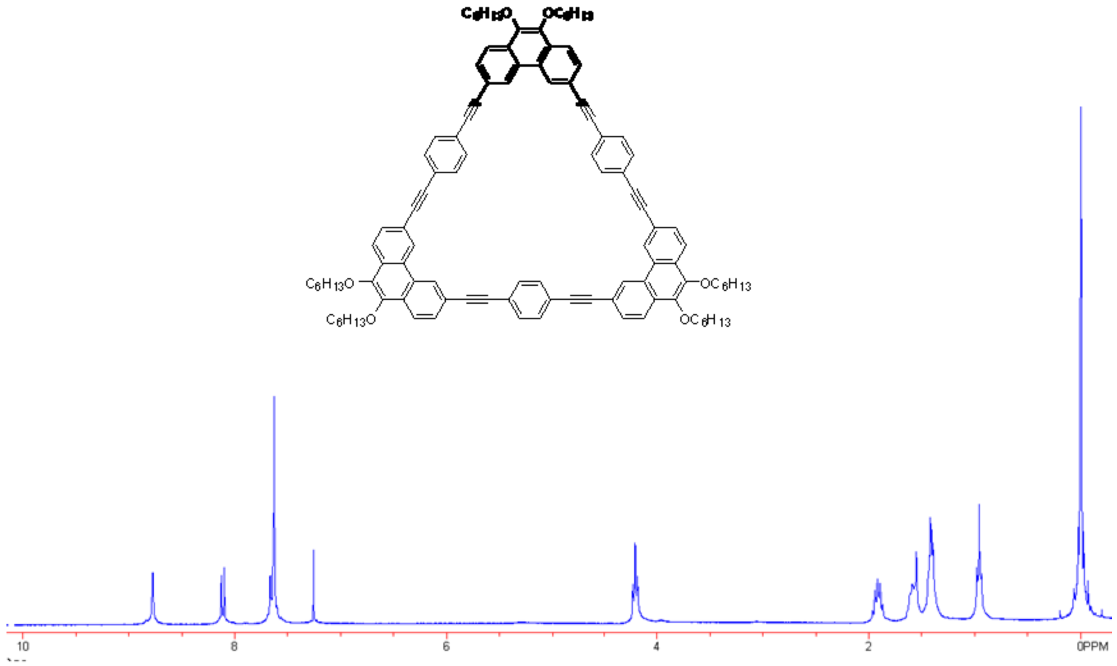


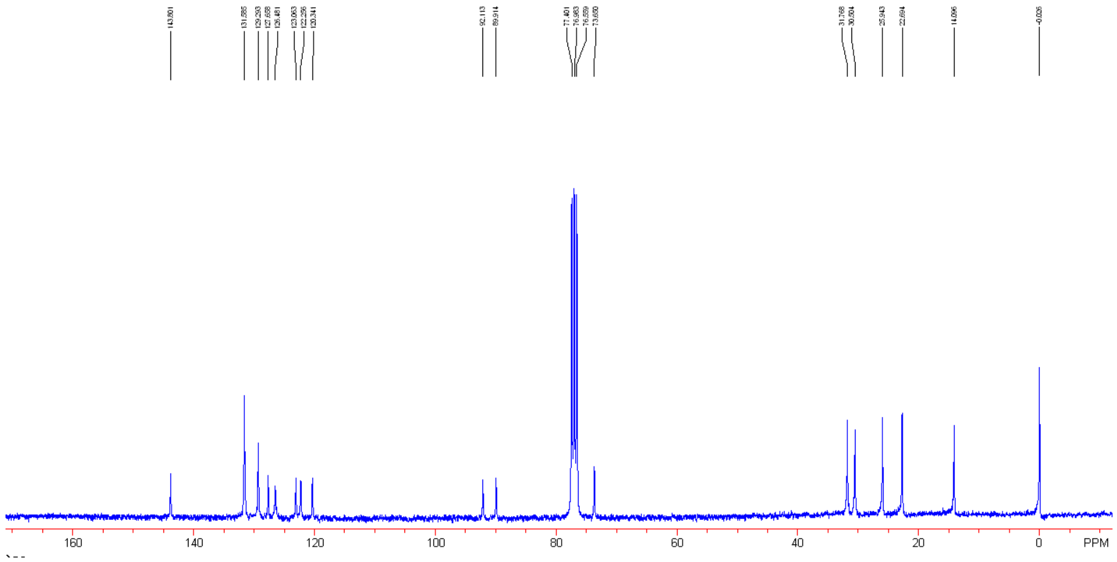
^{1}H and ^{13}C NMR spectrum of AEM **4**





^{1}H and ^{13}C NMR spectrum of AEM **5**





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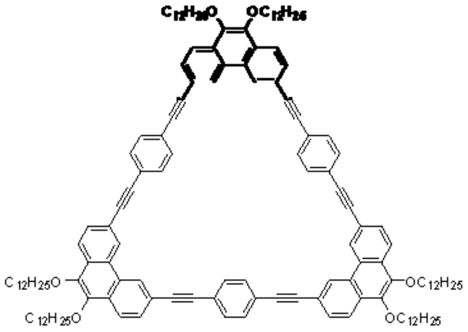
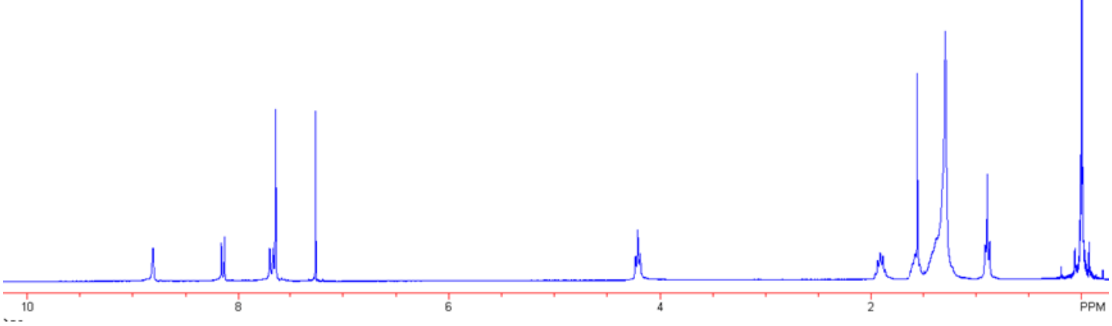
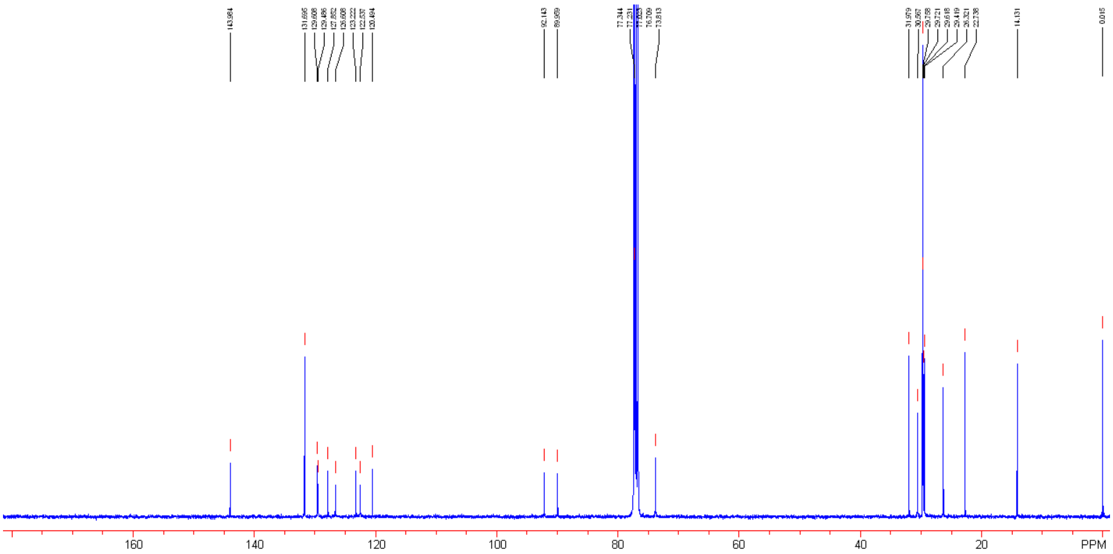
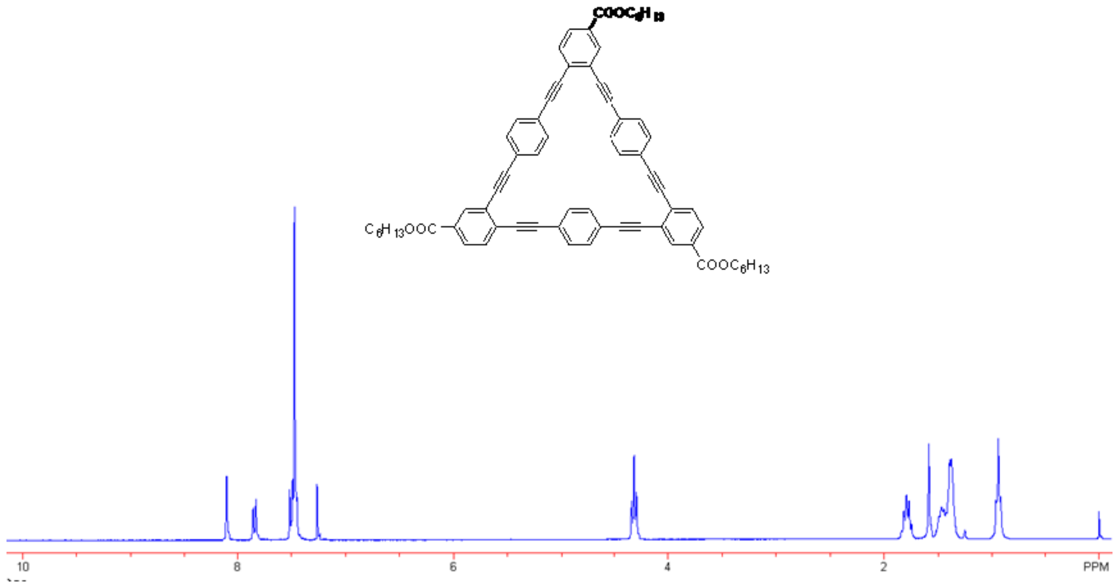
^{1}H and 13C NMR spectrum of AEM **6**

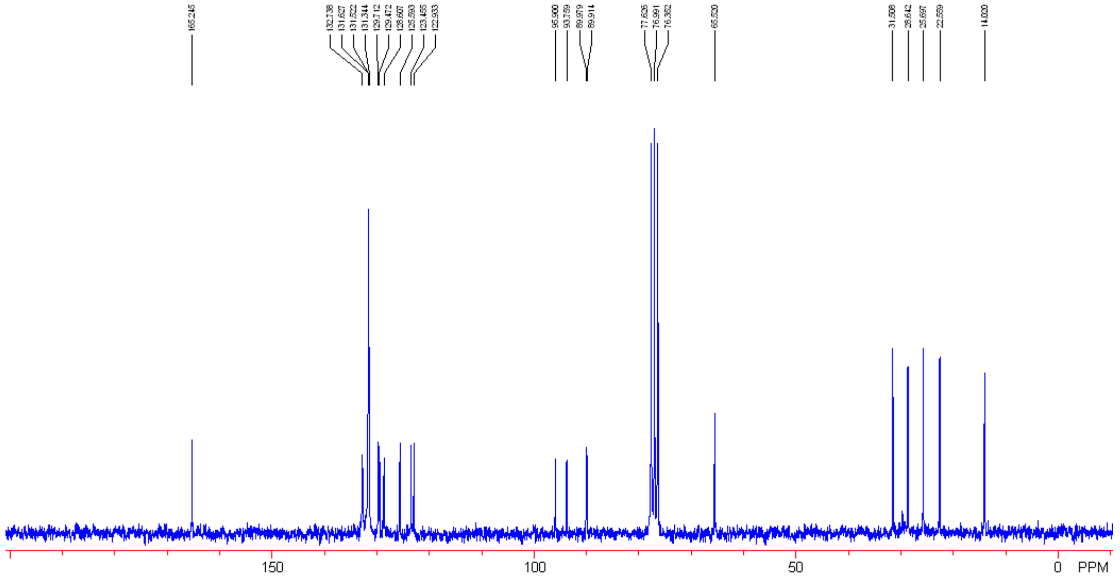




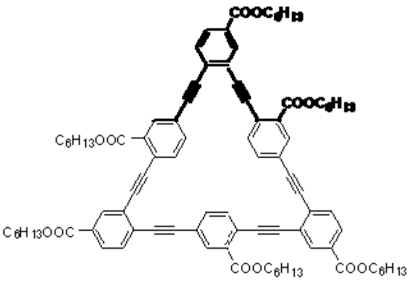


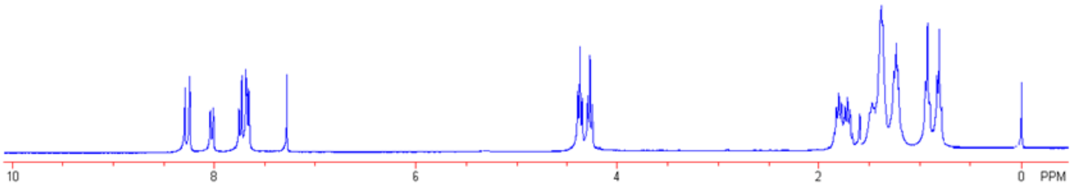
^{1}H and ^{13}C NMR spectrum of AEM **7**

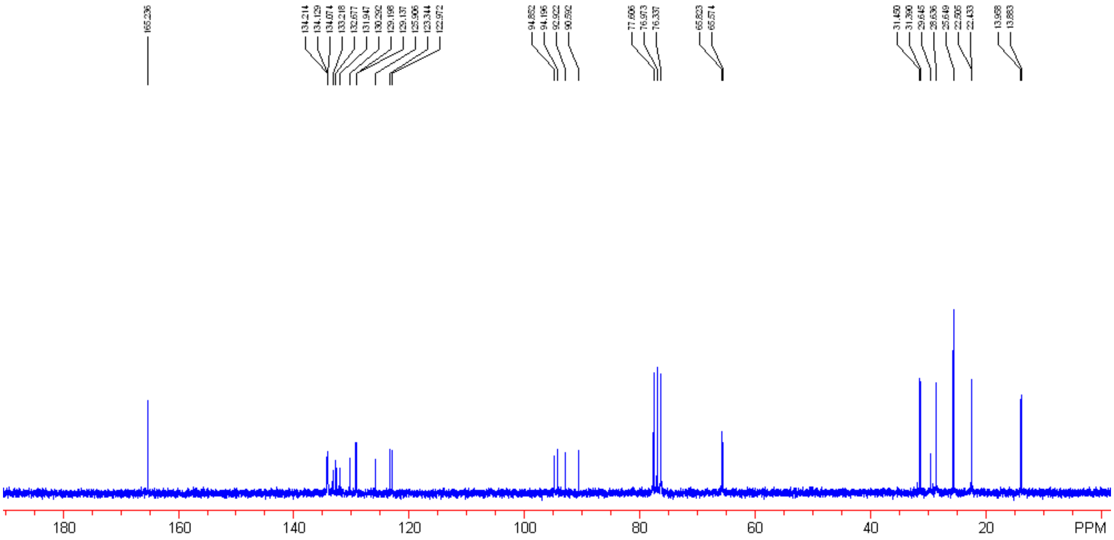




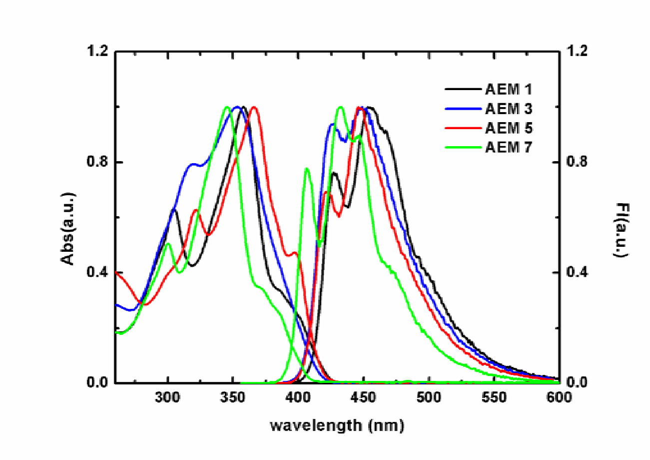
^{1}H and ^{13}C NMR spectrum of AEM **8**







III. Absorption and emission spectra of AEMs 1-8



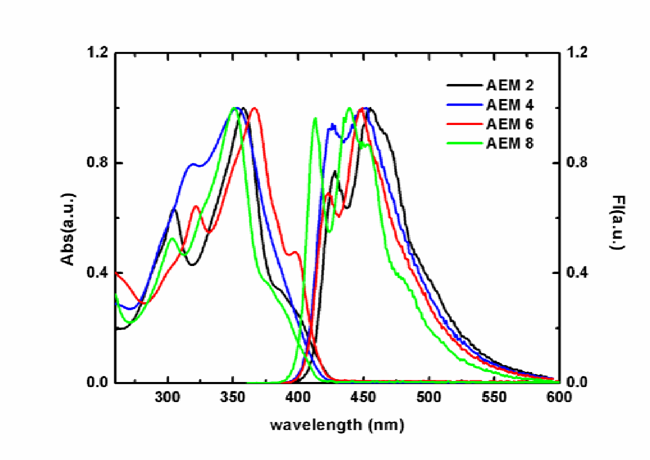


Fig. S1. Absorption and fluorescence emission spectra of AEMs **1-8** in dichloromethane.

IV. DSC, POM and XRD Characterizations of AEMs

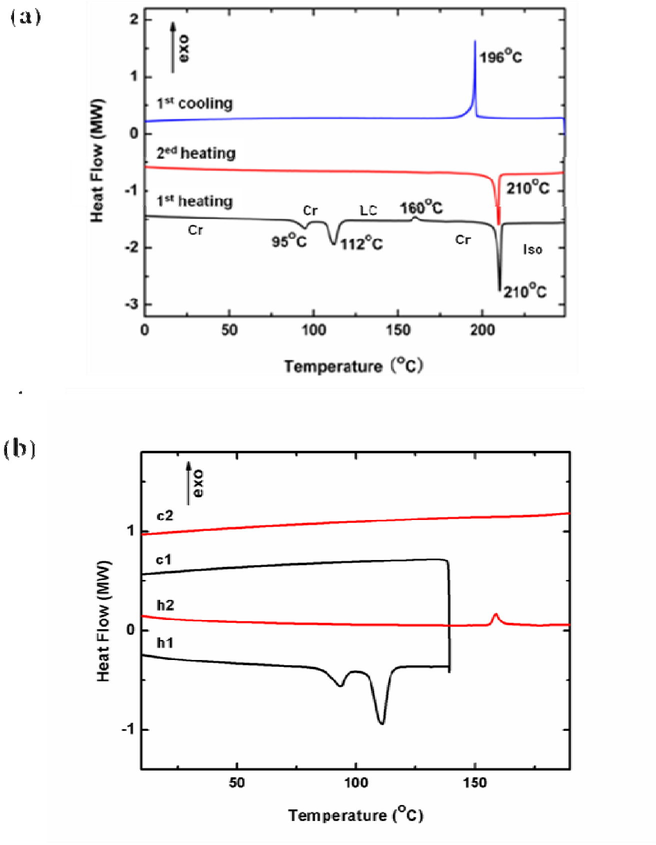


Fig. S2. DSC traces of AEM **1** at a scan rate of 5 °C min^{-1}; (a) the 1st and 2nd heating and 1st cooling cycles of a crystalline sample obtained from solution; (b) the solution-processed sample was first heated from 10 °C to 140 °C (h1), then cooled from 140 °C to 10 °C (c1), and heated again from 10 °C to 190 °C (h2) before cooled from 190 °C to 10 °C. The mesophase was preserved when the sample from cooled during c1 and h2 till the sample underwent another transition into a different crystalline state.

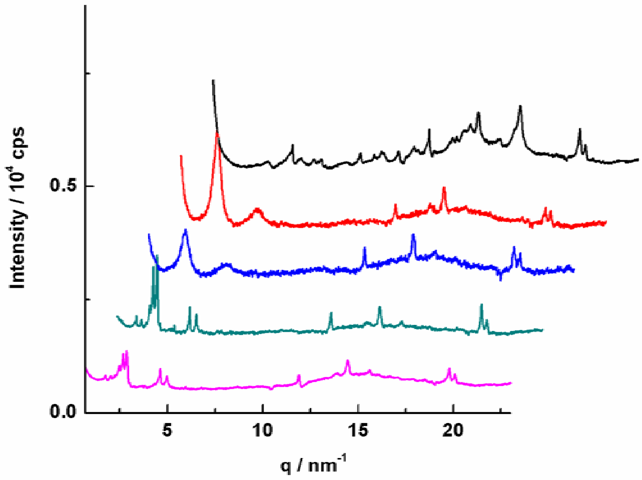


Fig. S3. XRD profiles of AEM **1** at different temperatures. Blank line: at 25 °C in the 1st heating cycle; red line: at 140 °C in the 1st heating cycle; blue line: at 25 °C when the sample was cooled upon 1st heating to 140 °C; cyan line: upon heating to 190 °C for the first time; purple line: at 25 °C when the sample giving cyan line was cooled from 190 °C. The two major small-angle diffraction peaks in the blue and red lines are index to (100) and (110) planes of a disordered hexagonal columnar phase.

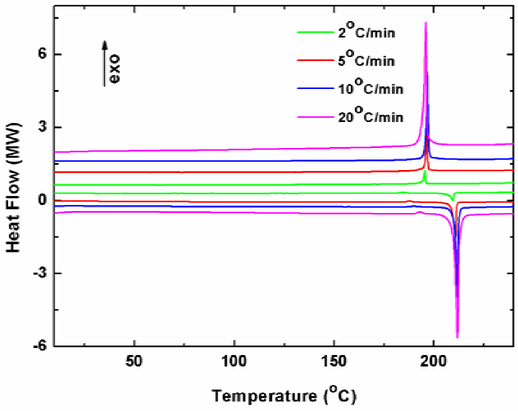


Fig. S4. DSC traces of AEM **1** at varied scan rates after thermal annealing (the small exothermic peak before the melting point in each heating scan was due to a cold crystallization process, which was observed in many polymer systems, since no crystal lattice change was detected by XRD above and below that temperature).

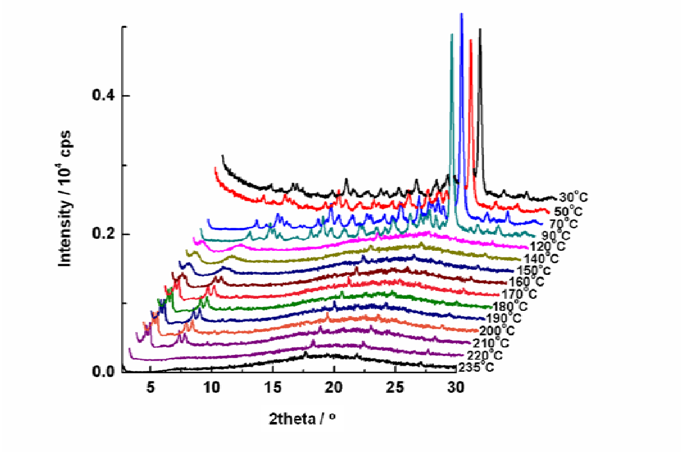


Fig. S5. WAXD of AEM **1** at varied temperatures in the 1st heating cycle.

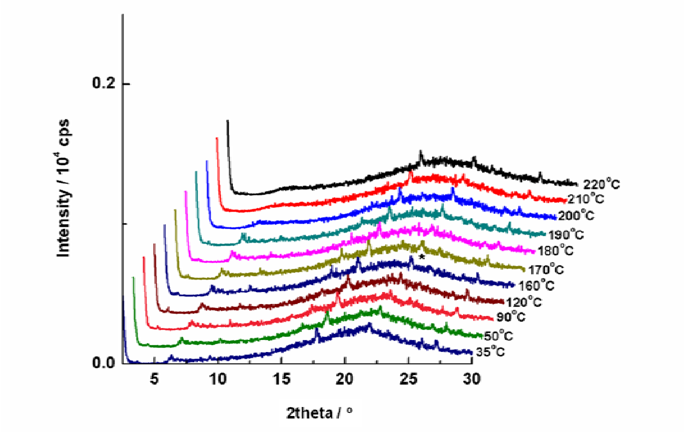


Fig. S6. WAXD of AEM **1** at varied temperatures in the 1st cooling cycle.

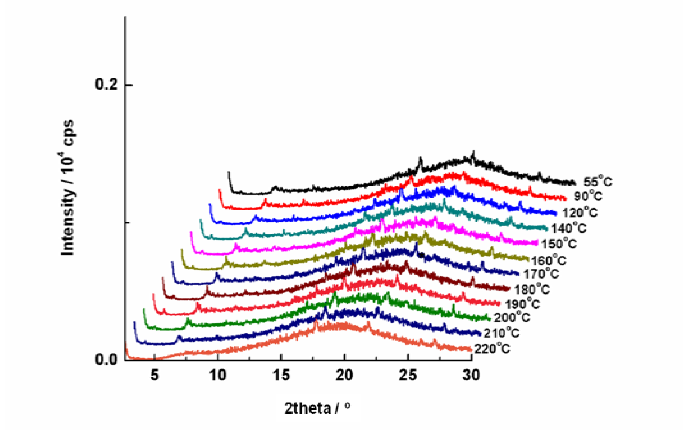


Fig. S7. WAXD of AEM **1** at varied temperatures in the 2nd heating cycle.

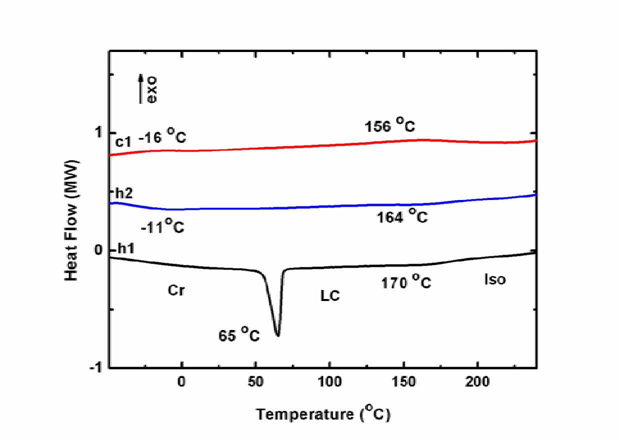


Fig. S8. DSC traces of AEM **2** at a rate of 5 °C min^{-1} (h1: the 1st heating cycle; c1: the 1st cooling cycle; h2: the 2nd heating cycle).

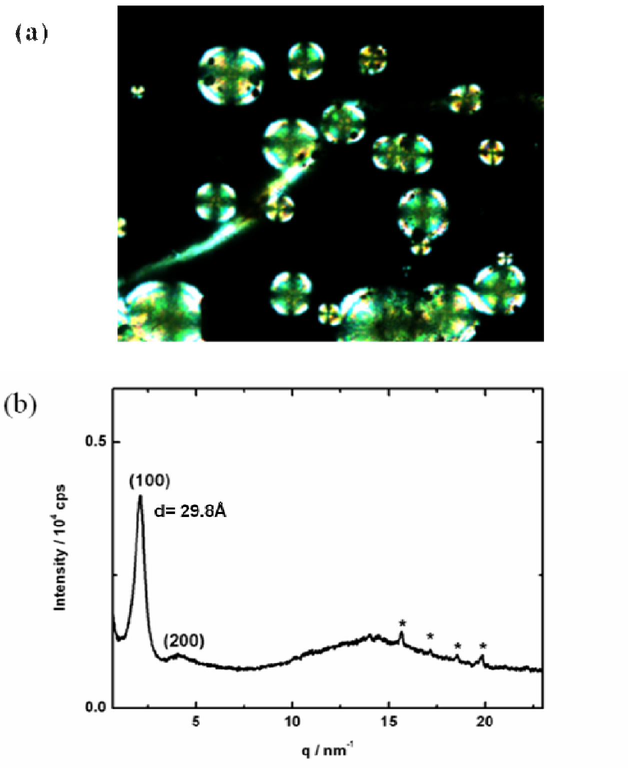


Fig. S9. (a) Optical microscopic image of AEM **2** showing focal conic texture typical of Col$_h$ phase in the 1st heating cycle (under crossed polarizer, ×200); (b) XRD patterns of AEM **2** (recorded at 80 °C in the 1st heating cycle).

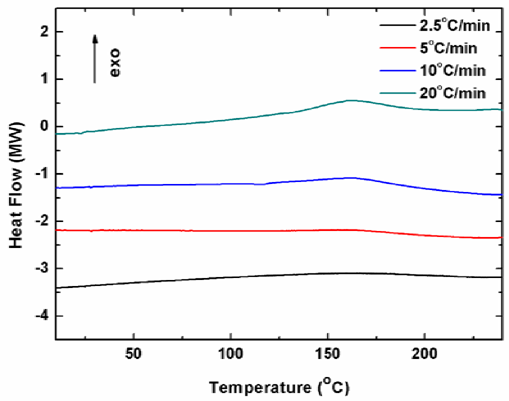


Fig. S10. DSC cooling traces of AEM **2** at varied rates.

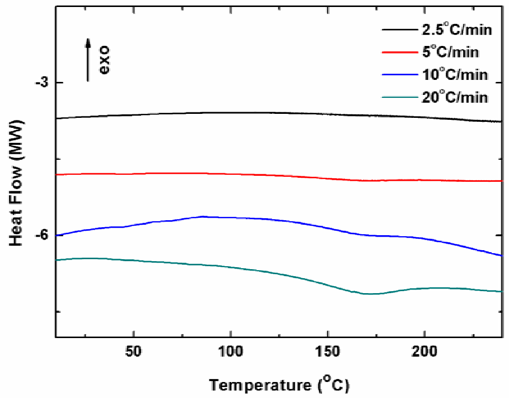


Fig. S11. DSC heating traces of AEM **2** at varied rates.

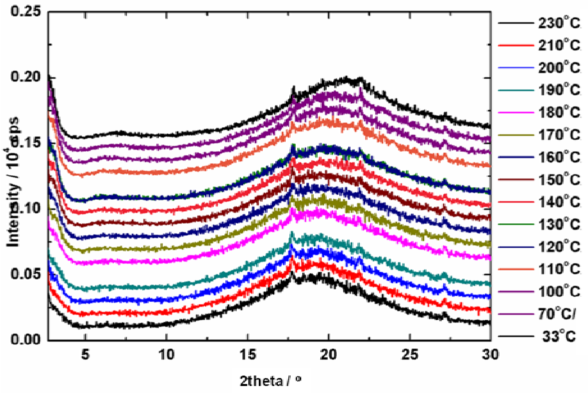


Fig. S12. WAXD of AEM **2** at varied temperatures in the 1st cooling cycle.

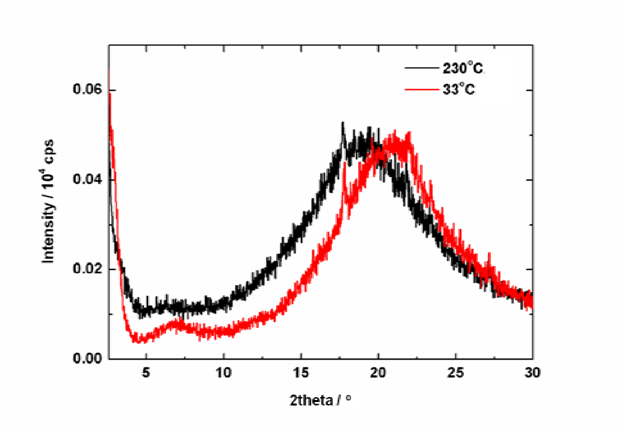


Fig. S13. WAXD of AEM **2** at the two temperatures in **Fig. S12**.

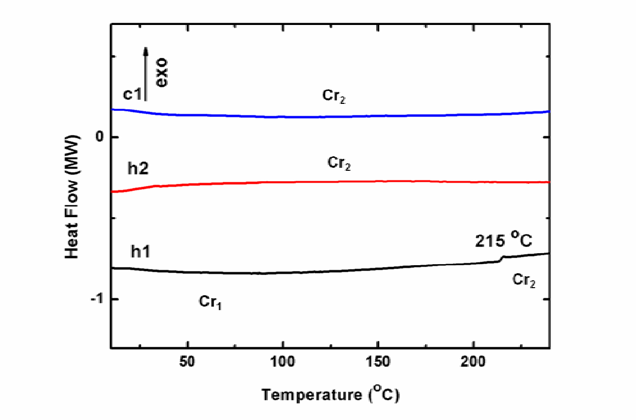


Fig. S14. DSC traces of AEM **3** at a rate of 5 °C min^{-1} (h1: the 1st heating cycle; c1: the 1st cooling cycle; h2: the 2nd heating cycle).

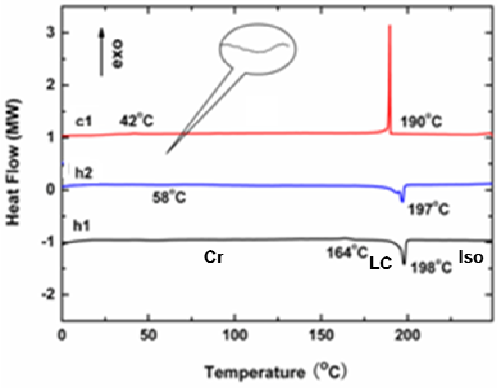


Fig. S15. DSC cycles of AEM **4** at a scan rate of 5 °C min^{-1} (h1: the 1st heating cycle; c1: the 1st cooling cycle; h2: the 2nd heating cycle).

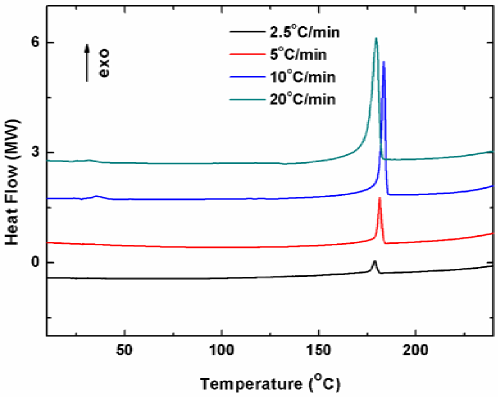


Fig. 16. DSC cooling traces of AEM **4** at varied rates.

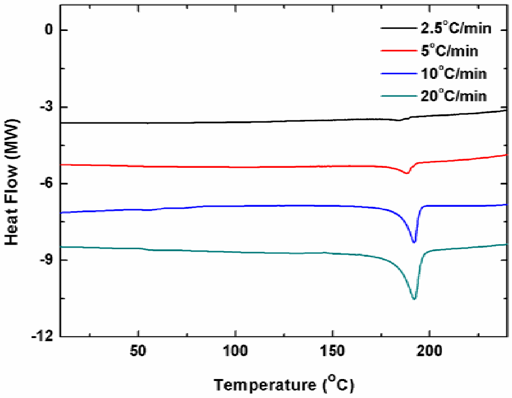


Fig. S17. DSC heating traces of AEM **4** at varied rates.

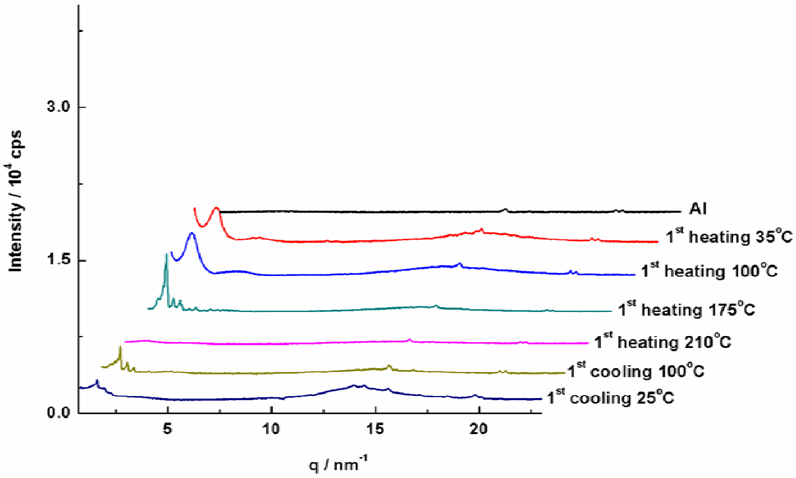


Fig. S18. XRD profiles of AEM **4** at different temperatures.

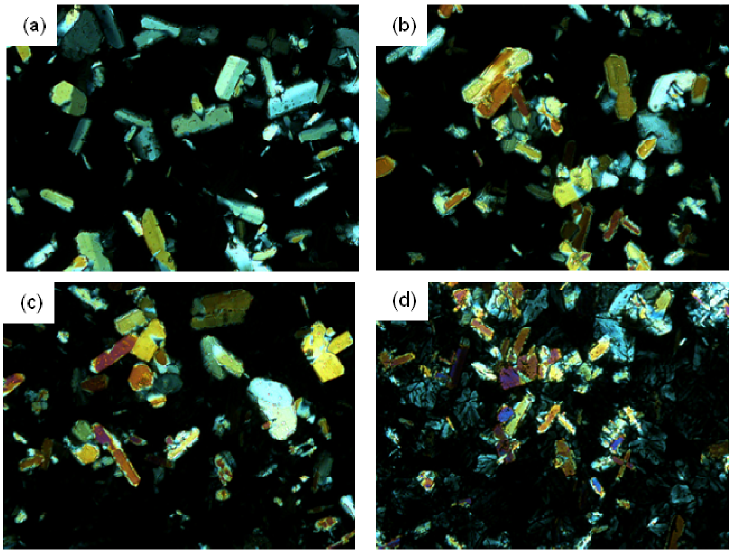


Fig. S19. Optical images of AEM **4** under POM at varied temperatures in the cooling cycle: (a) 159 ^{o}C; (b) 155 ^{o}C; (a) 117 ^{o}C; (b) 17 ^{o}C.

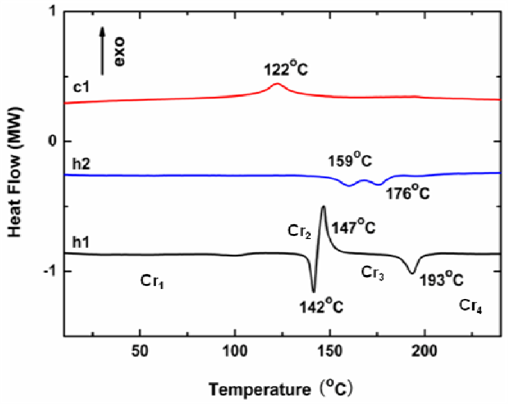


Fig. S20. DSC traces of AEM **5** at a rate of 5 ^{o}C min^{-1} (h1: the 1st heating cycle; c1: the 1st cooling cycle; h2: the 2nd heating cycle).

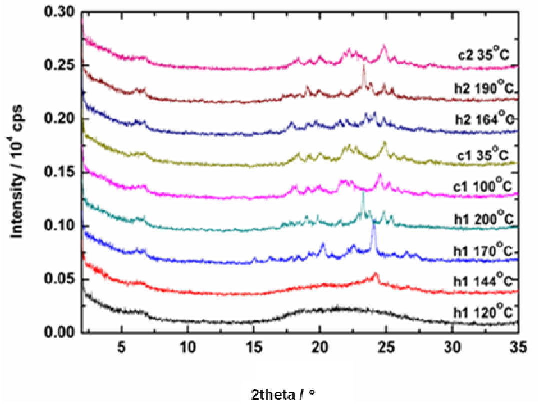


Fig. S21. WAXD profiles of AEM **5** (h1: the 1st heating cycle; c1: the 1st cooling cycle; h2: the 2nd heating cycle; c2: the 2nd cooling cycle).

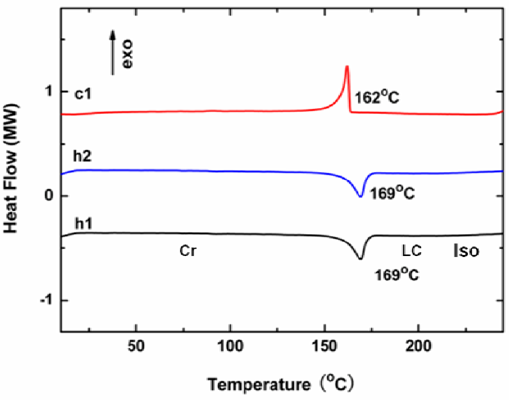


Fig. S22. DSC traces of AEM **6** at a rate of 5 °C min^{-1} (h1: the 1st heating cycle; c1: the 1st cooling cycle; h2: the 2nd heating cycle).

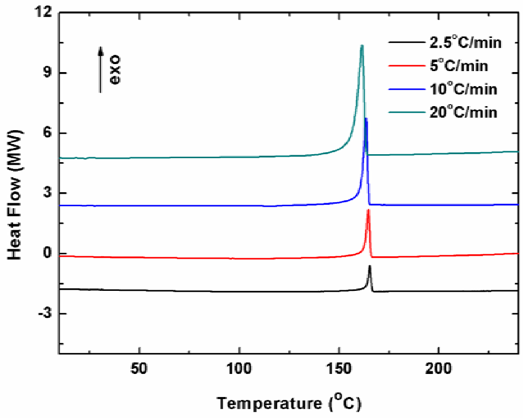


Fig. S23. DSC cooling traces of AEM **6** at varied rates.

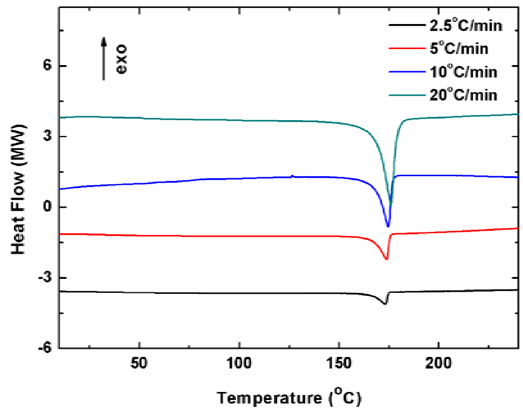


Fig. S24. DSC heating traces of AEM **6** at varied rates.

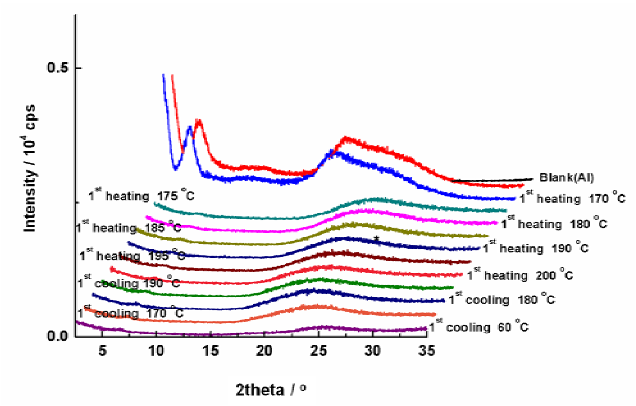


Fig. S25. WAXD profiles of AEM **6** at different temperatures.

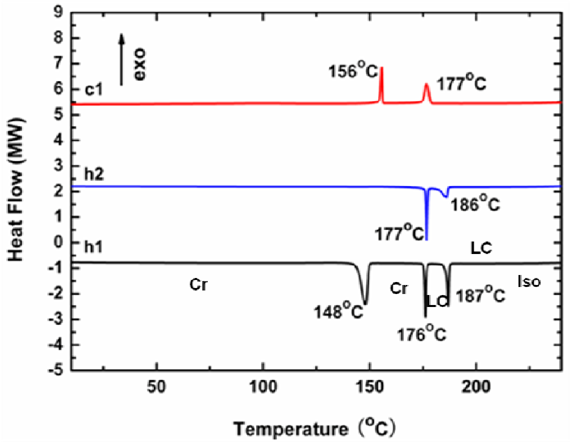


Fig. S26. DSC traces of AEM **7** at a rate of 5 °C min^{-1}(h1: the 1st heating cycle; c1: the 1st cooling cycle; h2: the 2nd heating cycle).

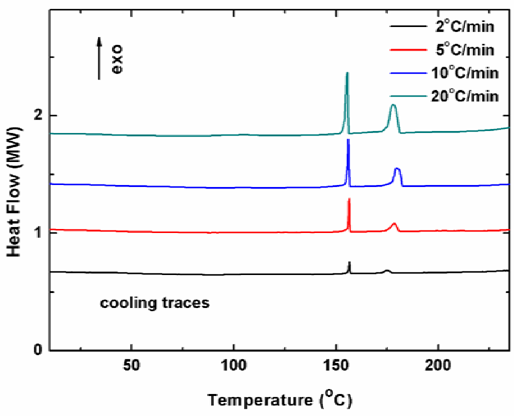


Fig. S27. DSC cooling traces of AEM **7** at varied rates.

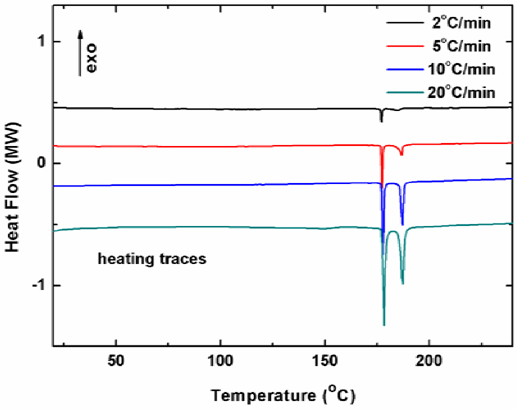


Fig. S28. DSC heating traces of AEM **7** at varied rates.

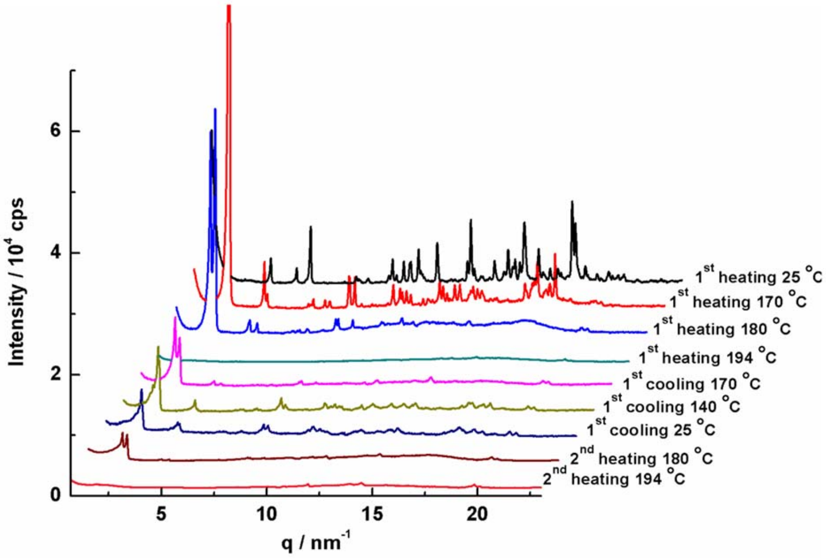


Fig. S29. XRD profiles of AEM **7** at varied temperatures.

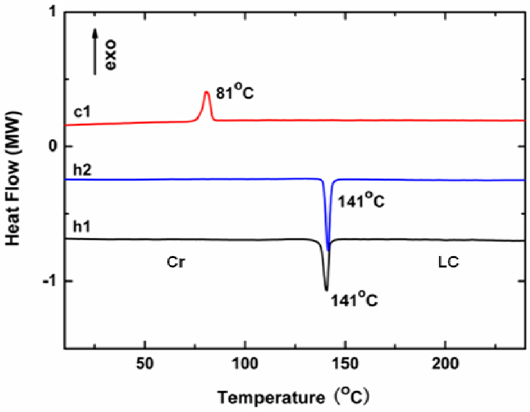


Fig. S30. DSC trace of AEM **8** at a rate of 5 °C min^{-1} (h1: the 1st heating cycle; c1: the 1st cooling cycle; h2: the 2nd heating cycle).

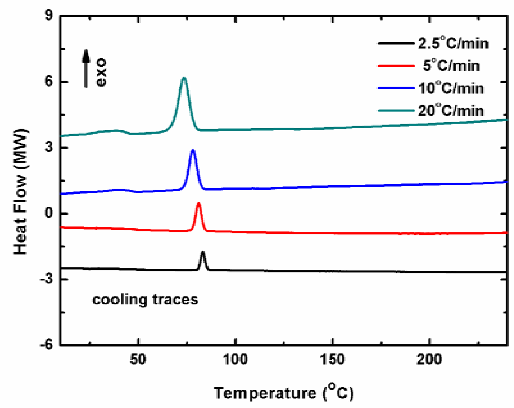


Fig. S31. DSC cooling traces of AEM **8** at varied rates.

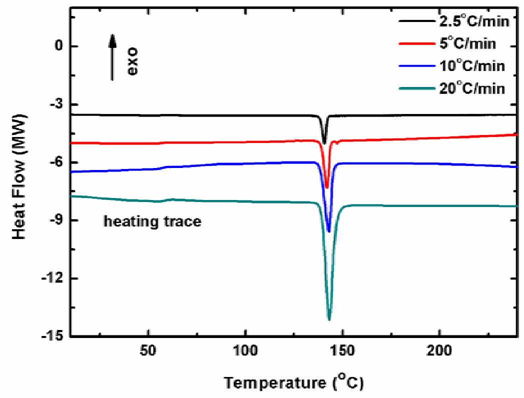


Fig. S32. DSC heating traces of AEM **8** at varied rates.

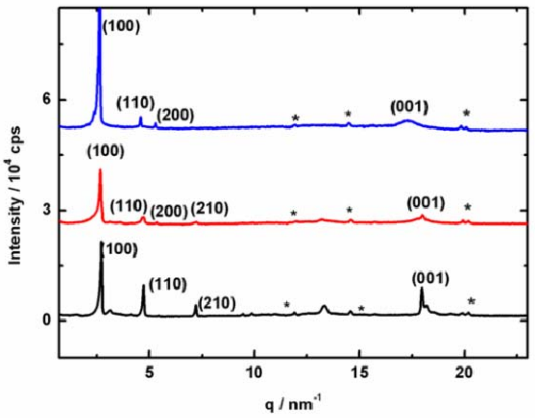


Fig. S33. XRD profiles of AEM **8** at varied temperatures (blank line: 25 °C; red line: 180 °C; blue line: 240 °C).

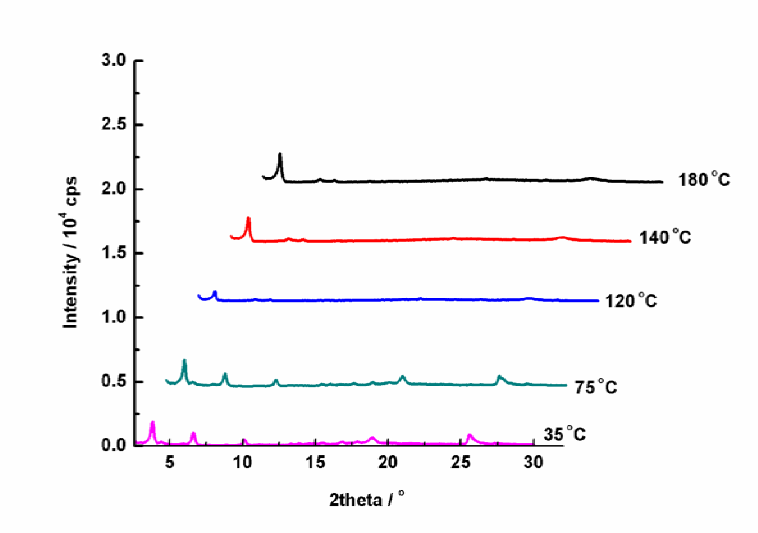


Fig. S34. WAXD profiles of AEM **8** at varied temperatures in the cooling cycle.

V. DFT Calculations of AEMs

Density functional calculations (DFT) were carried out using Gaussian03 program.[8] Molecular geometry was optimized using B3LYP hybrid functional[9] with 6-31G basis set. Molecular geometries were visualized by Chem3D program.

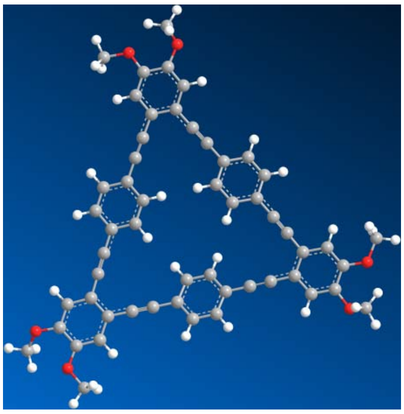


Fig. S35. DFT calculation of model compound of AEMs **1** & **2**

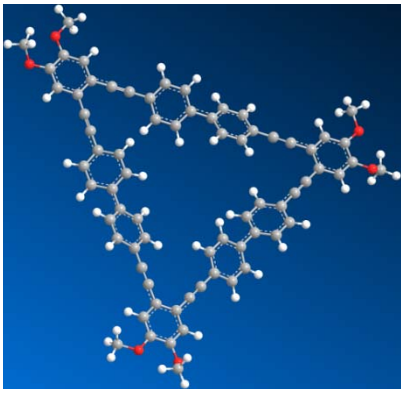


Fig. S36. DFT calculation of model compound of AEMs **3** & **4**

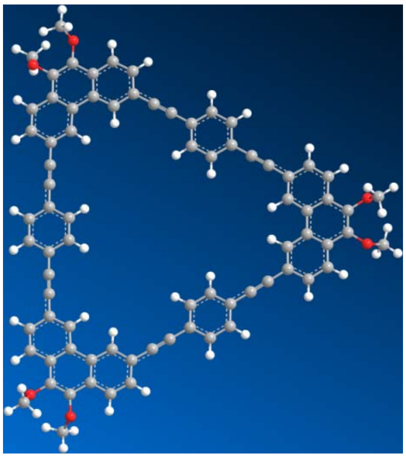


Fig. S37. DFT calculation of model compound of AEMs **5** & **6**

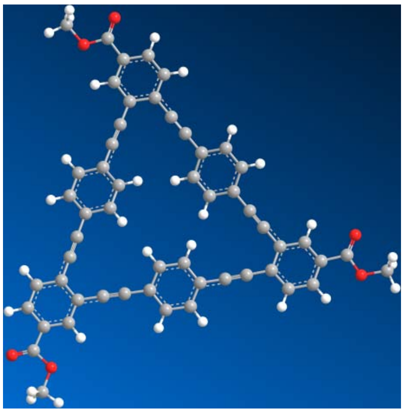


Fig. S38. DFT calculation of model compound of AEM **7**

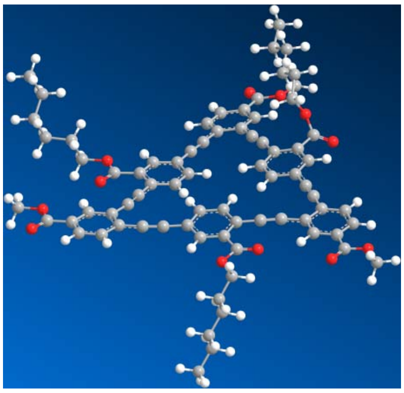


Fig. S39. DFT calculation of model compound of AEM **8**

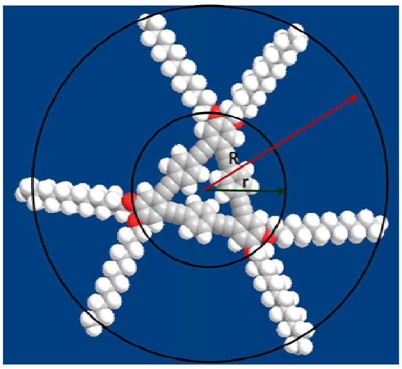


Fig. S40. Representations of r and R in **Table 3**.

Reference

1. J. Luo, Q. Yan, Y. Zhou, T. Li, N. Zhu, C. Bai, Y. Cao, J. Wang, J. Pei and D. Zhao, *Chem. Commun.* 2010, 5725-5727.
2. Z. Li, M. Wong, Y. Tao and M. *J.* D'Iorio, *Org. Chem.* 2004, **69**, 921-927.
3. N. Zhu, W. Hu, S. Han, Q. Wang and D. Zhao, *Org. Lett*. 2008, **10**, 4283-4286.
4. M. Slutsky, S. Jason and J. Phillip, G. Tew, *New J. Chem*., 2008, ***32***, 670–675
5. I. Hisaki, Y. Sakamoto, H. Shigemitsu, N. Tohnai, M. Miyata, S. Seki, A. Saeki and S. Tagawa, *Chem. Eur. J.* 2008, **14**, 4178 – 4187
6. A. Flatt, B. Chen and J. Tour. *J. Am. Chem. Soc.* 2005, **127**, 8918-8919.
7. S. Khansole, S. Junne, M. Sayyed, Y. Vibhute, *Synth. Comm..* 2008, **38**, 1792-1798.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria. M. A. Robb, J. R. Cheeseman, J. A. J. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y.Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, Revision C.02; Gaussian Inc.: Wallingford CT, 2004.
9. (a) A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098. (b) C. Lee, W. Yang and G. G. Parr, *Phys. Rev. B* 1988, **37**, 785.