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Aggregation-Induced Red-shifted Emission and Fluorescent Patterning of Poly(aryleneethynylene) with a Lateral AIEgen Substituent

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General

Commercially available reagents were used without further purification. Solvents were purified and dried according to standard procedures. All reactions were performed under nitrogen with magnetic stirring unless otherwise stated, monitored by thin layer chromatography (TLC), and the compounds were visualized with UV irradiation at 254 and 365 nm. Flash chromatography was carried out using silica gel as the stationary phase for separation and purification.

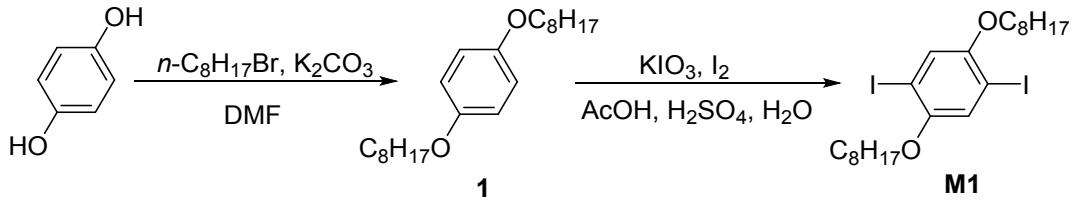

Figure S1. Synthesis of monomer **M1**.

1. Synthesis of monomer M1

1,4-bis(octyloxy)benzene (1): 1-bromo octane (15.7 mL, 90 mmol) was added to the DMF solution of hydroquinone (3.3 g, 30 mmol), and then K_2CO_3 (16.6g, 120 mmol) was added. The mixture was stirred overnight at 80 ºC and monitored by TLC. After cooled down, the solvents was evaporated under vacuum, and the mixture was extracted by CH_2Cl_2 (3×50 mL). The product was purified using column chromatography on silica gel eluented by n-hexane to afford a white solid (8.6 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 6.82 (s, 4H), 3.90 (t, J = 6.0 Hz, 4H), 1.74–1.65 (m, 4H), 1.34–1.27 (m, 20H), 0.89 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 153.4, 115.6, 68.9, 32.0, 29.7, 29.6, 29.5, 26.3, 22.8, 14.3.

M1: 1,4-bis(octyloxy)benzene (3.3 g, 10 mmol) was dissolved in 110 mL of a mixed solvent (CH_3COOH : H_2O : H_2SO_4 = 50 : 4 : 1) at 80 °C, followed by addition of KIO_3 (0.87 g, 4 mmol) and I_2 (3.3 g, 26 mmol). The mixture was stirred for 10 h, upon cooling to room temperature, the precipitate was collected by filtration and washed with Na_2CO_3 (~10%), $NaHSO_3$ (~5%) and water. The crude material was further purified by column chromatography with the eluent of *n*-hexane/CH_2Cl_2 (v/v = 1/1) to provide the product as a white solid (4.8 g, 82 %). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): δ 7.17 (s, 2H), 3.92 (t, J = 6.4 Hz, 4H), 1.79 (tt, J = 6.4 Hz, J = 6.8 Hz, 4H), 1.49 (q, J = 6.8 Hz, 4H), 1.32 (m, 16H), 0.89 (t, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 152.9, 122.8, 86.3, 70.4, 31.8, 29.2 (2C), 29.1, 26.0, 22.7, 14.1.

2. Synthesis of monomer M2

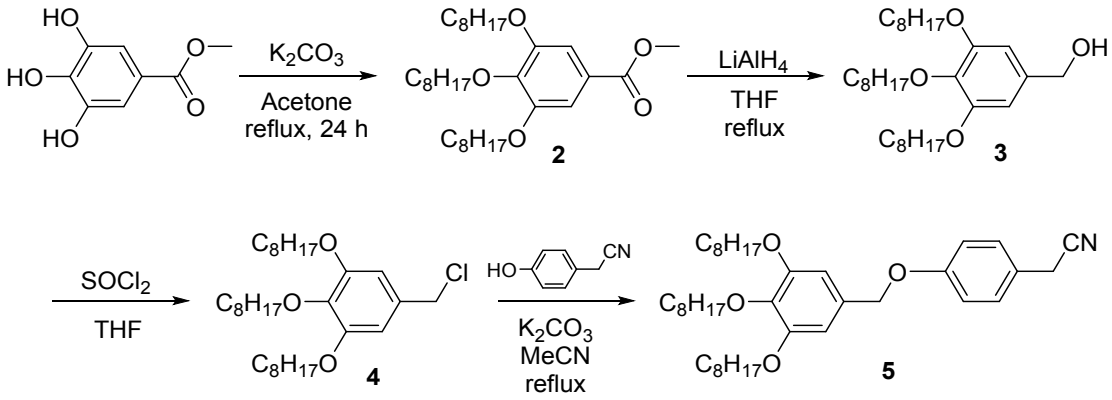

Figure S2. Synthetic routes of **5**.

Ethyl-3,4,5-tris(octyloxy)benzoate (2): Methyl-3,4,5-trihydroxybenzoate (3.68 g, 0.02 mol), 1-bromooctane (10.5 mL, 0.06 mol) and K_2CO_3 (16.56 g, 0.12 mol) were added to a round-bottomed flask with 100 mL of DMF. The mixture was stirred for 24 h at 75 °C. The mixture was then poured into 150 mL of water and extracted with EtOAc for three times. The combined organic extracts were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified on a silica gel column eluting with a CH_2Cl_2/hexane mixture (v/v = 1/4) mixture to give 9.37 g (90 %) of a colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 7.25 (s, 2H), 4.04-4.00 (m, 6H), 3.89 (s, 3H), 1.85–1.71 (m, 6H), 1.51-1.43 (m, 6H), 1.33–1.29 (m, 24H), 0.88 (t, J = 6.8 Hz, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz, δ/ppm): 153.2, 137.4, 136.2, 105.2, 73.4, 69.0, 68.0, 65.5, 31.8, 31.6, 30.3, 29.4, 25.8, 25.6, 22.7, 22.6, 14.1, 14.0.

3,4,5-Tris(octyloxy)benzyl alcohol (3): To a solution of ethyl-3,4,5-tris(octyloxy)benzoate (10.5 g, 0.02 mol) in THF was added $LiAlH_4$ (1.9 g, 0.05 mol) slowly at 0 °C. The mixture was stirred at 80 °C for 10 h and was then quenched by slow addition of isopropyl alcohol (3 mL), water (10 mL) and 30 % aq. NaOH (2 mL) successively. The mixture was extracted with EtOAc for three times and the combined

organic extract was dried by anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was obtained and further recrystallized from EtOAc to give pure product (8.4 g, 85 %). ^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 6.54 (s, 2H), 4.59 (d, 2H), 3.97 (t, 4H, J = 7.0 Hz), 3.94 (t, 2H, J = 6.8 Hz), 1.84-1.71 (m, 6H), 1.50–1.42 (m, 6H), 1.31–1.28 (m, 24H), 0.88 (t, J = 6.8 Hz, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz, δ/ppm): 153.2, 138.3, 132.3, 107.0, 73.4, 69.1, 68.0, 47.0, 31.8, 31.6, 30.3, 29.3, 25.8, 25.6, 22.7, 22.6, 14.1, 14.0.

5-(chloromethyl)-1,2,3-tris(octyloxy)benzene (4): The compound **3** (5.4 g) was dispersed in 30 mL of THF, and then 3.5 mL of SO_2Cl_2 was slowly added to the solution. The mixture was stirred vigorously for 3 h at room temperature, and then quenched by water. After extracted by CH_2Cl_2, the product **4** was obtained as an oil (5.04 g, 90 %). ^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 6.57 (s, 2H), 4.61 (d, 2H), 4.00-3.92 (m, 6H), 1.89-1.67 (m, 6H), 1.50–1.42 (m, 6H), 1.40–1.22 (m, 24H), 0.88 (t, J = 8 Hz, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz, δ/ppm): 153.2, 138.4, 132.3, 107.1, 73.4, 69.2, 46.9, 31.9, 31.8, 30.4, 29.6, 29.4(2), 29.3, 26.1(2), 22.7, 22.7, 14.1.

2-(4-((3,4,5-tris(octyloxy)benzyl)oxy)phenyl)acetonitrile (5): To a solution of **4** (1.10g, 2.15 mmol) in 20 mL of acetonitrile was added 2-(4-hydroxyphenyl)acetonitrile (0.29 g, 2.15 mmol), and then excess K_2CO_3 (0.89 g, 6.45 mmol) was added. The mixture was refluxed for 12 h and then cooled down to room temperature, the solvents were removed and the crude products were extracted for three times by CH_2Cl_2. After purification by column chromatography, the target compound **5** was isolated as a coleless oil (1.06 g, 81 %).^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 7.29 (d, J = 5.2 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.64 (s, 2H), 4.98 (s, 2H), 4.02-4.00 (m, 6 H), 3.82 (s, 2H), 1.85-1.80 (m, 6H), 1.53-1.48 (m, 6H), 1.40-1.28 (m, 24H), 0.9 (t, J = 6.8 Hz, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz, δ/ppm): 158.6, 153.3, 138.0, 131.5, 129.1, 122.1, 118.2, 115.5,

106.1, 73.4, 70.5, 69.1, 53.4, 31.8, 31.6, 30.3, 29.4(2), 25.8(2), 22.7, 22.6, 14.1(2).

1,4-dibromo-2-(bromomethyl)benzene (6): To a solution of 2,5-dibromotoluene (1 ml, 7.26 mmol) in chloroform (20 ml) was added *N*-bromosuccinimide (1.422 g, 8.00 mmol) and benzoyl peroxide (176.8 mg, 0.73 mmol). The mixture was stirred for 1 h at room temperature and then heated at the reflux temperature overnight. Afterwards, the mixture was filtered and the solvent removed to give a residual solid which was purified by chromatography on a silica gel column using *n*-hexane as eluent. The 1,4-dibromo-2-(bromomethyl)benzene was isolated as a white solid (2.10 g, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.60 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 2.4 Hz, 1H), 4.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 139.0, 134. 7, 134.0, 133.1, 123.0, 121.5, 32.2.

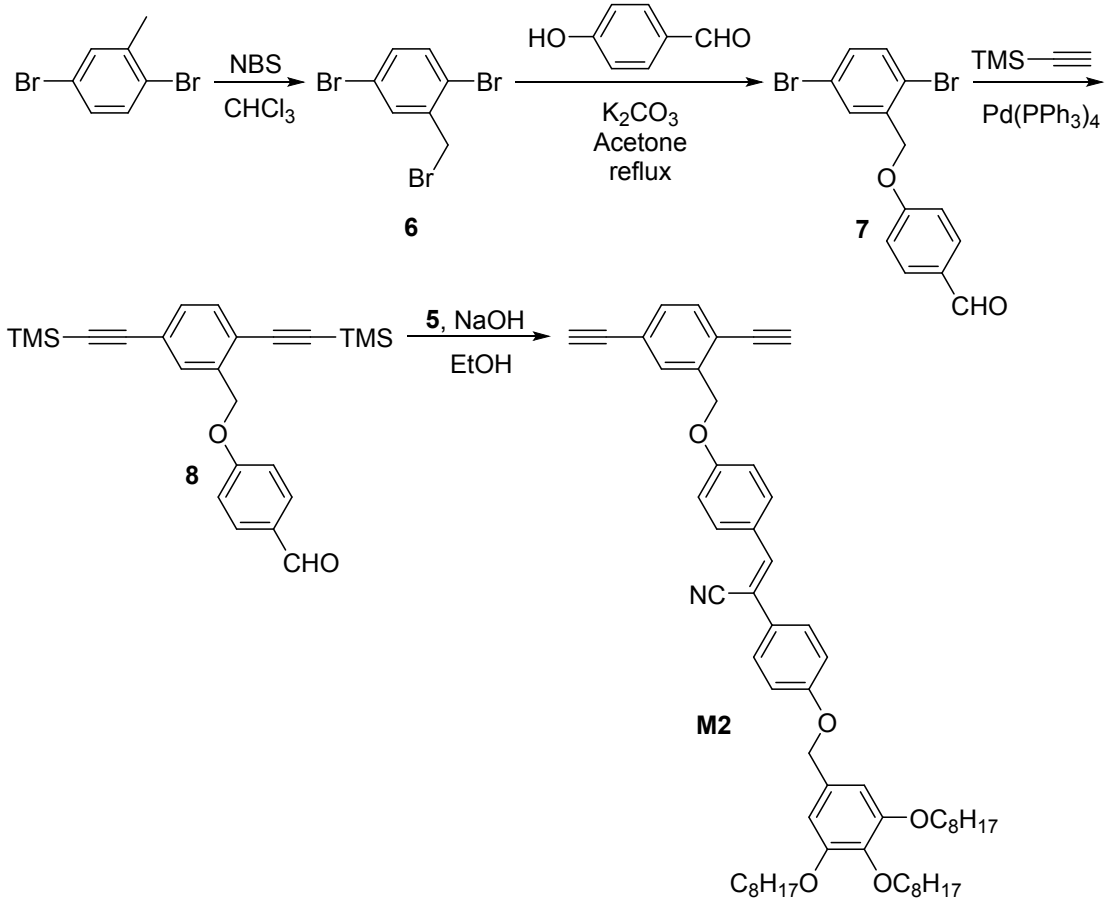

Figure S3. Synthesis of monomer **M2**.

4-((2,5-dibromobenzyl)oxy)benzaldehyde (7): To a solution of **6** (1.9 g, 5.8 mmol) in 20 mL of acetone was added 4-hydroxybenzaldehyde (0.85 g, 6.96 mmol), and then excess K_2CO_3 (1.6 g, 11.6 mmol) was added. The mixture was refluxed for 12 h and then cooled down to room temperature, the solvents were removed and the crude products were extracted by CH_2Cl_2 for three times. After purification by column chromatography, the target compound **7** was obtained as a white solid (1.72 g, 80 %).^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 9.83 (s, 1H), 7.80 (d, J = 8.8 Hz, 2H), 7.61 (s, 1H), 7.39 (d, J = 8.48 Hz, 1H), 7.27 (d, J = 2.44 Hz, 1H), 7.04 (d, J = 8.72 Hz, 2H), 5.09 (s, 2H).

4-((2,5-bis((trimethylsilyl)ethynyl)benzyl)oxy)benzaldehyde (8): To a solution of **7** (0.74 g, 2 mmol) in CH_2Cl_2/Et_3N (v/v = 1/1) was added $Pd(PPh_3)_4$ (50 mg) and CuI (30 mg). After the solution was stirred for 30 min at 0 °C, trimethylsilylacetylene (2 mL) was added and the suspension was heated to 75 °C for 24 h, then the mixture was cooled down to room temperature and the volatile solvents were removed, the residue was purified by column chromatography on silica gel using *n*-hexane/CH_2Cl_2 (v/v = 3/1) as the eluent to provide compound **8** (0.63 g, 78%). ^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 9.89 (s, 1H), 7.85 (d, J = 8.8 Hz, 2H), 7.59 (s, 1H); 7.44 (d, J = 7.88 Hz, 1H), 7.38 (dd, J = 7.96 Hz, 1.6 Hz, 1H), 7.09 (d, J = 8.72 Hz, 2H), 5.25 (s, 2H), 0.24 (s, 9H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz, δ/ppm): 190.7, 163.6, 138.1, 132.4, 132.0, 131.9, 131.6, 131.2, 130.6, 123.7, 121.7, 115.2, 114.9, 104.2, 102.3, 101.5, 96.8, 68.0, -0.1, -0.2(2).

M2: The reacting reagents of 2-(4-((3,4,5-tris(octyloxy)benzyl)oxy)phenyl)acetonitrile (0.78 g, 1.28 mmol) and 4-((2,5-

bis((trimethylsilyl)ethynyl)benzyl)oxy)benzaldehyde (0.52 g, 1.28 mmol) was dissolved in 40 mL of EtOH and 4 mL of THF, and then NaOH (0.21 g, 5.12 mmol) was added under nitrogen, the mixture was stirred at room temperature for 5 h under dark. The precipitate was filtered and washed by EtOH. The product was collected and dried to give the monomer M2 (0.98 g, 90%). ^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 7.86 (d, J = 8.84 Hz, 2H), 7.68 (s, 1H), 7.59 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 7.96 Hz, 1H), 7.41 (dd, J = 8.88, 1.48 Hz, 1H), 7.36 (s, 1H), 6.63 (s, 2H), 5.27 (s, 2H), 4.99 (s, 2H), 4.00-3.94 (m, 6H), 3.46 (s, 1H), 3.19 (s, 1H), 1.84-1.72 (m, 6H), 1.49-1.44 (m, 6H), 1.33-1.29 (m, 24 H), 0.89 (t, J = 6.76 Hz, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz, δ/ppm): 159.9, 159.3, 153.4, 139.8, 139.0, 138.0, 132.7, 131.4, 131.3, 131.0, 130.7, 129.0, 127.5, 127.2, 123.0, 120.7, 118.6, 115.3, 115.2, 108.6, 106.1, 84.5, 82.9, 80.2, 79.4, 73.5, 70.6, 69.1, 67.6, 32.0, 31.9, 30.4, 29.6, 29.4 (2), 26.2 (2), 22.8, 22.7, 14.2.

3. Synthesis of monomer M3

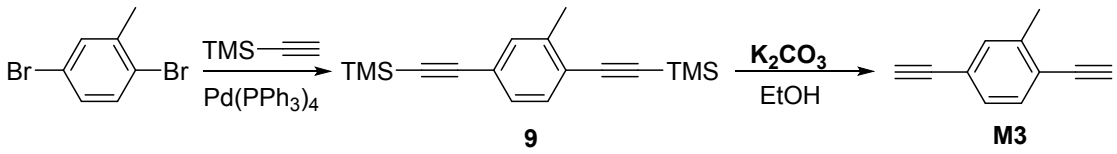

Figure S4. Synthesis of monomer **M3**.

((2-methyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (9): To a solution of 2,5-dibromotoluene (0.5 g, 2 mmol) in CH_2Cl_2/Et_3N (v/v = 1/1) was added the catalysts $Pd(PPh_3)_4$ (50 mg) and CuI (30 mg). After the solution was stirred for 30 min at 0 °C, trimethylsilylacetylene (2 mL) was added and then the suspension was heated to 75 °C for 24 h. The reaction was monitored by TLC, after cooled down, the

solvents were removed and the residue was purified by column chromatography on silica gel using n-hexane as the eluent to provide compound **9** (1.78 g, 81%). ^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 7.35 (d, J = 7.92 Hz, 1H), 7.31 (s, 1H), 7.22 (d, J = 7.96 Hz, 1 H), 2.39 (s, 3H), 0.26 (s, 9H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz, δ/ppm): 140.5, 132.7, 131.9, 129.0, 123.1, 122.9, 104.8, 103.5, 100.2, 95.7, 20.4, -0.0, -0.1.

M3: The compound of ((2-methyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (0.2 g, 0.7 mmol) was dissolved in 20 mL of EtOH and then excess K_2CO_3 (0.39 g, 2.8 mmol) was added. The mixture was stirred for 6 h and then extracted by CH_2Cl_2 for three times. The organic phase was combined and evaporated under vacuum. The crude product was purified using column chromatography on silica gel using n-hexane as the eluent to provide **M3** in a quantitative yield. ^{1}H NMR ($CDCl_3$, 400 Hz, δ/ppm): 7.23 (d, J = 7.92 Hz, 1H), 7.16 (s, 1H), 7.09 (d, J = 7.72 Hz, 1H), 3.18 (s, 1H), 2.96 (s, 1H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz, δ/ppm): 140.8, 133.0, 132.4, 129.2, 122.6, 12.3, 83.3, 82.8, 82.0, 78.6, 20.4.

4. Synthesis of **P1** and **P2**

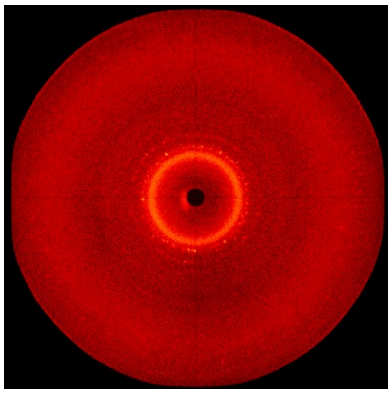

Figure S1. 2D-XRD pattern of **P2**.