Supporting Information of

"*Synthesis and Characterizations of Conjugated Poly(9, 10-Bisarylethynyl -2,6-anthrylene)s and Poly(9,10-Bisalkynyl-2,6-anthrylene)*" by

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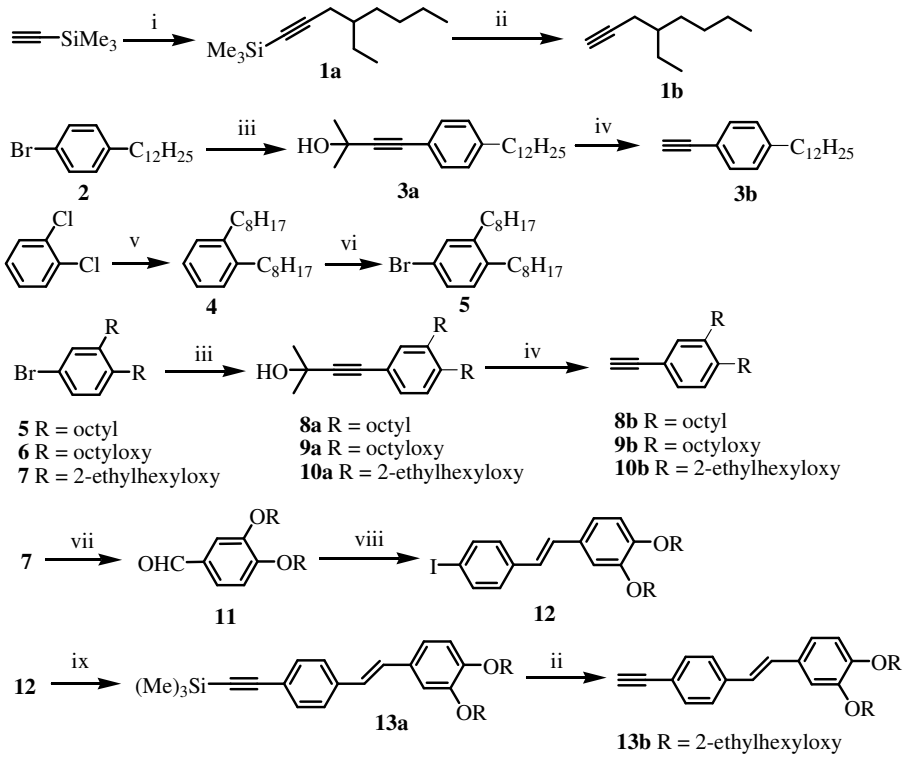
Scheme 1. Synthetic route of the intermediates.[a]



[a]Reagents and conditions: i) *n*-BuLi, HMPT, 2-ethylhexylbromide, THF, 0 ^{o}C to room temperature. ii) K_2CO_3, MeOH, room temperature. iii) $Pd(PPh_3)_2Cl_2$, CuI, 2-methylbut-3-yn-2-ol, Et_3N, reflux. iv) NaOH, THF, reflux. v) $C_8H_{17}MgBr$, $Ni(dppp)Cl_2$, Et_2O, reflux. vi) Br_2, $FeCl_3$, $CHCl_3$, 0 ^{o}C to room temperature. vii) (1) *n*-BuLi, THF, -78 ^{o}C; (2) DMF, -78 ^{o}C to room temperature. viii) diethyl(4-iodophenyl)methylphosphonate, *t*-BuOK, THF, 0 ^{o}C to room temperature. ix) trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, THF/Et_3N, room temperature.

4-Ethyl-1-trimethylsilyl-1-octyne (1a). To a solution of trimethylsilylacetylene (1.96 g, 20.0 mmol) in THF (40 mL) was dropwised *n*-BuLi (8.00 mL, 20.0 mmol, 2.5 M in hexane) at 0 ^{o}C. One hour later, HMPT (3.58 g, 20.0 mmol) were added into the mixture followed by 2-ethylhexyl bromide (1.93 g, 10.0 mmol). After stirred at room temperature overnight, the resulting mixture was poured into water and extracted with petroleum ether (PE). The organic layer was washed with brined and dried over anhydrous $MgSO_4$ On removal of the solvent, he residue was purified with column chromatography on silica gel with PE (30 -60 ^{o}C) as eluent to yield a colorless liquid, which was used for next step directly. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.14-0.18 (m, 9H), 0.83-0.92 (m, 6H), 1.27-1.40 (m, 8H), 1.54 (s, 1H), 2.19 (d, *J*= 5.17 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.09, 14.03, 22.94, 23.78, 26.08, 28.97, 32.70, 38.66, 85.14, 106.39, 113.71.

4-Ethyl-1-octyne (1b). A mixture of **1a**, K_2CO_3 (4.15 g, 30.0 mmol) and methanol (20 mL) was stirred for 5 hours. The resulting mixture was poured into water and extracted with petroleum ether. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. On removal of the solvent the, the residue was purified with column chromatography on silica gel with petroleum ether as eluent to yield **3** (0.71 g, total yield 50 %) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.82-0.90 (m, 6H), 1.26-1.44 (m, 8H), 1.50 (s, 1H), 1.55 (s, 1H), 2.16-2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.05, 14.07, 22.22, 22.93, 25.87, 29.01, 32.64, 38.45, 68.82, 83.82.

4-(4-Dodecylphenyl)-2-methylbut-3-yn-2-ol (3a). To a mixture of 1-bromo-4-dodecylbenzene (**2**, 7.00 g, 21.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.45 g) and CuI (0.24 g) was added Et_3N (40 mL).

2-Methylbut-3-yn-2-ol (2.17 g, 25.8 mmol) was added dropwise and the mixture was stirred at reflux for 5 h. The precipitate was filtrated and washed with petroleum ether (PE). The organic phase was washed with brine, dried over anhydrous $MgSO_4$. On removal the solvent, the residue was purified by column chromatography on silica gel (PE:Et_2O= 4:1) to yield **3a** (4.36 g, 78.5 %) as a colorless oil. ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) 0.85-0.89 (m, 3H), 1.24-1.27 (m, 20 H), 1.60 (s, 1H), 2.57 (t, *J*= 7.68 Hz, 2H), 7.10 (d, *J*= 8.1 Hz, 2H), 7.31 (d, *J*= 8.1 Hz, 2H).

1-Dodecyl-4-ethynylbenzene (3b). To a mixture of **3a** (1.50 g, 4.57 mmol) and NaOH (0.912 g, 22.8 mmol) was added THF (10 mL). The mixture was heated under reflux for 26 h. The resulting mixture was poured into water and extracted with PE. The organic extracts were washed with brine and dried over anhydrous $MgSO_4$. On removal of the solvent, the residue was purified with column chromatography on silica gel (PE:Et_2O=4:1) to yield **3b** (1.10 g, 88.7 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.86-0.90 (m, 3H), 1.25-1.30 (m, 18H), 1.57-1.61 (m, 2 H), 2.59 (t, *J*= 7.68 Hz, 2H), 3.03 (s, 1H), 7.13 (d, *J*= 7.95 Hz, 2H), 7.40 (d, *J*= 8.07 Hz, 2H).

1,2-Dioctylbenzene (4):

Grignard reagent prepared from Mg (5.16 g, 212 mmol), and octyl bromide (41.0 g, 212 mmol) in diethyl ether (150 mL) was added to the mixture of *o*-dichlorobenzene (10.4 g, 70.7 mmol) and Ni(dppp)Cl_2 (125 mg) in diethyl ether (70 mL) at 0 ^{o}C. The mixture was heated to reflux for 12 h. After being cooled, the mixture was hydrolyzed with 1 M HCl and extracted with diethyl ether. The organic extracts were washed with brine, and dried over anhydrous $MgSO_4$. On removal of the solvent, the residue was purified with column chromatography on silica gel with

petroleum ether as eluent and then distilled to yield **5** (15.0 g, 70.0 %) as colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.80-0.90 (m, 6H), 1.26-1.33 (m, 10H), 1.52-1.59 (m, 4H), 2.56-2.62 (m, 4H), 7.12-7.14 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 14.11, 22.74, 29.36, 29.50, 29.79, 31.41, 31.98, 32.77, 125.71, 129.10, 140.51.

4-Bromo-1,2-dioctylbenzene (5):

To a mixture of **4** (2.73 g, 9.03 mmol), $FeCl_3$ (32 mg) in chloroform (15 mL) was dropwised bromine (1.65 g) at 0 ^{o}C. After stirred over night at room temperature, the mixture was poured into water and extracted with PE. The organic extracts were washed with brine and dried over anhydrous $MgSO_4$. On removal of the solvent, the residue was purified with column chromatography on silica gel with PE as eluent to yield **5** as a colorless liquid, which was used for next step directly. ^{1}H NMR (300 MHz, CDCl3) δ (ppm) 0.85-0.90 (m, 6H), 1.26-1.30 (m, 20H), 1.51-1.55 (m, 4H), 2.50-2.57 (m, 4H), 6.99 (d, J= 8.4 Hz, 1H), 7.22 (dd, J_1= 8.0 Hz, J_2= 2.0 Hz, 1H), 7.36 (s, 1H).

4-(3,4-Dioctylphenyl)-2-methylbut-3-yn-2-ol (8a):

The procedure was the same as the preparation of **3a** but from **5** and 2-methybut-3-yn-2-ol (1.26 g, 15.0 mmol). On removal of the solvent, the residue was purified with column chromatography on silica gel (PE:Et_2O= 4:1) to yield **8a** (2.00 g, 52 % in two step) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.86-0.90 (m, 6H), 1.28-1.64 (m, 30H), 2.02 (s, 1H), 2.52-2.60 (m, 4H), 7.06 (d, J= 7.8 Hz, 1H), 7.16 (dd, J_1= 7.8 Hz, J_2= 1.5 Hz, 1H), 7.20 (s, 1H).

1,2-Dioctyl-4-ethynylbenzene (8b):

The procedure was the same as the preparation of **3b** but from of **8a** (1.50 g, 3.90 mmol), sodium hydroxide (0.468 g, 11.7 mmol) and THF (15 mL). On removal of the solvent, the residue was purified with column chromatography on silica gel (PE:Et_2O= 4:1) to yield **8b** (1.13 g, 89.0 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.86-0.90 (m, 6H), 1.29-1.33 (m ,16 H), 1.41-1.50 (m, 4H), 1.76-1.86 (m, 4H), 2.98 (s, 1H), 3.95-4.01 (m, 4H), 6.79 (d, *J*= 8.28 Hz, 1H), 6.99 (d, *J*= 1.89 Hz, 1H), 7.06 (dd, J_1= 8.23 Hz, J_2= 1.90 Hz, 1H).

4-(3,4-Dioctyloxyphenyl)-2-methylbut-3-yn-2-ol (9a):

The procedure was the same as the preparation of **3a** but from **6** (5.00 g, 12.1 mmol), and 2-methybut-3-yn-2-ol (1.32 g, 15.7 mmol).On removal of the solvent, the residue was purified with column chromatography on silica gel (PE:Et_2O= 4:1) to yield **9a** (4.47 g, 83.1 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.83-0.90 (m, 6H), 1.28-1.31 (m, 22H), 1.39-1.48 (m, 4H), 1.78-1.83 (m, 4H), 1.98 (s, 1H), 3.94-4.00 (m, 4H), 6.77 (d, *J*= 7.23 Hz, 1H), 6.92 (d, *J*= 1.86 Hz, 1H), 6.97 (dd, J_1= 8.26 Hz, J_2= 1.90 Hz, 1H).

1,2-Dioctyloxy-4-ethynylbenzene (9b):

The procedure was the same as the preparation of **3b** but from **9a** (2.00 g, 4.80 mmol), sodium hydroxide (0.960 g, 24.0 mmol) and THF (20 mL). On removal of the solvent, the residue was purified with column chromatography on silica gel (petroleum ether: ether= 4:1) to yield **9b** (1.38 g, 80.2 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.85-.89 (m, 6H), 1.27-1.32 (m, 16H), 1.40-1.54 (m, 4H), 1.75-1.85 (m, 4H), 2.97 (s, 1H), 3.94-4.00 (m, 4H), 6.78 (d, *J*= 8.28 Hz, 1H), 6.98 (d, *J*= 1.83 Hz, 1H), 7.05 (dd, J_1= 8.23 Hz, J_2= 1.90 Hz, 1H).

4-(3,4-Di(2-ethylhexyloxy)phenyl)-2-methylbut-3-yn-2-ol (10a):

The procedure was the same as the preparation of **2a** but from **7** (2.00 g, 4.08 mmol), $Pd(PPh_3)_2Cl_2$ (102 mg), CuI (55 mg), triethylamine (7 mL) and 2-methybut-3-yn-2-ol (0.528 g, 6.28 mmol).On removal of the solvent, the residue was purified with column chromatography on silica gel (petroleum ether: ether= 4:1) to yield **10a** (1.40 g, 70.0 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.88-0.95 (m, 12H), 1.31-1.54 (m, 16H), 1.61 (m, 6H), 1.75 (m, 2H), 1.97 (s, 1H), 3.83-3.86 (m, 4H), 6.77 (d, *J*= 8.22 Hz, 1H), 6.91 (d, *J*= 1.83 Hz, 1H), 6.96 (dd, J_1= 8.17 Hz, J_2= 1.87 Hz, 1H).

1,2-Di(2-ethylhexyloxy)-4-Ethynylbenzene (10b):

The procedure was the same as the preparation of **2b** but from **10a** (1.16 g, 2.78 mmol), sodium hydroxide (0.330 g, 8.25 mmol) and THF (10 mL). On removal of the solvent, the residue was purified with column chromatography on silica gel (petroleum ether: ether= 4:1) to yield **10b** (0.97 g, 97 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.88-0.95 (m, 12H), 1.31-1.53 (m, 16H), 1.71-1.79 (m, 2H), 2.98 (s, 1H), 3.83-3.87 (m, 4H), 6.78 (d, *J*= 8.1 Hz, 1H), 7.02 (d, *J*= 1.8 Hz, 1H), 7.08 (dd, J_1= 8.4 Hz, J_2= 1.8 Hz, 1H).

3,4-Di(2-ethylhexyloxy)benzaldehyde (11):

To **7** (4.00 g, 9.68 mmol) in THF (50 mL) was added *n*-BuLi (4.30 mL, 10.6 mmol, 2.5 M in hexane) dropwise at -78 ^{O}C. After 45 min, DMF (0.90 mL, 11 mmol) was added dropwise. The mixture was stirred at room temperature overnight, and then poured into water, extracted with PE. The organic extracts were washed with brine, dried over anhydrous $MgSO_4$. On removal the solvent, the residue was purified with column chromatography on silica gel (PE:DCM= 4:1-1:1)

to yield **11** as a colorless oil (3.30 g, 94.0 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.90-0.96 (m, 12H), 1.31-1.35 (m, 8H), 1.50-1.57 (m, 8H), 1.78-1.84 (m, 2H), 3.87-3.99 (m, 4H), 6.94 (d, *J*= 8.01 Hz, 1H), 7.38-7.43 (m, 2H), 9.83 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 11.6, 14.4, 23.4, 24.3, 29.5, 31.0, 39.8, 71.8, 111.0, 111.9, 126.9, 130.2, 150.2, 155.5, 191.4.

(*E*)-4-(4-Iodostyryl)-1,2-di(2-ethylhexyloxy)benzene (12):

To a solution of diethyl 4-iodobenzylphosphonate (3.75 g, 10.6 mmol) and **8** (3.20 g, 8.83 mmol) in THF (60 mL) was dropwised *t*-BuOK (22 mL, 1.0 M in THF) at 0 ^{O}C. After stirred at room temperature overnight, the mixture was poured into water, extracted with PE. The organic extracts were washed with brine, dried over anhydrous $MgSO_4$. On removal the solvent, the residue was purified with column chromatography on silica gel (PE:DCM= 10:1) to yield **12** as a colorless oil (4.68 g, 94.0 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.85-0.97 (m, 12H), 1.32-1.34 (m, 8H), 1.48-1.55 (m, 8H), 1.77-1.78 (m, 2H), 3.87-3.92 (m, 4H), 6.85 (t, *J*=7.80 Hz), 6.99-7.06 (m, 3H), 7.23 (d, *J*= 8.40 Hz, 2H), 7.65 (d, *J*= 8.25 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 11.2, 14.1, 22.7, 23.1, 23.9, 29.1, 30.6, 39.6, 39.7, 71.6, 92.1, 111.2, 113.5, 120.1, 125.2, 128.0, 129.6, 129.9, 137.3, 137.7, 149.7, 149.9.

1-[(*E*)-(4-(3,4-Di(2-ethylhexyloxy)styryl)phenyl]-2-trimethylsilylacetylene (13a):

To a mixture of **12** (4.00 g, 7.10 mmol), $PdCl_2$ $(PPh_3)_2$ (100 mg), CuI (53 mg) was added THF/Et_3N (64 mL/ 16 mL). Then trimethylsilylacetylene (0.84 g, 8.5 mmol) was added dropwise. The resulting mixture was stirred overnight. The precipitate was filtrated and washed with PE. The organic phase was washed with brine, dried over anhydrous $MgSO_4$. On removal the solvent, the residue was purified with chromatography on silica gel (PE: DCM= 8:1) to yield **13a** as a

colorless oil (3.70 g, 97.0 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.24-0.25 (m, 12H), 0.85-0.98 (m, 12H), 1.33-1.34 (m, 8H), 1.48-1.54 (m, 8H), 1.77-1.81 (m, 2H), 3.87-3.92 (m, 4H), 6.85 (t, *J*= 7.10 Hz, 2H), 6.93-7.08 (m, 3H), 7.39-7.46 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 0, 11.2, 14.1, 22.7, 23.1, 24.0, 29.1, 30.6, 39.6, 71.6, 94.8, 105.8, 111.2, 113.4, 120.1, 121.5, 125.7, 126.0, 129.7, 130.0, 132.3, 137.9, 149.7, 149.8.

1,2-Di(2-ethylhexyloxy)-(*E*)-4-(4-Ethynylstyryl)benzene (13b):

A mixture of **13a** (1.00 g, 1.88 mmol), K_2CO_3 (0.52 g, 3.8 mmol) and MeOH/CH_2Cl_2 (40 mL/ 5 mL) was stirred at room temperature for 2 h, and then poured into water for extraction with Et_2O. The organic layer was washed with brine, dried over anhydrous $MgSO_4$. On removal the solvent, the residue was purified with chromatography on silica gel (PE:DCM= 5:1) to yield **13b** as a colorless oil (0.86 g, 99 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.88-0.98 (m, 12H), 1.32-1.37 (m, 8H), 1.48-1.54 (m, 8H), 1.77-1.79 (m, 2H), 3.12 (s, 1H), 3.84-3.96 (m, 4H), 6.86 (t, *J*= 8.31 Hz, 2H), 6.94-7.09 (m, 3H), 7.42-7.48 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 11.2, 14.1, 23.1, 24.0, 29.2, 30.7, 39.6, 71.6, 77.7, 83.9, 111.3, 113.4, 120.2, 120.5, 125.6, 126.1, 130.0, 132.4, 138.3, 149.7, 149.9.