Supporting information:

All reactions were conducted in an inert atmosphere. The dry solvents were used freshly distilled.

octyl 4'-bromobiphenyl-4-carboxylate (1)

6.62 g (21.2 mmol) 4,4'-dibromobiphenyl was dissolved in 150 mL THF, 8.5 mL (21.2 mmol, 1 equiv) 2.5 M *n*-butyllithium in hexane was added dropwise at -78 ^{o}C during a period of 30 min. The reaction mixture was stirred at -78 ^{o}C further for 2 hours, then CO_2 was bubbled into the flask. After 2 hours, the reaction temperature was raised to room temperature for over night. The reaction was quenched by adding 100 mL water, THF was removed under vacuum, the residue was filtered and the filtrate was acidified with concentrated hydrochloric acid to PH = 2. The suspension was filtered and washed with water, dried under vacuum to give 4.66 g white solid. The crude product was used directly in the next step without purification.

4.66 g crude product **1**, 3.2 mL (20.3 mmol, ~ 1.2 equiv) *n*-octanol, 11 g (42.0 mmol, ~ 2.5 equiv) PPh_3 (triphenylphosphine) were suspended in 120 mL THF, 8.3 mL (42.2 mmol, ~ 2.5 equiv) DIAD (diisopropylazodicarboxylate) in 10 mL THF was added dropwise at 0 ^{o}C. The reaction mixture was stirred at room temperature over night. The organic solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, PE (petralether) : CH_2Cl_2 (dichloromethane) = 5:1) to get 5.35 g white solid **1** in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.105 (d, J = 8.4 Hz, 2H), 7.606 (m, 4H), 7.486 (d, J = 8.4 Hz, 2H), 4.339 (t, J = 6.4 Hz, 2H), 1.786 (p, J = 7.2 Hz, 2H), 1.458 (m,

2H), 1.296 (b, 8H), 0.890 (t, J = 6.4 Hz, 3H)

^{13}C NMR (400 MHz, $CDCl_3$): δ ppm 166.640, 144.485, 139.237, 132.300, 130.407, 129.941, 129.064, 127.045, 122.748, 65.476, 32.022, 29.484, 29.423, 28.985, 26.287, 22.866, 14.299

MS: m/z = 388 (EI+); calcd. For $C_{21}H_{25}BrO_2$ m/z = 389.33

octyl 4'-((trimethylsilyl)ethynyl)biphenyl-4-carboxylate (2)

2.42 g (6.23 mmol) **1**, 71 mg (0.37 mmol, 6 mol%) CuI, 130 mg (0.19 mmol, 3 mol%) $PdCl_2(PPh_3)_2$ were successively added into flask, then 30 mL NEt_3 was added, the solution was stirred for 10min, then added 1.7 mL (12.05 mmol, 2 equiv) trimethylsilylacetylene. The reaction mixture was refluxed for 2 days. Stopped the reaction, the solvent was removed under vacuum, the residue was purified by column chromatography (PE : CH_2Cl_2 = 5:1) to get 2.3 g light yellow solid **2** in 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.102 (d, J = 8.4 Hz, 2H), 7.647 (d, J = 8 Hz, 2H), 7.559 (s, 4H), 4.337 (t, J = 6.4 Hz, 2H), 1.785 (p, J = 7.2 Hz, 2H), 1.456 (m, 2H), 1.294 (b, 8H), 0.889 (t, J = 6.4 Hz, 3H), 0.270 (s, 9H)

^{13}C NMR (400 MHz, $CDCl_3$): δ ppm 166.680, 144.782, 140.160, 132.725, 130.333, 129.849, 127.234, 127.110, 123.200, 104.904, 95.760, 65.451, 32.017, 29.480, 29.421, 28.974, 26.281, 22.864, 14.303, 0.181

MS: m/z = 407.72 (APCI+); calcd. For $C_{26}H_{34}O_2Si$ m/z = 406.63

octyl 4'-ethynylbiphenyl-4-carboxylate (3)

1.424 g (3.51 mmol) **2** and 17 mg K_2CO_3 (0.12 mmol, 3.5 mol%) in 15 mL methanol and 3.5 mL dichloromethane was reacted at room temperature. The reaction was monitored by TLC, stopped before obvious transesterification happened. The reaction was quenched by adding 50 mL water, then extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was washed with water and brine, dried over Na_2SO_4. The organic solvent was removed under vacuum, the residue was purified by column chromatography (PE : CH_2Cl_2 = 5:1) to get 938 mg white solid **3** in 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.112 (d, *J* = 8.4 Hz, 2H), 7.649 (d, *J* = 8.4 Hz, 2H), 7.588 (s, 4H), 4.340 (t, *J* = 6.4 Hz, 2H), 3.153 (s, 1H), 1.786 (p, *J* = 7.2 Hz, 2H), 1.477 (m, 2H), 1.296 (b, 8H), 0.890 (t, *J* = 6.4 Hz, 3H)

^{13}C NMR (400 MHz, $CDCl_3$): δ ppm 166.619, 144.671, 140.560, 132.876, 130.344, 129.931, 127.348, 127.131, 122.135, 83.502, 78.488, 65.443, 32.003, 29.466, 29.408, 28.958, 26.264, 22.850, 14.291

MS: m/z = 334 (EI+); calcd. For $C_{23}H_{26}O_2$ m/z = 334.45

dioctyl 4',4''-(ethyne-1,2-diyl)dibiphenyl-4-carboxylate (4)

1.167 g (3 mmol) **1**, 1.102 g (3.3 mmol, 1.1 equiv) **3**, 340 mg (0.21 mmol, 7 mol%) CuI, 73 mg (0.10 mmol, 3.5 mol%) $PdCl_2(PPh_3)_2$ were successively added into flask, then 10 mL dioxane and 40 mL NEt_3 was added, the reaction mixture was refluxed for 2 days. Stopped the reaction, the solvent was removed under vacuum, the residue was purified by column chromatography (PE : CH_2Cl_2 = 2:1 then 2:3 then pure CH_2Cl_2) to give brown solid. The solid was washed with a small portion of acetone, recrystallized

from CH_2Cl_2 and PE to get 962 mg white solid **4** in 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.124 (d, *J* = 8.4 Hz, 4H), 7.683 (d, *J* = 8.4 Hz, 4H), 7.644 (s, 8H), 4.347 (t, *J* = 6.4 Hz, 4H), 1.794 (p, *J* = 6.8 Hz,4H), 1.465 (m, 4H), 1.302 (b, 16H), 0.895 (t, *J* = 6.4 Hz, 6H)

^{13}C NMR (400 MHz, $CDCl_3$): δ ppm 166.682, 144.777, 140.110, 132.408, 130.376, 129.893, 127.436, 127.115, 123.238, 90.528, 65.465, 32.022, 29.483, 29.432, 28.986, 26.288, 22.867, 14.303

MS: m/z = 642.4 (MALDI-TOF); calcd. For $C_{44}H_{50}O_4$ m/z = 642.87

hexakis(4”-n-octylcarbonylbiphenyl)benzene (5)

415 mg (0.65 mmol) **4** and 22 mg (0.065 mmol, 10 mol%) $Co_2(CO)_8$ were added into flask, then 20 mL dioxane was added, the reaction mixture was refluxed for 2 days. Stopped the reaction, the solvent was removed under vacuum, the residue was purified by column chromatography (CH_2Cl_2 then CH_2Cl_2 : EtOAc = 100:1) to give light brown solid, the solid was washed with a small portion of PE to give 287 mg white solid **5** in 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.973 (d, *J* = 8.4 Hz, 12H), 7.475 (d, *J* = 8.4 Hz, 12H), 7.216 (d, *J* = 8.4 Hz, 12H), 7.001 (d, *J* = 8.4 Hz, 12H), 4.286 (t, *J* = 6.4 Hz, 12H), 1.744 (p, *J* = 6.8 Hz, 12H), 1.414 (m, 12H), 1.268 (b, 48H), 0.871 (t, *J* = 6.8 Hz, 18H)

^{13}C NMR (300 MHz, $CDCl_3$): δ ppm 166.735, 145.047, 140.538, 140.431, 137.031, 132.196, 130.115, 129.234, 126.768, 125.900, 65.339, 31.993, 29.444, 29.391, 28.927,

26.230, 22.844, 14.296

MS: m/z = 1928.92(APCI+); calcd. For $C_{132}H_{150}O_{12}$ m/z = 1928.60

hexakis(4”-carboxylbiphenyl)benzene (HPB-6pa)

305 mg (0.16 mmol) **5** and 538 mg (9.6 mmol, 60 equiv) KOH in 20 mL water and 20 mL THF was refluxed for 3 days. Stopped the reaction, THF was removed under vacuum. The aqueous layer was extracted by CH_2Cl_2 three times, then acidified to PH = 2 with concentrated hydrochloric acid. The suspension was filtered and washed with water, dried under vacuum, recrystallized from DMF and diethyl ether to get 180 mg white solid **HPB-6pa** in 90% yield.

^{1}H NMR (400 MHz, DMSO-D6): δ ppm 12.79 (b, 6H), 7.846 (d, *J* = 8.4 Hz, 12H), 7.586 (d, *J* = 8.4 Hz, 12H), 7.358 (d, *J* = 8.4 Hz, 12H), 7.129 (d, *J* = 8.4 Hz, 12H)

^{13}C NMR (400MHz, DMSO-D6): δ ppm 167.867, 144.085, 141.018, 140.742, 136.466, 132.695, 130.734, 130.262, 127.066, 125.973

IR: 3448.2, 3024.8, 2920.3, 1720.3, 1685.9, 1607.7, 1497.3, 1419.7, 1387.9, 1273.9, 1229.6, 1176.8, 1176.8, 1100.4, 1006.0, 835.2, 766.1, 594.9 cm^{-1}

Elemental Analysis: Calculated for $C_{84}H_{54}O_{12}$·0.75DMF·H_2O: C 78.00, H 4.65, N 0.79 O 16.56; Found: C 77.88, H 4.65, N 0.76