Construction of Supramolecular Hyperbranched Polymers *via* "Tweezering Directed Self-Assembly" Strategy

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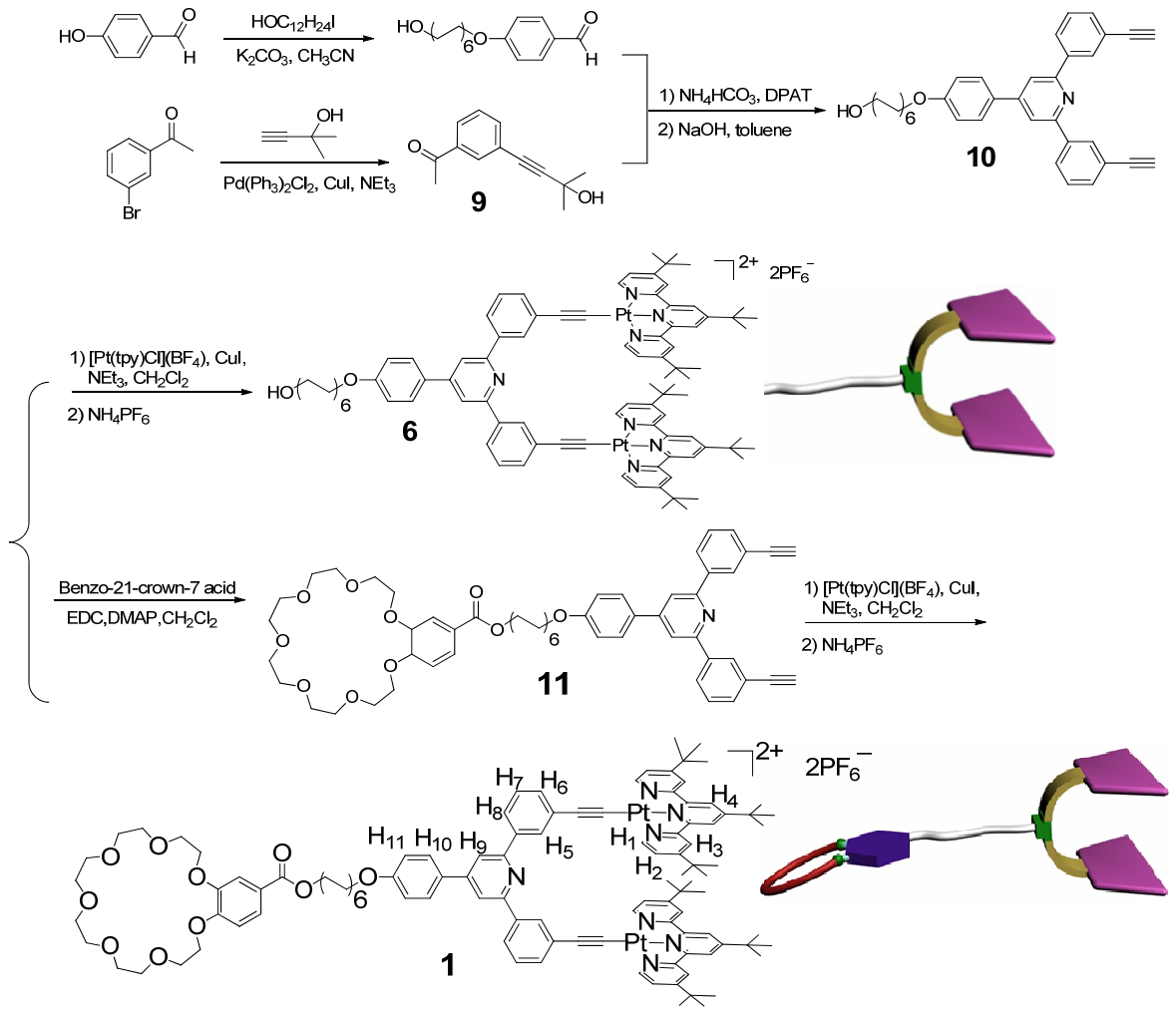
Supporting Information

1. Materials and Methods

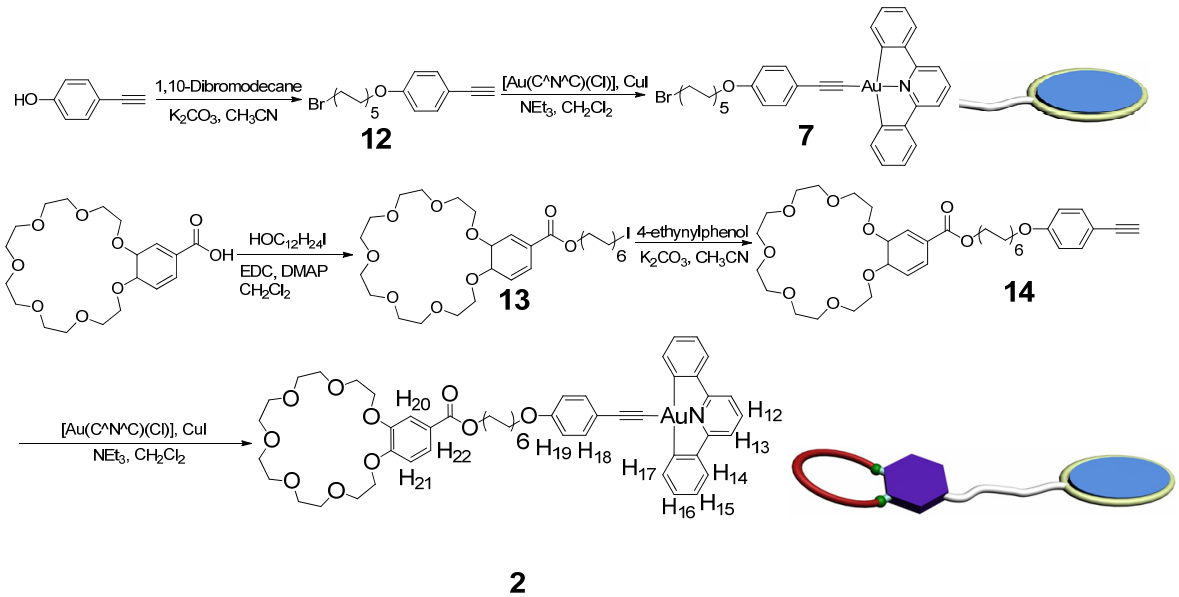
Diphenylammonium triflate (DPAT), 2-methyl-3-butyn-2-ol, copper(I) iodide (CuI), 3-bromoacetephenone, N-(3-(dimethylamino)propyl)-N'-ethylcarbodiimide hydrochloride (EDC·HCl), 4-dimethylamino pyridine (DMAP), and trimethylsilylacetylene were reagent grade and used as received. [Pt(tpy)Cl](PF_6),[S1] Benzo-21-crown-7 acid,[S2] compound **8**,[S2] [Au(C^N^C)Cl] (C^N^C = 2,6-diphenylpyridine),[S3] 4-ethenylphenol,[S4] and 4-((10-bromodecyl)oxy)benzaldehyde[S5] were synthesized according to the previously reported procedures. Compounds **6**, **9**, **10** and 4-[(12-hydroxydodecyl)oxy]benzaldehyde were synthesized according to our previously reported paper.[S6] Other reagents and solvents were employed as purchased.

^{1}H NMR spectra were collected on a Varian Unity INOVA-300 or INOVA-400 spectrometer with TMS as the internal standard. ^{13}C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometer at 100 MHz. Two-dimensional COSY experiments were performed on a Varian Unity INOVA-400 MHz spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany) equipped with an ESI interface and ion trap analyzer. Time-of-flight mass spectra (TOF-MS) were obtained on matrix-assisted laser desorption/ionization TOF/TOF MS (autoflex speed TOF/TOF, Bruker). UV/Vis spectra were recorded on a UV-1800 Shimadzu spectrometer.

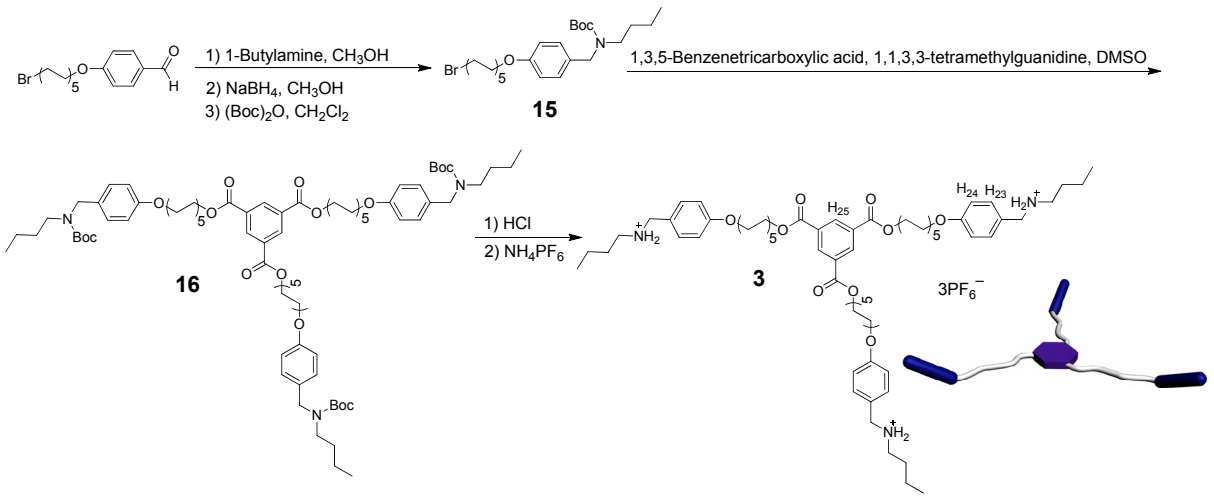
*2. Synthetic route to the targeted monomers **1–3***



Scheme S1. Synthetic route to monomer **1**.

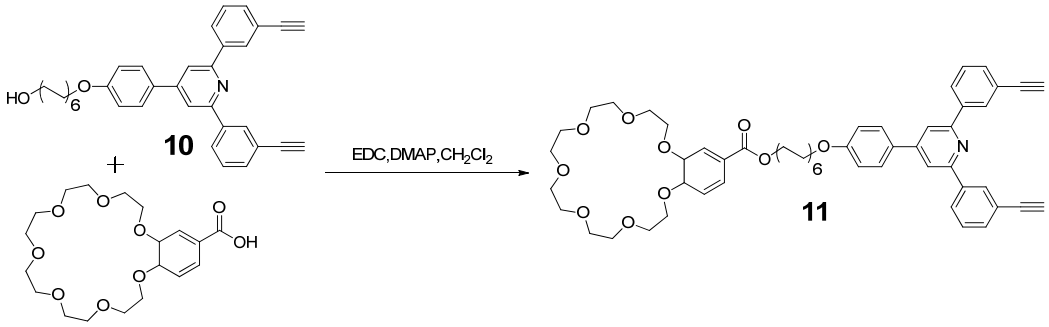


Scheme S2. Synthetic route to monomers **2**.



Scheme S3. Synthetic route to monomer **3**.

*2.1. Synthesis of compound **11***



Benzo-21-crown-7 acid (520 mg, 1.30 mmol), compound **10** (620 mg, 1.30 mmol), EDC·HCl (600 mg, 3.16 mmol) and DMAP (50.0 mg, 0.41 mmol) in 30 mL CH_2Cl_2 were placed in a 50 mL round-bottom flask and the mixture was stirred for 24 hours at room temperature. After the reaction was complete, the solvent was extracted with H_2O/CH_2Cl_2. The combined organic extracts were removed with a rotary evaporator and the residue was purified by flash column chromatography (ethyl acetate/CH_2Cl_2, 1 : 2 *v*/*v* as the eluent) to provide compound **11** as a colorless oil (788 mg, 66%). The ^{1}H NMR spectrum of compound **11** is shown in Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): 8.29 (s, 2H), 8.21 (d, J = 7.8 Hz, 2H), 7.86 (s, 2H), 7.70 (d, J = 8.7 Hz, 2H), 7.65 (m, 1H), 7.56 (m, 3H), 7.48 (t, J = 7.7 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.5 Hz, 1H), 4.28 (t, J = 6.6 Hz, 2H), 4.24–4.15 (m, 4H), 4.04 (t, J = 6.5 Hz, 2H), 3.94 (m, 4H), 3.80 (m, 4H), 3.74 (m, 4H), 3.67 (m, 8H), 3.15 (s, 2H), 1.89–1.72 (m, 6H), 1.31 (s, 14H). The ^{13}C NMR spectrum of compound **11** is shown in Figure S2. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 166.4, 160.2, 156.4, 152.8, 150.0, 148.2, 139.7, 132.6, 130.7, 130.5, 128.8, 127.7, 123.8, 123.3, 122.5, 116.9, 115.1, 114.6, 112.2, 83.7, 71.3, 71.2, 71.1, 71.0, 70.6, 69.6, 69.5, 69.3,

69.1, 68.2, 65.0, 60.4, 29.6, 29.5, 29.4, 29.3, 29.2, 28.8, 26.0. ESI–MS m/z: $[M + H]^+$, $C_{58}H_{68}NO_{10}$, 938.48358.

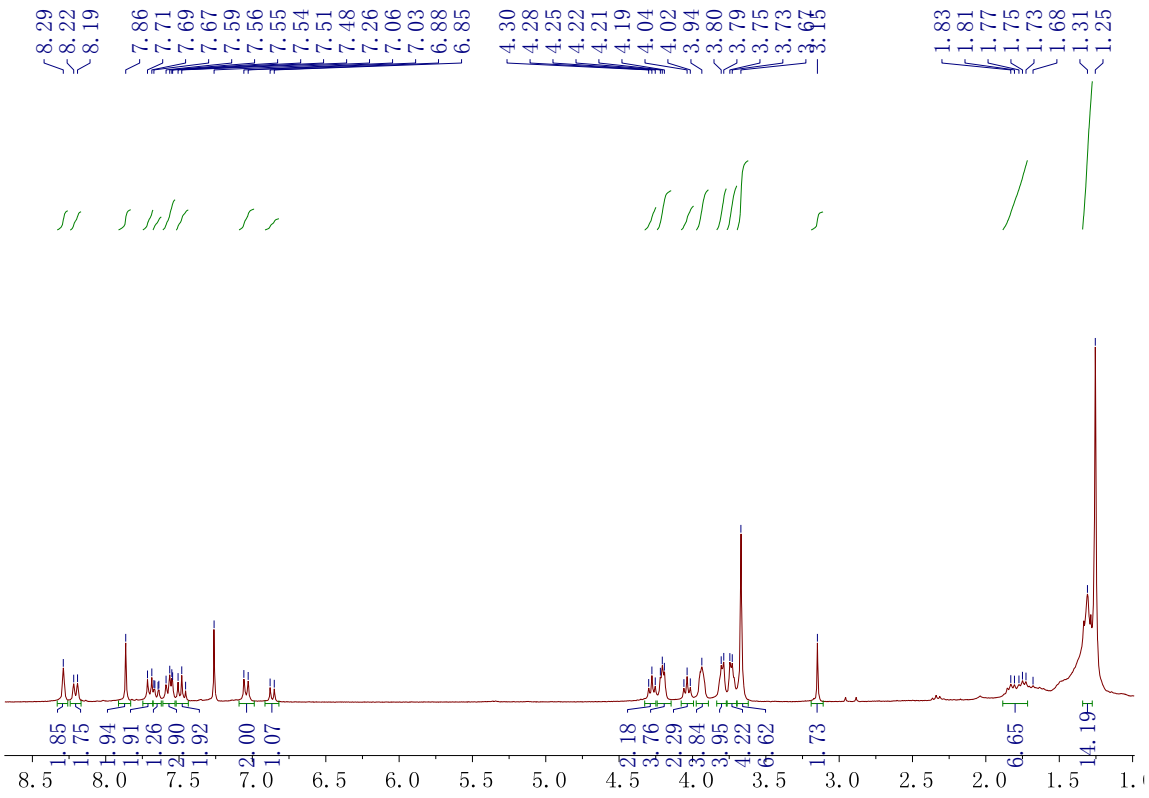


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of compound **11**.

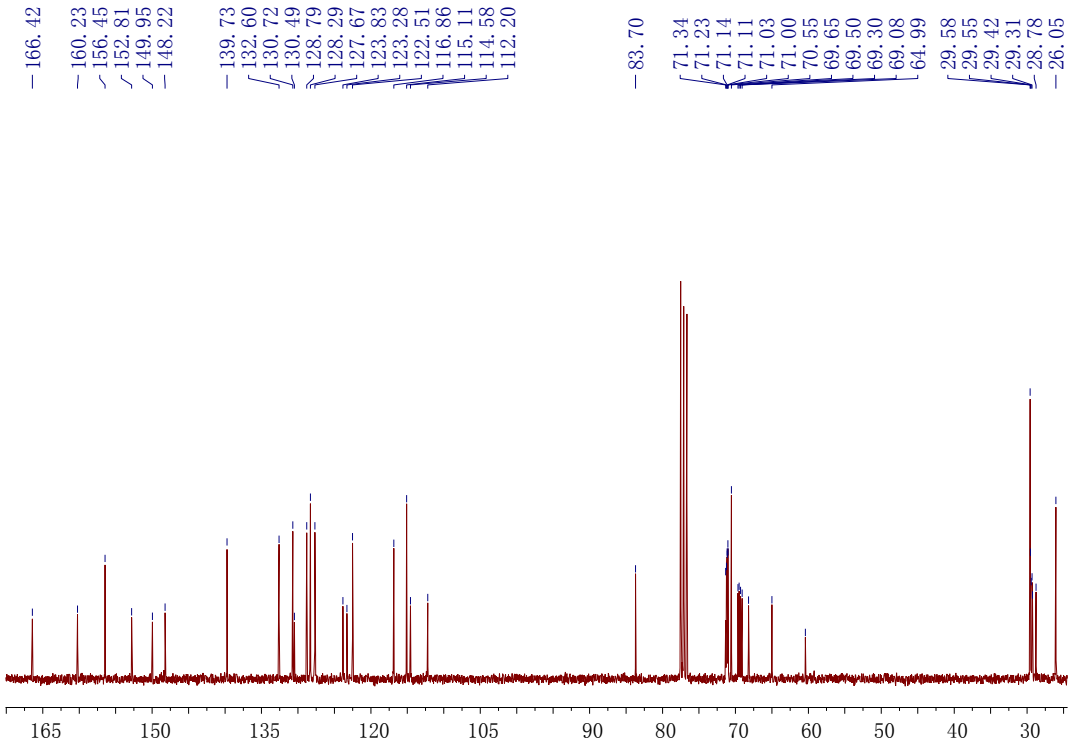
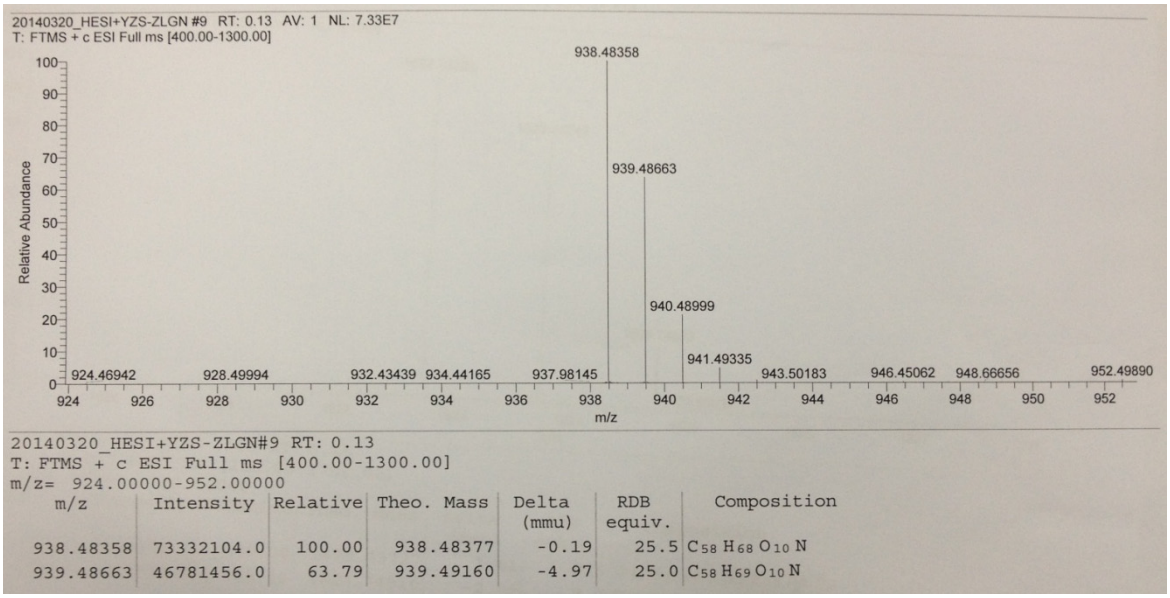


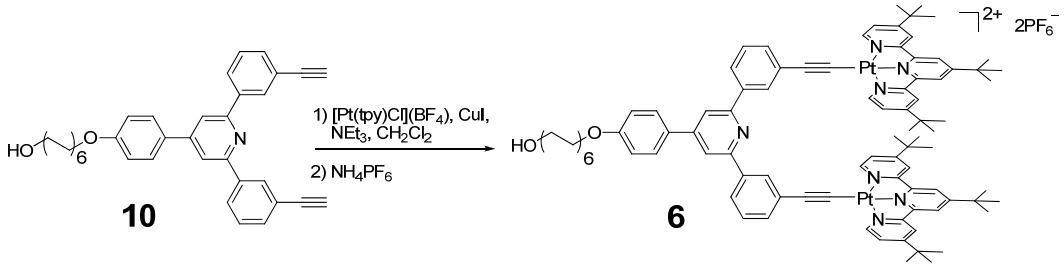
Figure S2. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of compound **11**.



m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
938.48358	73332104.0	100.00	938.48377	-0.19	25.5	$C_{58}H_{68}O_{10}N$
939.48663	46781456.0	63.79	939.49160	-4.97	25.0	$C_{58}H_{69}O_{10}N$

Figure S3. Electrospray ionization spectrum of compound **11**.

*2.2. Synthesis of compound **6***



Compound **10** (150 mg, 0.27 mmol), [Pt(tpy)Cl](BF$_4$) (430 mg, 0.60 mmol), CuI (10.0 mg, 0.05 mmol) and NEt$_3$ (5 mL) in 50 mL CH_2Cl_2 were stirred at room temperature for 48 hours under nitrogen atmosphere. The mixture was evaporated under reduced pressure and the residue was purified by flash column chromatograph (acetone/CH_2Cl_2, 1 : 20 *v*/*v* as the eluent) to afford a yellow solid. The solid was dissolved in CH_3CN and the NH_4PF_6 was added. The resulting solution was stirred at room temperature for 1 hour and washed with H_2O/CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and evaporated with a rotary evaporator to afford compound **6** as a red solid (300 mg, 54%). Mp: 210.0−213.5 ^{o}C. The ^{1}H NMR spectrum of compound **6** is shown in Figure S4. The aromatic protons on **6** display severe signal broadening phenomenaon in ^{1}H NMR spectrum, which probably results from the irregular capture of one diphenylpyridine unit by another molecular tweezer unit to form disordered self-recognition structures. The ^{13}C NMR spectrum of compound **6** is shown in Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 166.6, 165.1, 160.4,

157.7, 155.8, 153.5, 153.0, 138.4, 132.3, 131.9, 130.3, 129.7, 128.4, 127.8, 125.5, 125.3, 121.8, 120.6, 115.3, 111.5, 102.8, 98.1, 68.2, 63.0, 47.6, 36.8, 36.0, 32.8, 31.9, 30.2, 30.0, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 25.8. ESI–MS m/z: $[M - 2PF_6]^{2+}$, $C_{93}H_{109}N_7O_2Pt_2$, 873.4.

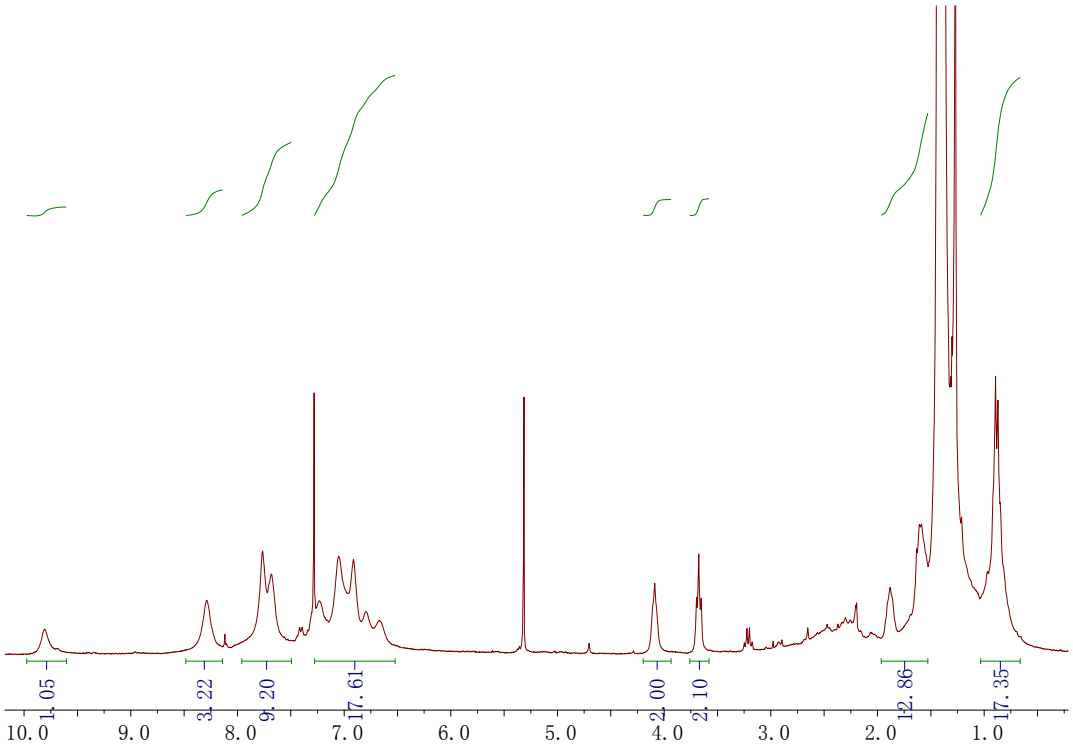


Figure S4. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of compound **6**.

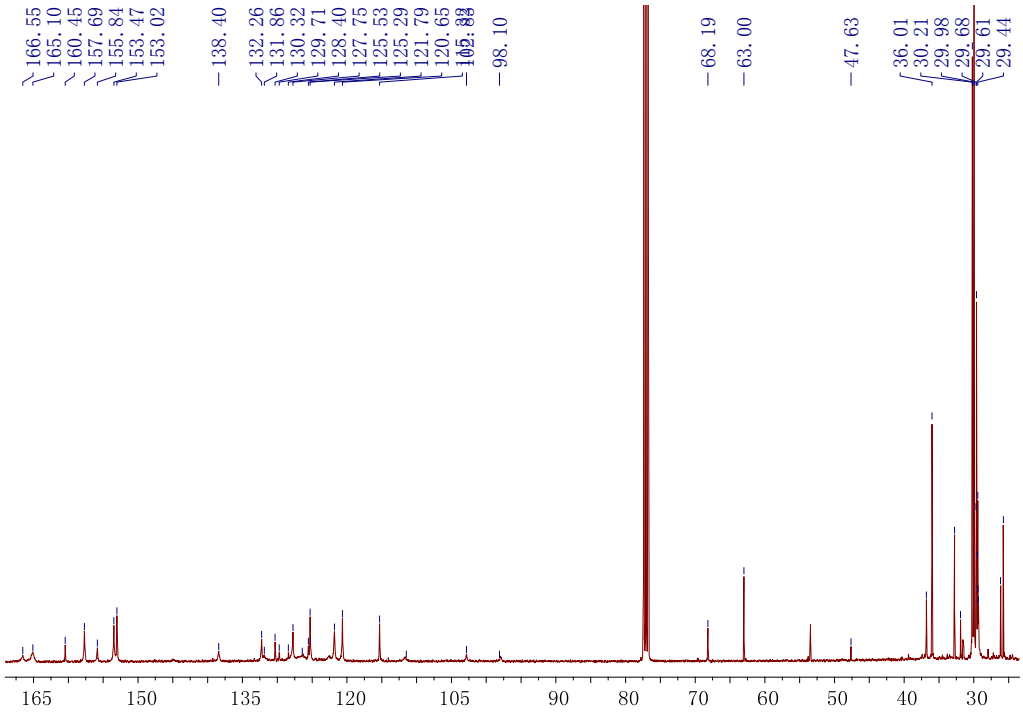


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of compound **6**.

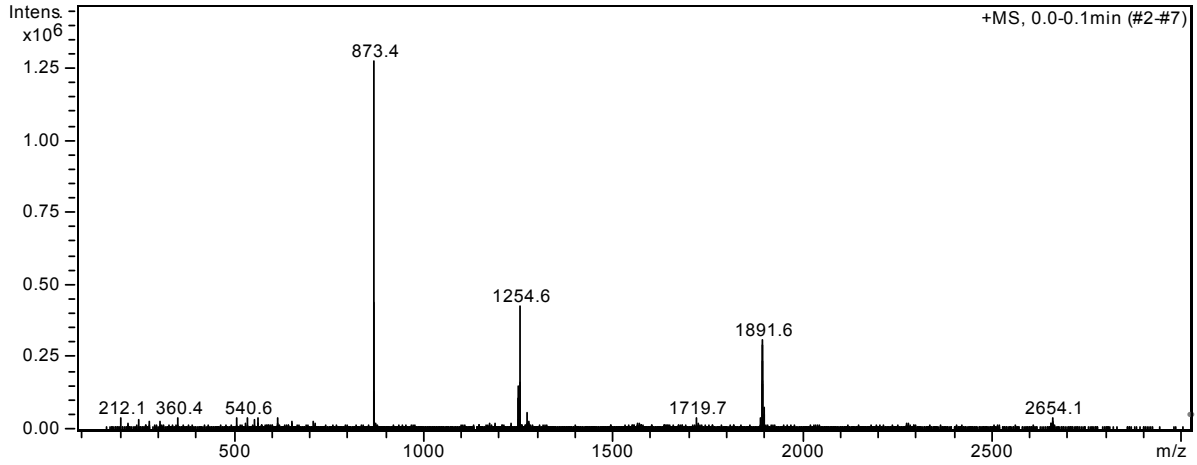
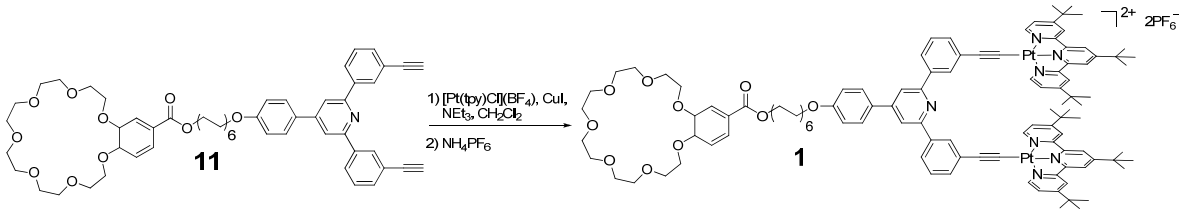


Figure S6. Electrospray ionization spectrum of compound **6**.

*2.3. Synthesis of monomer **1***



Compound **11** (230 mg, 0.25 mmol), [Pt(tpy)Cl](BF$_4$) (390 mg, 0.54 mmol), CuI (10.0 mg, 0.06 mmol) and NEt_3 (3 mL) in 30 mL CH_2Cl_2 were stirred at room temperature for 48 hours under nitrogen atmosphere. After the reaction was complete, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (acetone/CH_2Cl_2, 1 : 20 *v*/*v* as the eluent) to afford a red solid. The solid was dissolved in CH_3CN and then NH_4PF_6 was added. The result solution was stirred at room temperature for 1 hour, and then washed with H_2O/CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and evaporated with a rotary evaporator to afford compound **1** as a red solid (310 mg, 51%). Mp: 180.1−182.8 ^oC. The ^1H NMR spectrum of compound **1** is shown in Figure S7. Similar to **6**, the aromatic protons on **1** also display signal broadening phenomena in ^1H NMR spectrum, which probably results from the irregular capture of one diphenylpyridine unit by another molecular tweezer unit to form disordered self-recognition structures. The ^{13}C NMR spectrum of compound **1** is shown in Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 166.4, 165.1, 160.5, 157.7, 155.8, 153.5, 153.0, 152.8, 148.2, 139.2, 138.4, 132.2, 127.7, 125.3, 123.9, 123.3, 122.6, 121.8, 120.6, 115.4, 114.7, 114.0, 112.3, 102.8, 97.8, 71.2, 71.1, 71.0 70.9, 70.5, 69.6, 69.5, 69.3, 69.0, 68.2, 65.0, 36.8, 36.0, 33.8,

31.9, 30.3, 30.2, 30.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 28.9, 28.8, 26.2, 26.1, 22.7. MALDI–TOF MS *m*/*z*: $[M - PF_6]^+$, $C_{112}H_{135}PF_6N_7O_{10}Pt_2$, 2272.9208.

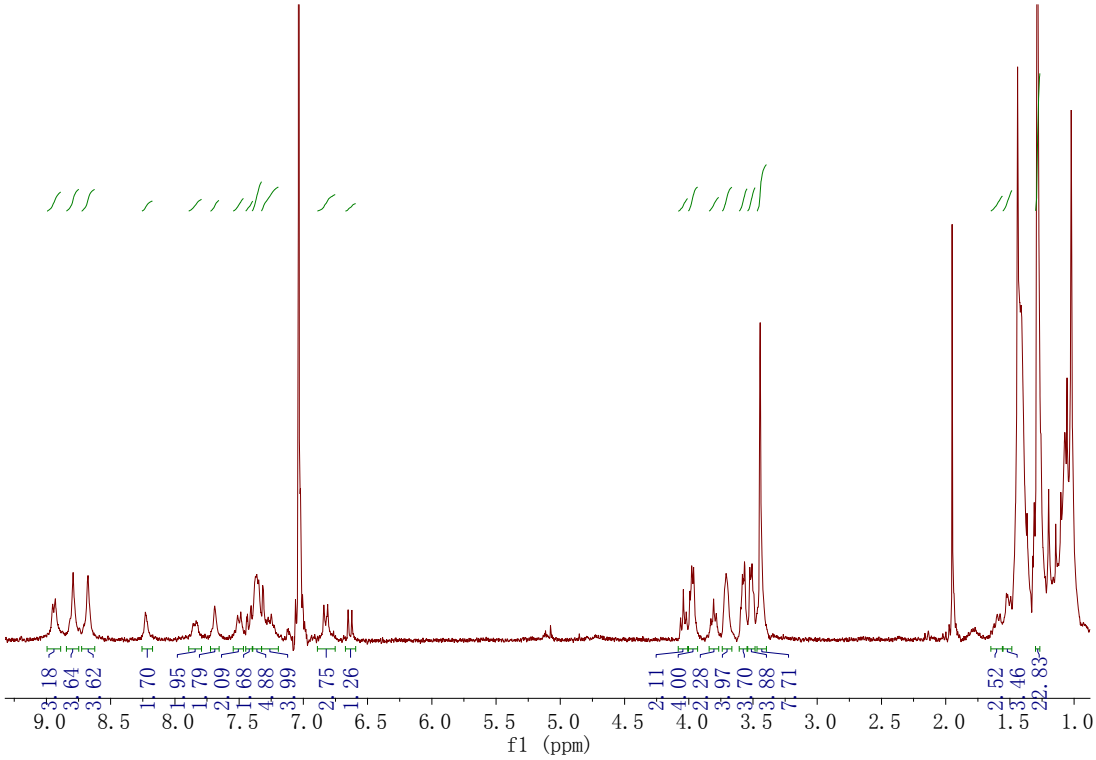


Figure S7. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of monomer **1**.

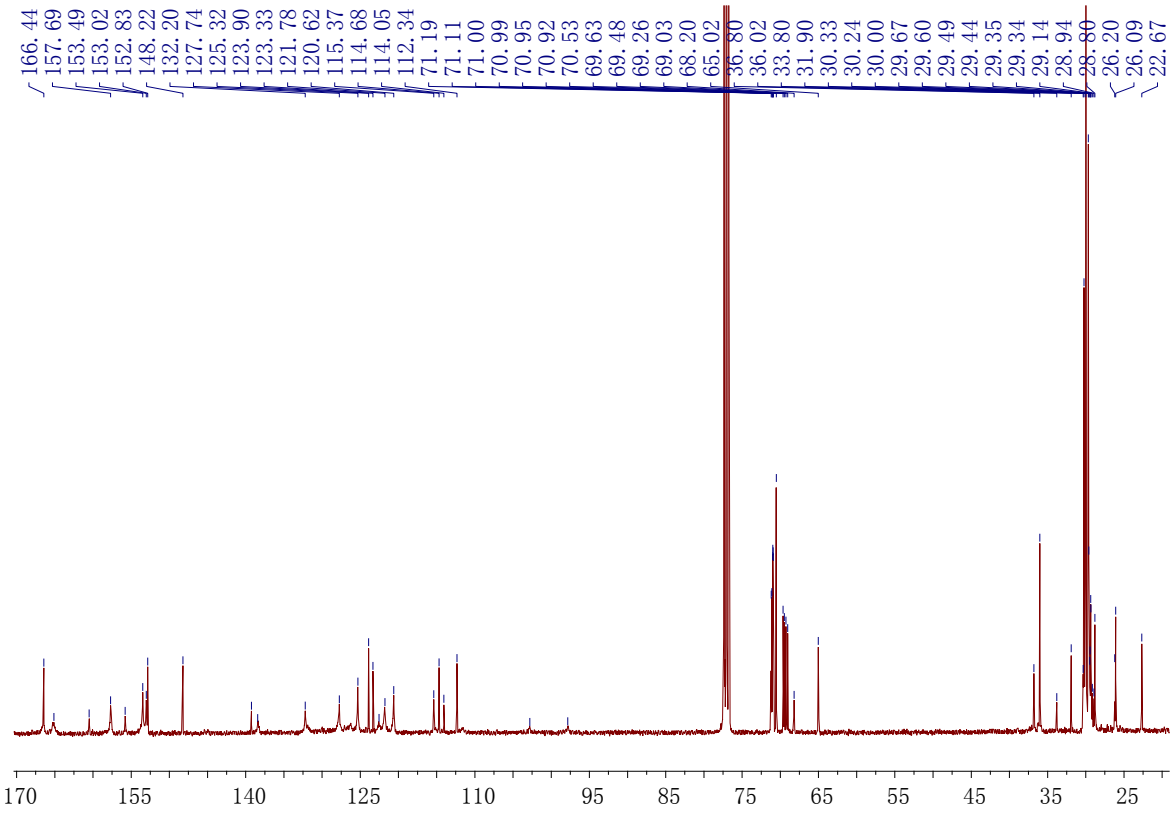


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of monomer **1**.

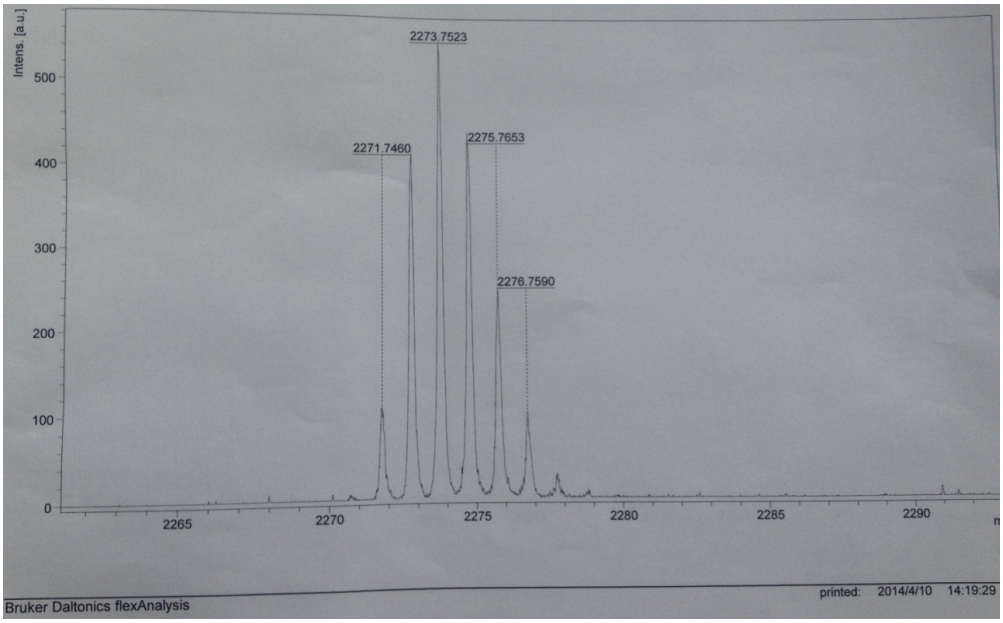
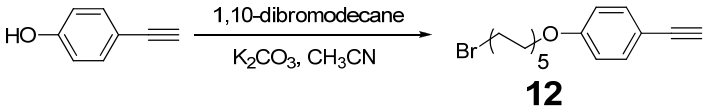


Figure S9. MALDI–TOF spectrum of monomer **1**.

*2.4. Synthesis of compound **12***



12

4-Ethynylphenol (500 mg, 4.23 mmol) and K_2CO_3 (2.00 g, 14.5 mmol) were placed in a 150 mL round-bottom flask. 1,10-Dibromodecane (6.00 g, 20.0 mmol) in CH_3CN (100 mL) was added and the resulting mixture was stirred at 50 ^oC for 36 hours. The solvent was evaporated under reduced pressure and the residue was extracted with H_2O/CH_2Cl_2. After the combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated with a rotary evaporator, the residue was purified by flash column chromatography (petroleum ether as the eluent) to afford compound **12** as a yellow solid (1.10 g, 77%). Mp: 66.5−68.7 ^oC. The ^1H NMR spectrum of compound **12** is shown in Figure S10. ^1H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): 7.39 (d, J = 8.3 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 3.93 (t, J = 6.4 Hz, 2H), 3.39 (t, J = 6.8 Hz, 2H), 2.97 (s, 1H), 1.91–1.68 (m, 4H), 1.40 (m, 4H), 1.29 (m, 8H). The ^{13}C NMR spectrum of compound **12** is shown in Figure S11. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 159.5, 133.6, 114.4, 113.9, 83.8, 75.7, 68.0, 34.1, 32.8, 29.4, 29.3, 29.2, 28.8, 28.2, 26.0. EI–MS m/z: $[M - e]^+$, $C_{18}H_{25}O^{81}Br$, 338.1063.

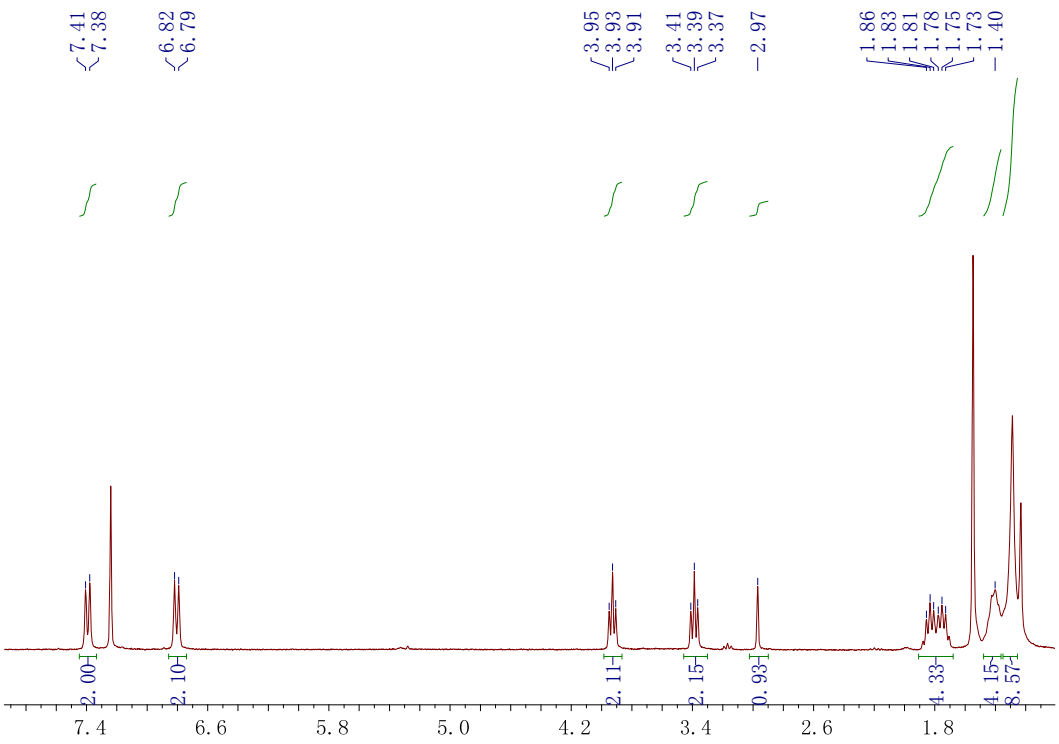


Figure S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of compound **12**.

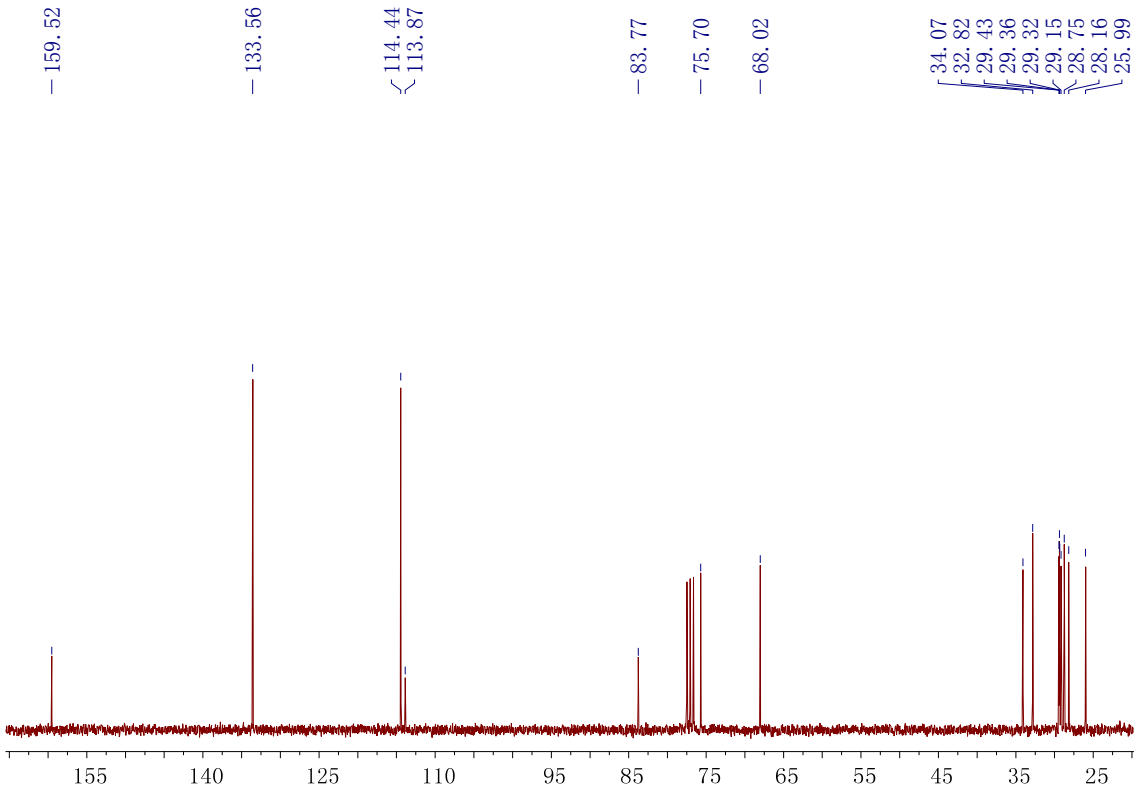


Figure S11. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of compound **12**.

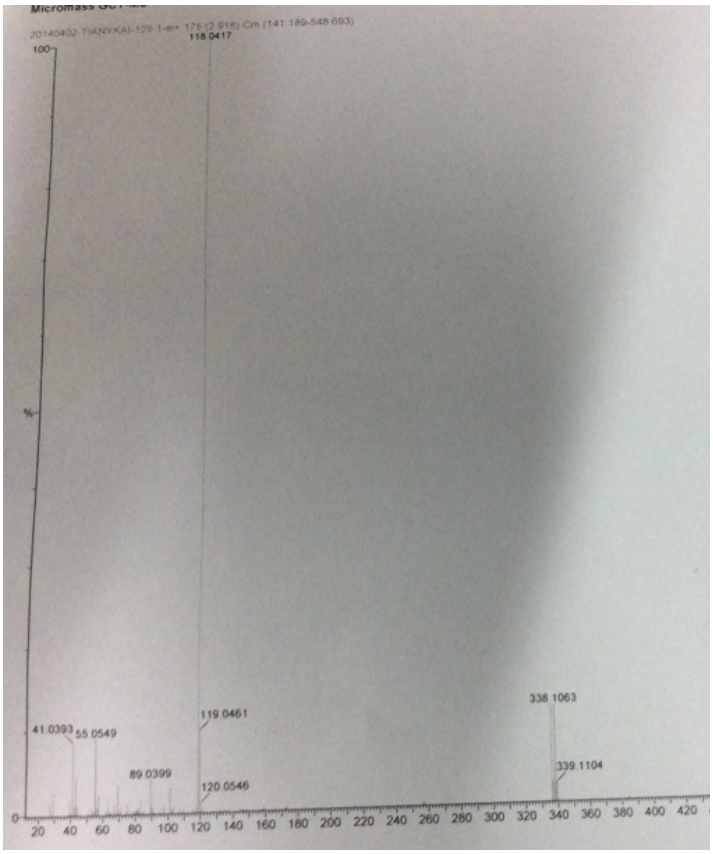
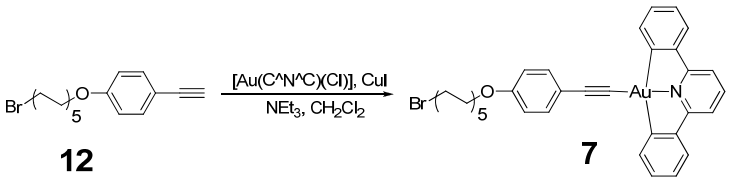


Figure S12. Electron ionization spectrum of compound **12**.

2.5. Synthesis of compound 7



12 **7**

Compound **12** (80.0 mg, 0.24 mmol), [Au(C^N^C)(Cl)] (100 mg, 0.22 mmol), CuI (9.50 mg, 0.05 mmol) and NEt_3 (0.50 mL) in 5 mL CH_2Cl_2 were stirred at room temperature for 48 hours under nitrogen atmosphere. After the reaction was complete, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (petroleum ether/CH_2Cl_2, 3 : 1 *v*/*v* as the eluent) to afford compound **7** as a yellow solid (120 mg, 72%). Mp: 120.1−122.0 ^oC. The ^1H NMR spectrum of compound **7** is shown in Figure S13. ^1H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): 8.09 (d, J = 7.2 Hz, 2H), 7.84 (t, J = 7.9 Hz, 1H), 7.53 (d, J = 8.0 Hz, 4H), 7.46 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.24 (m, 2H), 6.84 (d, J = 8.2 Hz, 2H), 3.96 (t, J = 6.3 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.91–1.71 (m, 4H), 1.42 (m, 4H), 1.30 (m, 8H). The ^{13}C NMR spectrum of compound **7** is shown in Figure S14. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 166.9, 164.8, 158.2, 149.0, 142.1, 136.6, 133.1, 131.8, 126.6, 125.2, 118.8, 116.8, 114.3, 100.6, 89.3, 68.0,

34.1, 32.8, 29.5, 29.4, 29.3, 28.8, 28.2, 26.0. MALDI–TOF MS *m*/*z*: $[M - e]^+$, $C_{35}H_{35}AuBrNO$, 761.1443.

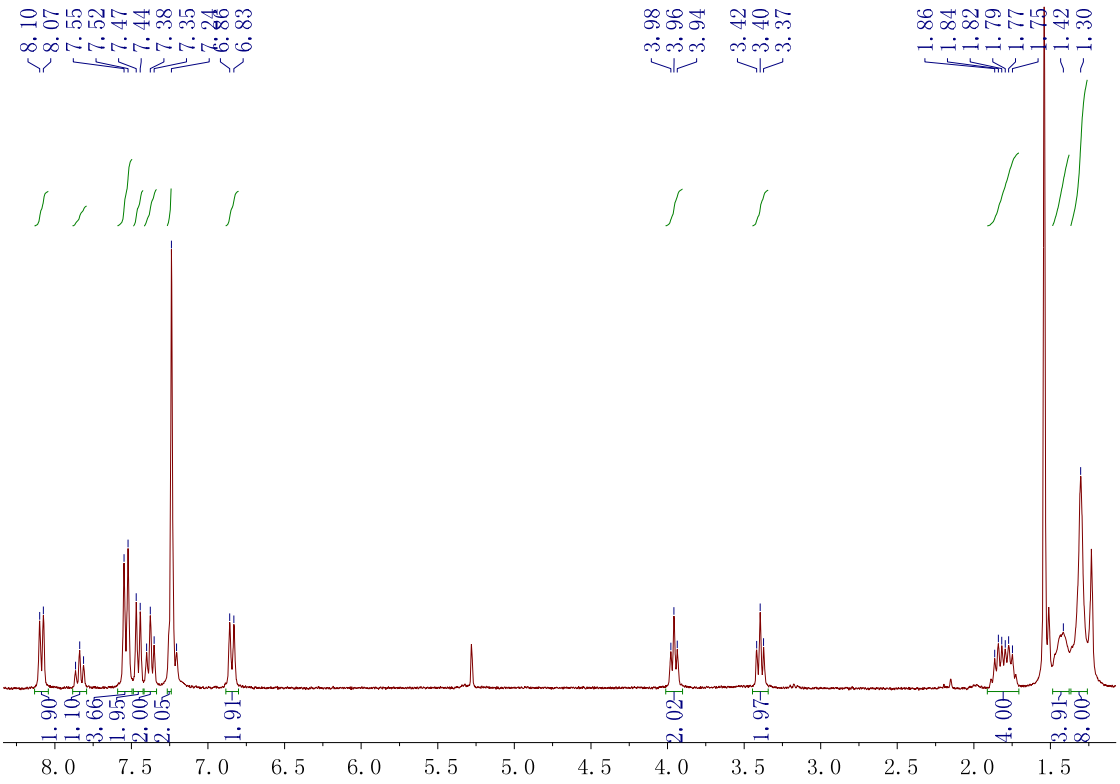


Figure S13. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of compound **7**.

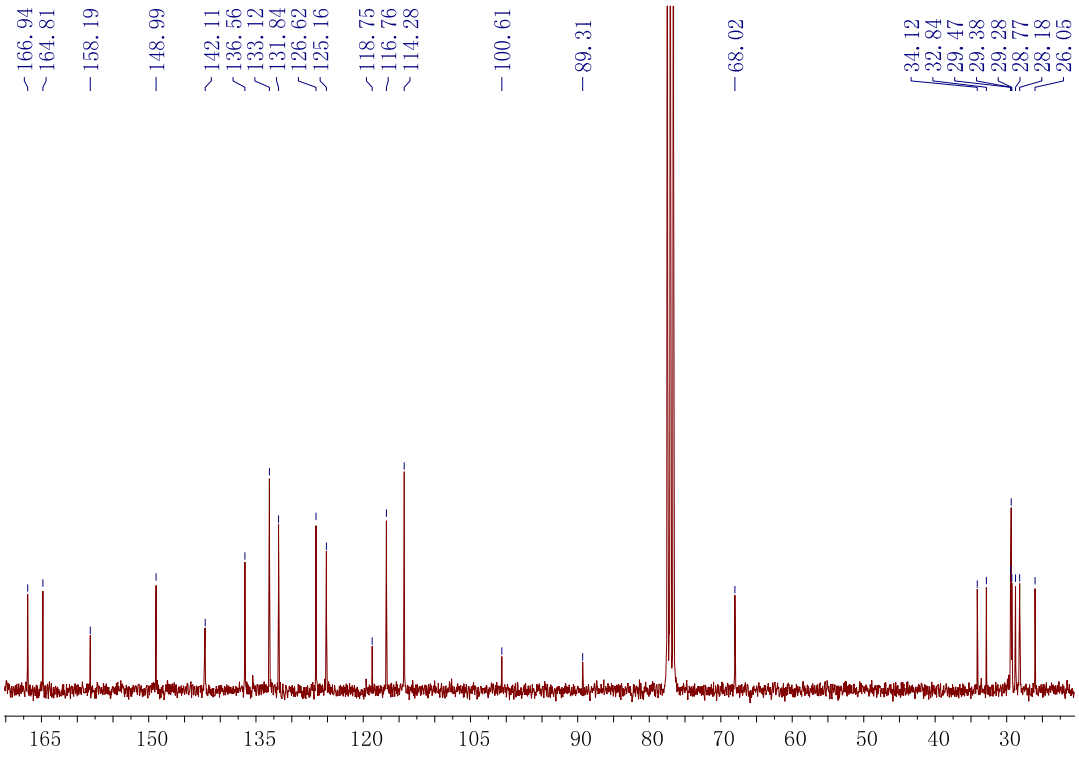


Figure S14. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of compound **7**.

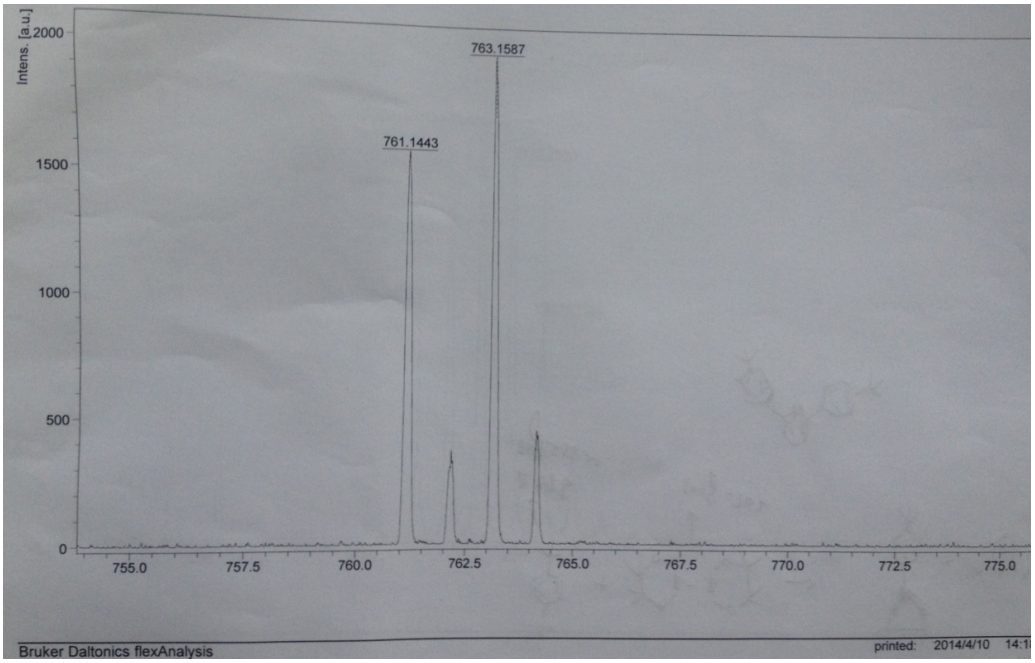
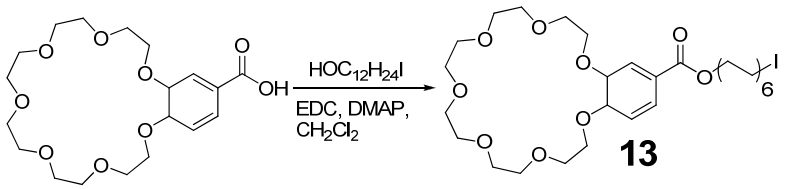


Figure S15. MALDI–TOF spectrum of compound **7**.

*2.6. Synthesis of compound **13***



Benzo-21-crown-7 acid (3.50 g, 8.75 mmol), 12-iododododecanol (2.50 g, 8.00 mmol), EDC·HCl (3.00 g, 15.7 mmol) and DMAP (300 mg, 2.45 mmol) in CH_2Cl_2 (50 mL) were placed in a 100 mL round-bottom flask and the mixture was stirred for 24 hours at room temperature. After the reaction was complete, the solvent was extracted with H_2O/CH_2Cl_2. The combined organic extracts were removed with a rotary evaporator and the residue was purified by flash column chromatography (ethyl acetate as the eluent) to provide compound **13** as a colorless oil (3.40 g, 61%). The ^{1}H NMR spectrum of compound **13** is shown in Figure S16. ^{1}H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): δ 7.66 (dd, J = 8.4, 2.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 4.27 (t, J = 6.7 Hz, 2H), 4.24–4.17 (m, 4H), 3.97–3.90 (m, 4H), 3.84–3.78 (m, 4H), 3.78–3.71 (m, 4H), 3.71–3.63 (m, 8H), 3.19 (t, J = 7.0 Hz, 2H), 1.86–1.69 (m, 4H), 1.37 (m, 4H), 1.28 (m, 12H). The ^{13}C NMR spectrum of compound **13** is shown in Figure S17. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 166.4, 152.8, 148.2, 123.8, 123.3, 114.6, 112.2, 71.4, 71.2, 71.1, 71.0, 70.6, 69.6, 69.5, 69.3, 69.1, 65.0, 33.6, 30.5, 29.5, 29.4, 29.3, 28.8, 28.5, 26.0. ESI–MS m/z: $[M + H]^+$,

$C_{31}H_{52}IO_9$, 695.26501.

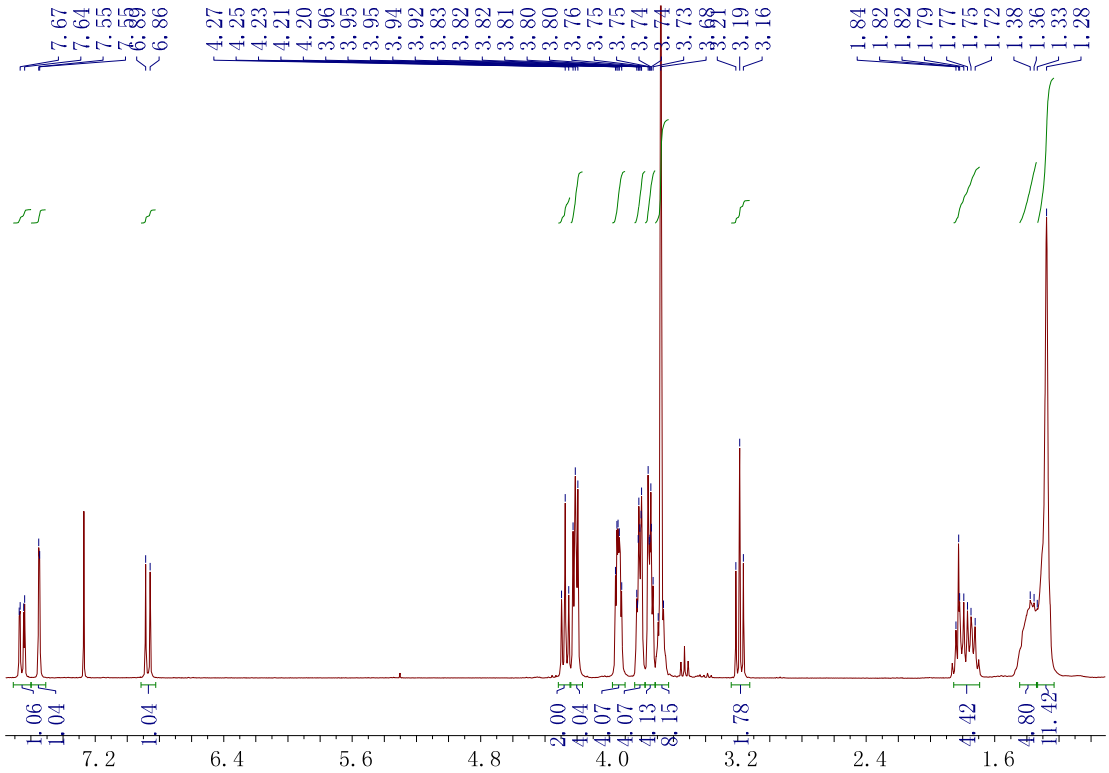


Figure S16. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of compound **13**.

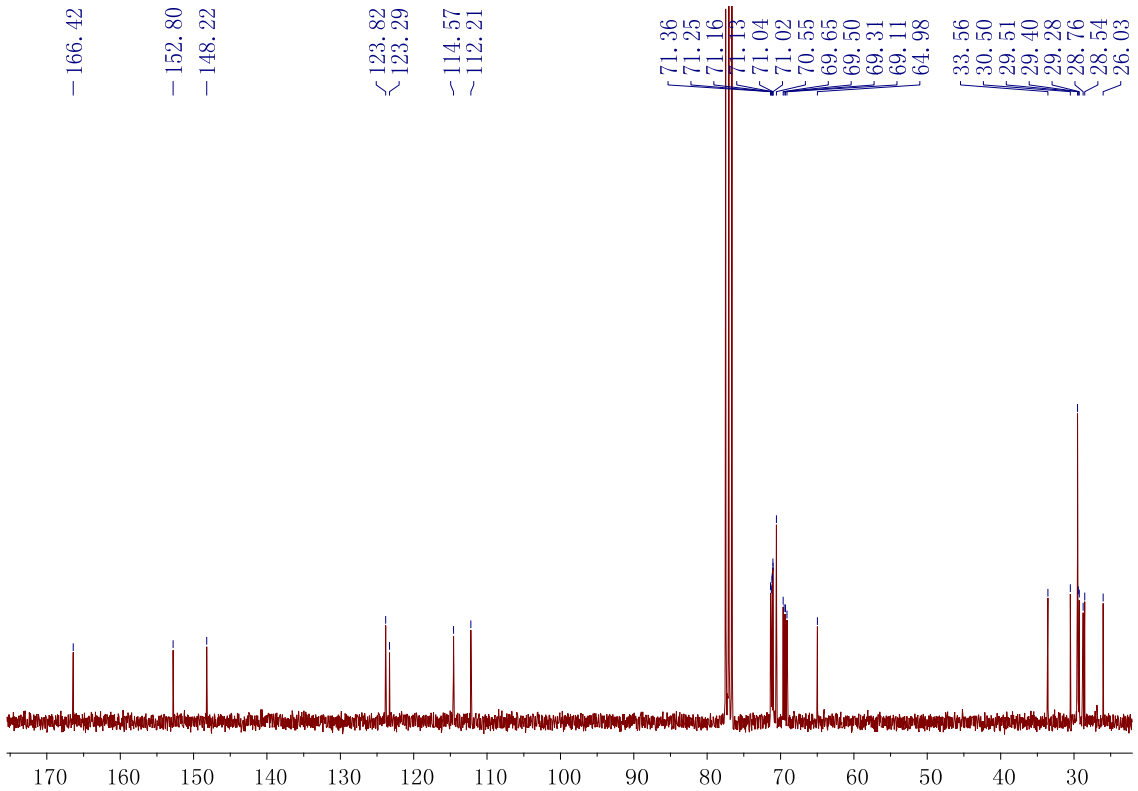


Figure S17. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of compound **13**.

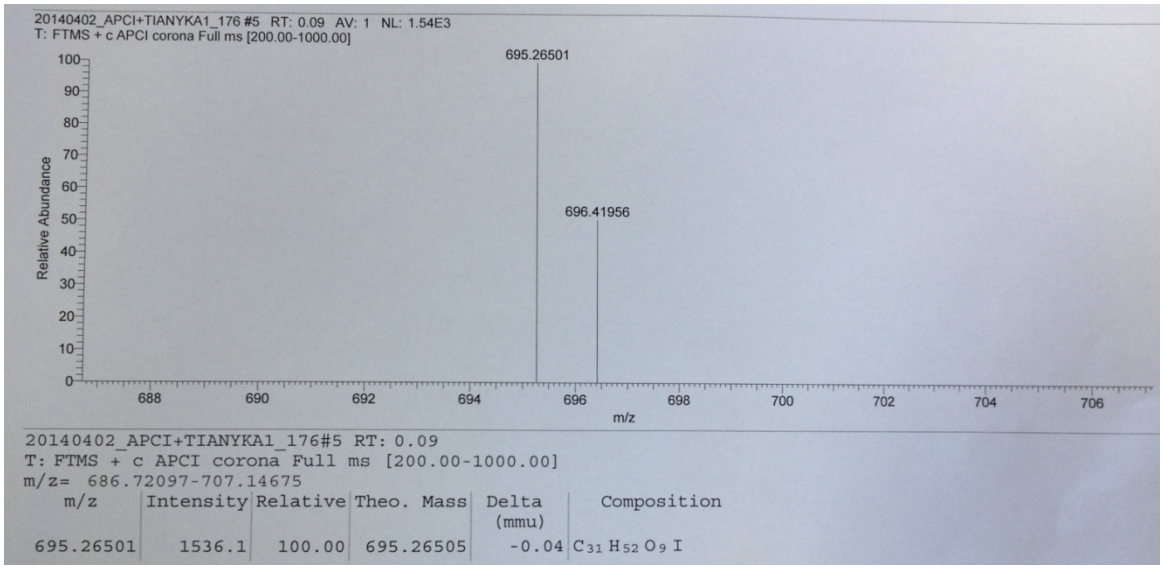
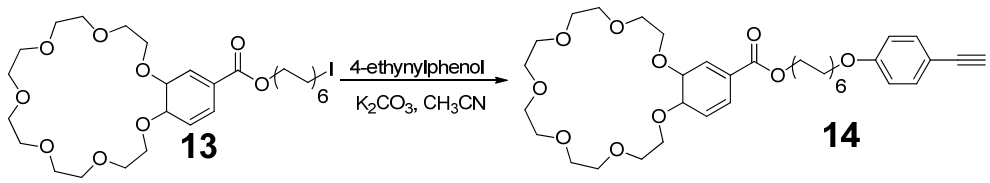


Figure S18. Electrospray ionization spectrum of compound **13**.

*2.7. Synthesis of compound **14***



4-Ethynylphenol (0.40 g, 3.39 mmol) and K_2CO_3 (0.70 g, 5.07 mmol) were placed in a 150 mL round-bottom flask. Compound **13** (1.70 g, 2.45 mmol) in CH_3CN (40 mL) was added and the resulting mixture was stirred at 90 ^oC for 24 hours. The solvent was evaporated under reduced pressure and the residue was extracted with H_2O/CH_2Cl_2. After the combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated with a rotary evaporator, the residue was purified by flash column chromatography (CH_3OH/CH_2Cl_2, 1 : 20 *v*/*v* as the eluent) to afford compound **14** as a yellow oil (1.40 g, 84%). The ^1H NMR spectrum of compound **14** is shown in Figure S19. ^1H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): 7.65 (m, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.45–7.37 (m, 2H), 6.91–6.79 (m, 3H), 4.27 (t, J = 6.7 Hz, 2H), 4.24–4.16 (m, 4H), 3.92–3.97 (m, 6H), 3.84–3.78 (m, 4H), 3.76–3.72 (m, 4H), 3.71–3.63 (m, 8H), 2.99 (s, 1H), 1.76 (m, 4H), 1.49–1.37 (m, 4H), 1.29 (m, 12H). The ^{13}C NMR spectrum of compound **14** is shown in Figure S20. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 166.4, 159.5, 152.8, 148.2, 133.6, 123.8, 123.3, 114.6, 114.4, 113.8, 112.2, 83.8, 75.7, 71.3, 71.2, 71.1, 71.0, 69.6, 69.5, 69.3, 69.1, 68.0, 65.0, 29.5, 29.4, 29.3, 29.2, 28.8, 26.0. ESI–MS m/z: $[M + H]^+$, $C_{39}H_{57}O_{10}$, 685.39453.

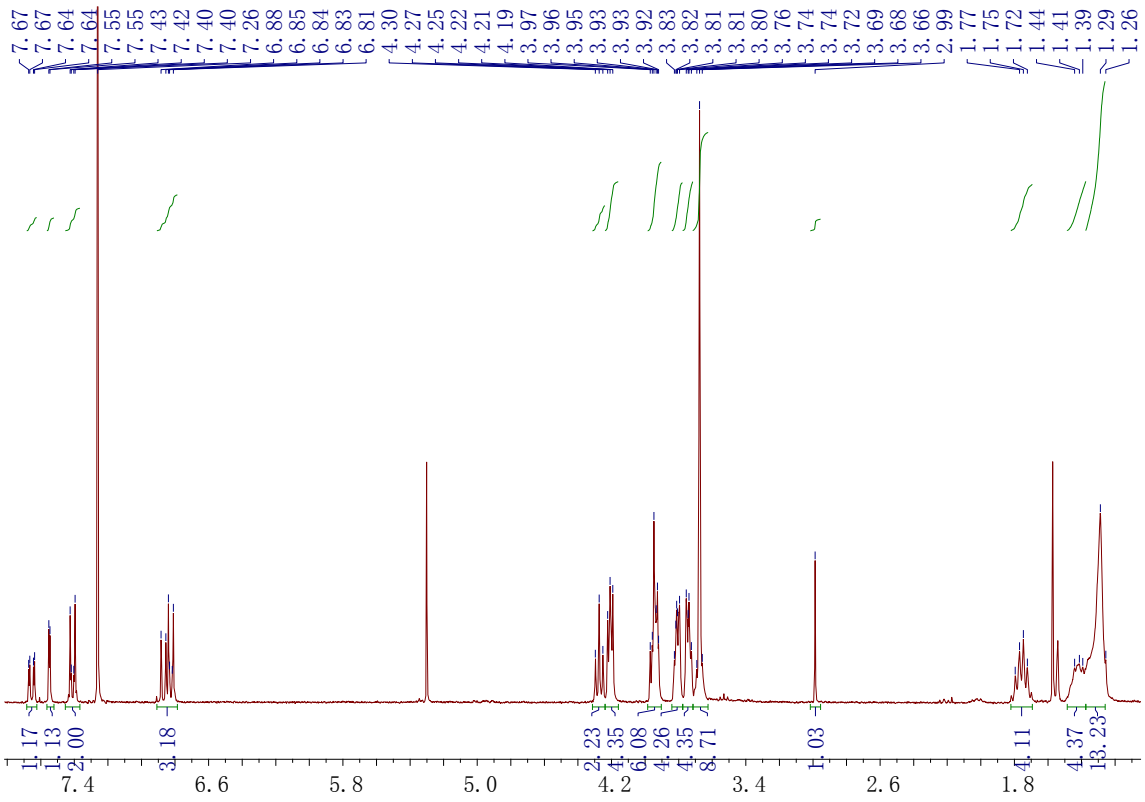


Figure S19. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of compound **14**.

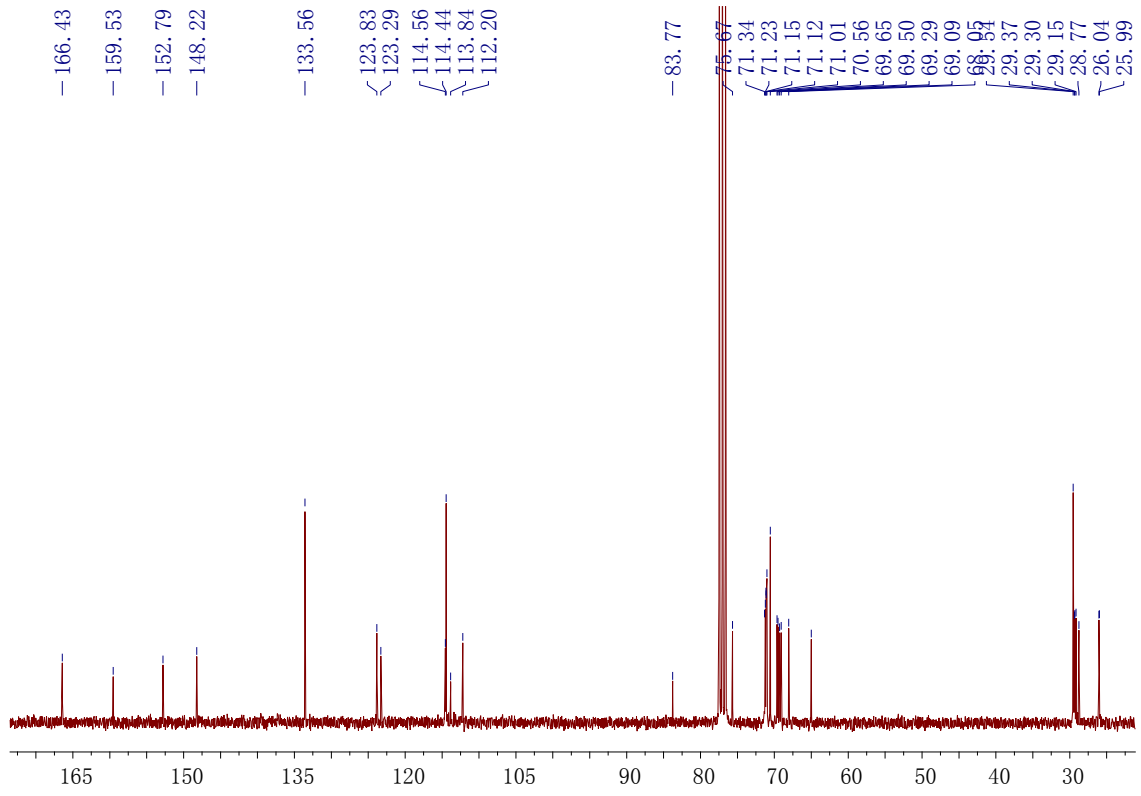
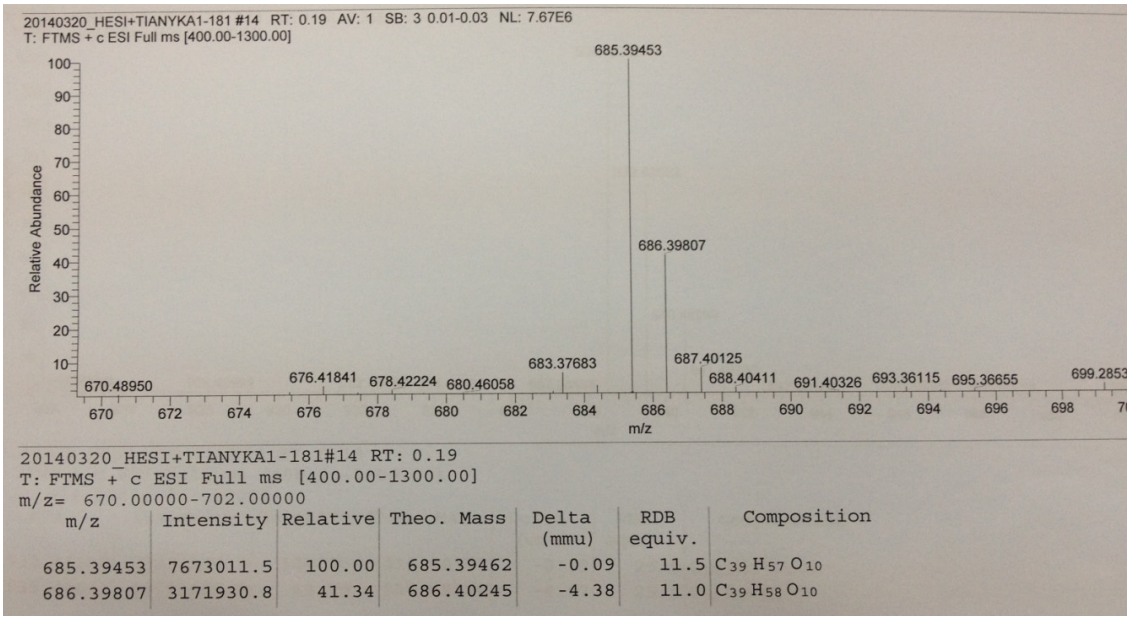


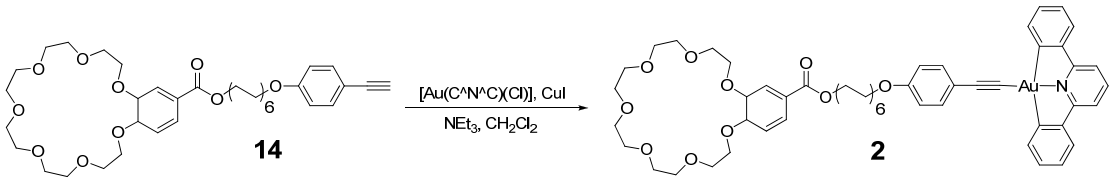
Figure S20. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of compound **14**.



m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
685.39453	7673011.5	100.00	685.39462	-0.09	11.5	$C_{39}H_{57}O_{10}$
686.39807	3171930.8	41.34	686.40245	-4.38	11.0	$C_{39}H_{58}O_{10}$

Figure S21. Electrospray ionization spectrum of compound **14**.

*2.8. Synthesis of monomer **2***



Compound **14** (310 mg, 0.45 mmol), [Au(C^N^C)(Cl)] (210 mg, 0.46 mmol), CuI (20.0 mg, 0.10 mmol) and NEt_3 (2 mL) in 30 mL CH_2Cl_2 were stirred at room temperature for 48 hours under nitrogen atmosphere. After the reaction was complete, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (CH_2Cl_2/CH_3OH, 100 : 1 *v*/*v* as the eluent) to afford compound **2** as a yellow oil (420 mg, 84%). The ^1H NMR spectrum of compound **2** is shown in Figure S22. ^1H NMR (300 MHz, $CDCl_3$, room temperature) δ (ppm): 8.08 (d, J = 7.2 Hz, 2H), 7.84 (t, J = 8.0 Hz, 1H), 7.65 (m, 1H), 7.54 (t, J = 7.8 Hz, 5H), 7.45 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.23 (m, 2H), 6.87 (m, 3H), 4.28 (t, J = 6.7 Hz, 2H), 4.24–4.17 (m, 4H), 3.99 (m, 2H), 3.96–3.90 (m, 4H), 3.84–3.78 (m, 4H), 3.78–3.71 (m, 4H), 3.67 (m, 8H), 1.84–1.60 (m, 6H), 1.30 (s, 14H). The ^{13}C NMR spectrum of compound **2** is shown in Figure S23. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 166.9, 166.4, 164.7, 158.2, 152.8, 149.0, 148.2, 142.1, 136.5, 133.1, 131.8, 126.6, 125.2, 123.8, 123.3, 126.6, 125.2, 123.8, 123.3, 118.8, 116.8, 114.5, 114.3, 112.2, 100.5, 89.4, 71.3, 71.2, 71.1, 71.0, 70.6, 69.6, 69.5, 69.3, 69.1, 68.0, 65.0, 29.7, 29.6, 29.4, 29.3, 28.8, 26.1. ESI–MS m/z: $[M + K]^+$, $C_{56}H_{66}AuKNO_{10}$, 1148.5.

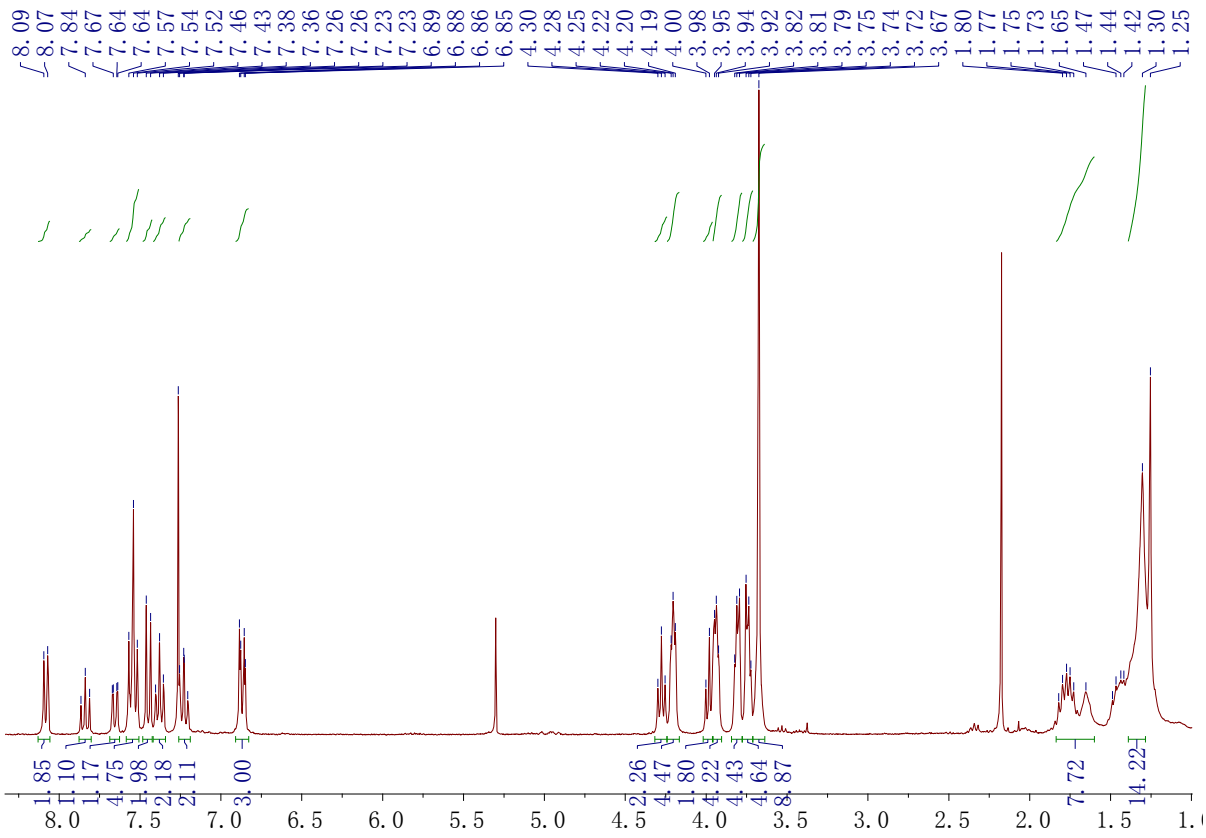


Figure S22. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of monomer **2**.

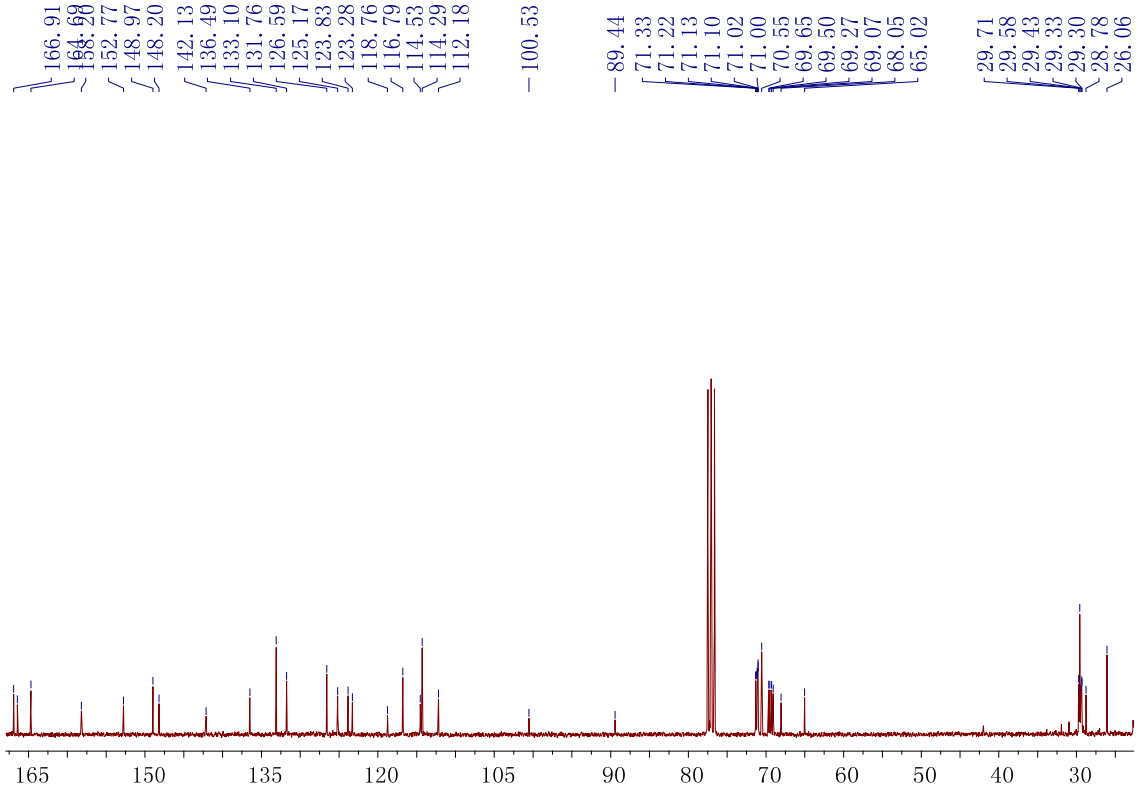


Figure S23. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of monomer **2**.

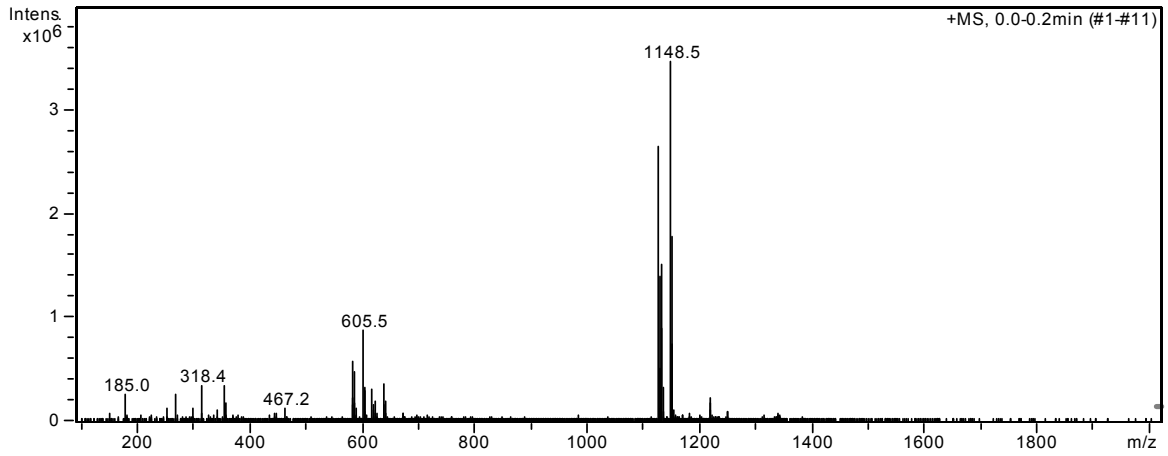
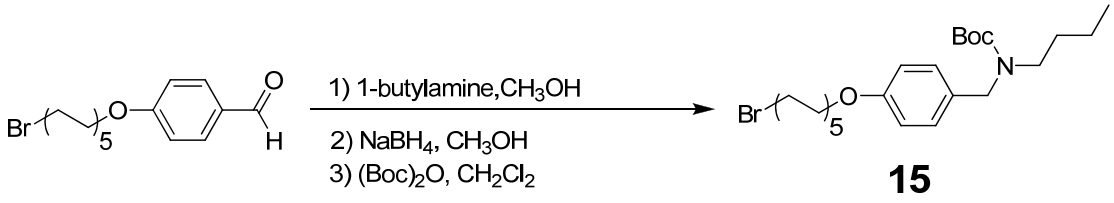


Figure S24. Electrospray ionization spectrum of monomer **2**.

*2.9. Synthesis of compound **15***



A solution of 4-((10-bromodecyl)oxy)benzaldehyde (10.0 g, 29.3 mmol) and 1-butylamine (6.42 g, 88.0 mmol) in MeOH (100 mL) was stirred at room temperature overnight. Then $NaBH_4$ (0.91 g) was added and stirred at room temperature for 6 hours. After the quench of reaction by addition of water, the resulting solution was extracted with H_2O/CH_2Cl_2. The organic extracts was dried over anhydrous Na_2SO_4 and evaporated to afford a crude product. The mixture of the crude product, di-*tert*-butyl dicarbonate (6.40 g, 29.3 mmol) and Et_3N (3.00 g, 29.6 mmol) in MeOH (100 mL) was stirred at room temperature overnight. The solvent was removed and the residue was purified by flash column chromatography (petroleum ether/CH_2Cl_2, 5 : 1 *v*/*v* as the eluent) to afford **15** as a colorless oil (9.27 g, 63%). The ^{1}H NMR spectrum of compound **15** is shown in Figure S25. ^{1}H NMR (300 MHz, $CDCl_3$, room temperature) δ 7.13 (br, 2H), 6.82 (d, J = 8.6 Hz, 2H), 4.34 (s, 2H), 3.92 (t, J = 6.5 Hz, 2H), 3.39 (t, J = 6.9 Hz, 2H), 3.23–3.01 (br, 2H), 1.92–1.70 (m, 4H), 1.44 (m, 12H), 1.35–1.19 (m, 11H), 0.89 (m, 3H). The ^{13}C NMR spectrum of compound **15** is shown in Figure S26. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 158.3, 130.5, 129.0, 128.4, 79.4, 68.0, 49.7, 49.1, 46.0, 34.0, 32.8, 30.1, 29.7, 29.4, 29.3, 28.7, 28.5, 28.2, 26.0, 20.0, 13.9. ESI–MS m/z: $[M + H]^+$, $C_{26}H_{45}O_3NBr$, 498.25787.

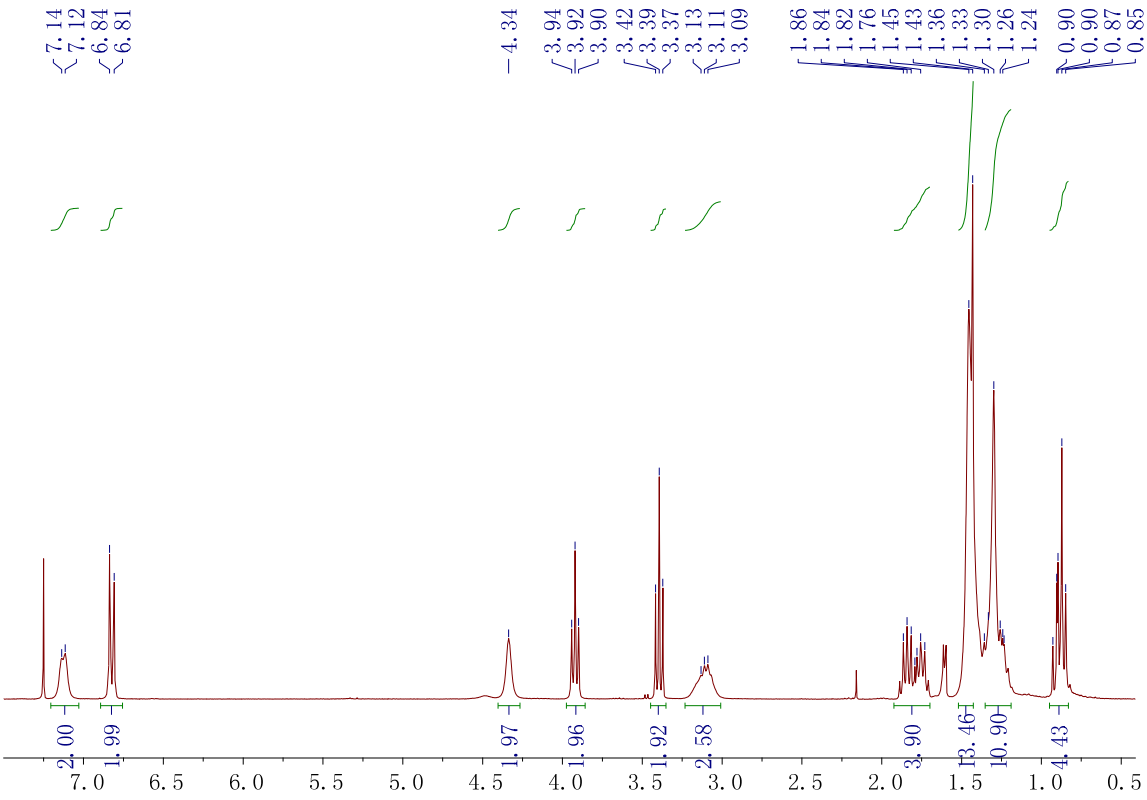


Figure S25. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of compound **15**.

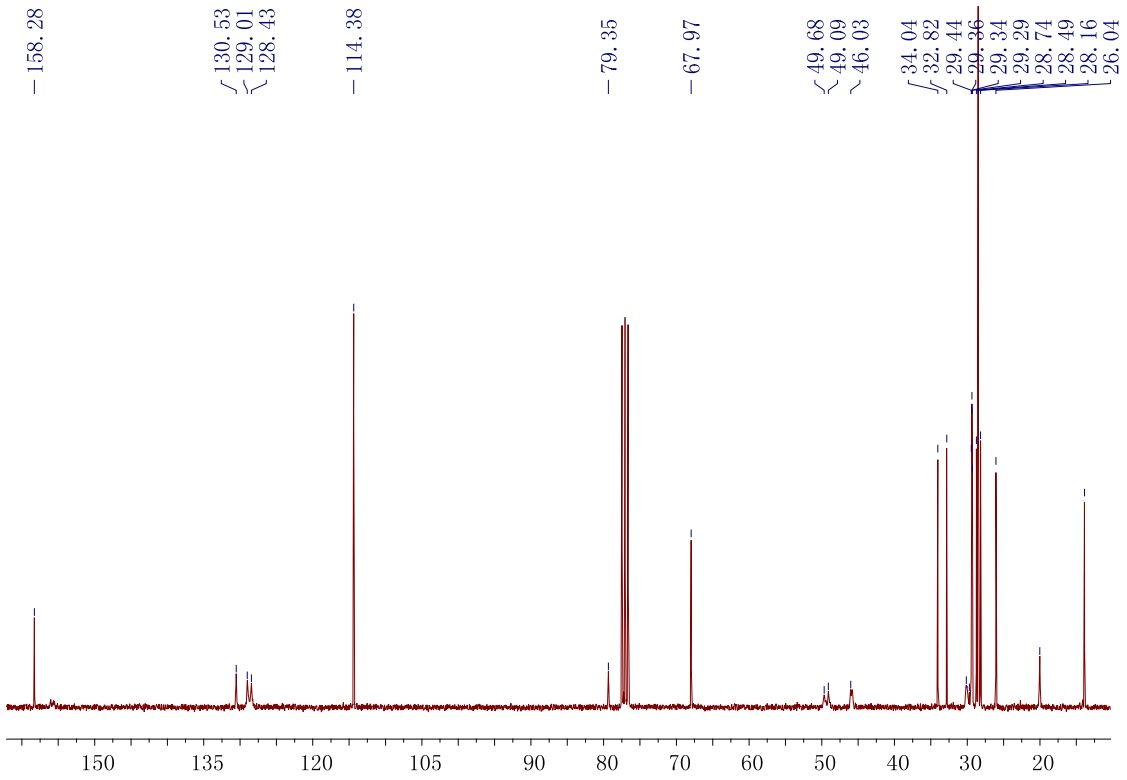
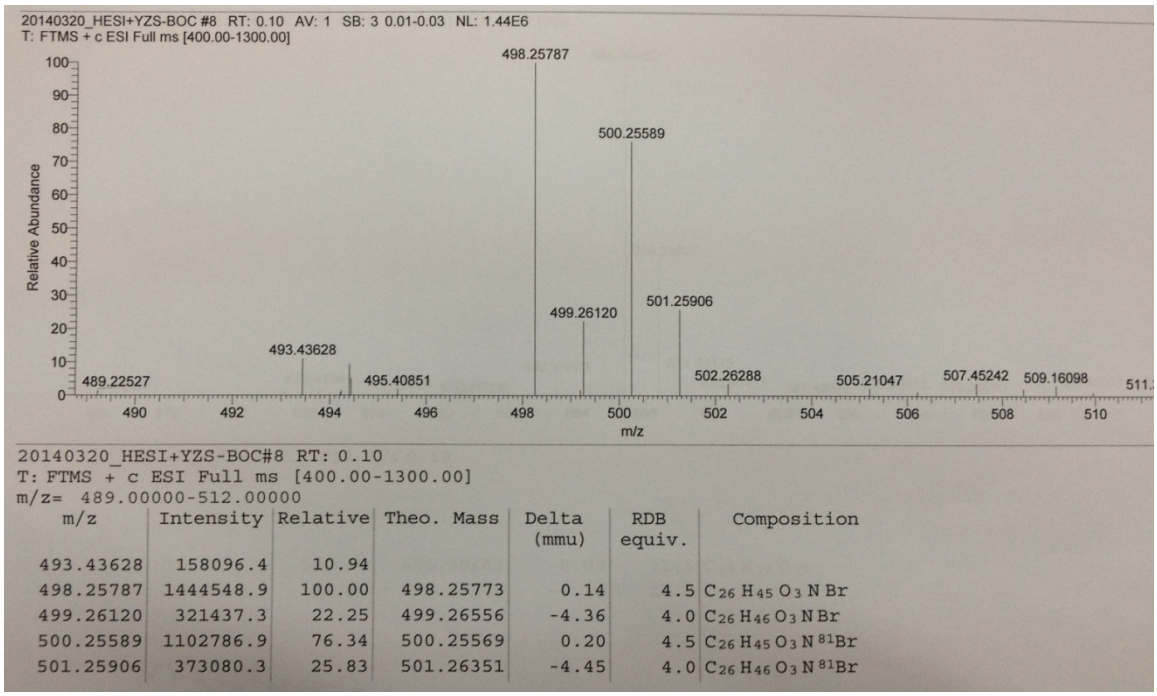


Figure S26. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of compound **15**.

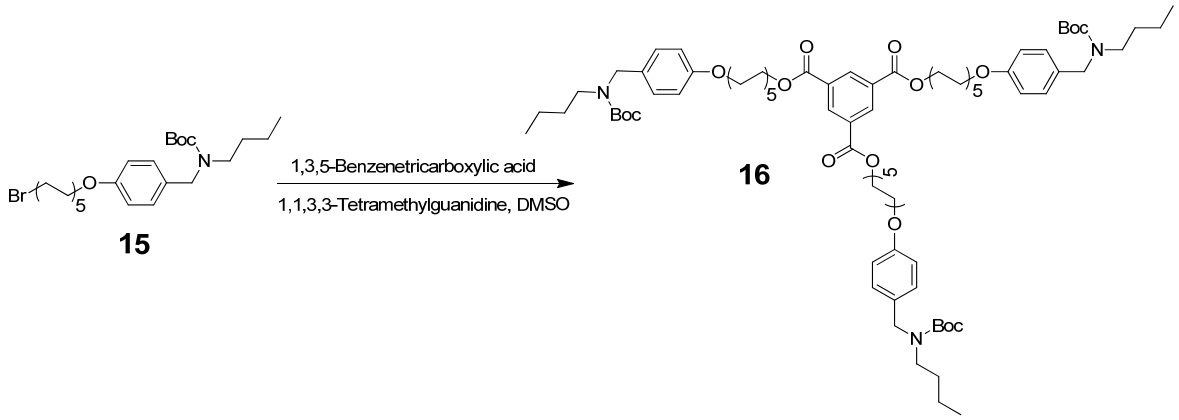


20140320_HESI+YZS-BOC#8 RT: 0.10
T: FTMS + c ESI Full ms [400.00-1300.00]
m/z= 489.00000-512.00000

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
493.43628	158096.4	10.94				
498.25787	1444548.9	100.00	498.25773	0.14	4.5	$C_{26}H_{45}O_3NBr$
499.26120	321437.3	22.25	499.26556	-4.36	4.0	$C_{26}H_{46}O_3NBr$
500.25589	1102786.9	76.34	500.25569	0.20	4.5	$C_{26}H_{45}O_3N^{81}Br$
501.25906	373080.3	25.83	501.26351	-4.45	4.0	$C_{26}H_{46}O_3N^{81}Br$

Figure S27. Electrospray ionization spectrum of compound **15**.

*2.10. Synthesis of compound **16***



Compound **15** (5.00 g, 10.0 mmol), 1,3,5-benzenetricarboxylic acid (0.53 g, 2.50 mmol) and 1,1,3,3-tetramethylguanidine (0.87 g, 7.55 mmol) in 50 mL DMSO were stirred at room temperature for 48 hours.[S7] After the reaction was complete, the solvent was extracted with H_2O/CH_2Cl_2. The organic extracts was dried over anhydrous Na_2SO_4 and evaporated with a rotary evaporator. The residue was purified by flash column chromatograph (petroleum ether/CH_2Cl_2, 2 : 1 *v*/*v* as the eluent) to afford compound **16** as a colorless oil (9.27 g, 63%). The ^{1}H NMR spectrum of compound **16** is shown in Figure S28. ^{1}H NMR (300 MHz, $CDCl_3$, room temperature) δ 8.84 (s, 3H), 7.13 (br, 6H), 6.82 (d, J = 8.6 Hz, 6H), 4.36 (t, J = 6.7 Hz, 12H), 3.92 (t, J = 6.5 Hz, 6H), 3.09 (br, 6H), 1.78 (m, 12H), 1.46 (m, 42H), 1.38–1.21 (m, 33H), 0.88 (t, J = 7.3 Hz, 9H). The ^{13}C NMR spectrum of compound **16** is shown in Figure S29. ^{13}C NMR (75 MHz, $CDCl_3$, room temperature) δ (ppm): 165.1, 158.3, 134.4, 131.5,

130.5, 129.0, 128.4, 114.4, 79.3, 68.0, 65.8, 49.7, 45.8, 30.1, 29.7, 29.5, 29.4, 29.3, 28.7, 28.5, 26.1, 26.0, 20.0, 13.9. ESI–MS m/z: $[M + H]^+$, $C_{87}H_{136}O_{15}N_3$, 1462.99634.

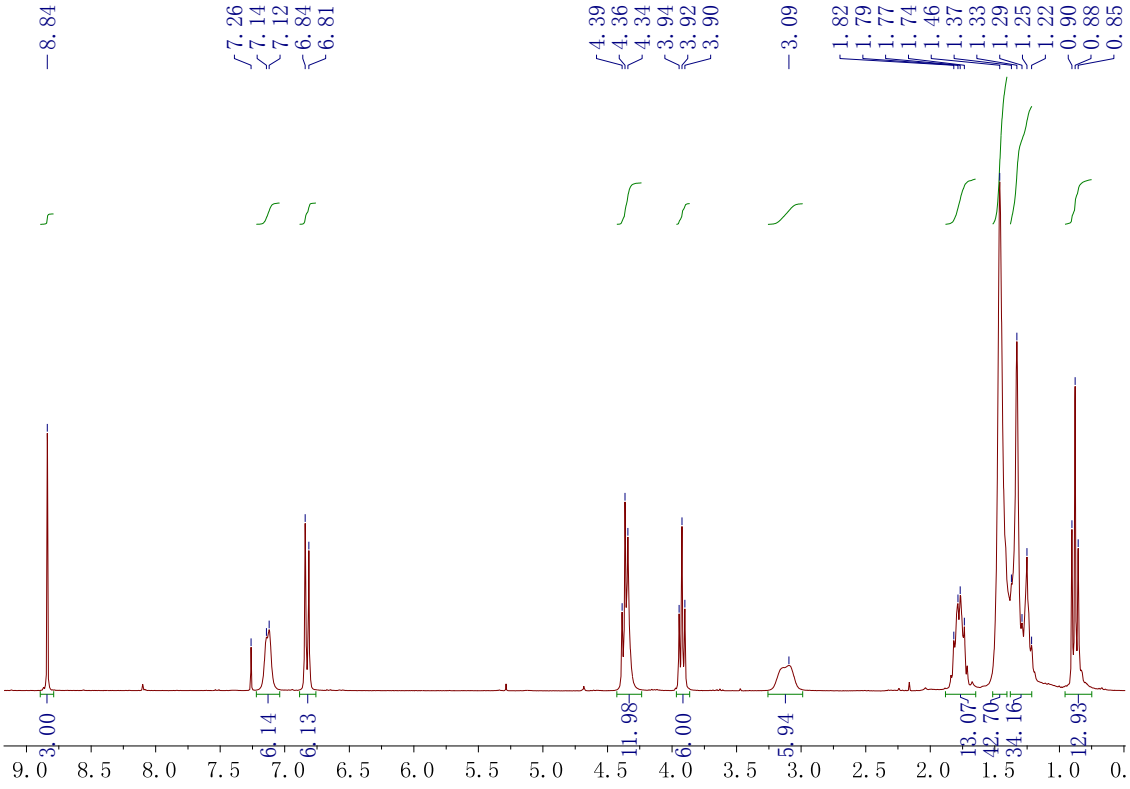


Figure S28. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, room temperature) of compound **16**.

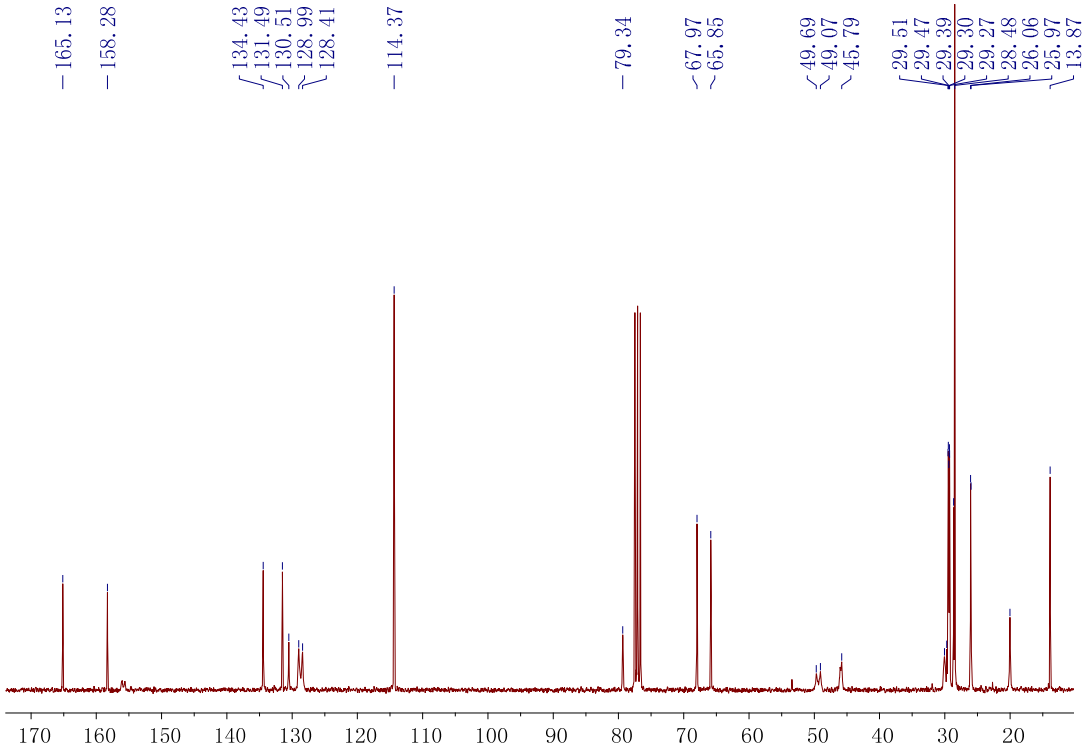
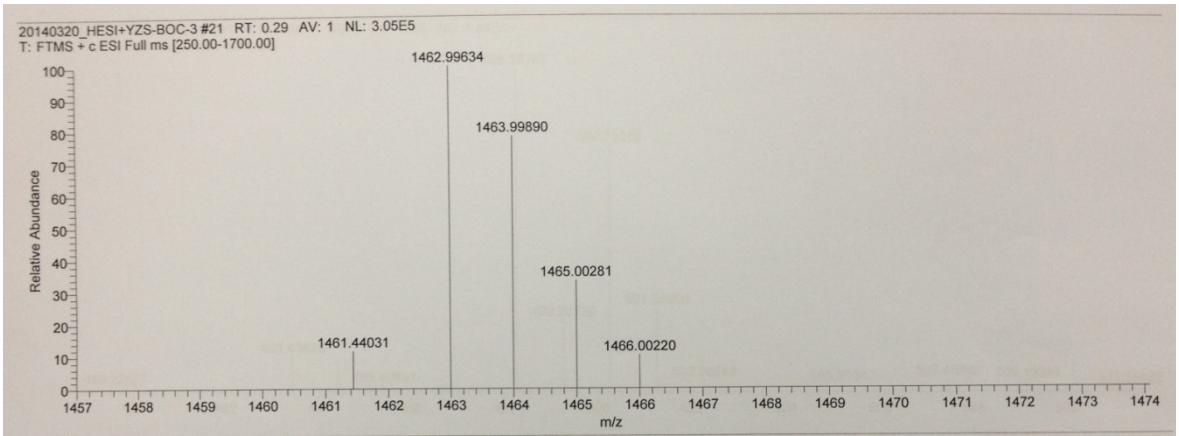


Figure S29. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, room temperature) of compound **16**.

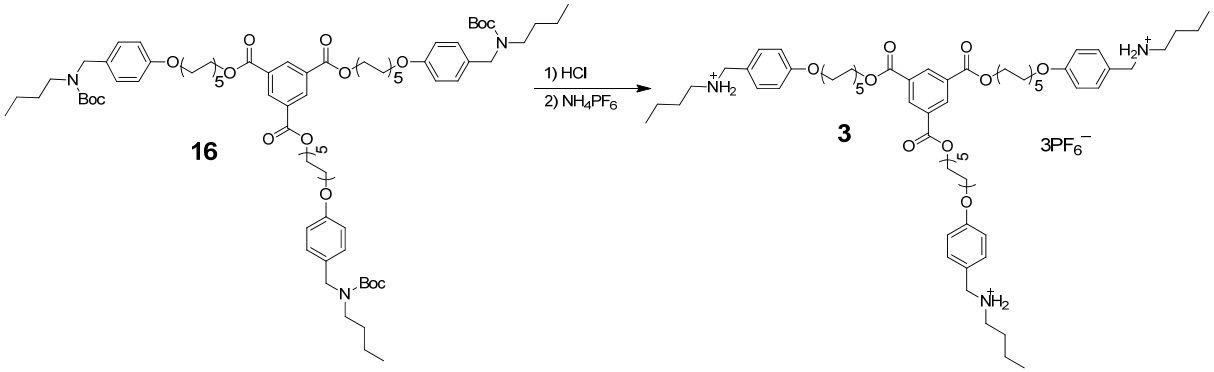


20140320_HESI+YZS-BOC-3#21 RT: 0.29
T: FTMS + c ESI Full ms [250.00-1700.00]
m/z= 1457.00000-1473.00000

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
1462.99634	304955.1	100.00	1462.99660	-0.26	21.5	$C_{87}H_{136}O_{15}N_3$
1463.99890	238591.5	78.24	1464.00442	-5.52	21.0	$C_{87}H_{137}O_{15}N_3$

Figure S30. Electrospray ionization spectrum of compound **16**.

*2.11. Synthesis of monomer **3***



Compound **16** (2.00 g, 1.37 mmol) was dissolved in 10% HCl/ethyl acetate (100 mL) and stirred overnight. After the reaction, the white solid was filtered, washed with ethyl acetate thoroughly, and dissolved in water/acetone (200 ml). The saturated aqueous solution of NH_4PF_6 was added and stirred at room temperature for 3 hours. Then acetone was evaporated with a rotary evaporator to afford a white precipitate, which was filtered off and washed with deionized water to afford monomer **3** as a white solid (1.45 g, 66%). Mp: 196.3−197.5 ^{o}C. The ^{1}H NMR spectrum of compound **3** is shown in Figure S31. ^{1}H NMR (300 MHz, CD_3CN, room temperature) δ 8.66 (s, 3H), 7.28 (d, J = 8.6 Hz, 6H), 6.88 (d, J = 8.2 Hz, 6H), 4.29 (t, J = 6.3 Hz, 6H), 3.99 (s, 6H), 3.91 (t, J = 6.6 Hz, 6H), 2.96–2.85 (m, 6H), 1.69 (m, 12H), 1.53 (m, 6H), 1.44–1.17 (m, 42H), 0.87 (t, J = 7.3 Hz, 9H). The ^{13}C NMR spectrum of compound **3** is shown in Figure S32. ^{13}C NMR (75 MHz, CD_3CN, room temperature) δ (ppm): 164.3, 159.8, 133.3, 131.4, 131.3, 122.0, 114.4, 67.6, 65.4, 50.7, 47.0, 28.9, 28.7, 28.6, 28.0, 27.2,

25.4, 19.0, 12.4. $[M + Na]^+$, $C_{72}H_{114}O_9N_3NaP_3$, 1622.73828.

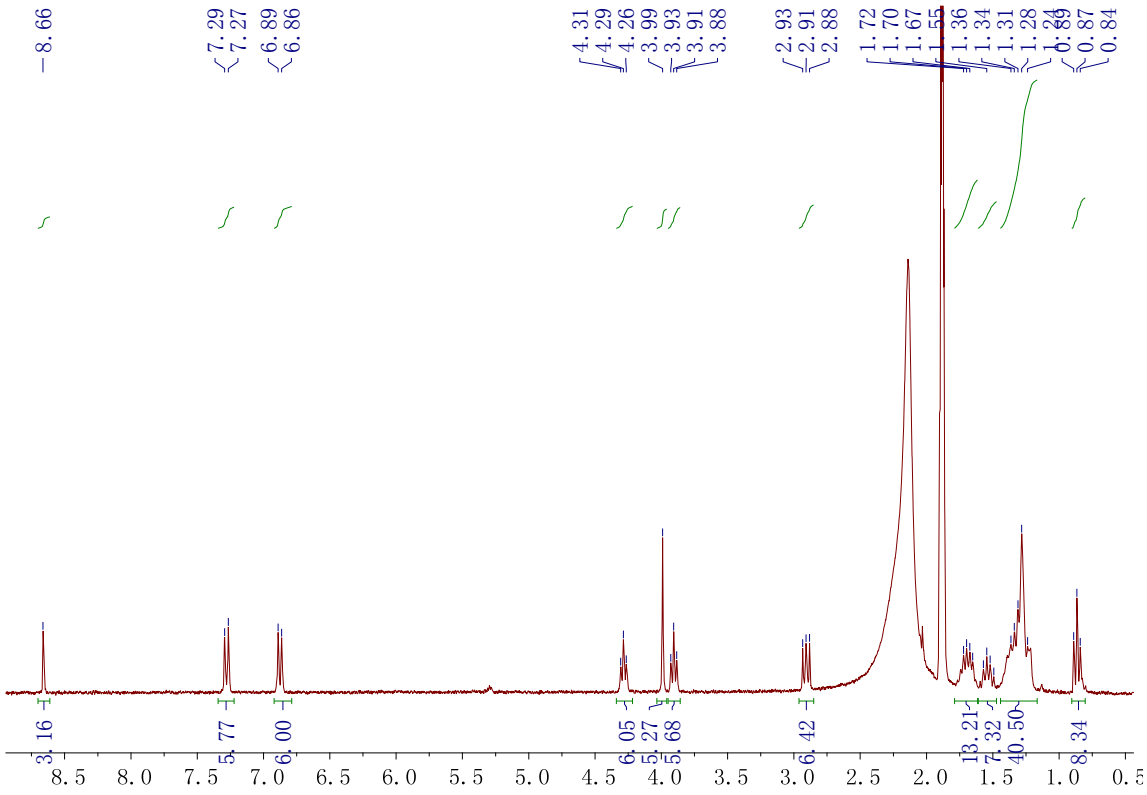


Figure S31. ^{1}H NMR spectrum (300 MHz, CD_3CN, room temperature) of compound **3**.

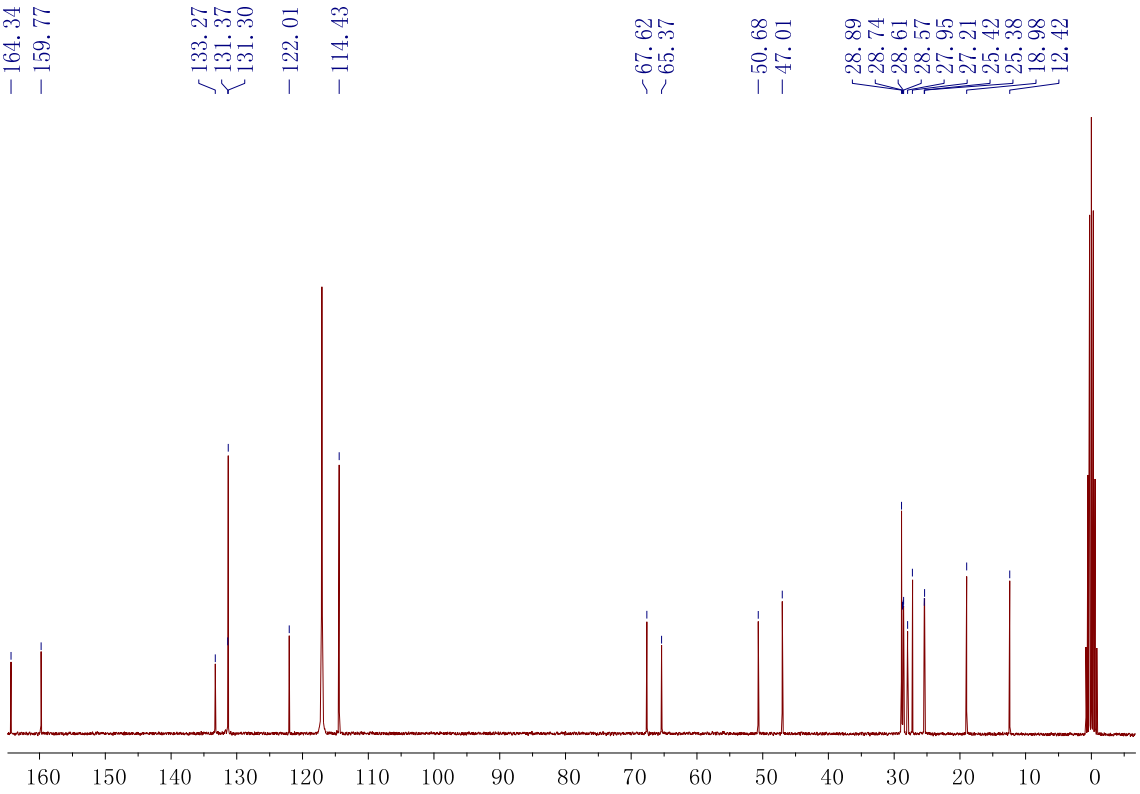
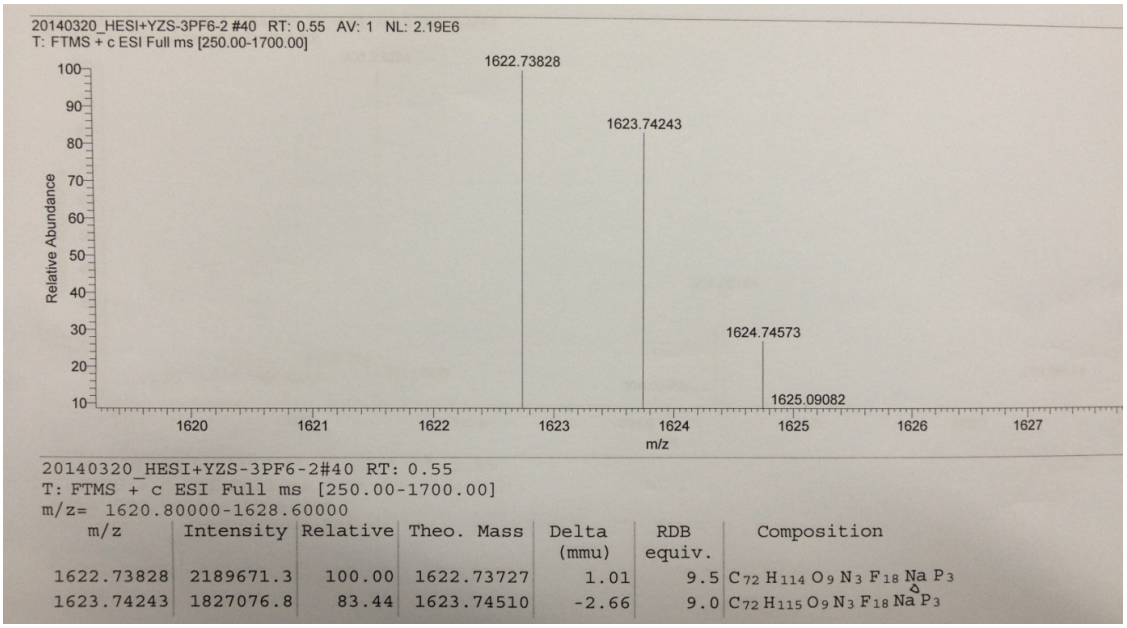


Figure S32. ^{13}C NMR spectrum (75 MHz, CD_3CN, room temperature) of compound **3**.



20140320_HESI+YZS-3PF6-2#40 RT: 0.55
T: FTMS + c ESI Full ms [250.00-1700.00]
m/z= 1620.80000-1628.60000

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
1622.73828	2189671.3	100.00	1622.73727	1.01	9.5	$C_{72}H_{114}O_9N_3F_{18}NaP_3$
1623.74243	1827076.8	83.44	1623.74510	-2.66	9.0	$C_{72}H_{115}O_9N_3F_{18}NaP_3$

Figure S33. Electrospray ionization spectrum of compound **3**.

*3. UV/Vis titration between **6** and pyrene*

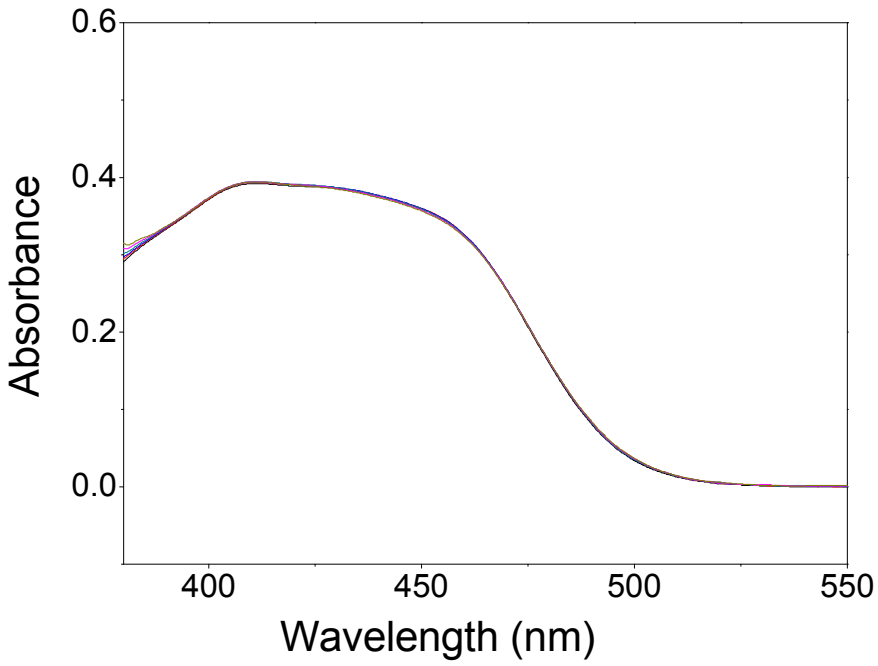


Figure S34. UV/Vis absorption spectra change upon stepwise addition of pyrene to monomer **6** at 5.00×10^{-5} M in $CHCl_3/CH_3CN$ (2/1, *v*/*v*). The weak binding affinity for **6**/pyrene is manifested by the very slight absorption changes in UV/Vis spectra. Therefore, the bis-alkynylplatinum(II) terpyridine molecular tweezer/pyrene recognition motif is not a suitable candidate for the fabrication of supramolecular hyperbranched polymers.

*4. ^{1}H NMR titration between **6** and **7***

^{1}H NMR titration experiments were performed between the monotopic compounds **6** and **7**, for which the initial concentration of compound **7** was kept constant at 5.00 mM while concentration of compound **6** was systematically varied (Figure S35). Based on the molar ratio plot (Figure 1a in the maintext), the complexation stoichiometry between compound **6** and compound **7** is determined to be 1 : 1 at room temperature.

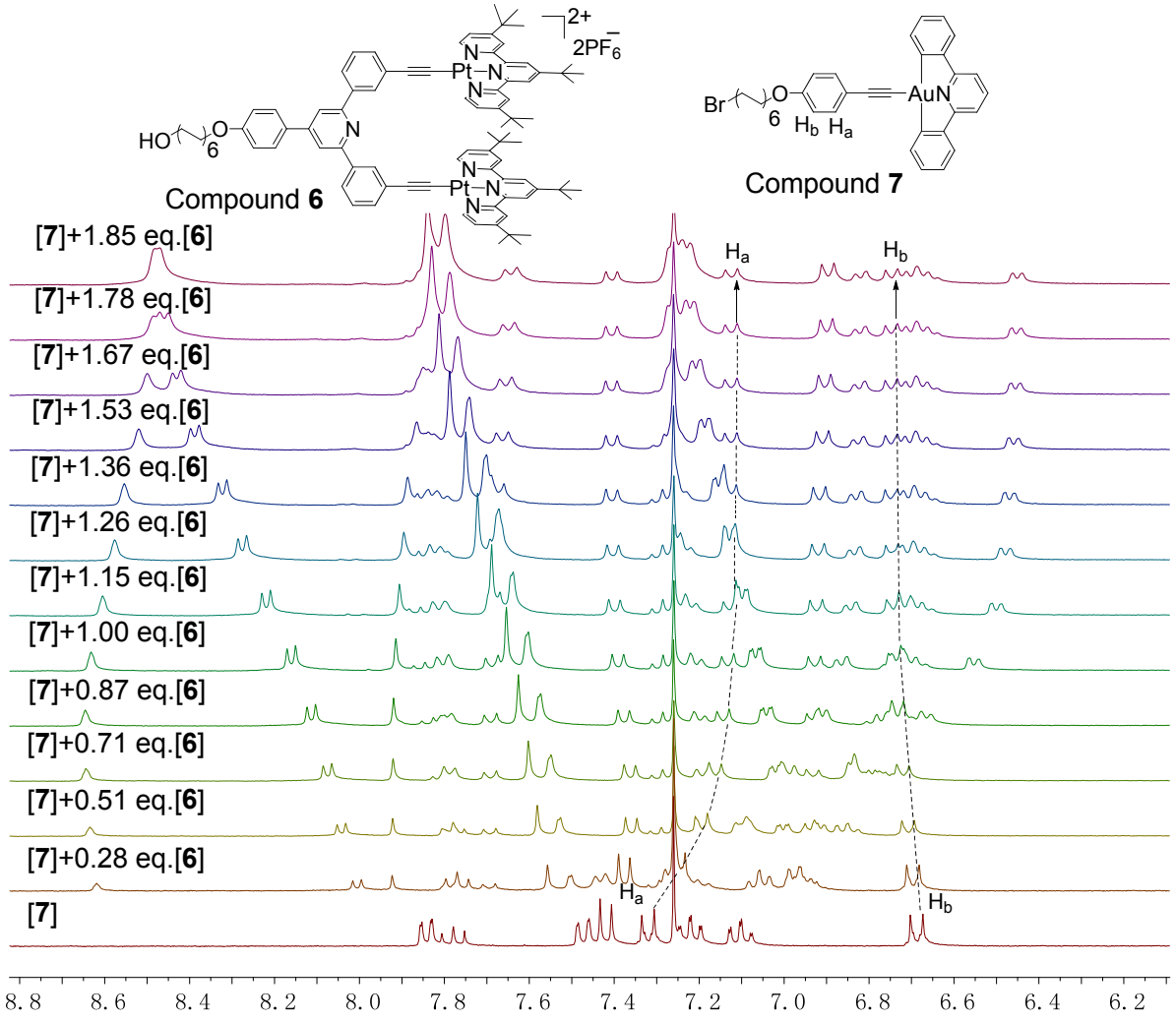


Figure S35. ^{1}H NMR titration spectra (300 MHz, $CDCl_3/CD_3CN$ (2/1, *v*/*v*), room temperature) of compound **7** at the concentration of 5.00 mM upon stepwise addition of compound **6**.

*5. UV/Vis titration experiments for complexes **6**/**2** and **1**/**2***

Progressive addition of **2** to the tweezer-containing compounds such as **1** and **6** led to a gradual decrease of the intensity for MLCT/LLCT absorption bands in UV/Vis spectra (Figure S36–37). Hence, treatment of the collected absorbance data at 460 nm (A) *vs* the concentration of guest added (C_A) with a non-linear least-squares curve-fitting equation affords the association constants. Specifically, for 1 : 1 host/guest complexation, binding constants are calculated according to the following equation:[S8]

$$A = A_0 + \frac{A_{\text{lim}} - A_0}{2C_0}\left[C_0 + C_A + 1/K_S - \left[\left(C_0 + C_A + 1/K_S\right)^2 - 4C_0C_A\right]^{1/2}\right] \qquad \text{(Equation S1)}$$

A_0 and A are the absorbance of the host at a selected wavelength with and without presence of the guest, respectively, [C_0] is the total concentration of the host, [C_A] is the concentration of the guest, A_{lim} is the limiting value of absorbance with the presence of excess guest and K_S is the binding constant.

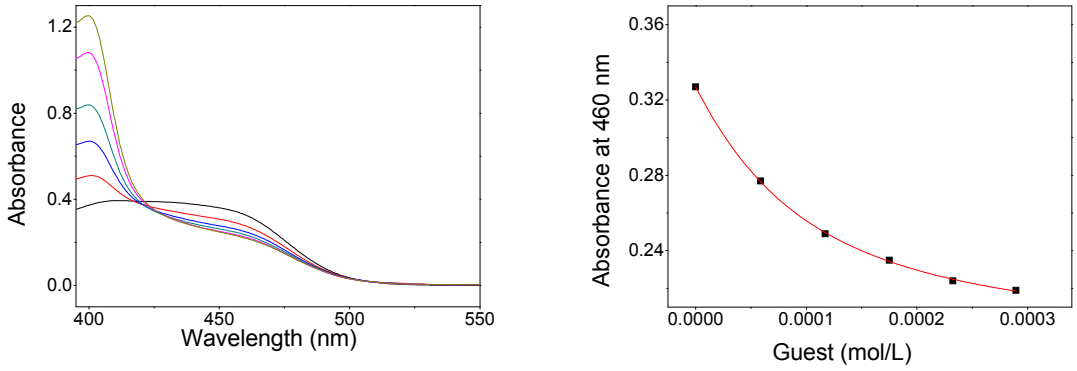


Figure S36. *Left*: UV/Vis absorption spectra change upon stepwise addition of **2** to **6** at 5.00 × 10^{-5} M in $CHCl_3/CH_3CN$ (2/1, *v*/*v*); *right*: UV/Vis absorption spectra change at 460 nm. The red line was obtained from the non-linear curve-fitting. $K_{\mathbf{6}\cdot\mathbf{2}} = (1.43 \pm 0.61) \times 10^4$ M^{-1}.

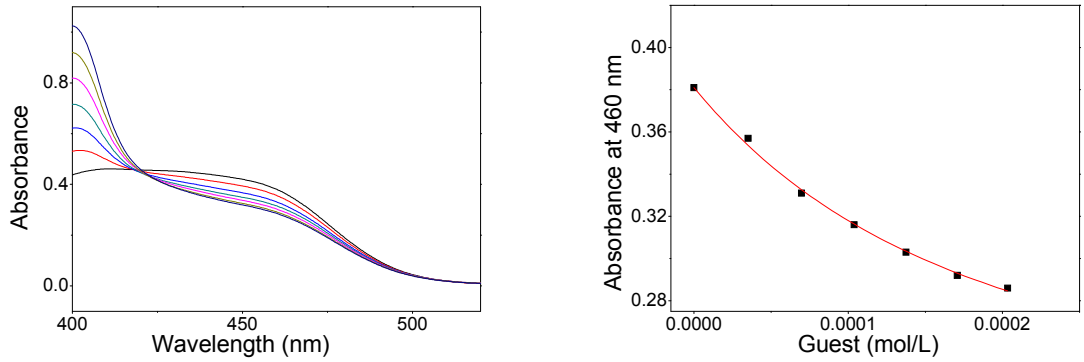


Figure S37. *Left*: UV/Vis absorption spectra change upon stepwise addition of **2** to **1** at 5.00 × 10^{-5} M in $CHCl_3/CH_3CN$ (2/1, *v*/*v*); *right*: UV/Vis absorption spectra change at 460 nm. The red line was obtained from the non-linear curve-fitting. $K_{\mathbf{1}\cdot\mathbf{2}} = (6.66 \pm 1.11) \times 10^3$ M^{-1}.

6. Molecular recognition studies for the four monotopic compounds

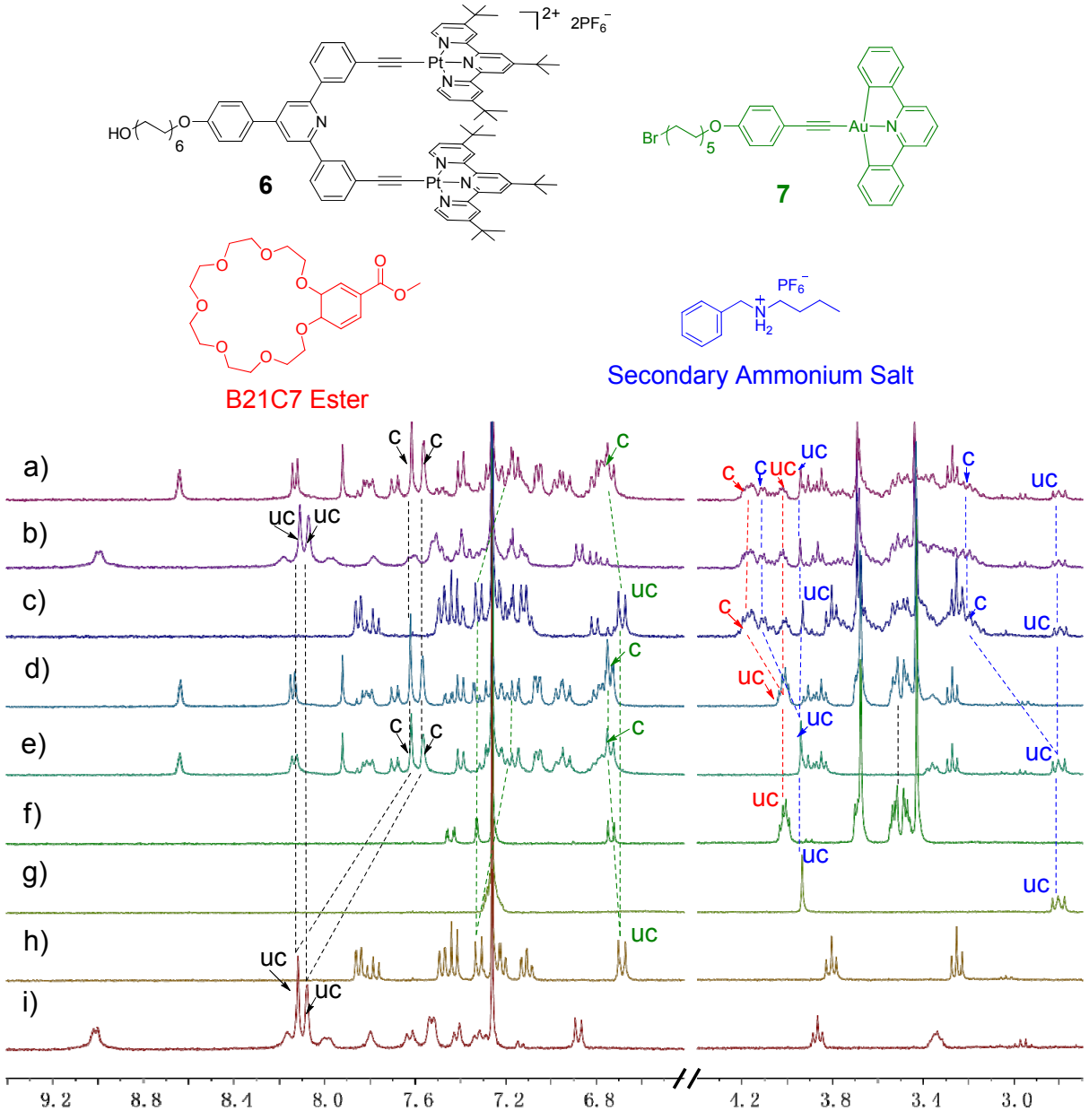


Figure S38. ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ (2/1, *v*/*v*), room temperature) of a) **6, 7**, B21C7 ester and secondary ammonium salt with 1 : 1 : 1 : 1 molar ratio; b) **6,** B21C7 ester and secondary ammonium salt with 1 : 1 : 1 molar ratio; c) **7**, B21C7 ester and secondary ammonium salt with 1 : 1 : 1 molar ratio; d) **6, 7** and B21C7 ester with 1 : 1 : 1 molar ratio; e) **6, 7** and secondary ammonium salt with 1 : 1 : 1 molar ratio; f) B21C7 ester; g) secondary ammonium salt; h) **7**; i) **6**. Peaks corresponding to complexed and uncomplexed units are designated as "c" and "uc", respectively. Based on Figure S38d–e, preferential recognition between molecular tweezer/gold(III) alkynyl complexes is confirmed without the participation of B21C7 ester or secondary ammonium salt. Meanwhile, specific recognition between B21C7 ester and secondary ammonium salt motifs is also demonstrated, without the involvement of **6** or **7** (Figure S38b–c). Moreover, after mixing equivalent amounts of monotopic compounds together, the resulting spectra (Figure S38a) are almost the overlapping ^{1}H NMR spectra of the corresponding **6**/**7** and B21C7/secondary ammonium salt complexes, definitely supporting the non-interfering complexation properties for the two non-covalent recognition motifs.

*7. Complexation studies for **1**–**3** via step-wise self-assembly pathway*

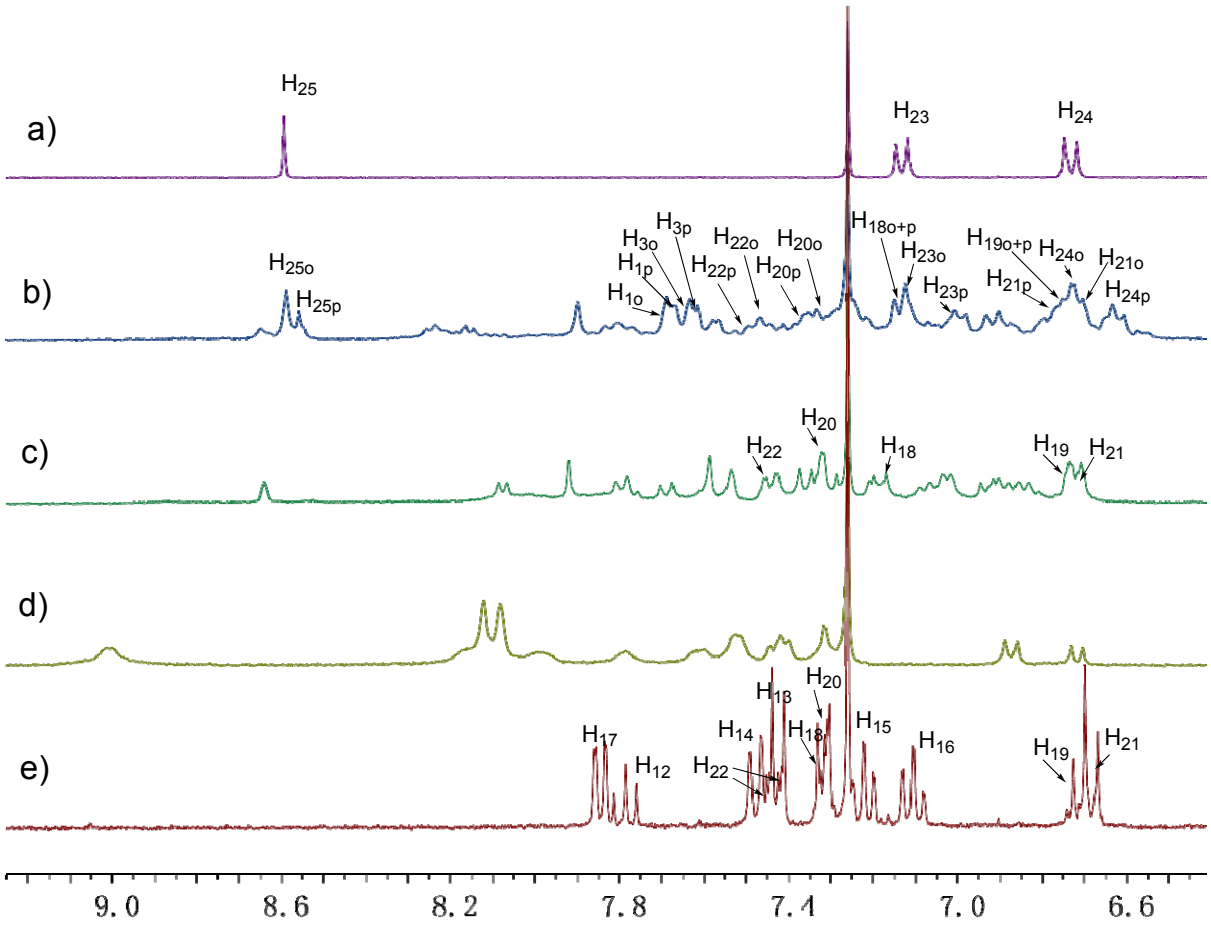


Figure S39. ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ (2/1, *v/v*), room temperature) of a) **3**; b) mixture of **1**, **2** and **3** with 3 : 3 : 2 molar ratio; c) mixture of **1** and **2** with 1 : 1 molar ratio; d) **1;** e) **2**. [**1**] = [**2**] = 9 mM, [**3**] = 6 mM. Here "p" and "o" denote the polymeric and oligomeric species, respectively.

*8. COSY NMR spectra for the mixture of **1–3***

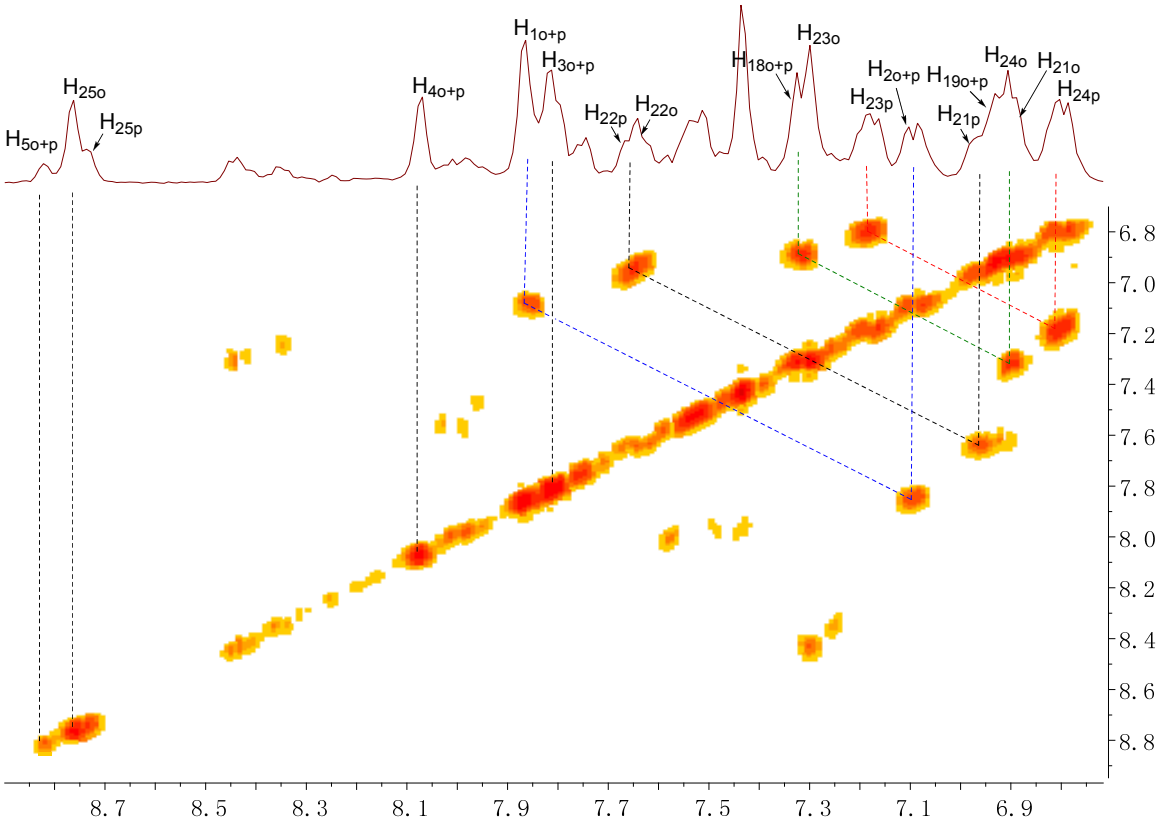


Figure S40. ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3/CD_3CN$ (2/1, *v/v*), room temperature) of the mixture of **1, 2** and **3** with 3 : 3 : 2 molar ratio (concentration of **1** is 9.0 mM). The spectrum facilitates the accurate proton assignments. Strong correlations could be seen between the protons H_1 and the neighbouring proton H_2 on the molecular tweezer unit. Moreover, the correlations between H_{18} and the neighbouring protons H_{19} on **2**, H_{24} and H_{23} on **3** could also be observed. For the neighbouring B21C7 ester protons the correlations could also be visulized. Here "p" and "o" denote the polymeric and oligomeric species, respectively.

9. DOSY experiments for the linear and hyperbranched supramolecuar polymers

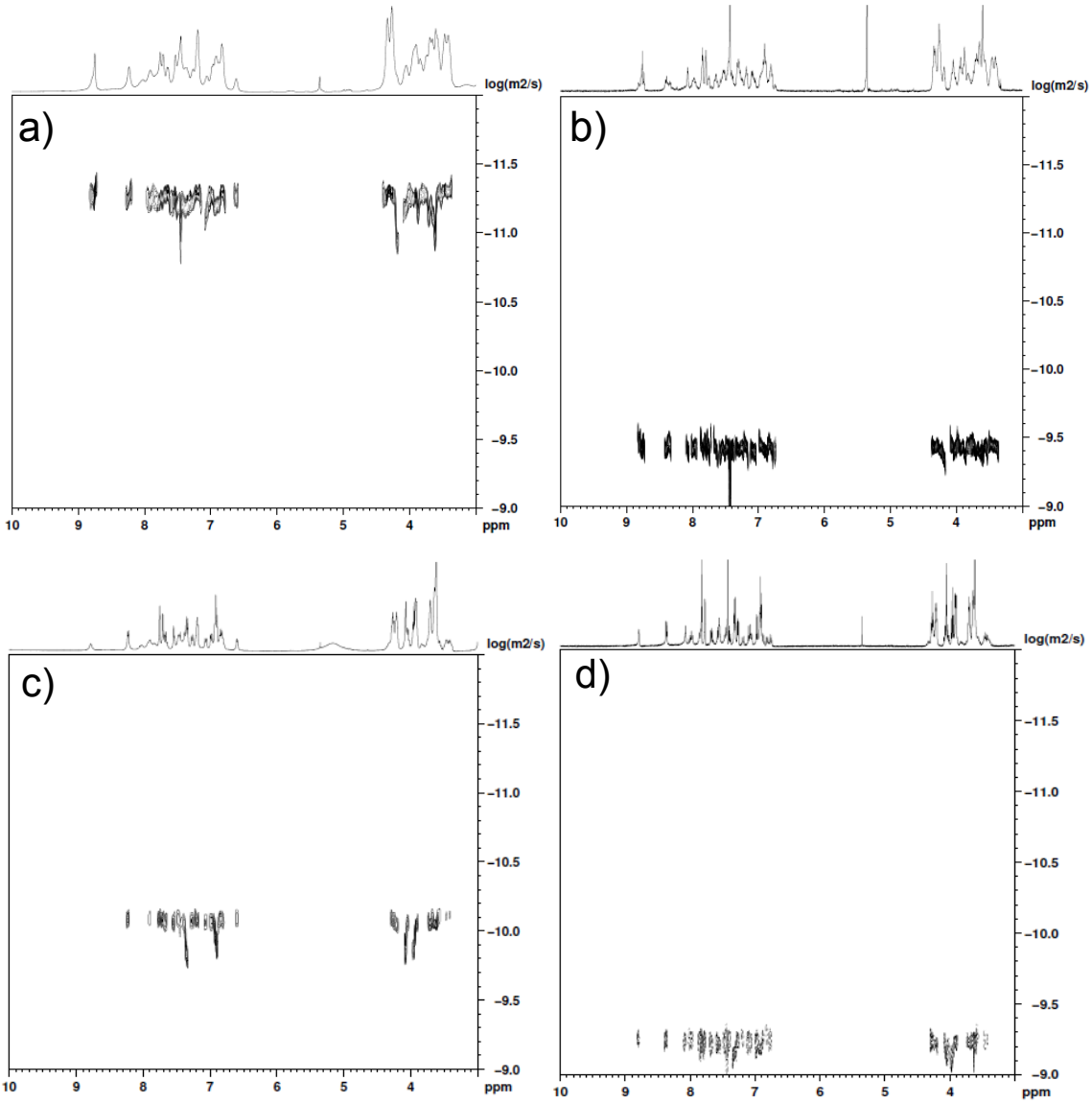


Figure S41. Two-dimensional diffusion-ordered NMR (DOSY) spectra of the supramolecular hyperbranched polymers (a and b) and the linear polymers (c and d) in $CDCl_3/CD_3CN$ (2/1, *v/v*) at different monomer concentrations: (a) and (c), 70.0 mM; (b) and (d), 5.00 mM for **1**. As the monomer concentration increases from 5.00 mM to 70.0 mM, the measured diffusion coefficients decrease dramatically from 3.75×10^{-10} to 5.12×10^{-12} m^2 s^{-1}. Similar trend is also observed for the linear supramolecular polymer, which declines from 5.83×10^{-10} to 8.49×10^{-11} m^2 s^{-1} under the same conditions. When compared with the results, it is obvious that the self-assembling architectures exert significant impacts on the size of the resulting supramolecular assemblies.

10. Stimuli-responsive properties for ***5***

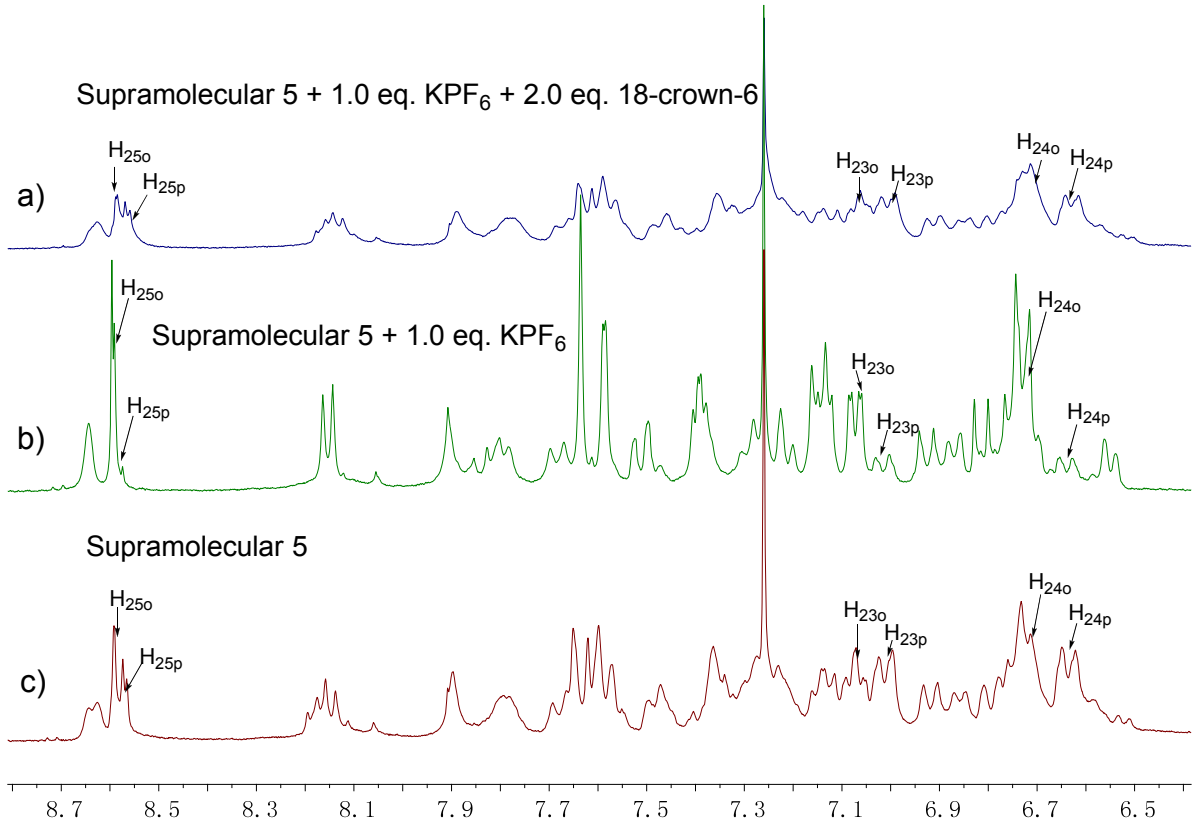


Figure S42. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ (2/1, *v/v*), 298 K) of the supramolecular hyperbranched polymers **5** (8.0 mM based on monomer **1**) with successive addition of KPF_6 and 18-crown-6, respectively. Here "p" and "o" denote the polymeric and oligomeric species, respectively.

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