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Supporting Information

Step-Wise Self-assembly of Discrete Molecular Honeycomb Using Multitopic Metallo-Organic Ligand

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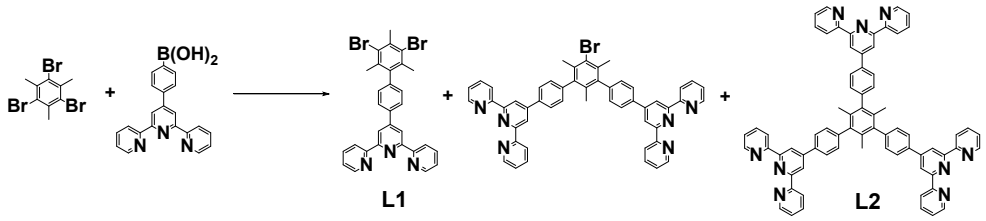
General

Solvents used in the experimental processes were purified, prior to use. All materials were directly purchased through J & K Chemical Technology and used without farther purification. Analytical thin layer chromatography (TLC) was performed on aluminum-backed sheets precoated with Al_2O_3 150 F254 adsorbent (0.25 mm thick; Merck, Germany). Column chromatography was conducted using neutral Al_2O_3 (200-300 mesh) from Sinopharm Chemical Reagent Co. The ^1H NMR spectra were recorded at 25°C on a Bruker spectrometer operating at either 400, 500 or 80, 100 MHz for ^1H or ^{13}C, respectively. Chemical shifts were reported in parts per million (ppm) referenced to the residual solvent peak for ^1H and solvent peak for ^{13}C NMR, respectively. Analytical characterization was performed on a Q-TOF mass spectrometer with an ESI probe which produced by XEVO. Matrix-assisted laser desorption/ionization coupled with time-of-flight detector (MALDI TOF) mass spectrometry was conducted on Bruker Microflex series spectrometer equipping nitrogen 337 nm laser. 1.0 μL of 2,5-dihydroxybenzoic acid (DHB) matrix solution (10 mg/mL in CH_3CN) was first deposited on a MALDI plate

and air-dried. Aliquots of sample solution (1 mg/mL in $CHCl_3$) were then added onto the matrix spots for characterization. UV-visible spectrophotometer and were corrected for the background spectrum of the solvent. Transmission microscopy measurements were performed on a JEM-2100F TEM operating at 200 kV.

Synthesis of organic ligand:

1,3,5-tribromo-2,4,6-trimethylbenzene[1], 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine[2] were synthesized according to the literatures.

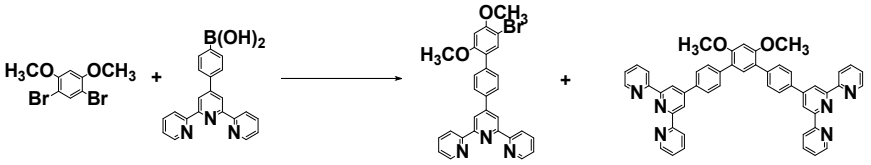


L**1** and L**2** were prepared through a single-pot reaction: To a 3-necked round bottom flask, 1,3,5-tribromo-2,4,6-trimethylbenzene (715 mg, 2 mmol), 4'-(4-boronatophenyl)-2,2':6',2"-terpyridine (2.12 g, 6 mmol), Na_2CO_3 (3.18 g, 30 mmol), and a solvent mixture of water (150 mL), toluene (150 mL), and Me_3COH (50 mL) were added. The system was freeze-pump-thaw (3×), back-filled with nitrogen; and then $PdCl_2(PPh_3)_2$ (210 mg, 300 μmol) was added. The resultant suspension was refluxed for 48 h under nitrogen. After cooling to 25°C, the aqueous layer was extracted with $CHCl_3$ (3×80 mL). The combined organic phase was dried ($MgSO_4$), and concentrated *in vacuo* to give a brown residue, which was purified by flash column chromatography (Al_2O_3), eluting with $CHCl_3$ to give L**1** and L**2** in turn, as white solid.

L**1** (26%); m.p.= 268°C; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.82 (s, 2H, Tpy-$H^{3',5'}$), 8.77-8.76 (d, J= 5Hz, 2H, Tpy-$H^{6,6"}$), 8.73-8.72(d, J= 5Hz, 2H, Tpy-$H^{3,3"}$), 8.00-7.99(d, J= 5Hz, 2H, Ph-H^{j}), 7.94-7.90 (m, 2H, Tpy-$H^{4,4"}$), 7.41-7.38 (m, 2H, Tpy-$H^{5,5"}$), 7.26-7.24 (d, J= 10Hz, 2H, Ph-H^{k}), 2.77 (s, 3H, CH_3), 2.16 (s, 6H, CH_3); ^{13}C NMR (101

MHz, $CDCl_3$) δ: 156.21, 156.03, 149.98, 149.18, 142.30, 141.06, 137.59, 136.92, 135.41, 129.57, 127.78, 125.85, 123.90, 121.36, 118.97, 25.99, 22.80; MALDI-TOF MS (*m/z*): Calcd. For: 586.03134; Found For: 586.03259 $[M+H]^+$.

L**2** (44%)[3].

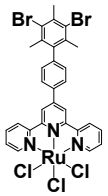


L**3** and L**4** were prepared through a single-pot reaction: To a solution of 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine (1.4 g, 4 mmol) and 1,3-dibromo-2,5-dimethoxybenzene (592 mg, 2 mmol) in THF (150 mL), aqueous NaOH (480 mg, 12 mmol) (1 M) was added. The system was degassed for 10 minutes, then $Pd(PPh_3)_4$ (231 mg) was added. After refluxing for 2 days under N_2, the solvent was removed *invacuo* to give a residue that was dissolved in $CHCl_3$ and washed with water. The organic layer was dried (anhydrous $MgSO_4$), concentrated *in vacuo* to give a residue that was purified by flash column chromatography (Al_2O_3) eluting with $CHCl_3$ to give L**3** and L**4** in turn, as white solid.

L**3** (28%); m.p.= 214°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (s, 2H, Tpy-*H*$^{3',5'}$), 8.79-8.78 (d, J= 5Hz, 2H, Tpy-*H*$^{6,6"}$), 8.73-8.72 (d, J= 5Hz, 2H, Tpy-*H*$^{3,3"}$), 8.01-7.99 (d, J= 10Hz, 2H, Ph-*H*^{j}), 7.95-7.92 (m, 2H, Tpy-*H*$^{4,4"}$), 7.67-7.65 (d, J= 10Hz, 2H, Ph-*H*^{k}), 7.59 (s, 1H, Ph-*H*^{b}), 7.42-7.39 (m, 2H, Tpy-*H*$^{5,5"}$), 6.63 (s, 1H, Ph-*H*^{a}), 4.00 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.99, 156.26, 156.12, 150.03, 148.94, 137.97, 137.14, 136.80, 134.34, 129.89, 127.07, 124.01, 123.87, 121.52, 118.94, 102.47, 97.27, 56.60, 56.09; MALDI-TOF MS (*m/z*): Calcd. For: 526.09522; Found For: 526.09564 $[M+H]^+$

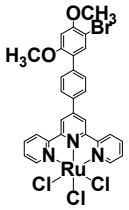
L**4** (54%)[4].

Synthesis of terpyridine-mono-Ru^{III} adduct:



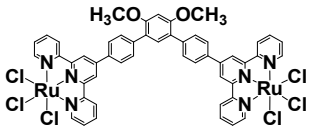
5

5: L**1** (176 mg, 300 μmol) and $RuCl_3 \cdot 3H_2O$ (86 mg, 330 μmol) were added into EtOH (50 mL), the mixture was refluxed for 18h. Then it was filtered to give a solid which was washed by MeOH to afford **5**, as a brown solid: 191.2 mg (Yield: 80.3%), m.p.>300°C. It was used directly without further purification.



6

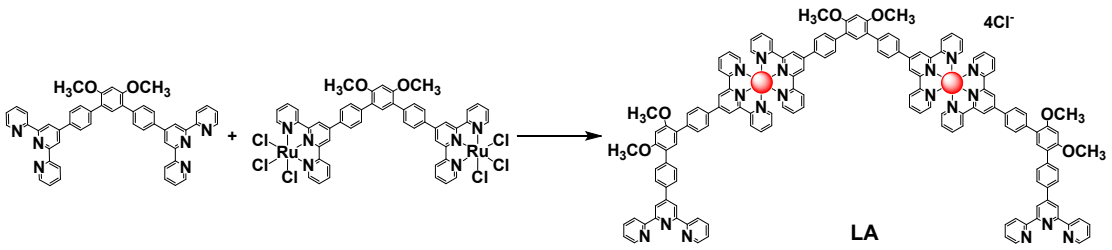
6: L**3** (210 mg, 400 μmol) and $RuCl_3 \cdot 3H_2O$ (115 mg, 440 μmol) were added into EtOH (60 mL), the mixture was refluxed for 18h. Then it was filtered to give a solid which was washed by MeOH to afford **6**, as a brown solid: 244.7 mg (Yield: 83.6%), m.p.>300°C. It was used directly without further purification.



7

7: L**4** (150.6 mg, 200 μmol) and $RuCl_3 \cdot 3H_2O$ (115 mg, 440 μmol) were added into EtOH (80 mL), the mixture was refluxed for 18h. Then it was filtered to give a solid which was washed by MeOH to afford **7**, as a brown solid: 193 mg (Yield: 73%), m.p.>300°C. It was used directly without further purification.

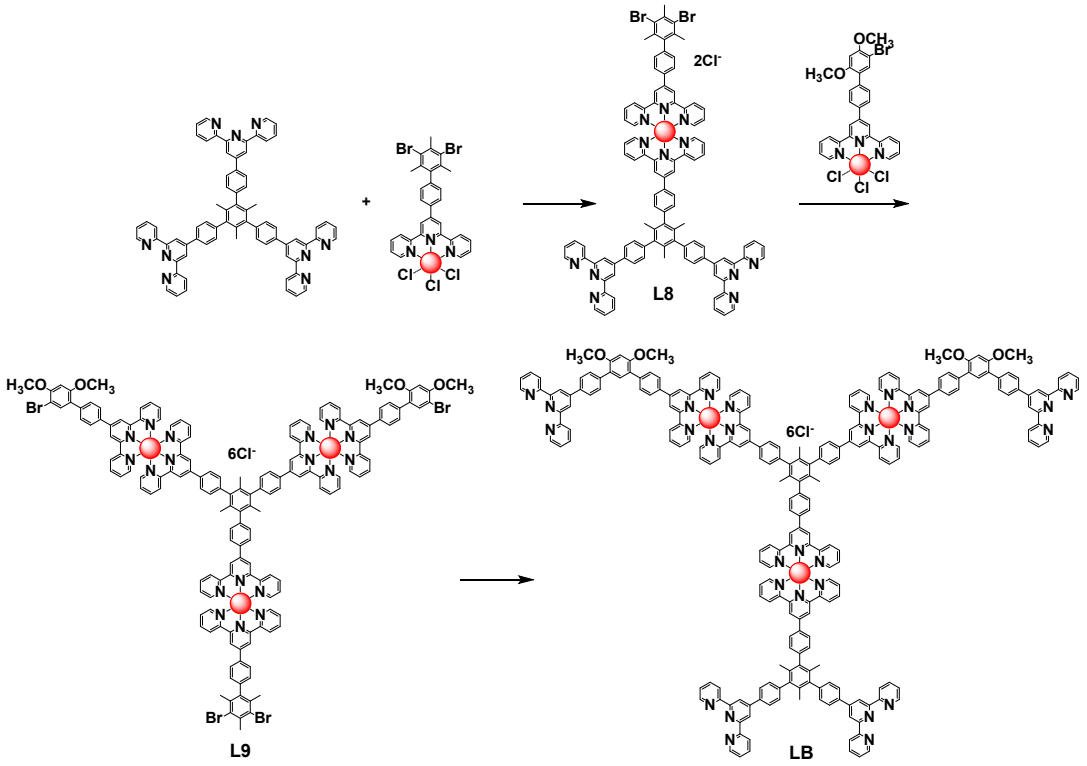
Synthesis of LA:



LA

L**A**: A suspension of L**4** (188 mg, 0.25 mmol) and **7** (116.7 mg, 0.1 mmol) in $CHCl_3$:CH_3OH=1:1 (160 mL), N-ethylmorpholine (4 drops) was added, the mixture was heated for 24 h. After the reaction mixture was cooled, the resulting deep red solution was filtered through Celite. Solvent and volatiles were removed in *vacuo*, the residue was column-chromatographed (Al_2O_3) eluting with an CH_2Cl_2/CH_3OH solution to afford a red solid: 137 mg (Yield: 45%), m.p.>300°C. ^{1}H NMR (500 MHz, CD_3OD) δ 9.38 (s, 4H, ^{A}Tpy-*H*$^{3',5'}$), 9.37 (s, 4H, ^{B}Tpy-*H*$^{3',5'}$), 8.97-8.94 (m, 8H, ^{A,B}Tpy-*H*$^{3,3''}$), 8.80 (s, 4H, ^{C}Tpy-*H*$^{3',5'}$), 8.77-8.74 (m, 8H, ^{C}Tpy-*H*$^{6,6'',3,3''}$), 8.43-8.41 (d, J= 10Hz, 4H, ^{A}Ph-*H*^{j}), 8.39-8.37 (d, J= 10Hz, 4H, ^{B}Ph-*H*^{j}), 8.11-8.05 (m, 16H, ^{C}Ph-*H*^{j}, ^{A,B,C}Tpy-*H*$^{4,4''}$), 8.03-7.98 (m, 8H, ^{A,B}Ph-*H*^{k}), 7.85-7.84 (d, J= 5Hz, 4H, ^{C}Ph-*H*^{k}), 7.64-7.62 (m, 8H, ^{A,B}Tpy-*H*$^{6,6''}$), 7.58-7.56 (m, 6H, Ph-*H*^{a,b}, ^{C}Tpy-*H*$^{5,5''}$), 7.34-7.31 (m, 8H, ^{A,B}Tpy-*H*$^{5,5''}$), 7.04 (s, 2H, Ph-*H*^{d}), 6.99 (s, 2H, Ph-*H*^{c}), 4.08 (s, 6H, OCH_3), 4.06 (s, 6H, OCH_3), 4.03 (s, 6H, OCH_3). ^{13}C NMR (126 MHz, CD_3OD) δ 158.49, 157.98, 155.87, 155.59, 155.55, 151.96, 148.69, 138.04, 130.38, 130.36, 130.04, 127.56, 127.14, 127.05, 126.39, 124.59, 124.23, 121.73, 121.11, 118.31, 96.51, 72.26, 70.17, 70.14, 70.00, 69.98, 60.83, 55.18, 55.13. ESI-TOF-MS (*m/z*): +4 (*m/z*= 615.11) (Calcd. : *m/z*= 615.17), +3 (*m/z*= 832.13) (Calcd. : *m/z*= 832.22), +2 (*m/z*= 1265.67) (Calcd. : *m/z*= 1266.31).

Synthesis of LB:



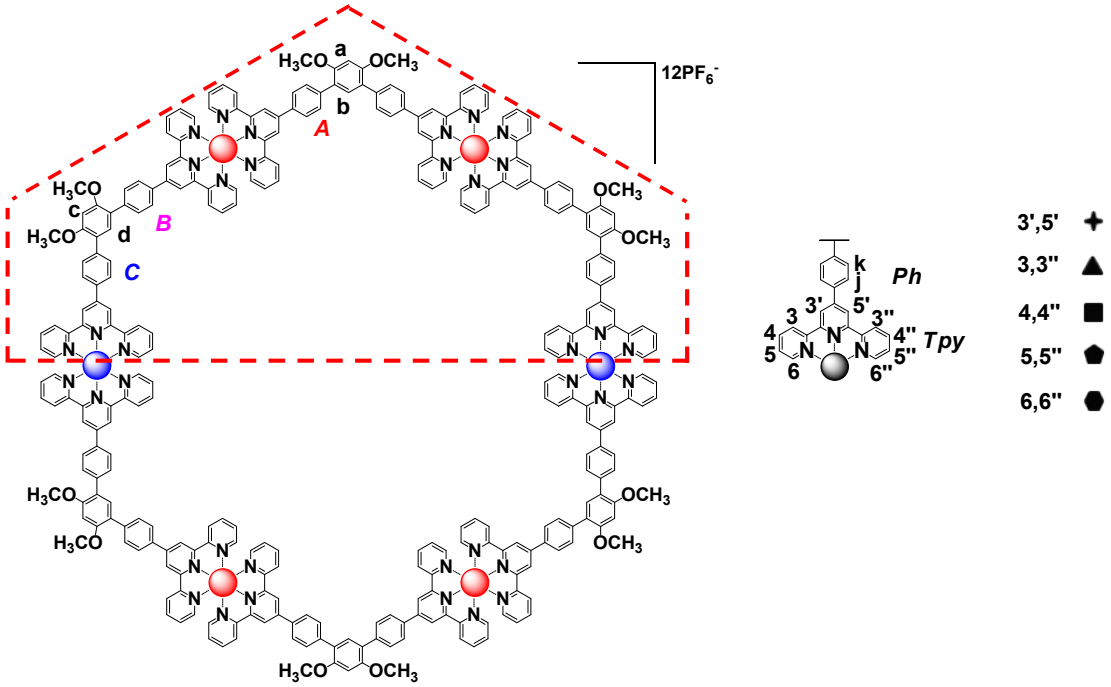
L8: A suspension of **5** (200 mg, 0.252 mmol) and **L2** (262.6 mg, 0.252 mmol) in $CHCl_3$:CH_3OH=1:1 (160 mL), N-ethylmorpholine (4 drops) was added, the mixture was heated for 16 h. The resulting red solution was allowed to cool down and evaporated under reducing pressure, then the residue was purified by flash column chromatography (Al_2O_3) (CH_2Cl_2/CH_3OH=100/2) to give a red solid (217.4 mg, 47%). m.p. > 300°C. ^{1}H NMR (500 MHz, CD_3OD) δ 9.24 (s, 2H, ^{C}Tpy-*H*$^{3',5'}$), 9.23 (s, 2H, ^{A}Tpy-*H*$^{3',5'}$), 8.87-8.83 (m, 4H, ^{A,C}Tpy-*H*$^{3,3''}$), 8.75 (s, 4H, ^{B}Tpy-*H*$^{3',5'}$), 8.72-8.71(d, J= 5Hz, 4H, ^{B}Tpy-*H*$^{6,6''}$), 8.69-8.67(d, J= 10Hz, 4H, ^{B}Tpy-*H*$^{3,3''}$), 8.36-8.34(m, 4H, ^{A,C}Ph-*H*^{j}), 8.09-8.08 (d, J= 10Hz, 4H, ^{B}Ph-*H*^{j}), 8.02-8.00 (m, 4H, ^{A,C}Tpy-*H*$^{4,4''}$), 7.99-7.97 (d, J= 10Hz, 4H, ^{B}Tpy-*H*$^{4,4''}$), 7.70-7.68 (d, J= 10Hz, 2H, ^{C}Ph-*H*^{k}), 7.52-7.46 (m, 14H, ^{A,B}Ph-*H*^{k}, ^{A,C}Tpy-*H*$^{6,6''}$, ^{B}Tpy-*H*$^{5,5''}$), 7.34-7.31 (m, 4H, ^{A,C}Tpy-*H*$^{5,5''}$), 2.77 (s, 3H, CH_3), 2.20(s, 6H, CH_3), 1.91(s, 6H, CH_3), 1.89(s, 3H, CH_3). ^{13}C NMR (126 MHz, CD_3OD) δ 158.26, 155.61, 155.57, 155.47, 151.87, 150.37, 148.51, 143.31, 139.55, 138.33, 137.96, 136.54, 135.03, 132.70, 130.78, 130.31, 130.22, 129.54, 128.12, 127.97, 127.81, 127.33, 125.63, 124.85, 124.53, 124.34, 123.83, 122.00, 121.51, 118.84, 34.60, 32.99, 31.71, 31.15, 30.71, 29.64, 29.39, 29.11, 29.01, 26.84, 25.54, 22.40, 22.06, 20.28, 18.89. ESI-TOF-MS (*m/z*): +2 (*m/z*= 864.06) (Calcd. : *m/z*= 864.18), +1 (*m/z*= 1763.09) (Calcd. : *m/z*= 1763.33).

L9: A suspension of **6** (123 mg, 0.168 mmol) and **L8** (144 mg, 0.080 mmol) in $CHCl_3$:CH_3OH=1:2 (150 mL), N-ethylmorpholine (4 drops) was added, the mixture was heated for 48 h. The resulting red solution was allowed to cool down and evaporated under reducing pressure, then the residue was purified by flash column

chromatography (Al_2O_3) (CH_2Cl_2/CH_3OH=100/2) to give a red solid (224.3 mg, 84%). m.p. > 300°C. ^{1}H NMR (400 MHz, CD_3OD) δ 9.44 (s, 6H, ^{A}Tpy-*H*$^{3',5'}$), 9.39 (s, 2H, ^{C}Tpy-*H*$^{3',5'}$), 9.36 (s, 4H, ^{B}Tpy-*H*$^{3',5'}$), 9.00-8.94 (m, 12H, ^{A,B,C}Tpy-*H*$^{3,3''}$), 8.56-8.55 (d, J= 4Hz, 6H, ^{A}Ph-*H*^{i}), 8.48-8.46 (d, J= 8Hz, 2H, ^{C}Ph-*H*^{i}), 8.37-8.35 (d, J= 8Hz, 4H, ^{B}Ph-*H*^{i}), 8.09-8.05 (m, 12H, ^{A,B,C}Tpy-*H*$^{4,4''}$), 7.89-7.87 (d, J= 8Hz, 4H, ^{B}Ph-*H*^{k}), 7.77-7.75 (d, J= 8Hz, 6H, ^{A}Ph-*H*^{k}), 7.64-7.63 (m, 14H, ^{A,B,C}Tpy-*H*$^{6,6''}$, Ph-*H*^{b}), 7.56-7.54 (d, J= 8Hz, 2H, ^{C}Ph-*H*^{k}), 7.35-7.32 (m, 12H, ^{A,B,C}Tpy-*H*$^{5,5''}$), 6.90 (s, 2H, Ph-*H*^{a}), 4.03 (s, 6H, OCH_3), 3.98 (s, 6H, OCH_3), 2.81 (s, 3H, CH_3), 2.26(s, 6H, CH_3), 2.06 (s, 9H, CH_3); ^{13}C NMR (101 MHz, CD_3CN) δ 157.80, 157.56, 157.26, 157.17, 157.09, 156.17, 155.96, 155.55, 154.36, 154.31, 154.18, 152.09, 151.12, 150.76, 150.66, 150.62, 147.32, 136.82, 136.70, 134.15, 132.24, 129.31, 129.28, 128.86, 126.82, 126.75, 126.27, 126.23, 125.79, 125.77, 123.38, 123.34, 123.27, 120.15, 120.10, 120.09, 119.81, 115.59, 95.94, 95.91, 95.90, 54.25, 53.85, 52.01, 20.40, 20.33, 17.20. ESI-TOF-MS (*m/z*): +6 (*m/z*= 496.69) (Calcd. : *m/z*= 496.72), +5 (*m/z*= 603.02) (Calcd. : *m/z*= 603.06).

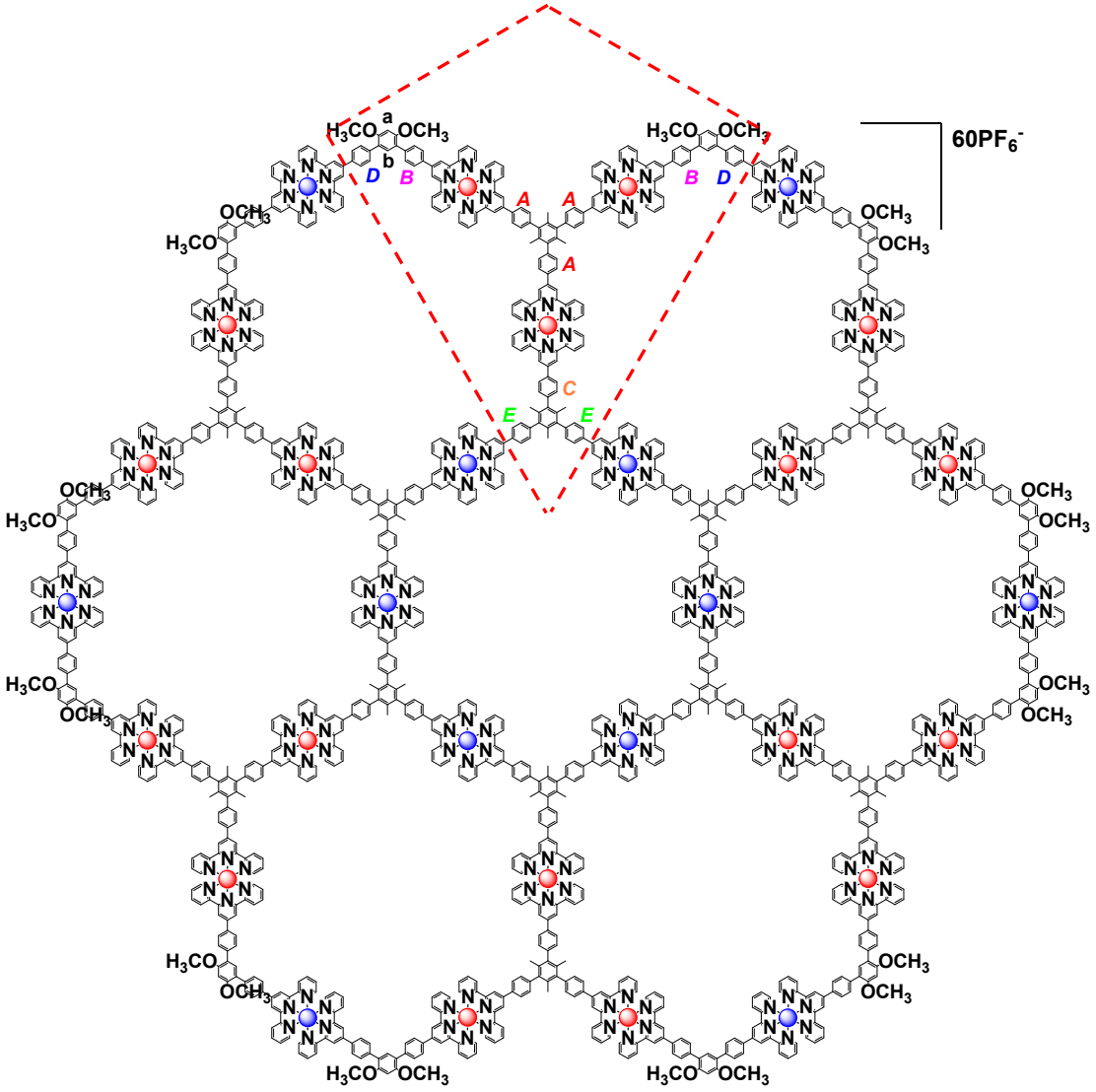
LB: K_2CO_3 (26 mg, 0.19 mmol) was added to a solution of **L9** (50 mg, 15.7 μmol) and (4-([2,2':6',2''-terpyridine]4'-yl)-phenyl boronic acid (134 mg, 397 μmol) in 60 ml CH_3CN, following the addition of catalyst tetrakistriphenylphosphine palladium (28 mg), the mixture was then refluxed at 85 ºC for 96 h under N_2. After cooling to the room temperature, the solvent was evaporated under reducing pressure and the residue was purified by flash column chromatography (Al_2O_3) (CH_2Cl_2/CH_3OH=100/2.5) to give a red solid (36.4 mg, 53%). m.p. > 300°C. ^{1}H NMR (400 MHz, CD_3OD) δ 9.42 (s, 6H, ^{A}Tpy-*H*$^{3',5'}$), 9.39 (s, 2H, ^{C}Tpy-*H*$^{3',5'}$), 9.37 (s, 4H, ^{B}Tpy-*H*$^{3',5'}$), 8.98-8.94 (m, 12H, ^{A,B,C}Tpy-*H*$^{3,3''}$), 8.82 (s, 4H, ^{E}Tpy-*H*$^{3',5'}$), 8.80 (s, 4H, ^{D}Tpy-*H*$^{3',5'}$), 8.76-8.73 (m, 16H, ^{D,E}Tpy-*H*$^{6,6''}$, ^{D,E}Tpy-*H*$^{3,3''}$), 8.55-8.53 (d, J=8Hz, 6H, ^{A}Ph-*H*^{i}), 8.48-8.46 (d, J= 8Hz, 2H, ^{C}Ph-*H*^{i}), 8.39-8.37 (d, J= 8Hz, 4H, ^{B}Ph-*H*^{i}), 8.16-8.14 (d, J= 8Hz, 4H, ^{E}Ph-*H*^{i}), 8.10-8.05 (m, 24H, ^{D}Ph-*H*^{i}, ^{A,B,C,D,E}Tpy-*H*$^{4,4''}$), 8.00-7.98 (d, J= 8Hz, 4H, ^{B}Ph-*H*^{k}), 7.85-7.83 (m, 6H, ^{D}Ph-*H*^{k}, Ph-*H*^{b}), 7.77-7.75 (d, J= 8Hz, 6H, ^{A}Ph-*H*^{k}), 7.71-7.69 (d, J= 8Hz, 2H, ^{C}Ph-*H*^{k}), 7.65-7.62 (m, 12H, ^{A,B,C}Tpy-*H*$^{6,6''}$), 7.56-7.53 (m, 12H, ^{D,E}Tpy-*H*$^{5,5''}$, ^{E}Ph-*H*^{k}), 7.35-7.32 (m, 12H, ^{A,B,C}Tpy-*H*$^{5,5''}$), 6.99 (s, 2H, Ph-*H*^{a}), 4.05 (s, 6H, OCH_3), 4.03 (s, 6H, OCH_3), 2.06 (s, 9H, CH_3), 1.96 (s, 6H, CH_3), 1.93(s, 3H, CH_3). ^{13}C NMR (126 MHz, CD_3OD) δ 158.24, 157.83, 157.58, 156.06, 156.03, 155.96, 155.91, 155.54, 155.43, 151.83, 150.24, 149.08, 148.75, 144.56, 141.01, 139.59, 139.40, 138.43, 137.60, 136.21, 134.23, 133.02, 132.77, 132.26, 130.81, 130.57, 130.21, 130.10, 129.60, 128.20, 127.89, 127.35, 127.21, 126.64, 125.03, 124.89, 124.21, 122.67, 121.94, 121.54, 121.23, 118.73, 118.57, 96.56, 55.54, 31.71, 29.52, 29.39, 29.30, 29.02, 26.88, 25.57, 22.42, 19.09, 19.01. ESI-TOF-MS (*m/z*): +6 (*m/z*= 649.01) (Calcd. : *m/z*= 649.02), +5 (*m/z*= 785.80) (Calcd. : *m/z*= 785.82), +4 (*m/z*= 991.24) (Calcd. : *m/z*= 991.27). LB as PF_6^- salt: ESI-TOF-MS (*m/z*): +6 (*m/z*= 648.96) (Calcd. : *m/z*= 649.02), +5 (*m/z*= 807.74) (Calcd. : *m/z*= 807.82), +4 (*m/z*= 1045.92) (Calcd. : *m/z*= 1046.02).

Self-Assembly:



Hexagon **A**

Hexagon **A**: $Zn(NO_3)_2$•$6H_2O$(0.298 mg, 1 μmol) was added to a solution of **LA** (2.6 mg, 1 μmol) in CH_3Cl/CH_3OH=1/1(6 ml). The mixture was stirred at 25ºC for 2 h, then excess KPF_6 was added, generating a red precipitate which was washed with water and then MeOH to give the desired product (2.81 mg, 97%).^{1}H NMR (500 MHz, CD_3CN) δ 9.12 (m, 16H, ^{A,B}Tpy-$H^{3',5'}$), 9.09(s, 8H, ^{C}Tpy-$H^{3',5'}$), 8.80-8.79(d, J= 5Hz, 8H, ^{C}Tpy-$H^{3,3"}$), 8.73-8.72(m, 16H, ^{A,B}Tpy-$H^{3,3"}$), 8.36-8.32(m, 24H, ^{A,B,C}Ph-H^{j}), 8.06-7.99(m, 48H, ^{A,B,C}Ph-H^{k}, ^{A,B,C}Tpy-$H^{4,4"}$), 7.91-7.90(d, J= 5Hz, 8H, ^{C}Tpy-$H^{6,6"}$), 7.71-7.68(m, 6H, Ph-$H^{d,b}$), 7.51-7.46(m, 24H, ^{A,B}Tpy-$H^{6,6"}$, ^{C}Tpy-$H^{5,5"}$), 7.25-7.23(m, 16H, ^{A,B}Tpy-$H^{5,5"}$), 7.03-7.02(m, 6H, Ph-$H^{c,a}$), 4.08(m, 36H, OCH_3), the signals of CH_3 were incorporated into the signals of CD_3CN. ESI-MS (*m/z*): 12+ (*m/z*= 421.03) (Calcd. : *m/z*= 421.04), 11+ (*m/z*= 472.48) (Calcd. : *m/z*= 472.47), 10+ (*m/z*= 534.22) (Calcd. : *m/z*= 534.21). 9+ (*m/z*= 609.59) (Calcd. : *m/z*= 609.70), 8+ (*m/z*= 704.10) (Calcd. : *m/z*= 704.01), 7+ (*m/z*= 825.30) (Calcd. : *m/z*= 825.29), 6+ (*m/z*= 987.02) (Calcd. : *m/z*= 987.00).



Honeycomb fractal **H**

Honeycomb fractal **H**: The synthesis process is the same as Hexagon **A** which gave a red solid (3.91 mg, 98%). ^{1}H NMR (500 MHz, CD_3CN) δ 9.16 (m, 48H, ^{D,E}Tpy-*H*$^{3',5'}$), 9.13 (m, 36H, ^{A}Tpy-*H*$^{3',5'}$), 9.09 (m, 36H, ^{BC}Tpy-*H*$^{3',5'}$), 8.81-8.79 (m, 36H, ^{B,C}Tpy-*H*$^{3,3''}$), 8.75-8.74 (m, 84H, ^{A,D,E} Tpy-*H*$^{3,3''}$), 8.47-8.45 (m, 48H, ^{D,E}Ph-*H*^{i}), 8.34-8.31 (m, 72H, ^{A,B,C}Ph-*H*^{i}), 8.24-8.22 (m, 36H, ^{B,C}Tpy-*H*$^{4,4''}$), 8.06-8.05 (m, 72H, ^{A,B,C}Ph-*H*^{K}), 8.02-8.01 (m, 84H, ^{A,D,E} Tpy-*H*$^{4,4''}$), 7.91-7.90 (m, 36H, ^{B,C}Tpy-*H*$^{6,6''}$), 7.77-7.75 (m, 48H, ^{D,E}Ph-*H*^{K}), 7.70 (s, 12H, Ph-*H*^{b}), 7.52-7.51 (m, 84H, ^{A,D,E} Tpy-*H*$^{6,6''}$), 7.47-7.45 (m, 36H, ^{B,C}Tpy-*H*$^{5,5''}$), 7.25-7.24 (m, 84H, ^{A,D,E} Tpy-*H*$^{5,5''}$), 7.02 (s, 12H, Ph-*H*^{a}), 4.09-4.05 (m, 72H, OCH_3), the signals of CH_3 were incorporated into the signals of CD_3CN. ESI-MS (*m/z*): 30+ (*m/z*= 949.71) (Calcd. $[M\text{-}30PF_6^-]^{30+}$: *m/z*= 949.80), 29+ (*m/z*= 990.41) (Calcd. $[M+2CH_3CN\text{-}29PF_6^-]^{29+}$: *m/z*= 990.40), 28+ (*m/z*= 1033.76) (Calcd. $[M+4CH_3CN\text{-}28PF_6^-]^{28+}$: *m/z*= 1033.85), 27+ (*m/z*= 1074.57) (Calcd. $[M+2CH_3CN\text{-}27PF_6^-]^{27+}$: *m/z*= 1074.48), 26+ (*m/z*= 1121.32) (Calcd. $[M+2CH_3CN\text{-}26PF_6^-]^{26+}$: *m/z*= 1121.38), 25+ (*m/z*= 1172.07) (Calcd. $[M+2CH_3CN\text{-}25PF_6^-]^{25+}$: *m/z*= 1172.03), 24+ (*m/z*= 1223.53) (Calcd. $[M\text{-}24PF_6^-]^{24+}$: *m/z*= 1223.49), 23+ (*m/z*= 1283.04) (Calcd. $[M\text{-}23PF_6^-]^{23+}$: *m/z*= 1282.99), 22+ (*m/z*= 1347.95)

(Calcd. [M-22PF_6^-]$^{22+}$: *m/z*= 1347.90), 21+ (*m/z*= 1419.03) (Calcd. [M-21PF_6^-]$^{21+}$: *m/z*= 1418.98), 20+ (*m/z*= 1497.24) (Calcd. [M-20PF_6^-]$^{20+}$: *m/z*= 1497.18).

^{1}H NMR spectra

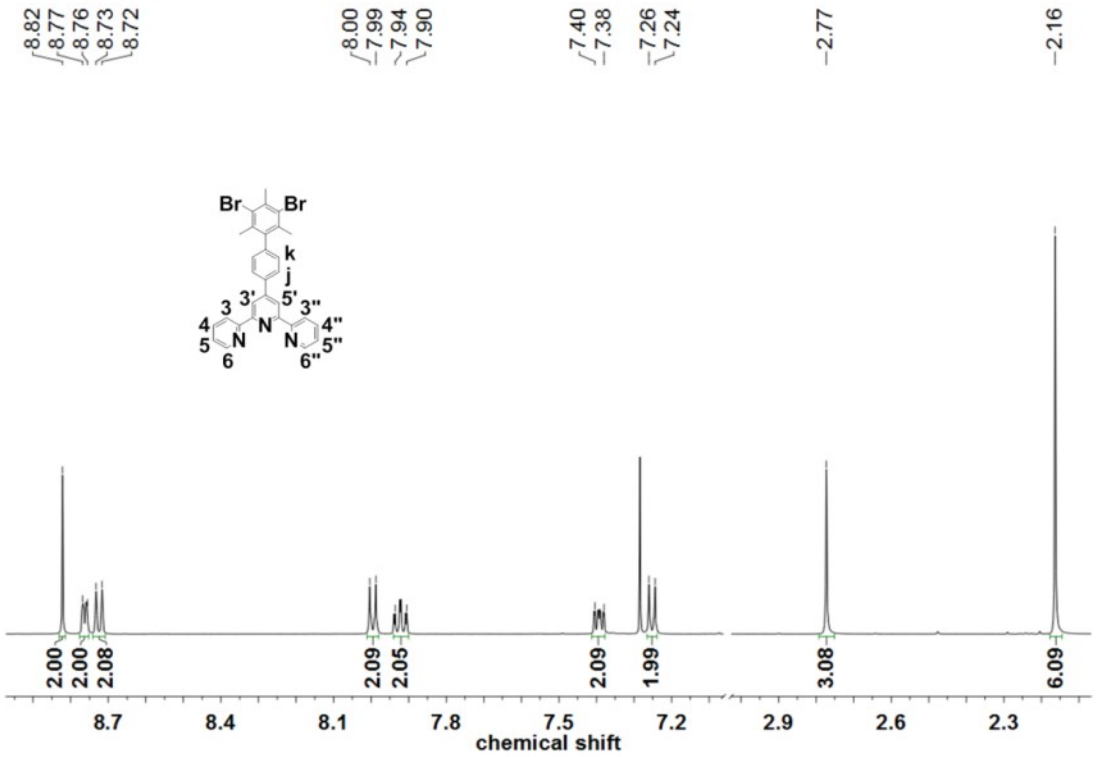


Figure S1. ^{1}H NMR spectrum of **L1**.

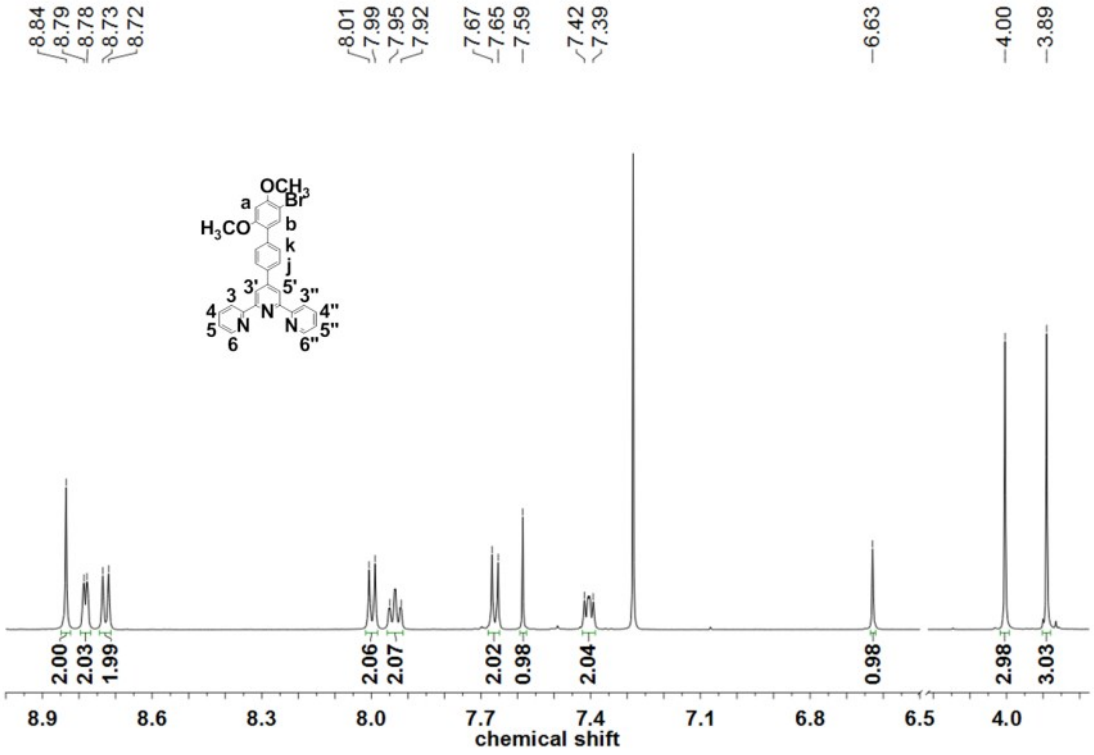


Figure S2. [1]H NMR spectrum of **L3**.

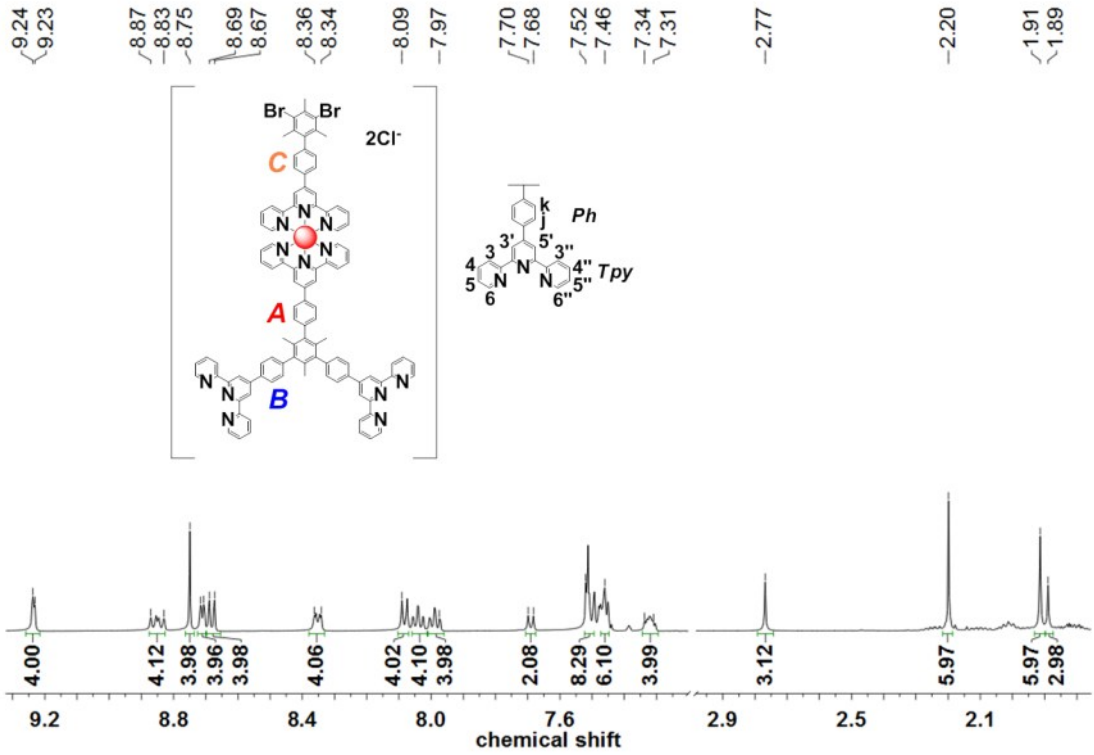


Figure S3. [1]H NMR spectrum of **L8**.

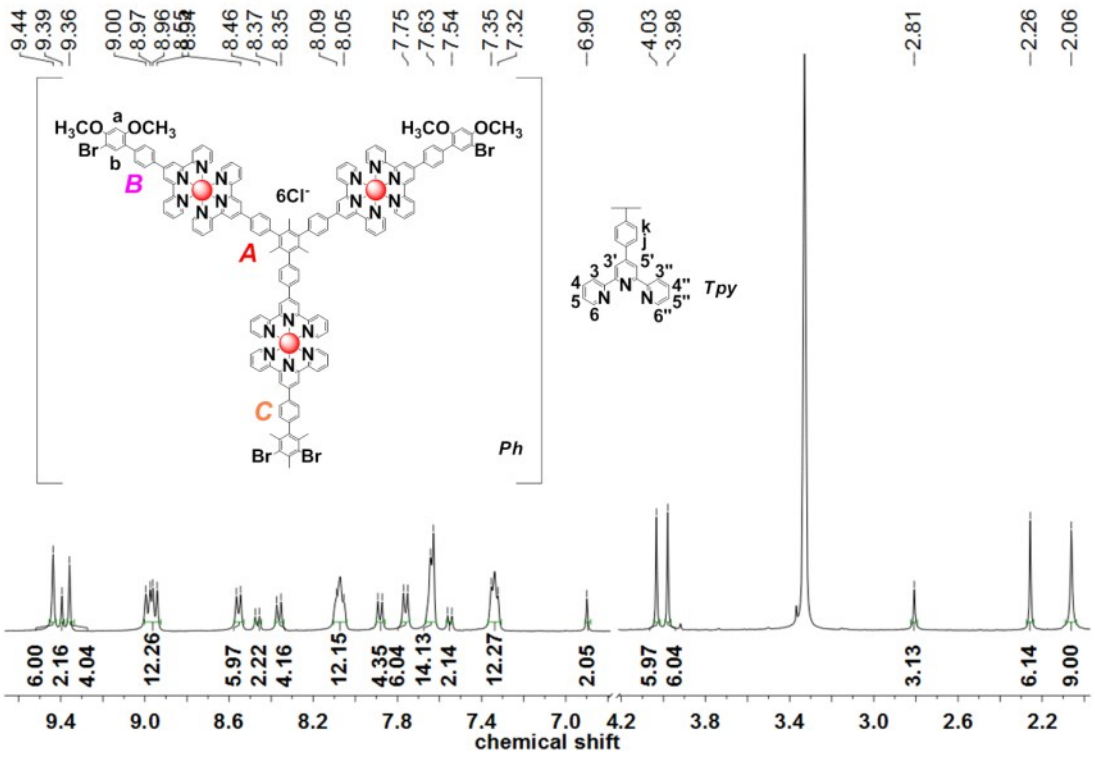


Figure S4. ^{1}H NMR spectrum of **L9**.

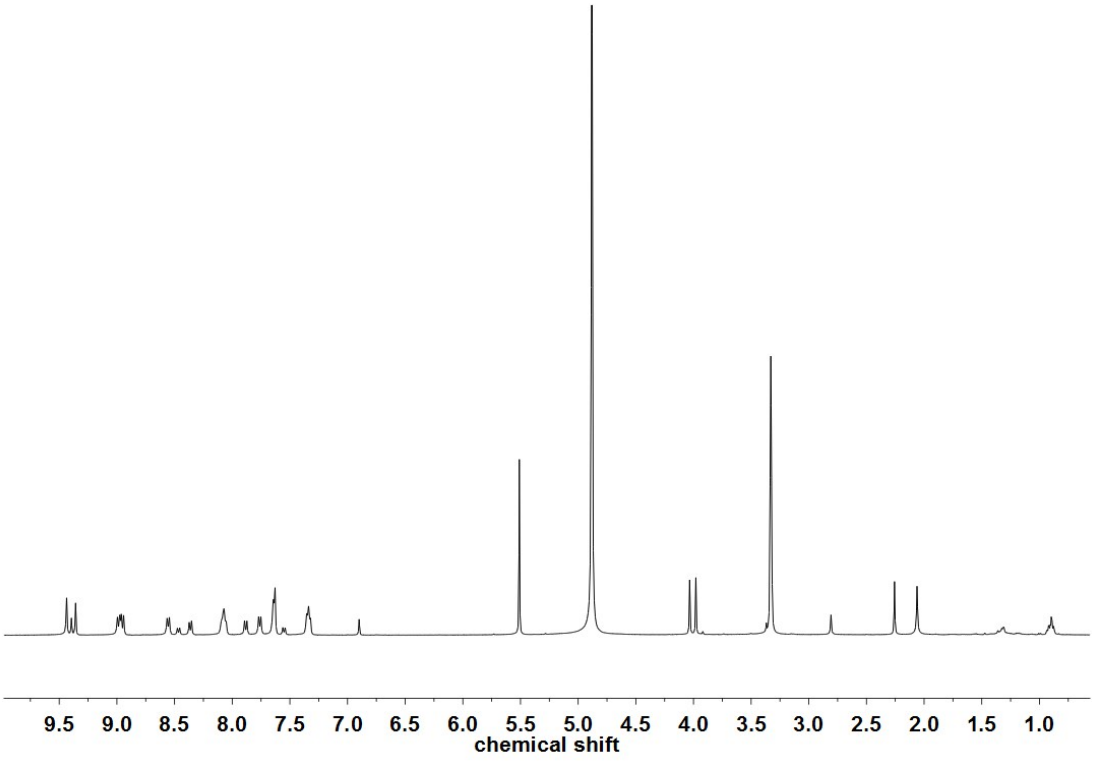


Figure S5. Full ^{1}H NMR spectrum of **L9**.

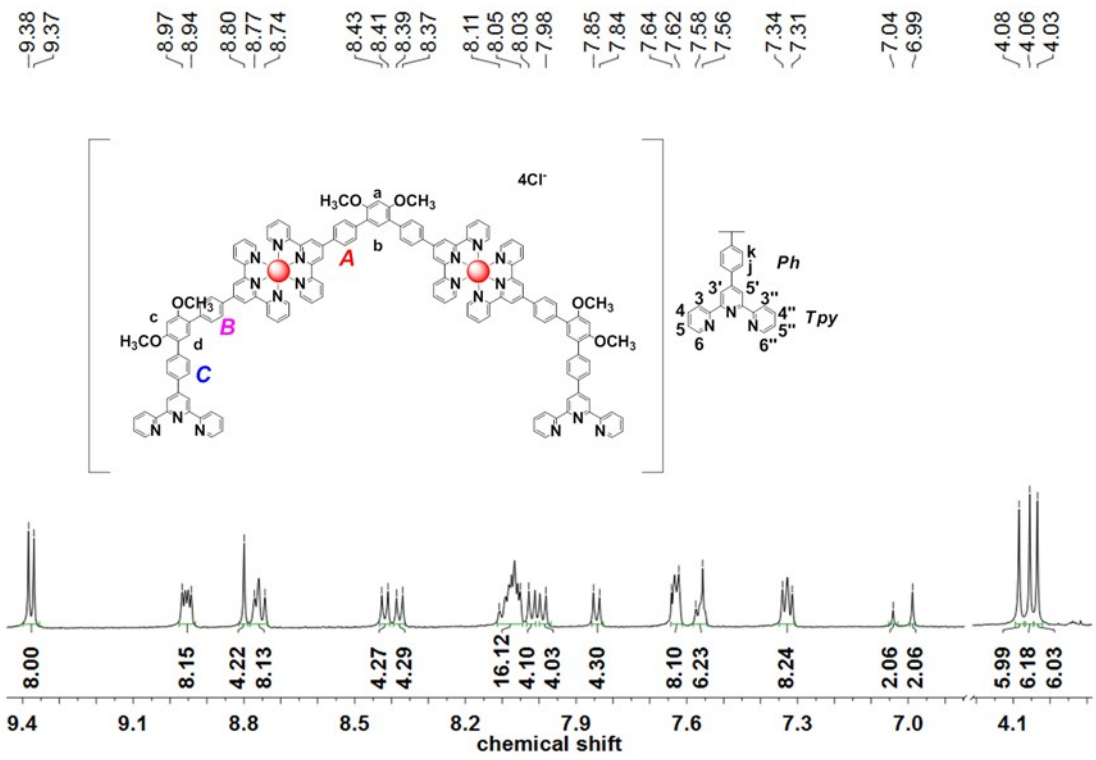


Figure S6. ^{1}H NMR spectrum of **LA**.

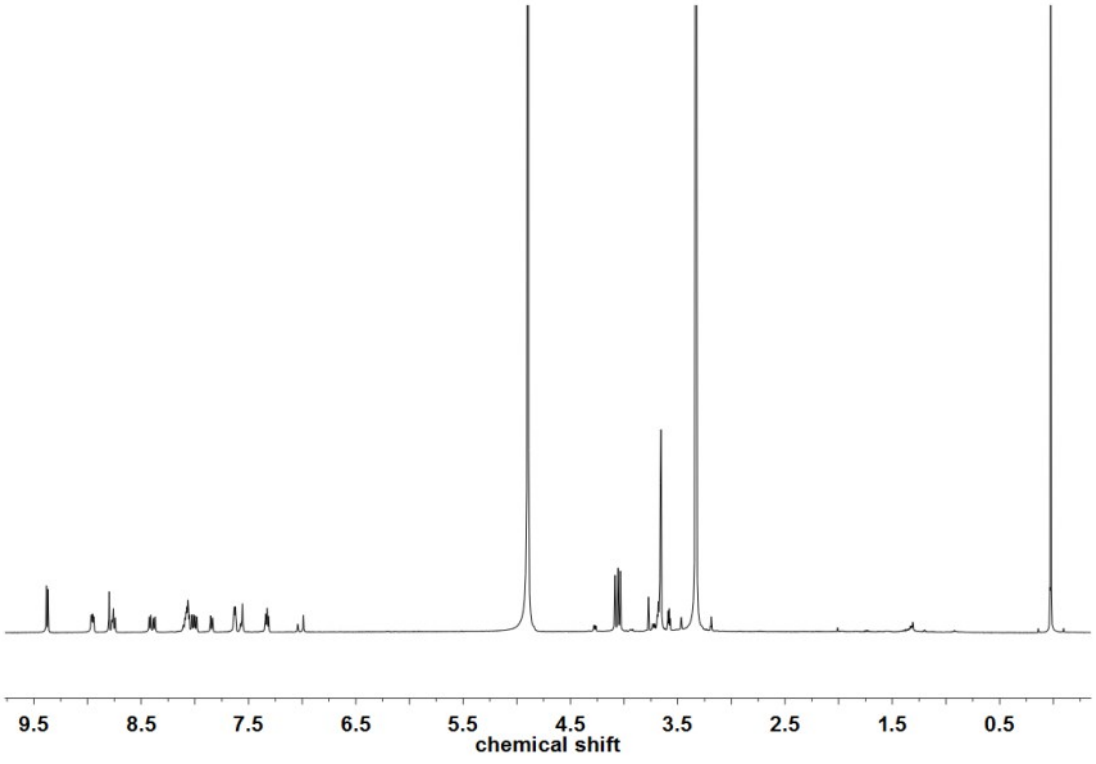


Figure S7. Full ^{1}H NMR spectrum of **LA**.

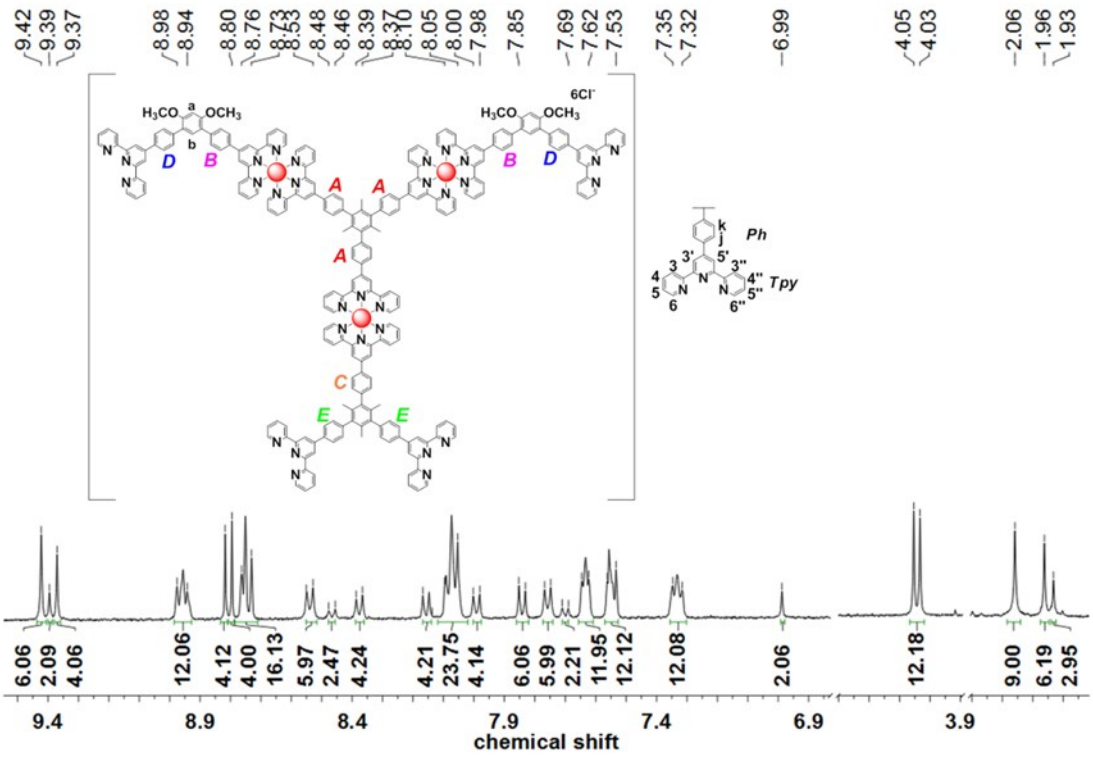


Figure S8. ^{1}H NMR spectrum of **LB**.

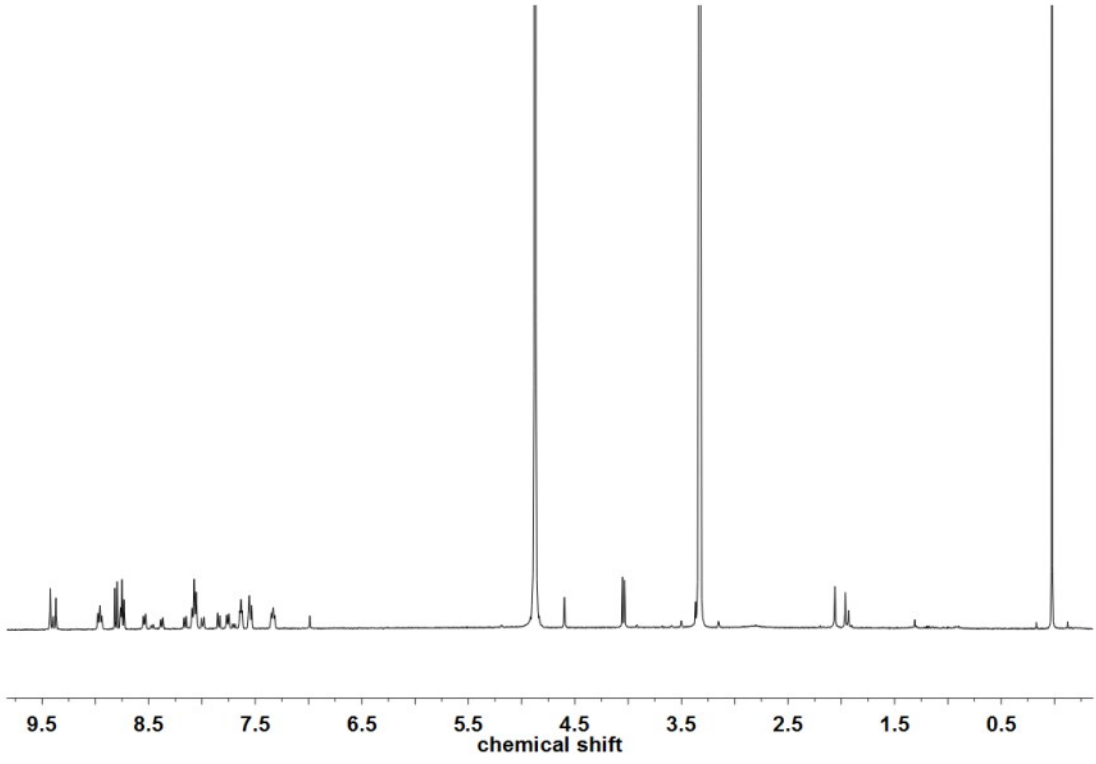


Figure S9. Full ^{1}H NMR spectrum of **LB**.

^{13}C NMR spectra

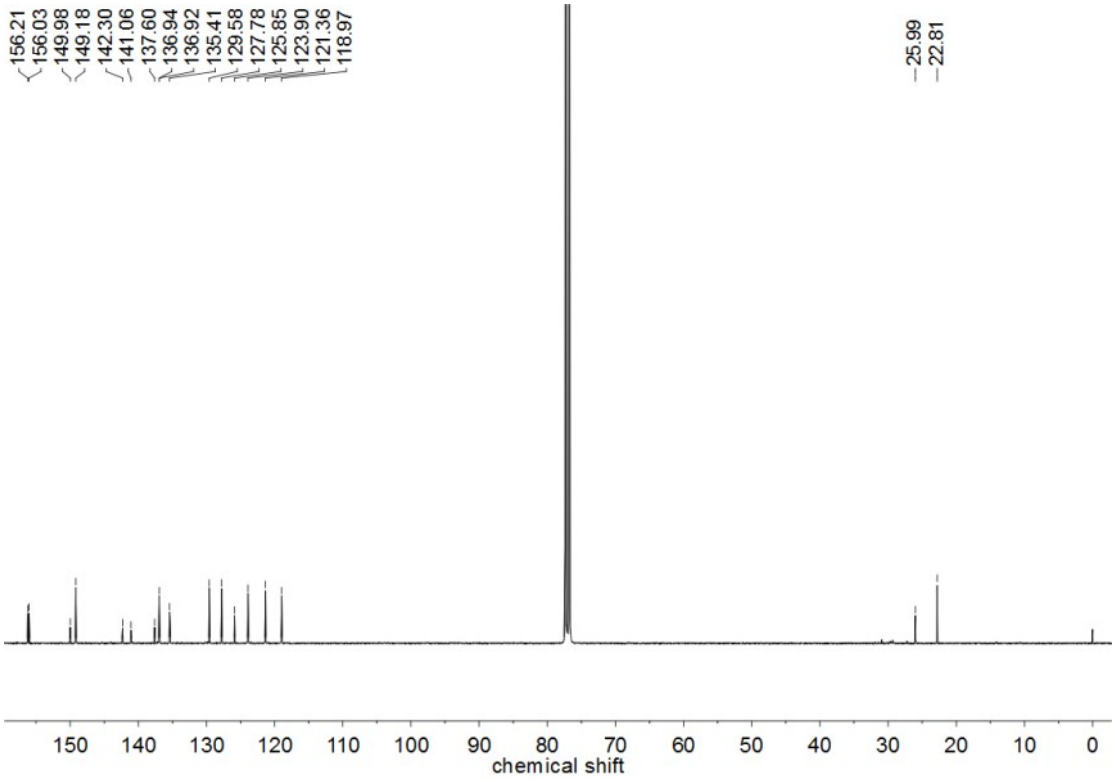


Figure S10. ^{13}C NMR spectrum of **L1**.

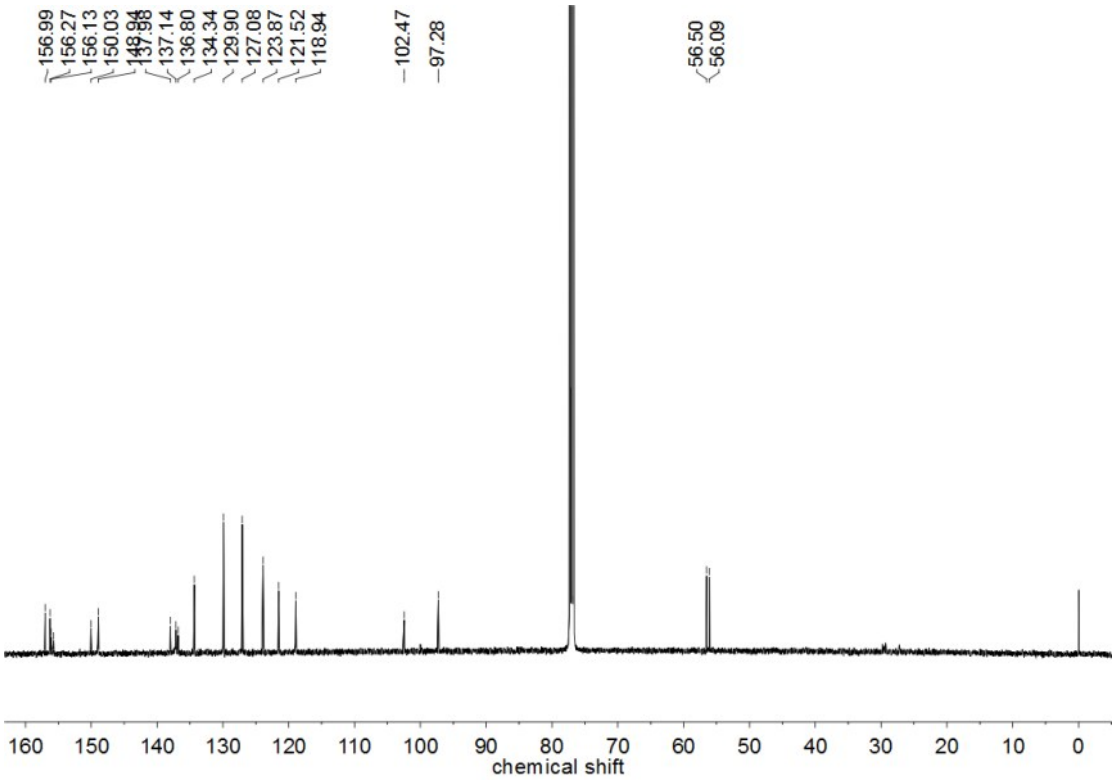


Figure S11. ^{13}C NMR spectrum of **L3**.

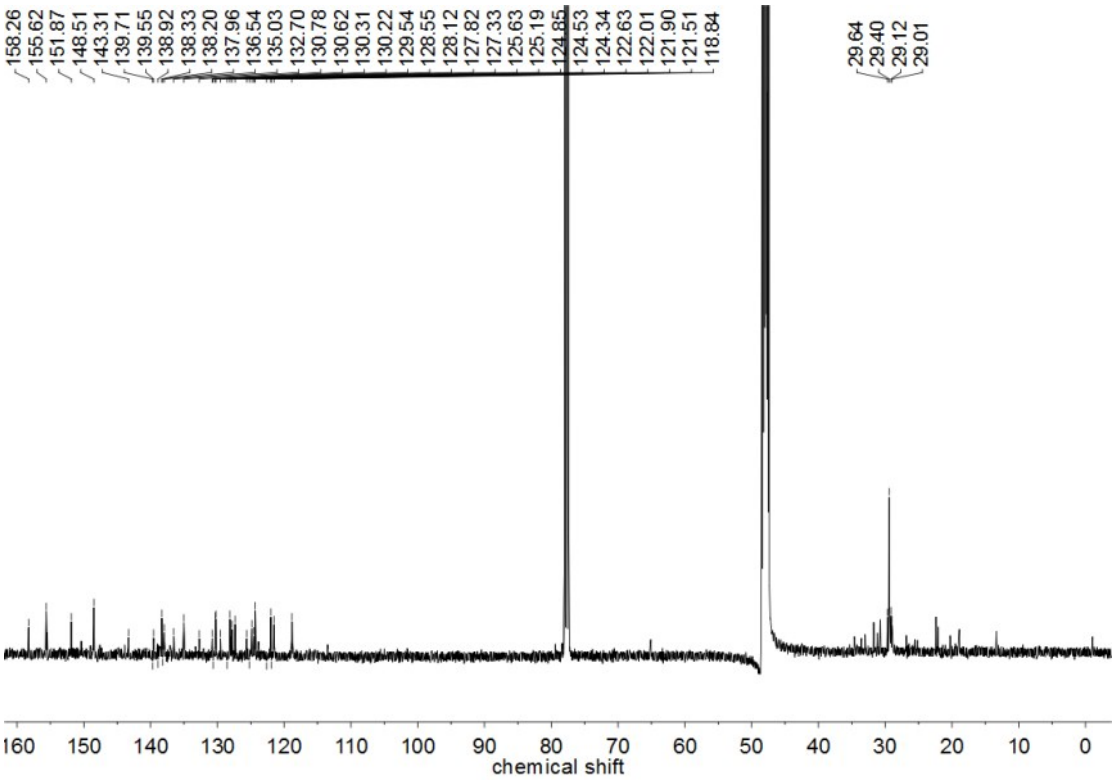


Figure S12. ^{13}C NMR spectrum of **L8**.

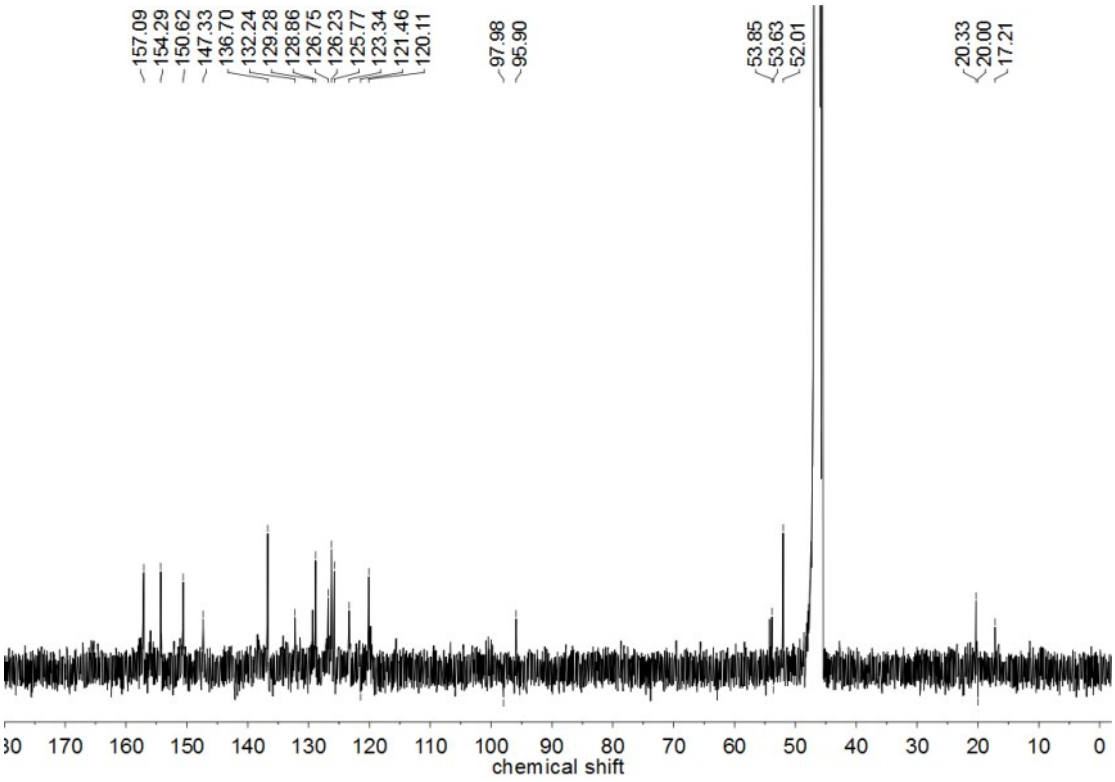


Figure S13. ^{13}C NMR spectrum of **L9**.

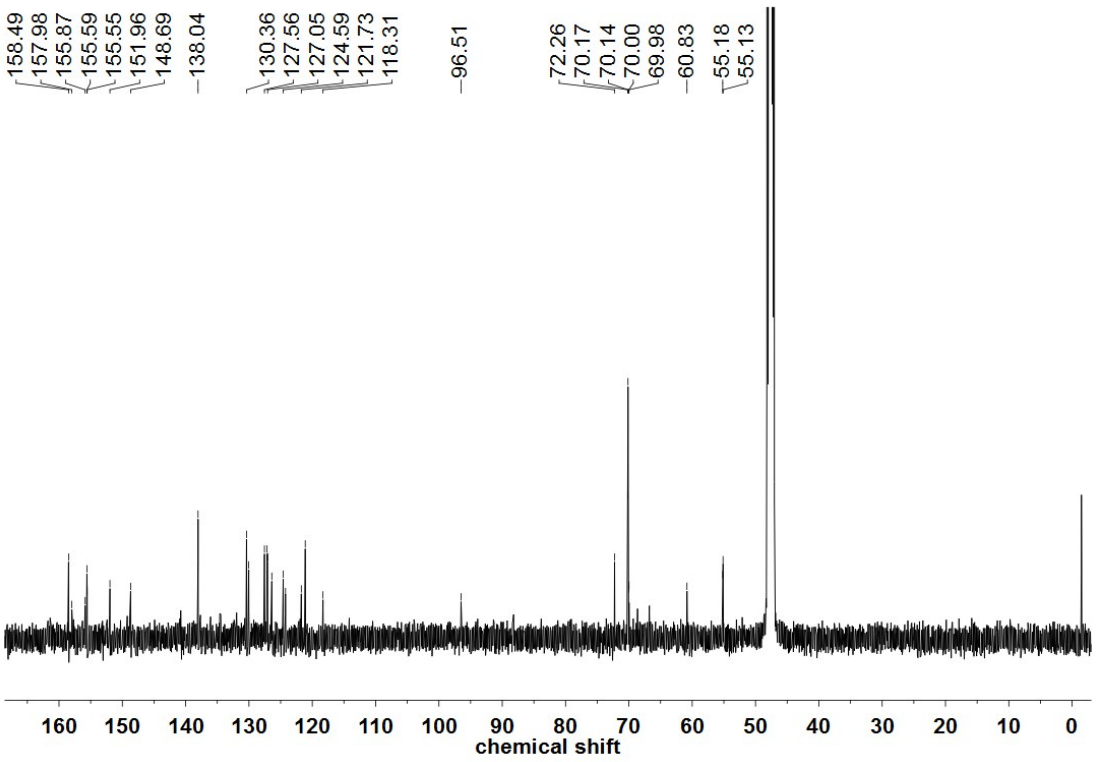


Figure S14. ^{13}C NMR spectrum of **LA**.

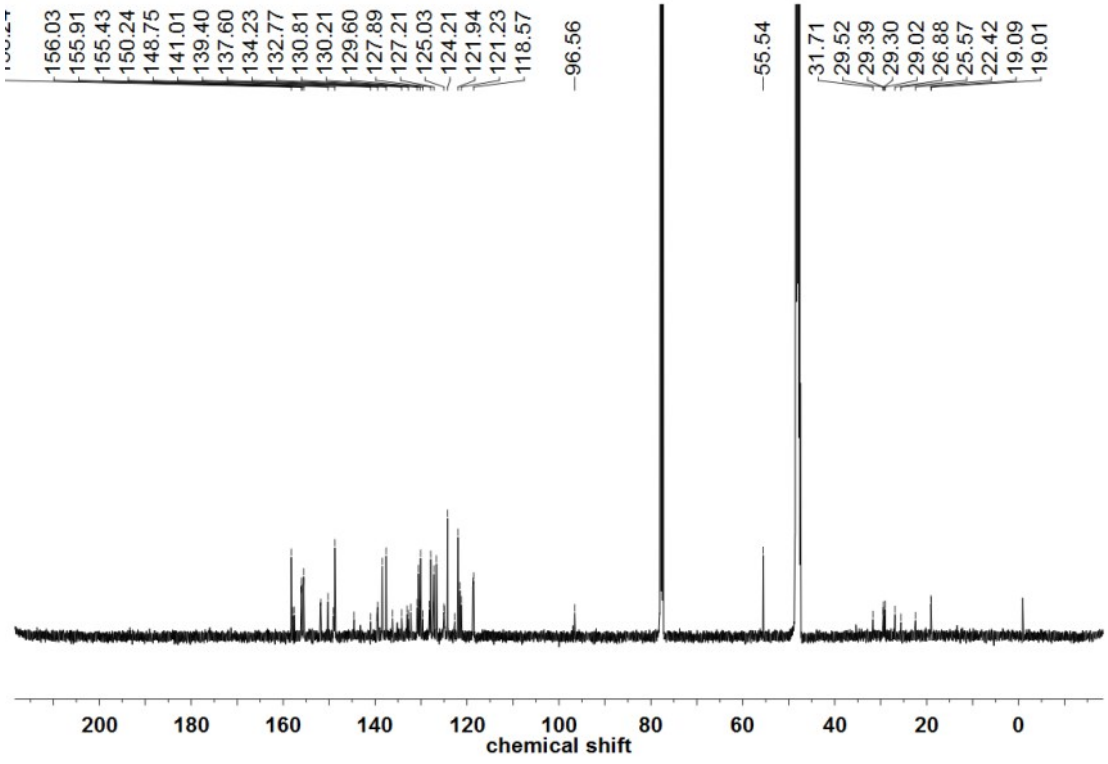


Figure S15. ^{13}C NMR spectrum of **LB**.

2D COSY NMR spectra

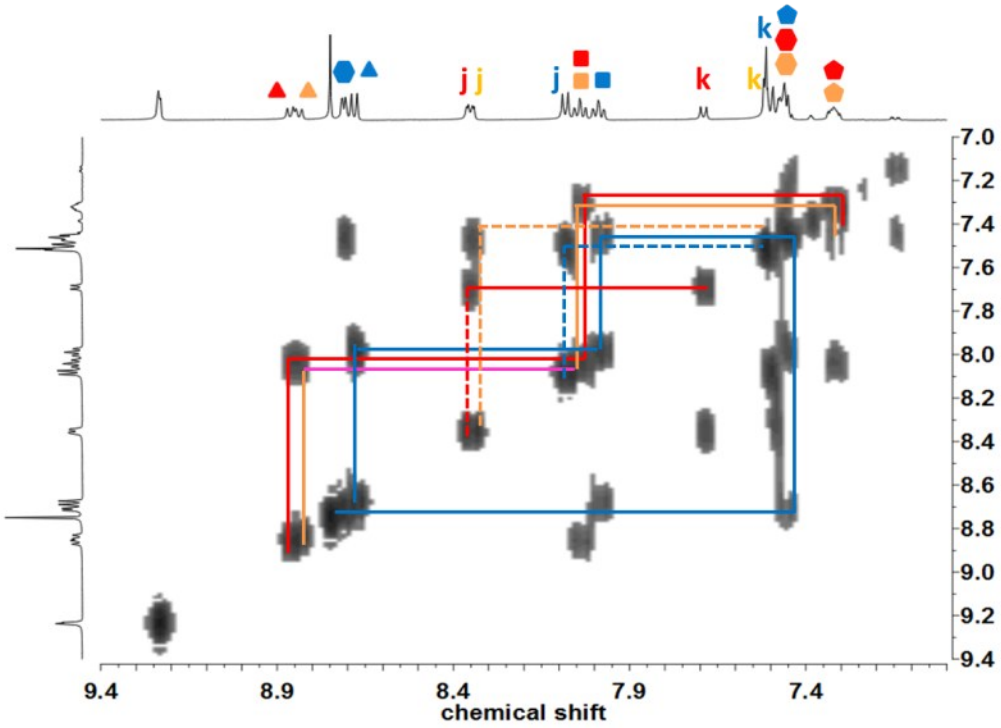


Figure S16. COSY NMR spectrum of **L8**. Cross peaks between Ph-kand Ph-j are denoted as dotted line; all the other cross peaks are illustrated as solid lines.

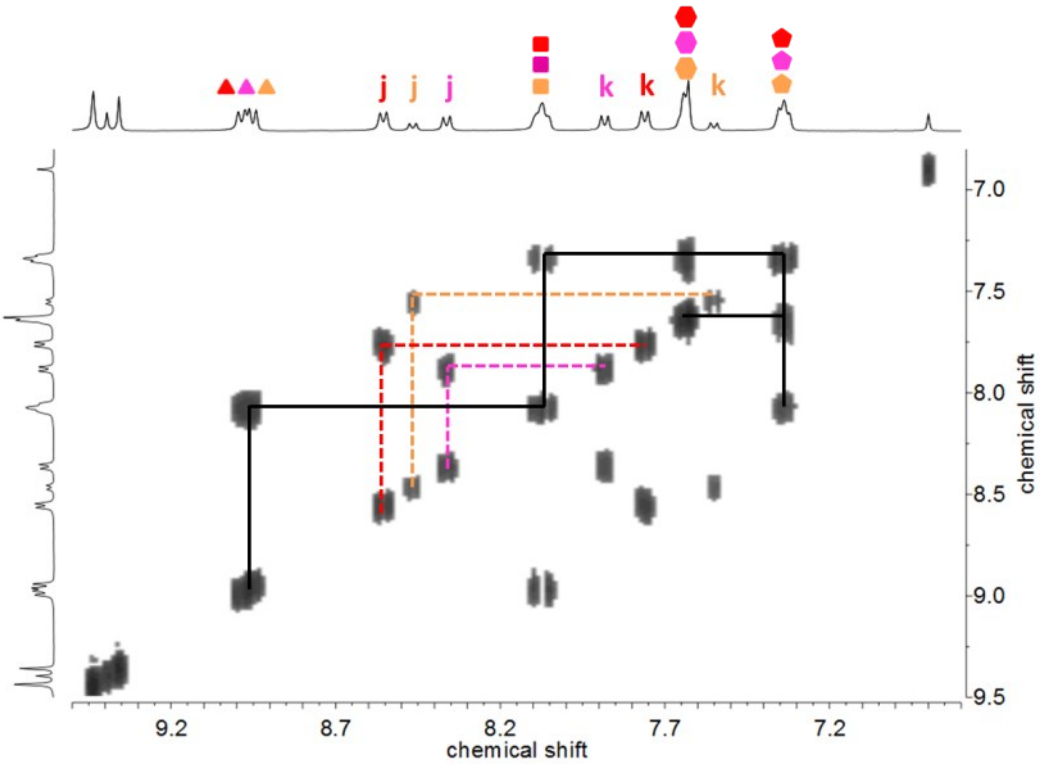


Figure S17. COSY NMR spectrum of **L9**. Because signals of Tpy-A, Tpy-B, Tpy-C merged into one broad peak,

cross peaks of these three kinds tpys were colored with black. Cross peaks between Ph-kand Ph-j are denoted as dotted line; all the other cross peaks are illustrated as solid lines.

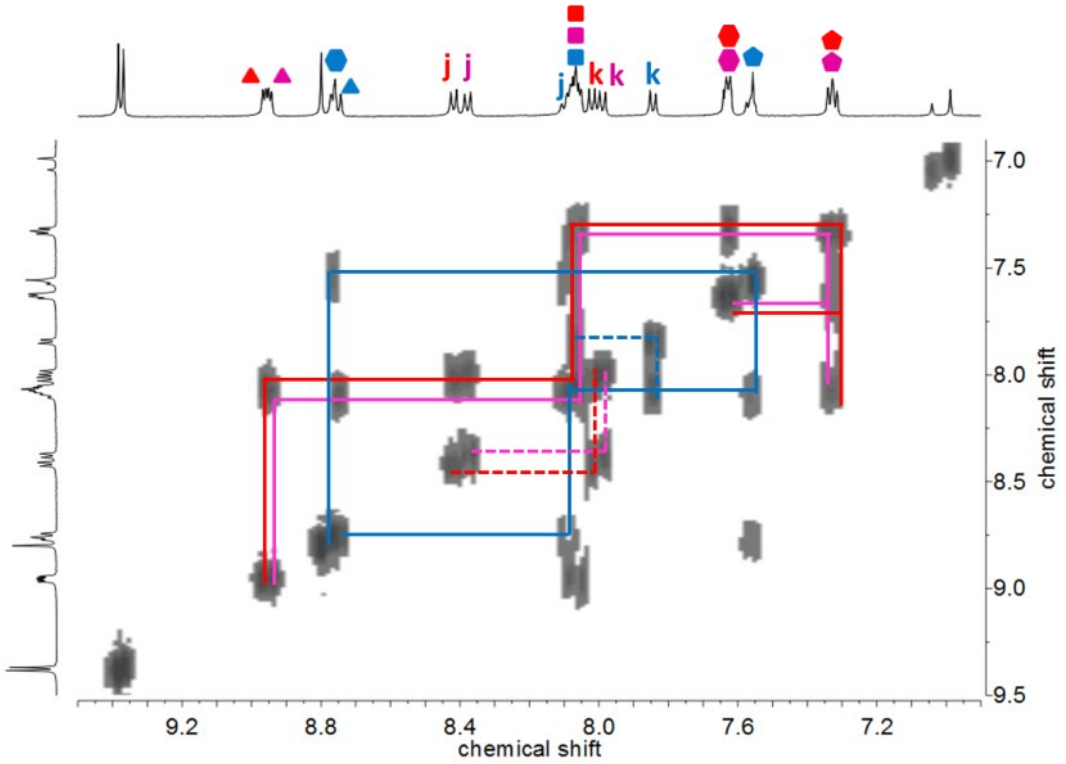


Figure S18. COSY NMR spectrum of **LA**. Cross peaks between Ph-kand Ph-j are denoted as dotted line; all the other cross peaks are illustrated as solid lines.

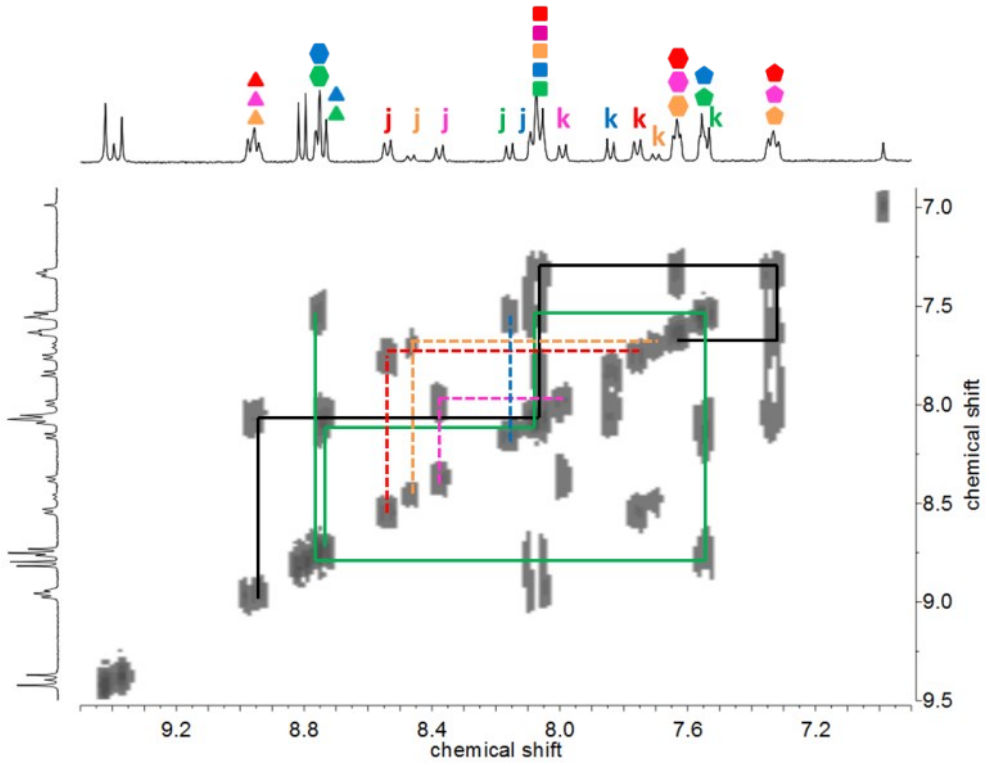


Figure S19. COSY NMR spectrum of **LB**. Because signals of Tpy-D, Tpy-E merged into one broad peak, cross peaks of these two kinds tpys were colored with green. Cross peaks between Ph-kand Ph-j are denoted as dotted

line; all the other cross peaks are illustrated as solid lines.

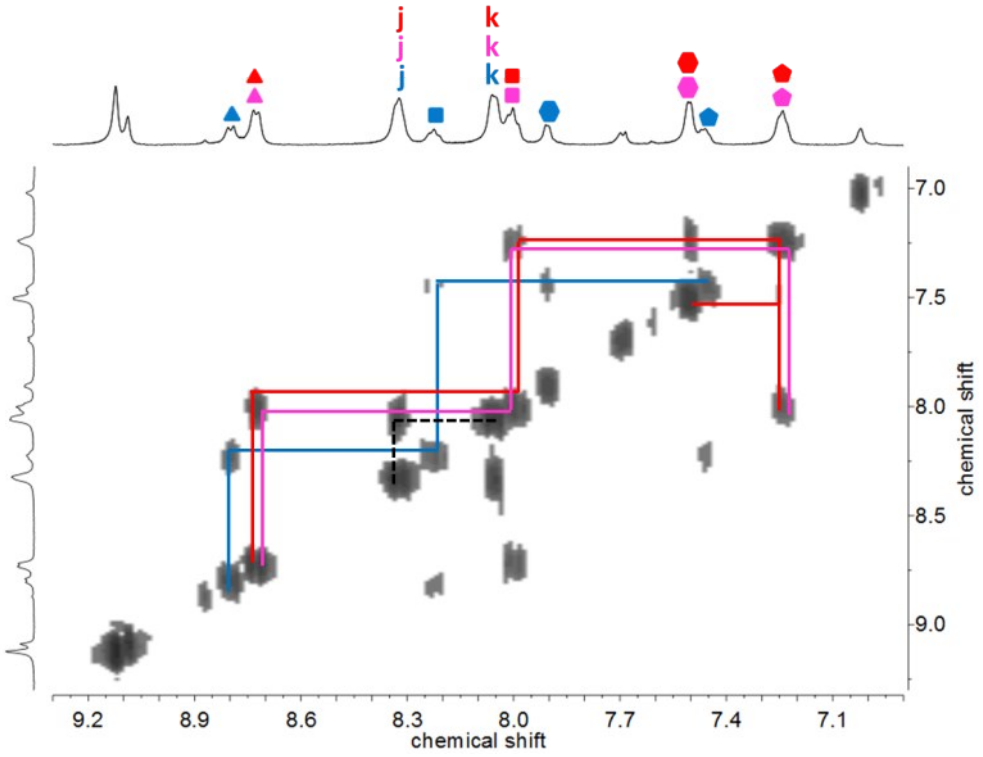


Figure S20. COSY NMR spectrum of Hexagon **A**. Because signals of Ph-k and Ph-j for Tpy-A, Tpy-B, Tpy-B merged into one broad peak, cross peaks of these three kinds protons were colored with black. Cross peaks between Ph-k and Ph-j are denoted as dotted line; all the other cross peaks are illustrated as solid lines.

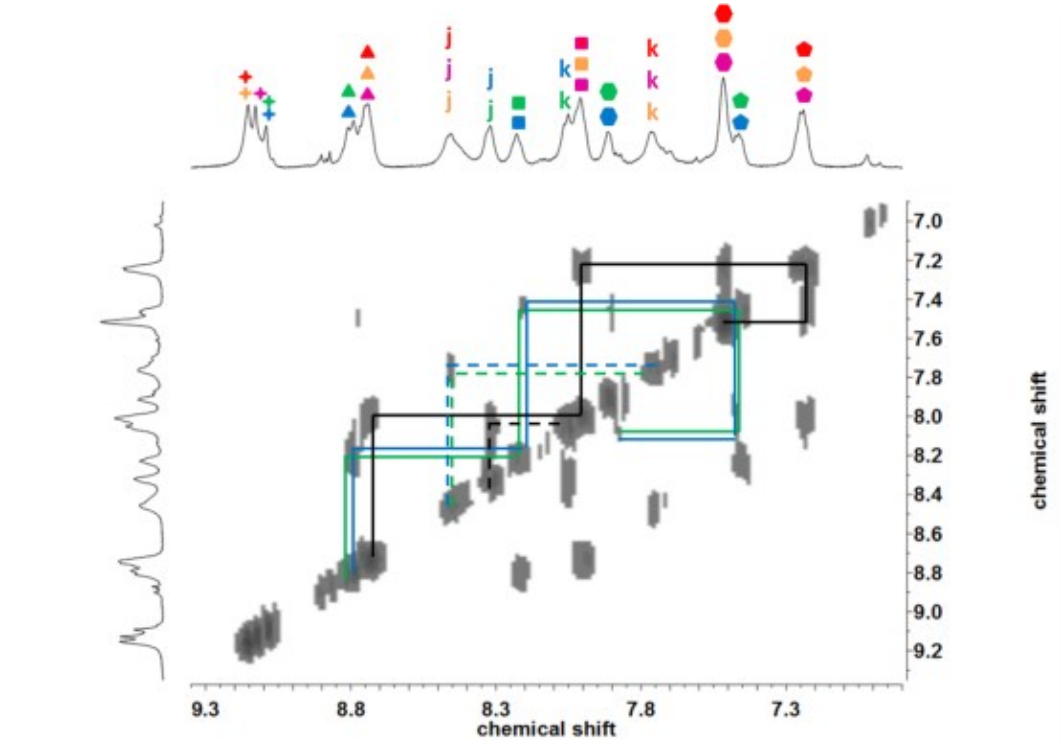


Figure S21. COSY NMR spectrum of Honey comb fractal **H.** All of cross peaks were labeled in one figure: Tpy-A (red), Tpy-B (purple), TpyC (orange), TpyD (blue), TpyE (green). Because signals of Tpy-A, Tpy-D, Tpy-E merged into one broad peak, cross peaks of these three kinds tpys were colored with black. Cross peaks between Ph-kand

Ph-j are denoted as dotted line; all the other cross peaks are illustrated as solid lines.

2D ROESY NMR spectra

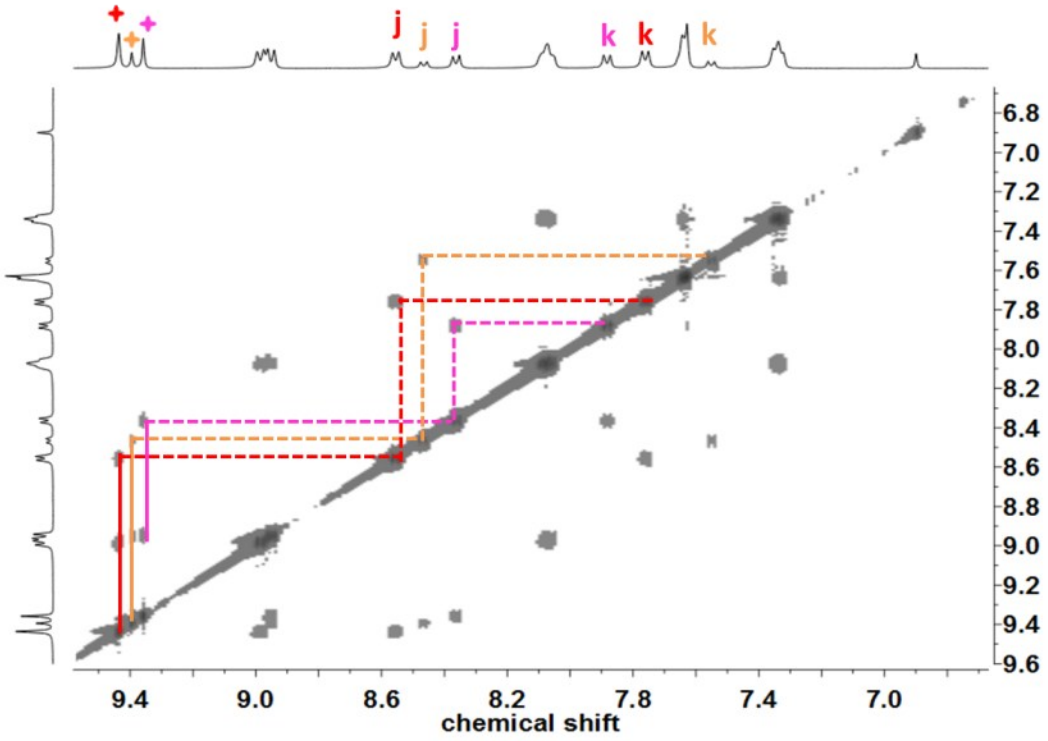


Figure S22. ROESY NMR spectrum of **L9**. Cross peaks between Ph-kand Ph-j are denoted as dotted line; all the other cross peaks are illustrated as solid lines.

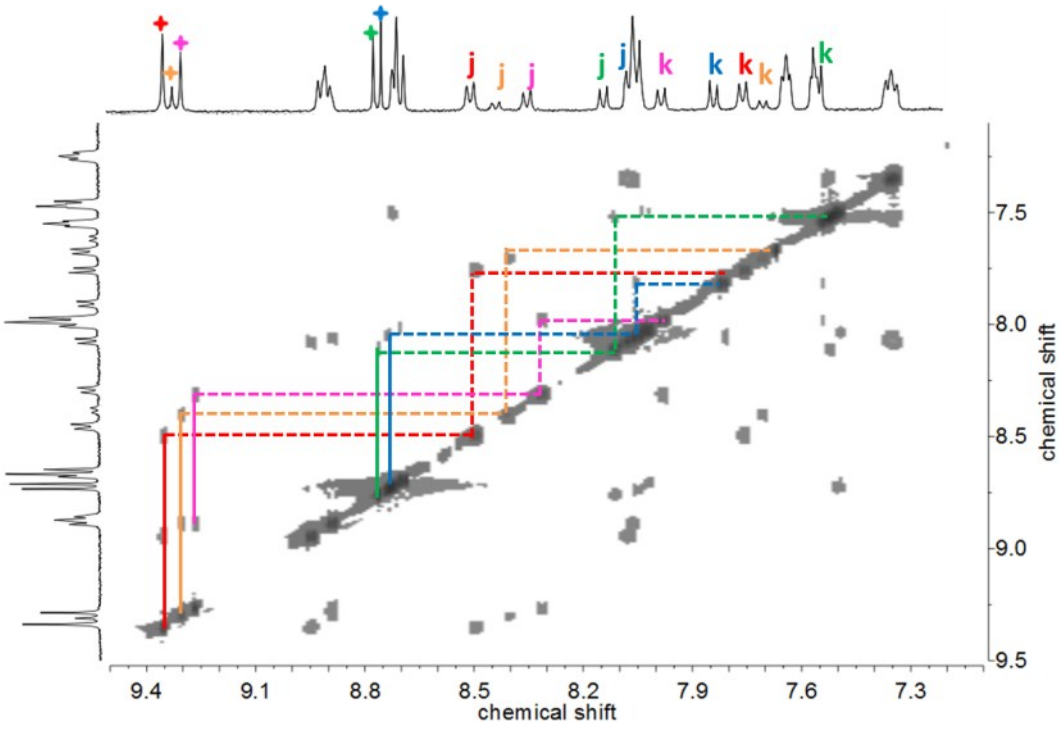


Figure S23. ROESY NMR spectrum of **LB**. Cross peaks between Ph-kand Ph-j are denoted as dotted line; all the other cross peaks are illustrated as solid lines.

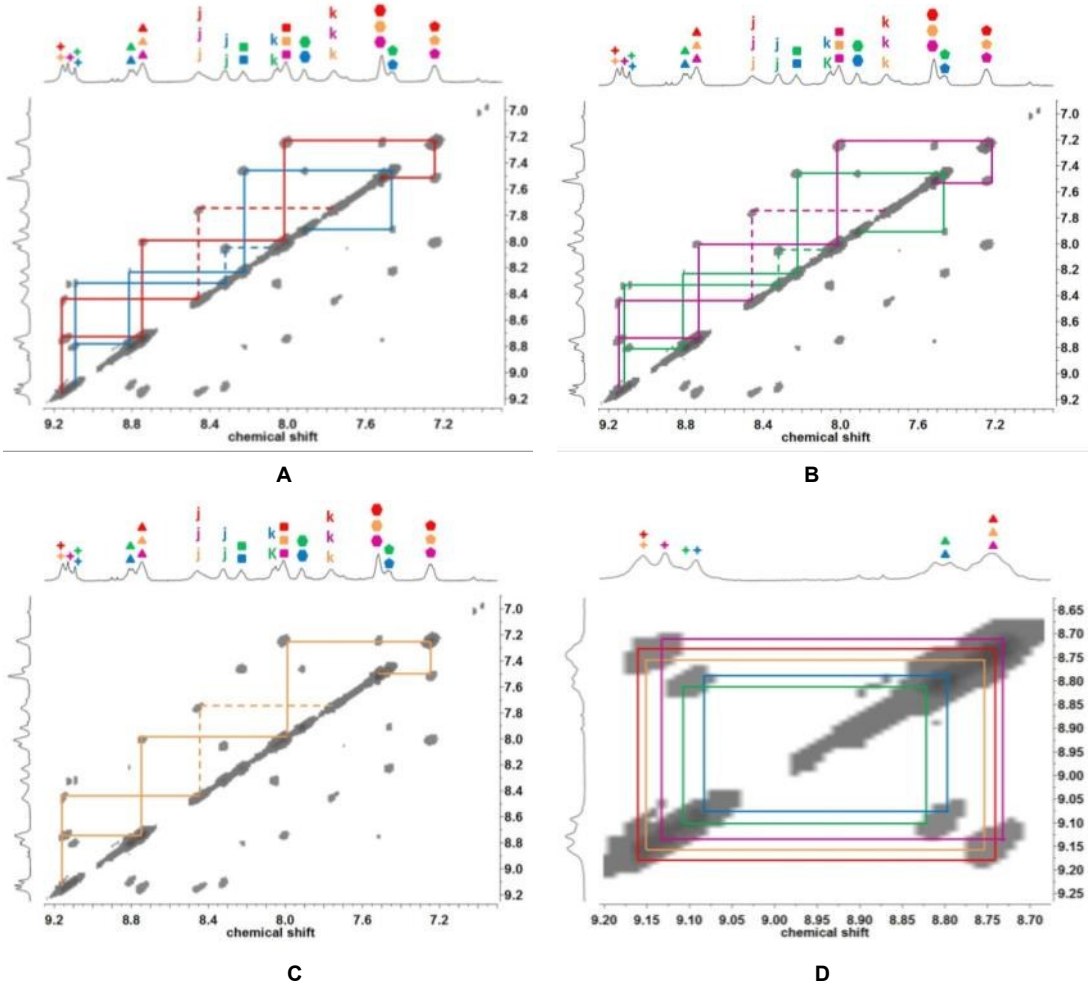


Figure S24. ROESY NMR spectrum of Honey comb fractal **H.** Cross peaks were labeled in three figures: Tpy-A (red), Tpy-E (blue) were labeled in the figure-A; Tpy-B (purple), Tpy-E (green) were labeled in the right figure-B; Tpy-C (orange) was labeled in the right figure-C. Cross peaks between Ph-j and Ph-k are denoted as dotted line; all the other cross peaks are illustrated as solid lines.

MS spectrum and isotope patterns

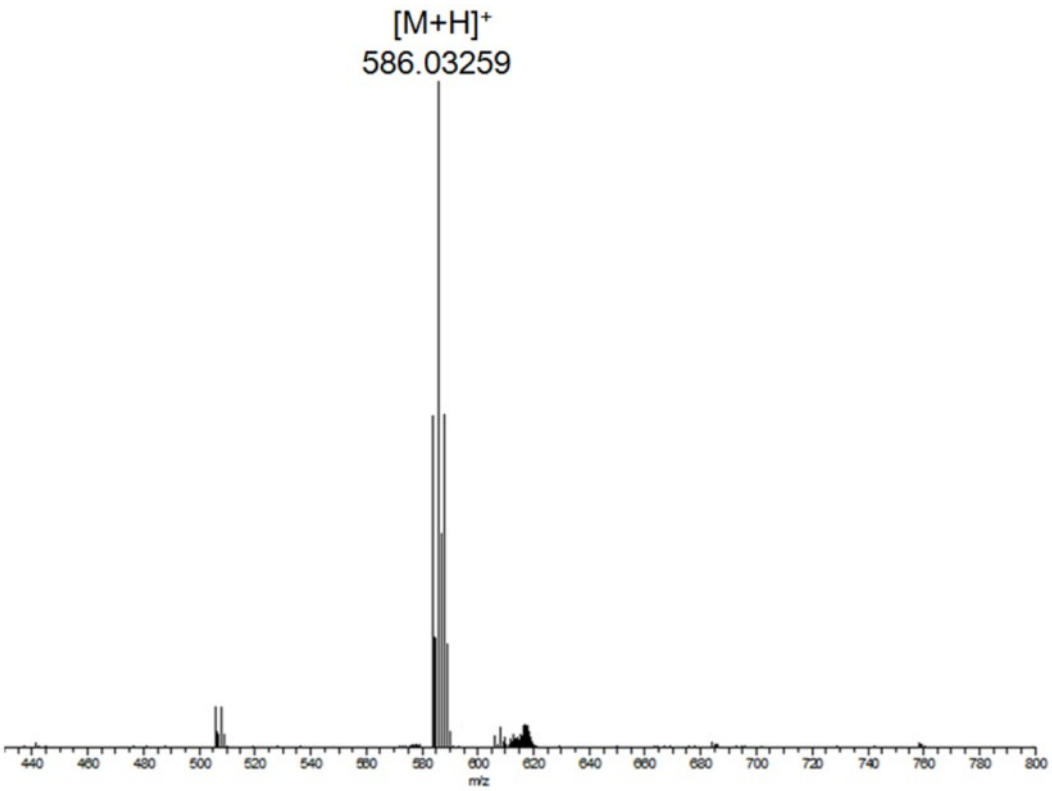


Figure S25. MALDI-TOF-MS spectrum of **L1**.

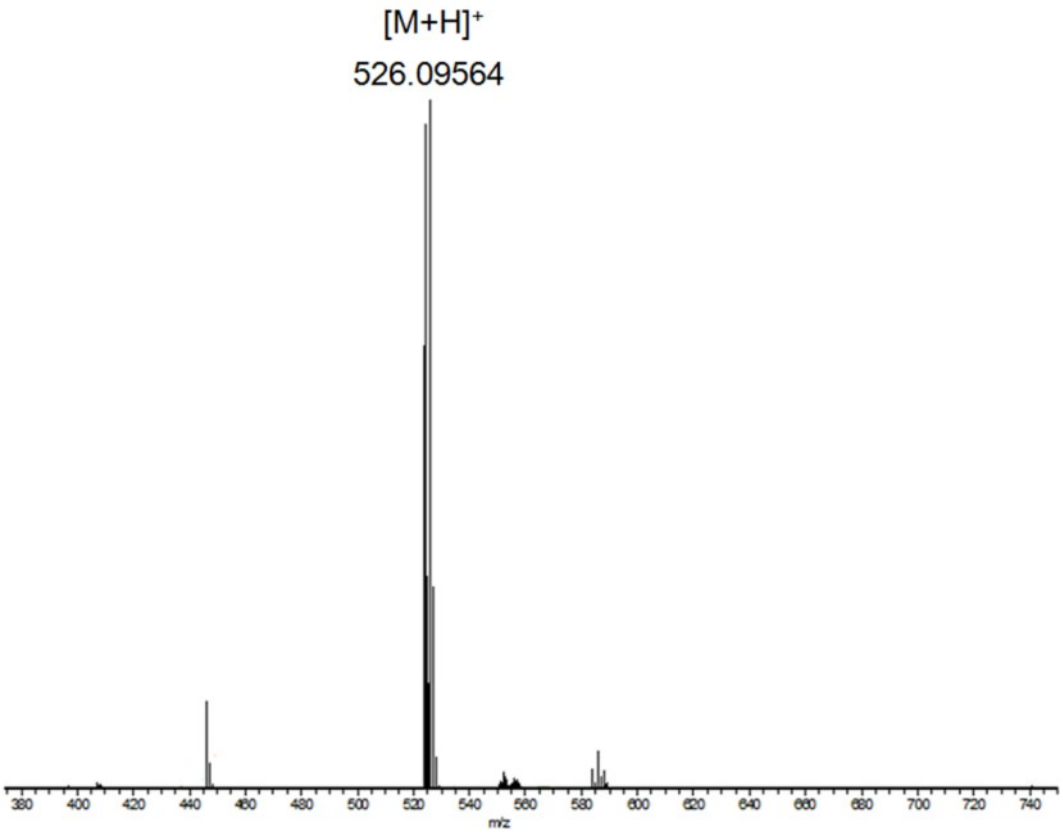


Figure S26. MALDI-TOF-MS spectrum of **L3**.

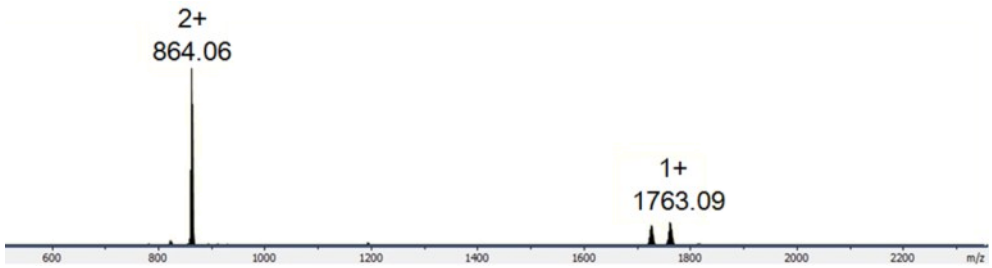


Figure S27. ESI-MS spectrum of **L8**.

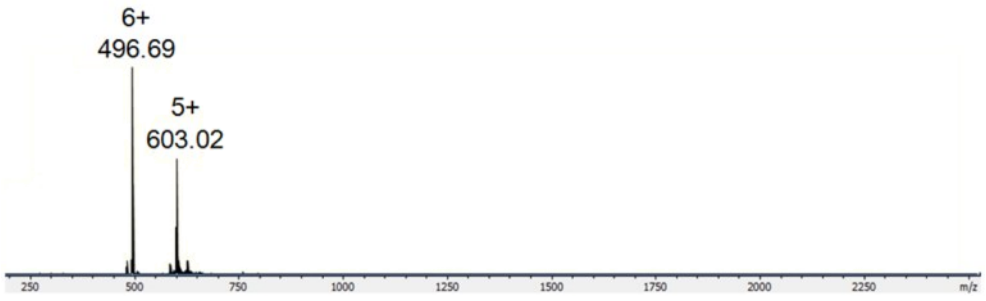


Figure S28. ESI-MS spectrum of **L9**.

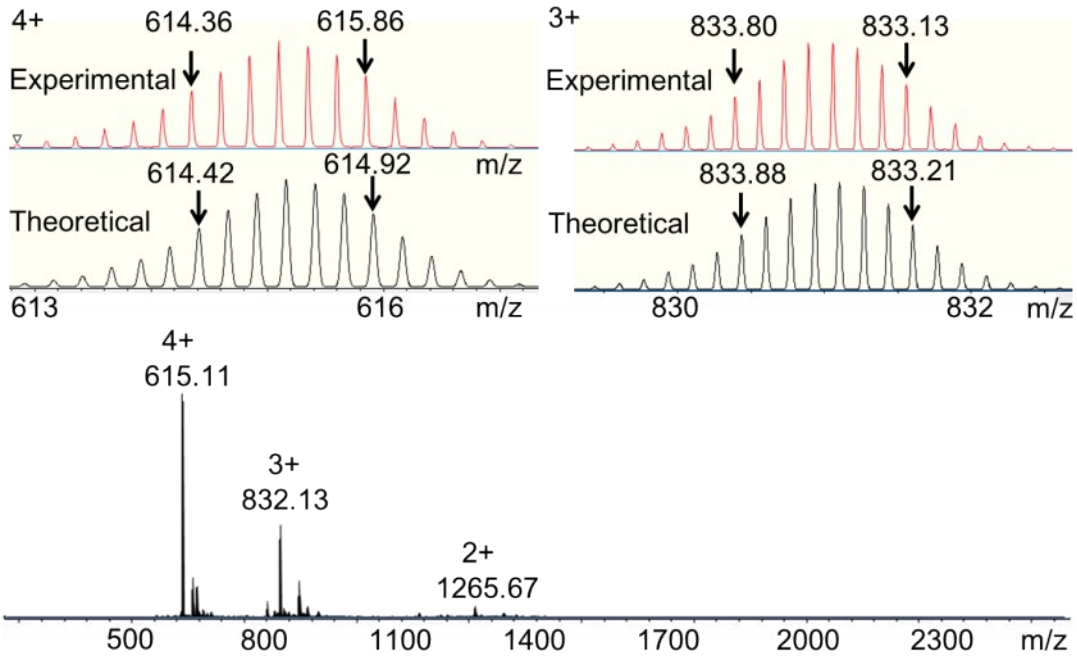


Figure S29. ESI-MS spectrum of **LA**.

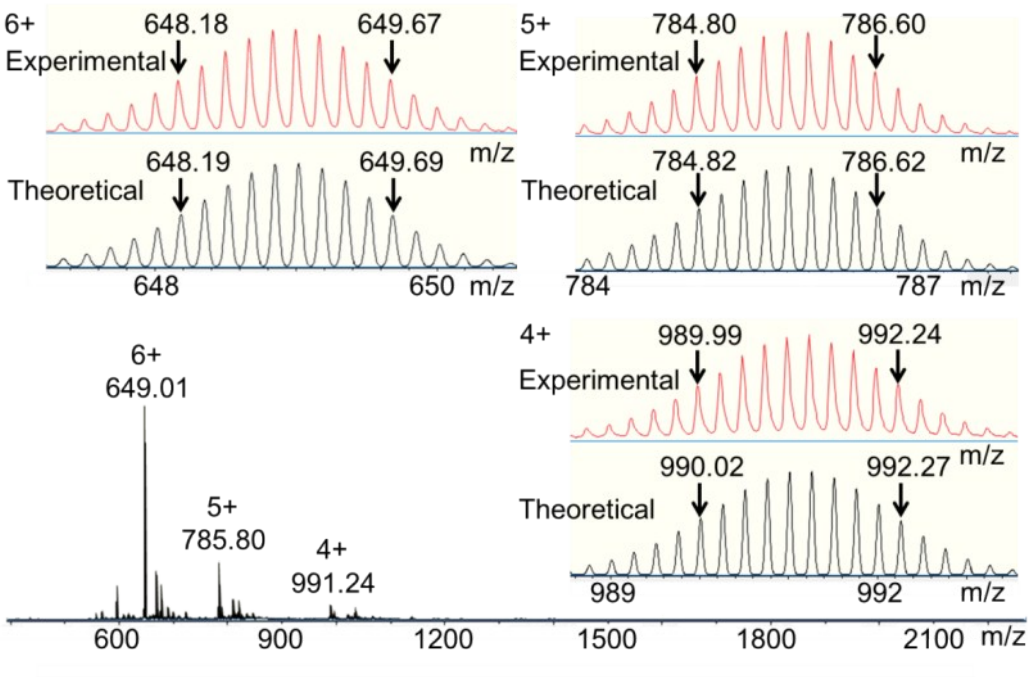


Figure S30. ESI-MS spectrum of **LB**.

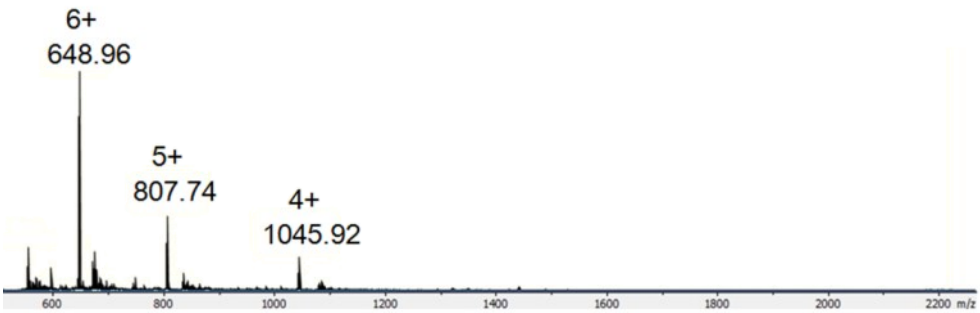


Figure S31. ESI-MS spectrum of **LB** as PF_6^- salt.

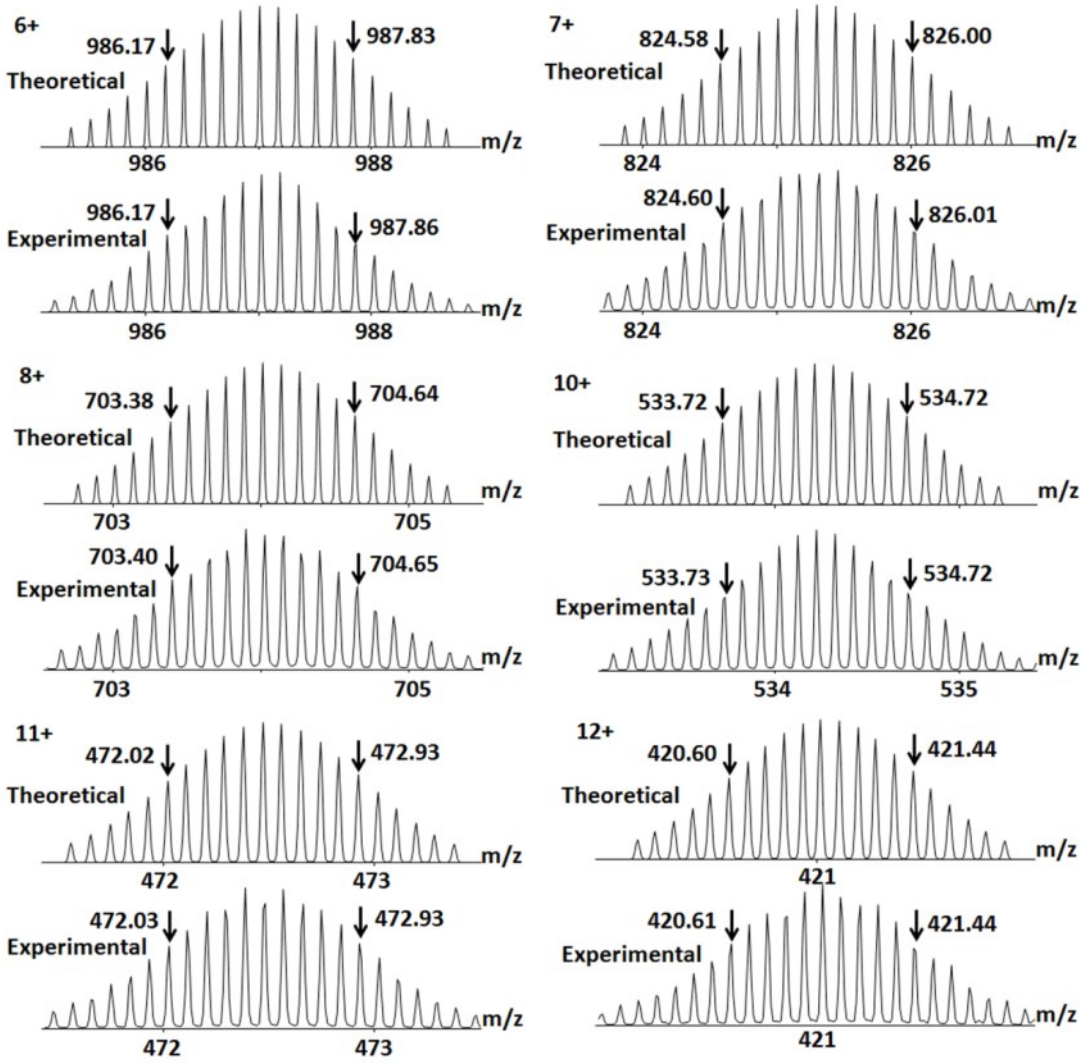


Figure S32. The experimental and theoretical isotope patterns for each charge states of hexagon **A**.

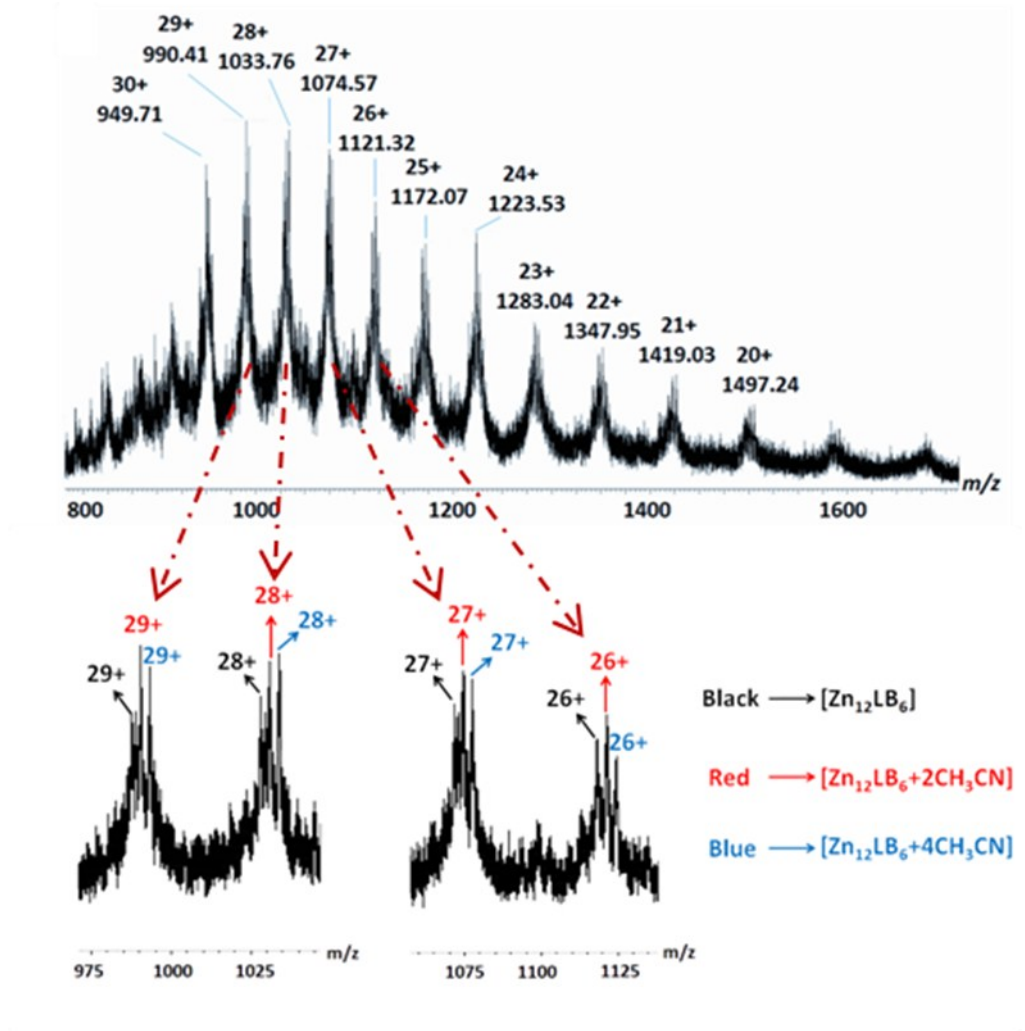


Figure S33. ESI-MS spectrum clearly confirmed the encapsulation of CH_3CN in the large cavities or surface of honeycomb fractal **H**.

Molecular modeling

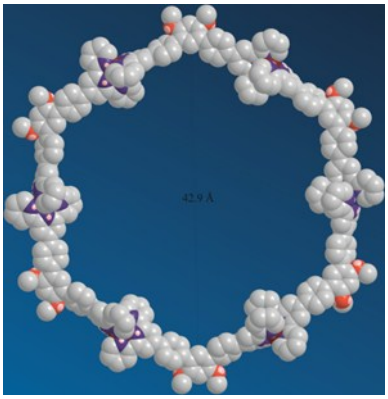


Figure S34. Energy-minimized structure of hexagon **A**.

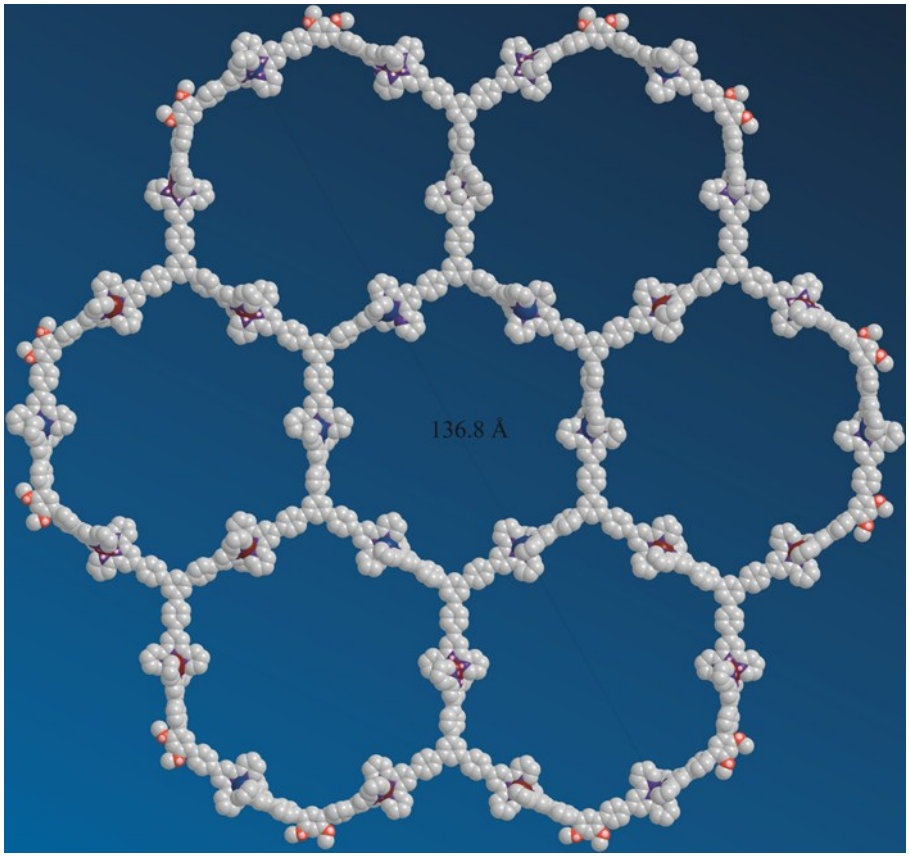


Figure S35. Energy-minimized structure of honeycomb fractal **H**.

2D DOSY NMR

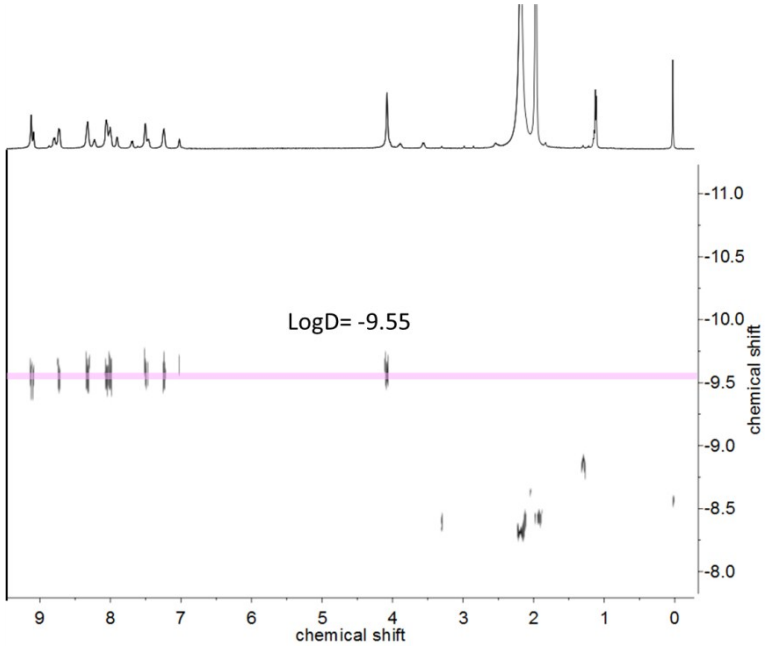


Figure S36. 2D DOSY NMR spectra of hexagong **A**.

Reference

1. D. Bruns, H. Miura, K. P. Vollhardt, *Org. Let.* **2003**, *5*(4), 549–552.
2. J. L. Wang, X. Li, X. Lu, I.-F. Hsieh, Y. Cao, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng, G. R. Newkome, *J. Am. Chem. Soc.* **2011**, *133*, 11450–11453.
3. X. C. Lu, X. P. Li, Y. Cao, A. Schultz, J. L. Wang, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng, G. R. Newkome, *Angew. Chem. Int. Ed.* **2013**, *52*, 7728 –7731.
4. A. Schultz, X. P. Li, C. N. Moorefield, C. Wesdemiotis, G. R. Newkome, *Eur. J. Inorg. Chem.* **2013**, 2492–2497.