

Bi-directional geometric constraints in the construction of giant dual-rim nanorings

Wanying Zhong,^a Zhantao Wang,^a Wei-Dong Yu,^c Ning Wang,^a Fan Fu,^a Jun Wang,^a He Zhao,^b Die Liu,^b Zhilong Jiang^{*a}, Pingshan Wang^{*a,b}, Mingzhao Chen^{*a}

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1. General Procedures

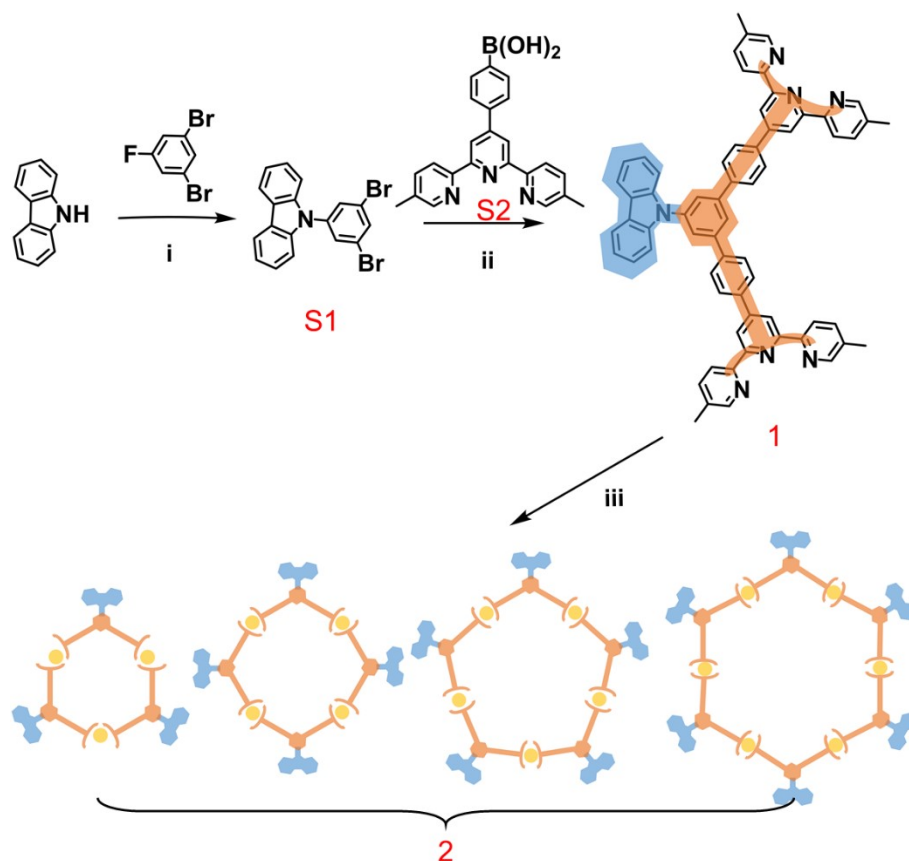
All starting materials were purchased from Aldrich, Alfa Aesar and used without further purification. Compounds **S2/S7** ((4-(5,5"-dimethyl-[2,2':6',2"-terpyridin]-4'-yl)phenyl)boronic acid, 4'-(2-(hexyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2':6',2"-terpyridine) and **5** (2,7-dibromo-9-(3,5-dibromophenyl)-9H-carbazole) were synthesized according to the reported methods[1, 2]. Column chromatography was conducted by using basic Al₂O₃ (sinopharm chemical reagents co., Ltd, 200-300 mesh) or SiO₂ (Qingdao Haiyang Chemical co., Ltd, 200-300 mesh). The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 400-MHz and 500-MHz NMR spectrometer in CDCl₃, and CD₃CN with TMS as the inner standard. Transmission Electron Microscopy (TEM) was obtained on JEOL 2010. Electro-spray ionization (ESI) mass spectra were recorded with a Bruker Q-TOF Qualification Standard Kit., using solutions of 0.1 mg sample in 10 mL of CHCl₃/ MeCN (1:3, v/v) for ligands or 1 mg in 5 mL of MeCN or MeCN/MeOH (3:1, v/v) for complexes. Energy minimization of the macrocycles was conducted with the Materials Studio version 6.1 program, using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted. SCXRD analysis was performed on a Bruker APEX3 diffractometer. The structure was solved with the ShelXT structure solution program using intrinsic phasing and refined with the ShelXL refinement package using least squares minimization. The Solvent Mask routine of the OLEX2 software was implemented to remove the contributions of DMF solvent and dichloromethane solvent to observed structure factors.

ESI. ESI mass spectrometry and traveling wave ion mobility (TWIM) experiments were conducted on a Waters Synapt HDMS G2 instrument with a LockSpray ESI source, using the following parameters: ESI capillary voltage, 1.3-3.0 kV; sample cone voltage, 20-25 V; extraction cone voltage, 1.1-3 V; desolvation gas flow, 800 L/h (N₂); trap collision energy (CE), 4 V; transfer CE, 0 V; trap gas flow, 2.0 mL/min (Ar); source temperature, 30 °C; and desolvation temperature, 30 °C. All samples were dissolved in CH₃CN or CH₃CN/CH₃NO₂ (1:1, v/v) and then infused into the -100, KD Scientific). Data were collected and analyzed by using MassLynx 4.1 and DriftScope 2.4 (Waters).

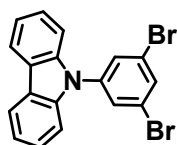
Transmission Electron Microscopy (TEM). The sample was dissolved in CH₃CN at a concentration of ~10⁻⁷ M. The solutions were dropped cast on to a carbon-coated Cu grid (300-400 mesh) and extra solution was absorbed by filter paper to avoid aggregation. The TEM images of the drop cast samples

were taken with a JEOL 2010 Transmission Electron Microscope. Scanning tunneling microscopy (STEM), and STEM mapping analysis was conducted from Titan G2 60-300 (FEI, U.S.) at an acceleration voltage of 300 kV.

2. Synthesis of the ligand 1 and macrocycles 2

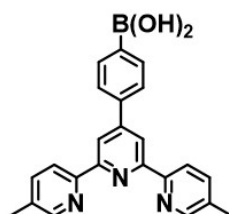


Scheme S1. Ligand **1** assembled with Zn²⁺ to form a mixture of trimer, tetramer, pentamer, and hexamer macrocycles (**2**). Reagents and conditions: (i) Cs₂CO₃, DMF, N₂, 24h, reflux; (ii) NaOH, Pd(PPh₃)₄, H₂O, THF, N₂, 48h, reflux; (iii) 1 equiv Zn(NTf₂)₂, CHCl₃/MeOH (2:1), 12h, reflux.

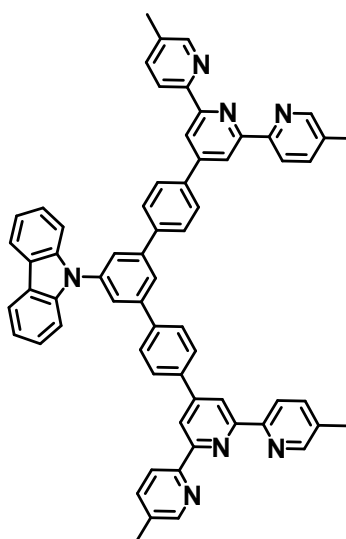


Compound S1: Carbazole (1.5 g, 8.97 mmol), 1,3-Dibromo-5-fluorobenzene (9.2 g, 35.88 mmol) was added to a 100 mL flask, then N,N-Dimethylformamide (40 mL) and Cs₂CO₃ (11.7 g, 35.88 mmol) was added. The mixture was stirred at 150°C under nitrogen for 24 h. After cooled to ambient temperature, the solvent was evaporated in vacuo followed by washed with CH₃OH, and filtered to

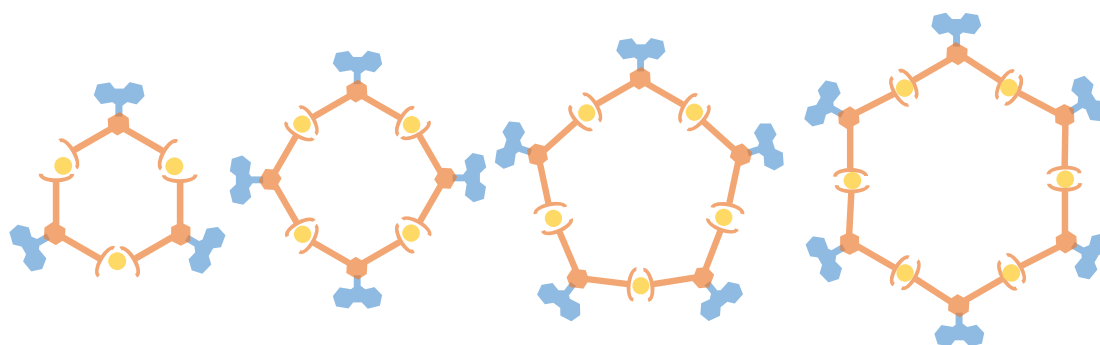
pure the product, as light gray solid: 2.5 g, 69.5%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.15-8.10 (m, 2H, H^i), 7.79-7.75 (m, 1H, H^p), 7.72-7.69 (m, 2H, H^n), 7.47-7.39 (m, 4H, H^q, H^g), 7.35-7.29 (m, 2H, H^m); ESI-MS (401.10 calcd. For $\text{C}_{18}\text{H}_{11}\text{Br}_2\text{N}$): m/z 402.9476 $[\text{M} + \text{H}^+]^+$ (calcd m/z : 402.9415).



Compound S2: 4-Formylphenylboronic acid (5 g, 33.91 mmol), 1-(5-Methylpyridin-2-yl)ethanone (11 g, 81.38 mmol) were added to a 500 mL flask, then $\text{CH}_3\text{CH}_2\text{OH}$ (90 mL) and NaOH (4 g, 135.65 mmol) was added. The mixture was stirred at room temperature for 12 h. Then $\text{NH}_3 \cdot \text{H}_2\text{O}$ (120 mL) was added to the mixture. The mixture was stirred at 80°C for 24 h. After cooled to 4°C , the solid was collected by filtration and was washed with isopropanol to give the product as a white solid: 6.4 g, 49%. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.74-8.68 (d, $J = 24$ Hz, 2H, $\text{H}^{3',5'}$), 8.66-8.61 (dd, $J = 12, 8$ Hz, 2H, $\text{H}^{3',3''}$), 8.60-8.54 (dd, $J = 8, 16$ Hz, 2H, $\text{H}^{6,6''}$), 8.05 (dd, $J = 28, 32$ Hz, 2H, H^k), 7.87-7.80 (m, 2H, $\text{H}^{4,4''}$), 7.72 (dd, $J = 60, 32$ Hz, 2H, H^i), 2.44-2.36 (d, $J = 32$ Hz, 6H, $\text{H}^{\text{Me-5},5''}$); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.42, 138.74, 134.32, 129.18, 124.43, 124.21, 121.95, 121.66, 120.35, 112.81; ESI-MS (381.24 calcd. For $\text{C}_{23}\text{H}_{20}\text{BN}_3\text{O}_2$): m/z 381.1687 $[\text{M} + \text{H}^+]^+$ (calcd m/z : 381.1685).



Compound 1: Compound S1 (0.3 g, 0.75 mmol), Compound S2 (0.68 g, 1.80 mmol) were added to a 100 mL flask, then THF (30 mL) and NaOH (0.18 g, 4.49 mmol) in 4.5 mL of water was added. The $\text{Pd}(\text{PPh}_3)_4$ (0.10 g, 0.09 mmol) as the catalyst was added and the system was degassed using N_2 . The mixture was stirred at 85°C under nitrogen for 48h. After cooled to ambient temperature, the solvent was evaporated in vacuo followed by washed with CH_3OH . After Filtered to obtain solid, and the solid was recrystallized with CH_2Cl_2 and CH_3OH to pure the product, as white solid: 0.856 g, 61%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.75 (s, 4H, $\text{H}^{3',5'}$), 8.59-8.55 (m, 8H, $\text{H}^{3',3''}$, $\text{H}^{6,6''}$), 8.22-8.18 (d, $J = 16$ Hz, 2H, H^i), 8.08-8.05 (m, 5H, H^j, H^p), 7.91-7.87 (m, 6H, H^n, H^k), 7.71-7.67 (m, 4H, $\text{tpy-H}^{4,4'}$), 7.61-7.58 (d, $J = 12$ Hz, 2H, H^g), 7.50-7.46 (t, 2H, H^q), 7.36-7.31 (t, 2H, H^m), 2.44 (s, 13H, tpy-H^{Me}); ESI-MS (914.13 calcd. For $\text{C}_{64}\text{H}_{47}\text{N}_7$): m/z 915.4046 $[\text{M} + \text{H}^+]^+$ (calcd m/z : 915.4049).



Macrocycles 2: Ligand **1** (10.00 mg, 0.011 μmol) and $\text{Zn}(\text{NTf}_2)_2$ (7.19 mg, 0.011 μmol) was added to a 100 ml flask, then a solvent mixture of CH_3OH and CHCl_3 (40 ml, V:V=1:2) was added. The mixture was refluxed for 12 h. After cooled to ambient temperature, excess bistrifluoromethanesulfonimide lithium salt (LiNTf_2) in CH_3OH was added to get dark yellow precipitate, which was filtered and washed with CH_3OH to generate a dark yellow solid: 15 mg, 87.3%. The composition of **2** is a mixture of **Zn₃1₃**, **Zn₄1₄**, **Zn₅1₅** and **Zn₆1₆**. ^1H NMR (400 MHz, CD_3CN) δ 9.02-8.98 (m, 4H, $^{\text{tpy}}\text{-H}^{3',5'}$), 8.68-8.62 (d, $J = 16$ Hz, 4H, $^{\text{tpy}}\text{-H}^{3,3''}$), 8.44-8.36 (d, $J = 32$ Hz, 2H, H^i), 8.33-8.26 (m, 5H, H^j , H^p), 8.22-8.18 (m, 2H, H^n), 8.03-7.96 (d, $J = 28$ Hz, 4H, H^k), 7.95-7.89 (s, 4H, $^{\text{tpy}}\text{-H}^{6,6''}$), 7.74-7.66 (m, 6H, $^{\text{tpy}}\text{-H}^{4,4''}$, H^g), 7.60-7.54 (t, $J = 24$ Hz, 2H, H^q), 7.44-7.37 (t, $J = 28$ Hz, 2H, H^m), 2.20-2.17 (s, 12H, $^{\text{tpy}}\text{-H}^{\text{Me}}$).

Zn₃1₃. ESI-MS (m/z): 1259.4209 [M-3NTf] $^{3+}$ (calcd m/z : 1259.64), 874.4438 [M-4NTf] $^{4+}$ (calcd m/z : 874.45), 643.4419 [M-5NTf] $^{5+}$ (calcd m/z : 643.73), 489.4450 [M-6NTf] $^{6+}$ (calcd m/z : 489.75).

Zn₄1₄. ESI-MS (m/z): 1259.3909 [M-4NTf] $^{4+}$ (calcd m/z : 1259.64), 951.5995 [M-5NTf] $^{5+}$ (calcd m/z : 951.80), 746.1029 [M-6NTf] $^{6+}$ (calcd m/z : 746.38), 599.4463 [M-7NTf] $^{7+}$ (calcd m/z : 599.73).

Zn₅1₅. ESI-MS (m/z): 1259.4209 [M-5NTf] $^{5+}$ (calcd m/z : 1259.64), 1003.0399 [M-6NTf] $^{6+}$ (calcd m/z : 1003.04), 819.6668 [M-7NTf] $^{7+}$ (calcd m/z : 819.70), 682.0152 [M-8NTf] $^{8+}$ (calcd m/z : 682.22), 575.0616 [M-9NTf] $^{9+}$ (calcd m/z : 575.29).

Zn₆1₆. ESI-MS (m/z): 1259.4209 [M-6NTf] $^{6+}$ (calcd m/z : 1259.64), 1039.6440 [M-7NTf] $^{7+}$ (calcd m/z : 1039.64), 874.3638 [M-8NTf] $^{8+}$ (calcd m/z : 874.69), 746.0029 [M-9NTf] $^{9+}$ (calcd m/z : 746.38), 643.3619 [M-10NTf] $^{10+}$ (calcd m/z : 643.73).

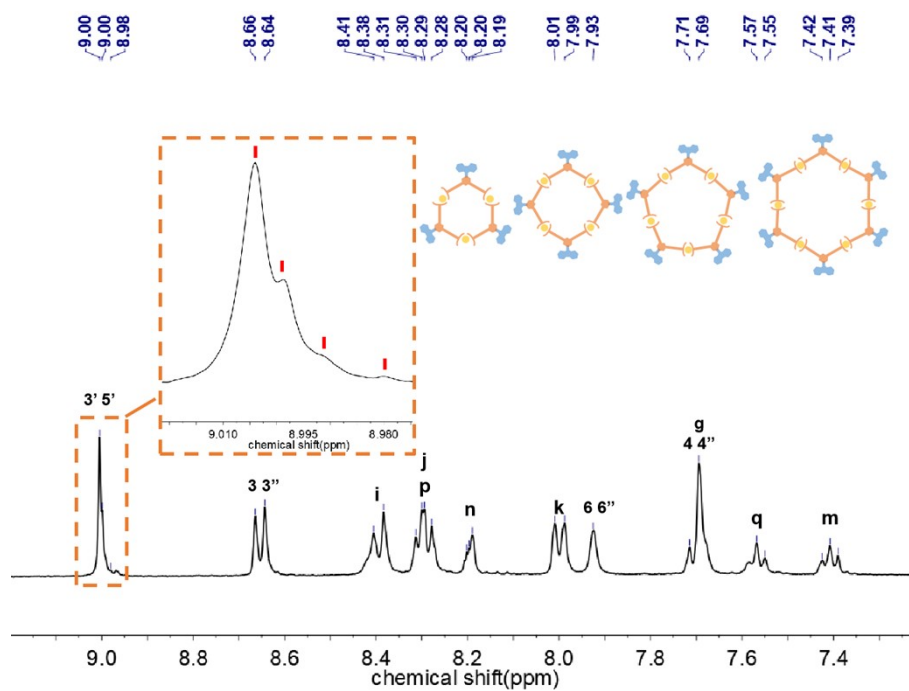


Figure S1. ^1H NMR spectrum (400 MHz) of macrocycles **2** in CD_3CN .

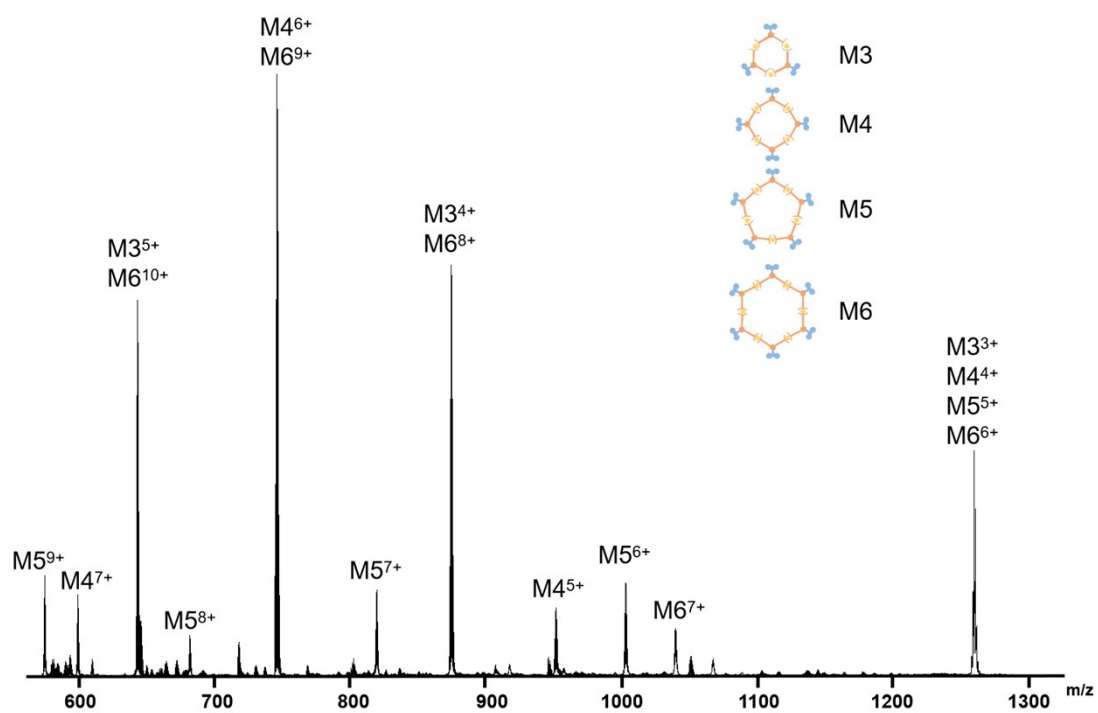


Figure S2. ESI-MS spectra of mixture of macrocycles **2** (M3, M4, M5 and M6).

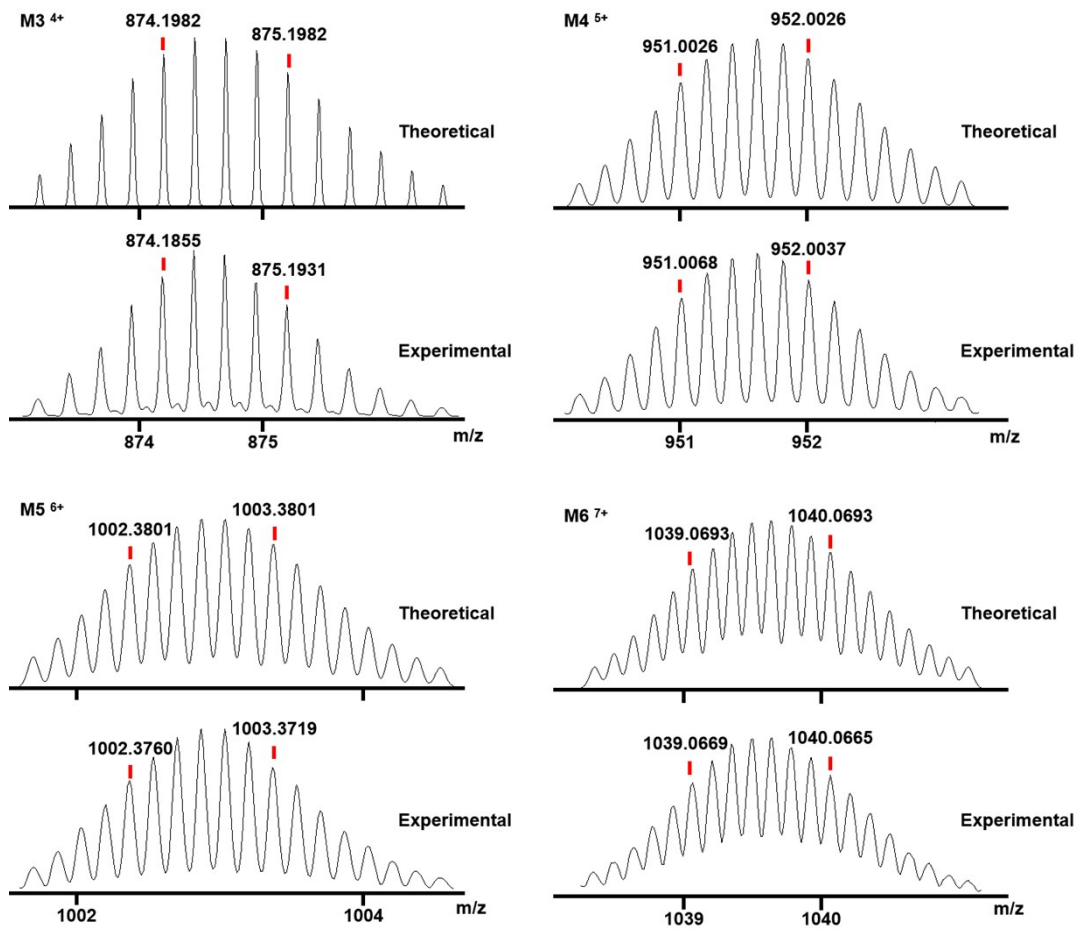
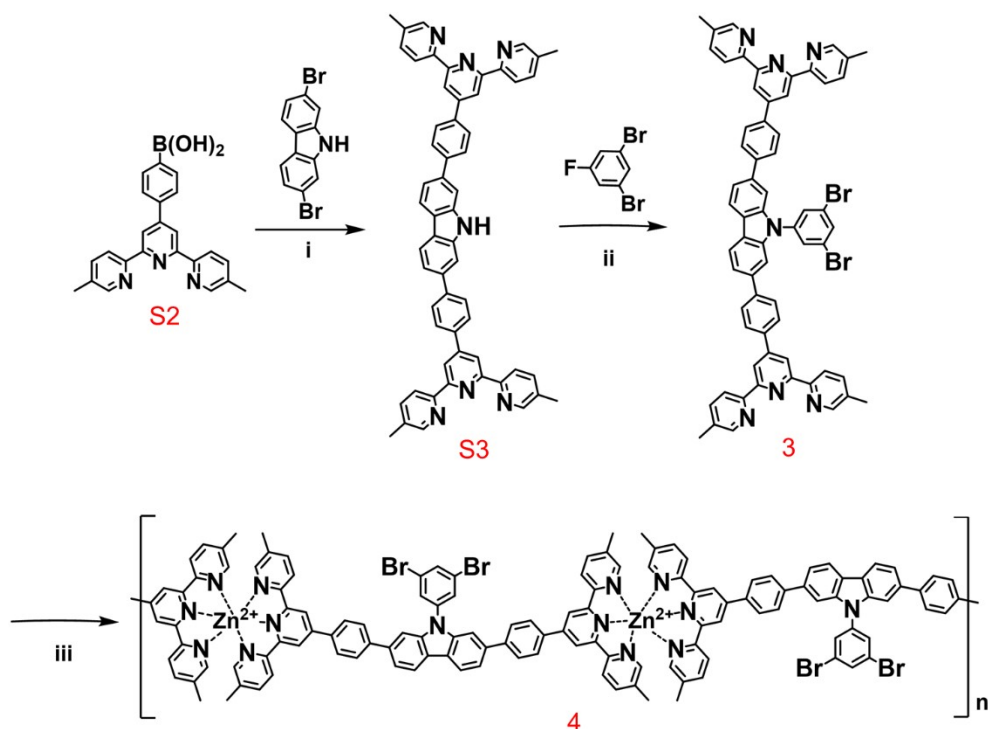
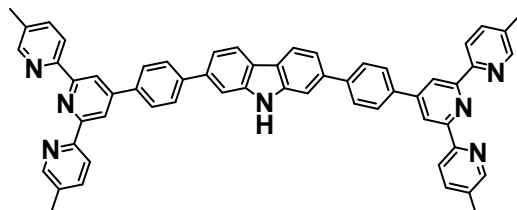


Figure S3. Theoretical (top) and experimental (bottom) isotope patterns for the different charge states observed from macrocycles **2** (NTf_2^- as counterion).

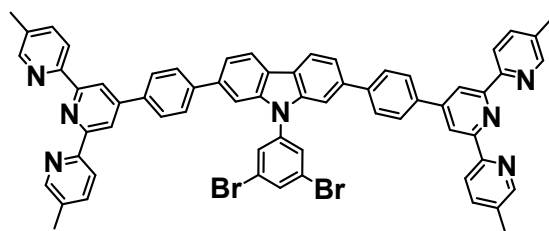
3. Synthesis of the ligand 3 and polymer 4



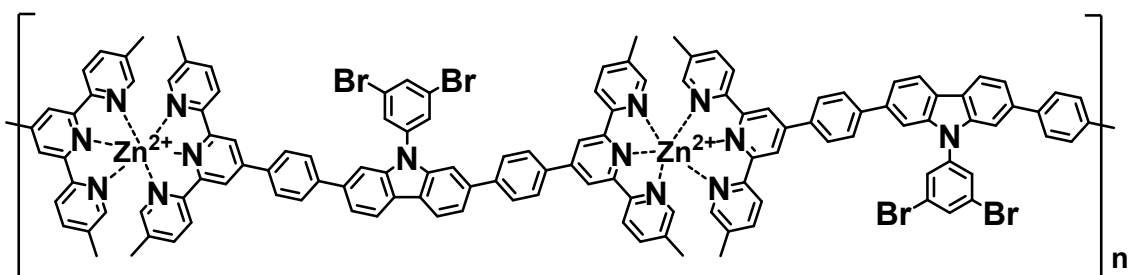
Scheme S2. Self-assembly polymer directed by Zn(II) ions. Reagents and conditions: (i) NaOH, Pd(PPh₃)₄, H₂O, THF, N₂, 48h, reflux; (ii) Cs₂CO₃, DMF, N₂, 24h, reflux; (iii) 1 equiv Zn(NTf₂)₂, CHCl₃/MeOH (2:1), 12h, reflux.



Compound S3: 2,7-Dibromo-9H-carbazole (2.13 g, 6.56 mmol), Compound S2 (6.00 g, 15.74 mmol) were added to a 250 mL flask, then THF (130 mL) and NaOH (1.57 g, 39.35 mmol) in 39.5 mL of water was added. The Pd(PPh₃)₄ (0.76 g, 0.66 mmol) as the catalyst was added and the system was degassed using N₂. The mixture was stirred at 85°C under nitrogen for 48h. After cooled to ambient temperature, the solvent was evaporated in vacuo followed by dissolution with CH₂Cl₂. The solvent was washed with CH₂Cl₂ and MeOH, then filtered to afford compound **3** as a yellow solid: 4.25 g, 77%. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 4H, H^{3',5'}), 8.59-8.54 (m, 8H, H^{3,3''}, H^{6,6''}), 8.36 (s, 1H, H^{NH}), 8.19-8.15 (d, J = 16 Hz, 2H, Hⁱ), 8.03-7.98 (d, J = 20 Hz, 4H, H^j), 7.85-7.80 (d, J = 20 Hz, 4H, H^k), 7.71-7.66 (m, 6H, H^{4,4''}, H^g), 7.61-7.56 (dd, 2H, H^m), 2.44 (s, 12H, ^{tpy}-H^{Me}); ESI-MS (838.03 calcd. For C₅₈H₄₃N₇): m/z 838.3659 [M + H⁺]⁺ (calcd m/z: 838.3658).



Ligand 3: compound **S3** (3.00 g, 3.58 mmol), 1,3-Dibromo-5-fluorobenzene (3.64 g, 14.32 mmol) was added to a 500 mL flask, then N,N-Dimethylformamide (150 mL) and Cs₂CO₃ (4.67g, 14.32 mmol) was added. The mixture was stirred at 150°C under nitrogen for 24 h. After cooled to ambient temperature, the solvent was evaporated in vacuo followed by ultrasonic treatment with methanol for 1 hour. And then filtered to obtain flesh-colored solid: 3.5 g, 91%. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 4H, H^{3',5'}), 8.59-8.54 (m, 8H, H^{3,3''}, H^{6,6''}), 8.25-8.21 (d, J = 16 Hz, 2H, Hⁱ), 8.05-8.00 (d, J = 20 Hz, 4H, H^j), 7.87-7.84 (t, J = 28 Hz, 1H, H^p), 7.83-7.78 (dd, 6H, H^{n,k}), 7.71-7.64 (td, 6H, H^{4,4''}, H^m), 7.62 (s, 2H, H^g), 2.44 (s, 12H, t^{py}-H^{Me}); ESI-MS (1071.92 calcd. For C₆₄H₄₅Br₂N₇): m/z 1072.2189 [M + H]⁺ (calcd m/z: 1072.2181).



Polymer 4: Ligand **3** (10.00 mg, 9.3 μmol) and Zn(NTf)₂ (6.13 mg, 9.8 μmol) was added to a 100 ml flask, then a solvent mixture of CH₃OH and CHCl₃ (40 ml, V:V=1:2) was added. The mixture was refluxed for 12 h. After cooled to ambient temperature, which was filtered and washed with CH₃OH to obtain a slight yellow solid:14 mg, 86.8%.

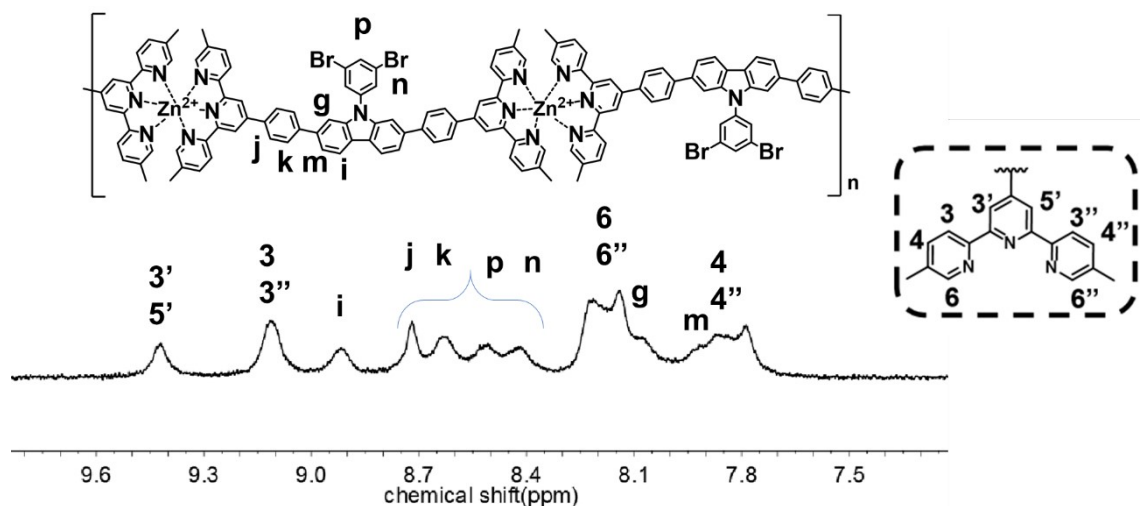


Figure S4. ¹H NMR spectrum (400 MHz) of Polymer **4** in DMSO-d₆.

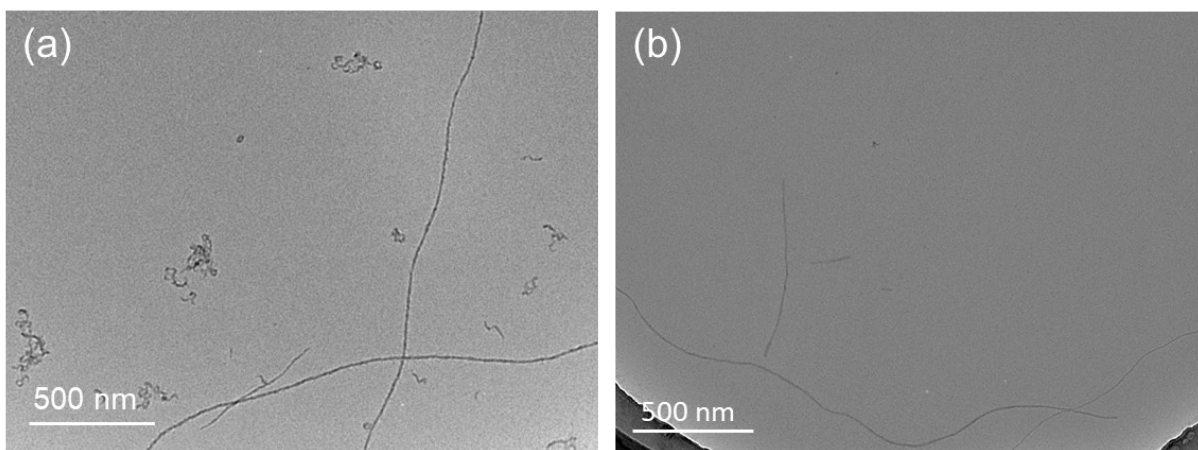
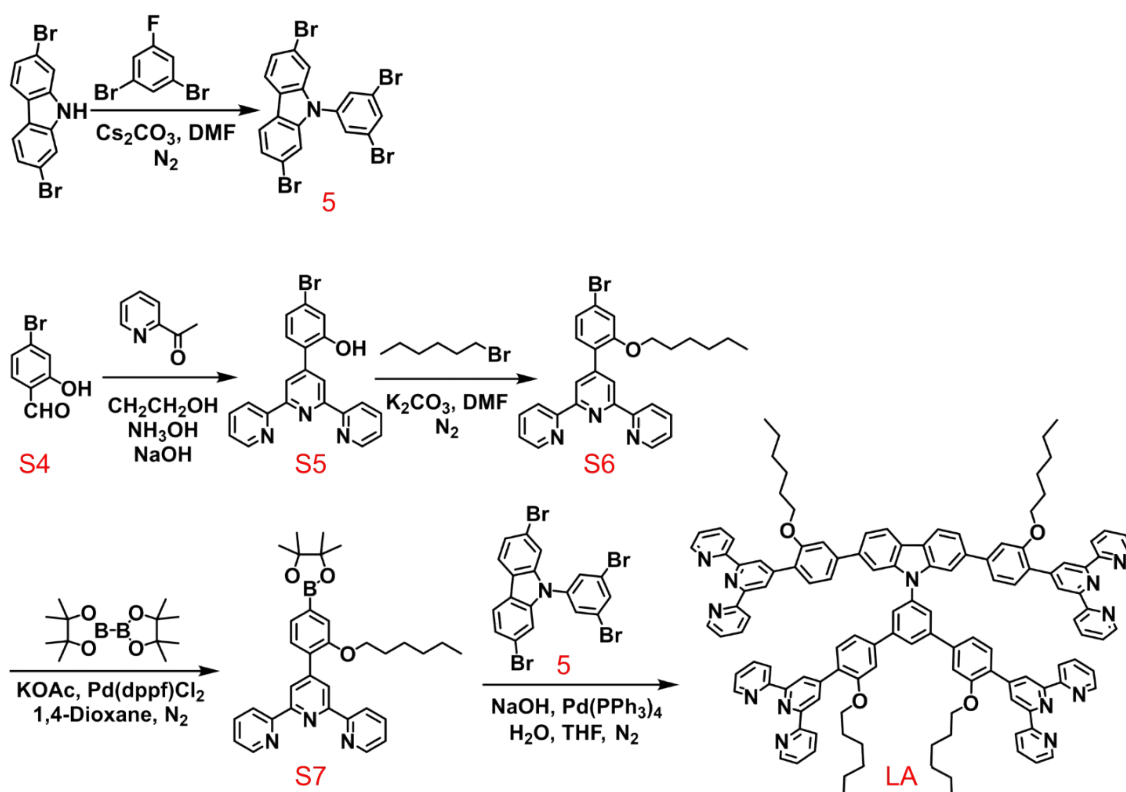
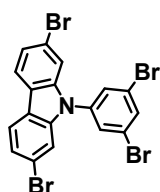


Figure S5. TEM images of polymer **4** on a carbon-coated Cu grid.

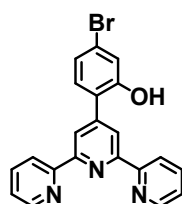
4. Synthesis of the ligand LA and supramolecular macrocycles SA



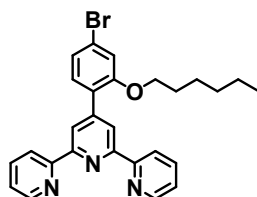
Scheme S3: The synthetic route of the Ligand LA.



Compound 5: 2,7-Dibromo-9H-carbazole (1.00 g, 3.08 mmol), 1,3-Dibromo-5-fluorobenzene (3.125 g, 12.31 mmol) was added to a 50 mL flask, then N,N-Dimethylformamide (30 mL) and Cs₂CO₃ (4.010 g, 12.31 mmol) was added. The mixture was stirred at 150°C under nitrogen for 24 h. After cooled to ambient temperature, the solvent was evaporated in vacuo followed by extraction with CH₂Cl₂ and saturated sodium chloride solution for three times. The combined organic layer was dried over anhydrous Na₂SO₄, and the solvent was evaporated in vacuo and the residue was purified by column chromatography (silica gel), eluting with the mixture of petroleum ether and CH₂Cl₂ to pure the product, as ivory solid: 1.3 g, 75%. ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.91 (dd, J = 8, 8 Hz, 2H, Hⁱ), 7.87-7.83 (t, J = 16 Hz, 1H, H^p), 7.63-7.61 (d, J = 8 Hz, 2H, H^g), 7.46-7.44 (d, J = 8 Hz, 3H, H^{m,n}), 7.43-7.41 (d, J = 8 Hz, 1H, H^m); ¹³C NMR (101 MHz, CDCl₃) δ 141.42, 138.74, 134.32, 129.18, 124.43, 124.21, 121.95, 121.66, 120.35, 112.81; ESI-MS (558.89 calcd. For C₁₈H₉Br₄N): m/z 559.7409 [M + H]⁺ (calcd m/z: 559.7468).

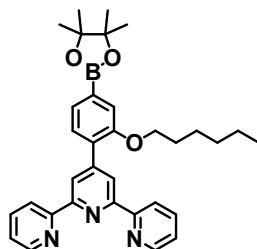


Compound S5: 4-Bromo-2-hydroxybenzaldehyde (12.0 g, 59.7 mmol), 1-(Pyridin-2-yl)ethanone (15.9 g, 131.3 mmol) and NaOH (7.2 g, 179.1 mmol) was added to a 500 mL flask, then CH₃CH₂OH(150 mL) was added. The mixture was stirred at room temperature for 12 h. The NH₃·H₂O was added to the mixture, and then the mixture was stirred at 80°C for 24 h. After cooled to ambient temperature, the precipitate was filtered and washed with isopropanol to afford compound 2 as a yellow solid (13.3 g, 55%). ¹H NMR (400 MHz, MeOD) δ 8.69 (s, 2H, H^{3',5'}), 8.67-8.63 (d, J = 16 Hz, 2H, H^{3,3''}), 8.59-8.54 (d, J = 20 Hz, 2H, H^{6,6''}), 8.00-7.93 (td, 2H, H^{4,4''}), 7.46-7.40 (ddd, 2H, H^{5,5''}), 7.29-7.25 (d, J = 16 Hz, 1H, H^j), 6.94-6.90 (d, J = 16 Hz, 1H, Hⁱ), 6.67-6.63 (dd, 1H, H^k); ¹³C NMR (101 MHz, MeOD) δ 167.18, 156.82, 154.92, 151.53, 148.62, 137.19, 130.33, 126.25, 123.51, 123.47, 123.27, 121.72, 121.46, 116.01; ESI-MS (404.27 calcd. For C₂₁H₁₄BrN₃O): m/z 405.0393 [M + H]⁺ (calcd m/z: 405.0398).

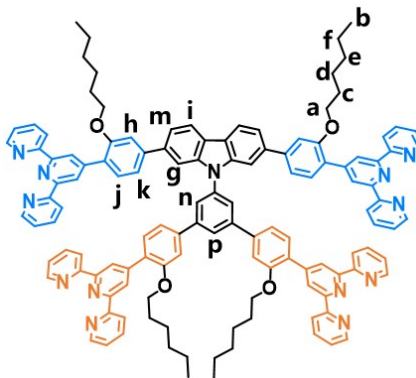


Compound S6: Compound S5 (3 g, 7.42 mmol), bromohexane (2.5 g, 14.84 mmol) was added to a 100 mL flask, then N,N-Dimethylformamide (30 mL) and K₂CO₃ (3 g, 22.26 mmol) was added. The mixture was stirred at 55°C under N₂ for 12 h. After the reaction mixture cooled to ambient temperature, the solvent was evaporated under reduced pressure. The resultant residue was dissolved in CH₂Cl₂ (100 mL) and washed twice with water (100 mL). The organic phase was combined and dried over anhydrous Na₂SO₄, the solvent was evaporated to give compound 3 (3.414 g, 93.8%) as SandyBrown solid. ¹H NMR (400 MHz, CDCl₃) δ 8.72-8.67 (d, J = 20 Hz, 2H, H^{3,3''}), 8.67-8.63 (t, 4H, H^{3',5'}, H^{6,6''}), 7.90-7.83 (td, 2H, H^{4,4''}), 7.45-7.40 (d, J = 20 Hz, 1H, H^j), 7.35-7.29 (ddd, 2H, H^{5,5''}), 7.22-7.17 (dd, 1H, H^k), 7.15-7.11 (d, J = 16 Hz, 1H, H^b), 4.11-3.91 (t, 2H, H^a), 1.84-1.57 (m, 6H, H^{c,d,e,f}), 0.81-0.65 (t, 3H, H^b); ¹³C NMR (101 MHz, MeOD) δ 167.18, 156.82, 154.92, 151.53, 148.62,

137.19, 130.33, 126.25, 123.51, 123.47, 123.27, 121.72, 121.46, 116.01; ESI-MS (488.43 calcd. For $C_{27}H_{26}BrN_3O$): m/z 489.1338 $[M + H]^+$ (calcd m/z : 489.1337).

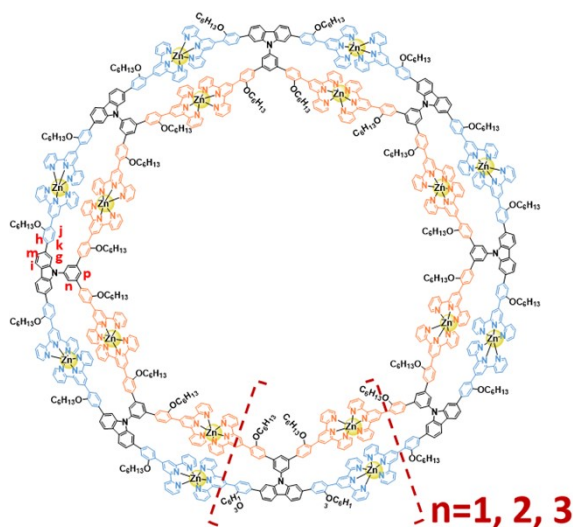


Compound S7: Compound **S6** (6.9 g, 14.13 mmol), Bis-(pinacolato)diboron (8.9 g, 35.32 mmol), KOAc (4.2 g, 42.38 mmol), Pd(dppf)Cl₂ (0.4 g, 0.57 mmol) was added to a 250 mL three-necked flask. The system was degassed with N₂ for 10 min, and then anhydrous 1,4- Dioxane (85 mL) was injected into the flask. The mixture was stirred at 80°C under N₂ for 12 h. After cooled to ambient temperature, the solvent was evaporated under reduced pressure, then concentrated in vacuo followed by column chromatography (Al₂O₃), eluting with the mixture of petroleum and CH₂Cl₂ to pure the product, as white thick solid: 6.5 g, 86%. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 2H, H^{3',5'}), 8.70-8.67 (d, J = 12 Hz, 2H, H^{3,3''}), 8.67-8.62 (d, J = 20 Hz, 2H, H^{6,6''}), 7.88-7.82 (td, 2H, H^{4,4''}), 7.60-7.55 (d, J = 20 Hz, 1H, H^j), 7.52-7.46 (d, J = 24 Hz, 1H, H^k), 7.40 (s, 1H, H^h), 7.34-7.28 (ddd, 2H, H^{5,5''}), 4.14-4.00 (t, 2H, H^a), 1.80-1.61 (m, 4H, H^{c,d}), 1.37 (s, 12H, H¹²), 1.18-1.05 (m, 4H, H^{e,f}), 0.76-0.67 (t, 3H, H^b); ¹³C NMR (101 MHz, CDCl₃) δ 156.44, 155.82, 155.02, 149.00, 148.27, 136.62, 131.05, 129.91, 127.31, 123.47, 121.77, 121.12, 117.90, 83.85, 83.38, 77.56, 77.24, 76.92, 68.44, 31.47, 29.15, 25.77, 24.96, 24.85, 24.80, 24.75, 24.52, 22.30, 13.90; ESI-MS (535.50 calcd. For C₃₃H₃₈BN₃O₃): m/z 536.3124 $[M + H]^+$ (calcd m/z : 536.3121).



Ligand LA: Compound **5** (0.50 g, 0.89 mmol) and compound **S7** (2.87 g, 5.35 mmol) was added to a 250 mL flask, then THF (66 mL) and NaOH (0.43 g, 10.74 mmol) in 11 mL of water was added. The system was degassed for 10 min, and Pd(PPh₃)₄ (0.21 g, 0.18 mmol) as the catalyst was added. The mixture was stirred at 85°C under nitrogen for 4 days, after cooled to ambient temperature, then concentrated in vacuo followed by column chromatography (Al₂O₃), eluting with the mixture of petroleum ether and CH₂Cl₂ to pure the product, as white solid: 544 mg, 32%. ¹H NMR (400 MHz, CDCl₃) δ 8.79-8.74 (d, J = 20 Hz, 8H, ^{A,B}-tpy-H^{3',5'}), 8.71-8.62 (m, 16H, ^{A,B}-tpy-H^{3',3'',6',6''}), 8.34-8.29 (d, J = 25 Hz, 2H, Hⁱ), 8.08 (s, 1H, H^p), 8.02-1.99 (d, J = 12 Hz, 2H, Hⁿ), 7.89-7.81 (td, 10H, ^{A,B}-tpy-H^{4',4''}, H^g), 7.77-7.73 (d, J = 16 Hz, 2H, ^B-tpy-H^j), 7.71-7.66 (d, J = 20 Hz, 4H, ^A-tpy-H^j, H^m), 7.51-7.47 (dd, 2H, ^B-tpy-H^k), 7.42-7.38 (dd, 2H, ^A-tpy-H^k), 7.38-7.35 (d, J = 12 Hz, 2H, ^B-tpy-H^h), 7.33-7.28 (m, 10H, ^{A,B}-tpy-H^{5,5''}, ^A-tpy-H^h), 4.14-4.07 (dd, 8H, H^a), 1.78-1.69 (m, 8H, H^c), 1.44-1.36 (m, 8H, H^d), 1.17-1.02 (m, 16H, H^{e,f}), 0.71-0.63 (m, 12H, H^b); ¹³C NMR (101 MHz, CDCl₃) δ 141.42,

138.74, 134.32, 129.18, 124.43, 124.21, 121.95, 121.66, 120.35, 112.81; ESI-MS (1873.38 calcd. for $C_{126}H_{113}N_{13}O_4$): m/z 1874.9193 $[M + H]^+$ (calcd m/z : 1874.9194).



Supramolecular macrocycles SA: Ligand LA (11.15 mg, 5.95 μmol) and $\text{Zn}(\text{NTf}_2)_2$ (7.45 mg, 11.90 μmol) was added to a 100 ml flask, then a solvent mixture of MeOH and CHCl_3 (30 ml, V:V=1:2) was added. The mixture was refluxed for 12 h. After cooled to ambient temperature, excess bistrifluoromethanesulfonimide lithium salt (LiNTf_2) in MeOH was added to get a faint yellow precipitate, which was filtered and washed with MeOH to generate a faint yellow solid: 17 mg, 91.4%. The composition of SA is a mixture of $\text{Zn}_{16}\text{LA}_8$, $\text{Zn}_{18}\text{LA}_9$ and $\text{Zn}_{20}\text{LA}_{10}$. ^1H NMR (400 MHz, CD_3CN) δ 9.24-9.03 (m, 8H, A,B-tpy- $\text{H}^{3',5'}$), 8.81-8.57 (m, 8H, A,B-tpy- $\text{H}^{3,3''}$), 8.49 (m, 2H, H^i), 8.32 (m, 1H, H^p), 8.19-7.82 (m, 11H, A,B-tpy- $\text{H}^{4,4''}$, $\text{H}^{n,g}$), 7.77-7.62 (m, 14H, A,B-tpy- $\text{H}^{6,6''}$, H^j , H^m), 7.40-7.25 (m, 16H, A,B-tpy- $\text{H}^{5,5''}$, H^h , H^k), 4.51-4.17 (m, 4H, H^a), 1.89-1.68 (m, 4H, H^c), 1.47-1.21 (m, 4H, H^d), 1.08-0.78 (m, 4H, H^e), 0.77-0.45 (m, 4H, H^f), 0.37-0.06 (m, 4H, H^b). **$\text{Zn}_{16}\text{LA}_8$.** ESI-MS (m/z): 2844.6199 $[\text{M}-8\text{NTf}_2^-]^{8+}$ (calcd m/z : 2844.6400), 2794.2146 $[\text{M}-9\text{NTf}_2^-]^{9+}$ (calcd m/z : 2497.4422), 2219.6289 $[\text{M}-10\text{NTf}_2^-]^{10+}$ (calcd m/z : 2219.684), 1992.3918 $[\text{M}-11\text{NTf}_2^-]^{11+}$ (calcd m/z : 1992.4273), 1803.1204 $[\text{M}-12\text{NTf}_2^-]^{12+}$ (calcd m/z : 1803.0467), 1642.8075 $[\text{M}-13\text{NTf}_2^-]^{13+}$ (calcd m/z : 1642.8015), 1505.4685 $[\text{M}-14\text{NTf}_2^-]^{14+}$ (calcd m/z : 1505.4486), 1386.4355 $[\text{M}-15\text{NTf}_2^-]^{15+}$ (calcd m/z : 1386.4093), 1282.2284 $[\text{M}-16\text{NTf}_2^-]^{16+}$ (calcd m/z : 1282.2500), 1190.3326 $[\text{M}-17\text{NTf}_2^-]^{17+}$ (calcd m/z : 1190.3447), 1108.6614 $[\text{M}-18\text{NTf}_2^-]^{18+}$ (calcd m/z : 1108.6511), 1035.5750 $[\text{M}-19\text{NTf}_2^-]^{19+}$ (calcd m/z : 1035.5568), 969.6026 $[\text{M}-20\text{NTf}_2^-]^{20+}$ (calcd m/z : 969.7720), 910.3305 $[\text{M}-21\text{NTf}_2^-]^{21+}$ (calcd m/z : 910.2524), 856.1362 $[\text{M}-22\text{NTf}_2^-]^{22+}$ (calcd m/z : 856.1436). **$\text{Zn}_{18}\text{LA}_9$.** ESI-MS (m/z): 1728.7234 $[\text{M}-14\text{NTf}_2^-]^{14+}$ (calcd m/z : 1728.6471), 1594.6934 $[\text{M}-15\text{NTf}_2^-]^{15+}$ (calcd m/z : 1594.7280), 1477.4442 $[\text{M}-16\text{NTf}_2^-]^{16+}$ (calcd m/z : 1477.5488), 1374.1235 $[\text{M}-17\text{NTf}_2^-]^{17+}$ (calcd m/z : 1374.1553), 1282.2284 $[\text{M}-18\text{NTf}_2^-]^{18+}$ (calcd m/z : 1282.2500), 1200.0233 $[\text{M}-19\text{NTf}_2^-]^{19+}$ (calcd m/z : 1200.0189), 1125.9264 $[\text{M}-20\text{NTf}_2^-]^{20+}$ (calcd m/z : 1126.0110), 1059.0728 $[\text{M}-21\text{NTf}_2^-]^{21+}$ (calcd m/z : 1059.0514), 998.1652 $[\text{M}-22\text{NTf}_2^-]^{22+}$ (calcd m/z : 998.1791), 942.4628 $[\text{M}-23\text{NTf}_2^-]^{23+}$ (calcd m/z : 942.6000), 891.6550 $[\text{M}-24\text{NTf}_2^-]^{24+}$ (calcd m/z : 891.6525), 844.7531 $[\text{M}-25\text{NTf}_2^-]^{25+}$ (calcd m/z : 844.7808). **$\text{Zn}_{20}\text{LA}_{10}$.** ESI-MS (m/z): 2123.5181 $[\text{M}-13\text{NTf}_2^-]^{13+}$ (calcd m/z : 2123.5369), 1951.8488 $[\text{M}-14\text{NTf}_2^-]^{14+}$ (calcd m/z : 1951.8457), 1803.1204 $[\text{M}-15\text{NTf}_2^-]^{15+}$ (calcd m/z : 1803.0467), 1672.7977 $[\text{M}-16\text{NTf}_2^-]^{16+}$ (calcd m/z : 1672.8475), 1557.9265 $[\text{M}-17\text{NTf}_2^-]^{17+}$ (calcd m/z : 1557.9659), 1455.9407 $[\text{M}-18\text{NTf}_2^-]^{18+}$

(calcd m/z : 1455.8489), 1364.4136 $[M-19NTf_2^-]^{19+}$ (calcd m/z : 1364.4811), 1282.2284 $[M-20NTf_2^-]^{20+}$ (calcd m/z : 1282.2500), 1207.8102 $[M-21NTf_2^-]^{21+}$ (calcd m/z : 1207.8505), 1140.1382 $[M-22NTf_2^-]^{22+}$ (calcd m/z : 1140.2145), 1078.3562 $[M-23NTf_2^-]^{23+}$ (calcd m/z : 1078.4600), 1021.9628 $[M-24NTf_2^-]^{24+}$ (calcd m/z : 1021.8517).

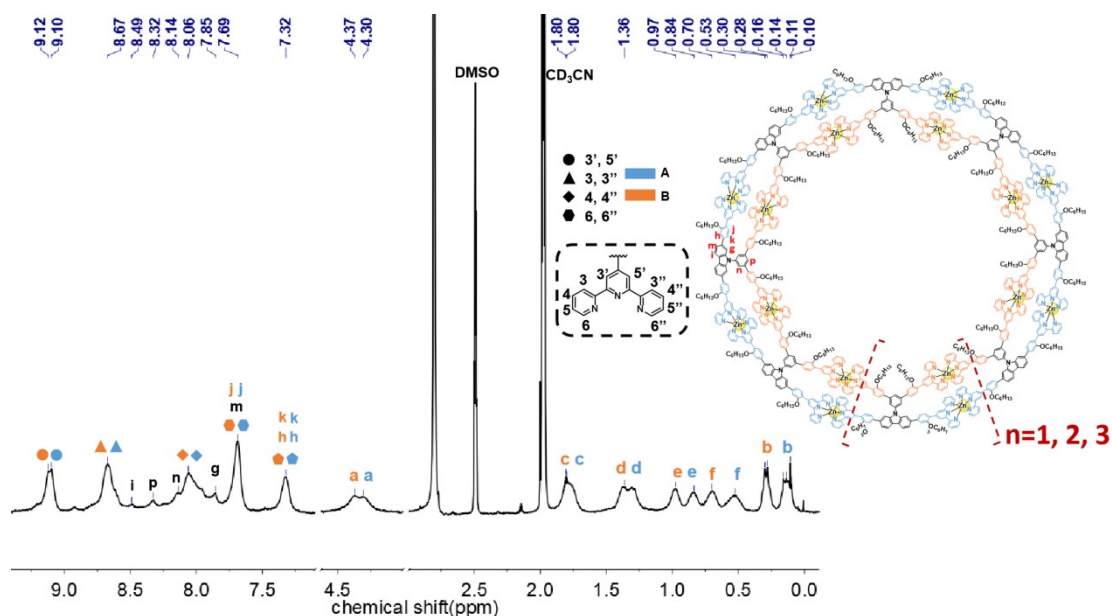


Figure S6. 1H NMR spectrum (400 MHz) of supramolecular macrocycles SA in DMSO- d_6 /CD $_3$ CN (1:9).

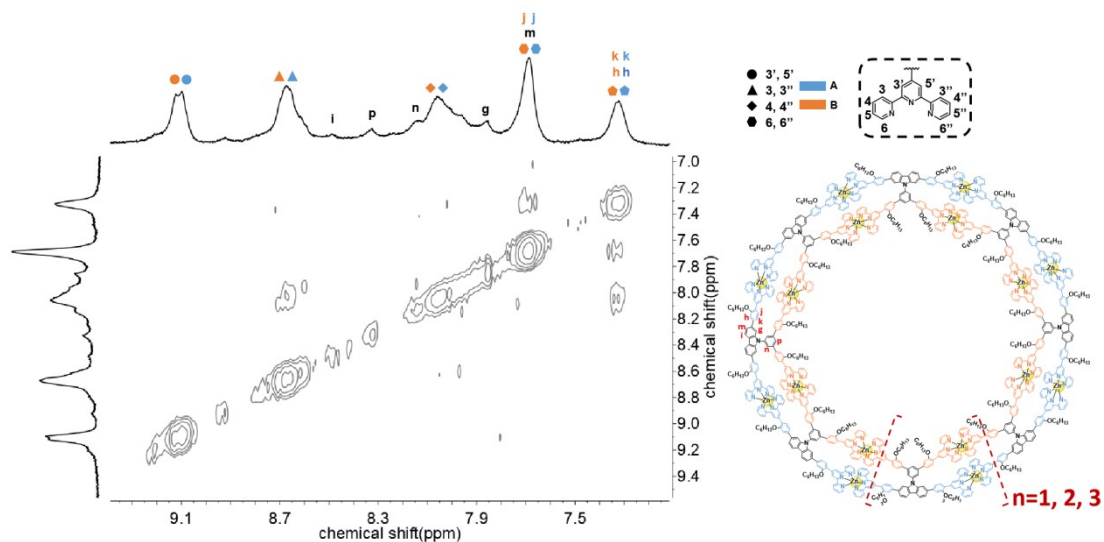


Figure S7. 2D COSY NMR spectrum (400 MHz) of supramolecular macrocycles SA in DMSO- d_6 /CD $_3$ CN (1:9).

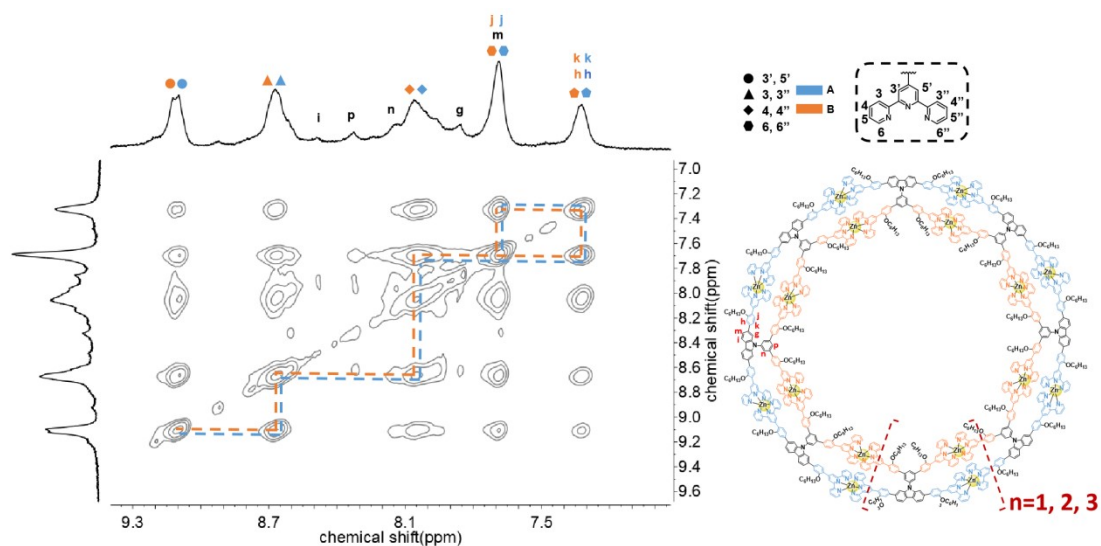


Figure S8. 2D NOESY NMR spectrum (400 MHz) of supramolecular macrocycles SA in DMSO- d_6 /CD $_3$ CN (1:9).

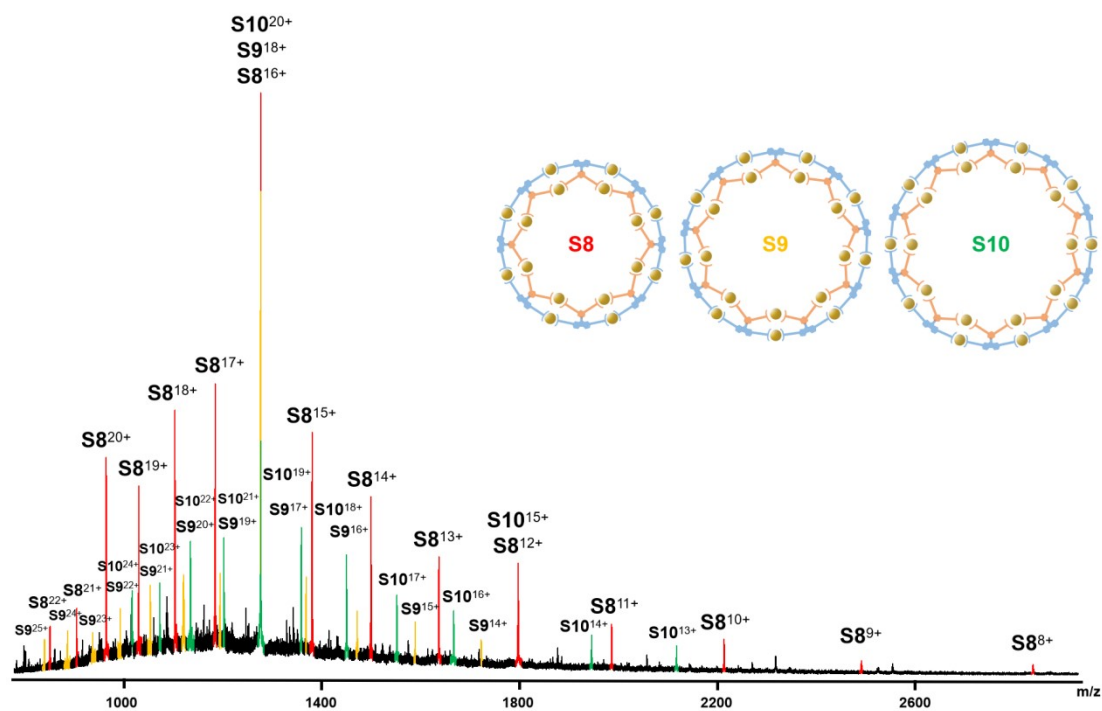


Figure S9. ESI-MS spectrum of supramolecular macrocycles SA (NTf_2^- as counterion).

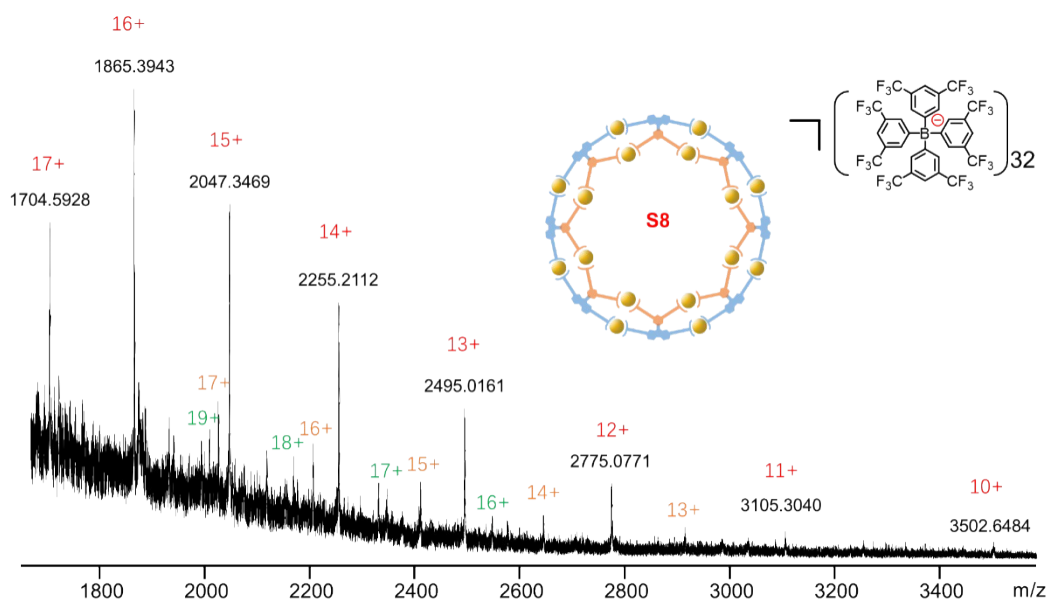


Figure S10. ESI-MS spectrum of supramolecular macrocycles SA ($C_{32}H_{12}BF_{24}^-$ as counterion), which displayed a series of major ESI-MS peaks that derived from the giant dual-rim octamer nanoring.

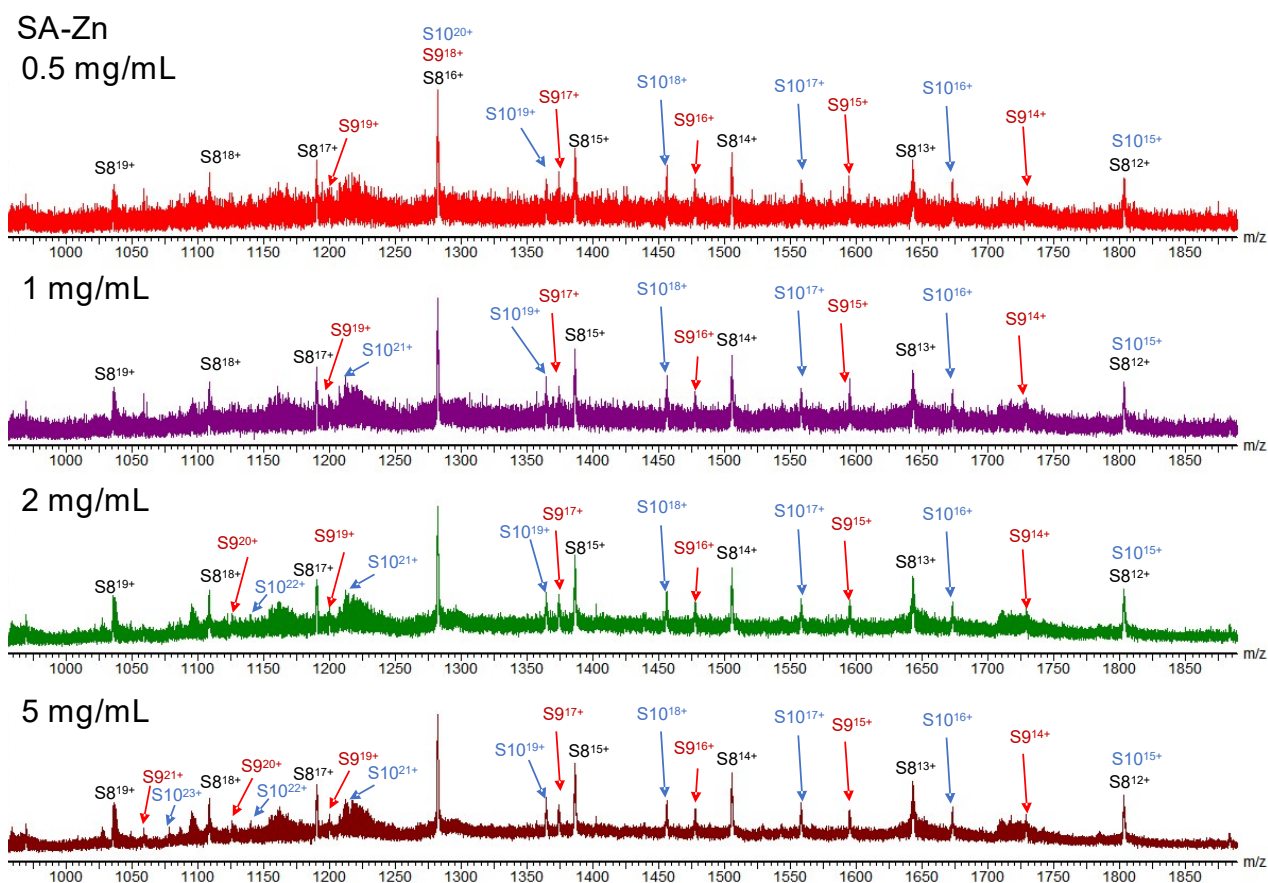
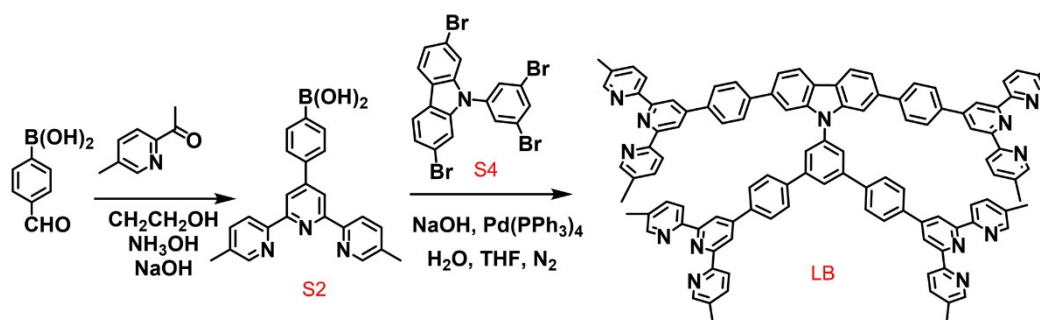
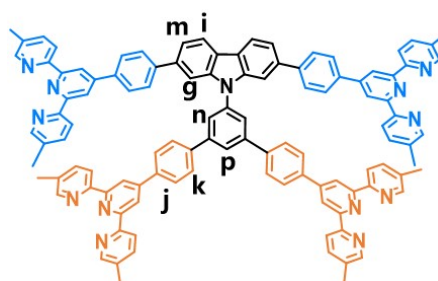


Figure S11. ESI-MS spectrum of the SA-Zn with concentration ranging from 0.5 mg/mL to 5 mg/mL.

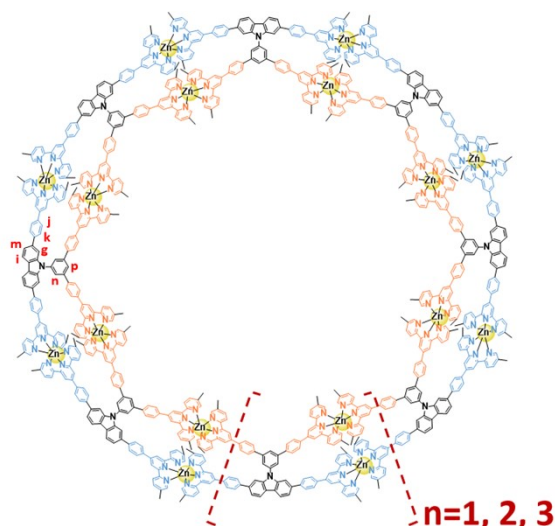
5. Synthesis of the ligand LB and supramolecular macrocycles SB



Scheme S2: The synthetic route of the Ligand LB.



Compound LB: Compound **1** (0.5 g, 0.89 mmol), Compound **5** (1.774 g, 4.65 mmol) were added to a 250 mL flask, then THF (80 mL) and NaOH (0.429 g, 10.74 mmol) in 11 mL of water was added. The Pd(PPh₃)₄ (0.2 g, 0.18 mmol) as the catalyst was added and the system was degassed using N₂. The mixture was stirred at 85°C under nitrogen for 4 days, after cooled to ambient temperature, then concentrated in vacuo followed by column chromatography (Al₂O₃), eluting with the mixture of petroleum ether and CH₂Cl₂ to pure the product, as golden yellow solid: 0.856 g, 61%. ¹H NMR (600 MHz, CDCl₃) δ 8.73-8.67 (d, J = 36 Hz, 8H, ^{A,B}-tpy-H^{3',5'}), 8.51 (m, 16H, ^{A,B}-tpy-H^{3'',3''',6,6''}), 8.27-8.23 (d, J = 24 Hz, 2H, Hⁱ), 8.09 (s, 1H, H^p), 8.05-8.01 (d, J = 24 Hz, 4H, ^A-tpy-H^j), 7.99-7.95 (d, J = 24 Hz, 4H, ^B-tpy-H^j), 7.94 (s, 2H, H^g), 7.89-7.85 (d, J = 24 Hz, 4H, ^A-tpy-H^k), 7.83-7.79 (d, J = 24 Hz, 6H, Hⁿ, ^B-tpy-H^k), 7.68-7.60 (m, 10H, ^{A,B}-tpy-H^{4,4''}), 2.38 (s, 24H, ^{A,B}-Me-H^{5,5''}). ¹³C NMR (101 MHz, CDCl₃) δ 141.42, 138.74, 134.32, 129.18, 124.43, 124.21, 121.95, 121.66, 120.35, 112.81; ESI-MS (1584.95 calcd. For C₁₁₀H₈₁N₁₃): m/z 1585.6815 [M + H]⁺ (calcd m/z: 1585.6816).



Supramolecular macrocycles SB: Ligand **LB** (5.22 mg, 3.29 μmol) and $\text{Zn}(\text{NTf}_2)_2$ (4.12 mg, 6.59 μmol) was added to a 100 ml flask, then a solvent mixture of MeOH and CHCl_3 (30 ml, V:V=1:2) was added. The mixture was refluxed for 12 h. After cooled to ambient temperature, excess bistrifluoromethanesulfonimide lithium salt (LiNTf_2) in MeOH was added to get a faint yellow precipitate, which was filtered and washed with MeOH to generate a faint yellow solid: 8 mg, 85.6%. The composition of **SB** is a mixture of **Zn₁₆LB₈**, **Zn₁₈LB₉** and **Zn₂₀LB₁₀**. ^1H NMR (400 MHz, CD_3CN) δ 9.25-8.96 (d, $J = 116$ Hz, 8H, $^{\text{A, B}}$ -tpy- $\text{H}^{3,5'}$), 8.80-8.50 (m, 10H, $^{\text{A, B}}$ -tpy- $\text{H}^{3,3''}$, H^{i}), 8.49-8.32 (m, 10H, H^{j} , H^{p}), 8.31-8.09 (m, 10H, H^{k} , H^{g}), 8.08-7.95 (m, 2H, H^{n}), 7.71-7.30 (m, 18H, $^{\text{A, B}}$ -tpy- $\text{H}^{4,4''}$, $^{6,6''}$, H^{m}), 1.92-1.79 (m, 12H, $^{\text{A, B}}$ -tpy- H^{Me}). **Zn₁₆LB₈**. ESI-MS (m/z): 1989.0968 [$\text{M}-10\text{NTf}_2^-$] $^{10+}$ (calcd m/z : 1988.9400), 1782.6381 [$\text{M}-11\text{NTf}_2^-$] $^{11+}$ (calcd m/z : 1782.6600), 1610.7992 [$\text{M}-12\text{NTf}_2^-$] $^{12+}$ (calcd m/z : 1610.7600), 1465.181 [$\text{M}-13\text{NTf}_2^-$] $^{13+}$ (calcd m/z : 1465.3062), 1340.4917 [$\text{M}-14\text{NTf}_2^-$] $^{14+}$ (calcd m/z : 1340.6314), 1232.4807 [$\text{M}-15\text{NTf}_2^-$] $^{15+}$ (calcd m/z : 1232.5800), 1137.9879 [$\text{M}-16\text{NTf}_2^-$] $^{16+}$ (calcd m/z : 1138.0350), 1054.4823 [$\text{M}-17\text{NTf}_2^-$] $^{17+}$ (calcd m/z : 1054.6129), 980.5468 [$\text{M}-17\text{NTf}_2^-$] $^{17+}$ (calcd m/z : 980.4600). **Zn₁₈LB₉**. ESI-MS (m/z): 2040.8651 [$\text{M}-11\text{NTf}_2^-$] $^{11+}$ (calcd m/z : 2040.5100), 1847.2660 [$\text{M}-12\text{NTf}_2^-$] $^{12+}$ (calcd m/z : 1847.1225), 1683.7830 [$\text{M}-13\text{NTf}_2^-$] $^{13+}$ (calcd m/z : 1683.4869), 1543.1353 [$\text{M}-14\text{NTf}_2^-$] $^{14+}$ (calcd m/z : 1543.2279), 1421.6132 [$\text{M}-15\text{NTf}_2^-$] $^{15+}$ (calcd m/z : 1421.6700), 1315.1100 [$\text{M}-16\text{NTf}_2^-$] $^{16+}$ (calcd m/z : 1315.3069), 1221.5123 [$\text{M}-17\text{NTf}_2^-$] $^{17+}$ (calcd m/z : 1221.4571), 1137.9879 [$\text{M}-18\text{NTf}_2^-$] $^{18+}$ (calcd m/z : 1138.0350), 1063.0372 [$\text{M}-19\text{NTf}_2^-$] $^{19+}$ (calcd m/z : 1063.3942), 996.0065 [$\text{M}-20\text{NTf}_2^-$] $^{20+}$ (calcd m/z : 996.2175). **Zn₂₀LB₁₀**. ESI-MS (m/z): 2083.8386 [$\text{M}-12\text{NTf}_2^-$] $^{12+}$ (calcd m/z : 2083.4850), 1901.8301 [$\text{M}-13\text{NTf}_2^-$] $^{13+}$ (calcd m/z : 1901.6677), 1745.5701 [$\text{M}-14\text{NTf}_2^-$] $^{14+}$ (calcd m/z : 1745.8243), 1610.7992 [$\text{M}-15\text{NTf}_2^-$] $^{15+}$ (calcd m/z : 1610.7600), 1492.6056 [$\text{M}-16\text{NTf}_2^-$] $^{16+}$ (calcd m/z : 1492.5788), 1388.5630 [$\text{M}-17\text{NTf}_2^-$] $^{17+}$ (calcd m/z : 1388.3012), 1295.5450 [$\text{M}-18\text{NTf}_2^-$] $^{18+}$ (calcd m/z : 1295.6100), 1212.4930 [$\text{M}-19\text{NTf}_2^-$] $^{19+}$ (calcd m/z : 1212.6758), 1137.9879 [$\text{M}-20\text{NTf}_2^-$] $^{20+}$ (calcd m/z : 1138.0350), 1070.0546 [$\text{M}-21\text{NTf}_2^-$] $^{21+}$ (calcd m/z : 1070.5029), 1009.0050 [$\text{M}-22\text{NTf}_2^-$] $^{22+}$ (calcd m/z : 1009.1100).

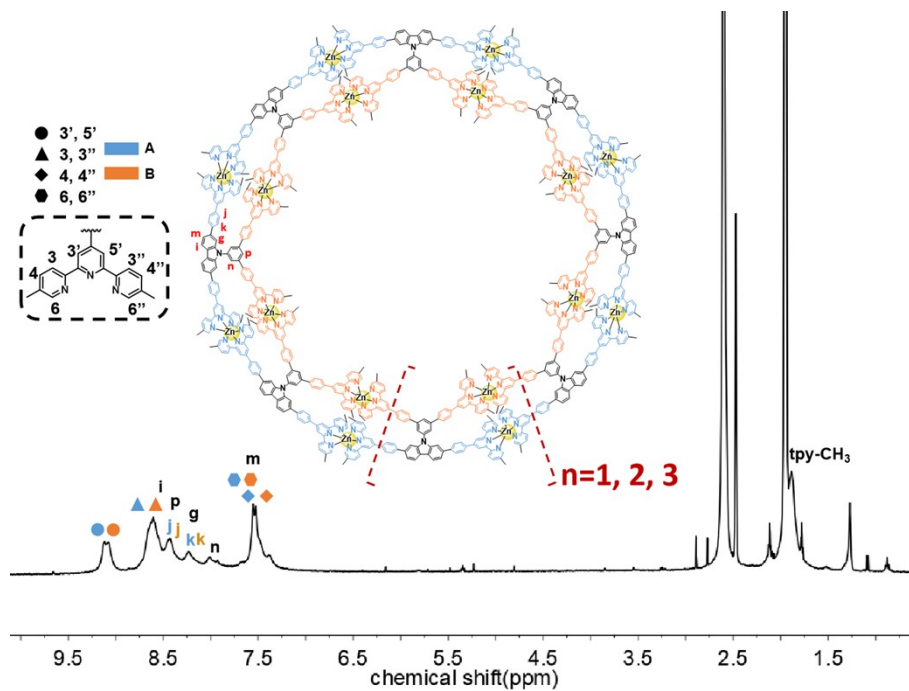


Figure S12. ^1H NMR spectrum (400 MHz) of supramolecular macrocycles **SB** in $\text{DMSO-d}_6/\text{CD}_3\text{CN}$ (1:9).

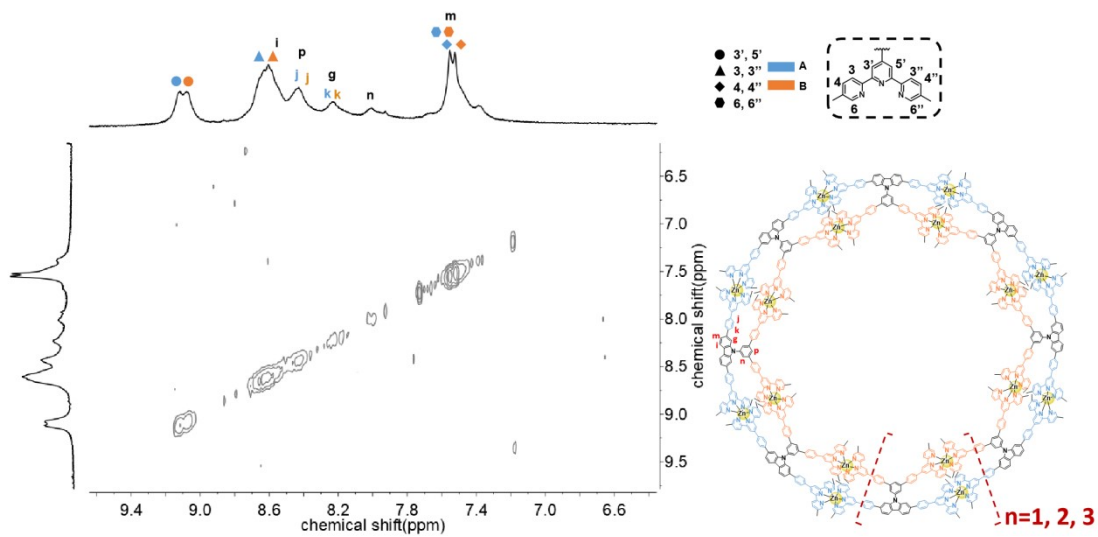


Figure S13. 2D COSY NMR spectrum (400 MHz) of supramolecular macrocycles **SB** in $\text{DMSO-d}_6/\text{CD}_3\text{CN}$ (1:9).

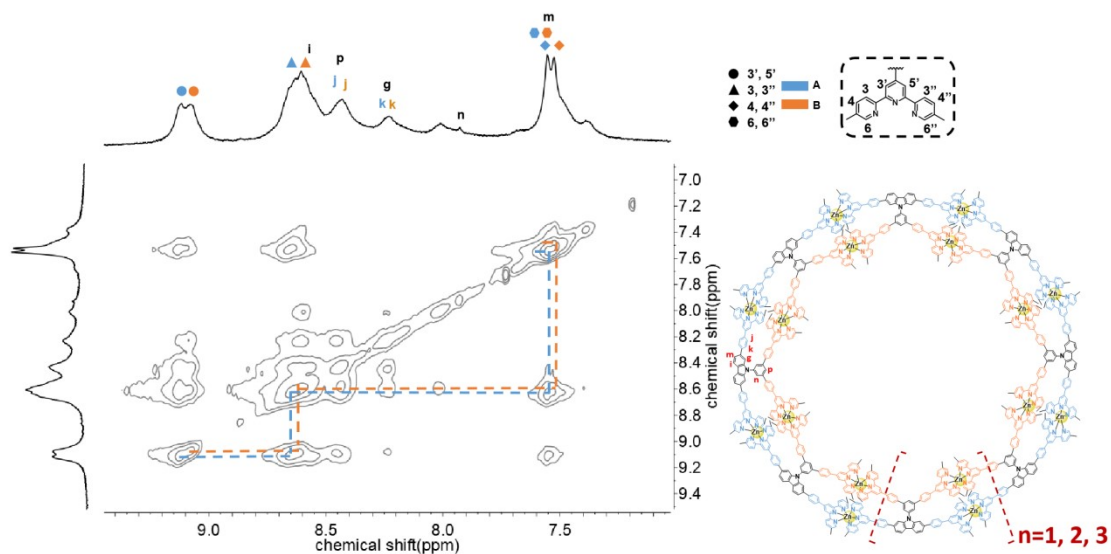


Figure S14. 2D NOESY NMR spectrum (400 MHz) of supramolecular macrocycles **SB** in DMSO- d_6 /CD $_3$ CN (1:9).

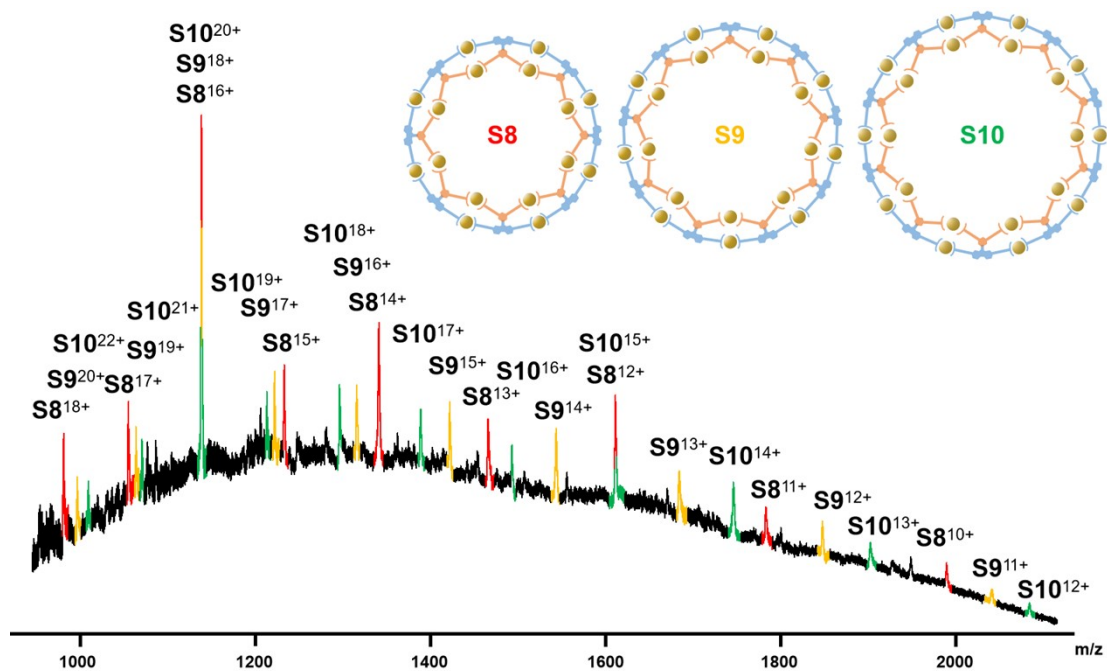
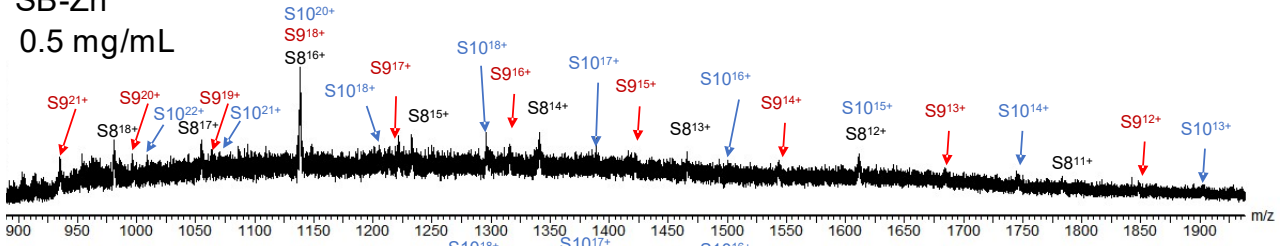


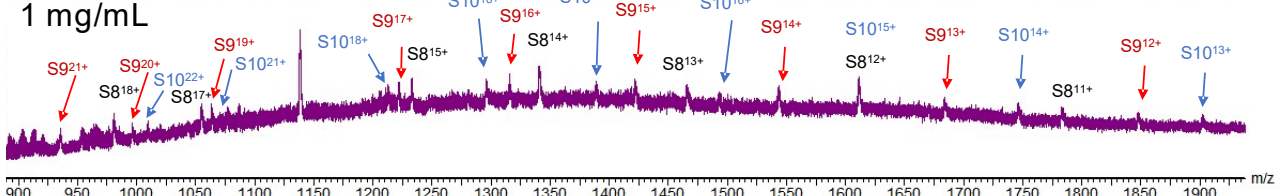
Figure S15. ESI-MS spectrum of supramolecular macrocycles **SB** (NTf $_2^-$ as counterion).

SB-Zn

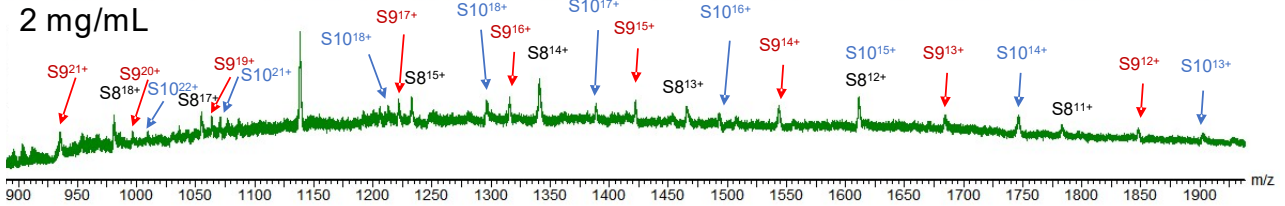
0.5 mg/mL



1 mg/mL



2 mg/mL



5 mg/mL

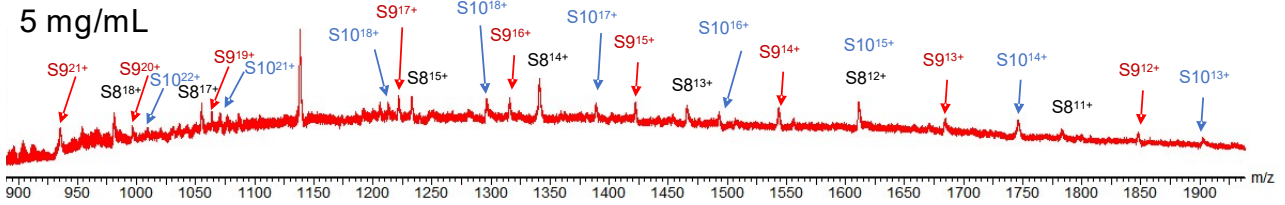


Figure S16. ESI-MS spectrum of the SB-Zn with concentration ranging from 0.5 mg/mL to 5 mg/mL.

6. ^1H NMR, ^{13}C NMR, COSY and NOESY NMR spectra of other compounds

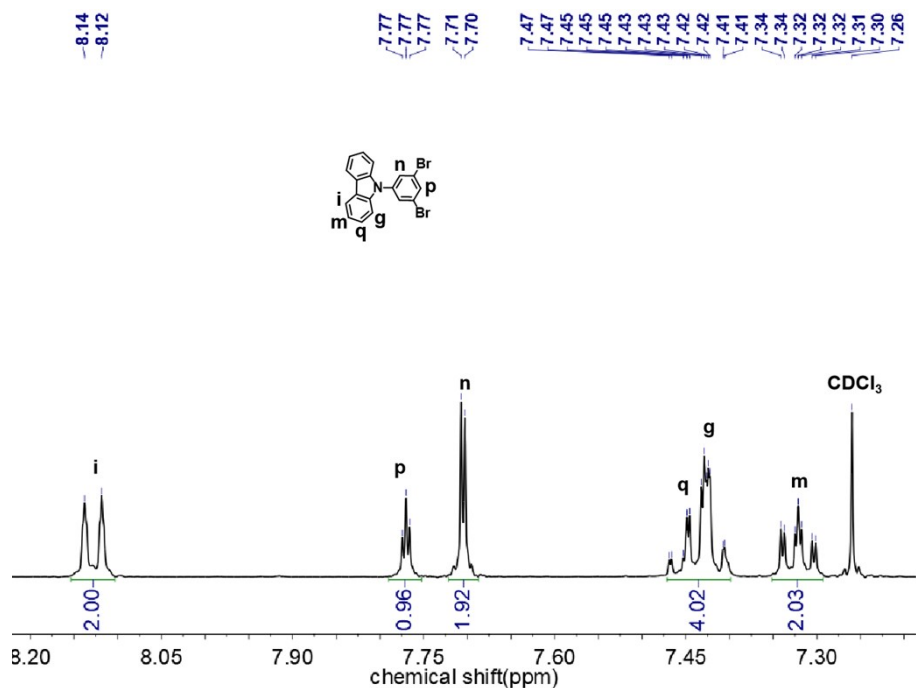


Figure S17. ^1H NMR spectrum (400 MHz) of Compound S1 in CDCl_3 .

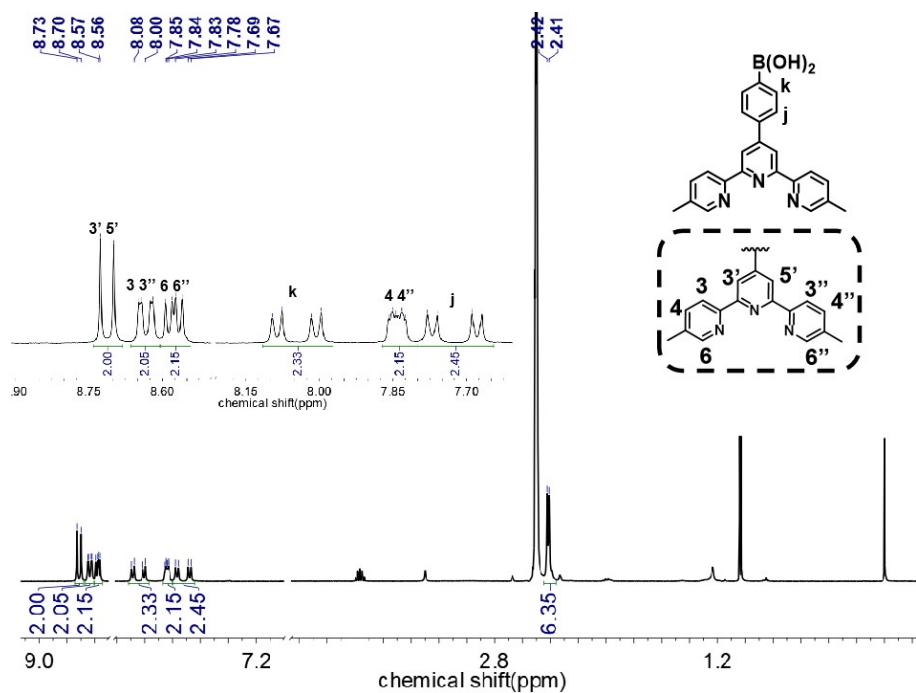


Figure S18. ^1H NMR spectrum (400 MHz) of S2 in CD_3OD .

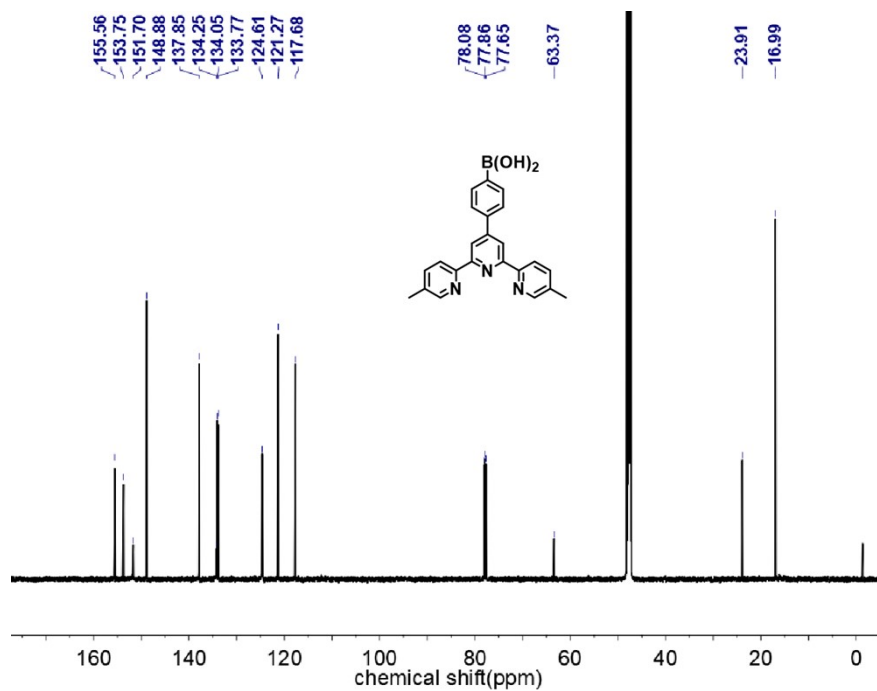


Figure S19. ¹³C NMR spectrum (101 MHz) of S2 in CD₃OD.

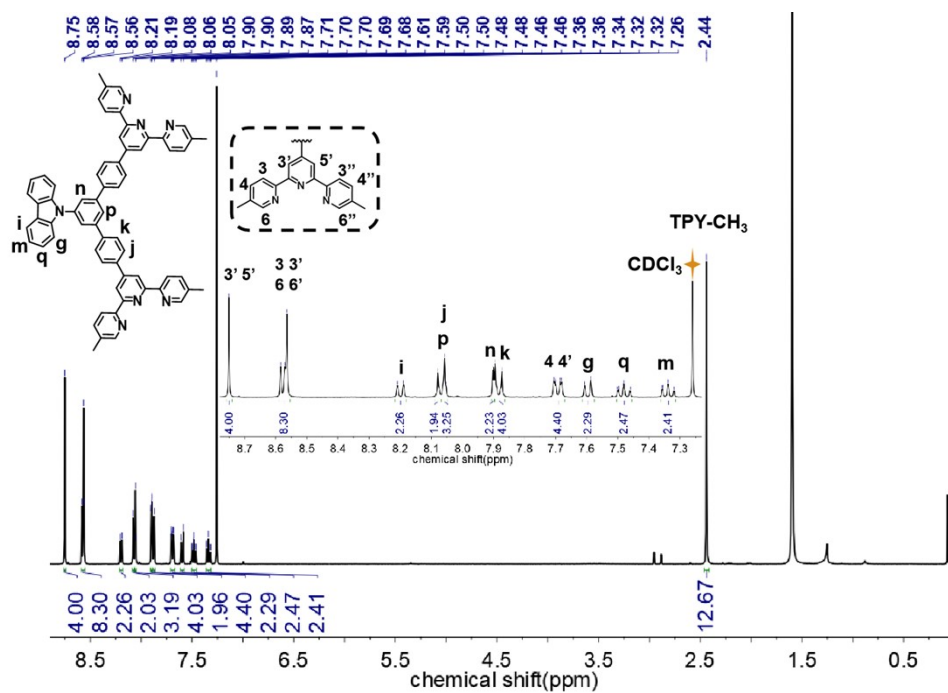


Figure S20. ¹H NMR spectrum (400 MHz) of Ligand 1 in CDCl₃.

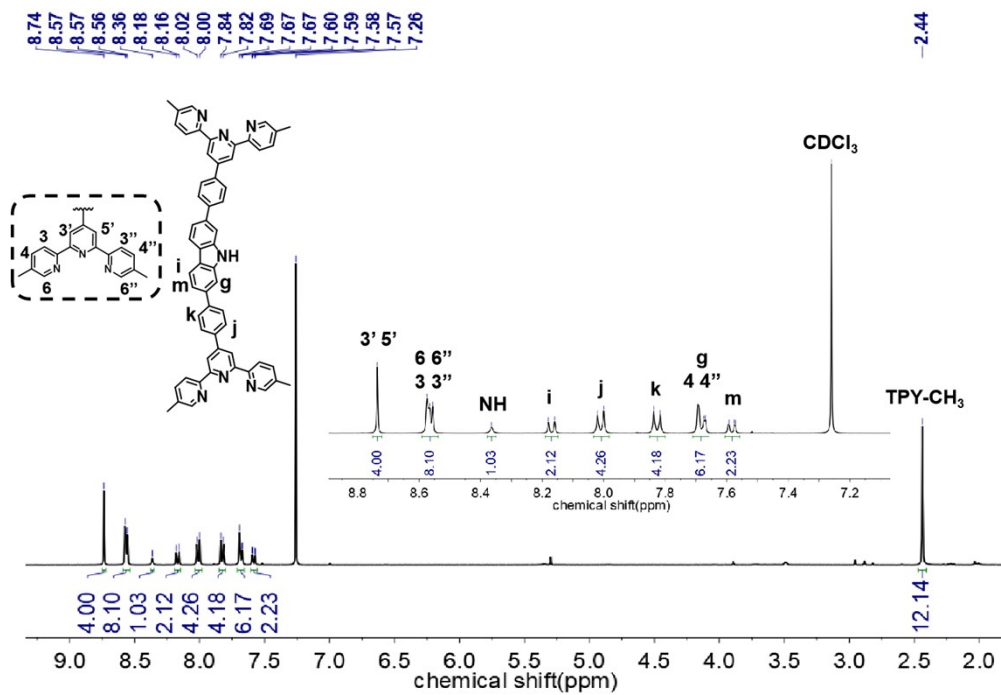


Figure S21. ¹H NMR spectrum (400 MHz) of Compound S3 in CDCl₃.

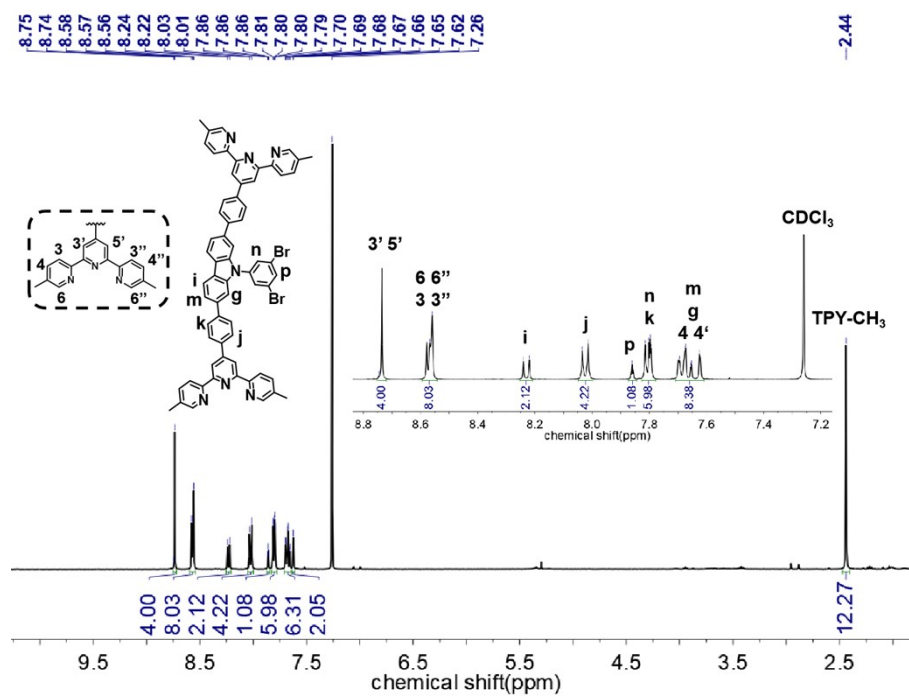


Figure S22. ¹H NMR spectrum (400 MHz) of Ligand 3 in CDCl₃.

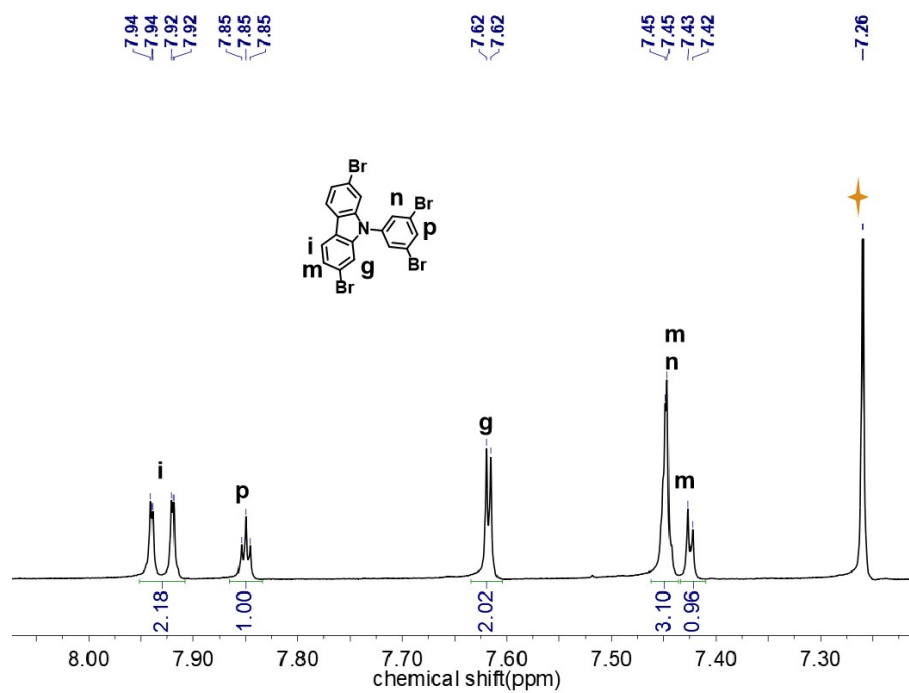


Figure S23. ^1H NMR spectrum (400 MHz) of **5** in CDCl_3 .

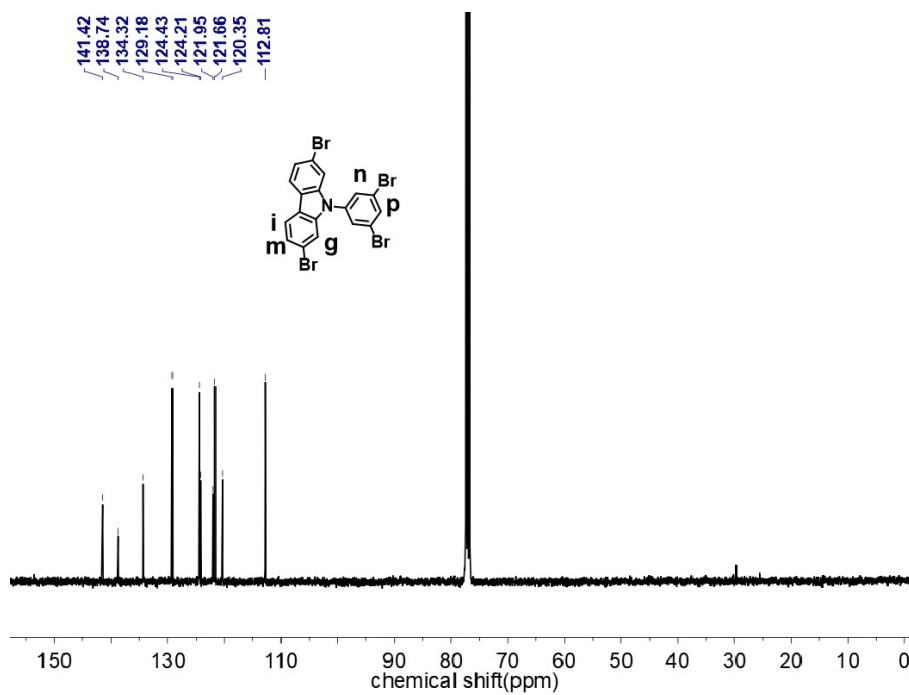


Figure S24. ^{13}C NMR spectrum (101 MHz) of **5** in CDCl_3 .

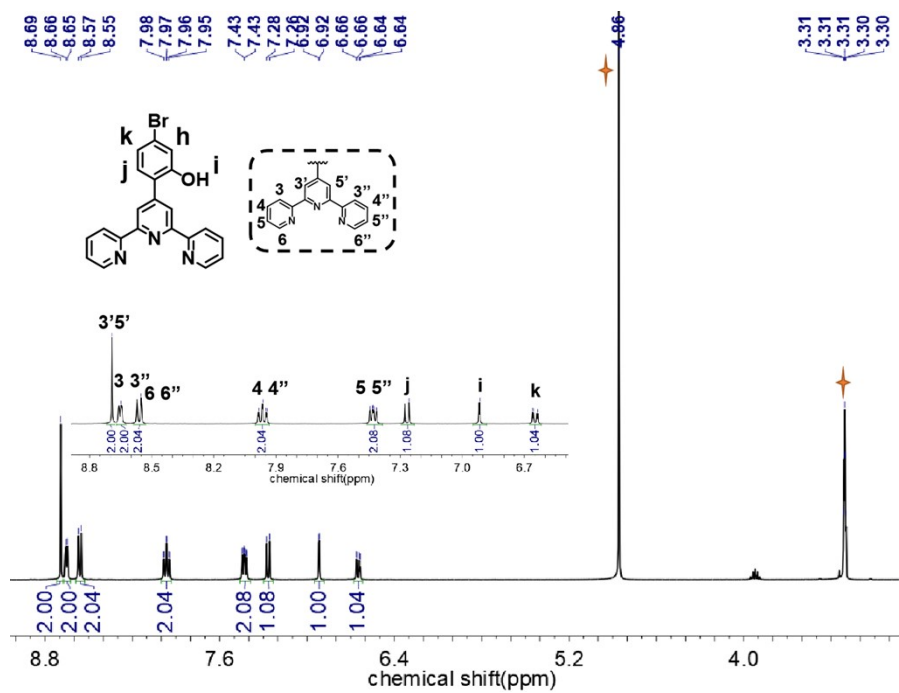


Figure S25. ¹H NMR spectrum (400 MHz) of S5 in CD₃OD.

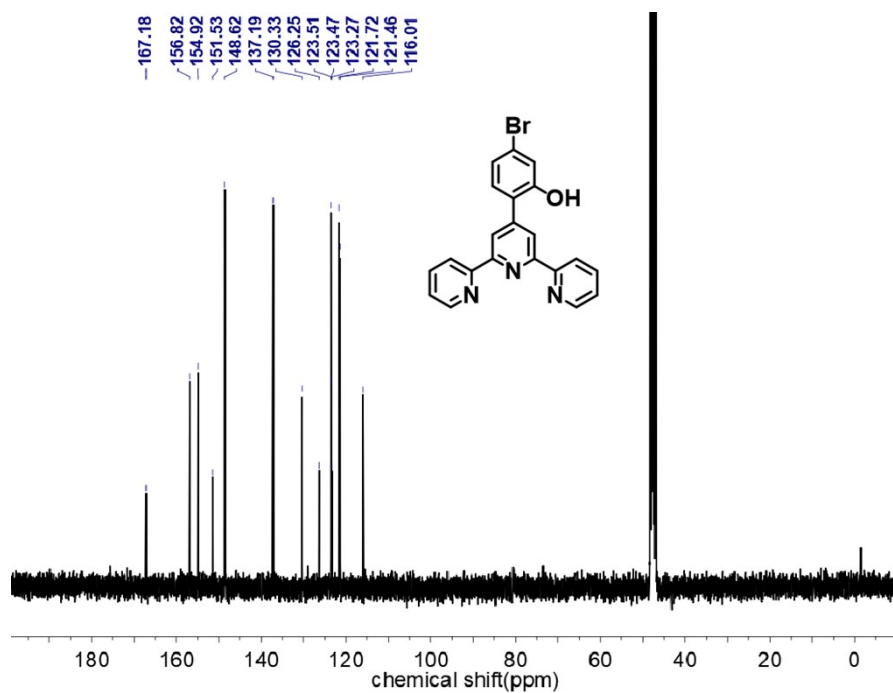


Figure S26. ¹³C NMR spectrum (101 MHz) of S5 in CD₃OD.

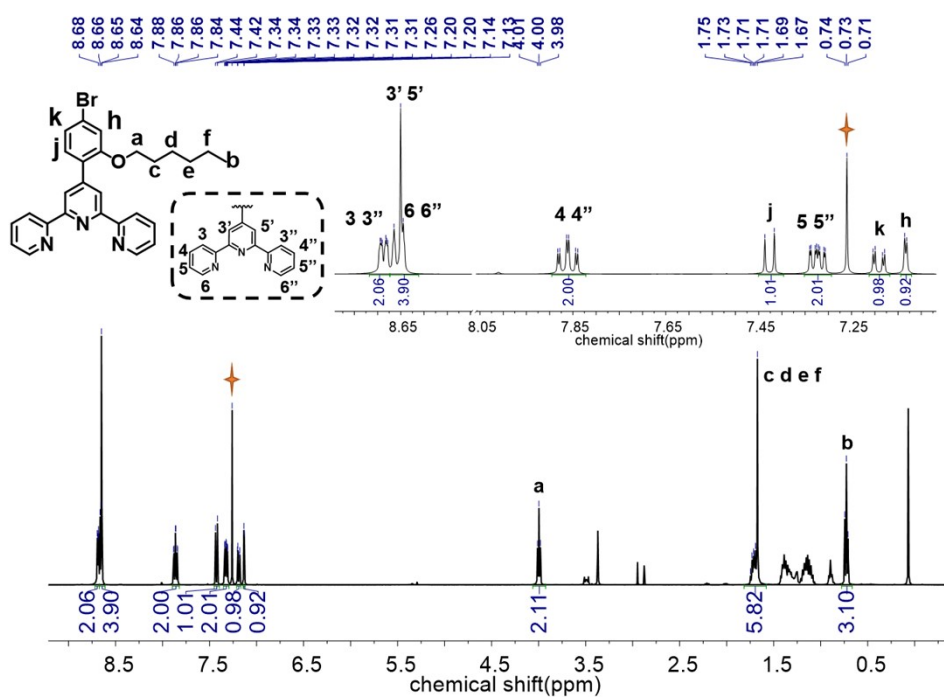


Figure S27. ¹H NMR spectrum (400 MHz) of **S6** in CDCl₃.

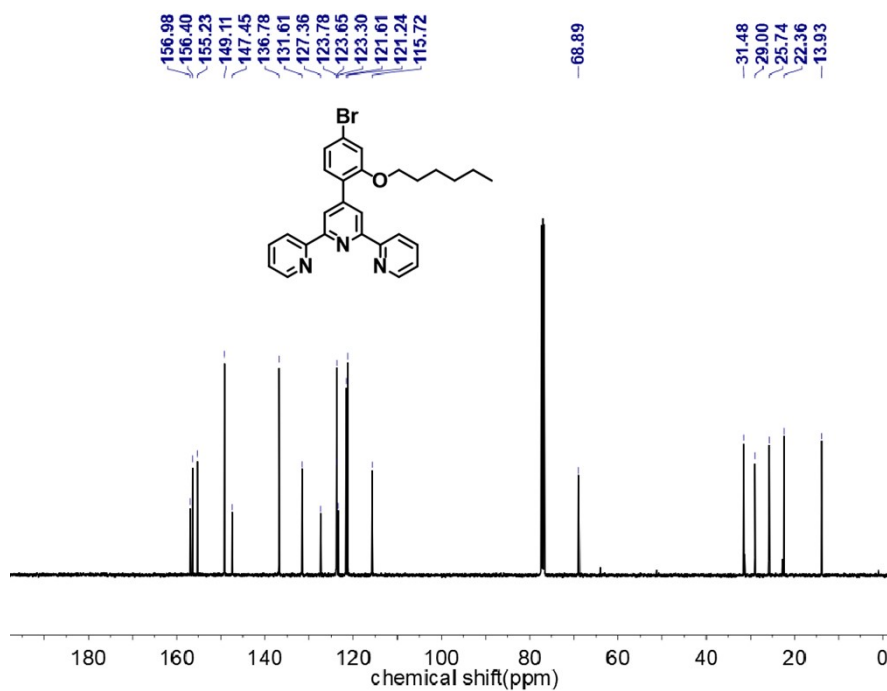


Figure S28. ¹³C NMR spectrum (101 MHz) of **S6** in CDCl₃.

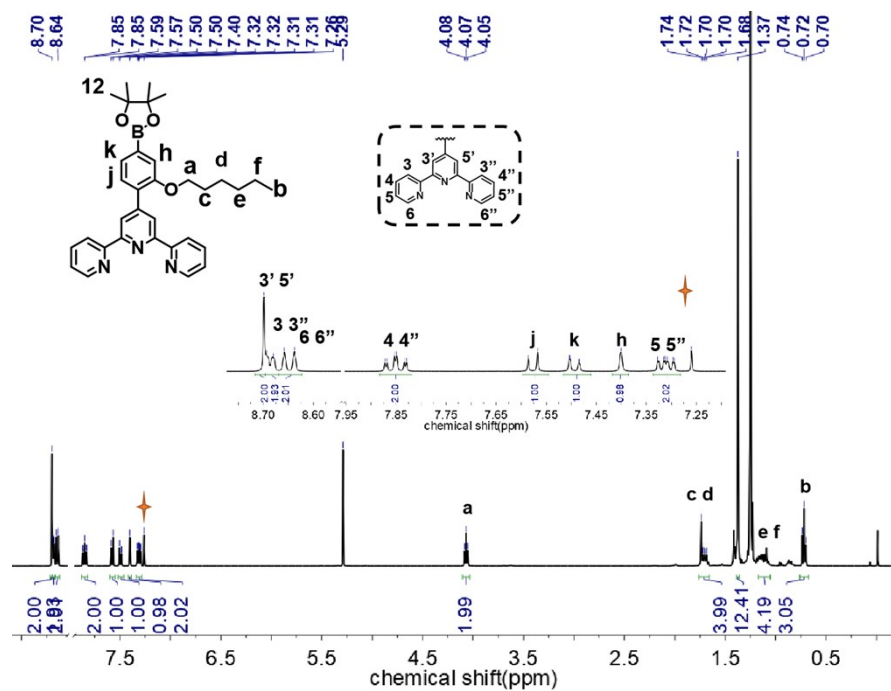


Figure S29. ¹H NMR spectrum (400 MHz) of S7 in CDCl₃.

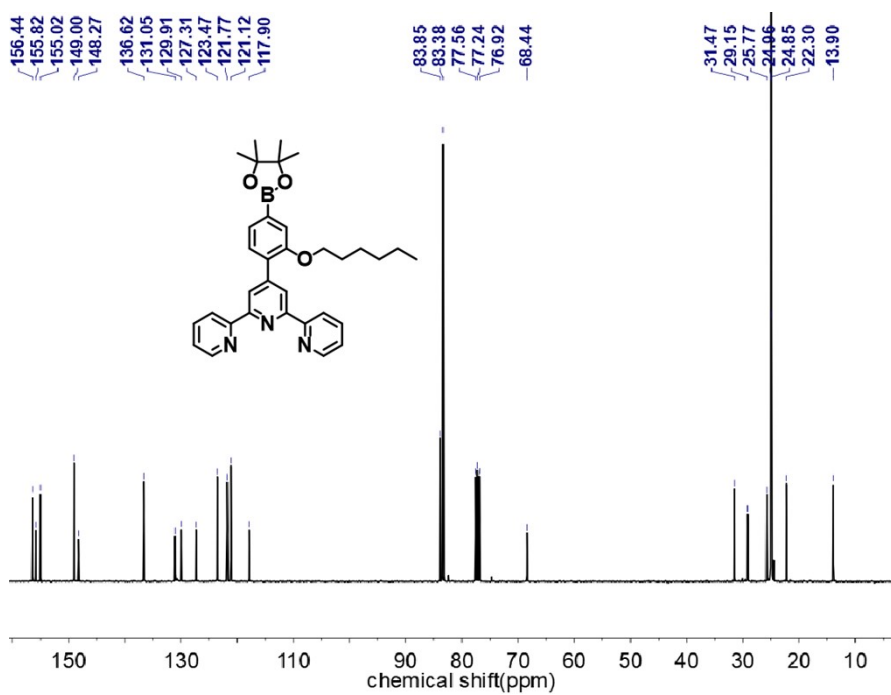


Figure S30. ¹³C NMR spectrum (101 MHz) of S7 in CDCl₃.

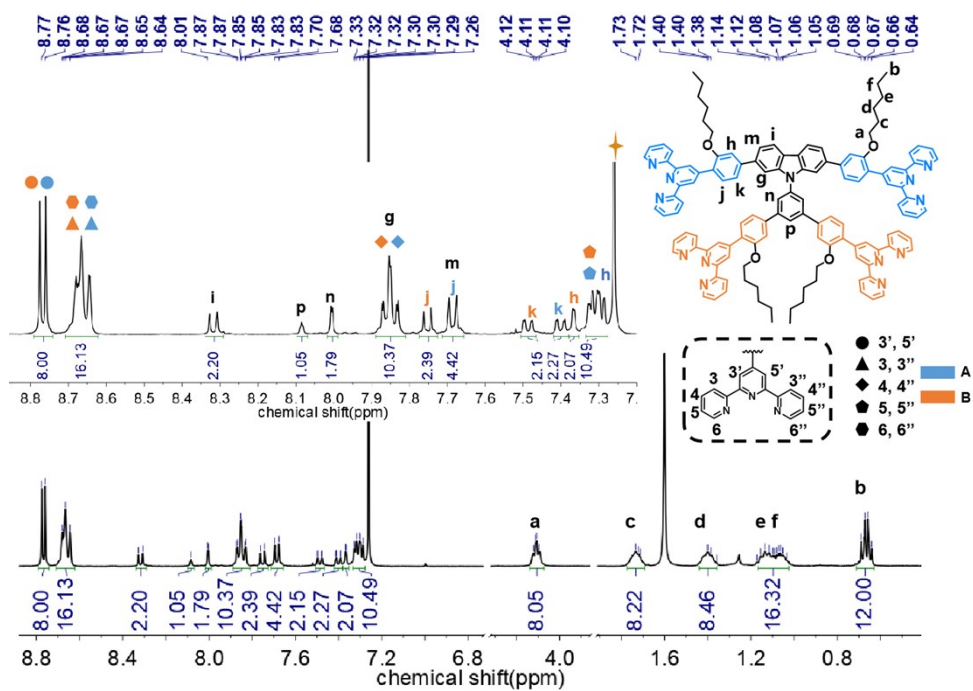


Figure S31. ^1H NMR spectrum (400 MHz) of ligand LA in CDCl_3 .

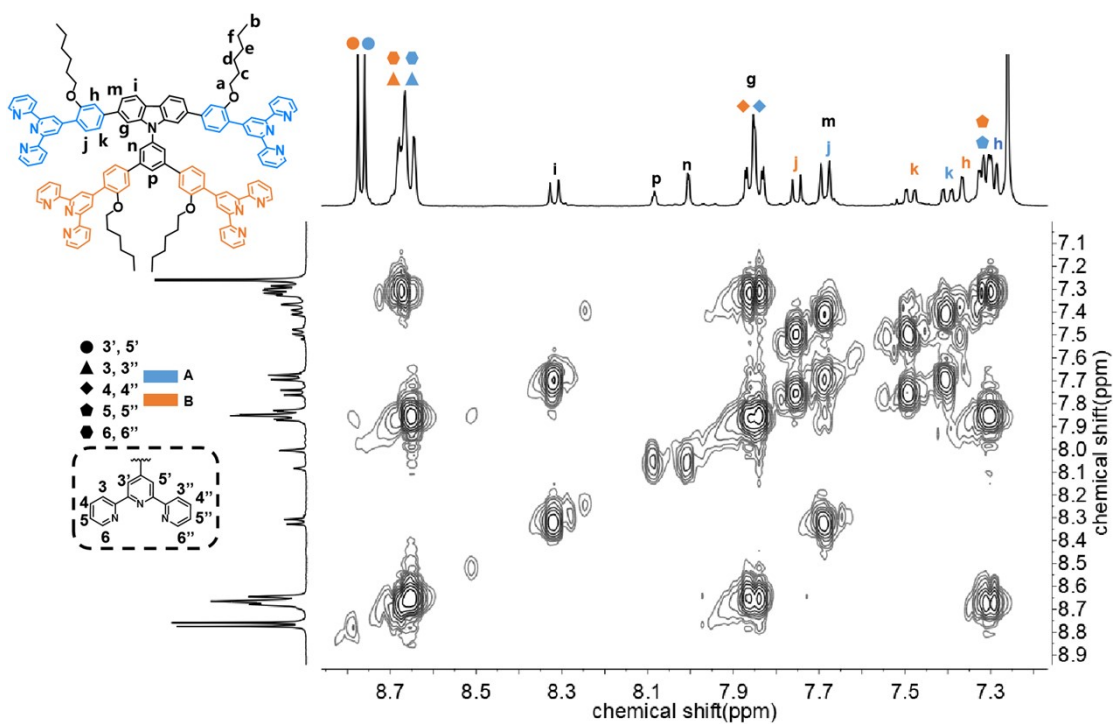


Figure S32. 2D COSY NMR spectrum (400 MHz) of ligand LA in CDCl_3 .

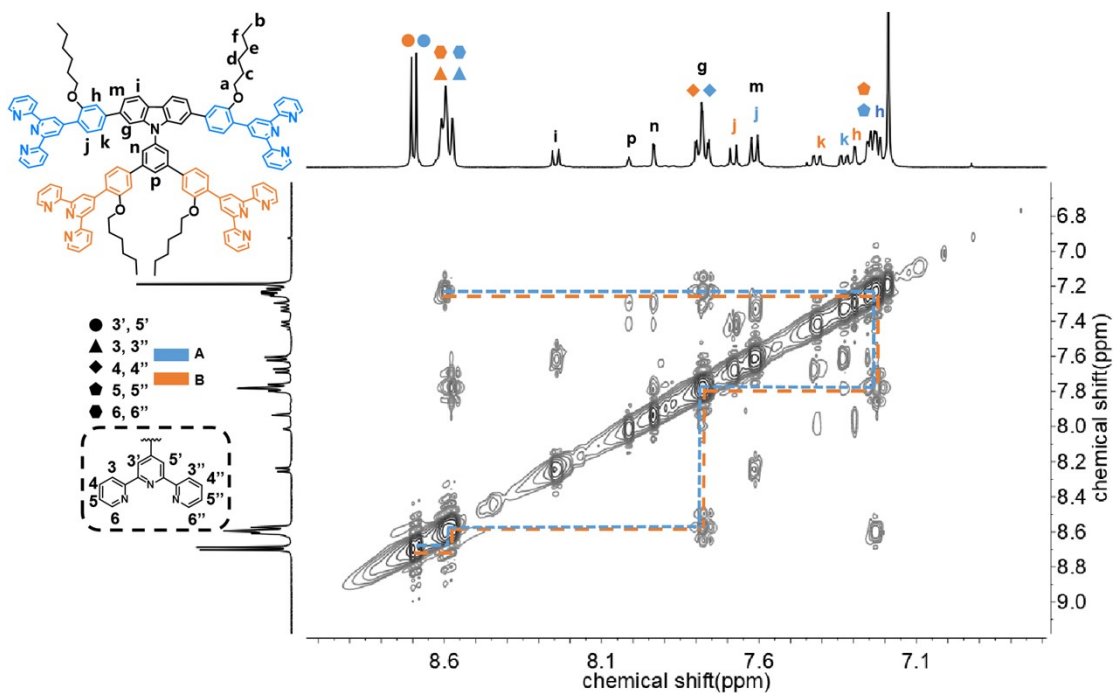


Figure S33. 2D NOESY NMR spectrum (400 MHz) of ligand **LA** in CDCl_3 .

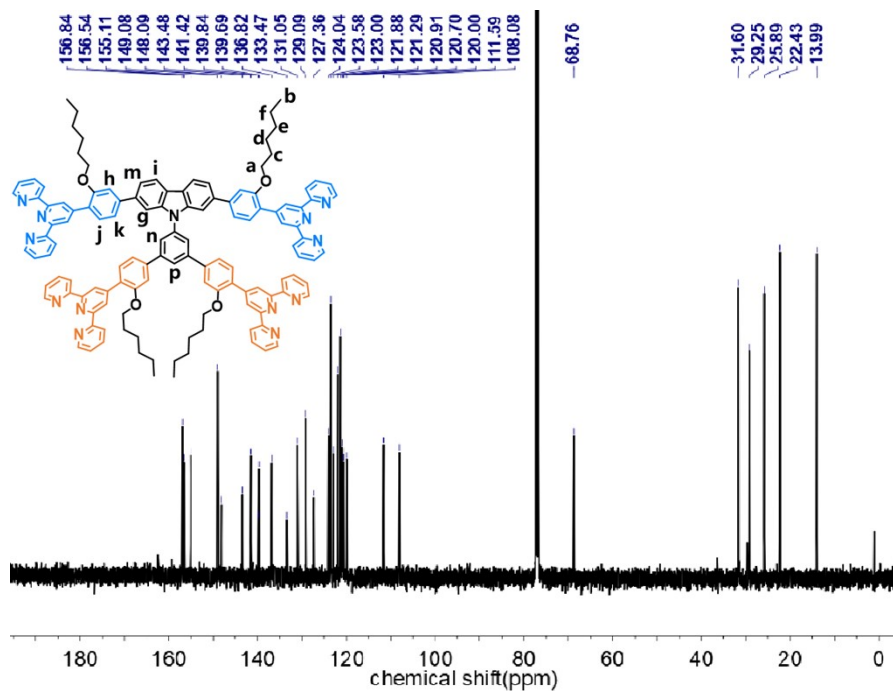


Figure S34. ^{13}C NMR spectrum (101 MHz) of ligand **LA** in CDCl_3 .

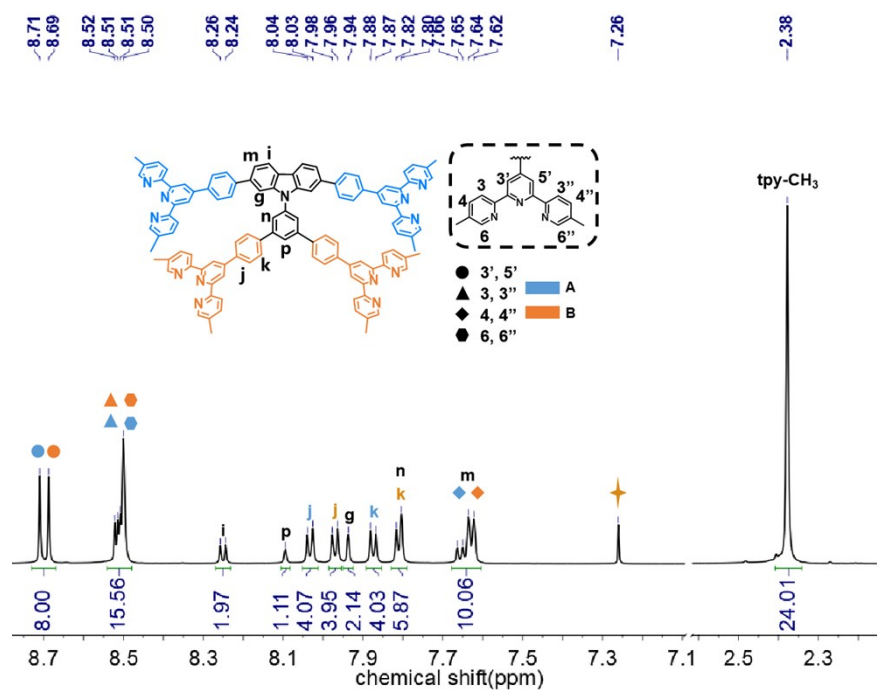


Figure S35. ¹H NMR spectrum (600 MHz) of ligand **LB** in CDCl₃.

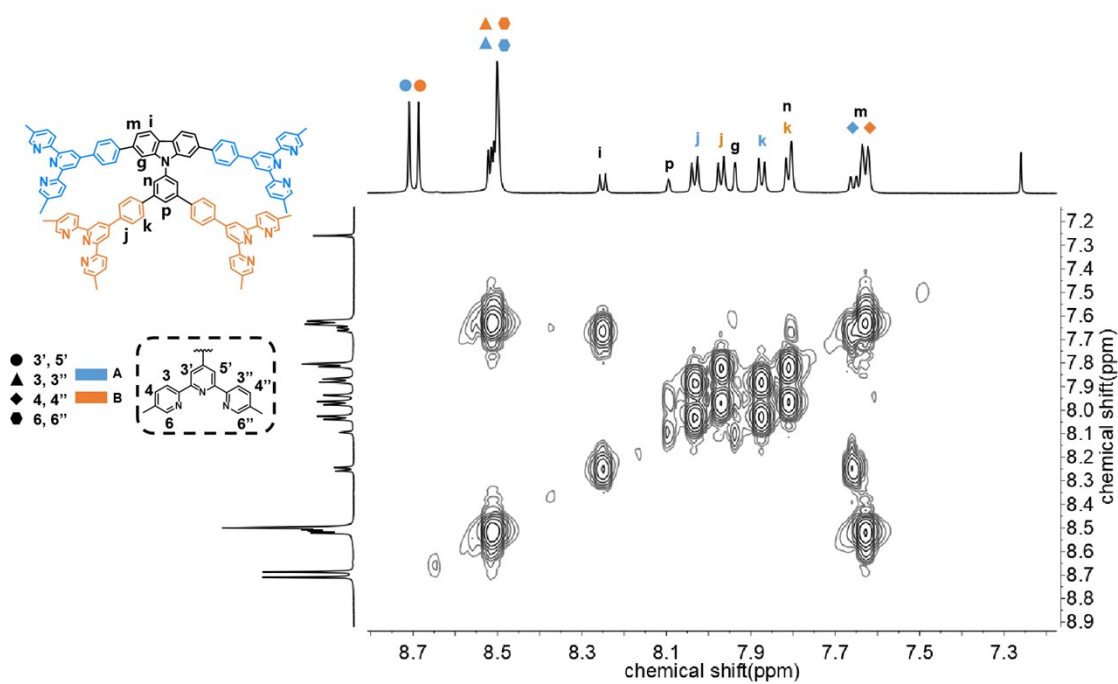


Figure S36. 2D COSY NMR spectrum (600 MHz) of ligand **LB** in CDCl₃.

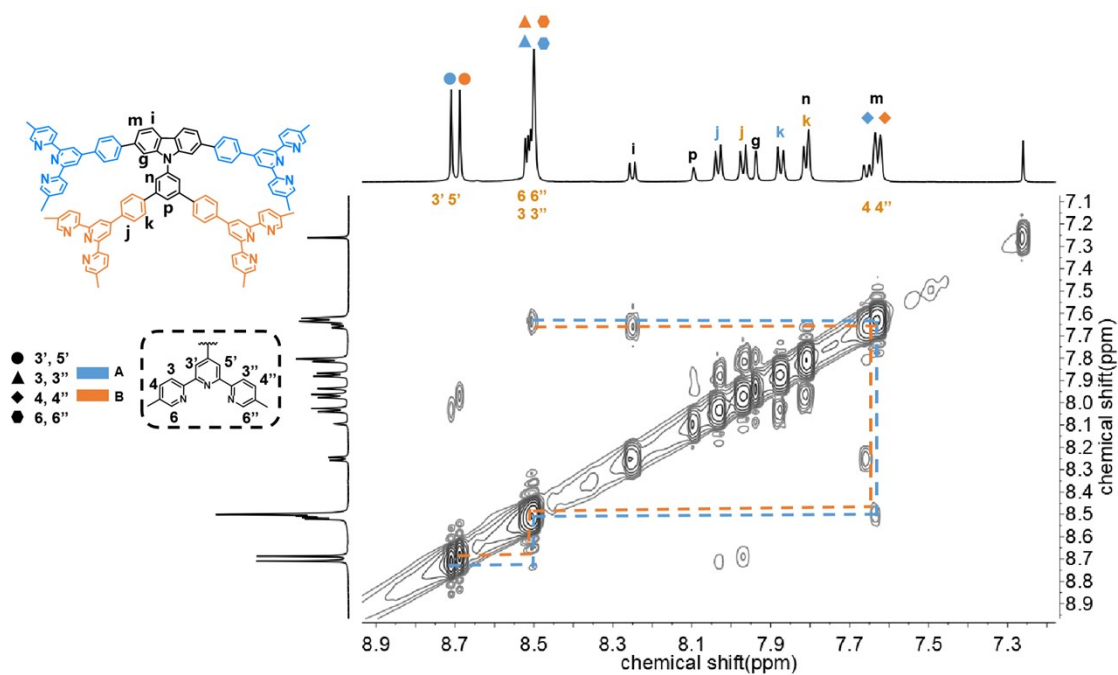


Figure S37. 2D NOESY NMR spectrum (600 MHz) of ligand **LB** in CDCl_3 .

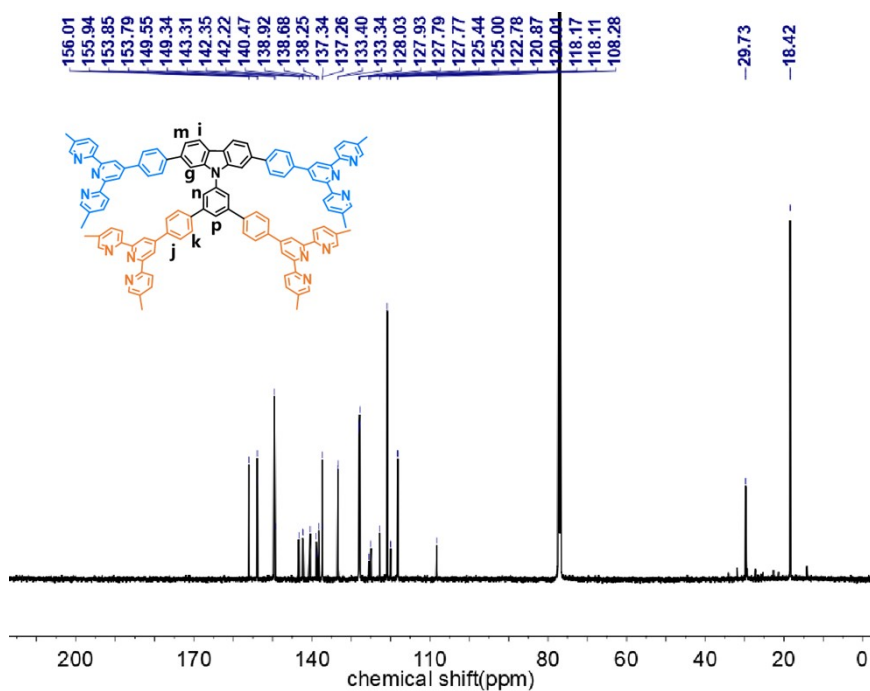


Figure S38. ^{13}C NMR spectrum (101 MHz) of ligand **LB** in CDCl_3 .

7. ESI-MS spectrum of ligands and other compounds

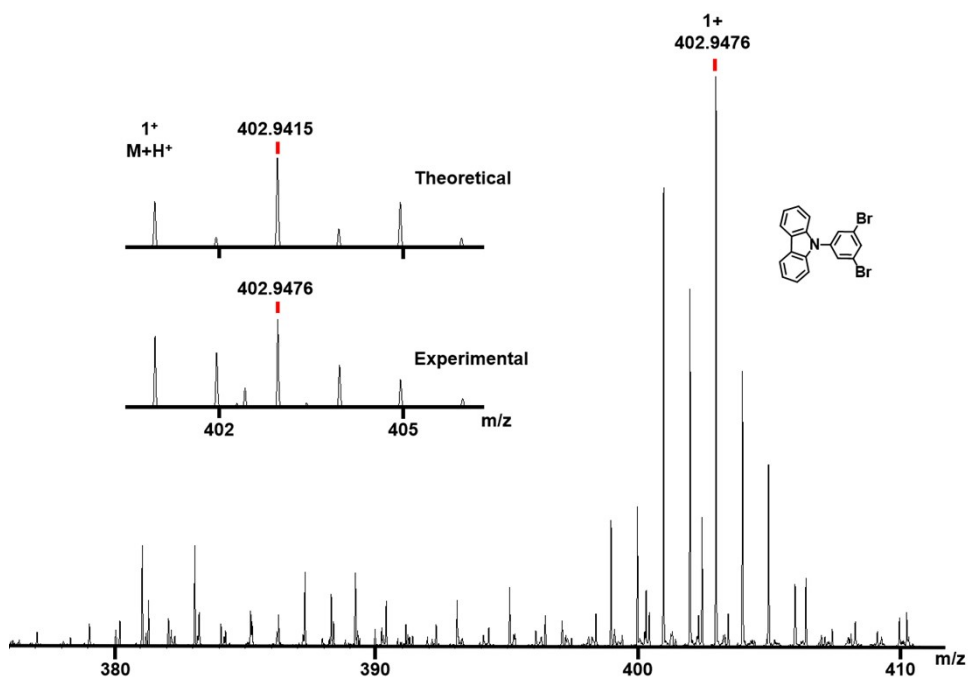


Figure S39. Isotope patterns and ESI-MS spectrum of S1.

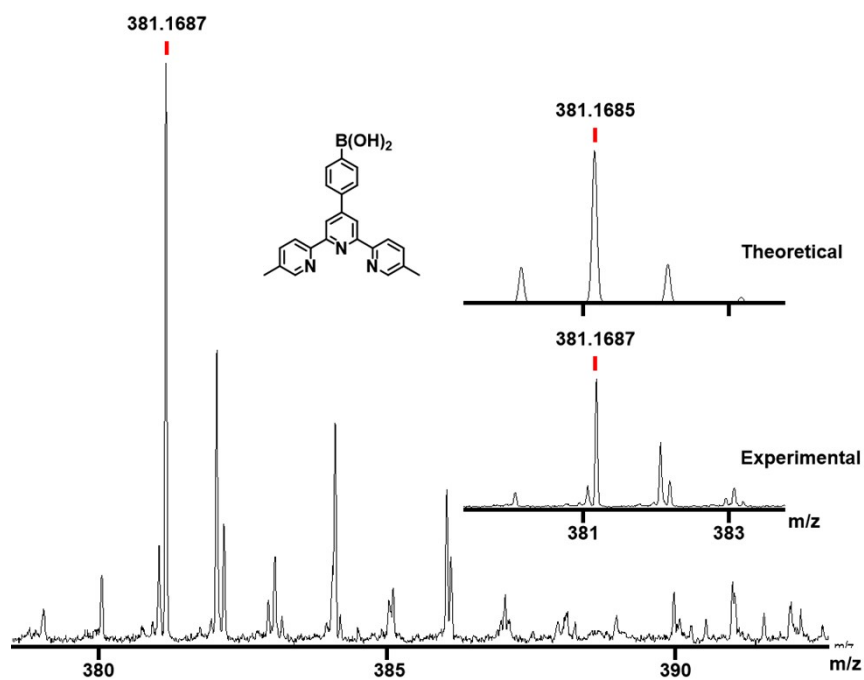


Figure S40. Isotope patterns and ESI-MS spectrum of S2.

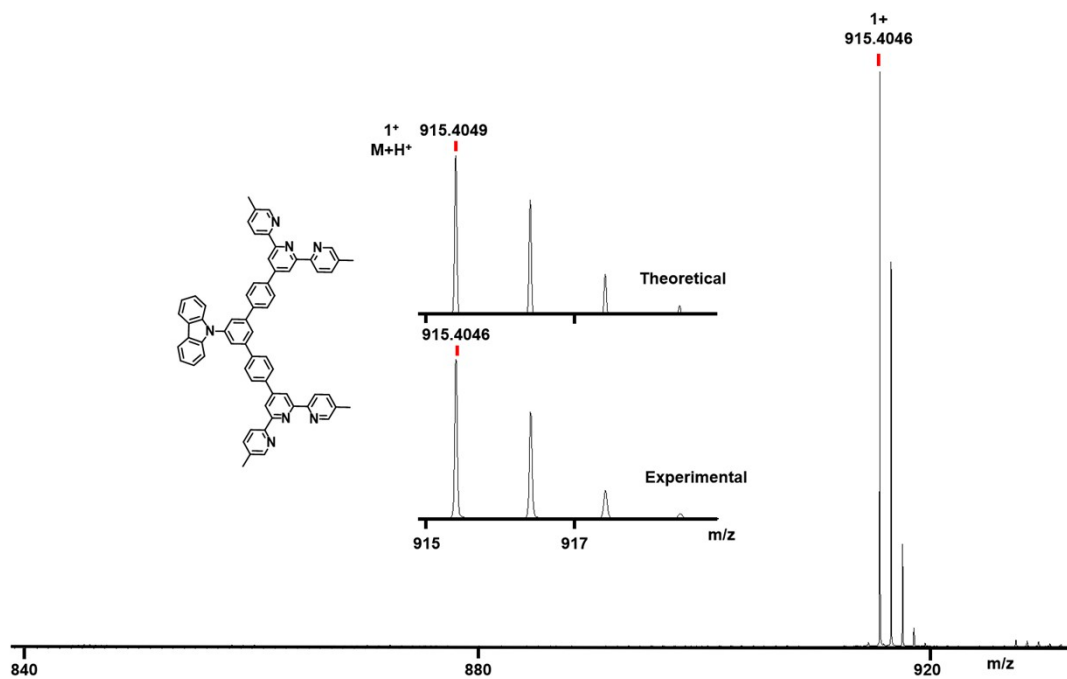


Figure S41. Isotope patterns and ESI-MS spectrum of ligand **1**.

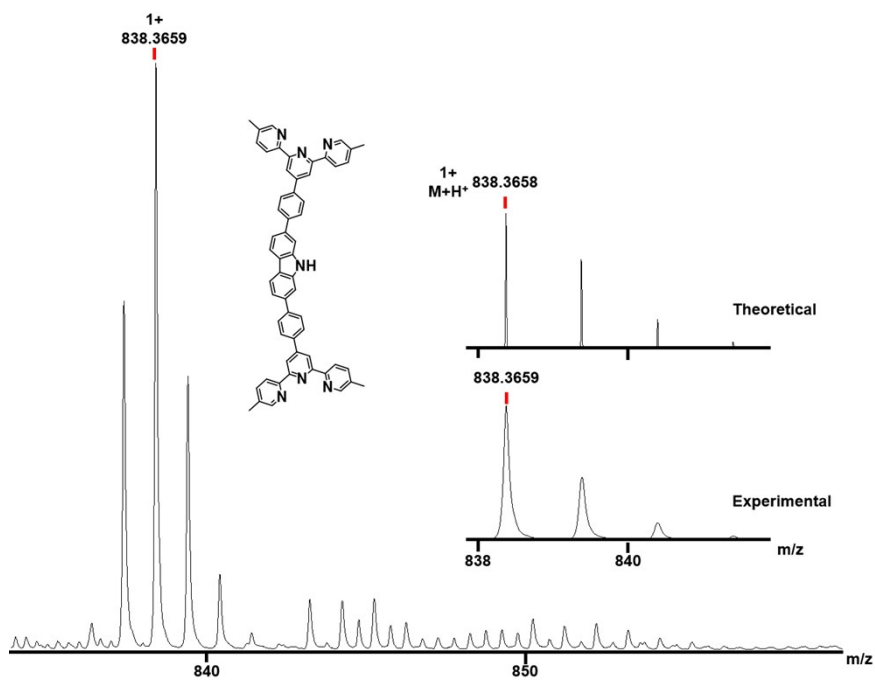


Figure S42. Isotope patterns and ESI-MS spectrum of **S3**.

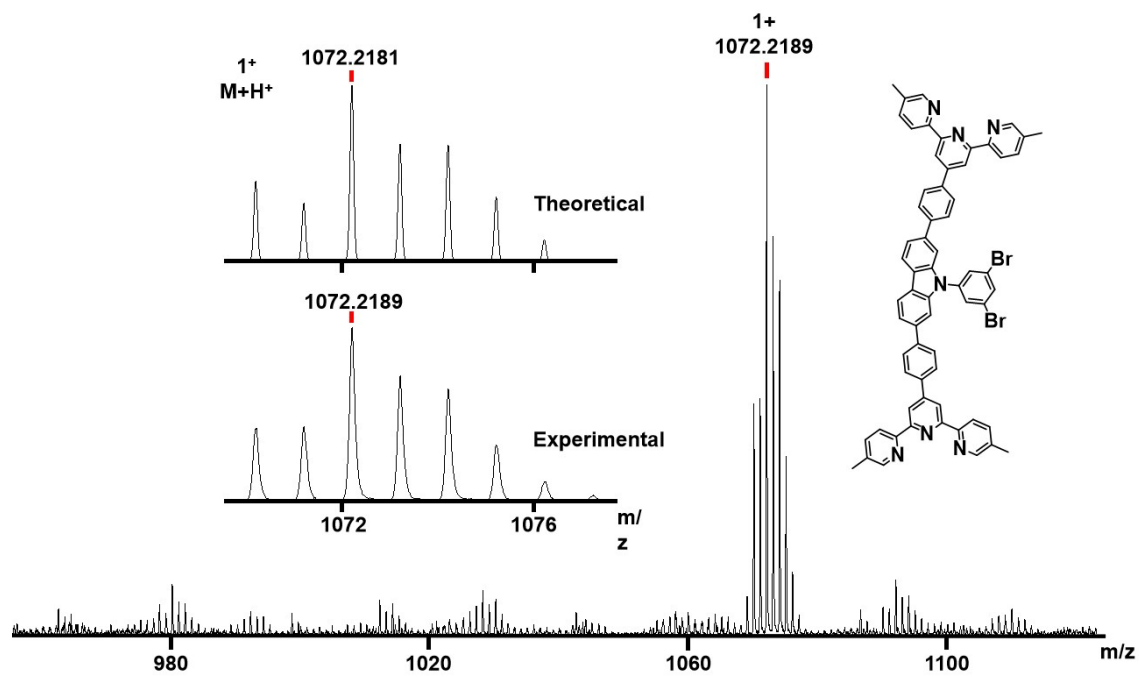


Figure S43. Isotope patterns and ESI-MS spectrum of 3.

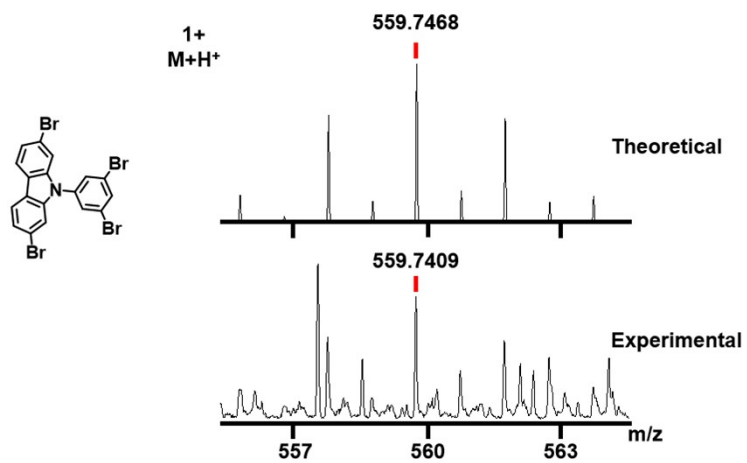


Figure S44. Isotope patterns and ESI-MS spectrum of 5.

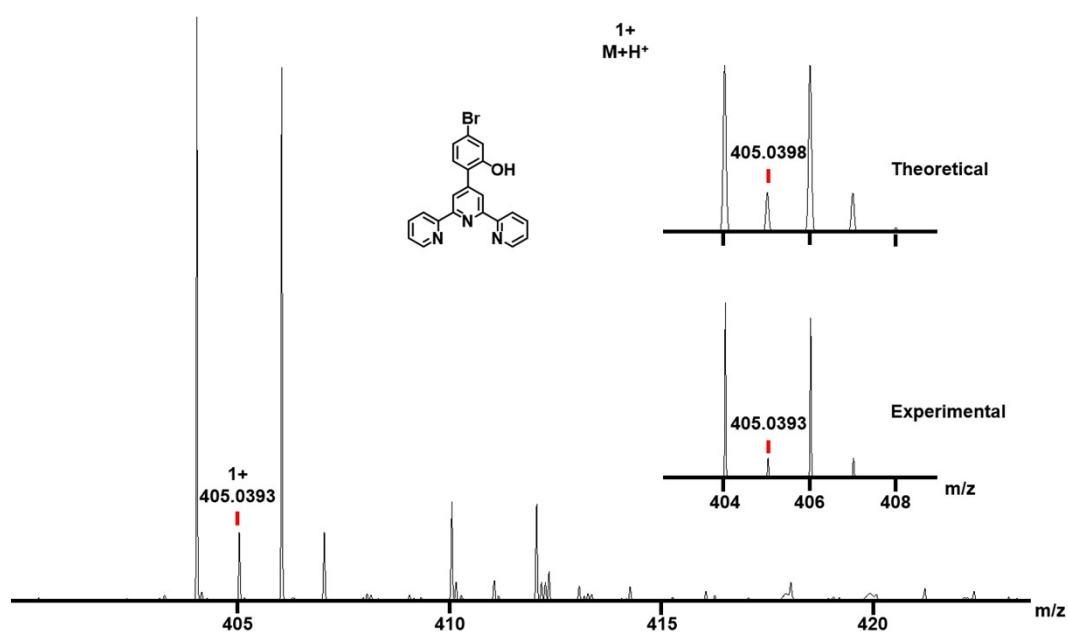


Figure S45. Isotope patterns and ESI-MS spectrum of S5.

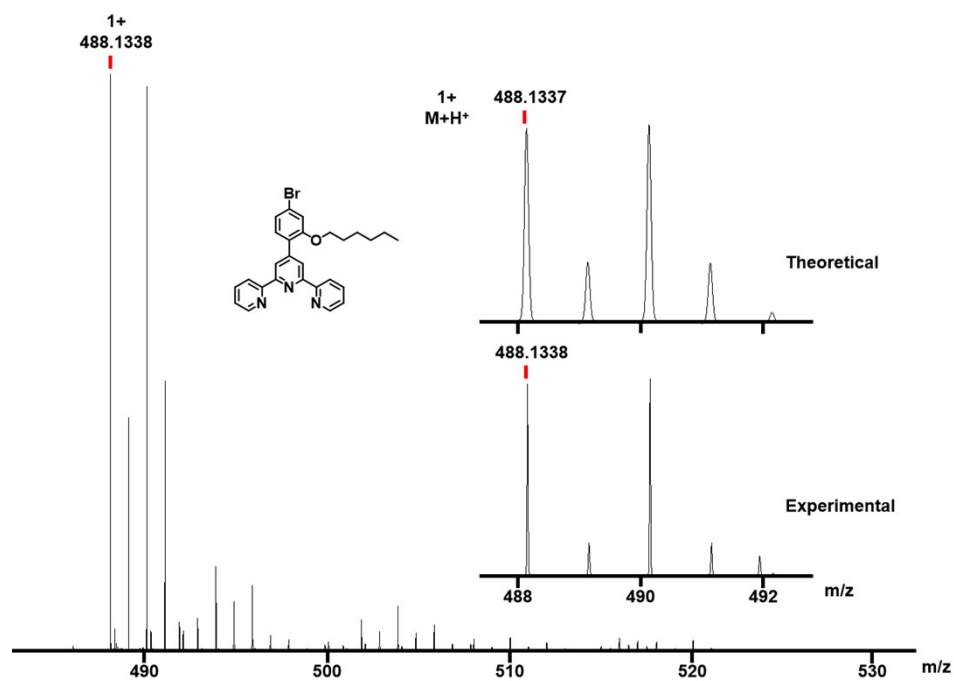


Figure S46. Isotope patterns and ESI-MS spectrum of S6.

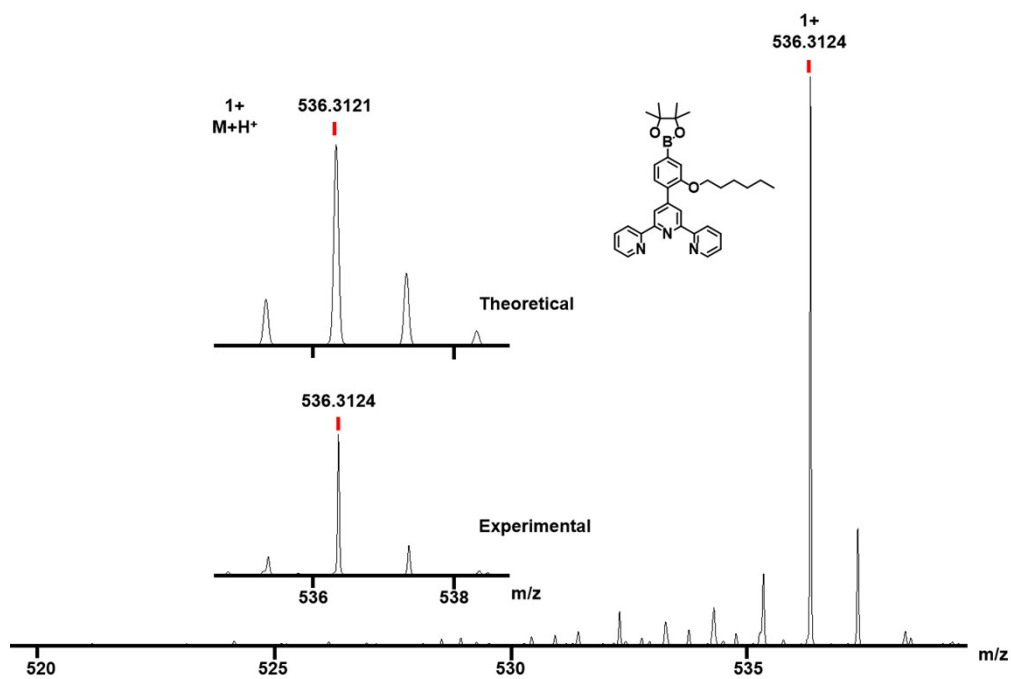


Figure S47. Isotope patterns and ESI-MS spectrum of S7.

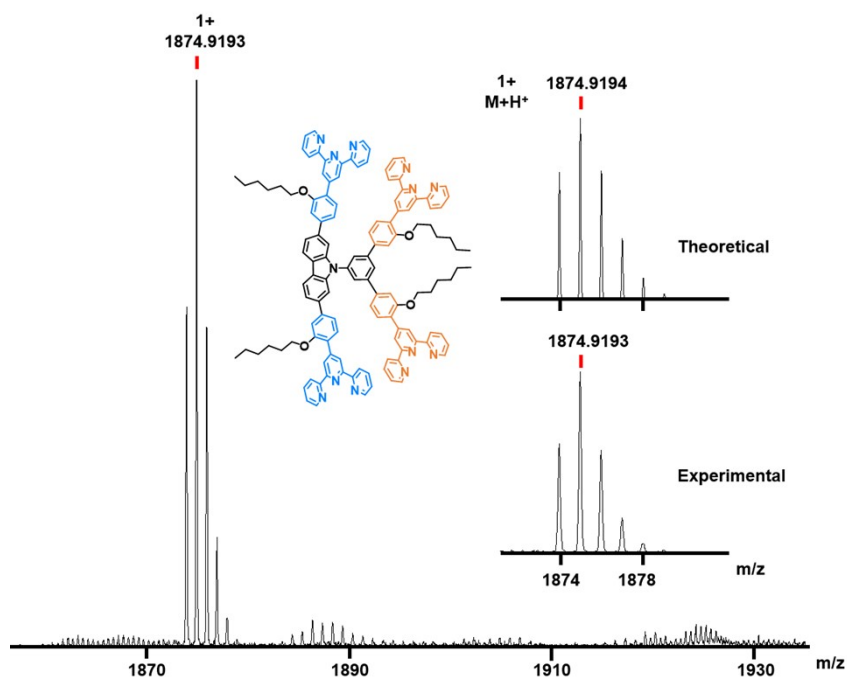


Figure S48. Isotope patterns and ESI-MS spectrum of LA.

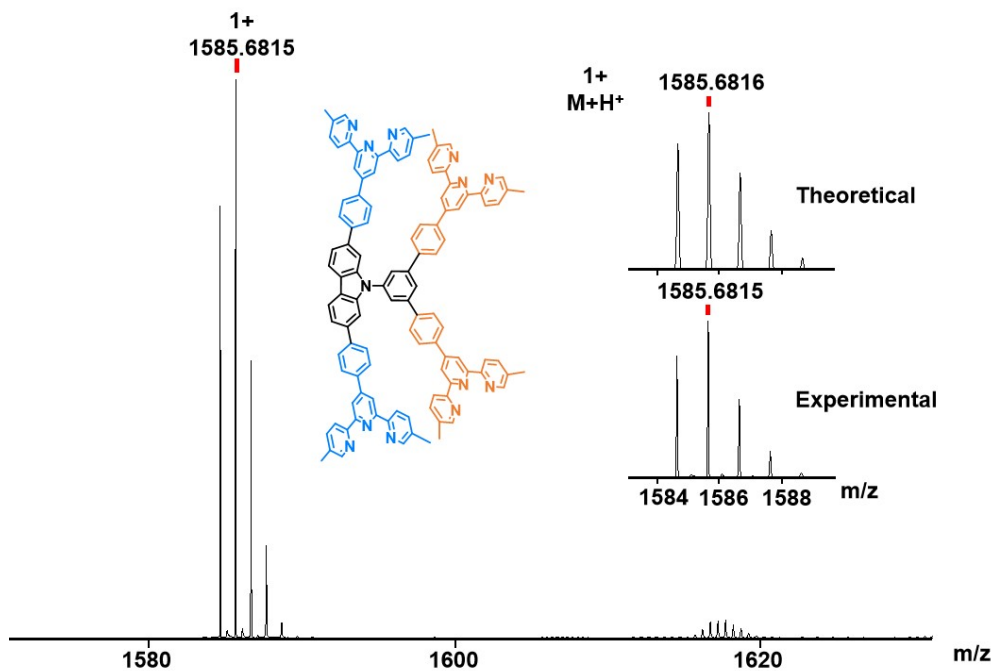


Figure S49. Isotope patterns and ESI-MS spectrum of LB.

8. The self-assembly process of ligands LA and LB.

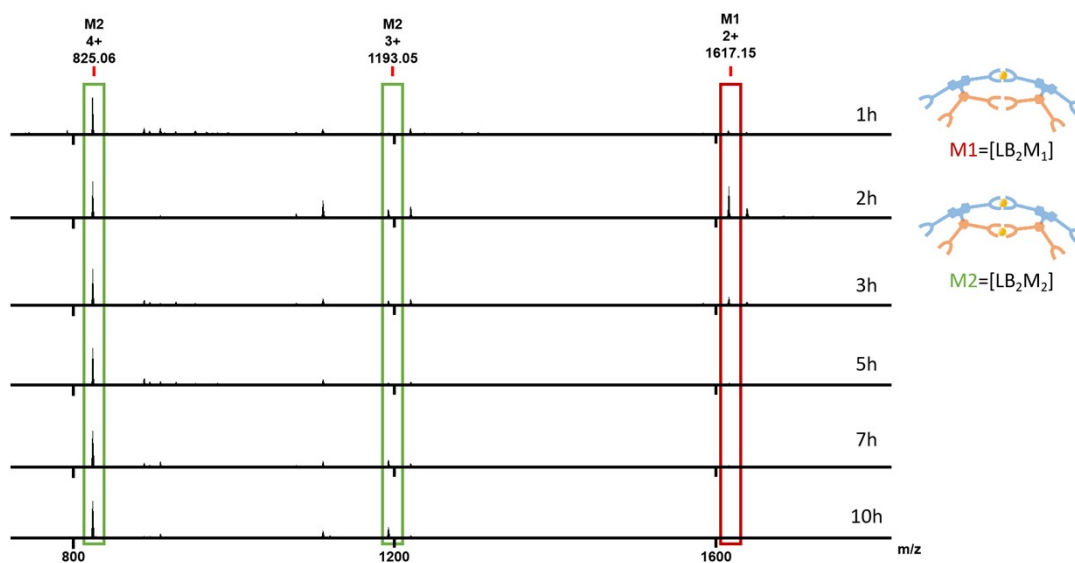


Figure S50. ESI-MS spectrum of self-assembly with LB and Zn^{2+} in the beginning (NTf_2^- as counterion).

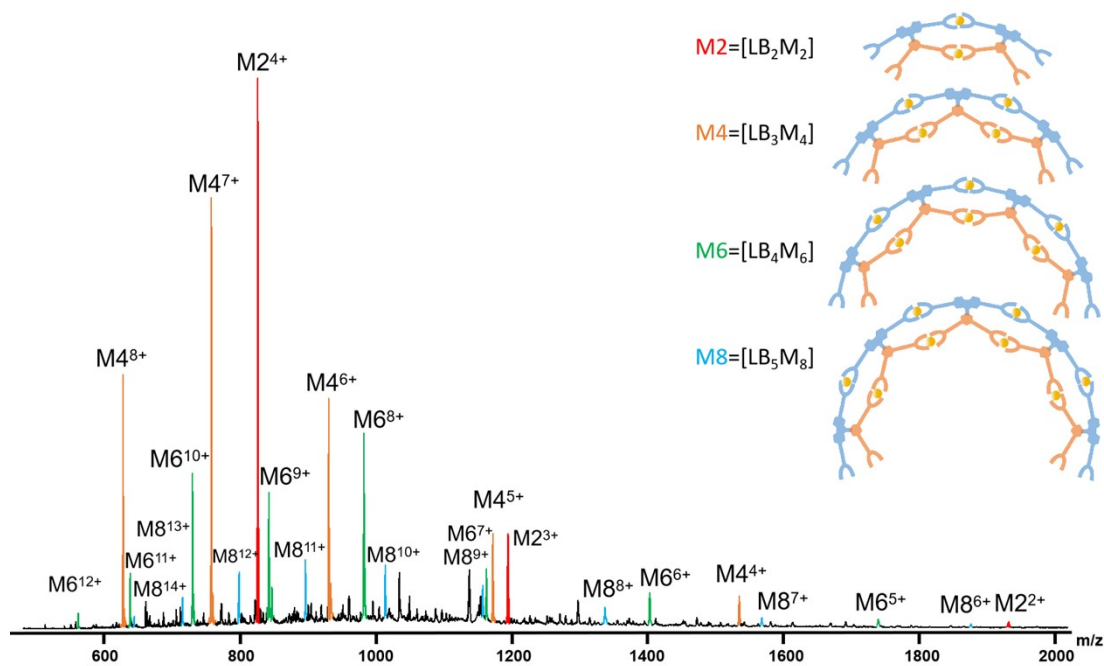


Figure S51. ESI-MS spectrum of the intermediates obtained by self-assembly of **LB** with Zn²⁺ at a molar ratio of 1:1.5 (NTf₂⁻ as counterion).

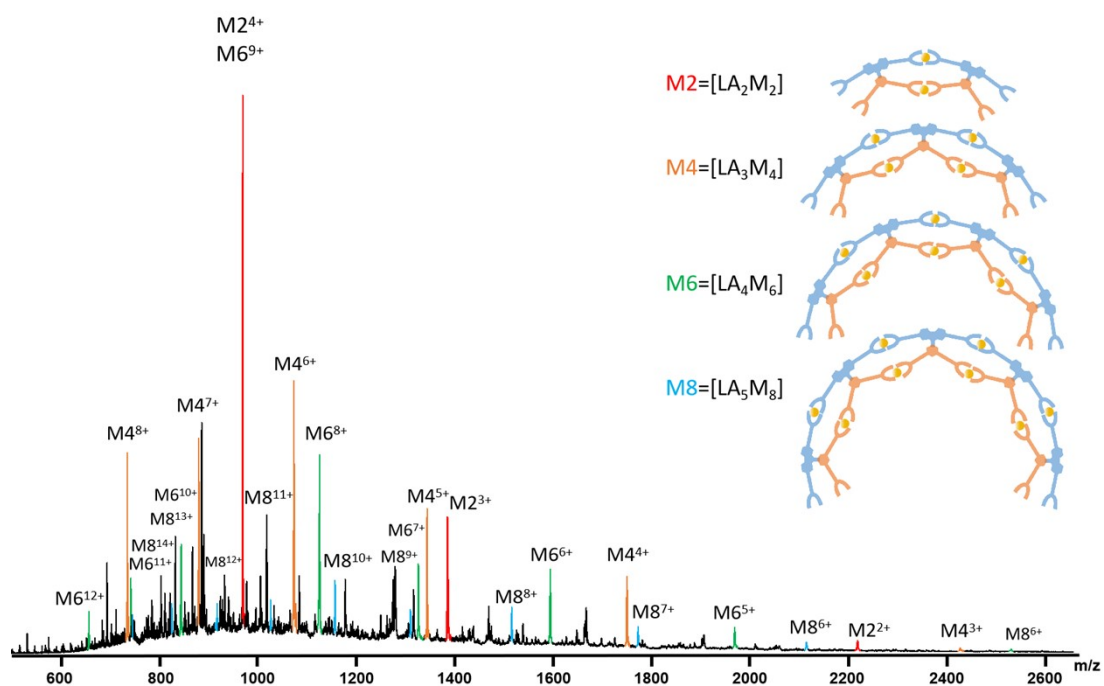


Figure S52. ESI-MS spectrum of the intermediates obtained by self-assembly of **LA** with Zn²⁺ at a molar ratio of 1:1.5 (NTf₂⁻ as counterion).

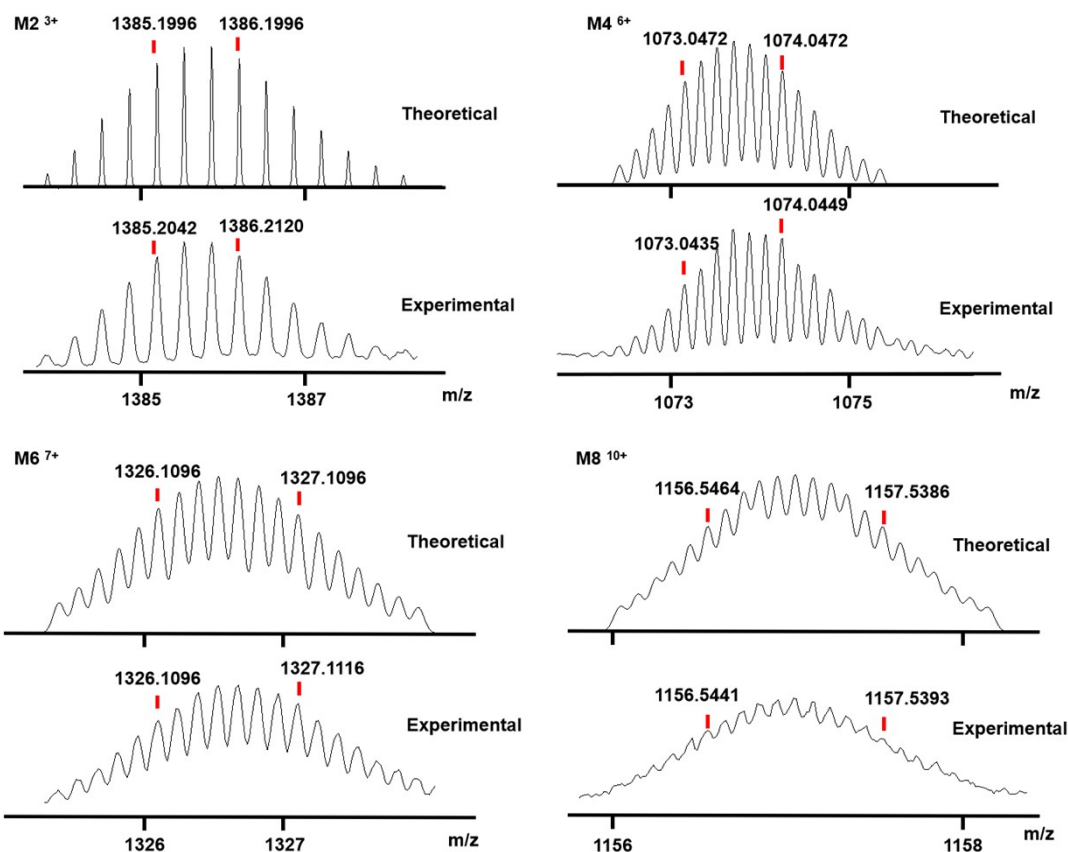


Figure S53. Theoretical (top) and experimental (bottom) isotope patterns for the different charge states observed from **MA** (NTf_2^- as counterion).

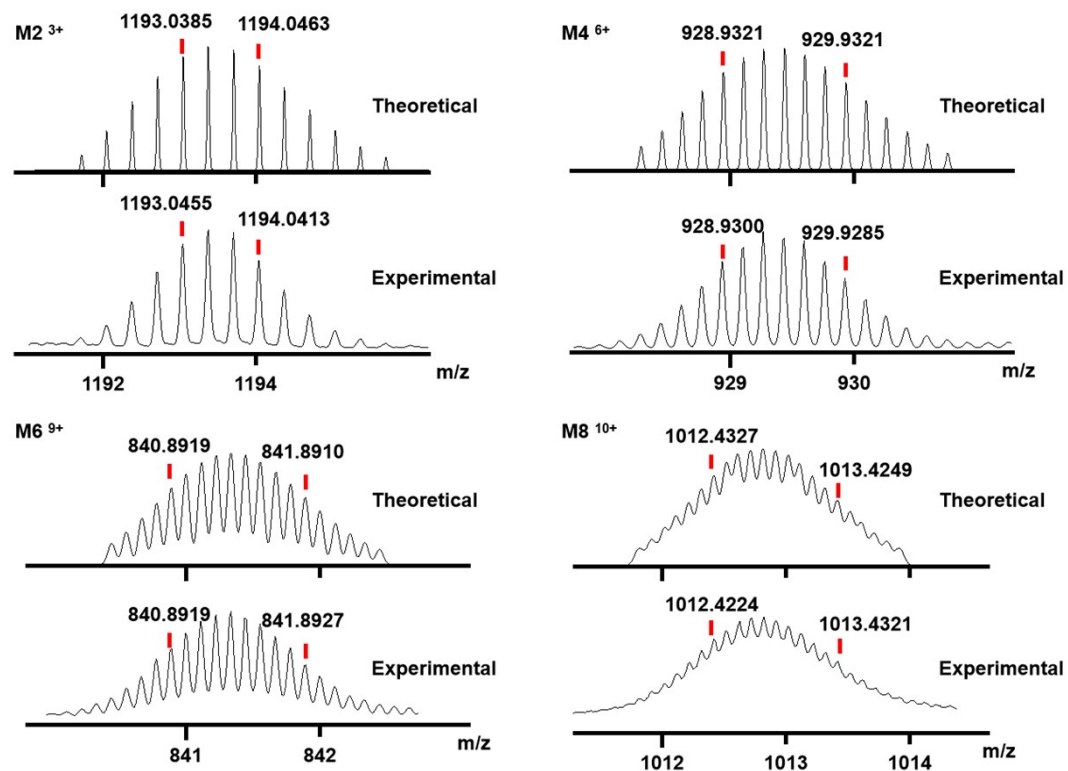


Figure S54. Theoretical (top) and experimental (bottom) isotope patterns for the different charge states observed from **MB** (NTf_2^- as counterion).

Table S1. Theoretical and experimental m/z ratios for [Zn₁₆LA₈].

Charge state	Composition	Theoretical m/z	Experimental m/z
8+	[M-8NTf ₂] ⁸⁺	2844.6400	2844.6199
9+	[M-9NTf ₂] ⁹⁺	2497.4422	2794.2146
10+	[M-10NTf ₂] ¹⁰⁺	2219.6840	2219.6289
11+	[M-11NTf ₂] ¹¹⁺	1992.4273	1992.3918
12+	[M-12NTf ₂] ¹²⁺	1803.0467	1803.1204
13+	[M-13NTf ₂] ¹³⁺	1642.8015	1642.8075
14+	[M-14NTf ₂] ¹⁴⁺	1505.4486	1505.4685
15+	[M-15NTf ₂] ¹⁵⁺	1386.4093	1386.4355
16+	[M-16NTf ₂] ¹⁶⁺	1282.2500	1282.2284
17+	[M-17NTf ₂] ¹⁷⁺	1190.3447	1190.3326
18+	[M-18NTf ₂] ¹⁸⁺	1108.6511	1108.6614
19+	[M-19NTf ₂] ¹⁹⁺	1035.5568	1035.5750
20+	[M-20NTf ₂] ²⁰⁺	969.7720	969.6026
21+	[M-21NTf ₂] ²¹⁺	910.2524	910.3305
22+	[M-22NTf ₂] ²²⁺	856.1436	856.1362

Table S2. Theoretical and experimental m/z ratios for [Zn₁₈LA₉].

Charge state	Composition	Theoretical m/z	Experimental m/z
14+	[M-14NTf ₂] ¹⁴⁺	1728.6471	1728.7234
15+	[M-15NTf ₂] ¹⁵⁺	1594.7280	1594.6934
16+	[M-16NTf ₂] ¹⁶⁺	1477.5488	1477.4442
17+	[M-17NTf ₂] ¹⁷⁺	1374.1553	1374.1235
18+	[M-18NTf ₂] ¹⁸⁺	1282.2500	1282.2284
19+	[M-19NTf ₂] ¹⁹⁺	1200.0189	1200.0233
20+	[M-20NTf ₂] ²⁰⁺	1126.0110	1125.9264
21+	[M-21NTf ₂] ²¹⁺	1059.0514	1059.0728
22+	[M-22NTf ₂] ²²⁺	998.1791	998.1652
23+	[M-23NTf ₂] ²³⁺	942.6000	942.4628
24+	[M-24NTf ₂] ²⁴⁺	891.6525	891.6550
25+	[M-25NTf ₂] ²⁵⁺	844.7808	844.7531

Table S3. Theoretical and experimental m/z ratios for [Zn₂₀LA₁₀].

Charge state	Composition	Theoretical m/z	Experimental m/z
13+	[M-13NTf ₂] ¹³⁺	2123.5369	2123.5181

14+	[M-14NTf ₂] ¹⁴⁺	1951.8457	1951.8488
15+	[M-15NTf ₂] ¹⁵⁺	1803.0467	1803.1204
16+	[M-16NTf ₂] ¹⁶⁺	1672.8475	1672.7977
17+	[M-17NTf ₂] ¹⁷⁺	1557.9659	1557.9265
18+	[M-18NTf ₂] ¹⁸⁺	1455.8489	1455.9407
19+	[M-19NTf ₂] ¹⁹⁺	1364.4811	1364.4136
20+	[M-20NTf ₂] ²⁰⁺	1282.2500	1282.2284
21+	[M-21NTf ₂] ²¹⁺	1207.8505	1207.8102
22+	[M-22NTf ₂] ²²⁺	1140.2145	1140.1382
23+	[M-23NTf ₂] ²³⁺	1078.4600	1078.3562
24+	[M-24NTf ₂] ²⁴⁺	1021.8517	1021.9628

Table S7. Theoretical and experimental m/z ratios for [Zn₁₆LB₈].

Charge state	Composition	Theoretical m/z	Experimental m/z
10+	[M-10NTf ₂] ¹⁰⁺	1988.9400	1989.0968
11+	[M-11NTf ₂] ¹¹⁺	1782.6600	1782.6381
12+	[M-12NTf ₂] ¹²⁺	1610.7600	1610.7992
13+	[M-13NTf ₂] ¹³⁺	1465.3062	1465.1810
14+	[M-14NTf ₂] ¹⁴⁺	1340.6314	1340.4917
15+	[M-15NTf ₂] ¹⁵⁺	1232.5800	1232.4807
16+	[M-16NTf ₂] ¹⁶⁺	1138.0350	1137.9879
17+	[M-17NTf ₂] ¹⁷⁺	1054.6129	1054.4823
18+	[M-18NTf ₂] ¹⁸⁺	980.4600	980.5468

Table S8. Theoretical and experimental m/z ratios for [Zn₁₈LB₉].

Charge state	Composition	Theoretical m/z	Experimental m/z
11+	[M-11NTf ₂] ¹¹⁺	2040.5100	2040.8651
12+	[M-12NTf ₂] ¹²⁺	1847.1225	1847.2660
13+	[M-13NTf ₂] ¹³⁺	1683.4869	1683.7830
14+	[M-14NTf ₂] ¹⁴⁺	1543.2279	1543.1353
15+	[M-15NTf ₂] ¹⁵⁺	1421.6700	1421.6132
16+	[M-16NTf ₂] ¹⁶⁺	1315.3069	1315.1100
17+	[M-17NTf ₂] ¹⁷⁺	1221.4571	1221.5123
18+	[M-18NTf ₂] ¹⁸⁺	1138.0350	1137.9879
19+	[M-19NTf ₂] ¹⁹⁺	1063.3942	1063.0372
20+	[M-20NTf ₂] ²⁰⁺	996.2175	996.0065

Table S9. Theoretical and experimental m/z ratios for [Zn₂₀LB₁₀].

Charge state	Composition	Theoretical m/z	Experimental m/z
12+	[M-12NTf ₂] ¹²⁺	2083.4850	2083.8386
13+	[M-13NTf ₂] ¹³⁺	1901.6677	1901.8301
14+	[M-14NTf ₂] ¹⁴⁺	1745.8243	1745.5701
15+	[M-15NTf ₂] ¹⁵⁺	1610.7600	1610.7992
16+	[M-16NTf ₂] ¹⁶⁺	1492.5788	1492.6056
17+	[M-17NTf ₂] ¹⁷⁺	1388.3012	1388.5630
18+	[M-18NTf ₂] ¹⁸⁺	1295.6100	1295.5450
19+	[M-19NTf ₂] ¹⁹⁺	1212.6758	1212.4930
20+	[M-20NTf ₂] ²⁰⁺	1138.0350	1137.9879
21+	[M-21NTf ₂] ²¹⁺	1070.5029	1070.0546
22+	[M-22NTf ₂] ²²⁺	1009.1100	1009.50

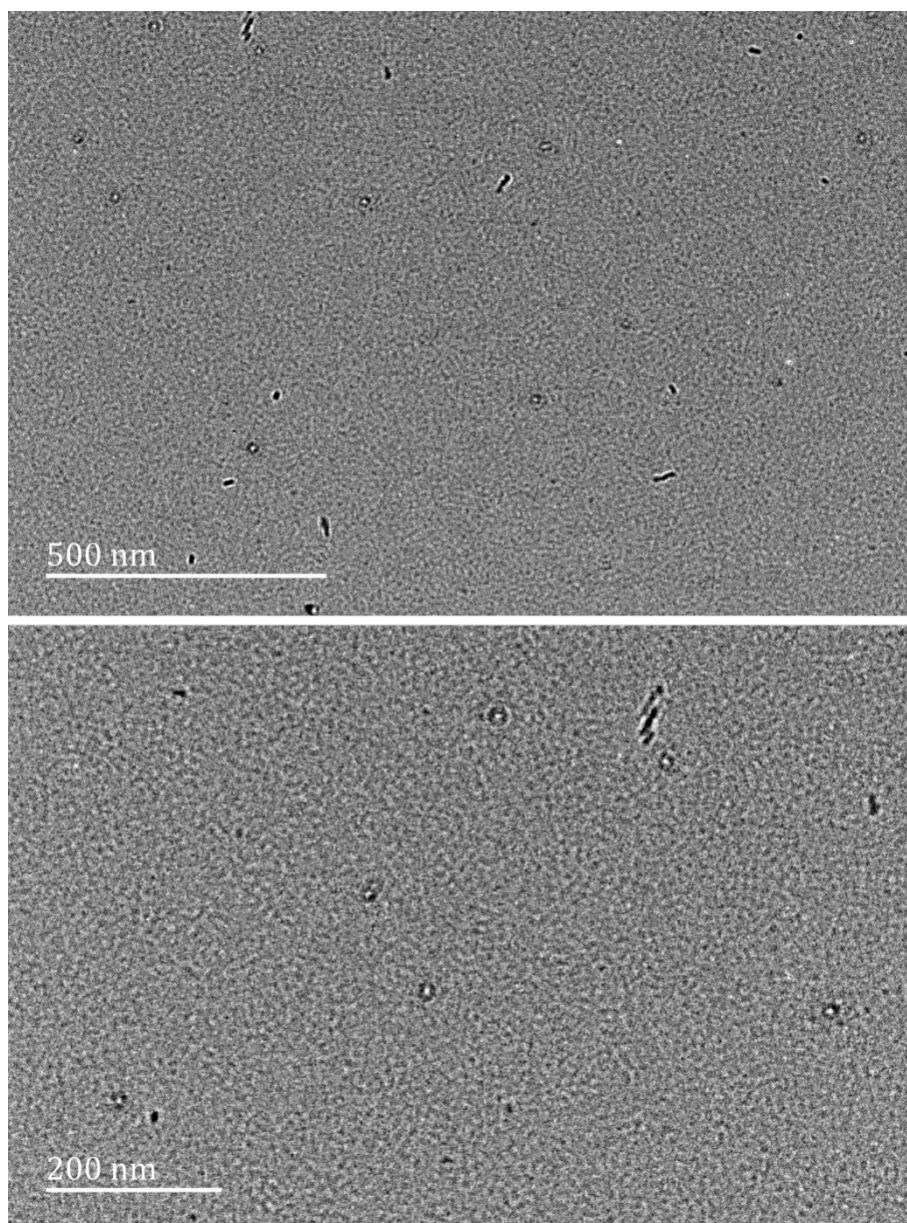


Figure S55. TEM images of supramolecular macrocycles SA. In the film, we observed the particles of complex SA with clear hollow structure.

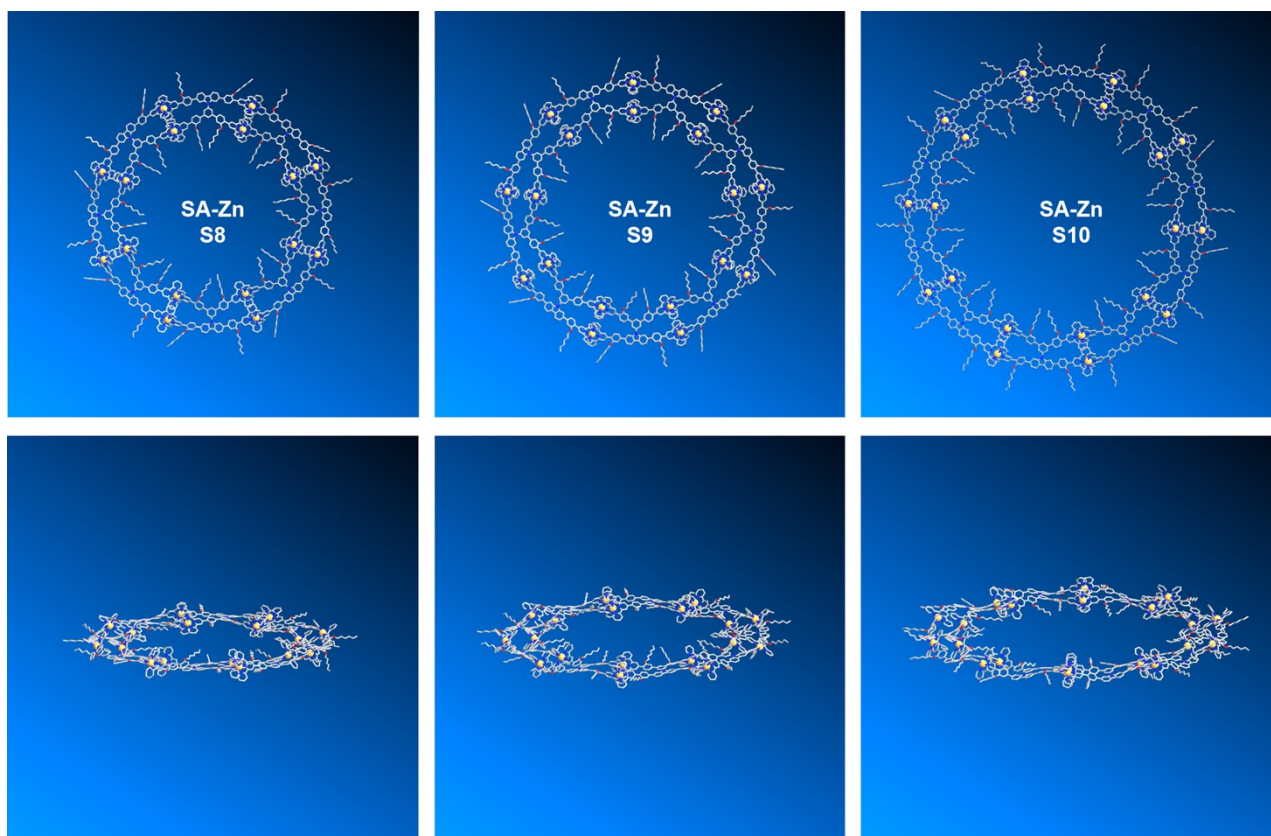


Figure S56. Representative energy-minimized structures from molecular modeling of **SA-Zn**.

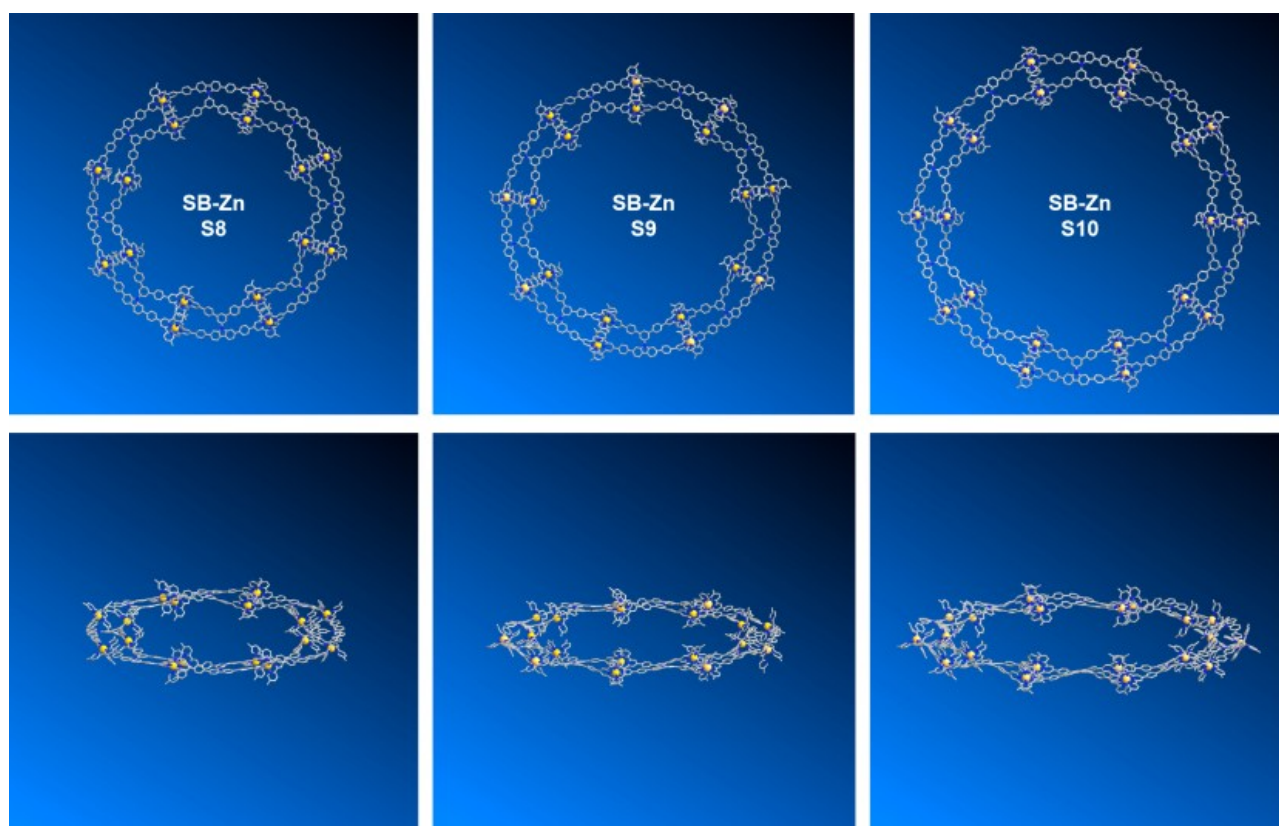


Figure S57. Representative energy-minimized structures from molecular modeling of **SB-Zn**.

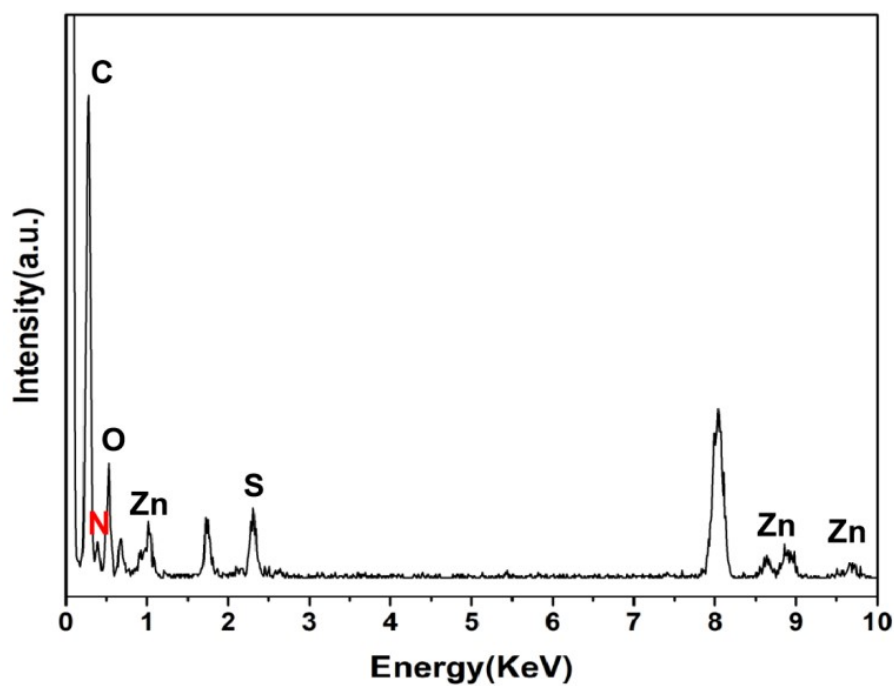
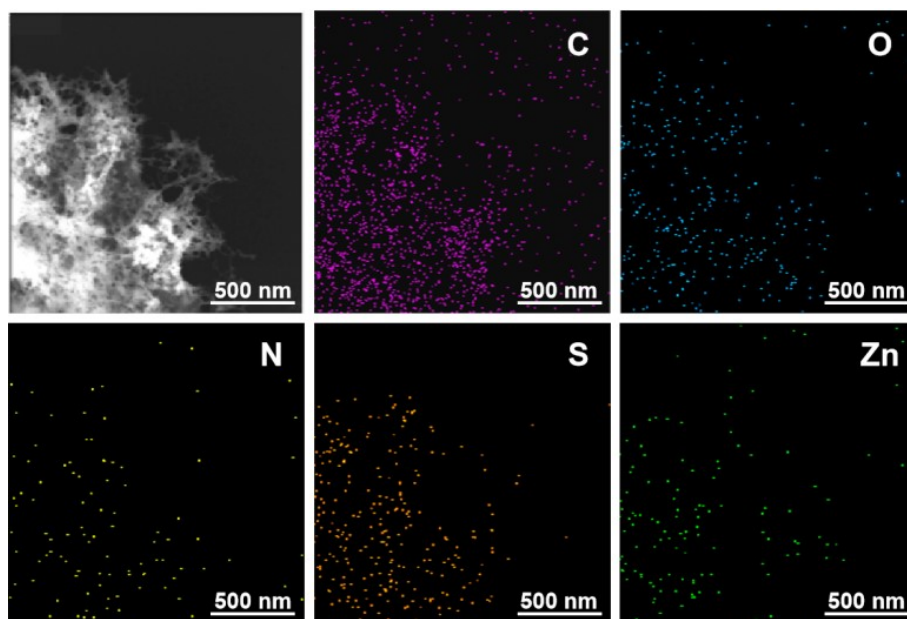


Figure S58. EDS elemental mapping and spectrum of the supramolecular macrocycles **SB** with heparin.

Table S10. Crystal data and structure refinement for compound **3** and ligand **LB**.

Compound	Compound 3	ligand LB
CCDC	2242709	2245970
Formula	$C_{64}H_{42}Br_2N_7$	$C_{114.29}H_{90.18}N_{14.3}O_1$
Temperature (K)	100(2)	120.00(10)
Formula weight (g/mol)	1068.86	1692.62
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1

<i>a</i> (Å)	11.3268(2)	15.1349 (2)
<i>b</i> (Å)	15.5229(3)	24.4882 (3)
<i>c</i> (Å)	17.3816(3)	26.4272(3)
α (°)	101.4560(16)	66.8300(10)
β (°)	98.3563(16)	87.7140(10)
γ (°)	107.5337(16)	88.7170(10)
<i>V</i> (Å ³)	2786.38(9)	8997.2(2)
<i>Z</i>	2	2
Calculated density		
(g cm ⁻³)	1.274	1.250
μ (mm ⁻¹)	1.500	0.594
2 θ (°)	2.291 to 30.896	5.844 to 147.658
F (000)	1096	3562.0
Reflections collected	10873	130851
<i>R</i> _{int}	0.0710	0.0469
Data/restraints/parameters	0/662	35268/215/2602
Goodness-off-fit on F ²	1.062	1.222
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ =0.0659	<i>R</i> ₁ = 0.0967
	<i>wR</i> ₂ =0.1199	<i>wR</i> ₂ = 0.2886
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0429	<i>R</i> ₁ = 0.1320
	<i>wR</i> ₂ =0.1199	<i>wR</i> ₂ = 0.3252

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right]^{1/2}$$

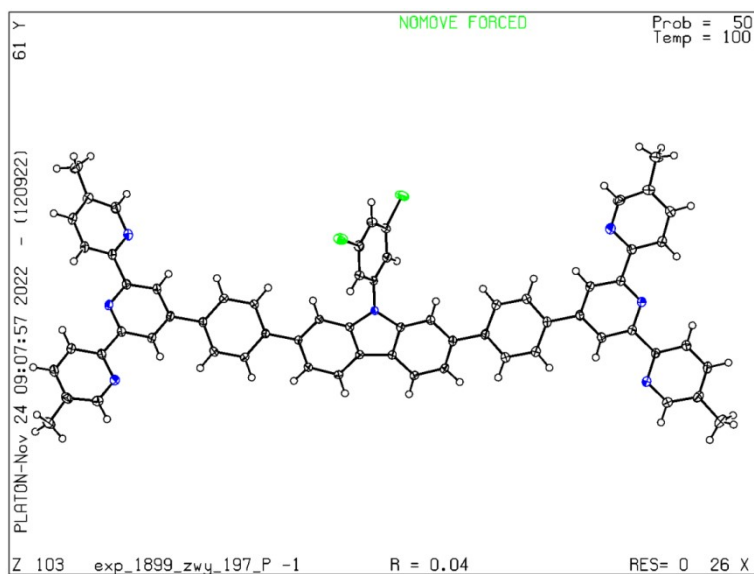


Figure S59. Ortep drawing of ligand **3**. The thermal ellipsoids are drawn at 50% probability.

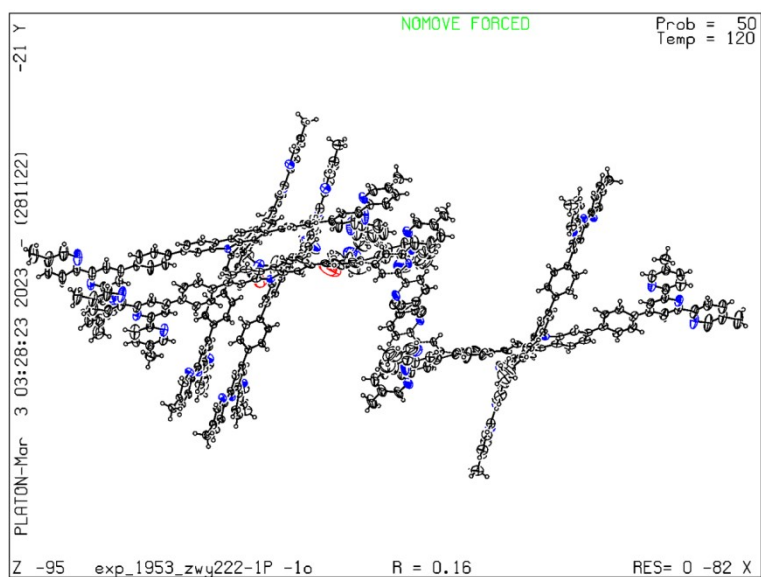


Figure S60. Ortep drawing of ligand **LB**. The thermal ellipsoids are drawn at 50% probability.

9. Reference

1. Dai, B., et al., *Site-Selective N-Arylation of Carbazoles with Halogenated Fluorobenzenes*. *Synthesis*, 2015. **48**(05): p. 737-750.
2. Wang, J., et al., *Construction of Macromolecular Pinwheels Using Predesigned Metalloligands*. *Journal of the American Chemical Society*, 2020. **142**(52): p. 21691-21701.