Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information:

Facile Thermodynamic Conversion of Linear Metallopolymer to Self-assembled Hexameric Metallomacrocycle

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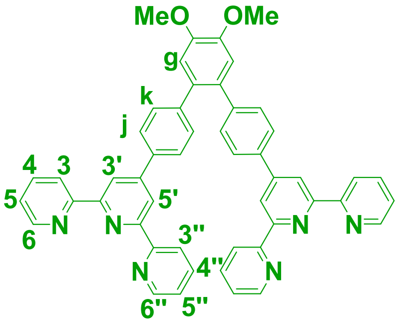
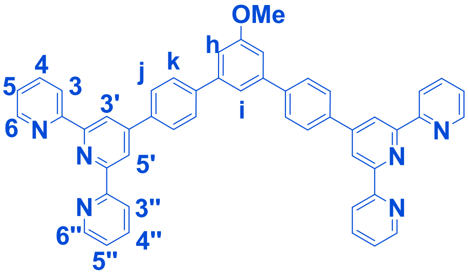
General Procedures

Solvents are 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.1,2-Dibromo-4,5-dimethoxybenzene, 1,3-dibromo-5-methoxybenzene and $RuCl_3·3H_2O$ were also purchased through J & K Chemical Technology. 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 ^{1}H NMR spectra were recorded at 25 °C on a Bruker spectrometer operating at either 500 or 100 MHz for ^{1}H or ^{13}C, respectively. Chemical shifts were reported in parts per million (ppm) referenced to the residual solvent peak for ^{1}H and solvent peak for ^{13}C NMR, respectively. Mass spectra were obtained on a Bruker Esquire electrospray ion trap mass spectrometer (ESI-MS). Electronic absorption spectra were recorded with a VARIAN Cary-50 UV-visible spectrophotometer and were corrected for the background spectrum of the solvent. Cyclic voltammetry measurements were performed on a Metrohm Autolab PGSTAT30 potentiost at with a standard three-electrode configuration using a glass-carbon working electrode, a platinum-rod auxiliary electrode, and a saturated calomel electrode reference electrode. CV experiments measurements in CH_2Cl_2 or MeCN, and 0.1 M $[(n\text{-}Bu)_4N][PF_6]$. Transmission microscopy measurements were performed on a JEM-2100F TEM operating at 200 kV.

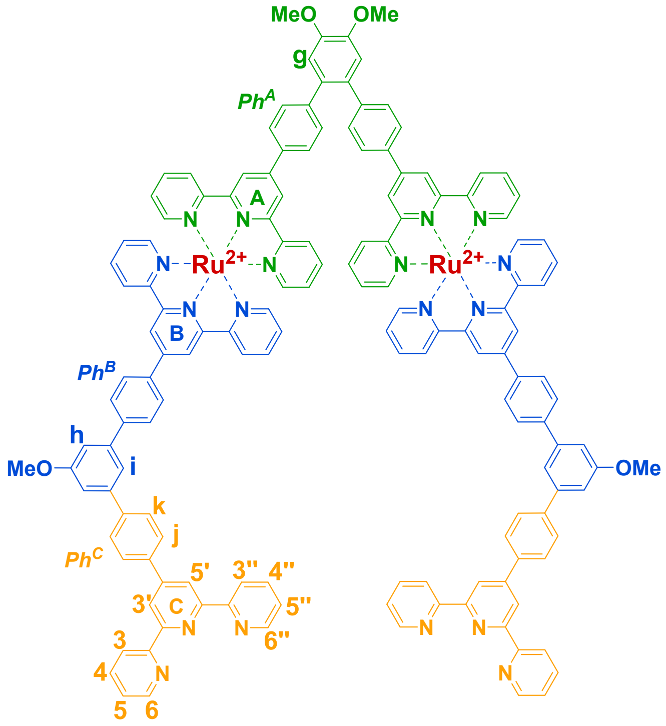


Bis-*o*-terpyridine 2 was synthesized by a published[1,2] procedure: mp 297-305°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (s, 4H, $H^{3',5'}$), 8.71-8.70 (d, J =5 Hz, 4H, $H^{6,6''}$), 8.67-8.66 (d, J =5 Hz, 4H,$H^{3,3''}$), 7.89-7.86 (m, 4H, $H^{4',4''}$), 7.86-7.84 (d, J =10 Hz,4H, H^{j}), 7.36-7.34 (d, J =10 Hz, 4H, H^{k}), 7.35-7.32 (m, 4H, $H^{5',5''}$), 7.28 (s, $CHCl_3$), 7.05 (s, 2H, H^{g}), 4.03 (s, 6H, OCH_3).



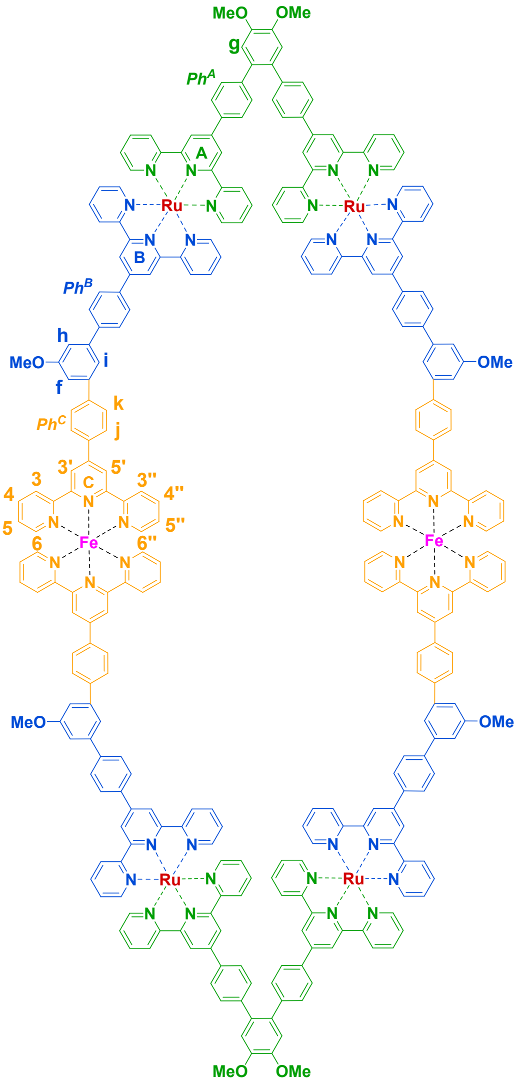
Bis-*m*-terpyridine 3: To a solution of 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine (**1**) (602 mg, 1.7 mmol) and 1,3-dibromo-5-methoxybenzene (150 mg, 560μmol) in THF (60 mL), aqueous K_3PO_4 (724mg, 3.4mmol) was added. The system was degassed for 10 minutes, then $Pd(PPh_3)_4$ (126 mg) was added. After refluxing for 2 days under N_2, the solvent was removed *invacuo* to give a residue that was dissolved in CH_2Cl_2 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 CH_2Cl_2/CH_3OH and petroleum ether to give **3**, as a white solid: 251mg, 62%; mp: 200-204°C; Elemental analysis: chemical formula, $C_{49}H_{34}N_6O\cdot MeOH\cdot CH_2Cl_2$, calculated: C 72.94; H 4.80; N 10.01%; found: C 75.82, H 4.82, N 9.73%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 4H, $H^{3',5'}$), 8.78-8.77 (d, J =5 Hz, 4H, $H^{6,6''}$), 8.73-8.71 (d, J =10 Hz, 4H, $H^{3,3''}$), 8.08-8.06 (d, J =10 Hz, 4H, H^{j}), 7.94-7.91 (m, 4H, $H^{4',4''}$), 7.85-7.84 (d, J =5 Hz, 4H, H^{k}), 7.57 (s, 1H, H^{i}), 7.41-7.39 (m, 4H, $H^{5',5''}$), 7.28 (s, $CHCl_3$), 7.25 (s, 2H, H^{h}), 4.01 (s, 3H, OCH_3); ^{13}C NMR (500 MHz, $CDCl_3$) δ: 160.50, 156.25, 155.98, 149.79, 149.13, 142.56, 141.73, 137.68, 136.96, 127.83, 127.81, 123.88, 121.44, 118.86, 118.81, 112.13, 55.61.

***bis*Ru^{3+}adduct 4:** Monomer **2** (188 mg, 250μmol) and $RuCl_3\cdot 3H_2O$ (137.3 mg, 525 μmol) were added into MeOH (50 mL), then the mixture was refluxed for 18h. The mixture was filtered giving a solid that was washed by MeOH (3X) and CH_2Cl_2 to afford (65%) **4**, as a brown solid: 189.8mg, mp: >300°C. Elemental analysis: chemical formula, $C_{50}H_{36}Cl_6N_6O_2Ru_2\cdot CH_2Cl_2$, calculated: C 48.90; H 3.06; N 6.71%; found: C 46.62, H 2.82, N 6.71%;



bisRu^{2+} trimer 5: The *m*-monomer **3** (51mg, 44 µmol) was dissolved in a 1:1 solution of $CHCl_3$: MeOH (60mL). After the solution was heated to reflux, **4** (63.6 mg, 88 µmol) in MeOH (10mL) was added then ultrasonically dispersed for 5min, then added dropwise to the solution. After refluxing for 48h, the solvent was removed *in vacuo* to give a residue that was column chromatography (Al_2O_3, $CHCl_3$ then to $CHCl_3$:MeOH=100:3) to afford **5**, as a red powder: 58mg, 55%; mp: >300°C; Elemental analysis (using PF_6^- as the counterions, since the ionic compounds are easy to separate by simply adding NH_4PF_6 or KPF_6 to form the precipitations): chemical formula, $C_{148}H_{104}N_{18}O_4Ru_2\cdot4PF_6$, calculated: C 59.64, H 3.52, N 8.46%; found: C 60.89, H 4.58, N 7.67%; ^{1}H NMR (500 MHz, MeOD/$CDCl_3$) δ 9.27 (s, 4H, $\mathrm{tpy}^{A}H^{3',5'}$), 9.24 (s, 4H, $\mathrm{typ}^{B}H^{3',5'}$), 8.95-8.93 (d, J =10 Hz, 4H, $\mathrm{tpy}^{A}H^{3,3''}$), 8.88-8.86 (d, J =10 Hz, 4H, $\mathrm{tpy}^{B}H^{3,3''}$), 8.76 (s, 4H, $\mathrm{typ}^{C}H^{3',5'}$), 8.76-8.75 (d, J =5 Hz, 4H, $\mathrm{tpy}^{C}H^{6,6''}$), 8.73-8.72 (d, J =5 Hz, 4H, $\mathrm{tpy}^{C}H^{3,3''}$), 8.38-8.36 (d, J =10 Hz, 4H, $\mathrm{Ph}^{B}H^{j}$), 8.26-8.24 (d, J =10 Hz, 4H, $\mathrm{Ph}^{A}H^{j}$), 8.12-8.10 (d, J =10 Hz, 4H, $\mathrm{Ph}^{C}H^{j}$), 8.09-8.06 (m, 4H, $\mathrm{tpy}^{A}H^{4',4''}$), 8.08-8.06 (d, J =10 Hz, 4H, $\mathrm{Ph}^{B}H^{k}$), 8.04-8.01 (m, 8H, $\mathrm{tpy}^{B}H^{4',4''}$, $\mathrm{tpy}^{C}H^{4',4''}$), 7.93-7.91 (d, J =10 Hz, 4H, $\mathrm{Ph}^{C}H^{k}$), 7.67-7.65 (d, J =10 Hz, 4H, $\mathrm{Ph}^{A}H^{k}$), 7.65 (s, 2H, H^{i}), 7.55-7.53 (m, 4H, $\mathrm{tpy}^{C}H^{5',5''}$), 7.49-7.48 (d, J =5 Hz, 4H, $\mathrm{tpy}^{A}H^{6,6''}$), 7.44-7.43 (d, J =5 Hz, 4H, $\mathrm{tpy}^{B}H^{6,6''}$), 7.35-7.33 (m, 4H, $\mathrm{tpy}^{A}H^{5',5''}$), 7.31(s, 4H, H^{h}), 7.30-7.28 (m, 4H, $\mathrm{tpy}^{B}H^{5',5''}$), 7.19 (s, 2H, H^{g}), 4.08 (s, 6H, OCH_3), 4.04(s, 6H, OCH_3); ^{13}C NMR (101 MHz, MeOD:$CDCl_3$=1:1): δ 160.63, 160.19, 158.07, 157.83, 155.37, 155.22, 151.98, 151.58, 150.16, 148.99, 148.96, 148.65, 148.45, 147.40, 143.91, 143.35, 142.65, 141.85, 141.76, 139.21, 138.67, 138.52, 138.24, 137.29, 135.23, 134.34, 132.20, 131.32, 129.66, 128.50, 128.18, 127.97, 127.90, 127.72, 125.40, 124.96, 124.49, 122.20, 121.64, 121.27, 119.12, 118.73, 113.89, 112.38, 56.20, 55.57; ESI/MS: (*m*/*z*) 600.622 $[M\text{-}4Cl^{-}]^{4+}$ (calcd *m*/*z*=600.165).

Polymer 6: $FeCl_2\cdot 4H_2O$ (dissolved in MeOH) was added dropwise into a solution of **5** in $MeOH/CHCl_3$, the mixture was stirred at 25 °C for 8 h. Then the solvent was evaporated *in vacuo*to afford **6**, as a violet powder, mp: >300°C. Elemental analysis (using PF_6^{-} as the counterions): chemical formula, $[C_{152}H_{111}C_{l9}FeN_{18}O_5Ru_2\cdot 6PF_6^{-}\cdot 3CHCl_3\cdot MeOH]_n$, calculated: C 49.12; H 3.01; 6.78 %; found: C 49.15, H 3.30, N 6.55%;



Hexamer 7: Polymer **6** (20mg) was dissolved in MeOH (15 mL), then heated at 80℃ for 16 hours. There sultant solution was added to excess NH_4PF_6 in MeOH to afford a red purple precipitate, which was filtered and washed with MeOH to generate (>90%) a dark purple solid **7**: mp>300°C; ^1H NMR (500 MHz, CD_3OD): δ 9.59 (s,

8H, typ$^{\mathrm{C}}H^{3',5'}$), 9.40 (s, 8H, typ$^{\mathrm{B}}H^{3',5'}$), 9.35 (s, 8H, tpy$^{\mathrm{A}}H^{3',5'}$), 8.98-8.96 (d, J =10Hz, 8H, tpy$^{\mathrm{B}}H^{3,3''}$), 8.96-8.94 (d, J=10 Hz, 16H, tpy$^{\mathrm{A}}H^{3,3''}$, tpy$^{\mathrm{C}}H^{3,3''}$), 8.64-8.62 (d, J=10 Hz, 8H, Ph$^{\mathrm{C}}H^{j}$), 8.52-8.50 (d, J=10 Hz, 8H, Ph$^{\mathrm{B}}H^{j}$), 8.34-8.32 (d, J=10 Hz, 8H, Ph$^{\mathrm{A}}H^{j}$), 8.25-8.23 (d, J=10 Hz, 8H, Ph$^{\mathrm{C}}H^{k}$), 8.21-8.19 (d, J=10 Hz, 8H, Ph$^{\mathrm{B}}H^{k}$), 8.07-8.02 (m, 24H, tpy$^{\mathrm{A}}H^{4',4''}$, tpy$^{\mathrm{B}}H^{4',4''}$, tpy$^{\mathrm{C}}H^{4',4''}$), 7.86 (s, 4H, H^{i}), 7.72-7.70 (d, J =10 Hz, 8H, Ph$^{\mathrm{A}}H^{k}$), 7.62-7.60 (m, 16H, tpy$^{\mathrm{A}}H^{6,6''}$, tpy$^{\mathrm{B}}H^{6,6''}$), 7.49 (s, 4H, H^{f}),7.48 (s, 4H, H^{h}), 7.39-7.38 (d, J=5 Hz, 8H, tpy$^{\mathrm{C}}H^{6,6''}$), 7.34-7.30 (m,16H, tpy$^{\mathrm{A}}H^{5',5''}$, tpy$^{\mathrm{B}}H^{5',5''}$), 7.26(s, 4H, H^{g}), 7.26-7.23 (m, 8H, tpy$^{\mathrm{C}}H^{5',5''}$), 4.10(s, 12H, OCH_3), 4.07(s, 12H, OCH_3); ^{13}C NMR (101 MHz, CD$_3$CN) δ: 161.00, 160.39, 158.25, 158.10, 155.52, 155.50, 153.11, 152.44, 150.56, 149.82, 149.28, 148.28, 147.68, 147.64, 143.90, 143.04, 142.85, 142.00, 141.53, 138.79, 138.07, 138.03, 136.16, 136.02, 135.90, 134.77, 132.00, 131.36, 130.46, 128.55, 128.46, 128.34, 127.50, 127.43, 127.36, 126.77, 124.61, 124.58, 121.53, 121.48, 121.32, 118.43, 113.91, 112.69, 55.83, 55.48; ESI/MS: (m/z) 519.9255 [M-10PF$_6^-$]$^{10+}$, (calcd m/z=519.9121); 459.5691 [M-11PF$_6^-$]$^{11+}$, (calcd m/z = 459.5596).

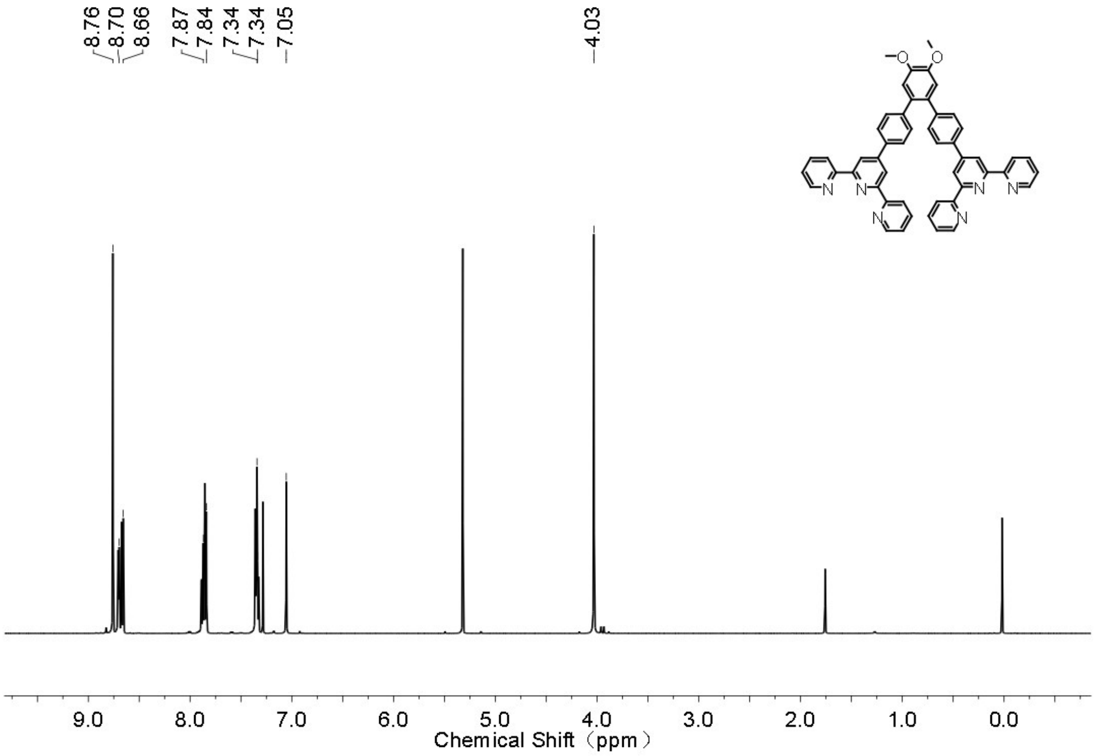


Figure S1. ^{1}H NMR spectrum of **2**.

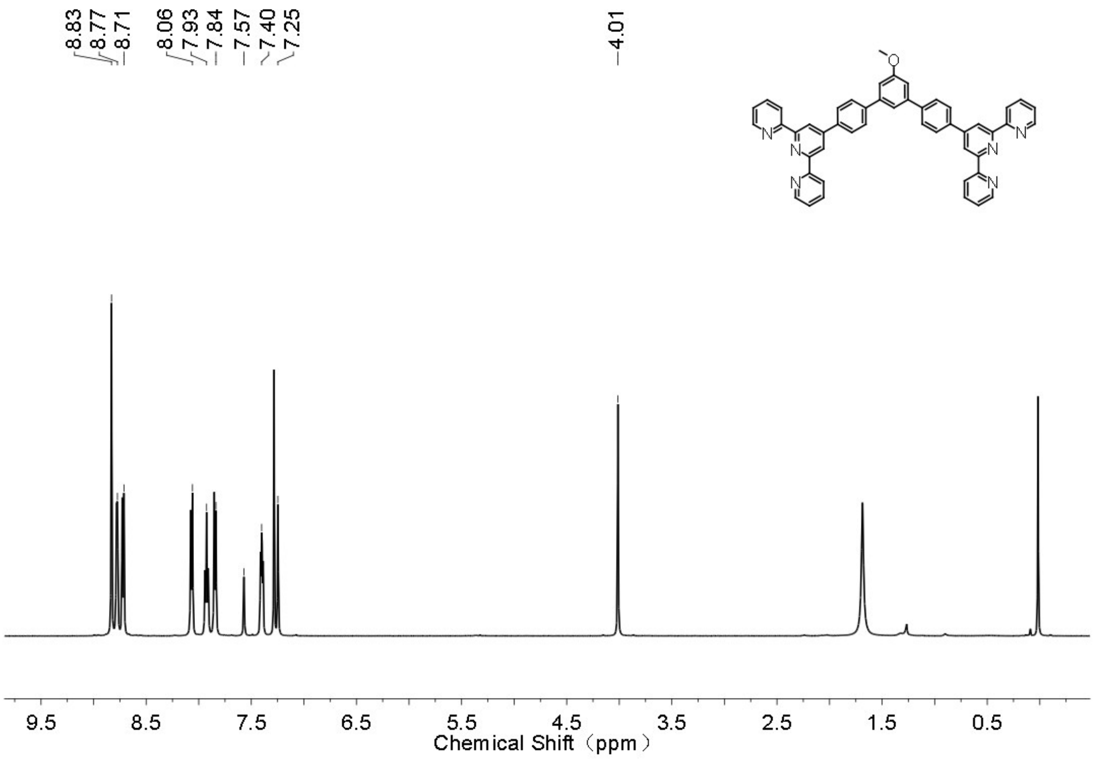


Figure S2. ^{1}H NMR spectrum of **3**.

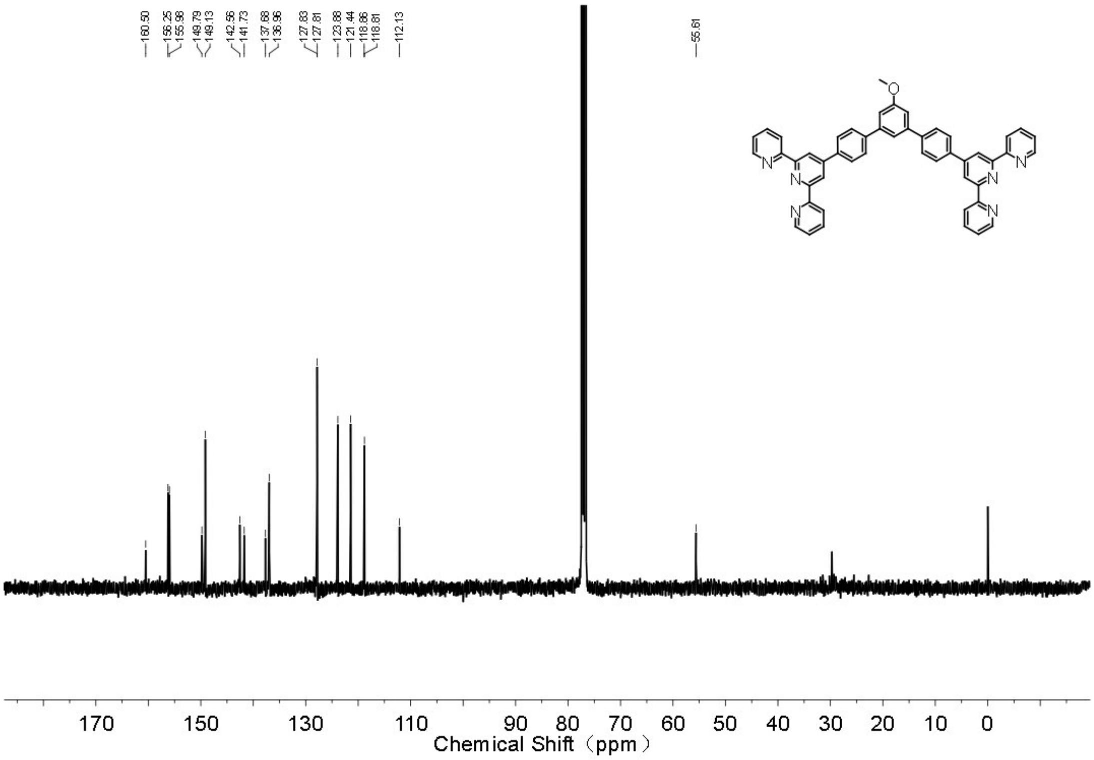


Figure S3. ^{13}C NMR spectrum of **3**.

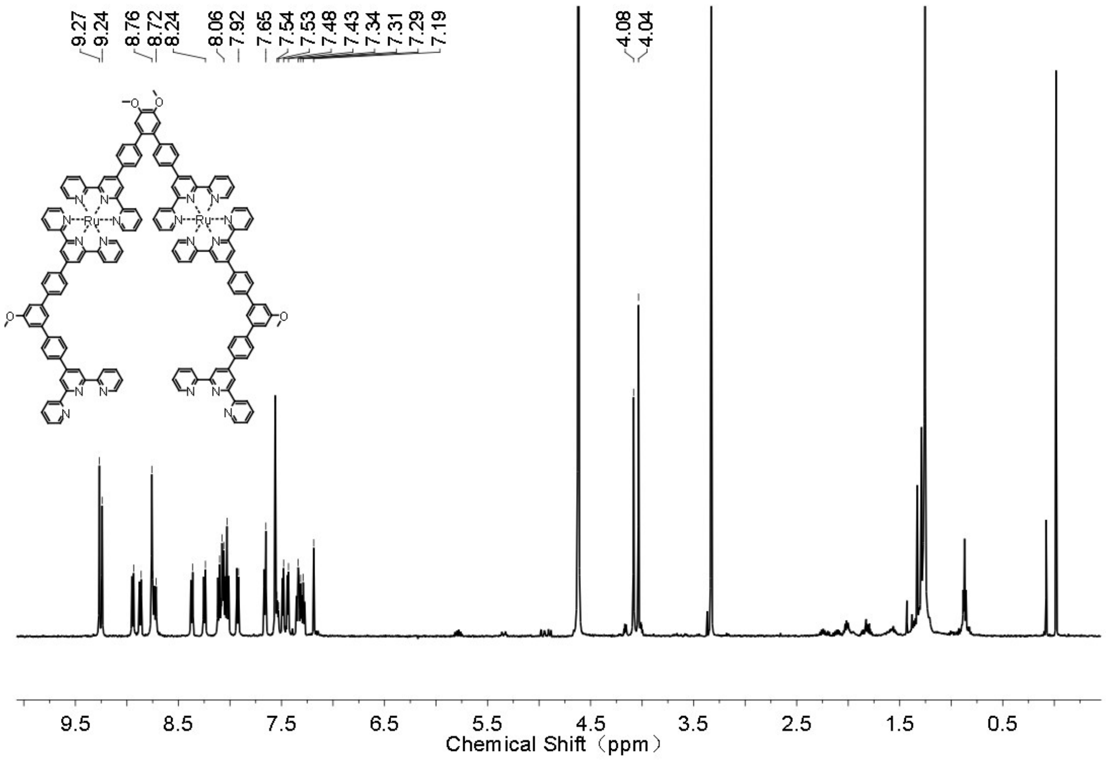


Figure S4. ^{1}H NMR spectrum of **5**.

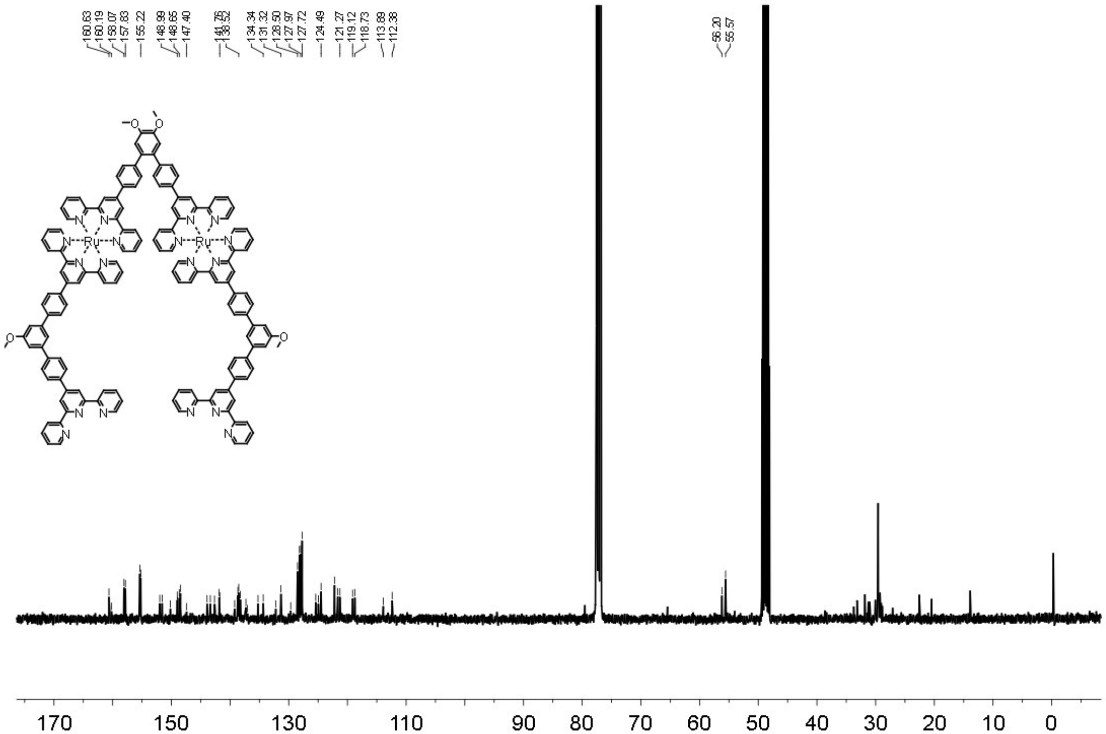


Figure S5. ^{13}C NMR spectrum of **5**.

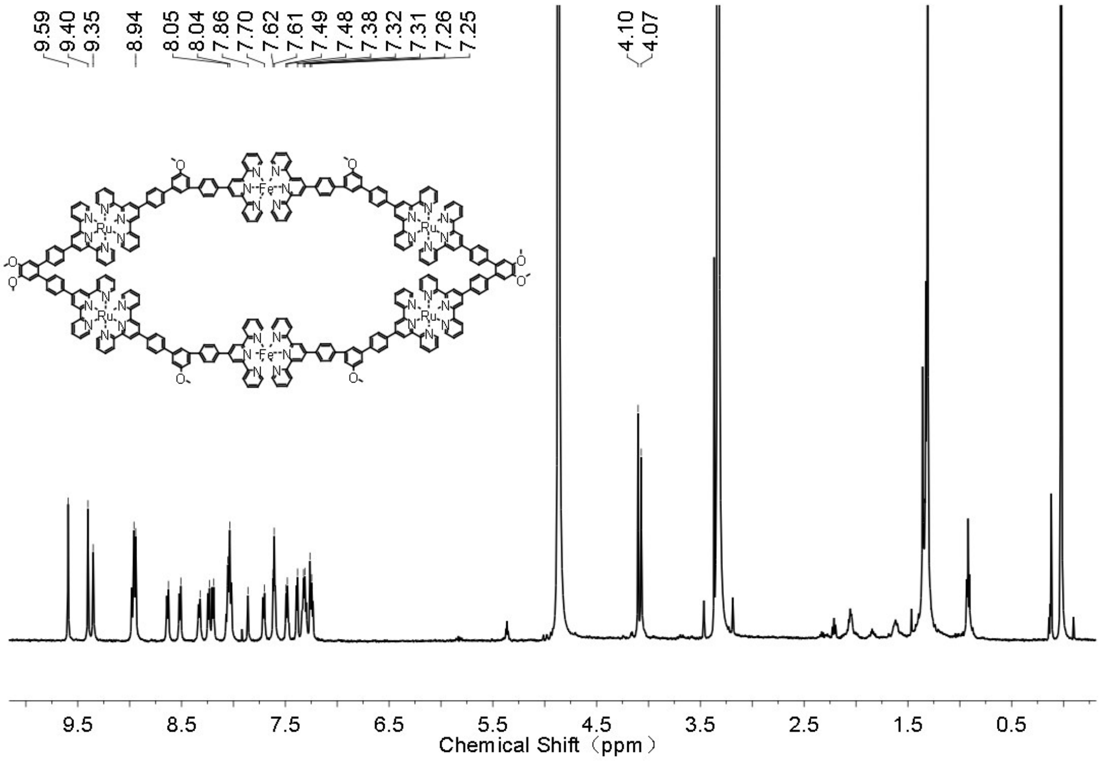


Figure S6. ^{1}H NMR spectrum of **7**.

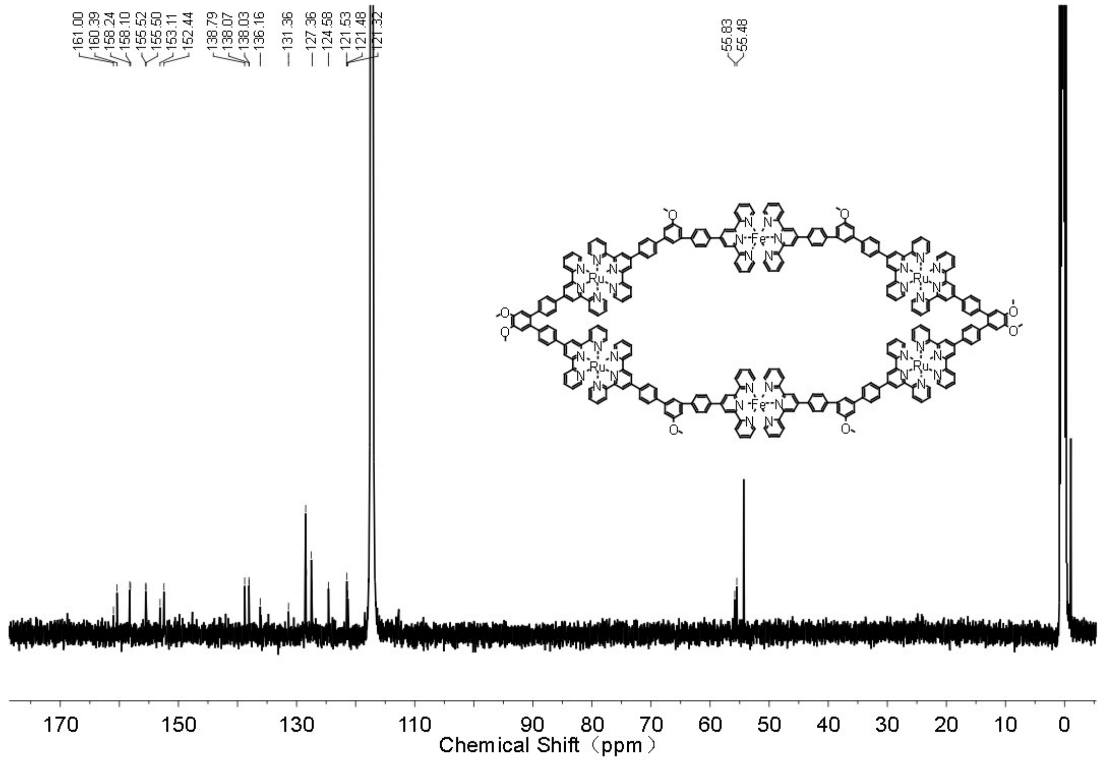


Figure S7. ^{13}C NMR spectrum of **7**

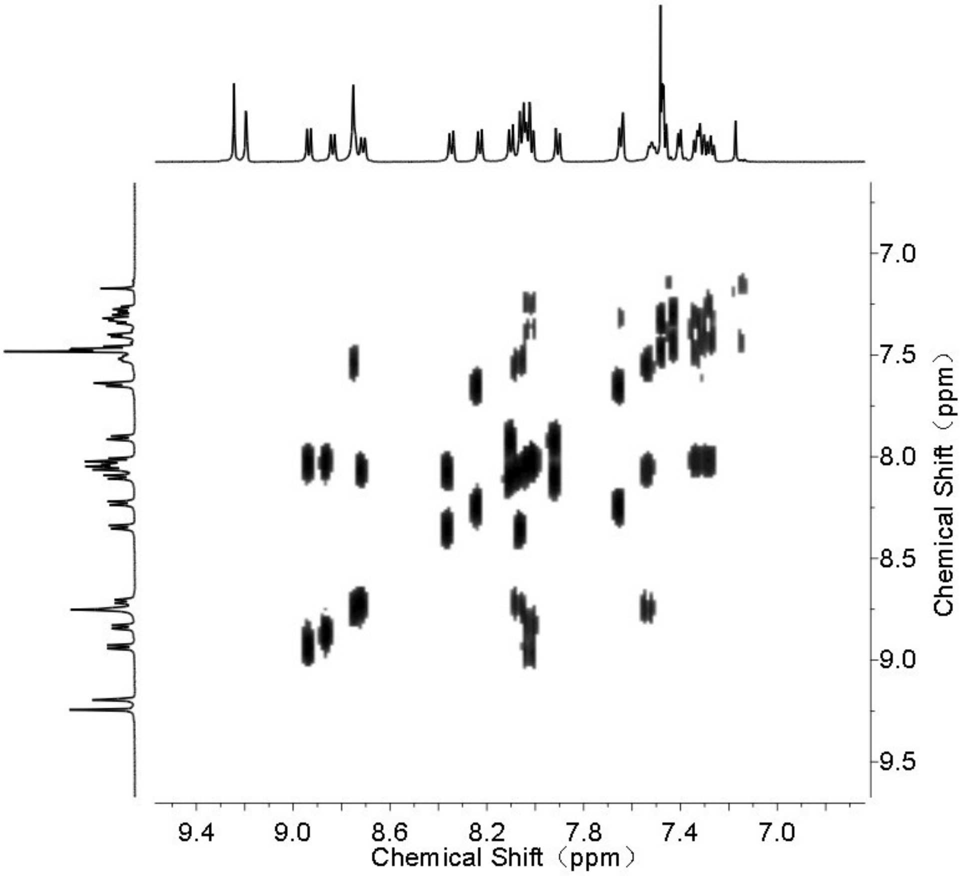


Figure S8. COSY spectrum of **5**.

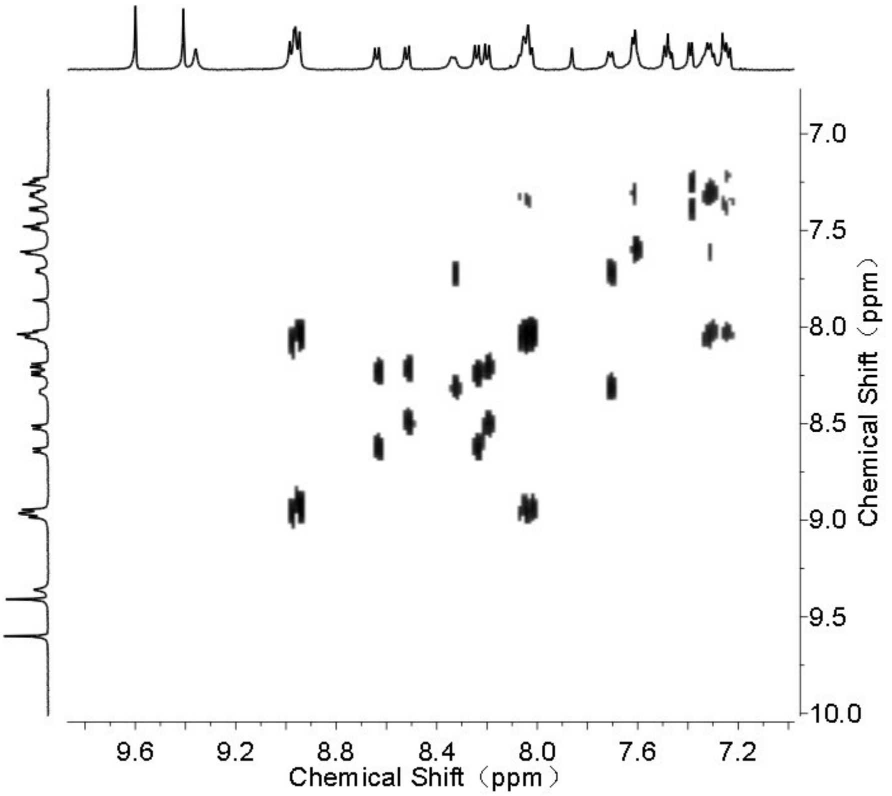


Figure S9. COSY spectrum of **7**.

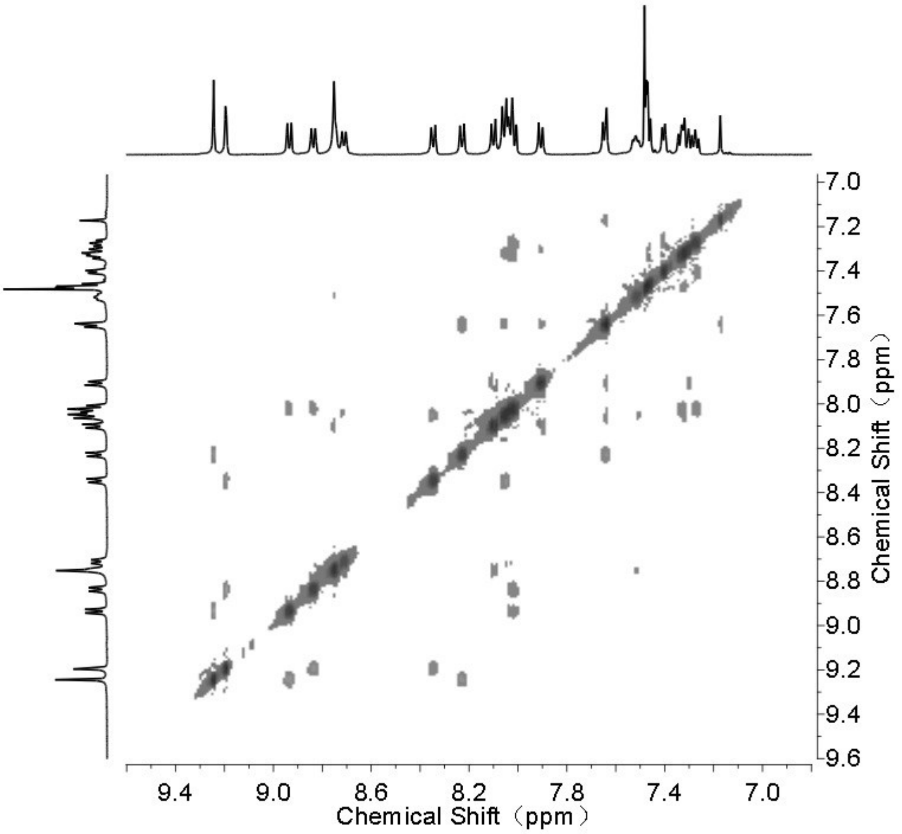


Figure S10. 2D ROESY spectrum of **5**.

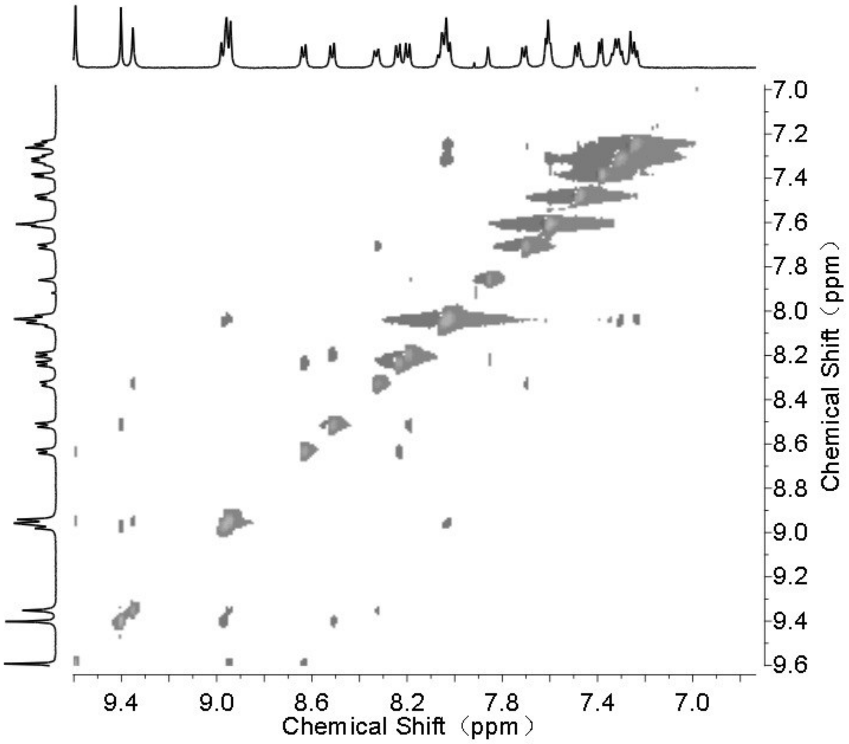


Figure S11. 2D ROESY spectrum of **7**.

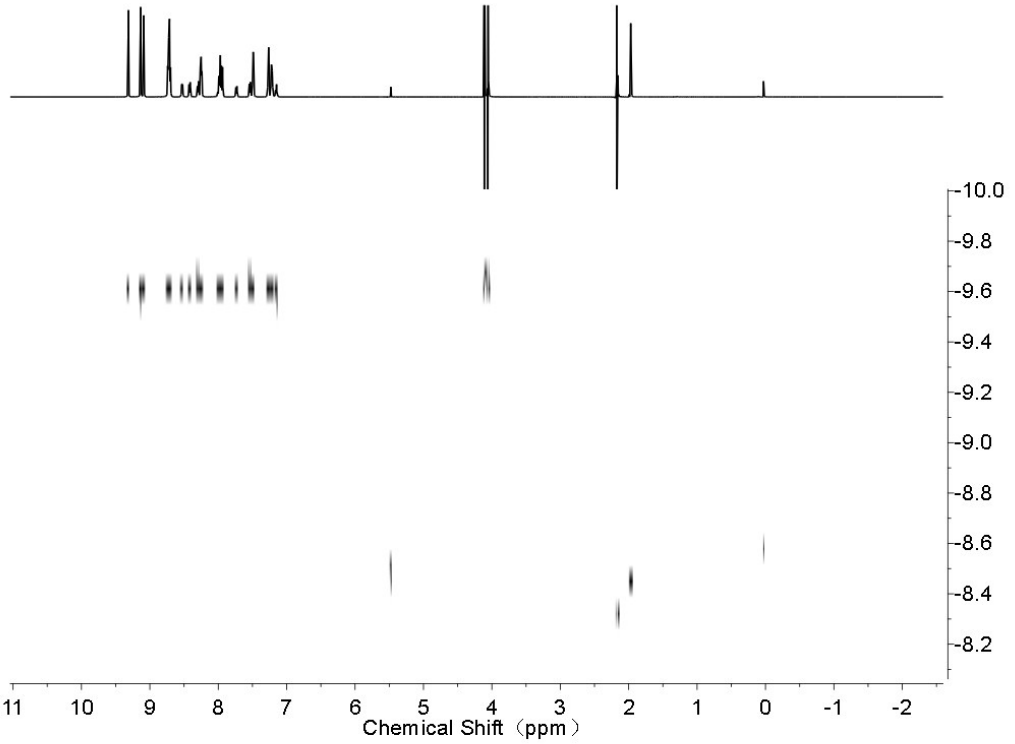


Figure S12. DOSY spectrum of **7**.

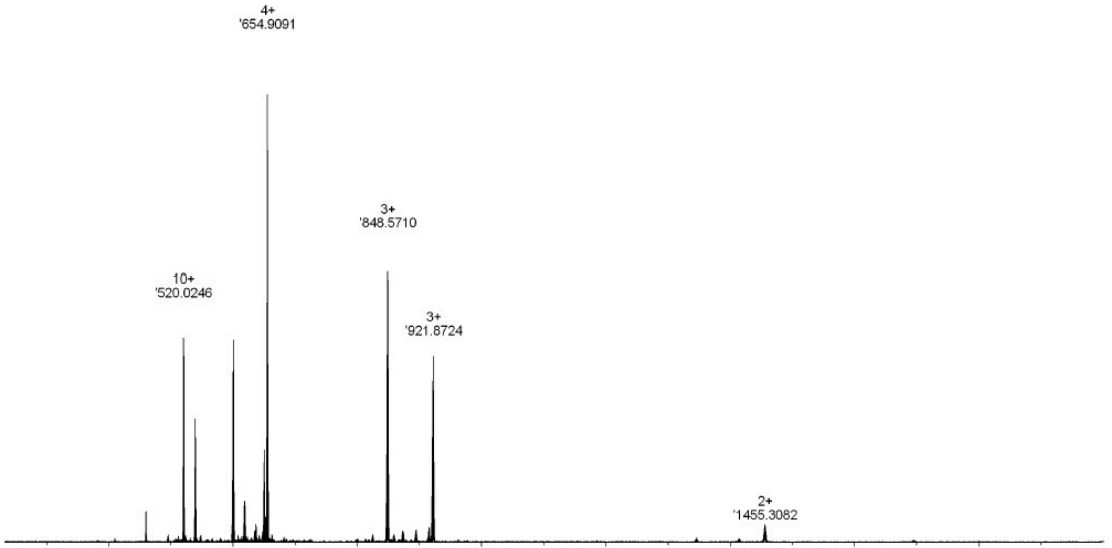


Figure S13. ESI-MS spectrum of **7**.

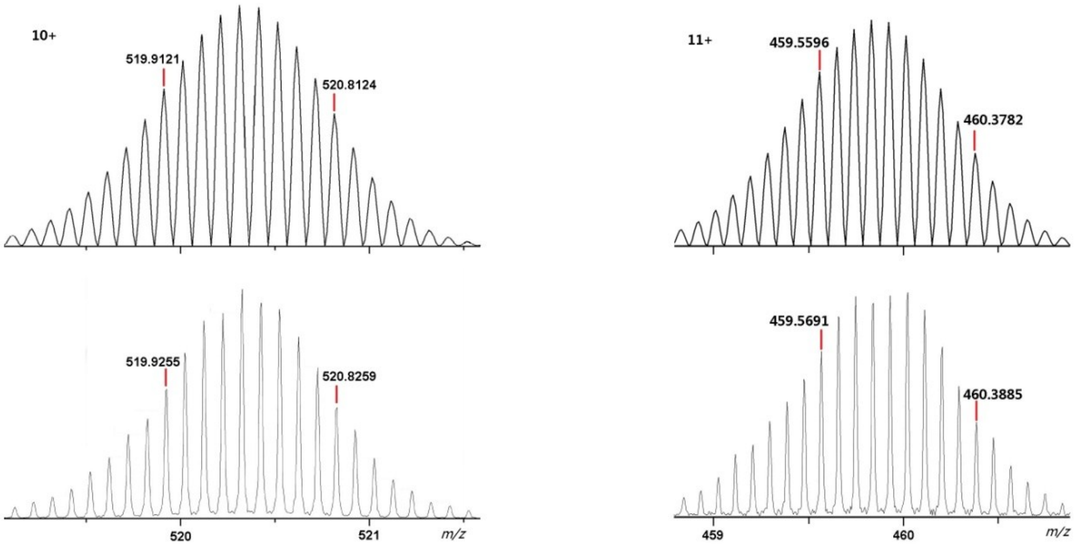


Figure S14. Calculated (top) and measured (bottom) isotope patterns for the different charge states (10+ and11+) observed from **7** (PF_6^-, as counterion).

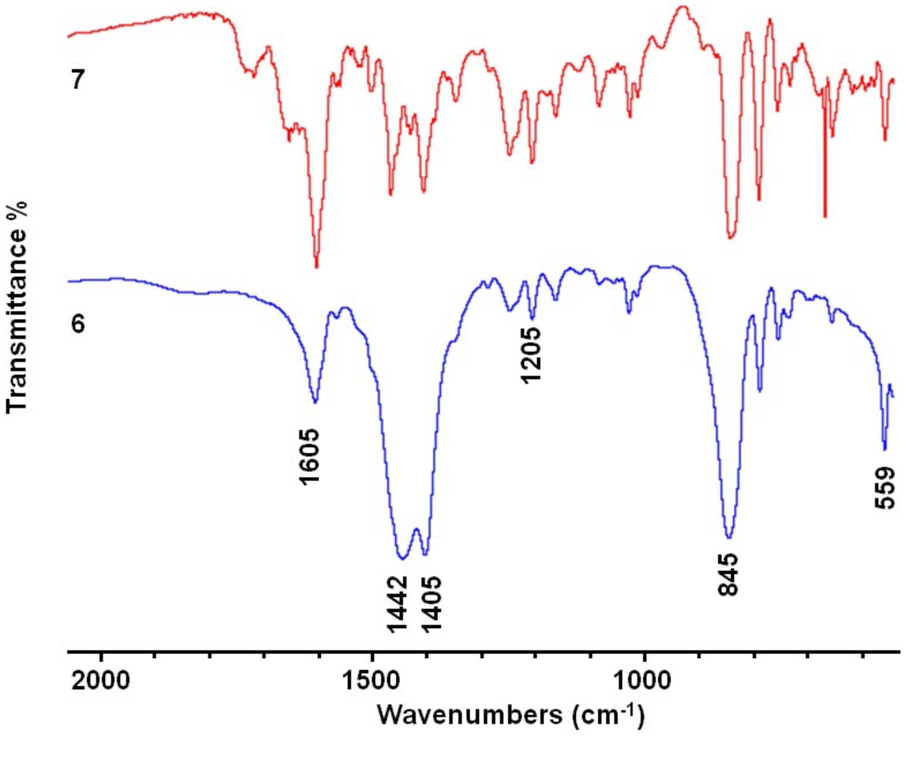


Figure S15. The FT-IR spectrum of polymer **6** and hexamer **7**

The transformation from polymer **6** to heaxmer **7** was also proved by FT-IR spectrum. Polymer **6** showed broader absorptions than **7**, which could indicate **6** as a polymer. The characteristic absorption bands due to terpyridine and benzene structures are situated at 1605 cm^{-1}, 1442 cm^{-1}, 1405 cm^{-1}, 1205 cm^{-1} for the symmetric stretching of C=C and C=N, the peak at 845cm^{-1} and 559cm^{-1} were attribute to the symmetric stretching and bending vibrations of P-F (PF_6^-), respectively.

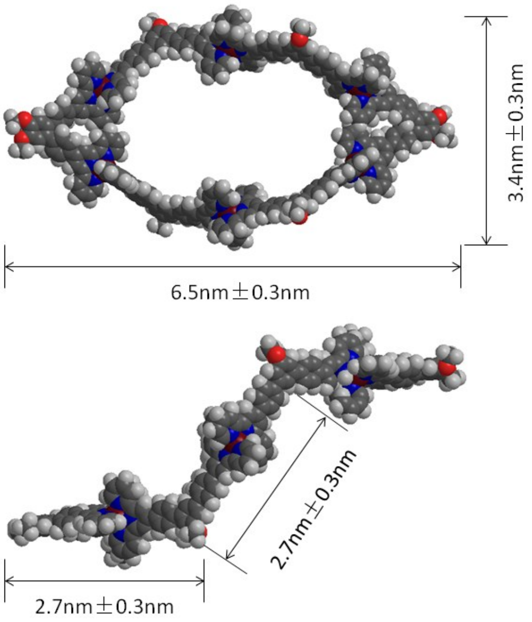


Figure S16. Representative energy-minimized structure of **7**.

References

1 Schultz, A.; Li, X.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Eur. J. Inorg.Chem.* **2013**, 2492.

2 Schultz, A.; Li, X.; McCusker, C. E.; Moorefield, C. N.; Castellano, F. N.; Wesdemiotis, C.; Newkome, G. R. *Chem. Eur. J.* **2012**, *18*, 11569.