

Supporting Information

Macrocycle with Equatorial Coordination Sites Provides New Opportunity for Structure-Diverse Metallacages

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Table of Contents

Section I. Synthesis and characterization of self-assembled metallacages...	S2-S22
Section II. Single-crystal structures of TP3 and M2.....	S23-S26

Section I. Synthesis and characterization of self-assembled metallacages

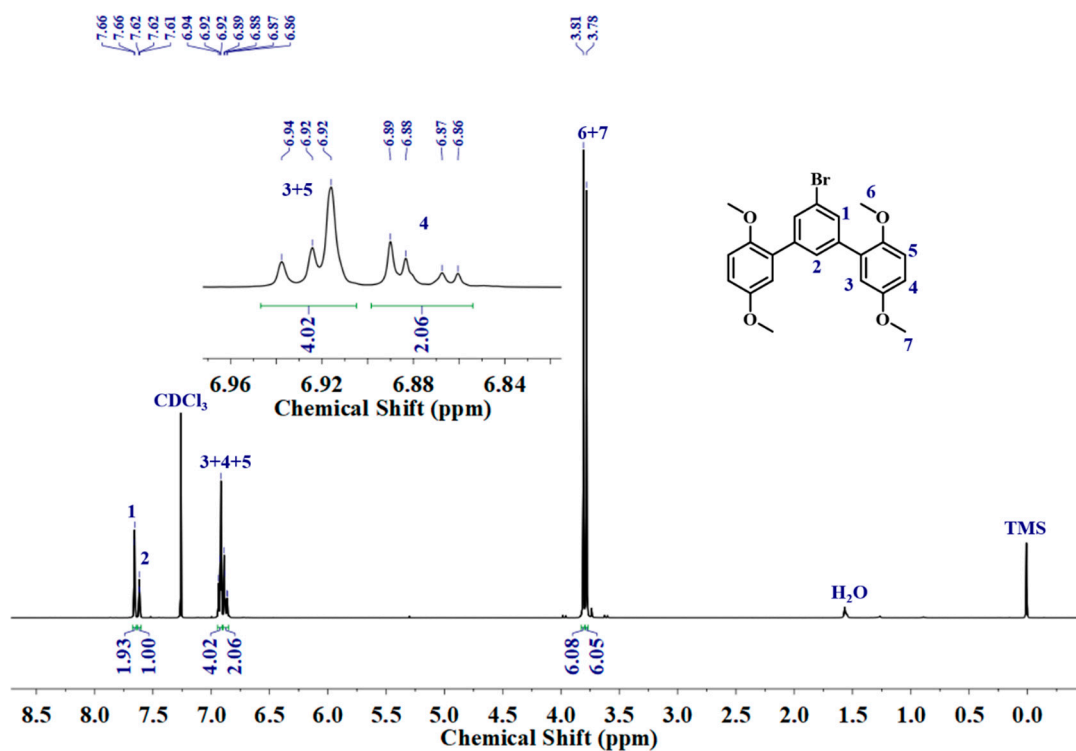


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of 5'-bromo-2,2'',5,5''-tetramethoxy-1,1':3',1''-terphenyl.

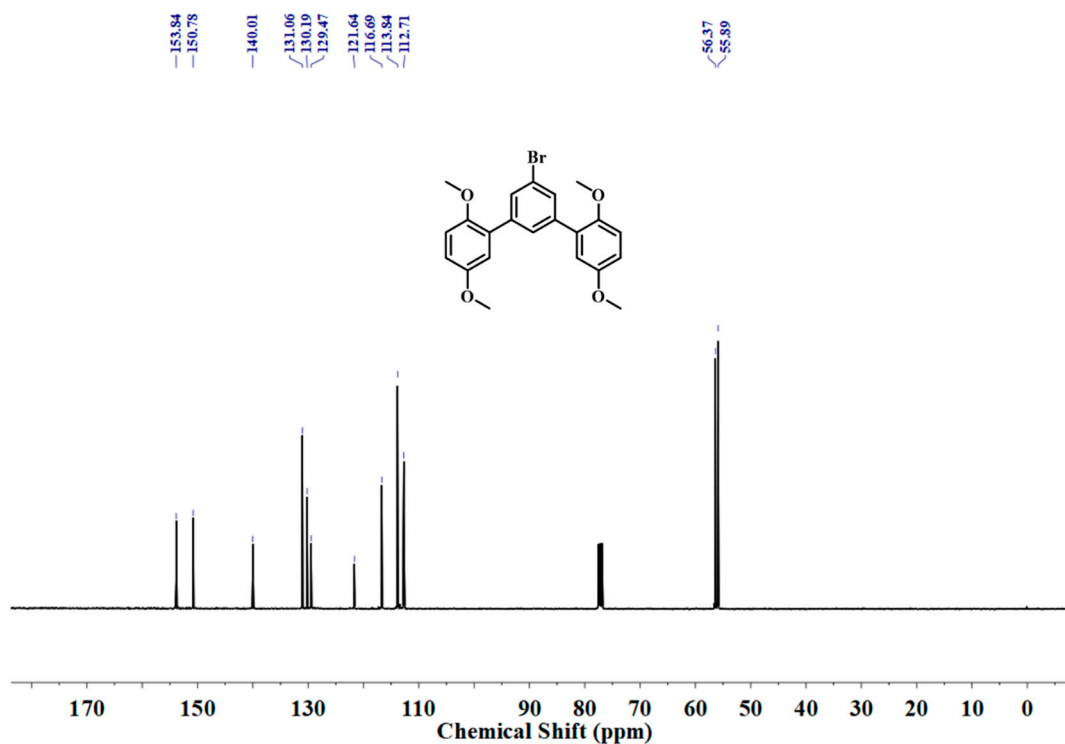


Figure S2. ¹³C NMR spectrum (100 MHz, CDCl₃, 298 K) of 5'-bromo-2,2'',5,5''-tetramethoxy-1,1':3',1''-terphenyl.

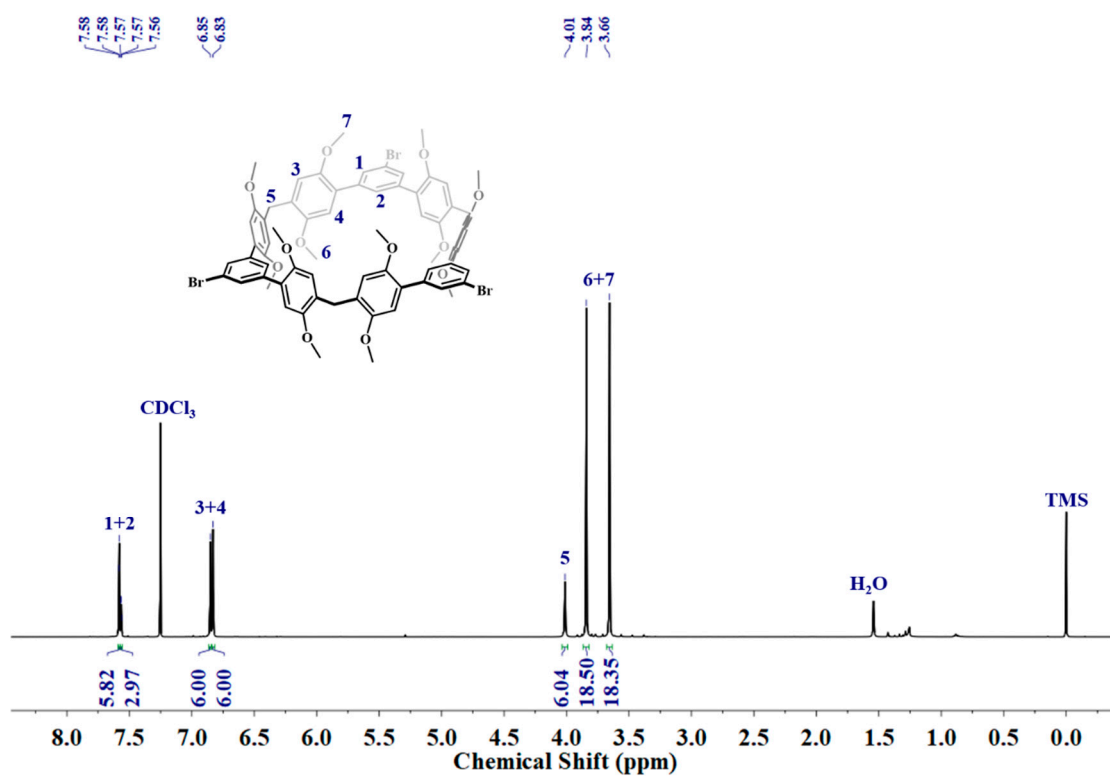


Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of TP3-Br.

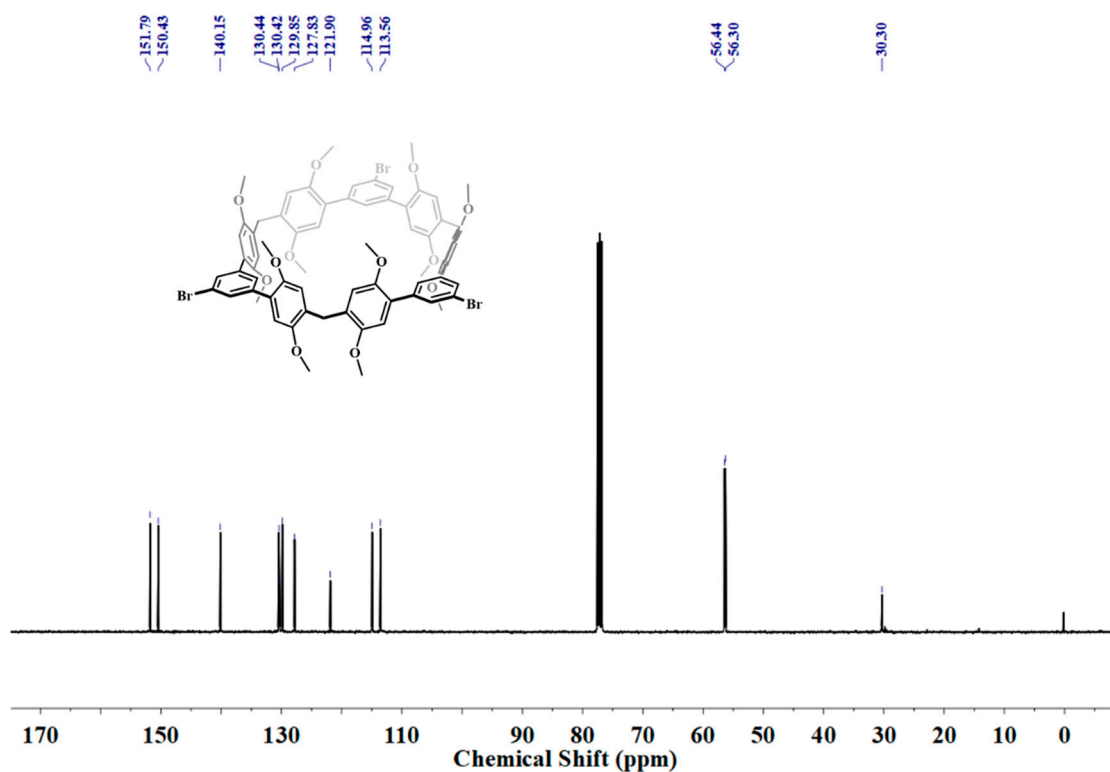


Figure S4. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of TP3-Br.

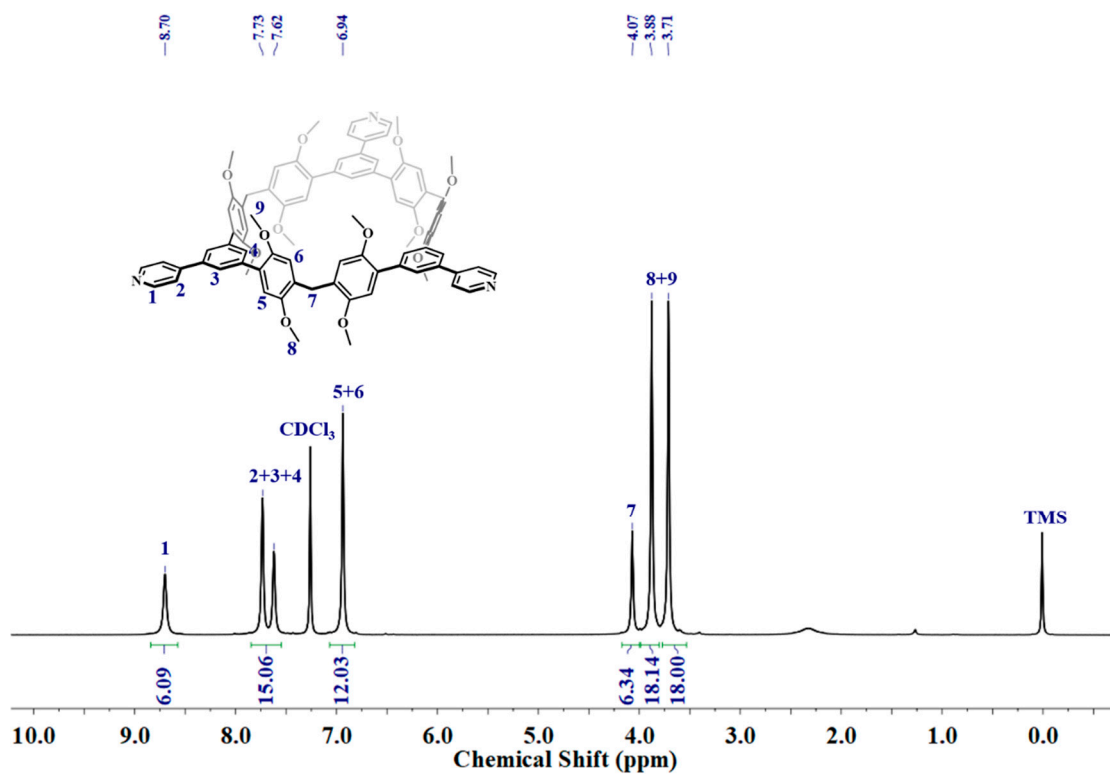


Figure S5. ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of TP3.

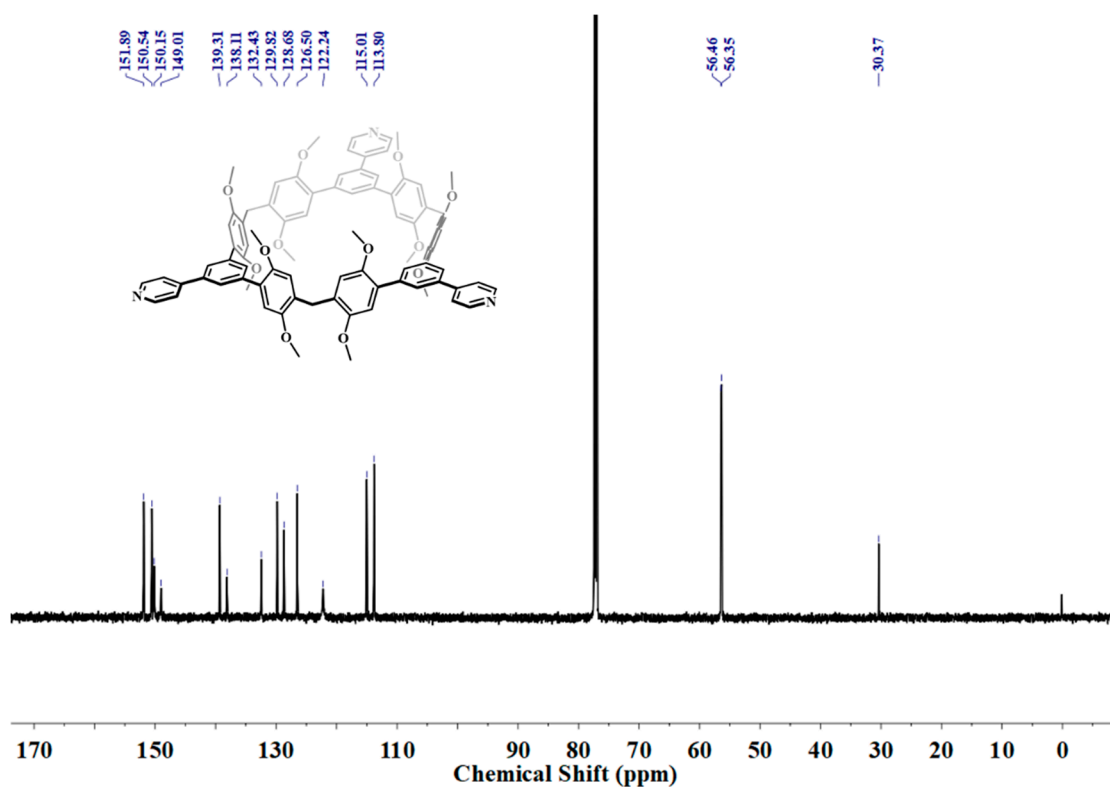


Figure S6. ¹³C NMR spectrum (100 MHz, CDCl₃, 298 K) of TP3-Br.

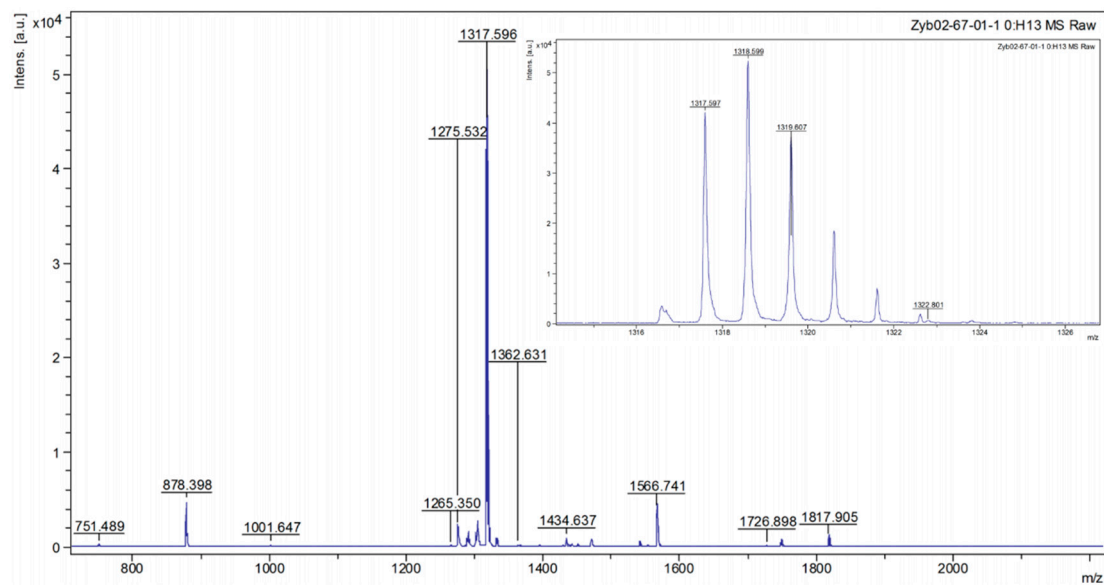


Figure S7. MALDI-TOF MS of TP3-Br.

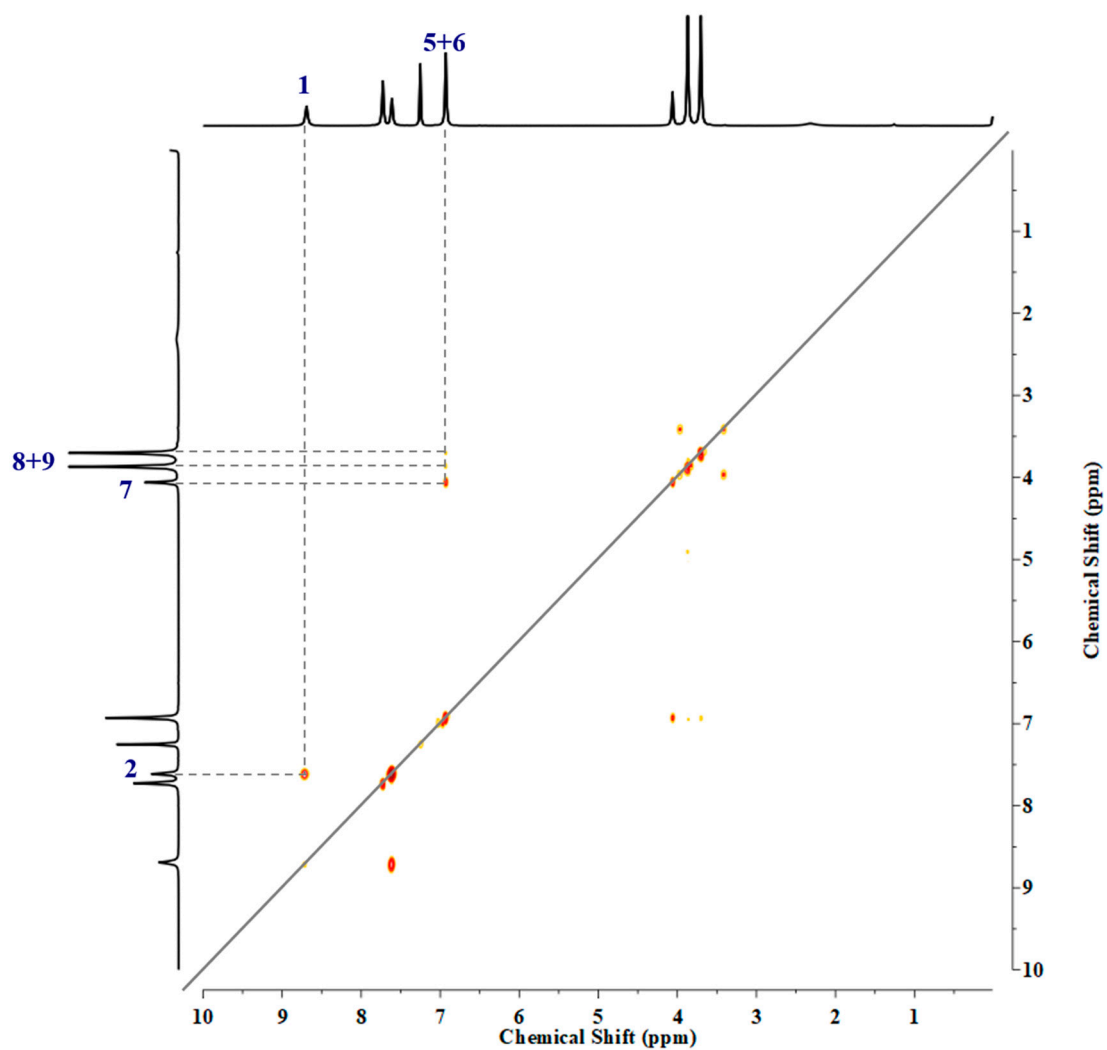
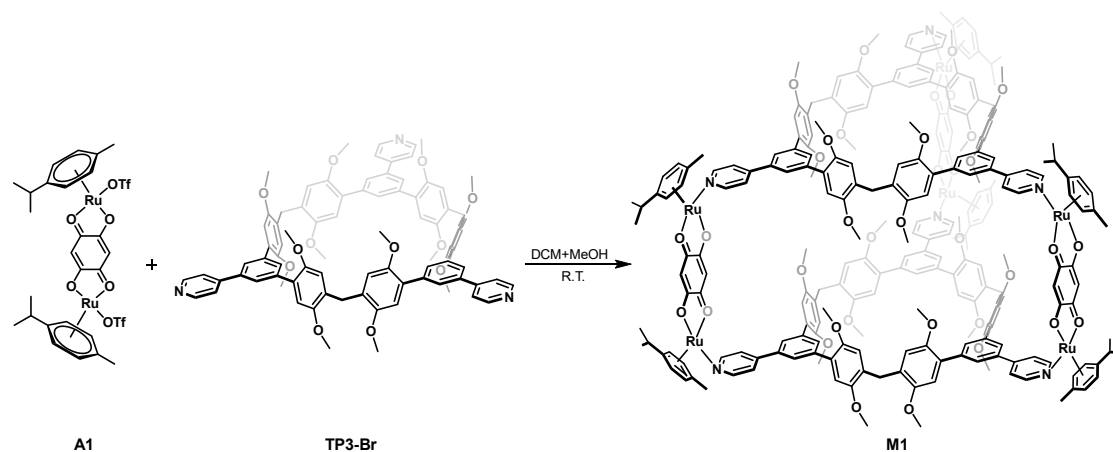


Figure S8. 2D COSY spectrum (400 MHz, CDCl₃, 298 K) of TP3-Br.



Scheme S1. Synthetic routes for the **M1**.

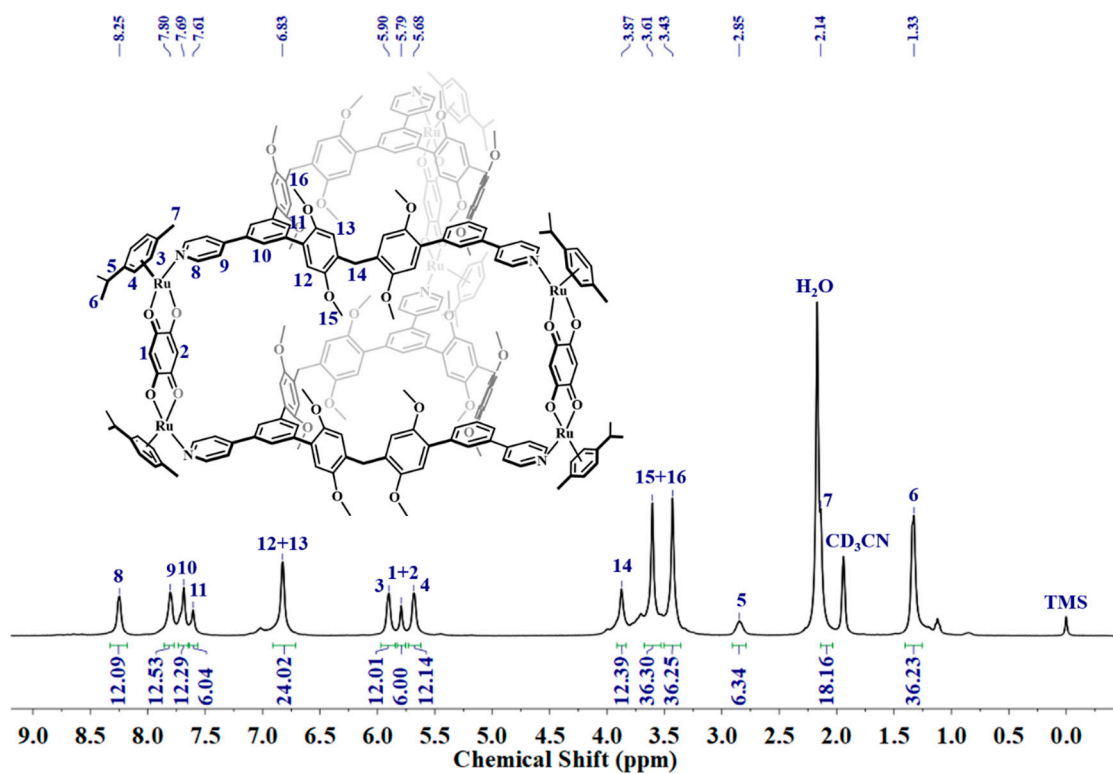


Figure S9. ^1H NMR spectrum (400 MHz, CD_3CN , 298 K) of **M1**.

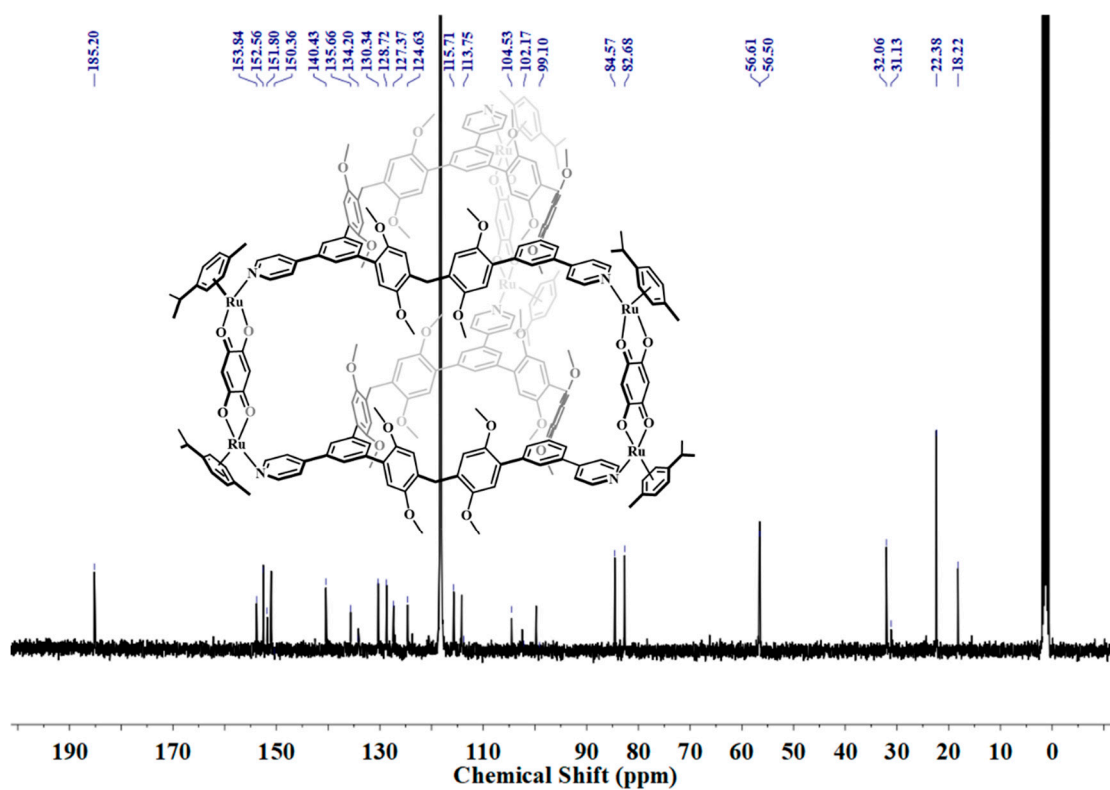


Figure S10. ^{13}C NMR spectrum (100 MHz, CD_3CN , 298 K) of **M1**.

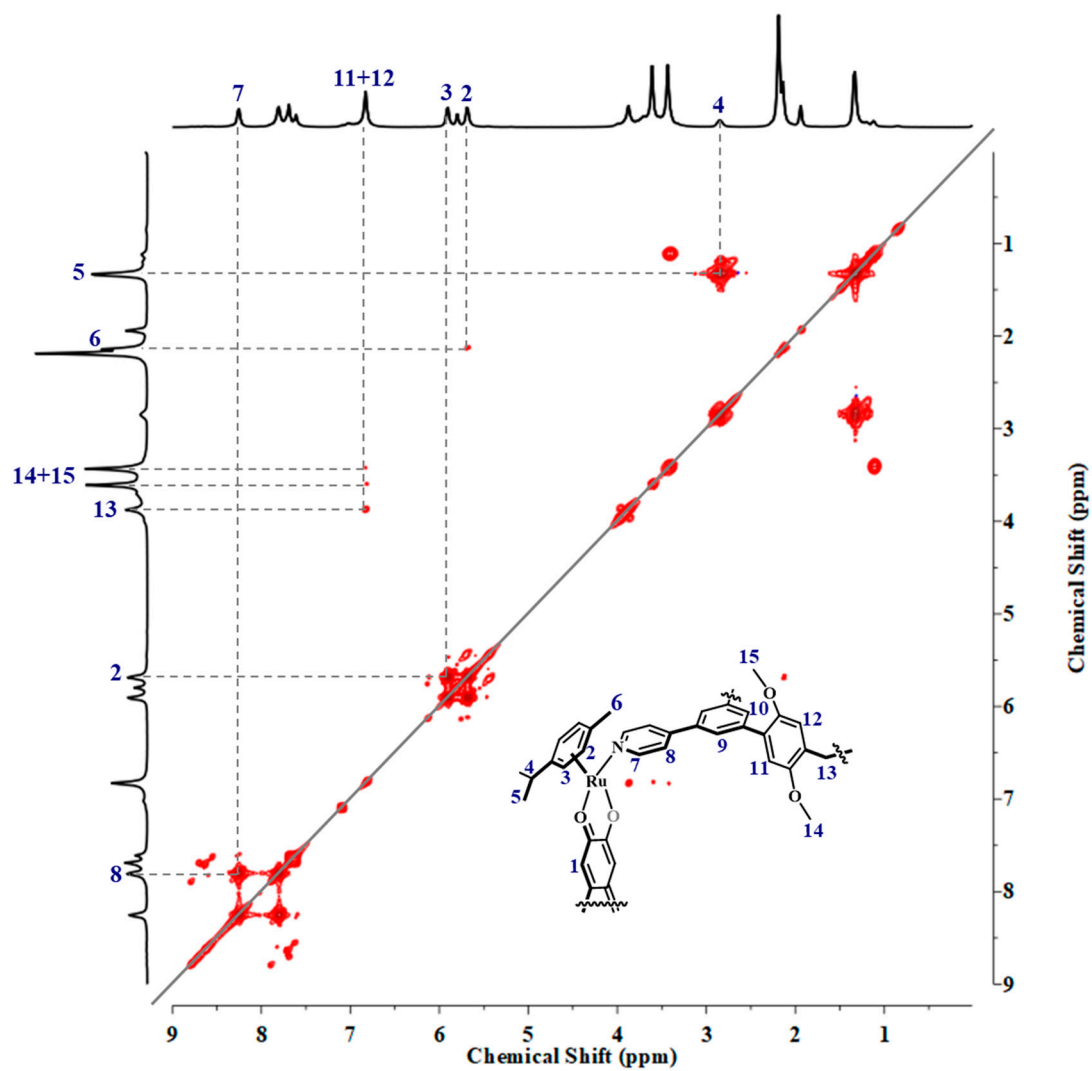


Figure S11. 2D COSY spectrum (400 MHz, CD₃CN, 298 K) of **M1**.

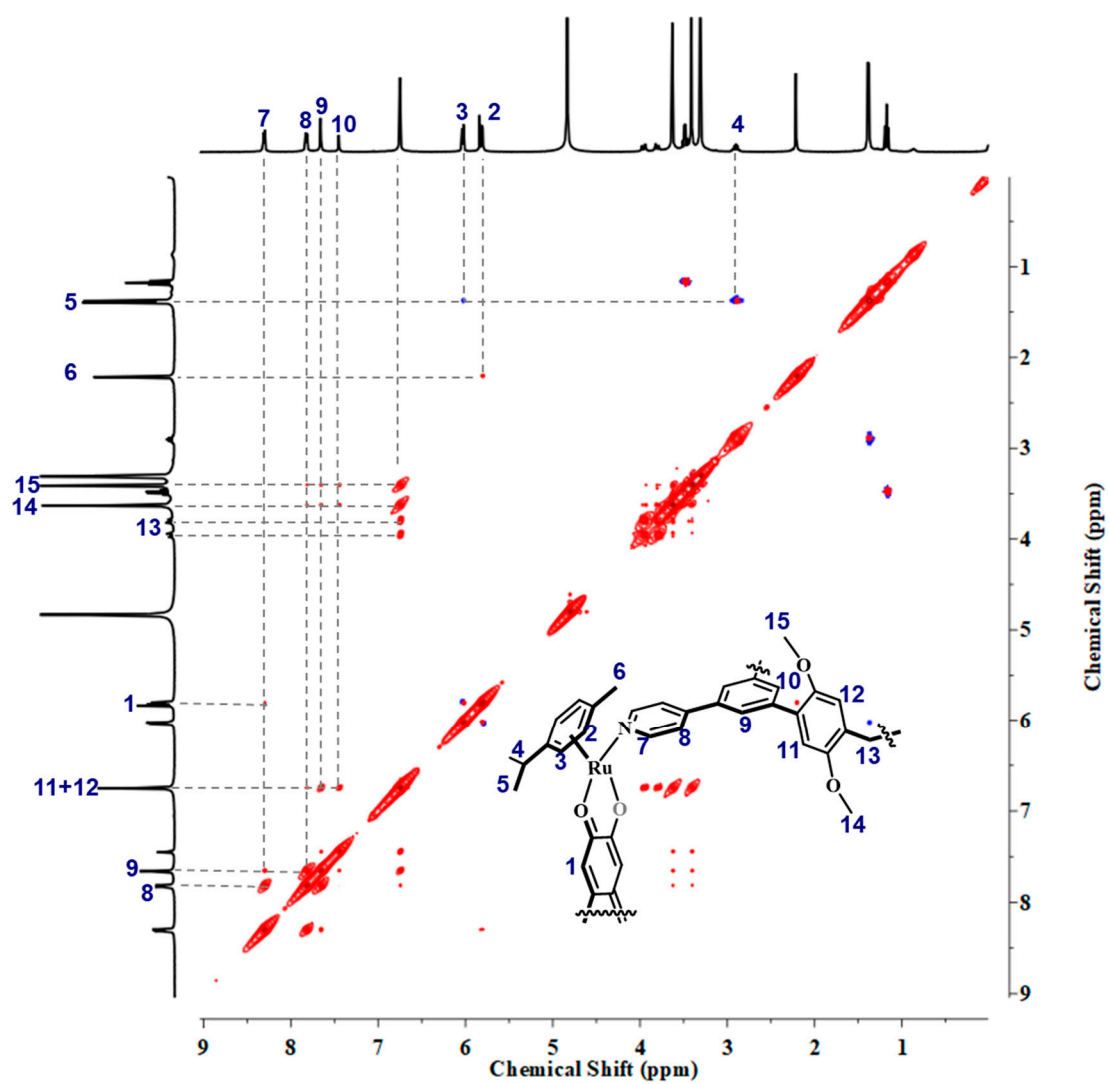


Figure S12. 2D NOESY spectrum (400 MHz, CD₃CN, 298 K) of **M1**.

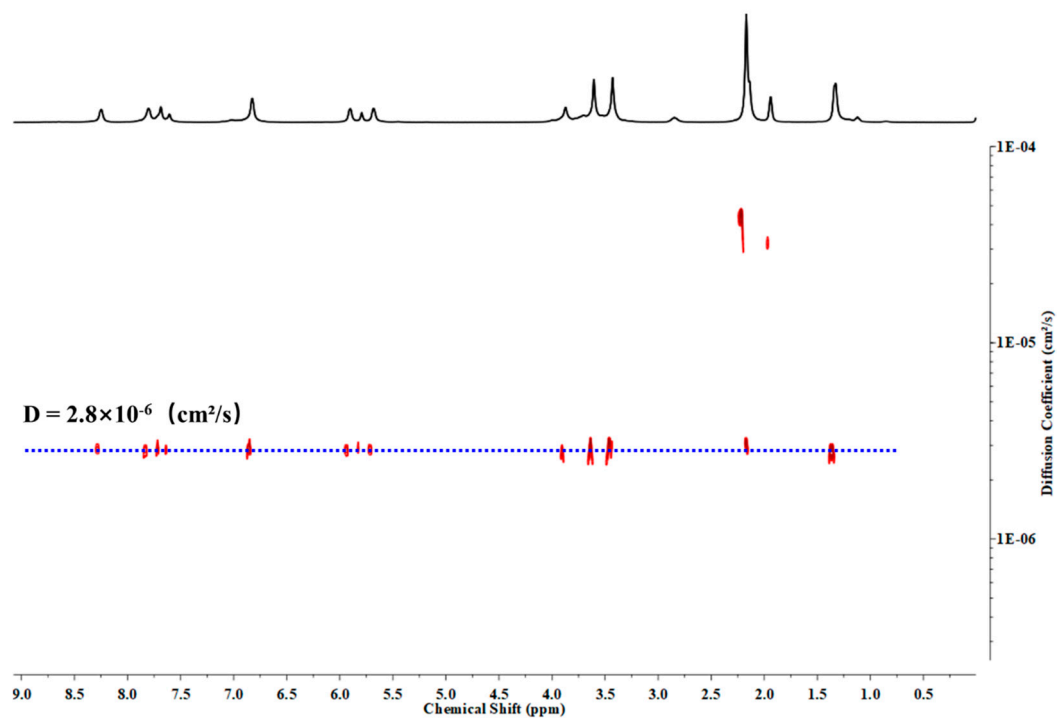
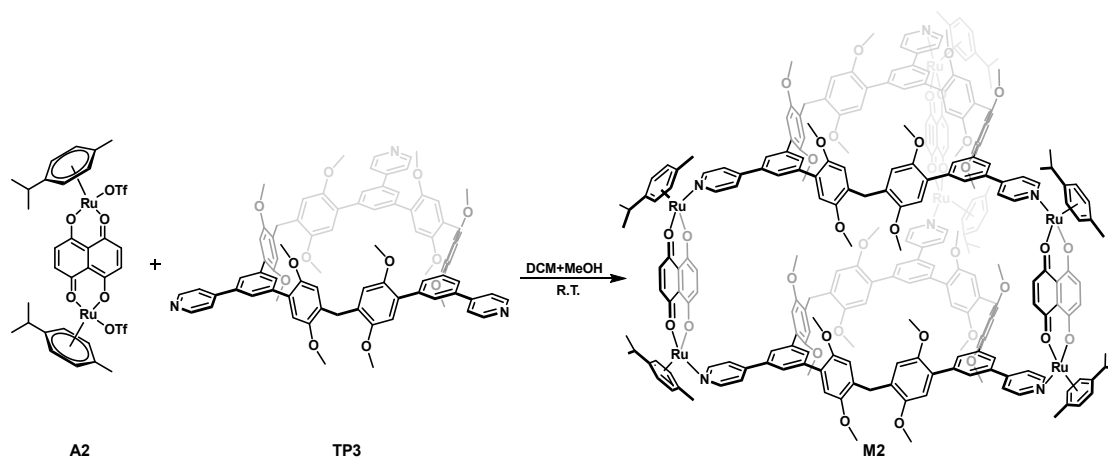


Figure S13. DOSY spectrum (400 MHz, CD₃CN, 298 K) of **M1**.



Scheme S2. Synthetic routes for the **M2**.

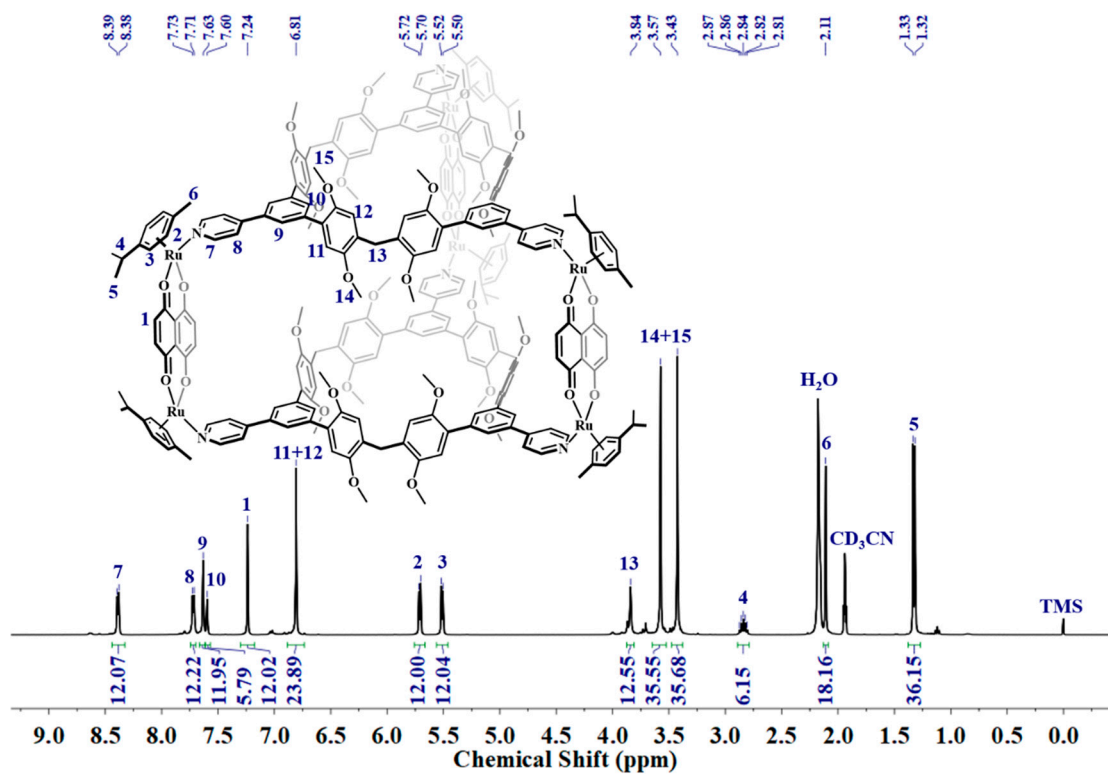


Figure S14. ¹H NMR spectrum (400 MHz, CD₃CN, 298 K) of **M2**.

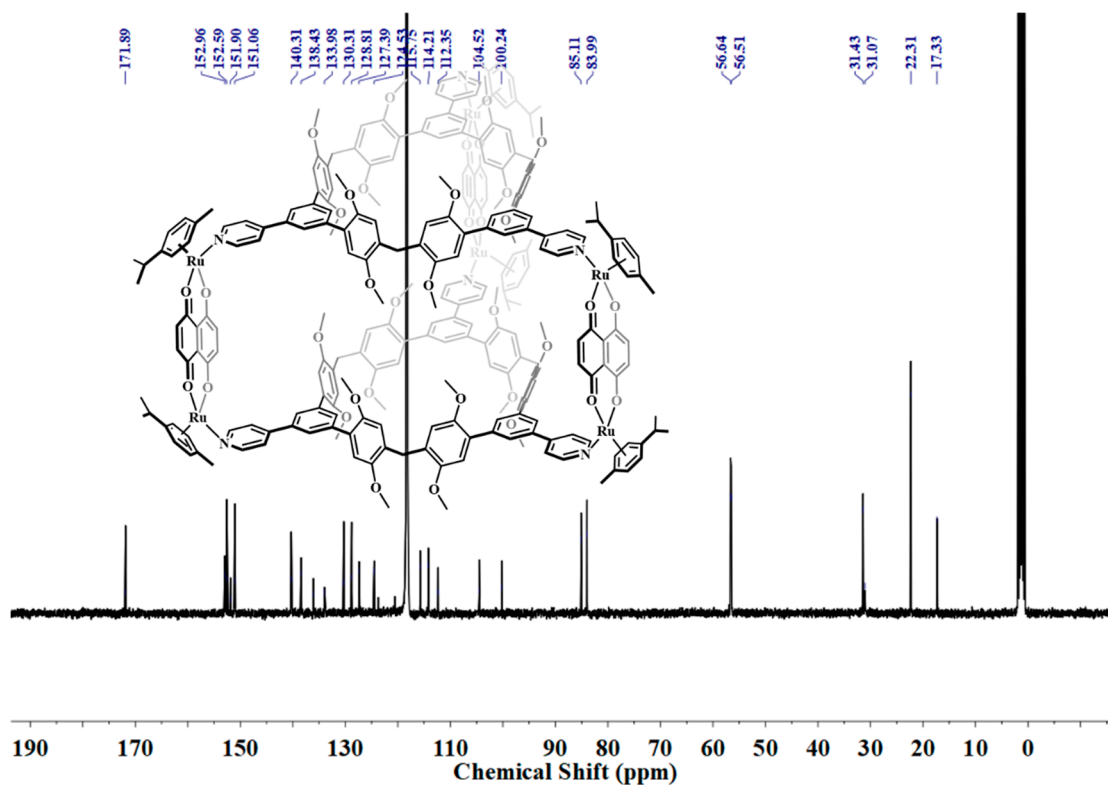


Figure S15. ¹³C NMR spectrum (100 MHz, CD₃CN, 298 K) of **M2**.

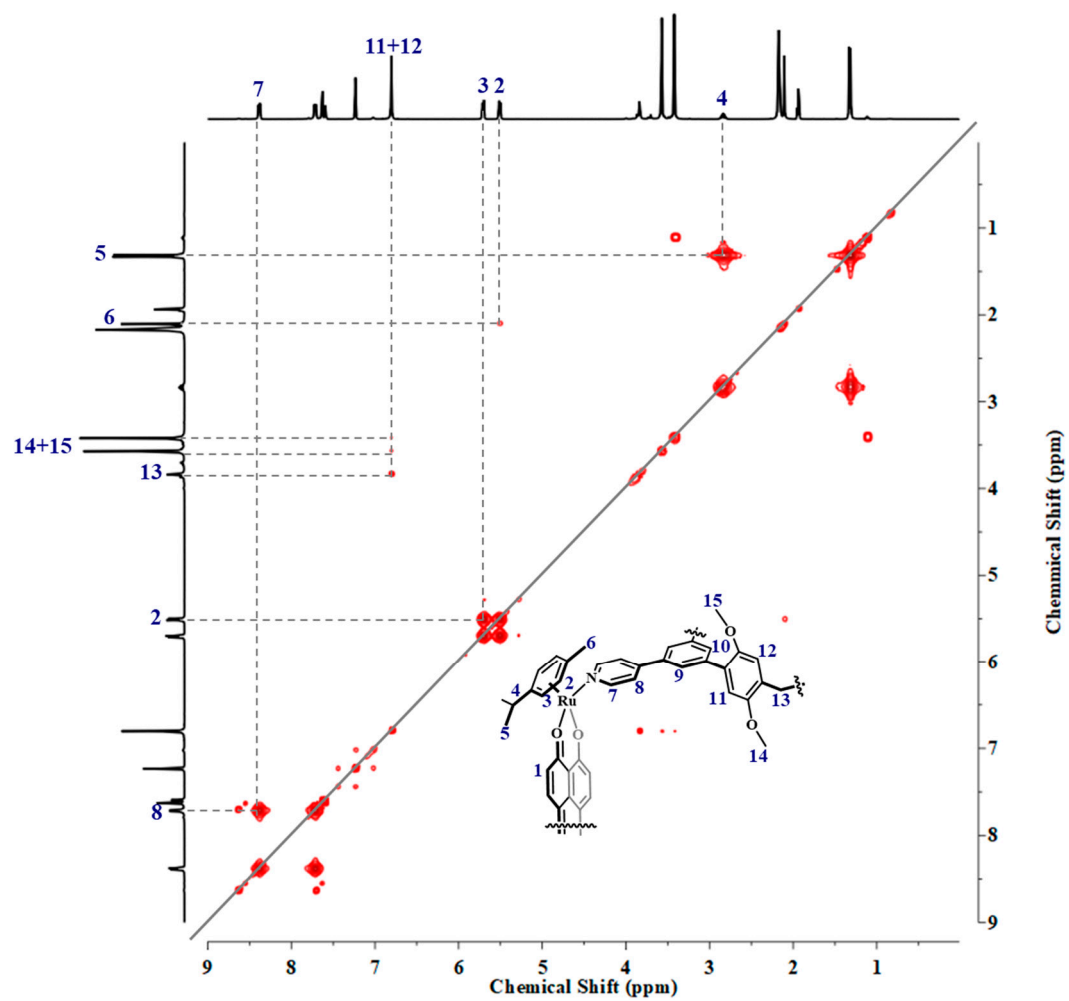


Figure S16. 2D COSY spectrum (400 MHz, CD₃CN, 298 K) of **M2**.

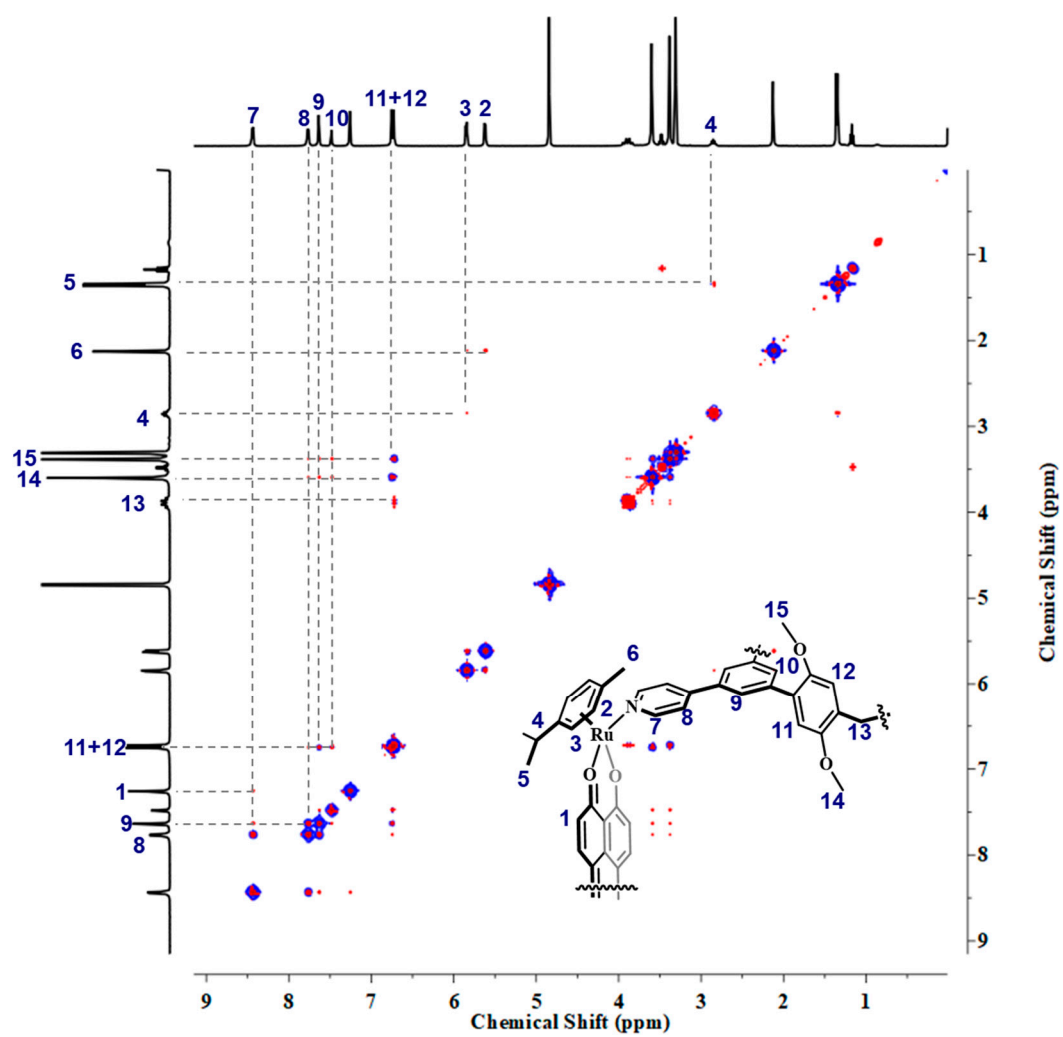


Figure S17. 2D NOESY spectrum (400 MHz, CD₃CN, 298 K) of **M2**.

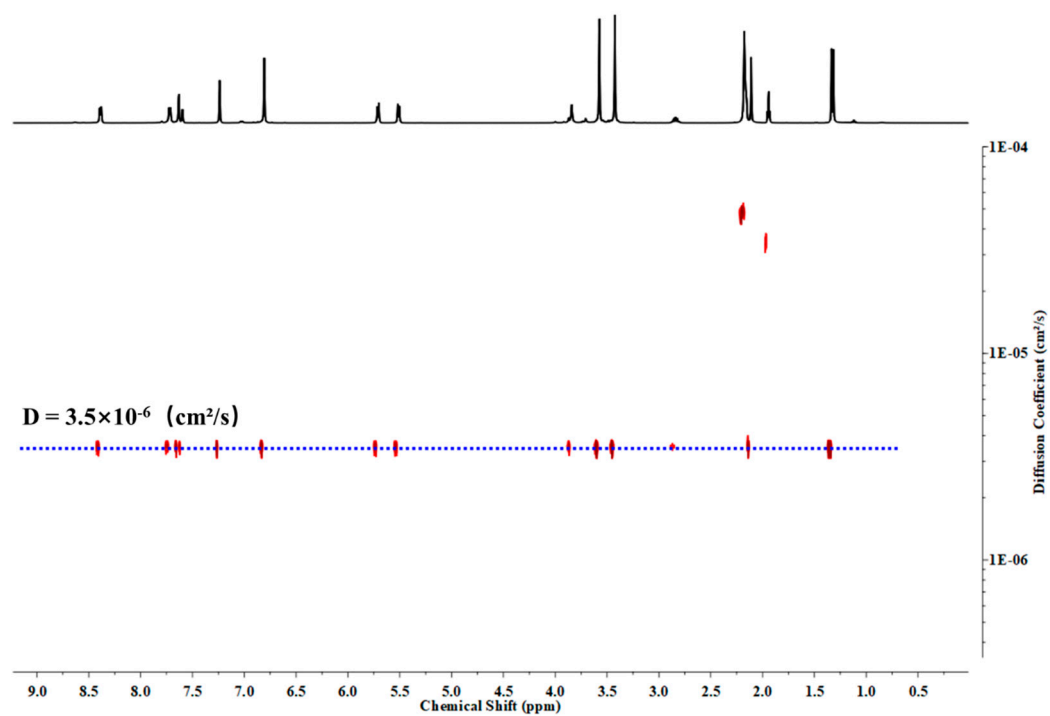
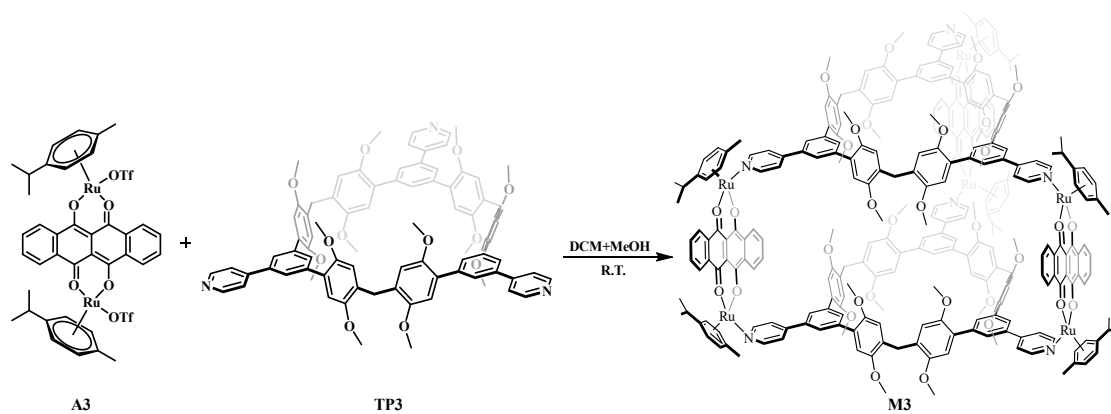


Figure S18. DOSY spectrum (400 MHz, CD₃CN, 298 K) of **M2**.



Scheme S3. Synthetic routes for the **M3**.

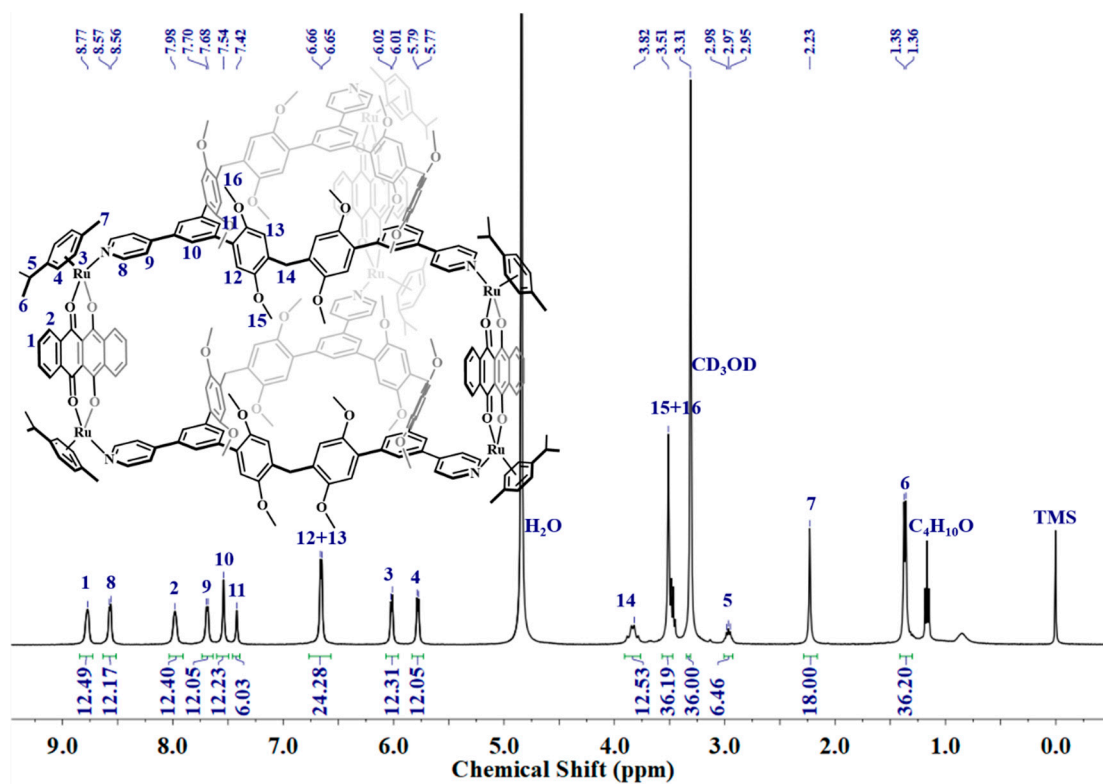


Figure S19. ^1H NMR spectrum (400 MHz, CD_3OD , 298 K) of **M3**.

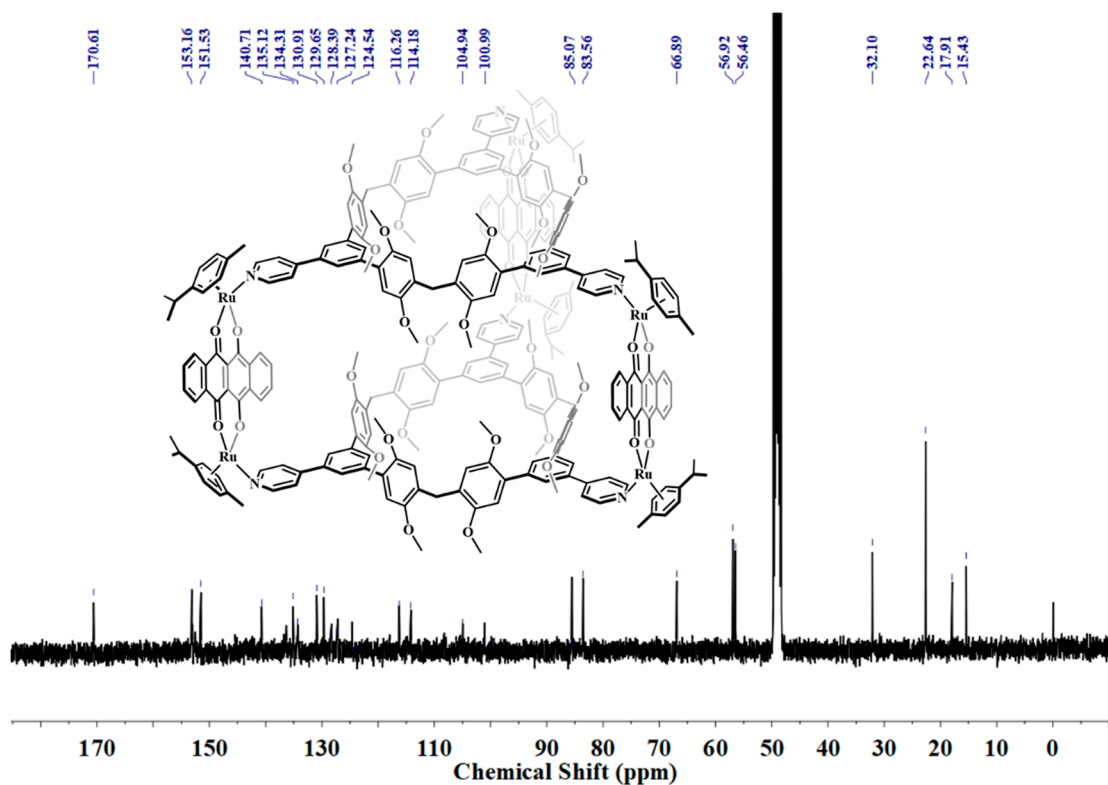


Figure S20. ^{13}C NMR spectrum (100 MHz, CD_3OD , 298 K) of **M3**.

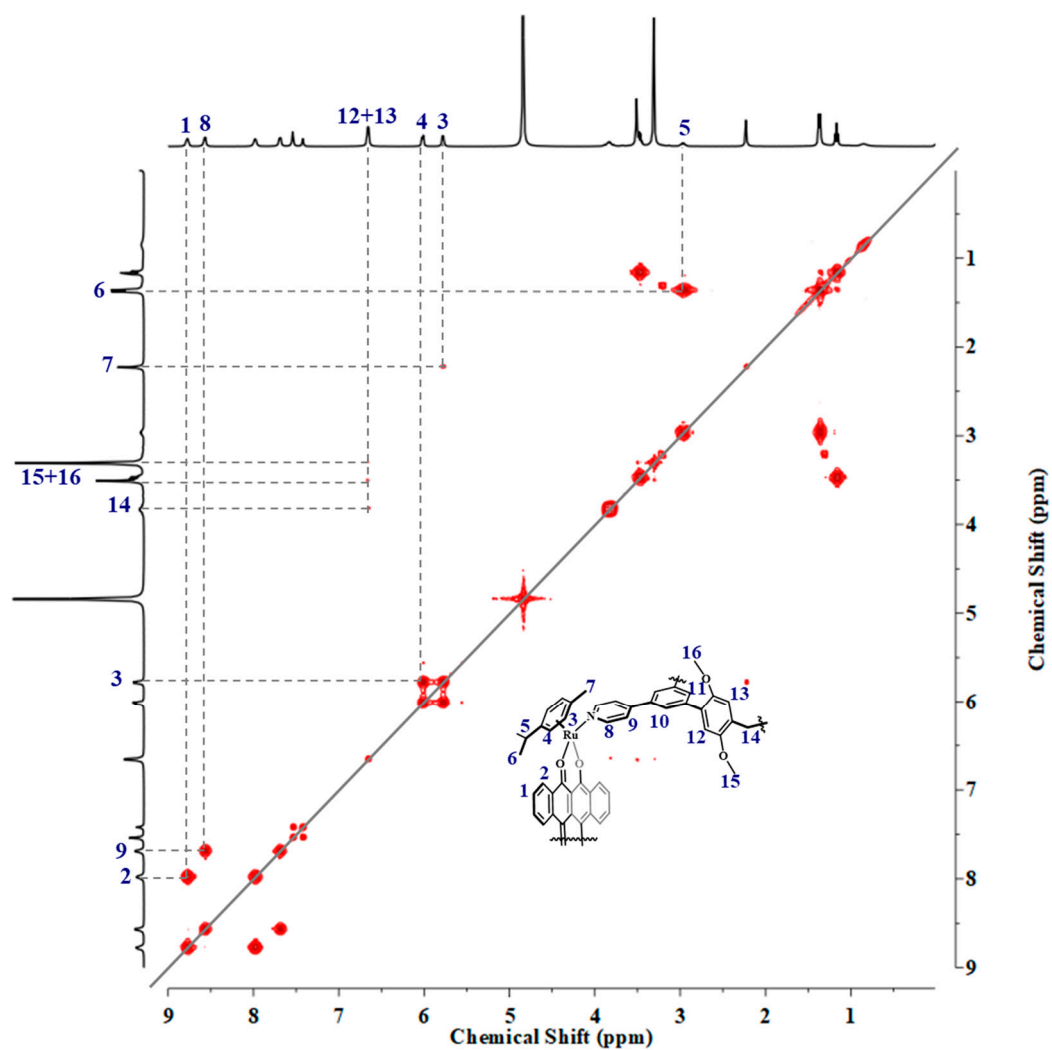


Figure S21. 2D COSY spectrum (400 MHz, CD₃OD, 298 K) of **M3**.

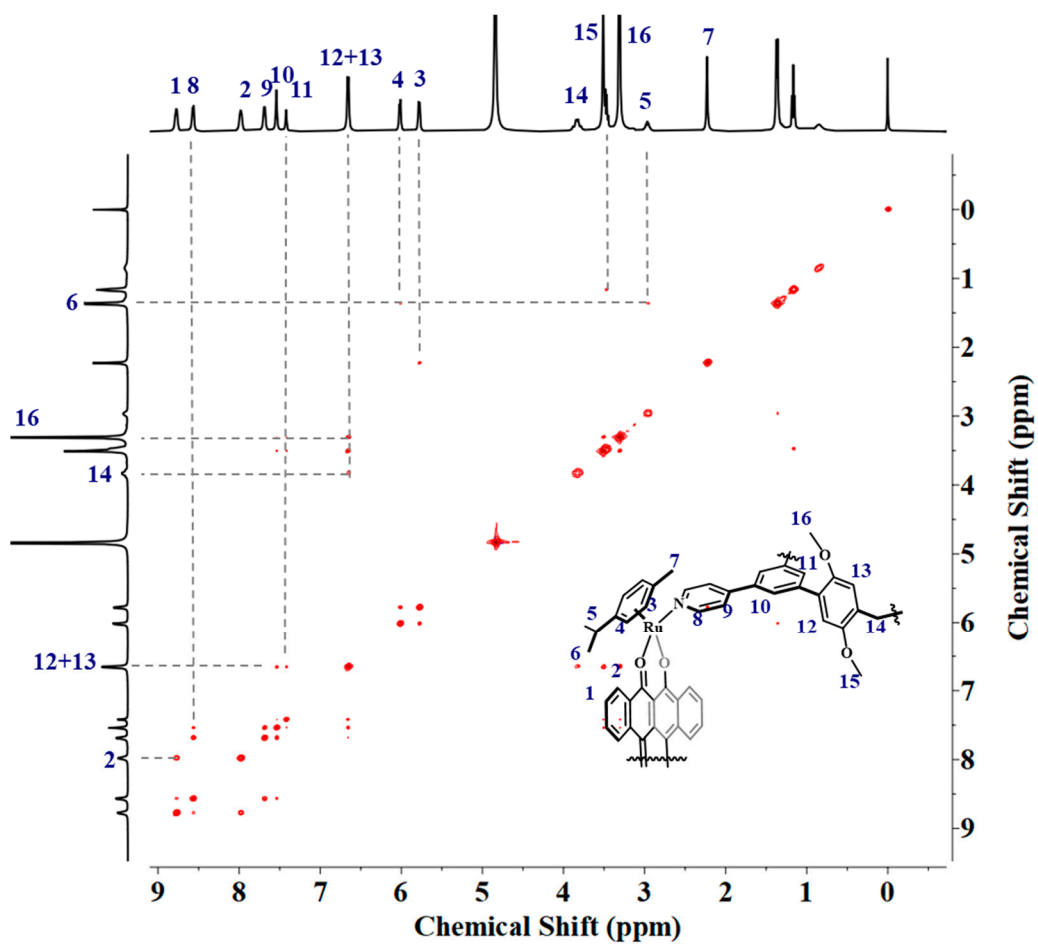


Figure S22. 2D NOESY spectrum (400 MHz, CD₃OD, 298 K) of **M3**.

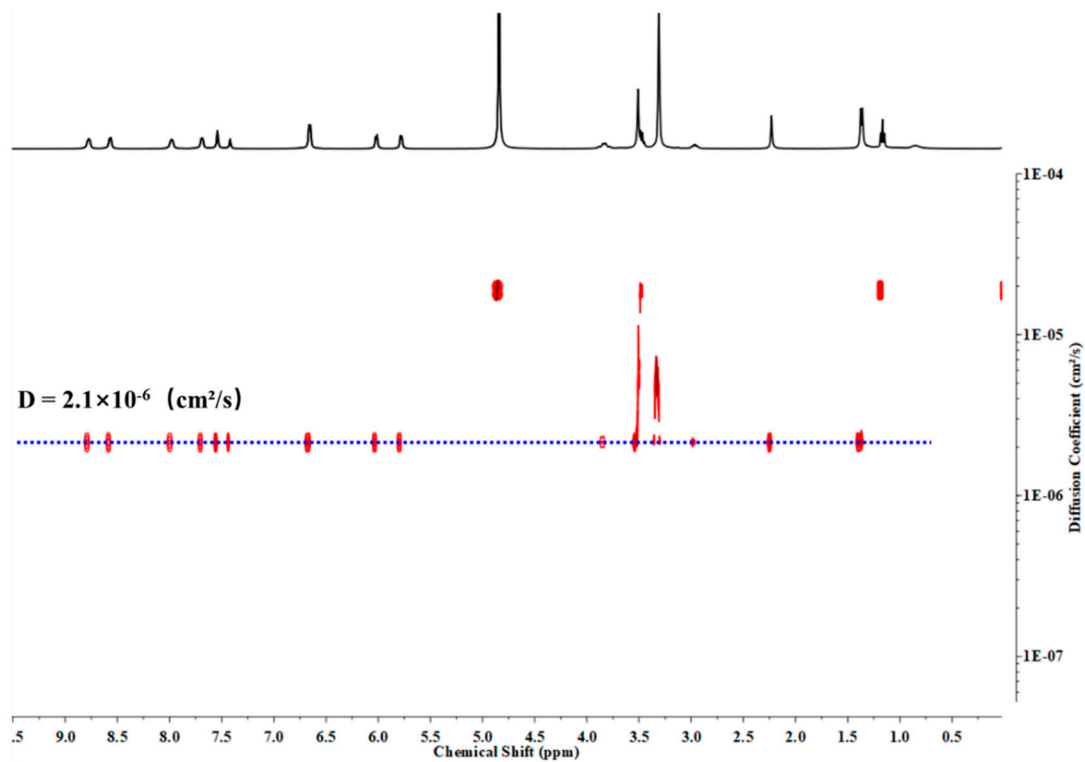


Figure S23. DOSY spectrum (400 MHz, CD₃CN, 298 K) of **M3**.

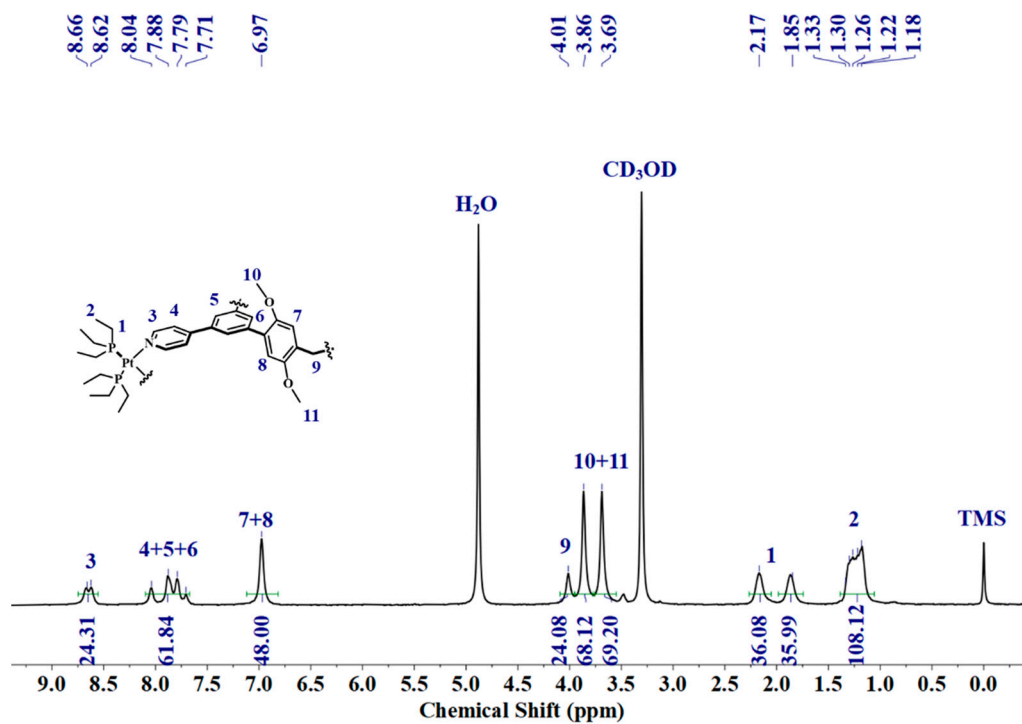


Figure S24. ¹H NMR spectrum (400 MHz, CD₃OD, 298 K) of **M4**.

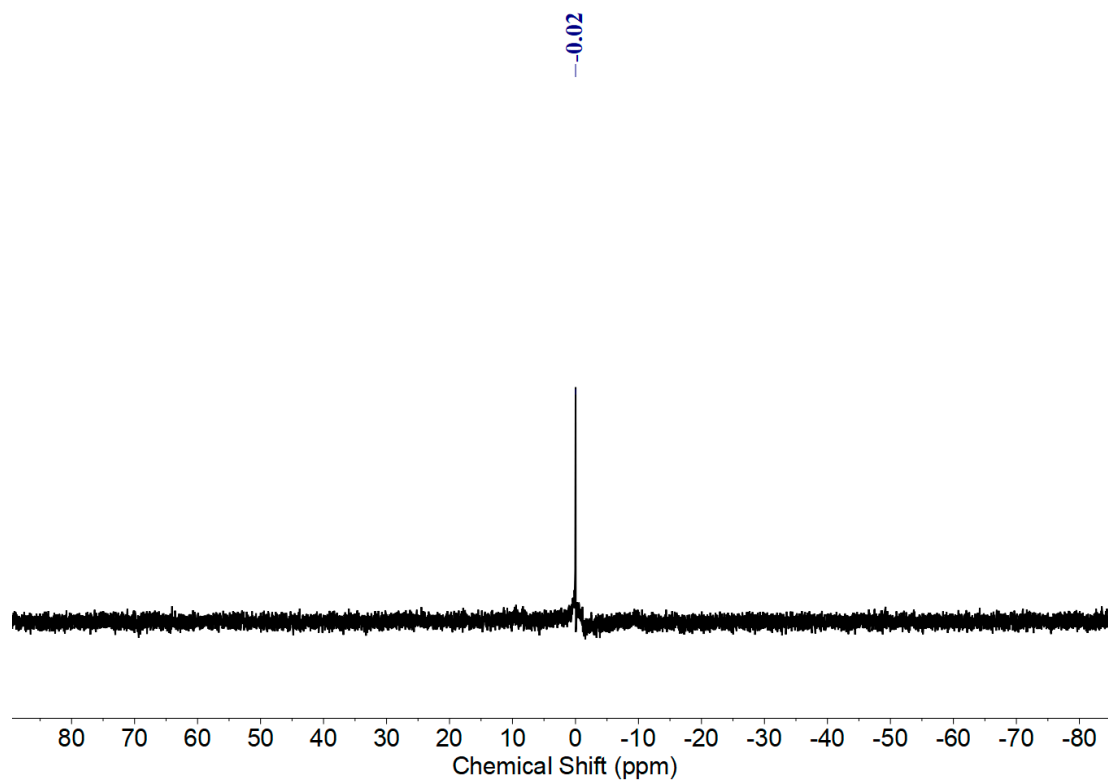


Figure S25. ³¹P{¹H} NMR (162 MHz, CD₃OD, 25 °C) spectrum of **M4**.

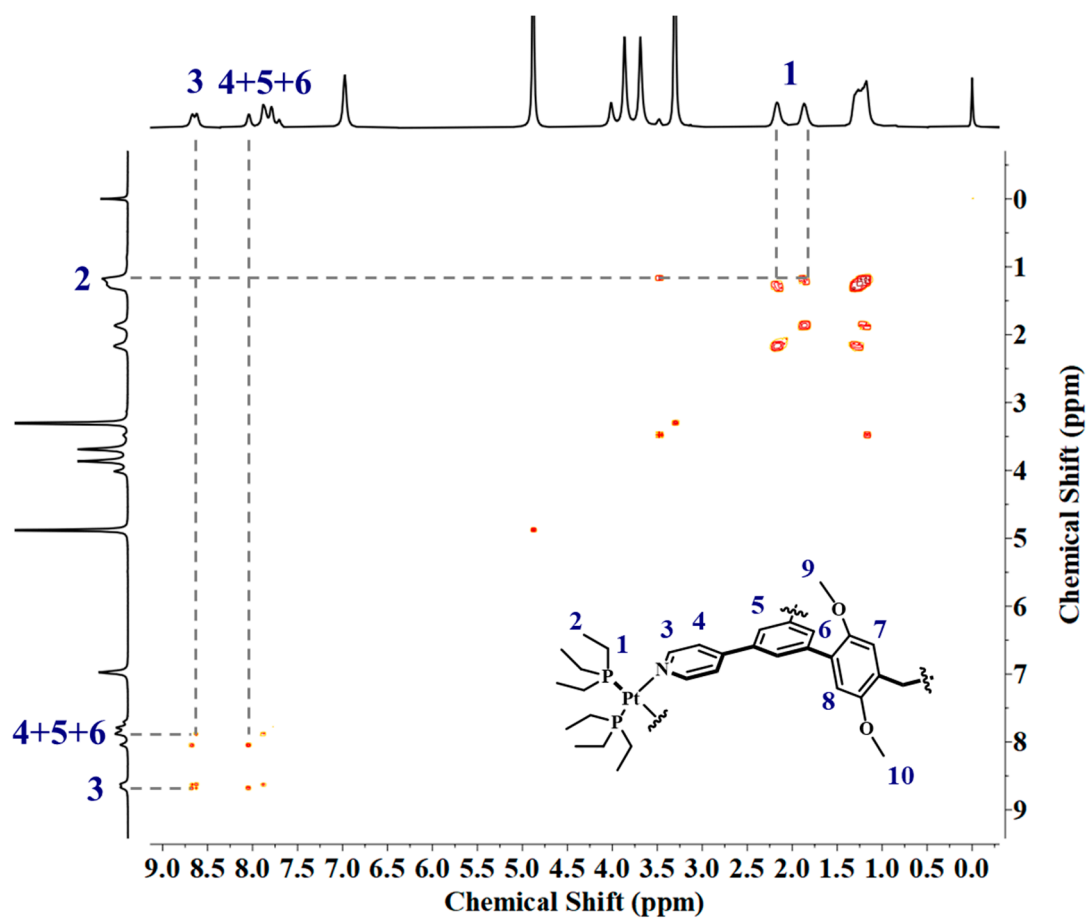


Figure S26. 2D COSY spectrum (400 MHz, CD₃OD, 298 K) of **M4**.

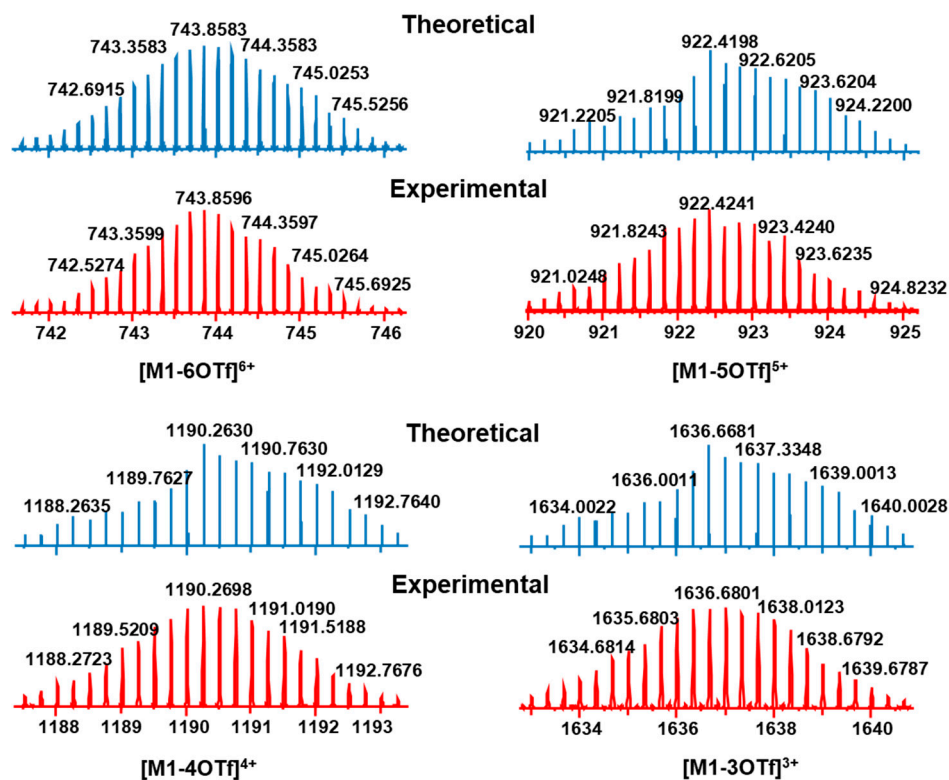


Figure S29. ESI-MS spectra of M1.

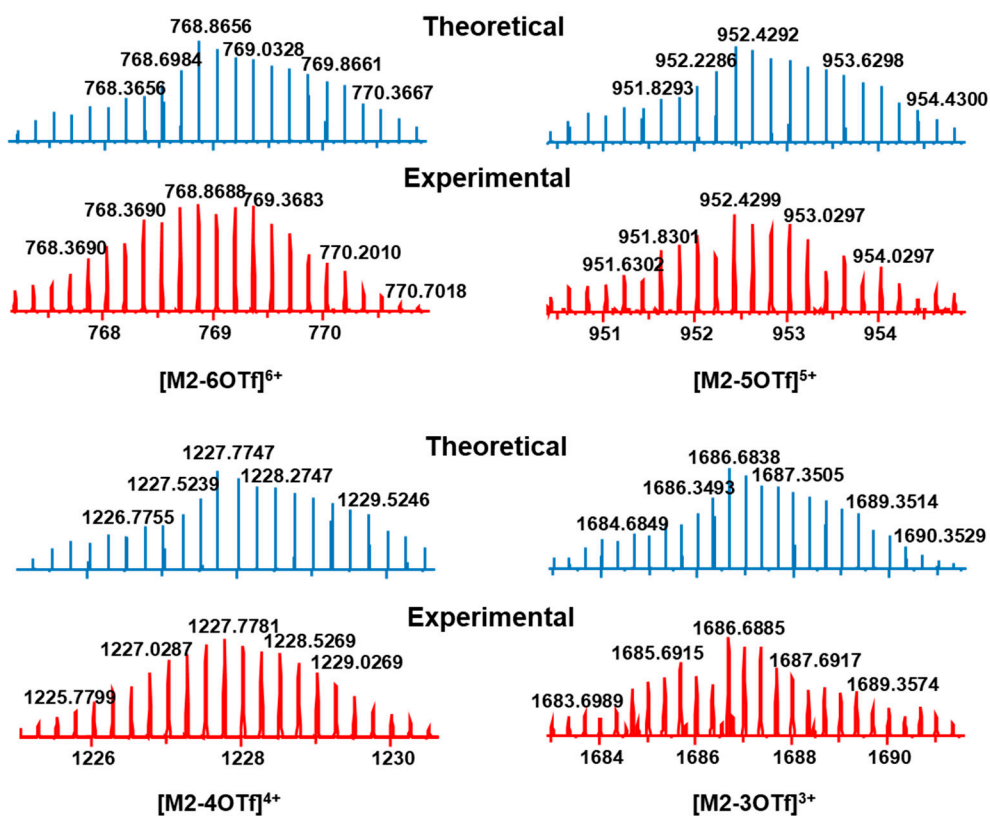


Figure S30. ESI-MS spectra of M2.

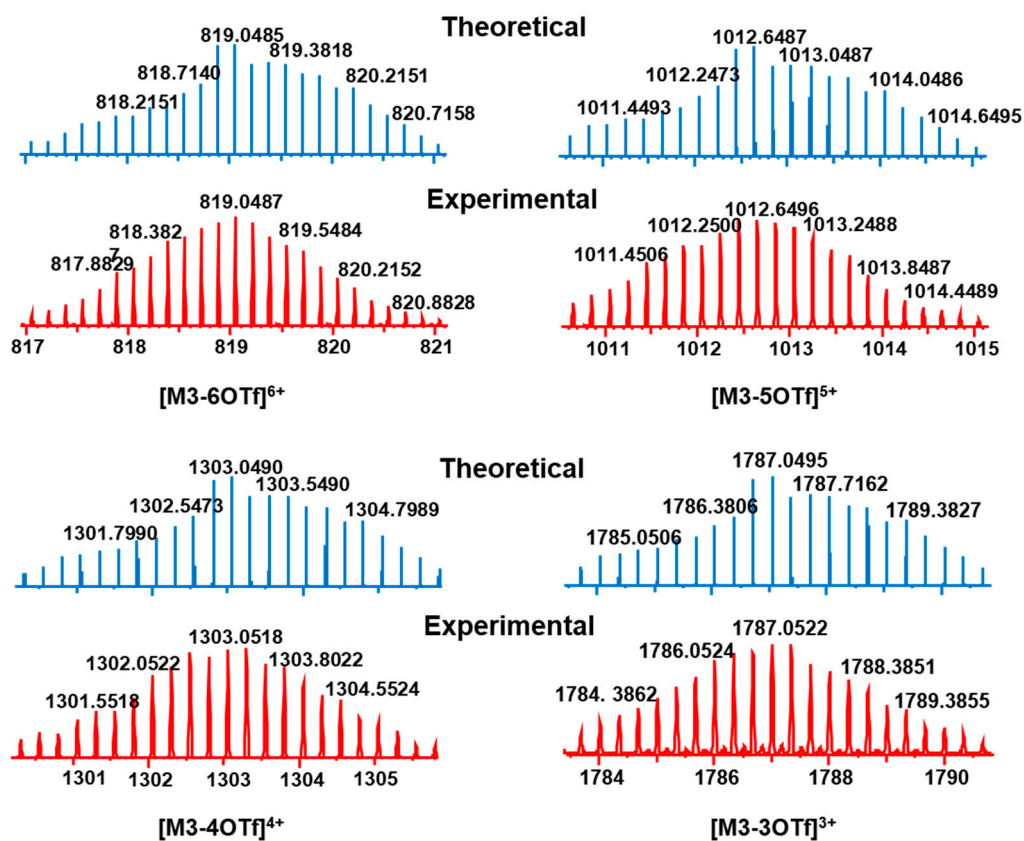


Figure S31. ESI-MS spectra of M3.

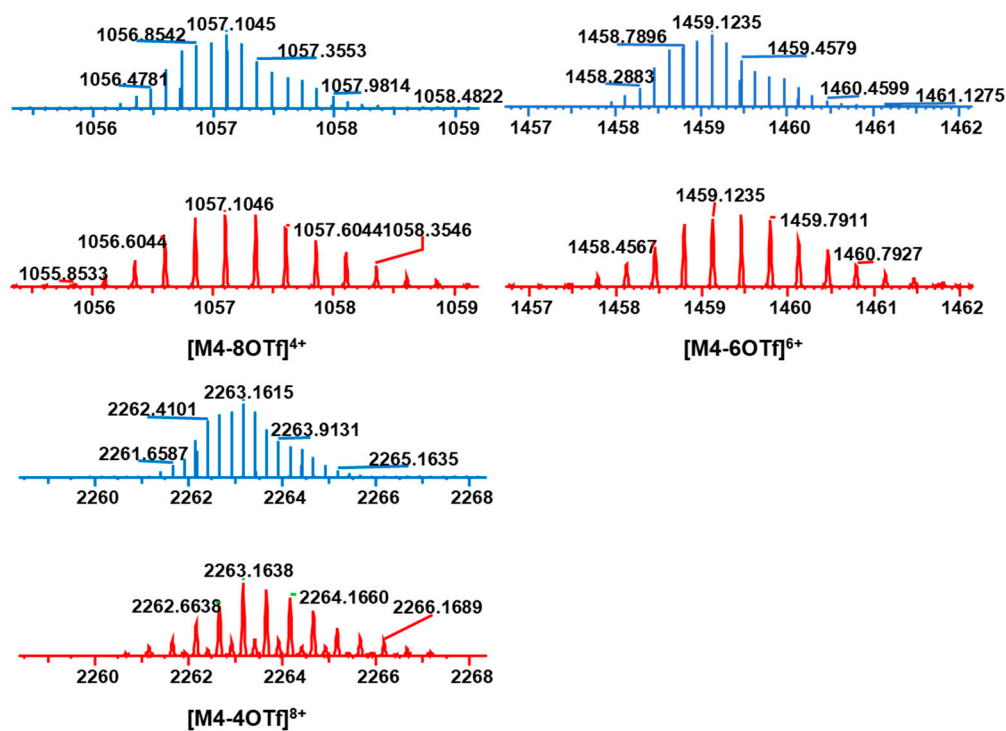


Figure S32. ESI-MS spectra of M4.

Section III. Single-crystal structures of TP3

Table S1. Crystal data of **TP3**.

Name	TP3
CCDC number	2238729
Empirical formula	C ₈₄ H ₇₅ N ₃ O ₁₂
Formula weight	1318.47
Temperature / K	293(2)
Radiation / Å	CuKα (λ= 1.54184)
Crystal system	monoclinic
Space group	P2 ₁ /n
a / Å	15.9766(11)
b / Å	25.8315(16)
c / Å	22.530(2)
α / °	90
β / °	104.916(2)
γ / °	90
Volume/ Å ³	8985.0(13)
Z	4
Density (calculated)	0.975 g/cm ³
μ / mm ⁻¹	0.524
F(000)	2784.0
Crystal size (mm ³)	0.22×0.2×0.18
2θ range / °	5.308 to 134.16
Index ranges	-12 ≤ h ≤ 19 -29 ≤ k ≤ 30 -26 ≤ l ≤ 21
Reflections collected	34957
Independent reflections	15949
R(int)	0.0787
Data/restraints/parameters	15949/126/904
Goodness-of-fit on F ²	1.063
Final R indices [I>2σ(I)]	R ₁ = 0.1610 wR ₂ = 0.4034
R indices (all data)	R ₁ = 0.2388 wR ₂ = 0.4969
Largest diff. peak/hole / e Å ⁻³	0.79/-0.40

Table S2. Crystal data of **M2**.

Name	M2
CCDC number	2238728
Empirical formula	C ₂₈₈ H ₂₅₈ F ₁₈ N ₆ O ₅₄ Ru ₆ S ₆
Formula weight	5807.00
Temperature / K	99.98(13)
Radiation / Å	CuK α (λ = 1.54184)
Crystal system	monoclinic
Space group	I2/a
a / Å	40.6464(6)
b / Å	25.0517(3)
c / Å	34.0854(6)
α / °	90
β / °	108.460(2)
γ / °	90
Volume/ Å ³	32921.9(9)
Z	141
Density (calculated)	1.232 g/cm ³
μ / mm ⁻¹	0.737
F(000)	12900.0
Crystal size (mm ³)	0.15×0.11×0.1
2 θ range / °	4.462 to 149.622
Index ranges	-48 ≤ h ≤ 50 -30 ≤ k ≤ 26 -41 ≤ l ≤ 42
Reflections collected	96284
Independent reflections	32132
R(int)	0.0265
Data/restraints/parameters	32132/42/1555
Goodness-of-fit on F ²	2.401
Final R indices [I>2sigma(I)]	R ₁ = 0.2146 wR ₂ = 0.5356
R indices (all data)	R ₁ = 0.2375 wR ₂ = 0.5551
Largest diff. peak/hole / e Å ⁻³	6.25/-1.46

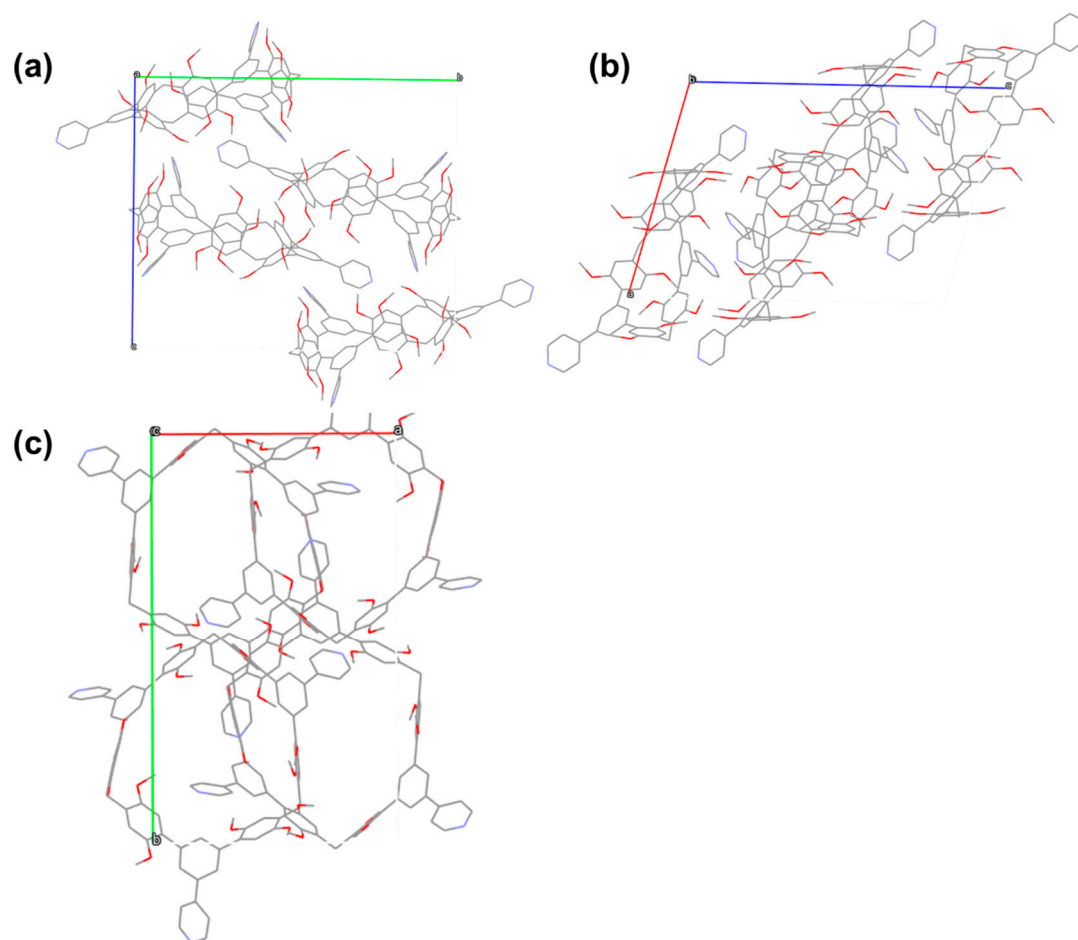


Figure S33. Packing diagram of **TP3** view along the (a) a-axis, (b) b-axis, and (c) c-axis.

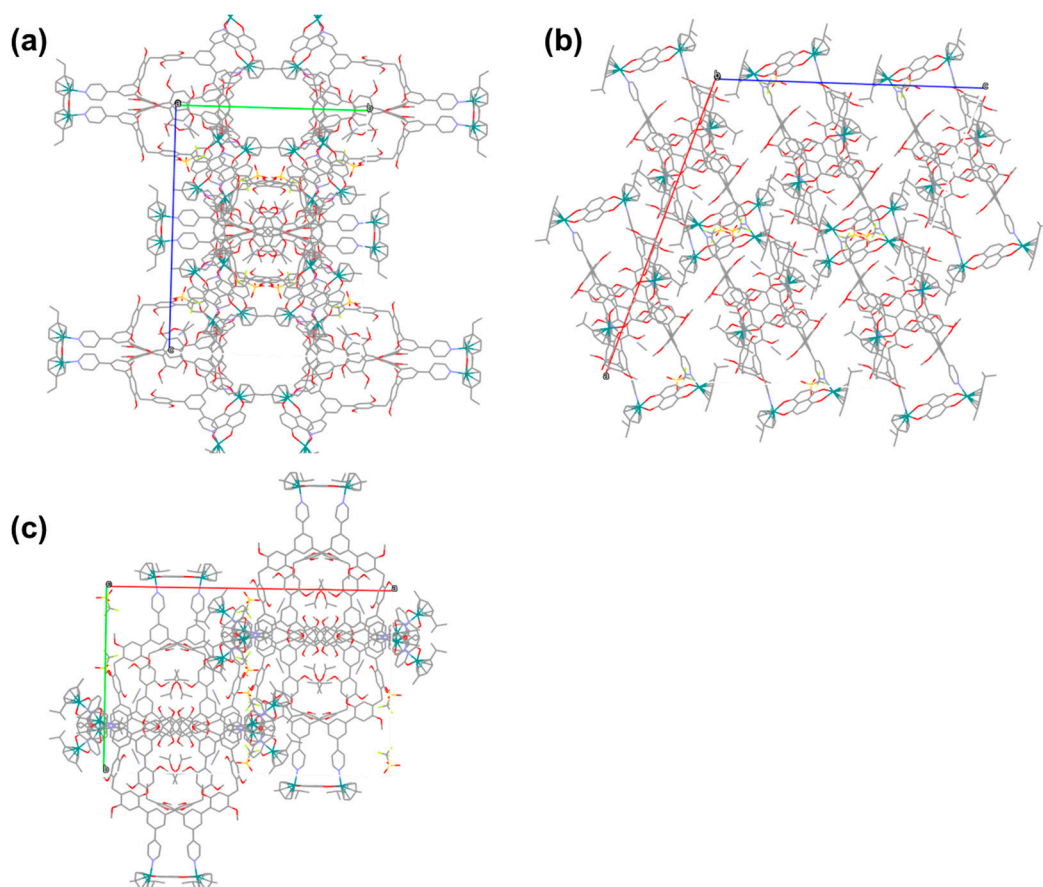


Figure S34. Packing diagram of **M2** view along the (a) a-axis, (b) b-axis, and (c) c-axis.