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Stacking Interactions Induced Host-Guest Chemistry and Borromean Rings Based on a Polypyridyl Ligand

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1. Materials and methods

All reagents and solvents were purchased from commercial sources and used as supplied unless otherwise mentioned. The starting materials $[Cp^*MCl_2]_2$ (Cp*=η^5-pentamethylcyclopentadienyl, M = Rh/Ir) and the ligands tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine (**TPPHZ**) and 1,4-bis(pyridin-4-ylethynyl)benzene (**L_3**) were prepared by the literature method.[S1, S2, S3] NMR spectra were recorded on Bruker AVANCE I 400. NMR Spectra were recorded at room temperature and referenced to the residual protonated solvent for NMR spectra. Proton chemical shift δ H = 3.31 (CD_3OD) and δ C values 49.00 (CD_3OD) are reported relative to the solvent residual peak. Coupling constants are expressed in hertz. Elemental analyses were performed on an Elementar Vario EL III analyzer. IR spectra of the solid samples (KBr tablets) in the range 400-4000 cm^{-1} were recorded on a Nicolet AVATAR-360IR spectrometer. ESI-MS spectra were recorded on a Micro TOF II mass spectrometer. The efficient full ^{13}C NMR spectrum for these metallarectangles cannot be obtained due to its limited solubility in the MeOH or MeCN even after 24 h.

2.1 Synthesis of 1a

$[(Cp^*RhCl_2)_2]$ (30 mg, 0.04854 mmol) was added to a solution of **TPPHZ** (18.6 mg, 0.04854 mmol) in methanol (10 mL) and stirred at ambient temperature. After 12 h the color of solution from light yellow to orange and then AgOTf (49.7 mg, 0.1942 mmol) was added to the resulting solution. The mixture was sheltered from light and was stirred at ambient temperature for another 12 h. The mixture was then filtered and concentrated to 1 mL under vacuum and diethyl ether was added to precipitate the light yellow solid which was filtered, washed with diethyl ether and dried to gain the light yellow crystalline solid. Yield: 61 mg, 86.4%. Anal. calcd for $C_{48}H_{42}F_{12}N_6O_{12}Rh_2S_4$: C, 39.57; H, 2.91; N, 5.77. Found: C, 39.65; H, 3.12; N, 5.63. ^1H NMR (400 MHz, CD_3OD, ppm): δ 10.43 (d, *J* = 8.0 Hz, 4H), 9.81 (d, *J* = 8.0 Hz, 4H), 8.61 (m, 4H), 1.80 (s, Cp*, 30H). ^{13}C NMR (101 MHz, CD_3OD): δ 155.53, 150.28, 141.65, 139.63, 131.58, 130.20, 100.20, 9.05. ^{19}F NMR (376 MHz, CD_3OD, ppm): δ = -80.15 (s, OTf^-). FT-IR spectrum (KBr, ν, cm^{-1}): 3449 (m), 3089 (w), 2964 (w), 2925 (w), 1653 (w), 1630 (w), 1617 (w), 1491 (m), 1466 (w), 1428 (w), 1400 (m), 1375 (m), 1262 (s), 1227 (m), 1164 (m), 1099 (w), 1057 (w), 1031 (s), 819 (m), 804 (m), 759 (w), 730 (m), 639 (s), 575 (m), 563 (w), 518 (m). ESI-TOF-MS: *m/z* 579.03 (calcd for $[M - 2OTf^-]^{2+}$ 579.03), 1307.01 (calcd for $[M - OTf^-]^+$ 1307.01).

2.2 Synthesis of 1b

Prepared by the same procedure as described above for **1a**, using $[(Cp^*IrCl_2)_2]$ (38.7 mg, 0.04854 mmol) and **TPPHZ** (18.6 mg, 0.04854 mmol). Yield: 70.6 mg, 88.9%. Anal. calcd for $C_{48}H_{42}F_{12}N_6O_{12}Ir_2S_4$: C, 35.25; H, 2.59; N, 5.14. Found: C, 35.30; H, 2.71; N, 5.30. ^1H NMR (400 MHz, CD_3OD, ppm): δ 10.43 (d, *J* = 8.0 Hz, 4H), 9.82 (d, *J* = 8.0 Hz, 4H), 8.62 (m, 4H), 1.87 (s, Cp*, 30H). ^{13}C NMR (101 MHz, CD_3OD): δ 155.51, 151.84, 141.81, 140.03, 132.01, 130.62, 91.84, 8.92. ^{19}F NMR (376 MHz, CD_3OD, ppm): δ = - 80.11 (s, OTf^-). FT-IR spectrum (KBr, ν, selected peaks): 3473 (m), 3103 (w), 2970 (w), 2925 (w), 1654 (w), 1630 (w), 1613 (w), 1494 (m), 1458 (w), 1414 (w), 1404 (m), 1389 (w), 1383 (w), 1370 (w), 1277 (s), 1258 (s), 1226 (m), 1164 (m), 1108 (w), 1075 (w), 1075 (w), 1061 (w), 1031 (s), 819 (m), 759 (w), 727 (w), 639 (s), 575 (m) 518 (w). ESI-TOF-MS: *m/z* 669.09 (calcd for $[M - 2OTf^-]^{2+}$ 669.09), 1487.13 (calcd for $[M – OTf^-]^+$ 1487.13).

2.3 Synthesis of 2a

The ligand 4,4′-bipyridine (3.8 mg, 0.02427 mmol) was added to a solution of complex **1a** (35.3 mg, 0.02427 mmol) in methonal (10 mL) and stirred at ambient temperature. After 24 h the resulting solution was concentrated to 1 mL under vacuum and diethyl ether was added to precipitate the light yellow solid which was filtered, washed with diethyl ether and dried to gain the light yellow crystalline solid. Yield: 37.4 mg, 95.7%. Anal. calcd for $C_{116}H_{100}F_{24}N_{16}O_{24}Rh_4S_8$: C, 43.18; H, 3.12; N,6.95. Found: C, 43.27; H, 3.21; N, 6.89. ^{1}H NMR (400 MHz, CD_3OD): δ 10.20 (d, J = 8.57 Hz, TPPHZ-H, 8H), 9.81 (d, J = 5.26 Hz, TPPHZ-H, 8H), 8.55 (dd, J = 13.42, 3.02 Hz, TPPHZ-H, 8H), 8.51 (d, J = 6.47 Hz, bpy-H, 8H), 7.76 (d, J = 6.50 Hz, bpy-H, 8H), 1.79 (s, Cp*-H, 60H). FT-IR spectrum (KBr, ν, cm^{-1}): 3463 (m), 3096 (w), 2963 (w), 2924 (w), 1652 (w), 1630 (w), 1610 (m), 1492 (m), 1466 (w), 1427 (w), 1412 (w), 1401 (m), 1375 (m), 1275 (s), 1259 (s), 1225 (m), 1163 (m), 1102 (w), 1072 (w), 1059 (w), 1030 (s), 818 (m), 758 (w), 730 (m), 639 (s), 574 (w), 563 (w), 518 (m).

2.4 Synthesis of 2b

Prepared by the same procedure as described above for **2a**, using complex **1b** (39.7 mg, 0.02427 mmol) and the ligand 4,4′-bipyridine (3.8 mg, 0.02427 mmol). Yield: 40.5 mg, 93.1%. Anal. calcd for $C_{116}H_{100}F_{24}N_{16}O_{24}Ir_4S_8$: C, 38.88; H, 2.81; N,6.25. Found: C, 38.93; H, 2.93; N, 6.33. ^{1}H NMR (400 MHz, CD_3OD): δ 10.21 (d, J = 8.0 Hz, TPPHZ-H, 8H), 9.78 (d, J = 4.0 Hz, TPPHZ-H, 8H), 8.57-8.53 (m, TPPHZ-H and bpy-H, 8H), 7.75 (d, J = 8.0 Hz, bpy-H, 8H), 1.74 (s, Cp*-H, 60H). FT-IR spectrum (KBr, ν, selected peaks): 3472 (m), 3102 (w), 2970 (w), 2924 (w), 1654 (w), 1639 (w), 1613 (m), 1494 (m), 1457 (w), 1413 (w), 1405 (m), 1385 (w), 1369 (m), 1278 (s), 1258 (s), 1227 (s), 1164 (m), 1107 (w), 1075 (w), 1061 (w), 1031 (s), 819 (m), 759 (w), 727 (m), 640 (s), 575 (w), 518 (m)

2.5 Synthesis of 3

The ligand *trans*-1,2-bis(4-pyridyl)-ethylene (4.4 mg, 0.02427 mmol) was added to a solution of complex **1a** (35.3 mg, 0.02427 mmol) in acetonitrile (10 mL) and stirred at ambient temperature. After 24 h the resulting solution was concentrated to 1 mL under vacuum and diethyl ether was added to precipitate the light yellow solid which was filtered, washed with diethyl ether and dried to gain the light yellow crystalline solid. Yield: 36.4 mg. (91.7%). Anal. calcd for $C_{120}H_{104}F_{24}N_{16}O_{24}Rh_4S_8$: C, 43.96; H, 3.20; N,6.84. Found: C, 44.07; H, 3.35; N, 6.78. ^{1}H NMR (400 MHz, CD_3OD): δ 10.25 (d, J = 9.1 Hz, TPPHZ-H, 8H), 9.82 (d, J = 6.2 Hz, TPPHZ-H, 8H), 8.58 (dd, J = 8.3, 5.3 Hz, TPPHZ-H, 8H), 8.41 (d, J = 6.7 Hz, bpe-H, 8H), 7.53 (d, J = 6.8 Hz, bpe-H, 8H), 7.27 (s, bpe-H, 4H), 1.78 (s, Cp*-H, 60H). FT-IR spectrum (KBr, ν, cm^{-1}): 3489 (m), 3093 (w), 2970 (w), 2924 (w), 1653 (w), 1630 (w), 1610 (m), 1466 (w), 1451 (w), 1428 (w), 1400 (m), 1375 (m), 1274 (s), 1261 (s), 1225 (m), 1162 (m), 1103 (w), 1059 (w), 1031 (s), 820 (w), 758 (w), 730 (w), 639 (s), 574 (w), 558 (w), 557 (w), 518 (w).

2.6 Synthesis of 4(BRs)

The ligand 1,4-bis(pyridin-4-ylethynyl)benzene (6.8 mg, 0.02427 mmol) was added to a solution of complex **1a** (35.3 mg, 0.02427 mmol) in methonal (10 mL) and stirred at ambient temperature. After 24 h the resulting solution was concentrated to 1 mL under vacuum and diethyl ether was added to precipitate the light yellow solid which was filtered, washed with diethyl ether and dried to gain the light yellow crystalline solid. Yield: 39.4 mg. (93.6%). Anal. calcd for $C_{408}H_{324}F_{72}N_{48}O_{72}Rh_{12}S_{24}$: C, 47.01; H, 3.13; N,6.45. Found: C, 47.08; H, 3.19; N, 6.39. ^{1}H NMR (400 MHz, CD_3OD): δ 10.33 (d, J = 8.1 Hz, TPPHZ-H, 16H), 10.19 (d, J = 8.9 Hz, TPPHZ-H, 8H), 9.92 (d, J = 5.5 Hz, TPPHZ-H, 8H), 9.85 (d, J = 9.6 Hz, TPPHZ-H, 16H), 8.91 (d, J = 5.9 Hz, bpeb-H, 8H), 8.67-8.60 (m, TPPHZ-H, 16H), 8.51 (d, J = 7.3 Hz, bpeb-H, 8H), 8.47 (d, J = 5.9 Hz, bpeb-H, 16H), 7.51 (d, J = 5.5 Hz, bpeb-H, 8H), 7.58 (s,

bpeb-H, 8H), 7.46 (d, J = 5.9 Hz, bpeb-H, 16H), 7.43 (s, bpeb-H, 16H), 1.93 (s, Cp*-H, 60H), 1.81 (s, Cp*-H, 120H). FT-IR spectrum (KBr, ν, cm^{-1}): 3473 (m), 3091 (w), 2964 (w), 2923 (w), 2220 (w), 1653 (w), 1630 (w), 1608 (m), 1492 (m), 1466 (w), 1425 (w), 1400 (m), 1375 (m), 1262 (s), 1225 (m), 1157 (m), 1120 (w), 1058 (w), 1031 (s), 818 (m), 757 (w), 730 (w), 639 (s), 574 (w), 518(w).
Characterization details for **4**(monomeric rectangle) follow. ^{1}H NMR (400 MHz, CD$_3$OD): δ 10.33 (d, J = 7.2 Hz, TPPHZ-H, 8H), 9.85 (d, J = 4.6 Hz, TPPHZ-H, 8H), 8.67-8.60 (m, TPPHZ-H, 8H), 8.47 (d, J = 5.8 Hz, bpeb-H, 8H), 7.46 (d, J = 5.8 Hz, bpeb-H, 8H), 7.43 (s, bpeb-H, 8H), 1.81 (s, Cp*-H, 60H).

2.7 General Method for the Study of Host−Guest Chemistry.

The guest Coronene (6 mg, 0.02 mmol) was added to a solution of complex **2a** (32.2 mg, 0.01 mmol) or complex **2b** (35.8 mg, 0.01 mmol) in dry methonal (10 mL) and stirred at ambient temperature. After 24 h the color of solution from light yellow to orange and then the resulting solution was concentrated to 1 mL under vacuum and diethyl ether was added to precipitate the orange solid which was filtered, washed with diethyl ether and dried to gain the orange crystalline solid.
Characterization details for **5a** follow. Yield: 36.1 mg. (94.5%). Anal. calcd for $C_{164}H_{124}F_{24}N_{16}O_{24}Rh_4S_8$: C, 51.47; H, 3.27; N, 5.86. Found: C, 51.60; H, 3.29; N, 5.78. ^{1}H NMR (400 MHz, CD$_3$OD): δ 9.63 (d, J = 4.0 Hz, TPPHZ-H 8H), 9.48 (d, J = 8.0 Hz, bpy-H, 8H), 9.14 (d, J = 4.0 Hz, bpy-H, 8H), 8.04 (m, TPPHZ-H, 8H), 7.95 (d, J = 8.0 Hz, TPPHZ-H, 8H), 6.33 (s, coronene, 24H), 1.58 (s, Cp*-H, 60H). FT-IR spectrum (KBr, ν, cm^{-1}): 3464 (m), 3103 (w), 2969 (w), 2925 (w), 1675 (w), 1653 (w), 1630 (w), 1607 (w), 1577 (w), 1571 (w), 1560 (w), 1493 (m), 1466 (w), 1451 (w), 1427 (w), 1411 (w), 1400 (m), 1374 (m), 1315 (w), 1276 (s), 1259 (s), 1225 (m), 1163 (m), 1100 (w), 1069 (w), 1058 (w), 1030 (s), 858 (m), 820 (m), 758 (w), 729 (m), 639 (s), 575 (w), 563 (w), 518 (m).
Characterization details for **5b** follow. Yield: 39.9 mg. (95.5%). Anal. calcd for $C_{164}H_{124}F_{24}N_{16}O_{24}Ir_4S_8$: C, 47.08; H, 2.99; N, 5.36. Found: C, 47.12; H, 3.05; N, 5.47. ^{1}H NMR (400 MHz, CD$_3$OD): δ 9.59 (d, J = 4.0 Hz, TPPHZ-H, 8H), 9.53 (d, J = 4.0 Hz, bpy-H, 8H), 9.14 (d, J = 8.0 Hz, bpy-H, 8H), 8.04 (m, TPPHZ-H, 8H), 7.95 (d, J = 8.0 Hz, TPPHZ-H, 8H), 6.38 (s, coronene, 24H), 1.54 (s, Cp*-H, 60H). FT-IR spectrum (KBr, ν, selected peaks): 3444 (m), 3098 (w), 2960 (w), 2923 (w), 1682 (w), 1657 (w), 1646 (w), 1634 (w), 1613 (w), 1574 (w), 1557 (w), 1540 (w), 1494 (m), 1456 (w), 1451 (w), 1416 (w), 1404 (m), 1385 (m), 1374 (m), 1313 (w), 1277 (s), 1258 (s), 1225 (m), 1161 (m), 1107 (w), 1074 (w), 1061 (w), 1030 (s),849 (m), 817 (m), 758 (w), 726 (m), 638 (s), 574 (w), 543 (w), 517 (m).

3. Single-Crystal Structure Determination

X-ray Crystallography Details. Single crystals of **2a**, **3**, **4**, **5a** and **5b** suitable for X-ray diffraction study were obtained at room temperature. X-ray intensity data of data of **3** and **4** were collected at 173 K**,** data of **5b** was collected at 213 K and **2b** and **5a** were collected at 223 K on a CCD-Bruker SMART APEX system. In these data, the disordered solvent molecules which could not be restrained properly were removed using the SQUEEZE route.

In asymmetric unit of **2a**, there were disordered cation and solvents (one protonated triethylamine cation, eight methanol and six water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. 2 ISOR and 5 DFIX instructions were used to restrain anions and Cp* fragments so that there were 17 restraints in the data.

In asymmetric unit of **3**, there were disordered anions and solvents (two triflate anions, four acetonitrile, six methanol and eight water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them.

In asymmetric unit of **4**, there were disordered anion and solvents (one triflate anion, eight methanol, thirteen acetonitrile and twelve water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One pentamethylcyclopentadienyl ligand (Cp* for short) and one triflate anion were disordered and they were divided into two parts (56:44 for Cp* and 67:33 for anion). 102 ISOR, 3 SIMU and 40 DFIX instructions were used to restrain anions, ligands, solvent molecules and Cp* fragments so that there were 760 restraints in the data. Hydrogen of methanol molecules could not be found and others were put in calculated positions

In asymmetric unit of **5a**, there were disordered solvents (half of a methanol molecule) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One methanol molecule was disordered and it was divided into two parts (57:43). 15 ISOR and 4 DFIX instructions were used to restrain anions and solvents so that there were 94 restraints in the data. Hydrogen of methanol and water molecules could not be found and others were put in calculated positions.

In asymmetric unit of **5b**, there were disordered anion and solvents (one triflate anion, one methanol and one water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. Two of four triflate anions were disordered and they were divided into two parts (46:54 and 45:55). 36 ISOR, 3 SIMU and 30 DFIX instructions were used to restrain disordered anions so that there were 324 restraints in the data. Hydrogen of methanol molecules could not be found and others were put in calculated positions.

4. X-Ray crystal structure parameters of compounds 2a, 3, 4, 5a and 5b

Table S1. Crystal data and structure refinement for complex **2a**.

Empirical formula	$C_{142}H_{220}F_{18}N_{18}O_{46}Rh_4S_6$	
Formula weight	3861.35	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.772(3) Å	α = 67.479(3)°.
	b = 17.560(3) Å	β = 69.242(3)°.
	c = 19.223(4) Å	γ = 86.897(3)°.
Volume	4578.2(15) Å^3	
Z	1	
Density (calculated)	1.401 Mg/m^3	
Absorption coefficient	0.518 mm^{-1}	
F(000)	2004	
Crystal size	0.410 x 0.370 x 0.350 mm^3	
Theta range for data collection	1.230 to 25.999°.	
Index ranges	-19<=h<=19, -21<=k<=21, -23<=l<=23	
Reflections collected	29755	
Independent reflections	17787 [*R*(int) = 0.0321]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.563 and 0.499	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17787 / 17 / 803	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)][a]	R_1 = 0.0795, wR_2 = 0.2415	
R indices (all data)	R_1 = 0.1071, wR_2 = 0.2645	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.275 and -1.099 e.Å^{-3}	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2Fc^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S2. Crystal data and structure refinement for complex **3**.

Empirical formula	$C_{148}H_{208}F_{24}N_{24}O_{52}Rh_4S_8$	
Formula weight	4279.49	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 21.482(3) Å	$\alpha = 90°$.
	b = 12.4683(16) Å	$\beta = 101.321(2)°$.
	c = 38.691(5) Å	$\gamma = 90°$.
Volume	10161(2) $Å^3$	
Z	2	
Density (calculated)	1.399 Mg/m^3	
Absorption coefficient	0.501 mm^{-1}	
F(000)	4408	
Crystal size	0.200 x 0.180 x 0.120 mm^3	
Theta range for data collection	1.009 to 26.998°.	
Index ranges	-26<=h<=27, -15<=k<=11, -49<=l<=49	
Reflections collected	70233	
Independent reflections	22096 [*R*(int) = 0.1127]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.801 and 0.663	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22096 / 0 / 749	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)][a]	$R_1 = 0.1172$, $wR_2 = 0.3289$	
R indices (all data)	$R_1 = 0.1750$, $wR_2 = 0.3703$	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.706 and -7.080 $e.Å^{-3}$	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2Fc^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S3. Crystal data and structure refinement for complex **4**.

Empirical formula	$C_{168}H_{192}F_{24}N_{28}O_{40}Rh_4S_8$	
Formula weight	4367.60	
Temperature	173.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 26.607(4) Å	α = 90°.
	b = 31.867(5) Å	β = 94.492(3)°.
	c = 33.813(5) Å	γ = 90°.
Volume	28581(8) $Å^3$	
Z	6	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	0.532 mm^{-1}	
F(000)	13440	
Crystal size	0.42 x 0.35 x 0.33 mm^3	
Theta range for data collection	0.879 to 25.150°.	
Index ranges	-31<=h<=23, -38<=k<=37, -40<=l<=40	
Reflections collected	165754	
Independent reflections	51040 [*R*(int) = 0.1345]	
Completeness to theta = 25.150°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6466 and 0.5246	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	51040 / 760 / 2586	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)][a]	R_1 = 0.1563, wR_2 = 0.3705	
R indices (all data)	R_1 = 0.2228, wR_2 = 0.4106	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.119 and -1.475 e.$Å^{-3}$	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2Fc^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S2. Crystal data and structure refinement for complex **5a**.

Empirical formula	$C_{169}H_{148}F_{24}N_{16}O_{31}Rh_4S_8$	
Formula weight	4023.15	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 37.464(5) Å	α = 90°.
	b = 13.3075(16) Å	β = 112.998(2)°.
	c = 36.173(4) Å	γ = 90°.
Volume	16601(4) Å^3	
Z	4	
Density (calculated)	1.610 Mg/m^3	
Absorption coefficient	0.598 mm^{-1}	
F(000)	8184	
Crystal size	0.280 x 0.240 x 0.230 mm^3	
Theta range for data collection	1.327 to 27.000°.	
Index ranges	-39<=h<=47, -16<=k<=16, -46<=l<=36	
Reflections collected	45291	
Independent reflections	17992 [*R*(int) = 0.0756]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.658	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17992 / 94 / 1146	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)][a]	$R_1 = 0.1014$, $wR_2 = 0.2766$	
R indices (all data)	$R_1 = 0.1643$, $wR_2 = 0.3093$	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.572 and -1.239 e.Å^{-3}	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2Fc^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S2. Crystal data and structure refinement for complex**5b**.

Empirical formula	$C_{170}H_{152}F_{24}Ir_4N_{16}O_{32}S_8$	
Formula weight	4412.35	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.945(8) Å	α = 90°.
	b = 14.605(6) Å	β = 101.754(7)°.
	c = 31.218(12) Å	γ = 90°.
Volume	8903(6) $Å^3$	
Z	2	
Density (calculated)	1.646 Mg/m^3	
Absorption coefficient	3.174 mm^{-1}	
F(000)	4384	
Crystal size	0.360 x 0.140 x 0.120 mm^3	
Theta range for data collection	1.043 to 27.292°.	
Index ranges	-24<=h<=25, -18<=k<=18, -39<=l<=40	
Reflections collected	62498	
Independent reflections	19842 [*R*(int) = 0.0782]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.491 and 0.347	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19842 / 324 / 1192	
Goodness-of-fit on F^2	0.904	
Final R indices [I>2sigma(I)][a]	$R_1 = 0.0518$, $wR_2 = 0.1233$	
R indices (all data)	$R_1 = 0.1034$, $wR_2 = 0.1395$	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.715 and -1.331 e.$Å^{-3}$	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2Fc^2]/3$(also with $F_0^2>2\sigma F^2$)

5. ESI-MS spectra

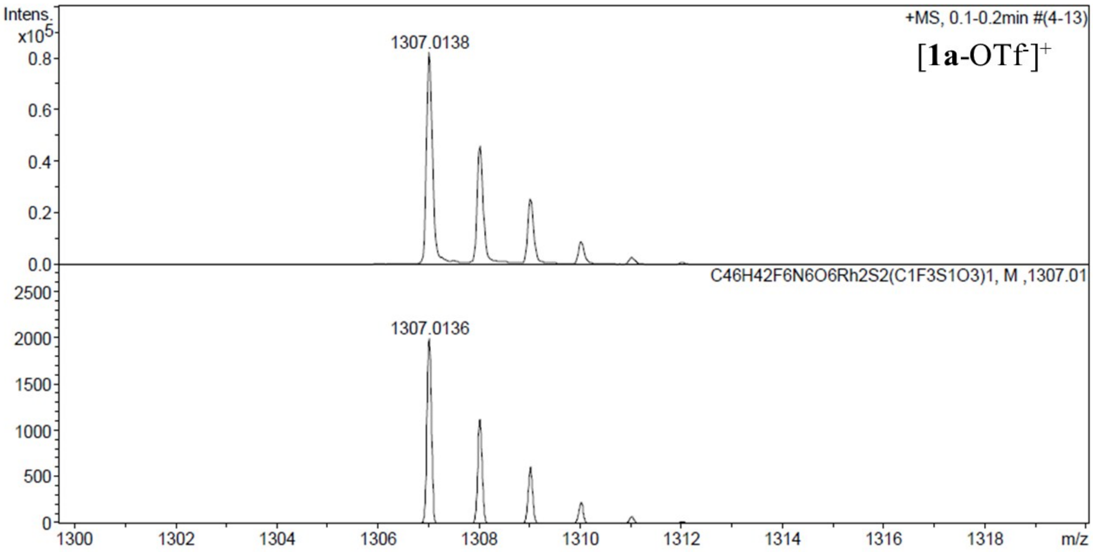

Figure S1. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **1a** (1).

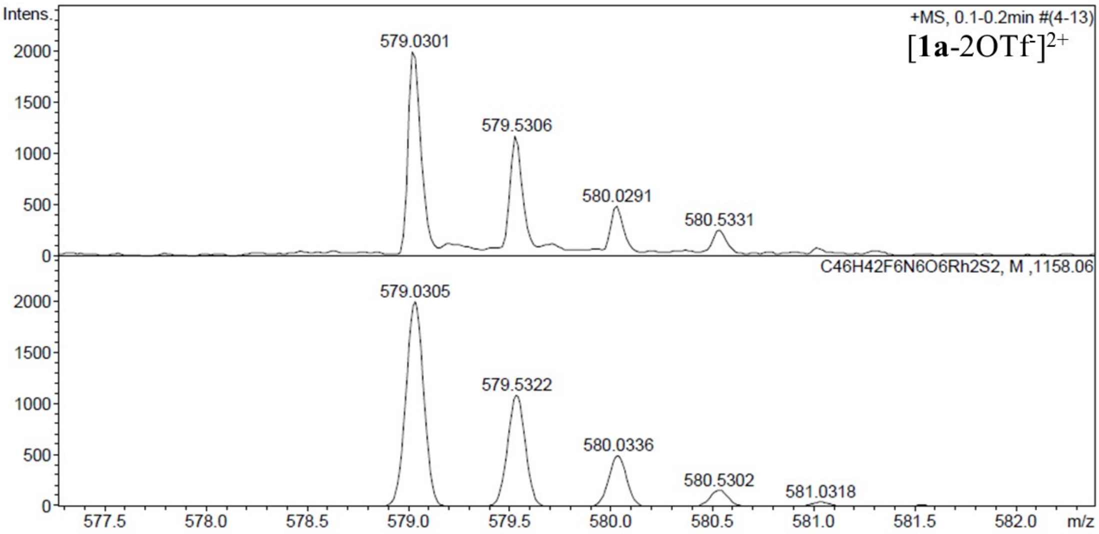

Figure S2. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **1a** (2).

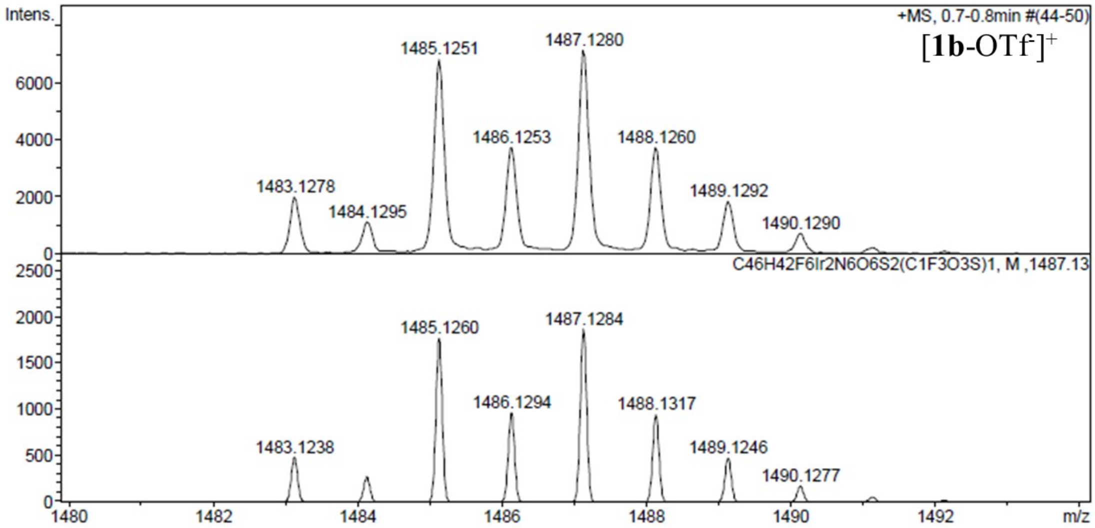

Figure S3. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **1b** (1).

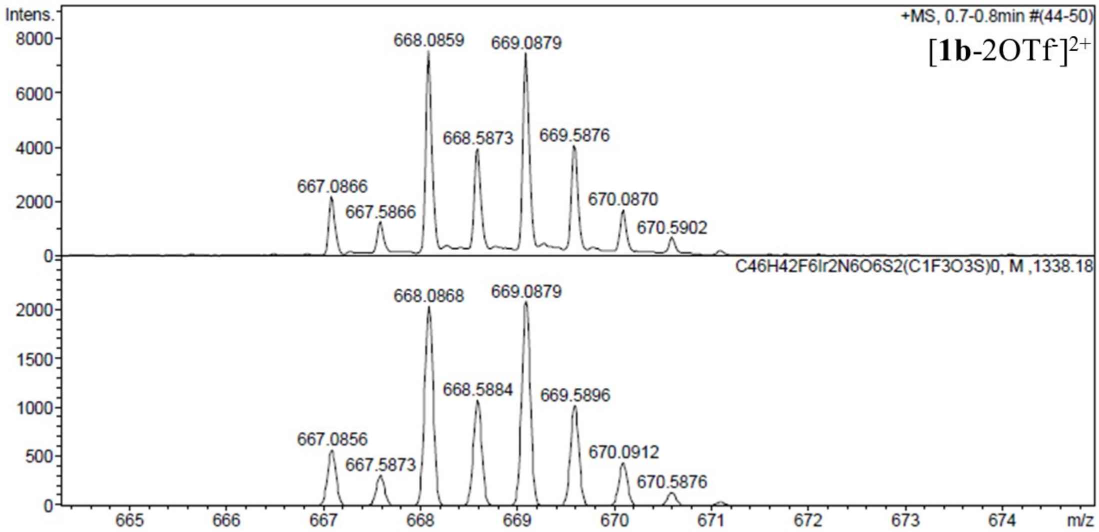

Figure S4. Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **1b** (2).

6. UV/Vis spectrum

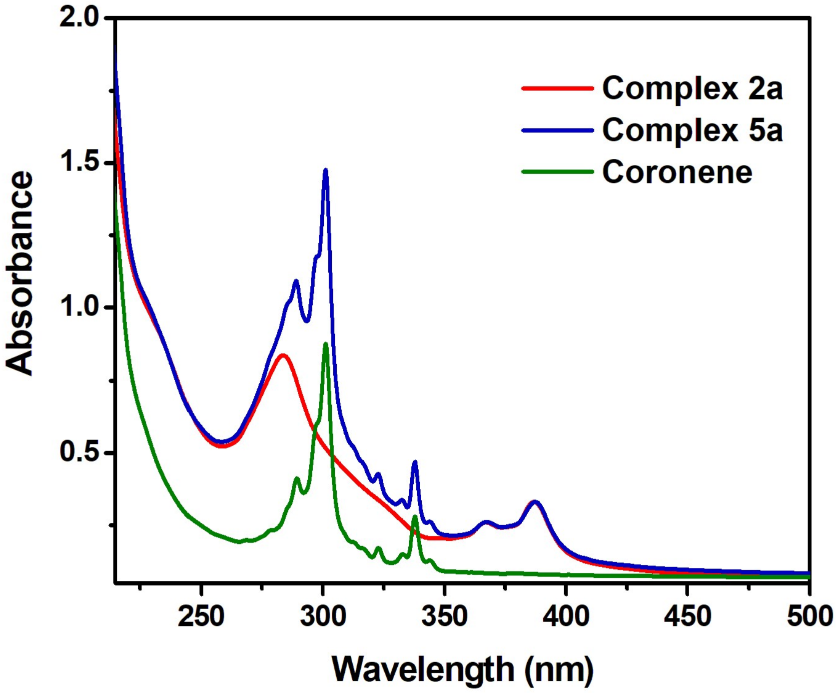

Figure S5. The UV/Vis spectrum of complex **5a**. *c* (complex **2a**) = 10^{-5} M, *c* (complex **5a**) = 10^{-5} M and *c* (coronene) = 10^{-5} M.

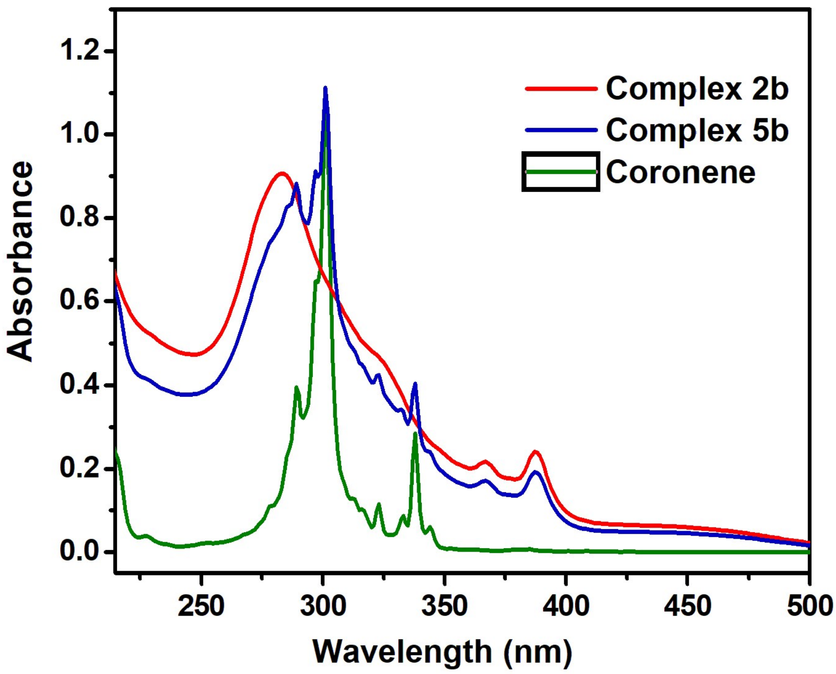

Figure S6. The UV/Vis spectrum of complex **5b**. *c* (complex **2b**) = 10^{-5} M, *c* (complex **5b**) = 10^{-5} M and *c* (coronene) = 10^{-5} M.

7. NMR spectra

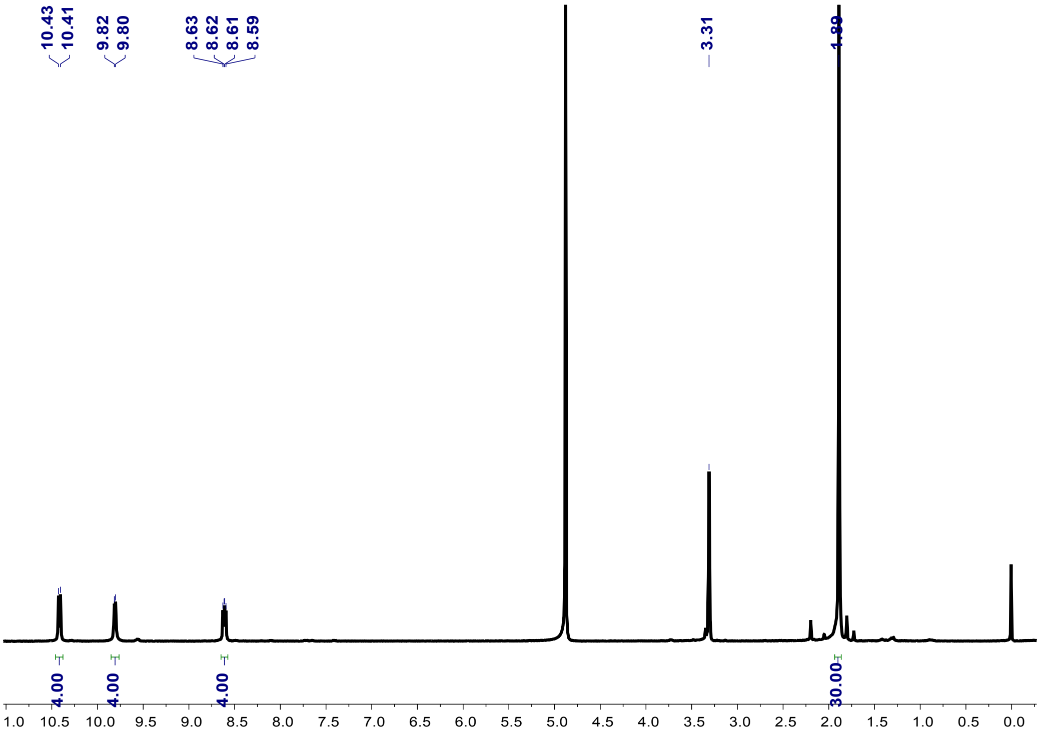

Figure S7. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **1a**.

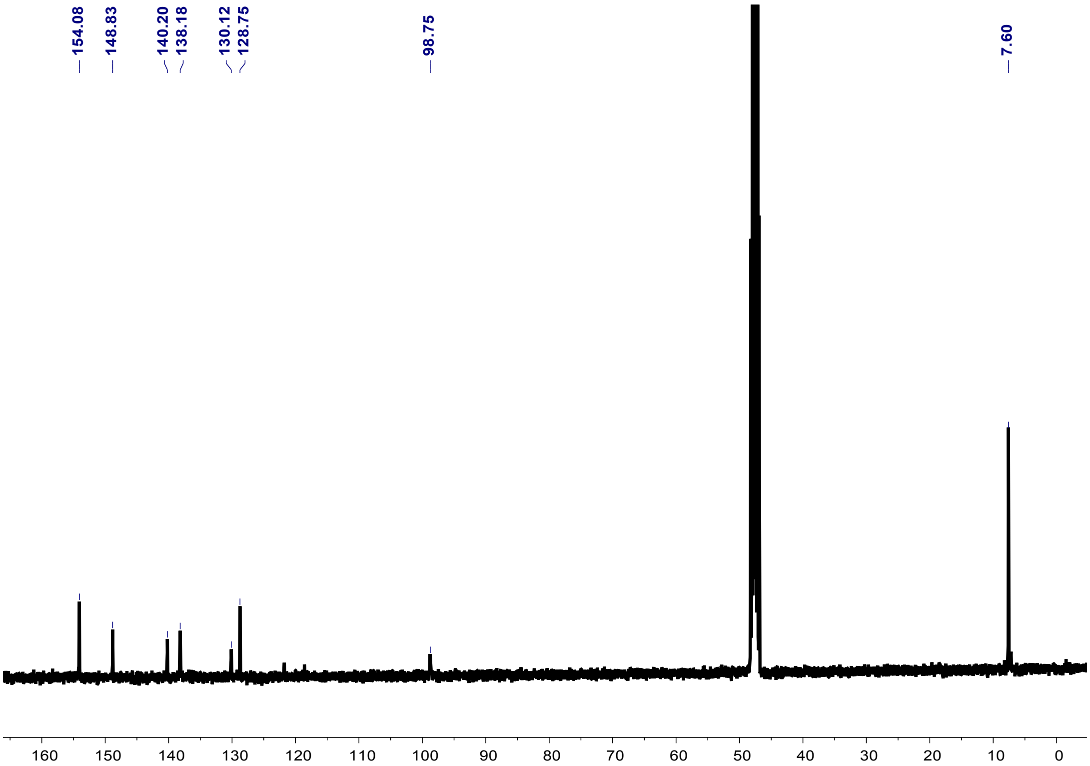

Figure S8. ^{13}C NMR (101 MHz, CD_3OD, ppm) for **1a**.

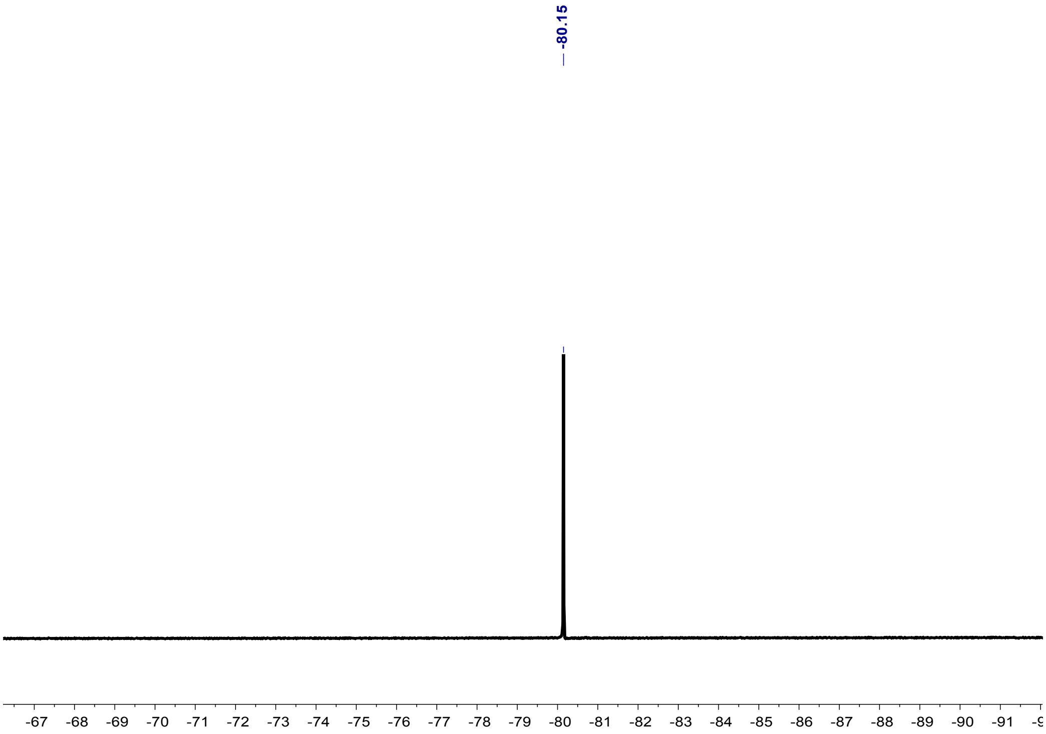

Figure S9. ^{19}F NMR (376 MHz, CD_3OD, ppm) for **1a**.

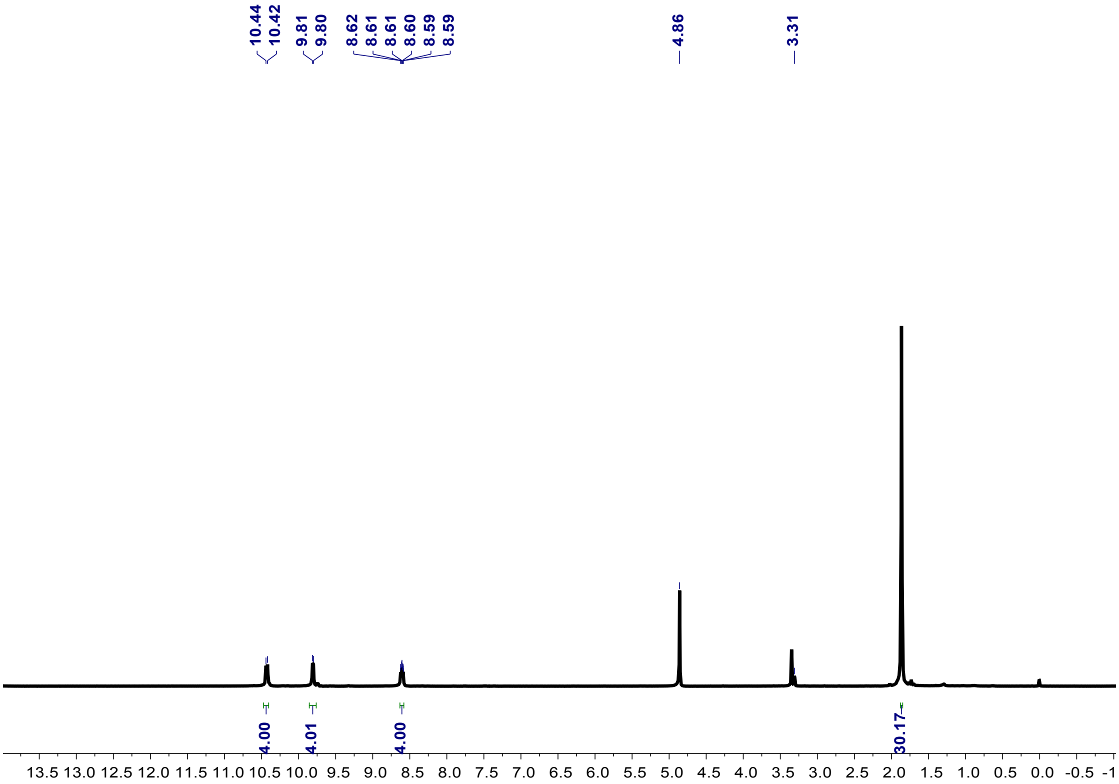

Figure S10. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **1b**.

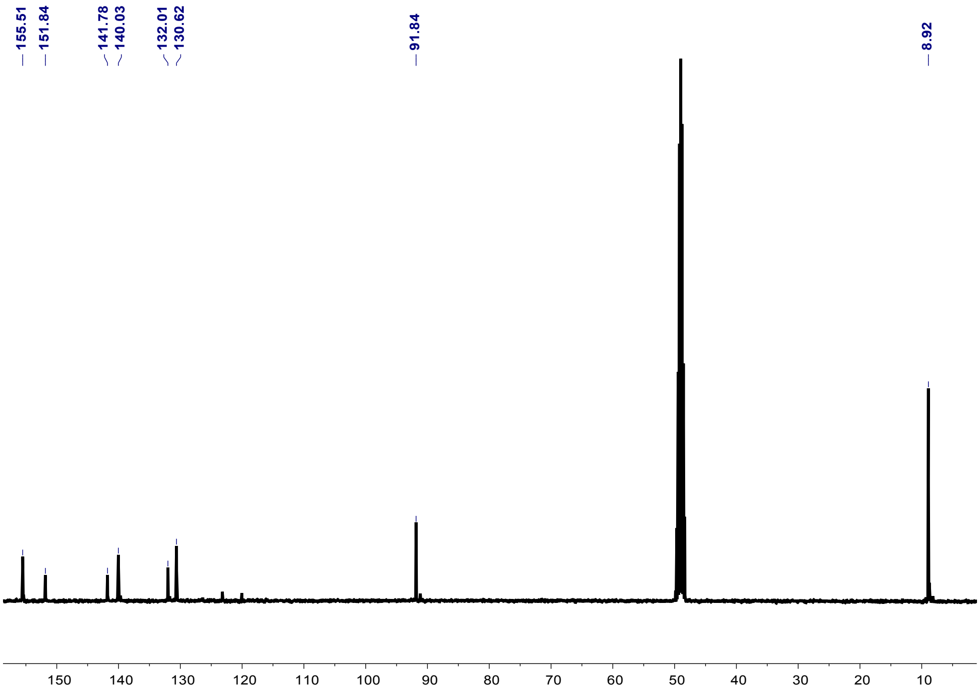

Figure S11. ^{13}C NMR (101 MHz, CD_3OD, ppm) for **1b**.

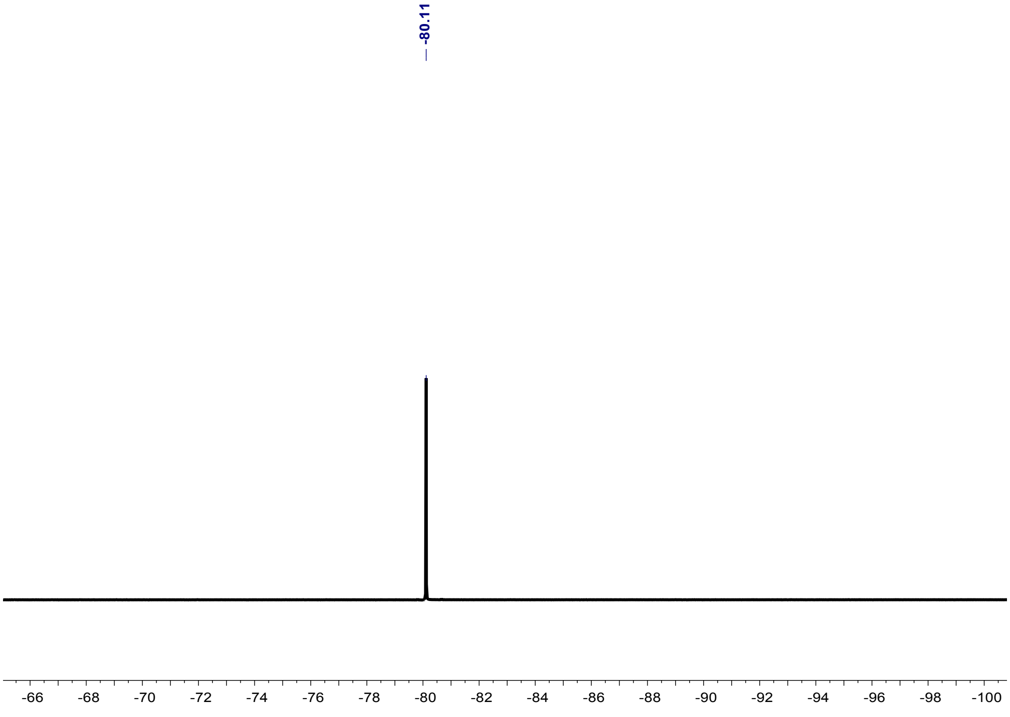

Figure S12. ^{19}F NMR (376 MHz, CD_3OD, ppm) for **1b**.

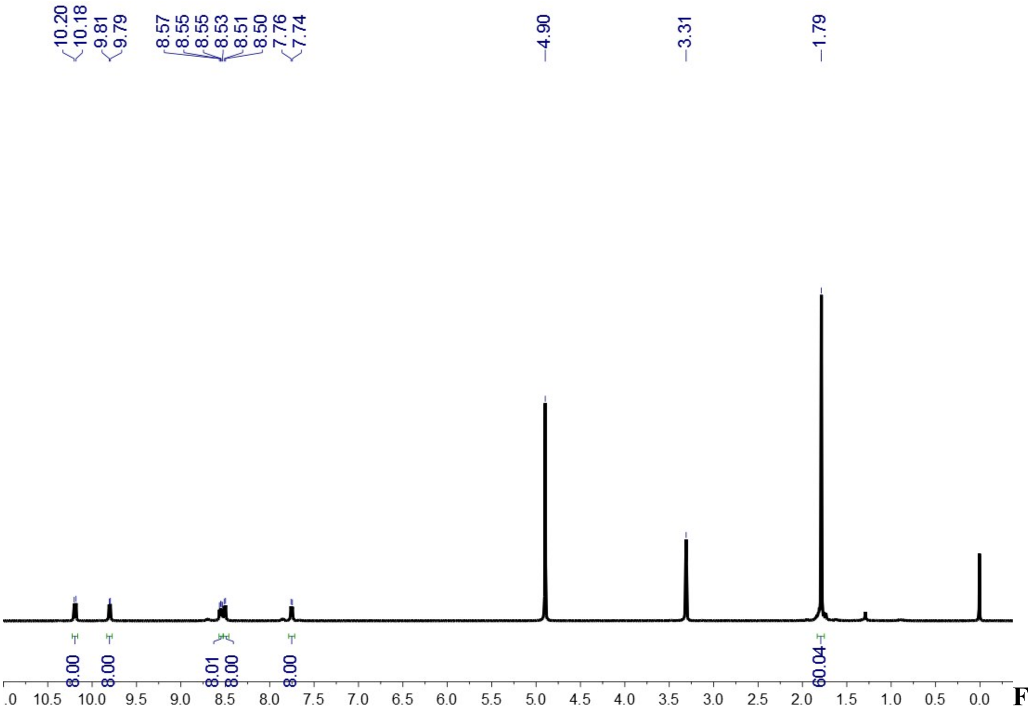

Figure S13. ^{1}H NMR (400 MHz, CD$_3$OD, ppm) for **2a**.

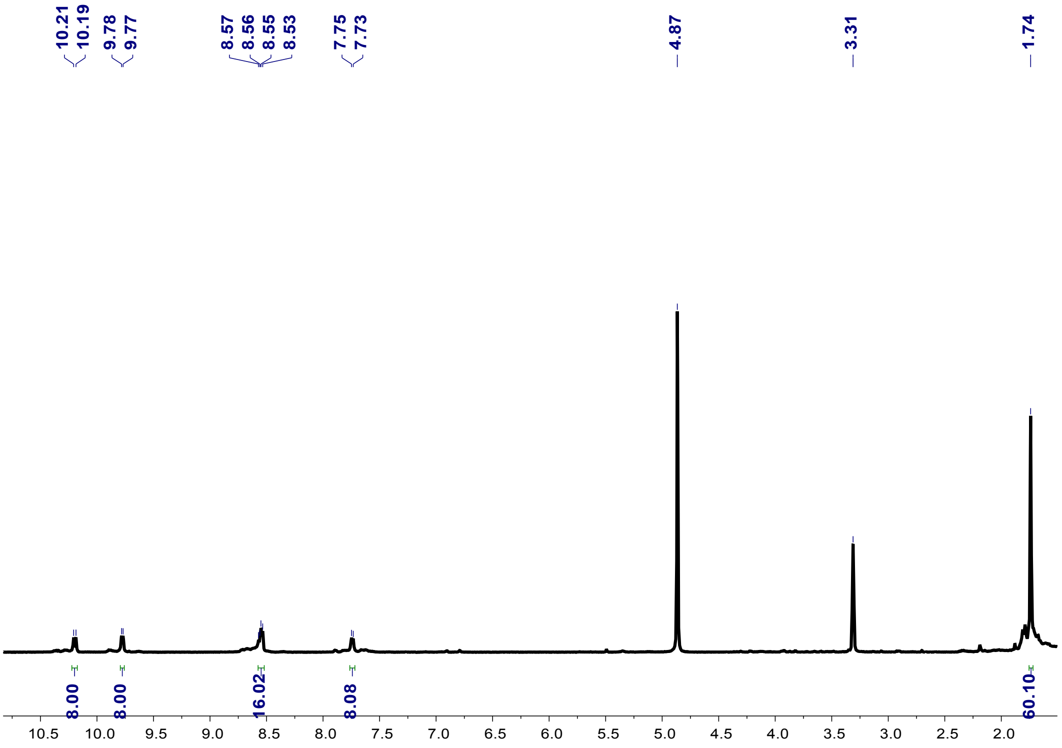

Figure S14. ^{1}H NMR (400 MHz, CD$_3$OD, ppm) for **2b**.

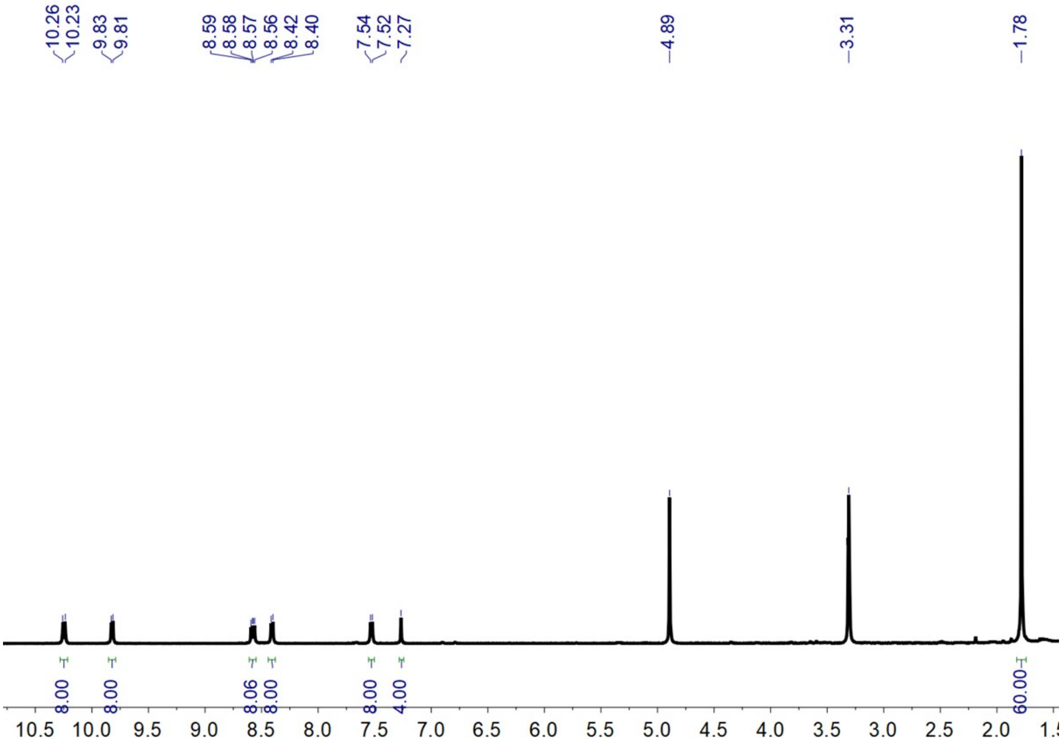

Figure S15. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **3**.

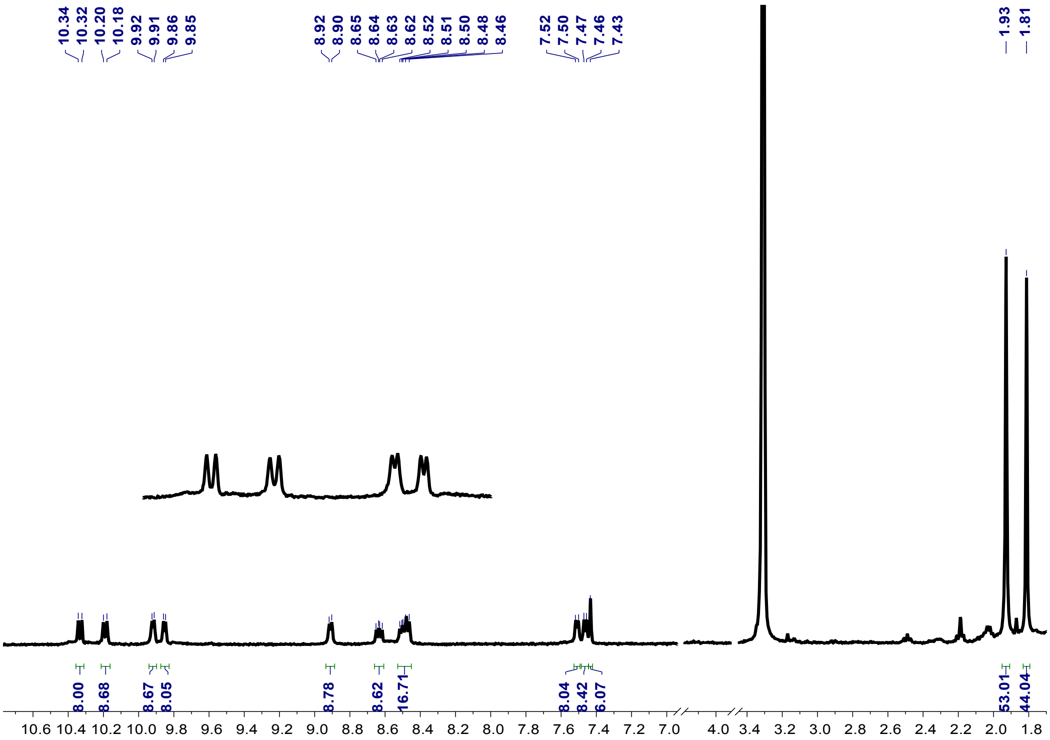

Figure S16. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **4 (BRs + monomeric rings)**, *c* = 2.0 mM.

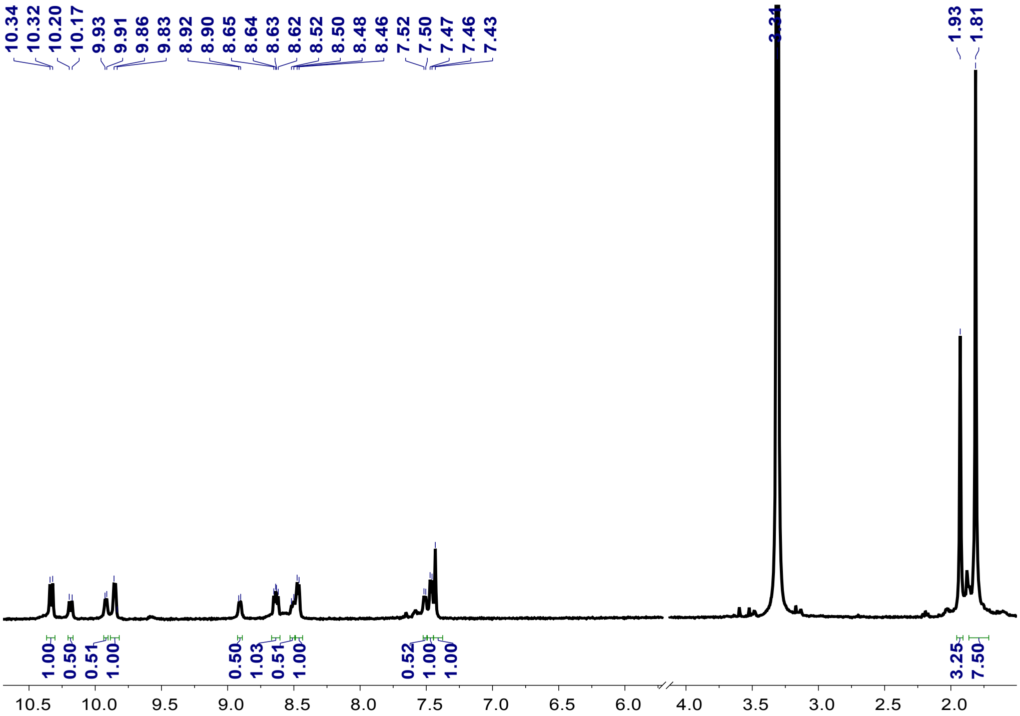

Figure S17. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **4 (BRs + monomeric rings)**, *c* = 1.0 mM.

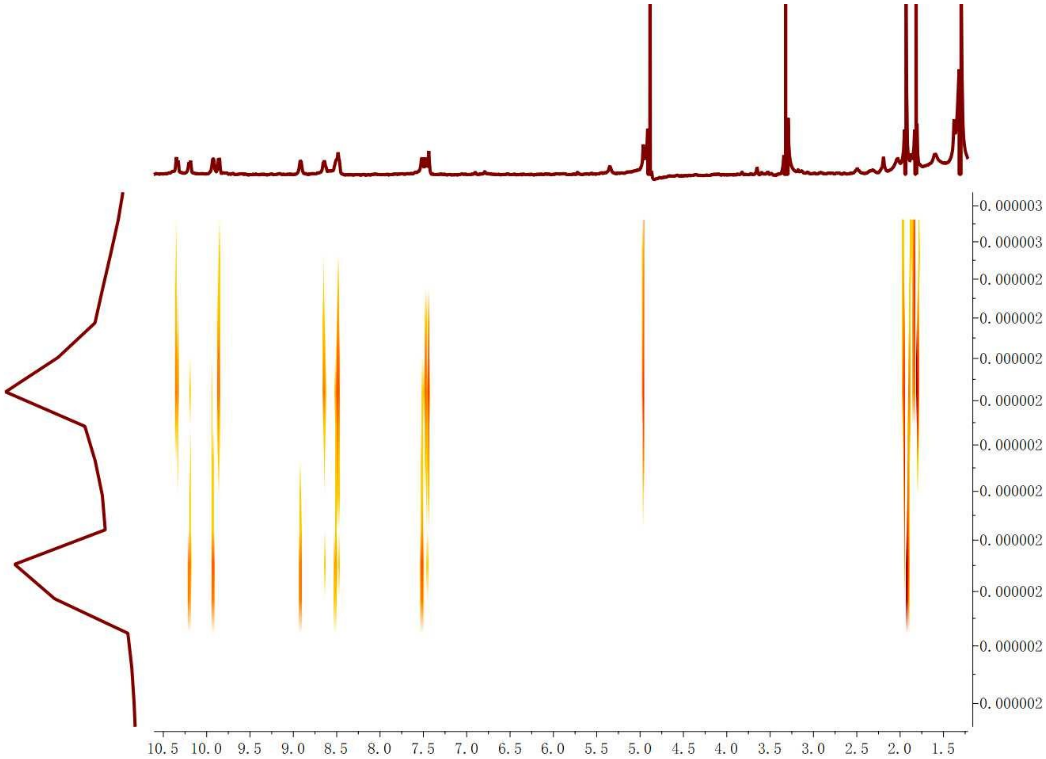

Figure S18. ^{1}H DOSY NMR (400 MHz, CD_3OD, ppm) for **4 (BRs + monomeric rings)**, *c* = 2.0 mM.

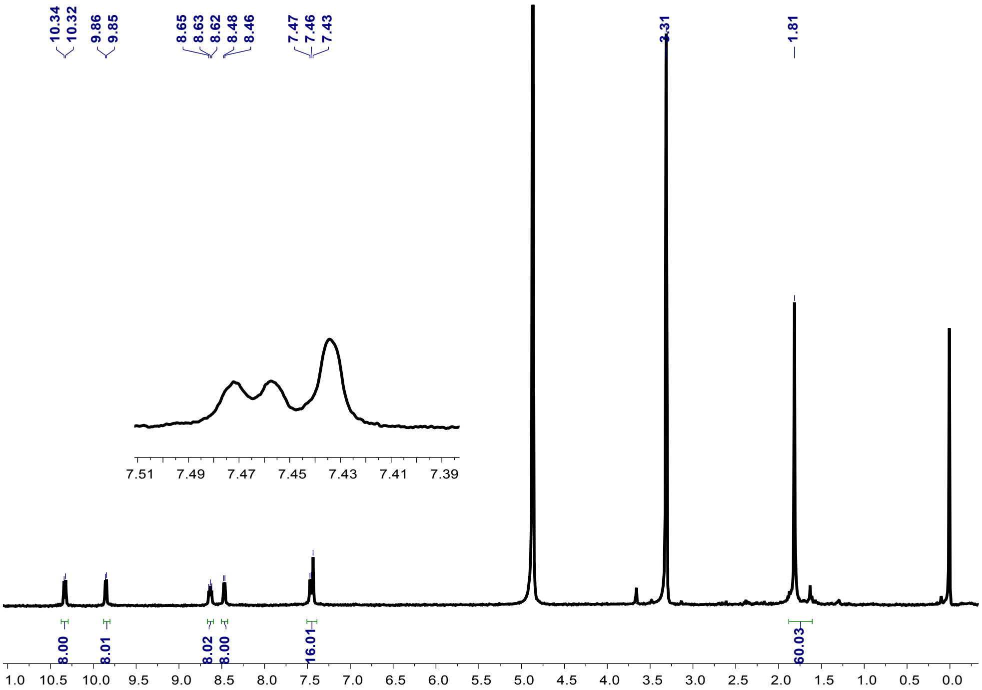

Figure S19. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **4 (monomeric rings)**, *c* = 0.5 mM.

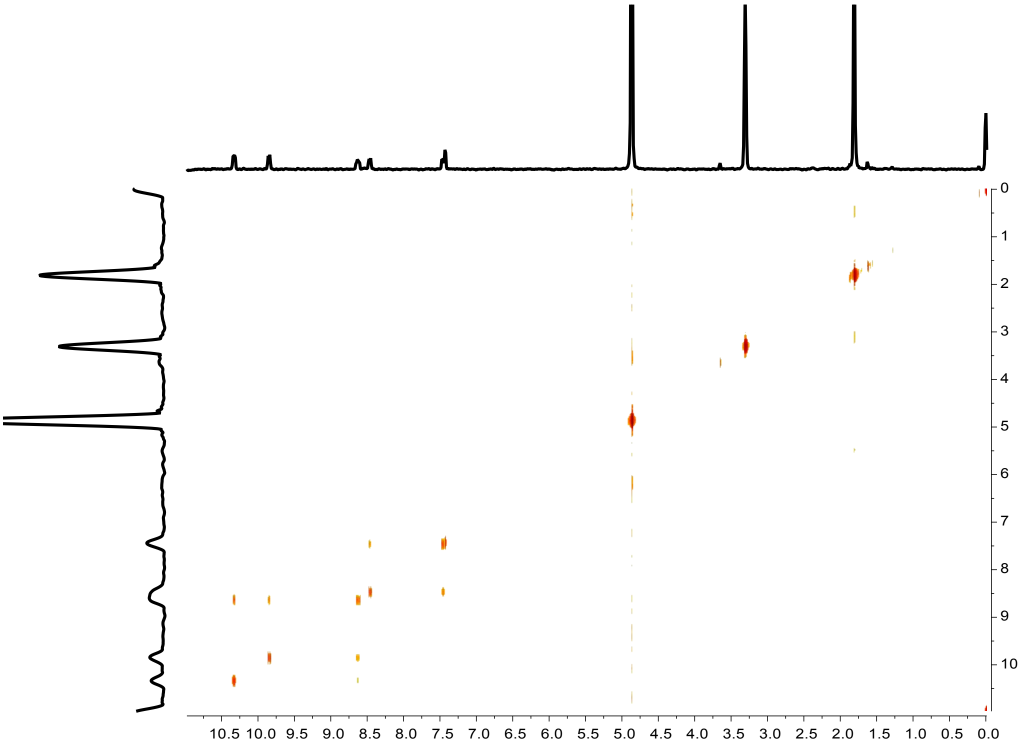

Figure S20. ^{1}H – ^{1}H COSY NMR (400 MHz, CD_3OD, ppm) for **4 (monomeric rings)**, *c* = 0.5 mM.

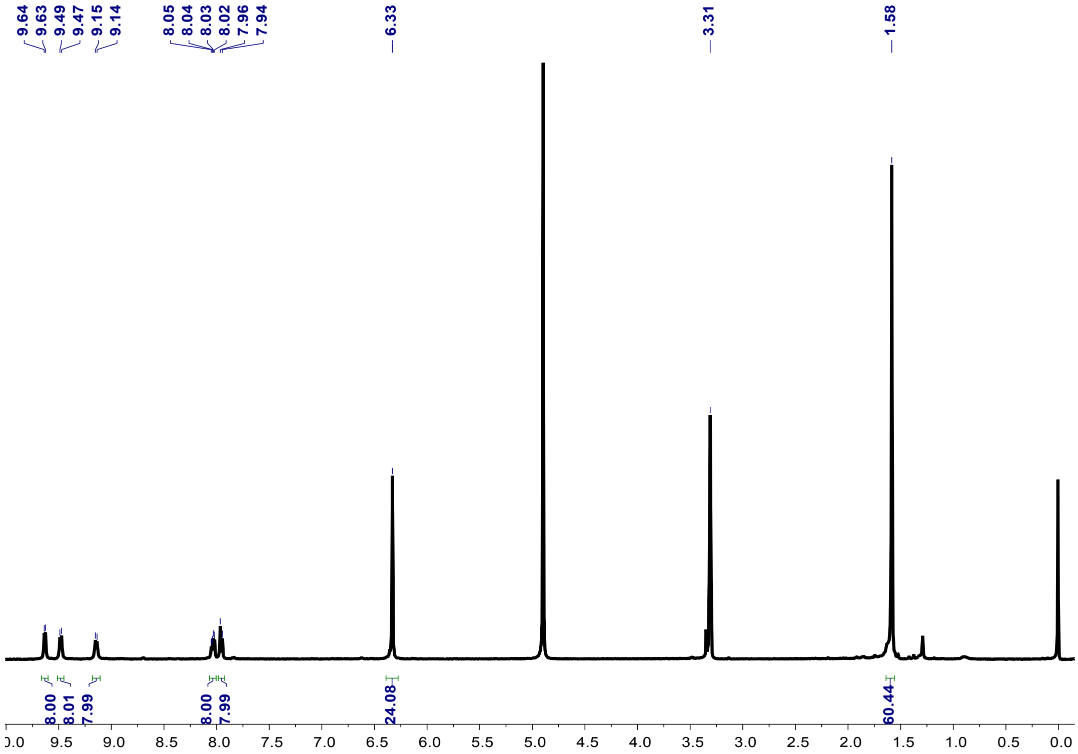

Figure S21. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **5a**.

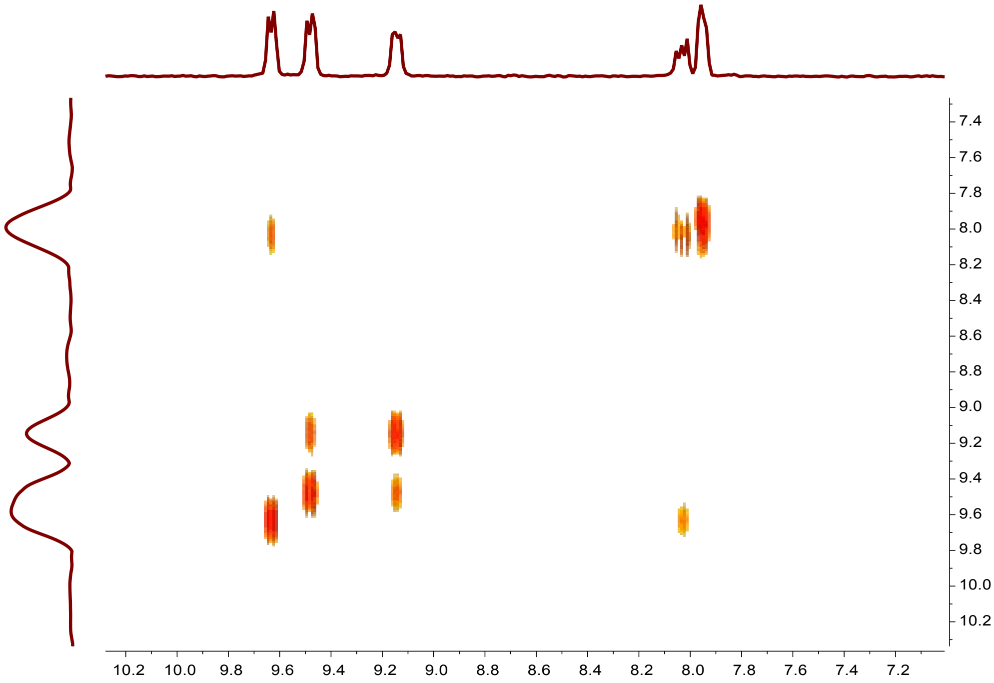

Figure S22. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3OD, ppm) for **5a**.

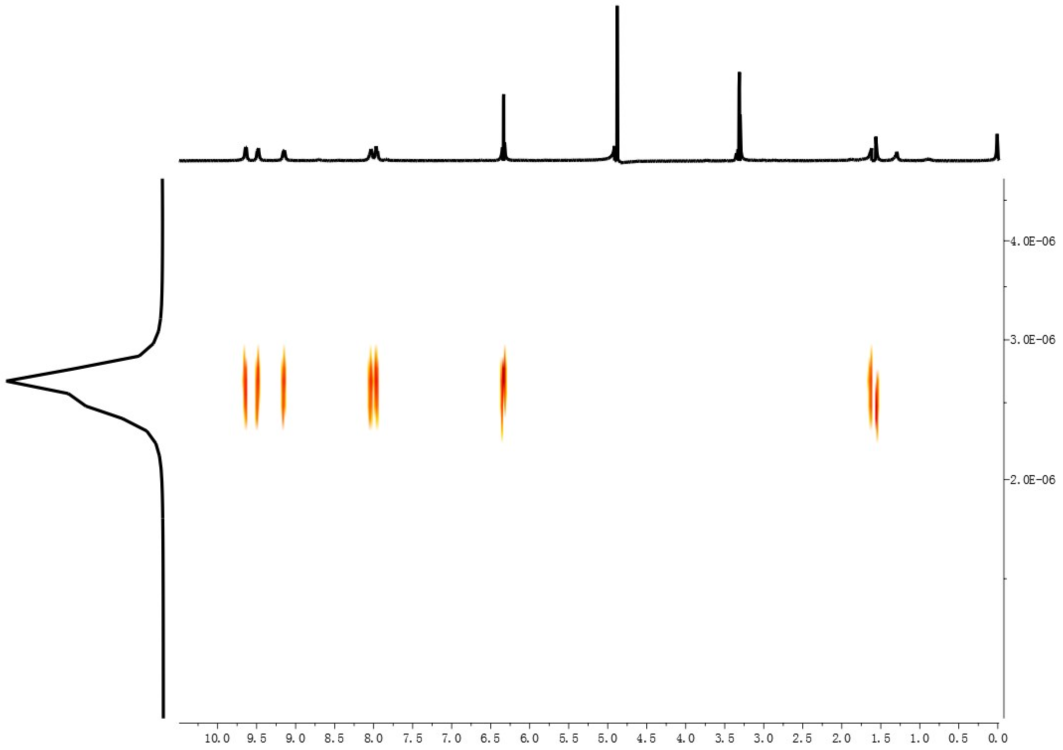

Figure S23. ^{1}H DOSY NMR (400 MHz, CD_3OD, ppm) for **5a**.

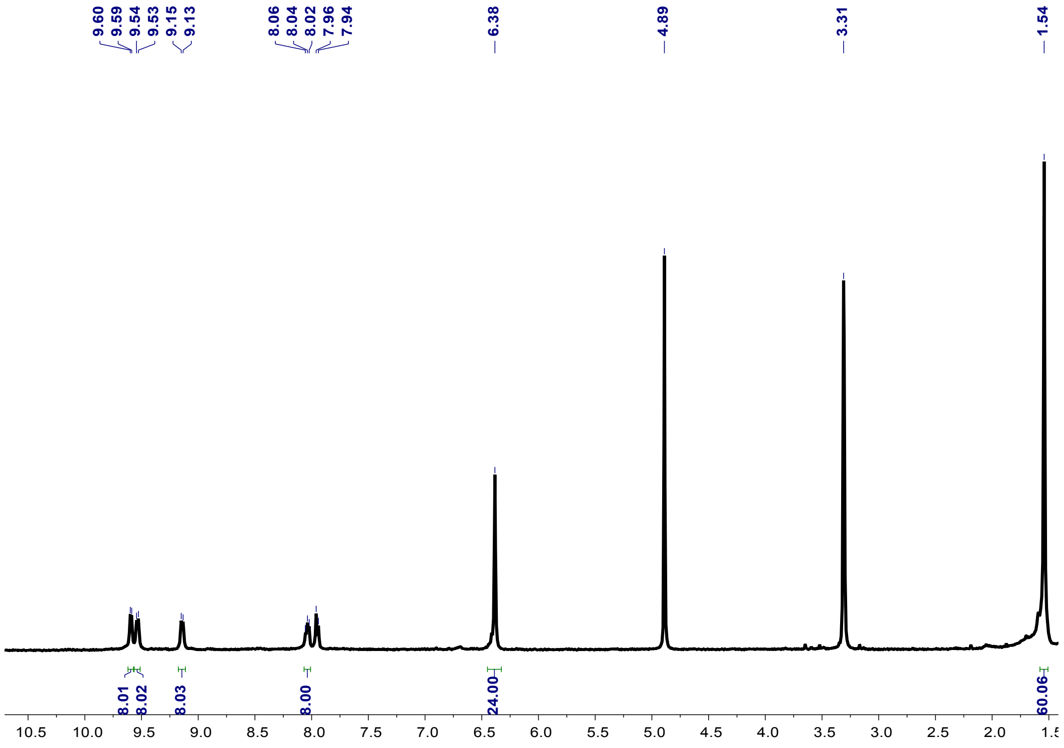

Figure S24. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **5b**.

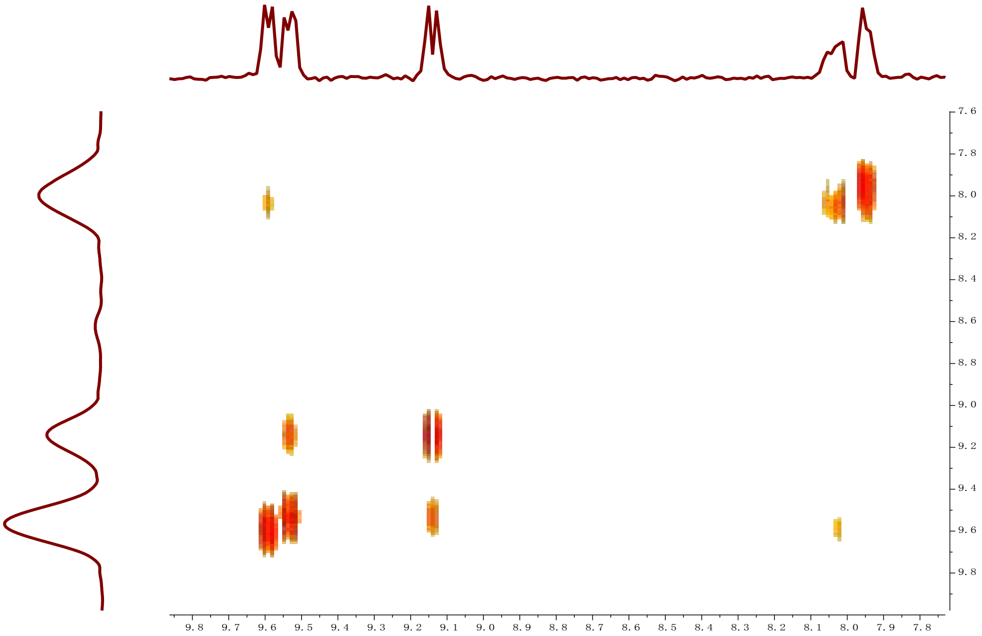

Figure S25. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3OD, ppm) for **5b**.

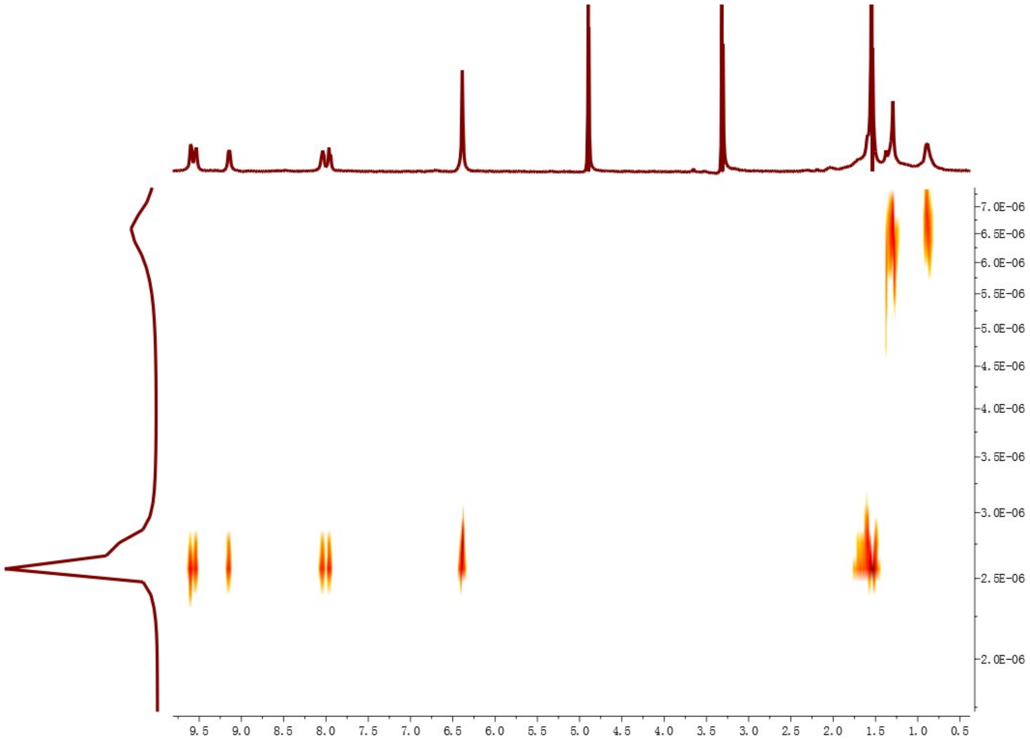

Figure S26. ^{1}H DOSY NMR (400 MHz, CD_3OD, ppm) for **5b**.

8. Single-crystal X-ray structure of 5b

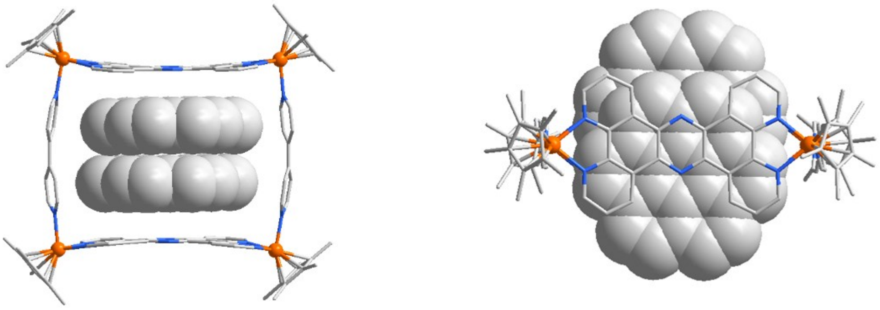

Figure S29. (left) side view; (right) top view. All hydrogen atoms, anions, and solvent molecules are omitted for clarity, all hydrogen atoms are omitted for clarity, Ir orange; N blue; C gray.

9. References

S1 C. White, A. Yates, P. M. Maitlis and D. M. Heinekey, *Inorg. Synth.*, 1992, **29**, 228.

S2 J. Bolger, A. Gourdon, E. Ishow, and J. -P. Launay, *Inorg. Chem.*, 1996, **35**, 2937.

S3 D. P. Lydon, L. Porrès, A. Beeby, T. B. Mardera and P. J. Low, *New J. Chem.*, 2005, **29**, 972.