Supplementary Information

Construction of half-sandwich multinuclear complexes including tunnel architectures via C–H-activation-directed assembly

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Information for Single-crystal X-ray structure determination

In asymmetric unit of data **2b**, all non-hydrogen atoms were refined anisotropically. 23 ISOR, 1 DELU, 3 SADI and 22 DFIX instructions were used to restrain anions and Cp* fragments so that there were 165 restraints in the data. In asymmetric unit of data **2c**, there were disordered solvent molecules (three acetonitrile molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One pyridyl group and one triflate anion were disordered and they were divided into two parts (50:50 for pyridyl group and 57:43 for anion). 41 ISOR, 2 FLAT, 3 SIMU and 17 DFIX instructions were used to restrain anions, bipyridine ligand, acetonitrile molecule and Cp* fragments so that there were 287 restraints in the data. In asymmetric unit of data **2g**, there were disordered solvents (two dichloromethane and two methanol molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. 45 ISOR and 6 DFIX instructions were used to restrain anions, ligands and Cp* fragments so that there were 276 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 data **3a**, 37 ISOR, 1 SIMU, 2 DELU and 20 DFIX instructions were used to restrain anions, cations, ligands and Cp* fragments so that there were 286 restraints in the data.

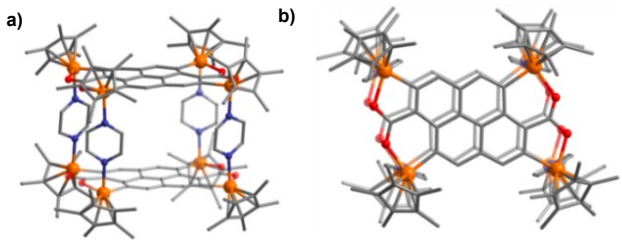


Fig. S1 (a) Crystallographically-derived structure of **1**; (b) top view. All hydrogen atoms, solvent molecules and counterions are omitted for clarity. Color code: N, blue; O, red; C, gray; Ir, orange.

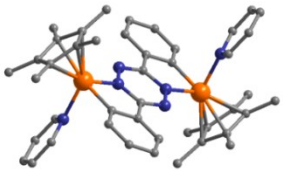
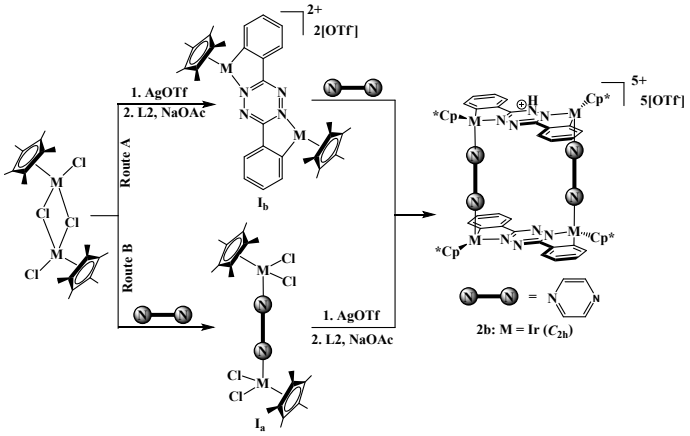


Fig. S2 Crystallographically-derived structure of **2a**. All hydrogen atoms, solvent molecules, and counterions are omitted for clarity. Color code: N, blue; C, gray; Ir, orange.



Scheme S1 Synthesis of tetranuclear complexes **2b**.

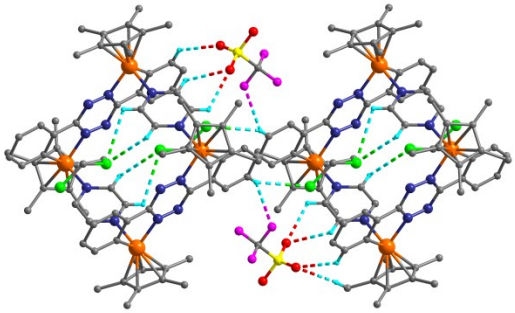


Fig. S3 hydrogen-bond interactions between two neighboring macrocycles in **2b** through OTf anions and dichloromethane guests. Hydrogen atoms, solvent molecules, and counterions are selectively omitted for clarity. Color code: N, blue; C, gray; H, cyan; O, red; S, yellow; F, pink; Cl, green; Ir, orange.

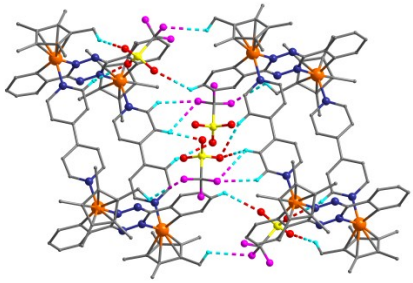


Fig. S4 hydrogen-bond interactions between two neighboring macrocycles in **2c** through OTf anions. Hydrogen atoms, solvent molecules, and counterions are selectively omitted for clarity. Color code: N, blue; C, gray; H, cyan; O, red; S, yellow; F, pink; Ir, orange.

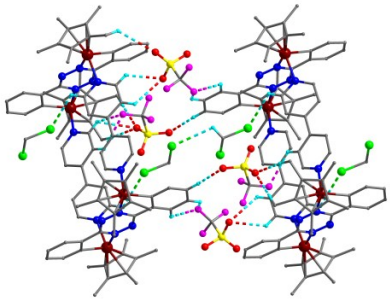


Fig. S5 hydrogen-bond interactions between two neighboring macrocycles in **2d** through OTf anions and dichloromethane guests. Hydrogen atoms, solvent molecules, and counterions are selectively omitted for clarity. Color code: N, blue; C, gray; H, cyan; O, red; S, yellow; F, pink; Cl, green; Rh, red.

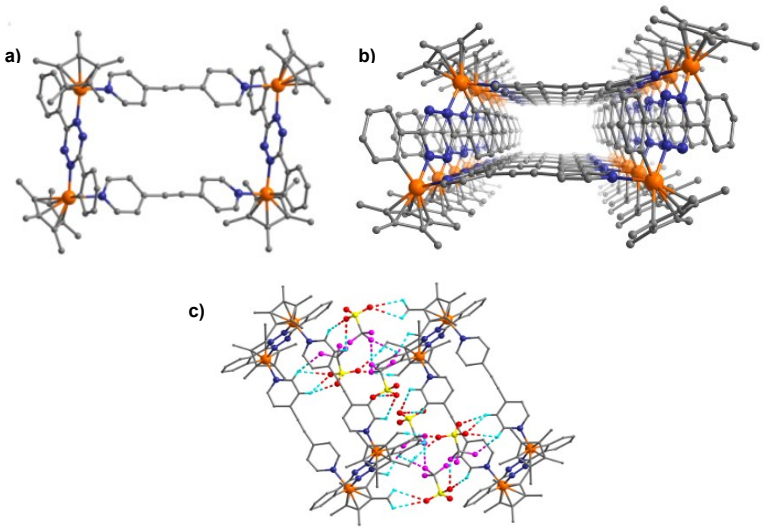


Fig. S6 (a) Crystallographically-derived structure of **2e**-C_{2h}; (b) view showing the packing of macrocycles to generate a channel; (c) hydrogen-bond interactions between two neighboring macrocycles in **2e**-C_{2h} through OTf anions. Hydrogen atoms, solvent molecules, and counterions are selectively omitted for clarity. Color code: N, blue; C, gray; H, cyan; O, red; S, yellow; F, pink; Ir, orange.

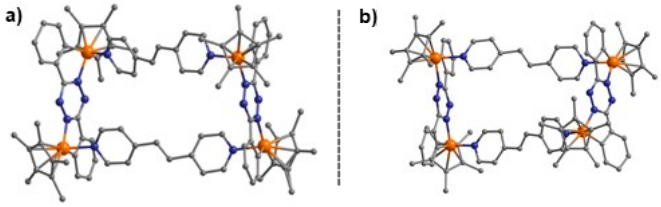


Fig. S7 (a) Crystallographically-derived structure of (*S*,*S*)-(*S*,*S*)-**2f**-D_2; (b) Crystallographically-derived structure of (*R*,*R*)-(*R*,*R*)-**2f**-D_2. All hydrogen atoms, solvent molecules, and counterions are omitted for clarity. Color code: N, blue; C, gray; Ir, orange.

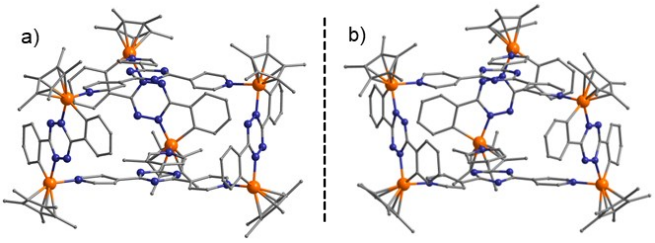


Fig. S8 (a) Crystallographically-derived structure of (*S*,*S*)-(*S*,*S*)-(*S*,*S*)-**2h**; (b) Crystallographically-derived structure of (*R*,*R*)-(*R*,*R*)-(*R*,*R*)-**2h**. All hydrogen atoms, solvent molecules, and counterions are omitted for clarity. Color code: N, blue; C, gray; Ir, orange.

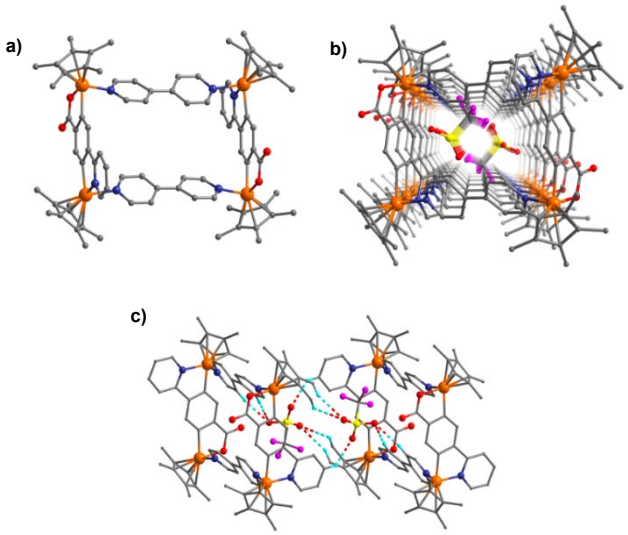


Fig. S9 (a) crystallographically-derived structure of **3b**; (b) view showing the packing of macrocycles **3b** to generate a channel containing OTf anions; (c) hydrogen-bond interactions between two neighboring macrocycles in **3b** through OTf anions. All hydrogen atoms, selected solvent molecules and counterions are omitted for clarity. Color code: N, blue; C, gray; H, cyan; O, red; S, yellow; F, pink; Ir, orange.

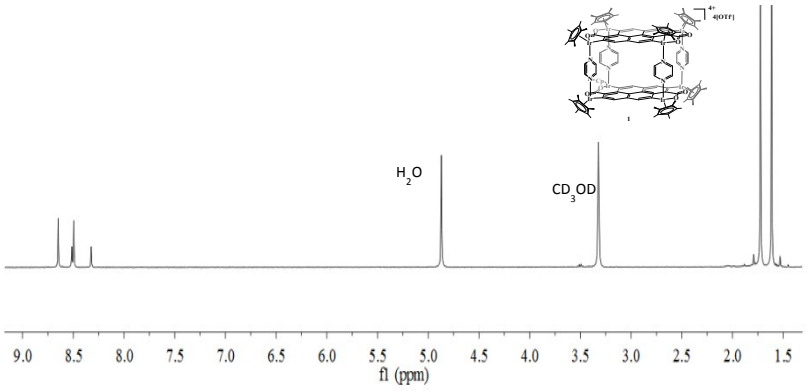


Fig. S10 ^{1}H NMR spectrum of **1**.

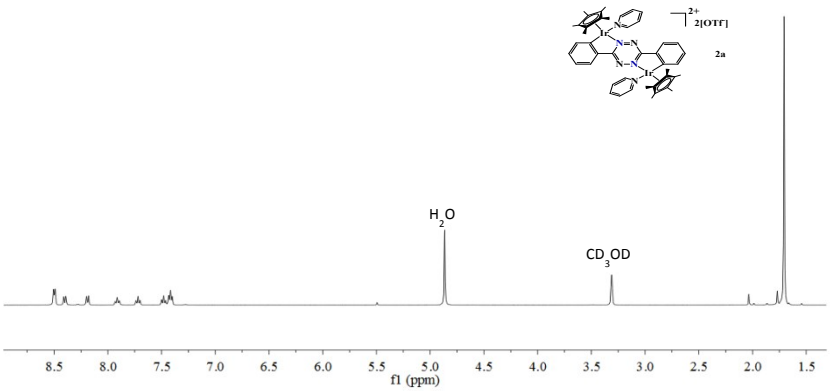


Fig. S11 ^{1}H NMR spectrum of **2a**.

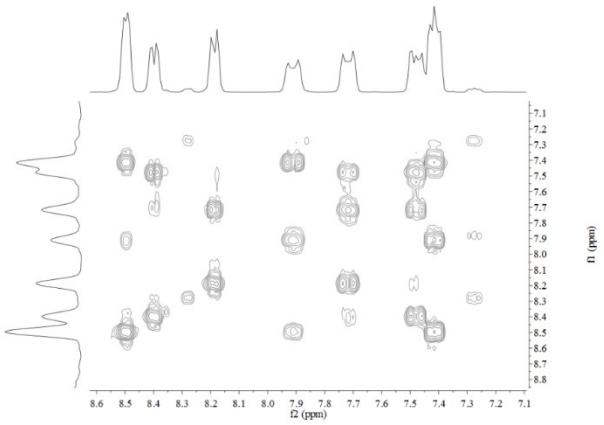


Fig. S12 ^{1}H-^{1}H COSY NMR spectrum of **2a**.

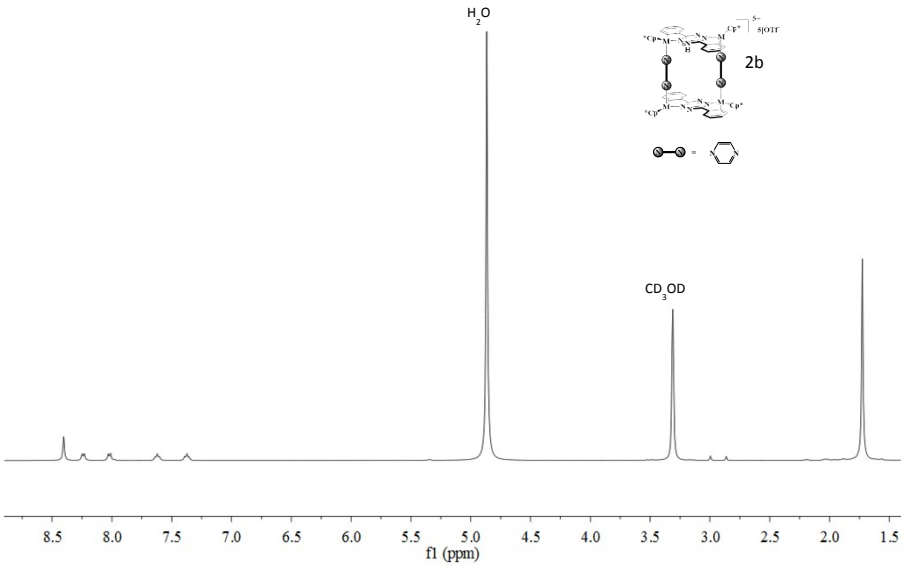


Fig. S13 ^{1}H NMR spectrum of **2b**.

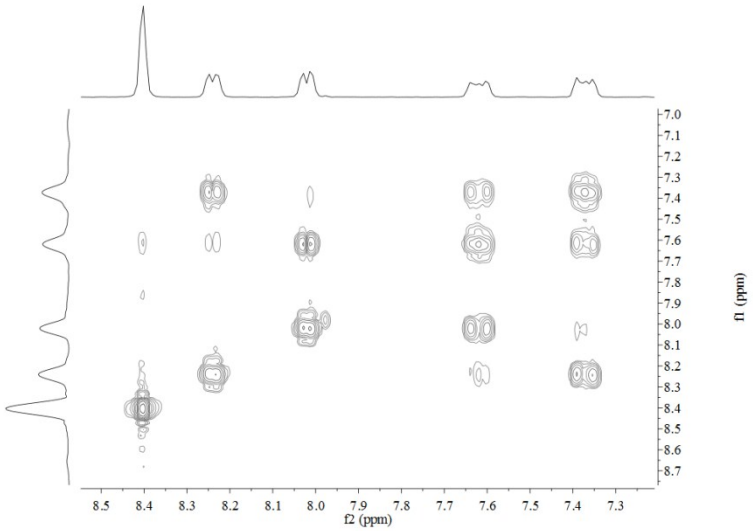


Fig. S14 ^{1}H-^{1}H COSY NMR spectrum of **2b**.

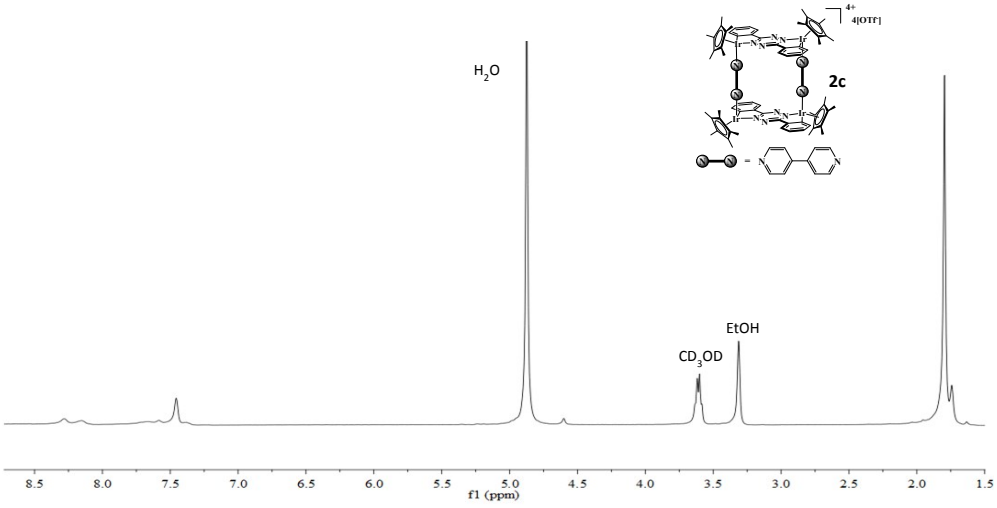


Fig. S15 ^{1}H NMR spectrum of **2c**.

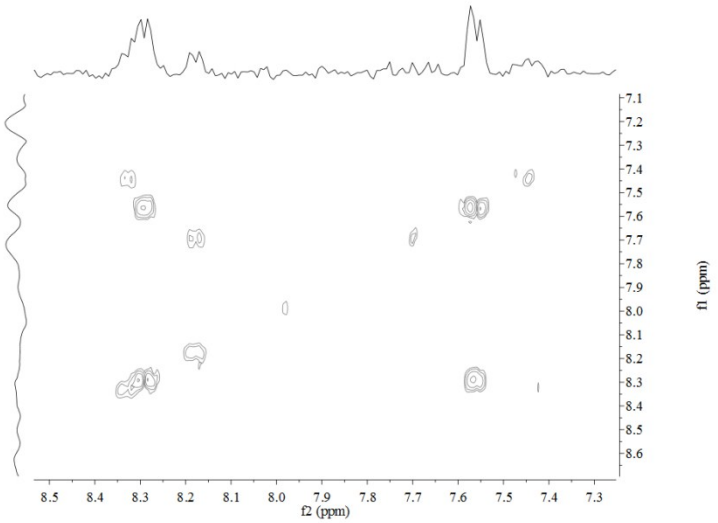


Fig. S16 ^{1}H-^{1}H COSY NMR spectrum of **2c**.

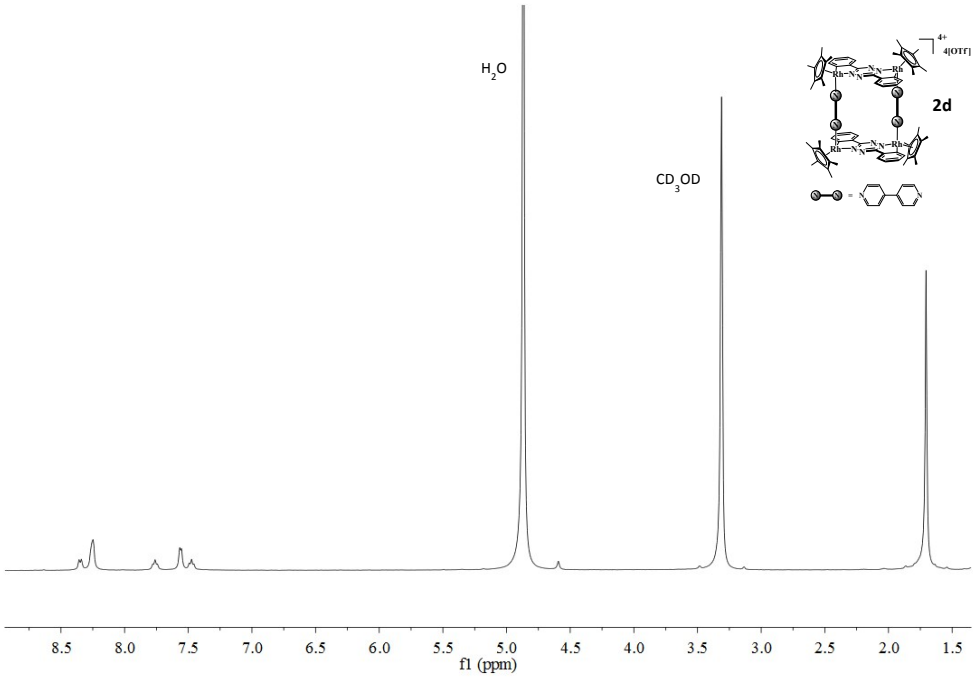


Fig. S17 ^{1}H NMR spectrum of **2d**.

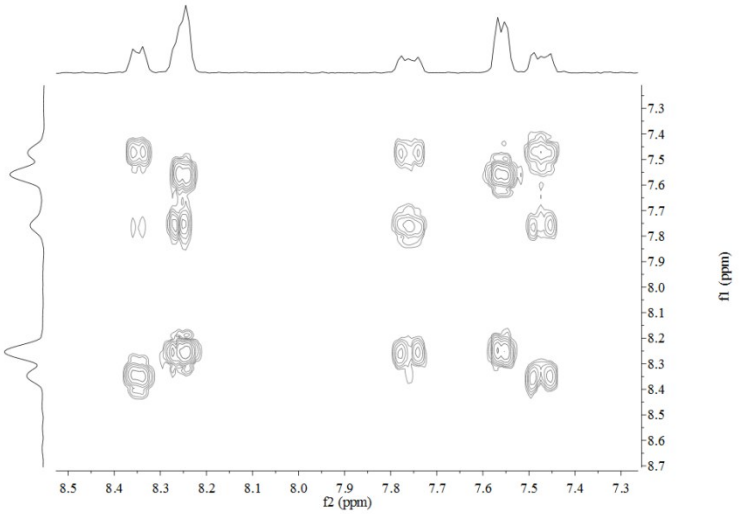


Fig. S18 ^{1}H-^{1}H COSY NMR spectrum of **2d**.

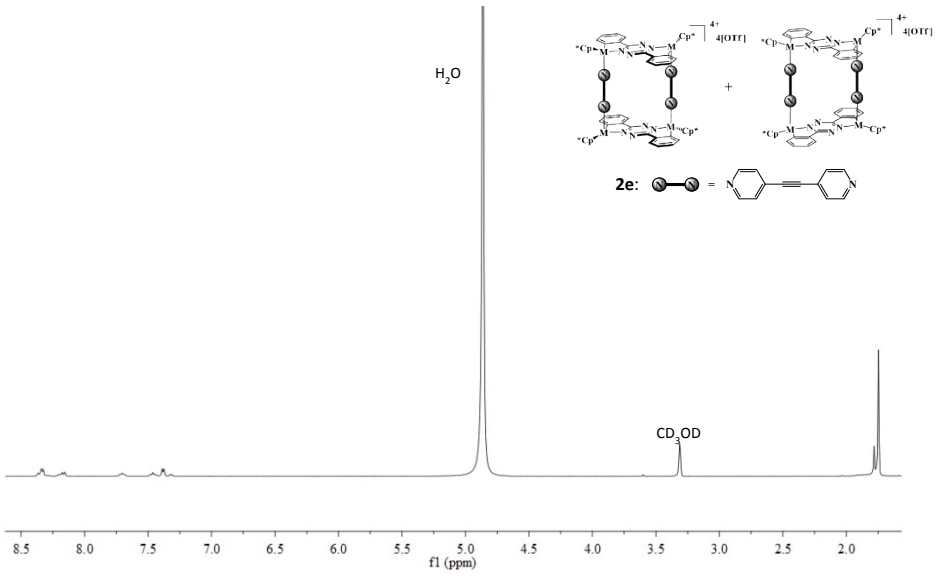


Fig. S19 ^{1}H NMR spectrum of **2e**.

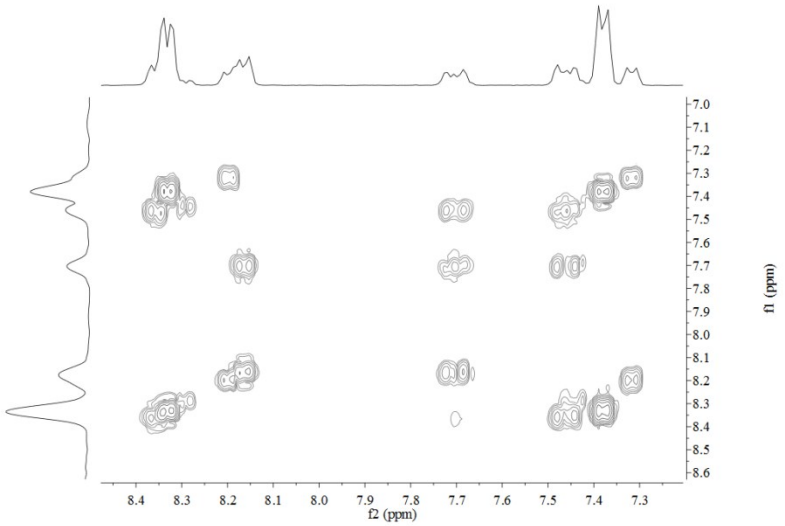


Fig. S20 ^{1}H-^{1}H COSY NMR spectrum of **2e**.

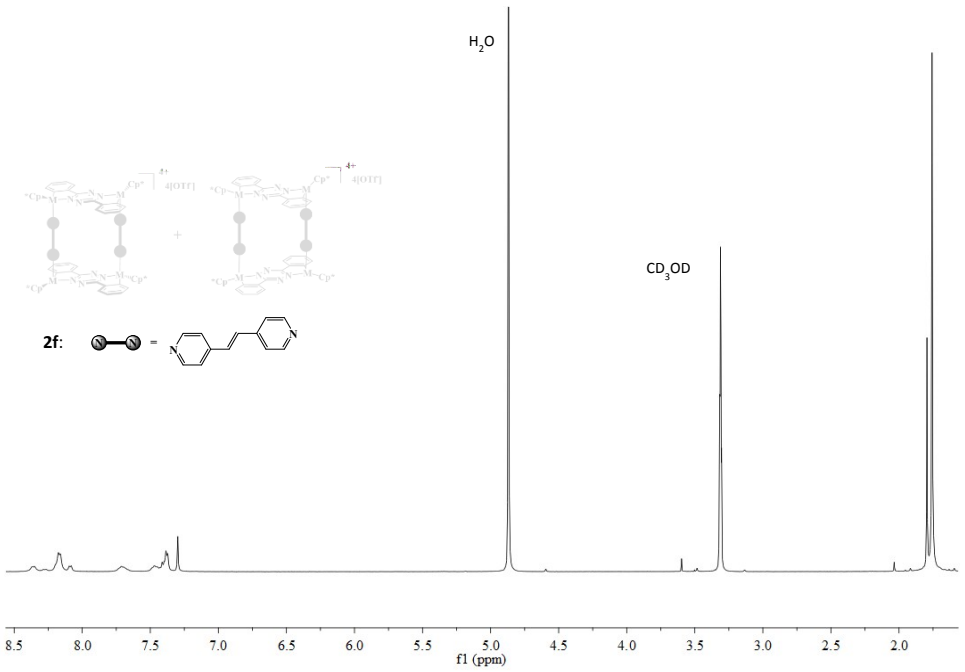


Fig. S21 ^{1}H NMR spectrum of **2f**.

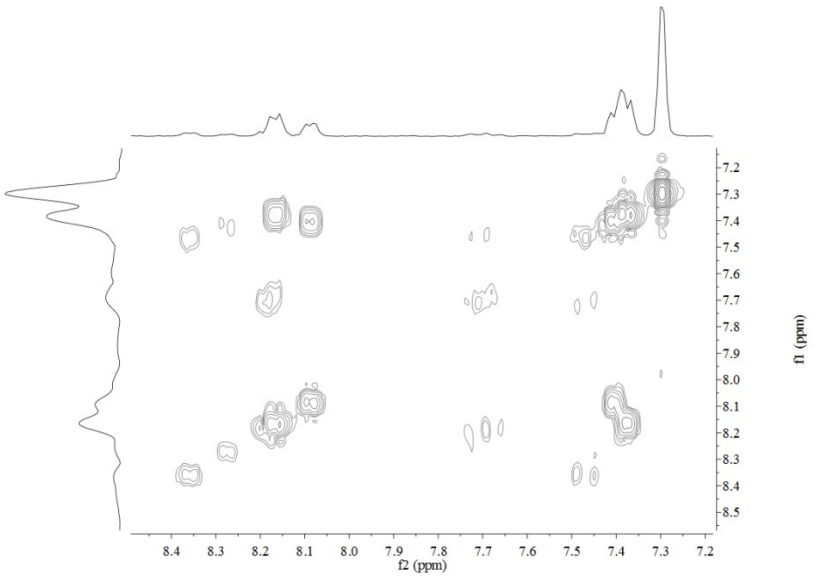


Fig. S22 ^{1}H-^{1}H COSY NMR spectrum of **2f**

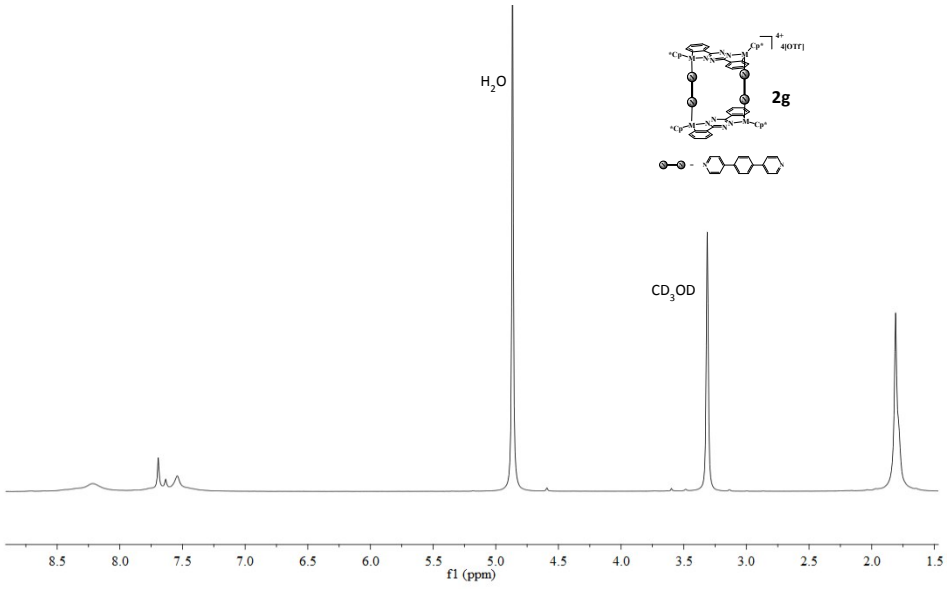


Fig. S23 ^{1}H NMR spectrum of **2g**.

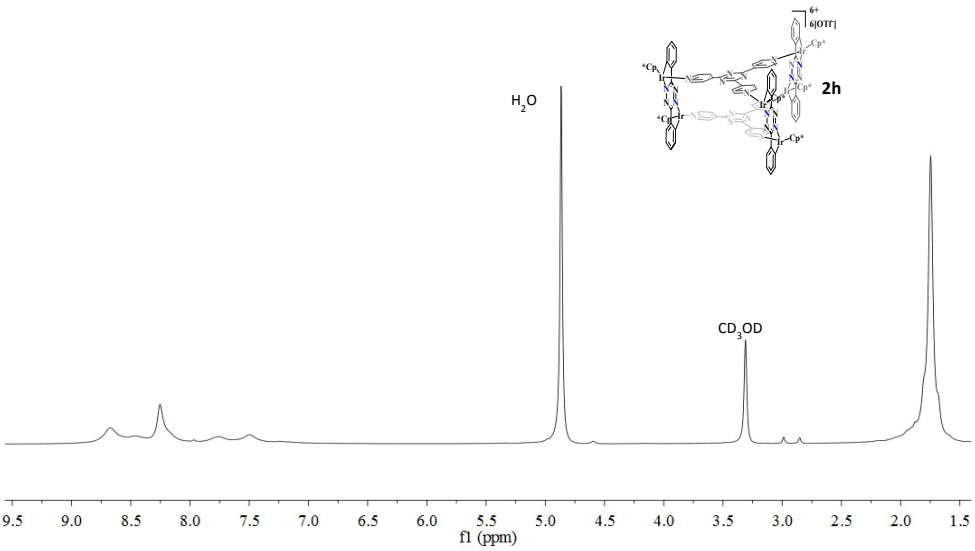


Fig. S24 ^{1}H NMR spectrum of **2h**.

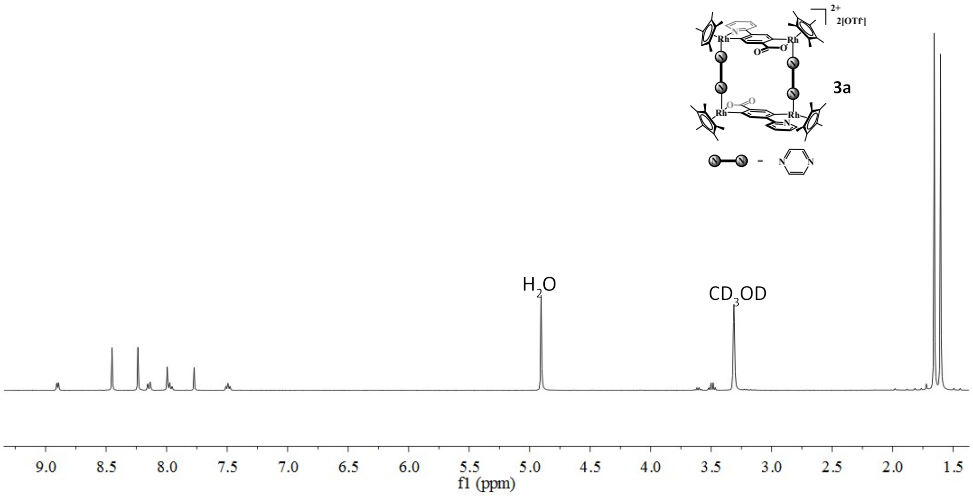


Fig. S25 ^{1}H NMR spectrum of **3a**.

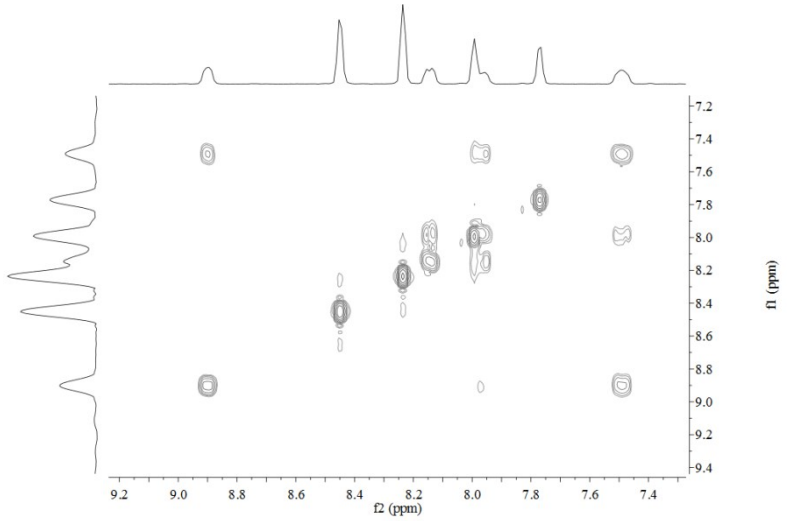


Fig. S26 ^{1}H-^{1}H COSY NMR spectrum of **3a**.

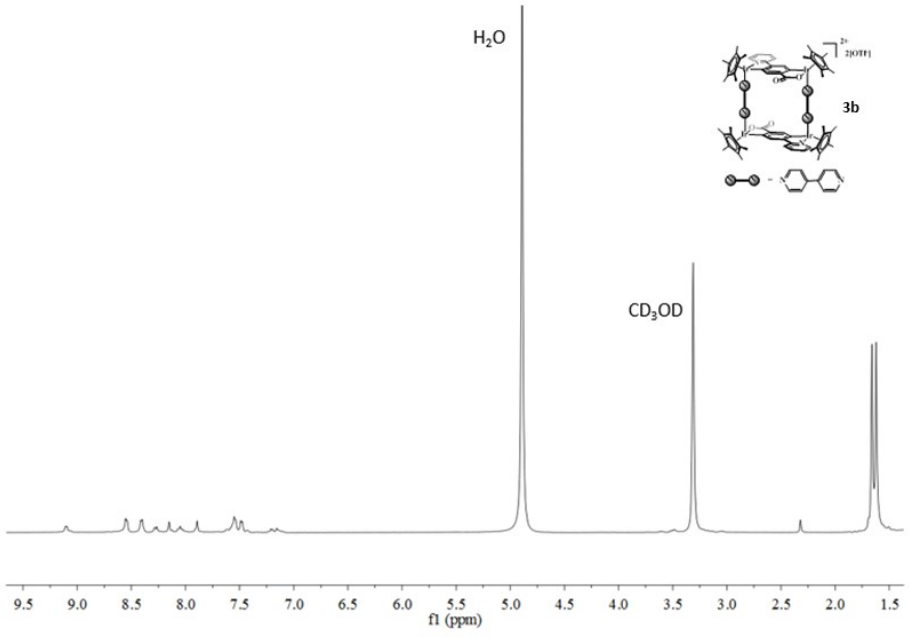


Fig. S27 ^{1}H NMR spectrum of **3b**.

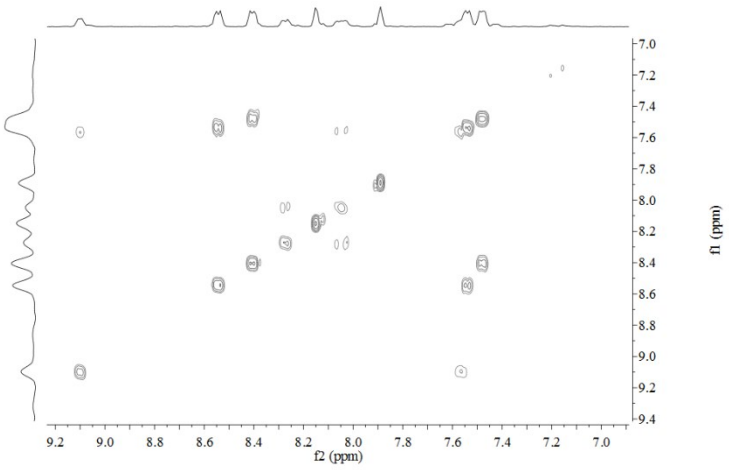
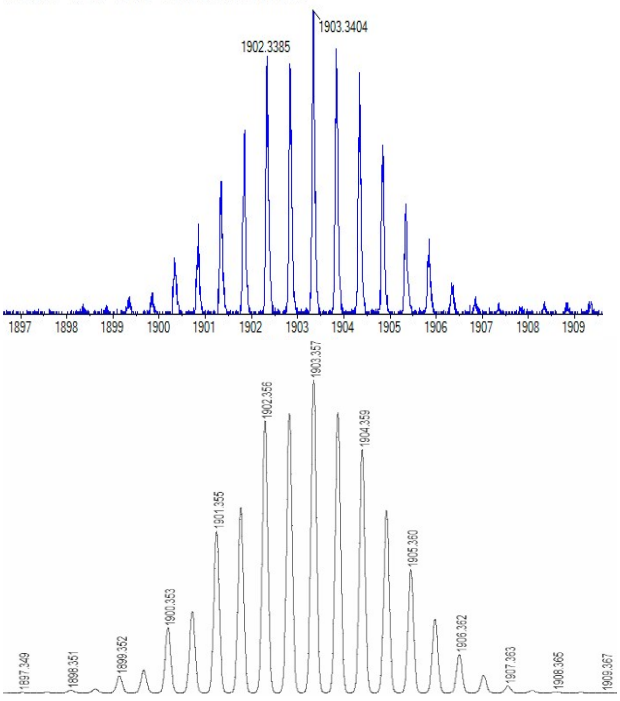
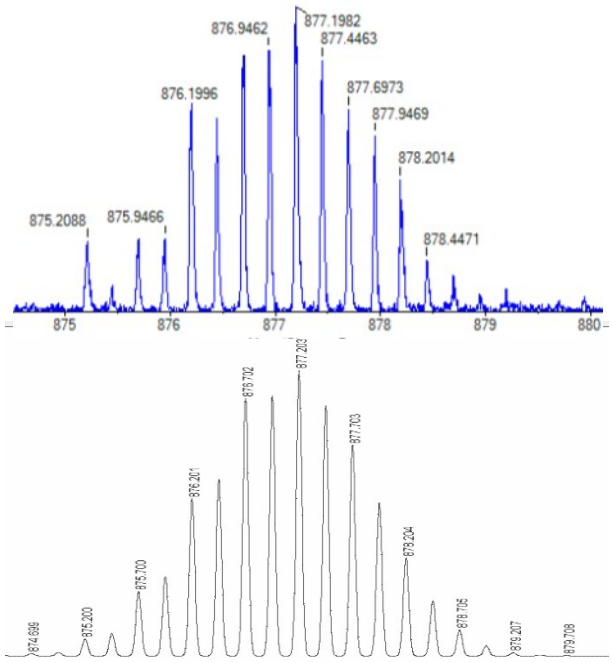


Fig. S28 ^{1}H-^{1}H COSY NMR spectrum of **3b**.

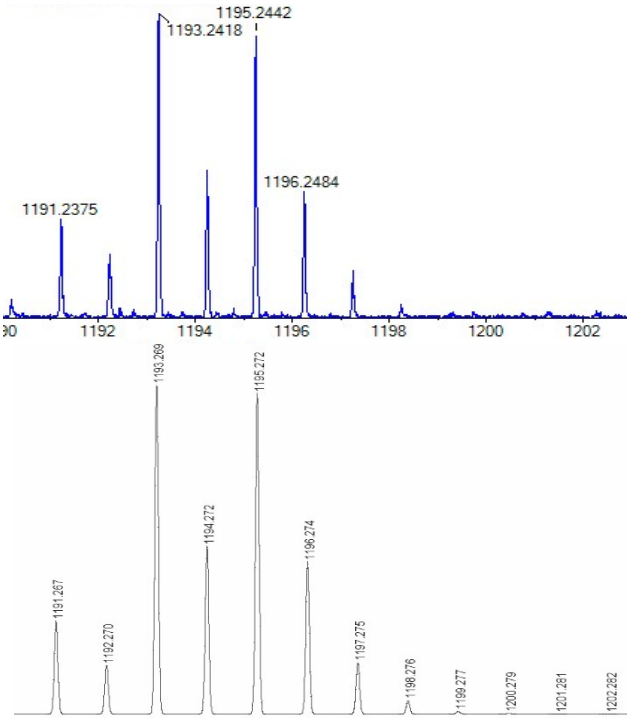


ESI-MS (positive ions) for $[C_{136}H_{144}Ir_8N_8O_{20}S_4F_{12}\text{-}2OTf^-]^{2+}$: Top (tested) and bottom (Calcd)

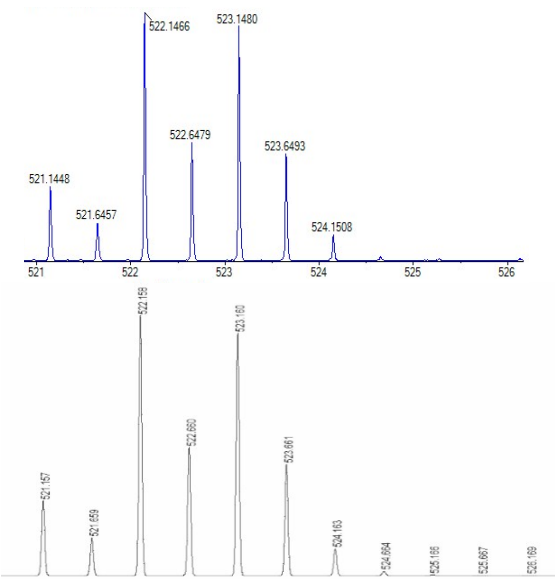


ESI-MS (positive ions) for $[C_{136}H_{144}Ir_8N_8O_{20}S_4F_{12}\text{-}4OTf^-]^{4+}$: Top (tested) and bottom (Calcd)

Figure S29. ESI-MS spectra of **1**.

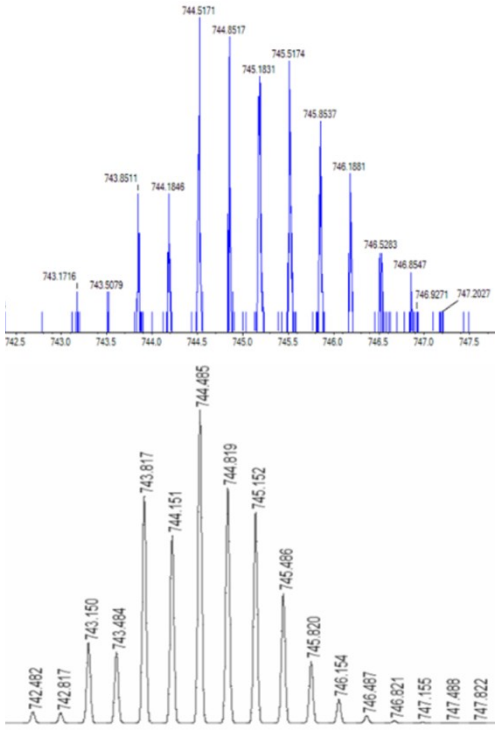


ESI-MS (positive ions) for $[C_{46}H_{48}Ir_2N_6O_6S_2F_6\text{-}OTf]^+$: Top (tested) and bottom (Calcd)



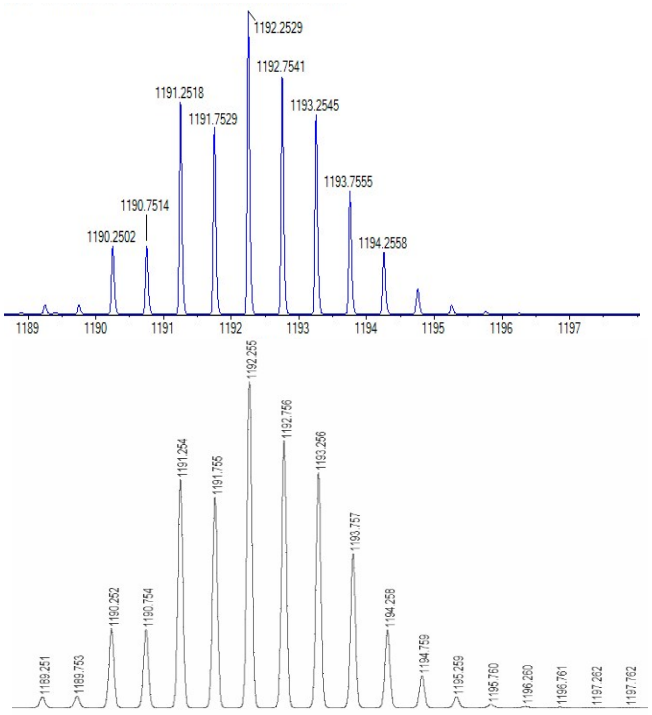
ESI-MS (positive ions) for $[C_{46}H_{48}Ir_2N_6O_6S_2F_6\text{-}2OTf]^{2+}$: Top (tested) and bottom (Calcd)

Figure S30. ESI-MS spectra of **2a**.



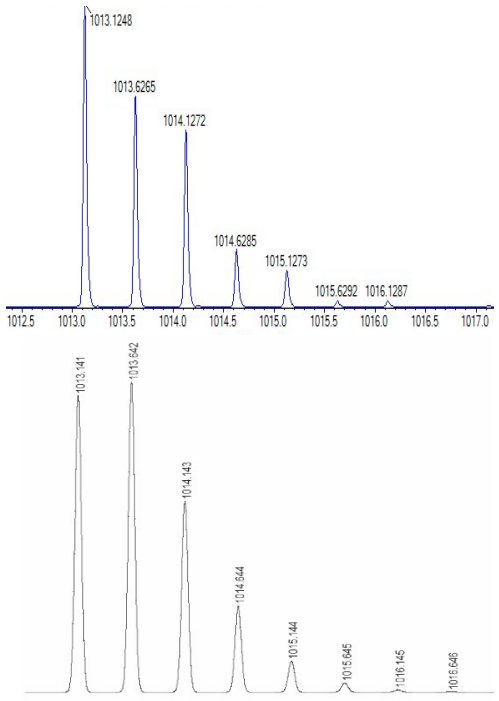
ESI-MS (positive ions) for $[C_{81}H_{85}Ir_4N_{12}O_{15}S_5F_{15}\text{-}3OTf]^{3+}$: Top (tested) and bottom (Calcd)

Figure S31. ESI-MS spectra of **2b**.

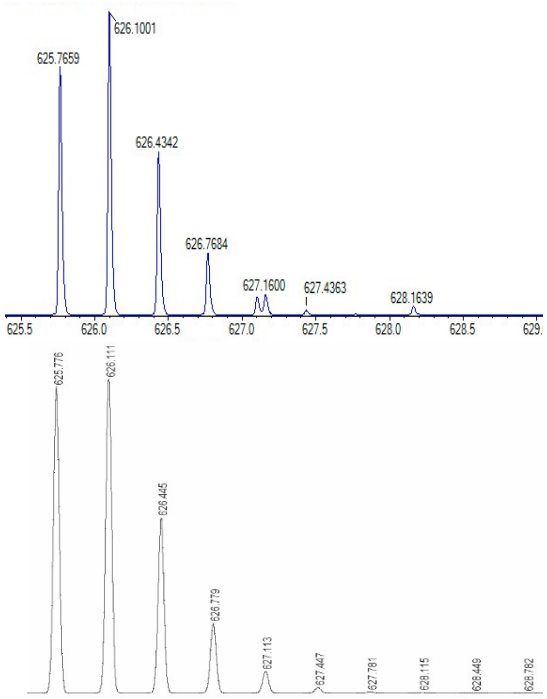


ESI-MS (positive ions) for $[C_{92}H_{92}Ir_4N_{12}O_{12}S_4F_{12}\text{-}2OTf]^{2+}$: Top (tested) and bottom (Calcd)

Figure S32. ESI-MS spectra of **2c**.

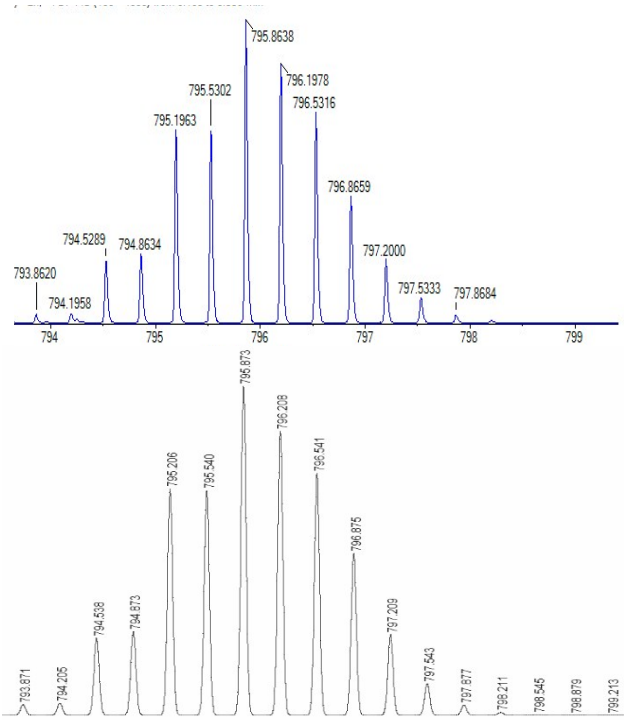


ESI-MS (positive ions) for $[C_{92}H_{92}Rh_4N_{12}O_{12}S_4F_{12}\text{-}2OTf]^{2+}$: Top (tested) and bottom (Calcd)



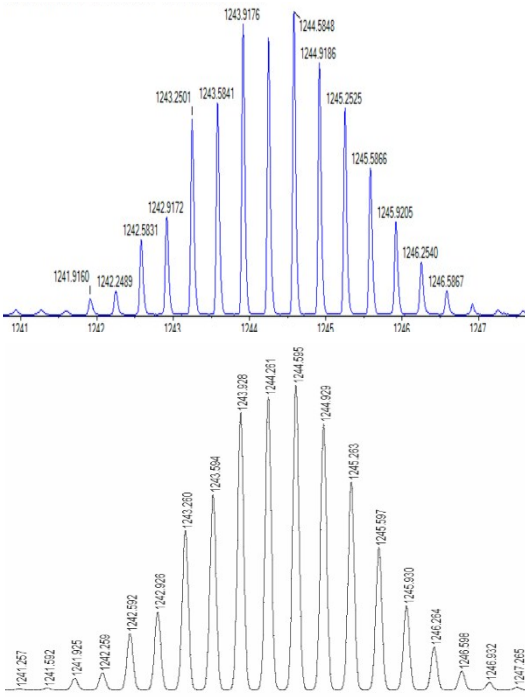
ESI-MS (positive ions) for $[C_{92}H_{92}Rh_4N_{12}O_{12}S_4F_{12}\text{-}3OTf]^{3+}$: Top (tested) and bottom (Calcd)

Figure S33. ESI-MS spectra of **2d**.

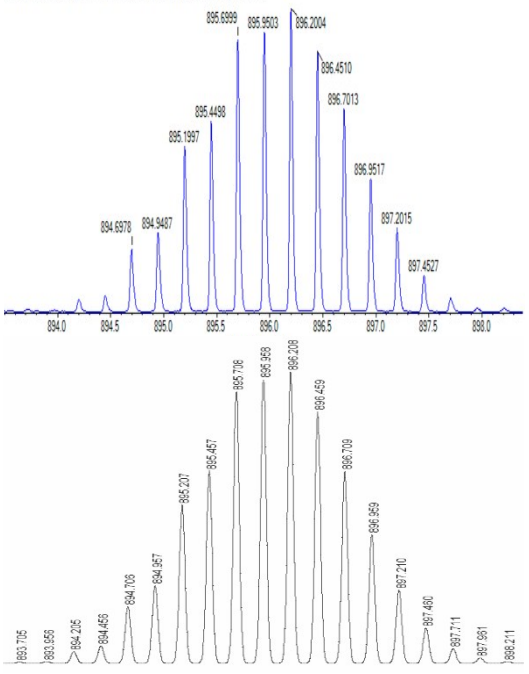


ESI-MS (positive ions) for $[C_{104}H_{100}Ir_4N_{12}O_{12}S_4F_{12}\text{-}3OTf]^{3+}$: Top (tested) and bottom (Calcd)

Figure S34. ESI-MS spectra of **2g**.

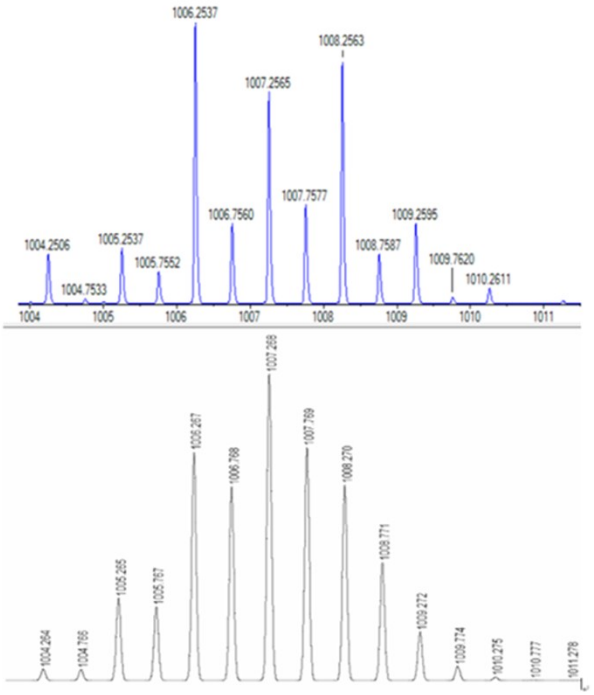


ESI-MS (positive ions) for $[C_{144}H_{138}Ir_6N_{24}O_{18}S_6F_{18}\text{-}3OTf]^{3+}$: Top (tested) and bottom (Calcd)



ESI-MS (positive ions) for $[C_{144}H_{138}Ir_6N_{24}O_{18}S_6F_{18}\text{-}4OTf]^{4+}$: Top (tested) and bottom (Calcd)

Figure S35. ESI-MS spectra of **2h**.



ESI-MS (positive ions) for $[C_{86}H_{88}Ir_4N_6O_{10}F_6S_2\text{-}2OTf]^{2+}$: Top (tested) and bottom (Calcd)

Figure S36. ESI-MS spectra of **3b**.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{155}H_{200}Cl_{14}F_{12}Ir_8N_8O_{29}S_4$	
Formula weight	5029.36	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 18.126(3) Å	α = 91.618(2)°.
	b = 18.204(3) Å	β = 90.640(2)°.
	c = 27.529(4) Å	γ = 102.873(2)°.
Volume	8851(2) $Å^3$	
Z	2	
Density (calculated)	1.887 Mg/m^3	
Absorption coefficient	6.328 mm^{-1}	
F(000)	4888	
Crystal size	0.220 x 0.200 x 0.180 mm^3	
Theta range for data collection	1.148 to 25.250°.	
Index ranges	-21<=h<=21, -20<=k<=21, -33<=l<=24	
Reflections collected	53838	
Independent reflections	31638 [R(int) = 0.0642]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.262 and 0.174	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	31638 / 813 / 1641	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.1021, wR2 = 0.2958	
R indices (all data)	R1 = 0.1624, wR2 = 0.3395	
Extinction coefficient	n/a	
Largest diff. peak and hole	6.520 and -3.482 $e.Å^{-3}$	

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

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

Empirical formula	$C_{54}H_{60}F_6Ir_2N_{10}O_6S_2$	
Formula weight	1507.64	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.218(2) Å	α = 66.499(3)°.
	b = 12.760(3) Å	β = 85.579(4)°.
	c = 14.795(4) Å	γ = 80.838(4)°.
Volume	1404.3(6) $Å^3$	
Z	1	
Density (calculated)	1.783 Mg/m^3	
Absorption coefficient	4.887 mm^{-1}	
F(000)	742	
Crystal size	0.600 x 0.200 x 0.150 mm^3	
Theta range for data collection	1.758 to 26.995°.	
Index ranges	-10<=h<=10, -16<=k<=8, -18<=l<=18	
Reflections collected	9413	
Independent reflections	6022 [R(int) = 0.0344]	
Completeness to theta = 25.242°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.492 and 0.193	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6022 / 190 / 413	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0657, wR2 = 0.1738	
R indices (all data)	R1 = 0.0847, wR2 = 0.2016	
Extinction coefficient	n/a	
Largest diff. peak and hole	8.442 and -2.079 e.$Å^{-3}$	

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

Table 3. Crystal data and structure refinement for **2b**.

Empirical formula	$C_{83}H_{89}Cl_4F_{15}Ir_4N_{12}O_{15}S_5$	
Formula weight	2850.56	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.7097(17) Å	α = 111.475(2)°.
	b = 13.8806(18) Å	β = 99.521(2)°.
	c = 14.7785(19) Å	γ = 107.062(2)°.
Volume	2381.4(5) $Å^3$	
Z	1	
Density (calculated)	1.988 Mg/m^3	
Absorption coefficient	5.891 mm^{-1}	
F(000)	1382	
Crystal size	0.550 x 0.250 x 0.200 mm^3	
Theta range for data collection	1.556 to 26.000°.	
Index ranges	-16<=h<=16, -12<=k<=17, -18<=l<=17	
Reflections collected	15415	
Independent reflections	9217 [R(int) = 0.0299]	
Completeness to theta = 25.242°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.421	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9217 / 161 / 663	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R_1 = 0.0405, wR2 = 0.1131	
R indices (all data)	R_1 = 0.0565, wR2 = 0.1308	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.938 and -1.607 e.$Å^{-3}$	

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

Table 4. Crystal data and structure refinement for **2c**.

Empirical formula	$C_{108}H_{116}F_{12}Ir_4N_{20}O_{12}S_4$	
Formula weight	3011.24	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.5713(16) Å	α = 71.237(2)°.
	b = 13.5763(16) Å	β = 76.757(2)°.
	c = 18.221(2) Å	γ = 65.095(2)°.
Volume	2866.0(6) $Å^3$	
Z	1	
Density (calculated)	1.745 Mg/m^3	
Absorption coefficient	4.789 mm^{-1}	
F(000)	1480	
Crystal size	0.080 x 0.060 x 0.020 mm^3	
Theta range for data collection	1.187 to 26.999°.	
Index ranges	-17<=h<=17, -16<=k<=17, -15<=l<=23	
Reflections collected	20208	
Independent reflections	12326 [R(int) = 0.0423]	
Completeness to theta = 25.242°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.801 and 0.613	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12326 / 251 / 759	
Goodness-of-fit on F^2	0.957	
Final R indices [I>2sigma(I)]	R_1 = 0.0640, wR2 = 0.1832	
R indices (all data)	R_1 = 0.1075, wR2 = 0.2222	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.766 and -1.768 $e.Å^{-3}$	

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

Table 5. Crystal data and structure refinement for **2d**.

Empirical formula	$C_{100}H_{106}Cl_8F_{12}N_{14}O_{12}Rh_4S_4$	
Formula weight	2747.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7585(8) Å	α = 78.1940(10)°.
	b = 13.7394(8) Å	β = 71.3620(10)°.
	c = 18.3544(11) Å	γ = 66.5160(10)°.
Volume	2785.1(3) $Å^3$	
Z	1	
Density (calculated)	1.638 Mg/m^3	
Absorption coefficient	0.934 mm^{-1}	
F(000)	1388	
Crystal size	0.600 x 0.200 x 0.120 mm^3	
Theta range for data collection	1.175 to 26.999°.	
Index ranges	-16<=h<=16, -17<=k<=17, -23<=l<=21	
Reflections collected	19788	
Independent reflections	11985 [R(int) = 0.0196]	
Completeness to theta = 25.242°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.767 and 0.678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11985 / 9 / 700	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1376	
R indices (all data)	R1 = 0.0603, wR2 = 0.1838	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.910 and -1.918 $e.Å^{-3}$	

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

Table 6. Crystal data and structure refinement for **2e**.

Empirical formula	$C_{104}H_{112}F_{12}Ir_4N_{16}O_{16}S_4$	
Formula weight	2967.13	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.8751(18) Å	α = 70.157(2)°.
	b = 13.1571(19) Å	β = 71.057(2)°.
	c = 19.026(3) Å	γ = 78.940(2)°.
Volume	2855.3(7) $Å^3$	
Z	1	
Density (calculated)	1.726 Mg/m^3	
Absorption coefficient	4.807 mm^{-1}	
F(000)	1456	
Crystal size	0.210 x 0.080 x 0.040 mm^3	
Theta range for data collection	1.186 to 27.000°.	
Index ranges	-16<=h<=11, -16<=k<=16, -24<=l<=24	
Reflections collected	20048	
Independent reflections	12298 [R(int) = 0.0563]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.547	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12298 / 154 / 668	
Goodness-of-fit on F^2	0.951	
Final R indices [I>2sigma(I)]	R_1 = 0.0679, wR2 = 0.1830	
R indices (all data)	R_1 = 0.1317, wR2 = 0.2614	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.575 and -2.691 e.$Å^{-3}$	

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

Table 7. Crystal data and structure refinement for **2f**.

Empirical formula	$C_{114}H_{148}F_{12}Ir_4N_{12}O_{20}S_4$	
Formula weight	3131.48	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 33.264(3) Å	α = 90°.
	b = 25.002(2) Å	β = 96.766(2)°.
	c = 28.645(3) Å	γ = 90°.
Volume	23657(4) $Å^3$	
Z	8	
Density (calculated)	1.758 Mg/m^3	
Absorption coefficient	4.648 mm^{-1}	
F(000)	12448	
Crystal size	0.250 x 0.220 x 0.180 mm^3	
Theta range for data collection	1.021 to 26.797°.	
Index ranges	-42<=h<=42, -29<=k<=31, -34<=l<=36	
Reflections collected	81332	
Independent reflections	25157 [R(int) = 0.0802]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.441	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25157 / 85 / 1179	
Goodness-of-fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R_1 = 0.0720, wR2 = 0.2102	
R indices (all data)	R_1 = 0.1157, wR2 = 0.2365	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.221 and -1.453 $e.Å^{-3}$	

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

Table 8. Crystal data and structure refinement for **2g**.

Empirical formula	$C_{111}H_{122}Cl_8F_{12}Ir_4N_{12}O_{16}S_4$	
Formula weight	3288.84	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 25.984(2) Å	α = 90°.
	b = 16.1535(13) Å	β = 93.8870(10)°.
	c = 29.502(3) Å	γ = 90°.
Volume	12354.6(18) $Å^3$	
Z	4	
Density (calculated)	1.768 Mg/m^3	
Absorption coefficient	4.619 mm^{-1}	
F(000)	6464	
Crystal size	0.240 x 0.110 x 0.030 mm^3	
Theta range for data collection	1.011 to 25.999°.	
Index ranges	-32<=h<=32, -19<=k<=16, -31<=l<=36	
Reflections collected	79739	
Independent reflections	24139 [R(int) = 0.1150]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.560	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24139 / 276 / 1434	
Goodness-of-fit on F^2	0.996	
Final R indices [I>2sigma(I)]	R_1 = 0.0680, wR2 = 0.1772	
R indices (all data)	R_1 = 0.1505, wR2 = 0.2342	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.975 and -1.192 $e.Å^{-3}$	

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

Table 9. Crystal data and structure refinement for **2h**.

Empirical formula	$C_{172}H_{190}F_{18}Ir_6N_{38}O_{23}S_6$	
Formula weight	4845.17	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.1650(15) Å	α = 90°.
	b = 25.599(3) Å	β = 91.925(2)°.
	c = 54.172(6) Å	γ = 90°.
Volume	19632(4) $Å^3$	
Z	4	
Density (calculated)	1.639 Mg/m^3	
Absorption coefficient	4.203 mm^{-1}	
F(000)	9568	
Crystal size	0.400 x 0.100 x 0.030 mm^3	
Theta range for data collection	0.752 to 25.250°.	
Index ranges	-16<=h<=17, -30<=k<=30, -65<=l<=58	
Reflections collected	118496	
Independent reflections	35405 [R(int) = 0.1054]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.647 and 0.418	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	35405 / 1017 / 1838	
Goodness-of-fit on F^2	1.191	
Final R indices [I>2sigma(I)]	R_1 = 0.1909, wR2 = 0.4005	
R indices (all data)	R_1 = 0.2182, wR2 = 0.4134	
Extinction coefficient	n/a	
Largest diff. peak and hole	4.457 and -7.576 e.$Å^{-3}$	

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

Table 10. Crystal data and structure refinement for **3a**.

Empirical formula	$C_{106}H_{150}Cl_6F_{18}N_{10}O_{22}Rh_4S_6$	
Formula weight	3075.05	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.5885(5) Å	α = 90°.
	b = 25.6240(9) Å	β = 91.106(2)°.
	c = 17.9554(7) Å	γ = 90°.
Volume	6710.8(4) $Å^3$	
Z	2	
Density (calculated)	1.522 Mg/m^3	
Absorption coefficient	6.660 mm^{-1}	
F(000)	3144	
Crystal size	0.400 x 0.400 x 0.300 mm^3	
Theta range for data collection	3.005 to 69.996°.	
Index ranges	-16<=h<=17, -31<=k<=30, -21<=l<=21	
Reflections collected	34648	
Independent reflections	12017 [R(int) = 0.0690]	
Completeness to theta = 67.679°	96.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.171 and 0.048	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12017 / 286 / 791	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R_1 = 0.0865, wR2 = 0.2241	
R indices (all data)	R_1 = 0.1131, wR2 = 0.2473	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.939 and -1.399 $e.Å^{-3}$	

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

Table 11. Crystal data and structure refinement for **3b**.

Empirical formula	$C_{112}H_{156}F_6Ir_4N_6O_{18}S_2$	
Formula weight	2821.34	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.1290(9) Å	α = 96.702(2)°.
	b = 14.4978(10) Å	β = 100.567(2)°.
	c = 15.9684(10) Å	γ = 98.155(3)°.
Volume	2925.7(3) $Å^3$	
Z	1	
Density (calculated)	1.601 Mg/m^3	
Absorption coefficient	9.543 mm^{-1}	
F(000)	1408	
Crystal size	0.270 x 0.190 x 0.130 mm^3	
Theta range for data collection	2.846 to 68.784°.	
Index ranges	-15<=h<=15, -17<=k<=17, -19<=l<=19	
Reflections collected	37460	
Independent reflections	10346 [R(int) = 0.0410]	
Completeness to theta = 67.679°	96.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753 and 0.563	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10346 / 58 / 602	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R_1 = 0.0745, wR2 = 0.1806	
R indices (all data)	R_1 = 0.0821, wR2 = 0.1855	
Extinction coefficient	n/a	
Largest diff. peak and hole	9.960 and -1.762 $e.Å^{-3}$	

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