

Supporting Information

Stepwise Assembly of “Organometallic Boxes” with Half-Sandwich Ir, Rh and Ru Fragments

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Experimental Section

All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were dried and deoxygenated by MBraun Solvent Purification System (4464) and collected just before use. $[\text{Cp}^*\text{IrCl}_2]_2$ (**1a**)^[1], $[\text{Cp}^*\text{RhCl}_2]_2$ (**1b**)^[1], $[(p\text{-cymene})\text{-RuCl}_2]_2$ (**1c**)^[2], $[(p\text{-cymene})_2\text{Ru}_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)]\text{Cl}_2$ (**4c**)^[3], $[(p\text{-cymene})_2\text{Ru}_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)(\text{MeOH})_2](\text{OTf})_2$ (**5c**)^[3], $[(\text{Cp}^*)_2\text{Ir}_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)]\text{Cl}_2$ (**4a**)^[4] and were prepared according to literature methods. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer, Elemental analyses were carried out by Elementar III Vario EI Analyzer, the samples were dried in vacuum for 48 h before to analyses. ¹H-NMR (500 MHz) spectra were obtained on a Bruker DMX-500 spectrometer in $[\text{D}_6]\text{-DMSO}$ or CDCl_3 solution.

Synthesis of **2a** $[\text{Cp}^*_4\text{Ir}_4(\mu\text{-H}_2\text{TPyP})\text{Cl}_8]$

To a solution of **1a** (160 mg, 0.20 mmol) in CH_2Cl_2 (30 mL) was added H_2TPyP (62 mg, 0.10 mmol) at room temperature. After stirring for 18 h, the solvent was evaporated under reduced pressure and the dark red residue was washed by diethyl ether. The dark red solids (217 mg, 98%) were gained through recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ at -18°C . ¹H-NMR (500 MHz, CDCl_3 , 25°C , TMS): $\delta = 9.47$ (m, 8H; $\text{H}_{\text{pyridyl}}$), 8.83 (d, 8H; $\text{H}_{\text{pyrrole}}$), 8.20 (m, 8H; $\text{H}_{\text{pyridyl}}$), 1.78 (s, 30H; Cp^*), 1.56 (s, 30H; Cp^*), -2.97 (s, 2H; NH) ppm; elemental analysis (%) calcd. for $\text{C}_{80}\text{H}_{86}\text{C}_{18}\text{Ir}_4\text{N}_8$: C 43.44, H 3.92, N 5.07; found: C 43.21, H 4.06, N 4.97.

Synthesis of **3a** $[\text{Cp}^*_8\text{Ir}_8(\mu\text{-H}_2\text{TPyP})_2(\mu\text{-Cl})_8](\text{OTf})_8$

AgOTf (102 mg, 0.40 mmol) was added to a solution of **2a** (220 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) at room temperature and stirred for 3 h, The solvent was removed and the residue was extracted with CH_2Cl_2 . The filtrate was concentrated to about 3 mL and diethyl ether was added. giving red solids of **3a** (202 mg, 76%). ¹H-NMR (500 MHz, $[\text{D}_6]\text{-DMSO}$, 25°C , TMS): $\delta = 9.08\text{-}9.36$ (m, 16H; $\text{H}_{\text{pyridyl}}$), 8.85 (m, 16H; $\text{H}_{\text{pyrrole}}$), 8.12 (d, 16H; $\text{H}_{\text{pyridyl}}$), 1.87 (s, 120H; Cp^*), -2.92 (s, 4H; NH) ppm; elemental analysis (%) calcd. for $\text{C}_{168}\text{H}_{172}\text{C}_{18}\text{F}_{24}\text{Ir}_8\text{N}_{16}\text{O}_{24}\text{S}_8$: C 37.84, H 3.25, N 4.20, S 4.81; found: C 37.59, H

3.06, N 4.18, S 4.67.

Synthesis of **4b** [$\text{Cp}^*_2\text{Rh}_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)\text{Cl}_2$]

(NH_4)₂C₂O₄·H₂O (140 mg, 1 mmol) was added to a solution of **1b** (618 mg, 1 mmol) in CH₃OH (20 mL), The suspension was kept stirring at 55°C for 5h. The solvent was then evaporated to dryness under vacuum, the residue was extracted with CH₂Cl₂. Yield: 86%; ¹H-NMR (500 MHz, [D₆]-DMSO, 25°C, TMS): δ = 1.65 (s, 30H; Cp*) ppm; elemental analysis (%) calcd. for C₂₂H₃₀Cl₂O₄Rh₂: C 41.60, H 4.76; found: C 41.92, H 4.84.

Synthesis of **5a** [$\text{Cp}^*_2\text{Ir}_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)](\text{OTf})_2$]

AgOTf (51 mg, 0.20 mmol) was added to a solution of **4a** (82 mg, 0.10 mmol) in CH₃OH (20 mL) at room temperature and stirred for 3 h, The solvent was removed and the residue was extracted with CH₂Cl₂. The filtrate was concentrated to about 3 mL and diethyl ether was added, giving yellow solids of **5a** (71 mg, 78%). ¹H-NMR (500 MHz, [D₆]-DMSO, 25°C, TMS): δ = 1.63 (s, 30H; Cp*) ppm; elemental analysis (%) calcd. for C₂₄H₃₀F₆Ir₂O₁₀S₂: C 27.69, H 2.90, S, 6.16; found: C 27.34, H 3.04, S, 6.12.

Synthesis of **5b** [$\text{Cp}^*_2\text{Rh}_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)](\text{OTf})_2$]

AgOTf (51 mg, 0.20 mmol) was added to a solution of **4b** (64 mg, 0.10 mmol) in CH₃OH (20 mL) at room temperature and stirred for 3 h, The solvent was removed and the residue was extracted with CH₂Cl₂. The filtrate was concentrated to about 3 mL and diethyl ether was added, giving yellow solids of **5b** (71 mg, 83%). ¹H-NMR (500 MHz, [D₆]-DMSO, 25°C, TMS): δ = 1.61 (s, 30H; Cp*) ppm; elemental analysis (%) calcd. for C₂₄H₃₀F₆O₁₀Rh₂S₂: C 33.42, H 3.51, S 7.44; found: C 33.64, H 3.68, S 7.85.

Synthesis of **6a** [$\text{Cp}^*_8\text{Ir}_8(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)_4((\mu\text{-H}_2\text{TPyP})_2)](\text{OTf})_8$]

The first method: (NH_4)₂C₂O₄·H₂O (28 mg, 0.2 mmol) was added to a solution of **3a** (265 mg, 0.05 mmol) in CH₃OH (20 mL), The suspension was kept stirring at 55°C for 5h. The solvent was then

evaporated to dryness under vacuum, the residue was extracted with CH₂Cl₂. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **6a** as purple solids. Yield: 143mg, 65%.

The second method: AgOTf (0.2 mmol) was added to a suspension of **4a** (0.1 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then H₂TPyP (0.05 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15h. The solvent was then removed and the residue was extracted with CH₂Cl₂. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **6a** as purple solids. Yield: 110.5 mg, 82%; IR: = 1631 cm⁻¹(C=O); ¹H-NMR (500 MHz, [D₆]-DMSO, 25°C, TMS): δ = 9.02-9.34 (m, 16H; H_{pyridyl}), 8.57-8.85 (m, 16H; H_{pyrrole}), 8.10 (d, 16H; H_{pyridyl}), 1.86 (m, 120H; Cp*), -2.93 (s, 4H; NH) ppm; elemental analysis (%) calcd. for C₁₇₆H₁₇₂F₂₄Ir₈N₁₆O₄₀S₈: C 39.13, H 3.21, N 4.15, S 4.75; found: C 38.98, H 3.06, N 3.97, S 4.62.

Synthesis of **6b** [Cp*₈Rh₈(μ-η⁴-C₂O₄)₄((μ-H₂TPyP)₂](OTf)₈

AgOTf (0.2 mmol) was added to a suspension of **4b** (0.1 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then H₂TPyP (0.05 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15h. The solvent was then removed and the residue was extracted with CH₂Cl₂. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **6b** as purple solids. Yield: 91.4 mg, 78%; IR: = 1634 cm⁻¹(C=O); ¹H-NMR (500 MHz, [D₆]-DMSO, 25°C, TMS): δ = 9.06-9.08 (m, 16H; H_{pyridyl}), 8.88 (m, 16H; H_{pyrrole}), 8.17 (d, 16H; H_{pyridyl}), 1.57 (m, 120H; Cp*), -2.92 (s, 4H; NH) ppm; elemental analysis (%) calcd. for C₁₇₆H₁₇₂F₂₄Rh₈N₁₆O₄₀S₈: C 45.10, H 3.70, N 4.78, S 5.47; found: C 45.03, H 3.57, N 4.55, S 5.32.

Synthesis of **6c** [(*p*-Cymene)₈Ru₈(μ-η⁴-C₂O₄)₄((μ-H₂TPyP)₂](OTf)₈

AgOTf (0.2 mmol) was added to a suspension of **4c** (0.1 mmol) in methanol (20 mL) at room

temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then H₂TPyP (0.05 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15h. The solvent was then removed and the residue was extracted with CH₂Cl₂. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **6c** as purple solids. Yield: 92.1 mg, 79%; IR: $\nu = 1630 \text{ cm}^{-1}$ (C=O); ¹H-NMR (500 MHz, [D₆]-DMSO, 25°C, TMS): $\delta = 8.96\text{-}9.09$ (m, 16H; H_{pyridyl}), 8.55 (m, 16H; H_{pyrrole}), 8.30 (d, 16H; H_{pyridyl}), 6.18-6.28 (m, 16H; Ar_{p-cym}), 5.99-6.15 (m, 16H; Ar_{p-cym}), 3.35 (m, 8H; CH(CH₃)₂), 3.35 (s, 24H; CH₃), 1.16-1.40 (m, 48H; CH(CH₃)₂), -3.07 (s, 4H; NH) ppm; elemental analysis (%) calcd. for C₁₇₆H₁₆₄F₂₄Ru₈N₁₆O₄₀S₈: C 45.32, H 3.54, N 4.80, S 5.50; found: C 45.13, H 3.37, N 4.65, S 5.21.

X-ray Structure Determination.

All single crystals were immersed in mother solution and sealed in thin-walled glass Data were collected on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method.

All the calculations were carried out with the SHELXTL^[5] program. In complex **6a**, three triflate anions could be well refined, but some carbon, oxygen and fluorine atoms in the other five anions were never found. Therefore, new data sets corresponding to omission of the missing anions were generated with the SQUEEZE algorithm^[6] and the structures were refined to convergence. In the structure of **6a**, 93 restraints were used in the refinement: ISOR instructions were applied to restrain 15 atoms (atom N2, N4, N12, C4, C5, C10, C18, C20, C45, C89, C90, C125, C126, C159, C162, each ISOR command line corresponds to 6 restraints) and 3 bond distances were restrained by DFIX instructions. Similarly, in the structure of **6c**, 2 atoms were restrained by ISOR (C85, C112) and 3 bond distances by DFIX. All the

hydrogen atoms were included in calculated positions, one of the hydrogen atoms in the solvent water molecules could be found by differential Fourier method.

All of figures were drawn with Diamond.

Crystal data for **5b**: C₂₆H₃₄Cl₄F₆Rh₂O₁₀S₂, $M_r = 1032.27$, Crystal dimensions 0.25 x 0.20 x 0.18 mm³, monoclinic, space group $P2(1)/n$, $Z = 2$, $\rho_{\text{calcd}} = 1.823 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 1.352 \text{ mm}^{-1}$, $F(000) = 1028$, $a = 14.50(2)$, $b = 9.437(14)$, $c = 14.50(2) \text{ \AA}$, $\beta = 108.711(16)^\circ$, and $V = 1880(5) \text{ \AA}^3$. $R = 0.0738$ [$I > 2\sigma(I)$], $R_w = 0.1864$ (for all data), $\text{GOF} = 0.935$.

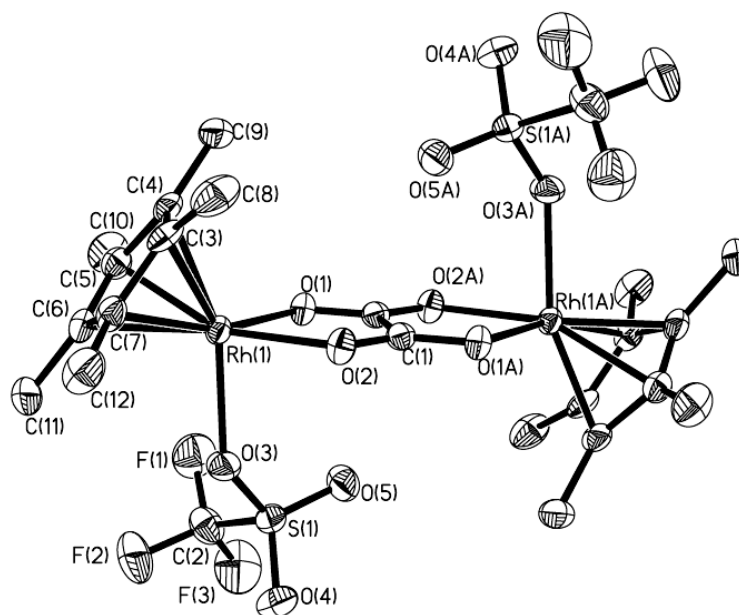


Figure S1 Molecular structure of **5b** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity. The symmetry operators are: $a = 1-x$; $b = 2-y$; $c = 1-z$.

References

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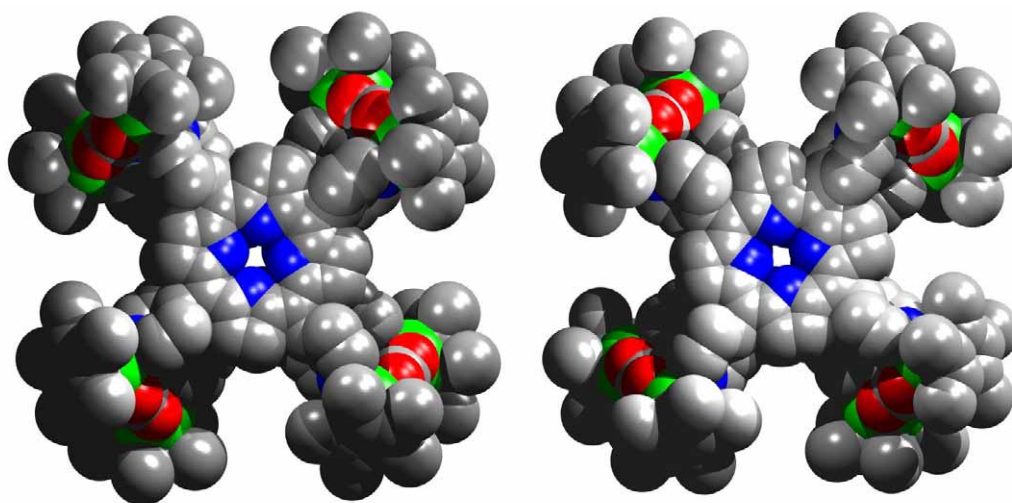


Figure S2 Crystal structure of the cationic part of **6a**. Space-filling model of **6a** viewed along the *b* axis showing the **D** (clockwise) configuration (left) and the **L** (counterclockwise) configuration (right). Carbon atoms are shown as gray, oxygen as red, nitrogen as blue and iridium as green.

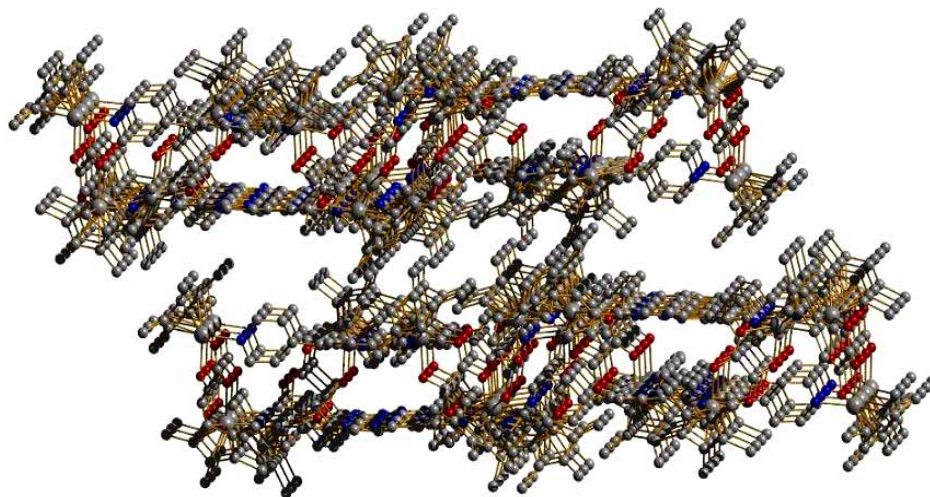


Figure S3 Crystal packing diagram of **6a** showing the open channels. Hydrogen atoms, anions are omitted.

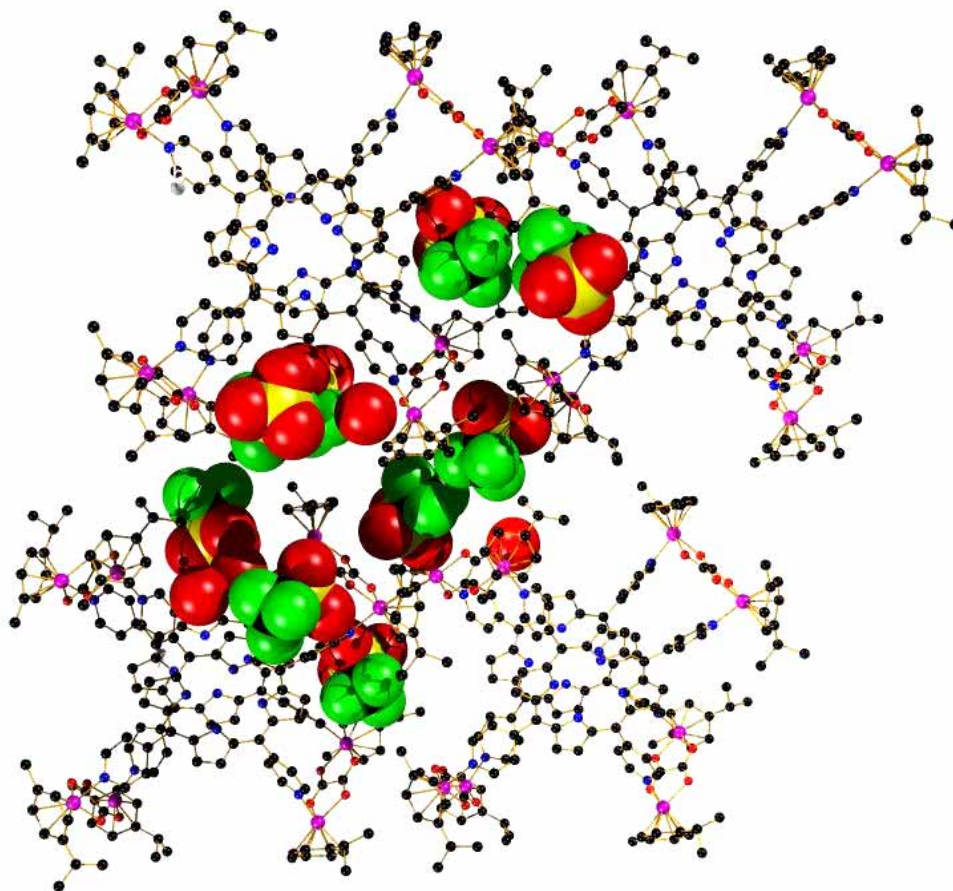


Figure S4 The existence of the counteranions and disordered H₂O molecules are located outside of box **6c**. Carbon atoms are shown as black, oxygen as red, sulfur as yellow, fluorine as green and ruthenium as rosy.

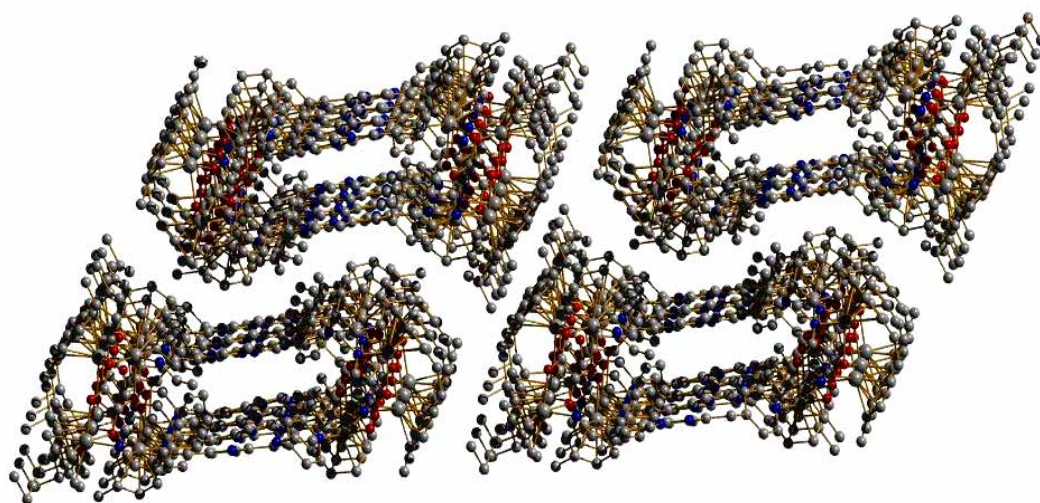


Figure S5 Crystal packing diagram of **6c** showing the open channels. Hydrogen atoms, anions and H₂O molecules are omitted.

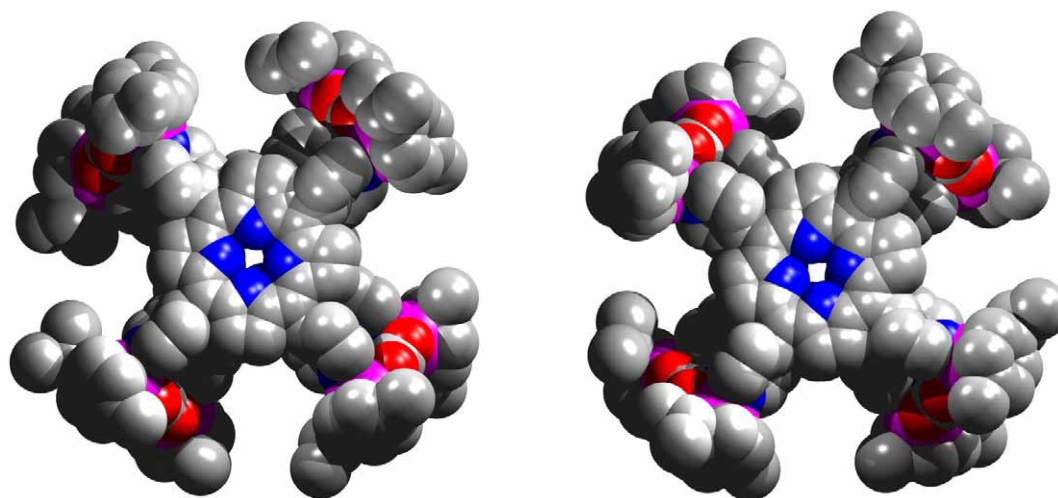


Figure S6 Crystal structure of the cationic part of **6c**. Space-filling model of **6c** viewed along the *b* axis showing the **D** (clockwise) configuration (left) and the **L** (counterclockwise) configuration (right). Carbon atoms are shown as gray, oxygen as red, nitrogen as blue and iridium as green.

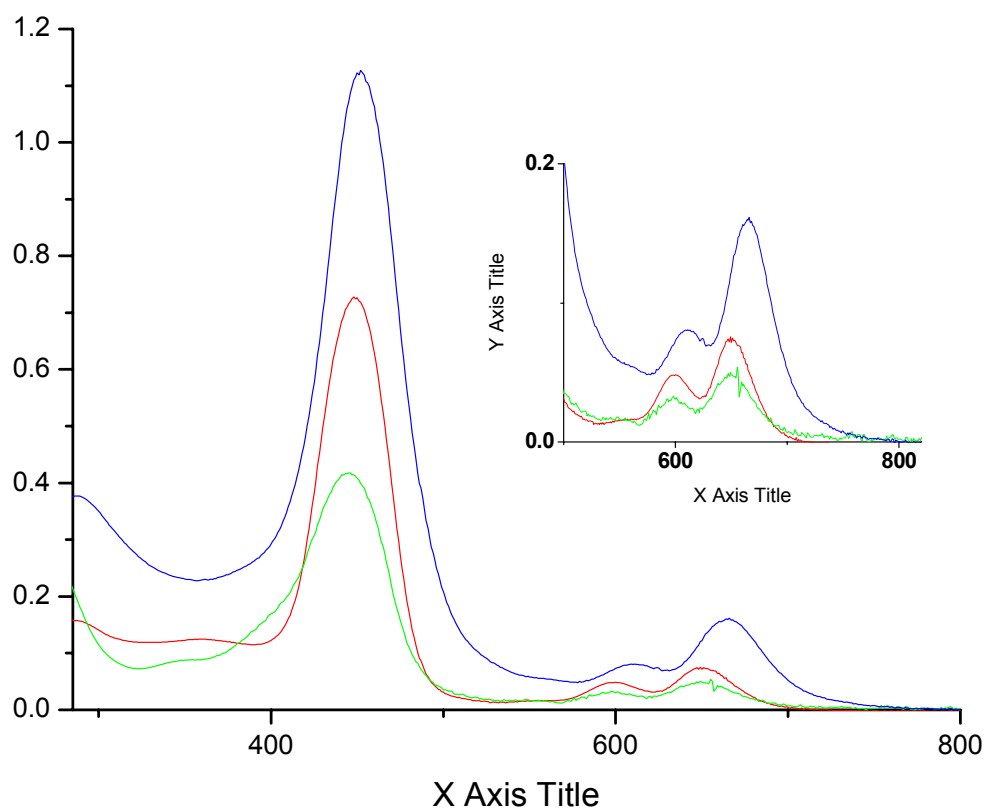


Figure S7 UV-vis absorption spectra in dichloromethane of **6a** (red line), **6b** (green line) and **6c** (blue line) at room temperature.