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Supporting Information

Selective Electrochemical CO₂ Conversion with a Hybrid Polyoxometalate

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General Experimental

¹H and ³¹P NMR spectra were measured on a Bruker AVANCE 400 spectrometer at room temperature. Chemical shifts (δ) are reported in ppm. Where appropriate, chemical shifts in ¹H spectra were referenced to the residual (partially) non-deuterated solvent according to Fulmer et al.¹ ³¹P NMR spectra were referenced through the solvent lock (2H) signal according to the IUPAC-recommended secondary referencing method following Bruker protocols.²

Cyclic voltammograms (CV) were recorded on an ALS BAS Model 620E cyclic voltametric analyser. Measurements were carried out in N₂- and CO₂-purged acetonitrile or *N*-methylpyrrolidone (NMP) solutions using a glassy carbon working electrode (d = 3 mm), a Pt-wire counter electrode, and a standard calomel reference electrode (SCE, +244 mV vs. NHE). The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($^{n}Bu_{4}NPF_{6}$), which was purified by triple recrystallization from ethanol and dried in vacuo. The potentials were corrected by employing a ferrocene | ferrocenium (Fc|Fc⁺) couple as an internal standard, where the Fc|Fc⁺ couple was observed at +400 mV vs. SCE in acetonitrile. Herein, the quoted potentials have been converted to be vs. NHE.

Controlled potential absorption spectra were recorded using a Shimazu UV-3150 spectrometer combined with an ALS BAS Model 620E potentiostat in degassed NMP. A Pt-mesh working electrode, Pt-coil counter electrode and SCE reference electrode were used in combination with a specialized quartz spectro-electrochemical cell, incorporating a 0.5 mm cuvette and fitted with rubber septum. The supporting electrolyte was 0.1 M ^{*n*}Bu₄NPF₆. The stated potentials were applied until the solution reaches an equilibrium state.

Bulk electrolysis was performed in an air-tight H-cell, constructed using two L-shape glass cells which are jointed together and separated using a Nafion[®] (Nafion115) membrane between the cathode and anode compartments. The working electrode was carbon paper, and the counter electrode was Pt-wire, with 0.1 M $^{n}Bu_{4}NPF_{6}$ as supporting electrolyte in acetonitrile.

Gas chromatography (GC) was recorded on a Shimazu GC-2014 Gas Chromatograph (Carrier gas: Ar, flow rate: 33 mL/min, column: SHINCARBON ST (6m x ϕ 3mm), detector: TCD-2014 and FID-2014) connected with MTN-1 methaniser in series. Capillary electrophoresis was used for detection of formic acid.

Materials and Synthesis

Materials: 4,4'-Dimethyl-2,2'-dipyridy (**dmbpy**) was purchased commercially (reagent grade) and used without further purification. The 4'-(4-phosphonophenyl)-2,2':6',2"-terpyridine (**ppt**) ligands,³ $K_{10}[P_2W_{17}O_{61}]$,⁴ ruthenium complexes [Ru(dmbpy)(ppt-Et₂)Cl]Cl (**[Ru]**) and [Ru(dmbpy)(ppt-H₂)Cl]Cl,⁵ were synthesised following reported methods. All other chemicals and solvents were purchased commercially and used as received, unless otherwise noted.



[Ru(dmbpy)(ppt-H₂)Cl)]Cl

[Ru(dmbpy)(ppt-Et₂)Cl)]Cl ([Ru])

Figure S1. Ruthenium complexes prepared according to literature procedures,⁵ **[Ru]** was also used in electrolysis studies.

Preparation of (*n***Bu**₄**N**)₃**H**[(**Ru**(dmbpy)(ppt)**C**I)₂**P**₂**W**₁₇**O**₅₇] (1): [Ru(dmbpy)(ppt-H₂)Cl]Cl (138 mg, 0.185 mmol), K₁₀[P₂W₁₇O₆₁] (400 mg, 0.088 mmol), *n*Bu₄NBr (208 mg, 0.647 mmol) and 12 M HCl (40 µL, 0.48 mmol) were suspended in *N*,*N'*-dimethylacetamide (12 mL) and heated at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate poured into ether. The precipitate was collected by centrifuge and washed by EtOH and ether before drying, yielding 447 mg (0.0747 mmol, 85 %) of hybrid POM **1** as a purple powder. **CHN elemental analysis**; calc. H 2.60 C 21.93 N 2.92; found. H 2.64 C 22.14 N 3.12. **¹H NMR** (400 MHz, DMSO-d₆) δ 9.94 (dmbpy, d, *J* = 5.4 Hz, 2H), 9.29-9.19 (ppt, m, 4H), 9.00-8.95 (ppt, m, 4H), 8.80 (dmbpy, s, 2H), 8.51-8.25 (dmbpy, 2ppt, m, 10H), 8.02 (ppt, m, 4H), 7.93 (dmbpy, d, *J* = 5.6 Hz, 2H), 7.64 (ppt, m, 4H), 7.41-7.38 (ppt, m, 4H), 7.23 (dmbpy, d, J = 5.9 Hz, 2H), 6.96 (dmbpy, d, *J* = 6.2 Hz, 2H), 3.17 (*n*Bu₄N, t, *J* = 8.2 Hz, 24H), 2.76 (dmbpy, s, 3H), 2.33 (dmbpy, s, 3H), 1.59-1.53 (*n*Bu₄N, m, 24H), 1.38-1.33 (*n*Bu₄N, m, 24H), 0.93 (*n*Bu₄N, t, *J* = 7.3 Hz, 36H). **³¹P{¹H} NMR** (162 MHz, DMSO-d₆) δ 14.33, -11.26, -12.88.

Crystallographic Details (1-TMA)

Crystals suitable for single-crystal diffraction studies were obtained by diffusing petroleum ether into a solution of **1** (15 mg) and tetramethylammonium tetrafluoroborate (5 mg) in NMP (2 mL) over a period of one week resulting in dark red blocks identified as the tetramethyl ammonium (TMA) salt of hybrid POM [(Ru(dmbpy)(ppt)Cl)₂P₂W₁₇O₅₇] (**1-TMA**). Single crystal X-ray diffraction measurements were performed on a Bruker SMART Apex II CCD diffractometer using a Mo-K α source (λ = 0.71073 Å). Crystals were mounted on a flexible-loop micro-mount, and data were collected at –173 °C. Structures were solved within Olex2⁶ by dual space iterative methods (SHELXT)⁷ and all non-hydrogen atoms refined by full-matrix least-squares on all unique F2 values with anisotropic displacement parameters (SHELXL).⁸

The crystals of the hybrid POM complex contain large regions of diffuse solvent and counter ion residues which result in weak diffraction intensities with particularly limited data quality at high angles. Many attempts were made to collect data on crystals of this sample which were also prone to twinning. The data used in this refinement was collected on a Bruker Apex II system and reprocessed in CrysAlisPro⁹ to allow the efficacy of various different adsorption correction methods to be assessed. Without adsorption correction the R_{int} (calculated to resolution 0.037 %A) was 10.61%. An attempt was made to index the faces of the crystal which were largely obscured by the protective oil around the sample. Using the estimated crystal faces to perform an empirical and face adsorption correction (Gaussian) in CrysAlisPro resulted in an Rint (same resolution) of 6.54%. Performing an empirical and spherical adsorption correction (using an equivalent radius of 0.06 mm) resulted in an identical R_{int} to the face indexed correction (same resolution) of 6.52%. The spherically corrected data was used for the refinement as it was considered that in this situation the face-based correction did not provide any improvement over the spherical model.

Although the data to parameter ratio of 30:1 is quite high for a model of a large molecule from weak diffraction data, it was found that a large number of restraints were needed to develop and converge a chemically sensible model. A contributing factor to this requirement is the significant disorder of the POM core described below. Rigid bond and similarity restraints were applied to the anisotropic displacement parameters of all atoms in the structure (RIGU, SIMU) and geometric similarity restraints were applied to the bond lengths of all chemically similar parameters of the peripheral hybrid ruthenium coordination complex moieties (SAME, SADI). The phenyl and pyridyl rings were additionally restrained to have planar geometries (FLAT). Attempts to refine the structure with fewer or no restraints on the anisotropic displacement parameters resulted in nonsensical ellipsoid geometries or non-positive definite ellipsoids. The anisotropic displacement parameter of methyl carbon atom C27D was found to be excessively elongated, even for a methyl group on a mobile peripheral ligand, and hence, was restrained to have more isotropic character (ISOR).

Residual electron density peaks around the Wells-Dawson POM core indicated the presence of a minor disorder component consisting of a closely overlapping POM core slightly shifted from the major component and possessing a different isomeric arrangement of the bottom three tungsten atoms. Only the tungsten atoms of the minor disorder component could be observed in the electron density map; the oxygen and phosphorous atoms were not observed and not included in the model. The minor component tungsten atoms were refined with isotropic displacement parameters and the distances between neighbouring tungsten atoms restrained to be similar to those in the major disorder component (SADI). The occupancies of the disorder components were refined and constrained to sum to unity resulting in values of 0.94(1) and 0.06(1). No minor disorder counterpart atom could be modelled for tungsten atom W8. The absence of an electron density peak between the two functionalised phosphorous atoms indicates that the minor component residue is also a hybrid POM rather than co-crystallised W₁₈-plenary POM.

Four *N*-Methyl-2-pyrrolidone (NMP) solvent residues and two tetramethylammonium counter ions were apparent in the electron density map and included in the model. The occupancies of three of the solvent residues were refined giving values of 0.93(1), 0.89(2) and 0.88(1). The atoms of the solvent residues and counter ions were refined with isotropic displacement parameters. The isotropic displacement parameters of the atoms of solvent residues S and T were fixed to be identical and each refined to a common value. The geometries of the solvent residues were restrained to be similar and planar (SAME, FLAT). The geometries of the counter ions were restrained to be similar and reflect their tetrahedral symmetry (SAME).

All hydrogen atoms were geometrically placed and refined using a riding model. A proton is expected to be found between the close lying oxygen atoms of the two phosphonate moieties according to charge balance considerations and compositional analysis of complex **1**. The proton was not observed unambiguously in the electron density map and was not included in the model, however, it was included in the unit cell contents.

Further regions of diffuse solvent for which models could not be developed were treated with the solvent mask routine in Olex2. A solvent mask was calculated, and 1634 electrons were determined in a volume of 6765 Å³ in 1 void per unit cell. The missing solvent and counter ion residues were assigned as one tetramethylammonium counter ion, four NMP solvent residues and 120 water molecules per asymmetric unit for a total of 1459 missing electrons. No elemental analysis was conducted to support this assignment of disordered residues. The assignment of disordered residues was made based on charge balance and the number of NMP and water residues that could plausibly fit into the void volume (assuming atomic volumes of 18 Å³ for solvent residues and 25 Å³ per water residue). The assignment of missing residues was chosen to match the void volume rather than the calculated electrons as the void was considered to be the more reliable metric given the absence of many strong low angle reflections obscured by the beam stop.

For further details please see the cif file which can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data request/cif</u> or from the Cambridge Crystallographic Data Centre (email: deposit@ccdc.cam.ac.uk). The CCDC deposition number is **2283230**.

 Table S1. Crystallographic experimental details.

	1-TMA							
CCDC Deposit	2283230							
Chemical formula	$W_{17}O_{63}P_4C_{66}H_{53}Ru_2Cl_2\cdot 3(C_4H_{12}N)\cdot 8(C_5H_9NO)\cdot 120(H_2O)$							
M _r	8553.84							
Crystal system, space group	Triclinic, P ¹							
Temperature (K)	100							
<i>a</i> , <i>b</i> , <i>c</i> (Å)	21.8379 (6), 22.3937 (6), 26.6266 (7)							
α, β, γ (°)	80.380 (2), 82.354 (2), 79.212 (2)							
$V(Å^3)$	12541.4 (6)							
Z	2							
Radiation type	Μο Κα							
μ (mm ⁻¹)	8.05							
Crystal size (mm)	0.1 × 0.1 × 0.05 × 0.08 (radius)							
	Data collection							
Diffractometer	Bruker APEX-II CCD							
Absorption correction	For a sphere <i>CrysAlis PRO</i> 1.171.43.63a (Rigaku Oxford Diffraction, 2023) Spherical absorption correction using equivalent radius and absorption coefficient. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.							
T_{\min}, T_{\max}	0.417, 0.428							
No. of measured, independent, and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	57896, 42251, 22782							
R _{int}	0.058							
(sin θ/λ) _{max} (Å ⁻¹)	0.595							
	Refinement							
$\begin{array}{c} R[F^2 > 2\sigma(F^2)], \ wR(F^2), \\ S \end{array}$	0.068, 0.172, 0.99							
No. of reflections	42251							
No. of parameters	1685							
No. of restraints	4078							
$\Delta \Box_{max}, \Delta \Box_{min}$ (e Å-3)	2.11, -2.15							



Figure S2. ORTEP diagram of hybrid POM 1-TMA.



Figure S3. UV-Vis absorption spectra of [Ru] and 1 collected in NMP.



Figure S4. CV and differential pulse voltammetry (DPV) of 1 in NMP (1.0 mM).



Figure S5. CV of 1 and [Ru] in CO₂-saturated NMP (1.0 mM).



Figure S6. Controlled potential UV-Vis-NIR absorption spectra of **1** in NMP. Reduction potentials are quoted vs. NHE. The 1st to 4th reduced states of the POM cluster are highlighted for reference (as in the legend, shown right). As the POM is reduced, subsequent broad IVCT bands can be observed in the mid-visible and NIR regions, respectively, whilst the sharp MLCT band associated with the Ru-polypyridyl moieties is found at *ca*. 550 nm. Upon reduction of the pyridyl ligands, a new band ascribed to radical transitions can be observed.



Figure S7. Controlled potential UV-Vis absorption spectra of **1** in NMP highlighting the different spectroscopic behaviour of the complex under N_2 and in the presence of CO_2 . Under a N_2 atmosphere, scanning of the potential beyond -1.0 V results in the decrease and eventual loss of the MLCT band and the formation of a new radical-based band at higher energy as the ligands are reduced. Under saturated CO_2 conditions, however, the MLCT band is unaffected by scanning to negative potentials, indicating that the reduced ligand state is highly reactive towards CO_2 (where the ligand radical state is rapidly quenched via reaction with a suitable substrate).

Catalysis Connectivity Studies

As indicated in **Figure S4**, under bulk electrolysis conditions (-1.56 V vs. NHE) POM **1** undergoes four reduction events at the POM body, while the polypyrdinyl ligands are also reduced to their corresponding radical anions (**Scheme S1**). This reduced hybrid POM species (**S2**) is the proposed active catalyst as the polypyridyl radical anions are rapidly quenched in the presence of CO₂ as shown in **Figure S7**. In the first instance, the ligated chloride anions at the ruthenium centers of **S2** dissociate and solvates and/or CO₂ coordination occurs intilising the catalytic cycle.¹⁰ This is supported by cyclic voltametry (**Figure S8**) where the reduction peak of the ppt ligand at -1.23 V undergoes a positive shift due to the replacement of the anionic chloride ligand over multiple scans, as has been observed previously in analogous systems.¹⁰



Scheme S1. Representation of change in oxidation state of hybrid POM **1** under bulk electrolysis conditions followed by chloride dissociation and solvation to the proposed active catalyst. Only one ruthenium polypyridyl complex is shown fully for clarity, however, both moieties undergo the described process.



Figure S8. CV over multiple scans of **1** (1.0 mM) in NMP under CO₂. Note that the reduction peak of the ppt ligand at -1.23 V undergoes a positive shift due to the replacement of the anionic chloride ligand over multiple scans, as has been observed previously in analogous systems.¹⁰

Following 1 h of bulk electrolysis, the reaction mixture (0.03 mM of **1** in MeCN with 0.1 M n BuN₄PF₆) was analysed by NMR spectroscopy and CV. The ¹H NMR spectrum showed significant quantities of n BuN₄PF₆ with evidence of solvent/electrolyte degradation, as well as new hybrid POMs (**Figure S9**). Close inspection of the polypyridyl ligand region (**Figure S10**) suggests that hybrid POM **1** is no longer the predominate species.

Phosphonate hybridised Wells-Dawson POMs are known to undergo hydrolytic cleavage at the phosphonate groups which may account for the new aromatic resonances (**Scheme S2**).¹¹⁻¹² Comparison of cleaved polypyridyl phosphonate complex and post-electrolysis ¹H NMR spectra (**Figure S11**) suggests that the connectivity of the hybrid material is maintained following 1 h of bulk electrolysis as no free phosphonic acid is observed. Retained structural connectivity is further supported by CV (**Figure S12**) as the key redox processes of the hybrid-POM complex are observed. Should hydrolysis have occurred, the corresponding peaks for $[P_2W_{17}O_{61}]^{10-}$ or $[P_2W_{18}O_{62}]^{6-}$ species would present with a substantial negative shift in the redox potential of the first redox event. Evidence suggests that the new polypyridyl resonances observed post-bulk electrolysis is likely a de-chlorinated ruthenium-hybrid POM species (**S2**) bearing ligated acetonitrile, CO₂ reduction products, or undetermined intermediates, however, spectrum is further complicated by the paramagnetic broadening of the spectrum after electrolysis, attributed to the reduced POM.



Figure S9. ¹H NMR spectrum (400 MHz, DMSO-d₆) taken of concentrated MeCN solution of hybrid **1** (0.03 mmol) and $^{n}Bu_{4}NPF_{6}$ (0.1 M) that had been subjected to 1 h of controlled potential electrolysis at -1.56 V vs. NHE under saturated CO₂ conditions.



Figure S10. Comparison of the ¹H NMR spectra (400 MHz, DMSO-d₆) of **1** taken before and after 1 h of controlled potential electrolysis at -1.56 V vs. NHE in acetonitrile (0.03 mM, 0.1 M ^{*n*}Bu₄NPF₆) under saturated CO₂ conditions. Despite some paramagnetic broadening of the spectrum after electrolysis (attributed to the reduction of the POM), all signals corresponding to the hybrid Ru-phosphonate-POM connectivity are maintained following the electrocatalytic reaction, albeit, a new coordination sphere has resulted due to chloride anion dissociation.

Scheme S2. Hydrolysis pathway of arylphosphonate hybrid Wells-Dawson phosphotungstates.¹¹⁻¹² Evidence suggest this does not occur for hybrid **1** after 1 h of bulk electrolysis.



Figure S11. Comparison of ¹H NMR spectroscopies (400 MHz, DMSO-d₆) of [Ru(dmbpy)(ppt-H₂)Cl]Cl and the postelectrolysis solution (controlled potential electrolysis of **1** at -1.56 V vs. NHE in acetonitrile (0.03 mM) under saturated CO₂ conditions for 1 h).



Figure S12. CV of **1** following 1 h controlled potential electrolysis at -1.56 V vs. NHE in acetonitrile (0.03 mM) under saturated CO₂ conditions, showing that the key redox processes of the hybrid-POM complex are maintained. Note that in the event the POM hybrid is decomposed (for example through hydrolysis to the corresponding [P₂W₁₇O₆₁]¹⁰⁻ or [P₂W₁₈O₆₂]⁶⁻ species), substantial negative shifts in the redox potential of the first redox event would be observed.



Figure S13. Concentration dependent CVs of **1** in NMP (1.0 mM) in the presence of AcOH under N_2 . Note that the redox potential of the POM reduction processes is positively shifted in response to increasing acid concentration, indicating proton-coupled redox processes. The voltammograms are cut-off at the onset point of the hydrogen evolution wave.



Figure S14. (*Left*) CVs of **1** in NMP (1.0 mM) under N₂ and CO₂, showing the increased catalytic current upon addition of AcOH; (*right*) CVs showing titration of AcOH into solutions of **1** in NMP (1.0 mM) under N₂. Note that after addition of 1 equivalent of acid, the redox potential of the 3^{rd} POM reduction is positively shifted, indicating a proton-coupled process (*i.e.* protonation of the POM) prior to the reduction potential of the catalytically active Ru-polypyridyl groups. This supports the involvement of POM-bound protons in the reduction of CO₂ to formic acid upon addition of AcOH. Furthermore, whilst a ligand-centred catalytic wave (located at the potential of the second ligand reduction) becomes apparent at increasing acid concentrations, a sharp HER wave is not observable until significantly more than 10 equivalents AcOH have been added (see **Figure S13** above), overwhelming the buffering capacity of the POM.

Bulk Electrolysis Outputs



Figure S15. Chromatograms from GC-TCD for Table 1. TCD used for determining hydrogen (H₂) content. Head space sampled contains atmospheric oxygen and nitrogen gasses observed at approximetly 7.5 and 8 min.



Figure S16. Chromatograms from GC-FID for Table 1. FID used for determining carbon monoxide (CO) content. Head space sampled contains excess carbon dioxide observed after 30 min.



Figure S17. Formic acid (HCOOH) content was determined by capillary electrophoresis. The recorded area associated with HCOOH is plotted for each entry corresponding to Table 1.

Summary of Related Ru Catalysts for CO₂ Electroreduction

The following table is adapted from the recent review by Zhang, S and co-authors, please see for a comprehensive analysis of ruthenium pincer ligand complexes as electrocatalysts.¹³

	Controlled Potential Electrolysis				Majar	EE	то	Dof
Catalyst	Electrolyte/solvent	Working electrode	Duration (h) or Charge (C)	Applied potential (V)	products	г с %	N	rter
	ⁿ Bu ₄ NPF ₆ /MeCN	CP	1 h	-1.56 V vs. NHE	H ₂	91	38	
Hybrid	″Bu₄NPF₀/MeCN/H₂O (10 equiv)	CP	1 h	−1.56 V vs. NHE	H ₂	74	33	
POM 1	ⁿ Bu ₄ NPF ₆ /MeCN/AcOH (10 equiv)	СР	1 h	−1.56 V vs. NHE	НСООН	67	22	
S3	ⁿ Bu₄NPF₀/MeCN	GC	5 h	-1.52 V vs. NHE	CO	76	5	10
S3	^{<i>n</i>} Bu ₄ NPF ₆ /MeCN/H ₂ O (10%)	GC	5 h	-1.20 V vs. NHE	CO	>90	7	<u>14</u>
S4	LiCI/DMF/H ₂ O (2:8)	Hg pool	80 C	−1.20 V vs. Ag Ag⁺	CO HCOOH H ₂	35 30 20	n.a.	<u>15</u>
S5	ⁿ Bu₄NPF₀/MeCN	GC	5 h	−1.20 V vs. Fc Fc⁺	CO, HCO ₃ ⁻	94.7	n.a.	16
S6	^{<i>n</i>} Bu ₄ NPF ₆ /MeCN/H ₂ O (10%)	GC	6 h	−1.55 V vs. Fc Fc⁺	CO H₂ HCOO⁻	34.4 12.6 6.9	2.5	<u>17</u>
S7	ⁿ Bu ₄ NPF ₆ /MeCN	Hg pool	1 h	−2.3 V vs. Fc Fc⁺	HCOO⁻ CO	5.9 4.1	n.a.	<u>18</u>
S 8	ⁿ Bu ₄ NPF ₆ /MeCN/H ₂ O (7%)	GC	12 h	−1.53 V vs. Fc Fc⁺	HCOO-	42	5.2 5	<u>19</u>

Table S2. Summary of ruthenium bpy/tpy derived complexes for electrochemical reduction of CO₂.

CP = Carbon Paper Electrode, GC = Glassy Carbon Electrode, n.a. = Data not available.



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Author Contributions

H.O., J.M.C. & G.N.N. conceived and supervised the project, and wrote the manuscript. Sa.K., T.F., K.D.J., Sh.K., R.S., Y.T., T.Y. & T.S. implemented the synthetic and analytical experiments. O.I. helped interpret the catalytic data. S.P.A. processed the single crystal diffraction data.