Supporting Information

Co-immobilization of a Rh catalyst and a Keggin Polyoxometalate in the UiO-67 Zr-based Metal-Organic-Framework: in Depth Structural Characterization and Photocatalytic Properties for CO₂ Reduction

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Table of Contents

Synthesis of Cp*Rh@UiO-67.	S3
Figure S1 . Powder X-ray diffraction patterns of UiO-67, PW ₁₂ @UiO-67, Cp*Rh@UiO-67, (PW ₁₂ ,Cp*Rh)@UiO-67 before and after catalysis.	S4
Figure S2. IR spectra of POM@MOF and (POM,Cat)@MOF solids.	S 5
Figure S3. Raman spectra of PW ₁₂ , Cp*Rh, PW ₁₂ @UiO-67, Cp*Rh@UiO-67, (PW ₁₂ ,Cp*Rh)@UiO-67.	S 6
Figure S4 . N ₂ adsorption/desorption isotherm (77 K, $P/P_0 = 1$ atm.) of UiO-67 and the PW ₁₂ @UiO-67, and (PW ₁₂ ,Cp*Rh)@UiO-67 composites.	S7
Figure S5 . Plot of the $(Ahv)^2$ versus photon energy (hv) of $(PW_{12}, Cp*Rh)@UiO-67, Cp*Rh@UiO-67, PW_{12}@UiO-67 and UiO-67.$	S7
Figure S6. Solid state NMR spectra of (PW ₁₂ ,Cp*Rh)@UiO-67 compared to that of the precursors.	S8-S9
Figure S7. Computed PW ₁₂ @UiO-67 and (PW ₁₂ ,Cp*Rh)@UiO-67 models.	S10
PDF data description and peak assignment for UiO-67.	S11
Figure S8. PDF analysis of UiO-67.	S12
Figure S9. Differential PDF for PW_{12} encapsulated in UiO-67.	S13
Comments on the coupling between PDF and DFT.	S14
Figure S10. Experimental and differential PDF data for (PW ₁₂ ,Cp*Rh)@UiO-67 before catalysis.	S15
Figure S11 . Experimental and differential PDF data for (PW ₁₂ ,Cp*Rh)@UiO-67 after catalysis.	S15

Figure S12 . Evolution of H_2 and HCOO ⁻ TONs over time during a CO ₂ photoreduction reaction.	S16
Figure S13 . Formate and H_2 TONs during a CO_2 photoreduction reaction.	S16
Figure S14. Photoreduction of CO ₂ overtime by a (PW ₁₂ ,Cp*Rh)@UiO-67 composite.	S17
Figure S15. SEM images and EDS mapping of (PW ₁₂ ,Cp*Rh)@UiO-67 before and after catalysis.	S17
Figure S16. HOMO and LUMO orbitals and energies of the Rh-complex and the PW ₁₂ @Rh-complex.	S18
Figure S17. Proposed mechanism for CO ₂ reduction by (PW ₁₂ ,Cp*Rh)@UiO-67.	S19
Figure S18. Recyclability of (PW ₁₂ ,Cp*Rh)@UiO-67 thin films.	S20
Table S1. EDS analyses.	S21
Table S2. Elemental Analysis.	S21
Table S3. Structural parameters and characteristic distances of first atomic pairs obtained from d-PDF	600
$[PW_{12}O_{40}]$ polyoxometalate structural model.	S 22
References.	S23

Synthesis of Cp*Rh@UiO-67. Cp*Rh@UiO-67 with a Cp*Rh loading of 7 % was synthesized by a slight variation of the reaction conditions used for the synthesis of the Cp*Rh@UiO-67 with a Cp*Rh loading of 10 %. ¹ In a 10 mL glass flask, UiO-67 (50 mg) and Cp*Rh(bpydc)Cl₂ (17 mg, 3.10⁻⁵ mol) were suspended in 10 mL degassed deionized water. This solution was stirred at room temperature for 24 h. The solid was isolated by centrifugation and suspended in 5 mL of DMF. After standing at room temperature for 1 h the suspension was centrifuged and the solvent was decanted. The obtained yellow solid (~ 40 mg) was then washed with ethanol and finally dried under reduced pressure at room temperature.



Figure S1. Powder X-ray diffraction patterns (PXRD) of POM@MOF and (POM,Cat)@MOF solids. PXRD are shown for UiO-67, $PW_{12}@UiO-67$, Cp*Rh@UiO-67 and $(PW_{12},Cp*Rh)@UiO-67$ before and after catalysis. All the diffraction peaks are unambiguously attributed to the UiO-67 crystalline structure.² Apart from the diffuse scattering observed in $PW_{12}@UiO-67$ (common to all POM-containing composites), the PXRD patterns of UiO-67 and $PW_{12}@UiO-67$ are strictly comparable in terms of 20 peak positions and intensities, prohibiting any further structural investigations, showing here the limit of conventional PXRD analysis to retrieve structural information in the case of the immobilization of a guest inside a MOF porous network without ordering/symmetry.



Figure S2. IR spectra of POM@MOF and (POM,Cat)@MOF solids. IR spectra of $PW_{12}@UiO-67$, Cp*Rh@UiO-67 and (PW₁₂,Cp*Rh)@UiO-67 composites are compared to those of the POM and Cp*Rh complex precursors and of the pristine UiO-67. The regions with characteristic peaks of the MOF, the POM and the Cp*Rh species are highlighted in grey, light blue and light orange respectively.



Figure S3. Raman spectra of A, B) POM, (POM,Cat)@MOF and Cat@MOF and C) POM@MOF, (POM,Cat)@MOF and Cat solids measured at 532 nm excitation wavelength. The main bands of POM at 1011 (stretching of P-O) and 996 cm⁻¹ (stretching of W=O)³ are detected in the (PW₁₂,Cat)@UiO-67. The two vibrational bands of the Cat@MOF are still observed in the 960-1040 cm⁻¹ area although not dominated (Fig. S3A et S3B). The presence of Cp*Rh in the (PW₁₂,Cat)@UiO-67 can be observed by the characteristic bands (Stars in Fig. S3C) at 440 (δ (N-Rh-N)), 1324 and 1506 cm⁻¹ (ν (C=N) + ν (C=C)).⁴ Those involving the COOH group disappear from the free Cp*Rh molecules after its insertion into the MOF, as the C=O 1738 cm⁻¹ band, as expected.



Figure S4. N₂ adsorption/desorption isotherms of UiO-67 and the PW₁₂@UiO-67, and (PW₁₂,Cp*Rh)@UiO-67 composites (77K, $P/P_0 = 1$ atm.). Inset shows the pore distributions.



Figure S5. Plot of the $(Ah\nu)^2$ versus photon energy $(h\nu)$ of $(PW_{12},Cp*Rh)@UiO-67$ (red), Cp*Rh@UiO-67 (blue), $PW_{12}@UiO-67$ (green) and UiO-67 (black).



Figure S6A. Solid state ¹H MAS NMR spectra of $PW_{12}@UiO-67$, Cp*Rh@UiO-67 and $(PW_{12},Cp*Rh)@UiO-67$ composites compared to that of the Cp*Rh complex precursor and UiO-67.



Figure S6B. Solid state ¹³C{¹H} CPMAS NMR spectra of $PW_{12}@UiO-67$, Cp*Rh@UiO-67 and (PW₁₂,Cp*Rh)@UiO-67 composites compared to that of the Cp*Rh complex precursor and UiO-67. The signals in range 20 to 80 ppm correspond to spinning side bands of aromatic C signals at 120 to 160 ppm.



Figure S7. Computed $PW_{12}@UiO-67$ and $(PW_{12},Cp*Rh)@UiO-67$ models. Computed position of PW_{12} in $PW_{12}@UiO-67$ and $(PW_{12},Cp*Rh)@UiO-67$ as obtained from SA and DFT-D3 level geometry optimizations. The POM and the Rh-catalytic center are modeled within the same cage ("*in*" position) or different cages ("*out*" position). For describing the "out" position, one inorganic Zr-cluster was omitted to illustrate the interactions of the POM with the Cp*Rh moiety. Interatomic distances and interaction energies between PW_{12} and the MOF host are given for each model. WO₆, blue polyhedra; ZrO₈, yellow polyhedra; Rh, dark green sphere; O, red spheres; C, H, grey; N, dark blue; Cl, green spheres.

PDF data description and peak assignment for UiO-67

For the r-range from 1 Å to 6.5 Å, all the peaks could be assigned to characteristic distances within the $Zr_6O_4(OH)_4$ clusters (Figure S8-a). The first chemically relevant peak (A) at ~ 1.3 Å corresponds to covalent C-C (benzene ring) and C-O (carboxylate group) bond lengths from the bpdc linkers. The second peak at 2.0 Å (B) corresponds to the Zr first coordination sphere, i.e. Zr-O bond lengths. The third peak at 3.5 Å (C) is assigned to the Zr-Zr second coordination sphere distances between two neighboring Zr atoms of a Zr_6 -cluster. The next peaks below 6.0 Å (D, E and F) are attributed to clearly identified Zr-O and Zr-Zr distances within the $Zr_6O_4(OH)_4$ cluster. The longer r-range from 6.5 Å to 15.0 Å exhibits many overlapping peaks of lower intensities characteristics of C-C, C-O and Zr-C distances. However, the higher scattering power of Zr atoms compared to that of O or C atoms implies we mainly observe the peaks corresponding to Zr-C distances. The peak broadening induced by the overlapping of the many contributions of close Zr-C distances renders nevertheless precise assignment challenging. Intense peaks (G to K) are visible from 15.0 Å to 22.0 Å and are clearly attributed to Zr-Zr distances between two $Zr_6O_4(OH)_4$ clusters separated by one bpdc linker (Figure S8-b). The other peaks at higher r value were assigned to Zr-Zr distances between further distant Zr clusters, in line with the excellent crystallinity of the UiO-67 framework.



Figure S8. PDF analysis of UiO-67. (a) PDF data of UiO-67. A-F labels of peak below 6.5 Å correspond to the indicated correlations within the $Zr_6O_4(OH)_4$ cluster. (b) Two $Zr_6O_4(OH)_4$ units connected by a bpdc linker and relevant Zr-Zr distances corresponding to the longer r features (G-K). Zr-grey, O-red, C-light grey, H-white. Presentation inspired from Bennett *et al.*⁵



Figure S9. Differential PDF for PW_{12} encapsulated in UiO-67. (a) Blue: Experimental d-PDF for PW_{12} encapsulated in UiO-67 determined by subtracting the PDF of UiO-67 from the PDF of $PW_{12}@UiO-67$, Red: theoretical d-PDF determined by subtracting the PDF of UiO-67 (DFT-calculated) from the PDF of $PW_{12}@UiO-67$ (DFT-calculated). The corresponding partial W-W and W-Zr calculated pair distribution function are show below in grey. (b) Structural model of $PW_{12}@UiO-67$ obtained from DFT. The black, orange and red arrows are used as guideline to highlight respectively the intra POM W-W distances, the inter POM-POM W-W distances and the inter POM-MOF Zr-distances.

Comments on the coupling between PDF and DFT

As expected, for the short-range order (1-8 Å), the experimental d-PDF and the DFT-calculated d-PDF are very similar showing a good agreement (Figure S9-a). All the peaks of the DFT-calculated d-PDF can thus be attributed to the $[PW_{12}O_{40}]^{3-}$ characteristics distances. However, extra-contributions are observable for higher radial distances on the DFT-calculated d-PDF (Figure S9-a). As the UiO-67 peaks are erased by the d-PDF, only the $[PW_{12}O_{40}]^{3-}$ contributions, namely POM-POM and POM-MOF interactions, are here represented. Knowing the atomic diffusion factors, we expect that the most intense and distinguishable peaks mainly arise from distances involving heavy atoms such as W and Zr. The distance analysis from the model obtained from DFT (Figure S9 a,b) confirms that they mainly correspond to inter-POM $[PW_{12}O_{40}]^{3-}$ W-W distances and $[PW_{12}O_{40}]^{3-}$ -UiO-67 W-Zr distances. This phenomenon comes from an ordering of the POM inside the MOF network induced by the DFT calculations. The peak absence at middle- and long-range order on the experimental d-PDF can then be explained on one hand by the random immobilization of the POM inside the UiO-67 network and on the other hand by the POM rotational disorder from one octahedral to another one.



Figure S10. Top: Experimental PDF data for $(PW_{12}, Cp*Rh)@UiO-67$ before catalysis (black) and the POM-free UiO-67 (red). Bottom: the resulting d-PDF for PW_{12} in $(PW_{12}, Cp*Rh)@UiO-67$ before catalysis (magenta) determined by subtracting the PDF of UiO-67 from the PDF of $(PW_{12}, Cp*Rh)@UiO-67$ before catalysis.



Figure S11. Top: experimental PDF data for $(PW_{12}, Cp*Rh)@UiO-67$ after catalysis (black) and the POM-free UiO-67 (red). Bottom: the resulting d-PDF for PW_{12} encapsulated in $(PW_{12}, Cp*Rh)@UiO-67$ after catalysis (navy blue) determined by subtracting the PDF of UiO-67 from the PDF of $(PW_{12}, Cp*Rh)@UiO-67$ after catalysis.



Figure S12. Evolution of a) H₂ and b) HCOO⁻ TON over time during a CO₂ photoreduction reaction by (PW₁₂,Cp*Rh)@UiO-67 compared to Cp*Rh@UiO-67. Reactions conditions: 0.17 µmol of catalyst in suspension, 0.8 mL of CH₃CN/TEOA 5:1, 1 mM Ru(bpy)₃Cl₂, 280 W, $\lambda > 415$ nm.



Figure S13. Formate (green) and H₂ (orange) TONs during a CO₂ photoreduction reaction by (PW₁₂,Cp*Rh)@UiO-67 and Cp*Rh@UiO-67 composites after 180 min illumination (CH₃CN/TEOA 5:1, Ru(bpy)₃Cl₂ 1 mM, 280 W, $\lambda > 415$ nm) from data shown in Figure S12.



Figure S14. Photoreduction of CO₂ overtime by a (PW₁₂,Cp*Rh)@UiO-67 composite (CH₃CN:TEOA 5:1, Ru(bpy)₃Cl₂ 1 mM, 280 W, $\lambda > 415$ nm). A fresh solution of Ru(bpy)₃Cl₂ photosensitizer was added to the reaction after 120 min.



Figure S15. a) SEM image of (PW₁₂,Cp*Rh)@UiO-67, b), c), d) EDS mapping of Rh, W, Zr respectively before catalysis and e) SEM image of (PW₁₂,Cp*Rh)@UiO-67, f), g), h) EDS mapping of Rh, W, Zr respectively after catalysis.

DFT calculations investigating the impact of the POM on the Rh-complex electronic structure.

Simplified cluster systems of the POM and the Rhodium complex were extracted from the VASP periodic calculations of the most stable "*in*" version of the PW₁₂@UiO-67-Rh model - *i.e.* where the POM is facing the Cp* ligand of the Rh-complex. The carboxylates of the bipyridine were neutralized by the addition of an hydrogen atom on each carboxylate and the resulting carboxylic acid functions were optimized at HSE06/6-31g(d,p)/LanL2DZ(Rh, W) level of theory using Gaussian 16 Revision B.01 software⁷ while the rest of the system was frozen as obtained from the periodic system optimized with VASP, thus not altering the interaction between the PW₁₂ and the Rh-complex for the subsequent computational steps. The HSE06 functional⁸ was elected as it was previously used for the POM-free system.¹ The authors would like to mention that B3P86, APFD and B3LYP functionals were also tested and gave similar trends than those reported here when using HSE06. Also, the HOMO-LUMO energy of the PW₁₂O₄₀³⁻ moiety computed with the HSE06 functional is in excellent agreement with the experimental value reported by Hiskia *et al.* in 2001.⁹

The single point calculations were performed at the HSE06/6-311++g(d,p)/LanL2DZ level of theory incorporating acetonitrile solvent effect via the Polarizable Continuum Model (PCM).¹⁰ They were done on the complete { $Na_2PW_{12}O_{40} + 2,2$ '-bpydcRhCp*Cl} system and also on the 2,2'-bpydcRhCp*Cl,PF₆ alone fully re-optimized at the HSE06/6-31g(d,p)/LanL2DZ(Rh) where PF₆⁻ was added to prevent charge effects on the electronic levels. The Total and Partial Density Of State (TDOS + PDOS) were analyzed using Multiwfn software allowing the extraction of the POM's and the Rh-complex's contributions.¹¹ The ionization potential of the two systems (Rh-complex with and without the POM) was used to align the Highest Occupied Molecular Orbitals (HOMO) of the two systems with the vacuum.



Figure S16. HOMO and LUMO orbitals and energies of the Rh-complex and the $PW_{12}@Rh-complex$ (a) HOMO-LUMO levels and corresponding surfaces for the {2,2'-bpydcRhCp*Cl – PF₆} molecular complex; (b) HOMO-LUMO levels and corresponding surfaces for the {Na₂PW₁₂O₄₀ + 2,2'-bpydcRhCp*Cl} cluster. All HOMOs energies are aligned with the corresponding ionization potential. Calculations are done at HSE06/6-311++g(d,p)/LanL2DZ level of theory. The reference redox potentials are reported in CH₃CN.¹²



Figure S17. Proposed mechanism for CO₂ reduction by $(PW_{12}, Cp*Rh)@UiO-67$ based on the mechanism presented by Pan et al. for the POM-free Cp*Rh@UiO-67 system.¹³ The oxidative quenching mechanism for CO₂ reduction into formate and H₂ by the composite involves the Rh catalytic complex which is assisted by the PW₁₂ polyoxometalate as a proton relay.



Figure S18. Recyclability of $(PW_{12}, Cp*Rh)@UiO-67$ thin films for photocatalytic CO₂ reduction. Normalized formate TONs (a) after 30 min illumination, (b) after 180 min (CH₃CN:TEOA 5:1, Ru(bpy)₃Cl₂ 1 mM, 280 W, $\lambda > 415$ nm). The TON after 180 min is equal to 175 for the first run for $(PW_{12}, Cp*Rh)@UiO-67$ thin films and 126 for (Cp*Rh)@UiO-67 thin films. The recyclability for H₂ production could not be performed on thin films. Indeed, the H₂ productions with and in absence of thin films are almost the same due to the majority contribution of $[Ru(bpy)_3]^{2+}$ in these conditions.

We have considered the following formulae (which ensure the electroneutrality of the compounds):

 $PW_{12} @UiO-67: Zr_6O_4(OH)_4(C_{14}O_4H_8)_{5.67}(PW_{12}O_{40})_{0.22} (M = 2674.31 \text{ g mol}^{-1})$

The twelve negative charge compensating the twelve positive charge are brought by the biphenyl dicarboxylate linkers (charge -2) and the POM (charge -3)

5.67x2 + 0.22x3 = 12

	Calc	Exp
W/Zr	0.44	0.45

Cp*Rh@UiO-67: $Zr_6O_4(OH)_4(C_{14}O_4H_8)_{5.56}(RhC_{22}H_{21}N_2O_4Cl_2)_{0.44}$ (M = 2251.26 g mol⁻¹)

The twelve negative charge compensating the twelve positive charge are brought by the biphenyl dicarboxylate linkers (charge -2) and the Cp*Rh complex with one chlorine atom bound to the Rh metal and one extra chloride ion (charge -2) 5.56x2+0.44x2 = 12

	Calc	Exp
Rh/Zr	0.070	0.073

 $(PW_{12}, Cp*Rh) @UiO-67: Zr_6O_4(OH)_4(C_{14}O_4H_8)_{5.45}(RhC_{22}H_{21}N_2O_4Cl)_{0.44}(PW_{12}O_{40})_{0.22}.7DMF (M = 3352.14 \text{ g mol}^{-1})$

A chlorine default has been identified by EDS measurements, suggesting a loss of chloride ion in the Cp*Rh complex. We thus propose that the twelve negative charge compensating the twelve positive charge are brought by the biphenyl dicarboxylate linkers (charge -2), the Cp*Rh complex with only one chlorine atom bound to the Rh metal (charge -1) and the POM (charge -3)

5.45x2 + 0.44x1 + 0.22x3 = 12

Before catalysis

	Calc	Exp
Rh/Zr	0.070	0.071
W/Zr	0.44	0.38

After catalysis

	Calc	Exp
Rh/Zr	0.070	0.070
W/Zr	0.44	0.39

Table S2. Calculated and experimental values of elemental analysis for (PW₁₂,Cp*Rh)@UiO-67

	С	Η	Ν	W	Zr	Rh
Calcd	38.22	3.17	3.28	14.48	16.33	1.29
Exp	38.27	4.79	3.55	14.80	16.70	1.40

Table S3. Structural parameters and characteristic distances of $[PW_{12}O_{40}]^{3-}$ polyoxometalate obtained from d-PDF refinement from a PW₁₂@UiO-67. For a comparison purpose, the structural parameters of the Keggin $[PW_{12}O_{40}]^{3-}$ reference are reminded.

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Structural data		Refined values	Reference	
			(JCPDS 00-50-0304)	
Structural	a (Å)	12.156	12.156	
parameters	$\mathbf{P}_{X_P} = y_P = z_P$	0.750 ; 0.750 ; 0.750	0.750 ; 0.750 ; 0.750	
	$O_p x_{O1} = y_{O1} = z_{O1}$	0.825	0.820	
	$O_2 x_{Ob1} = y_{Ob1}; z_{Ob1}$	0.675 ; 0.490	0.656 ; 0.507	
	$O_3 x_{Ob2} = y_{Ob2}; z_{Ob2}$	0.872 ; 0.027	0.870 ; 0.026	
	$O_t x_{04}; y_{04} = z_{04}$	0.730 ; 0.055	0.735 ; 0.053	
	$\mathbf{W} \mathbf{x}_{\mathrm{W}}$; $\mathbf{y}_{\mathrm{W}} = \mathbf{z}_{\mathrm{w}}$	0.758 ; 0.957	0.758 ; 0.957	
	B _{iso} P (Å ²)	1.13	0.50	
	B _{iso} O (Å ²)	1.65	0.47	
	$\mathbf{B}_{\mathbf{iso}} \mathbf{W}(\mathbf{\mathring{A}}^2)$	0.48	1.57	
First dis-	P-O _t (Å)	1.58	1.47	
lances	W-O _{octahedron} (Å)	$1.72 < d_{W-O} < 2.41$	$1.69 < d_{W-O} < 2.45$	
	W-W (Å)	3.42;3.70	3.40 ; 3.68	
Refiner	nent quality (R _{w)}	0.282	/	

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