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Supplementary Information

Light-driven hydrogen evolution catalyzed by a cobaloxime catalyst incorporated in a MIL-101(Cr) metal–organic framework

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General methods and instrumentation

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, VWR, Fluorochem, and Alfa-Aesar) and used without further purification, unless stated otherwise. Solvents were dried using appropriate drying agents (sodium for diethyl ether and THF; calcium hydride for dichloromethane and acetonitrile) and freshly distilled under argon before use. Co(dmgH)(dmgH$_2$)Cl$_2$ (dmgH = dimethylglyoxime) [1] and Co(dmgH)$_2$(4-methylpyridne)Cl[2] was synthesized according to literature method.

^{1}H-NMR spectra were measured using a JEOL 400 MHz spectrometer at 293 K. Powder X-ray diffraction patterns (PXRD) were obtained using a Simons D5000 Diffractometer (Cu Kα, λ = 0.15418 nm) at 45 kV and 40 mA, using a step size of 0.02°. The SEM images were taken by a Leo 1550 FEG microscope (Zeiss, Oberjochen, Germany) equipped with an InLens detector at 5 kV acceleration voltage. Samples were coated with Pd-Ir sputter coater for 30 s. EDX data was collected with a 80 mm^2 Silicon Drift Detector using AZtec (INCA energy) software at a working distance of 6.5 nm. BET surface area measurements were carried out using a Micromeritics ASAP 2060 and the N$_2$ sorption isotherm was recorded at 77 K. Prior to measurement, materials were activated under dynamic vacuum (1×10^{-4} Pa) using a Micromeritic SmartVacPrep sample preparation unit.

XAS at the Co K-edge was performed at beamline KMC-3 at BESSY-II (Berlin) using the previously described standard set-up (storage ring operated in top-up mode at 250 mA, double-crystal Si[111] monochromator, 13-element energy-resolving Ge detector (Canberra) for fluorescence monitoring, sample held in a cryostat (Oxford) at 20 K)**.[3]** Up to four monochromator scans on powder samples of the materials (grounded with boron nitride, 1:10 w/w) were

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[1] Trogler *et al*, *Inorg. Chem.*, 1974, **13**, 1564

[2] Panagiotopoulos *et al*, *Dalton trans.*, 2016, **45**, 6732

[3] Schuth *et al*, *Proc. Natl. Acad. Sci.*, 2017, **114**, 8556

averaged after detector dead-time and self-absorption correction, normalized to derive XANES spectra, and EXAFS spectra were extracted as described earlier.[4] EXAFS simulations were carried out using phase functions calculated with FEFF9 and in-house software.

Cyclic voltammetry was performed on a conventional three electrode set up with a glassy carbon working electrode (3 mm diameter), glassy carbon rod counter electrode, and Ag/AgNO$_3$ (10 mM in MeCN) reference electrode. A 0.1 M solution of *n*-Bu$_4$NPF$_6$ in DMF was used as supporting electrolyte. Prior to measurement, the solutions were purged with argon for 10 min. Metrohm Autolab potentiostat/galvanostat (PGSTAT302) with a GPES electrochemical interface was used for recording CVs.

Synthesis of Co(dmgH)$_2$(4-HEP)Cl, (4-HEP = 4-(2-hydroxyethyl)pyridine) (compound 1): To a suspension of Co(dmgH)(dmgH$_2$)Cl$_2$ (0.36 g, 1 mmol) in methanol (30 mL), triethylamine (0.14 mL, 1 mmol) was added to form a brown solution. The reaction mixture was stirred at 40° C for 10 min followed by addition of 4-(2-hydroxyethyl)-pyridine (0.12 mL, 1 mmol). After stirring for 2 h, the reaction mixture was cooled to room temperature and the volume was reduced to 10 mL. Diethyl ether (20 mL) was added to the solution which caused precipitation of a brown solid. The precipitate was collected by filtration, and washed with water (2×1 mL), ethanol (2×5 mL), and ether (4×5 mL). Yield: 0.163 g (36 %). ^{1}H NMR (400 MHz, dmso-d$_6$): δ = 18.47 (s, 2H), 7.88 (d, 2H), 7.34 (d, 2H), 4.72 (t, 1H), 3.59 (m, 2H), 2.68 (t, 2H), 2.32 (s, 12H). ^{13}C NMR (100 MHz, dmso-d$_6$): δ = 154.41, 159.95, 149.75, 127.54, 60.32, 37.86, 13.16.

Synthesis of MIL-101(Cr): MIL-101(Cr) was synthesized from chromium nitrate and benzene-1,4-dicarboxylic acid according to a literature procedure.[5] The as-synthesized MIL-101(Cr) were activated by washing with warm DMF (60°C), 1M HCl, H$_2$O, ethanol and dried in vacuo. The dried MIL-101(Cr) was used for chloromethylation.

Synthesis of MIL 101(Cr)-CH$_2$Cl: MIL-101-CH$_2$Cl was synthesized as described previously.[6] A Schlenk flask equipped with a stir bar was charged with MIL-101(Cr) (200 mg) and nitromethane (14 mL) under Ar atmosphere. AlCl$_3$·6H$_2$O (380 mg, 1.6 mmol) and metoxyacetyl chloride (80 mg, 0.74 mmol) were added sequentially to the vigorously stirred suspension. The mixture was heated at 100°C overnight. After cooling to room temperature, the green chloromethylated product was collected by centrifugation. The product was activated using water (60 mL) at 60°C for 4 h, ethanol (60 mL) at 85°C for 4 h and after that with THF (60 mL) at 65°C for 4 h. Finally, the green powder was collected by centrifugation and dried under vacuum at 80°C.

Synthesis of MIL-101-CH$_2$@1: 100 mg of MIL-101-CH$_2$Cl, 140 mg of [Co(dmgH)$_2$)(4-HEP)Cl], and 100 mg of K$_2$CO$_3$ were suspended in 30 mL acetone under Ar atmosphere. The resulting reaction mixture was refluxed at 65°C for 24 h. The solid was collected by centrifugation and washed extensively with water (3×30 mL), methanol (4×30 mL), ethanol (3×30 mL), and further purified by Soxhlet extraction for 12 h with acetone. The final product was dried under vacuum at 80 °C.

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[4] Petukar *et al*, *Dalton Trans.*, 2017, **46**, 907

[5] Edler *et al*, *CrystEngComm* 2011, **13**, 6916.

[6] Kapteijn *et al*, *CrystEngComm*, 2012, **14**, 4109.

Catalyst loading from ICP-AES: The amount of cobalt and chromium in MIL-101-CH_2@**1** samples were determined by ICP-AES after digesting the MOF by microwave heating in piranha solution (2:1 c. H_2SO_4/30% H_2O_2). Using reported chemical formula for pristine MIL-101(Cr),[7] we derived the following formula for MIL-101-CH_2@**1**: $[Cr_3(\mu_3\text{-}O)(OH)(H_2O)_2](BDC)_{3-x}(BDC\text{-}\mathbf{2})_x].nH_2O$ (x = number of cobaloxime-functionalized linkers per molecule).

Table S1: ICP-AES data for MIL-101-CH_2@**1**

Sample	Weight (mg)	Volume (mL)	[Cr] (µg/mL)	[Co] (µg/mL)	Cr:Co (atomic ratio)	functionalized BDC-linkers	[Co] (µmol/mg MOF)
MIL-101-CH_2@**1**	2.08	5	67.2	8.95	8.3:1	12%	0.36
MIL-101- CH_2@$\mathbf{1}_{\mathbf{low}}$	3.00	5	92.6	2.6	40.4:1	2.5%	0.07

Average number of cobaloxime units per cage: Loading of cobaloxime units per cage (n_{Co}) of the hybrid MOF catalyst was calculated using the reported crystal structure of MIL-101(Cr). Each vertex of MIL-101(Cr) is composed of four trimeric Cr-O clusters with one μ_3-O and four bidentate carboxylates. Six 1,4-benzenedicarboxylate (BDC) ligands extends from each cluster along the edges to form a 'super tetrahedron' (ST) sub-unit. The large and small cages in MIL-101(Cr) are delimited by 28 and 20 ST respectively.[7] The crystal structure shows that every ST is bordered by four cages, leading to each ST contributing 1.5 BDC linkers to each cage. Thus, the large and small cages consist of ($28 \times 1.5 =$) 42 and ($20 \times 1.5 =$) 30 BDC units, respectively. This numbers are combined with the ICP-AES data to calculate the number of catalyst units per cage.

Table S2. Cobaloaxime loading per cage in the MOF-catalyst

Sample	Cobaloxime-functionalized BDC-linkers	$(n_{Co})_{\text{large-cage}}$	$(n_{Co})_{\text{small-cage}}$
MIL-101-CH_2@**1**	12%	~5	~3.6
MIL-101- CH_2@$\mathbf{1}_{\mathbf{low}}$	2.5%	~1	~0.7

Estimation of the pore volume and the space occupied by the catalyst and the photosensitizer: The volumes of large and small pores of MIL-101(Cr) are ~20.6 and ~15.6 nm^3, respectively. From the crystal structures, the approximate space occupied by of $[Co(dmgH)_2(pyr)Cl]$[8] and eosin Y[9] could be estimated to be ~0.6 and ~0.7 nm^3, respectively. The size of the cobaloxime catalyst is ~10 Å × 9.5 Å and that of eosin Y is ~11 Å × 10 Å.

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[7] Férey *et al*, *Science*, 2005, **309**, 2040

[8] Geremia *et al*, *Inorg. Chim. Acta*, 1994, **216**, 125

[9] Quint *et al*, *J. Am. Chem. Soc.*, 2016, **138**, 7436

Photocatalysis: In a typical experiment, MIL-101-CH_2@**1** material (4.7 mg) was suspended in acetonitrile (4 mL) and an aqueous solution of triethanolamine (TEOA, 10% v/v, pH adjusted to 7.0 by HCl), followed by ultra-sonication for 15 min to obtain an uniform suspension. An aqueous solution of eosin Y (0.05 mL 8 mM solution, 0.4 µmol) was added to the MOF-suspension and the reaction vessel was sealed. For photocatalysis in homogeneous mixture, the molecular catalyst, $Co(dmgH)_2$(4-methylpyridine)Cl (2.5 µmol), was dissolved in 1:1 water/acetonitrile (12 mL) containing EY (0.05 mM) and TEOA (5% v/v) at pH 7.

After sparging with argon for 30 min, the mixture was irradiated with a cold light source (Leica CLS 150XE) fitted with a GG455 long-pass filter. The amounts of evolved hydrogen were determined by sampling aliquots of the headspace in a Perkin Elmer Clarus 580 gas chromatograph equipped with a molecular sieve column (60/80 mesh) and a thermal conductivity detector (TCD).

Reactivation of MOF-catalyst after loss of activity: After 23 h photocatalysis, the deactivated MOF-material (13.5 mg) was collected by centrifugation, thoroughly washed with 1:1 water/acetonitrile (2×15 mL), 1:1 acetonitrile/methanol (2×15 mL), and methanol (2×15 mL), and dried under vacuum for 2 h. A methanolic solution of $[Co(dmgH)(dmgH_2)Cl_2]$ (24 mg in 5 mL) containing 1 equiv. trimethylamine (0.01 mL) was added to the dry MOF, and stirred under Ar for 12 h. Afterwards, the MOF was separated from the reaction mixture by centrifugation, washed with methanol until the washings were colorless (6×10 mL), and dried under vacuum. The reactivated MOF-catalyst was used for photocatalytic hydrogen evolution under same condition.

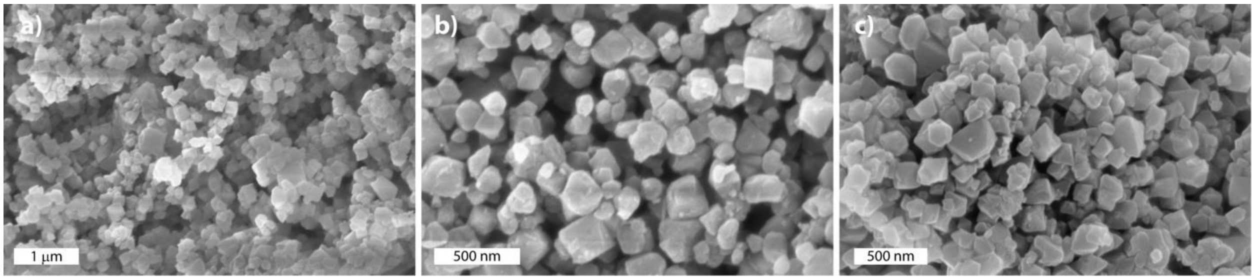

Figure S1. SEM image of (a) MIL-101(Cr), (b) MIL-101-CH_2Cl, and (c) MIL-101- CH_2@**1**

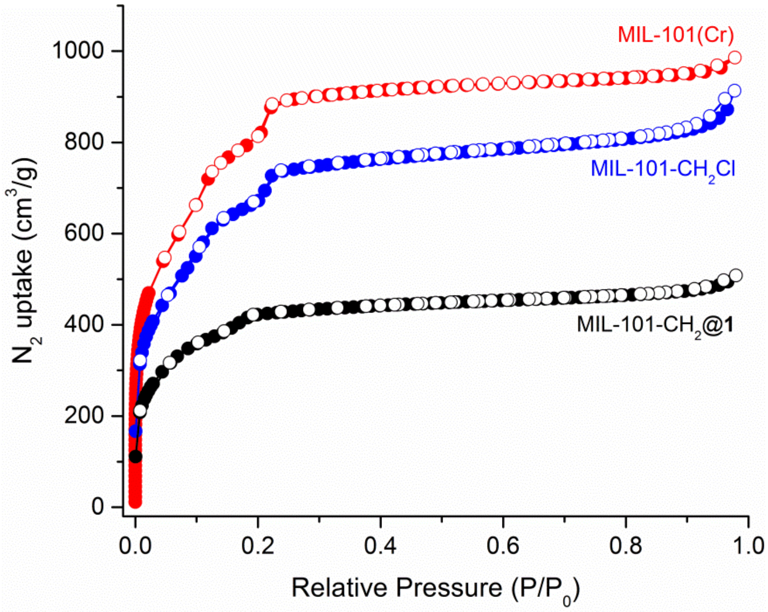

Figure S2. N_2 gas sorption isotherms of MIL-101(Cr), MIL-101-CH_2Cl and MIL-101-CH_2@**1**. Solid and open circles represent adsorption and desorption processes, respectively.

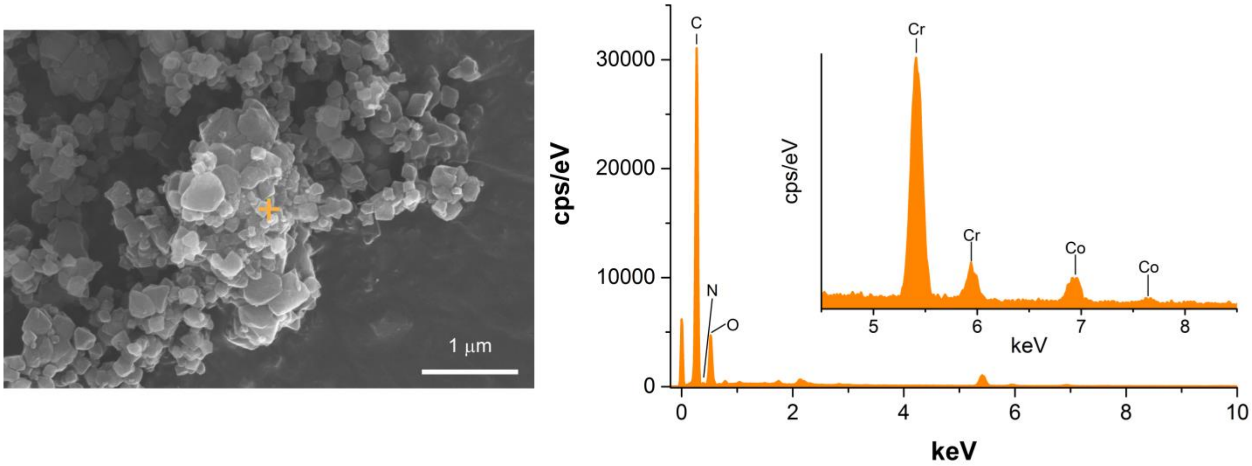

Figure S3. EDX analysis of MIL-101-CH_2@**1** (the orange cross on the SEM micrograph shows the point that was analyzed).

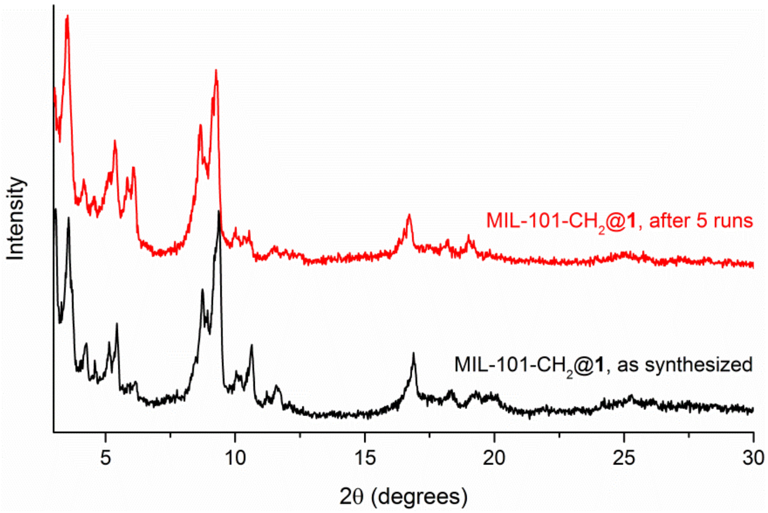

Figure S4. PXRD of freshly prepared MIL-101-CH$_2$@**1** and that of the material recovered after five 1 h photocatalysis cycles.

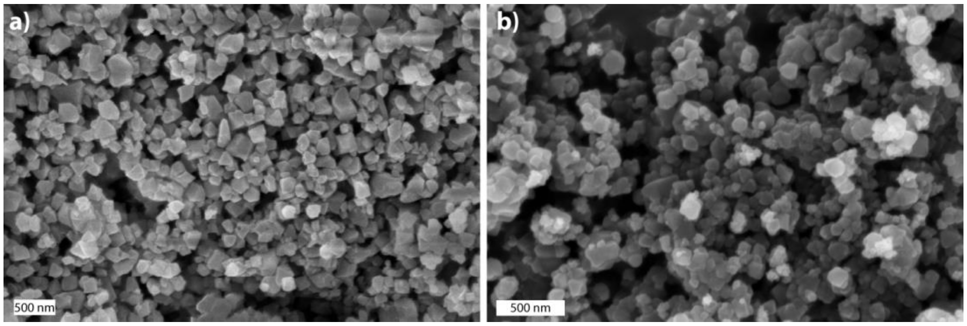

Figure S5. SEM image of MIL-101-CH$_2$@**1** (a) as synthesized and (b) after 20 h photocatalysis
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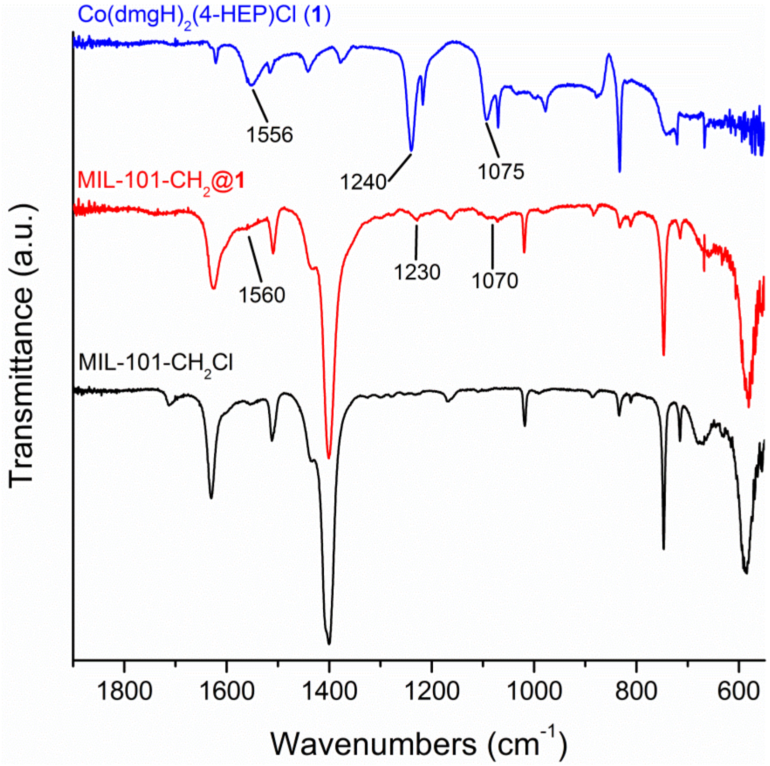

Figure S6. Attenuated total reflectance IR spectra of Co(dmgH)$_2$(4-HEP)Cl, MIL-101-CH$_2$Cl, and MIL-101-CH$_2$@**1**. The IR data do not confirm the presence of cobaloxime unit conclusively as the MIL-101(Cr) signals mask the characteristic C=N stretching bands of cobaloxime units (Fig. S4). However, appearance of a weak v(NO) stretching band at 1230 cm-1 suggests incorporation of the cobalt complex inside the MOF-scaffold.[10]

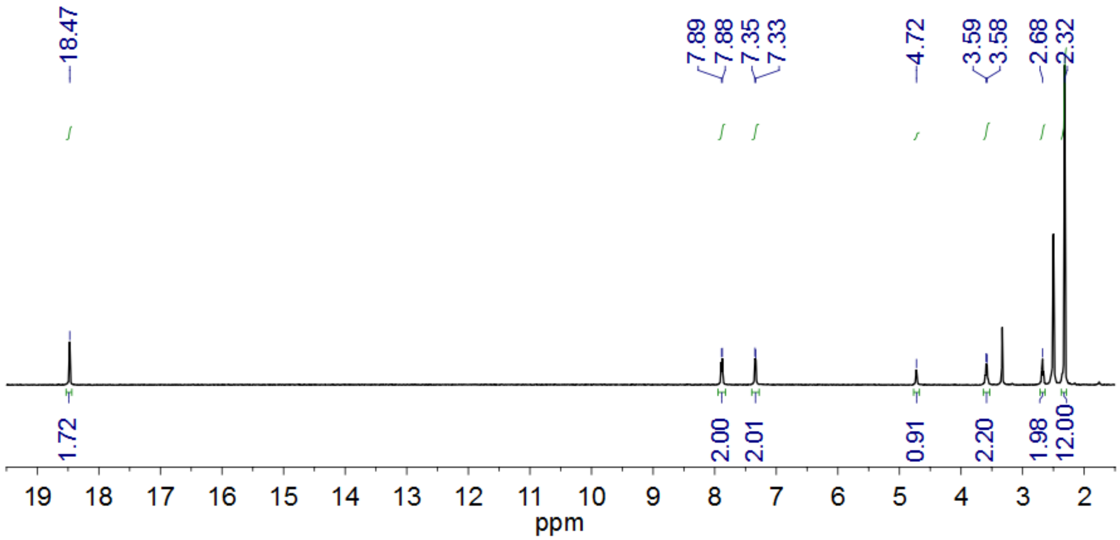

Figure S7. ^{1}H NMR of Co(dmgH)$_2$(4-HEP)Cl (**1**) in dmso-d$_6$.

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[10] Reuillard *et al*, *Angew. Chem. Int. Ed.*, 2016, **55**, 3952

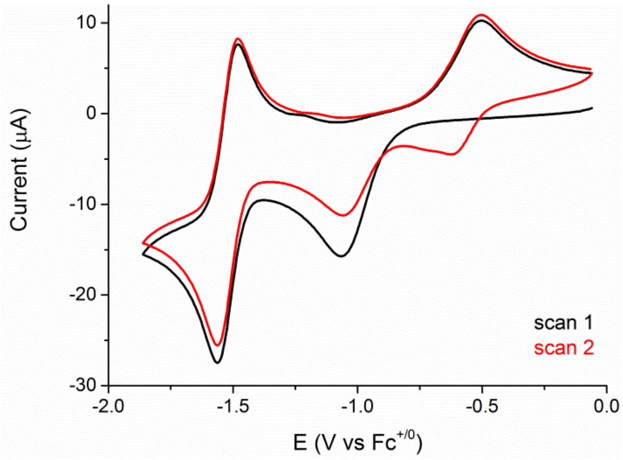

Figure S8. Cyclic voltammogram of Co(dmgH)$_2$(4-HEP)Cl (1 mM) recorded at 0.1 V s^{-1} in DMF containing 0.1 M n-Bu$_4$PF$_6$ supporting electrolyte

Table S2: EXAFS fit parameters.[a]

sample	fit	shell	N [per Co]	R [Å]	$2\sigma^2$ x10^3 [Å^2]	R_F [%]
1	1	Co-N(dmgH)	4*	1.90	2*	11.9
		Co-N(py)	1*	1.83	2*	
		Co-Cl	0.9	2.24	2*	
		Co-O	2*	3.33	2*	
		Co-O	2*	3.16	2*	
		Co-C	4*	2.90	2*	
		Co-C	2*	2.75	2*	
	2	Co-N(dmgH)	4*	1.90	2*	10.3
		Co-N(py)	1*	1.83	2*	
		Co-Cl	$0.8^{\#}$	2.24	2*	
		Co-O	$0.2^{\#}$	2.42	2*	
		Co-O	2*	3.32	2*	
		Co-O	2*	3.16	2*	
		Co-C	4*	2.89	2*	
		Co-C	2*	2.74	2*	
MIL-101-**CH$_2$@1**	3	Co-N(dmgH)	4*	1.92	2*	13.4
		Co-N(py)	1*	1.82	2*	
		Co-Cl	0.1	2.40	2*	
		Co-O	2*	3.22	2*	
		Co-O	2*	3.36	2*	
		Co-C	4*	2.89	2*	
		Co-C	2*	2.72	2*	
	4	Co-N(dmgH)	4*	1.92	2*	11.8
		Co-N(py)	1*	1.81	2*	
		Co-O	1.2	1.95	2*	
		Co-O	2*	3.23	2*	
		Co-O	2*	3.37	2*	
		Co-C	4*	2.90	2*	
		Co-C	2*	2.74	2*	

[a] N, coordination number; R, interatomic distance; $2\sigma^2$, Debye-Waller parameter; R_F, fit error sum calculated for reduced distances of 1-3 Å. *Values that were fixed in the fits to chemically and/or physically reasonable numbers, $^{\#}$coordination numbers of Cl and O ligands were coupled to yield a sum of 1. Fit parameters refer to EXAFS spectra shown in Fig. 2. The first fit approach for each compound determines the number of Cl^- ligands per Co ion (fits 1 and 3), the second fit approach includes an additional O-atom, which replaces the Cl^-.

Table S3. Comparison of the photocatalytic HER performance of MIL-101-2@[Co] with previously reported MOF-based photocatalysts.

Catalyst	**MOF-support**	**External Sensitizer**	**H_2 evolution rate (mmol h^{-1} g^{-1} MOF)**	**Ref.**
$Co(dmgH)_2(4\text{-}HEP)Cl$	MIL-101(Cr)	Eosin Y	1.50	This work
$[Co(DO)(DOH)pn]Cl_2$	MIL-125-NH_2 (Ti)	-	0.38	[11]
[Co(TPA)Cl]Cl	MIL-125-NH_2 (Ti)	-	0.55	[12]
$Fe_2(\mu\text{-}dcbdt)(CO)_6$	UiO-66	$Ru(bpy)_3Cl_2$	0.28	[13]
$Fe_2(c_1bdt)(CO)_6$	MIL-101-NH_2(Cr)	$Ru(bpy)_3Cl_2$	0.59	[14]
$Fe_2[\mu\text{-}SCH_2)_2\text{-}NC(O)C_5H_4N](CO)_6$	Zr-PF [PCN-222(Zn)]	-	0.30	[15]
Polyoxometalate (POM)[a]	UiO-67-Ru_{bpy}[b]	-	0.70	[16]
Pt-nanoparticle	UiO-66	Rhodamine B	0.12	[17]
Pt-nanoparticle	MIL-101-NH_2(Cr)	Rhodamine B	0.58	[18]
Cu-RSH[c]	Cu-RSH[d]	Eosin Y	7.88	[19]
$[Ru_2(p\text{-}BDC)_2]_n$	$[Ru_2(p\text{-}BDC)_2]_n$[e]	$Ru(bpy)_3Cl_2$	3.00	[20]

[a]POM = $[P_2W_{18}O_{62}]^{6-}$; [b]Ru_{bpy} = $[Ru(dcbpy)(bpy)_2Cl_2]$; [c]H_2RSH = 3-formyl-4-hydroxybenzoic acid); [d]Cu-RSH = coordination polymer; [e]$[Ru(p\text{-}BDC)_2]_n$ = porous polymer (BDC: terephthalic acid).

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[11] Nasalevich *et al*, *Energy Environ. Sci.*, 2015, **8**, 364

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[18] Wen *et al*, *Chem. Commun.*, 2014, **50**, 11645

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