Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Heterogenization of molecular cobalt catalysts in robust metal-organic frameworks for efficient photocatalytic CO_2 reduction

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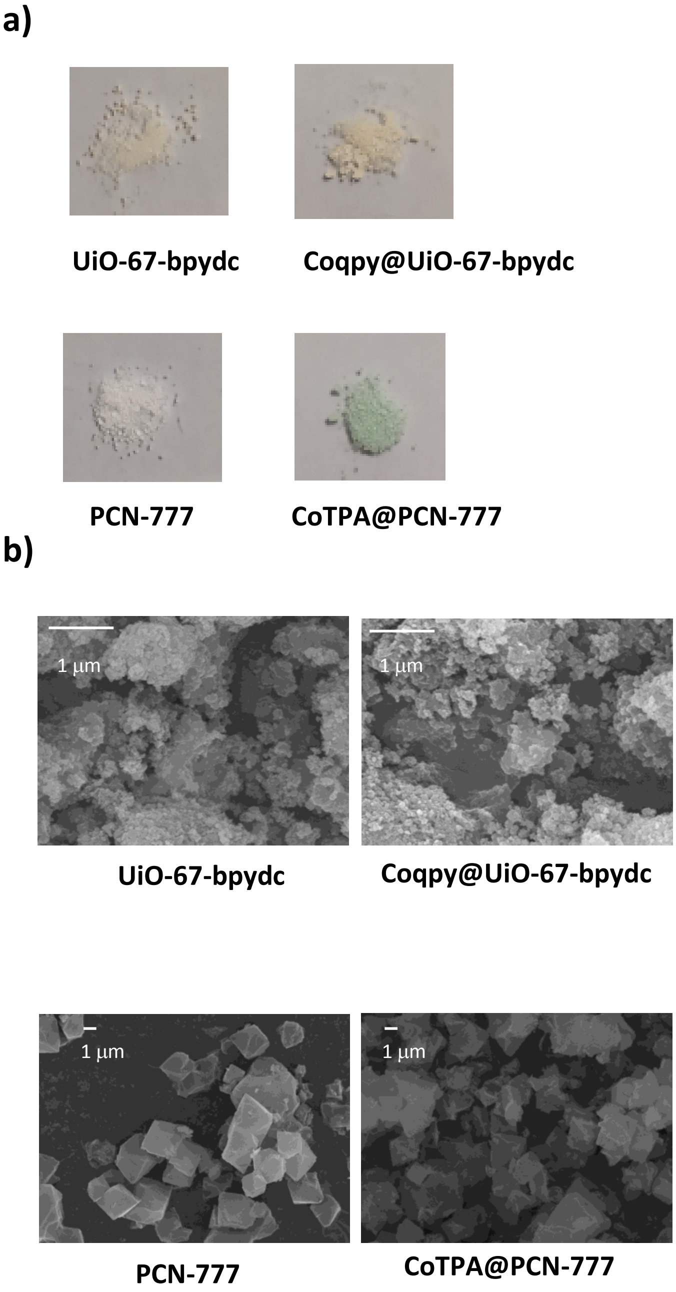

Figure S1. a) Pictures and b) SEM images of the crystallites of MOFs before and after impregnation.

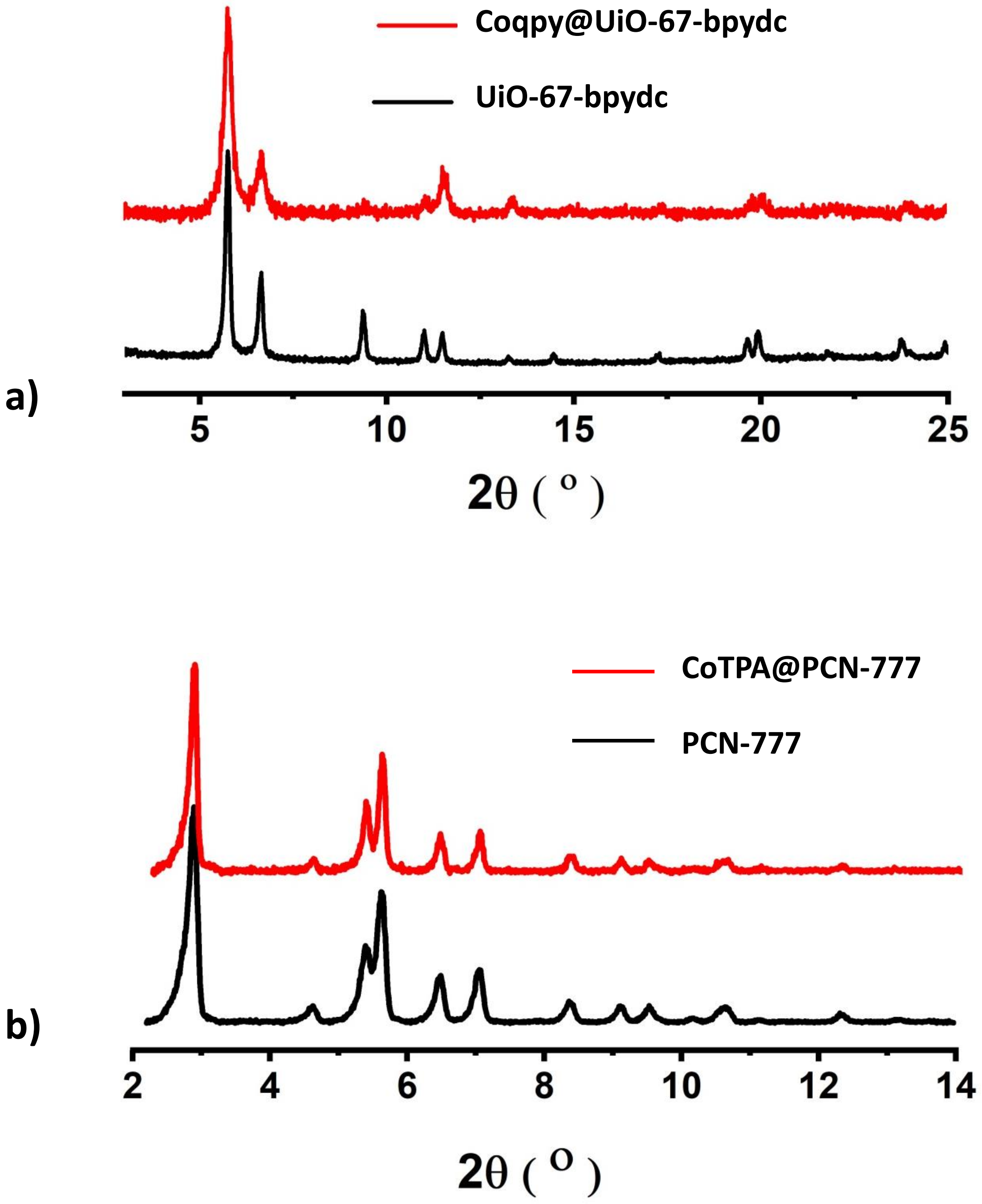

Figure S2. Experimental powder X-ray diffraction patterns of a) UiO-67-bpydc and **Coqpy@UiO-67-bpydc** and b) PCN-777 and **CoTPA@PCN-777**.

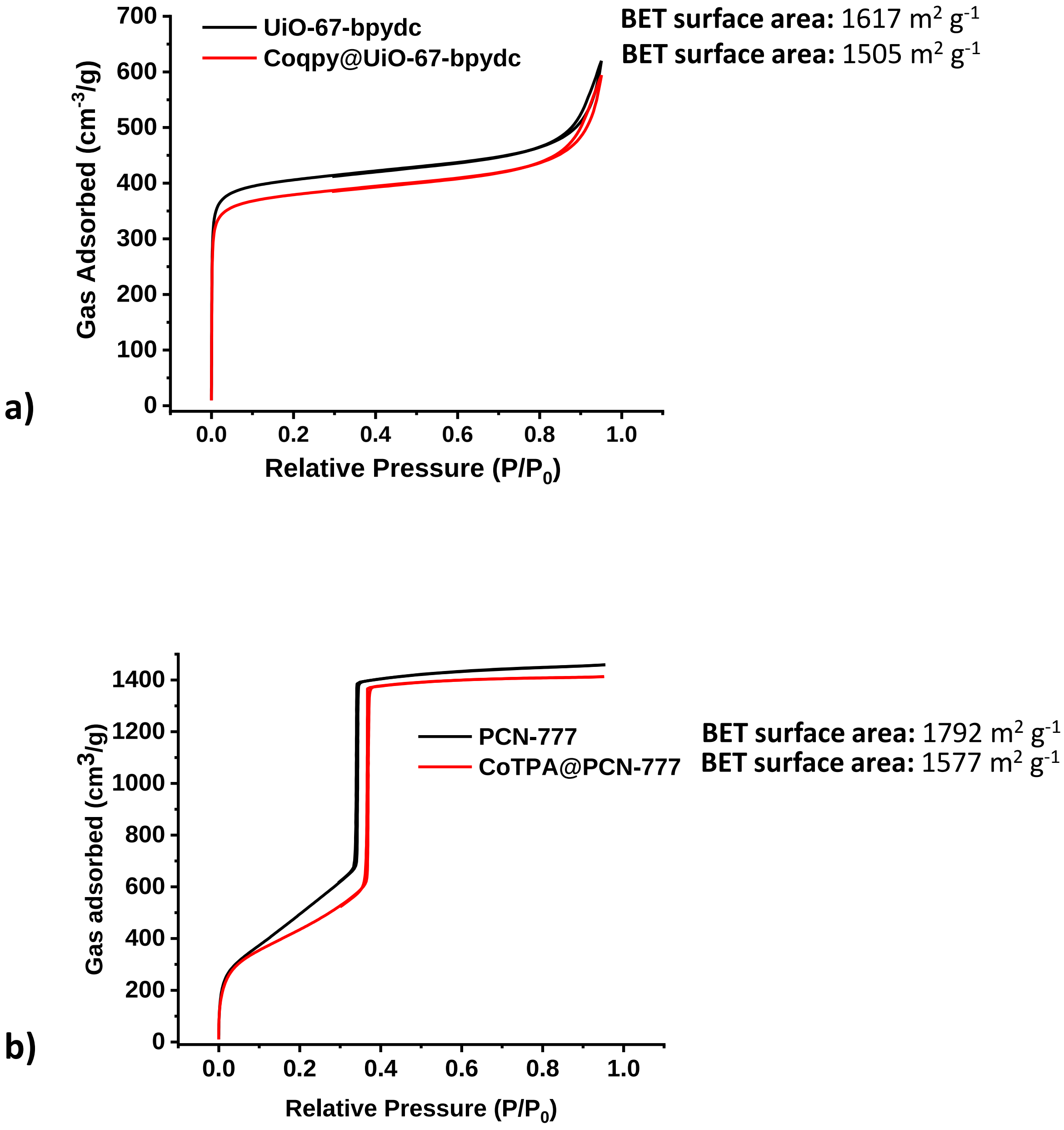

Figure S3. N_2 adsorption isotherms at 77 K of a) UiO-67-bpydc and **Coqpy@UiO-67-bpydc**, and b) PCN-777 and **CoTPA@PCN-777**.

Table S1. Comparison between the Co/Zr_6, Cl/Zr_6 and Ru/Zr_6 ratios determined by EDS analysis (Exp.) and the ratios calculated (Calc.) using the formula indicated below for **Coqpy@UiO-67-bpydc** and **CoTPA@PCN-777** before and after the photocatalytic events.

	Co/Zr_6		**Cl/Zr_6**		**Ru/Zr_6[a]**
	Calc.	**Exp.**	**Calc.**	**Exp.**	**Exp.**
Coqpy@UiO-67-bpydc	0.10	0.11	0.20	0.18	-
Coqpy@UiO-67-bpydc after catalysis	0.10	0.10	0.20	0.18	0.40
CoTPA@PCN-777	0.04	0.04	0.08	0.09	-
CoTPA@PCN-777 after catalysis	0.04	0.05	0.08	0.08	0.45

[a] The presence of Ru detected in both samples by EDS measurements indicates that a small amount of PS has been immobilized in the MOFs during the catalytic events.

We have considered the following formulae, deduced from EDS measurements and TGA analyses (see below):

For **Coqpy@UiO-67-bpydc:**

$[Zr_6O_4(OH)_8(H_2O)_4][C_{12}H_6N_2O_4]_4[Co(C_{20}N_4H_{14})(H_2O)_2]_{0.10}(ClO_4)_{0.20}\cdot 3H_2O$

For **CoTPA@PCN-777**:

$[Zr_6O_4(OH)_{10}(H_2O)_6][C_{24}H_{12}N_3O_6]_2[CoC_{18}N_4Cl]_{0.04}Cl_{0.04}\cdot 11H_2O\cdot 2DEF$ with DEF = diethylformamide

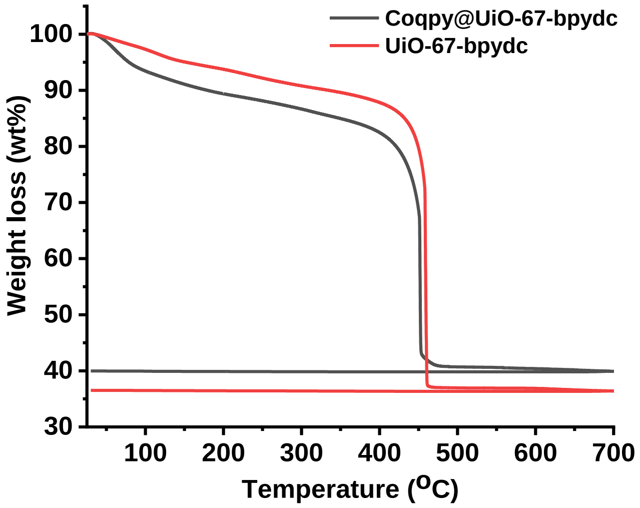

Figure S4. Thermogravimetric curves of UiO-67-bpydc and **Coqpy@UiO-67-bpydc**.

Two main weight losses are observed: the first loss below 200°C corresponds to the removal of solvent molecules, the weight loss between 200 and 450°C corresponds to linker combustion along with the formation of inorganic oxides. For a non-defective UiO-67-bpydc MOF of formula $Zr_6O_4(OH)_4(bpydc)_6$ this second weight loss, corresponding to the formation of ZrO_2, should be around 65%. The lower experimental weight loss (~56%) indicates the presence of linker deficiencies.[13] It has been reported that $bpydc^{2-}$ linkers are replaced by modulator molecules, in this study acetate, and also by formate coming from the decomposition of DMF. NMR spectroscopy of UiO-67-bpydc digested in NaOD solution allowed to estimate the ratios between the different organic molecules (bpydc/acetate/formate) (Fig. S6). The other missing linkers are replaced by OH^- and H_2O molecules.

Table S2. Comparison between calculated and experimental weight losses (corresponding to solvent departure) and residual weight after the formation of oxides determined by TGA analysis for UiO-67-bpydc and **Coqpy@UiO-67-bpydc**.

	Weight loss (solvent departure)		**Residual weight (oxides)**	
	Calc.	**Exp.**	**Calc.**	**Exp.**
UiO-67-bpydc	7.3	7.9	35.8	36.4
Coqpy@UiO-67-bpydc	6.8	8.8	38.9	39.9

We have considered the following formulae:
$[Zr_6O_4(OH)_{5.4}(H_2O)_{1.4}][C_{12}H_6N_2O_4]_{4.6}[CH_3CO_2]_{0.8}[HCO_2]_{0.6}\bullet 1.7DMF$ (M = 2041 g mol^{-1}) for UiO-67-bpydc

$[Zr_6O_4(OH)_8(H_2O)_4][C_{12}H_6N_2O_4]_4[Co(C_{20}N_4H_{14})(H_2O)_2]_{0.10}(ClO_4)_{0.20}\bullet 3H_2O$ (M = 1903 g mol^{-1}) for **Coqpy@UiO-67-bpydc**

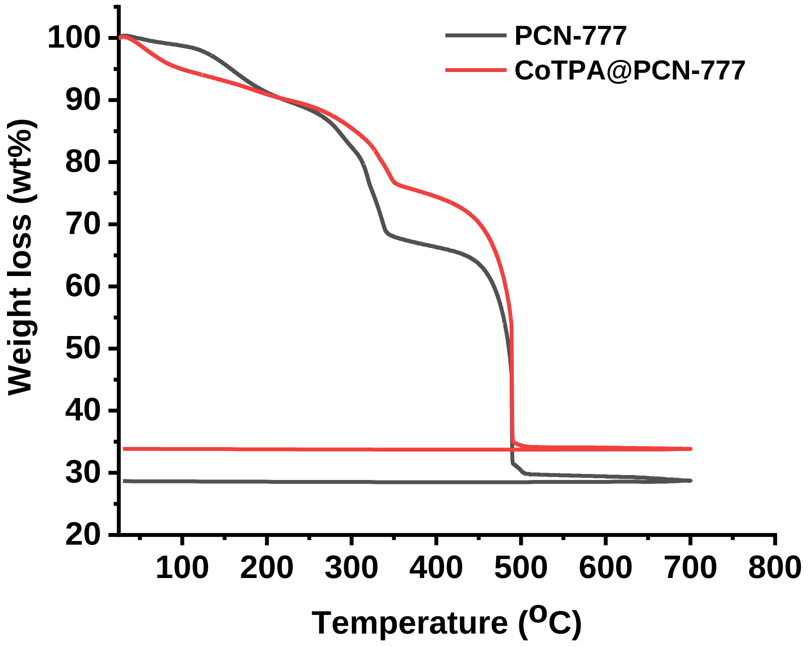

Figure S5. Thermogravimetric curves of PCN-777 and **CoTPA@PCN-777**.

Table S3. Comparison between calculated and experimental weight losses (corresponding to solvent departure) and residual weight after the formation of oxides determined by TGA analysis for PCN-777 and **CoTPA@PCN-777**.

	Weight loss (solvent departure)		**Residual weight (oxides)**	
	Calc.	**Exp.**	**Calc.**	**Exp.**
PCN-777	31.0	31.8	28.7	28.7
CoTPA@PCN-777	18.4	23.5	34.0	33.8

We have considered the following formulae:

$[Zr_6O_4(OH)_{10}(H_2O)_6][C_{24}H_{12}N_3O_6]_2 \bullet 8DEF$ (M = 2575 g mol^{-1}) for PCN-777

$[Zr_6O_4(OH)_{10}(H_2O)_6][C_{24}H_{12}N_3O_6]_2[CoC_{18}N_4Cl]_{0.04}Cl_{0.04} \bullet 11H_2O \bullet 2DEF$ (M = 2182 g mol^{-1}) for **CoTPA@PCN-777**

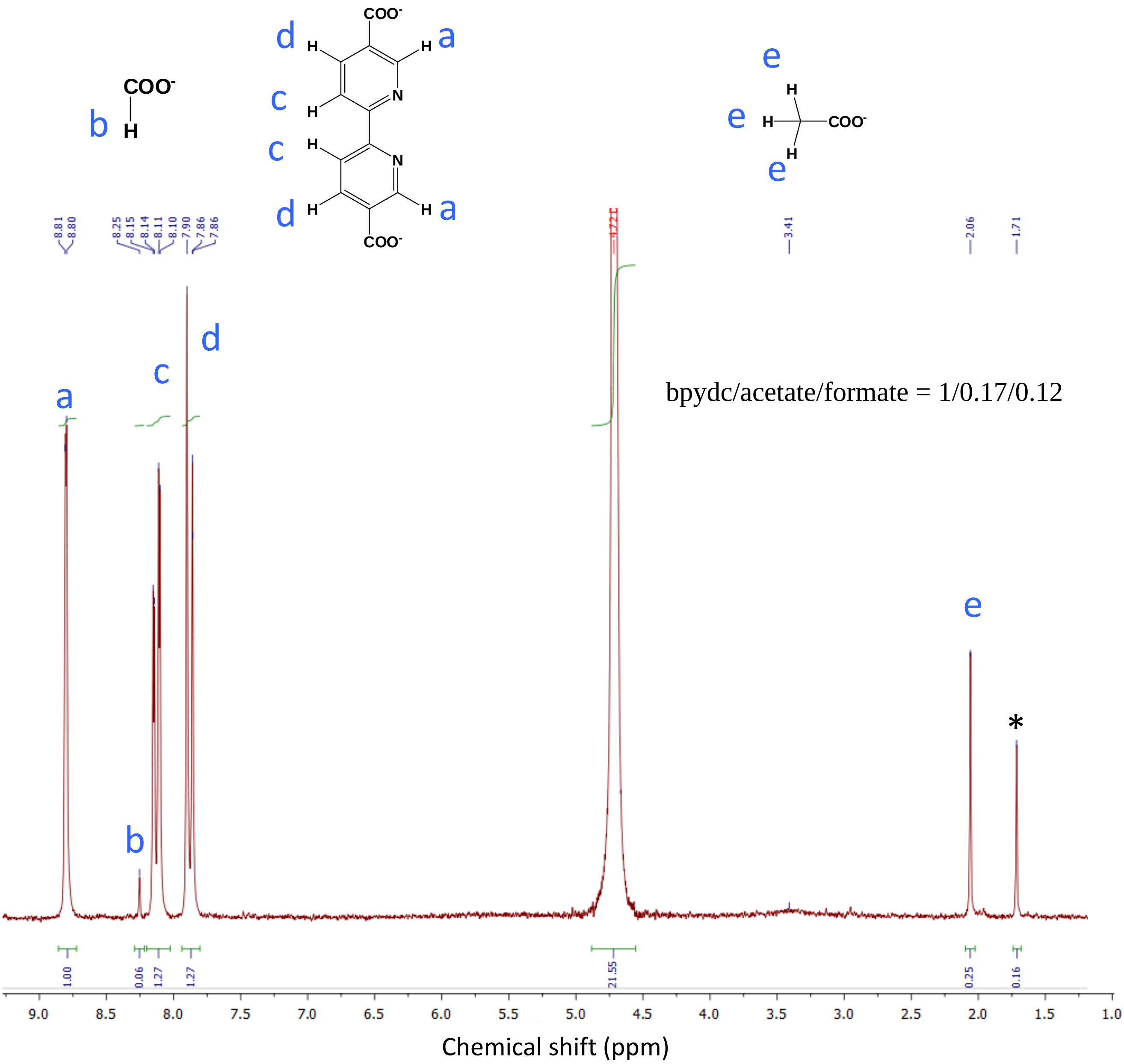

Figure S6. ^{1}H NMR spectrum of UiO-67-bpydc digested in NaOD with the attribution of H in the various molecules. The star refers to acetone impurity.

Table S4. Photocatalytic CO_2 reduction experiments using **Coqpy@UiO-67-bpydc** as catalyst.[a]

Entry	**SED**	**Photosensitizer**	**CO (μmol)**	**H_2 (μmol)**	**Selectivity CO (%)**
1	TEOA (0.2 mL)	$[Ru(bpy)_3]Cl_2$ (0.5 mM)	2.77	0.97	74
2	TEA (0.2 mL)	$[Ru(bpy)_3]Cl_2$ (0.5 mM)	0.76	1.57	33
3	BIH (5 mM)	$[Ru(bpy)_3]Cl_2$ (0.5 mM)	5.89	0.20	95
4[b]	BIH (5 mM)	$[Ru(bpy)_3]Cl_2$ (0.5 mM)	0	0.23	0
5	-	$[Ru(bpy)_3]Cl_2$ (0.5 mM)	0	0	0
6	BIH (5 mM)	-	0	0	0
7	BIH (20 mM)	$[Ru(bpy)_3]Cl_2$ (1 mM)	9.20	0.32	97
8	BIH (20 mM)	$[Ru(phen)_3](PF_6)_2$ (1 mM)	14.80	1.06	93

[a] Reaction conditions: **Coqpy@UiO-67-bpydc** (1.0 mg), photosensitizer $[Ru(bpy)_3]Cl_2$ (0.5 to 1 mM) or $[Ru(phen)_3](PF_6)_2$ (1 mM) and sacrificial electron donor (SED) (TEOA (0.2 mL) or TEA (0.2 mL) or BIH (5 to 20 mM)) in 3 mL (2.5 mL CH_3CN + 0.5 mL H_2O) solutions and irradiated with a solar simulator AM 1.5G with a 400 nm cut-off filter, CO_2 (99.999%), reaction time 24 h. [b] Argon was used instead of CO_2.

Table: S5. CO_2 photocatalytic activity of **Coqpy@UiO-67-bpydc** and UiO-67 using $[Ru(phen)_3](PF_6)_2$ as photosensitizer.[a]

Entry	**Catalyst**	**Solvent**	**Product yield (μmol)**			**Selectivity CO (%)**
			CO	**H_2**	**$HCOO^-$**	
1	**Coqpy@UiO-67-bpydc**	CH_3CN+H_2O	14.80	1.06	0.54	90
2	-	CH_3CN+H_2O	1.07	0.34	1.29	40
3	**Coqpy@UiO-67-bpydc**	CH_3CN	0	0	1.15	0
4[b]	**Coqpy@UiO-67-bpydc**	CH_3CN+H_2O	11.70	5.81	2.61	58
5	UiO-67-bpydc	CH_3CN+H_2O	0.97	0.32	1.36	36

[a] Reaction conditions: **Coqpy@UiO-67-bpydc** (1.0 mg) or UiO-67-bpydc (1.0 mg), photosensitizer $[Ru(phen)_3](PF_6)_2$ (3 mg, 1 mM) and sacrificial electron donor (SED) (BIH (20 mM)) in 3 mL (2.5 mL CH_3CN + 0.5 mL H_2O) solutions and irradiated with a solar simulator AM 1.5G with a 400 nm cut-off filter, CO_2 (99.999%), reaction time 24 h.[b] Sacrificial electron donor (SED) = BIH (20 mM)+TEOA (0.1 mL).

Table S6. Photocatalytic CO_2 reduction experiments using **CoTPA@PCN-777** as catalyst.[a]

Entry	SED	Photosensitizer	CO (μmol)	H_2 (μmol)	Selectivity CO (%)
1	TEOA (0.2 mL)	$[Ru(phen)_3](PF_6)_2$ (0.3 mM)	3.02	0.12	93
2	TEA (0.2 mL)	$[Ru(phen)_3](PF_6)_2$ (0.3 mM)	2.84	1.89	60
3	BIH (5 mM)	$[Ru(phen)_3](PF_6)_2$ (0.3 mM)	5.85	1.02	85
4[b]	BIH (5 mM)	$[Ru(phen)_3](PF_6)_2$ (0.3 mM)	0	0.26	0
5	-	$[Ru(bpy)_3](Cl)_2$ (0.5 mM)	0	0	0
6	BIH (5 mM)	-	0	0	0
7	BIH (5 mM)	$[Ru(bpy)_3](Cl)_2$ (0.5 mM)	3.81	2.37	61
8	BIH (20 mM)	$[Ru(phen)_3](PF_6)_2$ (1 mM)	7.09	0.59	93

[a] Reaction conditions: **CoTPA@PCN-777** (1.0 mg), photosensitizer $[Ru(bpy)_3]Cl_2$ (0.5 to 1 mM) / $Ru(Phen)_3(PF_6)_2$ (0.3 mM to1 mM)] and sacrificial electron donor (SED), (TEOA (0.1 mL) or TEA (0.1 mL) or BIH (5 to 20 mM)), solution 3 mL (2.5 mL CH_3CN + 0.5 mL H_2O) irradiated with a solar simulator AM 1.5G with a 400 nm cut-off filter, CO2 (99.999%), reaction time (24 h). [b]Argon was used instead of CO_2.

Table: S7. CO_2 photocatalytic activity of **CoTPA@PCN-777** and PCN-777 using $[Ru(phen)_3](PF_6)_2$ as a photosensitizer.[a]

Entry	Catalyst	Solvent	Product yield (μmol)			Selectivity CO (%)
			$HCOO^-$	CO	H_2	
1	**CoTPA@PCN-777**	CH_3CN+H_2O	0.84	8.89	0.59	83
2	-	CH_3CN+H_2O	0	0	0	0
3	**CoTPA@PCN-777**	CH_3CN	0.52	0.03	0	6
4	PCN-777	CH_3CN+H_2O	1.30	1.15	0.34	41

[a] Reaction conditions: **CoTPA@PCN-777** or PCN-777 (1.0 mg), photosensitizer $[Ru(Phen)_3](PF_6)_2$ (3 mg, 1mM) and sacrificial electron donor (SED) (BIH (20 mM)) in 3 mL (2.5 mL CH_3CN + 0.5 mL H_2O) solutions and irradiated with a solar simulator AM 1.5G with a 420 nm cut-off filter, CO_2 (99.999%), reaction time 24 h.

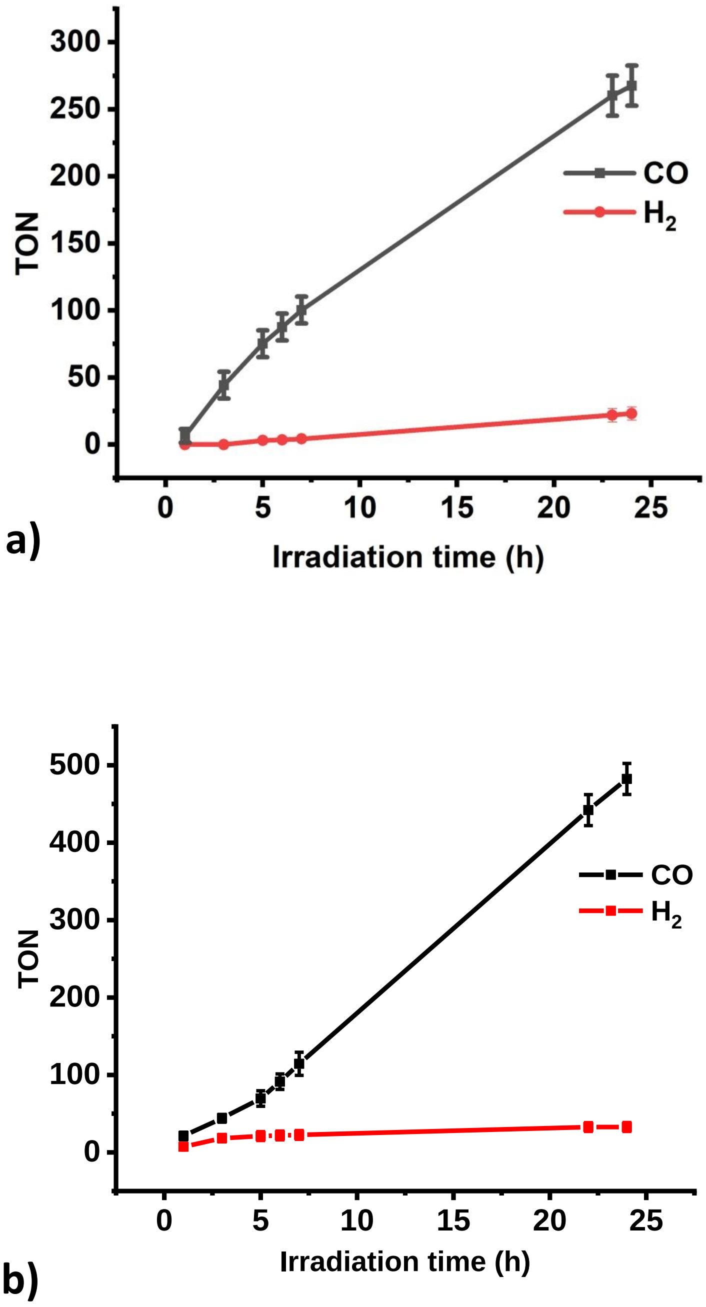

Figure S7. CO (black) and H_2 (red) TONs as a function of time during irradiation of a CO_2-saturated CH_3CN/H_2O (2.5 mL/0.5 mL) solution containing b) **Coqpy@UiO-67-bpydc** (1 mg) or **CoTPA@PCN-777** (1 mg), 1 mM $[Ru(phen)_3](PF_6)_2$ and 20 mM BIH, based on the averaged results of three parallel reaction runs.

Table S8. Photocatalytic production of CO and H_2 for **Coqpy@UiO-67-bpydc** and **CoTPA@PCN-777** as a function of time.

Catalyst	**Time**	**Product Yield (μmol)**		**CO TON**	**CO selectivity (%)**
		CO	**H_2**		
Coqpy@UiO-67-bpydc	1 h	0.29	0	6	100
	3 h	2.03	0	38	100
	5 h	4.86	0.13	92	97
	23 h	13.78	1	260	93
	24 h	14.18	1.06	268	93
CoTPA@PCN-777	1 h	0.38	0.13	21	74
	3 h	0.80	0.33	44	71
	5 h	1.27	0.38	70	77
	6 h	1.66	0.39	91	81
	22 h	8.11	0.59	442	93
	24 h	8.82	0.59	482	94

[a] Reaction conditions: Coqpy@UiO-67-bpydc (1.0 mg), photosensitizer $[Ru(phen)_3](PF_6)_2$ (3 mg, 1 mM) and sacrificial electron donor (SED) (BIH (20 mM)) in 3 mL (2.5 mL CH_3CN + 0.5 mL H_2O) solutions irradiated with a solar simulator AM 1.5G with a 400 nm cut-off filter, CO_2 (99.999%).

Table S9. Photocatalytic activity of **Coqpy@UiO-67-bpydc** and **CoTPA@PCN-777** compared to other Cat@MOFs based photocatalytic systems.

Heterogeneous Cat@MOFs catalysts[a] (mass)	**CO rate (µmol g^{-1} h^{-1})**	**H_2 rate (µmol g^{-1} h^{-1})**	**HCOOH rate (µmol g^{-1} h^{-1})**	**CO TON (time)**	**Selectivity CO (%)**	**PS**	**SD**	**Solvent/ Proton donor**	**Wavelength**	**Reference**
CoTPA@PCN-777 (1 mg)	**368**	**25**	**-**	**482 (24 h)**	**94**	**$Ru(phen)_3$**	**BIH**	**CH_3CN/H_2O**	**>400**	**This work**
Coqpy@UiO-67-bpydc (1 mg)	**617**	**44**	**-**	**268 (24 h)**	**93**	**$Ru(phen)_3$**	**BIH**	**CH_3CN/H_2O**	**>400**	**This work**
$Re(bpydc)(CO)_3Cl$@PCN-222(Zn) (3 mg)	1070	-	-	1893 (59 h)	100	TCPP(Zn) (MOF linker)	BIH	DMF/H_2O	>500	*ACS Appl. Mater. Interfaces* 2021, **13**, 2710
($Re(bpydc)(CO)_3Br$, $Ru(bpy)_2(bpydc)$)@NH_2-MIL-101(Al) (3.5 mg)	NM[b]	-	-	9.2 (10 h)	100	$Ru(bpy)_2(bpdc)$ (MOF linker)	TEOA	CH_3CN	450	*ACS Catal.* 2021, **11**, 871
($Re(bpymc)(CO)_3Cl$, $Ru(bpy)_2(bpymc)$)@MBA-MOF-808 (3 mg)	440	-	-	28 (30 h)	>99	$Ru(bpy)_2(bpymc)$	H_2O	H_2O	400-800	*Energy Environ. Sci.* 2021, **14**, 2429
(Cu(bpydc)(pyridine)Cl, $Ru(bpy)_2(bpydc)$)@EuMOF (2 mg)	96 (10h)	-	-	NM	100	$Ru(bpy)_2(bpdc)$ (MOF linker)	TIPA	CH_3CN/H_2O	>400	*J. Am. Chem. Soc.* 2021, **143**, 6114
($Ru(bpydc)(CO)_2Cl_2$, $Ru(bpy)_2(bpydc)$@MOF-253(Al) (5 mg)	46	18	121	7.3 (8 h)	24.9	$Ru(bpy)_2(bpdc)$ (MOF linker)	TEOA	CH_3CN	420-800	*Chem. Commun.* 2015, **51**, 2645
(Ni(bpet), $Ru(bpy)_2(bpydc)$)@UiO-67 (20 mg)	426	-	-	581 (20 h)	99	$Ru(bpy)_2(bpdc)$ (MOF linker)	BIH + TEOA	DMF/H_2O	~420	*Science Bulletin* 2019, **64**, 976
$Co(bpydc)Cl_2$@UiO-67 (1 mg)	3292	7095	-	49 (4 h)	31.7	$Ru(bpy)_3$	TEOA	CH_3CN/H_2O	400-800	*ACS Appl. Mater. Interfaces* 2020, **12**, 24059
$Re(bpydc)(CO)_3Cl$@UiO-67 (1 mg)	412	227	-	10 (4 h)	64.5	$Ru(bpy)_3$	TEOA	CH_3CN/H_2O	400-800	*ACS Appl. Mater. Interfaces* 2020, **12**, 24059

[a] The formula of the molecular catalyst (Cat) is written in blue, [b]NM = not mentioned

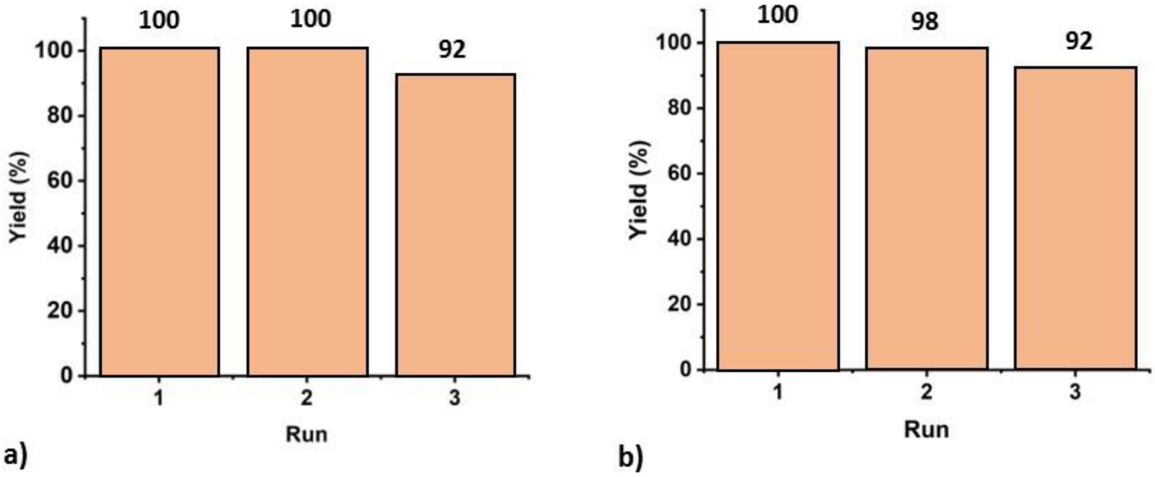

Figure S8. Recyclability tests in three consecutive experiments of a) **Coqpy@UiO-67-bpydc** and b) **CoTPA@PCN-777** catalysts towards photocatalytic production of CO in the presence of $[Ru(phen)_3](PF_6)_2$ (1 mM) and BIH (20 mM) in a CO_2-saturated CH_3CN/H_2O (2.5 mL / 0.5 mL) solution after 6 h and 24 h catalytic runs, respectively.