Electronic Supplementary Material (ESI) for CrystEngComm.
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Supplementary Information

Two Zr−based heterometal−organic frameworks for efficient CO_2 reduction under visible light

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Experimental

Materials

Zirconocene dichloride, isonicotinic acid, $MnCl_2·4H_2O$, $NiCl_2·6H_2O$, other chemicals and solvents for the synthesis were purchased from Alfa, all of them were used without further purification.

Characterization

The elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Powder X-ray diffraction (PXRD) patterns were carried out on an X-ray diffractometer of Rigaku, Rint 2000.Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer TG-7 analyzer heated from 25 °C to 800 °C under N_2 at a heating rate of 10 °C min^{-1}. Field emission-scanning electron microscopy (FE-SEM; Hitachi S-5500) was performed to observe the micro-structures of the hybrid photocatalysts. The UV−Vis absorption spectra of 200−800 nm were obtained on a Shimadzu UV−2550 spectrophotometer. The Fourier transform infrared (FT−IR) spectra were acquired using a Matton Alpha−Centauri FT−IR spectrophotometer with KBr pellets, in the range of 4000–400 cm^{-1}.

Crystal structure determination

Single-crystal X-ray diffraction data for **1** and **2** were collected by Bruker Apex-II CCD diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 173 K. The structures were solved by the direct method of SHELXS and full−matrix least−squares on F^2 was applied using the SHELXL program to further refinement. The disordered guest water molecules in this structure were removed by SQUEEZE in structural refinement. The crystallographic data and structure refinement parameters for **1** and **2** are summarized in Table S1.

Electrochemical Measurements

The photoelectron chemical characterizations were performed on the electrochemical workstation with a three-electrode configuration using the assembled photoelectrodes as the working electrode, Pt as counter electrode and 0.2 M Na_2SO_4 as electrolyte. The test was measured at frequencies of 800 Hz, 1000 Hz and 1200 Hz.

Results and discussion

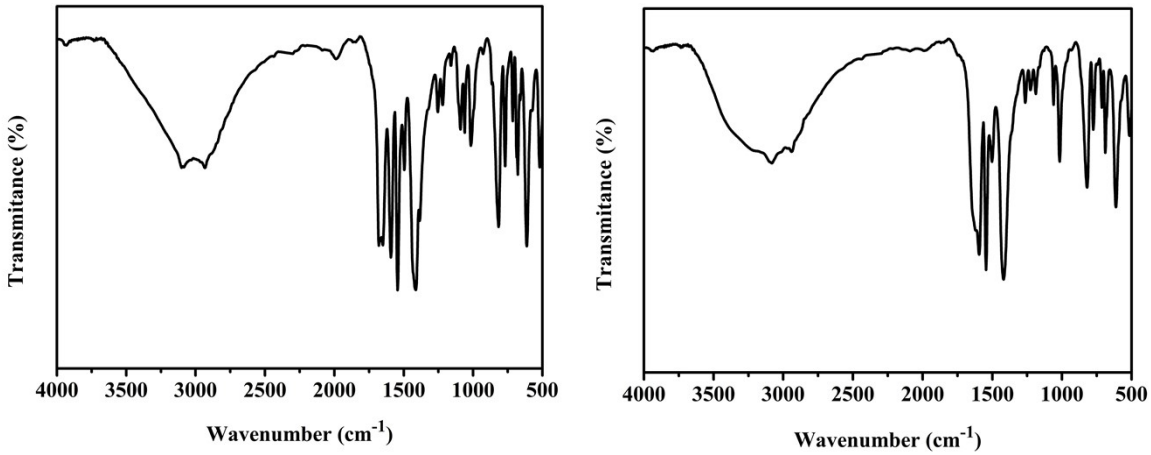

Fig. S1. IR spectra of **1** (left) and **2** (right).

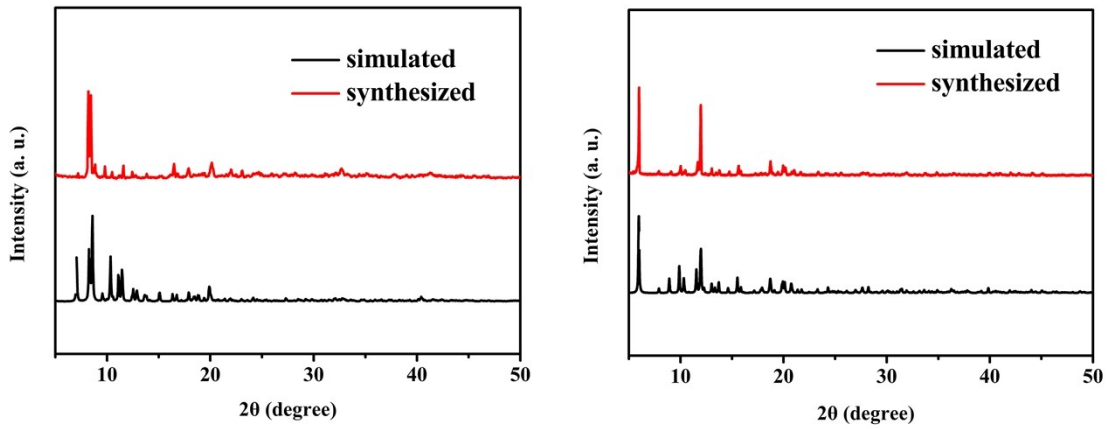

Fig. S2. PXRD patterns of **1** (left) and **2** (right) with simulated (black line), as-synthesized (red line).

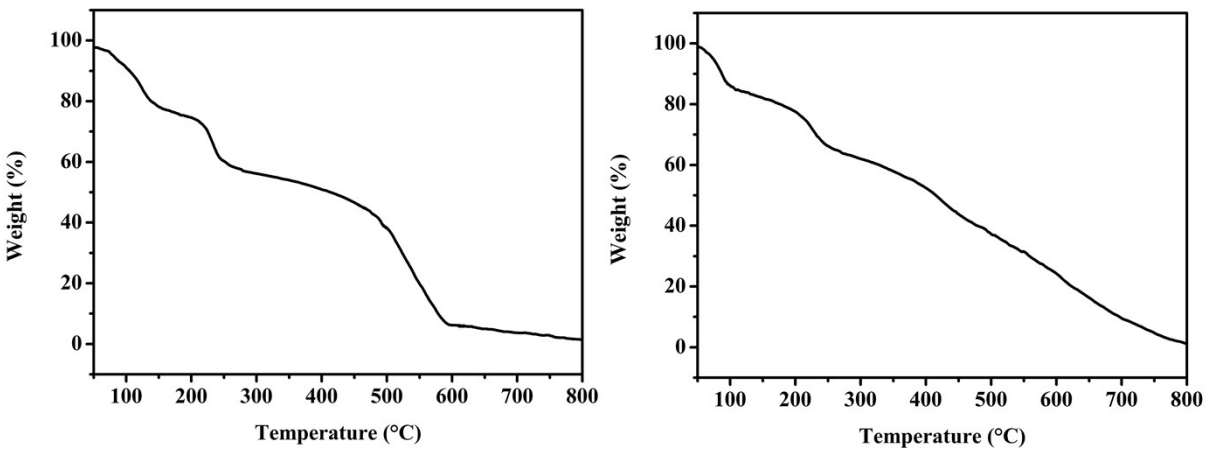

Fig. S3. TG curves of **1** (left) and **2** (right).

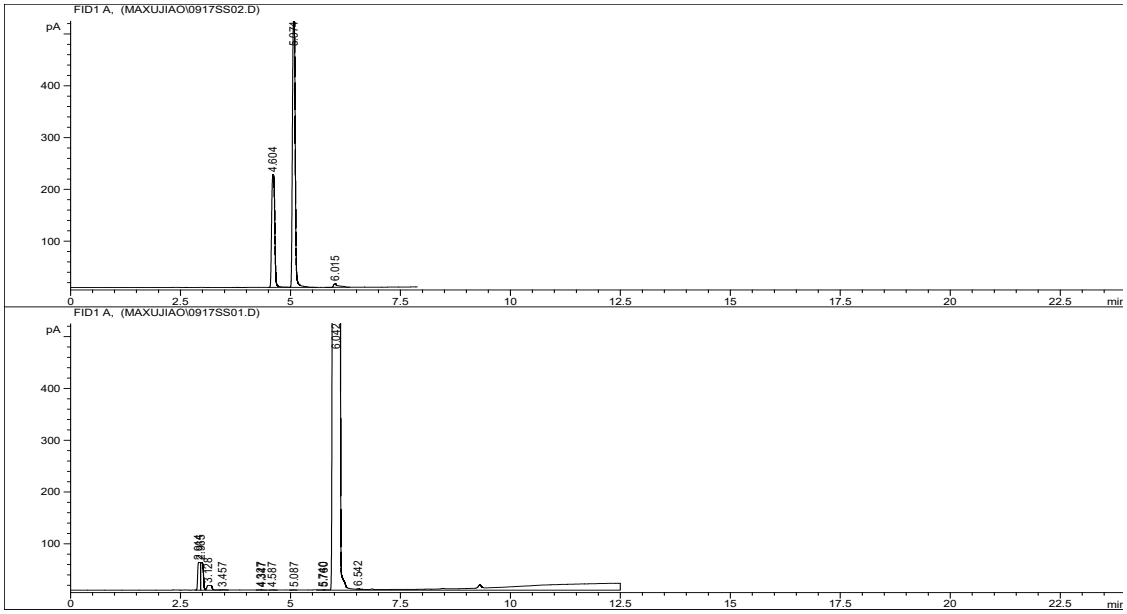

Fig. S4. High-performance liquid chromatography of compound **1** (top) and compound **2** (bottom).

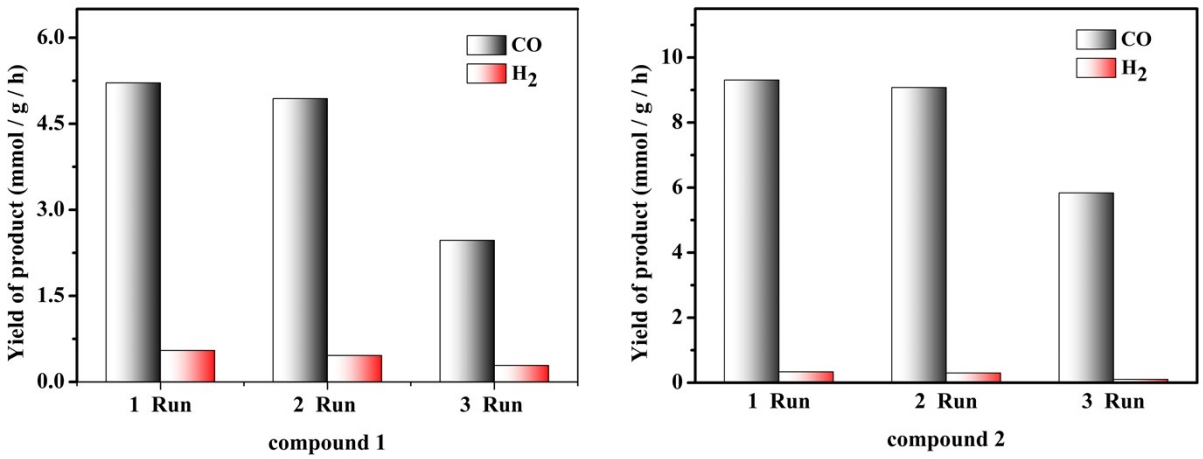

Fig. S5. The recyclability of the **1** (left) and **2** (right) system after each one hour of reaction.

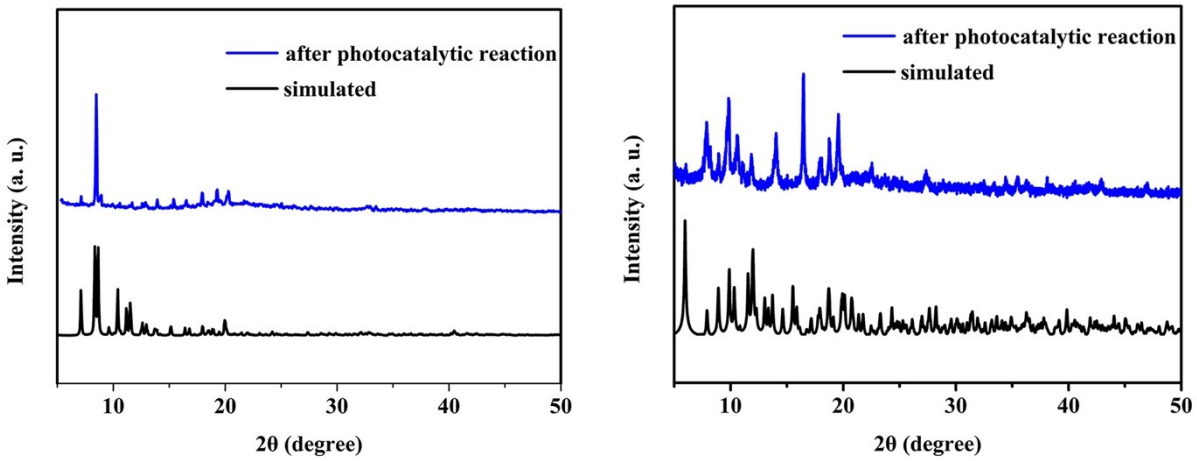

Fig. S6. PXRD patterns of **1** (left) and **2** (right) with simulated (black line), after photocatalytic reaction (blue line).

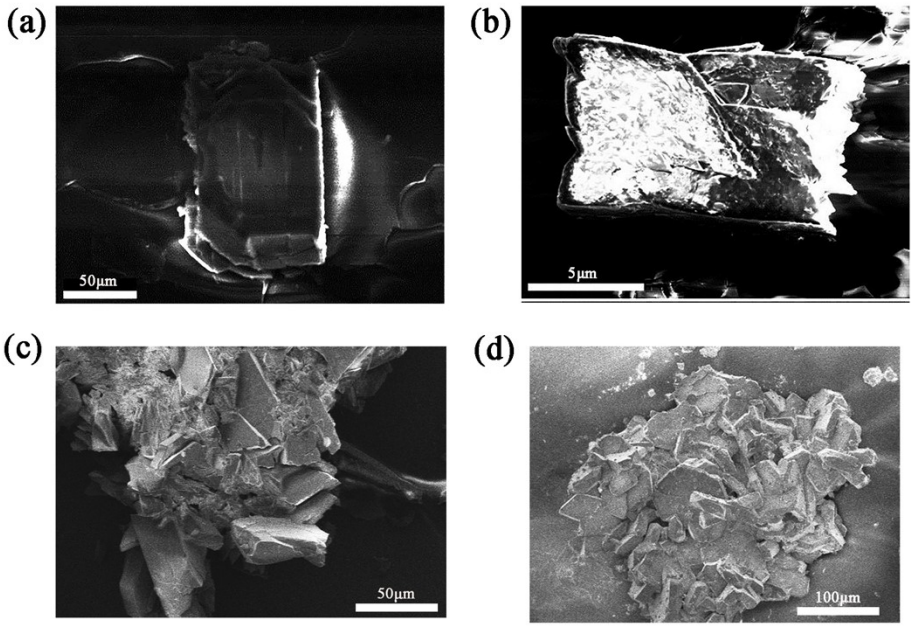

Fig. S7. SEM images of **1** (a) and after reaction (c). **2** (b) and after reaction (d).

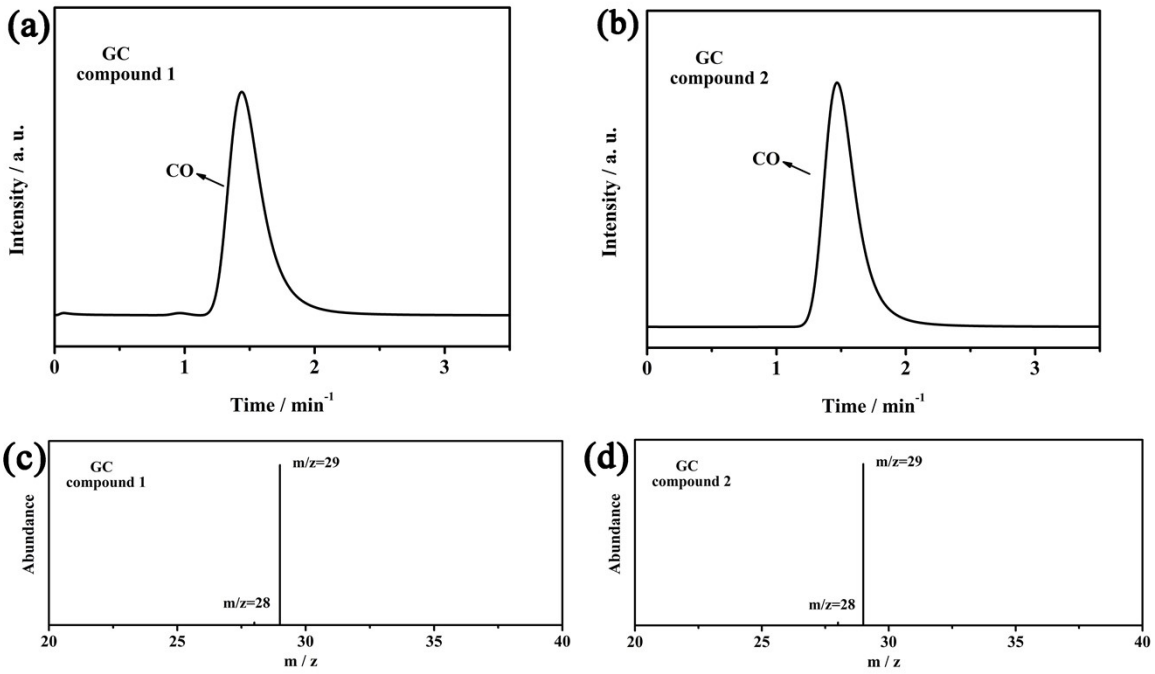

Fig. S8. Gas chromatogram of compound **1** (a) and compound **2** (b). mass spectra analyses of the generated gas in the photocatalytic reduction of $^{13}CO_2$ by compound **1** (c) and compound **2** (d).

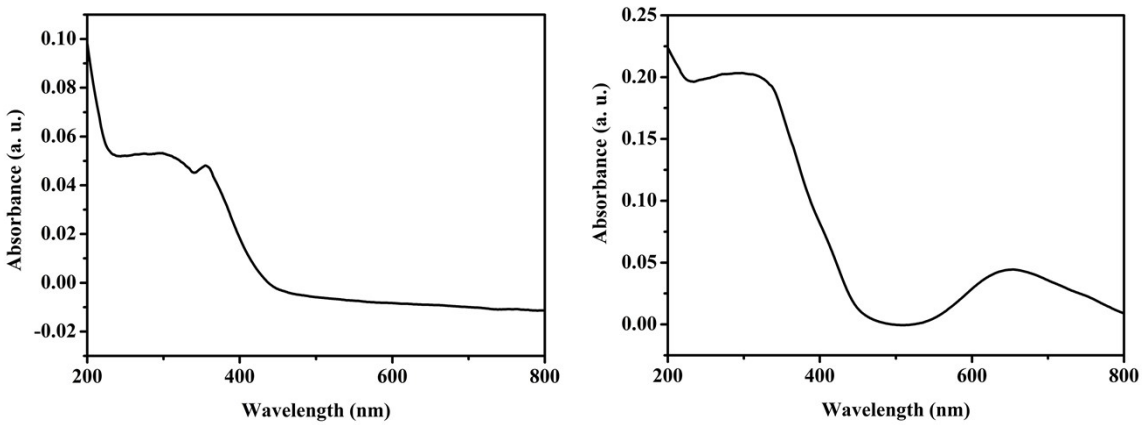

Fig. S9. UV-Vis spectra of **1** (left) and **2** (right).

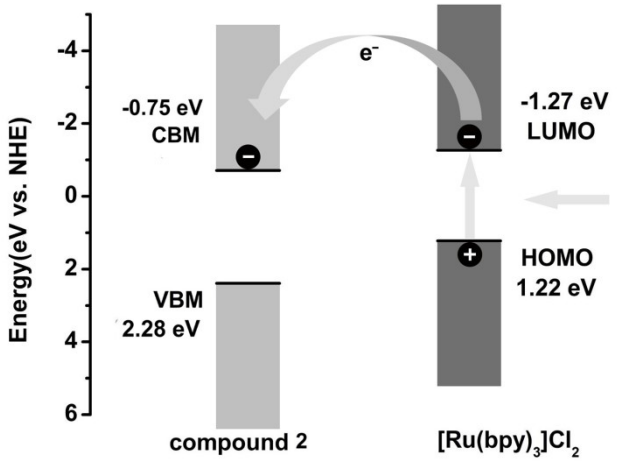

Fig. S10. Energy−level diagrams with electron transfer from $[Ru(bpy)_3]Cl_2$ to compound **2**.

Table S1. Crystal data and structure refinement for **1** and **2.**

compound	1	2
Empirical formula	$C_{72}H_{76}Cl_4MnN_8O_{22}Zr_6$	$C_{36}Cl_3H_{52}N_4NiO_{19}Zr_3$
Formula weight	2149.46	1283.53
Temperature/K	173.02	173.02
Crystal system	triclinic	orthorhombic
Space group	P-1	$P2_12_12_1$
a/Å	11.1927(10)	10.510(4)
b/Å	12.9714(11)	16.988(7)
c/Å	21.8377(19)	29.610(12)
α/°	80.980(5)	90
β/°	77.033(5)	90
γ/°	76.035(5)	90
Volume/Å^3	2980.6(5)	5287(4)
Z	1	4
ρ_{calc}g/cm^3	1.196	1.613
μ/mm^{-1}	0.748	1.147
F(000)	1071.0	2588.0
2θ Range /°	5.778 - 50.266	4.76 - 50.344
Reflections collected	73007	39850
Independent reflections	10595 [R_{int} = 0.2068, R_{sigma} = 0.1150]	9415 [R_{int} = 0.1561, R_{sigma} = 0.1407]
Goodness-of-fit on F^2	1.038	0.990
Final R indexes [I>=2σ (I)]	R_1 = 0.0635, wR_2 = 0.1572	R_1 = 0.0559, wR_2 = 0.1086
Final R indexes [all data]	R_1 = 0.1330, wR_2 = 0.1865	R_1 = 0.1168, wR_2 = 0.1264

[a]$R_1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$. [b]$wR_2=[\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Table S2. Comparison of the photocatalytic performance of compounds 1 and 2 with Zr-MOF and its derivatives.

Catalyst	Light source (nm)	Slovent	Product (μmol g^{-1} h^{-1})	
Compound 1	420	TEOA/MeCN/H_2O	CO = 5211.33	This work
Compound 2	420	TEOA/MeCN/H_2O	CO = 9304.29	This work
UiO-66	300W Xe lamp 400–800	MeCN/TEOA	CO = 0	1
NH_2-UiO-66	500W Xe lamp	Acetonitrile/TEOA	CO = 40	2
CdS/NH_2-UiO-66	300W Xe lamp 400 - 760	Acetonitrile/TEOA/H_2O	CO = 87	3
UiO-66/CNNS	300W Xe lamp 400 - 760	Acetonitrile/TEOA/H_2O	CO = 9.9	4
ZrPP-1-Co	300W Xe lamp 420	Acetonitrile/TEOA	CO = 14	5

References

1 L. Shi, T. Wang, H. Zhang, K. Chang and J., Ye, *Adv. Funct. Master.*, 2015, **25**, 5360-5367.
2 D. Sun, Y. Fu, W. Liu, L. Ye, D. Wang, L. Yang, X. Fu and Z. Li, *Chem. Eur. J.*, 2013, **19**, 14279- 14285.
3 H. Zhao, X. Yang, R. Xu, J. Li, S. Gao and Cao, R., *J. Master. Chem. A.*, 2018, **6**, 20152-20160.
4 L. Shi, T. Wang, H. Zhang, K. Chang and Ye, J. *Adv. Funct. Master.,* **2015**, 25, 5360-5367.
5 E. X. Chen, M. Qiu, Y. F. Zhang, Y. S. Zhu, L. Y. Liu, Y. Y. Sun, X. Bu, J. Zhang, and Q. Lin, *Adv. Mater.* 2018, **30**, 1704388-1704395.