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Nickel metal-organic frameworks for visible-light CO_2 reduction under mild reaction conditions

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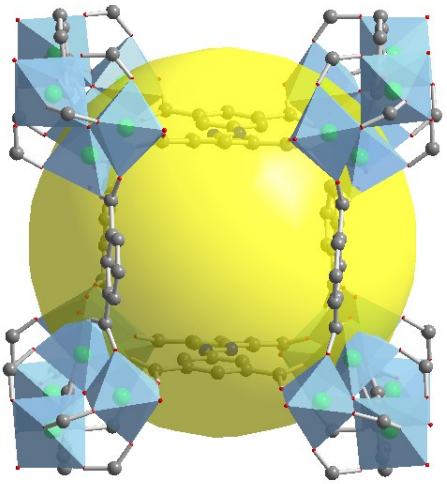

Fig. S1. Polyhedral structure. The large cavity is indicated by the yellow spheres. H atoms have been omitted for clarity.

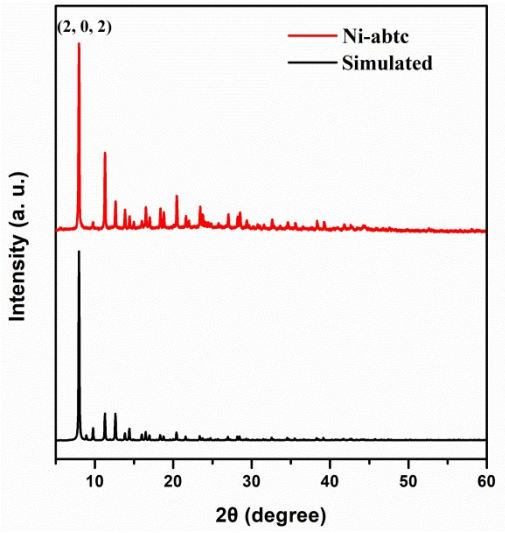

Fig. S2. Experimental and simulated XRD patterns for Ni-abtc sample.

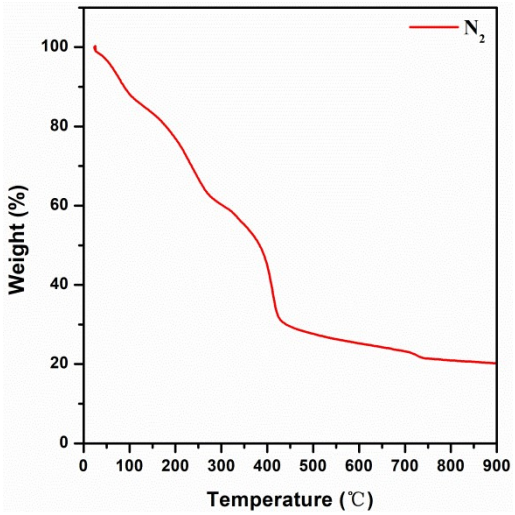

Fig. S3. The TG analysis of Ni-abtc in N_2 atmosphere.

Thermal stability of Ni-abtc was proved by thermogravimetric analyzer under N_2 atmosphere at a heating temperature rate of 10 °C min^{-1} up to 900 °C. The weight loss between 100 °C to 280 °C was ascribed to the leaving of coordinated water molecule, coordinated OH^- and physisorbed DMF in Ni-abtc. The weight loss between 280 °C to 900 °C was due to decomposition of the organic ligands.

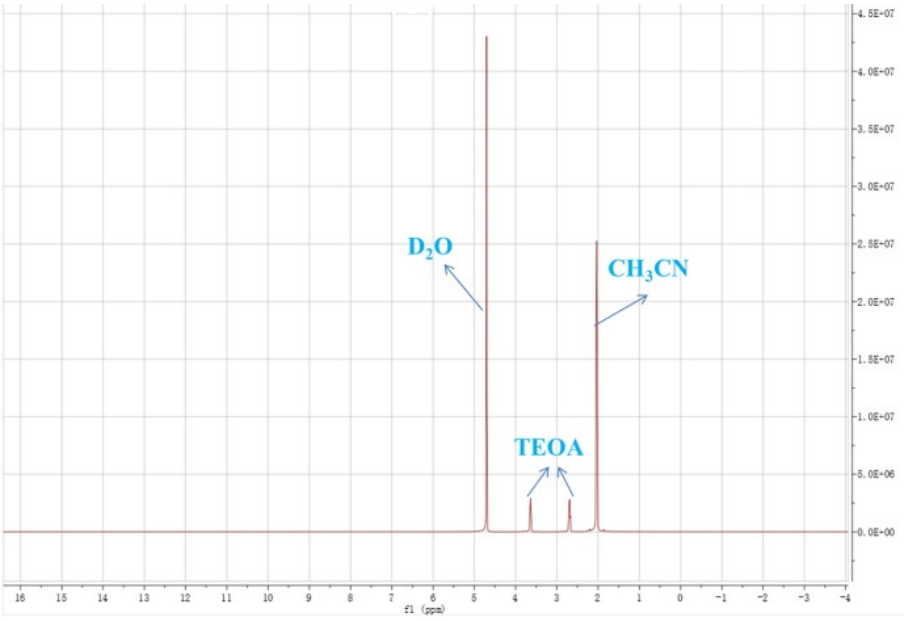

Fig. S4. The ^1H NMR spectrum for the liquid phase after CO_2 photoreduction reaction.

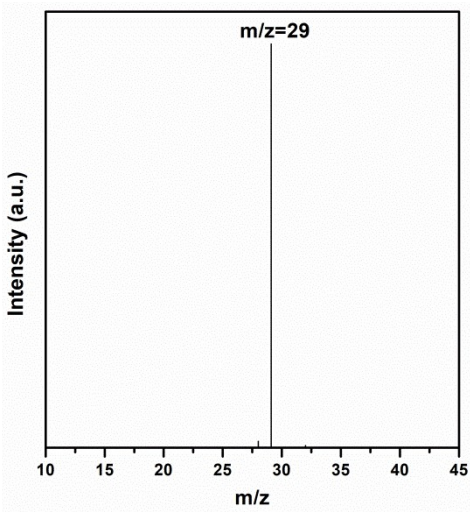

Fig. S5. GC-MS analysis of the generated ^{13}CO from $^{13}CO_2$ isotope experiment.

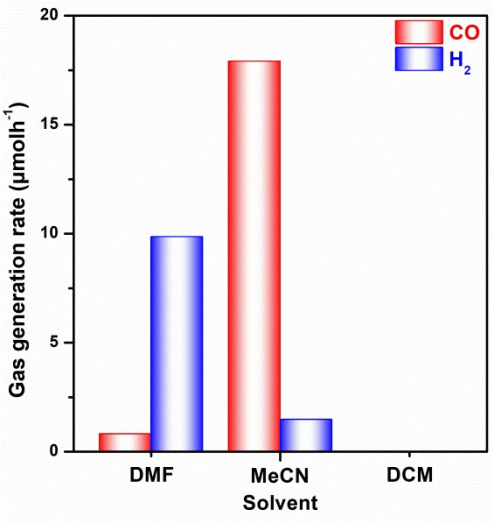

Fig. S6. The influence of the solvent on CO_2 photoreduction. (DMF, N,N-dimethylformamide; MeCN, acetonitrile; DCM, dichloromethane).

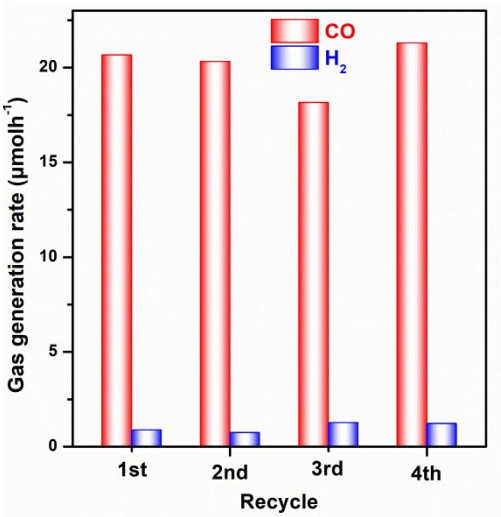

Fig. S7. Stability test of CO_2 photoreduction by Ni-abtc.

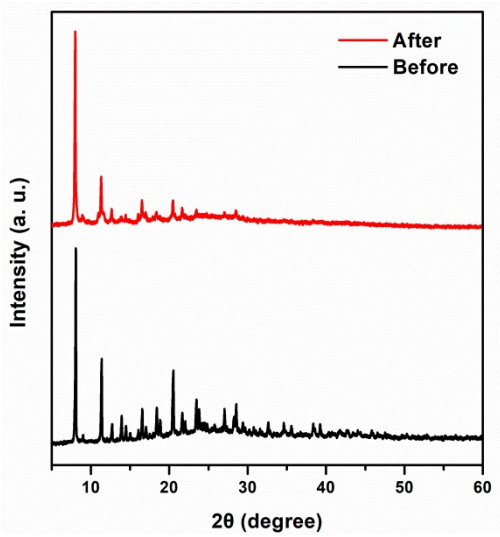

Fig. S8. XRD patterns of Ni-abtc samples before and after reaction.

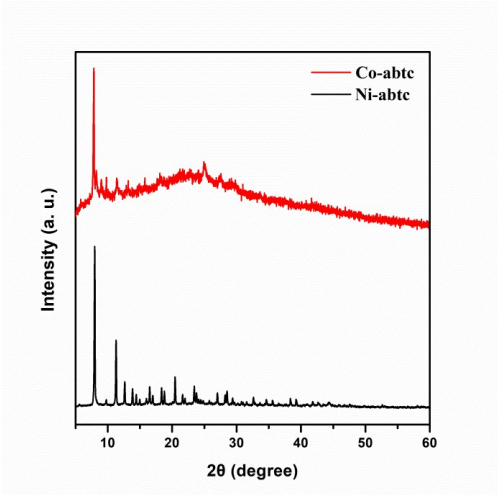

Fig. S9. XRD patterns of Co-abtc and Ni-abtc samples.

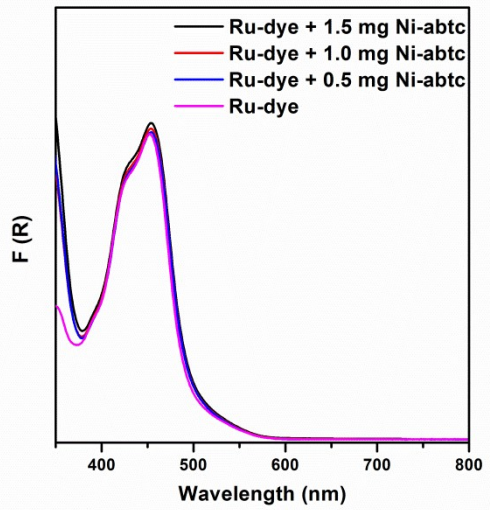

Fig. S10. UV-vis DRS spectra of photosensitizer **Ru-dye** upon the addition of increasing amounts of Ni-abtc, in solution of CH_3CN/H_2O (v:v = 3:2).

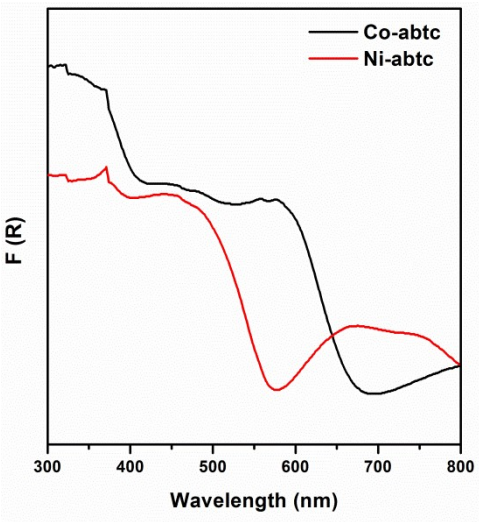

Fig. S11. UV-vis DRS spectra of Ni-abtc and Co-abtc samples.

Table S1. Crystal data and structure refinements for Ni-abtc.

Compounds	Ni-abtc
Formula	$C_{32}H_{12}N_4Ni_4O_{21.33}$
Formula weight	1028.63
T (K)	240
Space group	R-3
Crystal system	trigonal
a (Å)	31.3566 (3)
b (Å)	31.4566 (3)
c (Å)	38.3643 (5)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	32667.5 (6)
Z	6
Dcalcd (g cm^{-3})	0.941
μ(Mo Ka) (mm^{-1})	1.604
R_{int}	0.037
reflns collected	65579
Data Completeness measured	99.4
h,k,lmax	39,39,48
Tmin,Tmax	0.824,1.000
R_1, wR_2 [all data]	0.067, 0.2068
Mink Peak, Max Peak	-0.6, 1.9
Goodness-of-fit on F^2	1.031
R1, wR2 [I > 2σ(I)]	0.0679, 0.2007

Table S2. Comparison of the performance of CO_2 photoreduction.

Catalyst	Photosensitizer	Sacrificial agent	Major products evolution rate ($\mu molh^{-1}$)	CO_2 reduction selectivity	Ref
$LaCoO_3$	$Ru(bpy)_3^{2+}$	TEOA	CO: 44.2 H_2: 12.5	78 %	S[1]
$ZnCo_2O_4$	$Ru(bpy)_3^{2+}$	TEOA	CO: 25.1 H_2: 8.7	74.3 %	S[2]
$MnCo_2O_4$	$Ru(bpy)_3^{2+}$	TEOA	CO: 27 H_2: 8	77.1 %	S[3]
$CoSn(OH)_6$	$Ru(bpy)_3^{2+}$	TEOA	CO: 19.3 H_2: 3.0	86.5 %	S[4]
NiCoOPNPs@MHCFs	$Ru(bpy)_3^{2+}$	TEOA	CO: 16.6 H_2: -	-	S[5]
NC@$NiCo_2O_4$	$Ru(bpy)_3^{2+}$	TEOA	CO: 26.2 H_2: 3.4	88.6 %	S[6]
Co/C	$Ru(bpy)_3^{2+}$	TEOA	CO: 69 H_2: 2.1	64.2 %	S[7]
Co_3O_4	$Ru(bpy)_3^{2+}$	TEOA	CO: 200.1 H_2: 59.6	77.1 %	S[8]
$Ni(OH)_2$	$Ru(bpy)_3^{2+}$	TEOA	CO: 14.4 H_2: 0.58	96.1%	S[9]
Co-ZIF-67	$Ru(bpy)_3^{2+}$	TEOA	CO: 29.6 H_2: 14.8	66.6 %	S[10]
Co-ZIF-9	$Ru(bpy)_3^{2+}$	TEOA	CO: 41.8 H_2: 29.9	58 %	S[11]
Ni(TPA/TEG)	$Ru(bpy)_3^{2+}$	TEOA	CO: 26.6 H_2: -	100 %	S[12]
$Ni_3(HITP)_2$	$Ru(bpy)_3^{2+}$	TEOA	CO: 69 H_2: 2.1	97 %	S[13]
Ni MOLs	$Ru(bpy)_3^{2+}$	TEOA	CO: 12.5 H_2: 0.28	97.8 %	S[14]
Co-ZIF-67	$Ru(bpy)_3^{2+}$	TEOA	CO: 4.1 H_2: 2.4	63 %	S[15]
Ni-MOL-100	$[Ru(phen)_3]^{2+}$	TEOA	CO:11.89 H_2: 0.47	96.2 %	S[16]
Co MOLs	$Ru(bpy)_3^{2+}$	TEOA	CO: 4.61 H_2: 2.34	66.3 %	S[17]
BIF-29	$Ru(bpy)_3^{2+}$	TEOA	CO: 3.33 H_2: 0.7	82.6 %	S[18]
MAF-X27I-OH	$Ru(bpy)_3^{2+}$	TEOA	CO: 6.37 H_2: 0.12	98.2 %	S[19]
$[Ni(bpet)]^{2+}$	$Ru(bpy)_3^{2+}$	BIH	CO: 0.085	99 %	S[20]

Ni-abtc	$Ru(bpy)_3^{2+}$	TEOA	H_2: 0.008 CO: 19.13 H_2: 1.78	91.4 %	this work
Co-abtc	$Ru(bpy)_3^{2+}$	TEOA	CO: 11.6 H_2: 17.3	40.1 %	this work

References

[1] J. Qin, L. Lin, X. Wang, *Chem. Commun.* **2018**, *54*, 2272-2275.

[2] S. Wang, Z. Ding, X. Wang, *Chem. Commun.* **2015**, *51*, 1517-1519.

[3] S. Wang, Y. Hou, X. Wang, *ACS Appl. Mater. Interfaces.* **2015**, *7*, 4327-4335.

[4] Y. Gao, L. Ye, S. Cao, H. Chen, Y. Yao, J. Jiang, L. Sun, *ACS Sustainable Chem. Eng.* **2018**, *6*, 781-786.

[5] Y. Wang, S. Wang, X. W. Lou, *Angew. Chem. Int. Ed.* **2019**, *58*, 17236-17240.

[6] S. Wang, B. Y. Guan, X. W. Lou, *Energy Environ. Sci.* **2018**, *11*, 306-310.

[7] K. Zhao, S. Zhao, C. Gao, J. Qi, H. Yin, D. Wei, M. F. Mideksa, X. Wang, Y. Gao, Z. Tang, R. Yu, *Small* **2018**, *14*, 1800762.

[8] C. Gao, Q. Meng, K. Zhao, H. Yin, D. Wang, J. Guo, S. Zhao, L. Chang, M. He, Q. Li, H. Zhao, X. Huang, Y. Gao, Z. Tang, *Adv. Mater.* **2016**, *28*, 6485-6490.

[9] Y. Su, Z. Song, W. Zhu, Q. Mu, X. Yuan, Y. Lian, H. Cheng, Z. Deng, M. Chen, W. Yin, Y. Peng, *ACS Catal.* **2021**, *11*, 345-354.

[10] J. Qin, S. Wang, X. Wang, *Appl. Catal. B: Environ.* **2017**, *209*, 476-482.

[11] S. Wang, W. Yao, J. Lin, Z. Ding, X. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 1034-1038.

[12] K. Niu, Y. Xu, H. Wang, R. Ye, H. L. Xin, F. Lin, C. Tian, Y. Lum, K. C. Bustillo, M. M. Doeff, M. T. M. Koper, J. Ager, R. Xu, H. Zheng, *Sci. Adv.* **2017**, *3*, e1700921.

[13] W. Zhu, C. Zhang, Q. Li, L. Xiong, R. Chen, X. Wan, Z. Wang, W. Chen, Z. Deng, Y. Peng, *Appl. Catal. B: Environ.* **2018**, *238*, 339-345.

[14] B. Han, X. Ou, Z. Deng, Y. Song, C. Tian, H. Deng, Y.-J. Xu, Z. Lin, *Angew. Chem. Int. Ed.* **2018**, *57*, 16811-16815.

[15] M. Wang, J. Liu, C. Guo, X. Gao, C. Gong, Y. Wang, B. Liu, X. Li, G. G. Gurzadyan, L. Sun, *J. Mater. Chem. A.* **2018**, *6*, 4768-4775.

[16] W. Yang, H.-J. Wang, R.-R. Liu, J.-W. Wang, C. Zhang, C. Li, D.-C. Zhong, T.-B. Lu, *Angew. Chem. Int. Ed.* **2020**, 60, 409-414.

[17] H.-X. Zhang, Q.-L. Hong, J. Li, F. Wang, X. Huang, S. Chen, W. Tu, D. Yu, R. Xu, T. Zhou, J. Zhang, *Angew. Chem. Int. Ed.* **2019**, *58*, 11752-11756.

[18] Y. Wang, N.-Y. Huang, J.-Q. Shen, P.-Q. Liao, X.-M. Chen, J.-P. Zhang, *J. Am. Chem. Soc.* **2018**, *140*, 38-41.

[19] D. Hong, Y. Tsukakoshi, H. Kotani, T. Ishizuka, T. Kojima, *J. Am. Chem. Soc.* **2017**, *139*, 6538-6541.

[20] T. Nakajima, Y. Tamaki, K. Ueno, E. Kato, T. Nishikawa, K. Ohkubo, Y. Yamazaki, T. Morimoto, O. Ishitani, *J. Am. Chem. Soc.***2016**, *138*, 13818-13821.