

Supporting Information

Hexanuclear Cobalt Metal–Organic Frameworks for Efficient CO₂ Reduction under Visible Light

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Computational details

Our first-principle calculation was based on density functional theory (DFT) and performed in the SIESTA (Spanish Initiative for the Electronic Simulations of Thousand of Atoms) program package.^[1-3]In this calculation, the double zeta basis set plus polarization (DZP) function was used for all elements. The exchange and correlation potential was used in the generalized gradient approximation (GGA) in the scheme of Perdew, Burke and Ernzerrof (PBE).^[4]All the geometry structure was relaxed until energy and force are converged to 10⁻⁴ eV and 0.02 eV/Å. A cutoff of 250 Ry was used for the real-space integration grid. Brillouin zone was sampled by 2×2×4 k-points grid for optimized and a more refined 4×4×6 k-points grid for energy. In this calculation, supercells which is combined by double unit cell was composed 304 atoms and the lattice constant (*a*₀) was 17.766. And we artificially set six Co atoms spin up and six Co atoms spin down as mentioned in the article. The calculation of frontier molecular orbital was also finished in SIESTA program. To investigate the behavior of CO₂ absorption on the MOFs, the absorption energy (*E*_{ads}) was put forward and defined as $E_{ads} = E_{total} - (E_{MOFs} + E_{CO_2})$ where *E*_{total} was the total energy of adsorbate (i.e. CO₂) on MOFs, and *E*_{MOFs} and *E*_{CO₂} were the total energy of MOFs and adsorbate, respectively. In this condition, the more negative value of *E*_{ads} stood for more stable adsorption.

In the reduction process, two electrons are required to convert CO₂ to CO, therefore, photochemical quantum yield (Φ) can be calculated using the following equations.

$$\Phi_{\text{CO}} (\%) = \frac{2 \text{ mol of CO yield}}{\text{moles of photon absorbed by catalyst}} \times 100\%$$

The photon energy at a certain wavelength can be calculated using the following equation, where h is the Planck constant, c indicates speed of light, and λ is the wavelength. The average photon energy thus can be estimated.

$$E_{\text{photon}} = \frac{h c}{\lambda}$$

The following constants were used for calculation of Φ_{CO} :

The wavelength of light: 420 nm

Light intensity: 5.78 mW/cm²

Irradiation area: 3 cm²

Average photon energy: 4.735×10^{-19} J

Yield of CO in 3 hours under the irradiation of $\lambda = 420$ nm: 2.49 μ mol

Based on equations, Φ_{CO} was calculated as 0.758 %.

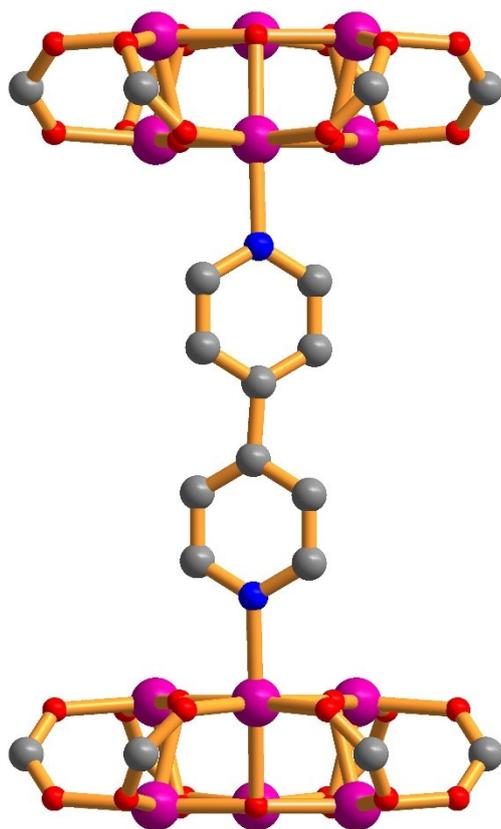


Fig. S1 The coordination environment of 4,4'-bpy. All hydrogen atoms have been omitted for clarity. Magenta = Co; gray = C; red = O; blue = N.

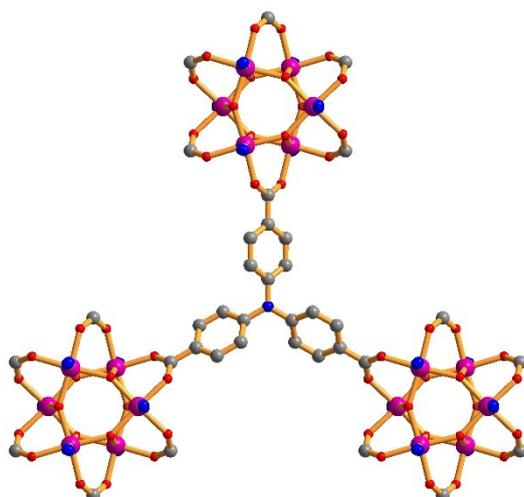


Fig. S2 The coordination environment of NTB. All hydrogen atoms have been omitted for clarity. Magenta = Co; gray = C; red = O; blue = N.

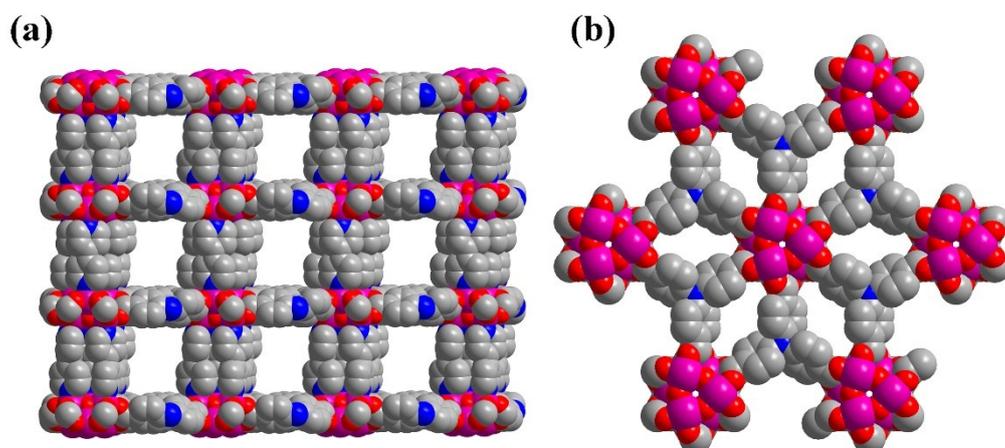


Fig. S3 The representation of the 3D packing framework. All hydrogen atoms have been omitted for clarity. Magenta = Co; gray = C; red = O; blue = N.

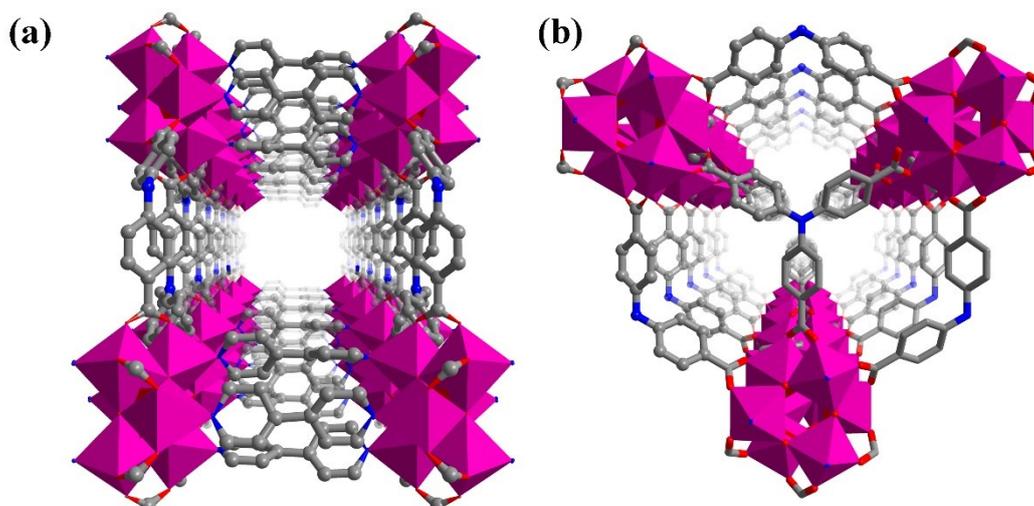


Fig. S4 (a) and (b) The square and diamond metal–organic nanotubes along the b (a) axis and c axis in the Co₆-MOF. All hydrogen atoms have been omitted for clarity. Magenta = Co; gray = C; red = O; blue = N.

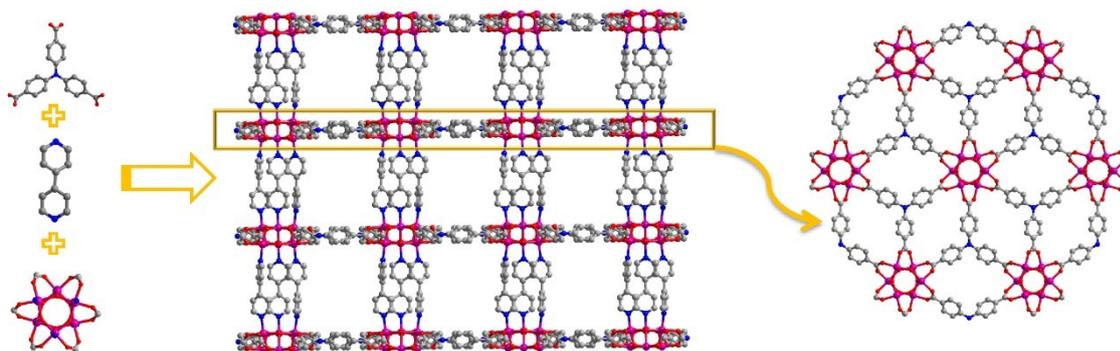


Fig. S5 Ball-and-stick representations of the 3D structure of Co₆-MOF. The layer is formed by Co₆(μ₃-OH)₆ clusters and NTB. All hydrogen atoms have been omitted for clarity. Magenta = Co; gray = C; red = O; blue = N.

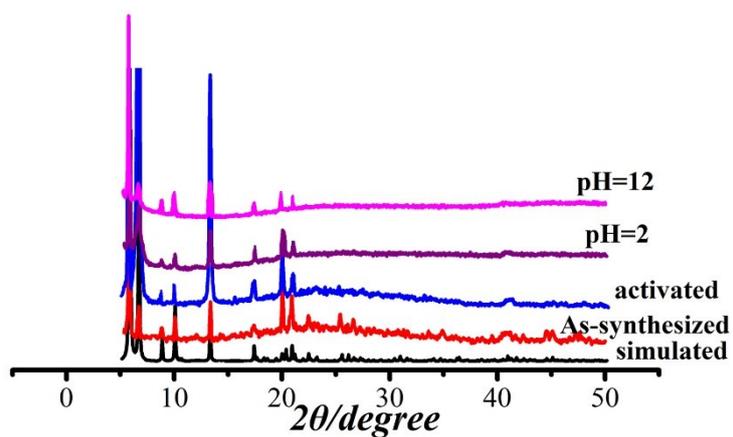


Fig. S6 X-Ray powder diffraction patterns of simulated Co₆-MOF (black), as-synthesized (red), activated (blue), samples placed in hydrochloric acid solution (pH = 2) (purple), samples placed in sodium hydroxide solution (pH = 12) (magenta).

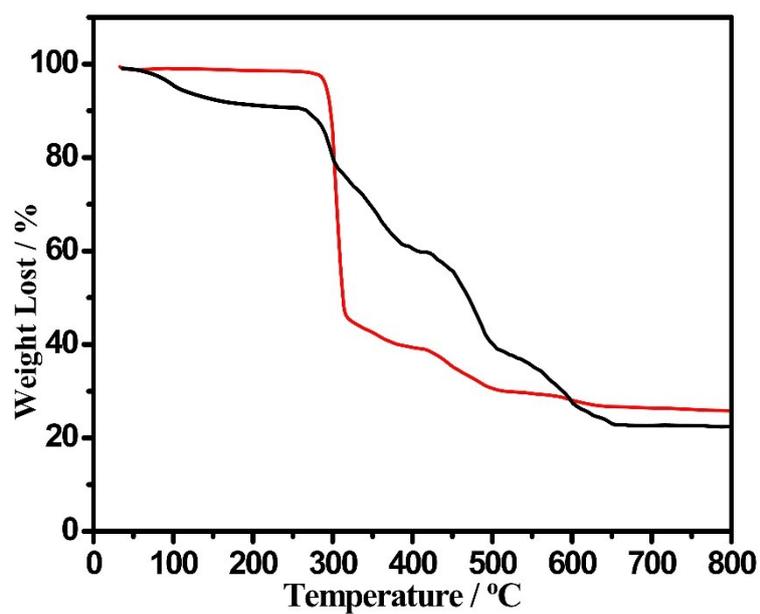


Fig. S7 TG curves of Co₆-MOF and desolvated Co₆-MOF.

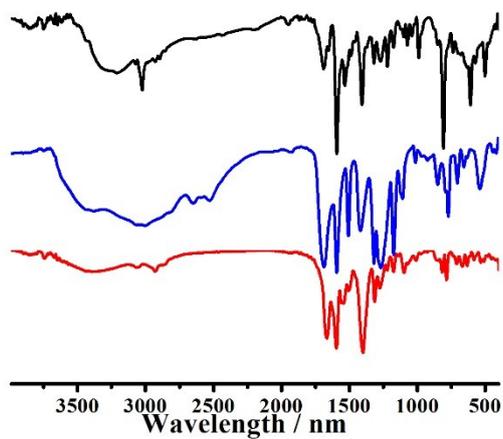


Fig. S8 The FT-IR curves for Co₆-MOF (black), 4,4'-bpy (blue), NTB (red).

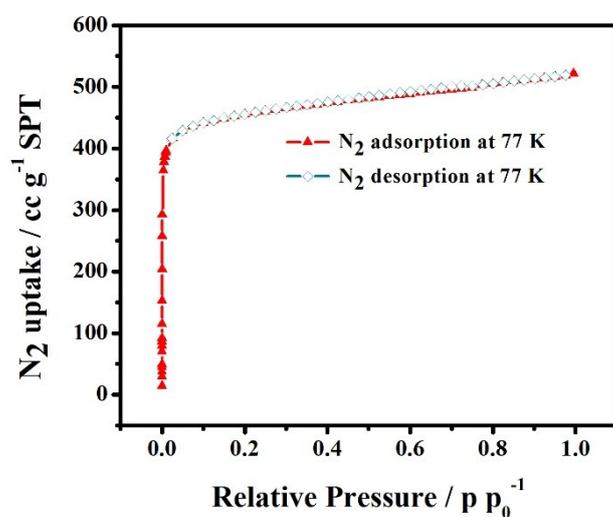


Fig. S9 N₂ sorption isotherms of Co₆-MOF soaked by water for 24 h.

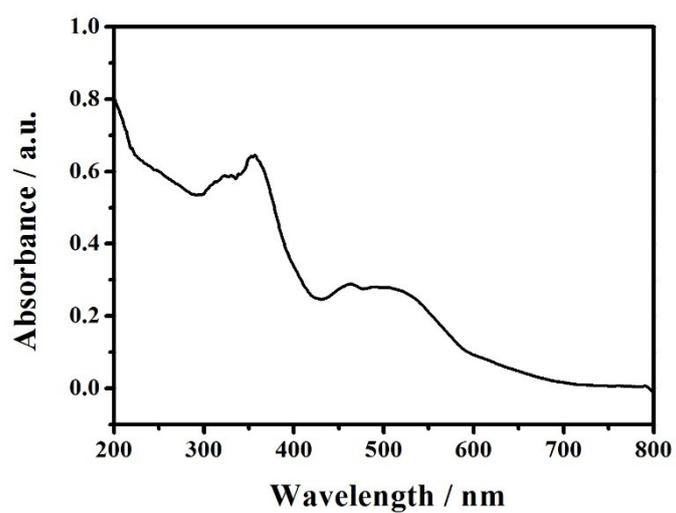


Fig. S10 The UV/Vis curves for Co₆-MOF.

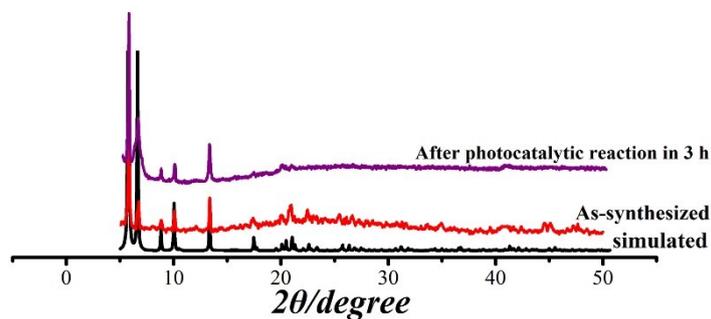


Fig. S11 X-Ray powder diffraction patterns of simulated $\text{Co}_6\text{-MOF}$ (black), as-synthesized (red), after photocatalytic reaction in 3 h (purple).

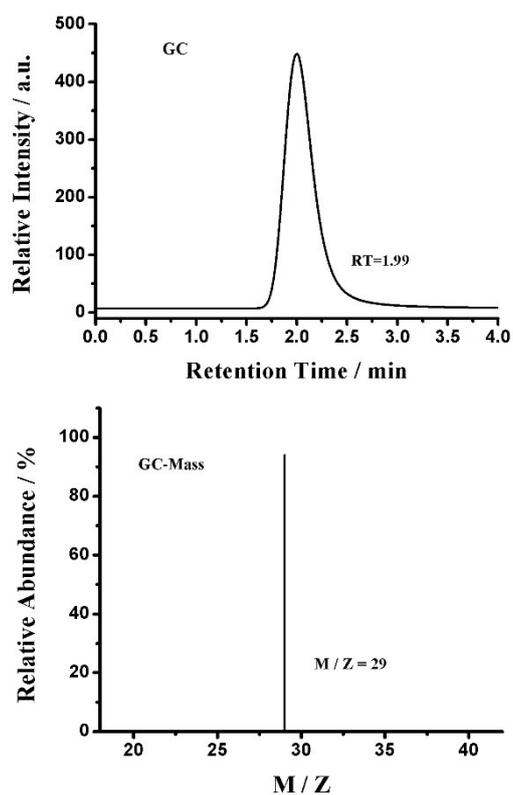


Fig. S12 Gas chromatogram and mass spectra ($m/z = 29$) analyses of the carbon source of the generated CO in the photocatalytic reaction of $^{13}\text{CO}_2$ by $\text{Co}_6\text{-MOF}$ as a cocatalyst.

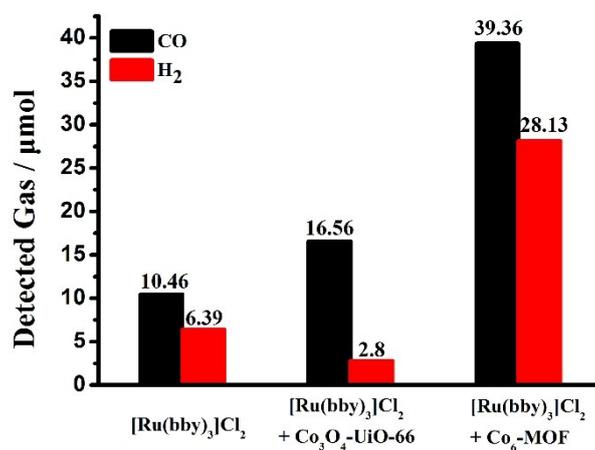


Fig. S13 The catalytic effect of Co₃O₄-Uio-66 as co-catalyst on the CO₂ photoreduction system.

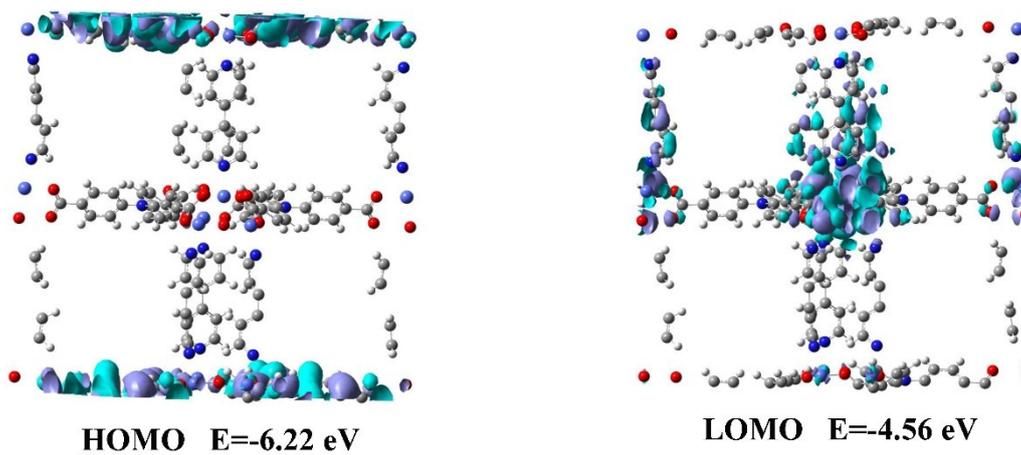


Fig. S14 HOMO and LOMO energy gaps of Co₆-MOF.

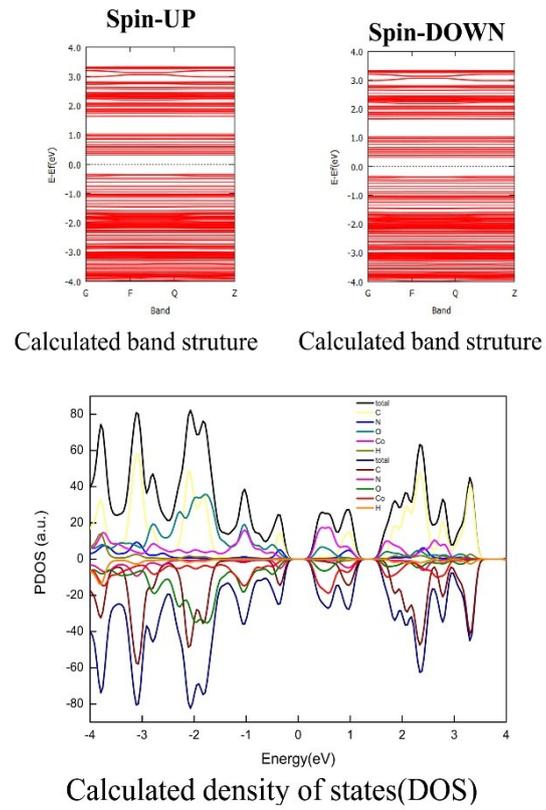


Fig. S15 Calculated band structure and Calculated density of states of Co₆-MOF.

Table S1 Reported MOF materials for converting CO₂ to CO under visible light irradiation.

MOFs	Condition			CO[μ mol]	H ₂ [μ mol]	TON	Reference
	Quantity[μ mol]	Light[nm]	Time[h]				
Co ₆ -MOF	5	$\lambda \geq 420$	3	39.36	28.13	13.5	This work
Co-MOF-74	0.8	$\lambda \geq 420$	0.5	11.7	7.3	23.8	Ref. 1 ^a
Mn-MOF-74	0.8	$\lambda \geq 420$	0.5	1.5	2.9	5.5	Ref. 1 ^a
Zn-ZIF-8	0.8	$\lambda \geq 420$	0.5	2.1	2.4	5.5	Ref. 1 ^a
Zr-UiO-66-NH ₂	0.8	$\lambda \geq 420$	0.5	1.2	2.2	4.3	Ref. 1 ^a
C ₁₀ H ₁₀ Co	0.8	$\lambda \geq 420$	0.5	5.0	2.7	9.6	Ref. 1 ^a
Co-ZIF-9	4	$\lambda > 420$	2	20.8	3.3	6.0	Ref. 2 ^b
Zr ₆ (μ -O) ₄ (μ -OH) ₄ (bpdc) _{5.83} (Re(CO) ₃ (dcbpy) _{0.17})Cl _{0.17}	1	$\lambda = 300$	6	5.0	0.5	5.5	Ref. 3 ^c

a) Ref. 1: S. B. Wang, W. S. Yao, J. L. Lin, Z. X. Ding and X. C. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 1034. b) Ref. 2: S. B. Wang, J. L. Lin and X. C. Wang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 14656. c) Ref. 3: C. Wang, Z. G. Xie, K. E. deKrafft, and W. B. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 13445.

~~Angew. Chem. Int. Ed., 2014, 53, 1034. b) Ref. 2: S. B. Wang, J. L. Lin and X. C. Wang, Phys. Chem. Chem. Phys., 2014, 16, 14656. c) Ref. 3: C. Wang, Z. G. Xie, K. E. deKrafft, and W. B. Lin, J. Am. Chem. Soc., 2011, 133, 13445.~~

Table S2 Crystal data and structure refinements for Co₆-MOF.

Chemical formula	C ₄₁ H ₃₈ Co ₃ N ₅ O ₁₀
Formula weight	937.55
Crystal system	Hexagonal
Space group	P6 ₃ /mcm
a (Å)	17.7662(12)
b (Å)	17.7662(12)
c (Å)	26.7970(2)
α (°)	90.00
β (°)	90.00
γ (°)	120.00
V (Å ³)	7324.9(11)
Z	4
Temperature (K)	296
D _{calcd} [g/cm ³]	0.850
F(000)	1920
Reflections collected	39887
R(int)	0.1187
Goodness-of-fit on F ²	1.078
R ₁ [I>2σ (I)] ^a	0.0669
wR ₂ [I>2σ (I)] ^b	0.1847
R ₁ ^a (all data)	0.0920
wR ₂ ^b (all data)	0.2094
^a R ₁ = Σ F _o - F _c /Σ F _o , ^b wR ₂ = [Σw(F _o ² - F _c ²) ² /Σw(F _o ²) ²] ^{1/2}	

Table S3 Selected Bonds Lengths (Å) and Angles (°) for Co₆-MOF.

Co ₆ -MOF			
Co ₁ -O ₁	2.056(3)	Co ₁ -O ₁ ³	2.056(3)
Co ₁ -O ₂	2.072(12)	Co ₁ -O ₂ ¹	2.072(12)
Co ₁ -O ₂ ²	2.156(3)	Co ₁ -N ₂	2.136(6)
O ₁ -Co ₁ -O ₁ ³	86.60(2)	O ₁ -Co ₁ -O ₂	89.81(15)
O ₁ ³ -Co ₁ -O ₂	174.6(14)	O ₁ -Co ₁ -O ₂ ¹	174.6(14)
O ₁ ³ -Co ₁ -O ₂ ¹	89.81(15)	O ₂ -Co ₁ -O ₂ ¹	93.50(2)
O ₁ -Co ₁ -N ₂	89.03(15)	O ₁ ³ -Co ₁ -N ₂	89.03(15)
O ₂ -Co ₁ -N ₂	94.91(15)	O ₂ ¹ -Co ₁ -N ₂	94.91(15)
O ₁ -Co ₁ -O ₂ ²	96.50(12)	O ₁ ³ -Co ₁ -O ₂ ²	96.49(12)
O ₂ -Co ₁ -O ₂ ²	79.94(14)	O ₂ ¹ -Co ₁ -O ₂ ²	79.94(14)
N ₂ -Co ₁ -O ₂ ²	172.4(2)		

References

- [1] P. Ordejo'n, E. Artacho, J. Soler, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *53*, R10441;
- [2] D. Sa'nchez-Portal, P. Ordejo'n, E. Artacho, J. M. Soler, *Int. J. Quantum Chem.* **1997**, *65*, 453;
- [3] J. M. Soler, E. Artacho, J. D. Gale, A. Garcı'a, J. Junquera, P. Ordejo'n, D. Sa'nchez-Portal, *J. Phys. Condens. Matter* **2002**, *14*, 2745.
- [4] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.