Electronic Supporting Information for:

Cobalt substitution in a flexible metal-organic framework: modulating soft paddle-wheel unit for tunable gate-opening adsorption

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1. Materials and General Procedures.

All reagents were purchased from commercial sources and used without further purification. Thermogravimetric (TGA) analyses were investigated with a Mettler Tolepo TGA/SDTA 851 analyzer under N_2 flow from room temperature to 800 °C with a heating rate of 10 K min^{-1}. Elemental analysis was measured on an Elementar Vario EL III microanalyzer. Scanning electron microscope mapping (SEM-mapping) measurement was tested on FEI Nova NanoSem 450 scanning electron microscope with voltage of 15kV. X-ray powder diffraction (XRD) patterns were measured using a Bruker D8 powder diffractometer at 40 kV, 40 mA for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 0.2 s/step and a step size of 0.05 °(2θ). CO_2 sorption isothermal at different temperature were carried out on ASAP 2020 apparatus. Before gas sorption, the samples (about 100 mg) were exchanged with dichloromethane (10 mL for three times) and then degassed at 140 ^{o}C overnight. ^{1}H NMR spectra were recorded on a Bruker Avance III HD spectrometer (400 MHz). UV-Vis spectra were measured on a PerkinElmer Lambda 650S UV-Vis spectrophotometer at room temperature. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) were measured using a PerkinElmer Avio 200 Optical Emission Spectrometer.

2. Synthesis and single-crystal-to-single-crystal structural transformation

Synthesis of MAC-6-Zn_2: MAC-6-Zn_2 was synthesized according to our previously reported method. [1]

Synthesis of MAC-6-$Zn_{2-x}Co_x$ (where x = 0.5, 1, 1.5): Taking x = 1 for example: $Co(OAc)_2·4H_2O$ (0.2 mmol, 0.050 g), $Zn(OAc)_2·2H_2O$ (0.2 mmol, 0.044 g), [1,1'-biphenyl]-3,3',5,5'-tetracarboxylic acid (H_4bptc, 0.2 mmol, 0.066 g) and 1*H*-1,2,4-triazole-3,5-diamine (Hdatrz, 0.2 mmol, 0.020 g) were dissolved in DMF (4.5 mL), the solution was stirred at room temperature for 10 min, and then 0.5 mL H_2O was added. Then 15 drops of nitric acid were added and the mixture was further stirred for another 10 min. Finally, the mixture was sealed in a Teflon-lined stainless-steel autoclave (15 mL) and heated at 140 ^oC for 3 days, followed by cooling down to room temperature. Rhombic purple crystals were collected by filtration, washed with DMF (5 mL × 3) and acetone (5 mL × 3) respectively. Yields: 60 % based on H_4bptc. Elemental analysis calc. (%) C 38.27, H 3.05, N 13.39. Found (%) C, 37.98, H 3.43, N 13.23.

Synthesis of MAC-6-Co_2: $CoCl_2·6H_2O$ (0.4 mmol, 0.095 g), H_4bptc (0.2 mmol, 0.067 g) and Hdatrz (0.2 mmol, 0.021 g) were dissolved in DMF (8 mL), the solution was stirred at room temperature for 10 min, and then 0.5 mL H_2O was added. Then 10 drops of nitric acid were added and the mixture was further stirred for another 10 min. Finally, the mixture was sealed in a Teflon-lined stainless-steel autoclave (15 mL) and heated at 140 ^oC for 3 days, followed by cooling down to room temperature. Rhombic dark-purple crystals were collected by filtration, washed with DMF (5 mL × 3) and acetone (5 mL × 3) respectively. Yields: 56 % based on H_4bptc. Elemental analysis calc. (%) C 38.67, H 3.08, N 13.57. Found (%) C, 38.20, H 3.65, N 13.40.

Single-crystal-to-single-crystal (SC-SC) transformation: High quality crystals of **MAC-6-Zn_1Co_1**, **MAC-6-Co_2** samples were picked out and put on a glass slide. After heating at 90 ^oC for 2 hours in air conditions, detectable crystal structural transferred samples **MAC-6'-Zn_1Co_1** and **MAC-6'-Co_2** were then isolated carefully.

3. Single X-ray Crystallographic Study

Data collection for **MAC-6-Zn_1Co_1, MAC-6-Co_2, MAC-6'-Zn_1Co_1** and **MAC-6'-Co_2** were carried out on a Bruker Apex Duo diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K. Data reduction was performed with SAINT, and empirical absorption corrections were applied by SADABS program. Structures were solved by direct method using SHELXS program and refined with SHELXL program.[3a, 3b] Heavy atoms and other non-hydrogen atoms were directly obtained from difference Fourier map. Final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. C-bonded H atoms were placed geometrically and refined as riding modes. The H atoms of coordinated and guest water molecules were not placed because of their disorders. The SQUEEZE method[3c] was used for **MAC-6-Co_2** and **MAC-6-Zn_1Co_1**, respectively. Crystallographic data are listed in Table S2, for detailed bond length and angles, please see in CIFs.

4. Preparation of **TMA@MAC-6-Zn$_{2-x}$Co$_x$ (x = 0, 0.5, 1, 1.5, 2)**

Following our previously reported method, [2] guest-cations in **MAC-6-Zn$_{2-x}$Co$_x$** was exchanged with tetramethylammonium cations (TMA$^+$). Generally: (a) as-synthesized **MAC-6-Zn$_{2-x}$Co$_x$** (50 mg) was rinsed with DMF (5 mL × 3); (b) the sample was soaked in DMF solution (3 mL), and then 1 mL of aqueous solution of TMA$^+$Br$^-$ (0.3 M) was added; (c) the mixture was then put in a shaker incubator with 280 rpm and at 25 ^{o}C; the solution was then removed after 2 h exchange; (d) the processes of steps b and c were cycled 15 times for a complete exchange; (e) the exchanged sample was rinsed with a mixed solution of DMF and H_2O (5:1, 12 mL × 3) to get the **TMA@MAC-6-Zn$_{2-x}$Co$_x$**.

5. Calculation method

The structural model of H_2O, $[Zn_{2-x}Co_x(\mu_{1,2}\text{-}CH_3COO)_2(\eta_1\text{-}CH_3COO)_2(Hdatrz)_2\cdot H_2O]$ to paddle-wheel unit $[Zn_{2-x}Co_x(\mu_{1,2}\text{-}CH_3COO)_4(Hdatrz)_2]$ were directly obtained from single-crystal diffraction and re-built with the Visualizer Program from Accelrys, Inc. The geometry optimization calculations were carried using the program DMOL^3. [4] The DNP basis set with fine precision was used. DFT Semi-core Pseudopots (DSPP) was used for the treatments of core electrons. The GGA (PBE) function was used in the calculation. To make the model the same as that in the crystal structure, constraints are used for metal ions and the atoms connected to the metal ion, then the geometry was optimized until convergence.

Table S1. Concentration and relative ratio of metals found for **MAC-6-$\mathbf{Zn_{2\text{-}x}Co_x}$**.

Zn (mg/L)	Co (mg/L)	Zn (mmol/L)	Co (mmol/L)	Found (Co/Zn)	Feeding (Co/Zn)
171.5	0	2.6220	0	0	0
64.29	19.98	0.9829	0.3390	0.3449	0.333
28.31	27.2	0.4328	0.4615	1.066	1.0
27.85	77.63	0.4258	1.3171	3.093	3.0
0	95.24	0	1.6162	n/a	n/a

n/a, not applicable

Table S2. Crystal structure parameter and refinement data of **MAC-6-Co$_2$, MAC-6’-Co$_2$, MAC-6-Zn$_1$Co$_1$,** and **MAC-6’-Zn$_1$Co$_1$**.

Crystallographic data	**MAC-6-Co$_2$**	**MAC-6’-Co$_2$**	**MAC-6-Co$_1$Zn$_1$**	**MAC-6’-Co$_1$Zn$_1$**
Empirical formula	$C_{20}H_{24}N_6O_{11}Co_2$	$C_{20}H_{21}N_6O_{9.5}Co_2$	$C_{20}H_{31}N_6O_{14.5}ZnCo$	$C_{20}H_{21}N_6O_{9.5}ZnCo$
Formula weight	642.31	615.29	711.81	621.73
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/m	*P*c	*C*2/m	*P*c
a / Å	16.9139(17)	8.097(3)	17.414(2)	8.1101(13)
b / Å	20.364(2)	21.414(9)	19.927(2)	21.350(3)
c / Å	12.255(2)	14.114(6)	12.8456(16)	14.109(2)
β / °	124.4410(10)	105.123(5)	126.5710(10)	105.008(2)
V / Å^3	3481.0(8)	2362.5(17)	3579.9(8)	2359.7(6)
Z	4	4	4	4
D_{calc} / g·cm^{-3}	1.226	1.724	1.321	1.745
μ / mm^{-1}	1.004	1.471	1.196	1.786
F(000)	1312	1244	1464	1256
Data / restraints / parameters	3192 / 0 / 153	8198 / 235 / 609	3284 / 0 / 153	6543 / 725 / 680
GOF on F^2	1.057	1.132	1.017	1.072
$R_1{}^a$ / wR$_2{}^b$ [I>2σ(I)]	0.0289 / 0.0775	0.1145 /	0.0403 / 0.1092	0.0439/ 0.1225
R indices (all data)	0.0379 / 0.0808	0.1611 /	0.0442 / 0.1109	0.0496 / 0.1305
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$	0.410 / -0.374	1.860 / -1.463	0.476 / -0.782	1.451 / -0.707

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

Figure S1. (a) The TG curve of **MAC-6-Zn$_{2-x}$Co$_x$**; (b) - (f) The temperature-dependent PXRD pattern of **MAC-6-Zn$_{2-x}$Co$_x$ (x = 0, 0.5, 1, 1.5, 2)**.

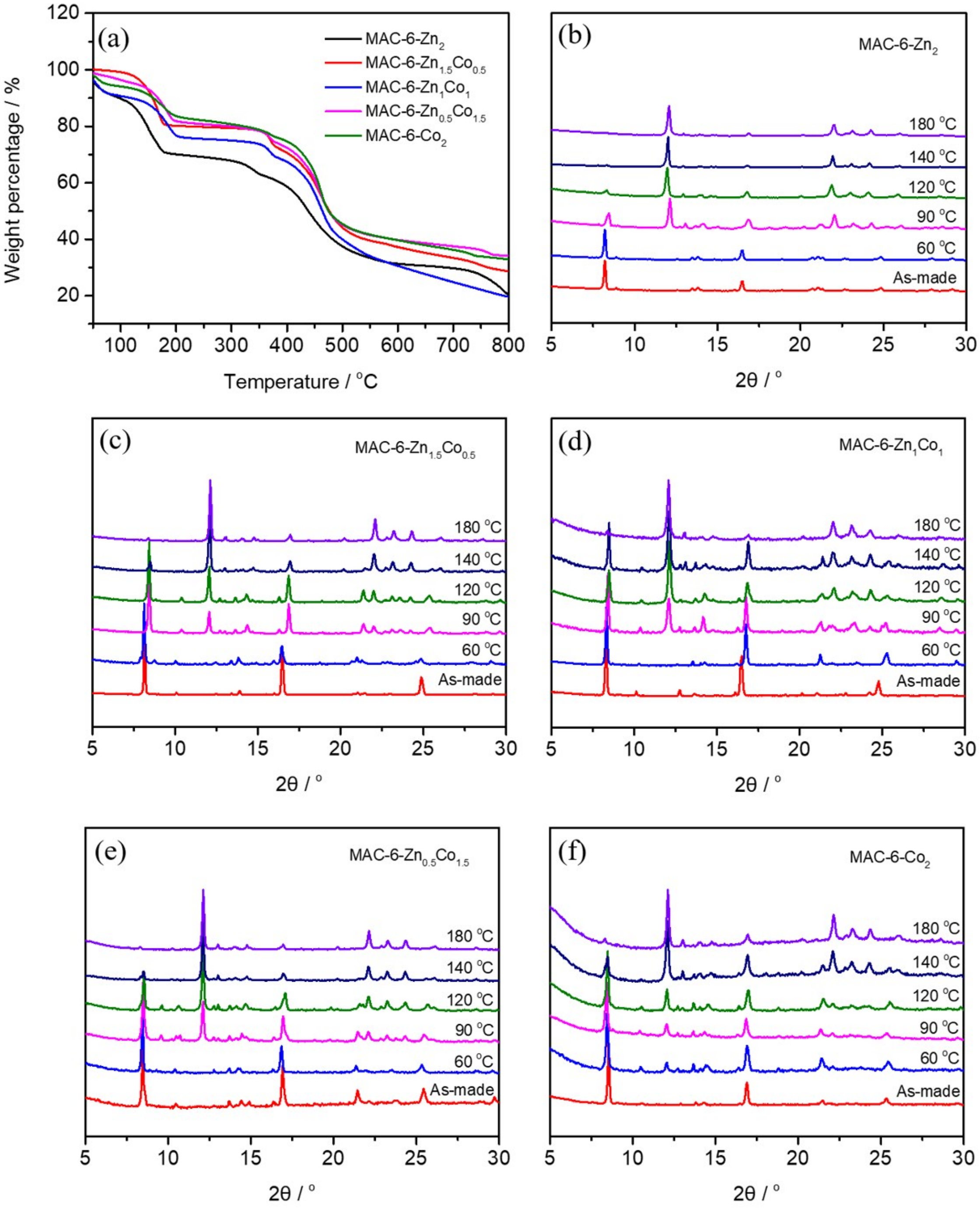


Figure S2. (a)-(b) PXRD patterns of **MAC-6-Zn$_1$Co$_1$** and **MAC-6-Co$_2$** indicating the reversible the structural transformation from open pore to closed pore; (b) Reversible phase transformation PXRD patterns of; (c)-(d) UV-Vis spectra of **MAC-6-Zn$_1$Co$_1$** and **MAC-6-Co$_2$** indicating reversible dissociation of paddle-wheel unit.

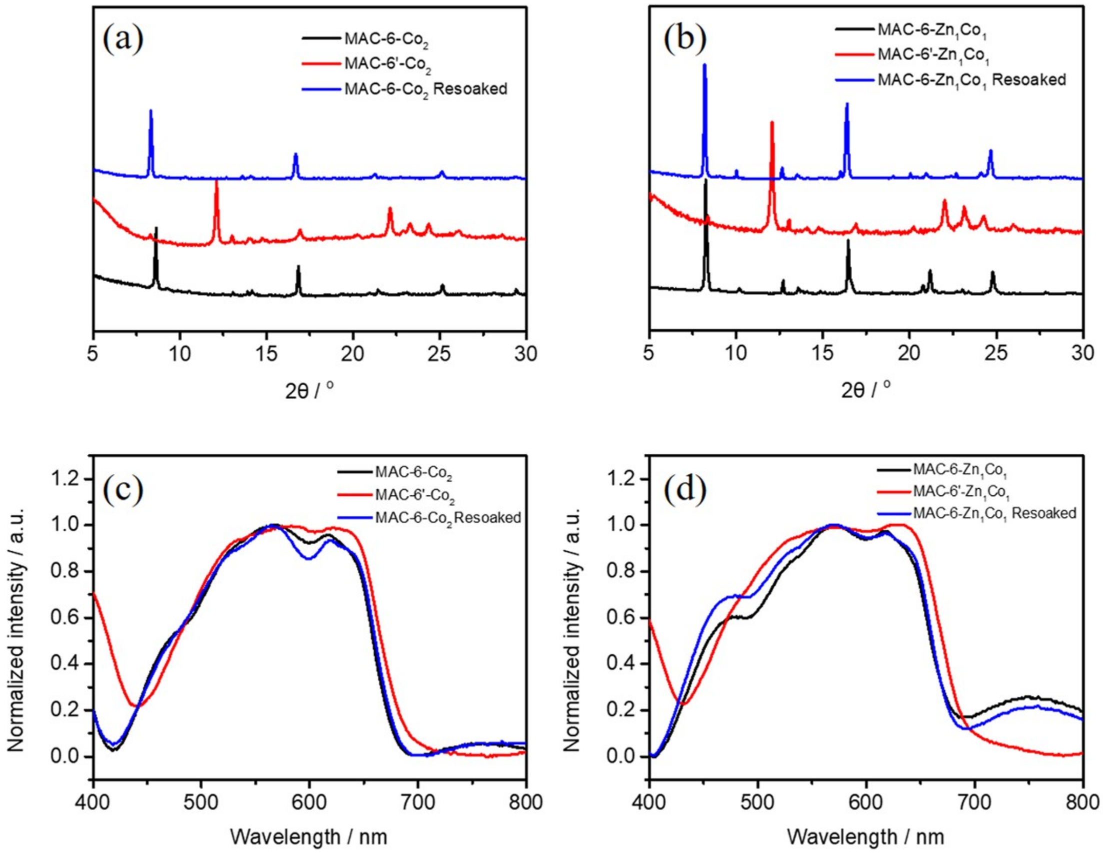


Figure S3. The ^{1}H NMR analysis of **TMA@MAC-6-Zn$_{2\text{-}x}$Co$_x$** indicating the incorporation of TMA cations (samples were deconstructed by DCl in DMSO-d$_6$ solution, (a) **TMA@MAC-6-Zn$_{1.5}$Co$_{0.5}$**, (b) **TMA@MAC-6-Zn$_1$Co$_1$**, (c) **TMA@MAC-6-Zn$_{0.5}$Co$_{1.5}$**, (d) **TMA@MAC-6-Co$_2$**. The rhombus labels the two kinds of H on the bptc ligand respectively. The triangle labels the position of DMSO-d$_6$ at 2.5 ppm.

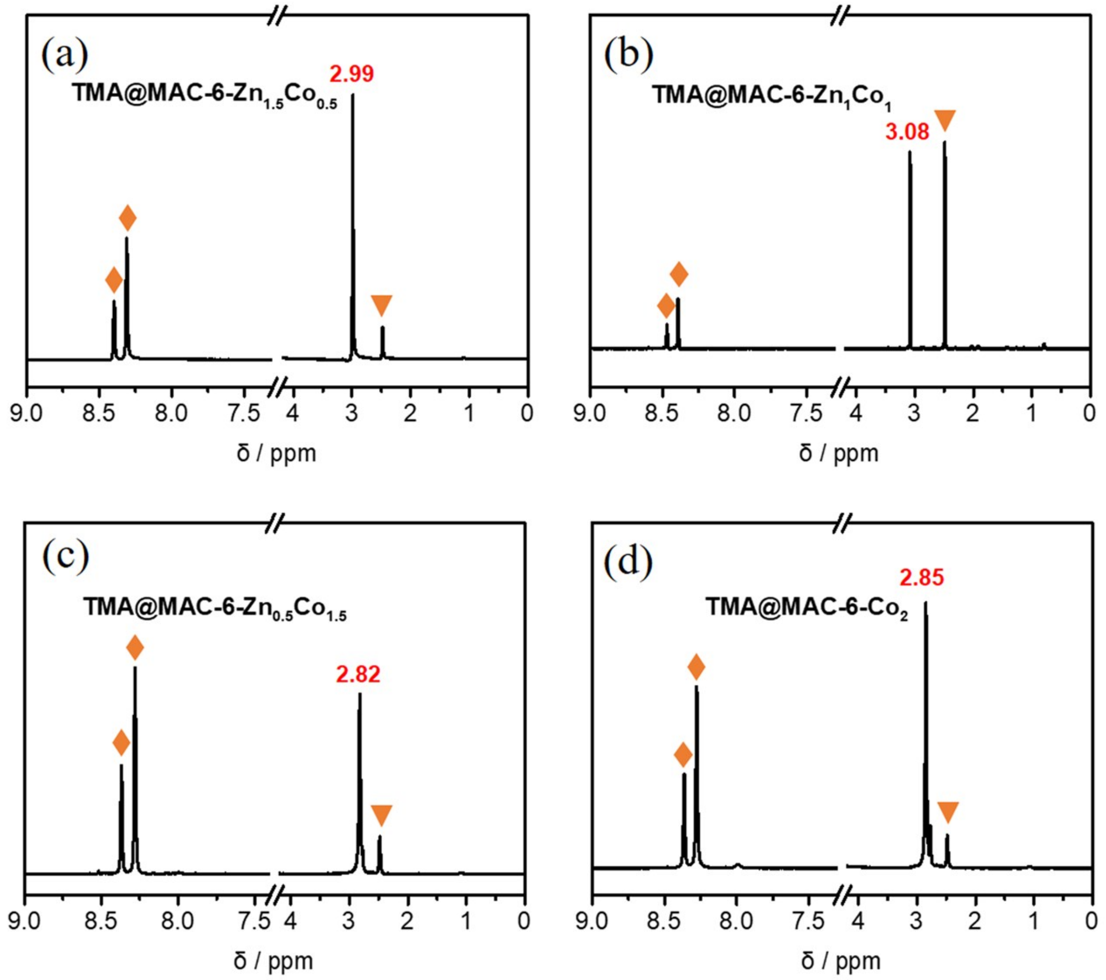


Figure S4. Variable-temperature PXRD pattern of **TMA@MAC-6-Zn$_{2-x}$Co$_x$** (**x = 0.5** (a)**, 1** (b)**, 1.5** (c)**, 2** (d)). The shift of diffraction peak to the larger angle confirms the transformation from open pore to closed pore, giving the formation of **TMA@MAC-6'-Zn$_{2-x}$Co$_x$**.

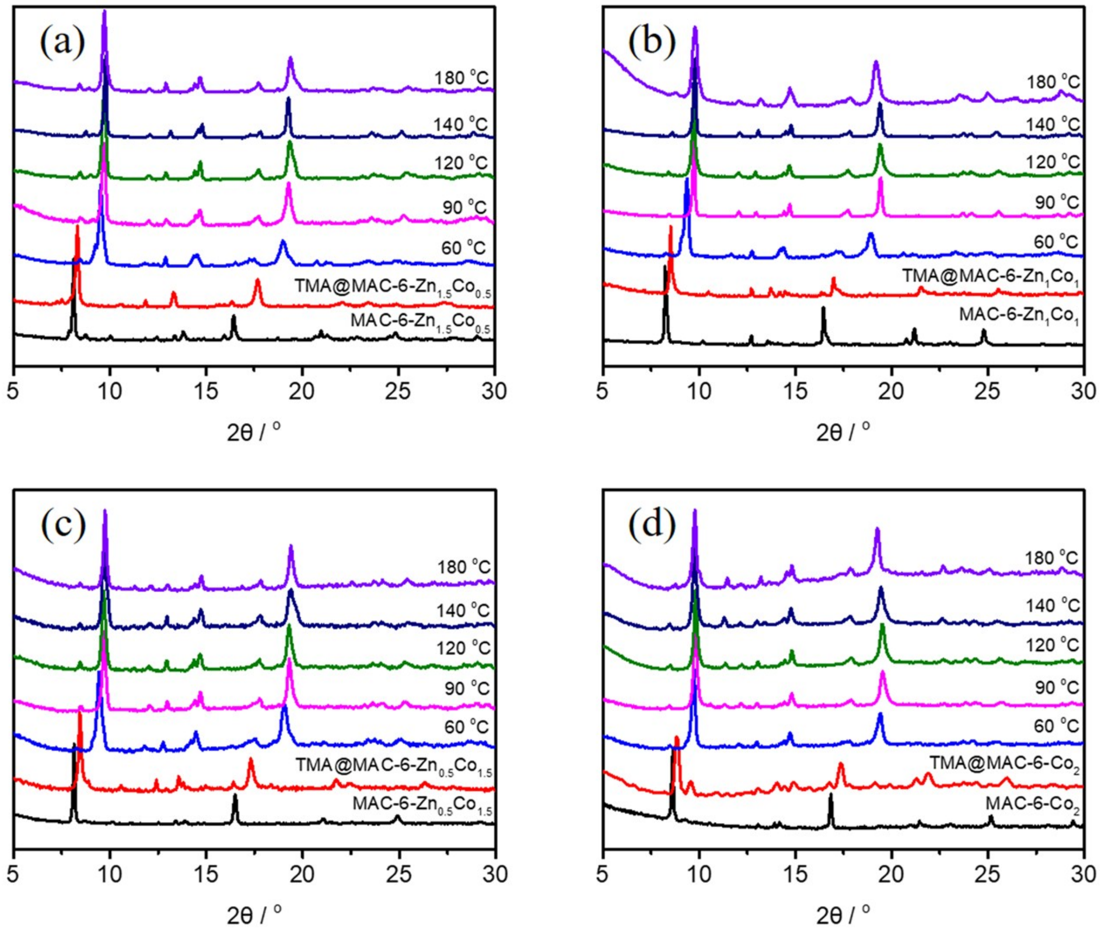


Figure S5. The CO_2 adsorption isotherm of (a) **TMA@MAC-6-Zn$_{1.5}$Co$_{0.5}$**, (b) **TMA@MAC-6-Zn$_1$Co$_1$**, (c) **TMA@MAC-6-Zn$_{0.5}$Co$_{1.5}$**, (d) **TMA@MAC-6-Co$_2$** at 258, 273 and 298 K.

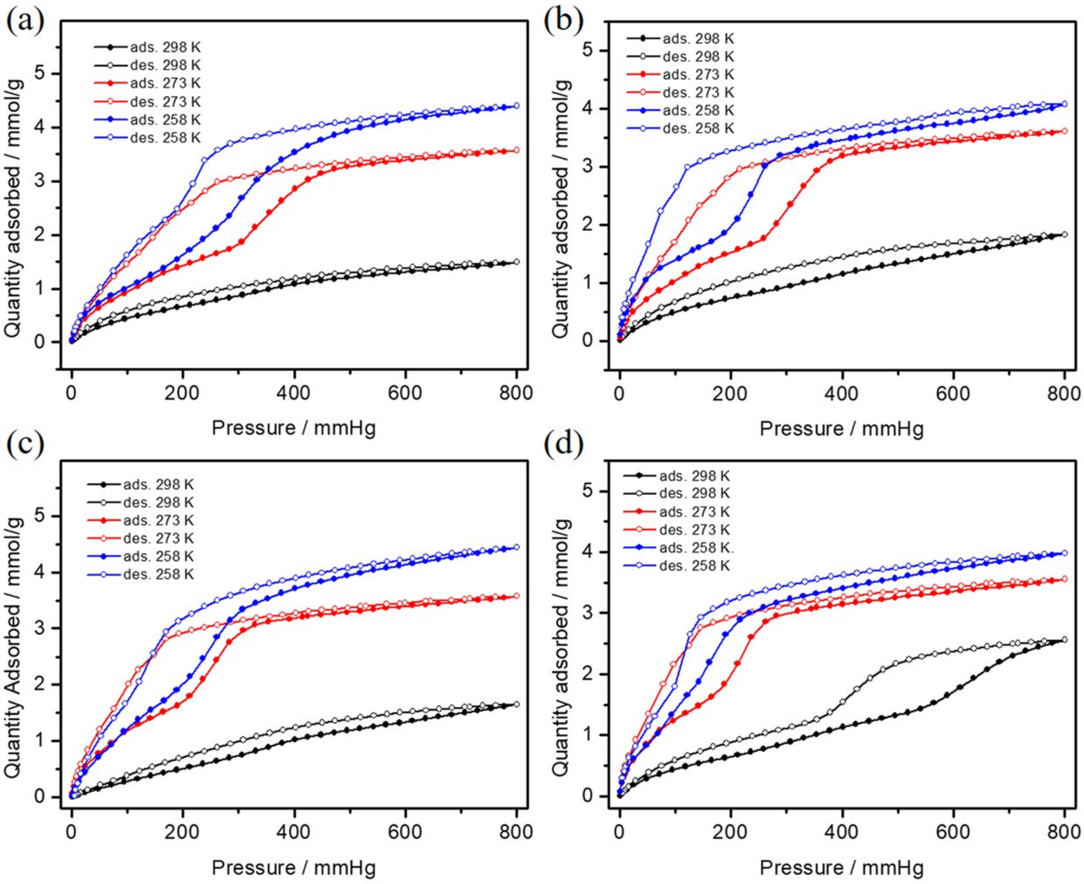


Figure S6. The adsorption enthalpy of (a) **TMA@MAC-6-$Zn_{1.5}Co_{0.5}$**, (b) **TMA@MAC-6-Zn_1Co_1**, (c) **TMA@MAC-6-$Zn_{0.5}Co_{1.5}$**, (d) **TMA@MAC-6-Co_2**.

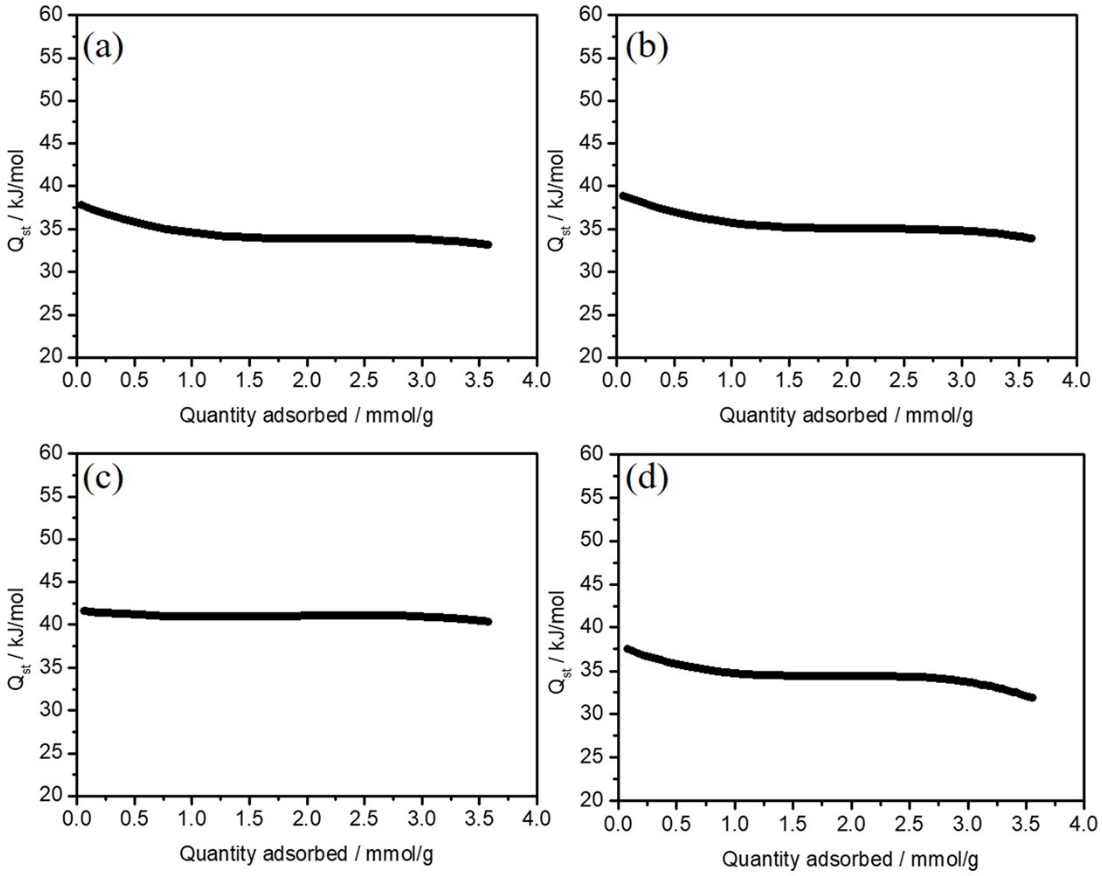


Figure S7. PXRD patterns and UV-Vis spectra of (a) & (c) **TMA@MAC-6-Zn$_1$Co$_1$**, (b) & (d) **TMA@MAC-6-Co$_2$** after CO$_2$ adsorption.

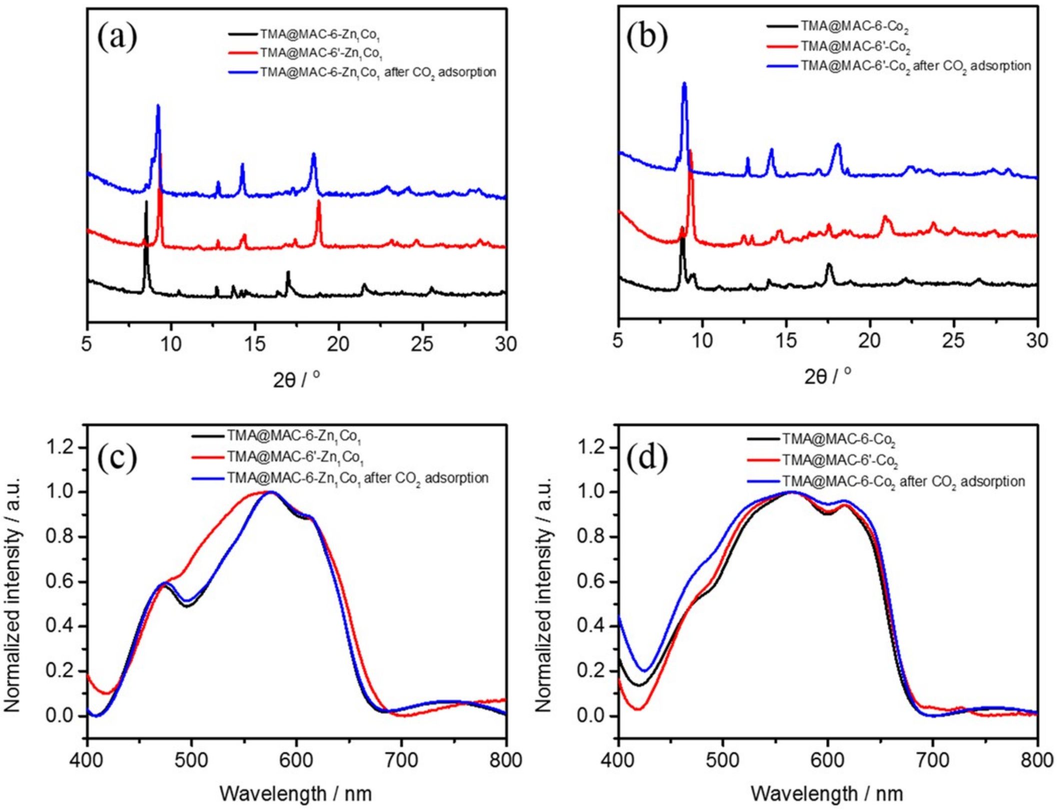
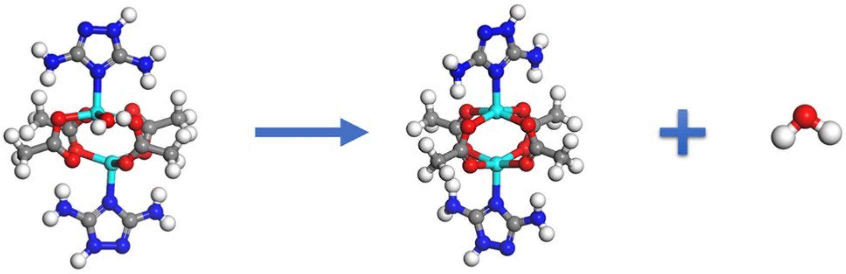


Figure S8. Reaction energy calculation of [$Zn_{2-x}Co_x(\mu_{1,2}-CH_3COO)_2(\eta_1-CH_3COO)_2(Hdatrz)_2 \cdot H_2O$] to paddle-wheel unit [$Zn_{2-x}Co_x(\mu_{1,2}-CH_3COO)_4(Hdatrz)_2$] and water. (In the calculation, T_d symmetrical site of the reactant was defined as Co since the blue color of bulk crystal samples after dissociation of paddle-wheel unit.)



	Reactant (total energy in Ha)	Products (total energy in Ha) Paddle-wheel	 H_2O	ΔE (kcal/mol)
x = 0	-2204.141757	-2127.777293	-76.37872	-8.95
x = 1	-2116.530405	-2040.205015	-76.37872	-33.5
x = 2	-2028.948581	-1952.649438	-76.37872	-49.9

Reference

[1] F. Yang, Q. Zheng, Z. Chen, Y. Ling, X. Liu, L. Weng and Y. Zhou, *CrystEngComm*, 2013, **15**, 7031.

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