Electronic Supplementary Information (ESI) for

Room-temperature synthesis of bimetallic Co-Zn based Zeolitic Imidazolate Frameworks in water for enhanced CO_2 and H_2 uptakes

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Reagents and chemicals

All of the chemicals were of analytical grade and used as received without further purification. These chemicals included zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 96% purity, Merck), Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 98% purity, SDFCL) and 2-methyl imidazole (Hmim 99%, purity, Sigma Aldrich).

Characterization

The powder X-ray diffraction (PXRD) patterns of the samples were recorded using Rigaku smart lab automated multipurpose X-ray diffractometer system with $CuK\alpha_1$ radiation (λ = 1.540593 Å) in 2θ range of 5-40 ° at scanning speed of 3 ° per minute and 0.01 ° scan step size. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were taken on a Carl Zeiss Supra-55 scanning electron microscope and EDS Oxford instruments model X-Max, energy dispersive X-ray spectroscopy. Images were captured under 5 kV acceleration voltage and scale (100 nm and 200 nm). Sample preparation was done by dispersing the material into methanol by sonication and a drop of resulting suspension was placed on a sample holder disk, dried at room temperature and coated using gold sputter coating for SEM analysis. EDS analysis of materials were obtained by increasing the acceleration voltage up to 20 kV. SEM-elemental mapping were performed on Hitachi S-5000 with ZIF powder samples on a carbon tape. To check the thermal stability, thermo gravimetric analysis (TGA) was done using Mettler Toledo TGA/DSC 1 analyser. The apparatus was loaded with approximately 4 mg samples under flow of nitrogen gas at a heating rate of 5 °C/min from room temperature to 800 °C. Transmission electron microscopy (TEM) images were obtained using a JEM-1400 microscope (JEOL) operated at 100-120 kV. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was performed using ARCOS, Simultaneous ICP Spectrometer. UV-visible spectral studies were

performed on a Agilent Cary 60 spectrophotometer. The N_2 gas adsorption isotherms were performed at 77 K on automatic volumetric adsorption equipment (Belsorp max). The equipment used for the CO_2 adsorption experiments was Autosorb IQ, Quantachrome sorptometer. Samples were out gassed prior to measurements being taken. Some adsorption experiments were also conducted after the samples were outgassed at 160 °C for 6 h (increasing rate 5 °C/min). The data was collected at 298 K from 0.025 bar to 1 bar (40 point system). H_2 adsorption experiments were conducted at 77 K using automatic volumetric adsorption equipment (Belsorp-max) in the pressure range of 0 to 1 bar.

Synthesis of bimetallic CoZn-ZIF-8 frameworks

Zn-ZIF-8 was prepared according to the previously reported procedure of Zhiping Lai *et al.* [S1], with slight modification to prepare bimetallic organic framework i.e. Co_xZn_{100-x}-ZIF-8 (x = 0-100). An aqueous solution of zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ and/or cobalt nitrate hexahydrate $Co(NO_3)_2 \cdot 6H_2O$ (total 0.98 mmol) (Molar percentages of $Co(NO_3)_2 \cdot 6H_2O$ used was 0%, 25%, 50%, 75%, 90% 100% to obtain Zn-ZIF-8, $Co_{25}Zn_{75}$-ZIF-8, $Co_{50}Zn_{50}$-ZIF-8, $Co_{75}Zn_{25}$-ZIF-8, $Co_{90}Zn_{10}$-ZIF-8 and Co-ZIF-8 frameworks, respectively) were prepared by dissolving the appropriate amounts in 2 mL of distilled water. Another aqueous solution was prepared by dissolving 2-methyl imidazole (5.675 g, 69.11 mmol) in 20 mL distilled water and filtered. The molar ratio of 2-methylimidazole to zinc and/or cobalt was 70:1. Material was synthesized via rapid pouring of aqueous solution of zinc nitrate hexahydrate and/or cobalt nitrate hexahydrate into the aqueous solution of 2-methyl imidazole, and the mixture was stirred at room temperature for 10 min. The product was collected by centrifugation (6500 rpm, 15-30 min) and washed with distilled water for 3 times. Further, it was dried at 65 °C overnight in a drying oven, after cooling to room temperature stored in tightly capped vials at room temperature.

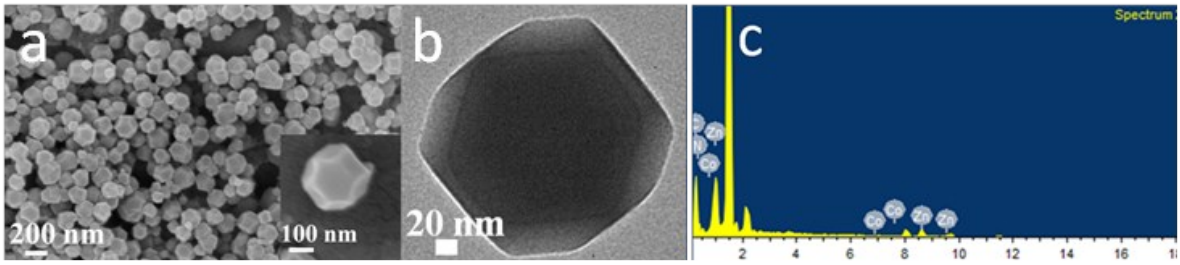

Figure S1 a) SEM, b) TEM micrographs and c) EDS spectra for $Co_{25}Zn_{75}$-ZIF-8

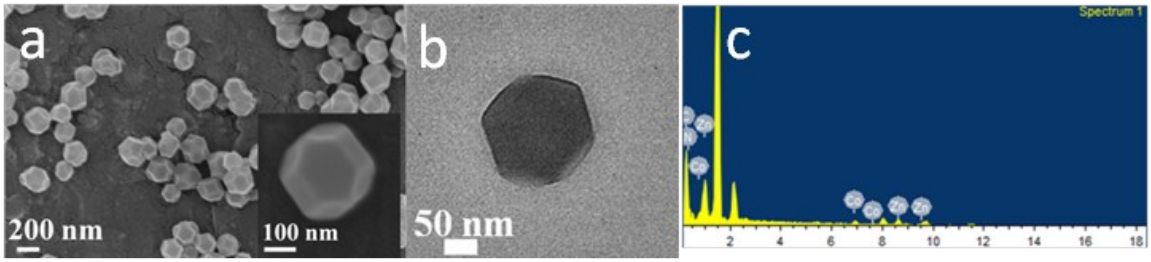

Figure S2 a) SEM, b) TEM micrographs and c) EDS spectra for $Co_{50}Zn_{50}$-ZIF-8

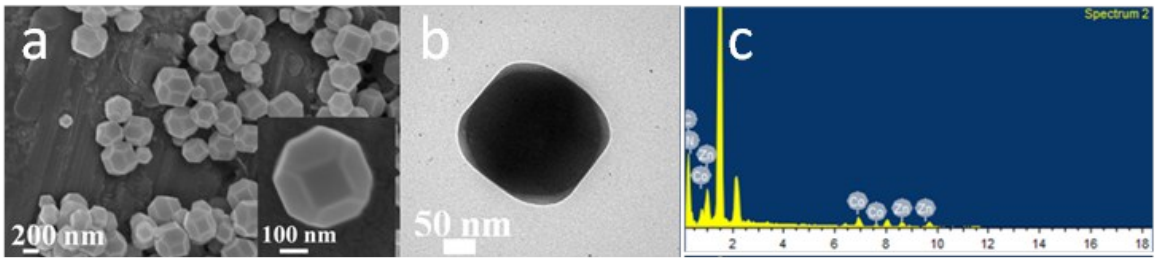

Figure S3 a) SEM, b) TEM micrographs and c) EDS spectra for $Co_{75}Zn_{25}$-ZIF-8

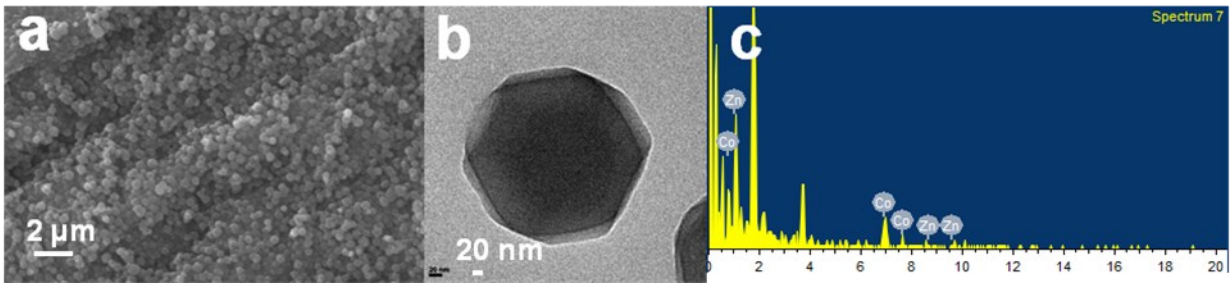

Figure S4 a) SEM, b) TEM micrographs and c) EDS spectra for $Co_{90}Zn_{10}$-ZIF-8

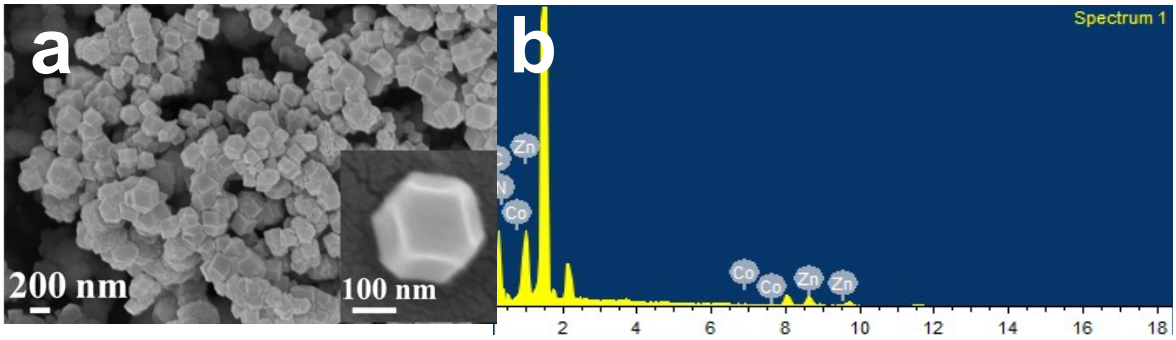

Figure S5 a) SEM micrograph and b) spectra for Zn-ZIF-8

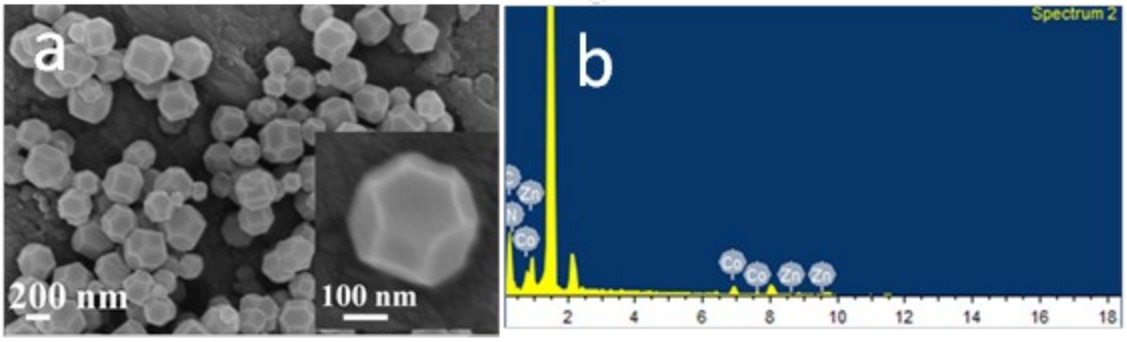

Figure S6 a) SEM micrograph and b) EDS spectra for Co-ZIF-8

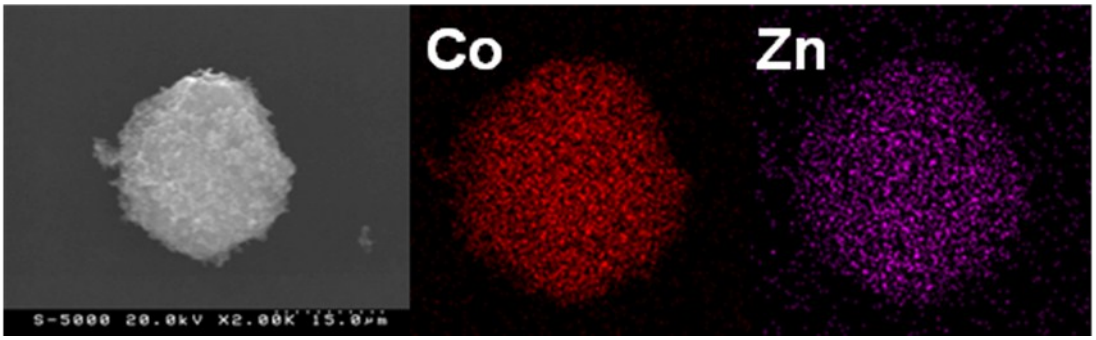

Figure S7 Elemental mapping of the $Co_{75}Zn_{25}$-ZIF-8

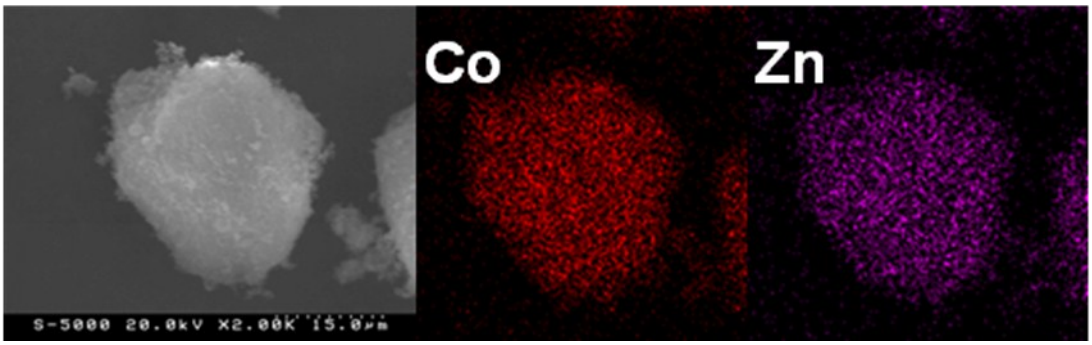

Figure S8 Elemental mapping of the $Co_{50}Zn_{50}$-ZIF-8

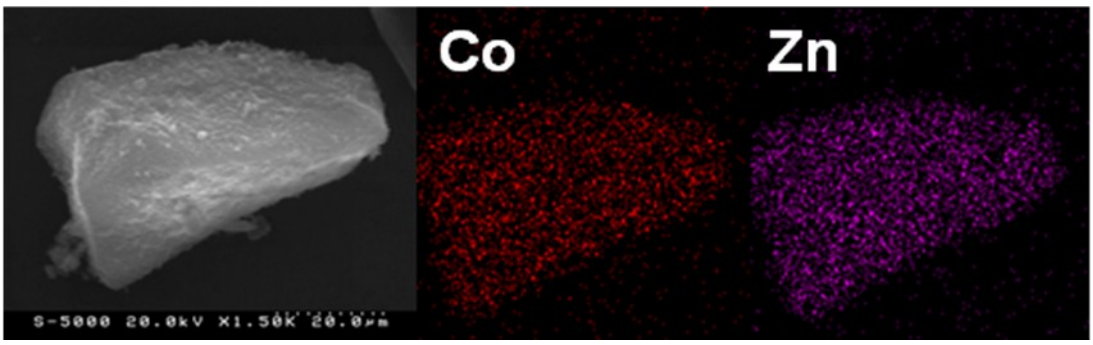

Figure S9 Elemental mapping of the $Co_{25}Zn_{75}$-ZIF-8

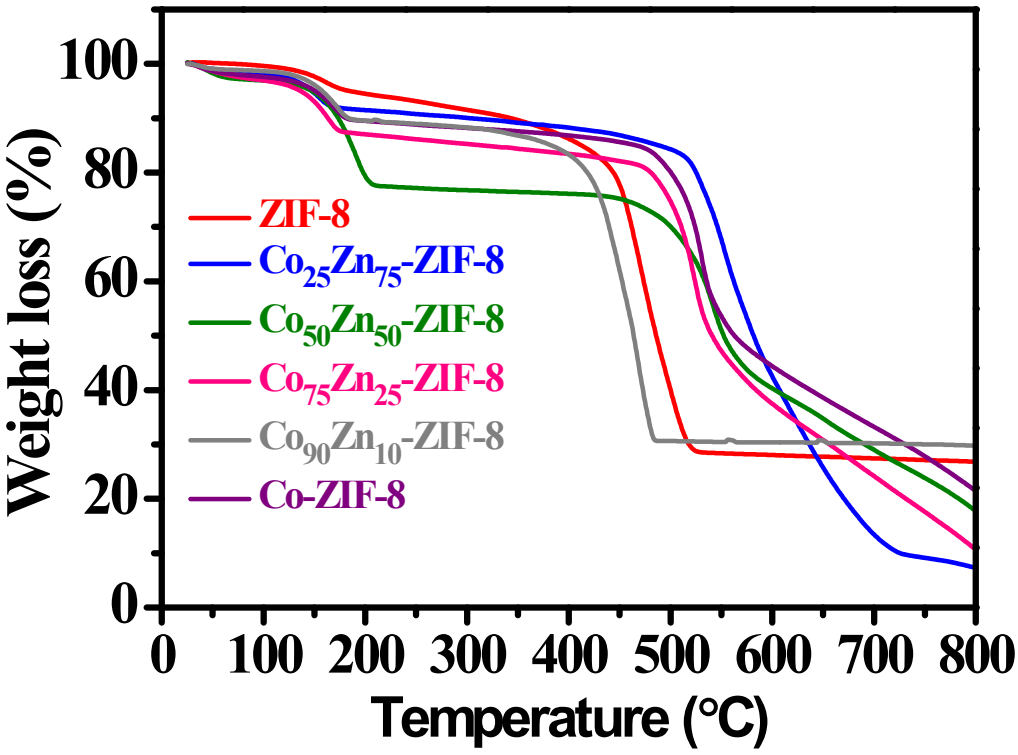

Figure S10 TGA curves for Zn-ZIF-8, CoZn-ZIF-8 and Co-ZIF-8

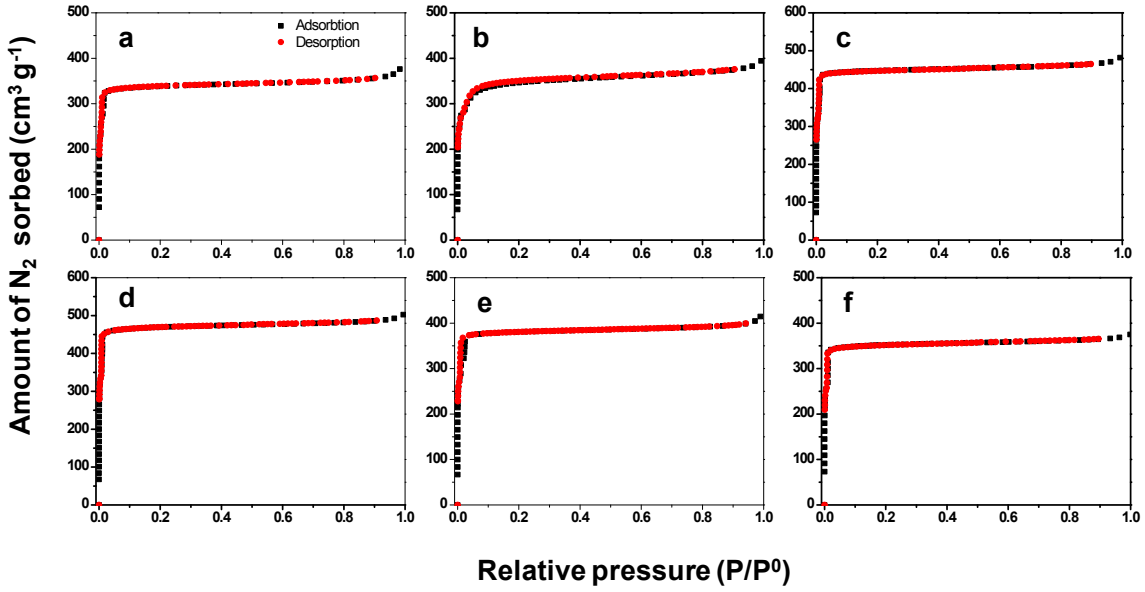

Figure S11 Adsorption-desorption N_2 isotherm of a) Zn-ZIF-8, b) $Co_{25}Zn_{75}$-ZIF-8, c) $Co_{50}Zn_{50}$-ZIF-8, d) $Co_{75}Zn_{25}$-ZIF-8 e) $Co_{90}Zn_{10}$-ZIF-8 and f) Co-ZIF-8 at 77 K

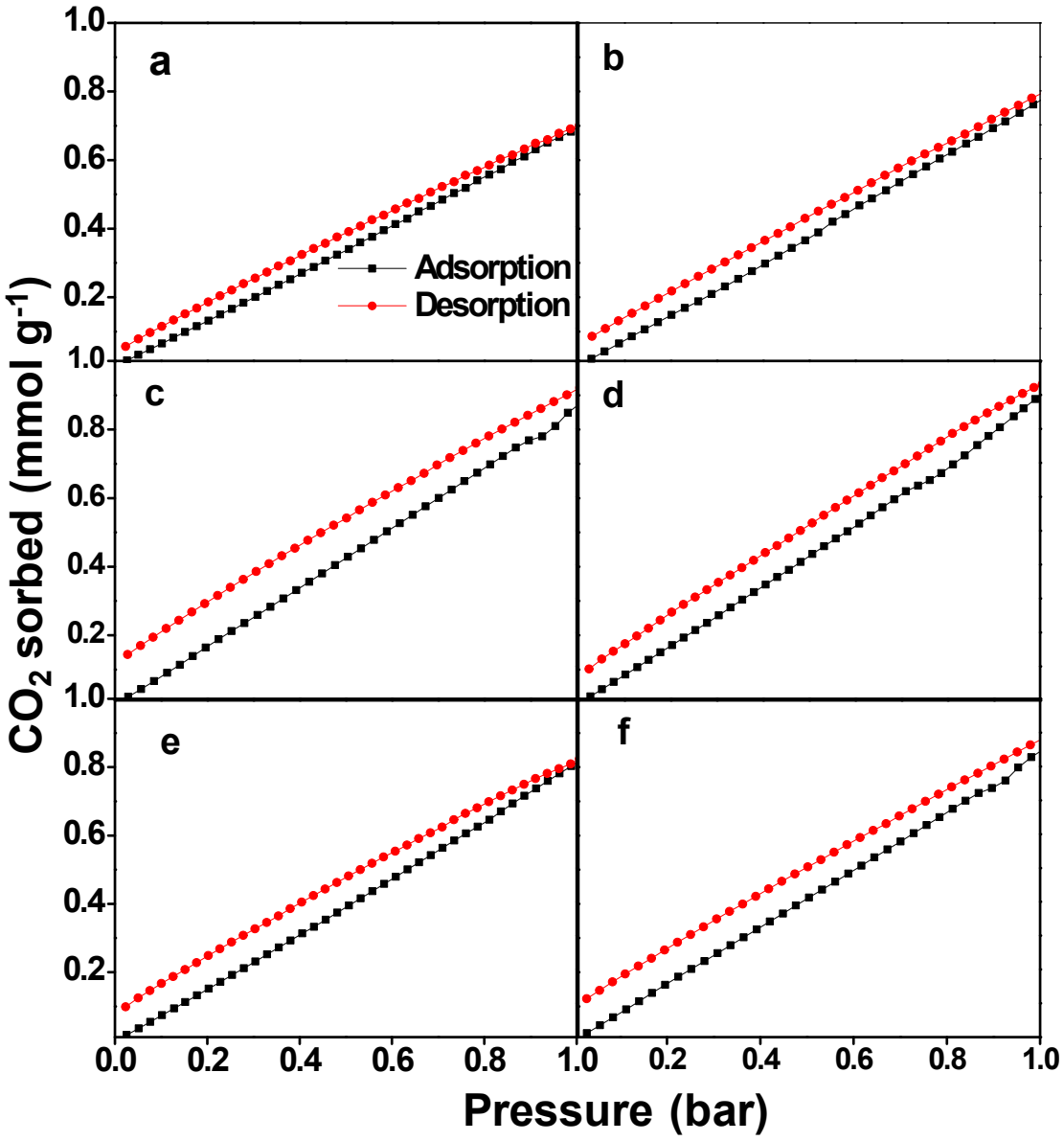

Figure S12 Adsorption-desorption CO_2 isotherm of a) Zn-ZIF-8, b) $Co_{25}Zn_{75}$-ZIF-8, c) $Co_{50}Zn_{50}$-ZIF-8, d) $Co_{75}Zn_{25}$-ZIF-8 e) $Co_{90}Zn_{10}$-ZIF-8 and f) Co-ZIF-8 at 298 K

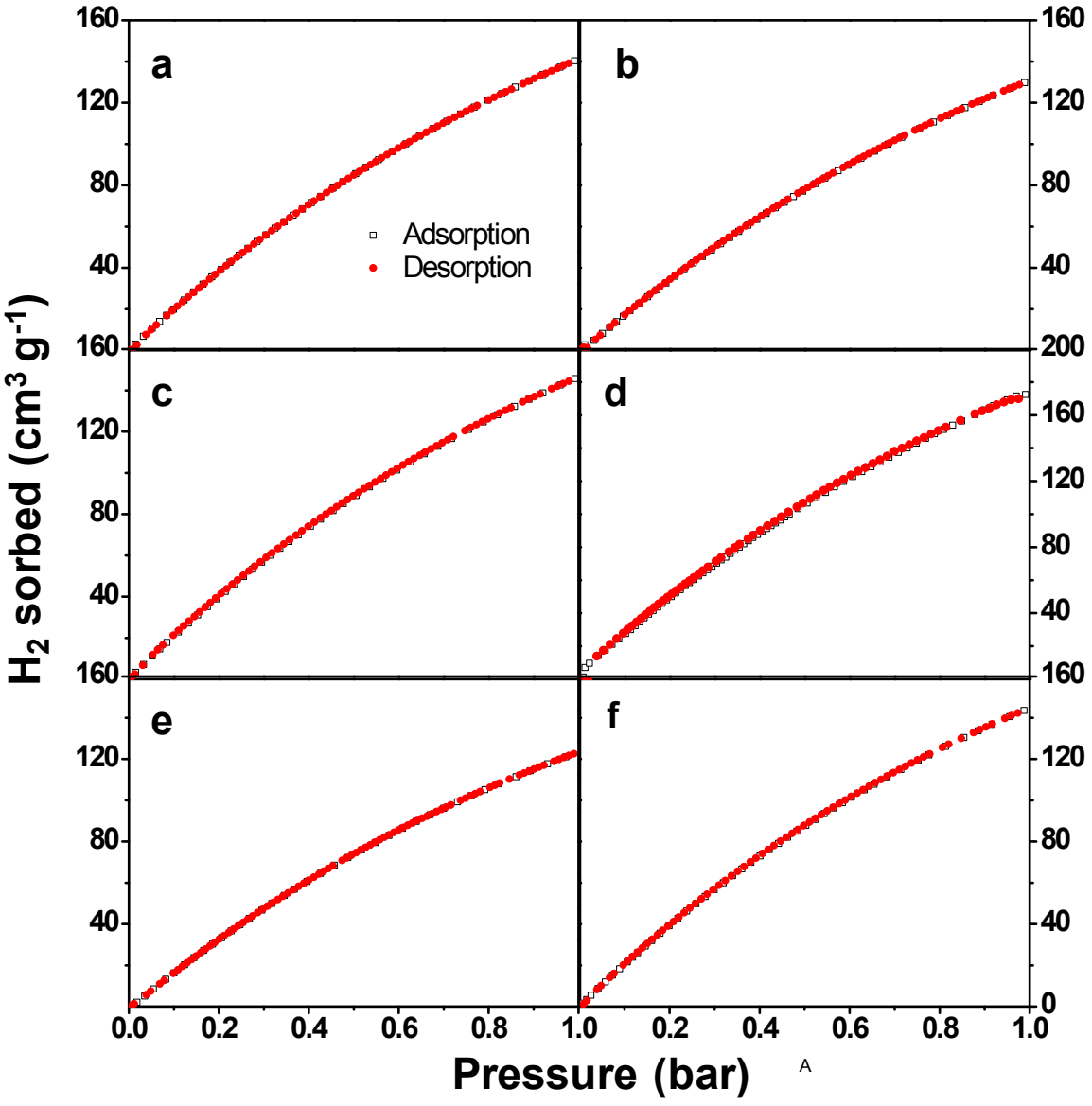

Figure S13 Adsorption-desorption H_2 isotherm of a) Zn-ZIF-8, b) $Co_{25}Zn_{75}$-ZIF-8, c) $Co_{50}Zn_{50}$-ZIF-8, d) $Co_{75}Zn_{25}$-ZIF-8 e) $Co_{90}Zn_{10}$-ZIF-8 and f) Co-ZIF-8 at 77 K

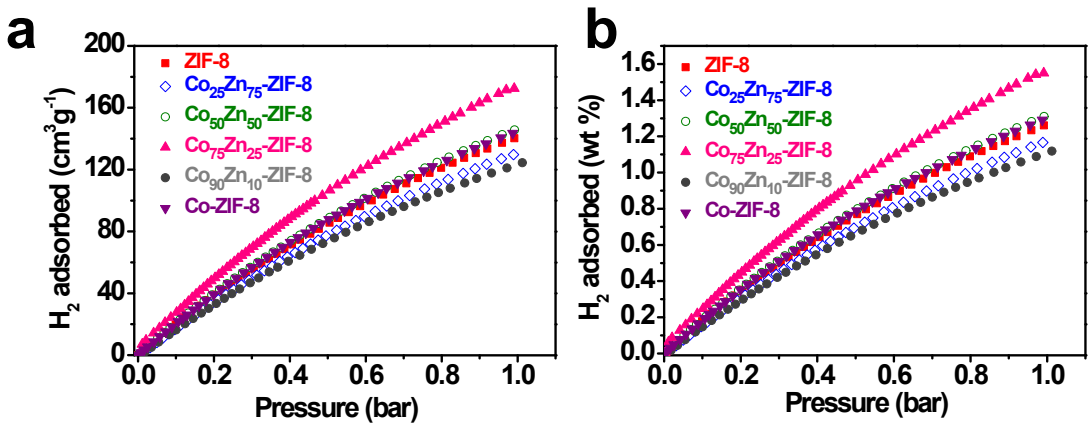

Fig. 14 H_2 adsorbtion isotherm at 77 K of Zn-ZIF-8, CoZn-ZIF-8 and Co-ZIF-8

Table S1 ICP-AES and EDS data in accordance with intended content of Co in CoZn-ZIF-8

Entry	ZIF frameworks	Co content (mol%) based on precursor materials used	EDS	ICP-AES
1	$Co_{25}Zn_{75}$-ZIF-8	25	24.8	22.3
2	$Co_{50}Zn_{50}$-ZIF-8	50	50.5	48.9
3	$Co_{75}Zn_{25}$-ZIF-8	75	77.9	74.8
4	$Co_{90}Zn_{10}$-ZIF-8	90	85	

Table S2 BET surface area, pore volume and pore diameter for Zn-ZIF-8, CoZn-ZIF-8 and Co-ZIF-8

Entry	ZIF frameworks	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (Å)	Surface area ($m^2\ g^{-1}$)
1	Zn-ZIF-8	0.5819	20.6	1131.1
2	$Co_{25}Zn_{75}$-ZIF-8	0.6086	21.0	1160.1
3	$Co_{50}Zn_{50}$-ZIF-8	0.7435	19.6	1518.8
4	$Co_{75}Zn_{25}$-ZIF-8	**0.7750**	**19.7**	**1571.7**
5	$Co_{90}Zn_{10}$-ZIF-8	0.6414	21.8	1180.0
6	Co-ZIF-8	0.5776	19.4	1191.2

Reference

S1 Y. Pan, Y. Liu, G. Zeng, L. Zhao and Z. Lai, *Chem. Commun*., 2011, **47**, 2071-2073.