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Electronic Supplementary Information

Synthesis of nanoporous cobalt/carbon materials by carbonized zeolitic imidazolate framework-9 and adsorption of dyes

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Experimental

1.1 Chemicals

$Co(CH_3COO)_2 \cdot 4H_2O$ (98%), benzimidazole (Hbim, 98%), anhydrous methanol and N,N-dimethylformaide (DMF) were purchased from commercial suppliers. Rhodamine 6G (98%), rhodamine B (98%), methylene green (96%), malachite green (98%), crystal violet (98%), rosanilin (98%), methyl blue (AR), methyl orange (AR), acid red 18 (98%), acid orange 7 (98%), orange G (98%) and congo red (98%) were used without further purification.

1.2 Synthesis of ZIF-9

ZIF-9 was prepared according to the procedures reported previously.[1] 100 mL

anhydrous methanol solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (10 mmol) was added rapidly to 100 mL DMF solution of Hbim (20 mmol). Then, the resultant mixture was stirred at room temperature (~25 °C) for 6 h to complete the crystallization. The obtained purple precipitate (ZIF-9) was collected by centrifugation and washed with anhydrous methanol for 4 times, and then dried at 80 °C under vacuum. The powder X-ray diffraction (PXRD) pattern, FT-IR spectrum and scanning electron microscope (SEM) image of the synthesized ZIF-9 were given in Fig. S1. By comparing with the reported literature, the characterizations indicate that ZIF-9 was successfully synthesized.[2]

1 N. L. Torad, M. Hu, S. Ishihara, H. Sukegawa, A. A. Belik, M. Imura, K. Ariga, Y. Sakka and T. Yamauchi, *Small,* 2014, **10**, 2096.

2 S. S. Yan, S. X. Ouyang, H. Xu, M. Zhao, X. L. Zhang and J. H. Ye, *J. Mater. Chem. A*, 2016, **4**, 15126.

1.3 Characterization

The PXRD measurements were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu K_α radiation (λ = 0.154 nm) and 2θ ranging from 7 to 80°. The FT-IR spectroscopy was conducted using a Mattson Alpha Centauri spectrometer on KBr pellets from 4000-400 cm^{-1}. SEM images were obtained on Hitachi SU8010, and the samples were mounted on aluminum studs by using adhesive graphite tape and sputter coated with gold before analysis. Raman spectra were performed with a Jobin Yvon HR800 micro-Raman spectrometer using a 488 nm line from a He-Cd laser. The N_2 adsorption-desorption experiments at 77 K were conducted

on automatic volumetric adsorption equipment (V-Sorb 2800S). Pore size distributions were calculated using density functional theory method.

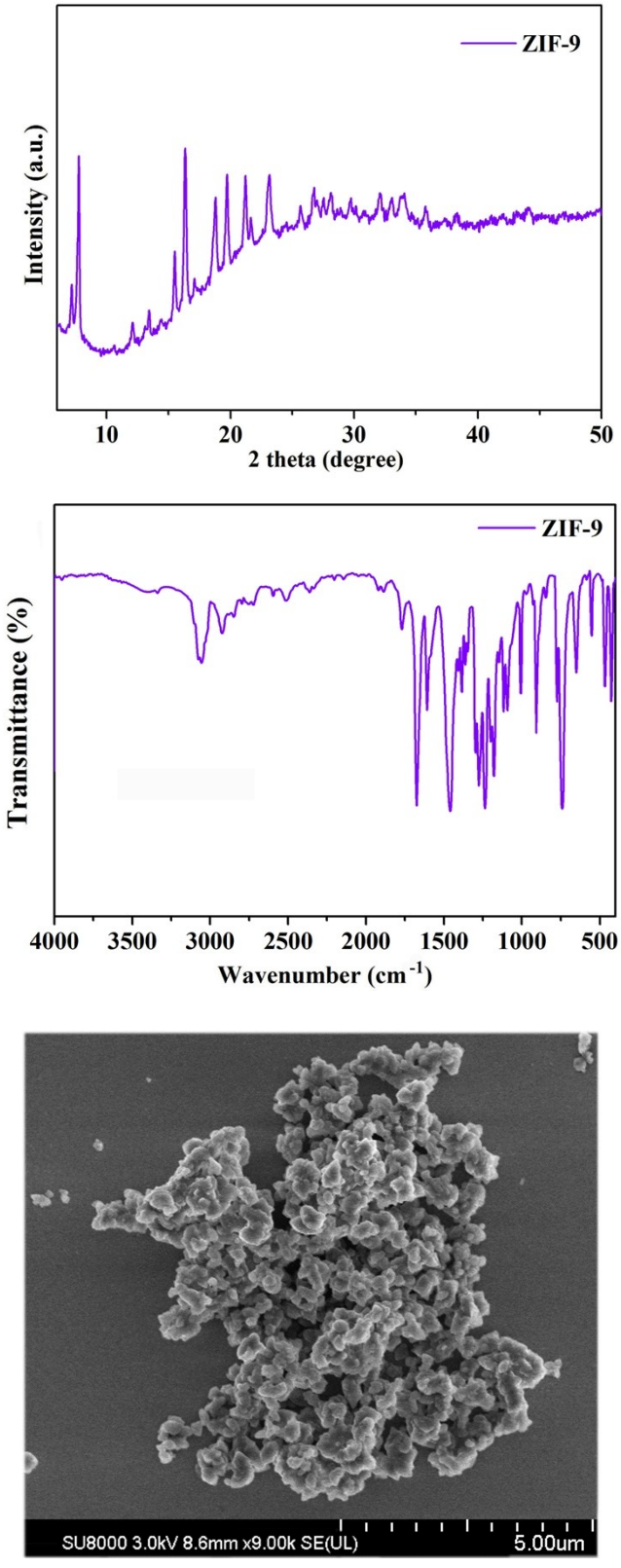
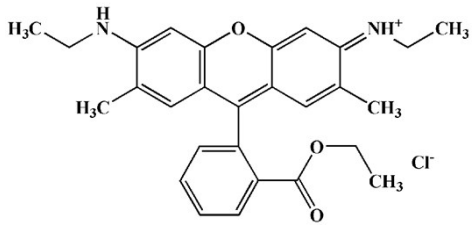
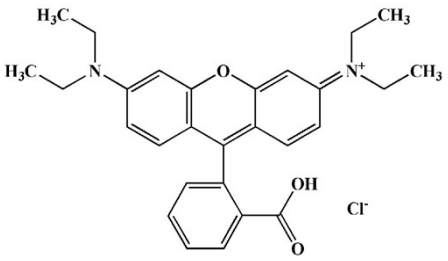
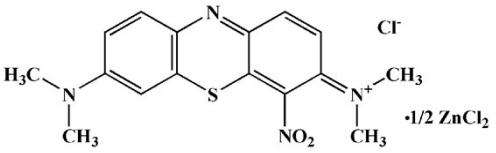
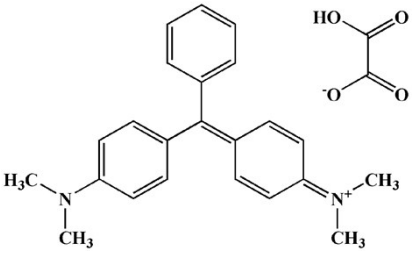
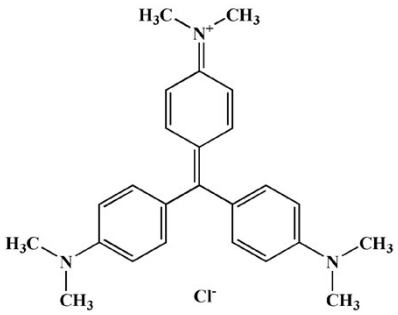
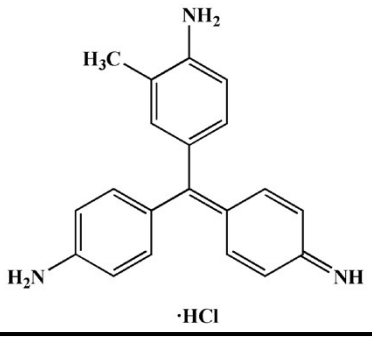


Fig. S1 PXRD pattern, FT-IR spectrum and SEM image of as-synthesized ZIF-9.

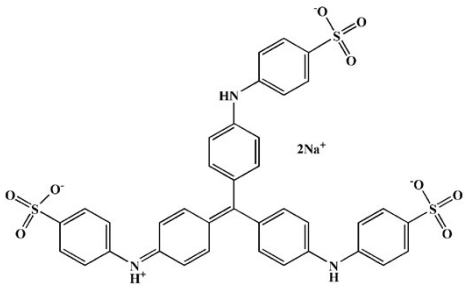
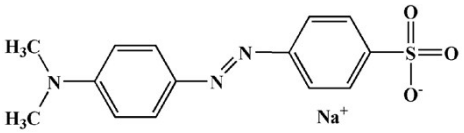
Table S1 The molecular structures, molecular weights (M_W) and calibrated UV-vis absorption wavelengths (λ) of dye molecules.

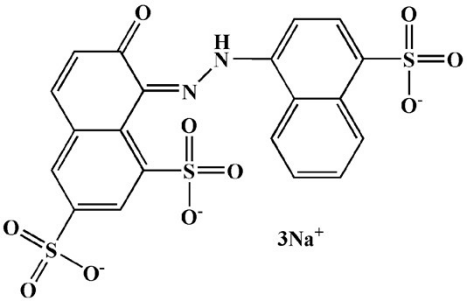
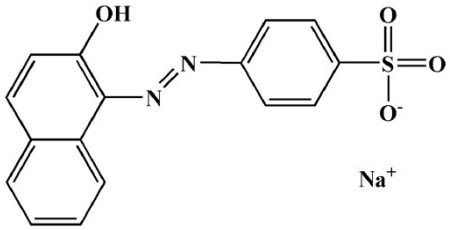
Dyes	Rhodamine 6G (R6G)	Rhodamine B (RHB)
M_W	479.0	479.0
λ (nm)	565	554
Molecular structures		

Dyes	Methylene green (MeG)	Malachite green (MaG)
M_W	433.0	463.5
λ (nm)	656	617
Molecular structures		

Dyes	Crystal violet (CV)	Rosanilin (RO)
M_W	372.5	337.8
λ (nm)	583	543
Molecular structures		

Dyes	Methyl blue (MB)	Methyl orange (MO)
M_W	799.0	327.4
λ (nm)	627	464

Molecular structures		

Dyes	Acid red 18 (AR)	Acid orange 7 (AO)
M_W	604.5	350.3
λ (nm)	507	484
Molecular structures		

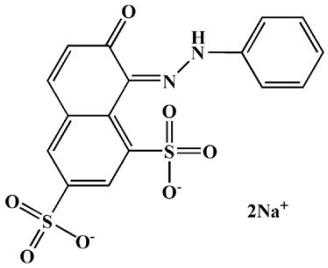
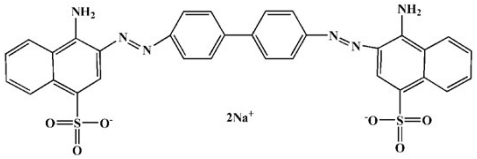
Dyes	Orange G (OG)	Congo red (CR)
M_W	452.4	696.7
λ (nm)	478	495
Molecular structures		

Table S2 Porosity properties of the as-prepared Z9-600, Z9-700, Z9-800 and Z9-900.

Samples	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Langmuir Surface area (m^2/g)	Pore size distribution (nm)
Z9-600	354.9	0.48	477.1	0.75-2.30
Z9-700	270.6	0.43	376.8	0.75-2.25
Z9-800	218.1	0.36	297.8	0.63-2.20
Z9-900	143.7	0.31	194.1	0.70-2.20

Table S3 Parameters of pseudo-second-order kinetic model and intraparticle diffusion

kinetic model of dyes adsorbed on Z9-600.

Dyes	Second-order kinetics			Intraparticle diffusion kinetics					
	q_e (mg/g)	K (g/mg•h)	R^2	K_{i1} (g/mg•h$^{0.5}$)	C_1	R_1^2	K_{i2} (g/mg•h$^{0.5}$)	C_2	R_2^2
MeG(C_0=0.5×10^{-4})	14.3	0.127	0.999	1.73	8.33	0.86	0.01	14.03	0.22
MeG(C_0=0.8×10^{-4})	23.1	0.066	0.999	3.19	12.04	0.87	0.02	22.63	0.22
MeG(C_0=1.0×10^{-4})	29.5	0.023	0.999	6.89	5.39	0.93	0.03	28.32	0.22
MeG(C_0=2.0×10^{-4})	58.2	0.024	0.999	3.86	41.54	0.98	0.29	55.29	0.51
MeG(C_0=2.5×10^{-4})	72.9	0.012	0.999	7.63	40.78	0.97	0.87	65.03	0.96
MaG(C_0=2.0×10^{-4})	61.6	0.136	0.994	13.78	33.93	0.95	0.02	62.29	0.76
CR(C_0=1.0×10^{-4})	50.2	0.006	0.997	12.98	0.81	0.97	0.43	43.87	0.66
RO(C_0=2.0×10^{-4})	46.4	0.041	0.996	14.11	18.73	0.93	0.57	41.75	0.92
AR(C_0=1.0×10^{-4})	56.8	0.001	0.996	8.56	-6.71	0.98	3.13	18.84	0.86
OG(C_0=1.0×10^{-4})	34.0	0.004	0.994	6.99	-2.88	0.99	0.76	23.91	0.78
CV(C_0=1.0×10^{-4})	28.2	0.013	0.998	6.27	2.82	0.95	0.61	22.30	0.72
AO(C_0=1.0×10^{-4})	23.9	0.029	0.998	4.71	6.62	0.87	0.11	22.34	0.75
MO(C_0=1.0×10^{-4})	23.5	0.010	0.997	6.36	-2.71	0.99	0.01	21.21	0.70
MB(C_0=1.0×10^{-4})	62.6	0.001	0.996	8.18	-4.72	0.98	2.06	32.47	0.94
RHB(C_0=1.0×10^{-4})	30.3	0.006	0.997	2.31	13.70	0.99	0.93	19.32	0.98
R6G(C_0=1.0×10^{-4})	27.6	0.009	0.995	0.88	19.01	0.99	0.35	22.90	0.97

Table S4 Fitting parameters of two kinds of isothermal models of MeG adsorbed on Z9-600.

Langmuir	q_m (mg/g)	K_L (L/mg)	R_l^2
	71.4	7.8	0.924
Freundlich	K_F (mg/g)	n	R_f^2
	62.6	3.0	0.851

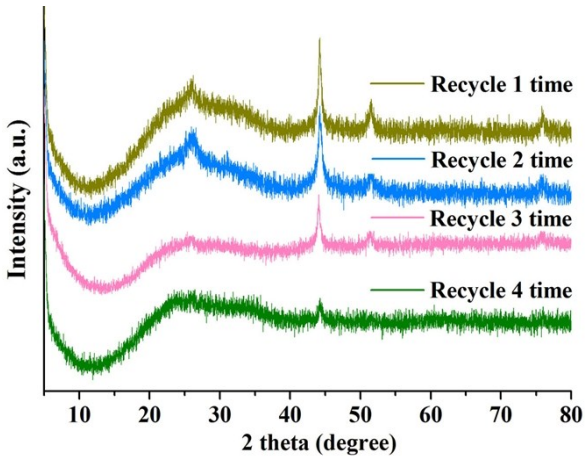


Fig. S2 PXRD patterns of regenerated Z9-600 after 4 cycles.