

Supporting Information for:

**Three novel Co(II)-based MOFs: Syntheses, structural diversity, and
adsorption properties**

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Text S1. Materials and general measurements, syntheses of MOFs 1-3.

3-(3,5-dicarboxylphenoxy)-6-carboxypyridine(H_3L), 1,3,5-tris(1-imidazolyl)benzene (tib), 4,4'-bis(imidazolyl)biphenyl (bibp), 3,5-bis(imidazolyl-1-yl)toluene (bip) were obtained from Jinan Henghua Sci. Tec. Co. Ltd. $Co(NO_3)_2 \cdot 6H_2O$, and different kinds of aromatic dyes, namely Congo Red (CR), Orange II (OII), Orange IV (OIV), Rhodamine B (RhB), Methylene blue (MB) and Acriflavine hydrochloride (AH) were purchased from Aladdin Industrial Corporation. The solvents were purchased from Sinopharm Chemical Reagent Co, Ltd. All reactants and solvents in analytical grade were obtained from commercial sources and were used without further purification.

Elemental analyses (C, H, N) were performed in a model 2400 PerkinElmer analyzer. The X-ray diffraction (XRD) patterns were performed on a D/max 2200 vpc diffractometer (Rigaku Corporation, Japan) with the $Cu-K\alpha$ radiation. The powder X-ray diffractions (PXRD) were collected on an Enraf-Nonius CAD-4 X-ray single-crystal diffractometer with $Cu-K\alpha$ radiation. Dye concentrations were tested by spectrophotometer (Shanghai Yuanxi, UV-1250). Zeta potential were measured by Zetasizer Nano-ZS90 (Malvern Panalytical, Britain). The porosities and BET surface areas of the samples were recorded by N_2 adsorption-desorption isotherms (Micromeritics ASAP 2460 surface area and porosity analyzer). Infrared spectra in the $4000 - 500\text{ cm}^{-1}$ region was recorded on a Nicolet 170SX spectrometer using KBr powder. Thermogravimetric analyses (TG) were conducted on a PerkinElmer TGA-7 analyzer under N_2 conditions from room temperature to $800\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Absorption spectra were collected via the HITACHI F-4500 UV-Vis Spectrophotometer and the ultrasonic cleaner type was 42 kHz working frequency with 200 W ultrasonic power.

Synthesis of $\{[Co(HL)(tib)(H_2O)] \cdot 2H_2O\}_n$ (1)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.058g, 0.2 mmol), H_3L (0.030 g, 0.1 mmol), tib (0.055 g, 0.2 mmol), N,N-dimethylformamide (DMF) (5 mL) and H_2O (5 mL) were stirred for 0.5 hour in air. And then the solution was transformed into the Teflon-lined stainless-steel vessel (15 mL), sealed and heated to $130\text{ }^\circ\text{C}$ and kept for 3 days. Subsequently, the vessel

was cooled to the room temperature at the degree of $5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$. Orange red block crystals were collected with the yield of 83.7 % (based on cobalt). Anal. Calcd for $\text{C}_{29}\text{H}_{21}\text{CoN}_7\text{O}_8\cdot 2(\text{H}_2\text{O})$: C, 50.45; H, 3.65, N, 14.20 %. Found: C, 50.12; H, 3.46; N, 13.89 %. IR (KBr disk, cm^{-1}): 3122 (w), 2363 (w), 1622 (s), 1561(m), 1510 (s), 1241 (m), 1072 (m), 1015 (w), 937 (w), 764 (m), 660 (w).

Synthesis of $[\text{Co}_3(\text{L})_2(\text{bibp})_4(\text{H}_2\text{O})_2]_n$ (**2**)

Changing the tib of **1** to bibp (0.029 g, 0.1 mmol) and the solvent to DMF (3 mL) and H_2O (5 mL), other conditions remained unchanged. Pink block crystals were collected with the yield of 81.5 % (based on cobalt). Anal. Calcd for $\text{C}_{100}\text{H}_{72}\text{Co}_3\text{N}_{18}\text{O}_{16}$: C, 61.33; H, 3,71, N, 12.87 %. Found: C, 61.16; H, 3.58; N, 12.76 %. IR (KBr disk, cm^{-1}): 3133 (m), 1559 (s), 1517(vs), 1363 (m), 1305 (m), 1248 (m), 1124 (w), 1063 (m), 963 (m), 819 (m), 776 (w), 719 (w), 653 (w).

Synthesis of $[\text{Co}_2(\text{L})(\text{bip})(\mu_3\text{-OH})]_n$ (**3**)

Changing the tib of **1** to bip (0.022 g, 0.2 mmol), and the solvent to DMF (6 mL) and H_2O (3 mL), other conditions remain unchanged. Purple block crystals were collected with the yield of 75.4 % (based on cobalt). Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{Co}_2\text{N}_5\text{O}_8$: C, 49.26; H, 2.76; N, 10.64 %. Found: C, 49.15; H, 2.51; N, 10.43 %. IR (KBr disk, cm^{-1}): 2359 (w), 1653 (m), 1615 (s), 1565 (s), 1507 (m), 1457 (w), 1386 (s), 1249 (w), 1058 (w), 781 (w), 718 (w).

X-ray crystal structure determination

The suitable crystals of the coordination polymers were collected for single crystal X-ray diffraction. The data were collected on a Bruker Apex Smart CCD diffractometer, using graphite-monochromated Mo- $\text{k}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) by using the ω - 2θ scan mode at 150 K. The structure was solved by direct methods using SHELXS-97. The non-hydrogen atoms were defined by the Fourier synthesis method. Positional and thermal parameters were refined by the full matrix least-squares method (on F^2) to convergence.

Text S2. Adsorption kinetics models

The pseudo-first-order equation is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where q_t is the adsorption capacity at time t ($\text{mg}\cdot\text{g}^{-1}$), and k_1 is the equilibrium rate constant (h^{-1}).

The pseudo-second-order equation is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where q_t and q_e are the adsorption capacity at time t and equilibrium, respectively ($\text{mg}\cdot\text{g}^{-1}$); k_2 is the equilibrium rate constant ($\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$).

Text S3. Adsorption isotherms

In order to designate the adsorption behavior and to assess the adsorption capacity, adsorption isotherms were studied by Langmuir and Freundlich isotherm models.

The Langmuir isotherm model describes the equilibrium of the adsorbate between the adsorbent surface and the solution in the form of a monolayer reversible equilibrium. The model assumes the presence of a certain number of uniformly distributed adsorption sites on the adsorbent surface, the design, fluorescence sensing and adsorption properties of a new transition system metal-organic framework and that its adsorption form is single-molecule type. The linear form is shown in the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$$

where c_e is the concentration of dyes at equilibrium; q_e is the corresponding adsorption capacity; q_m is the maximum adsorption capacity of the adsorbent and K_L is the Langmuir isotherm constant.

The Freundlich isotherm model is used to study multilayer adsorption in non-ideal multiphase adsorption systems. Assuming that the adsorption surface is not uniformly distributed, the adsorption equilibrium constant is related to the coverage of the adsorbent surface. Its linear form is shown in the following equation is shown.

$$\ln q_e = \ln K_F + \frac{1}{n}(\ln c_e)$$

where K_F is the Freundlich constant related to the adsorption capacity and adsorption strength per unit volume concentration. n is the adsorption strength constant under the Freundlich model, which indicates the goodness of adsorption. If $n > 1$, it indicates that the adsorption process is favorable.

Table S1 Selected bond lengths (Å) and angles (°) for **1-3**

1			
Co1—O1	2.089 (2)	Co1—N2	2.111 (3)
Co1—O3	2.075 (2)	Co1—N4 ⁱ	2.146 (3)
Co1—N1	2.143 (3)	Co1—N7 ⁱⁱ	2.155 (3)
O1—Co1—N1	78.24 (10)	O3—Co1—N7 ⁱⁱ	90.13 (10)
O1—Co1—N2	90.90 (10)	N1—Co1—N4 ⁱ	87.52 (10)
O1—Co1—N4 ⁱ	91.19 (10)	N1—Co1—N7 ⁱⁱ	88.68 (10)
O1—Co1—N7 ⁱⁱ	87.67 (9)	N2—Co1—N1	168.74 (11)
O3—Co1—O1	172.97 (9)	N2—Co1—N4 ⁱ	89.79 (10)
O3—Co1—N1	95.04 (10)	N2—Co1—N7 ⁱⁱ	93.87 (10)
O3—Co1—N2	95.92 (10)	N4 ⁱ —Co1—N7 ⁱⁱ	176.18 (10)
O3—Co1—N4 ⁱ	90.57 (10)		
Symmetry codes: (i) -x+1, -y, -z+1; (ii) -x, y+1/2, -z+1/2.			
2			
Co1-O2	2.038 (3)	Co2-O10	2.278 (4)
Co1-O5 ^{iv}	2.068 (3)	Co2-N10	2.066 (4)
Co1-N9 ^{iv}	2.136 (3)	Co2-N14	2.059 (4)
Co1-O1	2.171 (3)	Co3-O11	2.073 (3)
Co1-N5	2.158 (3)	Co3-O16 ⁱ	2.077 (3)
Co1-N1	2.088 (4)	Co3-O12	2.198 (3)
Co2-O9	2.090 (3)	Co3-N13 ⁱⁱ	2.083 (3)
Co2-O8	2.092 (3)	Co3-N18 ⁱ	2.105 (3)
Co2-O7	2.201 (3)	Co3-N8 ⁱⁱⁱ	2.163 (3)
O2—Co1—O5 ^{iv}	170.58 (12)	O10—Co2—C87	29.96 (13)
O2—Co1—N9 ^{iv}	92.46 (12)	N10—Co2—O9	95.01 (14)
O2—Co1—O1	86.30 (12)	N10—Co2—O8	111.12 (14)
O2—Co1—N5	87.23 (12)	N10—Co2—O7	84.60 (13)
O2—Co1—N1	97.58 (13)	N10—Co2—O10	154.40 (13)
O5 ^{iv} —Co1—N9 ^{iv}	78.59 (11)	N10—Co2—C32	96.34 (15)
O5 ^{iv} —Co1—O1	96.81 (12)	N10—Co2—C87	124.62 (15)
O5 ^{iv} —Co1—N5	90.01 (12)	N14—Co2—O9	109.54 (15)
O5 ^{iv} —Co1—N1	91.56 (13)	N14—Co2—O8	98.44 (14)
N9 ^{iv} —Co1—O1	91.69 (14)	N14—Co2—O7	158.10 (14)
N9 ^{iv} —Co1—N5	91.38 (13)	N14—Co2—O10	88.36 (15)
N5—Co1—O1	172.96 (13)	N14—Co2—N10	95.93 (15)
N1—Co1—N9 ^{iv}	169.23 (14)	N14—Co2—C32	128.17 (15)
N1—Co1—O1	85.10 (15)	N14—Co2—C87	98.12 (15)
N1—Co1—N5	92.99 (14)	O11—Co3—O16 ⁱ	172.41 (11)

O9—Co2—O8	139.38 (14)	O11—Co3—O12	87.49 (11)
O9—Co2—O7	92.18 (13)	O11—Co3—O12	87.49 (11)
O9—Co2—O10	59.98 (12)	O11—Co3—N18 ⁱ	94.05 (12)
O9—Co2—C32	119.21 (15)	O11—Co3—N8 ⁱⁱⁱ	85.92 (12)
O9—Co2—C87	30.16 (13)	O16 ⁱ —Co3—O12	95.24 (12)
O8—Co2—O7	61.45 (11)	O16 ⁱ —Co3—N13 ⁱⁱ	90.13 (12)
O8—Co2—O10	93.07 (13)	O16 ⁱ —Co3—N18 ⁱ	78.96 (11)
O8—Co2—C32	30.95 (13)	N13 ⁱⁱ —Co3—O12	91.05 (12)
O8—Co2—C87	119.19 (15)	N13 ⁱⁱ —Co3—N18 ⁱ	168.98 (13)
O7—Co2—O10	100.62 (13)	N13 ⁱⁱ —Co3—N8 ⁱⁱⁱ	94.37 (13)
O7—Co2—C32	30.73 (12)	N18 ⁱ —Co3—O12	88.47 (12)
O7—Co2—C87	99.54 (15)	N18 ⁱ —Co3—N8 ⁱⁱⁱ	87.36 (13)
O10—Co2—C32	100.76 (15)	N8 ⁱⁱⁱ —Co3—O12	171.93 (12)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+1/2, -y+3/2, z+1/2$; (iii) $x, -y+1, z+1/2$;
(iv) $-x+1, -y+1, -z+1$.

3

Co1—O7	2.162 (2)	Co2—O7 ⁱⁱⁱ	2.183 (2)
Co1—O1 ⁱⁱ	2.078 (2)	Co2—O8 ^{iv}	2.099 (2)
Co1—O4	2.065 (2)	Co2—O3	2.095 (2)
Co1—N3	2.094 (3)	Co2—O2 ^v	2.112 (2)
Co1—N5 ⁱ	2.136 (3)	Co2—N1	2.095 (3)
O8—Co1—O7 ⁱ	80.84 (9)	O8 ^{iv} —Co2—O7 ⁱⁱⁱ	78.63 (9)
O8—Co1—O1 ⁱⁱ	91.45 (10)	O8—Co2—O7 ⁱⁱⁱ	90.25 (9)
O8—Co1—O4	101.89 (9)	O8—Co2—O8 ^{iv}	80.77 (9)
O8—Co1—N3	102.59 (10)	O8—Co2—O3	99.60 (9)
O8—Co1—N5 ⁱ	155.09 (10)	O8—Co2—O2 ^v	178.85 (9)
O1 ⁱⁱ —Co1—O7 ⁱ	96.33 (9)	O8 ^{iv} —Co2—O2 ^v	98.30 (9)
O1 ⁱⁱ —Co1—N3	84.37 (10)	O8—Co2—N1	93.01 (10)
O1 ⁱⁱ —Co1—N5 ⁱ	81.73 (10)	O3—Co2—O7 ⁱⁱⁱ	164.92 (9)
O4—Co1—O7 ⁱ	90.45 (9)	O3—Co2—O8 ^{iv}	91.61 (10)
O4—Co1—O1 ⁱⁱ	165.87 (9)	O3—Co2—O2 ^v	81.08 (10)
O4—Co1—N3	88.14 (10)	O3—Co2—N1	91.91 (11)
O4—Co1—N5 ⁱ	87.90 (10)	O2 ^v —Co2—O7 ⁱⁱⁱ	88.91 (9)
N3—Co1—O7 ⁱ	176.49 (10)	N1—Co2—O7 ⁱⁱⁱ	99.00 (10)
N3—Co1—N5 ⁱ	100.55 (11)	N1—Co2—O8 ^{iv}	173.28 (11)
N5 ⁱ —Co1—O7 ⁱ	76.18 (10)	N1—Co2—O2 ^v	87.89 (10)

Symmetry codes: (i) $-x+1/2, -y+3/2, -z+1$; (ii) $x-1/2, -y+3/2, z$; (iii) $x, y, z+1$;
(iv) $-x+1/2, -y+3/2, -z+2$; (v) $-x+1, y, -z+2$.

Thermogravimetric analysis (TGA) under dinitrogen in the range of 30 - 790 °C at a heating rate of 10 °C min⁻¹ was carried out on **1-3** to investigate their thermal stability.

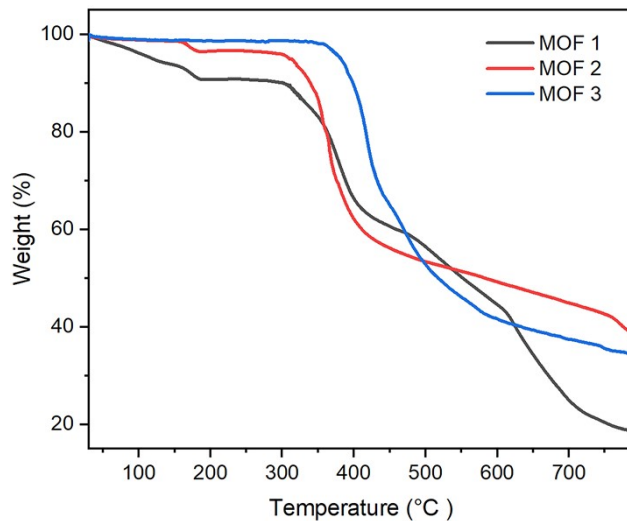


Fig. S1 TG curve of **1-3**.

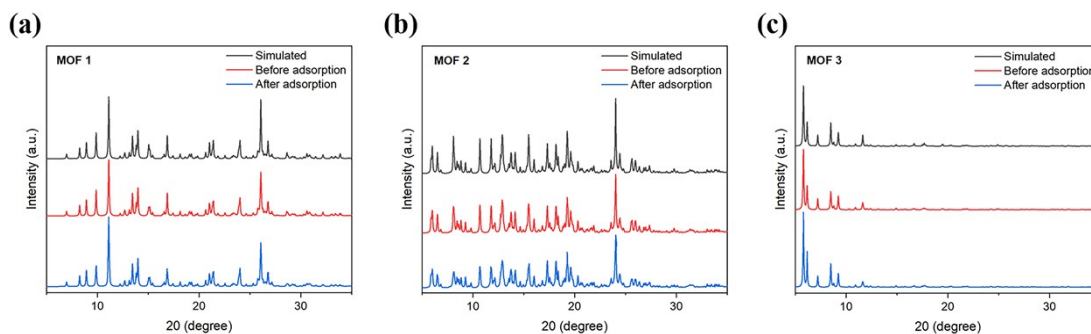


Fig. S2 The PXRD patterns of **1-3** before and after soaking and adsorption.

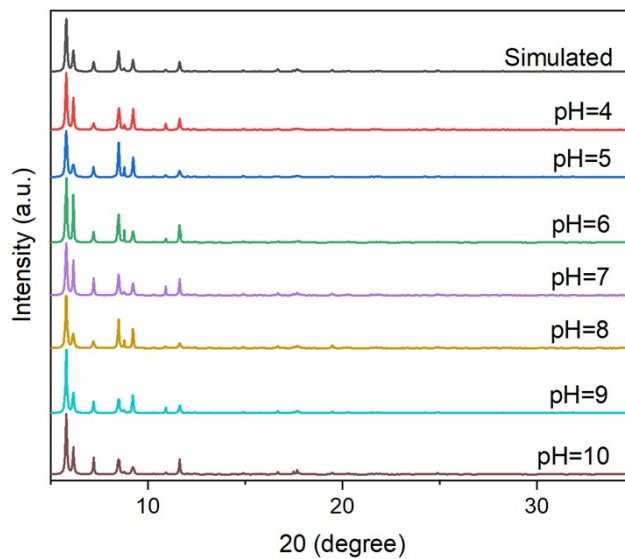


Fig. S3 The PXRD patterns of **3** at different pH.

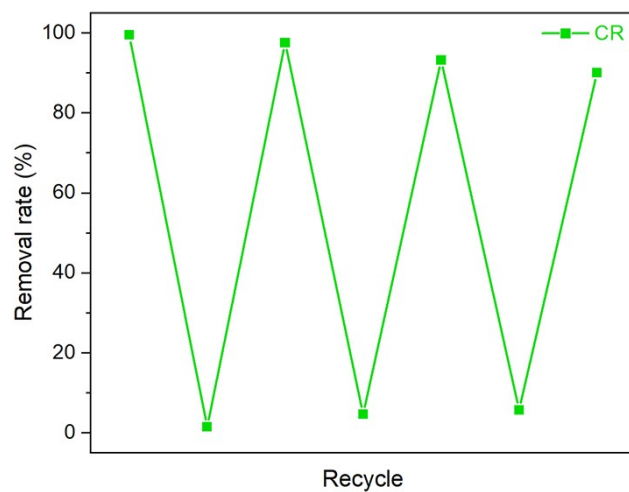


Fig. S4 The repeated adsorptions of CR for **3**.

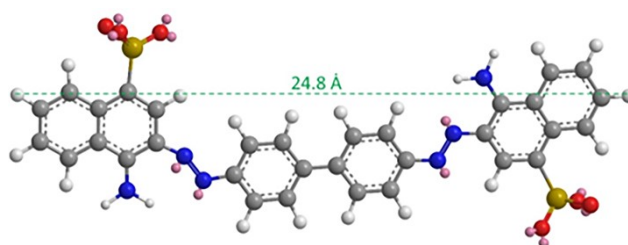


Fig. S5 Structural formula of Congo red.

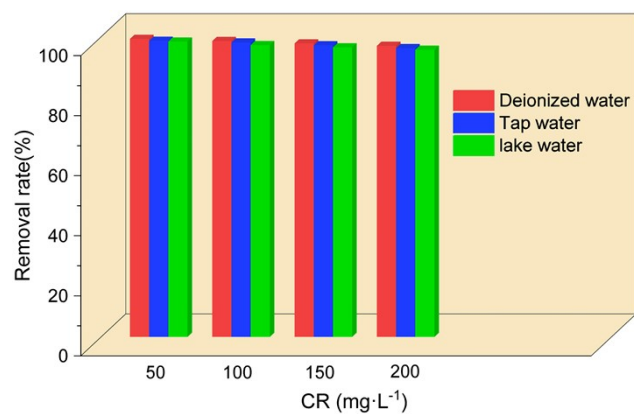


Fig. S6 Removal rates of CR at different concentrations by **3** in actual water samples.