Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Three Neutral Metal–Organic Frameworks with Micro- and Meso-pores for Adsorption and Separation of Dyes

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Synthesis of complex 2: A solution of **1** (0.5 mmol), pz (0.4 mmol) in DMF (10 mL) was heated at 90 °C for 3 days. The resulting turquoise octahedral crystals were collected, washed with ethanol, and dried at room temperature. Elemental analysis for $C_{408}H_{592}Cu_{24}N_{76}O_{196}$ (11218.04) (%): calcd. C 43.67 H 5.31 N 9.49; found C 43.62 H 5.35 N 9.50.

Synthesis of complex 3: A solution of **1** (0.5 mmol), bpy (0.4 mmol) in DMF (10 mL) was heated at 90 °C for 3 days. The resulting turquoise octahedral crystals were collected, washed with ethanol, and dried at room temperature. Elemental analysis for $C_{609}H_{1001}Cu_{24}N_{131}O_{251}$ (15699.37) (%): calcd. C 46.59 H 6.43 N 11.69; found C 46.57 H 6.41 N 11.71.

Synthesis of complex 4: A solution of **1** (0.5 mmol), bpe (0.4 mmol) in DMF (10 mL) was heated at 90 °C for 3 days. The resulting turquoise octahedral crystals were collected, washed with ethanol, and dried at room temperature. Elemental analysis for $C_{678}H_{1194}Cu_{24}N_{150}O_{270}$ (17292.69) (%): calcd. C 47.09 H 6.96 N 12.15; found C 47.02 H 6.98 N 12.13.

Dye adsorption:

Freshly prepared **3** were added into to DMF solutions containing Methylene Blue (**MB**), Rhodamine B (**RB**) and Methyl Orange (**MO**) in the dark at room temperature, respectively.

UV/Vis spectra were employed to measure the adsorption ability of **3** after certain time intervals.

Dye release:

3 loaded with **MB** were transferred to pure DMF and NaCl with different qualities in DMF solution, respectively.

UV/Vis spectra were employed to measure release process of **3** after certain time intervals.

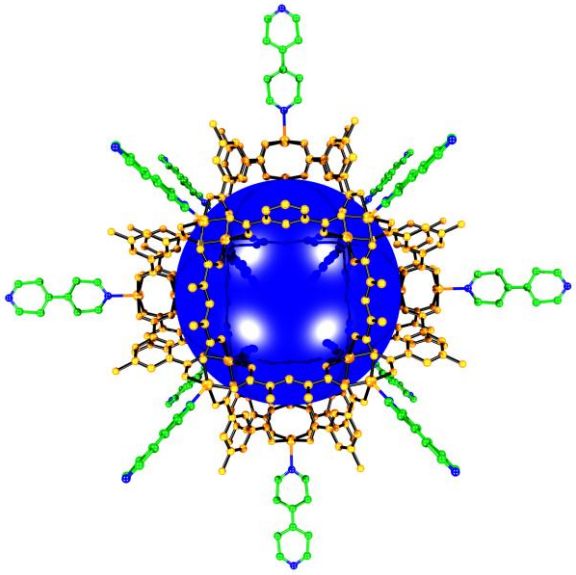
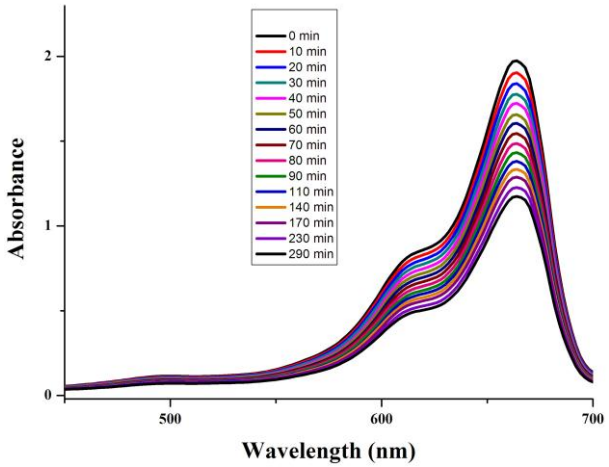


Fig. S1 The micropore surrounded by 12 bpy ligands.



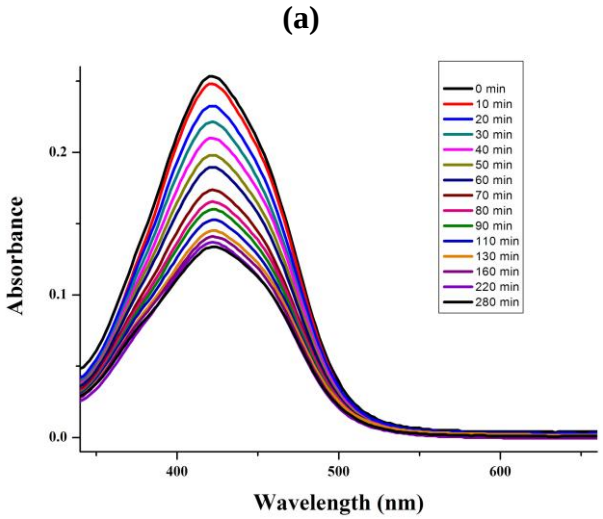


Fig. S2 UV/vis absorption spectra for (a) **MB** and (b) **MO** adsorption by 10 mg of **3** in 3 mL of dye-contaminated DMF.

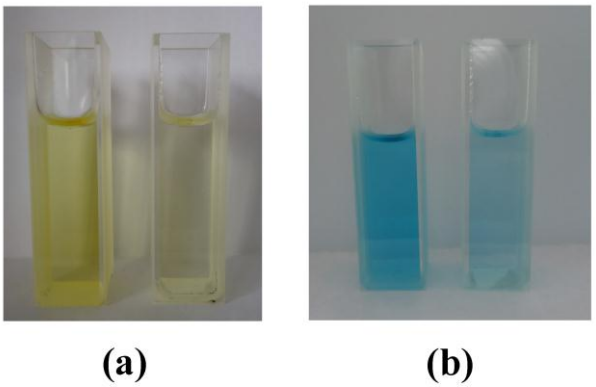


Fig. S3 Color changes of solutions containing (a) **MO**, (b) **MB** before (left) and after (right) addition of **3** (300 min).

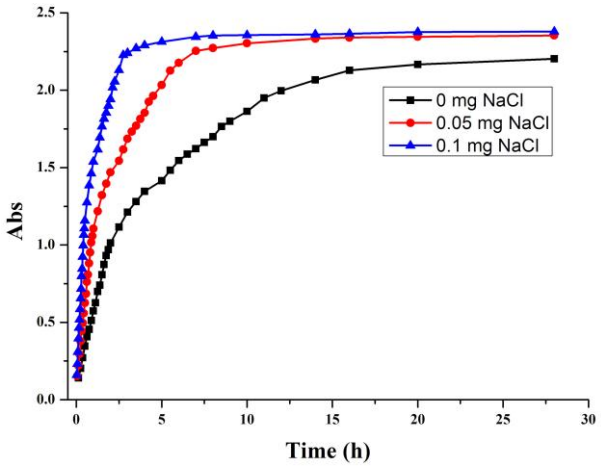


Fig. S4 The dye release from **3**@**MB** crystal.

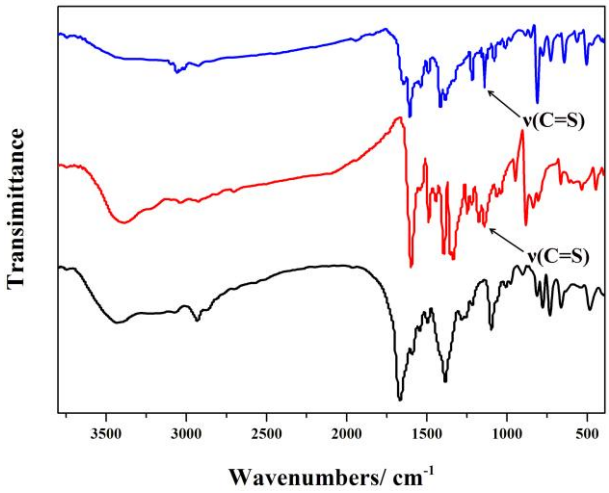


Fig. S5 IR spectra of **3** (black), **MB** (red) and **3** loaded with **MB** (blue).

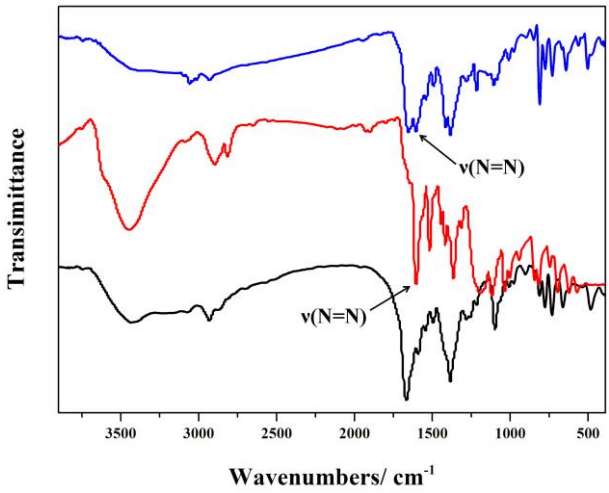


Fig. S6 IR spectra of **3** (black), **MO** (red) and **3** loaded with **MO** (blue).

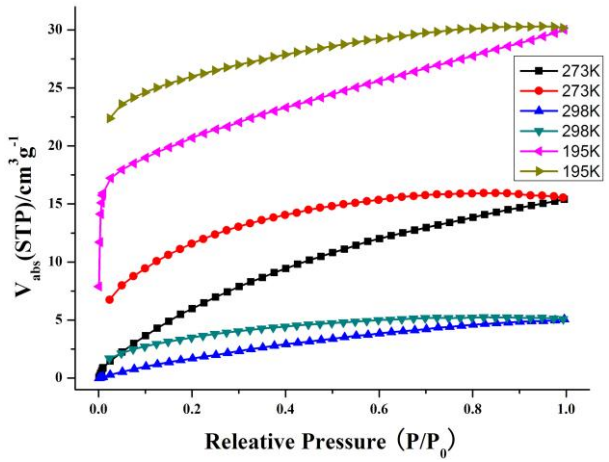


Fig. S7 CO_2 sorption isotherms of **3** under different temperatures.

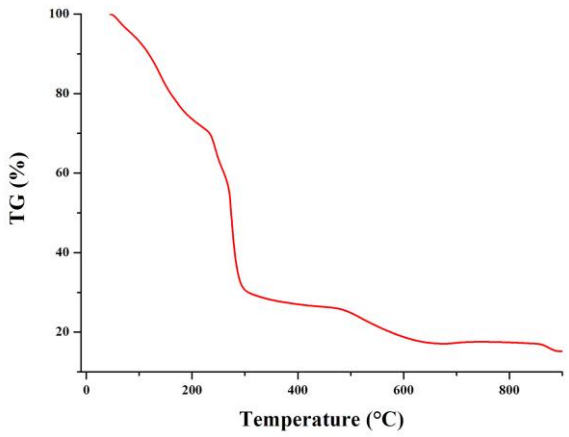


Fig. S8 The TG curve of **3**.

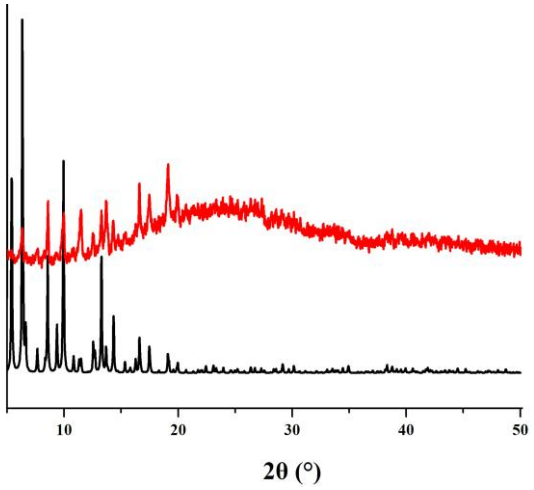


Fig. S9 Experimental and simulated powder X-Ray diffraction patterns for **3** (black: simulated; red: experimental).

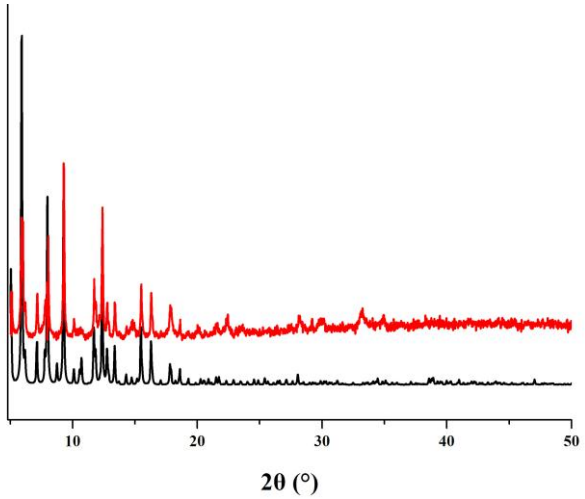


Fig. S10 Experimental and simulated powder X-Ray diffraction patterns for **4** (black: simulated; red: experimental).

Table S1 Crystal data and structure refinement for **2–4**.

Compound	**2**	**3**	**4**[1]
formular	$C_{408}H_{592}Cu_{24}N_{76}O_{196}$	$C_{609}H_{1001}Cu_{24}N_{131}O_{251}$	$C_{678}H_{1194}Cu_{24}N_{150}O_{270}$
weight	11218.04	15699.37	17292.69
space group	*Fm*-3*m*	*Fm*-3*m*	*Fm*-3*m*
a [Å]	40.0928(17)	46.1730	49.352(3)
b [Å]	40.0928(17)	46.1730	49.352(3)
c [Å]	40.0928(17)	46.1730	49.352(3)
α [deg]	90	90	90
β [deg]	90	90	90
γ [deg]	90	90	90
ρ_{cald} [gcm^{-3}]	1.156	1.059	-
V [$Å^3$]	64446(5)	98438	-
Z	4	4	4
wavelength (Å)	0.71069	0.71069	0.71069
F (000)	23339	33104	16536
Reflns collcd/unique	82270/2824	84904/2564	33296/968
GOF on F^2	1.085	1.060	-
[a] $R_1[I> 2\sigma(I)]$	0.0449	0.0723	-
[b] wR_2(all data)	0.1399	0.2234	-

1 Because of the absence of macroscopic crystals, a reasonable cif of **4** was not structurally characterized employing X-Ray method.