

Supporting Information

A nested Cu₂₄@Cu₇₂-based copper-organic polyhedral framework for selective adsorption of cationic dyes

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Section S1 Synthesis and Methods

Synthesis of $[\text{Cu}_5(\text{bdc})_4(\text{ina})_2(\text{H}_2\text{O})_3] \cdot \text{solvent}$ (**1**): $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ (0.10 mmol, 40 mg), CuI (0.42 mmol, 80 mg), Hina (0.32 mmol, 40 mg), 1,3-bdc (0.16 mmol, 27 mg) and NaClO_4 (0.28 mmol, 40 mg) were dissolved in 5 mL DMA in a 20 mL vial, and then the mixture was heated at 100 °C for 4 days and cooled to room temperature. Green cube crystals of **1** suitable for X-ray diffraction experiments were obtained by filtration, washed with DMA and air-dried. Yield: about 48 % (based on CuI). IR (KBr pellet, ν/cm^{-1}): 3408(s), 2934(w), 1608(vs), 1499(m), 1439(m), 1259(m), 1184(m), 1056(m), 1014(s), 950(m), 881(w), 644(w), 579(m).

Single-crystal structure analysis: Crystals were collected on a Bruker APEX II diffractometer at room temperature equipped with a fine focus, 2.0 kW sealed tube X-ray source (Cu K radiation, $\lambda = 1.54178 \text{ \AA}$) operating at 50 kV and 30 mA. The empirical absorption correction was based on equivalent reflections. Structures were solved by direct methods followed by successive difference Fourier methods. Computations were performed using SHELX-2014 and final full-matrix refinements were against F^2 . All non-hydrogen atoms were refined anisotropically. The disordered solvent molecules in **1** were removed using the SQUEEZE method in PLATON. CCDC-1854578 for **1** and CCDC-1916202 for **MB@1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Others: Powder XRD patterns were obtained using a RIGAKU-Miniflex II diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). IR spectra were recorded on PerkinElmer Spectrum One FT-IR infrared spectrophotometer with pressed KBr pellets in the range of 4000-400 cm^{-1} . Thermal analyses were performed in a dynamic air atmosphere with a heating rate of 10 °C/min, using a NETZSCH STA 449C thermal analyzer. UV-vis spectra were performed on a SHIMADZU UV-2600 UV-visible spectrophotometer by using the same solvent as the blank.

Dye adsorption: Freshly prepared **1** (20 mg) were added into to DMA solutions (10 mL) containing rhodamine B (RhB) ($6.0 \times 10^{-5} \text{ mol/dm}^3$), methylene blue (MB) ($2.0 \times 10^{-5} \text{ mol/dm}^3$), crystal violet (CV) ($2.0 \times 10^{-5} \text{ mol/dm}^3$), methyl orange (MO) ($2.0 \times 10^{-5} \text{ mol/dm}^3$), congo red (CR) ($2.0 \times 10^{-5} \text{ mol/dm}^3$), acid orange (AO) ($2.0 \times 10^{-5} \text{ mol/dm}^3$) and solvent yellow 2 (SY) (2.0

$\times 10^{-5}$ mol/dm³) on 20 mL sealed glass in the dark at room temperature, respectively. UV/Vis spectra were employed to measure the adsorption ability of **1** after certain time intervals.

Dye release: The **1** samples loaded with MB and CV (20 mg) were transferred into pure DMA and a saturated solution of NaNO₃ in DMA (10 mL) in cuvettes (4 mL), respectively. UV/vis spectra were employed to monitor the adsorb and release process of **MB@1** and **CV@1** after certain time intervals.

Dye separation: Freshly prepared **1** (40 mg) were added into to DMA solutions (10 mL) containing RhB & MB (concentration ratio: 3:1), MB & MO (concentration ratio: 1:5) and CV & SY (concentration ratio: 1:3) on 20 mL sealed glass in the dark at room temperature. The UV/Vis spectra and photographs were employed to measure the selective adsorption abilities of **1** after certain time intervals.

The following equations are used to calculate the adsorption efficiency and the quantity:

$$\text{dye removal}(\%) = \frac{C_0 - C_t}{C_0} \times 100$$

$$Q(\text{quantity}) = \frac{C_0 - C_t}{m} \times V \times M$$

In which C_0 is the initial concentration of dye solution and the C_t represents the concentration of **1** that adsorbs the dyes at t min, V is the volume of the solution (L), m and M are the mass of adsorbent **1** and the molar mass of dyes, respectively.

Synthesis discussion: During our synthesis, we have tried to replace different copper salt (e.g., Cu(NO₃)₂·6H₂O, CuCl₂·2H₂O, Cu(Ac)₂·H₂O, CuSO₄·5H₂O) or different 3d metals salts (e.g., Zn²⁺, Co²⁺, Cd²⁺, Mn²⁺, Ni²⁺) with CuI, unfortunately, no analogous products were obtained. The Cu²⁺ cations in of **1** come from the oxidation of Cu⁺ according to the reported literature.¹ Notably, the In(NO₃)₃·4.5H₂O plays a crucial role in the formation of **1**, though it does not enter the final products. According to the reported literature, **CPM-24**² with a nested Co₂₄@Co₄₈, indium nitrate was also added in synthesis process. Therefore, we speculated that indium salt may play a role as a mineralizer in the reaction. The indium salt induce the formation of such few nested cage-within-cage-based structures.

Section S2 Additional Table

Table S1 Crystal Data and Structure Refinement for **1**

	1	MB@1
Empirical formula	C ₄₄ H ₃₀ N ₂ O ₂₃ Cu ₅	C ₄₄ H ₃₀ Cu ₅ N ₂ O ₂₃
Formula weight	1272.40	1272.40
Crystal system	Cubic	Cubic
Space group	<i>Pm</i> ³ <i>m</i> (#. 221)	<i>Pm</i> ³ <i>m</i> (#. 221)
<i>a</i> (Å)	27.5681(4)	27.5914(2)
<i>b</i> (Å)	27.5681(4)	27.5914(2)
<i>c</i> (Å)	27.5681(4)	27.5914(2)
<i>V</i> (Å ³)	20951.8(9)	21004.9(5)
<i>Z</i>	6	6
<i>F</i> (000)	3822	3822
crystal size / mm ³	0.258 × 0.255 × 0.252	0.266 x 0.264 x 0.263
θ range / °	1.602 to 58.917	7.178 to 66.540
limiting indices	-30 ≤ <i>h</i> ≤ 29 -27 ≤ <i>k</i> ≤ 29 -26 ≤ <i>l</i> ≤ 29	-31 ≤ <i>h</i> ≤ 27 -32 ≤ <i>k</i> ≤ 30 -30 ≤ <i>l</i> ≤ 29
ρ_{calcd} (g cm ⁻³)	0.605	0.604
Temperature (K)	175(2)	175(2)
μ (mm ⁻¹)	1.107	1.104
Refl. Collected	46256	56419
Independent refl.	2975	3595
Parameters	106	106
<i>R</i> _{int}	0.0454	0.0450
GOF on <i>F</i> ²	1.098	1.082
Final <i>R</i> indices (<i>I</i> = 2σ(<i>I</i>))	<i>R</i> _{<i>I</i>} = 0.0400, <i>wR</i> ₂ = 0.1240	<i>R</i> _{<i>I</i>} = 0.0616, <i>wR</i> ₂ = 0.2032
<i>R</i> indices (all data)	<i>R</i> _{<i>I</i>} = 0.0465, <i>wR</i> ₂ = 0.1279	<i>R</i> _{<i>I</i>} = 0.0669, <i>wR</i> ₂ = 0.2100

^a*R*₁ = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|, ^b*wR*₂ = [Σ*w*(*F*_o² - *F*_c²)²/*w*(*F*_o)²]^{1/2}, *w* = 1/[σ²(*F*_o²) + (*xP*)² + *yP*], *P* = (*F*_o² + 2*F*_c²)/3, where *x* = 0.090750, *y* = 0 for **1** and *x* = 0.139900, *y* = 7.732200 for **MB@1**.

Section S3 Additional Figures

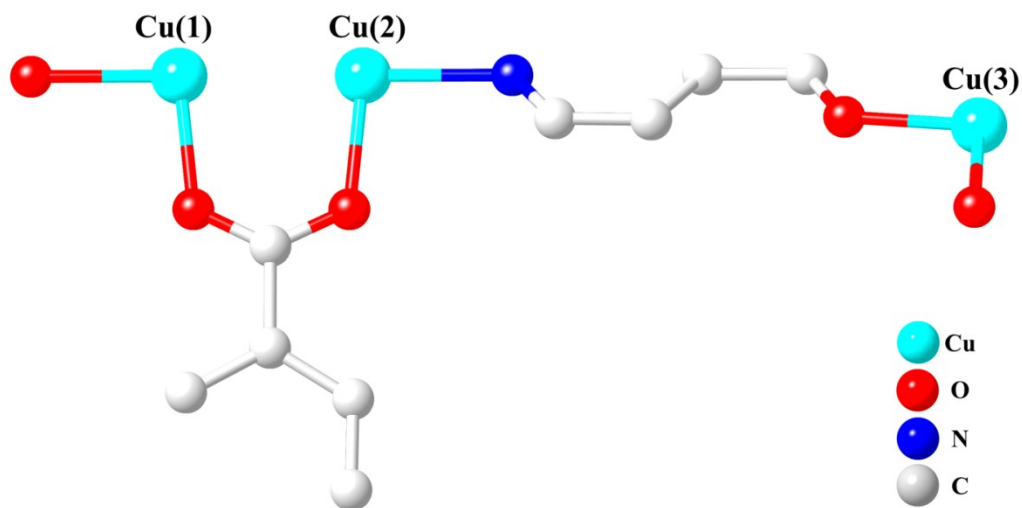


Fig. S1. The asymmetric unit of **1**.

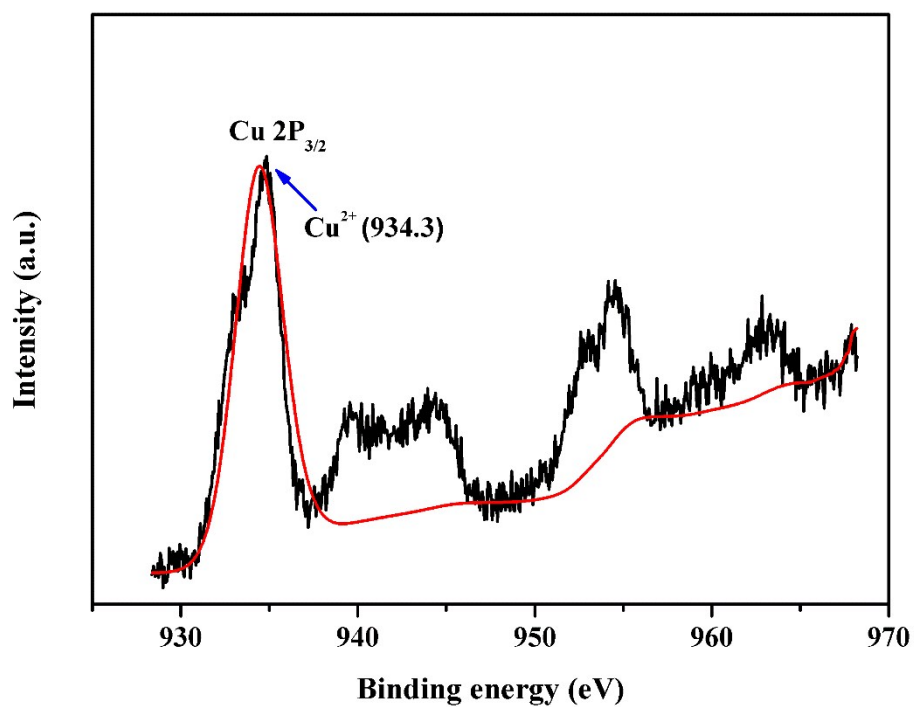


Fig. S2. X-ray photoelectron spectroscopy of **1**.

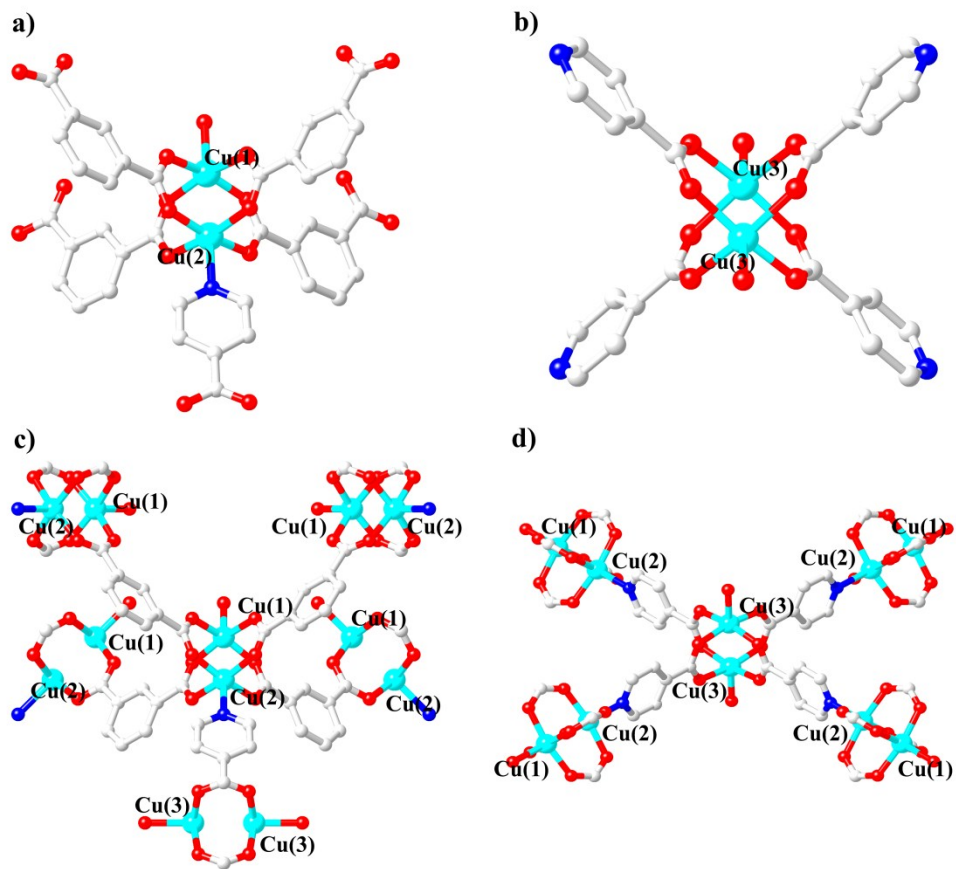


Fig. S3. The connection mode of two different types of paddlewheels $\text{Cu}_2(\text{COO})_4$ clusters.

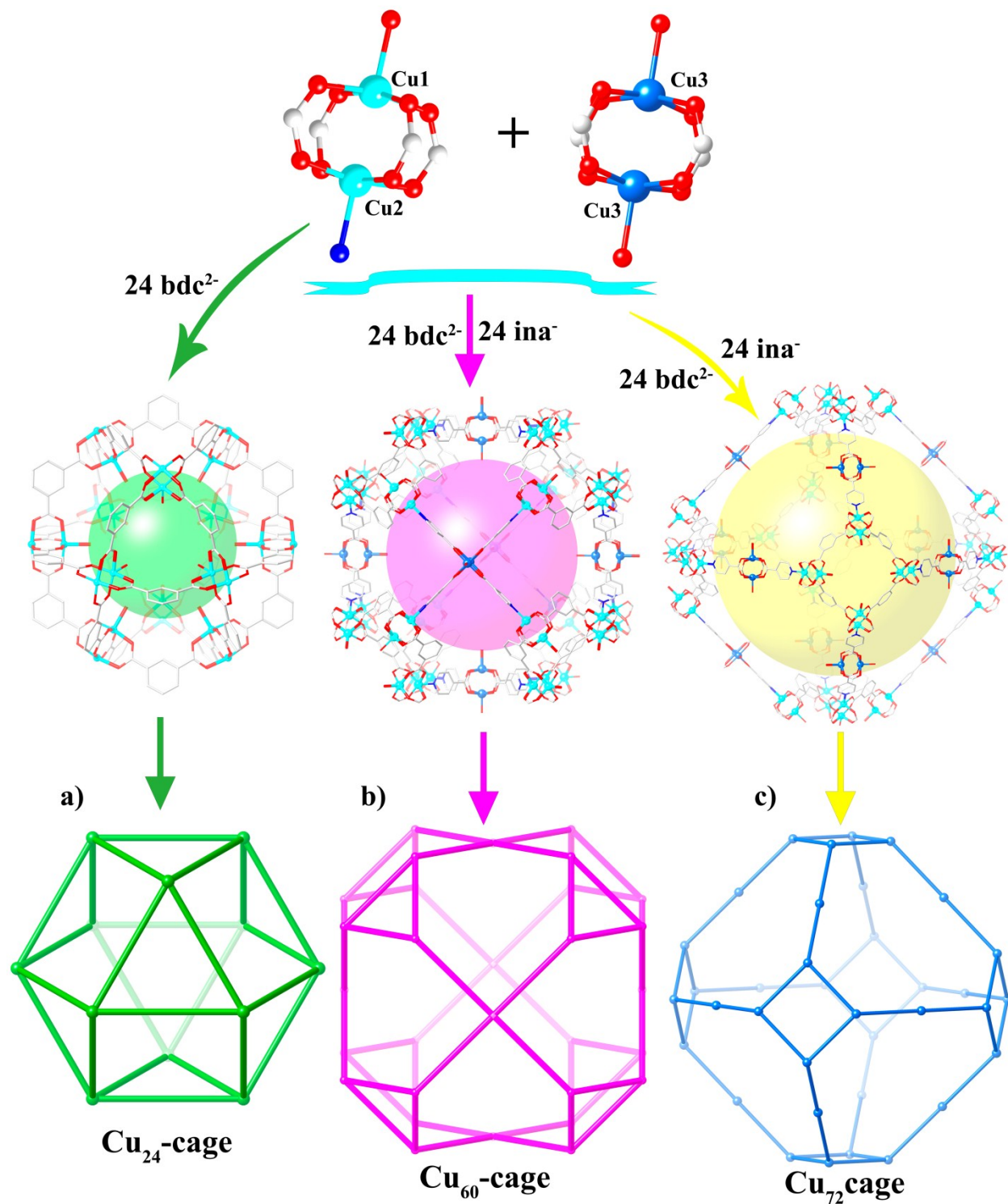


Fig. S4. Three types of cage in 1: a) Cu_{24} -cage, b) Cu_{60} -cage, c) Cu_{72} -cage.

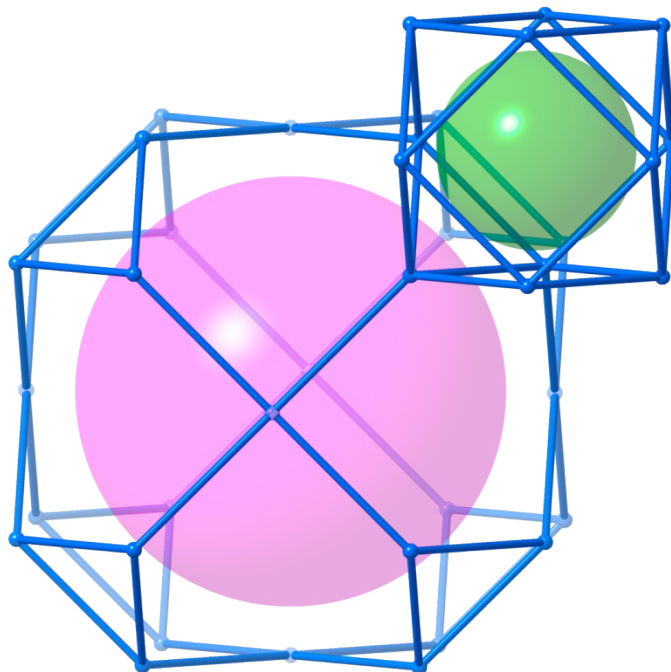


Fig. S5. The simplified representation of the linkage of Cu_{60} -cage and Cu_{24} -cage.

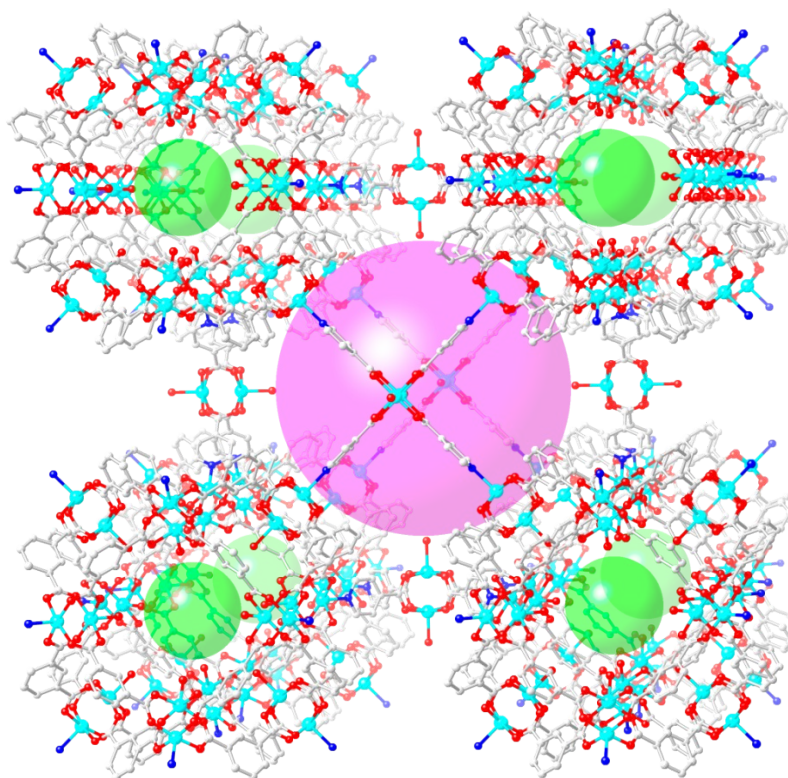


Fig. S6. The connection of the Cu_{60} -cage with eight small Cu_{24} -cages .

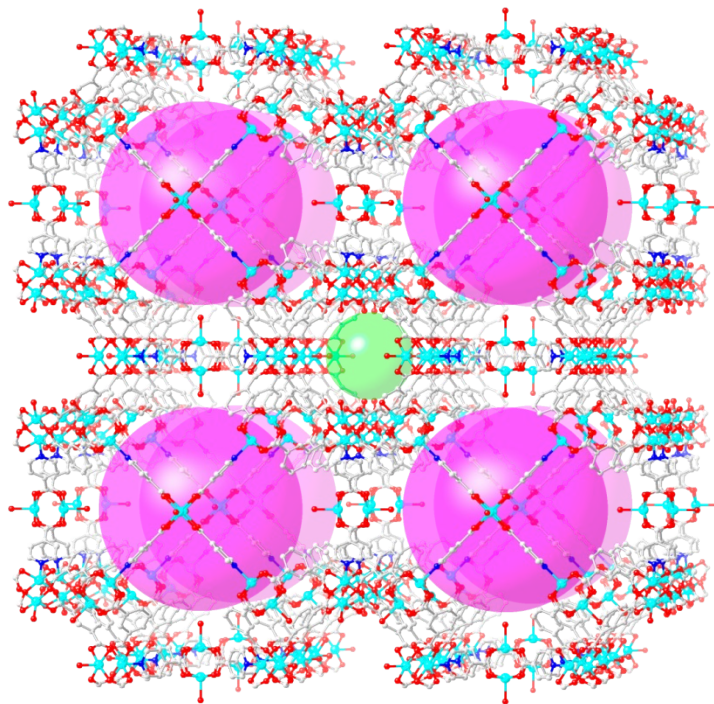


Fig. S7. The connection mode of the small Cu_{24} -cage with eight Cu_{60} -cages.

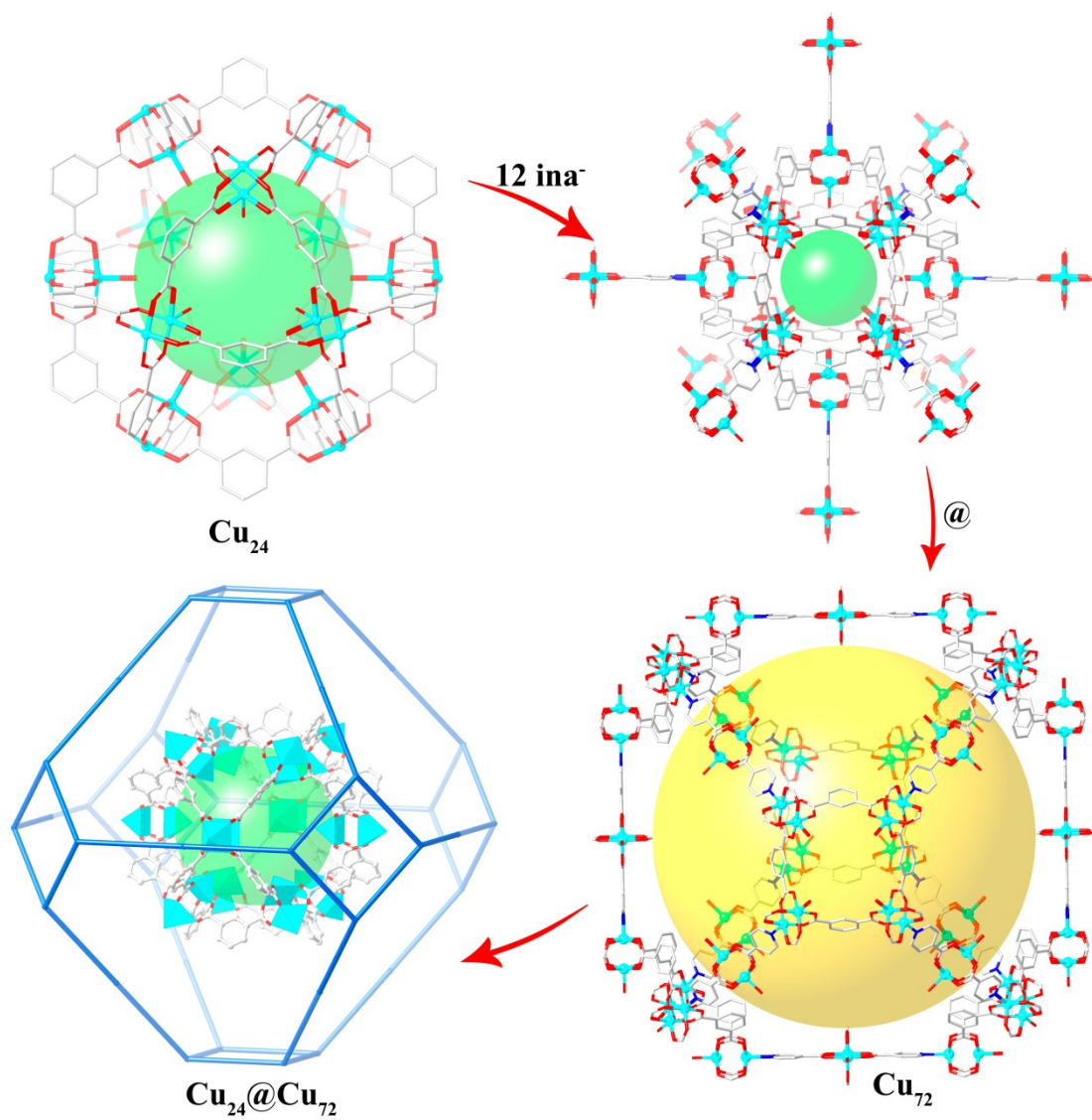


Fig. S8. The structural assembly route of $\text{Cu}_{24}@\text{Cu}_{72}$ structure.

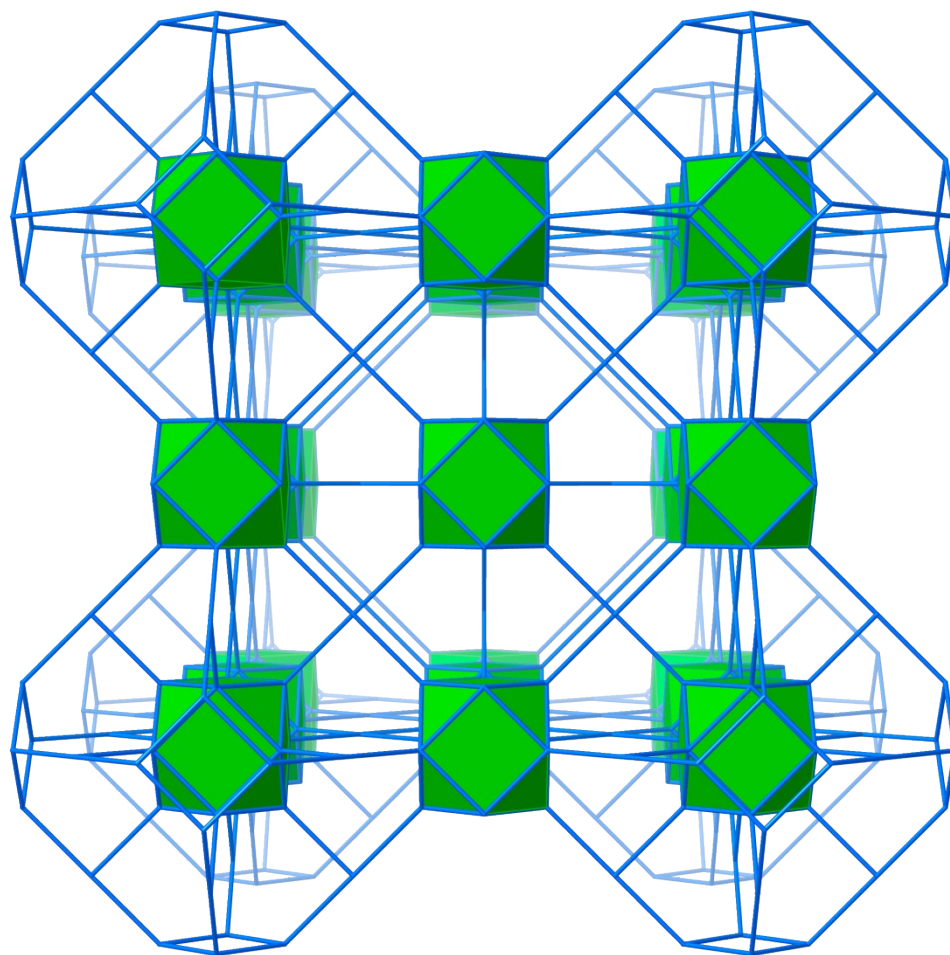


Fig. S9. The topology of **1** viewed along the *c* direction.

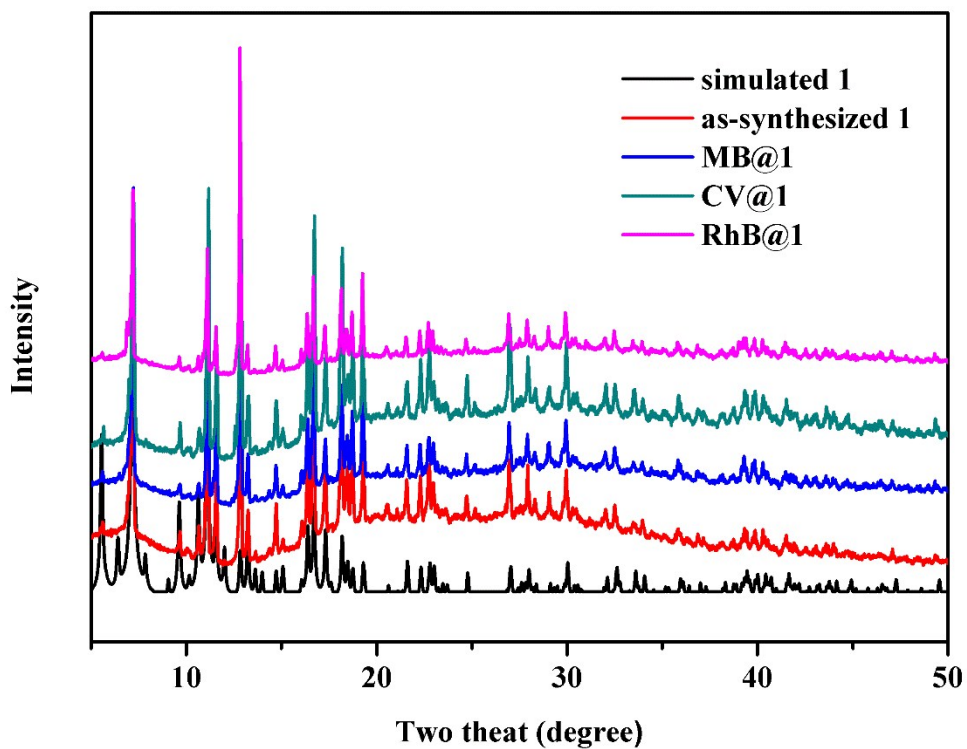


Fig. S10. PXRD patterns of as-synthesized and dye-adsorbed samples for 1

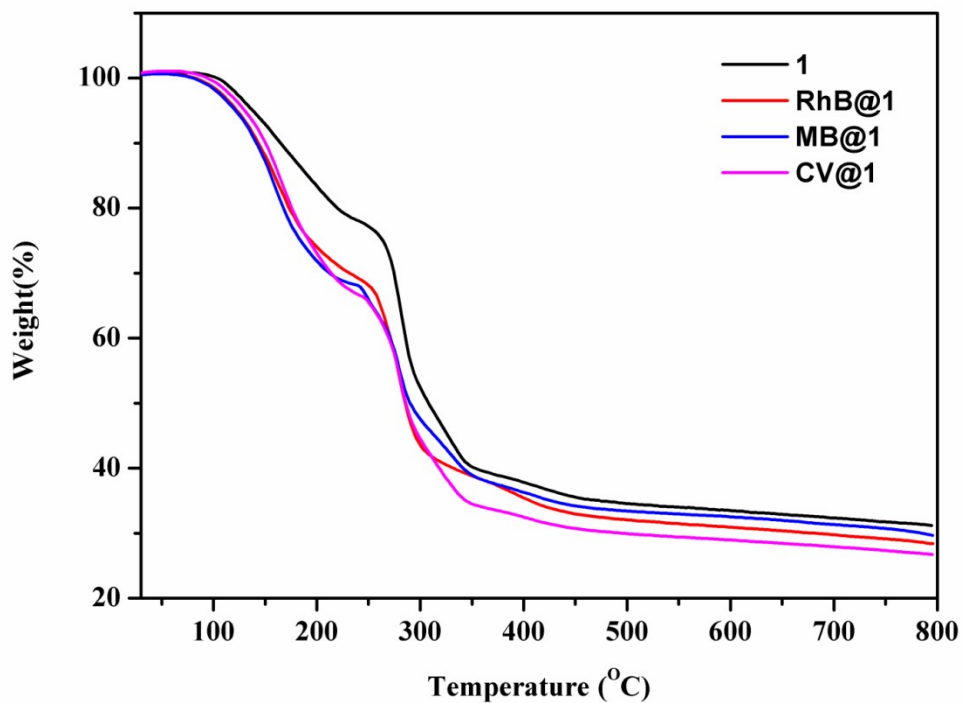


Fig. S11. TG curves of 1, RhB@1, MB@1 and CV@1.

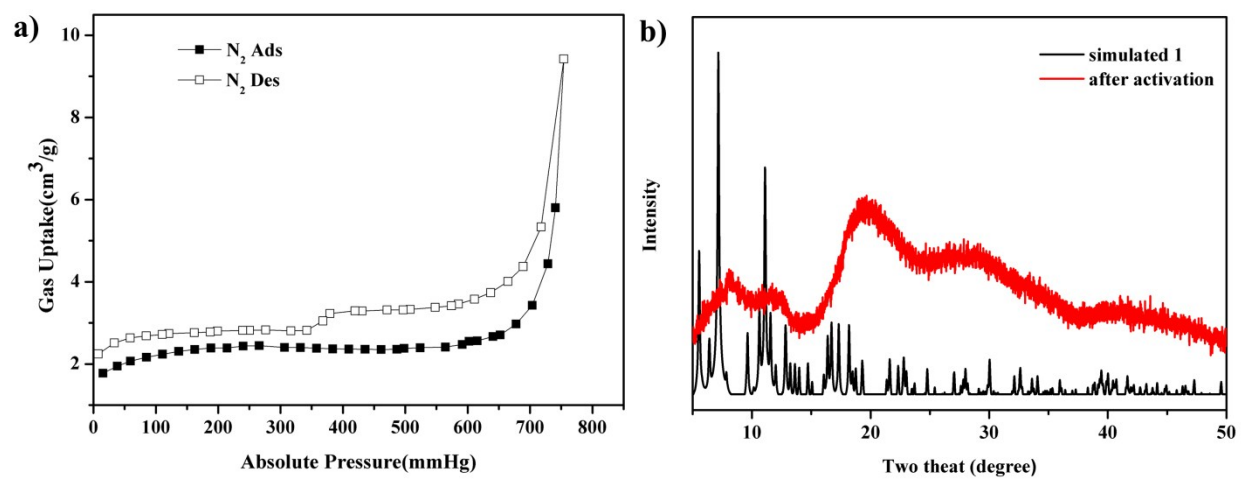


Fig. S12. a) N₂ sorption isotherms at 77 K under 800 mmHg and b) PXRD pattern after N₂ sorption for **1**.

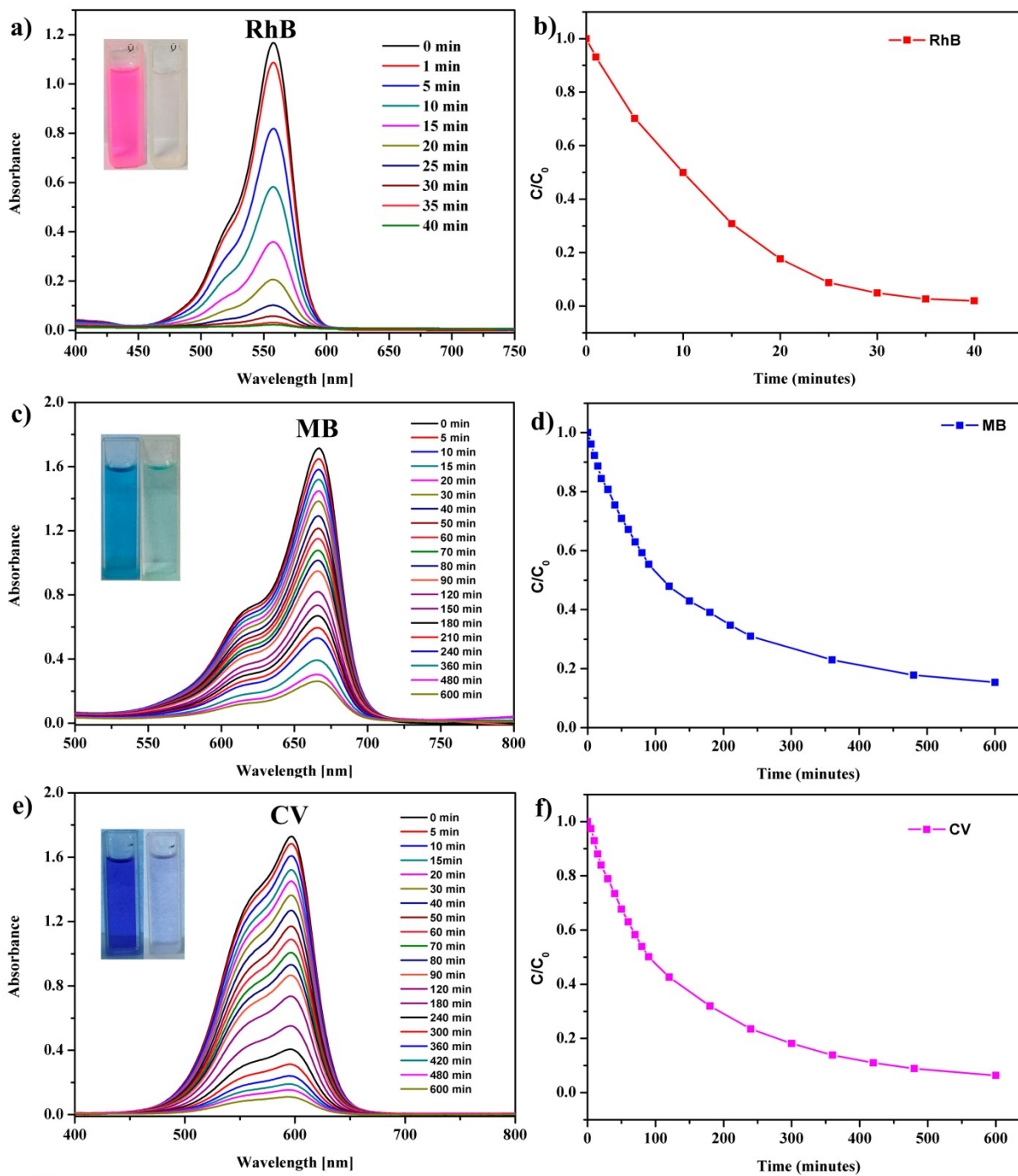


Fig. S13. UV/vis absorption spectra for a) RhB, c) MB, e) CV adsorption by 20 mg of **1** in 10 mL of dye-contaminated DMA and b), d) and f) their adsorption rate of **1**.

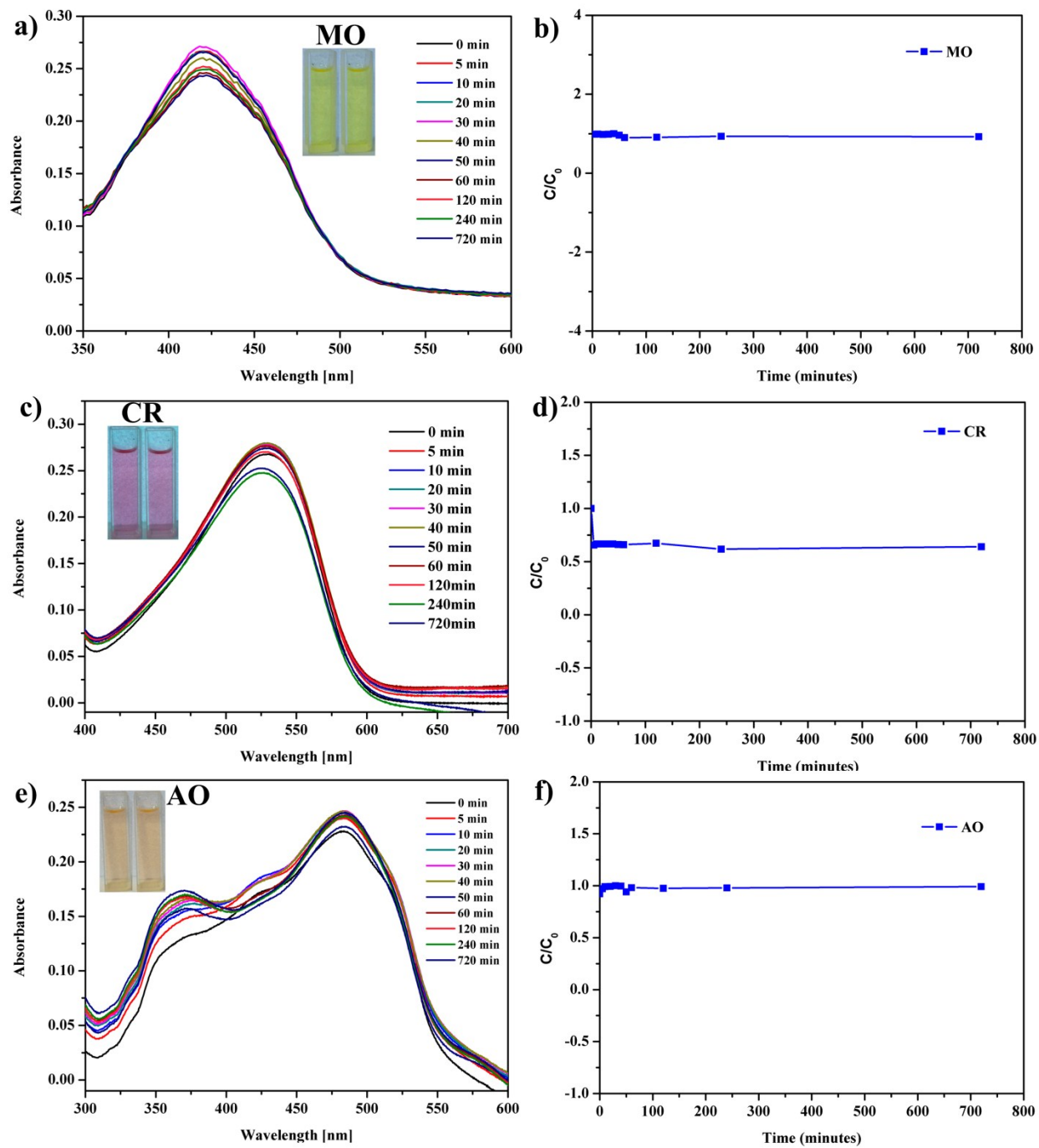


Fig. S14. UV-vis absorption spectra for a) MO, c) CR and e) AO adsorption by 20 mg of **1** in 10 mL of dye-contaminated DMA and b),d) and f) their adsorption rate of **1**.

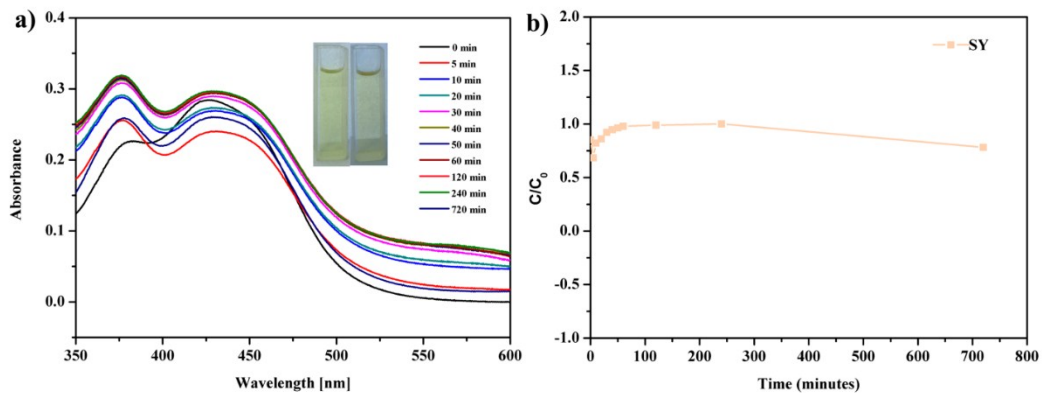


Fig. S15. UV/vis absorption spectra for a) SY adsorption by 20 mg of **1** in 10 mL of dye-contaminated DMA and b) its adsorption rate of **1**.

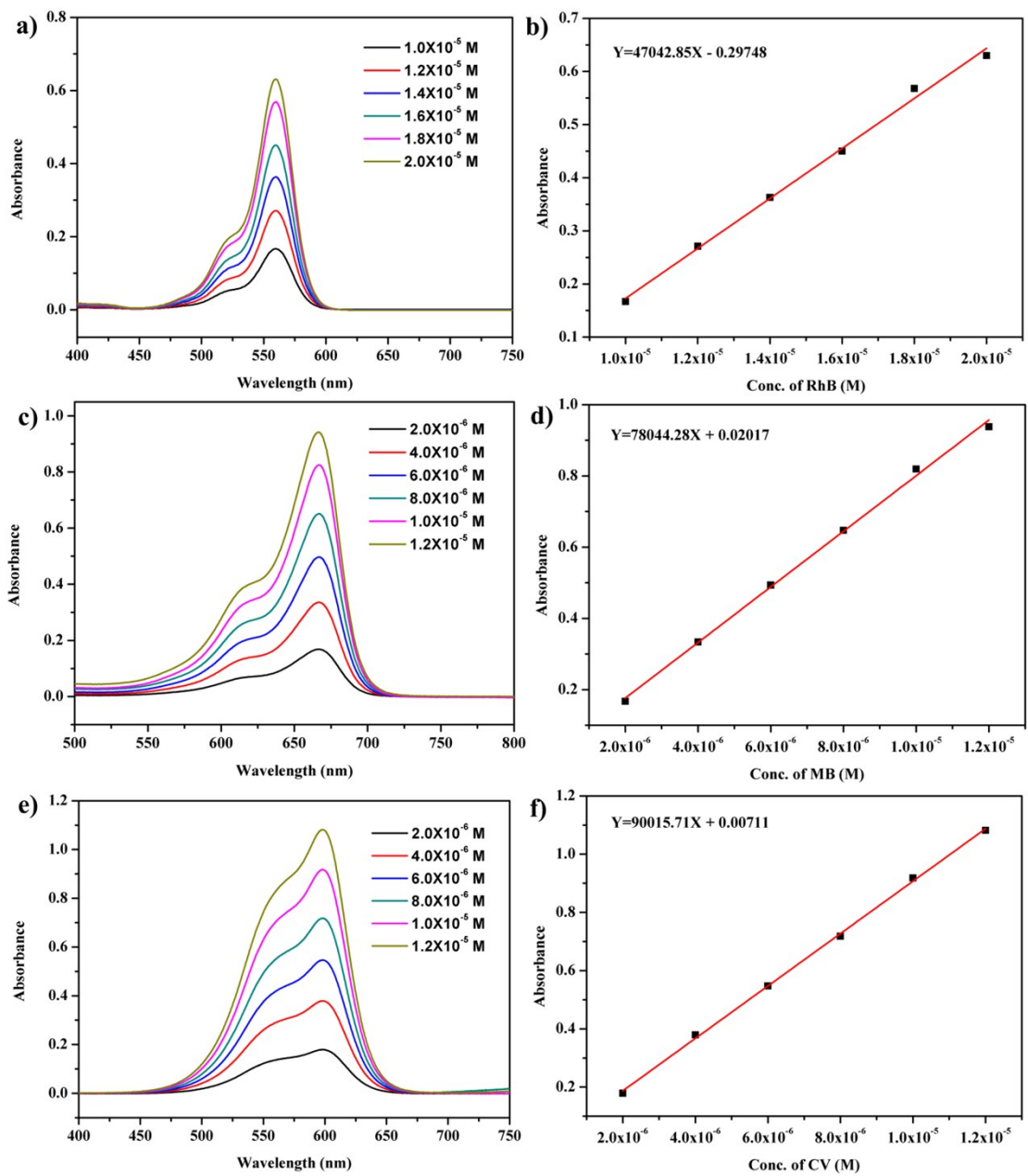


Fig. S16. Calibration plots of standard RhB, MB and CV (a & c & e) by UV-Vis spectra in DMA solution and their fitting of Abs. vs concentration of respective dye values (b & d & f).

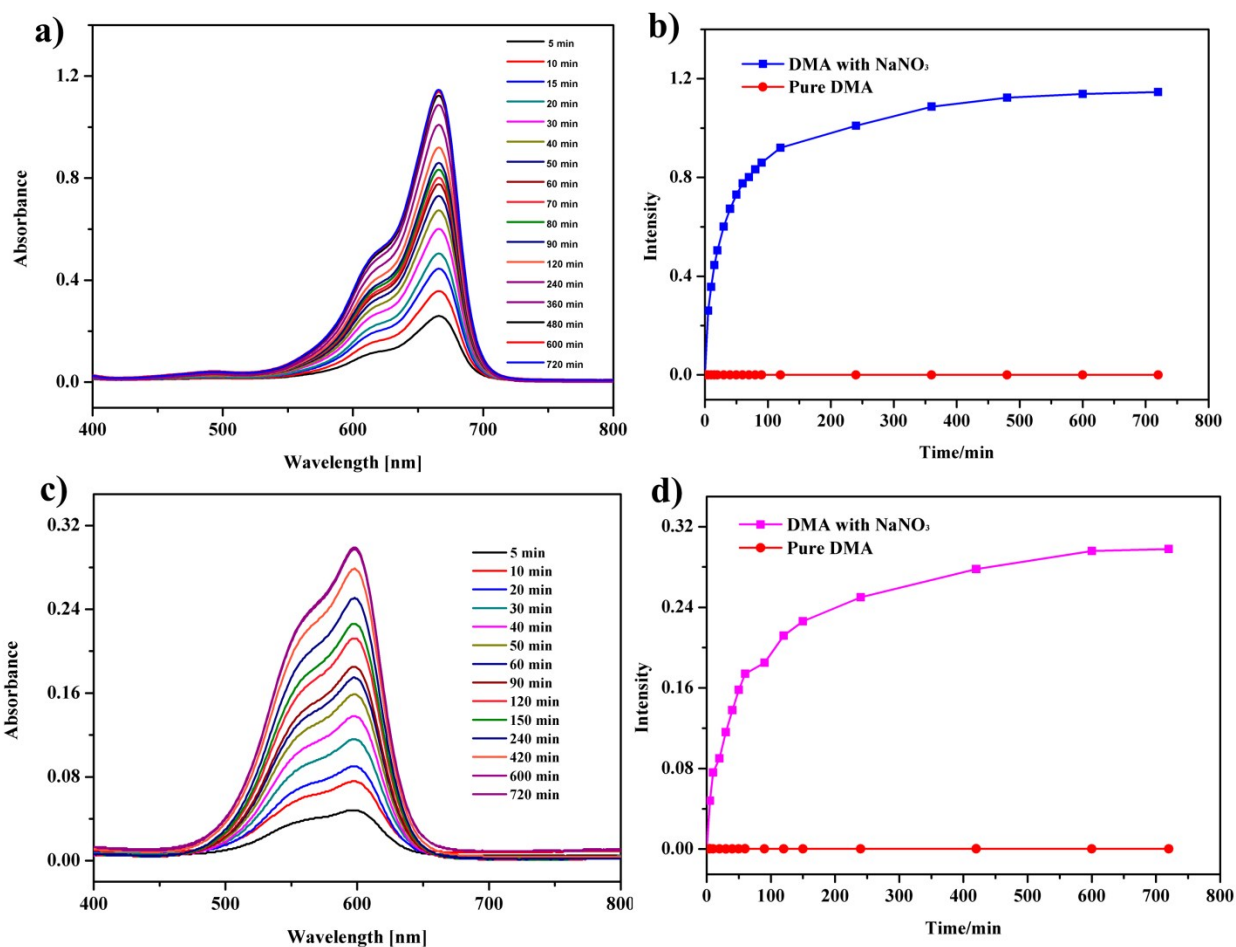


Fig. S17. a) The MB released from the **MB@1** in a saturated solution of NaNO_3 in DMA monitored by UV absorption spectra; b) The release-rate comparison of MB from **MB@1** in pure DMA and a saturated solution of NaNO_3 in DMA; c) The CV released from the **CV@1** in a saturated solution of NaNO_3 in DMA monitored by UV absorption spectra; d) the release-rate comparison of CV from **CV@1** in pure DMA and a saturated solution of NaNO_3 in DMA.

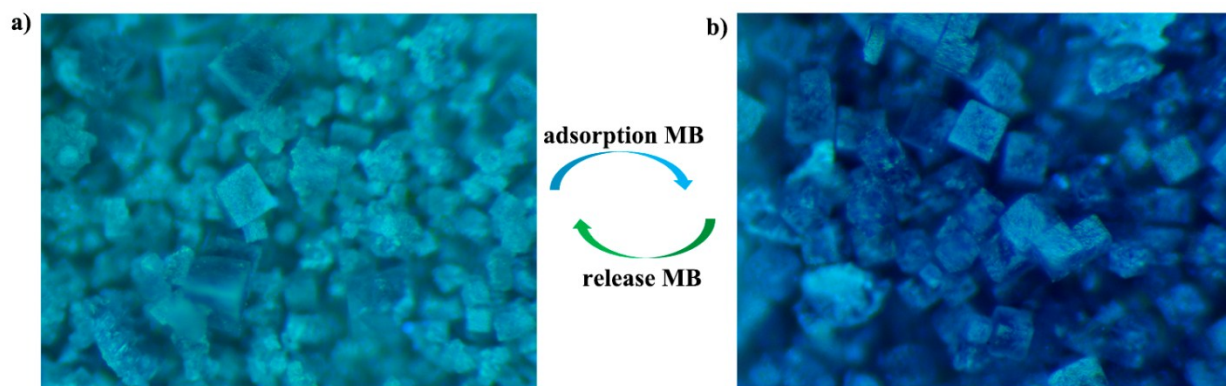


Fig. S18. Crystal morphology of **1** before and after MB adsorption under optical microscope.

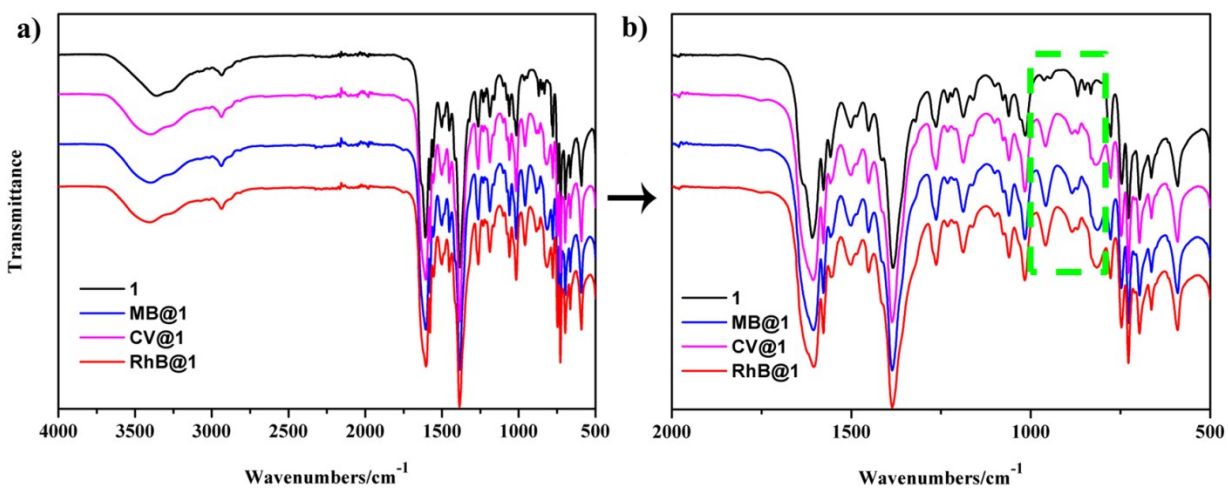
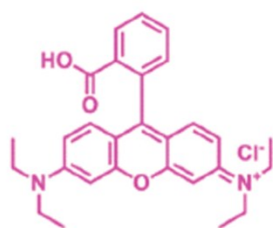
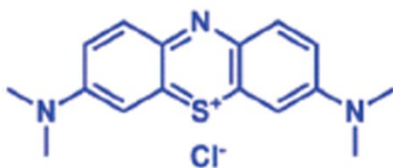


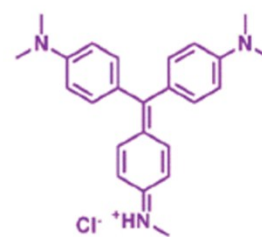
Fig S19. FT-IR spectra of **1** and **dye@1** for MB, CV and RhB.



rhodamine B (RhB)



methylene blue (MB)



crystal violet (CV)

Fig. S20 Molecular Parameters of the Dyes.

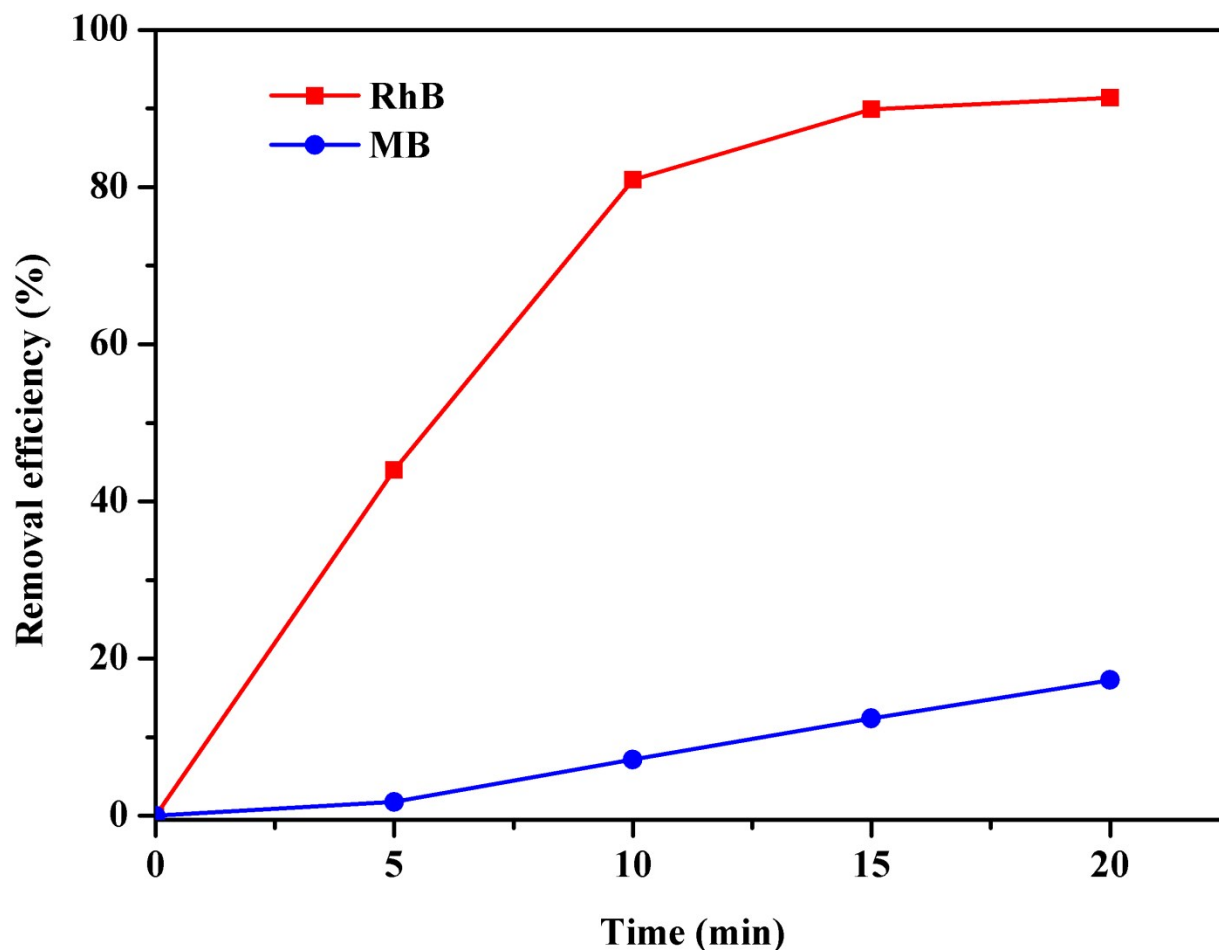


Fig. S21. The removal efficiency with time for mixtures RhB & MB.

Section S4 References

- (1) H. M. He, F. X. Sun, S. Q. Ma and G. S. Zhu, *Inorg. Chem.* 2016, **55**, 9071-9076.
- (2) S.-T. Zheng, T. Wu, B. Irfanoglu, F. Zuo, P. Y. Feng and X. H. Bu, *Angew. Chem. Int. Ed.*, 2011, **123**, 8184 -8187.