Supplementary Material (ESI) for CrystEngComm

An ideal metal-organic rhombic dodecahedron for highly efficient adsorption of dyes in an aqueous solution

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Materials and methods

All chemicals and solvents used in syntheses were purchased from commercial sources and used without further purification. The FT-IR spectra of the compounds were measured in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. The C, H and N elemental analysis were conducted on a Perkin–Elmer 2400CHN elemental analyzer. X-ray powder diffractions were carried out on a Rigaku Dmax 2000 X-ray diffractometer. TGA was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 °C under nitrogen gas. UV/vis absorption spectra were recorded at room temperature on a Cary 500 UV–VIS–NIR spectrophotometer.

X-ray crystallography

Single-crystal X-ray diffraction data for **1** was recorded at a temperature of 293 (2) K on a Bruker Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97[1] and refined by full-matrix least-squares techniques using the SHELXL-97 program[2] within WINGX.[3] All hydrogen atoms on carbon atoms were generated geometrically and refined using a riding model with d(C–H) = 0.93 Å, U_{iso} = 1.2U_{eq}(C) for aromatic and d(C–H) = 0.97 Å, U_{iso} = 1.2U_{eq}(C) for CH$_2$ atoms. The aqua hydrogen atoms were not included in the model. The SQUEEZE function in PLATON was applied to remove residual electron density which could not sensibly modeled as solvents or anions.[4] Thermogravimetric analysis indicates the presence of ca. 9 DMA molecules and 3 free water molecules in the structure of MOP-**1**.

References

1 G. M. Sheldrick, SHELXS-97, *Programs for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

2 G. M. Sheldrick, SHELXL-97, *Programs for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

3 L. J. Farrugia, WINGX: *A Windows Program for Crystal Structure Analysis*;
University of Glasgow: Glasgow, UK, 1988.

4 A. L. Spek, Single-crystal structure validation with the program PLATON. *J. Appl.
Crystallogr.*, 2003, **36**, 7.

Synthesis of H₃L

A mixture of 2,4,6-tris(bromomethyl)-mesitylene (10 mmol, 3.99 g), methyl 3-hydroxybenzoate (30 mmol, 4.56 g), and NaOH (30 mmol, 1.20 g) in N,N-dimethylformamide (DMF) (50 mL) was stirred under basic conditions and reluxed for 10 h. The solvent was removed by rotary evaporation. The residue was cooled to room temperature, and poured into 300 mol distilled water. The white solid trimethyl 2,4,6-tris[1-(3-carboxyl-phenoxy)-ylmethyl]-mesitylene formed immediately, and was then filtered off, washed successively with distilled water before drying at 60 °C. Trimethyl 2,4,6-tris[1-(3-carboxyl-phenoxy)-ylmethyl]-mesitylene (10 mmol, 6.13 g) and NaOH (60 mmol, 2.40 g) was added to 150 mL ethanol in a 250 mL round-bottom flask. Stirring at 80 °C was maintained for 8 h. The resulting solvent was removed by rotary evaporation, giving a white precipitate. The white precipitate was solved in 200 mL distilled water. The pH value was adjusted to 1-2 via conc. HCl. The white solid H₃L was collected by filtration, washed with distilled water and dried at 60 °C (yield: 82%).
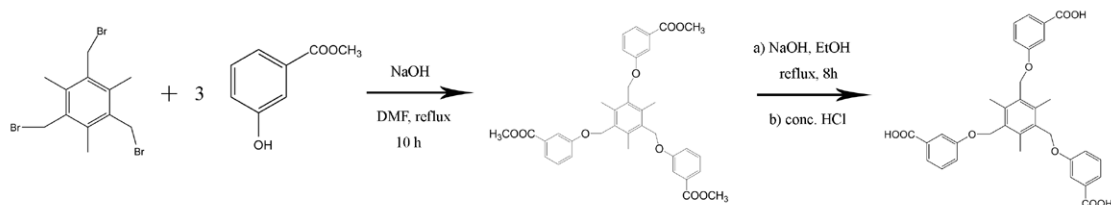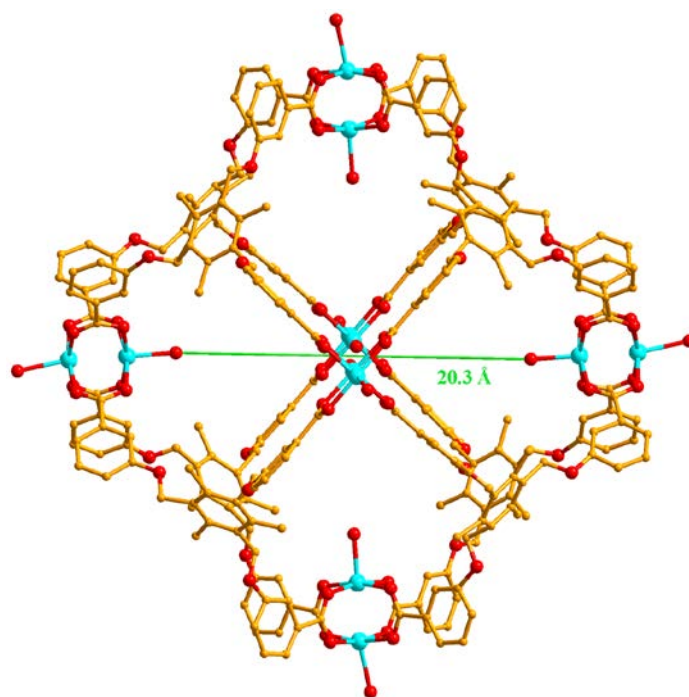

Scheme S1. Synthetic procedures for H₃L.

Methylene Blue (MB)

Rhodamine B (RB)

Methyl Orange (MO)

Congo Red (CR)
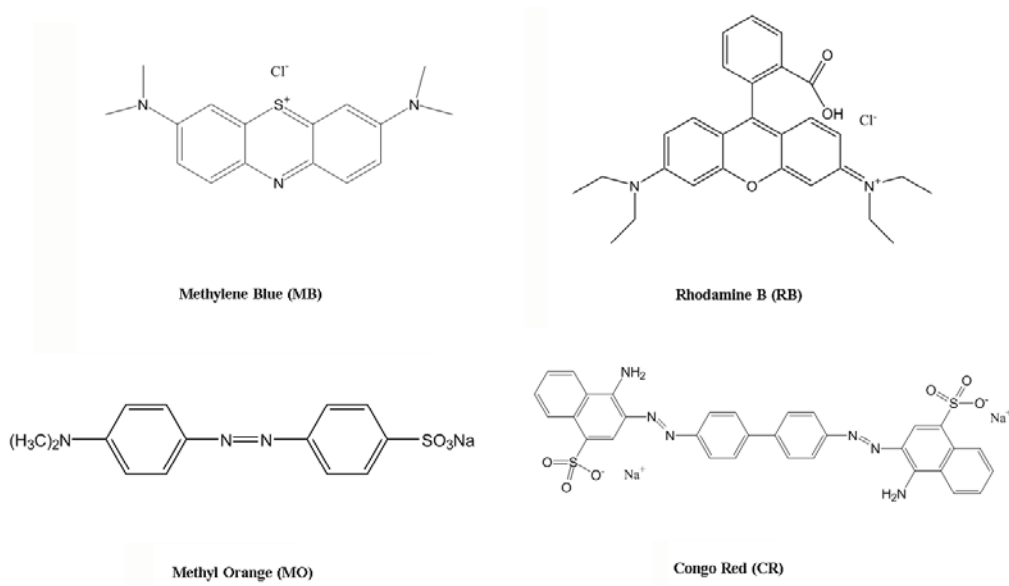
Scheme S2. Chemical structures of dyes used for adsorption.

(a)
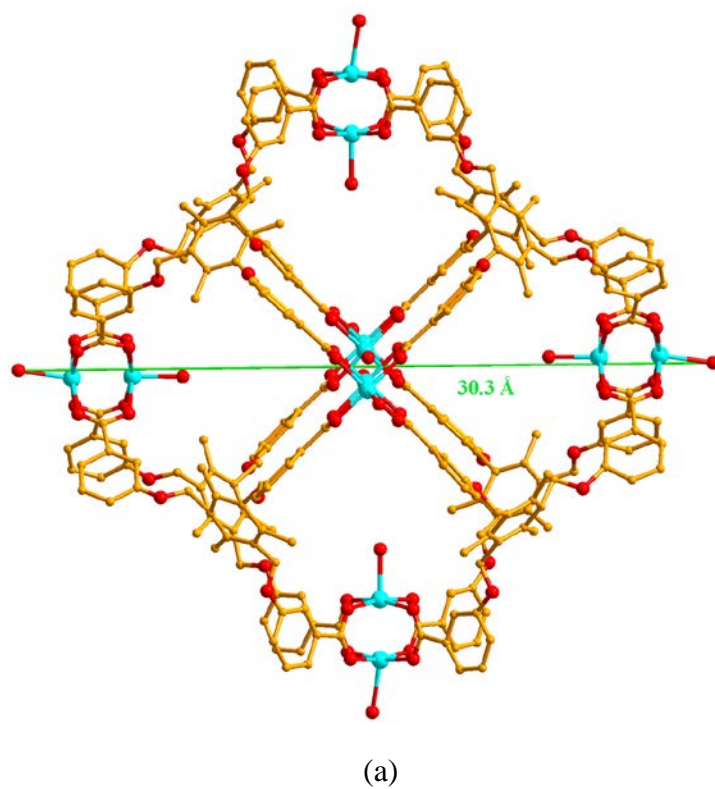
(b)

Fig. S1 (a) and (b) View of the rhombic dodecahedral polyhedron showing external and inner diameters with the corresponding sizes.
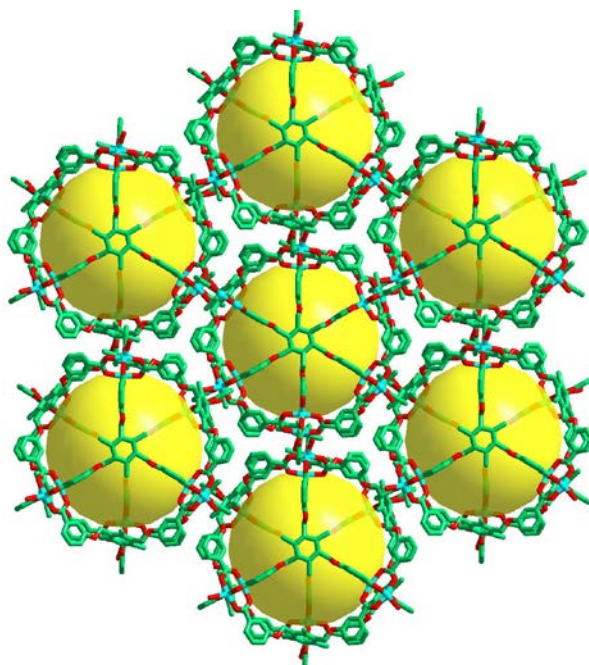

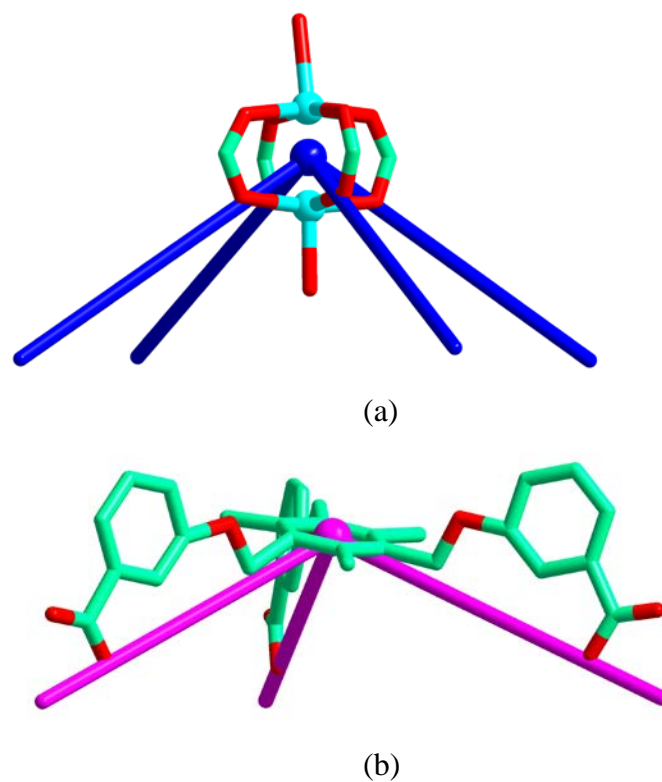
Fig. S2 Stacking diagram of neighboring MOP-**1** polyhedra.

(a)

(b)

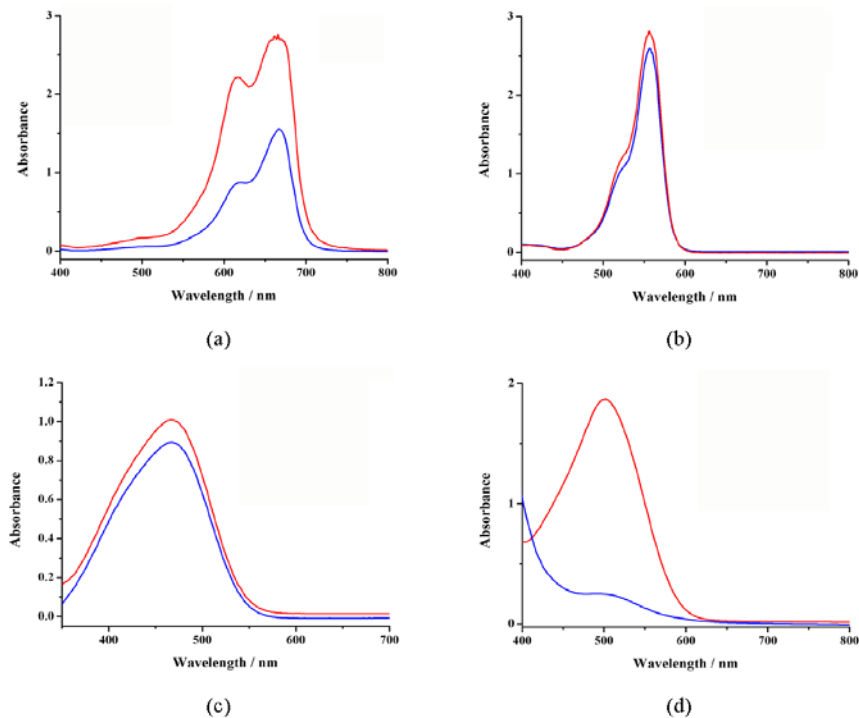**Fig. S3** (a) The square vertice defined by paddlewheel unit and (b) triangular vertice defined by the L ligand.

(a)

(b)

(c)

(d)

Fig. S4 UV-vis spectra of (a) **MB**, (b) **RB**, (c) **MO**, and (d) **CR** before (red lines) and after (blue lines) the addition of solid MOP-**1** (after 6 days).
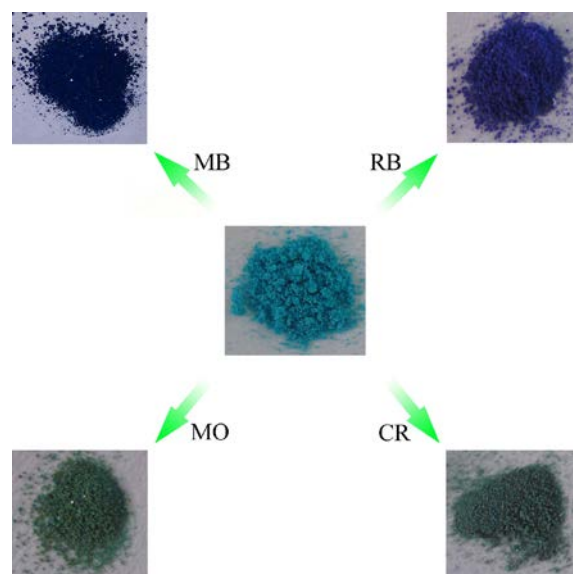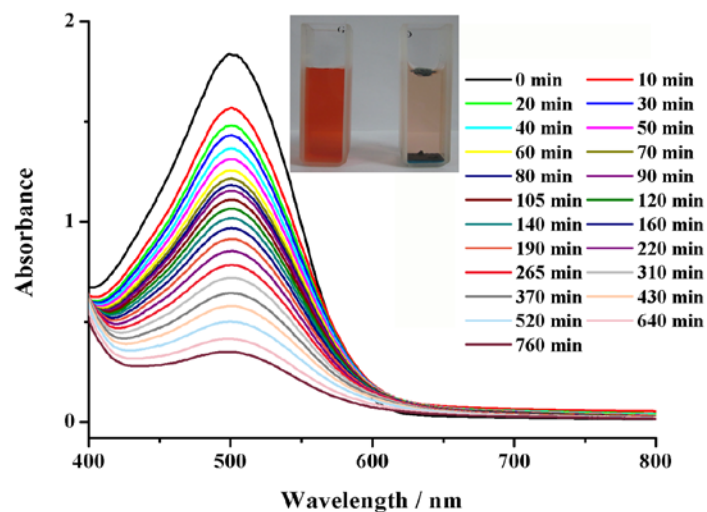
Fig. S5 Color changes of MOP-**1** after adsorption of dyes.
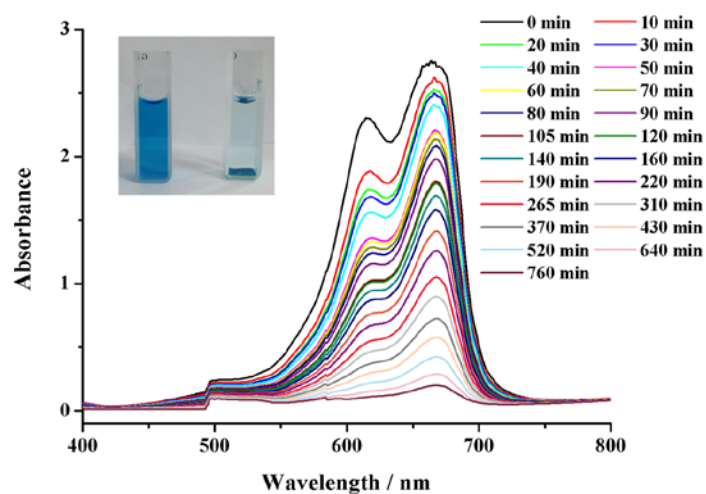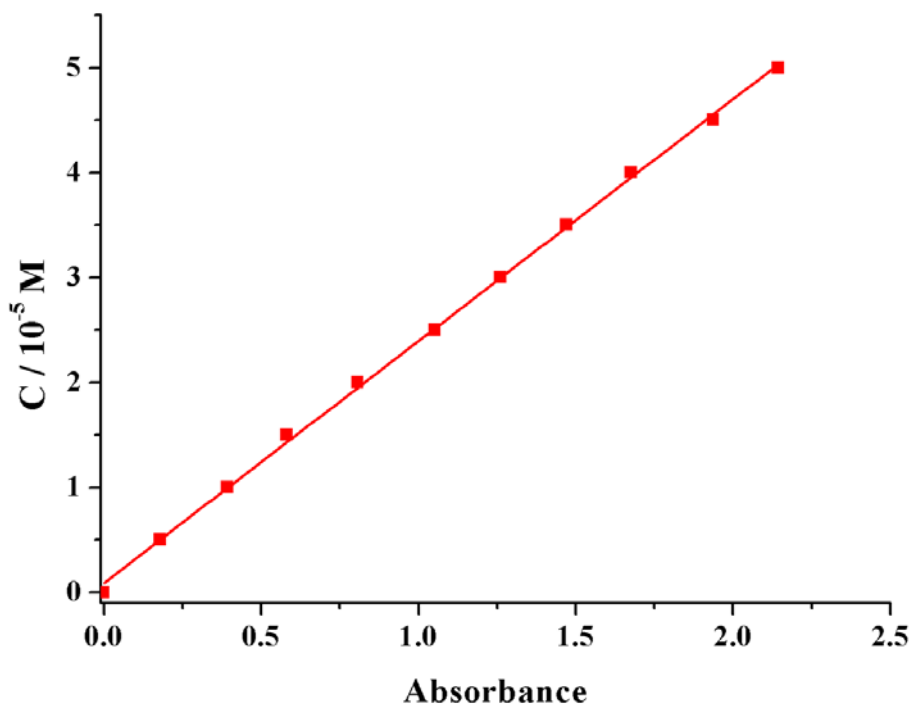

(a)
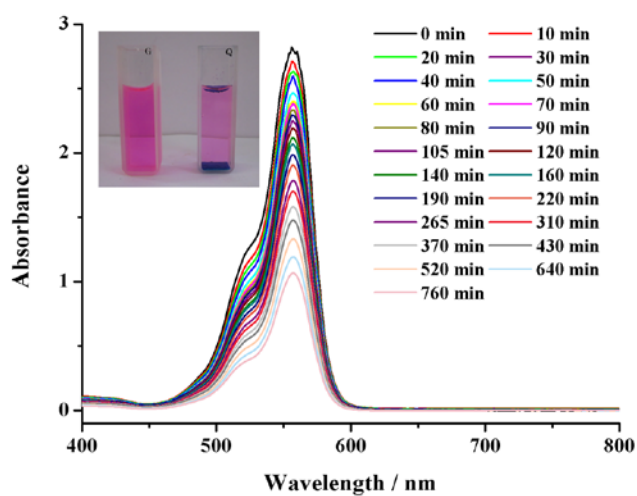
(b)
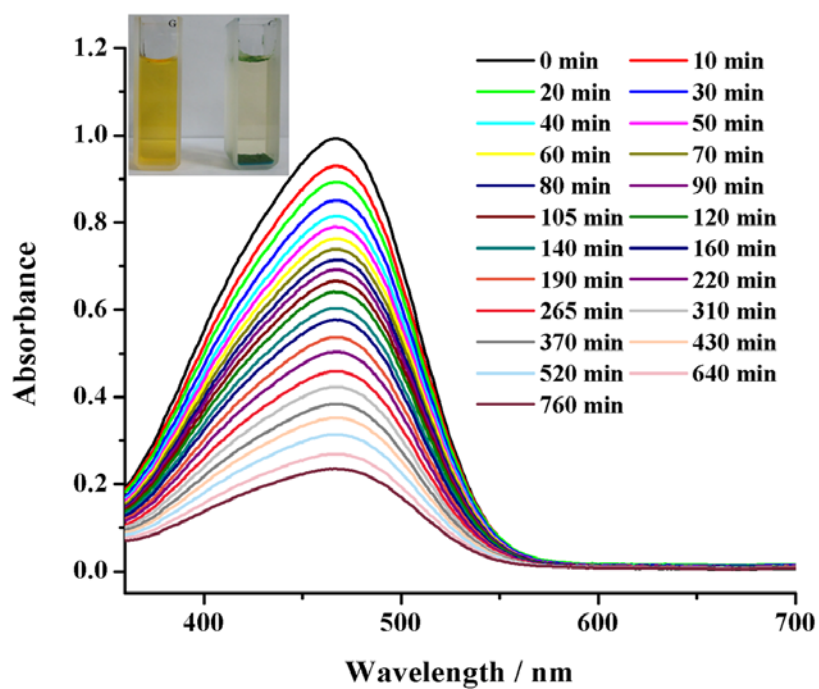
(c)

(d)

Fig. S6 Temporal evolution of UV/vis absorption spectra for (a) **MB,** (b) **RB**, (c) **MO**, and (d) **CR** adsorption by 50 mg of MOP-**1** in 3 mL of dye-contaminated water.
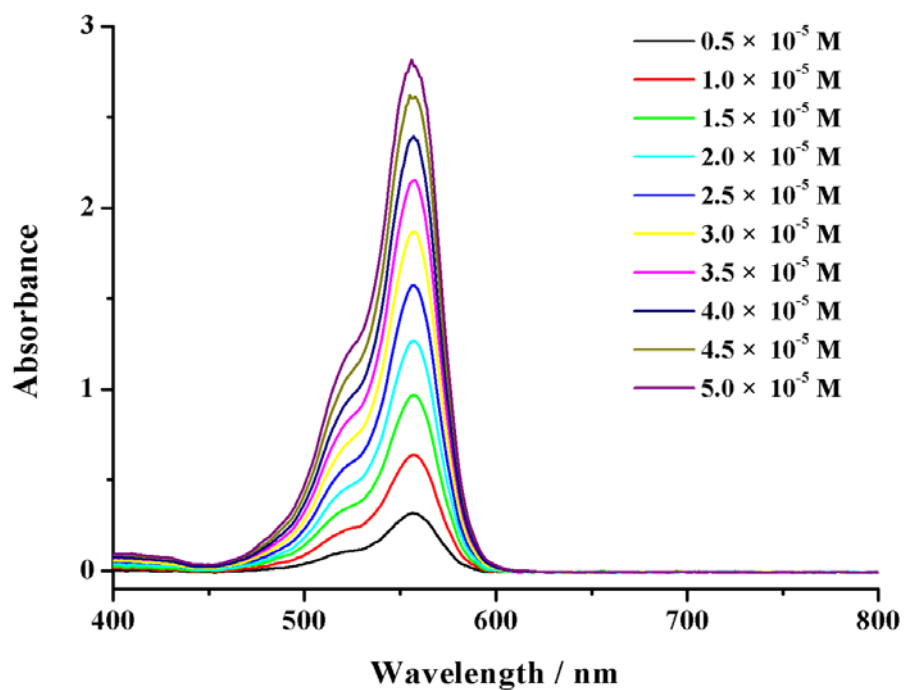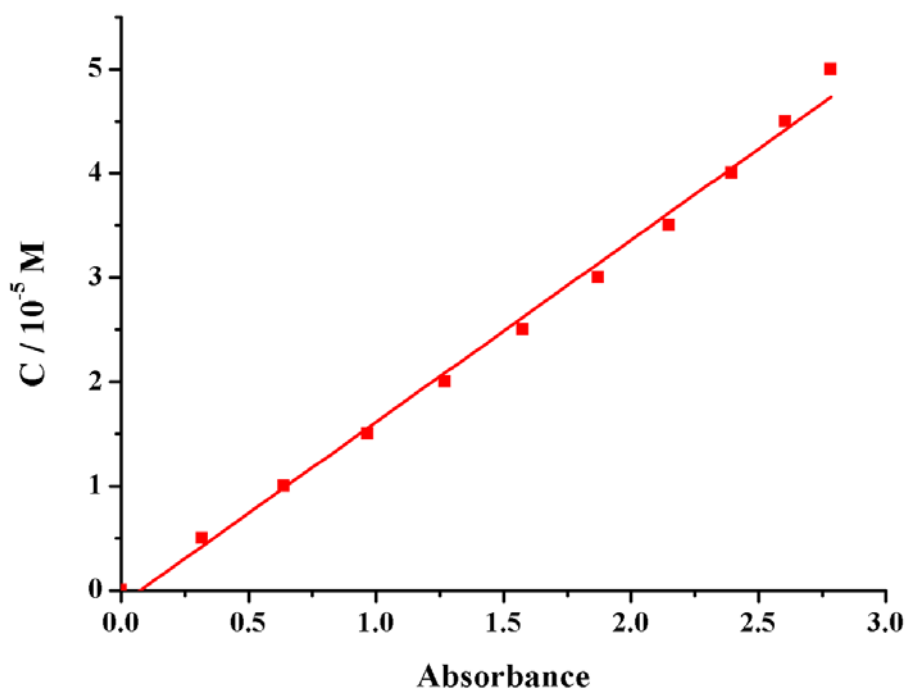
8
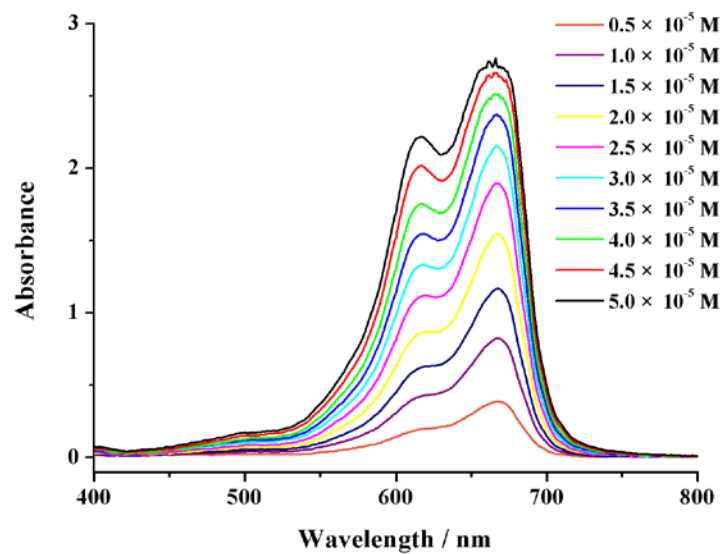
(a)

(b)

Fig. S7 (a) Calibration plot of standard **MB** by UV/vis spectra in an aqueous solution and (b) the fitting of concentration of **MB** *vs* Abs value.
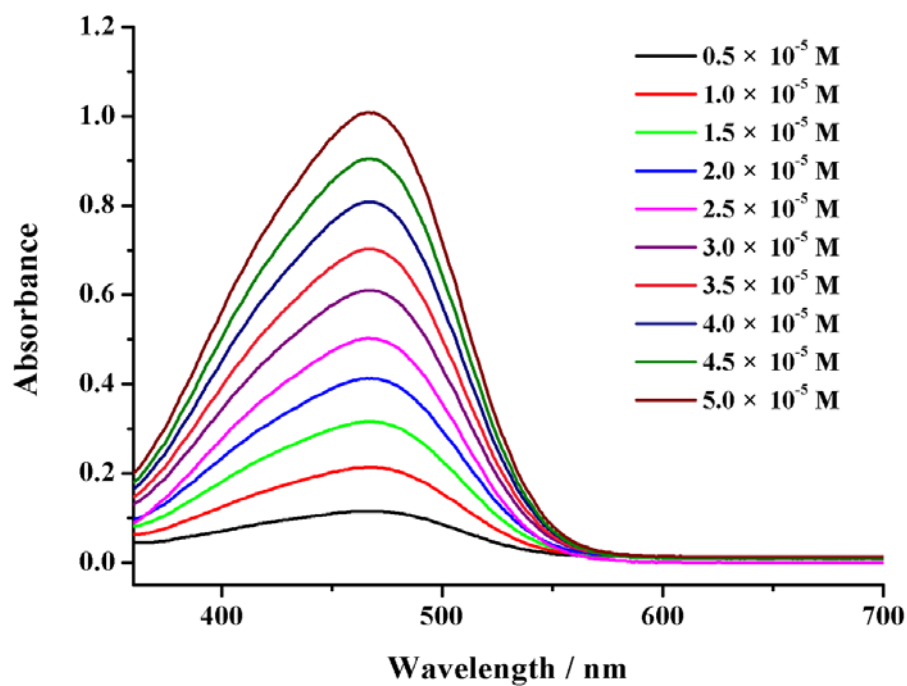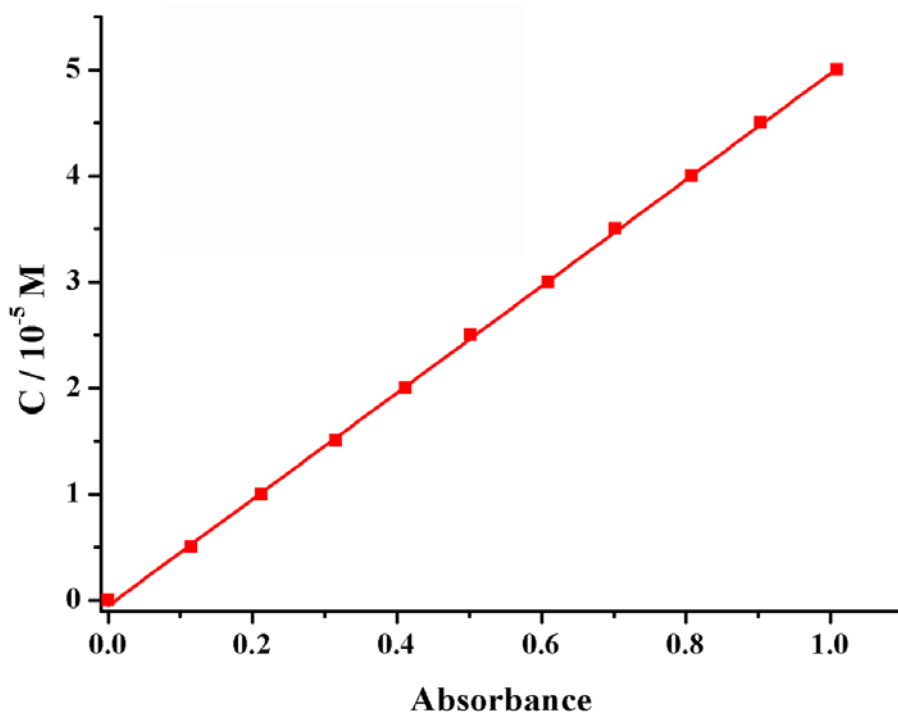
(a)

(b)

Fig. S8 (a) Calibration plot of standard **RB** by UV/vis spectra in aqueous solution and

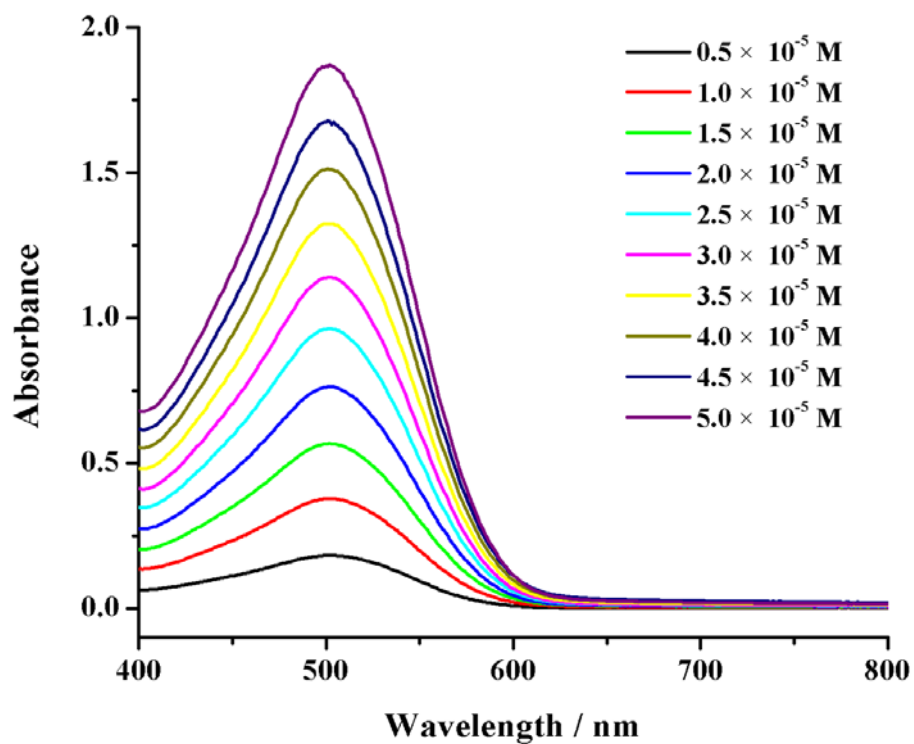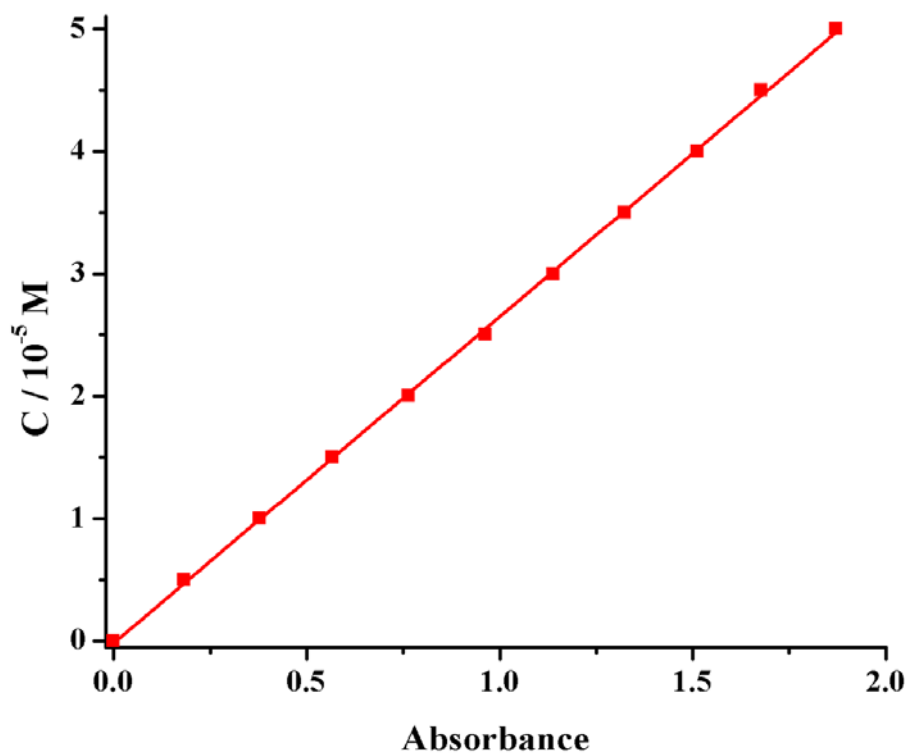(b) the fitting of concentration of **RB** *vs* Abs value.

(a)

(b)

Fig. S9 (a) Calibration plot of standard **MO** by UV/vis spectra in aqueous solution and (b) the fitting of concentration of **MO** *vs* Abs value.

(a)

(b)

Fig. S10 (a) Calibration plot of standard **CR** by UV/vis spectra in aqueous solution and (b) the fitting of concentration of **CR** *vs* Abs value.
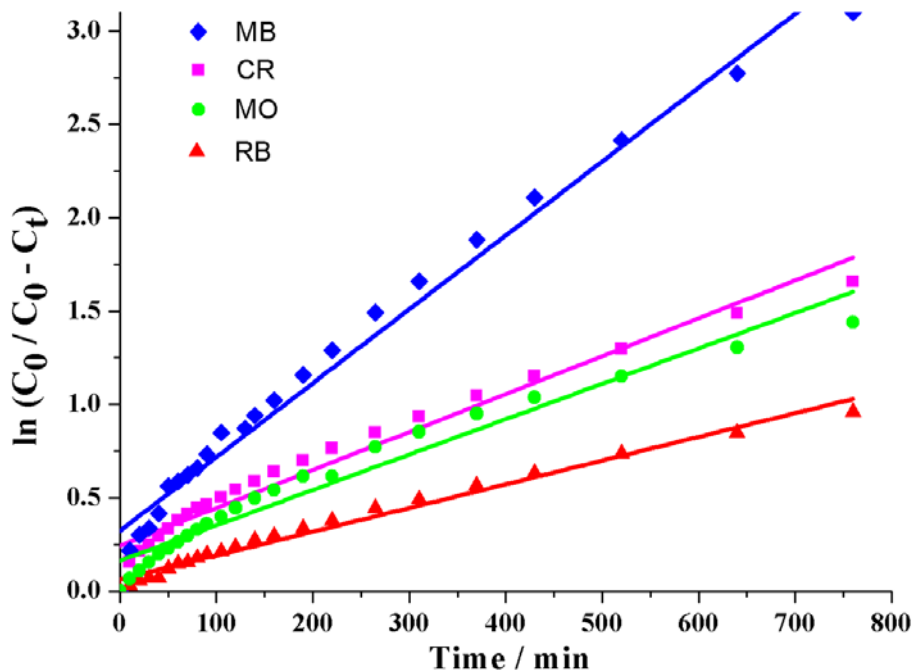
Fig. S11 Plots of first-order rates for adsorption of MB, CR, MO and RB onto MOP-**1** adsorbent. (The well-known first- and two-order equations were used to calculate the adsorption kinetics constants of the MOP-**1** for dyes, respectively (*ACS Appl. Mater. Interfaces*, 2010, **2**, 1483). The calculated results through the equations show that the plots of first-order rates for adsorptions of **MB**, **CR**, **MO** and **RB** onto MOP-**1** adsorbent are liner fits. Therefore, in the plots of first-order rates, the kinetics constants are the slopes of the lines.).
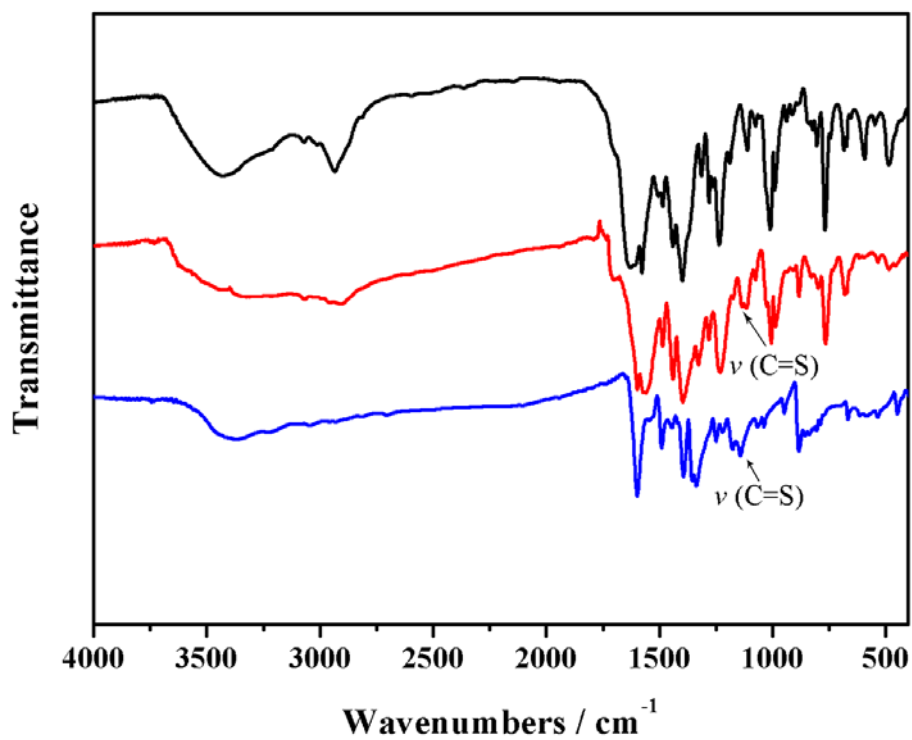
Fig. S12 IR spectra of MOP-**1** (black), MOP-**1** loaded with **MB** (red) and **MB** (blue).
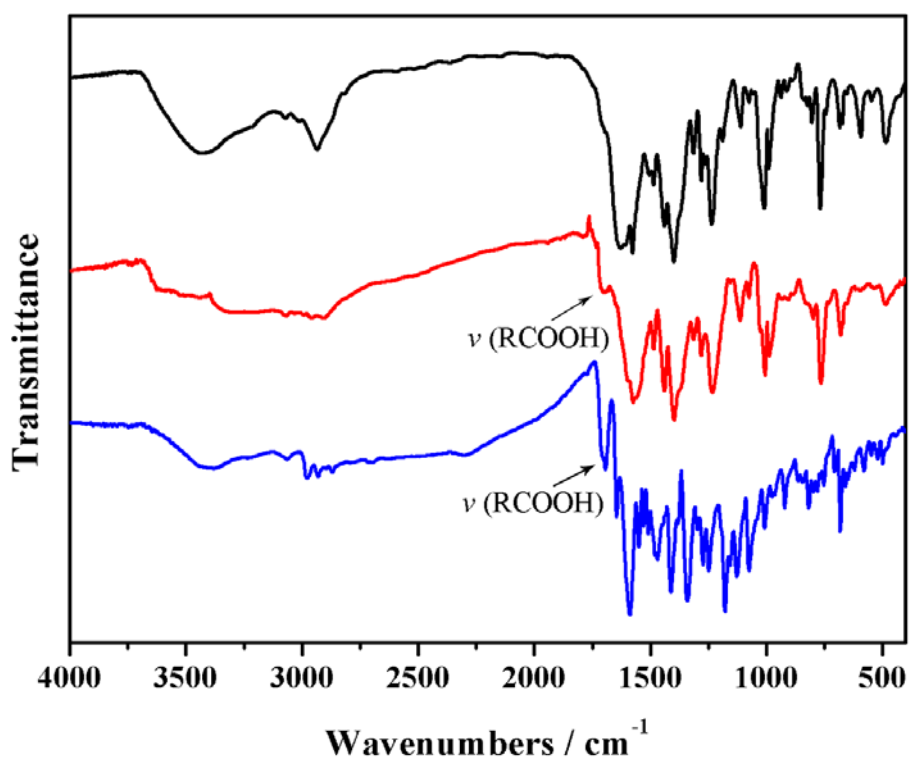

Fig. S13 IR spectra of MOP-**1** (black), MOP-**1** loaded with **RB** (red) and **RB** (blue).

Fig. S14 IR spectra of MOP-**1** (black), MOP-**1** loaded with **MO** (red) and **MO** (blue).

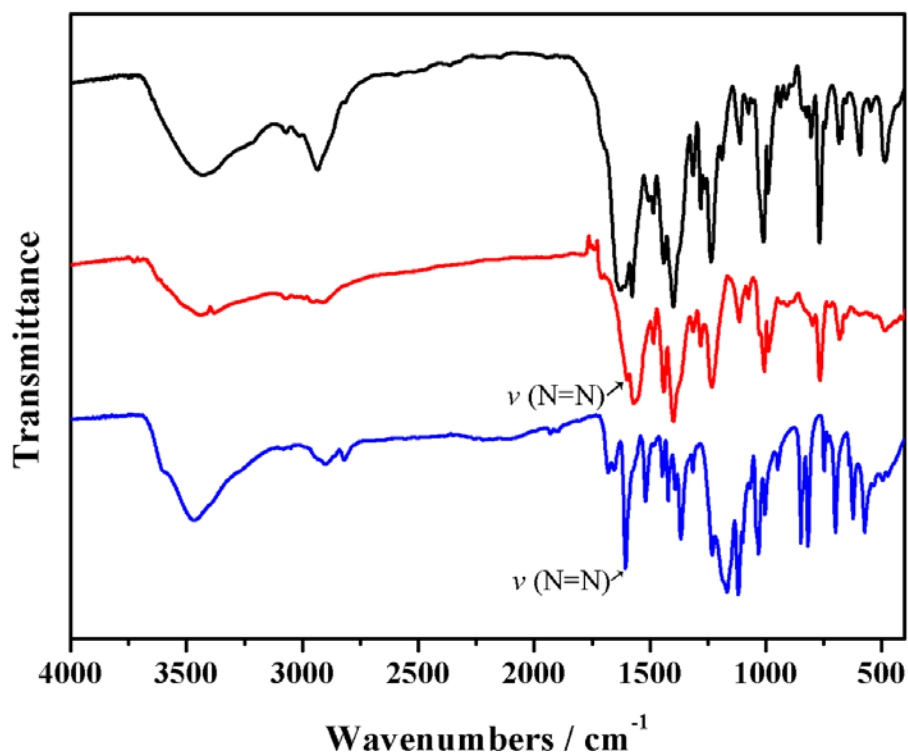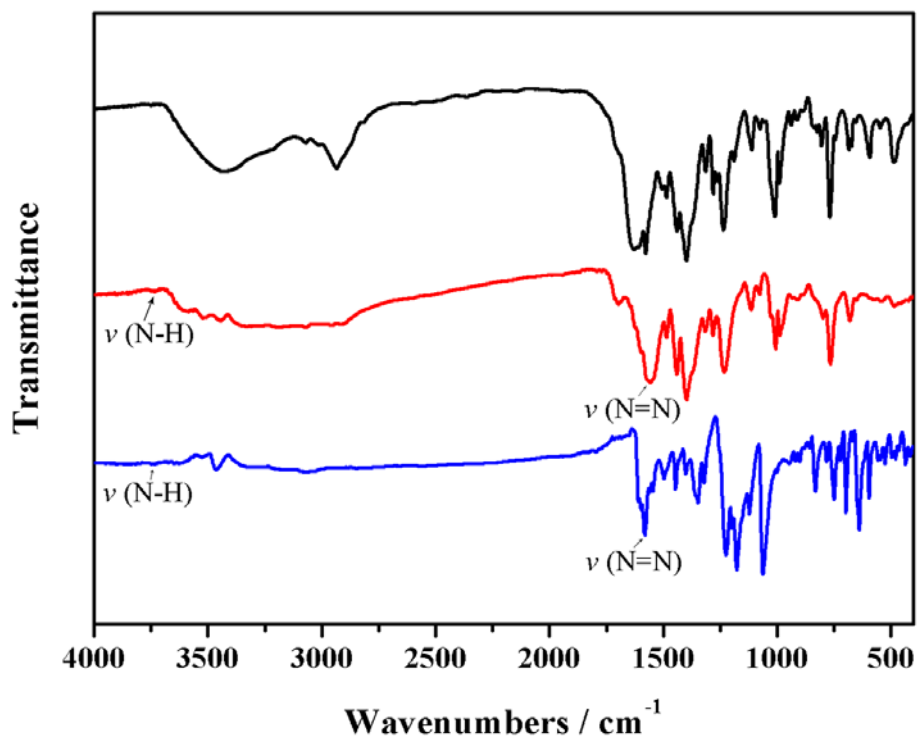**Fig. S15** IR spectra of MOP-**1** (black), MOP-**1** loaded with **CR** (red) and **CR** (blue).
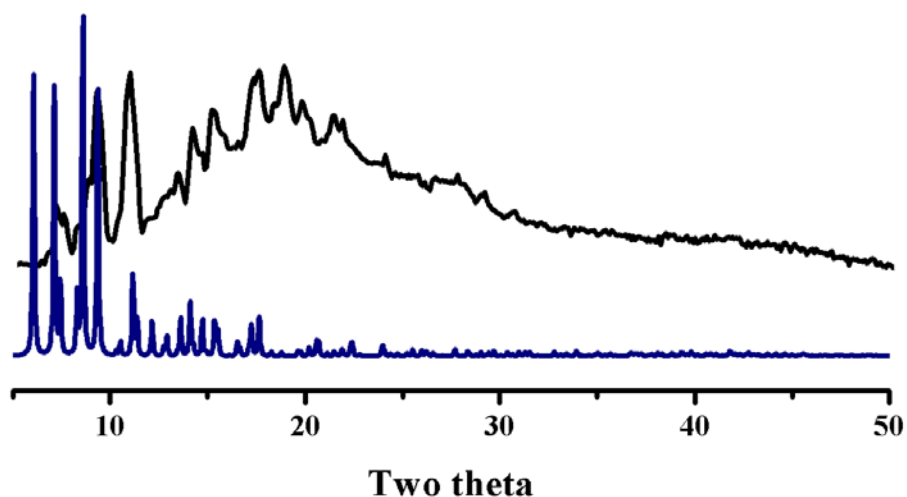
Fig. S16 The simulated (blue) and experimental (black) PXRD patterns for MOP-**1**.
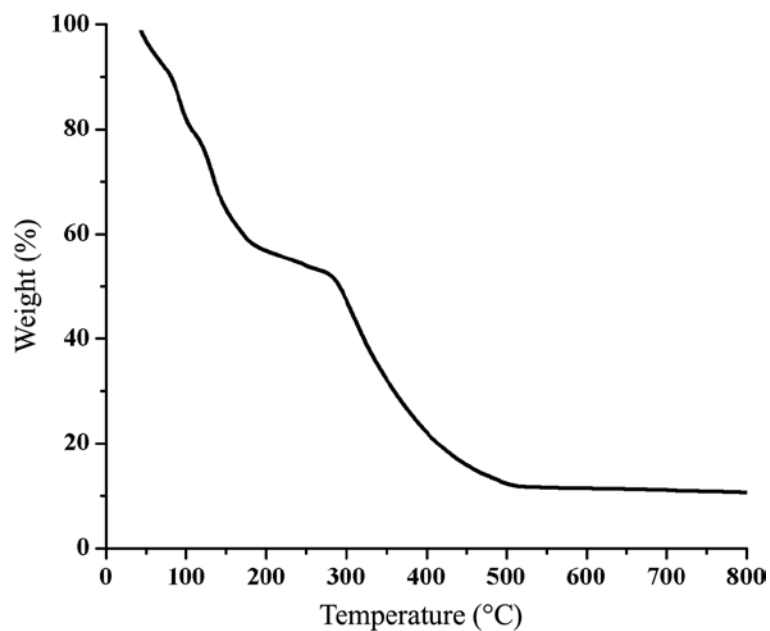

Fig. S17 The TG curve of MOP-**1.** The weight loss corresponding to the solvent molecules is observed over the temperature range from room temperature to 160 °C (found: 38.94%, calcd: 39.12%). The number of solvent molecules is calculated by TGA and also demonstrated by element analysis.

Table S1. Crystal data and structure refinement for MOP-**1.**

Compound	**1**
Formula	$C_{412}H_{609}Cu_{12}N_{37}O_{139}$
Fw	9066.84
Crystal system	Trigonal
Space group	R-3
a /Å	41.110(5)
b /Å	41.110(5)
c /Å	31.944(8)
α / °	90
β / °	90
γ / °	120
V /Å^3	46754(13)
Z	3
D_c/ g cm^{-3}	0.966
$F(000)$	14400
R(int)	0.1097
GOF on F^2	1.023
R_1 [$I > 2\sigma(I)$]	0.0691
wR_2 (all data)	0.0951

^{a} $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. ^{b} $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma |w(F_o)^2|^{2 \, 1/2}$.