

Electronic Supplementary Information

Facile preparation of a hierarchically porous metal-organic nanocomposite with excellent catalytic performance

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S1. Reagents and Materials

Cyanuric chloride, 5-aminoisophthalic acid, 4-nitrophenol (4-NP), sodium hydroxide (NaOH), sodium bicarbonate (NaHCO₃), 1,4-dioxane, hydrochloric acid (HCl), copper nitrate hydrate [Cu(NO₃)₂·3H₂O], sodium borohydride (NaBH₄), dimethyl sulfoxide (DMSO), N,N-dimethyl acetamide (DMA), N,N-dimethyl formamide (DMF), ethanol (EtOH) and methanol (MeOH) were purchased from Shanghai Civi Chemical Technology Co., Ltd. (Shanghai, China). Ultrapure water (18.2MU cm) was obtained from a Water Pro Water Purification System (Labconco Corporation, Kansas City, USA). All chemicals and reagents were analytical grade and used as received without further purification.

S2. Instrumentation

The scanning electron microscope (SEM) images were recorded on a Hitachi S-4800 at 15.0 kV. The transmission electron microscopy (TEM) images were taken with a JEM-1010 transmission electron microscope. The sample was dispersed in absolute ethanol by sonication

and dropped onto a carbon-coated copper grid. Powder X Ray Diffraction (PXRD) data were collected on a D8 FOCUS Powder X-ray Diffractometer (Germany, BRUKER AXS GMBH). Pore volume and pore size distribution were determined on an AutoPore IV 9500 mercury intrusion porosimetry (Micromeritics, Norcross, GA, USA). For pores below 100 nm, pore size and size distribution were analyzed by nitrogen sorption investigation using a equipment (BET, Quantachrome, Nora 200E).

S3. Synthesis of H₆L ligand, 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine

H₆L ligand was synthesized according to the method of the literature ^[S1] with minor modifications. 5-aminoisophthalic acid (15.2 g, 0.084 mol), sodium hydroxide (5.36 g, 0.134 mol), and sodium bicarbonate (8.74 g, 0.104 mol) were added to 140 mL H₂O. The mixture was stirred at 0 °C for 10 min, followed by dropwise addition of cyanuric chloride (3.68 g, 0.02 mol) in 1,4-dioxane (50 mL). The mixture was then refluxed for 24h. The resulting solution was adjusted to pH=1 with hydrochloric acid. The H₆L solid was collected by filtration, rinsed several times with distilled water, and dried at 80 °C (11.50 g, yield: 94%).

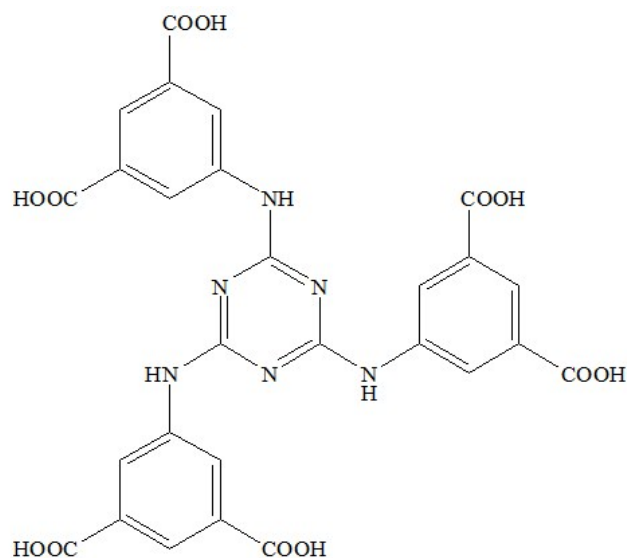


Fig.S1. The structural formula of H₆L ligand

S4. Preparation of the *hpCuL*

In a typical synthesis, H₆L ligand (30mg) was ultrasonically dissolved in 100 μ L of DMSO, 95 μ L of DMA and 10 μ L of H₂O, pH value of solution was adjusted to 5-6 with 1.0 M NaOH aqueous

solution. $\text{Cu}(\text{NO}_3)_2$ (165 mg) was dissolved in 75 μL of DMSO and 70 μL of DMA. The two solutions were mixed with vigorous agitation at room temperature, and a homogeneous green gel was observed in less than 20 seconds, which was confirmed by the inverted test tube method. The synthesized gel was then aged for 24h at 100 °C and subsequently washed three times with DMA followed by ethanol to exchange the DMSO and DMA. The *hpCuL* product as a green powder was harvested by centrifugation followed by drying at 60 °C. Exchanging the initial DMSO/DMA solvents with water, N,N-dimethyl formamide, ethanol or methanol yielded viscous precipitates, indicating that gel formation is dependent on the nature of the solvents.

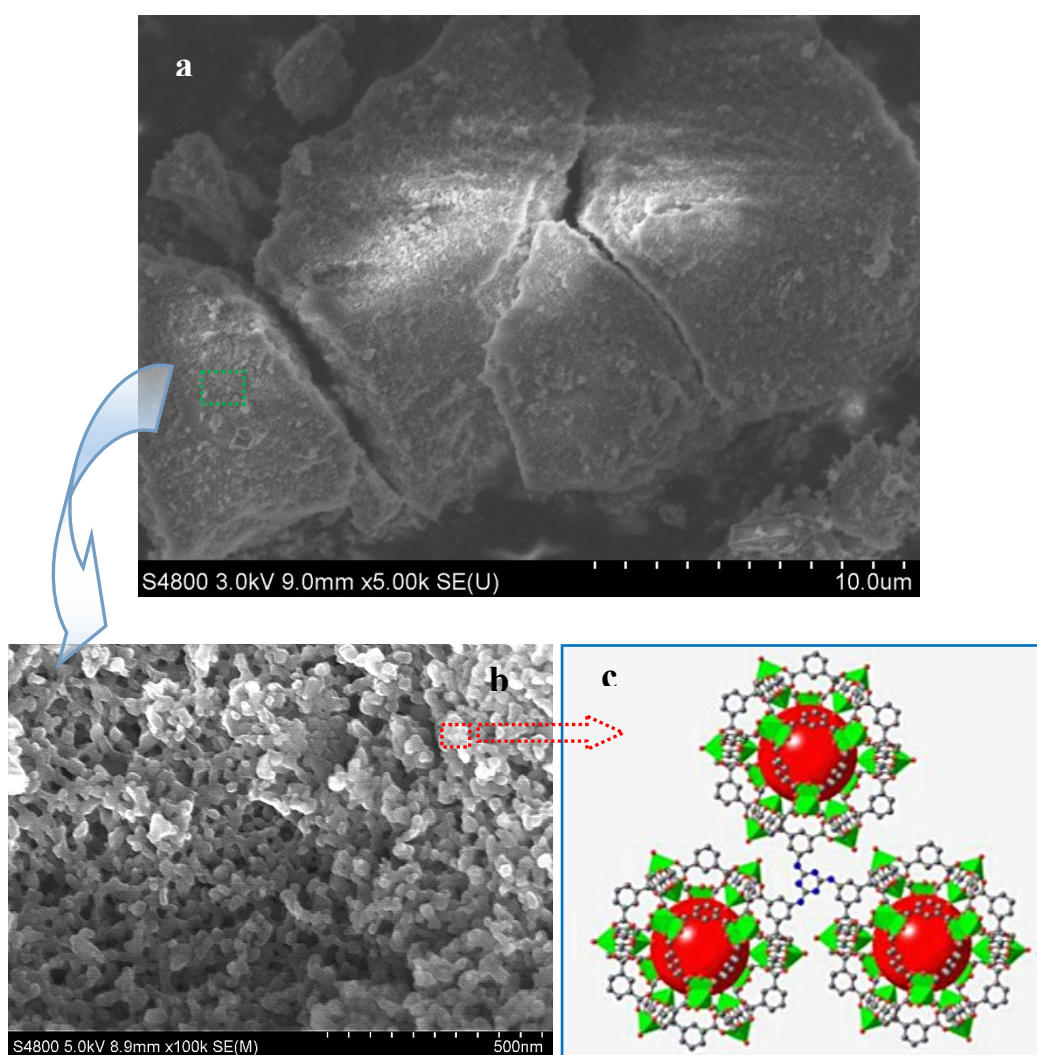


Fig.S2. (a) and (b) SEM images of the *hpCuL* with different magnifications originating from the gel prepared at pH 5.5 and aged at 100 °C for 12h; (c) the supramolecular building block of the *hpCuL*

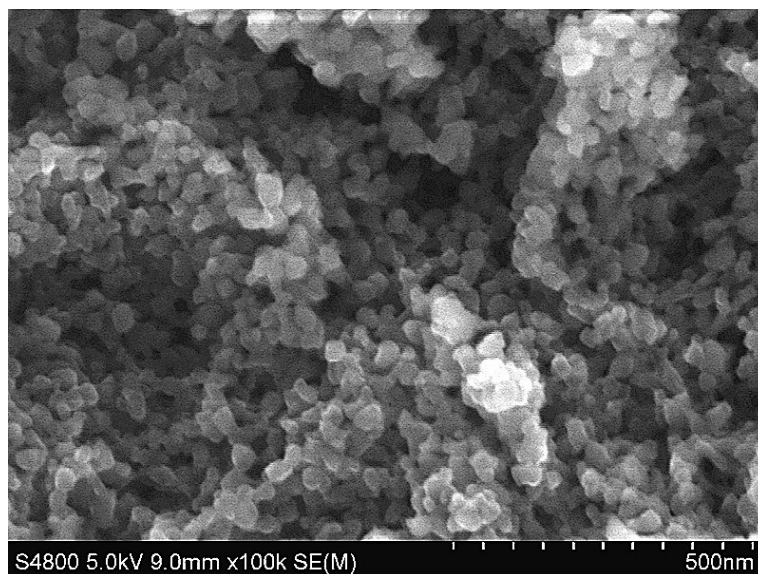


Fig.S3. SEM image of *hpCuL* originating from the gel prepared at pH 5.5 aged for 24h

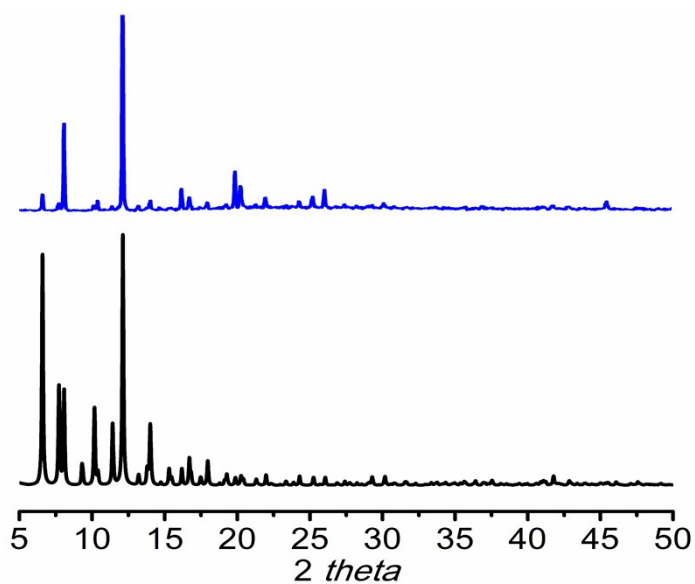


Fig.S4. PXRD patterns of simulated **1** from the single crystal data (black) and the product originating from the gel prepared at pH 4.8 aged for 24h

S5. Water stability investigation of the *hpCuL* framework.

25 mg of the *hpCuL* was placed in a vial containing 5 mL of H₂O. The sample was allowed to

sit at room temperature for 24 h. The samples were filtered and the solid was recovered for PXRD examination.

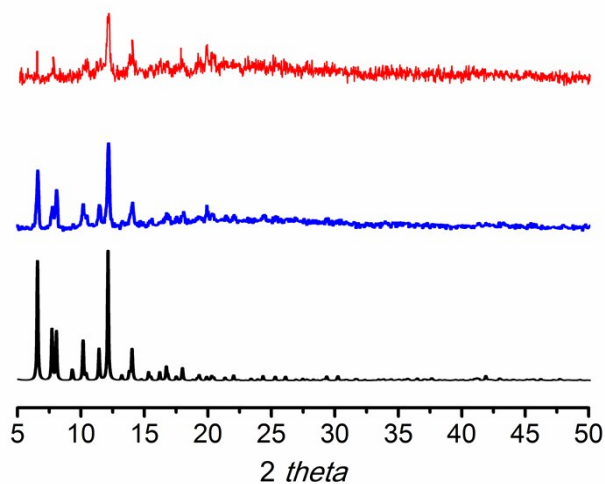


Fig.S5. PXRD patterns of the *hpCuL* exposed to air for 30 days at room temperature (blue) and soaked in water for 24h (red) in comparison with simulated patterns of single-crystal data of 1 (black)

S6. Catalytic reduction of 4-NP

Aqueous solutions of *hpCuL* (0.68mg/mL) and 4-NP (0.18 mmol/L) were prepared. To a mixture of 40 mg of NaBH_4 freshly dispersed in 5 mL of H_2O , 15 mL of 4-NP solution was added. Subsequently, 1mL of the *hpCuL* solution was added to the solution with the 4-NP and NaBH_4 under continuous stirring. The initial concentration of 4-NP is 0.13 mmol/L. The reaction was carried out at room temperature. Parts of the reaction mixture were taken and measured at certain time in the range of 250-500 nm with a UV-Visible absorption spectrometer. The apparent pseudo-first-order reaction rate constant (k_a) of the reaction was determined from the linear correlation of $\ln(A_t/A_0)$ obtained in absorbance at 400 nm versus reaction time.

The reduction of 4-NP in the absence of the *hpCuL* with excess NaBH_4 in water was exactly as above, except that *hpCuL* was not used.

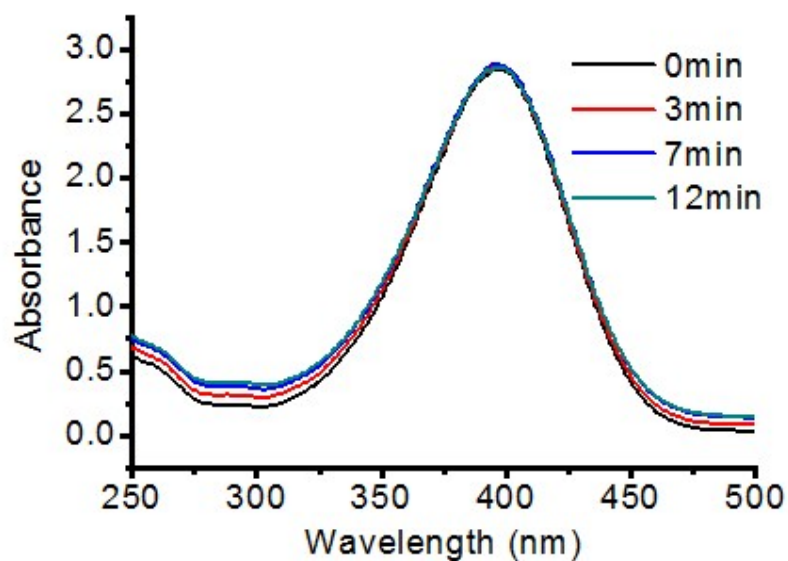


Fig. S6. UV-Vis absorption spectra for 4-NP reduction in the absence of the *hpCuL*.

S7. Adsorption of 4-NP

5 mL of H₂O was mixed with 15 mL of 4-NP solution (0.18 mM). The pH value of solution was adjusted to 12 with 10% NaOH (aq) for simulating the reduction solution with NaBH₄. 1 mL of the *hpCuL* solution (0.68mg/mL) was added. Parts of the mixture were taken and measured at certain time in the range of 300-800 nm with a UV-Visible absorption spectrometer. The adsorption process was carried out at room temperature under continuous stirring at 150 rpm rate. The relative concentration ratio of residual 4-NP were calculated according to the following equations:

$$\text{Re (\%)} = \frac{C_t}{C_o} \times 100\%$$

where C_o and C_t are the residual and initial concentration of aqueous 4-NP, respectively; because the ratio of A_t/A_o is directly proportional to the ratio of C_t/C_o , the C_t/C_o is expressed with A_t/A_o in absorbance at 400 nm.

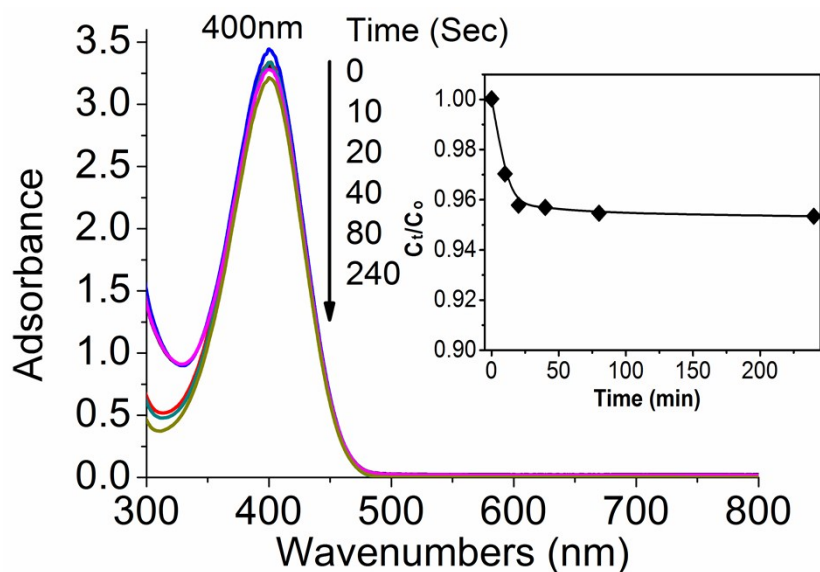


Fig. S7. UV-Vis absorption spectra of 4-NP at pH 12 in the absence of NaBH₄; the insert is the relative concentration ratio of residual 4-NP with an initial concentration of 0.13 mmol/L.

S8. Synthesis of crystals of **1**, Cu₃L(H₂O)₃·10H₂O·5DMA

Crystals of **1** were synthesized by hydrothermal appropriate methods according to the method of the literature ^[S1] with minor modifications. H₆L ligand (0.030 g, 0.049 mmol) was dissolved in DMA (2mL), DMSO (2mL), H₂O (100 μL), Cu(NO₃)₂·3H₂O (0.164g, 0.68 mmol). Upon adding 0.9 mL of HBF₄, the mixture was sealed in a small vial and heated at 85 °C for 3 d. After cooling to room temperature, blue octahedral crystals were filtered and washed with DMA. Yield 0.028 g, 74% (based on ligand).

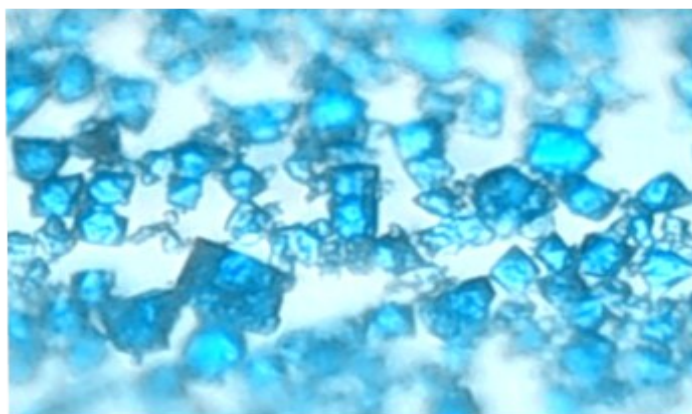
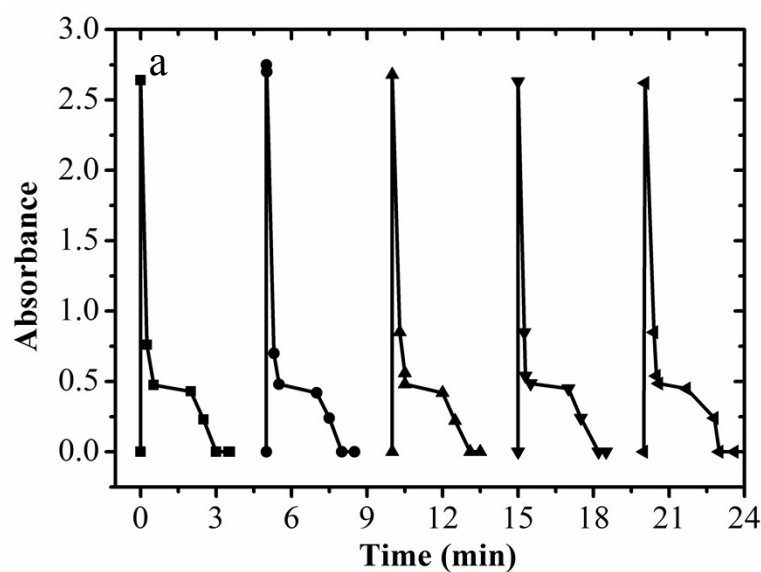


Fig.S8. The photograph of crystals of **1**

S9. Reusability test

Aqueous solutions of *hpCuL* (0.68mg/mL) and 4-nitrophenol (0.18 mM) were prepared. To a mixture of 40 mg of NaBH_4 freshly dispersed in 5 mL of H_2O , 15 mL of 4-nitrophenol solution and 1mL of *hpCuL* solution was added to the solution under continuous stirring. The reaction was carried out at room temperature for 5 min. Parts of the reaction mixture were taken and measured at certain time in the range of 250-500 nm with a UV-Visible absorption spectrometer. And then, the *hpCuL* was filtered, washed with distilled water, and placed into another mixed solution containing 40 mg of NaBH_4 freshly dispersed in 6 mL of H_2O and 15 mL of 4-nitrophenol solution. After five successive reactions, the *hpCuL* were filtered, washed with distilled water, dried for SEM examination.



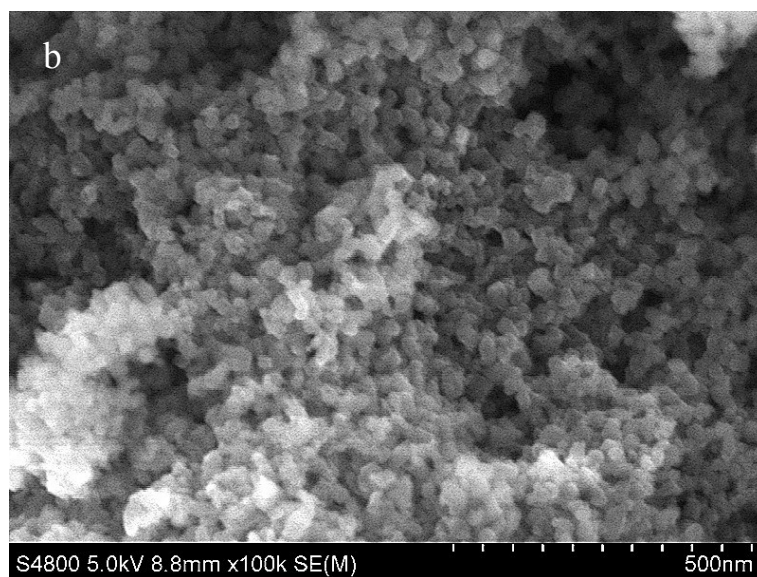
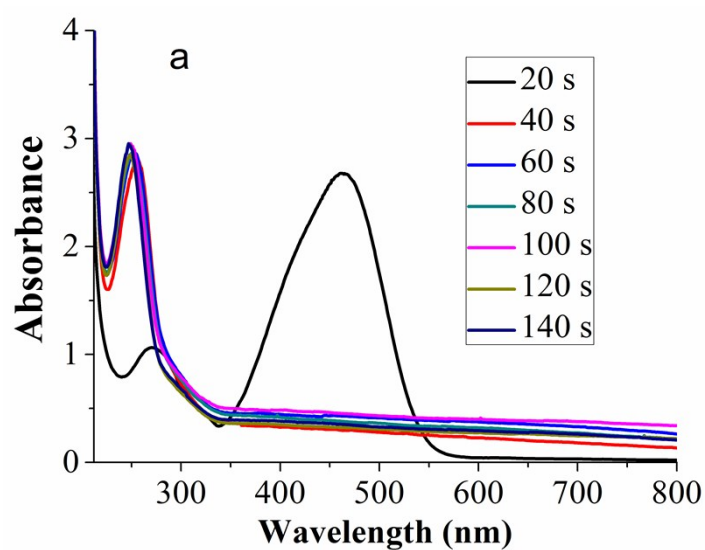


Fig. S9. (a) Catalytic kinetics of 4-nitrophenol (400 nm) and (b) the SEM image of the *hpCuL* with the same batch of *hpCuL* after the five cycle reactions

S10. Catalytic reduction of methyl orange, bromophenol blue and bromocresol green

10mg of the *hpCuL* and 130 mg of NaBH_4 was added to aqueous solutions of methyl orange, bromophenol blue or bromocresol green (25mL, $1\text{g}\cdot\text{L}^{-1}$) under continuous stirring. The reaction was carried out at room temperature. Parts of the reaction mixture were taken and measured at certain time in the range of 200-800 nm with a UV-Visible absorption spectrometer.



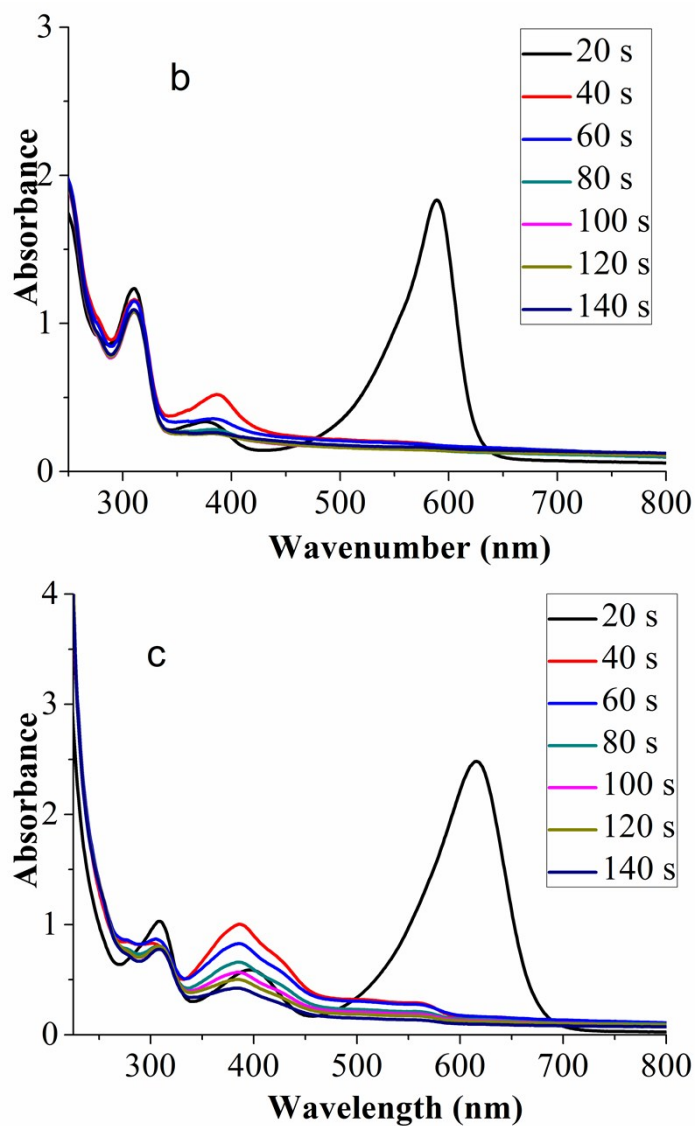


Fig. S10. UV-Vis absorption spectra for the reduction of methyl orange (a), bromophenol blue (b) and bromocresol green (c) catalysed by *hpCuL*.

Reference

[S1] B. Y. Li, Z. J. Zhang, Y. Li, K. X. Yao, Y. H. Zhu, Z. Y. Deng, F. Yang, X. J. Zhou, G. H. Li, H. H. Wu, N. Nijem, Y. J. Chabal, Z. P. Lai, Y. Han, Z. Shi, S. H. Feng and J. Li. *Angew. Chem. Int. Ed.*, 2012, **51**, 1412.