Supporting information

Copper based metal – organic molecular ring with inserted Keggin-type polyoxometakate: a stable photofunctional host-guest molecular system

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Experimental Section

General: All the reagents were purchased from commercial channels and used without further purification; TPT was synthesized as reported. A TA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the TGA curve in N_2 at a rate of 10 ºC min^{-1}. UV-Visible spectral measurements were carried out using a HITACHI U-3010 spectrometer. IR spectra were characterized by a Bruker Tensor 27 FTIR spectrometer in the range of 4000-400 cm^{-1} using a KBr disk. The C, H and N microanalyses were carried out with a Vario EL III elemental analyzer.

A solution of $CuCl_2 \cdot 2H_2O$ (0.324g, 2mmol), TPT (0.252g, 0.8mmol), H_3PO_4 (5 mL, 85%) and H_2O (180 mL) was stirred for 60min. 10 mL of the above suspension, $Na_2WO_4 \cdot 2H_2O$ (0.667mmol, 0.22g), NH_4VO_3 (0.085mmol, 0.01g) was mixed and stirred for 10 min, and the pH was adjusted to 3.51 with 2M NaOH. The mixture was sealed in a 25ml Teflon-lined steel bomb and heated at 170ºC for 6000min. Brown block-like crystals were collected in 29% yield. Elemental Anal. Calc. (%) for $C_{72}H_{56}Cu_5N_{24}O_{46}PW_{12}$ (4548.28): C, 19.01; H, 1.24; N, 7.39. Found: C, 18.82; H, 1.31; N, 7.48%.

Photocatalytic degradation experiments:

The photochemical experiment was performed in a 250mL Pyrex reactor with a AHD 150W xenon lamp as a light source. H_2O_2 (1.5 mmol/L, 1 mL) and powder of compound **1** (0.15g) were added to the MO solution (15mg/L, pH = 6.3) with continuous shaking at room temperature. At a certain interval of light irradiation, the decolorization rate of the solution was analyzed on a HITACHI U-3010 UV-Visible spectrometer by application of the Lamber–Beer law with one of its maximum bands at 465 nm. The calculating formula is listed as follows:

$$D = \frac{C_0 - C_1}{C_0} \times 100\% = \frac{A_0 - A_1}{A_0} \times 100\%.$$

All photocatalytic experiments are carried out at the same conditions except the difference of chemical reactants: (1) MO/ compound **1** for line **a;** (2) MO/ H_2O_2 for line **b**; (3) MO/compound **1** /H_2O_2 for line **c.**

X-ray structural analyses: Suitable crystal of compound **1** (brown block, 0.45 × 0.38 × 0.15 mm^3) was selected and mounted on a glass fiber. The measurement was made on a Brucker-axs Smart APEX CCD diffractormeter with MoKα radiation (λ = 0.71073 Å). Data were collected at 173K, using the ω and φ scans to a maximum θ value of 25.03°. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method. Since the crystal did not show any sign of decay during data collection a decay correction was deemed unnecessary. The structure was solved by direct methods SHELXS-97. The hydrogen atoms associated with water molecules and hydroxyl groups were located from the difference Fourier map and refined with distance restraints of O-H = 0.82 (3)Å. Other hydrogen atoms attached to carbon atoms were included at geometrically idealized position as a riding mode with default SHELXTL parameters. Four oxygen atoms (O22, O23, O24 and O25) were symmetric disordered over two positions with occupation factors of 0.5/0.5. All non-hydrogen atoms were refined anisotropically except those disordered atoms.

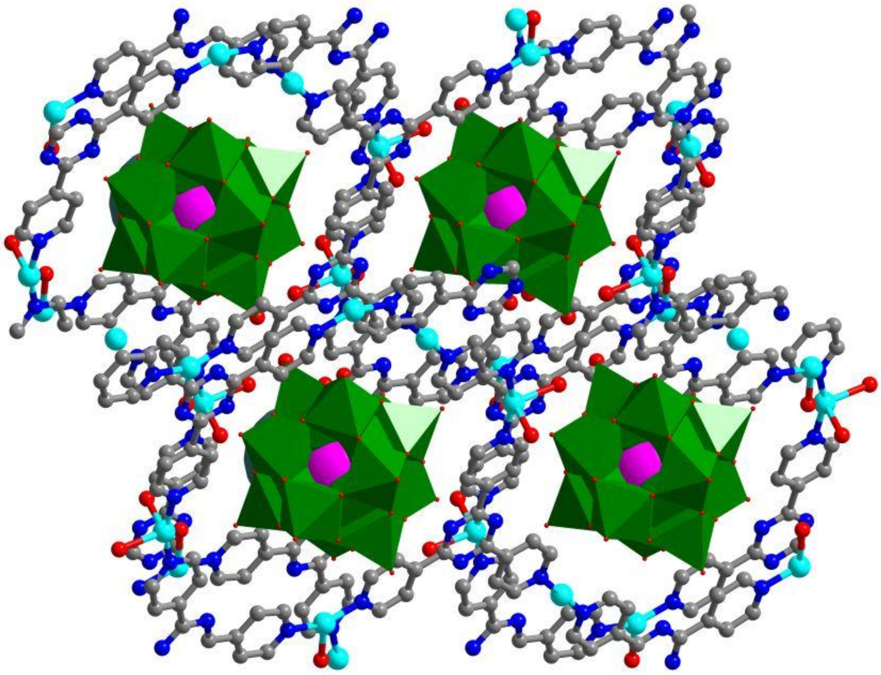


Figure S1 Crystal packing along the *c*-axis showing that the polyanions penetrate the stacking layers

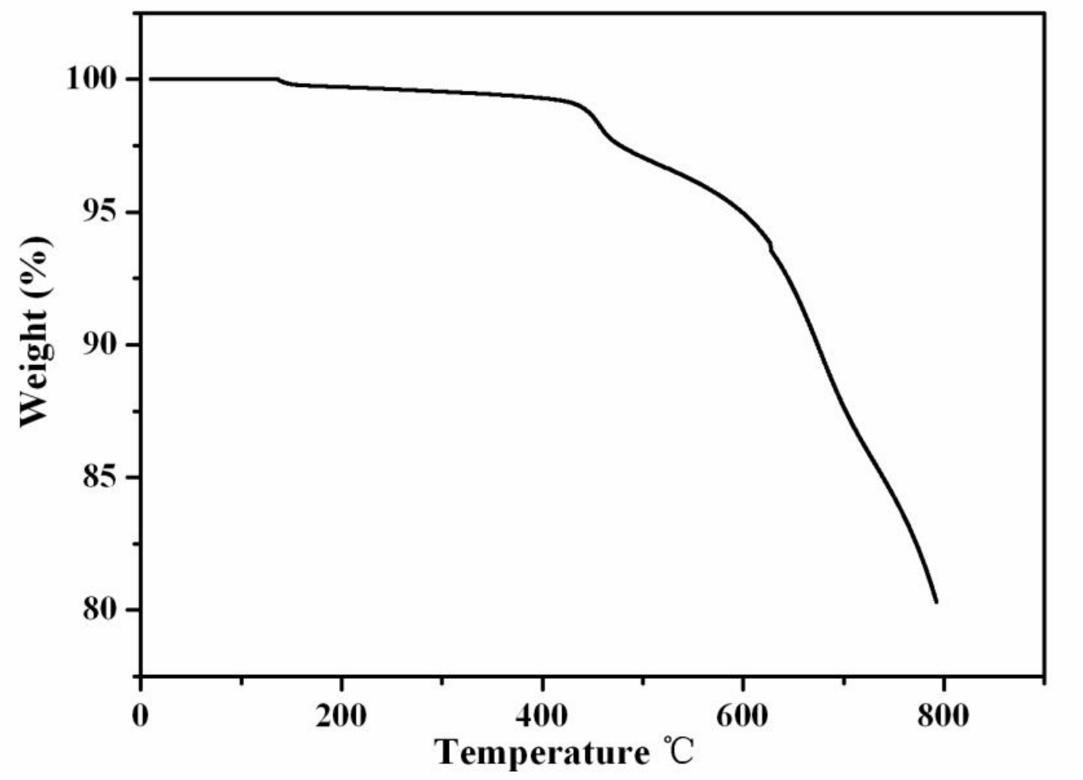


Figure S2 Thermal gravimetric curve of compound **1.**

The TG curve of **1** shows an initial weight loss of ca. 0.8% between 150ºC and 250ºC, corresponding to the removal of two coordinated water molecules (0.79% calculated). The decomposition of the whole framework starts at 430 ºC. From 430 to 800 °C, the TGA trace showed a sharp decline to give a total weight loss of ca. 20% (20.6% calculated), for the loss of three TPT molecules per formula unit.

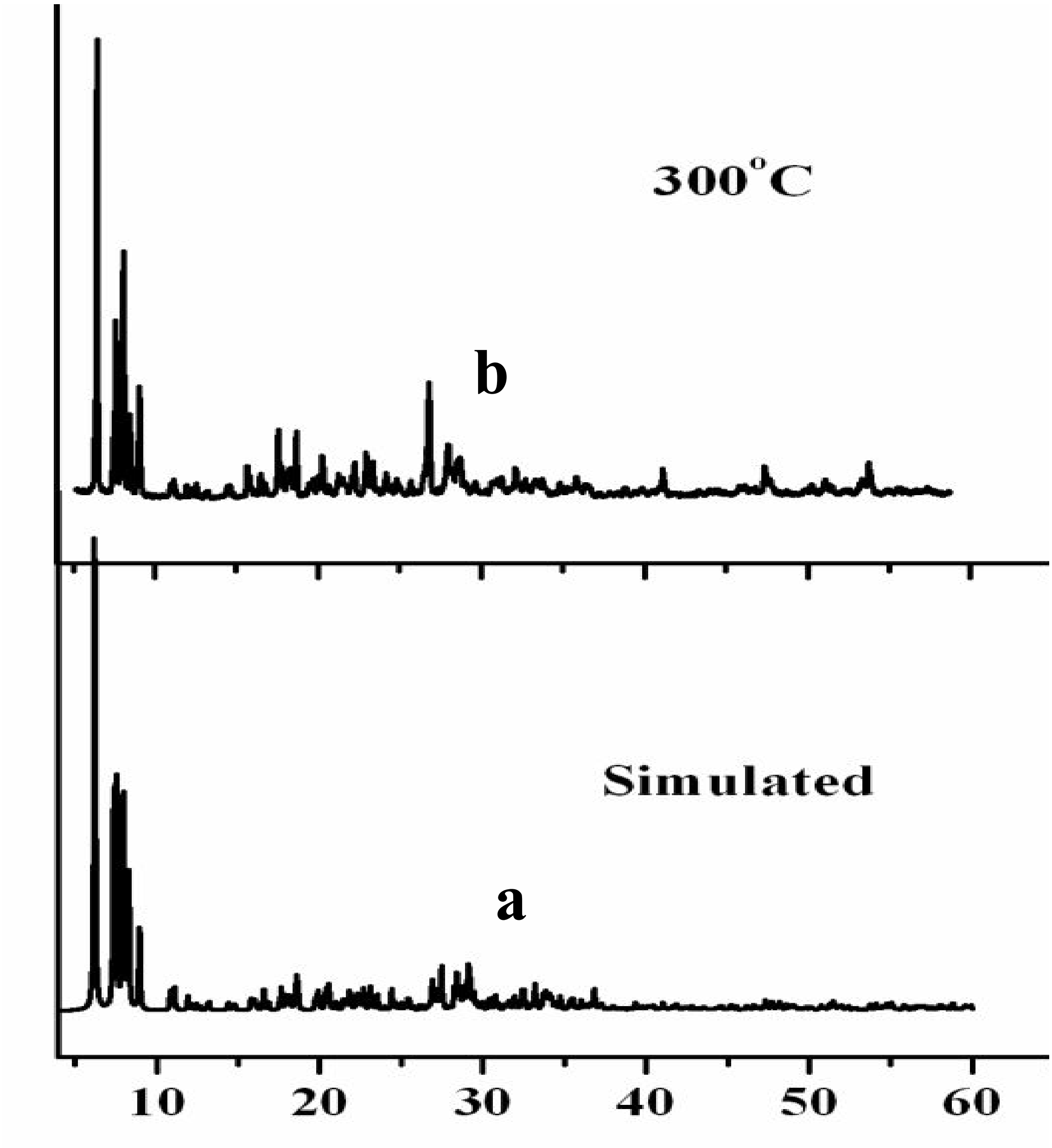


Figure S3 Powder XRD patterns: (a) simulated; (b) calcined at 300°C.

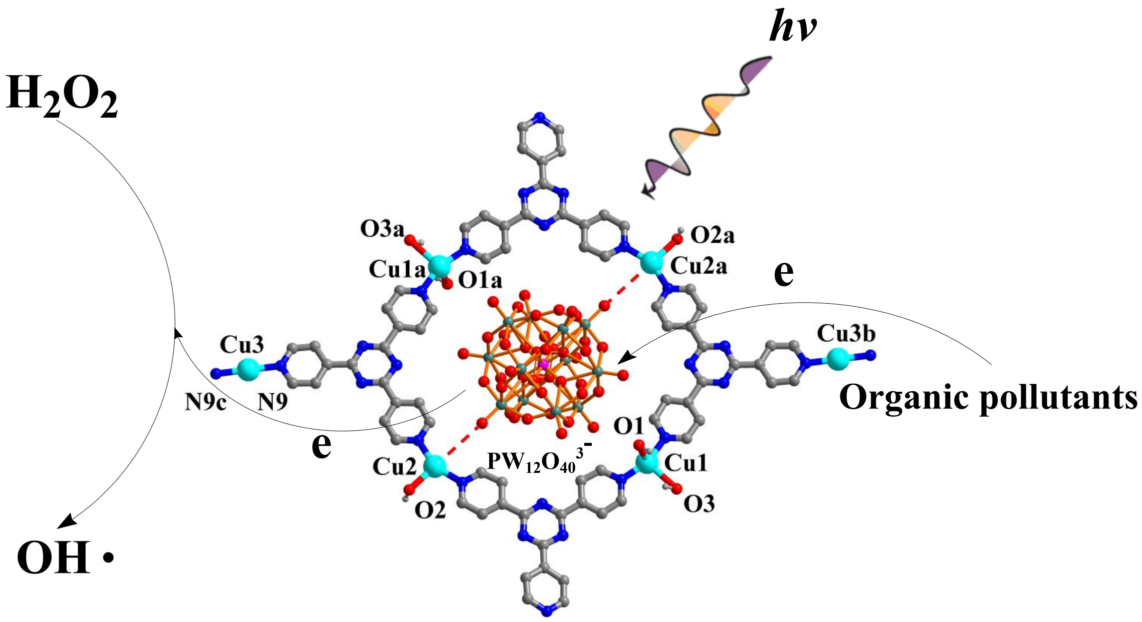


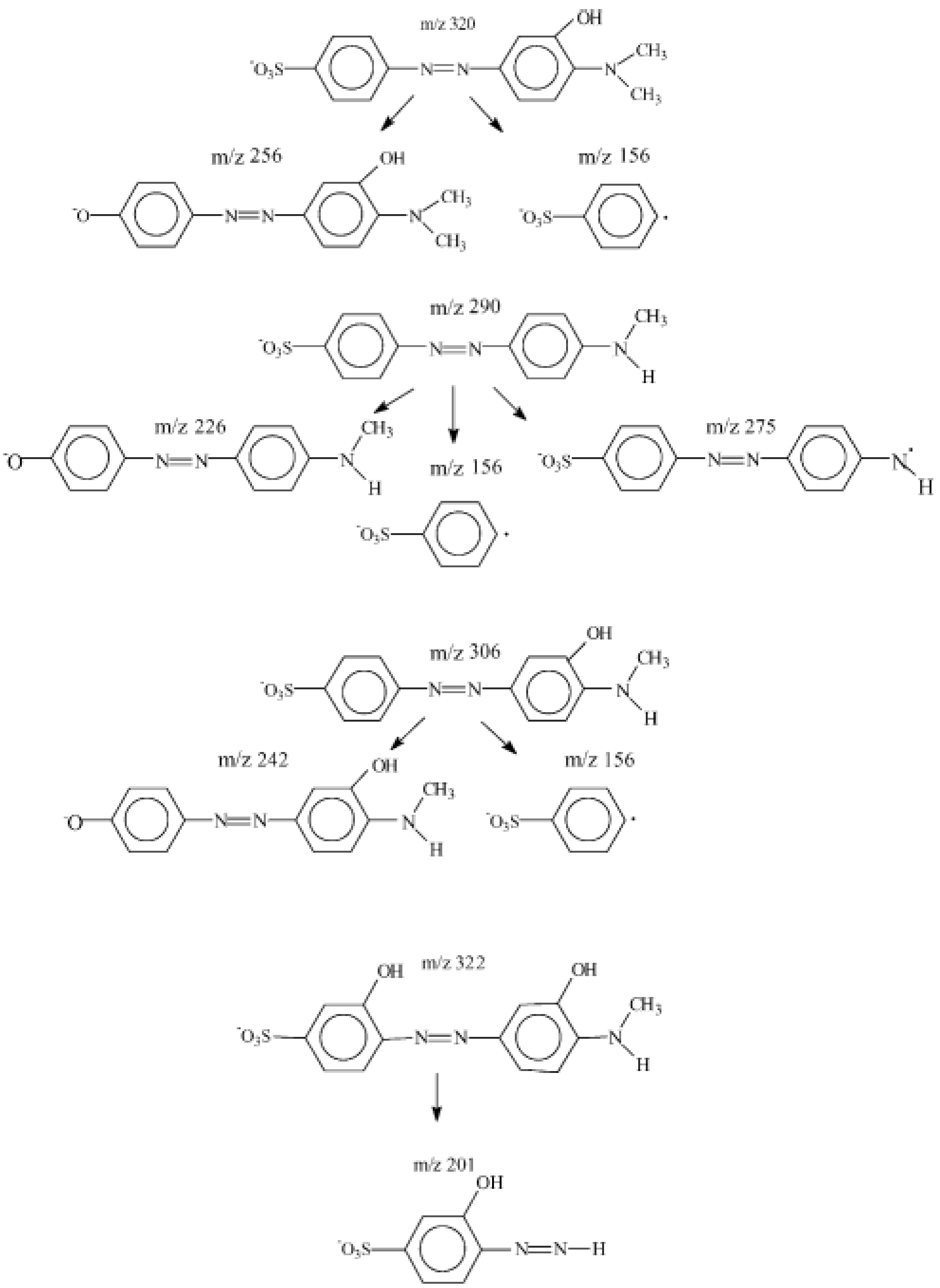
Figure S4 The proposed photodegradation mechanism**.**

Photocatalytic mechanism for the generation of •OH radical with polyphosphotungstate cluster as catalyst has been well reported.[1] The presence of H_2O_2 in solutions exposed to light irradiation provokes the generation of hydroxyl radicals •OH according to the following equation[2]:

$H_2O_2 + e \rightarrow \bullet OH + OH^-$

$\bullet OH + Dye \rightarrow Dye\bullet + H_2O \rightarrow$ Degradation products

The degradation products have been characterized by HPLC/UV–VIS diode array and HPLC/MS techniques. [3] The degradation products in solution were reported to contain a mixture of organic fragments (listed as follows):



Fragmentation scheme of methyl orange degradation products.[3]

[1] (a) A. Hiskia, A. Mylonas and E. Papaconstantinou, *Chem. Soc. Rev.*, 2001, **30**, 62; (b) H. X. Yang, T. F. Liu, M. N. Cao, H. F. Li, S. Y. Gao and R. Cao, *Chem. Commun.*, 2010, **46**, 2429.

[2] S. Haji, B. Benstaali and N. Al-Bastaki, *Chem. Eng. J.,* 2011, **168**, 134.

[3] C. Baiocchi, M. C. Brussino, E. Pramauro, A. B. Prevot, L. Palmisano and G. Marcì, *Int. J. Mass spectrom.* 2002, **214**, 247.