Supporting Information

A Hybrid Metal Phosphate-Phosphite Material Grafted with Electron Deficient Organic Component Showing Interesting Fluorescent and Photosensitive Properties

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Experimental Section

General: All the reagents were purchased from commercial channels and used without further purification; tris (4-pyridyl) triazine was synthesized as reported. UV-Visible spectral measurements were carried out using a HITACHI U-3010 spectrometer. The emission/excitation spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer. The ESR spectra were recorded at room temperature with a Bruker EMX-10/12 Electron Spin Resonance 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.

Synthesis of $Zn_9(TPT)_3(H_2PO_4)_2(HPO_4)_4(HPO_3)_4 \cdot 6H_2O$ **1**: $Zn(NO_3)_2 \bullet 6H_2O$ (0.2975g, 1mmol) was added to a mixture of H_3PO_3 (0.246g, 3mmol), and TPT (0.0624, 0.2mmol) in H_2O (4mL). The mixture was sealed in a 25ml Teflon-lined steel bomb and heated at 140ºC for 72h. Yellow needle-like crystals were collected in 35.6% yield (based on TPT) after filtration, washed by water, and dried at room temperature. Elemental Anal. Calc. (%) for $C_{54}H_{60}N_{18}O_{42}P_{10}Zn_9$ (2531.23): C, 25.62; H, 2.39; N, 9.96. Found: C, 25.45; H, 2.41; N, 9.85. IR (KBr): ν = 3427 (m), 3109(w), 3058(w), 1652(w), 1618(m), 1517(s), 1377(s), 1319(m), 1110(s), 912(m), 806(s), 663(m), 601(m), 518(m) cm^{-1}.

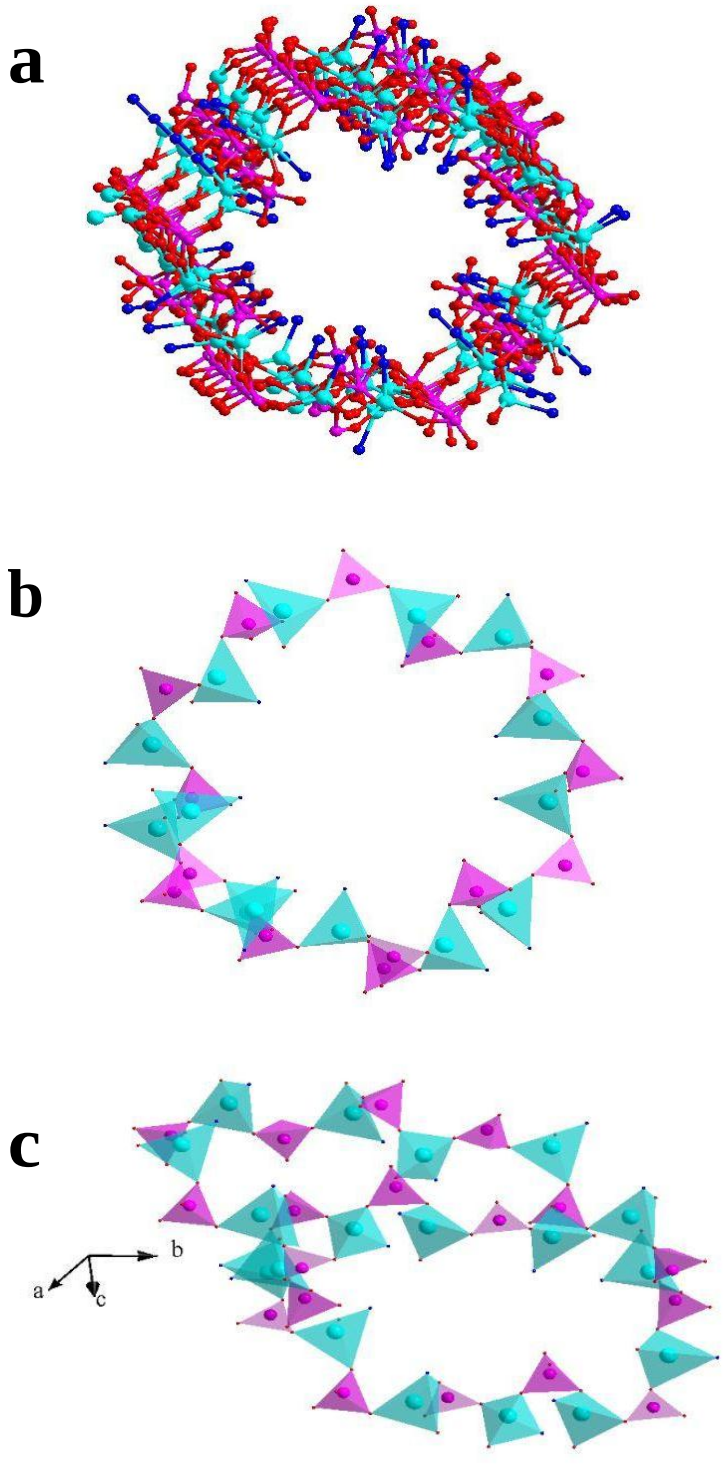

Fig. S1 (a) the structure of the 24-ring viewed along the c direction; **(b)** the tetragonal array of the 24-ring channel; **(c)** the corner-sharing 4-ring, 8-ring, 12-ring and 24-ring structure.

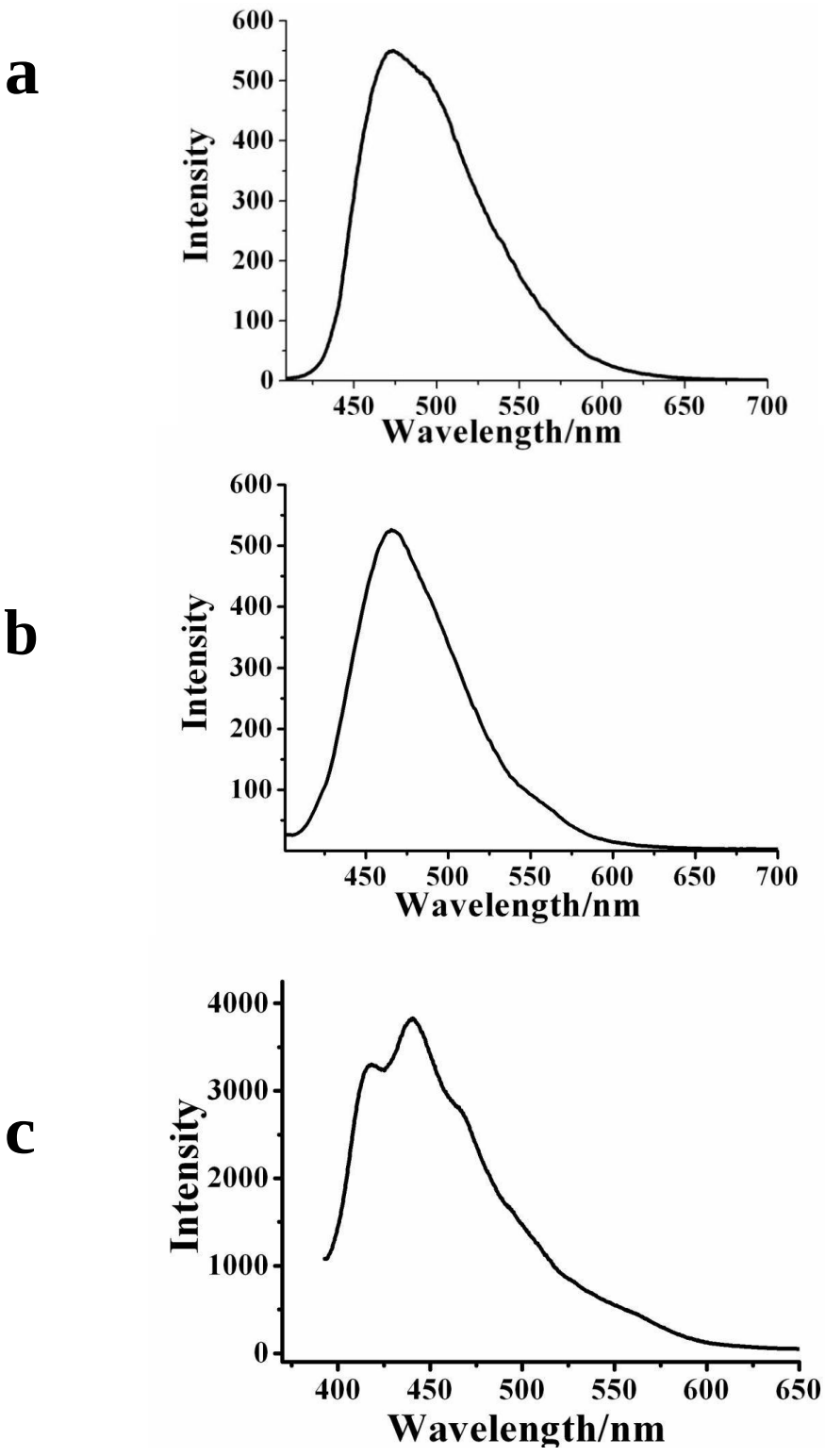

Fig. S2 (a) the fluorescence emission spectrum of TPT in ethylene glycol monoethyl ether solution (λ_{exc} = 370 nm); (b) the solid-state fluorescence emission spectrum of TPT (λ_{exc} = 370 nm); (c) the solid-state fluorescence emission spectrum of compound **1** (λ_{exc} = 370 nm).

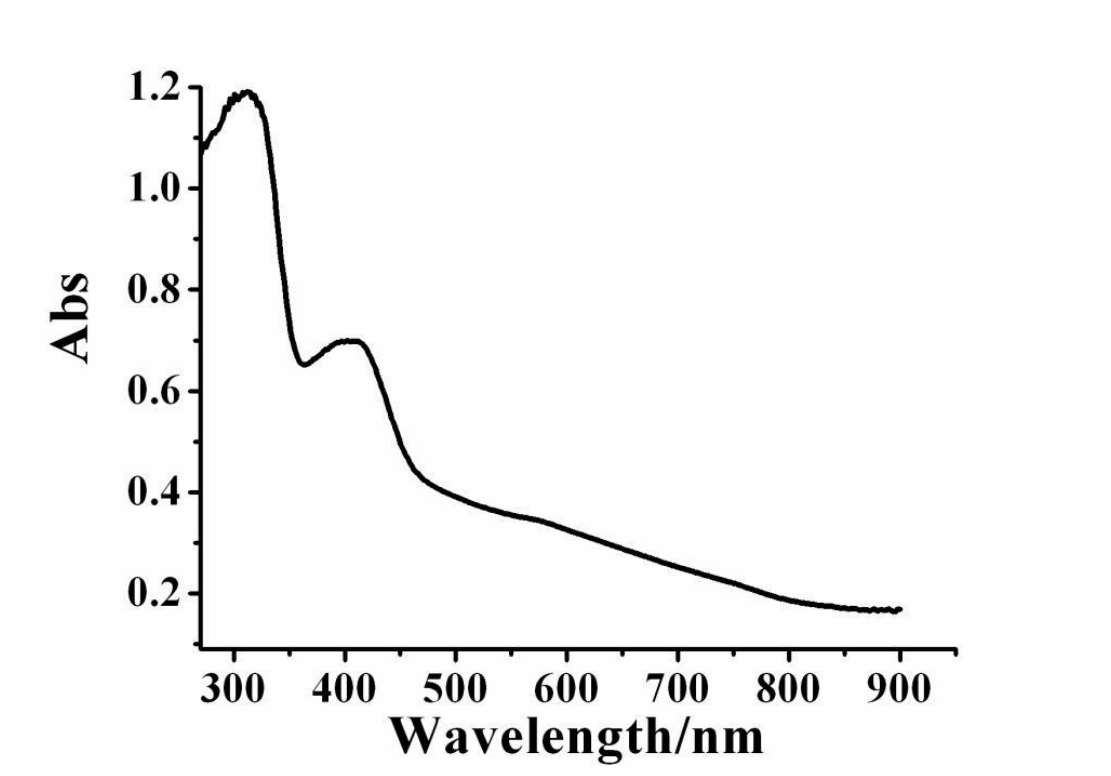

Fig. S3 UV-vis spectrum of TPT.

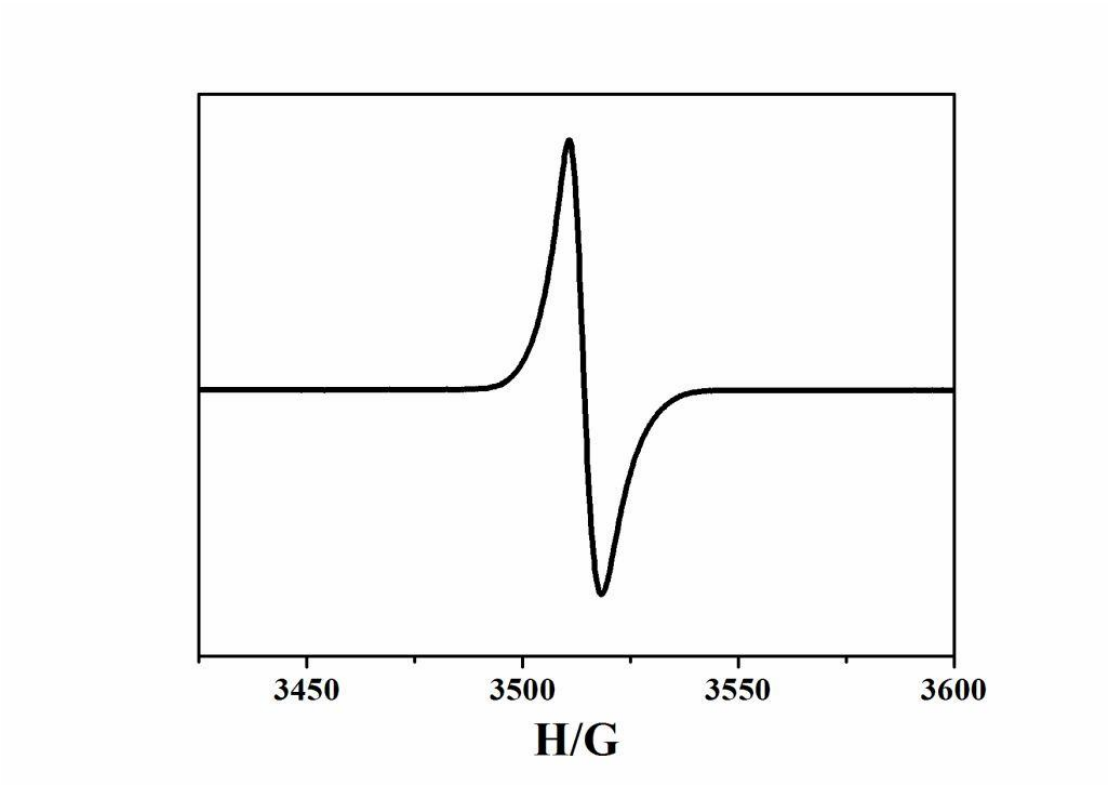

Fig. S4 ESR spectrum of the blue-green crystals of **1.**

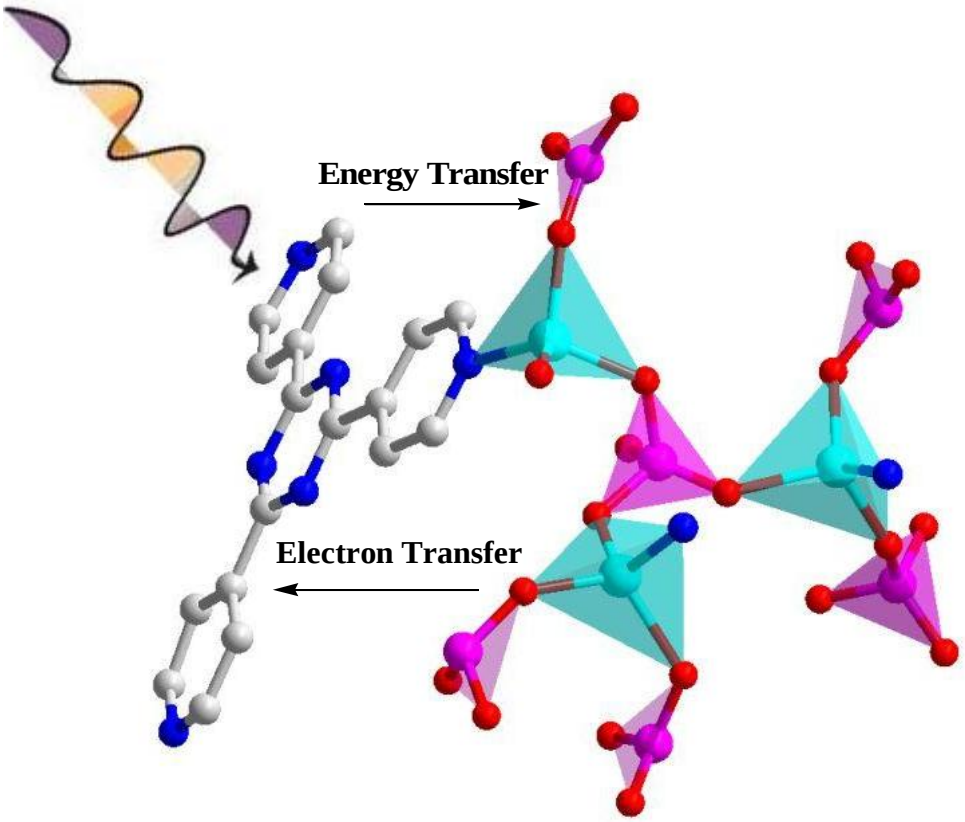

Fig. S5 The proposed photo-responsive mechanism**.**

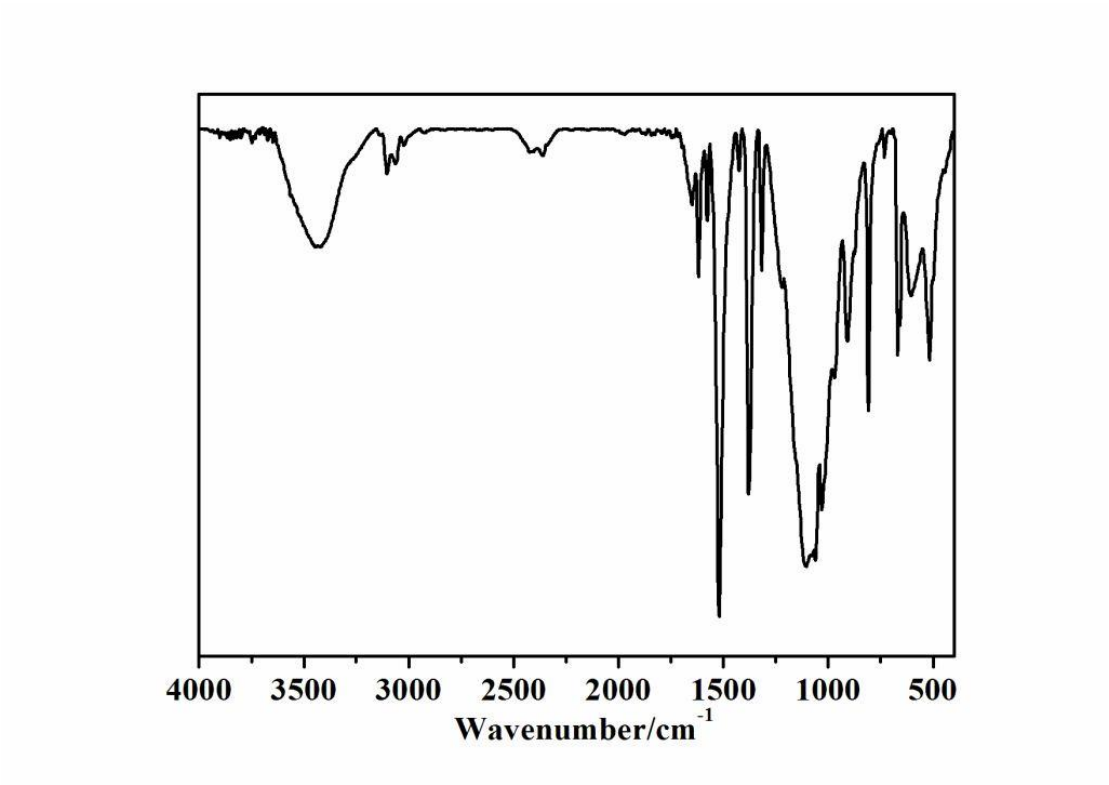

Fig. S6. IR spectrum of **1**