Photo- and thermoinduced coloration of a crystalline MOF accompanying electron transfer and long lived charge separation in a stable host-guest system

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Experimental Section

General: All the reagents were purchased from commercial channels and used without further purification; viologen diacetic acid dichloride was synthesized as reported.^{S1} A TA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the TGA curve in N_2 at a rate of 10 °C 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.

Synthesis of $[Zn_3(m-BDC)_4]$ -MV 1: $Zn(NO_3)_2 \cdot 6H_2O$ (59.4mg, 0.2mmol) was added to a mixture of viologen diacetic acid dichloride (4,4'-bipyridinium-1,1'-diacetic acid dichloride) (69 mg, 0.2mmol), and m-H₂BDC (33.2mg, 0.2mmol) in DMF (5ml), C₂H₅OH (5ml) and H₂O (2ml). The mixture was sealed in a 25ml Teflon-lined steel bomb and heated at 85°C for 48h. Yellow block-like crystals were collected by filtration, washed by water, and dried at room temperature (0.033mmol, 33.9mg, 66% yield based on m-H₂BDC).

References: S1 A. D. Phillips, Z. Fei, W. H. Ang, R. Scopelliti and P. J. Dyson, *Cryst. Growth. Des.*, 2009, **9**, 1966. \ddagger Crystal data for 1: C₄₄H₃₀N₂O₁₆Zn₃, $fw = 1038.81 \text{ g} \cdot \text{mol}^{-1}$, Triclinic, space group *P-1*, a = 9.5200(19) Å, b = 10.160(2) Å, c = 11.490(2) Åa = 102.50(3) $\beta =$ 110.19(3)°, $\gamma = 94.42(3)$ °, V = 1004.3(3) Å³, Z = 1, $\rho_{calcd} = 1.718$ g cm⁻³, final RI =0.0310 and wR2 = 0.0787 for 3048 independent reflections $[I \ge 2\sigma(I)]$. The data were measured on a Rigaku R-AXIS SPIDER CCD diffractometer with MoK α radiation (λ = 0.71073 Å) at 298K. The structure was solved by direct methods and refined by full-matrix leastsquares methods with SHELXL. CCDC 883810 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.ukf/data request/cif.

The calculation of kinetic rate constants:

UV-Vis spectra are recorded after irradiation and the calculations of kinetics of light/thermal reversion base on the intensity values of the wavelength at 618 nm. The kinetic rate constants are determined by the literature calculation method.^{S2} The following equation is used for data treatment:

$$In\frac{A_{\infty}-A_{0}}{A_{\infty}-A_{t}}=kt$$

where A_0 , A_t , A_∞ are the observed absorption data (618 nm) at the beginning, versus time, and at the end of the reaction, respectively.

S2 T. Kawato, H. Koyama, H. Kanatomi and M. Isshiki, *J. Photochem.*, 1985, **28**, 103.



Figure S1 The structural unit of compound **1.** Symmetry code: a = 1-x, -y, -z; b = 2-x, -y, -z; c = -1+x, y, z; d = x, 1+y, z; e = -x, 1-y, 1-z.



Figure S2 Views of the layer with encapsulated MV^{2+} cations.



Figure S3 Crystal packing along the *b*-axis showing that the MV^{2+} cations penetrate the layer.



Figure S4 Thermal gravimetric curve of compound 1.



Figure S5. IR spectrum of 1