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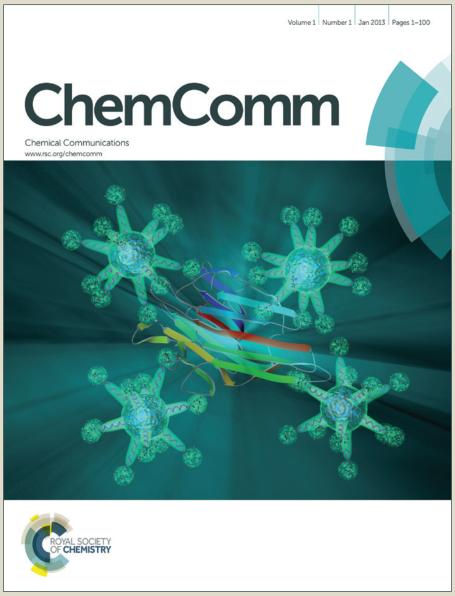

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Photo- and thermo-activated electron transfer system based on a luminescent europium organic framework with spectral response from UV to visible range

Hengjun Chen,[a] Guiming Zheng,[a] Min Li,[a] Yifang Wang,[a] Yang Song,[a] Conghui Han,[a] Jingcao Dai[b] and Zhiyong Fu*[a]

A dual stimuli-responsive system was constructed by introducing methyl viologen into a luminescent europium-organic framework with a compact packing mode. Besides its absorption and emission characters are sensitive to both light and heat involving electron/energy transfer processes, the photoactive MOF has a spectral response from UV to visible region.

Lanthanide-based metal-organic frameworks (Ln-MOFs) have manifested promising prospects for the applications in ion sensing,[1] small molecules sensing,[2] humidity sensing,[3] explosive detection[4] and temperature measurement[5] benefiting from the exceptional luminescent nature of lanthanide ions and their optical properties being sensitive to the chemical environment of the metal centers.[6] Recently, responsive molecular switches that involve electron transfer (ET) and color change processes under outer stimuli (such as light, heat and oxygen), showed an increased interest for discovering the intrinsic reaction mechanism and potential utilities in optoelectronic devices,[7] X-ray detectors,[8] thermosensors,[9] oxygen detectors[10]. Interesting photoactive MOFs are built *via* organizing photo- or redox-active components into the network structures by taking advantage of the building-block strategy.[11] Recognizing the potential of a facile complex approach, we have embarked on a program aimed at introducing viologen unit, a species complex with good electron accepting abilities, into the structure of lanthanide-based metal-organic frameworks. This approach may help to create a system that Ln-based photoluminescence (PL) is coupled with the stimuli-triggered ET processes. Herein, we report a unique multifunctional MOF, $Eu_2(m\text{-}BDC)_4(MV)$ (**1**) (m-BDC = 1,3-benzenedicarboxylate, MV = methyl viologen), featuring photo- and thermo dual stimuli-responsive characters. Accompanying the electron transfer and energy transfer processes, its photochromic and thermochromic reactions are coupled with the luminescent emissions. More interestingly, this photoactive complex displays a wide range of spectral response from UV to visible range. Developing photosensitive devices that can extend photo-response to visible range is urgent for the utilization of solar energy since the UV region accounts for only 3-5% of the solar spectrum.[12] Compound **1** is the first crystalline photoinduced electron transfer (PET) material producing a stable charge-separated state with UV and visible light response.

The title material was prepared *via* an *in situ* solvothermal reaction (See ESI†). Single crystal analysis reveals that the photo-responsive complex is constructed by the $[Eu_2(m\text{-}BDC)_4]^{2-}$ anionic host framework and MV^{2+} guest cations. The Eu^{3+} center is eight-coordinated with two chelating carboxylate groups and four oxygen atoms from four bidentate carboxylate groups respectively (Fig. S1, ESI†). The adjacent Eu^{3+} ions are connected by bidentate carboxylate groups to form a zigzag chain (Fig. 1a). Further assembly of the chains and the bridging benzenedicarboxylate ligands gives rise to an extended 3D network with a square cavity (7.2 × 7.2 Å) that shelters the MV^{2+} dications (Fig. 1b), presenting a compact packing mode (Fig. 1c). The interplanar distance between the paralleled pyridinium ring and the benzene ring of the host framework is

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[a] *Key Lab for Fuel Cell Technology of Guangdong Province, Guangdong, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China. E-mail: zyfu@scut.edu.cn; Fax: (+86) 20 8711-2965*
[b] *Institute of Materials Physical Chemistry, Huaqiao University, Quan- zhou, Fujian, 362021, China. E-mail: jcdai@hqu.edu.cn.*

† Electronic Supplementary Information (ESI) available: details about synthesis and general characterizations, crystal data, additional graphics, PXRD, band gap calculation, kinetic rate constants and emission lifetimes, luminescent quantum yields, additional UV-vis and PL spectra, ESR, TGA and IR data. CCDC 1016434. See DOI: 10.1039/c000000x/

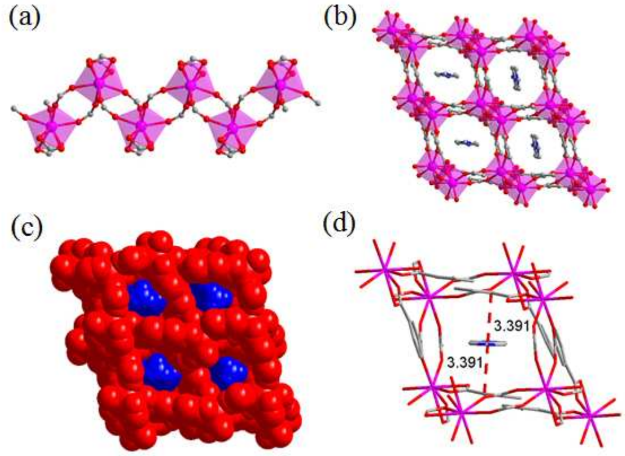


Fig. 1 Crystal structure of Eu$_2$(m-BDC)$_4$(MV): (a) 1D chain with bridging carboxylate groups; (b) extended 3D framework showing square cavity; (c) space-filling diagram (Red: Eu-BDC framework; blue: MV^{2+} ions); (d) interplanar distance between benzenecarboxylate and methyl viologen.

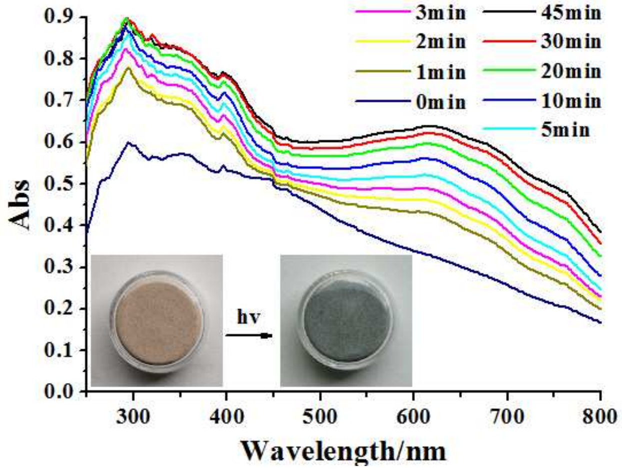


Fig. 2 Solid state diffuse reflectance spectral changes of **1** upon light irradiation. The insets show photographs of the sample before and after irradiation.

3.391 Å (Fig. 1d). The void volume of **1** is merely 4.0% of the cell volume (calculated by PLATON). Such compact structural arrangement not only suggests its potential light harvesting capability due to the high density of chromophores but also provides opportunities for the electron transfer reactions from the electron-rich anionic metal-benzenecarboxylate framework to the electron-deficient viologen moieties.

Phase purity of the as-synthesized bulky sample was verified by the powder X-ray diffraction (PXRD) data (Fig. S2, ESI†). Solid-state diffuse reflectance spectrum of **1** shows broad absorption from ultraviolet to visible region (Fig. 2). Upon light irradiation (xenon lamp or sunlight), a new strong band centered at 616 nm gradually emerged, which can be attributed to the characteristic band of MV$^{\bullet+}$ radicals formed *via* PET reaction.[13] The color of the brown solid **1** turned green at the same time. Interestingly, the photochromic reaction was also observed under visible light illumination ($\lambda > 400$ nm) (Fig. S9, ESI†), whereas other reported viologen-based PET systems can only be activated by UV or X-ray radiation.[8,10,14,21] The calculation based on the diffuse reflectance spectrum indicates that compound **1** exhibits a relatively low optical band gap energy (E_g) (2.25 eV) (Fig. S3, ESI†). This result supports that its has significant solar energy harvesting ability and intrinsic electrical conductivity.[15] The detected ESR signal of the photocolored product (g = 2.0020, Fig. S4, ESI†), which corresponds to the reported viologen free radicals,[16] further confirms the electron transfer process. Besides, the facile ET is also anticipated due to the close distance (3.391Å) from electron-donating framework to electron-accepting methyl viologens that is much smaller than the reported donor-acceptor distance threshold (3.82Å) in a viologen-based PET system.[17]

Compound **1** displays characteristic emission bands of Eu(III) ion located at 578 nm, 592 nm, 616 nm, 652 nm and 702 nm, which can be assigned to $^5D_0 \rightarrow {}^7F_J$ $_{(J\ =\ 0\text{-}4)}$ transitions. Upon exposure to continuous photoirradiation, the emission intensity of compound **1** decreases dramatically and is basically quenched after 45 min (I_{0min}/I_{45min} = 22.4, at 616 nm) (Fig. 3). This phenomenon originates from good spectral overlap between the emission bands of the luminescent complex and the arisen broad absorption bands around 616 nm of the colored photochromic unit. Such overlap results in intermolecular resonance energy transfer (RET) from the excited luminescent center to methyl viologen radicals (Scheme. 1).[18] Kinetic calculations based on diffuse reflectance and PL spectra also reveal that the enhancement of UV absorbance is proportional to the reduction of emission intensity (Fig. S5, ESI†). In addition, luminescent quantum yields (Φ_{Ln}) and lifetimes (τ) were measured to acquire radiative (k_r) and nonradiative (k_{nr}) rate constants before and after irradiation. The related data are summarized in table S2 (ESI†). The k_r, which is related to the ligand field of Eu^{3+},[19] decreases from 64.54 s^{-1} to 37.81 s^{-1} after the irradiation. This can be ascribed to the loss of electrons from the ligands after the PET reaction. Meanwhile the k_{nr} of the irradiated sample is 1.36 times larger than that of the as-synthesized sample. It further confirms the energy transfer from

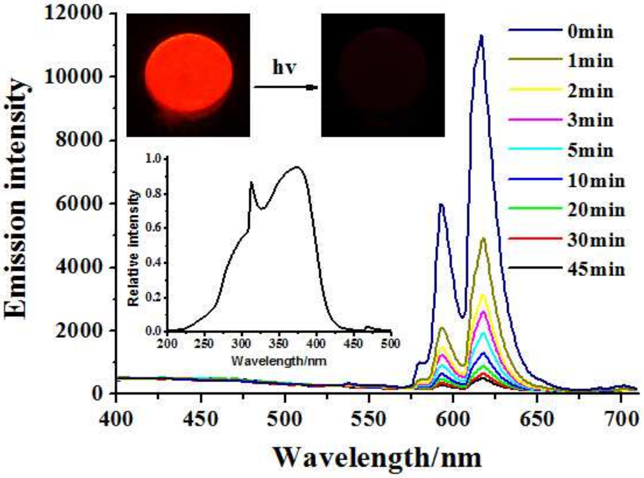
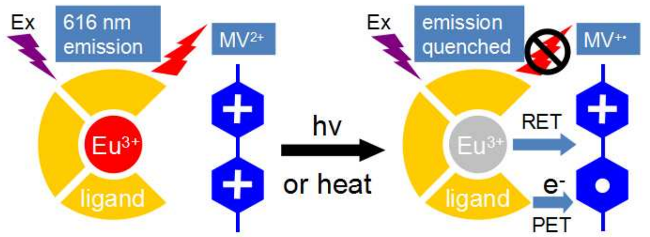


Fig. 3 Photoluminescence spectral variations (Ex: 375 nm) of compound **1** upon light irradiation. The insets show excitation spectrum monitored at 616 nm and photographs of the sample before and after irradiation.



Scheme 1 Schematic illustration of the stimuli-triggered PL quenching.

the luminophore to the $MV^{•+}$ radicals through nonradiactive dipole-dipole coupling.

As the generation of long-lived charge separation is considered as the key for converting solar energy to chemical energy,[20] the stability of the photogenerated radical is investigated. Although it is documented that colored viologen-based materials tend to fade in the air due to the charge recombination reactions induced by oxygen,[21] we find that the photocolored sample of **1** is stable in the air for at least two weeks (Fig. S7, ESI†). Its long-lived charge-separated state could be attributed to the dense packing mode that prevents contacts of the generated radicals with outer oxygen.

ET reaction of **1** can also be triggered by heat (>100°C) and it develops with elongated heating time or elevated temperature, leading to the variation of diffuse reflectance and PL spectra (Fig. 4). Similar to the photoactivation process, the thermal reaction also results in the generation of the $MV^{•+}$ radicals ($g = 2.0021$, Fig. S4, ESI†). Thermoinduced electron transfer is rare since charge-recombination is facilitated at higher temperature.[22] The temperature-dependent chromogenic and luminescent properties of **1** indicate its potential application in thermal sensing devices. TG and PXRD data reveal that **1** maintains crystalline phase up to 350ºC (Fig. S8, ESI†), displaying a stable system as thermosensitive or solar energy converting material.

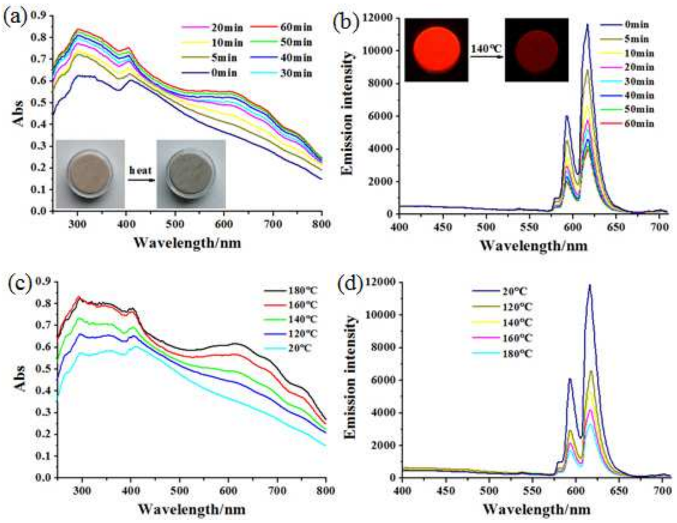


Fig. 4 (a) Solid state diffuse reflectance, (b) PL spectral changes of **1** upon heating at 140ºC. The insets are photographs of the sample before and after thermal treatment. (c) Solid state diffuse reflectance, (d) PL spectral changes of **1** after heated at different temperature for 20 min.

In conclusion, a multifunctional stimuli-responsive Eu-MOF has been synthesized and characterized. Its photo-/thermo-induced electron transfer and energy transfer process are investigated. The luminescent-photochromic dyad with dense packing mode presents the following interesting features: (a) the compact arrangement of molecules results in closer D-A distances that facilitate ET reactions; (b) a relatively low optical band gap of this Eu-MOF endows it a wide range of spectral response from UV to visible range; (c) europium-based luminescence is coupled with the ET processes; (d) oxygen that quenches free radicals are expelled, leading to a long-lived charge-separated state in the functional MOF. This work provides a new strategy for the fabrication of an efficient stimuli-responsive and light-harvesting assembly.

The authors thank the program for NCET (130209), the Fundamental Research Funds for the Central Universities (2014GD0004) and the SRP program for financial support.

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