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Journal Name

COMMUNICATION

## Viologen-functionalized chiral Eu-MOF as a platform for multifunctional switchable material

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**A novel viologen-functionalized chiral europium-based metal-organic framework (Eu-MOF) that possesses multi-switchable features including photochromism, photo-modulated luminescence, photoswitchable NLO and piezoelectric properties was obtained for the first time.**

Switchable materials have been a research hotspot in the past decades due to their ability to manifest two stable physical properties in response to external stimuli (light, temperature, and electric field) and potential application in the fields of photonic devices, optoelectronic technology and optical information storage.<sup>1-5</sup> Metal-organic frameworks (MOFs) have been recognized as a promising class of switchable materials for their characteristic features.<sup>6-16</sup> First, under external stimuli, a MOF with adaptable conformation can turn to another stable state by phase transition,<sup>6,7</sup> redox reaction,<sup>8</sup> release of solvated molecules,<sup>9-11</sup> or change in coordination environment of the metal centers,<sup>12</sup> resulting in reversible transformation of its physical (optical, electrical, and magnetic) properties. Second, transition between the two states can be monitored by crystal structure analysis, which provides valuable information to the mechanism study of switchable materials.<sup>13-15</sup> In practice, a variety of switchable materials can be realized by constructing multifunctional MOFs that possess tunable inorganic nodes and modifiable organic linkers.<sup>16</sup> Among them, lanthanide metal-organic frameworks (Ln-MOFs)<sup>17-19</sup> are an ideal candidate for switchable materials owing to the ligand-to-metal energy transfer process is sensitive to pH, temperature and solvent, which makes Ln-MOFs widely used as pH sensor,<sup>20</sup> luminescent thermometer,<sup>21,22</sup> sensor of small molecules (volatile organic compounds, explosives, solvent vapors) and ions,<sup>23-26</sup> as well as in biosensing and biomedical

imaging.<sup>27</sup>

Since its first discovery, viologen has been widely applied in photochemical devices and organic electrical conductors due to its inherent photoinduced electron transfer property.<sup>28-32</sup> Guo's group creatively introduced viologen into crystalline inorganic-organic hybrid materials and clearly demonstrated the electron-transfer mechanism of the photochromic process.<sup>34</sup> Photoreversible viologen-containing materials have also been proved to be remarkable candidates for photo-switchable materials, since photoinduced electron transfer could bring up two states with divergent electron disposition, which may display distinct physical properties.<sup>35-37</sup>

As is well known, non-centrosymmetric MOFs are of special interest by virtue of their distinctive physical properties, such as second-harmonic generation and piezoelectricity.<sup>38-40</sup> Recently, a novel acentric zinc-MOF composed of infinite zigzag chains and endowed with photo-switchable nonlinear optical (NLO) properties concomitant with photochromic process has been reported.<sup>37</sup> However, its second-harmonic generation (SHG) efficiency is only 0.8 times that of  $\text{KH}_2\text{PO}_4$  (KDP). So far, although a few crystalline MOF-based switchable materials have been reported, integrating multi-switchable physical properties (luminescence, second harmonic generation, piezoelectricity and magnetism) into one molecular material is still a challenge that remains largely unexplored.<sup>41</sup> Taking the above factors into consideration, we aim to achieve multifunctional switching by incorporating chirality, viologen functionalized ligands, and luminescent rare earth ions into a novel MOF with targeted synthesis.

In this work, we assemble  $\text{Eu}^{3+}$  ions with 1-(2,5-dicarboxybenzyl)-4,4'-bipyridinium nitrate ( $\text{H}_2\text{L}^+\text{NO}_3^-$ ) to obtain an interesting chiral Eu-MOF  $\{[\text{Eu}(\mu_2\text{-OH})(\text{L})(\text{H}_2\text{O})]\cdot\text{NO}_3\cdot\text{H}_2\text{O}\}_n$  which crystallizes in space group  $P2_1$ . Reversible photochromism from light yellow to pale blue is implemented, which reversibly modulates the luminescence intensity of the framework, resulting in photoinduced luminescence switching. More interestingly, Eu-MOF is SHG-active, and its efficiency is reversibly modified by a coloring/bleaching process. Moreover

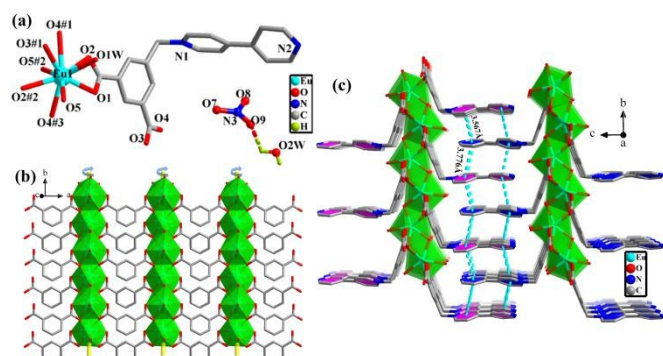
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† Electronic Supplementary Information (ESI) available: Experimental details, structure refinement, powder X-ray diffraction, thermal analysis, additional Fig.s. CCDC 1406260. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x.

Eu-MOF is piezoelectricity-silent but it displays a piezoelectric response after irradiation.

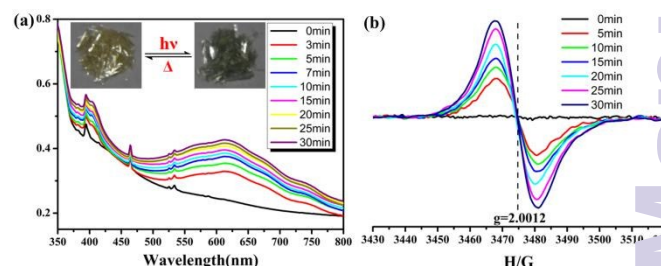
The solvothermal reaction of  $\text{H}_2\text{L}^+\text{NO}_3^-$  and  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in a mixture of water and acetonitrile at 120 °C yielded light yellow crystals. Single-crystal X-ray diffraction revealed that Eu-MOF crystallized in chiral space group  $P2_1$ . The asymmetric unit contains a crystallographically independent  $\text{Eu}^{3+}$  ion, an anionic  $\text{L}^-$  ligand, a  $\mu_2\text{-OH}^-$ , an aqua ligand, a solvated water molecule, and a uncoordinated nitrate ion (Fig. 1a). The Eu1 center is coordinated by nine oxygen atoms: six (O1, O2, O3#1, O4#1, O2#2, O4#3) from four different ligands, two coordinated  $\mu_2\text{-OH}$  groups (O5, O5#2) and one aqua ligand, completing a twisted capped square antiprismatic coordination sphere (Fig. S1, ESI<sup>†</sup>). The Eu–O bond lengths range from 2.328 (9) to 2.669 (7) Å, comparable to those reported for other europium–oxygen complexes. Each ligand connects four  $\text{Eu}^{3+}$  ions in  $\mu_4\text{-}\eta^1, \eta^2, \eta^1, \eta^2$  mode (Fig. S2, ESI<sup>†</sup>). Adjacent  $\text{Eu}^{3+}$  ions are bridged with carboxylate groups and  $\mu_2\text{-OH}^-$  ligands to form rod-like, infinite chains along the  $b$  axis with Eu...Eu distance of 3.751 (2) Å (Fig. S3, ESI<sup>†</sup>). Utilization of these rod-like secondary building units (SBUs) has been shown to be an efficient strategy for the construction of robust porous lanthanide–organic frameworks.<sup>42,43</sup> Interestingly, each rod-like SBU features three co-axial helical chains, with one being left-handed, and the other two right-handed (Fig. S4, ESI<sup>†</sup>). These chiral helix chains are further bridged by V-shaped ligands, forming a metal-organic layer (Fig. 1b). Notably, the face-to-face  $\pi\cdots\pi$  interactions between pyridyl rings, with the distances of 3.567 Å and 3.776 Å respectively, contribute to the interdigital architecture (Fig. 1c).<sup>44</sup> The aqua ligands, interlayer free nitrate ions, water molecules, and carbon atoms of pyridyl rings, are associated by hydrogen bonds, forming H-bond nets to stabilize the 3D supramolecular architecture (Fig. S5, ESI<sup>†</sup>).



**Fig. 1** (a) The asymmetric unit of Eu-MOF. Symmetry codes: #1:  $-x, y - 1/2, -z + 2$ ; #2:  $-x + 1, y + 1/2, -z + 2$ ; #3:  $-x, y + 1/2, -z + 2$ . (Dotted line represent hydrogen bond  $\text{O2W}\cdots\text{H2WA}\cdots\text{O9} = 2.921$  Å). (b) The 2D layer structure. (c) The interdigital structure constructed from face-to-face  $\pi\cdots\pi$  interaction. (Hydrogen atoms are omitted for clarity).

Eu-MOF shows interesting photoresponse, as shown in Fig. 2. The sample color changes from light yellow to pale blue in response to exposure to sunlight or 300 W xenon lamp in air. The colored photoproduct can undergo reverse transformation in the dark for two days or under heating at 120 °C for 30 minutes. In the solid-state UV–Vis diffuse reflectance spectrum,

a broad absorption band appears around 613 nm, which is the characteristic absorption of the viologen radical. Its intensity increase with continuous irradiation by the xenon lamp suggests that the photochromism of Eu-MOF presumably results from generation of the viologen radical (Fig. 2a).<sup>45,46</sup> Room-temperature ESR spectral measurement of Eu-MOF gave no ESR signal before irradiation, but a symmetric single-line radical signal ( $g = 2.0012$ ) appeared upon irradiation (Fig. 2b). Therefore, the photochromic process arises from photo-induced free radical generation of the viologen units.<sup>47</sup>

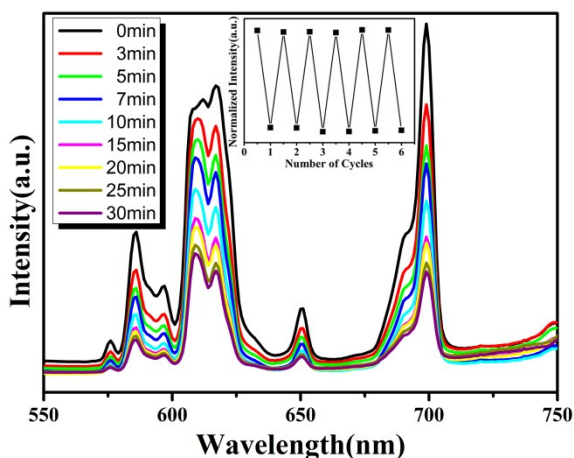


**Fig. 2** (a) Time-dependent UV-Visible diffuse reflectance spectrum; The inset shows photographic images of the photochromic effects. (b) The ESR response with different irradiation time.

As shown in Fig. S6 (ESI<sup>†</sup>), Eu-MOF displays good stability against the thermal bleaching temperature, and the powder X-ray diffraction (PXRD) spectrum remains unchanged after coloring/bleaching cycles (Fig. S7, ESI<sup>†</sup>), which further demonstrates that photochromism is unrelated to photoinduced isomerization or photolysis. Therefore photochromic property likely originates from electron-transfer process: the carboxylate oxygen atoms are efficient electron donors and the face-to-face aromatic  $\pi\cdots\pi$  interaction can also provide an electron-transfer pathway.<sup>48</sup> In Eu-MOF, the distance between carboxylate oxygen atoms (O3) and viologen nitrogen atoms (N1) is 3.744 (11) Å, which satisfies the electron transfer criterion between the carboxylate group donor and viologen acceptor units.<sup>49</sup> The highly ordered  $\pi\cdots\pi$  stacking interactions (3.776 Å and 3.567 Å) between pyridyl rings of the adjacent viologen groups also offer a reasonable electron-transfer pathway for the photochromic process (Fig. S8, ESI<sup>†</sup>).

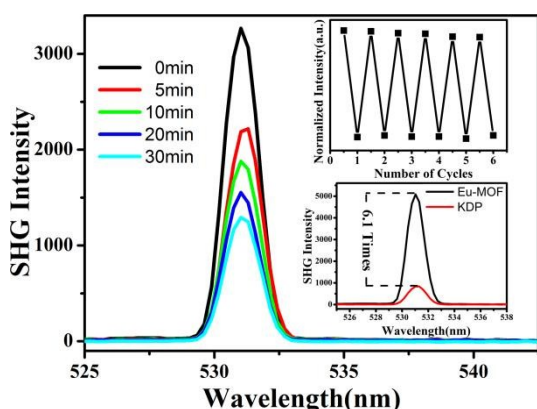
In the excitation spectrum of Eu-MOF, characteristic sharp peaks centered at 361, 381, 393, 413, 463 and 532 nm can be identified as  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$ ,  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$ ,  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ ,  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$ ,  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_2$  and  ${}^7\text{F}_1 \rightarrow {}^5\text{D}_1$  electronic transitions, respectively, of the  $\text{Eu}^{3+}$  center (Fig. S9, ESI<sup>†</sup>). The complex shows characteristic emission bands of the  $\text{Eu}^{3+}$  ion at 586, 617, 651 and 699 nm, which can be assigned to the f–f  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $j = 1-4$ ) transitions. Interestingly, with the reversible color change, the fluorescent on/off switch process occurs naturally. The fluorescence intensity decreases with the duration of irradiation and increases when the colored samples return to light-yellow. The reversibility of such fluorescent on/off behavior has been examined several times without obvious loss in emission intensity (Fig. 3). In view of the good overlap between the characteristic emission peaks of  $\text{Eu}^{3+}$  center and the broad absorption around 613 nm of the viologen radical,

intramolecular energy transfer from the excited luminescent center to the colored state of the ligands accounts for fluorescent quenching (Fig. S10, ESI†).



**Fig. 3.** The fluorescent emission spectrum of Eu-MOF under different irradiation time. The inset shows the modulation of the fluorescence intensity at 618 nm due to alternating UV irradiation and heating treatment.

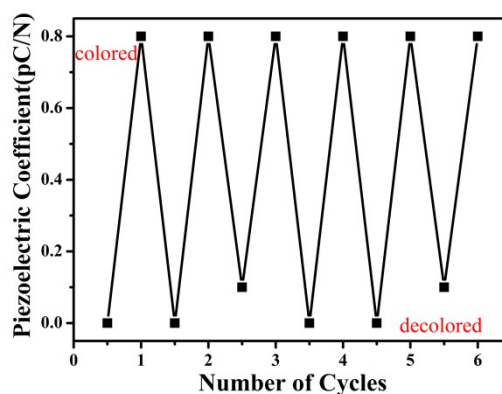
As Eu-MOF crystallizes in chiral space group  $P2_1$ , it is worthwhile to investigate its SHG property. Powder SHG measurement using a pulsed laser at a wavelength of 1064 nm resulted in emission of a green light, showing that the material is SHG-active. Powder KDP samples ground and sieved into different grain sizes were used as references. As shown in Fig. 4, the SHG efficiency of Eu-MOF is approximately 6.1 times that of KDP in the same particle size, which is relatively high in MOF materials.<sup>38</sup> The most intriguing behavior of Eu-MOF is that its SHG efficiency decreases as the irradiation time increases, and reaches 39% of the initial value. Meanwhile, the SHG intensity of the colored sample is restored to the original level along with the blue sample turning back to yellow. The photoswitching of NLO property can be maintained for at least six coloring/bleaching cycles. It is difficult to ensure whether the material is phase-matchable or not in the maximum particle size (300  $\mu\text{m}$ ) that can be obtained (Fig. S11, ESI†).



**Fig. 4** SHG intensity of Eu-MOF under different irradiation time. Inset: the normalized SHG intensity of the NLO switch process (up). The SHG intensity of the Eu-MOF and KDP as a reference in the same particle size (down).

Due to the inherent polarity of the chiral structure, SHG activity mainly originates from asymmetric disposition of electron densities between the donor and the acceptor.<sup>48</sup> The photoinduced electron transfer between carboxylate donor groups and viologen acceptor units attenuates respectively electron densities and then significantly lowers the polarity of the Eu-MOF complex, thereby resulting in a decrease in its SHG intensity.<sup>37</sup>

The piezoelectric coefficients<sup>51,52</sup> of twenty larger single crystals of Eu-MOF were recorded on a ZJ-6A Quasi-Static test system at room temperature. The piezoelectric signal of these yellow polar Eu-MOF crystals could not be observed before irradiation. Interestingly, after coloring by irradiation, the tested crystals all gave an obvious piezoelectric response with coefficient values in the range of 0.8–1.0 pC/N. Similar to the photomodulated fluorescence and SHG effects, the process is reversible, and the piezoelectric signal disappears when the crystals color returns to primitively yellow. As a result, reversible photo-regulated piezoelectric switching can be realized to accompany the reversible photochromic process, as shown in Fig. 5. We found that Eu-MOF exhibits excellent piezoelectric reversibility that the measured coefficient remains unchanged even after six coloring/bleaching cycles.



**Fig. 5** Reversible change of piezoelectric coefficient for the cyclic coloring/bleaching process.

According to previous reports<sup>36-38</sup> and the above discussion, photoinduced electron transfer in viologen-based complexes occurs among different groups and therefore leads to spatial charge separation during the photochromism process. Under the impact of external force, the separated charges possibly migrate and then accumulate on the surface of the crystal, resulting in piezoelectric response manifested by the colored samples. Therefore, photoinduced electron transfer may be responsible for the switchable piezoelectricity.<sup>51</sup>

In summary, a novel crystalline luminescent Eu-MOF combining both chirality and photoactive viologen groups has been assembled. Introduction of the viologen unit endows Eu-MOF with excellent photochromism and photo-modulated fluorescence switch properties. Furthermore, Eu-MOF displays interesting second-order nonlinear optical and piezoelectric switch properties resulting from the combination of inherent chirality and photo-induced charge separation upon irradiation.



Our work successfully integrates photochromism, luminescence, NLO, and piezoelectric properties into a single MOF, and points the way to an effective strategy for constructing multifunctional MOF-based switchable materials.

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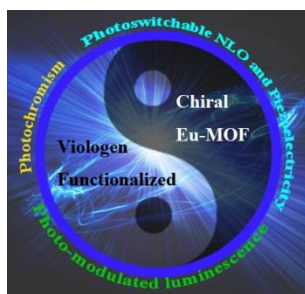
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Hai-Yang Li, Hong Xu, Shuang-Quan Zang\* and Thomas C. W. Mak



A novel crystalline Europium-organic framework (Eu-MOF) incorporates chirality and viologen, thereby combining photochromism, photo-modulated luminescence, photoswitchable NLO and piezoelectric properties.