Electron transfer photochromism of Ln-based (Ln = Dy, Tb) coordinated polymers for reversibly switching off/on single-molecule magnetic behavior

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ABSTRACT Switching on/off single-molecule magnets (SMMs) at room temperature is still a challenge in molecule-based magnets. Herein, two photochromic Ln-based (Ln = Dy, Tb) phosphonate coordinated polymers were synthesized with regulable SMM behavior. The reversible room-temperature photo-coloration was an electron transfer process with a generation of relatively stable radicals, characterized by structural analyses, ultraviolet-visible, luminescence and electron spin resonance spectra and magnetic measurements. Importantly, owing to the antiferromagnetic coupling interactions between Ln³⁺ ions and photogenerated radicals, the room-temperature light irradiation surprisingly switched off the SMM behavior, showing the first example of radical-quenched SMMs in the molecule-based magnets. Moreover, the silent SMM behavior could be recovered after eliminating photogenerated radicals *via* heat treatment, showing a reversible off/on switch of SMMs *via* light and heat. This work constructs a system for switching off/on SMMs through electron transfer photochromism, providing a visual operation way *via* naked-eye-detectable coloration for the switchable SMMs.

Keywords: electron transfer, photochromism, photogenerated radicals, single-molecule magnets, switch off

INTRODUCTION

Single-molecule magnets (SMMs), exhibiting slow magnetic relaxation resulting from the bistable magnetic ground states, can serve as attractive candidates for next generation high-density information storage devices [1–3]. Since the discovery of the well-known nanoscale Mn₁₂ molecule, many efforts have been devoted to exploring excellent SMMs based on transition metals. More recently, in pursuing the preparation and construction of SMMs with large effective energy barriers and blocking temperatures, lanthanide (Ln)-containing complexes soon stand out from the crowd due to their large single-ion magnetic anisotropy produced by the strong intrinsic spin-orbit coupling and the crystal-field effect [4–7]. However, most of the Ln-based SMMs with attractive high-performance are organometallic or air-sensitive complexes, the harsh synthetic conditions and intrinsic instability in air greatly restrict their future application [8–10].

On the other hand, switchable Ln-based SMMs *via* external stimuli, such as light, solvents, protonation, magnetic and electric fields, are of great importance and have attracted more attention in chemistry, physics and materials science [11–18]. Especially, light irradiation becomes an efficiently applied stimulus due to its convenient and rapid response for dynamic remote control and matched energy between different electronic states. A general approach is developed by incorporating photochromic moieties into the SMM system, including dithienylethene [19–21] with open and close forms, 1,2-bis(4-pyridyl)ethene [22–26] and 9-anthrylmethylphosphonic acid [27] with photochemical cycloaddition, spiropyran-merocyanine [28,29] with *cis-trans* isomerization and viologens [30,31] with photogenerated radicals.

In general, the slow magnetic relaxation in the spin crossover or metal-metal electron transfer complexes can be easily on/off switched *via* alternative light [32]. By comparison, SMM behaviors in the photochromic Ln-based SMMs could only be slightly tuned in the effective energy barrier and magnetic relaxation time. Actually, the construction of room-temperature light switchable on/off SMMs is still challenging in electron transfer photochromic materials. Recently, a Dy-based photochromic complex with photogenerated radical-actuated SMMs was realized in our previous work [30], showing the first example of SMMs in electron transfer photochromic materials. This motivates us to further explore the possibility of tunable SMMs *via* electron transfer photochromic complexes [32–38]. Especially, it is a challenging but interesting issue for switching off SMMs in these photochromic system. Furthermore, the operating temperature of light switch in these photochromic materials can be improved to room temperature, which is helpful for practical application.

Considering the above thoughts, two photochromic Ln-based complexes [Ln₃(H-HEDP)₂(H₂-HEDP)₂(H₃-HEDP)₂·H₃-TPP·11H₂O (Ln = Dy (1), Tb (2); TPP = 2,4,6-tris(4-pyridyl)pyridine; HEDP = hydroxyethylidene diphosphonate) with changeable photomagnetic properties were reported. In these structures, electron-rich HEDP components served as electron donors, while electron-deficient H₃-TPP motifs acted as acceptors; electron transfer process could occur after light irradiation *via* H-bonding interactions. As a result, remarkable photochromic behavior was reversibly observed in both compounds, accompanied with the photogeneration of HEDP[•] and H₃-TPP[•] radi-

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cals. The magnetic behavior in these complexes was studied with characteristic single-molecule magnetic behavior. Importantly, originated from the antiferromagnetic couplings between the photogenerated radicals and Ln^{3+} ions, the SMM behavior in both compounds could be switched off after room-temperature light irradiation, showing the first example of radical-quenched SMM in molecule-based magnets. Furthermore, the SMM behavior in both compounds could be recovered to the initial state after eliminating photogenerated radicals *via* annealing treatment or pitting the colored samples in dark, providing a visual way for photo-switchable SMM performance.

EXPERIMENTAL SECTION

Materials and methods

All the reagents and solvents for the syntheses of complexes were purchased from commercial sources and used as received. TPP ligand was purchased from Chemsoom and recrystallized in methanol solvent. Fourier transform infra-red (FT-IR) spectra were recorded in the range of 4000–400 cm^{-1} on a MAGNA-560 (Nicolet) FT-IR spectrometer (Canada). Powder X-ray diffraction (PXRD) patterns were collected with a Rigaku standard MiniFlex600 diffractometer (Japan). Ultraviolet-visible (UV-vis) spectra were measured using a Puxi Tu-1901 spectrophotometer (China). Elemental analyses for C, H and N were determined on a PerkinElmer 240C analyzer (America). The fluorescence measurements were carried out on an F-4700 fluorescence spectrometer. Electron paramagnetic resonance (EPR) spectra were respectively collected at 298 and 100 K using a Bruker E500 EPR spectrometer (Germany). Magnetic measurements were obtained with the usage of a Quantum Design MPMS3 superconducting quantum interference device (SQUID) magnetometer (America).

Synthesis of $[\text{Dy}_3(\text{H-HEDP})_2(\text{H}_2\text{-HEDP})_2(\text{H}_3\text{-HEDP})_2] \cdot \text{H}_3\text{-TPP} \cdot 11\text{H}_2\text{O}$ (**1**)

Dy_2O_3 (0.091 g, 0.244 mmol), HEDP (0.207 g, 0.924 mmol), LiF (0.062 g, 2.08 mmol, acting as a mineralizer), TPP (0.037 g, 0.119 mmol) were dissolved in the mixed solvents of methanol/water (3 mL/2 mL) in a 25-mL Teflon-lined stainless steel vessel and heated at 120°C for 168 h. The crystals were obtained by slowly cooling to 30°C in 12 h. Yield: ca. 30% based on TPP ligands. **1a** was obtained by Xe-lamp irradiation of compound **1** at room temperature for 40 min. Elemental analysis for **1** (%): calcd for $\text{C}_{52}\text{H}_{92}\text{N}_8\text{O}_{53}\text{P}_{12}\text{Dy}_3$ (2536.47): C, 24.62; H, 3.65; N, 4.42. Found: C, 24.55; H, 3.73; N, 4.29. IR of **1** (KBr pellets, cm^{-1}): 3244(m), 3099(s), 2935(m), 2366(w), 2145(w), 1635(m), 1506(w), 1409(w), 1148(s), 1079(s), 925(m), 814(m), 656(w), 563(s), 463(w), 424(w). IR of **1a** (KBr pellets, cm^{-1}): 3247(m), 3099(s), 2938(m), 2363(w), 2145(w), 1635(m), 1505(w), 1406(w), 1150(s), 1081(s), 922 (m), 814(m), 654(w), 563(s), 462(w), 423(w).

Synthesis of $[\text{Tb}_3(\text{H-HEDP})_2(\text{H}_2\text{-HEDP})_2(\text{H}_3\text{-HEDP})_2] \cdot \text{H}_3\text{-TPP} \cdot 11\text{H}_2\text{O}$ (**2**)

Tb_4O_7 (0.089 g, 0.119 mmol), HEDP (0.189 g, 0.843 mmol), LiF (0.054 g, 2.08 mmol), TPP (0.041 g, 0.133 mmol) were dissolved in the mixed solvents of methanol/water (3 mL/2 mL) in a 25-mL Teflon-lined stainless steel vessel and heated at 120°C for 168 h. The crystals were obtained by slowly cooling to 30°C in 12 h. Yield: ca. 33% based on TPP ligands. **2a** was obtained by

Xe-lamp irradiation of compound **2** at room temperature for 40 min. Elemental analysis for **2** (%): calcd for $\text{C}_{52}\text{H}_{92}\text{N}_8\text{O}_{53}\text{P}_{12}\text{Tb}_3$ (2525.73): C, 24.73; H, 3.67; N, 4.43. Found: C, 24.60; H, 3.85; N, 4.33. IR of **2** (KBr pellets, cm^{-1}): 3424(s), 3252(m), 3101(m), 2921(m), 2851(m), 2363(w), 2158(w), 1635(m), 1505(w), 1411(w), 1148(s), 1082(s), 923(w), 814(w), 654(w), 564(m), 464(w), 421(w). IR of **2a** (KBr pellets, cm^{-1}): 3426(s), 3248(m), 3100(m), 2919(m), 2851(m), 2363(w), 2158(w), 1632(m), 1507(w), 1411(w), 1148(s), 1082(s), 922(w), 814(w), 654(w), 563(m), 465(w), 421(w).

RESULTS AND DISCUSSION

Description of crystal structures

The single-crystal XRD analyses revealed that complexes **1** and **2** were isomorphic and belong to the orthorhombic crystal system with the space group $C222_1$ (Table S1). Due to their same structures, complex **1** was discussed for clarity. The asymmetric unit was composed of one and a half Dy^{3+} ions, one protonated TPP ligand, three coordinated diphosphonate units, and several solvent water molecules (Fig. 1a). The distances of Dy–O were in the range of 2.224(6)–2.487(7) Å (Table S2), which was similar to those of previously reported Dy^{3+} complexes based on diphosphonate ligands [30]. The neighboring two Dy^{3+} ions were connected through diphosphonate groups to form a linear shaped chain (Fig. 1b). The closest intra-chain and inter-chain Dy...Dy distances were 4.8114(4) and 11.4279(9) Å, respectively, indicating the dominant intra-chain interactions. Abundant H-bonding interactions were formed between N atoms in the TPP ligand and the coordinated diphosphonate O atoms (Fig. S1 and Table S3), with an average H-bonding distance of 2.050 Å. These hydrogen bonds linked the chains to form a three-dimensional (3D) supramolecular framework (Fig. 1c). Furthermore, the strong H-bonding interactions connected the HEDP electron donor and TPP acceptor, contributing to the fast electron transfer photochromism upon light irradiation. The geometrical configurations for Ln^{3+} ions were analyzed using SHAPE 2.0. As shown in Fig. 2, the Dy1 center was eight-coordinated by all O atoms from four distinct diphosphonate ligands, whereas Dy2 center adopted a hepta-coordination mode with the chelating phosphonate oxygen atoms, displaying a square antiprism and capped trigonal prism geometry, respectively (Tables S4 and S5), which was helpful for constructing molecular magnets with slow magnetic relaxation. The bond lengths and angles of **2** were similar with **1** and shown in Tables S6–S9.

Photochromic properties

The photochromic behavior of pure TPP ligand was firstly explored at solid state due to the large π -conjugated property and electron acceptability. After Xe-lamp light illumination, the color of TPP powders turned to faint yellow (Fig. S2, inset), showing the characteristics of the photochromism. The solid-state UV-vis and photoluminescence spectra were recorded to quest the light-induced color variations, with an appearance of a broad peak in UV-vis spectra and a decrease in emission spectra after irradiation, suggesting the generation of $\text{TPP}^{\bullet}$ radicals (Figs S2 and S3). Therefore, complexes **1** and **2** containing TPP ligands may display photochromic behavior due to photo-induced electron transfer from electron-rich groups to TPP ligand *via* hydrogen-bonding interactions. As expected, both complexes were very sensitive to light, and naked-eye-detectable

Figure 1 (a) Asymmetric unit for compound **1**. For clarity, water and H atoms were omitted; (b) 1D linear shaped chain for compound **1**; (c) 3D supramolecular structure of compound **1**. Atom legend: P, pink; N, blue; O, red; C, gray-40%; Dy, light orange.

Figure 2 Coordination environments of Dy^{3+} ions in compound **1**.

and rapid color changes from yellow to purple were observed upon exposure to Xe-lamp for 1 min at room temperature (Fig. 3, inset). The photosensitive products could be decolorized *via* putting photoactivated samples in dark for three days or heating the samples at 140°C for 5 h, showing a completely reversible photochromism. The reversibility of coloration and decoloration process for both compounds was also performed using the *in-situ* fluorescence spectra, which could be cycled for at least five times (Fig. S4). The unchanged PXRD and IR patterns in both compounds during reversible photochromism indicated that the photochromism was not caused by structural transformation or photolysis (Figs S5–S7). The solid-state time-dependent UV-vis spectra showed that the photoproducts of **1** and **2** generated new absorption bands around 570 nm, which was ascribed to the photogeneration of $\text{H}_3\text{-TPP}^{\bullet}$ free radicals (Fig. 3a, b). The intensities of the peaks gradually increased with the prolonged irradiation time, showing a radical-induced photochromic process. After decoloration, this $\text{H}_3\text{-TPP}^{\bullet}$ radical peak disappeared and the curve returned to the as-prepared state, showing a reversible photochromic process. By contrast,

the HEDP electron donor lost electrons and formed the $\text{HEDP}^{\bullet}$ radicals *via* migrating electrons to $\text{H}_3\text{-TPP}$ units, providing additional spin carriers to magnetically couple with Ln^{3+} ions and tune SMM behavior.

To confirm the generation of radicals, the solid-state electron spin resonance (ESR) spectra of both complexes before and after irradiation were measured. As shown in Fig. 3c, d, the original samples **1** and **2** revealed the signal of the rare-earth metal ions between 500 and 6500 G, and the weak signals may be due to the fast spin-lattice relaxation. After light irradiation, sharp signals centered at $g = 2.014$ and 1.996 occurred for **1a** and **2a**, characteristic of the free radicals (2.0023), and the small deviations should originate from the couplings between Ln^{3+} ions and photogenerated radicals. Therefore, the photochromic behaviors of both complexes should be stemmed from the photogeneration of radicals *via* ligand-to-ligand electron transfer process. To in-depth explore the variations of magnetic couplings between Ln^{3+} ions under the presence of photogenerated radicals, low-temperature EPR spectra of **1** and **2** were collected at a frequency of 9.41 GHz at 100 K before and after light irradiation, in which weak exchanges could be better defined even though the fast spin-lattice relaxation of the Ln^{3+} ions. As shown in Figs S8–S11, the signals assigned to Ln^{3+} ions largely enhanced after irradiation, and the radical...Ln exchange remarkably perturbed the EPR spectra of both compounds upon lowering the temperature, further indicating magnetic couplings between photogenerated $\text{HEDP}^{\bullet}$ radicals and Ln^{3+} ions. The decreased intensity in radical signal also implied the singlet diradicals in these structures [39]. Furthermore, room- and low-temperature EPR spectra also suggested anisotropy of g factor, which made it possible to treat these compounds as Ising systems at low temperatures [40].

The solid-state luminescence spectra for both compounds were also studied at room temperature. As depicted in Fig. 4a, the emission maximum was obtained at 376 nm for **1** ($\lambda_{\text{ex}} =$

Figure 3 Time-dependent UV-vis spectra of **1** (a) and **2** (b). Insets: color changes during UV-vis spectral measurements. Room-temperature ESR spectra of **1** and **1a** (c), **2** and **2a** (d) at solid state.

Figure 4 The variation of emission spectra of **1** (a) and **2** (b) at different irradiation time points.

270 nm), which was attributed to the π^* - π transition in TPP ligand. Moreover, the $4F_{9/2} \rightarrow 6H_J$ ($J = 15/2$) transition of Dy^{3+} ion caused a small emission peak at 467 nm. Similar with **1**, the strongest emission peak of **2** was located at 376 nm, which was also corresponded to the transition of ligand. The emission spectrum of **2** (Fig. 4b) consisted of the main bands at 488.8, 544.8, 585, 619.6 nm, such emission originated from the f-f transition lines within the $4f^8$ electron configuration of Tb^{3+} , assigned to $^5D_4 \rightarrow ^7F_J$ ($J = 6-3$) transitions of the Tb^{3+} ion [41–44]. Interestingly, with the extension of irradiation time, the intensities in both compounds decreased gradually, and finally unchanged after 90-min irradiation. Since the absorption of H_3 -TPP * radicals covered the emission of Dy^{3+} and Tb^{3+} ions, the characteristic emission of Ln^{3+} ions after irradiation showed a

decreasing trend, resulting in the reduction of all fluorescence emission peaks. This indicated that both **1** and **2** possessed photomodulated fluorescence behaviors. The quenched phenomenon could be attributed to the intermolecular energy transfer from the luminescent excited Ln^{3+} centers to the photogenerated radicals.

Magnetic studies

Due to the anisotropy of Dy^{3+} and Tb^{3+} ions, the magnetic measurements were performed to explore the switch of SMM behavior *via* photogenerated radicals. The direct current (DC) magnetic susceptibility under a DC field of 1000 Oe for both compounds (Fig. 5) showed that, the $\chi_M T$ value (χ_M is the molar susceptibility and T is the temperature) at 300 K was 42.62 and

Figure 5 Temperature-dependent of $\chi_M T$ products for **1** and **2** before and after light irradiation under a 1000-Oe DC field.

35.21 cm³ K mol⁻¹ for **1** and **2**, respectively, which was close to the expected value for three uncoupled Dy³⁺ (42.51 cm³ K mol⁻¹ K, $S = 5/2$, $L = 5$, $g = 4/3$) and Tb³⁺ (35.46 cm³ K mol⁻¹ K, $S = 3$, $L = 3$, $g = 3/2$) ions. As the temperature decreased, the $\chi_M T$ values decreased gradually and reached a minimum value of 33.8 and 26.8 cm³ K mol⁻¹ at about 4 K, which was attributed to the decrease of m_J sublevels and commonly seen in other Ln-based complexes. Then the $\chi_M T$ values slightly increased, suggesting weak ferromagnetic couplings between the intrachain Ln³⁺ centers. After being irradiated with a Xe-lamp at room temperature for about 40 min, large radicals *via* photogeneration could induce magnetic couplings with Ln³⁺ centers. As shown in Fig. 5, the $\chi_M T$ values at room temperature decreased to 41.79 and 33.33 cm³ K mol⁻¹ for **1** and **2**. Apparently, the decreases in light-response magnetization were due to the antiferromagnetic couplings between Ln³⁺ ions and photogenerated stable radicals, similar to other electron-transfer photochromic materials [33]. Then $\chi_M T$ - T curves directly decreased at low temperatures, dif-

ferent from the curves of the as-prepared samples. The magnetization values for both compounds in the M - H curves (M is the magnetization and H is the magnetic field) at 2 K exhibited obvious decreases at high fields after light irradiation, indicating the appearance of antiferromagnetic exchange interactions between these spin carriers (Figs S12 and S13).

To comprehensively understand the effect of photogenerated radicals on dynamic magnetic properties, the temperature dependence of alternating current (AC) magnetic susceptibilities were measured on microcrystalline samples for both compounds. For **1**, both the in-phase (χ') and out-of-phase (χ'') components in the frequency-dependent AC susceptibility data exhibited frequency dependence under a zero DC and 3.5-Oe AC field (Fig. S14), showing the slow magnetic relaxation behavior. However, originated from fast quantum tunnelling of magnetization (QTM), no peaks for both χ' and χ'' components were observed even at 2 K. To restrain the rapid relaxation of magnetization, a DC magnetic field of 2000 Oe was applied [45] and the χ' and χ'' components showed more obvious frequency dependence (Fig. 6a), indicating the presence of magnetic relaxation and field-induced single-molecule magnetic behavior. The Debye model based on $\ln(\chi''/\chi') = \ln(\omega\tau_0) + E_a/k_B T$ was also utilized to estimate the energy barrier E_a and preexponential factor τ_0 , where ω is the frequency and k_B is the Boltzmann constant. A linear fitting result yielded $E_a/k_B = 16.9$ K and $\tau_0 = 8.4 \times 10^{-6}$ s (Fig. S15), consistent with a superparamagnetic-like character of the relaxation dynamics and confirming the SMM behavior [46,47]. Interestingly, the irradiated samples of **1a** showed a different dynamic magnetic behavior from that of complex **1**. The frequency dependence in both χ' and χ'' components nearly disappeared after light irradiation even in an applied 2000-Oe DC field (Fig. S16), showing a photogenerated radical-quenched SMM behavior. After decoloration, both the χ' and χ'' components in the AC data returned to the initial state of the as-prepared samples of **1** (Fig. S17), showing the switchable off/on SMMs *via* light and heat treatment. For **2**, both the χ' and χ'' components (Fig. 6b) showed frequency dependence under a

Figure 6 Temperature dependence of the in-phase (χ') and out-of-phase (χ'') AC susceptibilities for **1** (a) and **2** (b) measured at different frequencies in a 3.5-Oe AC and 2000-Oe DC field.

2000-Oe DC field, with $E_a/k_B = 12.1$ K and $\tau_0 = 8.1 \times 10^{-6}$ s (Fig. S18). After light irradiation, the photogenerated HEDP[•] radicals antiferromagnetically coupled with Tb³⁺ ions, inducing the total disappearance of slow magnetic relaxations, even measured the AC data with a 2000-Oe DC field (Fig. S19).

CONCLUSIONS

In summary, two Ln-based chain complexes were synthesized and their structures, photochromic behavior and photomagnetic properties were investigated. The room-temperature reversible photo-coloration phenomenon was induced by photogenerated radicals with an electron transfer process from electron-rich diphosphonate units to electron-deficient H₃-TPP components, characterized by structural analyses, UV-vis, luminescence and ESR spectra and magnetic measurements. Both complexes showed obviously field-induced SMM behavior before light irradiation. Interestingly, accompanied with coloration, the SMM behavior could be switched off/on through light irradiation and heat treatment, for the first time realizing the off SMM behavior by photogenerated radicals in the molecule-based magnets. Based on electron transfer-triggered photochromism, this work constructs a system for switchable SMMs, providing a visual operation way through eye-detectable coloration for the on-off switchable SMMs. More studies on the photogenerated radicals switched SMMs are on the way.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper. CCDC 2097403 and 2097404 for **1** and **2** 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.uk/data_request/cif.

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Ln基($\text{Ln} = \text{Dy}, \text{Tb}$)配合物的电子转移光致变色及其可逆开关单分子磁体行为

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摘要 室温下实现单分子磁体(SMM)的开关行为仍然是分子磁体研究中的一个挑战。本文合成了两例具有SMM行为的光致变色Ln基($\text{Ln} = \text{Dy}, \text{Tb}$)膦酸盐配合物。结构分析、紫外-可见光谱、发光光谱、电子自旋共振光谱和磁性测量等手段共同表明, 目标产物的室温可逆光致变色行为是光生自由基诱导的电子转移过程。重要的是, 由于 Ln^{3+} 与光生自由基间的反铁磁耦合作用, 首次观测到室温光照可猝灭SMM行为。此外, 通过热处理消除光生自由基后, SMM的行为得以恢复, 因而通过光照和加热实现了可逆的SMM关/开变化。本工作在电子转移光致变色体系实现SMM的可控开/关, 为可控的SMM提供了一种可视化的操作方式。