Photochromic Lanthanide(III) Materials with Ion Sensing Based on Pyridinium Tetratetrazolate Zwitterion

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ABSTRACT: Lanthanide(III) ion (Ln(III)) sensing has become a major research area owing to its intriguing prospect in clinic, biology, and environmental studies. However, the existing methods have limitations like requirement of expensive instrumentation, long analytical times, and sample pretreatments, revealing the necessity of other methods. In this work, by using N-methyl-4-pyridinium tetratetrazolate (mptz) zwitterion as an electron acceptor, we obtained several new Ln(III) compounds with electron-transfer (ET) photochromic properties: [Ln(NO3)3(H2O)4]·mptz [Ln = Sm (1), Eu (2), Gd (3), La (4), Ce (5), Pr (6), Nd (7), Tb (8), Dy (9), Ho (10), Er (11), Tm (12), Yb (13), Lu (14)]. Notably, different Ln(III) ions in these compounds can be visually identified by their different photoinduced color changes related to the ET process. This work may not only contribute to the more understanding of the structure–photosensitivity relationships of pyridinium-based compounds, but also provide a new approach for Ln(III) ion sensing.

INTRODUCTION

Interest in the determination and sensing of specific lanthanide(III) ions (Ln(III)) has grown considerably in the last decade because of their significant roles in environmental and biological systems.1–6 Based on spectrophotometry or fluorescence, there are already some commonly used non-destructive methods for the Ln(III) ion sensing.7–10 However, these methods can only be used to analyze a small amount of samples because they have limitations such as time-consuming analysis, high cost, and sample preprocessing. Thus, the instantaneous sensing of an individual Ln(III) simply and economically is still a challenge.

In recent years, several electrode sensors have been developed to select Eu(III).11–14 They make the analysis simpler and are able to detect specific species in situ and in real time. These results inspired us to explore the combination of Ln(III) ions with electron-transfer (ET) photochromic behavior, which may allow us to achieve a unique way to Ln(III) ion sensing. Photochromic materials have attracted considerable attention in recent years due to their appealing applications.15–20 As a typical example, photochromic materials with N,N’-disubstituted bipyridinium (viologen) show the proverbial ligand-related ET photochromic behavior,21–27 and structure varieties after ligand modification.28–32 Previously, we chose the N-methyl-4-pyridinium tetratetrazolate (mptz) zwitterion to achieve two new ET photochromic compounds, [Zn(mptz)2]Br2 and [Cd(mptz)2Cl6]·4nH2O,33 revealing the electron-accepting ability of mptz in ET photochromic process for the first time. These results are very helpful for our further investigation on the sensing ability of the photochromic rare-earth compounds with mptz.

In this work, based on mptz, we found a new series of rare-earth coordination compounds, [Ln(NO3)3(H2O)4]·mptz [Ln = Sm (1), Eu (2), Gd (3), La (4), Ce (5), Pr (6), Nd (7), Tb (8), Dy (9), Ho (10), Er (11), Tm (12), Yb (13), Lu (14)]. Notably, after light-induced electron transfer from nitrate anion to mptz, most of these compounds showed obvious color changes (Figure 1), and different Ln(III) ions of these compounds can be visually distinguished by their different color changes.

RESULTS AND DISCUSSION

Crystal Structure and Characterization. Compounds 1–14 were obtained by the hydrothermal reaction of mptz with Ln(NO3)3. The phase purities of their crystalline products were verified by PXRD determinations and elemental analysis (Table 2, and Figure S1 and Table S2 in the Supporting Information (SI)). Structural analysis by single-crystal X-ray diffraction shows that complexes 1–14 crystallize in the triclinic space group P1 and exhibit discrete mononuclear Ln(III)–mptz unit. The asymmetrical structure unit contains one [Ln(NO3)3(H2O)4] molecule and one isolated mptz unit. As shown in Figure 2, the Ln(III) unit has one Ln(III) atom teacordinated by six O atoms of three nitrate anions and four
water molecules. Since compounds 1–14 are all isostructural, we choose 1–3 to make a general description of the structures of 1–14.

In compounds 1–3, one Ln(III) unit is linked to three adjacent mptz through five O–H···N bonds between coordinated water and azole ring of mptz (Table S4, and Figure S4a in the SI). Powder X-ray diffraction (PXRD) patterns (Figure S1 in the SI) and TG analysis data (Figure S3 in the SI) indicate that 1–3 are stable up to 99 °C, and then show a weight loss between 104 and 194 °C, in accordance with the removal of four water molecules (found: 12.32, 12.65, and 12.07%; calculated: 12.65, 12.62, and 12.51% for 1–3, respectively). Besides, π–π stacking of centroid-to-centroid (3.581/3.974 Å (1), 3.580/3.958 Å (2), and 3.581/3.945 Å (3)) between the adjacent mptz molecules further strengthens the stability of structures (Table S5 and Figure S4b in the SI).

**Photochromic Properties.** After illumination by a 300 W Xe lamp in atmosphere, compounds 1–14 displayed different color changes in 1 min and no clear crystal structure changes by PXRD determinations (Figure S1 in the SI). No further color change was observed by the naked eye after 40 min irradiation, demonstrating the saturation of coloration (Figure 3, and Figure S5 in the SI) and giving different new UV–vis absorption bands (380 nm for 5, 516 nm for 7, 574 nm for 13, 582 nm for 14, and 530–550 nm for other compounds). Such changes in the UV–vis spectrum are similar to those in our previous work. The photoproducts of 1–14 can last up to at least 3 weeks in the dark, but can be decolored completely in air by heating at 95 °C for 1 day.

The light-responsive wavelength of 1–14 is ca. 290–360 nm, and the optimal wavelength is 315–330 nm, respectively. Such characteristic wavelength dependence property indicates a photoinduced coloration mode but not a photothermal one.28 Besides, the transformation between coloration and decoloration can be repeated several cycles upon illumination and annealing. It can be best exemplified by monitoring the S36 nm absorption band of 1 (Figure S6 in the SI) that implies typical photochromic behaviors.

We further investigated whether these compounds have photochromic behavior after water loss, finding that they did not show clear color changes, which may be due to the structure collapse that we studied before. Since the collapsed structures of 1–14 after losing water are difficult to be figured out, the special cause of loss of photochromic behavior for these compounds after removing water remains to be studied.

**Photochromic Mechanism.** As mentioned above, compounds 1–14 have shown the similarity of structure and photochromic behaviors. Since the compounds 1–3 have shown the most obvious color change after irradiation, and the Sm(III), Eu(III), and Gd(III) in 1–3 are the most commonly used ions in luminescence studies of Ln(III) compounds, we choose 1–3 to further study the photochromic mechanism of these compounds for clarity. As depicted in PXRD and IR analyses (Figures S1–S2 in the SI), the crystal structures of 1–3 experienced no obvious changes after illumination, indicating that the coloration of 1–3 should not result from photolysis or photoinduced isomerization. No ESR signal could be observed in the spectra of 1 and 2 before irradiation, but the radical signals with g = 2.0042 and 2.0028 appeared after coloration, and the ESR spectra of 3 are shown in Figure S7 in the SI (Figures S7a–S7c).

The signal shape and g values are very similar to those in compounds [Zn(mptz)2]Br2 and [Cd(mptz)2Cl]4nH2O, indicating the generation of mptz...
radicals. Thus, the new absorption peak of 1 and 2 at 536 nm should belong to the generation of mptz radicals. Unlike the other two, the radical signal of 3 cannot be observed directly, which may be blurred by the strong ESR signal of Gd(III) with half-filled electronic configuration $f^7$, with the value of $g$ factor equal to 2 in this state.

Total and partial DOS were calculated by VASP to theoretically elucidate ET processes of 1–3. As shown in Figure 4, similar DOS results can be found on 1 and 3. The

![Figure 4. Total and partial DOS of 1 (a), 2 (b), and 3 (c). Positions of Fermi levels set at 0 eV by default.](image)

Sm/Gd atoms and water molecules contribute little to the top of the valence bands (VBs) or the bottom of the conduction bands (CBs). VBs are primarily contributed by $p-\pi$ orbitals of the nitrate anions, while the CBs are mainly dominated by $p-\pi^*$ antibonding orbitals of the mptz. Accordingly, the photochromism of 1 and 3 can be considered as the result of photoinduced nitrate anions $\rightarrow$ mptz ET. This conclusion can also be confirmed by the interactions between mptz and adjacent nitrate anions. There exist intermolecular C–H…O H-bonds between nitrate anions and mptz in the structure with the C…O distances in the range of ca. 3.253–3.461 Å. Moreover, the nearest distances between nitrate anion donors and mptz acceptors in one molecule are even shorter, with the O…N' lengths of ca. 2.917, 2.914, and 2.919 Å for 1, 2, and 3, respectively (O–N' in 1 are shown in Figure S7 in the SI), revealing the possible photochromic mechanism, ET from nitrate anions to mptz, of these compounds.

On the other hand, the DOS of 2 shows a slight difference. As shown in Figure 4b, VBs are mainly dominated by $p-\pi$ orbitals of the nitrate anions with some contribution of mptz $p-\pi$ orbitals, while the contribution for CBs is similar to that in 1 and 3. These results reveal that the photochromism of 2 is similar to that of 1 and 3, with different VBs that may be ascribed to the influence of Eu(III) on the Ln(III)–mptz coordination sphere.

**Lanthanide Ion Sensing.** It is known that major efforts for developing Ln(III) ion sensing were focused on the design of fluorescent sensor molecules in recent years. However, these methods may not be suitable for the Ln–mptz compounds in this work, due to the significant interference from other ions or ligands. As Figure 5 illustrates, the excitation and emission spectra of free mptz, 1 and 3, at room temperature are similar, while only 2 shows distinguished patterns. On the other hand, as mentioned above, the Ln–mptz compounds have shown different photoinduced visible color changes, which are based on ET photochromic process affected by different Ln(III) ions. It is then theoretically feasible that these color changes can be used to identify the Ln(III) ions in these samples. Further investigations on the potential application of Ln(III) sensing are merited.

To further study the sensing ability of these color changes toward different Ln(III) ions, finely grained crystalline samples (50 mg each) of 1–14 were deposited on glass plates for the photoinduced color change studies. With the same condition as UV–vis measurement, all of the samples were irradiated by Xe lamp at room temperature for 70 min to ensure the saturation. As shown in Figure 1, the samples showed different photoinduced visible color changes in solid state, while the shape and position of new absorption peaks of these compounds are also clearly related to the identity of the Ln(III) ion (Figure S5 in the SI), confirming the relationship between certain Ln(III) ions and the specific color changes of related Ln–mptz compounds in the solid state. Interestingly, these visible color changes can be roughly divided into three types: turn into red (Sm, Eu, Gd, Tb); become brown (La, Pr, Nd, Ho, Er, Tm, Yb, Lu), and change slightly (Ce, Dy). Besides, it is notable that some samples also show unique color before irradiation. For example, only the Pr–mptz (6) sample shows green-yellow, and the samples of La (4), Ho (10), and Lu (14) are clear brown-yellow. These color differences can also favor the Ln(III) ion sensing.

Such results inspired us to find the reason for these particular color changes. As mentioned above, compound 2 has a different VB from 1 and 3, which not only shows the influence of Eu(III) on the Ln(III)–mptz coordination sphere, but also has an effect on the photoinduced color changing of Ln(III)–mptz compounds. This variation can be attributed to the different interactions between Ln(III) center and protonated mptz group in the structure of [Ln(mptz)(NO$_3$)$_3$]·4H$_2$O. It is speculated that such interactions, depending on the nature of Ln(III) ions, would differently affect the energy transfer efficiency from nitrate anions to nearby mptz, leading to the particular color changes.

**CONCLUSIONS**

Based on previous studies about mptz zwitterion and ET photochromic process, we further investigated a new family of
photochromic rare-earth materials, \([\text{Ln(mptz)(NO}_3\text{)}_3\]) \([\text{Ln} = \text{Sm} (1), \text{Eu} (2), \text{Gd} (3), \text{La} (4), \text{Ce} (5), \text{Pr} (6), \text{Nd} (7), \text{Tb} (8), \text{ Dy} (9), \text{Ho} (10), \text{Er} (11), \text{Tm} (12), \text{Yb} (13), \text{Lu} (14)].\) They show distinct color changes after photoinduced ET from nitrate anions to mptz, with the generation of stable radicals in ambient condition at room temperature. Notably, based on their different photoinduced visible color changes, the compounds also show the possibility of Ln(III) ion sensing in solid state by ET photochromic process. However, as some of the complexes show similar color changes, it is not sufficient to determine the composition of an unknown sample containing two or more Ln by ET photochromic process, unless their absorption peaks are significantly different. This work may not only go far toward understanding the structure—photosensitivity relationships of pyridinium-based systems, but also provide a new idea that can complement the existing sensing methods of Ln(III) ion sensing.

**EXPERIMENTAL SECTION**

**Materials and Measurements.** mptz was synthesized by the literature procedure. Other chemicals of AR grade purity were purchased commercially and used without further purification.

All measurements except for thermogravimetric (TG) analysis and elemental analyses were performed in atmosphere at room temperature. The elemental analyses of C, H, and N were carried out on an Elemental Vario EL III microanalyzer. Powder X-ray diffraction (PXRD) patterns of 1–14 were collected on a Rigaku MiniFlex II diffractometer powered at 30 kV and 15 mA using Cu Kα (\(\lambda = 1.54056 \text{ Å}\)), with a scan rate of 2° min\(^{-1}\). Simulated patterns were achieved using the free Mercury software (http://www.ccdc.cam.ac.uk/products/mercury/) and the reported single-crystal X-ray diffraction data. UV–visible absorption spectra were measured at room temperature in the diffuse reflectance mode on a PerkinElmer Lambda 900 UV/vis/near-IR spectrophotometer with an integrating sphere attachment and BaSO\(_4\) plate as a reference.

**Synthesis.** Synthesis of \([\text{Ln(NO}_3\text{)}_3\text{·}(\text{H}_2\text{O})_3\text{·}3\text{mptz}]\). The reaction mixture of \(\text{Ln(NO}_3\text{)}_3\text{·}3\text{xH}_2\text{O}\) (0.40 mmol), mptz (64 mg, 0.40 mmol), and water (4 mL) were sealed in a 25 mL Teflon-lined autoclave and then heated to 120 °C at 2 °C/min and kept at this temperature for 1 day. Then, the mixture was cooled to room temperature at 2 °C/h to gain a clear yellow solution. By slow evaporation of the solution, blocky single crystals (35–45% yield based on mptz) were obtained and washed with ethanol. Anal. Calc’d (%) and Found (%) for 1–14 (\(\text{C}_{19}\text{H}_{15}\text{N}_8\text{O}_{13}\text{Ln}\)) are listed in Tables 2 and S2 (in the SI), and the phase purities of 1–14 were checked via PXRD (Figure S1 in the SI).

**X-ray Crystallographic Study.** X-ray diffraction data of the single crystals of 1–14 were recorded at 298(2) K in air on a Rigaku Pilatus 200 K diffractometer using graphite-monochromatic Mo Kα (\(\lambda = 0.71073 \text{ Å}\)). All absorption corrections were performed by using the multiscan program and the structures were solved by direct method and refined by full-matrix least-squares techniques on \(\text{F}^2\) with SHELXTL-2014 program package of crystallographic software. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms in mptz were generated geometrically and refined isotropically. The hydrogen atoms in water molecules were located in the idealized positions and refined with O–H distances restrained to a target value of 0.85 Å, the H–O distance to 1.34 Å, and \(U_{iso}(\text{H}) = 1.5 \times U_{iso}(\text{O})\). Crystallographic parameters and structure refinement details for 1–14 are summarized in Table 1 (1–3) and Table S1 (4–14), and the selected bond distances are given in Table S3 (in the SI). The entries of CCDC 1530985–1530987, 1559748–1559753, and 1560044–1560048 contain the supplementary crystallographic data for 1–14 (Table 2).

**Theoretical Calculation.** The crystallographic data of compounds 1–3 determined by X-ray single-crystal diffraction

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**Table 1. Data and Structure Refinements for 1–3**

| formula | 1 | 2 | 3 |
|---------|---|---|---|
| C\(_{19}\text{H}_{15}\text{N}_8\text{O}_{13}\text{Sm}\) | \(\text{C}_{19}\text{H}_{15}\text{N}_8\text{O}_{13}\text{Sm}\) | \(\text{C}_{19}\text{H}_{15}\text{N}_8\text{O}_{13}\text{Eu}\) | \(\text{C}_{19}\text{H}_{15}\text{N}_8\text{O}_{13}\text{Gd}\) |
| anal. calcd/% | C, 14.76; H, 2.65; N, 19.67 | C, 14.72; H, 2.65; N, 19.62 | C, 14.58; H, 2.62; N, 19.44 |
| found/% | C, 14.76; H, 2.65; N, 19.67 | C, 14.72; H, 2.65; N, 19.62 | C, 14.58; H, 2.62; N, 19.44 |

**Table 2. Elemental Analyses for 1–3**

| | anal. calcd/% | found/% |
|---|---|---|
| 1 | C, 14.76; H, 2.65; N, 19.67 | C, 14.41; H, 2.52; N, 19.78 |
| 2 | C, 14.72; H, 2.65; N, 19.62 | C, 14.36; H, 2.49; N, 19.82 |
| 3 | C, 14.58; H, 2.62; N, 19.44 | C, 14.46; H, 2.45; N, 19.33 |

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were used to calculate their electronic structures, and no further geometry optimization was performed in theoretical studies. The calculations employed the projector augmented wave method encoded in the Vienna ab initio simulation package (VASP),

![Image](http://example.com/image.png)

with the local density approximation and the plane wave cutoff energy of 500 eV. The numerical integration of the Brillouin zone was performed using a 2 × 1 × 1 Monkhorst-Pack k-point sampling for the three compounds.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03662.

Crystal data (Table S1); elemental analyses (Table S2); selected bond lengths (Table S3); bond distances and angles (Table S4); π−π interactions scheme (Table S5); PXRD patterns (Figure S1); IR spectra (Figure S2); TG curve (Figure S3); O−H···N bonds between coordinated water and azole ring (Figure S4); time-dependent UV–vis spectra (Figure S5); UV–vis absorbance of 1 at S36 nm vs the number of cycles (Figure S6); and interactions between mptz acceptors and adjacent donors (Figure S7) (PDF)

Crystallographic data (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF)

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### Notes

The authors declare no competing financial interest.

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