Photochromism

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Reversible Switching of the Luminescence of a Photoresponsive Gadolinium(III) Complex**

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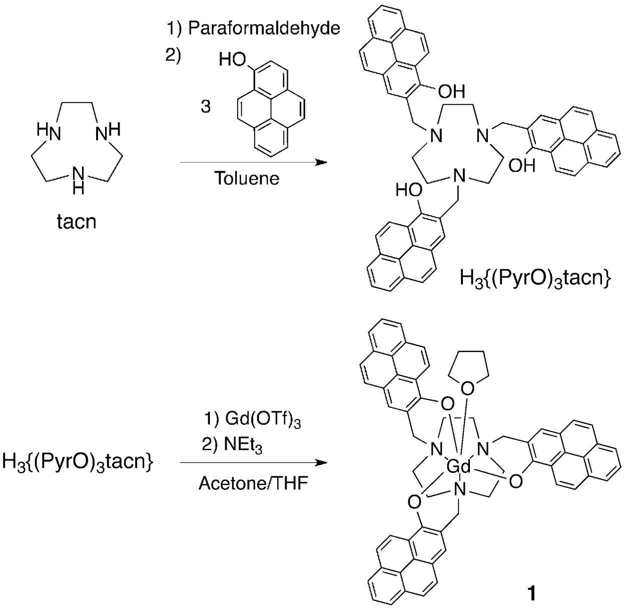
Photochromism is a light-induced reversible change of color, and the fundamental concept and its applications have always fascinated scientists.[1] Recently, photochromic metal complexes have been appealing because of their diverse structures and functions.[2–5] Recent developments have been dominated by the metal complexes that connect well-established organic photochromic molecules such as diarylethenes, azobenzenes, and spiropyrans.[2,4] However, the photochromic metal complexes based on their intrinsic light-induced behavior, which could open a new field of photochromic chemistry, are rare because of limited methodologies to construct the photochromic systems and compounds.[3,5]

In our efforts to develop a new class of luminescent lanthanide complexes with a novel light-harvesting hexadentate ligand ({(PyrO)$_3$tacn}$^{3-}$ = {(CH$_2$C$_{16}$H$_8$O)$_3$C$_6$H$_{12}$N$_3$}$^{3-}$),[6] we have serendipitously found an unprecedented luminescence photochromism of a gadolinium(III) complex [{(PyrO)$_3$tacn}Gd(THF)] (**1**) in THF at room temperature: Upon irradiation ($\lambda_{irr} < 405$ nm)[7], blue emission of **1** changes to intense red emission that reverts to the original blue emission after O$_2$ exposure (Scheme 1, Figure 1, and Movie S1 in the Supporting Information). In this photochromic system, room-temperature phosphorescence in solution, which is one of the rare properties of luminescent compounds,[8,9] plays a key role. Herein we report the synthesis, structure, and luminescence properties of **1** and disclose a principle for the luminescence photochromism of **1** in THF at room temperature.

The N$_3$O$_3$ hexadentate trianionic ligand {(PyrO)$_3$tacn}$^{3-}$ was synthesized through a Mannich reaction of 1,4,7-triazacyclononane (tacn) with 1-pyrenol and was isolated in the triprotonated form (H$_3${(PyrO)$_3$tacn} = 1,4,7-tris[2-(1-hydroxypyrenyl)methyl]-1,4,7-triazacyclononane) in high yield (81 %, Scheme 1, see the Supporting Information).[10] The



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Scheme 1. Preparation of the photoresponsive gadolinium(III) complex **1**.

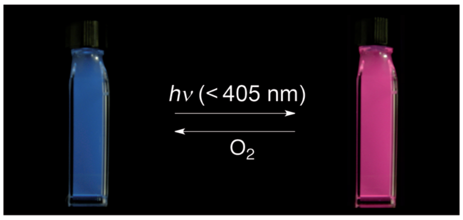

Figure 1. Unique luminescence photochromism of **1** (3.3×10^{-6} M) in THF at room temperature ($\lambda_{ex} = 365$ nm). Also see Movie S1 of the reversible switching of the luminescence of **1** by alternating light irradiation and O$_2$ exposure.

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protonated ligand $H_3\{(PyrO)_3tacn\}$ was characterized by X-ray diffraction analysis and ^{1}H NMR, ^{13}C NMR, UV/Vis, and luminescence spectroscopy (Figures S1–S3 in the Supporting Information). In luminescent lanthanide complexes, energy levels of the lowest singlet and triplet ligand-centered excited states are crucial factors determining the photoinduced properties and can be estimated by measuring the photophysical properties of the gadolinium(III) complexes with the newly developed ligands.[6h,11]

Reaction of $H_3\{(PyrO)_3tacn\}$ with $Gd(OTf)_3$ in acetone/THF at room temperature led to the formation of the gadolinium(III) complex **1** as a yellow powder (76%, Scheme 1, see the Supporting Information).

Yellow crystals suitable for X-ray diffraction analysis were grown from a saturated THF/AcOEt solution of **1** at room temperature. The obtained crystals consist of four complexes **1**, five THF molecules, and three AcOEt molecules per asymmetric unit. The solid-state molecular structure of one of the four crystallographically independent complexes **1** in the crystals of 4**1**·5THF·3AcOEt is depicted in Figure 2. The trivalent gadolinium ion in **1** is coordinated by three nitrogen and four oxygen atoms. The coordination polyhedron of the seven-coordinate gadolinium ion can be described as face-capped octahedron, in which the oxygen atom of THF caps the triangular face formed by the oxygen atoms of the $\{(PyrO)_3tacn\}^{3-}$ ligand. The observed geometry of **1** is similar to that of the reported trivalent uranium complex with an N_3O_3 hexadentate trianionic ligand $[\{(^{tBu}ArO)_3tacn\}U(CH_3CN)]$[6f] ($\{(^{tBu}ArO)_3tacn\}^{3-} = \{(CH_2tBu_2C_6H_2O)_3\text{-}C_6H_{12}N_3\}^{3-}$) rather than those of the corresponding trivalent lanthanide complexes $[\{(^{tBu}ArO)_3tacn\}Ln]$ (Ln = Sm, Eu, Lu).[6a]

Figure 3a displays the UV/Vis absorption spectrum of **1** in THF at room temperature. The absorption bands at 288, 366, 384, and 405 nm ($\varepsilon = 8.90\times10^4$, 7.27×10^4, 8.38×10^4, $10.35\times10^4\,\text{M}^{-1}\,\text{cm}^{-1}$, respectively) are mainly corresponding to the $\pi\rightarrow\pi^*$ transition of the hydroxypyrenato moieties. The absorption bands are slightly red-shifted relative to those of $H_3\{(PyrO)_3tacn\}$ (Figure S2 in the Supporting Information).

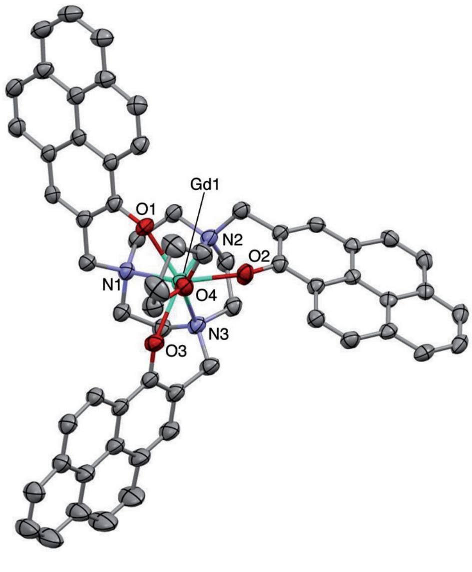

Figure 2. An ORTEP drawing of gadolinium(III) complex **1**. One of the four independent complexes in the crystals of 4**1**·5THF·3AcOEt is shown. Hydrogen atoms and cocrystallized solvent molecules (THF and AcOEt) are omitted for clarity; thermal ellipsoids are at the 50% probability level. Selected bond distances [Å] and angles [°]: Gd1–N1 = 2.555(4), Gd1–N2 = 2.621(3), Gd1–N3 = 2.604(4), Gd1–O1 = 2.216(3), Gd1–O2 = 2.189(3), Gd1–O3 = 2.219(3). Gd1–O4 = 2.447(3), N1-Gd1-N2 = 68.40(9), N1-Gd1-N3 = 68.58(11), N2-Gd1-N3 = 66.56(11), O1-Gd1-O2 = 111.08(11), O1-Gd1-O3 = 118.34(9), O2-Gd1-O3 = 115.01(11).[18]

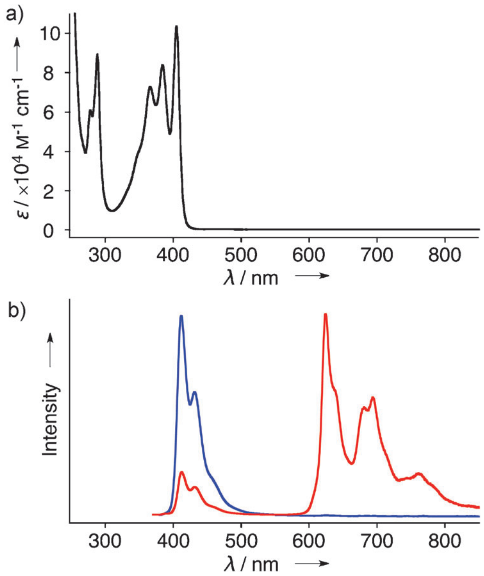

Figure 3. a) UV/Vis absorption spectrum of **1** (7.0×10^{-6} M). b) Corrected luminescence spectra of **1** (3.1×10^{-7} M) in nondegassed (blue) and degassed (red) THF at room temperature ($\lambda_{ex} = 285$ nm).

Under the excitation of **1** at $\lambda_{ex} < 405$ nm,[7] blue emission was observed in nondegassed THF at room temperature (Figure 3b, blue). Owing to the small Stokes shift and short emission lifetime (τ), the blue emission can be assigned to the fluorescence from an intraligand excited state ($\lambda_{em}{}^{max} = 412$ nm, $\tau < 50$ µs, quantum yield (Φ) = 0.01; Figure S3).[12,13] Surprisingly, continuous irradiation of **1** at $\lambda_{irr} < 405$ nm[7] induces a change of the emission color from blue to red at room temperature. The obtained spectrum (Figure S4 in the Supporting Information, black dots), in which the original fluorescence band ($\lambda_{em}{}^{max} = 412$ nm) is still observed with the same Φ, is identical to the emission spectrum of **1** in degassed THF at room temperature (Figure 3b, red). The red color originates mainly in a new emission band from 600 to 850 nm ($\lambda_{em}{}^{max} = 625$ nm, $\tau = 430$ µs, $\Phi = 0.12$; Figure S5 in the Supporting Information). The red emission is quenched by O_2 and goes back to the blue fluorescence only. On the basis of these results, the photoinduced red emission can be assigned to the phosphorescence from an intraligand excited state.[13] The excitation spectra monitored at 460 and 625 nm (fluorescence and phosphorescence, respectively) are identical to the absorption spectrum of **1** (Figure S6a and S6b in the Supporting Information). Thus, the luminescence photochromism is based on the fluorescence and room-temperature phosphorescence of **1**. The heavy-atom effect of the Gd^{3+} ion and the chelate effect of the ligand in **1** contribute to the observed rare room-temperature phosphorescence in solution. The proposed principle of the luminescence photochromism of **1** in THF at room temperature is summarized in Figure 4. Upon irradiation, **1** sensitizes triplet oxygen ($^3O_2$) in nondegassed THF to generate singlet oxygen ($^1O_2$), which readily reacts with THF to produce tetrahydrofuran hydroperoxide (THF-OOH).[14] Through these processes, $^3O_2$ is taken away from the system, and the red phosphorescence of **1** at room temperature becomes visible. The generation of $^1O_2$ was confirmed by the $^1O_2$-trapping reaction with 1,5-dihydroxynaphthalene in CH_2Cl_2/MeOH and by the observation of $^1O_2$ luminescence at 1275 nm in air-saturated CH_2Cl_2 (Figures S7 and S8 in the Supporting Information). The production of THF-OOH was analyzed by using the iodine test (Figure S9 in the Supporting Information). The light-induced processes involving the THF-OOH production are additionally supported by the fact that the luminescence photochromism of **1** does not occur in benzene, toluene, and CH_2Cl_2. Thus, the catalytic photooxidation of THF by **1** is indispensable to show the room-temperature phosphorescence of **1**. The backward process is simple phosphorescence quenching by $^3O_2$.[15] Notably, the switching of the luminescence of **1** in THF at room temperature is reversible with alternating irradiation (365 nm) and O_2 exposure for at least ten cycles (Figure 5). This indicates that **1** has the appropriate stability toward the light irradiation, $^1O_2$, and THF-OOH.

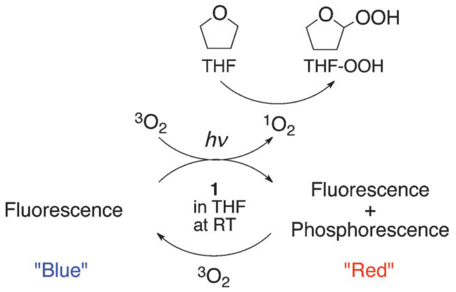

Figure 4. The proposed principle of the luminescence photochromism of **1** in THF at room temperature.

In conclusion, we have demonstrated that the photoresponsive gadolinium(III) complex **1** is a useful compound to construct a unique luminescence photochromic system. The gadolinium(III) complexes have been widely investigated as magnetic resonance imaging (MRI) contrast agents.[16] However, other functions, especially photofunctions, of the gadolinium(III) complexes have been scarcely explored so far.[9,17] Our findings offer attractive new insights into not only the construction of switchable and sensing materials but also the development of photo-oxidation catalysts, "photosensitizers", by using the photoresponsive gadolinium(III) complexes. Further work is currently in progress on the basis of these approaches.

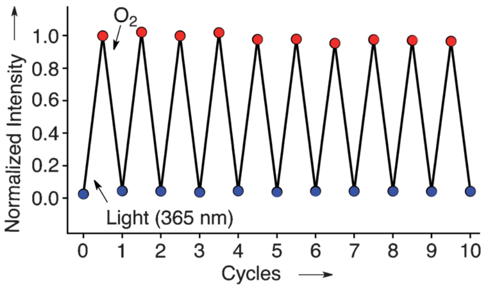

Figure 5. Reversible switching of the phosphorescence intensity of **1** (7.7×10^{-6} M) in THF at room temperature by alternating light irradiation (λ_{irr} = 365 nm, 810 µW cm^{-2}) and O_2 exposure. The phosphorescence was monitored at 625 nm.

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[18] CCDC-932725 (**1**) 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.