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Supporting Information

Photoactivatable Europium Luminescence Turn-On by Photo-Oxygenation of β-Diketone Having Pyrrole Rings

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Table of Contents

Experimental Section

General. ^1H NMR spectra were measured with JEOL ECX-400P (400 MHz). Chemicals were purchased from Wako Pure Chemical Industries Ltd. and used as received without further purification. Europium(III) trifluoromethanesulfonate and the other lanthanide(III) salts were obtained from Aldrich. Oxygen-$^{18}O_2$ (99 atom %) was purchased from Sigma-Aldrich. 1,3-Bis(1-methyl-1H-pyrrol-2-yl)propane-1,3-dione (LH_2) was prepared according to a procedure described previously.[1] The emission lifetimes were recorded using FluoroCube (HORIBA, 3000U-YSP). Mass spectra were measured with mass spectrometer (JEOL AccuTOF JMS-T100LC for ESI). The emission quantum yield (ϕ_{em}) was measured using a calibrated integrating sphere system (JASCO IL-533) in acetonitrile upon excitation of the ligand absorption band. The quantum yield (ϕ_{pr}) of the photo-oxygenation of LH_2 was determined using photoreaction quantum yield evaluation system (SHIMADZU, QYM-01) in an acetonitrile solution of LH_2 (1.0×10^{-4} M) containing Eu^{3+} (3.3×10^{-4} M) under atmospheric pressure of oxygen. The emission and UV-vis absorption spectra for the photoreaction were measured at room temperature using JASCO FP-6500 and V-660, respectively. Near-IR luminescence emission spectra were measured on a SPEX Fluorolog fluorescence spectrophotometer. Cyclic voltammetry measurements were performed using an ALS electrochemical analyzer in deaerated MeCN containing 0.1 M Bu_4NClO_4 (TBAP) as the supporting electrolyte at 298 K.

Crystallography. Suitable crystals of the photoproduct (LHOH) was obtained by slow evaporation of the acetonitrile solution of LHOH. Single crystal of LHOH was mounted with epoxy resin on a glass fiber. X-ray diffraction intensity was collected with a Rigaku RAXIS RAPID (3 kW) imaging plate area detector with graphite monochromated Mo Kα radiation at 123 K. All calculations were performed with the Rigaku CrystalStructure 3.8.1 software. In the crystal structures of LHOH, there are two LHOH molecules in the unit cell, where one of which has a disordered. For the purpose of clarity, Fig. 3e shows the other crystal structure of LHOH.

Photoreaction Procedure for Spectral Measurements. In most cases, a negatively charged β-diketonate ligand forms a neutral and stable ML_3 complex with trivalent lanthanide(III) ions. Therefore, we initially tried to synthesize the photoreactive lanthanide(III) complexes using the standard procedure for synthesis of tris(β-diketonates)lanthanide(III) complexes. However, during the course of experiments, we realized that the photoreactive europium(III) complex is labile, and the β-diketone ligands (LH_2) are partially dissociated from the metal ion during the isolation processes. In such circumstances, the photoreactive lanthanide(III) complexes were generated in situ by the addition of the metal ions to a stock solution of LH_2 prior to use. In order to avoid the existence of uncoordinated LH_2, excess amount of lanthanide(III) ions was added to the stock solution of LH_2. The UV-vis absorption titration experiment indicates that 3 equiv of metal ions is sufficient for that almost all LH_2 to form the complex (Fig. S1). These experimental conditions enable us to conduct the photoactivatable europium(III) luminescence experiments with good reproducibility. The reaction solution containing LH_2 (1.0×10^{-4} M) and Eu^{3+} (3.3×10^{-4} M) in acetonitrile (3 mL) begins to exhibit a bright red emission within 60 seconds photoirradiation ($\lambda = 365$ nm) by UV hand lamp (AS ONE SLUV_6) under atmospheric pressure of oxygen [Fig. 1b and see the supporting material: PA-Eu.mp4].

Formation of the photoreactive complex $[Eu^{3+}(LH^{-})_3]$ was confirmed by HRMS (ESI): *m*/*z* calcd for $C_{39}H_{40}EuN_6O_6$ $[Eu(LH)_3 + H]^+$ 841.22216, found 841.22293. The β-diketonate chelate (LH_2) forms complexes with various lanthanide(III) ions (e.g., Eu^{3+}, Tb^{3+}, Sm^{3+}, Gd^{3+}). Complex formation between LH_2 and lanthanide(III) ions occurs with clear isosbestic points in the presence of 0–4 equiv of metal ions (Fig. S1), suggesting the formation of a single complex species between LH_2 and the metal ions irrespective of the molar ratio. Therefore, the binding stoichiometry was determined by Job analysis. The Job plot indicates the 3:1 binding stoichiometry between LH_2 and the metal ion, suggesting the formation of the ML_3 type complex. It should be noted that the photoactivatable europium(III) luminescence can be observed even in the presence of a small amount (0.33 equiv) of Eu^{3+} (Fig. S3). In the other cases, excess amount of lanthanide(III) ions was used to avoid the uncoordinated LH_2, leading to increase the photoactive complex concentration in situ. The photoreaction proceeds with clear isosbestic points during the photoirradiation 0–2400 s (Fig. 4a), suggesting quantitative conversion of the photoreactive complex $[Eu(LH)_3]$ to the photo-generated complex $[Eu(LH)_2(LHOH)]$. Thus, no complex dissociation should take place upon photo-activation.

The emission and UV-vis absorption spectral changes during the photoreaction were measured by JASCO FP-6500 and V-660, respectively. In both experiments, fluorescence spectrometer Xe lamp (USHIO INC. UXL-159) was used as a light source for the photoreaction ($\lambda_{irr} = 344$ nm slit width of 20 nm). The 344 nm wavelength is the isosbestic point of the photoreaction (see Fig. 4a). Typically, an acetonitrile solution (3 mL) of LH_2 (1.0×10^{-4} M) containing Eu^{3+} (3.3×10^{-4} M) was irradiated in the cell chamber of the spectrophotometer with the Xe light source ($\lambda_{irr} = 344$ nm slit width of 20 nm). The emission spectra were recorded every 120 s with minimum excitation slit width (slit width of 1 nm) to minimize the effect of the photoirradiation during the spectral measurement (Fig. 2). The UV-vis absorption spectra were measured every 60 s under the same experimental conditions as employed for emission spectral measurements. The photoreaction of LH_2 in the presence of Yb^{3+} ions for was investigated with a SPEX Fluorolog fluorescence spectrophotometer.

Photoreaction Procedure and Product Isolation. Typically, LH_2 (13 mg) was added to a recovery flask that contained an acetonitrile solution (300 mL) containing $Eu(OSO_2CF_3)_3$ ($3.3 \times$

10^{-4} M) under atmospheric pressure of oxygen. Then, the solution was irradiated with UV-visible light (λ_{irr} = 365 nm) from a Xe lamp (UVP, Black-Ray-B-100AP) at room temperature for 5 h. The reaction solution was analyzed by UV-vis absorption spectra. The photoreaction was complete within 5 h photoirradiation under these conditions. The solvent was removed by reduced pressure. Then, the photoreaction product was separated from the Eu^{3+} ions by silica column chromatography (ethyl acetate), and purified by GPC with chloroform to provide a yellow powder (12 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (dd, *J* = 4.4, 1.6 Hz, 2H), 6.88 (dd, *J* = 2.6, 1.6 Hz, 2H), 6.16 (dd, *J* = 4.2, 2.6 Hz, 2H), 5.64 (d, *J* = 6.4 Hz, 1H), 4.73 (d, *J* = 6.9 Hz, 1H), 3.93 (s, 6H). HRMS (ESI) *m*/*z* calcd for $C_{13}H_{14}N_2NaO_3$ $[M+Na]^+$ 269.09021, found 269.09094.

Despite a great effort in performing several experiments for isolation of the photo-generated complex, the direct isolation has not been accomplished. The photo-generated lanthanide(III) complexes are still labile, and LHOH (or LH_2) was partially dissociated from the metal ion during the isolation processes. However, reconstruction of a europium(III) complex from the isolated photoreaction product (LHOH) facilitates the rationalization of the photoactivatable europium(III) luminescence phenomena (see in the text).

Photo Patterning. Typically, the filter paper (Tokyo Roshi Kaisha, Ltd.) was immersed for 1 min in an acetonitrile solution of LH_2 (1.0×10^{-4} M) containing $Eu(OSO_2CF_3)_3$ (3.3×10^{-4} M), and then irradiated UV light (λ_{irr} = 365 nm) for 1 min by UV hand lamp (AS ONE SLUV_6) and quickly dried by hot air.

Phosphorescence Spectral Measurements. The triplet (T_1) energy levels were estimated by referring to the highest energy band in the phosphorescence spectra of LH_2 and LHOH in the presence of gadolinium(III) ions (Gd^{3+}). The emission spectra were recorded at 298 K and 193 K. New emission bands appeared around λ_{em} = 500 nm with decreasing the temperature (Fig. S9 blue lines), and we assigned them as phosphorescence from the corresponding diketones. The highest energy band in the phosphorescence spectra were estimated from the difference spectra between the low and higher temperature spectra (Fig. S9 dashed lines).

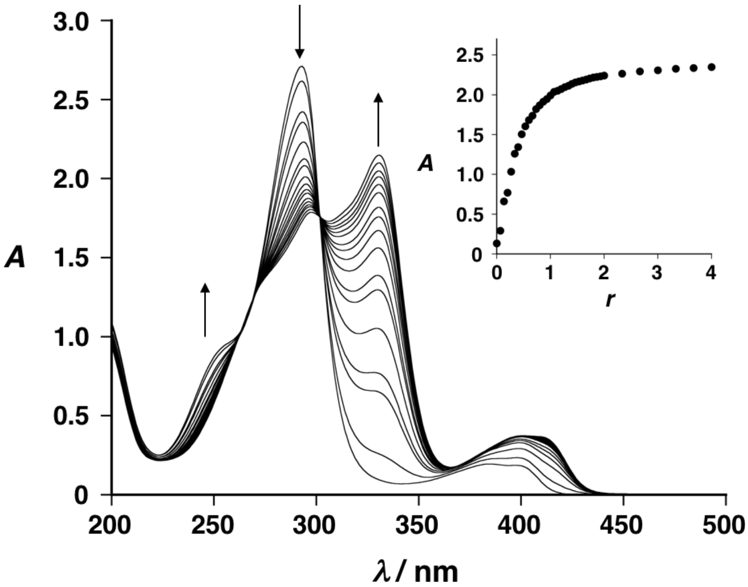

Fig. S1 UV–vis absorption spectra of LH_2 (1.0×10^{-4} M) in the presence of Tb^{3+} ($0–1.0 \times 10^{-4}$ M) in MeCN at 298 K. Inset: Plot of absorbance at 331 nm vs molar ratio (*r*).

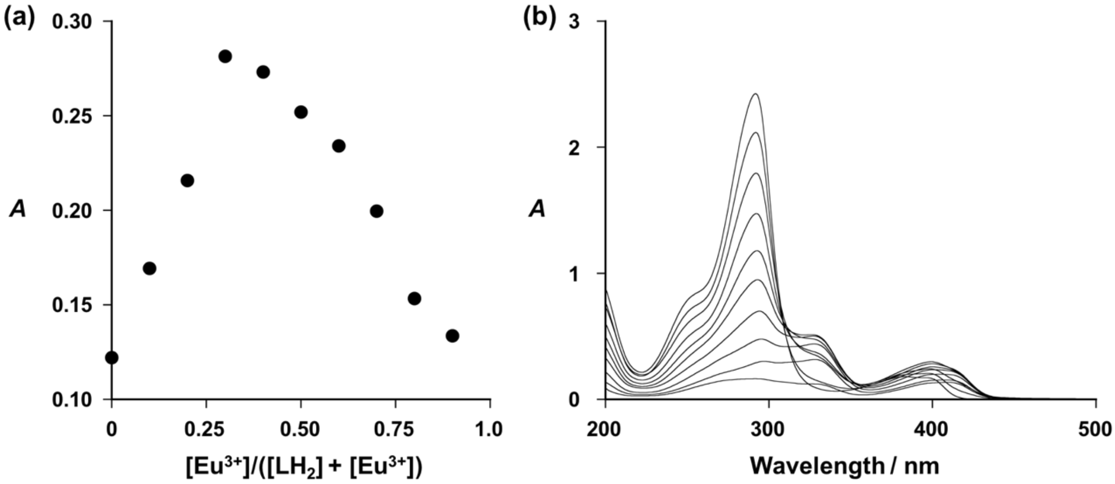

Fig. S2 (a) Plot of absorbance at λ = 405 nm versus $[Eu^{3+}]/([LH_2] + [Eu^{3+}])$, where the sum of the concentrations of the partners is fixed ($[LH_2] + [Eu^{3+}] = 1.0 \times 10^{-4}$ M). (b) The corresponding UV–vis absorption spectral changes. In this spectral change, no isosbestic point was present, because the total concentration of the ligand ($[LH_2]_0$) is not constant in the method of continuous variation (Job plot).

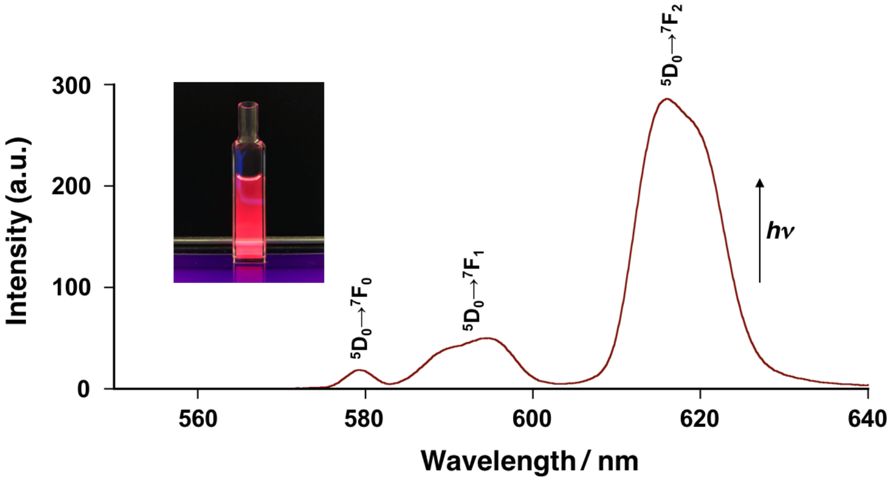

Fig. S3 Emission spectrum of the sample solution obtained by 180 s photoirradiation (λ_{irr} = 365 nm by UV hand lamp) of LH_2 (1.0×10^{-4} M) in the presence of Eu^{3+} (3.3×10^{-5} M) in MeCN at 298 K. Excitation wavelength: λ_{ex} = 344 nm. Inset: photographs of the solution under UV light (λ_{ex} = 365 nm).

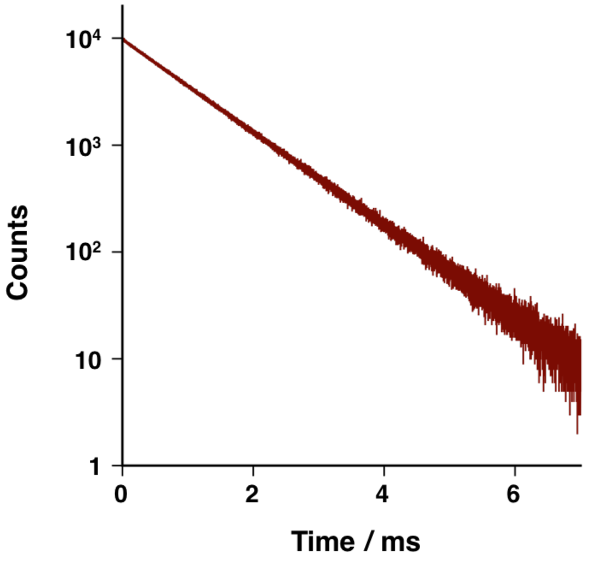

Fig. S4 Emission decay (λ_{em} = 614 nm) of the sample solution obtained by 1800 s photoirradiation (λ_{irr} = 344 nm) of LH_2 (1.0×10^{-4} M) in the presence of Eu^{3+} (3.3×10^{-4} M) in MeCN at 298 K. Excitation wavelength: λ_{ex} = 376 nm.

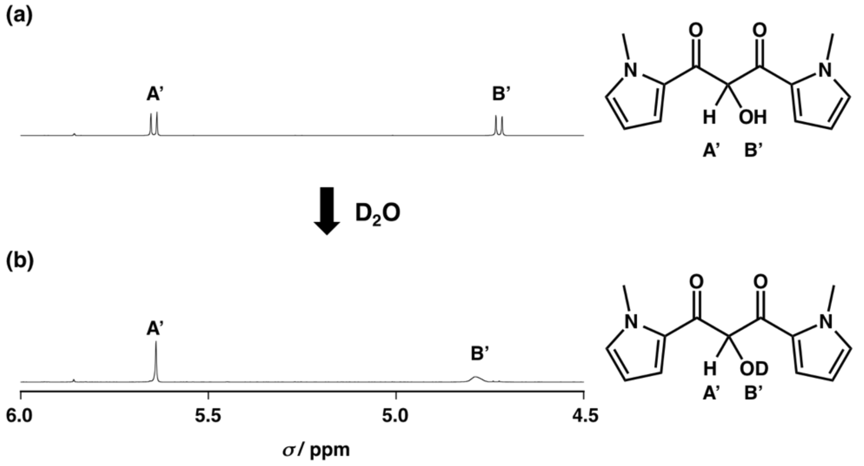

Fig. S5 ^{1}H NMR spectra of (a) the photoreaction product (LHOH) and (b) that in the presence of small amount of D_2O in $CDCl_3$ at 298 K.

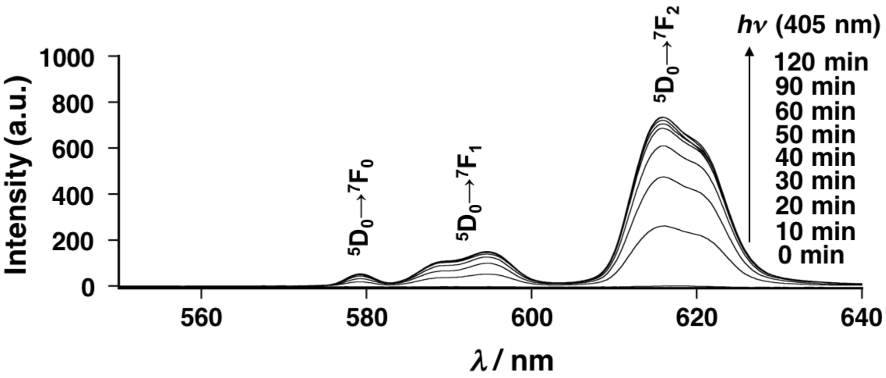

Fig. S6 Emission spectra of LH_2 (1.0×10^{-4} M) in the presence of Eu^{3+} (3.3×10^{-4} M) during photoirradiation (λ_{irr} = 405 nm) in MeCN at 298 K. Emission spectra were recorded with excitation wavelength of λ_{ex} = 344 nm by excitation slit width of 1 nm. The emission intensity increased upon photoirradiation at λ_{irr} = 405 nm (0–120 min; slit width of 20 nm).

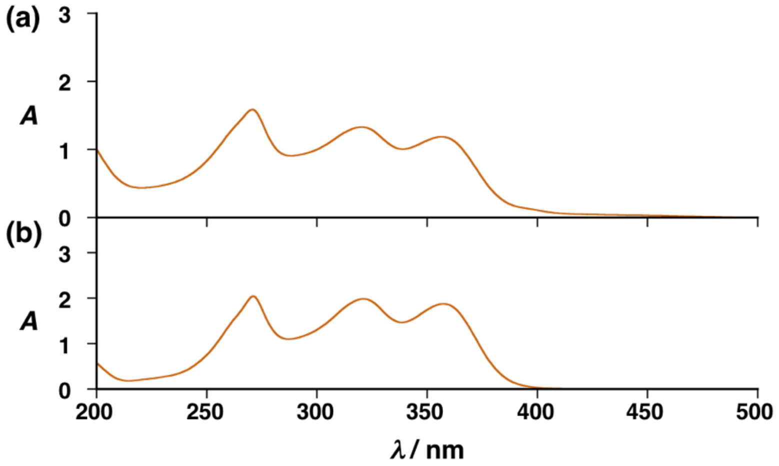

Fig. S7 (a) UV-vis absorption spectrum of the sample solution obtained by 5 h photoirradiation (λ_{irr} = 344 nm) of LH_2 (1.0×10^{-4} M) in the presence of Eu^{3+} (3.3×10^{-4} M) in MeCN at 298 K. (b) UV-vis absorption spectrum of LHOH (1.0×10^{-4} M) in the presence of Eu^{3+} (3.3×10^{-4} M) in MeCN at 298 K.

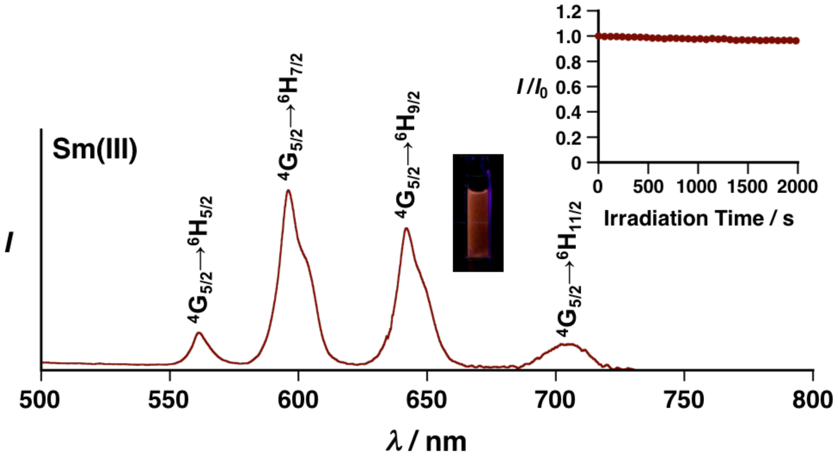

Fig. S8 Emission spectrum of LH_2 (1.0×10^{-4} M) in the presence of Sm^{3+} (3.3×10^{-4} M) in MeCN at 298 K. Excitation wavelength: λ_{ex} = 344 nm. Inset: Emission intensity changes at λ = 643 nm during photoirradiation at λ_{irr} = 344 nm, where I_0 denotes emission intensity before photoirradiation. Photographs of a MeCN solution of LH_2 (1.0×10^{-4} M) containing Sm^{3+} (3.3×10^{-4} M) under UV light (λ_{ex} = 365 nm).

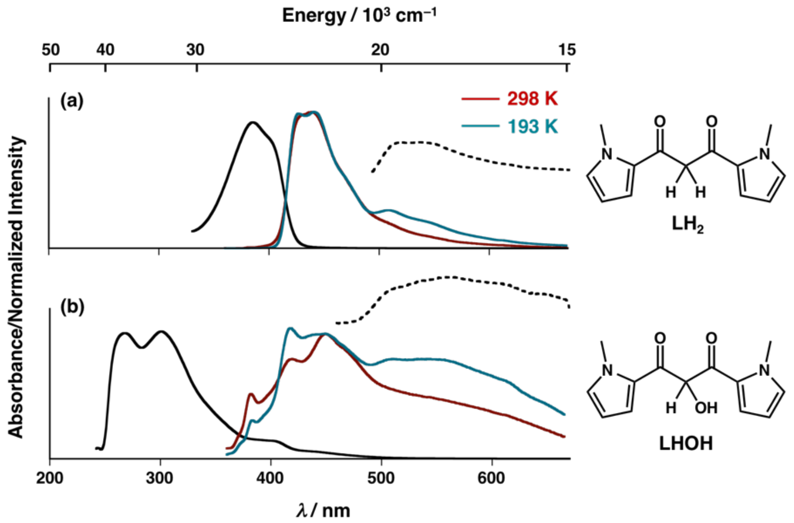

Fig. S9 Black solid lines show UV-vis absorption spectra of (a) LH_2 (1.0×10^{-4} M) and (b) LHOH (1.0×10^{-4} M) in the presence of Gd^{3+} (3.3×10^{-4} M) in propionitrile at 298 K. Emission spectra of (a) LH_2 (1.0×10^{-4} M) and (b) LHOH (1.0×10^{-4} M) in the presence of Gd^{3+} (3.3×10^{-4} M) in propionitrile at 298 K (red line) and 193 K (blue line). Dashed lines show the difference spectra between the low and higher temperature spectra. Excitation wavelength: λ_{ex} = 344 nm.

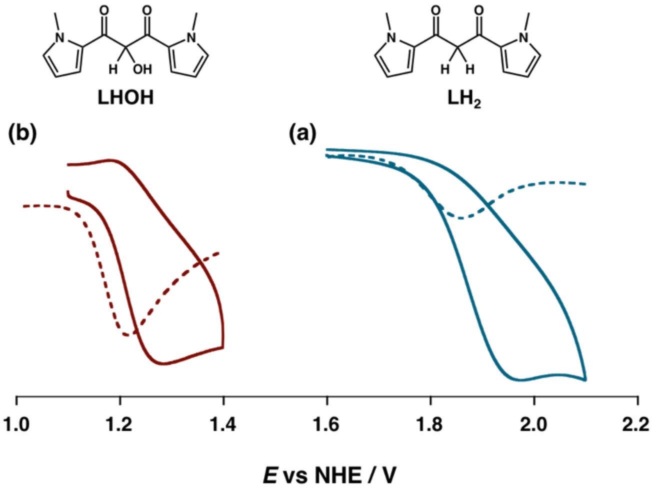

Fig. S10 Cyclic voltammograms (solid line) and differential pulse voltammograms (dashed line) of (a) LH_2 (9.5×10^{-4} M) and (b) LHOH (1.0×10^{-5} M) in deaerated MeCN containing 0.10 M TBAP with Pt electrode at 298 K.

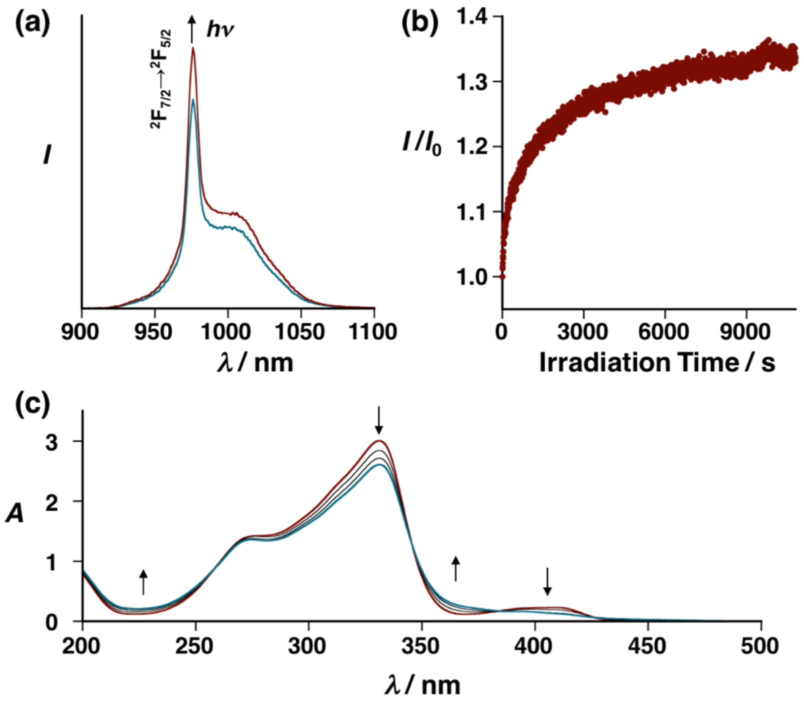

Fig. S11 (a) Emission spectra of LH_2 (1.0×10^{-4} M) in the presence of Yb^{3+} (3.3×10^{-4} M) before (blue line) and after 3 h photoirradiation (red line) at λ_{irr} = 344 nm in MeCN at 298 K. Excitation wavelength: λ_{ex} = 344 nm. (b) Emission intensity change at λ = 976 nm during photoirradiation at λ_{irr} = 344 nm, where I_0 denotes emission intensity before photoirradiation. (b) UV-vis absorption spectra of LH_2 (1.0×10^{-4} M) in the presence of Yb^{3+} (3.3×10^{-4} M) upon photoirradiation at λ_{irr} = 344 nm ([0 (blue line)–3 h (red line), every 1 h] in MeCN at 298 K.

REFERENCE

(1) H. Maeda and Y. Kusunose, *Chem.–Eur. J.*, 2005, **11**, 5661–5666.