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Spin-orbit coupling dependent energy transfer in luminescent nonanuclear Yb-Gd / Yb-Lu clusters

Shun Omagari[a], Takayuki Nakanishi[b,*], Yuichi Kitagawa[b], Tomohiro Seki[b], Koji Fushimi[b], Hajime Ito[b], Andries Meijerink[c], Yasuchika Hasegawa[b,*]

[a] Graduate School of Chemical Sciences and Engineering, Hokkaido University, N13 W8, Kita-Ku, Sapporo, Hokkaido 060-8628, Japan
[b] Faculty of Engineering, Hokkaido University, N13 W8, Kita-Ku, Sapporo, Hokkaido 060-8628, Japan
[c] Debye Institute, Department of Chemistry, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands

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ABSTRACT

In luminescent lanthanide (Ln(III)) complexes, the yield and the lifetime of triplet excited state of organic ligands are crucial factors that affect the ligands-to-Ln(III) energy transfer efficiency. Such factors are dependent on spin-orbit coupling induced by the Ln(III) ions that mixes different multiplicity states through heavy atom and paramagnetic effects. We investigated the role of these effects on the energy transfer efficiency in synthesized nonanuclear Yb-Gd / Yb-Lu clusters ([$Ln_9(\mu\text{-}OH)_{10}$(butyl salicylate)$_{16}$]NO_3, Ln_9 = $Yb_nGd_{9\text{-}n}$ or $Yb_nLu_{9\text{-}n}$, n = 0, 1, 3, 7, and 9). Based on the intensity of the fluorescence and phosphorescence of the ligands, the spin-orbit coupling strength was in the order of Yb(III) > Gd(III) > Lu(III). Various photophysical processes affecting the energy transfer efficiency in $Yb_nGd_{9\text{-}n}$ and $Yb_nLu_{9\text{-}n}$ clusters are discussed from the perspective of spin-orbit coupling and give insight in how to optimize energy transfer efficiencies.

1. Introduction

Over the past two decades, trivalent lanthanide (Ln(III)) complexes have been extensively studied for their unique spectroscopic properties such as high-chromaticity emission and long emission lifetimes that are advantageous for application to organic light-emitting diodes (OLEDs),[1,2] bioimaging,[3,4] and spectral converters.[5,6] Light-harvesting organic ligands play a major role in photosensitization of Ln(III) ions (photosensitized energy transfer, PSET), which are otherwise poor absorbers of light.[7] The mechanism of photosensitization is depicted in Fig. 1. When organic ligands absorb a photon, a transition from the singlet ground state (S_0) to the singlet excited state (S_1) occurs. Intersystem crossing (ISC) to the triplet excited state (T_1) immediately follows after the transition. Energy transfer to a Ln(III) ion typically proceeds from the T_1 state of the organic ligand.[8,9] Therefore, the efficiency of the PSET is high for Ln(III) complexes with fast $S_1 \rightarrow T_1$ ISC and slow $T_1 \rightarrow S_0$ relaxation.

While $S_1 \rightarrow T_1$ ISC and $T_1 \rightarrow S_0$ relaxation are spin-forbidden processes, they can become partially allowed processes by spin-orbit coupling (SOC).[10] The SOC in Ln(III) complexes is strong due to 1) large effective nuclear charge of Ln(III) ions (the "heavy atom effect"), and 2) the spin and orbital angular momentum of 4 f-electrons (the "paramagnetic effect"). As a result, $S_1 \rightarrow T_1$ ISC rate in Ln(III) complexes is assumed to be fast and ranges anywhere between 10^7 to 10^{10} s^{-1}.[11–13] Reports by Tobita [11] and Guldi [13] both showed that the difference in SOC arises predominantly from the paramagnetic effect rather than the heavy atom effect in the lanthanide series. For example, Gd(III) complex with methyl salicylate ligands showed an order of magnitude larger $S_1 \rightarrow T_1$ ISC and $T_1 \rightarrow S_0$ relaxation rates compared to Lu(III) complex despite Lu(III) being the heavier atom. Guldi and his coworkers further demonstrated that both $S_1 \rightarrow T_1$ ISC and $T_1 \rightarrow S_0$ relaxation rates are roughly proportional to the magnetic moment of the lanthanides.[13]

In terms of raising the PSET efficiency, we suggest that there is an optimum strength of SOC. PSET efficiency η_{sens} can be expressed as the product of $S_1 \rightarrow T_1$ ISC efficiency η_{ISC} and $T_1 \rightarrow Ln$ energy transfer efficiency $\eta_{T_1 \rightarrow Ln}$:

$$\eta_{sens} = \eta_{ISC} \times \eta_{T_1 \rightarrow Ln} = \frac{k_{ISC}}{k_{r,S_1} + k_{nr,S_1} + k_{ISC}} \times \frac{k_{T_1 \rightarrow Ln}}{k_{r,T_1} + k_{nr,T_1} + k_{T_1 \rightarrow Ln}}$$

where k_{ISC}, $k_{T_1 \rightarrow Ln}$, k_r, and k_{nr} are $S_1 \rightarrow T_1$ ISC, $T_1 \rightarrow Ln$ energy transfer, radiative, and nonradiative rate constants, respectively. Since SOC mixes different multiplicity states, k_{ISC} as well as $k_{r,T_1} + k_{nr,T_1}$ are raised in the presence of strong SOC. From the equation above, strong SOC

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* Corresponding authors.
E-mail addresses: nakanishi@eng.hokudai.ac.jp (T. Nakanishi), hasegaway@eng.hokudai.ac.jp (Y. Hasegawa).

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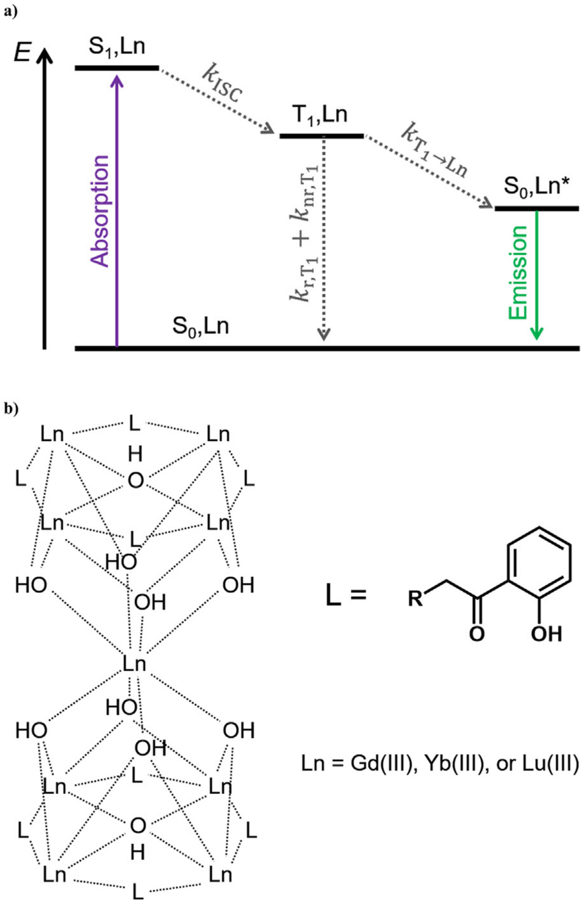

Fig. 1. a) Energy diagram of typical Ln(III) complexes showing various photophysical processes. S_0: ligand singlet ground state, S_1: ligand singlet excited state, T_1: ligand triplet excited state, Ln: ground state Ln(III) ion, Ln*: excited state Ln(III) ion. ISC: Intersystem crossing, ET: $T_1 \rightarrow Ln$ energy transfer. b) Nonanuclear Ln(III) clusters with ester salicylate ligands.

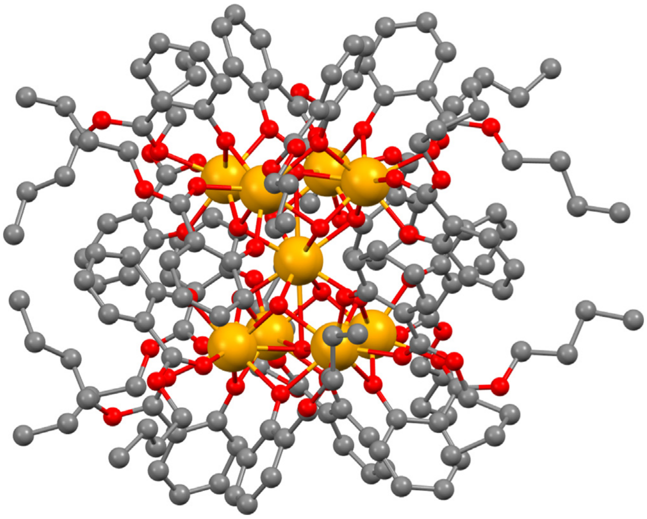

Fig. 2. Crystal structure of Yb_9 cluster. Orange: Yb atoms, red: oxygen atoms, and grey: carbon atoms. Hydrogen atoms as well as the random disorder of the butyl chains are omitted for clarity.

Table 1
Continuous shape measure calculation results for Gd_9, Yb_9, and Lu_9 clusters.

	Gd_9 cluster[a]		Yb_9 cluster		Lu_9 cluster	
	8-TDH	8-SAP	8-TDH	8-SAP	8-TDH	8-SAP
Ln1	2.976	4.725	2.573	4.578	2.565	4.455
Ln2	2.836	4.813	2.545	4.546	2.481	4.633
Ln3	2.704	4.588	2.413	4.776	2.447	4.622
Ln4	2.513	4.822	2.404	4.623	2.400	4.507
Ln5	2.976	4.725	2.573	4.578	2.565	4.455
Ln6	2.836	4.813	2.545	4.546	2.481	4.633
Ln7	2.704	4.588	2.413	4.776	2.447	4.622
Ln8	2.513	4.822	2.404	4.623	2.400	4.507
Ln9[b]	2.481	0.082	2.396	0.077	2.371	0.105

[a] Taken from reference [15].
[b] Center Ln(III) ion.

leads to high η_{ISC} but low $\eta_{T_1 \rightarrow Ln}$ while weak SOC leads to low η_{ISC} but high $\eta_{T_1 \rightarrow Ln}$. The opposite action of SOC on these two efficiencies determines the overall η_{sens} and indicates there is an optimum SOC to maximize the product of η_{ISC} and $\eta_{T_1 \rightarrow Ln}$. In order to experimentally observe this effect, we focused on nonanuclear Ln(III) clusters (Fig. 1). [14,15] Nonanuclear Ln(III) clusters are polynuclear Ln(III) complexes composed of nine "clustered" Ln(III) ions and sixteen surrounding ester salicylate ligands. The clusters allow control of SOC by mixing different Ln(III) ions without significantly distorting the structure. Yb(III), Gd (III), and Lu(III) ions were chosen for this work. The Yb(III) ion with its two-level 4f-states ($^2F_{7/2}$ and $^2F_{5/2}$ states) is suitable as the emissive center for the simplicity in discussing $T_1 \rightarrow Yb(^2F_{5/2})$ energy transfer process. Gd(III) and Lu(III) ions were chosen as the non-emissive paramagnetic and diamagnetic centers, respectively.

To investigate the effect of SOC strength induced by paramagnetic and diamagnetic Ln(III) ions on the PSET efficiency, we synthesized nonanuclear Yb_nGd_{9-n} and Yb_nLu_{9-n} clusters ($[Ln_9(\mu\text{-}OH)_{10}(\text{butyl salicylate})_{16}]NO_3$, Ln = Yb_nGd_{9-n} / Yb_nLu_{9-n}, $n = 0, 1, 3, 7, 9$). The clusters were identified with IR and mass spectroscopy as well as elemental analysis. The structural analysis was performed by the combination of powder and single-crystal XRD measurements. The effect of SOC was elucidated by emission spectra and lifetimes. We explore whether the PSET efficiency is reduced or raised in the presence of a strong SOC. Either result provides important insight into fundamental photophysics of Ln(III) complexes as well as factors to consider when designing them and to optimize the energy transfer efficiency.

2. Experimental section

2.1. Materials

$Gd(NO_3)_3 \cdot 6H_2O$ (> 99.95%) and $Lu(NO_3)_3 \cdot 4H_2O$ (> 99.95) were purchased from Kanto Chemical Co., and $Yb(NO_3)_3 \cdot 5H_2O$ (99.9%) was purchased from Sigma-Aldrich Japan. Butylsalicylate was purchased from Tokyo Chemical Industries. Methanol for spectroscopy was purchased from Wako Pure Chemical Industries, Ltd. All reagents were used without further purification.

2.2. Characterization

FAB-MS and ESI-MS spectra were measured on a JEOL JMS-700TZ and JEOL JMS-T100LP, respectively. Elemental analyses were performed by Exter Analytical CE440. Infrared spectra were recorded on a JASCO FT/IR-4600 spectrometer. XRD spectra were characterized by a RIGAKU SmartLab X-ray diffractometer. Single crystal X-ray diffractions were made on a RIGAKU RAXIS RAPID imaging plate area detector.

2.3. Synthesis

Yb_nGd_{9-n} and Yb_nLu_{9-n} clusters were synthesized following the procedures previously reported.[15]