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Luminescence Behaviour in Acetonitrile and in the Solid State of a Series of Lanthanide Complexes with a Single Helical Ligand†‡

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Luminescence mechanisms of Eu^{III}, Tb^{III}, Gd^{III} and Nd^{III} complexes with a hexadentate ligand (abbreviated to Eu**L**, Tb**L**, Gd**L**, and Nd**L**, respectively), which have two bipyridine moieties bridged by an ethylenediamine unit, have been examined. Our molecular design is that each complex forms a single helical polar structure based on the chelate ring to keep solubility in solutions. Eu**L** and Nd**L** show comparably bright emission from ff transitions both in acetonitrile solution and in the solid state. To understand the mechanism of the emission in detail, the energy level of triplet (T) state of the ligand **L** has been estimated based on the phosphorescence measurement of Gd**L,** because Gd^{III} shows no ff emission. The donor level of the T state of **L** and acceptor level of Eu^{III} or Nd^{III} can overlap, resulting that the excited photon localized on **L** has been used for the efficient ff emission, while not for $\pi\pi*$ emission. For Tb**L**, the luminescence quantum yield is significantly dependent on temperature and the state: In the solid state of Tb**L**, the quantum yield of ff emission is over 90 % at 77 K, while no luminescence is observed at room temperature, and in solution Tb**L** shows no emission. This observation suggests that the emissive f-level of Tb^{III} and the energy donor level of the excited T state of **L** are in thermal equilibrium. The described lanthanide complexes are stable and keep their molecular structure even in solutions and show characteristic luminescence behaviour based on the energy relaxation process of each lanthanide ion. Furthermore the Ho^{III} complex with **L** (Ho**L**) has been prepared and its structure has been analyzed. Ho**L** has a twisted arrangement of bpy moiety surrounding Ho^{III} due to the small ionic radius of Ho^{III}.

Introduction

Highly luminescent lanthanide (Ln) complexes have attracted much attention because they are applied to functional materials such as OLED,[1-6] solar cell systems,[7,8] and sensors in solutions.[9-13] Recently, intensive work has focused on the Ln complexes with organic ligands which exhibit significant luminescent properties.[14,15]

The spectral feature of their luminescence originated from ff-electronic transitions of Ln complexes, generally, is specific

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† Electronic supplementary information (ESI) available: Detailed preparation and characterizations of the complexes. CCDC 919427 – 919431 (a series of lanthanide complexes with **L**). Electronic absorption spectra of Nd**L** and Ho**L**, excitation spectra, luminescence decay curves, and representation of energy transfer mechanisms for the complexes.

‡ Dedicated to Dr. Toshihiko Hoshi, Professor Emeritus from Aoyama Gakuin University, on the occasion of his 77th birthday.
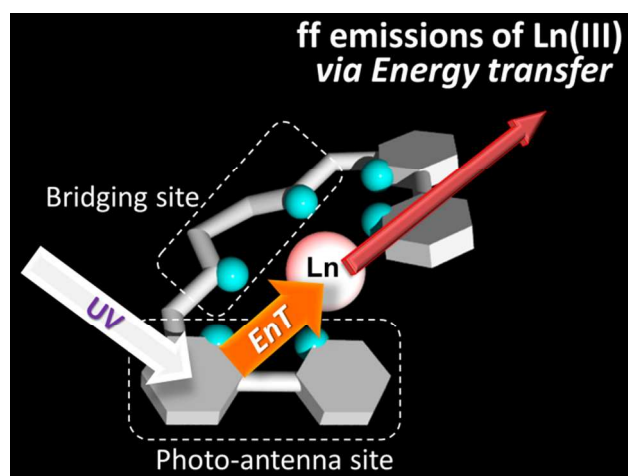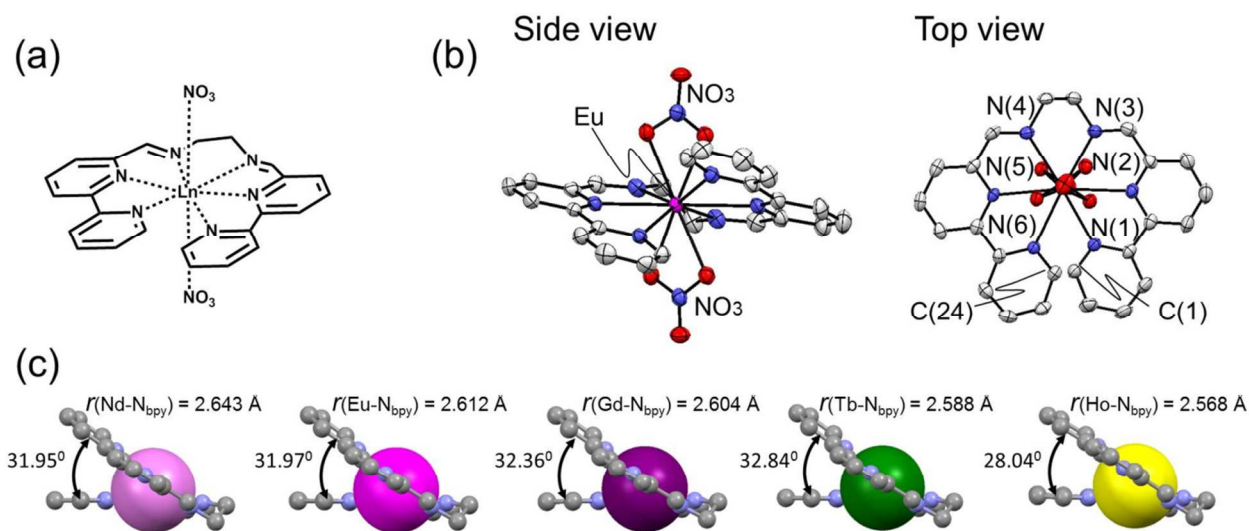

Fig. 1 Strategy to design a helical molecular structure to keep a strong dipole momentum to induce the ff-emission of Ln complexes. In this figure, *EnT* means the intramolecular energy transfer.

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Fig. 2 Top: Molecular structure of LnL (a) and the ORTEP drawing of EuL with 70% probability thermal ellipsoids (b) obtained from the single crystal X-ray analysis. Hydrogen atoms, PF$_6^-$ and acetonitrile are omitted for clarity. Bottom: (c) side views to compare the dihedral angles among two bipyridine moieties and averaged binding distances between a Ln ion and nitrogen atoms localized on bpy moieties for a series of LnL (Ln = Nd, Eu, Gd, Tb and Ho). Gray: carbon, blue: nitrogen, red: oxigen, lilac: neodimium, pink: europium, violet: gadrinium, green: terbium and yellow: hormium. For each of the illustrations, LnL has no NO$_3^-$ for clarity.

compared with that of fluorescence or phosphorescence of neat organic compounds[16,17]; the ff emission of Ln ion appears as narrow bands because of the inner-core transitions shielded from outer-sphere, and has been induced by the photo-excitation of π-electronic systems of the organic ligand moieties via an intramolecular energy transfer.[18-21] In other words, for these Ln complexes, the π-electronic moieties of the ligands act as photo-antennas and as energy donors, and splitter of f-level of Ln^{III} as an acceptor in the complexes. The energy differences between energy donor and acceptor based on molecular design affect directly the efficiency of ff-emissions. For instance, there are a number of papers to describe Ln complexes with organic ligand showing over 50 % or a 100 % efficiency in the luminescence.[16] These ligands also exert structural effects on the properties of the Ln complexes. For instance, such structural modifications lead to the tuning of luminescence efficiency and the band appearances of the ff emission[22-26]. Moreover, the enhanced ff emission may be induced, if the ligands act as a shield from outer-sphere with a stable structure in solution[23,27-30] or in the solid states.[24,31-35]

A chelate effect provides a fundamental but most useful technique to design stable metal complexes, and the coordination number of the chelate ring contributes to the stability constant of the coordination in solution. There are some manuscripts for metal complexes, eg. Co, Cu, Fe, Zn, Ag, Eu ion, with hexadentate ligand forming the helicate molecular structure.[36-38] It is well known that Constable and Tocher *et al.* reported various metal complexes having d- or f-block ions with helicate of a polypyridyl ligand. In their evolutionary of the molecular

preparation,[38] for instance, six pyridine moieties in the ligand demonstrated to have an ability to form a single-helical structure by coordinating with a Eu ion.

Our approach is to understand the emission mechanism of a series of lanthanide (Eu, Gd, Tb, and Nd) complexes, in view of photochemistry to realize efficient luminescent principle in the solid state and in solutions. Under the strategy, we designed a new hexadentate ligand to wind the Ln ion, and the formed complex would keep the strong dipole moment to dissolve into solution with emitting ability (Fig. 1). The target complexes would have five pentagonal-chelate-rings in a molecule to keep their stability in solution; so called as a chelate effect. It is expected that the molecular structure with the organic ligand would form a co-planar structure, and both sides of the structure would give two exchangeable/ flexible sites.

In the present study, electronic transitions of a series of new Ln complexes (abbreviated to LnL, Ln = Nd, Eu, Gd, Tb and Ho shown in Fig. 2) have been discussed. In particular, we have focused on the emission properties of the Eu and Tb complexes both in solution and the solid states. Here, we use a hexadentate ligand **L** having two bipyridine (abbreviated to bpy) moieties bridged by an ethylenediamine unit (abbreviated to en) designed based on the above strategy. Two bpy moieties may also act as photo-antenna to transport the excitation energy for the Ln excitation. The en group prevents conjugation of two bpy in LnL, and the excited state of π electronic system of the bpy can be treated as the same as those of simple bpy derivatives. The X-ray structural analysis of a series of LnL (Ln = Nd, Eu, Gd, Tb and

Ho) complexes were also performed to support spectral discussion concerning the molecular structure.

Results and discussion

1. Structural analyses

5 We have thus synthesized a new ligand **L** containing two bipyridine and a series of Ln**L** (Nd, Eu, Gd, Tb and Ho) complexes with L are abbreviated to Nd**L**, Eu**L**, Gd**L**, Tb**L** and Ho**L**, respectively).
The single crystal structures of Ln**L** have been determined by
10 each other in a van der Waals distance, r(C(1)-C(24)) = 3.176 Å

in Eu**L**. Furthermore, two nitrato anions bind to the Eu from both apical sites, and the Eu ion has total coordination number of ten. From the comparison of molecular shape of a series of Ln**L** (Ln = Nd, Eu, Gd, Tb and Ho), it is found that **L** can form the same
15 molecular structure with other Ln ions (Fig. S3 and Table 1). These metal ions are in the order corresponding to the ionic radii and atomic number, i.e., the ionic radius of Nd^{III} is larger than that of Ho^{III} known as the lanthanide contraction. The interatomic distance shows the averaged value of six Ln-N_{bpy} distance, r(Ln-
20 N_{bpy}), of each complex (Table S1 and S2). It is worth noting that the lanthanide contraction affects the length of Ln-N_{bpy} bonding and the distance of the terminal pyridyl group in the bpy skeleton

25 **Table 1** Crystallographic data for Ln**L**.

Ln	Nd	Eu	Gd	Tb	Ho
Formula	$C_{26}H_{23}F_6N_9NdO_6P$	$C_{26}H_{23}EuF_6N_9O_6P$	$C_{26}H_{23}F_6GdN_9O_6P$	$C_{26}H_{23}F_6N_9O_6PTb$	$C_{28}H_{26}F_6HoN_{10}O_6P$
Formula weight	846.74	854.46	859.75	861.42	908.49
Crystal size (mm)	0.13×0.09×0.02	0.15×0.11×0.08	0.18×0.16×0.10	0.22×0.10×0.08	0.13×0.09×0.02
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1	P-1
a (Å)	8.949(2)	8.9999(9)	9.0151(7)	9.0172(11)	9.961(3)
b (Å)	12.231(3)	12.2528(12)	12.2140(9)	12.2389(15)	13.593(4)
c (Å)	16.394(4)	16.2526(16)	16.1835(12)	16.133(2)	13.751(4)
α (°)	112.158(2)	112.3060(10)	112.0360(10)	112.0540(10)	68.307(3)
β (°)	104.132(2)	104.4460(10)	104.2970(10)	104.2690(10)	86.035(3)
γ (°)	92.428(3)	91.8160(10)	91.8260(10)	91.6220(10)	87.405(3)
V (Å^3)	1593.4(7)	1589.6(3)	1585.2(2)	1584.7(3)	1725.5(9)
Z value	2	2	2	2	2
D_{calcd} (Mg m^{-3})	1.765	1.785	1.801	1.805	1.749
μ (Mo Kα) (mm^{-1})	1.770	2.114	2.234	2.373	2.428
F(000)	838	844	846	848	896
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature (K)	100	100	100	100	100
$R1^a$ ($I > 2.00\sigma(I)$)	0.0308	0.0349	0.0325	0.0294	0.0378
$wR2^b$ ($I > 2.00\sigma(I)$)	0.0823	0.0947	0.0821	0.0807	0.0845
Goodness of fit	1.055	1.082	1.061	1.073	1.072
Largest peak and hole (e Å^{-3})	2.110, −1.090	2.639, −1.439	2.311, −1.227	2.870, −1.409	3.002, −1.530

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$
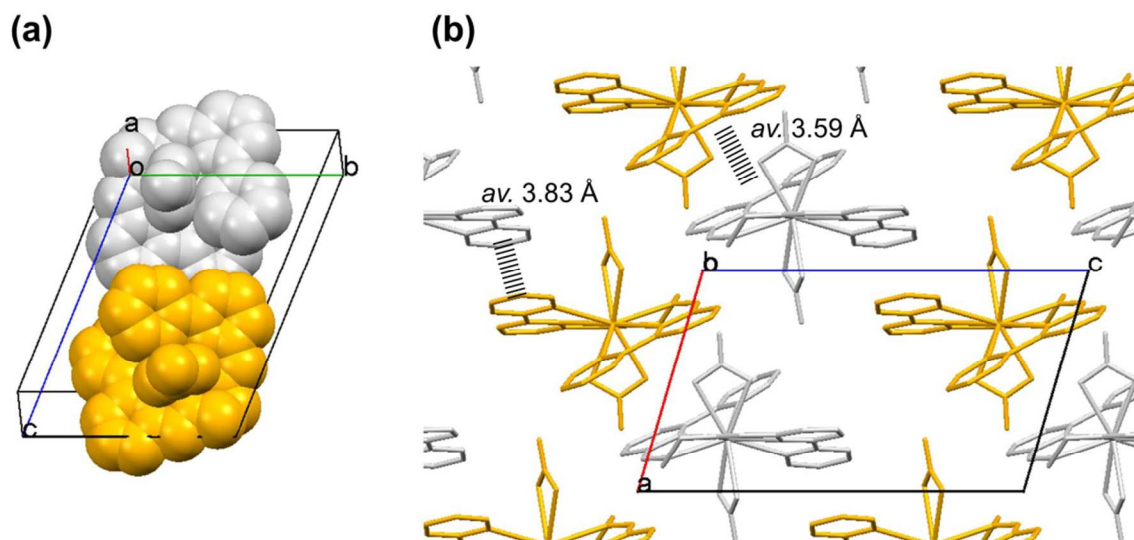
Fig. 3 (a) Two isomers in a unit cell of Eu**L**, having left-handed (gold) and right-handed (silver) isomers obtained from an X-ray single crystal structural analysis. (b) Molecular packings of Eu**L** projected from along the *b*-axis. (Hydrogen atoms, PF_6^- and acetonitrile are omitted for clarity)**.**

based on the periodicity of Ln ionic radii. The dihedral angle among two bipyridine moieties of the complex increases periodically in the increasing atomic numbers. It is reflected in their electronic repulsion among the terminal pyridyl group in the bpy skeleton, since the changes of distances of the $Ln-N_{bpy}$ bonding. In the case of Ho**L**, the dihedral angle is not on the periodicity, because of the distortion of bpy skeletons.

In a unit cell of Eu**L**, there are two molecules having chiralities; a right- and left-handed isomers (Fig. 3(a)). A couple of hexafluorophosphate and acetonitrile is also included into the unit cell of Eu**L** (Fig. S4(a)). As shown in Fig. 3(b), the molecular packing of Eu**L** suggests that two isomers between the neighbor unit cells interact through the intermolecular ππ interaction of their bpy skeletons in the distance of 3.58 – 3.87 Å. This interaction results in the formation of their independent column-like structure as shown in Fig. S4((b) and (c)), which is supported by the existence of PF_6^- ions and acetonitrile molecules.

X-ray structure analysis reveals that all complexes are isostructural with the each lanthanide counterpart, and the Nd, Eu, Gd, and Tb complexes are isomorphous with each other. Remarkably, the detailed crystallographic analysis clarified the void spaces in these complexes, which are placed around inversion centre of unit cell as shown in Fig. S5 and Table S3, originated from the desolvation of one acetonitrile. This means that 1.5 acetonitrile molecules were in asymmetric unit and totally three acetonitrile molecules were in unit cell before desolvation was occurred. In this case, the space group of the initial crystal should have lower symmetry, P1, compared to that of the desolvated crystal, P-1, because acetonitrile is not a symmetric molecule. The channel structure of the solvents makes it possible to desolvate easily from the crystal.

Among those complexes, Ho**L** is the only one complex that has two molecules of acetonitrile in asymmetric unit, meaning that there are totally four acetonitrile molecules in a unit cell.

2. Luminescence properties of Ln**L**

To discuss the luminescence spectra of Ln**L**, the electronic absorption spectra should be observed, because they generally give much information for their electronic and molecular structure. Fig. 4 shows the electronic spectra localized on the
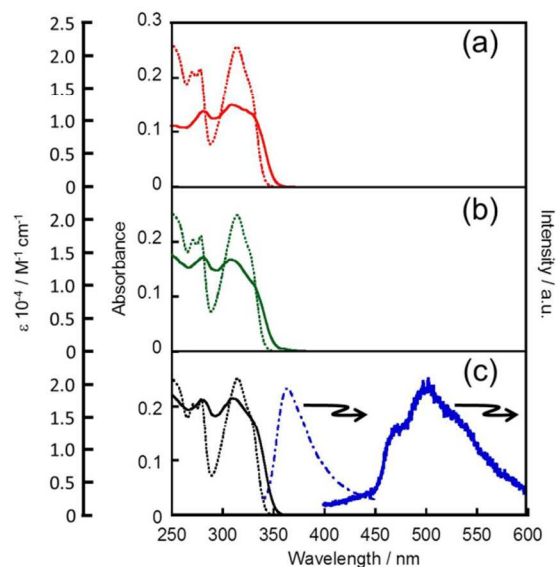
Fig.4 Electronic spectra of Eu**L** (a), Tb**L** (b), and Gd**L** (c) localized on the π electronic systems. Absorption spectra in acetonitrile (dotted line) and in the solid state (solid line) use the left vertical scales; emission spectra in the solid state at rt (dotted-dash) and 77 K (thick) the right one (λ_{ex} = 330 nm).
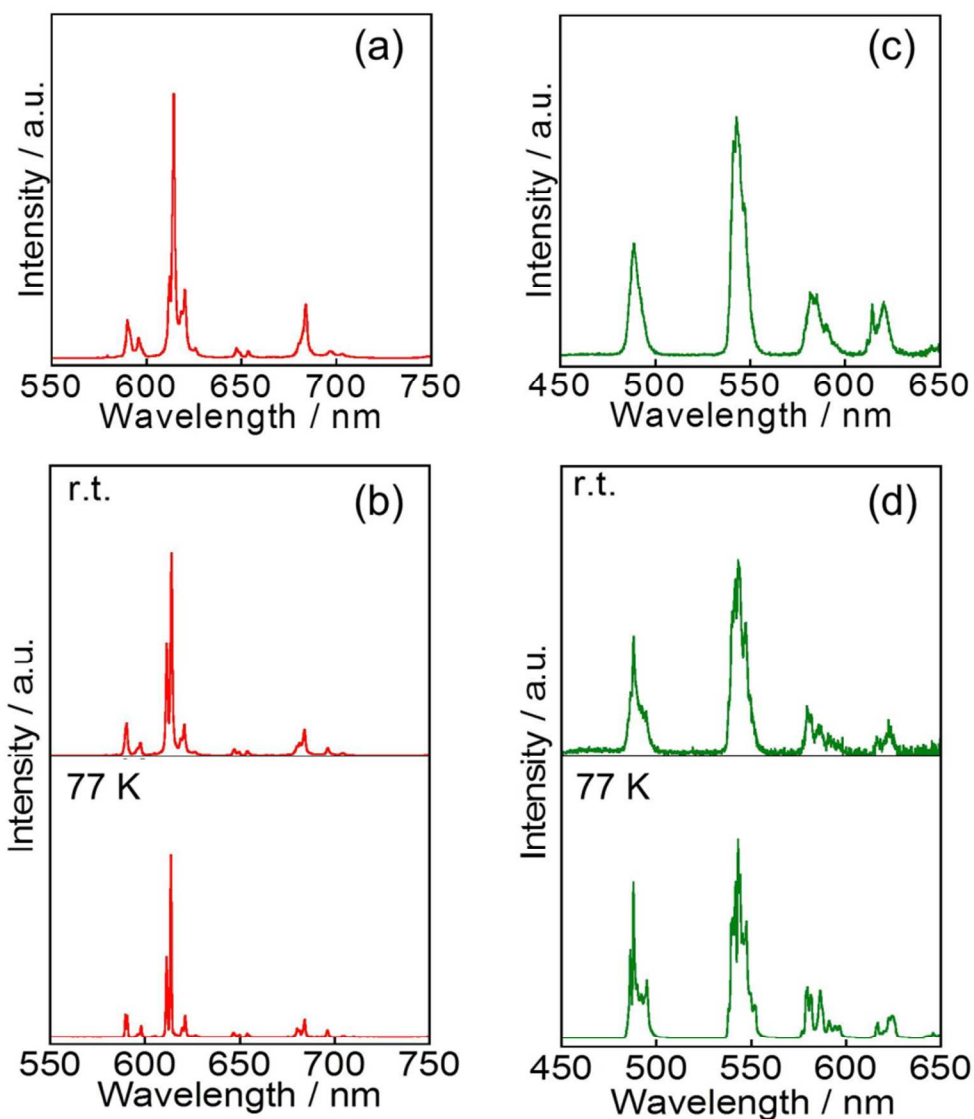
Fig. 5 Luminescence spectra of EuL ((a) and (b)) and TbL ((c) and (d)). (a) and (c) are in acetonitrile at rt, and (b) and (d) in the solid state at rt and 77 K (λ_{ex} = 330 nm).

5 **Table 2** Luminescence lifetimes τ_{obs} (amplitude) and absolute luminescence quantum yields Q^L_{Ln} of ff emissions of LnL (Ln = Eu and Tb).

		Temp.	τ_{obs} [ms] (Amp.)	Q^L_{Ln} [%][a]
EuL	in the solid state	rt	1.27 (1.0)	52.6 (±1.4)
		77 K	1.35 (1.0)	63.5 (±2.7)
	in acetonitrile	rt	1.55 (1.0)	12.0 (±0.5)
TbL	in the solid state	rt	0.0153 (0.96) 0.00234 (0.04)	1.0 (±0.2)
		77K	1.49 (1.0)	91.5 (±1.4)
	in acetonitrile	rt	n. d.	≈0

[a] the values of Ln emission were based on the ligand excitation.

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ligand moieties of EuL, GdL and TbL in the solid state and in acetonitrile. All complexes LnL show the $\pi\pi^*$ absorption bands of the ligand mainly at 280, 305 and 330 nm in the solid state. 15 Their corresponding bands appear at 275, 315 and 330 nm, respectively, in solution. This observation suggests that a series of LnL form molecular structures similar to those in solution and similar molecular arrangements in the solid state. ESI-TOF-MS spectra of these complexes in acetonitrile show a molecular ion 20 for each LnL unit (Fig. S2). The shape of the broadened absorption band in the solid state compared with that in the solution is attributed to the intermolecular interaction as above mentioned. The electronic absorption bands of EuL are observed in acetonitrile, and the band at 330 nm can be ascribed as the 25 lowest $\pi\pi^*$ transition experimentally. The $\pi\pi^*$ electronic absorption bands of NdL and HoL also appear at exactly corresponding position of those of EuL (Fig. S6). Additionally, NdL or HoL shows sharp absorption bands originated from the ff-transitions of Nd^{III} or Ho^{III} as shown below. 30 To estimate the energy donor level of L of LnL, luminescence

spectra of Gd**L** have been examined, since a split upper f-level of Gd[III], ^6P_J, locates in the vacuum ultra violet region meaning that Gd[III] shows no ff emission. Emission bands of Gd**L** are observed at 361 (27500) and *ca.* 500 nm (as a broadened band 21700 -
5 16600 cm^{-1}) mainly, at rt and 77 K, respectively (Fig. 4c).

The former transition and latter are assigned to the fluorescence ^{1}S and phosphorescence T band, respectively, localized on the bpy moiety of Gd**L**. It means that the excited T level of **L** is suitable to act as an energy donor to Eu[III] or Tb[III]. The complex,
10 Eu**L** or Tb**L** (also, Nd**L**), shows no $\pi\pi^*$ emissions, because the excited ligand-centred photon prevails for energy transfer to Eu[III] or Tb[III] relative to the $\pi\pi^*$ relaxations. It is notable that these ff emission properties in our present systems are unique, because the complexes have no $\pi\pi^*$ emission due to the efficient
15 intramolecular energy transfer from **L** to Ln[III].

The luminescence spectra of Eu**L** and Tb**L** in acetonitrile and in the solid state are shown in Fig. 5. Eu**L** in the solid state at rt shows the ff emission of trivalent Eu ion at 580, 593, 614, 650 and 684 nm, which are assigned to the $^5D_0\rightarrow^7F_0$, $^5D_0\rightarrow^7F_1$,
20 $^5D_0\rightarrow^7F_2$, $^5D_0\rightarrow^7F_3$ and $^5D_0\rightarrow^7F_4$ transitions, respectively. These bands of Eu**L** appear at the same position at 77 K. These corresponding bands are also observed at almost the same position in acetonitrile. Each excitation spectrum monitored at the ff emission band position reproduces well each electronic
25 absorption spectrum assigned to the lowest excited state of **L** (Fig. S7).

Absolute luminescence quantum yields Q^L_{Ln} and luminescence lifetimes τ_{obs} of Eu**L** and Tb**L** are estimated and the values are
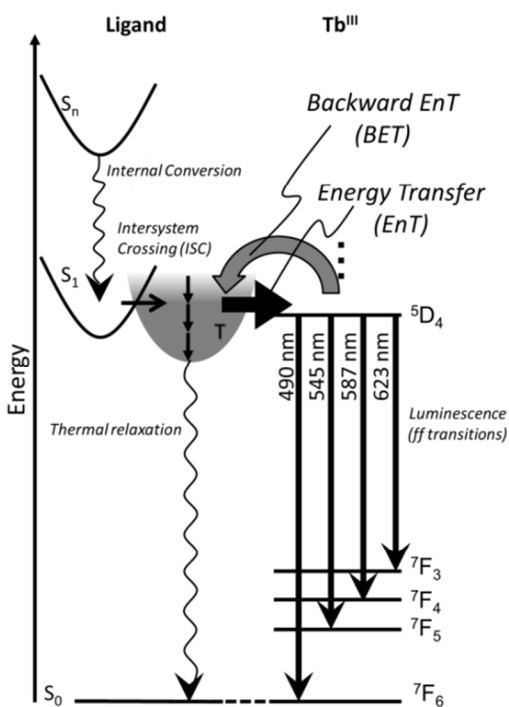
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Fig. 6 Schematic representation of a plausible energy diagram of the electronic transitions of Tb**L**.
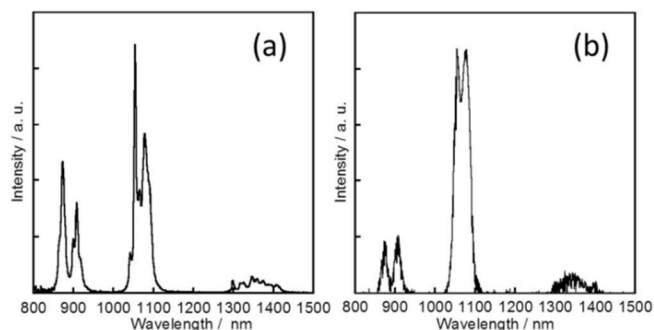

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Fig. 7 Luminescence spectra of Nd**L** (a) in the solid state and (b) in acetonitrile (λ_{ex} = 330 nm).

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given in Table 2. The τ_{obs} values for ff-emissions of Eu**L** in the solid state and in acetonitrile as well as Tb**L** in the solid state at 77 K are closer each other in 1.27 – 1.55 ms (Fig. S8). The Q^L_{Ln} values of Eu**L** in the solid state preserve over 50 % at ambient
45 and low temperatures. Furthermore, the Q^L_{Ln} value of Eu**L** in acetonitrile is 12 %, which is not all that high while enough to discuss photo properties even in solutions as same as those of other system[39].

It is generally known that the ff emissions of Tb[III] show thermal
50 sensitivity, which is caused by the thermal equilibrium on the energy transfer pathway between the T level of **L** and the energy acceptor level of Tb[III].[40] It is noteworthy that Tb**L** also leads to the efficient luminescence of Tb**L** at 77 K. Luminescence bands of Tb**L** in acetonitrile appear at 490, 545, 587 and 623 nm, which
55 are assigned to the $^5D_4\rightarrow^7F_6$, $^5D_4\rightarrow^7F_5$, $^5D_4\rightarrow^7F_4$ and $^5D_4\rightarrow^7F_3$ transitions, respectively (Fig. 5c). These band positions are almost the same as those in the solid state (Fig. 5d). Based on the estimation of Q^L_{Ln} values of Tb**L** (Table 2), the values at ambient temperature both in the solid state and in acetonitrile show
60 negligible low values. While, it is significant that at 77 K in the solid state, the Q^L_{Ln} value of Tb**L** drastically increases over 90 %. As far as we know, this value is the remarkably high value of quantum yields in Tb complexes[16a, 41], and thus drastic thermal effect on the value is unusual. The energy relaxation mechanism
65 of Tb**L** is shown in Fig. 6; the T level of **L** acts as an energy donor via intersystem crossing after the internal conversion. That is, this thermal sensing effect of Tb**L** is caused by the equilibrium between the emissive level of Tb[III] and the energy donating level of **L**. Also, it is known that molecular oxygen acts as a quencher
70 for the aromatic triplet excited state and similarly affect the lanthanide luminescence[42]. Thus, the significant low Q^L_{Ln} value of Tb**L** in acetonitrile might be affected by such oxygen molecule effect with thermal relaxation.

Emission and excitation spectra of Nd**L** in various conditions
75 are shown in Fig. 7 and S9, respectively. The ff emission bands of Nd[III] appear at 906, 1055 and 1345 nm assigned as the $^4F_{3/2}\rightarrow^4I_{9/2}$, $^4F_{3/2}\rightarrow^4I_{11/2}$ and $^4F_{3/2}\rightarrow^4I_{13/2}$ transition, respectively. Former two transitions are divided into two or more by the Stark effect. The emission efficiency is quite low and it is difficult to
80 estimate a quantitative value. However, it is found that the ligand **L** also acts as an energy donor and sensitizes the ff emissions of Nd[III] in the NIR region, since the excitation spectrum shows well
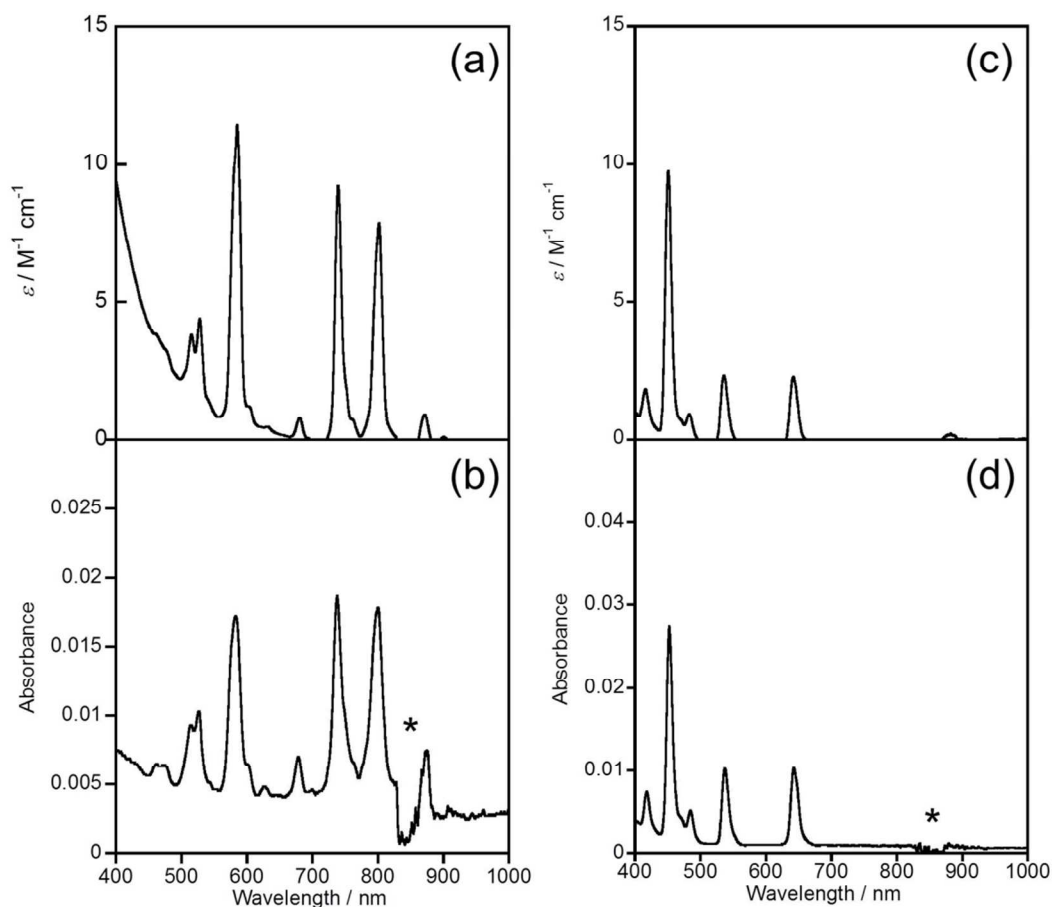
Fig. 8 Electronic absorption spectra of Nd**L** ((a) and (b)) and Ho**L** ((c) and (d)) in acetonitrile (upper) and in the solid state (bottom) (* due to apparatus).

correspondence with the absorption bands of **L**, not ff transitions of Nd^{III} (Fig. 8a and 8b). In the solid state, the ff-absorption bands of Nd**L** in the visible-NIR region appear at 468 (the $^4I_{9/2} \to {}^4G_{9/2}$ transition), 526 ($^4I_{9/2} \to {}^4G_{7/2}$), 584 ($^4I_{9/2} \to {}^4G_{5/2}$), 626 ($^4I_{9/2} \to {}^2H_{11/2}$), 679 ($^4I_{9/2} \to {}^4F_{9/2}$), 739 ($^4I_{9/2} \to {}^2H_{9/2}$), 800 ($^4I_{9/2} \to {}^4S_{3/2}$) and 874 ($^4I_{9/2} \to {}^4F_{3/2}$) nm. Corresponding ff-absorption bands of Nd**L** in the solid state were clearly observed in acetonitrile.

Ho**L** also shows the bands at 420 ($^5I_8 \to {}^5G_5$), 450 ($^5I_8 \to {}^5G_6$), 472 ($^5I_8 \to {}^3K_8$), 486 ($^5I_8 \to {}^5F_2$), 537 (overlap of $^5I_8 \to {}^5F_4$ and $^5I_8 \to {}^4S_2$) and 644 ($^5I_8 \to {}^5F_5$) nm in acetonitrile and in the solid state (Fig. 8c and 8d). Since small differences among the split f-levels of Ho^{III}, thermo-relaxation prevails over photo-relaxation (luminescence).

Energy diagrams of the relaxation process of Eu**L**, Gd**L** and Nd**L** are illustrated in Fig. S10. The phosphorescence band position and width of Gd**L** refer the energy donor level against Ln ions. Since the structural analyses and the electronic absorption spectra localized on **L** for these complexes are shown in accordance each other, it is considered that the donor level of **L** (triplet) of all complexes exist at the same energy level. The acceptor level of Eu^{III} is more overlapped with the donor (Fig. S10 (a)) than that of Nd^{III} (Fig. S10 (c)). These differences of Eu**L** and Nd**L** would affect the luminescence efficiencies.

Conclusions

The above presented new organic ligand forms stable Ln complexes with Nd, Eu, Gd, Tb and Ho. All of them formed similar helical molecular structure in crystalline state. Based on the above spectral results, Tb**L** is preferred to thermal energy relaxation, since the thermal equilibrium between energy donor and acceptor level has been more preferential than the vibration effect of intermolecular interactions among neighbour complexes. Furthermore, in solution, the ff-emission property of Eu**L** is still present although it is less pronounced than in the solid state. This seems to be due to its stable molecular structure. Also Nd**L** shows the respective ff-emission in the NIR region even in solution, despite its low efficiency probably due to its electronic structure. All complexes Ln**L** with ff-emission properties do not show $\pi\pi^*$ luminescence, meaning that the photo-antenna acts efficiently.

Experiments

Materials and synthesis

Synthesis of ligand (L). Most reagents and spectra-grade solvents were used without further purification. Bipyridine-6-aldehyde was obtained by mixing of 6-bromo-bipyridine 2.10 g (8.93 mmol; Isotech Laboratories, Inc.) and *n*-buthyl-lithium 6.80 g (10.9 mmol) in THF at − 80 ^{0}C for 30 min, then stirred for 1 h after addition of dimethylformamide[43] (0.670 mg, 3.64 mmol, 40.8 % yield). ^{1}H-NMR (500.00 MHz, CDCl$_3$); δ 10.2 (s, 1H), 8.72 (d, ^3J = 4.1 Hz, 1H), 8.64 (m, 1H), 8.57 (d, ^3J = 8.2 Hz, 1H), 8.00 (m, 2H), 7.86 (m, 1H), 7.23 (m, 2H), 7.38 (m, 1H).

The hexadentate ligand **L** was prepared by the reaction of bipyridine-6-aldehyde 200 mg and ethylene-diamine (Kanto Chemicals Co., Inc.) in methanol (160 mg, 0.408 mmol, 74.9 % yield). ^{1}H-NMR (500.00 MHz, CDCl$_3$); δ 8.64 (d, ^3J = 4.1 Hz, 2H), 8.53 (s, 2H), 8.41 (dd, ^3J = 7.8 and 7.3 Hz, 4H), 8.04 (d, ^3J =6.9 Hz, 2H), 7.80 (t, ^3J = 7.8 Hz, 2H), 7.73 (m, 2H), 7.23 (m, 2H), 4.10 (s, 4H). ^{1}H-NMR chart of above compounds are shown in Fig. S1.

Synthesis procedure for Ln complexes with L. Lanthanide complexes with **L**, Ln**L** (Ln = Nd, Eu, Gd, Tb and Ho), were obtained by the reaction between **L** and lanthanide nitrato *n*-hydrate in methanol. For the crystallization, one nitorato ion was exchanged to PF$_6$$^-$ by the NH$_4$PF$_6$ addition into their solution. The results with elemental analyses and ESI-TOF-MS (Fig. S2) for the complexes were summarized below.

NdL

50.4 mg (0.115 mmol) Nd(NO$_3$)$_3$ 6H$_2$O, 45.0 mg (0.115 mmol) **L** and NH$_3$PF$_6$ 18.7 mg (0.115 mmol). Yield 77.2 mg (80.1 %). Elemental analysis, calcd for [Nd(**L**)(NO$_3$)$_2$](PF$_6$) (C$_{24}$H$_{20}$N$_8$O$_6$NdPF$_6$); C 35.78, H 2.50, N 13.91; found; C 35.48, H 2.56, N 14.07; MS (ESI-TOF, acetonitrile); *m/z*, 657.94 [M - PF$_6$$^-$]$^+$ (calcd. 658.06).

EuL

51.3 mg (0.115 mmol) Eu(NO$_3$)$_3$ 6H$_2$O, 45.0 mg (0.115 mmol) **L** and NH$_3$PF$_6$ 18.7 mg (0.115 mmol). Yield 51.3 mg (55 %). Elemental analysis, calcd for [Eu(**L**)(NO$_3$)$_2$](PF$_6$) (C$_{24}$H$_{20}$N$_8$O$_6$EuPF$_6$); C 35.44, H 2.48, N 13.78; found; C 35.27, H 2.62, N 13.70; MS (ESI-TOF, acetonitrile); *m/z*, 668.97[M - PF$_6$$^-$]$^+$ (calcd. 669.07).

GdL

121 mg (0.270 mmol) Gd(NO$_3$)$_3$ 6H$_2$O, 105.6 mg (0.270 mmol) **L** and NH$_3$PF$_6$ 44.0 mg (0.270 mmol). Yield 58.4 mg (31 %). Elemental analysis, calcd for [Gd(**L**)(NO$_3$)$_2$](PF$_6$) (C$_{24}$H$_{20}$N$_8$O$_6$GdPF$_6$); C 35.21, H 2.46, N 13.69; found; C 35.12, H 2.68, N 13.62; MS (ESI-TOF, acetonitrile); *m/z*, 674.06 [M - PF$_6$$^-$]$^+$ (calcd. 674.08).

TbL

52.1 mg (0.115 mmol) Tb(NO$_3$)$_3$ 6H$_2$O, 45.0 mg (0.115 mmol) **L** and NH$_3$PF$_6$ 18.7 mg (0.115 mmol). Yield 68.3 mg (62 %). Elemental analysis, calcd for [Tb(**L**)(NO$_3$)$_2$](PF$_6$) (C$_{24}$H$_{20}$N$_8$O$_6$TbPF$_6$); C 35.14, H 2.46, N 13.66; found; C 35.26, H 2.70, N 13.50; MS (ESI-TOF, acetonitrile); *m/z*, 675.02 [M - PF$_6$$^-$]$^+$ (calcd. 675.08).

HoL

50.7 mg (0.115 mmol) Ho(NO$_3$)$_3$ 5H$_2$O, 45.0 mg (0.115 mmol) **L** and NH$_3$PF$_6$ 18.7 mg (0.115 mmol). Yield 79.4 mg (80.4 %). Elemental analysis, calcd for [Ho(**L**)(NO$_3$)$_2$](PF$_6$)·H$_2$O (C$_{24}$H$_{22}$N$_8$O$_7$HoPF$_6$); C 34.14, H 2.63, N 13.27; found; C 33.95, H 2.93, N 13.19; MS (ESI-TOF, acetonitrile); *m/z*, 680.97 [M - PF$_6$$^-$]$^+$ (calcd. 681.08).

Instrumentation

Electronic absorption and luminescence spectra were recorded on a Shimadzu UV3101PC and a Horiba Jobin-Ybon Fluorolog 3-22. The NIR emission was detected by the attachment C1452-AU on the above apparatus. The emission decay curves were measured by a Quantaurus-Tau C11367-12 (Hamamatsu Photonics K. K.) excited by Xenon flash lamp with band-path filter (λ_{ex} = 340 nm). The fluorescence quantum yields were measured by The C9920-02 Absolute PL Quantum Yield Measurement System (Hamamatsu Photonics K. K.).[44]

Electrospray ionization time of flight (ESI-TOF) mass spectra and elemental analyses for CHN were recorded on a LCT ESI-TOF spectrometer (Micromass), and MICRO CORDER (J-SCIENCE LAB), respectively.

X-ray crystallography

X-ray structural data for Ln**L** (Ln = Nd, Eu, Gd, Tb and Ho) were collected on a Bruker Smart APEX-II CCD diffractometer equipped with graphite monochromated Mo Kα radiation at 100 K. The data were collected to a maximum 2 h value of 55° and processed using the Bruker Apex2 software package.[45] The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELX-97.[46] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were located at idealized positions. Summaries of the fundamental crystal data and experimental parameters used to determine the structures of complexes Ln**L** are given in Supporting Information. CCDC 919427-919431 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Notes and references

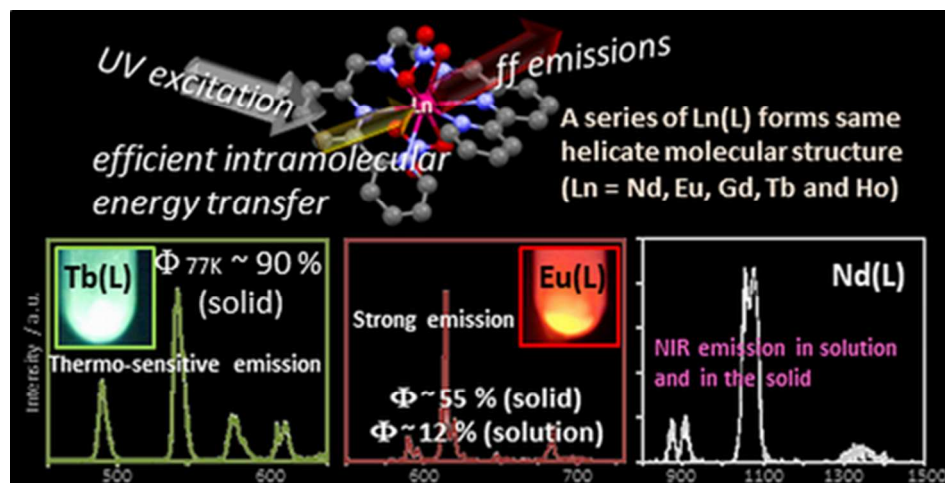1 (a) M. A. Katkova and M. N. Bochkarev, *Dalton Trans.*, 2010, **39**, 6599; (b) G. Zucchi, *Int. J. Inorg. Chem.*, 2011, **2011**, 92435; (c) J. Kido and Y. Okamoto, *Chem. Rev.*, 2002, **102**, 2357.

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