

REVIEW ARTICLE

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# Effective photosensitized, electrosensitized, and mechanosensitized luminescence of lanthanide complexes

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## Abstract

The 4f–4f emission of Tb(III), Eu(III), and Sm(III) complexes plays an important role in the design of monochromatic green, red, and deep-red luminescent materials for displays, lighting, and sensing devices. The 4f–4f emission of Yb(III), Nd(III), and Er(III) complexes is observed in the near-infrared (IR) region for bioimaging and security applications. However, their absorption coefficients are extremely small ( $\epsilon < 10 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). In this review, photosensitized luminescent lanthanide(III) complexes containing organic chromophores (ligands) with large absorption coefficients ( $\epsilon > 10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) are introduced. Organic molecular design elements, including (1) the control of the excited triplet ( $T_1$ ) state, (2) the effects on the charge-transfer (CT) band, and (3) the energy transfer from metal ions for effective photosensitized luminescence, are explained. The characteristic electrosensitized luminescence (electroluminescence) and mechanoluminescence (triboluminescence) of lanthanide(III) complexes are also explained. Lanthanide(III) complexes with well-designed organic molecules are expected to open avenues of research among the fields of chemistry, physics, electronics, and material science.

## Introduction

Lanthanides comprise a family of highly electropositive period 6 metals. According to the previous literature, lanthanides are defined as lanthanum (La) and 14 other elements (Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu)<sup>1</sup>. A general lanthanide is represented by the symbol Ln. Lanthanides in the stable (III) oxidation state are simply characterized by an incompletely filled 4f shell. The 4f orbital is shielded from the surroundings by the filled 5s<sup>2</sup> and 5p<sup>2</sup> orbitals (an image of the 4f radial distribution function: Fig. 1a). In a configurational coordinate diagram, these levels appear as parallel parabolas (a small offset case: Fig. 1b) because the 4f electrons are well shielded from their surroundings. Therefore, emission transitions yield sharp lines (full-width at half-maximum, FWHM <10 nm) in different spectra, which is a much different result from that seen for semiconductors,

transition materials, and organic molecules, as shown in Fig. 1c (in a large-stokes-shift case: FWHM >50 nm)<sup>2,3</sup>. The emission of light radiation for lanthanide(III) ions comes mainly from electric dipole transitions. Transitions formed in the 4f<sup>n</sup> inner shell of free ions are forbidden because they do not correspond to a change in parity. However, the transitions that are forbidden by odd-parity states become partially allowed by the mixing of the 4f and 5d orbitals through the ligand field. Since the parity does not change dramatically in such a transition, the lifetime of the excited state is long ( $\tau > \text{ms}$ ).

Lanthanide complexes with attached organic ligands are regarded as attractive luminescent materials because of their characteristic narrow emission bands and long emission lifetimes over a wide range of wavelengths (ultraviolet/visible/near-infrared (UV/vis/near-IR)). The 4f–4f emissions from Tb(III), Eu(III), and Sm(III) complexes play an important role in the design of monochromatic green, red, and deep-red luminescent materials for displays, lighting, and sensing devices, respectively

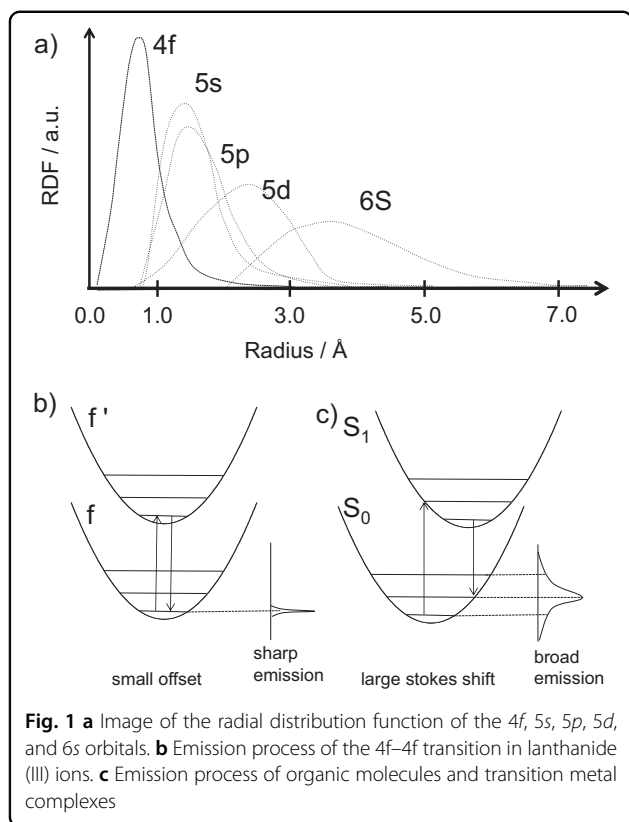
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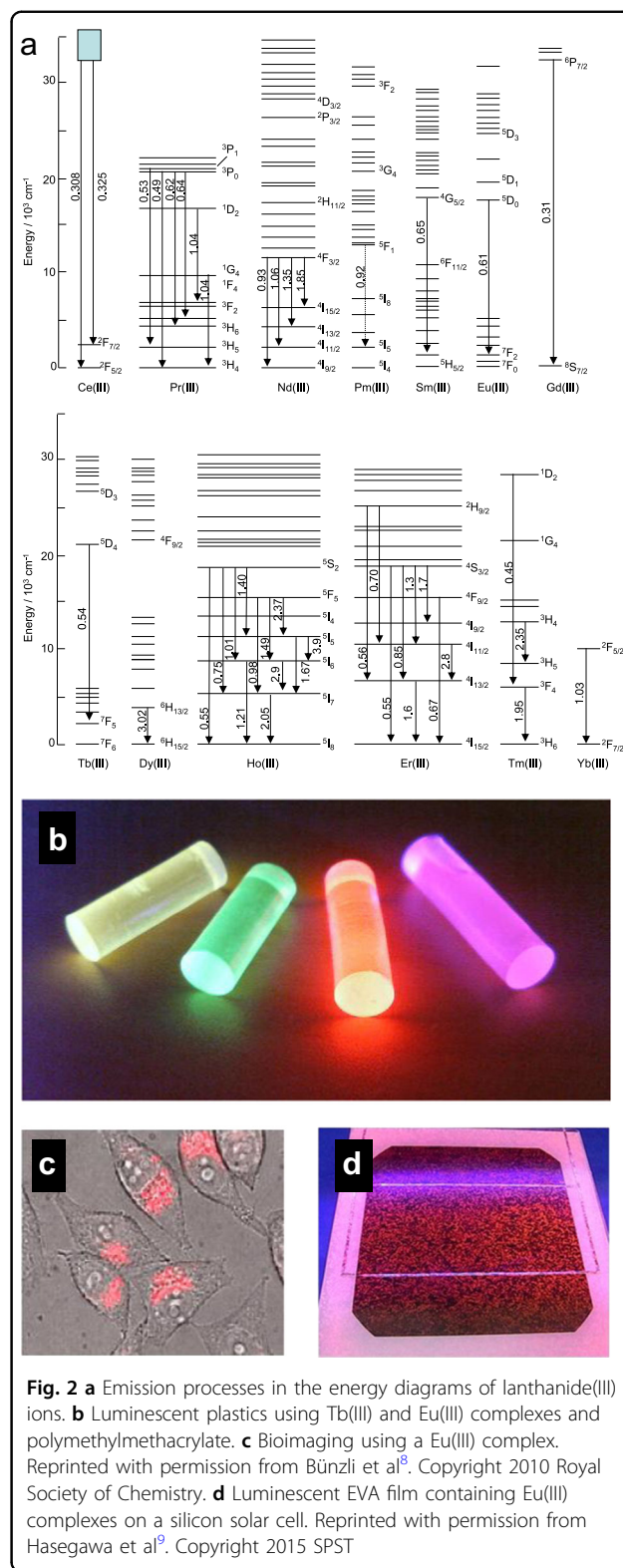


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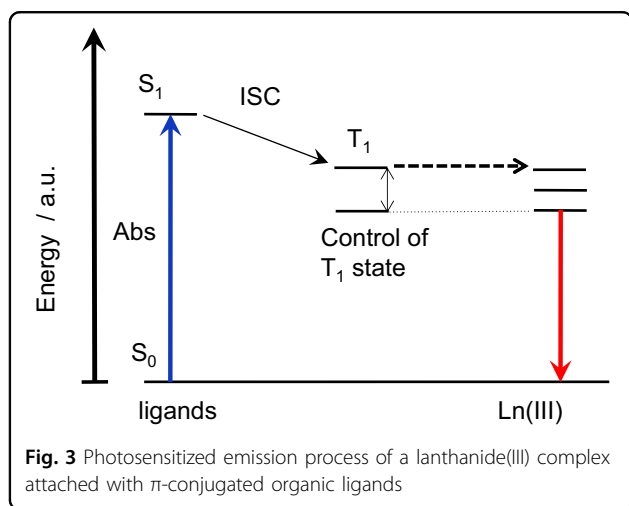


(Fig. 2a, b)<sup>3–8</sup>. The near-IR 4f–4f luminescence of Nd(III), Er(III), and Yb(III) complexes with long emission lifetimes is useful in bioimaging applications (Fig. 2c)<sup>8</sup>. Effective wavelength converters using lanthanide complexes for silicon solar cells have also been reported (Fig. 2d)<sup>9,10</sup>.

Here, we introduce the history of lanthanide complex studies. The 1930s and early 1940s witnessed the first spectroscopic studies of lanthanide ions in solution. Freed and co-workers<sup>11</sup> found that the relative intensities of the absorption bands of Eu(III) were different in different solvents, and Weissman<sup>12</sup> observed that complexes of Eu(III) with certain UV absorbing ligands were highly luminescent when excited with UV light. Since Eu(III) itself shows only a few very weak absorption bands, the solution of this ion does not offer very bright luminescence. Obviously, certain organic ligands can photosensitize the luminescence of lanthanide ions. It was also found that lanthanide ions quench the fluorescence of organic ligands<sup>13</sup>. Such studies can be considered as the starting points for the research and development of luminescent lanthanide complexes. It took, however, approximately 20 years for photochemists and coordination chemists to take a serious interest in these materials. At the beginning of the 1980s, the field received a new impulse when it became clear that lanthanide complexes could find widespread use in medical diagnostics<sup>14</sup>. In the past 40 years, lanthanide ions also started to receive the



attention of the growing number of organic and supra-molecular chemists. At the present stage, many types of luminescent lanthanide complexes have been reported<sup>15,16</sup>.



The focus of this review is photosensitized and electrosensitized luminescence of lanthanide complexes with effective organic ligands. The absorption coefficients of  $4f-4f$  transitions in Ln(III) ions are extremely small ( $4f-4f$  transition bands:  $\epsilon < 10 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The photosensitized and electrosensitized energy transfer from an organic ligand to a lanthanide(III) ion is a key point for achieving effective luminescence of lanthanide(III) complexes. Various types of organic chromophores (ligands) have been developed to photosensitize the luminescence of lanthanide(III) ions. Luminescent lanthanide(III) complexes with large absorption coefficients ( $\pi-\pi^*$  transition band:  $\epsilon > 10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) have been promising molecules as luminescent materials in the fields of optoelectronics, analytical chemistry, photophysical, and biomedical science.

Organic molecular designs that include (1) the control of the excited triplet ( $T_1$ ) state, (2) the effect on the charge-transfer (CT) band, and (3) the energy transfer from metal ions for effective photosensitized luminescence are explained in the next chapter. The transition bands provide effective photosensitized luminescence of lanthanide complexes. We also summarize the electroluminescence (EL) and mechanoluminescence of lanthanide(III) complexes as energy transfer from the electroexcitation of the organic ligand. The EL of lanthanide(III) complexes has been studied for the development of display devices. The historical reports and recent progress of EL using lanthanide complexes are introduced in this review.

The mechanoluminescence of lanthanide(III) complexes has also been studied over the past several decades. Mechanoluminescence is also called triboluminescence, which is the emission of light from bulk solid materials that originates from mechanical stress. While there have been extensive discussions on the origin of triboluminescence in molecular crystals, some studies have

indicated a contribution from the piezoelectric effect upon breaking non-centrosymmetric bulk crystals. Their EL and mechanoluminescence are dependent on the energy transfer process from the ligands in lanthanide complexes.

The molecular design and the strategies for the development of strong luminescent lanthanide(III) complexes are reviewed to illustrate novel developments in the fields of molecular science, photophysics, electronics, and material science.

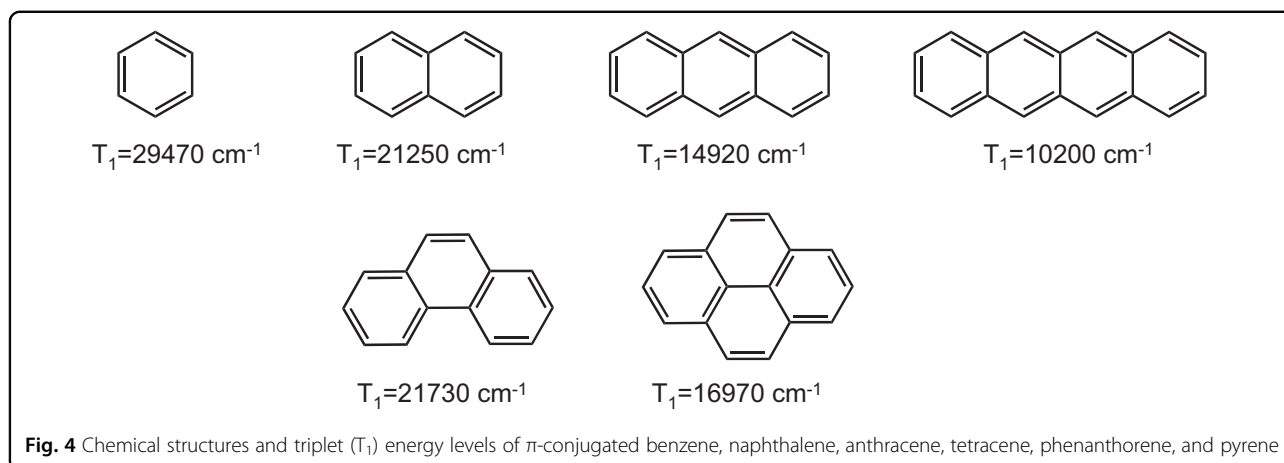
## Photosensitized luminescence from an organic ligand

### Control of the $T_1$ state

First, we introduce the photosensitized energy transfer from organic ligands to lanthanide ions for the development of a strong luminescent lanthanide(III) complex. Effective photosensitized energy transfer is achieved by excitation at the  $\pi-\pi^*$  bands of organic ligands. The  $\pi-\pi^*$  bands of organic ligands can transition and have large absorption coefficients ( $\epsilon > 10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). In the case of a lanthanide(III) complex, the  $S_1$  state of the organic ligand irradiated at the  $\pi-\pi^*$  band rapidly changes to a  $T_1$  state because of the heavy metal effect of the lanthanide(III) ions. For this reason, energy transfer efficiency between the  $T_1$  state and lanthanide(III) ion is key for effective photosensitization.

Here, the photosensitized energy transfer process is explained by using a simple schematic diagram (Fig. 3). First, the organic ligand in the lanthanide(III) complex is excited by photoirradiation at the  $\pi-\pi^*$  transition band, and then, a  $T_1$  state of the ligand is formed. The energy transfer process between the  $T_1$  and  $4f-4f$  transition bands of the lanthanide ion ( $4f-4f'$ ) is generally explained by the Förster and Dexter mechanisms<sup>15,16</sup>. Effective energy transfer (forward energy transfer) between the  $T_1$  (donor) and  $4f-4f'$  (acceptor) leads to the formation of an excited Ln(III) complex. However, a small energy gap between the  $T_1$  state and emitting level of the Ln(III) ion promotes energy back transfer from the  $4f-4f'$  emitting level (donor) to the  $T_1$  state (acceptor), resulting in the prevention of effective forward energy transfer. Thus, effective energy transfer is dependent on the energy gap between the  $T_1$  state and the emitting level in lanthanide (III) complexes.

In Eu(III) complexes with  $\beta$ -diketonate, pyridyl, and carboxylate ligands, the ideal energy gaps between the  $T_1$  state and the emitting level (Tb(III):  ${}^7F_6-{}^5D_4$ , Eu(III):  ${}^7F_0-{}^5D_0$ ) for the suppression of energy back transfer are estimated to be more than 2400 and 2500  $\text{cm}^{-1}$ , respectively<sup>17-24</sup>, although effective energy transfer with a small energy gap between the  $T_1$  state and emitting level ( ${}^7F_0-{}^5D_0$ ) has also been reported<sup>22,23</sup>. The effective energy



transfer between an organic ligand and lanthanide(III) ion is dependent on the ligand moiety.

Generally, the expansion of the  $\pi$ -conjugated system in a ligand leads to a decrease in the  $T_1$  level. However, the emitting level of lanthanide(III) ion is not changed by the surrounding media, such as an organic ligand and solvent. The emitting levels of the Eu(III), Tb(III), Sm(III), Yb(III), Nd(III) and Er(III) ions have been estimated to be 17,293, 20,500, 17,900, 10,260, 11,100, and 6535  $\text{cm}^{-1}$ , respectively<sup>3</sup>. When the energy level of the  $T_1$  state is lower than that of the emitting level, the lanthanide complex does not emit photons. Typical  $\pi$ -conjugate systems and their  $T_1$  energy levels are summarized in Fig. 4<sup>25–27</sup>. When the energy gap between the  $T_1$  and the emitting levels is also  $<2500 \text{ cm}^{-1}$ , energy back transfer from Ln(III) to the ligand is observed. From the photophysical findings, the expansive limitation of the  $\pi$ -conjugate structure in an organic ligand should be required for effective energy forward transfer from the  $T_1$  state of an organic ligand to the emitting level of a lanthanide(III) ion.

The overall emission quantum yield of an Ln(III) complex excited at the  $\pi$ - $\pi^*$  band of an organic ligand,  $\Phi_{\pi-\pi^*}$ , is calculated as follows:

$$\Phi_{\pi-\pi^*} = \Phi_{f-f} \times \eta_{sens} = \frac{k_r}{k_r + k_{nr}} \times \eta_{sens}, \quad (1)$$

where  $\Phi_{f-f}$ ,  $\eta_{sens}$ ,  $k_r$ , and  $k_{nr}$  are the lanthanide(III)-centered emission quantum yield, efficiency of the sensitization process, and radiative and non-radiative rate constants, respectively. Knag et al.<sup>28</sup> reported the photosensitized luminescence of Nd(III), Yb(III), and Er(III) complexes with anthracene-attached diketonate ligands. The  $\eta_{sens}$  values of the Nd(III) and Er(III) complexes were estimated to be 0.89% and 0.086%, respectively (Fig. 5a). Reddy and co-workers<sup>29</sup> described efficient photosensitized energy transfer of Nd(III) complexes with pyrene-attached diketonate ligands ( $\eta_{sens}$  of Nd(III) complex: 44%) (Fig. 5b). He also showed highly efficient

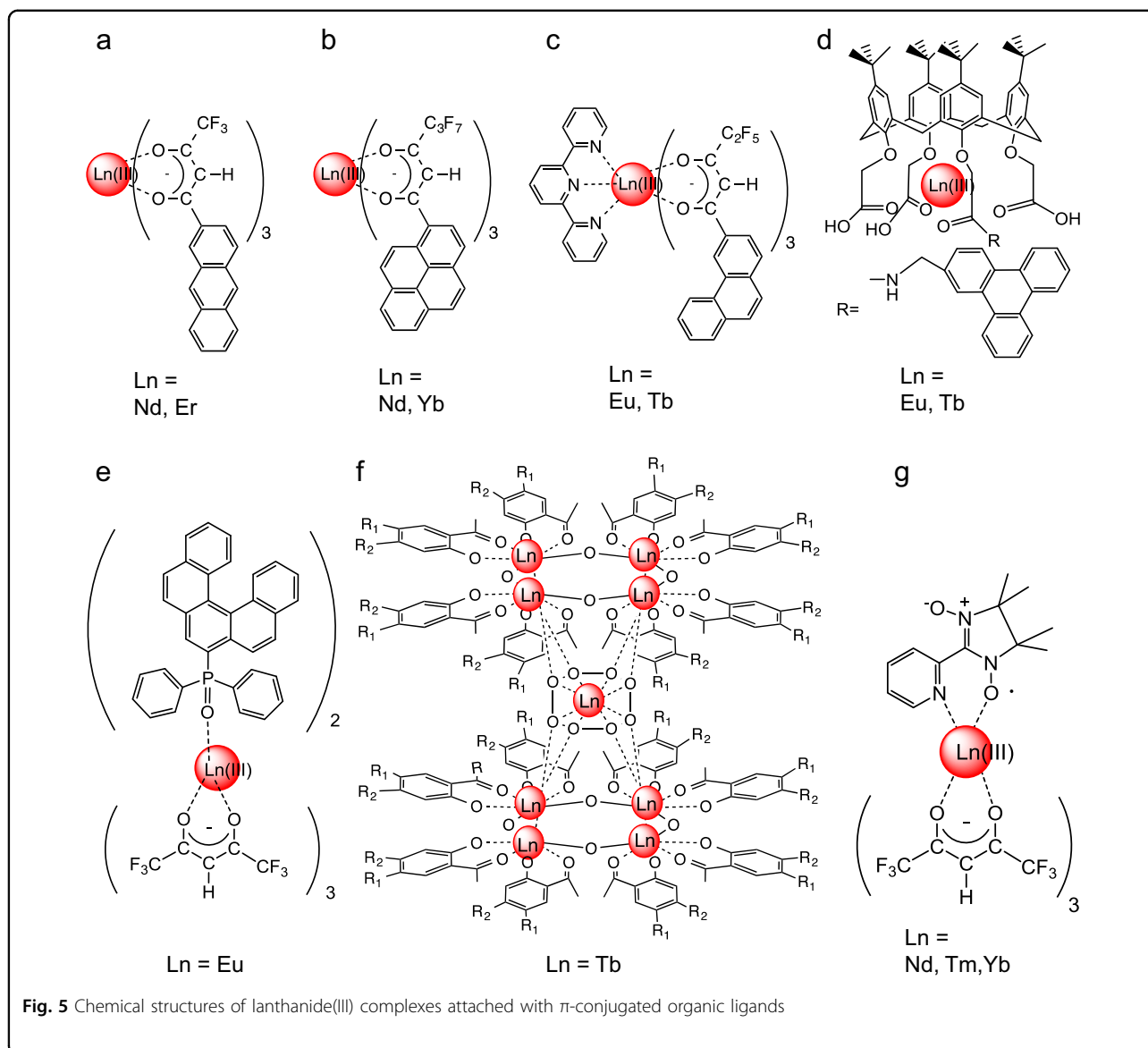
photosensitized energy transfer of Eu(III) complexes with phenanthrene-attached diketonate (Fig. 5c)<sup>30</sup>. In another case, the photosensitized luminescence of Eu(III) and Tb(III) ions with triphenylene in calix [4] arene systems has been reported (Fig. 5d);<sup>31</sup> however, the expansion of  $\pi$ -conjugated systems in aromatic ligands leads to a decrease in the energy level of the  $T_1$  state, resulting in energy back transfer from the excited Ln(III) ions to the  $T_1$  state of the aromatic ligands.

We have suggested a novel molecular strategy for the expansion of  $\pi$ -conjugated systems for the effective photosensitization of a lanthanide(III) complex using a helical-shaped helicene unit (Fig. 5e)<sup>32,33</sup>. We here explain the concept of molecular design for the effective photosensitization of a lanthanide(III) complex. The equation for the  $T_1(-S_0)$  level of the molecules is as follows:

$$E(T_1) = E_f - E_i - J_{ij}, \quad (2)$$

where  $E$  is the orbital energy and  $J$  is a coulombic integral that represents the electrostatic repulsion between the orbital charge distributions. The subscripts  $i$  and  $f$  are the occupied and unoccupied orbitals related to the  $T_1$  states, respectively. The  $J_{ij}$  value tends to decrease with the increasing delocalization of the electronic orbital density, when the  $\pi$ -conjugated system is extended. Herein, we consider a simple molecular design for maintaining the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels for extended  $\pi$ -conjugated systems using the fragment molecular orbital (FMO) method and DFT calculations (Gaussian 03, B3LYP/6-31G(d))<sup>34,35</sup>.

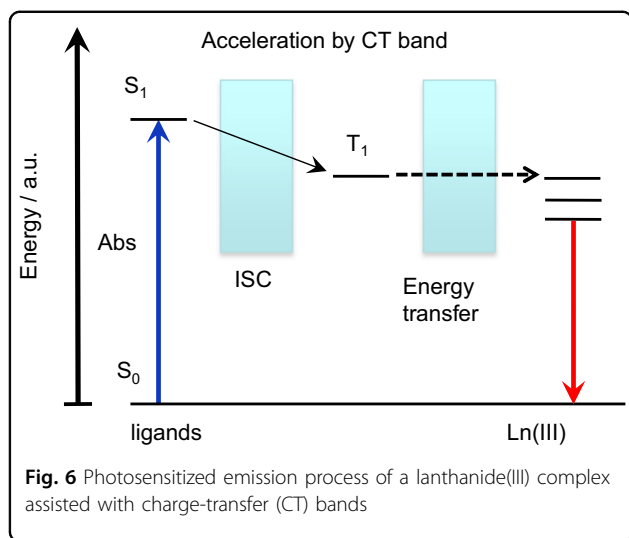
As a standard for  $\pi$ -conjugated molecules, we used naphthalene, which has a higher energy of the excited state (21,250  $\text{cm}^{-1}$ ) than those of the emitting levels of Eu(III), Tb(III), and Sm(III) ions. Extending the  $\pi$ -conjugation by coupling naphthalene and butadiene results in anthracene or phenanthrene molecules. For phenanthrene, the HOMOs (5.79 and 6.19 eV) and



LUMOs (0.96 and 0.82 eV) are electronically coupled, resulting in nearly unchanged HOMO (5.73 eV) and LUMO (0.99 eV) energies relative to those of naphthalene. Therefore, the  $T_1$  level of phenanthrene is almost unchanged ( $21,740 \text{ cm}^{-1}$ ). Based on this conceptual design, an extended  $\pi$ -conjugated structure by coupling phenanthrene and butadiene provides [4]-helicene ( $T_1 = 19,980 \text{ cm}^{-1}$ ). By using the molecular design based on the FMO and DFT, we successfully synthesized a phosphine oxide ligand containing a helical [5]-helicene unit (HPO ligand,  $T_1 = 18,410 \text{ cm}^{-1}$ )<sup>32</sup>. For an Eu(III) complex with an HPO ligand,  $[\text{Eu}(\text{hfa})_3(\text{HPO})_2]$  (hfa: hexafluoroacetylacetonate), the longer wavelength excitation ( $\lambda_{\text{ex}} = 430 \text{ nm}$ ) of the HPO ligands induces the photosensitized luminescence of the Eu(III) complex ( $\eta_{\text{sens}} = 10\%$ ) (Fig. 5e)<sup>32,33</sup>.

We also reported the effective photosensitized luminescence of Eu(III) and Tb(III) nonanuclear clusters with 16 salicylate derivative ligands (Fig. 5f)<sup>36,37</sup>. The Tb(III) clusters showed large absorption coefficients ( $\epsilon > 55,000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The photosensitized energy transfer efficiency is dependent on the  $T_1$  state of the aromatic ligands. The emission quantum yield of Tb-4-methylsalicylate ( $R_1 = \text{H}$ ,  $R_2 = \text{CH}_3$ ;  $\Phi_{\pi-\pi^*} = 31\%$ ) was found to be 13 times larger than that of Tb-5-methylsalicylate ( $R_1 = \text{CH}_3$ ,  $R_2 = \text{H}$ ;  $\Phi_{\pi-\pi^*} = 2.4\%$ ). The photophysical characterization and DFT calculations revealed the effect of the methyl group on the electronic structure of the methyl salicylate ligand.

Photosensitized luminescence of lanthanide(III) complexes with  $\pi$ -conjugated radical ligands has also been reported (Fig. 5g)<sup>38-40</sup>. The  $\pi$ -conjugated radical ligands



show large absorption coefficients; however, the absorption bands of radical ligands are generally lying in the vis region (wavelength  $>700$  nm). The absorption bands in the vis region prevent the photosensitized luminescence of Eu(III) and Sm(III) complexes<sup>38</sup>. Near-IR luminescence of Nd(III), Tm(III), and Yb(III) complexes with radical ligands has been reported<sup>39,40</sup>. The control and consideration of the energy level of the lowest excited state in an organic chromophore are the most important aspects for developing strong luminescent lanthanide(III) complexes.

### Effect on CT band

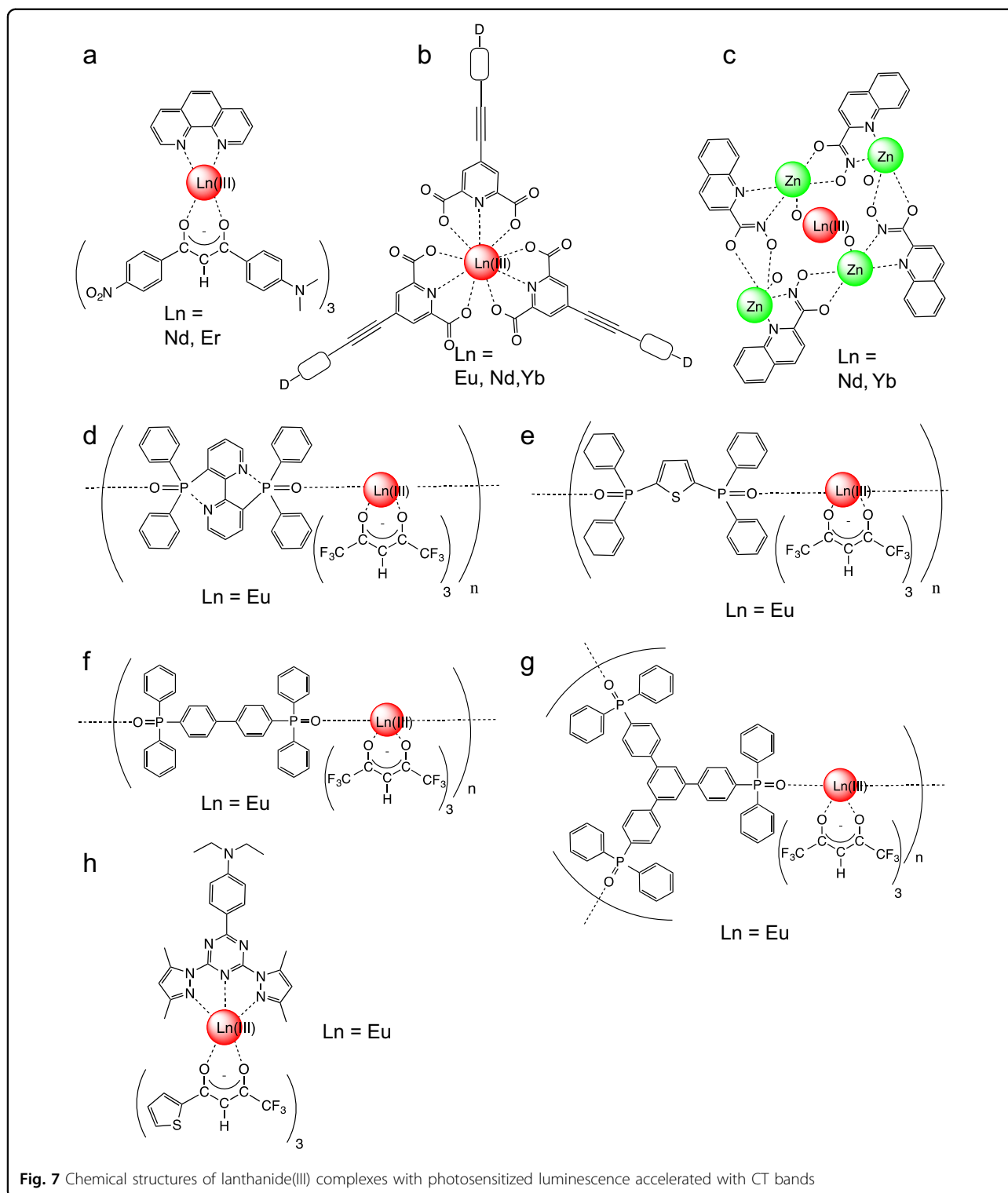
The photosensitized luminescence of lanthanide complexes is influenced by a specific band, for example, the CT band in a lanthanide complex. The CT band located in the vis region affects the effective energy transfer from the ligand to the lanthanide(III) ion. The CT transition is categorized into three types: (1) intra-ligand CT (intra-LCT), (2) inter-ligand CT (inter-LCT), and (3) ligand-to-metal CT (LMCT). The CT bands affect the intersystem crossing process or the energy transfer process between the ligand and the lanthanide(III) ion (Fig. 6).

According to the photosensitized luminescence of lanthanide(III) complexes accelerated by intra-LCT, Eu(III), Yb(III), Nd(III), and Er(III) complexes with donor amine-attached diketonate ligands have been reported ( $\Phi_{\pi-\pi^*}$ : Nd = 0.0078%, Yb = 0.04%, Fig. 7a)<sup>41,42</sup>. The effective luminescence of lanthanide(III) complexes with donor pyridine-attached ligands has been reported ( $\Phi_{\pi-\pi^*}$ : Eu = 43%, Nd = 0.22%, Yb = 0.59%, Fig. 7b)<sup>43</sup>. Lanthanide(III) complexes with donor pyridine-attached ligands also show solvatochromic properties, which are dependent on the organic solvent as a sounding medium.

The first example of photosensitized energy transfer from inter-LCT was presented using Eu(III) and Tb(III)

complexes with hfa ligands in a solid<sup>44</sup>. The emission quantum yield and energy transfer efficiency of the Eu(III) complex were estimated to be 58% and 81%, respectively. The effective formation of an inter-LCT state using an Eu(III) complex with phenanthroline ligands was later observed<sup>45</sup>. The inter-LCT-supported near-IR luminescence of Yb(III), Nd(III), and Er(III) complexes using crown-type ligands was also reported (Fig. 7c)<sup>46</sup>.

Generally, effective photosensitized luminescence accelerated by intra- and inter-LCT bands is observed in the solid state. Eliseeva et al.<sup>44</sup> recently reported that the formation of low-lying inter-LCT states contributes to the improvement of the ligand-to-metal energy transfer efficiency. Characteristic intra-LCT and inter-LCT bands are formed in the tightly packed crystals. The tightly packed crystals can be built as a polymeric structural design with a large strain in the  $\pi$ -conjugated ligands. The wavelength of the inter-LCT transition band of the strained ligand in solid media is longer than that of corresponding  $\pi-\pi^*$  transition bands of a normal ligand in liquid media. We observed an effective inter-LCT band using Eu(III) coordination polymers (Fig. 7d)<sup>47</sup>. The coordination polymers were composed of luminescent Eu(hfa)<sub>3</sub> parts and joint organic ligands, bipypo (bipypo: 3,3'-bis(diphenylphosphoryl)-2,2'-bipyridine). The effective inter-LCT band of the diketonate ligands was observed at approximately 400 nm in the solid state. The quantum efficiency accelerated by the inter-LCT in the solid state,  $\Phi_{\pi-\pi^*}$ , was found to be 61%. We also consider that luminescent lanthanide(III) coordination polymers with a characteristic inter-LCT band can be constructed by a zig-zag chained polymer. The tightly packed zig-zag structure of the Eu(III) coordination polymers was prepared using zig-zag-shaped joint ligands, dpt (2,5-bis(diphenylphosphoryl)thiophene), to enhance the photosensitized luminescence supported by the inter-LCT (Fig. 7e)<sup>48</sup>. They exhibit a high intrinsic emission quantum yield (75%) due to their asymmetrical and low-vibrational coordination structures around the Eu(III) ions. The characteristic alternative zig-zag orientation of the substituents also contributes to the dramatically high energy transfer efficiencies supported by the inter-LCT of up to 80% in the solid state. The high  $\eta_{\text{sens}}$  might be due to the formation of inter-LCT states induced by the densely packed zig-zag orientation. We estimated the dipole moment  $D$  of the bridging ligands by DFT calculations (B3LYP/6-31G (d)) based on the CIF data of their X-ray single-crystal analysis data. Compared to the linear-type Eu(III) coordination polymer [Eu(hfa)<sub>3</sub>(dppb)]<sub>n</sub> (Fig. 7f, dppb: 4,4'-bis(diphenylphosphoryl)-1,1'-biphenyl,  $D = 0.0005$ ), the zig-zag-type Eu(III) coordination polymers show large  $D$  values (1.1664 for [Eu(hfa)<sub>3</sub>(dpt)]<sub>n</sub> and 4.2992 for [Eu(hfa)<sub>3</sub>(dpedot)]<sub>n</sub> (dpedot: 2,5-bis(diphenylphosphoryl)ethylenedioxythiophene). The polar character of the bridging ligands



resulted in a characteristic alternative orientation of the inter-polymer or intra-polymer chains.

We also reported the strong photosensitized luminescence of a three-dimensional Eu(III) coordination

polymer with an attached triangular spacer ligand, tppb (1,3,5-tris(4-diphenylphosphorylphenyl)benzene). The intrinsic and photosensitized emission quantum yields,  $\Phi_{f-f}$  and  $\Phi_{\pi-\pi^*}$ , were calculated to be 82%, and 64%,

respectively. The energy transfer efficiency,  $\eta_{sens}$ , was calculated to be 78%, which is similar to that of the zig-zag-shaped Eu(III) coordination polymers (Fig. 7g)<sup>49</sup>.

The LMCT bands of some Eu(III) complexes are observed at approximately 400 nm. The LMCT band in a lanthanide(III) complex does not generate effective energy transfer. In Eu(III) complexes, the LMCT band from the  $S_0$  state of the ligand to the Eu(III) ion leads to effective quenching of the excited Eu(III) complex<sup>50-55</sup>. The results of the detailed analysis of quenching by the LMCT band using a dinuclear Eu(III) complex have been reported<sup>56,57</sup>. Studies on photosensitized luminescence assisted by the LMCT band of lanthanide(III) complexes are limited; however, the photosensitized luminescence of some Eu(III) and Sm(III) complexes assisted by the LMCT bands have been reported as specific examples (Fig. 7h)<sup>58-60</sup>.

Generally, the standard electrode reduction potential of Eu(III) in water is estimated to be  $-0.35$  V, which is smoothly transformed to meta-stable Eu(II) ions. For this reason, the excitation of the LMCT band in an Eu(III) complex promotes the intramolecular photoreduction of the Eu(III) ion and the formation of the Eu(II) ion<sup>61,62</sup>. Using the photoreduction technique, we also observed the decomposition of Eu(III) complexes and the formation of Eu(II) compounds (EuO and EuS nanoparticles) under the condition of LMCT band excitation<sup>63-65</sup>. Decomposition processes using gas-phase and laser-assisted MOCVD techniques have also been reported<sup>66,67</sup>.

The effective photosensitized luminescence of lanthanide(III) complexes is assisted by the presence of (1) an intra-LCT band formed by the introduction of donor parts in the organic ligands and (2) an inter-LCT band formed by the steric strain in the organic ligands in the crystals. The design of intra-LCT and inter-LCT is a promising strategy for developing a strong luminescent lanthanide(III) complex.

## Photosensitized luminescence from a metal complex

### Light and transition metal complexes

The photosensitized luminescence of lanthanide(III) complexes attached with metal complexes has been widely reported. There are three species of metal complexes for photosensitization: (1) light metal complexes, (2) transition metal complexes, and (3) lanthanide(III) complexes.

First, the photosensitized luminescence of lanthanide(III) complexes excited at the transition bands in light metal complexes are explained. Xu et al.<sup>68</sup> reported the photosensitized luminescence of polynuclear Eu(III), Nd(III), and Yb(III) hfa complexes attached with three Al(III) quinolate complexes (Fig. 8a). Aluminum (Al) is an element in family 13 (IIIA) in the periodic table. Al(III)

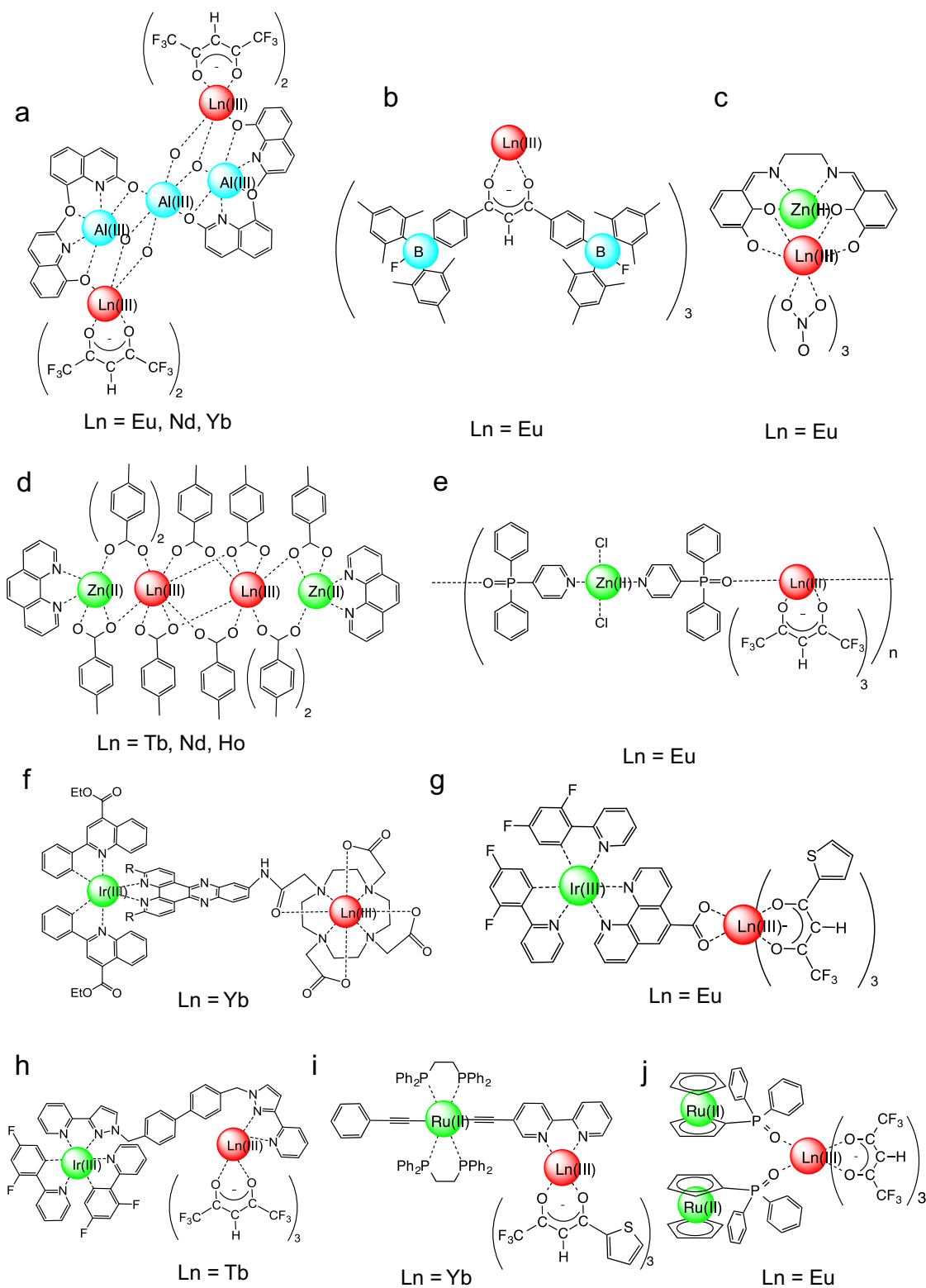
quinolate complexes are well known as green luminescent chromophores for EL devices<sup>69</sup>. The emission quantum yield of Eu(III) complexes with photosensitized Al(III) parts was estimated to be 6.1%. Furthermore, Smith et al.<sup>70</sup> reported the photosensitized luminescence of Eu(III) complexes with monodentate and bidentate boron complexes in diketone ligands (Fig. 8b). Boron complexes with three aryl groups, triarylborons, are transformed by the presence of fluorine ions, resulting in the formation of a B-F bond in the triarylboron unit. The formation of a B-F compound in the triarylboron unit accelerates the photosensitized luminescence of the Eu(III) complex. Eu(III) complexes with monodentate and bidentate triarylboron units are sensitive to fluorine ions in liquid media.

Next, the photosensitized luminescence of lanthanide(III) complexes with transition metal complexes are introduced. Various types of transition metal complexes for the photosensitization of lanthanide(III) complexes have been reported. Among them, luminescent Zn(II), Ir(III), and Ru(II) complexes are generally used for the photosensitized luminescence of lanthanide(III) complexes.

The metal-to-ligand CT (MLCT) bands in Zn(II) complexes are observed in the UV region. The energy levels of their MLCT bands are higher than those of the emitting levels of Tb(III) and Eu(III) ions. The MLCT bands promote effective photosensitized energy transfer in Zn(II)-Ln(III) hybrid complexes. Dinuclear Zn(II)-Ln(III) complexes with Schiff base ligands show effective photosensitized luminescence (Fig. 8c)<sup>71-74</sup>. Luminescent polynuclear Zn(II)-Ln(III) complexes with Zn(II) quinolate, terpyridine, phenanthroline, and a Schiff base have also been reported (Fig. 8d)<sup>75-80</sup>. We synthesized an Eu(III) coordination polymer cross-linked with a Zn(II) complex as a joint ligand (Fig. 8e)<sup>81</sup>. The intrinsic emission quantum yield ( $\Phi_{f-t}$ ) was estimated to be 59%.

Various types of lanthanide(III) complexes attached with Ir(III) complexes have also been reported (Fig. 8f)<sup>82-85</sup>. Generally, Ir(III) complexes show blue, green, and red luminescence at room temperature based on the MLCT transition bands. The MLCT transition of an Ir(III) complex leads to efficient luminescence with a high-emission quantum yield<sup>86</sup>. The emission color of an Ir(III) complex is dependent on the energy level of the organic ligands. Blue and green luminescent Ir(III) complexes are used for the photosensitized luminescence of lanthanide(III) complexes. The effective photosensitization of a polynuclear Ir(III)-Eu(III) complex has been reported. The emission quantum yield excited at the MLCT band is estimated to be 44% (Fig. 8g)<sup>84</sup>. Bian and Ward reported the photosensitized luminescence of red luminescent Ir(III)-Eu(III) and green luminescent Ir(III)-Tb(III) systems (Fig. 8h)<sup>87-90</sup>.





**Fig. 8** Chemical structures of lanthanide(III) complexes with Al, B, Zn, Ir, and Ru complexes

The Ru(II)–Ln(III) complex is also a popular system for the photosensitized luminescence of a lanthanide (III) complex. Generally, the emission band of an Ru(II) complex is observed at approximately 600 nm. The red luminescence of an Ru(II) complex is effective for the photosensitization of near-IR luminescence of Yb(III) and Nd(III) complexes. Gunnlaugsson, Charbonnière, and Faulkner<sup>91,92</sup> reported the near-IR luminescence of Ru(II)–Ln(III) (Ln = Nd(III) and Yb(III)) complexes in water media. Rigaut and co-workers<sup>93</sup> reported Yb(III) complexes with a carbon-rich ruthenium antenna (Fig. 8i). Sun made a molecular architecture composed of Ru(II) bipyridyl complexes and Ln(III) acetates<sup>94</sup>. Furthermore, organometallic ruthenocene [Ru(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] exhibits a white color, and the MLCT band is located in the UV region. We reported luminescent Eu(III) complexes attached with ruthenocene units (Fig. 8j)<sup>95</sup>. Ward<sup>96</sup> reviewed the energy transfer of Ru(II)–Ln(III) complexes.

Photosensitized luminescence using Re–Ln(III)<sup>92,97</sup>, Pt–Ln(III)<sup>98–100</sup>, Au–Ln(III)<sup>99,101</sup>, Ag–Ln(III)<sup>99,102</sup>, Cd–Ln(III)<sup>103,104</sup>, and Os–Ln(III)<sup>96</sup> systems has also been reported. In general, their CT (MLCT, LMCT, metal-metal-to-ligand CT, etc.) bands of Re, Au, Ag, Cd, and Os complexes show emission in the vis region. From these photophysical findings, the near-IR luminescence of Nd(III) and Yb(III) complexes with Re, Au, Ag, Cd, and Os complexes has been described.

#### Active use of energy transfer in lanthanide complexes

The energy transfer between the Ln(III) ions in polynuclear lanthanide(III) complexes and the clusters leads to characteristic emission properties, energy migration, temperature-dependent luminescence, multi-color component emission (triple luminescence), and upconversion luminescence. In this section, characteristic luminescence related to energy transfer between Ln(III) ions is described.

We reported the effective energy migration of a Tb(III) cluster composed of 9 Tb(III) ions and 16 salicylate ligands (Fig. 5f)<sup>105</sup>. The energy migration in a Tb(III) nonanuclear cluster leads to a decrease in the energy back transfer from the excited Tb(III) ions to the T<sub>1</sub> state of the ligands, resulting in thermal relaxation and a decrease in the emission quantum yield. The kinetics analysis of the temperature dependence of emission lifetimes using Tb(III)/Gd(III) mixed nonanuclear clusters showed that the energy transfer between Tb(III) ions competes with the energy back transfer. The results provide a new molecular design strategy to improve the efficiency of the luminescence of lanthanide(III) complexes.

We also reported the temperature-dependent luminescence of lanthanide coordination polymers composed of Tb(III) and Eu(III) complexes, [Tb,Eu(hfa)<sub>3</sub>(dpbp)]<sub>n</sub> (Tb(III)/Eu(III) = 99), for temperature sensing between 200

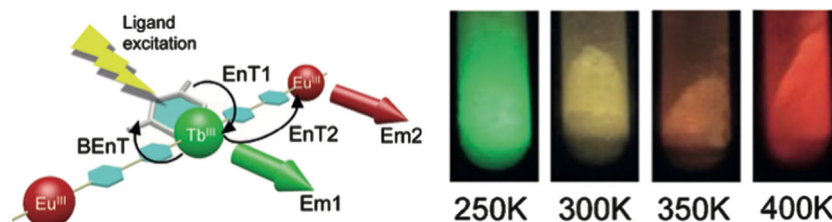
and 500 K (Fig. 9)<sup>106</sup>. The remarkable thermosensitive properties of [Tb<sub>0.99</sub>Eu<sub>0.01</sub>(hfa)<sub>3</sub>(dpbp)]<sub>n</sub> are influenced by the energy transfer efficiency between the Tb(III) and Eu(III) ions in the coordination polymer matrix. The energy transfer efficiency between the Tb(III) and Eu(III) ions is estimated by

$$\eta_{Tb-Eu} = 1 - (\tau_{obs}/\tau_{Tb}), \quad (3)$$

where  $\tau_{obs}$  and  $\tau_{Tb}$  are the emission lifetimes of [Tb,Eu(hfa)<sub>3</sub>(dpbp)]<sub>n</sub> and [Tb(hfa)<sub>3</sub>(dpbp)]<sub>m</sub>, respectively. Using this equation, the values of  $\eta_{Tb-Eu}$  at 200, 250, 275, and 300 K are estimated to be 1%, 19%, 26%, and 38%, respectively. The value of  $\eta_{Tb-Eu}$  increases with the increase in temperature. We observed the temperature-dependent energy transfer efficiency of a [Tb,Eu(hfa)<sub>3</sub>(dpbp)]<sub>n</sub> crystal. Previously, the energy transfer from Tb(III) ions to Eu(III) ions was studied by using mononuclear and dinuclear lanthanide complexes in homogeneous organic and aqueous media. We consider that the energy transfer mechanism of [Tb,Eu(hfa)<sub>3</sub>(dpbp)]<sub>n</sub> is different from those in previously reported homogeneous systems in solution. Regarding the energy transfer mechanism of [Tb,Eu(hfa)<sub>3</sub>(dpbp)]<sub>m</sub>, Hatanaka et al.<sup>107</sup> and Hatanaka and Morokuma<sup>108</sup> first reported the presence of the activation energy on organic joint ligands determined by quantum calculations. A collaborative study using quantum calculations as additional experiments is expected to open up a new field of photophysical theory of the energy transfer process. The development of thermosensitive luminophores using the energy transfer in Ln(III) polynuclear complexes, coordination polymers and clusters has also been explored<sup>109–118</sup>.

The multi-color component emission (triple luminescence) of a photosensitized lanthanide(III) system using Eu(III)/Tb(III)/Gd(III) MOF (metal–organic framework) systems<sup>119–121</sup> cross-linked with aromatic joint parts containing pyridyl, sulfonyl, and/or carbonyl groups has been reported. The multi-color emission is composed of a red luminescent Eu(III) complex, a green luminescent Tb(III) complex, and a blue luminescent ligand (phosphorescence) in the Gd(III) parts (the emitting level of the Gd(III) ion is higher than the T<sub>1</sub> state of the organic ligands). The triple component emission of the Eu(III)/Tb(III)/Gd(III) MOF system plays a role in precise color tuning for the naked eye and the creation of white lighting. Eu(III)/Tb(III)/La, Eu(III)/Tb(III)/Gd(III)/Zn(II), and Eu(III)/Tb(III)/ligand MOF systems have also been reported<sup>122–124</sup>.

In the field of inorganic material science and engineering, the upconversion luminescence of lanthanide compounds is well known as a wavelength conversion phenomenon from lower to higher photon energy. The upconversion luminescence is based on the energy transfer between metal and lanthanide ions<sup>125</sup>. In 2011, Piguet and co-workers<sup>126</sup> reported the first example of the



**Fig. 9** Temperature-dependent color changing properties of a Tb(III)/Eu(III) mixed coordination polymer  $[\text{Tb}_x\text{Eu}_{1-x}(\text{hfa})_3(\text{dppb})]_n$ . Color pictures of  $[\text{Tb}_{0.99}\text{Eu}_{0.01}(\text{hfa})_3(\text{dppb})]_n$  under UV (365 nm) irradiation, which show brilliant green, yellow, orange, and red emission. Reprinted with permission from Iki et al.<sup>106</sup> Copyright 2013 Wiley-VCH Verlag GmbH & Co

upconversion luminescence of an Er(III) helical complex with two Cr(III) units (Fig. 10a). The result of detailed analysis of the Er(III) helical complex with two Cr(III) units has also been reported<sup>127</sup>. Charbonnière and co-workers<sup>128,129</sup> reported the upconversion luminescence of a dinuclear Er(III) complex (Fig. 10b) and a polynuclear Tb(III)/Yb(III) complex. Faulkner and co-workers<sup>130</sup> reported the upconversion luminescence of a mononuclear Tm(III) complex in solution. A hybrid system composed of Yb(III)/ $\text{Tm}_2\text{O}_3$  interfacial coordination nanoparticles was also reported (Fig. 10c)<sup>131</sup>. Lanthanide coordination compounds are expected to play an important role in the molecular-level analysis of upconversion luminescence.

The photosensitized luminescence from neighboring lanthanide(III) ions in a coordination system promotes not only the enhancement of the emission intensity but also the characteristic energy migration luminescence, temperature-dependent luminescence, multi-color component emission (triple luminescence), and upconversion luminescence. The photosensitized luminescence from activated lanthanide ions is a key phenomenon for the creation of new advanced luminescent materials in the future.

### Electrosensitized luminescence

Lanthanide(III) complexes on glass electrodes or semiconductor crystals are expected to be useful for applications in display devices, such as organo-EL or electrochemically luminescent devices, light-emitting diode (LED) tip devices, and photovoltaic polymer memories. Kido et al.<sup>132</sup> was first to report the EL of a Tb(III) acetylacetonate complex in EL devices (Fig. 11a). We also reported the near-IR EL of an Nd(III) complex (Fig. 11b)<sup>133</sup>. Kido and Okamoto<sup>5</sup>, de Bettencourt-Dias<sup>6</sup> and Xu et al.<sup>134</sup> have written reviews of lanthanide complex-based emitting materials in the field of LEDs. Wang et al.<sup>135</sup> also reported the EL of Eu(III) complexes with hfa and phosphine monodentate oxide ligands. The EL luminance was estimated to be  $>90 \text{ cd m}^{-2}$ .

The performance of EL devices depends on the molecular structure of the lanthanide(III) coordination

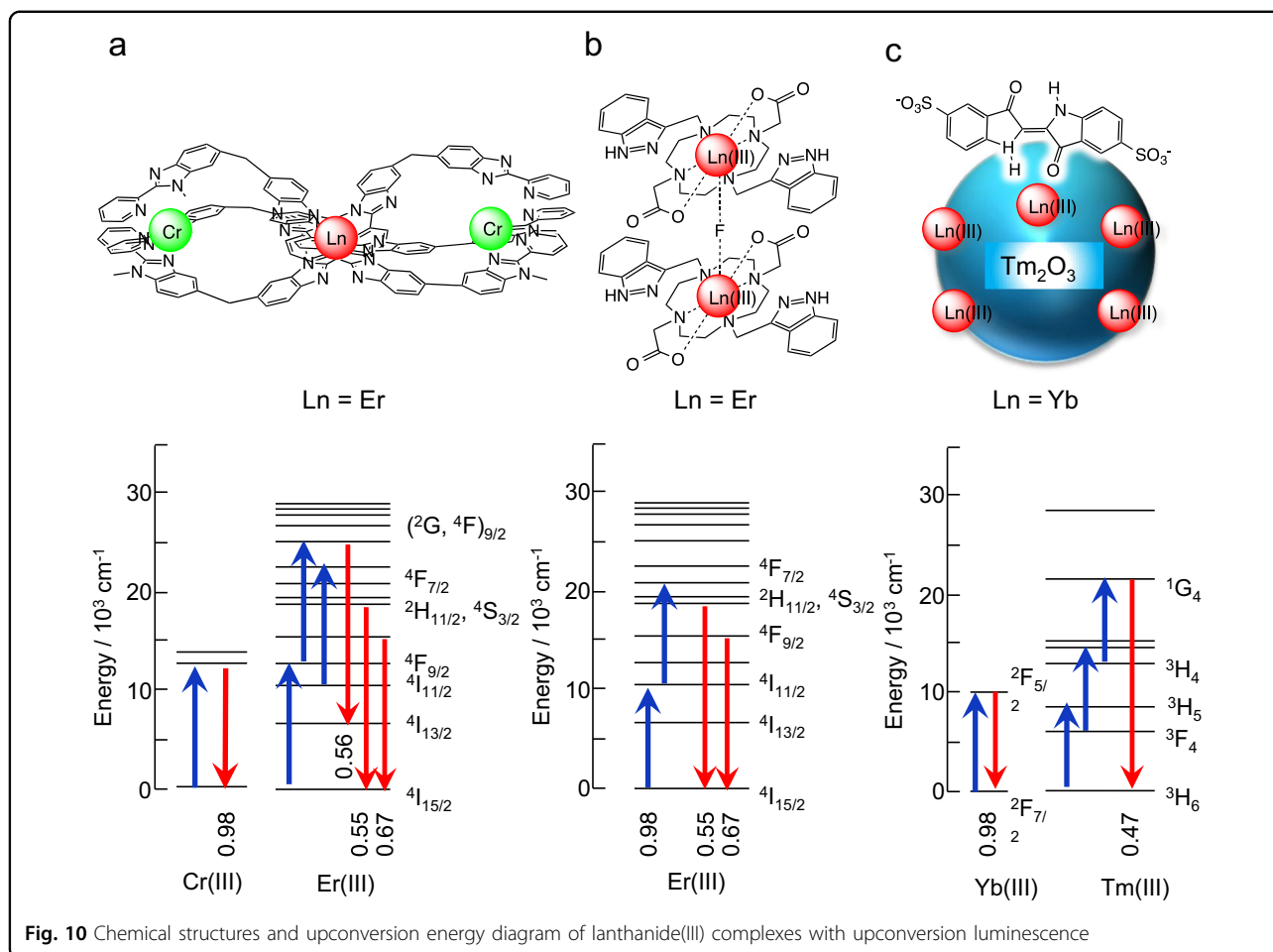
compounds. Recently, thermo-stable polymer materials attached with lanthanide complexes have been synthesized (Fig. 11c)<sup>136</sup>. The glass transition temperature and EL luminance were estimated to be  $220^\circ\text{C}$  and  $149 \text{ cd m}^{-2}$ , respectively. We also reported Eu(III) coordination nanoparticles on glass electrodes for EL devices<sup>137</sup>. The thermostability of a luminescent lanthanide complex is one of important factors for the fabrication of EL devices.

The characteristic EL performance has been reported. White EL using an Eu(III) coordination polymer has also been reported (Fig. 11d)<sup>138</sup>. Bari and co-workers<sup>139</sup> showed effective circularly polarized EL using a chiral Eu(III) complex (Fig. 11e). Zhang and co-workers<sup>140</sup> reported high-performance EL combined with an Ir(III) complex, a Tb(III) complex and a Gd(III) complex in devices ( $145,071 \text{ cd m}^{-2}$ ).

Various types of organic EL devices using organic molecules and transition metal complexes have been extensively studied. Highly efficient Ir(III) complexes and the characteristic TADF (thermally activated delayed fluorescence) of organic dyes have been studied for the fabrication of bright luminescent EL devices<sup>141–144</sup>. The EL properties of lanthanide(III) complexes are greatly different from those of organic molecules and transition metal complexes. The 4f–4f emissions of lanthanide(III) complexes play an important role in the design of monochromatic luminescent materials for display devices (narrow emission band:  $\text{FWHM} < 10 \text{ nm}$ )<sup>145</sup>, although EL devices using organic dye and transition metal complexes show broad emission spectra ( $\text{FWHM} > 50 \text{ nm}$ ). At present, the luminance of EL devices using lanthanide complexes is smaller than that of EL devices using organic molecules and transition metal complexes. However, lanthanide(III) complexes with characteristic EL are expected to be key materials for future displays.

### Mechanosensitized luminescence

The luminescence generated upon grinding solid materials is called triboluminescence (tribo-sensitized luminescence). In the seventeenth century, it was first noted by Francis Bacon who mentioned that “It is well



**Fig. 10** Chemical structures and upconversion energy diagram of lanthanide(III) complexes with upconversion luminescence

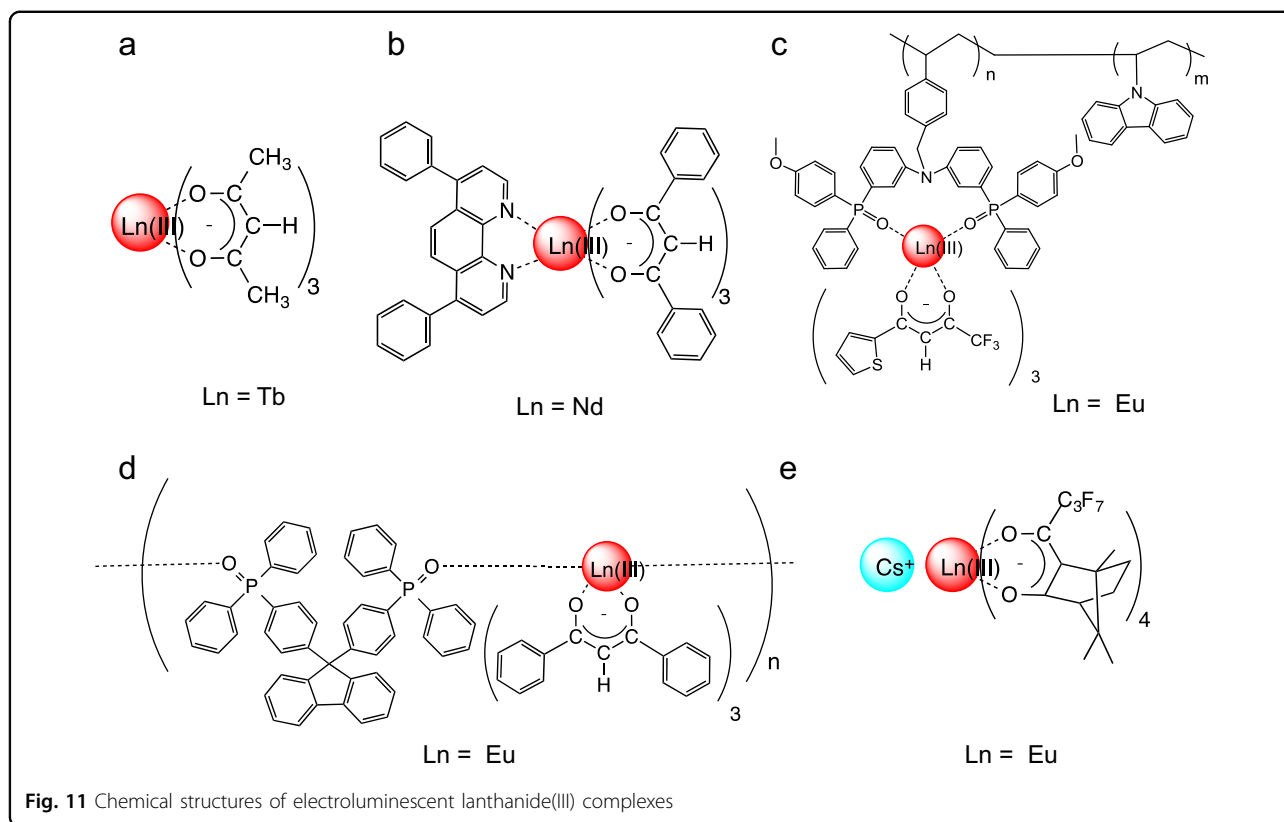
known that all sugar, whether candied or plain, if it be hard, will sparkle when broken or scraped in the dark.” Triboluminescent materials, unlike well-known photoluminescence materials, have the advantage of emission without requiring a light source<sup>146–148</sup>. The fracture-induced luminescent properties of triboluminescent materials make them attractive for applications as structural damage sensors and pressure sensors and for advanced security marking techniques<sup>149–152</sup>.

Different types of materials that exhibit triboluminescence, such as organic crystals, polymers, and metal complexes, have been studied. The first example of triboluminescence using a lanthanide(III) complex was reported in 1966 (Fig. 12a)<sup>153</sup>. In 1987, Sweeting and Rheingold<sup>154</sup> showed the importance of charge separation and recombination in solid state lanthanide(III) complexes. Some triboluminescence phenomena of lanthanide(III) complexes in crystals and polymer matrices have also been reported (Fig. 12b, c)<sup>155–166</sup>. Chen et al.<sup>167</sup> suggested that strongly luminescent lanthanide coordination polymer crystals with non-centrosymmetric structures are expected to show efficient triboluminescence because of the generation of opposite electric charges on opposing

faces of cracks perpendicular to their polar axes. Charge recombination on the crystal faces produces triboluminescence. From this point, triboluminescence is regarded as electrosensitized luminescence.

Eliseeva et al.<sup>168</sup> reported triboluminescence from a lanthanide coordination polymer composed of lanthanide(III) hfa complexes and 1,4-dimethylterephthalate joint ligands (Fig. 12d). We also reported strong triboluminescence from an Eu(III) coordination polymer with phosphine oxide joint ligands,  $[\text{Eu}(\text{hfa})_3\text{bipy}]_n$  (Fig. 7d)<sup>47</sup>. The Eu(III) coordination polymer with a specific coordination structure of low-vibrational frequency and coordination networks exhibits intense triboluminescence upon breaking, which is clearly observed even at ambient temperatures in daylight (Fig. 13). The triboluminescence of a supramolecular lanthanide(III) coordination system has also been reported (Fig. 12e)<sup>169</sup>.

Triboluminescence-active compounds are known to show photoluminescence as well. Triboluminescence and photoluminescence occur from distinct stimuli, namely, grinding and photoirradiation, respectively; however, their spectra usually exhibit similar profiles. The relationship



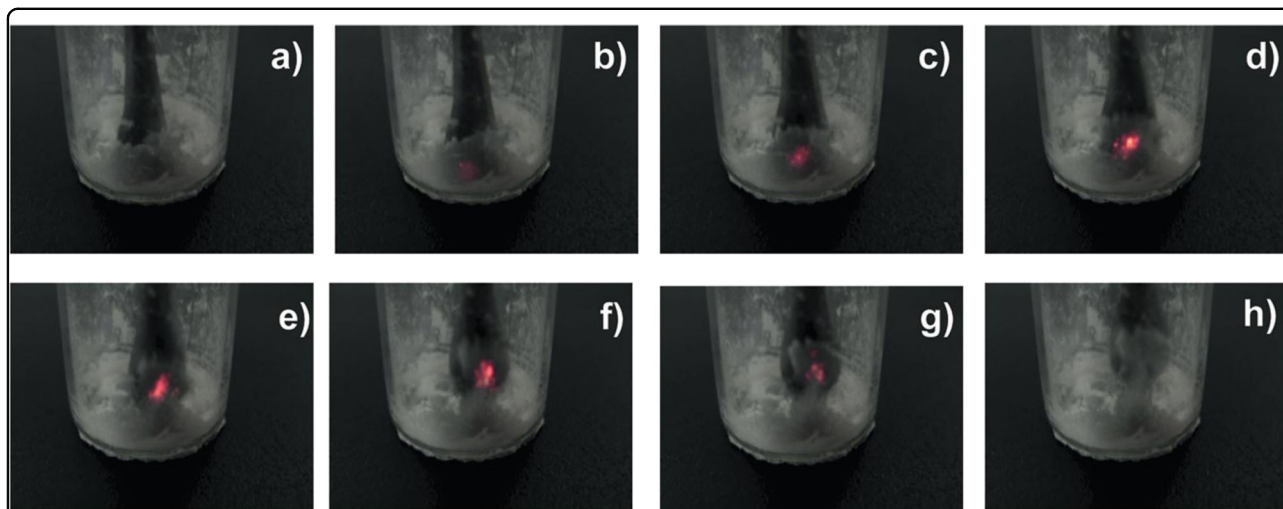
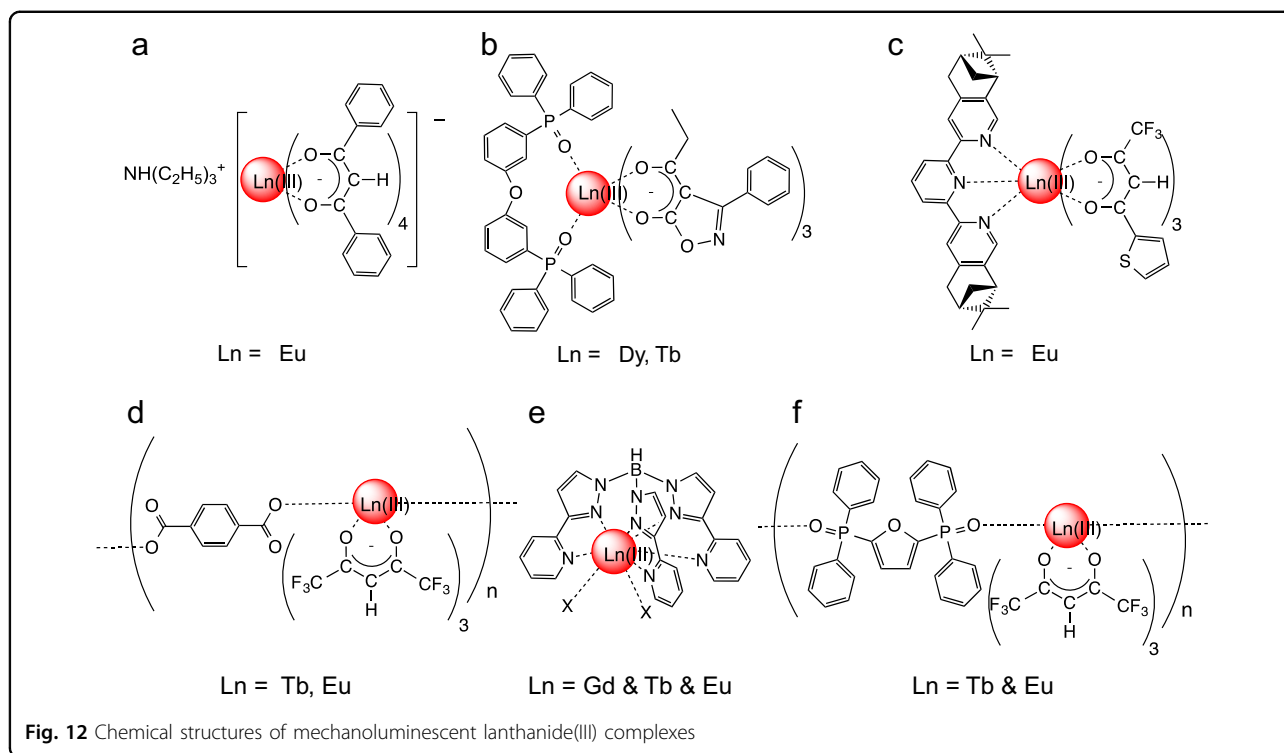
**Fig. 11** Chemical structures of electroluminescent lanthanide(III) complexes

between triboluminescence and photoluminescence is still being discussed from a scientific point of view.

Reddy and co-workers<sup>156</sup> recently demonstrated bright red triboluminescence and photoluminescence of [Eu(DPPF)<sub>3</sub>(DDXPO)] (DPPF = 1-(4-(diphenylphosphino)phenyl)-4,4,5,5,5-pentafluoropentane-1,3-dione, DDXPO = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene oxide). They also reported a slight decrease in the triboluminescence intensity when dispersed in PMMA films compared with that in the solid state. Teotonio et al.<sup>170</sup> and Mikhalyova et al.<sup>171</sup> suggested the possibility of triboluminescent energy transfer using lanthanide(III) complexes. Based on the difference between photoluminescence and triboluminescence properties, we discussed the spectral difference using a polar furan-linked Tb(III)/Eu(III) mixed coordination polymer with strong triboluminescence, [Tb/Eu(hfa)<sub>3</sub>(dpf)]<sub>n</sub> (dpf: 2,5-bis(diphenylphosphoryl)furan) (Fig. 12f)<sup>172</sup>. The Tb and Eu units in [Tb/Eu(hfa)<sub>3</sub>(dpf)]<sub>n</sub> show strong photosensitized luminescence. The intrinsic emission quantum yield and energy transfer efficiency of the Eu(III) unit [Eu(hfa)<sub>3</sub>(dpf)]<sub>n</sub> are estimated to be 73% and 88%, respectively. The intrinsic emission quantum yield and energy transfer efficiency of the Tb(III) units [Tb(hfa)<sub>3</sub>(dpf)]<sub>n</sub> is also calculated to be 88% and 45%, respectively. By using a Tb(III)/Eu(III) mixed coordination polymer [Tb/Eu(hfa)<sub>3</sub>(dpf)]<sub>n</sub>, we successfully observed a drastic spectral difference between the triboluminescence and

photoluminescence. Based on the results, we consider the triboluminescence of the lanthanide(III) coordination compounds to be responsible for both the ligand excitation and direct Ln(III) excitation, unlike the selective excitation with specific wavelengths (for example,  $\lambda_{\text{ex}} = 380 \text{ nm}$ ) in photoluminescence. We also assume that the Tb(III)-to-Eu(III) energy transfer occurs in both triboluminescence and photoluminescence with the same efficiency and that it is not responsible for the drastic color difference between the triboluminescence and photoluminescence.

Quantitative estimation of the triboluminescence efficiency is important to clarify the mechanism of triboluminescence and to develop strong triboluminescent materials. Generally, the drop-tower method is used to estimate the triboluminescence efficiency<sup>173–175</sup>. However, it is difficult to use the drop-tower method as a quantitative estimation (for calculations of the radiative and non-radiative rate constants). The development of a quantitative estimation method is needed to advance the field of triboluminescent material science. We developed a method to quantitatively estimate the triboluminescence using shockwave laser irradiation. The value of  $k_{\text{nr}}$  for triboluminescence is four times larger than that for photoluminescence in [Eu<sub>3</sub>(hfa)<sub>9</sub>(tppb)<sub>2</sub>]<sub>n</sub> crystals (tppb = tris(4-diphenylphosphorylphenyl)benzene) (Fig. 7g)<sup>49</sup>. These results indicate that the mechanical crushing of molecular crystals leads to an enhanced non-radiative transition in



**Fig. 13 a–h** Observed sequential images of triboluminescence from  $[\text{Eu}(\text{hfa})_3(\text{bipypo})]_n$  powder upon pushing with a black stick at ambient temperature and in daylight. Reprinted with permission from Hasegawa and co-workers<sup>47</sup>. Copyright 2011 Wiley-VCH Verlag GmbH & Co

the quantum process. The shockwave irradiation is considered to promote the effective mechanical crushing of organic crystals and the formation of an excited state of the ligands.

A highly photosensitized luminescence efficiency in Eu (III) coordination compounds should be the key to observing triboluminescence. The effective molecular design and a suitable experimental analysis method for triboluminescent lanthanide(III) coordination compounds are expected

to open a research pathway between coordination chemistry, materials chemistry, and photophysical chemistry.

## SUMMARY AND OUTLOOK

The photo and electrosensitized luminescence of lanthanide(III) complexes can be manipulated by the ligand design. The luminescence of lanthanide(III) complexes can be realized and enhanced by designing ligands that coordinate to the lanthanide(III) ions.

In the section on photosensitized luminescence, the importance of two factors, (1) the control of the  $T_1$  state of the ligand and (2) the presence of intra-LCT and inter-LCT, was explained. These ligand designs lead to the development of a strong luminescent lanthanide(III) complex. The energy transfer processes from neighboring light metal, transition metal, and lanthanide(III) complexes were also described. The characteristic energy migration, temperature-dependent luminescence, multi-color luminescence, and upconversion luminescence for polynuclear lanthanide(III) complexes, clusters, coordination polymers and nanoparticles are expected to lead to the development of new molecular materials for photonic and opto-electronic devices.

We then described electrosensitized luminescence (EL) and mechanosensitized luminescence (triboluminescence) as electric field sensitization phenomena. EL using lanthanide(III) complexes can provide highly pure green and red luminescence with a narrow FWHM, which is fundamental toward the fabrication of full-color display devices. Invisible near-IR EL can also be achieved by a lanthanide(III) complex for industrial security applications. These characteristic EL properties of lanthanide(III) complexes are greatly different from those of corresponding organic and transition metal complexes. The construction of novel lanthanide complexes with efficient carrier injection is required for the development of EL materials. The study of the triboluminescence of molecular crystals started in the seventeenth century; however, the mechanism of triboluminescence has still not been clarified. Determination of the excited state concentrations is required to gain a more complete understanding of the triboluminescence mechanism. The study of the triboluminescence of lanthanide(III) complexes is expected to open up a new research avenue in the field of material science.

In this review, we introduced different molecular designs for the enhancement of the photosensitized luminescence properties of lanthanide(III) complexes. The emission quantum efficiency of a lanthanide(III) complex is also dependent on its coordination geometry and vibrational structure. We reported the importance of the radiative  $k_r$  constant depending on the lanthanide(III) coordination geometry<sup>176–185</sup> and the non-radiative  $k_{nr}$  constant depending on the vibrational structure of the organic ligands<sup>186–197</sup>. Control of the  $k_r$  and  $k_{nr}$  constants in an excited lanthanide(III) complex is also important for the development of a strong luminescent lanthanide(III) complex.

Luminescent materials that include lanthanide(III) complexes are desirable for applications in novel organic lanthanide(III) devices, such as organic lasers, luminescent plastics, optical fibers, lasers, displays, lighting, wavelength converters for solar cells, and physical and biomedical sensors. The study of the photosensitized luminescence of lanthanide(III) complexes is expected to

open research avenues among the fields of chemistry, physics, electronics, and materials science.

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#### Conflict of interest

The authors declare that they have no conflict of interest.

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