Excitation energy transfer between $D_{3h}$ melamines and Pr(III) in the solid state

Miki Hasegawa *, Ayumi Ishii, Koji Habu, Hiroko Ichikawa, Kazuma Maeda, Shinobu Kishi, Yuzo Shigesato *

Department of Chemistry and Biological Science, College of Science and Engineering, Aoyama-Gakuin University, 5-10-1 Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan

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Abstract

Melamine or melem forms a coordination compound with Pr(III). From detailed measurements of electronic absorption and luminescence spectra reported here, it can be concluded that the excitation energy transfer of the Pr(III)–melamine complex occurs via an electron exchange mechanism, whereas the Pr(III)–melem follows a Coulomb mechanism.

Keywords: Pr(III) complex; Melamine; Luminescence spectra; Excitation energy transfer

1. Introduction

From the point of view of functional material science including the developments of biological agents, recent attention has been focused on metal complexes with organic compounds. Because the order and the coordination of metal ions and ligands are very flexible, the metal complex might yield new functional molecules with completely new properties. For instance, a Cu complex with 2,3-pyrazinedicarboxylate produces a framework, which keeps oxygen or hydrogen molecules in the solid state [1–3]. This plays an important role to storage gas molecules in a small space. There is also much attention to utilize new magnetic [4] or emissive materials [5]. Diamagnetic property of a metal or a metal ion can be controlled by using organic ligands, in other words metal complexes have also been investigated as single molecular magnets or even single chain magnets.

Optical emission properties of metal complexes have been reported for Pt(II), Ru(II), Ir(III), lanthanide(III) (abbreviated as Ln(III)), etc. [6]. Ir(III) complexes are useful as a blue-emitter originated from the triplet MLCT (metal to ligand charge transfer) level in an electro-luminescence system. Pt(II) complexes emit red, orange, yellow, etc. from the triplet MMLCT (metal–metal to ligand CT) level with a Pt–Pt interaction through the overlap between each $d_{z^2}$ orbital. Eu(III) complexes are very useful when applied as a DNA probe or a light source of the laser, etc. due to their strong red-emission. The emissive process of Ln(III) complexes differs from the above 3d transition metal systems, i.e. the ligand acts as a light-trigger and gives the energy to the center metal in the relaxation process, and the Ln(III) luminesces from the split f levels. According to the Dieke’s energy diagram [7], the emission property of Ln(III) depends on the ff transition energy; in a visible wavelength region, Eu(III) has only a few f-levels and brightly emits, while Nd(III) relaxes without emission due to the existence of many split f-levels. However, the energy transfer mechanism of the Ln(III) is very difficult to describe. The f-orbitals of Ln(III) exist inner sphere than the d-orbitals which contribute to the hybridization with the organic ligand in the coordination compound. Therefore, the emissions of Ln(III) appear independently as sharper bands which can hardly be influenced and shifted. Hitherto, we succeeded to select the emissive f levels by the modification of the light-trigger of Pr(III) complexes [8]. For instance, the Pr(III) complex with phenanthroline luminesces sequentially from the ligand and each of the split f-levels, as can be seen from picosecond time-resolved luminescence spectra. Also the measurement of phosphorescence of phenanthroline, and the decay curves of the respective luminescence band was compared with the theoretical approach; namely the excitation...
energy transfer pathway of the Pr(III) complex occurs from the excited $\pi\pi^*$ to the $^1I_6$ level of Pr(III) via the $T_1$ level of the ligand by $k(T_1 \rightarrow I_6)=3.3 \times 10^8 \text{ s}^{-1}$. The energy level of the $T_1$ of phenanthroline is controlled by the modification of the fluorophore, e.g. with the phenyl or with the methyl group, which results in the different energy pathway and the emissions between these molecules.

In the present paper, we report about new excitation energy transfer mechanism between the metal ion and the organic compound using novel emissive Pr(III) complexes. Triamino-s-triazine (abbreviated as melamine) is a unique formation exhibiting a $D_{3h}$ symmetry. It is commonly used as a source compound of polymer materials. The molecule has three bays to interact metal ions through non-bonding electron of nitrogen atoms. However, there are no reports about a coordination with Ln(III). Another $D_{3h}$ compound, triamino-tri-s-triazine (abbreviated as melem), has similar N-donor behavior based on the same symmetry as melamine [9]. Fortunately, the Pr(III) complexes with both compounds were synthesized, and the excitation energy pathway of two Pr(III) complexes was discussed from the measurement of luminescence spectra.

2. Experimental procedure

2.1. Materials

Melamine (Kanto Chemical Co.) was recrystallized from water. The available neat sample of melem was used [9]. PrCl$_3$$\cdot$7H$_2$O (0.19 g; 0.5 mol) is stirred with melamine (0.06 g; 0.5 mol) in a 1:1 mixed solvent (30 ml) of methanol and water for 7 days. The complex Pr–melamine is obtained as pale green powder (yield; 50%). The complex Pr–melem has been prepared in analogy to the above method in a hot methanol for 2 h (yield; 26%). Elemental analyses: found for Pr–melamine C=16.13, H=3.26, N=34.69; calcd for C$_{16}$H$_{40}$N$_{40}$O$_{40}$Cl$_{40}$Pr$_2$ [PrCl$_3$:melamine:H$_2$O:methanol = 2:5:3:1] C=15.86, H=3.33, N=34.70, found for Pr–melem C=6.60, H=2.45, N=12.98; calcd for C$_8$H$_{22}$N$_{10}$O$_4$Cl$_6$Pr$_3$ [PrCl$_3$:melem:H$_2$O = 3:1:8] C=6.53, H=2.01, N=12.69.

2.2. Instrumentation and MO calculation

Electronic absorption and luminescence spectra were recorded on Shimadzu UV3101 and Hitachi F3010, respectively.

To estimate the excited wavefunctions of the chromophore, the extended PPP calculation was used [10], which was modified to use a non-bonding electron on the nitrogen atom.

3. Results and discussion

Fig. 1 shows electronic absorption spectra of the Pr(III) complex with melamine or melem in the solid state. Melamine itself has weak $\pi\pi^*$ and $\pi\pi^*$ electronic transitions in the wavelength region of 200–350 nm, because of the highly $D_{3h}$ symmetry as described later. The ff absorption bands of the Pr(III) complex with melamine (abbreviated as Pr–melamine) are observed at 22,263 (449), 21,256 (470), 20,404 (490) and 16,685 cm$^{-1}$ (599 nm) with shoulders appearing at a shorter wavelength side by 362 cm$^{-1}$, which assigned as the $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$, respectively, and at 21,462 cm$^{-1}$ (466 nm) as the $^3H_4 \rightarrow ^1I_6$. Comparing to the Pr–melamine, the Pr(III) complex with melem (abbreviated as Pr–melem) exhibits much sharper spectrum for the ff transitions. It indicates that the ligand field affects to the f-orbital of Pr–melamine stronger than that of Pr–melem, and each f-level of Pr–melamine is split into two or more. Thus, melamine may build a higher symmetrical ligand field around Pr(III).

Luminescence spectra of Pr–melamine and the ligand in the solid state are shown in Fig. 2. The $\pi\pi^*$ fluorescence of melamine (around 28,100 cm$^{-1}$, 356 nm) is shifted to red after coordinating with Pr(III) in the solid state, and appears around 27,200 cm$^{-1}$ (368 nm). Similarly, the phosphorescence of Pr–melamine appears in a red-side around 24,000 cm$^{-1}$ (420 nm), than that of melamine. In the Pr(III) complex with organic chromophores, in general, the energy transfer pathway from the T$_1$ level of the ligand to a singlet of Pr(III) is possible [8]. In the case of Pr–melamine, the T$_1$ level exists almost like the one shown in Fig. 2(a), however, ff emissions are not observed. It is necessary for the energy transfer that the transition energy of the electron donor level (T$_1$) and that of the acceptor (1I$_6$, etc.) are almost equivalent. The difference of energy levels between the T$_1$ of melamine and the 1I$_6$ of Pr(III) is strongly pronounced (ca. 2500 cm$^{-1}$). Furthermore, the transition energy of the $\pi\pi^*$ transition of melamine is very weak from the observed (ca. 310 nm) and the calculated result (277.8 nm). From the MO calculation, the first $\pi\pi^*$ transition is constructed mainly of a mixture of excited wavefunctions; one is from nitrogen atoms to the neighbor carbon, and another is from other nitrogen to other carbons (Fig. 3). This means that the number of excitation photons as $\pi\pi^*$ is not large enough to lead to the energy transfer. Three degenerate $\pi\pi^*$ transitions result from the calculation as the second, the third and the fourth electronic transitions of melamine. Luminescence spectra of Eu–melamine were also shown in Fig. 2(c) for the
comparison. This complex shows the $\pi\pi^*$ transition and the T$_1$ of melamine at 27,300 (366) and 22,000 cm$^{-1}$ (456 nm), respectively. Eu–melamine also shows some ff emissions, the $^5D_0/^7F_1$ and the $^5D_0/^7F_2$ at 16,968 and 16,338 cm$^{-1}$, respectively. Therefore, the energy pathway from melamine to Ln(III) exists; however, melamine may not have enough energy for the ff-emission of Pr(III). The intramolecular energy transfer of Eu–melamine may occur as T$\rightarrow$S$^J$ via the Dexter mechanism [11,12]. The $^5D_0/^7F_1$ transition band of Eu–melamine, which corresponds to the magnetic dipole

$$\pi\pi^* (277.8 \text{ nm}): \Psi_1 = -0.6986X_{1,1} - 0.6986X_{1,1}$$
$$\pi\pi^* (235.5 \text{ nm}): \Psi_2 = -0.8562X_{1,1} + 0.2947X_{1,1}$$
$$\pi\pi^* (235.5 \text{ nm}): \Psi_3 = 0.8281X_{1,1} + 0.4781X_{1,1} + 0.2927X_{1,1}$$
$$\pi\pi^* (235.5 \text{ nm}): \Psi_4 = -0.8281X_{1,1} + 0.4781X_{1,1} + 0.2927X_{1,1}$$

Vacant orbitals

$\phi_{16}(\sigma^*)$

Occupied orbitals

$\phi_3(\sigma^*)$

Fig. 3. Excited state wavefunctions and diagrammatical representations of MO’s for melamine. The wavelength in each bracket shows the calculated transition energy.

![Excited state wavefunctions and diagrammatical representations of MO’s for melamine.](image1)

![Excited state wavefunctions and diagrammatical representations of MO’s for melame](image2)

![Excited state wavefunctions and diagrammatical representations of MO’s for melame](image3)

transition, is observed strongly. This indicates that the Eu(III) is surrounded by a strong and high-symmetrical sphere [13].

Pr–melem and Eu–melem show the $\pi\pi^*$ fluorescence at 390 nm (25,600 cm$^{-1}$), originating from the melem moiety, and there are no differences each other as shown in Fig. 4. Similarly to the case of Ln–melamine, the ff emissions appear in the spectra of Eu–melem, but no ff emissions in Pr–melem. However, Ln–melem has no phosphorescence, meaning that melem keeps a stable singlet level even in a complexation state. Thus, the intramolecular energy pathway of Ln–melem differs from the Ln–melamine, i.e. the excited singlet state of melem acts as an electron donor, and the energy transports to Ln(III) via the Förster mechanism [14]. The calculation was also performed about melem, and the result is shown in Fig. 5. The singlet $\pi\pi^*$ transition contributes to the intramolecular charge transfer transition from the six nitrogen atoms of the three bays to the center nitrogen and to the three carbons existing as a neighbor of amino groups. This indicates that the two ligands with the same symmetry D$_{3h}$, melamine and melem, have

$$\pi\pi^* (335.3 \text{ nm}): \Psi_1 = -0.9460X_{16,16} - ...$$

![Excited state wavefunctions and diagrammatical representations of MO’s for melame](image4)

![Excited state wavefunctions and diagrammatical representations of MO’s for melame](image5)
different electronic structure. As described above, the intramolecular excitation energy pathway of Pr–melamine differs from that of Pr–melem. In conclusion, melamine uses the triplet state as an energy donor to Pr(III), while, melem does the singlet (Fig. 6). From the above discussion, in the case of such an $D_{3h}$ organic molecule acting as the energy donor, the essential of the differences of intramolecular energy pathway in the Ln(III) system will be visualized from the electronic structural points of view. To clarify the useful differences of the energy mechanisms, we try to measure the fluorescence spectra of new compounds prepared with modified melamines, as well as we construct molecular thin films for detailed investigations.

4. Conclusion

The two kinds of Pr(III) complex both with a $D_{3h}$ symmetry-chromophore show completely different intramolecular energy transfer pathway from the measurements of electronic absorption and luminescence spectra in the solid state. Pr–melamine forms a strong ligand field, however, shows luminescences (fluorescence and phosphorescence) without any ff-emission. In contrary, Pr–melem shows only a singlet $\pi\pi^*$ luminescence without phosphorescence of the ligand and ff-emissions of Pr(III). According to the emission properties of two Eu(III) complexes, the energy transfer level of Ln–melamine occurs from the excited triplet level of melamine to the Ln(III), and that of Ln–melem does from the excited singlet of melem. These results shed light on the intramolecular energy transfer of Ln(III) compounds with the $D_{3h}$ chromophores. In continuation of this work we are preparing Ln(III) complexes with the mentioned chromophores expecting further information on these mechanisms.

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