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Photophysics of lanthanide double-decker compounds with mixed octaethylporphyrinato and 2,3-naphthalocyaninato ligands

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Abstract

Ground state electronic absorption and luminescence spectra for M^{III}(OEP)(Nc) (M = La, Eu, Lu; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinate; Nc = 2,3-naphthalocyaninate) and Ce(OEP)(Nc) are recorded and comparatively studied. Strong $\pi-\pi$ interactions are present in these highly π-conjugated systems. The central metal ions seem to play no direct role either in the absorption spectra or in the emissions, but have great influences on the properties of the complexes revealed by both absorption and emission spectra through tuning the ring-to-ring separation and thus ring-to-ring interaction. The absorption bands of the complexes M^{III}(OEP)(Nc) are dependent on the lanthanide ionic radius, red- or blue-shifted, respectively (depending on the electronic transition nature), along with the lanthanide contraction. Ce(OEP)(Nc) displays particularly different electronic absorption features in comparison with the other three tervalent metal complexes. The fast deactivation process for the sandwich double-decker complexes is mainly caused by the additional $\pi-\pi$ interactions and electronic transition states arising from the coupling of the two macrocycles. The lanthanide ions in the complexes also facilitate the deactivation processes through heavy atom enhancement of intersystem crossing rate, or opening new pathways by ligand-field or ring-metal charge transfer states lying below the normally emissive (π,π^*) states.

Keywords: Porphyrin; Naphthalocyanine; Lanthanide; Sandwich; Fluorescence

1. Introduction

Lanthanide tetrapyrrole sandwich-type complexes, in which two or three macrocycles are connected by one or two lanthanide ions to a close proximity, are an important species of compounds presenting strong $\pi-\pi$ interactions between the adjacent macrocycles, which gives a good model to assess the novel properties of the multichromophoric species and thus help to reveal the distinctive properties of the reaction center of the special pair. In the past several decades, efforts in search of novel advanced molecular materials have extended the research into both homoleptic and heteroleptic porphyrinato or phthalocyaninato as well as mixed (porphyrinato)-(phthalocyaninato) lanthanide sandwich complexes [1–4]. The mixed sandwich complexes containing both porphyrin and phthalocyanine in one molecule are especially interesting because when porphyrin and phthalocyanine are combined together, the absorptions

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of the formed compounds cover almost the whole visible region. This will promote the efficiency of solar energy absorption, and afford potential high-qualified energy transition and storage materials such as solar cells.

Few reports deal with the excited states of the homoleptic double- and triple-decker complexes due to the lack of fluorescence of most of the sandwich tetrapyrrole metal complexes. One good example is the work of Holten and co-workers who have investigated the photophysics of a series of bis- and tris(octaethylporphyrinato) lanthanide complexes [5–9], among which fluorescence quenching has been observed for some compounds. Almost nothing is known about the luminescence properties of the mixed (porphyrinato)(phthalocyaninato) lanthanide complexes, to the best of our knowledge, not to mention those of the novel mixed (porphyrinato)(naphthalocyaninato) rare earth complexes reported very recently by this group [10–13]. Herein, we report the ground state electronic absorption and emission properties of four mixed ring lanthanide double-decker complexes, namely M^{III}(OEP)(Nc) (M = La, Eu, Lu) and Ce(OEP)(Nc), in which one porphyrinato and one naphthalocyaninato macrocycles are connected by lanthanide ions to close proximity, 3.056–2.652 Å (Fig. 1, [10]). Also, we propose the excited state relaxation pathways and dynamics of the complexes by analogy to those of the reported homoleptic OEP lanthanide compounds.

2. Experimental

The synthesis and characterizations of complexes M^{III}(OEP)(Nc) (M = La, Eu, Lu) and Ce(OEP)(Nc) were reported elsewhere [11–13]. Ground state electronic absorption spectra were recorded on an HP 7530G spectrophotometer. Emission spectra were obtained on an FLS920 spectrofluorometer with a high-pressure xenon lamp as excitation source. All samples were measured for solutions in $CHCl_3$ with concentration of 10^{-5} mol cm^{-3} at room temperature.

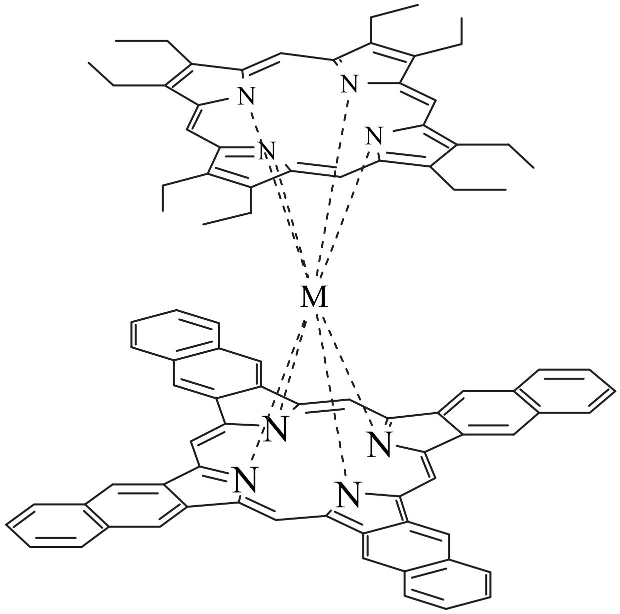

Fig. 1. The schematic molecular structure of M(OEP)(Nc).

3. Results and discussion

3.1. Electronic ground state absorption

The electronic ground state absorption spectra of M^{III}(OEP)(Nc) (M = La, Eu, Lu) and Ce(OEP)(Nc) are illustrated in Fig. 2. All the compounds show strong absorption bands lying at 327–325 and 406–393 nm, which are deduced from Soret bands of Nc and OEP ligands, respectively. No dramatic change has been found for these two Soret absorptions with the central metal ions changing from tervalent La, Eu and Lu to intermediate Ce. In the electronic ground state absorption spectra of M^{III}(OEP)(Nc) (M = La, Eu, Lu), several visible bands are observed in the region of 500–800 nm that can be ascribed to the Q bands of the macrocycles. In particular, the most intense Q (0,0) band appears at 612–594 nm with one shoulder in the higher energy region around 549–521 nm. The latter of which was assigned as Q (1,0) transition in OEP homoleptic double-decker complexes [9]. Two weak and broad absorption bands located at 683 and 759, 653 and 779 nm, respectively, were observed for the medium and heavy lanthanide Eu and Lu compounds, but become indiscernible for the light lanthanide compound of La.

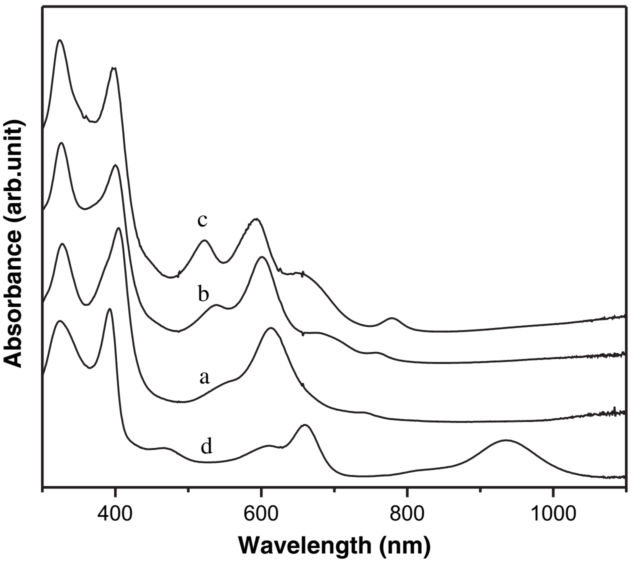

Fig. 2. Electronic absorption spectra of (a) La(OEP)(Nc), (b) Eu(OEP)(Nc), (c) Lu(OEP)(Nc), and (d) Ce(OEP)(Nc).

The positions of these absorption bands also depend on the ionic radii of the metal center, which shift bathochromically or hypsochromically along with decreasing central lanthanide ionic size. The absorption spectrum for the cerium complex Ce(OEP)(Nc) in the Q band region is remarkably different from the above three complexes, but represents the same features with those of reduced species $[M^{III}(OEP)(Nc)]^-$ [11–13]. The intensity of the main Q (0,0) absorption band of Ce(OEP)(Nc) gets weakened compared to that of the other three neutral tervalent lanthanide complexes. But the lower energy shoulder band at 660 nm becomes stronger. A new broad absorption band with relatively strong intensity at 936 nm is also found for this cerium compound. In addition to these changes, a new weak band emerging at about 463 nm between the Soret and Q bands for Ce(OEP)(Nc) is assigned to the $\pi-\pi^*$ electronic transition arising from molecular orbitals delocalized over both Nc and OEP macrocycles by analogy with that for $[Eu(OEP)(Nc)]^-$ [11–13].

3.2. Fluorescence behavior

Fig. 3 shows the emission spectra of the complexes M^{III}(OEP)(Nc) (M = La, Eu, Lu) and Ce(OEP)(Nc) under the excitation wavelength of 400 nm. Unlike the homoleptic OEP triple-decker complexes reported by Wittmer and Holten [9], the three tervalent lanthanide complexes show discernable fluorescence emitted from Q (π,π^*) state, which presents good mirror image with the absorption spectra. However, the emission is extremely weak compared with the reference compound H_2OEP. This indicates that the fluorescence of the photoexcited complexes is mostly non-radiatively decayed. Excitation at 400 nm induced one prominent emission at 625 nm, that is characteristic fluorescence emitted from Q (0,0) state with fine structures and the two weak vibronic bands.

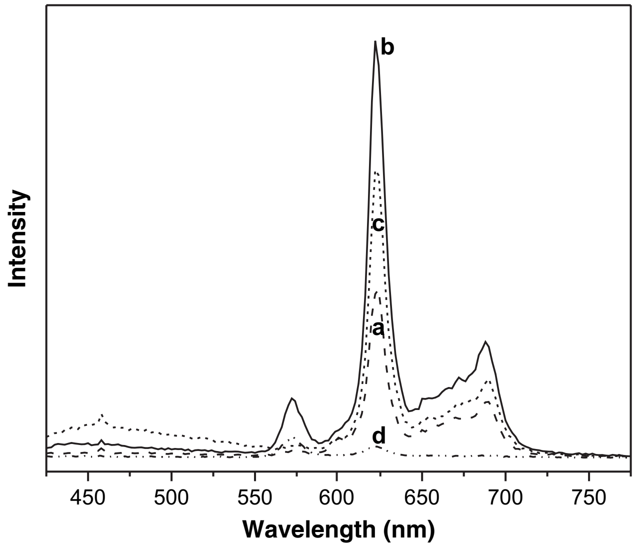

Fig. 3. Fluorescence spectra of (a) La(OEP)(Nc), (b) Eu(OEP)(Nc), (c) Lu(OEP)(Nc), and (d) Ce(OEP)(Nc) under the excitation wavelength of 400 nm.

As can be clearly seen from Fig. 3, no significant difference is observed among the emission features of the three tervalent lanthanide complexes. This indicates that the central metal ion does not play a direct role for the photophysical behavior of the mixed ring double-decker complexes. In contrast to the tervalent lanthanide complexes, Ce(OEP)(Nc) shows no discernable fluorescence under the same experimental conditions (Fig. 3).

3.3. Q absorption bands of the complexes

When one porphyrinato macrocycle and one naphthalocyaninato ring are combined together, the electronic ground state absorption of the complex in the Q band region becomes stronger than the homoleptic porphyrinato rare earth derivatives, suggesting strong interactions between the porphyrinato and naphthalocyaninato macrocycles.

Recently, the electronic absorption features of M^{III}(OEP)(Nc) in near-IR region by MCD measurement have been studied. The electronic energy levels for both tervalent lanthanide and intermediate cerium double-decker complexes have been illustrated in Fig. 4.

The Q (0,0) band is derived from the electron transition from the second HOMO to the LUMO state for compound M^{III}(OEP)(Nc). With the central metal ions changing from La to Lu (except for Ce), the interaction between OEP and Nc rings turns stronger owing to the drop in the distance between the two macrocycles, resulting in the increase in the energy of the first HOMO and decrease in the energy of the second HOMO [11]. Therefore, the splitting between the second HOMO and the first semi-occupied HOMO increases. It is worth noting that no significant change has been detected for the energy level of the first LUMO according to the electrochemical studies [11]. This is also true for the second LUMO. Consequently, the energy gap between the second HOMO and second LUMO increases in the same order, which is corresponding with the hypsochromic shift of the Q bands for the series of the tervalent metal complexes.

When the compound is reduced to $[M(OEP)(Nc)]^-$, the electronic absorption spectra display obvious change especially in the visible region due to one more electron being added to the semi-occupied HOMO of this π-conjugated system [11–13]. This is also true for Ce(OEP)(Nc). For this compound, the energy between HOMO and the second HOMO as well as that between LUMO and the second LUMO decreases due to the increase in the OEP-to-Nc ring distance associated with the addition of one more electron to the anti-bonding HOMO of the molecule. This induces the increase in the

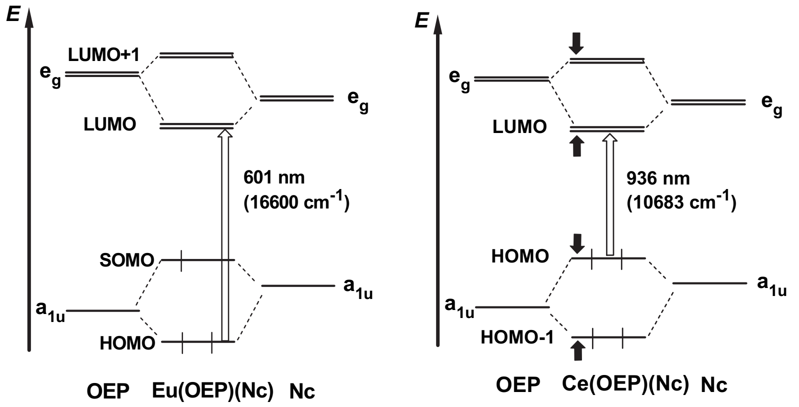

Fig. 4. Molecular orbital diagram of the complexes Eu(OEP)(Nc) and Ce(OEP)(Nc). The black arrows denote the energy level changes caused by altering the central metal ions.

energy gap between the HOMO and LUMO. As a result, the near-IR absorption band deduced from one electron transfer from HOMO to LUMO blue-shifts to 936 nm. Moreover, one new π–π* electronic transition emerges at 469 nm. The coupling of the two electrons in the HOMO of Ce(OEP)(Nc) diminishes the probability of the transition from the second HOMO to LUMO and thus weakens the intensity of the main Q (0,0) absorption.

3.4. Photophysical behavior and excited state deactivation pathways

The coupling of the porphyrinato and naphthalocyaninato macrocycles by lanthanide ions leads to fluorescence decay through electronic states located at lower energy levels deduced from π–π interactions between the macrocycles with participation of the central metal ions. It is well known that the quick deactivation behavior often takes place for the aggregated phthalocyaninato derivatives since strong π–π interactions are induced by aggregation. Thus, one can expect that similar decay process will take place for the face-to-face coupled sandwich-type mixed OEP and Nc double-deckers. Meanwhile, by comparing the emission features of the OEP and Nc double-deckers of different lanthanide metals shown in Fig. 3, no direct relationship between the fluorescent properties and the altering of the central metals is found. This demonstrates that the lanthanide metal ions play no direct part in the deactivation of the sandwich complexes, but have some impact on facilitating the deactivation process by heavy atom enhancement of intersystem crossing rate and low-lying ligand-field or ring-metal CT states.

Herein, we would like to propose that the deactivation processes of the excited sandwich complexes are mainly nonradiative deactivation through internal conversion, intersystem crossing and other energy and electronic transfer processes. At the same time, the metal ions chelated between the two macrocycles should take part in the deactivation processes of the complexes by opening new pathways.

La(III) and Lu(III) ions in our investigated double-decker complexes have the f^0 and f^{14} electronic configuration, respectively. Therefore, no low-lying ligand-field (f,f) excited states participate in the deactivation of the excited lowest singlet state $^1(\pi,\pi^*)$ of the complexes. Moreover, the tervalent lanthanide ions in the double-deckers are very difficult to be reduced under the present research conditions according to their electrochemical investigations [11], which indicates that the ring-π metal charge transfer states are too high to affect the decay of the photoexcited complexes. Hence, the heavy atom effect is suggested to be the primary way by which the metal ions participate in the deactivation process.

Eu(III) ion will not take part in the deactivation process through RMCT states either, due to the same reason mentioned above for the La and Lu analogues. However, the contribution of the ligand-field (f,f) excited states to the decay process in this compound cannot be excluded at this stage because of the f^6 electronic configuration of the Eu(III) ion.

The emission properties of Ce(OEP)(Nc) is a bit different from the other three tervalent metal complexes, which presents even faster decay process when excited. This can be understood on the basis of the difference in the central metal ions sandwiched between the two macrocyclic ligands. According to the XANES spectroscopic investigation, cerium ion in Ce(OEP)(Nc) employs an intermediate valent state, close to tetravalence [13]. The cyclic volammogram of Ce(OEP)(Nc) shows the first reduction at −0.19 V (SCE), which is attributed to the cerium-centered reduction process. And the first ring oxidation appears at +0.20 V for Ce(OEP)(Nc). Based on these data, the ring-to-metal CT state of the cerium double-decker is estimated to be ca. 0.39 eV. Probably, this should be responsible for the ultrafast

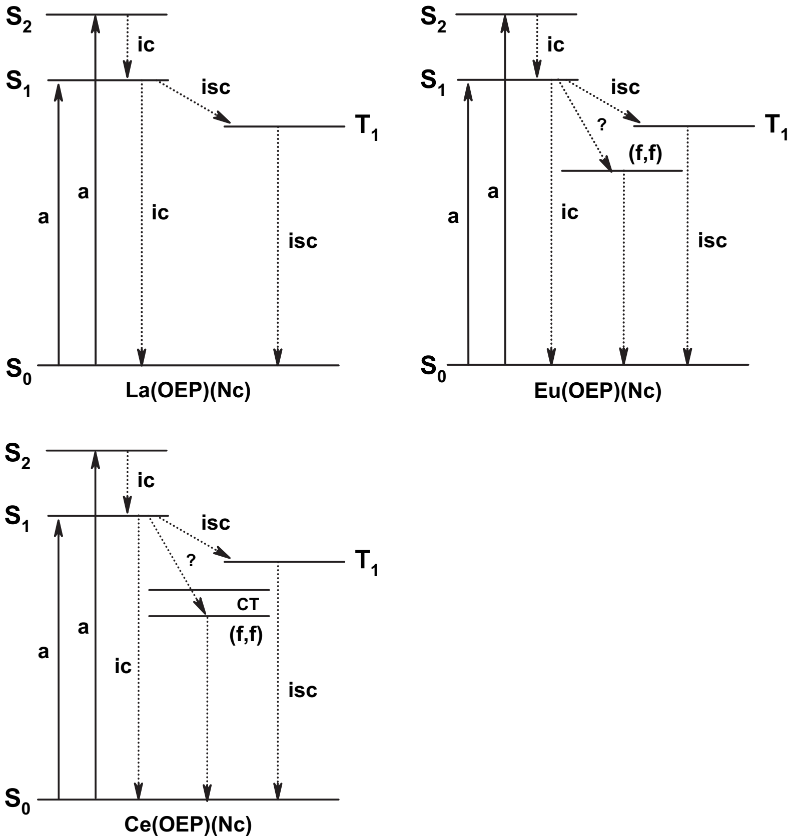

Fig. 5. Proposed photodynamics of La(OEP)(Nc) [or Lu(OEP)(Nc)], Eu(OEP)(Nc) and Ce(OEP)(Nc).

deactivation of the $^1(\pi,\pi^*)$ state ($\sim$2.0 eV above the ground state) to the ground state. Therefore, the cerium ion may influence the photophysical behavior of excited states of Ce(OEP)(Nc) through the involvement of the ligand-field and charge transfer states, as well as heavy atom effect. It is noteworthy that the very weak intensity of the Q (0,0) absorption is responsible for the very low luminescence of Ce(OEP)(Nc) with the excitation of Xe light at 400 nm. The proposed photodynamics and the deactivation processes of the photoexcited complexes are summarized in Fig. 5.

4. Conclusion

By studying the electronic ground state absorption spectra and steady state emission spectra of M^{III}(OEP)(Nc) (M = La, Eu, Lu) and Ce(OEP)(Nc), the electronic structures and photophysical behavior of the complexes are revealed. Strong π–π interactions are exhibited for the series of highly π-conjugated complexes. The central metal ions play no direct role but have significant effects on the spectroscopic properties of the complexes through affecting the ring-to-ring interactions. Along with the lanthanide contraction, the absorption bands shift to the red or blue, respectively, depending on the electronic transition nature. For photodynamic properties of the photoexcited complexes, the lanthanide ions promote the deactivation processes by means of heavy atom enhancement of intersystem crossing rate or ligand-field (f,f) states that lie below the normally emissive (π,π^*) states of the macrocycles, which opens a new route for deactivation. Ce(OEP)(Nc) shows remarkably different properties compared to the tervalent metal complexes due to the intermediate valent cerium ion in this compound.

Acknowledgments

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