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Electronic Characteristics of Sandwich-Type Lanthanide Octaethylporphyrinates

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The electronic behaviors of sandwich-type rare earth octaethylporphyrinates Ln(oep)$_2$ and Ln$_2$(oep)$_3$ (Ln=Ce, Pr, and Eu) were characterized by measurements of the near infrared or UV-vis spectra and D.C. conductivity. However, no remarkable change induced by oxidation of the ligand from (oep)$^{2-}$ to (oep·)$^-$ was observed on the conductivity.

A series of macrocyclic compounds such as metallophthalocyanides or metalloporphyrinates have been intensively studied as prospective materials for the electrical device such as organic semiconductors$^{1)}$ for several decades. Since the lanthanide phthalocyanine complexes with a sandwich structure of which the lanthanide ion was located between two phthalocyanine ligands were synthesized for the first time in 1965,$^{2)}$ a great interest has been paid especially to this kind of compounds, because they show high electrical conductivity values in the order of 10^{-5} to 10^{-7} S cm^{-1} and furthermore the substantial increase to the order of 10^{-2} S cm^{-1} is attained after the partial oxidation of complexes with iodine.$^{3)}$ Recently, a series of lanthanide porphyrinates have been synthesized and their molecular structure has been determined to be of the same sandwich-type as the lanthanide phthalocyanides.$^{4,5)}$ In this paper, the electronic characteristics of the double- or triple-decker lanthanide porphyrinates, Ln(oep)$_2$ or Ln$_2$(oep)$_3$, and their partially oxidized counterparts with iodine, Ln(oep)$_2^+$·I$_x$ and Ln$_2$(oep)$_3^+$·I$_x$, were discussed on the basis of their near IR or UV-vis spectra and electrical conductivity.

The complexes Ln(oep)$_2$ and Ln$_2$(oep)$_3$ were prepared according to the procedure of Buchler et al.$^{6)}$ The resulting complexes were identified by elemental analysis and UV-vis or near IR spectra. The iodine-doped materials were prepared by a modified procedure employed by Padilla et al. for Ln(Pc)$_2$·I$_x$.$^{3)}$ A solution of 2 ml benzene containing 10 mg of Ln(oep)$_2$ was mixed with another 2 ml benzene solution of 10 mg I$_2$, followed by a subsequent stirring for 2 h at room temperature. The violet-black product was isolated by filtration, and then the resulting solid was repeatedly washed with benzene and dried for several hours in vacuum. In the case of $Ln_2(oep)_3$, toluene was used instead of benzene. The iodine contents were evaluated from the elemental analysis to be x=2.7-3.0 and x=6.5-7.0 for $Ln(oep)_2 \cdot I_x$ and $Ln_2(oep)_3 \cdot I_x$, respectively.

The most typical property of the single-hole double-decker lanthanide porphyrin complexes consisting of a noninteracting central metal ion Ln^{3+}, a porphyrinate bivalent anion $(Por)^{2-}$, and a porphyrinate monovalent anion radical $(Por\cdot)^-$ is characterized by the near IR absorption spectra in the region of 1100-1500 nm, deriving from the internal charge transfer between $(Por)^{2-}$ as a donor and $(Por\cdot)^-$ as an acceptor.7) The peak positions reported are 1480 nm for $La(oep)_2$ and 1135 nm for $Lu(oep)_2$.7) The complexes, $Pr(oep)_2$ and $Eu(oep)_2$, prepared in this work also gave the near IR absorption bands at 1400 and 1280 nm, respectively, while no absorption spectrum was found on $Ce(oep)_2$, indicating that the valence states of Ce and (Por) are +IV and -II. For the iodine-doped $Ce(oep)_2 \cdot I_x$, however, the similar near IR absorption band appeared at 1240 nm (Fig. 1). This means that the porphyrinate monovalent anion radical $(oep\cdot)^-$ is formed in $Ce^{IV}(oep)_2 \cdot I_x$. The near IR absorption band of $Eu^{III}(oep)_2$ was also blue shifted from 1280 to 880 nm after the iodine-doped reaction, suggesting that the internal charge-transfer interaction gets stronger between the two $(oep\cdot)^-$ of $Eu(oep)_2 \cdot I_x$ after the iodine-doping than between the $(oep)^{2-}$ and $(oep\cdot)^-$ in $Eu^{III}(oep)_2$. However, the absorption band for the triple-decker complexes, $Ln_2(oep)_3$ and $Ln_2(oep)_3 \cdot I_x$, was never found.

The UV-vis absorption spectra of $Eu(oep)_2$ complex are shown in Fig. 2. The spectral patterns between the undoped and doped specimens for a series of lanthanide porphyrinates were almost similar to each other. The Soret and Q band maxima of both the iodine-doped complexes, $Ln(oep)_2 \cdot I_x$ and $Ln_2(oep)_3 \cdot I_x$, are blue-shifted compared with those of their neutral counterparts, $Ln(oep)_2$ and $Ln_2(oep)_3$, in a similar manner as the $Ln_2(oep)_3^+$ complex prepared by electrochemical oxidation of $Ln_2(oep)_3$.8) Therefore, this is another evidence of the formation of porphyrin π -cation-radicals although no absorption band is observed in the near IR region for $Ln_2(oep)_3 \cdot I_x$.

Two-probe D.C. electrical conductivity measurements were performed on pressed pellets with a size of ca. 3 mm in diameter and ca. 0.5 mm in thickness at room temperature. The conductivity values on both the double- and triple-decker lanthanide porphyrinates before and after the partial oxidation with iodine are summarized in Table 1.

The electrical conductivity values of the undoped lanthanide porphyrinates were distributed in a range of 6×10^{-8} to 9×10^{-7} S cm^{-1}. However, the apparent difference in the conductivity was not observed among the complexes of Ce, Pr, and Eu, and the order of magnitude of the values was about the same as that of the corresponding lanthanide phthalocyanines, $Ln(Pc)_2$,[3] but higher than that of transition metal monophthalocyanides.[9] This indicates that the overlap between the π orbitals of the face-to-face porphyrin units contributes to the relatively high conductivity in a similar way as $Ln(Pc)_2$. Unlike their phthalocyanine analogues, however, no apparent increase in conductivity was observed on the iodine-doped lanthanide porphyrinates and the values measured were still in the same order of magnitude as those of undoped specimens.

Since the near IR and UV-vis absorption spectra of iodine-doped lanthanide porphyri-

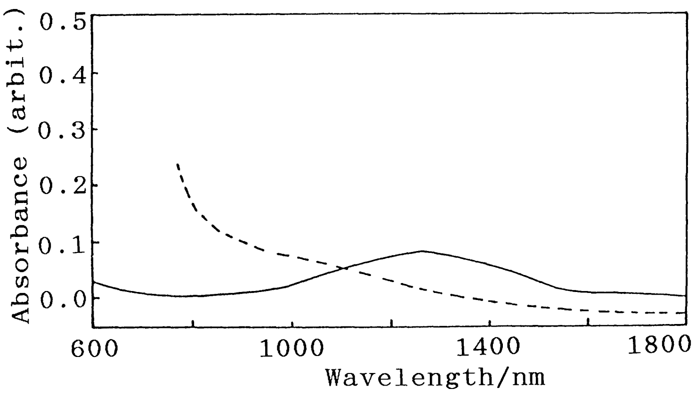

Fig.1. Near IR absorption spectrum of $Ce(oep)_2\cdot I_x$ (solid line) and $Ce(oep)_2$ (dashed line).

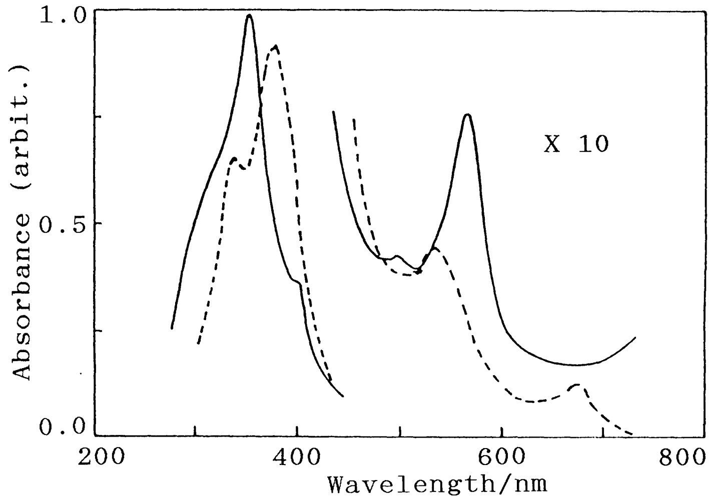

Fig.2. UV-vis absorption spectrum of $Eu(oep)_2\cdot I_x$ (solid line) and $Eu(oep)_2$ (dashed Line).

Table 1. D. C. electrical conductivity σ (S cm^{-1}) of sandwich-type $Ln(oep)_2$ and $Ln_2(oep)_3$ at room temperature before and after the partial oxidation with iodine

Compound	σ	Compound	σ
$Ce(oep)_2$	2×10^{-7}	$Ce(oep)_2\cdot I_x$	7×10^{-7}
$Pr(oep)_2$	2×10^{-7}	$Pr(oep)_2\cdot I_x$	1×10^{-6}
$Eu(oep)_2$	2×10^{-7}	$Eu(oep)_2\cdot I_x$	6×10^{-8}
$Ce_2(oep)_3$	9×10^{-7}	$Ce_2(oep)_3\cdot I_x$	7×10^{-7}
$Pr_2(oep)_3$	6×10^{-8}	$Pr_2(oep)_3\cdot I_x$	5×10^{-6}
$Eu_2(oep)_3$	3×10^{-7}	$Eu_2(oep)_3\cdot I_x$	2×10^{-7}

nates give the clear evidence of the formation of (oep·)$^-$ radical by oxidation with the iodine, the experimental result that the iodine-doping hardly contributes to increase of the electrical conductivity of Ln(oep)$_2$ or Ln$_2$(oep)$_3$ may be elucidated as follows: From the three-dimensional X-ray analysis of Ln(oep)$_2$ and Ln$_2$(oep)$_3$,$^{4)}$ the distance between the face-to-face oep ligands has been determined to be 3.4 to 3.5 Å and is short enough to interact between their π orbitals. However, the ethyl groups of oep ligands are oriented to the outside of molecule by the repulsion between the face-to-face oep ligands, and thus three-dimensional packing of complex molecules is expected to become loose from a kind of steric effect. Therefore, although the intramolecular π -orbital interaction gets stronger after the iodine oxidation, the intermolecular interaction may not be improved any more even after the partial oxidation with iodine because of the expanded spacing between the complex molecules.

It is concluded from the near IR and UV-vis absorption spectra that the Ce(oep)$_2$ and Ln$_2$(oep)$_3$ complexes consist only of (oep)$^{2-}$ but the Pr(oep)$_2$ and Eu(oep)$_2$ complexes contain the (oep·)$^-$ radical species as well as (oep)$^{2-}$. Furthermore, one (oep)$^{2-}$ ligand of Ce(oep)$_2$ or Ln$_2$(oep)$_3$ is oxidized to (oep·)$^-$ by the iodine-doping. However, such change of the electronic state never contributes to increase of the electrical conductivity and this may be due to the steric effect of molecular packing.

References

1) B. M. Hoffmann and J. A. Ibers, Acc. Chem. Res., **16**, 15 (1983).
2) I. S. Kirin, P. N. Moskalev, and Y. A. Makashev, Russ. J. Inorg. Chem., **10**, 1065 (1965).
3) J. Padilla and W. E. Hatfield, Syn. Met., **29**, F45 (1980).
4) J. W. Buchler and M. Knoff, "Optical Properties and Structure of Tetrapyrroles," ed by G. Blauer and H. Sund, Walter de Gruyter & Co, Berlin (1985), pp.91-105.
5) J. Jiang, K. Machida, and G. Adachi, Bull. Chem. Soc. Jpn., **65**, 1991 (1992).
6) J. W. Buchler, A. D. Cian, J. Fischer, M. Kihn-Botuliski, H. Paulus, and R. Weiss, J. Am. Chem. Soc., **108**, 3652 (1988).
7) J. W. Buchler, K. Elsasser, M. Kihn-Botulinski, B. Scharbert, and S. Tansil, ACS Symposium Series, **321**, 96 (1986).
8) J. K. Duchowski and D. F. Bocian, J. Am. Chem. Soc., **112**, 8807 (1990).
9) J. L. Peterson, C. S. Schramm, D. R. Stojakovic, B. M. Hoffmann, and T. J. Marks, J. Am. Chem. Soc., **99**, 287 (1977).

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