

## V-H Structures and Properties of Lanthanoid-Metallofullerenes

Lanthanoid-containing metallofullerenes with  $C_{82}$  cages,  $M@C_{82}$  ( $M$  is a lanthanoid metal atom), are the most widely investigated metallofullerenes. Accordingly to the oxidation state of the metal atom inside, they are classified into two groups; in one the metal atom takes the divalent state, and in the other it takes the trivalent state. Whether the two types of metallofullerenes have a common cage have been one of questions of lanthanoid-metallofullerenes. Recently we revealed that two types of metallofullerenes have a common cage and investigated the correlation between the absorption spectra and the cage structures on lanthanoid-metallofullerenes.

### V-H-1 Spectroscopic Studies of Endohedral Metallofullerenes

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We have measured the absorption spectra of the cations of  $La@C_{82}$  and  $Ce@C_{82}$ , which are trivalent-type metallofullerenes. The obtained spectra resemble not only each other but also those of the neutral species of  $Ca@C_{82}(IV)$  and  $Tm@C_{82}(III)$ , which are divalent-type metallofullerenes. Moreover we found that four metallofullerenes have an identical cage. To assign the absorption spectra, we performed a semi-empirical calculation at the level of single configuration interaction for  $Ca@C_{82}(IV)$ . It was revealed that any charge

transfer transitions from the  $C_{82}$  cage to the encapsulated metal atom cannot have large oscillator strength.

### V-H-2 Structural Study of Three Isomers of $Tm@C_{82}$ by $^{13}C$ NMR Spectroscopy

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The  $^{13}C$  NMR spectra were measured for three isomers of  $Tm@C_{82}$ , which is one of the divalent metallofullerenes. The molecular symmetries were determined for each isomer: isomer I has  $C_s$  symmetry, isomer II has  $C_2$  symmetry, and isomer III has  $C_{2v}$  symmetry. Moreover the cage structure of  $Tm@C_{82}(III)$  was found to be  $C_{82}(9)$ . As a result, it was revealed that  $Tm@C_{82}(III)$  has a cage identical to that of  $La@C_{82}$ , which is one of the trivalent metallofullerenes.

## V-I Development of Organic Superconductors

Since the discovery of superconductivity in a series of salts of TMTSF, TCF (tetrachalcogenafulvalene) derivatives have served as  $\pi$ -electron donors for the development of new organic superconductors. Although considerable research effort in this field has focused on the construction of TCF-type donors with extended  $\pi$ -conjugation, these donors, except for the DTEDT donor, failed to yield any organic superconductors. Besides TCF derivatives, our reported BDA-TTP donor gives three superconducting salts, but its  $\pi$ -electron system is the as that of TCF derivatives. Then it is possible that donor molecules with a less extended  $\pi$ -system that that of TCF derivatives produce superconductor? We attempted to find an answer to this question in the DHTTF donor system. We have also investigated the properties other salts of BDA-TTP.

### V-I-1 New Organic Superconductors Consisting of an Unprecedented $\pi$ -Electron Donor

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We designed and synthesized the DODHT donor with a reduced  $\pi$ -system as well as a bulky cis-fused dioxane ring. This donor forms crystalline salts with  $AsF_6$  and  $PF_6$  that display a variety of the pressure-induced resistive behavior and become superconducting at 3.3 and 3.1 K under 16.5 kbar pressure. X-ray analy-

sis show the donor molecules stacked head-to-tail to form the  $\beta''$ -type arrangement with weak intermolecular interactions in both salts.

### V-I-2 Tetrachloroferrate (III) Salts of BDH-TTP and BDA-TTP: Crystal Structures and Physical Properties

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Three  $\text{FeCl}_4$  salts based on non-TTF donors, BDH-TTP and BDA-TTP, have been prepared and characterized as  $\kappa$ -(BDH-TTP) $_2\text{FeCl}_4$ ,  $\beta$ -(BDA-TTP) $_2\text{FeCl}_4$ , and (BDA-TTP) $_3\text{FeCl}_4 \cdot \text{PhCl}$ . The  $\kappa$ -(BDH-TTP) $_2\text{FeCl}_4$  salt, with a room-temperature conductivity ( $\sigma_{\text{rt}}$ ) of  $39 \text{ Scm}^{-1}$ , is metallic down to 1.5 K, and its magnetic susceptibility obeys the Curie-Weiss law with a Curie constant ( $C$ ) of  $4.25 \text{ emuKmol}^{-1}$  and a Weiss constant ( $\theta$ ) of 0.041 K.  $\beta$ -(BDA-TTP) $_2\text{FeCl}_4$  exhibits metallic behavior ( $\sigma_{\text{rt}} = 9.4 \text{ Scm}^{-1}$ ) with a sharp metal-to-insulator (MI) transition ( $T_{\text{MI}} = 113 \text{ K}$ ) and antiferromagnetic ordering with the Néel temperature of near 8.5 K, whereas the solvated (BDA-TTP) $_3\text{FeCl}_4 \cdot \text{PhCl}$  salt is a semiconductor with a thermal activation energy of 0.11 eV ( $\sigma_{\text{rt}} = 2.0 \times 10^{-2} \text{ Scm}^{-1}$ ) and exhibits Curie-Weiss behavior ( $C = 4.42 \text{ emuK mol}^{-1}$ ,  $\theta = -0.35 \text{ K}$ ).