# V-D 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. Recently we investigated the cage structures and the motions of endohedral metal in metallofullerenes of the former group by <sup>13</sup>C NMR spectroscopy.

#### V-D-1 Structural Study of Four Ca@C<sub>82</sub> Isomers by <sup>13</sup>C NMR Spectroscopy

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The <sup>13</sup>C NMR spectra of four Ca@C<sub>82</sub> isomers have been measured. The symmetry of isomers I, II, III and IV are assigned to be  $C_s$ ,  $C_{3v}$ ,  $C_2$  and  $C_{2v}$ , respectively. For isomer IV, the cage is specified to be  $C_{2v}(9)$ . Our experimental results regarding the symmetry of cage structure coincide with the theoretical predictions.

## V-E 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. And we succeeded in developing two superconductors from DODHT, with a less extended  $\pi$ -system that that of TCF derivatives. Recently other superconductors have been produced from these donors.

#### V-E-1 A New Organic Superconductor, (DODHT)<sub>2</sub>BF<sub>4</sub>H<sub>2</sub>O

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In addition to two organic superconductors  $(DODHT)_2X$  [DODHT = (1,4-dioxane-2,3-diyldithio)dihydro-tetrathiafulvalene; X = PF<sub>6</sub> and AsF<sub>6</sub>] previously reported by us, the BF<sub>4</sub> salt of DODHT containing one water molecule [(DODHT)\_2BF\_4H\_2O] has been found to undergo a superconducting transition at 3.2 K under a hydrostatic pressure of 15.5 kbar.

### V-E-2 A New Organic Superconductor, $\beta$ -(BDA-TTP)<sub>2</sub>GaCl<sub>4</sub> [BDA-TTP = 2,5-(1,3-Dithian-2-Ylidene)-1,3,4,6-Tetrathiapentalene]

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The preparation, crystal structure and physical properties of  $\beta$ -(BDA-TTP)<sub>2</sub>GaCl<sub>4</sub> has been investigated; the salt exhibits superconductivity at 3.1 K (onset) under a hydrostatic pressure of 7.6 kbar.