Study on the electron spin state of $La_2@C_{80}$ anion

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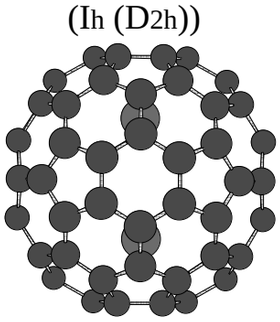
Spectroscopic study on fullerenes offers the likely playground for the discussion of molecular symmetry in 3-D fashion.[1,2] And a multi-metallofullerene (a fullerene with a metal cluster inside the hollow spherical carbon cage) is an interest in terms of the chemical trap of an active metal cluster in stable form under the atmosphere. Lanthanum monomers with various C_n cages ($La@C_n$)[3, 4] and an anion form of a lanthanum dimer with C_{80} cage ($La_2@C_{80}^-$) were measured by an ESR spectrometer.

A systematic characterization of the series of $La@C_n$s by using the temperature dependent ESR study in solution was performed. The anisotropic ESR parameters of g factor (Δg), the hyperfine coupling (hfc) tensor (Δa), and nuclear quadrapole interaction (NQI) were determined by the quantitative analysis of the line width under the assumption of molecular rotational correlation time (τ_r)of the hydrodynamics in solution. As a result, it was found that the electronic structures of all $La@C_n$s was stabilized by the intramolecular charge transfer and described as $La^{3+}@C_n^{3-}$. An interesting feature of the spin dynamics beyond the hydrodynamics in solution was deduced for $La@C_{80}$-I and $La@C_{84}$-II.

The enormous hyperfine coupling term (more than 30mT) of lanthanum nuclear spin in an anion form of $La_2@C_{80}$ was observed, which was due to the big spin density on the σ-bond of the lanthanum dimer. The enormous hyperfine coupling term together with the anisotropic g-factor gave the complicated x-band spectrum, however, the analysis of the x-band spectrum combined with that of the w-band one attains the complete simulation of both spectra. The full determination of parameters (g_{xx}, g_{yy}, g_{zz}, a_{xx}, a_{yy}, and a_{zz}) made it possible to deduce the nuclear quadrapole interaction (NQI) and the rotational correlation time (τ_r). Obtained τ_r surprisingly coincides with the value predicted by the assumption for the case of La@Cn.

La2@C80 anion (Ih (D2h))



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