

From neutral complexes to ionic compounds of fullerenes with magnetic transitions and metallic conductivity

Konarev D.V.*¹, Lyubovskaya R.N.¹, Khasanov S.S.²

¹*Institute of Problems of Chemical Physics RAS, 142432, Chernogolovka, Russia*

²*Institute of Solid State Physics RAS, 142432, Chernogolovka, Russia*

*e-mail: konarev@icp.ac.ru

Fullerenes are π -acceptors with spherical shape of the molecule, high symmetry and polarizability, and unusual band structure. Donor-acceptor complexes can be precursors in the design of new materials possessing metallic conductivity, superconductivity and ferromagnetism as well as showing magnetic transitions. Here we present different approaches to the synthesis of fullerene compounds, discuss their structures and properties.

Only neutral complexes of fullerenes can be obtained with relatively weak organic and organometallic donors such as saturated amines, metalloporphyrins and metal dithiocarbamates. Though they do not show dark conductivity, photoinduced charge transfer and relatively high photoconductivity are possible in some of them.

For preparation of ionic complexes we used direct fullerene reduction by strong donors or cationic metathesis reaction. These methods can be varied by the multi-component approach which allows one to introduce different neutral organic and organometallic compounds (D_2) into the ionic complexes to form the $(D_1^+) \cdot (\text{Fullerene}^{\bullet-}) \cdot (D_2)$ complexes which show a wide variety of crystal structures and properties.

The preparation of various ionic complexes showed that fullerene radical anions have strong tendency to dimerize to form diamagnetic singly bonded $(C_{60}^-)_2$ and $(C_{70}^-)_2$ dimers [1]. Their formation is accompanied by phase transitions in the 120-320 K range and results in the reversible transition of the compound from paramagnetic to diamagnetic state. Fullerene radical anions can also coordinate to cobalt(II) porphyrins and form diamagnetic σ -bonded $(\text{Co}^{\text{II}}\text{porphyrin} \cdot C_{60}^-)$ structures.

In the absence of dimerization and close contacts between fullerenes, compounds can demonstrate high conductivity and magnetic interaction of spins. The layered complex $(\text{MDABCO}^+) \cdot (C_{60}^{\bullet-}) \cdot \text{TPC}$ (MDABCO^+ is the cation of *N*-methyldiazabicyclooctane; TPC is triptycene) obtained by us is a unique pure organic quasi-two dimensional metal with unusual properties. The coexistence of metallic layers with nonmetallic layers having antiferromagnetic interaction of spins is observed in the 200-360 K range, whereas nonmetallic layers transfer to the metallic state below 200 K due to the ordering of $C_{60}^{\bullet-}$ [2]. In the series of C_{60} salts with *d*- metal cations: $(C_{60}^{\bullet-})_2 \cdot \{(M^{2+}) \cdot (\text{DMF})_x\}$ ($M = \text{Co}, \text{Fe}, \text{Ni}$ and Cd ; $x = 2.4 - 4$) high conductivity ($0.4-12 \text{ S} \cdot \text{cm}^{-1}$) coexists with antiferromagnetic interaction of spins localized on the metal cations [3]. The preparation of the complexes with partial charge transfer possessing metallic conductivity is also discussed.

- [1] D.V. Konarev, S.S. Khasanov, G.R. Mukhamadiyeva, L.V. Zorina, A. Otsuka, H. Yamochi, R.N. Lyubovskaya, *Inorg. Chem.* **49**, 3881 (2010).
- [2] D.V. Konarev, S.S. Khasanov, A. Otsuka, M. Maesato, G. Saito, R.N. Lyubovskaya, *Angew. Chem.* **49**, 4829 (2010).
- [3] D.V. Konarev, R.N. Lyubovskaya, *Russ. Chem. Bull.*, **57**, 1944-1954 (2008).