Division of Synthetic Chemistry
– Structural Organic Chemistry –

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Prof LEVITT, Malcolm	School of Chemistry, University of Southampton, 31 October
Mr MATEOS GIL, Jaime	Organic Chemistry Department, Complutense University of Madrid, 6 June–8 July

Scope of Research

Fundamental studies are being conducted for creation of new functional π-systems with novel structures and properties, and for evaluation of their application as organic semi-conducting materials toward photovoltaic and electroluminescent devices. The major subjects are: organo-chemical transformation of fullerenes C_{60} and C_{70}, specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of ionic fullerene species and their application for the synthesis of functional material; synthesis of new carbon-rich materials by the use of transition metal complex; creation of new functional π-materials with unique photoelectric properties.

KEYWORDS

π-Conjugated Systems
Open-Cage Fullerenes
Endohedral Fullerenes
Functional Dyes
Organic Solar Cell

Selected Publications

Kurotobi, K.; Murata, Y., A Single Molecule of Water Encapsulated in Fullerene C_{60}, *Science*, **333,** 613-616 (2011).

Murata, M.; Morinaka, Y.; Murata, Y.; Yoshikawa, O.; Sagawa, T.; Yoshikawa, S., Modification of σ-Framework of [60]Fullerene for Bulk-heterojunction Solar Cells, *Chem. Commun.*, **47,** 7335-7337 (2011).

Frunzi, M.; Jockusch, S.; Chen, J. Y.-C.; Calderon, R. K.; Lei, X.; Murata, Y.; Komatsu, K.; Guldi, D. M.; Lawler, R. G.; Turro, N. J., A Photochemical On-Off Switch for Tuning the Equilibrium Mixture of H_2 Nuclear Spin Isomers as a Function of Temperature, *J. Am. Chem. Soc.*, **133,** 14232-14235 (2011).

Beduz, C.; Carravetta, M.; Chen, J. Y.-C.; Concistre, M.; Denning, M.; Frunzi, M.; Horsewill, A. J.; Johannessen, O. G.; Lawler, R.; Lei, X.; Levitt, M. H.; Li, Y.; Mamone, S.; Murata, Y.; Nagel, U.; Nishida, T.; Ollivier, J.; Rols, S.; Room, T.; Sarker, R.; Turro, N. J.; Yang, Y., Quantum Rotation of *Ortho* and *Para*-water Encapsulated in a Fullerene Cage, *Proc. Natl. Acad. Sci. USA*, **109,** 12894-12898 (2012).

Zoleo, A.; Lawler, R.; Lei, X.; Li, Y.; Murata, Y.; Komatsu, K.; Valentin, M. D.; Ruzzi, M.; Turro, N. J., ENDOR Evidence of Electron-H_2 Interaction in a Fulleride Embedding H_2, *J. Am. Chem. Soc.*, **134,** 12881-12884 (2012).

Topics

Quantum Rotation of *Ortho* and *Para*-water Encapsulated in a Fullerene Cage

The synthetic procedure known as “molecular surgery” involves opening an orifice in fullerene C_{60} cages by a series of chemical reactions, insertion of small molecules into the cavity, and resealing of the cage by further reactions. This procedure has made available, in macroscopic quantities, a class of pure, stable, substances in which closed fullerene cages encapsulate small molecules. These systems provide “nano-laboratories” in which the small molecules are isolated in a geometrically well-defined, highly symmetrical environment. The recently-synthesized water-endofullerene $H_2O@C_{60}$ is particularly intriguing. Like H_2, water exhibits spin isomerism, with *ortho*- and *para*-forms, but unlike H_2, water has an electric dipole moment.

We study the energy levels, spin isomerism and quantum dynamics of single water molecules enclosed in fullerene cages, using three complementary physical methods: inelastic neutron scattering (INS), far-infrared spectroscopy (FIR), and nuclear magnetic resonance (NMR). In all cases, the homogeneous and symmetric environment provided by the fullerene cages isolates the *ortho* and *para* spin isomers, and gives rise to relatively narrow and unambiguous spectral features. We observe the existence of metastable *ortho*-water molecules, follow the slow conversion of *ortho*-water into *para*-water, and detect an energy splitting in the *ortho*-water rotational ground state, which is a signature of broken symmetry.

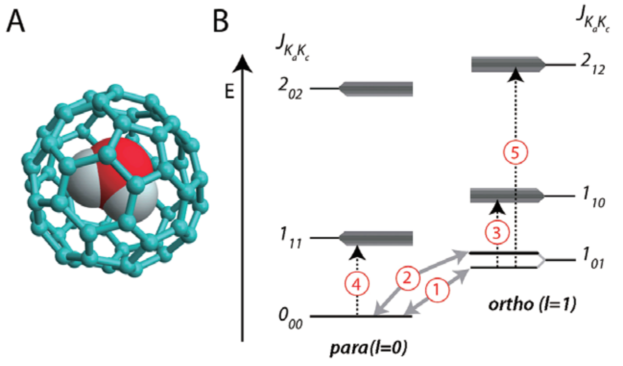

Figure 1. (A) Molecular structure of $H_2O@C_{60}$; (B) Energy level diagram, showing the principal transitions detected by INS (grey arrows) and IR spectroscopy (dashed arrows).

Elucidation of π-Conjugation Modes in Diarene-Fused 1,2-Dihydro-1,2-diborin Dianions

Boron-containing heterocycles have gained widespread attention, not only from a fundamental point of view, but also as potential materials for various applications, such as optoelectronics and sensors. Of particular interest is the fact that the incorporation of an electron-deficient boron atom, which has a vacant p-orbital, into a π-conjugated cyclic skeleton enables the production of an electron-accepting π-system with effective p-π* conjugation.

We have synthesized a series of diarene-fused 1,2-dihydro-1,2-diborins, B-B-bond-containing polycyclic π-electron systems, and investigated their intriguing orbital interactions between the π-framework and the diborane moiety. A dithieno-fused 1,2-dihydro-1,2-diborin derivative with a 3,3’-bithiophene skeleton was synthesized, which showed an absorption band at longer wavelength compared to that of the parent 3,3’-bithiophene. Upon two-electron reduction to the dianion, the 6π aromatic character in the diborin moiety was enhanced. This trend was different from that observed for the 2,2’-bithiophene analogue, the dianion of which had a peripheral π-conjugation that was extended over the tricyclic framework. Moreover, both of these dianions showed significant countercation effects in the absorption spectra, with drastic color changes. These results have provided deep insights into the fundamental nature of boron-containing π-conjugated systems and their potential applicability as a new type of optoelectronic materials.

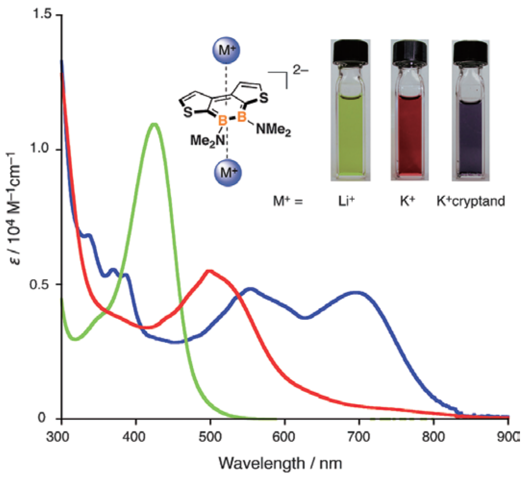

Figure 2. Absorption spectra of salts of 1,2-diborin dianion (Li^+, K^+, and K^+-([2.2.2]cryptand) in THF, together with photographs of their solutions in THF.