

Synthesis and Properties of Multiple C60/extended-TTF Systems

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The design and synthesis of artificial photosynthetic systems has recently been carried out as an important task for synthetic chemists due to the interest of transforming sunlight into chemical energy by mimicking the primary processes involved in photosynthesis.[1]

Among the different photo- and electroactive molecules used to construct artificial photosynthetic systems, [60]fullerene has played a very important role because of the large size and spherical shape of its delocalized and highly symmetric π -electron system. The resulting low reorganization energy of C60 and its remarkable chemical reactivity make it an excellent candidate as electron acceptor for the preparation of C60-based electroactive systems by covalent linkage to a wide variety of electron donor molecules. [2] These dyads undergo photoinduced singlet energy and/or electron transfer (ET) from the donor unit to the fullerene, generating a charge-separated state (CS) which, eventually, goes back to the ground state through a charge-recombination (CR) process. [3]

The ongoing quest for new C60-based dyads is driven by two goals: i) a rapid charge separation process to form the CS state, and ii) a slow down of the charge recombination process to the ground state, thus allowing to carry out a chemical work. For photovoltaic applications, the lifetime of the CS state has been evaluated to be in the range of $1\mu\text{s}$. We have recently reported that aromatization of the donor moiety upon oxidation in the formation of the CS state represents an important concept for a further stabilization of the formed radical pair. In this regard, we have covalently attached the tetrathiafulvalene (TTF) molecule to C60 to form C60-TTF dyads (1, 2) exhibiting remarkable lifetimes for the CS state, in the range of nanoseconds, due to the gain of aromaticity of the 1,3-ditholium cation formed upon oxidation. [4] In an effort to evaluate the photophysical effect of a second C60 unit covalently connected to the TTF moiety, we have synthesized very recently a C60-TTF-C60 triad in which the TTF unit is incorporated as an electroactive spacer between both C60 units. In this communication we will present our recent advances on the synthesis and properties of novel C60/extended-TTF systems

References.

[1](a) J. Deisenhofer, O. Epp, K. Miki, R. Huber, H. Michel, *J. Mol. Biol.* 1984, 180, 385. (b) W. Rettig, *Angew. Chem. Int. Ed. Engl.* 1986, 25, 971. (c) T.J. Meyer, *Acc. Chem. Res.* 1989, 22, 163. (d) H. Kurreck, M. Huber, *Angew. Chem. Int. Ed. Engl.* 1995, 34, 849.

[2] (a) *Fullerenes and Related Structures* (Ed.: A. Hirsch) Springer, Berlin, 1999, pp.199. (b) N. Martín, L. Sánchez, B. Illescas, I. Pérez, *Chem. Rev.* 1998, 98, 2527-2548. b) H. Imahori, Y. Sakata, *Adv. Mater.* 1997, 9, 537. c) H. Imahori, Y. Sakata, *Eur. J. Org. Chem.* 1999, 2445.

[3] D.M. Guldi, *Chem. Commun.* 2000, 321.

[4] a) N. Martín, L. Sánchez, M.A. Herranz, D.M. Guldi, *J. Phys. Chem. A.* 2000, 104, 4648. b) D.M. Guldi, S. González, N. Martín, A. Antón, J. Garn, J. Orduna, *J. Org. Chem.* 2000, 65, 1978.