

Rational design and synthesis of C₆₀-acene and C₆₀-[N]phenylene dyads towards efficient photoinduced charge transfer.

Taillemite, S. and Fichou, D.
CEA Saclay - DSM/DRECAM/SPCSI
LRC Semi-Conducteurs Organiques
CNRS - CEA - Paris 6 Univ.
91191 Gif-Sur-Yvette - France

C₆₀ can be easily functionalized by a variety of chemical structure, and therefore has been tested as an active component for biological and material applications. In 1992, Wudl and al.¹ observed a photoinduced electron transfer from a poly(phenylene vinylene) derivative (PPV) to C₆₀ and proposed a new approach to the preparation of photovoltaic devices². Interpenetrating blends of PPV donors and C₆₀ acceptors exhibit conversion yield up to 3 %, i.e. one of the best yield of organic solar cell today. Similarly to polymer/C₆₀ blends, a number of covalently bound C₆₀-donor dyads show a fast photoinduced electron transfer from the donor moiety to the fullerene acceptor followed by a slow charge recombination. This electronic process is at the origin of the high photovoltaic efficiency of these materials and is mainly due to the low reorganization energy of the fullerene derivatives. These last few years, a variety of donors have been covalently attached to C₆₀ such as ferrocene, oligo(phenylene vinylene)³, porphyrins⁴, ruthenium complexes, tetrathiafulvalenes... But, the acene derivatives have never been studied as donors, although pentacene proved to be a promising photovoltaic material⁵. We are also interested by other linear fused polycyclic aromatic molecules like [N]phenylene derivatives⁶ (Fig. 1) which have never been studied as donor or photovoltaic material.

First, we report here on the rational molecular design of C₆₀-acene dyads by combining both the Weller thermodynamic equation with the Marcus kinetic model. In particular, we have considered the importance of charge separation and recombination rate constants for various substituents on the donor moiety. For each substituted acene series, we build a diagram showing the dependence of the first singlet excited state energy (¹*E) on oxidation potential (E_{ox}). It allows to easily identify which substituents induce efficient charge separation. Our approach highlights electron-deficient acenes as virtually efficient donors.

Finally, we also report here on the synthesis of several C₆₀-tetracene (Fig. 2) and C₆₀-[3]phenylene dyads. Our synthetic strategy is based upon cobalt catalyzed [2+2+2] cycloaddition for the synthesis of the donors and Bingel reaction to link the donor moiety to C₆₀.

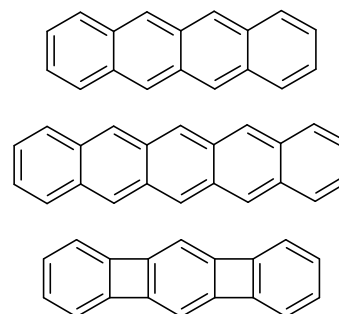


Fig. 1: chemical structures of tetracene, pentacene and [3]-phenylene.

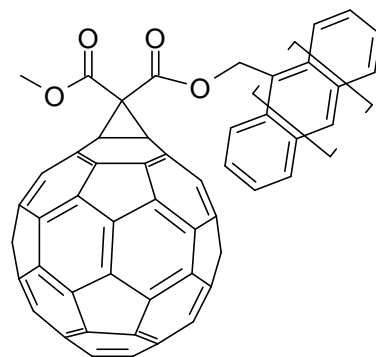


Fig. 2: Example of C₆₀-acene dyads (n = 1,2).

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⁴ Guldi, D. M. *Chem. Soc. Rev.* **2002**, 31, 22-36.

⁵ Videlot, C.; Fichou, D.; Garnier, F. *J. Chim. Phys.* **1998**, 95, 1335-1338.

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