

Design and Synthesis of Fullerene-based Dyads for Solid-Phase Photoinduced Charge Transfer.

Alexander Efimov, Nikolai Tkachenko, Helge Lemmetyinen.

Institute of Materials chemistry, Tampere University of Technology.

P.O. Box 541, 33101, Tampere, Finland.

Solid-phase photoinduced charge transfer is one of the most important phenomena in nanotechnology. Our research group pays lot of efforts on creating the donor-acceptor (DA) systems that are able to transform the light energy into electrical charge. The Langmuir-Blodgett technique is used as a method of DA organisation, allowing the preparation of the monomolecular DA-layers with controlled orientation. The donor-acceptor dyad used in the LB-technique should have some special properties like distinct hydrophilic and hydrophobic parts, size, solubility, dense intramolecular packing, low aggregation ability etc., making the molecular design a challenging task.

Two different approaches were considered when the linker between porphyrin and fullerene was designed. The first, where donor and acceptor moieties are separated one from another by four bonds and no ground-state interaction can be observed (1). In this case, the rings C and D of phytychlorin contain hydrophilic groups, such as carbomethoxyl, ketone, or hydroxyl, appearing to be enough for orientation of the molecule in LB-film. When the phytychlorin moiety is attached to the nitrogen atom, the structure of the hydrophobic part might be varied by substitution on position 2 of pyrrolidine ring. Finally, the hydrophobic-hydrophilic properties, as well attaching the bridge either on A or B ring of the phytychlorin can vary the intramolecular geometry. Overall seven different dyads (Fig. 1, comp. 1-7) were synthesized to explore all the possibilities.

The second global approach is to link the dyad components on "pi-stack" to ensure the ground-state porphyrin-fullerene interaction as a primary step in the charge transfer. Bingel's bis-adducts (2, 3) synthetic methodology was used in this case. The synthetic procedure was modified to introduce the hydrophilic groups into porphyrin to guarantee the uniform arrangement of the dyad in the LB-film (Fig. 2 comp. 8). The main disadvantage of compounds the 1-8 in terms of Langmuir-Blodgett technique is that they all are oriented the same way in the film, due to the location of the hydrophilic groups on the porphyrin part of the dyad. The compound 9 represents the reversed type of orientation where two carboxylic groups are attached on fullerene and the porphyrin ring is bearing two di-tert-butylphenyl groups, which form the hydrophobic part. In the same time such bulky fragments greatly improve the solubility of the whole molecule, making it easy to handle and study.

The detailed photochemical studies of dyads in solutions and LB-films are under way.

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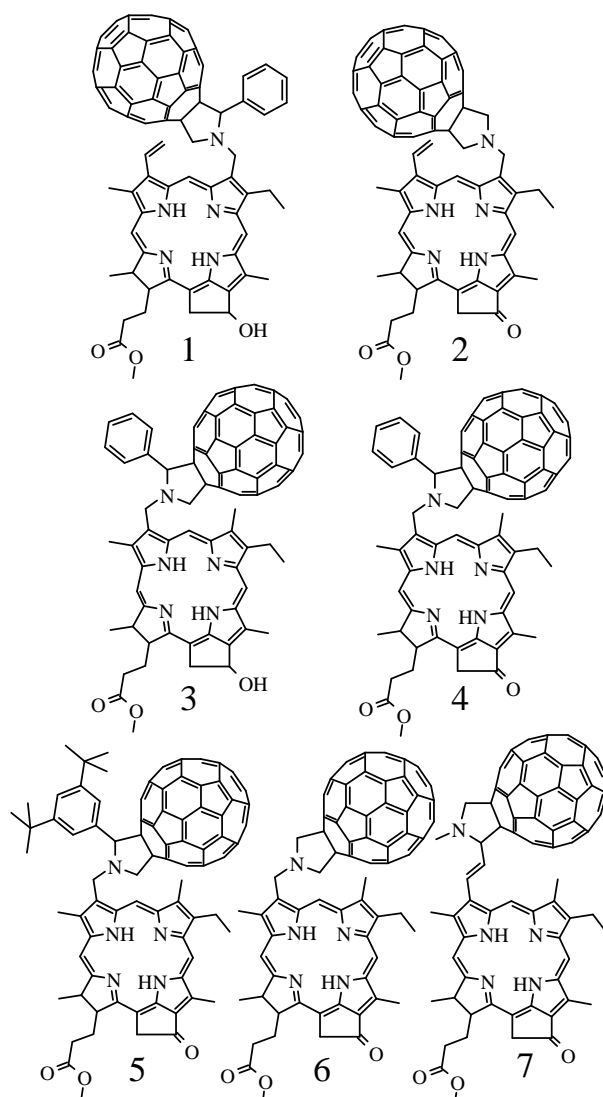


Fig. 1. Phytychlorin-fullerene dyads.

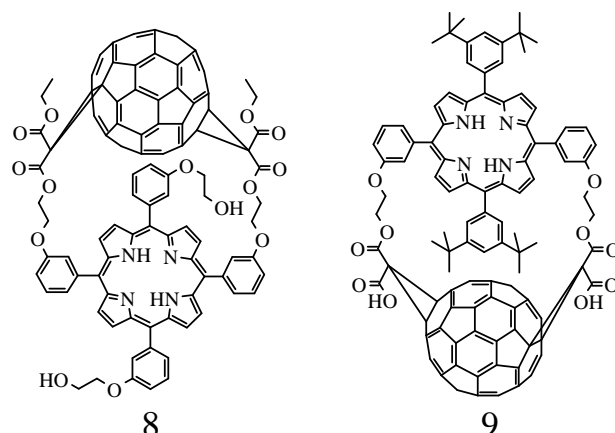


Fig. 2. Porphyrin-fullerene dyads.