

## Fullerene as an Electron Acceptor in Photoinduced Intra- and Interlayer Electron Transfer in LB Films

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Langmuir-Blodgett (LB) technique is well known and relatively simple method, which allows one to fabricate solid highly ordered monomolecular films of organic and bioorganic compounds [1]. It can be used to build a molecular device, which utilizes interaction of functional molecules in organized molecular system. In particular, one can construct a device capable of performing vectorial photoinduced electron transfer (VPET) [2].

Recently we have demonstrated that phytychlorin-fullerene (**PF**) donor-acceptor (DA) dyads can be used successfully for this purpose [2]. Except of being a good electron acceptor, the fullerene has two additional important functions in LB films: a) it is highly hydrophobic molecule and helps to keep high degree of ordering of the DA dyads; b) it is rather bulky molecule and prevents aggregation of the phytychlorin chromophores. This study is aimed to 1) optimize intralayer VPET functionality of **PF**-like dyads, 2) extend the primary intralayer VPET to an interlayer multi-step PVET, and 3) look for another molecular architecture for intra- and interlayer VPET.

(1) The ET process of **PF** compounds involves exciplex as the precursor of the complete charge separated (CCS) state [2]. In non-polar media exciplex relaxes directly to the ground state, which reduce efficiency of VPET in LB films. This, however, can be tuned by molecular design. A series of modified phytychlorin-fullerene compounds was synthesized (Fig. 1) and studied in solutions and films. The compounds with longer linker between donor and acceptor, **PpF** and **PtF**, undergo ET even in non-polar solvents. e.g. in toluene ET time constant is ~25 ps and charge recombination time is a few nanoseconds. In LB films we observed a gradual increase in efficiency of the VPET (Fig. 3, the strongest photovoltage response was observed from **PpF**).

(2) The intralayer VPET can be extended to an interlayer multistep VPET by alternating layer of DA molecules with a layer of molecules acting as a secondary donor or acceptor. We have used **PHT** (Fig. 2) as the secondary donor. When the **PHT** monolayer is placed at the phytychlorin moiety side of the **PF** monolayer, the amplitude and the lifetime of the photovoltage response increases gradually. Thus, **PHT** donates an electron to phytychlorin cation resulting in interlayer charge transfer state:  $(\text{PHT})^+ \text{PF}^-$ .

(3) LB technique opens new opportunities for molecular device engineering. Under certain conditions separate donor and acceptor molecules may form associated DA pairs in LB films. For example, this type of interaction is observed for mixture of **TBP** and **C<sub>60</sub>pyr** (see Fig. 2) in octadecylamine matrix (photoresponse is shown in Fig. 3). Yet another approach is to place donor and

acceptor in separate layers. Using this approach VPET was achieved between **PHT** layer (donor) deposited on top of **C<sub>60</sub>** (acceptor), which was supported by calixarene layer.

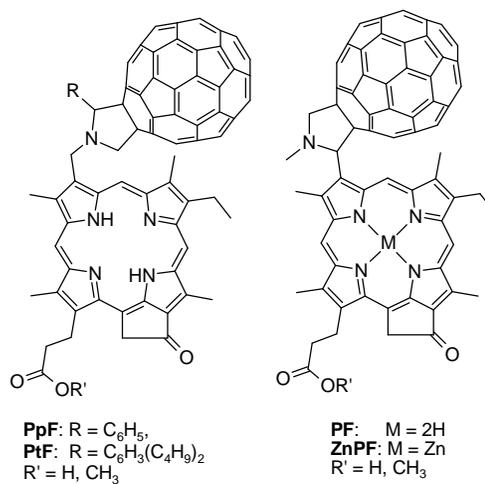


Fig. 1. DA dyads for intralayer photoinduced ET

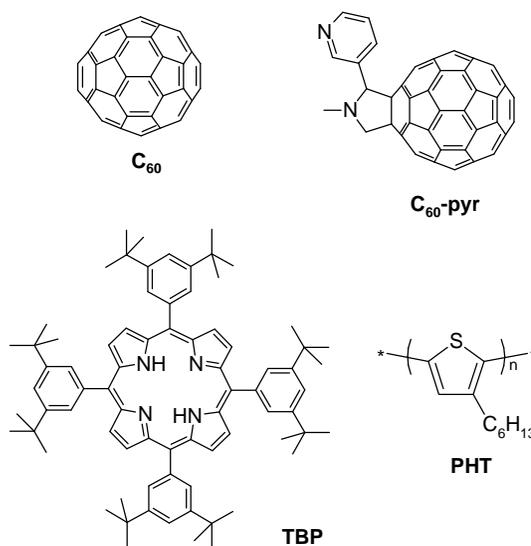


Fig. 2. Compounds for interlayer photoinduced ET.

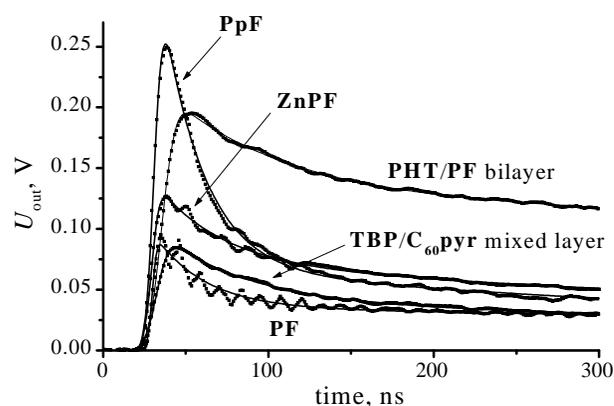


Fig. 3. Photo-voltage responses of different DA systems measured using time-resolved Maxwell charge displacement technique.

### References

- [1] G. Roberts, Langmuir-Blodgett films, Plenum, New York, 1990.
- [2] N.V.Tkachenko, E.Vuorimaa, T.Kesti, A.S.Alekseev, A.Tauber, P.H.Hynninen, H.Lemmetyinen, *J. Phys. Chem. B* (2000) **104**, 6371.