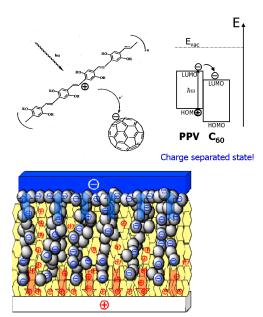
Organic Semiconductor Photophysics/Photochemistry for Solar Energy Conversion into Electricity and Synthetic Fuels

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Organic photovoltaic devices have a long history ranging back to 1970s. The first technologically interesting patent and publication on organic photovoltaic elements goes back to Ching Tang in Kodak labs in 1978. Therein, a vacuum evaporated double layer of phtalocyanine and perylenediimide inbetween two electrical contacts (sandwich geometry) showed photovoltaic action giving around 1% solar to electricity power conversion efficiency. Our contribution to the field of organic photovoltaics goes back to the discovery of an ultrafast photoinduced electron transfer from semiconducting polymers onto fullerenes (see Fig. 1) and the use of this phenomenon in photovoltaic elements in 1992.



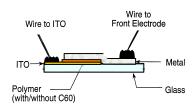


Fig. 1: Schematic illustration of photoinduced electron transfer from semiconducting conjugated polymers onto fullerenes. Energy level diagramme shows the absorption on the PPV polymer and the subsequent electron transfer from LUMO of the donor to the LUMO of the acceptor creating a positive charge (radical cation) on the polymer backbone and a negative charge (radical anion) on the fullerene. The charges are then transported to the respective electrodes in the donor and acceptor phases within the bulk heterojunction mixture. The OPV device is a simple sandwich geometry, where the photoactive layer is inbetween two electrodes.

In Sariciftci, Heeger patent in 1992, we described the definition and the making of "bulk heterojunction solar cells" as follows: Claim #2: "...where a heterojunction between conjugated polymer and acceptor material is formed *in situ* by controlled segregation during solidification from a solution containing both the donor and the acceptor moeities".

This strategy enables the fabrication of efficient photovoltaic elements by heavily increasing the contact interface between the donor and acceptor all over the volume. Second and important

photophysical advantage lies in the exciton harvesting potential, which leads to nearly 100% quantum efficiency of photoinduced charge generation. Today the world record organic photovoltaic elements perform around 10% power conversion efficiency using bulk heterojunction concept [Mitsubishi, Somitomo, Konarka, Heliatek, Solarmer].

We need new concepts and ideas in this field to open up new avenues to higher efficiencies and to new science. In this presentation we will present a photoelectrochemical route to organic bulk heterojunction solar cells to widen up the research in this field into the avenue of bulk heterojunction electrochemical devices and photochemical conversion of CO₂.

We will use the organic donor-acceptor bulk heterojunctions in electrochemical configuration as photoactive electrode materials as described in Fig. 2.

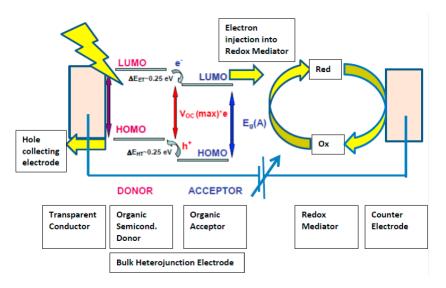


Fig. 2: Schematic description of the proposed use of bulk heterojunction electrodes in photoelectrochemical solar cells.

If we take the photoinduced electron transfer in organic donor-acceptor bulk heterojunctions, than after less than 1 picosecond a charge separated state is established: *i.e.* a radical cation on the organic semiconductor donor and a radical anion on the organic semiconductor acceptor. This charge separated state lasts milliseconds which gives enough time to do some chemistry/ electrochemistry using this radical anion to reduce CO₂ and/or split water.

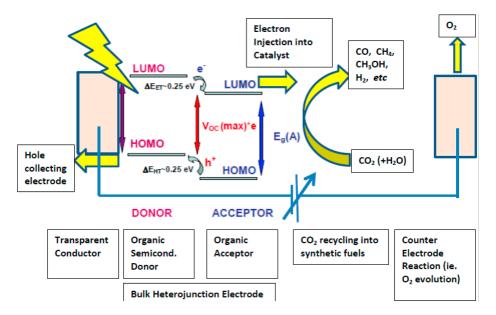


Fig. 3: The CO₂ reduction in a photoelectrochemical configuration using organic donor-acceptor bulk heterojunction electrodes