PHOTOPHYSICS AND PHOTOVOLTAIC DEVICES OF A π-EXTENDED TETRATHIAFULVALENE-FULLERENE DYAD

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ABSTRACT

Fullerenes have advantageous properties for photovoltaic application like strong electron affinity and high electron mobility. Yet, their absorption in the visible range, important for solar photovoltaics, is weak.
We present a novel fullerene dyad, consisting of a pi-extended tetrathiafulvalene donor, a phenylene-vinylene bridge and C_{60} as acceptor. The donor shows strong absorption in the range between 400 and 500 nm. Photoinduced charge separation is demonstrated by photoluminescence and photoinduced absorption spectroscopy. Spectroscopic evidence for the donor cation and fullerene anion is shown. The dyad molecule acts as photoactive material in thin film organic photovoltaic cells with a modest power conversion efficiency under simulated solar light.

INTRODUCTION

Organic materials gain interest for photovoltaic application in the last decades.[1,2,3]
Bulk heterojunction devices, consisting a blend of conjugated polymer and fullerene, are one interesting approach and have power conversion efficiencies > 3% today.[4,5] Main research topics are the development and implementation of red-shifted (low band gap materials), strongly absorbing materials[6] and the control of morphology on a nanoscale level.[7]
Fullerenes have advantageous properties for solar cells. They are strong electron acceptors, which give, in combination with many π-conjugated systems, rise to efficient splitting of excitons into charges.[8] Further, fullerenes have sufficiently high electron mobility ($\mu = $ 2-4.5 * 10^{-3} cm^2 V^{-1}s^{-1})[9] for the charge transport to the electrodes in thin layer (d ~ 100 nm) devices.
Yet, in fullerenes the HOMO-LUMO transitions is dipole symmetry forbidden. The optical absorption in the visible/ near infrared range, where the maximum of the solar photon flux is located, is therefore weak.
Fullerene chemistry has made great advances in the recent year and a variety of molecules with different functionalization is available. However, device development has mainly concentrated on bare C_{60} and the fullerene derivative 1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6)C61 PCBM. Other fullerene derivatives and dyad molecules[10,11,12,13] have not been largely investigated for their device performance, yet.[14]
In this contribution, we present a π-extended tetrathiafulvalene-wire-fullerene (ex-TTF-C_{60}) dyad as alternative fullerene material for organic solar cells. We demonstrate evidence for

photoinduced charge transfer between the ex-TTF and C_{60} unit. Preliminary devices are fabricated and characterized for this novel dyad molecule.

EXPERIMENTAL

Figure 1 shows the chemical structure of ex-TTF-C_{60} dyad and the donor part ex-TTF with a phenylene-vinylene wire, respectively. The later compound was used for reference experiments. The synthesis of the compounds were published elsewhere.[15]

Electrochemical measurements were performed in a dichlorobenzene: acetonitrile 4:1 solution with 0.1 M Bu_4NClO_4 as electrolyte. A glassy carbon electrode served as working electrode, a SCE as reference electrode and a platinum wire as counter electrode. Scan rate was 200 mV/s.

Optical absorption was measured on a HP 8453 spectrometer. Photoluminescence (PL) and Photoinduced Absorption (PIA) were measured with a homemade setup at 80 K. PL was measured under excitation at 476 nm light from an Ar^+ laser or at 664 nm light from a diode laser with a monochromator and Si detector. PIA was measured with a halogene lamp as probe and the Ar^+ laser as pump. The changes of the probe transmission resulting from the mechanically chopped laser pump beam were detected with a Si/ InGaAsSb sandwich detector and recorded with a lock-in-amplifier.

Photovoltaic devices were made in sandwich geometry. Photoactive layer were spin cast from chlorobenzene solutions. ITO, coated with PEDOT:PSS and evaporated LiF/ Al layer served as positive and negative contacts, respectively. Metal evaporation and device characterization were done under Ar atmosphere.

Current-voltage characteristics of the devices were measured in the dark and under illumination with 80 mW cm-2 from a solar simulator. Incident photon to current efficiencies IPCE were measured with monochromatic light from a Xe lamp, detecting the photocurrent with a lock-in-amplifier.
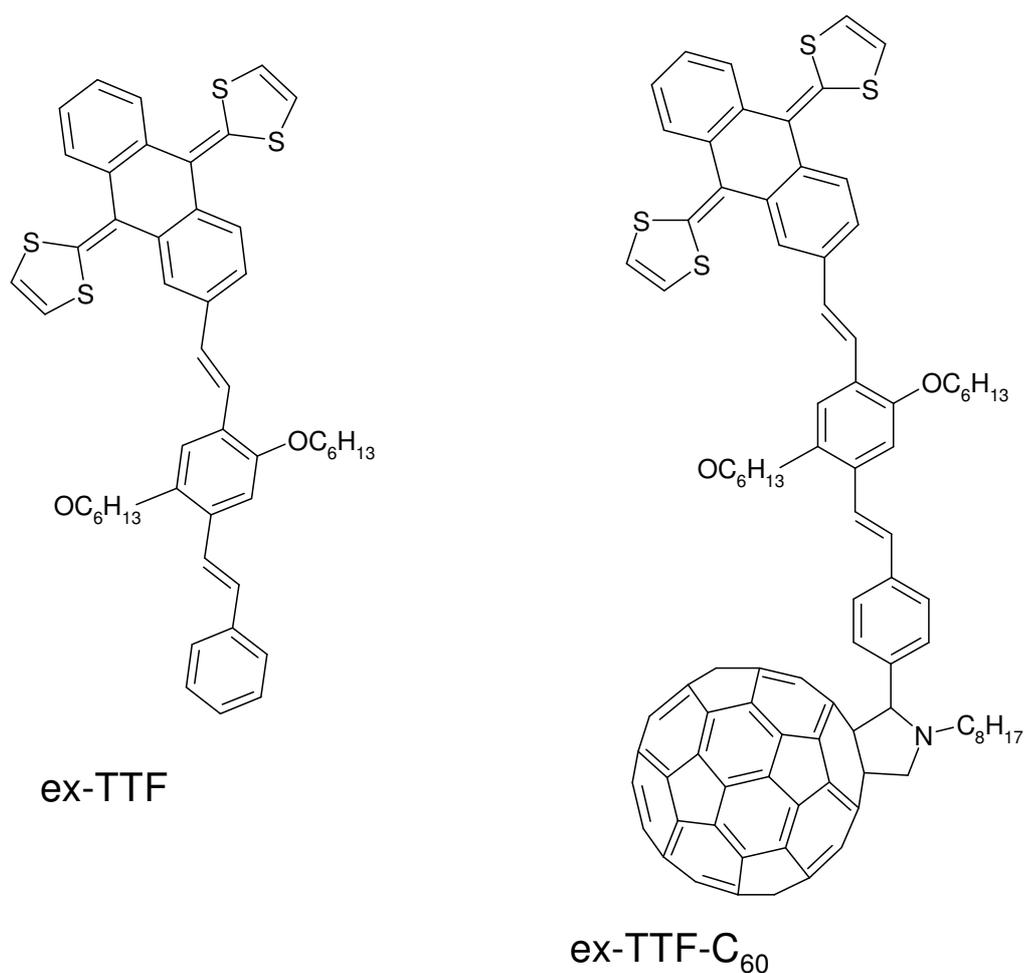
Figure 1: Chemical structure of the π-extended tetrathiafulvalene with the phenylene-vinylene wire group (ex-TTF) and the π-extended tetrathiafulvalene-C_{60} dyad (ex-TTF-C_{60}).

RESULTS AND DISCUSSION

The electrochemical HOMO-LUMO energy gap of ex-TTF in solution is determined with 1.98 eV. The onset for the optical absorption in CH_2Cl_2 solution with 2.3 eV and in solid state with 2.1 eV is significantly higher. The reduction peak of fulleropyrrolidine (C_{60}-P) at -700 mV vs. SCE is in comparable range with other [6,6] substituted fullerenes.

The oxidation and reduction potential of the dyad are in the range of the ex-TTF (donor) oxidation and C_{60}-P (acceptor) reduction, respectively. Figure 2 shows the energy diagram, derived from electrochemical measurements, for the donor, the acceptor and the dyad molecule.
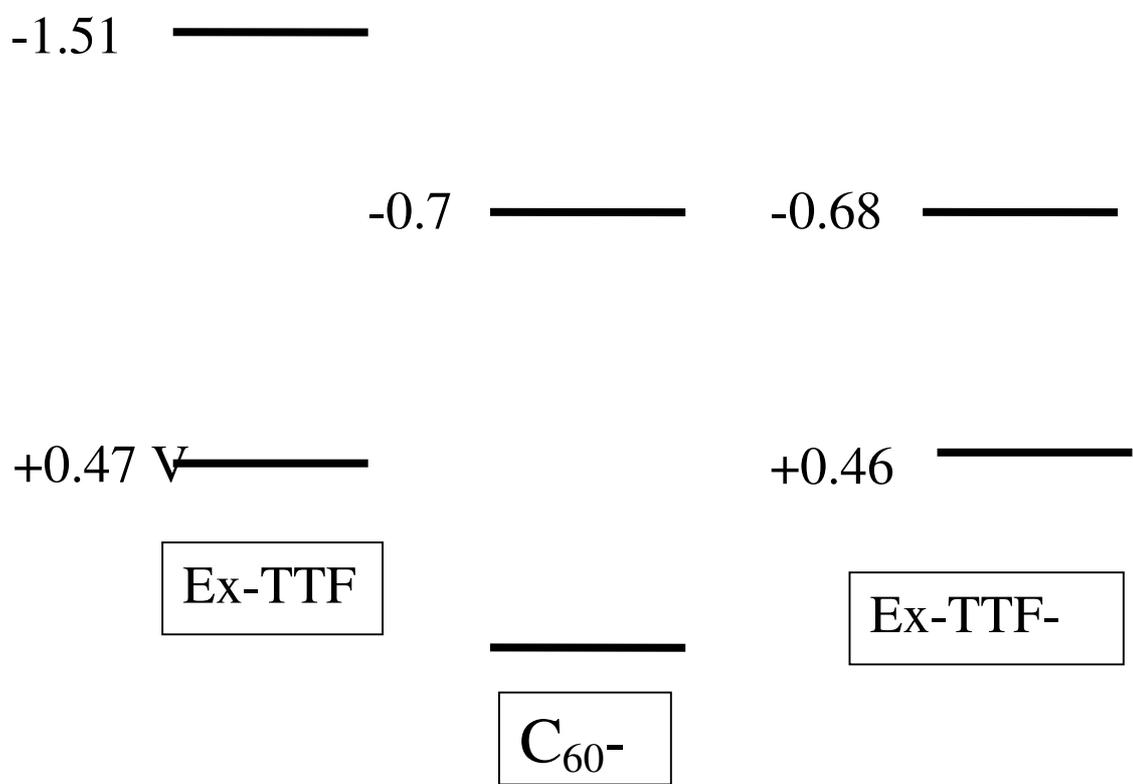
-1.51 ⎯⎯⎯

-0.7 ⎯⎯⎯   -0.68 ⎯⎯⎯

+0.47 V⎯⎯⎯   +0.46 ⎯⎯⎯

| Ex-TTF |

| C$_{60}$- |

| Ex-TTF- |

Figure 2: Energy diagram for ex-TTF, C$_{60}$-pyrrolidine (C$_{60}$-P) and the dyad ex-TTF-C$_{60}$, energy values are taken from electrochemical measurements. The first reduction peak is assigned to the LUMO, the first oxidation peak to the HOMO. For C$_{60}$-P, no electrochemical oxidation is observed. The bandgap is estimated from the absorption with 1.8 eV.
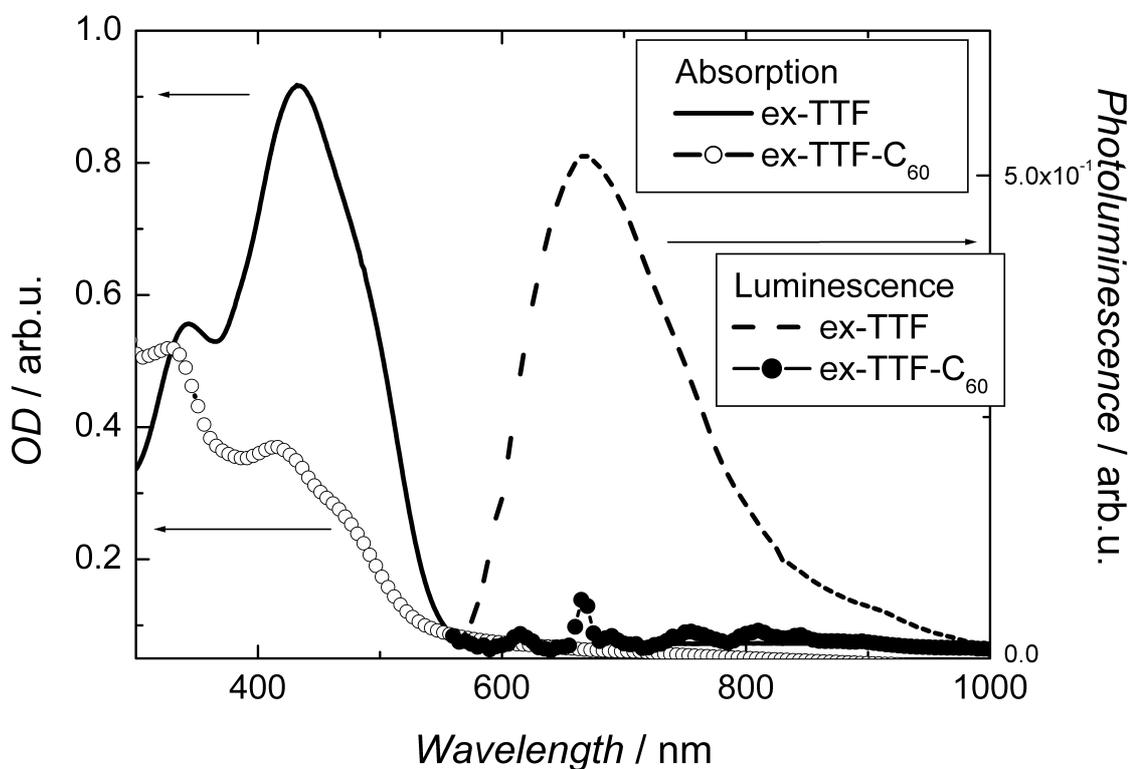
Figure 3: Absorption and luminescence of ex-TTF and ex-TTF-C_{60} spin cast film, thickness 50-70 nm, on glass substrates. Excitation was done with 40 mW at 476 nm.

Figure 3 shows the absorption and photoluminescence of ex-TTF and the ex-TTF-C_{60}. The ex-TTF-C_{60} molecule shows the absorption around 450 nm from ex-TTF and around 330 from C_{60}. Ex-TTF shows a luminescence with a maximum around 700 nm. In the dyad, the photoluminescence is quenched. The sample was excited either at 476 nm (ex-TTF absorbs predominantly) or 664 nm (C_{60} absorbs exclusively). This is an indication for photoinduced charge transfer.

In Figure 4, the PIA spectra of ex-TTF and ex-TTF-C_{60} are compared. The ex-TTF shows a broad peak around 1.7 eV and a shoulder at 0.8 eV. The dependence on the chopper frequency is shown for the peak as well as the shoulder in Figure 5. Distinct differences are observed. For the peak at 1.57 eV, a mean lifetime of 0.17 ms is determined, fitting the data with a dispersive recombination model.[16] The signal at 0.83 eV could not be fitted with this model. The PIA peak at 1.6 eV might be assigned to a triplet-triplet transition. The shoulder at low energies originates from a different species, its nature is unclear.

The PIA spectrum in the dyad molecule differs from the spectrum of ex-TTF. A series of peaks in the range between 1.8 eV and 2.3 eV is observed. An other peak is observed around 1 eV, a side peak at 1.2 eV and a shoulder at 0.8 eV. The high part is comparable with the absorption spectrum of ex-TTF cation in solution.[17] All peaks show similar dependence on the chopper frequency with lifetimes around 0.8 ms, see Figure 6.

The sharp absorption at 1.2 eV is assigned to C_{60}^-. The broad low energy peak at 1 eV is tentatively assigned to the ex-TTF cation as well.

Also the PIA measurements, the quenching of the peak at 1.6 eV in the ex-TTF, which is assigned to the triplet state, and the quenching of the ex-TTF photoluminescence, indicates photoinduced charge separation in the dyad.
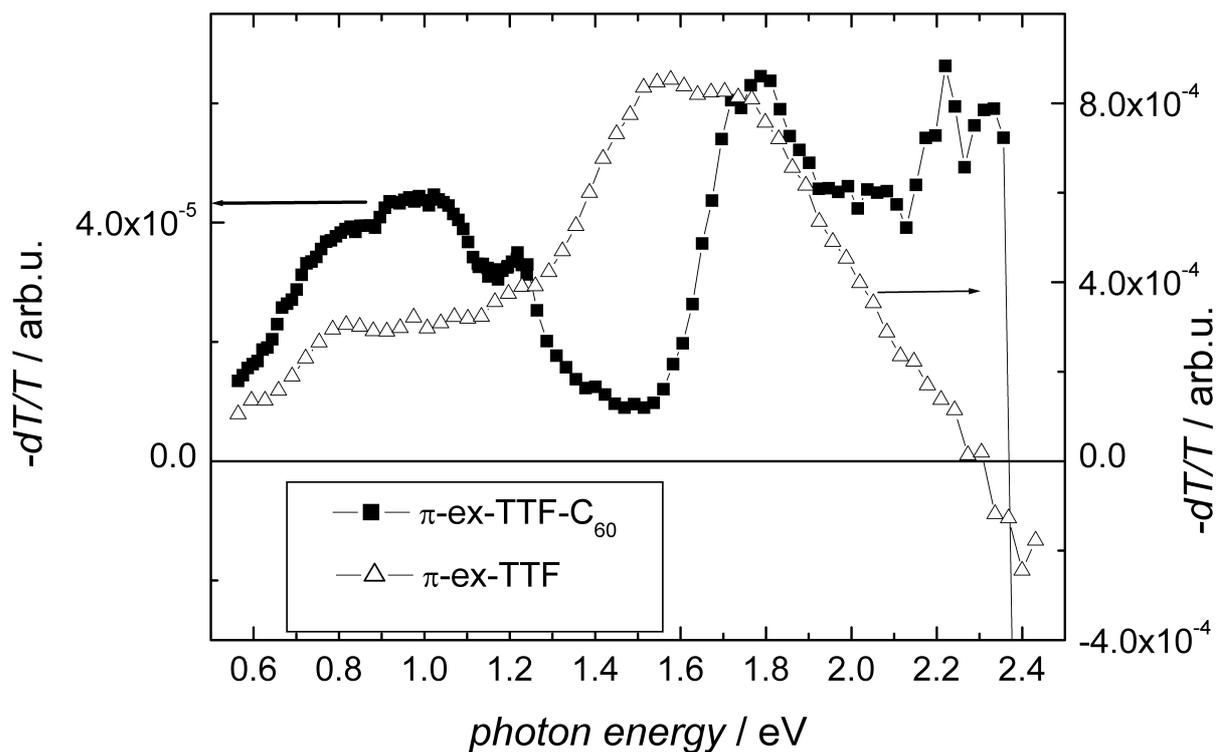

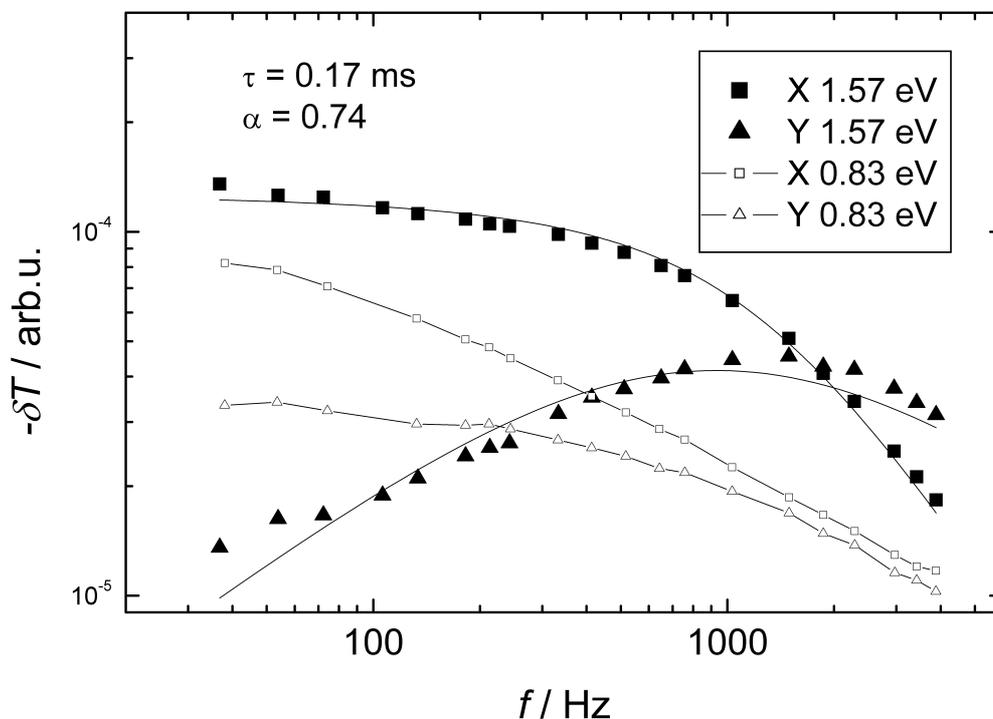**Figure 4:** PIA of ex-TTF and ex-TTF-C_{60} at 80 K, excitation at 476 nm (2.6 eV) with 40 mW.

Figure 5: Modulation frequency dependence of ex-TTF at 80 K, excitation with 40 mW at 476 nm (2.6 eV). The signal at 1.57 eV is fitted by dispersive recombination model. The signal at 0.83 eV could not be fitted by this model, the line is guide for the eye.
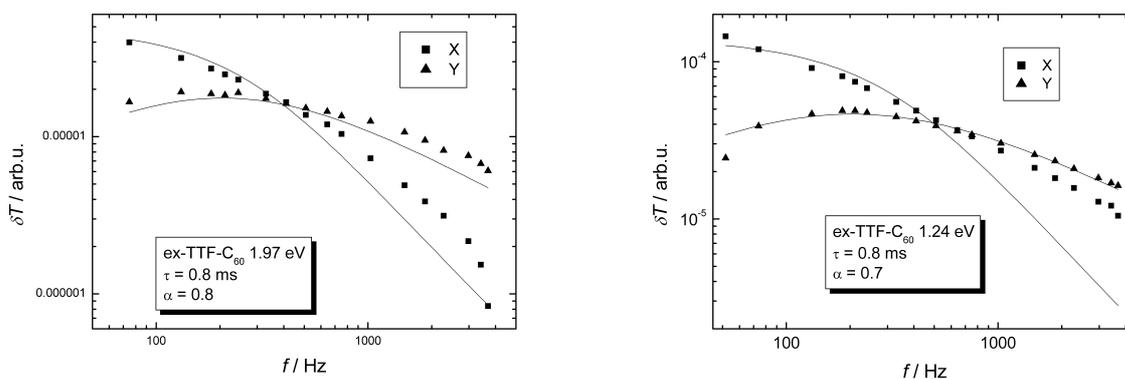

Figure 6: Modulation frequency dependence of ex-TTF-C_{60} at 80 K, excitation with 40 mW at 476 nm (2.6 eV) at 1.97 eV and 1.24 eV. Fits are done by the dispersive recombination model.

Photovoltaic devices are made with ex-TTF-C_{60}, spin cast from chlorobenzene solution. The devices show a clear photovoltaic effect, see Figure 7. The power conversion efficiency is 0.02 % under solar simulated light with 80 mW cm-2. The photocurrent spectrum shows a maximum at 400 nm, which is slightly blue-shifted to the ex-TTF absorption maximum at 450 nm. The onset of the photocurrent matches with the absorption onset around 600.

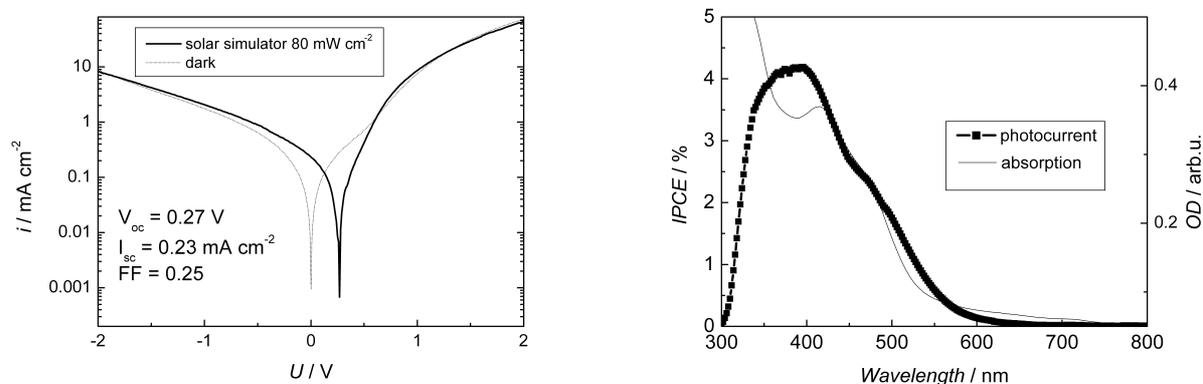Further devices studies, both with the pure dyad and with blend with conjugated polymers, are in progress.

Figure 7: I-V characteristics (left) of an ex-TTF-C_{60} dyad device in the dark and illumination from a solar simulator, active are thickness is 50-70 nm, photocurrent spectrum in comparison with the absorption spectrum (right).

CONCLUSIONS

The presented ex-TTF- C_{60} molecule acts as donor-acceptor dyad system upon photoexcitation. Quenching of the ex-TTF photoluminescence and triplet-triplet absorption is demonstrated by photoluminescence and photoinduced absorption experiments. Optical signature of the photoexcited ex-TTF cation as well as for the fullerene anion is assigned. Thus, the intramolecular photoinduced electron transfer from the ex-TTF unit onto the fullerene moiety within this molecule is concluded. The ex-TTF- C_{60} dyad acts as photovoltaic active material in thin film devices and show extended absorption range as compared to bare C_{60}

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