

## Control of electron transfer in conjugated polymer/fullerene heterostructures

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### Abstract

We investigate electron transfer in conjugated polymer/fullerene heterostructures prepared by a combination of spin-coating and self-assembly methods. Via insertion of ultrathin (<10nm) spacer layers of varying thickness between the conjugated polymer layer and a self-assembled monolayer of a functionalized fullerene, it is possible to control the electron transfer between the photoexcited conjugated polymer acting as a donor and the electron accepting fullerene.

*Keywords:* ( Fullerenes and derivatives, Conjugated Polymers, Photoluminescence, Heterojunctions)

### 1. Introduction

Electron transfer (ET) from a photoexcited conjugated polymer to a fullerene molecule has been demonstrated in blend systems as well as in heterostructures prepared from these two materials. The efficient ET causes a dissociation of the neutral excited state and can be utilized to increase the photocarrier yield in polymer optoelectronic devices [1,2]. Most of the experiments performed so far have been limited to the investigation of simple blend systems where the fullerene and the polymer are mixed in the same solvent and then spin-coated onto a substrate. For a better understanding of the electron transfer dynamics and for various applications, it is necessary to fabricate heterostructures with a well defined structure instead of disordered blend systems. One promising approach for a controlled deposition of such heterostructures is the method of self-assembly (SA) [3]. We have recently developed an SA-technique for a controlled mono- and multilayer deposition of a functionalized fullerene [4]. Using such layers in conjunction with a spin-coated conjugated polymer film of varying thickness, it was possible to determine the excitation diffusion length in ladder-type poly(p-phenylene) (LPPP) [5].

In this contribution we demonstrate that the electron transfer from a photoexcited conjugated polymer to a fullerene monolayer can be controlled by the insertion of an insulating spacer layer also deposited using an SA-technique.

### 2. Experimental

The structure of the samples used in our experiments is shown in Fig. 1. First, a glass substrate is functionalized by a monolayer of polyethyleneimine (PEI). Afterwards, half of the substrate is covered by a monolayer of the fullerene derivative, namely fullerene carboxylic acid (C<sub>60</sub>H<sub>8</sub>O<sub>2</sub>). Then the sample is again immersed into the PEI-solution. Subsequently, we deposit a spacer layer consisting of a varying number of polyallylamine hydrochloride (PAH) and polystyrenesulfonate (SPS) monolayers. Using these two polymers, an insulating spacer layer with variable thickness can be prepared by consecutive polyanion/polycation adsorption from liquid solution. For the deposition conditions used in our experiments the thickness of one SPS/PAH-bilayer is 2.2 nm. On top of the spacer layer we spin-cast a film of LPPP with a thickness of 5 nm.

The photoinduced electron transfer from LPPP to the fullerene relies on the spatial wavefunction overlap. Since the SPS/PAH-layer acts as a barrier, the overlap and thus the overall rate for the electron transfer should be controllable by varying the spacer thickness.

The electron transfer is detected using photoluminescence (PL) experiments. We measure the conjugated polymer PL from the two different parts of the sample and use the PL-quenching induced by the fullerene layer as an indicator for the electron transfer. The ET opens an additional non-radiative deactivation channel for photoexcitations in the conjugated polymer and thus suppresses the PL. We note that the PL from LPPP is not altered by an adjacent PAH/SPS spacer-layer alone (without a fullerene layer below). This proves that ET to the fullerene layer causes the observed PL-quenching.

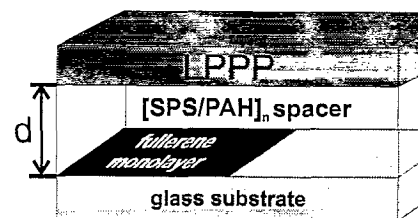


Fig. 1: Structure of the investigated samples. A self-assembled fullerene monolayer on half of the substrate is covered by SPS/PAH-bilayers with a thickness  $d$ . The top layer is a film of the conjugated polymer LPPP with a thickness of 5 nm.

### 3. Results and Discussion

Fig. 2 compares the PL spectra of LPPP for the different investigated samples. The highest PL-intensity is observed for the LPPP-film deposited directly on the glass substrate. The spectra for the heterostructures comprising an LPPP film of the same thickness are normalized to this reference spectrum. The strongest PL-quenching (greater than 90 %) is observed when the LPPP film is spin coated directly on the fullerene layer. Since the diffusion length of 14 nm in LPPP [5] is larger than the film

thickness basically all excitations can reach the interface and thus can undergo an electron transfer.

The other two spectra displayed in Fig. 2 show the emission spectra with a spacer consisting of one and two SPS/PAH-bilayers, respectively. When the fullerene layer is covered with a spacer layer prior to spin coating, the emission intensity is enhanced compared to the case without these additional layers.

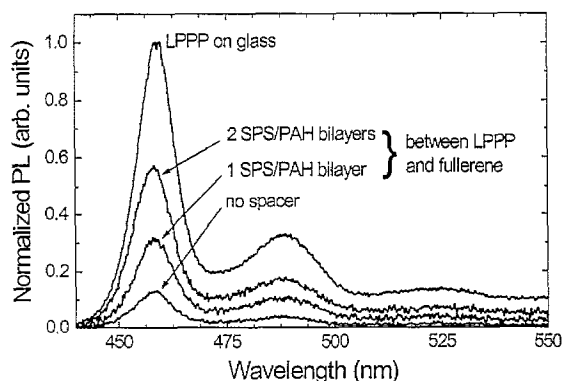


Fig. 2: PL spectra of an LPPP-film (thickness 5 nm) deposited directly on a glass substrate (uppermost curve). The other curves represent the emission spectra for the different heterostructures. The PL is reduced by the electron transfer to the fullerene layer.

The relative PL-quenching  $\Delta I/I_0$  (with  $\Delta I = I_0 - I$  being the PL-quenching with  $I$  and  $I_0$  denoting the PL with and without the fullerene layer, respectively) versus the number of spacer layers is plotted in Fig. 3. The upper x-axis indicates the thickness of the spacer layer. The relative PL-quenching varies systematically with the thickness of the spacer-layer. With 4 SPS/PAH-bilayers the electron transfer is almost completely suppressed, and the PL is nearly as strong as without electron acceptor layer.

Empirically, our results give a direct measure for the number of SA-layers that need to be introduced in order to suppress an electron transfer. The results presented here should also be valid for a modification of electrodes in light emitting diodes where SA-layers can be used as carrier blocking layers to enhance quantum efficiencies.

From a fundamental point of view a more detailed discussion of the distance dependence is important. For an idealized structure the electron transfer rate can be calculated using a simple hopping ansatz. For the dependence of the ET-rate on the thickness of the spacer layer, we find that the rate is (after integration over the entire layer of electron accepting sites):

$$f(d) = f_0 \left(1 + \frac{2d}{L}\right) e^{-\frac{2d}{L}}$$

Here  $L$  denotes the localization length of the excitations and  $f_0$  is a prefactor with the dimension of a rate. Using this equation we have calculated the expected time-integrated value for the PL quenching in dependence on the spacer thickness and have used the localization radius  $L$  as a fitting parameter. The result is shown in Fig. 3 as a dashed line.

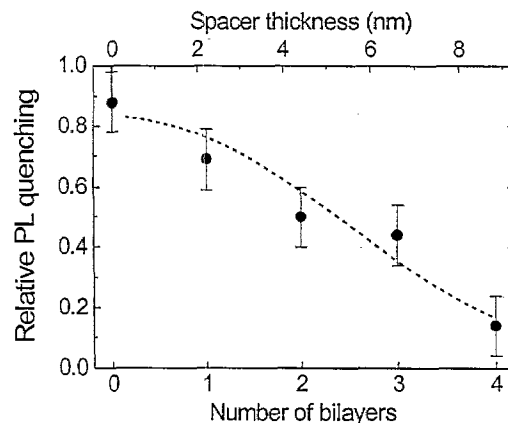


Fig. 3. Measured relative PL-quenching in the polymer versus the number of SPS/PAH-bilayers. The upper x-axis indicates the thickness of the different spacer layers. The dashed line shows the result of a hypothetical model calculation as described in the text.

The experimentally found thickness dependence can be well reproduced using a value of  $L=3.5$  nm. Although the agreement between experiment and the modeling is rather good, this value for the localization length seems to be surprisingly large. Earlier studies using Langmuir-Blodgett spacers on a  $\pi$ -conjugated molecular crystal have revealed much smaller values [6]. There are several effects that could explain the highly efficient PL quenching for thick spacers. The spacer layers have a roughness of 1.3 nm (as determined by X-ray-reflectivity studies). A rough interface leads to a smaller effective thickness of the spacer since the electron transfer preferentially occurs between sites that are much closer to each other than the nominal separation given by the average spacer thickness. Also, impurities incorporated during the SA-preparation might lead to an enhanced electron transfer rate by lowering the effective barrier.

#### 4. Summary and Conclusion

In conclusion we have demonstrated the control of electron transfer from a conjugated polymer to a fullerene layer via the insertion of ultrathin spacer layers prepared by the self-assembly technique. Four SPS/PAH-bilayers corresponding to a thickness of 9 nm are enough to suppress the electron transfer almost completely.

#### 5. References

- [1] N.S. Sariciftci and A.J. Heeger, *Int. Journ. of Mod. Phys. B* 8 (1994) 237
- [2] J.J.M. Halls *et al.*, *Appl. Phys. Lett.* 68 (1996) 3120
- [3] G. Decher *et al.*, *Thin Solid Films* 210/211 (1992) 831
- [4] C. Kallinger *et al.* in *Molecular Nanostructures*, H. Kuzmany (Ed), p. 515 (1998), World Scientific
- [5] A. Haugeneder *et al.* in *Fullerenes and Photonics IV*, Z.H. Kafafi (Ed.), *Proc. of SPIE Vol. 3142*, p. 140 (1997).
- [6] H. Killesreiter and H. Bässler, *Chem. Phys. Lett.* 11 (1971) 411.