

# EFFICIENT CHARGE GENERATION IN CONJUGATED MOLECULES

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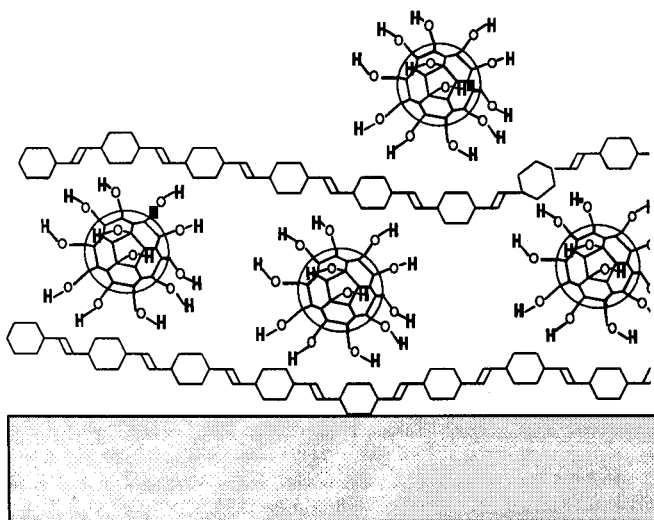
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## Introduction

The ultrafast photoinduced electron transfer between conjugated molecules of appropriately chosen levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) has allowed the production of efficient organic photovoltaic devices.<sup>1,2</sup> Although there has been rapid progress in recent years, very fundamental questions of optical charge generation and transport in organic materials are not yet resolved, which span fields from quantum mechanics to chemical engineering.<sup>3,4,5,6</sup> The absorption of light in a conjugated polymer primarily creates bound electron-hole pairs in their singlet state, singlet excitons (SE). It has become clear that the charge generation process in "pure" layers of conjugated molecules is driven by defects which serve as exciton dissociation centers.<sup>7,8</sup> In this sense, the incorporation of an electron accepting guest, such as the pure fullerene C<sub>60</sub>,<sup>9</sup> derivatized fullerenes<sup>10</sup> or others<sup>11</sup> in a poly(*para*-phenylene-vinylene) (PPV) host can be seen as an introduction of "defects". Since the exciton diffusion length in conjugated polymers is on the order of 10nm,<sup>12</sup> however, the charge generation can only occur if the dissociation site is within this distance of any given optically excited electron-hole pair.

A special variation of the dip coating approach produces exceptionally homogeneous thin films through the ionically self-assembled monolayer (ISAM) process. This method was developed by Decher and coworkers<sup>13,14</sup> and used for polymer light emitting diodes by Rubner and coworkers<sup>15,16</sup> as well as for nonlinear optical applications by us.<sup>17</sup> The ISAM method involves the alternate dipping of a charged substrate into an aqueous solution of a cation followed by dipping in an aqueous solution of an anion at room temperature (see Figure 1)



**Figure 1:** Composition of the PPV- C<sub>60</sub>(OH)<sub>24</sub> ISAM films on a molecular level. This is a "magnification" of the schematic bilayer structure. The grey area represents the substrate.

## Experimental

In a related detailed study, the parameters of the dipping solutions for the absorbance of the films and thus, the thickness of the films were optimized.<sup>18</sup> In general the ISAM layer structure is described by the scheme in Figure 1. In particular, we show a bilayer system based on PPV and

C<sub>60</sub>(OH)<sub>24</sub>. The data for the samples used in this study are compiled in Figure 1. All optical and electrical measurements were performed in air at room temperature.

The basic constituents of the ISAM films in this study are PPV and poly(methacrylic acid) (PMA) as oppositely charged film forming agents. The conjugated PPV precursor is prepared via the classic route<sup>19</sup> and has already been used successfully for ISAM-based devices.<sup>15</sup> PMA was purchased from Polysciences. For an interface study, which was also conducted for light emitting diodes,<sup>18</sup> we used several polymers. The polythiophene acetic acid (PTAA) was prepared according to Ref. <sup>20</sup>. Poly(allylamine hydrochloride) (PAH) and Cu-Phthalocyanine tetrasulfonic acid tetrasodium salt were purchased from Aldrich, and poly(sodium 4-styrenesulfonate) (PSS) was purchased from Polysciences. We have chosen C<sub>60</sub>(OH)<sub>n</sub> as a water-soluble ionizable fullerene derivative which was purchased from MER Corporation in Tucson, AZ. When C<sub>60</sub>(OH)<sub>n</sub> is synthesized, it yields a range of products which are not easily separated. The product we have used has an n-range of 22-26 for average composition of C<sub>60</sub>(OH)<sub>24</sub>. The pH and the ionic strength were adjusted as described below for the different studies. We will only report a selection of these parameters, which are described comprehensively in Ref.18. The film preparation process is described in detail in Ref. <sup>21</sup>

**Table 1: Overview of a selection of the samples used in this investigation.**

The peak response describes the maximum photocurrent for each of the 14 classes of devices we have investigated. Furthermore, we want to note that the photocurrent action spectra are normalized to the incident intensity and not to the absorbed intensity. We have used the following terminology: (A/B)<sub>x</sub>, where A, B denote the constituents of the bilayers and x denotes the number of bilayers. \* characterizes "thick" films.<sup>21</sup>

Sample #	Sample Composition	Peak Response [10 <sup>-5</sup> A/W]
1	(PPV/PMA) <sub>10</sub>	1
2	(PPV/PMA) <sub>20</sub>	4
3	(PPV/PMA) <sub>40</sub>	3.6
4	(PPV/PMA) <sub>32</sub>	90*
5	(PPV/ C <sub>60</sub> (OH) <sub>24</sub> ) <sub>32</sub>	0.55
6	(PPV/ C <sub>60</sub> (OH) <sub>24</sub> ) <sub>32</sub>	32*
7	(PAH/PT) <sub>3</sub> (PPV/PMA) <sub>20</sub>	34*
8	(PAH/PSS) <sub>3</sub> (PPV/PMA) <sub>20</sub>	55*
9	(PPV/PMA) <sub>20</sub>	19*
10	(PPV/PMA) <sub>20</sub> (PAH/PT) <sub>20</sub>	12*
11	(PPV/PMA) <sub>20</sub> (PAH/PSS) <sub>3</sub>	36*
12	(PPV/CuPc) <sub>30</sub>	170*
13	(PPV/CuPc/PPV/PMA) <sub>15</sub>	30*
14	(PPV/PMA) <sub>30</sub>	20*

The photovoltaic characterization was done with an Oriel 66002 light source, using a 150 W ozone free Xe lamp. The beam was passed through quartz lenses, an optical chopper and a CM 110 monochromator, equipped with a 2400 grooves/line grating, blazed at 250 nm. The area of the illuminated spot on the sample was 3 mm<sup>2</sup> with the excitation density on the order of 330 μW/ cm<sup>2</sup>. For the modulation measurements we used a chopper-frequency of 42 Hz. The photocurrent signal was picked up by a Stanford Research System lock-in amplifier SR 830

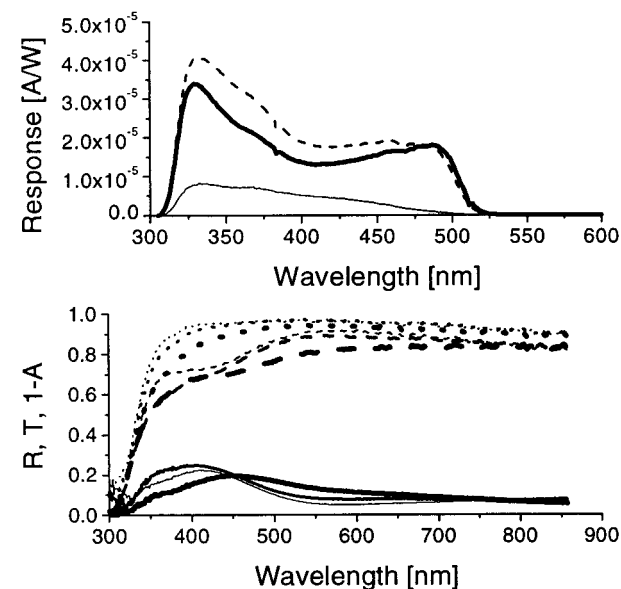
For the optical characterization, we have used an F20-UV thin-film measurement system by Filmetrics. The measurements yield two spectra:

- (i) **the reflection spectrum R(λ)** - i.e. the fraction of light reflected by the complete layered structure.
- (ii) **the transmission spectrum T(λ)** - i.e. the fraction of light transmitted through the complete layered structure.  
These two spectra can be used to *calculate*
- (iii) **the absorption spectrum A(λ)** - i.e. the fraction of light absorbed by the complete layered structure.

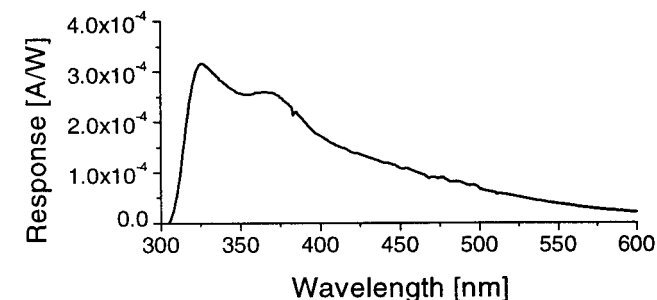
The calculation of A(λ) is based on the assumption that 1 = A(λ) + T(λ) + R(λ).

Figure 2 shows the photocurrent action spectra as well as the optical spectra of the thin device layers (samples # 1-3 in Table 1) in the region where

no Al is deposited. The photocurrent response for these devices as well as the others is summarized in Table 1. The very low absolute values of the photocurrent response for all three samples can be understood easily when looking at the optical data. The very thin ISAM films do not show any signature of absorption by the PPV: we show this by plotting  $1 - A(\lambda)$ , which represents the transmitted intensity after correction for reflection. The reflectivity clearly shows the presence of the very thin PPV film – the dips in the transmission spectra are primarily due to the peaks in the reflection, which are caused by the strong dispersion in the resonant region. Also, the photocurrent action spectra clearly show the onset for the PPV photocurrent at around 525 nm. The apparent peak in photovoltaic response at 330 nm is characteristic for the device and not for the PPV since we normalize our spectra with the incident radiation and not with the absorbed one. Therefore the strong decrease in photovoltaic response in these and all the following spectra represents the absorbance by glass and ITO. In order to obtain thicker films, we changed the film formation parameters as described in Ref. 21.



**Figure 2:** Top: photocurrent action spectra of the thin  $(PPV/PMA)_n$  devices; thin line:  $n=10$ , dashed line:  $n=20$ , thick solid line:  $n=40$ . Bottom: measured reflection spectrum  $R(\lambda)$  – solid lines – and measured transmission spectrum  $T(\lambda)$  – dashed lines; calculated  $R(\lambda) + T(\lambda)$  – dotted lines. The latter corresponds to  $1 - A(\lambda)$ . The different line thickness denotes the three devices: thin line:  $n=10$ , medium line:  $n=20$ , thick line:  $n=40$ .



**Figure 3:** Photocurrent action spectra of the thick  $(PPV/C_{60}(OH)_{24})_{32}$  devices.

The suppression of the observed electrical and optical PPV signatures is also observed in a thick sample, consisting of 32 bilayers of  $(PPV/C_{60}(OH)_{24})$  as shown in

Figure 3. In addition, also the time-constants observed in these devices are completely different from what is observed for the thick  $(PPV/PMA)_{32}$  devices. Therefore the  $(PPV/C_{60}(OH)_{24})_n$  devices contain relatively low amounts of PPV – we are observing the photovoltaic properties of  $C_{60}(OH)_{24}$ .

In order to overcome this shortcoming,  $(PPV/PMA/PPV/C_{60}(OH)_{24})_n$  devices are being produced. However, there are also other potential molecular dopands, which are expected to increase the photovoltaic response. We have decided to use Cu-Phthalocyanine tetrasulfonic acid tetrasodium salt (CuPc) and report the results in Table 1.

## Conclusions

In summary, we have described how to produce thin and thick ISAM films with a comparable amount of bilayers and quantitatively discussed the influence of thickness and incorporating other materials into the ISAM layers. Moreover, we have given a detailed description of the optical properties of the devices.

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