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Intramolecular charge separation in spirobifluorene-based donor–acceptor compounds adsorbed on Au and indium tin oxide electrodes

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ABSTRACT

Surface photovoltage (SPV) measurements were performed with a Kelvin-probe in spirobifluorene-based donor (diphenylamine)–acceptor (dicyano or cyanoacrylic acid moieties) compounds adsorbed from highly diluted solutions onto Au and indium tin oxide electrode surfaces. Strong intramolecular charge separation (negative SPV signals up to more than 0.1 V) due to directed molecule adsorption was observed only for spirobifluorene donor–acceptor compounds with carboxylic acid moiety. SPV signals and onset energies of electronic transitions depended on ambience conditions.

1. Introduction

A crucial point in organic optoelectronic systems is the interface between the inorganic substrate and the organic layer. The efficiency of heterojunction devices strongly depends on the charge injection process (of holes or electrons) between the metal electrodes and the active organic layers [1]. For example, in organic photovoltaic (OPV) devices, current losses arising from recombination and poor charge carrier injection due to energetic barrier result in low energy conversion efficiency [2]. Thus, the oriented deposition of surface dipoles and the formation of chemical bonds are important issues for organic/inorganic interface engineering. It can be realized, for example, by forming self-assembled monolayers [3], chemical grafting via hydrosilylation [4] or electrochemical grafting of organic molecules [5,6]. The presence of oriented molecules with intrinsic dipole over conductive surfaces produces changes in the metal work function [7–11], and the interface dipole can act as an improvement route for charge injection [12,13]. Hotchkiss et al. [14] showed that the introduction of monolayers of phosphonic acids in the inorganic/organic junction produces remarkable effects in the interface properties. Also it was demonstrated that triphenylamine-carboxylic acid monolayers produce changes in surface potential and work function of ITO (indium tin oxide) improving OLED (organic light emitting diode) performance [15]. Thus, a possible strategy to engineer surface work functions is related to the deposition of oriented dyad molecules holding donor (D) and acceptor (A) groups linked by a molecular bridge. This makes them interesting for applications in molecular electronics and solar cells [16,17]. The appropriate choices of the molecular geometry and the D–A moieties characteristics allow the control of the dipole direction and magnitude. The oriented deposition of molecules demands rather sophisticated deposition techniques. The introduction of molecular building blocks with fixed spatial structure such as spiro compounds [18] may simplify the situation. The spiro linkage improves the morphological stability of the materials while retaining their electrical properties [18]. Moreover, the perpendicular arrangement of the two molecular halves leads to a high steric demand of the resulting rigid structure, efficiently suppressing molecular interactions between the π-systems [18]. Spiro compounds can be used, for example, in charge transfer components with increased dimensionality [19] or in solid state dye sensitized solar cells (DSSC) as hole-transporting medium [20].

In this work, D–A molecules linked via conjugated bridges with spirobifluorene (SSD1, SSD2, and CN2) and without (NSD2) spiro-configuration (Fig. 1) were investigated in order to analyze their capacity for the generation of surface photoinduced dipoles. In previous papers we demonstrated that SSD1 and SSD2 showed to be useful in the construction of OPVs, with remarkable energy conversion efficiency [21,22]. The D–A dyads were adsorbed onto the Au and ITO electrode surfaces. The change of the contact potential (ΔCPD) of Au and ITO by the adsorbed molecules and by the photo-generated charge carriers (ΔCPD corresponds to the negative surface photovoltage — SPV) has been investigated with a Kelvin probe and surface photovoltage

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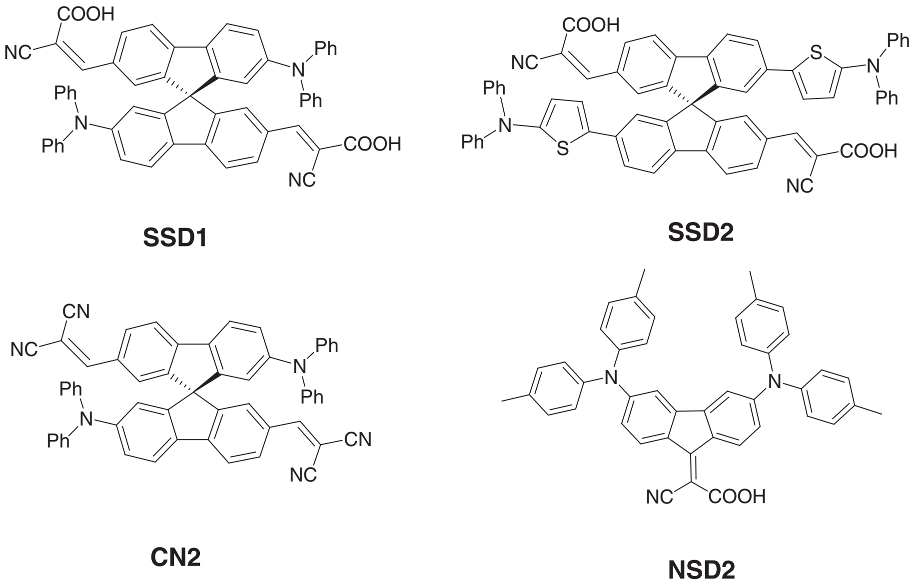

Fig. 1. Chemical structure of the donor–acceptor spirobisfluorene (CN2, SSD1, and SSD2) and non-spiro (NSD2) compounds.

spectroscopy [23]. We will show that molecules with spiro configuration holding cyanoacrylic acid groups produce the highest photoinduced contact potential difference.

2. Experimental details

CN2, SSD1, SSD2 and NSD2 molecules were prepared by procedures described recently [21,22]. The molecules were adsorbed from highly diluted solutions (0.05 μM in methylene chloride) onto Au (evaporated on glass substrates) and ITO (PGO company) electrode surfaces. The preparation method (deep coating and solvent evaporation) allows supposing that there is no reason to assume drastic differences in the adsorption of the molecules from highly diluted solution, i.e. there were not significant differences of surface coverage. The CPD of Au, measured versus a gold grid reference electrode, was larger than the CPD of ITO by 0.58 V in high vacuum and by 0.72 V in Ar atmosphere that is in good agreement with the general behavior of the work functions of Au [24] and ITO [24,25]. Agglomeration of the investigated molecules can be neglected under the given experimental conditions. Samples were placed into a home-made vacuum chamber for spectral dependent measurements of ΔCPD with a Kelvin probe (Delta phi Besocke). Illumination was performed from the front side of the electrodes with a 150 W halogen lamp (Müller Elektronik GmbH), and a quartz prism monochromator (SPM2, Carl Zeiss Jena). All the measurements were done at room temperature.

3. Results and discussion

Changes in ΔCPD depend on all processes which may influence ΔCPD within the time of measurement, and the relaxation kinetics of ΔCPD signals can depend on the nature of adsorbed molecules. To demonstrate qualitative changes in relaxation kinetics, measurements were performed in a repetitive regime and results were documented with scales of time and photon energy which was varied in time steps. Time monitoring of ΔCPD with interval of 1 s is shown in Fig. 2 for molecules adsorbed on Au during the cycles of measurement. Monitoring and evacuation were started after placing a sample into the chamber (pressure $2\cdot10^{-3}$ Pa). ΔCPD became more negative for the D–A spirobifluorene compounds within 10…15 min during pumping. For the D–A non-spiro compound (NSD2) ΔCPD dropped rapidly to a more negative value but increased slightly within the following 1…2 min. The waiting time was of the order of 10…20 min before two subsequent spectral measurements in vacuum (spectra S1 and S2) were started. The measurement of one spectrum from 0.4 to 4.0 eV with a step of 0.05 eV took about 10 min. The chamber was filled with Ar after measuring S1 and S2 and two subsequent spectral measurements in Ar (spectra S3 and S4) were performed.

All values of ΔCPD decreased in comparison to the bare Au substrate (Fig. 2). Before filling the chamber with Ar, ΔCPD decreased by 0.53, 0.80, 0.69 and 0.71 V in comparison to Au for CN2, SSD1, SSD2 and NSD2, respectively. For ITO substrates ΔCPD decreased by 0.59, 0.92, 0.80, 0.96 and 0.71 V in comparison to Au for bare ITO and ITO with adsorbed CN2, SSD1, SSD2 and NSD2 molecules, respectively. The ΔCPD decrease could be interpreted as a preferential orientation of −CN or cyanoacrylic groups towards the electrode surfaces. The strong surface binding ability of the cyano nitrogen is known. Surface-enhanced Raman spectroscopy of a series of nitrile compounds adsorbed on gold indicated the formation of σ-bonding of the nitrile nitrogen o the metal surface [26,27]. Also it has been

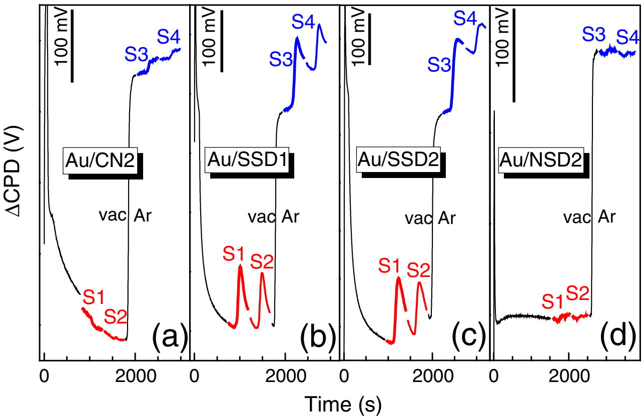

Fig. 2. Time dependence of the contact potential difference during the subsequent measurement regimes consisting of evacuation to high vacuum in the dark, two spectral dependent measurements under vacuum (S1 and S2), venting with Ar in the dark and two spectral dependent measurements in Ar atmosphere (S3 and S4) for CN2, SSD1, SSD2 and NSD2 (a–d, respectively) adsorbed at Au. The bars mark the potential difference of 100 mV.

reported that carboxylic groups bind to Au and ITO [22,28,29]. Thus, it is not unlikely that the studied molecules acquire a preferential orientation over electrode surface.

The values of ΔCPD increased for all samples after filling the chamber with Ar. The Ar induced increase of the ΔCPD signals amounted to 0.46 (0.31), 0.37 (0.28), 0.36 (0.32), 0.42 (0.32) and 0.29 (0.27) V for bare Au (ITO) and CN2, SSD1, SSD2 and NSD2 adsorbed at Au (ITO), respectively.

Relatively large values of −SPV (order of 100 mV) were obtained as peaks in S1–4 for SSD1 and SSD2 at Au and ITO electrodes (Figs. 2b and c and 3b and c). The negative sign of SPV means that photo-generated electrons were separated towards the external surface. At gold substrate, for subsequent measurements the values of −SPV decreased by 1.1 and 1.25 times for SSD1 and SSD2, respectively, in vacuum, and by 1.5 and 2.4 times for SSD1 and SSD2, respectively, in Ar. For molecules adsorbed at ITO a similar behavior was observed for successive measurements. This shows that the relaxation of the separated charge can be quite slow for SSD1 and SSD2. Also relaxation is slower in Ar atmosphere and relaxation is slower for the molecule with the longer molecular chain. The −SPV signals were much smaller for CN2 and NSD2 than for SSD1 and SSD2 adsorbed at both Au and ITO.

All time dependent signals of S1-4 were transferred to a spectral dependence. Figs. 4 and 5 show the S1–4 spectra for CN2 (a) and SSD2 (b) adsorbed on Au and ITO respectively. Comparing S3 and S4, ΔCPD of S4 started at the value at which S3 finished, i.e. most of the separated charge carriers did not recombine within several minutes. The ΔCPD spectra correlate with the absorption spectra of dyes in solution [22], indicating that the molecules are responsible of the observed surface photovoltage effects. The transitions observed in solution for CN2, SSD1, SSD2, and NSD2 have been assigned to charge-transfer transitions [22,30,31].

The onset of the photo induced response (E_{on}) was determined from the intersection of helping lines dominated by the relaxation and by the spectral response parts (see Figs. 4 and 5). The sign of −SPV was negative for S1 but positive for S2–4 for CN2 while the values of E_{on} amounted to 2.07 and about 2.20 eV for S1 and S2–4, respectively. For SSD2 the values of E_{on} were 1.80, 1.78, 1.93 and 2.00 eV for S1–4, respectively. Being more precise, for SSD2 an influence of photo generation on ΔCPD started already at photon energies below E_{on} as demonstrated by the dashed lines in Fig. 4.

The values of E_{on} (a and b) and of the SPV (c and d) signals for all dyes are summarized in Fig. 6 for Au (a and c) and ITO (b and d) substrates. There was a general trend of an increase of E_{on} in Ar atmosphere by 0.1–0.2 eV for all molecules adsorbed on ITO and for SSD1 and SSD2 adsorbed on Au. For CN2 and NSD2 adsorbed on Au the increase of E_{on} in Ar atmosphere was less significant or absent. The missing influence of the substrate on E_{on} in SSD1 and SSD2 systems gives evidence that internal photoemission was not important for charge separation processes.

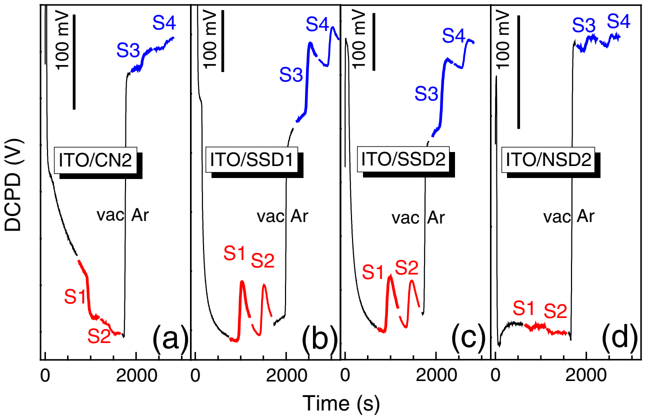

Fig. 3. Time dependence of the contact potential difference during the subsequent measurement regimes consisting of evacuation to high vacuum in the dark, two spectral dependent measurements under vacuum (S1 and S2), venting with Ar in the dark and two spectral dependent measurements in Ar atmosphere (S3 and S4) for CN2, SSD1, SSD2 and NSD2 (a–d, respectively) adsorbed at ITO. The bars mark the potential difference of 100 mV.

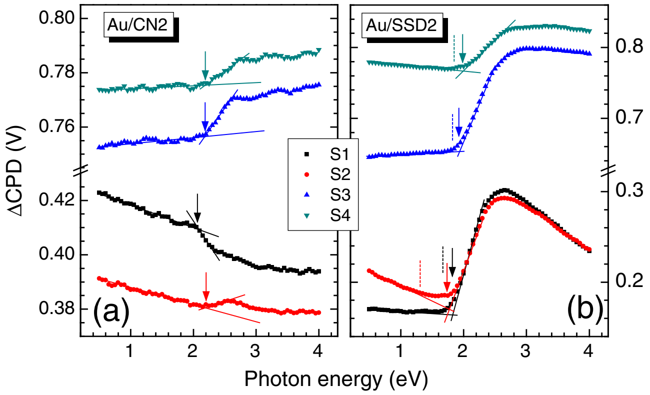

Fig. 4. Subsequent spectra of the contact potential difference for CN2 and SSD2 molecules adsorbed at Au (a and b, respectively) measured in vacuum (S1 and S2) and Ar atmosphere (S3 and S4). The arrows mark the onset energies of electronic transitions, and dashed lines mark the starting influence of photo generation on ΔCPD.

The lowest SPV signals were observed for NSD2. The SPV signals of SSD1 and SSD2 molecules were larger by about one order of magnitude than for NSD2 molecules. NSD2, SSD1 and SSD2 molecules had the same acceptor and similar donor groups and there was no reason to assume drastic differences in the adsorption of these molecules from highly diluted solution, i.e. there were not drastic differences of surface coverage. Therefore the striking difference in charge separation between NSD2 molecules at the one and SSD1 and SSD2 molecules at the other side was caused by the spiro bond in SSD1 and SSD2 molecules concomitant with preferential orientation of adsorbed molecules. As mentioned above, the acceptor groups were pointing preferentially towards the internal interface. The negative sign of SPV can be explained by refilling of D if assuming that electrons were partially transferred from D to A before illumination (intramolecular charge separation). Surprisingly the SPV signal of CN2 molecules changed the sign depending on ambience while the strongest change for repetitive measurements was observed for CN2 molecules

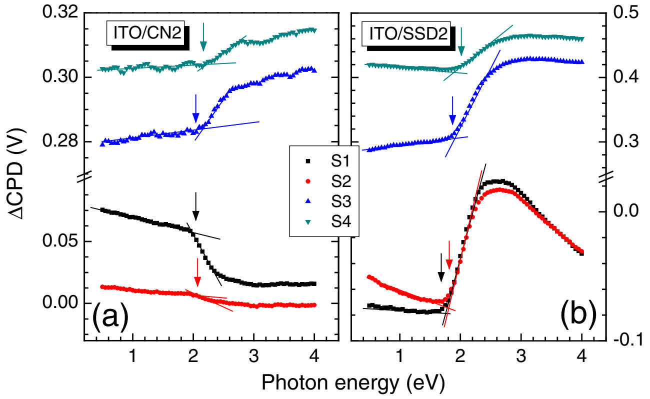

Fig. 5. Subsequent spectra of the contact potential difference for CN2 and SSD2 molecules adsorbed at ITO (a and b, respectively) measured in vacuum (S1 and S2) and Ar atmosphere (S3 and S4). The arrows mark the onset energies of electronic transitions, and dashed lines mark the starting influence of photo generation on ΔCPD.

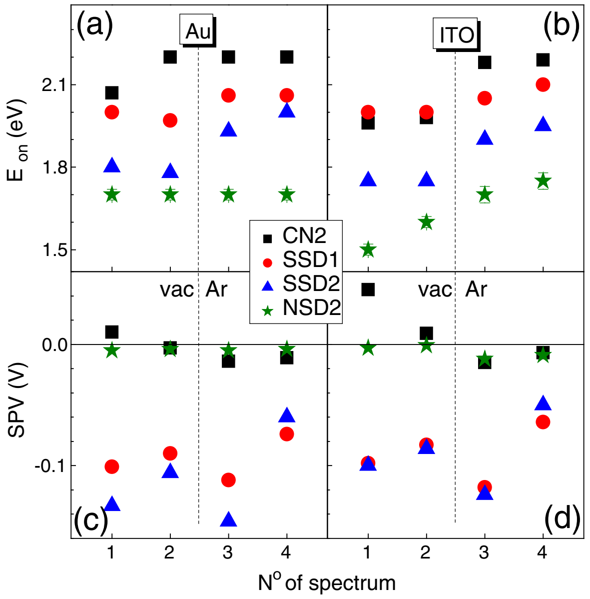

Fig. 6. Summarized values of the onset energies (a and b) and of the SPV amplitudes (c and d) for Au (a and c) and ITO (b and d) substrates with adsorbed CN2, SSD1, SSD2 and NSD2 (squares, circles, triangles and stars, respectively) as a function of the number of the measured spectra. The dashed lines separate the values obtained in vacuum or Ar atmosphere.

in vacuum. The shift of E_{on} to higher energy with changing sign of SPV for CN2 might be caused by changed occupation of states strongly affected by the ambient gas.

4. Conclusions

It has been demonstrated that molecular architectures with spiro links and carboxylic acceptor groups open more opportunities for oriented adsorption and well directed charge separation in molecular layers. SPV measurements give the principal opportunity to investigate the influence of relaxation and of ambient atmosphere on transition energies and charge separation. Correlation of SPV measurements with experiments giving time dependent information about geometry, charge state and coverage of adsorbed molecules will be needed for getting a deeper understanding about the processes in spiro-compounds under excitation and charge separation.

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