

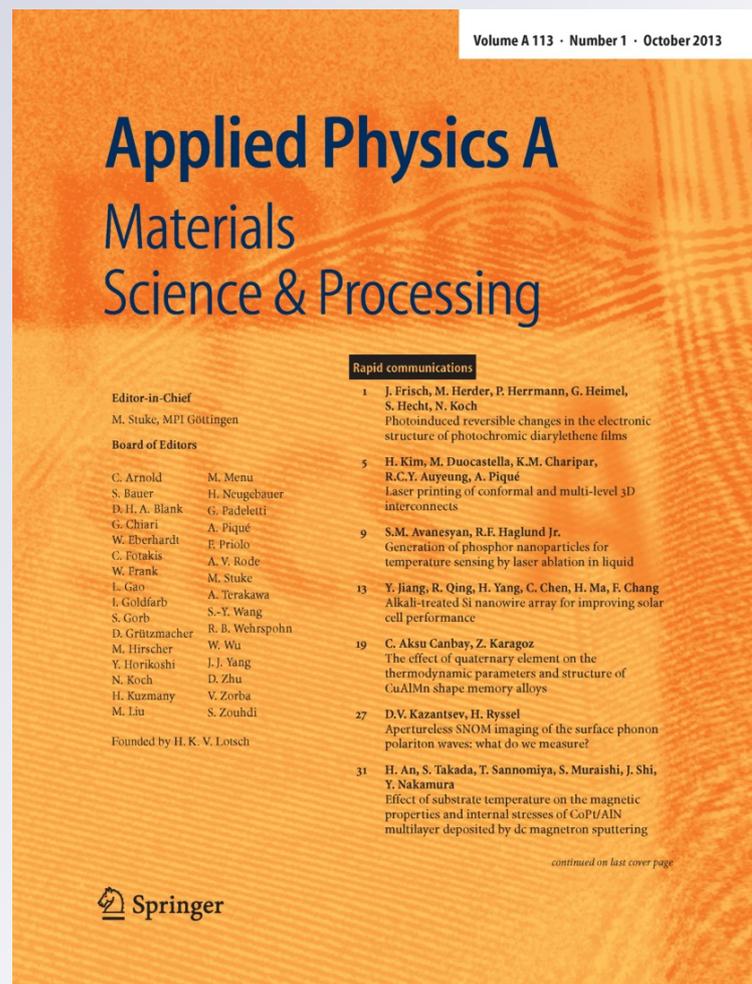
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Photoinduced reversible changes in the electronic structure of photochromic diarylethene films

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Abstract The change in the valence electronic structure upon switching of two photochromic diarylethene derivatives, i.e. 1,2-bis(2-methyl-5-p-tolylthiophen-3-yl)cyclopent-1-ene (DAE1) and 1,2-bis(5-(4-hexyloxycarbonylphenyl)-2-methylthiophen-3-yl)cyclopent-1-ene (DAE2), was measured by photoelectron spectroscopy. Switching between open and closed forms was followed in situ upon illumination. The increase of the ionization energy from the closed to the open form was 0.85 eV for DAE1 and 0.80 eV for DAE2. For DAE1, the work function also decreased by 0.25 eV upon switching, which is explained by a decrease of the intrinsic molecular dipole moment and a preferential orientation of molecules in thin films.

1 Introduction

Photochromic organic materials (PCOMs) grant access to optical switches and memories and to variable electrical currents in organic electronic devices. Photochromism is defined as a reversible photoinduced transformation between two isomers with different absorption spectra. During the photoisomerization, not only the absorption spectra but also other molecular properties, such as refractive indices, dielectric constants, dipole moments, and electronic structure, can be changed reversibly [1]. Particularly, the elec-

tronic structure change can be used to tune charge injection properties in organic devices by inserting a thin PCOM layer between one electrode and the organic semiconductor [2, 3]. Furthermore, the current in an organic device can be modulated by forming photoswitchable charge traps or charge barriers in a solid-state blend with a semiconducting polymer host [4, 5]. These applications of PCOMs enable a nondestructive readout method of a photon-mode optical memory using photocurrent detection [6–8]. Diarylethene (DAE) photochromes are promising candidates for photochemically controlled bi-stable building blocks for molecular switches [9]. The photoisomerization of DAE molecules and their derivatives has a huge influence on the energy position of the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level of the individual isomers, which results in a difference of the ionization energy (IE) and optical gap between the open- and closed-ring isomers of hundreds of meV [1]. An important issue for all current-related applications is the position of the frontier energy levels of both open- and closed-ring forms with respect to the Fermi level (E_F) of the electrodes and the transport levels of the organic semiconductor. For instance, to control the injection of holes in organic light emitting diodes the energy difference between the HOMO level of the PCOM and E_F of the anode should be minimized for one of the two configurations and maximized by the photochromic reaction. For blends of PCOM and the semiconducting polymer host, only proper matching of the energy levels will enable good charge transport. As a result, switching of the molecules changes the PCOMs to act either as traps or as barriers for charge carriers. Unfortunately, for PCOM thin films or in solid-state blends it often proves difficult to retain the molecular electronic properties as known from solution measurements [10]. This capricious behavior originates from the close packing of the molecules

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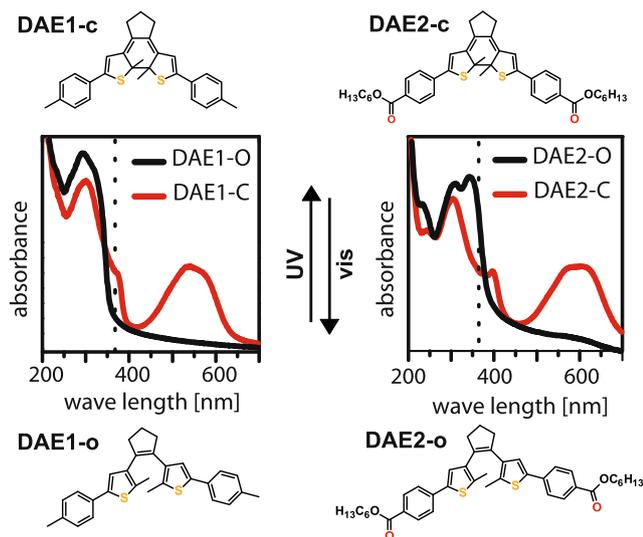


Fig. 1 Chemical structure of the closed (c) and open (o) forms of DAE1 and DAE2 and their thin-film absorption spectra. The cutoff wavelength of ~ 370 nm of the used lamp that limits sample illumination between 300 and 370 nm during in situ UPS experiments is indicated by the dotted line

in films or within the blend, generating steric constraints for conformational changes. Consequently, a detailed analysis of the molecular electronic properties of PCOMs in films and the influence of the photochromic reaction on their properties in relevant device structures is mandatory, as well as the fraction of PCOM molecules that can actually be switched. Ultraviolet photoelectron spectroscopy (UPS) is a suitable technique for investigating the electronic structure and provides direct information of the hole transport level of the material and was applied on photochromic diarylethene films before [11]. We performed in situ UPS measurements on thin films of two new DAE derivatives 1,2-bis(2-methyl-5-p-tolylthiophen-3-yl)cyclopent-1-ene (DAE1) and 1,2-bis(5-(4-hexyloxy-carbonylphenyl)-2-methylthiophen-3-yl)cyclopent-1-ene (DAE2); for chemical structures and respective absorption spectra, see Fig. 1. They were designed to feature different IEs of their open and closed isomers with respect to the IE of regioregular poly(3-hexylthiophene). We found that the photochromic reaction yield is close to 100 % at the surface of thin films and that the IEs of DAE1 and DAE2 films changed significantly by ~ 0.8 eV between the open and closed forms. It is noteworthy that the change of the HOMO level with respect to E_F was even larger than the IE change due to an additional decrease of the DAE1 film work function due to molecular dipole contributions.

2 Experimental section

Ultraviolet photoelectron spectroscopy experiments were performed at a custom-made multi-chamber ultra-high-

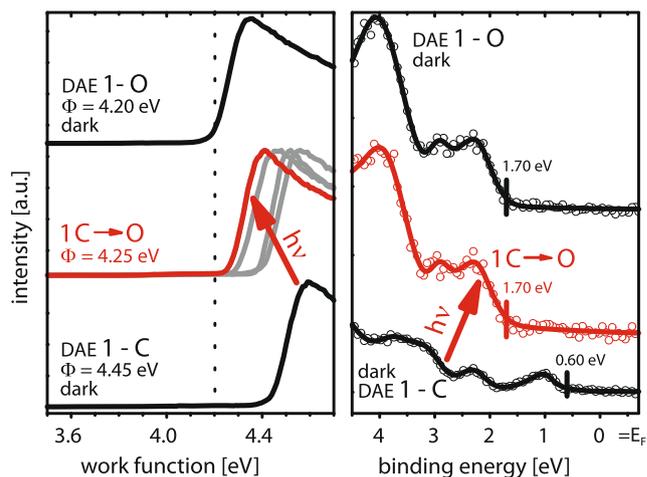


Fig. 2 SECO (left) and valence spectra (right) of freshly prepared (black lines) films of DAE1 in the open (top) and in the closed (bottom) forms measured in darkness (the open and closed forms of the molecules are indicated by O and C, respectively). In situ irradiation of the DAE1 film containing the closed isomer with a white light halogen lamp leads to a transition of the spectra to resemble those of the open DAE1 form (red line). Gray lines in the SECO spectra show the in situ change of Φ during the transition from the closed to the open form

vacuum system. Photoelectrons were excited with 21.2 eV photons (He-discharge lamp) at very low excitation density (approx. 100 times attenuated compared to standard commercial sources) and measured with a hemispherical spectrometer (SPECS Phoibos 100). The secondary electron cutoff (SECO) spectra were recorded with samples biased at -10 V to clear the analyzer work function. Samples were prepared by spin coating the DAE derivatives from chloroform solution onto solvent-cleaned coupons of indium-tin-oxide-coated glass in an inert-gas box, and they were transferred to ultra-high vacuum within 5 min to reduce possible contamination from air. During sample preparation, transfer, and measurements the samples were either kept in dark or exposed to low-intensity red light to avoid unintended switching. The films were irradiated in situ during UPS measurements through a glass window with a white light halogen lamp (SoLux, 4700 K, 35 W, 36°, EIKO). For synthesis of open and closed diarylethene isomers DAE1 and DAE2, see Ref. [12]. Density functional theory (DFT) calculations were performed using a PBE0 functional [13] applying a 6-31+g(d,p) basis set.

3 Results and discussion

Black lines in Fig. 2 show the valence electron region and the SECO spectra of freshly prepared DAE1 films in the open and closed forms (before any in situ light irradiation). The obtained IE values differ by 0.85 eV, i.e. decreasing from 5.90 eV for the open configuration to only 5.05 eV

for the closed form. It is noteworthy that the energy difference between the HOMO level onset position of the open (-O) and closed (-C) configurations is even larger (1.10 eV). This is caused by the fact that the work function (Φ) of DAE1-O is 0.25 eV lower compared to that of DAE1-C, which translates into the additional shift of the HOMO level with respect to E_F . The difference in sample Φ can be explained by different magnitudes of the intrinsic dipole moments of DAE1-O and DAE1-C, provided that a preferential orientation of the molecules at the surface persists. The calculated dipole moment of DAE1 is twice as large for the closed form (2.1 D) as for the open form (0.8 D). It has been shown that oriented dipoles can significantly affect the sample Φ [14–16]. Therefore, changes in the dipole magnitude due to the photochromic ring-closure/opening reaction can be responsible for the different Φ of the DAE1-C and DAE1-O films. Assuming a preferential orientation of the molecules in the film so that the dipoles point away from the surface, we can estimate the Φ change of a monolayer of DAE1 molecules using the difference of the dipole moments ($\Delta\mu = 1.3$ D) and the Helmholtz equation:

$$\Delta\Phi = \frac{en\Delta\mu}{\epsilon_0\epsilon_r} \quad (1)$$

with e the elementary charge, n the surface dipole density, $\Delta\mu$ the change of the dipole moment perpendicular to the surface, ϵ_0 the vacuum permittivity, and ϵ_r the relative dielectric constant. In a fairly simple approximation we assume a density of one molecule per nm^2 , which represents a dense-packed layer, and $\epsilon_r = 1$, which results in a Φ decrease when going from the open to the closed form in the order of 0.3 eV. The good agreement with the experimental Φ change, however, does not imply that all molecules at the surface have the same orientation; molecules below the surface also contribute to the overall Φ change, and thus we can only conclude a preferential orientation of molecules in the entire sample. The Φ decrease was also monitored in situ by measuring Φ during illumination of a DAE1-C film with a halogen lamp (grey SECO spectra in Fig. 2). The photochromic ring-opening reaction is accompanied by both a change of the film color (from pink to transparent) and valence spectra shape. After 1 min of illumination, the HOMO feature of the DAE1-C film at ~ 1 eV binding energy completely disappeared and spectral shape and Φ of the freshly prepared DAE1-O film were fully reproduced (red spectra in Fig. 2). Consequently, almost 100 % of the DAE1-C molecules at the film surface (UPS surface sensitivity is ~ 3 nm) are transformed to the open form (1C \rightarrow O) due to the photochromic reaction. In contrast, in situ illumination of a DAE1-O film has no impact on either Φ or valence spectra shape with our experimental parameters. Because sample illumination is achieved using a special lamp with a cutoff wavelength of ~ 370 nm, our light intensity to initiate the photochromic reaction is not sufficient for the

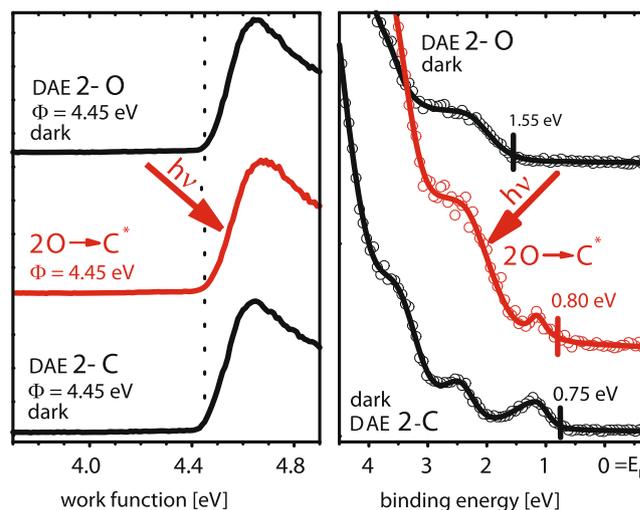


Fig. 3 SECO (*left*) and valence spectra (*right*) of freshly prepared (*black lines*) films of DAE2 in the open (*top*) and in the closed (*bottom*) forms measured in darkness. The appearance of the HOMO feature in the DAE2-C valence band spectrum was achieved by in situ irradiation of the open DAE2 film with a white light halogen lamp. Due to the absorption of both the open and closed forms of the DAE2 molecule (as explained in the text), the measured spectrum represents a mixture of both configurations, predominated by the closed one indicated by C*

open form of DAE1 that only absorbs light up to 360 nm (see absorption spectra in Fig. 1). UPS spectra of the SECO and the valence region of as-prepared DAE2 films are shown in Fig. 3 (black lines). In contrast to DAE1, Φ 's of DAE2 films in the open and closed forms do not differ. This indicates that DAE2 in thin films is not preferentially orientated with respect to the sample surface, as switching induces a $\Delta\mu$ as well (see DAE1 discussion above). Therefore, the difference of the IEs of the two molecular configurations is equivalent to the difference in the HOMO onset binding energy. The IE amounts to 5.20 eV for DAE2-C and 6.00 eV for DAE2-O. In the case of DAE2, in situ white light illumination of the closed form does not lead to a photochromic reaction that can be clearly evidenced by UPS measurements. Due to the red-shifted absorption spectra of DAE2 in comparison to DAE1 (see Fig. 1), the open and the closed forms of DAE2 significantly absorb light at wavelengths longer than 370 nm. Therefore, both transitions from the open to the closed form and vice versa take place simultaneously. However, the photochromic ring-closure reaction predominates and the majority of DAE2 molecules in a freshly prepared film under white light illumination is in the closed form because of a significantly higher quantum yield of the open DAE2 molecule [12]. Thus, the photochromic reaction of DAE2 in films can be followed in situ by UPS starting from DAE2-O. In situ illumination of the DAE2-O film results in the appearance of a new peak in the valence spectra close to E_F , attributed to emission from the HOMO of DAE2-C (red line in Fig. 3). Certainly, white light illumination of the

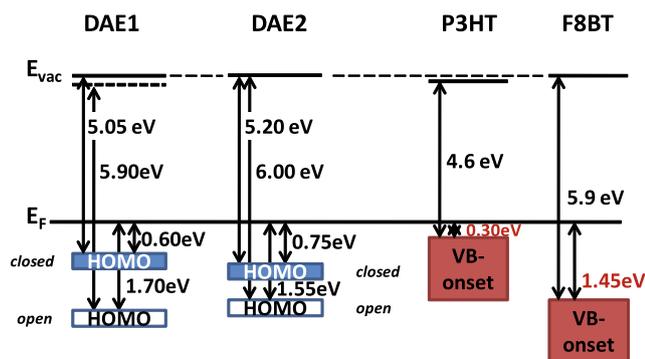


Fig. 4 Schematic energy level diagram of DAE1 and DAE2 in open and closed forms in comparison to hole transport levels of P3HT and F8BT, to act either as shallow or as deep traps for charge carriers (see text)

DAE2-O film did not cause a complete conversion from the open to the closed form but to a mixture of both molecular configurations ($O \rightarrow C^*$). The shape differences between the valence spectra of the DAE2-C film and the illuminated DAE2-O film (especially the less intense HOMO feature) confirm the co-existence of both conformations. Nonetheless, the photoresponsive change in the molecular conformation and electronic structure in the film is evident. The energy levels of both molecules in both forms are summarized in Fig. 4. For comparison, the energy levels of the hole transporting material poly(3-hexylthiophene) (P3HT) [17] and the light emitter poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT) [18] are also shown. Both DAE derivatives have already been exploited in blends with P3HT in organic thin-film transistors for optically induced reversible modulation of the output current [12]. This originated from the different energy positions of the HOMO levels in the open or closed forms of DAE with respect to the hole transport levels of P3HT. Whereas the HOMO positions of the closed DAE1 and DAE2 molecules almost match the valence band maximum of P3HT, thus acting as shallow traps [12], the open forms of both molecules are not accessible for holes within the DAE/P3HT blend, and thus do not impede charge transport. However, the subtle differences between the DAE1 and the DAE2 HOMO levels are reflected in the different device performances. DAE1, with its HOMO closer to the transport manifold of P3HT, shows a higher light-induced current modulation as compared to DAE2. For F8BT the situation is predicted to be rather different. Assuming a common vacuum level also for blends with the DAEs, the HOMO level of both open forms matches the valence band maximum of F8BT, thus enabling good charge transfer. In contrast to P3HT, where the DAEs in their closed form act as shallow traps, they should behave as deep traps for holes in the case of F8BT.

4 Conclusion

The photoresponsive change in the electronic structure of DAE1 and DAE2 in thin films was observed in situ by photoelectron spectroscopy. The variation of the electronic structure accompanying the photochromic reaction appeared clearly for both molecules in the valence band region, with DAE1 having a virtually 100 % yield. In addition, preferential orientation of DAE1 in thin films changed Φ due to the photochromic effect. This also influences the HOMO level position with respect to the substrate E_F and needs to be taken into consideration for application of DAE molecules as switchable components in blends with organic semiconductors. Finally, chemical substitution of DAEs enables the precise tuning of energy levels at interfaces and in blends with organic semiconductors, allowing for efficient photo-control of charge transport in organic electronic devices.

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