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N-Type Doping of Organic Semiconductors: Immobilization via Covalent Anchoring

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ABSTRACT: Electrical doping is an important tool in the design of organic devices to modify charge carrier concentration in and Fermi-level positon of organic layers. The undesired diffusion of dopant molecules within common transport materials adversely affects both, lifetime and device performance. To overcome this drawback, we developed a strategy to achieve immobilization of dopants through their covalent attachment to the semiconductor host molecules. Derivatization of the commonly employed n-type dopant 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazole (***o*-MeO-DMBI**) with a phenylazide enables the resulting ***o*-AzBnO-DMBI** to photochemically generate a reactive nitrene, which subsequently binds covalently to the host material, 6,6-phenyl-C_{61}-butyric acid methyl ester (PCBM). Both the activation and addition reaction are monitored by mass spectrometry as well as optical and photoelectron spectroscopy. A suppression of desorption and a decrease in volatility of the DMBI derivative in UHV was observed after activation of a bilayer structure of PCBM and ***o*-AzBnO-DMBI**. Electrical measurements demonstrate that the immobilized ***o*-AzBnO-DMBI** can i) dope the PCBM at conductivities comparable to values reported for ***o*-MeO-DMBI** in literature and ii) yield improved electrical stability measured in a lateral two terminal device geometry. Our immobilization strategy is not limited to the specific system presented herein, but should also be applicable to other organic semiconductor-dopant combinations.

INTRODUCTION

The applications and benefits of electrical or electrochemical doping in organic semiconductors are manifold.[1,2] Suitable dopants increase the conductivity of organic layers by several orders of magnitude, for example in charge transport layers of organic light emitting diodes (OLEDs).[3] Promising thermoelectric devices can be realized with doped conjugated polymers due to their low thermal conductivity.[4–6] Most importantly, doped layers enable quasi-Ohmic contacts to metal electrodes which greatly improves charge carrier injection and mitigates contact resistances due to offsets in energy level alignment.[7–9] A prerequisite for applying doped layers in dedicated device stacks is stability, since diffusion of dopants into adjacent active layers has been identified as a degradation mechanism (e.g. exciton quenching), detrimental to photo-active devices.[10–14] Moreover diffusion of dopants can be problematic in organic hole transport layers for planar perovskite solar cells.[15] Consequently, stable and efficient doping of organic materials is of high interest in present-day device fabrication. Replacing atomic dopants such as halides or alkali metals by small molecular p- and n-type dopants reduces volatility significantly.[16] However, some host-dopant systems still exhibit diffusivity of organic electron donors/acceptors.[17,18] This effect is more pronounced within conjugated polymers compared to molecular host materials.[19–21] Even though the dopant lacks diffusion in the host matrix, this might change when an electric field is applied. Recently, the migration of molecular dopants in an electric field has been reported in poly(3-hexylthiophene) (P3HT), and considered as drift effect.[22] To suppress dopant diffusion and drift, certain strategies have been proposed and demonstrated, e.g. introduction of a dense dopant blocking interlayer or filling of dopant pathways using a second redox-inactive transport material.[23–25] However, processing becomes more difficult and possible complications concerning charge transport or energy level alignment arise from the additional dopant blocking materials.[26] Furthermore, polar side chains were introduced to a polymer to increase its dopant affinity, yielding an improved thermal stability of molecular dopants and a higher melting temperature.[25] Larger molecular dopants offer a better morphological stability as demonstrated by thermally activated diffusion of dopants in molecular host systems.[27] Beside physical modifications like size or morphology, increased intermolecular interaction also reduces the mobility of dopants. These include dispersion force, dipole-dipole interactions, π-π interactions or even hybridization.[28] Charged dopants are much less diffusive than neutral dopants due to electrostatic interactions.[21,29] A covalent bond between the dopant and the host molecule would allow much stronger “fixation” and ideally to an immobilization of both neutral and charged dopants. A pre-modification of the host with a functional group that introduces self-doping was already used to localize dopants in assembled thin films.[30,31] For covalent bond formation after blending, host and dopant have to have complementary functional groups.[32–34] This concept requires modification of each transport material to fit the corresponding dopant, which is not practical given the plethora of materials in use. In order to be generally compatible with a wide scope of host material, an anchor group for dopants needs an unspecific binding method, e.g. by attachment to aliphatic C-H or olefinic C=C bonds present in almost any organic semiconductor without introduction of severe degradation or traps. A practical solution for this issue can be derived from photochemical cross-linking as desolubilization protocol:[35] The utilization of various bis-azides for cross-linking, thus preventing polymer strands from re-dissolution in solution-processed heterostructures, is not limited to one specific polymer.[36,37] The azide is activated by deep-ultraviolet light (UV, 254 nm), inducing photolysis and generating reactive singlet nitrenes. When properly substituted, these predominantly insert into aliphatic CH-bonds and side-reactions[38] involving triplet pathways, aromatic insertion, attack upon other functional groups or ketenimine ring expansion are suppressed.[36,39,40] The latter is found to be dominating only in solution for non-fluorinated aryl azides,[39,41] whereas in thin films or matrices, C-H insertion prevails.[42–45]

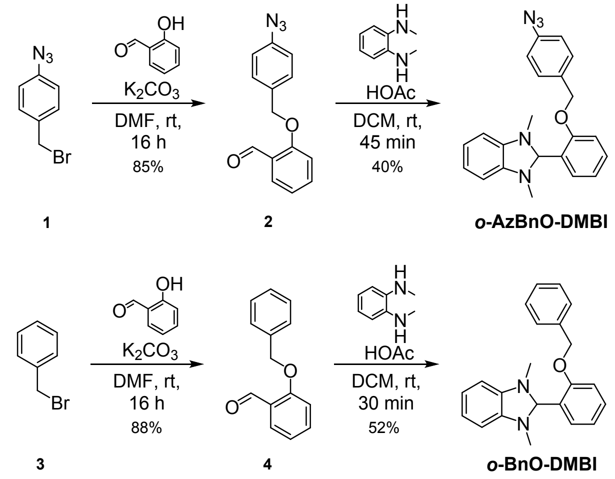
1,3-Dimethyl-2-phenyl-2,3-dihydro-1*H*-benzoimidazole (DMBI) derivatives are effective, air-stable and thus easy-to-handle, solution-processable n-type dopants. DMBIs are often used to dope n-channel semiconductors, preferably PCBM[46–51] or n-type polymers.[47,52] However, they seem to be more effective, in terms of achieved maximum conductivity, in combination with PCBM than with polymers like P(NDI2OD-T2) due to the poor miscibility of dopant and polymer.[6,47,53] Although the doping mechanism of DMBI derivatives in, for example, PCBM has been investigated, it is still under debate.[48,51,54] The initial step either involves a hydride transfer to the host or a hydrogen radical transfer with a subsequent electron transfer – both mechanisms lead to the generation of cationic DMBIs and PCBM radical anions responsible for the doping effect.

In this work, we report the successful anchoring of an azide-functionalized DMBI-based dopant in PCBM, employing a non-specific immobilization strategy through covalent attachment to the host while retaining its dopant strength compared to a non-functionalized counterpart. We detail the synthesis of ***o*-AzBnO-DMBI** and ***o*-BnO-DMBI**, in which the *ortho*-methoxy group of ***o*-MeO-DMBI**[55,56] is substituted by a (4-azidobenzyl)oxy) and a benzyloxy functional group, respectively, and investigate their doping and anchoring properties in blends with PCBM. Infrared and photoelectron spectroscopy are employed to analyze the CH-insertion or cycloaddition reaction and conductivity measurement to verify doping with and without UV trigger. High-resolution mass spectrometry verifies a covalent linkage of the dopant to PCBM. Our immobilization strategy *via* nitrene generation is generally applicable and not limited to a specific host-dopant system. Furthermore, it is destined to improve stability, lifetime and performance of doped organic devices by ideally suppressing both detrimental diffusion *and* drift effects.

RESULTS AND DISCUSSION

Synthesis and Immobilization Reactions

DMBI dopants are easily accessible via simple condensation reactions according to Scheme 1. Introduction of a phenylazide is achieved after etherification of salicylaldehyde employing 1-azido-4-(bromomethyl)benzene (**1**) in DMF at room temperature furnishing compound **2** in 85% yield, followed by condensation with *N^1*,*N^2*-dimethylbenzene-1,2-diamine to afford ***o*-AzBnO-DMBI** in 40% yield. The characteristic IR absorption band of the azde stretching vibration at 2109 cm^{-1} (see Figure 4 b and Figure S11) confirms the azide functionalization.[57]



Scheme 1. Synthesis of ***o*-AzBnO-DMBI** and ***o*-BnO-DMBI.**

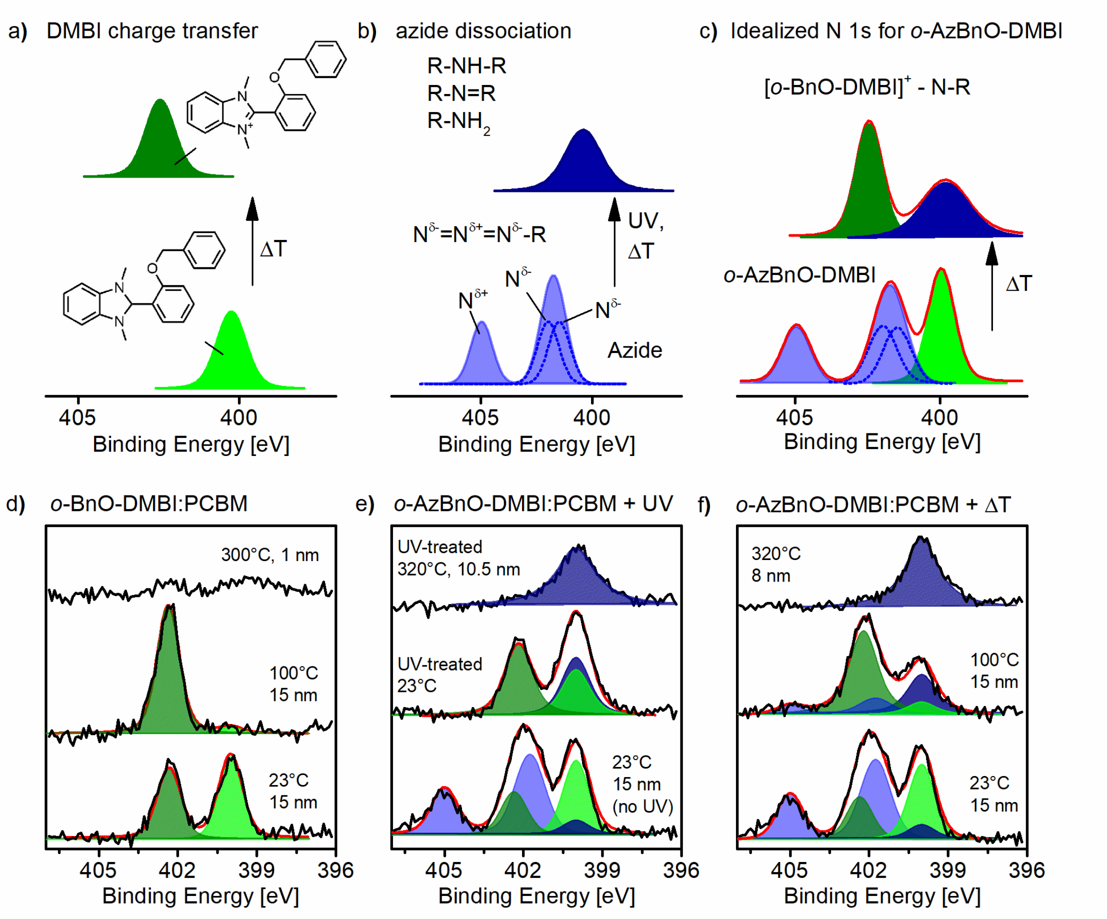


Figure 1. XPS measurements of the N 1s core-level spectra of thermally annealed PCBM films doped with **o-BnO-DMBI** and **o-AzBnO-DMBI** in (d)-(f). A schematic cartoon of N 1s peak components and their transformation in (a)-(c). Recorded spectra of PCBM doped with **o-BnO-DMBI** in (d) for different annealing temperatures. The N 1s signal of PCBM doped with **o-AzBnO-DMBI** is shown in (e) together with the spectrum measured after UV-activation and after annealing of the UV-activated film to 320 °C. A direct annealing of the **o-AzBnO-DMBI:PCBM** film without UV-treatment is given in (f). The assignment of peak composition in (d)-(f) is inferred from contributions of DMBI in green and from the azide in blue. The expected peak components of DMBI upon charge transfer and decomposition of pure azide are sketched in (a) and (b), respectively. For **o-AzBnO-DMBI** both reactions of (a) and (b) can occur as illustrated in (c). The peak shapes of (a) and (b) are fitted to the data in (e)-(f) using a constrained model (see SI for details). In the component fit, there is already a considerable fraction of charged dopants in (d)-(f) and possibly dissociated azide in (e) and (f) at room temperature. The initial film thickness at room temperature is 15 nm, and changes in (d)-(f) for higher temperatures.

To elucidate the influence of the azide group on immobilization, we synthesized the non-azido functionalized analogue and thus non-immobilizable **o-BnO-DMBI** employing benzyl bromide (**3**) for the Williamson ether synthesis. Both new dopants were isolated after crystallization from petroleum ether/methanol or DCM/hexane, respectively. The obtained colorless single crystals were suitable for X-ray crystal analyses, unambiguously proving their structure (see Supporting Information). In order to optimize the processing parameters, we studied the stability of the newly synthesized dopants as well as the literature known **o-MeO-DMBI** in solution (see Supporting Information, Figure S13). NMR spectroscopy revealed that the dopants are only fairly stable in solution: after one day at ambient conditions (sunlight and air) in chloroform, oxidized species can be seen. However, the dopant appears to be stable for processing within several hours. In the solid state at -10°C however, no degradation was observed over months.

In acetonitrile, the UV-vis spectrum of **o-BnO-DMBI** exhibits absorption features at $\lambda = 221$ nm, 274 nm and 313 nm, whereas for **o-AzBnO-DMBI** an additional absorption band at 253 nm is detected and attributed to the azide functional group (Figure S14).[42,58] Irradiation at 254 nm excites the azide and induces nitrene generation.[42,45] Throughout this work, this wavelength is used to initiate the immobilization process. Thermogravimetric analysis (see Figure S15) of **o-AzBnO-DMBI** shows irreversible mass loss at 117 °C corresponding to the extrusion of nitrogen. During additional heating/cooling cycles below the decomposition temperature of 240 °C no further mass loss is observed. Similar to the azide-functionalized dopant, **o-BnO-DMBI** exhibits a rather low melting point at 108 °C (86 °C for **o-AzBnO-DMBI**) and decomposes at 200 °C. To achieve maximum doping effects for the host:DMBI blend annealing at 75°C is required.[48] Thus, **o-AzBnO-DMBI** is stable enough to test doping of the PCBM host upon thermal treatment.

In the following, we provide spectroscopic data to corroborate successful anchoring of the **o-AzBnO-DMBI** dopant. From X-ray photoelectron spectroscopy (XPS) core-level spectra we gain insight into the activation mechanism of both the dopant and the anchor group as well as possible decomposition reactions. In order to additionally test the thermal stability of the DMBI derivative in the blend we annealed thin films of high doping concentration (50 mol%) in ultra-high vacuum (UHV, 10^{-9} mbar) and measured XPS at each temperature step (for details see Figure S20). The N 1s emission of ***o*-AzBnO-DMBI** contains a contribution of the functional azide group and the DMBI core, illustrated in Figure 1c in blue (azide) and in green (DMBI).

To assign the N 1s peak components of ***o*-AzBnO-DMBI** correctly, it is instructive to analyze spectral changes expected from DMBI and the azide group, sketched in Figure 1a and 3b, respectively. The spectra of ***o*-BnO-DMBI** in Figure 1d only exhibit peak components of DMBI core located at 402.5 eV and 400 eV. We identify the nitrogen emission at 402.5 eV as charged dopants having formed a radical and transferred an electron to PCBM. This assignment agrees with the N 1s emission of the ionic DMBI salt at ca. 402.5 eV reported in literature.[59] With rising temperature the peak component at 400 eV transforms into charged DMBI species at 402.5 eV, which correlates with an increase in conductivity observed for annealed PCBM films doped with DMBI. The N 1s signal reported for pure azides sketched in Figure 1b has three components whereas two components coincide between 400 eV and 402 eV leaving a single peak component isolated at high binding energies.[60,61] From density functional theory (DFT) calculations it is known that the central nitrogen in R-N=N$^{\delta+}$=N$^{\delta-}$ is electron-deficient and has an N 1s level at high binding energies.[62] Azide decomposition triggered by UV light or thermal energy leads to nitrogen release and ideally to the generation of singlet nitrene, which can then form new carbon nitrogen bonds. Regarding the azide in ***o*-AzBnO-DMBI**, the peak component at 405 eV in Figure 1e was therefore assigned to the central nitrogen and the contribution of the lateral nitrogen atoms to be between 400 eV and 402 eV. Upon UV activation at room temperature in Figure 1e, the former peak at 405 eV vanishes completely, reducing the peak area around 402 eV and increasing at 400 eV. During annealing of the doped PCBM film in Figure 1f the N 1s emission at 405 eV disappears above 100 °C suggesting that the azide group becomes thermally activated and produces a nitrene. As a result, carbon nitrogen bonds are formed causing an additional N 1s emission at 400 eV which persists at temperatures higher than 300 °C. At the same time, the DMBI part of ***o*-AzBnO-DMBI** donates an electron, similar to ***o*-BnO-DMBI**, thus transferring the peak component at 400 eV into the charged DMBI species at 402.5 eV. When reaching higher temperature in UHV, pure and ***o*-BnO-DMBI**-doped PCBM completely evaporates from the substrate at 300 °C and 200 °C, respectively. Interestingly, the film doped with ***o*-AzBnO-DMBI** is stable even beyond 300 °C and only a partial decrease in coverage is observed. However, from the N 1s emission we infer that the N 1s peak component at 402.5 eV, attributed to charged dopants, disappears almost completely above 210 °C leaving only carbon-nitrogen-bonds at 400 eV when approaching 320 °C in Figure 1 (for details see Figure S20).

At room temperature, pure and untreated ***o*-AzBnO-DMBI** is volatile under UHV conditions as observed by XPS. However, when ***o*-AzBnO-DMBI** is sequentially processed on top of PCBM in monolayer-range thickness, a desorption experiment in UVH at room temperature reveals that the anchoring of **o-AzBnO-DMBI** also appears to be quantitative, rendering ***o*-AzBnO-DMBI** completely resistant to desorption after UV-activation (see SI for details). A similar trend is observed for thicker bilayer structures, which means that in pure dopant films ***o*-AzBnO-DMBI** may also react with neighboring dopants (see Figure S19).

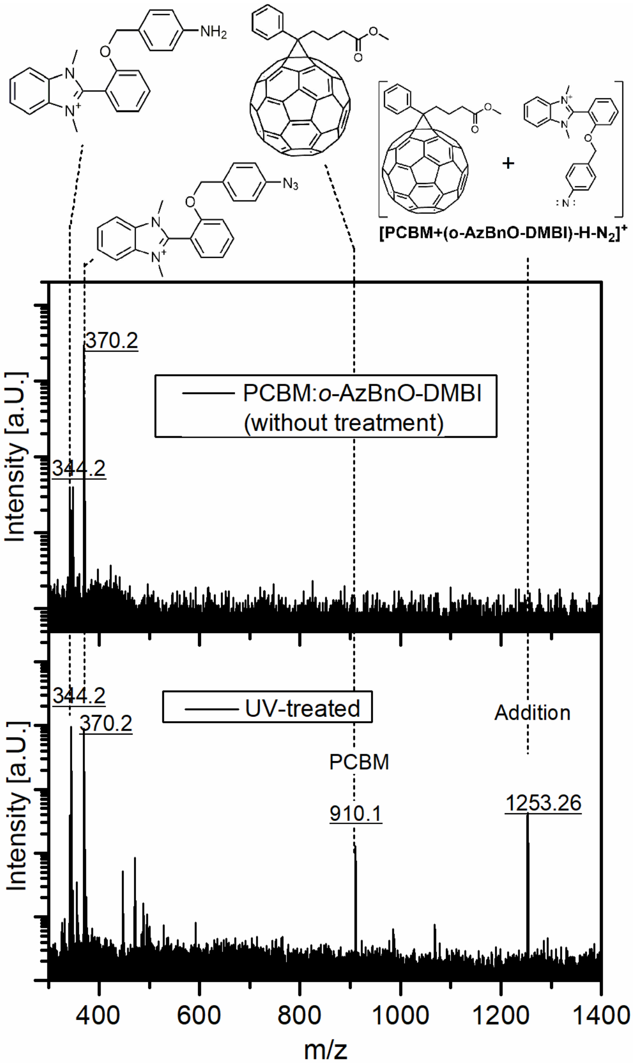


Figure 2. MALDI high-resolution mass spectrometry data are plotted for a blend of PCBM and ***o*-AzBnO-DMBI** in (a) and after UV-treatment in (b) on a log-scale. In principle, the MALDI laser used for desorption can cause azide decomposition but we find a pronounced main peak at 370.2 m/z assigned to intact ***o*-AzBnO-DMBI** in (a). Comparable ESI spectra can be found in Figure S24-S26. Only trace amounts of unfavorable amine products are detected at 344.2 m/z in both (a) and (b) relative to ***o*-AzBnO-DMBI** at 370.2 m/z.

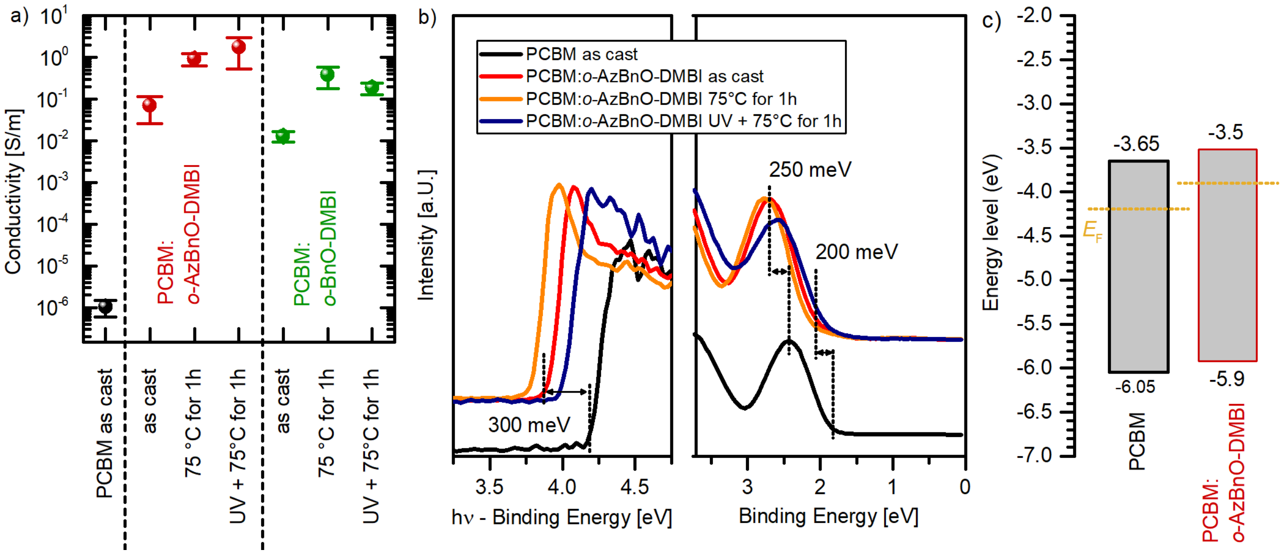


Figure 3. a) Conductivities of pure and doped PCBM layers with a molar doping ratio of 10:1 as cast, after UV treatment and after subsequent annealing. b) UPS spectra of pure and doped PCBM layers with a molar doping ratio of 10:1 as cast, after UV treatment and after subsequent annealing. The secondary electron cutoff with respect to the vacuum level as well as the homo onset with respect to the Fermi level are given. c) Calculated energy levels of pure and doped PCBM layers with a band gap of 2.4 eV.

Concerning the anchoring mechanism, it is known that azides react with fullerenes in a 1,3-dipolar [3+2] cycloadditions affording triazolines,[63,64] which, upon thermal treatment, undergo loss of nitrogen,[65,66] or [2+1] cycloaddition with nitrenes yield aziridinofullerenes or azafulleroids.[67,68] Additionally, CH-insertion into the alkyl chains of PCBM, though much less probable, may occur. To demonstrate covalent attachment of the dopant to the host, blends of ***o*-AzBnO-DMBI** and PCBM were analyzed by electrospray-ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) high-resolution mass spectrometry. We prepared blends of PCBM and ***o*-AzBnO-DMBI** at 25 mol% in a solution of chlorobenzene which were subsequently dried in vacuo. Azide activation was achieved by either annealing at 135 ° C or UV-activation of spin-cast thin films, which were redissolved and the material dried afterwards. Whereas no [3+2] cycloaddition products are found after simple blending, additional peaks of *covalent* PCBM-nitrene adducts at 1253.2 m/z (attributed to [PCBM+(***o*-AzBnO-DMBI**)-H-N_2]$^+$) are detected after heating to 135 °C (thermal azide generation) or photochemical activation (Figure 2 and Figure S24, S26). Photochemical activation is the more benign method as in the ESI spectra (Figure S25) fragmentation of the ether bond within the thermal activated blends is detected. We find comparably small mass peaks for amines (these may also be a fragment of mass spectroscopy created during ionization)[69,70] and unreacted azide from the UV-activated blends (Figure 2). We attribute the latter to the slightly modified sample preparation for mass spectroscopy because IR- and XPS experiments (Figure 4 and 3) demonstrate quantitative azide photolysis.

Doping and Functional Characterization

The conductivity measurements were performed under nitrogen on pure and doped PCBM layers (host-to-dopant ratio: 10:1), spuncast from chlorobenzene onto pre-structured silver contacts on glass substrates (Figure 3a and Figure S17). Whereas neat PCBM thin films exhibit conductivities in the range of 10^{-6} S/m, this characteristic value rises up to 0.1 S/m and 0.01 S/m for *as-cast* films doped with ***o*-AzBnO-DMBI** and ***o*-BnO-DMBI**, respectively. A final annealing step for doped films at 75 °C increases the conductivity further to 1 S/m. After UV-treatment (254 nm) of as-cast films, the conductivities of the doped PCBM layers decrease by roughly half an order of magnitude in comparison to as-cast blends. The subsequent thermal treatment (1 h at 75°C) increases the conductivities for both dopants by more than two orders of magnitude to 1 S/m. In total this is a gain of six orders of magnitude compared to neat PCBM layers (see Figure 3a).

UV-photoelectron spectroscopic (UPS) measurements of corresponding PCBM layers on silicon are presented in Figure 3b. The secondary electron cutoffs of ***o*-AzBnO-DMBI**-doped PCBM reveal strong shifts which translate to a reduction of the work function of ca. 300 meV compared to the neat PCBM layer. Additionally, in doped layers the highest occupied molecular orbital (HOMO) broadens and the HOMO maximum shifts by 250 meV to higher binding energies compared to undoped PCBM, and is accompanied by a shift of the core-level emission lines (see Figure S19). For a comparison, Naab et al. observed a Fermi-level shift of 500 meV in a PCBM blend with 1 wt% ***o*-MeO-DMBI** on ITO.[51]

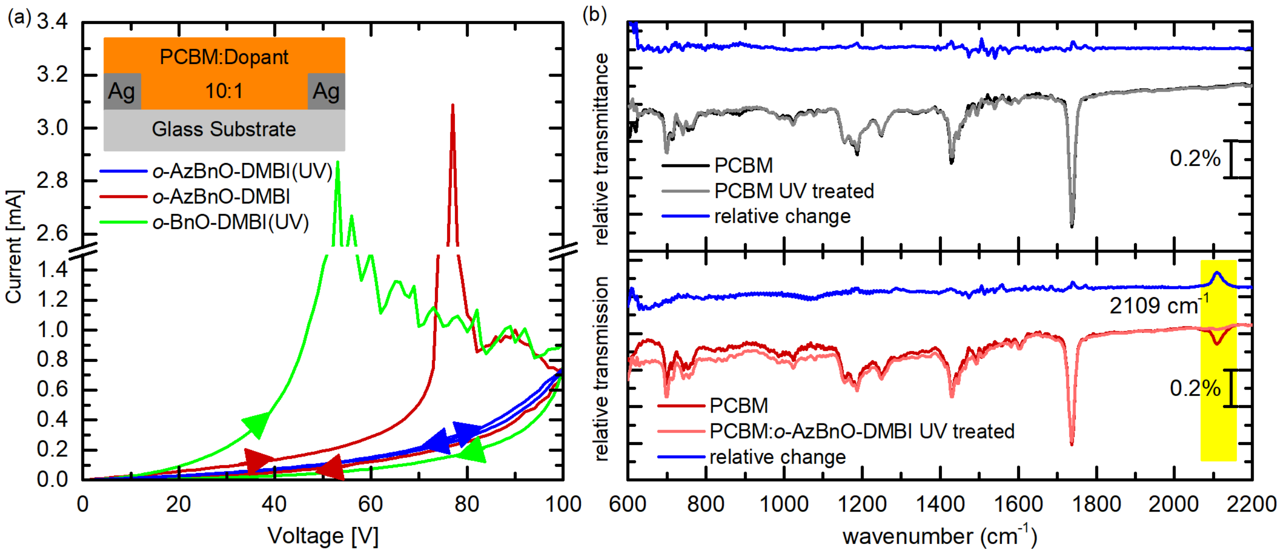


Figure 4. a) I-V curves of annealed layers as cast and after UV treatment. b) Relative IR transmission spectra of 30 nm thick pure and doped PCBM layers with a molar doping ratio of 10:1. The spectra were measured on as cast layers and after UV treatment as given in the legend. Dividing of the spectra after the UV treatment by the as cast spectra reveal the relative spectral change caused by the UV treatment. The vibrational mode of the azide group at 2109 cm^{-1} is marked in (b) and strongly reduced by the UV treatment.

The Fermi-level shift goes along with an increase of free charge carrier concentration and thus leads to an increased conductivity revealing a strong n-type doping effect of both DMBI derivatives in PCBM. Annealing of the thin film results in an additional shift of the Fermi-level towards the LUMO of ca. 50-100 meV for **oAzBnO-DMBI** arriving at a total 350-400 meV shift. Furthermore, we find a broadening of the emission of the HOMO level, yielding an increase of tail states for doped PCBM films. The results of the UPS measurements were used to calculate the energy level diagrams of pure and doped PCBM layer that are depicted in Figure 3c), assuming a constant band-gap of ca. 2 - 2.5 eV.[71–73]

Figure 4a shows I-V curves of doped ***o*-AzBno-DMBI** and ***o*-Bno-DMBI** PCBM layers *as-cast* and after UV treatment. At high electric field strength, the untreated films including ***o*-AzBnO-DMBI** features pronounced rise and subsequent fall-off in current. As a result, the I-V curve displays a distinct hysteresis, which can be also observed when repeating the cycle (slightly shifted to higher voltages). This can be explained either by contact modification and/or by ionic migration. A drift of charged dopant molecules away from a contact causes a similar hysteresis in IV curves which was found for films of poly(3-hexylthiophen-2,5-diyl) (P3HT) doped with the p-dopants 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and molybdenum tris[1-(methoxycarbonyl)-2-(trifluoromethyl)-ethane-1,2-dithiolene] ($Mo(tfd\text{-}CO_2Me)_3$)).[22] On the other hand, the I-V curve of a ***o*-AzBnO-DMBI** doped layer that was UV treated (followed by a final annealing step) display no or reduced hysteresis on average. This observation is a first indication for a successful dopant immobilization after nitrene generation. Moreover, hysteresis persists in ***o*-BnO-DMBI**-doped and UV-treated PCBM, suggesting that the observed characteristic is not due to changes in morphology during UV irradiation but reactions of ***o*-AzBnO-DMBI**.

The HOMO level of PCBM broadens after UV exposure which is attributed to an oxidation of the thin film surface most likely from residual oxygen in the glovebox triggered by UV light (measured by XPS in Figure S18). IR transmission measurements of PCBM layers before and after UV exposure, given in Figure 4b, do not show an oxidation of the PCBM bulk material meaning that the observed oxidation takes place only at the surface. Unfortunately, this hinders the further evaluation of the UV treated doped PCBM layers by UPS since the observed surface degradation strongly influences the measured Fermi-level position. IR transmission measurements of PCBM layers doped with ***o*-AzBnO-DMBI** before and after UV treatment are presented in Figure 4b. (See SI for additional spectra). Due to the doping concentration of 10 mol%, most of the observed vibrational modes stem from PCBM and fail to reveal a change caused by the UV treatment. Only the characteristic vibrational mode of the dopant's azide group at 2109 cm^{-1} vanishes completely, revealing a quantitative activation and dissociation of the azide by UV light.

CONCLUSION

In this work, we detail the synthesis of ***o*-AzBnO-DMBI**, a derivative of the literature known ***o*-MeO-DMBI**. An azidophenyl group is introduced to DMBI by etherification of salicylaldehyde employing 1-azido-4-(bromomethyl)benzene and a subsequent condensation with *N*^{1},*N*^{2}-dimethylbenzene-1,2-diamine. The modification of DMBI with a reactive azide aims at providing a universally applicable anchor-like functional group which should be able to covalently bind to a wide scope of common organic semiconductors. By creating a covalent bond with the host material the dopant is expected to be immobilized or at least rendered significantly less mobile, which ideally reduces problems in devices arising from diffusion or drift of dopants. In an exemplary study, ***o*-AzBnO-DMBI** was blended with PCBM and activated by UV light in order to generate highly reactive nitrenes to ultimately form covalent carbon-nitrogen bonds between PCBM and the dopant. The azide activation was monitored by infrared- and photoelectron spectroscopy. High resolution mass spectrometry reveals addition products, firmly demonstrating the covalent attachment of the dopant to PCBM molecules. The thermal stability of ***o*-AzBnO-DMBI** in the blend was tested by annealing thin films of high doping concentration in UHV and by measuring temperature dependent XPS. We find that the activated dopant renders the doped film more resistant to desorption when approaching the desorption temperature of PCBM in UHV. At room temperature activation of ***o*-AzBnO-DMBI** in a bilayer structure was shown to prevent desorption from PCBM under UHV. IV-measurements further prove that UV-activated ***o*-AzBnO-DMBI** maintains its doping properties giving rise to conductivities typical for blends of DMBI and PCBM. At high electric field strength, the UV-activated doped PCBM films show no or neglectable hysteresis, but a pronounced hysteresis is observed if ***o*-AzBnO-DMBI** is not exposed to UV light. The increased electrical stability can be explained by a suppression of dopant drift due to anchoring of the dopant to PCBM after activation.

The great advantage of our approach is the use of unspecific binding of the intermediately generated reactive dopand towards the host material, offering instant application to a plethora of organic semiconductors. Although chemical derivatization of dopants, either n- or p-type, may be challenging due to the instabilities resulting from their extreme frontier molecular orbital energies, azide incorporation is possible and has the potential to reduce undesired drift and diffusion in multilayer stacks of OLEDs or OPV and can be applied for p-n homo-junctions based on polymers. The appropriate chemical derivatization of p-type dopants such as F4TCNQ and F6TCNNQ is on-going in our laboratories.

EXPERIMENTALS

Synthesis. All reactions requiring exclusion of oxygen and moisture were carried out in heat-gun dried glassware under a dry and oxygen free nitrogen or argon atmosphere using Schlenk and glovebox techniques. All reagents were obtained from commercial suppliers and were used without further purification if not otherwise stated. Deuterated solvents were purchased from Sigma-Aldrich Laborchemikalien GmbH (Seelze, Germany).

Sample Preparation for Analysis. If not noted otherwise, the dopants and PCBM were dissolved separately in chlorobenzene at a concentration of 5 g L^{-1} for XPS, 10 g L^{-1} for IRs/IV-measurements and were mixed right before spin-coating. The dopants were kept in solution for 5-10 min but the PCBM solution was stirred over night at 50 °C. The films were spin-coated at 1000 rpm for 60 s in a nitrogen glovebox on cut n-doped Silicon wafer for XPS, intrinsic silicon for IR and on glass for IV-measurements. Activation by UV light was performed with a mercury-vapor lamp GPH135T5L/4 from Peschl UV-products with a nominal UV-C power of 1.2 W at 254 nm in the glovebox. The penlight was mounted on a stand at a distance of 10 cm above the sample. We measured a UV-intensity at the sample position using a Newport power-meter 1936-C equipped with a photodiode 818-UV plus attenuator and obtain a power density of 0.8 mW cm^{-2} for a 20 min exposure time.

IR-spectroscopy. For IR transmission measurements a Fourier-Transform IR spectrometer (Vertex80v, Bruker) was used. To prevent absorptions from ambient air (H_20 and CO_2) the spectrometer was evacuated to 3 mbar. All samples were recorded near normal transmittance (7°) with a MCT detector and a resolution of 4 cm^{-1}. For each spectrum 200 scans were averaged.

Electrical Measurements. IV measurements were performed under nitrogen atmosphere at room temperature. For this purpose finger-like structured silver contacts with channel lengths between 25 μm and 30 μm were used. Voltages were applied on these contacts using the Semiconductor Parameter Analyzer 4155C by Agilent Technologies which reads out corresponding currents for conductivity determination. Conductivities were then calculated from a set of at least three different samples.

Photoelectron spectroscopy. Photoelectron spectroscopy (PES) measurements were carried out using a PHI5000 Versa Probe scanning photoelectron spectrometer which was equipped with a monochromated Al Kα X-ray source at 1486.7 eV photon energy for X-ray photoelectron spectroscopy (XPS) and a differentially pumped helium discharge lamp operated to achieve He-I emission at 21.2 eV photon energy for ultraviolet photoelectron spectroscopy (UPS). The focused X-ray spot is approximately 200 μm in diameter and be moved to a different position on the sample for longer acquisition in order to avoid radiation damage.

Mass spectrometry. The mass spectra were recorded using the following instruments: JEOL JMS-700 magnetic sector (EI); Bruker ApexQehybrid 9.4 T FT-ICR (ESI, DART); Finnigan LCQquadrupole ion trap (DART); Bruker Autoflex Speed (MALDI).

ASSOCIATED CONTENT

Supporting Information: Synthesis, NMR spectroscopy, Crystal structure, IR-spectroscopy, NMR stability test, UV-Vis absorption, TGA/DSC, ESI Mass spectra, XPS analysis.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzoimidazole (**DMBI**), 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazole (***o*-MeO-DMBI**), 2-(2-(benzyloxy)phenyl)-1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazole (***o*-BnO-DMBI**), ; 2-(2-((4-azidobenzyl)oxy)phenyl)-1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazole (***o*-AzBnO-DMBI**).

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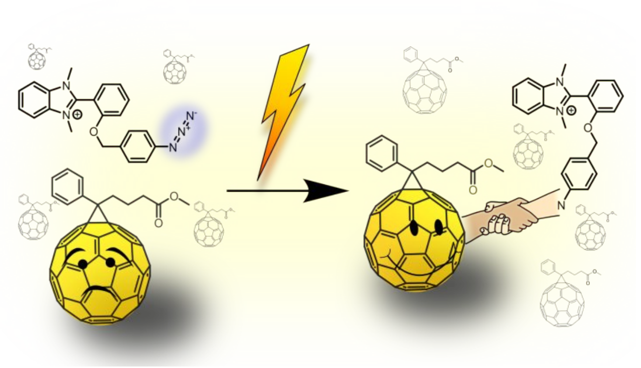

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