FULL PAPER

Passivation of Molecular n-Doping: Exploring the Limits of Air Stability

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Molecular doping is a key technique for flexible and low-cost organic complementary semiconductor technologies that requires both efficient and stable p- and n-type doping. However, in contrast to molecular p-dopants, highly efficient n-type dopants are commonly sensitive to rapid degradation in air due to their low ionization energies (*IE*s) required for electron donation, e.g., *IE* = 2.4 eV for tetrakis(1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinato) ditungsten(II) ($W_2(hpp)_4$). Here, the air stability of various host:$W_2(hpp)_4$ combinations is compared by conductivity measurements and photoemission spectroscopy. A partial passivation of the n-doping against degradation is found, with this effect identified to depend on the specific energy levels of the host material. Since host-$W_2(hpp)_4$ electronic wavefunction hybridization is unlikely due to confinement of the dopant highest occupied molecular orbital (HOMO) to its molecular center, this finding is explained via stabilization of the dopant by single-electron transfer to a host material whose energy levels are sufficiently low for avoiding further charge transfer to oxygen–water complexes. Our results show the feasibility of temporarily handling n-doped organic thin films in air, e.g., during structuring of organic field effect transistors (OFETs) by lithography.

1. Introduction

Reliable fabrication of organic semiconductor devices is challenging due to the air sensitivity of the organic materials used. In particular, simultaneous processing of both p- and n-type doped transistors for organic complementary semiconductor technology[1–3] is critical since several process steps like photolithography are usually performed under ambient conditions rather than in inert atmosphere or vacuum. Exposing these devices to air might lead to oxidation or reduction of the π-conjugated organic molecules due to electron donation or acceptance to/from oxygen and/or water species, respectively. Here, various redox reactions could be envisioned, e.g., reduction of water via $2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$ supported by oxidation of a donor type molecule, or oxidation of water via $2H_2O \leftrightarrow O_2 + 4H + 4e^-$ under reduction of an electron accepting molecule,[4] however, these redox reactions actually require proper catalysts in order to take place.[5,6] Although it has previously been argued that either oxygen[7] or moisture[8] plays the major role in the degradation of the semiconducting properties of conjugated polymers, recent work points to $O_2(H_2O)_n$ complexes as the likely source of performance degradation of organic field effect transistors (OFET)s under ambient conditions.[9] In any case, the redox potentials of the involved organic materials determine whether electron donation or acceptance is feasible, i.e., if the (charged) organics are stable in air. In particular, n-dopant compounds used for molecular (redox) doping are sensitive to immediate oxidation in atmosphere due to their high-lying energy levels, which is a requirement for efficient electron donation to typical transistor materials like pentacene (P5).[1,10]

Hence, research on the development of air stable n-dopant compounds has been actively pursued. In these approaches, the actual n-dopant is either preserved within a precursor molecule,[11–15] or present as the corresponding dimer with sufficient low energy levels to resist oxidation.[16–20] In all of these cases, n-type doping of fullerene films, i.e., [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) or C_{60} (electron affinity *EA* = 4.0 eV), was demonstrated.[12,14,19] Moreover, successful n-doping of copper-phthalocyanine (CuPc, *EA* = 3.5 eV) with dimeric forms of rhodocene was reported.[18] Attempts to dope host materials with even smaller *EA*s, e.g., of 6,13-bis(tri isopropylsilylethynyl)pentacene (TIPS-P5, *EA* = 3.0 eV), mostly resulted in trap-filling.[21,22]

In contrast, the di-metal complex $W_2(hpp)_4$ with its remarkable low ionization energy of just 2.4 eV is not only able to

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efficiently n-dope C_{60},[23] but also host materials with much lower *EA*s like zinc-phthalocyanine (ZnPc, *EA* = 3.4 eV) or even P5 (*EA* = 2.7 eV).[1,24] While this dopant has the drawback of immediate degradation in atmosphere,[25,26] we showed that the strong n-doping effect in C_{60}:$W_2(hpp)_4$ thin films, which disappears upon air exposure, can partially be recovered by returning the doped films back to vacuum and subsequent thermal annealing.[26] This unexpected effect was referred to as a self-passivation mechanism of molecular n-doping and explained either by charge transfer from $W_2(hpp)_4$ to C_{60} accompanied by a down shift of the dopant energy levels or by the formation of hybridized $W_2(hpp)_4$-C_{60} electronic states,[27] protecting the dopant species from oxidation in air.[26] The observed conductivity drop in air was hence attributed to formation of electron traps in C_{60},[28] which can be removed by post annealing in vacuum.

To gain deeper insight into the physics of the passivation mechanism, we investigate here the air stability of various n-doped films, using host materials of varying *EA* (cf. **Figure 1**): P5 (*EA* = 2.7 eV), ZnPc (*EA* = 3.4 eV), *N*,*N*-bis(fluorene-2-yl)-naphthalenetetracarboxylic diimide (bis-HFl-NTCDI, EA_{CV} = 3.8 eV), and the proprietary electron transport material NET108 (EA_{CV} = 4.0 eV). While no passivation effect is observed for the former two hosts, bis-HFl-NTCDI:$W_2(hpp)_4$ and NET108:$W_2(hpp)_4$ films exhibit fairly high n-type conductivities even in air. These findings are supported by ultraviolet and X-ray photoemission spectroscopy (UPS/XPS) measurements. From the density functional theory (DFT)-calculated highest unoccupied moleculat orbital (HOMO) distribution of a $W_2(hpp)_4$ molecule, we conclude that, it is a single-electron transfer to a host with sufficiently deep-lying energy levels that stabilizes the n-dopant against oxidation, rather than host-dopant hybridization. Moreover, we argue that in air, single-electron transfer to oxygen–water complexes such as $O_2(H_2O)_n$ leads to degradation, in particular, if the host's *EA* is not sufficiently high to avoid charge transfer to those complexes. These results do not only indicate the general presence of $O_2(H_2O)_n$-related electron traps in small-molecule thin films, they furthermore quantify the limits of air stable n-doping of organic semiconductors in general and thus extend the basic understanding of the molecular doping process. Finally, our findings are also helpful for establishing future design rules of emerging organic complementary semiconductur technologies.

2. Results

2.1. ZnPc:$W_2(hpp)_4$ and P5:$W_2(hpp)_4$

First, the air stability of a 36 nm ZnPc thin film n-doped by 18 wt% $W_2(hpp)_4$ is investigated. The initial conductivity of the freshly prepared film is 0.011 S cm^{-1} in vacuum. Exposing this sample to air yields an immediate drop of the conductivity by several orders of magnitude, reaching the experimental resolution limit of approximately 10^{-9} S cm^{-1} within a few seconds (cf. **Figure 2**a). Re-evacuating the measurement chamber after 16 min does not lead to any (restoration) effect on the conductivity, which had previously been observed for C_{60}:$W_2(hpp)_4$ films after the same air exposure time.[26] Only a marginal increase to ≈10^{-7} S cm^{-1} is observed when heating the sample slowly to 120 °C and keeping it at this temperature for 1 h (cf. Figure 2b). The final conductivity at room temperature (RT) is still five orders of magnitude below the initial value of the fresh film, clearly demonstrating that the n-doping effect of $W_2(hpp)_4$ to ZnPc vanished upon air exposure.

This conclusion is confirmed by UPS measurements on another n-doped ZnPc film (10 nm, 18 wt%) evaporated on silver foil and stepwise exposed to air for cumulated 15/555/1095 s.

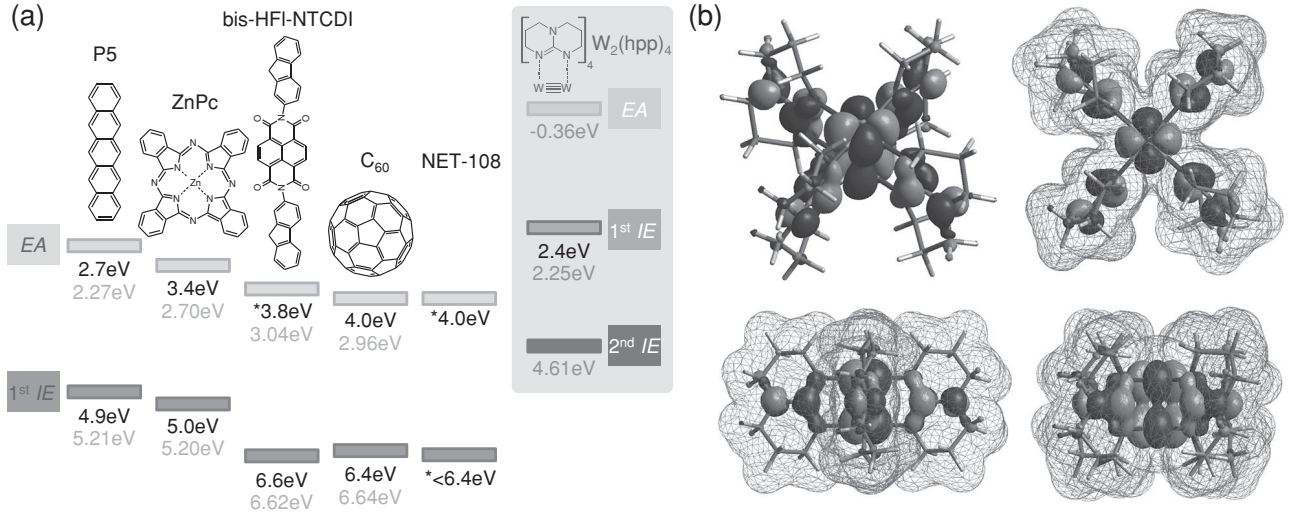

Figure 1. a) Chemical structures and state energies of the investigated organic materials. Black values indicate thin film *IE*s (*EA*s) measured by UPS (IPES), star labeled values are estimated by cyclic voltammetry (IE_{CV}/EA_{CV}), and gray values have been calculated by DFT. The chemical structure of the electron transport material NET108 is the property of Novaled GmbH, and its *IE* has crudely been estimated by EA_{CV}+$E_{gap,optical}$ (which neglects the exciton binding energy). Molecular n-doping is achieved by charge transfer from the highest occupied molecular orbital (HOMO) of $W_2(hpp)_4$ to the lowest unoccupied molecular orbital (LUMO) of a host molecule. b) DFT-calculated HOMO wavefunction (isovalue of 0.02 electrons$^{1/2}$/bohr$^{3/2}$) as well as van der Waals surface (gray mesh) of a $W_2(hpp)_4$ molecule from different perspectives.

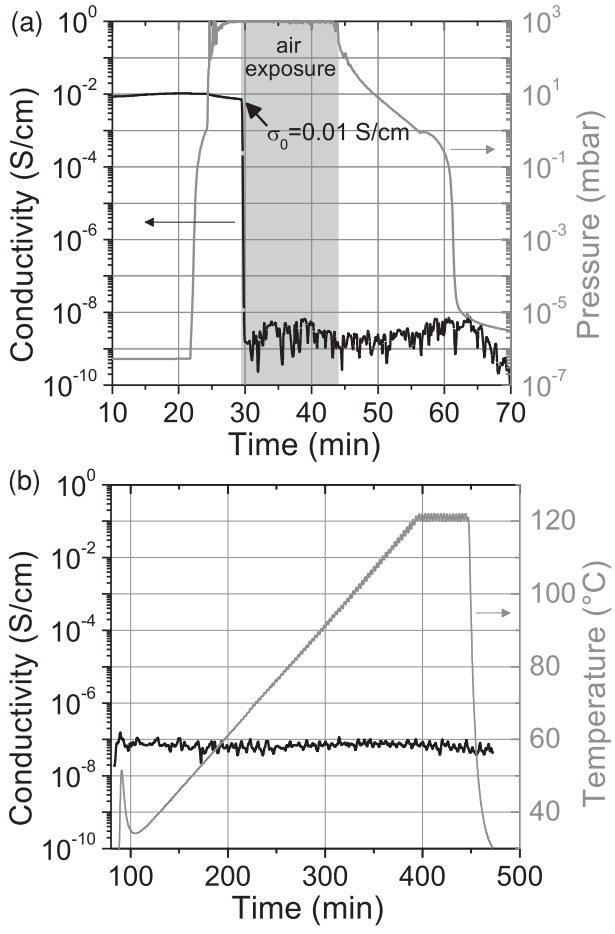

Figure 2. Conductivity of a ZnPc:$W_2(hpp)_4$ (36 nm, 18 wt%) thin film during air exposure a) and thermal annealing after re-evacuation b). The initial value of $\sigma_0 = 1.1 \times 10^{-2}$ S cm^{-1} is measured under vacuum conditions.

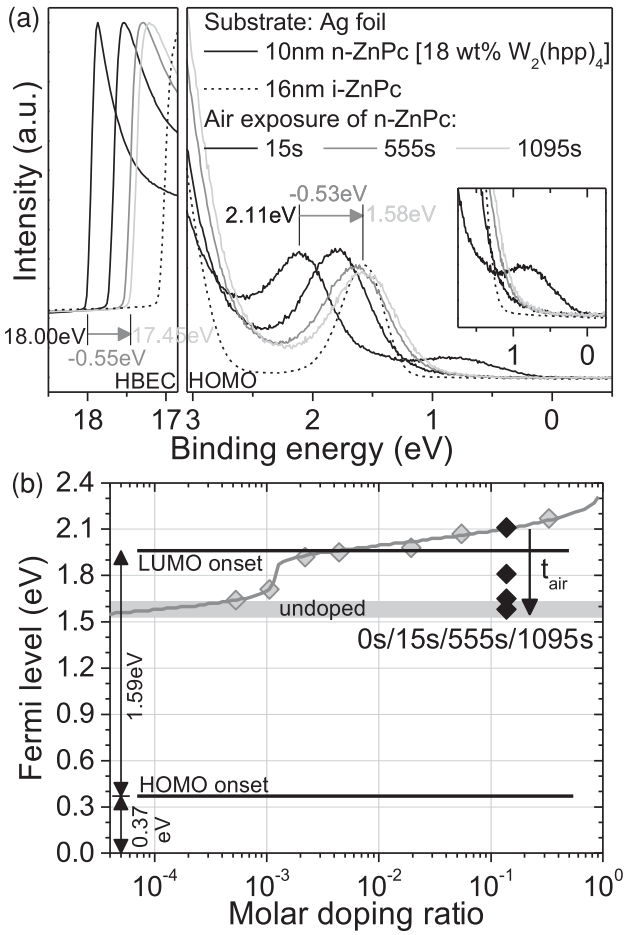

Figure 3. a) Evolution of UPS spectra of an Ag/ZnPc:$W_2(hpp)_4$ (10 nm, 18 wt%) sample under 0/15/555/1095 s of cumulated air exposure. b) Determined Fermi level positions for the consecutive air exposure steps (dark symbols) compared to other fresh samples with varying doping concentration (data taken from ref.[24]).

The obtained UPS spectra are shown in **Figure 3**a. After 15 s of air exposure, the spectrum of the n-doped film is shifted by 0.30 eV toward lower binding energies, i.e., the Fermi level lies at 1.81 eV above the HOMO peak center whereas it was at 2.11 eV for the freshly prepared film. Exposing the sample for additional 9 min to air (cumulated 555 s) decreases the Fermi level position even more to E_F = 1.65 eV and an air exposure of further 9 min (cumulated 1095 s) reduces it to E_F = 1.58 eV, which is equal to that of a fresh but undoped sample (cf. Figure 3a, dashed line). The shift of the Fermi level upon air exposure is further illustrated in Figure 3b, i.e., compared to values determined from fresh samples with varying doping concentrations.[24] Already after the first 15 s of air exposure, the Fermi level is shifted below values that have been measured for fresh samples with doping concentrations of one hundredths of 18 wt%, i.e., only at most 1% of the initial $W_2(hpp)_4$ molecules still provide free electrons. With increasing air exposure time, this trend proceeds and after 1095 s, the n-doping effect completely vanishes.

In this context, a degradation of n-doped (anionic) ZnPc molecules cannot be excluded. Therefore, the C1s and Zn2p3 core levels are scanned by XPS (cf. **Figure 4**). The peak shapes are in fact not significantly affected by the air exposure and just shifts towards lower binding energies by 0.47 eV and 0.57 eV after t_{air} = 1095 s are found (exact peak positions are given in Table S1, Supporting Information), which basically matches the corresponding shifts of the HOMO peak (–0.53 eV) and UPS HBEC (–0.55 eV). As long as the core level peaks follow the work function shift, which has been shown to occur for doped organic semiconductors,[29–31] additional chemical modification (degradation) of ZnPc causing respective changes in the core levels is unlikely or can even be excluded. Hence, these data indicate that the ZnPc host molecules are stable in air and that the observed conductivity drop is predominantly caused by degradation of the n-dopant. Experimental evidence for degradation of pure $W_2(hpp)_4$ thin films in air has previously been shown by XPS and laser desorption/ionization time-of-flight mass spectroscopy (LDI-TOF-MS) experiments, from which a cleavage of the dopant molecule at its W—N and W—W bonds upon air exposure was concluded.[26] In particular, a splitting of the W4f core level signal into two doublets, attributed either to intact (same binding energy) or degraded (W4f shifted to

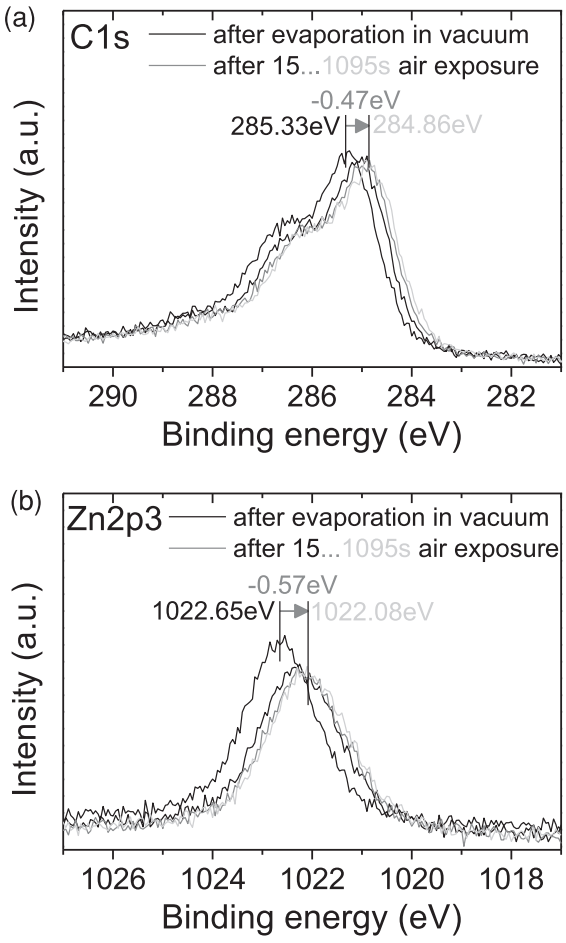

Figure 4. Evolution of the C1s and Zn2p3 core level peaks of an Ag/ZnPc:$W_2(hpp)_4$ (10 nm, 18 wt%) sample under 0/15/555/1095 s of cumulated air exposure.

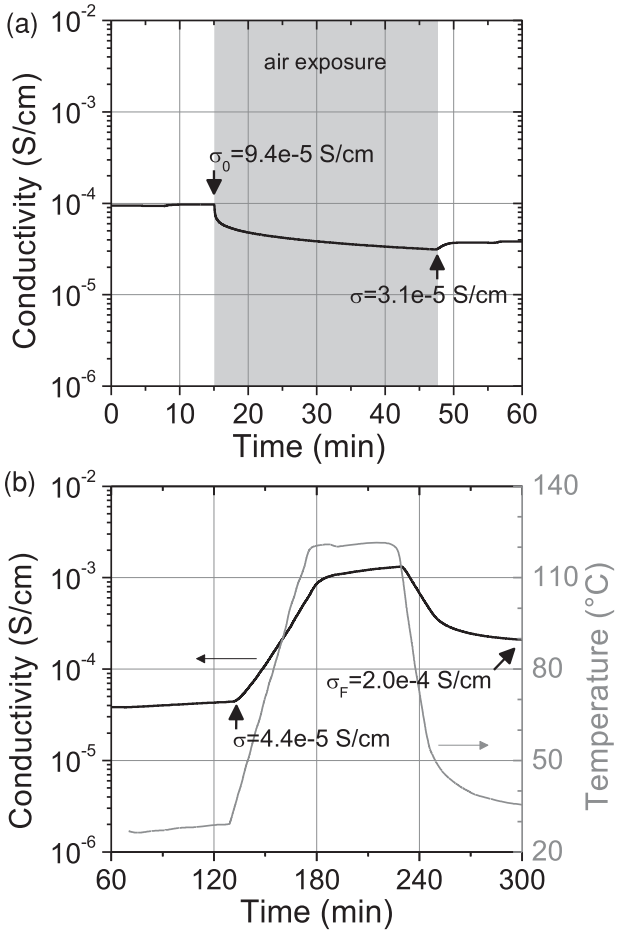

Figure 5. Conductivity of a bis-HFl-NTCDI:$W_2(hpp)_4$ (35 nm, 7 wt%) thin film during air exposure a) and thermal annealing after re-evacuation b). The initial value of $\sigma_0 = 9.4 \times 10^{-5}$ S cm^{-1} is measured under vacuum conditions.

higher binding energies) dopants, was found. The same result is basically observed for the air exposed ZnPc:$W_2(hpp)_4$ films here as well (cf. Figure S1, Supporting Information).

In general, P5:$W_2(hpp)_4$ exhibits a similar behavior when exposed to air. Experimental details are given in the Supporting Information. First, exposing a 16 wt% n-doped 60 nm thin P5 film to air leads to a conductivity drop by roughly 3 orders of magnitude within 5 min (cf. Figure S2, Supporting Information). Subsequent thermal annealing in a glove box does not provide recovery of the conductivity. Second, UPS/XPS measurements confirm this trend. Compared to a freshly prepared 16 wt% n-P5 film (E_F = 2.67 eV), the Fermi level is shifted away from the vacuum level by 0.31 eV upon air exposure for cumulated 375 s (cf. Figure S3a, Supporting Information). The film work-function is similarly increased by 0.35 eV while the C1s core level peak shifts by 0.38 eV toward lower binding energies, again, possesses the same shape before and after air exposure (cf. Figure S4b, Supporting Information). A splitting of the dopant-related W4f core level, indicating chemical decomposition of the $W_2(hpp)_4$ molecules, is found here as well (cf. Figure S4a, Supporting Information). Therefore, we conclude that the n-doping effect in P5:$W_2(hpp)_4$ films is also not stable in air.

2.2. Bis-HFl-NTCDI:$W_2(hpp)_4$ and NET108:$W_2(hpp)_4$

In the case of bis-HFl-NTCDI:$W_2(hpp)_4$, a passivation effect similar to the one previously reported for C_{60}:$W_2(hpp)_4$ is observed. The conductivity during air exposure of a 35 nm bis-HFl-NTCDI thin film doped by 7 wt% of $W_2(hpp)_4$ (MR = 0.05) is shown in **Figure 5**a. Starting at an initial value of $\sigma = 9.4 \times 10^{-5}$ S cm^{-1} measured in situ under high-vacuum conditions, the conductivity immediately drops after venting the chamber with ambient air. However, the observed decrease is much weaker than for n-doped ZnPc, P5, or C_{60} films. Within 5 min of air exposure, the conductivity drops by just a factor of two. During the following 25 min, it decreases only slowly to 3.1×10^{-5} S cm^{-1}, which is 33% of the initial value. This finding is remarkable since it means that the n-doping effect is practically active in air and also not (significantly) hindered by trap formation as observed for n-C_{60}.[26] Re-evacuation of the measurement chamber only marginally affects the conductivity, with just a slight increase to 4.4×10^{-5} S cm^{-1} within 1 h. However, thermal annealing at 120 °C for an additional hour and re-cooling to room temperature increase the conductivity

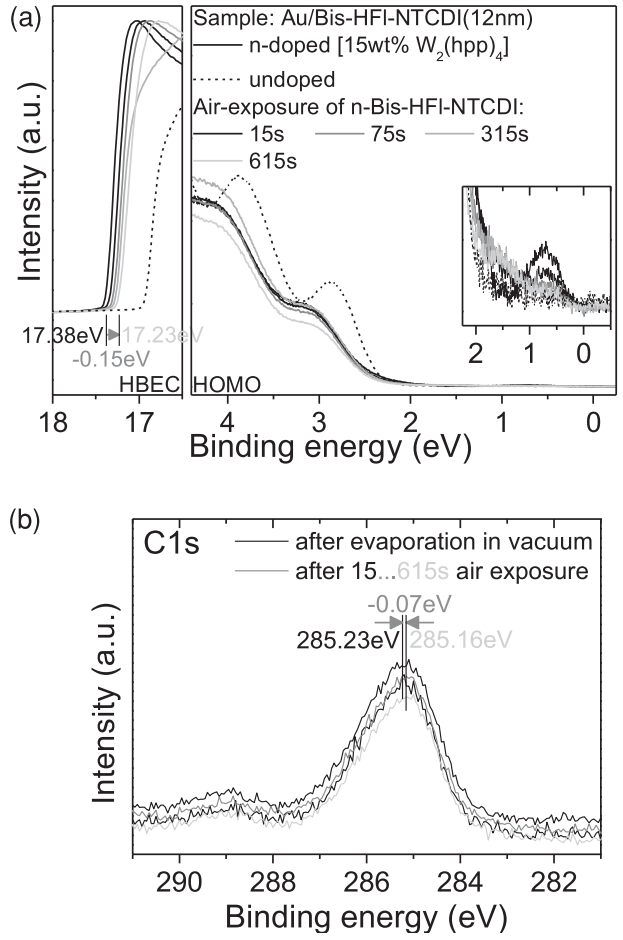

Figure 6. a) Evolution of UPS spectra of an Au/bis-HFl-NTCDI:$W_2(hpp)_4$ (12 nm, 15 wt%) sample under 0/15/75/315/616 s of cumulated air exposure. For comparison, the spectrum of an undoped bis-HFl-NTCDI thin film is shown. b) Corresponding evolution of the C1s core level peak during the air exposure.

by almost one order of magnitude to 2.0×10^{-4} S cm^{-1} (cf. Figure 5b), which is even twice as high as the initial value of the fresh film. Following previous conductivity studies on n-doped bis-HFl-NTCDI,[32] this finding can be attributed to an advantageous morphological modification that increases the carrier mobility. An additional (thermal) activation of the n-doping effect seems unlikely because efficient electron transfer from $W_2(hpp)_4$ to NTCDI molecules can be expected when considering the respective energy levels (cf. Figure 1a).

UPS measurements on a bis-HFl-NTCDI:$W_2(hpp)_4$ (12 nm, 15 wt%) thin film evaporated on Au-foil confirm the observed passivation effect. The UPS sample has been exposed to air for cumulated 15/75/315/615 s and the corresponding UPS spectra are shown in **Figure 6**a in comparison to an undoped reference sample. For the latter, the Fermi level lies 2.87 eV above the lowest binding energy (HOMO) peak center, whereas it is shifted to E_F = 3.20 eV for the freshly prepared n-doped film. Surprisingly, no significant shifts of the UPS spectra are observed under air exposure. The determined Fermi level positions are 3.18/3.17/3.14/3.14 eV, i.e., even after 615 s of air exposure the Fermi level is shifted by only 0.06 eV back towards the gap center. Furthermore, the shapes of the UPS spectra of the doped film, which significantly differ from that of the undoped sample, do not change upon air exposure, which is in contrast to what has been observed for n-P5 and n-ZnPc (see Figure 3a). There, a transition more towards the shape of the respective undoped reference sample is visible. In agreement with the UPS spectra, the C1s core level peak of the n-bis-HFl-NTCDI film is hardly affected by air exposure as well. Only a shift by 0.07 eV towards lower binding energies is found here, which is much less than observed for n-P5 and n-ZnPc. All together, these findings clearly confirm that the n-doping effect from $W_2(hpp)_4$ to bis-HFl-NTCDI does not suffer to any significant extent from air exposure, which is a remarkable effect even stronger than that previously observed for C_{60}:$W_2(hpp)_4$.[26]

Finally, the air stability of an n-doped NET108 film is analyzed since this electron transport material possesses similar energy levels as C_{60}, which means a similar passivation effect is expected here as well. The conductivity of a thermally evaporated 30 nm NET108 thin film n-doped by 4 wt% $W_2(hpp)_4$ and exposed to air for 16 min is shown in **Figure 7**a. For the freshly prepared film, $\sigma = 2.8 \times 10^{-5}$ S cm^{-1} is measured,

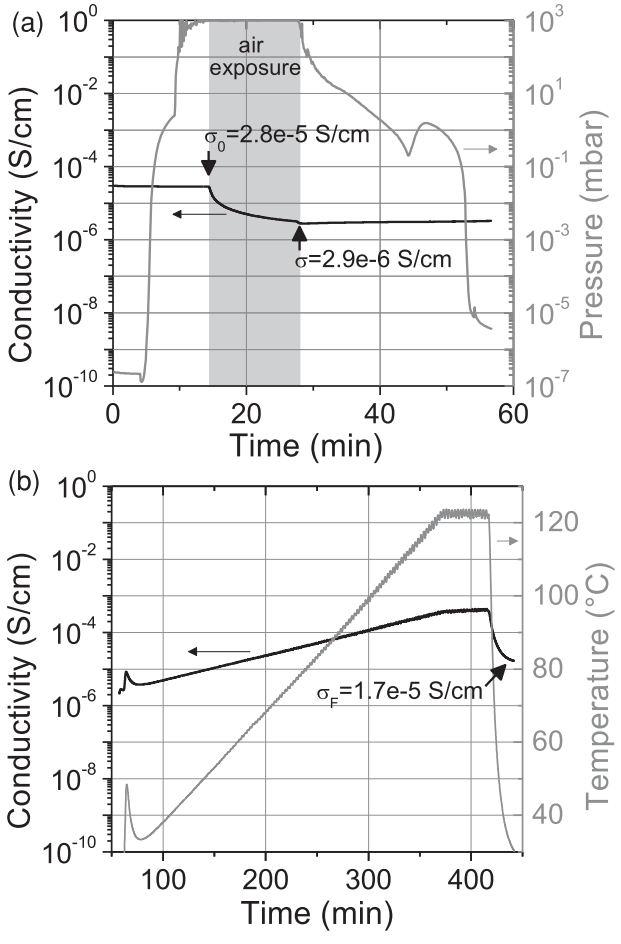

Figure 7. Conductivity of a NET108:$W_2(hpp)_4$ (30 nm, 4 wt%) thin film during air exposure a) and thermal annealing after re-evacuation b). The initial value of $\sigma_0 = 2.8 \times 10^{-5}$ S cm^{-1} is measured under vacuum conditions.

which is approximately five orders of magnitude lower than that of a similar C_{60} sample.[26] Exposing the n-NET108 film to air leads to a drop in the conductivity by one order of magnitude. Re-evacuation of the measurement chamber keeps the conductivity constant at $\sigma = 2.9 \times 10^{-6}$ S cm^{-1}, and a subsequent thermal annealing at 120 °C for 1 h recovers the conductivity to 1.7×10^{-5} S cm^{-1}, which is 61% of the initial value (cf. Figure 7b). In contrast, only 33% recovery has been observed for n-C_{60}.[26]

3. Discussion

The results presented above show that the n-doping effect of $W_2(hpp)_4$ to bis-HFl-NTCDI and NET108 stays fairly active in air and can partially be recovered by postannealing in vacuum for C_{60}. Instead, it completely vanishes for n-ZnPc and n-P5 after air exposure. Since the latter two hosts possess the lowest *EA*s (cf. Figure 1a), a correlation between the strength of the self-passivation effect and the depth of the host *EA* is suspected, which will be discussed in the following.

Blending small amounts of donor type molecules into an acceptor host basically yields two effects: single electron transfer from donor to acceptor or, if the spatial overlap of the frontier molecular orbitals of both species is sufficiently large, formation of donor–acceptor electronic hybrid orbitals.[27] Referring to our previous discussion in ref.[26] indeed, both mechanisms could in principle be used for explaining the experimental findings. More precisely, it was argued that doping $W_2(hpp)_4$ into a host material with lower lying *EA* leads either to a downshift of its HOMO level (cf. **Figure 8**a) or formation of a closed shell bonding dopant-host hybrid state, each lying below the LUMO of the involved host molecule. Thus, for both mechanisms, the resistance of $W_2(hpp)_4$ against oxidation is expected to be improved with increasing *EA* of the host material. However, the DFT-calculated HOMO wavefunction of $W_2(hpp)_4$ (cf. Figure 1b) strongly indicates that any host-$W_2(hpp)_4$ hybrid-orbital formation is very unlikely since the HOMO is essentially confined to the center (axes) of the molecule. This situation is very different from the exposed π-orbitals of flat molecules with no protection from steric bulk, e.g., as for F_4-TCNQ. To illustrate this point, the van der Waals surface of $W_2(hpp)_4$ is plotted in Figure 1b as gray mesh and illustrates that the HOMO is not close to the van der Waals surface, in particular not at the exposed edges of the hpp "paddles." Hybrid-orbital formation would therefore require penetration of the host molecule in-between two "paddles" of $W_2(hpp)_4$. This is unlikely due to the limited space, in particular, when considering the size of the buckyball C_{60} or the large molecule bis-HFl-NTCDI. To provide more evidence for that argument, calculated HOMO wavefunctions of $W_2(hpp)_4$ in interaction with an adjacent P5 molecule for three different mutual orientations are given in Figure S6 (Supporting Information). These represent the most plausible combination for possible electronic orbital hybridization due to the small size of P5. However, the HOMO remains mostly localized on the dopant molecule for this system as well.

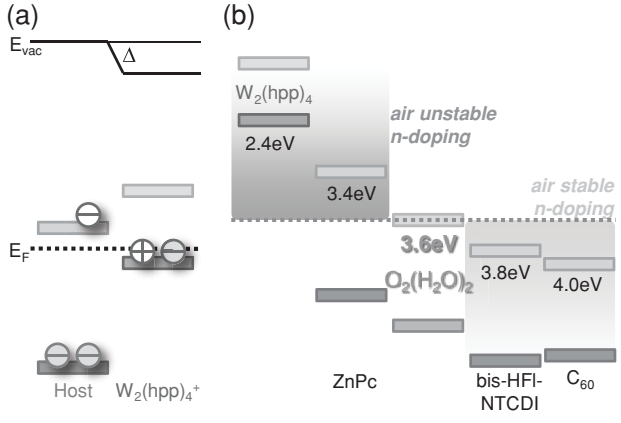

Figure 8. a) Schematic equilibrium energy-level alignment of an n-doped organic film, assuming single-electron transfer from $W_2(hpp)_4$ to host. b) Under ambient conditions, $O_2(H_2O)_2$ complexes represent electron traps, which become reduced if $EA(O_2(H_2O)_2) = 3.6$ eV > *EA*(host) or remain neutral otherwise. In the latter case, the n-doping effect remains active in air.

In the case of single-electron transfer, it is possible to explain the experimental findings by assuming that degradation of the organic materials is predominantly governed by reduction of $O_2(H_2O)_n$ complexes and subsequent chemical reactions. For instance, decomposition of $W_2(hpp)_4$ molecules in pristine dopant films in air is caused by electron transfer to $O_2(H_2O)$ and/or $O_2(H_2O)_2$ complexes, whose *EA*s within an organic matrix were estimated to be 2.9 and 3.6 eV, respectively.[9] These products are chemically highly reactive and, thus, lead to rapid decomposition of dopant molecules, likely by cleavage at their W—W and/or W—N bonds,[25,26] although the *IE* of the dopant cation $W_2(hpp)_4^+$ (4.61 eV, calculated by ωB97X-D3) is actually high enough to resist further oxidation. At first glance, the same processes are basically expected to happen in n-doped films as well. Furthermore, it has been suggested that $O_2(H_2O)_2$ complexes act as universal electron traps in conjugated polymer films,[33] with a corresponding trap depth at 3.6 eV below the vacuum level. Indeed, presence of such traps under ambient conditions also in small-molecule films could explain our experimental findings because reduction of $O_2(H_2O)_2$ complexes would only be possible if the *EA* of the host material is smaller than 3.6 eV (cf. Figure 8b). In that case, the n-doping effect vanishes in air and charged $O_2(H_2O)_2^{\bullet-}$ radicals can furthermore react with the dopant molecules, thus leading to their decomposition. In contrast, if the host *EA* exceeds 3.6 eV, electron transfer to the $O_2(H_2O)_2$-related trap is no longer possible and the n-doping effects stay active in air as observed for, e.g., bis-HFl-NTCDI:$W_2(hpp)_4$ films. In that sense, our findings – so far referred to as self-passivation of n-doping – reinforce the existence of the "universal electron trap" also in small-molecule films. Further experimental evidence for the same trap type has been reported in the literature for aluminum-tris(8-hydroxyquinoline) (Alq3).[34,35]

For all n-doped thin films, sub-gap features are visible in the UPS spectra (cf. insets of Figure 3a; Figure S3a, Supporting Information; Figure 6a), showing peaks at 0.8 eV below E_F for n-ZnPc, 1.3 eV for n-P5, and 0.7 eV for n-bis-HFl-NTCDI. Except for the latter host, these spectral features immediately disappear when exposing the films to atmosphere. Previously, the formation of gap states in doped polymer chains has theoretically been attributed to the presence of polarons and confirmed by distinct optical sub-gap absorption bands.[36,37] As

we excluded dopant-host electronic orbital hybridization, it is hence reasonable to identify the observed UPS sub-gap features with singly occupied orbitals of charged host molecules. In this case, electron transfer to $O_2(H_2O)_2$ complexes in atmosphere must lead to their disappearance as consistently observed for ZnPc and P5. For bis-HFl-NTCDI instead, charge transfer to the 3.6 eV trap is not possible; therefore, the gap states should remain present in air, which qualitatively matches the experimental findings (cf. inset Figure 6a). Additionally, the sub-gap features could be identified with residual occupied orbitals of $W_2(hpp)_4$ molecules according to Figure 8a. Thus, their disappearance would correspond to degradation of comparably large amounts of dopant molecules, which is consistent with the XPS results as briefly discussed in the following.

It was reported that exposing pure $W_2(hpp)_4$ thin films to air leads to a splitting of the corresponding W4f core level signal into two doublets, attributed either to intact (same binding energy) or degraded (W4f shifted to higher binding energies) $W_2(hpp)_4$ molecules.[26] Similar results are obtained for all n-doped films here as well (cf. Figures S1, S4, and S5, Supporting Information), i.e., also for bis-HFl-NTCDI:$W_2(hpp)_4$. Moreover, regardless of the host material, this degradation occurs on two time scales: ≈70% to 80% of the $W_2(hpp)_4$ molecules decompose within the first few seconds under air, whereas the remaining $W_2(hpp)_4$ molecules either degrade very slowly or perhaps even stay intact (cf. Figure S7, Supporting Information). In fact, this observation/interpretation is inconsistent with the aforementioned explanations and results. In particular, a recovery of the conductivity after air exposure to 33% or even 66% of the initial value has been found for n-bis-HFl-NTCDI and n-NET108 films, respectively, which is higher than expected from the W4f peak splitting/decay. An incomplete dopant contribution to the n-doping effect, i.e., a doping efficiency $p/N_D < 100\%$, e.g., caused by dopant aggregation, might resolve this inconsistency since aggregation of $W_2(hpp)_4$ molecules would allow for direct charge transfer to $O_2(H_2O)_2$ complexes in air, leading to their degradation. However, an equal dopant aggregation causing this effect in all the investigated systems seems unlikely, but cannot be excluded, particularly at the high doping ratios used. Furthermore, since dopant saturation has been concluded from E_F versus molecular doping ratio correlations for these n-doped systems,[24] further experimental and theoretical studies, in particular on the doping efficiency, are required in order to establish a complete picture.

4. Conclusion

The sensitivity against degradation in air of various n-doped organic thin films has been investigated by UPS and conductivity measurements. Although the n-dopant $W_2(hpp)_4$ is inherently air unstable (IE = 2.4 eV), a partial passivation against degradation in air is found when inserting it into a host material with sufficiently deep energy levels. In particular, $W_2(hpp)_4$:bis-HFl-NTCDI thin films possess high n-type conductivities even during air exposure times of up to half an hour. However, although $W_2(hpp)_4$ is capable to n-dope host materials with smaller EAs like pentacene (EA = 2.7 eV) and ZnPc (EA = 3.4 eV), no passivation of the n-doping effect against degradation in atmosphere is found for these materials. On the basis of DFT-ωB97X-D3 calculations, we were able to exclude the formation of electronic host-$W_2(hpp)_4$ hybrid orbitals as an explanation since the dopant HOMO is strongly confined to the molecule center. Instead, we argue that the n-doping effect is maintained in air due to single-electron transfer to host materials with sufficiently low-lying energy levels. In particular, air stable n-type conductive films are achieved as long as the EA of the host material lies deep enough to prevent reduction of $O_2(H_2O)_n$ complexes, i.e., if $EA > 3.6$ eV. For host materials with lower EAs, these complexes can be considered as electron traps with a "universal" trap depth.

In summary, these findings demonstrate the limits of air stable molecular n-doping. This is particularly helpful for the development of low-cost organic complementary semiconductor technologies since the required process steps like photolithography can only be performed with great effort in inert atmosphere or vacuum.

5. Experimental Section

The organic layers were deposited by thermal co-evaporation under high vacuum conditions (base pressure 10^{-8} mbar) in which the evaporation rates of host and dopant are monitored by two independent quartz crystal microbalances. The n-dopant molecule $W_2(hpp)_4$ as well as the proprietary electron transport material NET108 were both purchased from Novaled GmbH (Dresden, Germany) and used as delivered. Pentacene was supplied by Sensient (Wolfen, Germany) and purified threefold by 3-zone vacuum gradient sublimation. ZnPc was purchased from CreaPhys (Dresden, Germany) and purified three times as well. The host material bis-HFl-NTCDI was synthesized at IAPP and purified twice before evaporation in vacuum.[32] The chemical structures, and measured and calculated energy levels of all materials are summarized in Figure 1a.

All calculations were performed with the ORCA program package.[38] Geometries were optimized for isolated molecules using the B3LYP density functional method, accounting for dispersion effects using the D3 scheme with Becke–Johnson dampening.[39–44] Property analysis was done using single-point energies with the optimally tuned ωB97X-D3 density functional approximation[45,46] and the polarizable environment of the solid state was approximated with the conductor-like screening model (COSMO)[47] using a dielectric constant of $\varepsilon = 4$, a reasonable value for organic materials.[48] It should be noted that COSMO is a simplified model since it only accounts for isotropic polarizabilities.[49] All calculations made use of resolution of the identity with the chain of spheres approximation.[50,51] The def2-TZVP basis set[52] was used for all atoms; for tungsten, the def2-SD effective core potentials replaced the core electrons.[53] The energies reported in Figure 1a are vertical ionization energies and electron affinities. Additional computational details can be found in the Supporting Information.

For the UPS/XPS samples, either sputter-cleaned gold or silver foils (each 99.995%, MaTecK, Juelich, Germany) were used as substrates. The UPS/XPS experiments were performed with a Phoibos 100 system (Specs, Berlin, Germany, base pressure: 5×10^{-11} mbar) that is directly connected to the evaporation tool. For air exposure, the UPS samples were transferred through a glove box into a flow box, keeping times out of vacuum as short as possible to minimize surface contamination effects. The transfer time between high vacuum conditions and air exposure was estimated to be 6 min. Heating of the UPS samples was performed directly in the analysis chamber with two filaments positioned within the sample holder. The temperature was monitored by a thermocouple fixed on a contact clamp connecting the substrate to the metallic sample holder. Further experimental details of the UPS/XPS setup are explained elsewhere.[26]

Thin film conductivities were measured in lateral geometry either between two ITO or two silver contact pads, defining the width/length

ratio (w/l) of the organic channel (thickness d). A voltage sweep between ±10 V was applied to the contact pads while monitoring the current through the organic layer by Keithley SMUs. For symmetric (ohmic) I–V-characteristics, the film conductivity is calculated by

$$\sigma = \frac{I}{V}\frac{w}{l}\frac{1}{d}$$

in which the geometry ratio w/l defines the final resolution limit of the conductivity, which is 2×10^{-6} S cm^{-1} for the ITO and 2×10^{-9} S cm^{-1} for the silver contact pad geometry. The measurements were performed either in situ in vacuum, in a glove box, or under ambient conditions. For the latter, the relative humidity was within (40 ± 5)% at (24 ± 2) °C.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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