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Hybrid Modulation-Doping of Solution-Processed Ultra-Thin Layer of ZnO using Molecular Dopants

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In recent years, solution processable semiconductors such as metal oxides and organics have been attracting significant attention because of their tremendous potential for application in a wide range of emerging large-area electronics such as printable, flexible and potentially transparent opto-/electronics.^[1-6] Exploring the full potential of these material technologies, however, would most certainly require the development of efficient doping protocols and the necessary understanding of the underlying charge transfer/generation mechanism(s). In the area of oxides^[7] and organic^[8] thin-film transistors (TFTs), for instance, doping has been shown to facilitate accurate control of key device parameters such as charge

carrier mobility (μ),^[9-10] threshold voltage (V_T),^[11-12] reduction of parasitic contact resistance^[13-14] and in some cases, improved device-to-device performance uniformity - a critical parameter for the high yield manufacturing of large-area/large-volume electronics.^[15] Despite the obvious advantages, however, efficient doping of either, metal oxides or organics, has proven to be very challenging requiring either complex manufacturing techniques^[16] or high-temperature^[17] processes that are incompatible with inexpensive large-volume manufacturing and substrate materials such as plastic.

In the case of metal oxides substitutional doping represents an effective and versatile approach that has been used to control key material and device parameters.^[12] Unfortunately, the method offers limited flexibility in terms of processing since it often requires the use of complex techniques and high temperature process steps.^[10, 18] Unlike inorganics, organic semiconductors cannot be doped in the same manner due to the molecular nature of the solids. Instead, charge donating molecules – so-called donors or acceptors – are often incorporated into the organic host semiconductor in a process called molecular doping.^[19] Although p-type doping of organic conjugated materials is a relatively straight forward and well-understood process, n-doping has proven to be more challenging since the highest occupied molecular orbital (HOMO) of the dopant donor molecule has to be high enough in order to enable direct electron transfer to the host semiconductor. This rather strict requirement often leads to problems like poor chemical instability of the dopant molecule.^[20] In an effort to address this issue, a number of alternative molecular dopants have been developed in recent years including, cationic dyes,^[21] dimeric organometallic compounds^[22-24] and hydride transferring compounds.^[25-27] Depending on the molecular system, the doping effect is not always due to direct charge transfer from the dopant to the host semiconductor but it may rely on specific

reactions (e.g. hydride transfer) between the two materials^[27] although the exact mechanism is still being investigated.^[9]

In order to elucidate the inner workings of molecular doping, recent effort has been focusing on studying simple dopant/semiconductor blends as the active layer in diodes^[28] and TFTs.^[26] However, such systems are not ideal for fundamental studies since complex microstructural effects such as phase segregation, may dramatically affect the results. In an effort to overcome these complications, approaches similar to modulation-doping in inorganic hetero-junctions like $\text{Al}_{1-x}\text{Ga}_x\text{As}/\text{GaAs}$ ^[29] have been successfully applied to organic systems^[30-31] and more recently to oxide hetero-interfaces.^[32] Despite the promising results, the concept of modulation doping in organics and metal oxides, let alone hybrids, semiconductor systems remains underexploited. To this end charge transfer at oxide-organic hetero interfaces have been investigated using photospectroscopic techniques in the past.^[33-37] Further investigations into the charge transport mechanism across inorganic-organic interfaces with regards to complete versus partial transfer was recently carried out using density functional theory (DFT) calculations.^[38] However, to the best of our knowledge their applicability has only been demonstrated for work-function modulation of transparent conductive electrodes^[39] and in light-emitting devices.^[40]

Here, we report on an alternative doping approach that exploits the use of organic donor/acceptor molecules for the effective tuning of the carrier concentration in ultra-thin layers (≤ 6 nm) of zinc oxide (ZnO) acting as the transistor channels.^[41] The method is simple and can be implemented at room temperature in different ways. In its simplest form the dopant molecules can be solution deposited directly onto the ZnO layer at room temperature. Alternatively, the organic dopant can be blended in different concentrations with an organic

“host” semiconductor in solution which can then be subsequently deposited onto the ZnO. Through careful choice of molecular dopants, we demonstrate electron transfer from the dopant molecule to the ultra-thin ZnO layer, either directly or mediated by a charge transfer to the host organic semiconductor. By tuning the dopant concentration in the solution we are able to efficiently modulate the extrinsic electron concentration in the ZnO layer and dramatically alter the operating characteristics of the devices. Furthermore, the low-dimensional nature of ZnO allows accurate estimation of the electron density in the transistor channel with good accuracy. The fact that the blend organic doping layer can be applied at room temperature from solution, offers notable advantages and creates new opportunities for both organic and oxide electronics.

Figure 1a displays the schematic of the bottom-gate, top-contact (BG-TC) transistor architecture based on solution-processed layers of ZnO, while **Figure 1b** shows high-resolution transmission electron microscopy (HR-TEM) images of the device cross-section at different magnifications. Despite the low-temperature processing, the images show lattice fringes indicating the presence of polycrystalline ZnO in agreement with previous reports.^[41] As a result the Fast Fourier Transform (FFT) spectral image taken from the middle of the ZnO layer reveals multiple reflections. The lattice spacing of $\sim 2.4(\pm 0.4)$ Å, identified with the arrow, corresponds to the (101) plane of ZnO. The HR-TEM data also reveals the presence of a thin interlayer of AlO_x between ZnO and the top Al source/drain electrode. This is most probably the result of oxidation of the Al-ZnO interface during metal evaporation.^[33] Surface analysis of the ZnO channel by atomic force microscopy (AFM) reveals the presence of crystalline grains (**Figure 1c**) in line with the HR-TEM analysis. Despite their polycrystalline nature, ZnO layers are continuous with a root-mean-square (rms) surface roughness of ~ 0.42 nm.

Figure 1e displays a representative transfer characteristic measured at room-temperature for a BG-TC ZnO transistor. The device exhibits n-channel characteristics with minimum operating hysteresis and average electron mobility $\sim 1 \text{ cm}^2/\text{Vs}$. The excellent device performance indicates the presence of a uniform and continuous film in agreement with the HR-TEM and AFM data. Additional temperature dependent electron transport measurements were carried out in order to better understand the electron transport mechanism in these ultra-thin layers of ZnO. **Figure S1** displays the temperature dependence of electron mobility evaluated in the linear operating regime (μ_{LIN}) at different effective gate fields ($V_{\text{G}} - V_{\text{ON}}$). The noticeable reduction in μ_{LIN} with reducing T and its strong dependence on V_{G} indicates the existence of a partially energetically disordered semiconductor layer. This is corroborated by the exponential tail in the density of states (DOS) distribution below the conduction band minimum (CBM) calculated from the room-temperature transfer characteristics of the device using the Grünewald model (**Figure S2**).^[42]

Despite the non-ideal charge transport characteristics of the devices, the pseudo-two-dimensional (pseudo-2D) nature of ZnO and the proximity of the layer's surface to the electron conducting channel forming at the SiO_2/ZnO interface, provides an ideal platform for studying possible charge transfer-phenomena between a given dopant (organic or inorganic) and ZnO. Due to this proximity ($< 5 \text{ nm}$), any change in the areal electron density (ΔN_{areal}) within the ZnO channel could, in principle, be detected as a change in the device's turn-on voltage (V_{ON}) using:

$$\Delta N_{\text{AREAL}} = \frac{C_i \Delta V_{\text{ON}}}{e} \quad (1)$$

Here, $\Delta V_{\text{ON}} = V_{\text{ON}}^{\text{Doped}} - V_{\text{ON}}^{\text{Pristine}}$ is the shift in the V_{ON} between the pristine and the doped transistors, C_i the areal capacitance of the gate dielectric (8.64 nF/cm^2) and e the elementary charge of an electron ($-1.6 \times 10^{-19} \text{ C}$).

Unlike any previous reports, the pseudo-2D nature of ZnO layers employed here (**Figure 1b**) allows for the transistor channel to be approximated as a quasi-2-dimensional system.^[43] This unique feature enables estimation of the charge carrier density per unit volume ($N_{3\text{D}}$). By assuming that the channel thickness (d) is equal or comparable to the overall thickness of ZnO, the magnitude of $\Delta N_{3\text{D}}$ can be estimated using:

$$\Delta N_{3\text{D}} = \frac{\Delta N_{\text{AREAL}}}{d} \quad (2)$$

We note that the $\Delta N_{3\text{D}}$ in **Eq. 2** represents a lower limit since the electron concentration is expected to be higher near the dielectric-ZnO interface while **Eq. 2** assumes a homogeneous charge distribution. However, since the ZnO layer is only $\sim 5 \text{ nm}$ thick and the device is operated in the linear regime ($V_{\text{D}} = 10 \text{ V}$), the latter approximation is expected to hold.

To investigate the potential of the hybrid modulation-doping approach proposed, we studied the impact of different n-type molecular dopants starting with the well-known donor compound 1H-benzoimidazole (N-DMBI) (**Figure 2a**).^[26] Unlike the majority of dopant molecules, N-DMBI is air stable and only after cleaving a C-H bond in solution, a hydride or hydrogen atom transfer to the acceptor molecule is possible leading to a net charge transfer.^[27] This two-step charge-transfer process has been shown to be particularly effective in n-doping of various fullerenes and fullerene derivatives such as the phenyl-C61-butyric acid methyl ester (PC_{61}BM) shown in **Figure 2a**.^[9] On the basis of this energy band diagram one would expect electrons induced in the PC_{61}BM as a result of the hydride transfer from N-DMBI, to be subsequently transferred to ZnO due to its lower Fermi energy (E_{F}) level. To this end, we

note that the E_F of ZnO was determined via Kelvin probe measurements for several ultra-thin layers yielding values in the range -4.1 eV to -4.32 eV,^[43] while the HOMO and lowest unoccupied molecular orbital (LUMO) energy levels for N-DMBI and PC₆₁BM refer to bulk values reported in the literature.^[26, 44]

To test this hypothesis we first studied the n-doping process of PC₆₁BM with N-DMBI in solution. **Figure 2b** displays the absorption spectra for the neat and doped PC₆₁BM solutions. The data reveal the development of a new absorption peak in the near infrared region at ~1033 nm upon doping which is attributed to the formation of fullerene anions as a result of the efficient donation of an electron to the PC₆₁BM.^[27, 45] Having established that N-DMBI acts as an n-dopant for PC₆₁BM, we have fabricated three different types of transistors. Firstly, the neat solution of N-DMBI was spun onto the ZnO transistor channel (**Figure 3a**) under nitrogen atmosphere. The charge transfer capability of the dopant was then evaluated by recording the transfer characteristics of the transistors before and after N-DMBI deposition. As expected, no electron transfer to ZnO could be detected due to the absence of any hydride/hydrogen transfer from N-DMBI to ZnO. The second type of samples was realized by spin casting neat PC₆₁BM directly onto the ZnO channel. **Figure S3a** displays the transistor transfer characteristics measured before and after PC₆₁BM deposition together with a representative transfer characteristic of the neat PC₆₁BM transistor for comparison. As can be seen, addition of the PC₆₁BM layer has a negligible impact on the operating characteristics of the ZnO transistor. We attribute this to the negligible interactions between PC₆₁BM and Zn²⁺ ions and/or OH groups present and the significantly higher LUMO of PC₆₁BM.

Finally, the third type of devices was realized first by doping PC₆₁BM with N-DMBI in solution-phase (at different concentrations) and subsequently depositing the resulting

formulation onto the ZnO. The formed organic layers are extremely smooth with no evidence of phase segregation (**Figure 3b**). The most important observation, however, is the dramatic shift in the V_{ON} from 0 V to -50 V (**Figure 3c**) –or higher– depending on the doping concentration i.e. the amount of N-DMBI in PC₆₁BM. The measured shift was then used to estimate ΔN_{3D} using Eq. 2 yielding values of up to $4.6 (\pm 0.5) \times 10^{18} \text{ cm}^{-3}$ for a 0.5 % (molar ratio) doping. Increasing the N-DMBI concentration further (e.g. 10%) gradually leads to a significant increase in the transistor's OFF current due to increased conductivity of the N-doped PC₆₁BM layer which acts as a parallel channel to the SiO₂/ZnO interface. This dramatic doping effect is clearly illustrated in **Figure S3d** where ZnO/PC₆₁BM+N-DMBI(10%)-based transistors exhibit totally V_G -independent transfer characteristics. Because of this doping concentrations >1% were not quantitatively evaluated since the increased OFF current forbids meaningful analysis of the ΔV_{ON} evolution.

On the basis of the simplistic energy band diagram in **Figure 2a** we argued that other molecular n/p-dopants should in principle be able to either donate or accept electrons to/from the ZnO layer with similar efficiency, allowing for accurate tuning of the free carrier concentration. To test this hypothesis we investigated two additional dopant molecules namely decamethylcobaltocene^[22] (DMC) and tetracyanoquinodimethane^[46-47] (TCNQ). The chemical structure and the corresponding energy levels of these compounds are shown in **Figure 4a**. Based on the energetics, DMC is expected to donate electrons to ZnO via process (i), while TCNQ to withdraw electron from CBM/ E_F of ZnO via process (ii). Regarding the latter process, one can argue that electron transfer may be limited due to the similarity in the E_F of ZnO and the LUMO energy of TCNQ. To test whether such processes do take place, we have deposited thin dopant layers of DMC and TCNQ directly onto the ZnO channels (see device schematic in **Figure 4b**). **Figures 4c** and **4d** show the transfer characteristics of the

ZnO transistors measured before and after deposition of DMC and TCNQ (at different concentrations), respectively. As can be seen, the presence of a thin-layer of DMC or TCNQ on ZnO has a profound impact on the transistors' operating characteristics as evident by the dramatic shift in the device's switch-on voltage. In particular, deposition of a DMC layer from different solution concentrations leads to a controllable shift in V_{ON} towards more negative voltages indicating a drastic increase in N_{3D} (**Figure 4c**) in accordance with process (i). From the maximum ΔV_{ON} measured for DMC-doped (5 mg/ml solution) devices a value for $\Delta N_{3D} = 3(\pm 0.6) \times 10^{18} \text{ cm}^{-3}$ is calculated. Similar to ZnO/PC₆₁BM+N-DMBI-based transistors, the magnitude of ΔV_{ON} is proportional to the DMC concentration of the solution it was deposited from.

The opposite trend is observed when a TCNQ layer was spun from solutions of different concentrations directly onto ZnO. For the highest concentration of 2 mg/ml we observe a V_{ON} shift towards more positive V_G by up to +30 V (**Figure 4d**). This shift equates to a negative change in N_{3D} by approximately $-2(\pm 0.5) \times 10^{18} \text{ cm}^{-3}$ most likely indicating trapping/transfer of electrons from the CBM/ E_F of ZnO to the LUMO level of TCNQ [process (ii)]. On the basis of these results it is reasonable to assume that the efficiency with which electrons transfer/withdrawn to/from the ZnO channel correlates to the amount of dopant molecules present on the surface of the ZnO layer i.e. degree of coverage. To this end, surface analysis of the ZnO/DMC and ZnO/TCNQ structures by AFM (**Figures 4e** and **4f**, respectively) reveals that both dopants form rather thin layers as the characteristic morphology of the underlying 5 nm-thick ZnO is still visible making accurate evaluation of the degree of surface coverage difficult. Therefore, we cannot rule out that the dopant is distributed non-uniformly i.e. it forms incomplete layers when deposited on ZnO.

Besides the remarkable V_{ON} shift, the sub-threshold slope (SS) of the doped ZnO TFTs also reduces significantly. For ZnO/DMC devices, SS increases indicating enhanced electron scattering either within ZnO and/or at the ZnO/DMC interface. The increase in SS is also accompanied with a drop in the μ_{LIN} . This is most likely attributed to the proximity of the DMC layer to the transistor channel, i.e. the SiO₂/ZnO interface, due to Coulombic scattering. To confirm or refute this proposal, we carried out similar doping experiments in transistors comprising thicker layers of ZnO grown via atmospheric spray pyrolysis.^[48-50] Here the conducting channel is not assumed to extend across the entire ZnO layer thickness (~15 nm) and thus a significant separation between the conducting channel and the DMC layer should exist. The results from these experiments are presented in **Figure S4b**. As can be seen, μ_{LIN} remains nearly constant for both pristine and doped devices, clearly highlighting the absence of electron scattering seen in the ultra-thin layer ZnO TFTs of **Figure S4a**. This implies that the reduced μ_{LIN} in ultra-thin ZnO devices is most likely attributed to Coulombic scattering at the ZnO/DMC interface rather than the formation of electron traps. This conclusion is supported by the fact that the maximum channel current measured at $V_G - V_{ON} = 60 \text{ V}$ in ZnO devices remains constant before and after doping. On the contrary, in TCNQ-doped devices a drastic decrease in the maximum attainable channel current is observed (**Figure 4d**) and is most likely attributed to electron trapping at the ZnO/TCNQ interface.

In an effort to better understand the dominant scattering mechanism, the tail states for each investigated ZnO device were calculated using the Grünewald model (**Figure S5-S7**).^[42] Obtained results indicate that although there is no change in the tail states for DMC-doped ZnO, TCNQ and PCBM/N-DMBI-doped samples show an increase in tail states. Specifically, for TCNQ higher concentrations lead to a higher amount of tail states, whereas for PCBM/N-DMBI the amount of tail states remains dopant concentration independent. This can be

explained on the basis of the energy band diagrams shown in **Figures 2a** and **4a** where both PC₆₁BM and TCNQ are expected to act as electron traps due to their lower LUMO energies as compared to the CBM of ZnO. This also explains the observed independence of the calculated density of tail states to N-DMBI concentration. It can thus be concluded that in ZnO/DMC devices Coulombic scattering is the primarily mechanism responsible for the reduction in μ_{LIN} , whereas in ZnO/PC₆₁BM+N-DMBI and ZnO/TCNQ transistors, Coulombic scattering and charge trapping at the ZnO/dopant interface, both play a role.

Finally, it is noteworthy that our findings for the 15 nm-thick ZnO are in contradiction to the previously reported results presented by Yu *et al.* who proposed a charge transfer doping effect through the use of self-assembled monolayers (SAMs).^[51] In the latter study it was suggested that the doping effect vanishes at a ZnO thickness of ~8 nm, whereas in our 15 nm-thick ZnO the doping effect is still visible. Thus we argue that the doping effect described by Yu *et al.* might rather originate from polarization effects^[52-53] induced by the presence of the SAM which decrease with increasing layer thickness. Possible interaction of transported electrons with traps located on the film's surface may also play a role. This process has been shown to be critical in ZnO layers with thickness ≤ 10 nm due to Coulomb interactions of the field-induced electrons with the surface charges.^[45] However, this apparent discrepancy may well be attributed to other unknown extrinsic effects the role of which has not been considered.

In conclusion, the hybrid modulation doping approach in combination with the low-dimensional transistor architectures discussed here not only allow for accurate control and evaluation of the electron concentration in ultra-thin layers of ZnO but also provides a complementary tool to other optical spectroscopy-based techniques for studying fundamental

charge transfer processes between molecular dopants and inorganic/organic semiconductors. Importantly, the principle of hybrid modulation doping in such co-planar device configuration is expected to be universal and as such applicable to a wide range of materials combinations and devices. Envisaged applications include large-area oxide electronics where control of key transistor operating parameters such as threshold voltage, is of paramount importance for low-cost manufacturing. Due to its simplicity, the hybrid modulation doping approach could also be exploited in fundamental studies in the field of two-dimensional electron gases (2DEGs) formed between semiconducting heterointerfaces based on Si, III-V as well as complex oxide interfaces.

Experimental Section

Material Preparation and Device Fabrication: ZnO precursor solutions were prepared by dissolving 8 mg/ml of ZnO•2 H₂O (Sigma Aldrich, 97%) in aqueous ammonium hydroxide solution (NH₄OH, 50% v/v aqn. soln., Alfar Aesar) under constant stirring at room temperature for at least 30 min. The as-prepared solution was spin cast onto doped silicon wafers with a 400 nm-thick thermally grown SiO₂ acting as the gate dielectric. Before spin casting, the Si⁺⁺/SiO₂ wafers were cleaned in ultrasonic baths of deionized water (18.2 M Ω), acetone and isopropanol (HPLC grade) for 10 min each. The wafers were then exposed to UV-Ozone for 15 min to remove any unwanted organic residues. The ZnO precursor solution was deposited by spin casting at 3000 rpm for 30 s, followed by an annealing step at 200 °C for 30 min in ambient air (50% RH). The spin casting step was repeated three times. Finally, 40 nm-thick Al source/drain contacts were deposited through a shadow mask using vacuum sublimation. The channel length (L) and width (W) of the resulting transistors were 1000 μ m and 40 μ m, respectively. As-prepared transistors were post-annealed for 15 h at 170 °C in nitrogen atmosphere. Organic dopant solutions were prepared in nitrogen atmosphere.

Specifically, 25 mg of decamethylcobaltocene (DMC, Sigma Aldrich) and tetracyanoquinodimethane (TCNQ, Sigma Aldrich) were dissolved in 5 ml tetrahydrofuran and chlorobenzene respectively while stirring for at least 30 min at room temperature. The solutions were then filtrated in order to remove undissolved materials due to solubility saturation. Lower concentrations were achieved by diluting the filtered saturated solution. The actual concentration of the resulting solution was determined by weighing the solution before and after the complete evaporation of the solvent. N-DMBI and PC₆₁BM/N-DMBI solutions were prepared by dissolving N-DMBI (Sigma Aldrich, 97%) and PC₆₁BM (Solenne B.V., 99.5%) in CB with concentrations of 11.74 mg/ml and 20 mg/ml, respectively, and stirring for at least 30 min at room temperature. Deposition of the dopant layer was carried out in nitrogen atmosphere by spin casting the dopant solutions directly onto the ZnO devices at 1500 rpm for 20 s for pristine DMC, TCNQ and N-DMBI, and 2000 rpm for 30 s for PC₆₁BM/N-DMBI blends. An additional post-doping annealing step was introduced in order to remove solvent residues. The post-doping annealing was carried out in dry nitrogen at 75 °C for 10 min (for TCNQ, N-DMBI and PCBM/N-DMBI) and 125 °C for 10 min (for DMC) respectively. Electrical characterization of the pristine and doped transistors was carried out in dry nitrogen using an Agilent dual source-measurement system.

Electron Microcopy Measurements: Cross-section Transmission Electron Microscopy (TEM) micrographs were recorded with a Titan 80–300 Super Twin microscope (FEI Company) operating at 300 kV, equipped with a US4000 charged couple device (CCD) camera (Gatan Inc.). High-resolution transmission electron microscopy (HRTEM) images were recorded using a charged couple device (CCD) camera (Model: US1000, Gatan Inc.). In order to acquire scanning transmission electron microscopy (STEM) images, an annular dark-field (DF4) detector was used at 38 mm camera length. A Gatan Image Filter (GIF, Triediem 665) was utilized to perform the electron energy loss spectrum (EELS) line scan with 0.2

sec/pixel collection time and spectrum image with 0.1 sec/pixel. Samples were prepared on a Helios 400s focused ion beam (FIB; FEI Company) and the foils were lifted out in-situ using an Omniprobe nano-manipulator (AutoProbe300). In order to protect the semiconductor layer surface against the ion beam bombardment during ion beam milling, electron beam assisted carbon and platinum deposition was performed on the sample. The sample was attached to a Cu grid using a lift-out method after cutting it from the bulk using a Ga ion beam (30 kV, 9 nA). The sample was subsequently thinned down to ca. 50 nm thickness (30 kV, 93 pA) and cleaned (2 kV, 28 pA) to get rid of areas of the sample damaged during the thinning process.

Atomic Force Microscopy Measurements: Atomic Force Micrographs were recorded using an Agilent Technologies 5500 AFM / AC Mode III module in tapping mode with a scanning speed of 1 line/s and a resolution of 512 × 512 pixels in an area of 1 μm².

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Figures

Figure 1. (a) Schematic of the bottom-gate, top-contact transistor architecture employed. (b) Different magnification HR-TEM images of the transistor channel cross-section indicating the presence the Al electrode, a thin layer of native oxide (AlO_x), the SiO₂ gate dielectric and an ultra-thin layer of ZnO with the associated FFT analysis. (c) AFM topography image of the polycrystalline ZnO layer with a mean surface roughness of 0.42 nm. (d) Representative transfer characteristic measured for a ZnO transistor in the linear operating regime ($V_D = 10$ V).

Figure 2. (a) Energy levels of N-DMBI, PC₆₁BM and ZnO revealing possible charge transfer routes. (b) Absorption spectra of neat and N-DMBI doped PC₆₁BM solutions showing the formation of PC₆₁BM anions. In (a) SOMO, HOMO and LUMO energies represent bulk values while the CBM and VBM energies for ZnO have been determined experimentally.

Figure 3. (a) Structure of ZnO devices doped with PC₆₁BM/N-DMBI blends. (b) AFM micrograph of a device treated with N-DMBI doped PC₆₁BM. (c) Shift of transfer characteristics of the ZnO devices doped with different PC₆₁BM/N-DMBI blends.

Figure 4. (a) Simplified energy level diagram of DMC, ZnO and TCNQ without taking into consideration any interfacial band alignment effects. Processes (i) and (ii) represent possible electron transfer steps taking place at the ZnO/DMC and ZnO/TCNQ interfaces. (b) Schematic of the DMC and TCNQ doped ZnO devices. Shift of transfer characteristics of the ZnO devices doped with different amounts of DMC (c) and TCNQ (d). AFM micrographs of the channel ZnO layers coated with thin layers of DMC (e) and TCNQ (f).

Figure 5. (top) Calculated change in electron density (ΔN_{3D}) in DMC and TCNQ-doped ZnO devices. (bottom) Calculated ΔN_{3D} in PC₆₁BM/N-DMBI-doped ZnO transistors.

The Table of Contents Entry

An alternative doping approach that exploits the use of organic donor/acceptor molecules for the effective tuning of free electron concentration in quasi-two-dimensional ZnO transistor channel layers is reported. The method relies on the deposition of molecular dopants/formulations directly onto the ultra-thin ZnO channels. Through careful choice of materials combinations, we demonstrate electron transfer from the dopant molecule to ZnO (Image) and vice versa.

Keyword: doping, molecular doping, organic semiconductors, metal oxide semiconductors, modulation doping

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Title: Hybrid Modulation-Doping of Solution-Processed Ultra-Thin Layer of ZnO using Molecular Dopants

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Supporting Information

Hybrid Modulation-Doping of Solution-Processed Ultra-Thin Layer of ZnO using Molecular Dopants

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Section S1. Experimental Results

Figure S1. (a) Field-effect electron mobility calculated in the linear operating regime (μ_{LIN}) versus inverse temperature ($1/T$) and (b) activation energy (E_A) obtained from the Arrhenius fits in (a) versus effective gate voltage ($V_G - V_{ON}$) indicating a decrease in the temperature dependence of the mobility with increased V_G .

Figure S2. Tail states below the conduction band minimum estimated from room temperature transfer characteristics of pristine ZnO TFTs with the method developed by Grünewald et al. [1] Zero energy is set to the Fermi level under flat-band conditions.

Figure S3. Control samples for N-DMBI/PC₆₁BM analysis: (a) Comparison of pristine ZnO with bilayer ZnO+PC₆₁BM and the pristine PC₆₁BM TFTs with; (b) 0.1% N-DMBI, (c) with 1% N-DMBI and (d) with 10% N-DMBI added in the PC₆₁BM layer. For high doping concentrations of $\geq 1\%$ N-DMBI, the conductivity of the N-DMBI/PC₆₁BM layer increases leading to a low resistivity transistor channel. As a result the channel's off current increases, making the evaluation of the doping effect problematic. Most importantly, the results suggest that the change in transfer characteristics by doping is not originating from a superposition of the PC₆₁BM and the ZnO TFT.

Figure S4. Comparison of the normalized electron field-effect mobility (linear) of TFT based on 5 nm-thick (a) and 15 nm-thick (b) layers ZnO doped with DMC. Thin ZnO layers were fabricated as described in the experimental section. 15 nm-thick layers of ZnO were fabricated by atmospheric spray pyrolysis using a zinc acetate dihydrate precursor following previously published protocols [2-4]. Four spraying steps were conducted at a liquid feed rate of 2.5 ml/min and a gas pressure of 2 bar onto a substrate pre-heated to 400 °C. Samples were immediately removed from the hotplate after deposition. In order to avoid parasitic channel currents, the ZnO layers were patterned during the deposition using a stencil shadow mask.

Figure S5. Example for the tail states estimated by the method developed by Grünwald et al. [1] for pristine and DMC-doped ZnO TFTs. Zero energy is set to the Fermi level (E_F) under flat-band conditions.

Figure S6. Example for the tail states estimated by the method developed by Grünwald et al. [1] for pristine and TCNQ-doped ZnO TFTs. Zero energy is set to the Fermi level (E_F) under flat-band conditions.

Figure S7. Example for the change in the tail states estimated by the method developed by Grünwald et al. [1] for ZnO TFTs coated with PC₆₁BM and PC₆₁BM/N-DMBI layers. Zero

energy is set to the Fermi level under flat-band conditions. Data points were fitted in order to obtain values for the three-dimensional density of states.

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