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# Use of a 1*H*-Benzoimidazole Derivative as an *n*-Type Dopant and To Enable Air-Stable Solution-Processed *n*-Channel Organic Thin-Film Transistors

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The design of circuits utilizing organic complementary metal oxide semiconductor (CMOS) architecture requires the development of both *p*-channel and *n*-channel semiconductors with high performance and air-stability. Compared to highly developed *p*-channel organic semiconductors, the availability of high-performance, air-stable *n*-channel materials, in particular with solution processability, remains considerably limited.[1] This is attributed to the vulnerability of electrons to trapping by ambient oxidants, such as $O_2$ and $H_2O$.[2] These ambient traps result in significant decreases of the density of mobile electrons in *n*-channel organic thin-film transistors (OTFTs) and, thus, poor air-stability. The difficulties encountered in the development of new, air-stable *n*-channel semiconductors prompted us to seek a new approach to increase the density of mobile electrons to compensate for the trapped electrons under ambient conditions. We hypothesized that controlled *n*-type doping might fulfill this requirement. Previous attempts at intentional doping have increased film conductivities as a result of increased charge carrier density,[3] with the approach resulting in highly efficient organic light-emitting diodes (OLEDs)[4] and organic photovoltaics (OPVs).[5] However, the design of *n*-type (vs *p*-type) dopants is considerably challenging owing to the requirement of high-lying dopant highest occupied molecular orbital (HOMO) levels, making *n*-type dopants unstable against $O_2$.[3e] A promising strategy involves the formation of the active dopant species through thermal activation or photoactivation, allowing the active *n*-type dopants to transfer electrons to the host matrix and form stable cations.[3b,d] However, most previously reported dopants were processed by vacuum deposition and required high conversion temperatures. These dopants were thus incompatible with solution-processed materials and demonstrated weak doping effects (i.e., insufficient to render the device air-stable). Therefore, it is essential to design new *n*-type dopants for solution-processed *n*-channel OTFTs.

1,3-Dimethyl-2-phenyl-2,3-dihydro-1*H*-benzoimidazole (DMBI) derivatives have been reported as effective reagents for reductive transformations of organic compounds.[6] These materials are also known to promote hydrogen- and/or electron-transfer reactions via radical formation.[7] Thus, these solution-processable moieties present an ideal class of *n*-type dopants, as they readily form neutral radicals and H radical.[6] In this Communication, we report the use of (4-(1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazol-2-yl)phenyl)dimethylamine (N-DMBI, Figure 1a) as an *n*-type dopant and demonstrate improved air-stability of N-DMBI-doped *n*-channel OTFTs by solution processing.

To characterize the doping effect of N-DMBI, film conductivities of a well-known solution-processable *n*-channel semiconductor, [6,6]-phenyl $C_{61}$ butyric acid methyl ester (PCBM),[8] were explored. N-DMBI and PCBM were mixed at varying ratios and spin-coated from chlorobenzene solutions to form thin films. The dopants were activated by heating the films at 80 °C overnight in a $N_2$-filled glovebox. The conductivities of N-DMBI-doped films increased considerably (Figure 2a), with the highest conductivity (ca. $1.9 \times 10^{-3}$ S/cm) being more than 4 orders of magnitude higher than that of undoped PCBM film ($8.1 \times 10^{-8}$ S/cm). These values approach the highest reported conductivities for *n*-type doped organic semiconductors,[3b,c,9] indicating the strong doping ability of N-DMBI. The film conductivities increased superlinearly with regard to the doping concentration of N-DMBI. This can be attributed to the tendency of N-DMBI for aggregation (Figure 2a, inset) and the localization of the donated electrons around dopant molecules in the films.[10]

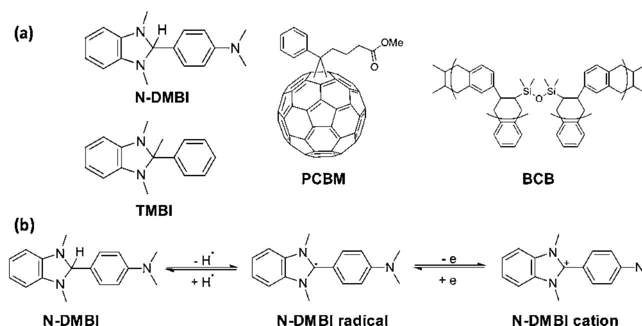


***Figure 1.*** (a) Chemical structures of the materials. (b) Proposed mechanism of hydrogen and electron transfer for *n*-type doping.

PCBM transistors were fabricated with a bottom-gate, top-contact configuration. A thin (20 nm), thermally cross-linked divinyltetramethyldisiloxane bis(benzocyclobutene) (BCB) layer was used to eliminate electron traps that can arise from surface hydroxyl groups on $SiO_2$.[1d,2c,8b] The use of BCB increased the electron mobility of PCBM transistors by 1 order of magnitude ($1.24 \times 10^{-1}$ cm$^2$/(V·s), in $N_2$) as compared to that of transistors fabricated directly on $SiO_2$ dielectric ($1.68 \times 10^{-2}$ cm$^2$/(V·s), in $N_2$).

The performance of N-DMBI-doped PCBM OTFTs in a $N_2$-filled glovebox is shown in Figure 2b. The threshold voltage ($V_t$) of OTFTs is typically employed to evaluate the minimum gate bias ($V_{gs}$) required to fill trap states so that mobile charges start to move under drain−source bias. From the transfer characteristics of the doped devices, $V_t$ systematically negatively shifted with increasing doping concentration. This indicates that a lower gate voltage is needed to turn on the transistors after *n*-type doping. Hysteresis was not observed with all doping concentrations (Figure S3, Supporting Information (SI)). At low doping concentrations (0.5 and 2 wt%), the mobilities remained around 0.1 cm$^2$/(V·s). At high doping concentrations (5 and 10 wt%), the off-current increased by more than 5 orders of magnitude compared to that of the undoped PCBM device. However, there was no significant difference in the on-current at the same $V_{gs}$.

The lowest unoccupied molecular orbital (LUMO) level of PCBM is around −3.80 eV,[11] which is much higher than the HOMO of N-DMBI (−4.67 eV).[6] This means that electron transfer cannot

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spontaneously occur between N-DMBI and PCBM molecules. However, Gaussian 03[12] calculations reveal the singly occupied molecular orbital (SOMO) level of the neutral radical of N-DMBI after hydrogen removal to be −2.36 eV. Thus, the neutral radical species allows for electron transfer from the N-DMBI neutral radical to the PCBM. Besides, a stable *n*-type doping effect could be obtained by stabilizing the N-DMBI cation by the adjacent electron-rich phenyl ring and two nitrogen atoms, making the electron-transfer process irreversible. Therefore, the highly energetic radicals are presumed to be responsible for the strong doping effect of N-DMBI. Moreover, the vis−NIR absorption spectra of the doped film also indicated electron transfer from N-DMBI to PCBM (Figure S4, SI).[13] To further elucidate the nature of the mechanism, 1,2,3-trimethyl-2-phenyl-2,3-dihydro-1*H*-benzoimidazole (TMBI) was used as the dopant, wherein the imidazole core hydrogen was replaced with a methyl group (Figure 1a). No obvious *n*-type doping effect was observed in TMBI-doped transistors (i.e., negative $V_t$ shift and decrease of on−off ratio) (Table S1, SI). This is consistent with our hypothesis on the doping mechanism.

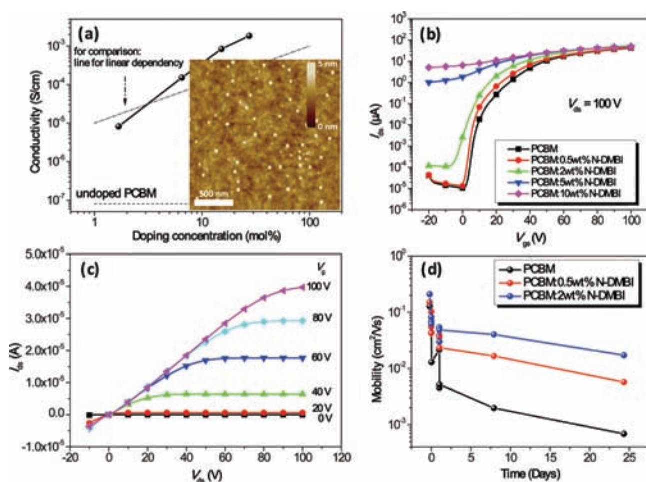


***Figure 2.*** (a) Conductivities of undoped and N-DMBI-doped PCBM films at varying doping concentrations. Inset: AFM image of 2 wt% N-DMBI-doped PCBM film. (b) Transfer characteristics of N-DMBI-doped PCBM OTFTs at varying doping concentrations in a glovebox. (c) Output characteristics of 0.5 wt% N-DMBI-doped PCBM OTFTs in a glovebox. (d) Changes of field-effect mobilities in air as a function of time for undoped and 0.5 and 2 wt % N-DMBI-doped PCBM OTFTs.

The long-term air-stability of undoped and 0.5 and 2 wt% N-DMBI-doped PCBM transistors was monitored by measuring the performance as a function of time (Figure 2d). For undoped OTFT, the performance degraded rapidly, although the $SiO_2$ surface was passivated by the hydroxyl-free BCB layer. The introduction of N-DMBI dopants improved the air-stability of PCBM OTFTs. Significantly, the mobility of 2 wt% N-DMBI-doped PCBM OTFTs remained higher than $10^{-2}$ $cm^2/(V \cdot s)$, even after 20 days. We attribute this improved stability to the compensatory effect of the dopant on the $O_2$ electron traps. To our knowledge, this is the first successful demonstration of an *n*-type dopant enabling air-stability in *n*-channel OTFTs, although there were reports of *n*-type doping on *n*-channel OTFTs for increasing conductivity or crystallization.[9,14] Preliminary results also indicate that this methodology can enable air-stability in vapor-processed *N*,*N*′-ditridecyl perylene diimide OTFTs. These results indicate *n*-type doping is a promising method to incorporate existing air-sensitive *n*-channel semiconductors for practical applications.

In summary, we have developed a new, solution-processable *n*-type dopant, N-DMBI. PCBM can be effectively doped with N-DMBI by solution processing, and the conductivities of doped films are significantly increased. We demonstrate that N-DMBI neutral radicals are the key species enabling *n*-type doping. Furthermore, we utilized this dopant to enable and improve the air-stability of *n*-channel OTFTs by compensating for the ambiently trapped electron charge carriers. Our successful demonstration of *n*-type doping opens up new opportunities for the development of air-stable *n*-channel semiconductors. We also envision potential applications to solution-processed OLEDs and OPVs. Systematic studies on doping mechanisms and the development of additional DMBI derivatives for both solution processing and vacuum deposition are underway.

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**Supporting Information Available:** Details of experimental procedures, discussion on the doping mechanism, complete ref 12, vis−NIR absorption spectra of the thin films of undoped and 10 wt% N-DMBI-doped PCBM, and OTFT data. This material is available free of charge via the Internet at http://pubs.acs.org.

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