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# 2-(2-Methoxyphenyl)-1,3-dimethyl-1*H*-benzoimidazol-3-ium Iodide as a New Air-Stable n-Type Dopant for Vacuum-Processed Organic Semiconductor Thin Films

Peng Wei,<sup>†</sup> Torben Menke,<sup>‡</sup> Benjamin D. Naab,<sup>†</sup> Karl Leo,<sup>‡</sup> Moritz Riede,<sup>‡</sup> and Zhenan Bao<sup>\*,†</sup>

<sup>†</sup>Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States

<sup>‡</sup>Institut für Angewandte Photophysik, Technische Universität Dresden, George-Bähr-Str. 1, 01069 Dresden, Germany

## S Supporting Information

**ABSTRACT:** 2-(2-Methoxyphenyl)-1,3-dimethyl-1*H*-benzoimidazol-3-ium iodide (*o*-MeO-DMBI-I) was synthesized and employed as a strong n-type dopant for fullerene C<sub>60</sub>, a well-known n-channel semiconductor. The coevaporated thin films showed a maximum conductivity of 5.5 S/cm at a doping concentration of 8.0 wt% (14 mol %), which is the highest value reported to date for molecular n-type conductors. *o*-MeO-DMBI-I can be stored and handled in air for extended periods without degradation and is thus promising for various organic electronic devices.

Controllable molecular doping of organic semiconductors<sup>1</sup> has important advantages for organic light-emitting diodes (OLEDs),<sup>2</sup> organic solar cells (OSCs),<sup>3</sup> and organic thin-film transistors (OTFTs).<sup>4</sup> Previous studies on doping of organic semiconductors showed that the addition of strong electron donors or acceptors as dopants can generate extra electrons or holes, respectively. This leads to a shift in the Fermi level and improves the film conductivity.<sup>1</sup> Furthermore, an Ohmic contact can be formed by a highly doped layer at the interface between the metal electrode and the organic semiconductor layer, allowing good charge injection or extraction to be achieved in spite of energy barriers between the electrode and the organic semiconductor layer.<sup>5</sup> For example, efficient doping in organic transporting layers resulted in very low operational voltages of OLEDs with a high power efficiency of 90 lm/W.<sup>2c</sup> Doping also enabled the fabrication of tandem structures for efficient OSCs using a versatile organic recombination contact.<sup>3a,f,6</sup> Additionally, our group has recently reported that intentional n-type doping can improve the air stability of n-channel OTFTs.<sup>4</sup>

A number of molecular p-type dopants have been investigated, such as F<sub>4</sub>-TCNQ<sup>7</sup> and C<sub>60</sub>F<sub>36</sub>.<sup>8</sup> Recently, n-type molecular doping has drawn interest to replace the reactive alkali metals as dopants to prevent high diffusivity and difficulty in handling.<sup>9</sup> However, efficient n-type molecular doping is challenging since the dopant's highest occupied molecular orbital (HOMO) level must be above the lowest unoccupied molecular orbital (LUMO) level of the organic semiconductor matrix in order to make the electron transfer process favorable. The required HOMO of the dopant is usually so shallow that it is unstable in air,<sup>1,3d,10</sup> complicating the fabrication process and

limiting the applications of such dopants in organic electronics. One approach is to use new dopants with shallow HOMOs that are still stable in air, such as tetrathianaphthacene (TTN).<sup>11</sup> However, they are not strong enough donors to obtain n-type-doped films with high conductivity. Another approach is to use a stable cationic salt precursor, such as pyronin B (PyB) chloride,<sup>12</sup> the triphenylmethane cationic dye crystal violet (CV),<sup>13</sup> or acridine orange base [3,6-bis(dimethylamino)-acridine, AOB],<sup>14</sup> to generate the volatile electron donor for n-type doping in situ upon heating. Recently, a series of air-stable dimers of sandwich compounds, including rhodocene and (pentamethylcyclopentadienyl)(arene)ruthenium and -iron derivatives, have been reported as highly reducing n-type dopants for a variety of electron-transporting materials processed by either vacuum or solution, with electron affinities as small as 2.8 eV.<sup>15</sup> In this approach, a thermodynamically unfavorable reversible cleavage of the dimer occurs, followed by a rapid irreversible electron transfer from the highly reactive monomer radical. In comparison with the precursor approach (e.g., PyB), chemical side reactions are minimized, and electron-transporting materials with high LUMOs can be n-type-doped using these dimers. Although several air-stable molecular n-type dopants have been reported,<sup>4b,10a,11,12a,13–16</sup> the highest reported conductivity for an n-type-doped organic film with air-stable molecular dopants is still low, only ca. 4.9 × 10<sup>−2</sup> S/cm with C<sub>60</sub> as the matrix.<sup>14</sup> Therefore, it remains challenging to develop molecular n-type dopants that are air-stable and have strong doping ability to achieve high film conductivities for applications in organic electronic devices.

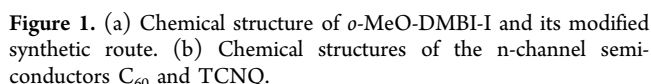
Recently, our group introduced (4-(1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazol-2-yl)phenyl)dimethylamine (N-DMBI) as a solution-processable dopant with efficient n-type doping ability<sup>4b</sup> and showed that the conductivity of an N-DMBI-doped [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) film was significantly increased. In this communication, we demonstrate the use of its cationic derivative, 2-(2-methoxyphenyl)-1,3-dimethyl-1*H*-benzoimidazol-3-ium iodide (*o*-MeO-DMBI-I; Figure 1), as an n-type dopant for vacuum-processed n-channel semiconductors. A film conductivity as high as 5.5 S/cm was obtained.

There was only one previous paper reporting the synthesis of *o*-MeO-DMBI-I via a two-step reaction from 1,2-diaminoben-

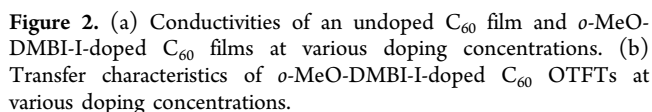
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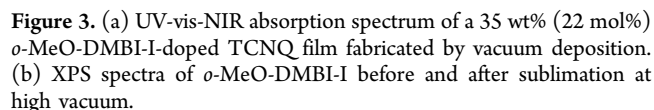


To characterize the n-type doping ability of *o*-MeO-DMBI-I, the film conductivity of fullerene C<sub>60</sub>, a well-known n-channel semiconductor, was investigated. n-Type doping of C<sub>60</sub> was previously shown to be essential for the fabrication of efficient tandem solar cell structures.<sup>3a,f,6</sup> Effective n-type doping of C<sub>60</sub> is needed to create low-loss contacts between the stacked cells while maintaining a very thin doped C<sub>60</sub> layer to minimize parasitic absorption losses.<sup>3a</sup> In our experiments, C<sub>60</sub> and *o*-MeO-DMBI-I were codeposited from separate sources at high vacuum onto smooth glass substrates to give 30 nm thick films. Different doping concentrations were achieved by accurate control of the deposition rates of the matrix and dopant materials using separate quartz microbalances. The conductivity of *o*-MeO-DMBI-I-doped C<sub>60</sub> films were measured in high vacuum, and the results are shown in Figure 2a. The



sulfoxide (DMSO) or ethylene glycol (EG) is in the range 0.1–1 S/cm.<sup>20d</sup> This indicates the strong n-type doping ability of *o*-MeO-DMBI-I, which makes it promising for applications in organic electronic devices. At a higher doping concentration of 12 wt% (21 mol%), the conductivity decreased slightly to 1.8 S/cm, which can be attributed to the tendency of *o*-MeO-DMBI-I to aggregate and the localization of the donated electrons around dopant molecules in the films (Figures S5 and S6 in the Supporting Information).<sup>7c,21</sup>

To study the origin of the n-type doping effect of *o*-MeO-DMBI-I, we measured UV-vis-NIR absorption spectra of doped C<sub>60</sub> films fabricated by vacuum deposition. In our experiments, we could not observe the C<sub>60</sub> anion peaks at 1000–1200 nm arising from electron transfer because the C<sub>60</sub> anion is too unstable in air to be detected as a result of its high LUMO level.<sup>13</sup> Therefore, to confirm the electron transfer from *o*-MeO-DMBI-I to the n-channel matrix, we doped 7,7,8,8-tetracyanoquinodimethane (TCNQ), another well-known n-channel semiconductor that has a much lower LUMO level (−4.8 eV),<sup>23</sup> with *o*-MeO-DMBI-I. In this case, the anion peaks could be observed in the absorption spectra even under ambient conditions. We fabricated the *o*-MeO-DMBI-I-doped TCNQ films by vacuum codeposition at a doping concentration of 35 wt% (22 mol%). In the absorption spectra, the strong TCNQ anion peaks (764 and 865 nm)<sup>13,24</sup> were observed in air (Figure 3a), indicating that efficient electron transfer from *o*-MeO-DMBI-I to TCNQ molecules had occurred.





In our previous work on the solution-processable n-type dopant N-DMBI,<sup>4b</sup> we speculated that the key species enabling effective n-type doping was its neutral radical, whose singly occupied molecular orbital (SOMO) level is very high ( $-2.36$  eV according to B3LYP/6-31G\* calculations using Gaussian 03<sup>25</sup>). Thus, the neutral radical could potentially allow for electron transfer from the dopant to the n-channel semiconductor. However, our recent Electron Paramagnetic Resonance (EPR) experiments indicated that the radical intermediate was not present. The reported studies on the cationic salts of PyB and CV showed that their protonated leuco bases can be generated in situ during vacuum deposition.<sup>12,13,26</sup> In our case, mass spectra were measured in situ in the vacuum chamber during evaporation of *o*-MeO-DMBI-I at its deposition temperature ( $180$ – $200^\circ\text{C}$ ). A peak at  $254.3$  amu was clearly observed (Figure S7), which is assigned to 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1*H*-benzimidazole (*o*-MeO-DMBI, molecular weight  $254.3$  amu), indicating the formation of *o*-MeO-DMBI during evaporation. But no mass peak for a neutral radical was observed in our experiments. Therefore, we hypothesized that *o*-MeO-DMBI-I was reduced during evaporation under high vacuum to form *o*-MeO-DMBI, which underwent electron transfer to  $\text{C}_{60}$  molecules. To elucidate the doping mechanism further, X-ray photoelectron spectroscopy (XPS) measurements were performed on pure *o*-MeO-DMBI-I films fabricated by either vacuum deposition or drop-casting from ethanol solution (Figure 3b). By comparison, no iodide peak was observed in the XPS spectrum of the neat *o*-MeO-DMBI-I film fabricated by vacuum deposition, indicating that *o*-MeO-DMBI-I was reduced and lost  $\text{I}^-$  during evaporation; this also demonstrated that the lost  $\text{I}^-$  in this precursor approach did not contaminate the doping films. Moreover, we also fabricated *o*-MeO-DMBI-I-doped PCBM films at a doping concentration of  $2.0$  wt% ( $4.7$  mol%) by solution spin-coating deposition. The entire process was carried out below  $100^\circ\text{C}$ . In this case, we found no n-type doping effect by both conductivity and transistor measurements. These results indicate that *o*-MeO-DMBI-I is an n-type dopant precursor and that the doping effect can be obtained by heating to form the neutral compound, *o*-MeO-DMBI, which is responsible for the strong n-type doping effect. Moreover, our preliminary results showed that *o*-MeO-DMBI-I can also effectively accomplish n-type doping of organic semiconductors with LUMO levels as high as  $-3.0$  eV. Our further investigation of the n-type doping effect of *o*-MeO-DMBI-I on different organic semiconductors with higher LUMOs ( $>-3.0$  eV) is still in progress to explore further the limit of the n-type doping achievable with *o*-MeO-DMBI-I.

In summary, we have synthesized a new air-stable n-type dopant, *o*-MeO-DMBI-I, for vacuum-processed organic thin films.  $\text{C}_{60}$  can be highly doped by *o*-MeO-DMBI-I, as shown by measurements of film conductivity and transistors. The highest film conductivity obtained in this work was  $5.5$  S/cm, indicating that it is promising for applications in various organic electronic devices. Systematic studies on the doping mechanisms of *o*-MeO-DMBI-I and other DMBI-I derivatives as well as their applications in solar cells are underway.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Details of experimental procedures, synthetic route for *o*-MeO-DMBI-I, complete ref 25, undoped and *o*-MeO-DMBI-I-doped  $\text{C}_{60}$  transistor data, AFM images of undoped and *o*-MeO-

DMBI-I-doped  $\text{C}_{60}$  films, and the mass spectrum obtained in the vacuum chamber during evaporation of *o*-MeO-DMBI-I. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

zbao@stanford.edu

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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## ■ REFERENCES

- (1) Walzer, K.; Maennig, B.; Pfeiffer, M.; Leo, K. *Chem. Rev.* **2007**, *107*, 1233.
- (2) (a) Pfeiffer, M.; Leo, K.; Zhou, X.; Huang, J. S.; Hofmann, M.; Werner, A.; Blochwitz-Nimoth, J. *Org. Electron.* **2003**, *4*, 89. (b) Meerheim, R.; Lussem, B.; Leo, K. *Proc. IEEE* **2009**, *97*, 1606. (c) Reineke, S.; Lindner, F.; Schwartz, G.; Seidler, N.; Walzer, K.; Lussem, B.; Leo, K. *Nature* **2009**, *459*, 234.
- (3) (a) Drechsel, J.; Männig, B.; Kozłowski, F.; Pfeiffer, M.; Leo, K.; Hoppe, H. *Appl. Phys. Lett.* **2005**, *86*, No. 244102. (b) Chan, C. K.; Zhao, W.; Kahn, A.; Hill, I. G. *Appl. Phys. Lett.* **2009**, *94*, No. 203306. (c) Schwartz, G.; Maennig, B.; Uhrich, C.; Gnehr, W.; Sonntag, S.; Erfurth, O.; Wollrab, E.; Walzer, K.; Pfeiffer, M. *Proc. SPIE* **2009**, *7416*, No. 74160K. (d) Cho, N.; Yip, H.-L.; Hau, S. K.; Chen, K.-S.; Kim, T.-W.; Davies, J. A.; Zeigler, D. F.; Jen, A. K. Y. *J. Mater. Chem.* **2011**, *21*, 6956. (e) Meiss, J.; Menke, T.; Leo, K.; Uhrich, C.; Gnehr, W.-M.; Sonntag, S.; Pfeiffer, M.; Riede, M. *Appl. Phys. Lett.* **2011**, *99*, No. 043301. (f) Riede, M.; Uhrich, C.; Widmer, J.; Timmreck, R.; Wynands, D.; Schwartz, G.; Gnehr, W.-M.; Hildebrandt, D.; Weiss, A.; Hwang, J.; Sundarraj, S.; Erk, P.; Pfeiffer, M.; Leo, K. *Adv. Funct. Mater.* **2011**, *21*, 3019.
- (4) (a) Oh, J. H.; Wei, P.; Bao, Z. *Appl. Phys. Lett.* **2010**, *97*, No. 243305. (b) Wei, P.; Oh, J. H.; Dong, G.; Bao, Z. *J. Am. Chem. Soc.* **2010**, *132*, 8852.
- (5) Olthof, S.; Meerheim, R.; Schober, M.; Leo, K. *Phys. Rev. B* **2009**, *79*, No. 245308.
- (6) Timmreck, R.; Olthof, S.; Leo, K.; Riede, M. K. *J. Appl. Phys.* **2010**, *108*, No. 033108.
- (7) (a) Blochwitz, J.; Pfeiffer, M.; Fritz, T.; Leo, K. *Appl. Phys. Lett.* **1998**, *73*, 729. (b) Gao, W.; Kahn, A. *Appl. Phys. Lett.* **2001**, *79*, 4040. (c) Maennig, B.; Pfeiffer, M.; Nollau, A.; Zhou, X.; Leo, K.; Simon, P. *Phys. Rev. B* **2001**, *64*, No. 195208.
- (8) Meerheim, R.; Olthof, S.; Hermenau, M.; Scholz, S.; Petrich, A.; Tessler, N.; Solomeshch, O.; Lüssem, B.; Riede, M.; Leo, K. *J. Appl. Phys.* **2011**, *109*, No. 103102.
- (9) Kido, J.; Matsumoto, T. *Appl. Phys. Lett.* **1998**, *73*, 2866.
- (10) (a) Chan, C. K.; Amy, F.; Zhang, Q.; Barlow, S.; Marder, S.; Kahn, A. *Chem. Phys. Lett.* **2006**, *431*, 67. (b) Chan, C. K.; Zhao, W.; Barlow, S.; Marder, S.; Kahn, A. *Org. Electron.* **2008**, *9*, 575.
- (11) Tanaka, S.; Kanai, K.; Kawabe, E.; Iwahashi, T.; Nishi, T.; Ouchi, Y.; Seki, K. *Jpn. J. Appl. Phys.* **2005**, *44*, 3760.
- (12) (a) Werner, A. G.; Li, F.; Harada, K.; Pfeiffer, M.; Fritz, T.; Leo, K. *Appl. Phys. Lett.* **2003**, *82*, 4495. (b) Werner, A.; Li, F. H.; Harada, K.; Pfeiffer, M.; Fritz, L.; Leo, K.; Machill, S. *Adv. Funct. Mater.* **2004**, *14*, 255.
- (13) Li, F. H.; Werner, A.; Pfeiffer, M.; Leo, K.; Liu, X. J. *J. Phys. Chem. B* **2004**, *108*, 17076.

- (14) Li, F.; Pfeiffer, M.; Werner, A.; Harada, K.; Leo, K.; Hayashi, N.; Seki, K.; Liu, X.; Dang, X.-D. *J. Appl. Phys.* **2006**, *100*, No. 023716.
- (15) Guo, S.; Kim, S. B.; Mohapatra, S. K.; Qi, Y.; Sajoto, T.; Kahn, A.; Marder, S. R.; Barlow, S. *Adv. Mater.* **2012**, *24*, 699.
- (16) Nollau, A.; Pfeiffer, M.; Fritz, T.; Leo, K. *J. Appl. Phys.* **2000**, *87*, 4340.
- (17) Fekner, T.; Gallucci, J.; Chan, M. K. *Org. Lett.* **2003**, *5*, 4795.
- (18) (a) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1997**, *119*, 2722. (b) Zhu, X.-Q.; Zhang, M.-T.; Yu, A.; Wang, C.-H.; Cheng, J.-P. *J. Am. Chem. Soc.* **2008**, *130*, 2501.
- (19) Bostai, B.; Novák, Z.; Bényei, A. C.; Kotschy, A. *Org. Lett.* **2007**, *9*, 3437.
- (20) (a) Kim, J. Y.; Jung, J. H.; Lee, D. E.; Joo, J. *Synth. Met.* **2002**, *126*, 311. (b) Ouyang, J.; Xu, Q.; Chu, C.-W.; Yang, Y.; Li, G.; Shinar, J. *Polymer* **2004**, *45*, 8443. (c) Crispin, X.; Jakobsson, F. L. E.; Crispin, A.; Grim, P. C. M.; Andersson, P.; Volodin, A.; van Haesendonck, C.; Van der Auweraer, M.; Salaneck, W. R.; Berggren, M. *Chem. Mater.* **2006**, *18*, 4354. (d) Elschner, A. *PEDOT: Principles and Applications of an Intrinsically Conductive Polymer*; CRC Press: Boca Raton, FL, 2011.
- (21) Ha, S. D.; Kahn, A. *Phys. Rev. B* **2009**, *80*, No. 195410.
- (22) (a) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194. (b) Zhang, X.-H.; Domercq, B.; Kippelen, B. *Appl. Phys. Lett.* **2007**, *91*, No. 092114. (c) Wöbkenberg, P. H.; Bradley, D. D. C.; Kronholm, D.; Hummelen, J. C.; de Leeuw, D. M.; Cölle, M.; Anthopoulos, T. D. *Synth. Met.* **2008**, *158*, 468.
- (23) Yamagishi, M.; Tominari, Y.; Uemura, T.; Takeya, J. *Appl. Phys. Lett.* **2009**, *94*, No. 053305.
- (24) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374.
- (25) Frisch, M. J.; et al. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (26) Chan, C. K.; Kim, E. G.; Brédas, J.-L.; Kahn, A. *Adv. Funct. Mater.* **2006**, *16*, 831.