

Supporting Information

A 1*H*-Benzoimidazole Derivative as an *n*-Type Dopant and Its Use to Enable Air-Stable Solution-Processed *n*-Channel Organic Thin-Film Transistors

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Chemicals

[6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) was purchased from Nano-C. (4-(1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazole-2-yl)-phenyl)-dimethyl-amine (N-DMBI) was purchased from Sigma-Aldrich. 1,2,3-Trimethyl-2-phenyl-2,3-dihydro-1*H*-benzoimidazole (TMBI) was purchased from ChemBridge Corporation. Divinyltetramethyldisiloxane bis(benzocyclobutene) (BCB) was purchased from Dow Chemicals. The remaining chemicals and solvents were purchased from Sigma-Aldrich. All of the chemicals were used as received without further purification.

Instruments

A Digital Instruments (DI) MMAFM-2 scanning probe microscope was used to perform tapping mode AFM on the samples with a silicon tip of 300 kHz frequency. DI Nanoscope software was used to process the raw AFM images. UV/VIS/NIR was recorded with a Varian Cary 6000i UV-vis spectrophotometer in ambient condition. All electrical measurements were measured with a Keithley 4200 semiconductor parameter analyzer. All devices were measured without encapsulation.

Discussion On the Doping Mechanism

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. They are also known to promote radical reactions, where they act as hydrogen donor and/or electron transfer reagents.^{1,2} Among DMBI derivatives, DMBI was already widely studied and utilized as a reducing reagent for carbonyl compounds in organic synthesis.¹ For example, at $^{\circ}\text{C}$ α -haloacetophenones can be reduced by DMBI to their corresponding carbonyl compounds.^{1b} Because the neutral radicals of DMBI derivatives are highly reactive, direct detection and characterization by electron paramagnetic resonance (EPR) spectroscopy was not possible, as reported in previous publications.^{2,3} However, in the reported references,¹ the mechanism of the reduction reactions by DMBI derivatives was proved to be a radical process by the addition of radical initiators or radical inhibitors. Zhu X. Q. et al. also systematically studied the enthalpy changes and

energy levels of DMBI derivatives.² Their results indicated that N-DMBI can form radicals similar to DMBI, although there is no report on reduction reactions of N-DMBI.

In the N-DMBI doped PCBM system, we hypothesize N-DMBI neutral radicals formed by heating in a N₂-filled glovebox. This neutral radical has extremely high singly occupied molecular orbital level (SOMO, -2.36 eV by Gaussian 03' calculation) so that an electron can be immediately transferred to the lowest unoccupied molecular orbital (LUMO) of PCBM (Figure S1), leading to the formation of a stable N-DMBI cation. Therefore, PCBM is reduced by electron transfer from the neutral radicals of N-DMBI. This was proved by the observation of the PCBM radical anion absorption band over 800~1100 nm in vis-NIR (Figure S4).

Moreover, to have a better understanding of the doping mechanism of N-DMBI, we used TMBI to replace N-DMBI, where the hydrogen at imidazole core was replaced with a methyl group (Figure 1a) so that the neutral radicals cannot be easily formed as N-DMBI with hydrogen abstraction process. In our experiments, we indeed could not observe an obvious *n*-type doping effect, which is consistent with our hypothesis on the doping mechanism.

The systematical studies are underway to make a better understanding on the doping mechanism.

Full Reference Citation for Ref. 12 in the Communication

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, J. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Nalick, D. K.; Rabuck, A. D.; Raghavachari, J.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, G.; Clifford, S.;

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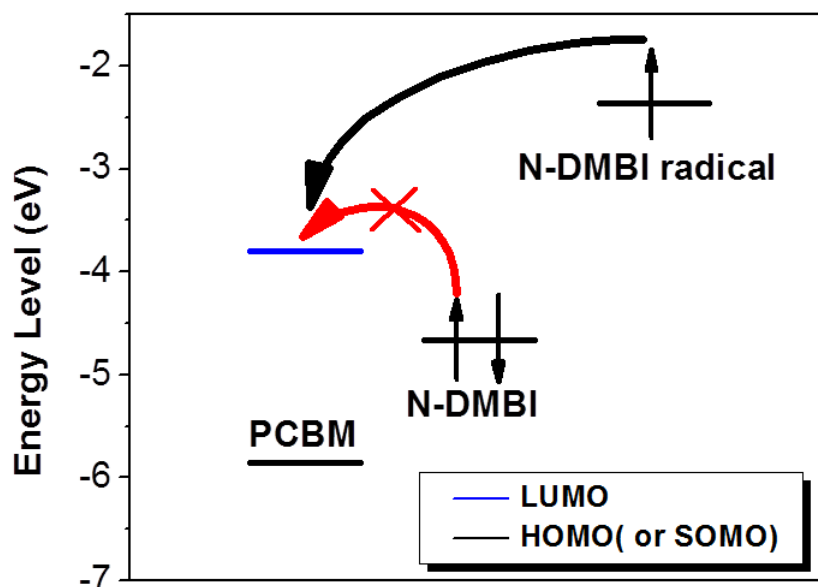


Figure S1. Energy diagram of PCBM, N-DMBI and N-DMBI neutral radical. The SOMO level of N-DMBI neutral radical was calculated by Gaussian 03’.

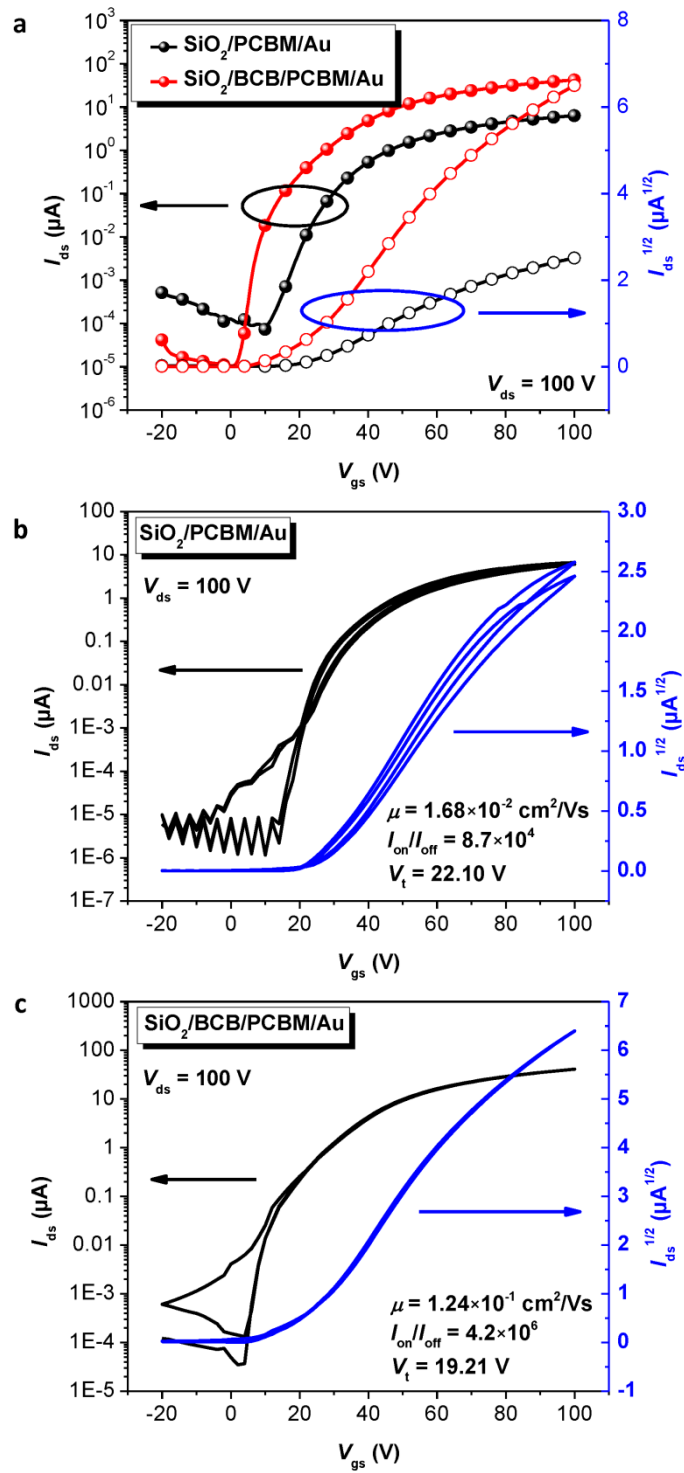


Figure S2. Comparison of the transfer ($V_{ds} = 100$ V) and hysteresis characteristics with/without the hydroxyl-free BCB interlayer for PCBM OTFTs in a N_2 -filled glovebox.

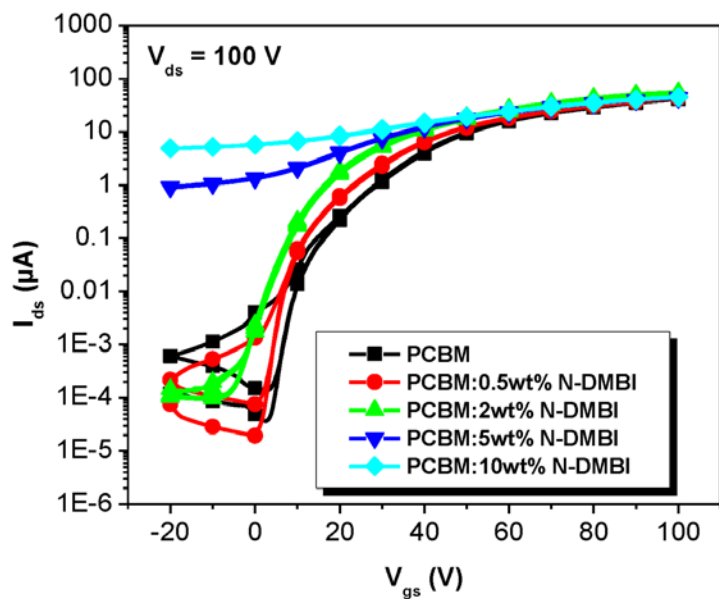


Figure S3. Hysteresis characteristics of the undoped and N-DMBI doped PCBM transistors at different doping concentrations in a N₂-filled glovebox.

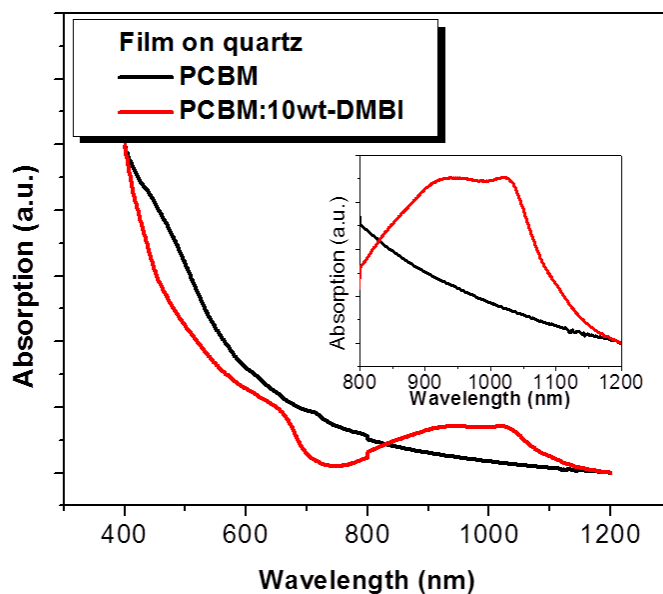


Figure S4. Vis/NIR absorption spectra of the thin films of undoped PCBM and 10wt% N-DMBI doped PCBM measured in ambient condition within 5 min exposure to air from a N₂-filled glovebox. The inset shows the comparison of NIR absorption spectra with undoped PCBM and 10wt% N-DMBI doped PCBM films.

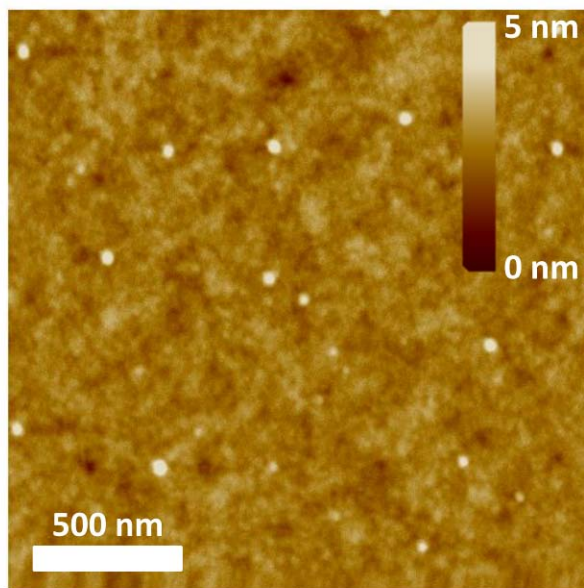


Figure S5. AFM image of 0.5wt% N-DMBI doped PCBM film.

Table S1. OTFT electrical properties for undoped, N-DMBI and TMBI doped PCBM transistors at different doping concentrations measured in the N₂-filled glovebox. The calculated mobilities at high doping concentrations (5wt% and 10wt% N-DMBI doping) are lower as the devices are almost completely conductive and the on-off ratios are lower than 100.

	Glovebox		
	μ^a (cm ² /Vs)	I_{on}/I_{off}	V_t (V)
PCBM	1.25×10^{-1}	4.67×10^6	19.10
PCBM:0.5wt%N-DMBI	1.18×10^{-1}	2.73×10^6	13.73
PCBM:2wt%N-DMBI	1.02×10^{-1}	4.77×10^5	6.43
PCBM:5wt%N-DMBI	6.47×10^{-2}	4.33×10^1	-15.60
PCBM:10wt%N-DMBI	3.82×10^{-2}	9.20×10^0	-23.38
PCBM:0.5wt%TMBI	1.07×10^{-1}	3.30×10^6	18.31

PCBM:2wt% TMBI	1.22×10^{-1}	5.27×10^6	26.76
PCBM:5wt% TMBI	1.04×10^{-1}	4.80×10^6	22.57
PCBM:10wt% TMBI	0.81×10^{-1}	4.01×10^6	19.94

a, All the data are the average of at least 3 devices.

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