N-type doping in organic semiconductor thin films by using a dendritic oligoarylamine-substituted benzimidazole dopant

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Organic n-type doping with donor dopants has not been established well because of air instability of conventional donor dopants. With this background, we have focused on imidazole-based compounds as solution-processable and pure organic n-type dopants. These compounds are known as strong single-electron reductants. However, these dopants are quickly oxidized in solution phase in ambient condition. In this work, we report an approach for increasing the stability of benzimidazole dopant molecule in solution phase by attachment dendritic oligoarylamine (N,N-bis[4-(di-4-anisyl-amino) phenyl]amine) at the 2-position of the imidazole ring (N3-DMBI-H shown in Fig. 1)[1].

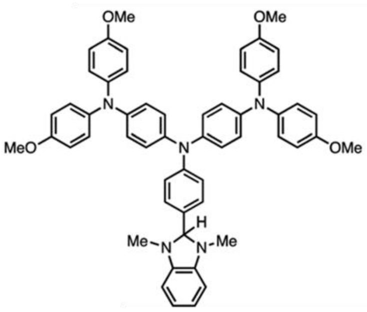

Figure 1. Molecular structure of N3-DMBI-H.

N3-DMBI-H was newly synthesized by ourselves. N3-DMBI-H solution in chlorobenzene (CB) revealed much better stability in ambient air than solutions of other benzimidazole dopants. [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) solution (in CB) was dropcast onto Si substrates covered with 200 nm-thick SiO_2 layer. Doping concentrations of N3-DMBI-H were 0, 0.5, 2 and 5 wt%. After that, the dropcast films were dried and heated at 100°C overnight to activate the dopants. The above processes were performed in a N_2-filled glovebox. After Au electrodes (thickness: 25 nm) were deposited onto the PCBM film surfaces by vacuum evaporation, we measured two-terminal current-voltage (I-V) characteristics of PCBM films under a vacuum condition (10^{-2} Pa).

Figure 2 shows two-terminal I-V characteristics of undoped and N3-DMBI-H doped PCBM films. The gap distance between the two contact electrodes was 50 µm. As shown in Fig. 2, doping N3-DMBI-H into PCBM increased the current value by more than five orders of magnitude. The electrical conductivity of the N3-DMBI-H-doped PCBM thin film was reported to be 6.39×10^{-4} cm^{-1}(undoped PCBM: 6.62×10^{-9} S cm^{-1}). This result suggests that the electric resistance of PCBM thin films considerably decreased by N3-DMBI-H doping, due to carrier (electron) doping effects.

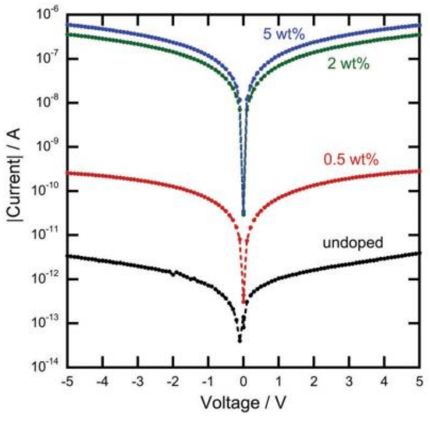

Figure 2. I-V characteristics of undoped and N3-DMBI-H doped PCBM thin films.

[1] M. Uebe, Y. Yoshihashi, K. Noda, M. Matsubara, A. Ito, *J. Mater. Chem. C* 2018, **6**, 6429-6439

Supplementary information:

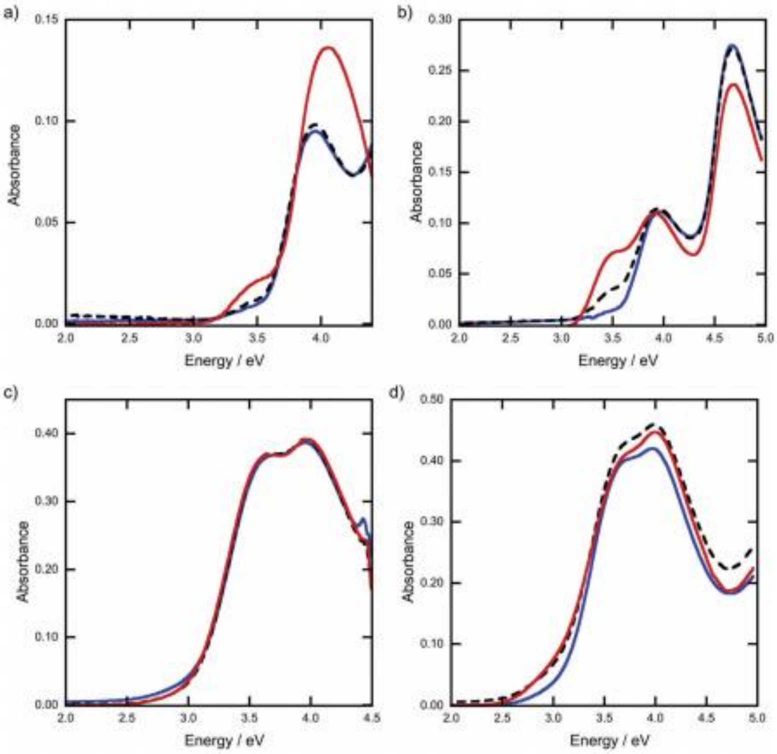

Figure S1. Change of absorption spectra of **N-DMBI-H** in (a) chlorobenzene (1 × 10^{-4} M)[as-prepared solution (blue line); after 1 day (broken line); after 4 days (red line)] and (b) CH_2Cl_2 (1 ×10^{-4} M) [as-prepared solution (blue line); after 1 day (broken line); after 4 days (red line)], and of **N3-DMBI-H** in (c)chlorobenzene (1 ×10^{-4} M) [as-prepared solution (blue line); after 1 day (broken line); after 4 days (red line)] and (d) CH_2Cl_2 (1 × 10^{-4} M) [as-prepared solution (blue line); after 1 day (broken line); after 4 days (red line)], at room temperature under ambient light and air.

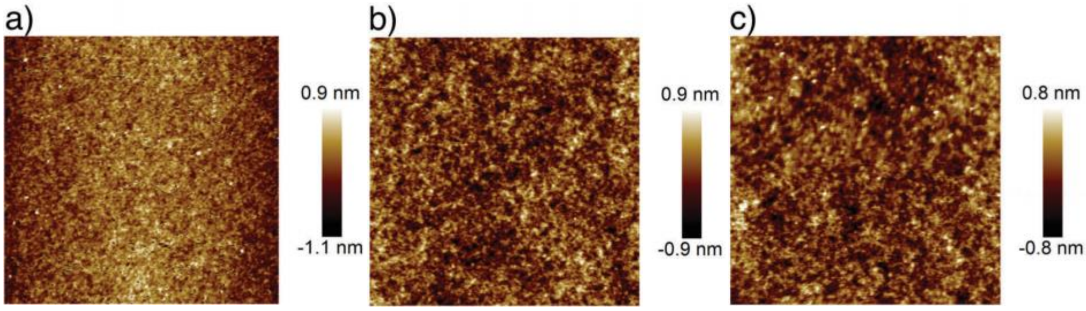

Figure S2. AFM images of (a) undoped, (b) 2 wt% N3-DMBI-H-doped and (c) 5wt% N3-DMBI-H-doped PCBM thin films (scan area: 3 μm × 3 μm). Typical root-mean-square surface roughness for the three samples were estimated to be 0.28, 0.25, and 0.23 nm, respectively.