

## Supporting Information

### **Molecular Doping of Organic Near-Infrared Photodetectors for Photoplethysmogram Sensors**

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## Experimental Section

### *Materials*

PC<sub>61</sub>BM and PMDPP3T were purchased from Solenne BV Corporation and Luminescence Technology Corp., respectively. Zinc acetate dehydrate was purchased from Wako Pure Chemical Industries. BCF and N-DMBI was purchased from Sigma. BV was synthesized by following previous procedures.<sup>1</sup>

### *Fabrication of OPDs*

The ITO glass substrates were first treated with oxygen plasma (10 s at 300 W), then a 20 nm-thick ZnO layer was formed by spin-coating (5,000 rpm. for 30 s). A ZnO precursor solution was prepared by dissolving zinc acetate dehydrate (0.5 g) and ethanolamine (0.16 ml) in 2-methoxyethanol (5 ml). The substrate was annealed in air at 180 °C for 30 min. The active layer was obtained from a PMDPP3T and PC<sub>61</sub>BM solution with a weight ratio of 1:3 in mixed solvent (chloroform and o-dichlorobenzene with a volume ratio of 4:1) to yield a total of 20 mg mL<sup>-1</sup>. The solution was deposited by spin-coating at 400 rpm for 4 min to form the thicker active layer (~280 nm). Finally, 10 nm-thick MoOx and 80 nm-thick Ag was deposited as the top electrode.

### *Characterization*

*Electrical test.* OPDs with an area of 4 mm<sup>2</sup> was used for electrical characterization by using a semiconductor device analyzer (B1500A, Agilent Technology) or a Keithley 2400 source measure unit. The NIR LED with a wavelength of 850 nm and a calibrated intensity of 2.64 mW cm<sup>-2</sup> was purchased from Nissan Electronics (Japan) with EQE values under varying voltages were measured using a Hyper Monolight SM-250 system (Bunkoh-Keiki, Japan). The light intensity was modulated using a series of neutral density filters (Newport Optics). The response time and recovery time were measured by device current waveform analyzer (Keysight Technologies, CX3324A), no bias was applied on the OPD devices during test. Long-term storage test was conducted by repeatedly measuring the identical devices in air after storing in glovebox or in air for certain time.

*Pulse wave test.* The finger was directly attached to OPD devices and NIR LEDs (IRTD-HS1512, Nissan Electronics) with a wavelength of 850 nm were placed just above the other side of the finger. The light intensity of the LEDs was 30 mW cm<sup>-2</sup>.

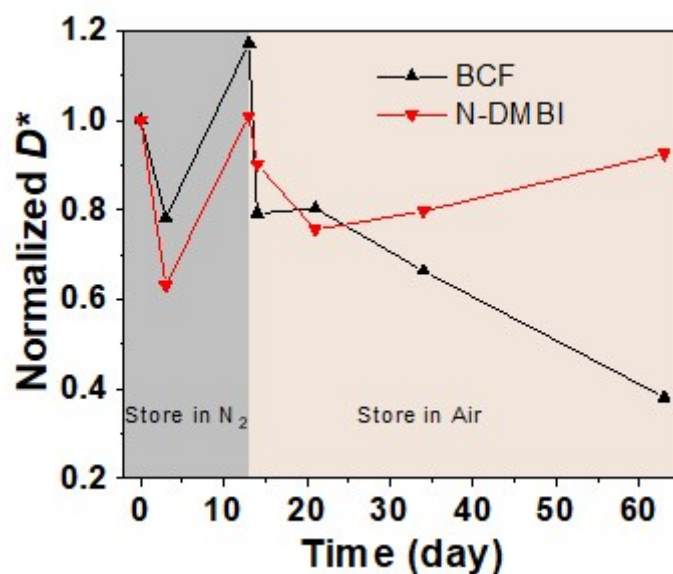


Fig. S1. The  $D^*$  stability of OPDs with 0.02 wt% BCF and N-DMBI dopants in  $N_2$  and air atmosphere.

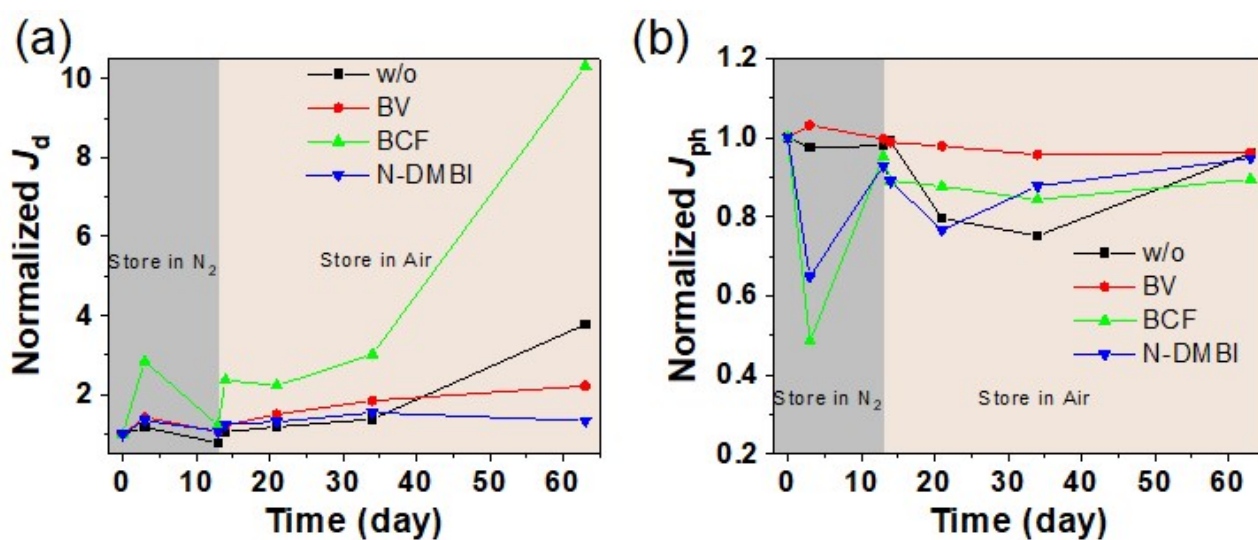


Fig. S2. The (a)  $J_d$  and (b)  $J_{ph}$  stability of OPDs without and with 0.02 wt% dopants in  $N_2$  and air atmosphere.

## Reference

1. Y. Lin, Y. Firdaus, M. I. Nugraha, F. Liu, S. Karuthedath, A. H. Emwas, W. Zhang, A. Seitkhan, M. Neophytou, H. Faber, E. Yengel, I. McCulloch, L. Tsetseris, F. Laquai and T. D. Anthopoulos, *Adv. Sci.*, 2020, **7**, 1903419.