[Supporting Information]

Solution-Processable All-Small Molecular Bulk Heterojunction Films for Stable Organic Photodetectors: Near UV and Visible Light Sensing

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This supporting information contains following data:

- 1. Optical absorption spectrum of chlorobenzene (solvent).
- 2. Optical absorption spectrum of EHTPPD-MT in chlorobenzene for checking the absorption edge.
- 3. Optical absorption spectrum of the $PC_{61}BM$ film.
- 4. Fast photoresponse of the OPDI with the EHTPPD-MT: $PC_{61}BM$ (1:2) layer under quick on/off modulation of the high intensity green light.
- 5. Analysis of 2D GIXD image for the pristine EHTPPD-MT film.
- 6. Assignment of carbon atoms in the EHTPPD-MT molecule for ¹³C-NMR spectrum analysis.



Figure S1. Optical absorption spectrum of chlorobenzene used as a solvent for the optical absorption measurement of EHTPPD-MT in Figure 1b.



Figure S2. Optical absorption spectrum of EHTPPD-MT in solution (solvent: CB (chlorobenzene)): The absorption edge is measured as 780 nm (1.6 eV) from the onset point given with the green guidelines.



Figure S3. Optical absorption spectrum of the $PC_{61}BM$ film. As shown in Figure 1b and Figure 2c, the strong absorption of the BHJ layers at the wavelength of <400 nm can be attributed to the contribution of $PC_{61}BM$ in the presence of relatively small EHTPPD-MT absorption (300~470 nm).



Figure S4. Fast photoresponse of the OPDI with the EHTPPD-MT:PC₆₁BM (1:2) layer under quick on/off modulation of the high intensity green light (532 nm, $P_{IN} = 133.4 \text{ mW/cm}^2$). The rise and decay response was much faster than those in Figure 6, even though the applied voltage was increased. Note that there was still a limit in quick data acquisition because the electrometer (Keithley 2400) used in this work could read only 7~8 current values per second.



Figure S5. (a) 2D GIXD image for the pristine EHTPPD-MT film coated on the ITO-glass substrate. (b) The simulation result using the original 2D GIXD image in (a) by employing a software (Anaelu 1.0) [D. W. Breiby, O. Bunk, J. W. Andreasen, H. T. Lemke, M. M. Nielsen, *J. Appl. Cryst.*, 2008, 41, 262]. (c) Illustration of crystal structures and parameters on the basis of the simulated result in (c). (d) Possible alignment of EHTPPD-MT molecules in the viewing direction normal to the (*a,c*) plane. We note that the present analysis refers to following two references: (1) A. K. Palai, J. Lee, T. J. Shin, A. Kumar, S. –U. Park, and S. Pyo, *Chem. Commun.*, 2014, 50, 8845; (2) V. S. Gevaerts, E. V. Herzig, M. Kirkus, K. H. Hendriks, M. M. Wienk, J. Perlich, P. Müller-Buschbaum, R. A. J. Janssen, *Chem. Mater.*, 2014, 26, 916.



Figure S6. Assignment of carbon atoms in the EHTPPD-MT molecule in order to confirm the molecular structure using ¹³C-NMR spectroscopy. The chemical shift (ppm) for each carbon atoms measured are given in the experimental section.