Supplementary Materials for

Electron doping of a crystalline conjugated polymer through cation exchange

Yu Yamashita, Shinya Kohno, Elena Longhi, Samik Jhulki, Shohei Kumagai, Stephen Barlow, Seth R. Marder, Jun Takeya, and Shun Watanabe

Correspondence and requests for materials should be addressed to YAMASHITA.Yu@nims.go.jp (Y.Y.) and swatanabe@edu.k.u-tokyo.ac.jp (S.W.).

1. Materials and doping methods

The polymeric semiconductor poly[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5'-(2,2'-bithiophene) (P(NDI2OD-T2)) is a widely studied n-type organic semiconductor (OSC). P(NDI2OD-T2) was purchased from Ossila with following indices, Mw:202,261, Mn:90,982, and PDI:2.22. *o*-Dichlorobenzene (*o*DCB) was purchased from Fujifilm Wako and used as a solvent for P(NDI2OD-T2). $CoCp_2$ as a reducind agent was purchased from Sigma-Aldrich. Salt compounds of tetrabutylammonium hexafluorophosphate (TBA-PF_6), tetraphenylphosphonium chloride(TPP-Cl), 1,3-dimesitylimidazolium chloride (DMIM-Cl) were purchased from Tokyo Chemical Industry. A salt compound of Tetrabutylammonium bis(trifluoromethanesulfonylimide) (TBA-TFSI) was purchased from Sigma-Aldrich. Redox agents of $(RuCp^*Mes)_2$ and N-$DMIM_2$ were synthesized following the reported procedures[1].

Low-impurity EAGLE XG glass substrates were employed for UV-Vis absorption measurements. EAGLE XG glass substrates with patterned Cr/Au electrodes were employed for electrical measurements. EAGLE XG glass or Si substrates with naturally oxidised layers were employed for the X-ray scattering measurements. EAGLE XG glass substrates covered with Cr/Au electrodes were employed for XPS and PYS measurements. P(NDI2OD-T2) thin films were deposited via spin-coating in a glove box. 1 wt% P(NDI2OD-T2) solution in *o*-DCB and substrates were heated at 100°C before the spin-coating. The coating condition was 2000 rpm for 60 s. After drying the thin films at 100°C, the films were further baked at 180°C for 30 min, followed by slow cooling down. The film thicknesses were determined to be 70 ± 5 nm by a Dektak surface profilometer.

The P(NDI2OD-T2) thin films were doped by immersing the thin films into dopant solutions for 5 min at in an N_2-purged glove box. For $CoCp_2$ and cation exchange doping,

acetonitrile was employed as the solvent. Concentrations of $CoCp_2$ was 2.5 mM and that of salt compounds was 12.5 mM. Solution was heated at 45°C during the doping process. After the doping process, the doping solution was cooled down to room temperature before bringing the sample out from the solution. After bringing the the sample out from the doping solution, the sample was heated at 60°C for 5 min. For doping with $(RuCp^*Mes)_2$ and $(N\text{-}DMBI)_2$, *n*-butylacetate was employed as the solvent for doping solution. Concentrations of dopants were 2 mM. Doping process is the same as cation exchange doping except that the solution was heated at 60°C during the doping process, and the sample was baked at 80°C after the doping process.

2. X-ray scattering images.

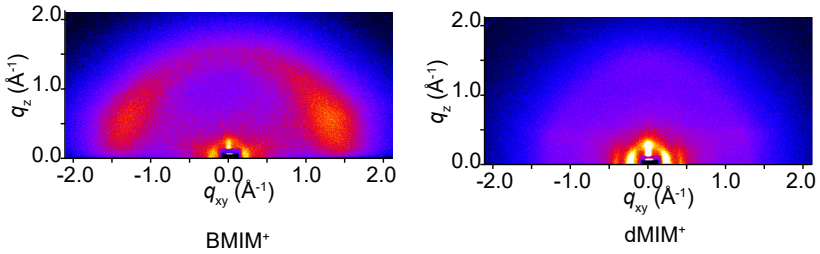

Figure S1: X-ray scattering images of doped P(NDI2OD-T2) with imidazolium-based cations. 1-butyl-3-methylimidazolium ($BMIM^+$, left) and 1,3-dimethylimidazolium ($dMIM^+$, right) salts with chloride anion were employed in cation exchange doping.

3. Supplementary References

[1] Un, H.-I. *et al.* Understanding the effects of molecular dopant on n-type organic thermoelectric properties. *Advanced Energy Materials* **9**, 1900817 (2019).