

## Supplementary materials

# **Elucidating the Doping Mechanism in fluorene-dithiophene based hole selective layer employing ultra-hydrophobic Ionic Liquid Dopant**

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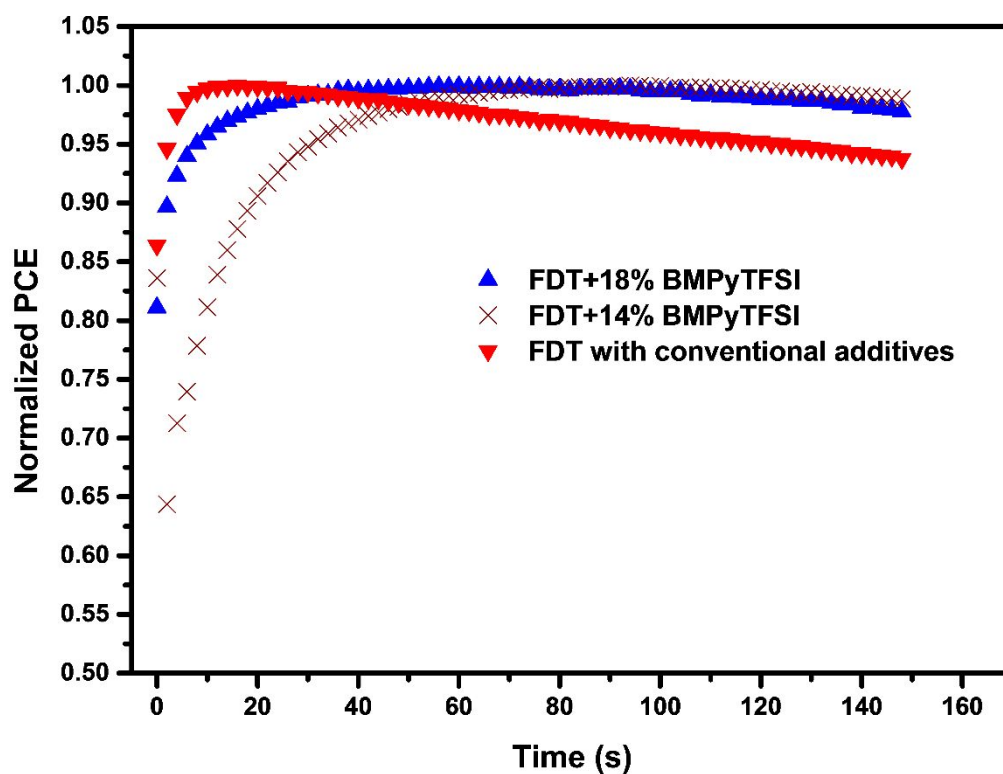


Fig.S1: Maximum power tracking for power conversion efficiency of conventional doped FDT and with 14 and 18 mol % BMPyTFSI.

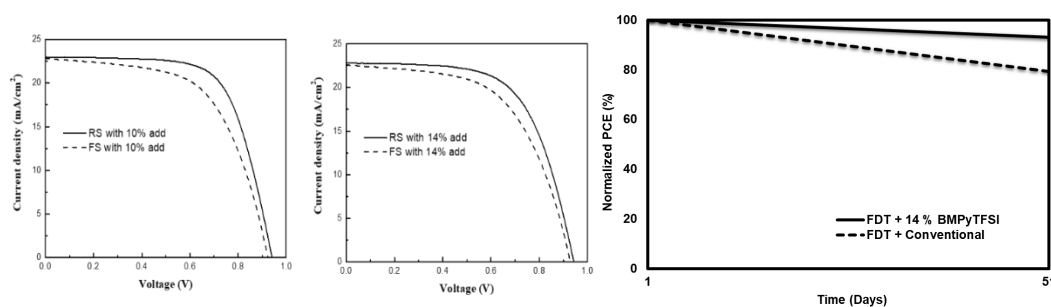


Fig.S2: Forward and reverse  $J$ - $V$  scan of FDT with 10 and 14 mol% BMPyTFSI, and environmental stability of un-encapsulated devices fabricated with conventional doped FDT and with 14 mol % BMPyTFSI in 50% RH.

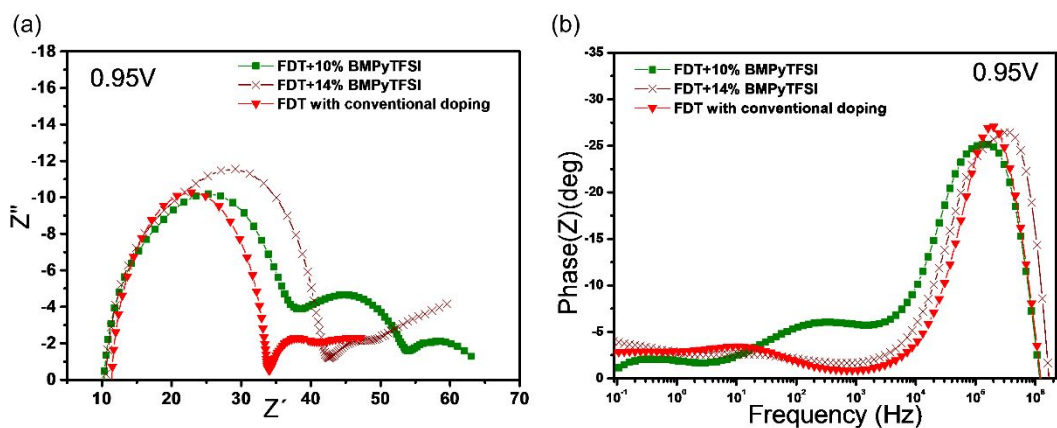


Fig.S3: a) Nyquist and b) Bode plot of samples using different concentration of FDT-BMP HTL and both references FDT and Spiro-OMeTAD respectively at open circuit voltage conditions.

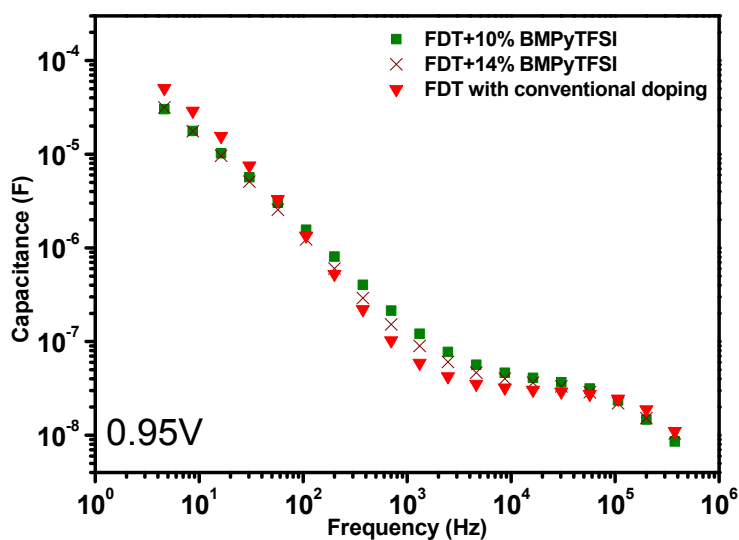


Fig.S4: Capacitance vs frequency at open circuit condition of samples using different concentration of FDT-BMP HTL and both references FDT and Spiro-OMeTAD respectively.

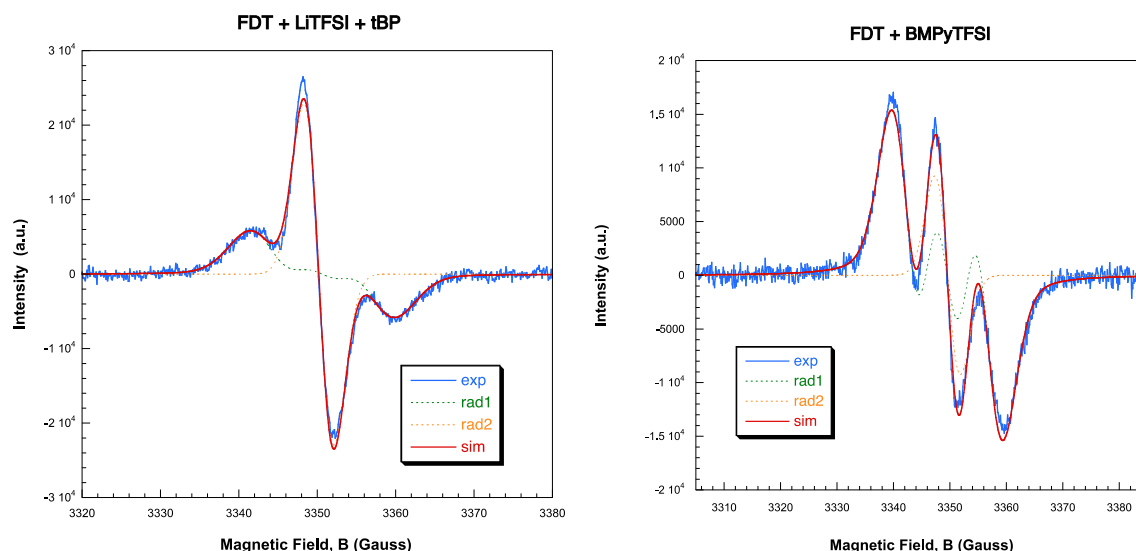


Fig.S5: Optimized simulations of the X-band EPR spectra of FDT+BMPyTFSI and FDT+LiTFSI+t-BP samples. The fitting parameters are compiled in Table 2 (main text).

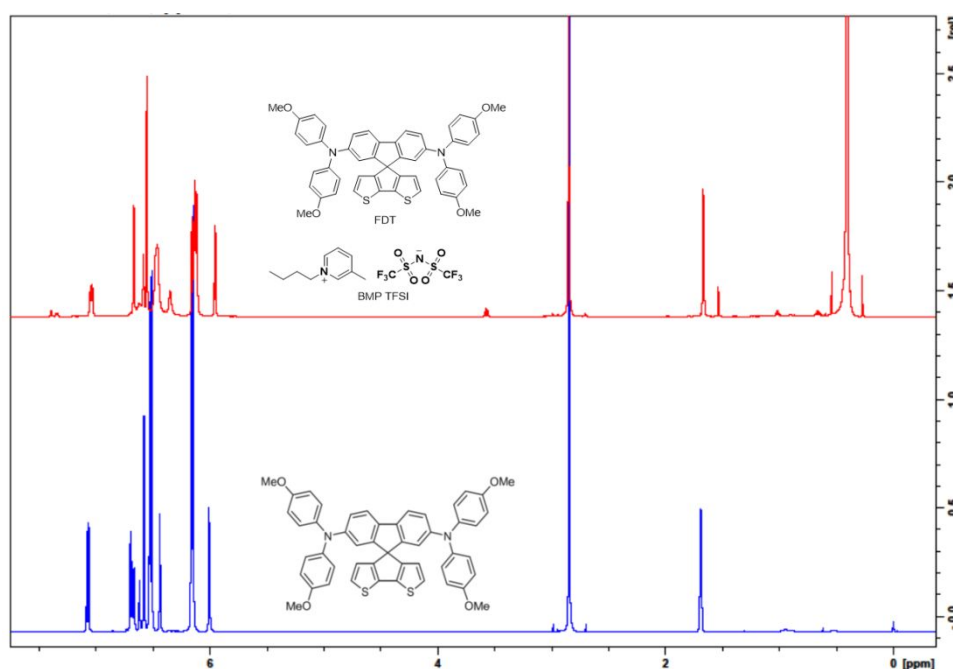


Fig.S6:  $^1\text{H}$ -NMR spectra of FDT and BMPyTFSI doped FDT.

The NMR spectra of FDT is well defined. It has 38 protons, each kind of similar protons showing integral values and peaks at different position respectively. When it is doped with BMPyTFSI change in the NMR spectra of FDT was noted. We can see generation of new peaks (0.9ppm –triplet, 1.06 and 1.4 –multiplet, 4.0- triplet 7.7- a singlet, 7.75- a doublet) and spectral changes in few of them. The other peaks corresponds to the peaks of FDT parent molecule. The peak at 6.89 becomes broader.

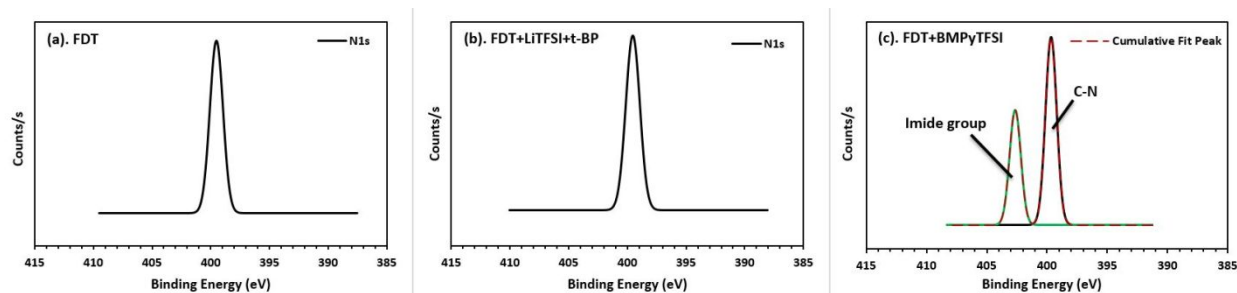


Fig.S7: High resolution XPS of N1s. (a). FDT, (b) FDT+LiTFSI+t-BP and (c) FDT+BMPyTFSI.

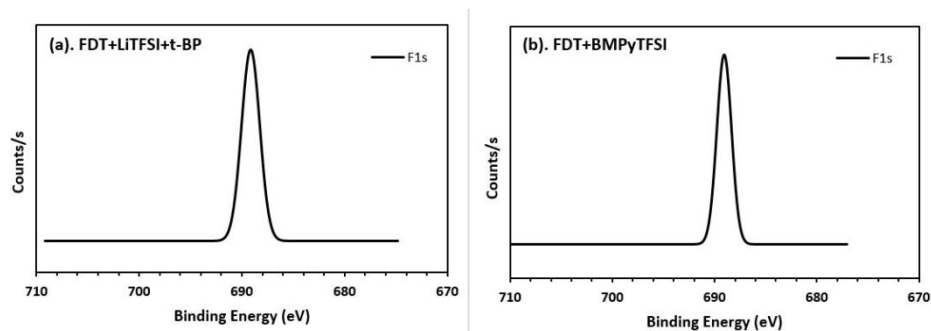


Fig.S8: High resolution XPS of S2p. (a) FDT+LiTFSI+t-BP and (b) FDT+BMPyTFSI.