

## **ELECTRONIC SUPPLEMENTARY INFORMATION**

### **Donor-acceptor interface modification by zwitterionic conjugated polyelectrolytes in polymer photovoltaics**

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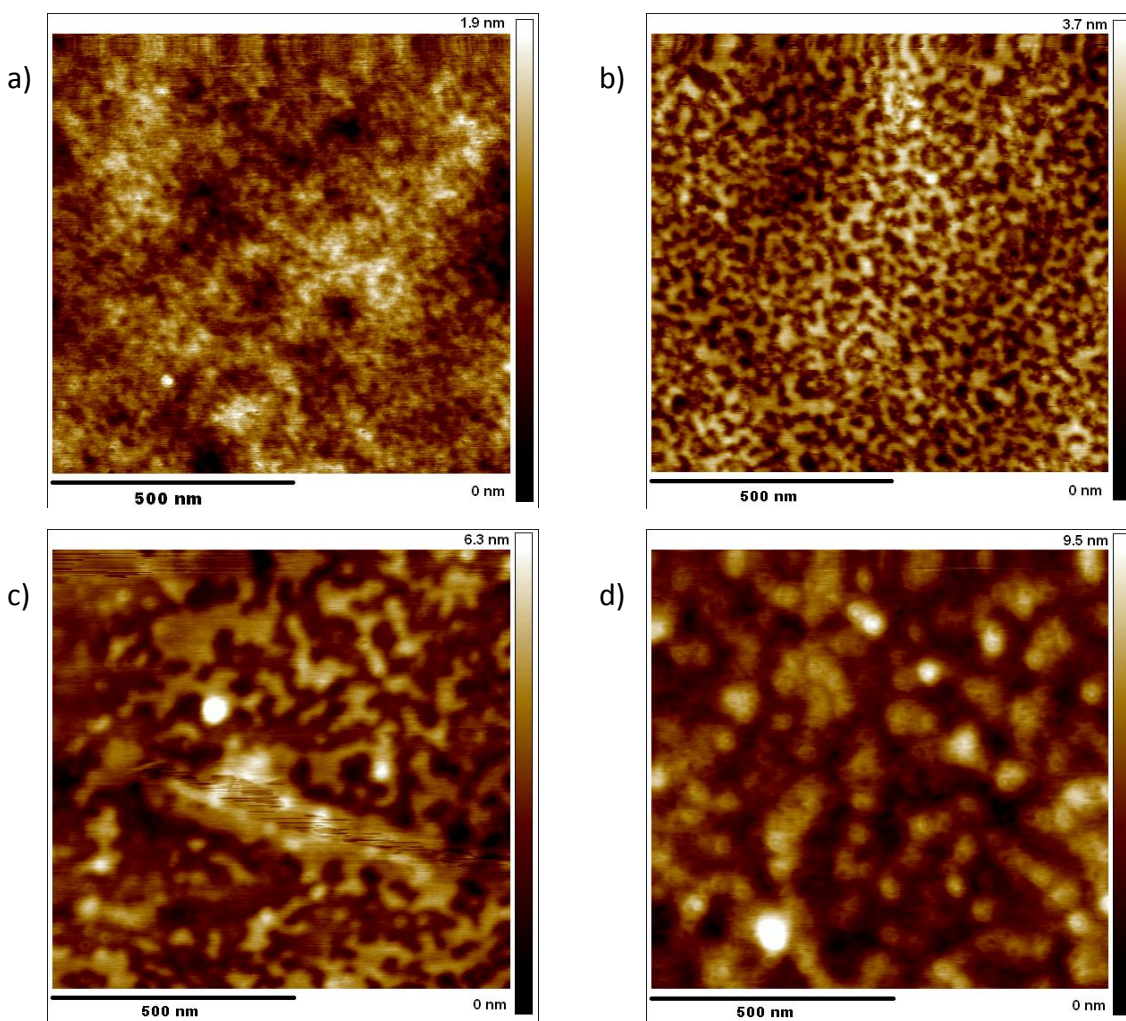
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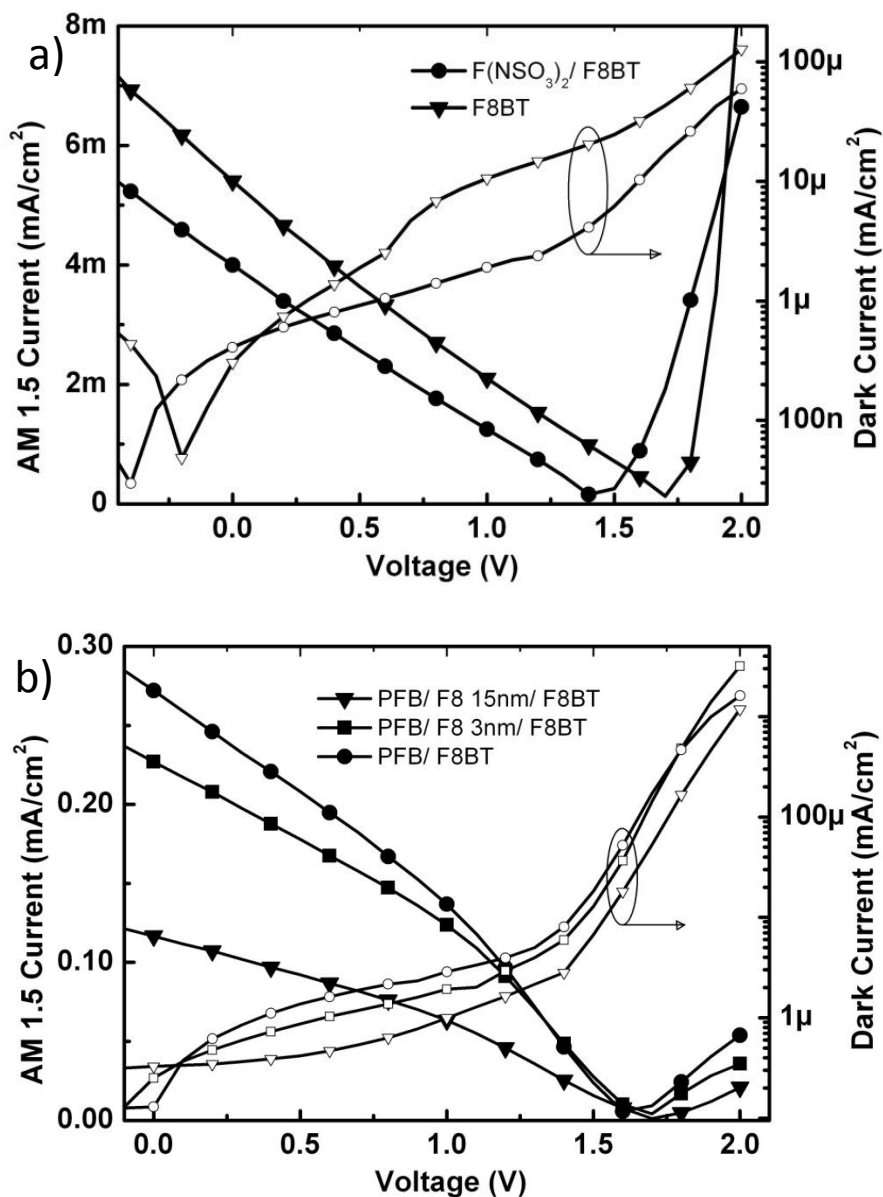
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The morphology of the F(NSO<sub>3</sub>)<sub>2</sub> layer on top of the crosslinked PFB was investigated with Atomic Force Microscopy. In Figure S1 we present: a) bare crosslinked PFB; b) a 2nm layer of F(NSO<sub>3</sub>)<sub>2</sub> spun on top of PFB; c) 5nm thick F(NSO<sub>3</sub>)<sub>2</sub> spun on top of PFB, and d) a 14nm thick F(NSO<sub>3</sub>)<sub>2</sub> spun on top of PFB (the processing conditions for the PFB and F(NSO<sub>3</sub>)<sub>2</sub> were kept as described in the main text for the device structures). The bare PFB layer is quite smooth as expected, the roughness (Ra, arithmetic average of the absolute values of the surface height deviations measured from the mean plane) for the film was 0.2 nm. Figure S1-b shows a discontinuous layer with uniformly distributed 2nm thick islands. This is likely to be a self-assembled monolayer of F(NSO<sub>3</sub>)<sub>2</sub> as expected from the amphiphilic nature of the zwitterionic polymer. The darker areas in the picture are associated to regions of bare PFB, showing the possibility for the F8BT top layer to access this interface in the final device structure. At higher concentration, multilayer structures start forming providing an increase of the average thickness to ~5nm, however is still possible to find few areas of uncovered PFB. At even higher F(NSO<sub>3</sub>)<sub>2</sub>

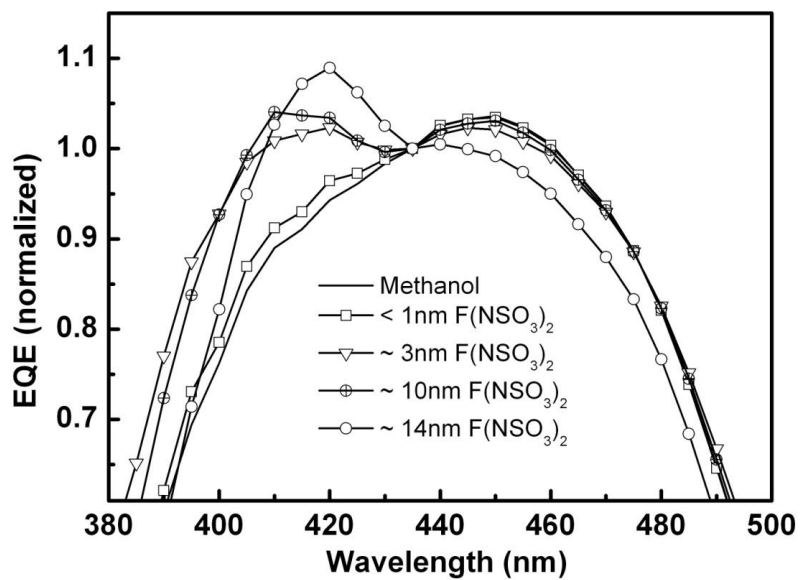
solution concentrations, a more uniform thin film is formed (~14nm thick) and the underlying PFB layer cannot be accessed by the scanning tip.



SI Figure 1. AFM scan of the (a) bare PFB film, (b) ~2nm F(NSO<sub>3</sub>)<sub>2</sub>, (c) ~5nm F(NSO<sub>3</sub>)<sub>2</sub>, and (d) ~14nm F(NSO<sub>3</sub>)<sub>2</sub> layer on top of PFB layer respectively.

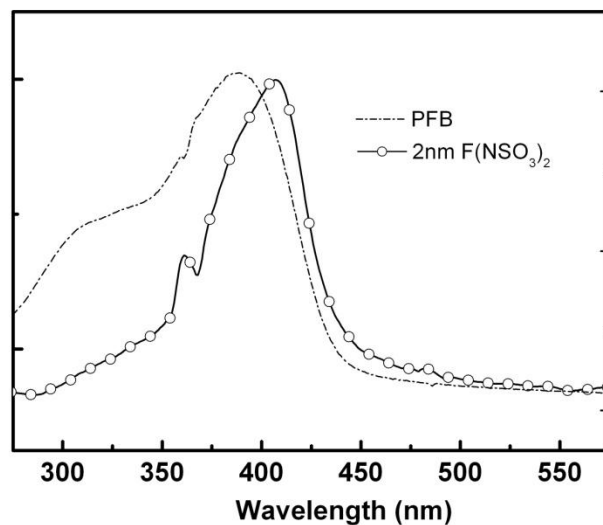


SI Figure 2. (a) J-V characteristics of bilayer F8BT and F(NSO<sub>3</sub>)<sub>2</sub>/F8BT devices under AM1.5 illumination and in dark. (b) J-V characteristics of the PFB/F8BT, PFB/F8-3nm/F8BT, and PFB/F8-15nm/F8BT devices under AM1.5 illumination and in dark.

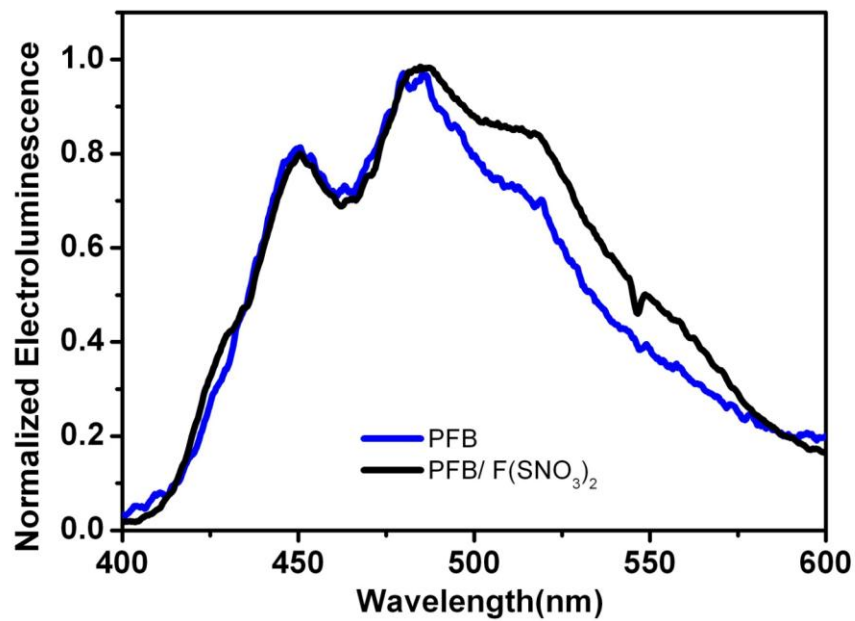


SI Figure 3. Normalized EQE spectra of PFB/F8BT devices treated with methanol, and with increasing concentrations of  $\text{F(NSO}_3)_2$ . The spectra were normalized at 435nm. The  $\text{F(NSO}_3)_2$  thickness was estimated from its optical absorption.

The UV-VIS absorption of the 2nm thick layer of  $F(NSO_3)_2$  (on top of 40nm thick PFB layer) were measured. The absorption profile is plotted in figure SI 4. The PFB absorption was set as background to measure the  $F(NSO_3)_2$  absorption. The disappearance of PFB peak at 388nm and emergence of peak at 400nm confirms the presence of  $F(NSO_3)_2$  on top of PFB.



SI Figure 4. The figure plots the absorption spectra of 2nm  $F(NSO_3)_2$  on top of PFB. The absorption spectra of PFB plotted at background for spectral comparison.



SI Figure 5. Electroluminescence spectrum of PFB and PFB/F(NSO<sub>3</sub>)<sub>2</sub> devices.

Material	Dielectric constant $\epsilon_r$
F8	3.23
F(NSO <sub>3</sub> ) <sub>2</sub>	49.38

SI Figure 6. Table showing the measured dielectric constant of F(NSO<sub>3</sub>)<sub>2</sub> and F8 (the polymer with same backbone but no zwitterionic side chain).

Capacitance measurements were done on Al/ F(NSO<sub>3</sub>)<sub>2</sub>/Al and Al/F8/Al parallel plate capacitor devices using a Hewlett Packard Impedance Analyzer. The thickness of the F(NSO<sub>3</sub>)<sub>2</sub> film was 80nm and of the F8 film was 160nm. The dielectric constant was calculated using formula  $\epsilon_r = (C.d)/(\epsilon_0.A)$ , where  $C$  is the capacitance measured by impedance spectroscopy at 1.1 kHz,  $d$  is the thickness of the polymer film measured by AFM,  $A$  is the surface area of the Al electrode, and  $\epsilon_0$  is the dielectric constant of free space. The differential capacitance was found to be independent of d.c. bias voltage.