## **Supporting Information**

## The role of emissive charge transfer states in two polymer/fullerene organic photovoltaic blends: tuning charge photogeneration through the use of processing additives

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**Figure S1.** Summary of device data for PCPDTTTz:PCBM and PDTSiTTZ:PCBM, showing average efficiency, FF, J<sub>sc</sub> and V<sub>oc</sub> over several devices of differing optical density (OD).



Figure S2. Transient absorption spectra of PCPDTTTz:PCBM belnd films measured with and without DIO.



**Figure S3.** The photoluminescence decays in the 670-700 nm spectral range for pristine PDTSiTTz and PCPDTTTz films as compared to solutions in o-dichlorobenzene (a). The photoluminescence decays with time for pristine PDTSiTTz and PCPDTTTz (on encapsulated quartz) measured in the spectral range at the emission maximum of 670 – 700 nm, compared to PCPDTBT and Si-PCPDTBT (on encapsulated glass) (b).



**Figure S4.** The photoluminescence decays with time for pristine PCPDTTTz and blends with PCBM, varying the weight percentage of PCBM and measuring in the spectral range of 1000-1100 nm (c).



Figure S5. Steady-state absorption spectra of pristine PCPDTTTz and PDTSiTTZ solutions (o-DCB) and thin films.