Supporting Information for:

Effects of Surface Passivation on Trap States, Band Bending, and Photoinduced Charge Transfer in P3HT-TiO₂ Hybrid Inverse Opals

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SUPPORTING FIGURES



Figure S1. XRD patterns for non-passivated (black) and 0.05 M TiCl4 (red) treated inverse opal powders produced by co-assembly. Miller indices corresponding to anatase are noted above each diffraction peak. Approximately 20 films of each condition were scraped off the glass substrate and the powders were redeposited on low-background substrate.



Figure S2. Tauc plot of the absorption coefficient of TiO₂ as a function of photon energy for TiO₂ inverse opals treated with various concentrations of TiCl₄. The energy of the TiO₂ bandgap is extrapolated from the x-intercept of the tangent line (dashed grey).



Figure S3. Reflectance spectra of TiO₂ inverse opals treated with 0 M (a), 0.025 M (b), 0.05 M (c) and 0.05 M twice (d) TiCl4. Experimental total reflectance spectra are shown in black, and simulated specular reflectance spectra obtained from scalar-wave approximation using both real (n) and imaginary (k) refractive indices of TiO₂ are shown in blue, compared to simulated spectra using only the real refractive index of TiO₂ shown in red. Simulated spectra are scaled for clarity. Strong absorption (incorporating k) suppresses photonic stop band reflection, however the refractive indices of nanocrystalline TiO₂ could deviate from bulk values. The weak reflectivity centered at ~260 – 295 nm (λ_{sb}) for the different samples can be modelled by excluding the absorption effects (using only n). The red shift and increase in the intensity of the stop band correlate with increasing amount of TiO₂. The composition of the framework (26 vol% of the fcc structure) for each sample is shown. Overall the total vol% of TiO₂ increases from 12 % (i.e. 47 % x 26 %) for unpassivated inverse opal to 18 % (i.e. 69 % x 26 %) for 0.05 M twice-passivated inverse opal.



Figure S4. Analytical fitting of the absorbance spectra of P3HT/TiO₂ with different TiCl₄ treatments: 0 M (a), 0.025 M (b), 0.05 M (c) and 0.05 M twice (d). Fits to the equation:

$$A \propto \sum_{m=0} \left(\frac{e^{-S}S^m}{m!}\right) \left(1 - \frac{We^{-S}}{2E_p} \sum_{n \ (\neq m)} \frac{S^n}{n!(n-m)}\right)^2 \times exp\left(-\frac{(E-E_{0-0}-mE_p)}{2\sigma^2}\right), \text{ where } m \text{ is the } m \text{ is } m \text{ is$$

vibrational level, *n* is the vibrational quantum number, *S* is the Huang-Rhys factor (1), *Ep* is the intermolecular vibrational energy (0.179 eV for C=C symmetric stretch), $E_{0.0}$ is the 0-0 transition energy, *W* is the exciton bandwidth, and σ is the Gaussian linewidth are shown in red. The last three parameters and a proportionality constant are the fitting variables. The spectra were fitted in the range of 1.9 to 2.25 eV to obtain the aggregate spectra (red), which were subtracted from the experimental data (black) to give the amorphous spectra (grey). The fitted values are shown in Table S1; small differences are found, where an increase in disorder and fraction of unaggregated P3HT are observed with increasing TiCl4 treatment.



Figure S5. UPS spectrum of neat P3HT: (a) secondary cut off region, and (b) HOMO region. The ionization potential of P3HT was determined to be (21.22 eV - (17.30 eV - 0.68 eV)) = 4.60 eV.

SUPPORTING TABLE

TiCl₄ (M)	E ₀₋₀ (eV)	W (eV)	Ep (eV)	σ	% aggregated
0	2.045	0.0902	0.179	0.0793	51.7
0.025	2.055	0.0850	0.179	0.0810	51.3
0.05	2.060	0.0860	0.179	0.0802	49.9
0.05x2	2.060	0.0855	0.179	0.0825	48.0

Table S1. Summary of the fitted parameters of data shown in Figure S4.