Experimental Procedures:

Materials synthesis and instrumentation. High aspect ratio anatase TiO_2 nanorods were synthesized by hydrolyzing titanium tetraisopropoxide according to our previous study[1]. Oleic acid (OA, 120 g) was vigorously stirred at 120◦C for one hour in a three-neck flask under Ar flow to remove moisture. The reactant was then cooled to 98◦C and titanium tetraisopropoxide (17 mmol, Aldrich, 99.999%), as the precursor, was added into the flask and stirred for 5 min to mix with the oleic acid. Trimethylamine-N-oxide dihydrate (34 mmol, Acros, 98%) in 17 ml of water was rapidly injected into the flask to catalyze the polycondensation reaction. This reaction was continued for 9 h to complete the hydrolysis and crystallization. Subsequently, the TiO_2 nanorods were obtained. The TiO_2 nanorods were purified through several cycles of washing and precipitation using methanol to remove any unreacted oleic acid or impurities. P3HT was synthesized by Industrial Technology Research Institute (ITRI, Taiwan) with a molecular weight of 61881 g mol-1 (Mw), polydispersity index (PDI) of 1.48 and a regioregularity (RR) of 97.2%. Tris(perfluorophenyl)borane ($B(C_6F_5)_3$, BCF) was purchased from Aldrich and used as received. 2,6- (2,3,5,6- ditetrafluorobenzonitrile)- 4,4'- dihexyl- 4H- cyclopenta [2,1-b:3,4-b'] dithiophene (FBN-CPDT) was synthesized by Stille cross-coupling reaction in a similar fashion according to our previously reported compounds[2,3]. UV-visible absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV-visible absorption spectroscopy. The film thickness was determined by an alpha-stepper (Veeco, Dektak 6M 24383). The cross-section areas of the hybrid films were observed by a scanning electron microscopy (SEM, FEI, XL 30).

UV/Visible absorption measurement. The absorption spectra of fluorinated molecules were recorded in chloroform solution. The absorption spectra of P3HT/TiO_2 nanorods hybrid films were obtained from the hybrid solution spin cast onto a glass substrates. The absorption spectra were normalized to have equal film thickness.

Cross-section SEM images. The hybrid films were deposited on the Si substrate covered with ~ 40 nm PEDOT:PSS by spin coating of hybrid solution with and without fluorinated molecule. The PEDOT:PSS layer was spin coated onto Si substrate and baked at 120°C for 30 min. The cross-sectional images of the hybrid films were obtained by breaking the film crosswise along a diamond knife scratched line on Si in liquid nitrogen.

Hybrid solar cell fabrication and characterization. The surface of TiO_2 nanorods was modified by pyridine first, and then the TiO_2 nanorods are dissolved in a co-solvent consisting of pyridine, dichloromethane and chloroform in a volumetric ratio of 1:2:3. The TiO_2 nanorods were mixed with P3HT which was dissolved in chlorobenzene. The fluorinated molecules, BCF and FBN-CPDT, were dissolved in chloroform first and then mixed with the P3HT/TiO_2 hybrid solution to form a ternary solution. The hybrid solution was prepared by blending the P3HT with TiO_2 nanorods in 47 : 53 wt/wt ratios. The P3HT/TiO_2/fluorinated molecule hybrid films were fabricated in a weight ratio of 46/53/1 respectively. For the fabrication of solar cell, a thin active hybrid layer of P3HT/TiO_2 nanorods ca. 120 nm thick was spin coated onto ITO glass covered with about ~ 40 nm PEDOT:PSS (Baytron P, 4083). A thin active hybrid layer of P3HT/TiO_2 nanorods/fluorinated molecules was also spin coated onto ITO/PEDOT:PSS substrates and the thickness of the hybrid films with fluorinated molecules is ca. 180 nm. The PEDOT:PSS layer was spin coated onto ITO glass and baked at 120°C for 30 min. An additional layer of TiO_2 nanorods was deposited between the hybrid film and the Al electrode to act as a hole blocking layer. The Al electrode was then deposited onto the TiO_2 nanorods layer by thermal evaporation under vacuum at 5 x 10^{-6} torr. The performance of these devices were evaluated under AM 1.5 G irradiation (100 mW/cm2) using a solar simulator (Oriel Inc.). J-V curves were recorded with a Keithley 2400 digital source meter.

Charge mobility measurement. The charge carrier mobility in the hybrid film was calculated by using the space charge limited current (SCLC) model. The structure of hole-only device was ITO/PEDOT:PSS/ P3HT:TiO_2:fluorinated molecule/Au and that of electron-only device was Al/P3HT:TiO_2:fluorinated molecule/Al.

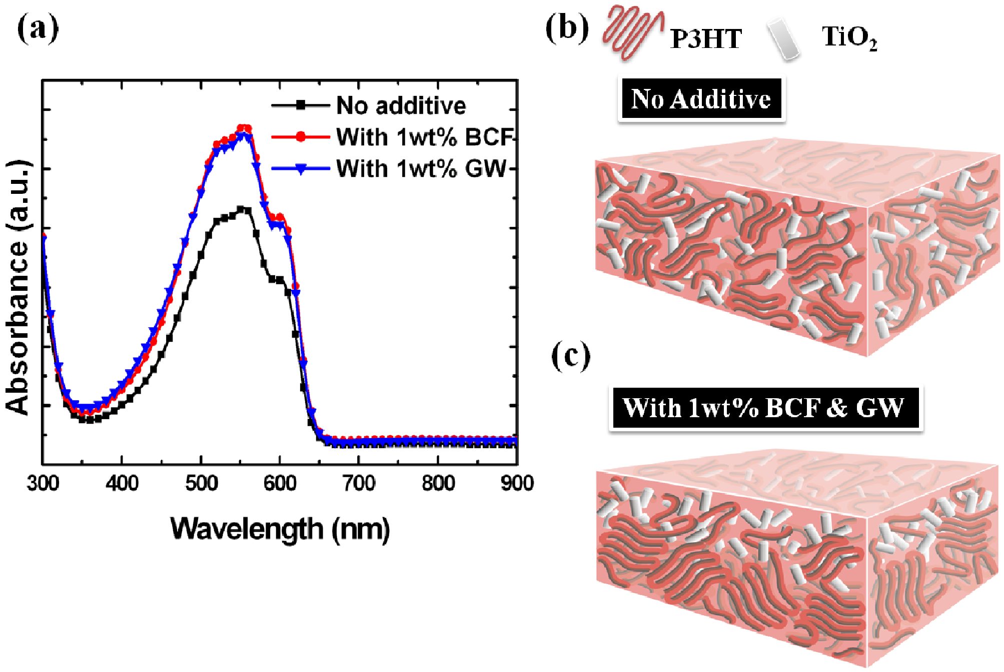

Fig. 1S (a) Absorption spectra of P3HT/TiO_2/fluorinated molecule hybrid system. Schematics of the distribution of P3HT and TiO_2 in active layer (b) without and (c) with fluorinated molecule.

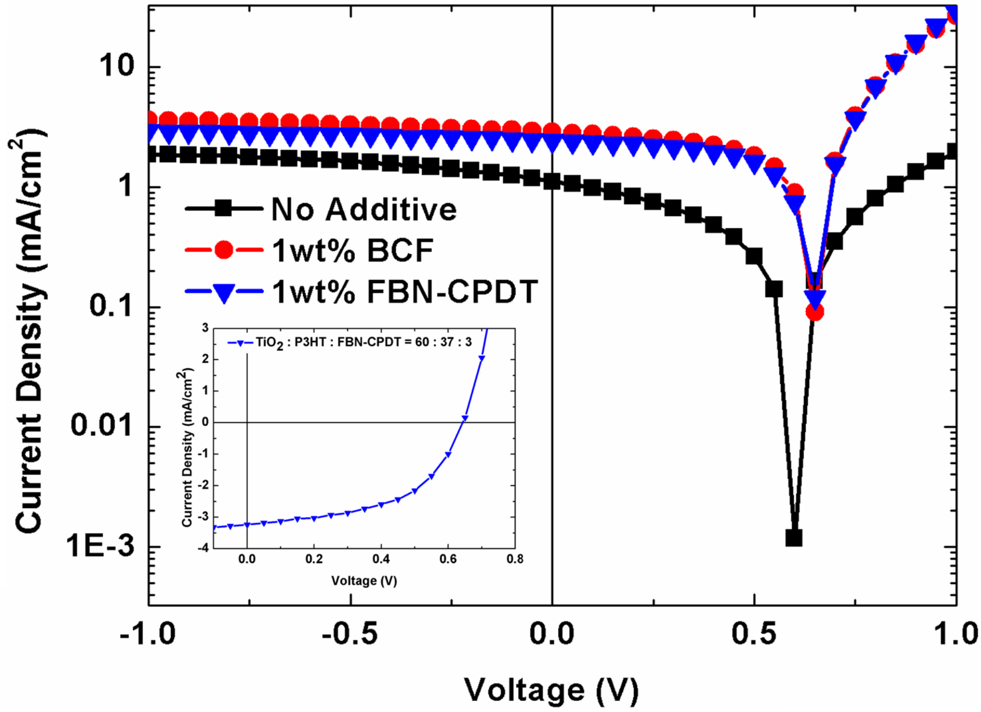

Fig. 2S J-V curves of hybrid solar cells based on P3HT/TiO_2, P3HT/TiO_2/BCF and P3HT/TiO_2/FBN-CPDT under AM 1.5 illumination (100 mW/cm^2). Inserted image is the J-V curve of P3HT/TiO_2/FBN-CPDT in a weight ratio of 37/60/3.

Table 1S. Performance and charge mobility of hybrid solar cells fabricated from different materials of P3HT/TiO_2, P3HT/TiO_2/BCF and P3HT/TiO_2/FBN-CPDT

Device	**V_{oc} (V)**	**J_{sc} (mA/cm^2)**	**FF**	**η (%)**	**μ_h (cm^{2}V^{-1}s^{-1})**	**μ_e (cm^{2}V^{-1}s^{-1})**
No fluorinated molecule	**0.60**	**1.11**	**0.33**	**0.22**	**2.32×10^{-4}**	**3.52×10^{-5}**
1wt% BCF	**0.64**	**2.87**	**0.50**	**0.92**	**4.97×10^{-4}**	**4.33×10^{-4}**
1wt% FBN-CPDT	**0.63**	**2.43**	**0.51**	**0.78**	**4.08×10^{-4}**	**5.01×10^{-4}**
3wt% FBN-CPDT	**0.65**	**3.23**	**0.53**	**1.11**	**--**	**--**

References

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2. G. C. Welch, R. Coffin, J. Peet and G. C. Bazan, *J. Am. Chem. Soc.*, 2009, **131**, 10802
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