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Perovskite solar cells by using aligned TiO_2 nanobundles grown on sputtered Ti layer and benzothiadiazole dopant free hole transporting material

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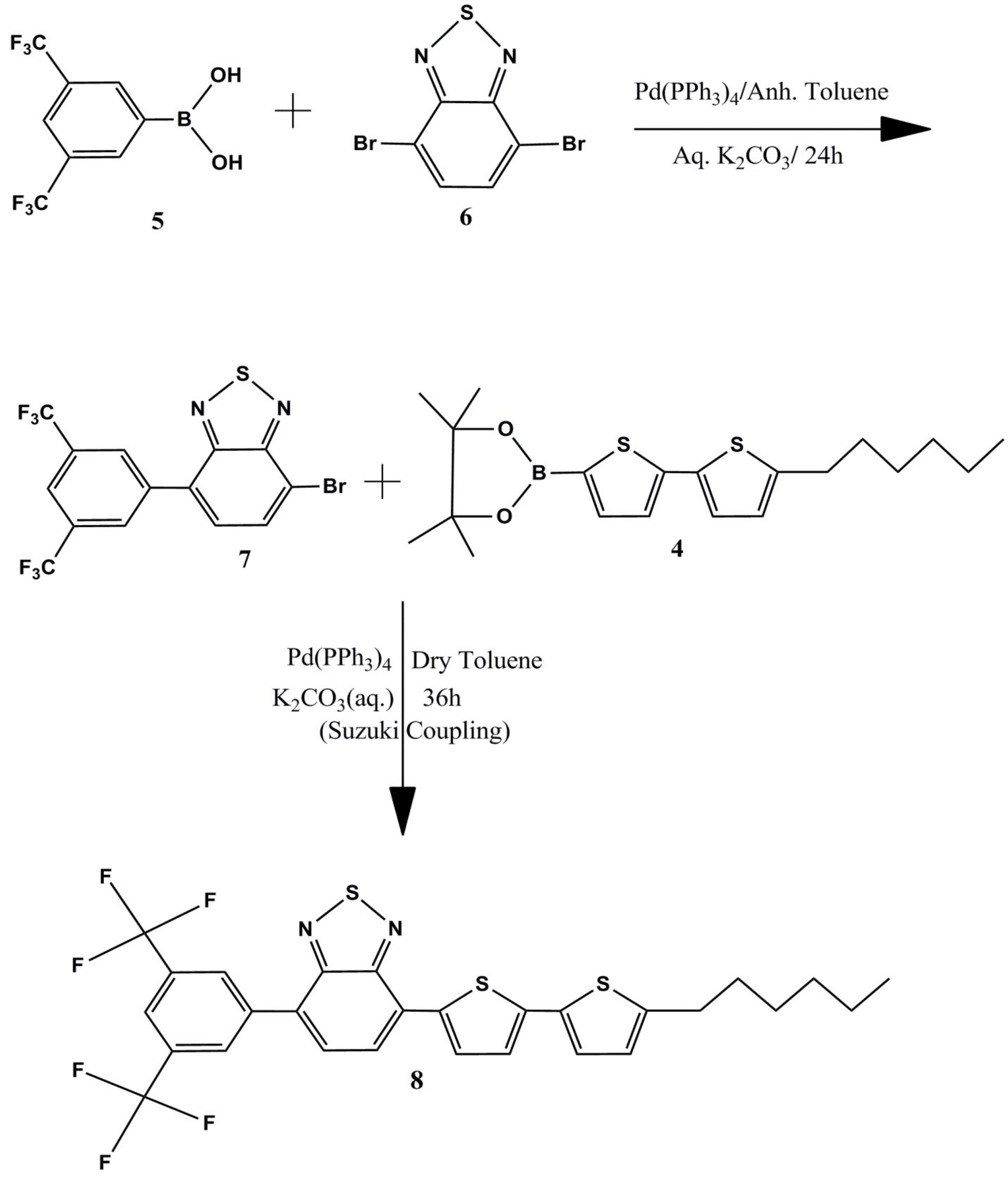
Experimental

Synthesis of CF-BTz-ThR

The synthetic route of benzothiadiazole-based organic chromophore, CF-BTz-ThR is shown in Scheme 1. The monomeric precursors **2**, **3**, of n-hexyl bithiophene boronic acid pinacole ester, **4** and 2,7-dibromo-9,9′-benzothiadiazole, **6** intermediates were synthesized as previously reported procedures [39-41]. The intermediate product, **7** (CF-BTz-Br) was obtained by the Suzuki cross-coupling reaction between 2,7-dibromo-9,9′-benzothiadiazole, **6** and 3,5-bis(trifluoromethyl)phenyl boronic acid, 5 using Pd(0) catalyst (3 mol %) and potassium carbonate as a base in anhydrous toluene solvent and then finally coupled again with n-hexyl bithiophene boronic-acid pinacole ester, 4 by Suzuki coupling using $Pd(PPh_3)_4$ catalyst (5 mol %) and potassium carbonate as a base in anhydrous toluene solvent under inert atmosphere to give a final product, **8** named as CF-BTz-ThR. The synthesized chromophore was purified by flash column chromatography and then recrystallized in the mixed solvent of dichloromethane/methanol (2:1, v/v) as red solid (Yield: 72.2 %).



Scheme S1. Synthetic route of CF-BTz-ThR

2-(7-bromo-9,9′-benzothiadiazole-2-yl)-5-(3,5-bis(trifluoromethyl)benzene (7)

3,5-bis(trifluoromethyl)phenyl boronic acid, **5** (0.411 gm, 2 mmol), and 2,7-dibromo-9,9′-benzothiadiazole, **6** (0.948 g, 2 mmol) and $\mathrm{Pd(PPh_3)_4}$ (15 mg, 5 mol%) were refluxed in degassed toluene (～10 mL) with an aqueous K_2CO_3 solution (2 M) (4 mL) for 24 h under an inert atmosphere. The reaction was cooled and DI was added to quench the reaction and then diluted with hexane (10 ml). The organic layer was extracting with dichloromethane (20 ml), washed with DI water, brine solution and dried over anhydrous $MgSO_4$. The solvent evaporated by rotary evaporator and the obtained compound was dried in vacuo. The crude product was purified by flash column chromatography by using hexane : DCM (2:1, v:v) followed by recrystallization from DCM:methanol (5:1, v:v) to get pale yellow solid (0.641 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.82–0.88 (t, 3H), 1.17–1.26 (m, 6H), 1.85 (t, 2H), 3.45 (t, 2H), 6.70 (d, 1H), 6.76 (d, 1H), 6.78 (d, 1H), 7.06-7.12 (t, 4H), 7.18-7.20 (d, 2H), 7.36 (d, 2H), 7.41-7.51 (d, 4H), 7.63 (s, 2H), 7.76 (d, 2H) . ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 150.62, 147.43, 147.13, 141.77, 139.72, 131.20, 128.36, 128.16, 127.41, 126.96, 126.67, 123.45, 121.96, 121.45, 120.88, 120.46, 120.35, 119.37, 31.65, 30.69, 30.52, 30.27, 28.83, 28.46, 27.62, 27.34, 22.77, 22.69, 14.22 14.16. FTIR (KBr pellets, cm^{-1}): 3439, 3028, 2962, 2855, 1731, 1653, 1587, 1485, 1404, 1323, 1256, 1228, 1099, 1022, 976, 948, 836, 792, 691.

2-(7-(3,5-bis(trifluoromethyl)phenyl)-9,9'-benzothiadiazole-2-yl)-5-(5-hexylthiophen-2-yl)thiophene (8)

A solution of 32-(5-(5-Decylthiophen-2-yl) thiophen-2-yl) -4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 4 (0.381 g, 1 mmol), and intermediate bromide, 7 (0.642, 1 mmol) were added in aqueous solution (2 M) of K_2CO_3 (5 ml) and Pd $(PPh_3)_4$ catalyst (10 mg, 0.01 mmol) in anhydrous toluene (~10 ml) solvent. The reaction mixture was degassed several times, heated to reflux under inert atmosphere for 24 h. After completion, the reaction (as monitored by TLC) was cooled at room temperature and diluted with hexane (10 ml). To ensure the completion of the coupling reaction, the boronic acid was used in access. The organic layer was extracted with dichloromethane (20 ml) and washed with DI water, brine and dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography using hexane:DCM (5:1, v:v), followed by recrystallization from DCM:methanol (2:1, v:v) to get the red solid (0.46 g, 72.2%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.84–0.88 (t, 3H), 1.18–1.28 (m, 6H), 1.82 (t, 2H), 3.42 (t, 2H), 6.64 (d, 1H), 6.70 (d, 1H), 6.76 (d, 1H), 6.78 (d, 1H), 7.06-7.12 (t, 4H), 7.18-7.20 (d, 2H), 7.36 (d, 2H), 7.43-7.52 (d, 4H), 7.62 (s, 3H), 7.79 (d, 2H) . ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 150.62, 147.43, 147.13, 141.77, 139.72, 131.20, 128.36, 128.16, 127.41, 126.96, 126.67, 123.45, 121.96, 121.45, 120.88, 120.46, 120.35, 119.37, 119.26, 36.09, 30.69, 30.56, 30.42, 28.70, 28.46, 27.62, 27.34, 22.19, 21.69, 13.61, 13.07. FT-IR (KBr pellets, cm^{-1}): 3439, 3062, 3026, 2954, 2922, 2850, 1590, 1486, 1463, 1423, 1378, 1302, 1278, 1234, 1072, 972, 828, 786, 747, 693, 612, 522. MS (ESI): *m*/*z* calc. for $[C_{47}H_{34}F_6S_2]^+$: 596.12; found: 596.98 [M^+].

1-(5-(thiophen-2-yl) thiophen-2-yl)hexan-1-one (2)

Hexanoyl chloride (4.07 ml, 20.0 mmol) was added to a solution of 2,2’-bithiophene 1 (3.17 g, 19.1 mmol) in anhydrous benzene (20 ml) at room temperature. $TiCl_4$ solution (2.25 ml, 20.5 mmol) was added slowly at 0 °C to the reaction mixture and then stirred for 15 min at 0 ^{o}C. Ice water was added to quench the reaction, and the resulting mixture was diluted with dichloromethane (50 ml), washed successively with DI water (200 ml) and saturated aqueous solution of $NaHCO_3$ (100 ml), then dried over $MgSO_4$ and evaporated under reduced pressure evaporator to obtain 5.00 g (85%) of yellow solid as expected from the desired ketone intermediate. The intermediate was used without purification for next step reaction.

A suspension of $LiAlH_4$ (4.6 g, 121 mmol) and $AlCl_3$ (4.03 g, 30.3 mmol) in anhydrous Et_2O (100 ml) was added to toluene (40 ml) solution of ketone intermediate at 0 ^{o}C under inert atmosphere. The reaction was stirred for 1 h at room temperature, then cooled at 0 ^{o}C. Afterward, ethyl acetate (20 ml) and HCl (6 M) solution (50 ml) were added to the reaction mixture. The resulting mixture was extracted with diethyl ether (300 ml), washed with brine solution and DI water (50 ml), dried over $MgSO_4$ and evaporated in an vacuum oven. The obtained yellow residue was purified by flash column chromatography on silica gel (hexane) to obtain colorless oil (6.00 g, 93%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.17 (dd, 1H), 7.13 (dd, 1H), 6.95 (dd, 1H), 6.97 (d, 1H), 6.66 (d, 1H), 2.74 (t, 2H), 1.67 (m, 2H), 1.37 (m, 14H), 0.92 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 146.5, 145.3, 138.1, 134.7, 127.4, 125.5, 124.4, 123.9, 123.7, 123.2, 32.1, 31.6, 30.3, 29.7, 29.5, 29.1, 22.7, 14.1.

5-Bromo-5'-decyl-2,2'-bithiophene (3)

N-bromo succinimide (NBS) (1.22 g, 6.86 mmol) was added slowly in a compound **2** (2.00 g, 6.53 mmol) solution in dimethylformamide (30 ml), and the obtained reaction mixture was stirred for 30 min in a dark. The reaction mixture was diluted with hexane (50 ml), and washed with saturated aqueous solution of NH_4Cl (50 ml), dried over $MgSO_4$ and evaporated under reduced pressure. The obtained residue was purified by flash column chromatography on silica gel (hexane) to obtain a white solid (2.36 g, 94%), mp 35-38 °C; ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.96 (d, 1H), 6.91 (d, 1H), 6.87 (d, 1H), 6.69 (d, 1H), 2.75 (t, 2H), 1.65 (m, 2H), 1.37 (m, 14H), 0.93 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 145.3, 139.7, 133.6, 130.1, 130.7, 124.5, 123.5, 123.3, 110.5, 32.3, 31.5, 30.6, 29.7, 29.5, 29.1, 22.7, 14.2.

2-(5-(5-Decylthiophen-2-yl) thiophen-2-yl) -4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

n-BuLi (1.6 M, 3.17 mmol) was added to tetrahydrofuran (20 ml) solution of **3** (1 g, 2.6 mmol) at -78 °C under nitrogen atmosphere. Then the temperature was slowly increased to -50 °C within 20 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.58 ml, 5.27 mmol) solution was added dropwise by syringe at -50 °C and the temperature was increased slowly up to the room temperature. The reaction mixture was stirred for 3 h at room temperature then 2N HCl (20 ml) was added. The obtained reaction mixture was extracted with diethyl ether (30 ml), washed with brine and DI water (500 ml), dried over $MgSO_4$, and then evaporated under reduced pressure. The obtained solid residue was recrystallized in hexane (10 ml) to receive a white solid (0.84 g, 93%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.57 (d, 1H), 7.24 (d, 1H), 7.07 (d, 1H), 6.73 (d, 1H), 2.86 (t, 2H), 1.75 (m, 2H), 1.35 (m, 14H), 0.93 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 146.3, 144.8, 137.7, 134.5, 124.7, 124.2, 84.4, 31.8, 31.3, 30.3, 29.8, 29.5, 29.2, 24.6, 22.5, 14.4.

Results and Discussion

Morphological studies

The morphology, quantitative and roughness parameters of aligned TiO_2 NBs are further confirmed by the topographic and three dimensional (3D) AFM images, as shown in Fig. S1. From topographic image (Fig. S1 (a)), the bright dots like morphology with aggregates are visible in aligned TiO_2 NBs thin film. The aligned morphology of NBs is similar to the FESEM observations. Similar morphology is well matched with AFM image at 3D mode, as shown in Fig. S1(b). The roughness analysis from AFM image reveals that the grown aligned TiO_2 NBs exhibits quite high root mean roughness (R_{rms}) of ~65.8 nm. In general, the larger and rough surface of TiO_2 nanostructured thin film might increase the photo-scattering efficiency and simultaneously promote the high light absorption.[1] Herein, aligned TiO_2 NBs with several aggregates and large R_{rms} might helpful for enhancing the photoabsorption and scattering properties.

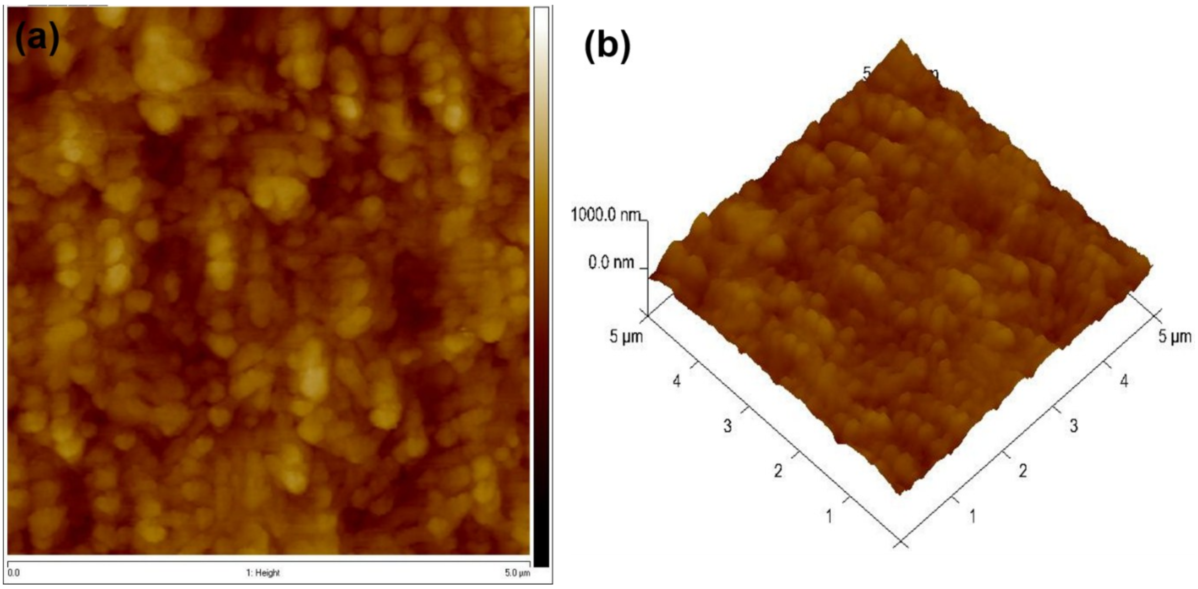


Fig. S1. Topographic (a) and three dimensional (b) AFM images of aligned TiO_2 NBs thin film

Optical and transmittance properties

The transmittance spectra of Ti/FTO and aligned TiO_2 NBs/FTO are shown in Fig. S2 (a). Ti/FTO thin film presents low transmittance of ~22%, which is significantly improved after the conversion of Ti to TiO_2 NBs. The aligned TiO_2 NBs/FTO thin film exhibits the average transmittance of ~79% in the wavelength range of 400-800 nm. Whereas, TiO_2 NPs/FTO thin film presents slightly low average transmittance of ~74% in the same wavelength range. The XRD patterns of $CH_3NH_3PbI_3$/ TiO_2 NPs/FTO and $CH_3NH_3PbI_3$/aligned TiO_2 NBs/FTO thin films are shown in Fig. S2(b). Both thin films show the presence of perovskite, TiO_2 and FTO phases, indicating the sensitization of perovskite over the TiO_2 surface.

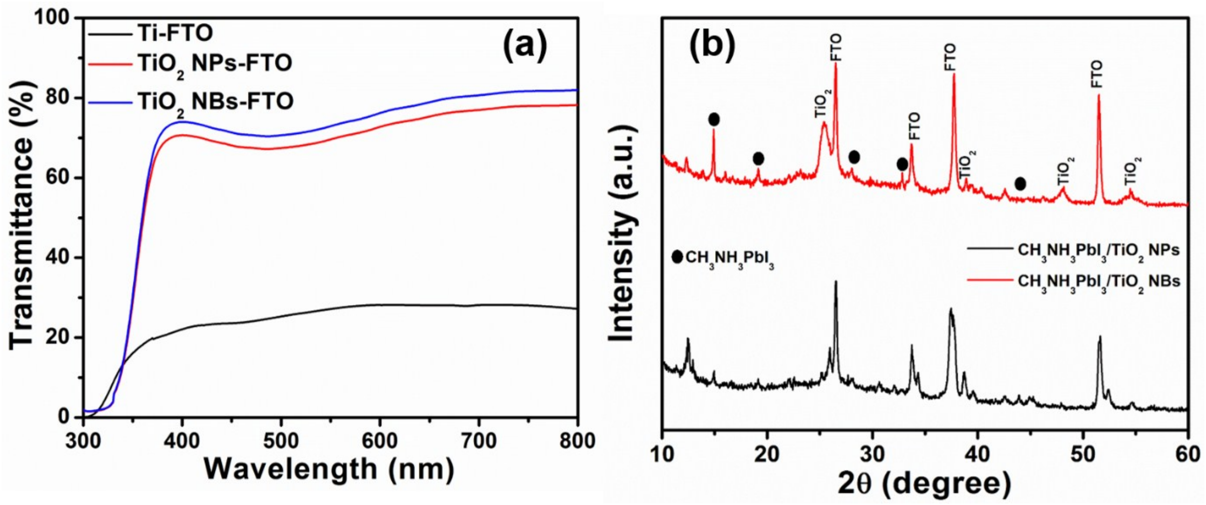


Fig. S2. (a) The transmittance spectra of Ti/FTO, TiO_2 NPs/FTO and aligned TiO_2 NBs/FTO thin films and (b) XRD patterns of $CH_3NH_3PbI_3$/aligned TiO_2 NBs and $CH_3NH_3PbI_3$/TiO_2 NPs thin films

The ultraviolet-visible (UV-vis) spectroscopy is measured to quantify and notice the effects of adsorbed $CH_3NH_3PbI_3$ on aligned TiO_2 NBs. Aligned TiO_2 NBs/FTO thin film (Fig. S3 exhibits the absorption edge at ~386 nm, which is consistent with other reports.[2] It is assumed that the grown aligned TiO_2 NBs could provide enough surfaces for high loading of $CH_3NH_3PbI_3$ sensitizer.

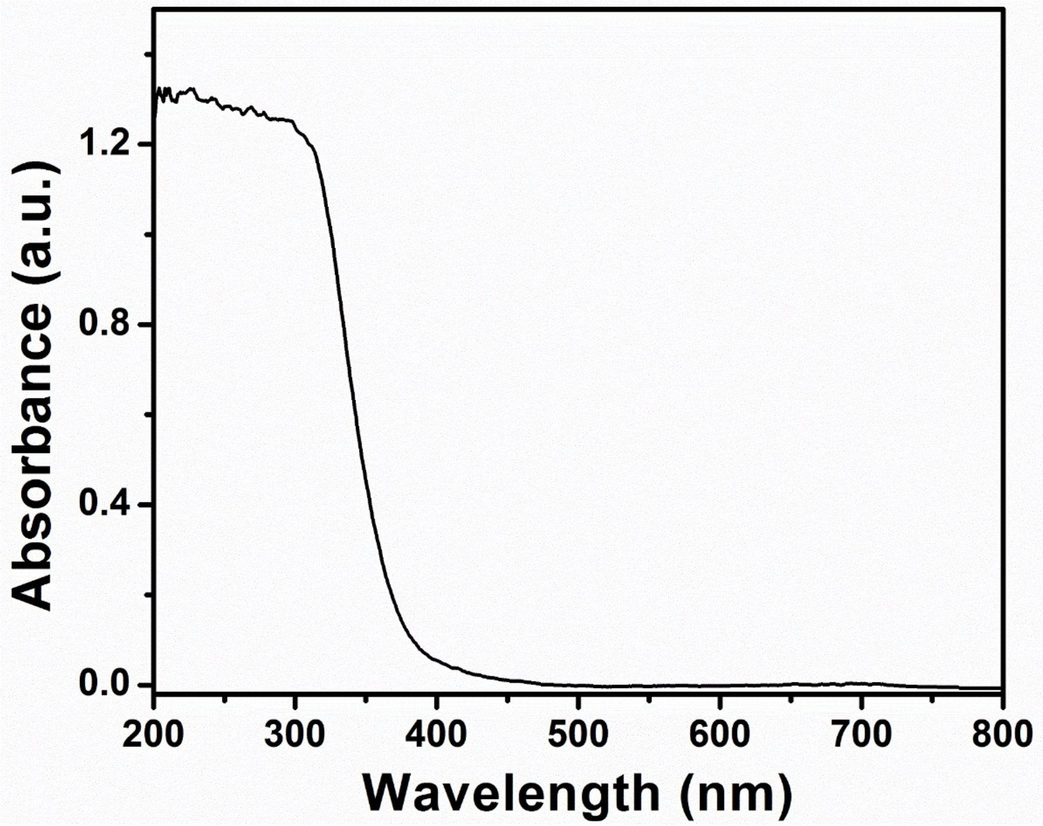


Fig. S3. UV-vis spectroscopy of aligned TiO_2 NBs/FTO thin film

Thermal studies of CF-BTz-ThR

For CF-BTz-ThR characterizations, the thermal properties are investigated by measuring differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) under inert atmosphere, as displayed in Fig. S4. The CF-BTz-ThR molecule possesses a high glass transition temperature (T_g) at ~61 ^{o}C which is associated to alkyl chain and phenyl rings. The CF-BTz-ThR shows only ~2% weight loss and the high decomposition temperature at ~312 ^{o}C, indicating good thermal stability. In addition, the organic chromophore has shown liquid-crystalline (LC) properties by detecting two melting transitions (T_m) at ~178 ^{o}C and ~252 ^{o}C along with the three crystallization transitions (T_c) at ~163 ^{o}C, ~214 ^{o}C and ~278^{o}C, which represent the self-organization of the organic chromophore.[3]

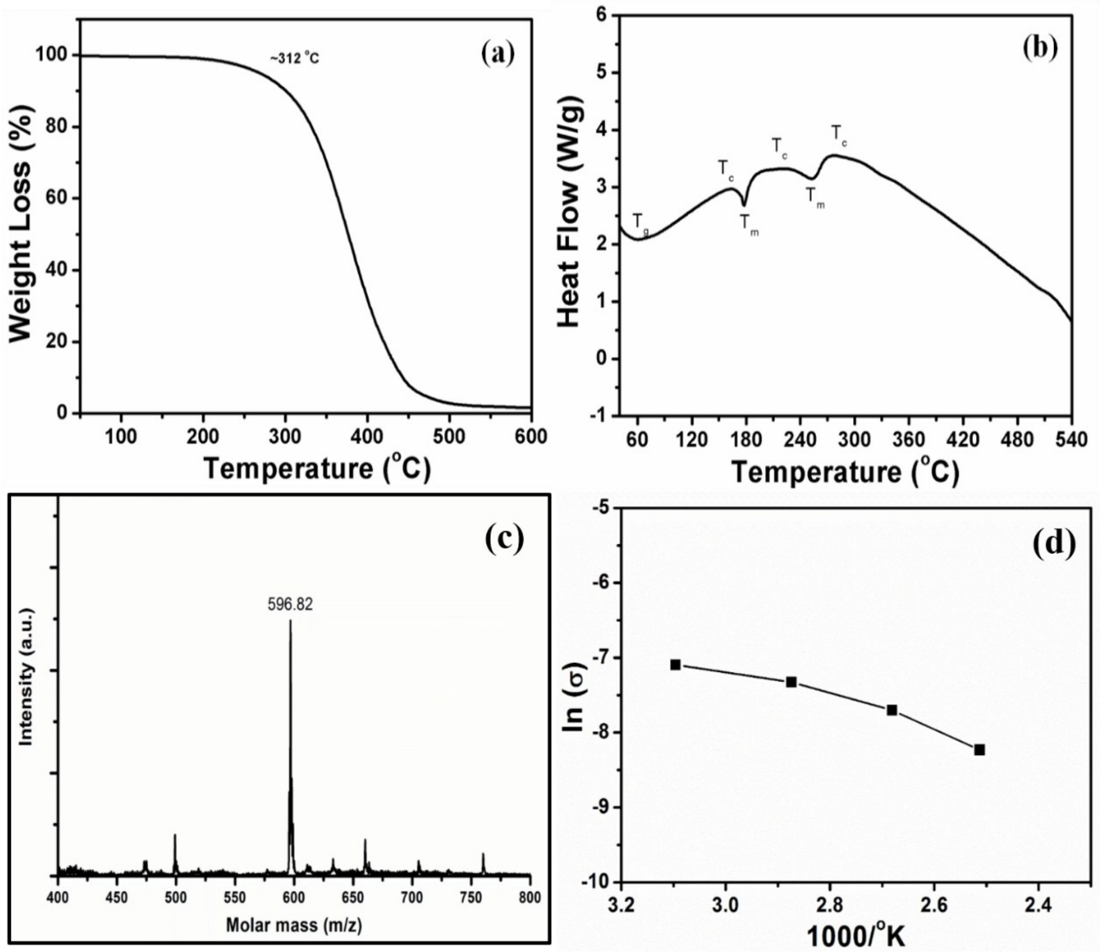


Fig. S4. (a) Thermogravimetric analysis (TGA), (b) differential scanning calorimetry (DSC) plots, (c) mass spectroscopy and (d) electrical conductivity of CF-BTz-ThR molecule

The Mass spectroscopy has been analyzed to determine the mass of CF-BTz-ThR HTM. In the Fig. S4(c), a strong mass peak at m/z = 596.82 is obtained which is almost similar to the formula mass of CF-BTz-ThR molecule. This observation clearly confirms that the mass of the synthesized CF-BTz-ThR HTM is 596.8.

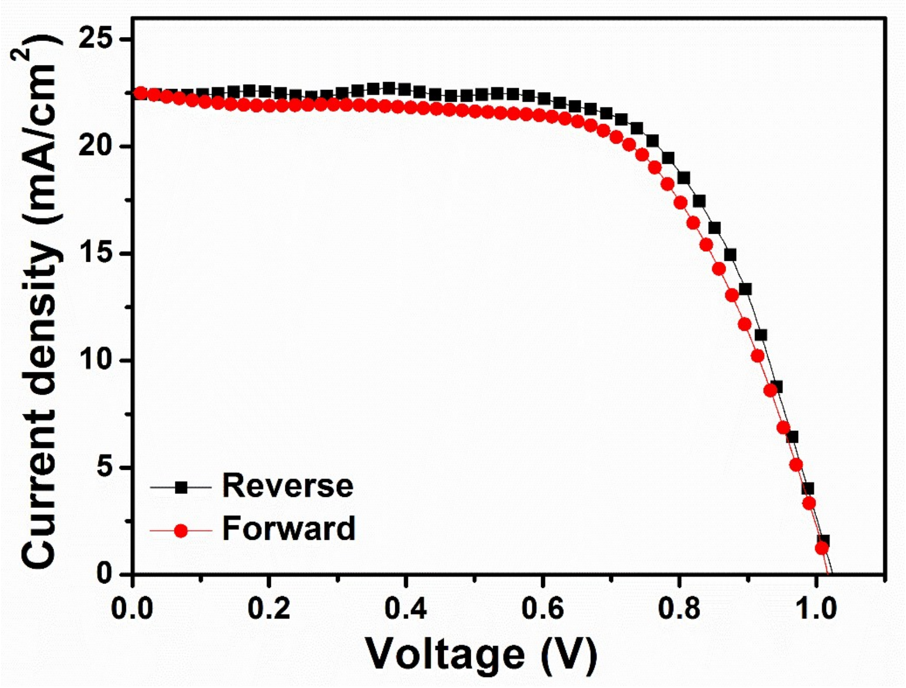


Fig. S5. Reverse and forward scan direction-dependent I−V curves of the Au/CF-BTz-ThR/$CH_3NH_3PbI_3$/TiO_2 NBs/FTO device

J−V hysteresis of the fabricated Au/CF-BTz-ThR/$CH_3NH_3PbI_3$/TiO_2 NBs/FTO device is shown in Fig. S5. From J-V curve, a negligible difference is seen in J_{SC} at short-circuit condition and almost a similar V_{OC} is observed in both the reverse and forward scans. A small hysteresis is observed in both the scans, suggesting the existence of small accumulated capacitive current in TiO_2 NBs based device.

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