Supplementary Information:

Organic Dyes with Remarkably High Absorptivity; All Solid-State Dye Sensitized Solar Cell and Role of Fluorine Substitution

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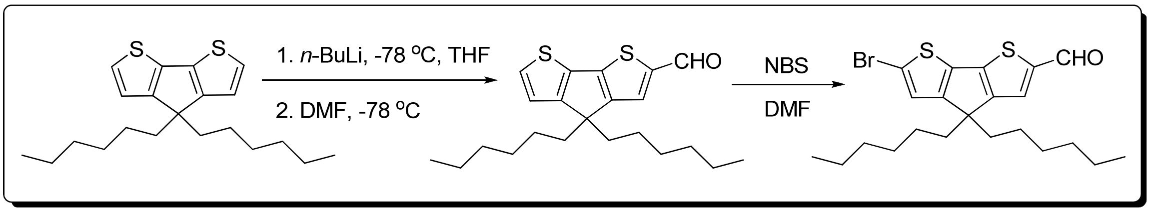
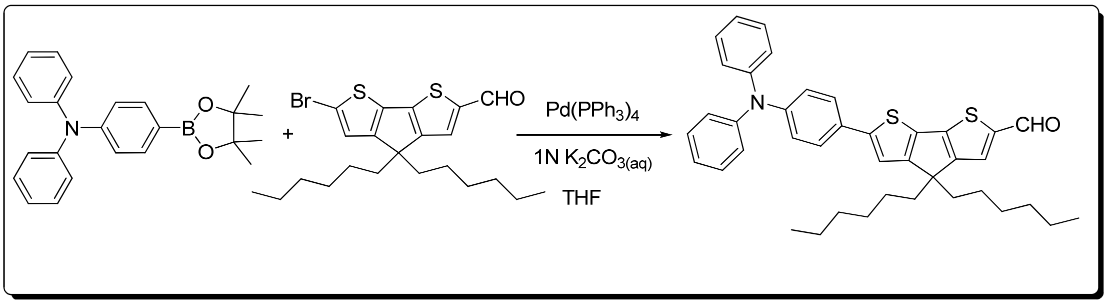
General procedures: All reactions were performed under nitrogen atmosphere and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV254). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.



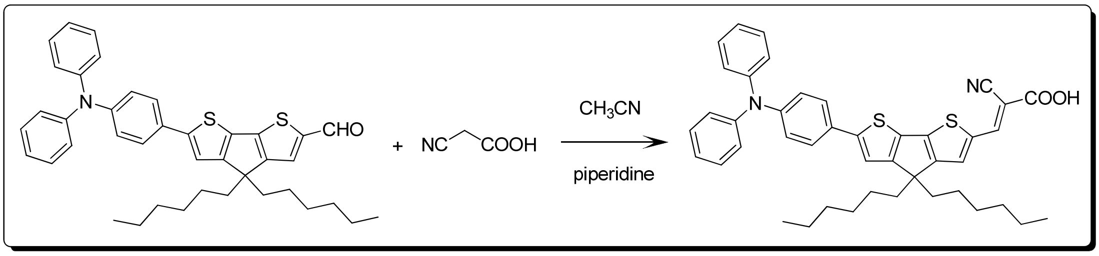
Synthesis of 7-bromo-4,4′-dihexylclopentadithiophene-2-carbaldehyde (T1). To a THF (10 mL) solution of 4,4′-dihexylcyclopenta[2,1-b:3,4-b]dithiophene (0.811 g, 2.30 mmol) maintained at −78 °C, *n*-butyl lithium (1.0 mL, 2.5 M, 2.58 mmol) was added dropwise over a period of 15 mins. After then, anhydrous DMF (0.21 mL, 2.86 mmol) was added and the mixture was allowed to attain RT. After two hours, the reaction was quenched by pouring into an ice-water mixture. The organic product was extracted with CH_2Cl_2 and purified by silica gel column chromatography eluting with a 2:1 mixture of CH_2Cl_2 and hexane. After then, the isolated product was dried under vacuum and dissolved into a DMF (10 mL) solution of N-bromosuccinimide (NBS, 0.379 g, 2.11 mmol). After stirring at RT for two hours, the mixture was poured over crushed ice (20 g) to obtain the desired orange precipitate; yield: 0.785 g, 74%.

Spectral data of T1: HRESI-MS (m/z): $[M]^+$ calcd. for $C_{22}H_{29}BrOS_2$, 452.0843; Found 452.0832. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 9.81 (s, 1H), 7.53 (s, 1H), 6.99 (s, 1H), 1.87 ~ 1.71 (m, 4H), 1.26 ~ 1.10 (m, 12H), 0.95 ~ 0.85 (m, 4H), 0.80 (t, J_{HH} = 7.2 Hz, 6H). ^{13}C−{^{1}H} NMR (100 Hz, $CDCl_3$, 298K): δ 182.49, 161.02, 157.09, 146.70, 143.45, 135.85, 129.83, 124.85, 124.50, 116.59, 54.53, 37.45, 31.45, 29.47, 24.43, 22.49, 13.91.



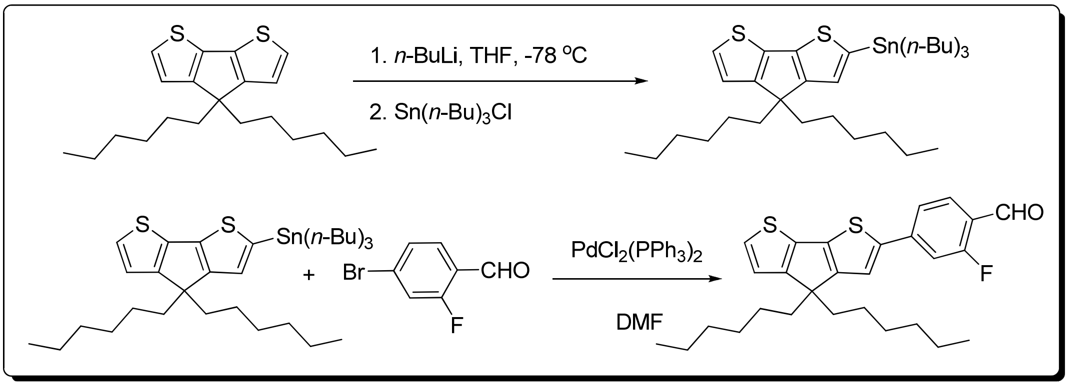
7-(4-(diphenylamino)phenyl)-4,4´-dihexylclopentadithiophene-2-carbaldehyde (T2). N,N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (0.838 g, 2.26 mmol) was treated with **T1** (0.785 g, 1.74 mmol) in the presence of $Pd(PPh_3)_4$ (0.1 g, 0.09 mmol), 1N aqueous solution of K_2CO_3 (5.2 mL) and THF (40 mL). The solution was refluxed for 24 hours. After the completion of the reaction, the solvent was removed under vacuum and the residue was dissolved into minimal amount of CH_2Cl_2. It was then filtered and purified by silica gel column chromatography using a 2:1 mixture of CH_2Cl_2 and hexane as the eluent (R_f = 0.47) to obtain orange solid (747 mg, 1.22 mmol, 70 %).

Spectral data of T2: HRESI-MS (m/z): $[M]^+$ calcd. for $C_{40}H_{43}NOS_2$, 617.2786; Found 617.2726. ^1H NMR (400 MHz, $CDCl_3$, 298K): δ 9.80 (s, 1H), 7.53 (s, 1H), 7.47 (d, J_{HH} = 8.8 Hz, 2H), 7.26 (t, J_{HH} = 8.0 Hz, 4H), 7.11 (d, J_{HH} = 7.6 Hz, 5H), 7.07 ~ 7.02 (m, 4H), 1.92 ~ 1.80 (m, 4H), 1.19 ~ 1.13(m, 12H), 0.96 ~ 0.93 (m, 4H), 0.79 (t, J_{HH} = 7.2 Hz, 6H). $^{13}C-\{^1H\}$ NMR (100 Hz, $CDCl_3$, 298K): δ 181.87, 163.31, 157.12, 149.29, 147.82, 147.56, 147.02, 142.73, 133.58, 129.16, 127.99, 126.16, 124.43, 123.16, 116.49, 53.87, 37.54, 31.37, 29.43, 24.36, 22.40, 13.86.



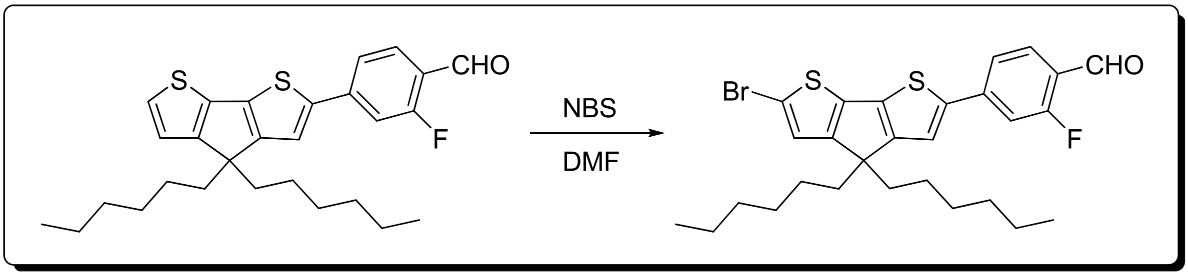
2-Cyano-3-(7-(4-(diphenylamino)phenyl)-4,4´-dihexylclopentadithiophene-2-yl)acrylic acid (A1). An acetonitrile solution (20 mL) solution of **T2** (51 mg, 0.083 mmol), cyanoacrylic acid (15 mg, 0.17 mmol) and piperidine (0.04 mL, 0.43 mmol) was heated at reflux for 6 hours. After cooling to RT, the mixture was poured into excess of water to yield a precipitate. It was filtered and thoroughly washed with water and hexane. The dark red solid was obtained by slow diffusion of hexane into a THF solution at RT (46 mg, 0.067 mmol, 80 %).

Spectral data of A1: FAB-MS (m/z): $[M+1]^+$ calcd for $C_{43}H_{44}N_2O_2S_2$, 684; Found 685. ^{1}H NMR (400 MHz, d_6-DMSO, 298K): δ 8.41 (s, 1H), 7.93 (s, 1H), 7.61(d, J_{HH} = 8.8 Hz, 2H), 7.55 (s, 1H), 7.33 (t, J_{HH} = 7.6 Hz, 4H), 7.11 ~ 7.04 (m, 6H), 6.98 (d, J_{HH} = 8.4 Hz, 2H), 1.89 ~ 1.87 (m, 4H), 1.13 ~ 1.09 (m, 12H), 0.87 (m, 4H), 0.75 (t, J_{HH} = 7.2 Hz, 6H). $^{13}C-\{^1H\}$ NMR (176 Hz, d_6-DMSO, 298K): δ 164.72, 164.69, 157.83, 150.04, 149.15, 147.78, 147.59, 147.15, 136.26, 133.74, 133.64, 130.14, 128.12, 126.87, 124.89, 124.10, 123.29, 118.15, 117.85, 94.23, 53.86, 37.27, 31.41, 29.37, 24.48, 22.45, 14.30. Anal. Calcd for $C_{43}H_{44}N_2O_2S_2$: N, 4.09; C, 75.32; H, 6.47. Found: N, 4.16; C, 75.40; H, 6.54.



2-Fluoro-4-(4,4´-dihexylclopentadithiophen-2-yl)benzaldehyde (T3-F). To a THF solution (20 mL) of **T1** (0.99 g, 2.86 mmol) at −78°C, *n*-butyl lithium (1.4 mL, 2.5 M) was added dropwise. After stirring for 10 min, tributyltin chloride (1.0 mL, 3.69 mmol) was added and the mixture was allowed to attain RT. After 12 h of reaction, the content was quenched by pouring into an ice-water mixture to afford a yellow oily material. After drying under vacuum, 4-bromo-2-fluorobenzaldehyde (0.480 g, 2.38 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.084 g, 0.120 mmol) and DMF (8 mL) solvent were added and stirred at 100°C for 8 h to complete the coupling reaction. Finally, DMF solvent was evaporated and the remaining solid was separated by silica gel column chromatography eluting with a 1:2 mixture of CH$_2$Cl$_2$ and hexane (R$_f$ = 0.57). The product (**T3-F**) was isolated as yellow powder; yield: 0.421 g, 38%.

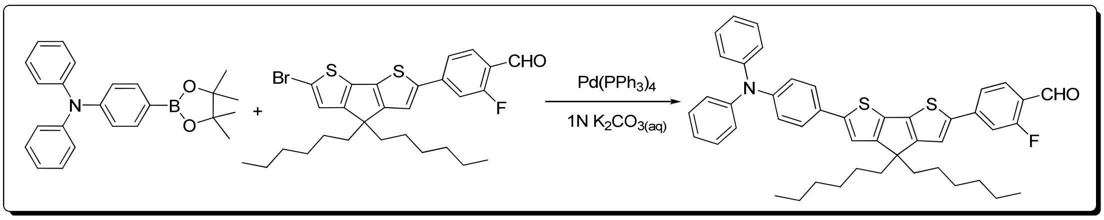
Spectral data of T3-F: HRESI-MS (m/z): $[M]^+$ calcd. for $C_{28}H_{33}FOS_2$, 468.1956; Found 468.1952. ^{1}H NMR (400 MHz, CDCl$_3$, 298K): δ 10.28 (s, 1H), 7.83 (t, J_{HH} = 8.0 Hz, 1H), 7.46 (d, J_{HH} = 8.0 Hz, 1H), 7.36 ~ 7.33 (m, 2H), 7.25 (d, J_{HH} = 4.4 Hz, 1H), 6.94 (d, J_{HH} = 4.8 Hz, 1H), 1.85 (t, J_{HH} = 8.0 Hz, 4H), 1.19 ~ 1.16 (m, 12H), 0.97 ~ 0.92 (m, 4H), 0.79 (t, J_{HH} = 7.2 Hz, 6H). ^{13}C−{^{1}H} NMR (100 Hz, CDCl$_3$, 298K): δ 186.22, 166.44, 163.88, 159.28, 159.18, 143.50, 140.73, 139.54, 135.95, 129.32, 126.68, 121.70, 120.76, 120.30, 111.75, 111.52, 53.88, 37.76, 31.58, 29.64, 24.51, 22.58, 13.99. ^{19}F−{^{1}H} NMR (376 Hz, CDCl$_3$, 298K): δ −121.64.



2-Fluoro-4-(7-bromo-4,4´-dihexylclopentadithiophen-2-yl)benzaldehyde (T4-F). A DMF (10 mL) solution of **T3-F** (0.421 g, 0.90 mmol) and N-bromosuccinimide (0.194 g, 1.08 mmol) was stirred at RT for one hour. It was then poured over crushed ice (20 g). The solid was extracted with diethyl ether, and the solution was washed with water, dried over anhydrous MgSO$_4$ and filtered. The desired orange product was recovered upon passing through a short silica gel column and removal of the solvent; yield: 0.39 g, 78%

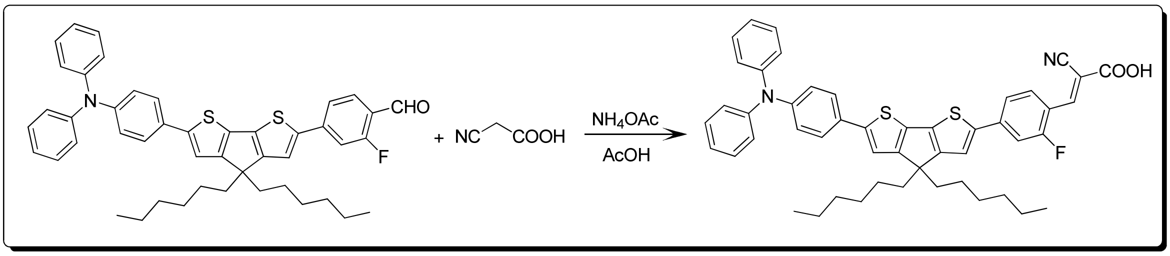
Spectral data of T4-F: RESI-MS (m/z): $[M]^+$ calcd. for $C_{28}H_{32}BrFOS_2$, 546.1062; Found 546.1042. ^{1}H NMR (400 MHz, CDCl$_3$, 298K): δ 10.28 (s, 1H), 7.83 (t, J_{HH} = 8.0 Hz, 1H), 7.45 (d, J_{HH} = 8.4 Hz, 1H), 7.34 (d, J_{HH} = 11.6 Hz, 1H), 7.30 (s, 1H), 6.96 (s, H), 1.83 ~ 1.79 (m, 4H), 1.20

~ 1.13 (m, 12H), 0.93 (m, 4H), 0.80 (t, J_{HH} = 7.2 Hz, 6H). ^{13}C−{^{1}H} NMR (100 Hz, $CDCl_3$, 298K): δ 186.06, 186.00, 158.25, 157.79, 141.21, 138.73, 136.28, 129.30, 129.28, 124.70, 120.75, 120.72, 120.07, 112.86, 111.78, 111.56, 54.68, 37.30, 31.52, 29.57, 24.45, 22.56, 13.96. ^{19}F−{^{1}H} NMR (376 Hz, $CDCl_3$, 298K): δ −122.37.



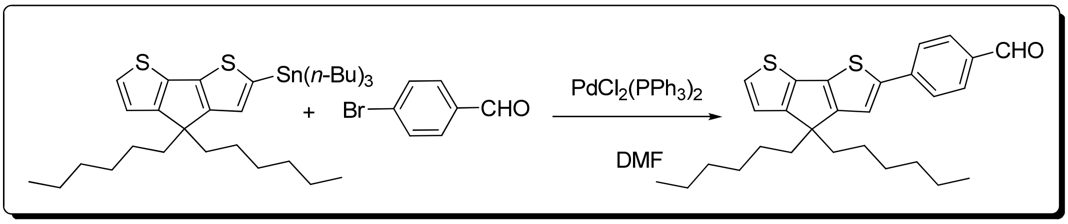
2-Fluoro-4-(7-(4-(diphenylamino)phenyl)-4,4′-dihexylclopentadithiophen-2-yl)benzaldehyde (T5-F). The synthesis followed the method reported for **T2**, giving the desired product as orange solid; yield: 76%.

Spectral data of T5-F: FAB-MS (m/z): $[M+1]^+$ calcd. for $C_{46}H_{46}FNOS_2$, 711; Found 712. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 10.28 (s, 1H), 7.83 (t, J_{HH} = 8.0 Hz, 1H), 7.49 ~ 7.45 (m, 3H), 7.36 ~ 7.33 (m, 2H), 7.26 (t, J_{HH} = 8.0 Hz, 4H), 7.12 ~ 7.02 (m, 9H), 1.90 ~ 1.86 (m, 4H), 1.21~ 1.15 (m, 12H), 0.99 (m, 4H), 0.80 (t, J_{HH} = 7.2 Hz, 6H).



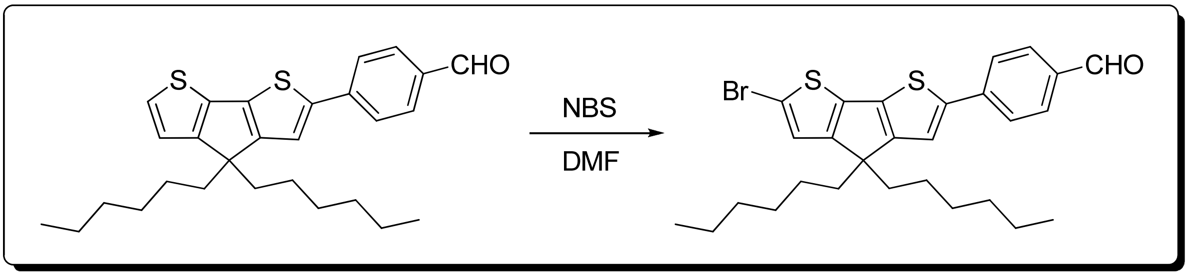
(E)-2-Cyano-3-(4-(7-(4-(diphenylamino)phenyl)-4,4′-dihexylclopentadithiophen-2-yl)-2-fluorophenyl) acrylic acid (A2-F). The synthesis followed the method reported for **A1**, giving the desired product as dark brown solid; yield: 78%.

Spectral data of A2-F: FAB-MS (m/z): $[M+1]^+$ calcd. for$C_{49}H_{47}FN_2O_2S_2$,778; Found 779. ^1H NMR (400 MHz, d_6-DMSO, 298K): δ 8.28 (s, 1H), 8.25 (t, J_{HH} = 8.0 Hz, 1H), 7.91 (s, 1H), 7.75 (d, J_{HH} = 1.2 Hz, 1H), 7.68 (d, J_{HH} = 9.6 Hz, 1H), 7.58 (d, J_{HH} = 8.4 Hz, 2H), 7.49 (s, 1H), 7.32 (t, J_{HH} = 8.0 Hz, 4H), 7.09 ~ 7.03 (m, 6H), 6.97 (d, J_{HH} = 8.8 Hz, 2H), 1.89 (t, J_{HH} = 8.0 Hz, 4H), 1.10 ~ 1.92 (m, 12H), 0.85 (m, 4H), 0.75 (t, J_{HH} = 6.8 Hz, 6H). $^{13}C-\{^1H\}$ NMR (125 MHz, d_6-DMSO, 298K): δ 163.01, 162.40, 160.71, 160.48, 158.84, 146.78, 146.63, 145.67, 143.73, 141.51, 140.47, 139.01, 133.69, 129.55, 129.30, 128.32, 125.96, 124.10, 123.29, 121.80, 117.60, 117.22, 116.01, 110.95, 104.08, 53.69, 36.91, 30.92, 28.95, 23.99, 21.96, 13.77. $^{19}F-\{^1H\}$ NMR (563 Hz, d_6-DMSO, 298K): δ −111.67. Anal. Calcd for $C_{49}H_{47}FN_2O_2S_2\cdot1/2H_2O$: N, 3.55; C, 74.68; H, 6.14. Found: N, 3.63; C, 74.82; H, 5.93.



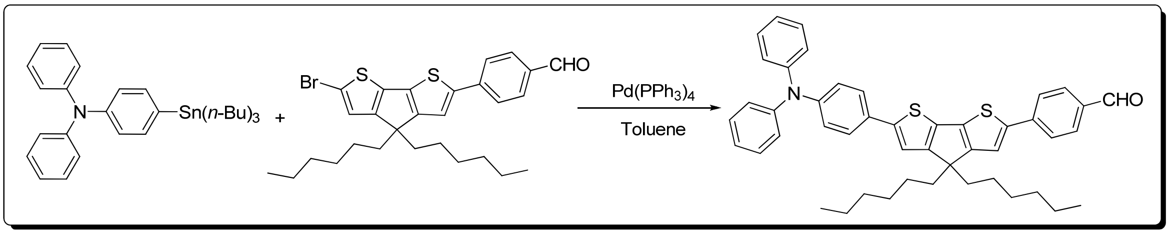
4-(4,4´-dihexylclopentadithiophen-2-yl)benzaldehyde (T3-H). The synthesis followed the method reported for **T3-F**, giving the desired product as red powder; yield: 49%.

Spectral data of T3-H: HRESI-MS (m/z): $[M]^+$ calcd. for $C_{28}H_{34}OS_2$, 450.2051; Found 450.2051. ^1H NMR (400 MHz, $CDCl_3$, 298K): δ 9.95 (s, 1H), 7.84 (d, J_{HH} = 8.0 Hz, 2H), 7.72 (d, J_{HH} = 8.4 Hz, 2H), 7.32 (s, 1H), 7.22 (d, J_{HH} = 4.8 Hz, 1H), 6.93 (d, J_{HH} = 5.2 Hz, 1H), 1.84 (t, J_{HH} = 8.0 Hz, 4H), 1.18 ~ 1.15 (m, 12H), 0.97 ~ 0.85 (m, 4H), 0.78 (t, J_{HH} = 7.2 Hz, 6H). $^{13}C-\{^1H\}$ NMR (100 Hz, $CDCl_3$, 298K): δ 190.99, 159.07, 158.74, 141.95, 140.95, 138.53, 136.05, 134.35, 130.36, 126.05, 124.83, 121.56, 119.54, 53.68, 37.65, 31.47, 29.56, 24.42, 22.49, 13.91.



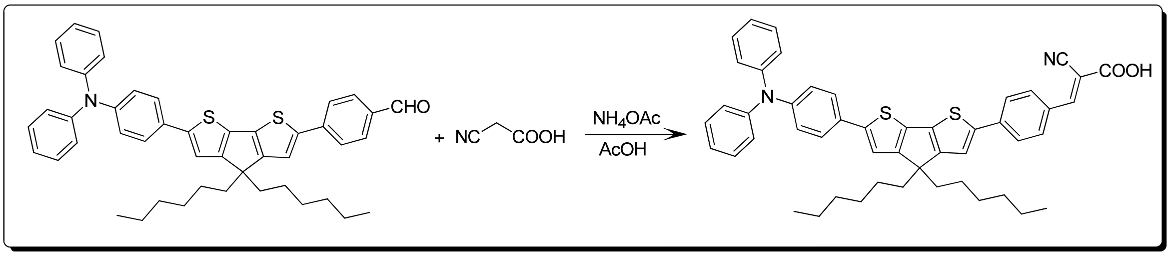
2-Fluoro-4-(7-bromo-4,4′-dihexylclopentadithiophen-2-yl)benzaldehyde (T4-H). The synthesis followed the method reported for **T4-F**, giving the desired product as dark red powder; yield: 90%.

Spectral data of T4-H: HRESI-MS (m/z): $[M]^+$ calcd. for $C_{28}H_{33}BrOS_2$, 528.1156; Found 528.1142. ^1H NMR (400 MHz, $CDCl_3$, 298K): δ 9.96 (s, 1H), 7.85 (d, J_{HH} = 8.8 Hz, 2H), 7.71 (d, J_{HH} = 8.4 Hz, 2H), 7.30 (s, 1H), 6.95 (s, 1H), 1.83 ~ 1.78 (m, 4H), 1.24 ~ 1.12 (m, 12H), 0.93 ~ 0.87 (m, 4H), 0.78 (t, J_{HH} = 7.2 Hz, 6H). $^{13}C-\{^1H\}$ NMR (100 Hz, $CDCl_3$, 298K): δ 191.24, 158.30, 157.40, 142.61, 140.87, 137.93, 136.56, 134.62, 130.52, 125.06, 124.72, 119.46, 112.26, 54.68, 37.68, 31.56, 29.62, 24.48, 22.59, 13.98.



4-(7-(4-(diphenylamino)phenyl)-4,4′-dihexylclopentadithiophen-2-yl)benzaldehyde (T5-H). The synthesis followed the method reported for **T5-F**, giving the desired product as orange solid; yield: 79%.

Spectral data of T5-H: HRESI-MS (m/z): $[M]^+$ calcd. for $C_{46}H_{47}NOS_2$, 693.3099; Found 693.3262. ^1H NMR (400 MHz, $CDCl_3$, 298K): δ 9.95 (s, 1H), 7.84 (d, J_{HH} = 8.4 Hz, 2H), 7.72 (d, J_{HH} = 8.0 Hz, 2H), 7.47 (d, J_{HH} = 8.8 Hz, 2H), 7.23 (s, 1H), 7.27 ~ 7.23 (m, 5H), 7.11 ~ 7.00 (m, 8H), 1.88 ~ 1.84 (m, 4H), 1.26 ~ 1.17 (m, 12H), 1.15 ~ 0.98 (m, 4H), 0.78 (t, J_{HH} = 7.2 Hz, 6H). $^{13}C-\{^1H\}$ NMR (100 Hz, $CDCl_3$, 298K): δ 190.93, 159.67, 158.46, 147.26, 146.97, 145.79, 141.93, 140.91, 138.91, 134.62, 134.22, 130.37, 129.18, 128.91, 125.91, 124.81, 124.70, 124.29, 123.69, 122.97, 119.40, 116.62, 54.04, 37.77, 31.53, 29.60, 24.44, 22.52, 13.94.



(E)-2-Cyano-3-(7-(4-(diphenylamino)phenyl)-4,4′-dihexylclopentadithiophen-2-yl) acrylic acid (A2-H). The synthesis followed the method reported for **A2-F**, giving the desired product as dark brown solid; yield: 73%.

Spectral data of A2-H: FAB-MS (m/z): $[M+1]^+$ calcd. for $C_{49}H_{48}N_2O_2S_2$, 760; Found 761. ^1H NMR (400 MHz, d_6-DMSO, 298K): δ 8.27 (s, 1H), 8.06 (d, J_{HH} = 8.4 Hz, 2H), 7.85 (s, 2H), 7.83 (d, J_{HH} = 3.6 Hz, 1H), 7.57 (d, J_{HH} = 8.4 Hz, 2H), 7.48 (s, 1H), 7.31 (t, J_{HH} = 7.6 Hz, 4H), 7.08 ~ 7.02 (m, 6H), 6.97 (d, J_{HH} = 8.8 Hz, 2H), 1.89 (t, J_{HH} = 8.0 Hz, 4H), 1.14 ~ 1.09 (m, 12H), 0.91 (m, 4H), 0.74 (t, J_{HH} = 6.4 Hz, 6H). ^{13}C NMR (125 MHz, d_6-DMSO, 298K): δ 163.48, 160.07, 158.89, 153.14, 146.81, 146.57, 145.14, 141.83, 138.98, 137.98, 133.89, 131.73, 129.59, 128.44, 125.95, 124.70, 124.09, 123.33, 120.81, 117.65, 116.50, 101.90, 53.69, 36.95, 30.95, 28.96, 24.00, 21.98, 13.79. Anal. Calcd for $C_{49}H_{48}N_2O_2S_2\cdot H_2O$: N, 3.60; C, 75.54; H, 6.47. Found: N, 3.79; C, 75.51; H, 6.16.

Fabrication of solid-state DSSCs

An 80 nm compact-layer of TiO_2 was deposited on the F-doped SnO_2, FTO, Tech 8 grade) by spray pyrolysis at 450°C. After then, TiO_2 (~20 nm in size) paste was spin coated on the compact-layered TiO_2 and sintered at 500°C for 30 min, forming the mesoporous TiO_2 film, for which its thickness varies from 1.0 μm to 3.0 μm in an aim to maximize the device performance. Subsequently, the sensitizers were applied to the as-prepared TiO_2 film by a dipping method in 300 μM dye solution for 10 hrs, followed by the spin coating with hole-transporting materials (a mixture composed of spiro-MeOTAD, *tert*-butylpyridine, and $Li(CF_3SO_2)_2N$ in the chlorobenzene). Finally, the counter electrodes, Ag, were thermally evaporated onto the top of spiro-MeOTAD blend. Note that no antireflective coating was applied in this application.

Measurement of Light-to-electricity conversion efficiency values

I-V curve of Photovoltaic devices were measured by using a modified light source, 450 W Xe lamp (Oriel, 6266), an Oriel 81088 Air Mass 1.5 Global Filter and a digital source meter (Keithley Instruments Inc). The incident light intensity was calibrated by using a standard solar cell composed of a crystalline silicon solar cell and an IR cutoff filter (Schott, KG-5), giving the photoresponse range of amorphous silicon solar cell. The potential and current density were measured using a Keithley model 2400 digital source meter.

Computational Methodology.

Restricted formalism was adopted in the singlet state geometry optimizations for all studied dyes using the density functional theory (DFT) with B3LYP hybrid functional[1] associated with 6-31G* basis set.[2] Time-dependent DFT (TDDFT) calculations using the B3LYP functional were then performed based on the optimized structures at ground states.[3] Oscillator strengths were deduced from the dipole transition matrix elements (for singlet states only). All calculations were carried out using the Gaussian 03 package.[4]

Furthermore, geometry optimizations of the A2-H and A2-F dye absorbed on TiO_2 surface, modeled by a $(TiO_2)_{38}$ cluster, were performed with a spin-polarized DFT method within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) functional form[5] implemented in the DMOL3 package.[6] The all-electron double numerical basis set with polarized function (the DNP basis set) was employed. The real-space global cutoff radius was set to be 4.5 Å and the Brilliouin zone was sampled by 4 x 4 x 1 k-points using the Monkhorst-Pack scheme. During the optimization, the forces on every atom were relaxed to be less than 0.0002 au/Å.

Table S1. Absorption (in 1:1 (v/v) acetonitrile: *tert*-butanol) and adsorptivity of organic sensitizers, A1, A2-H, A2-F.

sensitizers	λ_{max} [nm]	ε	adsorptivity
		at λ_{max} [$M^{-1}cm^{-1}$]	[10^{-8}mol]
A1	477	51,660	2.96
A2-H	450	52,560	3.08
A2-F	460	53,740	2.90

Figure S1. Frontier orbitals mainly involved in the lower-lying electronic transitions of **A1**.

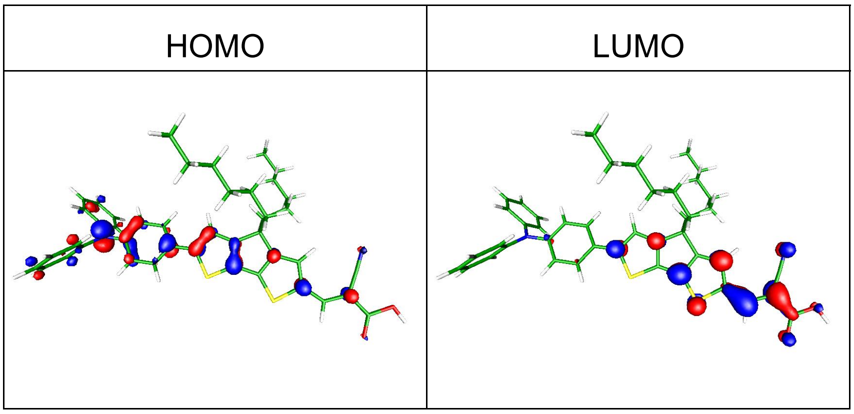


Figure S2. Frontier orbitals mainly involved in the lower-lying electronic transitions of **A2-F**.

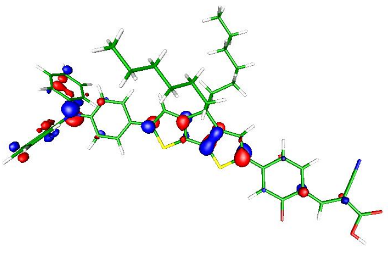
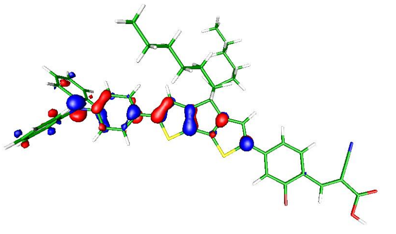
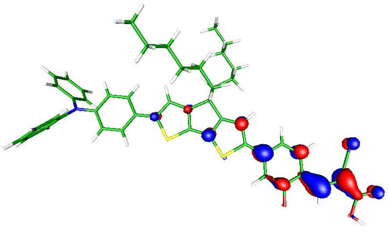
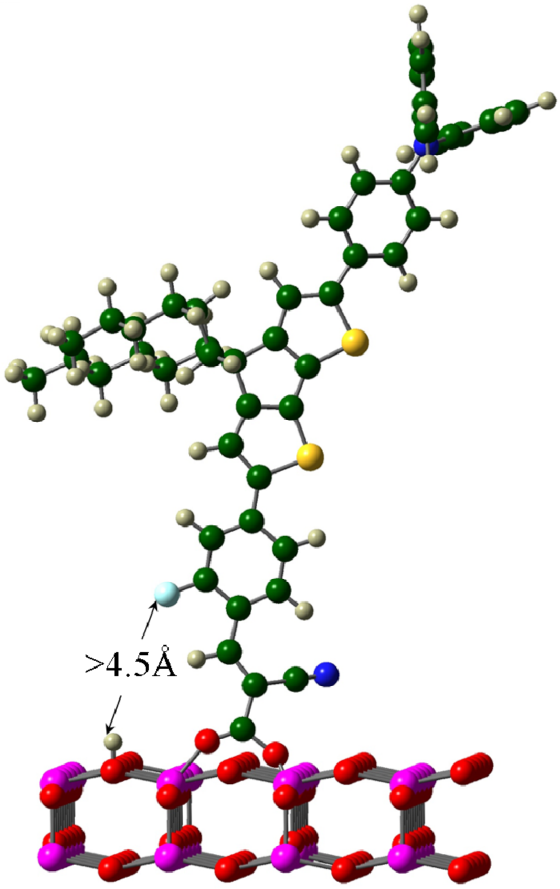
HOMO-1	HOMO	LUMO
		

Figure S3. The illustration of hydrogen-bonding (F-H) interaction between **A2-F** and TiO_2 upon geometry optimization. (see text for detail). Color illustration: Ti (pink), O (red), (blue) N, (grey) C, (light blue) F, (yellow) S.



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