Supporting Information

## Effect of Fluorine Substituent of Benzothiadiazole-based D-π-A'-π-A Photosensitizer of Dye-sensitized Solar Cells

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^{1}H NMR in $CDCl_3$ were recorded on a Varian INOVA 500NMR apparatus. Chemical shifts were calibrated against TMS as an internal standard. Mass spectra (MALDI–TOF MS) were measured on Micromass GCT–MS spectrometer.

1. Synthetic route to **LS101** and **LS102** dyes
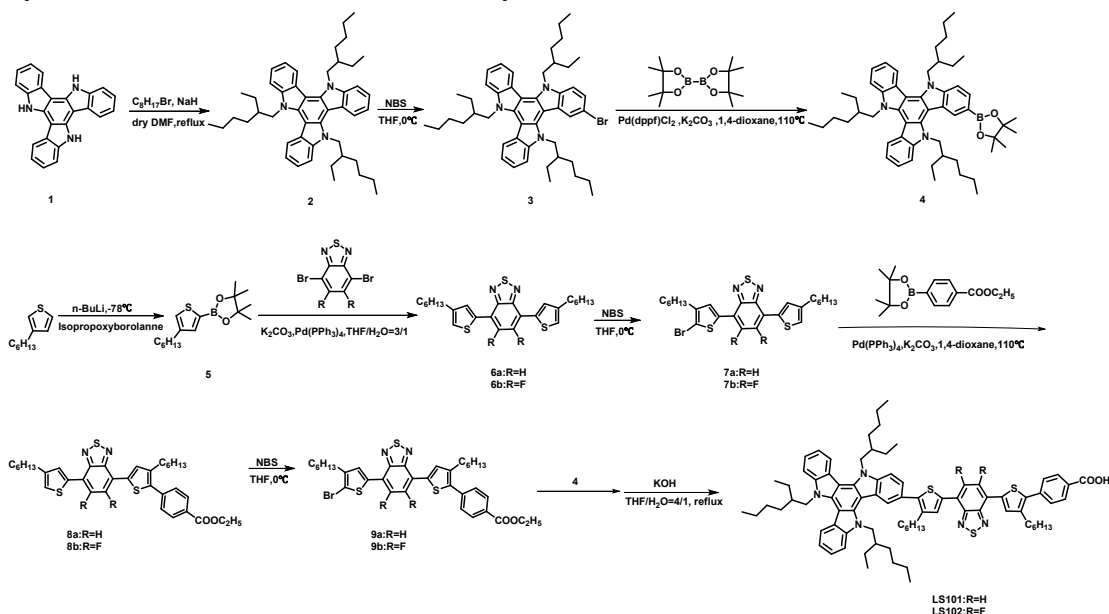
Scheme S1. Synthetic routes of **LS101** and **LS102** dyes

Compounds 1, 2, 3, 4[1], 5, 6, 7[2] and ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate[3] are synthesized by following the cited literature procedures.

ethyl4-(5-(7-(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophen-2-yl)benzoate(9a): Compound **7a** (684 mg, 1.25 mmol, 1eq.), ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (414 mg, 1.5 mmol, 1.2 eq.), K_2CO_3 (864 mg, 6.25 mmol, 5 eq.), $Pd(PPh_3)_4$ (10 mg/mmol) were dissolved in THF/H_2O (5:1, v/v) under N_2, and then the mixture was refluxed for 12 h. When the reaction was cooled to the room temperature, the mixture was poured into water, followed by extraction with DCM. The combined organic phase was dried by anhydrous $MgSO_4$ and solvent was removed by rotary evaporation. The crude product

was purified by silica gel column chromatography with petroleum ether/ DCM (1/1) as eluent to give out product **8a** (576 mg, 75% yield). Compound **8a** (576mg, 0.9 mmol, 1 eq.) was added in 50 mL THF, followed by bromination with NBS (192 mg, 1.08 mmol, 1.2 eq.) at 0 ℃. The addition of the NBS was needed to be very slow, and then the mixture was stirred for 6 h at 0-5 ℃. The resultant mixture was extracted three times with DCM before the organic phase was dried over $MgSO_4$. The product was isolated off on a silica gel column with 50% DCM in petroleum ether to give the desired product as a red solid **9a** (468 mg, 72% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 2H), 7.95 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 6.4 Hz, 2H), 7.56 (dd, J = 30.0, 8.3 Hz, 2H), 4.35 (d, J = 7.1 Hz, 2H), 2.63 (dt, J = 56.2, 7.8 Hz, 4H), 1.62 (tt, J = 15.3, 7.7 Hz, 4H), 1.36 (s, 15H), 0.82 (d, J = 16.4 Hz, 6H). MS (MALDI-TOF) m/z calculated for $C_{35}H_{39}BrN_2O_2S_3$: 694.1352; found:694.1334.

ethyl4-(5-(5,6-difluoro-7-(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophen-2-yl)benzoate(8b): Synthetic steps was in accordance with the **8a** synthesis method to accept light red solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.8, 7.1 Hz, 4H), 7.53 (d, J = 8.1 Hz, 2H), 7.13 (s, 1H), 4.35 (d, J = 7.1 Hz, 2H), 2.66 (d, J = 23.9 Hz, 4H), 1.62 (d, J = 5.4 Hz, 4H), 1.38 – 1.12 (m, 15H), 0.81 (dd, J = 14.7, 7.3 Hz, 6H). MS (MALDI-TOF) m/z calculated for $C_{35}H_{38}F_2N_2O_2S_3$: 652.2058; found: 652.2113.

4-(3-hexyl-5-(7-(4-hexyl-5-(5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazol-3-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)benzoic acid (LS101): In a 100 mL two-neck round-bottom flask equipped with a magnetic stirring bar was added compound **4** (500 mg, 0.62 mmol,1eq.), compound **9a** (475 mg, 0.62 mmol,1eq.), K_2CO_3(428 mg, 3.1 mmol, 5 eq.) and $Pd(PPh_3)_4$ (72 mg, 0.1 eq.) under an nitrogen atmosphere. Then, THF/H_2O (5:1, v/v) was added to the reaction mixture, which was heated at 80°C for 12 h. After cooling to room temperature, the solution was washed with water and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. After solvent removal, the crude product was purified by chromatography on silica gel using CH_2Cl_2: petroleum ether (3:2, v/v) to afford 0.63g red solid (78% yield). Then, to a mixture of the compounds obtained (500 mg, 0.38 mmol), KOH (1.08 g, 20 mmol) dissolved in water (5.0 mL), and THF (15.0 mL) in a round bottom flask was stirred at reflux for 36 h. After cooling to room temperature, the reaction was quenched with water, to which was then added 2 M HCl for neutralizing to pH = 1-3. Then the organic layer was extracted with CH_2Cl_2 and dried by anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified by chromatography (DCM/ methanol = 15/1) on silica gel to accept the final red solid (95% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.23 (s, 4H), 7.98 (s, 2H), 7.83 (s, 3H), 7.59 (s, 2H), 7.37 (s, 5H), 7.27 (s, 2H), 4.89 (s, 6H), 2.72 (s, 4H), 1.98

(s, 4H), 1.68 (dd, J = 50.7, 23.6 Hz, 9H), 1.27 (dd, J = 51.3, 17.8 Hz, 30H), 0.88-0.65 (m, 24H). MS (MALDI-TOF) m/z calculated for $C_{81}H_{97}N_5O_2S_3$: 1267.6799; found: 1267.6791.

4-(5-(5,6-difluoro-7-(4-hexyl-5-(5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazol-3-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophen-2-yl)benzoic acid (LS102): **LS102** is synthesized in the same way as **LS101**. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.32 (s, 1H), 8.20 (d, J = 14.8 Hz, 4H), 8.11 (s, 2H), 7.67 (s, 1H), 7.54 (s, 2H), 7.37 (s, 4H), 7.27 (d, J = 6.2 Hz, 3H), 4.88 (s, 6H), 2.72 (s, 4H), 1.97 (s, 4H), 1.68 (dd, J = 17.0, 8.5 Hz, 9H), 1.22 (d, J = 30.5 Hz, 30H), 0.88 (d, J = 6.3 Hz, 24H). MS (MALDI-TOF) m/z calculated for $C_{81}H_{95}F_2N_5O_2S_3$: 1303.6610; found: 1303.6564.

2. Material of DSSCs

[Co(bpy)$_3$](TFSI)$_2$ and [Co(bpy)$_3$](TFSI)$_3$ were purchased from Dyenamo AB. Sweden. 4-tert-butylpyridine (TBP) was purchased from TCI. Lithium bis(trifluoromethanesulphonyl)imide (TFSILi) was purchased from Alfa Aesar. 18-NRT Titania paste was purchased from Dyesol. TPP200, Surlyn films and counter electrodes (Pt-coated FTO conducting glass) were purchased from Dalian Hepta Chroma Solar Tech Co. Ltd. All the other solvents and chemicals were purchased through commercial channels.

3. Characterization of DSSCs

The UV-vis data was recorded by Agilent 8453 spectrophotometer. Current-voltage characteristics were recorded using a digital source meter (Keithley 2400). Cyclic voltammograms were recorded with a CHI660E (CH Instruments, Inc.) electrochemical workstation in a three-electrode electrochemical cell, and glassy carbon, Ag/AgCl and platinum wire were treated as working electrode, reference electrode and counter electrode, respectively. The electrochemical impedance spectroscopy (EIS) measurements were carried out at an impedance/gain-phase analyzer (Zahner Zennium, Serial No. 40037) electrochemical work station and the data was fitted with the Zahner software package. The Photocurrent Density-Voltage (*J-V*) data of DSSCs were measured under a simulate irradiation (100 mW cm^{-2}, AM 1.5G) provided by Sol3A Class AAA Solar Simulator (Newport USA, Model: 94023A) with a 450 Watt Xenon source. Newport-provided standard Silica-based reference cell (Newport USA, Model: 91150V) was used to calibrate the light intensity. Incident photo-to-current conversion efficiency (IPCE) data was acquired by a Hyper mono lighter (SM-25, Jasco Co. Ltd., Japan). In this method, a standard silicon solar cell was used as reference before the sample was measured.

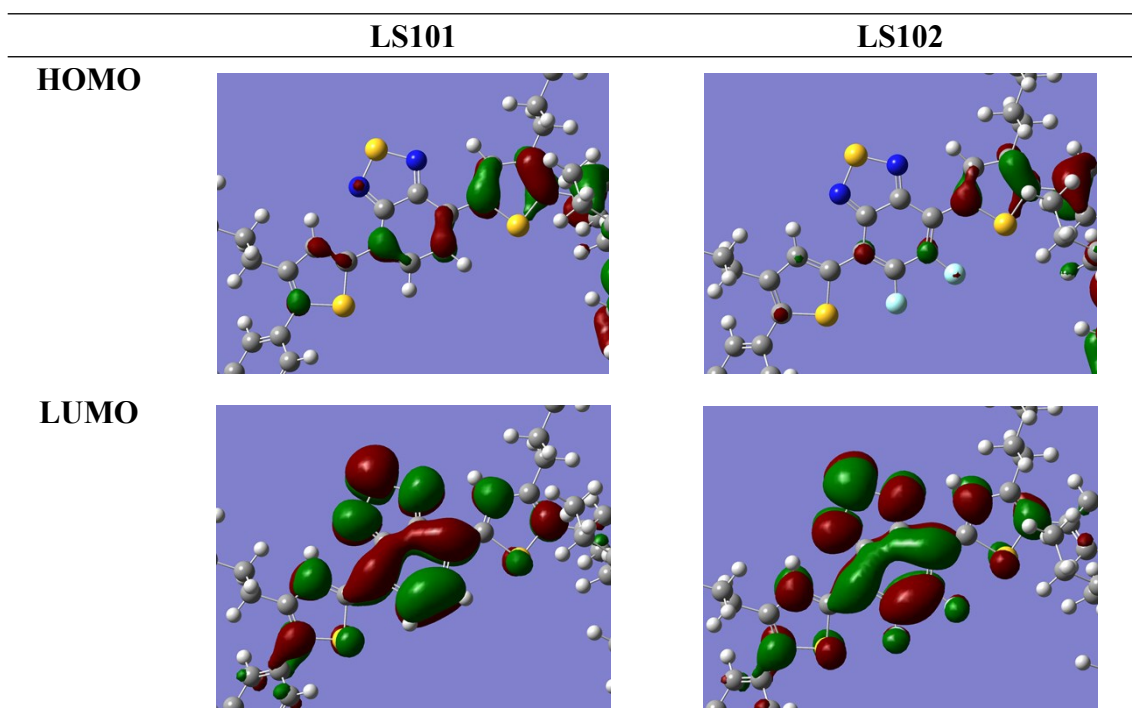4. The partial enlarged orbitals of **LS101** and **LS102**

	LS101	LS102
HOMO		
LUMO		

Figure S1. The partial enlarged orbitals of **LS101** and **LS102**

5. The measurement of dye loading amount on the surface of TiO_2 film

Firstly, the standard UV-visible absorption spectrum about a certain concentration of dye (1×10^{-5} mol•L^{-1}) in the THF/H_2O (V: V=1:1) solution of sodium hydroxide (NaOH) were recorded, obtaining the molar absorption coefficients of the dye. Then, two sensitized TiO_2 films (area: 4mm×4mm) were immersed in the solution mentioned above. After the dye was desorbed and dissolved in the solution completely, the obtained solution was constant volume to 10 ml by a volumetric bottle. By measuring the UV-visible absorption spectrum, the concentration of the solution can be calculated according to A= ε·bc, thus the dye loading amount on the film can be estimated.

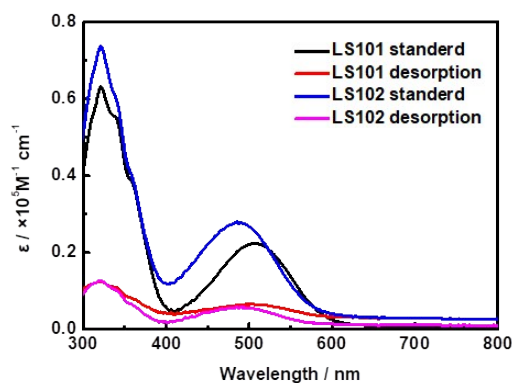Table S1. The adsorption amount of **LS101** and **LS102** dyes on TiO_2 film.

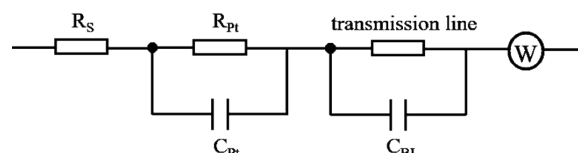| Dye	Standard ε at λ_{max} (M^{-1} cm^{-1})	Desorbed ε at λ_{max} (M^{-1} cm^{-1})	Dye-load mol•cm^{-2}($\times 10^{-8}$)
LS101	22623	6762	9.3
LS102	27723	5774	6.5

6. Equivalent circuit model

Figure S3. Equivalent circuit model of EIS data

7. Stability of solar cells

The stability of devices based on **LS101** and **LS102** were measured under dark condition for 1000h, the variation tendency of J_{sc}, V_{oc}, FF and PCE were recorded in Figure S4. The J_{sc} of both dyes had a relatively obvious decline, while the V_{oc} almost unchanged. The FF of **LS101** floated slightly, but that of **LS102** had a greater degree of increase. As a result, the PCEs maintained 89% and 94% of the initial level after 1000h under dark condition for **LS101** and **LS102** respectively.
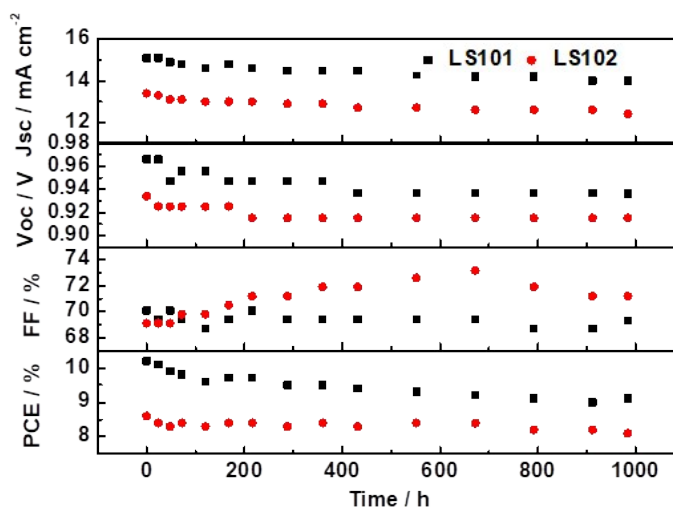

Figure S4. Evolution of photovoltaic parameters of devices based on the **LS101** and **LS102** sensitizers within 1000 hours
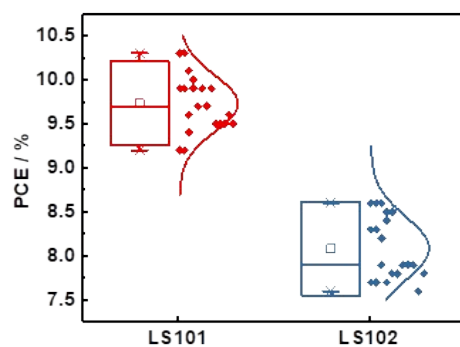
8. Repeatability of solar cells

Figure S5. *J-V* characteristics values shown as box plots for PCE distributions of 20 **LS101** and **LS102** devices.

References:

1.	L. Zhang, X. Yang, W. Wang, G. G. Gurzadyan, J. Li, X. Li, J. An, Z. Yu, H. Wang, B. Cai, A. Hagfeldt and L. Sun, *ACS Energy Lett.*, 2019, **4**, 943-951.

2.	J.-C. Li, E.-O. Seo, S.-H. Lee and Y.-S. Lee, *Macromolecular Research*, 2010, **18**, 304-307.

3.	L. Blank, M. Fagnoni, S. Protti and M. Rueping, *Synthesis*, 2019, **51**, 1243-1252.