Electronic Supporting Information

for

Significant Light Absorption Enhancement by Single Heterocyclic Unit Change in π-Bridge Moiety from Thieno[3,2-b]benzothiophene to Thieno[3,2-b]indole for High Performance Dye-Sensitized and Tandem Solar Cells

Yu Kyung Eom^a, Sung Ho Kang^a, In Taek Choi^a, YoungJun Yoo^b, Jeongho Kim^b and Hwan Kyu Kim^a,*

^aGlobal GET-Future Lab. & Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-ro, Sejong 339-700, Korea

^bDepartment of Chemistry, Inha University, 100 Inha-ro, Incheon 402-751, Korea

Detailed methods of materials and measurements

Materials and Synthesis

All reactions were carried out under a nitrogen atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma–Aldrich, TCI and Alfar Aesar. Tributyl(thiophen-2-yl)stannane,¹ bis(2',4'-dihexyloxybiphenyl-4-yl)-amine,² and 4-(4-bromobenzo[c][1,2,5]thiadiazol-7-yl)benzaldehyde³ were synthesized according to the literature with slight modifications.

Measurements

The ¹H NMR spectroscopy study was conducted on a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; d = 0 ppm) as the internal standard. Chemical shifts for ¹H NMR spectra were recorded on a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; d = 0 ppm) as the internal standard. The ¹³C NMR spectroscopy study was conducted on a Bruker Biospin Gmbh AVAVCE II 900 spectrometer using tetramethylsilane (TMS; d =0 ppm) as the internal standard. MALDI-TOF mass spectra were recorded by a Voyager-DETM STR biospectrometry workstation.

Time-resolved photoluminescence

The steady-state emission spectra of the dye sensitizers were measured with a FluoroLog-322 (Horiba) spectrometer equipped with a 450W Xe arc lamp. Time-resolved photoluminescence (TR-PL) was measured using a time-correlated single-photon counting spectrometer (FluoTime 200, PicoQuant) equipped with a picosecond diode laser (LDH-P-C-390, PicoQuant) and a hybrid photomultiplier detector (PMA Hybrid 50, PicoQuant). The film samples consisting of dyes adsorbed on a layer of TiO₂ (3.5 μ m thickness) or Al₂O₃ (4.0 μ m thickness) were excited by ~100 ps laser pulses of 393 nm centre wavelength; the

emission was measured at $\lambda_{em max}$ for each dye. The time resolution of the TR-PL measurement was ~190 ps nominally but effectively reduced to < 50 ps by deconvolution of the instrument response function.

Transient photovoltage and photocurrent decay measurements

In transient photovoltage measurements, DSSCs were irradiated by a diode LED (635 nm), and the decay of open-circuit voltage, caused by a stepwise decrease of a small fraction of the laser intensity, was measured. The resulting photovoltage decay transients were collected and the τ values are determined by fitting the data to the equation exp ($-t/\tau$).

DSSC fabrications

FTO glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a mucasol liquid cleaner (Aldrich) in an ultrasonic bath for 30 min, then rinsed with deionized water and ethanol. The FTO glass plates were immersed in 40 mM TiCl₄ (aqueous) at 70 °C for 30 min, then washed with deionized water and ethanol. A transparent nanocrystalline layer on the FTO glass plate was prepared by repeated screen printing with TiO₂ paste (Dyesol, 18NR-T) and then dried at 120 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. A paste for the scattering layer containing 400 nm anatase particles (CCIC, PST-400C) was deposited by screen printing and then dried for 1 h at 25 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 325 °C for 5 min, at 375 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min. The resulting layer was composed of a 4.0 µm thick transparent layer and a 3.5 µm thick scattering layer. The thickness of the transparent layer was measured using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA). The TiO₂ electrodes were again treated with TiCl₄ at 70 °C for 30 min and sintered at

500 °C for 30 min. The TiO₂ electrodes were immersed in the dye solution (0.3 mM in THF/EtOH=1:2 containing 20 mm CDCA) and kept at room temperature for 2 h. The FTO plate (Pilkington TEC Glass-TEC 8, solar 2.3 μ m thickness) used as the counter electrode was cleaned in an ultrasonic bath in H₂O, acetone and 0.1 M HCl aqueous. The counter electrodes were prepared by coating with a drop of H₂PtCl₆ solution (2 mg of Pt in 1 mL of ethanol) on an FTO plate and heated at 400 °C for 15 min. The dye adsorbed on the TiO₂ electrode and the Pt-counter electrode were assembled into a sealed sandwich-type cell by heating at 80 °C with a hot-melt film (25 μ m thick Surlyn) as a spacer between the electrodes. A drop of the electrolyte solution was placed on a drilled hole in the counter electrode of the assembled cell and driven into the cell through vacuum backfilling. Finally, the hole was sealed using additional Surlyn and cover glass (0.1 μ m thick).

Photoelectrochemical measurements of DSSC

Photoelectrochemical data were measured using a 1000 W xenon light source (Oriel, 91193) that was focused to provide 100 mW cm⁻², the equivalent of one sun at AM 1.5 G at the surface of the test cell. The light intensity was adjusted with a Si solar cell that was double-checked with an NREL-calibrated Si solar cell (PV Measurement, Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current–voltage characteristics of the cells under these conditions were determined by biasing the cell externally and measuring the photocurrent generated. This process was fully automated using Wavemetrics software. IPCE was measured in AC mode under bias light using a specially designed IPCE system (PV measurement Inc.) equipped with a 75 W xenon lamp as a light source for monochromatic beam and a 75 W–12 V halogen lamp as a bias light source. The IPCE (λ) curve is expressed in the following equation: IPCE (λ) = 1240

 (J_{sc}/λ_{ϕ}) , where λ is the wavelength, J_{sc} is the current at short circuit (mA cm⁻²), and ϕ is the incident radiative (W m⁻²), which can be derived from the measured absorption spectrum of the DSSC for comparison.

Experimental Section

2-(4-bromo-2-nitrophenyl) thiophene (1)

A mixture of tributyl (thiophen-2-yl) stannane (5.15 g, 13.80 mmol), 1,4-dibromo-2nitrobenzene (4.0 g, 13.80 mmol), Pd (PPh₃)₂Cl₂ (0.78 g, 1.1 mmol), and 200 mL toluene was refluxed at 110°C for 12 hrs under nitrogen, then extracted with CH₂Cl₂. The organic layer was washed with brine and water and dried over magnesium sulfate, filtered and concentrated in a vacuum. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/*n*-hexane (ν/ν , 1:2) as eluent to afford **1** as an oil (2.83g, 94%). ¹H NMR (300 MHz, CDCl₃) δ : 7.89 (d, J = 1.8 Hz, 1H), 7.68-7.71 (dd, $J_1 = 1.8$ Hz, $J_2 = 8.4$ Hz,1H), 7.41-7.44 (m, 2 H), 7.08 (d, J = 7.5 Hz, 2H). ¹³C NMR (300 MHz, CDCl₃) δ : 121.84, 126.76, 127.14, 127.29, 127.90, 128.48, 133.07, 133.98, 134.85, 135.68.

6-bromo-4*H*-thieno[3,2-*b*]indole (2)

A mixture of compound **1** (1.69 g, 5.95 mmol) and triphenylphophine (4.68 g, 17.84 mmol) in 1,2-dichlorobenzene (50 mL) was refluxed for 12 hrs under nitrogen, then extracted with CH₂Cl₂. The organic layer was washed with brine and water and dried over magnesium sulphate, filtered and concentrated in vacuum. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/*n*-hexane (v/v, 2:1) as eluent to yield **2** as a white powder (0.6 g, 40%). ¹H NMR (300 MHz, CDCl₃) δ : 8.18 (s, 1H), 7.58-7.61 (m, 2H), 7.39 (d, J = 5.4 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 5.1 Hz, 1H). ¹³C NMR (300 MHz,

CDCl₃) δ: 141.93, 128.48, 126.93, 122.44, 120.75, 119.37, 115.67, 114.25, 112.55, 110.68. HRMS (EI) *m/z* calculated (M⁺) for C₁₀H₆BrNS: 252.9384; found: 253.2161.

6-bromo-4-ethyl-4*H*-thieno[3,2-*b*]indole (3a)

Compound **2** (0.2 g, 0.79 mmol) and potassium hydroxide (0.45 g, 7.93 mmol) were dissolved in acetone (20 mL). Bromoethane (0.12 mL, 1.59 mmol) was added to the mixture. The mixture was stirred for 5 hr. After the reaction was finished, the reactant was extracted with CH₂Cl₂. The organic layer was washed with brine and water and dried over magnesium sulphate, filtered and concentrated under a vacuum. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/*n*-hexane (ν/ν , 1:2) as eluent to afford **3a** as a white powder (0.15 g, 67%). ¹H NMR (300 MHz, CDCl₃) δ : 7.58-7.61 (d, *J* = 9 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 5.1 Hz, 1H), 7.28 (d, *J*₁ = 1.8 Hz, *J*₂ = 1.8 Hz, 1H), 7.07 (d, *J* = 5.1 Hz, 1H), 4.25-4.32 (q, *J*₁ = 5.1 Hz, *J*₂ = 6.9 Hz, *J*₃ = 7.2 Hz, 2H), 1.42-1.47 (t, *J*₁ = 6.9 Hz, *J*₂ = 7.2 Hz, 3H). ¹³C NMR (300 MHz, CDCl₃) δ : 141.73, 128.20, 126.69, 120.92, 119.50, 115.87, 112.08, 111.30, 109.41, 40.10, 14.78. HRMS (EI) *m/z* calculated (M⁺) for C₁₂H₁₀BrNS: 280.9697; found: 281.1573.

6-bromo-4-hexyl-4H-thieno[3,2-b]indole (3b)

The mixture of compound **2** (0.3 g, 1.19 mmol) and potassium hydroxide (0.67 g, 11.9 mmol) was dissolved in acetone (10 mL). Then bromohexane (0.33 mL, 2.38 mmol) was added to the mixture. The mixture was stirred for 5 hr. After the reaction finished, the reactant was extracted with CH_2Cl_2 . The organic layer was washed with brine and water and dried over magnesium sulphate, then filtered and concentrated in a vacuum. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/n -hexane (v/v, 1:3) as eluent to afford **3b** as a yellow oil (0.25 g, 62%). ¹H NMR (300 MHz, CDCl₃) δ : 7.58-7.61 (d, J = 8.1

Hz, 1H), 7.53 (d, J = 1.8 Hz, 1H), 7.40 (d, J = 5.4 Hz, 1H), 7.28 (dd, J = 1.8 Hz, 1H), 7.06 (d, J = 5.4 Hz, 1H), 4.18-4.22 (t, $J_1 = 7.2$ Hz, $J_2 = 6.9$ Hz, 2H), 1.80-1.87 (m, 2H), 1.21-1.34 (m, 6H), 0.89 (t, $J_1 = 6.9$ Hz, $J_2 = 7.2$ Hz, 3H). ¹³C NMR (300 MHz, CDCl₃) δ : 142.15, 126.98, 126.56, 121.48, 120.89, 119.43, 115.79, 112.17, 111.43, 109.61, 45.55, 31.0, 29.80, 26.93, 22.67, 14.30. HRMS (EI) *m/z* calculated (M⁺) for C₁₆H₁₈BrNS: 337.0323; found: 337.1534.

N,*N*-Bis(2',4'-dihexyloxybiphenyl-4-yl)-*N*-ethylthieno[3,2-*b*][1]indole-6-amine (4a)

Bis(2',4'-dihexyloxybiphenyl-4-yl)-amine (0.23g, 0.32 mmol), compound **3a** (0.1 g, 0.36 mmol), Pd₂(dba)₃ (0.01 g, 0.01 mmol), P(*t*-Bu)₃ (0.01 ml, 0.01 mmol), and sodium tertbutoxide (0.05g, 0.48 mmol) in dry toluene (15 ml) was heat to reflux for 1 hr. After cooling to room temperature, saturated ammonium chloride solution was added to the reaction solution. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH₂Cl₂/*n*-hexane (*v*/*v*, 1:3) as eluent to afford **3a** as a yellow sticky solid (0.2 g, 66%). ¹H NMR (300 MHz, CDCl₃) δ : 7.66 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 4H), 7.33 (d, *J* = 5.1 Hz, 1H), 7.28 (m, 2H) 7.17 (d, *J* = 8.7 Hz, 4H), 7.02-7.06 (m, 3H), 6.52-6.54 (m, 4H), 4.17-4.22 (q, *J*₁ = 6.9 Hz, *J*₂ = 7.2 Hz, 2H), 3.93-4.00 (q, *J*₁ = 6.0 Hz, *J*₂ = 7.0 Hz, 8H), 1.84 (m, 8H), 1.28-1.48 (m, 24H), 0.84-0.94 (m, 15H). ¹³C NMR (300 MHz, CDCl₃) δ : 159.56, 157.10, 157.02, 146.72, 145.32, 143.38, 141.96, 141.93, 132.03, 131.60, 129.55, 129.30, 123.64, 123.21, 118.95, 118.44, 115.14, 106.62, 105.63, 100.76, 68.46, 68.23, 41.23, 31.77, 31.59, 29.46, 29.18, 25.88, 22.77, 22.71, 14.19. MS (MALDI-TOF) *m/z* calculated for C₆₀H₇₆N₂O₄S: 920.5526; found: 920.4792.

N,*N*-Bis(2',4'-dihexyloxybiphenyl-4-yl)-*N*-hexylthieno[3,2-*b*][1]indole-6-amine (4b)

Bis(2',4'-dihexyloxybiphenyl-4-yl)-amine (0.23g, 0.32 mmol), compound **3b** (0.2 g, 0.59 mmol), Pd₂(dba)₃ (0.015 g, 0.02 mmol), P(*t*-Bu)₃ (0.01 ml, 0.02 mmol), and sodium tert-

butoxide (0.08g, 0.80 mmol) in dry toluene (15 ml) was heated to reflux for 1 hr. After cooling to room temperature, saturated ammonium chloride solution was added to the reaction solution. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH₂Cl₂/*n*-hexane (v/v, 1:3) as eluent to yield **4b** as a yellow sticky solid (0.3 g, 62%). ¹H NMR (300 MHz, CDCl₃) δ : 7.66 (d, J = 8.7 Hz, 1H), 7.44 (d, J = 9.0 Hz, 4H), 7.32 (d, J = 5.1 Hz, 1H), 7.28 (m, 2H) 7.17 (d, J = 8.1 Hz, 4H), 7.02-7.05 (m, 3H), 6.52-6.55 (m, 4H), 4.14 (t, 2H), 3.93-4.00 (q, $J_1 = 8.1$ Hz, $J_2 = 6.6$ Hz, 8H), 1.73-1.84 (m, 10H), 1.27-1.48 (m, 30H), 0.80-0.94 (m, 15H). ¹³C NMR (300 MHz, CDCl₃) δ : 159.57, 157.13, 157.03, 146.73, 145.73, 143.27, 142.43, 131.98, 130.91, 129.96, 129.58, 129.21, 123.68, 123.26, 118.87, 118.39, 117.77, 106.64, 105.04, 100.88, 68.49, 68.23, 45.29, 32.51, 31.77, 29.85, 29.19, 26.92, 25.89, 22.72, 14.24 MS (MALDI-TOF) *m*/*z* calculated for C₆₄H₈₄N₂O₄S: 976.6152; found: 976.5311.

N,*N*-bis(2',4'-bis(hexyloxy)biphenyl-4-yl)-2-bromo-4-ethyl-4*H*-thieno[3,2-*b*]indol-6amine (5a)

Compound **4a** (0.57 g, 0.62 mmol) was dissolved in 100 mL of chloroform. NBS (0.11 g, 0.62 mmol) was added to one portion. The mixture was stirred for 1 hr, and the mixture was poured into water. Aqueous was extracted with dichloromethane, and the combined organic layer was dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH₂Cl₂/*n*-hexane (ν/ν , 1:2) as eluent to yield **5a** as a yellow sticky solid (0.6 g, 97%). ¹H NMR (300 MHz, CDCl₃) δ : 7.58 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 4H), 7.24-7.28 (m, 3H), 7.17 (d, *J* = 9.3 Hz, 4H), 7.10 (d, *J* = 5.4 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 7.03 (d, *J* = 1.8 Hz, 1H), 6.53-6.55 (m, 4H), 4.16 (q, *J* = 7.5 Hz, 2H), 3.94-4.01 (q, *J*₁ = 7.2 Hz, *J*₂ = 6.3 Hz, 8H), 1.85 (m, 8H), 1.28-1.47 (m, 24H), 0.84-0.94 (m, 15H). ¹³C NMR (300 MHz, CDCl₃) δ :

159.58, 157.08, 146.62, 144.04, 142.76, 140,78, 132.26, 131.10, 13091, 13013, 13001, 123.69, 122.87, 120.92, 118.91, 116.38, 113.08, 107.00, 105.44, 100.62, 68.49, 68.21, 39.92, 31.75, 29.46, 45.89, 22.76, 14.17.

N,*N*-bis(2',4'-bis(hexyloxy)biphenyl-4-yl)-2-bromo-4-hexyl-4*H*-thieno[3,2-*b*]indol-6amine (5b)

The compound **4b** (0.2 g, 0.2 mmol) was dissolved in 100 mL of chloroform. NBS (0.04 g, 0.2 mmol) was added to one portion. A mixture was stirred for 1 hr, and the mixture was poured into water. Aqueous was extracted with dichloromethane, and the combined organic layer was dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH₂Cl₂/*n*-hexane (ν/ν , 1:2) as eluent to afford **5b** as a yellow sticky solid (0.19 g, 88%). ¹H NMR (300 MHz, CDCl₃) δ : 7.58 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 4H), 7.25-7.29 (m, 3H), 7.18 (d, *J* = 9.0 Hz, 4H), 7.09 (d, *J* = 6.0 Hz, 1H), 7.06 (d, *J* = 1.8 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 6.53-6.56 (m, 4H), 4.11 (t, *J*₁ = 6.3 Hz, *J*₂ = 6.9 Hz, 2H), 3.95-4.02 (q, *J*₁ = 6.9 Hz, *J*₂ = 6.9 Hz, 8H), 1.72-1.86 (m, 10H), 1.27-1.49 (m, 30H), 0.84-0.95 (m, 15H). ¹³C NMR (300 MHz, CDCl₃) δ : 159.56, 157.08, 146.60, 143.57, 143.25, 141.24, 132.21, 131.35, 130.59, 130.20, 129.63, 123.73, 122.80, 121.91, 118.92, 116.21, 112.28, 107.25, 105.65, 100.79, 69.55, 68.51, 45.30, 31.59, 29.46, 29.19, 26.85, 25.89, 22.71, 14.24.

4-(7-(6-(Bis(2',4'-dihexyloxybiphenyl-4-yl)amino)-N-ethylthieno[3,2-b][1]indole-2-

y1)benzo[c][1,2,5]thiadiazol-4-yl)benzaldehyde (6a)

Compound **5a** (0.6 g, 0.60 mmol) was dissolved in distilled 70 mL THF and cooled down to-78 °C under a nitrogen atmosphere, then *n*-BuLi (0.72 mmol, 0.29 mL, 1.2 eq., 2.5 M in n-hexane) was added dropwise to the mixture. After stirring for 1 h at the same temperature, tri-

n-butyltin chloride (0.18 mL, 0.66 mmol, 1.1 eq.) was slowly injected into the reaction solution. After stirring for 1 h at the same temperature, the mixture was warmed to room temperature and stirred further overnight. The crude product was used without further purification. Dry toluene (20 mL), crude product (0.2 g, 0.63 mmol), 4-(4bromobenzo[c][1,2,5]thiadiazol-7-yl)benzaldehyde (0.91g, 0.75 mmol, 1.2 eq.) and Pd (PPh₃)₂Cl₂ (0.01 g, 0.02 mmol) were combined in a 50 mL round-bottom flask. The mixture was refluxed at 110°C for 12 hrs under nitrogen, then extracted with CH₂Cl₂. The organic layer was washed with brine and water and dried over magnesium sulphate, then filtered and concentrated in a vacuum. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/n -hexane (v/v, 1:1) as eluent to afford **6a** as purple oil (0.33 g, 46 %). ¹H NMR (300 MHz, CDCl₃) δ : 10.11 (s, 1H), 8.42 (s, 1H), 8.19 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 5.4 Hz, 1H), 7.82 (d, J = 4.5 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 6.9 Hz, 4H), 7.28-7.30 (m, 3H), 7.22 (d, J = 5.4 Hz, 4H), 7.09 (d, J = 1.8 Hz, 1H), 7.06 (d, J = 1.8 Hz, 1H), 6.56 (m, 4H), 4.31 (q, J = 6.9 Hz, 2H), 3.96-4.02 (q, $J_1 = 6.0$ Hz, $J_2 = 6.0$ Hz, 8H), 1.83 (m, 8H), 1.29-1.52 (m, 24H), 0.85-0.95 (m, 15H). ¹³C NMR (300 MHz, CDCl₃) δ: 192.06, 159.59, 157.12, 154.05, 152.69, 146.52, 14451, 143.40, 142.44, 139.24, 135.77, 132.46, 131.88, 131.09, 130.95, 130.39, 130.10, 130.16, 129.98, 129.24, 128.96, 124.18, 123.99, 123.13, 122.32, 122.09, 120.01, 119.66, 119.27, 118.66, 117.95, 117.68, 113.39, 112.15, 106.61, 105.85, 105.35, 101.69, 100.62, 100.45, 99.31, 68.49, 39.92, 31.75, 29.46, 25.89, 22.76, 14.16. MS (MALDI-TOF) *m/z* calculated for C₇₃H₈₂N₄O₅S₂: 1158.5727; found: 1158.4911.

4-(7-(6-(Bis(2',4'-dihexyloxybiphenyl-4-yl)amino)-*N*-hexylthieno[3,2-*b*][1]indole-2y1)benzo[c][1,2,5]thiadiazol-4-yl)benzaldehyde (6b)

Compound 5b (0.3 g, 0.28 mmol) was dissolved in 50 mL of distilled THF and cooled down

to -78 °C under a nitrogen atmosphere; then n-BuLi (0.34 mmol, 0.14 mL, 1.2 eq., 2.5 M in n-hexane) was added dropwise to the mixture. After stirring for 1 h at the same temperature, tri-n-butyltin chloride (0.1 mL, 0.31 mmol, 1.1 eq.) was slowly injected into the reaction solution. After stirring for 1 h at the same temperature, the mixture was warmed to room temperature and stirred further overnight. The crude product was used without further purification. In a 50 mL round bottom flask was added dry toluene (20 mL), the crude product (0.14 g, 0.44 mmol), 4-(4-bromobenzo[c][1,2,5]thiadiazol-7-yl)benzaldehyde (0.67g, 0.53 mmol, 1.2eq) and Pd(PPh₃)₂Cl₂ (0.01 g, 0.02 mmol). The mixture was refluxed at 110° C for 12 hrs under nitrogen, then extracted with CH₂Cl₂. The organic layer was washed with brine and water and dried over magnesium sulphate, filtered and concentrated in a vacuum. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/nhexane (v/v, 1:1) as eluent to afford **6b** as purple oil (0.27 g, 51 %). ¹H NMR (300 MHz, CDCl₃) δ : 10.11 (s, 1H), 8.39 (s, 1H), 8.20 (d, J = 7.5 Hz, 2H), 8.01-8.07 (m, 3H), 7.83 (d, J= 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.4 Hz, 4H), 7.30 (m, 3H), 7.21 (d, J =5.4 Hz, 4H), 7.08 (d, J = 8.4 Hz, 2H), 6.56 (m, 4H), 4.23 (t, 2H), 3.95-4.02 (q, $J_1 = 6.0$ Hz, J_2 = 6.9 Hz, 8H), 1.75-1.83 (m, 10H), 1.26-1.46 (m, 30H), 0.84-0.95 (m, 15H). ¹³C NMR (300 MHz, CDCl₃) δ: 192.08, 159.64, 127.13, 154.05, 152.76, 146.54, 146.31, 144.42, 143.45, 142.92, 139.19, 135.82, 132.47, 131.95, 131.28, 130.61, 130.43, 130.20, 130.01, 129.82, 129.45, 129.04, 124.45, 123.21, 122.82, 122.22, 120.36, 119.73, 119.48, 118.87, 117.95, 117.85, 112.53, 112.27, 106.76, 105.67, 105.25, 100.78, 100.38, 99.30, 68.54, 68.26, 45.25, 31.76, 29.47, 25.91, 22.72, 14.06. MS (MALDI-TOF) *m/z* calculated for C₇₇H₉₀N₄O₅S₂: 1214.6353; found: 1214.5425.

3-(4-(7-(6-(Bis(2',4'-dihexyloxybiphenyl-4-yl)amino)-*N*-ethylthieno[3,2-*b*][1]indole--2y1)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)-2-cyanoacrylic acid (SGT-136) The compound **6a** (0.33 g, 0.29 mmol), dissolved in CHCl₃ (15 mL) and acetonitrile (15 mL) was condensed with 2-cyanoacetic acid (0.25g, 2.88 mmol) in the presence of piperidine (0.12 g, 1.44 mmol). The mixture was refluxed for 12 h. After cooling the solution, the organic layer was removed from the vacuum. The dark purple solid of SGT-136 was obtained by silica gel chromatography (CH₂Cl₂/MeOH (ν/ν , 10:1)). Yield was 70% (0.25 g). ¹H NMR (300 MHz, THF- d_8) δ : 8.44 (s, 1H), 8.37 (s, 1H), 8.07 (m, 3H), 7.81 (s, 1H), 7.67 (s, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 7.5 Hz, 5H), 7.25 (s, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 4H), 6.89 (d, J = 8.7 Hz, 1H), 6.54 (s, 2H), 6.48 (d, J = 8.4 Hz, 2H), 3.90-3.96 (q, $J_1 = 5.4$ Hz, $J_2 = 6.3$ Hz, 8H), 1.95 (d, J = 4.5 Hz, 2H), 1.66-1.78 (m, 8H), 1.29-1.49 (m, 24H), 0.84-0.95 (m, 15H). ¹³C NMR (900 MHz, THF- d_8) δ : 169.04, 159.21, 156.60, 153.16, 151.97, 146.01, 145.30, 143.79, 141.95, 138.92, 132.24, 131.84, 130.06, 129.46, 129.28, 128.76, 127.94, 127.79, 122.49, 122.21, 120.19, 119.30, 117.97, 117.78, 117.24, 111.41, 106.20, 104.78, 99.75, 67.59, 67.16, 53.52, 31.51, 31.29, 31.06, 29.27, 28.99, 28.72, 19.55, 13.73. MS (MALDI-TOF) *m/z* calculated for C₇₆H₈₃N₅O₆S₂: 1225.5785; found: 1225.4487.

3-(4-(7-(6-(Bis(2',4'-dihexyloxybiphenyl-4-yl)amino)-*N*-hexylthieno[3,2-*b*][1]indole-2y1)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)-2-cyanoacrylic acid (SGT-137)

The compound **6b** (0.27 g, 0.22 mmol), dissolved in CHCl₃ (15 mL) and acetonitrile (15 mL) was condensed with 2-cyanoacetic acid (0.19 g, 2.22 mmol) in the presence of piperidine (0.09 g, 1.11 mmol). The mixture was refluxed for 12 h. After cooling the solution, the organic layer was removed by vacuum. The dark purple solid of SGT-137 was obtained by silica gel chromatography (CH₂Cl₂/MeOH (ν/ν , 10:1)). Yield was 67% (0.17 g). ¹H NMR (300 MHz, THF- d_8) δ : 8.46 (s, 1H), 8.36 (s, 1H), 8.04 (m, 3H), 7.76 (m, 1H), 7.64 (m, 1H), 7.47 (d, 1H), 7.41 (d, J = 7.2 Hz, 5H), 7.22 (s, 1H), 7.16 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 7.8 Hz, 1H), 6.54 (s, 2H), 6.45 (d, J = 7.2 Hz, 2H), 3.92 (m, 8H), 1.94

(m, 2H), 1.73 (m, 10H), 1.29-1.49 (m, 30H), 0.85-0.95 (m, 15H). ¹³C NMR (900 MHz, THF d_8) δ : 169.11, 159.19, 156.59, 153.13, 151.96, 145.98, 145.77, 143.66, 142.38, 139.45, 138.89, 132.21, 130.08, 129.47, 128.73, 127.89, 127.66, 124.56, 123.56, 122.50, 122.18, 120.18, 119.28, 117.93, 117.43, 116.99, 111.64, 108.83, 104.78, 99.77, 67.59, 67.16, 43.97, 39.63, 31.67, 29.27, 29.00, 28.81, 26.20, 19.56, 13.09. MS (MALDI-TOF) *m/z* calculated for C₈₀H₉₁N₅O₆S₂: 1281.6411; found: 1281.5063.

References

- (1) Ref [10] in manuscript.
- (2) Ref [11b] in manuscript.
- (3) Ref [9] in manuscript.



Figure S1. Cyclic voltammograms of π -bridge units.

The redox potentials of π -bridge moieties were measured at the same concentration of electrolyte (0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆)) in anhydrous acetonitrile. Measurements were carried using the Pt plate as working electrode together with a set of Pt wire and Ag/Ag⁺ as counter and reference electrode, respectively, with scan rate of 50 mV s⁻¹. The potential of the reference electrode was calibrated with Fc/Fc⁺ as an external reference using E_0 (Fc/Fc⁺) = 0.63 V vs. NHE.

	E ^{DFT a} (eV)	$E_{_{ m ox}}^{_{ m DFT a}}$ (eV)	$E_{_{ox}^{*}}^{_{ m DFT}a}$ (eV)	$\lambda_{absmax}^{DFT\ b}$ (nm)	f^{b}	MO transition ^b
ТВТ	4.60	-5.90	-1.30	287 294	0.21 0.32	H-1→L (70%), H→L (9%), H→L+1 (18%) H-1→L (9%), H→L (86%), H-1→L+1 (4%),
Ethyl-TI	4.57	-5.55	-0.98	291 306	0.34 0.14	H-1→L (74%), H→L (14%), H→L+1 (6%) H-1→L (15%), H→L (81%)
Hexyl-TI	4.51	-5.49	-0.98	291 307	0.34 0.13	H-1→L (73%), H→L (14%), H→L+1 (5%) H-1→L (15%), H→L (81%)

Table S1. Photophysical and electrochemical properties of sensitizers on DFT calculations

^aTheoretical frontier orbital energy levels are computed with the DFT method at the B3LYP/6-31G(d,p) level in tetrahydrofurn. Energy gaps ($E_{0.0}^{DFT}$) are calculated via $E_{0.0}^{DFT} = E_{0.0}^{DFT} - E_{0.0}^{DFT}$.

 ${}^{b}E_{0-0}$ was determined from the intersection of absorption and emission spectra in THF.

 ${}^{c} \lambda_{absmax}^{DFT b}$, *f*, and the corresponding transition were computed with the TD-DFT method at the B3LYP/6-31G(d,p) level in tetrahydrofurn.



Figure S2. Projected densities of states (PDOS) for (a) TBT (blue), (b) ethyl-TI (red) and (c) hexyl-TI (green) including benzene (navy), the core ring (yellow–green), alkyl (yellow), and outside thiophene (pink) as individual aromatic rings. Each total density of state is shown as a dashed line.

Table S2. Molecular orbital contributions (in %) of the HOMO and LUMO orbitals of each π -bridge

			Molecular orbital contribution (in %)						
			Core T ^a						
	Orbital	Energy (eV)	Benzene	Core N ^b	Alkyl in core ^b	Outside T			
ТВТ	LUMO	-1.31	36	3	3	32			
	номо	-5.89	36	45		18			
Ethyl-TI	LUMO	-0.92	41	22	1	36			
	номо	-5.43	34	48	1	17			
Hexyl-TI	LUMO	-0.9	41	22	1	36			
	номо	-5.4	34	48	1	17			



Figure S3. Cyclic voltammograms of all SGT sensitizers.

The redox potentials of dyes were measured at the same concentration of electrolyte (0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆)) in anhydrous acetonitrile (oxidation) or tetrahydrofuran (reduction). Measurements were carried using the TiO₂ films (oxidation) or Pt plate (reduction) as the working electrode, together with a set of Pt wire and Ag/Ag⁺ as counter and reference electrode, respectively, with scan rate of 50 mV s⁻¹. The potential of the reference electrode was calibrated with Fc/Fc⁺ as an external reference using E_0 (Fc/Fc⁺) = 0.63 V vs. NHE. Measurements were obtained using a 2 µm TiO₂ film deposited on conducting FTO glass in CH₃CN containing 0.1M TBAPF₆ as the supporting electrolyte with a 50 mV s⁻¹ scan rate.



Figure S4. Optimized structure, dihedral angles and lengths of all SGT sensitizers.



Figure S5. Simulated absorption spectra of the **SGT** sensitizers in THF calculated at the CAM-B3LYP/6-31G(d,p).

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	E ^{DFT a} (eV)	E ^{DFT a} (eV)	E ^{DFT a} ox [*] (eV)	$\lambda_{absmax}^{DFT\ a}$ (nm)	f^a	MO transition ^a
SGT-130	4.25	-6.01	-1.76	299 480	1.60 1.18	H→L+3 (78%), H-2→L+7 (2%) H-1→L (33%), H→L (50%)
SGT-136	4.07	-5.88	-1.81	305 512	1.57 1.20	H→L+3 (77%), H-1→L+3 (9%) H-1→L (27%), H→L (56%)
SGT-137	4.07	-5.88	-1.81	305 512	1.56 1.19	H→L+3 (77%), H-1→L+3 (9%) H-1→L (27%), H→L (56%)

 Table S3. Photophysical and electrochemical properties of sensitizers on DFT calculations

^aEnergy gaps ($E_{0.0}^{DFT}$), $\lambda_{absmax}^{DFT b}$, f, and the corresponding transition were computed with the TD-DFT method at the CAM-B3LYP/6-31G(d,p) level in THF. Energy gaps ($E_{0.0}^{DFT}$) are calculated via $E_{0.0}^{DFT} = E_{ox}^{DFT} - E_{ox}^{DFT}$.



Figure S6. Projected densities of states (PDOS) for (a) **SGT-130**, (b) **SGT-136** and (c) **SGT-137** including the donor (yellow–green), π -bridge unit (Stable, Ethyl-TI: red, Hexyl-TI: green), BTD-P (yellow) and CNCOOH (sky-blue) moieties as individual groups. Each total density of state is shown (black line).

			Molecular orbital contribution (in %)					
	Orbital	Energy (eV)	Donor	π-bridge	BTD-P	СNCOOH		
	LUMO	-1.76	0	11	71	18		
SGT-130	НОМО	-6.01	74	23	3	0		
	HOMO-1	-6.86	38	35	25	1		
	LUMO	-1.81	0	10	66	24		
SGT-136	НОМО	-5.88	67	28	4	0		
	HOMO-1	-6.66	31	47	21	1		
	LUMO	-1.81	0	10	66	24		
SGT-137	номо	-5.88	67	28	4	0		
	HOMO-1	-6.65	31	47	20	1		

Table S4. Molecular orbital contributions (%) of the HOMO and LUMO orbitals of the**SGT** sensitizer



Figure S7. Time-resolved PL decay traces of dye-adsorbed mesoporous Al₂O₃ (black line) and TiO₂ film (a) **SGT-130** (blue line); (b) **SGT-136** (red line); (c) **SGT-137** (green line). Excitation wavelength: 393 nm; Detection wavelength: $\lambda_{em max}$ of each sensitizer.

		$ au_1$ (ns)	A_1	τ ₂ (ns)	A_2	τ ₃ (ns)	A_3	<\alpha > av a (ns)	η_{inj} (%)
SGT- 130	Al_2O_3	3.49	12.71	1.29	49.02	0.38	38.26	1.22	74.15
	TiO ₂	2.71	2.03	0.66	18.39	0.17	79.58	0.32	
SGT- 136	Al ₂ O ₃	1.73	6.90	0.70	37.18	0.19	55.92	0.49	81.20
	TiO ₂	1.71	2.24	0.57	11.49	0.15	86.26	0.23	
SGT- 137	Al ₂ O ₃	1.91	4.94	0.71	36.51	0.19	58.55	0.47	82.98
	TiO ₂	0.88	7.41	0.15	92.59			0.21	

Table S5. Time coefficients and relative amplitudes of PL decay traces in Figure S7

^aThe values of τ_{av} were determined with $\langle \tau \rangle_{av} = \sum_{i=1}^{n} A_i \tau_i$



Figure S8. *J-V* characteristics of the DSSCs employing the iodine electrolyte under simulated AM 1.5 G.

Dye	J _{sc} (mA cm ^{□2})	$V_{ m oc}~({ m mV})$	FF (%)	PCE ^a (%)
SGT-130 ^b	15.27 ± 0.04	680 ± 0.07	74.80 ± 0.11	7.71 ± 0.01
SGT-136 ^b	16.67 ± 0.11	657 ± 2.40	68.55 ± 1.25	7.51 ± 0.22
SGT-137 ^b	18.05 ± 0.03	655 ± 1.27	66.12 ± 0.06	7.81 ± 0.01

Table S6. Photovoltaic performance of the DSSCs based on the various sensitizers underone-sun illumination (AM 1.5G) (mean of two DSSCs)

^aIrradiated light: AM 1.5G (100 mW cm⁻²); cell area tested with a metal mask: 0.141 cm².

The iodine-based electrolyte consists of 0.6 M DMPII, 0.5 M TBP, 0.05 M I_2 and 0.1 M LiI in CH₃CN.



Figure S9. (a) Nyquist and (b) Bode plots obtained from the DSSCs based on the various sensitizers in the dark with forward bias of -0.77 V. (c) and (d) The τ_n and τ_r derived from IMPS and IMVS of the DSSCs as a function of light intensity, respectively. (e) Equivalent circuit for EIS data fitting



Figure S10. a) Photocurrent transient dynamics of DSSCs. b) Open-circuit voltage decay (OCVD) curves for the same DSSCs. The inset is electron lifetime and V_{oc} values for the same DSSCs.



Figure S11. Long-term stability test under light soaking (100 mWcm⁻²) at 50 $^{\circ}$ C for DSSCs based on all SGT sensitizers.



Figure S12. Chemical structures of HC-A1, HC-A4 and SGT-021.



Figure S13. Histogram of the PCE of the devices made with (a) **SGT-137**, (b) **SGT-021**, and (c) PT-dsscs at full sun intensity.

NMR and MALDI-TOF spectra



Figure S14. ¹H NMR spectrum of 1 in CDCl₃.



Figure S15. ¹³C NMR spectrum of 1 in CDCl₃.



Figure S16. ¹H NMR spectrum of 2 in CDCl₃.











Figure S19. ¹³C NMR spectrum of **3a** in CDCl₃.



Figure S20. ¹H NMR spectrum of 3b in CDCl₃.



Figure S21. ¹³C NMR spectrum of **3b** in CDCl₃.











Figure S24. ¹H NMR spectrum of 4b in CDCl₃.



Figure S25. ¹³C NMR spectrum of 4b in CDCl₃.



Figure S26. ¹H NMR spectrum of 5a in CDCl₃.



Figure S27. ¹³C NMR spectrum of 5a in CDCl₃.



Figure S28. ¹H NMR spectrum of 5b in CDCl₃.



Figure S29. ¹³C NMR spectrum of 5b in CDCl₃



Figure S30. ¹H NMR spectrum of 6a in CDCl₃.



Figure S31. ¹³C NMR spectrum of 6a in CDCl₃.



Figure S32. ¹H NMR spectrum of 6b in CDCl₃.







Figure S34. ¹H NMR spectrum of SGT-136 in THF- d_8 .



Figure S35. ¹³C NMR spectrum of SGT-136 in THF- d_8 .



Figure S36. ¹H NMR spectrum of SGT-137 in THF- d_8 .



Figure S37. ¹³C NMR spectrum of SGT-137 in THF- d_8 .







Figure S39. HR-MS (EI) spectrum of 3.







Figure S41. MALDI-TOF spectrum of 4a.







Figure S43. MALDI-TOF spectrum of 6a.



Figure S44. MALDI-TOF spectrum of 6b.



Figure S45. MALDI-TOF spectrum of SGT-136.



Figure S46. MALDI-TOF spectrum of SGT-137.