Electronic Supporting Information

for

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

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**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)benzaldehyde\(^3\) were synthesized according to the literature with slight modifications.

**Measurements**
The \(^1\)H NMR spectroscopy study was conducted on a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; \(d = 0\) ppm) as the internal standard. Chemical shifts for \(^1\)H NMR spectra were recorded on a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; \(d = 0\) ppm) as the internal standard. The \(^{13}\)C NMR spectroscopy study was conducted on a Bruker Biospin GmbH AVANCE 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 TiO\(_2\) (3.5 \(\mu\)m thickness) or Al\(_2\)O\(_3\) (4.0 \(\mu\)m thickness) were excited by \(~\)100 ps laser pulses of 393 nm centre wavelength; the
emission was measured at \( \lambda_{\text{em max}} \) 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 \( \tau \) 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 TiCl\(_4\) (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 TiO\(_2\) paste (Dyesol, 18NR-T) and then dried at 120 °C. The TiO\(_2\) 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 TiO\(_2\) 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 \( \mu \)m thick transparent layer and a 3.5 \( \mu \)m thick scattering layer. The thickness of the transparent layer was measured using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA). The TiO\(_2\) electrodes were again treated with TiCl\(_4\) at 70 °C for 30 min and sintered at
500 °C for 30 min. The TiO$_2$ 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 µm thickness) used as the counter electrode was cleaned in an ultrasonic bath in H$_2$O, acetone and 0.1 M HCl aqueous. The counter electrodes were prepared by coating with a drop of H$_2$PtCl$_6$ 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 TiO$_2$ 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 µm 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 µm 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 ($\lambda$) curve is expressed in the following equation: IPCE ($\lambda$) = 1240
(\(J_{sc}/\lambda\phi\)), where \(\lambda\) is the wavelength, \(J_{sc}\) is the current at short circuit (mA cm\(^{-2}\)), and \(\phi\) 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-2-nitrobenzene (4.0 g, 13.80 mmol), Pd (PPh\(_3\))\(_2\)Cl\(_2\) (0.78 g, 1.1 mmol), and 200 mL toluene was refluxed at 110\(^\circ\)C for 12 hrs under nitrogen, then extracted with CH\(_2\)Cl\(_2\). 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 CH\(_2\)Cl\(_2\)/n-hexane (\(v/v\), 1:2) as eluent to afford \(1\) as an oil (2.83g, 94%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 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). \(^{13}\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\): 121.84, 126.76, 127.14, 127.29, 127.90, 128.48, 133.07, 133.98, 134.85, 135.68.

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

A mixture of compound \(1\) (1.69 g, 5.95 mmol) and triphenylphosphine (4.68 g, 17.84 mmol) in 1,2-dichlorobenzene (50 mL) was refluxed for 12 hrs under nitrogen, then extracted with CH\(_2\)Cl\(_2\). 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 CH\(_2\)Cl\(_2\)/n-hexane (\(v/v\), 2:1) as eluent to yield \(2\) as a white powder (0.6 g, 40%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 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). \(^{13}\)C 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 C₁₀H₁₆BrNS: 252.9384; found: 253.2161.

6-bromo-4-ethyl-4H-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 (v/v, 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, J₁ = 1.8 Hz, J₂ =1.8 Hz, 1H), 7.07 (d, J = 5.1 Hz, 1H), 4.25-4.32 (q, J₁ = 5.1 Hz, J₂ = 6.9 Hz, J₃ = 7.2 Hz, 2H), 1.42-1.47 (t, J₁ = 6.9 Hz, J₂ = 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 C₁₂H₁₆BrNS: 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 was finished, the reactant was 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 CH₂Cl₂/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, J1 = 7.2 Hz, J2 = 6.9 Hz, 2H), 1.80-1.87 (m, 2H), 1.21-1.34 (m, 6H), 0.89 (t, J1 = 6.9 Hz, J2 = 7.2 Hz, 3H). 13C NMR (300 MHz, CDCl3) δ: 142.15, 126.98, 126.56, 121.48, 121.48, 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 (0.23 g, 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 tert-butoxide (0.05 g, 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, J1 = 6.9 Hz, J2 = 7.2 Hz, 2H), 3.93-4.00 (q, J1 = 6.0 Hz, J2 = 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 (0.23 g, 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 CH$_2$Cl$_2$/n-hexane (v/v, 1:3) as eluent to yield **4b** as a yellow sticky solid (0.3 g, 62%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 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). $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$: 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 C$_{64}$H$_{84}$N$_2$O$_4$S: 976.6152; found: 976.5311.

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

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 MgSO$_4$. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH$_2$Cl$_2$/n-hexane (v/v, 1:2) as eluent to yield **5a** as a yellow sticky solid (0.6 g, 97%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 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). $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$: 
\[N,N\text{-bis}(2',4'\text{-bis(hexyloxy)biphenyl-4-yl})-2\text{-bromo-4-hexyl-4H-thieno}[3,2-b]\text{indol-6-amine} \text{ (5b)}\]

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 MgSO\(_4\). The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH\(_2\)Cl\(_2\)/n-hexane (\(v/v\), 1:2) as eluent to afford \(5b\) as a yellow sticky solid (0.19 g, 88%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 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). \(^{13}\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\): 159.56, 157.08, 146.60, 146.57, 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.

\[4-(7-(6-(\text{Bis(2',4'-dihexyloxybiphenyl-4-yl)amino})-N-\text{ethylthieno}[3,2-b][1]\text{indole-2-y1})\text{benzo}[c][1,2,5]\text{thiadiazol-4-yl})\text{benzaldehyde} \text{ (6a)}\]

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-(4-bromobenzol[1,2,5]thiadiazol-7-yl)benzaldehyde (0.91 g, 0.75 mmol, 1.2 eq.) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (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 CH<sub>2</sub>Cl<sub>2</sub>. 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<sub>2</sub>Cl<sub>2</sub>/n-hexane (v/v, 1:1) as eluent to afford 6a as purple oil (0.33 g, 46%).

1H NMR (300 MHz, CDCl<sub>3</sub>) 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<sub>1</sub> = 6.0 Hz, J<sub>2</sub> = 6.0 Hz, 8H), 1.83 (m, 8H), 1.29-1.52 (m, 24H), 0.85-0.95 (m, 15H). 13C NMR (300 MHz, CDCl<sub>3</sub>) 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 C<sub>73</sub>H<sub>82</sub>N<sub>4</sub>O<sub>5</sub>S<sub>2</sub>: 1158.5727; found: 1158.4911.

4-(7-(6-(Bis(2',4'-dihexyloxybiphenyl-4-yl)amino)-N-hexylthieno[3,2-b][1]indole-2-y1)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 (0.67 g, 0.53 mmol, 1.2 eq) 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/n-hexane (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, J₁ = 6.0 Hz, J₂ = 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, 112.27, 106.76, 105.67, 105.25, 100.78, 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--2-yl)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 (0.25 g, 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 (v/v, 10:1)). Yield was 70% (0.25 g). ¹H NMR (300 MHz, THF-d₈) 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, J₁ = 5.4 Hz, J₂ = 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-d₈) 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-2-y1)benzoc[1,2,5]thiadiazol-4-yl)phenyl)-2-cyano acrylic 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 (v/v, 10:1)). Yield was 67% (0.17 g). ¹H NMR (300 MHz, THF-d₈) 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). $^{13}$C 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 C$_{80}$H$_{91}$N$_5$O$_6$S$_2$: 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 \( E_0 (\text{Fc/Fc}^+) = 0.63 \) V vs. NHE.
### Table S1. Photophysical and electrochemical properties of sensitizers on DFT calculations

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{HOMO}}^{\text{ss}}$ (eV)</th>
<th>$E_{\text{LUMO}}^{\text{ss}}$ (eV)</th>
<th>$E_{\text{HOMO}}^{\text{ss}}$ (eV)</th>
<th>$\lambda_{\text{SS}}$ (nm)</th>
<th>$f^b$</th>
<th>MO transition$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBT</td>
<td>4.60</td>
<td>-5.90</td>
<td>-1.30</td>
<td>287</td>
<td>0.21</td>
<td>H-1→L (70%), H→L (9%), H→L+1 (18%)</td>
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<td></td>
<td></td>
<td>294</td>
<td>0.32</td>
<td>H-1→L (9%), H→L (80%), H-1→L+1 (4%)</td>
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<tr>
<td>Ethyl-TI</td>
<td>4.57</td>
<td>-5.55</td>
<td>-0.98</td>
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<td>0.34</td>
<td>H-1→L (74%), H→L (14%), H→L+1 (6%)</td>
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<td>306</td>
<td>0.14</td>
<td>H-1→L (15%), H→L (81%)</td>
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<tr>
<td>Hexyl-TI</td>
<td>4.51</td>
<td>-5.49</td>
<td>-0.98</td>
<td>291</td>
<td>0.34</td>
<td>H-1→L (73%), H→L (14%), H→L+1 (5%)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>307</td>
<td>0.13</td>
<td>H-1→L (15%), H→L (81%)</td>
</tr>
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</table>

$^a$Theoretical frontier orbital energy levels are computed with the DFT method at the B3LYP/6-31G(d,p) level in tetrahydrofuran. Energy gaps ($E_{\text{HOMO}}^{\text{ss}} - E_{\text{LUMO}}^{\text{ss}}$) are calculated via $E_{\text{HOMO}}^{\text{ss}} - E_{\text{LUMO}}^{\text{ss}}$.

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

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

**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

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy (eV)</th>
<th>Molecular orbital contribution (in %)</th>
<th>Core T&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Core T&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Benzene</td>
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<tr>
<td>LUMO</td>
<td>-1.31</td>
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<td>HOMO</td>
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<td>LUMO</td>
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<td>HOMO</td>
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<td>34</td>
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<tr>
<td>LUMO</td>
<td>-0.9</td>
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<td>41</td>
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<tr>
<td>HOMO</td>
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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 Fe/Fe⁺ as an external reference using $E_0$ (Fe/Fe⁺) = 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 S3.** Cyclic voltammograms of all SGT sensitizers.
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).

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

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{opt}}$ (eV)</th>
<th>$E_{\text{ox}}$ (eV)</th>
<th>$E_{\text{red}}$ (eV)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$f^a$</th>
<th>MO transition $^b$</th>
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<tr>
<td>SGT-130</td>
<td>4.25</td>
<td>-6.01</td>
<td>-1.76</td>
<td>299</td>
<td>1.60</td>
<td>H→L⁺3 (78%), H⁻2→L⁺7 (2%) H⁻1→L (33%), H→L (50%)</td>
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<tr>
<td>SGT-136</td>
<td>4.07</td>
<td>-5.88</td>
<td>-1.81</td>
<td>305</td>
<td>1.57</td>
<td>H→L⁺3 (77%), H⁻1→L⁺3 (9%) H⁻1→L (27%), H→L (56%)</td>
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<td>512</td>
<td>1.20</td>
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<td>SGT-137</td>
<td>4.07</td>
<td>-5.88</td>
<td>-1.81</td>
<td>305</td>
<td>1.56</td>
<td>H→L⁺3 (77%), H⁻1→L⁺3 (9%) H⁻1→L (27%), H→L (56%)</td>
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<td>512</td>
<td>1.19</td>
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$^a$Energy gaps ($E_{\text{opt}}$), $E_{\text{ox}}$, $f$, and the corresponding transition were computed with the TD-DFT method at the CAM-B3LYP/6-31G(d,p) level in THF. Energy gaps ($E_{\text{red}}$) are calculated via $E_{\text{red}} = E_{\text{ox}} - E_{\text{opt}}$. 
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).
Table S4. Molecular orbital contributions (%) of the HOMO and LUMO orbitals of the SGT sensitizer

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy (eV)</th>
<th>Donor</th>
<th>π-bridge</th>
<th>BTD-P</th>
<th>CNCOOH</th>
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<tbody>
<tr>
<td>LUMO</td>
<td>−1.76</td>
<td>0</td>
<td>11</td>
<td>71</td>
<td>18</td>
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<tr>
<td>SGT-130</td>
<td>HOMO</td>
<td>−6.01</td>
<td>74</td>
<td>23</td>
<td>3</td>
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<tr>
<td>HOMO-1</td>
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<td>LUMO</td>
<td>−1.81</td>
<td>0</td>
<td>10</td>
<td>66</td>
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<tr>
<td>SGT-136</td>
<td>HOMO</td>
<td>−5.88</td>
<td>67</td>
<td>28</td>
<td>4</td>
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<tr>
<td>HOMO-1</td>
<td>−6.66</td>
<td>31</td>
<td>47</td>
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<td>LUMO</td>
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<tr>
<td>SGT-137</td>
<td>HOMO</td>
<td>−5.88</td>
<td>67</td>
<td>28</td>
<td>4</td>
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<tr>
<td>HOMO-1</td>
<td>−6.65</td>
<td>31</td>
<td>47</td>
<td>20</td>
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</table>
Figure S7. Time-resolved PL decay traces of dye-adsorbed mesoporous Al$_2$O$_3$ (black line) and TiO$_2$ film (a) SGT-130 (blue line); (b) SGT-136 (red line); (c) SGT-137 (green line). Excitation wavelength: 393 nm; Detection wavelength: $\lambda_{\text{em max}}$ of each sensitizer.
**Table S5.** Time coefficients and relative amplitudes of PL decay traces in Figure S7

<table>
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<th>$\tau_1$ (ns)</th>
<th>$A_1$</th>
<th>$\tau_2$ (ns)</th>
<th>$A_2$</th>
<th>$\tau_3$ (ns)</th>
<th>$A_3$</th>
<th>$\langle \tau \rangle_{av}$ (ns)</th>
<th>$\eta_{inj}$ (%)</th>
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<td><strong>SGT-130</strong></td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>3.49</td>
<td>12.71</td>
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<td>2.03</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>1.73</td>
<td>6.90</td>
<td>0.70</td>
<td>37.18</td>
<td>0.19</td>
<td>55.92</td>
<td>0.49</td>
<td>81.20</td>
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<td>TiO$_2$</td>
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<td>2.24</td>
<td>0.57</td>
<td>11.49</td>
<td>0.15</td>
<td>86.26</td>
<td>0.23</td>
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<td><strong>SGT-137</strong></td>
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</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.91</td>
<td>4.94</td>
<td>0.71</td>
<td>36.51</td>
<td>0.19</td>
<td>58.55</td>
<td>0.47</td>
<td>82.98</td>
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<td>TiO$_2$</td>
<td>0.88</td>
<td>7.41</td>
<td>0.15</td>
<td>92.59</td>
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*The values of $\tau_{av}$ were determined with $\langle \tau \rangle_{av} = \sum A_i \tau_i$.*

**Figure S8.** $J-V$ characteristics of the DSSCs employing the iodine electrolyte under simulated AM 1.5 G.
Table S6. Photovoltaic performance of the DSSCs based on the various sensitizers under one-sun illumination (AM 1.5G) (mean of two DSSCs)

<table>
<thead>
<tr>
<th>Dye</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>PCE$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGT-130$^b$</td>
<td>15.27 ± 0.04</td>
<td>680 ± 0.07</td>
<td>74.80 ± 0.11</td>
<td>7.71 ± 0.01</td>
</tr>
<tr>
<td>SGT-136$^b$</td>
<td>16.67 ± 0.11</td>
<td>657 ± 2.40</td>
<td>68.55 ± 1.25</td>
<td>7.51 ± 0.22</td>
</tr>
<tr>
<td>SGT-137$^b$</td>
<td>18.05 ± 0.03</td>
<td>655 ± 1.27</td>
<td>66.12 ± 0.06</td>
<td>7.81 ± 0.01</td>
</tr>
</tbody>
</table>

$^a$Irradiated light: AM 1.5G (100 mW cm$^{-2}$); cell area tested with a metal mask: 0.141 cm$^2$.

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 CH$_3$CN.
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 $\tau_n$ and $\tau_r$ 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 mW/cm²) at 50°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. $^1$H NMR spectrum of 1 in CDCl$_3$.

Figure S15. $^{13}$C NMR spectrum of 1 in CDCl$_3$. 
Figure S16. $^1$H NMR spectrum of 2 in CDCl$_3$.

Figure S17. $^{13}$C NMR spectrum of 1 in CDCl$_3$. 
Figure S18. $^1$H NMR spectrum of 3a in CDCl$_3$.

Figure S19. $^{13}$C NMR spectrum of 3a in CDCl$_3$. 
Figure S20. $^1$H NMR spectrum of 3b in CDCl$_3$.

Figure S21. $^{13}$C NMR spectrum of 3b in CDCl$_3$. 
Figure S22. $^1$H NMR spectrum of 4a in CDCl$_3$.

Figure S23. $^{13}$C NMR spectrum of 4a in CDCl$_3$. 
Figure S24. $^1$H NMR spectrum of 4b in CDCl$_3$.

Figure S25. $^{13}$C NMR spectrum of 4b in CDCl$_3$. 
Figure S26. $^1$H NMR spectrum of 5a in CDCl$_3$.

Figure S27. $^{13}$C NMR spectrum of 5a in CDCl$_3$. 
Figure S28. $^1$H NMR spectrum of 5b in CDCl$_3$.

Figure S29. $^{13}$C NMR spectrum of 5b in CDCl$_3$. 
Figure S30. $^1$H NMR spectrum of 6a in CDCl$_3$.

Figure S31. $^{13}$C NMR spectrum of 6a in CDCl$_3$. 
Figure S32. $^1$H NMR spectrum of 6b in CDCl$_3$.

Figure S33. $^{13}$C NMR spectrum of 6b in CDCl$_3$. 
Figure S34. $^1$H NMR spectrum of SGT-136 in THF-$d_8$.

Figure S35. $^{13}$C NMR spectrum of SGT-136 in THF-$d_8$. 
Figure S36. $^1$H NMR spectrum of SGT-137 in THF-$d_8$.

Figure S37. $^{13}$C NMR spectrum of SGT-137 in THF-$d_8$. 
Figure S38. HR-MS (EI) spectrum of 2.

Figure S39. HR-MS (EI) spectrum of 3.
Figure S40. HR-MS (EI) spectrum of 4.

Figure S41. MALDI-TOF spectrum of 4a.
**Figure S42.** MALDI-TOF spectrum of 4b.

**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.