

Supporting Information

Silicon-Naphthalo/Phthalocyanine-Hybrid Sensitizer for Efficient Red-Response in Dye-Sensitized Solar Cells

Bogyu Lim,^{†,#} George Y. Margulis,^{†,Δ} Jun-Ho Yum,[§] Eva L. Unger,[#] Brian E. Hardin,¹ Michael Grätzel,[§] Michael D. McGehee,[#] and Alan Sellinger^{,#,1}*

[[#]] Department of Materials Science and Engineering, Stanford University, Stanford, California 94305-4045, USA

[^Δ] Department of Applied Physics, Stanford University, Stanford, California 94305-4045, USA

[[§]] Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Science, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

[¹] Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

[¹] Current address: Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, USA

[[†]] Both authors contributed equally to this work.

* E-mail: aselli@mines.edu

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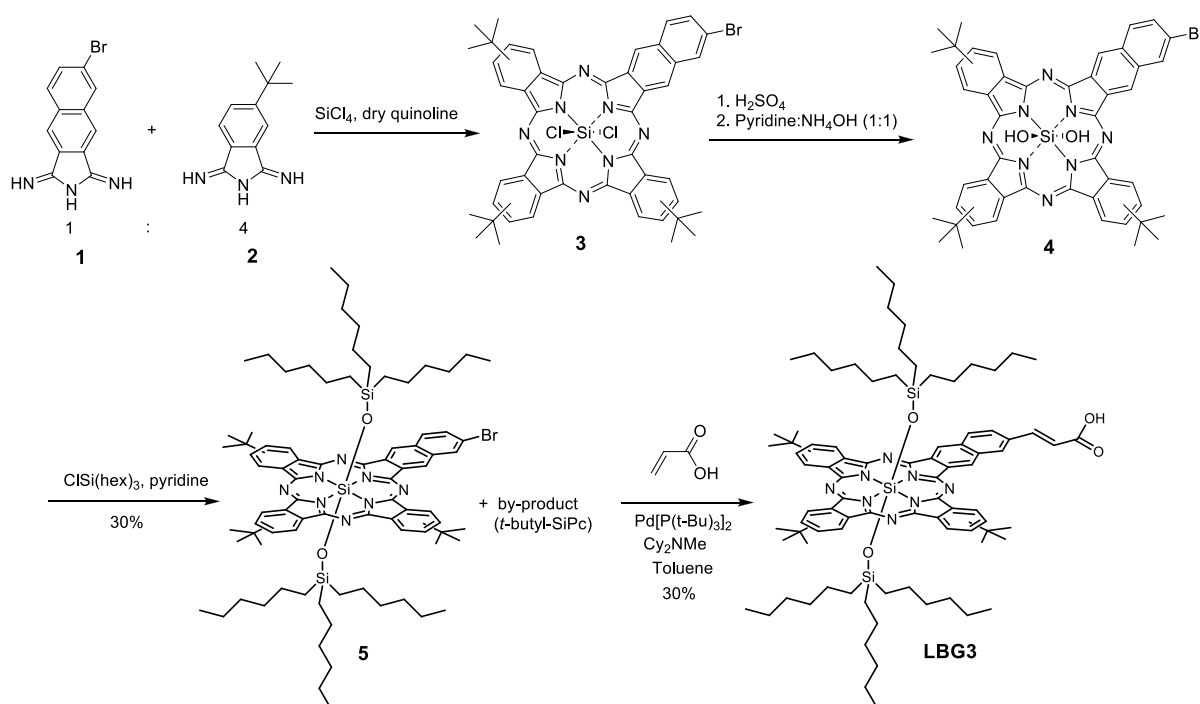
Figure S16: Dye absorption spectra of **LBG3** and **LBG1** on TiO_2 with various amounts of cDCA.

Section 1: Synthesis of dyes and dye-characterization

General Characterization: Materials were characterized by ^1H NMR spectroscopy (Varian 400 MHz) and ^{13}C NMR spectroscopy (Inova 500 MHz). Absorption and IR spectra were measured using a Cary 6000i UV/Vis spectrophotometer, and a Bruker Vertex 70 FTIR spectrometer, respectively. High resolution mass spectrum (HR-MS) was obtained from a direct injection ESI/MS on an Agilent 1260

HPLC and Bruker microTOF-Q II mass spectrometer. Full scan mass data was acquired in both positive and negative ion modes. Melting temperature was determined using a TA Instruments DSC. Cyclic voltammetry (CV) was conducted using a VMP3 (Bio-Logic) in a dichloromethane solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte, glassy carbon as the working electrode, Pt wire as the counter electrode and Ag wire as the reference electrode at a scan rate of 50 mV/s.

Materials: All starting materials and reagents were purchased from commercial supplies unless otherwise specified, and used without further purification. 6-bromo-1,3-diiminobenz[*f*]isoindoline (**1**) was prepared according to procedures in the literature.^[1]



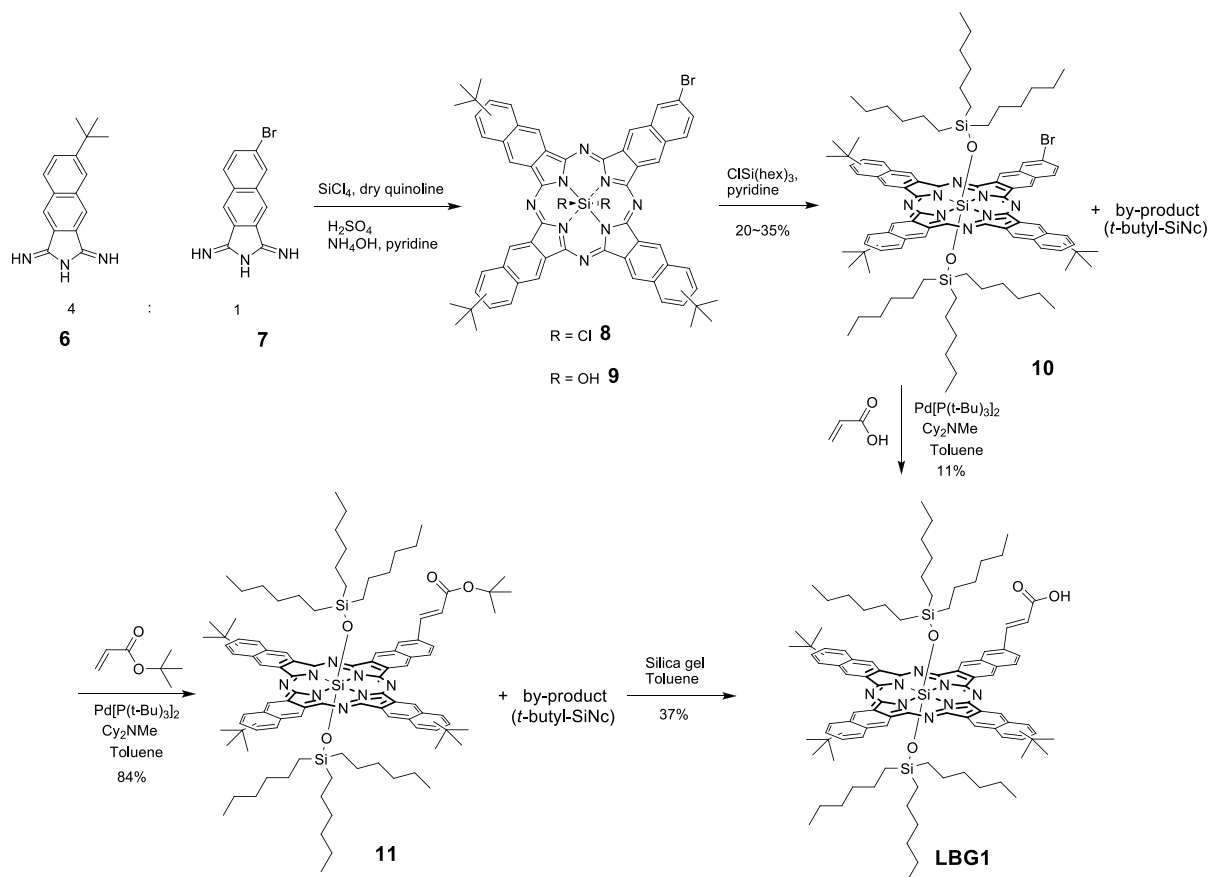
Scheme S1. Synthetic procedure for **LBG3**.

Synthesis of compound 4: Tetrachlorosilane (1.375 mL, 12 mmol) was added to a suspension of 6-bromo-1,3-diiminobenz[*f*]isoindoline (**1**) (0.55 g, 2 mmol) and 5-tert-butyl-1,3-diiminoisoindoline (**2**) (1.61 g, 8 mmol) in 20 mL of quinoline at room temperature under nitrogen. The mixture was heated to 210°C and stirred for 2 h. After cooling slowly, 70 mL of methanol was added and resulting mixture was stirred overnight. The reddish-brown mixture was filtered and washed with methanol and then dried (2.08 g), and then was used for subsequent reactions without further purification. The

bluish green solid (compound **3**) was then added to 20 mL in conc. H_2SO_4 while stirring for 2 h. The mixture was poured onto 20 g of ice and the resulting mixture was vigorously stirred overnight. The precipitate formed was filtered and washed with water and then methanol. The resulting bluish green solid (1.87 g) was refluxed in a 1:1 mixture of pyridine and 25 % NH_4OH (20 mL) for 10 h. After cooling to room temperature, the insoluble material was filtered, washed with water and ethanol, and then dried to give a crude mixture (1.54 g) of dark bluish green solid (compound **4**), that was used for subsequent reactions without further purification.

Synthesis of compound 5: Chlorotrihexylsilane (2.20 mL, 6 mmol) was added to a suspension of the **4** (1.54 g, 1.77 mmol) in 100 mL of dry pyridine, and the mixture was stirred for 2 h under reflux. After cooling, the reaction mixture was poured into 250 mL of ethanol/water (1:1), and the resulting mixture was stirred overnight. The precipitated bluish green solid was filtered, , and subsequently washed with water and then ethanol. The solid was purified by short column chromatography with hexane to obtain the 0.765 g of a mixture of product **5** and t-butyl SiPc as a dark-bluish green powder. Yield: 0.765 g (30 %).

Synthesis of compound LBG3: A flask was charged with bis(tri-tert-butylphosphine)palladium ($\text{Pd}(\text{P}(\text{t-Bu})_3)_2$) (0.0153 g, 0.03 mmol), a mixture of **5** and t-butyl SiPc (0.6467 g, 0.45 mmol), and purged with nitrogen. Toluene (15 mL) was added, and the mixture was stirred at room temperature, resulting in a homogeneous bluish green solution. N-methyldicyclohexylamine (Cy_2NMe) (0.21 mL, 1 mmol), and acrylic acid (0.21 mL, 3 mmol) were then added. The resulting mixture was allowed to stir at room temperature for 5 min, then heated to 100°C in an oil bath for 24 hr. The crude product was extracted with DCM and the combined organic layers were washed with plenty of water. The organic extracts were evaporated and purified with column chromatography on silica gel with hexane:DCM=5:1 as the eluant to obtain the product (**LBG3**) as a bluish green powder and t-butyl SiPc as a blue powder (160 mg). Yield: 0.19 g (30 %). M.p.: 143°C ; IR (KBr, cm^{-1}) IR (KBr, cm^{-1}) 2964, 2921, 2858 (O-H), 1694 (C=O), 1081, 1025 (Si-O); ^1H NMR (CDCl_3 , 400 MHz, [ppm]): δ 10.17 (t, 2H, $J = 44.81$ Hz), 9.65 (m, 3H), 9.55 (m, 3H), 8.80 (m, 2H), 8.39 (m, 3H), 8.29 (d, 1H, , $J = 15.81$ Hz), 8.19 (d, 1H, $J = 8.50$ Hz) 6.90 (d, 1H, $J = 15.81$ Hz), 1.85 (m, 27H), 0.81 (m, 12H), 0.59 (m, 18H), 0.37 (m, 12H), 0.06 (m, 12H), -1.17 (m, 12H), -2.30 (m, 12H); ^{13}C NMR (CDCl_3 , 500 MHz, [ppm]): δ 171.60, 154.47, 149.29, 147.18, 136.44, 134.95, 134.06, 133.11, 131.15, 128.68, 124.75, 123.28, 119.86, 118.43, 36.39, 32.94, 32.30, 31.13, 29.97, 22.60, 21.70, 14.32, 13.20; HR-MS: m/z 1427.8958, calcd for $\text{C}_{87}\text{H}_{123}\text{N}_8\text{O}_4\text{Si}_3$ 1427.8970.



Scheme S2. Synthetic procedure for **LBG1**.

Silicon-naphthalocyanine **LBG1** was synthesized using a similar procedure for **LBG3** from a 4:1 blending ratio of 6- *tert*-butyl -1,3-diiminobenz[*f*]isoindoline and 6-bromo-1,3-diiminobenz[*f*]isoindoline, respectively. Green powder. Yield: 11 %. M.p.: >290 °C; IR (KBr, cm⁻¹) 2964, 2921, 2858 (O-H), 1694 (C=O), 1081, 1025 (Si-O); ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 10.13 (s, 1H) 1.09 (m, 7H), 8.75 (s, 1H), 8.60 (m, 7H), 8.28 (d, 1H, *J* = 16.21 Hz), 8.13 (d, 1H, *J* = 8.48 Hz), 8.03 (m, 3H), 6.86 (d, 1H, *J* = 16.21 Hz), 1.65 (m, 27H), 0.61 (m, 12H), 0.39 (m, 18H), 0.17 (m, 12H), 0.07 (m, 12), -1.01 (m, 12H), -2.05 (m, 12H); ¹³C NMR (CDCl₃, 500 MHz, [ppm]): δ 171.24, 150.52, 149.19, 147.80, 147.10, 134.98, 134.31, 133.32, 132.93, 131.03, 129.95, 126.83, 125.23, 124.42, 123.14, 35.61, 33.39, 31.60, 31.39, 29.96, 22.68, 22.04, 14.14, 13.62; LC-MS: *m/z* 1577.8983, calcd 1577.94; HR-MS: *m/z* 1577.9374, calcd for C₉₉H₁₂₉N₈O₄Si₃ 1577.9439.

LBG1 was also synthesized though hydrolysis of *t*-butyl-ester SiNc (**11**)^[2]

Synthesis of compound 11: A flask was charged with bis(tri-*tert*-butylphosphine)palladium (Pd(P(*t*-Bu)₃)₂) (0.0036 g, 0.007 mmol), a mixture of **10** and *t*-butyl SiNc (0.1746 g, 0.11 mmol), and purged with nitrogen. Toluene (20mL) was added, and the mixture was stirred at room temperature resulting

in a homogeneous green solution. N-methyldicyclohexylamine (Cy₂NMe) (0.064 mL, 0.3 mmol), and *t*-butylacrylate (0.087 mL, 0.6 mmol) were then added. The resulting mixture was allowed to stir at room temperature for 5 min, then heated to 100°C in an oil bath for 24 hr. The crude product was extracted with DCM and the combined organic layers were washed with water. The organic extracts were evaporated and purified with column chromatography on silica gel with hexane as the eluant to obtain the product as a green powder and *t*-butyl SiNc as green powder. Yield: 0.1513 g (84 %). ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 10.07 (m, 8H), 8.69 (m, 8H), 8.08 (m, 5H), 6.76 (d, 2H, *J* = 15.90 Hz), 1.66 (m, 36H), 0.60 (m, 12H), 0.38 (m, 18H), 0.19 (m, 12H), 0.07 (m, 12H), -1.00 (m, 12H), -2.06 (m, 12H); ¹³C NMR (CDCl₃, 500 MHz, [ppm]): δ 150.19, 149.18, 148.37, 133.18, 132.50, 131.14, 130.25, 126.57, 125.45, 124.20, 33.54, 32.05, 31.82, 29.97, 23.30, 22.85, 15.31, 14.40; MALDI-TOF: *m/z* 1634.6, calcd 1634.00.

Synthesis of compound LBG1 through hydrolysis of 11: A solution of the **11** (0.1471g, 0.09 mmol) and silica gel (2.5 g, 230-400 mesh) in toluene (10 mL) was refluxed with vigorous agitation until the starting material was consumed (~24h). Upon cooling, the solution was diluted with 10% methanol in dichloromethane, Celite® was added, and the solution was filtered through a pad of Celite®. The solids were washed with methanol/ dichloromethane, and the filtrate was concentrated and purified with column chromatography on silica gel with hexane:DCM = 4:1 as the eluant to obtain the product as a green powder. Yield: 52.3 mg (36.8 %). M.p.: >290 °C; IR (KBr, cm⁻¹) 2964, 2921, 2858 (O-H), 1694 (C=O), 1081, 1025 (Si-O); ¹H NMR (CDCl₃, 400 MHz, [ppm]): δ 10.13 (s, 1H) 1.09 (m, 7H), 8.75 (s, 1H), 8.60 (m, 7H), 8.28 (d, 1H, *J* = 16.21 Hz), 8.13 (d, 1H, *J* = 8.48 Hz), 8.03 (m, 3H), 6.86 (d, 1H, *J* = 16.21 Hz), 1.65 (m, 27H), 0.61 (m, 12H), 0.39 (m, 18H), 0.17 (m, 12H), 0.07 (m, 12), -1.01 (m, 12H), -2.05 (m, 12H); ¹³C NMR (CDCl₃, 500 MHz, [ppm]): δ 171.24, 150.52, 149.19, 147.80, 147.10, 134.98, 134.31, 133.32, 132.93, 131.03, 129.95, 126.83, 125.23, 124.42, 123.14, 35.61, 33.39, 31.60, 31.39, 29.96, 22.68, 22.04, 14.14, 13.62; LC-MS: *m/z* 1577.8983, calcd 1577.94; HR-MS: *m/z* 1577.9374, calcd for C₉₉H₁₂₉N₈O₄Si₃ 1577.9439.

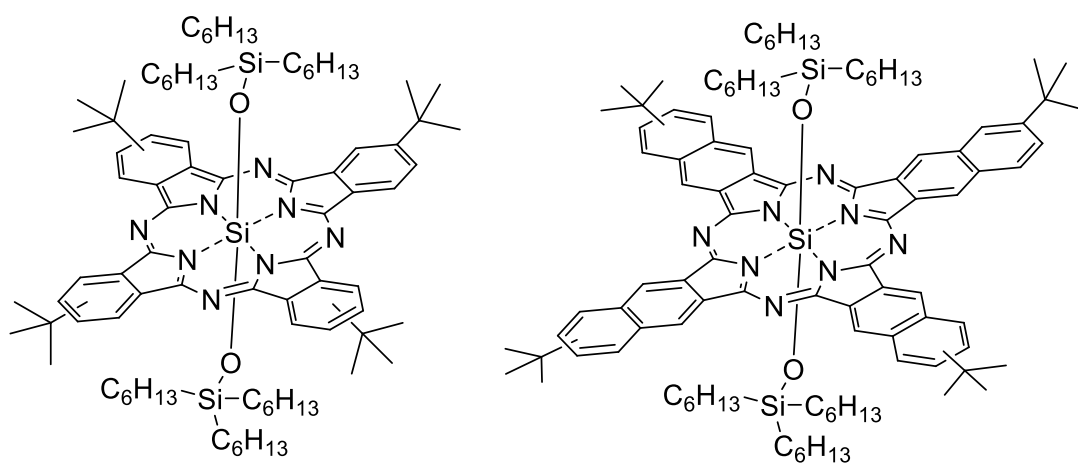


Figure S1. Molecular structure of *tert*-butyl silicon-phthalocyanine (*t*-butyl SiPc, left) and *tert*-butyl silicon-naphthalocyanine (*t*-butyl SiNc, right) as by-products.

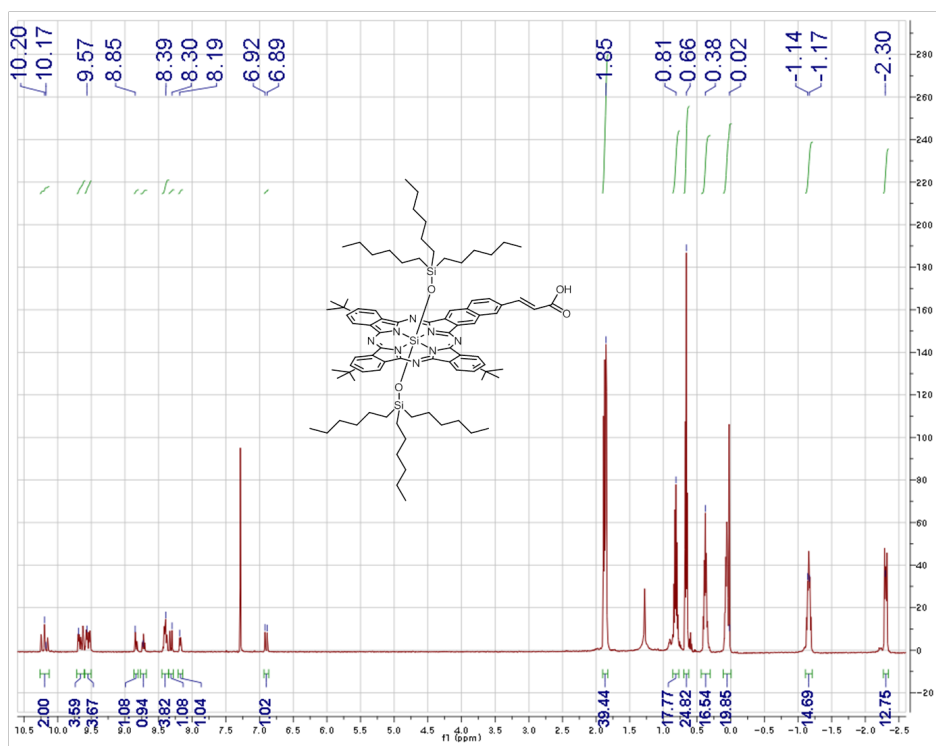


Figure S2. ^1H -NMR for LBG3.

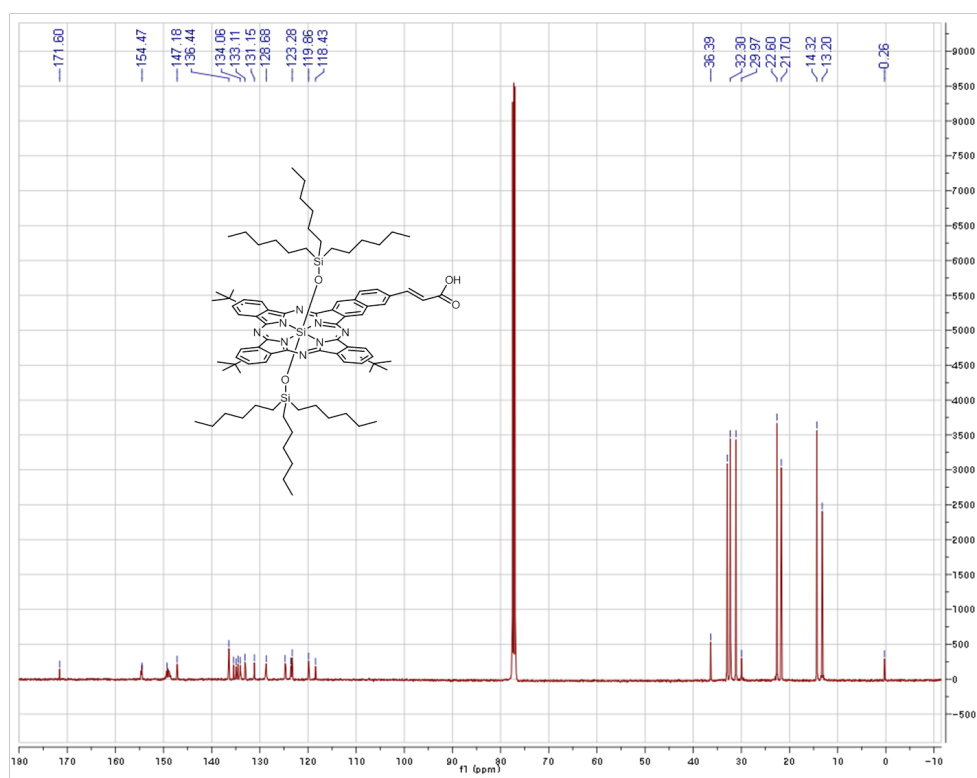


Figure S3. ^{13}C -NMR for LBG3.

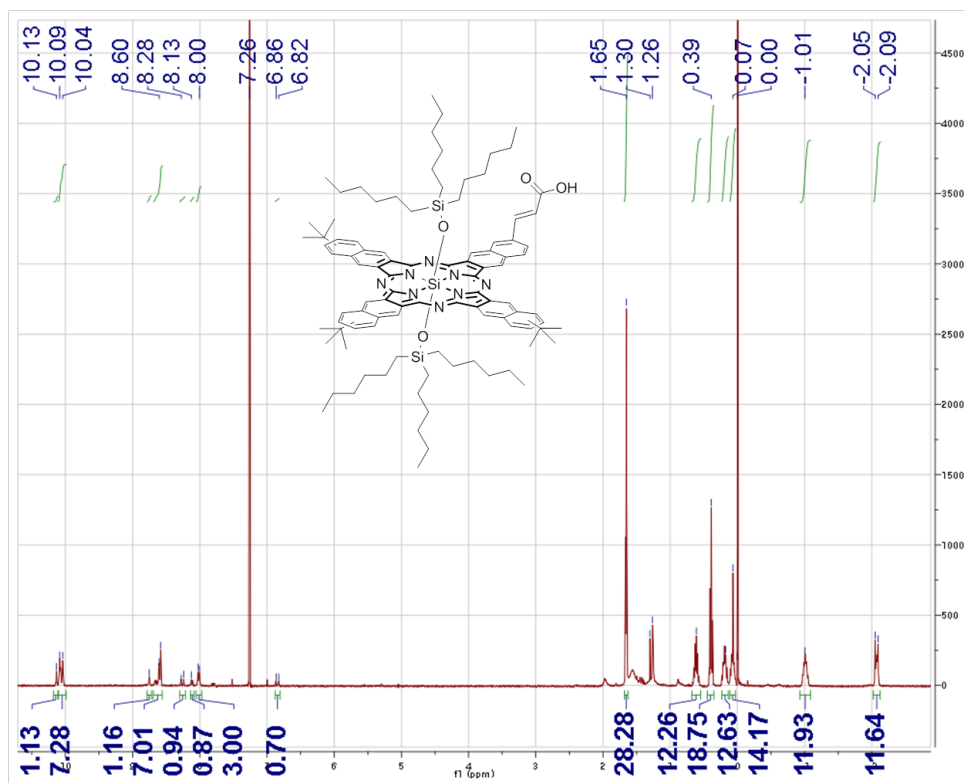


Figure S4. ¹H-NMR for LBG1.

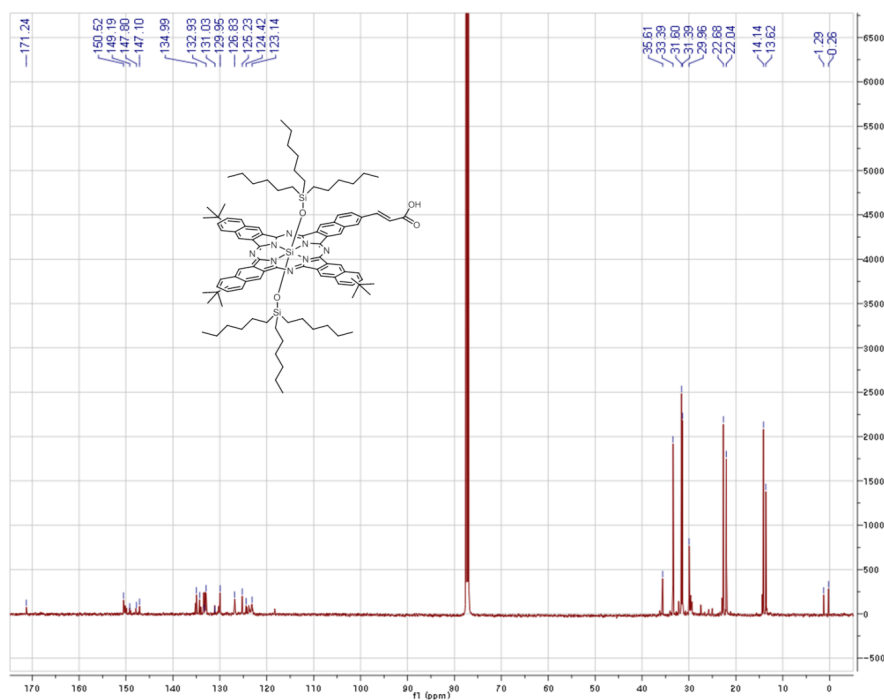


Figure S5. ¹³C-NMR for LBG1.

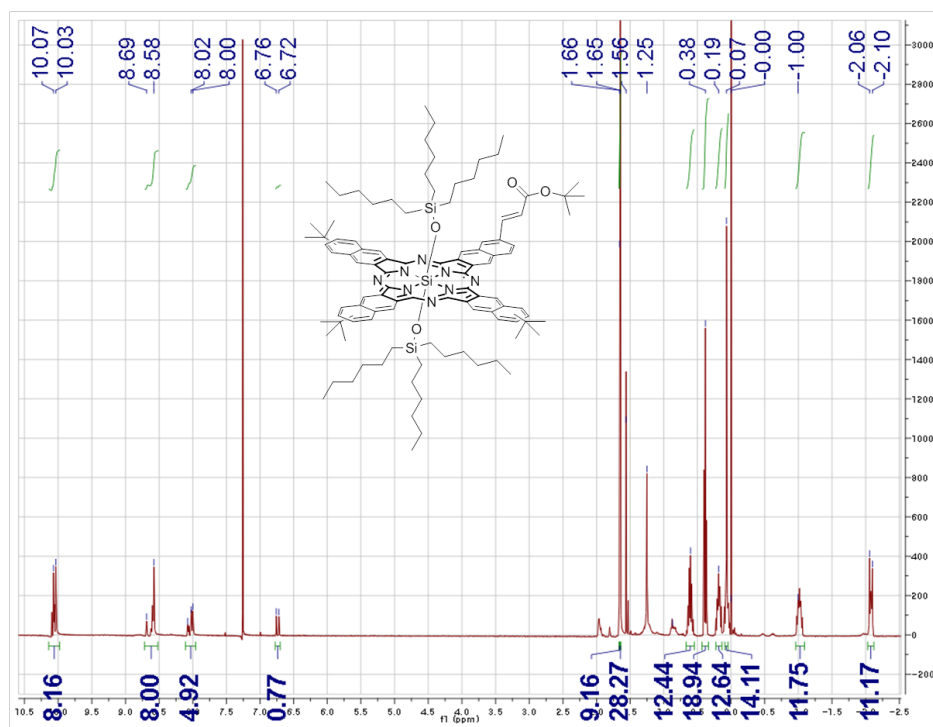


Figure S6. ¹H-NMR for 11.

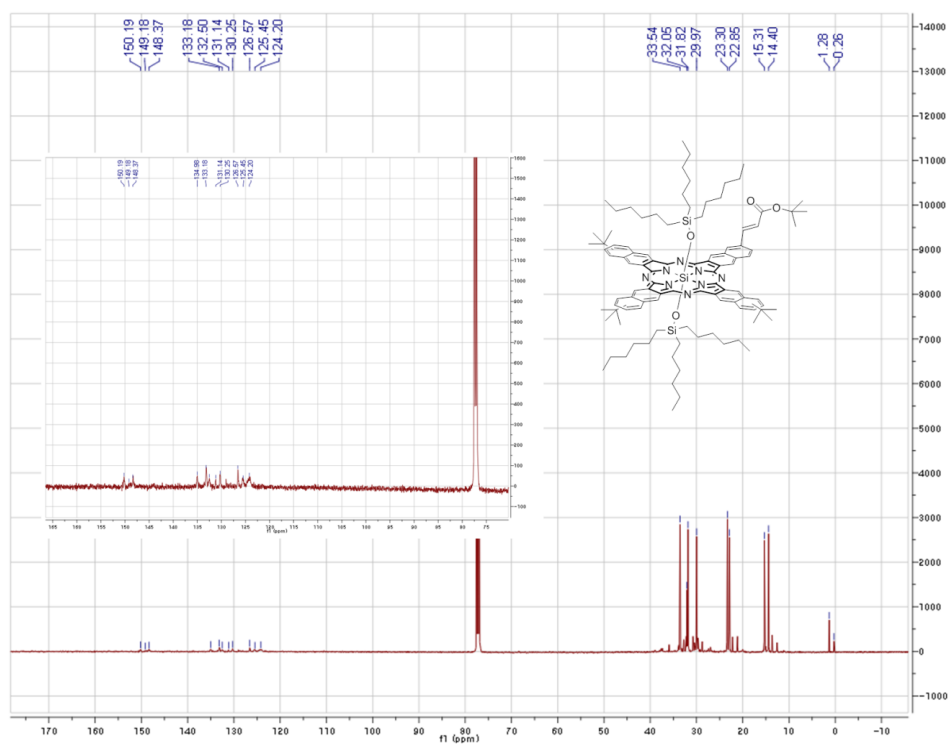


Figure S7. ¹³C-NMR for 11.

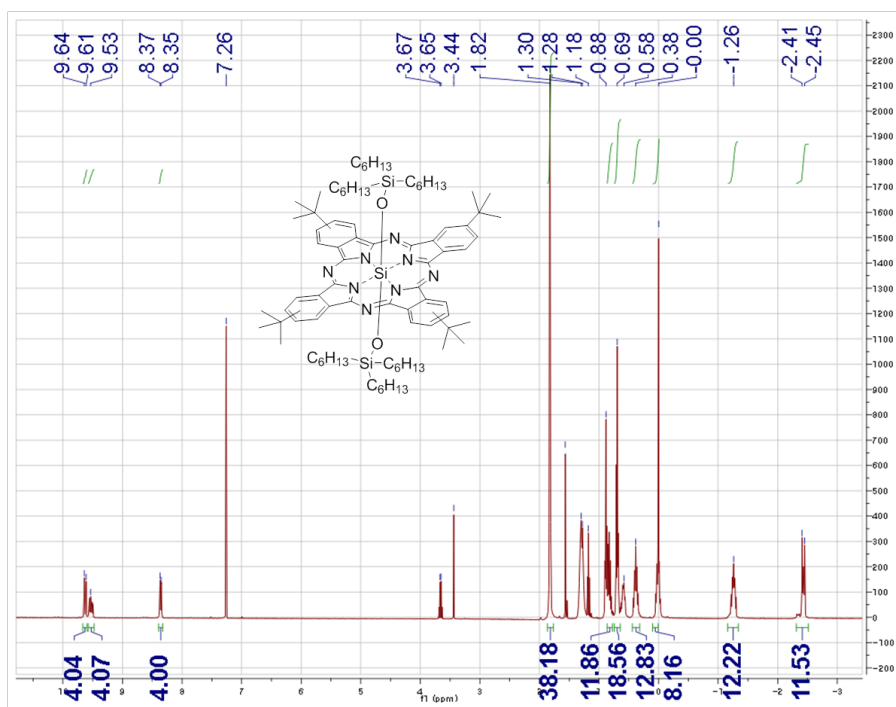


Figure S8. ^1H -NMR for *t*-butyl SiPc.

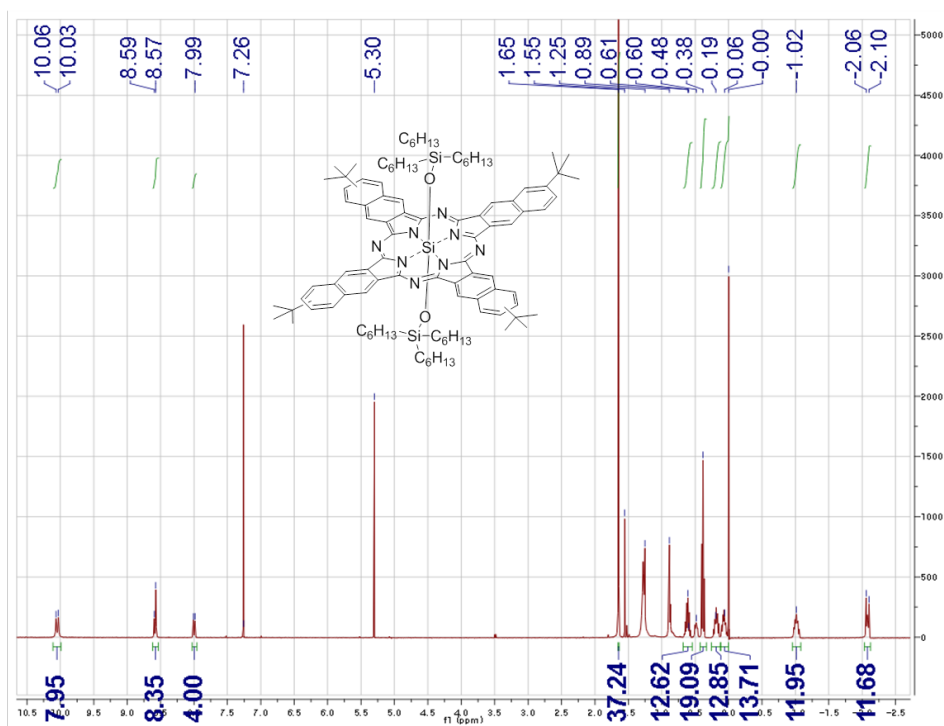


Figure S9. ^1H -NMR for *t*-butyl SiNc.

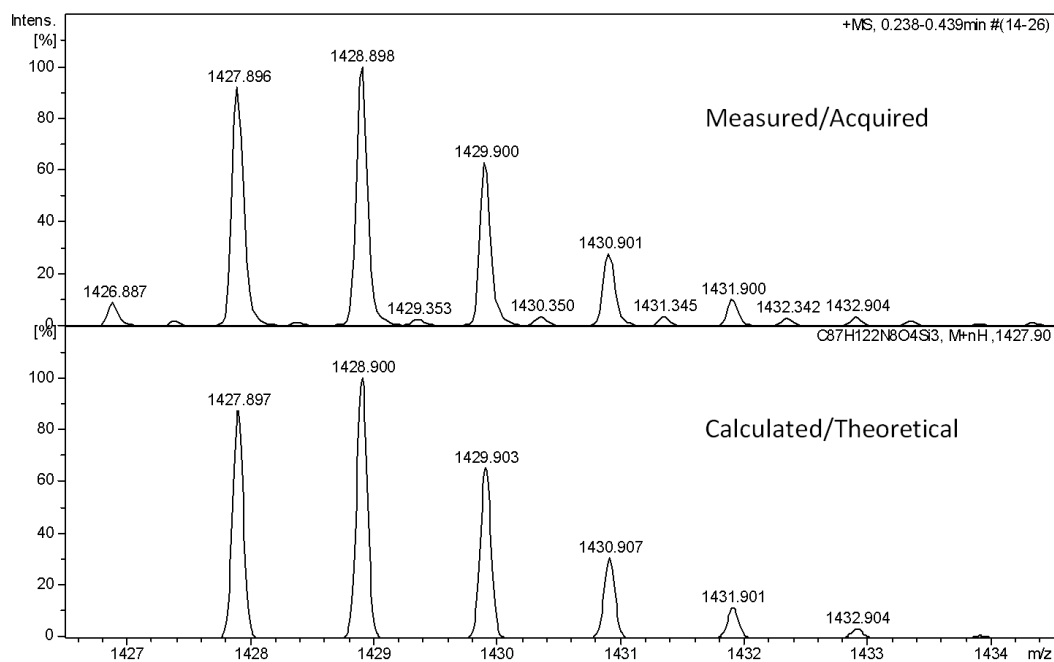


Figure S10. HR-MS spectra for **LBG3**; measured m/z (up), calculated m/z (down).

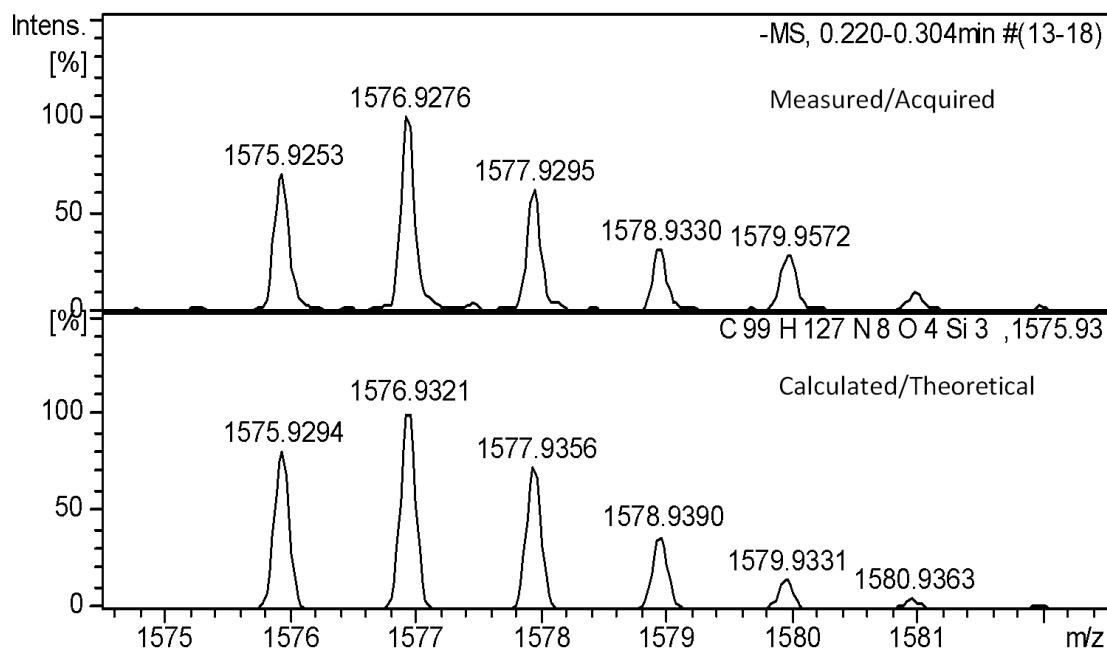


Figure S11. HR-MS spectra for **LBG1**; measured m/z (up), calculated m/z (down).

Section 2: Absorption spectra (solution) and electrochemistry

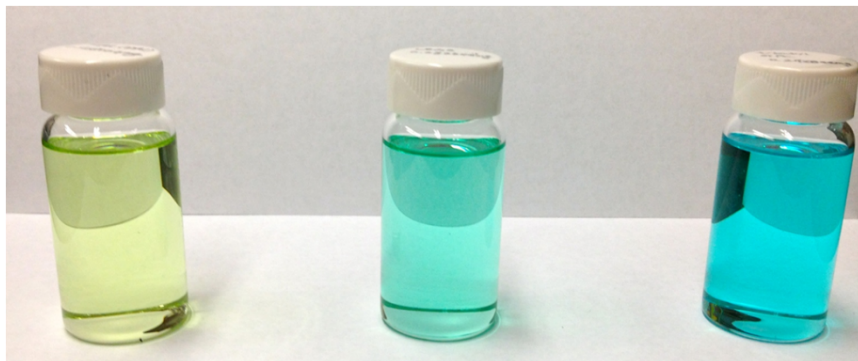


Figure S12. Dye solutions in CHCl_3 ($c = 10^{-5}$ M) of **LBG1** (left), **LBG3** (middle), and *t*-butyl SiPc (right).

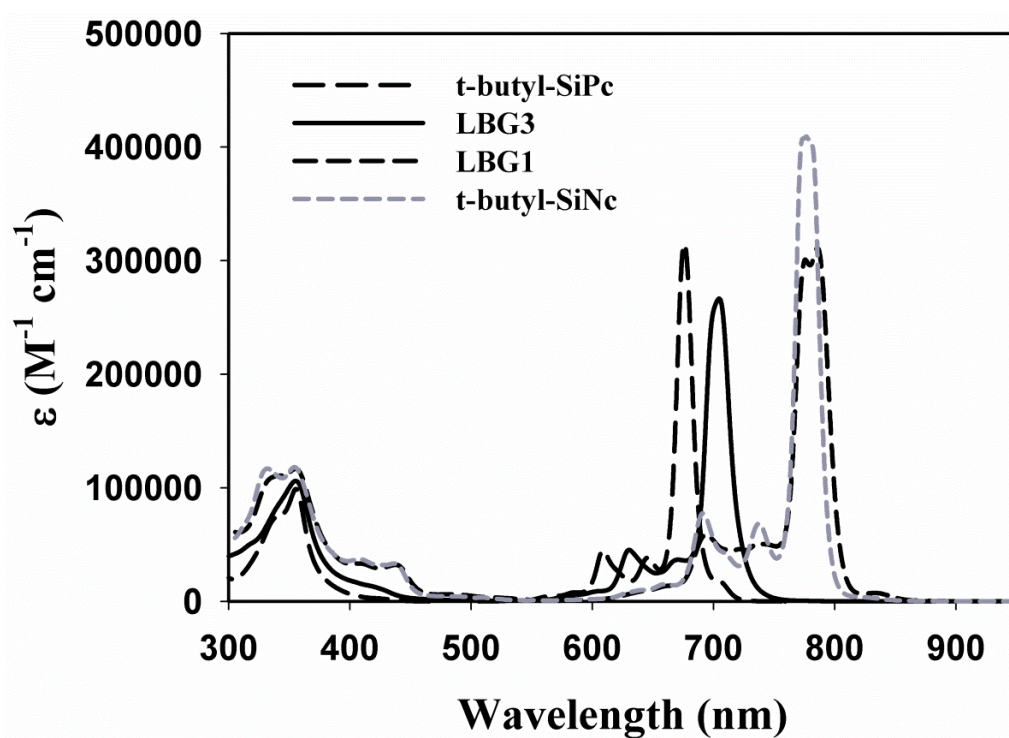


Figure S13. Electronic absorption spectra in CHCl_3 ($c = 10^{-5}$ M) of *t*-butyl SiPc (black long dashed line), **LBG3** (solid line), **LBG1** (black middle dashed line), and *t*-butyl SiNc (gray short dashed line).

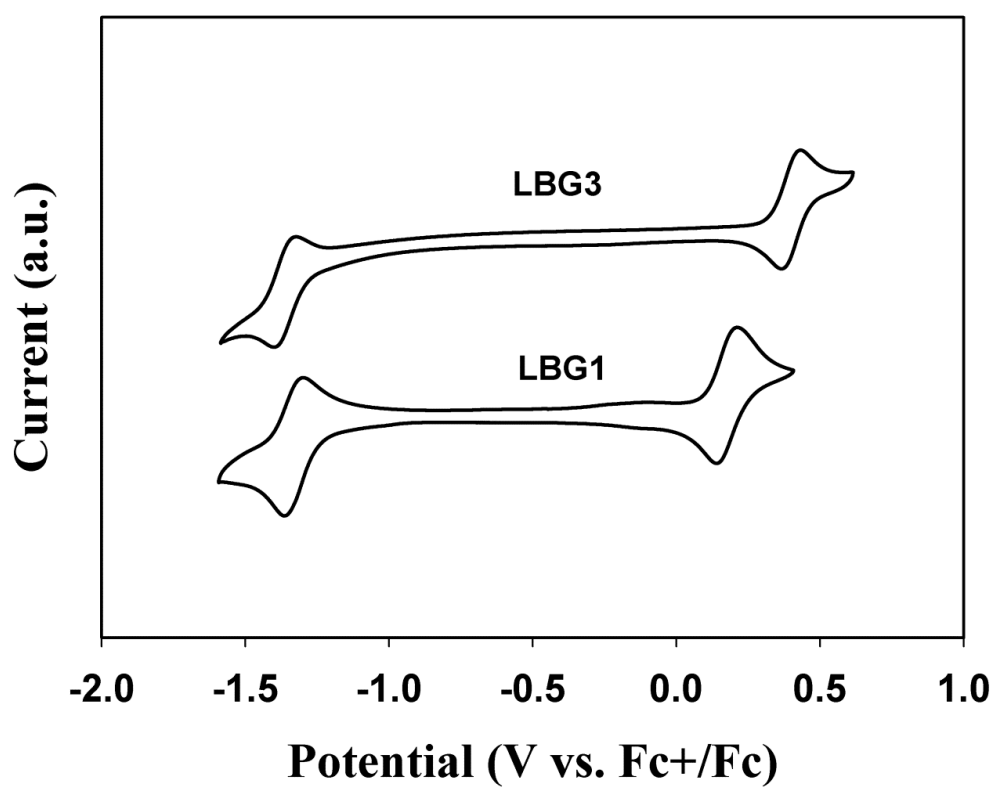


Figure S14. Cyclic voltammograms of **LBG1** and **LBG3** in dichloromethane containing 0.1 M TBAPF₆ at 25 °C.

Section 3: Solar cell devices manufacturing and characterization

Dye-sensitized solar cells: TiO_2 substrates for DSCs and counter electrodes were fabricated as previously reported with 8 microns of transparent 20nm size TiO_2 nanoparticles and a 5 micron scattering layer.^[3] Substrates were then sensitized in 0.1 mM **LBG1** or **LBG3** solution in ethanol with 1 mM cheno-deoxycholic acid (cDCA) 18 hours. The solar cell was completed by sealing the dyed TiO_2 substrate and counterelectrode with a 25 micron thick surlyn spacer (Solaronix). Electrolyte was made by dissolving 1.0 M LiI and 0.05 M I_2 in acetonitrile and inserted into the cell by vacuum backfilling. J-V curves were taken with a Keithley 2400 sourcemeter, under simulated AM 1.5G illumination with a Spectraphysics model 91160 solar simulator which has been calibrated using a hamamatsu Si photodiode with KG5 filter. The sample was masked with a 0.159 cm^2 area machined mask during J-V measurements. IPCE spectra were taken at a chopping rate of 2 Hz with a white light illumination bias of approximately 0.1 suns (supplied by a Lamina white light LED array). For the chopped IPCE signal, a Newport Apex monochromator illuminator was used in conjunction with a Princeton Instruments monochromator and a filter wheel. The signal from the DSC was put through a transimpedance amplifier and recorded on a Stanford Instruments lock-in amplifier.

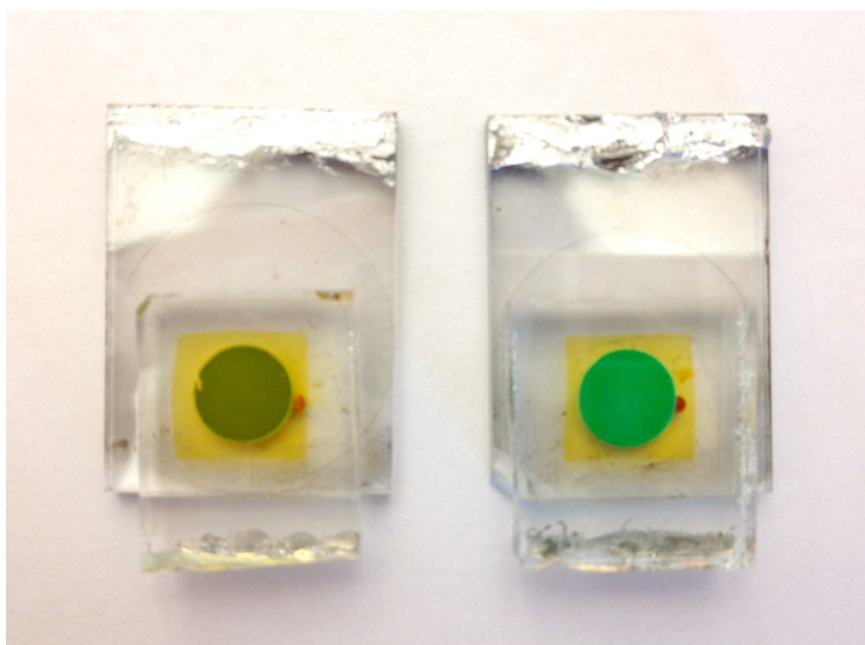


Figure S15. Images of **LBG1** (left) and **LBG3** (right) cells.

Section 4: Dye spectra on titania with various cDCA concentrations

Shown below are the absorption spectra of **LBG3** (left) and **LBG1** (right) on thin (1 μm) meso-porous titania films deposited on glass substrates. The films were dyed from solutions containing various amounts of the additive cheno-deoxycholic acid (cDCA). For the samples with high cDCA concentration (10 mM) we find that the spectrum on titania is comparable (with some spectral broadening) to the solution spectrum of the dyes. This should correspond to the absorption spectrum of dye monomers and no dye aggregates are visible at high cDCA concentrations. At lower cDCA concentration a band evolving at about 710 nm (LBG3) and 800 nm (LBG1) is observed. This indicated the formation of J-aggregates caused by the introduction of the lateral siloxane-groups, affecting the molecular organization on the titania surface.^[4] Without these side-chains, phthalocyanines and naphthalocyanines and hybrid naphthalo-phthalocyanines exhibit a dominant tendency to form H-aggregates.^[5, 6] In the solar cell devices investigated herein, the concentration of cDCA in the dye solution was 1 mM, which improved the performance considerably.

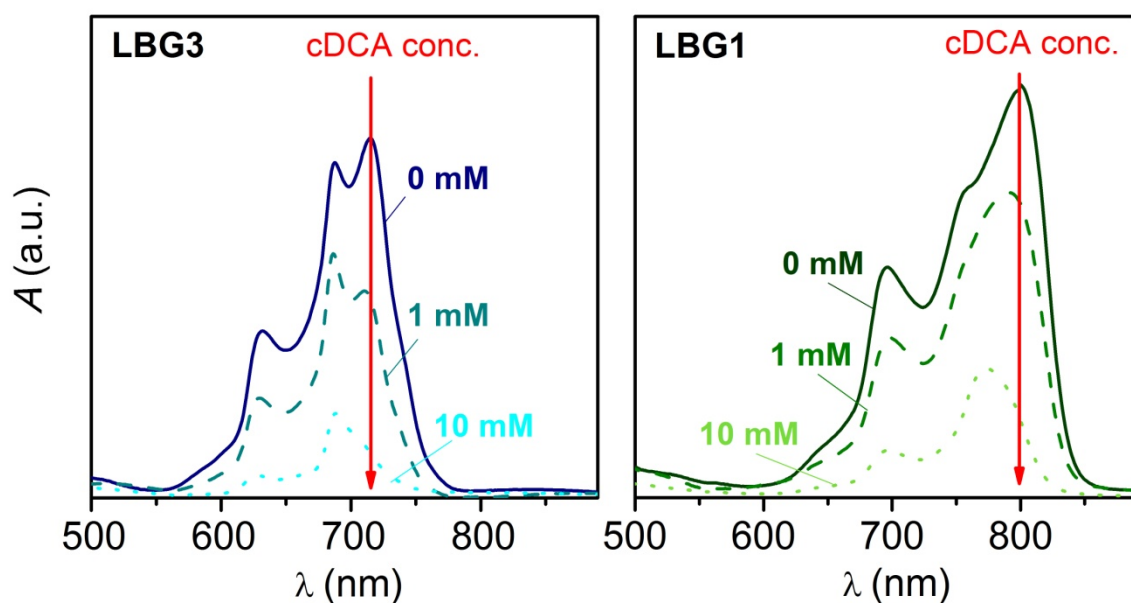


Figure S16. Absorption spectra of **LBG3** (left) and **LBG1** (right) adsorbed onto mesoporous TiO₂ films (ca. 1 μm) with varying amounts (0, 1, 10 mM) of the co-adsorbent cheno-deoxycholic acid (cDCA) added to the dye bath.

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