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Harvesting UV Photons for Solar Energy Conversion Applications

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Supporting Information

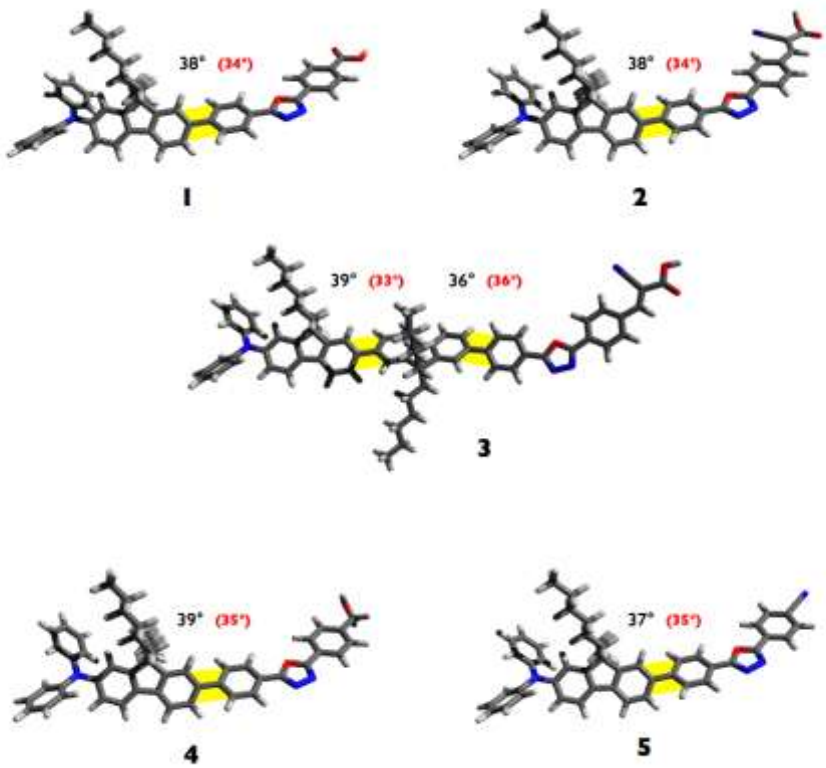


Figure S1. Optimized geometries of the dyes **1**-**5** with the corresponding dihedral angles in the neutral state (black) and the dihedral angles in the oxidized positively charged conformation (red) as mentioned in the manuscript. For consistency, for dye **3** diphenylamine replaces di(*p*-tolyl)amine.

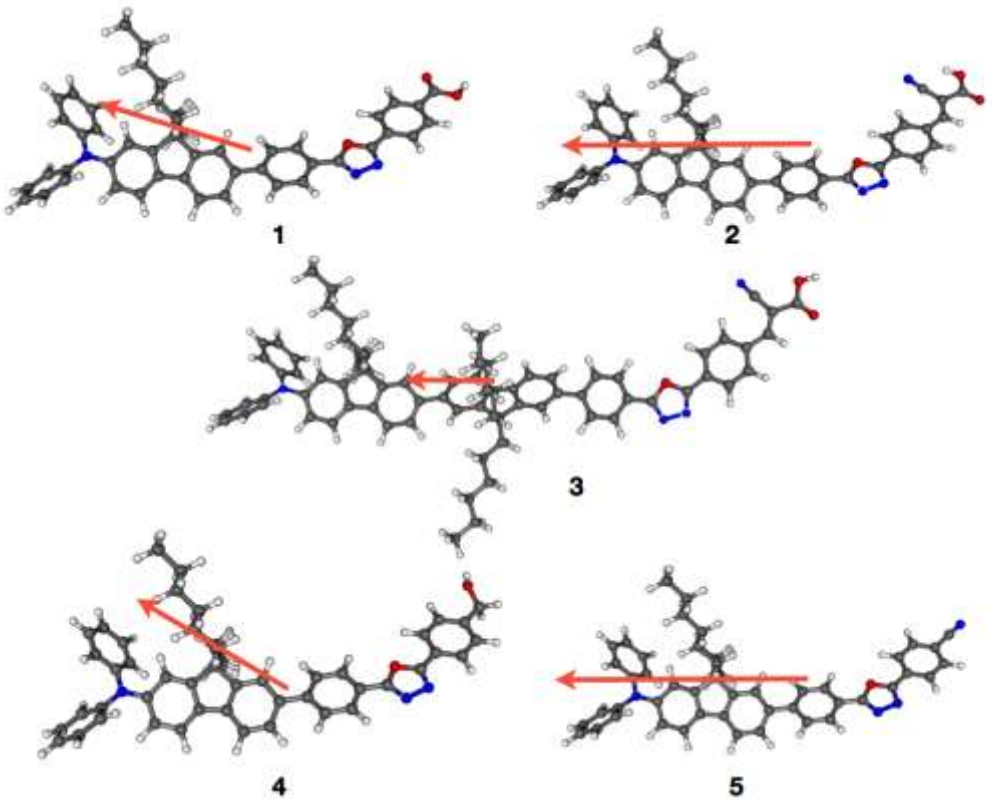


Figure S2. Representation of the calculated dipole moment vector for all the dyes. The length of the arrows are related to the absolute values of the dipole moments. For consistency, for dye **3** diphenylamine replaces di(*p*-tolyl)amine.

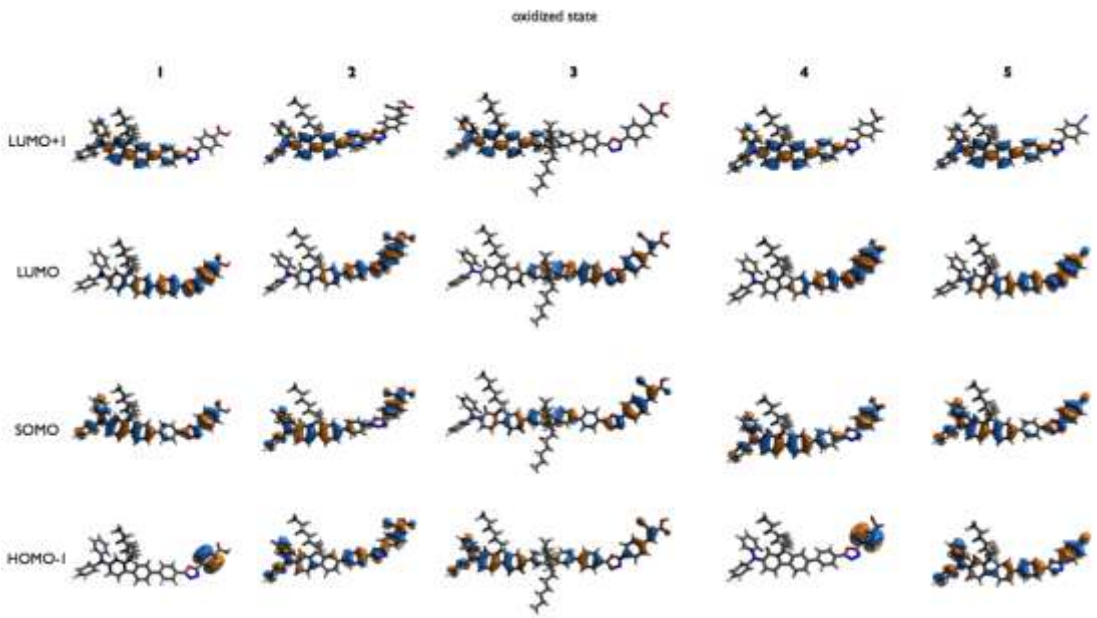


Figure S3. Representation of the frontier orbitals HOMO-1 to LUMO+1 of the positively charged *oxidized* state for all dyes.

Experimental Section.

Film preparation

5 µm thick transparent films of 20 nm sized TiO_2 particles were first screen-printed on normal flint glass slides. After annealing of the TiO_2 layers at 500 °C for 30 min, the films were cooled to 80 °C and immersed overnight into 0.1 mM tBuOH/MeCN (1:1 v/v mixture) solutions of the dyes. After washing the films for 30 min in pure solvent they were dried and were either coated with a drop of 3-methoxypropionitrile or with the Z960 electrolyte. The composition of Z960 is 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M I_2, 0.05 M lithium iodide, 0.1 M guanidinium thiocyanate and 0.5 M *tert*-butylpyridine in acetonitrile and valeronitrile solvent mixture (85:15 v/v).

Laser Studies

Time-resolved pump-probe transient absorption measurements were performed on the previously described dye-sensitized, 5 µm-thick, transparent TiO_2 mesoporous films in the presence and absence of the electrolyte Z960. For solution studies 1 mm quartz cuvettes have been employed.

The pump-probe technique uses a compact 1 kHz, Ti:Sapphire amplified femtosecond laser (CPA-2001, Clark-MXR), with a pulse width of about 120 fs and a pulse energy of 1 mJ at a central wavelength of 775 nm. The output beam was split into two parts for pumping a double-stage non-collinear optical parametric amplifier (NOPA) and to produce a white light continuum in a sapphire plate or 387 nm UV light by second harmonic generation of the CPA output in a thin BBO crystal. The NOPA was pumped by 200 µJ pulses at a central wavelength of 775 nm and the excitation wavelength was tuned to 400 nm to generate pulses of approximately 10 µJ. The output pulses of the NOPA were compressed in a SF10-glass prism pair compressor down to a duration of less than 60 fs (fwhm). Iris diaphragms were used to decrease the pulse energy down to a few µJ for the pump and to <1 µJ for the probe beam. Transient spectra were measured using a white light continuum (WLC) for probing.

The nanosecond laser flash photolysis employed 7 ns duration pulses to excite the sample at $\lambda = 420$ nm and using a 30 Hz repetition rate. An optical parametric oscillator (OPO-355, GWU Lasertechnik) pumped by a frequency-tripled Q-switched Nd:YAG laser (Powerlite 7030, Continuum) served as a light source. The OPO beam output was expanded by a planoconcave lens to irradiate a large cross-section of the sample, whose surface was kept at a 45° angle to the excitation beam. The laser fluence on the sample was kept at a low level (40 µJ cm^{-2} per pulse) to ensure that, on average, less than one electron is injected per TiO_2 nanoparticle on exposure to one laser pulse. The probe light, produced by a continuous wave xenon arc lamp, was first passed through a monochromator tuned at 750 and 900 nm, various optical elements, the sample, and then through a second monochromator, before being detected by a fast photomultiplier tube (Hamamatsu, R9110).

Device fabrication

The device consists of two electrodes made of FTO glass (NSG 10, Nippon Sheet Glass Co, Ltd. – photoanode and TEC7, Pilkington – counterelectrode). A multilayer of TiO_2 was screen printed onto the photoanode glass: on the bottom a transparent 8 µm-thick layer consisted of 20 nm ∅ particles and on the top 5 µm-thick scattering layer (400 nm ∅ particles) and then sintered at 500 ˚C. A hydrothermal $TiCl_4$ treatment (70 ˚C for 30 min) was conducted before final sintering at 450 ˚C for another 30 min prior to the immersion into dye solutions (dipped for 24 h). The device was assembled by binding the stained photoanode and a thermally platinized counter-electrode together with a 25 µm-thick hot-melt polymer film (Surlyn, DuPont). The electrolyte (1 M 1,3-dimethylimidazolium iodide, 0.03 M I_2, 0.1 M guanidinium thiocyanate, 0.5 M *t*-butylpyridine, 0.05 M lithium iodide in 85:15 v/v acetonitrile/valeronitrile) was driven into the device via a pre-drilled hole in the counter-electrode with the aid of vacuum system. The hole was sealed with the Surlyn piece and a covering glass. Metal contacts were placed on the edges of the cell.

IV and IPCE measurements

A homemade setup was used to characterize the photovoltaic performance of the devices. A 450 W xenon lamp (Oriel) served as a light source and the mismatch between the simulated light and real solar spectrum was corrected with a Schott K113 Tempax sunfilter (Präzisions Glas & Optik GmbH) in the range 350-750 nm. The voltage bias was applied on the device via a Keithley 2400 digital sourcemeter (Keithley), which also recorded the generated photocurrent. The IPCE setup used for measurements consisted of a 300 W xenon lamp (ILC Technology), a Gemini-180 monochromator (Jobin Yvon Ltd.), a set of white diodes to apply a constant light bias, a chopper and a Lock-In Amplifier (SR830, Stanford Research Systems). The cells were masked to define the illuminated area of 0.159 cm^2.

Materials and Molecular Synthesis.

General Experimental Procedures

All air-sensitive reactions were conducted under a blanket of argon which was dried by passage through a column of phosphorus pentoxide. All commercial chemicals were used without further purification unless otherwise stated. Anhydrous toluene, tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried through an HPLC column on an Innovative Technology Inc. solvent purification system. Anhydrous pyridine was dried over KOH pellets. Column chromatography was carried out using 40-60 µm mesh silica. Analytical thin layer chromatography was performed on 20 mm pre-coated plates of silica gel (Merck, silica gel $60F_{254}$), visualization was made using ultraviolet light (254 nm). NMR spectra were recorded on: Bruker Avance-400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 101 MHz), Varian Mercury-200 (^{1}H NMR: 200 MHz), Varian Mercury-400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 126 MHz), Varian Inova-500 (^{1}H NMR: 500 MHz, ^{13}C NMR 126 MHz) and Varian VNMRS-700 (^{1}H NMR: 700 MHz, ^{13}C NMR 176 MHz) spectrometers. Melting points were determined in open-ended capillaries using a Stuart Scientific SMP3 melting point apparatus at a ramping rate of 5 °C/min. Mass spectra were measured on a Waters Xevo OTofMS with an ASAP probe. Electron ionisation (EI) mass spectra were recorded on a Thermoquest Trace or a Thermo-Finnigan DSQ.

General Miyaura Borylation Procedure

In a flame-dried flask under an atmosphere of argon the aryl halide (1.0 equiv.) was dissolved in DMF (2 mL per mmol of halide) and degassed with argon for 20 min. To this stirred solution B_2pin_2 (1.4 equiv.) and potassium acetate (1.6 equiv.) were added and the mixture degassed for a further 10 min, after which time [$PdCl_2$(dppf)] (2 mol%) was added and the reaction mixture was heated to 80 °C for 15 h. The mixture was then cooled, water added and extracted with diethyl ether. The organic extracts are combined and the solvent removed under reduced pressure. The product was purified by column chromatography on silica gel.

General Suzuki-Miyaura Cross-Coupling Procedure

In a flame-dried flask under an atmosphere of argon the relevant aryl halide and boronic ester or acid were dissolved in anhydrous THF (2 mL per mmol of halide) and degassed for 20 min. To this stirred solution aqueous NaOH (2-2.5 equiv.) was added and the mixture degassed for a further 10 min. After this time [$PdCl_2(PPh_3)_2$] (2 mol%) was added and the reaction mixture heated to 65 °C for 15 h under argon. The reaction mixture was then allowed to cool, filtered through a plug of Celite, washed with water and extracted with diethyl ether. The solvent was removed from the combined organic extracts under reduced pressure and the crude product purified by column chromatography on silica gel.

4-(5-(4-Bromophenyl)-1,3,4-oxadiazol-2-yl)benzonitrile (C)

To a stirred solution of 4-cyanobenzoic acid (**A**) (2.00 g, 0.014 mol), 4-bromobenzohydrazide (**B**) (2.90 g, 0.014 mol) and TBTU (4.50 g, 0.014 mol) DIPEA (2.44 mL, 0.014 mol) were added. The reaction mixture was stirred at room temperature for 24 h. After this time it was poured onto water and extracted with ethyl acetate. The combined organic extracts were washed sequentially with saturated $NaHCO_3$ solution and then 1 M $NaHSO_4$ solution. The solvent was removed from the organic layers under reduced pressure. The crude 4-bromo-*N*'-(4-cyanobenzoyl)benzohydrazide was dissolved in $POCl_3$ (5 mL) and heated to reflux for 12 h. The excess $POCl_3$ was then removed by distillation and the crude product purified by column chromatography on silica gel using chloroform as eluent to yield **C** as a white solid (0.71 g, 16%). Mp: 220.3-221.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 9.0 Hz, 2H), 7.84 – 7.75 (d, 8.5 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.68, 163.21, 132.92, 132.62, 128.47, 127.59, 127.38, 127.09, 122.28, 117.82, 115.38; (HRMS ASAP$^+$) calcd for $C_{18}H_8{}^{79}BrN_3O$: 324.9851, Found: 324.9851.

4-(5-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzonitrile (D)

The standard Miyaura borylation procedure was followed using the following reagents: **C** (0.30 g, 0.92 mmol), B_2pin_2 (0.30 g, 1.20 mmol), [$PdCl_2$(dppf)] (20 mg, 0.03 mmol), KOAc (0.23 g, 2.3 mmol) and DMF (10 mL). The product was purified by column chromatography on silica gel using 1 : 1 (v/v) petroleum ether : DCM as eluent to yield **D** as a white solid (0.18 g, 51%). Mp: 241.9 – 243.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 1.38 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.40, 163.15, 135.42, 132.87, 127.77, 127.40, 126.12, 125.46, 117.88, 115.23, 84.32, 25.02, 24.90. HRMS (ASAP$^+$), calcd for $C_{21}H_{21}{}^{10}BN_3O_2$: 374.1753, Found: 374.1791.

4-(5-(4-(7-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzonitrile (5)

The general Suzuki-Miyaura cross-coupling procedure was followed using the following reagents: **D** (0.28 g, 0.75 mmol), **E**[1] (0.48 g, 0.83 mmol), [$PdCl_2(PPh_3)_2$] (25 mg, 0.04 mmol), NaOH (0.08 g in 5 mL H_2O) and THF (10 mL). The product was purified by column chromatography on silica gel using initially 7 : 3 (v/v) petroleum ether : diethyl ether changing to 1 : 1 (v/v) petroleum ether : diethyl ether as eluent to yield **5** as a yellow solid (0.25 g, 45%). Mp: 167.9 – 168.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 8.0 Hz, 2H), 7.84 (t, *J* = 7.5 Hz, 4H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.29 – 7.20 (m, 4H), 7.13 (d, *J* = 7.5 Hz, 5H), 7.02 (m, 3H), 2.00 – 1.80 (m, 4H), 1.19 – 0.94 (m, 12H), 0.78 (t, *J* = 7.0 Hz, 6H), 0.76 – 0.59 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.38, 162.98, 152.46, 151.60, 147.89, 147.54, 145.54, 141.42, 137.44, 135.38, 132.87, 129.17, 127.85, 127.69, 127.52, 127.33, 126.12, 123.91, 123.43, 122.61, 121.64, 121.17, 120.63, 119.53, 119.14, 117.90, 115.12, 55.22, 40.22, 31.48, 29.59, 23.78, 22.52, 14.01; HRMS (ASAP$^+$), calcd for $C_{52}H_{50}N_4O$: 746.3985, found: 746.3962.

4-(5-(4-(7-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzoic acid (1)

A mixture of **5** (0.065 mg, 0.09 mmol) and potassium hydroxide (0.13 g, 2.3 mmol) in 3 : 1 ethanol : water solution (10 mL) was heated to reflux for 15 h. After this time, when the solid had dissolved, the pH was altered to pH 3 by addition of dilute

hydrochloric acid. The resulting precipitate was filtered, dissolved in dichloromethane and washed with $NaHCO_3$ solution. The organic extracts were combined and the solvent removed under reduced pressure. The product was purified by column chromatography on silica gel using dichloromethane and then with dichloromethane and 5% acetic acid as eluent to yield **1** as a yellow solid (38 mg, 57%). Mp: 129.7 – 132.1 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ 8.16 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 7.0 Hz, 4H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.26 (m, 4H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.13 – 7.07 (m, 4H), 7.07 – 7.00 (m, 3H), 2.18 – 1.88 (m, 4H), 1.18 – 1.04 (m, 12H), 0.77 (t, *J* = 7.0 Hz, 6H), 0.72 (s, 4H); ^{13}C NMR (151 MHz, acetone-d_6): δ 170.96, 166.02, 165.71, 165.43, 152.46, 151.49, 148.00, 147.54, 144.73, 141.13, 137.96, 136.85, 135.92, 133.55, 131.24, 129.68, 129.25, 128.09, 127.61, 126.82, 126.12, 123.71, 123.50, 122.70, 121.33, 120.81, 119.65, 119.30, 55.18, 39.86, 31.30, 23.70, 22.23, 19.51, 13.34; HRMS (ASAP$^+$), calc for $C_{52}H_{52}N_3O_3$: 766.4009. Found: 766.4023.

2-(4-Bromophenyl)-5-*p*-tolyl-1,3,4-oxadiazole (H)
To a stirred solution of 5-*p*-tolyl-1*H*-tetrazole (**F**) (5.45 g, 33.0 mmol) in pyridine (50 mL) 4-bromobenzoyl chloride (**G**)(7.84 g, 36.0 mmol) was added and the mixture was heated to reflux for 72 h. The reaction mixture was cooled and poured onto water to precipitate **H** which was filtered, dried and isolated as a white solid (6.12 g, 57%). Mp: 205.0 – 206.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.92 (m, 4H), 7.68 (m, 2H), 7.36 – 7.31 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.93, 163.64, 142.50, 132.41, 129.83, 128.28, 126.94, 126.29, 122.96, 120.96, 21.68. MS (ASAP+) 314 (85%, M+), 179 (100), 119 (45); HRMS (ASAP$^+$) calcd for $C_{15}H_{12}N_2OBr$: 315.0133. Found: 315.0150.

2-(4-(Bromomethyl)phenyl)-5-(4-bromophenyl)-1,3,4-oxadiazole (I)
To a solution of **H** (2.00 g, 6.3 mmol) in 1,2-dichloroethane (50 mL) *N*-bromosuccinimide (1.07 g, 6.0 mmol) and benzoyl peroxide (0.30 g, 1.2 mmol) were added. The reaction mixture was heated to 70 °C for 15 h, then cooled and the solvent removed under reduced pressure. The product was purified by column chromatography using initially petroleum ether and then petroleum ether : ethyl acetate (1:1 v/v) as eluents. The product was further purified by recrystallization from acetonitrile and **I** was isolated as a white solid (1.12 g, 48%). Mp 184.2 – 186.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 4.54 (s, 2H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.25, 163.98, 141.62, 132.45, 129.77, 128.32, 127.37, 126.53, 123.60, 122.71, 32.15; HRMS (ASAP$^+$), for $C_{15}H_{10}Br_2N_2O$ calcd: 391.9160. Found: 391.9171.

4-(5-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzyl acetate (J)
The general Miyaura borylation procedure was followed using the following reagents: **I** (0.50 g, 1.6 mmol), B_2Pin_2 (1.02 g, 4 mmol), potassium acetate (0.31 g, 3.2 mmol) and [$PdCl_2$(dppf)] (35 mg, 0.5 mmol). The product was purified by column chromatography on silica gel using petroleum ether (b.p. 40 – 60 °C) with 10% then 30% ethyl acetate as eluent to yield **J** as a white solid (0.26 g, 48%). Mp: 168.1 – 169.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (m, 4H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 5.19 (s, 2H), 2,11 (s, 3H), 1.38 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.63, 164.70, 164.37, 139.86, 135.32, 128.53, 127.20, 125.98, 123.70, 84.24, 65.49, 24.89, 20.89; HRMS (ASAP$^+$), for $C_{23}H_{25}N_2O_5{}^{10}B$ calcd: 420.1971, found: 420.1964.

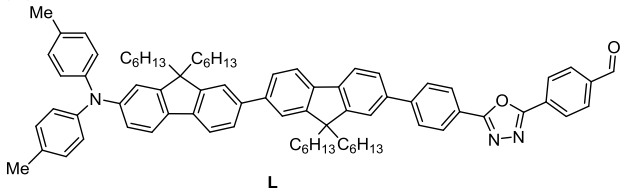
(4-(5-(4-(7-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)methanol (4)
The general Suzuki-Miyaura procedure was followed using the following reagents: **J** (0.10 g, 0.24 mmol), **E** (0.14 g, 0.25 mmol), sodium hydroxide (0.02 g, 0.57 mmol), H_2O (5 mL) and [$PdCl_2(PPh_3)_2$] (0.01 g, 0.01 mmol). The product was purified by column chromatography on silica gel using 1 : 1 (v/v) petroleum ether (b.p. 40 – 60 °C) : diethyl ether as eluent. The product **4** was isolated as a yellow solid (0.14 g, 76%). Mp: 73.9 – 76.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.5 Hz, 2H), 8.17 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.28 – 7.23 (m, 4H), 7.16 – 7.11 (m, 5H), 7.06 – 6.99 (m, 3H), 4.83 (s, 2H), 1.99 – 1.80 (m, 4H), 1.19 – 1.00 (m, 12H), 0.79 (t, *J* = 7.0 Hz, 6H), 0.77 – 0.65 (m, 4H) (OH not observed); ^{13}C NMR (151 MHz, $CDCl_3$): δ 164.55, 164.39, 152.45, 151.55, 147.91, 147.45, 145.00, 144.70, 141.24, 137.67, 135.49, 129.15, 127.58, 127.34, 127.24, 127.15, 126.08, 123.87, 123.45, 123.14, 122.56, 122.23, 121.18, 120.59, 119.49, 119.20, 64.70, 55.21, 53.38, 40.22, 31.47, 30.89, 29.58, 24.83, 23.78, 22.52, 14.00; HRMS (ASAP$^+$), calcd for $C_{52}H_{53}N_3O_2$: 751.4138, found: 751.4161.

4-(5-(4-(7-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzaldehyde (K)
To a solution of **4** (0.15 g, 0.20 mmol) in dichloromethane (5 mL) pyridinium chlorochromate (51 mg, 0.24 mmol) in dichloromethane (5 mL) was added dropwise. The resulting mixture was stirred at room temperature for 1 h. After this time the reaction mixture was filtered through a Celite plug. The product was then purified by column chromatography on silica gel using 1 : 1 (v/v) petroleum ether : diethyl ether as eluent to yield **K** as a yellow solid (89 mg, 60%). Mp: 148.3 – 149.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 2H), 8.20 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.51 (m, 3H), 7.26 – 7.18 (m, 4H), 7.12 – 7.05 (m, 5H), 7.04 – 6.94 (m, 3H), 1.97 – 1.76 (m, 4H), 1.15 – 0.96 (m, 12H), 0.75 (t, *J* = 7.0 Hz, 6H), 0.72 – 0.62 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 191.46, 165.53, 163.81, 152.72, 151.85, 148.16, 147.77, 145.66, 141.63, 138.42, 137.77, 135.68, 130.51, 129.43, 129.23, 127.93, 127.77, 127.70, 126.38, 124.16, 123.70, 122.86, 122.07, 121.44, 120.89, 119.79, 119.42, 55.48, 40.49, 31.74, 29.85, 24.05, 22.79, 14.28; HRMS (ASAP$^+$), calc for $C_{52}H_{51}N_3O_2$: 749.3981, Found: 749.3961.

2-Cyano-3-(4-(5-(4-(7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)acrylic acid (2)

To a solution of **K** (46 mg, 0.061 mmol) and ammonium acetate (1 mg, 0.012 mmol) in acetic acid (2 mL) was added cyanoacetic acid (15 mg, 0.18 mmol). This stirred mixture was heated to reflux for 15 h after which time it was cooled, poured onto water and filtered. The solid was dissolved in dichloromethane and washed with water. The solvent was removed from the combined organic extracts and the crude product was purified by column chromatography using initially dichloromethane, then dichloromethane:methanol (4:1 v/v) as eluent to yield **2** as a yellow solid (25 mg, 50%). Mp: 119.3 – 120.0 ^{o}C. ^{1}H NMR (400 MHz, CD_3OD/CS_2): δ 8.27 (m, 4H), 8.20 – 8.12 (m, 3H), 7.96 – 7.87 (m, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.70 – 7.59 (m, 3H), 7.31 – 7.19 (m, 4H), 7.16 – 7.07 (m, 5H), 7.03 (m, 3H), 2.12 – 1.85 (m, 4H), 1.25 – 1.00 (m, 12H), 0.87 – 0.78 (m, 6H), 0.73 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.62, 152.67, 151.68, 150.91, 148.14, 147.60, 141.31, 135.68, 129.37, 127.55, 126.38, 124.11, 122.78, 120.87, 119.77, 119.40, 55.42, 40.40, 31.63, 29.93, 29.75, 24.03, 22.68, 14.22; HRMS (ES^+), calc for $C_{55}H_{52}N_4O_3$: 816.4039, Found: 816.4042; IR (THF solution) cm^{-1}; 3372 (O-H), 3502 (O-H), 2217 (C≡N), 1641 (C=O), 1596 (C=N).

(4-(5-(4-(7'-(di-*p*-tolylamino)-9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzaldehyde (L)



L

Following literature precedents,[2] compound **L** was obtained as a yellow solid in 68% yield. Mp: 150.2 – 151.8 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.22 (dd, *J* = 26.3, 8.2 Hz, 5H), 8.08 – 7.93 (m, 4H), 7.70 – 7.61 (m, 2H), 7.60 – 7.50 (m, 7H), 7.43 (m, 2H), 7.00 – 6.86 (m, 8H), 2.22 – 1.90 (m, 14H), 1.10 – 0.56 (m, 44H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 191.26, 157.91, 156.73, 155.80, 155.72, 154.33, 151.99, 150.82, 149.55, 148.43, 148.40, 145.00, 144.02, 143.61, 142.30, 142.01, 141.10, 141.04, 141.00, 138.70, 137.55, 134.90, 134.13, 132.75, 131.94, 130.89, 130.39, 129.44, 129.21, 127.67, 126.55, 125.22, 125.19, 124.50, 124.20, 124.10, 123.66, 122.32, 122.01, 121.20, 60.00, 59.23, 44.21, 43.10, 42.01, 35.01, 34.88, 32.88, 32.51, 28.01, 25.90, 24.99, 23.54, 16.11; HRMS ($ASAP^+$), calc for $C_{79}H_{87}N_3O_2$: 1109.6798, Found: 1109.6796.

2-Cyano-3-(4-(5-(4-(7'-(di-p-tolylamino)-9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2'-bifluoren]-7-yl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)acrylic acid (3)

To a solution of the aldehyde precursor **L** (50 mg, 0.045 mmol) and ammonium acetate (0.7 mg, 0.01 mmol) in acetic acid (2 mL) was added cyanoacetic acid (11.5 mg, 0.135 mmol). The mixture was refluxed under argon for 15 h then poured onto water and filtered. The crude solid was dissolved in dichloromethane (20 mL) and washed with water (2x50 mL). The solvent was removed from the combined organic extracts and the crude product was purified by column chromatography using first dichloromethane then dichloromethane/methanol (4:1 v/v) mixture as eluent to yield **3** as a yellow solid (38 mg, 71%). Mp: 108.2 – 109.8 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$): δ 8.19 (dd, *J* = 26.3, 8.2 Hz, 5H), 8.08 (s, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.78 – 7.71 (m, 2H), 7.65 – 7.54 (m, 7H), 7.49 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.06 – 6.92 (m, 9H), 2.12 – 1.75 (m, 14H), 1.15 – 0.57 (m, 44H). ^{13}C NMR (101 MHz, $CDCl_3/CD_3OD$): δ 168.15, 166.72, 156.93, 155.33, 154.88, 154.72, 154.27, 151.64, 150.52, 149.31, 148.54, 148.48, 144.22, 143.96, 143.35, 142.32, 141.12, 141.02, 140.98, 138.22, 138.18, 137.98, 134.94, 134.01, 132.65, 130.74, 130.44, 130.30, 129.11, 129.03, 126.93, 126.68, 125.34, 125.13, 124.53, 124.33, 124.25, 124.10, 123.09, 122.09, 122.07, 121.23, 58.30, 58.00, 43.22, 43.11, 41.87, 34.38, 34.31, 32.49, 32.48, 26.68, 25.40, 25.39, 23.55, 16.84, 16.77. MS (MALDI-TOF) *m/z* (%): 1176.6.0 ($[M-H]^+$, 100); HRMS $ASAP^+$, calc for $[M-CO_2H]$ $C_{81}H_{87}N_4O$: 1131.6880, Found: 1131.6842; IR (THF solution) cm^{-1}; 3370 (O-H), 3500 (O-H), 2217 (C≡N), 1639 (C=O), 1590 (C=N).

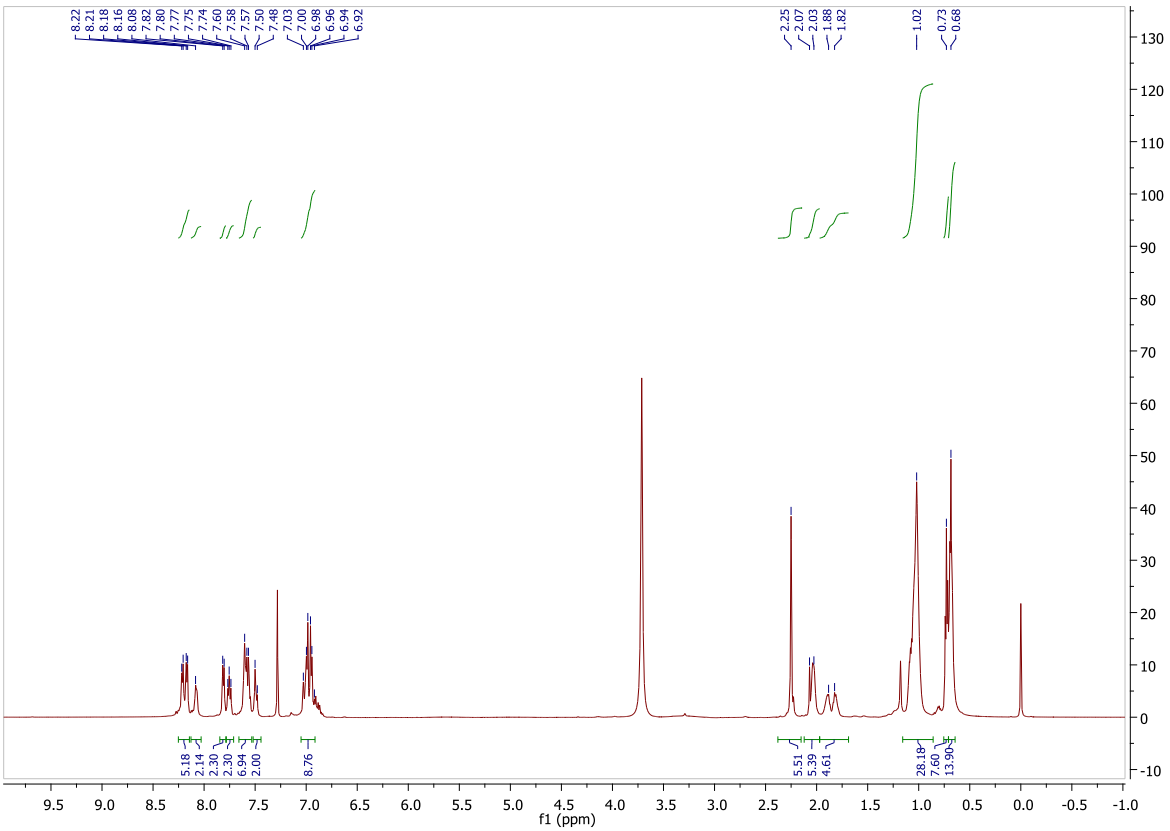


Figure S4. ^{1}H NMR spectrum of **3** in $CDCl_3/CD_3OD$.

References

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2 K. E. Linton, A. L. Fisher, C. Pearson, M. A. Fox, L.-O. Palsson, M. R. Bryce, M. C. Petty, *J. Mater. Chem*., 2012, **22**, 11816.