Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Modulating Dye $E_{(S+/S*)}$ with Efficient Heterocyclic Nitrogen Containing Acceptors for DSCs

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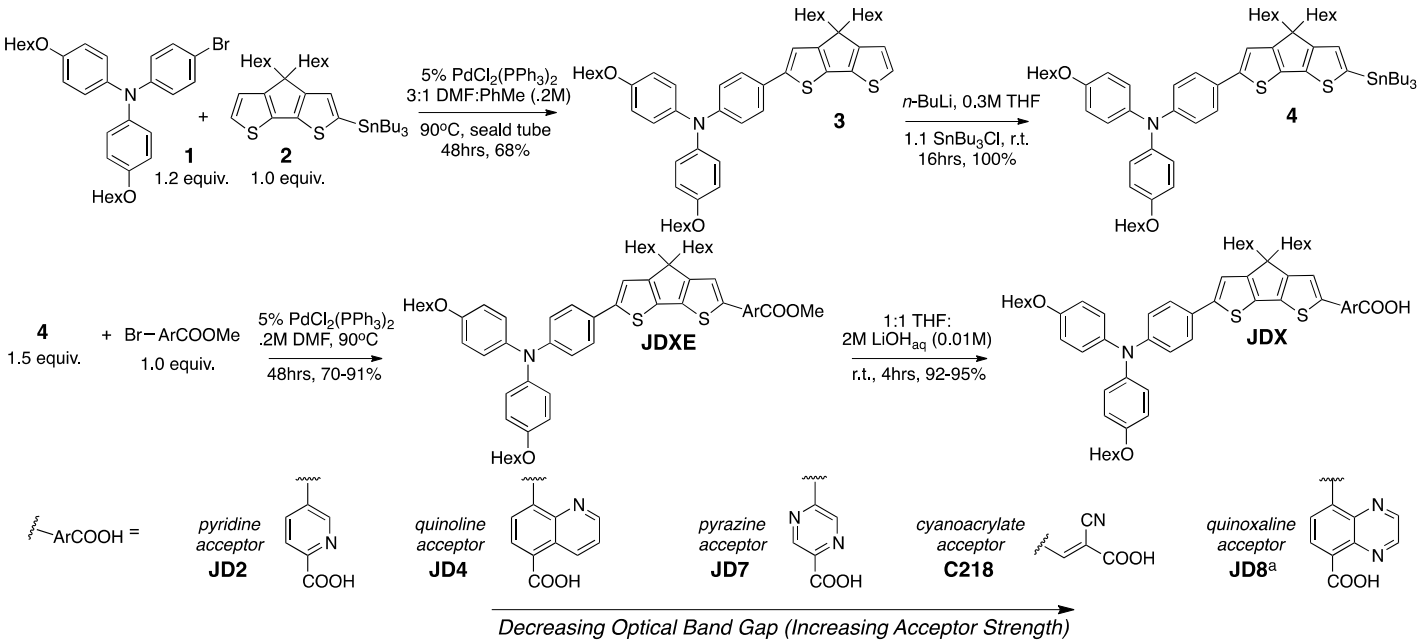
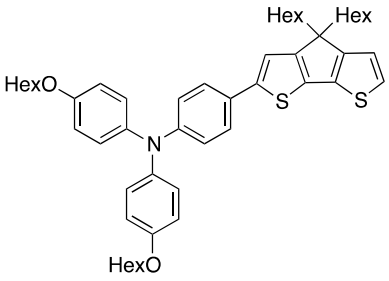
General Information: All commercially obtained reagents were used as received: 4H-cyclopenta[2,1-b:3,4-b']dithiophene (Astar Pharmaceuticals), methyl 5-bromopyrazine-2-carboxylate (Astatech, Inc.), methyl 8-bromoquinoline-5-carboxylate (Oakwood), and methyl 5-bromopyridine-2-carboxylate (Alfa Aesar). Anhydrous N,N-dimethylformamide (DMF) (Sure Seal) was obtained from Sigma-Aldrich and used as received. Anhydrous tetrahydrofuran (THF) (AcroSeal) was obtained from Acros and used as received. Thin-layer chromatography (TLC) was conducted with Merck KGaA precoated TLC Silica gel 60 F_{254} aluminum sheets and visualized with UV and potassium permanganate staining. Flash column chromatography was performed as described by Still using Silicycle UltraPure SilicaFlash P60, 40-63 μm (230-400 mesh).[1] ^{1}H NMR spectra were recorded on a Bruker Avance-400 (400 MHz), Bruker AvanceIII-400 (400MHz), or Bruker DPX-400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Avance-400 (100 MHz) or Bruker AvanceIII-400 (100MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.23 ppm). High-resolution mass spectra were obtained at the École Polytechnique Fédérale de Lausanne mass spectrometry laboratory (EPFL). UV-Vis spectrum were measured with a Hewlett Packard 8453 UV-Vis spectrometer. Cyclic voltammetry was measured with an Autolab Eco Chemie cyclic voltammeter. Emission spectrum were measured with a Fluorolog Horiba Jobin Yvon Model FL-1065.

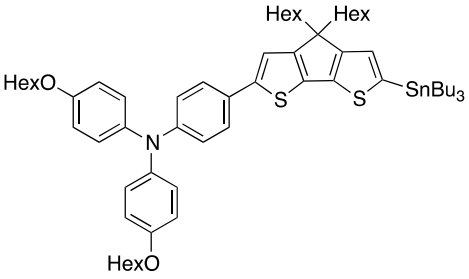
Photovoltaic Characterization: A 450W xenon lamp (Oriel, USA) was used as a light source to study the current-voltage characteristics of the DSSC. The spectral output of the lamp was filtered using a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) to reduce the mismatch between the simulated and actual solar spectrum to less than 2 %. The Keithley model 2400 digital source meter (Keithley, USA) was used for data acquisition. The photo-active area of 0.16 cm^2 was defined by a black mask of 6x6mm2. Incident photon-to-current conversion efficiency measurements were carried from the mono chromated visible photons, from Gemini-180 double monochromator Jobin Yvon Ltd. (UK), powered by a 300 W xenon light source (ILC Technology, USA) superimposed on a 10mW/cm^2 LED light. The monochromatic incident light was passed through a chopper running at 2 Hz frequency and the on / off ratio was measured by an operational amplifier.



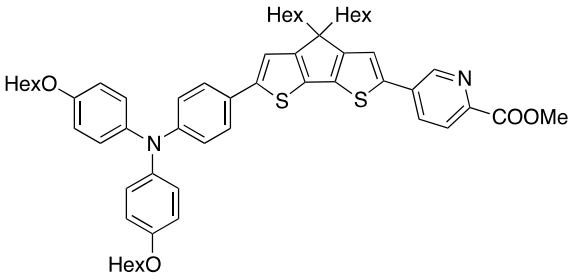
Scheme SI 1. Synthesis of D-π-A dyes **JD2**, **JD4**, **JD7** and **JD8** with nitrogen heterocycle acceptors. [a]Synthesized from the corresponding benzyl alcohol, followed by two step Swern/$NaClO_2$ oxidation to the final dye **JD8** (see below).



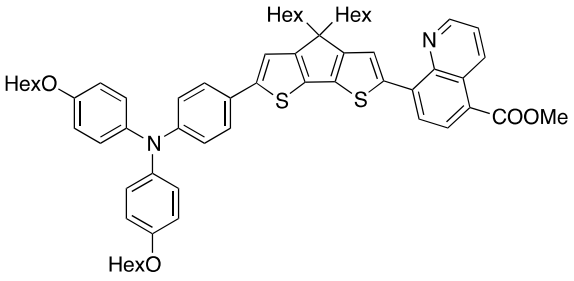
4-(4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline (3): To a 250 mL flame dried, N_2-filled round bottom flask charged with a stir bar was added 4-bromo-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline[2] (6.70 g, 12.8 mmol, 1.0 equiv.) and tributyl(4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-2-yl)stannane[3] (9.72 g, 15.3 mmol, 1.2 equiv.). Anhydrous DMF (64 mL, 0.20 M) was then added to the flask followed by dropwise addition of anhydrous toluene (20 mL, 0.64 M) until the stirred mixture became homogenous. A long needle was then placed in the reaction mixture and N_2 was bubble through the solution for 30 minutes through a needle vent. The flask was then charged with $PdCl_2(PPh_3)_2$ (448.0 mg, 0.64 mmol, 5 mol%), flushed with N_2 and sealed. The vessel was heated to 90°C for 48 hrs. The reaction was worked up by extraction with a 1:1 mixture of Et_2O:Hx (400 mL x 2) and H_2O (400 mL). The organic layers were combined and dried over $MgSO_4$. After removal of solvent, the mixture was purified via silica gel chromatography: 800 mL SiO_2, 10% CH_2Cl_2:Hx → 30% CH_2Cl_2:Hx (3L total) to give 4-(4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline, **3**, as a light orange oil (6.89g, 8.73 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 4.8 Hz, 1H), 7.05 (ap d, *J* = 9.2 Hz, 5H), 6.94-6.91 (m, 3H), 6.82 (d, *J* = 9.2 Hz, 4H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.95-0.75 (m, 48H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 157.5, 155.7, 148.1, 144.7, 140.8, 137.0, 134.8, 127.7, 126.6, 126.0, 124.4, 121.7, 121.1, 116.5, 115.5, 68.4, 53.8, 38.1, 34.9, 31.8, 29.9, 29.5, 27.1, 26.0, 24.7, 22.8. 14.3, 14.2. MS (MALDI) *m*/*z* calculated for $C_{51}H_{67}NO_2S_2$ $[M]^+$: 789.5, found 789.3.



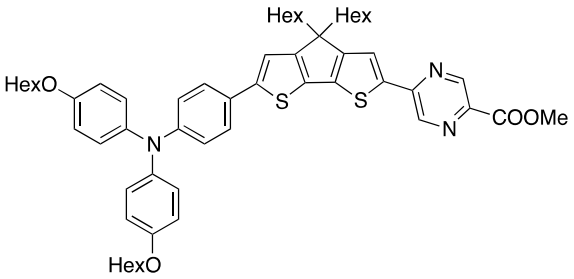
4-(4,4-dihexyl-6-(tributylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline (4): To a flame dried, N_2-filled 100 mL round bottom flask with stir bar was added **3** (5.39 g, 6.83 mmol, 1.0 equiv.) and anhydrous THF (30 mL, 0.23 M). The mixture was cooled to -78°C under N_2 and *n*-BuLi (2.73 mL, 6.83 mmol, 1.0 equiv., 2.5M) was added dropwise. After addition was complete, the mixture was maintained at -78°C for 2 hours. Then tributylchlorostannane (2.44 g, 2.03 mL, 7.51 mmol, 1.1 equiv.) was added via syringe dropwise. The mixture maintained at -78°C for 1 hour and then was allowed to warm to room temperature overnight. The reaction was worked up by extraction with 1:1 Et_2O:Hx (400 mL x 2) and H_2O (400 mL). The organic layers were combined and dried over $MgSO_4$. After removal of solvent, the crude mixture was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.05 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.91 (s, 1H), 6.83 (d, *J* = 9.2 Hz, 4H), 3.94 (t, *J* = 6.8 Hz, 4H), 1.90-0.75 (m, 75H). MS (MALDI) *m*/*z* calculated for $C_{63}H_{93}NO_2S_2Sn$ $[M]^+$: 1079.6, found 1079.3.



Methyl 5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)picolinate (JD2E): To a 10 mL sealed tube was added **4** (289.2 mg, 0.268 mmol, 1.5 equiv.), methyl 5-bromopicolinate (38.5 mg, 0.179 mmol, 1.0 equiv.), and DMF (0.89 mL, 0.3 M). The tube was capped with a needle vent and N_2 was bubbled through the mixture with a long needle for 30 minutes. $PdCl_2(PPh_3)_2$ (9.5 mg, 0.0134 mmol, 5.0 mol%) was then quickly added and the head space was flushed with N_2 and the tube was sealed. After heating for 72 hours at 90°C the reaction was cooled to room temperature. The reaction was diluted with 3 mL of CH_2Cl_2 and purified by column chromatography (200 mL SiO_2, 100% CH_2Cl_2 → 1.5% MeOH:CH_2Cl_2 → 3% MeOH:CH_2Cl_2) to yield the desired product, methyl 5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)picolinate **(JD2E)**, as a dark red oil which may solidify upon standing(115.6 mg, 0.125 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 2.4 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.95 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.35 (s, 1H), 7.06 (ap d, *J* = 8.8 Hz, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 4H), 4.02 (s, 3H), 3.94 (t, *J* = 6.8 Hz, 4H), 1.96-1.85 (m, 4H), 1.84-1.73 (m, 4H), 1.54-1.42 (m, 4H), 1.42-1.30 (m, 8H), 1.24-1.10 (m, 10H), 1.08-0.96 (m, 4H), 0.96-0.88 (m, 8H), 0.86-0.75 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 160.1, 158.5, 155.6, 148.3, 146.8, 145.7, 144.9, 140.4, 139.8, 138.0, 134.6, 133.9, 132.1, 128.6, 126.6, 126.0, 125.4, 120.6, 119.9, 116.2, 115.3, 68.3, 54.3, 52.8, 37.9, 31.6, 29.3, 28.2, 25.8, 24.5, 22.6, 17.4, 14.1 (2C), 13.6. MS (MALDI) *m*/*z* calculated for $C_{58}H_{72}N_2O_4S_2$ $[M]^+$: 924.49, found 924.48. UV-Vis λ_{max} = 466 nm ($CHCl_3$).

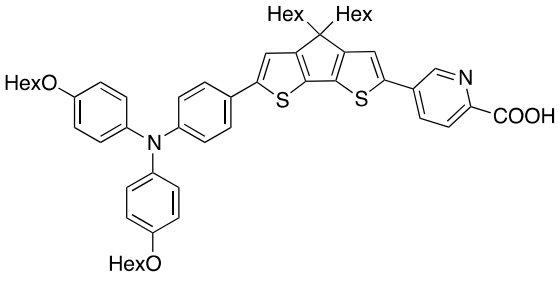


Methyl 8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-2-yl)quinoline-5-carboxylate (JD4E): To a 10 mL sealed tube was added **4** (289.2 mg, 0.268 mmol, 1.5 equiv.), methyl 8-bromoquinoline-5-carboxylate (48.0 mg, 0.179 mmol, 1.0 equiv.), and DMF (0.89 mL, 0.3 M). The tube was capped with a needle vent and N_2 was bubbled through the mixture with a long needle for 30 minutes. $PdCl_2(PPh_3)_2$ (9.5 mg, 0.0134 mmol, 5.0 mol%) was then quickly added and the head space was flushed with N_2 and the tube was sealed. After heating for 72 hours at 90°C the reaction was cooled to room temperature. The reaction was diluted with 3 mL of 1:1 CH_2Cl_2:Hx and purified by column chromatography (125 mL SiO_2, 1:1 CH_2Cl_2:Hx) to yield the desired product, methyl 8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)quinoline-5-carboxylate **(JD4E)**, as a dark red oil which may solidify upon standing(159.0 mg, 0.163 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ □□□□□□dd, *J* = 8.8, 2.0 Hz, 1H), 9.05 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.16 (br d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.58 (dd, *J* = 8.4, 3.6 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.07 (ap d, *J* = 8.8 Hz, 5H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 4H), 4.02 (s, 3H), 3.95 (t, *J* = 6.4 Hz, 4H), 1.96-1.87 (m, 4H), 1.85-1.74 (m, 4H), 1.53-1.41 (m, 4H), 1.40-1.31 (m, 8H), 1.24-1.00 (m, 16H), 0.98-0.85 (m, 6H), 0.85-0.75 (m, 6H). HRMS (MALDI) *m*/*z* calculated for $C_{62}H_{74}N_2O_4S_2$ $[M]^+$: 974.5090, found 974.4678. UV-Vis λ_{max} = 509 nm ($CHCl_3$).



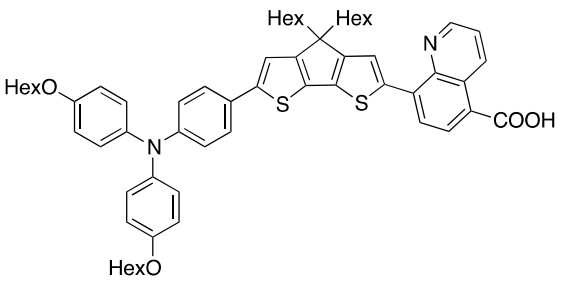
Methyl 5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-2-yl)pyrazine-2-carboxylate (JD7E): To a 10 mL sealed tube was added **4** (204.0 mg, 0.189 mmol, 1.5 equiv.), methyl 5-bromopyrazine-2-carboxylate (27.2 mg, 0.126 mmol, 1.0 equiv.), and DMF (0.63 mL, 0.2 M). The tube was capped with a needle vent and N_2 was bubbled through the mixture with a long needle for 30 minutes. $PdCl_2(PPh_3)_2$ (5.0 mg, 0.007 mmol, 5.0 mol%) was then quickly added and the head space was flushed with N_2 and the tube was sealed. After heating for 48 hours at 90°C the reaction was cooled to room temperature. The reaction was diluted with 3 mL of CH_2Cl_2 and purified by column chromatography (125 mL SiO_2, 100% CH_2Cl_2) to yield the desired product, methyl 5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)pyrazine-2-carboxylate **(JD7E)**, as a dark red oil which may solidify upon standing(105.6 mg, 0.114 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 1.6 Hz, 1H), 8.92 (d, *J* = 1.6 Hz, 1H), 7.62 (s, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.10-7.04 (m, 5H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 4H), 4.04 (s, 3H), 3.95 (t, *J* = 6.8 Hz, 4H), 1.95-1.85 (m, 4H), 1.85-1.74 (m, 4H), 1.54-1.41 (m, 4H), 1.40-1.30 (m, 8H), 1.25-1.10 (m, 12H), 1.05-0.95 (m, 4H), 0.95-0.87 (m, 6H), 0.81 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.4, 161.8, 158.8, 155.9, 151.9, 148.8, 148.5, 146.1, 144.4, 140.5, 139.5, 138.8, 134.2, 126.9, 126.8, 126.3, 122.3, 120.6, 116.4, 115.5, 68.5, 54.4, 53.1, 38.2, 31.8, 29.9, 29.5, 26.0, 24.7, 22.8 (2C), 14.3, 14.2, 13.8. MS (MALDI) *m*/*z* calculated for $C_{57}H_{71}N_3O_4S_2$ $[M]^+$: 925.5, found 925.4. MS (MALDI) *m*/*z* calculated for $C_{57}H_{71}N_3O_4S_2$ $[M + H]^+$: 912.49, found 912.41. UV-Vis λ_{max} = 508 nm ($CHCl_3$).

See the scheme below for the synthesis of **8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)quinoxaline-5-carboxylic acid (JD8)**.

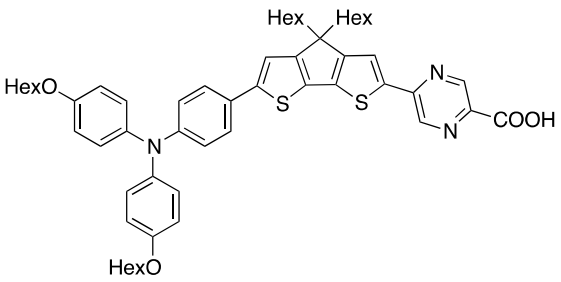


5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)picolinic acid (JD2): To a 100 mL

round bottom flask was added methyl 5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)picolinate, **JD2E** (115.6 mg, 0.125 mmol), followed by 20 mL of THF and 20 mL of 2M LiOH (aq.) solution. The mixture was stirred at room temperature until complete consumption of the starting material was observed by TLC (~2 hours). Upon completion, the reaction was diluted with CH_2Cl_2 (100 mL) and acidified with AcOH (10 mL). The mixture was rinsed with H_2O (100 mL x 2) and the organics dried over Na_2SO_4. The crude product was purified via column chromatography (125 mL SiO_2, 3% AcOH:20% MeOH:CH_2Cl_2) to give 5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)picolinic acid **(JD2)** as a dark red solid (108.2 mg, 0.119 mmol, 95%). Note: **JD2** does not give clearly resolved NMR signals in a variety of solvents tested, presumably due to strong aggregation in solution. Resolved peaks are observed if the sample is made dilute *and* significant tributyltin chloride is added to the NMR sample, presumably disrupting aggregation. Triethylamine was originally used as an additive; however, it was ambiguous as to weather the basicity or lipophilic alkyl chains were aiding in disrupting aggregation. To resolve this discrepancy the non-basic tributyltin chloride was added and aggregation was again suppressed. A possible hypothesis is the coordination of the lipophilic tributyltin with either the two alkyls on the CPDT, the two alkyls on the TPA, or both resulting in an effective large increase in steric bulk around the dye preventing aggregation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 1.6 Hz, 1H), 8.10 (dd, J = 8.0, 1.6 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.50 (s, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.07 (ap d, J = 8.8 Hz, 5H), 6.94 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 4H), 3.95 (t, J = 6.8 Hz, 4H). Remaining peaks are beneath tributyltin resonances (see above). HRMS (MALDI) m/z calculated for $C_{57}H_{70}N_2O_4S_2$ $[M]^+$: 910.4777, found 910.4790. UV-Vis λ_{max} = 466 nm ($CHCl_3$), λ_{max} = 461 nm (CH_2Cl_2). Emission (CH_2Cl_2) λ_{emis} = 644 nm (460 nm excitation wavelength). Elemental analysis (CHN): calculated C 75.12, H 7.74, N 3.07; found C 74.22, H 8.40, N 2.83.

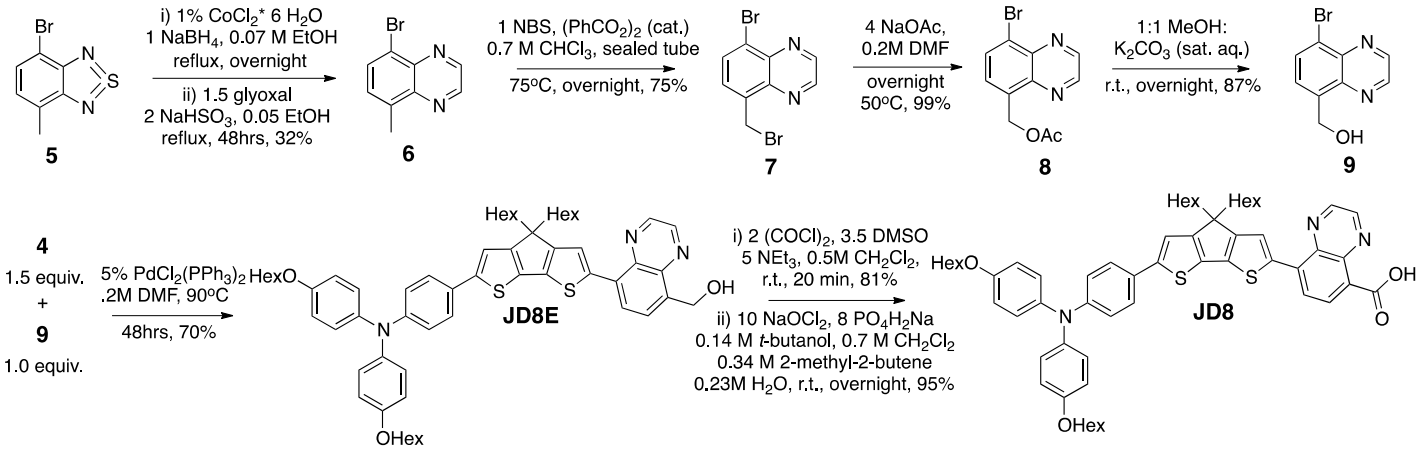


8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)quinoline-5-carboxylic acid (JD4): To a 100 mL round bottom flask was added methyl 8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)quinoline-5-carboxylate, **JD4E** (159.0 mg, 0.163 mmol), followed by 20 mL of THF and 20 mL of 2M LiOH (aq.) solution. The mixture was stirred at room temperature until complete consumption of the starting material was observed by TLC (overnight, > 6hrs). Upon completion, the reaction was diluted with CH_2Cl_2 (100 mL) and acidified with AcOH (10 mL). The mixture was rinsed with H_2O (100 mL x 2) and the organics dried over Na_2SO_4. The crude product was purified via column chromatography (125 mL SiO_2, 3% AcOH:10% MeOH:CH_2Cl_2) to give 8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)quinoline-5-carboxylic acid **(JD4)** as a dark red solid (144.1 mg, 0.150 mmol, 92%). Note: **JD4** displays rotamers at room temperature in $CDCl_3$ denoted as [multiplicity, major] and [multiplicity, minor] and aggregation unless a reagent is added to disrupt aggregation such as tributyltin chloride. Triethylamine was originally used as an additive; however, it was ambiguous as to weather the basicity or lipophilic alkyl chains were aiding in disrupting aggregation. To resolve this discrepancy the non-basic tributyltin chloride was added and aggregation was again suppressed. A possible hypothesis is the coordination of the lipophilic tributyltin with either the two alkyls on the CPDT, the two alkyls on the TPA, or both resulting in an effective large increase in steric bulk around the dye preventing aggregation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, J = 8.4 Hz, 1H), 9.05 [br s, minor] and 9.02 [br s, major] (1H), 8.43 [d, J = 7.2 Hz, minor] and 8.35 [d, J = 7.2 Hz, major] (1H), 8.16 (br s, 1H), 7.80 [br s, minor] and 7.74 [br s, major] (1H), 7.65-7.50 (m, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.07 (ap d, J = 8.4 Hz, 5H), 6.94 (br d, 7.6 Hz, 2H), 6.84 (d, J = 8.8 Hz, 4H), 3.95 (t, J = 6.8 Hz, 4H). Remaining signals overlap with the tributyltin chloride used to disrupt aggregation (see above). HRMS (MALDI) m/z calculated for $C_{61}H_{72}N_2O_4S_2$ $[M]^+$: 960.4934, found 960.4951. UV-Vis λ_{max} = 502 nm ($CHCl_3$), λ_{max} = 507 nm (CH_2Cl_2). Emission (CH_2Cl_2) λ_{emis} = 712 nm (500 nm excitation wavelength). Elemental analysis (CHN): calculated C 76.21, H 7.55, N 2.91; found C 75.50, H 7.52, N 2.54.

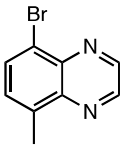


5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)pyrazine-2-carboxylic acid (JD7): To a 100 mL round bottom flask was added methyl methyl 5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)pyrazine-2-carboxylate, **JD7E** (105.6 mg, 0.114 mmol), followed by 20 mL of THF and 20 mL of 2M LiOH (aq.) solution. The mixture

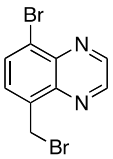
was stirred at room temperature until complete consumption of the starting material was observed by TLC (overnight, > 6hrs). Upon completion, the reaction was diluted with CH_2Cl_2 (100 mL) and acidified with AcOH (10 mL). The mixture was rinsed with H_2O (100 mL x 2) and the organics dried over Na_2SO_4. The crude product was purified via column chromatography (125 mL SiO_2, 100% Acetone → 3% AcOH: 5% MeOH:CH_2Cl_2 → 3% AcOH:10% MeOH:CH_2Cl_2) to give 5-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)pyrazine-2-carboxylic acid **(JD7)** as a dark red solid (98.8 mg, 0.108 mmol, 95%). Note: NMR is of the tetrabutylammonium salt for better resolved peaks. The parent compound gives poor signals, presumably due to aggregation. The compound is sparingly soluble in DMSO and requires heat to dissolve. Poor signals in DMSO were likely due to solubility problems. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (br s, 1H), 8.89 (br s, 1H), 7.53 (br s, 1H), 7.41 (d, J = 7.41, 2H), 7.05 (ap d, J = 8.4 Hz, 5H), 6.92 (d, J = 8.4, 2H), 6.82 (d, J = 8.4 Hz, 4H), 3.93 (t, J = 6.0 Hz, 4H), 3.36 (br s, 8H), 2.10-1.95 (m, 4H), 1.95-1.82 (m, 4H), 1.82-1.55 (m, 10H), 1.55-1.05 (m, 34H), 1.05-0.74 (m, 24H). HRMS (MALDI) m/z calculated for $C_{56}H_{70}N_3O_4S_2$ $[M + H]^+$: 912.4808, found 912.4838. UV-Vis λ_{max} = 505 nm ($CHCl_3$), λ_{max} = 508 nm (CH_2Cl_2). Emission (CH_2Cl_2) λ_{emis} = 693 nm (500 nm excitation wavelength). Elemental analysis (CHN): calculated C 73.73, H 7.62, N 4.61; found C 73.35, H 7.93, N 4.35.



Scheme SI 2. Synthetic scheme for quinoxaline dye **JD8**.

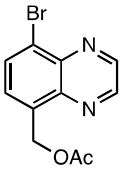


5-bromo-8-methylquinoxaline (6): To a 1L round bottom flask was added 4-bromo-7-methylbenzo[c][1,2,5]thiadiazole, **5** (7.21 g, 31.6 mmol, 1.0 equiv.) and EtOH (451 mL, 0.07M). With rapid stirring, $NaBH_4$ (1.2g, 31.6 mmol, 1.0 equiv.) was added slowly to minimize exotherm. After addition was complete, $CoCl_2$ catalyst (74.0 mg, 1.0 mol%) was added in one portion. The mixture was refluxed overnight. After complete consumption of the SM by TLC, the mixture was cooled to room temperature and the black solid was filtered off. The solvent was removed by rotary evaporator and the oil was extracted with Et_2O (400 mL) and H_2O (100 mL). The organic layer was dried over Na_2SO_4 and immediately 3-bromo-6-methylbenzene-1,2-diamine was used crude upon concentration. 3-bromo-6-methylbenzene-1,2-diamine (assumed quantitative yield) was dissolved in EtOH (600 mL, 0.05M) in a 1L round bottom flask. Glyoxal (5.4 mL [8.8 M H_2O solution], 47.4 mmol, 1.5 equiv.) and $NaHSO_3$ (6.5 g, 63.2 mmol, 2.0 equiv.) were added to the mixture. The reaction was warmed to reflux for 48 hours. The mixture was extracted with CH_2Cl_2 (400 mL x 2) and H_2O (400 mL). The organics were combined and concentrated to dryness. The crude mixture was purified by column chromatography (125 mL SiO_2, 7% ethyl acetate:hexanes) to give 5-bromo-8-methylquinoxaline (**6**) as a white solid (2.24 g, 10.1 mmol, 32% yield).

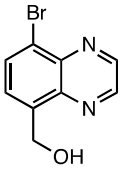


5-bromo-8-(bromomethyl)quinoxaline (7): To a 25 mL sealed tube was added 5-bromo-8-methylquinoxaline, **6** (1.03 g, 4.64 mmol, 1.0 equiv.), $CHCl_3$ (7 mL, 0.7M), NBS (1.07 g, 6.03 mmol, 1.3 equiv.), and benzoyl peroxide (20 mg). The reaction was sealed and heated to 75°C for 48hrs. Note: the reaction is stirred as a heterogeneous mixture for the first 1-2 hours after which the all components dissolve completely. Worked up by filtering through a pad of SiO_2 (125 mL) with 100% CH_2Cl_2. The filtrate was rotovapped down, and further purified with column chromatography (125 mL SiO_2, 75% CH_2Cl_2:Hexanes → 100% CH_2Cl_2) to yield 5-bromo-8-(bromomethyl)quinoxaline (**7**) as a white solid (1.03 g, 3.45 mmol,

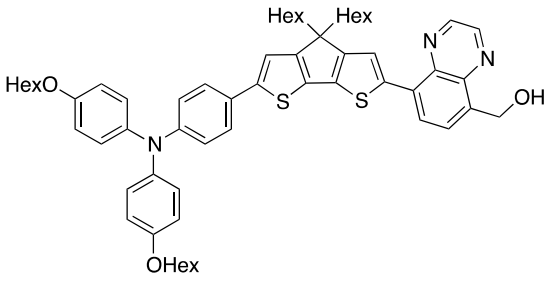
75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 1.6 Hz, 1H), 8.97 (d, *J* = 2.0 Hz, 1H), 8.08 (d, *J* = 8.0, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 5.14 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 145.2, 141.8, 141.0, 137.0, 133.7, 131.3, 125.1, 27.4. HRMS (ESI) *m*/*z* calculated for $C_9H_7Br_2N_2$ $[M+H]^+$: 300.8976, found 300.8973.



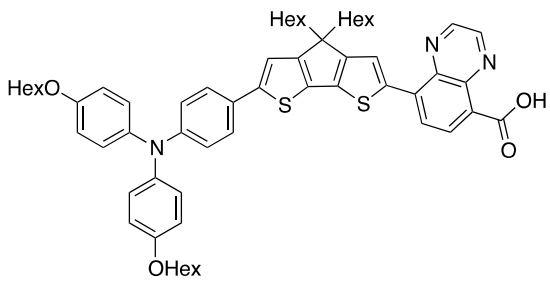
(8-bromoquinoxalin-5-yl)methyl acetate (8): To a 50 mL round bottom flask was added 5-bromo-8-(bromomethyl)quinoxaline, **7** (950.0 mg, 3.17 mmol, 1.0 equiv.), DMF (20 mL, 0.2M), and NaOAc (1.05 g, 12.7 mmol, 4.0 equiv.). The mixture was then heated to 50°C with stirring overnight. Upon completion, the product was extracted with CH_2Cl_2 (300 mL) and rinsed with H_2O (200 mL x 3). The organic layer was dried with $MgSO_4$ and purified with column chromatography (125 mL SiO_2, 100% CH_2Cl_2 → 2% MeOH:CH_2Cl_2) to yield (8-bromoquinoxalin-5-yl)methyl acetate (**8**) as a white solid (882 mg, 3.15 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 2.0 Hz, 1H), 8.93 (d, *J* = 1.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 5.78 (s, 2H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 145.7, 145.0, 142.0, 140.6, 135.0, 133.4, 129.7, 124.3, 61.7, 21.1. HRMS (ESI) *m*/*z* calculated for $C_{11}H_{10}BrN_2O_2$ $[M+H]^+$: 280.9926, found 280.9921.



(8-bromoquinoxalin-5-yl)methanol (9): To a 100 mL round bottom flask containing (8-bromoquinoxalin-5-yl)methyl acetate, **8** (882 mg, 3.15 mmol, 1.0 equiv.) was added MeOH (20 mL) and K_2CO_3 (sat. aq., 20 mL). The mixture was capped and stirred at room temperature overnight. Note: the starting material does not dissolve readily and takes about 2 hours to dissolve. Also, substantial white precipitate forms overnight. The reaction was diluted with CH_2Cl_2 (250 mL) and rinsed with H_2O (200 mL). The organic layer was dried over $MgSO_4$, concentrated and no further purification was needed. (8-bromoquinoxalin-5-yl)methanol (**9**) was isolated as a white solid (660 mg, 2.77 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, *J* = 2.0 Hz, 1H), 8.87 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 7.6, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 5.02 (s, 2H), 3.60 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 144.3, 142.6, 141.0, 139.3, 133.7, 128.9, 123.7, 63.0. HRMS (ESI) *m*/*z* calculated for $C_9H_8BrN_2O$ $[M+H]^+$: 238.9820, found 238.9817.

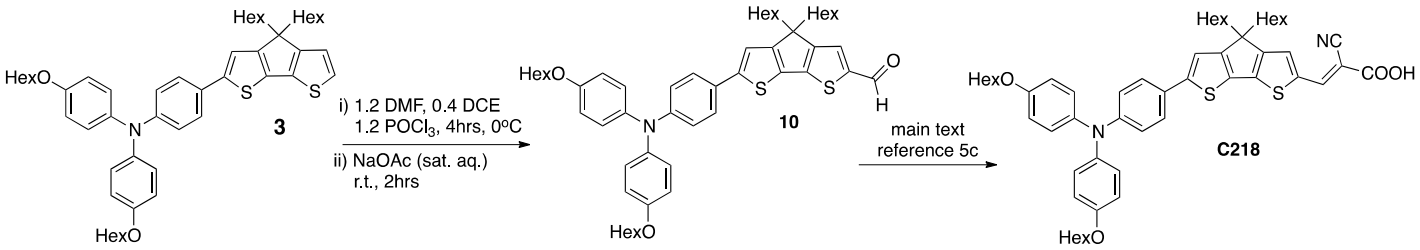


(8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)quinoxalin-5-yl)methanol (JD8E): To a 10 mL sealed tube was added **4** (333.0 mg, 0.309 mmol, 1.5 equiv.), (8-bromoquinoxalin-5-yl)methanol (49.0 mg, 0.206 mmol, 1.0 equiv.), and DMF (1.0 mL, 0.2 M). The tube was capped with a needle vent and N_2 was bubbled through the mixture with a long needle for 30 minutes. $PdCl_2(PPh_3)_2$ (7.2 mg, 0.01 mmol, 5.0 mol%) was then quickly added and the head space was flushed with N_2 and the tube was sealed. After heating for 48 hours at 90°C the reaction was cooled to room temperature. The reaction was diluted with 3 mL of CH_2Cl_2 and purified by column chromatography (125 mL SiO_2, 100% CH_2Cl_2 → 2% MeOH:CH_2Cl_2) to yield the desired product, methyl (8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)quinoxalin-5-yl)methanol **(JD8E)**, as a dark red oil which may solidify upon standing (136.7 mg, 0.144 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 1.6 Hz, 1H), 8.86 (d, *J* = 1.6 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.75-7.65 (m, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.12-7.02 (m, 5H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 4H), 5.22 (br s, 2H), 3.95 (t, *J* = 6.8 Hz, 4H), 3.87 (br s, 1H), 1.98-1.86 (m, 4H), 1.84-1.74 (m, 4H), 1.54-1.42 (m, 4H), 1.42-1.32 (m, 8H), 1.26-1.02 (m, 16H), 0.98-0.88 (m, 6H), 0.86-0.78 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 157.1, 155.7, 148.2, 145.7, 143.5, 143.4, 142.3, 141.8, 140.8, 139.9, 137.8, 136.6, 135.2, 134.2, 128.7, 127.6, 126.7, 126.4, 126.1, 121.5, 121.1, 115.5, 105.2, 68.5, 63.7, 54.1, 38.2, 31.9, 31.8, 30.0, 29.9, 29.5, 26.0, 24.8, 22.9, 22.8, 14.3. HRMS (ESI) *m*/*z* calculated for $C_{60}H_{73}N_3O_3S_2$ $[M]^+$: 947.5093, found 947.5405. UV-Vis λ_{max} = 502 nm ($CHCl_3$).

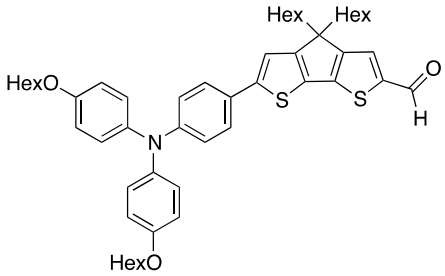


8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)quinoxaline-5-carboxylic acid (JD8): To a 5 mL round bottom flask was added CH_2Cl_2 (0.30 mL, 0.5M) and oxalyl chloride (27.3 µL, 40.0 mg, 0.316 mmol, 2.0 equiv.). The mixture was cooled to -78°C and DMSO (39.2 µL, 43.1 mg, 0.553 mmol, 3.5 equiv.) was added dropwise with stirring. The solution was stirred at -78°C for 15 minutes and then (8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-

b:5,4-*b′*]dithiophen-2-yl)quinoxalin-5-yl)methanol, **JD8E** (150.0 mg, 0.158 mmol, 1.0 equiv.) dissolved in CH_2Cl_2 (150 µL, 1.0M) was cannulaed into the reaction. The solution was maintained at -78°C for 40 minutes followed by addition of triethylamine (110 µL, 79.9 mg, 0.79 mmol, 5.0 equiv.). After 10 minutes at -78°C the mixture was warmed to r.t. for 20 minutes. The solution was filtered through a pad of silica gel (125 mL, 100% CH_2Cl_2) collecting only the purple solution. The solution was rotovapped down to a black oil and used as crude 8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophen-2-yl)quinoxaline-5-carbaldehyde without further purification (121.3 mg, 0.128 mmol, 81%). To a 5 mL flask was added crude 8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophen-2-yl)quinoxaline-5-carbaldehyde (35.0 mg, 0.037 mmol, 1.0 equiv.), *tert*-butanol (0.264 mL, 0.14M), CH_2Cl_2 (53 µL, 0.7M) and 2-methyl-2-butene (109.0 µL, 0.34M). $NaOCl_2$ (33.3 mg, 0.37 mmol, 10.0 equiv.) and PO_4H_2Na (26.4 mg, 0.30 mmol, 8.0 equiv.) were then added in H_2O (161 µL , 0.23M). The solution was stirred at room temperature overnight. A reaction aliquate NMR shows completion of the reaction. The solution was extracted with CH_2Cl_2 (100 mL) and rinsed with H_2O (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated to give 8-(6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophen-2-yl)quinoxaline-5-carboxylic acid (**JD8**) as a black solid (33.8 mg, 0.035 mmol, 95%). ^{1}H NMR (400 MHz, DMSO) δ 9.23 (s, 1H), 9.16 (s, 1H), 8.57-8.51 (m, 1H), 8.42-8.35 (m, 1H), 8.19 (s, 1H), 7.53 (d, *J* = 8.8, 2H), 7.44 (s, 1H), 7.05 (d, *J* = 8.8 Hz, 4H), 6.94 (d, *J* = 9.2 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.96 (t, *J* = 6.0 Hz, 4H), 2.00-1.90 (m, 4H), 1.80-1.67 (m, 8H), 1.50-1.37 (m, 4H), 1.37-1.05 (m, 16H), 1.02-0.83 (m, 10H), 0.83-0.72 (m, 6H). HRMS (MALDI) *m/z* calculated for $C_{60}H_{71}N_3O_4S_2$ $[M + H]^+$: 961.4886, found 961.4874. UV-Vis λ_{max} = 598 nm ($CHCl_3$), λ_{max} = 579 nm (CH_2Cl_2). Emission (CH_2Cl_2) λ_{emis} = not observed as more than a trace signal for all excitation wavelengths tested (500, 575, 600 and 675 nm excitation wavelengths). Elemental analysis (CHN): calculated C 74.88, H 7.44, N 4.37; found C 75.11, H 7.59, N 4.34.



Scheme SI 3. Modified synthetic route to **C218** beginning with intermediate **3** which synthetic details are provided for above.



6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophene-2-carbaldehyde (10): To a flame dried, N_2-filled 10 mL round bottom flask was added 4-(4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline, **3**, (500.0 mg, 0.63 mmol, 1.0 equiv.), dichloroethane (1.6 mL, 0.4 M) and DMF (55.0 mg, 58.0 µL, 0.76 mmol, 1.2 equiv.). The solution was cooled to 0°C and $POCl_3$ (116.0 mg, 70.5 µL, 0.76 mmol, 1.2 equiv.) was added dropwise. The solution was stirred for 4 hours at this temperature before NaOAc (sat. aq., 3.2 mL) was added. The solution was rapidly stirred at room temperature for 2 hours before transfer to separatory funnel with the addition of CH_2Cl_2 (50 mL) and 2M NaOH (50 mL). The organics were then separated, dried with $MgSO_4$ and concentrated. The crude mixture was purified via column chromatography (125 mL SiO_2, 40% CH_2Cl_2:Hexanes → 100% CH_2Cl_2) to yield the desired product, 6-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophene-2-carbaldehyde (0.29 g, 0.35 mmol, 56% yield) as an oil. Characterization data was similar to reported data for reference 5c from the main text.

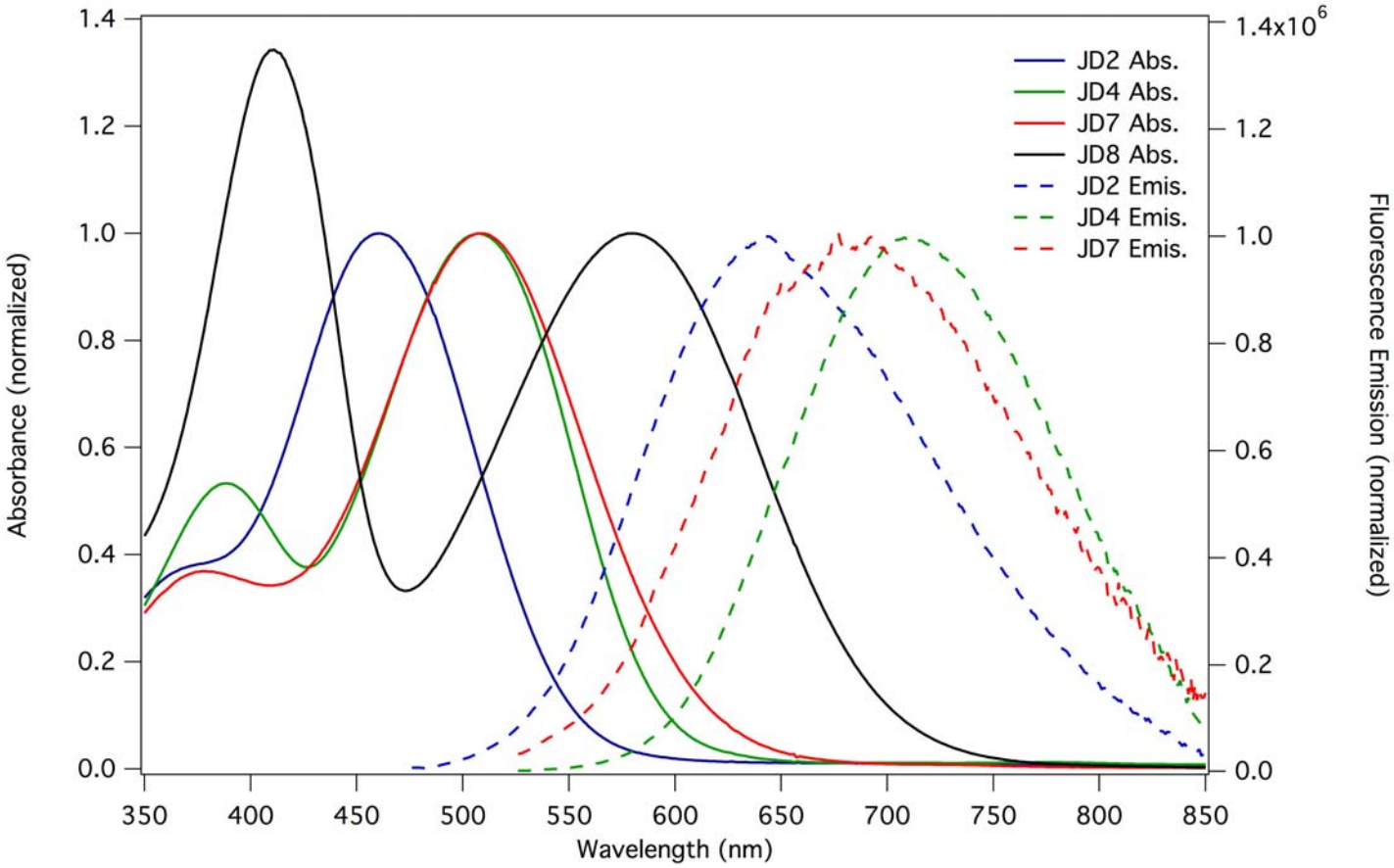


Figure SI 1. Absorption (solid lines) and emission (dashed lines) spectrum of **JD2**, **JD4**, **JD7** and **JD8** in methylene chloride.

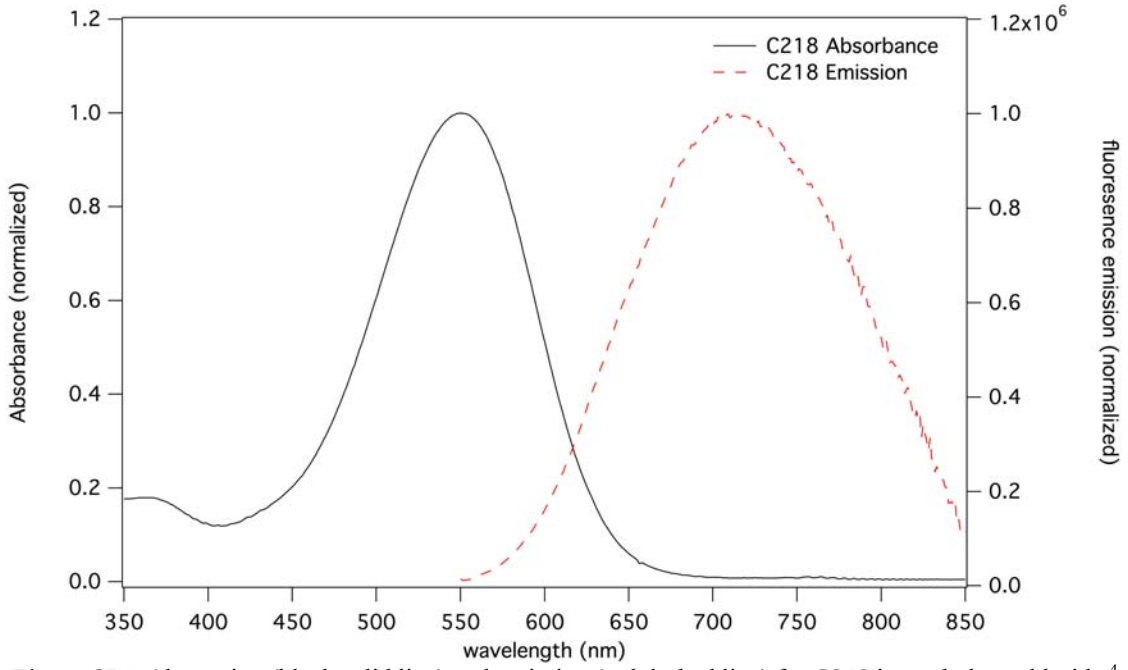


Figure SI 2. Absorption (black solid line) and emission (red dashed line) for **C218** in methylene chloride.[4]

Dye	λ_{max} (nm)[a]	λ_{emis} (nm)[a]	E_g^{opt} (eV)[b]	$E_{(0-0)}$ (eV)[c]	$E_{(S+/S)}$ (V)[d]	$E_{(S+/S^*)}$ (V)[e]	E_{red} (V)[c,f]
JD2	461	644	2.27	2.28	0.81	-1.46	-1.66
JD4	507	712	2.11	2.07	0.82	-1.29	-1.66
JD7	508	693	2.05	2.11	0.82	-1.23	-1.69
JD8	579	-----	1.79	-----	0.79	-1.00	-0.86, -1.69

Table SI 1. Optical and electrochemical data. [a]Measured in CH_2Cl_2. [b]Calculated from UV-Vis spectrum at λ_{onset}. [c]Measured at the intersection of the absorption and emission spectrum in CH_2Cl_2. [d]Measured in a 0.1 M Bu_4NPF_6 in CH_2Cl_2 solution with glassy carbon working electrode, Pt reference electrode, and Pt counter electrode with ferrocene as an internal standard. Values are reported versus NHE. [e]Calculated from $E_{(S+/S^*)} = E_{(S+/S)} - E_g^{opt}$. [f]Reduction potentials were not reversible and were taken at the onset of the reduction.

Dye Uptake Measurements: The amount of dye uptake on a 15µm TiO_2 films was measured by desorbing the sensitized dye in DMF containing tetrabutyl ammonium hydroxide (TBAOH). The film area was 0.16 cm^2. The absorbance of the resulting solution, measured by UV-visible spectrophotometry (model: Hewlett Packard 8452A diode array spectrophotometer), is implemented in the Beer-Lambert's law to calculate the concentration of the dye molecules considering the molar extinction coefficient of the dyes.

Dye	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	mmol/cm^2 loading with CDCA	mmol/cm^2 loading without CDCA
JD2 TBA	434	37,300	2.78×10^{-5}	2.96×10^{-5}
JD4 TBA	460	41,700	4.70×10^{-6}	3.15×10^{-5}
JD7 TBA	451	40,000	2.76×10^{-5}	5.03×10^{-5}
JD8 TBA	469	29,200	9.93×10^{-6}	3.59×10^{-5}

Table SI 2. Dye desorption studies with TBAOH (tetrabutylammonium hydroxide) to determine device dye loadings with and without CDCA (chenodeoxycholic acid). Dyes were desorbed from TiO_2 by submerging the sensitized semiconductor in a 0.1 M TBAOH/DMF solution overnight. The TiO_2 semiconductor was then removed and the solution absorbance measured by UV-Vis.

Device Fabrication: The photoanode consists of thin TiO_2 electrodes comprising a 9.5 µm mesoporous TiO_2 layer (particle size, 20 nm) and a 5.0 µm TiO_2 scattering layer (particle size, 400 nm). The working electrode was prepared by immersing the 14.5 µm (9.5 µm thick transparent layer + 5.0 µm thick scattering) TiO_2 film into the dye solution for 18 h. A thermally platinized FTO glass counter electrode and the working electrode were then sealed with a 25 mm thick hot-melt film (Surlyn, Dupont) by heating the system at 100°C. Devices were completed by filling the electrolyte by pre-drilled holes in the counter electrodes and finally the holes were sealed with a Surlyn sheet and a thin glass cover by heating. A black mask (6x6 mm^2) was used in the subsequent photovoltaic studies.

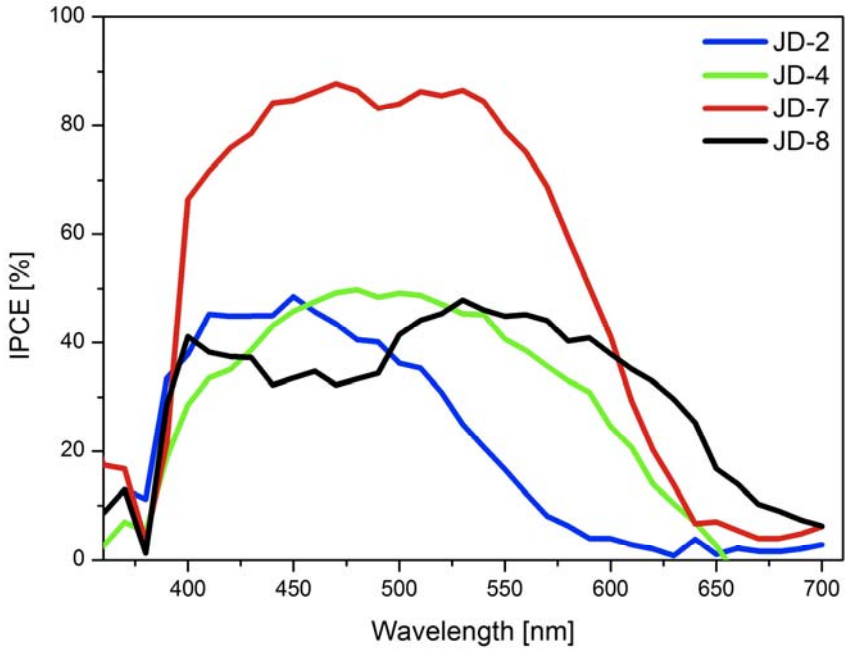


Figure SI 3. IPCE spectrum for dyes **JD2**, **JD4**, **JD7** and **JD8** without addition of CDCA.

Transient Voltage Decay: The transient open-circuit voltage decay measurements were performed with a white light bias generated from an array of diodes (Lumiled model LXHL-NWE8 whitestar) with red light pulsed diodes (LXHL-ND98 redstar, 0.2 s square pulse width, 100 ns rise and fall time) as the perturbation source controlled by a fast solid-state switch. The voltage dynamics were recorded on a PC-interfaced Keithley 2400 source meter with a 500 μs response time. The perturbation light source was set to a suitably low level so that the voltage decay kinetics were monoexponential. By varying the white light bias intensity, we could estimate the lifetime of the electrons over a range of cell potentials.

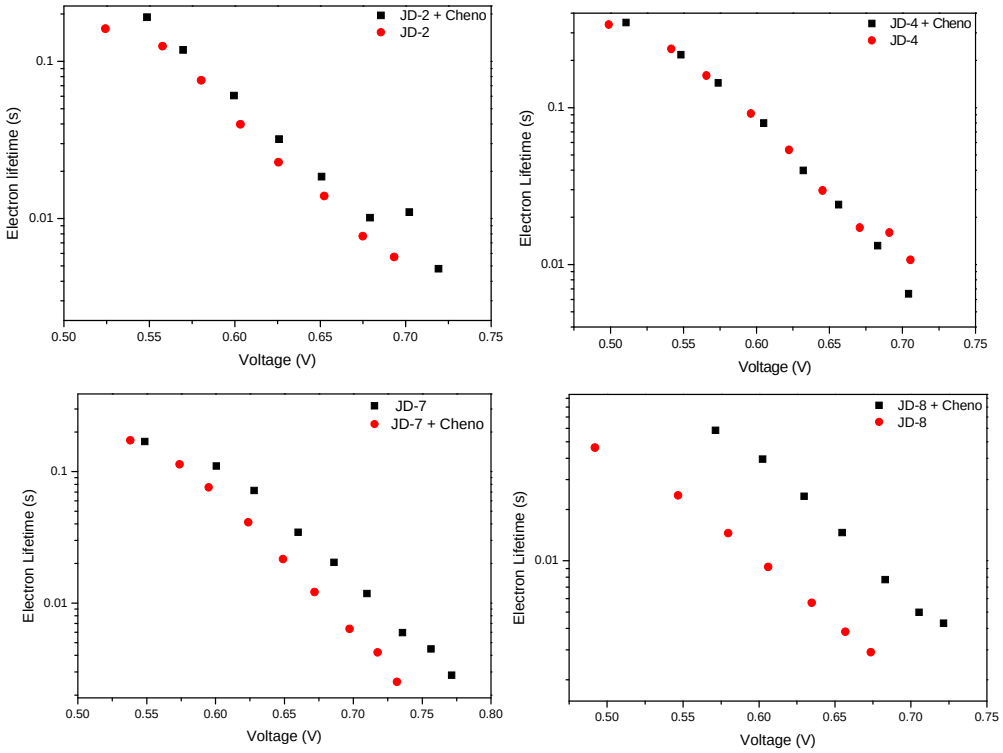


Figure SI 4. Transient voltage decay plots for dyes **JD2**, **JD4**, **JD7** and **JD8** with and without cheno (CDCA).

[1] Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[2] Prepared as outlined in the following reference with hexyl alkyl chains in place of octyl alkyl chains: Qian, G.; Dai, B.; Luo, M.; *Chem. Mater.* **2008**, *20*, 6208.

[3] 4H-cyclopenta[2,1-b:3,4-b']dithiophene is commercially available from Astar Pharmaceuticals. Alkylation: Li, R.; Liu, J.; Cai, N.; Zhang, M.; Wang, P. *J. Phys. Chem. B* **2010**, *114*, 4461. Stannylation: Karsten, B. P.; Bijleveld, J. C.; Viani, L.; Cornil, J.; Gierschner, J.; Janssen, R. A. J. *J. Mat. Chem.* **2009**, *19*, 5343.

[4] **C218** provides the best overall η of 8.95% when compared to any of the heterocyclic nitrogen containing acceptors based dyes. Pyridine, pyrazine and cyano acrylate accetpors all provide >85% IPCE spectrum with the TPA-CPDT donor-bridge; however, since cyanoacrylate is the strongest acceptor and the $E_{(S+/S*)}$ is still capable of injection into TiO_2, a greater current is observed for **C218** (see ref. 5c).