SUPPORTING INFORMATION

Molecular engineering of 2-quinolinone based anchoring groups for dye sensitized solar cells

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1. Materials and Methods

Experimental section

All the compounds synthesized in this thesis work were characterized by ^{1}H NMR, ^{13}C NMR and mass spectrometry. Triphenyl amine 4 was synthesised as per the literature procedure.[1] Thin-layer chromatography (TLC) was conducted with Merck KGaA precoated TLC Silica gel 60 F254 aluminum sheets and visualized with UV. Flash column chromatography was performed using Silicycle UltraPure SilicaFlash P60, 40-63 μm (230-400 mesh). ^{1}H and ^{13}C NMR spectra were obtained using a Bruker spectrometer (400 MHz), Bruker AvanceIII-400 (400MHz), Bruker DPX-400 (400 MHz) and are reported in ppm using solvent as an internal standard: Methylene Chloride-d_2, THF-d_8, $CDCl_3$-d, DMSO-d_6. Mass spectra were obtained with Bruker daltonics, FT-ICR/APEX II, ESI mode. MALDI-TOF mass spectra were recorded using Micromass Tof Spec 2E instrument. High-resolution mass spectra were obtained at the École Polytechnique Fédérale de Lausanne mass spectrometry laboratory (EPFL). Absorption spectral measurements were recorded using JASCO V630 UV–visible spectrophotometer. Emission measurements were carried out with JASCO FP-6500 spectrofluorimeter. From the intersection of the normalized absorption and emission spectra, the zero-zero transition energy ($E_{0–0}$) of the dye can be estimated. Cyclic voltammetry was measured with an Autolab Eco Chemie cyclic voltammeter in dichloromethane solvent. The experimental setup consisted of a glassy carbon working electrode, platinum wire counter electrode and platinum reference electrode. All samples were deaerated by bubbling with pure nitrogen gas for ca. 5min at room temperature. The system was initially calibrated with ferrocene/ferrocenium (Fc/Fc^{+}) redox couple. The FTIR spectra for all the samples were measured using a Digilab 7000 FTIR spectrometer. The ATR data were taken with the "Golden Gate" diamond anvil ATR accessory (Graseby-Specac) using, typically, 64 scans at a resolution of 2 cm^{-1}.

Device Fabrication

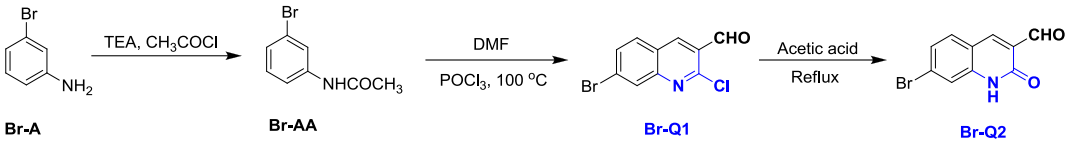
A screen-printed double layer of nanocrystalline TiO_2 particles was used as the photoelectrode. The FTO glass plates were immersed in a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. A 8 microns thick film of 20 nm sized TiO_2 particles was then printed on the FTO conducting glass and further coated with a 5 microns thick second layer of 400 nm light-scattering TiO_2 particles (400 nm diameter, Catalysts & Chemicals Ind. Co. Ltd. (CCIC), HPW- 400). Sintering was carried out at 500 °C for 15 min, which was gradually heated. The working electrode was prepared by immersing the 13.0 μm (8.0 μm thick transparent layer + 5.0 μm thick scattering) TiO_2 film into the dye solution for 12 h. To prepare the counter electrode, Pt catalyst was deposited on cleaned FTO glass by coating with a drop of H_2PtCl_6 solution (10 mM in 2-propanol solution) with heat treatment at 400 °C for 15 min. For the assembly of DSSCs, the dye-containing TiO_2 electrode and Pt counter electrode were assembled into a sandwich-type cell and sealed with a hot-melt gasket of 25 microns thickness made of the ionomer Surlyn 1702 (Dupont). 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 (6×6 mm^2) was used in the subsequent photovoltaic studies.

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 6×6 mm^2. Incident photon-to-current conversion efficiency measurements were measured using the mono chromated visible photons, from Gemini-180 double monochromator Jobin Yvon

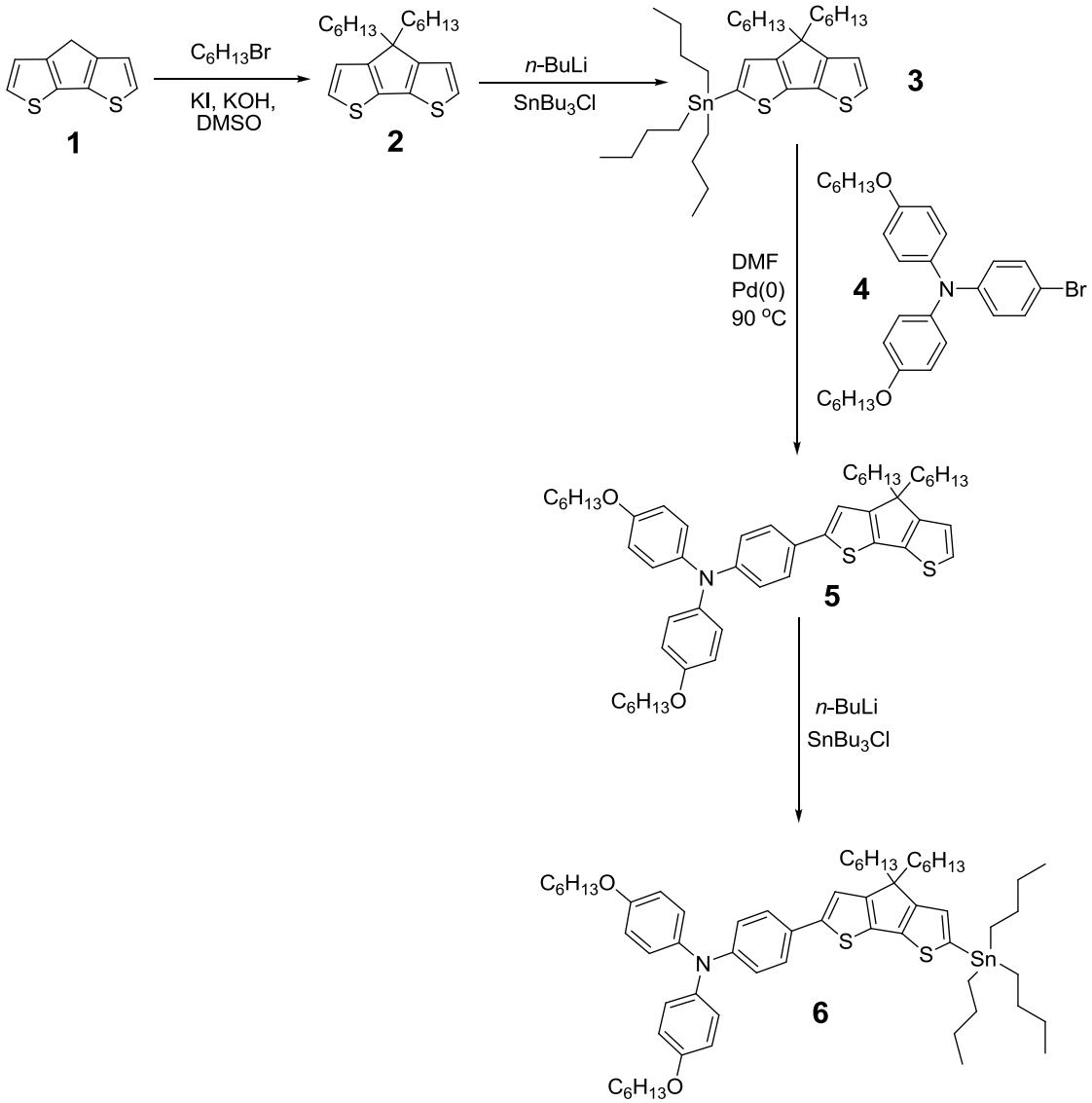
Ltd. (UK), powered by a 300 W xenon light source (ILC Technology, USA) superimposed on a 10 mW/cm^2 LED light. The monochromatic incident light was passed through a chopper running at 2 Hz frequency and the on / off ratio was measured by an operational amplifier. Photovoltage transients were observed by using a pump pulse generated by 4 red light emitting diodes controlled by a fast solid-state switch with a white light bias. The pulse of red light with widths of 50 ms was incident on the photoanode side of the cell, and its intensity was controlled to keep a suitably low level to generate the exponential voltage decay where the charge recombination rate constants are obtained directly from the exponential decay rate.

Scheme S1: Synthetic route for quinolinone type acceptor groups.

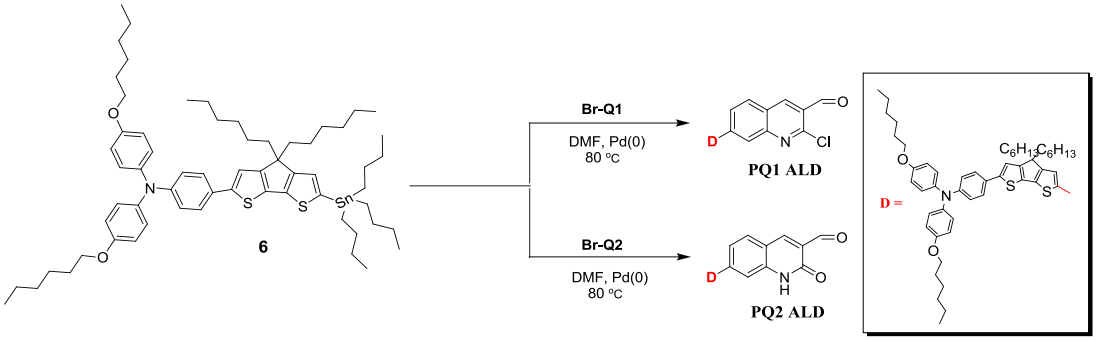


Br-A Br-AA Br-Q1 Br-Q2

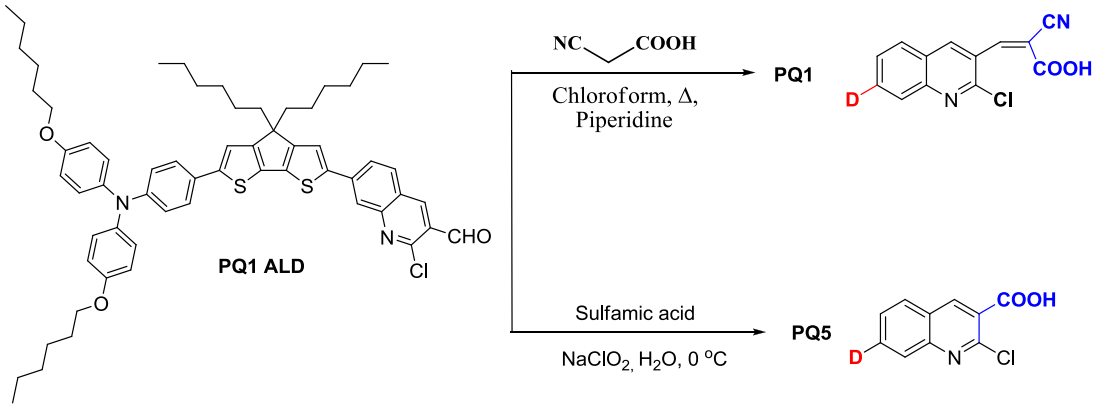
Scheme S2: Synthetic route for donor π spacer groups.



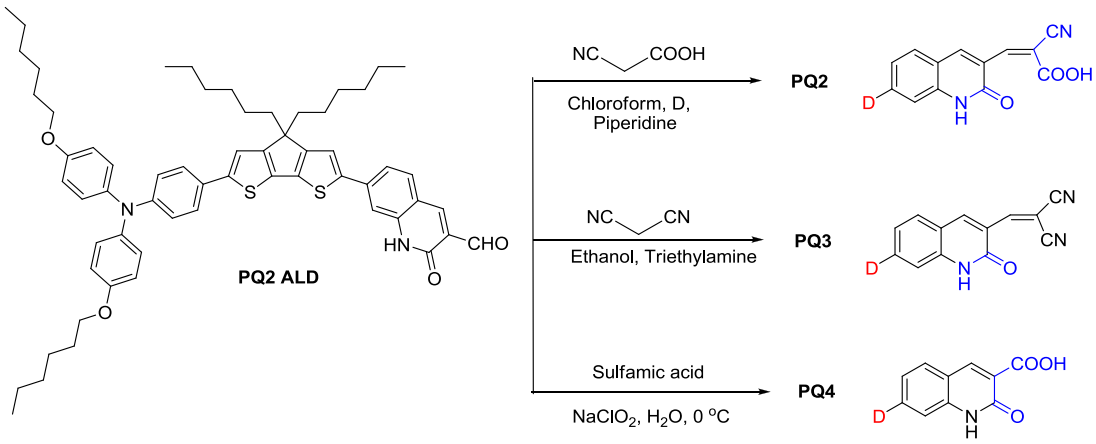
Scheme S3: Synthetic route for aldehyde precursors.



Scheme S4: Synthetic route for 2-chloro quinoline based final dyes.



Scheme S5: Synthetic route for 2-quinolinone based final dyes.



2. Synthetic details of various sensitizers.

Synthesis of N-(3-bromophenyl)acetamide (Br-AA)

A mixture of 3-bromoaniline (3.0g, 17.4 mmol) and triethylamine (2.92 ml, 20.9 mmol) dissolved in acetone (80.0 ml) was allowed to stir at room temperature for 2 h and the reaction mixture was cooled to 0–5 °C. To this cold mixture, acetyl chloride (1.49 ml, 20.9 mmol) was added slowly with constant stirring by maintaining the reaction temperature below 5 °C. After the completion of addition, the reaction mixture was warmed to room temperature and stirred until the complete formation of the product monitored by thin layer chromatography. The reaction mixture was quenched in ice water under slow stirring and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to afford **Br-AA** (3.5g, 94 %) as white solid. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.84 (t, J = 1.9 Hz, 1H), 7.58 (s, 1H), 7.42 – 7.38 (m, 1H), 7.27 – 7.18 (m, 2H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.44, 139.35, 130.23, 127.26, 123.16, 122.48, 118.67, 24.43. HRMS (ESI) *m/z* calculated for C_8H_8BrNO $[M+H]^+$: 213.9867, found 213.9510.

Synthesis of 7-Bromo-2-chloroquinoline-3-carbaldehyde (Br-Q1)

Phosphorous oxychloride (6.2 mL, 65.8 mmol) was added dropwise to dimethyl formamide (1.82 mL, 23.6 mmol) at 0 – 5 °C. After the completion of addition, the mixture was allowed to stir for about 15 min 0 – 5 °C. Br-AA (2.0 gm, 9.4 mmol) was added to the reaction mixture and the temperature was heated to 90 °C and stirred for 30 h. The reaction mixture was cooled to room temperature and then poured into crushed ice under stirring condition. The obtained precipitate was filtered and washed with water and dried to get **Br-Q1** (1.0 g, 40 %) as yellow solid. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 10.52 (s, 1H), 8.73 (d, J = 0.9 Hz, 1H), 8.25 (d, J = 1.9 Hz, 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.77 (dd, J = 8.7, 1.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ = 189.60,

149.32, 141.79, 140.12, 134.91, 132.38, 131.99, 130.38, 128.15, 125.74. MS (ESI) *m/z* calculated for $C_{10}H_5BrClNO$ $[M+H]^+$: 269.93, found 269.93.

Synthesis of 7-Bromo-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (Br-Q2)

BrQ1 (0.5 g) was added to the mixture of acetic acid (30 ml) and water (10 ml) at ambient temperature and the reaction mixture was heated to 110 °C and stirred for about 18 hrs. The reaction mixture was cooled to room temperature and poured into crushed ice under stirring. The obtained precipitate was filtered and washed with water (3 × 50 ml) and methanol (3 × 5 ml) to yield the compound **Br-Q2** (0.3 g) as yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.29 (s, 1H), 10.20 (t, *J* = 1.5 Hz, 1H), 8.50 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 7.45 – 7.42 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ = 190.00, 161.68, 142.41, 142.35, 133.16, 127.68, 126.35, 126.17, 118.18, 117.69. HRMS (ESI) *m/z* calculated for $C_{10}H_6BrNO_2$ $[M]^+$: 251.9660, found 251.9641.

Synthesis of 4,4-Dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (2)

To a solution of 4H-cyclopenta[2,1-b:3,4-b']dithiophene **1** (1.0 g, 5.61 mmol), 1-bromohexane (1.85g, 11.2 mmol) and potassium iodide (0.014 mmol) in dimethyl sulfoxide (30.0 ml) was added potassium hydroxide (0.63 g, 11.2 mmol) under nitrogen atmosphere and stirred overnight at room temperature. The crude product was extracted into diethyl ether and washed with saturated ammonium chloride aqueous solution (3 × 50 ml) and water (3 × 50 ml). The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was purified with gradient silica gel chromatography using 100 % hexane to give **2** (1.73 g, 84%) as colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 4.9 Hz, 2H), 6.93 (d, *J* = 4.9 Hz, 2H), 1.82 (dd, *J* = 7.8, 4.3 Hz, 4H), 1.13 (ddt, *J* = 10.1, 7.4, 4.6 Hz, 12H), 0.96 – 0.91 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 6H).

Synthesis of Tributyl(4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)stannane (3)

To a flame dried, nitrogen filled 100 mL round bottom flask with stir bar was added 4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene **2** (1.0 g, 2.9 mmol) and anhydrous THF (20 mL). The mixture was cooled to −78 °C under nitrogen atmosphere and 2.5 M solution of *n*-BuLi (1.27 mL, 3.18 mmol) was added dropwise. The resulting reaction mixture was maintained at −78 °C for 2 h and tributylchlorostannane (1.2 mL, 4.34 mmol) was added dropwise through a syringe. The resulting reaction mixture was maintained at -78 ˚C for 1 h and allowed to warm to room temperature overnight. Dichloromethane (20 ml) was added to the reaction mixture and washed with saturated ammonium chloride aqueous solution (3 × 40 ml) and water (3 × 40 ml). The organic layer was separated and dried over magnesium sulfate. After the evaporation of solvent, the crude mixture was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.11 (d, *J* = 4.8 Hz, 1H), 6.93 – 6.91 (m, 2H), 1.85 – 1.80 (m, 4H), 1.63 – 1.57 (m, 6H), 1.39 – 1.32 (m, 12H), 1.15 – 1.10 (m, 12H), 0.96 – 0.92 (m, 4H), 0.92 – 0.87 (m, 9H), 0.82 (t, *J* = 6.9 Hz, 6H).

Synthesis of 4-(4,4-Dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline (5):

To a 100 mL flame dried, nitrogen filled round bottom flask charged with a stir bar was added 4-bromo-N,N-bis(4-(hexyloxy)phenyl)aniline 4 (0.83 g, 1.6 mmol) and tributyl(4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)stannane 3 (1.5 g, 2.4 mmol). $Pd(PPh_3)_4$ (150 mg) was then added, followed by freeze–pump–thaw degassing procession. Anhydrous DMF (30 mL) was added and the reaction mixture was heated to 90 °C for 12 hours. Dichloromethane (50 ml) was added to the reaction mixture and washed with saturated sodium chloride aqueous solution (3 × 75 ml) and then with water (3 × 75 ml). The organic layer was separated and dried over magnesium sulfate. After the removal of solvent, the crude mixture was purified with gradient silica gel chromatography: 100 % Hexane to 60:40 Hexane : DCM to give **5** (1.1 g, 88 %) as light

orange oil. ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.43 – 7.40 (m, 2H), 7.14 (d, *J* = 4.8 Hz, 1H), 7.07 – 7.04 (m, 5H), 6.94 (d, *J* = 4.5 Hz, 2H), 6.92 (s, 1H), 6.85 – 6.81 (m, 4H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.81 (ddd, *J* = 14.8, 10.4, 7.0 Hz, 8H), 1.51 – 1.45 (m, 4H), 1.39 – 1.32 (m, 10H), 1.14 (h, *J* = 2.9, 2.1 Hz, 10H), 0.94 (qd, *J* = 6.9, 3.5 Hz, 11H), 0.82 (t, *J* = 6.9 Hz, 6H). ^{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.

Synthesis of 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 (6):

To a flame dried, N_2-filled 250 mL round bottom flask with stir bar 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 **5** (1.0 g, 1.27 mmol) and anhydrous THF (50 mL). The mixture was cooled to −78 °C under N_2 and 2.5 M solution of *n*-BuLi (0.56 mL, 1.4 mmol) was added dropwise. After addition was complete, the mixture was maintained at −78 °C for 2 hours. Then tributylchlorostannane (0.52 mL, 1.91 mmol) was added via syringe dropwise. The mixture maintained at −78 °C for 1 hour and then was allowed to warm to room temperature overnight. Dichloromethane (50 ml) was added to the reaction mixture and washed with saturated ammonium chloride aqueous solution (3 × 80 ml) and then with water (3 × 80 ml). The organic layer was separated and dried over magnesium sulfate. After removal of solvent, the crude mixture was used without further purification.^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.44 – 7.38 (m, 2H), 7.06 (s, 1H), 7.04 (d, *J* = 1.9 Hz, 4H), 6.95 – 6.92 (m, 2H), 6.91 (s, 1H), 6.85 – 6.81 (m, 4H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.78 (dd, *J* = 14.8, 6.8 Hz, 4H), 1.63 – 1.55 (m, 6H), 1.36 (dt, *J* = 7.4, 3.7 Hz, 12H), 1.16 – 1.11 (m, 12H), 0.95 – 0.88 (m, 13H), 0.82 (t, *J* = 7.0 Hz, 6H). MS (MALDI) *m/z* calculated for $C_{63}H_{93}NO_2S_2Sn$ $[M]^+$: 1079.6, found 1079.3.

Synthesis of PQ1 ALD

To a 100 mL flame dried, N_2-filled round bottom flask charged with a stir bar was added 7-bromo-2-chloroquinoline-3-carbaldehyde (Br-Q1) (0.1 g, 0.37 mmol) and 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 **6** (0.47 g, 0.44 mmol). $Pd(PPh_3)_4$ (100 mg) was then added, followed by freeze–pump–thaw degassing procession. Anhydrous DMF (20 mL) was then added and the reaction mixture was heated to 80 °C for 12 hours. Dichloromethane (50 ml) was added to the reaction mixture and washed with saturated sodium chloride aqueous solution (3 × 75 ml) and then with water (3 × 75 ml). The organic layer was separated and dried over magnesium sulfate. After the removal of solvent, the crude mixture was purified with gradient silica gel chromatography: 100: 0 to 40:50 (Hexane:DCM) to give **PQ1 ALD** (0.13 g, 36 %) as red colour semisolid. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 10.50 (s, 1H), 8.67 (d, *J* = 0.9 Hz, 1H), 8.27 (d, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.65 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.29 (s, 1H), 7.16 (s, 1H), 7.10 – 7.07 (m, 4H), 6.94 – 6.91 (m, 2H), 6.89 – 6.86 (m, 4H), 3.97 (d, *J* = 6.6 Hz, 4H), 1.99 – 1.94 (m, 4H), 1.83 – 1.78 (m, 4H), 1.50 (ddt, *J* = 7.8, 5.2, 2.3 Hz, 4H), 1.39 (dt, *J* = 6.8, 2.9 Hz, 10H), 1.21 – 1.17 (m, 10H), 1.06 (td, *J* = 9.2, 8.1, 4.1 Hz, 4H), 0.95 (q, *J* = 2.5 Hz, 6H), 0.83 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl2) δ = 191.04, 161.36, 158.70, 156.25, 154.23, 150.34, 148.86, 147.73, 142.98, 141.06, 140.64, 139.08, 134.42, 131.49, 130.90, 130.68, 127.68, 127.58, 127.18, 127.03, 126.28, 124.72, 120.51, 116.70, 115.67, 68.70, 54.78, 38.26, 32.03, 30.09, 29.72, 28.25, 27.33, 27.25, 26.14, 25.02, 23.04, 23.01, 17.88, 14.24, 14.20, 13.78. MS (MALDI) *m/z* calculated for $C_{61}H_{71}ClN_2O_3S_2$ $[M + 2Na]^+$: 1024.4, found 1024.3.

Synthesis of PQ2 ALD

To a 100 mL flame dried, N_2-filled round bottom flask charged with a stir bar was added 7-bromo-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (Br-Q2) (0.13 g, 0.51 mmol) and 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 **6** (0.72 g, 0.0.66 mmol). $Pd(PPh_3)_4$ (100 mg) was then added,

followed by freeze–pump–thaw degassing procession. Anhydrous DMF (20 mL) was then added and the reaction mixture was heated to 80 °C for 12 hours. Dichloromethane (50 ml) was added to the reaction mixture and washed with saturated sodium chloride aqueous solution (3 × 75 ml) and then with water (3 × 75 ml). The organic layer was separated and dried over magnesium sulfate. After the removal of solvent, the crude mixture was purified with gradient silica gel chromatography: 100 % Hexane to 10:85:5 (Hexane:DCM:MeOH) to give **PQ2 ALD** (0.25 g, 51 %) as purple colour solid. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 11.72 (s, 1H), 10.53 (s, 1H), 8.45 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.50 (s, 1H), 7.49 – 7.44 (m, 2H), 7.16 (s, 1H), 7.13 – 7.07 (m, 4H), 6.96 – 6.92 (m, 2H), 6.91 – 6.84 (m, 4H), 3.99 (t, *J* = 6.5 Hz, 4H), 2.03 – 1.94 (m, 4H), 1.85 – 1.78 (m, 4H), 1.55 – 1.49 (m, 4H), 1.40 (dq, *J* = 7.2, 3.5 Hz, 8H), 1.22 (dt, *J* = 12.1, 4.3 Hz, 12H), 1.06 (dd, *J* = 10.0, 6.0 Hz, 4H), 1.00 – 0.94 (m, 6H), 0.85 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl2) δ = 188.99, 163.65, 160.52, 158.70, 155.83, 148.39, 146.84, 141.92, 141.58, 141.25, 140.72, 140.26, 139.92, 134.59, 133.98, 131.20, 126.76, 125.82, 124.30, 120.55, 120.35, 120.15, 117.65, 116.33, 115.26, 109.98, 68.32, 54.33, 37.88, 31.65, 31.62, 29.71, 29.31, 25.76, 24.58, 22.63, 13.82, 13.80. MS (MALDI) *m/z* calculated for $C_{61}H_{72}N_2O_4S_2$ $[M]^+$: 960.4934, found 960.3173.

Synthesis of PQ1

PQ1 ALD (0.090 g, 0.1 mmol), 2-cyanoacetic acid (0.085 g, 1.0 mmol), and piperidine (0.17 g, 2.0 mmol) were dissolved in chloroform (30 mL). The reaction mixture was heated in a sealing tube at 85 °C overnight. The mixture was cooled to room temperature, and then 1 N HCl was added to the chloroform solution. After stirring for 30 min, the organic layer was separated and washed with 1 N HCl, water, and brine and dried with $MgSO_4$. The crude product was purified by silica gel column chromatography using Hexane: Ethylacetate: Acetic acid (0.7:0.25:0.05) as final eluent to yield **PQ1** (0.035 g, 37 %) as red colour solid. ^{1}H NMR (400 MHz, THF-d_8) δ 8.86 (s, 1H), 8.63 (s, 1H), 8.23 (d, *J* = 1.9 Hz, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.67 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.48 – 7.44

(m, 2H), 7.28 (d, *J* = 15.9 Hz, 2H), 7.04 – 7.00 (m, 4H), 6.92 – 6.88 (m, 2H), 6.86 – 6.82 (m, 4H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.97 (dd, *J* = 11.1, 5.6 Hz, 4H), 1.49 (ddd, *J* = 6.9, 5.4, 3.2 Hz, 4H), 1.36 (dp, *J* = 6.4, 3.3, 2.8 Hz, 10H), 1.18 (q, *J* = 4.3, 3.6 Hz, 12H), 1.08 – 1.01 (m, 4H), 0.93 (td, *J* = 7.2, 4.1 Hz, 8H), 0.82 – 0.78 (m, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ = 162.01, 159.21, 157.06, 153.92, 150.17, 149.64, 148.68, 143.74, 143.71, 141.54, 138.85, 135.19, 131.88, 131.08, 130.99, 128.10, 127.59, 127.01, 126.87, 126.68, 125.55, 124.85, 121.48, 117.32, 116.18, 68.93, 68.14, 55.36, 39.07, 32.77, 32.72, 30.90, 30.49, 29.07, 28.13, 26.93, 26.02, 23.72, 18.56, 14.56, 14.54, 14.30. MS (MALDI) *m/z* calculated for $C_{64}H_{72}ClN_3O_4S_2$ $[M]^+$: 1045.4653, found 1045.2324.

Synthesis of PQ2

PQ2 ALD (0.090 g, 0.094 mmol), 2-cyanoacetic acid (0.080 g, 0.0094 mmol), and piperidine (0.16 g, 1.88 mmol) were dissolved in chloroform (30 mL). The reaction mixture was heated in a sealing tube at 85 °C overnight. The mixture was cooled to room temperature, and then 1 N HCl was added to the chloroform solution. After stirring for 30 min, the organic layer was separated and washed with 1 N HCl, water, and brine and dried with $MgSO_4$. The crude product was purified by silica gel column chromatography using Dichloromethane: Acetic acid (1:0.02) as final eluent to yield **PQ2** (0.04 g, 41 %) as red colour solid. ^{1}H NMR (400 MHz, THF-d_8) δ 11.06 (s, 1H), 7.84 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.50 (s, 1H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 2H), 7.25 (s, 1H), 7.04 – 7.00 (m, 4H), 6.90 – 6.87 (m, 2H), 6.85 – 6.82 (m, 4H), 3.93 (t, *J* = 6.4 Hz, 4H), 1.98 – 1.93 (m, 4H), 1.76 (dd, *J* = 8.6, 6.3 Hz, 4H), 1.52 – 1.46 (m, 4H), 1.36 (q, *J* = 3.7 Hz, 8H), 1.21 – 1.16 (m, 12H), 1.06 (dt, *J* = 12.4, 3.7 Hz, 4H), 0.94 – 0.90 (m, 6H), 0.81 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ = 161.08, 159.52, 158.26, 155.84, 148.28, 146.14, 142.59, 140.41, 139.44, 137.77, 137.58, 137.37, 133.97, 129.08, 128.51, 127.09, 126.36, 125.56, 120.42, 119.11, 119.08, 118.08, 117.21, 116.21, 115.00, 109.59, 67.75, 65.98, 54.10, 37.84, 36.15, 31.61, 29.75, 29.33, 25.77,

22.56, 22.55, 19.76, 13.42, 13.40. MS (MALDI) *m/z* calculated for $C_{64}H_{73}N_3O_5S_2$ $[M]^+$: 1027.4992, found 1027.1824.

Synthesis of PQ3

To a solution of PQ2 ALD (0.050 g, 0.052 mmol) in ethanol (30 mL) were added malononitrile (0.011 g, 0.16 mmol) and few drops of triethylamine. The reaction mixture was refluxed for overnight under N_2 atmosphere. The mixture was cooled to room temperature and then water (30 ml) was added and stirred for 5 min. The organic layer was separated and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography using dichloromethane as eluent to yield **PQ3** (0.025 g, 48 %) as dark red colour solid. ^{1}H NMR (400 MHz, THF-d_8) δ 11.07 (s, 1H), 7.87 (s, 1H), 7.77 – 7.65 (m, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.50 (s, 1H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.42 (q, *J* = 1.9 Hz, 2H), 7.25 (s, 1H), 7.06 – 6.97 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.87 – 6.80 (m, 4H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.97 – 1.93 (m, 4H), 1.78 – 1.73 (m, 4H), 1.48 (dtd, *J* = 11.4, 7.0, 6.1, 3.2 Hz, 4H), 1.36 (dq, *J* = 7.2, 3.7 Hz, 8H), 1.18 (hept, *J* = 4.9 Hz, 12H), 1.08 – 1.02 (m, 4H), 0.95 – 0.89 (m, 6H), 0.81 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ = 161.59, 158.29, 155.87, 148.33, 146.21, 142.54, 140.44, 139.80, 139.49, 138.46, 137.86, 137.47, 134.94, 134.87, 134.81, 133.67, 133.57, 130.51, 129.51, 129.38, 128.45, 128.03, 127.98, 127.93, 127.10, 126.39, 125.59, 125.45, 120.44, 119.16, 119.13, 118.18, 116.23, 115.04, 113.29, 109.77, 67.79, 54.14, 37.88, 33.09, 31.62, 29.76, 29.67, 29.35, 25.78, 24.48, 22.57, 22.56, 21.05, 13.43, 13.41. MS (MALDI) *m/z* calculated for $C_{64}H_{72}N_4O_3S_2$ $[M + 2H]^+$: 1010.5202, found 1010.1122.

Synthesis of PQ4

PQ2 ALD (0.020 g, 0.021 mmol) was dissolved in THF (3.0 ml) and cooled to 0–5 °C. Sulfamic acid (0.008 g, 0.084 mmol) was added and stirred for 5 min. A solution of sodiumperchlorite (0.004 g, 0.042 mmol) in water (1.0 ml) was added slowly to the reaction mixture and stirred for 2 hours at 0–5 °C and then warmed to room temperature.

Dichloromethane (30 ml) was added to the reaction mixture and washed with saturated sodium chloride aqueous solution (3 × 50 ml) and then with water (3 × 50 ml). The organic layer was separated and dried over magnesium sulfate. After the removal of solvent, the crude mixture was purified with gradient silica gel chromatography using dichloromethane: methanol (1:0.05) as eluent to give **PQ4** (0.013 g, 64 %) as purple color solid. ^{1}H NMR (400 MHz, THF-d_8) δ 11.93 (s, 1H), 8.83 (s, 1H), 7.94 – 7.82 (m, 1H), 7.73 (ddd, *J* = 8.5, 6.6, 4.4 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.45 (dd, *J* = 9.0, 2.3 Hz, 2H), 7.15 – 6.97 (m, 4H), 6.95 – 6.79 (m, 6H), 3.94 (t, *J* = 6.3 Hz, 4H), 1.99 (td, *J* = 12.4, 10.7, 6.5 Hz, 4H), 1.76 (d, *J* = 2.6 Hz, 4H), 1.52 – 1.46 (m, 4H), 1.37 (dt, *J* = 7.6, 3.8 Hz, 8H), 1.23 – 1.15 (m, 12H), 1.09 – 0.99 (m, 4H), 0.94 – 0.90 (m, 6H), 0.80 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ = 162.81, 161.80, 159.27, 158.38, 156.70, 156.58, 155.01, 154.34, 154.04, 151.74, 150.48, 147.12, 146.92, 146.60, 145.15, 143.52, 141.08, 139.70, 138.75, 138.68, 138.47, 138.13, 138.10, 137.71, 137.49, 137.20, 136.47, 135.91, 131.83, 131.73, 131.31, 129.96, 129.59, 129.57, 128.74, 128.65, 126.76, 126.40, 126.28, 125.96, 125.17, 125.07, 124.99, 124.57, 123.77, 118.73, 118.51, 118.42, 117.14, 116.43, 115.42, 114.34, 113.33, 113.24, 113.15, 109.99, 108.36, 107.99, 68.68, 65.89, 65.12, 54.19, 52.31, 38.46, 35.99, 34.20, 31.43, 29.74, 29.62, 27.87, 27.79, 27.75, 27.64, 27.46, 23.90, 23.00, 20.71, 20.68, 20.63, 11.59, 11.55, 11.52. MS (MALDI) *m/z* calculated for $C_{61}H_{72}N_2O_5S_2$ $[M]^+$: 976.4883, found 976.5139.

Synthesis of PQ5

PQ1 ALD (0.020 g, 0.0204 mmol) was dissolved in THF (3.0 ml) and cooled to 0–5 °C. Sulfamic acid (0.008 g, 0.082 mmol) was added and stirred for 5 min. A solution of sodiumperchlorite (0.004 g, 0.041 mmol) in water (1.0 ml) was added slowly to the reaction mixture and stirred for 2 hours at 0–5 °C and then warmed to room temperature. Dichloromethane (30 ml) was added to the reaction mixture and washed with saturated sodium chloride aqueous solution (3 × 50 ml) and then with water (3 × 50 ml). The organic layer was separated and dried over magnesium sulfate. After the removal of

solvent, the crude mixture was purified with gradient silica gel chromatography using dichloromethane: methanol (1:0.05) as eluent to give **PQ5** (0.012 g, 59 %) as red color solid. ^{1}H NMR (400 MHz, THF-d_8) δ 10.87 (s, 1H), 8.43 (d, J = 21.8 Hz, 1H), 8.16 (d, J = 1.8 Hz, 1H), 7.95 (td, J = 17.3, 16.8, 8.7 Hz, 1H), 7.82 – 7.68 (m, 2H), 7.59 (dt, J = 8.5, 6.6 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.24 (s, 1H), 7.14 – 6.99 (m, 4H), 6.94 – 6.78 (m, 6H), 3.94 (t, J = 6.4 Hz, 4H), 1.93 (t, J = 8.0 Hz, 4H), 1.77 (s, 4H), 1.52 – 1.46 (m, 4H), 1.37 (dq, J = 7.7, 3.8 Hz, 10H), 1.18 (dd, J = 10.4, 5.3 Hz, 10H), 1.07 (dd, J = 10.2, 4.9 Hz, 4H), 0.92 (dd, J = 6.2, 3.0 Hz, 6H), 0.80 (t, J = 6.7 Hz, 6H). MS (MALDI) *m/z* calculated for $C_{61}H_{71}ClN_2O_4S_2$ $[M + 2Na]^+$: 1040.434, found 1040.218.

3. NMR spectra

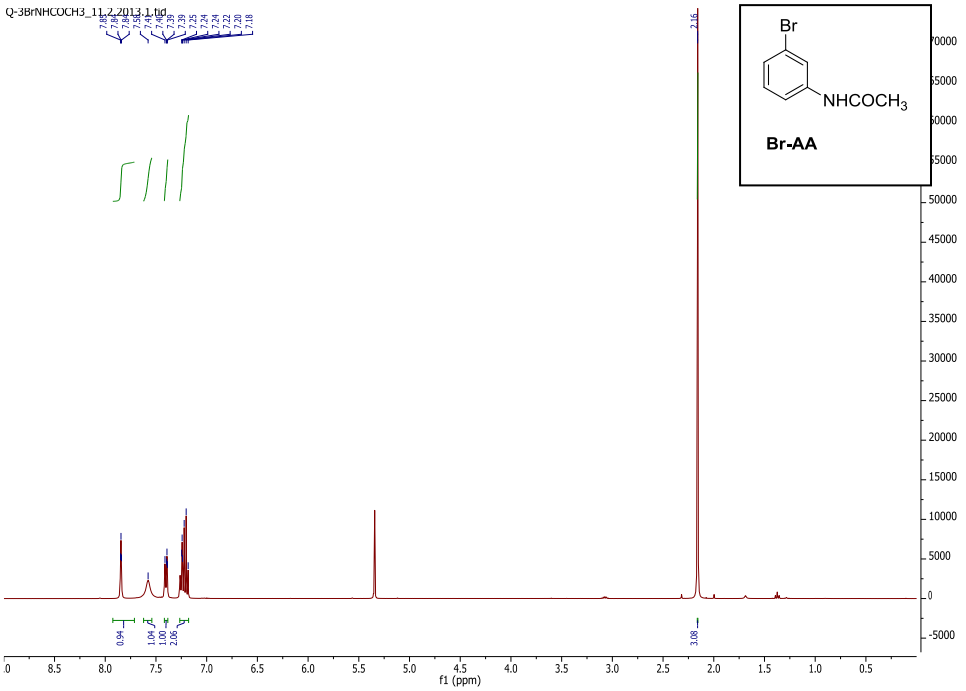


Figure S1: ^{1}H NMR of Br-AA

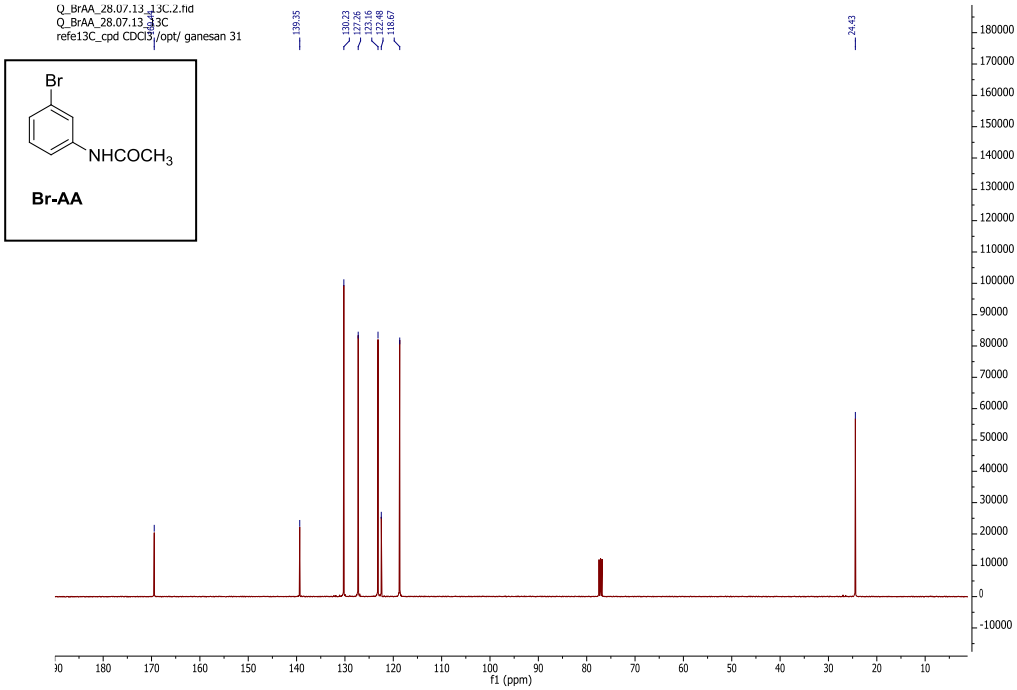


Figure S2: ^{13}C NMR of Br-AA

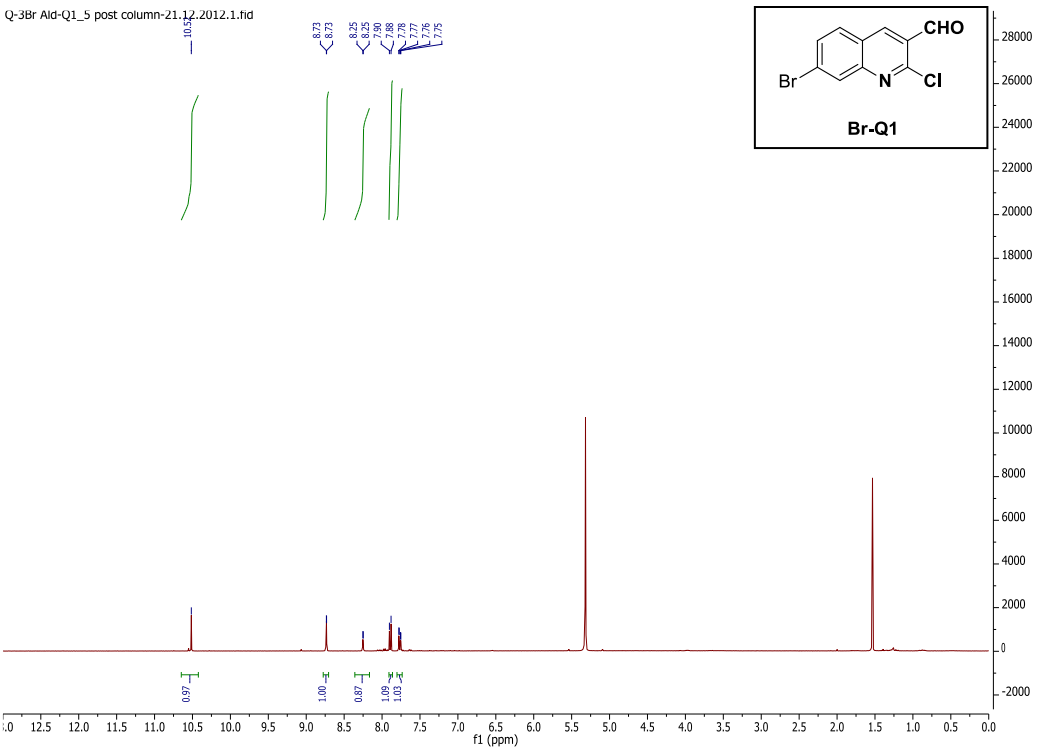


Figure S3: ^{1}H NMR of Br-Q1

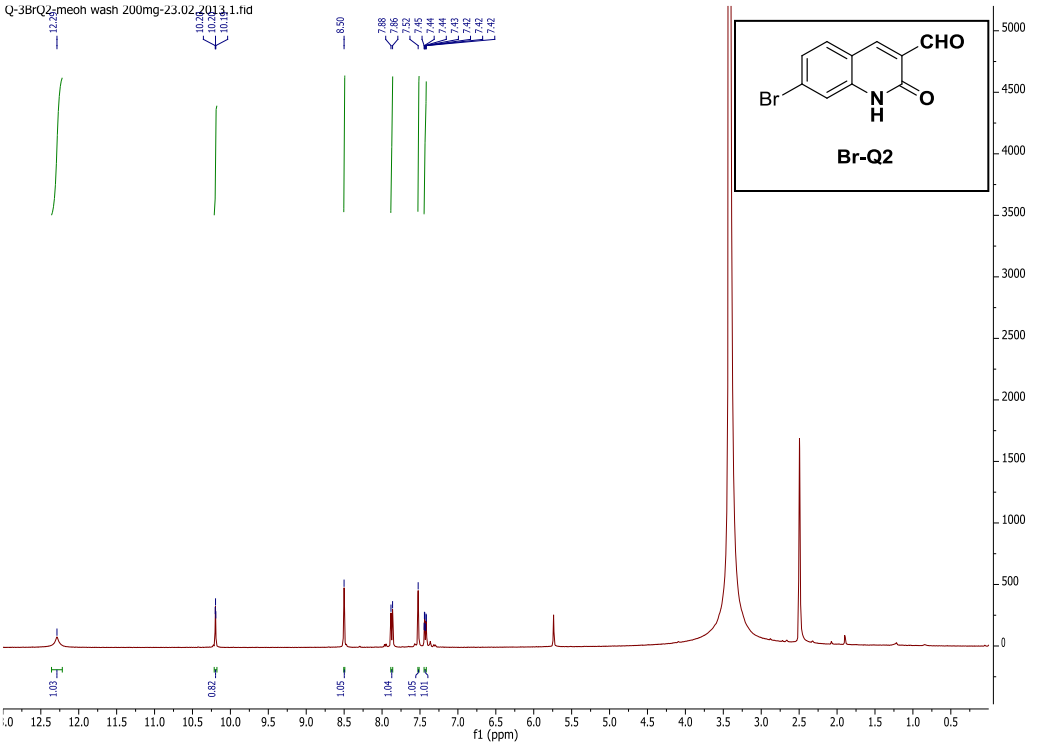


Figure S4: ^{1}H NMR of Br-Q2

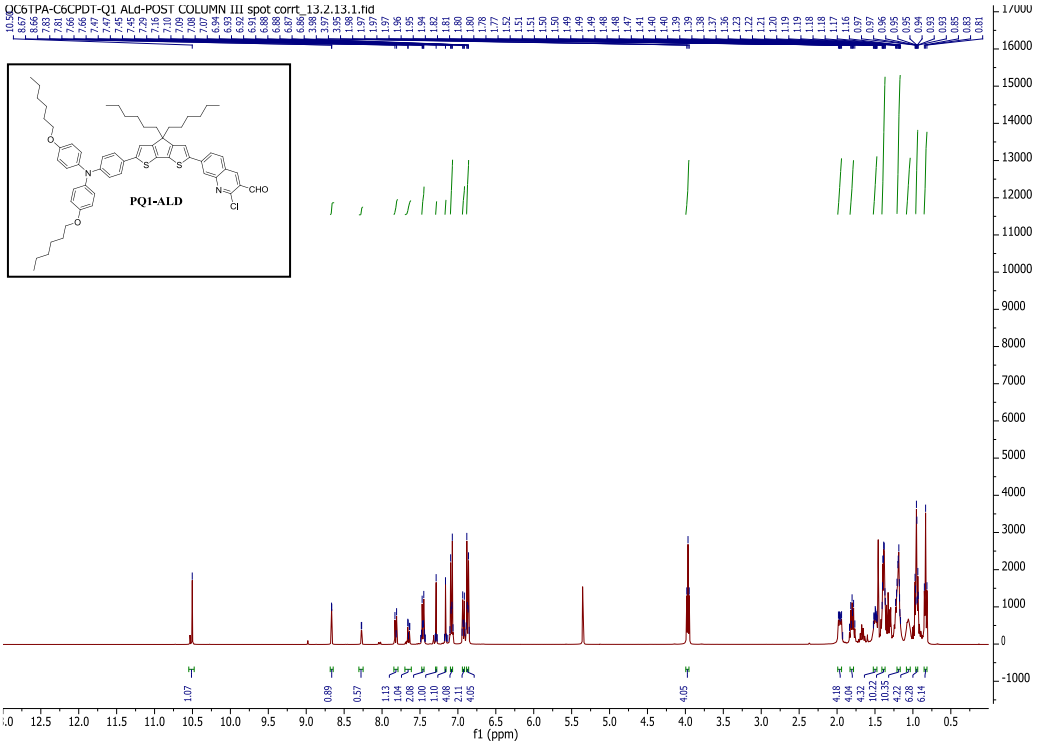


Figure S5: ^{1}H NMR of PQ1-ALD

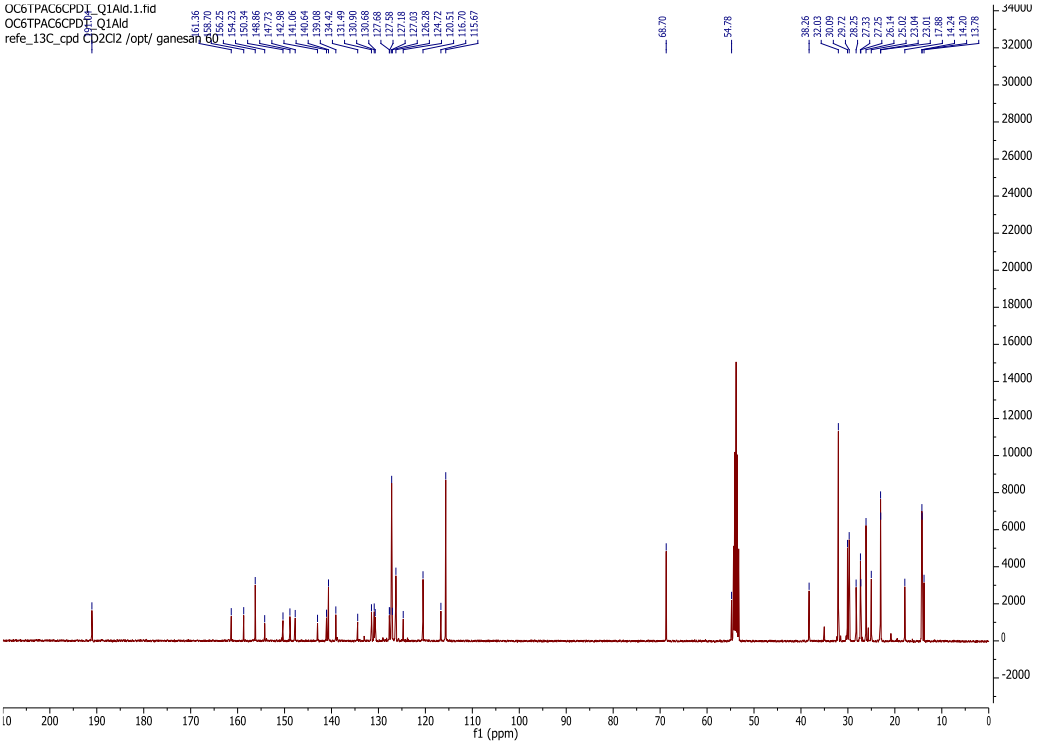


Figure S6: ^{13}C NMR of PQ1-ALD

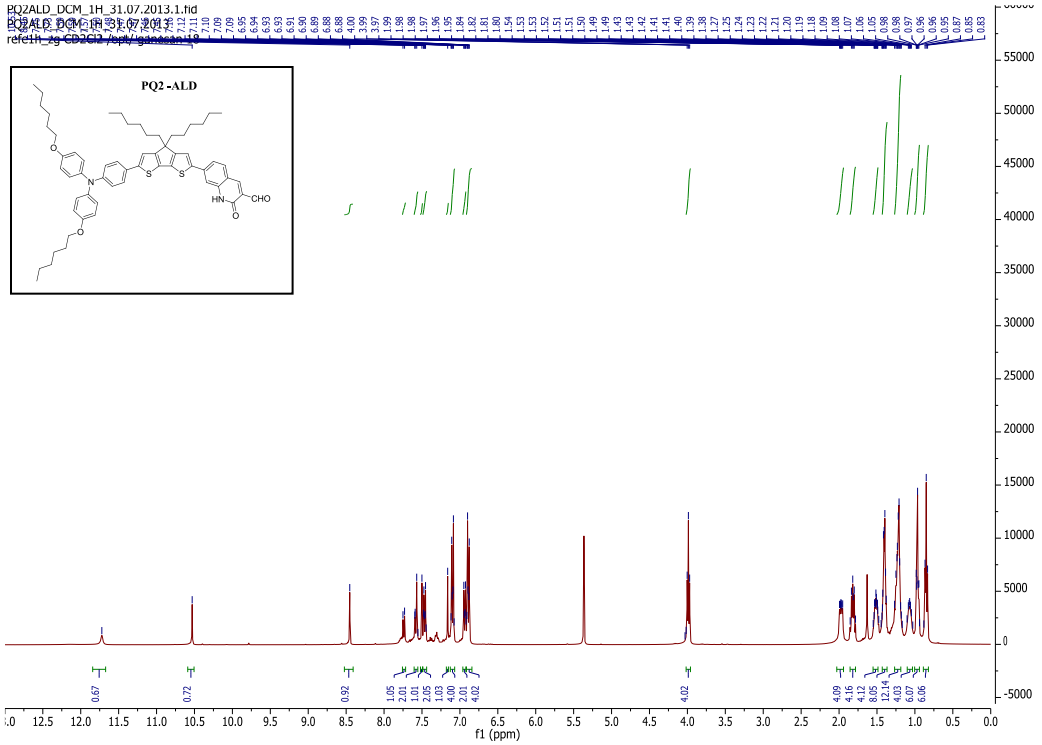


Figure S7: ^{1}H NMR of PQ2-ALD

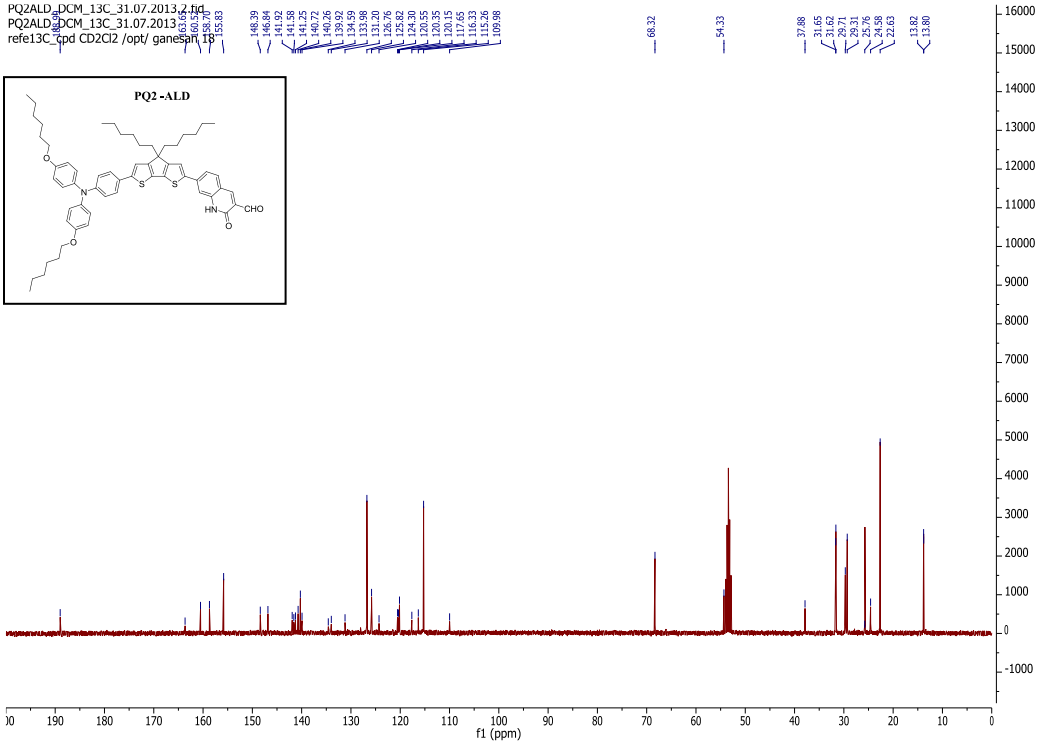


Figure S8: ^{13}C NMR of PQ2-ALD

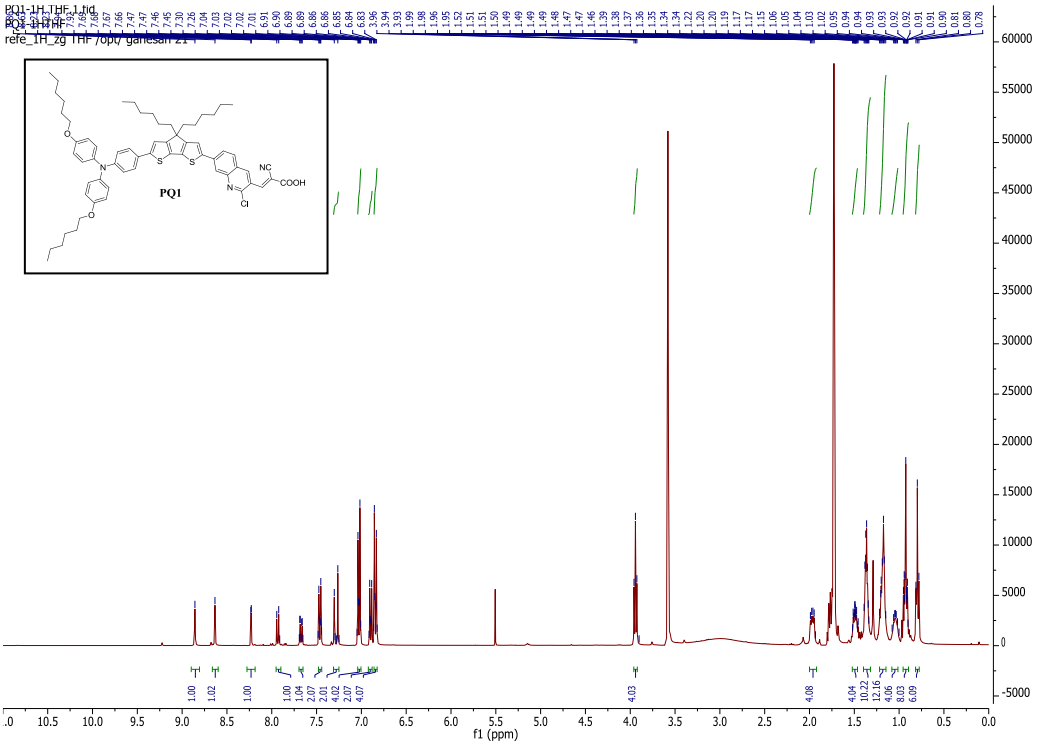


Figure S9: ^{1}H NMR of PQ1

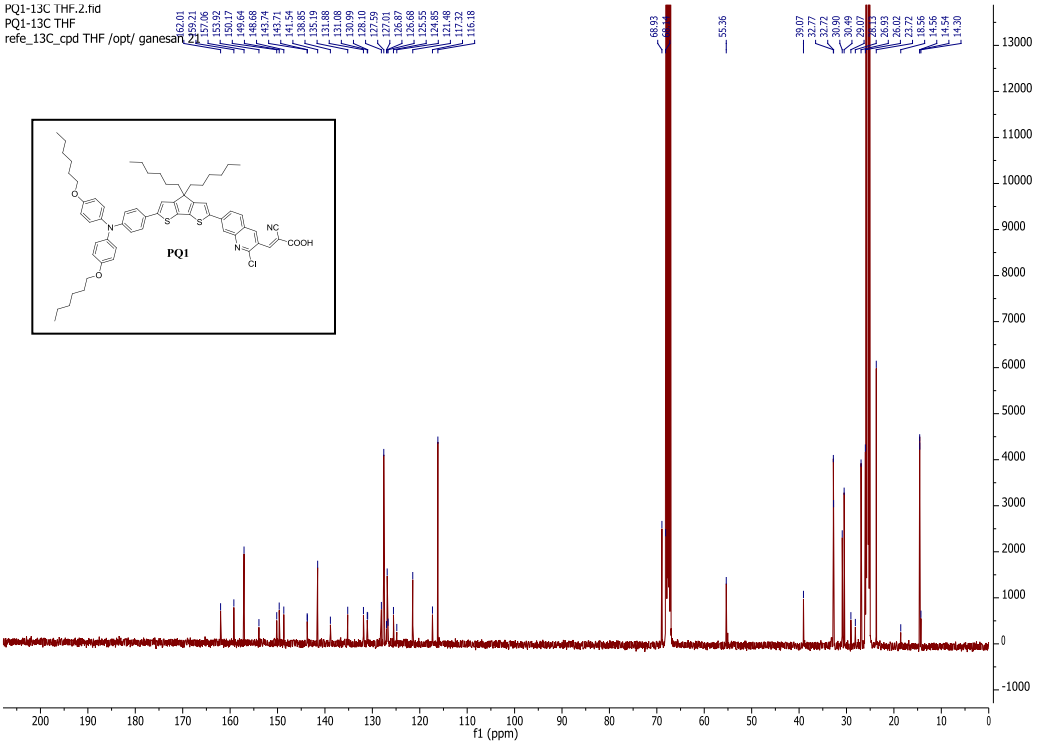


Figure S10: ^{13}C NMR of PQ1

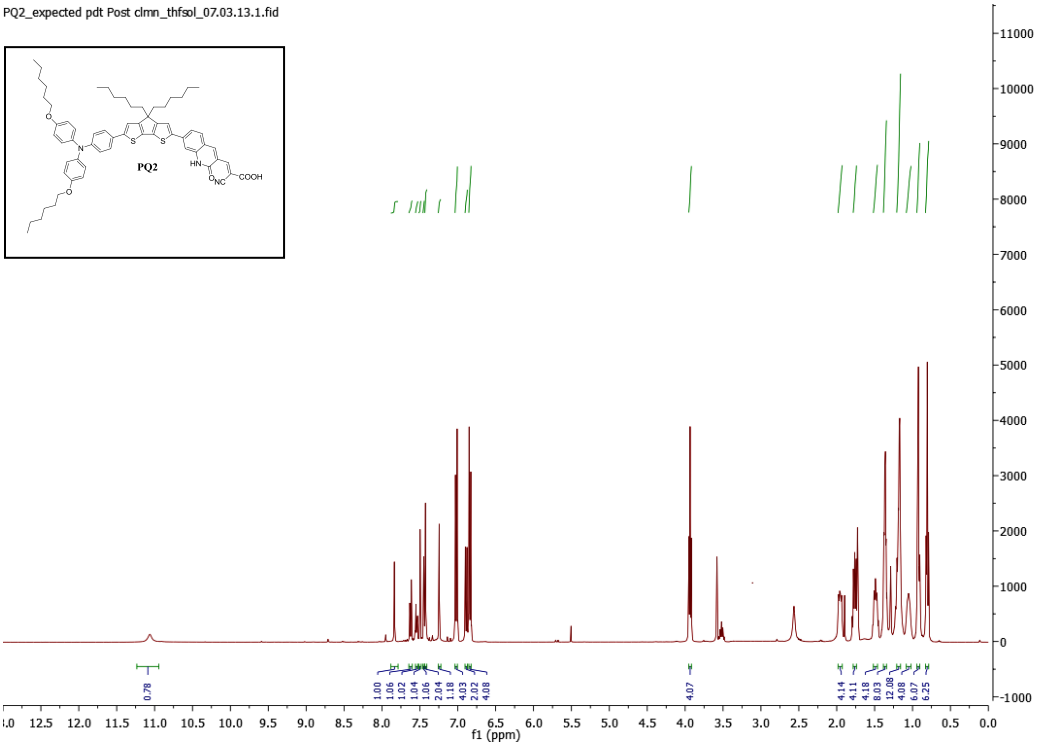


Figure S11: ^{1}H NMR of PQ2

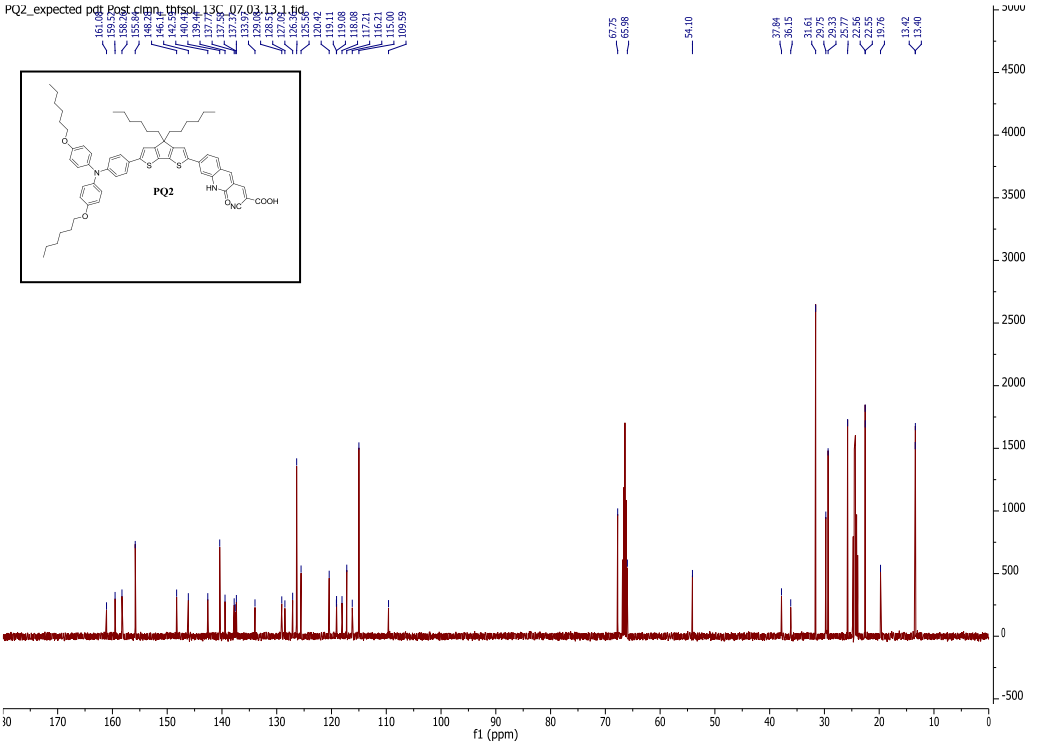


Figure S12: ^{13}C NMR of PQ2

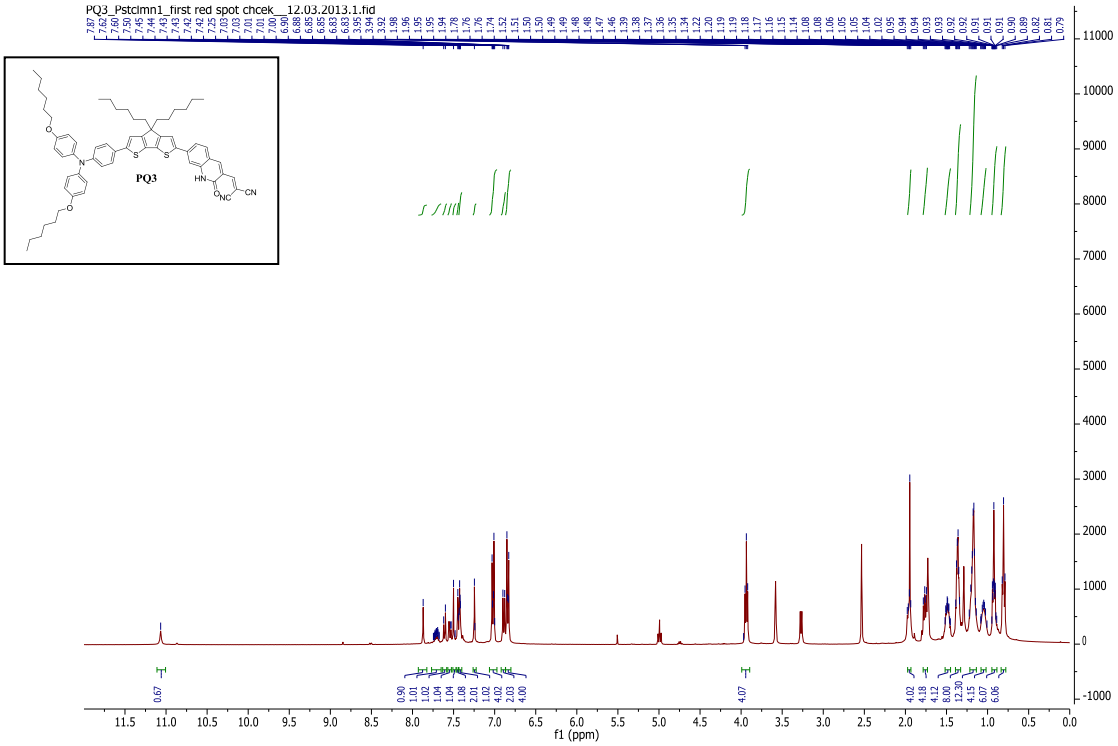


Figure S13: ^{1}H NMR of PQ3

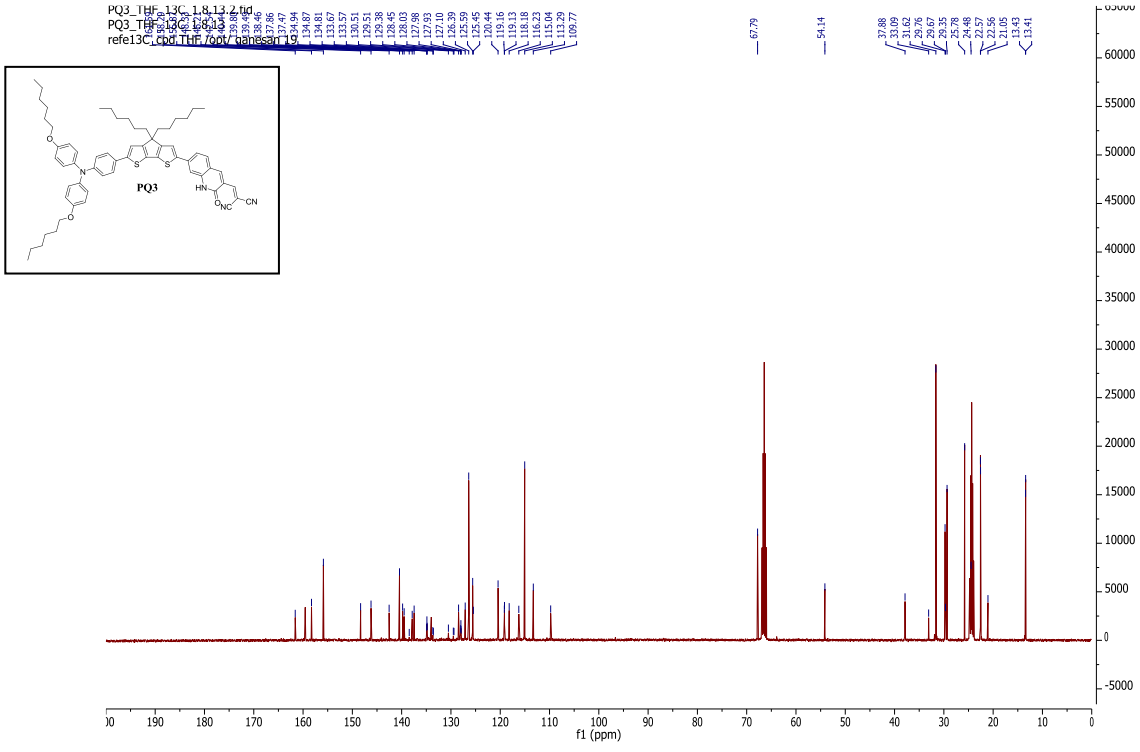


Figure S14: ^{13}C NMR of PQ3

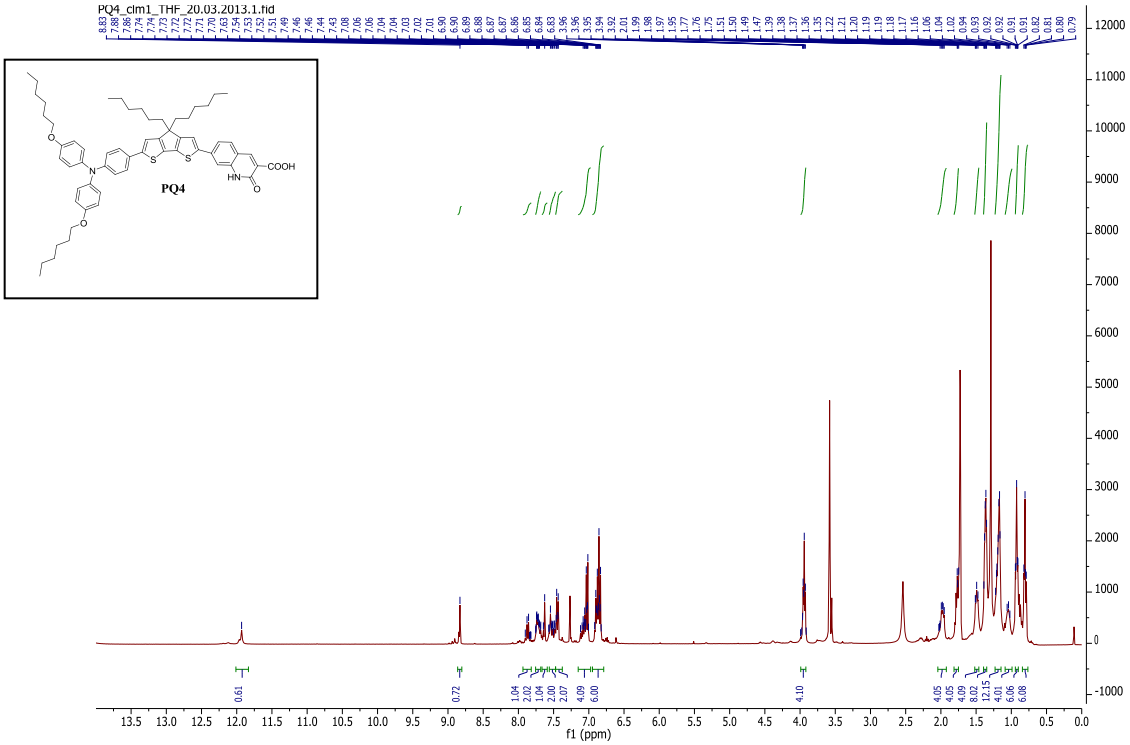


Figure S15: ^{1}H NMR of PQ4

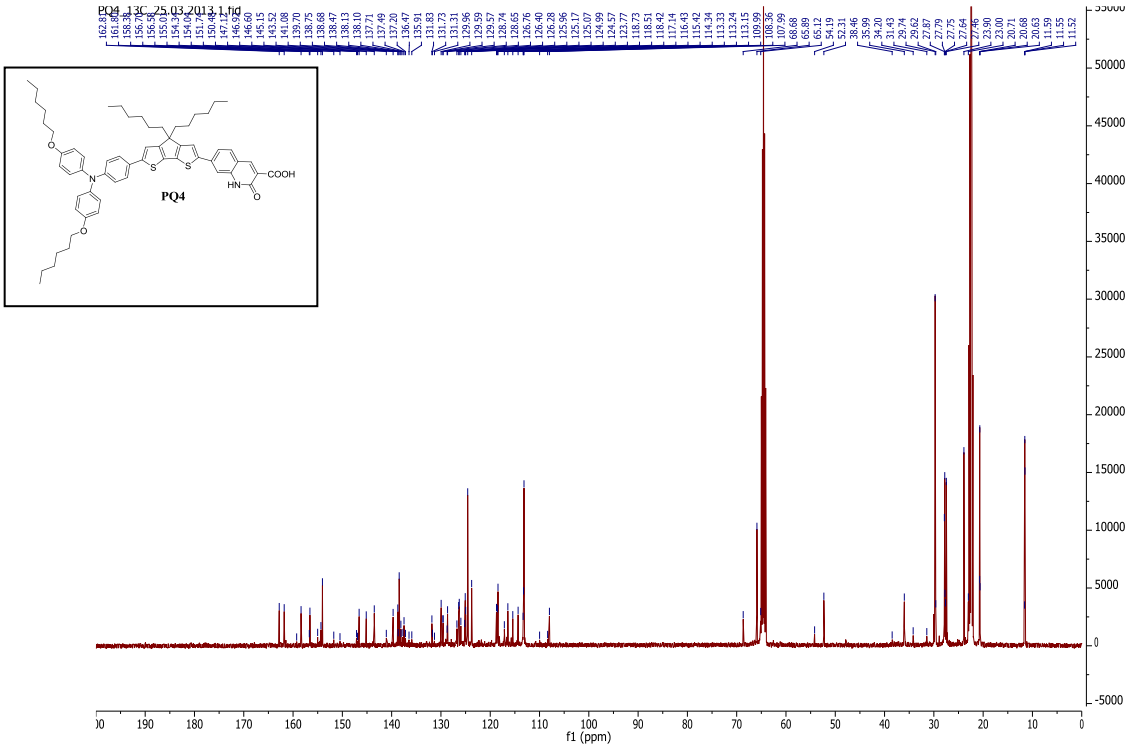


Figure S16: ^{13}C NMR of PQ4

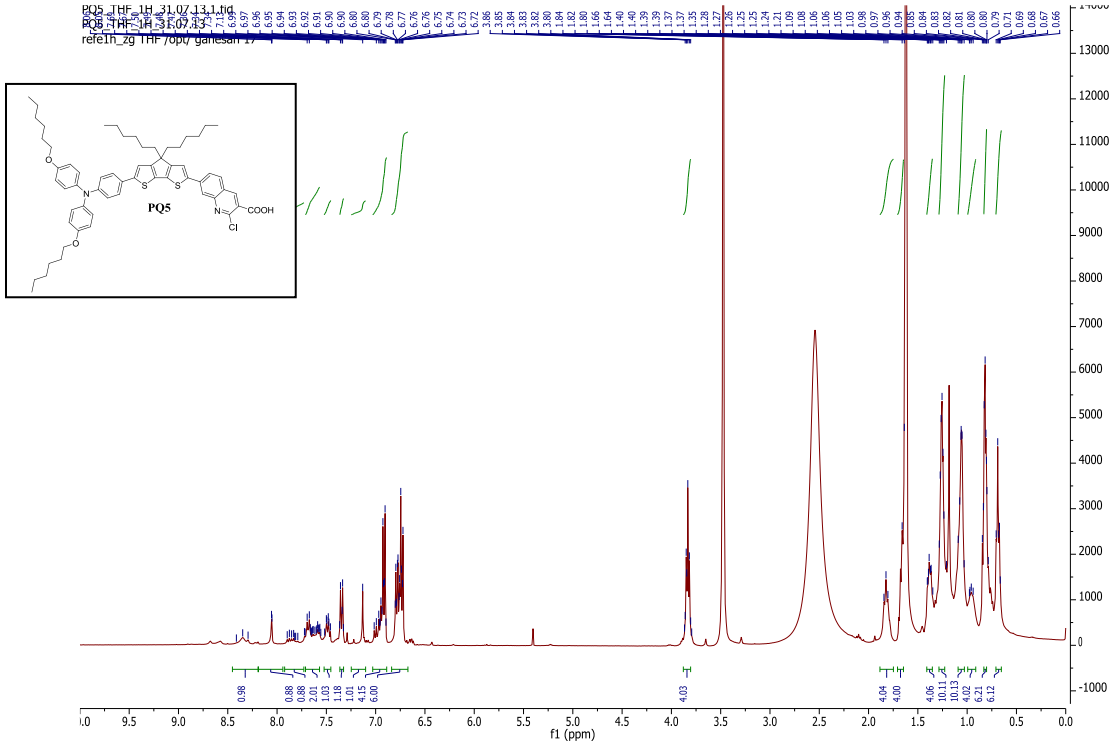


Figure S17: ^{1}H NMR of PQ5

4. Mass spectroscopy

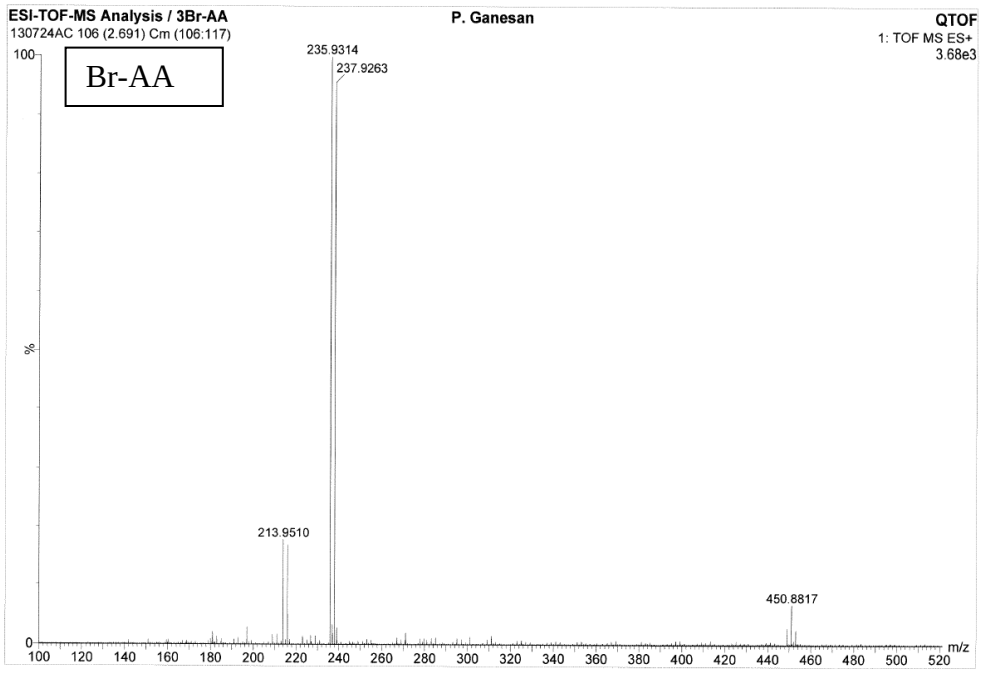


Figure S18: ESI-TOF-MS of Br-AA

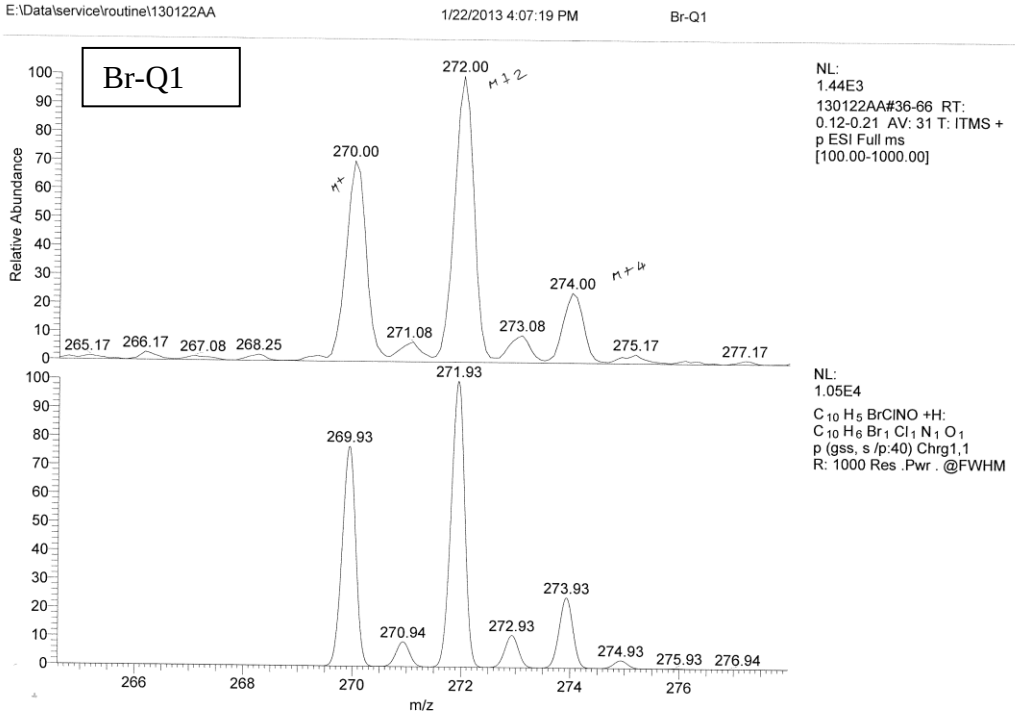


Figure S19: ESI-TOF-MS of Br-Q1

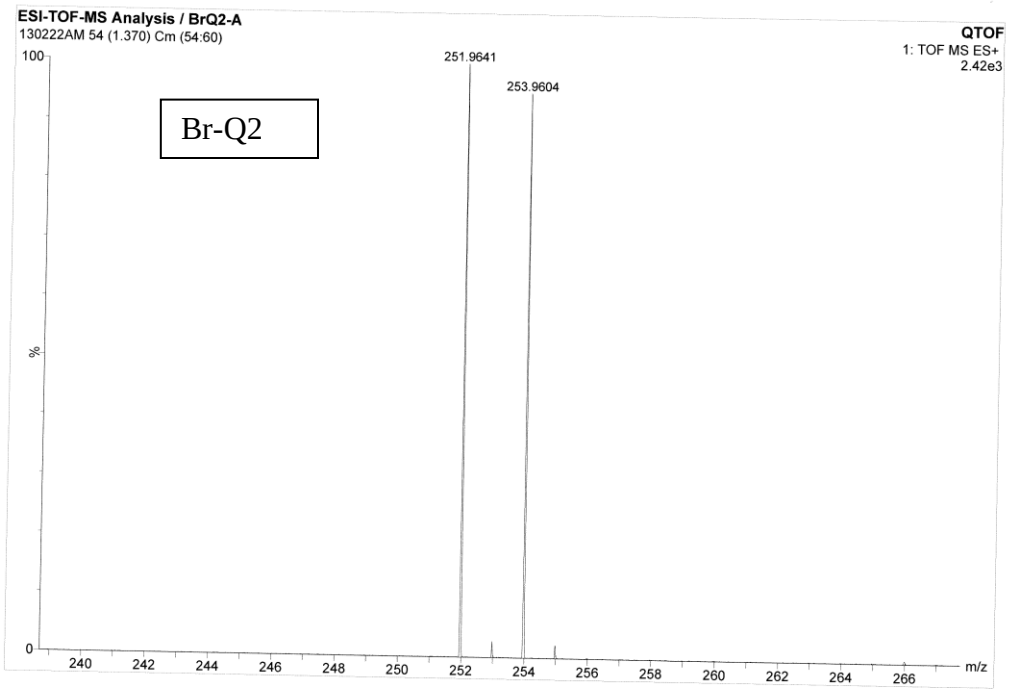


Figure S20: ESI-TOF-MS of Br-Q2

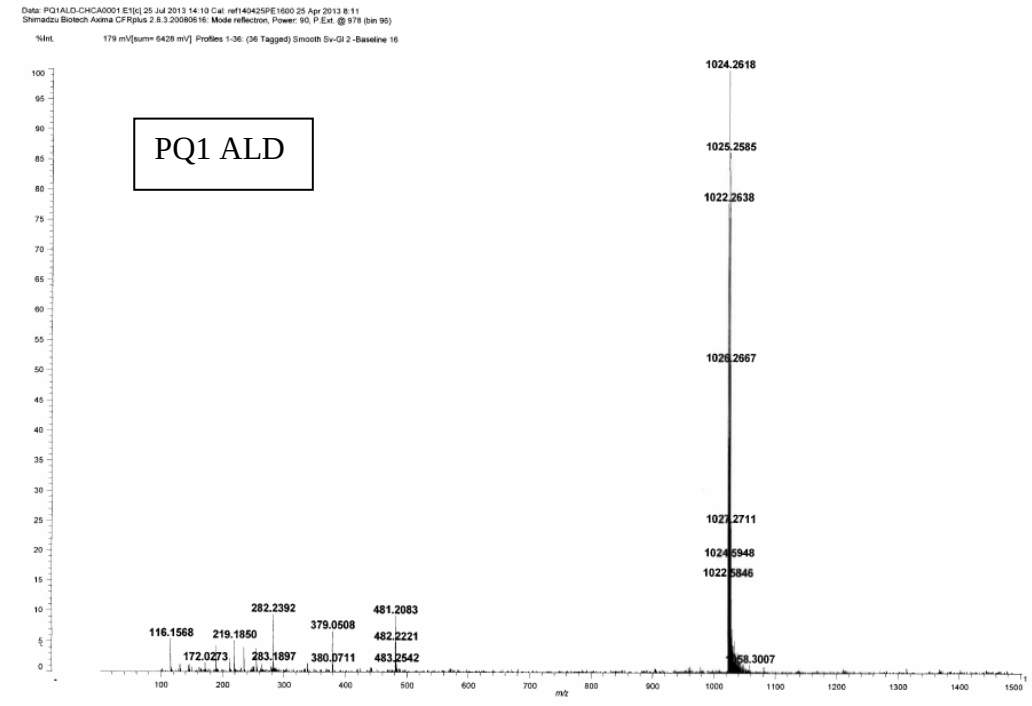


Figure S21: MALDI-MS of PQ1-ALD

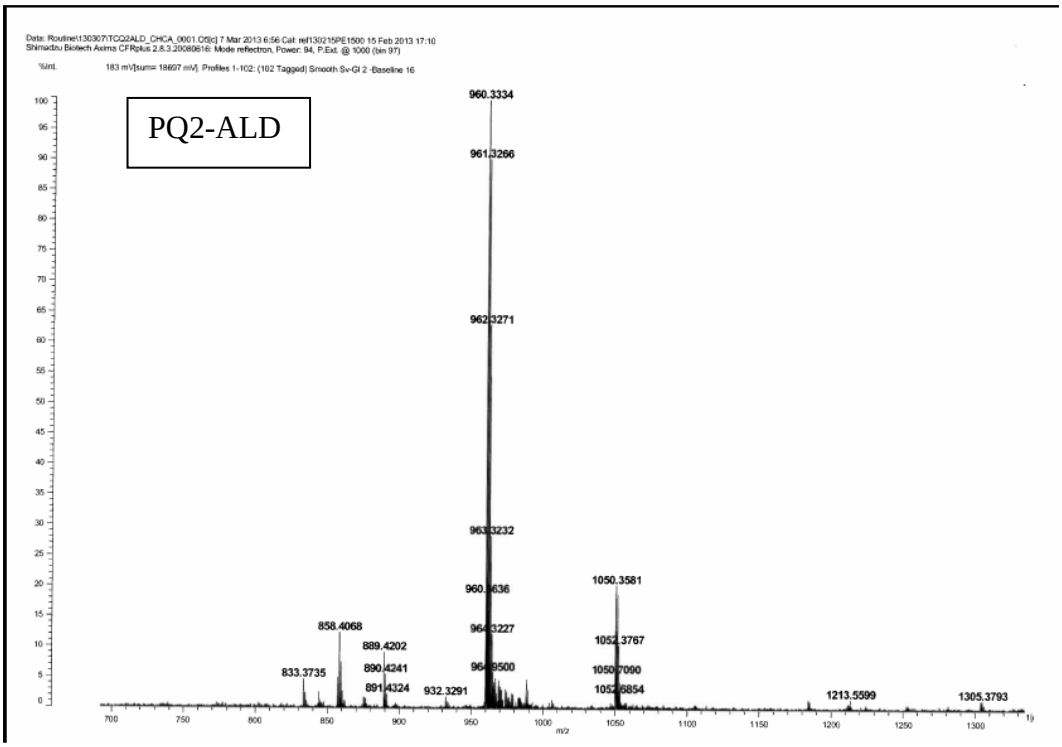


Figure S22: MALDI-MS of PQ2-ALD

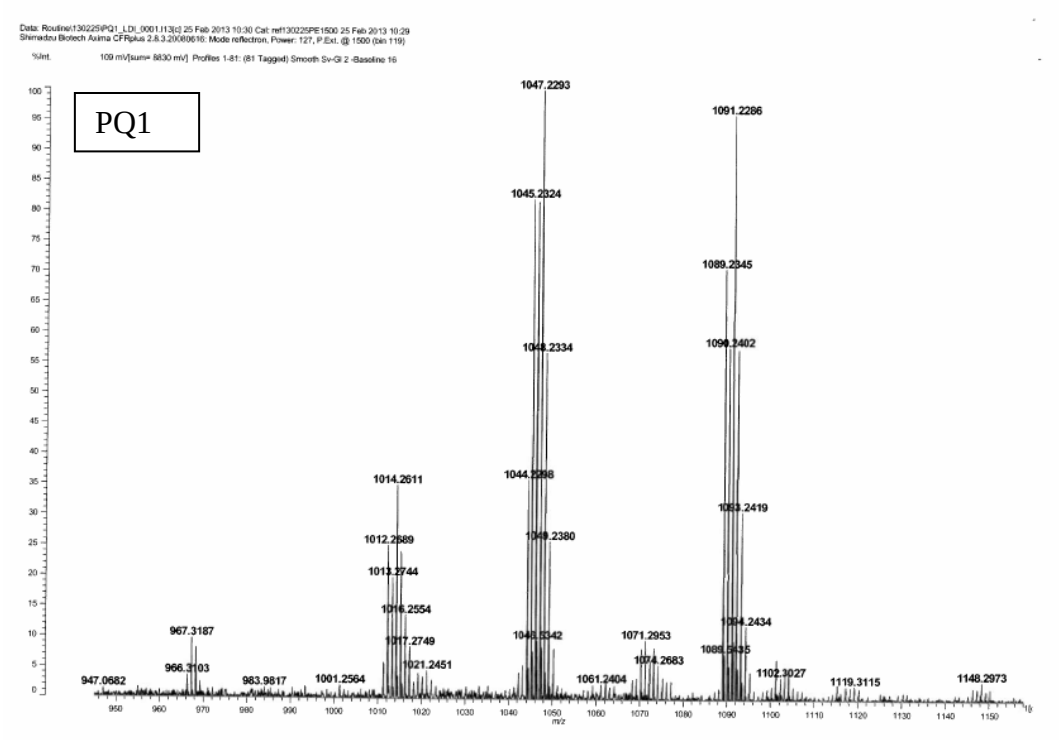


Figure S23: MALDI-MS of PQ1

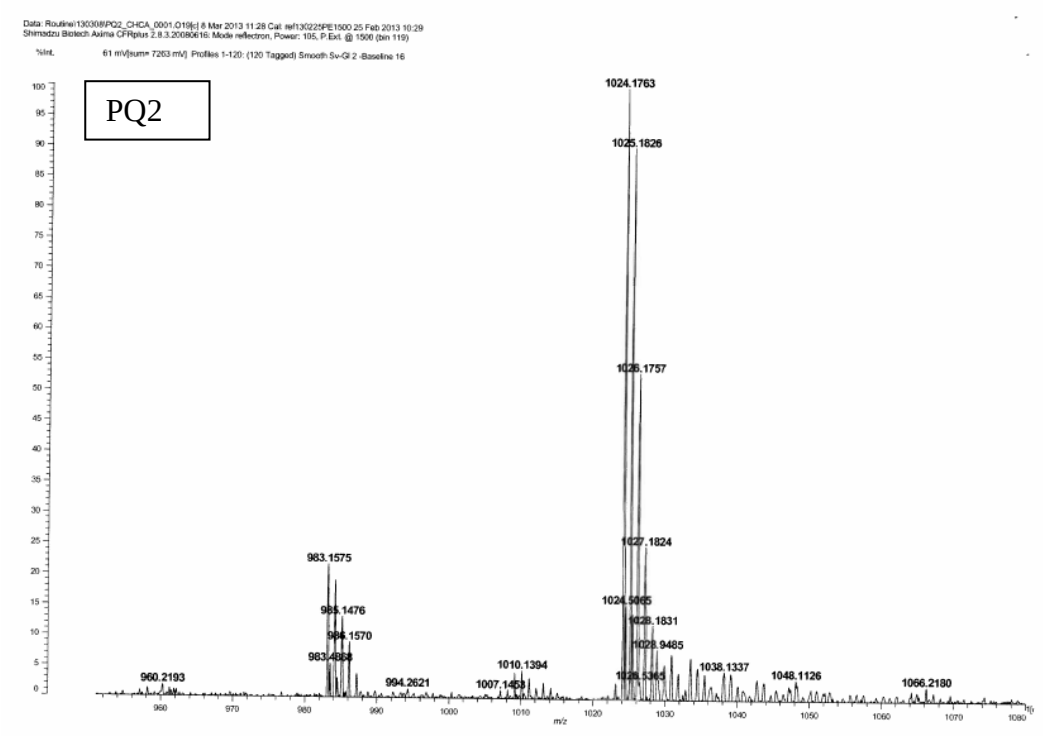


Figure S24: MALDI-MS of PQ2

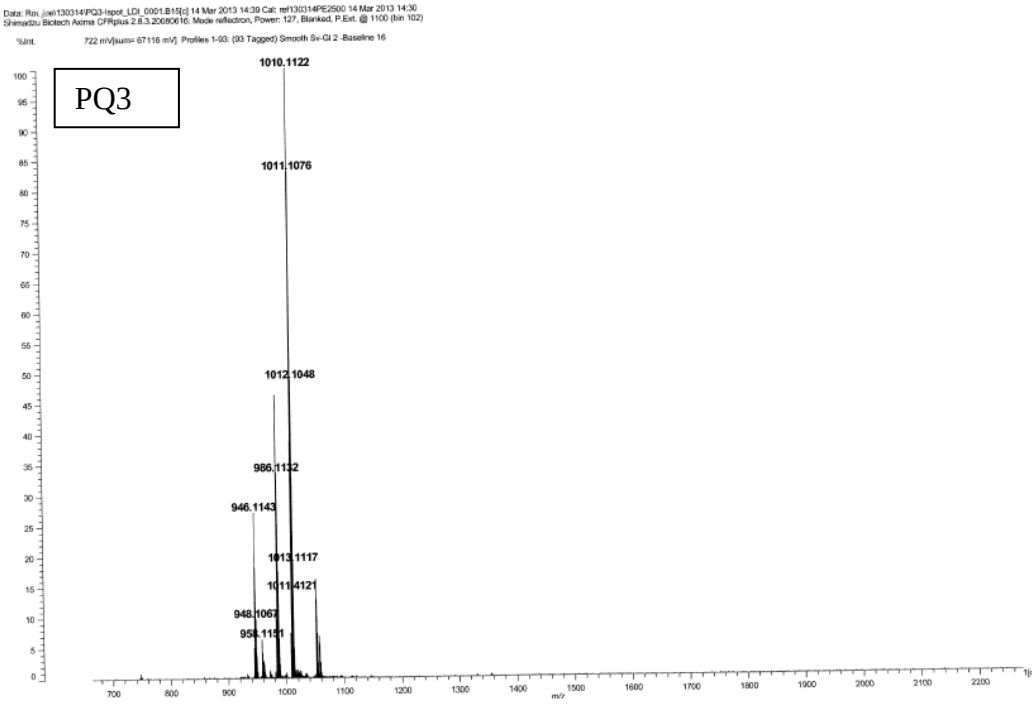


Figure S25: MALDI-MS of PQ3

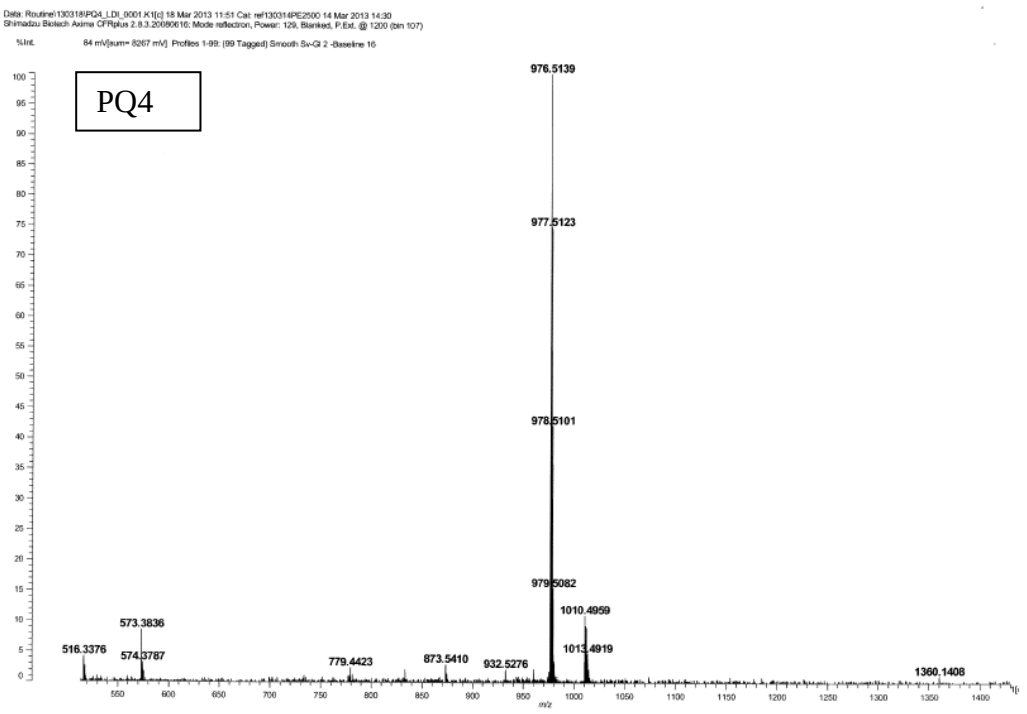


Figure S26: MALDI-MS of PQ4

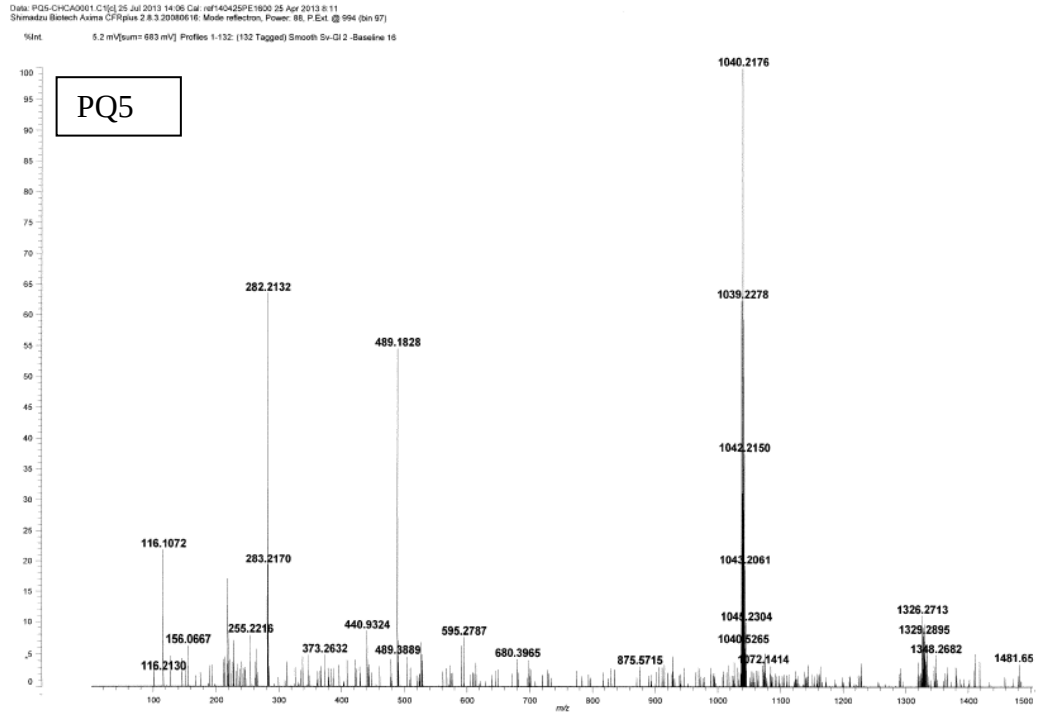


Figure S27: MALDI-MS of PQ5

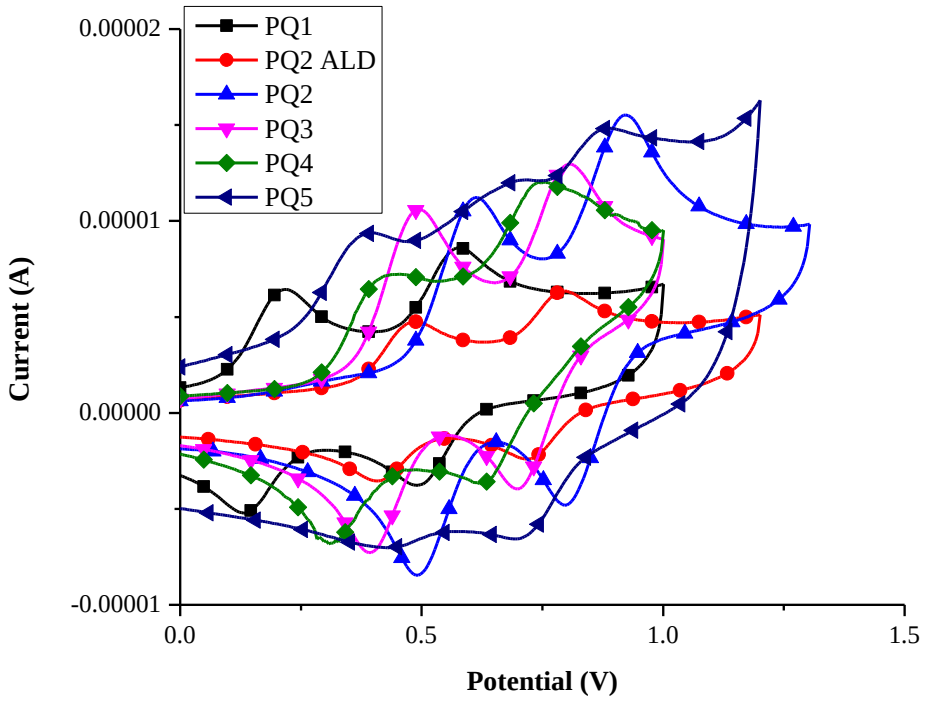


Figure S28: Cyclic Voltammograms of the sensitizers recorded in dichloromethane

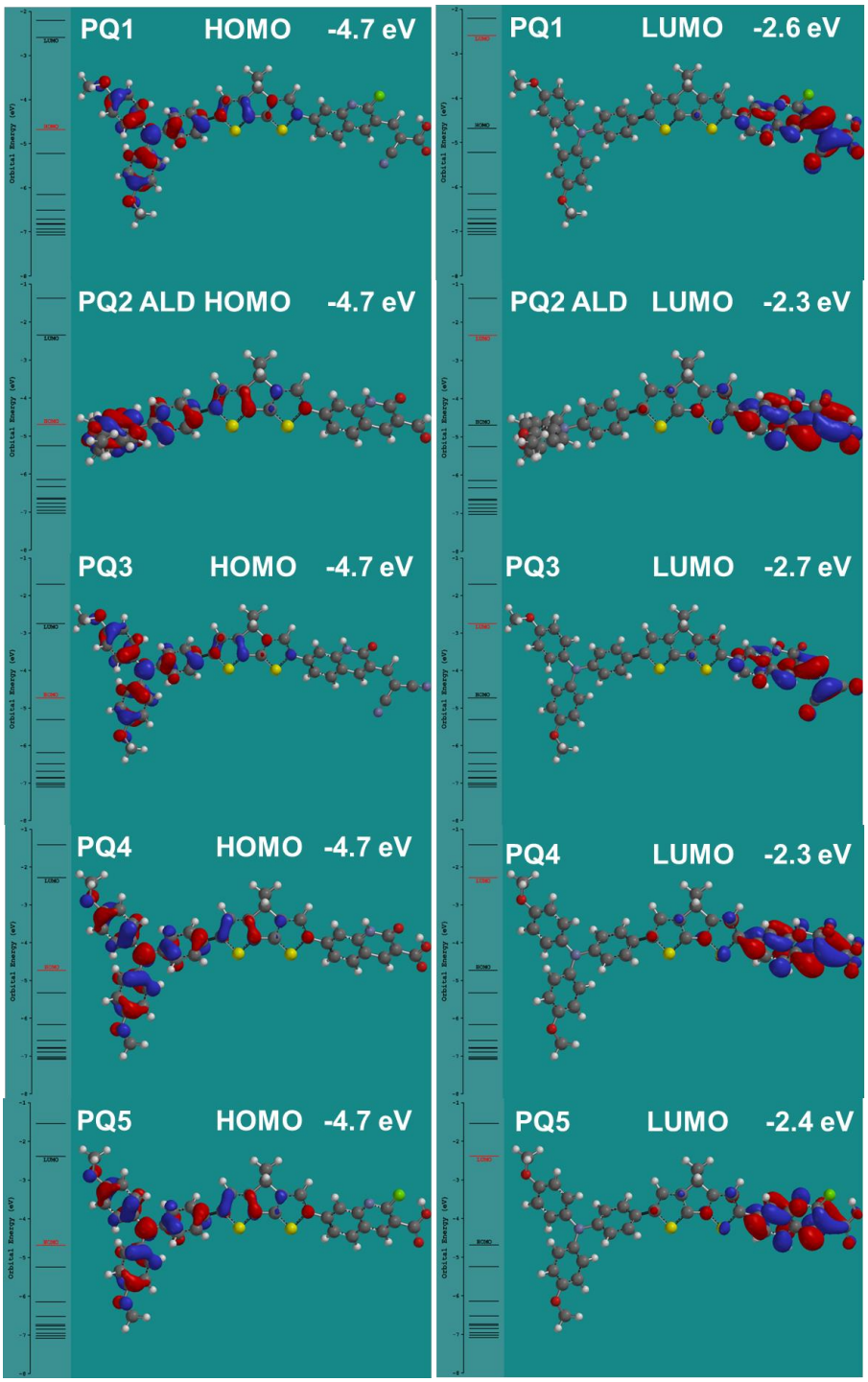


Figure S29: Frontier Molecular Orbitals (HOMO and LUMO) of Quinolinone based sensitizers (All calculations were carried out using Spartan '10 Windows run on Microsoft Windows XP, while. (3) Geometry optimization, energy levels, and frontier molecular orbitals of the dyes' HOMOs, LUMOs and LUMO-1s were calculated at the B3LYP/6-31G (d,p) level)

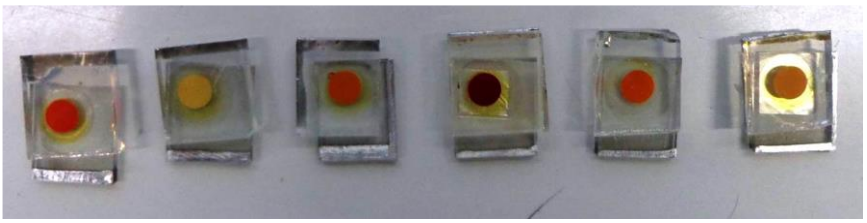


Figure S30: Dye sensitized solar cells of the sensitizers under investigation

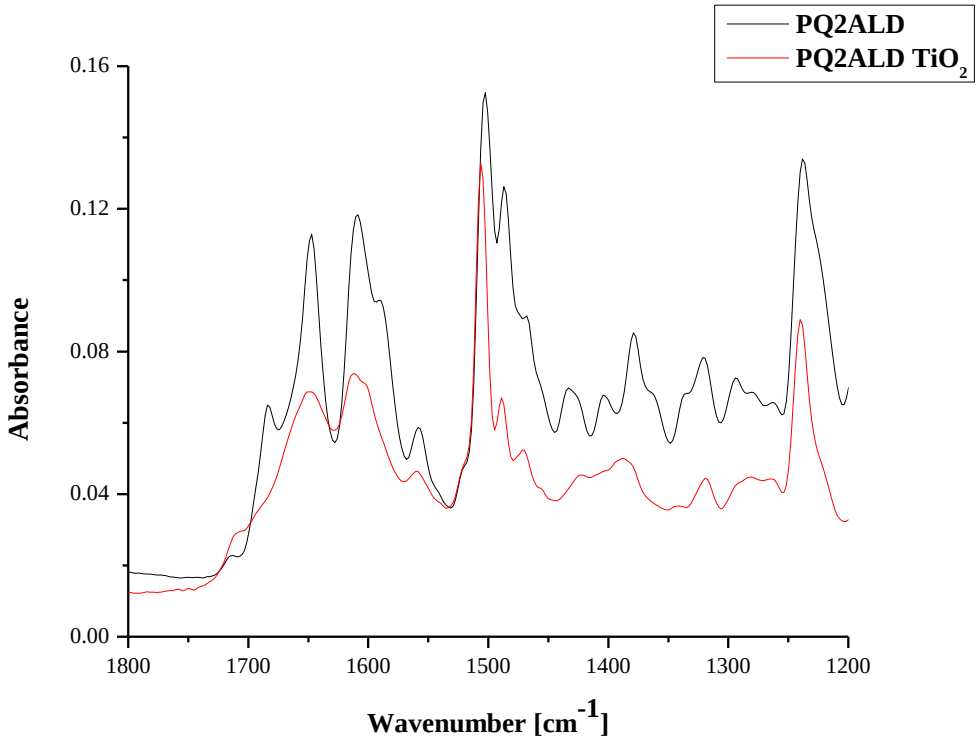


Figure S31: FTIR spectra of PQ2-ALD in solid state and dyes adsorbed on TiO_2 films.

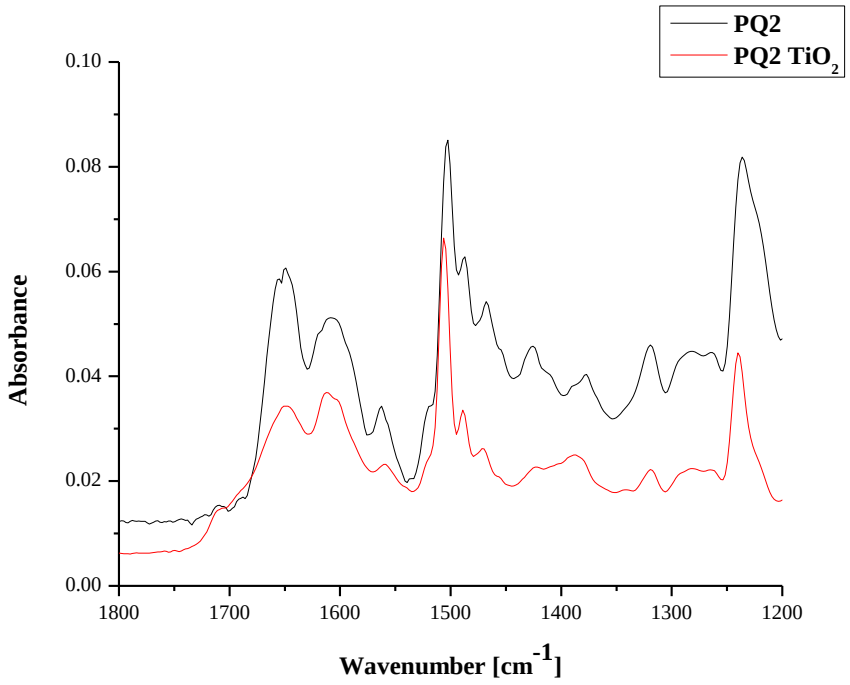


Figure S32: FTIR spectra of PQ2 dye in solid state and dyes adsorbed on TiO_2 films.

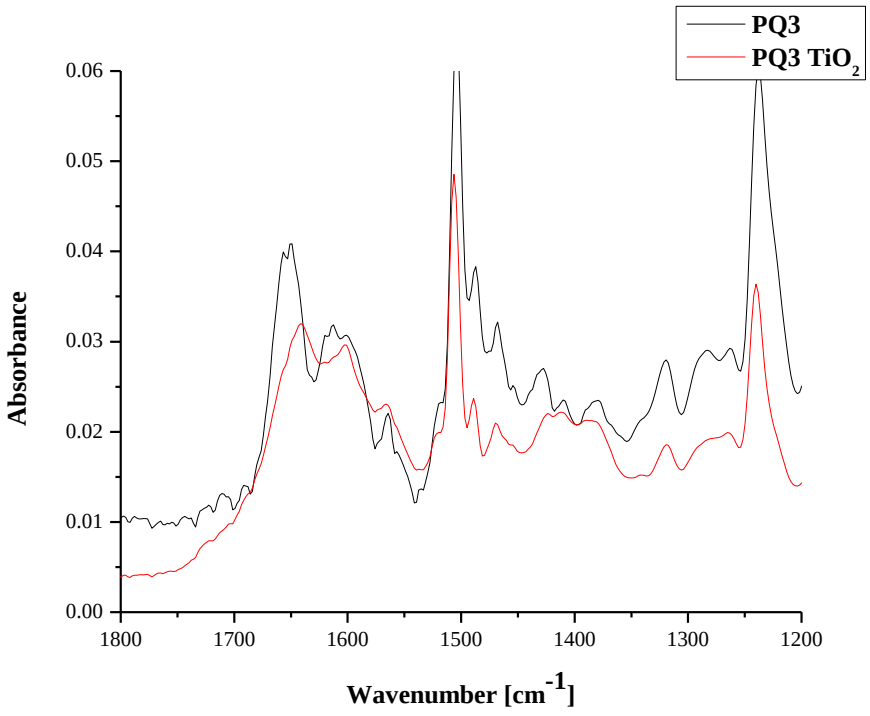


Figure S33: FTIR spectra of PQ3 in solid state and dyes adsorbed on TiO_2 films.

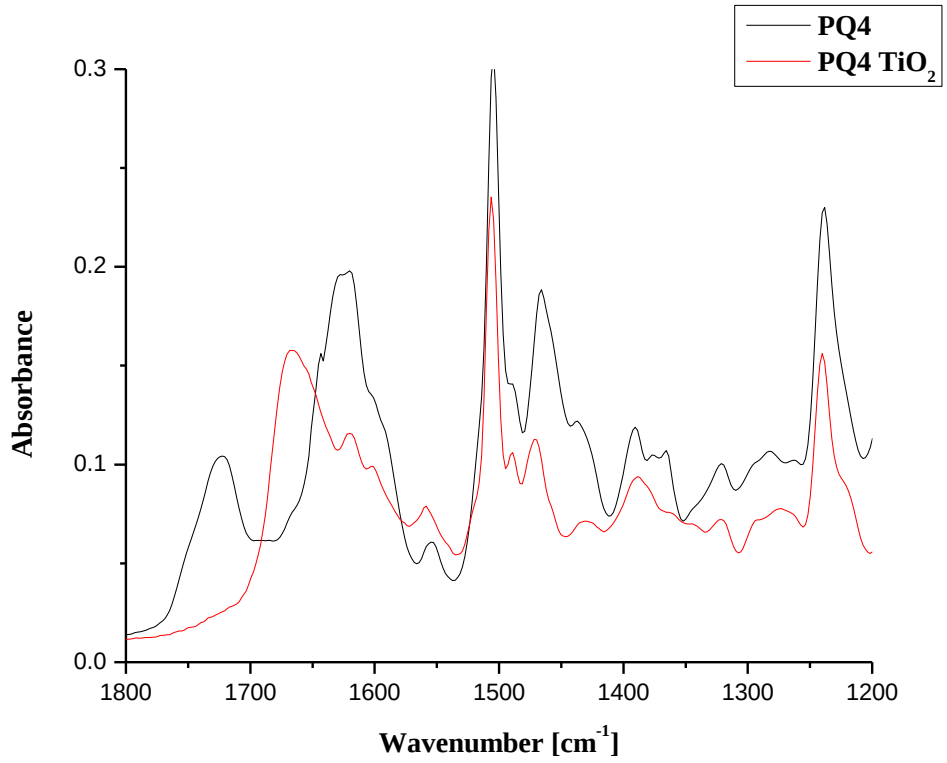


Figure S34: FTIR spectra of PQ4 in solid state and dyes adsorbed on TiO_2 films.

[1] Qian, G.; Dai, B.; Luo, M.; Yu, D.; Zhan, J.; Zhang, Z.; Ma, D.; Wang, Z. Y. Band Gap Tunable, Donor−Acceptor−Donor Charge-Transfer Heteroquinoid-Based Chromophores: Near Infrared Photoluminescence and Electroluminescence. *Chem. Mater.* **2008**, *20*, 6208–6216.