Supporting Information

Effect of Tetrahydroquinoline Dyes Structure on the Performance of Organic Dye Sensitized Solar Cells

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Contents:

(A) Synthesis and photophysical data for the intermediates and sensitizers:

General: ^{1}H NMR Spectra were recorded with a Varian INOVA 400NMR instrument. MS data were obtained with GCT CA156 (UK) high resolution mass spectrometer (HRMS) or HP1100 LC/MSD (USA) mass spectrometer. UV-vis spectra of the dyes in solutions were recorded in a quartz cell with 1 cm path length on a HP 8453 spectraphotometer. Melting-points were measured with a X-4 melting-point apparatus with microscope.

The several of π-conjugating spacers **5a-8a** were prepared using known procedures. **5a** and **6a** were prepared by Suzuki coupling of 2-thienylboronic acid with corresponding 2-bromothiophene and 2,5-dibromothiophene, respectively. **7a** was obtained in 3 steps from 3-bromothiophene according to the already reported procedures.[1,2] **8a** of *E*-configuration was prepared by McMurry coupling of 2-thiophenecarboxaldehyde.[3]

2,2,4-Trimethyl-1,2-dihydro-quinoline(**1a**)

To a solution of aniline (18.7 g, 0.2 mol) and toluenesulfonic acid (1.9 g) in cyclohexane (20 mL), acetone (42 mL, 0.57 mol) was added dropwise at 80~90 ºC for 8~10 h. The resulted water was removed by co-boiling with cyclohexane. Sodium carbonate (0.55 g) in water (20 mL) was poured into the reaction mixture after complete addition of acetone at 70 ºC. The reaction mixture was stirred overnight at r.t. The organic layer was washed with water and dried over magnesium sulfate. The unreacted acetone and solvent was romoved by rotary evaporation. The residue was distilled in *vacuo* to give **1a** as colorless oil (130 ºC/10 mmHg, 17 g, 49%). ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 1.27 (s, 6H), 1.98 (d, J = 1.2 Hz, 3H), 3.66 (s, 1H), 5.30 (d, J = 1.2 Hz, 1H), 6.43 (d, J = 7.8 Hz, 1H), 6.63 (dd, J_1 = 8.0 Hz, J_2 = 7.5 Hz, 1H), 6.97 (dd, $J_1 = J_2$ = 7.6 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H).

2,2,4-Trimethyl-1,2,3,4-dihydro-quinoline (**1b**)

To a solution of **1a** (12.05 g) in absolute ethanol was added a 50% (w/w) slurry of Raney nickel in ethanol (1 g). The reaction was hydrogenated over H_2 gas (1 MPa) at 130 ºC. The resulting solution was filtered carefully over celite and washed with

ethanol. The solvent was removed in *vacuo* and the residue (12 g, ~99%) was used for the next reaction without more purification. ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 1.15 (s, 3H), 1.21 (s, 3H), 1.32 (d, J = 6.7 Hz, 3H), 1.43 (dd, J_1 = 12.5 Hz, J_2 = 12.6 Hz, 1H), 1.71 (dd, J_1 = 5.6 Hz, J_2 = 12.9 Hz, 1H), 2.87-2.93 (m, 1H), 3.53 (s, 1H), 6.41 (d, J = 7.9 Hz, 1H), 6.64 (dd, J_1 = 7.5 Hz, J_2 = 7.4 Hz, 1H), 6.95 (dd, J_1 = 7.8 Hz, J_2 = 7.4 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H).

1,2,2,4-Tetramethyl-1,2,3,4-dihydro-quinoline (**1c**)

1b (1.75 g, 10 mmol) and $(CH_3)_2SO_4$ (0.76 g, 6 mmol) were dissolved in benzene. The mixture was refluxed for 2 h. 10% NH_4OH (10 mL) was added at 70 ºC and stirred for 1 h. The organic layer was dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane: hexane = 1:1) to provide 1.5 g (79%) of the title product as colorless oil. ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 1.18 (s, 3H), 1.25 (s, 3H), 1.32 (d, J = 6.7 Hz, 3H), 1.51 (dd, J_1 = 12.7 Hz, J_2 = 12.8 Hz, 1H), 1.75 (dd, J_1 = 4.5 Hz, J_2 = 12.9 Hz, 1H), 2.78 (s, 3H), 2.80-2.86 (m, 1H), 6.56 (d, J = 8.1 Hz, 1H), 6.65 (dd, J_1 = 7.4 Hz, J_2 = 8.2 Hz, 1H), 7.06-7.12 (m, 2H).

6-Formyl-1,2,2,4-tetramethyl-1,2,3,4-dihydro-quinoline (**1d**)

$POCl_3$ (0.49 mL, 5.4 mmol) was added dropwise with stirring to a solution of **1c** (1.008 g, 5.3 mmol) in fresh distilled DMF (1.3 mL, 16.7 mmol) at 15~20 ºC under N_2 protect. Then the mixture was held at 55 ºC for 6 h and then cooled, ice (100 g) was added, and then 5N NaOH to pH 6. The precipitate was filtered, dried under reduced pressure to give **1d** as green solid (631 mg, 55%). ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 1.28 (s, 3H), 1.34 (s, 3H), 1.40 (d, J = 6.6 Hz, 3H), 1.54 (dd, J_1 = 13.0 Hz, J_2 = 13.1 Hz, 1H), 1.83 (dd, J_1 = 4.5 Hz, J_2 = 13.1 Hz, 1H), 2.92 (s, 3H), 2.82-2.90 (m, 1H), 6.59 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 8.6 Hz, 1H), 7.64 (s, 1H), 9.71 (s, 1H).

6-Bromo-1,2,2,4-tetramethyl-1,2,3,4-dihydro-quinoline(**1e**)

1c (2.54g, 13.4mmol) and NBS (2.63g, 14.7mmol) were dissolved in 20 mL CCl_4. This solution was stirred at r. t. for 2h. The solvent was removed by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane: hexane = 1:2). **1e** (3.36g, 93%) was obtained as colorless solid. Mp.

37-46 ºC. ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 1.17 (s, 3H), 1.25 (s, 3H), 1.30 (d, J = 6.7 Hz, 3H), 1.47 (dd, $J_1 = J_2$ = 12.8 Hz, 1H), 1.75 (dd, J_1 = 4.5 Hz, J_2 = 13.0 Hz, 1H), 2.75 (s, 3H), 2.78-2.80 (m, 1H), 6.41 (d, J = 8.6 Hz, 1H), 7.15(dd, J_1 = 2.3 Hz, J_2 = 8.7 Hz, 1H), 7.17 (s, 1H).

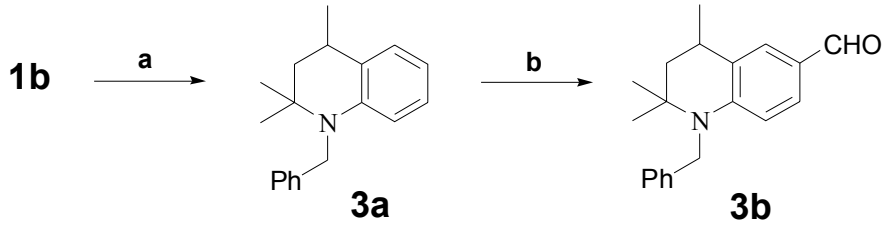
1,2,2,4-Tetramethyl-1,2,3,4-dihydro-quinoline-6-boronic acid (**1f**)

To a THF (20mL) solution of **1e** (540mg, 2mmol) was added a hexane solution of *n*-BuLi (2.57M, 0.85mL, 2.3mmol) at -78 ºC. After being stirred for 1h at this temperature, $B(OBu)_3$ (1mL, 3.7mmol) was added dropwise to this solution. After the mixture was stirred for another 1h at -78 ºC, it was warmed to ambient temperature and stirred overnight. The solution was partitioned between saturated aqueous NH_4Cl (50 mL) and ethyl acetate (50mL). The aqueous layer was extracted further with dichloromethane (3 × 20mL) and the combined organic layers were dried over $MgSO_4$. The product was purified by flash chromatography (silica gel, CH_2Cl_2:MeOH = 40:1) to provide the boronic acid as white solid (230mg, 50%). ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 1.25 (s, 3H), 1.33 (s, 3H), 1.46 (d, J = 6.6 Hz, 3H), 1.59 (dd, J_1 = 12.5 Hz, J_2 = 13.0 Hz, 1H), 1.82 (dd, J_1 = 4.3 Hz, J_2 = 12.9 Hz, 1H), 2.88-2.90 (m, 4H), 6.66 (d, J = 7.8 Hz, 3H), 7.96-7.80 (m, 2H).

(1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-methanol (**1g**) and (1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl-methyl)triphenylphosphonium bromide (**1h**)

To a solution of aldehyde **1d** (555mg, 2.56mmol) in absolute EtOH (10mL), an excess of $NaBH_4$ was added portionwise until consumption of the starting material as followed by TLC (CH_2Cl_2). After dilution with Et_2O, the mixture was hydrolyzed using 2 mL H_2O. The organic phase was dried over Na_2SO_4 and evaporated in *vacuo* to give the corresponding alcohol **1g** which was directively dissolved in $CHCl_3$ (20mL) in the presence of $HPPh_3Br$ (0.99g, 2.86mmol) (prepared from a solution of PPh_3 and gaseous HBr).[4] The reaction mixture was refluxed for 3h, and the solvent was evaporated after cooling. The residue was purified by chromatography (silica gel, CH_2Cl_2:MeOH = 20:1) and further triturated in the minimum of Et_2O leading to the precipitate of a white solid which was filtered to give a white powder **1h** (510mg,

37%). Mp. 190-191 ºC. ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 0.90 (d, J = 6.6 Hz, 3H), 1.12 (s, 3H), 1.25 (s, 3H), 1.37 (dd, J_1 = 13.0 Hz, J_2 = 13.1 Hz, 1H), 1.69 (dd, J_1 = 4.5 Hz, J_2 = 12.8 Hz, 1H), 2.61-2.64 (m, 1H), 2.72 (s, 3H), 4.97 (dd, J_1 = 13.4 Hz, J_2 = 14.5 Hz, 1H), 5.09 (dd, J_1 = 13.5 Hz, J_2 = 14.4 Hz, 1H), 6.34 (d, J = 8.1 Hz, 1H), 6.62 (s, 1H), 6.78 (d, J = 8.1 Hz, 1H), 7.64-7.79 (m, 15H). MS: API-ES positive: [quinoline-PPh_3^+] (*m/z* =464.5); API-ES negative: [Br^-] (*m/z* =79 and 81).



Scheme S1 Synthesis route of **3d**. a) i. *n*-BuLi, THF, -15 ºC; ii. benzyl bromide, 4h, 86%; b) $POCl_3$/DMF, CH_2ClCH_2Cl, reflux, 4h, 94%.

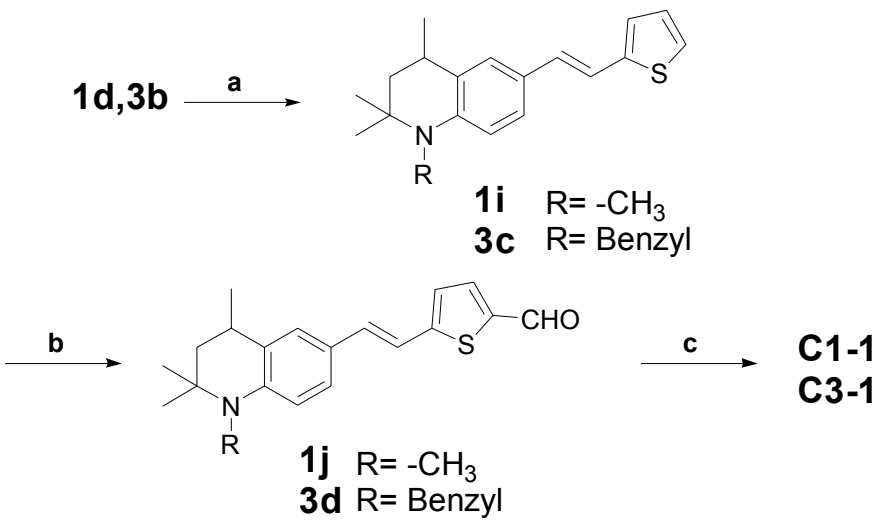
1-Benzyl-2,2,4-trimethyl-1,2,3,4-tetrahydro-quinoline (**3a**)

To a solution of **1b** (1.796g, 10.3mmole) in absolute THF (40mL) was added a solution of *n*-BuLi in hexane (2.57M, 4.4mL, 11.3mmole) at -15 ºC. After stirring for 30 min at this temperature, benzyl bormide (1.35mL, 11.3mmol) was added dropwise to this solution. The reaction mixture was stirred for another 4 h and the solvent was removed by rotary evaporator. After purification by chromatography (silica gel, CH_2Cl_2:hexane=1:5), the product was obtained as colorless oil (2.343 g, 86 %). ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 1.25 (s, 3H), 1.27 (s, 3H), 1.38 (d, J = 6.6 Hz, 3H), 1.76 (dd, J_1 = 12.6 Hz, J_2 = 12.8 Hz, 1H), 1.83 (dd, J_1 = 5.2 Hz, J_2 = 13.0 Hz, 1H), 3.03-3.09 (m, 1H), 4.24 (d, J = 17.9 Hz, 1H), 4.70 (d, J = 17.8 Hz, 1H), 6.30 (d, J = 8.3 Hz, 1H), 6.62 (dd, J_1 = 7.3 Hz, J_2 = 7.4 Hz, 1H), 6.91 (dd, J_1 = 7.5 Hz, J_2 = 8.0 Hz, 1H), 7.17-7.22 (m, 2H), 7.29-7.30 (m, 4H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{19}H_{23}N$, 265.1830; found, 265.1826.

1-Benzyl-6-formyl-2,2,4-trimethyl-1,2,3,4-tetrahydro-quinoline (**3b**)

To a solution of compound **3a** (927mg, 3.5mmol) and anhydrous DMF (0.4mL, 5.2mmol) in anhydrous 1,2-dichloroethane (10 mL) was added $POCl_3$ (0.5mL, 5.3mmol), and the mixture was refluxed for 4 h. After cooling, the mixture was

poured into ice water (50 mL) and stirred for 2 h. After neutralization using aqueous solution of sodium hydroxy (1M), the aquesous phase was extracted with CH_2Cl_2 (3×30mL). The organic fraction were gathered, dried over $MgSO_4$, and evaporated in *vacuo*. After chromatography on silica gel (CH_2Cl_2), green solid **3b** (964 mg, 94 %) were obtained. Mp. 86-87 ºC. ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 1.31 (s, 3H), 1.32 (s, 3H), 1.44 (d, J = 6.2 Hz, 3H), 1.76 (dd, J_1 = 12.9 Hz, J_2 = 13.0 Hz, 1H), 1.92 (dd, J_1 = 4.1 Hz, J_2 = 13.0 Hz, 1H), 4.43 (d, J = 17.9 Hz, 1H), 4.77 (d, J = 17.9 Hz, 1H), 6.35 (d, J = 8.4 Hz, 1H), 7.21-7.25 (m, 3H), 7.31 (d, J = 6.9 Hz, 2H), 7.40 (d, J = 8.2 Hz, 1H), 7.71 (s, 1H), 9.67 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{20}H_{23}NO$, 293.1780; found, 293.1782.



Scheme S2 Synthesis Route of **C1-1** and **C3-1** dyes. a) diethyl 2-thienylmethylphosphonate, *t*-BuOK, THF, 0 ºC, 2h; b) i. *n*-BuLi, THF, -15 ºC, 20 min; ii. DMF, -15 ºC, 2h; iii. water; c) cyano-acetic acid, CH_3CN, piperidine, reflux for 2h.

1,2,2,4-Tetramethyl-6-(2-thiphen-2-yl-vinyl)-1,2,3,4-tetrahydro-quinoline (**1i**)

To a solution of *t*-BuOK (353 mg, 3.15 mmol) in 10 mL fresh distilled THF, diethyl 2-thienylmethylphosphonate (725 mg, 3.1 mmol) was added dropwise at 0 ºC under protection of N_2. The mixture was vigorously stirred in an ice bath. Then **1d** (545 mg, 2.5 mmol) in 10 mL anhydrated THF was added dropwise in about 30 min and stirring was continued for 2 h. After removing the solvent, the residue was loaded on column chromatography (silica gel, CH_2Cl_2 as eluent). The desired product was obtained as a

yellow solid (706 mg, 95 %). Mp. 87-89 ^{o}C. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.21 (s, 3H), 1.30 (s, 3H), 1.36 (d, J = 6.7 Hz, 3H), 1.46 (dd, J_1 = 12.7 Hz, J_2 = 13.0 Hz, 1H), 1.85 (dd, J_1 = 4.5 Hz, J_2 = 12.9 Hz, 1H), 2.84 (s, 3H), 2.80-2.87 (m, 1H), 6.56 (d, J = 8.5 Hz, 1H), 6.88 (d, J =16.0 Hz, 1H), 6.99 (dd, J_1 = 3.5 Hz, J_2 = 5.1 Hz, 1H), 7.04 (d, J = 3.5 Hz, 1H), 7.15 (d, J =16.1 Hz, 1H), 7.23-7.24 (m, 2H), 7.31 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{19}H_{23}NS$, 297.1551; found, 297.1546.

5-[2-(1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-thiophene-2-carb aldehyde (**1j**)

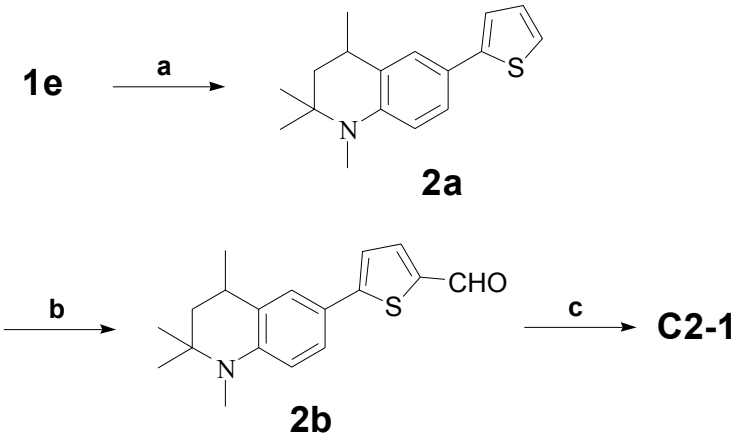
A solution of *n*-BuLi in hexane (2.57 M, 0.43 mL, 1.1 mmol) was added dropwise to a solution of **1i** (297 mg, 1 mmol) in anhydrated THF (20 mL) at -15 ºC under N_2 protection. Then the mixture was stirred for another 20 min at -15 ºC. Anhydrous DMF (0.09mL, 1.2 mmol) was added to the above reaction mixture. After stirring at -15 ºC for 2 h, the reaction mixture was poured into 50 mL of ice water. After extracted three times by CH_2Cl_2, the extraction was dried on magnesium sulfate and removed of solvent. The residue was subjected to column chromatography (silica gel, CH_2Cl_2 as the eluent), 182 mg (56 %) of red-brown solid was obtained. Mp. 138-139 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.24 (s, 3H), 1.32 (s, 3H), 1.37 (d, J = 6.6 Hz, 3H), 1.47 (dd, J_1 = 12.7 Hz, J_2 = 12.9 Hz, 1H), 1.87 (dd, J_1 = 4.4 Hz, J_2 = 13.0 Hz, 1H), 2.88 (s, 3H), 2.79-2.85 (m, 1H), 6.59 (d, J = 8.6 Hz, 1H), 7.20-7.22 (m, 3H), 7.33 (dd, J_1 = 1.7 Hz, J_2 = 8.5 Hz, 1H), 7.39 (s, 1H), 7.82 (d, J = 3.9 Hz, 1H), 9.85 (s, 1H); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{20}H_{23}NOS$, 325.1500; found, 325.1500.

1-Benzyl-2,2,4-trimethyl-6-(2-thiophen-2-yl-vinyl)-1,2,3,4-tetrahydro-quinoline (**3c**)

3c was prepared by the similar procedure of synthesizing **1i**. Yellow solid (yield 70 %). Mp. 119-120 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.31 (s, 3H), 1.32 (s, 3H), 1.42 (d, J = 6.6 Hz, 3H), 1.71 (dd, J_1 = 12.7 Hz, J_2 = 13.0 Hz, 1H), 1.95 (dd, J_1 = 4.7 Hz, J_2 = 12.9 Hz, 1H), 3.04-3.06 (m, 4H), 4.32 (d, J = 18.2 Hz, 1H), 4.82 (d, J = 18.3 Hz, 1H), 6.27 (d, J = 8.7 Hz, 1H), 6.84 (d, J = 16.1 Hz, 1H), 6.99 (dd, J_1 = 3.5 Hz, J_2 = 5.1 Hz, 1H), 7.02 (d, J = 2.7 Hz, 1H), 7.07 (dd, J_1 = 1.7 Hz, J_2 = 9.0 Hz, 1H), 7.13 (d, J = 16.3 Hz, 1H), 7.20-7.25 (m, 2H), 7.31-7.32 (m, 4H), 7.37 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{25}H_{27}NS$, 373.1864; found, 373.1854.

5-[2-(1-Benzyl-2,2,4-trimethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-thiophene-2-carbaldehyde (**3d**)

3d was prepared by the similar procedure of synthesizing **1j**. Orange solid (yield 65 %). Mp. 121-122 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.32 (s, 3H), 1.33 (s, 3H), 1.43 (d, J = 6.5 Hz, 3H), 1.72 (dd, J_1 = 12.8 Hz, J_2 = 13.0 Hz, 1H), 1.96 (dd, J_1 = 4.7 Hz, J_2 = 13.3 Hz, 1H), 3.04-3.07 (m, 4H), 4.37 (d, J = 18.4 Hz, 1H), 4.85 (d, J = 18.4 Hz, 1H), 6.31 (d, J = 8.9 Hz, 1H), 7.16-7.23 (m, 5H), 7.30-7.32 (m, 4H), 7.46 (s, 1H), 7.83 (d, J = 4.0 Hz, 1H), 9.85 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{26}H_{27}NOS$, 401.1813; found, 401.1821.



Scheme S3 Synthesis route of **C2-1** dye. a) 2-thienylboronic acid, K_2CO_3, $Pd(PPh_3)_4$, DME, reflux for 8h. 85%; b) i. *n*-BuLi, THF, -15 ºC, 20 min; ii. DMF, -15 ºC, 2h; iii. water; c) cyano-acetic acid, CH_3CN, piperidine, reflux for 2h.

1,2,2,4-Tetramethyl-6-thiophen-2-yl-1,2,3,4-tetrahydro-quinoline (**2a**)

$Pd(PPh_3)_4$ (100 mg, 0.09 mmol) was degassed in *vacuo* for 30 min and then 1,2-dimethoxy-ethane (DME, 20mL) was added. **1e** (290 mg, 1.08 mmol), aqueous K_2CO_3 (1mL, 2M, 2 mmol) and 2-thienylboronic acid (210 mg, 1.64 mmol) were added to the $Pd(PPh_3)_4$ solution and this mixture was degassed with a steady stream of argon for 20 min at room temperature. The reaction mixture was then heated to reflux for 8 h under argon. After cooled to room temperature, the reaction mixture was extracted by CH_2Cl_2 (3×30mL). The organic layer was collected and evaporated in *vacuo*, the residue was subjected to a column chromatography (silica gel,

CH_2Cl_2:hexane = 1:5 as eluent) to give the target compound **2a** as yellow oil (250 mg, 85%). ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.22 (s, 3H), 1.30 (s, 3H), 1.37 (d, J = 6.6 Hz, 3H), 1.47 (dd, J_1 = 12.8 Hz, J_2 = 12.9 Hz, 1H), 1.86 (dd, J_1 = 4.3 Hz, J_2 = 12.9 Hz, 1H), 2.84-2.86 (m, 4H), 6.59 (d, J = 8.5 Hz, 1H), 7.03 (dd, J_1 = 3.9 Hz, J_2 = 4.5 Hz, 1H), 7.21 (d, J = 3.0 Hz, 1H), 7.24 (d, J = 5.0 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.37 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{17}H_{21}NS$, 271.1395; found, 271.1391.

5-(1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-thiophene-2-carbaldehyde (**2b**). **2b** was prepared by the similar procedure of synthesizing **1f**. Green solid (yield 72%). Mp. 90-92 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.25 (s, 3H), 1.34 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H), 1.49 (dd, J_1 = 12.7 Hz, J_2 = 13.6 Hz, 1H), 1.89 (dd, J_1 = 4.7 Hz, J_2 = 13.0 Hz, 1H), 2.87-2.90 (m, 4H), 6.64 (d, J = 8.6 Hz, 1H), 7.44 (d, J = 3.7 Hz, 1H), 7.48-7.50 (m, 2H), 7.88 (d, J = 4.0 Hz, 1H), 9.85 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{21}NOS$, 299.1344; found, 299.1341.

Bis-formylation reaction for the synthesis of intermediates **5b-8b**

The general procedure for the synthesis of intermediates **5b-8b** was described. For example, the synthesis of compound **7b** was as follows. The compound **7a** (760 mg, 3.88 mmol) was dried in *vacuo* for 30 min, and then anhydrous THF (30mL) was added. A solution of *n*-BuLi in hexane (2.57 M, 3.2 mL, 8.2 mmol) was added dropwise at 0 ºC. After the addition of *n*-BuLi, the solution was stirred at r. t. for 1 h and then cooled to -78 ºC. After cooling, anhydrous DMF (1.5mL, 19.4 mmol) was added dropwise to this solution at -78 ºC. The mixture was stirred at -78 ºC for another 1 h and then warmed to r. t. slowly. After stirring at r. t. for 2 h, the mixture was poured into ice water (200mL). A lot of yellow solid was precipitated. The precipitate was filtered and dried in *vacuo* to give the target compound **7b** with enough purity for the next reaction. For other examples, a further purification procedure by chromatography on silica gel (CH_2Cl_2 as eluent) was needed.

5,5'-Diformyl-2,2'-bithiophene(**5b**)

Yellow solid (yield 50%). Mp. 212-213 ºC (lit. 185-195 ºC).[5] ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 7.71 (d, J = 3.9 Hz, 2H), 8.01 (d, J = 3.9 Hz, 2H), 9.99 (s, 2H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{10}H_6O_2S_2$, 221.9809; found, 221.9803.

5,5''-Diformyl-2,2';5',2''-terthiophene (**6b**)

Red brown solid (yield 76%). Mp. 202-207 ºC (lit. 203-205 ºC).[6] ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.30 (d, *J* = 4.0 Hz, 2H), 7.32 (s, 2H), 7.70 (d, *J* = 4.0 Hz, 2H), 9.89 (s, 2H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{14}H_8O_2S_3$, 303.9686; found, 303.9688.

2,6-Diformyl-dithieno[3,2-b;2',3'-d]thiophene (**7b**)

Yellow solid (yield 94%). Mp. >260 ºC (lit. 270 ºC, decomposition).[7] ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 8.48 (s, 2H), 10.11 (s, 2H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{10}H_4O_2S_3$, 251.9373; found, 251.9373.

E-1,2-Bis(2-formyl-5-thienyl)ethene (**8b**)

Brown solid (yield 48%). Mp. 197-205 ºC (lit. 203-205 ºC).[8] ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 7.49 (d, *J* = 3.9 Hz, 2H), 7.54 (s, 2H), 7.93 (d, *J* = 3.9 Hz, 2H), 9.95 (s, 2H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_8O_2S_2$, 247.9966; found, 247.9963.

Mono-Witting reaction for the synthesis of intermediates **5c-8c**

A typical preparation of the intermediates **5c-8c** was as follows for the particular case of the terthiophene spacer **6c**. The precursor dicarbaldehyde **6b** (304 mg, 1 mmol), anhydrous K_2CO_3 (276 mg, 2 mmol) and 18-crown-6-ether (15mg) were dried in vacuo for 30 min, and then added 40 mL of dry DMF. Ylide **1h** (544mg, 1 mmol) was dissolved in dry DMF (10mL) and added dropwise to the above solution slowly. After the addition the mixture was stirred at r. t. for another 2 h. The mixture was poured into ice water (200mL) and leading to precipitate red solid. The precipitate was filtered and purified by chromatography on silica gel with CH_2Cl_2-hexane (1:1) as eluent. The final compound **6c** was obtained as orange crystals.

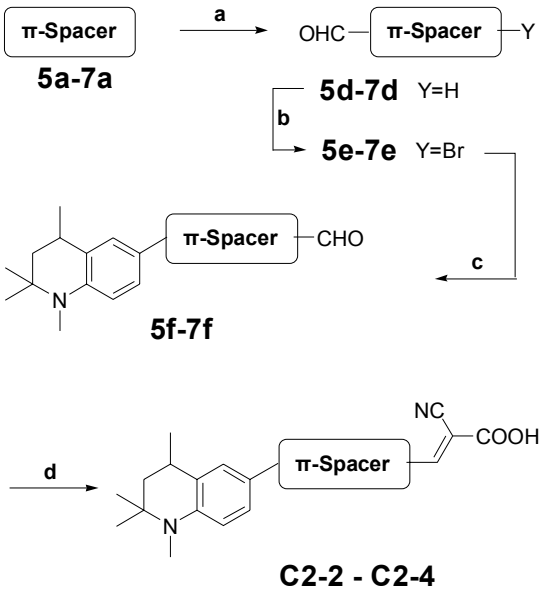
E-1-[1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl]-2-[5-formyl-2,2'-bithiophene-5'-yl]ethane(**5c**). Red brown solid (yield 56%). Mp. 148-150 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.23 (s, 3H), 1.31 (s, 3H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.47 (dd, J_1 = 12.7 Hz, J_2 = 13.0 Hz, 1H), 1.87 (dd, J_1 = 4.4 Hz, J_2 = 13.0 Hz, 1H), 2.85-2.86 (m, 4H), 6.59 (d, *J* = 8.6 Hz, 1H), 6.95 (d, *J* = 16.0 Hz, 1H), 7.08 (d, *J* = 3.7 Hz, 1H), 7.17 (d, *J* = 16.0 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.35 (s, 1H), 7.42-7.45 (m, 2H), 7.92 (d, *J* = 3.8 Hz, 1H), 9.91 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for

$C_{24}H_{25}NOS_2$, 407.1378; found, 407.1372.

E-1-[1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl]-2-[5-formyl-2,2';5',2''-terthiophene-5''-yl]ethane(**6c**). Red brown solid (yield 42%). Mp. 138-140 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.23 (s, 3H), 1.31 (s, 3H), 1.38 (d, J = 6.7 Hz, 3H), 1.47 (dd, J_1 = 12.7 Hz, J_2 = 13.8 Hz, 1H), 1.87 (dd, J_1 = 4.0 Hz, J_2 = 13.8 Hz, 1H), 2.85-2.86 (m, 4H), 6.58 (d, J = 8.9 Hz, 1H), 6.93 (d, J = 16.2 Hz, 1H), 7.03 (d, J = 3.9 Hz, 1H), 7.15 (d, J = 16.3 Hz, 1H), 7.28-7.30 (m, 3H), 7.34 (s, 1H), 7.49 (d, J = 4.1 Hz, 1H), 7.51 (d, J = 4.1 Hz, 1H), 7.95 (d, J = 3.9 Hz, 1H), 9.93 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{28}H_{27}NOS_3$, 489.1255; found, 489.1255.

E-1-[1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl]-2-[6-formyl-dithieno[3,2-b;2',3'-d]thiophene-2-yl]ethane(**7c**). Orange red solid (yield 60%). Mp. 185-190 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.24 (s, 3H), 1.32 (s, 3H), 1.38 (d, J = 6.6 Hz, 3H), 1.48 (dd, J_1 = 12.9 Hz, J_2 = 13.3 Hz, 1H), 1.87 (dd, J_1 = 4.4 Hz, J_2 = 12.9 Hz, 1H), 2.86-2.87 (m, 4H), 6.60 (d, J = 8.9 Hz, 1H), 7.06 (d, J = 16.1 Hz, 1H), 7.25-7.33 (m, 2H), 7.35 (s, 1H), 7.47 (s, 1H), 8.35 (s, 1H), 10.01 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{24}H_{23}NOS_3$, 437.0942; found, 437.0948.

E-1-[2-*E*-(1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-5-thienyl]-2-[2-formyl-5-thienyl]ethane (**8c**).Red brown solid (yield 54%). Mp. 115-118 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.23 (s, 3H), 1.31 (s, 3H), 1.37 (d, J = 6.6 Hz, 3H), 1.47 (dd, J_1 = 12.8 Hz, J_2 = 13.2 Hz, 1H), 1.86 (dd, J_1 = 4.5 Hz, J_2 = 13.0 Hz, 1H), 2.84-2.86 (m, 4H), 6.58 (d, J = 8.7 Hz, 1H), 6.93 (d, J = 16.0 Hz, 1H), 7.00 (d, J = 3.7 Hz, 1H), 7.11 (d, J = 15.7 Hz, 1H), 7.18 (d, J = 3.8 Hz, 1H), 7.26 (dd, J_1 = 2.0 Hz, J_2 = 8.6 Hz, 1H), 7.33-7.34 (m, 2H), 7.42 (d, J = 15.9 Hz, 1H), 7.87 (d, J = 3.9 Hz, 1H), 9.89 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{26}H_{27}NOS_2$, 433.1534; found, 433.1539.



Scheme S3 Synthesis route of **C2-2** - **C2-4** dyes. a) $POCl_3$/DMF, CH_2ClCH_2Cl, reflux, 4h; b) NBS, DMF, r. t. overnight; c) **1f**, $Pd(PPh_3)_4$, K_2CO_3, DME, reflux, overnight; d) cyano-acetic acid, CH3CN, reflux, 2h.

Mono-formylation reaction for the synthesis of intermidates **5d-7d**

As a representative example, a typical preparation of the intermediates **5d** was as follows. To a solution of compound **5a** (417 mg, 2.5 mmol) and anhydrous DMF (0.25 mL, 3.2 mmol) in anhydrous 1,2-dichloroethane (5mL) was added $POCl_3$ (0.24mL, 2.6mmol), and the mixture was refluxed for 4 h. After cooling, the mixture was poured into ice water (50mL) and stirred for 2 h. After separation of the organic phase by decantation, the aqueous phase was extracted with CH_2Cl_2 (3× 30mL). The organic fractions were gathered, dried over $MgSO_4$, and evaporated in *vacuo*. After chromatography on silica gel (CH_2Cl_2 as elute), yellow solid was obtained.

5-Formyl-2,2'-bithiophene (**5d**)

Yellow green solid (yield 68%). Mp. 55-56 ºC (lit. 57-58 ºC).[9] ^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.08 (dd, J_1 = 4.3 Hz, J_2 = 4.4 Hz, 1H), 7.26 (d, J = 3.8 Hz, 1H), 7.36-7.37 (m, 2H), 7.68 (d, J = 3.9 Hz, 1H), 9.87 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_9H_6OS_2$, 193.9860; found, 193.9854.

5-Formyl-2,2';5',2''-terthiophene (**6d**)

Orange solid (yield 65%). Mp. 132-133 ºC (lit. 140-141 ºC).[10] ^{1}H-NMR (Acetone-d_6, 400MHz, ppm): δ 7.13 (dd, J_1 = 3.9 Hz, J_2 = 4.9 Hz, 1H), 7.32 (d, J =

3.9 Hz, 1H), 7.40 (d, *J* = 3.4 Hz, 1H), 7.51 (m, 3H), 7.95 (d, *J* = 3.9 Hz, 1H), 9.94 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{19}H_8OS_3$, 295.9737; found, 295.9725.

2-Formyl-dithieno[3,2-b;2',3'-d]thiophene (**7d**)

White solid (yield 78%). Mp. 159-160 ºC (lit. 161-162 ºC).[11] ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 7.59 (d, *J* = 5.3 Hz, 1H), 7.87 (d, *J* = 5.3 Hz, 1H), 8.39 (s, 1H), 10.04 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_9H_4OS_3$, 223.9424; found, 223.9416.

NBS bromization reaction for the synthesis of intermidates **5e-7e**

A typical procedure of synthesis of compound **6e** was as follows. **6d** (210 mg, 0.76 mmol) and NBS (149mg, 0.84mmol) were dissolved in DMF (20mL) and stirred at r. t. for 24 h. The mixture was poured into water (100mL) and leading to precipitate red solid. The precipitate was filtered and purified by chromatography on silica gel (CH_2Cl_2 as eluent) to give the compound **6e** as orange solid.

5-Bromo-5'-fromyl-2,2'-bithiophene (**5e**)

Yellow solid (yield 96%). Mp. 139-140 ºC (lit. 145 ºC).[12] ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 7.25 (d, *J* = 3.8 Hz, 1H), 7.38 (d, *J* = 3.9 Hz, 1H), 7.47 (d, *J* = 3.9 Hz, 1H), 7.94 (d, *J* = 3.9 Hz, 1H), 9.94 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_9H_5BrOS_2$, 271.8965; found, 271.8967; 273.8947.

5-Bromo-5''-formyl-2,2';5',2''-terthiophene (**6e**)

Orange solid (yield 96%). Mp. 150-152 ºC (lit. 158 ºC).[13] ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 7.20 (d, *J* = 3.9 Hz, 1H), 7.22 (d, *J* = 3.9 Hz, 1H), 7.32 (d, *J* = 3.9 Hz, 1H), 7.51-7.52 (m, 2H), 7.95 (d, *J* = 4.0 Hz, 1H), 9.94 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_7BrOS_3$, 353.8842; found, 353.8838; 355.8810.

2-Bromo-6-formyl- dithieno[3,2-b;2',3'-d]thiophene (**7e**)

Yellow solid (yield 99%). Mp. 191 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 7.74 (s, 1H), 8.40 (s, 1H), 10.04 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_9H_3BrOS_3$, 301.8529; found, 301.8524; 303.8500.

Suzuki coupling reaction for the synthesis of intermediates **5f-7f**

A typical preparation of the intermediates **5f-7f** was as follows for the particular case of the compound **6f**. $Pd(PPh_3)_4$ (80mg, 0.07mmol) was degassed in *vacuo* for 30

min and then 1,2-dimethoxy-ethane (DME, 25mL) was added. The bromated intermediate **6e** (178mg, 0.5 mmol), aqueous K_2CO_3 (1mL, 2M, 2 mmol) and **1f** (140mg, 0.6mmol) were added to the $Pd(PPh_3)_4$ solution and this mixture was degassed with a steady stream of argon for 20 min at room temperature. The reaction mixture was then heated to reflux overnight (~15 h) under argon. After cooled to room temperature, the reaction mixture was extracted by CH_2Cl_2 (3×30mL). The organic layer was collected and evaporated in *vacuo*, the residue was subjected to a column chromatography (silica gel, CH_2Cl_2:hexane = 1:1 as eluent) to give the target compound **6f** as red-orange solid.

5'-(1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-[2,2']bithiophenyl-5-carbaldehyde (**5f**)

Red orange solid (yield 63%). Mp. 117-119 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.24 (s, 3H), 1.33 (s, 3H), 1.40 (d, J = 6.7 Hz, 3H), 1.49 (dd, J_1 = 12.6 Hz, J_2 = 12.8 Hz, 1H), 1.89 (dd, J_1 = 4.5 Hz, J_2 = 13.1 Hz, 1H), 2.88-2.89 (m, 4H), 6.63 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 3.9 Hz, 1H), 7.39-7.44 (m, 3H), 7.48 (d, J = 3.9 Hz, 1H), 7.92 (d, J = 4.0 Hz, 1H), 9.91 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{22}H_{23}NOS_2$, 381.1221; found, 381.1228.

5''-(1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-[2,2';5',2'']terthiophene-5-carbaldehyde (**6f**)

Red-orange solid (yield 80 %). Mp.: 140-145 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.24 (s, 3H), 1.32 (s, 3H), 1.39 (d, J = 6.7 Hz, 3H), 1.49 (dd, J_1 = 12.1 Hz, J_2 = 13.4 Hz, 1H), 1.89 (dd, J_1 = 4.3 Hz, J_2 = 12.3 Hz, 1H), 2.86-2.87 (m, 4H), 6.63 (d, J = 8.6 Hz, 1H), 7.24 (d, J = 3.8 Hz, 1H), 7.29 (d, J = 3.9 Hz, 1H), 7.32 (d, J = 3.7 Hz, 1H), 7.38 (d, J = 8.6 Hz, 1H), 7.41 (s, 1H), 7.48 (d, J = 4.0 Hz, 1H), 7.51 (d, J = 3.9 Hz, 1H), 7.94 (d, J = 4.0 Hz, 1H),9.93 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{26}H_{25}NOS_3$, 463.1098; found, 463.1090.

6-(1,2,2,4-Tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-dithieno[3,2-b;2',3'-d]thiophene-2-carbaldehyde (**7f**)

Red-orange solid (yield 44 %). Mp.: 183-184 ºC. ^{1}H NMR (Acetone-d_6, 400MHz, ppm): δ 1.26 (s, 3H), 1.34 (s, 3H), 1.42 (d, J = 6.6 Hz, 3H), 1.51 (dd, J_1 = 12.7 Hz, J_2

= 13.2 Hz, 1H), 1.91 (dd, J_1 = 5.0 Hz, J_2 = 12.4 Hz, 1H), 2.90 (s, 3H), 2.92 (m, 1H), 6.66 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.49 (s, 1H), 7.69 (s, 1H), 8.35 (s, 1H), 10.01 (s, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{22}H_{21}NOS_3$, 411.0785; found, 411.0781.

Knoevenagel condensation reaction for the synthesis of **C1** series, **C2** series and **C3-1** sensitizers

The **C1** series, **C2** series and **C3-1** sensitizers were synthesized under Knoevenagel condensation conditions. Cyanoacetic acid and corresponding aldehyde intermediates were refluxed in acetonitrile under the presence of piperidine as catalyst. After chromatography purfication procedure (silica gel, CH_2Cl_2:MeOH=10:1 as eluent), the target compounds were obtained as dark or red-brown solids.

2-Cyano-3-{5-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-thiophen-2-yl}-acrylic acid (**C1-1**). Black solid (yield 80%). Mp. 208-210 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.17 (s, 3H), 1.27 (s, 3H), 1.33 (d, J = 6.6 Hz, 3H), 1.41 (dd, J_1 = 12.6 Hz, J_2 = 12.9 Hz, 1H), 1.83 (dd, J_1 = 4.2 Hz, J_2 = 13.0 Hz, 1H), 2.77-2.80 (m, 4H), 6.54 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 16.1 Hz, 1H), 7.18 (d, J = 3.9 Hz, 1H), 7.21 (d, J = 16.0 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.34 (s, 1H), 7.59 (d, J = 3.9 Hz, 1H), 8.06 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{22}H_{24}N_2S$, 348.1660; found, 348.1656.

2-Cyano-3-{5'-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-[2,2']bithiophenyl-5-yl}-acrylic acid (**C1-2**). Black solid (yield 65%). Mp. 202-206 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.16 (s, 3H), 1.26 (s, 3H), 1.33 (d, J = 6.4 Hz, 3H), 1.40 (dd, J_1 = 12.7 Hz, J_2 = 13.5 Hz, 1H), 1.83 (dd, J_1 = 4.0 Hz, J_2 = 13.3 Hz, 1H), 2.78 (m, 4H), 6.53 (d, J = 8.6 Hz, 1H), 6.96 (d, J = 16.4 Hz, 1H), 7.12-7.19 (m, 2H), 7.26 (d, J = 8.5 Hz, 1H), 7.30 (s, 1H), 7.53 (m, 2H), 7.95 (d, J = 3.7 Hz, 1H), 8.46 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{26}H_{26}N_2S_2$, 430.1538; found, 430.1532.

2-Cyano-3-{5''-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-[2,2';5',2'']terthiophen-5-yl}-acrylic acid (**C1-3**). Black solid (yield 72%). Mp. 215-219 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.17 (s, 3H), 1.26 (s, 3H), 1.33 (d, J = 6.4 Hz,

3H), 1.41 (dd, J_1 = 12.6 Hz, J_2 = 13.4 Hz, 1H), 1.83 (dd, J_1 = 4.9 Hz, J_2 = 12.8 Hz, 1H), 2.79 (m, 4H), 6.53 (d, J = 8.8 Hz, 1H), 6.86 (d, J = 15.9 Hz, 1H), 7.08 (d, J = 3.8 Hz, 1H), 7.15 (d, J = 16.1 Hz, 1H), 7.25 (d, J = 9.0 Hz, 1H), 7.30 (s, 1H), 7.36 (m, 2H), 7.59 (d, J = 3.7 Hz, 1H), 7.97 (d, J = 3.8 Hz, 1H), 8.46 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{30}H_{28}N_2S_3$, 512.1415; found, 512.1414.

2-Cyano-3-{5"-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-dithieno[3,2-b;2',3'-d]thiophene-5-yl}-acrylic acid (**C1-4**). Dark brown solid (yield 77%). Mp. >260 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.18 (s, 3H), 1.27 (s, 3H), 1.35 (d, J = 6.7 Hz, 3H), 1.42 (dd, J_1 = 12.7 Hz, J_2 = 13.0 Hz, 1H), 1.84 (dd, J_1 = 4.0 Hz, J_2 = 12.7 Hz, 1H), 2.80 (m, 4H), 6.56 (d, J = 9.0 Hz, 1H), 6.96 (d, J = 16.2 Hz, 1H), 7.25-7.34 (m, 3H), 7.53 (s, 1H), 8.17 (s, 1H), 8.30 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{26}H_{24}N_2S_3$, 460.1102; found, 460.1107.

2-Cyano-3-[5-(2-{5-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-thiophen-2-yl}-vinyl)-thiophen-2-yl]-acrylic acid (**C1-5**). Black solid (yield 64%). Mp. >260 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.17 (s, 3H), 1.26 (s, 3H), 1.33 (d, J = 6.6 Hz, 3H), 1.41 (dd, J_1 = 12.8 Hz, J_2 = 13.4 Hz, 1H), 1.83 (dd, J_1 = 4.1 Hz, J_2 = 12.8 Hz, 1H), 2.79 (m, 4H), 6.53 (d, J = 9.0 Hz, 1H), 6.84 (d, J = 16.3 Hz, 1H), 7.04 (d, J = 3.5 Hz, 1H), 7.09-7.17 (m, 2H), 7.23-7.35 (m, 5H), 7.75 (s, 1H), 8.20 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{28}H_{28}N_2S_2$, 456.1694; found, 456.1693.

2-Cyano-3-[5-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-thiophen-2-yl]-acrylic acid (**C2-1**). Red brown solid (yield 83%). Mp. 185-190 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ1.19 (s, 3H), 1.29 (s, 3H), 1.34 (d, J = 6.5 Hz, 3H), 1.43 (dd, J_1 = 12.4 Hz, J_2 = 13.3 Hz, 1H), 1.86 (dd, J_1 = 4.2 Hz, J_2 = 13.0 Hz, 1H), 2.82-2.84 (m, 4H), 6.61 (d, J = 8.4 Hz, 1H), 7.42-7.45 (m, 2H), 7.49 (d, J = 3.7 Hz, 1H), 7.82 (d, J = 3.6 Hz, 1H), 8.27 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{20}H_{22}N_2S$, 322.1504; found, 322.1498.

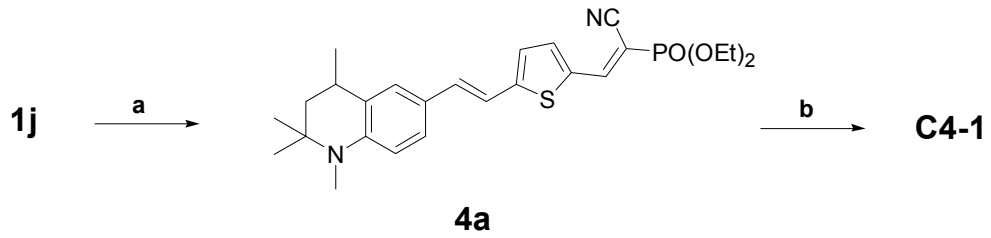
2-Cyano-3-[5'-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-[2,2']bithiophenyl-5-yl]-acrylic acid (**C2-2**). Black solid (yield 67%). Mp. 195-198 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.18 (s, 3H), 1.27 (s, 3H), 1.35 (d, J = 6.7 Hz, 3H), 1.43 (dd, J_1 = 12.5 Hz, J_2 = 13.0 Hz, 1H), 1.85 (dd, J_1 = 4.6 Hz, J_2 = 13.0 Hz, 1H),

2.80-2.82 (m, 4H), 6.58 (d, *J* = 8.6 Hz, 1H), 7.36-7.40 (m, 3H), 7.52 (d, *J* = 4.1 Hz, 1H), 7.55 (d, *J* = 3.9 Hz, 1H), 7.93 (d, *J* = 3.6 Hz, 1H), 8.42 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{24}H_{24}N_2S_2$, 404.1381; found, 404.1387.

2-Cyano-3-[5"-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-[2,2';5',2"]terthiophen-5-yl]-acrylic acid (**C2-3**). Black solid (yield 63%). Mp.: 196-200 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.18 (s, 3H), 1.27 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.43 (dd, J_1 = 13.2 Hz, J_2 = 13.4 Hz, 1H), 1.84 (dd, J_1 = 4.3 Hz, J_2 = 13.2 Hz, 1H), 2.80-2.82 (m, 4H), 6.58 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 4.1 Hz, 1H), 7.33-7.38 (m, 4H), 7.55 (m, 2H), 7.88 (d, *J* = 4.0 Hz, 1H), 8.36 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{28}H_{26}N_2S_3$, 486.1258; found, 486.1250.

2-Cyano-3-[6-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-dithieno[3,2-b;2',3'-d]thiophen-2-yl]-acrylic acid (**C2-4**). Black solid (yield 54%). Mp. 210-213 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.19 (s, 3H), 1.28 (s, 3H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.44 (dd, J_1 = 12.1 Hz, J_2 = 13.8 Hz, 1H), 1.87 (dd, J_1 = 4.6 Hz, J_2 = 13.8 Hz, 1H), 2.82-2.84 (m, 4H), 6.62 (d, *J* = 8.9 Hz, 1H), 7.41 (m, 2H), 7.82 (s, 1H), 8.36 (s, 1H), 8.55 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{24}H_{22}N_2S_3$, 434.0945; found, 434.0947.

3-{5-[2-(1-Benzyl-2,2,4-trimethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-thiophen-2-yl}-2-cyano-acrylic acid (**C3-1**). Dark brown solid (yield 82%). Mp. 202-207 ºC. ^{1}H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.33 (s, 3H), 1.34 (s, 3H), 1.73 (dd, J_1 = 13.0 Hz, J_2 = 13.1 Hz, 1H), 1.97 (dd, J_1 = 4.5 Hz, J_2 = 13.3 Hz, 1H), 3.08 (m, 4H), 4.38 (d, *J* = 18.1 Hz, 1H), 4.86 (d, *J* = 18.1 Hz, 1H), 6.31 (d, *J* = 8.7 Hz, 1H), 7.20-7.25 (m, 5H), 7.29-7.33 (m, 4H), 7.51 (s, 1H), 7.82 (d, *J* = 4.0 Hz, 1H), 8.35 (s, 1H). HRMS-EI (*m/z*): $[M\text{-}CO_2]^+$ calcd for $C_{28}H_{28}N_2S$, 424.1973; found, 424.1970.



Scheme S4 Synthesis route of **C4-1** dye. a) diethyl cyano-methylphosphonate, acetonitrile, piperidine, reflux for 2h, 78%; b) i) trimethylsilane iodide (TMSI), CH2Cl2, reflux for 1.5h; ii) CH_3OH, r.t. 1h, 93%.

(1-Cyano-2-{5-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-thioph en-2-yl}-vinyl)-phosphonic acid dithyl ester (**4a**)

To a solution of **1j** (65 mg, 0.2 mmol) and diethyl cyanomethyl-phosphonate (43 mg, 0.24 mmol) in 5 mL acetonitrile, 5 drop of piperidine was added. The reaction mixture was heated to reflux for 2 h under N_2. After removing of solvent the residue was column chromatographied (silica gel, CH_2Cl_2: EtOAc =10: 1 as eluent) to give a dark solid (75 mg, 78%). Mp. 112-113 ^oC. ^1H-NMR (Acetone-d_6, 400MHz, ppm): δ 1.24 (s, 3H), 1.33 (s, 3H), 1.34-1.39 (m, 9H), 1.47 (dd, J_1 = 12.9 Hz, J_2 = 13.0 Hz, 1H), 1.87 (dd, J_1 = 4.4 Hz, J_2 = 13.1 Hz, 1H), 2.80-2.89 (m, 4H), 4.14-4.21 (m, 4H), 6.60 (d, J = 8.5 Hz, 1H), 7.24-7.25 (m, 3H), 7.37 (d, J = 8.5 Hz, 1H), 7.44 (s, 1H), 7.79 (d, J = 4.0 Hz, 1H), 8.03 (d, J = 19.2 Hz, 1H). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{26}H_{33}N_2O_3PS$, 484.1949; found, 484.1953.

(1-Cyano-2-{5-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-vinyl]-thioph en-2-yl}-vinyl)-phosphonic acid (**C4-1**).

Trimethylsilane iodide (0.1 mL) was added dropwise to a solution of **4a** (48 mg, 0.1 mmol) in CH_2Cl_2 (10mL). After refluxing for 1.5h, the mixture was cooled to r. t. and CH_3OH (1mL) was added. The solvent was removed after stirring for 1h and the residue was loaded to a silica gel column chromatography. CH_3OH was used as eluent and gave brown solid (yield 93%). Mp.: 201-203 ºC. ^1H-NMR (DMSO-d_6, 400MHz, ppm): δ 1.16 (s, 3H), 1.26 (s, 3H), 1.32 (d, J = 5.8 Hz, 3H), 1.40 (dd, J_1 = 12.4 Hz, J_2 = 13.4 Hz, 1H), 1.82 (dd, J_1 = 4.0 Hz, J_2 = 12.8 Hz, 1H), 2.78 (m, 4H), 6.51 (d, J = 8.6 Hz, 1H), 6.93 (d, J = 16.0 Hz, 1H), 7.09 (s, 1H), 7.16 (d, J = 16.1 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 7.31 (s, 1H), 7.41 (s, 1H), 7.64 (d, J = 14.5 Hz, 1H). HRMS-EI (*m/z*): $[M\text{-}PO_3H]^+$ calcd for $C_{22}H_{24}N_2S$, 348.1660; found, 348.1665.

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(B) Photophysical properties of the tetrahydroquinoline sensitizers:

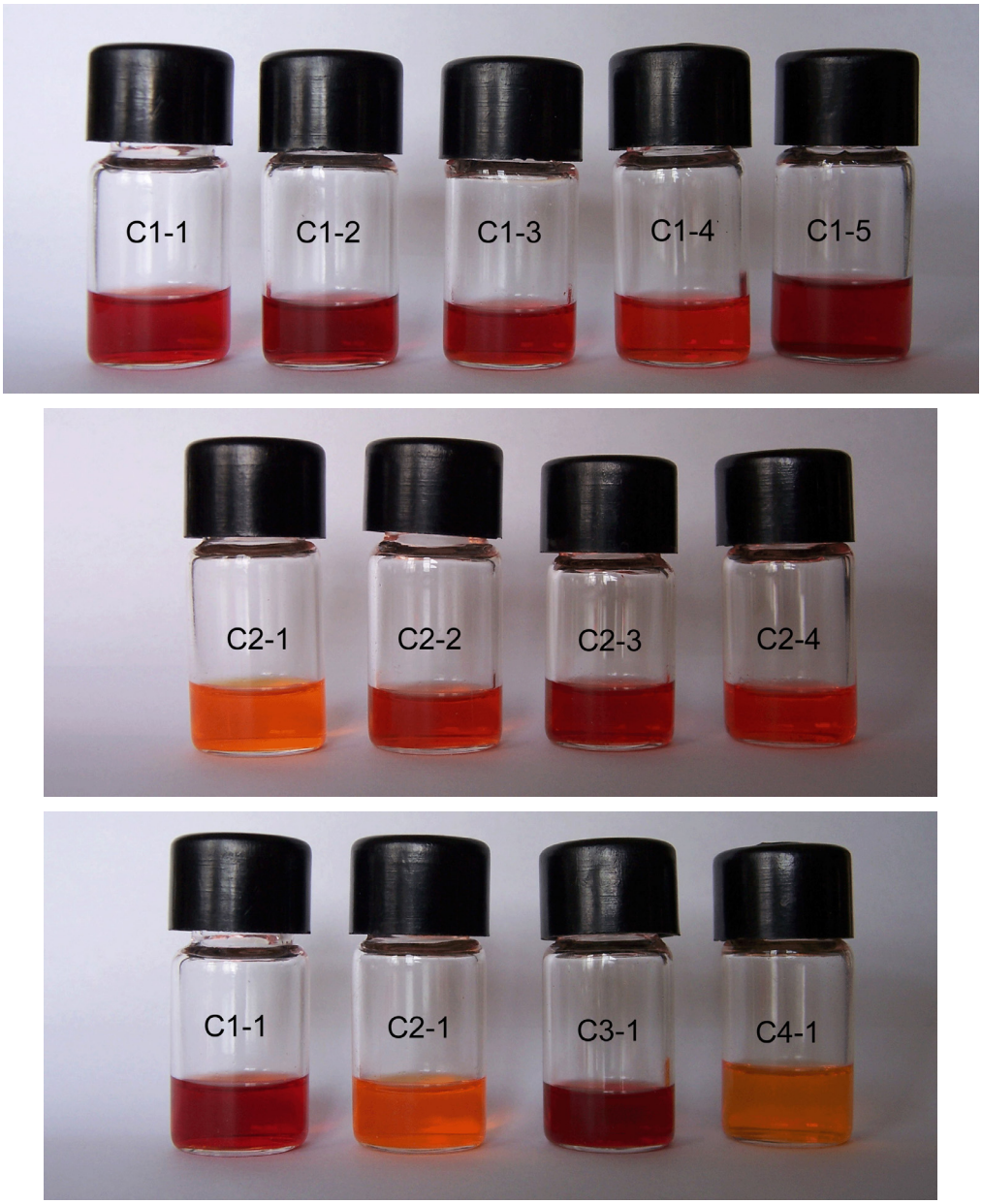


Figure S1. Image of the dye solutions.

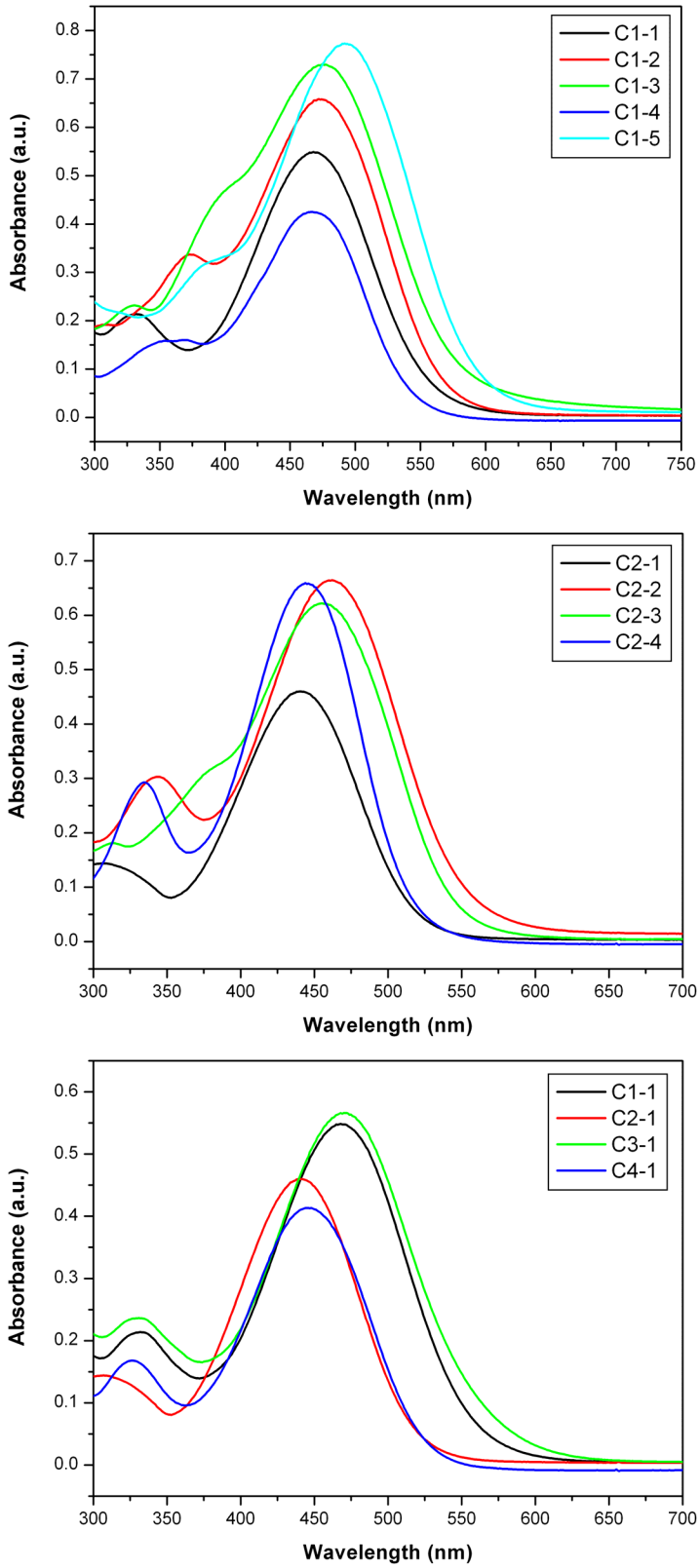


Figure S2 UV-vis spectra of the dyes in ethanol solutions (2×10^{-5} M) at 25 ºC. **C1-4**, **C2-3** and **C2-4** were measured in DMF solutions (2×10^{-5} M) at 25 ºC.

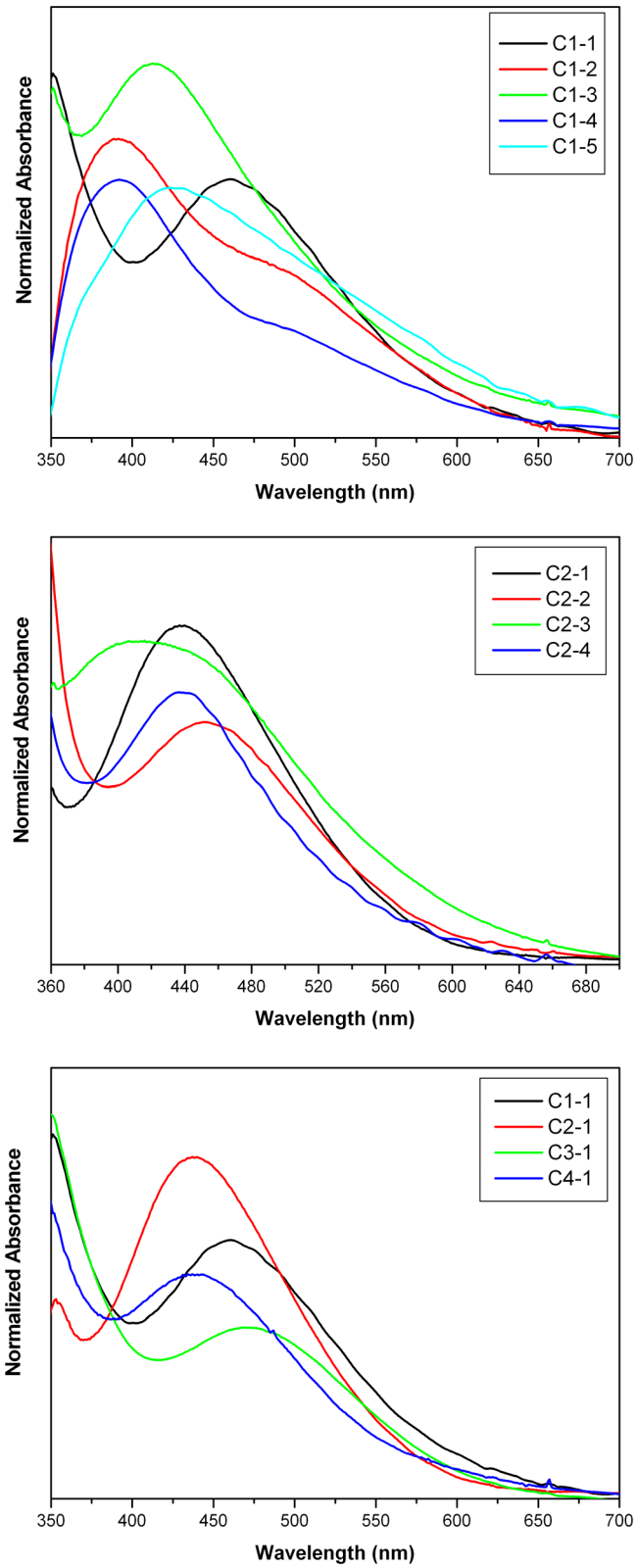


Figure S3. Absorption spectra of the dyes anchored on TiO_2 surface.

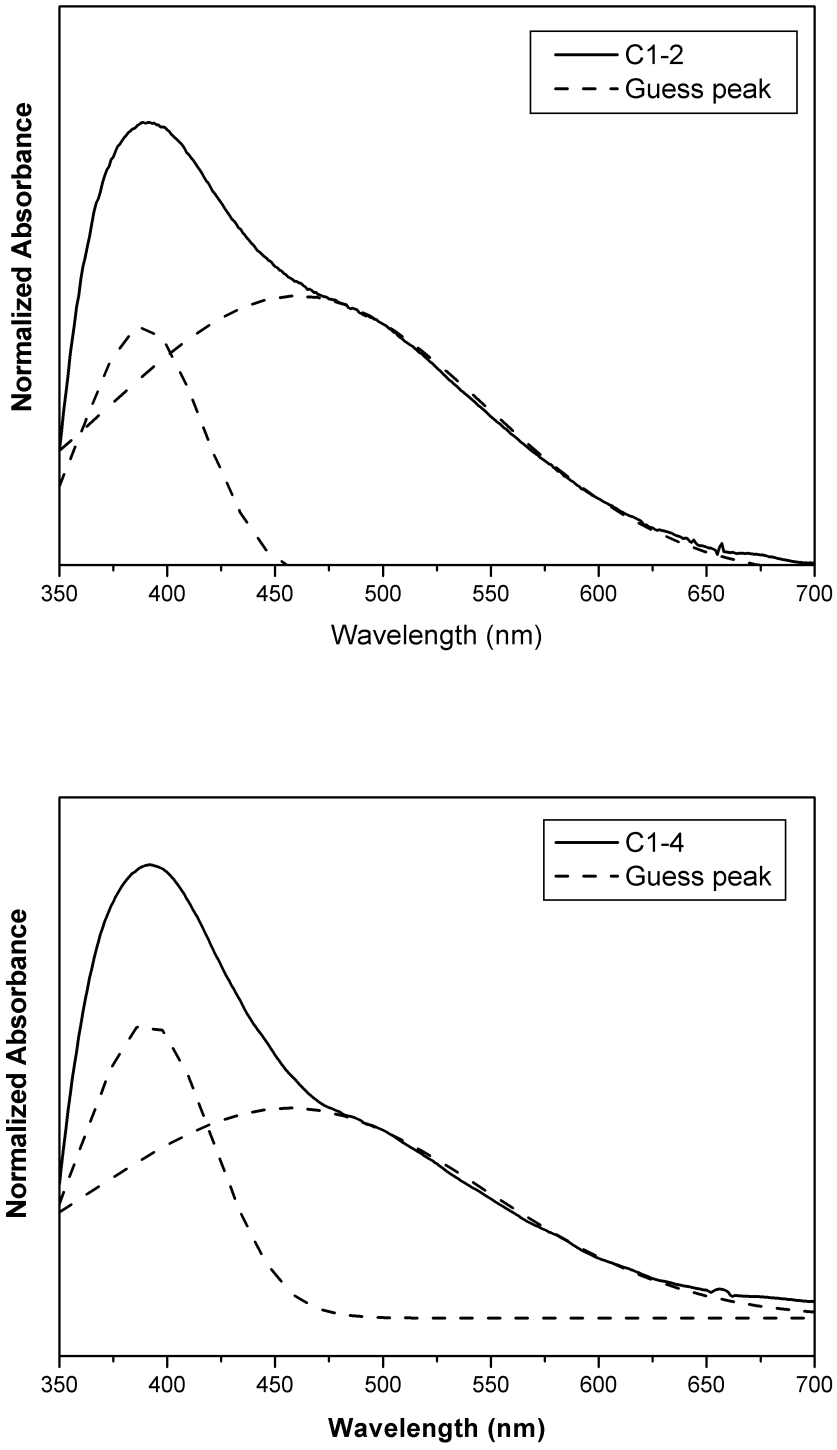


Figure S4 Absorption spectra and curve fitting of **C1-2** and **C1-4** dyes anchored on TiO_2.

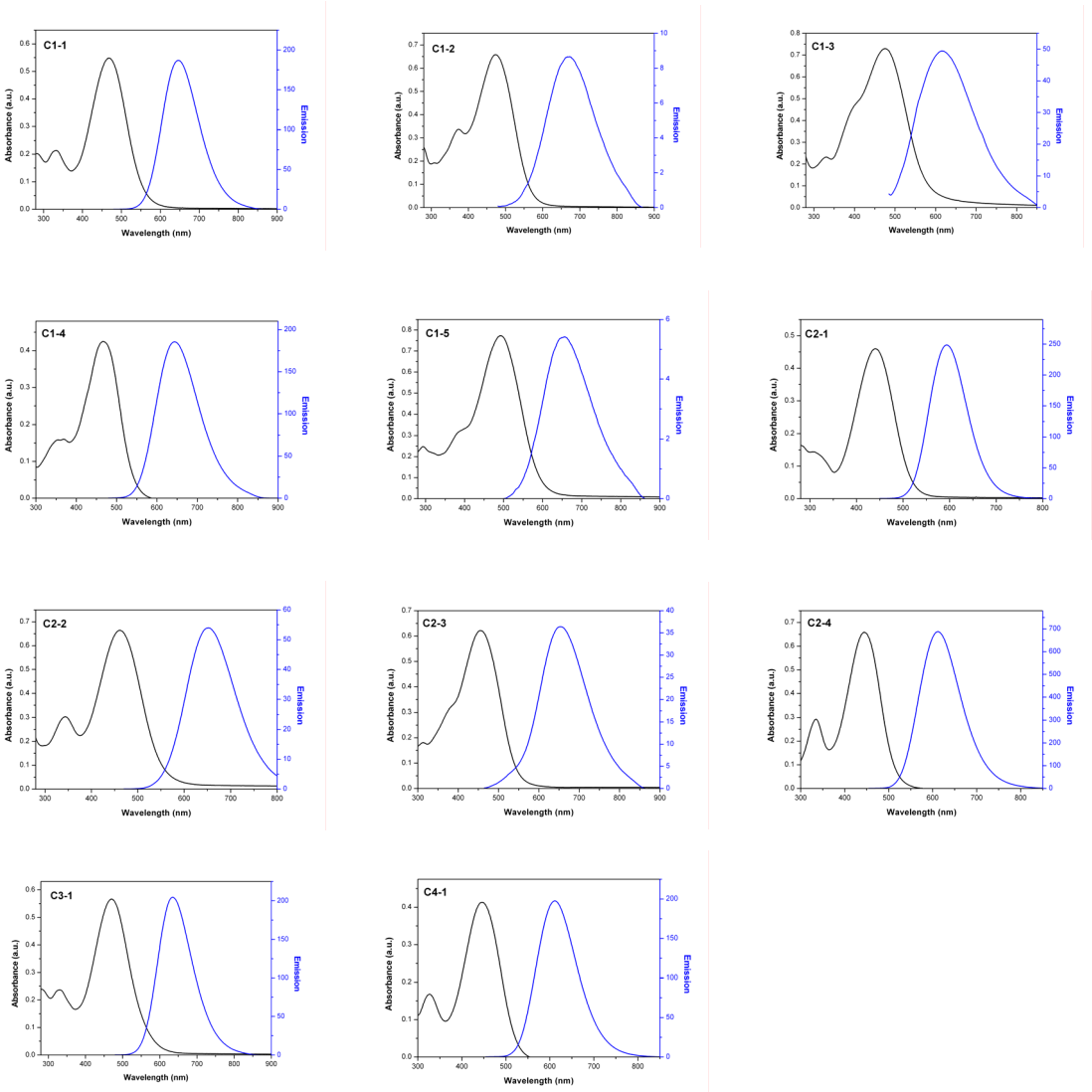


Figure S5. Absorption (black) and emission (blue) spectra of the dyes in ethanol solutions; **C1-4**, **C2-3** and **C2-4** were measured in DMF solutions.

(C) Characterization of the DSSCs:

Table S1 Photovoltaic performance of DSSCs based on the tetrahydroquinoline dyes with and without the addition of CDCA[a]

Dye	J_{sc} (mA/cm^2)	V_{oc} (mV)	Fill factor (*ff*)	η (%)
C1-1[b]	7.80	582	0.65	2.93
C1-1 CDCA[b]	8.48	583	0.64	3.17
C1-2	5.01	516	0.60	1.56
C1-2 CDCA	6.99	543	0.62	2.35
C1-3	4.68	500	0.56	1.32
C1-3 CDCA	6.39	521	0.57	1.91
C1-4[c]	6.38	495	0.56	1.78
C1-4 CDCA[c]	6.87	514	0.66	2.34
C1-5	3.39	532	0.66	1.19
C1-5 CDCA	7.22	542	0.59	2.32
C2-1[b]	11.3	600	0.66	4.47
C2-1 CDCA[b]	11.2	600	0.67	4.49
C2-2	9.82	590	0.65	3.74
C2-2 CDCA	12.0	597	0.63	4.53
C2-3[c]	10.00	537	0.64	3.44
C2-3 CDCA[c]	8.53	527	0.67	3.00
C2-4[c]	8.35	524	0.63	2.77
C2-4 CDCA[c]	8.84	522	0.63	2.92
C3-1[b]	7.50	560	0.64	2.70
C3-1 CDCA[b]	9.27	580	0.67	3.61
C4-1	4.79	554	0.67	1.79
C4-1 CDCA	8.54	568	0.67	3.27
N3[d]	14.03	695	0.63	6.16

[a] Conditions: Irradiated light: AM1.5 (100mW/cm^2); TiO_2 films thickness: 10 μm; Dye bath: ethanol solutions (1×10^{-4} M) with or without the addition of chenodexoycholic acid (CDCA, 3×10^{-3} M); Working area: 0.159cm^2; Electrolyte: 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide/ 0.1 M LiI/ 0.05 M I_2/ 0.5 M 4-*tert*-butylpyridine in 3-methoxyproponitrile. [b] Dye bath: ethanol solution (2×10^{-4} M) with or without the addition of CDCA (3×10^{-3} M); [c] Dye bath: DMF solution (1×10^{-4} M) with or without the addition of CDCA (3×10^{-3} M); [d] Dye bath: ethanol solution (3×10^{-4} M).

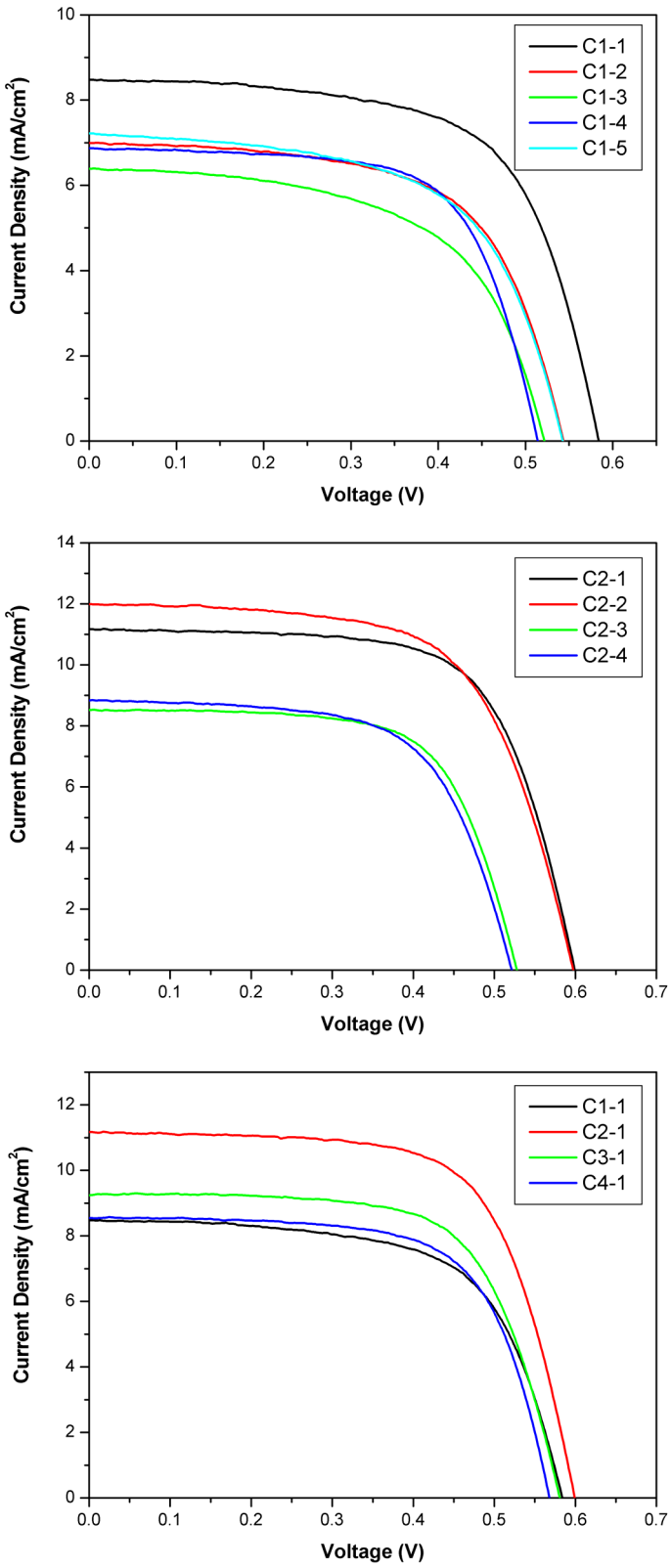


Figure S6 *J-V* curves of DSSCs based on tetrahydroquinoline dyes with the addition of CDCA into dye bath.

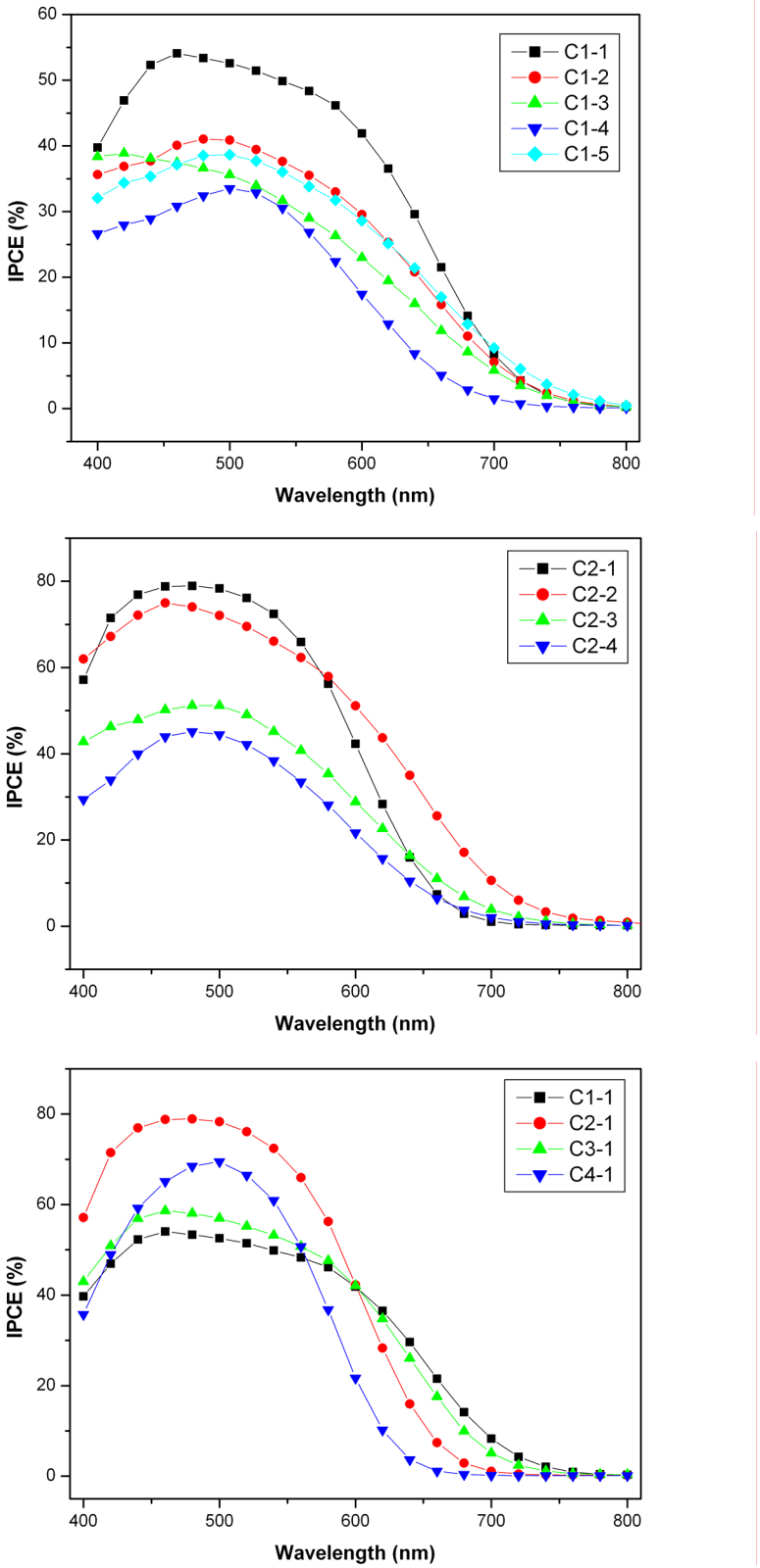
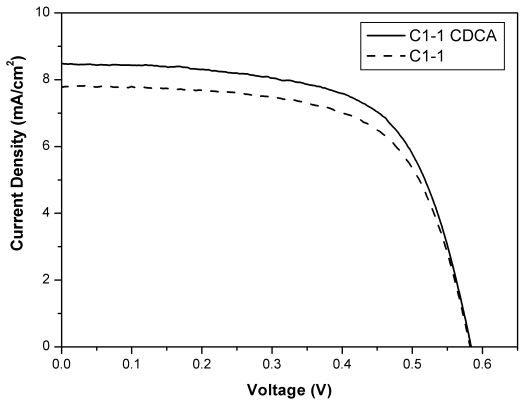
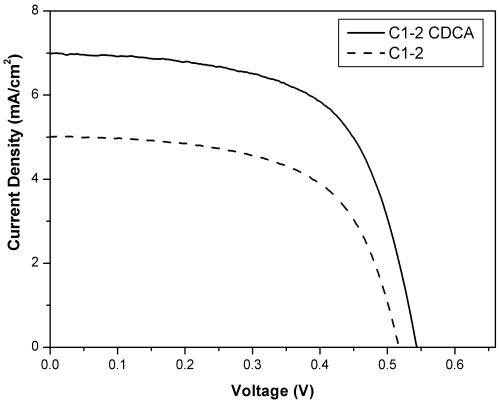
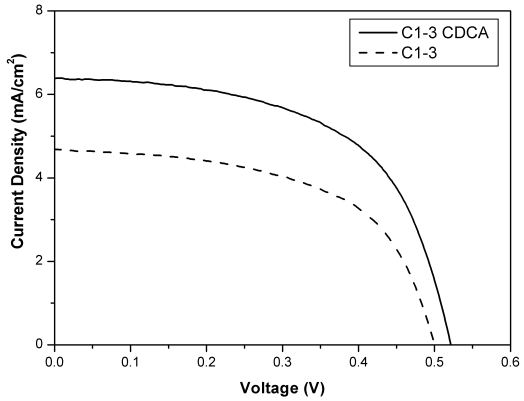
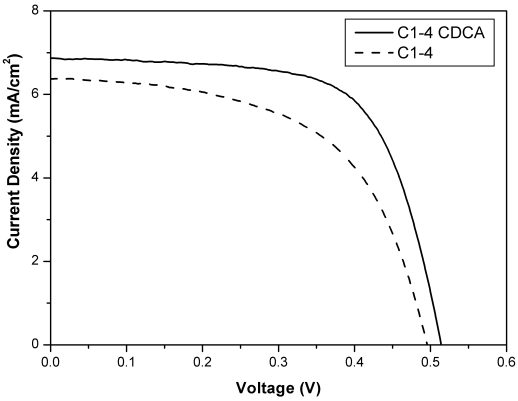


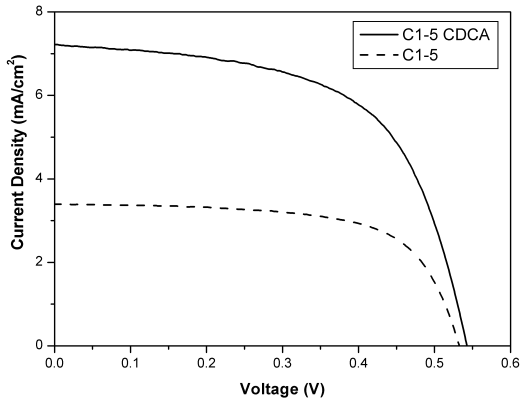
Figure S7 Incident photon-to-current conversion efficiencies of the DSSCs based on tetrahydroquinoline dyes.

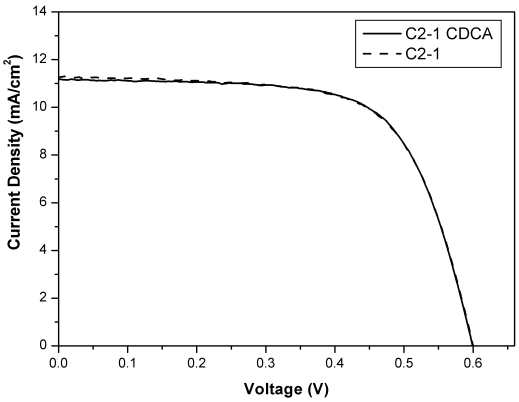

C1-1 CDCA
C1-1
Current Density (mA/cm^2)
Voltage (V)

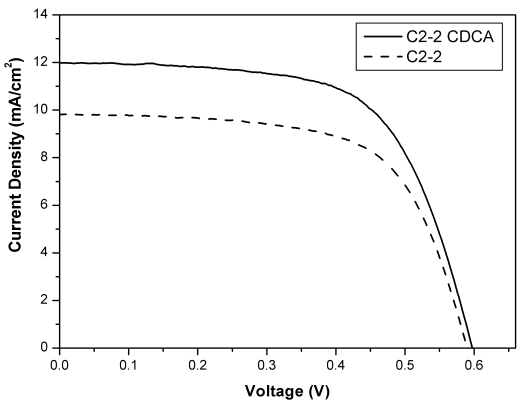

C1-2 CDCA
C1-2
Current Density (mA/cm^2)
Voltage (V)

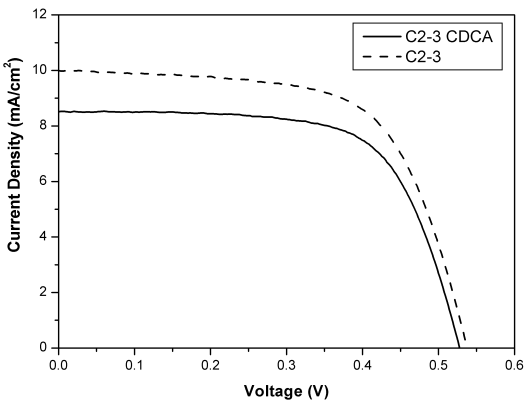

C1-3 CDCA
C1-3
Current Density (mA/cm^2)
Voltage (V)


C1-4 CDCA
C1-4
Current Density (mA/cm^2)
Voltage (V)


C1-5 CDCA
C1-5
Current Density (mA/cm^2)
Voltage (V)


C2-1 CDCA
C2-1
Current Density (mA/cm^2)
Voltage (V)


C2-2 CDCA
C2-2
Current Density (mA/cm^2)
Voltage (V)


C2-3 CDCA
C2-3
Current Density (mA/cm^2)
Voltage (V)

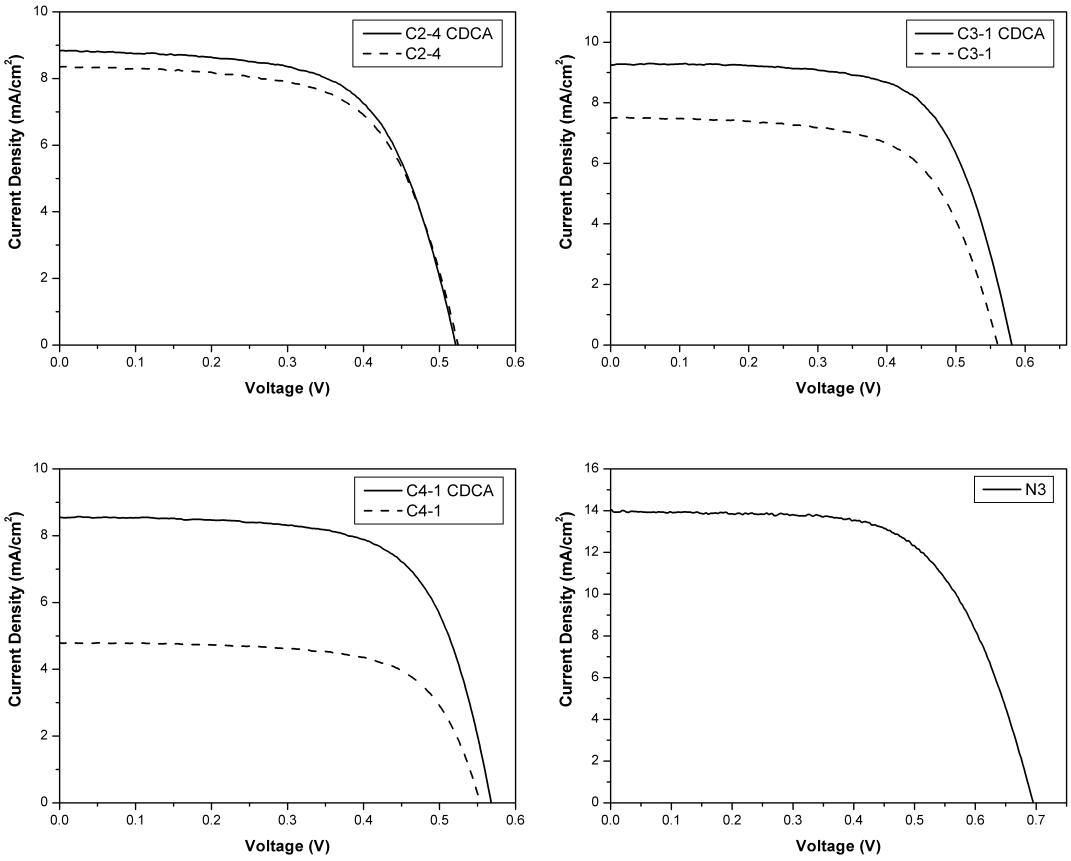


Figure S8 *J-V* curves of DSSCs based on the tetrahydroquinoline dyes with (—) or without (- - -) the addition of CDCA (3×10^{-3} M) into dye bath.

(D) Complete Reference 38

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