Accepted Manuscript

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PII: S0143-7208(18)32144-2

DOI: https://doi.org/10.1016/j.dyepig.2018.12.042

Reference: DYPI 7247

To appear in: Dyes and Pigments

Received Date: 27 September 2018

Revised Date: 12 November 2018

Accepted Date: 19 December 2018

Please cite this article as: Weldekirstos HD, Kuo M-C, Li S-R, Su W-L, Desta MA, Wu W-T, Kuo C-H, Sun S-S, New 2,3-diphenylquinoxaline containing organic D-A-π-A dyes with nickel oxide photocathode prepared by surfactant-mediated synthesis for high performance p-type dye-sensitized solar cells, *Dyes and Pigments* (2019), doi: https://doi.org/10.1016/j.dyepig.2018.12.042.

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New 2,3-Diphenylquinoxaline Containing Organic D-A- π -A Dyes with Nickel Oxide Photocathode Prepared by Surfactant-Mediated Synthesis for High Performance p-type Dye-Sensitized Solar Cells

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ABSTRACT

Dye-sensitized solar cells (DSSCs) are one of the most promising organic photovoltaics. The optimized efficiency of a tandem cell combined with both n- and p-type DSSCs was theoretically predicted to be 43%. The bottleneck for reaching the optimized performance is limited by the p-type half-cell, particularly the lacking of an appropriate semiconducting material as the photocathode. In this regard, we report the surfactant-mediated synthesis of nickel oxide nanomaterial using a chemical co-precipitation method. The new material was fully characterized by XRD, SEM, XPS, EDS, and BET. The BET result indicates the nickel oxide nanoparticles synthesized with surfactant attain higher surface area than the conventional one. In addition, the new organic dyes with electron-deficient diphenylquinoxaline incorporated within the molecular structure were prepared for p-type dye-sensitized solar cells with the newly prepared NiO as the photocathode. The new organic dyes consist of carboxylic acid as the anchoring group, triphenylamine as the electron donor, 2,3-diphenylquinoxaline as the auxiliary acceptor moiety, 2-methylenemalononitrile as electron acceptor, connected with thiophene, 3,4-ethylenedioxythiophene, and 2,2'-bithiophene as the π -spacer. Sensitizers with mono-anchoring

group (EH166, EH122, and EH174) performed better than their corresponding double-anchoring sensitizers (EH162, EH126, and EH170). Among these, dye EH174 exhibited the best conversion efficiency up to 0.207% with a short-circuit photocurrent density of 4.84 mAcm⁻², an open-circuit photovoltage of 137 mV, and a fill factor of 0.312. The current results indicate that the combination of electron-deficient quinoxaline motif with suitable π -linker in a D-A- π -A molecular structure is a promising design of p-type sensitizers for NiO-based p-DSSCs.

Graphic abstract:



Keywords: surfactant, nickel oxide, quinoxaline, p-type sensitizers, p-type dye-sensitized solar cells

1. Introduction

Solar energy is largely abundant, exceeding our current global annual energy needs. The total solar energy absorbed by earth's atmosphere, oceans and land masses is approximately 3.85 $\times 10^{24}$ joules per year[1]. Radical improvements in device manufacture led to a remarkable increase in solar energy conversion efficiencies and significant price cuts [2]. The dye-sensitized solar cell (DSSC) is one type of organic photovoltaics mimicking the process of natural photosynthesis [3]. Up to date, the majority of the research efforts on DSSCs has been focused on the development of n-type DSSCs (n-DSSCs) with the highest efficiency up to 14% [4, 5]. The interest in studying p-type DSSCs (p-DSSCs) [6] as an important component for the construction of tandem DSSCs (t-DSSCs) with n-DSSCs and for potential solar fuel with dye-

sensitized photoelectrochemcial cells has been a focus recently[7-9]. Theoretical prediction for the t-DSSC is projected to 43% when all components in the cell are optimized [10].

Compared to n-DSSCs, nevertheless, much less studies have been reported on the sensitization of p-DSSCs with wide band gap p-type semiconductors [11]. The highest efficiency of p-DSSC with iodide/triiodide based redox electrolyte is 0.61% using the sensitizer, TPA-6T-PMI (triphenylamine-sexithiophene-perylene monoimide), with a push-pull structural design [12]. The efficiency of TPA-6T-PMI sensitized p-DSSC was boosted to 1.3% with the cobalt based redox mediator and registered the highest open circuit voltage of 709 mV[13]. Recently, the efficiency of p-DSSC was further raised to a record high of 2.51% for the same sensitizer via iron based redox mediator[14]. The best efficiency for pn t-DSSC achieved 4.1% with a TiO₂ photoanode sensitized by dye D35 and a NiO photocathode sensitized by a diketopyrrolopyrrole dye [15].

The most commonly used photocathode material for p-DSSCs is NiO, which possesses a wide band gap of 3.5 eV with excellent chemical and thermal stability. However, NiO suffers significant drawbacks as the photocathode because of 1) small energy gap between the valence band of NiO and commonly used I/I_3^- redox couple that results in low photovoltage and 2) limited thickness due to the weak mechanical strength of NiO that reduces the amount of dye loading and lowers down the light harvesting ability, and 3) low intrinsic conductivity of NiO that slows down the hole mobility and reduces the charge collection efficiency and fill factor. In order to boost p-DSSCs with better performance, investigations have been carried out on both novel p-type semiconductors and light harvesting dyes[16-20]. The criteria for appropriate p-type semiconductors include good hole collection efficiency and better mechanical strength in comparison with conventional NiO [21-28]. The strategy of designing p-type photosensitizers aims at superior light harvesting efficiency, suitable energy level alignment with both the valence band of p-type semiconductor and the redox potential of redox mediator, and effective charge separation to suppress charge recombination[29-36].

Hole transport in the mesoporous film is one of the limiting factors to the performance of p-DSSCs, pointing out the need to improve the hole conductivity of the nickel oxide based electrode[37]. As yet, the efficiency of p-type system is limited by the intrinsically low open circuit potential caused by the small difference in potential between the quasi-Fermi level in the

semiconductor and the electrochemical potential of the redox mediator [38]. In addition, low photocurrent density due to fast charge recombination between the reduced dye and the holes generated in the nickel oxide as well as the low light-harvesting efficiency (LHE) resulting from the limited dye loading on the nickel oxide film all lead to low efficiencies [39-42].

In this work, we report the synthesis of dodecyltrimethylamonium bromide (DTAB) mediated nickel oxide with a uniform particle size and excellent morphology for photocathode material of p-DSSCs. Six new organic p-type sensitizers with a D–A– π –A framework were prepared with triphenylamine (TPA) as a donor, an electron deficient 2,3-diphenylquinoxaline as the auxiliary acceptor, various thiophene derivatives as the π -linkers, methylene malonitrile as the electron acceptor, and carboxylic acid as the anchoring group. The molecular structures of these dyes are shown in Fig 1. Organic dyes with electron-deficient quinoxaline incorporated within a D–A– π –A framework have been widely employed as photosensitizers for n-DSSCs [43-49]. Our findings here along with the literature report confirm that quinoxaline unit could also be an effective auxiliary acceptor for p-DSSCs [50].



Fig. 1: Molecular structures of p-type sensitizers EH122, EH126, EH162, EH166, EH170 and EH174

2. Experimental Section

2.1 Materials and Characterization Methods

All reagents are commercially available unless otherwise noticed. Powder X-Ray diffraction patterns were recorded 20 in the range of 20-90° using a Brüker D8 Advance diffractometer (Cu Ka, 40 kV, 40 mA). Morphology of nanoparticle and surface of the thin film analysis done by field-emission scanning electron microscope with model (ULTRA PLUS, a member of Carl Zeiss). The Brunauere-Emmete-Teller (BET) specific surface area measurements were carried out with a micrometrics ASAP 2020 surface area and porosity analyzer instrument using N₂ as gas analyzer. Elemental analysis was done using energy dispersive x-ray spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS). Work function measurements were done on an AC-2 model photoelectron spectrometer (Riken Keiki). The film thickness of each working electrodes were measured by surface profilometer-Dectack 50. Photocurrent-voltage characteristics of p-type solar cell devices were measured by using a LSQE-IV Class AAA solar simulator (SAN-EL Electric Co.) at a light intensity of 100 mWcm⁻² and calibrated by using an Oriel reference solar cell (Oriel 91150, New port S). Intensitymodulated photovoltage spectroscopy (IMVS) was carried out by using an electrochemical workstation (Zahner, Zennium) equipped with a frequency-response analyzer under an intensitymodulated (10 to 300 Wm⁻²) white-light-emitting diode. The frequency range was set from 1 kHz to 100 mHz. Cyclic voltammetry experiments were performed using a CH Instruments electro-chemical workstation (model 660A). The experiments were carried out under N₂ atmosphere in DMF solution containing 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) as a supporting electrolyte at a scan rate of 100 mV/s. The potentials are quoted against the ferrocene standard. UV-visible absorption spectroscopy measurements were carried out using Varian Cary 300 type UV-Vis spectrophotometer.

2.2 Surfactant mediated synthesis of nickel oxide

The surfactant mediated synthesis of nickel oxide was carried out according to the following procedure. The hexahydrate nickel(II) chloride (1 g) and DTAB (1 g) were dispersed and stirred in 40 mL of deionized (DI) water at room temperature. Subsequently, a sodium

hydroxide solution (0.94 g in 40 mL DI water) was added slowly to the nickel(II) chloride solution [42]. The combined solution was kept for 1 h with constant stirring before being centrifuged and washed with DI water to purify from spectator ions. The residue was dried at 90 °C to remove the solvent and produced the green nickel hydroxide (Ni(OH)₂). The thus obtained nickel hydroxide was calcined at 350 °C for 2 h to yield the desired NiO.

2.2 Synthesis of organic compounds

The synthetic procedures for precursors and sensitizers are depicted in Scheme S1-S3 in Supporting Information. Compounds **7** [51], **Q** [52], **5** [53], **TPA2** [54] were synthesized according to the literature procedures.

2.2.1 5'-(8-bromo-2,3-diphenylquinoxalin-5-yl)-[2,2'-bithiophene]-5-carbaldehyde (Q-BT)

A mixture in a 250-mL flask containing compound **7** (1.00 g, 4.76 mmol), compound **Q** (4.19 g, 9.52 mmol), Pd(PPh₃)₂Cl₂ (0.17 g, 0.24 mmol), Na₂CO₃ (1.77 g, 16.66 mmol) and 100 mL THF/H₂O mixed solvent (v/v = 4/1) was refluxed for 8 h. The solvent was evaporated and the residue was extracted with DCM and water. The organic layer was collected and dried over MgSO₄. Solvent evaporation afforded the crude compound **8**, which was dissolved in 7 mL DMF. To this DMF mixture was dropwisely added POCl₃ (6.6 mL) in an ice bath. The mixture was heated to reflux for 8 h and cooled to room temperature. The solution was neutralized by an aqueous NaHCO₃ in an ice bath followed by extraction with DCM/H₂O. The organic layer was collected and dried over MgSO₄. The desired product **Q-BT** was obtained by column chromatography flashed with EA/hexane (1/5) as a red solid (1.87 g, 71%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 9.89 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 4.0 Hz, 1H), 7.74-7.69 (m, 5H), 7.47-7.36 (m, 7H), 7.32 (d, *J* = 4.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 182.5, 153.5, 152.7, 147.5, 141.7, 139.5, 139.2, 138.8, 138.2, 138.0, 137.51, 137.48, 133.1, 131.7, 130.5, 130.3, 129.5, 128.39, 128.35, 127.5, 126.8, 125.7, 124.0, 123.3. HRMS (FAB) m/z: calcd for C₂₉H₁₈BrN₂OS₂: 553.0044; [M+H] ⁺ found: 553.0046.

2.2.2 7-(8-bromo-2,3-diphenylquinoxalin-5-yl)-2,3-dihydrothieno[3,4b][1,4]dioxine-5carbaldehyde (**Q-EDOT**)

A mixture in a 250-mL flask containing compound **5** (1.00 g, 5.88 mmol), compound **Q** (5.17 g, 11.75 mmol), $Pd(OAc)_2$ (0.21 g, 0.94 mmol), Na_2CO_3 (2.18 g, 20.57 mmol) and 100 mL

DMF solvent was refluxed for 8 h. The solvent was evaporated and the residue was extracted with DCM and water. The organic layer was collected and dried over MgSO₄. The desired product **Q-EDOT** was obtained by column chromatography flashed with EA/hexane (1/5) as a red solid (1.40 g, 45%). ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 10.01$ (s, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.72-7.67 (m, 4H), 7.42-7.34 (m, 6H), 4.46 (s, 4H). ¹³C NMR (125 MHz, CDCl₃, ppm): $\delta = 180.6$, 153.4, 152.7, 147.6, 140.0, 138.5, 138.2, 137.8, 132.9, 130.5, 130.3, 129.9, 129.6, 129.5, 129.4, 128.4, 128.3, 123.9, 123.0, 119.9, 64.9, 64.8. HRMS (FAB) m/z: calcd for C₂₇H₁₈BrN₂O₃S: 529.0222; [M+H]⁺ found: 529.0233.

2.2.3 Methyl 4-(bis(4-bromophenyl)amino)benzoate (12)

To a 250-mL flask containing compound **11** (1.00 g, 2.24 mmol) was added 100 mL of methanol and 2 mL H₂SO₄. The solution was heated to reflux for 8 h before being cooled to room temperature. The mixture was extracted with water/DCM. The organic layer was collected and dried over MgSO₄. A white solid of **12** (1.02 g, 99%) was obtained after solvent evaporation. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 4H), 7.00-6.97 (m, 6H), 3.88 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 166.8, 151.2, 145.6, 132.9, 131.2, 127.0, 123.6, 121.1, 117.5, 52.1. HRMS (FAB) m/z: calcd for C₂₀H₁₅Br₂NO₂: 458.9470; M⁺ found: 458.9481.

2.2.4 Dimethyl4,4'-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) azanediyl) benzoate (**TPA1**)

To a 250-mL flask containing compound **12** (1.26 g, 2.73 mmol), bis(pinacolato)diboron (1.46 g, 5.74 mmol), Pd(dppf)Cl₂ (0.20 g, 0.27 mmol), and KOAc (0.67 g, 6.83 mmol) was added 60 mL of 1,4-dioxane. The mixture was heated to reflux under nitrogen atmosphere for 12 h. After cooling to room temperature, the mixture was extracted with water/DCM. The organic layer was collected and dried over MgSO₄. The desired product of **TPA1** was obtained as a white solid (0.80 g, 53%) by column chromatography eluted with EA/hexane (1/20). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.87 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 4H), 7.11-7.04 (m, 6H), 3.88 (s, 3H), 1.34 (s, 24H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 166.9, 151.5,

149.4,136.3, 131.0, 124.4, 123.7,122.3, 83.9, 60.5, 52.0, 25.0. HRMS (FAB) m/z: calcd for $C_{32}H_{39}B_2NO_{6:}$ 555.2963; M⁺ found: 555.2970.

2.2.5 Methyl 4-(bis(4-(8-(5-formylthiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)phenyl)amino) benzoate (17)

To a 100-mL flask containing **Q-T** (1.00 g, 2.12 mmol), **TPA1** (0.59 g, 1.06 mmol), Pd(PPh₃)₂Cl₂ (0.08 g, 0.11 mmol), and Na₂CO₃ (0.56 g, 5.3 mmol) was added a 50 mL TH/H₂O mixed solvent (v/v = 4/1). The mixture was heated to reflux under nitrogen atmosphere for 8 h before being cooled to room temperature. The solution was evaporated to dryness and the residue was extracted with DCM and water. The organic layer was collected and dried over MgSO₄. The desired product of **17** was obtained as a red solid (0.44 g, 38%) by column chromatography eluted with EA/hexane (1/1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.0 (s, 2H), 8.27 (d, *J* = 7.6 Hz, 2H), 7.98-7.92 (m, 6H), 7.88 (d, *J* = 8.8 Hz, 4H), 7.84 (d, *J* = 4.0 Hz, 2H), 7.76-7.73 (m, 4H), 7.62-7.60 (m, 4H), 7.43-7.39 (m, 10H), 7.36-7.28 (m, 8H), 3.92(s, 3H). ¹³C NMR (150 MHz, CDCl₃, ppm): δ = 183.4, 166.8, 152.3, 152.2, 151.6, 148.5, 146.6, 145.1, 140.1, 138.7, 138.6, 138.3, 137.5, 135.7, 133.4, 132.1, 131.0, 130.4, 130.3, 130.1, 129.4, 129.2, 128.5, 128.3, 127.1, 126.1, 125.5, 124.7, 123.5, 122.0, 51.9. HRMS (FAB) m/z: calcd for C₇₀H₄₆N₅O₄S₂: 1084.2991; [M+H]⁺ found: 1084.3000.

2.2.6 4-(bis(4-(8-(5-formylthiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)phenyl)amino)benzoic acid (18)

To a 50-mL flask containing **17** (200 mg, 0.18 mmol) and LiOH (31 mg, 0.74 mmol) was added 21 mL of THF/MeOH/H₂O (v/v/v = 5/1/1) mixed solvent and the mixture was heated to reflux for 8 h. After cooling to room temperature, the solution was neutralized by dilute HCl. The precipitate was collected, washed with water, and dried under vacuum to afford a dark red solid of compound **18** (195 mg, 99%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.0 (s, 2H), 8.27 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 4.0 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 4H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.76-7.73 (m, 4H), 7.62-7.60 (m, 4H), 7.43-7.41 (m, 10H), 7.36-7.29 (m, 8H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 183.5, 170.8, 152.4, 152.3, 152.2, 148.4, 146.4, 145.0, 140.0, 138.7, 138.6, 138.3, 137.5, 135.7, 133.7, 132.1, 131.7,

130.4, 130.3, 130.1, 129.43, 129.39, 129.2, 128.5, 128.3, 128.2, 127.1, 125.0, 122.0, 121.5. HRMS (MALDI) m/z: calcd for C₆₉H₄₄N₅O₄S₂: 1070.2835; [M+H] ⁺ found: 1070.2828.

2.2.7 4-(bis(4-(8-(5-(2,2-dicyanovinyl)thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)phenyl)amino) benzoic acid (**EH122**)

To a 50-mL flask containing **18** (100 mg, 0.09 mmol) and malononitrile (14 mg, 0.21 mmol) was added 20 mL DCM. The solution was stirred at room temperature for 2 h. Subsequently, the mixture was concentrated to ~5mL followed by adding large amount of hexane to crash a red solid. The dark red solid was collected, washed with hexane, and dried under vacuum to afford **EH122** (48 mg, 44%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.33 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.96-7.94 (m, 4H), 7.90 (d, *J* = 8.4 Hz, 4H), 7.86 (s, 2H), 7.84 (d, *J* = 4.4 Hz, 2H), 7.82-7.80 (m, 4H), 7.63-7.61 (m, 4H), 7.45-7.41 (m, 10H), 7.36-7.30 (m, 8H). The ¹³C NMR spectrum was not obtained because of very low solubility of **EH122**. HRMS (FAB) m/z: calcd for C₇₅H₄₄N₉O₂S₂: 1166.3059; [M+H]⁺ found: 1166.3054.

2.2.8 Dimethyl 4,4'-((4-(8-(5-formylthiophen-2-yl)-2,3-diphenylquinoxalin-5-yl) phenyl) azanediyl) dibenzoate (19)

To a 100-mL flask containing **Q-T** (1.00 g, 2.12 mmol), **TPA2** (1.03 g, 2.11 mmol), Pd(PPh₃)₂Cl₂ (0.08 g, 0.11 mmol) and Na₂CO₃ (0.79 g, 7.43 mmol) was added 50 mL THF/H₂O mixed solvent (v/v = 4/1). The mixture was refluxed under nitrogen atmosphere for 8 h. After cooling the solution to room temperature, the mixture was extracted with DCM and water. The organic layer was collected and dried over MgSO₄. The desired product of **19** was obtained as a red solid (1.05 g, 66%) by column chromatography eluted with EA/hexane (1/1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10,00 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.98-7.95 (m, 5H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.87-7.83 (m, 3H), 7.75-7.72 (m, 2H), 7.60-7.58 (m, 2H), 7.43-7.41 (m, 3H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 4H), 3.92 (s, 6H). ¹³C NMR (150 MHz, CDCl₃, ppm): δ = 183.4, 166.6, 152.3, 152.2, 151.0, 148.4, 146.0, 145.1, 139.9, 138.62, 138.59, 138.3, 137.5, 135.7, 134.2, 132.3, 131.1, 130.5, 130.4, 130.1, 129.5, 129.4, 129.2, 128.5, 128.3, 128.2, 127.2, 125.2, 124.6, 123.1, 52.0. HRMS (FAB) m/z: calcd for C₄₇H₃₄N₃O₅S: 752.2219; [M+H]⁺ found: 752.2229.

2.2.9 4,4'-((4-(8-(5-formylthiophen-2-yl)-2,3-diphenylquinoxalin-5-yl) phenyl) azanediyl) dibenzoic acid (**20**)

Compound **20** was synthesized followed the same procedures for compound **18**. A dark red solid was obtained in a yield of 99%. ¹H NMR (400 MHz, DMSO- d_6 , ppm): $\delta \equiv 10.00$ (s, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 4.4 Hz, 1H), 8.12-8.08 (m, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 4H), 7.69-7.66 (m, 2H), 7.56 (d, J = 7.2 Hz, 2H), 7.47-7.44 (m, 3H), 7.43-7.34 (m, 3H), 7.30 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.8 Hz, 4H). ¹³C NMR (100 MHz, DMSO- d_6 , ppm): $\delta = 184.6$, 166.8, 152.1, 151.6, 150.2, 146.4, 145.5, 145.0, 138.9, 138.3, 138.0, 137.8, 137.0, 136.4, 133.5, 132.3, 131.0, 130.1, 129.8, 129.33, 129.28, 129.1, 128.5, 128.3, 128.1, 127.7, 125.1, 124.8, 122.8. HRMS (FAB) m/z: calcd for C₄₅H₃₀N₃O₅S: 724.1906; [M+H] ⁺ found: 724.1898.

2.2.10 4,4'-((4-(8-(5-(2,2-dicyanovinyl)thiophen-2-yl)-2,3-diphenylquinoxalin-5 yl) phenyl) azanediyl) dibenzoic acid (EH126)

To a 50-mL flask containing **20** (100 mg, 0.14 mmol) and malononitrile (11 mg, 0.17 mmol) was added 20 mL DCM and 5 mL EtOH. The solution was stirred at room temperature for 2 h. Subsequently, the mixture was concentrated to ~5mL followed by adding large amount of hexane to crash a red solid. The red solid was collected, washed with hexane, and dried under vacuum to afford **EH126** (67 mg, 63%). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ = 8.70 (s, 1H), 8.68 (d, *J* = 7.6 Hz, 1H), 8.30 (d, *J* = 4.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 4.8 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 4H), 7.77-7.75 (m, 2H), 7.59-7.57 (m, 2H), 7.42-7.34 (m, 6H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 4H). The ¹³C NMR spectrum was not obtained because of very low solubility of **EH126**. HRMS (FAB) m/z: calcd for C₄₈H₃₀N₅O₄S: 772.2019; [M+H]⁺ found: 722.2009.

2.2.11 Methyl4-(bis(4-(8-(7-formyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenyl quinoxalin-5-yl)phenyl)amino)benzoate (21)

To a 100-mL flask containing **Q-EDOT** (1.00 g, 1.89 mmol), **TPA1** (0.52 g, 0.94 mmol), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.10 mmol), and Na_2CO_3 (0.50 g, 4.72 mmol) was added a 50 mL TH/H₂O mixed solvent (v/v = 4/1). The mixture was heated to reflux under nitrogen atmosphere for 8 h before cooling to room temperature. The solution was evaporated to dryness and the

residue was extracted with DCM and water. The organic layer was collected and dried over MgSO₄. The desired product of **21** was obtained as a red solid (0.46 g, 41%) by column chromatography eluted with EA/hexane (1/1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.03 (s, 2H), 8.71 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 4H), 7.77-7.75 (m, 4H), 7.62-7.60 (m, 4H), 7.42-7.38 (m, 10H), 7.35-7.29 (m, 8H), 4.49 (s, 8H), 3.92 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 180.6, 166.9, 151.9, 151.7, 151.5, 147.8, 146.4, 139.8, 139.1, 138.8, 138.3, 138.2, 137.7, 133.6, 132.2, 132.1, 131.0, 130.5, 130.1, 129.8, 129.4, 129.3, 129.1, 128.8, 128.6, 128.4, 128.3, 124.7, 121.9, 119.5, 65.0, 64.8, 51.9. HRMS (FAB) m/z: calcd for C₇₄H₅₀N₅O₈S₂: 1200.3108; [M+H]⁺ found: 1200.3105.

2.2.12 4-(bis(4-(8-(7-formyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenylquinoxalin-5-yl)phenyl)amino)benzoic acid (**22**)

Compound **22** was synthesized followed the same procedures as compound **18**. A dark red solid was obtained in a yield of 99%. ¹H NMR (600 MHz, CDCl₃, ppm): $\delta = 10.02$ (s, 2H), 8.70 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 9.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.5 Hz, 4H), 7.77-7.75 (m, 4H), 7.61-7.59 (m, 4H), 7.42-7.38 (m, 10H), 7.34-7.28 (m, 8H), 4.48 (s, 8H). ¹³CNMR (125 MHz, CDCl₃, ppm): $\delta = 180.7$, 171.0, 152.3, 151.7, 151.3, 147.9, 146.1, 139. 9, 138.7, 138.20, 138.16, 137.5, 133.7, 132.1, 131.7, 130.5, 130.1, 129.6, 129.3, 129.2, 129.1, 128.7, 128.4, 128.3, 124.9, 123.9, 122.0, 121.3, 119.4, 116.7, 64.9, 64.7. HRMS (FAB) m/z: calcd for C₇₃H₄₈N₅O₈S₂: 1186.2944; [M+H] ⁺ found: 1186.2936.

2.2.13 4-(bis(4-(8-(7-(2,2-dicyanovinyl)-2,3-dihydrothieno[3,4-b] [1,4] dioxin-5-yl)-2,3diphenyl quinoxalin-5-yl) phenyl) amino) benzoic acid (**EH166**)

To a 50-mL flask containing **22** (118 mg, 0.10 mmol) and malononitrile (15 mg, 0.23 mmol) was added 20 mL DCM. The solution was stirred at room temperature for 2 h. Subsequently, the mixture was concentrated to ~5mL followed by adding large amount of hexane to crash a red solid. The dark red solid was collected, washed with hexane, and dried under vacuum to afford **EH166** (64 mg, 50%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.77 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.95 (s, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.88-7.83 (m, 6H), 7.62 (d, *J* = 6.8 Hz, 4H), 7.44-7.37 (m, 10H), 7.31-7.28 (m, 8H), 4.47 (s, 8H). The ¹³C NMR

spectrum was not obtained because of very low solubility of **EH166**. HRMS (MALDI) m/z: calcd for $C_{79}H_{47}N_9O_6S_2$: 1281.3085; M⁺ found: 1281.3065.

2.2.14 Dimethyl 4,4'-((4-(8-(7-formyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenyl quinoxalin-5-yl)phenyl)azanediyl)dibenzoate (23)

To a 100-mL flask containing **Q-EDOT** (1.00 g, 1.89 mmol), **TPA1** (0.92 g, 1.89 mmol), Pd(PPh₃)₂Cl₂ (0.07 g, 0.10 mmol), and Na₂CO₃ (0.70 g, 6.61 mmol) was added a 50 mL TH/H₂O mixed solvent (v/v = 4/1). The mixture was heated to reflux under nitrogen atmosphere for 8 h before cooling to room temperature. The solution was evaporated to dryness and the residue was extracted with DCM and water. The organic layer was collected and dried over MgSO₄. The desired product of **23** was obtained as a red solid (1.04 g, 68%) by column chromatography eluted with EA/hexane (1/1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.02 (s, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 4H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.77-7.74 (m, 2H), 7.60-7.57 (m, 2H), 7.42-7.40 (m, 3H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 4H), 4.48 (s, 4H), 3.91 (s, 6H). ¹³C NMR (150 MHz, CDCl₃, ppm): δ = 180.6, 166.7, 152.0, 151.6, 151.0, 147.8, 145.8, 139.9, 138.7, 138.3, 138.2, 137.7, 134.4, 132.3, 131.1, 130.5, 130.1, 129.8, 129.4, 129.3, 129.2, 129.0, 128.4, 128.3, 125.2, 124.6, 124.0, 123.0, 119.5, 65.0, 64.8, 52.0. HRMS (FAB) m/z: calcd for C₄₉H₃₆N₃O₇S: 810.2274; [M+H]⁺ found: 810.2280.

2.2.15 4,4'-((4-(8-(7-formyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenylquinoxalin-5-yl) phenyl)azanediyl)dibenzoic acid (**24**)

Compound **24** was synthesized followed the same procedures as compound **18**. A dark red solid was obtained in a yield of 99%. ¹H NMR (600 MHz, DMSO-*d*₆, ppm): $\delta = 9.97$ (s, 1H), 8.82 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 4H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.47-7.43 (m, 3H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.37-7.34 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 4H), 4.56 (d, *J* = 5.4 Hz, 4H). ¹³C NMR (125 MHz, DMSO-*d*₆, ppm): $\delta = 180.1$, 166.8, 151.8, 150.2, 148.4, 145.5, 140.4, 138.4, 137.9, 137.8, 137.6, 136.7, 133.6, 132.4, 131.1, 130.1, 129.8, 129.7, 129.5, 129.3, 129.1, 128.2, 128.1, 125.1, 124.9, 122.8, 121.7, 118.4, 65.0, 64.9. HRMS (ESI) m/z: calcd for C₄₇H₃₀N₃O₇S: 780.1804; [M-H]⁻ found: 780.1795.

2.2.16 4,4'-((4-(8-(7-(2,2-dicyanovinyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenyl quinoxalin-5-yl)phenyl)azanediyl)dibenzoic acid (**EH162**)

To a 50-mL flask containing **24** (100 mg, 0.13 mmol) and malononitrile (10 mg, 0.15 mmol) was added 20 mL DCM and 5 mL EtOH. The solution was stirred at room temperature for 2 h. Subsequently, the mixture was concentrated to ~5mL followed by adding large amount of hexane to crash a red solid. The dark red solid was collected, washed with hexane, and dried under vacuum to afford **EH162** (69 mg, 65%). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): $\delta = 8.89$ (d, *J* = 8.0 Hz, 1H), 8.25 (s, 1H), 8.11(d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 4H), 7.77-7.74 (m, 2H), 7.58-7.56 (m, 2H), 7.42-7.35 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 4H), 4.56 (s, 4H). The ¹³C NMR spectrum was not obtained because of very low solubility of **EH162**. HRMS (FAB) m/z: calcd for C₅₀H₃₂N₅O₆S: 830.2073; [M+H]⁺ found: 830.2081.

2.2.17 Methyl4-(bis(4-(8-(5'-formyl-[2,2'-bithiophen]-5-yl)-2,3-diphenyl quinoxalin-5-yl) phenyl) amino)benzoate (25)

To a 100-mL flask containing **Q-BT** (1.00 g, 1.81 mmol), **TPA1** (0.50 g, 0.90 mmol), Pd(PPh₃)₂Cl₂ (0.06 g, 0.09 mmol), and Na₂CO₃ (0.48 g, 4.52 mmol) was added a 50 mL THF/H₂O mixed solvent (v/v = 4/1). The mixture was heated to reflux under nitrogen atmosphere for 8 h before cooling to room temperature. The solution was evaporated to dryness and the residue was extracted with DCM and water. The organic layer was collected and dried over MgSO₄. The desired product of **25** was obtained as a red solid (0.45 g, 40%) by column chromatography eluted with EA/hexane (2/1). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 9.89 (s, 2H), 8.24 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 4H), 7.85 (d, *J* = 4.2 Hz, 2H), 7.79-7.77 (m, 4H), 7.72 (d, *J* = 3.6 Hz, 2H), 7.63-7.61 (m, 4H), 7.46-7.41 (m, 8H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.37-7.27 (m, 10H), 3.92 (s, 3H). ¹³CNMR (125 MHz, CDCl₃, ppm): δ = 182.5, 166.9, 152.1, 151.7, 151.6, 147.9, 146.4, 141.5, 140.4, 138.8, 138.7, 138.6, 138.5, 137.6, 137.0, 133.6, 132.0, 131.0, 130.8, 130.5, 130.1, 129.6, 129.3, 129.1, 128.3, 127.0, 126.6, 125.7, 124.8, 123.8, 123.2, 121.8, 51.9. HRMS (FAB) m/z: calcd for C₇₈H₅₀N₅O₄S₄: 1248.2746; [M+H] ⁺ found: 1248.2751.

2.2.18 4-(bis(4-(8-(5'-formyl-[2,2'-bithiophen]-5-yl)-2,3-diphenylquinoxalin-5-yl)phenyl) amino) benzoic acid (**26**)

Compound **26** was synthesized followed the same procedures as compound **18**. A dark red solid was obtained in a yield of 98%. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 9.90 (s, 2H), 8.26 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 4.0 Hz, 2H), 7.80-7.78 (m, 4H), 7.73 (d, *J* = 4.0 Hz, 2H), 7.64-7.62 (m, 4H), 7.47-7.40 (m, 12H), 7.38-7.28 (m, 10H). The ¹³C NMR spectrum was not obtained because of very low solubility of **26**. HRMS (FAB) m/z: calcd for C₇₇H₄₇N₅O₄S₄ :1234.2589; [M+H] ⁺ found: 1234.2593.

2.2.19 4-(bis(4-(8-(5'-(2,2-dicyanovinyl)-[2,2'-bithiophen]-5-yl)-2,3-diphenylquinoxalin-5-yl) phenyl) amino) benzoic acid (EH174)

To a 50-mL flask containing **26** (100 mg, 0.08 mmol) and malononitrile (12 mg, 0.18 mmol) was added 20 mL DCM and 5 mL EtOH. The solution was stirred at room temperature for 2 h. Subsequently, the mixture was concentrated to ~5mL followed by adding large amount of hexane to crash a red solid. The dark red solid was collected, washed with hexane, and dried under vacuum to afford **EH174** (49 mg, 45%). ¹H NMR (500 MHz, DMF- d_7 , ppm): δ = 8.63 (d, J = 7.5 Hz, 2H), 8.18 (d, J = 4.0 Hz, 2H), 8.14-8.10 (m, 8H), 7.90-7.88 (m, 6H), 7.75-7.73 (m, 6H), 7.61 (d, J = 3.5 Hz, 2H), 7.56-7.50 (m, 6H), 7.46-7.40 (m, 10H), 7.27 (d, J = 6.0 Hz, 4H). ¹³C NMR (100 MHz, DMF- d_7 , ppm): δ = 168.1, 160.5, 153.4, 152.6, 152.5, 152.3, 147.3, 141.5, 140.5, 140.2, 139.6, 139.4, 139.0, 138.8, 137.6, 135.1, 134.9, 133.4, 132.8, 132.2, 131.9, 131.7, 131.2, 130.41, 130.35, 130.1, 129.4, 129.3, 128.8, 127.8, 125.7, 125.4, 124.8, 122.7, 118.0, 117.7, 81.5. HRMS (FAB) m/z: calcd for C₈₃H₄₈N₉O₂S₄: 1330.2814; [M+H] ⁺ found: 1330.2799.

2.2.20 Dimethyl4,4'-((4-(8-(5'-formyl-[2,2'-bithiophen]-5-yl)-2,3-diphenyl quinoxalin-5-yl) phenyl) azanediyl)dibenzoate (27)

To a 100-mL flask containing **Q-BT** (1.00 g, 1.81 mmol), **TPA2** (0.88 g, 1.81 mmol), Pd(PPh₃)₂Cl₂ (0.06 g, 0.09 mmol), and Na₂CO₃ (0.67 g, 6.32 mmol) was added a 50 mL THF/H₂O mixed solvent (v/v = 4/1). The mixture was heated to reflux under nitrogen atmosphere for 8 h before cooling to room temperature. The solution was evaporated to dryness

and the residue was extracted with DCM and water. The organic layer was collected and dried over MgSO₄. The desired product of **27** was obtained as a red solid (1.02 g, 68%) by column chromatography eluted with EA/hexane (2/1). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 9.89 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 7.0, 2.0 Hz, 4H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.88-7.84 (m, 3H), 7.79-7.77 (m, 2H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.61-7.59 (m, 2H), 7.46-7.42 (m, 4H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.34-7.32 (m, 3H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 4H), 3.92 (s, 6H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 182.7, 166.9, 152.3, 151.8, 151.2, 148.0, 146.0, 141.7, 140.5, 139.1, 138.9, 138.8, 138.64, 138.59, 137.7, 137.2, 134.6, 132.4, 131.3, 131.2, 130.7, 130.3, 129.9, 129.5, 129.4, 128.5, 127.3, 126.8, 125.9, 125.5, 124.7, 124.0, 123.2, 52.2. HRMS (FAB) m/z: calcd for C₅₁H₃₅N₃O₅S₂: 833.2018; M⁺ found: 833.2014.

2.2.21 4,4'-((4-(8-(5'-formyl-[2,2'-bithiophen]-5-yl)-2,3-diphenylquinoxalin-5-yl)phenyl)azanediyl)dibenzoic acid (**28**)

Compound **28** was synthesized followed the same procedures as compound **18**. A dark red solid was obtained in a yield of 99%. ¹H NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 9.91$ (s, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 4.0 Hz, 1H), 8.07-8.04 (m, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.8 Hz, 4H), 7.76-7.73 (m, 3H), 7.60-7.57 (m, 3H), 7.50-7.47 (m, 3H), 7.42-7.37 (m, 3H), 7.29 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 4H). ¹³C NMR (125 MHz, DMSO- d_6 , ppm): $\delta = 184.2$, 167.3, 152.4, 151.6, 150.7, 146.5, 145.8, 141.5, 139.7, 139.3, 138.9, 138.8, 138.4, 138.2, 138.0, 136.3, 134.2, 132.7, 131.5, 130.7, 130.4, 130.3, 130.2, 129.8, 129.6, 128.68, 128.65, 128.4, 127.4, 126.7, 125.5, 125.4, 125.2, 123.2. HRMS (FAB) m/z: calcd for C₄₉H₃₂N₃O₅S₂: 806.1783; [M+H]⁺ found: 806.1773.

2.2.22 4,4'-((4-(8-(5'-(2,2-dicyanovinyl)-[2,2'-bithiophen]-5-yl)-2,3-diphenylquinoxalin-5-yl) phenyl) azanediyl)dibenzoic acid (EH170)

To a 50-mL flask containing **28** (100 mg, 0.15 mmol) and malononitrile (10 mg, 0.15 mmol) was added 20 mL DCM and 15 mL EtOH. The solution was stirred at room temperature for 2 h. Subsequently, the mixture was concentrated to ~5mL followed by adding large amount of hexane to crash a red solid. The dark red solid was collected, washed with hexane, and dried under vacuum to afford **EH170** (74 mg, 70%). ¹H NMR (600 MHz, DMSO-*d*₆, ppm): δ = 8.46 (s, 1H), 8.38 (d, *J* = 7.8 Hz, 1H), 7.95 (s, 1H), 7.88-7.84 (m, 6H), 7.74 (s, 1H), 7.64 (d, *J* = 7.2

Hz, 2H), 7.59 (s, 1H), 7.51 (d, J = 7.2 Hz, 2H), 7.48 (s, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.41-7.37 (m, 2H), 7.33-7.30 (m, 3H), 7.18 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 8.4 Hz, 4H). ¹³C NMR (150 MHz, DMSO- d_6 , ppm): $\delta = 167.2$, 152.4, 152.1, 151.3, 150.7, 149.2, 145.8, 143.1, 140.3, 138.9, 138.4, 138.2, 138.0, 137.9, 136.1, 134.0, 133.6, 132.6, 131.5, 130.7, 130.2, 130.1, 130.0, 129.8, 129.6, 128.8, 128.6, 128.2, 127.5, 127.1, 125.6, 125.2, 125.0, 123.2, 115.3, 114.5, 73.8. HRMS (MALDI) m/z: calcd for C₅₂H₃₂N₅O₄S₂: 854.1890; [M+H]⁺ found: 854.1899.

2.3 Solar cell device fabrication and measurements

For the preparation of nickel oxide film, the nickel oxide paste prepared by mixing 1 g of NiO, 2.7 mL ethanol, 0.342 g ethyl acetate, and 6 mL α -terpinol for each powders and then nickel oxide film was made using doctor blade method with two steps on FTO glass and sintered at 450 °C for 30 minutes. The film thickness and working area of each working electrodes were measured by a surface profilometer. Then the prepared NiO films were soaked in a 0.3 mM dye solution for 24 h. Platinized counter electrode was prepared by spraying H₂PtCl₆ on predrilled and cleaned FTO glass, followed by drying at 70 °C and sintered at 500 °C for 1 h. The dyed NiO working electrode was assembled face-to-face with platinized counter electrode in the presence 30 μ m surlyn outside the hole. The electrolyte was injected through the hole and covered with a microscopic glass and surlyn. The electrolyte is a combination of 0.6 M DMPII, 0.03 M I₂, 0.1 M GuSCN, 0.5 M TBP, and 0.05 M LiI in a dry acetonitrile. The amount of dye loading was determined by desorption of adsorbed dye on NiO with DMF. The concentration of dye in the desorption solution was determined by absorption spectrophotometry.

3. Results and Discussion

3.1 Synthesis and characterization of surfactant mediated nickel oxide photocathode materials

Here we used the cationic surfactant, DTAB, which has not been reported previously for the synthesis of nickel oxide. The synthetic procedures are shown in Scheme 1. Hexahydrate nickel (II) chloride (NiCl₂•6H₂O) was stirred with DTAB in a basic solution following the literature procedure with modifications [42]. The green nickel hydroxide, Ni(OH)₂, was collected by centrifugation. The desired nickel oxide nanoparticles were obtained after calcination. The powder X-ray diffraction (PXRD) patterns of nickel oxide nanoparticles prepared without and with DTAB as the surface-active agent are plotted in Fig.2. It can be seen that both samples show the same XRD patterns with high crystallinity. There exist five diffraction peaks at 2θ position of 37.1, 43.4, 62.7, 76.5, and 79.3°, which are indexed to (111), (200), (220), (311), and (222) of the cubic nickel oxide, respectively.



Fig. 2. XRD patterns for the nickel oxide nanoparticles prepared with and without DTAB.

80

60

20

40

Angle/20

The SEM images of the as-synthesized NiO nanoparticles without and with DTAB do not exhibit significant difference in their particle uniformity (Fig. S1). However, very distinct results were obtained in their annealed films. Fig. 3 shows the SEM images of NiO films prepared without (a, c) and with DTAB (b, d) on an ITO conductive substrate acquired from a top (a, b) and a cross-section view (c, d). From the top-view images, the NiO film in (a) formed with apparently smaller agglomerates of NiO nanoparticles compared with those on the film in (b). It indicates that the energy from input heat for preparation of a NiO film easily overcame interparticle affinity, and hence drove lateral diffusion of NiO nanoparticles without DTAB. Conversely, the existence of DTAB elevates inter-particle affinity so as to result in big chunks of NiO nanoparticle assemblies. From the cross-section images, it is clear in both cases that a thin annealed NiO films were formed homogeneously at the interfaces between ITO substrates and NiO chunks. The result infers the strong interaction between NiO and ITO. On the base film, agglomerates of NiO nanoparticles are short without DTAB and tall with DTAB, corresponding with those in top-view images. Hence, it is very likely the big NiO chunks came from DATBmodified surface property before annealing. Such difference by treating with DTAB induces rough surface morphologies of annealed NiO film that increases dye-loading quantity (Table 1). It is well known that the short-circuit current density is highly determined by the initial number of photo-generated charges. Here, the initial number of photo-generated charges could be significantly affected by differently structured films where the amount of light-harvesting dyes is different. The amount of dye adsorbed on nickel oxide surfaces was determined using UV-vis absorption spectroscopy and estimated to be 17.9 and 11.6 nmolcm⁻² for DTAB treated and untreated NiO, respectively, with Coumarin 343 (C343) as the p-type sensitizer (Table 1). The increase in dye loading originated from morphology difference of the DTAB assisted synthesis of nickel oxide nanoparticles which is responsible for enhancing the number of photo-generated charges.



Fig. 3. SEM images with the top views (a, b) and cross-section views (c, d) of NiO surfaces. NiO prepared without (a, c) and with DTAB (b, d).

Different physical parameters of nickel oxide nanoparticles including Fermi level, average particle size, and surface area are collected in Table 1. The Fermi level of the NiO nanoparticles was determined from the work function measurement of the thin film. The average particle size of nickel oxide nanoparticles estimated from SEM images from Figure S1 is about 12 nm for nickel oxide prepared from surfactant-assisted synthesis whereas the NiO particles prepared without surfactant are not well dispersed due to the agglomeration. DTAB-assisted synthesis of nickel oxide film resulted in enhanced dye loading by about 35% which leads to improved light harvesting ability.

Parameters	NiO	NiO-DTAB
Work function /eV from vacuum level	5.3	5.3
Dye loading/nmol cm ⁻²	11.6	17.9
Surface area, BET (m^2/g)	41.5	56.8
		Y

Table 1. Physical Parameters of Nickel Oxide Nanoparticles

The influence of DTAB on the different oxidation states of nickel in nickel oxide and the defect site on oxygen was studied by XPS spectra as illustrated in Fig. 4, which plotted at the Ni 2p and O 1s edge. All three satellites with fitting at the binding energy indicated in the inset of Fig. 4 in both samples are characteristic peaks of Ni²⁺ and Ni³⁺ oxidation states in NiO thin films [24]. This result confirms the addition of DTAB does not significantly affect the oxidation state of nickel in nickel oxide because the binding energies of the satellites are numerically close. Energy dispersive X-ray spectroscopy (EDS) data was also studied for further elemental analysis. The percentage atomic composition of nickel and oxygen in two materials is shown in Fig. 5. It turns out that the compositions of NiO nanoparticles with and without DTAB are pretty consistent, indirectly confiming the auxiliary role of DTAB only to assist the dispersion of nanoparticles.



Fig. 4. XPS study nickel oxide samples synthesized with and without DTAB.at the Ni 2p, O 1s edge



Fig. 5. EDS of nickel oxide samples synthesized with and without DTAB.

3.1.1 p-DSSC Performance Study

The newly synthesized NiO was evaluated as the photocathode material for p-DSSC. The photocurrent density versus photovoltage curve and the corresponding IPCE plots of the devices sensitized with C343 are shown in Fig.6 for both NiO nanoparticles. Among the two, the device with NiO prepared with DTAB produced better photocurrent density, photovoltage, and fill factor than the other. The DTAB-assisted synthesized NiO film with C343 achieved higher power conversion efficiency of 0.0418%, with a short-circuit current density (J_{sc}) of 0.963

mAcm⁻² and an open circuit potential (V_{oc}) of 121 mV. The detailed photovoltaic data are summarized in Table 2.



Fig. 6. (a) Current voltage characteristic curves and (b) IPCE plots for p-DSSCs sensitized by C343 for two different NiO films

	C343 (NiO)	C343 (NiO-DTAB)
$V_{ m oc}/{ m V}$	0.112	0.121
$J_{\rm sc}/{\rm mAcm}^{-2}$	0.621	0.963
FF	0.364	0.359
η (%)	0.0253	0.0418

Table 2. Photovoltaic Performance of p-DSSCs Sensitized by C343^a

^a The cells were composed of 4 μ m thick NiO. The electrolyte used was a mixture of 0.6 M DMPII, 0.03 M iodine, 0.1 M GuSCN, 0.5 M TBP and 0.05 M LiI in a dry acetonitrile.

Fig. 7 displays the results of intensity-modulated photovoltage spectroscopy (IMVS) measurements (a) and charge extraction analysis (b) to assess the detail information of the hole lifetime, Fermi level with photovoltage and also the hole density [55]. The results in Fig. 7(a) show that the hole lifetime in NiO nanoparticle prepared using DTAB is longer than that prepared without DTAB. The charge concentration as a function of open-circuit potential induced by various illumination intensities is shown in Fig. 7(b), in which the hole density of

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NiO film prepared with DTAB is higher than that prepared without DTAB. It is clearly demonstrated here that the NiO prepared from morphology-directing surfactant does produce more effective photocathode than the one with unmodified NiO.



Fig. 7. (a) Hole lifetime versus open circuit voltage and (b) charge density versus open circuit voltage

3.2 Design and Synthesis of Organic Dyes

Six new organic dyes with a general D-A- π -A framework were designed with the carboxylic acid as the anchoring group, triphenylamine as the electron donor, 2,3-diphenylquinoxaline as the auxiliary acceptor moiety, 2-methylenemalononitrile as the electron acceptor and various thiophene derivatives as the π -spacers. These dyes are classified into two categories: the mono-anchoring dyes (EH122, EH166, and EH174) and di-anchoring dyes (EH126, EH162, and EH170). The detail synthetic procedures are illustrated in Scheme 2 whereas for compounds 5, 7, TPA1 and TPA2 reported in supporting information (Scheme S1). In general, the synthesis of these dipolar organic dyes involved multiple synthetic steps including bromination, Miyaura borylation, condensation, and Suzuki coupling [53, 54, 56]. The purity and identity of these dyes were fully characterized by NMR spectroscopy and high-resolution mass spectrometry.



Scheme 2: Synthetic strategy of sensitizers': EH122, EH126, EH162, EH166, EH170 and EH174 Reagents and conditions: a, d, f, i) Pd(PPh₃)₂Cl₂, Na₂CO₃, THF:H₂O (4:1), reflux, 8 h; b, e) DMF, POCl₃, CH₂Cl₂, 65 °C, 8 h; c) Pd(OAc)₂, Na₂CO₃, DMF, reflux, 8 h; g, j) LiOH, THF:MeOH:H₂O (5:1:1), reflux, 8 h; h, k) pepperdine, malononitrile, CH₂Cl₂, rt, 2 h.

3.2.1 Photophysical and Electrochemical Properties

The UV-vis absorption spectra of all six sensitizers in DMF solutions and adsorbed on NiO films are depicted in Fig.8 and the data are summarized in Table 3. In general, the spectral coverages for all six new dyes reach nearly 600 nm. Two absorption bands were observed in solution for each case (Fig. 8(a)). The absorption band between 290-370 nm is assigned to a π - π *

transition and the other band located in the visible region between 450-600 nm is attributed to an intramolecular charge-transfer (ICT) transition. The extinction coefficients of mono-anchoring dyes (EH174, EH122 and EH166) are greater than those of with double anchoring groups (EH126, EH162 and EH170). EH174 and EH166 with the bithiophene and EDOT π -linkers, respectively, exhibited the molar extinction coefficients over 40000 M⁻¹ cm⁻¹ on both bands, signifying their excellent light harvesting ability. The absorption bands become broad over the range from 400 to 650 nm when these dyes are adsorbed onto NiO film indicative of some degree of dye aggregation on NiO surface. The optical band gaps (E_{0-0}) of all the new sensitizers were determined by the intersection of normalized absorption and emission spectra. The band gaps of EH dyes are comparable and ranged from 2.15-2.24 V as shown in Table 3.



Fig. 8. (a) UV-Vis absorption spectra of EH dyes in DMF solutions and (b) adsorbed on nickel oxide films.

Dye	λ_{max} , nm ($\varepsilon \times 10^4$, M ⁻¹ cm ⁻¹)	$\lambda_{em}^{}$, nm	E_{0-0} , eV^b
EH122	323 (5.41), 474 (3.40)	711	2.15
EH126	323 (3.61), 468 (1.84)	657	2.24
EH166	315 (5.53), 497 (4.59)	660	2.19
EH162	322 (3.85), 487 (2.31)	652	2.21
EH174	345 (8.36), 474 (4.38)	660	2.22
EH170	338 (3.32), 501 (2.22)	653	2.17

Table 3. Photophysical Parameters of EH Dyes^a

^{*a*} The absorption and emission spectra were measured in DMF solutions. ^{*b*} E_{0-0} was calculated

from the intersection of normalized absorption and emission spectra ($E_{0-0} = 1240 / \lambda$).

Cyclic voltammograms of six dyes were measured in DMF solutions to access the relative energy levels and feasibility of hole injection from the excited dyes into the valence band of NiO and electron transfer from the reduced dyes to redox couples in the electrolyte. The details of electrochemical parameters such as oxidation potential (E_{ox} (S⁺/S)), reduction potential (E_{red} (S/S⁻)), and exited state reduction potential ($E_{red}*(S*/S^-)$) are summarized in Table 4. The relative energy levels of all sensitizers, the valence band position of nickel oxide, and the redox mediator are depicted in Fig.9. The potential differences between the Fermi level of NiO and the HOMOs of sensitizers range from 0.89 to 1.03 V indicative of a sufficient driving force for hole injection. The high energy levels of LUMOs of these dyes also ensure favorable dye regeneration.

Dye	$E_{\mathrm{ox}}(\mathrm{S}^{+}/\mathrm{S}),\mathrm{V}$	$E_{\rm red}({\rm S/S}^{-}), {\rm V}$	$E_{\rm red}^*, V^b$
EH122	1.27	-0.70	1.45
EH126	1.32	-0.70	1.54
EH166	1.28	-0.67	1.52
EH162	1.18	-0.62	1.59
EH174	1.13	-0.68	1.54

Table 4. Electrochemical Potentials of EH Dyes^a

1.02

EH170

^{*a*} Oxidation potential ($E_{ox}(S^+/S)$) and reduction potential ($E_{red}(S/S^-)$) were measured in DMF solutions with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The potentials were calibrated with ferrocene/ferrocenium vs NHE. ^{*b*} The excited-state reduction potential (E_{red}^*) was calculated by $E_{red}(S/S^-) + E_{0-0}$

1.48

-0.69



Fig. 9. The energy levels of EH-series sensitizers relative to the valence band potential of nickel oxide and oxidation potential of the redox mediator

3.2.2 Theoretical Calculations

Theoretical studies based on density functional theory (DFT) calculations using the Gaussian 09 [57] program package at the mPW1K[58]/6-31G*[59] level of theory were carried out in the SMD [60] solvation model (DMF) for the six dyes to construct their geometries. The electron density difference maps of S_0 to S_1 and S_0 to S_2 transitions for the six dyes obtained by time-dependent density functional theory (TD-DFT) were calculated and the results are presented in Fig. 10. The molecular orbitals of HOMO and LUMO were depicted in Fig. S2 in supplementary information. The calculated absorption spectra and the transitions involved are also summarized in Figure S3 and Table S1 in supplementary information. The electron density of the HOMOs is mostly localized on the triphenylamine donor moiety with some charge diffusion towards the quinoxaline moiety, whereas the electron density of the LUMOs is delocalized from quinoxaline to the π -spacer and 2-methylenemalononitrile acceptor. Upon light excitation, the hole generated from charge transfer transition would be effectively injected into the valence band of NiO via the terminal anchoring groups. Sensitizers with bithiophene and thiophene π -spacers showed better charge separation than EDOT π -spacer resulted from the presence of less electron-rich group capable of facilitating charge separation. For the monoanchoring sensitizers, EH122 and EH174, the electron densities in the auxiliary fragments

(diphenylquinoxaline) further shift to the acceptor group. As a result, **EH122** and **EH174** have less charge retention on the 2,3-diphenylquinoxaline that results in a significant charge separation.





Fig. 10. Geometry-optimized structures of the six new dyes and the electron density distributions of frontier molecular orbitals from TD-DFT calculations. The yellow and red colors represent increase of electron density and decrease of electron density, respectively.

3.2.3 Photovoltaic Performance

The performances of p-DSSCs sensitized with six new dyes using DTAB mediated nickel oxide nanoparticles as photocathode and I^{-}/I_{3}^{-} as the redox couple were measured under standard AM 1.5G condition (100 mWcm⁻²). The photocurrent density/voltage curves and the incident photon-to-electron conversion efficiency (IPCE) plots for the DSSCs sensitized by six dyes are depicted in Fig. 11. The detailed photovoltaic data are summarized in Table 5. The device sensitized by the standard p-type sensitizer, P1, measured under the same experimental conditions is also included for comparison purpose [61]. In general, the mono-anchoring dyes displayed higher short-circuit current density (J_{sc}) , likely due to the nearly twice as high as the molar extinction coefficients than their corresponding di-anchoring congeners. Sensitizers with bithiophene linker showed slightly larger open-circuit photovoltage (V_{oc}) than dyes with thiophene and EDOT linkers. Among the dyes investigated, the p-DSSC sensitized by EH174 with a bithiophene π -linker and with one anchoring group exhibits the highest power conversion efficiency of 0.207% with a J_{sc} of 4.84 mAcm⁻², a V_{oc} of 0.137 V and a fill factor of 0.312. Whereas the EH162 with an EDOT π -linker and double anchoring groups displays the lowest cell performance of all. The cell performance follows the order of EH174 > EH122 > EH170 > **EH126** > **EH166** > **EH162**. The recorded IPCE values are over 25% between 450-550 nm for dyes EH174 and EH122. The higher photocurrent densities from devices sensitized by EH174 and EH122 than others can be considered the results of higher effective chromophores adsorbed on NiO. The amount of dye adsorbed on NiO for the mono-anchoring dyes is comparable to that of bi-anchoring dyes despite the larger molecular sizes of the mono-anchoring dyes. In other words, a more compact dye block layer on NiO for mono-anchoring dyes than their respective bi-anchoring dyes is expected, which may contribute to more effective suppression of the charge recombination between the injected holes and the reduced form of redox mediators. The photovoltages of devices sensitized by EH sensitizers follow the order of EH170~EH174~EH122 > EH166 > EH126 > EH115. A similar trend for the dark current was also recorded.



Fig. 11. (a) Current voltage characteristic curves and (b) IPCE plots of p-DSSCs sensitized by EH dyes

Sensitizers	$V_{\rm oc}/{ m V}$	J _{sc} /mAcm ⁻²	FF	η (%)	Dye loading, nmolcm ⁻²
EH122	0.134±0.005	4.39±0.05	0.303±0.004	0.178±0.020	31.4
EH126	0.122±0.006	3.93±0.02	0.304±0.003	0.146±0.006	37.4
EH166	0.131±0.003	3.47±0.01	0.284±0.003	0.129±0.005	22.1
EH162	0.115±0.006	1.79±0.02	0.304±0.007	0.062±0.004	34.3
EH174	0.137±0.008	4.84±0.03	0.312±0.006	0.207±0.014	29.4
EH170	0.139±0.012	3.47±0.03	0.315±0.007	0.152±0.007	29.1
P1	0.123	2.57	0.294	0.093	

Table 5. Photovotaic Parameters of the EH Dyes^a

^a The cells were composed of 4 μ m thick NiO. The electrolyte used is a mixture of 0.6 M DMPII, 0.03 M iodine, 0.1 M GuSCN, 0.5 M TBP and 0.05 M LiI in a dry acetonitrile. Dye solutions prepared as: **EH122** and **EH166** in DCM and the other four dyes in THF/DCM (1:4, v/v) mixed solution.

IMVS measurment and charge extraction analysis were carried out to evaluate the involvement of fermi level position of NiO and the charge density of the device upon the opencrcuit potential for each new dyes. Fig.12(a) presented hole lifetime versus open-circuit voltage. The longer hole lifetime specifies that the charge recombination by hole transfer from the injected hole in NiO film to the reduced redox mediator is well surpressed. The hole lifetimes decreased in the order of EH174 > EH122 > EH170 > EH166 > EH126 > EH162. The order of hole lifetime correlates well with the results from dark current measurements. The hole density as a function of photovoltage at various illumination intensities is shown in Fig. 12(b). At the same V_{oc} value, the hole density trend follows the order of EH174 > EH122 ≈ EH160 > EH126 > EH122 ≈ EH166 > EH126 > EH122 ≈ EH166



Fig. 12. (a) Hole lifetime versus open circuit voltage. (b) Charge density versus open circuit voltage

3.2.4 Long-term Stability Test

The long-term durability of the p-type devices were evaluated based on the two best performance dyes EH174 and EH122. The results are collected in Fig.13. The long-term

stability of the devices were carried out by continuous light soaking (100 mWcm⁻²) at 45 °C for 120 h. The photocurrent showed initial increase at the first 24-36 h followed by slow decay to reach steady values after 60 h. The fill factor showed a minor but steady enhancement up to 120 h whereas the devices displayed a trend of continuous photovoltage loss. The overall performance of device sensitized by dye EH122 remained at the same level after 120 h while the device sensitized by dye EH174 showed 6% efficiency drop. Based on these results, one could conclude that the p-type DSSCs sensitized by the EH sensitizers are promising with good long-term durability.



Fig. 13. Long-term stability test of p-DSSC devices based on dyes **EH122** and **EH174** measured under continuous light soaking (100 mWcm⁻²) at 45 °C.

4. Conclusion

In this work, we developed DTAB assisted synthesis of nickel oxide nanoparticles for photocathode material of p-DSSCs. The XRD pattern confirmed the cationic surfactant/DTAB

does not affect the nature of NiO and showed the same pattern at 20 values with the NiO synthesized in the absence of DTAB. The higher surface area of the NiO prepared by the surfactant-mediated synthesis directly attributes to a larger dye loading and better light harvesting ability. Six new organic sensitizers based on a D-A- π -A framework were designed to evaluate the newly developed surfactant-mediated synthesis of NiO as the photocathode material for p-DSSCs. Sensitizers with mono-anchoring group (EH166, EH122, and EH174) performed better than their corresponding double-anchoring sensitizers (EH162, EH126, and EH170). The electron density distributions of frontier molecular orbitals from TD-DFT calculations suggest that sensitizers with less electron-rich π -spacer neighboring to the acceptor group exhibit better charge separation which is beneficial for hole injection to the valance band of nickel oxide. Among the dyes investigated, the p-DSSC sensitized by EH174 with a bithiophene π -linker and with one anchoring group produced the highest power conversion efficiency of 0.207% with a J_{sc} of 4.84 mAcm⁻², a V_{oc} of 0.137 V and a fill factor of 0.312. The high molar extinction coefficient of EH174 and low dark current in the device all contribute to the promising conversion efficiency. The current results indicate that the combination of electron-deficient quinoxaline motif with suitable π -linker in a D-A- π -A molecular structure is a promising design of p-type sensitizers for NiO-based p-DSSCs.

Acknowledgments

We thank Ministry of Science and Technology of Taiwan, Academia Sinica (AS-KPQ-106-DDPP) and National Tsing Hua University for support of this research. H. D. W. is grateful for the fellowship supported by Taiwan International Graduate Program of Academia Sinica under the program of Molecular Science and Technology. We specially thank Ms. Mei-Ying Chung for carrying out the SEM analyses.

Appendix A. Supplementary Information

Supplementary data of this articles also included in supporting information section.

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Supporting Information

New 2,3-Diphenylquinoxaline Containing Organic D-A- π -A Dyes with

Nickel Oxide Photocathode Prepared by Surfactant-Mediated Synthesis

for High Performance p-type Dye-Sensitized Solar Cells

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Scheme S1. Synthetic procedures of precursors

Table S1. Calculated excitation energy, oscillator strength, and transitions involved for the low-lying excited states of EH series dyes

Fig. S1. SEM Images of nickel oxide nanoparticles without (A) and with (B) DTAB

Fig. S2. The electron density distributions of frontier molecular orbitals from TD-DFT calculations

Fig. S3: Calculated UV-Vis absorption spectra of the **EH** dyes in DMF solution. Red vertical lines represent the calculated singlet excitation energies

Fig. S4. ¹H NMR spectrum of compound Q-BT in CDCl₃

Fig. S5. ¹³C NMR spectrum of compound **Q-BT** in CDCl₃

Fig. S6. ¹H NMR spectrum of compound Q-EDOT in CDCl₃

Fig. S7. ¹³C NMR spectrum of compound Q-EDOT in CDCl₃

Fig. S8. ¹H NMR spectrum of compound 12 in CDCl₃

Fig. S9. ¹³C NMR spectrum of compound 12 in CDCl₃

Fig. S10. ¹H NMR spectrum of compound TPA1 in CDCl₃

Fig. S11. ¹³C NMR spectrum of compound TPA1 in CDCl₃

Fig. S12. ¹H NMR spectrum of compound 17 in CDCl₃

Fig. S13. ¹³C NMR spectrum of compound 17 in CDCl₃

Fig. S14. ¹H NMR spectrum of compound 18 in CDCl₃

Fig. S15. ¹³C NMR spectrum of compound 18 in CDCl₃

Fig. S16. ¹H NMR spectrum of compound EH122 in CDCl₃

Fig. S17. ¹H NMR spectrum of compound 19 in CDCl₃

Fig. S18. ¹³C NMR spectrum of compound 19 in CDCl₃

Fig. S19. ¹H NMR spectrum of compound **20** in DMSO- d_6

Fig. S20. ¹³C NMR spectrum of compound 20 in DMSO- d_6

- Fig. S21. ¹H NMR spectrum of compound EH126 in DMSO-*d*₆
- Fig. S22. ¹H NMR spectrum of compound 21 in CDCl₃
- Fig. S23. ¹³C NMR spectrum of compound 21 in CDCl₃
- Fig. S24. ¹H NMR spectrum of compound 22 in CDCl₃
- Fig. S25. ¹³C NMR spectrum of compound 22 in CDCl₃
- Fig. S26. ¹H NMR spectrum of compound EH166 in CDCl₃
- Fig. S27. ¹H NMR spectrum of compound 23 in CDCl₃
- Fig. S28. ¹³C NMR spectrum of compound 23 in CDCl₃
- **Fig. S29.** ¹H NMR spectrum of compound **24** in DMSO- d_6
- **Fig. S30.** ¹³C NMR spectrum of compound **24** in DMSO- d_6
- **Fig. S31.** ¹H NMR spectrum of compound **EH162** in DMSO- d_6
- Fig. S32. ¹H NMR spectrum of compound 25 in CDCl₃
- Fig. S33. ¹³C NMR spectrum of compound 25 in CDCl₃
- Fig. S34. ¹H NMR spectrum of compound 26 in CDCl₃
- Fig. S35. ¹H NMR spectrum of compound EH174 in DMF- d_7
- Fig. S36. ¹³C NMR spectrum of compound EH174 in DMF- d_7
- Fig. S37. ¹H NMR spectrum of compound 27 in CDCl₃
- Fig. S38. ¹³C NMR spectrum of compound 27 in CDCl₃
- **Fig. S39.** ¹H NMR spectrum of compound **28** in DMSO- d_6
- Fig. S40. ¹³C NMR spectrum of compound 28 in DMSO- d_6
- Fig. S41. ¹H NMR spectrum of compound EH170 in DMSO-*d*₆
- Fig. S42. ¹³CNMR spectrum of compound EH170 in DMSO-*d*₆



Scheme S1. Synthetic procedures of compounds: 5,6,7, TPA1 and TPA2



Fig. S1. SEM Images of nickel oxide nanoparticles without (A) and with (B) DTAB, both display monodispersive particle sizes





Fig. S2. The electron density distributions of frontier molecular orbitals from TD-DFT calculations.

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dye	excited state	composition ^a	λ_{cal} , nm	f^{b}
FH122	\mathbf{S}_1	$H-1 \rightarrow L+1 (16\%), H \rightarrow L (70\%)$	434	1.03
E11122	S_2	$H-1 \rightarrow L (18\%), H \rightarrow L+1$ (68%)	421	1,18

lying excited states of EH series dyes

EH126	S_1	H-1 → L+1 (30%), H → L (63%)	414	1.18
	S_2	H-1 \rightarrow L (56%), H \rightarrow L+1 (21%)	356	0.40
FH162	S_1	H-1 → L+1 (33%), H → L (62%)	439	1.12
EH102	S_2	H-1 → L (55%), H → L+1 (26%)	368	0.02
ги166	S_1	H-1 → L+1 (24%), H → L (62%)	455	1.93
EH100	S_2	H-1 → L (11%), H → L+1 (56%)	442	0.49
FH17 0	\mathbf{S}_1	$\begin{array}{c} \text{H-1} \rightarrow \text{L+1} \ (49\%), \ \text{H} \rightarrow \text{L} \\ (45\%) \end{array}$	450	1.82
EIII70	S_2	$H-1 \rightarrow L (35\%), H \rightarrow L (28\%), H \rightarrow L+1 (27\%)$	371	0.03
FH17 <i>1</i>	S_1	$H-2 \rightarrow L (20\%), H-1 \rightarrow L+1 (36\%), H \rightarrow L (36\%)$	457	2.06
E111/4	S_2	$H-2 \rightarrow L+1 (22\%), H-1 \rightarrow L (39\%), H \rightarrow L+1 (33\%)$	450	1.68

^a H = HOMO, L = LUMO ^b Oscillator strength





Fig. S3: Calculated UV-Vis absorption spectra of the **EH** dyes in DMF solution. Red vertical lines represent the calculated singlet excitation energies.





Fig. S3. ¹³C NMR spectrum of compound Q-BT in CDCl₃



Fig. S5. 13 C NMR spectrum of compound Q-EDOT in CDCl₃



Fig. S7. ¹³ C NMR spectrum of compound 12 in CDCl₃



Fig. S9. ¹³C NMR spectrum of compound TPA1 in CDCl₃





Fig. S11. ¹³C NMR spectrum of compound 17 in CDCl₃



Fig. S13. 13 C NMR spectrum of compound 18 in CDCl₃



Fig. S15. ¹H NMR spectrum of compound 19 in CDCl₃

Fig. S16. ¹³C NMR spectrum of compound 19 in CDCl₃



Fig. S18. ¹³C NMR spectrum of compound **20** in DMSO- d_6













Fig. S24. ¹H NMR spectrum of compound EH166 in CDCl₃



Fig. S26. ¹³C NMR spectrum of compound 23 in CDCl₃

Fig. S27. ¹H NMR spectrum of compound **24** in DMSO- d_6



Fig. S29. ¹H NMR spectrum of compound **EH162** in DMSO- d_6



Fig. S31. 13 C NMR spectrum of compound 25 in CDCl₃



Fig. S33. ¹H NMR spectrum of compound **EH174** in DMF- d_7



Fig. S35. ¹H NMR spectrum of compound **27** in CDCl₃



Fig. S37. ¹H NMR spectrum of compound **28** in DMSO- d_6



Fig. S39. ¹H NMR spectrum of compound **EH170** in DMSO- d_6



Fig. S40. ¹³C NMR spectrum of compound EH170 in DMSO- d_6

Highlights

- 1. A surfactant-mediated synthetic protocol for NiO nanoparticles used for the photocathode material of p-type dye-sensitized solar cells were developed.
- 2. The NiO prepared by surfactant-mediated synthesis exhibited higher surface area than the one prepared by conventional method.
- 3. A much better efficiency improvement of the p-type dye-sensitized solar cells with newly developed NiO nanoparticles as the photocathode materials.
- 4. New organic dyes with a D-A- π -A structural framework were designed for p-type sensitizers for p-type dye-sensitized solar cells with best performance up to 0.207%.