SUPPORTING INFORMATION

Enhanced Photocurrent Density by Spin-Coated NiO Photocathodes for N-annulated Perylene Based p-Type Dye-Sensitized Solar Cells

Xing Li, [a] Fengtao Yu, [a] Sebastian Stappert, [b] Chen Li, [b] Ying Zhou, [a] Ying Yu, [a] Xin Li, [c*] Hans Ågren, [c] Jianli Hua [a*] and He Tian [a]

[a] *Key Laboratory for Advanced Materials, Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science & Technology, 130 Meilong Road, Shanghai, 200237, PR China. Fax: 8621-64250940.*

[b] *Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany*

[c] *Division of Theoretical Chemistry and Biology, School of Biotechnology, KTH Royal Institute of Technology, SE-10691 Stockholm, Sweden*

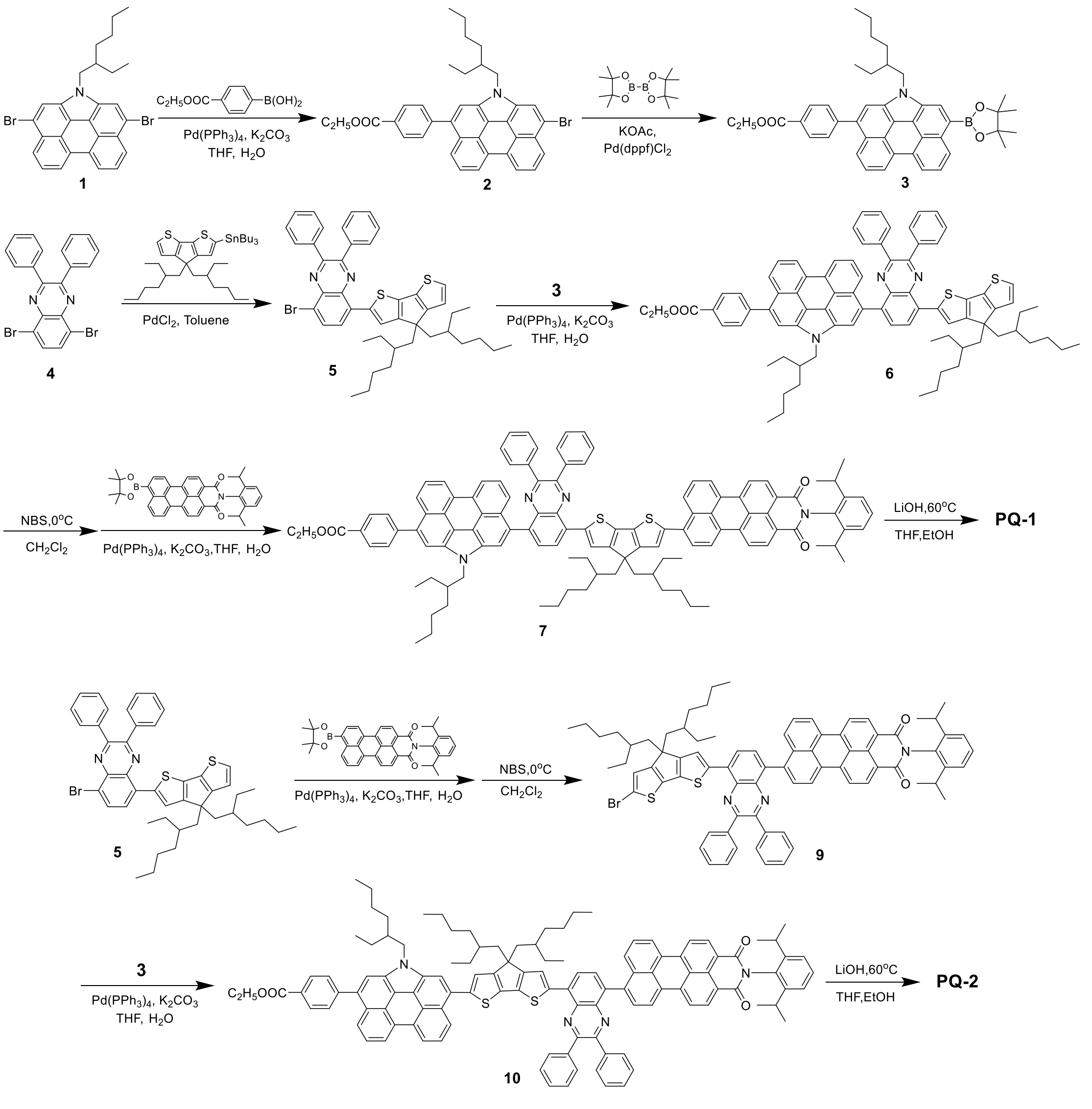
Email: jlhua@ecust.edu.cn (J.H.); lixin@theochem.kth.se (X.L.)

S1. Experimental Section

Materials

N-annulated perylene (1)[1], 5,8-dibromo-2,3-diphenylquinoxaline (4)[2] and 9-pinacolboronicester-(2,6-diisopropylphenyl)perylenemonoimide[3] were synthesized according to published procedures. All chemicals and solvents were purchased from commercial sources and were used without further purification.

Synthesis



Scheme S1. Synthetic Route of the PQ-1 and PQ-2 Dyes

Synthesis of **2**. Under an argon atmosphere, compound **1** (690 mg, 1.32 mmol),

K_2CO_3 (5 mL, 2 M aqueous solution) and $Pd(PPh_3)_4$ (42 mg, 0.036 mmol) were dissolved in 20 mL of THF. After stirring for half an hour, the mixture was heated to 50 ^{o}C and a solution of [4-(ethoxycarbonyl)phenyl]boronic acid (257 mg, 1.32 mmol) in THF (5 mL) was added slowly. The mixture was then refluxed for 4 h before cooling to room temperature and extracted with CH_2Cl_2. The organic layers were washed with brine water and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with PE/CH_2Cl_2 (4/1−2/1, v/v) as eluent to give compound **2** (280 mg, 36 % yield). ^{1}H NMR(400 MHz,$CDCl_3$, ppm): δ = 8.43 (d, *J* = 8.4 Hz, 2H), 8.31 (d, *J* = 8.2 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.2 Hz, 1H), 8.01-7.98 (m, 2H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 4.71 (d, *J* = 8.4 Hz, 2H), 4.76 (q, *J* = 8.4 Hz, 2H), 2.31-2.28 (m, 2H), 1.33-1.29 (m, 6H), 1.25-1.20 (m, 3H), 0.95 (t, *J* = 8.4 Hz, 2H), 0.95 (t, *J* = 8.4 Hz, 3H), 0.80 (t, *J* = 8.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 166.71, 147.22, 137.69, 133.20, 132.93, 131.25, 130.78, 130.46, 128.56, 126.56, 126.06, 125.34, 125.02, 122.75, 122.60, 121.88, 118.73, 118.09, 115.91, 61.58, 50.32, 41.96, 31.34, 24.79, 23.70, 14.68, 14.24, 11.07.

Synthesis of **3**. Under an argon atmosphere, compound **2** (500 mg, 0.82 mmol) and bis(pinacolato)diboron (270 mg, 1.06 mmol) were mixed together with potassium acetate(245 mg, 2.5 mmol) in 20 mL of dioxane. Then Pd(dppf)Cl_2 (44 mg, 0.1 mmol) was added, and the reaction mixture was stirred under argon atmosphere for 3 h at 70 °C. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 and washed twice with water. The CH_2Cl_2 layer was separated and dried over $MgSO_4$, and the crude product was purified by column chromatography with PE/CH_2Cl_2 (3/1−2/1, v/v) as eluent to give compound **3** (390 mg, 60 % yield). ^{1}H NMR(400 MHz,$CDCl_3$, ppm): δ = 9.02 (d, *J* = 8.4 Hz, 1H), 8.70 (dd, *J* = 4.2 Hz, *J* = 4.2 Hz, 2H), 8.46 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 8.4 Hz, 1H), 7.82-7.75 (m, 4H), 4.69-4.58 (m, 2H), 4.47 (q, *J* = 8.4 Hz, 2H), 2.29-2.26 (m,1H), 1.51(s, 12H), 1.48-1.45(m, 4H), 0.94 (t, *J* = 8.4 Hz, 3H), 0.86 (t, *J* = 8.4 Hz, 3H).

Synthesis of **5**. Under an argon atmosphere, compound **4** (450 mg, 1.02 mmol) and $PdCl_2$ (18 mg, 0.1 mmol) were dissolved in 20 mL of toluene. After stirring for half an hour, the mixture was heated to 50 °C and a solution of 1.5 mmol CPDT-tributylstannane in toluene (5 mL) was added slowly. The mixture was then refluxed for 6 h before cooling to room temperature, adding 1 mL saturated salt solution and extracted with CH_2Cl_2. The organic layers were washed with brine water and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with PE/CH_2Cl_2 (5/1−3/1, v/v) as eluent to give red compound **5** (165 mg, 21 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 1H), 7.97-7.94 (m, 1H), 7.79 (s, 1H), 7.74-7.67 (m, 4H), 7.44-7.35 (m, 6H), 7.19 (d, *J* = 4.4 Hz, 1H), 6.97 (dd, *J* = 4.4 Hz, *J* = 4.4 Hz, 1H), 1.98-1.87 (m, 4H), 1.39-1.25 (m, 2H), 1.01-0.90 (m, 16H), 0.75 (t, *J* = 8.8 Hz, 6H), 0.62-0.58 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 157.13, 153.19, 152.23, 141.88, 138.29, 137.73, 133.11, 130.51, 130.27, 129.31, 129.19, 128.33, 125.89, 125.06, 122.42, 121.86, 121.02, 53.44, 43.36, 35.09, 34.26, 34.12, 28.61, 28.58, 27.40, 22.80, 22.78, 14.10, 14.07, 10.71, 10.61. HRMS (m/z): [M+H$^+$] calcd for $C_{45}H_{50}BrN_2S_2$, 761.2599; found: 761.2607.

Synthesis of **6**. Under an argon atmosphere, compound **5** (420 mg, 0.55 mmol), K_2CO_3 (5 mL, 2 M aqueous solution) and $Pd(PPh_3)_4$ (42 mg, 0.036 mmol) were dissolved in 20 mL of THF. After stirring for half an hour, the mixture was heated to 50 ^oC and a solution of compound 3 (450mg, 0.69mmol) in THF (10 mL) was added slowly. The mixture was then refluxed for 6 h before cooling to room temperature and extracted with CH_2Cl_2. The organic layers were washed with brine water and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with PE/CH_2Cl_2 (3/1–2/1, v/v) as eluent to give red compound **6** (370 mg, 56 % yield). ^{1}H NMR(400 MHz,$CDCl_3$, ppm): δ = 8.76 (t, J = 8.8 Hz, 2H), 8.28 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 8.4 Hz, 1H), 8.10-8.08 (m, 1H), 8.03-8.02 (m, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.86-7.83 (m, 3H), 7.81-7.78 (m, 3H), 7.75-7.70 (m, 3H), 7.47-7.43 (m, 6H), 7.21 (d, J = 4.4 Hz, 1H), 7.12 (d, J = 8.8 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 4.62-4.60 (m, 2H), 4.48 (q, J = 8.4 Hz, 2H), 2.33-2.27 (m, 1H), 2.00-1.96 (m, 4H), 1.48 (t, J = 8.4 Hz, 3H), 1.29-1.25(m, 14H), 1.10-1.00(m, 12H), 0.81-0.78 (m, 9H), 0.67-0.64(m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 165.61, 146.05, 138.31, 137.41, 136.83, 135.45, 133.72, 131.54, 131.47, 129.44, 129.37, 128.90, 128.82, 128.44, 127.71, 127.45, 127.19, 126.73, 125.97, 125.11, 124.41, 124.21, 123.44, 122.96, 118.07, 109.63, 60.11, 53.25, 34.11, 33.84, 33.50, 30.91, 30.57, 30.41, 29.72, 29.16, 28.68, 28.68, 28.64, 28.41, 28.35, 27.57, 26.45, 25.89, 24.25, 23.11, 21.83, 21.67, 21.64, 13.41, 13.11, 9.81, 9.66. HRMS (m/z): [M+H$^+$] calcd for $C_{82}H_{84}N_3O_2S_2$, 1206.6005; found: 1206.6014.

Synthesis of **7**. Compound **6** (210 mg, 0.17 mmol) and N-bromosuccinimide (NBS) (35 mg, 0.2 mmol) were dissolved in anhydrous CH_2Cl_2 (30 mL) in an ice bath for 2 h. Then, a Suzuki coupling reaction was performed with 9-pinacolboronicester-(2, 6-diisopropylphenyl)perylenemonoimide by using a similar procedure to that of compound **6** to give an reddish black solid compound **7** (185 mg, 65 % yield). ^{1}H NMR (400 MHz,$CDCl_3$, ppm): δ = 8.77-8.74 (m, 2H),8.70-8.68 (m, 2H), 8.58-8.48 (m, 5H), 8.38 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 2H), 8.15-8.11 (m, 2H), 8.04 (d, *J* = 4.4 Hz, 1H), 8.00 (d, *J* = 4.4 Hz,1H), 7.92-7.90 (m, 1H), 7.86-7.78 (m, 8H), 7.73-7.69 (m, 1H), 7.48-7.45 (m, 4H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 4.4 Hz, 1H), 7.30-7.28 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.06-7.02 (m, 2H), 4.62-4.60 (m, 2H), 4.48 (q, *J* = 8.4 Hz, 2H), 2.82-2.76 (m, 2H), 2.31-2.26 (m, 1H), 2.11-2.07 (m, 4H), 1.48 (t, *J* = 8.4 Hz, 3H), 1.29-1.26 (m, 14H), 1.20 (d, *J* = 8.4 Hz,12H), 1.13-1.04 (m, 16H), 0.94-0.84 (m, 8H), 0.80-0.75 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 166.72, 164.04, 158.58, 157.37, 152.16, 151.56, 147.11, 146.82, 145.76, 145.49, 141.32, 140.67, 140.39, 139.86, 139.32, 138.92, 138.80, 137.48, 137.19, 137.14, 136.26, 136.20, 134.02, 133.09, 132.40, 132.29, 132.23, 131.95, 131.16, 130.82, 130.58, 130.46, 130.33, 129.99, 129.81, 129.48, 129.32, 129.16, 129.07, 129.02, 128.80, 128.72, 128.53, 128.50, 128.34, 128.30, 127.95, 127.31, 127.13, 126.67, 125.83, 125.05, 124.81, 124.69, 124.50, 124.41, 124.07, 123.73, 123.51, 121.67, 121.05, 120.84, 120.64, 120.23, 120.00, 119.14, 119.07, 117.29, 116.23, 114.30, 77.00, 61.09, 54.14, 49.75, 43.64, 41.28, 35.44, 35.37, 35.02, 34.91, 34.55, 33.86, 31.97, 31.55, 31.48, 30.90, 30.23, 30.17, 29.74, 29.70, 29.40, 29.22, 28.95, 28.80, 27.54, 24.11, 23.07, 22.94, 22.74, 14.49, 14.27, 14.23, 14.17, 14.06, 11.01, 10.96, 10.76. MALDI-TOF-MS: [M] calcd for $C_{116}H_{108}N_4O_4S_2$, 1684.7812; found: 1684.7667.

Synthesis of **PQ-1**. Compound **7** (160 mg, 0.095 mmol) and 10 mL LiOH aqueous solution (20 wt%), were dissolved in THF (30 mL) and EtOH (20 mL) mixed solution. The mixture was then refluxed for 6 h before cooling to room temperature. The pH value of mixture solution was adjusted to acid with diluted HCl and extracted with CH_2Cl_2. The organic layers were washed with brine water and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with Methanol/CH_2Cl_2 (1/20–1/10, v/v) as eluent to give reddish black solid compound **PQ-1** (70 mg, 44 % yield). ^{1}H NMR(400 MHz,THF-d_8, ppm): δ = 8.65 (d, *J* = 8.4 Hz, 2H), 8.50-8.44 (m, 8H),8.15-8.13 (m, 3H), 8.05-8.00 (m, 3H), 7.83-7.81 (m, 2H), 7.74-7.64 (m, 8H), 7.40-7.39 (m, 1H), 7.32-7.27 (m, 4H), 7.22-7.18 (m, 4H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.94-6.90 (m, 2H), 4.59-4.57 (m, 2H), 2.72-2.67 (m, 2H), 2.22-2.20 (m, 1H), 2.10-2.07 (m, 4H), 1.17 (s, 12H), 1.05-0.98 (m, 30H), 0.79-1.75(m, 6H), 0.70-0.64 (m, 18H). ^{13}C NMR (100 MHz, THF-d_8, ppm): δ = 173.56, 166.69, 163.37, 158.63, 157.21, 151.53, 146.48, 145.86, 140.40, 139.08, 138.99, 137.32, 136.96, 136.44, 135.96, 132.34, 132.16, 131.76, 131.46, 130.84, 130.43, 130.09, 129.84, 129.75, 129.70, 129.18, 128.80, 128.65, 128.36, 128.05, 127.66, 127.42, 127.20, 126.77, 124.86, 124.61, 124.41, 124.22, 123.81, 123.36, 121.29, 121.14, 120.98, 120.70, 120.46, 117.08, 114.51, 54.08, 49.28, 43.44, 41.39, 35.36, 34.47, 33.33, 31.90, 30.77, 29.67, 29.63, 29.52, 29.38, 29.34, 29.17, 29.03, 28.87, 28.68, 27.44, 27.04, 23.36, 22.93, 22.79, 22.59, 13.61, 13.58, 13.48, 13.40, 10.41, 10.12, 9.97. MALDI-TOF-MS: [M] calcd for $C_{114}H_{104}N_4O_4S_2$, 1656.7499; found: 1656.7200.

Synthesis of **9**. Under an argon atmosphere, compound **5** (230 mg, 0.30 mmol), K_2CO_3 (5 mL, 2 M aqueous solution) and $Pd(PPh_3)_4$ (42 mg, 0.036 mmol) were dissolved in 20 mL of THF. After stirring for half an hour, the mixture was heated to 50 ^{o}C and a solution of 2-(2, 6-diisopropylphenyl)perylene bisimide borate (250 mg, 0.41mmol) in THF (10 mL) was added slowly. The mixture was then refluxed for 6 h before cooling to room temperature and extracted with CH_2Cl_2. The organic layers were washed with brine water and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure to give crude intermediate product. Then, a bromination reaction was performed with NBS by using a similar procedure to that of compound 7 to give red solid compound 9 (185 mg, 65 % yield). ^{1}H NMR (400 MHz,$CDCl_3$, ppm): δ = 8.67 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, 2H), 8.58 (d, *J* = 8.8 Hz, 1H), 8.52-8.49 (m, 3H), 8.31-8.28 (m, 1H), 7.90 (t, *J* = 8.8 Hz, 2H), 7.83-7.79 (m, 2H), 7.75-7.72 (m, 2H), 7.58-7.54 (m, 1H), 7.49-7.43 (m, 4H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.29-7.27 (m, 2H), 7.22-7.18 (m, 1H), 7.13-7.10 (m, 2H), 7.02 (d, *J* = 4.4 Hz, 1H), 7.36 (d, *J* = 4.4 Hz, 1H), 7.30-7.28 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.06-7.02 (m, 2H), 2.83-2.76 (m, 2H), 2.01-1.88 (m, 4H), 1.20 (d, *J* = 8.4 Hz,12H), 1.06-0.96 (m, 16H), 0.83-0.79 (m, 6H), 0.74-0.64 (m,8H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 164.08, 156.75, 152.47, 145.75, 138.58, 137.92, 137.77, 136.45, 133.94, 132.07, 131.80, 131.13, 130.47, 129.94, 129.12, 128.91, 128.34, 128.03, 126.97, 126.66, 125.44, 124.03, 123.86, 123.53, 120.86, 120.79, 120.30, 120.18, 54.34, 43.32, 35.30, 35.16, 34.19, 34.15, 29.17, 28.62, 27.49, 24.05, 22.85, 14.14, 10.71. HRMS (m/z): [M+H$^+$] calcd for $C_{79}H_{75}BrN_3O_2S_2$, 1240.4484; found: 1240.4468.

Synthesis of **10**. Compound **10** was obtained by using a similar procedure to that of compound **6** (170 mg, 67% yield). ^{1}H NMR (400 MHz,$CDCl_3$, ppm): δ = 8.76 (t, *J* = 8.8 Hz, 2H), 8.70 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, 2H), 8.64-8.59 (m, 2H), 8.56-8.52 (m, 3H), 8.37-8.34 (m, 1H), 8.28 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.01-7.98 (m, 2H), 7.95-7.89 (m, 2H), 7.85-7.78 (m, 9H), 7.61-7.57 (m, 1H), 7.48-7.43 (m, 4H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31-7.28 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 4.65-4.63 (m, 2H), 4.48 (q, *J* = 8.8 Hz,2H), 2.83-2.78 (m, 2H), 2.33-2.27 (m, 1H), 2.16-2.06 (m, 4H), 1.48 (t, *J* = 8.8 Hz, 3H), 1.29-1.24 (m, 14H), 1.21(d, *J* = 8.8 Hz,12H), 1.15-1.06 (m, 16H), 1.00-0.97 (m, 6H), 0.89-0.86 (m, 6H), 0.80-0.74 (m,12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 166.71, 164.07, 158.79, 158.75, 156.80, 152.57, 151.82, 146.72, 145.78, 144.12, 144.06, 142.57, 140.27, 140.17, 138.78, 138.70, 138.30, 137.62, 137.45, 137.17, 137.06, 136.54, 136.20, 135.47, 134.34, 133.78, 132.41, 132.24, 131.90, 131.21, 130.59, 130.32, 129.94, 129.84, 129.48, 129.24, 129.11, 129.04, 128.91, 128.62, 128.35, 128.07, 127.36, 126.64, 126.50, 125.42, 124.90, 124.72, 124.08, 123.90, 123.75, 123.40, 122.76, 122.00, 121.32, 121.20, 120.64, 120.56, 120.04, 119.93, 117.19, 117.12, 114.73, 114.30, 61.11, 54.15, 53.45, 48.69, 46.83, 43.72, 41.38, 41.28, 36.11, 35.45, 35.36, 34.70, 34.56, 31.97, 31.63, 30.85, 30.23, 30.17, 29.74, 29.46, 29.24, 29.10, 28.99, 28.64, 27.71, 27.55, 26.95, 25.48, 25.32, 24.12, 23.11, 23.06, 22.98, 22.95, 22.84, 22.70, 20.48, 18.79, 17.77, 15.09, 14.48, 14.29, 14.24, 14.16, 14.08, 11.47, 10.86, 10.76. MALDI-TOF-MS: [M] calcd for $C_{116}H_{108}N_4O_4S_2$, 1684.7812; found: 1684.7893.

Synthesis of **PQ-2**. Compound **PQ-2** was obtained by using a similar procedure to that of compound **PQ-1** (55 mg, 43% yield). ^{1}H NMR (400 MHz,THF-d_8, ppm): δ = 8.75-8.71 (m, 3H), 8.63 (d, *J* = 8.8 Hz, 3H), 8.53 (d, *J* = 8.8 Hz, 3H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 3H), 8.05-8.01 (m, 2H), 7.90-7.87 (m, 2H), 7.78-7.67 (m, 8H), 7.51-7.47 (m, 2H), 7.33-7.28 (m, 4H), 7.22-7.19 (m, 4H), 7.08-7.06 (m, 1H), 7.02-6.98 (m, 2H), 4.69-4.67 (m, 2H), 2.26-2.24 (m, 1H), 2.11-2.07 (m, 4H), 1.24-1.22 (m, 12H), 1.06-1.04 (m, 30H), 0.91-0.87 (m, 6H), 0.76-0.69 (m, 12H). ^{13}C NMR (100 MHz, THF-d_8, ppm): δ =173.11, 166.24, 162.92, 158.18, 156.76, 151.08, 146.03, 145.42, 139.95, 139.46, 138.82, 138.64, 138.54, 136.87, 136.51, 135.99, 135.51, 133.64, 132.52, 131.98, 131.89, 131.72, 131.32, 131.01, 130.39, 129.98, 129.64, 129.40, 129.30, 129.26, 128.74, 128.36, 128.21, 127.91, 127.60, 127.21, 126.98, 126.75, 126.33, 124.41, 124.17, 123.96, 123.78, 123.36, 122.91, 120.84, 120.69, 120.53, 120.26, 120.02, 116.63, 114.07, 53.64, 48.83, 42.99, 40.94, 34.92, 34.02, 32.88, 31.46, 30.32, 29.22, 29.08, 28.94, 28.90, 28.73, 28.58, 28.42, 28.24, 26.99, 24.96, 22.91, 22.49, 22.15, 13.17, 13.14, 13.03, 12.95, 9.96, 9.67, 9.5. MALDI-TOF-MS: [M] calcd for $C_{114}H_{104}N_4O_4S_2$, 1656.7499; found: 1656.7563.

Characterization

^{1}H NMR and ^{13}C NMR spectra were measured at 400 and 100 MHz, respectively. Chemical shifts δ, were calibrated against TMS as an internal standard. HRMS measurements were performed by using a Waters LCT Premier XE spectrometer. The absorption spectra of the sensitizer dyes in solution and adsorbed on NiO films were measured with a Varian Cary 500 spectrophotometer. Transmission electron microscopy (TEM) images were taken with a S4800 transmission electron microscope operated at 15.0 kV. Powder X-ray diffraction (XRD) was performed on a Bruker D8-Advance X-ray diffractometer with monochromatized Cu Kα radiation (λ = 1.5418 Å). Gas adsorption/desorption isotherm was measured by volumetric adsorption analyzer V-Sorb 2800 after the sample was degassed at 150 °C for 12 h under vacuum. Brunauer-Emmett-Teller (BET) and t-plot model were used to determine the specific surface area and t-plot micropore area of the samples, respectively.

Cyclic Voltammograms

The cyclic voltammograms were determined by using a CHI660C electrochemical workstation (Chenhua Co. Ltd, Shanghai, China) in a three-electrode cell. The working electrode was a glassy carbon electrode, used in conjunction with a Pt auxiliary electrode and an Ag/AgCl wire reference electrode. The electrolyte consisted of 0.1 M TBAP solution in THF containing 10^{-3} M of dye. The Fc/Fc^+redox couple was used as an internal potential reference. The scan rate was 100 mV/s.

Preparation of NiO Films

Screen-printed NiO Films: NiO paste was prepared by mixing an ethyl cellulose solution in terpineol (50 wt %), ethanol (40 wt %), and NiO (10 wt %). The paste was screen-printed on FTO glass by a commercial semiautomatic screen printer.[4] The films were dried for 10 min at 125 °C, and then sintered in oven at 450 °C for 30 min. The film thickness is ca. 2 µm.

Spin-coated NiO Films: A triblock co-polymer F68-templated precursor solution of NiO was prepared by mixing $NiCl_2$ (1 g), co-polymer F68 (1 g), deionized water (3 g) and ethanol (6 g) according to the literature.[5] NiO film was made by spin-coating method with scotch tape on each side of FTO glass. The samples were spin-coated at 500 rpm for 6 s and then 2000 rpm for 20 s (IME-CAS, KW-4A, Beijing). After dried in air, the film was heated in oven at 40 °C for 30 mins. This spin-coating and heating procedure were repeated 4 times, named 4 layers. The film thickness is ca. 2 µm. The scotch tape was used on each side of FTO glass as a spacer for adjusting the film thinness, and it will be removed prior to thermal treatment. The scotch tape used in this work was purchased from 3M (China) company and the brand name is Scotch® Magic™ Tape.

Fabrication of the Solar Cells

Both films were then dipped into a dye solution either in a mixture of THF/EtOH (v/v: 3/1) at room temperature for 6 h. After washing with EtOH and drying with air flow, the sensitized NiO working electrode and the Pt-counter electrode were assembled together using a 25-µm-thick Surlyn gasket. The Pt-counter electrodes were prepared by spin coating of H_2PtCl_6 solution (20 mM in isopropanol) onto FTO glass at 400 °C for 15 min. The electrolyte contained 0.03 M I_2, 0.5 M tBP, 0.6 M BMII and 0.1 M GuSCN in acetonitrile. (tBP = tert-butylpyridine, BMII = 1-butyl-3-methylimidazolium iodide).

Photovoltaic Performance Measurements

Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a

300 W xenon lamp (Model No. 91160, Oriel). The power of the simulated light was calibrated to 100 mW cm^{-2} by using a Newport Oriel PV reference cell system (Model 91150 V). *J-V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640).

Electrochemical Impedance Spectroscopy (EIS)

A Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany) was employed to carry out the electrochemical impedance spectroscopy. The frequency range was 0.1 Hz-100 kHz and the applied bias was from 0.02 V to 0.16 V. The magnitude of the alternating signal was 5 mV.

Intensity-modulated photocurrent spectroscopy (IMPS)

IMPS spectra were recorded on a Zahner electrochemical workstation with a frequency-response analyzer under an intensity-modulated blue-light-emitting diode (30-150 W m^{-2}, $\lambda = 457$ nm) driven by a Zahner (PP211) source supply. The modulated light intensity was 10 % or lower than the base light intensity. The frequency range was set between 100 kHz and 0.1 Hz.

S2. Absorption spectra section

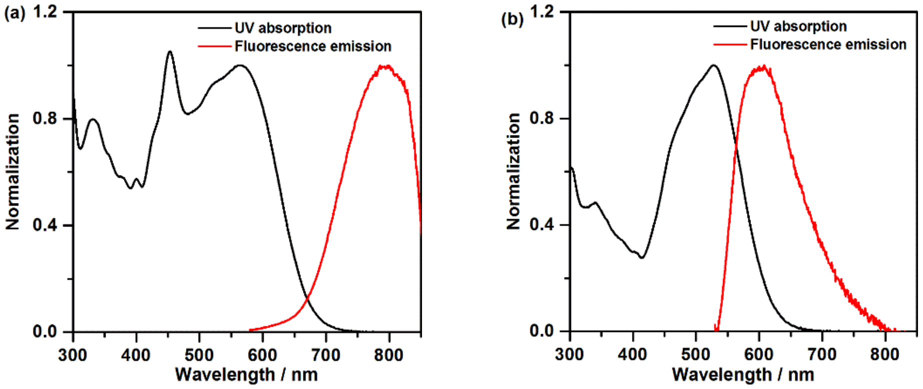


Figure S1. Normalized absorption and emission curves of (a) PQ-1 and (b) PQ-2 in THF

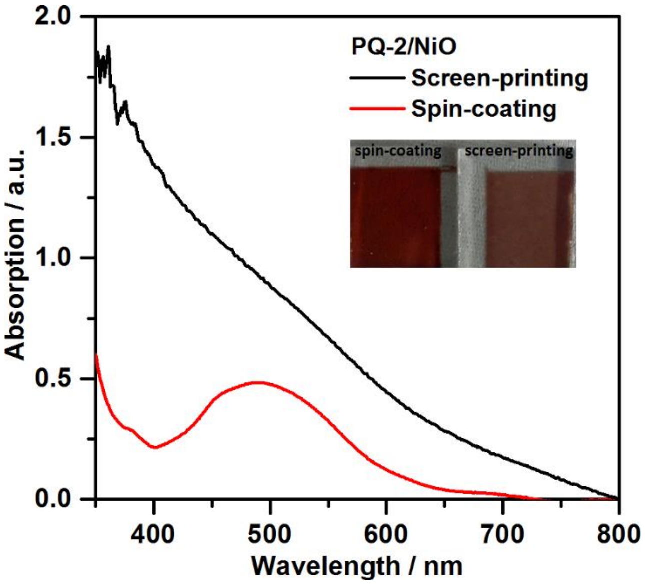
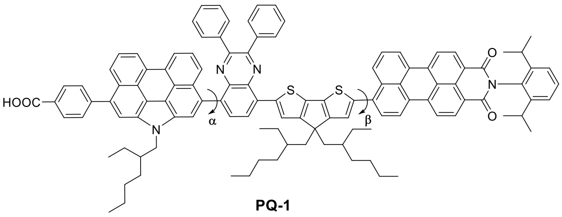


Figure S2. Absorption spectra of the PQ-2/NiO

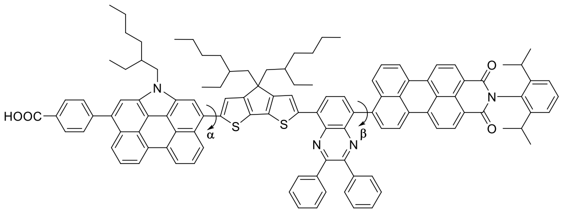
S3. Theoretical computation section

Table S1. Optimized dihedral angles.

	PQ-1	**PQ-2**
α (dihedral on the left side)	55.5°	44.9°
β (dihedral on the right side)	41.6°	57.9°



PQ-1



PQ-2

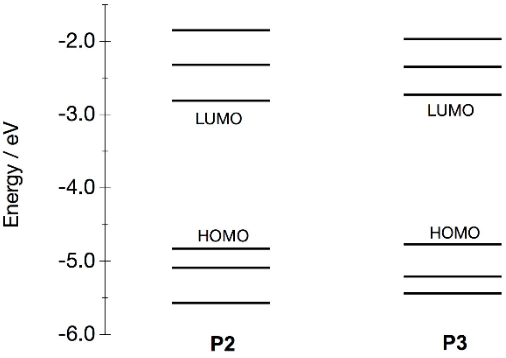


Figure S3. Computed energy levels of frontier molecular orbitals.

S4. Brunauer-Emmett-Teller (BET) and t-plot model

Table S2. Surface area of NiO prepared by screen-printing and spin-coating methods.

Preparation methods	Single point surface area [m^2/g]	BET surface area [m^2/g]	Langmuir surface area [m^2/g]	t-Plot External surface area
Screen-printing	44.26	45.32	60.81	50.83
Spin-coating	45.96	47.73	64.30	57.94

S5. References

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