Synthesis of Sensitizers

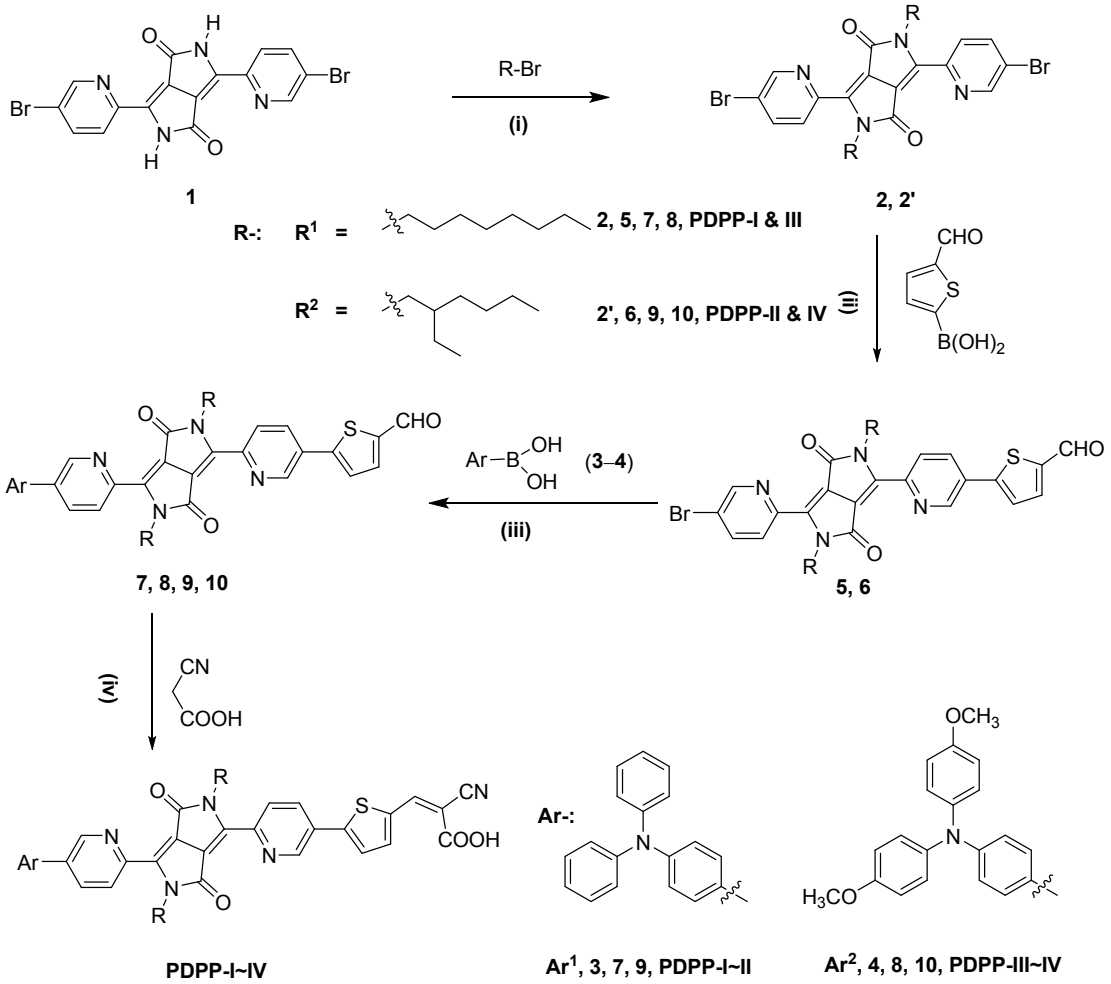

Fig. 1 Synthesis of the PDPP sensitizers: i) DMF, K_2CO_3, 125°C for 50 min; ii) K_2CO_3, $Pd(PPh_3)_4$, THF, 90°C for 16h; iii) K_2CO_3, $Pd(PPh_3)_4$, THF, 90°C for 16h; iv) CH_3COONH_4, CH_3COOH/THF (1:1, v/v), reflux for 2.5h.

3,6-bis(5-bromopyridin-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **(2)**: 3,6-bis(5-bromopyridin-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2**) (500mg, 1.12mmol) and K_2CO_3 (770 mg) were dispersed in 30mL dry DMF at 90°C for 30 min under a argon atmosphere. 1-bromooctane (860mg, 4.48mmol) was added by a

syringe, and then the mixture was stirring at 125°C for 50min. After stirring, the reactant was poured into 500mL deionized water. The precipitate was filtered and washed with water, then dried overnight in a vacuum desiccator. The residue was purified by a column chromatography on silica gel with eluent (petroleum ether/dichloromethane = 1:2, v/v) to yield a red solid (365mg, 48.5%). ^{1}H NMR (400 MHz, d_1-$CDCl_3$): δ 9.01 (d, J = 8.5 Hz, 2H), 8.77 (s, 2H), 8.02 (d, J = 7.5 Hz, 2H), 4.30 (s, 4H), 1.35 – 1.21 (m, 24H), 0.87 (d, J = 4.7 Hz, 6H).

3,6-bis(5-bromopyridin-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **(2')**: The synthetic method of compound **2'** was resembled that of compound **2**, with 3-(bromomethyl)heptane replacing 1-bromooctane. The compound was purified by column chromatography using eluent (petroleum ether/dichloromethane = 1:2, v/v) to afford a red solid (265mg, 35.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (d, J = 6.7 Hz, 2H), 8.75 (s, 2H), 8.03 (s, 2H), 4.30 (m, 4H), 1.40~1.13 (m, 18H), 0.84 (m, 12H).

5-(6-(4-(5-bromopyridin-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophene-2-carbaldehyde (**5**): The compound **2** (100mg, 0.15mmol), K_2CO_3 (400mg) and $Pd(PPh_3)_4$ (10mg) was added in 20 ml THF and 0.5 mL deionized water. The mixture was heated to 60°C under argon atmosphere for 30min. A solution of 5-formylthiophen-2-ylboronic acid (23.4 mg, 0.15 mmol) in 10 mL THF was dropped within 30min. the mixture was stirring at 90°C for 16h. After cooling to room temperature, the reactant was poured into 500mL deionized water

and extracted with dichloromethane. The combine organic layers were dried by anhydrous $MgSO_4$, and then concentrated by a rotate evaporator. The residue was purified by column chromatography with petroleum ether/dichloromethane mixture (3:1, v/v) as a gradient eluent to get compound **5** (dark red solid, 27.7 mg, yield: 26.2%). ^{1}H NMR(d-$CDCl_3$): 9.98(s, 1H), 9.22(d, 1H, J=8.02Hz), 9.05(d, 2H, J=8.24Hz), 8.80(s, 1H), 8.14(d, 2H, J=8.82Hz), 8.03(d, 1H, J=8.29Hz), 7.84(d, 1H, J=2.87Hz), 7.60(d, 1H, J=2.89Hz), 4.36(m, 4H), 1.66(s, 4H), 1.49~1.21(m, 20H), 0.89(m, 6H)

5-(6-(4-(5-bromopyridin-2-yl)-2,5-bis(2-ethylheptyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophene-2-carbaldehyde (**6**): The synthetic method of compound **6** was resembled that of compound **5**, with compound **2'** replacing compound **2** to afford a dark red solid (26.4 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 9.12 (d, *J* = 7.1 Hz, 1H), 9.08 – 8.92 (m, 2H), 8.75 (s, 1H), 8.14 (s, 1H), 8.03 (s, 1H), 7.82 (s, 1H), 7.58 (s, 1H), 4.33 (m, 4H), 1.32~1.10 (m, 18H), 0.84 (m, 12H)

5-(6-(4-(5-(4-(diphenylamino)phenyl)pyridin-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophene-2-carbaldehyde (**7**): Compound **5** (27.7mg, 0.039mmol), 4-(diphenylamino)phenylboronic acid (**3**) (30mg, 0.10mmol), K_2CO_3 (400mg) and $Pd(PPh_3)_4$ (10mg) was added into 30 mL THF and 0.5 mL deionized water, and then heated to 90°C, stirring for 16h under argon

atmosphere. After cooling, the mixture was extracted with CH_2Cl_2/water twice. The combine organic layers was dried by anhydrous $MgSO_4$, and then concentrated by a rotate evaporator. The residue was purified by column chromatography using ethyl acetate/dichloromethane mixture (1:10, v/v) as an eluent to yield a dark red powder (25.0 mg, 73.2 %). ^{1}H NMR (400 MHz, THF) δ 9.81 (s, 1H), 9.26 (d, *J* = 7.2 Hz, 2H), 9.04 (s, 1H), 8.94 (s, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.81 (s, 1H), 7.72 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 4H), 7.03 (t, *J* = 7.7 Hz, 6H), 6.96 (t, *J* = 7.4 Hz, 2H), 4.34 (d, *J* = 6.4 Hz, 4H), 1.24 – 1.16 (m, 24H), 0.76 (s, 6H).

5-(6-(4-(5-(4-(bis(4-methoxyphenyl)amino)phenyl)pyridin-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophene-2-carbaldehyde (**8**): The synthetic method of compound **8** was resembled that of compound **7**, with compound **4** replacing compound **3** to afford a dark red solid (27.6 mg, 71.1%). ^{1}H NMR (400 MHz, THF): δ 9.89 (s, 1H), 9.32 (s, 2H), 9.10 (s, 1H), 8.98 (s, 1H), 8.29 (s, 1H), 8.13 (s, 1H), 7.89 (s, 1H), 7.78 (s, 1H), 7.60 (d, *J* = 7.1 Hz, 2H), 7.08 (m, 4H), 6.97 (m, 2H), 6.88 (m, 4H), 4.44 (s, 4H), 3.77 (s, 6H), 1.28 (m, 24H), 0.86 (m, 6H).

5-(6-(4-(5-(4-(diphenylamino)phenyl)pyridin-2-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophene-2-carbaldehyde (**9**): The synthetic method of compound **9** was resembled that of compound **7**, with compound **6** replacing compound **5** to afford a dark red solid (29.5 mg, 70.6%). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 9.12 (m, 1H), 9.05 (m,1H), 9.01 (s, 1H), 8.94 (s, 1H), 8.14 (s, 1H), 8.07 (s, 1H), 7.82 (s, 1H), 7.55 (d, J = 8.7 Hz, 4H), 7.31 (m, 2H), 7.18 (m, 7H), 7.10 (m, 2H), 4.39 (s, 4H), 1.32~1.09 (m, 18H), 0.84 (m, 12H).

5-(6-(4-(5-(4-(bis(4-methoxyphenyl)amino)phenyl)pyridin-2-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophene-2-carbaldehyde (**10**): The synthetic method of compound **10** was resembled that of compound **8**, with compound **4** replacing compound **3** to afford a dark red solid (26.8 mg, 72.5%). ^{1}H NMR (400 MHz, d_1-$CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 9.14 (s, 1H), 9.02 (m, 2H), 8.93 (s, 1H), 8.14 (m, 1H), 8.06 (m, 1H), 7.82 (s, 1H), 7.57 (s, 1H), 7.50 (m, 2H), 7.12 (d, J = 7.3 Hz, 4H), 7.02 (m, 2H), 6.89 (m, 4H), 4.39 (s, 4H), 3.82 (s, 6H), 1.35~1.07 (m, 18H), 0.84 (m, 12H).

2-cyano-3-(5-(6-(4-(5-(4-(diphenylamino)phenyl)pyridin-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophen-2-yl)acrylic acid (**PDPP-I**): Compound **7** (48.3mg, 0.056mmol), cyanoacetic acid (47.5mg, 0.56mmol), ammonium acetate (60 mg) dissolved in THF (4 mL) and acetic acid (4 mL) at refluxing for 2.5h. After cooling to room temperature, the mixture was poured into 100 mL ice water. The precipitate was filtered and washed with water, ethanol and n-hexane to afford a black-red powder (20mg, 38.4%). ^{1}H NMR (400 MHz, THF) δ 9.27 (s, 2H), 9.07 (s, 1H), 8.95 (s, 1H), 8.31 (s, 2H), 8.13 (s, 1H), 7.85 (s, 1H), 7.75 (s, 1H), 7.62 (s, 2H), 7.18 (s, 4H), 7.04 (s, 6H), 6.96 (s, 2H), 4.36 (s, 4H), 1.25~1.05 (m,

24H), 0.76 (m, 6H). ^{13}C NMR (100 MHz, THF): δ 162.54, 162.33, 155.43, 149.52, 148.14, 147.46, 146.93, 146.41, 143.91, 139.44, 137.96, 137.38, 134.34, 134.20, 130.03, 129.97, 128.44, 128.08, 127.20, 125.65, 124.22, 123.65, 112.70, 111.79, 111.29, 91.95, 43.21, 32.62, 30.78, 30.70, 30.02, 27.58, 23.33, 14.22. HRMS (MALDI-TOF, m/z): [M + H] calcd for ($C_{58}H_{59}N_6O_4S$,), 935.4319; found, 935.4252.

2-cyano-3-(5-(6-(4-(5-(4-(diphenylamino)phenyl)pyridin-2-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophen-2-yl)acrylic acid (**PDPP-II**): **PDPP-II** was obtained as black-red powder using similar synthetic method of **PDPP-I** (12.5mg, 32%). ^{1}H NMR (400 MHz, THF) δ 9.34 (s, 2H), 9.15 (s, 1H), 9.03 (s, 1H), 8.41 (s, 2H), 8.23 (s, 1H), 7.96 (s, 1H), 7.84 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.14 (t, *J* = 8.2 Hz, 6H), 7.08 – 7.02 (m, 2H), 4.44 (s, 4H), 1.58 – 1.27 (m, 18H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, THF): δ 162.78, 162.72, 157.37, 150.21, 149.57, 149.39, 148.15, 147.29, 146.05, 139.35, 138.02, 137.20, 135.82, 134.51, 134.30, 130.70, 130.56, 129.98, 128.45, 127.20, 125.65, 125.41, 124.23, 123.69, 112.72, 112.40, 111.80, 96.88, 46.47, 40.52, 31.27, 30.53, 29.32, 23.74, 14.19, 10.83. HRMS (MALDI-TOF, m/z) [M + H] calcd for ($C_{58}H_{59}N_6O_4S$,), 935.4319; found, 935.4606.

3-(5-(6-(4-(5-(4-(bis(4-methoxyphenyl)amino)phenyl)pyridin-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophen-2-yl)-2-cyanoacrylic acid(**PDPP-III**): **PDPP-III** was obtained as black-red powder using

similar synthetic method of **PDPP-I** (23mg, 36%). ^{1}H NMR (400 MHz, THF) δ 9.37 (s, 2H), 9.17 (s, 1H), 9.02 (s, 1H), 8.41 (s, 2H), 8.18 (s, 1H), 7.95 (s, 1H), 7.85 (s, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 4H), 4.46 (s, 4H), 3.77 (s, 6H), 1.39~1.28 (m, 24H), 0.86 (s, 6H). ^{13}C NMR (100 MHz, THF) δ 163.52, 162.62, 157.59, 148.46, 147.23, 146.96, 145.92, 144.61, 140.90, 139.44, 135.96, 134.04, 133.77, 128.45, 128.14, 128.05, 127.81, 125.04, 123.69, 120.35, 116.18, 115.41, 111.65, 110.81, 91.01, 55.41, 43.17, 32.60, 31.85, 30.40, 30.00, 27.55, 23.32, 14.20. HRMS (MALDI-TOF, m/z) [M + H] calcd for ($C_{60}H_{63}N_6O_6S$,), 995.4530; found, 995.4554.

3-(5-(6-(4-(5-(4-(bis(4-methoxyphenyl)amino)phenyl)pyridin-2-yl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)pyridin-3-yl)thiophen-2-yl)-2-cyanoacrylic acid(**PDPP-IV**): **PDPP-IV** was obtained as black-red powder using similar synthetic method of **PDPP-I** (31mg, 42.1%). ^{1}H NMR (400 MHz, THF) δ 9.32 (m, 2H), 9.14 (s, 1H), 9.00 (s, 1H), 8.39 (m, 2H), 8.18 (s, 1H), 7.95 (s, 1H), 7.83 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 4H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 4H), 4.44 (s, 4H), 3.77 (s, 6H), 1.43~1.25 (m, 18H), 0.87 (s, 12H). ^{13}C NMR (100 MHz, THF) δ 163.58, 162.95, 162.66, 157.57, 150.53, 148.92, 148.49, 146.99, 146.68, 146.14, 146.01, 145.89, 144.04, 140.85, 139.44, 137.92, 137.64, 134.44, 133.80, 130.23, 128.46, 128.29, 128.13, 127.82, 127.16, 125.04, 123.70, 120.30, 116.22, 115.39, 112.74, 111.62, 101.42, 85.53, 55.41, 46.50, 40.49, 31.26, 30.41, 29.32, 23.76, 14.23, 10.83. HRMS (MALDI-TOF, m/z)

[M + H] calcd for ($C_{60}H_{63}N_6O_6S$,), 995.4530; found, 995.5020.

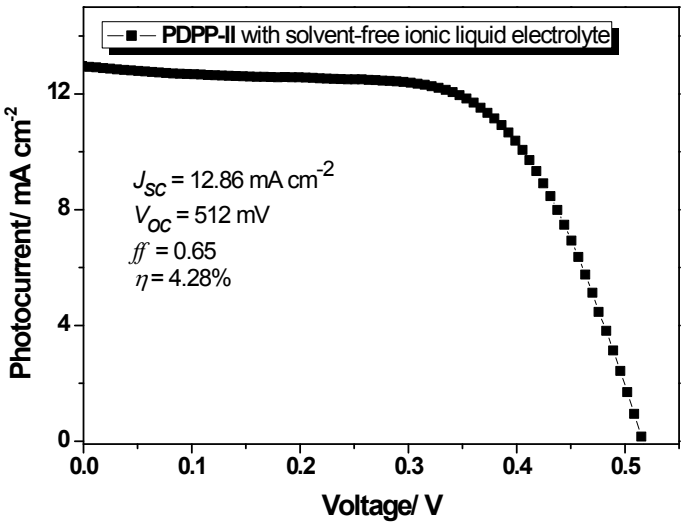

Figure S1 Photocurrent-voltage curve of **PDPP-II** based DSSC under standard global AM 1.5 illumination (100 mW cm^{-2}) with solvent-free ionic liquid electrolyte

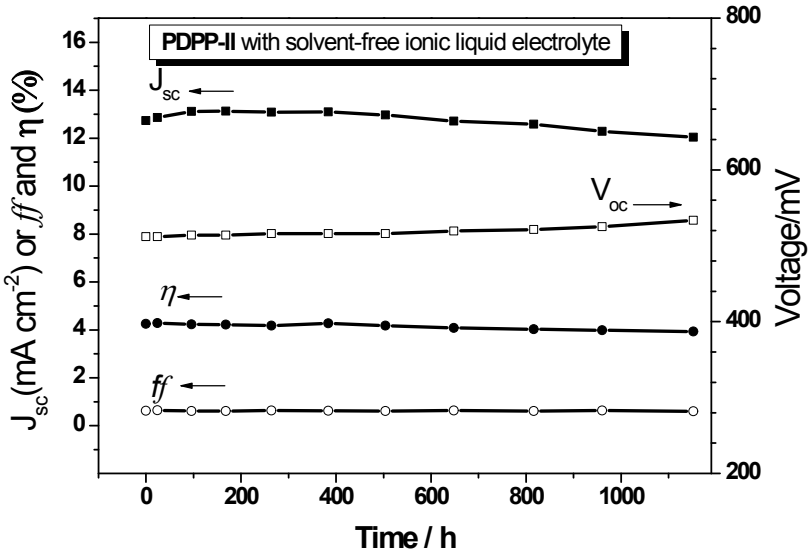

Figure S2 Stability test photovoltaic parameter (J_{sc}, V_{oc}, *ff*, and η) variations with aging time for the DSSCs based on **PDPP-II**-sensitized TiO_2 film with solvent-free ionic liquid electrolyte under visible-light soaking.