

Electronic Supplementary Information for

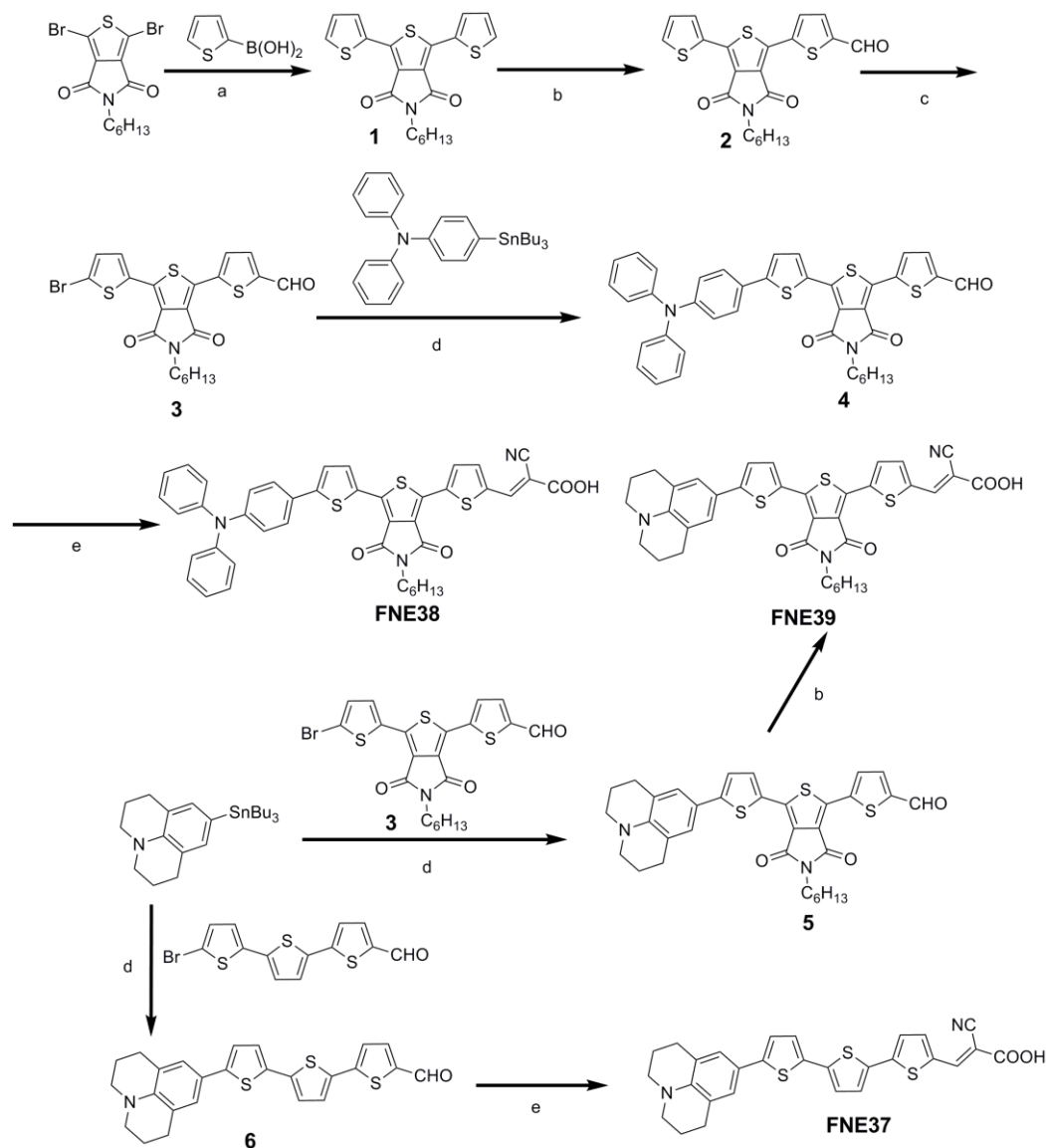
Synthesis and Photovoltaic Properties of Organic Sensitizers Incorporating Thieno[3,4-c]pyrrole-4,6-dione Moiety

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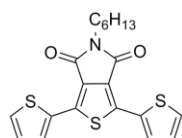
Experimental Section

All of the chemicals and reagents were purchased from a commercial supplier and used as received. THF was distilled from sodium benzophenone ketyl. CHCl_3 was distilled from CaH_2 . All reactions and manipulations were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. 1,3-Dibromo-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione^[S1] and 5''-bromo-5,2':5',2''-terthiophene-2-carbaldehyde^[S2] were synthesized according to literature procedures. The synthesis of 2-cyano-3-[5''-(4-(diphenylamino)phenyl)-[2,2',5',2'']terthiophene-5-yl]acrylic acid (**FNE31**) is described elsewhere.^[S2] 9-(tributylstannyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline was synthesized in a similar way as the preparation of *N,N*-diphenyl-4-(tributylstannyl)aniline.^[S3]

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Varian Mercury Plus - 400 spectrometer. Unless specified, data of ^1H NMR and ^{13}C NMR were recorded in CDCl_3 solutions. The chemical shifts were expressed in ppm downfield from tetramethylsilane (TMS). The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet).

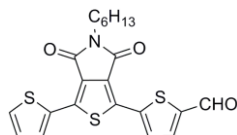


Scheme S1. Synthesis of dyes **FNE37-39**. a) Pd(PPh₃)₄, K₂CO₃, THF/H₂O, reflux, 16 h; b) POCl₃, DMF, CHCl₃, reflux, 20 h; c) NBS, CH₂Cl₂/HOAc, r.t., 12 h; d) Pd(PPh₃)₄, DMF, 100 °C, 12 h; e) cyanoacetic acid, piperidine, CHCl₃, reflux, 6 h.

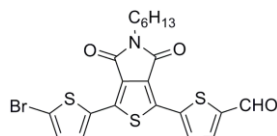


5-Hexyl-1,3-di(thiophen-2-yl)-thieno[3,4-c]pyrrole-4,6-dione (1). A mixture of 1,3-dibromo-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione (640 mg, 1.62 mmol), thiophen-2-ylboronic acid (456 mg, 3.56 mmol), Pd(PPh₃)₄ (80 mg, 0.08 mmol), K₂CO₃ (60 mg, 0.6 mmol), THF (30 mL) and H₂O (4 mL) was refluxed for 16 h under N₂. After cooling, water was added and the reaction mixture was extracted three times

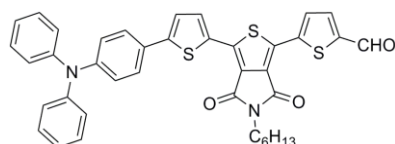
with CH₂Cl₂. The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/PE = 2/1) on silica gel to yield the product as a yellow solid, **1** (533 mg, 82%). ¹H NMR (400 MHz, CDCl₃, δ): 7.99 (d, *J* = 4.0 Hz, 2H), 7.42 (d, *J* = 4.0 Hz, 2H), 7.11 (t, *J* = 4.0 Hz, 2H), 3.64 (t, *J* = 7.3 Hz, 2H), 1.67 (m, 2H), 1.32 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 162.81, 136.68, 132.65, 130.07, 128.85, 128.63, 38.80, 31.64, 28.67, 26.84, 22.75, 14.28.



5-(5-hexyl-4,6-dioxo-3-(thiophen-2-yl)-5,6-dihydro-thieno[3,4-c]pyrrol-1-yl)thiophene-2-carbaldehyde (2) To a cold Vilsmeier reagent, which was prepared with 2 mL of POCl₃ in DMF (2 mL), was added a solution of **1** (420 mg, 1.05 mmol) in dry CHCl₃ (10 mL) at 0 °C. The mixture was stirred at 90 °C for 20 h, and quenched with 10% aqueous solution of NaOAc (30 mL) at 0 °C. After neutralization with 25% NaOH solution to pH 7, the mixture was extracted by CH₂Cl₂ three times. The combined organic layer was washed with H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/PE = 1/1) on silica gel to obtain aldehyde **2** (350 mg, 78%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃, δ): 9.90 (s, 1H), 8.14 (d, *J* = 4.0 Hz, 1H), 8.02 (d, *J* = 4.0 Hz, 1H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.46 (d, *J* = 4.0 Hz, 1H), 7.12 (d, *J* = 4.0 Hz, 1H), 3.66 (t, *J* = 7.3 Hz, 2H), 1.69 (m, 2H), 1.32 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 182.77, 162.44, 144.66, 140.99, 138.75, 136.86, 130.85, 130.37, 129.77, 128.85, 38.97, 31.60, 28.62, 26.82, 22.73, 14.27.

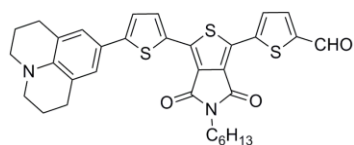


5-(3-(5-bromothiophen-2-yl)-5-hexyl-4,6-dioxo-5,6-dihydro-thieno[3,4-c]pyrrol-1-yl)thiophene-2-carbaldehyde (3) To the solution of **2** (315 mg, 0.73 mmol) in CH_2Cl_2 (30 mL) and glacial acid (30 mL) was added *N*-bromosuccinimide (391 mg, 2.20 mmol) in portions. The reaction mixture was stirred at room temperature for 12 hours, and quenched with water (10 mL). The mixture was extracted by CH_2Cl_2 three times. The combined organic layer was washed with H_2O and brine, dried over Na_2SO_4 , and evaporated under reduced pressure. The crude product was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{PE} = 1/1$) on silica gel to obtain compound **3** (316 mg, 85%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3 , δ): 9.87 (s, 1H), 8.08 (d, $J = 4.0$ Hz, 1H), 7.68 (d, $J = 4.0$ Hz, 2H), 7.61 (d, $J = 4.0$ Hz, 1H), 7.01 (d, $J = 4.0$ Hz, 1H), 3.60 (t, $J = 7.3$ Hz, 2H), 1.65 (m, 2H), 1.31 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 182.67, 162.25, 162.13, 144.84, 140.62, 136.94, 136.82, 134.29, 133.60, 131.56, 131.48, 130.53, 129.13, 117.81, 39.01, 31.58, 28.59, 26.82, 22.74, 14.28.

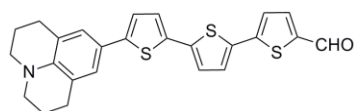


5-(3-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)-5-hexyl-4,6-dioxo-5,6-dihydro-thieno[3,4-c]pyrrol-1-yl)thiophene-2-carbaldehyde (4) A mixture of **3** (145 mg, 0.29 mmol), *N,N*-diphenyl-4-(tributylstannyl)aniline (187 mg, 0.35 mmol), $\text{Pd}(\text{PPh}_3)_4$ (50 mg, 0.05 mmol), and DMF (20 mL) was refluxed for 12 h under N_2 . After cooling, water was added and the reaction mixture was extracted three times with CH_2Cl_2 . The combined organic layer was washed with H_2O and brine, dried over anhydrous Na_2SO_4 , and evaporated under reduced pressure. The crude product was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{PE} = 1/1$) on silica gel to yield the

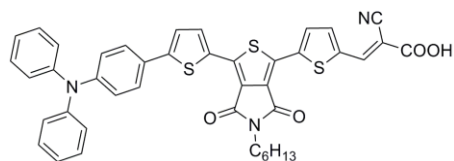
product as a red solid, **4** (154 mg, 79%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.90 (s, 1H), 8.14 (d, $J = 4.0$ Hz, 1H), 8.01 (d, $J = 4.0$ Hz, 1H), 7.71 (d, $J = 4.0$ Hz, 1H), 7.46 (d, $J = 8.6$ Hz, 2H), 7.29 (t, $J = 7.9$ Hz, 4H), 7.19 (d, $J = 4.0$ Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 4H), 7.06 (m, 4H), 3.65 (t, $J = 7.4$ Hz, 2H), 1.68 (m, 2H), 1.33 (m, 6H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 182.76, 162.56, 162.47, 149.07, 148.62, 147.32, 144.49, 141.21, 138.99, 136.97, 136.93, 133.47, 132.35, 131.91, 130.26, 130.15, 129.78, 129.67, 128.25, 127.06, 126.69, 125.43, 125.19, 123.87, 123.59, 122.95, 38.96, 31.63, 28.67, 26.86, 22.76, 14.30.



5-(3-(5-(1,2,3,5,6,7-Hexahydropyrido[3,2,1-ij]quinolin-9-yl)thiophen-2-yl)-5-hexyl-4,6-dioxo-5,6-dihydro-thieno[3,4-c]pyrrol-1-yl)thiophene-2-carbaldehyde (5). A mixture of 9-(tributylstannyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline (610 mg), **3** (138 mg, 0.27 mmol), $\text{Pd}(\text{PPh}_3)_4$ (100 mg, 0.09 mmol) in 10 mL DMF was heated at 100 °C overnight under N_2 atmosphere. The Solvent was removed and the residue was subjected to flash column chromatography on silica ($\text{CH}_2\text{Cl}_2/\text{PE} = 1/1$) to give the target compound **5** as a deep red solid (139 mg, 86%). ^1H NMR (400 MHz, CDCl_3 , δ): 9.93 (s, 1H), 8.18 (d, $J = 4.0$ Hz, 1H), 8.00 (d, $J = 4.0$ Hz, 1H), 7.76 (d, $J = 4.0$ Hz, 1H), 7.13 (d, $J = 4.0$ Hz, 1H), 7.11 (s, 2H), 3.67 (t, $J = 7.4$ Hz, 2H), 3.21 (t, $J = 5.6$ Hz, 4H), 2.78 (t, $J = 6.4$ Hz, 4H), 1.98 (m, 4H), 1.68 (m, 2H), 1.33 (m, 6H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 182.74, 162.67, 162.54, 151.19, 144.13, 143.74, 141.52, 139.70, 136.94, 132.69, 132.53, 131.91, 129.98, 128.23, 127.17, 124.94, 121.59, 121.53, 120.21, 50.11, 38.90, 31.66, 28.71, 27.89, 26.90, 22.78, 21.97, 14.32.

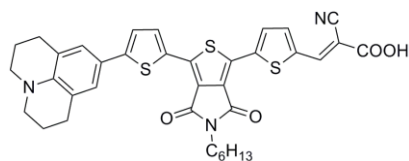


5''-(1,2,3,5,6,7-Hexahydropyrido[3,2,1-ij]quinolin-9-yl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (6). The Stille coupling reaction of 9-(tributylstannyl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline (450 mg) with 5''-bromo-5,2':5',2''-terthiophene-2-carbaldehyde (150 mg, 0.42 mmol) using Pd(PPh₃)₄ (100 mg, 0.09 mmol) as a catalyst in DMF (10 mL) was carried out in a similar manner to that for **5**. The crude product was purified by column chromatography (CH₂Cl₂/PE = 1/1) to yield aldehyde **6** as a red solid (126 mg, 0.28 mmol, 67%). ¹H NMR (400 MHz, CDCl₃, δ): 9.85 (s, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 4.0 Hz, 1H), 7.21 (d, *J* = 4.0 Hz, 1H), 7.13 (d, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 4.0 Hz, 1H), 7.04 (s, 2H), 7.01 (d, *J* = 4.0 Hz, 1H), 3.19 (t, *J* = 5.6 Hz, 4H), 2.78 (t, *J* = 6.4 Hz, 4H), 1.99 (m, 4H). ¹³C NMR (100 MHz, CDCl₃, δ): 182.63, 146.30, 143.15, 141.44, 140.30, 137.73, 133.64, 127.27, 125.64, 124.71, 123.95, 123.82, 121.77, 121.29, 50.15, 27.92, 22.11.

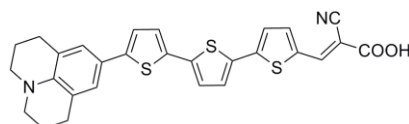


FNE38: A mixture of aldehyde **4** (138 mg, 0.21 mmol) with cyanoacetic acid (87 mg, 1.03 mmol) in chloroform (20 mL) was refluxed in the presence of piperidine (0.3 mL) for 12 h under N₂. After cooling, the mixture was diluted with CH₂Cl₂, and washed with water and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/methanol = 10/1) on silica gel to yield the product as a brown powder, **FNE38** (93 mg, 60%). ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.04 (s, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.96 (d, *J* = 4.0 Hz, 1H), 7.64 (d, *J* = 4.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 4.0 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 4H), 7.09 (m, 6H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.50 (t, *J* = 7.4 Hz, 2H), 1.59 (m, 2H), 1.29 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, THF-*d*₈, δ): 163.54, 163.20, 153.16, 152.40, 150.07, 149.34, 138.38, 137.58, 136.74, 134.00, 133.15, 131.31, 128.66, 126.88, 126.78, 125.40,

120.26, 115.40, 109.70, 106.25, 33.51, 31.74, 30.28, 28.71, 24.57, 15.59. HRMS (ESI, m/z): $[M - H]^-$ calcd for $(C_{42}H_{32}N_3O_4S_3)$, 738.1555; found, 738.1561.



FNE39 was obtained as brown powder in similar way with **FNE38** (yield 63%): ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.04 (s, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.91 (d, *J* = 4.0 Hz, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.22 (d, *J* = 4.0 Hz, 2H), 7.03 (s, 2H), 3.52 (t, *J* = 7.4 Hz, 2H), 3.19 (m, 4H), 2.69 (t, *J* = 6.4 Hz, 4H), 1.88 (m, 4H), 1.60 (m, 2H), 1.28 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, THF-*d*₈, δ): 168.18, 167.44, 167.12, 164.79, 161.63, 161.15, 160.43, 147.55, 143.99, 143.09, 138.67, 137.19, 137.14, 135.83, 132.22, 128.28, 126.27, 126.03, 125.36, 124.77, 123.82, 62.33, 40.38, 32.15, 31.66, 30.40, 29.92, 24.94, 22.92, 14.36. HRMS (ESI, m/z): $[M - H]^-$ calcd for $(C_{36}H_{32}N_3O_4S_3)$, 666.1555; found, 666.1554.



FNE37 was obtained as brown powder in similar way with **FNE38** (yield 55%): ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.44 (s, 1H), 7.95 (d, *J* = 4.0 Hz, 1H), 7.56 (m, 2H), 7.34 (d, *J* = 4.0 Hz, 1H), 7.30 (d, *J* = 4.0 Hz, 1H), 7.19 (d, *J* = 4.0 Hz, 1H), 7.02 (s, 2H), 3.14 (t, *J* = 5.6 Hz, 4H), 2.68 (t, *J* = 6.4 Hz, 4H), 1.85 (m, 4H). ¹³C NMR (100 MHz, THF-*d*₈, δ): 163.29, 149.25, 146.52, 146.43, 145.56, 139.59, 133.41, 132.45, 127.53, 125.69, 125.68, 125.64, 124.25, 124.09, 123.84, 121.42, 121.18, 49.92, 27.81, 22.16. MALDI-TOF-MS: m/z calcd for $(C_{28}H_{22}N_2O_2S_3)$, 514; found (M)⁺ 514.

References

- [S1] A. Najari, S. Beaupre, P. Berrouard, Y. P. Zou, J. R. Pouliot, C. Lepage-Perusse and M. Leclerc, *Adv. Funct. Mater.*, **2011**, *21*, 718.
[S2] P. Shen, Y. Liu, X. Huang, B. Zhao, N. Xiang, J. Fei, L. Liu, X. Wang, H. Huang and S. Tan, *Dyes Pigments*, **2009**, *83*, 187.

[S3] G. Qian, B. Dai, M. Luo, D. Yu, J. Zhan, Z. Zhang, D. Ma and Z. Y. Wang,
Chem. Mater., **2008**, *20*, 6208.