Supporting Information for

Near Infrared Thieno[3,4-b]pyrazine Sensitizers for Efficient Quasi-Solid-State Dye-Sensitized Solar Cells

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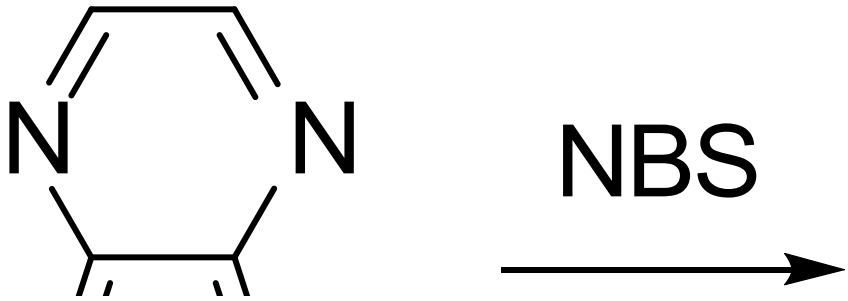
Experimental Section

Synthesis of Sensitizers.



Scheme S1. Synthetic route for sensitizer **FNE32**.

Synthesis of 5,7-dibromothieno[3,4-b]pyrazine (2). Compound **2** was synthesized accroding to previously reported literature. [S1]

Synthesis of 5,7-bis[3-(2-ethylhexylthiophenyl)]thieno[3,4-b]pyrazine (3). Under a nitrogen atmosphere, a mixture of compound **2**(790 mg, 2.69 mmol), tributyl(3-(2-ethylhexyl)thiophen-2-yl)stannane (3.20 g, 6.59 mmol) and $Pd(PPh_3)_4$ (105 mg, 0.09 mmol) in DMF (30 mL) was stirred and heated at 90 °C for 8 h. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, DCM/PE = 1:2). A dark red solid was obtained with a yield of 53% (751 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.54 (s, 2H); 7.42 (d, 2H, *J* = 5.2 Hz), 7.02 (d, 2H, *J* = 5.2 Hz), 2.82 (d, 4H, *J* = 7.2 Hz), 1.64-1.63 (m, 2H), 1.31-1.16 (m, 16H), 0.82-0.75 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.38, 141.57, 140.09, 130.39, 127.40, 127.12, 126.66, 40.41, 34.18, 32.79, 28.93, 25.97, 23.25, 14.35, 10.97.

Synthesis of 4-(2-ethylhexyl)-5-(7-(3-(2-ethylhexylthiophenyl))thieno[3,4- b]pyrazin-5-)thiophene-2-carbaldehyde (4). Under a nitrogen atmosphere, compound **3** (751 mg, 1.43 mmol) and N,N-Dimethylformamide (126 mg, 1.72 mmol) were dissolved in 20 mL DCM. To this solution, phosphorus oxychloride (264 mg, 1.72 mmol) was added slowly. The mixture was stirred for 20 min at room temperature and then heated to 70 °C for 10 h. After cooling to room temperature, 40 mL saturated sodium acetate solution was added to the dark red reaction solution and stirrer for 20 min. The mixture was poorer into ice water (80 mL) and neutralized (pH = 7) through the addition of sodium hydroxide solution. The product was extracted with DCM for three times. The combined organic solution was washed with sodium bicarbonate and sodium chloride solution and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, DCM/PE = 1:2). A dark red solid was obtained with a yield of 52% (451 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.92 (s, 1H), 8.62 (s, 2H), 7.66 (s, 1H), 7.47 (d, 1H, *J* = 5.2 Hz), 7.05 (d, 1H, *J* = 5.2 Hz), 2.89 (d, 2H, *J* = 7.2 Hz), 2.83 (d, 2H, *J* = 7.2 Hz), 1.62 (m, 2H), 1.36-1.16 (m, 16H), 0.82-0.76 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 183.05, 144.78, 144.58, 142.88, 142.13, 141.51, 140.88, 140.05, 138.70, 137.96, 130.49, 129.19, 127.84, 126.87, 124.28, 40.34, 39.92, 34.56, 34.27, 32.70, 32.66, 28.85, 28.81, 25.92, 25.84, 23.16, 14.26, 10.89, 10.81.

Synthesis of 5-(7-(5-bromo-3-(2-ethylhexyl)thiophenyl)thieno[3,4- b]pyrazinyl)-4-(2-ethylhexyl)thiophene-2-carbaldehyde (5). Under a nitrogen atmosphere, compound **4** (415 mg, 0.75 mmol) was dissolved in DCM (20 mL). To this solution, N-bromosuccinimide (267 mg, 1.50 mmol) was added. After the mixture was stirred at room temperature for 7 h, distilled water was added to quench the reaction. The solution was extracted with DCM for three times. The combined organic solution was washed with sodium hydroxide solution and sodium chloride solution and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, DCM/PE = 1:2). A dark red solid was obtained with a yield of 70% (334 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.92 (s, 1H), 8.61 (d, 2H, *J* = 5.5 Hz), 7.65 (s, 1H), 6.98(s, 1H), 2.88 (d, 2H, *J* = 7.2 Hz), 2.79 (d, 2H, *J* = 7.2 Hz), 1.71-1.67 (m, 2H), 1.36-1.20 (m, 16H), 0.84-0.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 182.48, 144.40, 143.95, 142.51, 141.65, 141.05, 140.17, 139.50, 138.12, 137.18, 132.35, 128.32, 127.22, 123.77, 114.91, 39.58, 39.39, 34.11, 34.09, 32.13, 28.29, 25.34, 22.65, 13.75, 10.34, 10.31.

Synthesis of amine 6. Under a nitrogen atmosphere, a mixture of compound **5** (150 mg, 0.24 mmol), N,N-diphenyl-4-(tributylstannyl)aniline (380 mg, 0.71 mmol) and $Pd(PPh_3)_4$ (27 mg, 0.02 mmol) in DMF (15 mL) was stirred and heated at 90 °C for 8 h. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, DCM/PE = 1:2). A dark red solid was obtained with a yield of 75% (142 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.90 (s, 1H), 8.59 (s, 2H), 7.64 (s, 1H), 7.53 (d, 2H, *J* = 7.8 Hz), 7.29-7.25 (m, 4H), 7.15-7.03 (m, 9H), 2.91-2.86 (m, 4H), 1.73-1.72 (m, 2H), 1.36-1.21 (m, 16H), 0.83-0.82 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 183.58, 148.45, 148.13, 146.80, 145.41, 144.68, 143.56, 143.29, 141.80, 141.53, 140.40, 139.34, 138.81, 130.22, 130.13, 128.53, 127.36, 126.69, 126.33, 125.42, 124.13, 124.05, 123.86, 40.67, 40.49, 35.52, 35.29, 33.33, 29.45, 28.90, 27.60, 26.56, 26.48, 23.82, 18.21, 14.93, 14.42, 11.53, 11.44.

Synthesis of dye FNE32. Under a nitrogen atmosphere, a mixture of compound **6** (130 mg, 0.16 mmol) with cyanoacetic acid (40 mg, 0.46 mmol) in acetonitrile (10 mL) was refluxed in the presence of piperidine (0.4 mL) for 8 h. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The combined organic solution was washed with water and sodium chloride solution and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, DCM/MeOH = 10:1). A black solid was obtained with a yield of 57% (80 mg). ^{1}H NMR (400 MHz, DMSO, δ ppm): 8.58 (d, 2H, *J* = 5.0 Hz), 8.10 (s, 1H), 7.62 (s, 1H), 7.45 (d, 2H, *J* = 8.3 Hz), 7.22-7.17 (m, 4H), 6.96-6.91 (m, 7H), 6.84 (d, 2H, *J* = 7.9 Hz), 2.69 (s, 4H), 1.55 (m, 2H), 1.13-0.98 (m, 16H), 0.63-0.59 (m, 12H). ^{13}C NMR (100 MHz, THF, δ ppm): 158.82, 158.60, 147.29, 147.19, 146.70, 145.07, 144.46, 144.44, 143.73, 143.63, 141.61, 140.15, 140.11, 139.11, 128.81, 127.86, 126.42, 125.91, 125.13, 124.05, 123.12, 122.68, 39.31, 39.09, 34.48, 34.07, 32.15, 28.25, 28.19, 25.34, 25.27, 22.63, 22.61, 13.16, 9.78, 9.72. HRMS (ESI, m/z): [M^+] calcd for $C_{52}H_{54}N_4O_2S_3$, 862.3409; found, 862.3400.

Scheme S2. Synthetic route for sensitizer **FNE34**.

Synthesis of 4-(2-ethylhexyl)-5-(10-(3-(2-ethylhexyl)thiophenyl)acenaphtho[1,2-b]thieno[3,4-e]pyrazinyl)thiophene-2-carbaldehyde (11). 8,10-bis(3-(2-ethylhexyl)thiophenyl)acenaphtho[1,2-b]thieno[3,4-e]pyrazine (**10**) was synthesized using modified strategy according to the literature.[S2] Compound **11** was synthesized similarly as described for synthesis of compound **4,** yield 86% (430 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.92 (s, 1H), 8.29-8.18 (m, 2H), 7.98-7.93 (m, 2H), 7.74-7.66 (m, 2H), 7.60 (s, 1H), 7.47 (d, 1H, J = 5.2 Hz), 7.03 (d, 1H, J = 5.2 Hz), 2.94 (d, 2H, J = 7.6 Hz), 2.90 (d, 2H, J = 7.2 Hz), 1.80-1.73 (m, 2H), 1.34-1.19 (m, 16H), 0.88-0.78 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 183.21, 154.10, 153.88, 142.28, 141.58, 140.60, 139.89, 139.39, 139.06, 138.58, 138.56, 131.51, 131.36, 130.44, 130.19, 129.52, 129.31, 128.82, 128.68, 128.14, 128.10, 127.63, 123.74, 122.14, 121.67, 40.14, 39.67, 35.06, 34.79, 32.85, 32.77, 28.99, 28.92, 26.08, 25.95, 23.30, 14.35, 11.00, 10.89.

Synthesis of 5-(10-(5-bromo-3-(2-ethylhexyl)thiophenyl)acenaphtho[1,2- b]thieno[3,4-e]pyrazinyl)-4-(2-ethylhexyl)thiophene-2-carbaldehyde (12). Compound **12** was synthesized similarly as described for synthesis of compound **5,** yield 61% (290 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.87 (s, 1H), 8.21-8.17 (m, 2H,) 7.95-7.93 (m, 2H), 7.70-7.65 (m, 2H), 7.53 (s, 1H), 6.88 (s, 1H), 2.87 (d, 2H, J = 6.5 Hz), 2.77 (d, 2H, J = 6.5 Hz), 1.78-1.68 (m, 2H), 1.39-1.23 (m, 16H), 0.89-0.83 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 183.18, 154.15, 154.05, 142.38, 141.30, 140.57, 139.54, 139.52, 139.29, 138.82, 138.57, 132.65, 131.28, 130.39, 130.33, 130.21, 129.61, 129.47, 128.88, 128.80, 127.47, 123.53, 122.26, 121.89, 115.53, 39.93, 39.68, 35.28, 32.81, 28.99, 26.04, 23.39, 14.45, 11.01, 10.98.

Synthesis of amine 13. Compound **13** was synthesized similarly as described for synthesis of compound **6,** yield 66% (80 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.92 (s, 1H), 8.37 (d, 1H, *J* = 6.7 Hz), 8.30 (d, 1H, *J* = 6.9 Hz), 8.06-8.02 (m, 2H), 7.81-7.75 (m, 2H), 7.61 (s, 1H), 7.58 (d, 2H, *J* = 8.3 Hz), 7.28 (t, 4H, *J* = 7.6 Hz), 7.17-7.05 (m, 9H), 2.97 (d, 2H, *J* = 7.2 Hz), 2.92 (d, 2H, *J* = 7.2 Hz), 1.82-1.77 (m, 2H), 1.40-1.22 (m, 16H), 0.94-0.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 183.24, 154.39, 154.37, 153.71, 147.83, 147.71, 145.81, 142.76, 142.31, 140.75, 140.71, 140.06, 139.54, 139.19, 138.70, 138.59, 131.70, 131.56, 130.37, 129.63, 129.43, 128.97, 128.86, 128.39, 127.17, 126.81, 125.88, 124.92, 123.75, 123.51, 122.30, 121.85, 40.05, 39.78, 35.27, 35.11, 32.89, 32.83, 28.98, 27.08, 26.11, 26.01, 23.34, 17.67, 14.38, 13.89, 11.04, 10.94.

Synthesis of dye FNE34. FNE34 was synthesized similarly as described for synthesis of **FNE32**, black solid, yield 73% (61 mg). ^{1}H NMR (400 MHz, DMSO, δ ppm): 8.13 (d, 1H, *J* = 6.9Hz), 8.06-7.98 (m, 4H), 7.67-7.64 (m, 2H), 7.46 (d, 2H, *J* = 8.2 Hz), 7.37 (s, 1H), 7.26-7.22 (m, 4H), 7.09-6.96 (m, 6H), 6.87-6.85 (m, 3H), 2.62-2.57 (m, 4H), 1.59-1.57 (m, 2H), 1.17-1.00 (m, 16H), 0.68-0.58 (m, 12H). ^{13}C NMR (100 MHz, THF, δ ppm): 163.56, 154.74, 153.06, 149.98, 149.47, 147.82, 139.58, 139.25, 139.13, 138.17, 131.55, 129.67, 129.38, 128.95, 128.88, 126.45, 124.69, 124.54, 123.89, 123.13, 121.31, 111.31, 109.69, 109.16, 39.72, 39.06, 32.63, 29.84, 28.80, 25.84, 23.24, 23.12, 13.73, 13.68, 10.32. HRMS (ESI, m/z): [M^+] calcd for $C_{62}H_{58}N_4O_2S_3$, 986.3772; found, 986.3695.

Scheme S3. Synthetic route for sensitizer **FNE36**.

Synthesis of amine 23. Compound **20** was synthesized using the modified strategy according to the literature.[S2] Under a nitrogen atmosphere, a mixture of 20 (200 mg, 0.48 mmol), N,N-diphenyl-4-(tributylstannyl)aniline (257 mg, 0.48 mmol), and $Pd(PPh_3)_4$ (58 mg,

0.05 mmol) in DMF (20 mL) was stirred and heated at 90 °C for 12 h. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The combined organic solution was washed with water and sodium chloride solution and dried over anhydrous sodium sulfate. After removal of the solvent, the residue **21** (540 mg, 0.72 mmol), 3',4-bis(2-ethylhexyl)-5'-(tributylstannyl)-[2,2'-bithiophene]-5-carbaldehyde (566 mg, 0.80 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), DMF(10 mL) were added into a Schlenk tube and the solution was stirred and heated at 90 °C for 8 h. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, DCM/PE = 1:1). A black solid **23** was obtained with a total yield 18% (80 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.00 (s, 1H), 8.21 (d, 1H, J = 6.9 Hz) 8.15-8.11 (m, 3H), 7.97-7.94 (m, 2H), 7.74-7.66 (m, 2H), 7.38 (s, 1H), 7.34-7.30 (m, 4H) 7.21-7.19 (m, 4H) 7.16-7.06 (m, 5H) 2.87 (d, 2H, J = 7.1 Hz), 2.73 (d, 2H, J = 7.1 Hz), 1.74-1.62 (m, 2H), 1.40-1.25 (m, 16H), 0.95-0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 181.88, 153.80, 153.59, 152.88, 147.91, 147.50, 145.83, 141.46, 139.37, 138.49, 138.23, 136.84, 134.89, 131.99, 131.82, 131.64, 131.24, 130.28, 129.62, 129.23, 129.06, 128.97, 128.93, 128.72, 128.67, 128.23, 127.01, 125.23, 123.70, 123.01, 121.41, 121.19, 41.88, 40.17, 34.17, 33.02, 32.78, 32.75, 29.93, 29.07, 28.92, 28.07, 27.08, 26.00, 25.94, 23.33, 23.26, 17.76, 14.40, 13.85, 11.09, 10.99.

Synthesis of dye FNE36. FNE36 was synthesized similarly as described for synthesis of **FNE32**, black solid, yield 69% (52 mg). ^{1}H NMR (400 MHz, THF, δ ppm): 8.39-7.45 (m, 9H), 7.22-7.19 (m, 5H), 6.99-6.96 (m, 5H), 7.10-7.06 (m, 4H), 2.80-2.77 (m, 4H), 1.78-1.76 (m, 2H), 1.29-1.18 (m, 16H), 0.87-0.78 (m, 12H). ^{13}C NMR (100 MHz, THF, δ ppm): 168.45, 162.95, 157.64, 156.67, 153.00, 147.61, 146.12, 146.07, 144.67, 138.27, 134.11, 132.62, 131.81, 131.67, 131.61, 131.25, 129.57, 129.48, 128.73, 125.33, 125.13, 123.57, 122.60, 109.71, 37.06, 36.98, 36.42, 35.51, 35.00, 32.42, 32.11, 31.99, 31.12, 29.87, 29.55, 28.70, 23.21, 22.80, 13.81, 10.21. HRMS (ESI, m/z): [$(M+Na)^+$] calcd for $C_{62}H_{58}N_4O_2S_3Na$, 1009.3620; found, 1009.3613.

References

[S1]B. Burkhart, P. P. Khlyabich, T. C. Canak, T. W. LaJoie, B. C. Thompson, *Macromolecules* **2011**, *44*, 1242.

[S2]R. Mondal, N. Miyaki, H. A. Becerril, J. E. Norton, J. Parmer, A. C. Mayer, M. L. Tang, J. L. Bredas, M. D. McGehee, Z. N. Bao, *Chem. Mater.* **2009**, *21*, 3618.

Figure S1. Chemical structure of the reference dye.

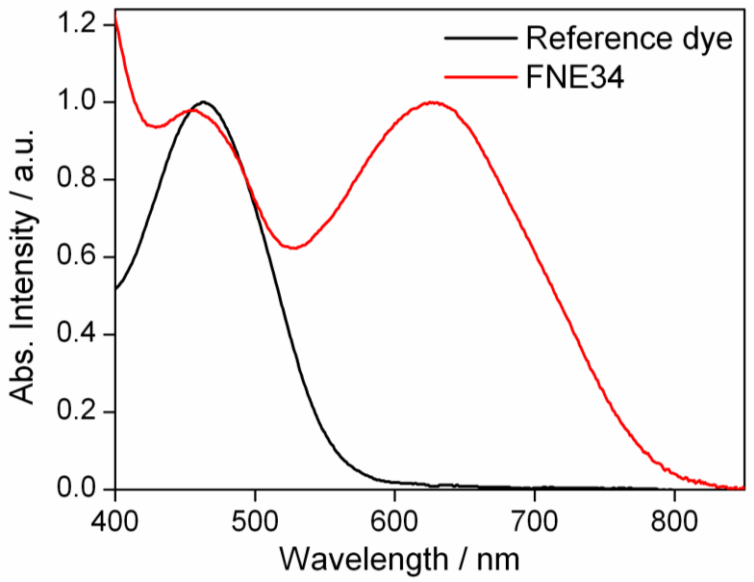


Figure S2. Normalized absorption spectra of the reference dye and **FNE34** in toluene solutions.

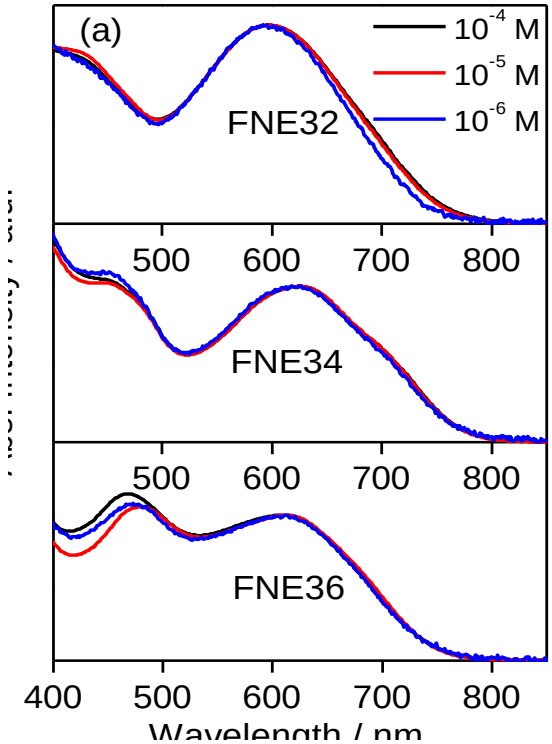


Figure S3. Absorption spectra of **FNE32**, **FNE34**, and **FNE36** in toluene solutions with different concentration.