Supporting Information for

Photoinduced Intramolecular Electron Transfer in Phenylene Ethynylene Naphthalimide Oligomers

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Experimental

Scheme S1. Synthesis of NI building block



(1). HAc, octylamine, reflux; (2). TMSA, NEt₃, CuI, (PPh₃)₂PdCl₂, rt; (3). K₂CO₃, methanol, rt;
 (4). 6, Pd(PPh₃)₂Cl₂, CuI, triethylamine, THF, rt.



Scheme S2. Synthesis of OPE building blocks

NiCl₂(dppp), BrMgC₆H₁₃, Et₂O, 50°C; (2). I₂, HIO₃, CCl₄, H₂SO₄, HAc, 120°C; (3).
 HC≡CCH₂OH, Pd(PPh₃)₂Cl₂, CuI, piperidine, THF, rt; (4). HC≡CTIPS, Pd(PPh₃)₂Cl₂, CuI, piperidine, THF, 50°C; (5).n-Bu₄NF, THF, rt; (6). 6, Pd(PPh₃)₂Cl₂, CuI, piperidine, THF, rt; (7).
 9, Pd(PPh₃)₂Cl₂, CuI, piperidine, THF, rt; (8). MnO₂, KOH, Et₂O, rt.



Scheme S3. Synthesis of designed compounds

12, Pd(PPh₃)₂Cl₂, CuI, piperidine, THF, rt; (2). 12, Pd(PPh₃)₂Cl₂, CuI, piperidine, THF, rt;
 (3). MnO₂, KOH, Et₂O, rt; (4). Iodobenzene, Pd(PPh₃)₂Cl₂, CuI, piperidine, THF, rt; (5). 3, Pd(PPh₃)₂Cl₂, CuI, triethylamine, THF, rt; (6). 12, Pd(PPh₃)₂Cl₂, CuI, triethylamine, THF, rt; (7). 14, Pd(PPh₃)₂Cl₂, CuI, triethylamine, THF, rt.

Compound 1. 4-Bromo-1,8-naphthalic anhydride (5 g, 0.018 mol) and octylamine (2.8 g, 0.022 mol) were dissolved in 100 ml ethanol, and refluxed for 12 hours. The precipitate was filtered out and washed with water. A yellow product (6.38 g, yield 91%) was obtained after the sample was dried under vacuum overnight. ¹H NMR (CDCl₃, 300 MHz): $\delta = 8.66$ (d, 1 H), 8.57 (d, 1 H), 8.41(d, 1 H), 8.04 (d, 1H), 7.84 (t, 1 H) 4.14 (t, 2H), 1.69 (m, 2 H), 1.27 (m, 10 H), 0.85 (t, 3 H).



Figure S1. ¹HNMR spectrum of 1.

Compound 2. Compound 1 (2.575 g, 6.63 mmol) was dissolved in 30 ml triethylamine and degassed for 30 min. CuI (75.8 mg, 0.4 mmol) and PdCl₂(PPh₃)₂ (0.279 g, 0.4 mmol) were added to the system and degassed further for about 15 min. (Trimethylsilyl)-acetylene (0.977 g, 10 mmol) was added to the solution and stirred for 12 hours at room temperature. The solvent was removed after the reaction was finished. H₂O: ethyl acetate (v:v=2:1) was added to dissolve the residue. The organic layer was separated, and the aqueous layer was extracted several times with ethyl acetate. The organic layers were combined and washed with brine, then dried over MgSO₄. A yellow product (1.779 g, yield 66%) was obtained after purification by column chromatography with hexane: ethyl acetate (v:v=10:1). ¹H NMR (CDCl₃, 300 MHz): δ = 8.63 (d, 1 H), 8.62 (d, 1 H), 8.51(d, 1 H), 7.88 (d, 1H), 7.80 (t, 1 H) 4.14 (t, 2H), 1.69 (m, 2 H), 1.27 (m, 10 H), 0.84 (t, 3 H), 0.36 (s, 9H).



Figure S2. ¹HNMR spectrum of 2.

Compound 3. Compound 2 (0.57 g, 1.41 mmol) and potassium carbonate (1.17 g, 8.43 mmol) were dissolved in 20 mL 1:1 (v:v) DCM:methanol. After 3h, TLC indicated that the reaction was completed. DI water was poured into the reaction system, which was then extracted with DCM several times. The organic layer was washed with DI water and brine three times, and then dried over MgSO₄. The product was further purified by column chromatography eluting with hexane: ethyl acetate (v:v=9:1) to give 0.37 g solid (yield 78%). ¹H NMR (CDCl₃, 300 MHz): δ = 8.65 (d, 1 H), 8.63 (d, 1 H), 8.53 (d, 1 H), 7.93 (d, 1H), 7.81 (t, 1 H) 4.15 (t, 2H), 3.73 (s, 1H), 1.70 (m, 2 H), 1.27 (m, 10 H), 0.86 (t, 3 H).

8.67 8.65 8.65 8.64 8.63 8.53 8.53 8.53 7.94 7.93 7.84 7.83 7.81



Figure S3. ¹HNMR spectrum of 3.

Compound 4. Compound 6 (2 g, 4 mmol) and compound 3 (0.67 g, 2 mmol) were dissolved in dry THF (20 mL) and triethylamine (10 mL). The system was degassed for at least 30 min. Then $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol) and CuI (19 mg, 0.1 mmol) were added into the system. The system was stirred overnight at room temperature. Diethyl ether and water were added to the resulting suspensions. Two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phase was then dried over MgSO₄. The pure product was obtained by flash chromatography with hexane to hexane: ethyl acetate (v:v= 10:1) (0.5 g, yield 35%). ¹H NMR (CDCl₃, 300 MHz): 8.72 (dd, 1 H), 8.67 (dd, 1 H), 8.58(d, 1 H), 7.96 (d, 1H), 7.85 (t, 1 H), 7.76 (s, 1H), 7.44 (s, 1H), 4.20 (t, 2H), 2.88 (t, 2H), 2.73 (t, 2H), 1.73 (m, 6H), 1.43 (m, 22H), 0.91 (m, 9 H).



Figure S4. ¹HNMR spectrum of 4.

Compound 5. 1,4-Dichlorobenzene (6.7 g, 0.02 mol) and NiCl₂(dppp) (74 mg, 0.14 mmol) were placed in 50 mL dry diethyl ether in a dry three-necked flask. The system was cooled to 0°C. The Grignard reagent (C₆H₁₃MgBr) (50 mL) was slowly added via dropping funnel to start the reaction, and the system was refluxed overnight. Then the reaction was carefully quenched by adding water and 1 mol/L HCl. The aqueous layer was separated and extracted several times with Et₂O, the combined organic layers were washed with water and brine and dried over MgSO₄. The pure product was obtained by removing the solvent and dried under vacuum (7.6 g, yield 70%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 7.11$ (s, 4 H), 2.57 (t, 4 H), 1.59 (m, 4H), 1.29 (m, 12 H), 0.89 (t, 6H).



Figure S5. ¹HNMR spectrum of 5.

Compound 6. Compound 5 (12 g, 0.05 mol) was dissolved in a solvent mixture of water (25 mL), CCl₄ (50 mL) and acetic acid (230 mL). H₃IO₆ (5.04 g, 0.02 mol), I₂ (11.2 g, 0.04 mol) and concentrated H₂SO₄ (7.8 mL) were added and the resulting mixture was refluxed for 24 h. The reaction was quenched by adding water at room temperature. Then the aqueous phase was extracted several times with pentane, and the combined organic layers were washed consecutively with saturated solutions of Na₂S₂O₃, Na₂CO₃, Na₂SO₄ and dried over MgSO₄. The product was obtained by removing the solvent and drying in an oven (19.8 g, yield 65%). ¹HNMR (CDCl₃, 300 MHz): $\delta = 7.60$ (s, 2 H), 2.56 (t, 4 H), 1.49 (m, 4H), 1.29 (m, 12 H) 0.88 (t, 6H).



Compound 7. Compound 6 (4 g, 8 mmol) and prop-2-ynol (0.224 g, 4mmol) were dissolved in dry THF (6 mL) and dry piperidine (12 mL). The system was degassed for at least 30 min. Then $Pd(PPh_3)_2Cl_2$ (56.2 mg, 0.08 mmol) and CuI (30.4 mg, 0.16 mmol) were added, and the system was stirred overnight at room temperature. Diethyl ether and water were added to the resulting suspensions. Two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phase was washed with 2M HCl and saturated NaCl (aq) and then dried over MgSO₄. The pure product was obtained by flash chromatography with hexane: ethyl acetate (v:v= 8:1) (1.41 g, yield 41%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 7.64$ (s, 1H), 7.22 (s, 1 H), 4.50 (d, 2 H), 2.60 (m, 4H), 1.55 (m, 4 H), 1.32 (m, 12H), 0.89 (m, 6H).



Figure S7. ¹HNMR spectrum of 7.

Compound 8. Compound 7 (1.40 g, 3.3 mmol) and (triisopropylsilyl)ethyne (2.39 g, 13.1 mmol) were dissolved in dry THF (30 mL) and dry piperidine (15 mL). The system was degassed for at least 30 min. Then Pd(PPh₃)₂Cl₂ (46 mg, 0.07 mmol) and CuI (25 mg, 0.13 mmol) were added, and the system was stirred overnight at 45°C. Diethyl ether and water were added to the resulting suspension. The two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phases were washed with 2M HCl and saturated NaCl(aq) and then dried over MgSO₄. The pure product was obtained by flash chromatography with hexane: dichloromethane (v:v= 1:1) (1.09 g, yield 70%). ¹H NMR (CDCl₃, 300 MHz): δ = 7.25 (s, 1H), 7.23 (s, 1 H), 4.52 (d, 2H), 2.66 (m, 4 H), 1.59 (m, 4H), 1.31 (m, 12 H), 1.14 (s, 21H), 0.88 (m, 6H).



Figure S8. ¹HNMR spectrum of 8.

Compound 9. Compound 8 (3.6 g, 7.0 mmol) was dissolved in 100 mL THF. 16 mL 1M TBAF in THF solution was added to the system and stirred for four hours at room temperature. The pure product was obtained by flash chromatography with hexane: dichloromethane (v:v= 4:1) to hexane: dichloromethane (v:v= 1:1) (1.50 g, yield 67%). ¹H NMR (CDCl₃, 300 MHz): δ = 7.29 (s, 1H), 7.24 (s, 1 H), 4.52 (d, 2 H), 3.28 (s, 1H), 2.66 (m, 4 H), 1.60 (m, 4H), 1.32 (m, 12 H) 0.86 (t, 6H).





7.29

Compound 10. Compound 6 (3.03 g, 6.08 mmol) and compound 9 (1.97 g, 6.07 mmol) were dissolved in dry THF (30 mL) and dry piperidine (15 mL). The system was degassed for at least 30 min. Then Pd(PPh₃)₂Cl₂ (213.4 mg, 0.30 mmol) and CuI (3.1 mg,0.30 mmol) were added to the system. The system was stirred overnight at 45°C. Diethyl ether and water were added to the resulting suspension. The two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phase was washed with 2M HCl and saturated NaCl (aq) and then dried over MgSO₄. The pure product was obtained by flash chromatography with hexane: dichloromethane (v:v= 1:1) (1.68 g, yield 40%). ¹H NMR (CDCl₃, 300 MHz): δ = 7.67 (s, 1H), 7.31 (s, 1H), 7.29 (s, 1H), 7.27 (s, 1 H), 4.53 (d, 2 H), 2.62 (m, 8 H), 1.60 (m, 8 H), 1.25 (m, 24H), 0.84 (m, 12H).



Figure S10. ¹HNMR spectrum of 10.

Compound 11. Compound 7 (2.57 g, 6.0 mmol) and phenylacetylene (1.23 g, 12.0 mmol) were dissolved in dry THF (40 mL) and dry piperidine (40 mL). The system was degassed for at least 30 min. Then Pd(PPh₃)₂Cl₂ (84.5 mg, 0.12 mmol) and CuI (22.9 mg, 0.12 mmol) were added to the system. The system was stirred overnight at 45°C. Diethyl ether and water were added to the resulting suspension. The two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phases were washed with 2M HCl and saturated NaCl (aq) and then dried over MgSO₄. The pure product was obtained by flash chromatography with hexane: dichloromethane (v:v= 4:1) (2.06 g, yield 86%). ¹H NMR (CDCl₃, 300 MHz): δ = 7.49 (m, 2H), 7.33 (m, 4H), 7.27 (s, 1 H), 4.53 (d, 2 H), 2.69 (m, 4H), 1.59 (m, 4 H), 1.30 (m, 12H), 0.84 (m, 6H).



Figure S11. ¹HNMR spectrum of 11.

Compound 12. Compound 11 (0.92 g, 2.3 mmol) was dissolved in 100 ml ethyl ether. Activated manganese oxide (3.0 g, 34.5 mmol) and potassium oxide (1.04 g, 18.5 mmol) were divided into four portions and added to the solution over eight hours. The system was stirred at 30°C. After TLC monitoring until no starting material was left, the reaction was diluted in 300 mL ethyl ether, and the solid was filtered. The product was collected after evaporating the solvent (0.54 g, yield 64%). ¹H NMR (CDCl₃, 300 MHz): δ = 7.50 (m, 2 H), 7.32 (m, 5 H), 3.29 (s, 1H), 2.71 (m, 4 H), 1.59 (m, 4H), 1.30 (m, 12 H), 0.85 (m, 6H).

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Figure S12. ¹HNMR spectrum of 12.

Compound 13. Compound 10 (0.44 g, 0.64 mmol) and compound 12 (0.28 g, 0.77 mmol) were dissolved in dry THF (10 mL) and dry piperidine (10 mL). The system was degassed for at least 30 min. Then $Pd(PPh_3)_2Cl_2$ (13.4 mg, 0.02 mmol) and CuI (3.6 mg, 0.02 mmol) were added to the system. The system was stirred overnight at room temperature. Diethyl ether and water were added to the resulting suspensions. The two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phases were washed with 2M HCl and saturated NaCl (aq) and then dried over MgSO₄. The product was obtained by flash chromatography with hexane: dichloromethane (v:v= 4:1). The pure product is really hard to separated, so compound 13 with little impurity were used in the next step without further purification since this compound is not final product. Compound 14 is pure product.

Compound 14. Compound 13 (0.286 g, 0.31 mmol) was dissolved in 100 mL ethyl ether. Activated manganese oxide (0.398 g, 4.58 mmol) and potassium oxide (0.137 g, 2.44 mmol) were divided into four portions and added to the solution over eight hours. The system was stirred at 30°C. After TLC monitoring until no starting material was left, the reaction was diluted in 300 mL ethyl ether and the solid was filtered. The product was collected after evaporation of the solvent (0.18 g, yield 64%). ¹H NMR (CDCl₃, 300 MHz): δ = 7.52 (m, 2 H), 7.34 (m, 9 H), 3.30 (s, 1 H), 2.72 (m, 12 H), 1.62 (m, 12 H), 1.34 (m, 38 H), 0.86 (m, 18 H).

7.55 7.54 7.54 7.52 7.52 7.52 7.33 7.35 7.35 7.35 7.35

0.88 0.88 0.88 0.93



Figure S13. ¹HNMR spectrum of 14.

OPE3. Compound 6 (0.31 g, 0.63 mmol) and phenylacetylene (0.14 g, 1.38 mmol) were dissolved in dry THF (15 mL) and dry (i-Pr)₂NH (8 mL). The system was degassed for at least 30 min. Then Pd(PPh₃)₄ (29.0 mg, 0.025 mmol) and CuI (4.8 mg, 0.025 mmol) were added, and the system was stirred overnight at 40°C. Diethyl ether and water were added to the resulting suspensions. The two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phases were washed with 2M HCl and saturated NaCl (aq) and then dried over MgSO₄. The crude product was purified by flash chromatography with pure hexane to hexane: dichloromethane (v:v= 9:1). The pure white solid was obtained by recrystallization from ethanol (0.23 g, yield 82%). ¹H NMR (CDCl₃, 300 MHz): δ = 7.50 (m, 4H), 7.33 (m, 8 H), 2.78 (t, 4 H), 1.66 (m, 4 H), 1.33 (m, 12 H), 0.85 (t, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ =142.24, 132.30, 131.48, 128.39, 128.23, 123.51, 122.52, 93.87, 88.44, 34.15, 31.76, 30.64, 29.25, 22.63, 14.10. ESI-MS; m/z: 579.2013 [M+Cs⁺]⁺; calcd. For C₃₄H₃₈: 579.2022.



Figure S15. ¹³CNMR spectrum of OPE3.

OPE5. Compound 14 (0.19 g, 0.21 mmol) and iodo benzene (0.039 g, 0.19 mmol) were dissolved in dry THF (15 mL) and dry (i-Pr)₂NH (8 mL). The system was degassed for at least 30 min. Then Pd(PPh₃)₄ (4.2 mg, 0.006 mmol) and CuI (1.1 mg, 0.006 mmol) were added, and the system was stirred overnight at 40°C. Diethyl ether and water were added to the resulting suspension. The two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phases were washed with 2M HCl and saturated NaCl (aq) and then dried over MgSO₄. The crude product was purified by flash chromatography with pure hexane to hexane: dichloromethane (v:v= 9:1). The pure white solid was obtained by recrystallization from ethanol (0.10 g, yield 52%). ¹H NMR (CDCl₃, 500 MHz): δ = 7.53 (m, 4H), 7.34 (m, 12H), 2.80 (m, 12 H), 1.68 (m, 12 H), 1.33 (m, 36H), 0.87 (m, 18H). ¹³C NMR (CDCl₃, 125 MHz): δ =142.27, 141.92, 132.46, 132.28, 131.48, 128.40, 128.25, 123.51, 122.79, 122.53, 93.94, 93.04, 93.01, 88.47, 34.19, 31.84, 31.77, 30.71, 30.68, 29.28, 22.67, 14.11. ESI-MS; m/z: 1115.6375 [M+Cs⁺]⁺; calcd. For C₇₄H₉₄: 1115.6405.



Figure S16. ¹HNMR spectrum of OPE5.



OPE1-NI. Compound 1 (0.39 g, 1 mmol), phenylacetylene (0.13 g, 1.2 mmol) and triphenyl phosphate (10 mg, 0.02 mmol) were dissolved in diisopropylamine (20 ml). The system was degassed for at least 30 min. Then Pd(PPh₃)₂Cl₂ (10 mg, 0.01 mmol) and CuI (10 mg, 0.01 mmol) were added, and the system was stirred for 24 hours at 70°C. Water was added to the resulting solution, which was extracted several times with ethyl acetate. The combined organic phase was then dried over MgSO₄. The pure product was obtained by flash chromatography with hexane to hexane: ethyl acetate (v:v= 10:1) (0.35 g, yield 85%). ¹H NMR (CDCl₃, 300 MHz): δ = 8.67 (dd, 1 H), 8.59 (dd, 1H), 8.50 (d, 1H), 7.89 (d,1H), 7.78 (t, 1H), 7.65 (m, 2H), 7.41 (m, 3H), 4.14 (t, 2 H), 1.70 (m, 2 H), 1.25 (m,10 H), 0.86 (m, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ = 163.89, 163.62, 132.21, 131.87, 131.52, 131.48, 130.66, 130.26, 129.37, 128.60, 127.90, 127.45, 127.35, 122.98, 122.23, 122.11, 98.97, 86.22, 40.56, 31.81, 31.58, 29.69, 29.33, 29.21, 28.12, 27.16, 22.63, 14.08. ESI-MS; m/z: 410.2127 [M+H⁺]⁺; calcd. For C₂₈H₂₇NO₂: 410.2115.



OPE3-NI. Compound 12 (97.6 mg, 0.26 mmol) and compound 4 (0.17 g, 0.24 mmol) were dissolved in dry THF (10 mL) and dry (i-Pr)₂NH (5 mL). The system was degassed for at least 30 min. Then Pd(PPh₃)₄ (11.1 mg, 0.01 mmol) and CuI (1.8 mg, 0.01 mmol) were added, and the system was stirred overnight at 40°C. Diethyl ether and water were added to the resulting suspensions. The two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phases were then dried over MgSO₄. The crude product was purified by flash chromatography with pure hexane to hexane: dichloromethane (v:v= 4:1). (0.10 g, yield 42%). ¹H NMR (CDCl₃, 300 MHz): δ = 8.76 (dd, 1 H), 8.68 (dd, 1H), 8.60 (d, 1H), 7.98 (d,1H), 7.85 (t, 1H), 7.54 (m, 3H), 7.46 (s, 1H), 7.37 (m, 5H), 4.19 (t, 2 H), 2.83 (m, 8 H),1.71 (m, 8H), 1.28 (m, 36 H) 0.87 (m, 15H). ¹³C NMR (CDCl₃, 125 MHz): δ =164.02, 163.76, 142.61, 142.32, 142.24, 141.98, 132.80, 132.71, 132.51, 132.32, 131.61, 131.56, 131.49, 130.75, 130.43, 128.41, 128.30, 128.17, 127.81, 127.39, 124.17, 123.45, 123.11, 122.79, 122.53, 122.10, 121.38, 98.27, 94.09, 93.83, 92.65, 90.76, 88.38, 40.62, 34.51, 34.19, 31.84, 31.77, 30.95, 30.71, 30.68, 29.71, 29.36, 29.28, 29.24, 28.15, 27.17, 22.67, 22.65, 14.10. ESI-MS; m/z: 946.6532 [M+H⁺]⁺; calcd. For C₆₈H₈₃NO₂: 946.6497.



Figure S20. ¹HNMR spectrum of OPE3-NI.



Figure S21. ¹³CNMR spectrum of OPE3-NI.

OPE5-NI. Compound 14 (77.5 mg, 0.09 mmol) and compound 4 (50.1 mg, 0.07 mmol) were dissolved in dry THF (8 mL) and dry (i-Pr)₂NH (4 mL). The system was degassed for at least 30 min. Then Pd(PPh₃)₄ (2.5 mg, 0.004 mmol) and CuI (0.7 mg, 0.004 mmol) were added, and the system was stirred overnight at 40°C. Diethyl ether and water were added to the resulting suspension. The two phases were separated, and the aqueous phase was extracted several times with diethyl ether. The combined organic phases were dried over MgSO₄. The crude product was purified by flash chromatography with pure hexane to hexane: dichloromethane (v:v= 4:1). (0.04 g, yield 40%). ¹H NMR (CDCl₃, 500 MHz): δ = 8.74 (d, 1H), 8.66 (d, 1H), 8.57 (d, 1H), 7.96 (d, 1H), 7.83 (t, 1H), 7.52 (m, 4H), 7.44 (s, 1 H), 7.34 (m, 8H), 4.17 (t, 2 H), 2.80 (m, 16 H), 1.72 (m, 16 H), 1.25 (m, 60 H), 0.86 (m, 27 H). ¹³C NMR (CDCl₃, 125 MHz): δ = 164.03, 163.76, 142.63, 142.28, 142.25, 142.01, 141.99, 141.94, 141.91, 132.81, 132.71, 132.46, 132.29, 131.62, 131.57, 131.48, 130.76, 130.43, 128.40, 128.26, 128.18, 127.81, 127.40, 93.86, 93.24, 93.11, 92.97, 92.73, 90.78, 88.45, 40.62, 34.52, 34.22, 31.84, 31.77, 30.96, 30.72, 30.69, 29.38, 29.36, 29.32, 29.29,

29.24, 28.16, 27.17, 22.68, 22.65, 14.12. ESI-MS; m/z: 1483.0841 $[M+H^+]^+$; calcd. For C₁₀₈H₁₃₉NO₂: 1483.0879.

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Figure S22. ¹HNMR spectrum of OPE5-NI.



Figure S23. ¹³CNMR spectrum of OPE5-NI.



Wavelength (nm) Figure S24. Fluorescence spectra of (a) OPE1-NI, (b) OPE3-NI and (c) OPE5-NI in different solvents.



Figure S25. Transient absorption spectra of OPE3 and OPE5 in THF (λ_{exc} =355 nm, 4 mJ/ pulse, 50ns initial delay, 100 ns delay increment).



Figure S26. Ultrafast transient absorption spectra of (a) OPE3 in hexane, (b) OPE3 in THF, (c) OPE5 in hexane, (d) OPE5 in THF at the indicated delays following a 340 nm laser excitation pulse for the OPE3 and at 370 nm for the OPE5.



Figure S27. Ultrafast transient absorption spectra of OPE1-NI at the indicated delays following a 370 nm laser excitation pulse in different solvents: (a) hexane, (b)THF and (c) DCM.



Figure S28. Ultrafast transient absorption spectra of (a) OPE3-NI and OPE5-NI in THF at the indicated delays following laser excitation pulse.

Sample	Solvent	τ ₁ (ps)	$\tau_2(ps)$	τ 3(ps)	τ 4(ps)
OPE3	HX	-	1	79.7±3.2 (0.4)	669±17(0.6)
OPE3	THF	-		88.4±5.6(0.4)	664±28(0.6)
OPE3	DCM	-		87.8±4.1(0.4)	697 ± 22 (0.6)
OPE5	НХ	-		12.0±3.0(0.1)	452±14(0.7)
OPE5	THF	-		10.9±1.0(0.3)	462±14(0.6)
OPE5	DCM	-		7.0±1.5(0.1)	417±14 (0.8)
OPE1-NI	НХ	-	-	75.6±9.4(0.2)	1350 ±72(0.6)
OPE1-NI	THF	2.5±0.3(0.3)	-	113±22(0.1)	1590±131(0.5)
OPE1-NI	DCM	1.9±0.2(0.3)	-	82.5±6.0(0.3)	$1637 \pm 85(0.3)$
OPE3-NI	HX	-	6.9±0.3(-0.3)	330±28(0.2)	1375±56(0.5)
OPE3-NI	THF	1.7±0.1(0.2)	14.0±0.9(-0.1)	395±31(0.2)	2029±108(0.5)

Table S2. Dynamics of OPEn-NI measured by femtosecond transient absorption.^a

OPE3-NI	DCM	1.2±0.1(0.4)	11.5±0.1(-0.1)	320±32(0.1)	2730±175(0.3)
OPE5-NI	HX	-	5.7±2.0(-0.2)	-	997±16(0.8)
OPE5-NI	THF	$1.9 \pm 0.1(0.2)$	11.2±1.5(-0.1)	-	1471±31(0.6)
OPE5-NI	DCM	$1.3 \pm 0.1(0.5)$	17.6±6.2(-0.1)	-	1406±46(0.4)

^a Monitored at TA band maximum, 550 – 650 nm. Numbers in parenthesis are the amplitudes of lifetime components.



Figure S29. Cyclic voltammetry of OPE_n -NI compounds in DCM solvent with 0.1M NBu_4PF_6 supporting electrolyte.

Compound	E_{ox}/V^a	E _{red} /V ^a	$\Delta E_{0,0}^{b}/eV$
OPE3	1.63	-	3.64
OPE5	1.55	-	3.24
OPE1-NI	1.89	-1.31	3.17
OPE3-NI	1.57	-1.29	3.46
OPE5-NI	1.45	-1.11	3.18

Table S3. Summary of electrochemistry data.

^a Data obtained by cyclic voltammetry measurements using 0.1M NBu₄PF₆ as supporting electrolyte in DCM, platinum wire as working and counter electrodes, and Ag/AgCl as a quasi-reference electrode with scan rate of 100 mV/s. Potentials are reported relative to the Ag/AgCl reference. External calibration showed that Fc/Fc⁺ is at 0.42 V vs the Ag/AgCl quasi-reference. ^b Zero-zero transition energy was estimated by $(E_{abs}^{max} + E_{em}^{max})/2$ in hexane solvent.

Table S4. Driving force and Charge-Transfer energy in hexane, THF and DCM

Compound		$\Delta G_{CS}^{a}/eV$	E_{CT}^{b}/eV
	Hexane	-0.35	-0.53
OPE3-NI	THF	-0.82	-0.78
	DCM	-0.85	-0.90
	Hexane	-0.20	-0.54
OPE5-NI	THF	-0.74	-0.62
	DCM	-0.77	-0.76

^aCalculated from eq. 5. ^bCalculated by the difference in the energy of the CT emission and the LE emission (weak emission in OPEn-NI on high energy side of CT emission).



Figure S30. Center-to-Center Distances for OPE_n-NI Series.