Supporting information materials for "Synthesis, photophysical and photovoltaic investigations of acceptor-functionalized perylene monoimide dyes for nickel oxide p-type dye-sensitized solar cells"

Loïc Le Pleux, Amanda L. Smeigh, Elizabeth Gibson, Yann Pellegrin, Errol Blart, Gerrit Boschloo, Anders Hagfeldt,* Leif Hammarström* and Fabrice Odobel*

General Methods:

Compounds N-(2,5-di-tert-butylphenyl)-perylene-1,6-di(4-tert-butylphenoxy)-9-bromo-3,4-dicarboximide (**1**),[1] benzyl 4-hydroxybenzoate,[2] N-Octylnaphthalene-1,8-dicarboxyanhydride-4,5-di-carboximide[3] (**4**), N-Amino-N′-octylnaphthalene-1,8:4,5-tetracarboxydiimide (**5**)[3], 1,6-di(4-tert-butylphenoxy)-9-bromo-perylene-3,4-dicarboxylicanhydride (**8**),[3] 4-(5,5-dimethyl-1,3-dioxan-2-yl)aniline (**9**),[4] N-(2,5-di-tert-butylphenyl)-perylene-1,6-di(4-tert-butylphenoxy)-9-(4-carboxyphenoxy)-3,4-dicarboximide (**19**)[5] were prepared according to literature methods.

Chemicals were purchased from Aldrich, Acros or ABCR and used as received. Air sensitive reactions were carried out under argon in dry solvents and glassware.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 MHz or AMX 400 MHz Brucker spectrometer. Chemical shifts for ^{1}H NMR spectra are referenced relative to residual protium in the deuterated solvent ($CDCl_3$ $\delta = 7.26$ ppm for ^{1}H and $\delta = 77.16$ ppm for ^{13}C). EI mass spectra were recorded on a EI-MS HP 5989A spectrometer. MALDI-TOF analyses were performed on a BRUKER Ultraflex III, micrOTOF Q spectrometer in positive linear mode at 20 kV acceleration voltage with 2,5-dihydroxybenzoïque acid (DHB) or dithranol as matrix.

Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F$_{254}$. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh) or with SDS neutral alumina (0.05-0.2 mm mesh).

Electrochemical measurements were performed with a potentiostat-galvanostat AutoLab controlled by resident GPES software (General Purpose Electrochemical System 4.9) using a conventional single-compartment three-electrode cell. The working electrode was a Pt electrode, the auxiliary was a Pt wire of 10 mm long and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supported electrolyte was 0.1 N Bu_4NPF_6 in dichloromethane and the solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s.

UV-Visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluoromax fluorimeter.

N-(2,5-di-tert-butylphenyl)-perylene-1,6-di(4-tert-butylphenoxy)-9-(4-carboxybenzylphenoxy)-3,4-dicarboximide (2)

1 (300 mg, 0.34 mmol), benzyl 4-hydroxybenzoate (310 mg, 1.4 mmol) and K_2CO_3 (530 mg, 1.6 mmol) in anhydrous DMF (10 mL) were refluxed for 1h.The reaction mixture was cooled to room temperature. Water (50 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3*50 mL). The combine organic layers were washed with brine and water and dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 7/3) to give the desired product in 85% yield as a red solid. ^{1}H NMR (300 MHz, *CDCl$_3$)* δ ppm 9.45 (dd, J = 7.86, 0.87 Hz, 1H, H_{pery}), 9.33 (d, *J* = 8.74 Hz, 1H, H_{pery}),), 8.32 (s, 1H, H_{pery}), 8.31 (s, 1H, H_{pery}), 8.27 (dd, *J* = 8.27, 0.84 Hz, 1H, H_{pery}), 8.17-8.06 (m, 2H, H_{phenyl}), 7.62 (t, *J* = 8.10 Hz, 1H, H_{pery}), 7.55 (d, *J* = 8.57 Hz, 1H, H_{pery}), 7.50-7.33 (m, 10H, 4 H_{Ar1} + 5 H_{benzyl} + H_{Ar2}), 7.19-7.03 (m, 7H, 4 H_{Ar1} + 2 H_{phenyl} + H_{Ar2}), 6.95 (d, *J* = 2.15 Hz, 1H, H_{Ar2}), 5.37 (s, 2H, CH_2), 1.35 (s, 9H, tBu), 1.33 (s, 9H, *t*Bu), 1.29 (s, 9H, *t*Bu), 1.27 (s, 9H, *t*Bu). ^{13}C NMR (75 MHz, *CDCl$_3$)* δ ppm 165.82, 165.71, 164.22, 161.36, 161.18, 153.9, 153.82, 153.27, 150.04, 149.92, 147.44-147.35, 147.31-147.20, 143.84-143.69, 136.14-136.02, 132.09, 129.63, 129.35, 128.77, 128.64, 128.22, 127.51, 127.21, 127.04, 126.61-126.48, 126.15-126.03, 125.56-125.43, 124.07, 123.81, 122.07-121.93, 121.49-121.33, 118.75, 118.60 , 118.31, 114.87, 66.72, 35.57, 34.48, 34.24, 31.81, 31.51, 31.25, 29.75, 14.30-14.19. HR-MS (MALDI-TOF): m/z: calcd for $C_{70}H_{65}NO_7$ $[M]^{+\bullet}$ 1031.4761 ; found 1031.4789.

1,6-di(4-tert-butylphenoxy)-9-(4-carboxyphenoxy)perylene-3,4-dicarboxylicanhydride (3)

A mixture of **2** (348 mg 0.34 mmol) and KOH (965 mg, 17.2 mmol) in 2-methyl-2-propanol (19 mL) was refluxed for 2h. The hot reaction mixture was poured into acetic acid (37 mL) and the mixture was vigorously stirred for 5 min at room temperature. CH_2Cl_2 was added and the product was extracted, washed with water until neutrality and dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography on silica gel (CH_2Cl_2/MeOH = 1/0 to 9/1) to give the desired product (203 mg) in 80% yield as a red solid. ^{1}H NMR (300 MHz, *CDCl$_3$)* δ ppm 9.45 (d, *J* = 7.94 Hz, 1H, H_{pery}), 9.34 (d, *J* = 8.45 Hz, 1H, H_{pery}), 8.32 (d, *J* = 8.47 Hz, 1H, H_{pery}), 8.21 (m, 2H, H_{pery}), 8.12 (d, *J* = 8.53 Hz, 2H, H_{phenyl}), 7.65 (t, *J* = 8.00 Hz, 1H, H_{pery}), 7.44 (m, 4H, H_{Ar1}), 7.09 (m, 6H, H_{Ar1} + H_{phenyl}), 1.36 (m, 18H, *t*Bu). HR-MS (MALDI-TOF): m/z: calcd for $[M]^{+\bullet}$ $C_{49}H_{38}O_8$ 754.2567 ; found 754.2554.

PMI-NDI

A mixture of **3** (145 mg, 0.192 mmol), N-Amino-N′-octylnaphthalene-1,8:4,5-tetracarboxydiimide (**5**) (91 mg, 0,231 mmol), zinc acetate dihydrate (11 mg, 0,050 mmol), and imidazole (1.37 g, 20.2 mmol) was heated at 140 °C for 2 h. Then the mixture was cooled to room temperature. The resulting solid was dissolved in 1N HCl aq (mL) and extracted with $CHCl_3$ (50 mL). The organic layer was washed with 1N HCl aq (50 mL) and brine (100 mL). The combine organic layers were dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography on silica gel (CH_2Cl_2/MeOH = 100/0 to 98/2) to give the desired product in 31 % yield as a red solid. ^1H NMR (400 MHz, *CDCl₃*) δ ppm 9.45 (d, J = 7.40 Hz, 1H, H_{pery}), 9.33 (d, J = 8.75 Hz, 1H, H_{pery}), 8.81-8.74 (m, 4H, H_{napht}), 8.31 (d, J = 8.63 Hz, 1H, H_{pery}), 8.30 (s, 1H, H_{pery}), 8.28 (s, 1H, H_{pery}), 8.05 (d, J = 8.10 Hz, 1H, H_{pery}), 7.63 (t, J = 8.10 Hz, 1H, H_{pery}), 7.44-7.32 (m, 6H, H_{phenyl} + H_{Ar1}), 7.13 (d, J = 8.29 Hz, 2H, H_{phenyl}), 7.08-7.00 (m, 6H, H_{phenyl} + H_{Ar1}), 4.23-4.14 (m, 2H, N-CH_2), 1.73 (m, 2H, CH_2 octyl chain), 1.33-1.22 (m, 28H, octyl chain + *t*Bu), 0.86 (t, J = 6.80 Hz, 3H, CH_3 octyl chain). HR-MS (MALDI-TOF): m/z: calcd for $[M]^{+\bullet}$ $C_{71}H_{59}N_3O_{11}$, 1129.4150 ; found, 1129.4155.

N-(4-*tert*-Butyl carbamate-aminophenyl)-N′-octylnaphthalene-1,8:4,5-tetracarboxydiimide (6)

5 (150 mg, 0.4 mmol) was dissolved in dry dimethylformamide (8 mL) and the solution was heated to 120 °C. Then, *tert*-Butyl carbamate protected *p*-phenylenediamine (150 mg, 0.40 mmol) was added, and the solution was further heated for 12 h. The reaction mixture was cooled to room temperature. After evaporation, CH_2Cl_2 was added and the mixture was washed with H_2O. The organic layer was dried over $MgSO_4$ and concentrated to dryness and the residue was subjected to column chromatography on silica gel (CH_2Cl_2/MeOH = 1/0 to 100/0.5) to give the desired product in 74 % yield as a yellow solid (167 mg). ^1H NMR (300 MHz, *CDCl₃*) δ ppm 8.79 (s, 4H, H_{napht}), 7.57 (d, J = 8.77 Hz, 2H, H_{phenyl}), 7.24 (d, J = 8.78 Hz, 2H, H_{phenyl}), 6.65 (s, 1H, NH), 4.30-4.12 (m, 2H, N-CH_2), 1.84-1.66 (m, 2H, CH_2 octyl chain), 1.58 (m, 2H, octyl chain), 1.54 (s, 9H, *t*Bu BOC), 1.48-1.19 (m, 8H, octyl chain), 0.88 (m, 3H, CH_3 octyl chain). ^{13}C NMR (75 MHz, *CDCl₃*) δ ppm 163.14, 162.82, 155.64, 152.51, 139.20, 131.39, 131.04, 129.07, 126.98, 126.76, 119.10, 41.10, 31.83, 29.32, 29.22, 28.36, 28.12, 27.13, 22.67, 14.12. HR-MS MALDI-TOF m/z: $[MNa^+]$ calcd for $C_{33}H_{35}N_3O_6Na$, 592,2424 ; found, 592,2450.

N-(4-aminophenyl)-N′-octylnaphthalene-1,8:4,5-tetracarboxydiimide (7)

6 (160 mg, 0,28 mmol) was treated by TFA (10 mL) and stirred at room temperature for 20’. Toluene was added and the resulting solution was concentrated. CH_2Cl_2 was added and the mixture was washed with saturated $NaHCO_3$ solution to reach pH ≈ 8. The organic layer was dried over $MgSO_4$ and concentrated to dryness. ^1H NMR (300 MHz, *CDCl₃*) δ ppm 8.76 (s, 4H, H_{napht}), 7.07 (d, J = 8.32 Hz, 2H, H_{phenyl}), 6.83 (d, J = 7.06 Hz, 2H, H_{phenyl}), 4.22-4.13 (m, 2H, N-CH_2), 3.39 (s, 2H, NH_2), 1.73 (m, 2H, CH_2 octyl chain), 1.30 (m, 10H, octyl chain), 0.85 (t, J = 6.40 Hz, 3H, CH_3 octyl chain). ^{13}C

NMR (75 MHz, *CDCl*$_3$) δ ppm 162.898, 131.339, 129.068, 126.843, 115.797, 49.687, 29.203, 28.093, 27.104, 22.642, 14.080. HR-MS CI m/z: [MH$^+$] calcd for $C_{28}H_{27}N_3O_4$, 470.2080 ; found, 470.20784.

PMI-PhNDI

A mixture of **3** (105 mg, 0.139 mmol), N-(4-aminophenyl)-N′-octylnaphthalene-1,8:4,5-tetracarboxydiimide (**7**) (78 mg, 0.167 mmol), zinc acetate dihydrate (7.9 mg, 0.036 mmol), and imidazole (995 mg) was heated at 140 °C for 2 h. Then the mixture was cooled to room temperature. The resulting solid was dissolved in 1N HCl aq (20 mL) and extracted with $CHCl_3$ (50 mL). The organic layer was washed with 1N HCl aq (50 mL) and brine (100 mL). The combine organic layers were dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography on silica gel (CH_2Cl_2/MeOH = 98/2) to give the desired product in 45 % yield as a red solid. ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 9.45 (m, 1H, H_{pery}), 9.40-9.28 (m, 1H, H_{pery}), 8.80 (s, 4H, H_{napht}), 8.33-8.24 (m, 2H, H_{phenyl}), 8.13-8.06 (m, 2H, H_{pery}), 7.50-7.36 (m, 6H), 7.19-7.00 (m, 6H), 4.25-4.16 (m, 2H, CH_2), 1.67 (m, 12H, octyl chain), 1.35 (m, 18H, *t*Bu), 0.88 (t, *J* = 6.34 Hz, 3H, CH_3). HR-MS MALDI-TOF m/z: [MH$^+$] calcd for $C_{77}H_{64}N_3O_{11}$, 1206.4541; found, 1206.4502.

N-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-perylene-1,6-di(4-tert-butylphenoxy)-9-bromo-3,4-dicarboximide (10)

A mixture of **1** (270 mg, 0.387 mmol), 4-(5,5-dimethyl-1,3-dioxan-2-yl)aniline (96 mg, 0.464 mmol), zinc acetate dihydrate (22.1 mg, 0.101 mmol), and imidazole (2.77 g) was heated at 140 °C for 2.5 h. Then, the mixture was cooled to room temperature. The resulting solid was dissolved in 1N HCl aq (20 mL) and extracted with $CHCl_3$ (50 mL). The organic layer was washed with 1N HCl aq (50 mL) and brine (100 mL). The combine organic layers were dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 2/8) to give the desired product (190 mg) in 55 % yield as a red solid. ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 9.36 (dd, *J* = 7.89, 0.82 Hz, 1H, H_{pery}), 9.13 (d, *J* = 8.56 Hz, 1H, H_{pery}), 8.33 (dd, *J* = 8.37, 0.86 Hz, 1H, H_{pery}), 8.24 (s, 1H, H_{pery}), 8.22 (s, 1H, H_{pery}), 7.86 (d, *J* = 8.56 Hz, 1H, H_{pery}), 7.71-7.60 (m, 3H, H_{pery} + 2 H_{phenyl}), 7.44-7.36 (m, 4H, H_{Ar1}), 7.27 (d, *J* = 8.16 Hz, 2H, H_{phenyl}), 7.09-6.95 (m, 4H, H_{Ar1}), 5.46 (s, 1H, CH), 3.79 (d, *J* = 11.11 Hz, 2H, CH_2), 3.67 (d, *J* = 10.85 Hz, 2H, CH_2), 1.56 (s, 3H, CH_3), 1.33 (s, 18H, *t*Bu), 0.82 (s, 3H, CH_3). HR-MS MALDI-TOF m/z: [M+] calcd for $C_{54}H_{48}BrNO_6$, 885.2665; found, 885,2669.

4-methoxybenzyl 4-iodobenzoate (13)

To a solution of 4-iodobenzoyl chloride (2574 mg, 9.7 mmol) in 50 mL of dry CH_2Cl_2 in a round-bottom flask equipped with a condenser in an ice bath was added dropwise Et_3N (1.35 mL, 9.7 mmol), DMAP (1134 mg, 9.7 mmol) and *p*-methoxybenzyl alcohol (1 mL, 8.05 mmol) in dry CH_2Cl_2 (20 mL) over 5’. After addition, the solution was stirred for 12 h at rt, diluted with 100 mL of CH_2Cl_2, washed with 70 mL of 1% HCl and water (3 x 30 mL), dried with anhydrous $MgSO_4$, and concentrated. The crude was purified by column chromatography on silica gel (CH_2Cl_2) to give the desired product

(1.5 g, 51 %) as a beige solid. ^{1}H NMR (300 MHz, *Acetone-d6*) δ ppm 8.57 (d, *J* = 8.41 Hz, 2H, H_{phenyl}), 8.45 (d, *J* = 7.37 Hz, 2H, H_{phenyl}), 8.12 (d, *J* = 8.57 Hz, 2H, H_{phenyl}), 7.64 (d, *J* = 8.58 Hz, 2H, H_{phenyl}), 5.99 (s, 2H, CH_2), 4.49 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, *Acetone-d6*) δ ppm 207.08, 167.08, 161.61, 139.61, 138.78-138.68, 132.72, 131.89, 129.90, 115.64, 101.98, 68.21, 62.67, 56.50, 55.85-55.76, 31.59, 15.50. MS EI m/z: [M^+] calcd for $C_{15}H_{13}IO_3$, 367.99; found, 367.90.

4-methoxybenzyl 4-(tributylstannyl)benzoate (14)

A solution of **13** (1.5 g, 4.07 mmol), hexabutylditin (3.09 µL, 6.1 mmol), and [$Pd(PPh_3)_4$] (20 mol%, 100 mg) in distilled toluene (68 mL) was refluxed for 24h in a Schlenk flask under argon. After complete conversion of the starting material the solvent was evaporated and the residue was dried in vacuo, and finally purified by column chromatography (silica gel, CH_2Cl_2) to yield **14** as colourless oil (1.16 g, 53 %). ^{1}H NMR (300 MHz, *CDCl₃*) δ ppm 8.01 (d, *J* = 6.66 Hz, 2H, H_{phenyl}), 7.57 (d, *J* = 7.09 Hz, 2H, H_{phenyl}), 7.41 (d, *J* = 8.57 Hz, 2H, H_{phenyl}), 6.93 (d, *J* = 8.62 Hz, 2H, H_{phenyl}), 5.32 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 1.61-1.48 (m, 6H, butyl chain), 1.42-1.27 (m, 6H, butyl chain), 1.18-1.04 (m, 6H, butyl chain), 0.91 (m, 9H, butyl chain). ^{13}C NMR (75 MHz, *$CDCl_3$*) δ ppm 166.84, 159.57, 149.62, 136.33, 129.80, 128.93-128.67, 128.42, 113.89, 66.33, 55.20, 30.61, 29.83-29.67, 28.99, 27.45, 26.91, 26.61, 16.72-16.41, 16.40, 13.60, 12.94-12.85, 12.12-11.88, 11.80, 9.94, 9.62, 7.66-7.45, 7.37. HR-MS MALDI-TOF m/z: [MNa^+] calcd for $C_{27}H_{40}O_3SnNa$, 551.1893; found, 551.1879.

N-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-perylene-1,6-di(4-tert-butylphenoxy)-9-(4-carboxy-*p*-methoxybenzylphenoxy)-3,4-dicarboximide (15)

A solution of **10** (188 mg, 0.21 mmol), stannyl derivative **14** (225 mg, 0.4 mmol), and [$Pd(PPh_3)_4$] (20 mol%, 49 mg) in dry toluene (20 mL) was refluxed for 20 h in a Schlenk flask under argon. The solvent was evaporated and the residue purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 2/8 to 0/1) to yield 15 (162 mg, 73 %) as a bright red solid. ^{1}H NMR (300 MHz, *$CDCl_3$*) δ ppm 9.45-9.29 (m, 2H, H_{pery}), 8.26 (s, 2H, H_{pery}), 8.20 (d, *J* = 8.29 Hz, 2H, H_{phenyl}), 7.91 (d, *J* = 8.35 Hz, 1H, H_{pery}), 7.64 (d, *J* = 8.19 Hz, 1H, H_{pery}), 7.61-7.49 (m, 3H, H_{pery} + 2 H_{phenyl}), 7.41 (m, 6H, 2 H_{phenyl} + 4 H_{Ar1}), 7.28 (m, 4H, H_{phenyl}), 7.05 (m, 4H, 4 H_{Ar1}), 6.94 (d, *J* = 8.66 Hz, 2H, H_{PMB}), 5.36 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 3.79 (d, *J* = 11.17 Hz, 2H, CH_2), 3.67 (d, *J* = 11.02 Hz, 2H, CH_2), 1.33 (s, 18H, *t*Bu). HR-MS MALDI-TOF m/z: [M+] calcd for $C_{69}H_{61}NO_9$, 1047.4346; found, 1047.4366.

N-(4-formylphenyl)-perylene-1,6-di(4-tert-butylphenoxy)-9-(4-carboxy-*p*-methoxybenzylphenoxy)-3,4-dicarboximide (16)

15 (162 mg, 0.155 mmol) was dissolved in a mixture of $CHCl_3$ (4 mL), trifluoroacetic acid (4 mL), and H_2SO_4 aq (1M, 3 mL). After stirring at room temperature for 23 h, the resulting mixture was poured into H_2O (20 mL). The separated aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layer was washed with brine (50 mL) and dried over $MgSO_4$. After filtration and evaporation, the residue was subjected to silica gel column chromatography (CH_2Cl_2) which gave **16** (72 mg, 48% yield) as a red solid. ^{1}H NMR (300 MHz, *CDCl$_3$)* δ ppm 10.09 (s, 1H, CHO), 9.35 (m, 2H, H_{pery}), 8.22 (s, 2H, H_{pery}), 8.20 (d, J = 7.89 Hz, 2H; H_{phenyl}), 8.02 (d, J = 8.35 Hz, 2H, $H_{phenyl'}$), 7.92 (d, J = 8.27 Hz, 1H, H_{pery}), 7.62-7.34 (m, 12H, 2 H_{pery} + 4 H_{Ar1} + 2 H_{PMB} + 2 $H_{phenyl'}$ + 2 H_{phenyl}), 7.04 (d, J = 8.75 Hz, 4H, H_{Ar1}), 6.94 (d, J = 8.67 Hz, 2H, H_{PMB}), 5.36 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 1.33 (s, 18H, *t*Bu). HR-MS MALDI-TOF m/z: [$M^{+\bullet}$] calcd for $C_{64}H_{51}NO_8$, 962.1109; found, 962.1108.

Dyad 17

To a solution of **16** (70 mg; 0.087 mmol) in anhydrous toluene (265 mL) were added C_{60} (126 mg; 0.175 mmol) and N-methylglycine (sarcosine) (78 mg ; 0.874 mmol). The reaction mixture was refluxed under nitrogen for 24h. After the solution was cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/toluene = 2/1 to CH_2Cl_2/toluene = 2/1) to afford **17** as a red product (99 mg, 66 %). ^{1}H NMR (300 MHz, *CDCl$_3$)* δ ppm 9.40 (d, J = 8.17 Hz, 1H, H_{pery}), 9.39 (dd, J = 7.87, 0.89 Hz, 1H, H_{pery}), 8.27 (s, 2H, H_{pery}), 8.20 (d, J = 8.44 Hz, 2H, $H_{phenyl'}$), 7.91 (dd, J = 8.40, 0.91 Hz, 1H, H_{pery}), 7.56 (m, 4H), 7.47-7.32 (m, 8H), 7.17 (m, 2H), 7.06 (m, 4H, H_{Ar1}), 6.93 (d, J = 8.73 Hz, 2H, H_{PMB}), 5.35 (s, 2H, CH_2), 5.00 (d, J = 9.01 Hz, 1H, CH_2 pyrrolidine), 5.01 (s, 1H, CH pyrrolidine), 4.29 (d, J = 9.47 Hz, 1H, CH_2 pyrrolidine), 3.83 (s, 3H, OCH_3), 2.83 (s, 3H, NCH_3), 1.32 (s, 18H, *t*Bu). HR-MS MALDI-TOF m/z: calcd for $[MH]^+$ $C_{126}H_{57}N_2O_7$ 1709.4087 ; found 1709.4085.

PMI-PhC$_{60}$

17 (30 mg, 0.018 mmol) was dissolved in a mixture of dry CH_2Cl_2 (2 mL) and trifluoroacetic acid (2 mL). After stirring at room temperature for 1 h, the resulting dark purple mixture was poured into H_2O (10 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was washed with brine (50 mL) and water until neutrality and dried over $MgSO_4$. After filtration and evaporation, the residue was subjected to silica gel column chromatography (CH_2Cl_2/MeOH = 100/0 to 95/5) which gave **17** (23 mg, 82 %) as a red solid. ^{1}H NMR (300 MHz, *CDCl$_3$)* δ ppm 9.27 (m, 2H, H_{pery}), 8.14 (s, 2H, H_{pery}), 8.07 (d, J = 8.01 Hz, 2H, H_{phenyl}), 7.82 (d, J = 8.09 Hz, 2H, H_{pery}), 7.60 (d, J = 6.16 Hz, 1H, H_{pery}), 7.55-7.37 (m, 6H), 7.26 (m, 7H), 6.94 (m, 4H, H_{Ar1}), 4.91 (s, 1H, CH pyrrolidine), 4.90 (d, J = 8.69 Hz, 1H, CH_2 pyrrolidine), 4.82 (d, J = 6.68 Hz, 1H, CH_2 pyrrolidine), 2.72 (s, 3H, NCH_3), 1.19 (s, 18H, *t*Bu). HR-MS MALDI-TOF m/z: calcd for $[MH]^+$ $C_{118}H_{49}N_2O_6$ 1589,35851 ; found 1589,36079.

N-(2,5-di-tert-butylphenyl)-perylene-1,6-di(4-tert-butylphenoxy)-9-(4-carboxyphenyl)-3,4-dicarboximide (18)

A Schlenk flask was charged with **1** (64 mg, 0.07 mmol), 4-carboxyphenylboronic acid (18 mg, 0.1 mmol), cesium fluoride (40 mg, 0.188 mmol), and silver$^{(I)}$ oxide (25 mg, 0.1 mmol), and the flask was evacuated and backfilled with nitrogen two times. Tetrakis(triphenylphosphine)palladium (8.4 mg, 10 mol%) was added. The flask was evacuated and backfilled with nitrogen three times. Subsequently, distilled DME (2.4 mL) was added by syringe. The resulting solution was purged with argon through 3 freeze-pump-thaw cycles. Subsequently, the reaction mixture was stirred at 80°C for 24 h with vigorous stirring. After being cooled to room temperature, CH_2Cl_2 was added and the mixture was washed with H_2O. The combined organic layer was dried over $MgSO_4$. and concentrated. The crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 1/0 to 9/1) to afford **18** as a red product (43 mg, 64 %). ^1H NMR (300 MHz, *CDCl$_3$*) ppm 9.36 (d, *J* = 8.13 Hz, 1H, H_{pery}), 9.35 (d, *J* = 7.30 Hz, 1H, H_{pery}), 8.28 (s, 2H, H_{pery}), 8.20 (d, *J* = 8.17 Hz, 1H, H_{pery}), 7.90 (d, *J* = 8.08 Hz, 1H, H_{pery}), 7.71-7.56 (m, 7H, 2 H_{Ar2} + H_{pery} + 4 H_{Ar1}), 7.56-7.31 (m, 4H, H_{phenyl}), 7.05 (m, 4H, H_{Ar1}), 6.90 (d, ^3J = 2.13 Hz, 1H, H_{Ar2}), 1.25 (m, 36H, *t*Bu). HR-MS MALDI-TOF m/z: calcd for $[MH]^+$ $C_{63}H_{60}NO_6$ 926,44152 ; found 926,43515.

References

1. Fuller, M. J.; Wasielewski, M. R., *J. Phys. Chem. B* **2001,** 105, 7216-7219.
2. Taylor, E. C.; Yoon, C.-m., *J. Org. Chem.* **1994,** 59, (23), 7096-7098.
3. Hayes, R. T.; Wasielewski, M. R.; Gosztola, D., *J. Am. Chem. Soc.* **2000,** 122, (23), 5563-5567.
4. Imahori, H.; Azuma, T.; Ajavakom, A.; Norieda, H.; Yamada, H.; Sakata, Y., *J. Phys. Chem. B* **1999,** 103, (34), 7233-7237.
5. Morandeira, A.; Fortage, J.; Edvinsson, T.; Le Pleux, L.; Blart, E.; Boschloo, G.; Hagfeldt, A.; Hammarstroöm, L.; Odobel, F., *J. Phys. Chem. C* **2008,** 112, (5), 1721-1728.

Table S1. Time constants obtained from global analysis of solution phase data

	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)
PMI-18	1.4 ± 0.2	120 ± 2.5	4.3 ± 0.07
PMI-19	2.8 ± 0.5	250 ± 7.6	4.5 ± 0.08
PMI-NDI	1.6 ± 0.2	44 ± 2.0	4.0 ± 0.14
PMI-PhNDI	2.8 ± 0.3	350 ± 15	3.9 ± 0.10
PMI-PhC$_{60}$	3.3 ± 0.2	28 ± 3.7	> 50

All molecules are in CH_2Cl_2.

Table S2. Time constants obtained from global analysis of PMI/NiO data in the presence of different electrolytes

		τ_{CS1} (ps)	τ_{CS2} (ps)	τ_{CR1} (ps)	τ_{CR2} (ps)
PMI-18	A	1.7 ± 0.04	18 ± 0.6	190 ± 5.7	9200 ± 340
	B	1.0 ± 0.02	13 ± 0.43	150 ± 5.3	13000 ± 560
	C	1.0 ± 0.02	13 ± 0.5	170 ± 7.0	18000 ± 1100
PMI-19	A	0.86 ± 0.07	5.5 ± 0.23	100 ± 1.9	6800 ± 270
	B	1.6 ± 0.04	16 ± 0.73	160 ± 5.4	8800 ± 370
	C	1.4 ± 0.05	12 ± 0.6	130 ± 3.7	8900 ± 340

Electrolyte solution: A is 0.1 M $LiClO_4$ in propylene carbonate, B 0.1 M LiI & 1 M I_2 in propylene carbonate, C is 0.1 M $[Co(dtb)_3](ClO_4)_2$ & 0.1 M $[Co(dtb)_3](ClO_4)_3$ & 0.1 M $LiClO_4$ in propylene carbonate.

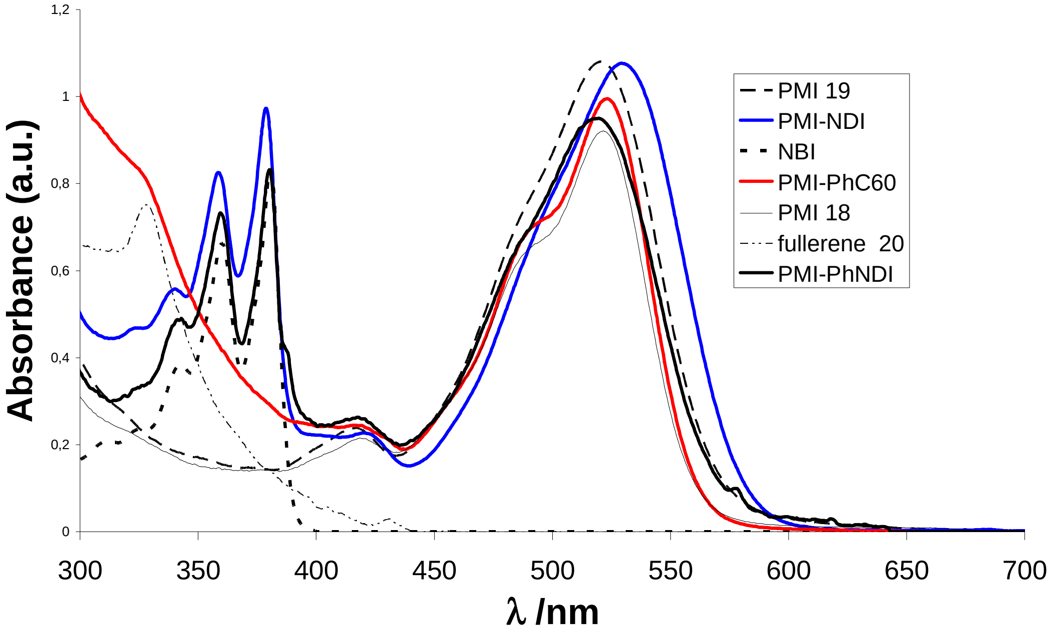
Table S3. Time constants obtained from global analysis for Dyads/ NiO in the presence of different electrolytes

		τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
PMI-NDI	A	0.21 ± 0.01	1.5 ± 0.06	28 ± 1.7	190 ± 22[1]
	B	0.35 ± 0.03	2.1 ± 0.16	30 ± 2.1	250 ± 30[1]
	C	0.27 ± 0.03	2.5 ± 0.21	25 ± 2.3	210 ± 30[1]
PMI-PhNDI	A	0.29 ± 0.03	3.0 ± 0.31	45 ± 2.6	300 ± 33
	B	0.28 ± 0.05	3.4 ± 0.33	46 ± 2.2	370 ± 27
	C	0.30 ± 0.04	3.6 ± 0.41	47 ± 3.4	320 ± 40
PMI-PhC$_{60}$	A	0.3 ± 0.01	2.3 ± 0.1	24 ± 0.7	-
	B	0.3 ± 0.015	2.5 ± 0.11	23 ± 0.8	-
	C	0.3 ± 0.01	2.5 ± 0.1	21 ± 0.7	-

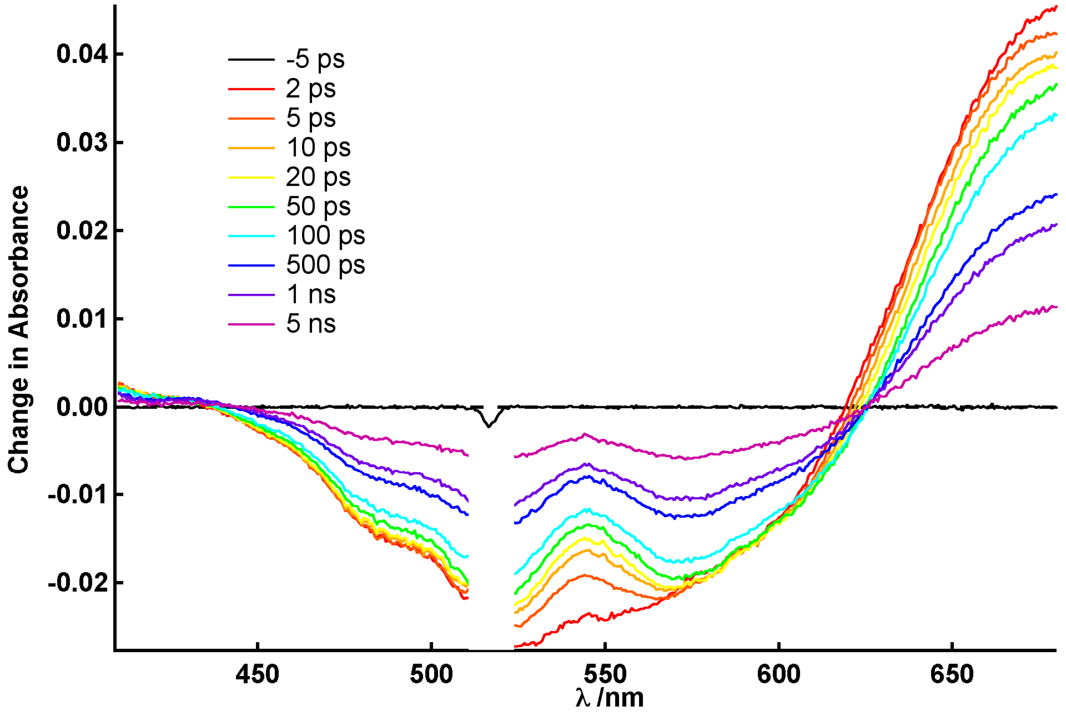
A) 0.1 M $LiClO_4$ in propylene carbonate, B) 0.1 M LiI, 1 M I_2 in propylene carbonate and C) 0.2 M $[Co(dtb)_3](ClO_4)_{2/3}$ with 0.1 M $LiClO_4$ in propylene carbonate

Fitting error is from global analysis values.

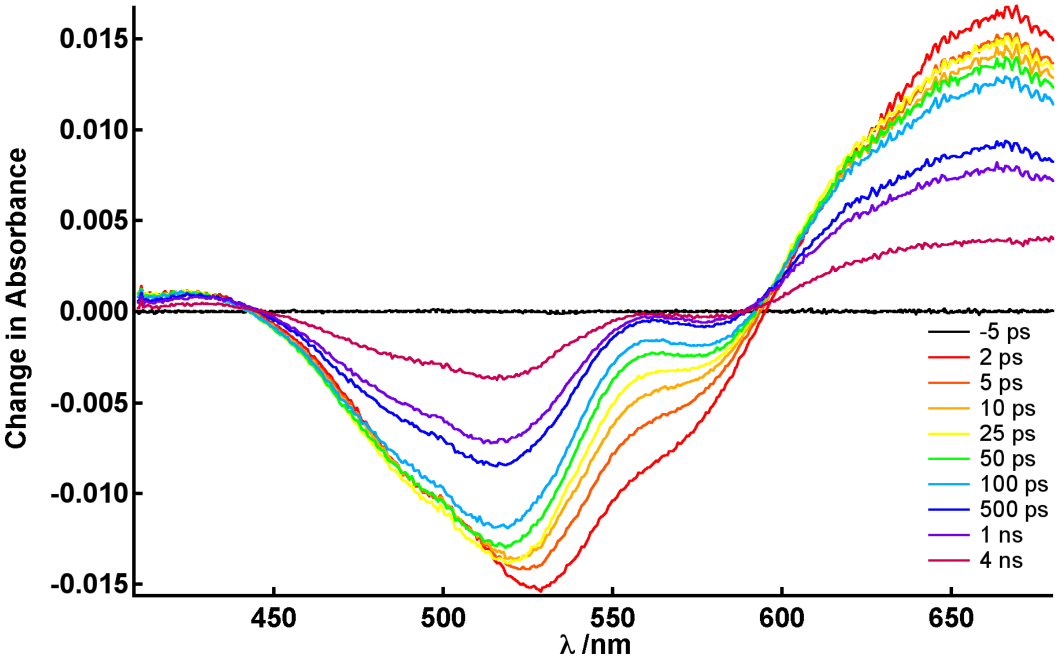
[1] Attributed to the kinetics associated with PMI monomer, which persists through the purification process.



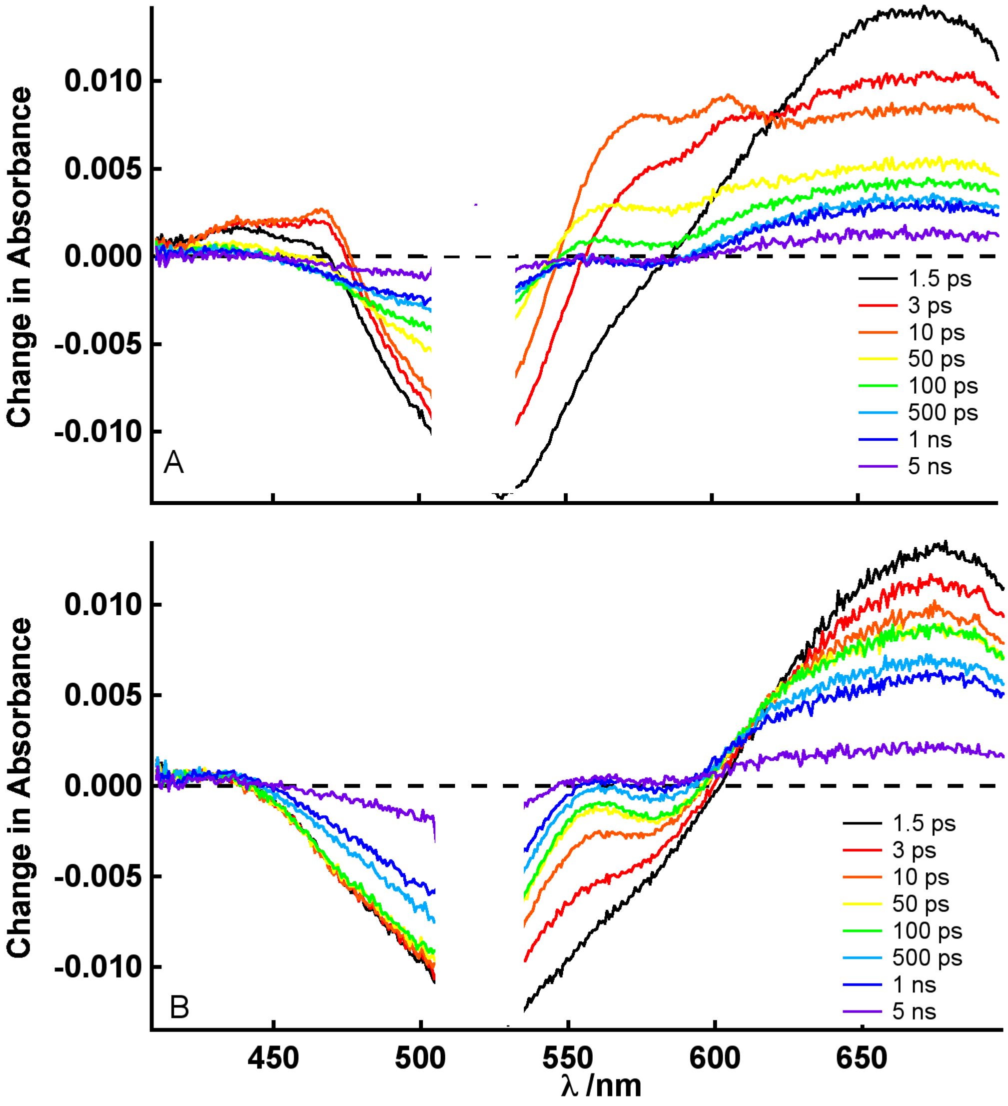
S1. Overlay of the absorption spectra of the dyads recorded in dichloromethane along with that of their constituents.



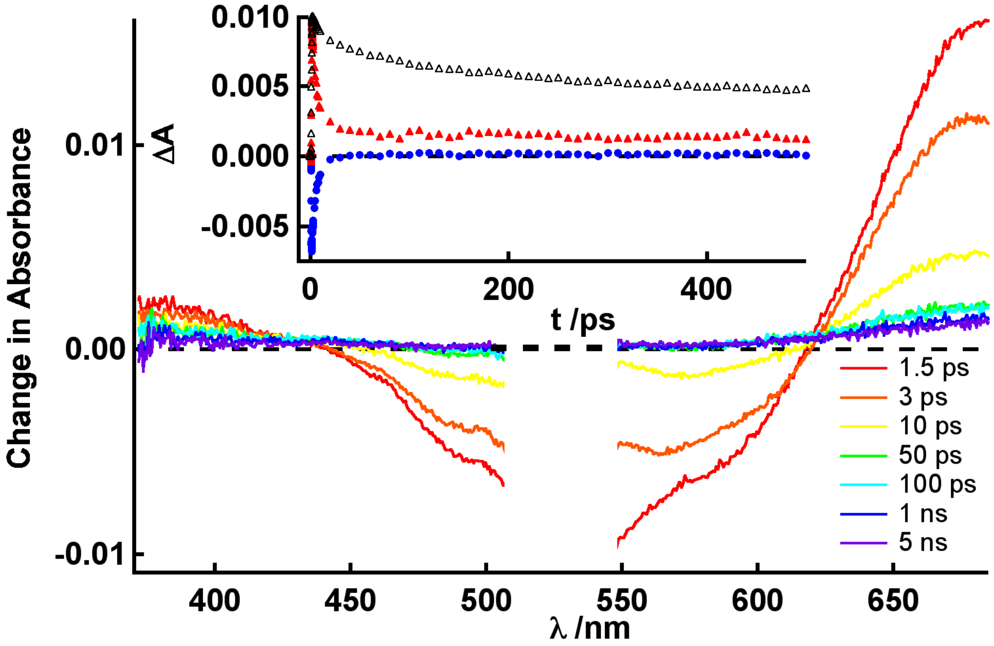
S2. Transient absorption spectra for PMI-**18** in CH_2Cl_2.
Transient absorption spectra at various delays after excitation at 520 nm (500 nJ)



S3. Transient absorption spectra for PMI-**19** in CH_2Cl_2.
Transient absorption spectra at various delays after excitation at 520 nm (500 nJ)

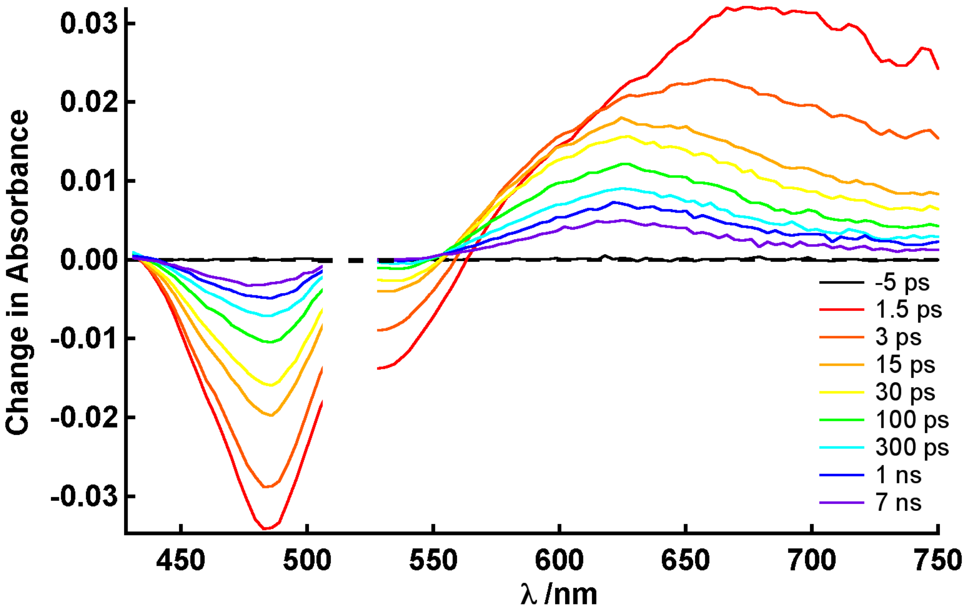


S4. Transient absorption spectra for **PMI-NDI** (top) and **PMI-PhNDI** (bottom) in CH_2Cl_2. Delay time after excitation with 520 nm (700 nJ)

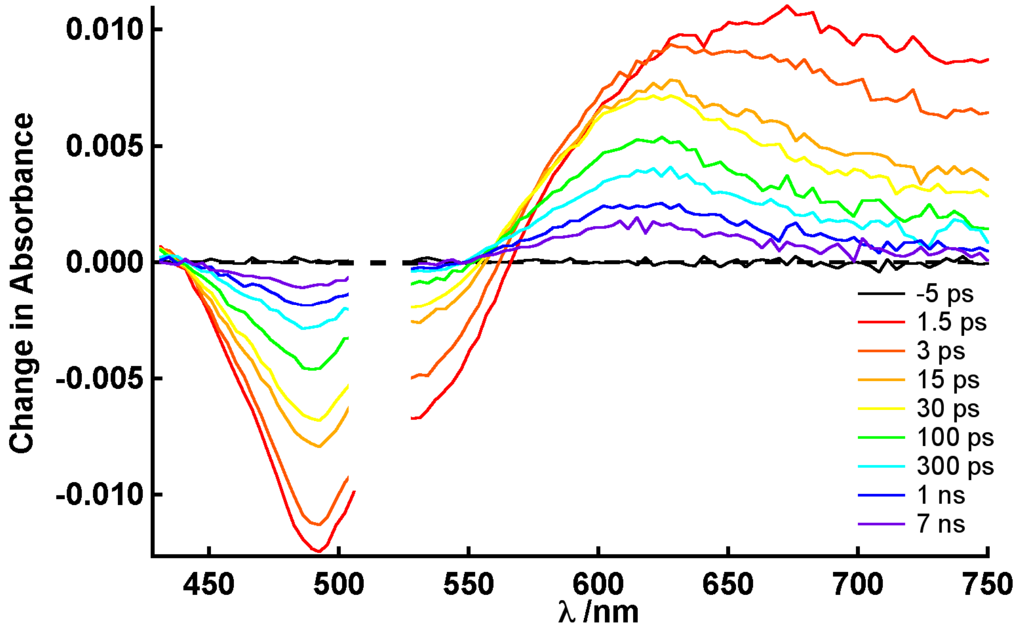


S5. Transient absorption spectra of **PMI-PhC$_{60}$** in CH_2Cl_2.

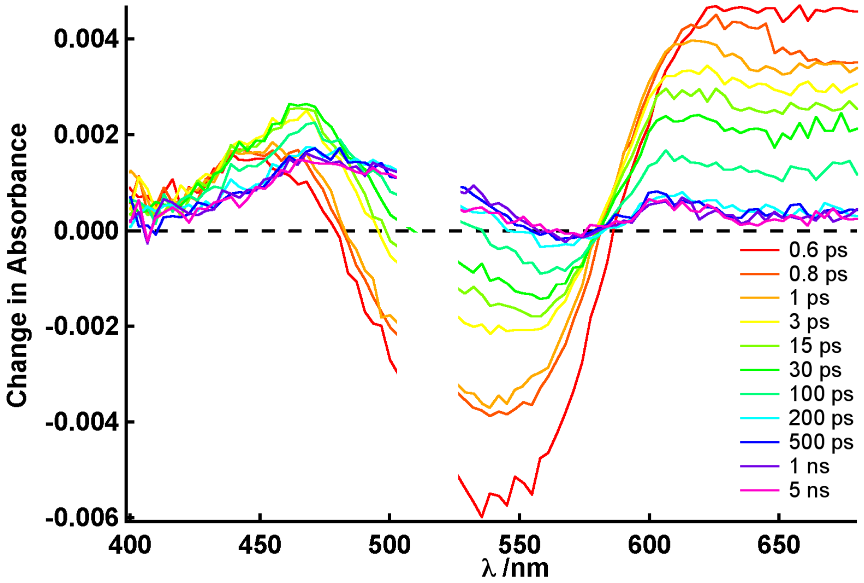
Spectra presented are at delay times indicated after excitation with 520 nm (200 nJ) Inset: Kinetic traces at 650 nm probe (positive signals) of PMI-18 (open black triangles) and PMI-PhC$_{60}$ (solid red triangles), and at 575 nm probe (negative signal) of PMI-PhC$_{60}$ (solid blue circles) in CH_2Cl_2; after 520 nm excitation.



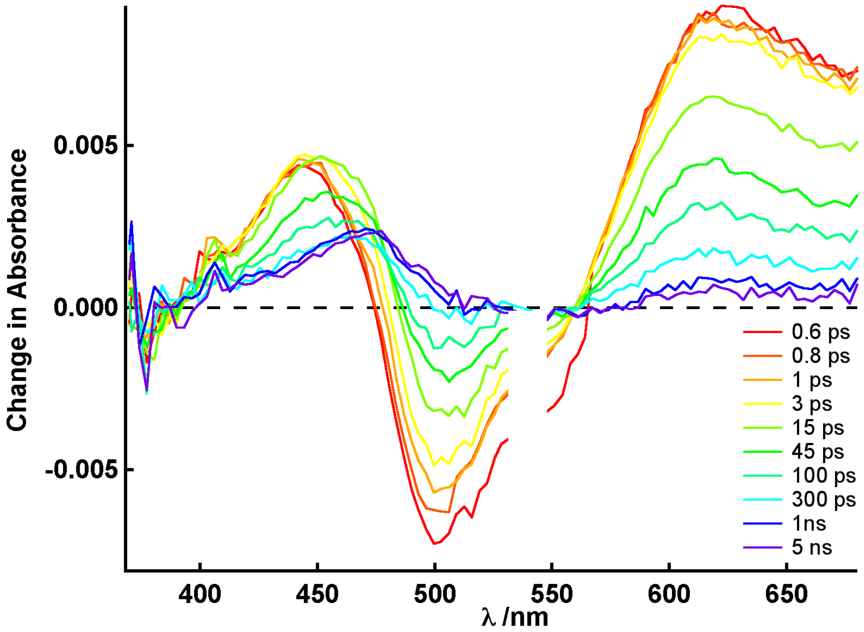
S6. Transient absorption spectra of PMI-**18**/NiO in the presence of the iodide mediator Excitation at 520 nm (480 nJ) in the presence of 0.1 M LiI/1.0 M I_2 in propylene carbonate



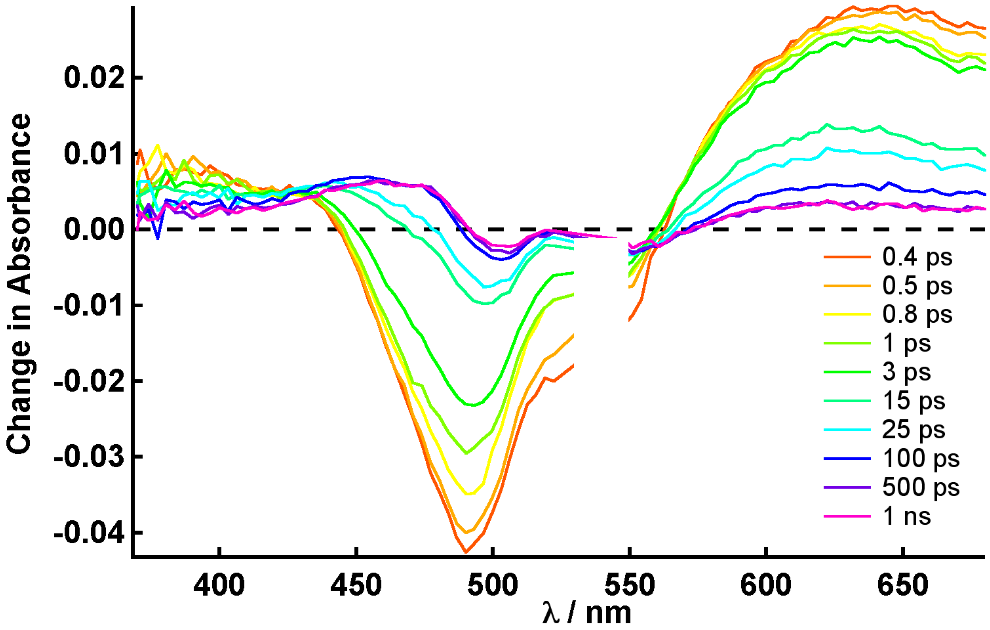
S7. Transient absorption spectra of PMI-**19**/NiO in the presence of the iodide mediator Excitation at 520 nm (480 nJ) in the presence of 0.1 M LiI/1.0 M I_2 in propylene carbonate



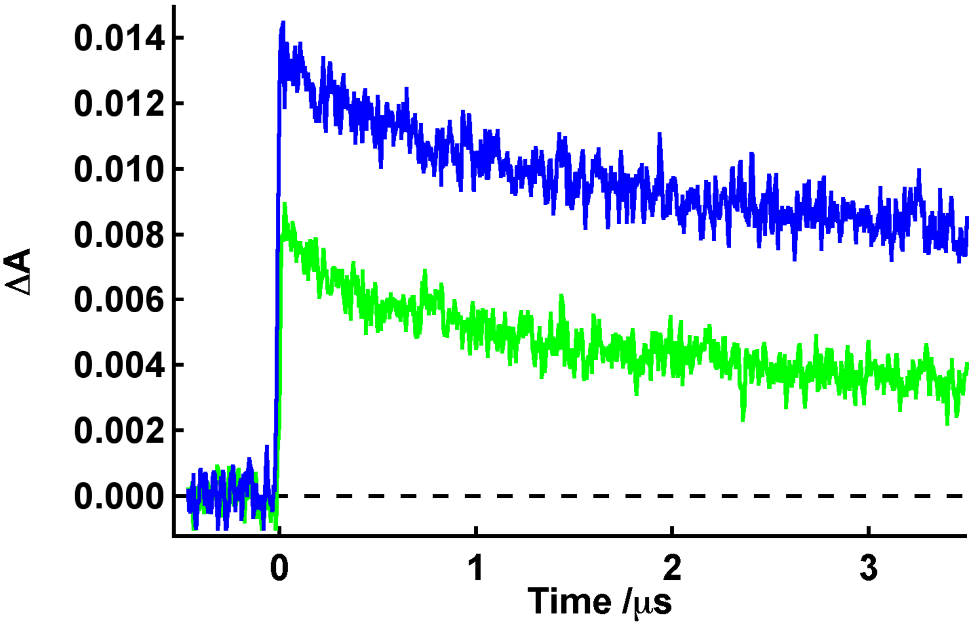
S8. **PMI-NDI**/NiO transient absorption spectra in the presence of cobalt mediator Excitation at 520 nm (400 nJ) in the presence of 0.1 M $[Co(dtb)_3]^{n+}$ in propylene carbonate



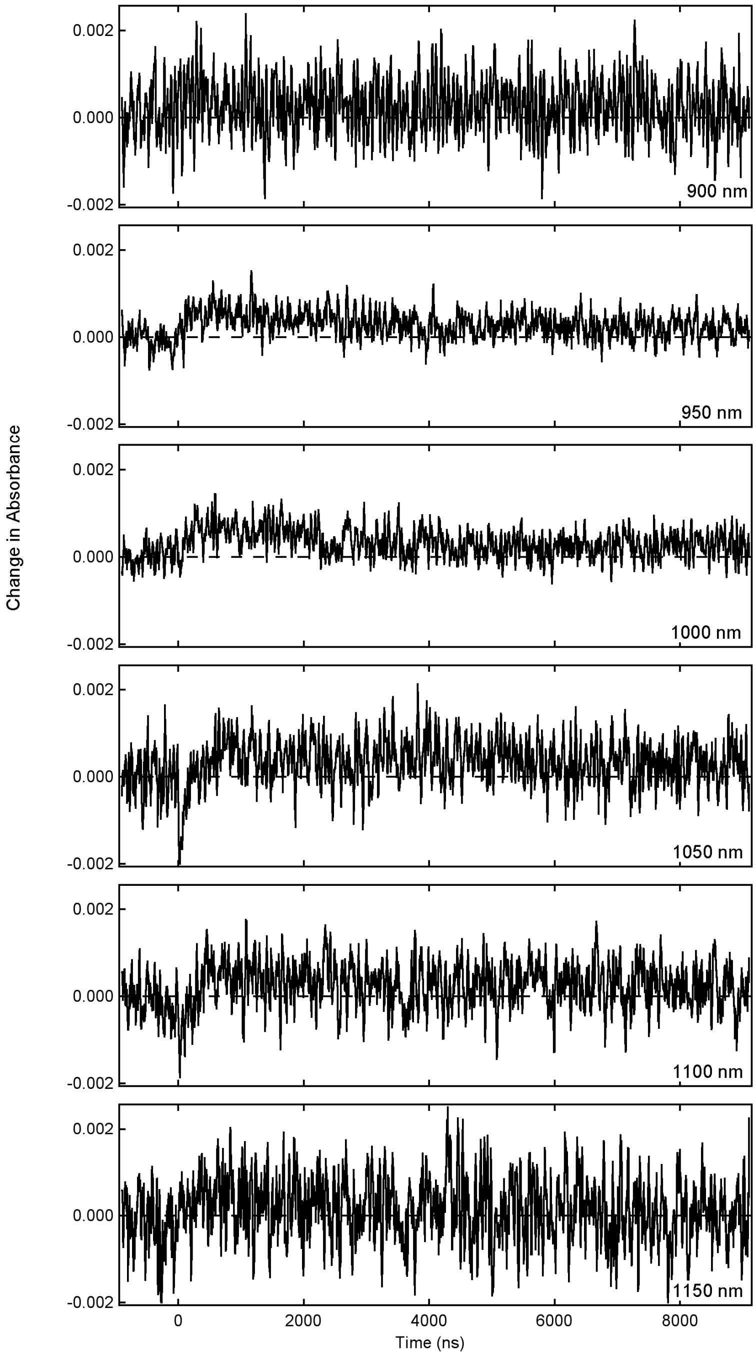
S9. **PMI-PhNDI**/NiO transient absorption spectra in the presence of cobalt mediator Excitation at 520 nm (400 nJ) in the presence of 0.1 M $[Co(dtb)_3]^{n+}$ in propylene carbonate



S10. **PMI-PhC$_{60}$**/NiO transient absorption spectra in the presence of the iodide mediator. Excitation at 540 nm (200 nJ) in the presence of 30 mM LiI and 3 mM I_2 in propylene carbonate.

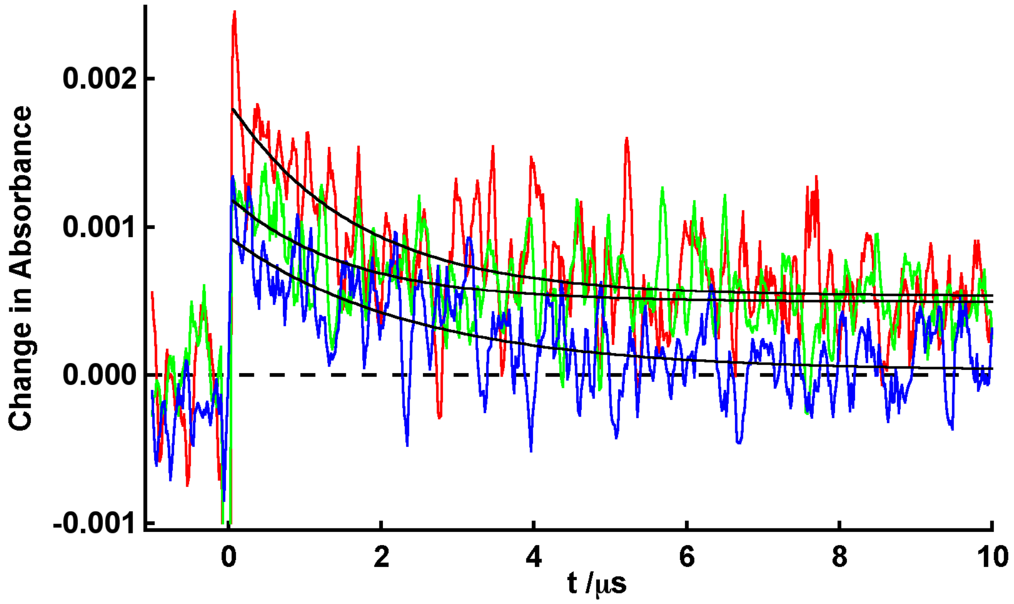


S11. Kinetic traces at 475 nm of **PMI-NDI**/NiO in the presence of $LiClO_4$ (blue) and $[Co(dtb)_3]^{n+}$ (green) electrolyte. The same sensitized film was used to measure both kinetic traces, indicating rapid quenching of the NDI^- state by the cobalt electrolyte when compared to the intrinsic NDI^- population.

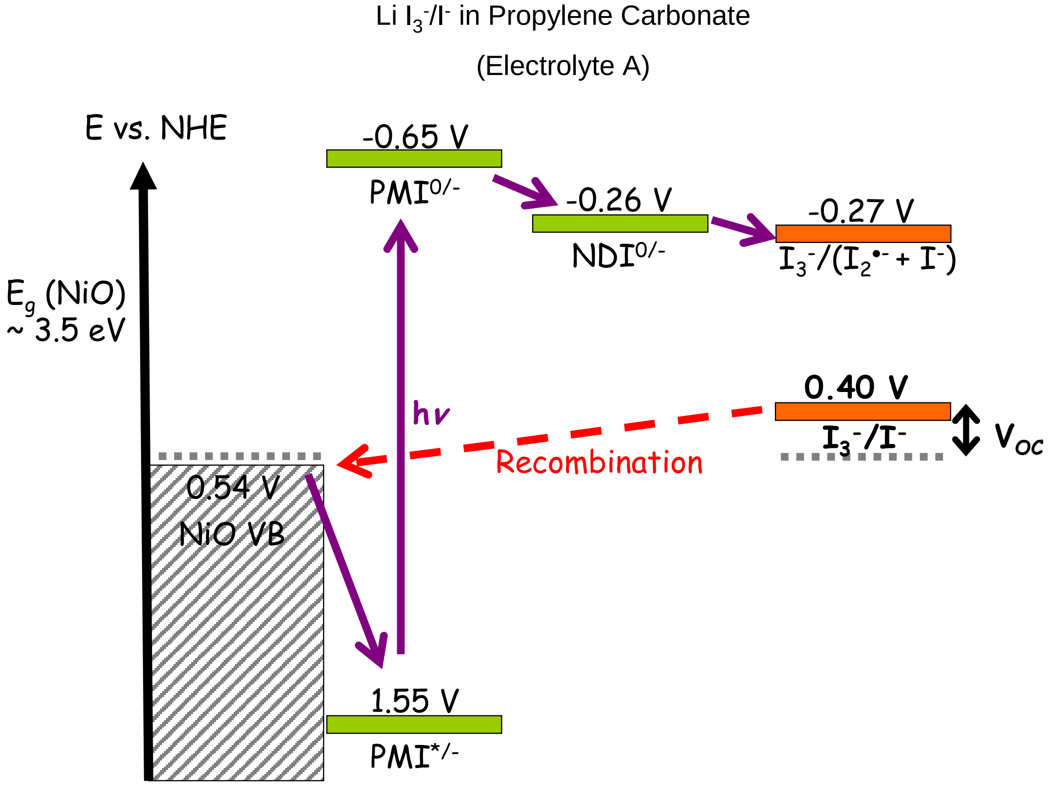


S12. NIR kinetic traces of **PMI-PhC$_{60}$**/NiO

Excitation at 540 nm of **PMI-PhC$_{60}$**/NiO in the presence of Li$^+$ at various NIR probes. The presence of a feature around 950 - 1050 nm supports the assumption that photoexcitation of **PMI-PhC$_{60}$**/NiO results in reduction of C$_{60}$, which recombines on the microsecond timescale.



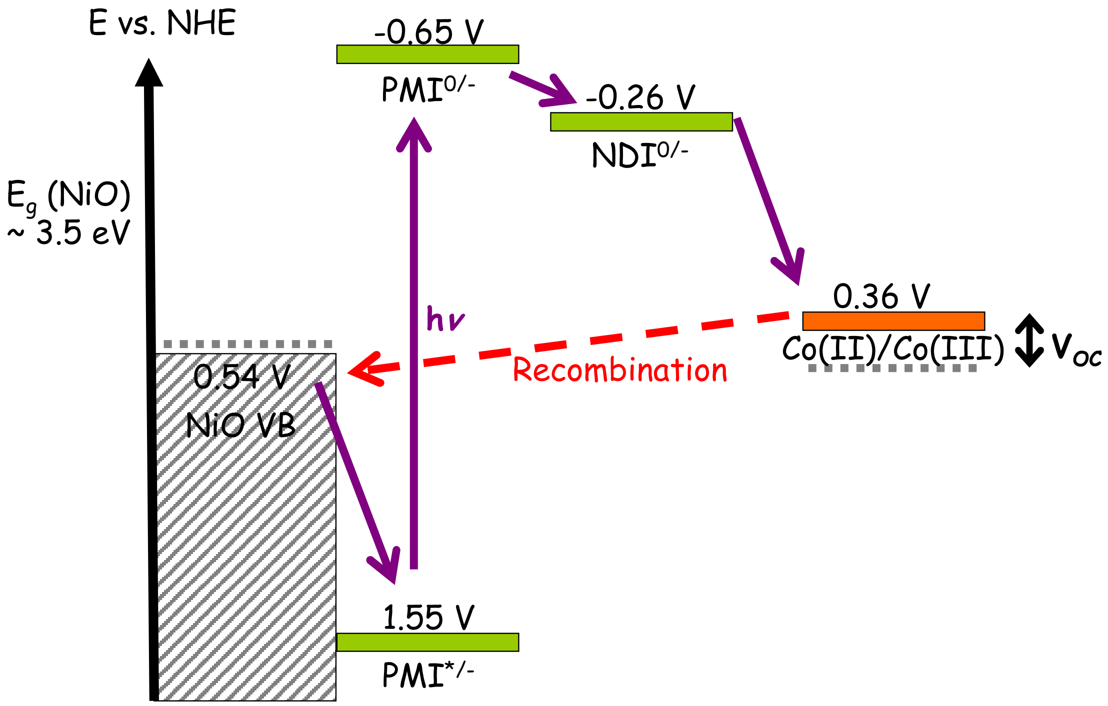
S13. Visible kinetic traces of **PMI-PhC$_{60}$**/NiO in the presence of various electrolytes $LiClO_4$ (blue), I^-/I_3^- (red) and $[Co(dtb)_3]^{n+}$ (green). Fits shown in black correspond to time constants reported in the main text Table 3.



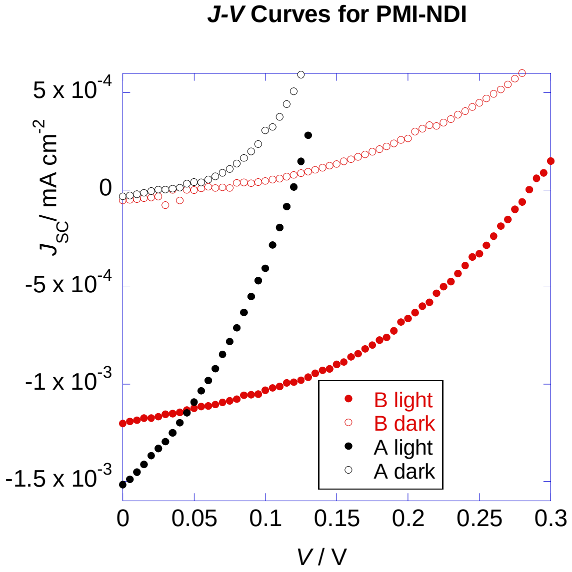
S14. Energy level diagram for **PMI-NDI**/NiO in the presence of 0.1 M LiI & 0.01 M I_2 in propylene carbonate.

Co(II/III) tris(4,4'-di*tert*-butyl-2,2'-dipyridyl) perchlorate in Propylene Carbonate

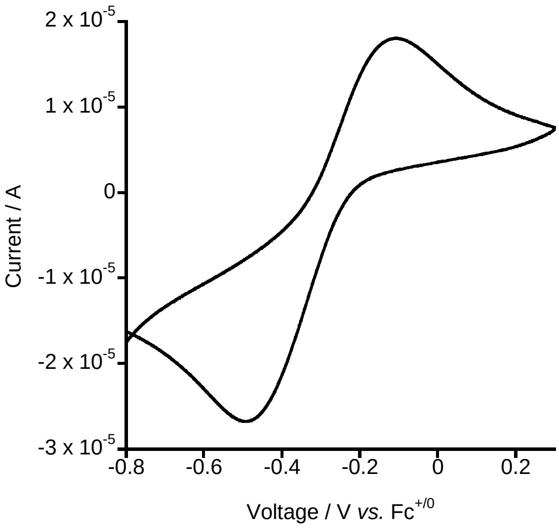
(Electrolyte B)



S15. Energy level diagram for **PMI-NDI**/NiO in the presence of cobalt electrolyte



S16. *J-V* curves for **PMI-NDI** in the dark (open symbols) and under illumination (filled symbols). Black symbols: I_3^-/I^- electrolyte; red symbols: $Co^{III/II}$ electrolyte.



S17. Current – voltage plot for tris(4,4'-di-*tert*-butyl-2,2'-bipyridene)cobalt(II/III) in propylene carbonate. 0.01 M each Co^{2+} and Co^{3+} in 0.1M $LiClO_4$, measured using a glassy carbon working electrode, Pt counter electrode, and Ag/Ag^+ reference electrode, calibrated against ferrocene in the same solvent. The rest potential of the triiodide/iodide electrolyte used was measured in a two electrode set up against a $Ag/AgNO_3$ in propylene carbonate reference electrode, calibrated against $Fc^{+/0}$.