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Electronic Supplementary Information for

Photo-driven Electron Transfer from the Highly Reducing Excited State of Naphthalene Diimide Radical Anion to a CO_2 Reduction Catalyst within a Molecular Triad

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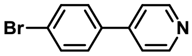
Characterization. ^{1}H NMR spectra were recorded on a Bruker Avance 500 TCI Cryoprobe Spectrometer. Chemical shifts are recorded in ppm (δ) in $CDCl_3$ (internal reference set to δ 7.26 ppm). ^{13}C NMR (126 MHz) spectra were recorded using a Bruker Avance III QNP Cryoprobe with simultaneous decoupling of ^{1}H nuclei and externally referenced to TMS set to 0 ppm. All spectra were recorded at 298 K. ESI-MS were performed by Northwestern University's Integrated Molecular Structure Education and Research Center.

Synthesis

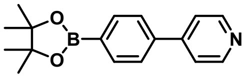
1.



2.0 g (16.39 mmol) 4-pyridinylboronic acid, 6.94 g (24.59 mmol) 1-Bromo-4-iodobenzene, and 13.9 g (131.12 mmol) Na_2CO_3 were combined in 300 mL THF and 100 mL DI H_2O in a 500 mL two-necked roundbottom flask and sparged 30 minutes with N_2. 0.9 g (0.8 mmol) $Pd(PPh_3)_4$ was added under flow of N_2 and the solution sparged for an additional ten minutes, then refluxed overnight. The flask was cooled to room temperature, and the solvents were removed under reduced pressure. The remaining solid was suspended in 300 mL of DCM and poured over a silica plug. The product was then eluted using ethyl acetate. The solvent was evaporated under vacuum to yield pure product. Yield: 0.86 g (22%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.70 – 8.61 (m, 2H), 7.66 – 7.59 (m, 2H), 7.54 – 7.42 (m, 4H).

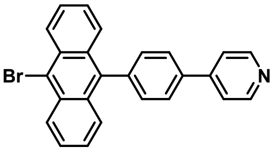
2.



3.2 g (13.5 mmol) **1** and 4.3 g (16.9 mmol) bispinacolatoboron (B_2pin_2) were combined with 4.0 g potassium acetate and 0.5 g (0.7 mmol) Pd(dppf)Cl_2 in a 500 mL two-neck round bottom flask fitted with a condensor. 300 mL dry dioxane was added into the flask and sparged 30 minutes with N_2. The solution was stirred at 100 °C overnight. The flask was cooled to RT and the solvent was under reduced pressure. The contents were suspended in 300 mL of DCM and pour over a silica plug. The product was eluted using ethyl acetate. The solvent was evaporated under reduced pressure and then sonicated in minimal pentane and gravity filtered. The solid was washed with cold pentane to yield pure product. Yield: 1.54 g (40%)**.**

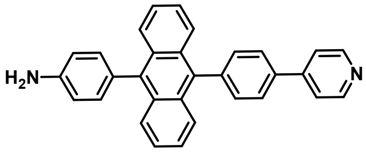
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.69 – 8.64 (m, 2H), 7.95 – 7.90 (m, 2H), 7.67 – 7.62 (m, 2H), 7.55 – 7.50 (m, 2H), 1.37 (s, 12H).

3.



1.3 g (4.6 mmol) **2**, 15.54 g (46.0 mmol) 9,10-dibromoanthracene, and 3.9 g (37.0 mmol) Na_2CO_3 were combined in 500 mL THF and 150 mL DI H_2O in a 1 L two-necked roundbottom flask and sparged 30 minutes with N_2. 0.3 g (0.05 mmol) $Pd(PPh_3)_4$ was added under flow of N_2 and the solution sparged for an additional ten minutes, then refluxed overnight. The flask was cooled to room temperature, and the solvents were removed under reduced pressure. The contents were suspended in 300 mL of DCM, poured over a silica plug and washed with DCM until the excess 9,10-dibromoanthracene had been removed. Ethyl acetate was used to elute the product. The solvent was evaporated under reduced pressure and then sonicated in minimal DCM and gravity filtered. The product was washed with copious amounts of cold methanol to afford the pure product. Yield 0.8 g (43%).

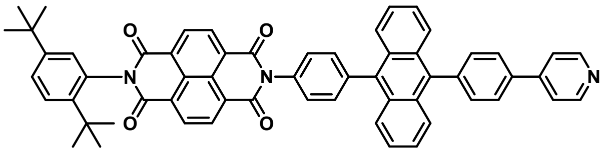
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.78 – 8.71 (m, 2H), 8.64 (d, *J* = 8.9 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.72 – 7.65 (m, 4H), 7.65 – 7.58 (m, 2H), 7.58 – 7.52 (m, 2H), 7.43 – 7.39 (m, 2H).



4.

0.8 g (2.0 mmol) **3**, 0.9 g (3.9 mmol) to 4-Aminophenylboronic acid pinacol ester, and 2.2 g (15.6 mmol) Na_2CO_3 were combined in 500 mL THF and 150 mL DI H_2O in a 1 L two-necked roundbottom flask and sparged 30 minutes with N_2. 0.3 g (0.05 mmol) $Pd(PPh_3)_4$ was added under flow of N_2 and the solution sparged for an additional ten minutes, then refluxed overnight. The flask was cooled to room temperature, and the solvents were removed under reduced pressure. The contents were suspended in 300 mL of DCM and pour over a silica plug. The product was eluted using ethyl acetate. Ethyl acetate was removed under reduced pressure. The solid was then sonicated in copious amounts of MeOH and then gravity filtered. The solid remaining was then sonicated in minimal DCM and copious amounts of MeCN and then gravity filtered and collected. Yield 0.68 g (80%).

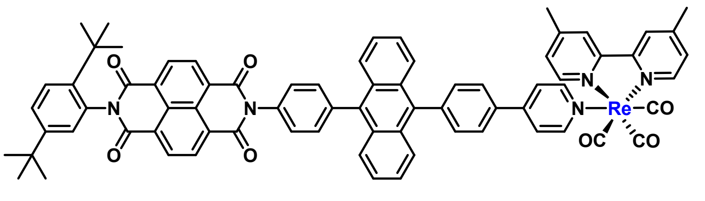
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.77 – 8.73 (m, 2H), 7.93 – 7.88 (m, 2H), 7.86 – 7.82 (m, 2H), 7.73 – 7.68 (m, 4H), 7.63 – 7.59 (m, 2H), 7.37 – 7.33 (m, 4H), 7.28 – 7.26 (m, 2H), 6.95 – 6.92 (m, 2H), 3.87 (bs, 2H).



5.

In an oven dried round bottom flask with a magnetic stirrer and reflux condenser, **4** (0.16 g, 0.427) and DtB-NIA (0.24 g, 0.53 mmol)[1] were dissolved in pyridine (50mL) and heated to 120 °C under N_2 overnight. The solution was cooled to room temperature and pyridine was removed in vacuo. The gooey residue was sonicated in ethanol until a solid precipitated, gravity filtered and collected. The solid was then dissolved in DCM and poured over silica plug. The product was eluted with ethyl acetate. The solvent was evaporated under reduced pressure and then sonicated in MeOH and filtered to afford the pure product. Yield 0.19 g (52%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.96 – 8.91 (m, 4H), 8.77 – 8.75 (m, 2H), 7.94 – 7.90 (m, 2H), 7.87 – 7.84 (m, 2H), 7.78 – 7.69 (m, 6H), 7.67 – 7.59 (m, 5H), 7.51 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.46 – 7.39 (m, 4H), 7.05 (d, *J* = 2.1 Hz, 1H), 1.35 (s, 9H), 1.30 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.95, 163.37, 150.58, 148.18, 143.83, 140.25, 140.13, 137.46, 136.71, 136.33, 134.12, 132.59, 132.31, 132.11, 131.75, 131.72, 130.02, 129.95, 129.21, 128.83, 127.68, 127.58, 127.53, 127.49, 127.25, 127.21, 126.91, 126.76, 125.62, 125.56, 121.81, 100.13, 77.41, 77.16, 76.91, 35.75, 34.47, 31.91, 31.37, 26.15 **HRMS-ESI** (*m/z*): calculated $C_{59}H_{45}N_3O_4$ $[M+H]^+$: 860.3489, found 860.3493



6.

In a nitrogen filled glove box, an oven dried pressure flask with a magnetic stirrer was filled with Re(dmb)$(CO)_3$Br (14 mg, 0.03 mmol), **5** (25g, 0.03 mmol), $AgPF_6$ (7.8 mg, 0.04 mmol), and dichloromethane (40 mL). The pressure flask was capped and brought out of the glovebox and heated to 80°C overnight. The solution was cooled to room temperature and filtered through celite. The solvent was removed under reduced pressure and then sonicated in copious amounts of toluene, gravity filtered and collected. The compound was then sonicated in minimal MeOH, gravity filtered and collected. The compound was then dissolved in minimal dichloromethane and layered with diethyl ether. Upon filtering, a brown solid was obtained. Yield 0.03 g (66%).

^{1}H NMR (500 MHz, Methylene Chloride-*d*$_2$) δ 9.02 (d, *J* = 5.8 Hz, 2H), 8.92 (d, *J* = 7.5 Hz, 2H), 8.89 (d, *J* = 7.5 Hz, 2H), 8.29 – 8.21 (m, 4H), 7.85 (dd, *J* = 10.2, 8.0 Hz, 4H), 7.73 – 7.58 (m, 13H), 7.57 – 7.50 (m, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.35 (m, 4H), 2.67 (s, 6H), 1.35 (s, 9H), 1.29 (s, 9H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 163.96, 163.35, 155.62, 154.93, 151.91, 151.67, 150.58, 143.83, 142.12, 140.06, 136.53, 136.05, 134.56, 134.12, 132.68, 132.56, 132.12, 131.74, 131.71, 129.95, 129.75, 129.47, 129.20, 128.81, 128.39, 128.16, 127.69, 127.57, 127.52, 127.47, 127.43, 127.27, 127.21, 127.18, 126.89, 126.78, 126.65, 125.70, 125.64, 124.65, 102.11, 77.41, 77.16, 76.91, 35.74, 34.46, 31.91, 31.36, 21.95. **HRMS-ESI** (*m/z*): calculated $C_{74}H_{57}N_5O_7Re$ [M−PF$_6$]$^+$: 1314.3816, found 1314.3865

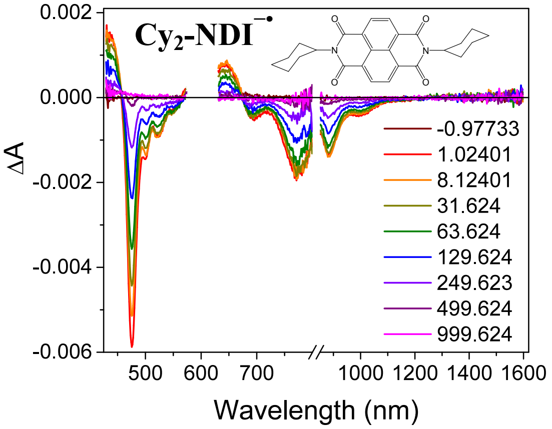


Figure S1. Visible and NIR transient absorption spectra of **Cy$_2$-NDI$^{-\bullet}$** (λ_{ex} = 605 nm). Reproduced from ref 9.

References

1. R. Carmieli, Q. X. Mi, A. B. Ricks, E. M. Giacobbe, S. M. Mickley and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2009, **131**, 8372-8373.