Supporting Information

High Power Organic Cathodes Using Thin Films of Electropolymerized Benzidine Polymers

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1. General Considerations

All manipulations of air and water sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk line techniques. ¹H NMR spectra were recorded on a Varian INOVA 400 (¹H, 400 MHz) and referenced with residual non-deuterated solvent shift (CHCl₃ = 7.26 ppm). ¹³C NMR spectra were recorded on Varian INOVA 500 (¹³C, 125 MHz) spectrometer and referenced to chloroform (77.16 ppm). High resolution mass spectrometry (HRMS) analyses were carried out on a Thermo Scientific Exactive Orbitrap MS system equipped with an Ion Sense DART ion source. Flash column chromatography was performed using silica gel (particle size 40-64 μ m, 230-400 mesh).

Electrochemistry experiments were performed at 22 °C using a Hokuto Denko HABF1510m or a Princeton Applied Research VersaSTAT 3 potentiostat. All cyclic voltammetry (CV) measurements were carried out in a fritted three compartment cell using a glassy carbon working electrode (GCE, 3 mm diameter), a large-area Pt counter electrode, and a Ag/Ag⁺ (0.05 M AgClO₄ and 0.1 M [NBu₄][ClO₄] in CH₃CN) reference electrode. The potential, 0 V, measured using a Ag/Ag⁺ reference electrode is +3.3 V vs. Li/Li⁺. UV-Vis absorption spectra were obtained using a HP 8453 diode array spectrophotometer using a fritted three compartment cell.

The thickness of the electropolymerized films on GCEs were measured with a contact profilometer (Tencor Alpha Step 500) after scraping away a section of the polymer film with a razor blade. Line scans were performed at different points along the film edge. The thickness readings were then averaged to determine the mean film thickness.

2. Materials

Tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃), DavePhos (2-(dicyclohexylphosphino)-2'-(*N*,*N*-dimethylamino))-1,1'-biphenyl), and sodium *tert*-butoxide (NaO'Bu) were purchased from Strem and used as received. Bromobenzene and acetonitrile were purchased from Sigma-Aldrich and distilled over CaH₂. *N*,*N'*-dimethylethylenediamine, *N*,*N'*dimethyl-1,3-propanediamine, and *N*,*N'*-dimethyl-1,6-hexanediamine were purchased from Sigma-Aldrich and distilled over KOH. HPLC grade toluene and dichloromethane were purchased from Fischer Scientific and dried over an alumina column. Tetrabutylammonium hexafluorophosphate was purchased from TCI America and recrystallized twice from absolute ethanol and dried under vacuum. Indium-tin oxide (ITO) coated glass slides (10 Ω /sq. in.) were purchased from Nanocs and cleaned by sonicating in acetone, and then isopropanol. All other reagents were purchased from commercial sources and used as received.

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3. Synthesis of Di- and Trianilinoalkane Monomers



N,*N*'-Dimethyl-1,4-butanediamine (3a)

N,*N*'-Dimethyl-1,4-butanediamine was prepared according to a literature procedure.¹ Formic acid (88% Macron, 35.2 mL, 0.821 mol) was added dropwise to 1,4-butanediamine (**1a**, Aldrich, 25 mL, 0.25 mol) at 0 °C. The solution was refluxed for 1 h, and then the pressure was lowered slowly until the reaction was refluxing under full vacuum for 4 h. A white precipitate crashed out of the cooled reaction and was collected by filtration. The intermediate **2a** was recrystallized using isoamyl alcohol and dried under reduced pressure to give a white powder (81% yield). The diamide (**2a**, 6.49 g, 45.0 mmol) was reduced using LiAlH₄ (7.25 g, 191 mmol) in 180 mL ether. After stirring overnight, the mixture was quenched with 20 mL water at 0 °C. The white mixture was filtered over Celite and washed with ether. The filtrate was dried over MgSO₄ and concentrated. Distillation under vacuum with KOH (b.p. 52 °C, 14 mmHg) afforded **3a** in 54 % isolated yield. ¹H NMR spectrum in ppm (CDCl₃, 400 MHz): δ 2.56 (m, 4H), 2.40 (s, 6H), 1.49 (m, 4H), 1.23 (br s, 2H) and was consistent with the literature.²



N-Methyl-*N'*-[2-(methylamino)ethyl]-1,2-ethanediamine trihydrochloride (3b)

The triamine hydrochloride were prepared by the method of Edwards.³ Diethylenetriamine (**1b**, Aldrich, 1.02 g, 9.89 mmol) was dissolved in methanol (15 mL) and di-*tert*-butyl dicarbonate (TCI America, 7.3 g, 33 mmol) was added and the reaction stirred overnight (12 h). Water was added and the product was extracted with ether, washed with brine, dried with MgSO₄, and concentrated. The clear, colorless oil crystallized on standing at 25 °C resulting in a white powder (88% yield). In the glovebox, NaH (Aldrich 95%, 0.56 g, 23 mmol) was added to a Schlenk flask. The solution of tris-Boc-protected diethylenetriamine (2.98 g, 7.38 mmol) dissolved in dry DMF (4.5 mL) was injected in under N₂. After the mixture was stirred at 25 °C for 1 h, methyl iodide (Aldrich, 1.4 mL, 22 mmol) was added in dropwise. After 12 h, the reaction was quenched with water and the product was extracted into CH₂Cl₂ and washed with brine. The crude product was purified via flash column chromatography using 30% ethyl acetate/hexanes as the eluent to give **2b** as a clear, viscous oil (42% isolated yield).

Compound **2b** (1.35 g, 3.13 mmol) was dissolved in absolute ethanol (8 mL) and 2 M HCl in ether (8 mL, 16 mmol) was added. After 5 h, the white precipitate was collected by filtration and dried under vacuum to give **3b** (89% isolated yield). ¹H NMR spectrum (D₂O, 400 MHz): δ 3.42-3.56 (m, 8H), 2.80 (s, 6H) and was consistent with previous literature.⁴

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N-Methyl-*N'*-[6-(methylamino)hexyl]-1,6-hexanediamine trihydrochloride (3c)

Bis(hexamethylene)triamine (1c, Aldrich, 0.50 g, 2.3 mmol) was dissolved in methanol (5 mL) and di-*tert*-butyl dicarbonate (TCI America, 1.68 g, 7.70 mmol) was added and the reaction stirred overnight (12 h). Water was added and the product was extracted with ether, washed with brine, dried with MgSO₄, and concentrated. The product was purified by column chromatography using 20% ethyl acetate/hexanes to obtain a clear, colorless oil (91% yield). In the glovebox, NaH (Aldrich 95%, 0.275 g, 11.4 mmol) was added to a Schlenk flask. The tris-Boc-protected bis(hexamethylene)triamine (1.47 g, 2.86 mmol) dissolved in dry DMF (6 mL) was injected in under N₂. After the mixture was stirred at 25 °C for 1 h, methyl iodide (Aldrich, 1.36 mL, 21.8 mmol) was added in dropwise. After 12 h, the reaction was quenched with water and the product was extracted into CH₂Cl₂ and washed with brine. The crude product was purified via flash column chromatography using 30% ethyl acetate/hexanes as the eluent to give **2c** as a clear, viscous oil (62% isolated yield).

Compound **2c** (0.82 g, 1.5 mmol) was dissolved in absolute ethanol (4 mL) and 2 M HCl in ether (10 mL, 20 mmol) was added. After 5 h, the white precipitate was collected by filtration and dried under vacuum to give **3c** (79% isolated yield). ¹H NMR spectrum (D₂O, 400 MHz): δ 3.02 (t, 8H), 2.70 (s, 6H), 1.69 (br s, 8H), 1.41 (br s, 8H).

Representative Pd-catalyzed Amination Procedure A



In the glovebox, $Pd_2(dba)_3$ (1 mol %), DavePhos (4 mol %) and NaO⁷Bu (2.3 equiv.) were added to an oven-dried Schlenk tube equipped with a magnetic stir bar. Then chlorobenzene (2.5 mL) was added, followed by bromobenzene (9 equiv.) and the diamine (1 equiv.). After sealing, the tube was heated in an oil bath set at 100 °C for 5 d. After cooling, the cooled mixture was filtered over Celite and washed with CH₂Cl₂. The filtrate was concentrated and evacuated under reduced pressured to remove excess bromobenzene and solvent. The crude product was purified by flash column chromatography.

Representative Pd-catalyzed Amination Procedure B

In the glovebox, NaO'Bu (2.8 equiv.) and bromobenzene (9 equiv.) were added to an ovendried Schlenk tube equipped with a magnetic stir bar. Then the diamine (1 equiv.) in 0.25 mL of toluene was added, followed by a mixture of $Pd_2(dba)_3$ (1 mol %) and DavePhos (4 mol %) in 0.5 mL toluene. After sealing, the tube was heated in an oil bath set at 50 °C overnight for 12 h, then at 100 °C for 12 h. After cooling, the cooled mixture was filtered over Celite and washed with CH₂Cl₂. The filtrate was concentrated and the crude product was purified by flash column chromatography.

Representative Pd-catalyzed Amination Procedure C



In the glovebox, $Pd_2(dba)_3$ (1 mol %), DavePhos (4 mol %) and NaO^tBu (6 equiv.) were added to an oven-dried Schlenk tube equipped with a magnetic stir bar. Then bromobenzene and the triamine (1 equiv.) were added. After sealing, the tube was heated in an oil bath set at 100 °C for 3 d. After cooling, the cooled mixture was filtered over Celite and washed with CH₂Cl₂. The filtrate was concentrated and evacuated under reduced pressured to remove excess bromobenzene. The crude product was purified by flash column chromatography.

N,*N*'-Dimethyl-*N*,*N*'-diphenylethylenediamine (DA-2)

Following the general procedure B, a mixture of bromobenzene (1.5 g, 9.6 mmol), *N*,*N*'dimethylethylenediamine (88 mg, 1.0 mmol), Pd₂(dba)₃ (9.5 mg, 10 µmol), DavePhos (16.7 mg, 42.4 µmol), NaO'Bu (272 mg, 2.83 mmol), and toluene (0.75 mL) was heated to 50 °C for 12 h then 100 °C for 12 h. The crude product was purified by flash column chromatography using 5% ethyl acetate/hexanes as the eluent ($R_f = 0.32$) to give a yellow powder (97% isolated yield). Spectroscopic characterization was consistent with that reported in previous literature.^{5 1}H NMR spectrum (CDCl₃, 400 MHz): δ 7.22-7.29 (m, 4H), 6.69-6.75 (m, 6H), 3.55 (s, 4H), 2.95 (s, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 148.98, 129.43, 116.36, 111.94, 49.85, 38.82. HRMS (DART-MS) m/z calculated for C₁₆H₂₀N₂⁺ (M + H⁺) 241.1621, found 241.1700.

N,*N*'-Dimethyl-*N*,*N*'-diphenyl-1,3-propanediamine (DA-3)

Following the general procedure A, a mixture of bromobenzene (1.5 g, 9.6 mmol), *N*,*N*'dimethyl-1,3-propanediamine (107 mg, 1.05 mmol), Pd₂(dba)₃ (9.5 mg, 10 µmol), DavePhos (20.7 mg, 52.6 µmol), NaO'Bu (230 mg, 2.39 mmol), and chlorobenzene (2.5 mL) was heated to 100 °C for 5 d. The crude product was purified by flash column chromatography using 5% ethyl acetate/hexanes as the eluent ($R_f = 0.24$) to give a yellow oil (88% isolated yield). ¹H NMR spectrum (CDCl₃, 400 MHz): δ 7.18-7.25 (m, 4H), 6.66-6.73 (m, 6H), 3.37 (t, 4H), 2.92 (s, 6H), 1.83-1.93 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz): δ 129.28, 116.43, 112.57, 50.61, 38.50, 24.28. HRMS (DART-MS) m/z calculated for C₁₇H₂₂N₂⁺ (M + H⁺) 255.1778, found 255.1854.

N,*N*'-Dimethyl-*N*,*N*'-diphenyl-1,4-butanediamine (DA-4)

Following the general procedure A, a mixture of bromobenzene (1.5 g, 9.6 mmol), **3a** (122 mg, 1.05 mmol), Pd₂(dba)₃ (9.2 mg, 10 µmol), DavePhos (22.7 mg, 57.7 µmol), NaO^{*t*}Bu (235 mg, 2.44 mmol), and chlorobenzene (2.5 mL) was heated to 100 °C for 5 d. The crude product was purified by flash column chromatography using 5% ethyl acetate/hexanes as the eluent (R_f = 0.23) to give a yellow powder (78% isolated yield). ¹H NMR spectrum (CDCl₃, 400 MHz): δ 7.20-7.26 (m, 4H), 6.66-6.72 (m, 6H), 3.34 (m, 4H), 2.92 (s, 6H), 1.59-1.64 (m, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ 149.37, 129.30, 116.14, 112.28, 52.80, 38.43, 24.56. HRMS (DART-MS) m/z calculated for C₁₈H₂₅N₂⁺ (M + H⁺) 269.2012, found 269.2012.



N,*N*'-Dimethyl-*N*,*N*'-diphenyl-1,6-hexanediamine (DA-6)

Following the general procedure B, a mixture of bromobenzene (1.5 g, 9.6 mmol), *N*,*N*'dimethyl-1,6-hexanediamine (146 mg, 1.01 mmol), Pd₂(dba)₃ (9.4 mg, 10 µmol), DavePhos (17 mg, 43 µmol), NaO'Bu (270 mg, 2.81 mmol), and toluene (0.75 mL) was heated to 50 °C for 12 h then 100 °C for 12 h. The crude product was purified by flash column chromatography using 5% ethyl acetate/hexanes as the eluent ($R_f = 0.26$) to give a yellow oil (82% isolated yield). Spectroscopic characterization was consistent with that reported in previous literature.^{6 1}H NMR spectrum (CDCl₃, 400 MHz): δ 7.19-7.25 (m, 4H), 6.66-.6.71 (m, 6H), 3.30 (t, 4H), 2.91 (s, 6H), 1.54-1.63 (m, 4H), 1.33-1.40 (m, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ 149.38, 129.23, 115.95, 112.17, 52.79, 38.38, 27.20, 26.75. HRMS (DART-MS) m/z calculated for C₂₀H₂₈N₂⁺ (M + H⁺) 297.2247, found 297.2325.



N-Methyl-*N'*-[2-(methylphenylamino)ethyl]-*N*,*N'*-diphenyl-1,2-ethanediamine (TA-2)

Following the general procedure C, a mixture of bromobenzene (2.5 g, 16 mmol), **3b** (128 mg, 0.532 mmol), $Pd_2(dba)_3$ (16 mg, 17 µmol), DavePhos (38 mg, 96 µmol), NaO'Bu (360 mg, 3.75 mmol) was heated to 100 °C for 3 d. The crude product was purified by flash column chromatography using 4% ethyl acetate/hexanes as the eluent ($R_f = 0.15$) to give a yellow powder (74% isolated yield). ¹H NMR spectrum (CDCl₃, 400 MHz): δ 7.18-7.29 (m, 5H), 6.63-6.76 (m, 9H), 3.50 (s, 8H), 2.90 (s, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 148.95, 147.57, 129.72,

129.47, 116.51, 116.37, 112.02, 111.58, 50.08, 48.24, 38.87. HRMS (DART-MS) m/z calculated for $C_{24}H_{30}N_3^+$ (M + H⁺) 360.2434, found 360.2434.



N-Methyl-*N*'-[6-(methylphenylamino)hexyl]-*N*,*N*'-diphenyl-1,6-hexanediamine (TA-6)

Following the general procedure C, a mixture of bromobenzene (2.5 g, 16 mmol), **3c** (470 mg, 1.33 mmol), Pd₂(dba)₃ (29 mg, 32 µmol), DavePhos (54 mg, 0.14 mmol), NaO'Bu (813 mg, 8.46 mmol) was heated to 100 °C for 3 d. The crude product was purified by flash column chromatography using 5% ethyl acetate/hexanes as the eluent ($R_f = 0.18$) to give a yellow oil (47% isolated yield). ¹H NMR spectrum (CDCl₃, 400 MHz): δ 7.17-7.24 (m, 6H), 6.61-6.70 (m, 9H), 3.30 (t, 4H), 3.23 (t, 4H), 2.91 (s, 6H), 1.54-1.62 (m, 8H), 1.33-1.37 (m, 8H). ¹³C NMR (CDCl₃, 125 MHz): δ 149.41, 148.14, 129.33, 129.26, 115.98, 115.35, 112.19, 111.83, 52.83, 51.10, 38.42, 27.35, 27.23, 26.79. The γ -carbon to aniline groups (27.23 ppm) exhibit chemical shift equivalence. HRMS (DART-MS) m/z calculated for C₃₂H₄₅N₃⁺ (M + H⁺) 471.3608, found 471.3686.

4. Electrochemical Measurements

4.1 Cyclic Voltammetry (CV) & Chronoamperometry

CV and chronoamperometry measurements were taken in a three-electrode cell configuration using a 3 mm diameter GCE working electrode, a Ag/Ag^+ reference electrode and a coiled Pt wire counter electrode in separate compartments connected by medium porosity glass frits. The GCEs were polished with 1.0 µm, 0.3 µm, and 0.05 µm alumina (EXTEC) mixtures, rinsed with distilled water and acetone, sonicated in acetone for 1 min, and dried prior to use. The Pt counter electrode was flame annealed prior to use.

Films of **PDA-6** were prepared on GCEs by anodic electrochemical polymerization of 5 mM **DA-6** in 0.5 M [NBu₄][PF₆]/CH₂Cl₂ at 20 mV s⁻¹ between -0.5-0.8 V for two cycles, unless specified otherwise. After the polymerization, the modified electrodes were rinsed gently with CH₂Cl₂ and CH₃CN. After air-drying, the electrodes were dried under vacuum for at least 4 h. Throughout this report, the first couple refers to the electron transfer between the neutral and radical cation species, while the second couple refers to the electron transfer between the radical cation and dicationic species.

For the movies, **PDA-6** was prepared on an ITO electrode by electropolymerization of 5 mM **DA-6** in 0.1 M [NBu₄][PF₆]/CH₂Cl₂ at 20 mV s⁻¹ between -0.5-0.8 V. After the polymerization, the modified electrodes were rinsed gently with CH₂Cl₂ and CH₃CN. The modified electrode was cycled in 0.5 M [NBu₄][PF₆]/CH₃CN at 20 mV s⁻¹ between -0.5-0.6 V.

| Name | $E^{0'}{}_1$ | $\Delta E_{\rm p1}$ | $E^{0'}{}_{2}$ | $\Delta E_{\rm p2}$ | Theoretical capacity |
|-------|--------------|---------------------|----------------|---------------------|----------------------|
| | (V) | (V) | (V) | (V) | $(mA h g^{-1})$ |
| PDA-2 | - | - | - | - | 223 |
| PDA-3 | 0.067 | 0.192 | 0.452 | 0.029 | 211 |
| PDA-4 | 0.068 | 0.285 | 0.381 | 0.044 | 200 |
| PDA-6 | 0.002 | 0.041 | 0.354 | 0.058 | 181 |
| PTA-2 | - | - | - | - | 224 |
| PTA-6 | 0.019 | 0.089 | 0.350 | 0.083 | 170 |
| | | | | | |

Table S1. The electrochemical values for polymer films from Figure 1b.



Figure S1. (a) Sweep rate dependent CVs of 10 mM N,N,N',N'-tetramethylbenzidine (TMB, Aldrich) in 0.1 M [NBu₄][PF₆]/CH₃CN. (b) The dependence of the peak currents of the two redox couples of TMB on the square root of the scan rate. The linear fits indicate that TMB undergoes two reversible one-electron transfers in solution.



Figure S2. (a) The difference in peak potentials (ΔE_p) of the two redox couples of **PDA-6** at various scan rates. (b) The dependence of the anodic and cathodic peak currents (i_{pa} and i_{pc} , respectively) of the first and second couples of **PDA-6** on scan rate. The decrease in ΔEp is expected at slower sweep rates since the electrolyte ions have more time to diffuse into the polymer film. The linear correlation is expected for redox-active polymers that are confined to the surface of the electrode, and undergo kinetically facile electron transfers. The films on GCE were cycled in 0.5 M [NBu₄][PF₆]/CH₃CN between -0.3-0.6 V.



 $\label{eq:potential} \begin{array}{l} \mbox{Potential / V vs. Ag/Ag}^{*} \\ \mbox{Figure S3. Cyclic voltammograms of 10 mM DA-6 in 0.1 M [NBu_4][PF_6]/solvent on the 1^{st} (--) \\ \mbox{and 2^{nd} cycle (---). All CVs on 100 μA scale. Scan rate: 20 mV s^{-1}. \end{array}$



Figure S4. (a) Successive CVs of 5 mM **DA-6** in 0.5 M [NBu₄][PF₆]/CH₂Cl₂ during electropolymerization at 20 mV s⁻¹. (b) CVs of **PDA-6** films that were prepared by different deposition cycles, cycled in 0.5 M [NBu₄][PF₆]/CH₃CN at 20 mV s⁻¹. (c) Dependence of the anodic and cathodic peak currents (i_{pa} and i_{pc} , respectively) of **PDA-6** on the number of deposition cycles during film preparation. These plots indicate that the polymer film growth follows a linear correlation with the number of electropolymerization cycles.



Figure S5. The performance of polymer films, deposited on GCE as in Fig. 1a, cycled in 0.1 M $[NBu_4][PF_6]/CH_3CN$ at 20 mV s⁻¹.

Laviron Analysis

The Laviron method⁷ was used for the determination of the charge transfer rate constants of adsorbed species. The same CVs used for Figure S2 (scan rate dependence of **PDA-6**) were used for the analysis. The dependence of the difference between peak potentials (E_p) and the formal redox potential (E^{0}) was plotted vs. the logarithm of the scan rate (log(v)). The plot yields two straight lines per redox couples when log(scan rate) > -1.0. The electron transfer coefficient, α , and the electron transfer rate constant, k_s , were calculated using equation 1 and the straight lines from Figure S6.⁸

$$E_{\rm p} = E^{0'} - \frac{RT}{cnF} \ln\left(\frac{cnF}{RTk_s}\right) - \frac{RT}{cnF} \ln(\nu) \tag{1}$$

where *R* is the gas constant (8.314 J K⁻¹ mol⁻¹), *T* is the temperature (293 K), *n* is the number of electrons, and *F* is the Faraday constant (96,485 C mol⁻¹). The constants were determined to be

 α =0.42 and $k_s = 0.4 \text{ s}^{-1}$ for the first redox couple, and α =0.46 and $k_s = 0.5 \text{ s}^{-1}$ for the second redox couple.



Figure S6. Dependence of the difference between peak potentials (E_p) and the formal redox potential $(E^{0'})$ on the logarithm of the scan rate $(\log(v))$.

Determination of Diffusion Coefficient

Chronoamperometry was performed by holding the potential at 0.8 V for several seconds, and measuring the current with time. The graph, known as a Cottrell plot, of the current vs. the reciprocal square root of time was plotted. The slope of the linear portion of the plot was used to determine the diffusion coefficient of **PDA-6** film as 2.4×10^{-9} cm² s⁻¹.



Figure S7. Cottrell plot of PDA-6 in 0.1 M [NBu₄][PF₆]/CH₃CN.



Figure S8. Cyclic voltammogram of **PDA-6** cycled in 0.5 M [NBu₄][PF₆]/CH₃CN at 10 mV s⁻¹. Shown in the plot are the differences in the peak potentials (ΔE_p) of the two redox couples as well as the charge (*Q*) for each peak after subtraction of the contribution from the double layer (shown in blue lines).

4.2 Spectroelectrochemical Experiments

ITO coated glass slides were cut to 5x75 mm sized electrodes and copper tape was wrapped around the top of the electrode to facilitate electrical contact. For the *in situ* spectroelectrochemical studies, **PDA-6** was deposited on an ITO electrode by electropolymerization of 0.5 mM **DA-6** in 0.1 M [NBu₄][PF₆]/CH₂Cl₂ at 20 mV s⁻¹ between -0.5–0.8 V. After the polymerization, the modified electrodes were rinsed gently with CH₂Cl₂ and CH₃CN. The modified ITO electrode was placed facing the light path in a fritted three compartment glass cell, along with the Ag/Ag⁺ reference electrode and a coiled Pt wire counter electrode. The modified electrode was cycled in 0.1 M [NBu₄][PF₆]/CH₃CN at 10 mV s⁻¹ between -0.5–0.6 V and UV-Vis spectra were collected every 8 seconds.

For the switching time experiments, the ITO electrodes were deposited as described above. For measuring the switching time for the dication from the neutral polymer, the potential was held at -0.2 V and 0.5 V for 3 cycles of 5, 2, 1, 0.5 seconds, and the absorbance was measured at 469 nm. For measuring the switching time for the radical cation, the potential was held at -0.2 V and 0.3 V for 3 cycles of 5, 2, 1, 0.5 seconds, and the absorbance was measured at 400 nm.

| Label | Potential | λ (nm) | Absorbance |
|--------------|-------------------|----------------|------------|
| | $(V vs. Ag/Ag^+)$ | | (AU) |
| Ι | -0.093 | 457 | 0.086 |
| II | 0.067 | 414 | 0.107 |
| | | 731 | 0.079 |
| III | 0.207 | 399 | 0.154 |
| | | 729 | 0.101 |
| IV | 0.347 | 401 | 0.154 |
| | | 472 | 0.125 |
| | | 721 | 0.093 |
| \mathbf{V} | 0.587 | 469 | 0.252 |
| VI | 0.373 | 467 | 0.207 |
| VII | 0.223 | 397 | 0.154 |
| | | 729 | 0.097 |
| VIII | 0.063 | 400 | 0.117 |
| | | 732 | 0.084 |
| IX | -0.087 | 450 | 0.086 |

 Table S2. Spectroelectrochemical data from Figure 2.



Figure S9. Simultaneously acquired (a) absorbance at 400 nm and (b) current measurements at set (c) applied potentials of **PDA-6** deposited onto an ITO electrode in 0.5 M $[NBu_4][PF_6]/CH_3CN$. The switching time between the neutral, colorless polymer film and the green-colored **PDA-6**⁺⁺ is 0.9 seconds.



Figure S10. Simultaneously acquired (a) absorbance at 469 nm and (b) current measurements at set (c) applied potentials of **PDA-6** deposited onto an ITO electrode in 0.5 M $[NBu_4][PF_6]/CH_3CN$. The switching time between the neutral, colorless polymer film and the dicationic, marigold-colored **PDA-6**²⁺ is 1.8 seconds.

4.3 Galvanostatic Cycling

Galvanostatic charge-discharge measurements were taken in a three-electrode cell configuration using the modified GCE, a Ag/Ag⁺ reference electrode and a Pt wire counter electrode in 0.5 M [NBu₄][PF₆]/CH₃CN. Initially, a CV at 10 mV s⁻¹ of the electrode was taken between -0.3-0.2 V to determine the amount of charge (capacity) stored for the initial oneelectron process (charge of reduction peak). Then, the applied current was calculated to obtain the desired C-rate. The |applied current| was the same for charging and discharging, unless specified otherwise. The polymer was charged and discharged in 0.5 M [NBu₄][PF₆]/CH₃CN between -0.1-0.5 V.

C rate
$$(h^{-1}) = \frac{\text{applied current }(\mu A)}{\text{capacity }(\mu C)}$$
 (2)

applied current=
$$\frac{C \text{ rate}}{3600} \times \text{capacity}$$
 (3)

The capacities (mA h g⁻¹) were calculated from galvanostatic cycling experiments using the total charge (mA h) passed during charge/discharge and the approximate mass of the polymer film (w). The mass, w, of the film was calculated by the following equation: $w = h\rho A$. The film thickness, h, was determined by profilometry, the density, ρ , was estimated to be 1.0 g cm⁻³, and the area, A, of the GCE was 0.0707 cm². The Coulombic efficiency (%) was calculated from the capacity of the film after discharging divided by the capacity from charging.



Figure S11. Performance of **PDA-6** films cycled at various C rates over 100 cycles. The polymer films on GCE were galvanostatically charged and discharged in 0.5 M $[NBu_4][PF_6]/CH_3CN$ between -0.1-0.5 V. The |applied current| was the same for the charge and discharge except for 100 C which was charged at 1000 C and discharged at 100 C.



Figure S12. Discharge curves of **PTA-6** in 0.5 M [NBu₄][PF₆]/CH₃CN at an applied current of 36 μ A. Inset: The relative capacities between the two couples with cycling, where the first reduction occurs between +0.2 and -0.1 V and the second reduction is between +0.5 and +0.2 V vs. Ag/Ag⁺. Relative capacities = capacity(1st reduction)/capacity(2nd reduction).

5. ¹H and ¹³C NMR Spectra

N,*N*'-Dimethyl-*N*,*N*'-diphenylethylenediamine (DA-2)



N,*N*'-Dimethyl-*N*,*N*'-diphenyl-1,3-propanediamine (DA-3)

¹H NMR spectrum (400 MHz, CDCl₃)





N,*N*'-Dimethyl-*N*,*N*'-diphenyl-1,4-butanediamine (DA-4)

¹H NMR spectrum (400 MHz, CDCl₃)





N,N'-Dimethyl-*N,N'*-diphenyl-1,6-hexanediamine (DA-6)

¹H NMR spectrum (400 MHz, CDCl₃)





N-Methyl-*N'*-[2-(methylphenylamino)ethyl]-*N*,*N'*-diphenyl-1,2-ethanediamine (TA-2)

¹H NMR spectrum (400 MHz, CDCl₃)





N-Methyl-*N'*-[6-(methylphenylamino)hexyl]-*N*,*N'*-diphenyl-1,6-hexanediamine (TA-6)



¹H NMR spectrum (400 MHz, CDCl₃)



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