

Supporting Information

Investigation of Triphenylamine Thiophene Azomethines Derivatives: Towards Understanding Their Electrochromic Behavior

Marie-Hélène Tremblay, Thomas Skalski, Yohan Gautier, Grégory Pianezzola, W. G. Skene*

Laboratoire de caractérisation photophysique des matériaux conjugués
Département de chimie
Université de Montréal
CP 6128, Centre-ville
Montreal, QC

1. Materials and General Details.

All reagents were commercially available and they were used as received, unless otherwise stated. Commercial grade solvents were dried and deoxygenated with an aluminum column purification system. NMR spectra were recorded on a 700 MHz spectrometer with a TBI probe with the appropriate deuterated solvents, unless otherwise stated.

Synthesis

1 was prepared according to known methods and it was recrystallized from an acetone/hexane mixture (1/1 v/v).^{S1-3}

2-Amino-4,5,6,7-tetrahydrobenzo(b)-3-thiophenecarbonitrile (**2**).^{S4-7} In a 50 mL double neck round-bottomed flask were added cyclohexanone (1.47 mL, 14.2 mmol), malononitrile (0.98 mL, 15.6 mmol), and sulphur (0.5 g, 15.6 mmol). The reagents were dissolved in absolute ethanol (14 mL) followed by the addition of morpholine (10 mL). The mixture was then heated for three hours at 90 °C. After cooling the reaction mixture to room temperature, it was poured into ice water. The resulting precipitate was filtered after the ice melted. The solid was recrystallized in propan-2-ol/hexane (1/1 v/v) to afford the title compound as brown crystals (88 %). ¹H NMR (DMSO-d₆) δ=6.96 (br, s, 2H), 2.41 (t, 2H, *J* = 5.6 Hz), 2.34 (td, 2H, *J* = 6.0 Hz), 1.71 (m, 4H). ¹³C NMR (DMSO-d₆) δ=163.2, 131.5, 117.2, 116.6, 83.6, 24.3, 23.9, 23.4, 22.3. HRMS (+) (C₉H₁₉N₂S)H⁺: calculated: 179.0643; found: 179.0639. M.p. 146 – 149 °C.

4-(Diphenylamino)benzaldehyde (**3**).^{S8} In a two-neck round bottom flask were added triphenylamine (1.0 g, 4.08 mmol), 1,2-dichloroethane (25 mL), and dimethylformamide (0.47

mL, 6.11 mmol). The solution was deoxygenated for thirty minutes with nitrogen, afterwards it was cooled to -5 °C. Phosphorous oxychloride (0.56 mL, 6.11 mmol) was then added dropwise. The reaction mixture was slowly warmed to room temperature and then it was refluxed at 75 °C overnight. The reaction mixture was then cooled to 0 °C and water (10 mL) was added with intense stirring. A concentrated solution of sodium hydroxide was slowly added dropwise to adjust the pH=7. The product was extracted with dichloromethane. The organic layer was dried over magnesium sulphate, filtered, and the solvent was then evaporated. The crude product was purified by flash chromatography using a hexane/ethyl acetate gradient (100% decreased to 90%/10% v/v) as the eluent. The title compound was isolated as yellow crystals (0.98 g, 88 %). ¹H NMR (acetone-d₆) δ=9.85 (s, 1H), 7.75 (dt, 2H, *J*_D = 8.9 Hz), 7.43 (td, 4H, *J*_T = 7.2 Hz), 7.24 (dd, 4H, *J*_D = 8.6 Hz), 7.22 (s, 2H), 6.99 (dt, 2H, *J* = 8.9 Hz). HRMS (+) (C₁₉H₁₅NO)H⁺: calculated: 274.1232; found: 274.1233. M.p. 132 – 134 °C.

4,4'-(Phenylazanediy)dibenzaldehyde (**4**).^{S9} In a two-neck round bottom flask were added triphenylamine (1.0 g, 4.08 mmol), 1,2-dichloroethane (25 mL) and dimethylformamide (0.94 mL, 12.2 mmol). The solution was deoxygenated by bubbling with nitrogen for thirty minutes. The reaction mixture was then cooled to -5 °C and phosphorous oxychloride (1.12 mL, 12.2 mmol) was added dropwise. Afterwards, the reaction mixture was warmed to room temperature followed by refluxing at 75 °C overnight. The mixture was then cooled to 0 °C and water (10 mL) was added with vigorous stirring. A concentrated solution of sodium hydroxide was added dropwise to adjust the pH≈7. The crude product was then extracted with dichloromethane and washed with water and brine. The organic layer was dried over magnesium sulphate, filtered, and then the solvent was evaporated. The crude product was purified by flash chromatography with

hexane/ethyl acetate gradient (100% decreased to 80%/20% v/v). The product was obtained as yellow crystals (0.92 g, 75 %). $^1\text{H NMR}$ δ =9.95 (s, 2H), 7.87 (dt, 4H, $J_D = 8.4$ Hz, $J_t = 2.0$ Hz), 7.49 (tt, 2H, $J_T = 8.3$ Hz, $J_t = 1.9$ Hz), 7.33 (tt, 1H, $J_T = 7.5$ Hz, $J_t = 1.2$ Hz), 7.25 (tt, 4H, $J_T = 8.4$ Hz, $J_t = 0.8$ Hz), 7.23 (s, 2H). HRMS (+) ($\text{C}_{20}\text{H}_{15}\text{NO}_2$) H^+ : calculated: 302.1181; found: 302.1183. M.p. 143 – 144 °C.

4,4',4''-Nitrilotribenzaldehyde (**5**).^{S10} In a microwave vial (25 mL) were added triphenylamine (0.5 g, 2.04 mmol), 1,2-dichloroethane (5 mL) and dimethylformamide (5.6 mL, 61 mmol). The solution was deoxygenated for thirty minutes by bubbling with nitrogen. It was then cooled to -5 °C and phosphorous oxychloride (11.2 mL, 61 mmol) was added dropwise. The vial was sealed and it was heated in a microwave for one hour. Afterwards, it was cooled to 0 °C, unsealed, and the reaction mixture was then poured into a cooled flask. Water (10 mL) was added dropwise, then a concentrated solution of sodium hydroxide was added slowly with the temperature being kept at 10 °C and the pH adjusted to 7. The crude product was extracted with dichloromethane and washed with water and brine. The organic layer was dried over magnesium sulphate, filtered, and the solvent was then evaporated. The crude product was purified by flash chromatography with hexane/ethyl acetate gradient (90%/10% to 75%/25% v/v). The product was isolated as yellow crystals that were stored in the dark under nitrogen (0.42 g, 63 %). $^1\text{H NMR}$ (acetone- d_6) δ =10.01 (s, 3H), 7.95 (d, 6H, $J = 8.6$ Hz), 7.36 (d, 6H, $J = 8.6$ Hz). HRMS (+) ($\text{C}_{21}\text{H}_{15}\text{NO}_3$) H^+ : calculated: 330.1130; found 330.1132. M.p. 217 – 222 °C.

General procedure for the synthesis of **6-8**.^{S11}

In a round bottom flask (5 mL) were added the corresponding formylated triphenylamine (1 equivalent) and **1** (3 equivalents) in absolute ethanol (2.5 mL). A catalytic amount of trifluoroacetic acid (TFA) was added and the solution was heated with a heat gun for one minute. The flask was then cooled room temperature. The resulting precipitate was filtered and then washed with cold absolute ethanol (5 mL).

Diethyl (*E*)-2-amino-5-((4-(diphenylamino)benzylidene)amino)thiophene-3,4-dicarboxylate (**6**). Orange solid (71.3 mg, 95 %). ¹H NMR (DMSO-*d*₆) δ=7.99 (s, 1H), 7.85 (s, 2H), 7.63 (d, 2H, *J* = 8.8 Hz), 7.38 (t, 4H, *J* = 8.5 Hz), 7.16 (t, 2H, *J* = 8.4 Hz), 7.12 (d, 4H, *J* = 8.6 Hz), 6.92 (d, 2H, *J* = 8.8 Hz), 4.25 (q, 2H, *J* = 7.1 Hz), 4.14 (q, 2H, *J* = 7.1 Hz), 1.18 (t, 3H, *J* = 7.1 Hz), 1.21 (t, 3H, *J* = 7.1 Hz). ¹³C NMR (DMSO-*d*₆) δ=165.4, 163.8, 161.0, 152.2, 150.1, 146.7, 133.1, 130.3, 129.8, 129.2, 129.0, 125.8, 124.8, 121.1, 100.3, 61.1, 59.9, 14.6, 14.6. HRMS (+) (C₂₉H₂₇N₃O₄S)H⁺: calculated: 514.1801; found: 514.1782. M.p. 191 – 193 °C.

Tetraethyl 5,5'-(((1*E*,1'*E*)-((phenylazanediyl)bis(4,1-phenylene))bis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (**7**). Yellow solid (83.9 mg, 81 %). ¹H NMR (DMSO-*d*₆) δ=8.03 (s, 2H), 7.88 (br s, 4H), 7.69 (d, 4H, *J* = 8.8 Hz), 7.42 (t, 2H, *J* = 8.4 Hz), 7.22 (t, 1H, *J* = 7.5 Hz), 7.16 (d, 2H, *J* = 8.4 Hz), 7.06 (d, 4H, *J* = 9.8 Hz), 4.25 (q, 4H, *J* = 7.1 Hz), 4.14 (q, 4H, *J* = 7.1 Hz), 1.29 (t, 6H, *J* = 7.1 Hz), 1.21 (t, 6H, *J* = 7.1 Hz). ¹³C NMR (DMSO-*d*₆) δ= 165.3, 163.8, 161.2, 151.9, 149.1, 146.1, 132.8, 130.8, 130.5, 129.9, 129.5, 126.5, 125.6, 123.3, 100.4, 61.2, 59.9, 14.6, 14.6. HRMS (+) (C₄₀H₃₉N₅O₈S₂)H⁺: calculated: 782.2318; found: 782.2331. M.p. 249 – 252 °C.

Hexaethyl 5,5',5''-(((1*E*,1'*E*,1''*E*)-(nitrilotris(benzene-4,1-diyl))tris(methanylylidene))tris(azanylylidene))tris(2-aminothiophene-3,4-dicarboxylate) (8).
purple powder (98.1 mg, 77 %). ¹H NMR (DMSO-*d*₆) δ=8.06 (s, 3H), 7.90 (br s, 6H), 7.74 (d, 6H, *J* = 8.7 Hz), 7.15 (d, 6H, *J* = 8.7 Hz), 4.25 (q, 6H, *J* = 7.2 Hz), 4.15 (q, 6H, *J* = 7.1 Hz), 1.29 (t, 9H, *J* = 7.1 Hz), 1.21, (t, 9H, *J* = 7.1 Hz). ¹³C NMR (DMSO-*d*₆) δ=165.3, 163.8, 161.3, 151.8, 148.5, 132.7, 131.7, 129.9, 129.8, 124.5, 100.4, 61.2, 59.9, 14.6, 14.6. HRMS (+) (C₅₁H₅₁N₇O₁₂S₃)H⁺: calculated: 1050.2836; found: 1050.2799. M.p. 258 – 263 °C.

General procedure for the synthesis of **9-11**.^{S11}

In a round bottom flask were added the corresponding formyl triphenylamine (1 equivalent) and **2** (5 equivalents) in propan-2-ol (2.5 mL). A catalytic amount of TFA was added and the solution was heated for one minute. The solution was then cooled to room temperature and water was added (200 mL). The pH was adjusted to >12 by adding triethylamine (4 mL) and the resulting precipitate was collected by filtering. The precipitate was washed with cold propan-2-ol (5 mL) and then cold hexane (10 mL).

(*E*)-2-((4-(Diphenylamino)benzylidene)amino)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (**9**). Yellow solid (23.5 mg, 40 %). ¹H NMR (DMSO-*d*₆) δ=8.49 (s, 1H), 7.82 (d, 2H, *J* = 8.8 Hz), 7.42 (t, 4H, *J* = 8.1 Hz), 7.21 (t, 2H, *J* = 7.4 Hz), 7.17 (d, 4H, *J* = 7.4 Hz), 6.95 (d, 2H, *J*=8.8 Hz), 2.69 (m, 2H), 2.57 (m, 2H), 1.80 (m, 4H). ¹³C NMR (DMSO-*d*₆) δ=162.3, 161.2, 152.7, 147.2, 135.4, 132.8, 132.3, 131.3, 128.2, 127.2, 126.3, 120.7, 115.7, 105.6, 25.2, 24.4, 23.2, 22.1. HRMS (+) (C₂₈H₂₃N₃S)H⁺: calculated: 434.1691; found: 434.1683. M.p. 171 – 172 °C.

2,2'-(((1*E*,1'*E*)-(Phenylazanediyl)bis(4,1-phenylene))bis(methanylylidene))bis(azanylylidene))bis(4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile) (**10**). Orange powder (29.3 mg, 36 %). ¹H NMR (DMSO-*d*₆) δ=8.56 (s, 2H), 7.91 (d, 4H, *J* = 8.7 Hz), 7.47 (t, 2H, *J* = 7.6 Hz), 7.29 (t, 1H, *J* = 7.5 Hz), 7.21 (d, 2H, *J* = 7.5 Hz), 7.16 (d, 4H, *J* = 8.7 Hz), 2.70 (m, 4H), 2.58 (m, 4H), 1.80 (m, 8H). ¹³C NMR (DMSO-*d*₆) δ=161.8, 161.1, 151.4, 146.7, 135.6, 133.4, 132.3, 131.5, 130.6, 127.9, 127.2, 124.0, 115.6, 106.3, 25.2, 24.4, 23.2, 22.1. HRMS (+): (C₃₈H₃₁N₅S₂)H⁺: calculated: 622.2099; found: 622.2083. M.p. 219 – 222 °C.

2,2',2''-(((1*E*,1'*E*,1''*E*)-(Nitrilotris(benzene-4,1-diyl))tris(methanylylidene))tris(azanylylidene))tris(4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile) (**11**). Red powder (26.5 mg, 27 %). ¹H NMR (DMSO-*d*₆) δ=8.62 (s, 3H), 7.97 (d, 6H, *J* = 8.7 Hz), 7.27 (d, 6H, *J* = 8.7 Hz), 2.72 (m, 6H), 2.59 (m, 6H), 1.81 (m, 12H). ¹³C NMR (DMSO-*d*₆) δ=161.6, 161.0, 150.7, 135.7, 133.8, 132.4, 131.8, 125.7, 115.5, 106.6, 25.2, 24.4, 28.8, 22.1. HRMS (+): (C₄₈H₃₉N₇S₃)H⁺ calculated: 810.2507; found: 810.2509. M.p. 258 – 259 °C.

Diethyl 2,5-bis(((*E*)-4-(di-*p*-tolylamino)benzylidene)amino)thiophene-3,4-dicarboxylate (**12**). DABCO (2.5 mmol, 600 mg), **1** (61 mg, 0.24 mmol), and 4-(di-*p*-tolylamino)benzaldehyde (250 mg, 0.83 mmol) were added to a 50 mL two-neck round bottom flask under an inert atmosphere. After adding anhydrous toluene (20 mL), the reaction mixture was cooled to 0 °C and TiCl₄ (0.1 mL, 3.8 equivalents) was added. The reaction mixture was heated to reflux overnight. The

solvent was removed under reduced pressure once the reaction mixture was cooled. Acetone was then added and the solution was filtered to remove the titanium salts. The filtrate was evaporated and the crude product was purified by silica gel column chromatography (hexanes/AcOEt: 95/5 + 1% Et₃N). The title compound was isolated as a red solid (13.5 mg, 7%). ¹H NMR (CDCl₃) δ = 8.26 (s, 2H), 7.65 (d, 4H, *J*=8.8 Hz), 7.12 (d, 8H, *J*=8.2 Hz), 7.05 (d, 8H, *J*=8.4 Hz), 6.95 (d, 4H, *J*=8.8 Hz), 4.35 (q, 4H, *J*=7.1 Hz), 2.36 (s, 12H), 1.36 (t, 6H, *J*=7.1 Hz). ¹³C NMR (CDCl₃) δ = 163.8, 158.4, 151.9, 150.1, 144.1, 134.5, 130.8, 130.4, 127.5, 126.6, 126.1, 119.7, 61.3, 21.1, 14.5. HRMS (+) (C₅₂H₄₈N₄O₄S): calculated: 824.3396; found: 824.3398.

2. Measurements

2.1 Electrochemical measurements

Cyclic voltammetry was done on a three channel potentiostat. All compounds were dissolved in the anhydrous solvent (10⁻³ M). Either tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as the supporting electrolyte (0.1 M). The E_{ox}, corresponding to the maximum peak potential for the forward scan in cyclic voltammetry, was used to compare the oxidation potentials of the compounds. Ferrocene was added at the end of the measurements (in equal molar concentration to the triphenylamine when to possible) as an internal calibration (E_o'=400 and 380 mV vs. SCE for TBAPF₆ and TBAP, respectively).^{S12} The values in Table 2 were referenced against the reversible ferrocene redox couple by setting Fc/Fc⁺ (E_{forward}+E_{reverse})/2 as zero.

2.1 Spectroscopic measurements

Absorption measurements were done with a UV-visible-NIR spectrometer and fluorescence studies were carried out on a combined steady-state time-resolved fluorimeter after degassing the samples with nitrogen for 10 min. The compounds of study were dissolved in anhydrous dichloromethane. The emission spectra were measured by exciting the samples with the maximum absorption. For these measurements, nitrogen was bubbled for a minimum of 20 minutes to remove the dissolved oxygen. The fluorescence cuvettes were then sealed with a rubber septum to eliminate the diffusion of oxygen during the measurements. The oxidized state and its subsequent reduction to generate the neutral state were done with ferric chloride and hydrazine hydrate, respectively.

2.2 Spectroelectrochemical measurements

Measurements were done using a honeycomb electrode as a working electrode and Pt wire as the counter electrode. A Ag wire was used as the reference electrode. The honeycomb electrode was placed in a special 10 mm quartz spectroscopic cuvette in which there was a ca. 2 mm slit to hold the electrode. The absorption spectra were recorded after applying a given potential for a set period of time.

2.3 Theoretical calculations

Calculations were done with Gaussian 09 at the DFT level. The geometries of all the compounds were optimized using the same theoretical level; B3LYP hybrid functional with 6-31+G(d) basis set. Time-dependent density functional theory (TD-DFT) was used to calculate the optical transitions using the 6-31+G(d) basis set. The first six lowest transitions were calculated.

3. Additional Results

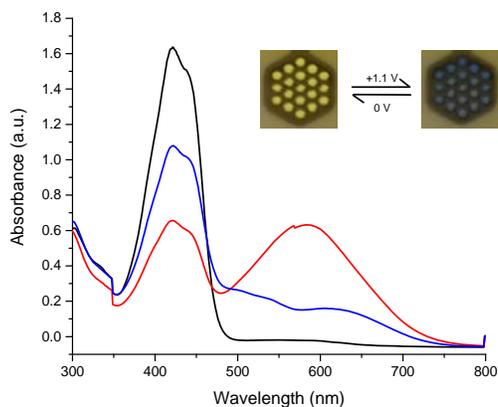


Figure S1. Spectroelectrochemistry of **6** measured in dichloromethane with applied potentials of 0 (—), 0.8 (—), and then 0 (—) V. Inset: photographs of the honeycomb electrode of the neutral (left) and oxidized (right) states with the corresponding applied potentials.

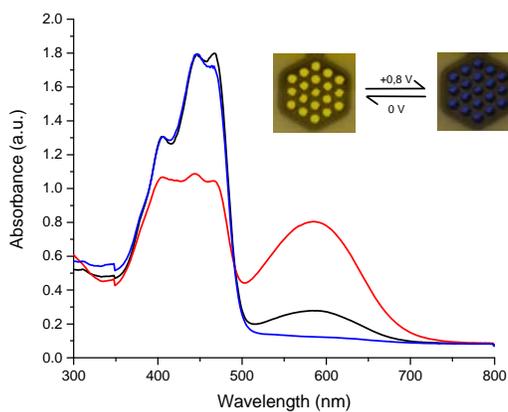


Figure S2. Spectroelectrochemistry of **7** measured in dichloromethane with applied potentials of 0 (—), 0.8 (—), and then 0 (—) V. Inset: photographs of the honeycomb electrode of the neutral (left) and oxidized (right) states with the corresponding applied potentials.

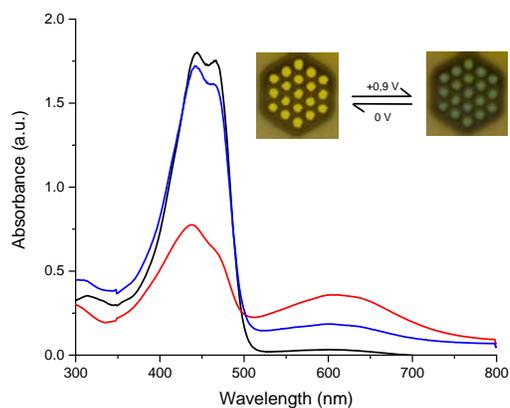


Figure S3. Spectroelectrochemistry of **8** measured in dichloromethane with applied potentials of 0 (—), 1.0 (—), and then 0 (—) V. Inset: photographs of the honeycomb electrode of the neutral (left) and oxidized (right) states with the corresponding applied potentials.

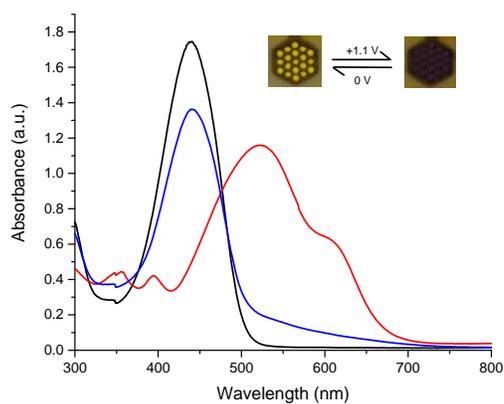


Figure S4. Spectroelectrochemistry of **9** measured in dichloromethane with applied potentials of 0 (—), 1.2 (—), and then 0 (—) V. Inset: photographs of the honeycomb electrode of the neutral (left) and oxidized (right) states with the corresponding applied potentials.

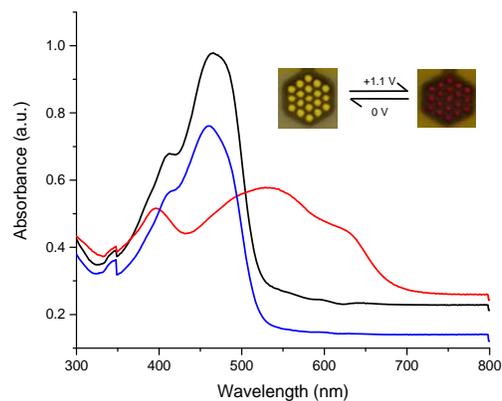


Figure S5. Spectroelectrochemistry of **10** measured in dichloromethane with applied potentials of 0 (—), 1.2 (—), and then 0 (—) V. Inset: photographs of the honeycomb electrode of the neutral (left) and oxidized (right) states with the corresponding applied potentials.

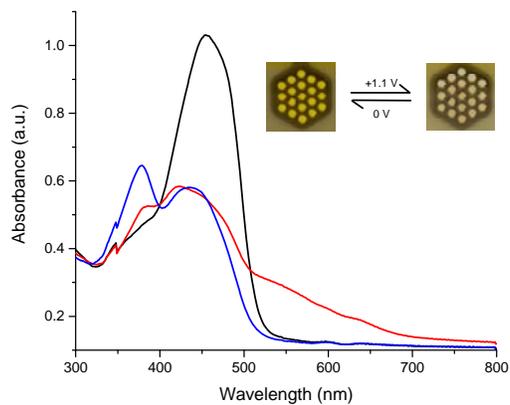


Figure S6. Spectroelectrochemistry of **11** measured in dichloromethane with applied potentials of 0 (—), 1.2 (—), and then 0 (—) V. Inset: photographs of the honeycomb electrode of the neutral (left) and oxidized (right) states with the corresponding applied potentials.

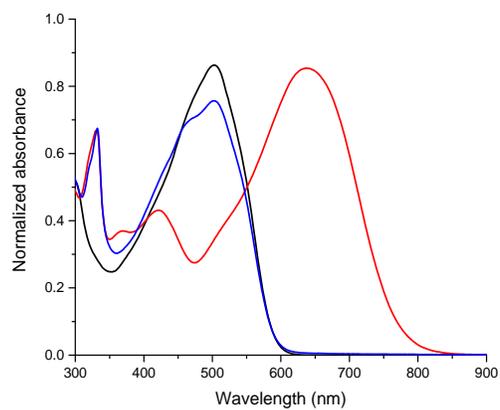


Figure S7. Normalized absorption spectra of **12**: neutral (—), oxidized with ferric chloride (—), and subsequently reduced with hydrazine (—).

Table S1. CIE coordinates with A, B and C illuminants with the 2° standard observer angle.^a

| | | Neutral State | | | Electrochemically Oxidized State | | |
|-----------|----------|---------------|------------|------------|----------------------------------|------------|------------|
| | | <i>L</i> * | <i>a</i> * | <i>b</i> * | <i>L</i> * | <i>a</i> * | <i>b</i> * |
| 6 | A | 85.4 | 3.2 | 42.7 | 62.0 | 1.1 | -12.0 |
| | B | 84.5 | -4.4 | 46.8 | 62.7 | -3.8 | -8.3 |
| | C | 84.1 | -10.4 | 48.3 | 63.1 | -5.8 | -6.7 |
| 7 | A | 80.1 | -3.1 | 76.3 | 36.7 | -12.1 | -51.4 |
| | B | 79.3 | -13.6 | 84.7 | 39.5 | -0.5 | -47.6 |
| | C | 78.9 | -21.1 | 87.2 | 40.7 | 7.7 | -45.8 |
| 8 | A | 96.6 | -3.6 | 94.3 | 75.6 | -10.3 | 27.7 |
| | B | 95.6 | -14.7 | 103.8 | 75.9 | -17.6 | 32.1 |
| | C | 95.0 | -22.9 | 106.6 | 75.9 | -22.1 | 33.4 |
| 9 | A | 90.3 | -1.0 | 92.5 | 61.3 | -26.3 | -17.7 |
| | B | 89.1 | -10.8 | 101.7 | 63.3 | -21.1 | -14.4 |
| | C | 88.5 | -18.5 | 104.6 | 64.0 | -17.5 | -13.3 |
| 10 | A | 77.9 | 5.0 | 54.2 | 62.3 | 10.9 | -2.3 |
| | B | 76.5 | 0.3 | 53.2 | 61.6 | 11.6 | 4.3 |
| | C | 75.9 | -4.0 | 52.3 | 61.4 | 11.9 | -4.9 |
| 11 | A | 87.5 | 2.5 | 70.7 | 79.3 | 7.9 | 28.2 |
| | B | 86.1 | -4.4 | 72.2 | 78.2 | 3.5 | 28.1 |
| | C | 85.4 | -10.2 | 72.1 | 77.8 | 0.0 | 27.9 |
| 12 | A | 98.3 | 11.3 | 6.8 | 101.4 | -0.9 | -1.0 |
| | B | 97.3 | 11.8 | 4.3 | 101.5 | -0.8 | 0.8 |
| | C | 96.9 | 11.5 | 3.4 | 101.6 | -0.6 | -0.8 |

^aMeasured between 360 and 830 nm.

References

- (S1) Gewalt, V. K.; Kleinert, M.; Thiele, B.; Hentschel, M. Zur Basenkatalysierten Reaktion von Methylenaktiven Nitrilen mit Schwefel. *J. Prak. Chem.* **1972**, *314*, 303-314.
- (S2) Gewalt, K.; Gruner, M.; Hain, U.; Süptitz, G. Zur Ringumwandlung von 2-Amino-thiophen-3-carbonsäureestern: Pyridon- und Pyridazinon-Derivate *Monatsh. Chem.* **1988**, *119*, 985-992.
- (S3) Gewalt, K. Methods for The Synthesis of 2-Aminothiophenes and Their Reactions (Review). *Chem. Heterocycl. Compd.* **1976**, *12*, 1077-1090.
- (S4) Hallas, G.; Towns, A. D. A Comparison of the Properties of Some 2-Aminothiophene-Derived Disperse Dyes. *Dyes Pigm.* **1996**, *31*, 273-289.
- (S5) Sabnis, R. W.; Rangnekar, D. W. Synthesis of Azo Benzo[B]Thiophene Derivatives and Their Application as Disperse Dyes. *Dyes Pigm.* **1989**, *10*, 295-302.
- (S6) Mohareb, R. M.; Sherif, S. M.; Moustafa, H. E.-D. The Reaction of Cyclohexan-1,3-dione with Cyanomethylenes: Synthesis of Thiophenes and Their Fused Derivatives with Antifungal Activities. *Phosphorus, Sulfur Silicon Relat. Elem.* **2009**, *184*, 2078-2096.
- (S7) Bai, R.; Liu, P.; Yang, J.; Liu, C.; Gu, Y. Facile Synthesis of 2-Aminothiophenes Using NaAlO₂ as an Eco-Effective and Recyclable Catalyst. *ACS Sustainable Chem. Eng.* **2015**, *3*, 1292-1297.
- (S8) Lai, G.; Bu, X. R.; Santos, J.; Mintz, E. A. Reinvestigation of the Vilsmeier-Haack Formylation of Triphenylamine. *Synlett* **1997**, *1997*, 1275-1276.
- (S9) Li, X.-C.; Liu, Y.; Liu, M. S.; Jen, A. K. Y. Synthesis, Properties, and Application of New Luminescent Polymers with Both Hole and Electron Injection Abilities for Light-Emitting Devices. *Chem. Mater.* **1999**, *11*, 1568-1575.
- (S10) Feng, J.; Zhang, C.; Li, Y.; Yang, M. Hyperbranched Polymer Based on Triphenylamine and Pyridine: Fluorescent Chemosensors for Palladium Ions. *J. Appl. Polym. Sci.* **2011**, *121*, 217-225.
- (S11) Skalski, T. Développement de composés conjugués en étoile de première génération incluant des liens azométhines et études électrochimiques et photophysiques. M. Sc. Université de Montréal, 2012.
- (S12) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96*, 877-910.