

Second Harmonic Generation in nonsymmetrical squaraines: tuning of the directional charge transfer character in highly delocalized dyes

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Supporting Information:

- 1. Synthetic details for the squaraines preparation**
- 2. Technical details for the Cyclic Voltammetry measurements**
- 3. Cyclic voltammetry for derivatives 13 and 15.**
- 4. References for the Supporting Information**

1. Synthetic details for the squaraines preparation

Materials.

All chemicals and solvents were purchased from Fluka or Adlrich and used as received unless explicitly stated. ^1H spectra were recorded using either a Bruker AMX-500 spectrometer or a Bruker AMX-200. ^{13}C NMR were recorder on a Bruker AMX-500 spectrometer operating at 125.70 MHz. Absorption spectrometry was performed using a Jasco V570 spectrophotometer. Melting points are uncorrected.

3-hydroxy-4-(1-methyl-5-diphenylhydrazone-1H-pyrrol-2-yl)cyclobut-3-ene-1,2-dione (5)

Squarilium chloride¹ (0.295 g, 1.95 mmol) was added directly as a solid to a colorless solution of hydrazone **4**² (0.538 g, 1.95 mmol) in dry Et₂O (75 ml). Color readily turns deep yellow and a red precipitate is formed. Mixture was stirred at r.t. for 1 h. The suspension was concentrated to about 20 ml volume and the red precipitate was filtered and washed with hexane directly on the filter. (0.430 g, 1.10 mmol, 57 % yield). Mp. 213-214 °C. ^1H NMR (500 MHz, CDCl₃) δ 7.51 (1H, d, J = 4.45 Hz), 7.48 (t, 4H, J = 7.96 Hz), 7.28 (t, 2H, J = 7.34 Hz), 7.18 (d, 4H, J = 7.64 Hz), 7.10 (s, 1H), 6.66 (d, 1H, J = 4.55 Hz), 4.23 (s, 3H).

The emichloride was immediately converted in the corresponding emisquaraine. The red precipitate was thus dissolved in 40 ml of acetone and 0.4 ml of N(Et)₃ were added. After 6 h stirring at r.t. solvent was removed and the brown solid residue was taken up with H₂O (50 ml). The yellow solution was filtered to remove any undissolved material. 5 % HCl was added dropwise till about pH = 2 and a red-brown solid was suddenly formed. The solid was filtered under reduced pressure and dried till constant weight. (0.310 g, 0.83 mmol, 75 % yield). Mp. 131-133 °C. ^1H NMR (500 MHz, CDCl₃) δ 7.41 (4H, t, J = 7.83 Hz), 7.20 (t, 2H, J = 7.34 Hz), 7.19 (d, 1H, J = 3.70 Hz), 7.14 (d, 4H, J = 7.86 Hz), 7.08 (s, 1H), 6.40 (d, 1H, J = 3.87 Hz),

4.23 (s, 3H).

**3-(5-(4-(dibutylamino)styryl)-1-hexyl-1H-pyrrol-2-yl)-4-hydroxycyclobut-3-ene-1,2-dione
(7).**

Squarilium chloride (0.250 g, 1.66 mmol) was added directly as a solid to a colorless solution of derivative **6**³ (0.630 g, 1.66 mmol) in dry Et₂O (30 ml). Color readily turns deep yellow and a red precipitate is formed. After 1 h stirring at r.t., the red precipitate was filtered and washed with hexane directly on the filter. (0.510 g, 1.03 mmol 62 % yield). ¹H NMR (DMSO-*d*₆) 7.59 (s, 1H), 7.41 (d, 2H, *J* = 8.60 Hz), 7.20 (d, 1H, *J* = 15.84 Hz), 6.82 (d, 1H, *J* = 4.57 Hz), 6.74 (d, 1H, *J* = 15.84 Hz), 6.66 (d, 2H, *J* = 8.57 Hz), 4.53 (t, 2H, *J* = 7.34 Hz), 3.36 (t, 4H, *J* = 7.54 Hz), 1.72 (m, 2H), 1.63 (m, 4H), 1.45-1.25 (m, 10H), 0.97 (m, 6H), 0.88 (m, 3H).

The emichloride was immediately converted in the corresponding emisquaraine. The red precipitate was thus dissolved in 20 ml of acetone and 0.3 ml of N(Et)₃ were added. After 6 h stirring at r.t. solvent was removed and the brown solid residue was taken up with H₂O (50 ml). The yellow solution was filtered to remove any undissolved material. 5 % HCl was added dropwise till the precipitation of a red-brown solid. The solid was filtered under reduced pressure and dried till constant weight. (0.393 g, 0.824 mmol, 80 % yield). Mp. 150 °C (dec). ¹H NMR (DMSO-*d*₆) 7.37 (d, 2H, *J* = 8.77 Hz), 6.92 (d, 1H, *J* = 3.95 Hz), 6.89 (d, 1H, *J* = 17.66 Hz), 6.85 (d, 1H, *J* = 17.65 Hz), 6.62 (d, 1H, *J* = 8.83 Hz), 6.53 (d, 1H, *J* = 3.98 Hz), 5.77 (s, 1H), 4.69 (t, 2H, *J* = 7.12 Hz), 3.29 (t, 4H, *J* = 7.76 Hz), 1.55-1.47 (m, 6H), 1.38-1.27 (m, 4H), 1.25-1.28 (m, 4H), 0.93 (t, 6H, *J* = 7.38 Hz), 0.82 (t, 3H, *J* = 6.65 Hz).

Squaraine 9.

A yellow suspension of emisquaraine **3**⁴ (0.200 g, 1.05 mmol), hexylbenzothiazolium iodide **8**⁵

(0.378 g, 1.05 mmol) and imidazole⁶ (0.170 g, 2.50 mmol) in 30 ml of a 3:1 BuOH:toluene mixture was refluxed for 4 h under a Dean-Stark trap to azeotropically remove the water formed. The color gradually turns green and eventually deep blue. All volatiles were removed under reduced pressure and the oily deep blue residue was taken up with 2 % HCl in order to dissolve the excess imidazole and the unreacted benzothiazolium salt. The resulting purple suspension was filtered to give a dark powder that was washed directly on the filter with 3 % NaOH to remove any unreacted emisquaraine and with deionized water. Crystallization from EtOH afforded an analytical sample. (0.250 g, 0.61 mmol, 59 % yield). Mp 208-210 °C. ¹H NMR (500 MHz, CDCl₃): δ 9.63 (s broad, 1H), 7.63 (d, 1H, *J* = 7.83 Hz), 7.44 (t, 1H, *J* = 7.49 Hz), 7.31 (t, 1H, *J* = 7.35 Hz), 7.27 (d, 1H, *J* = 8.31 Hz), 6.07 (s, 1H), 5.94 (s, 1H), 4.17 (t, 2H, *J* = 8.03 Hz), 2.55 (s, 3H), 2.29 (s, 3H), 1.82 (quint, 2H, *J* = 7.37 Hz), 1.50-1.40 (m, 2H), 1.40-1.30 (m, 4H), 0.88 (t, 3H, *J* = 7.37 Hz); ¹³C NMR (CDCl₃) δ 181.7, 163.5, 162.6, 140.6, 138.7, 132.1, 129.1, 127.7, 125.4, 122.4, 123.5, 114.0, 112.3, 88.0, 47.0, 31.4, 27.8, 26.5, 22.5, 13.9, 13.8, 13.0. Anal. Calcd for C₂₄H₂₆N₂O₂S: C, 70.90; H, 6.45; N, 6.89; Calcd for C₂₄H₂₆N₂O₂S * H₂O: C, 67.90; H, 6.65; N, 6.60; Found: C, 67.65; H, 6.63; N, 6.48.

Squaraine 10.

A yellow suspension of emisquaraine **5** (0.040 g, 0.10 mmol), hexylbenzothiazolium iodide **8** (0.036 g, 0.10 mmol) and imidazole (0.014 g, 0.21 mmol) in 30 ml of a 1:1 ¹PrOH:toluene mixture was refluxed for 6 h under a Dean-Stark trap to azeotropically remove the water formed. The color gradually turns greenish-blue. All volatiles were removed under reduced pressure and the oily deep blue residue was purified by chromatography (SiO₂ CH₂Cl₂) to give the pure title compound as a purple solid. (0.040 g, 0.068 mmol, 68 % yield). Mp 220-223°C. ¹H NMR (500 MHz, CDCl₃): δ 7.69 (d, 1H, *J* = 7.80 Hz), 7.48 (t, 1H, *J* = 7.34 Hz), 7.43 (t, 4H, *J* = 8.12 Hz), 7.39 (d, 1H, *J* = 4.25 Hz), 7.37 (t, 1H, *J* = 7.71 Hz), 7.33 (d, 1H, *J* = 8.33 Hz),

7.22 (t, 1H, $J = 7.42$ Hz), 7.17 (d, 2H, $J = 7.64$ Hz), 7.10 (s, 1H), 6.48 (d, 1H, $J = 4.27$ Hz), 6.27 (s broad, 1H), 4.35 (s, 3H), 4.26 (t, 2H, $J = 8.06$ Hz), 1.86 (quint, 2H, $J = 7.79$ Hz), 1.46 (quint, 2H, $J = 7.73$ Hz), 1.20-1.10 (m, 4H), 0.94 (t, 3H, $J = 7.90$ Hz). ^{13}C NMR (CDCl_3) δ 182.0, 180.0, 179.0, 164.3, 159.4, 143.1, 140.6, 137.7, 130.7, 130.1, 129.4, 128.1, 127.4, 126.0, 125.0, 122.8, 122.6, 118.2, 115.6, 113.1, 89.6, 47.5, 36.4, 31.5, 28.1, 26.6, 22.6, 14.1. Anal. Calcd for $\text{C}_{36}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$: C, 73.69; H, 5.84; N, 9.55; Calcd for $\text{C}_{36}\text{H}_{34}\text{N}_4\text{O}_2\text{S} \cdot 2\text{H}_2\text{O}$: C, 69.43; H, 6.15; N, 9.00; Found: C, 69.77; H, 6.60; N, 8.72.

Squaraine 11.

A yellow suspension of emisquaraine **7** (0.100 g, 0.21 mmol), hexylbenzothiazolium iodide **8** (0.076 g, 0.21 mmol) and imidazole (0.014 g, 0.21 mmol) in 30 ml of a 1:1 $^i\text{PrOH}$:toluene mixture was refluxed for 8 h under a Dean-Stark trap to azeotropically remove the water formed. The color gradually turns greenish-blue. All volatiles were removed under reduced pressure and the oily deep blue residue was purified by chromatography (SiO_2 AcOEt) to give the pure title compound as a purple solid. (0.073 g, 0.105 mmol, 50 % yield). Mp 158-160°C. ^1H NMR (500 MHz, benzene- d_6): δ 8.43 (d, 1H, $J = 4.08$ Hz), 7.37 (d, 2H, $J = 8.83$ Hz), 7.12 (d, 1H, $J = 16.04$ Hz), 6.91 (d, 1H, $J = 16.04$ Hz), 6.76 (t, 1H, $J = 8.28$ Hz), 6.72 (d, 1H, $J = 4.28$ Hz), 6.69 (d, 1H, $J = 7.29$ Hz), 6.62 (t, 1H, $J = 7.18$ Hz), 6.59 (d, 2H, $J = 9.04$ Hz), 6.28 (d, 1H, $J = 8.31$ Hz), 6.19 (s, 1H), 5.00 (t, 2H, $J = 7.56$ Hz), 3.04 (t, 2H, $J = 8.19$ Hz), 3.01 (t, 4H, $J = 8.02$ Hz), 1.86 (quint, 2H, $J = 7.75$ Hz), 1.54 (m, 4H), 1.40-1.10 (m, 12H), 1.00-0.90 (m, 11 H), 0.83 (t, 6H, $J = 7.31$ Hz), 0.81 (t, 3H, $J = 6.91$ Hz). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.72 (d, 1H, $J = 7.82$ Hz), 7.49 (d, 1H, $J = 7.75$ Hz), 7.43 (s, 1H, broad), 7.40-7.30 (m, 4H), 7.06 (d, 1H, $J = 14.89$ Hz), 6.78 (d, 1H, $J = 15.79$ Hz), 6.70 (s, 1H, broad), 6.64 (d, 2H, $J = 8.58$ Hz), 6.11 (s, 1H, broad), 4.71 (t, 2H, $J = 6.58$ Hz), 4.23 (t, 2H, $J = 7.38$ Hz), 3.31 (t, 4H, $J = 6.82$ Hz), 1.86 (quint, 2H, $J = 7.52$ Hz), 1.71 (quint, 2H, $J = 7.28$ Hz), 1.59 (quint, 4H, $J = 7.68$

Hz), 1.47 (quint, 2H, $J = 5.97$ Hz), 1.40-1.35 (m, 14H), 0.97 (t, 6H, $J = 7.34$ Hz), 0.91 (t, 3H, $J = 6.88$ Hz), 0.87 (t, 3H, $J = 7.02$ Hz). ^{13}C NMR (CD_2Cl_2) δ 181.5, 179.1, 178.5, 163.1, 161.0, 148.5, 142.1, 140.9, 132.0, 129.2, 128.1, 127.7, 125.2, 124.0, 122.7, 118.9, 112.8, 111.7, 110.6, 110.4, 88.2, 50.8, 47.1, 46.1, 32.1, 31.8, 31.5, 29.5, 27.8, 26.6, 26.3, 22.7, 22.6, 20.4, 13.9, 13.9. Anal. Calcd for $\text{C}_{44}\text{H}_{57}\text{N}_3\text{O}_2\text{S}$: C, 76.37; H, 8.30; N, 6.07; Found: C, 76.07; H, 8.69; N, 6.08.

Squaraine 13.

A yellow suspension of emisquaraine **7** (0.250 g, 0.53 mmol) and anhydrobase **12** (0.115 g, 0.53 mmol) in 40 ml of a 1:1 $i\text{PrOH}$:benzene mixture was refluxed for 4 h under a Dean-Stark trap to azeotropically remove the water formed. The color gradually turns green, than blue. All volatiles were removed under reduced pressure and the solid deep blue residue was purified by chromatography (SiO_2 CHCl_3 :MeOH 9:1) to give the pure title compound as a purple solid. (0.170 g, 0.250 mmol, 47% yield). Mp > 200 °C (dec). ^1H NMR (acetone- d_6) 8.12 (dd, 2H, $J = 6.63$ Hz, 1.72 Hz), 7.78 (d, 1H, $J = 4.50$ Hz), 7.54 (d, 2H, $J = 8.86$ Hz), 7.42 (d, 1H, $J = 16.01$ Hz), 7.38 (d, 1H, $J = 7.21$ Hz), 7.08 (d, 1H, $J = 16.01$ Hz), 6.99 (d, 1H, $J = 4.55$ Hz), 6.73 (d, 2H, $J = 8.93$ Hz), 6.02 (s, 1H), 4.96 (t, 2H, $J = 7.39$ Hz), 3.78 (s, 3H), 3.43 (t, 6H, $J = 7.67$ Hz), 1.87 (s, 6H), 1.74 (m, 2H), 1.61 (m, 4H), 1.20-1.50 (m, 10H), 0.98 (m, 6H), 0.85 (m, 3H). ^{13}C NMR (acetone- d_6) δ 184.6, 184.3, 183.5, 182.4, 181.8, 175.7, 171.0, 166.5, 149.0, 146.6, 139.3, 135.6, 130.6, 129.0, 129.0, 126.0, 125.8, 125.0, 123.8, 123.3, 122.2, 112.4, 111.6, 109.8, 89.2, 50.3, 48.9, 45.8, 31.9, 31.4, 29.7, 29.5, 26.2, 25.8, 22.4, 20.0, 13.4, 13.4. Anal. Calcd for $\text{C}_{43}\text{H}_{52}\text{N}_2\text{O}_4$: C, 76.41; H, 7.90; N, 6.22; Calcd for $\text{C}_{43}\text{H}_{52}\text{N}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$: C, 70.75; H, 8.15; N, 5.62; Found: C, 77.27; H, 6.65; N, 2.74.

Squaraine 15.

A yellow suspension of emisquaraine **14**⁷ (0.398 g, 1.35 mmol) and anhydrobase **12** (0.294 g, 1.35 mmol) in 60 ml of a 1:1 ⁱPrOH:toluene mixture was refluxed for 6 h under a Dean-Stark trap to azeotropically remove the water formed. The color gradually turns deep blue. All volatiles were removed under reduced pressure and the solid deep blue residue was taken up with 20 ml of a water:toluene 1:1 mixture. The resulting golden precipitate was filtered under reduced pressure and crystallized from MeOH to give an analytical sample. (0.300 g, 0.61 mmol, 45 % yield). Mp. >200 °C (dec). ¹H NMR (500 MHz, CDCl₃): δ 8.69 (s, 1H), 8.17 (dd, 1H, *J* = 8.29 Hz, 1.44 Hz), 8.13 (d, 1H, *J* = 1.80 Hz), 8.11 (d, 1H, *J* = 1.27 Hz), 7.60 (dd, 1H, *J* = 10.93 Hz, 1.68 Hz), 7.48 (d, 1H, *J* = 10.97 Hz), 7.16 (d, 1H, *J* = 8.37 Hz), 6.60 (s broad, 1H), 3.78 (s, 3H), 3.34 (s, 3H), 3.15 (quint, 1H, *J* = 6.97 Hz), 2.57 (s, 3H), 1.87 (s, 6H), 1.41 (d, 6H, *J* = 6.89 Hz). ¹³C NMR (500 MHz, CDCl₃): δ 169.3, 152.2, 150.2, 146.8, 142.3, 139.3, 137.8, 135.4, 134.2, 131.4, 130.4, 125.6, 124.2, 109.8, 49.6, 38.4, 32.1, 28.1, 26.7, 24.3, 13.0. Anal. Calcd for C₃₂H₃₁NO₄: C, 77.87; H, 6.33; N, 2.84; Calcd for C₂₈H₂₄N₄O₂* 1/4 H₂O: C, 77.16; H, 6.37; N, 2.81; Found: C, 77.27; H, 6.65; N, 2.74.

2. Cyclic Voltammetry Experimental procedure.

For the electrochemical characterization the squaraines were dissolved (concentration about 10^{-4} M) in the supporting electrolyte that was a 0.1 M solution of tetrabutylammonium *p*-toluenesulfonate (Fluka, electrochemical grade, $\geq 99.0\%$) in anhydrous acetonitrile (Aldrich, 99.8%). Cyclic Voltammetries at scan rate of 100 mV/s were carried out using a PARSTA2273 potentiostat in a single chamber three electrodes electrochemical cell in a glove box filled with Argon ($[O_2] \leq 1$ ppm). The working, counter and pseudo-reference electrodes were a Glassy Carbon (GC) disc, a Pt flag, and a Ag/AgCl wire, respectively. The GC disc was well polished with alumina 0.1 μm suspension, sonicated for 15 min. in deionized water and washed with 2-propanol before using. The Ag/AgCl pseudo-reference electrode was calibrated before and after each measurement using a 1 mM ferrocene solution in the electrolyte, no more than 5 mV in difference was observed between two successive calibrations.

Cyclic voltammetry for derivatives 13 and 15.

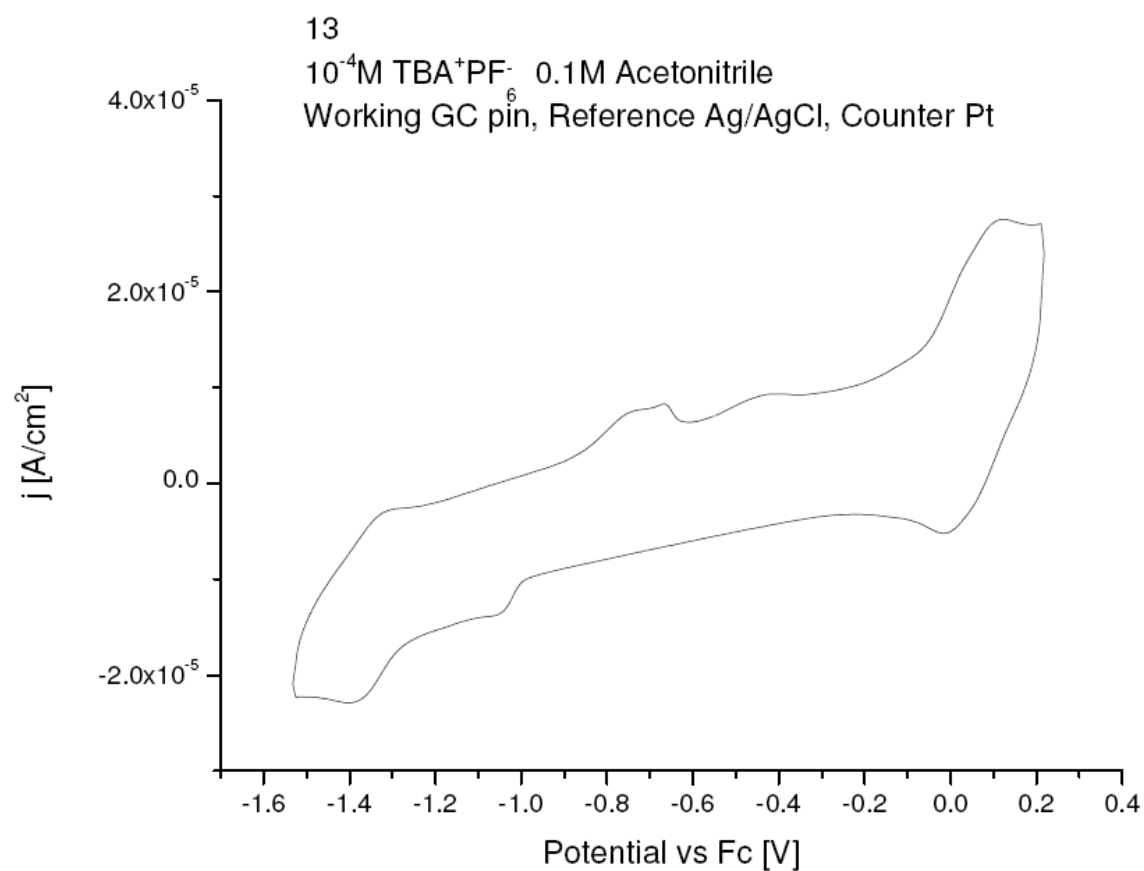


Figure SI01. Cyclic Voltammetry plot for squaraine **13** in CH₃CN with tetrabutylammonium hexafluorophosphate as the supporting electrolyte

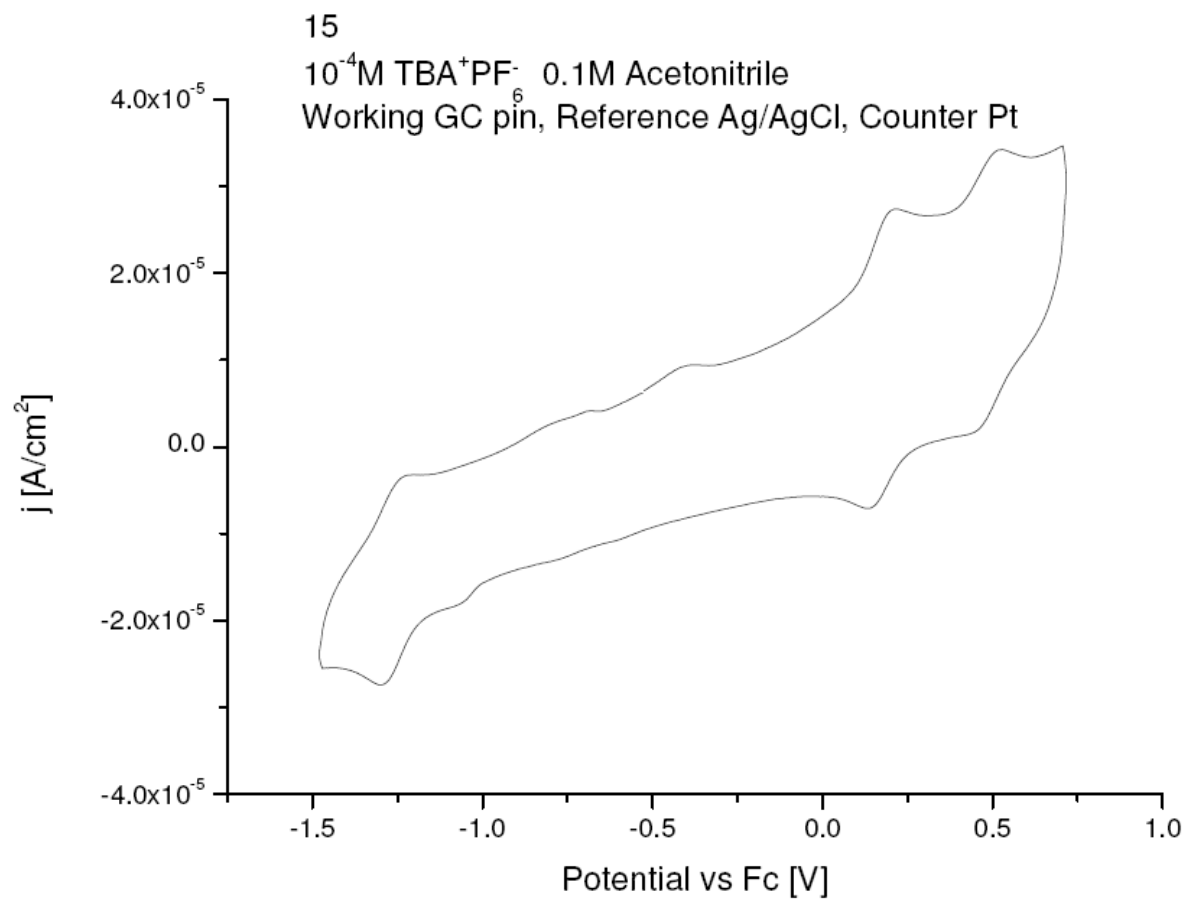


Figure SI02. Cyclic Voltammetry plot for squaraine **15** in CH₃CN with tetrabutylammonium hexafluorophosphate as the supporting electrolyte

4. References for the Supporting Information.

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 - 6 The original choice of imidazole instead of the more commonly employed quinoline enabled for an easier isolation of the pure compound from the reaction mixture. In fact, some of the compounds we made possess a basic residue preventing the use of diluted HCl to extract the excess base from the reaction mixture as the corresponding salt. Imidazole did not interfere with the purification process, even when in excess with respect to 8. Conversely the excess quinoline, whenever employed, was found to strongly interfere with the reaction mixture behaviour during chromatography.
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