Breaking Down Resonance: Non-Linear Transport and the Breakdown of Coherent Tunneling Models in Single Molecule Junctions

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S1 Additional Analysis and Data

S1.1 TDO4 in TCB



Figure S1: (a) Data presented in Figure 1d, with each trace offset horizontally such that the drop in current occurs at t=0. **(b)** Histogram of the peak-to-valley ratio extracted from each trace.

As detailed in the main manuscript, most of the I-V traces display abrupt NDR. However, this is not visible in Figure 1d as the location of the NDR is not the same in every IV curve. Figure S1a above shows a 2D plot where each IV trace is aligned relative to the time where the current is minimum after the threshold bias (which is the bias where the maximum current occurs). This figure demonstrates how sharp the current drops beyond the threshold bias. Although there are certainly some traces which display more gradual NDR, most traces have current dropping by a factor of 10 on a few millisecond time scale. The peak-tovalley current ratio of each trace is extracted from the data by taking the ratio of the current at the threshold bias (i.e. the maximum current in the trace) and the minimum current after the threshold bias. This is shown in Figure S1b.



Figure S2: (a) 2D-histogram of current traces versus time for TDO4 measured in PC after selecting for traces that do not rupture and display hysteresis. The applied bias trace overlaid in white. (b) 2D-histogram of threshold bias against fitted level alignment ε (energy difference between the transport orbital and the Fermi energy). The diagonal lines delineate the expected trend in a non-polar solvent $(V_{thresh}=2\varepsilon)$ or a perfectly effective polar-solvent where the level alignment is pinned to the substrate $(V_{thresh}=\varepsilon)$. The data falls between the two lines. Histograms of fitted **(c)** level alignment ε and **(d)** level broadening Γ , with the results before and after charging shown in blue and green, respectively.



Figure S3: Same as Figure S2, except for squaraine measured in TCB. Diagonal line in **(b)** is the V= 2ε limit expected for experiments performed in non-polar solvent. Level alignment is quoted as positive for convenience (HOMO conducting molecules have negative ε).



Figure S4: Same as Figure S2, except for squaraine in PC.

Note that the current is higher when the bias is positive, which indicates that the HOMO resonance is closer to Fermi than the LUMO resonance.

S1.4 Ramp Speed and Reversibility Experiments



Figure S5: (a) Normalized threshold bias versus ramp speed, *(b)* percent reversed versus hold bias, and *(c)* percent reversed versus hold time for squaraine measured in TCB (red triangles) and PC (black circles). *(d)*, *(e)*, and *(f)* are the corresponding experiments for TDO4.

The ramp speed experiments are performed as described in the manuscript. On the vertical axis we plot the "normalized" threshold bias rather than the actual threshold bias. This is necessary to compare experiments performed in polar solvent with those in non-polar solvent. To normalize, we divide the measured threshold bias by the bias at which the resonance of the transmission function is expected to enter the bias window, given by Equation S1 below. Note that this normalization is performed for each trace based on the fitted values of ε and α . α is fixed at 0 for junctions in non-polar solvent.

$$V_{resonance} = \frac{\varepsilon}{\frac{1}{2} + \alpha}$$
(S1)

An interesting observation is that the charged state of squaraine appears less stable in PC than in TCB as indicated by a higher reversibility in Figures S5b,c. We hypothesize that this is due the presence of water in PC which can protonate the molecule. Protonation serves as an additional driving force for discharging not present in TCB.

S2 Selection Algorithms



Figure S6: 2D-histogram of current traces versus time after **(a)** initial selection, **(b)** hysteresis test, and **(c)** rupture test. **(d)** Example trace (same as Figure 1c), zoomed in to highlight features used in selection algorithms. Each algorithm looks for specific features in the current at different points in time in the trace, indicated by the vertical lines. The initial selection (green) checks for the presence of the molecule. The hysteresis test (magenta) checks that the molecule has been charged. The rupture test (orange) distinguishes junctions that rupture upon charging from junctions that sustain.

S2.1 Initial Selection

Just before the I-V ramp is performed (at 75 ms in Figure S6d), the bias is held fixed and the conductance is measured. If the conductance matches the expected conductance of the molecule, the trace is selected for further analysis. The results from this initial selection are displayed in Figure S6a.

S2.2 Hysteresis Test

Due to the junction-to-junction variation in level alignment, not all junctions enter the resonant-tunneling regime within the maximum applied bias. Assuming that all junctions that enter the resonant-tunneling regime have a lower current during the return bias sweep due to junction rupture or hysteresis, we select traces that undergo charging by comparing the current at the threshold bias during the ramp up and during the ramp down. Specifically, we compare the average current for 50 points before the threshold bias during the ramp up (increasing bias) to the 50 points after the threshold bias during the ramp down (decreasing bias). If the difference between the two currents is at least half a decade, the trace is labeled as having entered the resonant-tunneling regime. Recall that the threshold bias is approximated as the

bias where the maximum current occurs. If the maximum bias is sufficiently large, most junctions will display hysteresis or junction rupture. The results after this selection are shown if Figure S6b.

S2.3 Rupture Test

Finally, to distinguish those junctions which display true hysteresis from those that rupture, we consider the points at the very end of the downward ramp (at 125 ms in Figure S6d). Junctions that rupture have a current at the instrumental noise even for biases as high as 0.1 V. At instrumental noise, the polarity of the current will oscillate between positive and negative. By rejecting those traces where the current and bias have opposite polarity close to zero bias, we are left with the traces that show true hysteresis. The results from this final selection is shown in Figure S6c.

S2.4 Polar Solvent

As explained in Section S3.3, fitting data collected in polar solvent requires acquiring data at both bias polarities. The initial selection algorithm is identical to that for experiments performed in non-polar solvent except one additional requirement. In addition to selecting for those traces that display the expected conductance before the voltage ramp, we reject those traces which fail the rupture test where the bias changes polarity (at 50 ms in Figure S2a). This is to reject traces that display strong capacitive back-current.

S2.5 Post-Fit Selection

The majority of traces before charging can be characterized through non-linear least-squares regression, as described in Section S3. A fraction of traces will return unrealistic values for the level alignment and/or level broadening for the fitting after charging. This is due to false negatives from the rupture test, i.e. junctions that actually rupture but pass the rupture test. This problem is worse for experiments performed in polar solvent compared to those performed in non-polar solvent. We reject those traces where one of the fitting parameters equals the constraint (see Section S3.5). We also reject those traces with level alignment greater than 10 eV or level broadening greater than 1 eV. The histograms of the fitted values of level alignment and level broadening are constructed out of traces after this selection algorithm has been applied. Without this selection, the qualitative behavior of the histograms is the same.

S2.6 Statistics

Molecule	Solvent	Total Collected	Initial Selection	w/ Hysteresis	w/o Rupture	Post-Fit Selection
TDO4	ТСВ	5000	3378	3030	568	461
TDO4	PC	50000	7829	5721	1310	843
Squaraine	ТСВ	21000	10660	8958	1913	1638
Squaraine	PC	5000	3550	3387	1504	957

Table S1: Number of traces after each selection algorithm.

S2.7 Reversibility Test

Finally, Figures S7 demonstrates the selection algorithm for the reversibility tests on squaraine in PC. The initial selection is the same except that the rupture test is applied just before the second ramp. In addition

to the standard rupture test, we check that the current is greater than instrument noise. The hysteresis test for both ramps is the same as described above. The rupture test is not performed after the second ramp, since junctions that rupture due to charging still count as reversed. Figures S7e,f show the same data as in Figures S7c,d, respectively, but zoomed in to highlight the second ramp to demonstrate the efficacy of the hysteresis test.



Figure S7: 2D-histograms of current traces versus time after (a) initial selection and (b) hysteresis test in ramp 1. The traces which display hysteresis in ramp 2 (i.e. those traces that reverse) and the traces which do not display hysteresis in ramp 2 are compiled in (c) and (d), respectively. The same data is presented in (e) and (f) to highlight the efficacy of the hysteresis test.

S3 Non-Linear Least-Squares Fitting Methods

S3.1 Fitting Algorithm

First, the current and voltage trace is loaded and the appropriate IV data is extracted. For example, for experiments performed in non-polar solvent, only the initial ramp up to the threshold bias is required. For experiments performed in polar solvent, the middle ramp where the bias sweeps the entire range is selected, not including points past the threshold bias. If the data after charging is being fit, the entire reverse ramp is selected. The current data is converted to log(current) data by multiplying the sign of the voltage at each data point before applying the base 10 logarithmic function, i.e. $log(I) \equiv log_{10}(I * sign(V))$. There may still be some points where the sign of current does not match the sign of the voltage; these points are removed. The remaining points are then smoothed using a boxcar smoothing algorithm (unweighted sliding-average) with a box width of 11 points. This step minimizes the number of outliers. Before fitting the data, the number of points is reduced to 200, with points being selected evenly from the remaining data. All fitting is performed using Levenberg-Marquardt least-squares method as implemented in Igor Pro Version 6.3.7.2.

S3.2 Curve-Fitting Near the Resonant Tunneling Regime



Figure S8: (a) Theoretical I-V curves generated using Eq S2 (blue) and Eq 1 (red). Example I-V data (black dots) with fits from logarithmically-scaled data (red) and linearly-scaled data (blue), displayed on a semilog plot **(b)** and on a linear plot **(c)**.

Many works in the past that have performed I-V fitting on room-temperature based single-molecule junction measurements do so within the 0 K approximation, where the Fermi-Dirac distributions are replaced with step functions^{1–7}. In the special case where the transmission function can be approximated with a Lorentzian function, the current can be computed analytically without performing numerical integration (Equation S2 below). Although this is a reasonable approximation in the non-resonant tunneling regime, as the bias approaches 2ε , the theoretical current deviates significantly from the low-temperature approximation, as demonstrated in Figure S8a. As a rule of thumb, if the bias exceeds ε , temperature must be taken into account and one must perform numerical integration. The requirement would be more stringent for experiments performed in polar solvent.

$$\lim_{T \to 0} I(V) = \frac{2e}{h} \int_{-\frac{eV}{2}}^{\frac{eV}{2}} dE \ T(E) = \frac{2e\Gamma}{h} \left[\tan^{-1} \left(\frac{V - 2\varepsilon}{2\Gamma} \right) + \tan^{-1} \left(\frac{V + 2\varepsilon}{2\Gamma} \right) \right]$$
(S2)

In addition, since the current can span on the order of three orders of magnitude when approaching the resonant tunneling regime, all fitting is done on a logarithmic scale, as using a linear scale fit results in systematic errors at low bias. This is illustrated in Figure S8b and S8c.

S3.3 Fitting Data in Polar Solvent

$$T(E) = \frac{\Gamma^2}{(E - \varepsilon - \alpha eV)^2 + \Gamma^2}$$
(S3)

The effect of polar solvent can be captured by a modified transmission function, given by Equation S3, where $0 \le \alpha \le 0.5$. The primary effect of the additional parameter is to introduce an asymmetry in the I-V curve³. In order to perform fitting without fixing α , data at both bias polarities must be collected. This is shown in Figures S2a and S4a. This asymmetry also allows us to determine whether the molecular orbital dominating transport is the HOMO or LUMO. If the current is higher at positive (negative) bias, the molecule is HOMO (LUMO) conducting.

When fitting the IV curve after charging, only data at one bias polarity is available. In order to fit this data, we fix α to be the same as that determined before charging.

S3.4 The Polaron Model in Polar Solvent

The polaron model requires that LUMO conducting molecules become HOMO conducting upon charging in order to explain NDR. More succinctly, the level alignment ε changes sign. Figure S9 summarizes the resulting fit if we enforce this change in sign for both TDO4 and squaraine measured in PC. The reorganization energy is then given by the equation $2\lambda = |\tilde{\varepsilon} - \varepsilon_0|$, where ε_0 and $\tilde{\varepsilon}$ are the level alignment before and after charging, respectively. Since ε_0 and $\tilde{\varepsilon}$ have opposite signs in the polaron model, this can be rewritten as $2\lambda = |\tilde{\varepsilon}| + |\varepsilon_0|$. We can then use Figures 2c and S3c to estimate the reorganization energy in TCB and Figures S9a,c to estimate the reorganization energy in PC. These reorganization energies are summarized in Table S2. If we assume the polaron model, the fits imply that the reorganization energy is on average smaller in PC, the polar solvent with a dielectric constant of 66^8 than in TCB, the non-polar solvent with a dielectric constant of 2.24^9 . This is the opposite of what is expected from Marcus' theory of charge transfer, and the work of Dzhioev and Kosov predicts that the reorganization energy should be almost double in PC¹⁰. We therefore conclude that the polaron model, in its current form, cannot explain our experimental results.

Table S2: Estimated reorganization energies	s (λ) for TDO4 and .	Squaraine measured in	TCB and PC
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	λ_{TCB} (eV)	λ_{PC} (eV)
TDO4	1.7	0.7
Squaraine	0.6	0.45

We note that this analysis cannot be applied to measurements performed in non-polar solvent. This is because the I-V curve for experiments performed in non-polar solvent is symmetric with respect to the

sign of ε . Unlike measurements in polar solvents, therefore, measurements in non-polar solvents require no assumptions about the sign of ε in order to perform fitting, and fits apply equally to both the polaron model and the blocking-state model.



Figure S9: Fitted values of level alignment and level broadening before (blue) and after (green) charging for TDO4 in PC (**(a)** and **(b)**) and squaraine in PC (**(c)** and **(d)**), assuming that the sign of the level alignment changes upon charging. The sign of the level alignment has been suppressed for simplicity.

S3.5 Fitting Constraints

For experiments performed in non-polar solvents, no constraints are necessary to obtain reasonable values for the level alignment and the level broadening. For convenience, we constrain the level alignment ε to be positive, since the model is symmetric with respect to the sign of ε . We also constrain the level broadening Γ to be greater than 1 µeV.

For experiments performed in polar solvent, in principle α should be constrained between 0 and 0.5, whereas ε is completely unconstrained. Negative values of ε would correspond to HOMO conducting molecules, and positive values of ε would correspond to LUMO conducting molecules. In practice, it is more useful to constrain ε to be positive and constrain α to lie between -0.5 and 0.5. Negative values of α correspond to HOMO conducting molecules, and positive values of a correspond to LUMO conducting molecules.

S3.6 Goodness of Fit

Figure S10 shows histograms of the root-mean square error (RMSE) for the various molecule-solvent combinations, both before and after charging. Because the fitting is performed on a semi-log scale, the RMSE should be interpreted in decades. For all fits, the RMSE is around 0.2 decades. To give a qualitative sense of what this means, a trace with an RMSE of 0.2 is shown in Figure S11a. The fitted curve captures the main features of the data. We conclude that a RMSE of 0.2 decades is reasonable.



Figure S10: Histograms of RMSE for fitted curves of (a) TDO4 in TCB, (b) TDO4 in PC, (c) squaraine in TCB, and (d) squaraine in PC.

In order to assuage any concerns that the correlation between the threshold bias and the fitted values of the level alignment is artificial, we took the exemplary data depicted in Figure 2a and performed fitting for different values of the threshold bias. That is, we performed fitting for a progressively smaller range of biases to simulate if the junction had ruptured at a bias much lower than 2ε . The result is summarized in Figure S11b. Although the assumed threshold bias and the fitted values for level alignment are correlated, the correlation due to fitting is not remotely large enough to account for the correlation we see in Figure 2b. Incidentally, the fictional threshold bias is also weakly correlated with the fitted value for the level broadening, but there is no evidence of this correlation for the experimental values. We are confident, therefore, that our fitting algorithm returns reasonable values for ε even in the case of low threshold bias.



Figure S11: (a) Example I-V data (red) with a fitted IV curve (blue) with RMSE of approximately 0.2 decades. **(b)** Figure 2b reproduced with fitted values of level alignment ε for five different artificial threshold bias values overlaid on top. The trend in the 2D-histogram is not reproduced by the dots, indicating that the correlation is not due to limitations of the fitting algorithm or model.



Figure S12: (a) Calculated transmission function of squaraine. Orbitals of the Au-squaraine-Au system corresponding to the *(b)* LUMO resonance and *(c)* HOMO resonance generated with Jmol.

We compute the transmission function of squaraine using the AITRANSS implementation of the nonequilibirium Green's function formalism within density functional theory (DFT)^{11,12}. AITRANSS is built on the FHI-aims package which uses numerical atom-centered basis functions^{13,14}, and we use the PBE exchange-correlation functional¹⁵.

The resulting transmission function is given in Figure S12a, which confirms that the molecule is HOMO conducting. Exact level alignment may not match experiment due to limitations of DFT¹⁶. The Ausquaraine-Au geometry is reproduced in Figures S12b,c. Each electrode consists of a pyramidal cluster of 55 Au atoms, arranged in 6 layers in the (111) direction with closest interatomic distance of 2.88 Å. The orbitals corresponding to the LUMO resonance and the HOMO resonance are shown in Figures S12b and S12c, respectively.

S5 Synthesis and Characterization of Squaraine

S5.1 Methods

Commercially available intermediates were purchased and used without further purification. ¹H, and ¹³C{¹H} NMR spectra were collected on a Bruker 400 MHz spectrometer. Deuterated solvents with tetramethylsilane as an internal standard were used. Mass spectra were measured on a VG Instruments 70-SE using the electron impact (EI) or fast-atom bombardment (FAB) mode and on an Applied Biosystems 4700 Proteomics Analyzer using MALDI mode. Elemental analyses were carried out by Atlantic Microlab using a LECO 932 CHNS elemental analyzer. Electronic spectroscopic data were collected in dichloromethane on a UV-Vis-NIR spectra in 1 cm quartz cuvette using an Agilent Cary 5000 spectrophotometer. Electrochemical measurements were carried out under an inert atmosphere in dry deoxygenated dichloromethane solution containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte. A CH-Instrument 620D potentiostat equipped with a conventional three-electrode cell utilizing a glassy carbon working electrode, platinum wire counter electrode, and a silver wire coated with silver chloride as the pseudo-reference electrode, was used for the measurements. Potentials were referenced to the ferrocenium/ferrocene (FeCp₂^{+/0}) using decamethyferrocenium/ decamethylferrocene (FeCp₂^{+/0} was determined to be -0.55 V vs. FeCp₂^{+/0} in dichloromethane). Cyclic voltammograms were recorded at a scan rate of 50 mV s⁻¹.



Figure S13: Preparation of the symmetric squaraine 5; (a) (i) 3-Methyl-2-butanone, ethanol, reflux, 1h; (ii) Acetic acid, reflux, overnight (b) Methyl iodide, acetonitrile, 55 °C, sealed pressure vessel, overnight (c) Sodium hydroxide (1M), toluene, room temperature, 2h (d) 3,4-Dihydroxy-3-cyclobutene-1 2-dione, toluene, 1-butanol, reflux, 20h.

S5.2 Synthetic Route

The [4-methylthio-phenylhyrdazine]hydrochloride, **1**, was synthesized according to literature procedure from the commercially available methylthio-aniline.¹⁷ The phenyl hydrazine **1** was transformed to the respective hydrazone upon reaction with 3-methyl-2-butanone,¹⁸ and then to the methylthio indole, **2**, via an acid catalyzed Fischer indole synthesis.¹⁹ Due to the instability of **2**, it was directly *N*-alkylated with methyliodide to get compound **3** as an ammonium salt.²⁰ The deprotonation of the quaternary salt **3** with sodium hydroxide yielded the *N*-alkylated indoline, **4**, which upon subsequent condensation with a squaric acid (3,4-dihydroxy-3-cyclobutene-1 2-dione), gives the symmetric squaraine **5**.²¹

S5.3 Synthetic Procedures

1,2,3,3-tetramethyl-5-(methylthio)-3H-indol-1-ium iodide (3)

2-(4-(methylthio)phenyl)hydrazin-1-ium chloride **1** (4.00 g, 20.9 mmol) and 3-methyl-2-butanone (3.61 g, 41.9 mmol) were dissolved in ethanol (60 mL) and refluxed under a nitrogen atmosphere for 1 hour. The ethanol was then removed under reduced pressure, acetic acid (60 mL) was added, and the reaction mixture was refluxed under nitrogen atmosphere overnight. The acetic acid was removed under reduced pressure, and to the resultant slurry was added water and ethanol (8:2, 100 mL). The organic layer was extracted with dichloromethane (3 × 150 mL) dried over anhydrous sodium sulfate, and solvent removed under reduced pressure to result in **2** as a red oil which was directly transferred into a 50 mL pressure flask, to which 10 mL of acetonitrile, and methyl iodide (7.5 mL, 121 mmol) were added and the content stirred at 55 °C overnight. The precipitate was filtered and washed with cold acetonitrile, methanol, dichloromethane and hexane, in this order, to get the desired compound **3**, as a mustard colored solid (2.5 g, 27% yield over 2 steps). ¹H NMR (400 MHz, (CH₃)₂SO-*d*₆) δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.77 (d, d, *J* = 1.8 Hz, 1H), 7.47 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.8 Hz, 1H), 3.95 (s, 3H), 2.74 (s, 3H), 2.58 (s, 3H), 1.53 (s, 6H). ¹³C{¹H} NMR (100 MHz, (CH₃)₂SO-*d*₆) δ 194.69, 142.99, 141.44, 139.83, 125.93, 120.85, 115.91, 54.27, 35.25, 22.16, 15.35, 14.51. HRMS (EI) *m/z*: [M–IH]⁺ Calcd for C₁₃H₁₇NS, 219.1082; found, 219.1080. Anal. Calcd for C₁₃H₁₃INS: C 44.96, H 5.22, N 4.03; found C 44.92, H 5.19, N 4.07.

1,3,3-trimethyl-2-methylene-5-(methylthio)indoline (4)

To a stirring solution of **3** (1.80 g, 5.18 mmol) in toluene (100 mL), an aqueous sodium hydroxide solution (1.0 M, 100 mL) was added, and the reaction mixture was stirred at room temperature and under nitrogen atmosphere for 2 hours. The yellow organic layer was separated and washed with brine solution (2 × 50 mL) and water (2 × 50 mL), dried with anhydrous sodium sulfate and solvent evaporated under reduced pressure to give **4** (0.70g, 62%) as a yellowish liquid, which rapidly turns to purple if left in air. ¹H NMR (400 MHz, CDCl₃) δ 7.20 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 1H), 7.15 (d, J = 1.8 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 3.78 (s, 2H), 3.05 (s, 3H), 2.46 (s, 3H), 1.36 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.53, 145.53, 138.63, 129.80, 125.48, 124.32, 105.31, 73.59, 44.13, 29.89, 28.83, 19.38. HRMS (EI) m/z: [M]⁺ Calcd for C₁₃H₁₇NS, 219.1082; found, 219.1079.

(Z)-3-oxo-4-((1,3,3-trimethyl-5-(methylthio)-3H-indol-1-ium-2-yl)methylene)-2-((E)-(1,3,3-trimethyl-5-(methylthio)indolin-2-ylidene)methyl)cyclobut-1-enolate (5)

Indoline **4** (0.35 g, 1.60 mmol), 3,4-Dihydroxy-3-cyclobutene-1 2-dione (0.091 g, 0.80 mmol) were dissolved in toluene/butanol mixture (3:1) and refluxed under nitrogen atmosphere overnight. The reaction was cooled down to 0 $^{\circ}$ C and the green metallic precipitates were filtered and washed with cold dichloromethane, methanol and hexane in this order to get **5** (0.30 g, 73%) as a green metallic solid. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 1.4 Hz, 2H), 7.27 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 1.91 (s, 2H), 3.56 (m, 6H), 2.54 (s, 6H), 1.79 (bs, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 182.80, 178.29, 170.28, 142.73, 141.19, 133.61, 127.21, 121.93, 109.69, 86.77, 49.20, 30.88, 26.99, 17.28. HRMS (MALDI) *m/z*: [M]⁺ Calcd for C₃₀H₃₂N₂O₂S₂; 516.1905; found, 516.1917. Anal. Calcd for C₃₀H₃₂N₂S₂O₂: C 69.73, H 6.24, N 5.42; found C 69.86, H 6.34, N 5.41.

S5.4 Electrochemistry and absorption measurements



Figure S14: Cyclic voltammetry measurements showing the oxidation and reduction potentials of the squaraine **5**. Potentials are referenced to decamethyferrocenium/ decamethylferrocene ($FeCp_2^{*+/0}$; $FeCp_2^{*+/0}$ was determined to be -0.55 V vs. $FeCp_2^{+/0}$ in dichloromethane). Cyclic voltamograms were recorded at a scan rate of 50 mV s⁻¹.

Table S3: Half-wave oxidation and reduction potentials converted to the $(FeCp_2^{+/0})$ scale as described above.



Figure S15: The absorption spectra of squaraine **5** in dichloromethane; absorption maximum is at 657 nm.

S5.5 NMR Spectra



Figure S16: ¹H NMR for compound 3



Figure S17: ¹³C{¹H} NMR for compound **3**



Figure S18: ¹H NMR for compound 4



Figure S19: ¹³C{¹H} NMR for compound 4



Figure S20: ¹H NMR for compound 5



Figure S21: ¹³C{1H} NMR for compound 5

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