On the association of neutral and cationic tris(tetrathiafulvaleno)dodecadehydro[18]annulenes

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ELECTRONIC SUPPLEMENTARY INFORMATION

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Synthesis and Characterization

General Methods. Chemicals were purchased from Aldrich and Merck and used as received. Dry solvents were obtained from a Solvent Purification System, Innovative Technology, Inc. All reactions were performed under an inert atmosphere of argon (and with solvents flushed by argon) if not otherwise stated. Hay catalyst refers to a freshly prepared solution of CuCl (100 mg, 1.0 mmol) and N,N,N',N'-tetramethylethylenediamine (TMEDA; 0.15 mL, 1.0 mmol) in CH₂Cl₂ (25 mL). LDA was prepared by adding BuLi (2.65 mL, 6.63 mmol, 2.5 M in hexanes) dropwise to a solution of i-Pr₂NH (0.6 mL, 4.25 mmol) in dry THF (4 mL) at -78 °C. The mixture was stirred for 15 min before use. Thin-layer chromatography (TLC) was carried out using aluminum sheets pre-coated with silica gel 60F (Merck 5554). The plates were inspected under UV light. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded on a Bruker instrument using the residual solvent as the internal standard. All chemical shifts are quoted on the δ scale (ppm), and all coupling constants (J) are expressed in Hz. Electrospray Ionization (ESI) mass spectra were recorded on a Bruker Micro-TOF Q II spectrometer and Matrix Assisted Laser Desorption Ionization (MALDI) mass spectra were recorded on a Bruker Daltonix Autoflex time-of-flight apparatus; HR-MS = High resolution mass spectrometry.

4,5-Bis(methylthio)-4’,5’-bis(triisopropylsilyl ethynyl)tetrathiafulvalene (4)

A solution of 2 (335.6 mg, 0.61 mmol) in i-Pr₂NH (30 mL) was degassed with argon in an ultrasound bath for 30 min, whereupon Pd(PPh₃)₄ (70.7 mg, 0.061 mmol), CuI (23.3 mg, 0.12 mmol) and triisopropylsilylacetylene (893.0 mg, 4.90 mmol, 1.10 mL) were added. The reaction mixture was stirred at rt for 5 h and was then filtered through a plug (SiO₂, heptane/CH₂Cl₂ 1:1) and then concentrated in vacuo. Column chromatography (SiO₂, heptane/CH₂Cl₂ 7:3) gave the product 4 as a red oil (128.0 mg, 32%). ¹H NMR (500 MHz, CDCl₃): δ = 2.42 (s, 6 H), 1.08 (s, 42 H). ¹³C NMR (125 MHz, CDCl₃): δ = 127.6, 121.0, 111.0, 110.9, 103.3, 96.4, 19.4, 18.8, 11.3.
4,5-Bis(ethylthio)-4',5'-bis(triisopropylsilyl)ethynyl)tetrathiafulvalene (5)

A solution of 3 (932.0 mg, 1.6 mmol) in \( \text{i-Pr}_2\text{NH} \) (50 mL) was degassed with argon in an ultrasound bath for 30 min, whereupon \([\text{Pd}(\text{PPh}_3)_4]\) (285.0 mg, 0.247 mmol), CuI (64.5 mg, 0.34 mmol) and triisopropylsilylacetylene (4.42 g, 24.3 mmol, 5.4 mL) were added. The reaction mixture was stirred at rt overnight. Heptane (10 mL) was added, and the mixture was filtered through a short plug (SiO\(_2\), heptane/CH\(_2\)Cl\(_2\) 1:1) and concentrated in vacuo. Column chromatography (SiO\(_2\), heptane/EtOAc 95:5) gave the product 5 as a red oil (703.3 mg, 64\%).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 2.85 \) (q, \( J = 7.4 \) Hz, 4 H), 1.31 (t, \( J = 7.4 \) Hz, 6 H), 1.08 (s, 42 H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta = 128.0, 121.1, 111.4, 110.2, 103.2, 96.4, 30.7, 18.8, 15.2, 11.3 \). MS (MALDI-TOF): \( m/z \) 684.1 [M\(^+\)].

HRMS (ESI): \( m/z \) 684.1910 [M\(^+\)] (calcd. for C\(_{32}\)H\(_{52}\)S\(_6\)Si\(_2\): 684.1926).

4,5-Bis(ethylthio)-4',5'-bis(trimethylsilyl)ethynyl)tetrathiafulvalene (6)

Argon-degassed \( \text{i-Pr}_2\text{NH} \) (25 mL) and trimethylsilylacetylene (1.85 mL, 13.0 mmol) were added to a mixture of 3 (500 mg, 0.868 mmol), CuI (33 mg, 0.17 mmol), and \([\text{Pd}(\text{PPh}_3)_4]\) (100 mg, 0.0865 mmol). The mixture was stirred for 4 h, filtered through a plug (SiO\(_2\), heptane/CH\(_2\)Cl\(_2\) 1:1) and concentrated under reduced pressure. Flash column chromatography (SiO\(_2\), CH\(_2\)Cl\(_2\)/heptane 1:9) gave 6 as a red oil (340 mg, 76%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 2.84 \) (q, \( J = 7.4 \) Hz, 4H), 1.31 (t, \( J = 7.4 \) Hz, 6H), 0.23 (s, 18H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta = 127.99, 121.83, 111.73, 109.87, 106.06, 94.69, 30.75, 15.21, -0.17 \). Anal. Calcd (C\(_{20}\)H\(_{28}\)S\(_6\)Si\(_2\)): C, 46.47; H, 5.46. Found: C, 46.47; H, 5.00. HRMS (ESI) \( m/z \): 516.0040 (calcd. for C\(_{20}\)H\(_{28}\)S\(_6\)Si\(_2^+\): 516.0048).
Hexakis(methylthio)-1,2,7,8,13,14-tris(tetrathiafulvaleno)-3,4,5,6,9,10,11,12,15,16,17,18-dodecadihydro[18]annulene (1f)

Bu₄NF (0.22 mL, 1 M in THF, 0.22 mmol) was added to a solution of 4 (143.9 mg, 0.22 mmol) in wet THF (10 mL) cooled to 0 °C under argon. The mixture was stirred at 0 °C for 5 min, whereupon full desilylation was observed according to TLC (SiO₂, heptane/CH₂Cl₂ 1:1). The mixture was passed through a plug (SiO₂, heptane/CH₂Cl₂ 1:1) and concentrated in vacuo to almost dryness. The crude product (7) was redissolved in CH₂Cl₂ (20 mL) and cooled to 0 °C. Hay catalyst (5 mL) was added, and the reaction mixture was stirred at 0 °C under air for 2 h, by which the mixture changed color from red to deep purple. MeOH (20 mL) was then added, and the solution was filtered through a sintered glass funnel, washed with MeOH (20 mL) and heptane (20 mL) on the filter and dried under vacuum. Due to insolubility, 1f could not be purified, nor fully characterized. MS (MALDI-TOF): m/z 1025.5 [M⁺].
Hexakis(ethylthio)-1,2,7,8,13,14-tris(tetrathiafulvaleno)-3,4,5,6,9,10,11,12,15,16,17,18-dodecadehydro[18]annulene (1g)

Bu$_4$NF (0.45 mL, 1 M in THF, 0.45 mmol) was added to a solution of 5 (317.4 mg, 0.46 mmol) in wet THF (10 mL) cooled to 0 °C under argon. The mixture was stirred at 0 °C for 10 min, whereupon full desilylation was observed according to TLC (SiO$_2$, heptane/CH$_2$Cl$_2$ 1:1). The mixture was passed through a short plug (SiO$_2$, heptane/CH$_2$Cl$_2$ 1:1) and concentrated in vacuo to almost dryness. The crude product was redissolved in CH$_2$Cl$_2$ (40 mL) and cooled to 0 °C. Hay catalyst (10 mL) was added, and the reaction mixture was stirred at 0 °C under air for 2 h, by which it changed color from red to deep purple. The mixture was washed with H$_2$O (2 x 100 mL), dried with MgSO$_4$, filtered and concentrated in vacuo. The crude product was passed through a short column (SiO$_2$, pentane/CH$_2$Cl$_2$ 1:1) to give a mixture of 1g and a product, which is tentatively assigned to the cyclic tetramer (see below). The products could be separated using size exclusion chromatography (Biobeads S-X3, CH$_2$Cl$_2$), affording dehydro[18]annulene 1g (25.0 mg, 15%) as a purple solid with a grey metallic sheen. Crystals for X-ray crystallography were grown by CH$_2$Cl$_2$ / MeOH vapour diffusion. $^1$H NMR (500 MHz, CDCl$_3$): δ = 2.89 (q, $J = 7.4$ Hz, 12 H), 1.35 (t, $J = 7.4$ Hz, 18 H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 128.1, 124.9, 115.1, 107.8, 85.0, 79.2, 30.8, 15.3. MS (MALDI-TOF): $m/z$ 1111.2 [M+H$^+$]. HRMS (ESI): $m/z$ 1109.7319 [M$^+$] (calcd. for C$_{42}$H$_{30}$S$_{18}$: 1109.7315).
Hexakis(ethylthio)-1,2,7,8,13,14-tris(tetrathiafulvaleno)-3,4,5,6,9,10,11,12,15,16,17,18-dodecadehydro[18]annulene (1g)

K$_2$CO$_3$ (50 mg, 0.36 mmol) was added to a solution of 6 (300 mg, 0.580 mmol) in THF (10 mL) and MeOH (10 mL). The mixture was stirred for 10 min, filtered through a short plug (SiO$_2$, heptane/CH$_2$Cl$_2$ 1:1) and concentrated to approximately 5 mL under vacuum. The residue was dissolved in CH$_2$Cl$_2$ (60 mL); then molecular sieves (3 g) and Hay catalyst (10 mL) were added at 0 °C. The mixture was stirred vigorously for 2 h in an open Erlenmeyer flask at 0 °C and then washed with water (2 x 100 mL), dried over Na$_2$SO$_4$ and concentrated in vacuo. Flash column chromatography (SiO$_2$, CH$_2$Cl$_2$/heptane 1:1) followed by size exclusion chromatography (Biobeads S-X3, CH$_2$Cl$_2$) gave 1g as a purple solid (61 mg, 28%).

By-product: dark grey solid; not stable in air at room temperature. Tentatively assigned to a cyclic tetramer. HR-MS (MALDI-TOF): $m/z$ 1479.6412 [M$^+$] (calcd. for C$_{56}$H$_{40}$S$_{24}$$^+$: 1479.6421).
By-product: cyclic tetramer.

Figure S1. $^1$H-NMR spectrum (CDCl$_3$) of product mixture of 1g and the assumed cyclic tetramer before size exclusion chromatography. Expanded region shows SCH$_2$ signals.
Figure S2. MALDI-TOF MS spectrum of product mixture of 1g and the assumed cyclic tetramer before size exclusion chromatography.
UV-Vis Absorption Spectroscopy

Figure S3. UV-Vis absorption spectra of 1g in different solvents

Figure S4. Solutions of 1g in THF (left) and in 1:1 THF/H₂O (right).
Figure S5. UV-Vis dilution studies of 1g in CH₂Cl₂

Figure S6. Lambert Beer plots from dilution experiments of 1g in CH₂Cl₂.
Figure S7. UV-Vis dilution studies of 1g in toluene.

Figure S8. Lambert Beer plots from dilution experiments of 1g in toluene.
Figure S9. UV-Vis dilution studies of 1g in 1:1 THF/H₂O.
NMR Spectroscopic Studies – Dilution Experiments

**Figure S10.** $^1$H-NMR dilution studies of 1g in CDCl$_3$ in the concentration range from $1.8 \cdot 10^{-3}$ M to $9.6 \cdot 10^{-5}$ M. Signals have been normalized.

**Figure S11.** $^1$H-NMR dilution studies of 1g in benzene-$d_6$ in the concentration range from $1.8 \cdot 10^{-3}$ M to $9.6 \cdot 10^{-5}$ M. Signals have been normalized.
UV-Vis-NIR Spectroscopy – Chemical Oxidation

Figure S12. UV-Vis-NIR absorption spectra of 1g upon chemical oxidation using “magic blue” ([N(C₆H₄-4-Br)₃][SbCl₆]). Samples were prepared and run straight away to avoid decomposition (see below).

Figure S13. Left: UV-Vis-NIR spectra showing the oxidized cationic species of 1g (black trace) and after a day in air (red trace). The spectrum of ‘magic blue’ is also included (blue trace). Right: Spectrum of a freshly prepared solution of 1g plus 0.5 equivalents of ‘magic blue’ (black trace) and the same sample ran again ca. 5 min later (red trace), showing signs of decay.
**Electrochemistry**

**General procedure.** Cyclic voltammetry and potential step chronocoulometry were carried out at room temperature (~24 °C) in solvents containing Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte using an Autolab PGSTAT12 potentiostat. The solvents were CH$_2$Cl$_2$, MeCN or a 7/1-mixture of CH$_2$Cl$_2$ and MeCN. Substrate concentrations are given in the figures or the figure captions. The working electrode was circular glassy carbon disk ($d = 3$ mm), the counter electrode was a platinum wire and the reference electrodes were silver wires immersed in the solvent-supporting electrolyte mixtures and physically separated from the solutions containing the substrate by a ceramic frit. When needed, the potentials of the reference electrodes were determined vs the ferrocene/ferrocenium (Fc/Fc$^+$) redox system in separate experiments. The voltage sweep rate was 0.1 Vs$^{-1}$. Solutions were purged with nitrogen saturated with solvent for ten minutes before the measurements were made. $iR$-Compensation was used in all experiments. When data recorded at substrate concentrations in the submillimolar range were needed, the data processing included subtraction of the background currents, obtained in separate experiments, from the raw data.

**Cyclic voltammetry of TTF – solvent dependence**

The cyclic voltammograms recorded for TTF in CH$_2$Cl$_2$ and MeCN, respectively, are shown below.

![Cyclic voltammogram for TTF (0.93 mM) in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$). Potentials are in V vs the Ag-reference electrode.](image)

**Figure S14.** Cyclic voltammogram for TTF (0.93 mM) in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$). Potentials are in V vs the Ag-reference electrode.
The characteristic sharp peaks observed for the 2nd one-electron transfer in CH$_2$Cl$_2$ results from an adsorption/desorption phenomenon caused by the poor solvation of TTF$^{2+}$ in the non-polar solvent. As seen, the 1st one-electron transfer (blue curve) is not affected. In contrast, two ‘normal’ one-electron transfer processes are observed in the more polar MeCN.

**Potential step chronocoulometry of TTF**

Potential step chronocoulometry is convenient for studying the relative number of electrons exchanged for a substrate that undergoes consecutive electron transfer processes, one advantage being that measurements may be carried out with the same setup of electrodes (and the same solution) as used for CV. The procedure is first illustrated by the oxidation of TTF in MeCN for which, as well-known and also illustrated above the electrochemical oxidation includes two reversible one-electron processes.

In short, in a series of experiments the potential is stepped from a value at which no current flows (in this case 0.0 V) to step-wise increasing values in the region encompassing the two one-electron transfer processes (in this case from +0.3 V to +1.1 V in 25 mV steps). During each potential step the charge ($Q$) exchanged between the working electrode and the substrate is recorded as a function of time ($t$). Typical $Q$-$t$ curves obtained for TTF are shown below.
**Figure S16.** $Q$-$t$ curves resulting from potential step chronoamperometry for TTF (1.02 mM) in MeCN (0.1 M Bu$_4$NPF$_6$); same solution as above. For clarity, only the curves obtained for 0.1 V increments of the potential are shown. Red +0.3 V; blue +0.4 V; green +0.5 V; cyan +0.6 V; black +0.7 V; magenta +0.8 V; light blue +0.9 V; light red +1.0 V; light green +1.1 V, in all cases in V vs the Ag-reference electrode.

It is seen that the curves fall into two groups, the first including the red, blue, green and cyan curves corresponding to the region of the 1st one-electron transfer process and the second including the black, magenta, light blue, light red and light green curves corresponding to the 2nd one-electron transfer process. By arbitrarily using the charge exchanged after 10 sec ($Q_{10}$) to monitor the oxidation process, a plot of $Q_{10}$ as a function of the potential provides information about the relative number of electrons exchanged in the two electron transfer processes.

**Figure S17.** Charge ($Q_{10}$)-potential curve for the oxidation of TTF (1.02 mM) in MeCN (0.1 M Bu$_4$NPF$_6$). Potentials are in V vs the Ag-reference electrode. The colored lines are explained in the text.
The value of $Q_{10}$ corresponding to the first electron transfer may now be obtained as the height of the plateau (red line) observed in the region around 0.6 V, that is in the potential region between the two electron transfers where the $\Delta Q_{10}$ curve has a minimum (here close 0). The value of $Q_{10}$ obtained in this way is $\sim 137 \ \mu$C. Similarly the value of $Q_{10}$ corresponding to the 1\textsuperscript{st} \textit{and} the 2\textsuperscript{nd} one-electron transfers (black line) is $\sim 261 \ \mu$C and, accordingly, the value of $Q_{10}$ corresponding to the 2\textsuperscript{nd} electron transfer only is $261-137 \ \mu$C = $134 \ \mu$C. It is seen that ratio between the $Q_{10}$ values for the 1\textsuperscript{st} and 2\textsuperscript{nd} electron transfer, 137/134, is close to 1/1 as expected for a compound that like TTF undergoes two consecutive one-electron transfer processes.

A similar approach was taken for the oxidation of 1g (0.45 mM) carried out in CH$_2$Cl$_2$/MeCN (7/1) where the adsorption phenomena are absent. Considering that 1g contains three TTF groups it seems fair to assume that that full oxidation of this compound would correspond to the formation of the hexacation, 1g$^{6+}$ in an overall six-electron process. The cyclic voltammogram in the solvent mixture has already been reproduced as Fig 3C in the paper, but is repeated here to facilitate the comparison with the chronocoulometry curves to follow.

![Cyclic voltammogram for 1g (0.45 mM) in CH$_2$Cl$_2$/MeCN = 7/1 (0.1 M Bu$_4$NPF$_6$). Potentials are in V \textit{vs} the Ag-reference electrode.](image)

**Figure S18.** Cyclic voltammogram for 1g (0.45 mM) in CH$_2$Cl$_2$/MeCN = 7/1 (0.1 M Bu$_4$NPF$_6$). Potentials are in V \textit{vs} the Ag-reference electrode.

As shown below, the curves obtained in the potential region corresponding to the first electron transfers are not as well separated as those obtained for TTF, obviously because of the close proximity of the first $E^{o+}$ values.
Figure S19. Charge-time curves resulting from potential step chronocoulometry for 1g (0.45 mM) in CH$_2$Cl$_2$/MeCN = 7/1 (0.1 M Bu$_4$NPF$_6$); same solution as above. For clarity, only the curves obtained for 0.1 V increments of the potential are shown. Red +0.3 V; blue +0.4 V; green +0.5 V; cyan +0.6 V; black +0.7 V; magenta +0.8 V; light blue +0.9 V; light red +1.0 V; light green +1.1 V; light cyan +1.2 V; light magenta +1.3 V, in all cases in V vs the Ag-reference electrode.

Figure S20. Charge ($Q_{10}$)-potential curve for the oxidation of 1g (0.45 mM) in CH$_2$Cl$_2$/MeCN = 7/1 (0.1 M Bu$_4$NPF$_6$). Potentials are in V vs the Ag-reference electrode. The colored lines are explained in the text.
The values of $Q_{10}$ where the $\Delta Q_{10}$ vs $E$ curve has its minima are in this case ~20 (red line), ~56 (black line) and ~109 µC (green line) leading to the following relative amounts of charge: 
$$\frac{20}{(56-20)/(109-56)} = \frac{20}{36/53} \approx \frac{1}{2/3},$$
which for a an overall six-electron process corresponds to the successive formation of the radical cation, $1g^+$ (peak 1), the radical trication, $1g^{3+}$ (peak 2) and the hexacation, $1g^{6+}$ (peak 3).
UV-Vis-NIR Spectroelectrochemistry


Speciation: Four readily identifiable species can be seen in an electrolysis experiment on a 0.2 mM solution of tris(tetrathiafulvaleno)dodecadehydro[18]annulene 1g using 0.1 M TBAPF in CH$_2$Cl$_2$. The conversion between the species can be followed by absorption spectroscopy, where clear isosbestic points can be found by cursory inspection of the spectra at different points of conversation. As a consequence it can be concluded that at these potentials only two species are present and that these interconvert. By comparing the resulting spectra following chemical oxidation with one equivalent of oxidation agent with that obtained by electrochemical oxidation it can be concluded that the speciation is the following upon electrolysis of 1g:

\[
1g = 1g^{+} + e^{-}
\]
\[
1g^{+} = 1g^{3+} + 2e^{-}
\]
\[
1g^{3+} = 1g^{6+} + 3e^{-}
\]

**Figure S21.** Absorption spectra of four redox states of 1g (0.2 mM) in CH$_2$Cl$_2$ + 0.1 M Bu$_4$NPF$_6$.

For the radical cation a new red-shifted low-intensity NIR absorption can be observed, assigned to an IVCT transition. It is only present in the radical cation $1g^+$ and disappears upon further oxidation to the trication $1g^{3+}$. The FWHM of low-energy band is 1600 cm$^{-1}$.

At higher concentrations, new bands appear in the spectra, indicating the occurrence of association phenomena in the monocation as well as the trication. Inspection of the electrochemical cell upon electrolysis, revealed a large quantity of black amorphous solids. Under the experimental conditions used we did not succeed in generating the dynamic equilibrium needed to study these association processes in greater detail.
Figure S22. Absorption spectra of 1g (0.2 mM) in CH\(_2\)Cl\(_2\) + 0.1 M Bu\(_4\)NPF\(_6\) during the course of an electrolysis experiment. The data are separated into three panels showing the progression from one redox state to the next.
Figure S23. NIR absorption spectra of 1g (1.8 mM) in CH₂Cl₂ + 0.1 M Bu₄NPF₆ during the course of an electrolysis experiment. The data are separated into two panels showing the progression from 1g to 1g⁺ (top) and 1g⁺ to 1g³⁺ (bottom). The arrows indicate the spectral changes. The red line indicates the maximum point of absorption of the initially formed species, while the blue line indicates the maximum of absorption for the second species formed.
Figure S24. NIR absorption spectra of 1g (1.8 mM) in CH₂Cl₂ + 0.1 M Bu₄NPF₆ during the course of an electrolysis experiment (potentials are uncalibrated). The spectra has been normalised at the maximum of the CT band. The peak moves from 2370 nm to 2050 nm upon further oxidation.
Figure S25. NIR absorption spectra of 1g (1.8 mM) in CH₂Cl₂ + 0.1 M Bu₄NPF₆ during the course of an electrolysis experiment. The data is separated into two panels showing the early part of the progression from 1g to 1g⁺ (top) and the first spectra normalised (bottom). The bold lines represent identical spectra in the two panels.
Figure S26. 3-Dimensional representation of the absorption spectra of 1g (1.8 mM) in CH$_2$Cl$_2$ + 0.1 M Bu$_4$NPF$_6$ during the course of an electrolysis experiment.
Figure S27. NIR absorption spectra of 1g (0.2 mM) in CH₂Cl₂ + 0.1 M Bu₄NPF₆ during the course of an electrolysis experiment. The data are separated into two panels showing the progression from 1g to 1g⁺ (top) and 1g⁺ to 1g³⁺ (bottom). The arrows indicate the spectral changes. The red line indicates the maximum point of absorption of the initially formed species, while the blue line indicate the maximum of absorption for the second species formed.
Figure S28. NIR absorption spectra of 1g (0.2 mM) in CH$_2$Cl$_2$ + 0.1 M Bu$_4$NPF$_6$ during the course of an electrolysis experiment. The data is separated into two panels showing the early part of the progression from 1g to 1g$^+$ (top) and the first spectra normalised (bottom). The bold lines represent identical spectra in the two panels.
Figure S29. NIR absorption spectra of $1g$ in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M Bu}_4\text{NPF}_6$ during the course of an electrolysis experiment for the first steps in the experiment at high (1.8 mM) and low (0.2 mM) concentration.

Table 1. Peak values observed in the NIR absorption spectra of $1g$ in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M Bu}_4\text{NPF}_6$ during the course of an electrolysis experiment, the progress of the oxidation from $1g$ to $1g^{3+}$ over $1g^+$ is indicated by the peak absorption. Note that no CT transition is observed from $1g^{3+}$.

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<th>Peak absorbance (nm)</th>
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Figure S30. Comparison between the spectral shape of NIR absorption spectra of 1g in CH₂Cl₂ + 0.1 M Bu₄NPF₆ during the course of an electrolysis experiment (from low potential, top, to high potential, bottom; potentials are uncalibrated) as a function of concentration (0.2 or 1.8 mM).
ESR/UV-Vis-NIR Spectroelectrochemistry

The spectroelectrochemical *in situ* ESR/UV-vis-NIR cyclovoltammetric experiments were carried out under an argon atmosphere in a special flat spectroelectrochemical cell (0.1 mm path length), suitable for an optical transmission ESR resonator (ER 4104 OR-C 9609) of an EMX EPR spectrometer (Bruker, Germany). As a supporting electrolyte 0.5 M TBAPF₆ was used. The working electrode was a laminated Pt mesh with a small hole in the foil coincident with the light beam, which limited the active surface area of the electrode. A Pt wire auxiliary (counter) electrode and an Ag wire pseudoreference electrode were used. The optical EPR resonator cavity was connected to the diode-array UV-vis-NIR spectrometer Avantes Avaspec (Avantes, Netherlands) by optical fibers. A deuterium-halogen lamp DH 2000 (Sentronic, Germany) was used as a light source. UV-vis-NIR spectra were processed by the proprietary AvaSoft 7.7 software package. Both EPR and UV-vis-NIR spectrometers were synchronized together by trigger pulses received from the potentiostat, to simplify the assignment of the potentials to the observed spectra.
Figure S3. *In situ* cyclic voltammogram of 0.04 mM 1g in CH$_2$Cl$_2$ + 0.2 M Bu$_4$NPF$_6$ (Pt-mesh working electrode, scan rate 1.85 mV s$^{-1}$) with color highlighted selected potential regions and (b) the corresponding 3D-view of the potential dependence of UV–vis-NIR spectra measured during the cyclic voltammetric scan.
Figure S3. 3D-view of the potential dependence of UV–vis-NIR spectra measured during the cyclic voltammetric scan of (a) 0.04 mM 1g and (b) 0.4 mM 1g in CH₂Cl₂ + 0.2 M Bu₄NPF₆ (Pt-mesh working electrode, scan rate 1.85 mV s⁻¹) with color highlighted selected spectra at the maximal monocation 1g⁺⁺ intensity in the forward voltammetric scan. (c) Comparison of the optical spectra of monocation 1g⁺⁺ at its maximal intensity in the forward scan for 0.04 mM 1g (blue line) and 0.4 mM 1g (red line), normalized to the absorbance intensity at 865 nm.
NMR Spectra

Compound 4

\[ \text{MeS} \cdots \text{S} \cdots \text{S} \cdots \text{Si}(\text{-Pr})_3 \]

\[ \text{MeS} \cdots \text{S} \cdots \text{S} \cdots \text{Si}(\text{-Pr})_3 \]
MeS$_2$S$_2$Si(\(\cdot\)Pr)$_3$
EtS

Si(Pr)3

EtS

Si(Pr)3
Compound 6
Compound 1g