Chapter 2

Three-State Switching of an Anthracene Extended Bis-thiaxanthylidene with a Highly Stable Diradical State

A multistable molecular switching system based on an anthracene-extended bis-thiaxanthylidene with three individually addressable states that can be interconverted by electrochemical, thermal, and photochemical reactions is reported. Besides reversible switching between an open-shell diradical- and a closed-shell electronic configuration, our findings include a third dicationic state and control by multiple actuators. This dicationic state with an orthogonal conformation can be switched electrochemically with the neutral open-shell triplet state with orthogonal conformation, which was characterized by EPR. The remarkably stable diradical shows kinetic stability as a result of a significant activation barrier for isomerization to a more stable neutral closed-shell folded geometry. We ascribe this activation barrier of $\Delta G^\circ(293 \text{ K}) = 25.7 \text{ kcal mol}^{-1}$ to steric hindrance in the fjord region of the overcrowded alkene structure. The folded closed-shell state can be converted back to the diradical state by irradiation with 385 nm. The folded state can also be oxidized to the dicationic state. These types of molecules with multiple switchable states and in particular stable diradicals show great potential in the design of new functional materials such as memory devices, logic gates, and OFETs.

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2.1 Introduction

Artificial molecular switches and motors play a prominent role in the transition from molecules with static function to dynamic molecular systems in contemporary chemistry.\textsuperscript{1,2,3} Taking inspiration from biology, e.g. the process of vision, it is evident that molecular switching offers numerous opportunities for the reversible control of material properties\textsuperscript{4}, molecular information content\textsuperscript{5} or biological function\textsuperscript{6}. Switching between redox- and geometric states can be induced by external stimuli including electricity, light and heat.\textsuperscript{7,8} A molecular switch can typically form either of two stable isomers, so called bistability, to control, e.g., magnetic, electronic and optical properties, supramolecular assembly and molecular recognition or complex functions such as catalysis.\textsuperscript{9,10,11,12,13,14,15}

Moving beyond bistability, the design of multiple switchable molecular systems that can reach various stable states triggered by distinct and orthogonal external inputs e.g. photochemical, thermal, electrochemical, remains particularly challenging. Herein, we report reversible switching between \textit{three states in a single molecule}, including a highly stable diradical state, controlled through multiple actuators (electricity, light, and heat). Stable organic diradicals feature unique electronic properties and therefore show great potential for applications in molecular electronics such as OFETs.\textsuperscript{16} Reversible switching between open-shell diradical (or diradicaloid)- and closed-shell electronic configurations of organic molecules is fascinating both experimentally and theoretically.\textsuperscript{17,18,19,20} The system we describe here adds a third state that is interconvertible with the open-shell diradical state via redox chemistry. We anticipate that such a system with three independently addressable states will open doors towards smart, tuneable electronics such as memory devices and logic gates.\textsuperscript{21}

The systems presented here are based on bistricyclic aromatic enes (BAEs)\textsuperscript{22}, a class of molecules that includes the overcrowded alkene light-driven molecular motors, which are robust examples of multistage switchable molecular systems.\textsuperscript{23} In BAEs, the steric crowding in the fjord region plays a key role in the relative stability of various isomers.\textsuperscript{22} Two such geometries are described as folded (F) and twisted (T) (Fig. 1). Facing the challenge to design orthogonal switching systems to allow ultimately more complex dynamic and responsive behavior, bisthiaxanthylidenes, a specific class of BAEs, offer the opportunity to combine multiple effectuators and states.\textsuperscript{12} Bisthiaxanthylidenes undergo geometrical changes induced either by redox or photochemical reactions. A photochemical-redox luminescent switch based on bisthiaxanthylidenes was developed earlier by our group, in which oxidation leads to a stable dicationic state with a nearly orthogonal (O) orientation of the two tricyclic aromatic moieties (Fig. 1a).\textsuperscript{12}
Recently, photochemical and thermal interconversion of stable closed-shell- and open-shell diradical states of an organic compound (with a concomitant geometry change) has emerged as a new modality of molecular switching. Organic compounds with an open-shell diradical resonance contributor in the ground state date back to Tschitschibabin’s hydrocarbon, reported in 1907 (Fig. 1b). Noting the importance of stable open-shell systems, other organic compounds with diradicaloid ground states have since been described. Bistability between open- and closed-shell states can be achieved when the activation barriers are sufficiently high, while low barriers (with respect to $k_B T$) lead to thermal equilibration over the states. The open-shell diradical configurations are stabilized by a combination of factors including steric hindrance, delocalization of spin density, and aromaticity. In 2020, Kubo reported an organic compound capable of controlled switching between open-shell diradical- and closed shell state: this BAE, based on the 9,10-dihydro-10,10-dimethyl-9-anthryl (DMA) motif, undergoes conversion from a triplet open-shell diradical state to a neutral closed-shell thermally, which can then be converted back to the open-shell state photochemically (Fig. 1c).

The anthracene-extended bis-thiaxanthylidene 1 described here allows for three-state reversible switching (Fig. 1d). In our design the peripheral thioxanthene motif enables redox switching by stabilizing a dicationic state ($I^{2+}$) by virtue of the sulfur heteroatom, which enables full conjugation to an “anthracene-like” delocalized structure facilitated by mesomeric electron donation (an effect that is entirely lacking in the DMA motif). The thioxanthenes also stabilize an open-shell diradical configuration (1-O) in the neutral form by spin density delocalization.
central anthracene linker induces additional kinetic stabilization to the diradical. The stable open-shell orthogonal diradical converts thermally to a lower energy closed-shell folded geometry (1-F), and irradiation restores the compound to its orthogonal diradical state. In contrast, the analogous benzene-bridged bis-thiaxanthylidene 2 (Fig. 1d) displays a thermal equilibrium between an open-shell diradical state (2-O) and a lower energy closed-shell folded state (2-F), which demonstrates the effect of steric crowding in the fjord region.

2.2 Results and discussion

2.2.1 Synthetic procedures

The arene-extended bisthioxanthylium salts 1²⁺ and 2²⁺, were prepared with anthracene and benzene spacers, respectively (Scheme 1). Thioxanthene-9-one 3 was iodinated to obtain 4, which was then functionalized with ethoxy groups through an Ullmann coupling to increase the solubility of these compounds in organic solvents. Dilithiation of 9,10-dibromoanthracene and 1,6-dibromobenzene and subsequent reaction with 5 produced diols 7 and 9, respectively, which after dehydration with aqueous HBF₄ yielded the dicationic BF₄⁻ salts 1²⁺ and 2²⁺. Characterization of compound 1²⁺ by ¹H-NMR spectroscopy was precluded by the presence of traces of paramagnetic species, which is probably a mono-radical impurity that facilitates fast electron exchange on the NMR time scale and consequent line broadening. The presence of a mono-radical impurity is supported by an EPR signal that is typical for a doublet species (Fig. S8). The salts 1²⁺ and 2²⁺ were reduced chemically with cobaltocene to obtain the neutral compounds 1-O and 2-F. The ¹H-NMR spectrum of compound 1-O (Fig. S2) shows paramagnetic shifts and broadening, consistent with open-shell diradical character. This is not the case for compound 2-F which we therefore expect to be in the lowest energy folded closed-shell state (DFT calculations vide infra) and we denote it as 2-F. Re-oxidation of 1-O and 2-F to their respective dicationic salts 1²⁺ and 2²⁺ was achieved with NOBF₄ (Fig. S2 and S3).
Scheme 1. Synthesis of compounds $1^{2+}$, $2^{2+}$, 1-O, and 2-F.

### 2.2.2 X-Ray crystallography

Single crystal X-ray analysis of $1^{2+}$ and 2-F revealed the structures shown in Fig. 2. DFT optimized structures of 1-O and $2^{2+}$ are shown in Fig. 3. Both the anthracene bridged dication $1^{2+}$ (Fig. 2a) and the benzene bridged dication $2^{2+}$ (DFT optimized structure, Fig. 3b) adopt an almost orthogonal conformation of the aromatic spacers relative to the thioxanthylum units with dihedral angles of 80° and 75°, respectively. In both structures the two thioxanthylum motifs are coplanar. For $1^{2+}$, the C1-C2 and C2-C3 distances are...
1.494 (3) Å and 1.407 (3) Å, respectively, which shows that it does not have a quinoidal structure. DFT calculations predict a similar quasi orthogonal conformation for 1-O similar to the dications with a dihedral angle of 82° between the anthracene spacer relative to the thioxanthenes (Fig. 3a). In contrast, 2-F has a double folded boat-like structure (Fig. 2b). Within one thiaxanthylidene the fold angle between the two C6H3OEt rings is 133°. The bond length of ~1.38 Å between C5-C8 and C1-C2, and ~1.35 Å between C6-C7 and C3-C4 are consistent with double bond character. On the other hand, single bond character was noted between C2-C7, C2-C3, C4-C5, and C5-C6 (~1.45 Å). This reveals that 2-F has a quinoidal closed-shell structure in the solid state.

![Figure 2. ORTEP drawings of the a) 1^{2+} and b) 2-F structures. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.](image)

![Figure 3. DFT optimized structures of the a) 1-O and b) 2^{2+} structures. Hydrogen atoms are omitted for clarity.](image)

### 2.2.3 Electronic Absorption and Emission Spectroscopy

The redox couple 1^{2+} and 1-O both display UV/Vis absorption spectra (Fig. 4a and 4c, Table 1) with absorptions at long wavelength in the visible region between 500-650 nm. These are common bands for twisted geometries. Thus, it seems likely that the conformation does not change significantly between 1^{2+} and 1-O. The absorption bands for 1^{2+} and 1-O between 325-400 nm with vibronic splitting are typical for anthracene. In contrast, the spectra of 2^{2+} and 2-F (Fig. 4b and 4d, Table 1) are consistent with a
major change in geometry. 2-F shows a broad absorption band between 350-550 nm. The absorption bands at shorter wavelength are typical of an increase in S0-S1 gap expected for a folded structure. Its spectrum is similar to that observed for the folded anthracene-bridged bis-DMA confirming its folded structure in solution while 22+ shows characteristic absorptions of a twisted conformation. Compound 12+ exhibits red emission (λmax = 641 nm), whereas 1-O is not luminescent as expected due to its triplet diradical character (vide infra). Furthermore, emission spectroscopy shows that reduction of 22+ to 2-F results in a change in luminescence with λmax shifting from 682 nm (red) to 569 nm (yellow), respectively.

![Figure 4](image.png)

**Figure 4.** UV/Vis absorption- and normalized emission-spectra (dotted lines) of a) 12+ (6.25 x 10^-6 M), b) 22+ (6.25 x 10^-6 M), c) 1-O (2.5 x 10^-5 M), and d) 2-F (1.25 x 10^-5 M) in DCM. Excitation wavelengths: a) 560 nm, b) 520 nm, and d) 450 nm.

**Table 1.** λmax values for 12+, 22+, 1-O, and 2-F.

|        | UV/Vis       | Emission (Φb) |
|--------|--------------|---------------|
| (a) 12+| 260, 299, 359, 377, 398, 448, 569 | 641 (0.02)    |
| (b) 22+| 253 (S°), 303, 376, 443, 561     | 682 (4.0)     |
| (c) 1-O| 264, 284, 340 (S), 360, 376, 397, 444, 614 | -             |
| (d) 2-F| 255, 391, 468                     | 569           |

a S = shoulder. b Φ = quantum yield in %.
2.2.4 EPR spectroscopy

1-O shows a typical EPR spectrum for a triplet diradical in toluene at 77 K (Fig. 5). Simulation (EasySpin, see SI) yields a g-value of 2.0023 and zero field splitting parameters $D = 183$ MHz (65.3 G) and $E = 3$ MHz. $D$ was used to estimate a spin-spin distance of 7.53 Å by the point-dipole approximation. This distance is greater than the distance between the two carbons at the 9-position (5.87 Å) which indicates delocalization of the unpaired electrons. The forbidden $\Delta m_s = 2$ signal is observed at 1722 G (effective g-value of 4.006) the intensity of which increases with decreasing temperature. The $\Delta m_s = 2$ double integrated intensity ($I_{EPR}$) vs. $1/T$ (temperature range 70-8.6 K) plot was fitted with the Bleaney-Bowers equation (eq. 1) where $C$ is the Curie constant, $J$ the electron exchange interaction, and $2J$ equals $\Delta E_{S,T} (=+22 \times 10^{-3}$ kcal mol$^{-1}$) and $J = +3.9$ cm$^{-1}$ (ferromagnetic coupling).

\[
I_{EPR} = \frac{C}{T} \frac{3e^{-2J/kB T}}{1 + 3e^{-2J/kB T}} \tag{1}
\]

From both the paramagnetic $^1$H-NMR and EPR spectral data we conclude that 1-O has a triplet diradical ground state with a singlet diradical state slightly higher in energy. As expected, for compound 2-F a signal was not observed consistent with its preferred closed-shell, folded (F) quinoidal structure (vide supra).

Figure 5. Left: EPR signal of compound 1-O (4.4 x 10$^{-4}$ M) in toluene at 77 K with inset: forbidden $\Delta m_s = 2$ signal at 40 K. Right: Curie plot of 1-O with fit to the Bleaney-Bowers equation (Adj. R-Square = 0.9939).
## 2.2.5 Computational studies

DFT calculations on 1 and 2 were performed to further investigate the stabilities of the folded quinoidal geometries relative to the orthogonal diradical conformations. Computational investigation at the B3LYP/6-31** level of theory (for the selection of the computational method, see SI) of the various possible geometries showed that the most stable geometry is a folded (F) structure for the neutral compounds 1 and 2 and an orthogonal (O) conformation for the dicationic compounds 1^{2+} and 2^{2+} (Table S4, S5).

More specifically, the most stable geometry of 1-F is in a doubly anti-folded state that minimizes steric hindrance with the anthracenyl bridge. For 2-F the steric hindrance is significantly lower and it has a syn-folded orientation as its most stable form.

However, the isomerization barriers of the neutral compounds differ greatly. Reduction of 1^{2+} leads to the diradical state 1-O without significant conformational change. 1-O is a local minimum (ΔE = 0.7 kcal mol\(^{-1}\) relative to 1-F, Fig. 6) kinetically trapped with a high barrier (ΔE\(^{1}\) = 30.6 kcal mol\(^{-1}\)) for isomerisation at room temperature towards the global minimum 1-F. Conversely, as deduced from electrochemistry (vide infra), the reduction of 2^{2+} does initially lead to 2-O, which subsequently isomerizes to 2-F. The calculated barrier for the latter process (ΔE\(^{1}\) = 9.5 kcal mol\(^{-1}\)) supports the experimental observations. The low barrier and relative energy differences between 2-O and 2-F provides a rational for the shape of the cyclic voltammogram (Fig. 7e), where a relatively fast equilibrium means that both the orthogonal and folded structures are present in solution. This isomerisation pathway was probed with a potential energy surface scan (Fig. S22 and S23). The relative energies of the diradical singlets and the corresponding triplets for 1-O and 2-O are sufficiently close for population of both states (ΔE\(_{ST}\) = \(-14 \times 10^{-3}\) kcal mol\(^{-1}\) for 1-O and ΔE\(_{ST}\) = \(-0.145\) kcal mol\(^{-1}\) for 2-O). The low ΔE\(_{ST}\) for 1-O is in accordance with EPR data, although experimentally a triplet ground state was observed. However, the calculated energy difference is less than the expected error margin and hence it can only be concluded that the energy levels are highly similar. For all diradical species we found that the spin density is mainly located on the thioxanthene motifs with negligible contribution from the bridging motifs.
Figure 6. Schematic and graphic representation of the thermal isomerisation pathway for the neutral geometries 1-O to 1-F and 2-O to 2-F based on DFT calculations (B3LYP/6-31G**). Hydrogens omitted for clarity.

2.2.6 Electrochemistry

Compounds $1^{2+}$ and $2^{2+}$ were characterized electrochemically by cyclic voltammetry in dichloromethane (DCM) at rt and both show reversible electrochemical switching (Fig. 7a and 7b, Table 2). For $1^{2+}$ splitting of the redox waves was seen in DCM whereas in MeCN (Fig. S9) a single reversible wave was observed. This difference is due to the better solvation of the radical cation in MeCN after the first reduction relative to DCM.$^{41}$ In solvents with poor donor properties, such as DCM, the singly occupied molecular orbital (SOMO) can be delocalized over the entire molecule, stabilizing the radical cation.$^{42}$
Figure 7. Cyclic voltammograms of a) $1^{2+}$, b) $2^{2+}$, c) 1-O, d) $2^{-}$F (0.1 Vs$^{-1}$), e) $2^{-}$F at different scanrates, and f) $2^{-}$F at -50 °C (0.1 Vs$^{-1}$) recorded in DCM with 5 x 10$^{-4}$ M analyte and 0.1 M TBAPF$_6$. 
Therefore, in DCM, the second reduction of $1^{2+}$ is shifted to more negative potentials. The radical cation of $2^{2+}$ is less stabilized and only a single reversible wave is observed independent of solvent. Cyclic voltammograms of $1$-$O$ and $2$-$F$ do not show hysteresis (Fig. 7c and 7d, Table 2). This suggests that $1$-$O$ has a structure similar to $1^{2+}$. The open-shell diradical $1$-$O$ indeed has an almost orthogonal conformation. In contrast, it is proposed that the folded closed-shell $2$-$F$ is in equilibrium with the orthogonal open-shell diradical $2$-$O$. This explains why $2$-$F$ exhibits a quasi-reversible cyclic voltammogram where the rapid prior equilibrium between $2$-$F$ and $2$-$O$ precedes the oxidation of $2$-$O$ to $2^{2+}$. Hysteresis is not observed as $2$-$O$ and $2^{2+}$ have similar conformations. At lower scan rate there is more time (within the timeframe of the electrochemical experiment) for the equilibrium to shift towards $2$-$O$ and the voltammogram shows increasing electrochemical reversibility (Fig. 7e). Cyclic voltammetry at $-50 \, ^\circ\text{C}$ shows the direct oxidation of $2$-$F$ to $2^{2+}$ (Fig. 7f, Table 2). At this temperature the $2$-$O$ state is not populated and the large geometrical change from the folded $2$-$F$ to the orthogonal $2^{2+}$ is responsible for the hysteresis.

Table 2. Peak- and half-wave potentials for $1^{2+}$, $2^{2+}$, $1$-$O$, and $2$-$F$.

|     | $E_{p, \text{ox}}$ | $E_{p, \text{red}}$ | $E_{1/2}$ |
|-----|-------------------|-------------------|----------|
| (a) $1^{2+}$ | -0.47/-0.36 | -0.42/-0.54 | -0.39/-0.50 |
| (b) $2^{2+}$ | -0.29 | -0.33 | -0.31 |
| (c) $1$-$O$ | -0.46/-0.34 | -0.40/-0.52 | -0.49/-0.37 |
| (d) $2$-$F$ | -0.12 | -0.35 | -0.24 |
| (e) $2$-$F$ ($-50 \, ^\circ\text{C}$) | 0.14 | -0.41 | - |

2.2.7 Thermal equilibrium between $2$-$F$ and $2$-$O$

DFT calculations indicated that the orthogonal diradical $2$-$O$ is thermally accessible. Variable temperature NMR (VT-NMR) spectroscopy studies of $2$-$F$ (Fig. 8a) show that the resolved signals at $25 \, ^\circ\text{C}$ become increasingly broadened with heating to $80 \, ^\circ\text{C}$, consistent with the population of the excited triplet diradical state ($2$-$O$). Returning to $25 \, ^\circ\text{C}$ recovers the original spectrum as expected from the low activation barrier for the $2$-$O$ to $2$-$F$ conversion. These results are consistent with our electrochemical data and show that there is a thermal equilibrium between $2$-$F$ and $2$-$O$. 

Figure 8. VT-NMR (500 MHz) spectroscopy studies of compounds a) 2-F and b) 1-O in toluene-\(d_8\).
2.2.8 Switching between 1-O and 1-F

DFT calculations predict that 1-F is more stable than 1-O but it was not observed after the chemical reduction of 1\(^{2+}\). We speculated that the as-synthesized 1-O was kinetically trapped. VT-NMR studies on the paramagnetic compound 1-O (Fig. 8b) showed resolved signals, which are assigned to 1-F, that emerged as the temperature was increased to 100°C. Cooling to 25°C, shows that the signals persist, consistent with a high activation barrier for interconversion between 1-F and 1-O. Full conversion to 1-F was achieved by holding the solution at 100°C until its \(^1\)H-NMR spectrum at rt shows highly resolved signals. 1-O was converted in toluene at 90°C to isolate and characterize 1-F. Single crystals of 1-F were grown and confirmed a double anti-folded geometry (Fig. 9a). Within one thiaxanthylidene the fold angle between the two C\(_6\)H\(_3\)OEt rings is 129°. A quinoidal structure was confirmed by the double bond character of the C5-C8 and C1-C2 bonds (~1.35 Å) and the single bond character of the C4-C5, C5-C6, C2-C7, and C2-C3 bonds (~1.50 Å).

Its UV/Vis absorption spectrum supports the hypothesis that a geometrical change from orthogonal to folded occurred as the longest wavelength absorption is shifted to 450 nm (Fig. 9b). The emission spectrum of 1-F has a maximum at 474 nm. Thus, by reversible switching between the 1\(^{2+}\), 1-O, and 1-F states (\textit{vide infra}) the luminescence can be changed between red, nonluminescent, and blue, respectively. The activation barrier for the 1-O to 1-F transition was determined by UV/Vis absorption spectroscopy in toluene. The decay in absorbance was monoexponential and rates were used in an Eyring-Polanyi plot (Fig. 9c). Eyring-Polanyi analysis yielded the free energy of activation \(\Delta G^\ddagger (293 \text{ K}) = 25.7 \text{ kcal mol}^{-1} \pm 0.2 \text{ kcal mol}^{-1}\). The activation barrier from 1-O to 1-F rationalizes why the reduction of 1\(^2+\) leads to trapping in the 1-O state as can be seen from the cyclic voltammograms of the 1\(^{2+}\)/1-O couple. The barriers are related to the increased steric hindrance in the fjord region and this behaviour is not seen for the 2O/2F couple. This restricted movement in the fjord region is also reflected in the onset of the oxidation potential of 1-F at 0.5 V (relative to the onset of the oxidation potential of 1-O at -0.6 V) (Fig. 9d). The lack of chemical reversibility for the oxidation of 1-F is the result of the fast (within the timeframe of the electrochemical experiment) chemical step 1-F\(^{2+}\) → 1\(^2+\).

This chemical step leads to the observation of the following small reduction waves: 1-F\(^{2+}\) → 1-F\(^+\) followed by 1-F\(^+\) → 1-F at peak potentials 0.7 V (shoulder) and 0.6 V respectively. Oxidation of 1-F (or 1-O) leads to 1\(^2+\) which can subsequently be reduced at -0.39 V and -0.50 V to 1-O in the return sweep (from 1 to -1 V). This hysteresis in the cyclic voltammogram is caused by a geometrical change.\(^{18,45}\) Irradiation at 385 nm leads to photochemical switching from 1-F to 1-O (Fig. 9e). In toluene a band at 615 nm assigned to 1-O is observed. Heating at 90°C results in this absorption band disappearing over 1 h. Repeated cycles of irradiation and heating confirm the excellent reversibility of this process not showing fatigue. Additional evidence for the photochemical back
reaction of 1-F to 1-O was provided by EPR spectroscopy. Irradiation at 385 nm of the EPR silent 1-F leads to the emergence of signals associated with 1-O (Fig. 9f).

Figure 9. a) ORTEP drawing of the 1-F structure (hydrogen atoms are omitted for clarity), b) UV/Vis absorption- and normalized emission spectrum ($\lambda_{\text{exc}} = 350$ nm) of 1-F (2.5 x $10^{-5}$ M) in DCM including $\lambda_{\text{max}}$ values (quantum yield = 6.9%), c) Eyring-Polanyi plot of the thermal conversion of 1-O to 1-F in toluene monitored at 615 nm obtained by fitting to the linearized form of the Eyring equation (Adj. R-Square = 0.9985). Dashed lines indicate 95% confidence intervals, d) Cyclic voltammogram of 1-F, $E_{\text{p,ox}} = 0.66$ V (shoulder) and $E_{\text{p,ox2}} = 0.75$ V ($5 \times 10^{-4}$ M in DCM/0.1 M TBAPF$_6$/0.1 Vs$^{-1}$), e) Cycles of irradiating ($1 \times 10^{-3}$ M) with 385 nm for 10 min (white areas) and heating at 90°C for 1 h (grey areas) while monitoring the absorbance at 615 nm, and f) EPR spectra of 1-F ($5.3 \times 10^{-4}$ M) in toluene at 77 K: before irradiation (red) and after irradiation with 385 nm at rt for 10 min (black).
2.2.9 Discussion

2.2.9.1 UV/Vis absorption spectra 1-F and 2-F
The absorption at longer wavelengths of 2-F compared to 1-F stems from the fact that 2-F has an increased “planar” structure relative to 1-F. Even though the fold angle between the two C₆H₅OEt rings are highly similar for both compounds (129° for 1-F and 133° for 2-F), the dihedral angles between the C₃-C₄-C₆-C₇ plane and the C₅-C₈-C₁₅-C₉ plane in 1-F and 2-F are 144° and 177°, respectively (Fig. 10). This means that 2-F has increased orbital overlap resulting in a reduction in the HOMO-LUMO gap and therefore has longer wavelength absorption bands compared to 1-F.

![ORTEP drawings of a) 1-F and b) 2-F with dihedral angles between the C₃-C₄-C₆-C₇ and the C₅-C₈-C₁₅-C₉ planes.](image)

The longer wavelength absorption for 2-F (relative to 1-F) could be caused by a thermal equilibrium between folded and twisted compounds, but the only compounds we have observed experimentally to be in thermal equilibrium are the syn-folded 2-F (which was isolated) and 2-O. Significant population of the 2-O state only occurs at elevated temperature (Fig. 8a) so its presence at rt was excluded. A twisted conformation could account for the electrochemical observations, but our calculations show that a twisted conformation (2-T) would be too high in energy to be present to any extent and the VT-¹H-NMR results (Fig. 8a) cannot be explained by the presence of 2-T (see below). We therefore expect that only the syn-folded 2-F was present during the UV/Vis absorption measurements at rt.
2.2.9.2 The electronic configuration of 2-O

Broadening of the aromatic signals in VT-1H-NMR spectra at high temperature with comparable compounds has been ascribed earlier to the formation of diradicals.\textsuperscript{30,31} The fact that both sets of protons from the –OEt groups show a decrease in intensity with an increase in temperature disfavors the proposal of possible closed-shell twisted conformation formation, because in that case you would expect a similar or higher intensity with faster exchange at higher temperature. We therefore think that the shift of the methylene protons is caused by fast exchange (within the timeframe of the NMR experiment) between the folded closed-shell 2-F geometry and orthogonal open-shell 2-O geometry. Broadening of the –OEt sets of protons is observed to a lesser extent (relative to the aromatic protons) since the paramagnetic center of 2-O mostly affects the protons in the aromatic region.

EPR spectra at higher temperature were also recorded for 2-F in 1,2-dichlorobenzene (Fig. 11). At 340 K a signal emerged which increased in intensity at 400 K. Fast freezing of the sample to 200 K did not lead to observable fine coupling and the signal persisted when bringing it to 280 K. This suggests that the signal is due to the formation of a paramagnetic $s = 1/2$ impurity. Even though these EPR spectra do not provide evidence for the formation of 2-O at higher temperatures, the broadening of the aromatic signals in the VT-1H-NMR spectra at higher temperatures in combination with its reversibility still point to a thermal equilibrium between 2-F and 2-O. An equilibrium of 2-F with another conformation such as the twisted 2-T also seems unlikely from our calculations.

Figure 11. Variable temperature EPR spectra of 2-F in 1,2-dichlorobenzene.
2.3 Conclusion

Here we report two arene-extended bis-thiaxanthylidines in which the introduction of an anthracene spacer allowed for redox switching between an orthogonal dicationic- $(1^{2+})$ and a diradical state $(1\text{-}O)$ while thermal and photochemical switching allows modulation between $1\text{-}O$ and the folded state $1\text{-}F$. The barrier between the neutral orthogonal open-shell triplet- $(1\text{-}O)$ to the folded closed-shell $(1\text{-}F)$ form is high $(\Delta G^\ddagger(293\text{ K}) = 25.7\text{ kcal mol}^{-1})$ showing that $1\text{-}O$ is a remarkably stable diradical. The reverse reaction from the closed-shell to the open-shell form has a higher activation barrier $(\Delta G^\ddagger = 31.3\text{ kcal mol}^{-1}\text{ (from DFT)})$. The resultant three stable states of this system shows that the reduction of $1^{2+}$ leads to the kinetically trapped $1\text{-}O$ which can be switched thermally to the more stable folded geometry $1\text{-}F$. Irradiation of $1\text{-}F$ switches it back to the open-shell $1\text{-}O$, while oxidation produces $1^{2+}$. For the benzene analogue, redox switching between an orthogonal dicationic- $(2^{2+})$ and a diradical state $(2\text{-}O)$ was observed. A thermal equilibrium was found between the neutral more stable folded closed-shell $(2\text{-}F)$ and orthogonal open-shell $(2\text{-}O)$ forms with a low activation barrier from the transient $2\text{-}O$ to $2\text{-}F$. At low temperature $2\text{-}F$ can be directly oxidized to $2^{2+}$. We ascribe the difference in activation barrier between $2\text{-}O$ to $2\text{-}F$ relative to $1\text{-}O$ to $1\text{-}F$ to the increased steric bulk in the fjord region. Overall, this means a robust three-state switch has been developed where the dication $1^{2+}$, diradical $1\text{-}O$, and $1\text{-}F$ states can be individually addressed and interconverted by electricity, temperature control or irradiation. This opens opportunities for the exploration of stable multistate photo-and electro-chemical responsive materials and devices.

2.4 Acknowledgements

Brian P. Corbet is acknowledged for performing DFT calculations and for writing the paragraph (2.6) on the results of these calculations. We would like to thank the Center for Information Technology of the University of Groningen for their support and for providing access to the Peregrine high-performance computing cluster. We would like to thank Stefano Crespi for comments and suggestions regarding the computational studies. Jelte S. Steen is acknowledged for assistance with spectroelectrochemical measurements. Renze Sneep is acknowledged for mass spectral analysis.
2.5 Experimental procedures

2.5.1 General information

All reagents and solvents were purchased from Sigma Aldrich, TCI Europe, Acros Organics or Alfa Aesar and were used without further purification. Dry solvents were obtained from an M Braun SPS-800 solvent purification system or from a system with \( \text{Al}_2\text{O}_3 \) (Fluka) columns, BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Sigma Aldrich, 4Å). Solvents were deoxygenated by performing at least three freeze-pump-thaw cycles. Flash column chromatography was performed on silica gel (Merck, type 9385, 230-400 mesh). Thin-layer chromatography (TLC) was carried out on silica coated aluminum sheets (60 F253) purchased from Merck. Visualization of compounds was performed with an UV-lamp and/or staining with a \( \text{KMnO}_4 \) solution.

NMR spectra \(^1\text{H} \) and \(^{13}\text{C} \) were recorded on a Varian Mercury-Plus 400 spectrometer or a Bruker Avance 600 NMR spectrometer at 298K. VT-NMR studies in anhydrous/deoxygenated toluene were performed on a Varian Unity Plus 500 NMR spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent signal. Coupling constants are reported in hertz (Hz). The splitting pattern is designated as follows: singlet (s), doublet (d), triplet (t), m (multiplet), br (broad), and doublet of doublets (dd).

High resolution mass spectrometry (HRMS) was performed on a LTQ Orbitrap XL spectrometer with electrospray ionization (ESI) as ionization technique. Single crystal X-ray diffraction data was obtained from a Bruker D8 Venture diffractometer.

Electronic absorption spectra were recorded on an Agilent 8453 UV/Vis Spectroscopy System in a 1 cm quartz cuvette. Emission spectra were recorded on a FS-5 spectrofluorometer (Edinburgh Instruments) in a 1 cm quartz cuvette. Absorption and emission spectra of \( \text{1-O, 1-F and 2-F} \) were recorded in anhydrous/deoxygenated DCM. Quantum yields were determined in aerated dichloromethane (with \( \text{[(2,2'-bipyridyl)]\text{Ru}(\text{PF}_6)_2} \) in aerated water as reference) using the following formula:

\[
\Phi = \frac{\Phi_{\text{ref}}}{I_{\text{ref}}} \frac{1 - 10^{-A_{\text{ref}}}}{n^2_{\text{ref}}} \frac{1 - 10^{-A}}{n^2}
\]

Where \( \Phi_{\text{ref}} \) is the emission quantum yield of the reference (0.04\(^\text{46}\)), \( I \) the integrated emission intensity, \( A \) the absorbance at the excitation wavelength, \( n \) the refractive index, and the subscript \( \text{ref} \) refers to the reference.

Electron paramagnetic resonance (EPR) spectra were collected on a Bruker ECS 106 spectrometer at 77 K using a finger dewar filled with liquid nitrogen. Low temperature
EPR measurements in the range between 8.6-70 K were performed on a Bruker EMX-plus spectrometer, equipped with an ER 4112HV-CF100 cryostat. The spectra were simulated with EasySpin, using the cwEPR 3.1 GUI.

Cyclic voltammograms were recorded using a three-electrode setup on a CHI600C (CH Instruments) or a VSP-300 Potentiostat/Galvanostat (Biologic Science Instruments) using an Ag/AgCl wire as pseudo-reference electrode (RE), glassy carbon (3 mm diameter) disc working electrode (WE), and a platinum wire as counter electrode (CE). The working electrode was polished with an aqueous aluminum oxide solution before every experiment. All cyclic voltammograms were recorded at room temperature, with scan rate 0.1 V/s under an argon atmosphere using anhydrous solvents (DCM or MeCN), and nBu₄NPF₆ (0.1 M) as electrolyte unless otherwise stated. All cyclic voltammograms were calibrated by the addition of ferrocene at the end of the experiment. Spectroelectrochemical measurements were performed in a glovebox under nitrogen atmosphere using a three-electrode setup on a CHI600C (CH Instruments) using an Ag/AgCl wire as reference electrode (RE), platinum wire as counter electrode (CE), and a graphite stick as working electrode (WE) in an anhydrous/deoxygenated MeCN solution with 0.1 M nBu₄NPF₆ as electrolyte. The graphite stick was equipped with a hole, drilled in the exact position of the path of the light beam coming from an Avantes Avalight-DHC light source. Constant potential experiments were performed while simultaneously absorption spectra were recorded every 2 s using an Avantes Starline AvaSpec-2048 spectrometer. The first absorption spectrum recorded, before applying a potential, was used as blank and difference absorbance spectra were plotted.

2.5.2 Compound preparation and characterization

![Chemical Structure]

2,7-diiodo-9H-thioxanthen-9-one. Compound 4. 9H-thioxanthen-9-one (4.04 g, 19.0 mmol) and iodine (5.80 g, 24.6 mmol) were placed in a three-neck flask, fitted with reflux condenser and magnetic stirring bar, containing CCl₄ (2.3 mL, 23.8 mmol), acetic acid (30 mL), and concentrated H₂SO₄ (1.5 mL, 95-97%). After stirring for 15 min HIO₃ (4.6 g, 26.1 mmol) was added and the mixture was heated at reflux for 16 h. After cooling to room temperature the yellow precipitate was filtered, washed with cold ethanol, and recrystallized from toluene to provide the title compound which was directly used in the next step without further purification. Yield: 3.81 g (43%).

¹H-NMR (400 MHz, CDCl₃): δ 8.91 (d, J = 2.0 Hz, 2H), 7.90 (dd, J = 8.5, 2.0 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H). ¹³C-NMR (151 MHz, CDCl₃): δ 177.46, 141.16, 138.86, 136.48,
130.39, 127.75, 91.32. **HRMS** (ESI, pos) m/z calcd for C$_{13}$H$_{12}$O$_{5}$S [M+H]$^+$ 464.83015, found 464.83015.

![Image](image_url)

**2,7-diethoxy-9H-thioxanthen-9-one. Compound 5.** In a round-bottom pressure flask with magnetic stirring bar under argon atmosphere, compound 4 (1.3 g, 2.8 mmol), CuI (0.212 g, 1.11 mmol), phenanthroline monohydrate (0.445 g, 2.24 mmol), and cesium carbonate (5 g, 15.3 mmol) were placed. After the addition of dry toluene (5 mL) and dry ethanol (8 mL) the reaction mixture was heated at 120°C for 48 h. The mixture was cooled to room temperature and poured into water and extracted with ethyl acetate. The combined organic layers were washed with an aqueous 10% HCl solution, brine, and dried over MgSO$_4$. After filtration the solution was concentrated under reduced pressure. The resulting solid was recrystallized from ethyl acetate to provide the title compound as a light yellow solid. Yield: 0.474 g (56%).

$^1$H-NMR (600 MHz, CDCl$_3$): δ 8.06 (d, J = 2.9 Hz, 4H), 7.49 (d, J = 8.8 Hz, 4H), 7.24 (dd, J = 8.8, 2.9 Hz, 4H), 4.18 (q, J = 7.0 Hz, 8H), 1.47 (t, J = 7.0 Hz, 12H). **$^{13}$C-NMR** (151 MHz, CDCl$_3$): δ 179.54, 157.71, 129.71, 129.44, 127.40, 111.02, 64.06, 14.85. **HRMS** (ESI, pos) m/z calcd for C$_{17}$H$_{17}$O$_3$S [M+H]$^+$ 301.08929, found 301.08947.

9,9'-(-anthracene-9,10-diyl)bis(2,7-diethoxy-9H-thioxanthen-9-ol). **Compound 7.** In an oven dried Schlenk flask with magnetic stirring bar, under an argon atmosphere, 9,10-dibromoanthracene (141 mg, 0.420 mmol) in dry THF (16 mL) was brought to -78°C whereupon 6 eq tBuLi (1.48 mL [1.7 M in hexane], 2.52 mmol) was added dropwise. The mixture was consecutively stirred at -78°C for 1 h and at room temperature for another 1 h. Then the mixture was brought to -78°C again and compound 5 (276 mg, 0.919 mmol), dissolved in 20 mL dry THF, was added dropwise whereupon it was stirred at room temperature overnight. After quenching with saturated aq. NH$_4$Cl (5 mL) the mixture was poured into brine after which the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3x) and the combined organic layers were dried
over Na₂SO₄. After filtration, the solution was concentrated under reduced pressure. The resulting crude was subjected to column chromatography (25% EtOAc/Pentane/1% Triethylamine) to provide the title compound as a brown/yellow solid. Yield: 138.2 mg (42%).

¹H-NMR (400 MHz, CDCl₃): δ 9.10 (br, 4H)*, 7.40 (d, J = 8.6 Hz, 4H), 7.02 (br, 4H), 6.81 (dd, J = 8.6, 2.6 Hz, 4H), 6.53 (br, 4H), 3.76-3.64 (m, 4H), 3.62-3.51 (m, 4H), 2.93 (br, 2H), 1.09 (t, J = 6.9 Hz, 12H). ¹³C-NMR (151 MHz, CDCl₃): δ 157.58, 141.39, 136.39, 131.53, 127.89, 127.26, 123.52, 121.12, 116.33, 114.89, 82.02, 63.58, 14.55.*Integral deviates from the expected value due to the broadness of the resonance.

HRMS (ESI, pos) m/z calcd for C₄₈H₄₁O₅S₂ [M-OH]⁺ 761.23899, found 761.23867.

9,9'-(1,4-phenylene)bis(2,7-diethoxy-9H-thioxanthen-9-ol). Compound 9. In an oven dried Schlenk flask with magnetic stirring bar, under an argon atmosphere, 1,4-dibromobenzene (52.6 mg, 0.223 mmol) in dry THF (6 mL) was brought to -78°C whereupon 4 eq tBuLi (0.52 mL [1.7 M in hexane], 0.892 mmol) was added dropwise. The mixture was consecutively stirred at -78°C for 1 h and at room temperature for another 1 h. Then the mixture was brought to -78°C again and compound 5 (147.4 mg, 0.491 mmol), dissolved in 10 mL dry THF, was added dropwise whereupon it was stirred at room temperature overnight. After quenching with saturated aq. NH₄Cl (2 mL) the mixture was poured into brine after which the organic layer was separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried over Na₂SO₄. After filtration, the solution was concentrated under reduced pressure. The resulting crude was subjected to column chromatography (30% EtOAc/Pentane/1% Triethylamine) to provide the title compound as a yellow solid. Yield: 67 mg (44%).

¹H-NMR (600 MHz, CDCl₃): δ 7.53 (d, J = 2.7 Hz, 4H), 7.24 (d, J = 8.4 Hz, 4H), 6.81 (s, 4H), 6.78 (dd, J = 8.4, 2.7 Hz, 4H), 4.06-4.00 (m, 8H), 2.65 (s, 2H), 1.40 (t, J = 7.0 Hz, 12H). ¹³C-NMR (151 MHz, CDCl₃): δ 158.32, 142.53, 141.52, 127.79, 126.94, 123.27, 114.25, 112.23, 77.32, 63.86, 14.98. HRMS (ESI, neg) m/z calcd for C₄₀H₃₇O₃S₂ [M-H]⁻ 677.20370, found 677.20412.
Chapter 2

9,9′-(anthracene-9,10-diyl)bis(2,7-diethoxythioxanthylum) di(tetrafluoroborate). Compound 1\(^{2+}\). A scintillation vial equipped with a magnetic stirring bar was charged with compound 7 (102.8 mg, 0.132 mmol) dissolved in acetone (2 mL). The mixture was brought to 0°C whereupon a solution of HBF\(_4\) (0.2 ml [50 wt% in H\(_2\)O], 1.6 mmol) in acetone (0.6 mL) was dropwise added. After the addition, the mixture was stirred for 1 h at 0 °C. Then Et\(_2\)O was added to precipitate the product which was separated and subsequently washed with more Et\(_2\)O. The product was dissolved in MeCN and precipitated with Et\(_2\)O (3x) and finally separated and washed with pentane. Drying under vacuum provided the title compound as a purple solid. Yield: 112.9 mg (93%). Crystals suitable for single crystal X-ray analysis were grown by layering Et\(_2\)O on a concentrated solution of 1\(^{2+}\) in MeCN at room temperature.

\(^1\)H-NMR (600 MHz, Acetone-\(d_6\)): δ 9.21 (d, \(J = 9.3\) Hz, 4H), 8.27 (dd, \(J = 9.3, 2.5\) Hz, 4H), 7.55-7.51 (m, 4H), 7.47-7.43 (m, 4H), 7.21 (d, \(J = 2.5\) Hz, 4H), 4.04 (q, \(J = 7.0\) Hz, 8H), 1.21 (t, \(J = 7.0\) Hz, 12H). \(^{13}\)C-NMR (151 MHz, Acetone-\(d_6\)): δ 161.02, 160.78, 142.67, 133.86, 132.28, 130.18, 129.93, 129.05, 128.47, 126.38, 111.97, 64.60, 13.35. HRMS (ESI, pos) m/z calcd for C\(_{48}\)H\(_{40}\)O\(_4\)S\(_2\) [M]\(^{2+}\) 372.11785, found 372.11792.

9,9′-(1,4-phenylene)bis(2,7-diethoxythioxanthylum) di(tetrafluoroborate). Compound 2\(^{2+}\). A round-bottom flask equipped with a magnetic stirring bar was charged with compound 9 (125 mg, 0.184 mmol) dissolved in acetone (4 mL). The mixture was brought to 0°C whereupon a solution of HBF\(_4\) (0.3 mL [50 wt% in H\(_2\)O], 2.4 mmol) in
acetone (1 mL) was dropwise added. After the addition, the mixture was stirred for 1 h at 0°C. Then Et₂O was added to precipitate the product which was separated and subsequently washed with more Et₂O and pentane. Drying under vacuum provided the title compound as a purple solid. Yield: 118.4 mg (79%).

\[ ^1H\text{-NMR} \ (400\ MHz, \text{CD}_3\text{CN}): \delta \ 8.78 \ (d, \ J = 9.3 \ Hz, \ 4H), \ 8.06 \ (dd, \ J = 9.3, \ 2.5 \ Hz, \ 4H), \ 7.96 \ (s, \ 4H), \ 7.50 \ (d, \ J = 2.5 \ Hz, \ 4H), \ 4.20 \ (q, \ J = 7.0 \ Hz, \ 8H), \ 1.44 \ (t, \ J = 7.0 \ Hz, \ 12H). \]

\[ ^{13}C\text{-NMR} \ (151\ MHz, \text{CD}_3\text{CN}): \delta \ 163.29, \ 161.29, \ 142.98, \ 138.44, \ 133.66, \ 131.36, \ 130.37, \ 130.19, \ 113.17, \ 65.86, \ 14.67. \]

HRMS (ESI, pos) m/z calcd for C₄₀H₃₆O₄S₂ [M]⁺ 744.23625, found 744.23555.

**Compound 1-O.** A scintillation vial with compound \(1^{2+} \) (140.7 mg, 0.153 mmol) was brought in a glovebox under nitrogen atmosphere where a solution of cobaltocene (116 mg, 0.613 mmol) in MeCN (10 mL) was prepared. The latter was added in one portion to compound \(1^{3+}\) dissolved in MeCN (5 mL). The precipitate, which emerged after leaving the vial overnight at -30°C, was isolated by decanting and washed multiple times with MeCN. Subsequently, it was dried under vacuum to provide the title compound as a green solid which was stored in the freezer (-30°C) of the glovebox. Yield: 90.0 mg (79%).

HRMS (ESI, pos) m/z calcd for C₄₈H₄₀O₄S₂ [M]⁺ 744.23625, found 744.23555.

**3,6-bis(2,7-diethoxy-9H-thioxanthen-9-ylidene)cyclohexa-1,4-diene. Compound 2-F.**
A scintillation vial with compound \(2^{2+} \) (21.6 mg, 0.0264 mmol) was brought in a glovebox under nitrogen atmosphere where a solution of cobaltocene (10 mg, 0.053 mmol) in
MeCN was (2 mL) prepared. The latter was added dropwise to compound 2\(2^+\) and the precipitate, which emerged after shaking the vial for 5 min, was isolated by decanting and washed multiple times with MeCN and was finally dried under vacuum to provide the title compound as an orange solid. Yield: 15.6 mg (92%). Crystals suitable for single crystal X-ray analysis were grown by layering MeCN on a concentrated solution of 2-F in DCM at room temperature.

\(^1\)H-NMR (600 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.40 (d, \(J = 8.6\) Hz, 4H), 7.24 (s, 4H), 7.13 (d, \(J = 2.7\) Hz, 4H), 6.82 (dd, \(J = 8.6, 2.7\) Hz, 4H), 4.07 (q, \(J = 7.0\) Hz, 8H), 1.42 (t, \(J = 7.0\) Hz, 12H). \(^{13}\)C-NMR (151 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 158.11, 137.79, 134.57, 129.96, 128.49, 128.03, 127.21, 115.94, 114.28, 64.50, 15.19. HRMS (ESI, pos) m/z calcd for C\(_{40}\)H\(_{36}\)O\(_4\)S\(_2\) [M]\(^+\) 644.20495, found 644.20344.

9,10-bis(2,7-diethoxy-9H-thioxanthen-9-ylidene)-9,10-dihydroanthracene.

**Compound 1-F.** In an oven dried Schlenk flask fitted with a reflux condenser and magnetic stirring bar, under an argon atmosphere, compound 1-O (42.7 mg, 0.057 mmol) was added together with 30 mL dry/degassed toluene. The reaction mixture was heated to 90\(^\circ\)C for 40 h and the toluene removed under reduced pressure. The crude mixture was then subjected to column chromatography (5% EtOAc/Pentane) to provide the title compound as a yellow solid. Yield: 36 mg (84%).

\(^1\)H-NMR (500 MHz, C\(_6\)D\(_6\)): \(\delta\) 7.49 (d, \(J = 8.5\) Hz, 4H), 7.18 (d, \(J = 2.7\) Hz, 4H), 7.12-7.07 (m, 4H), 6.66 (dd, \(J = 8.5, 2.7\) Hz, 4H), 6.51-6.45 (m, 4H), 3.68 – 3.56 (m, 8H), 1.02 (t, \(J = 7.0\) Hz, 12H). \(^{13}\)C-NMR (151 MHz, C\(_6\)D\(_6\)): \(\delta\) 157.83, 138.77, 138.23, 134.08, 133.42, 129.31, 128.94, 128.35, 125.96, 117.30, 114.76, 63.76, 14.73. HRMS (ESI, pos) m/z calcd for C\(_{40}\)H\(_{40}\)O\(_4\)S\(_2\) [M]\(^+\) 744.23625, found 744.23562.
2.5.3 X-Ray crystal structures

Single crystals of compounds 1$^{2+}$, 1-F and 2-F were mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3. The final unit cell was obtained from the xyz centroids of 9884 (1$^{2+}$), 9526 (1-F) and 9426 (2-F) reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS). The structures were solved by direct methods using SHELXT, and refinement of the structure was performed using SHLEXL.

For compound 1-F, refinement was frustrated by a disorder problem: three of the OEt groups were found to be disordered, which was incorporated in the refinement by a two-site occupancy model. For one of the C$_6$H$_3$OEt rings that makes up one half of a thioxanthylidene moiety the thermal displacement parameters indicated the presence of a minor degree of additional rotational disorder, but attempts to model this were unsuccessful. The second thioxanthylidene group was also affected by disorder, which in this case was found to extend also to the S atom. A two-site occupancy model was applied to the entire SC$_6$H$_3$OEt fragment (half of the thioxanthylidene). The six-membered aromatic ring of both disorder components was constrained to an idealized hexagon using the AFIX66 instruction. For some of the atoms in this disordered part the thermal displacement parameters turned to non-positive definite values when allowed to refine freely; ultimately, SIMU and RIGU instructions were applied to the disordered atoms to prevent this.

For all structures, the hydrogen atoms were generated by geometrical considerations, constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Crystal data and details on data collection and refinement are presented in Table S1.
Table S1. Crystallographic data for compounds 1^{2+}, 1-F and 2-F.

|                  | 1^{2+} | 1-F     | 2-F     |
|------------------|--------|---------|---------|
| chem formula     | C_{48}H_{40}O_{4}S_{2}B_{2}F_{8} | C_{40}H_{36}O_{4}S_{2}B_{2}F_{8} | C_{48}H_{40}O_{4}S_{2}B_{2}F_{8} |
| M_r             | 1000.65 | 744.92  | 644.81  |
| cryst syst      | triclinic | monoclinic | monoclinic |
| color, habit    | purple, block | yellow, block | orange, platelet |
| size (mm)       | 0.350 x 0.330 x 0.130 | 0.440 x 0.300 x 0.250 | 0.23 x 0.15 x 0.04 |
| space group     | P - 1 | P 21/n | P 21/c |
| a (Å)           | 8.4003(5) | 14.0808(4) | 11.0931(2) |
| b (Å)           | 10.6690(7) | 19.2501(5) | 10.1155(2) |
| c (Å)           | 14.3308(9) | 14.3787(4) | 28.8387(6) |
| α (°)           | 73.798(2) | 90      | 90      |
| β (°)           | 77.564(2) | 104.6090(10) | 93.1500(10) |
| γ (°)           | 85.150(3) | 90      | 90      |
| V (Å³)          | 1204.01(13) | 3771.44(18) | 3231.17(11) |
| Z               | 1      | 4      | 4      |
| ρ_{calc}, g.cm⁻³ | 1.380 | 1.312 | 1.325 |
| Radiation [Å]   | Mo Kα0.71073 | Mo Kα0.71073 | Cu Kα 1.54178 |
| μ(Mo Kα), mm⁻¹  | 0.190 | 0.188 | 1.829 |
| μ(Cu Kα), mm⁻¹  | 0.000000, 4.007100 | 0.0336, 2.1476 |
| F(000)          | 518    | 1568   | 1360   |
| Temp (K)        | 100(2) | 100(2) | 100(2) |
| θ range (°)     | 2.64 – 27.88 | 2.78 – 26.35 | 4.63 – 72.14 |
| data collected (h,k,l) | -10:10; -13:13; -18:18 | -17:17; -24:22; -17:17 | -13:13; -12:12; -35:35 |
| no. of rflns collected | 55478 | 45853 | 35920 |
| no. of indpndt collected | 5305 | 7689 | 6305 |
| Observed reflns F_o ≥ 2.0 σ | 4919 | 6907 | 5681 |
| R(F) (%)        | 6.53   | 4.93   | 3.09   |
| wR(F²) (%)      | 17.05  | 10.58  | 8.12   |
| GooF            | 1.037  | 1.204  | 1.042  |
| weighting a,b   | 0.0781, 2.2441 | 0.000000, 4.007100 | 0.0336, 2.1476 |
| params refined  | 319    | 608    | 419    |
| min, max resid dens | -0.921, 2.457 | -0.341, 0.478 | -0.280, 0.292 |

Figure S1. ORTEP drawings of the a) 1^{2+}, b) 2-F, and c) 1-F structures with carbon numbering. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.
2.5.4 Chemical oxidation of 1-O to $1^{2+}$

Figure S2. NMR studies: chemical oxidation of 1-O (under N$_2$ atmosphere): 1-O in $d_2$-DCM (red), 1-O in $d_3$-MeCN/$d_2$-DCM (green), addition of 6 eq of NOBF$_4$ forming $1^{2+}$ (blue), removal of solvent and addition of $d_6$-acetone (orange), and $1^{2+}$ in $d_6$-acetone reference (black). To ensure complete conversion for this spectroscopic measurement an excess of NOBF$_4$ was used (3-fold excess).
2.5.5 Chemical oxidation of 2-F to $2^{2+}$

**Figure S3.** NMR studies: chemical oxidation of 2-F (under N$_2$ atmosphere): 2-F in 1:1 $d_3$-MeCN/$d_2$-DCM (red), addition of 4 eq of NOBF$_4$ forming $2^{2+}$ in combination with minor unidentified chemical species (green), and $2^{2+}$ in $d_3$-MeCN reference (blue). To ensure complete conversion for this spectroscopic measurement an excess of NOBF$_4$ was used (2-fold excess).
2.5.6 Experimental and simulated EPR Spectra of 1-O

**Figure S4.** Top: Experimental and simulated EPR spectrum of 1-O in anhydrous/deoxygenated toluene. Experimental parameters: T = 77 K, Freq = 9.6453 GHz, Modulation Amplitude = 1 G. Microwave power = 0.0003162 mW. Simulation parameters S = 1 species: g-value = 2.0023, D = 183 MHz, E = 3 MHz, lwpp = [0.592, 0.144], weight = 1. Simulation parameters S = ½ species: g-value = 2.0022, lwpp = [0.88, 0.13], weight = 0.08 (7%). Bottom: Components contribution to the simulated spectrum. Component 2 is probably the one-electron oxidized form of 1-O.
**Figure S5.** Experimental and simulated EPR spectrum of 1-O (half-field) in anhydrous/deoxygenated toluene. Experimental parameters: $T = 40\, \text{K}$, $\text{Freq} = 9.6506\, \text{GHz}$, Modulation Amplitude = 4 G. Microwave power = 6.33 mW. Simulation parameters: $S = 1$, $g$-value = 2.0023, $D = 183\, \text{MHz}$, $E = 3\, \text{MHz}$, lwpp = [0.592, 0.144].

**Figure S6.** Experimental EPR spectrum of 1-O in the solid state. Experimental parameters: $T = \text{rt}$, $\text{Freq} = 9.6157\, \text{GHz}$, Modulation Amplitude = 0.1 G, Microwave power = 0.0001 mW. Intermolecular exchange coupling gives rise to a predominant $S = \frac{1}{2}$ signal dominating the $S = 1$ signal.
2.5.7 Characterization of compound 1^{2+}

Characterization of compound 1^{2+} by NMR spectroscopy was precluded by the presence of what was thought to be a mono-radical cation impurity (Fig. S7). Therefore, after following the synthetic procedure to produce 1^{2+}, an EPR spectrum was recorded to investigate whether a mono-radical cation was present. The EPR spectrum of compound 1^{2+} was taken in MeCN at 77K and a signal for a monoradical impurity was observed (Fig. S8). From double integration of the EPR signal, the impurity is estimated to be ~7%.

In an attempt to obtain resolved peaks in the NMR spectra it was tried to oxidize the mono-radical cation to 1^{2+} by adding a drop of HBF\(_4\) (50 wt% in H\(_2\)O) (Fig. S7) (to promote the oxygen reduction reaction) or AgBF\(_4\) (Fig. S7). This immediately resulted in resolved peaks associated with 1^{2+} (although with additional impurities in the case of AgBF\(_4\)). The same result could be obtained by simply stirring 1^{2+} in chloroform, removing the solvent, and dissolving it in acetone-d\(_6\). The \(^1\)H-NMR spectrum obtained by following this procedure can be found in section 2.5.2. The \(^{13}\)C-NMR spectrum was obtained by adding a drop of HBF\(_4\) (50 wt% in H\(_2\)O) to compound 1^{2+} in acetone-d\(_6\).

**Figure S7.** \(^1\)H-NMR spectra of compound 1^{2+} in acetone-d\(_6\) (red) with in experiment 1 the addition of a drop of HBF\(_4\) (50 wt% in H\(_2\)O) (green) and in experiment 2 the addition of AgBF\(_4\) (blue).
Figure S8. EPR signal of compound 1^{2+} (1 \times 10^{-3} \text{ M}) in MeCN at 77 K.
2.5.8 Electrochemistry

All cyclic voltammograms of 1-O and 1^{2+} were recorded using a 0.5 mM concentration at different scan rates. All solvents used were anhydrous while additionally the DCM used for 1-O and the MeCN used for 1^{2+} were deoxygenated. The obtained voltammograms are shown in Fig. S9.

**Figure S9.** Cyclic voltammograms of 1-O in DCM and 1^{2+} in DCM and MeCN.
All cyclic voltammograms of $2^-F$ and $2^{2+}$ were recorded using a 0.5 mM concentration at different scan rates. All solvents used were anhydrous and deoxygenated. The obtained voltammograms are shown in Fig. S10.

**Figure S10.** Cyclic voltammograms of $2^-F$ in DCM and $2^{2+}$ in DCM and MeCN.
2.5.9 Spectroelectrochemistry

Figure S11. Spectroelectrochemical data of a) $2^+$ and b) $2^{-}$ in MeCN. Insets: initial absorption spectra before applying a constant potential.
2.5.10 Eyring-Polany plot absorption spectra

Figure S12. Eyring-Polanyi analysis: UV/Vis absorption spectroscopy in toluene showing the decay in absorbance of the thermal conversion of I-O monitored at 615 nm (dashed lines) at different temperatures a) 55°C, b) 65°C, c) 75°C, d) 85°C, and e) 95°C (a-b: spectrum every 10 min, c-e: spectrum every 5 min). f) In an A/A$_0$ (Absorbance/Initial Absorbance) vs. time plot the decay in absorbance is fitted to a monoexponential ($y = A1*\exp(-x/t1)+y0$) for each temperature.
2.6 References

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