

Supplementary Information

Light-gated Redox Switching and Actuation in Polymer Hydrogels

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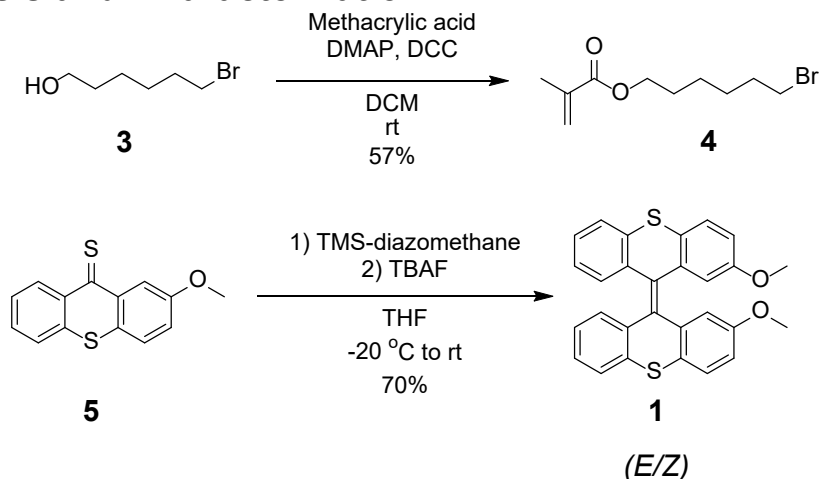
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Supplementary Methods and Discussions

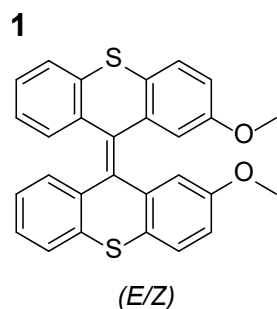
1 General Remarks

All reactions were performed under nitrogen atmosphere unless otherwise noted. Flash column chromatography was performed on silica gel Davisil LC60A (Merck type 9385, 230400 mesh), a Reveleris X2 Flash Chromatography system from Büchi or a Biotage Selekt system (MPLC) using the indicated solvents. NMR spectra (^1H and ^{13}C) were recorded on a Varian Mercury-Plus 400 (400 MHz), or a Bruker Avance Neo 600 (600 MHz) spectrometer at 298K (referenced to residual solvent signal: for ^1H detection, $\delta = 7.26$ ppm ; for ^{13}C detection, $\delta = 77.16$ ppm for CDCl_3). High resolution mass spectroscopy (HRMS) was performed on a LTQ Orbitrap XL spectrometer with electrospray ionization (ESI) as ionization technique. Rheological tests were performed on a TA instruments Discovery HR-2 rheometer. LEDs and power meter were purchased from Thorlabs (M455L4, M365L2, PM400 with sensor S401C).

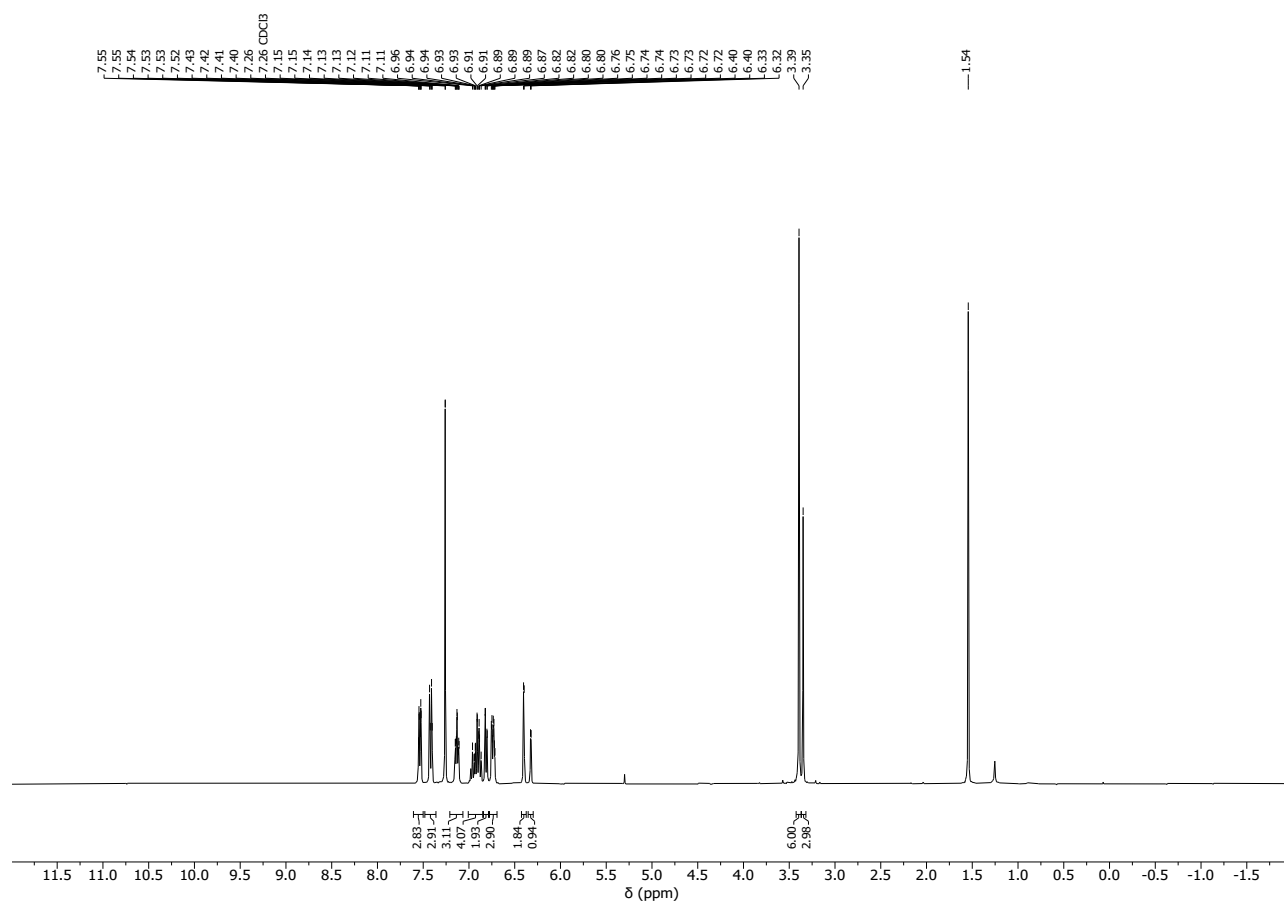
2 Synthesis and Characterization



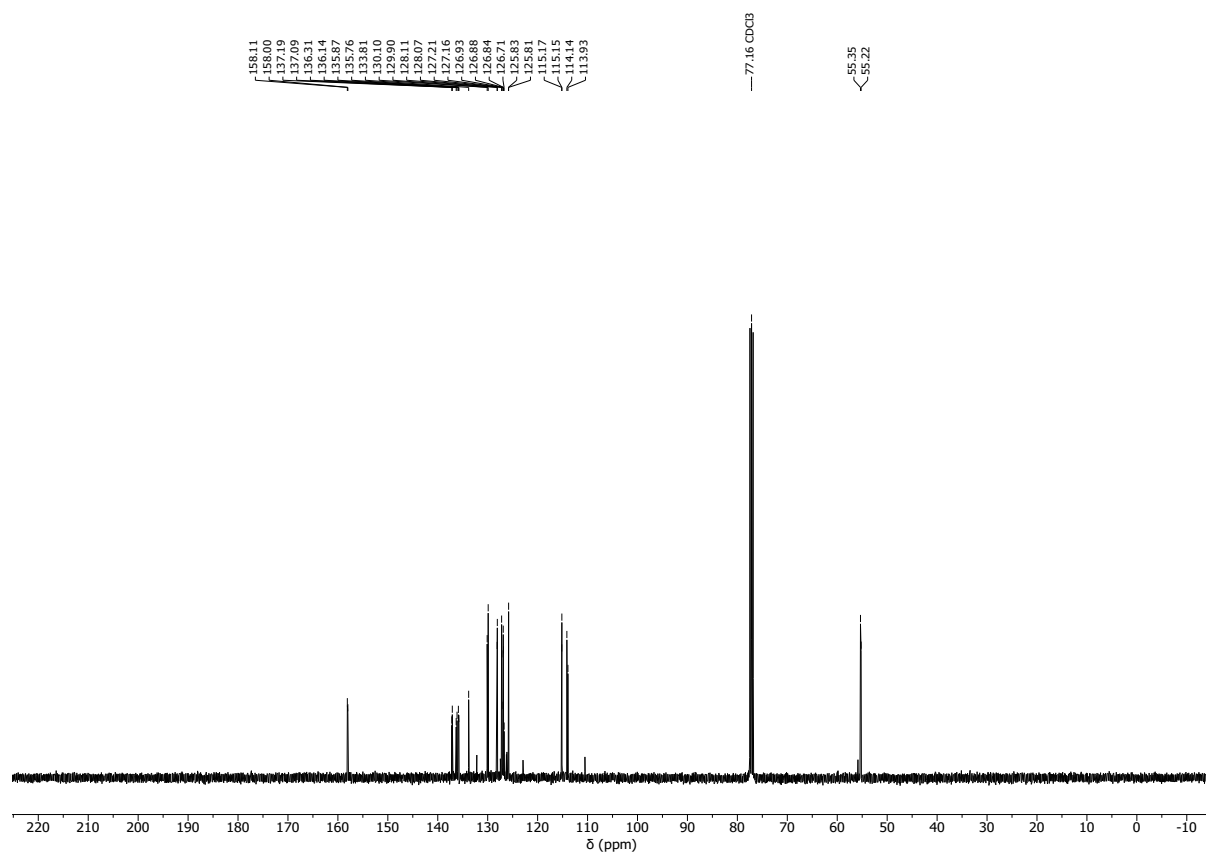
Supplementary Figure 1: Synthetic scheme of the synthesis of compound 1.



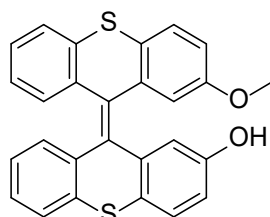
Synthesised according to a modified procedure¹: 2-methoxy-9H-thioxanthene-9-thione (2.4 g, 9.9 mmol) was dissolved in 70 mL dry THF (0.04 M). Of this solution, 60 mL was removed using a syringe and stored under nitrogen. The remaining 60 mL was cooled to -20 °C using an NaCl/ice bath. TMSCHN₂ (2.7 mL, 5.4 mmol, 0.55 equiv., 2.0 M in hexanes) was added and the mixture was allowed to warm to room temperature, resulting in a colour change from green/black to a clear, light yellow solution. The 60 mL solution of 2-methoxy-9H-thioxanthene-9-thione that was removed earlier was added back to the reaction flask and the resulting mixture was stirred at room temperature for 30 min. 1.0 M in THF tetrabutylammonium fluoride solution (20 mL, 20 mmol, 2.0 equiv.) was added, and the solution was left to stir for ten min. After concentration under reduced pressure the crude product was recrystallized twice from EtOAc. Spectroscopic data is in accordance with literature.¹



Supplementary Figure 2: ¹H NMR spectrum of compound **1**. 400 MHz in CDCl₃.



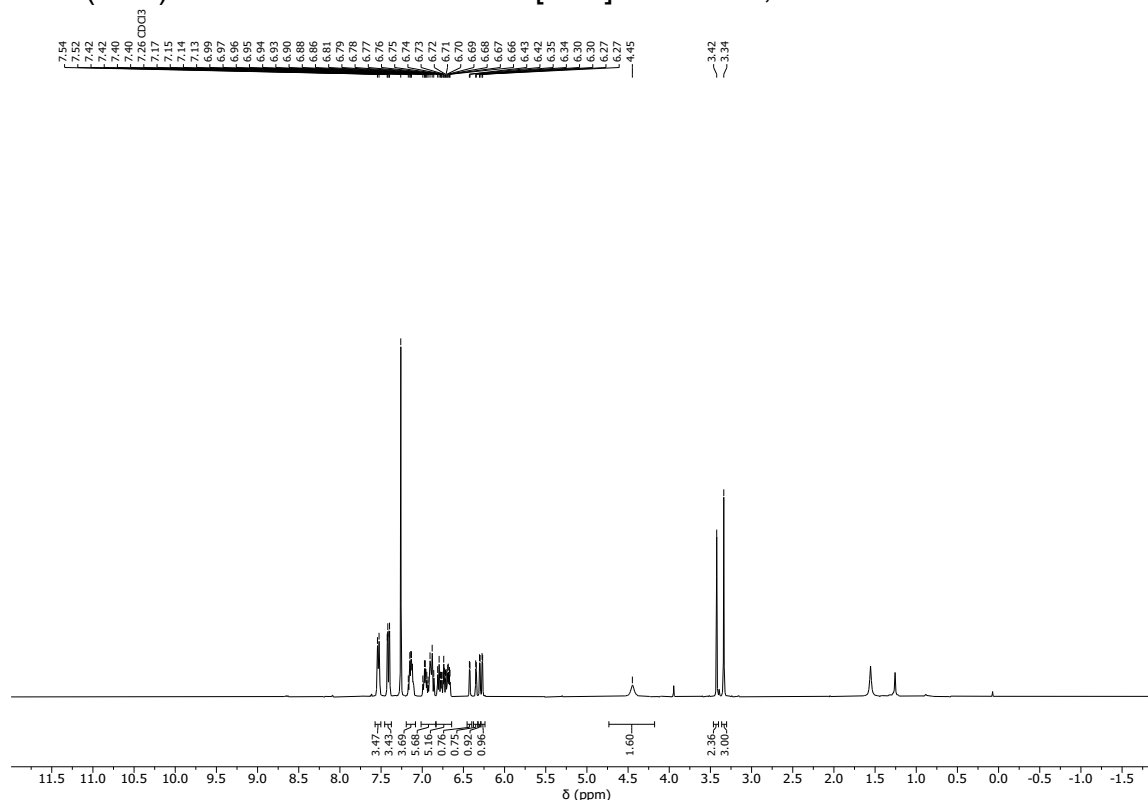
Supplementary Figure 3: ^{13}C NMR spectrum of compound **1**. 101 MHz in CDCl_3 .

2*(E/Z)*

To a stirred solution of **1** (2.5 g, 5.4 mmol) in 54 mL methylene chloride, BBr₃ solution (1 M in methylene chloride, 3.6 mL, 3.6 mmol, 0.7 equiv.) was added at 0 °C. The solution was left to stir at room temperature for 24 hr, after which it was quenched with water. The aqueous layer was extracted with methylene chloride (3 x 50 mL) and ethyl acetate (3 x 50 mL) to ensure that all BTX species are extracted. The combined organic layer was washed with brine, dried with MgSO₄ and concentrated in vacuo. The product mixture was dry-loaded on celite and purified by column chromatography (silica gel, pentane:CH₂Cl₂:MeOH 100:0:0 to 50:50:0 to recover **1** (29%) 50:50:0 to 0:100:0 to isolate both isomers of **2** (together 30%, 56:44 major:minor) and 0:100:0 to 0:90:10 to isolate the diphenolic species (fully demethylated) (29%).

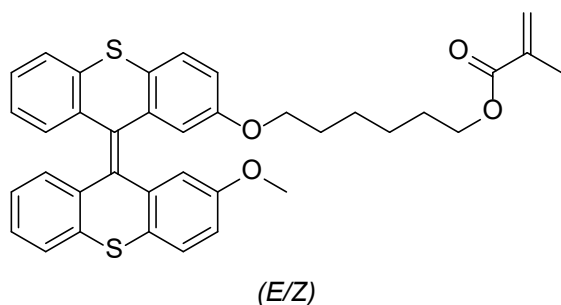
¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.49 (m, 2H_{major} + 2H_{minor}), 7.45 – 7.37 (m, 2H_{major} + 2H_{minor}), 7.18 – 7.09 (m, 2H_{major} + 2H_{minor}), 7.01 – 6.83 (m, 3H_{major} + 3H_{minor}), 6.83 – 6.63 (m, 3H_{major} + 3H_{minor}), 6.43 (d, J = 2.7 Hz, 1H_{minor}), 6.35 (d, J = 2.7 Hz, 1H_{minor}), 6.30 (d, J = 2.7 Hz, 1H_{major}), 6.27 (d, J = 2.7 Hz, 1H_{major}), 4.67 (s, 1H_{major} + 1H_{minor}), 3.42 (s, 3H_{minor}), 3.34 (s, 3H_{major}). Product was too insoluble for ¹³C NMR.

HRMS (ESI⁻): Calculated: C₂₇H₁₇O₂S₂⁻ [M-H]⁻ 437.0675, found : 437.0670.



Supplementary Figure 4: ¹H NMR spectrum of compound **2**. 400 MHz in CDCl₃.

BTX-MA

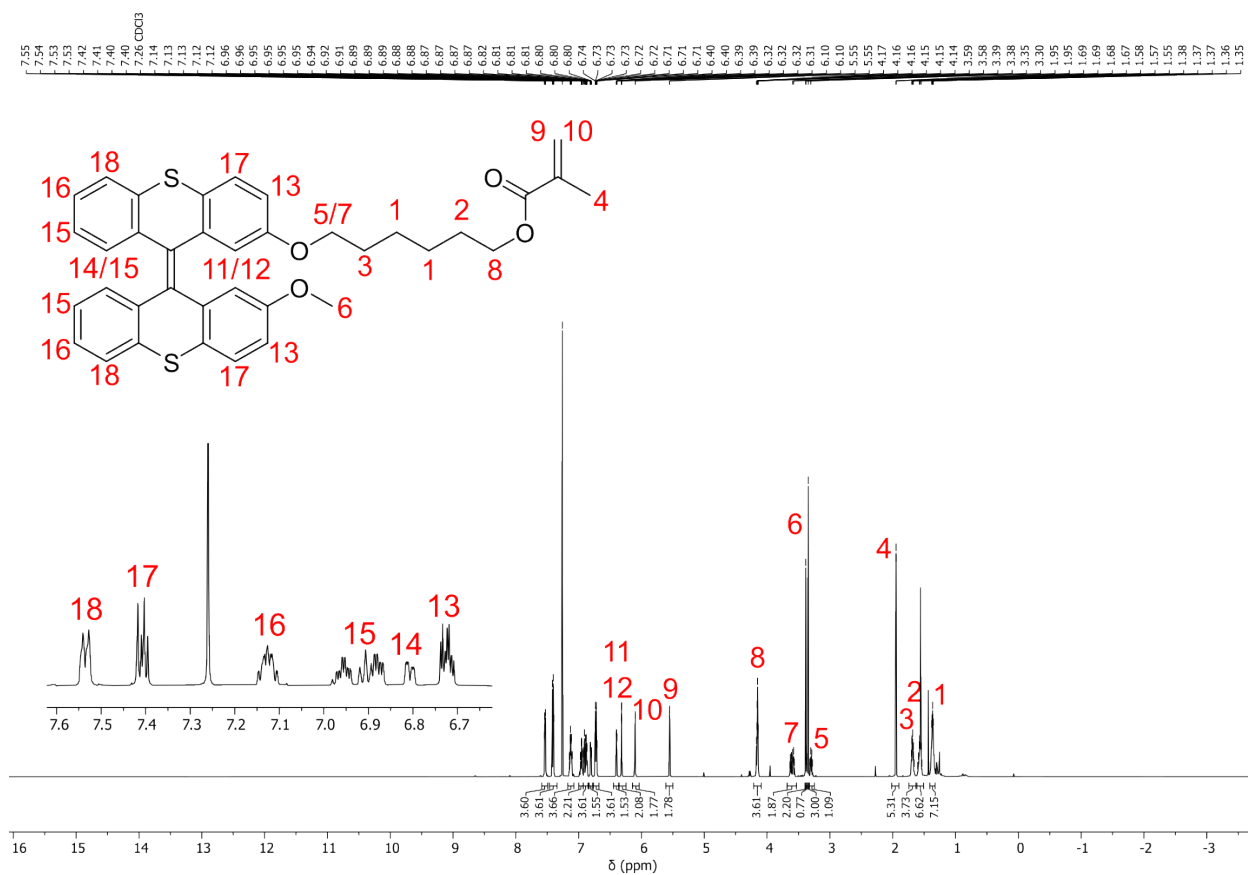


Compound **2** (50 mg, 0.11 mmol), Cs_2CO_3 (41 mg, 0.13 mmol, 1.1 equiv.) and 6-bromohexyl methacrylate (28 mg, 0.11 mmol, 1 equiv.) were dissolved in 1 mL acetone and heated to 60 °C for 16 hr while stirring. After cooling to room temperature, water was added and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was then washed with brine, dried with MgSO_4 and loaded on celite. Compound **3** was purified by column chromatography (silica gel, pentane: CH_2Cl_2 90:10:0 to 50:50:0) to give 45 mg of product (mixture of isomers, 60/40 major/minor) as an off-white solid (Yield 65%). When storing this compound for extended periods of time, we recommend adding a small amount of BHT to inhibit polymerization.

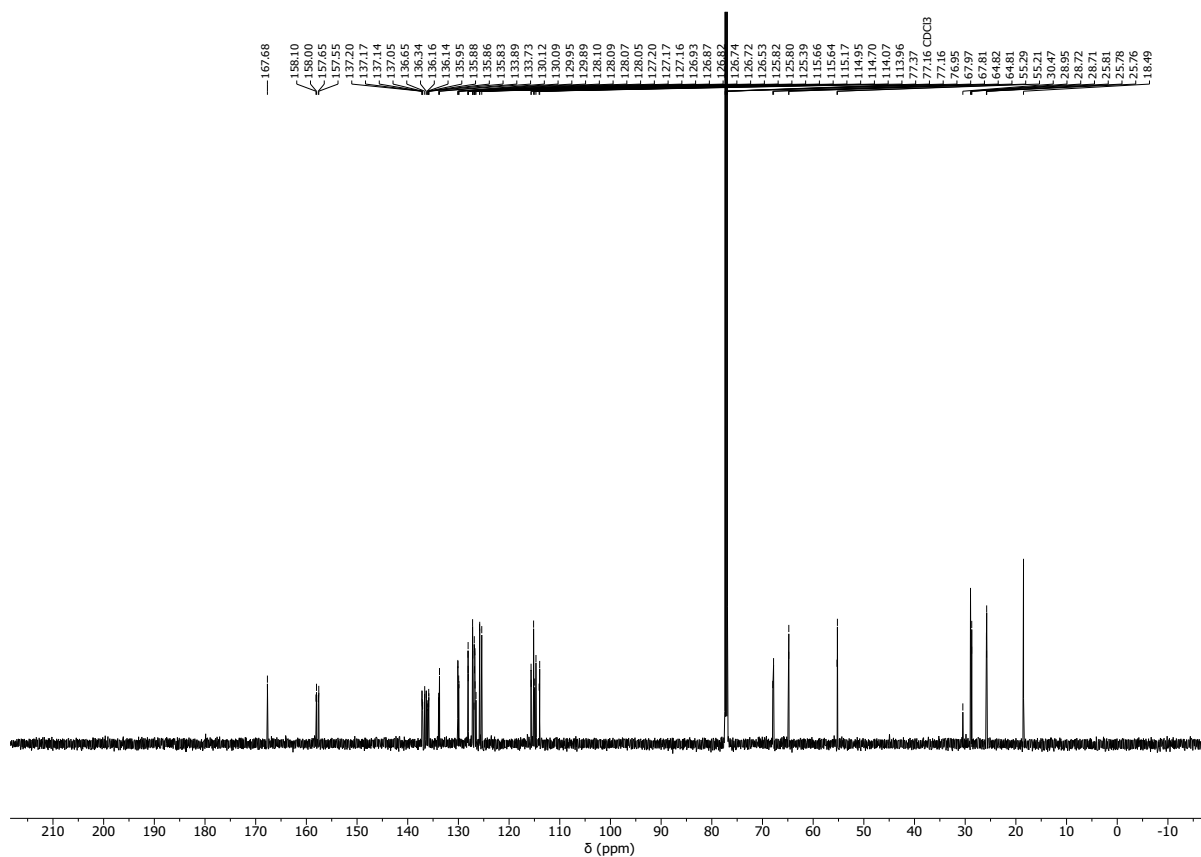
^1H NMR (400 MHz, CDCl_3) δ 7.54 (m, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 7.46 – 7.35 (m, $4\text{H}_{\text{major}} + 4\text{H}_{\text{minor}}$) (m, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 7.17 – 7.08 (m, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 7.00– 6.85 (m, $3\text{H}_{\text{major}} + 3\text{H}_{\text{minor}}$), (m, 1H) (m, $1\text{H}_{\text{major}} + 1\text{H}_{\text{minor}}$), 6.77 – 6.68 (m, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 6.45 – 6.36 (m, $1\text{H}_{\text{major}} + 1\text{H}_{\text{minor}}$), 6.36 – 6.25 (m, $1\text{H}_{\text{major}} + 1\text{H}_{\text{minor}}$), 6.10 (overlapping s, $1\text{H}_{\text{major}} + 1\text{H}_{\text{minor}}$), 5.55 (overlapping s, $1\text{H}_{\text{major}} + 1\text{H}_{\text{minor}}$), 4.21 – 4.10 (m, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 3.68 – 3.53 (m, $1\text{H}_{\text{major}} + 1\text{H}_{\text{minor}}$), 3.38 (s, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 3.34 (s, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 3.33 – 3.25 (m, $1\text{H}_{\text{major}} + 1\text{H}_{\text{minor}}$), 1.95 (overlapping s, , $3\text{H}_{\text{major}} + 3\text{H}_{\text{minor}}$), 1.74 – 1.63 (m, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 1.62 – 1.51 (m, $2\text{H}_{\text{major}} + 2\text{H}_{\text{minor}}$), 1.41 – 1.33 (m, $4\text{H}_{\text{major}} + 4\text{H}_{\text{minor}}$).
 ^{13}C NMR (151 MHz, CDCl_3) δ (major and minor signals strongly overlapping) 167.7, 158.1, 158.0, 157.6, 157.6, 137.2, 137.2, 137.1, 137.0, 136.6, 136.3, 136.2, 136.1, 135.9, 135.9, 135.9, 135.8, 133.9, 133.7, 130.1, 130.1, 129.9, 129.9, 128.1, 128.1, 128.1, 128.0, 127.2, 127.2, 127.2, 126.9, 126.9, 126.8, 126.7, 126.7, 126.5, 125.8, 125.8, 125.4, 115.7, 115.6, 115.2, 114.9, 114.7, 114.1, 114.0, 77.4, 77.2, 76.9, 68.0, 67.8, 64.8, 64.8, 55.3, 55.2, 29.0, 28.7, 28.7, 25.8, 25.8, 25.8, 18.5.

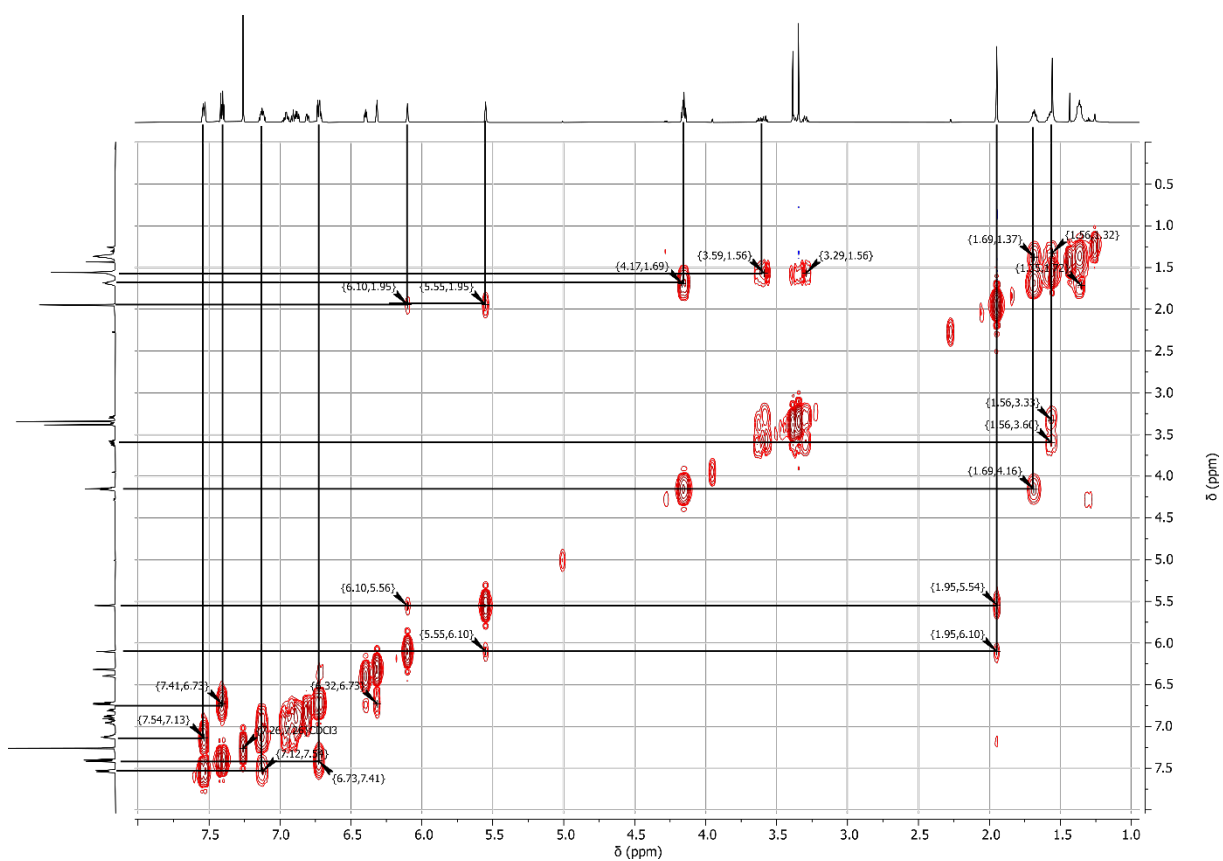
HRMS (ESI⁺): Calculated: $\text{C}_{37}\text{H}_{34}\text{O}_4\text{S}_2^+$ [M]⁺ 606.1893, found : 606.1896.

Elemental analysis (% calcd, % found for $\text{C}_{37}\text{H}_{34}\text{O}_4\text{S}_2$): C (73.24, 72.96), H (5.65, 5.98), N (0.00, 0.00)



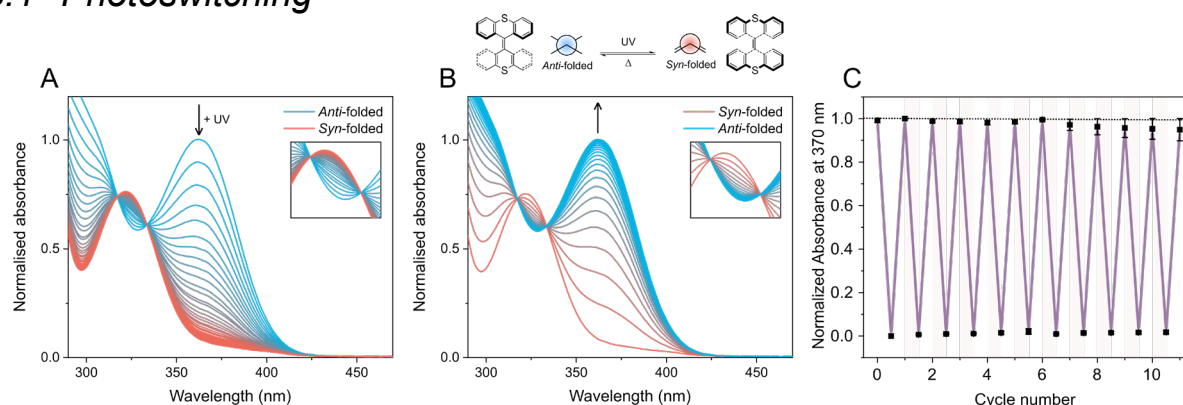
Supplementary Figure 5: ¹H NMR spectrum of compound **BTX-MA**. 600 MHz in CDCl₃.



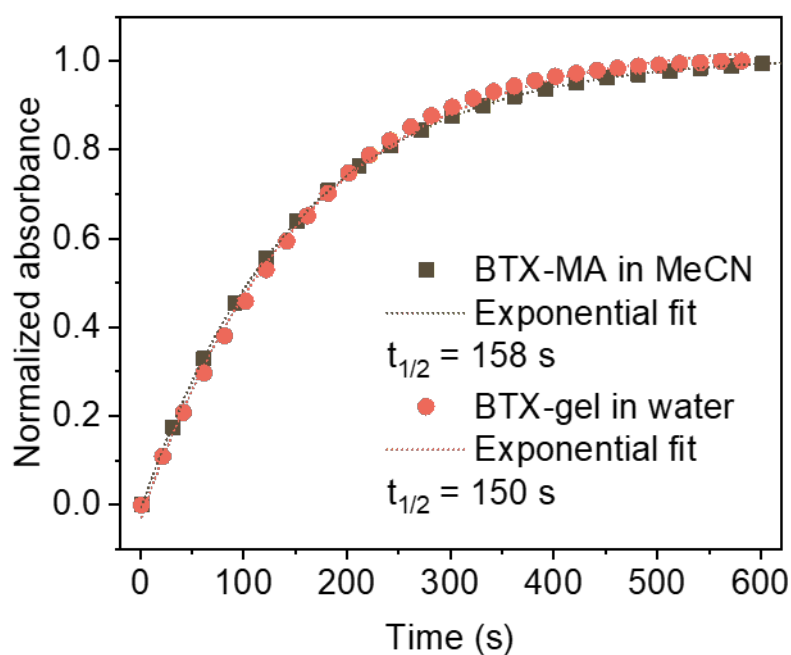


3 UV/Vis studies

3.1 Photoswitching

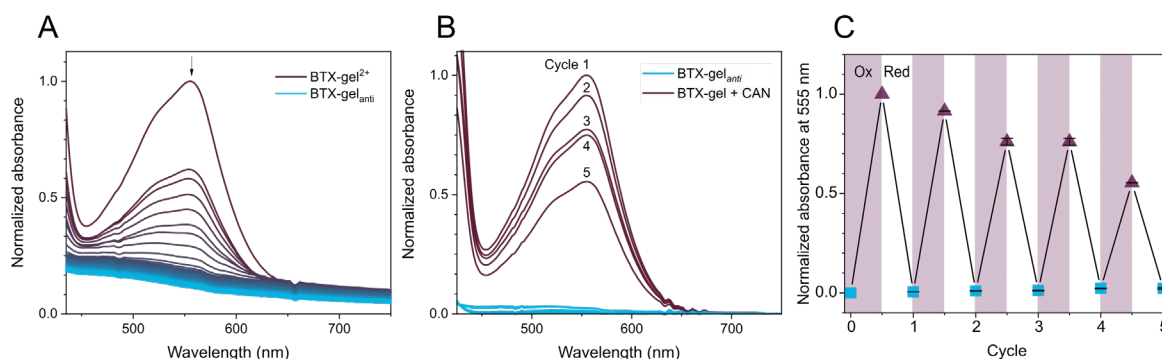


Supplementary Figure 8: Photo- and thermal switching of BTX-gel in water at 25 °C between *anti*- and *syn*-folded states as determined by UV/Vis spectroscopy. A) Changes in absorbance upon irradiation with 365 nm light. B) Changes in absorbance upon thermal relaxation. C) Photoswitching fatigue over 11 cycles followed by monitoring the absorbance at 370 nm. Error bars represent the standard deviation of two independent measurements.



Supplementary Figure 9: Absorbance changes at 370 nm at 25 °C of the thermal relaxation of the *syn*-folded state to the *anti*-folded state for **BTX-gel** in water and **BTX-MA** in MeCN.

3.2 Oxidation & Reduction



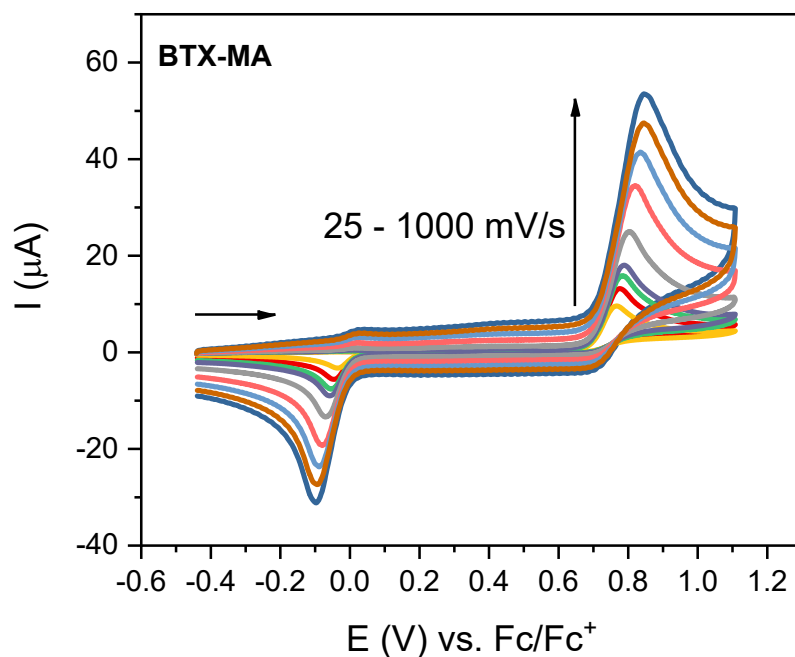
Supplementary Figure 10: A) UV/Vis spectra of **BTX-gel²⁺** in a 15 mM solution of ascorbic acid, leading to reduction of **BTX-gel²⁺** to neutral **BTX-gel**. Initially the *syn*-folded state is quantitatively formed which then thermally relaxes to the *anti*-folded state; in the depicted wavelength region neither of these species display any absorbance and due to the time scale of the experiment **BTX-gel_{anti}** will be the predominant species. B) Spectra showing the characteristic peak of **BTX-gel²⁺** over five cycles of alternating oxidation and reduction. C) The normalized absorbance at 555 nm from B). Error bars represent one standard deviation of independent duplicate experiments. Note that the error bars are so small that they are barely visible.

It is important to note that the slow fatigue of bulk redox switching (Supplementary Figure 10C) is most likely related to a small degree of side reactions during/after oxidation/reduction and not due to incomplete redox switching. Nevertheless, even though there is some loss of activity, the absorbance peak at 555 nm still has an optical density of 1 after five cycles, and visually there is only a small decrease in the intensity of the color of the material.

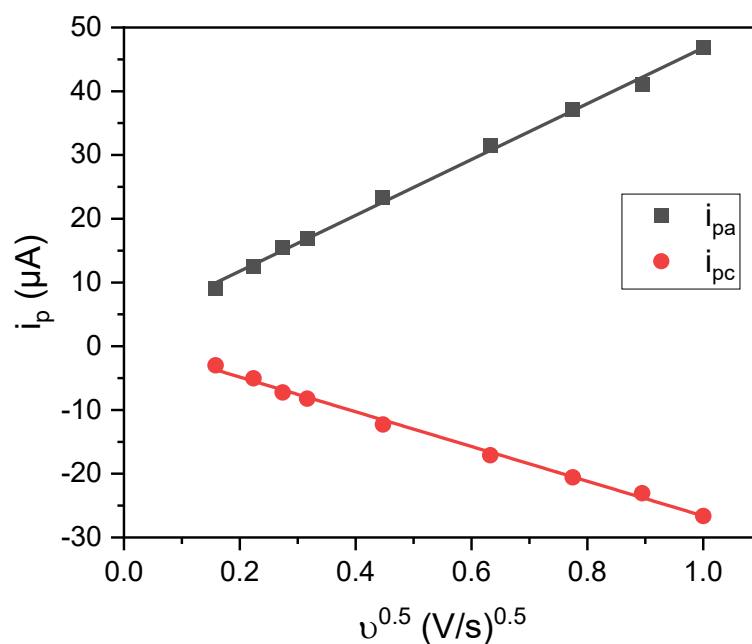
4 Electrochemistry, Redox Mechanisms and Theoretical Calculations

4.1 General Electrochemical Characterization

As shown in Figure S11, the voltammetric properties of the monomer **BTX-MA** are largely unchanged over a large range of scan rates. The excellent linear dependence of the peak currents on the square-root of the scan rate further confirms that this redox process is diffusion-controlled (Supplementary Fig. 12).



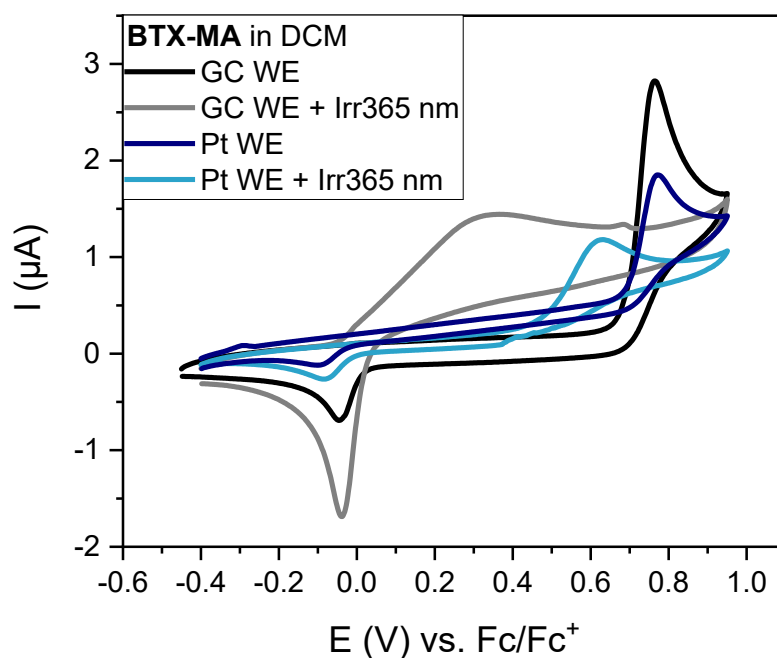
Supplementary Figure 11: CVs of 0.5 mM **BTX-MA** in CH_2Cl_2 , 100 mM TBAPF_6 at varying scan rates.



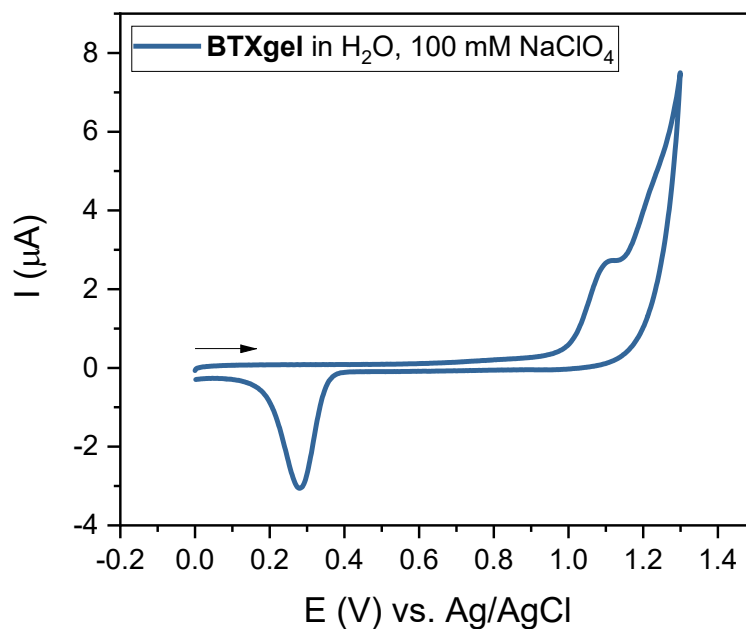
Supplementary Figure 12: Anodic and cathodic peak currents of 0.5 mM **BTX-MA** in CH_2Cl_2 , 100 mM TBAPF_6 as a function of the square-root of the scan rate including linear fits.

Shown in Figure S13 is a comparison of the CVs of the *anti*- and *syn*-folded states of **BTX-MA** using different working electrodes (GC or Pt). As shown in Figure 3E in the main text, a very significant cathodic voltammetric shift was observed when using GC (~ 400 mV), however the oxidation peak for the *syn*-folded state is very broad under these conditions. In contrast, when using a Pt working electrode, a better-defined oxidation peak shape was obtained, however with a smaller cathodic shift of ~ 140 mV.

In any case, the potential shift is clearly large enough to enable selective, light-gated redox switching with Fe^{3+} in water.



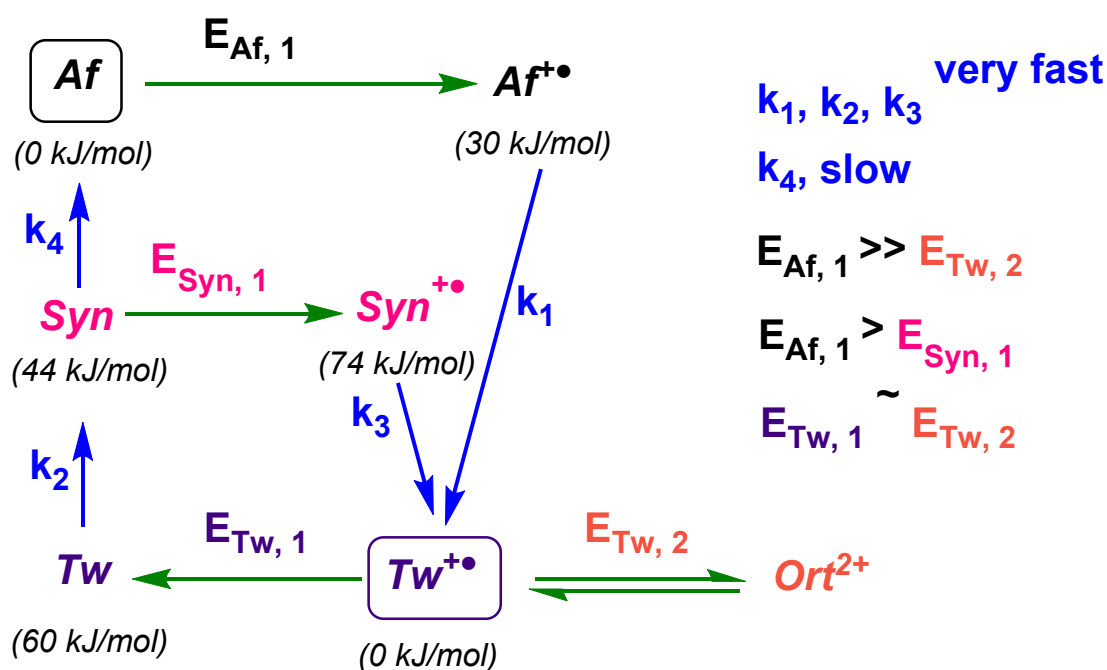
Supplementary Figure 13: CVs of 0.25 mM **BTX-MA** in CH_2Cl_2 , 100 mM TBAPF_6 at $v = 25$ mV/s in both the *anti*- and *syn*-folded states. The *syn*-folded state was generated by continuous, in situ irradiation of the solution with 365 nm light. The CVs in blue were measured with a Pt disk working electrodes while the CVs shown in black were measured using a GC disk electrode.



Supplementary Figure 14: CV of **BTX-gel** on ITO in H_2O , 100 mM NaClO_4 at $v = 25$ mV/s.

4.2 Mechanism of Redox Switching

Starting from the neutral, *anti*-folded state, one electron oxidation occurs at a high potential ($E_{Af,1}$) and transiently generates a radical cation in the same conformational state ($Af^{+\bullet}$, Figure S15). This species very quickly chemically rearranges to its most preferred conformational state ($Tw^{+\bullet}$, via k_1). This twisted radical cation now possesses a *lower* oxidation potential for removal of the second electron ($E_{Tw,2}$, with $E_{Tw,2} \ll E_{Af,1}$, i.e. potential inversion), such that the dicationic species in the twisted/orthogonal state (Ort^{2+}) is immediately generated (any redox potential sufficient to induce the first $E_{Af,1}$ process will automatically force the second electron transfer, such that both electrons are in effect transferred simultaneously and the intermediate radical cation $Tw^{+\bullet}$ is not formed in any significant amounts, giving rise to a simultaneous two-electron oxidation at ~ 0.8 V, see Figure 3 main text). In the forward direction (*anti*-folded $\rightarrow$ dication) the redox switching thus occurs via an ECE mechanism with a chemically irreversible first step, “ratcheted” by the favourable and fast geometric rearrangement of $Af^{+\bullet}$ to $Tw^{+\bullet}$). This was further supported by calculations of the relative conformer energies at the r²SCAN-3c level of theory, which confirm that for the radical cation charge state, the $Af^{+\bullet}$ conformer is ~ 30 kJ/mol higher in energy than $Tw^{+\bullet}$ (see Table S1), such that the first one-electron transfer is (rapidly) followed by a chemical rearrangement step.



Af – *anti*-folded

Syn – *syn*-folded

Tw – *twisted*

Ort – *orthogonal*

Supplementary Figure 15: Detailed square scheme depicting the relevant redox (green arrows) and structural (blue arrows) interconversions between all relevant redox states. The thermodynamically most stable and most relevant species for each oxidation state are highlighted with a box and for the neutral and radical cationic charge states the relative energies of all conformers are given in

parentheses (energy differences are given relative to the lowest lying conformer of each redox state, at 25 °C (vide infra). For simplicity, most pathways are depicted as only proceeding in one direction; however, in principle, all redox and structural processes are (reversible) equilibria; most depicted ET processes are rendered chemically irreversible through fast, subsequent rearrangements.

In principle, the second electron transfer between $Tw^{+\bullet}$ and Ort^{2+} is a fully reversible step as it occurs without any significant geometric rearrangements, or at least with very low barriers (Note that while for the BTX^{2+} dication, a perpendicular arrangement of the rotors has been confirmed crystallographically,² other more “twisted” conformations are energetically easily accessible by rotation around the central single-bond; in fact for a related derivative we recently crystallographically observed a 64° angle between the mean planes of the two rotors in the dicationic “orthogonal” state).³

In spite of this reversible interconversion, the $Tw^{+\bullet}$ state can still not be accessed by reduction of the dication (at least not for the homomeric BTX derivatives³). This is because at potentials at which the reduction can be achieved (~ -0.05 V, see Figure 3 main text), the reduction of the second thioxanthylum rotor also occurs as there is very little electronic communication between the two halves in the single-bonded orthogonal state (i.e. $E_{Tw,1} \sim E_{Tw,2}$, potential compression). As a result, during reduction simultaneous transfer of two electrons occurs easily, which transiently generates the neutral twisted state (Tw), which is an unfavored conformation for this charge state and thus very quickly rearranges to the *syn*-folded state (k_2). This was again confirmed by DFT calculations; for the neutral switch, Tw (~ 60 kJ/mol) is much higher in energy than the *syn*- (~ 44 kJ/mol) or *anti*-folded states (≈ 0 kJ/mol). The exclusive formation of *Syn* by reduction of Ort^{2+} (via the very unstable Tw) was confirmed previously.^{2,4} As discussed in the main text, *Syn* can then thermally relax to *Anti* (k_4), which is however much slower than the other chemical rearrangements ($t_{1/2} \sim 150$ s). As a result *Syn* can be quantitatively populated by irradiation and also oxidized, most likely via an ECE mechanism, this time via the $E_{Syn,1}$ and k_3 pathway and the transient generation of the $Syn^{+\bullet}$ state, whose relative energy is with 74 kJ/mol even higher than that of $Ar^{+\bullet}$ (~ 30 kJ/mol). It is important to note that, despite the chemical irreversibility of the EC and/or EEC steps, the overall redox process displays a very high degree of practical reversibility, i.e. repeat interconversion of the neutral and dicationic states without significant decomposition/formation of other side-products.

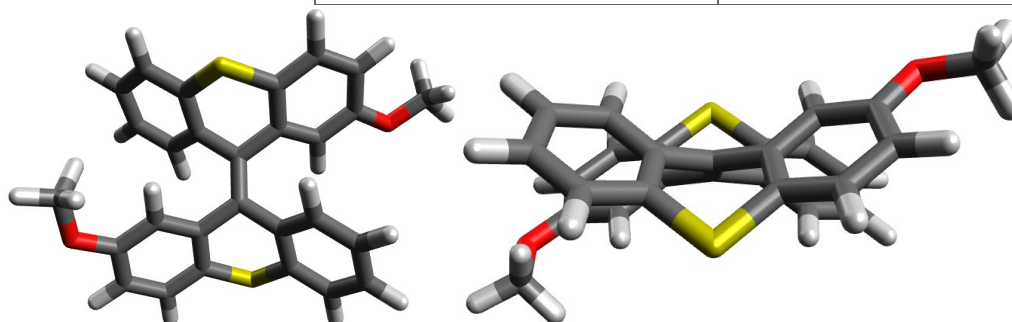
The calculated structures and energies of all the relevant conformational and charge states discussed above are shown in Table S1 and Figures S16-27. For simplicity these calculations, as well as the following electrochemical studies were carried out using the 2,2'-dimethoxy-BTX precursor **1** as a simpler analogue of the BTX-MA monomer. Substitution at one of the methoxy groups to give the monomer is not expected to affect the switching properties of the core, even more significant substitutions do not significantly alter the general (redox) switching properties of the system.^{1,4}

As shown in Table S1, the relative energies of the 2,2'-dimethoxy-BTX precursor **1** were calculated for both the *E* and *Z* isomers of all conformers and both the neutral and monocationic charge state. In all cases the energy difference between the *E* and

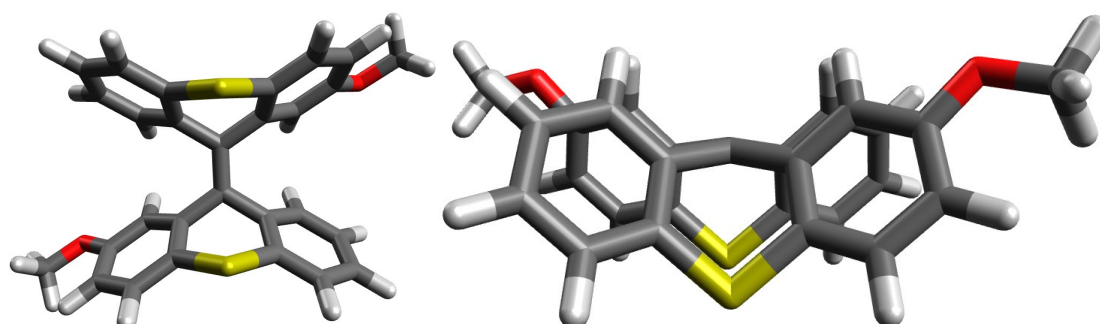
Z isomers is negligible, confirming that their (redox) switching behavior is the same, regardless which isomer is used (note we herein always use a mixture of both isomers).

Supplementary Table 1: Calculated Gibbs free energy differences (kJ/mol) at 25 °C of the different isomers of **1**, relative to the energy of the lowest isomer within each redox state. Calculations were performed at the r²SCAN-3c level of theory in the gas phase.

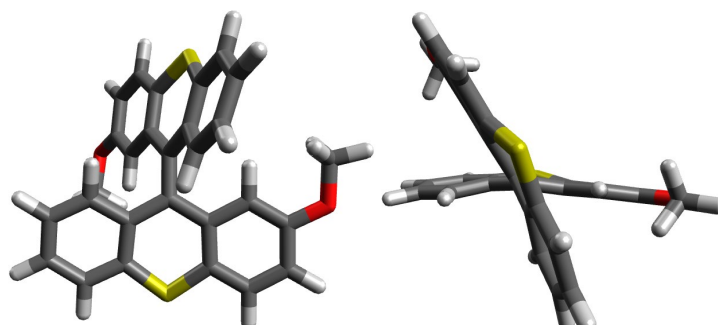
	Neutral	Radical Cation
<i>E-anti</i> -folded	0	29.5
<i>E-syn</i> -folded	43.5	74.1
<i>E</i> -twisted	59.0	0
<i>Z-anti</i> -folded	0.6	29.6
<i>Z-syn</i> -folded	44.5	74.6
<i>Z</i> -twisted	60.0	0.1



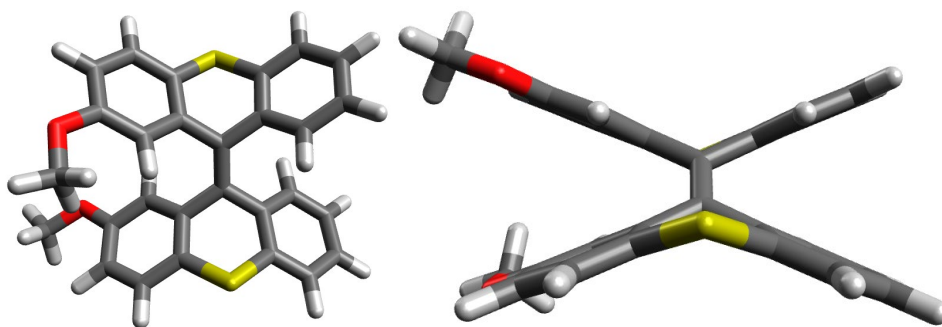
Supplementary Figure 16: Optimized geometry of the *E-anti* isomer of **1** (neutral state).



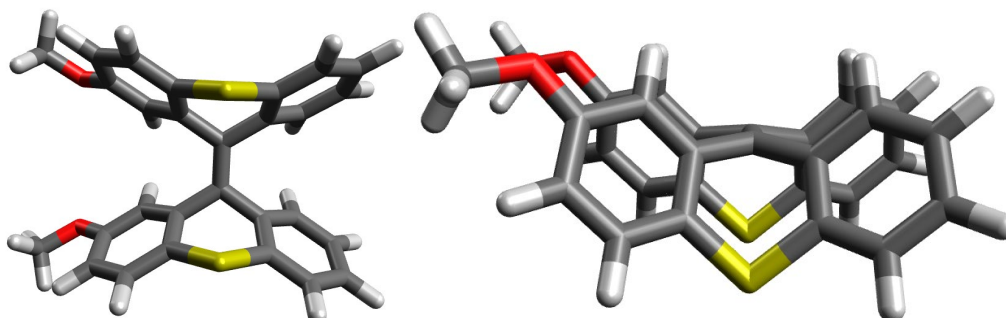
Supplementary Figure 17: Optimized geometry of the *E-syn* isomer of **1** (neutral state).



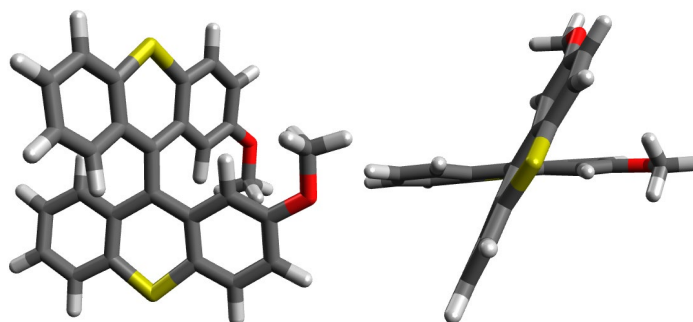
Supplementary Figure 18: Optimized geometry of the *E*-twisted isomer of **1** (neutral state).



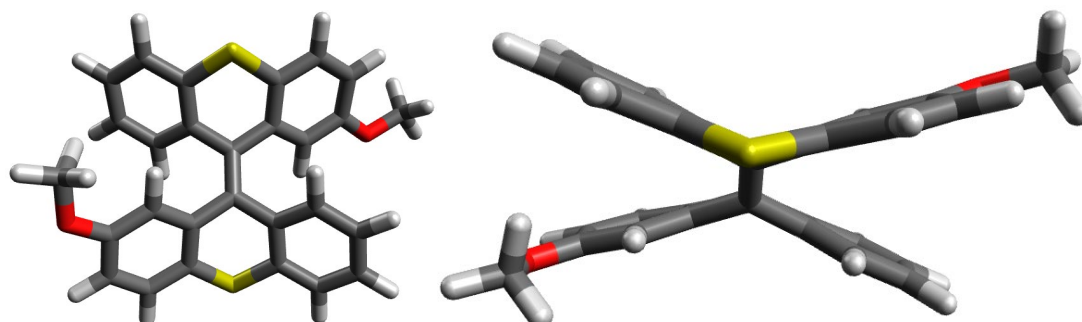
Supplementary Figure 19: Optimized geometry of the *Z-anti* isomer of **1** (neutral state).



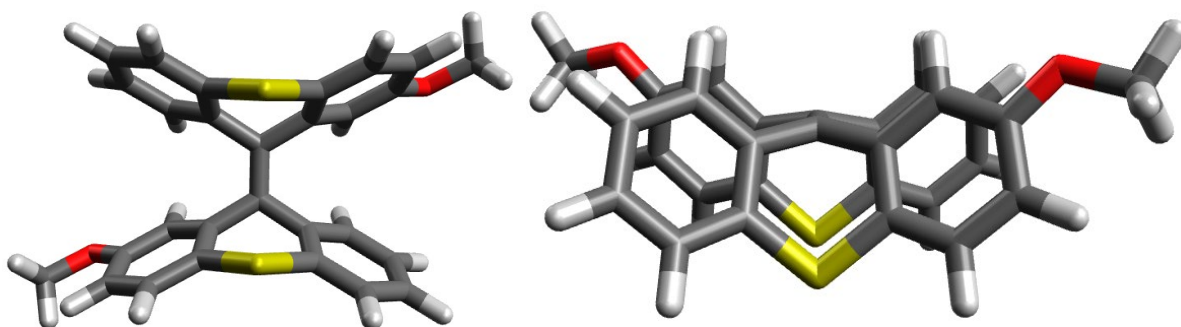
Supplementary Figure 20: Optimized geometry of the *Z-syn* isomer of **1** (neutral state).



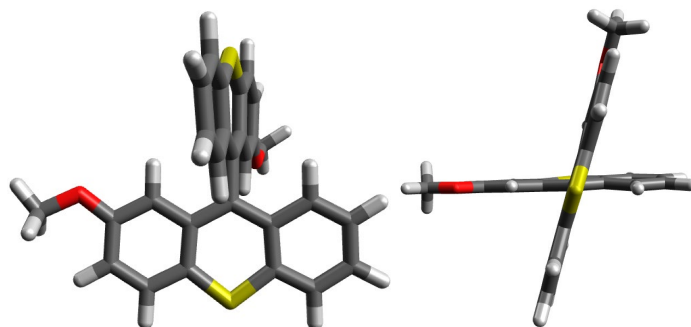
Supplementary Figure 21: Optimized geometry of the twisted *Z* isomer of **1** (neutral state).



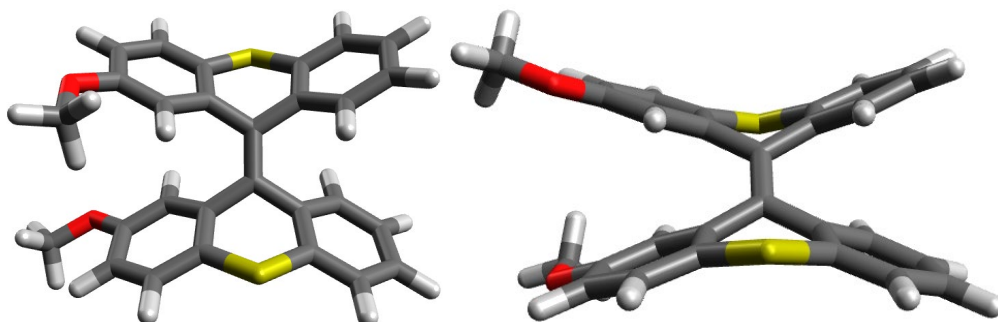
Supplementary Figure 22: Optimized geometry of the *E-anti* isomer of **1*+** (radical cationic state).



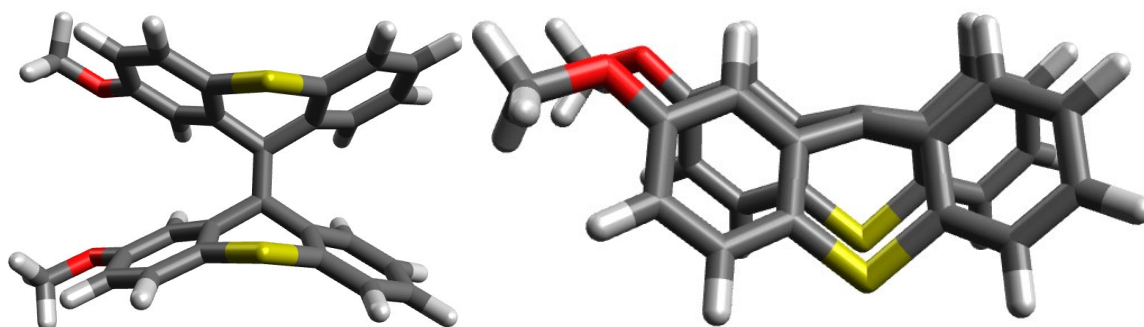
Supplementary Figure 23: Optimized geometry of the *E-syn* isomer of **1^{•+}** (radical cationic state).



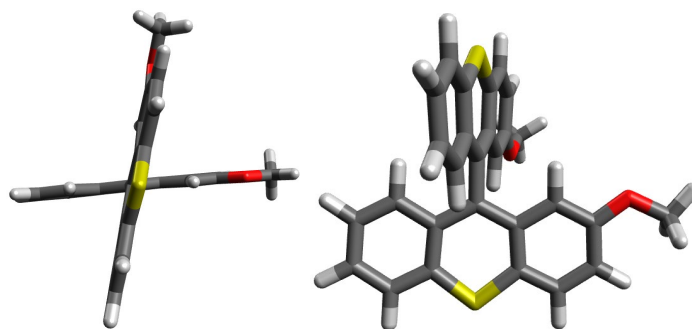
Supplementary Figure 24: Optimized geometry of the *E-twisted* isomer of **1^{•+}** (radical cationic state).



Supplementary Figure 25: Optimized geometry of the *Z-anti* isomer of **1^{•+}** (radical cationic state).



Supplementary Figure 26: Optimized geometry of the *Z-syn* isomer of **1^{•+}** (radical cationic state).



Supplementary Figure 27: Optimized geometry of the Z-twisted isomer of **1**^{•+} (radical cationic state).

Number of transferred electrons

To further confirm that the single oxidative wave observed in the CVs corresponds to transfer of two electrons, we carried out the following additional experiments.

The time-dependent current response at a microdisk electrode following a potential step is given by the following equation as derived by Shoup and Szabo:⁵

$$I = 4nFDcrf(\tau) \quad (\text{eqn. S1})$$

Where:

$$f(\tau) = 0.7854 + 0.8862 * \tau^{-0.5} + 0.214 * \exp [0.7823\tau^{-0.5}] \quad (\text{eqn. S2})$$

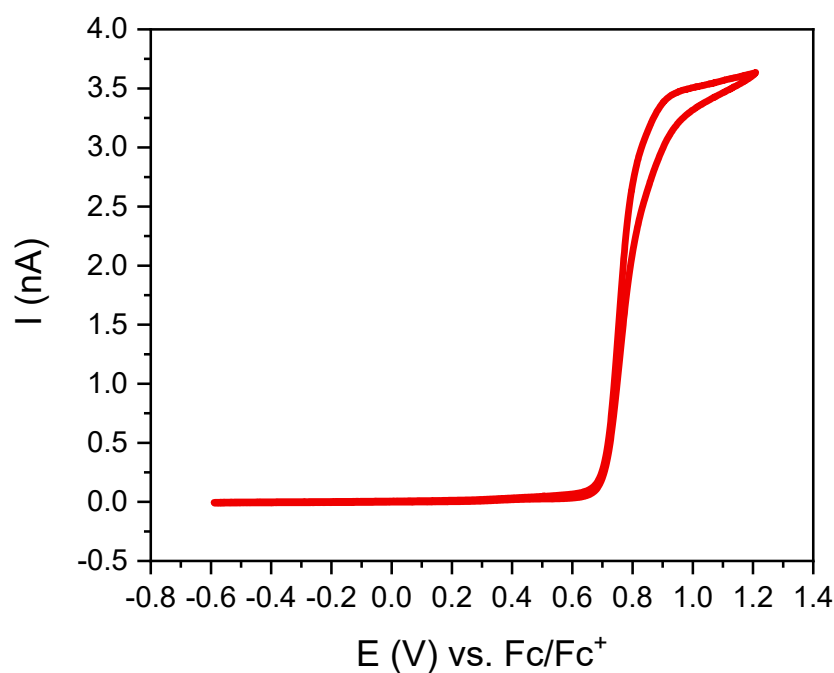
and:

$$\tau = \frac{4Dt}{r^2} \quad (\text{eqn. S3})$$

With c = bulk concentration, n = number of electrons transferred, D = diffusion constant, r = radius of the microdisk electrode and F = Faraday constant.

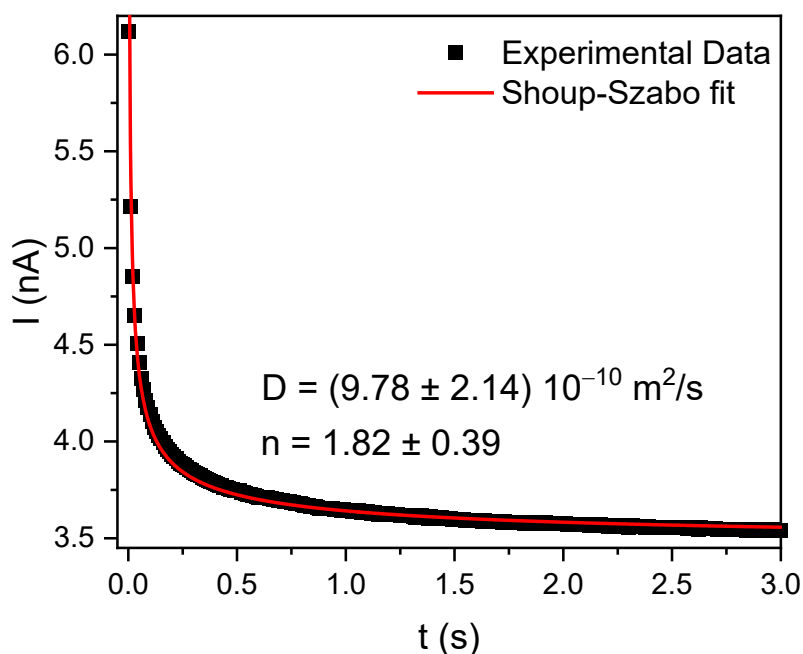
As shown by Compton and co-workers, both D and n can be simultaneously obtained by deconvolution of the current-response obtained from a simple chrono-amperometric experiment by non-linear curve fitting according to the equations above (when r and c are known).⁶

This analysis was carried out herein for **1** via chronoamperometry of a 1 mM solution of **1** in CH₂Cl₂, 100 mM TBAPF₆ using a Pt microdisk electrode ($r = 5 \mu\text{m}$) and OriginPro 2018. Figure S28 shows the CV under these conditions, while Figure S29 shows the CA current response.



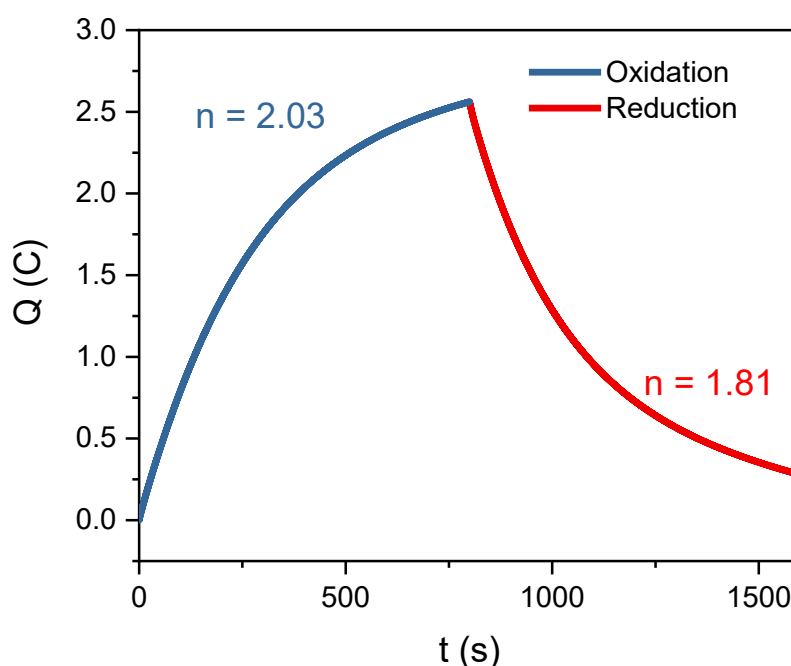
Supplementary Figure 28: CV of 1 mM **1** in CH_2Cl_2 , 100 mM TBAPF_6 at a Pt micro disk electrode ($r = 5 \mu\text{m}$) at $v = 100 \text{ mV/s}$.

Analysis of this current response according to the equations shown above affords a good fit to the experimental data with $D = 9.8 \times 10^{-10} \text{ m}^2/\text{s}$ and $n = 1.82$, confirming that the oxidation wave of the BTX derivatives corresponds to transfer of two electrons.



Supplementary Figure 29: Chronoamperometric current response ($E = 1.01 \text{ V}$) for the oxidation of 1 mM **1** in CH_2Cl_2 , 100 mM TBAPF_6 at a Pt micro disk electrode ($r = 5 \mu\text{m}$) including a fit according to the Shoup-Szabo equation.

This was further supported by controlled-potential bulk electrolysis of **1** in 1:1 (v/v) CH₃CN/CH₂Cl₂, 100 mM TBAPF₆ in a divided bulk electrolysis cell, which again confirmed that the oxidation wave is comprised of two electrons (Figure S30). Additionally, this confirmed that reduction also proceeds via two electrons. The mixed solvent system containing 50% CH₃CN was chosen to ensure good solubility of both the neutral and dicationic charge state of **1**.



Supplementary Figure 30: Controlled-potential chronocoulometry of 13.1 μ mol **1** in 1:1 (v/v) CH₃CN/CH₂Cl₂, 100 mM TBAPF₆ in a divided bulk electrolysis cell (WE: porous carbon, CE: Pt wire coil, RE: Ag/AgNO₃) confirming that both oxidation and reduction proceed via two electrons.

4.3 Mechanism for Change in Redox Potential Upon Irradiation

As mentioned in the main text, we hypothesized that the lowered oxidation potential of the *syn*-folded BTX switch state is related to its first ionization potential, i.e. its HOMO energy, for the first one electron oxidation ($E_{\text{Syn},1}$ and $E_{\text{Af},1}$ in Figure S15). According to Koopmans' theorem,⁷ within the Hartree-Fock approximation, the first ionization energy of a molecule is equal to the negative of the energy of the HOMO. While this theorem is not exact for DFT-calculated energies, numerous studies report accurate predictions of ionization potentials using this method at the DFT level.^{8,9}

Figures S31-32 and Table S2-3 show the valence orbitals energy diagram and highest occupied orbitals at the ω B97X-D4/def2-TZVPD level of theory for both folded isomers of *E*-**1** and *Z*-**1**, respectively. As shown in Figures S31 and S32, the HOMO energies for all isomers (*E* and *Z* as well as *syn*- and *anti*-folded) are very similar.

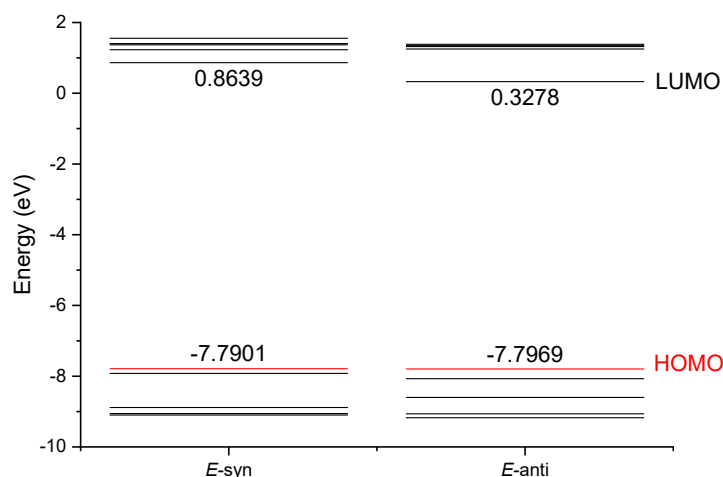
Specifically, at the ω B97X-D4/def2-TZVPD level of theory, the following difference in ionization potential (IP) are obtained between the *syn*- and *anti*- forms of the *E*- and *Z*-isomers:

$$\Delta IP_{anti/syn}(E-1) = IP_{anti}(E-1) - IP_{syn}(E-1) = -\epsilon HOMO(E-anti-1) - (-\epsilon HOMO(E-syn-1)) = 7.7969 - 7.7901 = \mathbf{0.0068 \text{ eV}} \quad (eqn. S4)$$

$$\Delta IP_{anti/syn}(Z-1) = IP_{anti}(Z-1) - IP_{syn}(Z-1) = -\epsilon HOMO(Z-anti-1) - (-\epsilon HOMO(Z-syn-1)) = 7.7915 - 7.7751 = \mathbf{0.0164 \text{ eV}} \quad (eqn. S5)$$

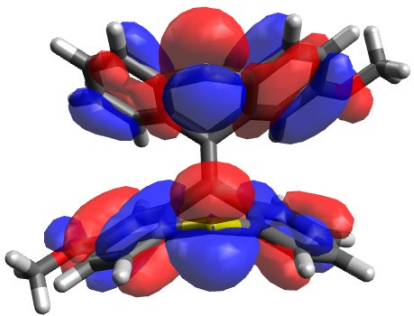
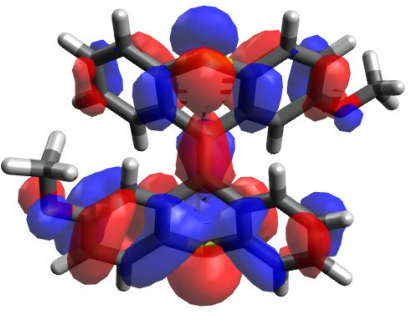
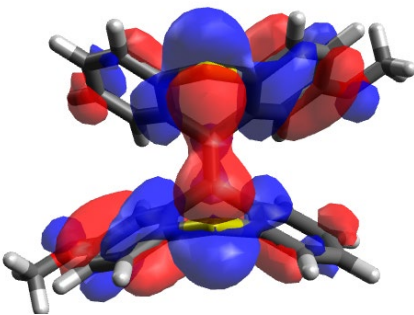
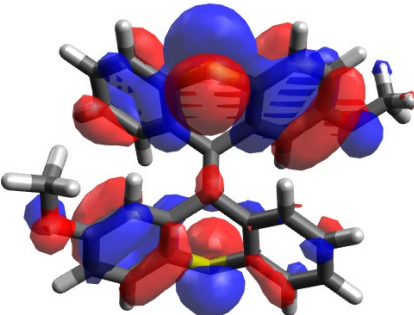
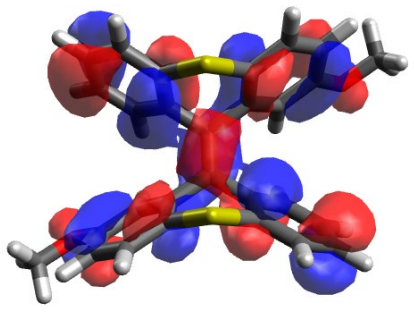
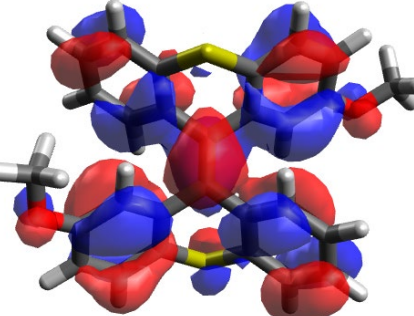
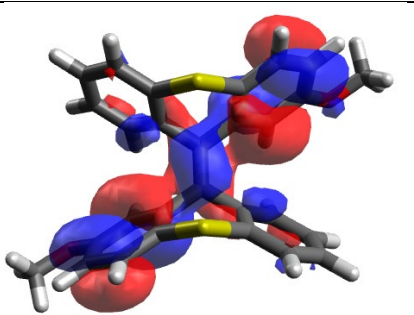
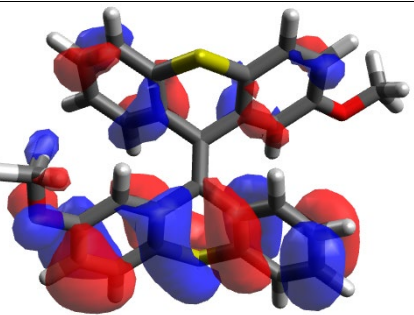
This suggests that the *syn*- form of both *E* and *Z* isomers are slightly easier to oxidize than the *anti*- form, with a difference of 7 and 16 mV respectively. However, these differences are too small to explain the experimentally observed difference in oxidation potential, whereby the *syn*-folded state displays at least 100 mV lower E_{Ox} (Figure S13). This suggests that other factors need to be considered to explain the full extent of the observed difference in oxidation potentials. Specifically, this could be related to the kinetics of the “C” step or a complete change in oxidation mechanism (e.g. CEE), however this requires further in-depth electrochemical and theoretical studies, which are beyond the scope of this work.

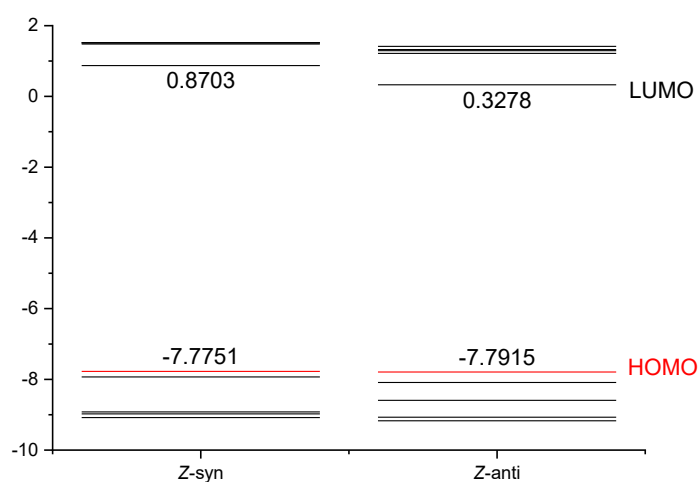
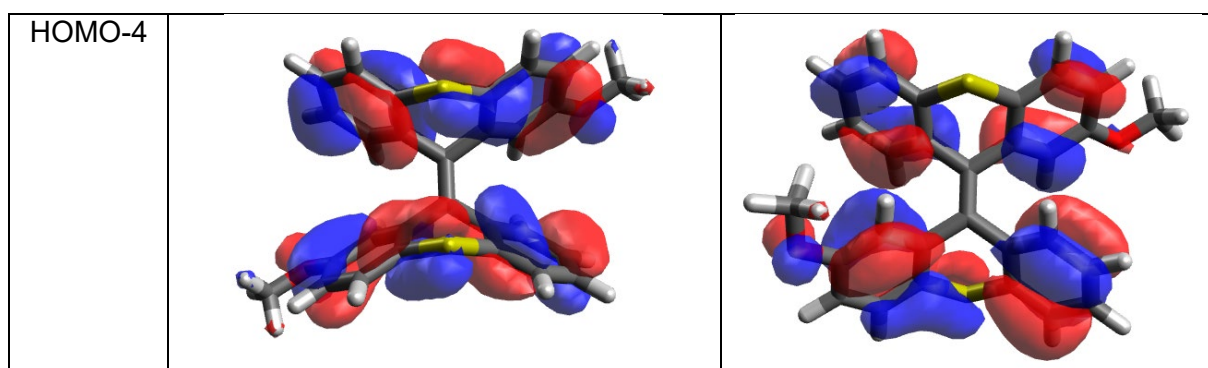
Lastly, we would also like to highlight that these calculations correctly predict an increase in HOMO-LUMO gap upon light-induced switching to the *syn*-folded state, as is indeed observed experimentally by a blue-shift in the absorbance spectrum (Figure 3B).



Supplementary Figure 31: Valence orbitals energy diagram (LUMO-4 to HOMO+4) for the *E*-*syn* and *E*-*anti* isomers of **1** at the ω B97X-D4/def2-TZVPD level of theory.

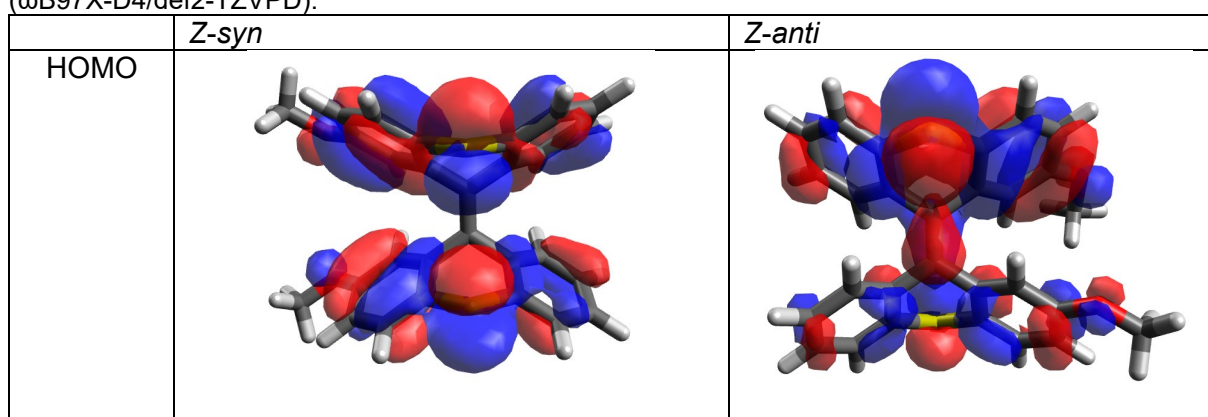
Supplementary Table 2: Plot of the highest occupied orbitals for the *E-syn* and *E-anti* isomers of **1** (ω B97X-D4/def2-TZVPD).

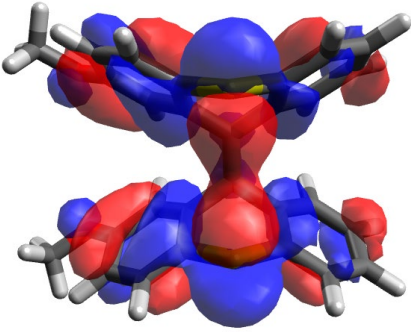
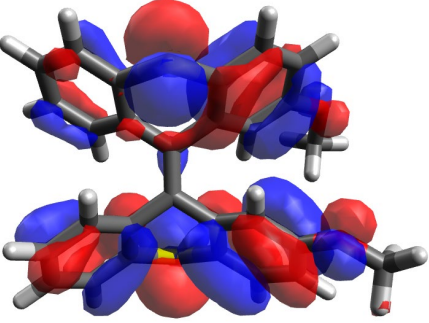
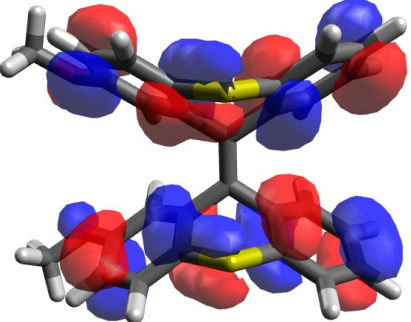
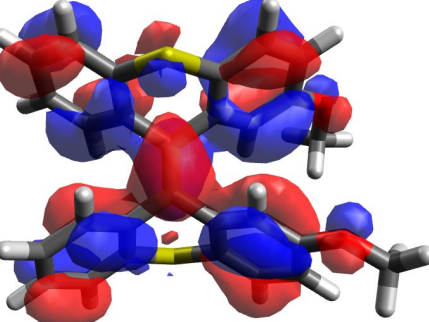
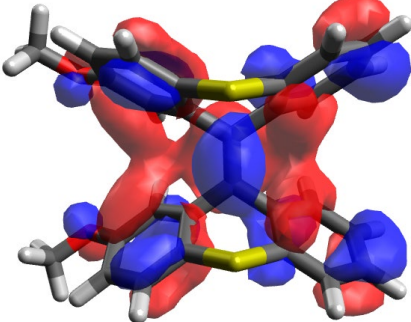
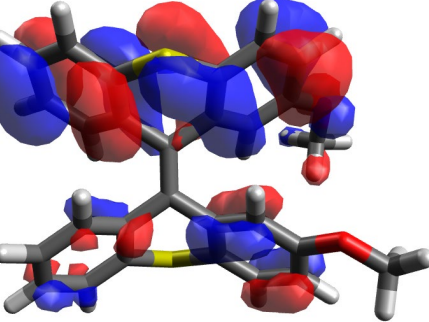
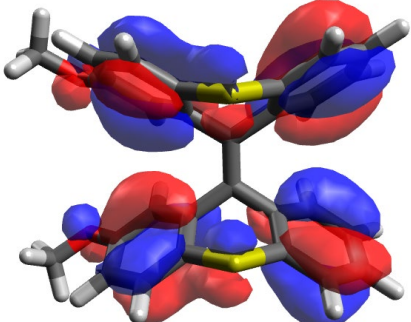
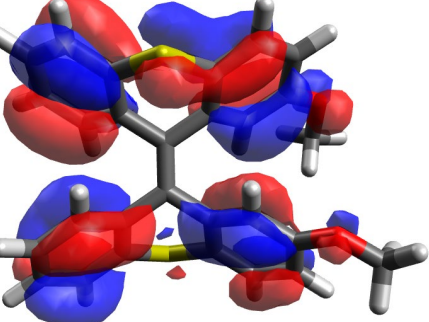
	<i>E-syn</i>	<i>E-anti</i>
HOMO		
HOMO-1		
HOMO-2		
HOMO-3		



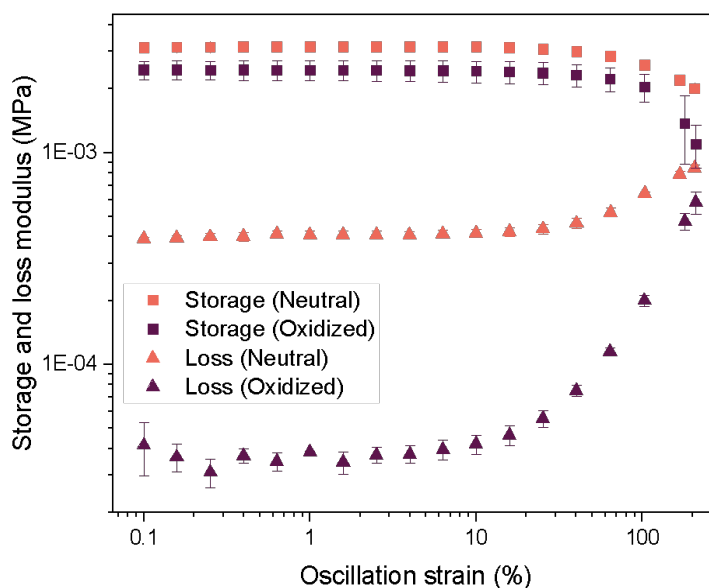
Supplementary Figure 32: Valence orbitals energy diagram (LUMO-4 to HOMO+4) for the Z-syn and Z-anti isomers of **1** at the ω B97X-D4/def2-TZVPD level of theory.

Supplementary Table 3: Plot of the highest occupied orbitals for the Z-syn and Z-anti isomers of **1** (ω B97X-D4/def2-TZVPD).

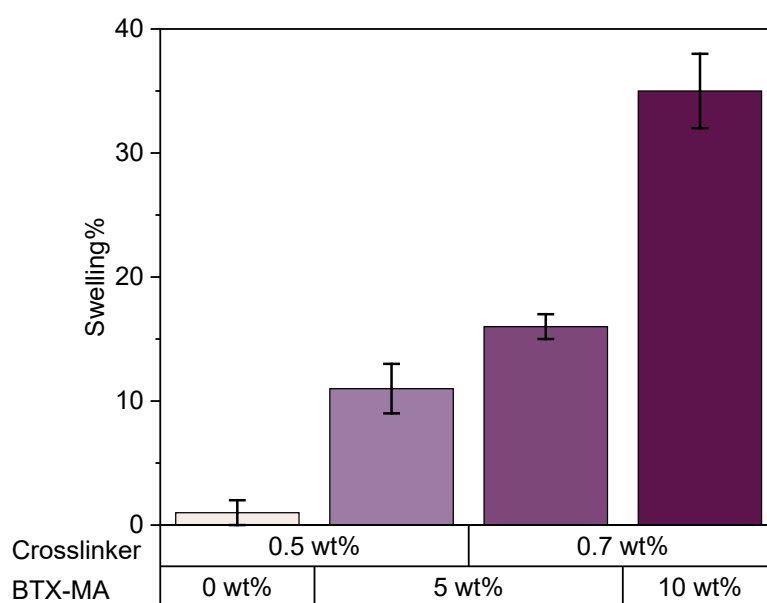


HOMO-1	 A 3D visualization of the HOMO-1 molecular orbital. The molecule is shown in a skeletal structure with red and blue isosurfaces representing the positive and negative phases of the orbital. The orbital is localized on the central part of the molecule, with large lobes on the nitrogen atoms and smaller lobes on the carbon atoms.	 A 3D visualization of the HOMO-1 molecular orbital from a different perspective. The red and blue lobes are clearly visible, showing the spatial distribution of the orbital across the molecule's framework.
HOMO-2	 A 3D visualization of the HOMO-2 molecular orbital. The orbital is distributed across the molecule, with significant lobes on the nitrogen atoms and some on the carbon atoms. The red and blue phases are well-defined.	 A 3D visualization of the HOMO-2 molecular orbital from a different perspective. The spatial distribution of the orbital is shown with red and blue lobes.
HOMO-3	 A 3D visualization of the HOMO-3 molecular orbital. The orbital is spread throughout the molecule, with large lobes on the nitrogen atoms and smaller lobes on the carbon atoms. The red and blue phases are clearly visible.	 A 3D visualization of the HOMO-3 molecular orbital from a different perspective. The spatial distribution of the orbital is shown with red and blue lobes.
HOMO-4	 A 3D visualization of the HOMO-4 molecular orbital. The orbital is distributed across the molecule, with significant lobes on the nitrogen atoms and some on the carbon atoms. The red and blue phases are well-defined.	 A 3D visualization of the HOMO-4 molecular orbital from a different perspective. The spatial distribution of the orbital is shown with red and blue lobes.

5 Material Optimization & Rheology



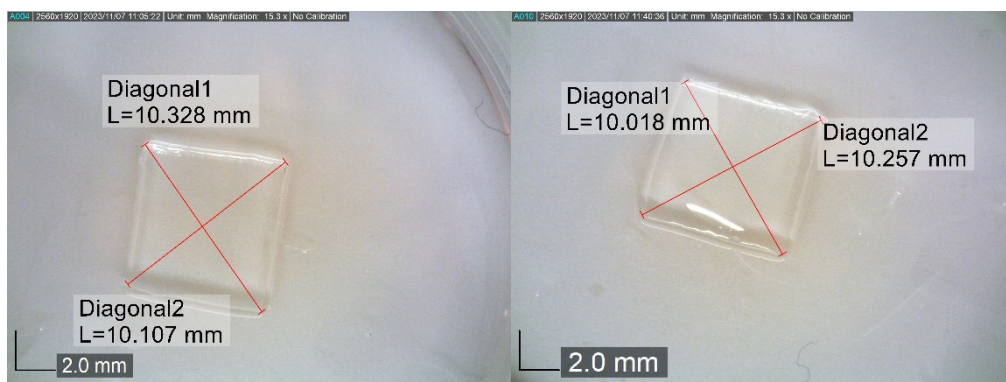
Supplementary Figure 33: Plot of the storage (G') and loss modulus (G'') of **BTX-gel** and **BTX-gel²⁺** vs. the oscillation strain. Error bars represent one standard deviation of independent triplicate experiments.



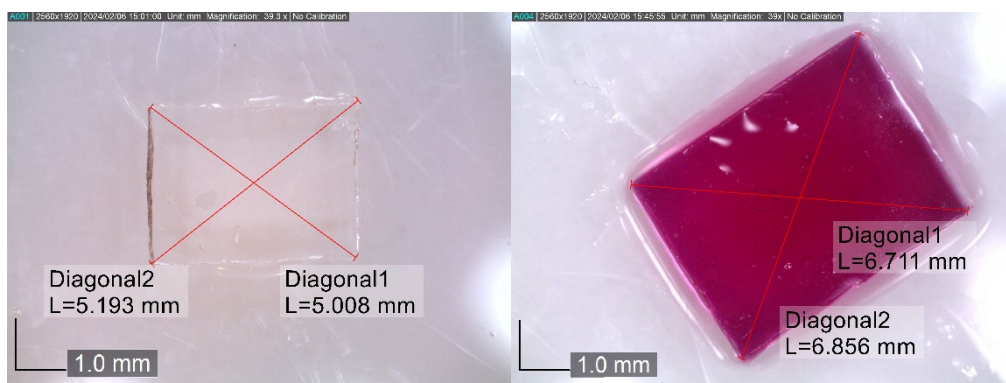
Supplementary Figure 34: Bar graph showing the oxidation-induced swelling for several different material compositions. Error bars represent one standard deviation of independent triplicate experiments.

6 Swelling

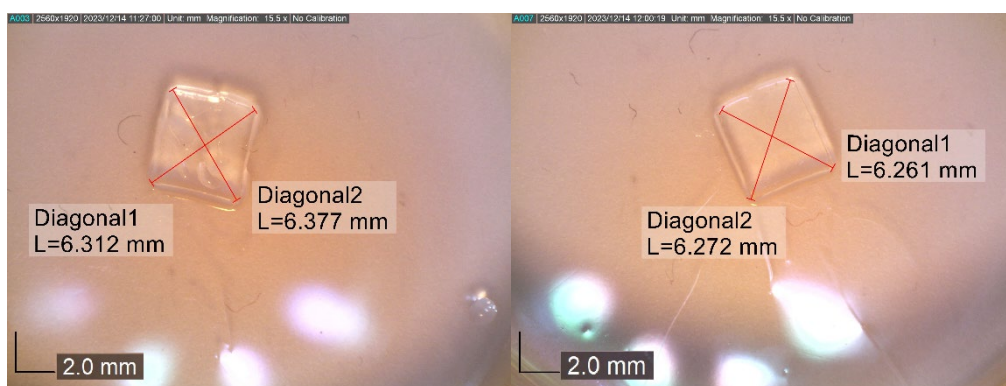
The effect of the oxidant strength (CAN or $\text{Fe}(\text{ClO}_4)_3$) and irradiation (dark or 365 nm light) on the swelling of the BTX hydrogels was studied and the results are summarized in Figure S40. For each condition, representative photographs of the hydrogel pieces are shown in Figures S36-39. To ensure that the swelling effect is due to BTX, a 'blank' gel consisting of the same components as the **BTX-gel** except **BTX-MA** was also treated with CAN. This did not lead to swelling, proving that the increase in size of the gels is due to oxidation from BTX to BTX^{2+} (Figure S35). Every experiment described below was repeated at least three times.



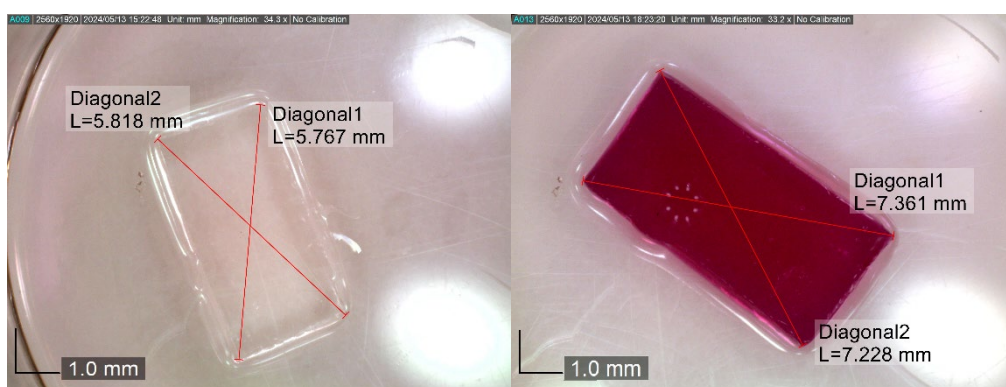
Supplementary Figure 35: Photographs of a piece of 'blank' gel consisting of 99% *N,N*-dimethylacrylamide, 0.7% *N,N*-methylenebisacrylamide and 0.3% IRG819, i.e. the polymer matrix without BTX, before (left) and after (right) treatment with 15 mM CAN. This experiment was performed to exclude any influence of CAN on the swelling of the polymer matrix without BTX. No change was observed in these gels after treatment with CAN.



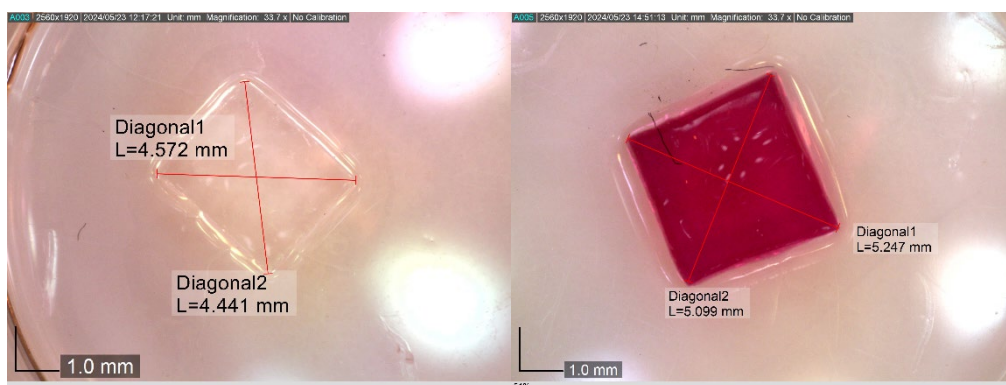
Supplementary Figure 36: Photographs of a piece of **BTX-gel** before (left) and after (right) treatment with 15 mM CAN in water.



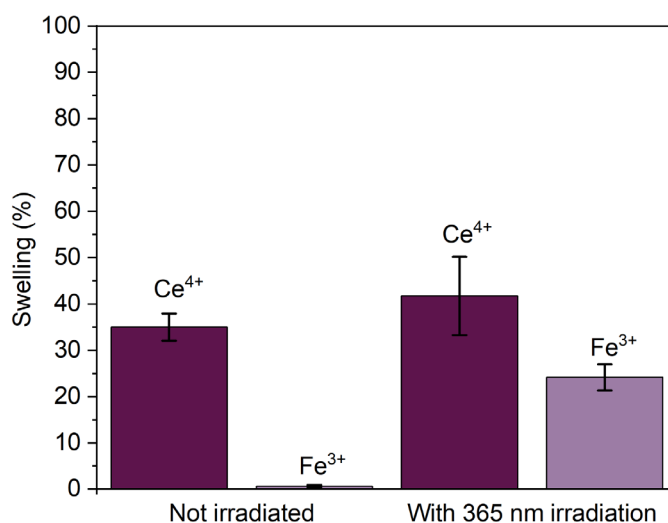
Supplementary Figure 37: Photographs of a piece of **BTX-gel** in water before (left) and after (right) treatment with 30 mM $\text{Fe}(\text{ClO}_4)_3$ without irradiation.



Supplementary Figure 38: Photographs of a piece of **BTX-gel** in water (left) and after treatment with 30 mM $\text{Fe}(\text{ClO}_4)_3$ and 365 nm light (right).



Supplementary Figure 39: Photographs of a piece of **BTX-gel** in water (left) and after treatment with 15 mM CAN and 365 nm light (right).



Supplementary Figure 40: Bar graph illustrating the %increase in characteristic length of **BTX-gel** squares in different oxidation conditions. Using CAN in the dark led to a $35 \pm 3\%$ increase in size, and $\text{Fe}(\text{ClO}_4)_3$ without irradiation had no effect on the size of the gel. CAN with 365 nm light irradiation caused the material to swell $42 \pm 8\%$ and $\text{Fe}(\text{ClO}_4)_3$ with 365 nm irradiation caused the material to swell $24 \pm 3\%$. Error bars represent one standard deviation of independent triplicate experiments.

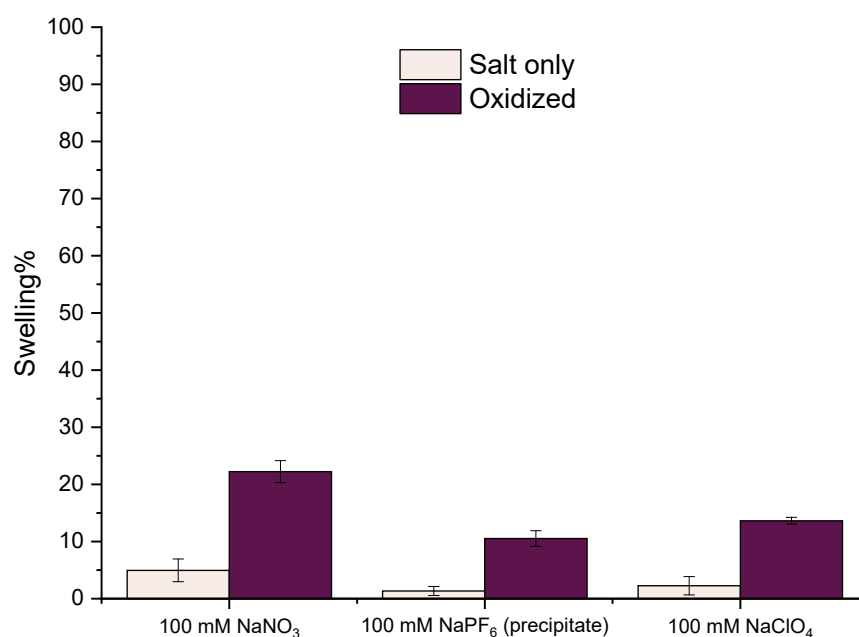
Swelling experiments in the presence of various salts and pH

In order to study the influence of various salt and pH conditions on the swelling behaviour of the neutral gel, as well as for the chemical oxidation with CAN, the following experiments were carried out:

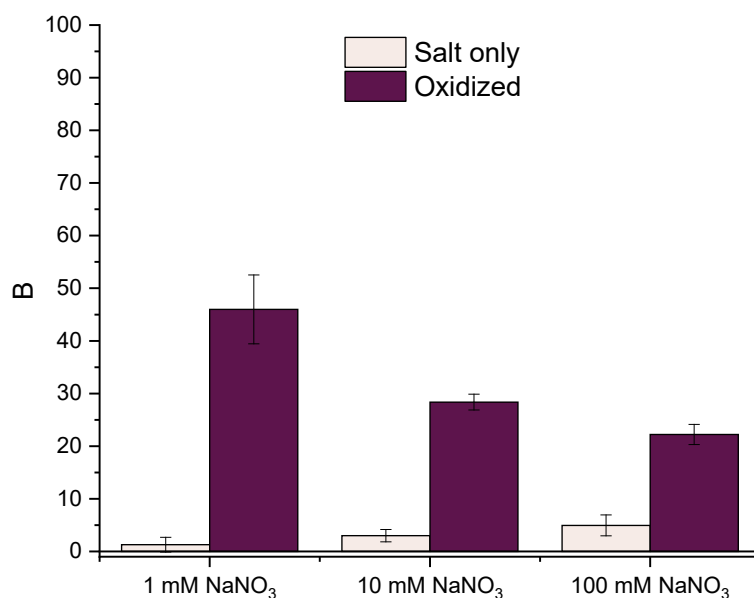
The size of the **BTX-gel** was first measured in pure water. The medium was then exchanged with the salt solution and after 30 minutes of equilibration the size was measured again. Afterwards, CAN was added (15 mM total, added as a stock solution of same salt concentration/pH) and the oxidized gels were equilibrated in the oxidant for 2 hours. The oxidized gels were then washed with pure salt solution and their size remeasured.

As shown in Figure S41, the nature of the counter anion (NO_3^- , PF_6^- or ClO_4^-) did not significantly alter the swelling properties of the gel, neither in the neutral state, nor after oxidation. Only for PF_6^- a slightly smaller swelling magnitude was observed after oxidation, however this can in part be attributed to some degree of precipitation formed by reaction between the CAN oxidant and the counter anion. Nevertheless, gel oxidation was still observed.

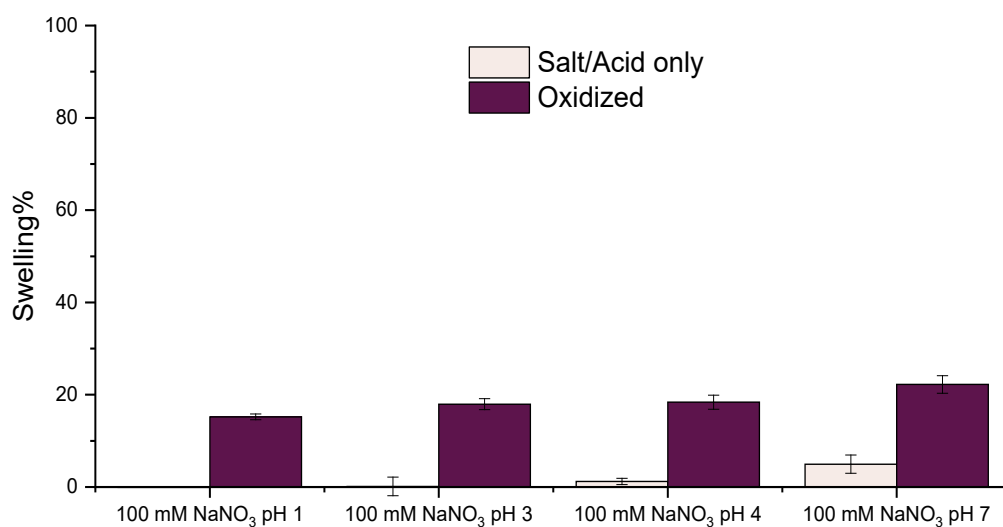
As shown in Figures S42 and S43, increasing the ionic strength (either by increase of the electrolyte concentration (NaNO_3) or by lowering the pH using HNO_3 (at a constants background concentration of 100 mM NaNO_3) induced a small decrease in the degree of swelling upon oxidation. For the swelling of the neutral gels upon exchange of the medium from pure water to the electrolyte, no clear trends that correlate with overall ionic strength were observed, however the change in gel size was comparably small in all cases ($\max 5 \pm 2\%$) for 100 mM NaNO_3 at pH 7.



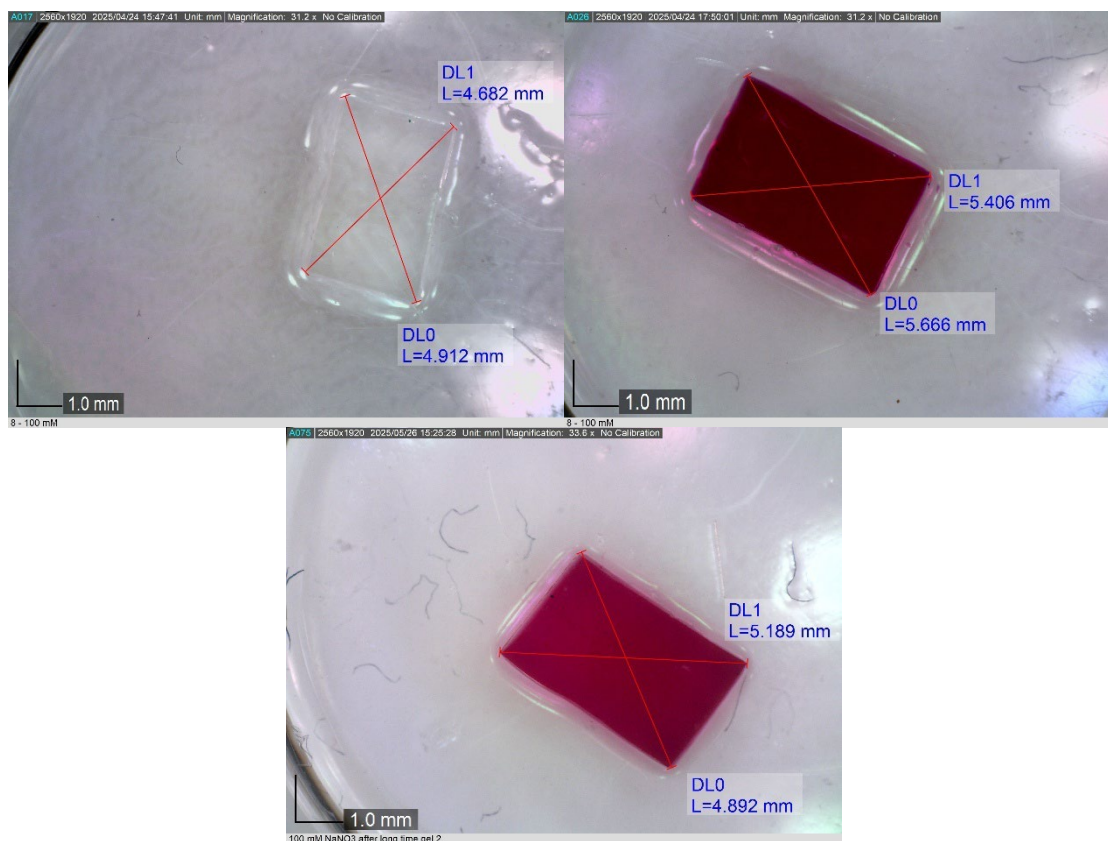
Supplementary Figure 41: Swelling percentage (% increase in the characteristic length) of **BTX-gel** after the exchange of the swelling medium from water to a 100 mM sodium salt solution (off-white bars) and after oxidation using CAN (15 mM) in the same salt solution (purple bars), relative to the size of the gel in water. Upon addition of CAN to the gel in 100 mM NaPF₆ some precipitate was observed, however the oxidation still took place. Error bars represent one standard deviation of independent triplicate experiments.



Supplementary Figure 42: Swelling percentage (% increase in the characteristic length) of **BTX-gel** after the exchange of the swelling medium from water to NaNO₃ solutions with different concentrations (off-white bars) and after oxidation using CAN (15 mM) in the same salt solution (purple bars), relative to the size of the gel in water. Error bars represent one standard deviation of independent triplicate experiments.

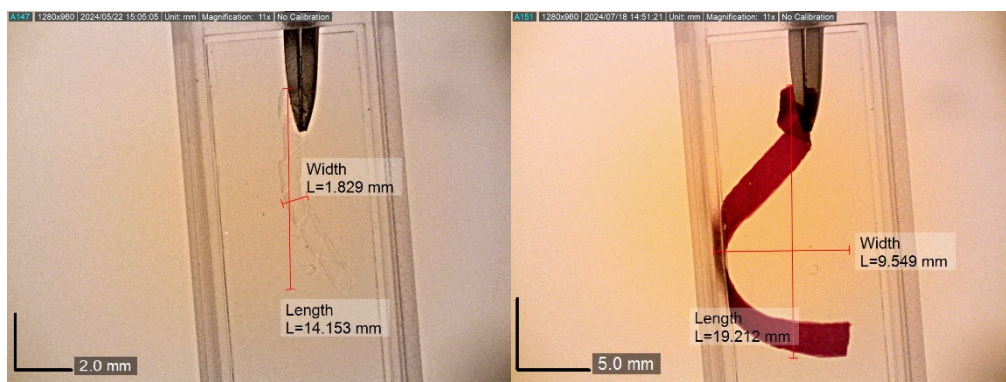


Supplementary Figure 43: Swelling percentage (% increase in the characteristic length) of **BTX-gel** after the exchange of the swelling medium from water to a 100 mM NaNO₃ solution with different pH (off-white bars) and after oxidation using CAN (15 mM, at the same pH; purple bars), relative to the size of the gel in water. The pH was adjusted using HNO₃. Error bars represent one standard deviation of independent triplicate experiments.

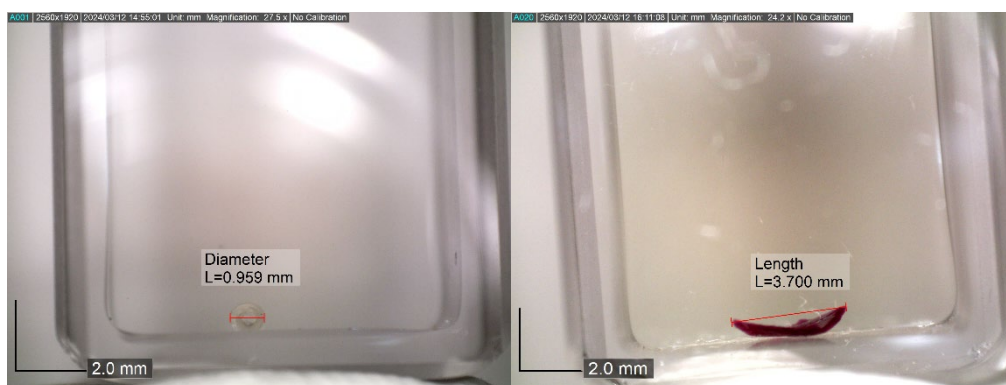


Supplementary Figure 44: Pictures of the BTX-gel in 100 mM NaNO₃ (top left), after oxidation with 15 mM CAN (top right) and after one month in the salt solution (due to some solvent evaporation the exact concentration of NaNO₃ is not known).

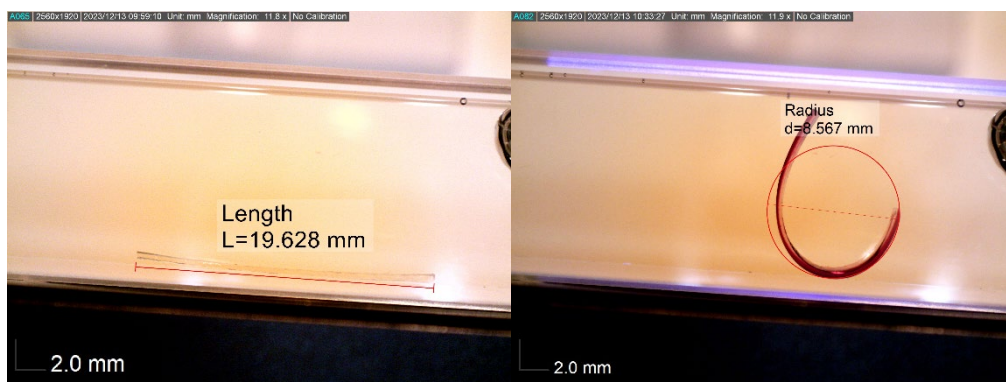
7 Actuation



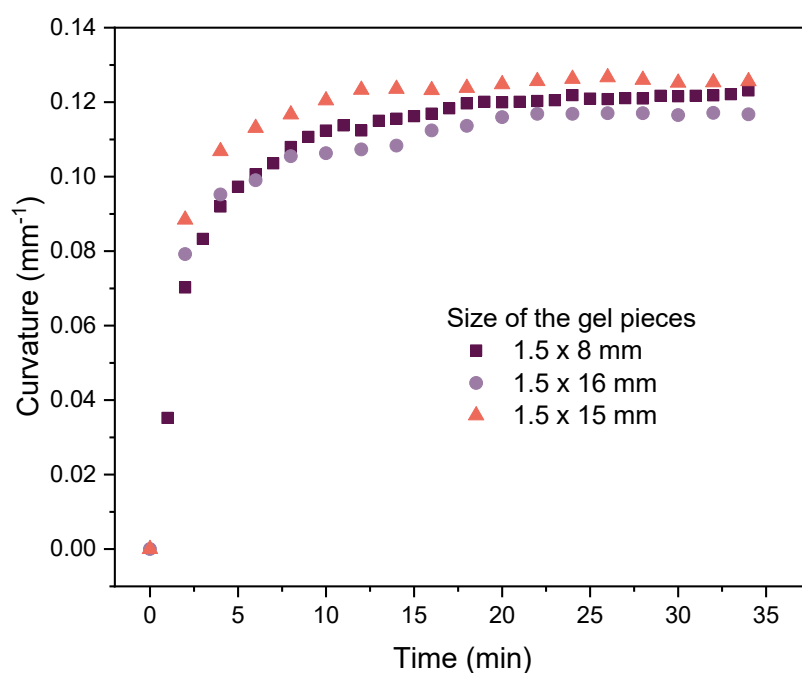
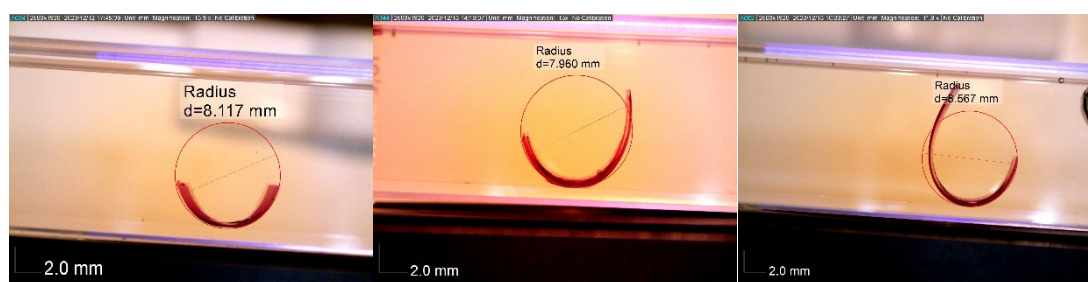
Supplementary Figure 45: BTX-gel helix prepared *via* Method 2 before (left) and after (right) oxidation with CAN.



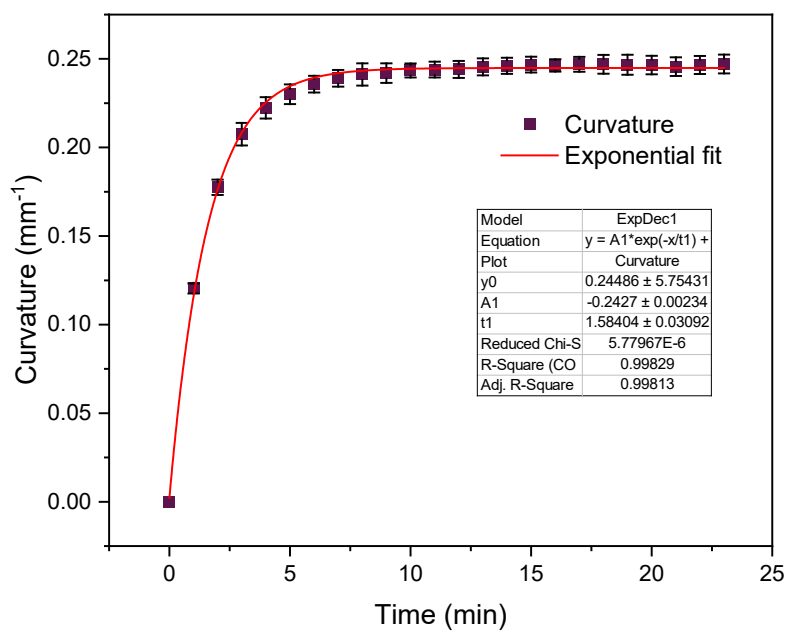
Supplementary Figure 46: BTX-gel curl prepared *via* Method 2 before (left) and after (right) oxidation with CAN.



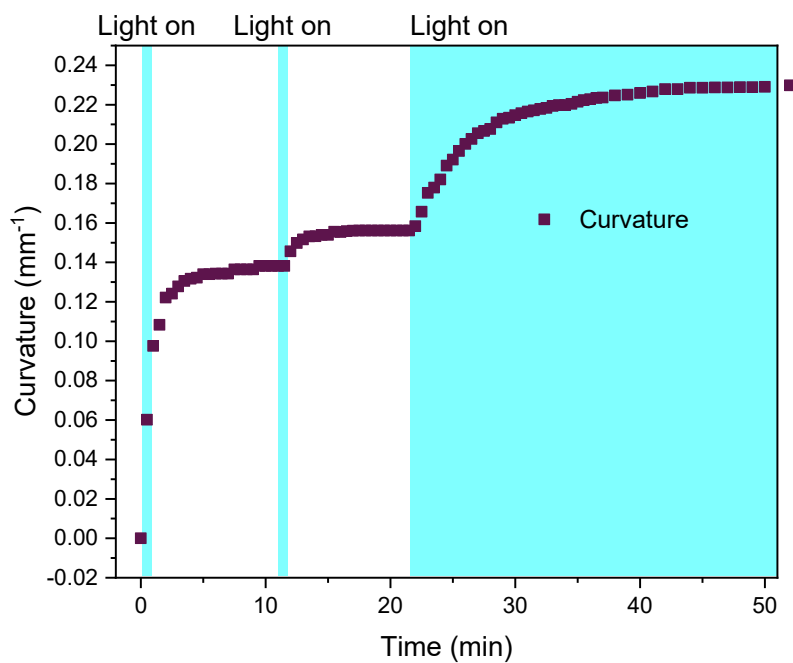
Supplementary Figure 47: Isotropic BTX-gel strip in 30 mM $\text{Fe}(\text{ClO}_4)_3$ prepared *via* Method 1 before (left) and after (right) continuous 365 nm irradiation from the bottom.



Supplementary Figure 48: (TOP) Images of three isotropic **BTX-gel** strips in 30 mM $\text{Fe}(\text{ClO}_4)_3$ prepared via Method 1 after irradiation and 365 nm irradiation from the bottom. (BOTTOM) Plot of the change in curvature ($1/r$, r = radius) over time of these three isotropic **BTX-gel** strips in 30 mM $\text{Fe}(\text{ClO}_4)_3$ prepared under continuous 365 nm irradiation from the bottom.

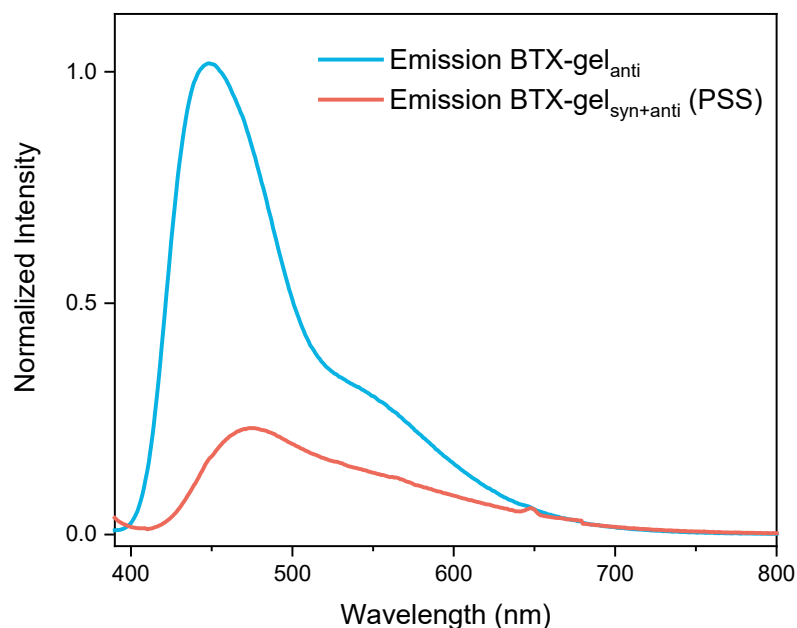


Supplementary Figure 49: Curvature of the gel strips over time under continuous 365 nm irradiation in the presence of 30 mM $\text{Fe}(\text{ClO}_4)_3$. Error bars represent one standard deviation of three independent samples sized 2 x 14 mm.

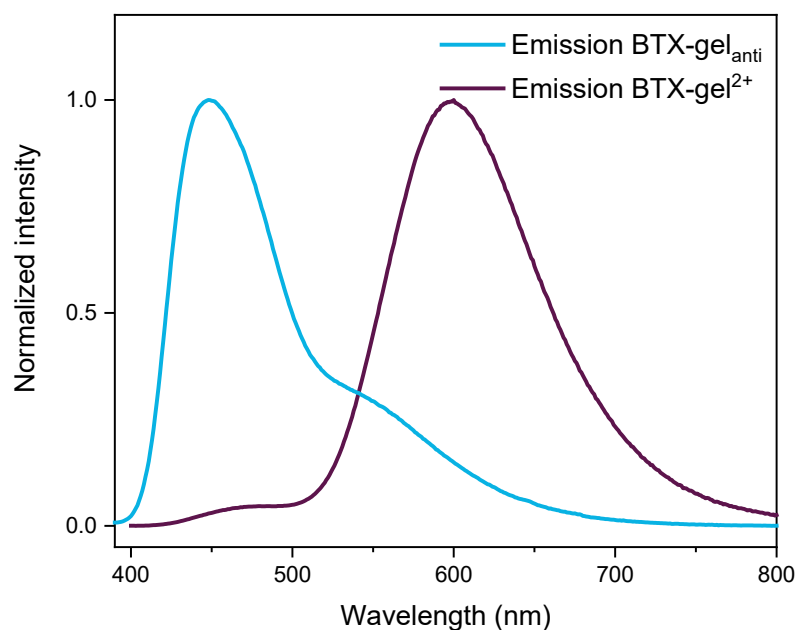


Supplementary Figure 50: Curvature of a gel strip over time with intermittent 365 nm irradiation (cyan) and in the dark (white) in the presence of 30 mM $\text{Fe}(\text{ClO}_4)_3$. The first two shorter irradiations were 20 s each.

8 Fluorescence



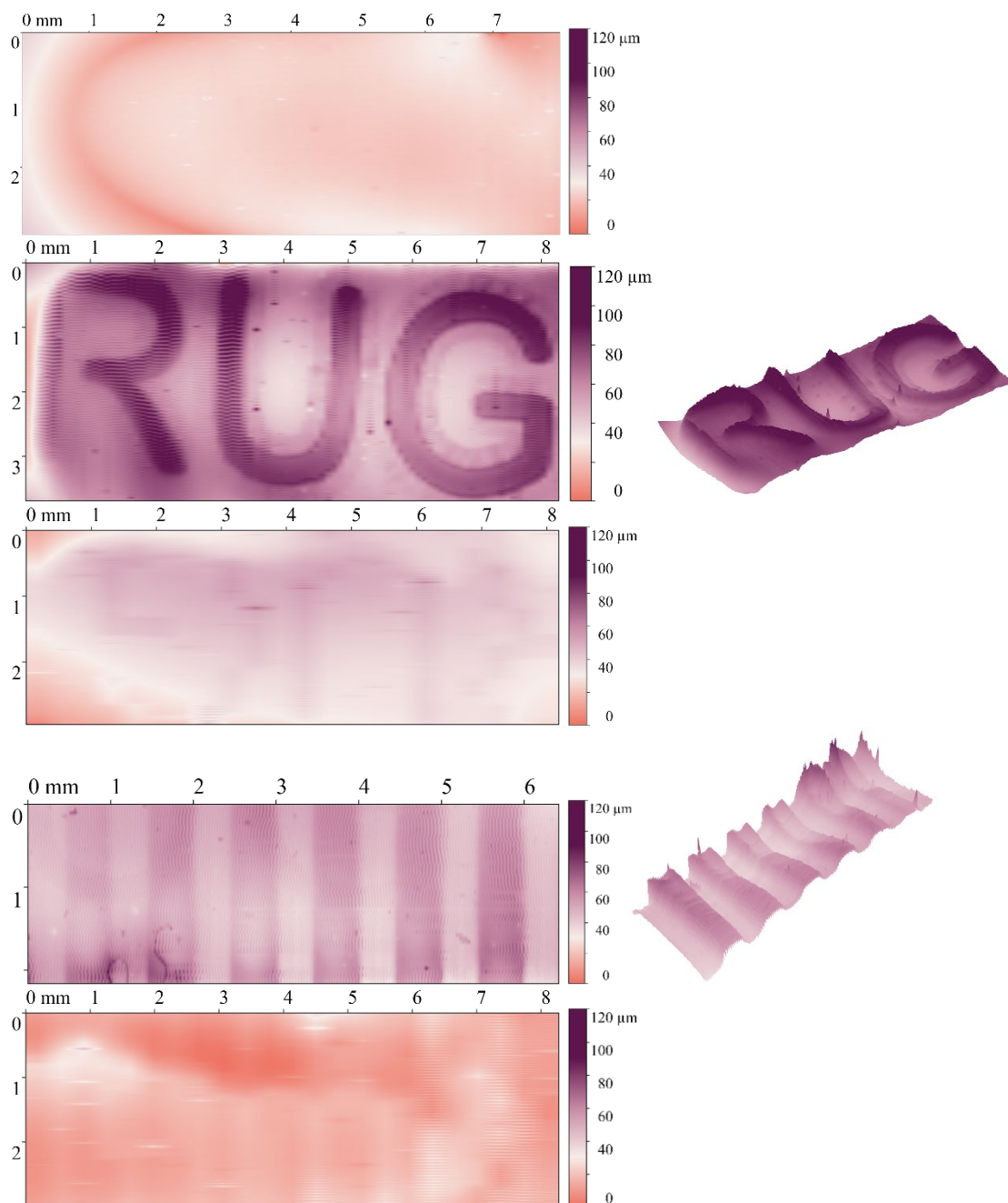
Supplementary Figure 51: Normalized fluorescence emission spectra ($\lambda_{ex} = 365$ nm) of **BTX-gel_{anti}** in water and after 5 min ex-situ irradiation with 365 nm light, corresponding to mostly **BTX-gel_{syn}**. There is some residual fluorescence because it was difficult to fully convert every *anti*-folded BTX into *syn*-folded inside the hydrogel. Additionally, it was not possible to irradiate with the 365 nm LED while recording the emission spectrum. Therefore, considering the half-life of *syn*-folded BTX, there is always going to be a small amount of relaxation during the measurement.



Supplementary Figure 52: Normalized fluorescence emission spectra of **BTX-gel_{anti}** ($\lambda_{ex} = 365$ nm) and **BTX-gel²⁺** (obtained by oxidation with 15 mM CAN) ($\lambda_{ex} = 350$ nm)

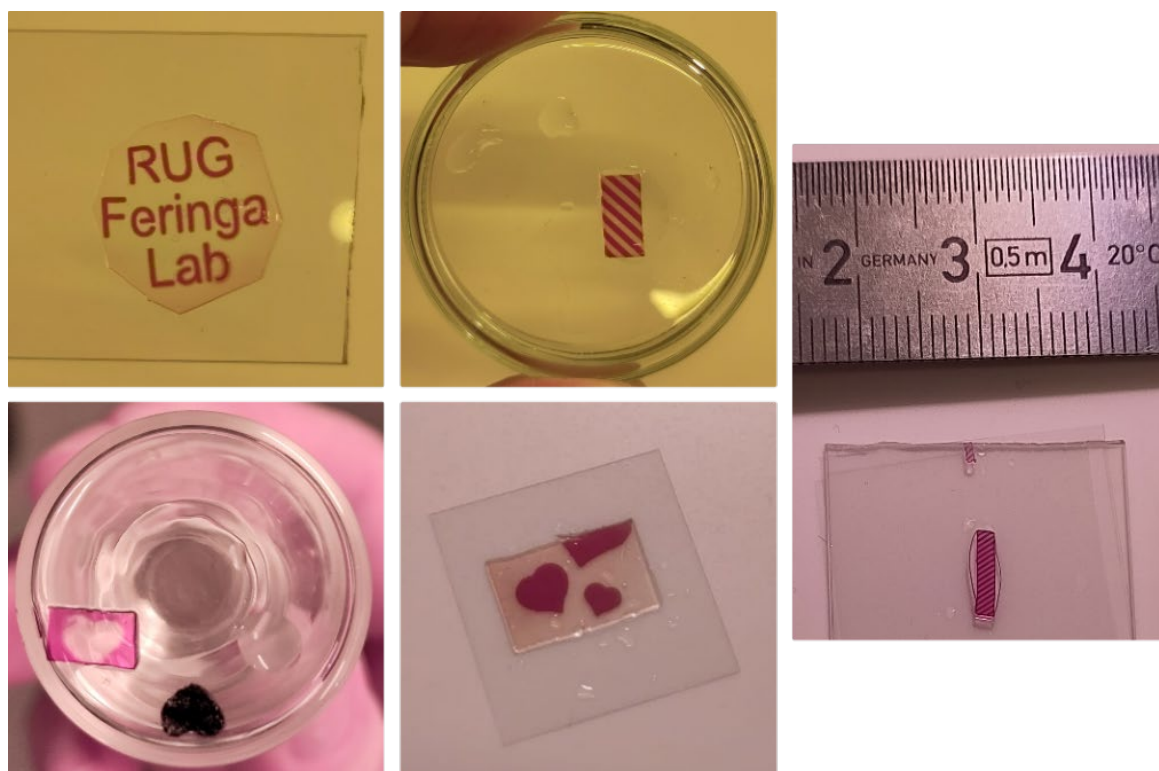
9 Profilometry

The line profile scans and 3D mapping of the surface topography were performed using a DektakXT Bruker profilometer with a stylus tip radius of 12.5 μm and 1 mg of stylus force. An average thickness of the polymer on the glass slide, when using a 100 μm spacer to prepare the polymer, was found to be 148.8 μm , which is in accordance with the size increase between the freshly polymerized gel and the gel in water.



Supplementary Figure 53: 2D and 3D profiles of **BTX-gel** after applying and erasing various patterns.

10 Patterning



Supplementary Figure 54: Photographs of different patterns on freestanding BTX-gel (Method 1) prepared via the patterning procedure described in the Extended Data. The bottom right (heart) photomask is also visible, drawn in black marker. The other samples were made using metal photomasks. Photographs taken using a Fairphone 4 camera.

11 Supplementary References

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