

Supporting Information

Highlighting spin selectivity properties of chiral electrode surfaces from redox potential modulation of an achiral probe under applied magnetic field

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SI.1 Experimental Procedures

SI.1.1. Synthesis

The monomer 2,2'-bis(2,2'-bithiophene-5-yl)-3,3'-bithianaphthene, BT_2T_4 , was synthesized as racemate [SI 1] and then resolved into the two enantiopure antipodes through chiral-HPLC according to the procedure described in [SI 2].

The enantiopure monomer (2*R*,3*R*)-2,3-dimethyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine, *c*-EDOT, was synthesized according to the procedure described in [SI 3].

Achiral 2,3-dihydrothieno[3,4-*b*][1,4]dioxine, EDOT, was purchased from Sigma Aldrich and used without further purification.

SI.1.2 Electrodeposition of thiophene-based thin films

Magnetochemistry measurements were carried out employing as working electrode (WE) a slice (0.8 × 4.5) cm² of ITO coated glass where a chiral enantiopure organic thin film or an achiral one was electrodeposited on an area of about 1 cm². Films were electrodeposited by potentiodynamic oxidation of the corresponding monomer at 0.2 V s⁻¹ in acetonitrile (ACN) + 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) supporting electrolyte by cycling the potential in a proper electrochemical window including the oxidation peak of the corresponding monomer. The three types of thiophene-based thin films were prepared according to the following protocols:

- Enantiopure oligo-(*R*) and oligo(*S*)- BT_2T_4 films: (*R*)- or (*S*)- BT_2T_4 monomer 5·10⁻⁴ M, by cycling from 1 to 10 times the potential in the 0-1.35 V vs SCE windows;
- Enantiopure *c*-PEDOT films: *c*-EDOT monomer 5·10⁻⁴ M, by cycling from X times the potential in the -0.2-1.1 V vs SCE windows;
- Achiral PEDOT films: EDOT monomer 5·10⁻⁴ M, by cycling from X times the potential in the -0.2-1.1 V vs SCE windows

It is important to underline that during the deposition step no external magnetic field was applied.

SI 1.3 Experimental magnetoelectrochemistry set-up

Magnetoelectrochemistry study was carried using a cuvette as working cell where the hybrid ITO| film WE, a Pt wire as counter electrode and an aqueous saturated calomel electrode (SCE) as reference one were immersed in a solution containing the achiral redox couple, made by:

- i)* an equimolar aqueous solution of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (indicated as Fe(III)/Fe(II)), each of them at 2.5 mM concentration, with 400 mM KCl as supporting electrolyte;
- ii)* a 2 mM solution of ferrocene in ACN with 0.1 M TBAPF₆ as supporting electrolyte.

A magnetic field perpendicular to the electrode surface was applied by placing a permanent magnet (nickel-coated NdFeB B88X0 Grade N42 K&J Magnet, Inc.) close to the WE, at a distance of around 2.6 mm (considering that the thickness of ITO-coated glass electrode and cuvette were ca. 1 mm and ca. 1.6 mm, respectively). The nominal magnetic field strength at the surface of the magnet is 6353 Gauss. Change in the orientation of the magnetic field was obtained by mechanically flipping the magnet around its magnetic axis (north vs south orientation).

Measurements changing the strength of the magnetic field were carried out by placing rigid plastic foils of different thickness (0.1 mm, 0.3 mm, 0.8 mm, 1 mm, 2 mm, 3 mm) between the cuvette and the permanent magnet and by recording CV signals of the achiral redox couples mechanically flipping the magnet. These additional tests were performed on enantiopure oligo-(*S*)-BT₂T₄ film that was electrodeposited on ITO electrode at constant protocol as described above.

Measurements changing the thickness of the inherently chiral films were obtained by electrodepositing enantiopure (*S*)-BT₂T₄ monomer by varying the number of deposition cycles (10, 4, 2, 1) and then recording CV signals of the achiral Fe(III)/Fe(II) couple mechanically flipping the magnet.

SI.2 Additional Data and Results

SI.2.1 Key parameters of magnetoelectrochemistry experiments related to Figure 2

Table SI.2.1. Key CV parameters (related patterns are shown in Figure 2) obtained for Fe(III)/Fe(II) redox couple recorded at 0.2 V s⁻¹ potential scan rate on: bare ITO electrode (without magnet), on hybrid ITO/oligo-(S)- and oligo-(R)-BT₂T₄ electrodes (with and without magnet), and on hybrid ITO/c-PEDOT interface (with magnet).

	$E_{p,an}/$ V vs. SCE	$E_{p,cat}/$ V vs. SCE	$E_{1/2}^a/$ V vs. SCE	$\Delta E_{1/2}^b/$ V
<i>Bare ITO</i>	0.25	0.13	0.19	
oligo-(S)-BT ₂ T ₄	0.29	0.08	0.18	
oligo-(R)-BT ₂ T ₄	0.29	0.08	0.18	
oligo-(S)-BT ₂ T ₄ - <i>South</i>	0.07	-0.06	-0.00	-0.47
oligo-(S)-BT ₂ T ₄ - <i>North</i>	0.52	0.42	0.47	
oligo-(R)-BT ₂ T ₄ - <i>South</i>	0.53	0.43	0.48	0.51
oligo-(R)-BT ₂ T ₄ - <i>North</i>	0.00	-0.07	-0.03	
c-PEDOT- <i>South</i>	0.10	-0.10	0.00	-0.15
c-PEDOT- <i>North</i>	0.25	0.05	0.15	

^a Half-wave potential, $E_{1/2}$, is calculated according to $E_{1/2} = (E_{p,an} + E_{p,cat})/2$.

^b $\Delta E_{1/2}$ corresponds to the difference between the $E_{1/2}$ related to the two specular cases: $E_{1/2}^{(S) \text{ film-South}} - E_{1/2}^{(S) \text{ film-North}}$ and/or $E_{1/2}^{(R) \text{ film-South}} - E_{1/2}^{(R) \text{ film-North}}$ obtained by flipping magnet orientation (*South* or *North*) and changing film configuration ((*R*) or (*S*)).

SI.2.2 Effect of the chiral film thickness on the shift of the Fe(III)/Fe(II) peak potential in magnetoelectrochemistry experiments

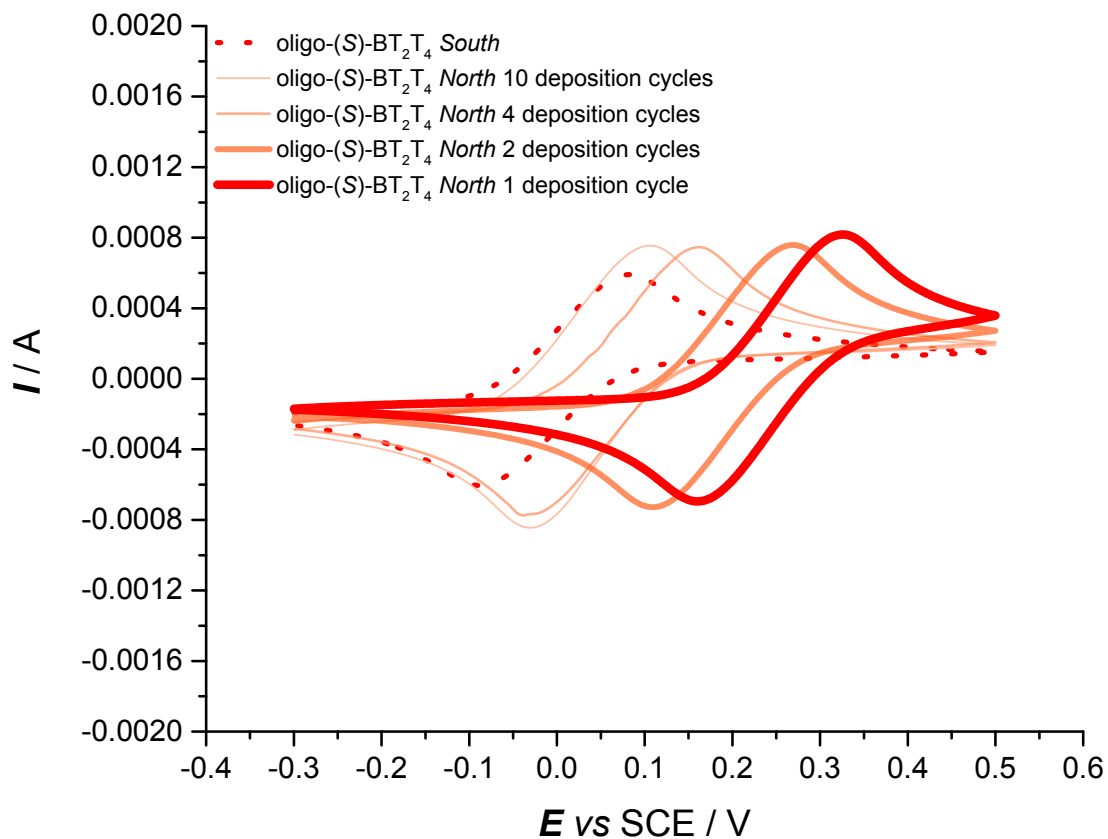


Figure SI.2.2. CV patterns recorded at 0.2 V s^{-1} for the Fe(III)/Fe(II) achiral redox couple on hybrid ITO/oligo-(S)-BT₂T₄ electrode as a function of the applied magnetic field orientation (solid lines *North* vs dashed line *South*) by increasing from 1 to 10 the electrodeposition cycles. For *South* orientation only one curve (1 cycle) has been reported, because all the CV patterns recorded by varying the deposition cycles are practically superimposed.

SI.2.3 Effect of the magnet distance on the shift of Fe(III)/Fe(II) peak potentials in magnetoelectrochemistry experiments

Table SI.2.3. Relevant data observed for the Fe(III)/Fe(II) achiral couple (**Figure 3 in the main paper**) by varying cuvette-magnet distance and the magnet orientation, using oligo-(S)-BT₂T₄ film. All peaks and half-wave potential values are referred to SCE electrode.

Cuvette-magnet distance / mm	South orientation			North orientation			$E_{1/2, \text{North}} - E_{1/2, \text{South}} / \text{V}$
	$E_{p, \text{an}} / \text{V}$	$E_{p, \text{cat}} / \text{V}$	$E_{1/2, \text{South}} / \text{V}$	$E_{p, \text{an}} / \text{V}$	$E_{p, \text{cat}} / \text{V}$	$E_{1/2, \text{North}} / \text{V}$	
3	0.24	0.11	0.18	0.25	0.12	0.19	0.01
2	0.23	0.12	0.18	0.27	0.15	0.21	0.03
1	0.20	0.09	0.15	0.25	0.16	0.21	0.06
0.8	0.18	0.07	0.13	0.27	0.17	0.22	0.09
0.3	0.15	0.05	0.10	0.30	0.20	0.25	0.15
0.1	0.11	-0.19	-0.04	0.32	0.22	0.27	0.31

^a Half-wave potential, $E_{1/2}$, is calculated according to $E_{1/2} = (E_{p, \text{an}} + E_{p, \text{cat}}) / 2$.

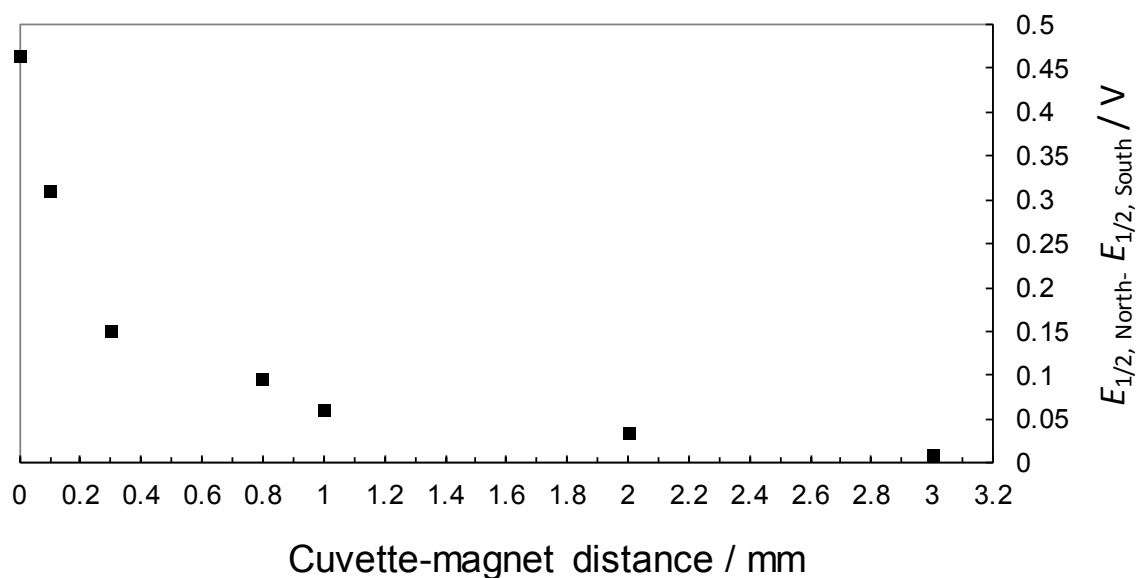


Figure SI.2.3. Relationship between cuvette-magnet distance and half-wave potential difference between the two voltammetric signals of the Fe(III)/Fe(II) redox couple related to north vs south orientations.

SI.2.4 Magnetochemistry experiments extended to a second probe (Fc⁺|Fc): CV patterns and related peak potentials as a function of the magnet distance

Figure SI.2.4.1. CV patterns recorded at 0.05 V s⁻¹ for the Fc⁺|Fc achiral couple in ACN + TBAPF₆ 0.1 M at hybrid ITO|oligo-(S)-BT₂T₄ interface, as a function of the applied magnetic field orientation (north vs south) and of the magnetic field strength (*i.e.*, modulated varying the magnet-cuvette distance).

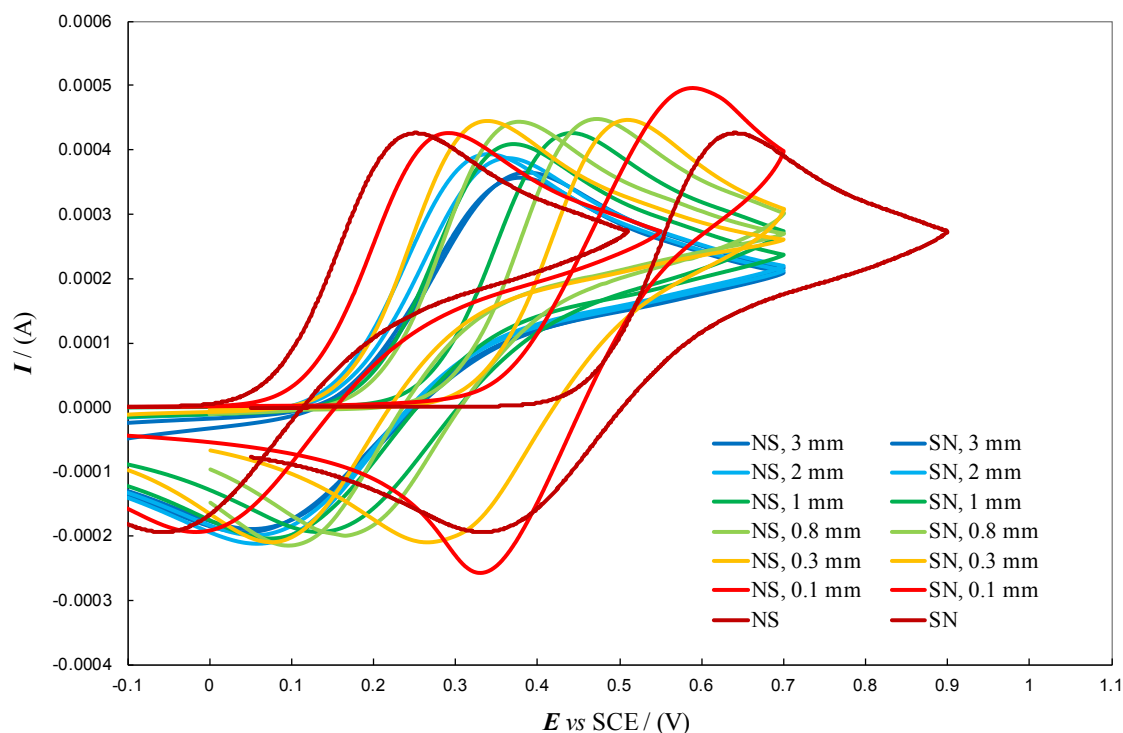
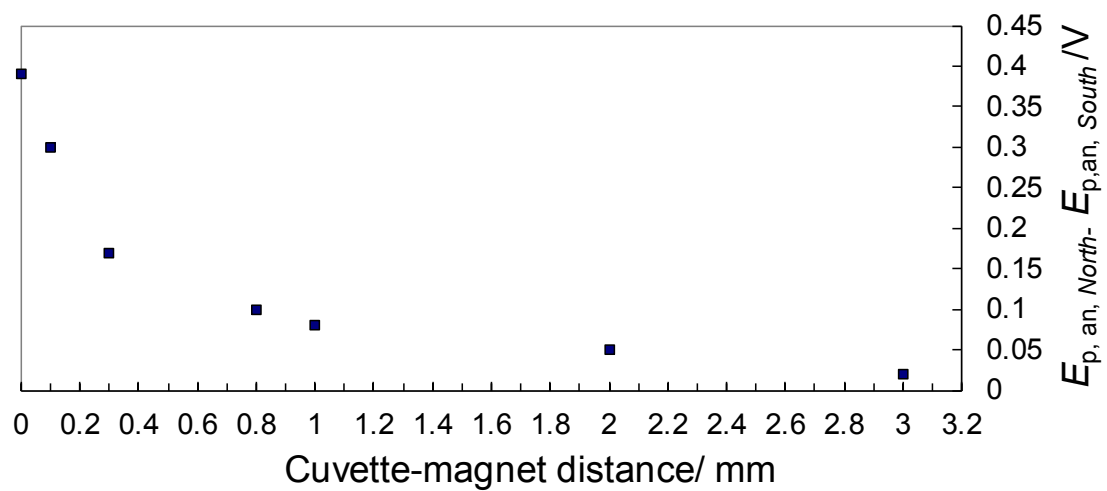


Table SI.2.4. Relevant data observed for the Fc⁺|Fc achiral couple by varying cuvette-magnet distance and the magnet orientation, depicted in **Figure SI.2.4.1**.

Cuvette-magnet distance / mm	$E_{p, an, South} /$ V vs SCE	$E_{p, an, North} /$ V vs SCE	$E_{p, an, North} - E_{p, an, South} /$ V vs SCE
3	0.37	0.39	0.02
2	0.33	0.38	0.05
1	0.36	0.44	0.08
0.8	0.37	0.47	0.10
0.3	0.34	0.51	0.17
0.1	0.29	0.59	0.30

^a Half-wave potential, $E_{1/2}$, is calculated according to $E_{1/2} = (E_{p,an} + E_{p,cat})/2$.

Figure SI.2.4.2. Relationship between cuvette-magnet distance and potential difference between the two voltammetric signals of $\text{Fc}^+|\text{Fc}$ redox couple related to north vs south orientations.



SI 2.5 "Control" magnetoelectrochemistry experiments with achiral PEDOT as thin film on ITO electrode

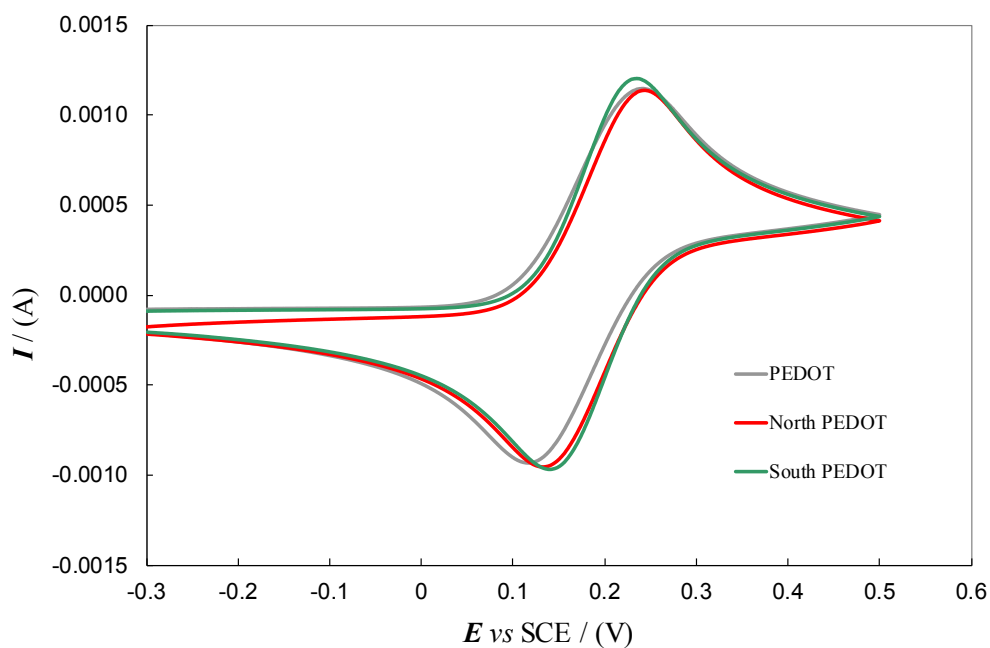


Figure SI.2.5. CV patterns recorded at 0.05 V s^{-1} for the Fe(III)/Fe(II) redox couple on hybrid ITO|achiral PEDOT electrode, without the external magnet (grey line) and as a function of the applied magnetic field orientation (red line: north orientation and green line: south orientation).

SI 2.6 Preliminary experiment on the temperature effect on the spin-related half-wave potential splitting of the $\text{Fc}^+|\text{Fc}$ achiral probe

Performing at low temperature (-35°C , in dry ice/methanol bath) the magneto-electrochemistry experiment with the achiral $\text{Fc}^+|\text{Fc}$ probe on oligo-(*R*)- BT_2T_4 films under application of the external magnetic field resulted in a significant increase of the half-wave potential splitting $\Delta E_{1/2}$, from ~ 0.39 V (room temperature) to ~ 0.50 V (-35°C).

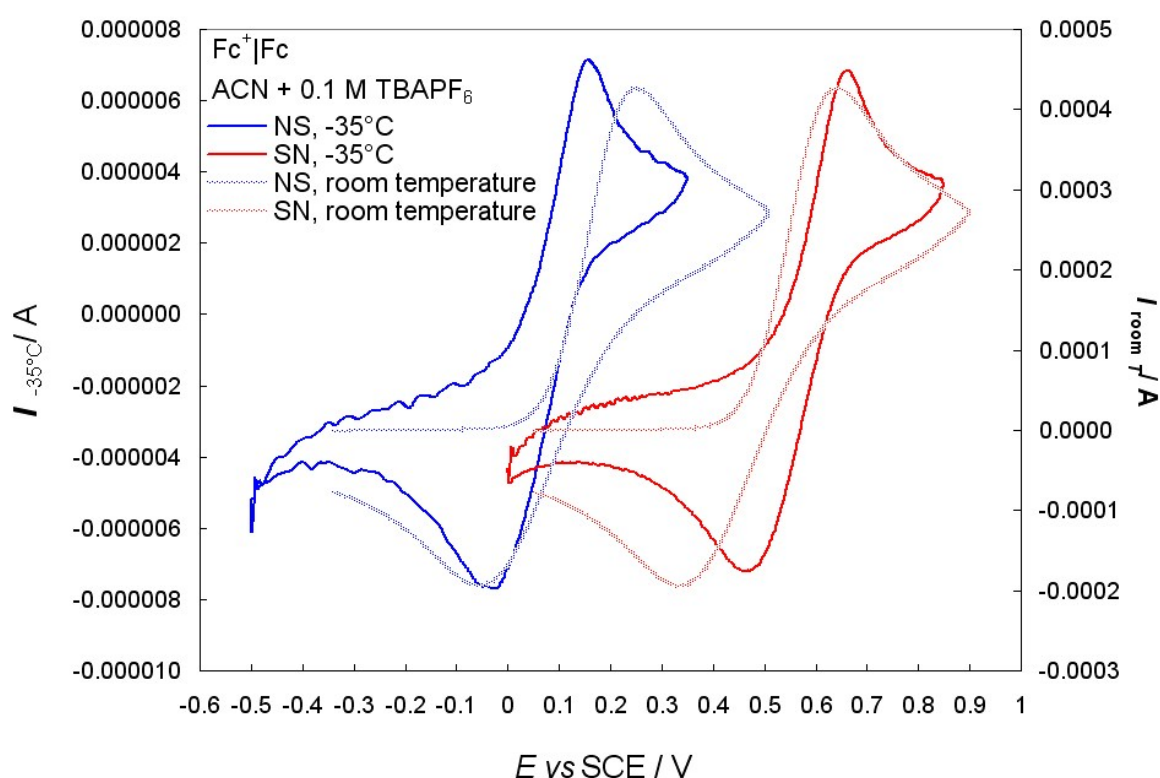


Figure SI.2.6. CV patterns recorded at 0.05 V s^{-1} for the $\text{Fc}^+|\text{Fc}$ achiral couple in ACN + TBAPF₆ 0.1 M at hybrid ITO|oligo-(*R*)- BT_2T_4 interface, as a function of the applied magnetic field orientation (north-south or south-north), at room temperature (shadowed lines, right-hand y axis) and at -35°C (solid lines, left-hand axis).

Interestingly, a similar effect can also be observed in magnetic CD, which, as mentioned in the main paper, shows striking analogies with our magneto-electrochemistry experiments.

The magnetic CD effect requires the achiral molecule to comply with at least one of three A, B, or C “Faraday terms”, each one representing a kind of interaction between ground states/excited states and external magnetic field.^{SI4} In particular, the C term is typical of paramagnetic molecules, like ferricinium Fc^+ and ferricyanide (III), the oxidized members of our reversible redox couples, which are low-spin paramagnetic complexes with an unpaired electron spin. It has been demonstrated that the C term originates from a Zeeman loss of degeneracy for the α or β spin configurations in the electron ground level energy under magnetic field. This results in a small excess for a spin configuration over the other one, remarkably increasing with decreasing temperature, with the CD spectrum becoming sharper and sharper at constant magnetic field. Actually, such temperature dependence is considered a diagnostic criterion for this effect.^{SI4}

SI.3. References

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[SI 4] B.Han, X. Gao, J. Lv, Z. Tang, *Adv. Mater.* **2018**, 1801491