Supporting Information

Spin Polarized Current in Chiral Organic Radical Monolayers

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1. Synthesis and monolayer deposition

FT-IR spectra were recorded with Spectrum Two FT-IR Spectrometer. ESI-MS spectra were recorded with a JEOL MStation JMS700. Melting points were measured with Stuart SMP50 Automatic Melting Point Apparatus. All the reactions were monitored and R_f was calculated by TLC on commercially available precoated plates (silica gel 60 F 254) and the products were visualized with acidic vanillin solution. Silica gel 60 (230–400 mesh) was used for column chromatography. Dry solvents were obtained by The PureSolv Micro Solvent Purification System unless otherwise specified. UV spectra were obtained on a Varian Cary 50 UV-Vis spectrophotometer. The HPLC resolution was performed on a HPLC Waters Alliance 2695 equipped with a 200 µL loop injector and a spectrophotometer UV Waters PDA 2996 using HPLC grade solvents purchased from Merck. The semipreparative resolution was carried out on a CHIRALPAK® IG semipreparative column (250 x 10 mm/ 5µm) purchased from Chiral Technologies Europe. The mobile phase, delivered at a flow rate 3.5 mL/min, was hexane/CH2Cl2 70/30 v/v. Enantiomeric excess was measured on a CHIRALPAK® IA analytical column (250 x 4.6 mm/ 5µm) purchased from Chiral Technologies Europe. The mobile phase, delivered at a flow rate 1.2 mL/min, was hexane/CH_2Cl_2 70/30 v/v. Elemental analysis was measured with a Thermoscientific FlashSmart Elemental Analyzer CHNS/O.

To a solution of (P)-NeuSAc or (M)-NeuSAc (25 mg, 0.04 mmol) in 2 mL of dry DCM, $AgSbF_6$ (17 mg, 0.05 mmol) was added. The dark solution was stirred at room temperature for 1 hour, then filtered through a sintered glass funnel and the volatiles were eliminated under reduced pressure. Dissolution of the crude material into a minimum amount of DCM and addition of n-hexane led to the precipitation of the desidered product (P)-RadESAc or (M)-RadESAc, as a dark blue solid (27 mg, 80%). mp 151-154 °C. UV-Vis (CH_2Cl_2): λ_{max} (ε) = 573 nm (8140), 396 nm (3150), 313 nm (15530). Anal. Calcd for $C_{39}H_{49}F_6NO_3S_3Sb$: C, 51.38; H, 5.42; N, 1.54; S, 10.55. Found: C, 51.40; H, 5.47; N, 1.58; S, 10.65

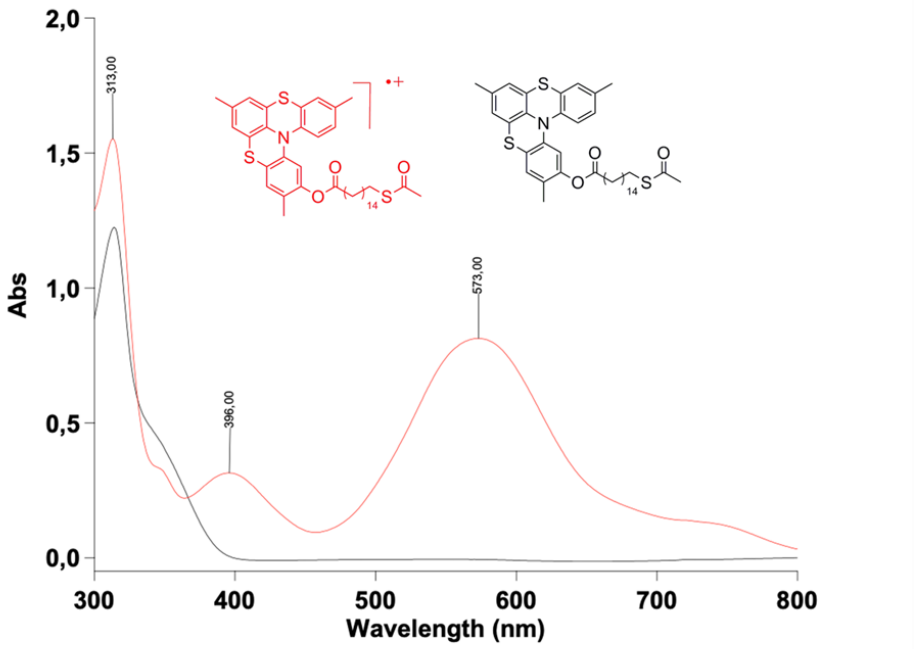

Figure S1 Uv-Vis Spectra of NeuSAc (black line) and of **RadESAc** (red line) in CH_2Cl_2 (10^{-4} M)

Substrates preparation and deposition of Self-Assembled Monolayer

The substrates for the XPS analysis were prepared by evaporating gold on mica slabs inside a vacuum chamber (≈ 10^{-6} mbar) with a deposition rate lower than 0.1 Å/s. The surface was prepared in ultra ultra-high vacuum (UHV) by sputtering cycles with Ar^+ ions and subsequent annealing at 430 K to induce the reconstruction of the Au(111) surface before proceeding with the deposition of the molecules. Surface cleanliness and reconstruction were controlled by XPS and STM measurements after preparation.
The substrates for the mc-AFM experiment were prepared using an e-beam evaporation, depositing on a clean Si wafer an adlayer of Ti (10 nm) followed by Ni (100 nm) and Au (10 nm). The substrate was then cleaned by immersing it in boiling acetone for 10 minutes and in boiling ethanol for additional 10 minutes. Finally, the substrate was kept under UV/ozone atmosphere for 15 minutes.
The molecular monolayer was prepared by incubating a precleaned substrate in a 2 mM solution of (P)-**RadESAc** or (M)-**RadESAc** in dichloromethane overnight at room temperature. The surface was then rinsed several times (3-4) with pure dichloromethane and dried under a N_2 atmosphere. The same solution used for the sample incubation was employed for the preparation of the dropcast sample to be used as reference in the XPS analysis.

2. XPS

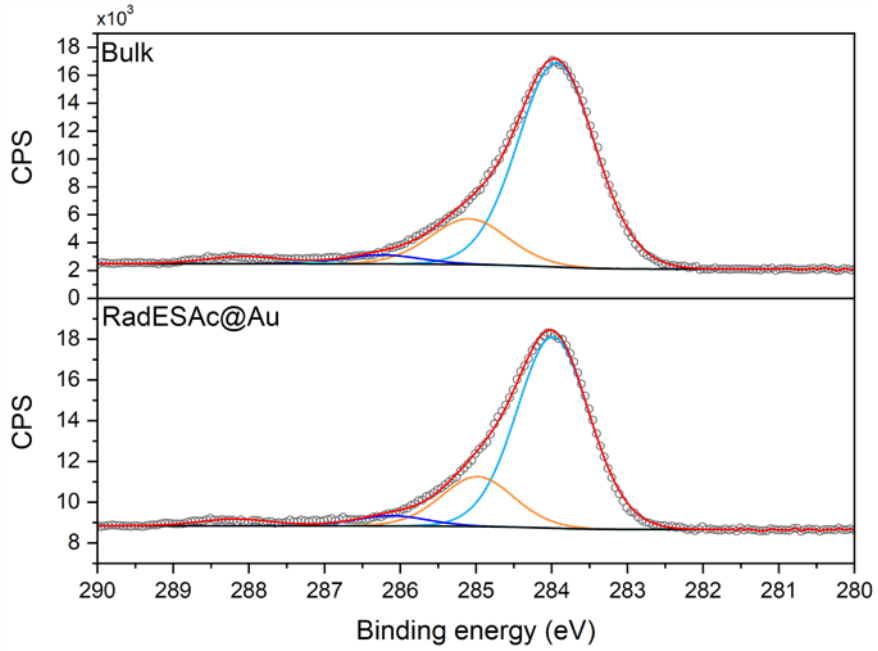

Figure S2 XPS C1*s* region of **RadESAc** bulk sample (top) and of **RadESAc@Au** (bottom)

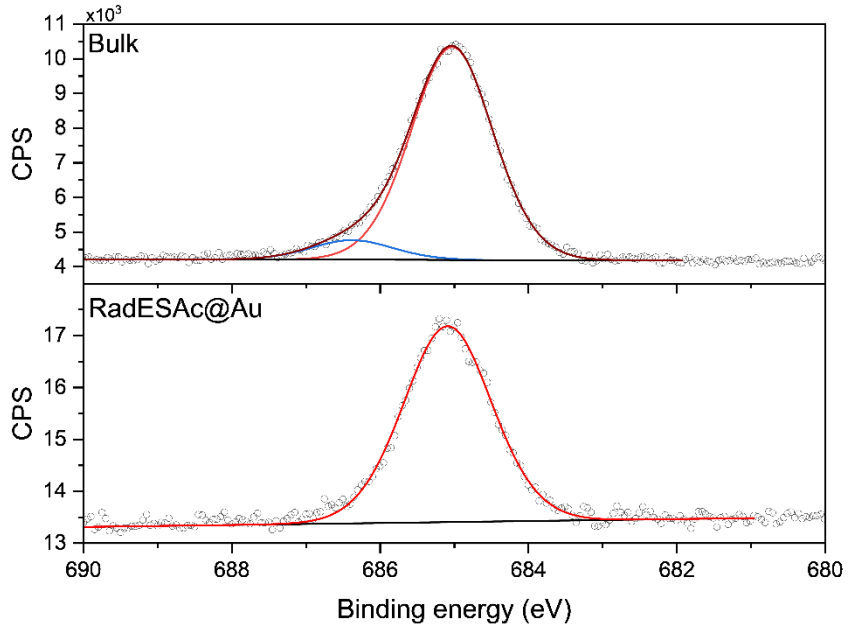

Figure S3 XPS F1*s* region of **RadESAc** bulk sample (top) and of **RadESAc@Au** (bottom)

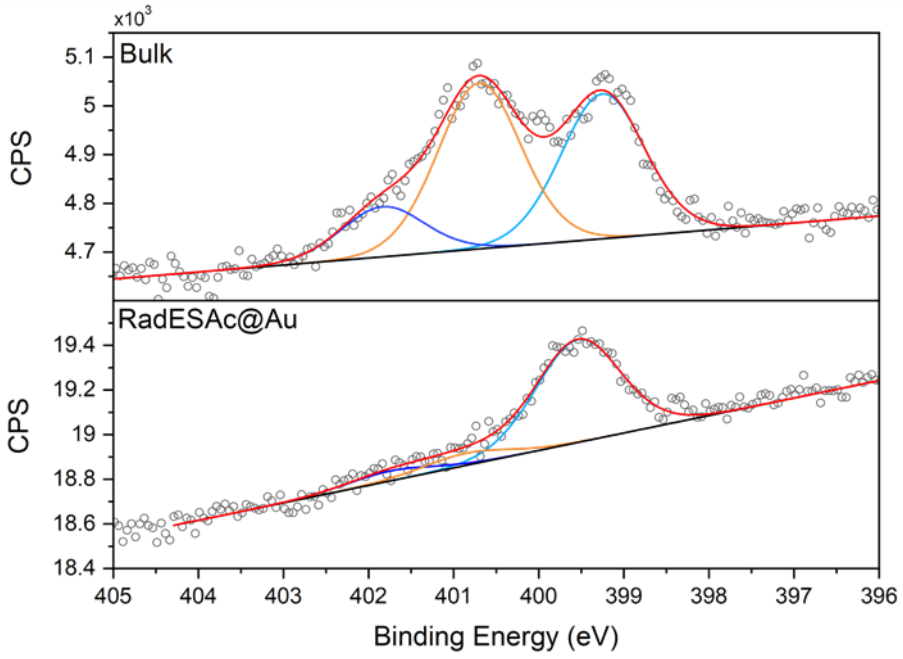

Figure S4 XPS N1*s* region of **RadESAc** bulk sample (top) and of **RadESAc@Au** (bottom)

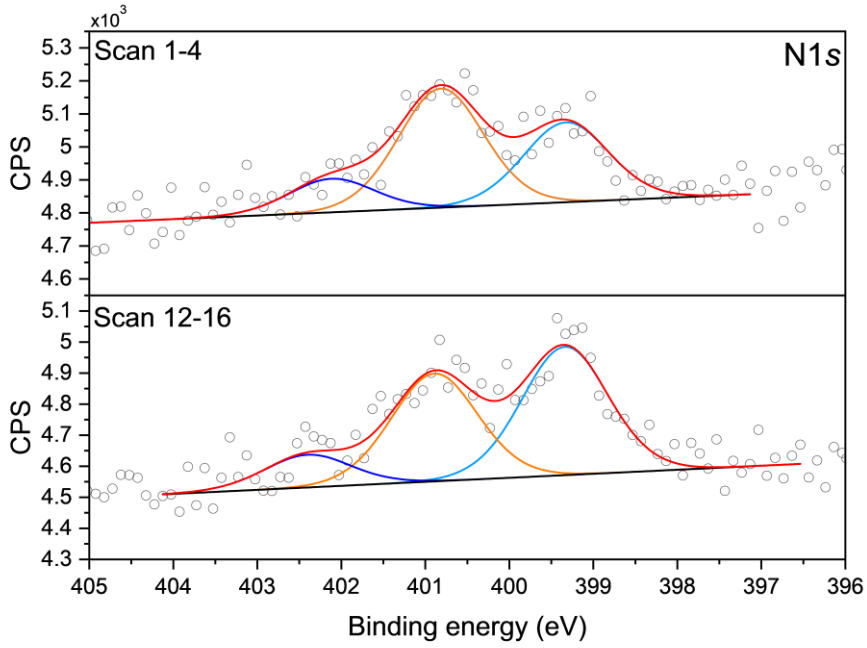

Figure S5 Time evolution of XPS N1*s* region of **RadESAc** bulk sample. The higher intensity of the light blue component at low binding energy confirms the photoreduction occurring during the exposure to X-rays.

Sample	***Bulk***		***RadESAc@Au***	
	Experimental (%)	*Theoretical (%)*	*Experimental (%)*	*Theoretical (%)*
C1*s*	91.2 ± 4.6	90.5	90.3 ± 4.5	90.0
S2*p*	6.9 ± 0.3	7.1	7.3 ± 0.4	7.5
N1*s*	1.9 ± 0.1	2.4	2.3 ± 0.1	2.5
S/N ratio	3.7	3	3.2	3
C-S-C/S-Au	---	---	2.6	2

Table S1 Semi-quantitative elemental analysis extracted from XPS characterization on **RadESAc** bulk sample as well as on **RadESAc@Au**

3. EPR

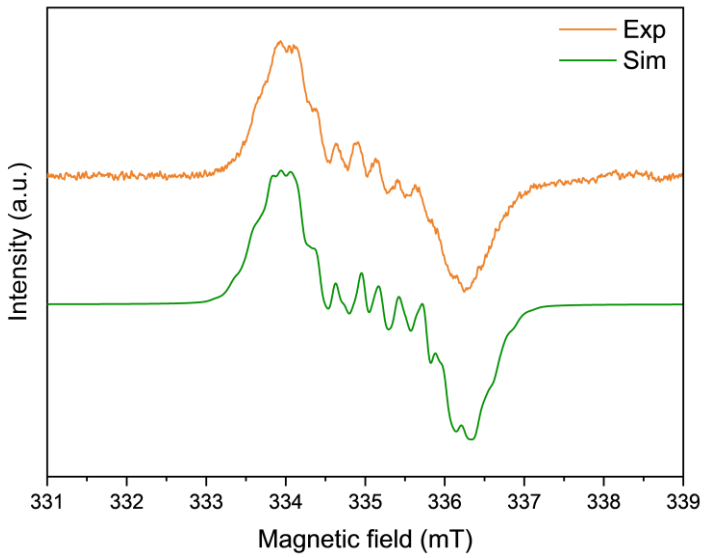

Figure S6 EPR spectra of a solution of **RadESAc** in CH_2Cl_2/toluene at 200 K and best simulation obtained using parameters reported in Table S2.

Fluid solution *g = 2.0071*		
Nucleus	Equivalent nuclei	A (MHz)
N	1	22.08
H	6	6.84
H	3	5.77
H	2	3.11

Table S2 *g* and hyperfine coupling values used for the simulation of EPR fluid solution spectrum of **RadESAc**. The spectrum features an isotropic *g* and the spectral contribution of hyperfine coupling.

RadESAc@Au monolayer experimental parameters:
The substrate (ca. 50 x 30 mm) was prepared following the procedure described above. Thus, EPR spectra on the monolayer was obtained averaging on 625 scans with a power of 6.713 mW and an attenuation of 15 dB. All the spectrum were registered using a modulation gain of 60 dB on 1024 points with a time constant of 1.28 ms and a conversion time equal to 40.96 ms.

4. MR Device

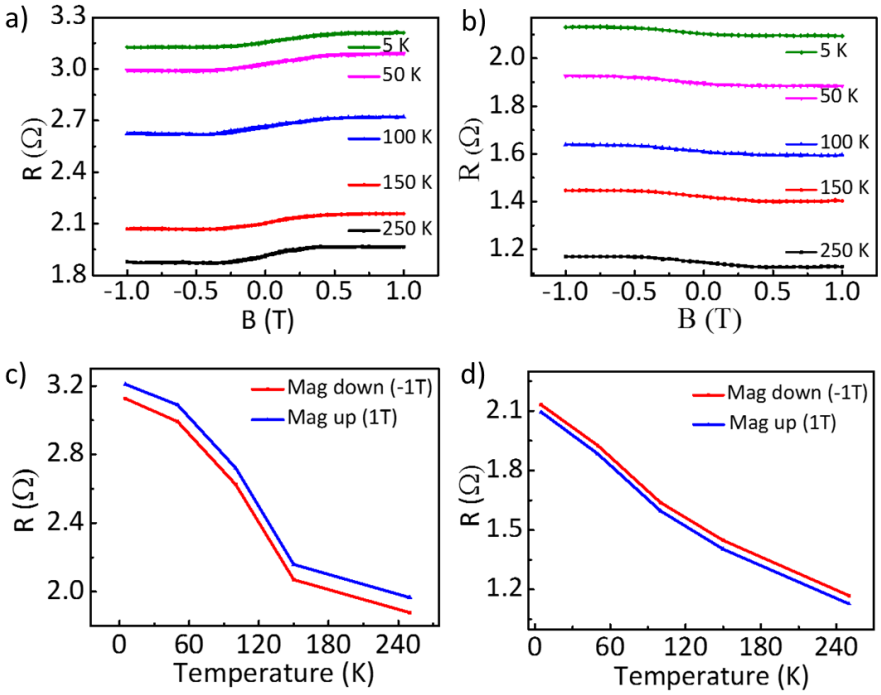

Figure S7 Temperature dependent magnetoresistance in the range ±1 T of a) ***(P)*-RadESAc** and b) ***(M)*-RadESAc** monolayers. c-d) The temperature interfacial resistance between top and bottom electrode in the presence of magnetic field.

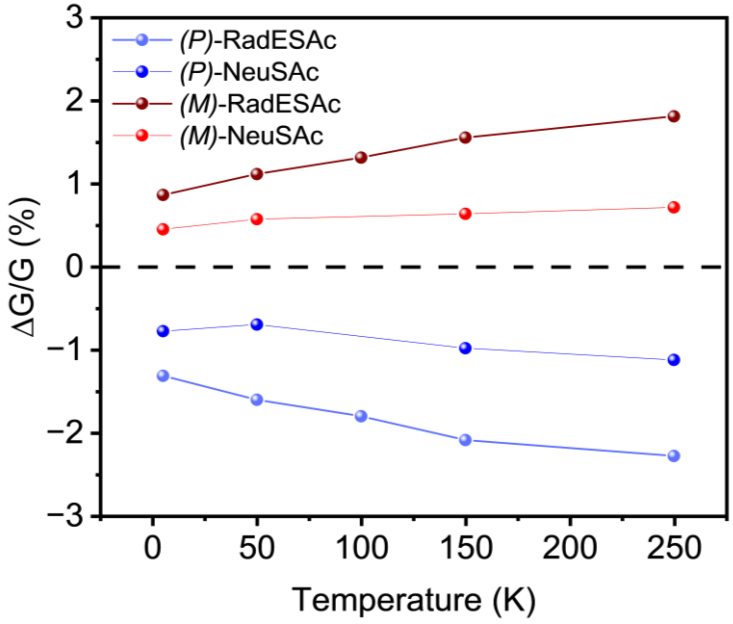

Figure S8 $\frac{\Delta G}{G}$ (%) values as a function of the temperature for the two enantiomers of **RadESAc** and the corresponding neutral species.