Supporting Information

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Chiral Conductive Polymers as Spin Filters

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Materials
R and S N,N-dimethyl-1-ferrocenylethylamine ferrocene, K₄Fe(CN)₆, K₃Fe(CN)₆, ferrocene, KCl, and tetrabutylammonium tetrafluoroborate (TBA-TFB) were purchased from Sigma Aldrich and were used as received. Solvents (AR grade) were purchased from Merck and used without any further purification. Single-crystal silicon <100> (400 Ω/cm²) of 525 ± 25 μm thickness (300 nm of thermal oxide on the surface) was purchased from University Wafers, Inc. (USA). All metals (Ni, Au, Ti, and Cr) used during evaporation were purchased from Kurt J. Lesker, USA.

Evaporation of Ni and Au on silicon:
An 8 nm Ti (Kurt, 99.9%) adhesive layer was deposited at a rate of 0.2 Å/s on a polished p-type single-crystal silicon wafer in an electron beam evaporator. 200 nm Ni (CERAC, 99.9995%) was deposited at a base pressure of 10⁻⁵ mbar at a deposition rate of 0.5-2 Å/s. A 150 nm gold (Kurt, 99.999%) layer was deposited at a slow evaporation rate of 0.2 Å/s on an 8 nm Cr (Kurt, 99.999%) adhesive layer deposited on silicon.

Formation of monolayers:
Freshly prepared Ni, Au substrates were properly cleaned in hot acetone and ethanol for 15 min each and then dried under N₂. Chiral conductive polymers were dissolved in anhydrous chloroform (0.5 mg/ml). The Au substrates were then plasma cleaned in oxygen (at ~0.4 Torr) for 1 min. Subsequently, the gold substrates were immediately immersed into the corresponding polymer solution for 22-24 h at room temperature. The modified gold substrates were rinsed several times with fresh chloroform and consequently dried in a stream of nitrogen and used immediately afterwards for characterization. The monolayer of polymer was formed on solvent-treated Ni surfaces by an electrochemical deposition method. This was carried out in chloroform containing a polymer solution (1 mg/ml) in the presence of 0.1 M tetrabutylammonium tetrafluoroborate (TBA-TFB) as a base electrolyte. Ni, a Pt-wire, and saturated calomel electrode were used as working, counter, and reference electrodes, respectively. The conducting polymer was deposited on Ni at -0.1 to -0.8 V for 10 cycles at a...
The polymer-coated nickel substrates were rinsed with chloroform, acetone, ethanol, and then dried under N₂ flow and used immediately for characterization.

**Characterization of monolayers:**
Fabrication of PCT-L film on Ni and Au substrates was confirmed by various complementary surface characterization techniques such as static water contact angle (CA) measurements, polarization modulation-infrared reflection-absorption spectroscopy (PM-IRRAS), ellipsometry, and atomic force microscopy (AFM) measurements. All measurements were performed at least three times to confirm their reproducibility.

**Ellipsometry measurement:**
SAM thickness was measured using a multiple wavelength ellipsometer (M 2000 V from J. A. Woollam Co., Inc.) at a constant incidence angle of 70º under ambient conditions and was analyzed using commercial software (WVASE32).

Ellipsometry-derived polymer film thickness was estimated as 20±3 Å. Notably, the optimized length of the polymer was calculated at ≈ 30 Å. This result shows that the polymer on surfaces is not standing strictly upright, rather, it is tilted by 40º with respect to the surface normal.

**Polarization modulation-infrared reflection-absorption spectroscopy (PM-IRRAS):**
Formation of the monolayer on Ni and Au was confirmed by infrared spectra, which were recorded in PM-IRRAS mode using a Nicolet 6700 FTIR, at an 80º incidence angle, equipped with a PEM-90 photoelastic modulator (Hinds Instruments, Hillsboro, OR).

The strong peak, which appeared at 1721 cm⁻¹, was designated as a carbonyl (C=O) stretching frequency in amide bond. Moreover, aromatic ring stretching vibrations in the lower ranges at 1438, 1458, and 1500 cm⁻¹ were also observed (see Fig. S1A). The peaks observed at 1369 and 1261 cm⁻¹ are due to CH₂ bending and the C-N stretching frequency, respectively. The presence of methylene (-CH₂-) and methyl (-CH₃) groups in the film structure was also confirmed from the spectrum. For instance, the peaks at 2960, 2925, 2872, and 2850 cm⁻¹ are related to asymmetric stretching vibrations of methyl, methylene (νₕ(CH₃), νₕ(CH₂)), and symmetric vibrations of the methyl, methylene (νₘ(CH₃), νₘ(CH₂)) groups, respectively (see Fig. S1B). A similar observation was made with polymer-coated Au surfaces.
Static Contact Angle (CA) measurements:
Aqueous contact angle measurements were performed with an automated goniometer (Rame-Hart, model 100), and microsyringe droplets (advancing drop method) of ca. 4 μL deionized water (Millipore, Inc.). Contact angle data were recorded immediately after the monolayer formation of polymer on gold and nickel substrates. The contact angle of the bare substrates was measured at 68±0.5° (see Fig. S2, left panel), whereas after polymer deposition it was increased to 90±0.5°. The above result further confirms the formation of a relatively hydrophobic layer (see Fig. S2, right panel).

AFM measurements:
AFM images were recorded on Multimode/Nanoscope-V (Bruker-Nano, Santa Barbara, CA). The topological images of the polymer-coated Ni/Au surfaces were acquired in semi-contact mode.
mode using a silicon probe (70-90 kHz resonance frequency) with a scan rate of 0.5 Hz under N₂ flow. Several images were recorded from different points to ensure the formation of polymer film. The topographical images of 500×500 nm² scans are presented for polymer-coated Ni and Au substrates (Fig. S3), indicating the formation of the polymer film. To measure the thickness of the polymer films on Ni/Au, the scratching procedure (nano shaving) was carried out on a Solver P47 SPM system (ND-MDT, Zelenograd Russia). The operation mode of the AFM was temporarily switched to the contact mode with a programmed script and the applied tip force was relatively high (160 nN). This force is enough to scratch away the monolayer, although it is not sufficient to scratch the substrate surface. The image is presented after scratching the polymers from the Ni surfaces (Fig. S4, left panel). The average polymer thickness was estimated from the height profile plot (Fig. S4, right panel) as ca. 3±1 nm. Similar results were obtained from ellipsometry measurements.

Figure S3: AFM topography of a polymer-coated Ni surface (500×500 nm²).
**Figure S4:** AFM topography polymer-coated Ni surface after scraping (left panel, 1200×900 nm$^2$). The island part shows the effect of scratching polymer from the nickel substrate. The average thickness was estimated from the height profile plot and it was found to be ca. 3 nm (right panel).

**Device characterization**

The current versus voltage was measured on the device used to obtained the MR data (Figure 6) and is shown in Figure S5. MR data were also obtained with devices composed of the PCT-D polymer. As mentioned in the manuscript, and as shown below the PCT-D polymer is less uniform than the PCT-L polymer and as result, it exhibits lower values of MR and the data were less reproducible. However, the MR data for PCT-D (Figure S6-left) clearly show a slope opposite that obtained with PCT-L. In Figure 6-right the MR curve is shown for a device composed of PCT-L deposited by spin coating. The curve is symmetric versus the magnetic field, indicating that the film conducts the two spins equally. The signal observed is only due to the agnetoresistance of the nickel itself.
Figure S5: I-V curves of the device measured at 15K.

Figure S6: Left- Magnetoresistance curves obtained with a solid-state device composed of PCT-D using an external magnetic field up to 0.5 T at different temperatures. Note that the MR values obtained with PCT-D are an order of magnitude smaller than those obtained with PCT-L. Right- Magnetoresistance curve measured with a device made by spin-coating the PCT-L polymer.
Polymer characterization

The synthesis and characterization of the L-monomer is reported in:

The D-monomer has been synthesized following the same procedure reported in the article, using as the starting material the D-serine derivative instead of the L-one. The characterization data for the D-monomer are reported here.

**Methyl N-(tert-Butoxycarbonyl)-5-3-thienyl-D-cysteinate**

$^1$H NMR (400MHz, CDCl$_3$): $\delta$=1.42 (s, 9 H, t-Bu), 3.58 (s, 3H, OCH$_3$), 3.20-3.27 (m, 2H, CH$_2$), 4.50-4.54 (br m, 1H, CH), 5.34 (br d, J=6.2Hz, 1H, NH), 7.04 (dd, J=4.9, 1.4Hz, 1H, 4-H), 7.27 (dd, J=3.0, 1.4Hz, 1H, 2-H), 7.30 (dd, J=4.9, 3.0Hz, 1H, 5-H).

MS (EI): m/z = 317 (48) [M+], 261 (32), 200 (96) 158 (26), 141 (48), 129 (100), 115 (38), 102 (34), 88 (42), 71 (20), 57 (55).

Anal. Calcd for C$_{13}$H$_{19}$NO$_4$S$_2$: C, 49.19; H, 6.03; N, 4.41; S, 20.20. Found: C, 49.4; H, 6.00; N, 4.39; S, 20.10.

Enantiomeric excess, determined on the trifluoroacetate derivative, was 97%.

**NMR**

$^1$H-NMR data (CDCl$_3$, 400MHz) of the two polymers PCT-L and PCT-D are shown in Figure S7. The main differences between the two polymers are the presence of a double peak at 3.40ppm in the PCT-D spectra (whereas the PCT-L spectra displays a single peak) and the presence of a peak at 1.30ppm (absent in the PCT-L spectra). These two peaks suggest a different regioregularity of the two polymers, with less regioregularity in PCT-D. This is probably due to a Br-Sn exchange during the synthesis, which is known to occur sometimes in Stille coupling reactions such as the one used for the polymerization.
**Figure S7**: $^1$H-NMR data (CDCl$_3$, 400MHz) of the two polymers PCT-L (top) and PCT-D (bottom).

**GPS**

GPC was carried out on a Hewlett-Packard system equipped with a Hewlett-Packard 5m mixed PLgel column and a diode-array UV detector, using THF as the eluant, with a flow rate of 1.0 mL min$^{-1}$, at room temperature. The GPC system was calibrated using a series of monodisperse polystyrene standards. The GPC data of PCT-L (Figure S8) show two major peaks, one with molecular weight (Mw) = 24036 and polydispersity index (PDI) = 1.15 and the other with Mw = 4683 and PDI = 1.5. The GPC data for PCT-D (Figure S9) also show two major peaks, the first one having Mw = 40414 and PDI = 1.18 and the second one Mw = 6458 and PDI = 1.36. The first peak of both the GPCs is attributed to an interchain aggregated form of the polymer, whereas the second peak is attributed to the free standing chain.
Figure S8: The GPC data obtained for PCT-L

Figure S9: The GPC data obtained for PCT-D
The CD optical spectra of PCT D and PCT-L are shown in Figure S10 (a) and (b), respectively. The UV-Vis spectrum of PCT-D shows an intense peak at 610nm, indicating the presence of aggregates in the solid state. In the PCT-L spectrum, the same peak is present but as a small shoulder, indicating that the interchain aggregation is less dominant, namely, the system favors an intrachain conformation.

**Figure S10**: The CD (a) optical (b) spectra of PCT D (green) and PCT-L (blue).