Low-Resistance Molecular Wires Propagate Spin Polarized Currents

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1. Materials and Instrumentation

General Materials:

All manipulations were carried out under insert gas previously passed through an O_2 scrubbing tower packed with Schweizerhall R3-11 catalyst and a drying tower packed with Linde 3 Å molecular sieves. Air-sensitive compounds were handled in a Braun 150-M glove box. Air-sensitive reactions are conducted by employing standard Schlenk technique. All reagents purchased from Sigma-Aldrich, TCI, Chem-Impex and Fisher Scientific were used as received without further purification. All solvents utilized in this work were obtained from Fisher Scientific and Sigma-Aldrich (HPLC Grade). CH_2Cl_2 and tetrahydrofuran (THF) were dried from a PURE SOLV (Innovative Technology) solvent purification system with 4 Å molecular sieves and degassed by freeze-pump-thaw cycles. Solid phase peptide synthesis (SPPS) was performed on 0.4-1.5 mmol•g^{-1} of substituted cysteamine 2-chlorotrityl resin. Flash and size exclusion column chromatography were performed on the bench top, using respectively silica gel (EM Science, 230–400 mesh) and Bio-Beads SX-1 as media.

Instrumentation:

NMR spectra were recorded on a 400 MHz AC-Brucker instrument. Chemical shifts for ^1H NMR spectra are reported relative to residual protium in the deuterated solvent ($CDCl_3$ = 7.26 ppm). Electronic spectra were recorded on a Varian 5000 UV/vis/NIR and SHIMADZU UV-1700 UV/vis spectrophotometer. Circular Dichroism were recorded on a model 435 AVIV Circular Dichroism Spectrometer. MALDI-TOF mass spectroscopic data were obtained on a Bruker Autoflex Speed LRF MALDI-TOF System using either a 2-(4-hydroxyphenylazo)benzoic acid (HABA) or a α-cyano-4-hydroxycinnamic acid (HCCA) matrix.

2. Synthetic Procedures and Characterization

Syntheses of Pro_8PZn_n:

Synthesis of the molecular wires **Pro_8PZn_n** (n = 1-3) consists of three steps. The first step consists of the preparation of ethyne-bridged *meso*-to-*meso* porphinato(zinc(II)) arrays **PZn_nEH** (n = 1-3) previously described in the literature.[1-6] In the second step, solid phase peptide synthesis was manually conducted in peptide synthesis vessels (Chemglass Life Sciences) to realize a polyproline **Pro_8** resin (Scheme S1).[7] In the third step, a copper(I)-catalyzed azide-alkyne cycloaddition reaction was employed, forming a covalent bond between **PZn_nEH** (n = 1-3) and **Pro_8** (Scheme S3).[8]

PZn_1EH

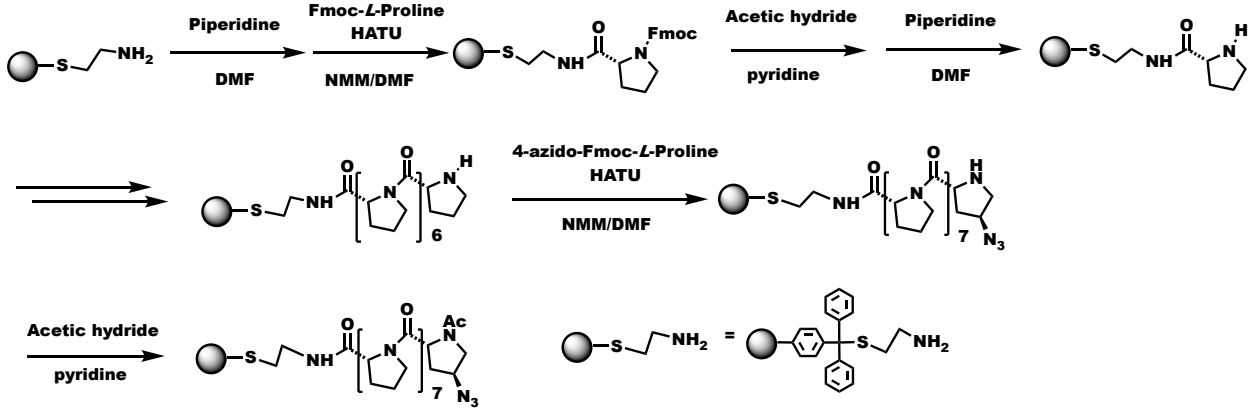
^{1}H NMR (400 MHz, $CDCl_3$ as 7.26 ppm): 10.08 (s, 1H), 9.72 (d, 2H), 9.24 (d, 2H), 8.96 (d, 2H), 8.93 (d, 2H), 7.72 (t, 4H), 7.03 (d, 8H), 4.12 (s, 1H), 3.90 (t, 8H), 0.91 (t, 8H), and 0.34 (s, 32H); MS (MALDI-TOF) m/z: 950.42 [(M^+), calcd 950.59].

PZn_2EH

^{1}H NMR (400 MHz, $CDCl_3$ as 7.26 ppm): 10.41 (d, 2H), 10.36 (d, 2H), 10.06 (s, 1H), 9.63 (d, 2H), 9.25 (d, 2H), 9.12 (d, 2H), 9.01 (d, 2H), 8.97 (d, 2H), 8.88 (d, 2H), 7.74 (t, 4H), 7.05 (d, 8H), 4.13 (s, 1H), 3.96 (t, 16H), 0.90 (t, 16H), and 0.34 (s, 32H); MS (MALDI-TOF) m/z: 1898.92 [(M^+), calcd 1899.16].

PZn_3EH

^{1}H NMR (400 MHz, $CDCl_3$ as 7.26 ppm): 10.44 (d, 2H), 10.36 (m, 6H), 10.06 (s, 1H), 9.64 (d, 2H), 9.26 (d, 2H), 9.14 (d, 2H), 9.04 (m, 6H), 8.97 (d, 2H), 8.88 (d, 2H), 7.74 (m, 6H), 7.07 (m, 12H), 4.13 (s, 1H), 3.99 (t, 24H), 0.94 (t, 24H), and 0.34 (s, 108H); MS (MALDI-TOF) m/z: 2841.22 [(M^+), calcd 2841.33].



Scheme S1. Synthetic route to the **Pro$_8$** resin.

Solid Phase Peptide Synthesis

The synthesis of the peptide **Pro$_8$** resin was performed by solid-phase synthesis techniques using cysteamine 2-chlorotrityl resin (Scheme S1). In the first stage, **Protocol A** was employed to neutralize the amine on the resin. Then, **Protocol B** was employed to complete the coupling, and **Protocol C** was used to cap the residual unreacted amine groups. After the coupling was completed, the resin was sequentially washed by DMF and DCM five times to remove the coupling reagent. In the following step, **Protocol D** led to the removal of the Fmoc protecting group providing free amine groups that were available for further coupling. The entire procedure was repeated until the desired sequence of the peptide **Pro$_8$** resin was obtained.

Protocol A: Amine neutralization

Cysteamine 2-chlorotrityl resin (1 g, *ca.* 0.5 mmol) was charged in 50 mL synthesis vessel. The resin was washed and swelled for one min with fresh DMF five times. Piperidine/DMF (v/v = 1:4) was injected to neutralize the primary amine for twenty min while bubbling with nitrogen. The resin was then washed with DMF five times to remove the piperidine.

Protocol B: Peptide coupling

Fmoc-*L*-proline (1.34 g, 4.0 mmol, 8 equiv.) or Fmoc-(4R)-azido-*L*-proline (1.89 g, 4.0 mmol, 8 equiv.) were mixed with HATU (1.52 g, 4.0 mmol, 8 equiv.) and dissolved in a minimal amount of N-methylmorpholine (NMM)/DMF (v/v = 1:4) solution and stirred for ten min. The orange

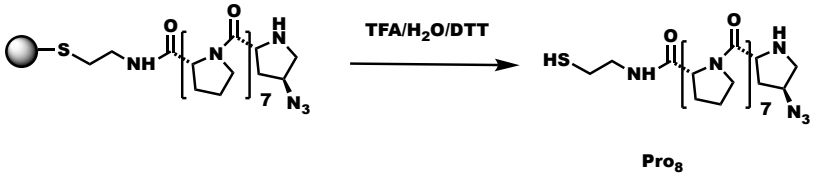
solution was then poured into the vessel containing the resin and the mixture was bubbled with nitrogen for 4 h and then washed by DMF and DCM five times, respectively. The completion of couplings was monitored using the chloranil test. This procedure was repeated as necessary to ensure that the coupling was complete.

Protocol C: N-terminal acetylation

Fresh capping solution was made by combining acetic anhydride and pyridine (v/v = 3:2). The solution was added to the resin and then bubbled with nitrogen for thirty min. at room temperature. The completion of capping was monitored using the chloranil test. The resin was then cleaned with DMF and DCM five time after the removal of the capping solution.

Protocol D: Fmoc deprotection

A solution mixed with piperidine/DMF (v/v = 1:4) was added to the resin and the mixture was purged with nitrogen for twenty min. The reaction was monitored using the chloranil test. Then resin was washed thoroughly using DCM and DMF five times, respectively.

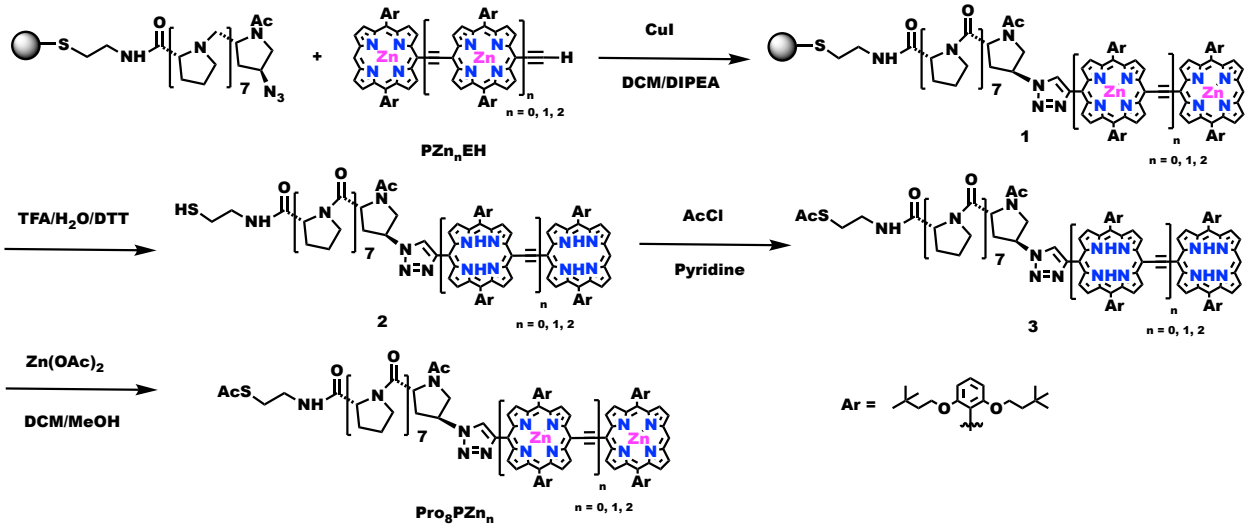


Scheme S2. Cleavage of **Pro$_8$** molecule from resin.

Pro$_8$

In Scheme S2, the resin (0.2 g, *ca.* 0.1mmol) containing **Pro$_8$** was charged in a 50 mL flask. The cleavage solution consisting of TFA/H_2O (v/v = 95/5, 10 mL) was prepared with 0.5% dithiothreitol (DTT) and transferred into the flask. The mixture was then gently stirred over fifty min. at room temperature. The green solution was filtered, and the resin washed with DCM (30 mL), following which the filtrate solution was reduced under reduced pressure. The crude product was precipitated with cold ether and filtered, yielding a white-yellow compound, which was subsequently purified by size-exclusion chromatography (Biobeads SX-1, eluent: THF) to

afford a yellow solid (56 mg, 57.1% yield based on the 0.15 mmol of 0.3 g starting resin). MS (MALDI-TOF) m/z: 897.60 [(M^+), calcd 895.46].



Scheme S3. Synthetic route to **Pro$_8$PZn$_n$** (n = 1-3)

Porphyrin-Proline Complex (1)

As outlined in Scheme S3, **PZn$_1$EH** (0.189 g, 0.2 mmol), **PZn$_2$EH** (0.357 g, 0.2 mmol), or **PZn$_3$EH** (0.535 g, 0.2 mmol) were charged into a 50 mL round bottom flask containing **Pro$_8$** resin (0.4 g, *ca.* 0.2mmol), and CuI (0.0019g, 0.01 mmol) under inert atmosphere. Dry, degassed DCM (20 mL) was cannulated into the flask and 0.5 mL DIPEA was injected via syringe. The flask was covered with aluminum foil and the mixture was stirred overnight. The resin was filtered and washed thoroughly with DCM until the filtrate was colorless. The purple-red beads were placed in a vial with DCM (20 mL) and then sonicated for 10 min. to remove unreacted porphyrin starting material on the resin, to afford resin **1**.

Porphyrin-Proline Complex (2)

As outlined in Scheme S3, the resin **1** (0.4 g, *ca.* 0.2mmol) was charged in a 50 mL flask. The cleavage solution consisting of TFA/H_2O (v/v = 95/5, 10 mL) was prepared with 0.5% dithiothreitol (DTT) and transferred into the flask. The mixture was then gently stirred over fifty min. at room temperature. The green solution was then filtered, and the resin was washed with

DCM until the filtrate was colorless. The solution was reduced under pressure to afford the green product **2**, which was used for the next reaction without further purification.

Porphyrin-Proline Complex (3)

As outlined in Scheme S3, product **2** (0.1 g) was charged in a 100 mL round bottom flask under inert atmosphere. Dry pyridine (10 mL) was cannulated into the flask to dissolve the product and cooled to 0 °C. AcCl (2 mL, 28 mmol) was injected via syringe, and the mixture was stirred for 10 min. before warming to room temperature. The mixture was then stirred for 30 min. and quenched by pouring into an ice/water mixture. The product was extracted by DCM three times (20 mL). The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure to afford product **3**, which was used for the next reaction without further purification.

Porphyrin-Proline Complex ($\mathbf{Pro_8PZn_n}$ (n = 1-3))

Product **3** (0.1 g) was charged into a 50 mL round bottom flask and dissolved in a solution of MeOH/DCM (v/v = 1:9, 25 mL) and zinc acetate dihydrate (0.5 g, 2.27 mmol) was added. The mixture was heated to reflux for 3 h. The mixture was then extracted with DCM three times (20 mL). The combined organic layers were dried over sodium sulfate, concentrated under reduced pressure and then dried under high vacuum. The crude product was purified by size-exclusion chromatography (Biobeads SX-1, eluent: THF) and silica gel with MeOH/DCM (v/v = 3:97) to afford the final $\mathbf{Pro_8PZn_n}$ product.

$\mathbf{Pro_8PZn_1}$

Purple solid (4.8 mg, 1.6% yield based on 0.15 mmol of starting resin). MS (MALDI-TOF) m/z: 1928.32 [(M^+), calcd 1929.75]; vis-NIR (DCM): 415, 482, 561, 654 nm.

$\mathbf{Pro_8PZn_2}$

Brown/black solid (2.6 mg, 0.6% yield based on 0.15 mmol of 0.3 g starting resin). MS (MALDI-TOF) m/z: 2878.63 [(M^+), calcd 2878.32]; vis-NIR (DCM): 409, 543 nm.

Pro_8PZn_3

Brown/black solid (5.7 mg, 1.0% yield based on 0.15 mmol of 0.3 g starting resin). MS (MALDI-TOF) m/z: 3827.10 [(M^+), calcd 3826.89]; vis-NIR (DCM): 412, 493, 730 nm.

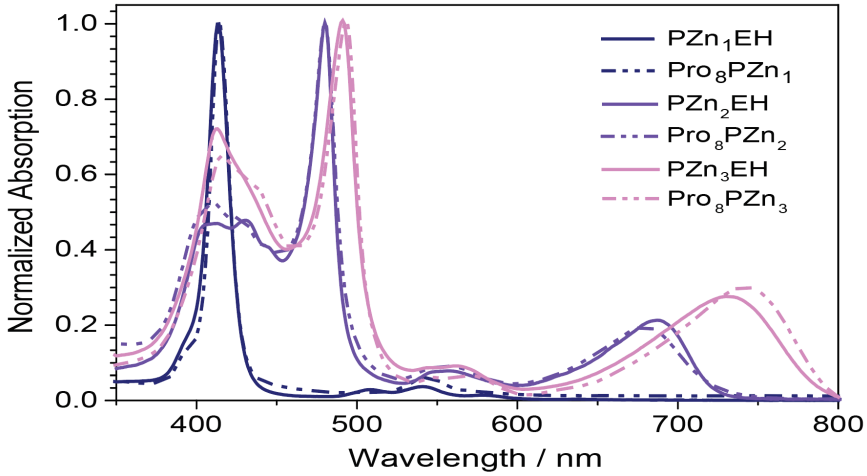


Figure S1. Electronic absorption spectra of PZn_nEH and Pro_8PZn_n in CH_2Cl_2 solvent. Blue solid and dashed lines represent PZn_1EH and Pro_8PZn_1, respectively. Purple solid and dashed lines represent PZn_2EH and Pro_8PZn_2, respectively. Pink solid and dashed lines represent PZn_3EH and Pro_8PZn_3, respectively.

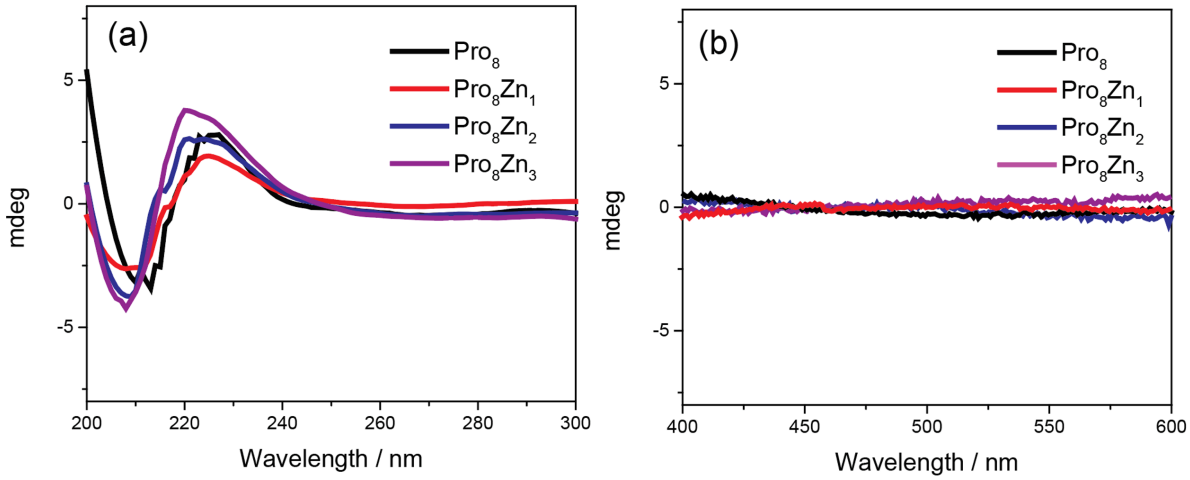


Figure S2. Circular dichroism spectra of Pro_8, Pro_8PZn_1, Pro_8PZn_2, and Pro_8PZn_3 dissolved in 1-propanol solvent recorded over a 200 to 300 nm (a) and 400 to 600 nm (b) spectral ranges.

3. Fabrication of Hall Devices

Hall Devices: For the fabrication of the Hall devices, AlGaN/GaN wafers on a sapphire substrate (from NTT) were used. The wafer is composed of a nucleation layer, and then an intrinsic-GaN layer of 1800-nm thickness. On top of the i-GaN layer, an intrinsic-AlGaN layer of thickness 20 nm was present. Finally, a capping layer of 2 nm thickness was present on i-AlGaN. All the Hall devices were prepared by standard photolithography in a class 1000 clean room. To prepare ohmic contacts, a metallic multilayer i.e., Ti (20 nm)/Al (100nm)/Ni (40 nm)/Au (40 nm) was annealed at 850°C. A size of 500 μm in length and 40 μm in width of the active area of the channel was also coated with 5nm Au for molecular adsorption. After growing the monolayers of the various molecules on the channel (discussed in Section 4), devices were glued to a sample holder using double-sided tape and all the pads of electrodes were connected to a chip holder using wire bonding and finally using a high-quality RTV silicone glue; all the connections were passivated to avoid short circuiting. For Hall and electrochemical measurements in an aqueous environment, a cell was prepared from PDMS (polydimethylsiloxane) having a capacity of 200 μL glued onto the device holder. For polarization experiments, a glass coverslip was coated with gold on the side facing away from the solution. This gold coverslip works as a gate electrode to provide the electric field for the polarization of the molecule. All measurements were collected in a dark Faraday cage.

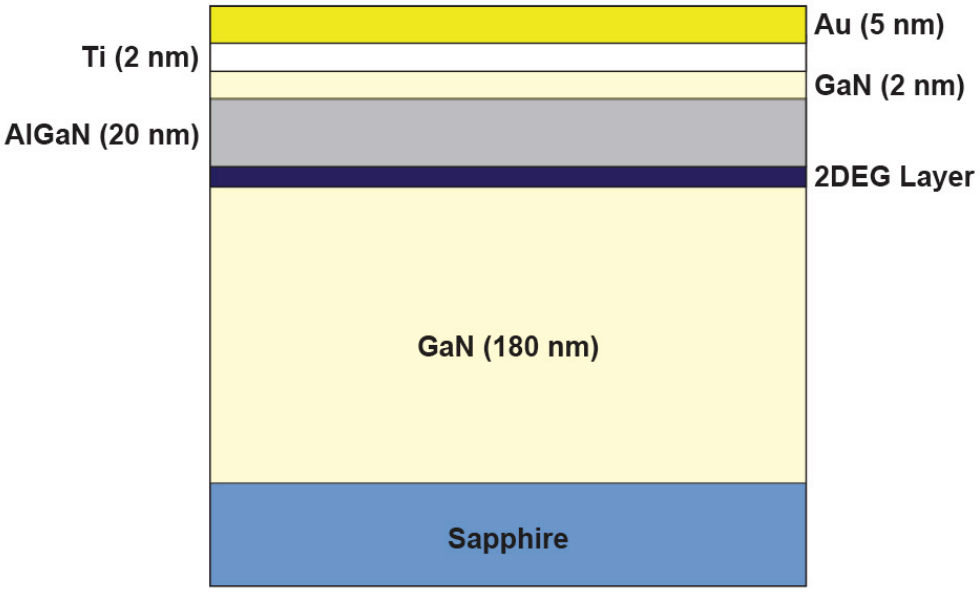


Figure S3. Schematic of the Hall device channel composition, where the top gold layer allows adsorption of thiolated **Pro$_8$** and **Pro$_8$PZn$_n$** monolayers.

4. Preparation and Characterization of Assembled Monolayers

Monolayer Growth: Before growing a monolayer of **Pro_8PZn_n** on the devices, their surfaces were cleaned by first boiling in acetone and then boiling in ethanol for 10 min. each. The surfaces then underwent UV/OX treatment for 10 min. and were subsequently immersed in ethanol for 30 min. Immediately afterwards, the surfaces were dried with a nitrogen stream and then placed in a **Pro_8PZn_n** solution for 24 h. After this period, the samples (devices) were rinsed twice with 0.4 M PBS and twice with de-ionized water.

Characterization setup: A constant current between the source (S) and drain (D) electrodes and varying gate voltages were applied using a dual channel Keithley 2636A source measuring unit. At the same time the Hall voltage (V_H) was recorded using a Keithley 2182A nanovoltmeter. In order to calibrate voltage due to the asymmetry of the Hall device, current was maintained in both the forward and backward directions. The Hall potential was calculated by adding the result, $\Delta V_H = V_{H+} - V_{H-}$. All the polarization experiments were performed in a wet environment in 0.1M PBS buffer. For the electrochemical characterization of the Hall device, an electrochemical workstation (Princeton Applied Research 263A) was configured with the Hall setup (Keithley 2636A+2182A). During the electrochemical measurement 0.1M PBS buffer was used as electrolyte. Ag/AgCl and platinum wire were used as the reference and counter electrodes during the measurement.

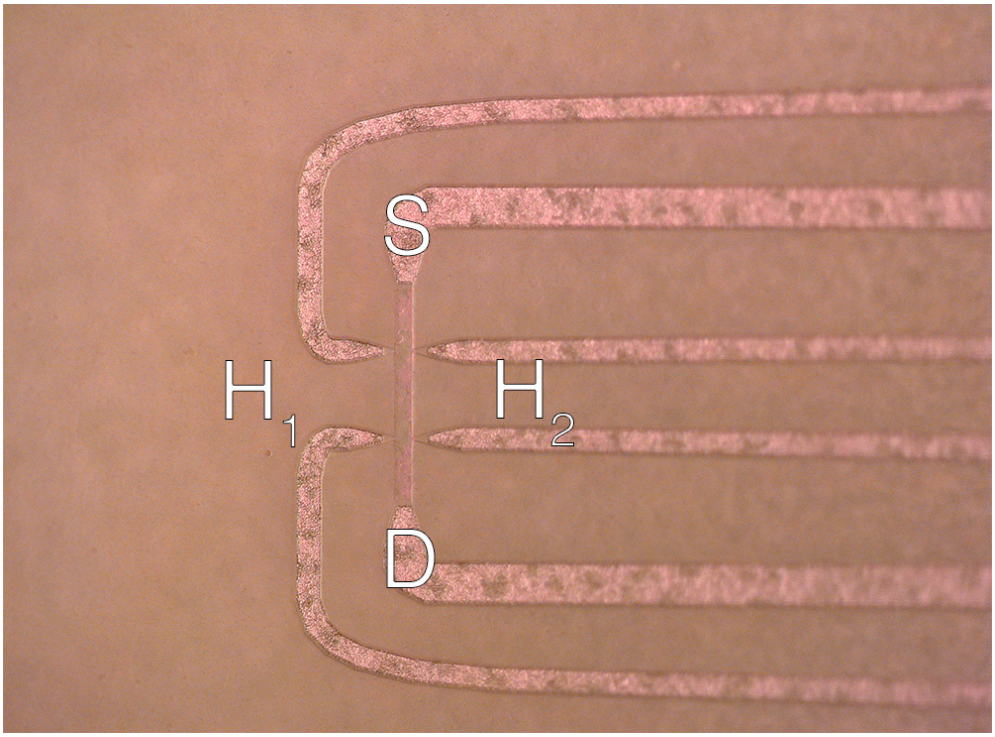


Figure S4. Optical microscopic image of the Hall device with a source-drain channel length of 500 μm. The width of the channel is 40 μm.

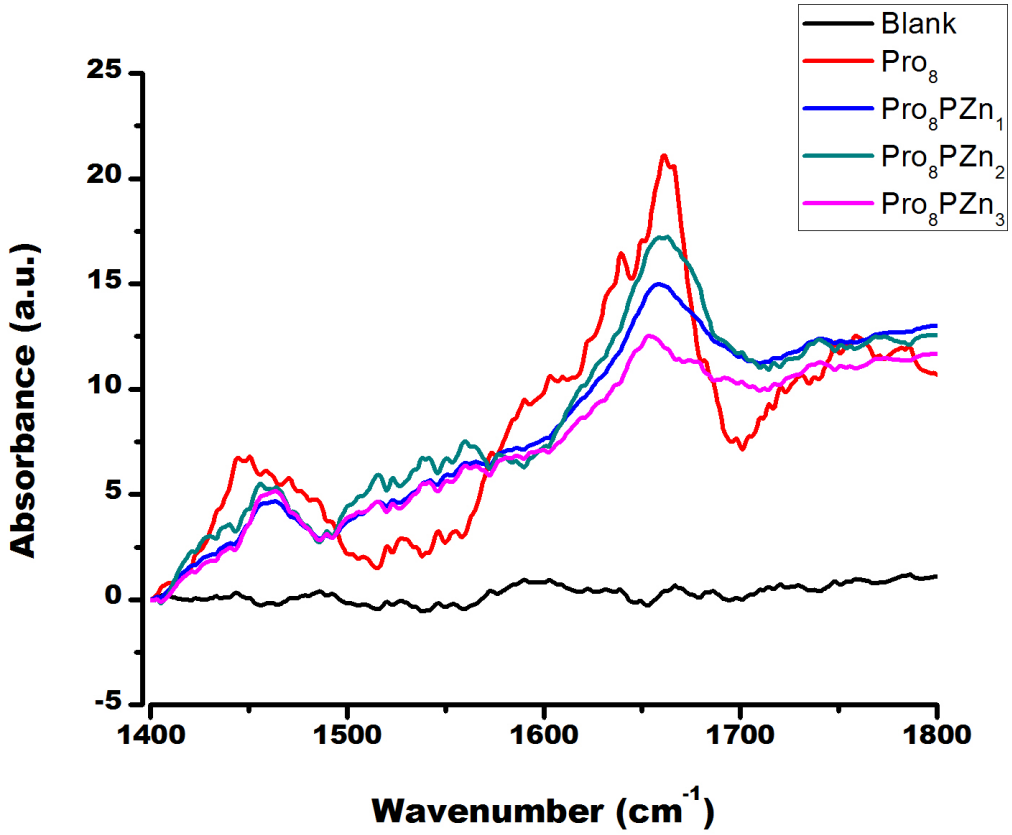


Figure S5. Polarization modulation-infrared reflection-adsorption spectroscopy data of pristine and self-assembled **Pro$_8$**- and **Pro$_8$PZn$_n$**-monolayer modified Au surfaces.

Table S1. Summary of PM-IRRAS and ellipsometry data indicating self-assembled monolayer angle deviation from perpendicular to the surface and monolayer height.

Molecule	Angle from Normal	Layer Height
Pro_8	42.3°	1.1 nm
Pro_8PZn_1	47.7°	1.68 nm
Pro_8PZn_2	44.2°	2.51 nm
Pro_8PZn_3	52.7°	2.73 nm

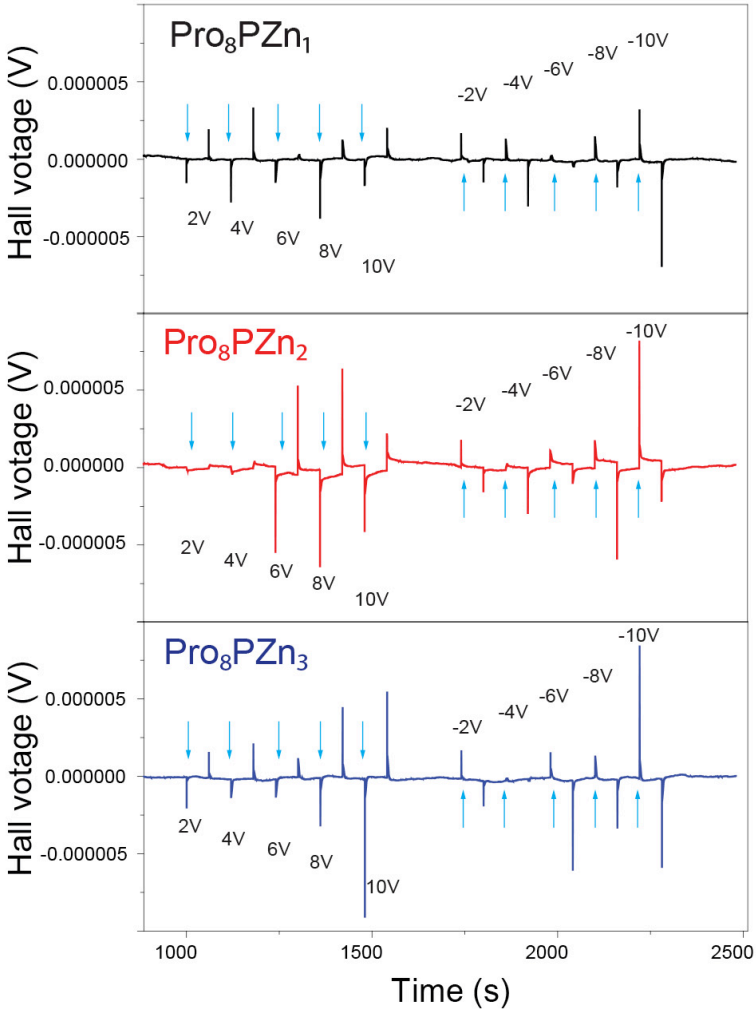


Figure S6. Polarization experiments for the self-assembled monolayers of the **Pro$_8$PZn$_n$** series measured using sequential gate pulses from -10 V to 10 V at 2 V intervals. The Hall bar served as the working electrode and a gold coated surface was utilized as the gate electrode. All measurements were carried out in 0.1M PBS buffer.

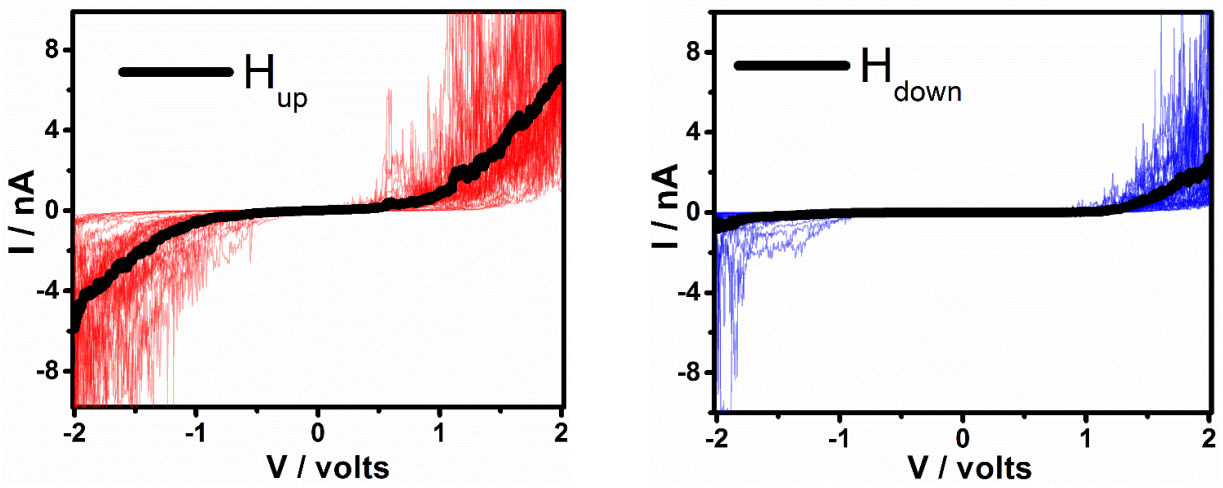


Figure S7. Spin dependent conduction through the **Pro$_8$PZn$_3$** molecule, measured with magnetic conducting atomic force microscopy with the Ni substrate magnetized in UP (left) and DOWN (right) orientations. Measurements were carried out on SAMs formed on Si wafers coated with successive thin layers of Ti:Ni:Au (10:120:10 nm). The panels highlight the I-V responses acquired over a -2 to 2 V potentiometric window. A permanent magnet (0.3 T) was aligned with the substrate to polarize electron spins within the substrate Ni layer.

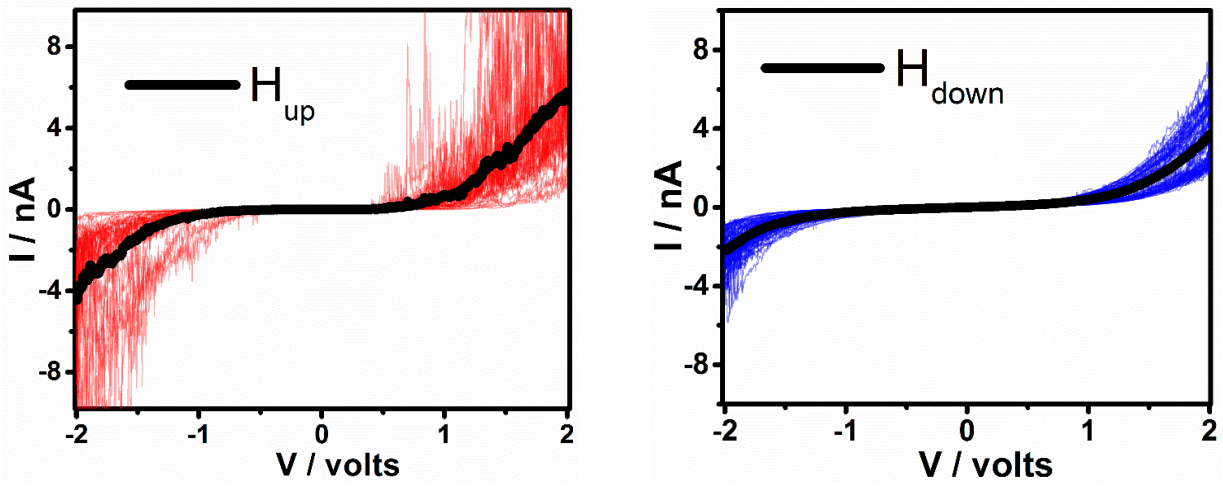


Figure S8. Spin dependent conduction through the **Pro$_8$PZn$_2$** molecule, measured with magnetic conducting atomic force microscopy with the Ni substrate magnetized in UP (left) and DOWN (right) orientations. Measurements were carried out on SAMs formed on Si wafers coated with successive thin layers of Ti:Ni:Au (10:120:10 nm). The panels highlight the I-V responses acquired over a -2 to 2 V potentiometric window. A permanent magnet (0.3 T) was aligned with the substrate to polarize electron spins within the substrate Ni layer.

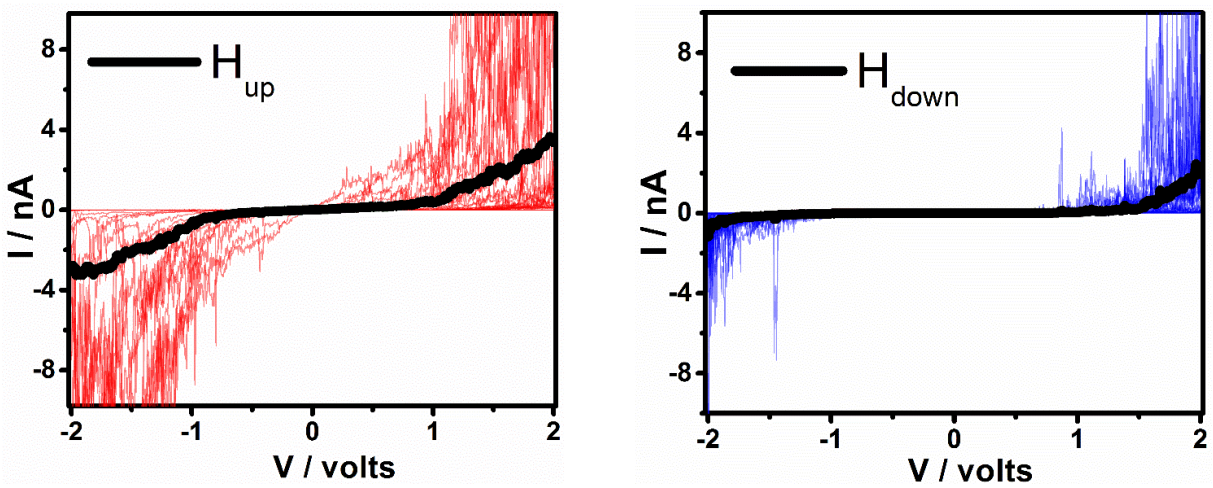


Figure S9. Spin dependent conduction through the **Pro$_8$PZn$_1$** molecule, measured with magnetic conducting atomic force microscopy with the Ni substrate magnetized in UP (left) and DOWN (right) orientations. Measurements were carried out on SAMs formed on Si wafers coated with successive thin layers of Ti:Ni:Au (10:120:10 nm). The panels highlight the I-V responses acquired over a -2 to 2 V potentiometric window. A permanent magnet (0.3 T) was aligned with the substrate to polarize electron spins within the substrate Ni layer.

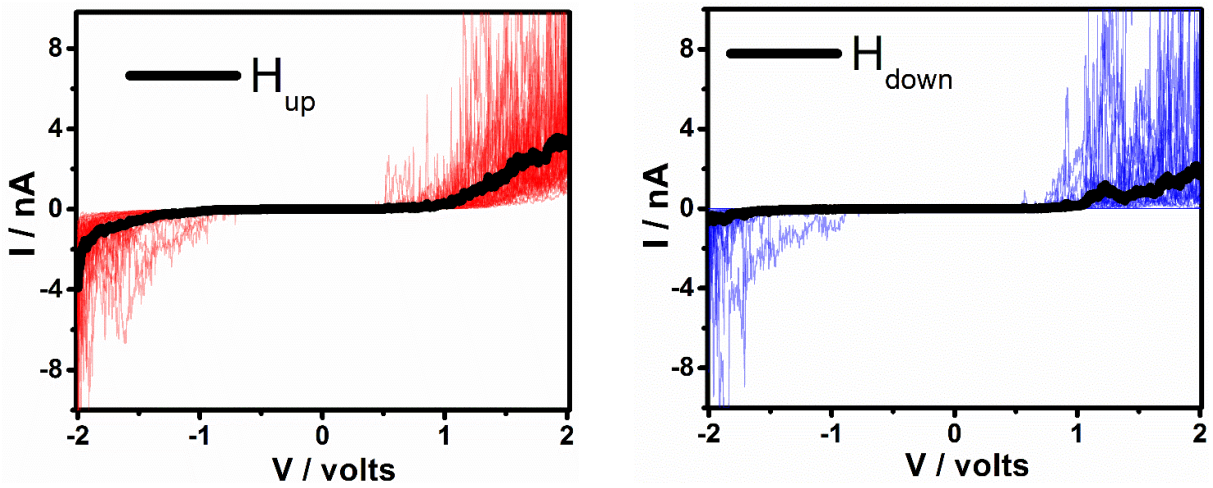


Figure S10. Spin dependent conduction through the **Pro$_8$** molecule, measured with magnetic conducting atomic force microscopy with the Ni substrate magnetized in UP (left) and DOWN (right) orientations. Measurements were carried out on SAMs formed on Si wafers coated with successive thin layers of Ti:Ni:Au (10:120:10 nm). The panels highlight the I-V responses acquired over a -2 to 2 V potentiometric window. A permanent magnet (0.3 T) was aligned with the substrate to polarize electron spins within the substrate Ni layer.

Table S2. Anodic cyclic voltammetric responses of self-assembled monolayers of Pro_8 and Pro_8PZn_n

1st Oxidation Potential, V vs. Fc/Fc^+				
Compound	Pro_8	Pro_8PZn_1	Pro_8PZn_2	Pro_8PZn_3
$E_{1/2}^{0/+}$	n/a [a]	0.88	0.53	0.29

[a] No oxidative electrochemical processes observed over the 0 to 1.2 V potentiometric window.

Cyclic voltammetric responses of **Pro_8** and **Pro_8PZn_n** (n = 1-3) self-assembled monolayers on Au working electrode were recorded in acetonitrile solvent. The Fc/Fc^+ redox couple was used as an internal potentiometric standard in these cyclic voltammetric studies. Experimental conditions: 0.1 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6), 200 mV/s scan rate, Au working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode.

5. References

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