By electrochemically coupling microbial and abiotic catalysts, bioelectrochemical systems such as microbial electrolysis cells and microbial electrosynthesis systems synthesize energy-rich chemicals from energy-poor precursors with unmatched efficiency. However, to circumvent chemical incompatibilities between the microbial cells and inorganic materials that result in toxicity, corrosion, fouling, and efficiency-degrading cross-reactions between oxidation and reduction environments, bioelectrochemical systems physically separate the microbial and inorganic catalysts by macroscopic distances, thus introducing ohmic losses, rendering these systems impractical at scale. Here we electrochemically couple an inorganic catalyst, a SnO₂ anode, with a microbial catalyst, Shewanella oneidensis, via a 2-nm-thick silica membrane containing -CN and -NO₂ functionalized p-oligo(phenylene vinylene) molecular wires. This membrane enables electron flow at 0.51 μA cm⁻² from microbial catalysts to the inorganic anode, while blocking small molecule transport. Thus the modular architecture avoids chemical incompatibilities without ohmic losses and introduces an immense design space for scale up of bioelectrochemical systems.
While bioelectrochemical systems have traditionally focused on electricity or hydrogen production, recently a new generation of bioelectrochemical systems has been developed to synthesize inorganic chemicals, fuels, and pharmaceuticals from wastewater or renewable energy\(^1\)–\(^7\). These systems use microbial cells and inorganic materials as separate catalysts for both oxidative and reductive reactions, and these two reactions are coupled to make products of interest at high thermodynamic efficiency. When the microbial catalysts perform oxidative reaction and the inorganic material, e.g., Pt\(^6\) or carbon cloth\(^9\), catalyzes the reductive reaction, these systems are called microbial electrolysis cells\(^8\)–\(^12\). Alternatively, in microbial electro-synthesis\(^13\)–\(^16\), biohybrid\(^17\)–\(^19\), or artificial photosynthesis\(^20\), \(^21\) systems, the direction of electron flow is reversed so that the inorganic material performs oxidative catalysis and the microbial catalyst carries out reductive reaction (Supplementary Fig. 1).

Independent of the direction of electron flow, a recognized challenge in these systems is that the microbial and inorganic catalysts require distinct chemical environments for optimal function\(^4\), \(^6\), \(^7\). For example, inorganic catalysts generate reactive oxygen species\(^15\), \(^19\) or leach heavy metal ions\(^19\), \(^20\), which kill the microbial catalysts, or microbial catalysts can corrode the inorganic catalyst\(^7\) or generate undesired products, i.e., CH\(_3\) in H\(_2\), via cross-reactions\(^3\), \(^6\). To achieve and sustain the chemically distinct environments, the biotic and abiotic catalysts are separated by millimeters to centimeters\(^15\), \(^16\), \(^22\) or by macroscale membranes\(^9\), \(^10\). This separation leads to crippling ohmic losses on the order of 25% of the cell voltage\(^20\), \(^21\) that impair system scale up\(^1\), \(^3\), \(^7\) and device architectures that are incongruent with large-scale manufacturing\(^23\). Thus new concepts to simultaneously chemically separate, yet electrochemically couple, microbial and inorganic catalysts on the shortest possible length scale are needed to render scale up of bioelectrochemical systems feasible.

Similar to abiotic and microbial catalysts, purely synthetic oxidation and reduction catalysts require separate chemical environments for optimal function. Recently, nanoscale silica membranes containing embedded molecular wires have been introduced as a platform to electrochemically couple these catalysts under separate reaction environments at the smallest possible length scale\(^24\). The 2 nm-thick amorphous silica layer of these membranes is impermeable to O\(_2\) and other small molecules but transmits protons\(^25\). Embedded in the silica layer, conjugated oligo-para(phenylene vinylene) molecules can rapidly transfer electrons at energies dictated by their orbital energetics\(^26\)–\(^28\) between the catalysts.

While these silica membranes with embedded wires offer the features needed, microorganisms that grow, live, and die offer a uniquely challenging physicochemical environment for chemical separation. Likewise, electron transfer in biological catalysts operates in a different kinetic and energetic regime than in synthetic catalysts.

Here we overcome these challenges and show that specifically tailored versions of these silica membranes can indeed couple inorganic catalysts with microbial catalysts on the shortest possible length scale—nanometers—while separating the incompatible abiotic and microbial environments. This proof-of-concept demonstration provides a platform to dramatically reduce ohmic losses associated with macroscale separation while avoiding chemical incompatibilities. This approach to integrate biotic and abiotic catalysts opens up an immense design space for building macroscale systems, thus providing an opportunity for scalable bioelectrochemical systems.

**Results**

**Designing the nanoscale membrane.** To explore this concept for the abiotic/biotic interface, we chose to test whether the bacterial catalyst, *Shewanella oneidensis* MR-1, could be electronically connected and yet chemically isolated from an inorganic catalyst, SnO\(_2\), using a nanoscale silica membrane (Fig. 1). *S. oneidensis* MR-1 can oxidize lactate and transfer electrons to a variety of metal oxides via outer membrane cytochromes (\(E^\circ \approx +200 \text{ mV}\) vs. normal hydrogen electrode (NHE); all redox potentials are vs. NHE) directly or in conjugation with flavins (\(E^\circ \approx 0\) mV, \(-200\) mV)\(^29\) to provide energy for cell maintenance and growth. We chose SnO\(_2\) as the abiotic component because its conduction units\(^30\) is far too negative, we designed an oligo-para(phenylene vinylene) molecule (abbrev. PV3) with strong electron withdrawing cyano (CN) and nitro (NO\(_2\)) substituents whose LUMO (lowest unoccupied molecular orbital) would be better matched to that of the *S. oneidensis* MR-1 outer membrane cytochromes.

**Tailoring electronic properties of molecular wires.** Our first steps were to synthesize this molecular wire and anchor it to the SnO\(_2\) anode. The compound \(4,4'-(1\text{Z},1\text{Z})-1,4\text{-phenylenebis}[2\text{-cyanoethene-2,1-diyl}]\text{bis}(3\text{-nitrobenzoic acid})\) (abbrev. PV3, Fig. 2) was prepared by Knoevenagel condensation strategy.
These molecules were covalently anchored on a Pt/SnO₂ film in a two-step process. First, the anchoring group 4-(trimethoxysilyl) aniline (abbrev. TMSA) was covalently attached to the oxide surface and its attachment was monitored by infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The good agreement between polarized Fourier transform infrared (FT-IR) reflection absorption (FT-IRRAS) spectra of free and anchored TMSA (Fig. 3a, traces (1) and (2)) indicates that the silyl aniline remained intact upon anchoring, as further described in Supplementary Methods. Additionally, a distinct N 1s peak at 399.8 eV (Fig. 3b, trace (2), and Supplementary Fig. 4) appeared in the XPS N 1s spectrum of the SnO₂ surface (Fig. 3b, trace (1)) upon TMSA anchoring, providing additional confirmation that TMSA is surface attached. It is worth noting that covalent attachment of the wire to the SnO₂ surface via the TMSA anchoring group likely causes electronic effects that determine the exact reduction potential of the wire in the complete assembly.

Next, PV3 was linked to the TMSA anchor via formation of an amide bond (Fig. 1a). Infrared spectroscopy of the resulting PV3 on Pt/SnO₂ showed that it shared key spectral features with that of solid PV3 with aniline end groups (Fig. 3a, traces (3) and (4), Supplementary Figures 4 and 6 and spectral assignments in Supplementary Methods). Furthermore, the XPS spectrum of PV3 attached to TMSA on Pt/SnO₂ (Fig. 3b, trace (3)) showed a N 1s band centered at 406.2 eV originating from the nitro groups along with overlapping nitrile and amide signals at 400 eV. Taken together, these infrared and XPS analyses confirm that the two-step anchoring method results in the attachment of the intact PV3 wire molecules on the Pt/SnO₂ surface.

To complete the nanoscale membrane, atomic layer deposition (ALD) was used to cast the PV3 wires on Pt/SnO₂ into SiO₂ with a thickness of 1.9 ± 0.3 nm as determined by ellipsometry. While the IRRAS measurement was challenging due to strong

**Fig. 2 Chemical structure of PV3 molecular wire**

**Fig. 3 Spectroscopic characterization of PV3 wire attachment and casting into SiO₂.** a FT-IR characterization. (1) Absorbance spectrum of TMSA powder in KBr. Scale bar is 0.008. (2) IRRAS of TMSA anchored on Pt/SnO₂ (using Pt/SnO₂ as reference) at 2 cm⁻¹ resolution, computed as the negative log of a single beam spectrum at p-polarization of a sample, divided by a single beam spectrum at s-polarization. Scale bar is 0.002. (3) Absorbance spectrum of powder of PV3 with the aniline groups attached on both ends of the wire molecule (model for TMSA anchored PV3) in KBr. Scale bar is 0.008. (4) IRRAS of PV3 attached to TMSA on Pt/SnO₂ (using SnO₂/PT as reference). PV3 bands highlighted in blue. Scale bar is 0.002. (5) IRRAS of pure SiO₂ layer on Pt/SnO₂ (using Pt/SnO₂ as reference). For clarity, raw spectrum shown in light trace is overlaid by computationally filtered (low bandpass) dark trace. Scale bar is 0.002. (6) IRRAS of SiO₂-encapsulated PV3 attached to TMSA on Pt/SnO₂ (using Pt/SnO₂ as reference). PV3 bands are shaded in black for clarity. Scale bar is 0.002. b XPS spectrum of the N 1s region of (1) Pt/SnO₂; (2) TMSA anchored on Pt/SnO₂ showing N 1s NH₂ peak; and (3) PV3 attached to TMSA on Pt/SnO₂ showing overlapping amide and cyano group signals centered at 399.5 eV and the nitro group at 406.2 eV. Two-component deconvolution is shown (see text). Binding energies are aligned with reference to adventitious C 1s peak at 284.8 eV. CPS counts per second. For completeness, bands for C 1s, O 1s, and Si 2p spectra are shown in Supplementary Fig. 4. c UV-Vis spectra of (1) 0.47 μM PV3 in aqueous solution and (2) difference spectrum of SiO₂-encapsulated PV3 on quartz/SnO₂ (transmission mode). Reference is pure SiO₂ on quartz/SnO₂. The gray line is a cubic fit for the background.
Chemically isolating two compartments on the nanoscale. To probe the ability of the PV3-SiO2 on Pt/SnO2 electrode (correct wire electrode) to both chemically separate and electrochemically connect the SnO2 and S. oneidensis catalysts, we needed to establish the level of chemical cross-talk in the absence of the SiO2 membrane and the level of current flow in the absence of embedded wires. Thus we synthesized Pt/SnO2 electrodes (bare electrode) as a negative control that should be unable to provide chemical separation and Pt/SnO2 overlaid with 2 nm SiO2 electrodes (no wire electrode) that should be unable to provide electrochemical coupling.

To probe whether the membrane could chemically separate yet protonically connect the SnO2 catalyst from the aqueous compartment that will contain S. oneidensis, we performed cyclic voltammetry in bioelectrochemical reactors (Fig. 4 inset) containing 1 mM KFeII(CN)6 and KFeIII(CN)6 solution in the aqueous compartment and bare, no wire, or the correct wire electrodes. The ferricyanide couple should be able to reduce and oxidize any accessible SnO2 surface but should be unable to reduce or oxidize the PV3 molecule in the no wire or correct wire electrodes. As expected for the bare electrode, a redox wave is observed at 314 mV (Fig. 4a, inset), confirming that ferricyanide can contact the electrode surface. By contrast, cyclic voltammograms of both the no wire and correct wire electrodes show no significant redox signal at 314 mV (Fig. 4a). (Note that in Fig. 4a the y axis of experiments with SiO2 membrane spans 0.25 mA cm−2, whereas the y axis of experiments with bare SnO2 (inset) spans 8 mA cm−2.) The absence of a redox wave with the no wire and correct wire samples indicates that the SnO2 surface is >99% inaccessible, demonstrating that the 2-nm-thick SiO2 membrane chemically separates the SnO2 catalyst from the aqueous compartment. It is also essential that this membrane allows H+ transport to enable full electrochemical coupling. The cathodic peak at −0.4 V in both the no wire and correct wire samples, which arises from the reaction of H+ with Pt to form H-Pt, also demonstrates that H+ can move through the silica layer in accordance with past observations. Thus we conclude that the casting of SnO2-anchored wires into a 2 nm silica layer creates a nanoscale membrane that can transmit H+ between the inorganic catalyst and aqueous compartment, while blocking small molecule transport.

Electron transport across the membrane with wires. We next sought to determine whether the SiO2 membranes with embedded wires could enable electron flow from the microbial catalyst to the SnO2 catalyst. To do so, we monitored current flow from S. oneidensis MR-1 expressing green fluorescence protein (GFP) to the bare, no wire, and correct wire electrodes in microaerobic
bioelectrochemical reactors (Supplementary Fig. 8). To ensure that the current we measured was limited by charge transport from \textit{S. oneidensis} to the SnO$_2$, we added lactate (the electron donor for \textit{S. oneidensis}) into excess, included Pt wire as a cathode, and poised all SnO$_2$ anodes to a potential of $+600$ mV vs. NHE (Supplementary Fig. 9). It is important to note that the use of the Pt/SnO$_2$ as an anode and an applied bias is only used to confirm current flow in these proof-of-concept experiments; in a bioelectrochemical system, the Pt layer would be replaced by an inorganic catalytic system. The chronoamperometric curves (Fig. 4b) present 28 h of bacterial current generation where additional lactate was introduced toward the end of the experiment to maintain the viability of the bacterial cells. To adjust for sample-to-sample variation in background (abiotic) current density, we calculated the difference between the maximal current produced by bacteria on the correct wire anode (Table 1) and the current density produced by the inorganic SnO$_2$ layer.

![Image]

**Table 1: Current density and bacterial cell density**

| Sample type                  | $I_f - I_s$ μA cm$^{-2}$ | Initial OD at 600 nm | Final OD at 600 nm | Cell density, μm cm$^{-2}$ |
|------------------------------|--------------------------|----------------------|--------------------|---------------------------|
| Bare anode Pt/SnO$_2$        | 4.92 ± 2.98              | 0.15 ± 0.00          | 0.24 ± 0.01        | N.D.                      |
| No wires SiO$_2$ on Pt/SnO$_2$| $-0.01 ± 0.01$           | 0.18 ± 0.05          | 0.07 ± 0.01        | 0.14 ± 0.18               |
| Correct wires PV3-SiO$_2$ on Pt/SnO$_2$ | 0.51 ± 0.42             | 0.14 ± 0.02          | 0.12 ± 0.01        | 0.41 ± 0.11               |
| Wrong wires PV3_SO$_2$ on Pt/SnO$_2$ | $-0.06 ± 0.09$           | N.D.                 | N.D.               | N.D.                      |

Data for different electrode and membrane combinations are shown.

Bacterial catalysts are viable in the presence of membrane. Under the reactor conditions, \textit{S. oneidensis} can use electron transfer to an extracellular electrode to maintain or increase cell mass. To determine whether the rate of electron transfer was sufficient to support maintenance or growth of the bacterial catalyst, we monitored the density of \textit{S. oneidensis} cells in solution via optical density at 600 nm (OD$_{600nm}$) and on the electrode via confocal microscopy. \textit{S. oneidensis} can attach and grow in the presence of different electrode surfaces under aerobic conditions and free of electrical bias (Supplementary Fig. 10), which confirms that the surfaces themselves are not toxic. Under microaerobic, polarized conditions, the initial cell density was similar in all the reactors independent of the electrode surface. After 2 days, the cell density in solution dropped by ~60% in the no wire electrodes, yet only decreased ~15% in the reactors containing correct wire electrodes (Table 1). In agreement with this trend, a significant density of bacterial cells (0.41 ± 0.11 cells μm$^{-2}$) were attached to the correct wire electrodes, while a much lower density (0.14 ± 0.18 cells μm$^{-2}$) were attached to the no wire electrode (Fig. 4c). These data indicate that the PV3 wires support electron transfer at a rate that enables \textit{S. oneidensis} to maintain biomass, thus fulfilling an important prerequisite for any bioelectrochemical system.

**Discussion**

While providing proof-of-concept of a nanoscale separation membrane for bioelectrochemical systems, the current density from the bacterial catalysts to the molecular wires is presently ~10% of the current density of the bacterial catalysts on the bare Pt/SnO$_2$ electrode. Thus additional understanding and optimization is required to fully realize the efficiency and scalability of this platform. We hypothesize that optimizing the wire redox potential and density will increase the current density from the bacterial catalysts to the inorganic surface via silica-embedded wires so that the rate and energy efficiency of this system will be limited solely by the catalytic components rather than charge transport between them. Specifically, for shifting the LUMO energetics of the wire molecules to more positive values, aryl moieties can be modified by CF$_3$ groups as previously reported for organic molecular wires.
While the planar configuration of the platform allowed proof-of-concept, bioelectrochemical systems featuring ultrathin separation membranes require the development of three-dimensional (3D) geometries for extending the separation across all length scales from nano to macro. At the same time, the high surface area of 3D systems will compensate for the relatively slow rate of heterogeneous electron transfer between an electrode and S. oneidensis or other microbial catalysts (−100 IA per cell). We envision core–shell microtube arrays where the core of each tube is the inorganic catalyst, while the shell is an ultrathin silica tube with embedded wires. Such core–shell tube arrays of ~5 cm² size are being developed in our laboratory48, 49 along with metal nanocatalyst attachment on the SnO2 layer for important reduction reactions such as the generation of hydrogen peroxide from O2 or conversion of nitrobenzene to aniline.

More broadly, the nanoscale membrane presented here is one specific implementation of a broader concept for improving scaling up in bioelectrochemical systems. In electrolysers systems13–15 and related bioelectrochemical systems19, 20, microbial catalysts can accept electrons from an electrode at redox potentials ranging from ~300 mV to +310 mV39–43 and utilize these electrons to synthesize biomass44 or precursors to energy-rich molecules.17 Since molecular wires with LUMOs spanning −0.5 to −1.7 V or HOMOs (highest occupied molecular orbitals) from +1.4 to over 2 V have already been demonstrated, a nanoscale membrane with the appropriate wires could be used as an interstitial layer between a water-splitting anode and the microbial catalysts, obviating the need for external wires (Supplementary Fig. 9). Electrons and protons from the water-splitting reaction would transit the silica membrane to reach the microbial catalysts, while toxic reactive oxygen species and metal ions would be blocked. Since the electrochemical cycle is closed on the nanoscale, ohmic losses between the water splitting and microbial catalyst would be ~10 mV compared the ~250 mV found in the state of the art. We also envision the nanoscale membrane described here could be used as current collectors44, 45 or separators46 to avoid corrosion or oxygen crossover in microbial fuel cells or microbial electrolysis cells (Supplementary Fig. 1; note that the ultrathin silica membrane is O2 impermeable). Additionally, the concept demonstrated here should apply to bioelectrocatalytic systems that harness the energy found in biomass or waste. The concept presented here also could be used as a proof-of-concept, bioelectrochemical systems featuring ultrathin silica membrane to drive a variety of bioelectrocatalytic processes, such as the generation of hydrogen peroxide from O2 or conversion of nitrobenzene to aniline.

In conclusion, we demonstrate a concept for completing the redox couple between a microbial catalyst and inorganic catalyst at the nanoscale while separating the incompatible anodic and cathodic reaction environments. This electron transport occurs only when the energetics of the microbial catalyst and molecular wires are matched, and it occurs rapidly enough to allow the microbial catalyst to maintain biomass. The ability to optimize this platform for different combinations of inorganic and microbial catalysts will drive development of scalable bioelectrochemical systems that harness the energy found in biomass or renewable sources to a variety of chemicals and materials.

**Methods**

**Pt deposition.** Pt 100 nm (99.99%) was deposited by e-Beam evaporation (Semi-core SC600 e-beam evaporator) at 2 x 10⁻⁸ Torr on a Si wafer with ~5 nm of Ti or Cr to improve adhesion.

**SnO2 deposition.** ALD of tin dioxide was carried out using an Oxford FlexAl-Plasma Enhanced Atomic Layer Deposition system. At a temperature of 200 °C and 80 mTorr (60 SCCM O2: 100 SCCM Ar; SCCM = standard cubic centimeters per minute), Sn precursor (tetraakis(dimethylamido)tin(IV) bubbled with 100 SCCM of Ar was injected into the chamber (~5 s pulse), 20 SCCM oxygen (Ar purge) was pulsed to the chamber (~5 s pulse), and the pulse was followed by purging 5 s with 60 SCCM O2 and 200 SCCM Ar. A 0.5 s pre-plasma step with pressure set at 15 mTorr (60 SCCM O2: 100 SCCM Ar) was followed by a 5 s step of 300 W plasma (60 SCCM O2: 20 SCCM Ar) and 1 s post of post-plasma purge with (60 SCCM O2: 100 SCCM Ar).

**TMSA attachment to SnO2.** Two 6.35 x 1.1 cm² substrates (either Si/Pt/SnO2 or fused quartz/SnO2) were cleaned by sonication in isopropanol for 5 min before being arranged back to back in a 25 mL Schlenk flask containing 5.4 mg (0.025 mmol) TMSA (90%; Geltex). The flask was sealed and evacuated for 1 h at ambient temperature before 25 mL of toluene (HPLC grade; Sigma Aldrich) was added by syringe. The content was sonicated for 5 min in a small sonication bath, and the solution was stirred for 12 h. After stirring, the substrates were transferred directly to the nanotube reactor and sonicated for 10 min, and the solvent was switched to a 50% vol. methanol–toluene mixture and sonicated for 10 min again before changing the solvent to methanol and sonication for another 10 min. As a final step, the substrates were dried with a N2 stream and immediately utilized for PV3 attachment or kept in a closed vial for further characterization.

**PV3 attachment to TMSA.** Two substrates with TMSA attached (either Si/Pt/ SnO2 or quartz/SnO2) were placed back to back in a 10 mL Schlenk flask such that the samples were vertical inside the flask. After addition of 3.1 mg (6.1 µmol) of PV3-CN:CO:CH (4.4’-((1,1’-Z)-1,4-phenylenebis(2-cyanoethene-2,1-diyl)) bis(3-nitrobenzoic acid)) and 5.4 mg (14 µmol) of HBF4 (N,N’,N’-tetramethyl-1-(1H-benzotriazol-1-yl)uronium hexafluorophosphate (Sigma Aldrich), the flask was sealed and evacuated on the Schlenk line for 2 h before 10 mL dimethyl formamide (DMF; anhydrous; Sigma Aldrich) was added by syringe with 0.1 mL (0.57 mmol) N,N-diisopropylethylamine (Alfa Aesar). The solution was stirred at 40 °C for 12 h. To clean the substrates, they were rinsed with water and transferred to a flask containing deionized water, sonicated for 5 min, and dried with N2. The cleaned substrates were transferred to the ALD chamber and sealed in the dark for further characterization.

**SiO2 atomic layer deposition.** SiO2 was deposited in a modified Savannah 100 Cambridge Nanotech ALD system equipped with a hollow cathode plasma source and a grounding grid above the sample. SiO2 deposition was carried out at 80 °C using a two-step following cycle. After a 30 s purge with (60 SCCM O2; 100 SCCM Ar, the chamber exhaust was closed and a 0.05 s pulse of tris-dimethylaminosilane (TMSA) was introduced to the chamber. The chamber was kept sealed for 60 s before purging with 40 SCCM of Ar for 30 s followed by a 5 s SCCM 45 s purge with O2. At a pressure of ~20 mTorr, the plasma was ignited for 30 s followed by purging with Ar for 45 s at 5 s SCCM. Twenty such cycles lead to a deposition of 2.28 ± 0.27 nm-thick SiO2 layer.

**IRRAS measurements.** IRRAS spectra were measured with a Bruker FT-IR spectrometer model Vertex 70 equipped with a LN2 cooled HgCdTe detector, a reflection accessory Bruker model AS15/Q, and wire-grid polarizer model F350. The mirror angle of the IRRAS accessory was fixed at 80° and the grid polarizers were switched between an s- and p-polarization (determined by scanning for maximum and minimum infrared throughput (ADC count) for each polarization). Ten spectra of 256 scans each were recorded and averaged to reduce the noise level after purging the sample compartment with N2 for 10–20 min. Sample single channel spectrum at p-polarization was divided by a single channel spectrum of the reference sample at the same polarization and the negative logarithm calculated. A similar spectrum of the s-polarization was calculated as well and the difference is shown in Fig. 3. Supplementary Figure 6 shows the single polarization spectrum of each sample.

**UV-Vis spectroscopy.** UV-Vis spectra were recorded using a monochromatic Al Kα source (λ = 1486.6 eV) operated at 225 W at a takeoff angle of 0° relative to the surface normal, and pass energy for narrow scan spectra of 20 eV. Spectral analysis was conducted with the software CasaXPS V2.3. Binding energy scale was corrected to adventitious C1s at 284.8 eV.

**Ultraviolet-visible (UV-Vis) measurements.** Fused quartz substrates were used for SnO2 deposition. Procedures for TMSA anchoring and subsequent attachment of PV3-CN:CO:CH were the same as for Si/Pt substrates. UV-Vis measurements were taken with a Shimadzu ultraviolet–visible spectrophotometer 2501PC using an integrating sphere accessory model ISR-2200. The beam is focused on a 2 x 2 mm² area of the sample. A 5 mm slit and slow scan was used to collect the spectra.
without any sample in the reference beam path. Difference spectra were calculated by taking the difference of a spectrum of Quartz/SnO2/PV3_CN_NO2_CO2_TMSA, with or without 0.1 M tert-butyl ammonium hexafluorophosphate (NBu4PF6), and the same substrate without PV3_CN_NO2_CO2_TMSA. Prior to recording of spectra, the back side of the substrate was cleaned by UV-ozone treatment for 5 min.

Absorption spectra of PV3_CN_NO2_CO2_H were dissolved in water with the assistance of a few ml of 1 M tetra-butyl ammonium hydroxide in methanol (final concentration 0.13 mM). The difference spectrum was calculated by subtracting spectrum of the same solution without PV3_CN_NO2_CO2_H.

The surface density of anchored wire molecules was calculated as follows: approximating the baseline in the 260–450 nm region by a third-order polynomial (gray curve of Fig. 3c, trace (2)), the absorbance of quartz/SnO2/PV3/SiO2 at 315 nm is determined as 0.006. Using Beer–Lambert law and a measured extinction coefficient for PV3 of ε = 20,280 L mol⁻¹ cm⁻¹, A/ε [PV3] is calculated as 2.97 × 10⁻⁵ mol cm⁻² or 1.79 molecules nm⁻².

**Electrochemical measurements.** Cyclic voltammetric measurements were carried out using a CH Instruments model CHI604E potentiostat equipped with a Ag/AgCl as reference electrode (Hart Scientific) reference electrode (Hart Scientific) reference electrode (Hart Scientific), 69–0053; 1 mm diameter; 3.4 M KCl) and Pt wire counter electrode housed in a custom-made photoelectrochemical cell. An aqueous solution of 1 mM of K3Fe(CN)6 (CN)₆ and KFe(CN)₆(CN)₆ was used for testing accessibility of the SnO₂ surface. Redox potentials of PV3 and PV3_S02₆⁻ molecules were calculated from cyclic voltammetry or linear sweep voltammetry measurements of 1 mM solution of these molecules with 0.1 M tert-butyl ammonium hexafluorophosphate (NBu₄PF₆) and ferrocene (1 mM) in dry DMF purged with Ar or N₂. The ferrocene (0/1) redox potential is 0.45 V vs. saturated calomel electrode (SCE). The LUMO of PV3_CN_NO2_CO2H is situated at −0.55 V vs. NHE, and the HOMO level was calculated from the intersection of optical absorption and ferrocene at 3.3 eV vs. NHE. Linear sweep voltammetry was used to determine the HOMO level of PV3_S02₆⁻ and redox potential is 0.45 V vs. saturated calomel electrode (SCE). The LUMO of PV3_CN_NO2_CO2H is situated at −0.55 V vs. NHE, and the HOMO level was calculated from the intersection of optical absorption and ferrocene at 3.3 eV vs. NHE. Linear sweep voltammetry was used to determine the HOMO level of PV3_S02₆⁻ and the same substrate without PV3_CN_NO2_CO2H.

**Bacterial strains and growth conditions.** Two strains of the S. oneidensis MR-1 expressing GFP were grown with 50 µg kanamycin. Two strains of the S. oneidensis MR-1 expressing GFP were grown with 50 µg kanamycin. S. oneidensis MR-1, a Gram-negative facultative anaerobe, was grown with 50 µg kanamycin.

**Bioelectrochemical characterization.** After overnight growth, S. oneidensis MR-1 cultures were washed 2 times and then diluted approximately ten-fold to a final OD₆₀₀ of ~0.15 (~2.5 × 10⁷ cells mL⁻¹). Two strains of the S. oneidensis MR-1 were used in this work. To visualize attachment of the bacteria to surfaces, we used S. oneidensis MR-1-expressing GFP. To probe the involvement of outer membrane cytochromes in electron transfer, we used a mutant S. oneidensis MR-1 that does not express outer membrane cytochrome c (S. oneidensis ΔmctB) Bacterial cultures were inoculated from frozen glycerol stocks into 5 mL of Luria-Bertani broth and grown at 30 °C with 225 rpm shaking overnight to early stationary phase. Cultures of S. oneidensis MR-1 expressing GFP were grown with 50 µg kanamycin.

**Data availability.** The data that support the findings of this study are available from the corresponding authors upon reasonable request.
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Author contributions

C.M.A.-F. and H.F. conceptualized the design, guided the experimental design and analysis and edited the manuscript. J.A.C. prepared the bacterial samples, developed together with E.E. the electrochemical cell, and conducted the electrochemical experiments and confocal microscopy. H.S. designed and executed the synthesis and spectroscopic characterization of molecular wires. E.E. prepared and spectroscopically characterized the membranes on inorganic substrates. All authors contributed to manuscript writing.

Additional information

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