

High-Durability Organosiloxane Nonskid Coatings

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Introduction: The 2006 Cost of Corrosion Study issued by the Office of the Secretary of Defense (OSD) identified nonskid decking coatings as one of the Fleet's "top five" cost drivers. The Navy installs nearly 3.7 million square feet of the nonskid coatings at a cost of roughly \$56.6 million per year. This is because the average life expectancy of traditional epoxy-based nonskid coating is at best 18 months.

The Office of Naval Research's (ONR) Future Naval Capability Program, together with NAVSEA's Capital Investment for Labor (CI-Labor) Program – Nonskid Initiative, aims to improve the state of the art of available nonskid coatings and materials. As the technical lead for ONR and NAVSEA, the Naval Research Laboratory is striving to extend the service life of Navy nonskid systems. This includes identifying or developing and testing next-generation non-epoxy alternatives for extended-durability flight and general deck performance, and addressing heat-resistant issues associated with current and future vertical launch aircraft requirements.

Currently, the Navy's traditional (MIL-PRF-24667) nonskid coatings are composed of an epoxy and an amine component, which are mixed together and applied over an anticorrosive deck primer. The coating is roll-applied to the deck using a phenolic roller to create a rough "peak and valley" profile, thereby providing a frictional surface that prevents the sliding or skidding of crew members, aircraft, storage containers, and machinery. To provide this aggressive profile, these coatings usually contain aluminum oxide or aluminum metal aggregate for general purposes areas (Type-G) or landing areas (Type-L), respectively. Typical MIL-PRF-24667 nonskid coatings are also modified with fillers (such as silicas, talc, and calcium carbonate) and thickening agents to yield a specified impact resistance and viscosity. Improper mixing of the two components, poor application, insufficient cleaning of the deck primer, outright lack of deck primer, as well as environmental/operating conditions, can all lead to premature or catastrophic failures, such as coating disbondment, corrosion seepage due to the cracks in the nonskid coating, and loss of slip resistance. Although the majority of these issues are examples of installer-related problems, the main problem with current nonskid technology is that the epoxy and amine components are not engineered to withstand the external environmental conditions that the U.S. Navy routinely encounters.

The epoxy component of traditional nonskid coatings is composed of aromatic epoxy resins, whereas the amine component is primarily composed of polyamine and/or amidoamine resins. Aromatic epoxy resins, which provide good hardness and chemical resistance, are notorious for degrading rapidly when exposed to external weathering conditions including UV radiation and oxygen. These resins are intended for use on internal structures, such as ballast tanks or floor primers, and are rarely used for the external coating of structures by the coating industry. As for the amine component, amidoamine resins contain chromophores that absorb external radiation and cause yellowing. The amide groups also impart high levels of hydrogen bonding, thereby increasing the level of solvent required to use the resin in a coating. Furthermore, polyamine and amidoamine resins can frequently cause "blushing," which is a reaction with CO₂ and water that creates an insoluble white film on the surface of the nonskid coatings.

Technology Description: Hybrid coating technology based on the incorporation of silicone-based resins with nonaromatic epoxy or amine chemistries can provide better performance characteristics than traditional coatings because silicone-oxygen bonds are much stronger than the carbon-carbon, carbon-hydrogen, or nitrogen-hydrogen bonds that are found in traditional nonskid coatings, not to mention the elimination of aromatic moieties that absorb UV radiation and easily degrade. This increased bond strength of siloxane groups leads to greater external durability because the silicone-oxygen bonds are already oxidized and do not absorb UV radiation, thereby extending the life of a coating and preventing the rapid chalking, fading, and cracking that occur with conventional nonskid formulations.

At the Naval Research Laboratory, we have recently formulated a novel siloxane-based nonskid coating (Fig. 1) that provides greater external durability, color retention, and chemical resistance than traditional



FIGURE 1
Close-up view of NRL's siloxane nonskid coating (rolled version).

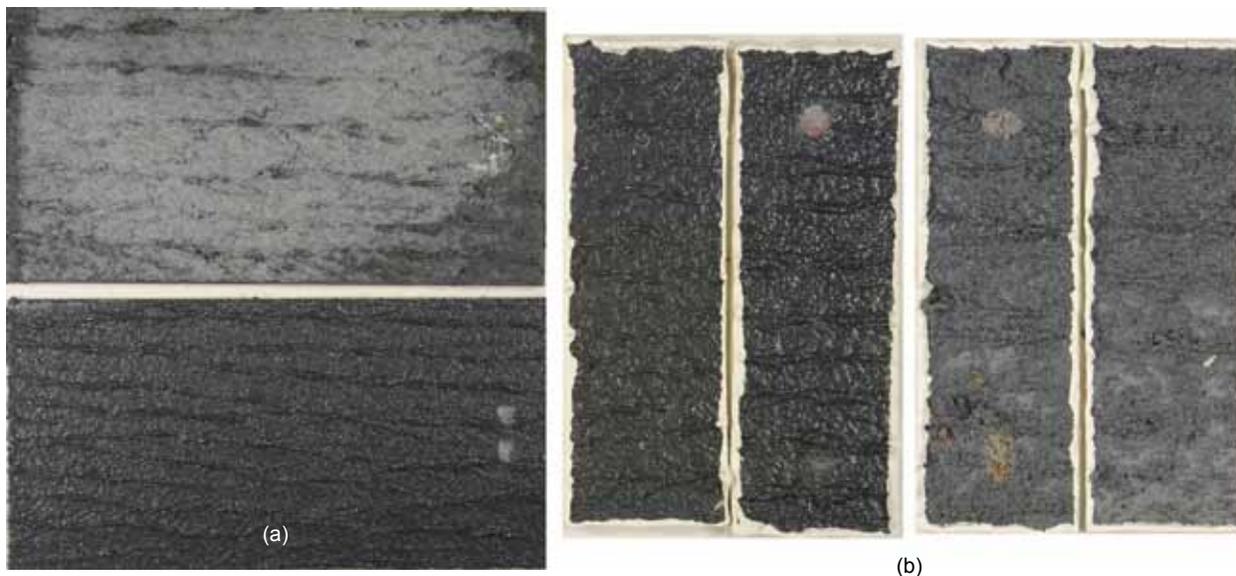


FIGURE 2

(a) NRL's siloxane nonskid (bottom) vs a commercial composition G epoxy (top) after 400 hours QUV-B exposure. (b) NRL's siloxane nonskid (left) vs a commercial epoxy (right) after 28 days of detergent immersion.

epoxy nonskid coatings. The newly developed coating can be applied over a primed surface or directly to clean and blasted steel, and applicators have the option of spraying or rolling the material. When subjected to numerous MIL-PRF-24667 tests, the siloxane nonskid coating greatly outperformed a traditional qualified nonskid epoxy coating, especially with regard to UV and chemical resistance (Fig. 2).

Technology Scale-Up and Demonstrations:

To expedite technology transition to the Fleet, NRL is directly working with a Navy approved coatings supplier to produce production batches and work out system scale-up issues. The siloxane nonskid has been

scaled-up to produce batches of over 160 gallons, thus allowing NRL to perform field demonstrations on several Norfolk, Virginia-based ships. For instance, the first trial occurred on USS *Ponce* in April 2010, where 50 gallons of siloxane nonskid was roll-applied on the 03 level – Aux Conn Station. Since then, both roll and spray trials have occurred on USS *Oak Hill* (May 2010), USS *Whidbey Island* (June 2010), USS *Mason* (June 2010), USS *Ramage* (August 2010), and USS *Cole* (December 2010). Figure 3 shows the siloxane nonskid adjacent to a traditional epoxy nonskid on the deck of USS *Mason*. One can easily see how after six months of exterior exposure, the traditional material has faded and begun to degrade, whereas the siloxane nonskid is color-fast and in nearly pristine condition.



FIGURE 3

NRL's siloxane nonskid (right) vs a commercial epoxy nonskid (left) after 6 months exposure on USS *Mason*. The commercial nonskid was dark blue when initially applied.

Technology Cost and Product Characteristics:

Currently, the cost of the siloxane nonskid is roughly \$100 per gallon, or \$500 for a 5 gallon kit (as supplied), whereas qualified Navy nonskid coatings range from \$70 to \$80 per gallon. However, it should be noted that this is not the final cost of the product, as price is based on manufactured volume and amount sold. When roll-applying the product, coverage is approximately 20 to 25 square feet per gallon. This number increases to approximately 45 square feet per gallon when spray application is used. It is anticipated that both application processes will be employed by the Fleet in the future; however, due to flight deck performance requirements, the roll application may be retained exclusively for aircraft carrier flight deck applications, whereas spray application may be employed for general traffic locations and rotary wing flight decks. It is anticipated that

the unit cost of the material will be significantly reduced as more material is specified for application in the Fleet when the product becomes approved for Navy use in the Qualified Product Database.

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Advanced Trace Explosives Detection Testbed

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Introduction: The Department of Defense (DoD) and the Department of Homeland Security (DHS) need improved explosives detection systems to protect personnel and platforms from attack from insurgents and terrorists both at home and abroad. Therefore, research is under way for the development of new materials and sensors for explosives vapor detection. However, uniform, reliable methods for evaluating new detection systems are limited, making assessment of the new products difficult. Drawing from much experience in hazardous chemical vapor generation and detection, the Naval Research Laboratory's Chemistry Division has developed a comprehensive testbed for trace explosives vapor generation and assessment of sensor technology.¹

A multidisciplinary team of scientists and engineers from the Chemistry Division came together to design and construct the state-of-the-art trace explosives detection testbed, shown in Fig. 4, which facilitates the development and evaluation of advanced trace explosives detection technologies. The testbed is a fully automated



FIGURE 4

Advanced Trace Explosives Detection System Testbed with touch screen GUI.

system using NRL-developed custom software that is controlled by a touch screen graphical user interface (GUI). Six sample ports are available for individual or multiple, simultaneous testing of novel sensors and materials. The testbed consists of SilcoNert™-treated stainless steel gas lines, a custom mixer, and a dual distribution manifold (see Fig. 5) enclosed in a custom oven, which can operate at temperatures up to 150 °C. The dual manifold was designed to permit rapid switching

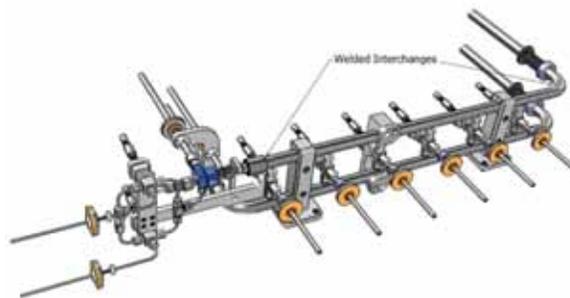


FIGURE 5

Dual manifold with six sample ports.

between clean air and the analyte sources, via computer-controlled actuators that drive custom feed-throughs to open and close all valves. All oven-enclosed components are bakeout-compatible, but the manifold may be easily exchanged with a duplicate manifold to prevent any possibility of cross contamination between different explosive analytes. The testbed employs a zero-grade air source with temperature and humidity control, and vapor generation systems for comprehensive testing of trace levels of explosives and potential interferents.

The touch screen interface allows a user to control and monitor all system components, enabling a wide variety of test conditions including different vapor concentrations, test mixtures, and test durations. Standard and custom test protocols are easily developed and implemented. The system was designed to enable the implementation of test protocols developed by any testbed-equipped laboratory, facilitating interagency sensor/material research collaborations and accelerating the validation of prototype commercial systems.

Custom sensor chambers, as shown in Fig. 6, were designed for evaluating materials and sensors. The Impactor Sample Chamber accommodates a variety of sensor types, directs the test vapor directly onto the sensor, and can be individually heated. An online verification system that uses a thermal desorption/gas chromatography/mass spectrometry/electron capture detector has also been incorporated into the testbed. The testbed was analytically characterized using both TNT and RDX for concentrations from parts per trillion (ppt) to parts per billion (ppb) in humid air from

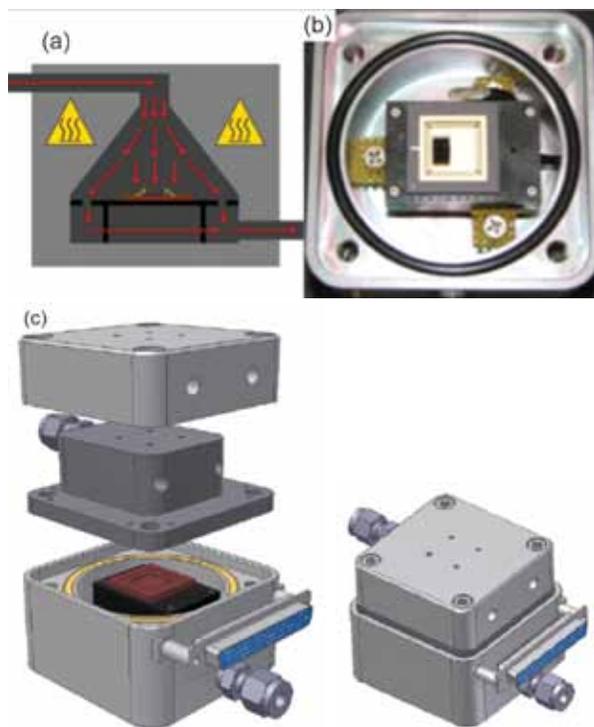


FIGURE 6
 (a) Schematic of the Impactor Sample Chamber with the red arrows indicating the gas flow into the chamber, onto the sensor, and out to the exhaust. (b) A prototype sensor array mounted in a pin grid array and loaded into the Impactor Sample Chamber. Electrical connections to the device are made through the packaging and the zero insertion force (ZIF) socket (black). (c) Impactor Sample Chamber.

20% to 85% relative humidity (RH). Consistent results were observed at all six sample ports.

The NRL testbed is the only one of its kind in the world to provide quantitative results for explosive vapors over such a wide concentration range. NRL is using the testbed to evaluate sensor systems under development in the Chemistry Division. We expect to use the system to evaluate new materials and sensors being developed by DHS in the future. A second testbed was constructed and delivered to the Transportation Security Laboratory for evaluating new detection systems of interest to DHS. The concepts used for the DHS testbed were applied to the development of another testbed using large domes to provide uniform vapors over a large area for the evaluation of entire instruments or arrays of sensors. Both testbeds are now being expanded to include more threats and potential interferences. The Advanced Trace Explosives Detection System will allow DoD and DHS to assess technologies in a consistent manner, thus providing our troops and TSA personnel the best technologies to safeguard personnel and platforms.

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Reference

¹ "NRL/DHS/TSL Advanced Trace Explosive Detection Testbed, Operations Manual," NRL/PU/6180--10-544, Naval Research Laboratory, September 2010.

Highly Conductive Molecular Wires for Electronic, Sensing, and Energy-Converting Devices

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Introduction: The construction of highly efficient molecular electronic, sensing, and energy-converting devices requires a high rate of signal transduction between molecules and electrodes. One of the promising molecules in the construction of these devices is oligo(phenylene vinylene), OPV. This molecule can be considered as a graphene ribbon with an extremely narrow width approaching the single phenyl ring. The molecule has delocalized molecular orbitals and performs efficient electron transfer (ET) at various conditions. However, OPV has a relatively large highest-occupied-molecular orbital/lowest-unoccupied-molecular orbital (HOMO-LUMO) band gap with molecular orbitals located far from the electrode Fermi level and thus requires the application of high bias voltages for the generation of current. To achieve efficient ET between a molecule and an electrode at low bias voltages, one needs a molecule that has an electronic energy level near the electrode Fermi level.

A New Conductive Molecule with a Low Band Gap and a High Level of Electron Delocalization:

To solve the problem, we synthesized a new molecule, oligo(phenylene vinylene) quinone, OPVQ, having OPV as the main component and a quinone with two oxygen atoms as an end group (Fig. 7). The molecule has a planar configuration allowing for efficient sp^2 hybridization and molecular orbital (MO) delocalization through the entire structure, and shows highly efficient conductivity at low biases in electrochemical and scanning tunneling microscopy (STM) measurements.^{1,2}

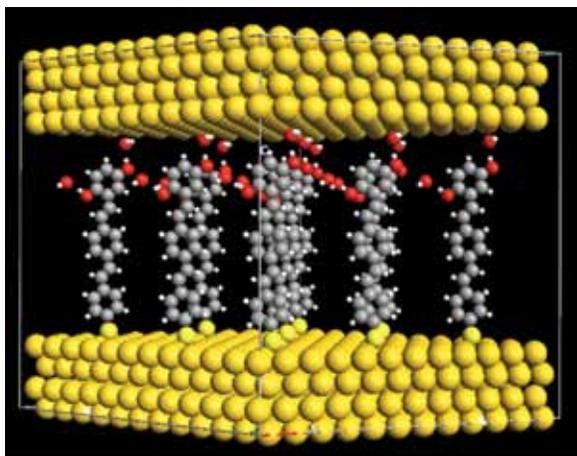


FIGURE 7
Model of the reduced and protonated form of OPVQH molecular wires including water between two gold electrodes.

The Narrow Transmission Band: The origin of the high conductivity of OPVQ lies in its molecular electronic structure and the electron transmission spectrum (ETS). The unique feature of OPVQ is the presence of a narrow transmission band near the gold electrode Fermi level (Fig. 8). This band has a Lorentzian shape and indicates extremely high rates of ET, 9.73×10^{12} and $2.26 \times 10^{12} \text{ s}^{-1}$, to the left and right electrode, respectively.³ The position of the band in the energy spectrum is very stable and only slightly shifts under either positive or negative bias without substantial changing of its width. In addition, no change in the band intensity under different bias voltages was observed.³

The Spatial Distribution of Electrostatic Potential:
The discovered effect of the two oxygen atoms on the

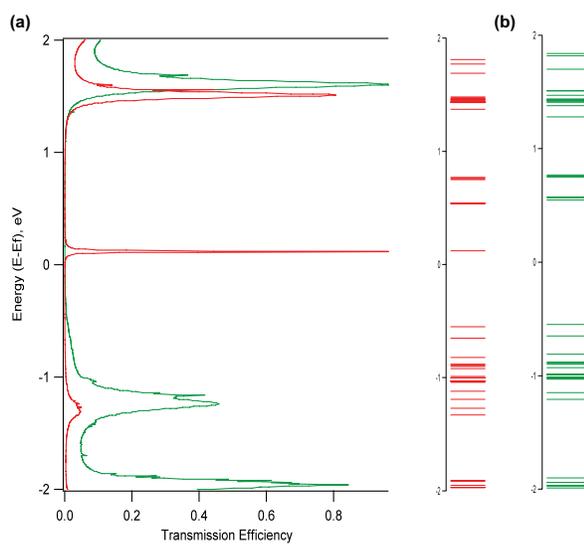


FIGURE 8
Electron transmission spectra (a) and energy spectra (b) for Au|OPVQ Au (red) and Au|OPV Au (green) junctions.

molecular conductivity is due to the spatial distribution of electrostatic potential at the molecule–electrode junction (Fig. 9). At zero bias, the potential profile has two barriers of different width located between the sulfur atom and the carbon ring at one contact and between the quinone ring and the right electrode at the other contact. In addition, the profile shows that oxygen atoms generate a field in the surrounding molecule area that forms a local negative barrier, which prevents a uniform potential distribution in the space between the electrodes. Application of a small bias between electrodes (0.4 V, more negative at the left electrode) completely eliminates the potential barrier between the molecule and the left electrode and changes the spatial distribution of the electrostatic potential allowing for efficient ET to the molecule from the right electrode. Now the molecule is in equilibrium with the left electrode, and this electrode determines the potential of the molecule. Such distribution of the potential does not

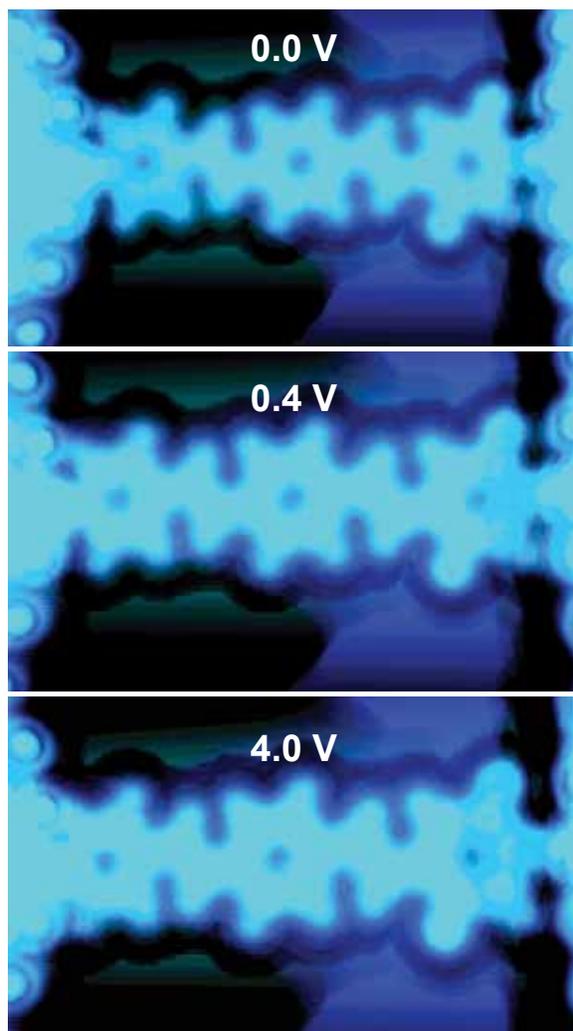


FIGURE 9
Real space effective potential for Au|OPVQ Au junction at biases = 0.0, 0.4, and 4.0 V (from top to bottom).

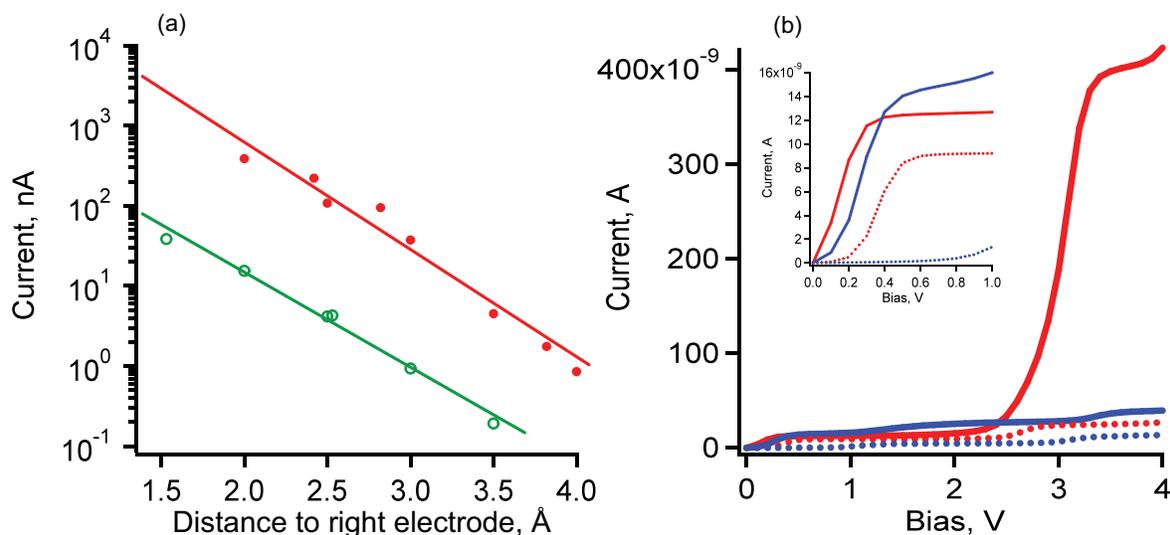


FIGURE 10

(a) Dependence of the current through Au|OPVQ Au (red) and Au|OPV Au junctions (green) on the distance between the molecule and the right electrode. Bias voltage = 0.4 V. Rings are the calculated data and the line is the linear fit. (b) I-V curves for the conductivity of OPVQ (red) and OPVQH (blue) between two gold electrodes in the absence (dashed) and presence (solid) of water. The distance between the electrodes is 25 Å. The current intensity at low biases is shown in the inset.

alter upon further increasing the bias. In addition, the potential profile shows the presence of a valley near one of the carbon atoms of the quinone ring that possibly specifies the main electron flow pathway through this carbon atom to the right electrode.

Distance Attenuation Factor: The tunneling through space is one of the most crucial factors determining the efficiency of molecular electronic devices. The current through OPVQ at increasing distances between the molecules and the electrode exponentially reduces with the decay attenuation factor $\beta = 2.69 \text{ \AA}^{-1}$ (Fig. 10(a)). OPV shows the same slope and a similar distance attenuation factor, but the current is about 100 times lower. Extrapolation of the fitted curve to 1.4 Å distance between the OPVQ and the electrode (corresponding to a single carbon chemical bond) approaches the theoretical limit of molecular conductance ($1 G_0$). Thus, being chemically bound to both electrodes, the OPVQ should have a conductance close to the quantum limit.³

Electrochemical Conductance Switching: One of the most interesting features of the constructed molecule is the possibility of reverse-switching its molecular conductance by changing the electrochemical potential of the surrounding medium (electrochemical conductance switching).² Our electrochemical STM experiments show that the reduction-protonation of OPVQ is reversible and can be done many times without changing the conductance efficiency.⁴ The electron transmission spectra show that the effect is due to appearance and disappearance of the narrow transmission band

around the Fermi level, which is typical for OPVQ, and is missing from OPVQH.

Long-Range Electron Transfer Through Water Molecules: Water molecules are a very important component in any chem/bio-sensing device.⁵ The ET spectra of oxidized and reduced forms of OPVQ reveal that water molecules stabilize and improve conductivity through the narrow transmission band. In addition, the water molecules induce the formation of new strong transmission bands below the Fermi level leading to the appearance of additional p-type conductivity channels.⁵ These effects of water lead to substantial changes in the I-V curves. For dry molecules at low source-drain biases (at about 0.4 V), the conductivity nearly turns off when the molecule is reduced-protonated (Fig. 10(b), inset). Instead, for wet devices at these biases, the reduced-protonated molecule has conductivity higher than the oxidized one. At biases between 3 and 4 V, when additional ET paths through water molecules become operational, the difference in conductivity for the wet configuration will be orders of magnitude (Fig. 10(b)). In addition to the increasing efficiency, the direct interaction of water molecules with OPVQ changes the pathway of ET, potentially allowing for its redirection.

Summary: Electron transfer at the organic-inorganic interface is a major roadblock in the construction of efficient chemical and biological sensing, soft optoelectronic, and energy-converting devices. We have shown that the problem can be overcome by the construction of innovative molecules with the efficient

electron delocalization and precise positioning of electron acceptor groups that allow for the efficient control of spatial charge distribution, and electron tunneling through space and solvent located between the molecule and the electrode. Our experimental and simulation results demonstrate that the conductance through the constructed molecules is highly efficient, coherent, and can achieve the theoretical limit of molecular conductance.

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