

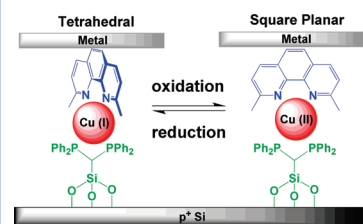
# Surface Immobilized Heteroleptic Copper Compounds as State Variables that Show Negative Differential Resistance

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**ABSTRACT** Surface immobilized bidentate heteroleptic Cu(I) compounds are synthesized using a surface outward sequential synthesis and are characterized using solid-state NMR and atomic force microscopy (AFM). Through use of chemical redox agents, the reversible switching characteristics of SiO<sub>2</sub>-immobilized Cu(I) compounds (tetrahedral) to Cu(II) (square planar) are verified via UV–visible absorption spectroscopy and electron paramagnetic resonance. Electrical properties of this system are characterized via preparation of a sandwich-type device using p<sup>+</sup> silicon and conductive AFM (cAFM). Current–Voltage (I–V) spectroscopy demonstrates that this system reproducibly switches between Cu(I) and Cu(II) states at approximately −0.8 and 2.3 V.

**SECTION** Nanoparticles and Nanostructures

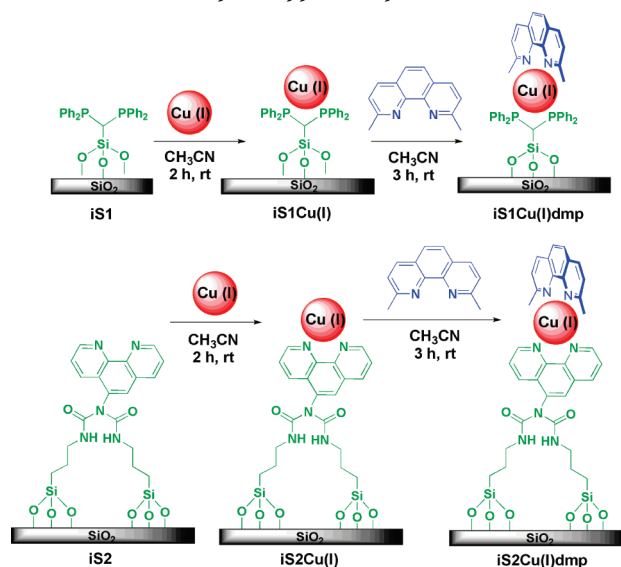


State variables<sup>1</sup> for silicon-based electronic devices are physical representations of information used to perform information processing via memory and logic functionality.<sup>2</sup> Silicon-based electronics are based on Boolean logic, i.e., 1 or 0, where a physical state variable must reside and be controlled in two distinguishable states. In order to optimize the current technology, many factors need to be considered, including maximum speed (time to perform a function), minimum physical area/volume (high device density per area), and minimum energy dissipation (reduced heat dissipation). Nanoscale electronics based on functional molecular units acting as state variables provide an attractive alternate to conventional metal-oxide-semiconductor field-effect transistor (MOSFET) technology due to their potential scalability, low-cost, low variability, highly integratable characteristics, and the capacity to exploit self-assembly processes. In this letter, copper compounds coordinated by bidentate ligands are shown to be promising state variables based on their well-known redox-induced isomerization between tetrahedral Cu(I) and square planar Cu(II) geometries.<sup>3–8</sup> A heteroleptic design is required because one ligand must bind to the native oxide layer of a silicon support, while the second ligand should have the possibility to rotate freely.

The synthesis of heteroleptic copper compounds in solution is difficult to achieve. An effective strategy for synthesizing heteroleptic copper compounds in solution utilizes bulky diaryl groups in the 2,9 and 4,7 positions of two different 1,10-phenanthroline ligands.<sup>9,10</sup> This strategy thermodynamically favors heteroleptic copper compounds via  $\pi$ – $\pi$  stacking interactions. Unfortunately, these interactions prohibit the isomerization of Cu(I) tetrahedral to Cu(II) square planar geometries. For the purpose of using heteroleptic copper compounds as a state variable, at least one ligand needs to be able to rotate

freely. Presented in this paper is the strategy of a surface outward sequential synthesis (Scheme 1) that ensures the formation of surface immobilized heteroleptic copper compounds, which have freedom of motion to allow the 90° relative rotational motion of the ligands that acts as a state variable.

**Scheme 1.** The Surface Outward Sequential Synthesis of SiO<sub>2</sub>-Immobilized Heteroleptic Copper Compounds

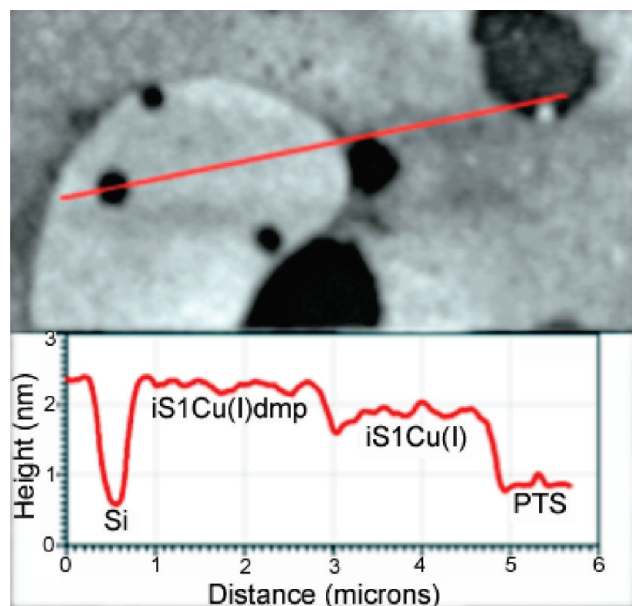


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The self-assembly synthetic approach, shown in Scheme 1, yields heteroleptic copper compounds that are covalently bonded to a solid support. The systems contain three subunits: a bifunctional linker (a bidentate ligand bonded to both a solid support and to a Cu center), the metal center (Cu), and a diimine free ligand. Four steps are involved in the preparation of surface immobilized heteroleptic copper compounds. The first step is to choose a support ( $p^+$  Si or  $\text{SiO}_2$ ), followed by covalent grafting of a linker ligand ([bis-(diphenylphosphino)-methyl]triethoxysilane<sup>11</sup> (iS1) or 5-*N,N*-di(amidopropyl)-triethoxysilane<sup>12</sup> (iS2) onto the support. The linker ligand is then used to chelate a copper center that subsequently bonds to the free ligand subunit 2,9-dimethyl-1,10-phenanthroline (dmp). In the case of  $p^+$  Si preparations, propyltriethoxysilane (PTS) was added to fill in any gaps between immobilized iS1 linkers (Scheme 2), followed by the addition of  $\text{Cu(I)}(\text{CH}_3\text{CN})_4\text{PF}_6$  and then dmp. The design shown in Scheme 2 contains four components: (i) a bidentate bifunctional linker, (ii) PTS as a gap filler, (iii) a copper metal center, and (iv) a bidentate free ligand.



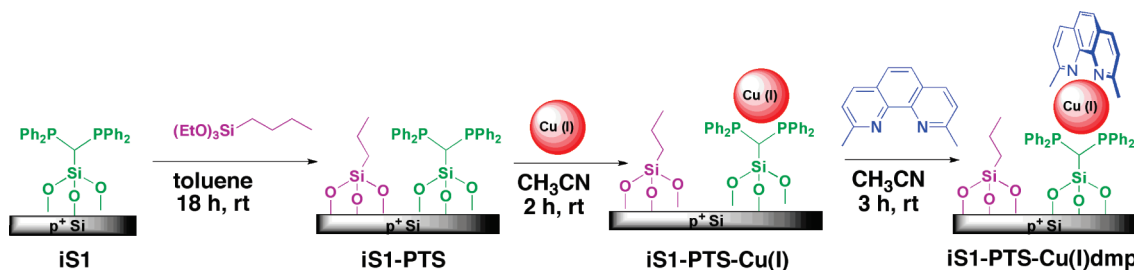
**Figure 1.** Representative tapping-mode AFM height image,  $7\ \mu\text{m} \times 3.5\ \mu\text{m}$  (X/Y)  $\times 3.7\ \text{nm}$  (Z), and cross-sectional profile of a  $p^+$  Si immobilized preparation.

Characterization and optimization of the synthetic scheme was carried out using atomic force microscopy (AFM), as shown in Figure 1. To demonstrate the presence of system components within a molecular monolayer, a sample with submonolayer coverage and incomplete complexation was deliberately prepared through the use of shorter reaction times. Subsequent imaging revealed discrete regions of variable height, with the bare  $p^+$  Si serving as a measurement baseline for measuring the step heights of the different components. Three distinct regions of interest were found, and cross-sectional linescan analysis revealed step heights that correlated directly with calculated molecular dimensions of the individual subunits. The gap-filler (PTS), iS1-Cu(I), and iS1Cu(I)dmp were distinguished with step heights of 0.45, 1.2, and 2.2 nm, respectively.

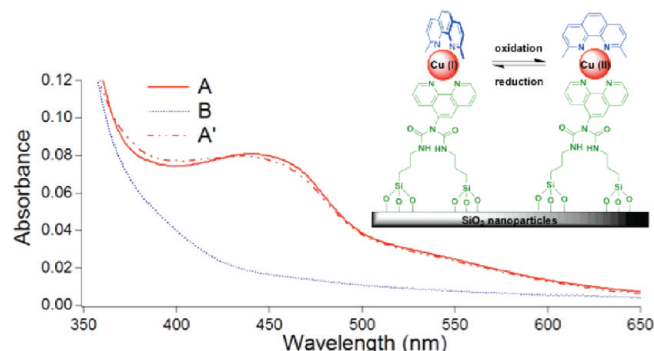
The  $\text{SiO}_2$ -immobilized copper compounds were characterized via solid-state NMR, UV–visible (UV–vis) absorption, and electron paramagnetic resonance (EPR) spectroscopies.  $^{29}\text{Si}$  CP/MAS was used to verify the immobilization of iS2, while  $^{31}\text{P}$  CP/MAS was used to confirm the immobilization of iS1 and iS1Cu(I)dmp. For absorption spectroscopy, the compounds were attached on highly dispersed silica nanoparticles ( $\sim 60$ – $100\ \text{nm}$ ).<sup>13</sup> Optical spectroscopy of a dimethyl sulfoxide (DMSO) suspension demonstrated the reversibility of the Cu(I)/Cu(II) immobilized compounds (Figure 2). Chemical redox agents were used to switch from Cu(I) to Cu(II) and then back to Cu(I). The iS2 linker was used for these studies because the iS1 linker is sensitive to redox agents.<sup>14,15</sup> iS2Cu(I)dmp, immobilized onto  $\text{SiO}_2$  nanoparticles and suspended in DMSO, has a metal-to-ligand charge transfer (MLCT) band at  $\sim 450\ \text{nm}$  (Figure 2, curve A). Upon the addition of hydrogen peroxide and then washing of the particles, iS2Cu(I)dmp was oxidized to Cu(II) (Figure 2, curve B). The presence of Cu(II) was observed by the disappearance of the MLCT band. The sample was reversibly reduced back to Cu(I) by the addition of ascorbic acid followed by a wash (Figure 2, curve A'). The MLCT band reappeared upon the reduction of Cu(II) to Cu(I).

The device architecture that was used for the electrical characterizations of the switching behaviors within an immobilized monolayer of iS1-PTS-Cu(I)dmp was prepared by the surface outward synthesis on the native oxide layer of a  $p^+$  Si wafer. Current–voltage (I–V) measurements were carried out using two different types of methods as the top electrodes: (1) highly localized conductive AFM (cAFM) and (2) bulk studies using macroscopic gold electrodes.<sup>16</sup> Samples were first studied using cAFM. In order to assess repeatability of the

**Scheme 2.** The Surface Outward Sequential Synthesis of  $p^+$  Si Immobilized Heteroleptic Copper Compounds



localized electrical switching characteristics within the monolayer device, high-resolution imaging of molecular layer was coupled with multiple I–V measurements sampled over a large area. After characterizing the surface preparation (Figure 3a–c), a  $5 \times 5$  grid at a spacing of 250 nm was used for I–V spectroscopy as shown in Figure 3b. Minimization and maintenance of the contact force applied by the cAFM probe provided a means of reducing perturbation to the molecule during the measurement and enhancing reproducibility. In addition, it served to eliminate spurious effects commonly observed in sandwich type devices. The I–V curves provided in Figure 3d–f reproducibly demonstrate bias-dependent

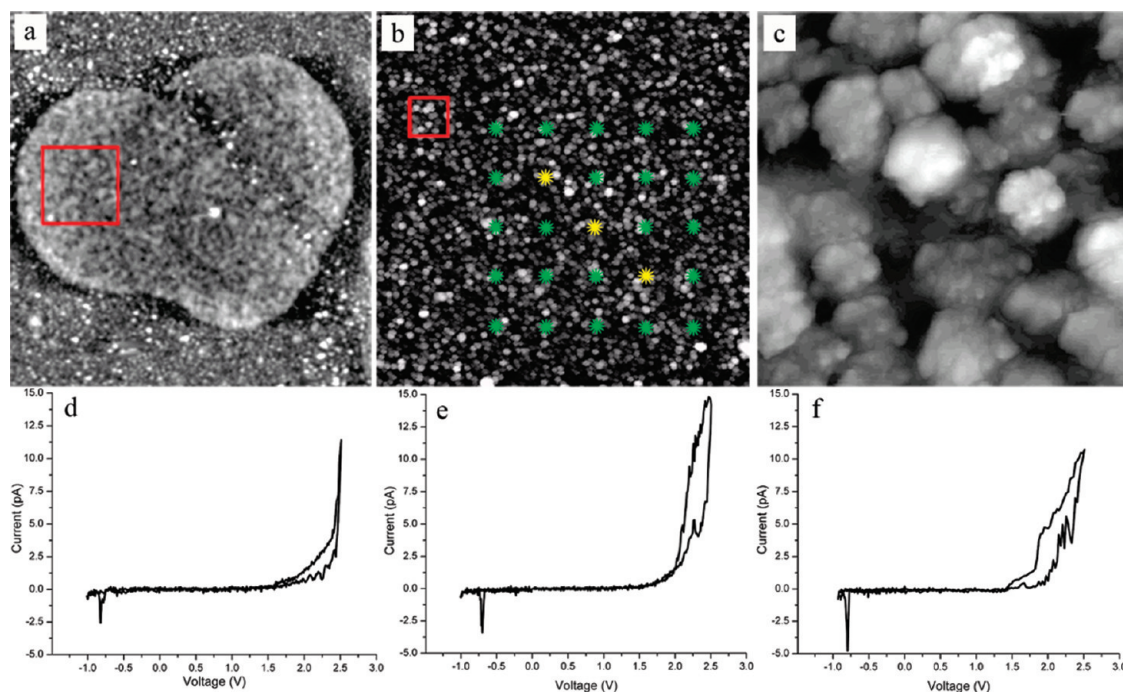


**Figure 2.** Switching characteristics induced by chemical redox agents and monitored optically. A 2.5 mL portion of the particle suspension (100  $\mu\text{g/mL}$ ) in DMSO was used. Curve A represents the Cu(I) heteroleptic copper compound immobilized onto  $\text{SiO}_2$  nanoparticles. Curve B represents the oxidation of Cu(I) to Cu(II) via the oxidizing agent,  $\text{H}_2\text{O}_2$ . Curve A' represents the return of Cu(II) to Cu(I) via the reducing agent, ascorbic acid.

switching events and represent typical results obtained over many areas on the sample.

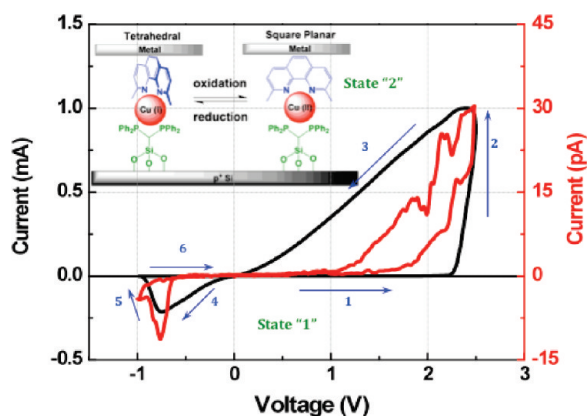
To ensure that the results shown in Figure 3 were reproducible, a second method (using a bulk device architecture) was carried out. The same exact samples studied locally by cAFM were next studied in bulk using evaporated gold. A direct-current (DC) electric field was applied between the  $\text{p}^+$  Si and first a Pt–Ir coated cAFM tip followed by a Ti/gold film and swept in the direction denoted by the arrows numerically as shown in Figure 4. I–V spectroscopy showed the two distinct states where state “1” represents the low-resistance state, and state “2” represents the high-resistance state. The turning voltages for the oxidation and reduction processes at the Cu center are  $\sim 2.3$  V and approximately  $-0.8$  V in the positive and negative region, respectively. For a given device, the I–V characteristics are stable and reproducible with consecutive positive and negative bias sweeps. Small fluctuations in the measured current are observed across devices owing to the nonuniformity of the active molecular layer.<sup>16</sup>

The results obtained via the collective I–V measurements are indicative of discrete, bias-dependent switching (with different current intensities) between Cu(I) and Cu(II) oxidation states. Through this design, the relative intramolecular, rotational motion of iS1 and dmp with respect to each other is not hindered by either the deposition of the macroscopic electrode or the cAFM tip due to the presence of an  $\text{sp}^3$  center within the iS1 linker. Preliminary temperature-dependent I–V measurements yielded an activation energy of  $\sim 0.3$  eV associated with the rotational movement of iS1 Cu(I)dmp. These as well as other recently reported results further support the conformational change of Cu(I) to Cu(II)



**Figure 3.** Representative sequential AFM images of the molecular layer at multiple length scales:  $5 \mu\text{m}^2$  (a),  $2 \mu\text{m}^2$  (b), and  $200 \text{ nm}^2$  (c), where the regions highlighted by a red box in a and b correspond to the areas shown in b and c, respectively. Within b, a schematic of the  $5 \times 5$  grid employed in cAFM I–V spectroscopy is shown. Spectra acquired at the positions denoted in yellow are provided in d–f.





**Figure 4.** Switching characteristics of the two copper states induced electrically and monitored via I–V spectroscopy using a  $p^+$  Si substrate and either a macroscopic Au/Ti film electrode (black curve) or a Pt–Ir-coated cAFM probe (red curve).

as the most likely mechanism for the induction of switching effects.<sup>16</sup>

In summary, we have designed, synthesized, characterized, and tested the potential of a bistable heteroleptic copper compound on a  $p^+$  Si support to act as a state variable using cAFM. The design included the use of two different linkers. The iS1 linker formed a rigid attachment onto a Si surface, whereas iS2, although floppy, is robust against chemical redox agents. UV–vis absorption, solid-state NMR, and EPR spectroscopies, as well as AFM imaging were used to characterize these systems on  $\text{SiO}_2$  nanoparticles and  $p^+$  Si wafers, respectively. Through use of UV–vis absorption and EPR spectroscopies and chemical redox agents, the  $\text{SiO}_2$ -immobilized  $\text{iS2Cu(I)dmp}$  showed two distinct conformational states based on tetrahedral Cu(I) or square planar Cu(II). I–V spectroscopy demonstrated robust electrical switching and conformation-dependent conductance characteristics of this system. Highly localized cAFM measurements showed excellent correlation with bulk evaporated gold electrodes. These results were reproducible under very different device architectures, suggesting that the heteroleptic copper compounds are sturdy and thus could have potential use in switching applications for molecular electronics.

## EXPERIMENTAL METHODS

**UV–vis Absorption Measurements of  $\text{SiO}_2$  Nanoparticle–Modified Heteroleptic Copper Compounds:** An amount of 0.2 g of  $\text{SiO}_2$  nanoparticles was prepared and modified with  $2 \times 10^{-4}$  M iS2. The subsequent addition of  $2 \times 10^{-4}$  M of  $[\text{Cu(I)}(\text{CH}_3\text{CN})_4]\text{PF}_6$  followed by  $2 \times 10^{-4}$  M of dmp was carried out. The reaction mixture was centrifuged, and the supernatant was removed. The modified  $\text{SiO}_2$  particles with  $\text{iS2Cu(I)dmp}$  were washed  $3 \times$  with  $\text{CH}_3\text{CN}$  and dried overnight under vacuum. A volume of 2.5 mL of  $\text{iS2Cu(I)dmp}$ -modified particles was suspended (100  $\mu\text{g/mL}$ ) in DMSO. Either hydrogen peroxide or ascorbic acid solutions were added into the suspension to oxidize or reduce the copper centers, respectively. After the addition of the redox agent, the particles were washed with and resuspended in DMSO to measure absorbance.

**Preparation of Si-Immobilized Heteroleptic Copper Compounds for I–V Measurements and AFM Characterization:** A  $p^+$  Si wafer was first washed with piranha (1 part 30%  $\text{H}_2\text{O}_2$  and 3 parts  $\text{H}_2\text{SO}_4$ ) and then aquaregia (1:3  $\text{HNO}_3$ : $\text{HCl}$ ) solutions. The wafer was then immersed into a  $1 \times 10^{-5}$  M solution of iS1 inside a test tube. The test tube was equipped with a stir bar and sealed under an  $\text{N}_2$  atmosphere. The wafer remained in this solution at ambient temperature for approximately 18 h. After washing away excess iS1 with toluene, the modified wafer containing immobilized iS1 linkers was subsequently immersed into a test tube containing  $1 \times 10^{-5}$  M solution of PTS, equipped with a stir bar, under an  $\text{N}_2$  atmosphere, at room temperature, for an additional 18 h. The wafer was washed with toluene to remove excess PTS and then placed in a test tube containing  $1 \times 10^{-5}$  M solution of  $\text{Cu(I)}(\text{CH}_3\text{CN})_4\text{PF}_6$  in  $\text{CH}_3\text{CN}$ , under an  $\text{N}_2$  atmosphere and stirred at ambient temperature for 3 h. A concentration of  $1 \times 10^{-5}$  M of dmp in  $\text{CH}_3\text{CN}$  was added to the reaction test tube, and the immersed wafer was allowed to stir under ambient condition and under an  $\text{N}_2$  atmosphere for an additional 2 h. The wafer was washed thoroughly with  $\text{CH}_3\text{CN}$  and dried o/n in a vacuum desiccator. For I–V measurements, the molecular layer (iS1  $\text{Cu(I)dmp}$ ) was immobilized onto a  $p^+$  Si wafer, and the device was completed by depositing a Ti/gold film through a shadow mask to form the top electrode or by use of a Pt–Ir cAFM tip (Figure 3).

All AFM-based methods were carried out using the NanoScope V Dimension Icon (Veeco Instruments) in ambient conditions. Topographic imaging in the dynamic mode (AM-AFM) employed phosphorus  $n^+$ -doped silicon cantilevers (PPP-FM, Nanosensors) with nominal spring constants of 2.1 N/m, first longitudinal resonance frequencies between 45 and 80 kHz, and nominal tip radii of  $< 10$  nm. Simultaneous height and phase images were acquired and reproduced from multiple samples. Simple plane fitting of the acquired images enabled subsequent cross-sectional analyses. Reported values demonstrated no significant variation between different samples or cantilever probes. I–V spectroscopic analyses by cAFM employed Pt–Ir coated silicon cantilevers (ContPt, NanoWorld) with calibrated spring constants between 0.12 and 0.15 N/m, first longitudinal resonance frequencies between 11.5 and 13 kHz, and nominal tip radii of  $< 25$  nm in contact mode. A minimum applied force was used so as to reduce sample perturbation during the measurement.

**I–V Measurements:** I–V spectroscopy of the molecular devices in ambient conditions was carried out in two parts. First, bulk device characteristics were characterized using a Keithley 4200 Semiconductor Characterization System. A probe station was used to ground the  $p^+$  Si substrate, and the bias voltage was applied to the top gold electrode. Sweep delay and hold times were set to be 3 s in order to average the nonuniformity of the molecular monolayer. Each sweep took approximately 10 min to complete for each device depending on the measured current level. Second, local nanoscale I–V characteristics were characterized by cAFM using the Veeco Extended TUNA applications module. The bias voltage was applied to the sample with respect to a virtually grounded cAFM probe tip. Bias voltage sweeps were carried out at rate of

0.25 V/s over the range of interest while maintaining a constant applied force throughout by means of the feedback loop. Individual data points were averaged five times to enhance the signal-to-noise (S/N) ratio, and the presented data are composed of a single sweep. In both cases, for a given device, the I–V characteristics were stable with repeated positive and negative bias sweeps. Small fluctuations were observed among different devices owing to the nonuniformity of the active molecular layer.

**SUPPORTING INFORMATION AVAILABLE** Experimental and spectral characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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