Optically Reconfigurable Monolayer of Azobenzene Donor Molecules on Oxide Surfaces

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ABSTRACT: The structural configuration of molecules assembled at organic—Inorganic interfaces within electronic materials strongly influences the functional electronic and vibrational properties relevant to applications ranging from energy storage to photovoltaics. Controlling and characterizing the structural state of an interface and its evolution under external stimuli is crucial both for the fundamental understanding of the factors influenced by molecular structure and for the development of methods for material synthesis. It has been challenging to create complete molecular monolayers that exhibit external reversible control of the structure and electronic configuration. We report a monolayer/inorganic interface consisting of an organic monolayer assembled on an oxide surface, exhibiting structural and electronic reconfiguration under ultraviolet illumination. The molecular monolayer is linked to the surface through a carboxylate link, with the backbone bearing an azobenzene functional group and the head group consisting of a rhenium—bipyridine group. Optical spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and X-ray reflection show that closely packed monolayers are formed from these molecules via the Langmuir—Blodgett technique. Reversible photoisomerization is observed in solution and in monolayers assembled on Si and quartz substrates. The reconfiguration of these monolayers provides additional means to control excitation and charge transfer processes that are important in applications in catalysis, molecular electronics, and solar energy conversion.

INTRODUCTION

The creation of materials incorporating optically reconfigurable interfaces between organic and inorganic components provides access to a wide range of new electronic and optical phenomena with both fundamental and practical importance. Dynamically reconfiguring the structure of an interfacial molecular monolayer through the use of external stimuli has the potential to provide precise control over charge transfer dynamics, energy offsets of interfacial electronic states, dipole moments or polarizations, and vibrational phenomena. In the past, various structural configurations were created by varying the conditions under which the monolayers were assembled. Such studies indicate that changes in the structural state can include change in the molecular height and conformation and an increase or decrease in the dipole moment and net polarization.

In addition to these modifications in the fundamental properties of the interfaces, computational studies proposed that it may be possible to create high-energy-density solar fuels through a mechanism in which energy is stored in the metastable molecular configuration and is released through isomerization into the stable trans isomeric state via optical absorption. This technology was recently realized through the creation of a high-energy-density azobenzene/graphene hybrid as a solar fuel exhibiting a high energy density of up to 112 W h kg$^{-1}$ with a half-life of 33 days. Additionally, a photosresponsive cross-linked azobenzene/polymer assembly has demonstrated its feasibility as a high-performance light-driven actuator. Similarly, the structural cues provided by azobenzene monolayers can drive photoinduced alignment in liquid crystal films and create surfaces with photoswitchable wettability.

A further range of opportunities to achieve reconfigurable interfacial control of material properties arises in organic donor/inorganic semiconductor materials through the incorporation of a photoexcitable molecular monolayer at the interface. Molecular donors deposited on semiconducting oxides such as TiO$_2$, ZnO, and SnO$_2$ can inject electrons into the oxide from their metal-to-ligand charge transfer excited state on the picosecond timescale. Molecular monolayers and thin films exhibit variation in molecular orientation, conformation, and binding motif as well as in macroscopic parameters including thickness, roughness,

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packing density, and aggregation, all of which can affect the charge transfer rates. Likewise, the rate of charge transfer, either through conjugated links or through space tunneling, depends on factors such as the composition and structure of the chromophore and the anchoring group, the extent of conjugation of the molecular bridge group, and macroscopic structural factors such as packing density and aggregation state. In this context, rhenium (Re)–bipyridine complexes have been extensively studied as photoabsorbers and electron donors. Donor molecule/semiconductor interfaces are electronically and structurally intriguing because of the strong connection between charge transfer rates and the spatial separation of the donating group and the substrate. This donor–surface distance can be manipulated through the incorporation of a reconfigurable group that changes the distance between the donor and the substrate in response to an external stimulus. The challenge has been to fabricate reconfigurable interfaces with a specific structure and to correlate the corresponding electronic kinetics systematically. Additionally, it is challenging to directly evaluate the structure and structural changes quantitatively during and after the external stimulus in these reconfigurable systems.

Reconfigurability can be introduced into organic/inorganic interfaces by assembling molecules containing azo-groups at the interfaces. The azo group switches from trans to cis configuration following electronic excitation by a photon resonant with the π-to-π* transition at a wavelength of 320–350 nm. The cis-to-trans transformation can be induced by exciting the n-to-π* transition via the absorption of blue light at a wavelength of 400–450 nm. In solution, the azobenzene molecule reconfigures on a 10 ps timescale. Thermal isomerization back to the thermodynamically stable trans state occurs much more slowly, on the order of milliseconds to days, depending on the stability and steric bulk of the other constituents of the azobenzene-containing molecule. The timescale on which the trans-to-cis ratio in an ensemble changes is often much longer because of the different probabilities of the elementary isomerization processes. This change in the ensemble ratio of the trans and cis isomers has commonly been observed to be on the timescale of seconds. The photoisomerization leads to changes in the molecular conformation, from the planar, elongated trans isomer to the compact three-dimensional (3D) cis isomer, which is accompanied by a change in the dipole moment, a decrease in the intensity of the π-to-π* peak, and an increase in the intensity of the n-to-π* peak in the absorption spectra.

Steric hindrance and the restricted free volume available due to dense molecular packing limit the photoisomerization rates of azobenzene monolayers, prolonging the timescale of the initial reconfiguration to the order of seconds. Additional insight into the role of mesoscopic effects is observed in scanning tunneling microscopy (STM) experiments, which show that chains with widths of a few molecules and lengths of 20–300 Å photoisomerize more slowly under UV radiation than their isolated counterparts and exhibit concerted switching. The concerted switching phenomenon observed using STM was described as arising from intermolecular electronic coupling due to enhanced π-orbital overlap of the neighboring azobenzene groups. These previous experimental results offer insight into the behavior of localized and isolated sets of molecules but do not describe the behavior of complete monolayers.

In this work, we report the synthesis of a novel photoisomerizable donor (ReAzoC) molecule (Figure 1) and its assembly on oxide surfaces. The molecules were organized into an ordered monolayer using Langmuir–Blodgett (LB) deposition, an approach we previously developed for a series of other Re–bipyridine complexes. Structural characterization shows that the LB assembly yields a monolayer structure with the Re–bipyridine complex as the head group and carboxylic acid anchored to the substrate, as shown in Figure 1b. The molecules show spectroscopic evidence of photoisomerization in solution and as deposited in a monolayer. The structure is thus further tunable using the trans-to-cis photoisomerization of the azobenzene group. Additionally, the LB assembly can be reproducibly used to create monolayers with a series of different molecular coverages by varying the surface pressure and an optimized single monolayer when deposited under the correct conditions.

The order resulting from this simple deposition process permits more precise structural characterization of the molecular reconfiguration than has been possible in the past. The incorporation of the Re metal complex in the monolayer increases the electron density contrast, enabling precise X-ray reflectivity (XRR) studies of the mechanisms of structural
reconfiguration. XRR quantitatively characterizes the structure and structural changes in large areas of complete monolayers with sensitivity to in-plane structural roughness on the 100 nm lateral length scale and the molecular configuration on the Angstrom scale. The XRR studies reported here characterize the degree of order within the monolayer, the orientation of molecules on the surface, the isomerization state, and the evolution of the structure under optical exposure.

The combination of structural and spectroscopic characterization studies described below shows that ReAzoC can be organized into a closely packed complete monolayer. Optical absorption measurements indicate that 13−15% of the molecules on the surface can be reversibly optically driven between structural states by illumination with alternating ultraviolet (UV) and blue light and that larger fractions of up to 47−52% can be irreversibly transformed at a high optical power. X-ray and optical spectroscopies provide independent and consistent estimates of the fraction of isomerized molecules and the resultant monolayer structure. At low optical power, a small fraction of molecules isomerize in a spatially random distribution. At higher optical powers, where optical absorption indicates that UV light isomerizes approximately 50% of molecules, there is an inhibition of the cis-to-trans reverse photosomerization. XRR measurements show that the mean height of the donor groups within the monolayer is reproducibly changed as a result of the trans-to-cis isomerization.

**EXPERIMENTAL SECTION**

**ReAzoC Synthesis.** Synthesis of 4′-Bromomethyl-4-methyl-2,2′-bipyridine (3) (Modified Synthetic Conditions from Ref 32). A solution of 4,4′-dimethyl-2,2′-dipyridine (1, 1.00 g, 5.43 mmol) in anhydrous tetrahydrofuran (THF, 30 mL) was prepared under protection of argon (Ar) and precooled at −78 °C. Lithium diisopropylamide (LDA) stock solution (2.85 mL, 2.0 M in THF) was then added dropwise to the reaction mixture. A dark brown solution formed and was stirred at room temperature for an additional 2 h. The solution was cooled to −78 °C before adding chlorotrimethylsilane (1.5 mL, 11.8 mmol). After 5 min, the reaction was quenched with ethanol (3 mL) and stirred for 10 min. The final reaction mixture was isolated and purified using a yellow powder as the final product (240 mg, 83%).

**Synthesis of 4′-Methoxyl-4-methyl-2,2′-bipyridyl-phenyl)diazenyl-benzoic Acid Methylester (6) (Optimized Synthetic Conditions on Different Reactants According to Ref 34).** A solution of compound 3 (1.43 g, 5.43 mmol) in DMF (30 mL) was reacted with compound 5 (1.43 g, 5.58 mmol), K2CO3 (1.2 g, 8.68 mmol), and 18-crown-6 (75 mg, 0.28 mmol) at 65 °C overnight. The resultant redish solution was concentrated using a rotary evaporator and recrystallized in chloroform/methanol three times to yield a yellow solid (1.85 g, 78%).

**Synthesis of 4-(2-[4′-(4′-Methoxy-4-methyl-2,2′-bipyridyl)-phenyl]diazenyl)-benzoic Acid (7).** DMF (30 mL) was used to dissolve compound 6 (300 mg, 0.684 mmol). Sodium hydroxide (NaOH, 80 mg, 2 mmol) was first dissolved in water (1 mL) and then added to the DMF solution of 6. The reaction was carried out at 90 °C for 18 h; followed by the removal of DMF. The crude yellow slush was then dissolved in water/methanol (10:1, v/v) and then recrystallized using ethyl acetate/hexane to obtain a yellow powder as the final product (100 mg, 33%).

**Synthesis of 4-(2-[4′-(4′-Methoxy-4-methyl-2,2′-bipyridyl)-phenyl]diazenyl)-benzoic Acid Re Complex (8).** Compound 7 (300 mg, 0.263 mmol) and pentafluorochlorochlororphenium(I) (93.7 mg, 0.260 mmol) were dissolved in degassed DMF (15 mL) under Ar. The solution was stirred at 70 °C for 15 h. DMF was pumped off under vacuum, and the solid crude product was recrystallized using a mixture of diethyl ether and hexane. A bright orange powder was obtained as the final product (8, 141 mg, 82%).

**Substrate Materials and Preparation.** Quartz substrates were purchased from Structure Probe, Inc., available under the trade name SPI SuperSmooth Quartz Slides. The manufacturer’s specification for the root-mean-square (rms) roughness of these quartz slides is less than 0.5 nm. Minimizing substrate roughness maximizes the quality of XRR data, which can be achieved through both improvements in the vertical alignment of the electron-rich portion of the molecule and a reduction in the interfacial roughness. Si/SiO2 substrates were purchased from Montco Silicon Technologies. Si/SiO2 and quartz substrates were cleaned using the piranha process (7:3 H2SO4:H2O2) at 90 °C for 30 min and rinsed with DI water.

Phenol (685 mg, 7.28 mmol) was dissolved in a mixture of acetic acid and water (1:2, v/v) and then slowly added to the prepared solution of compound 4 at room temperature. The reaction was quenched with a saturated solution aqueous solution of NaHCO3 in an ice bath until the formation of gas bubbles ceased. A light yellow solid precipitated, which was filtered and washed using large amounts of water, as the final product (1.70 g, 98%).

**XRR Studies.** The combination of structural and spectroscopic characterization studies described below shows that ReAzoC can be organized into a closely packed complete monolayer. Optical absorption measurements indicate that 13−15% of the molecules on the surface can be reversibly optically driven between structural states by illumination with alternating ultraviolet (UV) and blue light and that larger fractions of up to 47−52% can be irreversibly transformed at a high optical power. X-ray and optical spectroscopies provide independent and consistent estimates of the fraction of isomerized molecules and the resultant monolayer structure. At low optical power, a small fraction of molecules isomerize in a spatially random distribution. At higher optical powers, where optical absorption indicates that UV light isomerizes approximately 50% of molecules, there is an inhibition of the cis-to-trans reverse photosomerization. XRR measurements show that the mean height of the donor groups within the monolayer is reproducibly changed as a result of the trans-to-cis isomerization.
LB Deposition. LB characterization and deposition experiments were performed using a LB trough (KSV KIMA Medium size KN2002, Helsinki, Finland). The surface pressure–area (σ–A) isotherm of the donor molecules was measured using a Wilhelmy balance (Pt plate). The water subphase was treated to have a resistivity of 18.2 MΩ cm using a Milli-Q water filtration station (Millipore, Inc.). The molecular layers were transferred to the solid substrates using the LB dipping technique at a set surface pressure. A ReAzoC solution with a concentration of 200 μL of (1 mg/mL CHCl3/THF = 9:1) was used. The solvent was allowed to evaporate for 30 min before compression of the monolayer. A drop-cast film was prepared for comparison by dropping ReAzoC solution (1 mg/mL CHCl3/THF = 9:1) onto a Si substrate prepared via the piranha treatment and allowing it to evaporate for 24 h in vacuum.

Atomic Force Microscopy (AFM). The surface morphology of the monolayers of ReAzoC molecules was imaged using a Nanoscope III Multimode atomic force microscope (Digital Instruments). A noncontact imaging mode was used for the AFM measurement. A triangular cantilever with an integral pyramidal Si3N4 tip was used. The typical imaging force was on the order of 1 nN. The thickness of the monolayer was determined using line profiles through pinholes in the film.

Ultraviolet–Visicible (UV–vis) Spectroscopy. UV–vis absorption measurements were performed in a transmission geometry in a wavelength range of 200–800 nm using a Shimadzu PC-2401 spectrometer.

Light Sources. Two different light sources were used to photoisomerize the molecules. Prizmatix FC8-LEDs with wavelengths of 365 and 465 nm were used for the UV–vis studies. Light emitting diode (LED) sources (Engin LZ1-00DB00 and LZ1-00UV00, with peak wavelengths of 460 and 365 nm, respectively) were used for XRR studies and studies of sequential XRR measurements and optical exposures.

X-ray Photoelectron Spectroscopy (XPS). A Thermo Scientific K-Alpha X-ray photoelectron spectrometer was used for the compositional analysis of films deposited on Si/SiO2 substrates. The XPS instrument used a microfocused monochromated Al Kα X-ray source with a spot size of 400 μm. A pass energy of 50 eV was used to collect the survey spectra. Spectra were analyzed using the manufacturer’s Avantage software, and peak fitting was performed using a Gaussian/Lorentzian peak shape and a Shirley/Smart baseline.

The surface coverage, defined as the number of molecules per unit area on the substrate, was determined using the formula

$$N_v = \frac{A_x \phi_{Si,SiO_2} \lambda_{Si,SiO_2} \sin(\theta)}{A_{Si} S_{x,organic}} \frac{\epsilon^{(1/\lambda_{organic} \sin \theta)}}{\epsilon^{(1/\lambda_{organic} \sin \theta)}}$$

(1)

where $N_v$ is the number of atoms per unit area for element $x$, and $A_x$, $A_{Si}$, and $S_{x,organic}$ / $S_{Si}$ are the ratio of integrated peak areas for element $x$ and the ratio of the sensitivity factors of element $x$ on the substrate Si, respectively. The factor $\phi_{Si,SiO_2}$ is the number of Si atoms per unit volume in SiO2, and $\lambda_{Si,SiO_2}$ is the inelastic mean free path (IMFP) of Si photoelectrons in SiO2. The layer thickness is $t$, and $\lambda_{organic}$ is the IMFP for the electrons emitted from element $x$ in the molecular monolayer.

XRR. XRR measurements were performed at the University of Wisconsin (UW)—Madison and at the National Institute for Materials Science (NIMS). Measurements at NIMS used a custom-built X-ray reflectometer, with an X-ray source operated at 1.6 kW, producing Cu Kα radiation. The incident beam width measured using a knife edge was 42.6 μm. Measurements conducted at UW—Madison used a Panalytical XPERT MRD using Cu Kα radiation at a source power of 1.8 kW, for which the incident beam width was 220 μm. The analysis of the experimentally acquired XRR intensity distributions was conducted using GenX software package.10 The GenX package uses a curve-fitting algorithm that adjusts the values of the interface roughness, layer thickness, and density to optimize a figure of merit

$$\log(R_1) = \sum \frac{[\log(Y_i) - \log(S_i)]}{\sum [\log(Y_i)]}$$

(2)

where $Y_i$ is the measured reflected intensity, $S_i$ is the corresponding simulated value, and the sum spans the series of data points.

## RESULTS AND DISCUSSION

**Design and Synthesis of ReAzoC.** We designed a unique azo-based chromophore ReAzoC that contains three moieties relevant to the XRR studies. The head group containing the bipyridine group can form a complex with transition metal ions to increase the electron density contrast and hence the X-ray
scattering cross section. The middle unit of the molecule contains the photoswitchable azo group that is used to reconfigure the monolayer by photoisomerization from the trans to the cis form. The tail group of the molecule is a polar carboxylic acid group that anchors the molecule at the water subphase during the assembly and subsequently to the oxide substrate.

Our initial attempts to connect the bipyridine head group to the azobenzene unit via an ester link were unsuccessful because the bipyridine is labile either under low pH or in the presence of acyl halides, in traditional esterification reactions. Mitsunobu esterification requires an organophosphate catalyst, which interferes with azobenzene in the chromophore and thus cannot be used in this case. The Steglich esterification showed good compatibility with azobenzene in our previous work, but it led to low yields when hydroxy-azobenzene was reacted with aromatic acid. Thus, we choose an ether linker via SN2 substitution of 4′-bromomethyl-4-methyl-2,2′-bipyridine (3) by activated methyl-4′-hydroxy-4-azobenzylcarboxylate (5) under mild reaction conditions. These two precursors were obtained with over 90% yields under optimized conditions. As a final step, the carboxylic acid was deprotected using basic hydrolysis. It was essential to conduct the deprotection as the very last step because the carboxylic acid of 5 has low solubility in most organic solvents, leading to low yields of methyl-4′-(4-methyl-2,2′-bipryridyl-4′-methoxyl)-4-azobenzylcarboxylate (6) and 4′-(4-methyl-2,2′-bipryridyl-4′-methoxyl)-4-azobenzylcarboxylic acid (7). To form the carboxylic acid from sodium carboxylate salt, the pH was adjusted to 4.5 because the bipyridine group is acid-sensitive. On the basis of these observations, an eight-step (Scheme 1) synthesis was carried out to achieve the final material with an overall yield of 48%, and the purity was confirmed using proton/carbon nuclear magnetic resonance (1H/13C NMR) and high-resolution mass spectrometry (MS).

**LB Deposition.** The LB method is typically used to assemble amphiphilic molecules such as lipids at the air–water interface and to transfer the ordered monolayer onto a substrate. Although not truly amphiphilic, the ReAzoC molecule has a more polar carboxylic acid tail group, which makes it a good candidate for stabilization at the air/water interface and to preferentially interact with oxide substrates. Although not truly amphiphilic, the ReAzoC molecules at the air/water interface and to transfer the ordered monolayer onto a substrate.

Figure 2. Surface pressure–mean molecular area isotherm of ReAzoC spread from chloroform and THF (9:1) with a concentration of 1.0 mg/mL. Regions of gas, liquid, and solid phases are defined by slope discontinuities at 125 and 50 Å².

**Figure 3.** AFM characterization of a monolayer of ReAzoC donor molecules deposited at 25 mN/m surface pressure: (a) 5 × 5 and (b) 1 × 1 μm² regions. The inset in (b) shows a height line profile taken along the dashed line. The height difference between the molecular layer and the substrate in the line profile is 2.3 nm.

by Dominey et al., the trans state of the molecule theoretically occupies an area of 37.44 Å². The 50 Å² mean molecular area observed at a surface pressure of 25 mN/m is thus close to the theoretical cross-sectional area of ReAzoC in the thermodynamically favored trans conformation. The pressure–area curve suggests that transferring a monolayer of ReAzoC to a solid substrate at the transition point between the solid and liquid phases in the isotherm produces the most densely packed single monolayer that can be deposited. This hypothesis is supported by a detailed XPS characterization given below.

**AFM images of monolayers transferred from the LB trough to a substrate at a surface pressure of 25 mN/m are shown in Figure 3.** AFM images in Figure 3a exhibit a low rms surface roughness of 0.218 nm, far less than the total thickness of the molecule. The holes evident in Figure 3a,b allow the thickness of the film to be measured. The height profile inset in Figure 3b shows a height difference of 2.3 nm between the top and the bottom of the monolayer, which corresponds to the height of the ReAzoC molecule. This height is predicted to be 2.4 nm based on the bonding configurations given in ref 46.

**XPS Characterization of Molecular Coverage.** The surface concentration of ReAzoC molecules within layers deposited at different surface pressures (5, 15, 25, and 40 mN/m) and via drop-casting was measured using XPS. The drop-cast film that was expected to be disordered was used as a comparison. The XPS data for N(1s), Cl(2p), and Re(4f) transitions for a monolayer transferred at a surface pressure of 25 mN/m and for a drop-cast film are shown in Figure 4a,b, respectively. The N(1s) peak at 399–404 eV, Cl(2p) peak at 198–204 eV, and Re(4f) peaks at 41–49 eV together confirm that the ReAzoC molecules have been transferred to the substrate. The surface coverages calculated from the Cl(2p), Re(4f), and N(1s) peaks in the XPS spectrum are shown in Table 1.

The dependence of the molecular coverage on the surface pressure is shown in Figure 5. The surface coverage of the ReAzoC molecules in LB films transferred at the optimum surface pressure of 25 mN/m is 1.84 molecules/nm². This is consistent with the estimate of 2 molecules/nm² from the LB
The theoretical maximum coverage of a single monolayer of ReAzoC is 2.7 molecules/nm², calculated from the molecular dimensions estimated based on Dominey et al.46 When taken together, the XPS spectra, the AFM profile, and the LB isotherm confirm the formation of an optimized ReAzoC monolayer at a surface pressure of 25 mN/m.

UV−Vis Spectroscopy. The trans−cis photoisomerization of ReAzoC thin films deposited on a transparent quartz substrate was monitored using UV−vis transmission spectroscopy. The absorption spectrum before irradiation (black curve, Figure 6a) exhibits a strong peak at 360 nm, arising from the π−π* electronic transition of trans-azobenzene. Absorption spectra of ReAzoC at a concentration of 2.74 × 10⁻⁶ M in a chloroform−THF (9:1) solution are shown in Figure 6b. Absorption spectra were acquired under ambient room light, and the initial configuration thus consisted of a mixture of trans and cis states. The two absorption peaks at 244 and 285 nm arise from the π−π* transition of the Re−bipyridine group.47,48
Illumination of the transferred LB film at a wavelength of 365 nm leads to a decrease in the absorbance of the 360 nm absorption band, reaching a photostationary state after a 10 s exposure at 16.9 mW/cm² (Figure 6a). The absorbance of the 360 nm peak recovered to its initial value after a 10 s exposure to 465 nm wavelength illumination at 9.5 mW/cm². The photostationary state observed in the spectra of the thin film is consistent with the observations in solution, as shown in Figure 6b. The change in the optical spectrum provides direct evidence for the trans–cis photoisomerization of both monolayer and solution forms of ReAzoC.

The absorption cross section was estimated using the UV–vis spectra shown in Figure 6. In solution, the absorption cross section at 352 nm was $6.8 \times 10^{-16}$ cm² for the trans isomer and $4.0 \times 10^{-16}$ cm² for the cis isomer. The absorption cross section of the molecular monolayer was $1.8 \times 10^{-16}$ cm² for the trans isomer and $1.6 \times 10^{-16}$ cm² for the cis isomer. The difference between the absorption cross section of ReAzoC in solution and the ReAzoC monolayer can be in part attributed to the anisotropic distribution of the molecular orientation in the monolayer. The transition dipole moment of the azobenzene $\pi^* - \pi^*$ transition is oriented approximately parallel to the long axis of the azobenzene group and is thus oriented nearly along the monolayer surface normal. The electric field vector of the incident radiation is in a plane perpendicular to the surface normal under the normal-incidence conditions used for the UV–vis measurements. The absorbance under these conditions is proportional to $3/2 \sin^2(\theta)$, where $\theta$ is the angle between the transition dipole moment of azobenzene and the surface normal. With the molecules oriented approximately normal to the surface as is the case in the ReAzoC monolayer, this factor serves to reduce the absorbance in comparison to the solution.

The absorption cross section of the $\pi - \pi^*$ transition in an azobenzene-containing monolayer can be estimated from the values given in ref 30. With a correction based on the approximately 20% quantum yield of the reorientation transition, the total absorption cross section from ref 30 is on the order of $3.5 \times 10^{-17}$ cm². The peak position of the $\pi - \pi^*$ transition in the LB monolayer was red-shifted by 8 nm relative to that in solution. The origin of this red shift is unclear at this point. However, multiple factors such as the tilt of the molecular orientation with respect to the surface normal, contributions to the maximum at 360 nm from the S2 $\pi - \pi^*$ transition in the Re–bipyridine group, and possible solvatochromic effects influencing the S2 transition may play a role.

The optical absorption spectra were used to estimate the fraction of molecules that undergo the trans-to-cis isomerization. The 360 nm absorption band has contributions from the absorbance of the azobenzene group in both the cis and trans isomers and a small contribution from the Re–bipyridine head group. However, if this small contribution is neglected, an estimation of the lower limit for the fraction of molecules isomerized can be estimated by an extension of Beer’s law

$$A = \varepsilon_{\text{trans}}N_{\text{trans}} + \varepsilon_{\text{cis}}N_{\text{cis}}$$

where $\varepsilon_i$ is the absorption constant for the isomer and $N_i$ is the number of molecules of each isomer in the optical beam path, and $N_{\text{trans}} + N_{\text{cis}} = N_{\text{total}}$. The absorption constants of the trans and cis isomers are related by a scalar $n$, the wavelength-dependent ratio of the trans–cis isomer absorption constants.

Thus, the absorbance of the peak can be rewritten as a function of a single isomer independent absorption constant.

$$A = \varepsilon N_{\text{trans}} + \varepsilon N_{\text{cis}}$$

The fractional change in the absorbance can be related to the fraction of molecules isomerized by computing the fractional change $(A - A')/A$, where $A$ is the absorbance of the initial state and $A'$ is the absorbance of the final state. Using eq 4, we find the following expression for the fractional change in absorbance

$$A - A' = \frac{n\varepsilon\Delta N_{\text{trans}} + \varepsilon\Delta N_{\text{cis}}}{n\epsilon N_{\text{trans}} + \varepsilon N_{\text{cis}}}$$

Here $\Delta N_{\text{trans}}$ and $\Delta N_{\text{cis}}$ are the differences between the number of molecules of the trans and cis states present in the initial and final states, respectively. Necessarily, $\Delta N_{\text{trans}} = -\Delta N_{\text{cis}} = \Delta N$, thus

$$A - A' = (n - 1) \frac{\Delta N}{nN_{\text{trans}} + N_{\text{cis}}}$$

We assume that the initial state before UV exposure can be reasonably approximated as consisting only of trans isomers, which is applicable because the trans state of the azobenzene group is the thermodynamically stable state. In this approximation, $N_{\text{trans}} = N$ and $N_{\text{cis}} = 0$, and eq 6 becomes

$$\frac{\Delta N}{N} = \frac{n}{n - 1} \frac{\Delta A}{A}$$

Literature values of $n$ lie between 5 and 10. The absorption spectra of ReAzoC molecules in solution (Figure 6b) have $\Delta A/A = 40\%$, and thus between 44 and 50% of the molecules in solution are photoisomerized. When deposited as a monolayer (Figure 6a), $\Delta A/A = 12\%$, and thus only 13–15% of the molecules on the surface are photoisomerized by a UV intensity of 16.9 mW/cm². This limited photoisomerization is commonly observed in para-substituted azobenzens as a result of very rapid thermal relaxation that makes the creation of large fractions of cis isomers difficult.

The reversibility of the trans–cis photoisomerization of ReAzoC was characterized by alternating 10 s periods of illumination at wavelengths of 365 and 465 nm at optical intensities of 16.9 and 9.5 mW/cm², respectively. A decrease and recovery of the absorbance of the monolayer at 352 nm in solution and at 360 nm is evident in the summaries of the absorption peak heights after repeated exposures shown in Figure 6c,d. At low optical intensities, the molecules in solution deposited in a monolayer undergo reversible photoisomerization.

**XRR Structural Characterization.** The fractional intensity of an incident X-ray beam reflected by a thin film on a substrate depends on the electron density profile of the interface along the surface normal direction. A model consisting of the substrate, the monolayer, and the ambient environment was used to interpret the XRR measurement. The model parameters are $\rho_{\text{sub}}$, the electron density of the substrate, which is held constant; $\sigma_{\text{sub}}$, the roughness of the substrate–monolayer interface, and $L_{\text{monolayer}}$, $\rho_{\text{monolayer}}$, and $\sigma_{\text{monolayer}}$, which are the thickness, electron density, and roughness of the monolayer–air interface, respectively. An initial point for the refinement of the reflectivity model was obtained by predicting the height using the distance along the long axis of the ReAzoC molecule from the literature values of bond angles and bond
The initial electron density estimate was obtained by counting the number of electrons within the theoretical volume occupied by the molecule. On the basis of the model for the ReAzoC molecule, an ideally packed monolayer of trans conformation molecules is expected to have an electron density of 0.396 e⁻/Å³, thickness of 24 Å, and substrate roughness near that of bare silicon. A corresponding monolayer of cis conformation molecules is expected to have an electron density of 0.521 e⁻/Å³ and a thickness of 8.45 Å. Additional geometric and experimental parameters such as sample width, beam width, and direct beam intensity are measured to allow the fit to match the measured intensity with no overall scaling parameter. Further discussion of the geometric model is given in ref 31.

An XRR measurement of a ReAzoC monolayer deposited at a surface pressure of 25 mN/m is shown in Figure 7a. The XRR of a (a) ReAzoC monolayer deposited at a surface pressure of 25 mN/m, (b) ReAzoC monolayer deposited at a surface pressure of 15 mN/m, (c) drop-cast ReAzoC film, and (d) bare Si/SiO₂ substrate. The red line shows the best fit using the model and parameters in Table 2. Insets show model electron density profiles.

Reflectivity curve for the 25 mN/m samples exhibits total external reflection at incident angles lower than 2θ = 0.4° and a single broad reflectivity fringe, including an intensity minimum at 2θ = 1.4° and a maximum at 2θ = 1.8°. Only one fringe is observed as a result of the small thickness of the monolayer and the limited dynamic range of the laboratory-based X-ray instrumentation. The reflectivity from a monolayer deposited at 15 mN/m (Figure 7b) shows a weak reflectivity fringe, as seen by the changes in the curvature of the reflected intensity near 2θ = 1.5° and 2.25°. The reflectivity signal from the drop cast film (Figure 7c) and bare silicon (Figure 7d) do not exhibit interference fringes. The extracted electron density profiles of each sample are shown in the inset of the reflectivity curves. Fitting parameters for the XRR curves are summarized in Table 2. For a monolayer deposited at a surface pressure of 25 mN/m, the substrate—monolayer roughness and the electron density of the single layer agree with the theoretical model. This indicates that the monolayer is closely packed, with the molecules orientated and ordered with their long axis more or less normal to the surface.

A systematic XRR study of several samples shows small variations in the apparent monolayer thickness of films deposited under nominally identical deposition conditions. Thicknesses are consistent for samples in a single batch but are different in different deposition events and substrates. The mean molecular thickness obtained by averaging the thicknesses measured for each sample is 29.6 Å, with a standard deviation of 3.2 Å. A further difference between the predicted and measured heights can arise from the roughness of the substrate, which is nearly one-third the height of the molecule. The physical interpretation of the parameters of the XRR model is thus complicated by the relative magnitudes of the molecular length and surface roughness and of the molecules.

An alternative to the single layer model is to conceptually split the molecule into two layers of different densities, with a boundary between the two layers placed at the ether group connecting the head and the bridge groups. The result is a two-layer model with an electron-rich head group, with a density of 0.718 e⁻/Å³ and a thickness of 8.3 Å, and an electron-poor bridge and attachment groups with a density of 0.226 e⁻/Å³ and a thickness of 15.7 Å. The substrate—air interface roughness of the silicon substrate is fit to be 7.6 Å rms. The interface can be modeled as a monolayer of molecules, assuming this two-box model, conformally coating a rough silicon substrate. In this case, the out-of-plane electron density profile created by integrating the density along the in-plane direction appears to form a single layer with average density and increased thickness as a result of the comparable magnitudes of the molecular length and surface roughness and the comparable densities of the molecular head group and the Si substrate.

The XRR results exhibit a clear difference in the electron density profiles of samples deposited with different surface densities. The model fit of the monolayer deposited using a surface pressure of 15 mN/m shows a reduction in the magnitude of the thickness and electron density parameters. This reduction in the magnitude of the thickness and electron density is indicative of a reduced monolayer coverage with the fit parameters being a weighted average between the densities

Table 2. XRR Fit Parameters

<table>
<thead>
<tr>
<th>sample</th>
<th>substrate—monolayer interface roughness (Å)</th>
<th>monolayer thickness (Å)</th>
<th>monolayer electron density (e⁻/Å³)</th>
<th>monolayer—air interface roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 mN/m ReAzoC monolayer</td>
<td>5.9</td>
<td>33</td>
<td>0.41</td>
<td>13.2</td>
</tr>
<tr>
<td>15 mN/m ReAzoC monolayer</td>
<td>8.8</td>
<td>28.7</td>
<td>0.34</td>
<td>15.2</td>
</tr>
<tr>
<td>drop-cast ReAzoC monolayer</td>
<td>12.4</td>
<td>8</td>
<td>0.29</td>
<td>8.2</td>
</tr>
<tr>
<td>Si/SiO₂ substrate</td>
<td>7.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of the molecular monolayer and air. This weighted average interpretation is used to account for samples with a submonolayer coverage to account for the lack of lateral homogeneity. The reflectivity pattern is indicative of a surface with the molecules organized into closely packed islands because of the spatial constraint imposed by the lateral coherence length of X-rays. The weighted average model estimates the surface coverage for the 15 mN/m film to be 75% of the value of the complete single monolayer, as compared with 68% as observed via XPS. This discrepancy arises from the uncertainty in accounting for the interfacial roughness for the bare silicon and the complete monolayer films used in the weighted average model. Further reduction in these parameters in the case of the drop-cast films is consistent with a randomly distributed array of molecules or the formation of 3D aggregates.

**XRR Characterization of Isomerization.** XRR provides insight into the structural changes, including changes in the thickness of the molecular layer, resulting from optical illumination. XRR studies of the reconfiguration were conducted using monolayers deposited at a surface pressure of 25 mN/m. The experimental procedure used for the structural studies of the reconfiguration process consisted of a series of alternating exposures to UV and blue light at wavelengths of 365 and 460 nm, respectively. The UV and blue optical intensities for this structural study were 94 and 100 mW/cm², respectively, far higher than the intensities used to obtain the optical spectra in Figure 6.

XRR measurements of the as-deposited structure are shown in Figure 8a. Following this initial configuration, the monolayer was exposed to blue light for 30 s, and the XRR curve was remeasured. As expected, no change in the structure was observed (Figure 8a, solid blue line) because the initial state is composed of molecules in the *trans* isomeric state. The same sample was then exposed to 30 s initially and then to 360 s of UV light. After the UV exposure, there is an increase in intensity near the local minimum (Figure 8a, solid violet line). This increase in intensity near the local minimum is consistent with a change in the structure because of the photo-isomerization of the monolayer from the *trans* state to the *cis* state.

The XRR data can be used to estimate the fraction of the monolayer isomerized as a result of UV exposure. Using the simple structural model described above, the reflected intensity curve can be modeled as the weighted average of the reflectivity from the starting structure, which is assumed to be dominated by the *trans* isomer, and the reflectivity from a theoretical 100% *cis* monolayer. Adding the intensities in this way is appropriate for sample configurations in which the isomeric domains have lateral extents on the order of the X-ray transverse coherence length, which is 350 nm for the experimental geometry used here. An analysis of the XRR data shown in Figure 7 using this two-domain model gives an isomerization of 11 ± 2% of the area of the monolayer. An analysis of UV-vis studies under these optical conditions using eq 7 gives an isomerized fraction of 47−52%, depending on the value of the constant n. Difference between these fractions may arise because the X-ray measurements are insensitive to the isomerized areas that are smaller than the lateral X-ray coherence length on the order of 100 nm.

When the XRR experiment was performed under the same optical conditions as those for the UV-vis spectroscopy studies, no statistically significant change in the reflected intensity was observed. The combination of X-ray and spectral data thus suggests that for experiments conducted with low-intensity light, the isomerized molecules are randomly distributed, rather than grouped into domains, because a change in the XRR curve is not observed under low-intensity illumination.

The return to the *trans* state was probed by studying the structure under blue illumination following UV illumination. The initial UV exposure was followed by exposures with durations of 360 s (Figure 8d, solid blue line), 720 s (Figure 8, dashed red line), and 1440 s (Figure 8, dotted black line) to light with 460 nm wavelength at an optical intensity of 100 mW/cm². An XRR measurement was performed after each of these exposures, but no evidence of a structural change in the monolayer was observed in the XRR signal.

To further investigate the monolayer structural changes, the molecular structure was probed by a series of alternating XRR and UV-vis spectroscopy measurements performed with the same power density and exposure times as used for the measurements shown in Figure 8. A 25 mN/m LB sample was prepared on a quartz substrate, its initial structure was probed using XRR, and a subsequent series of measurements were conducted using alternating optical illumination and XRR. The 365 nm illumination was carried out at a power density of 100 mW/cm² for 360 s. The 460 nm illumination was performed at a power density of 100 mW/cm² for 720 s. Optical spectroscopy measurements were performed before and after each XRR measurement. The resulting XRR measurements are shown in Figure 9a.

The reflectivity curve from the starting structure in Figure 9a (black curve) shows a local minimum at 2θ = 2°. Upon exposure to UV light (violet), the intensity at the local minimum decreases and the reflectivity fringe becomes less pronounced. Upon subsequent exposure to blue light, the reflectivity curve remains unchanged. This progression in the reflectivity curves is consistent with the results observed in Figure 8.

The UV-vis spectra resulting from the high-power and long-duration optical exposure are shown in Figure 9b. The starting UV-vis spectrum (black, solid) remains unchanged after the X-ray measurement (black, dashed). After UV exposure (violet, solid), the absorption peak at 360 nm is reduced from 0.031 to 0.018, a decrease of 42%. After the XRR measurement, the magnitude of the absorbance increases to 0.021, a recovery of 23% of the original transformation. After blue light exposure,
The molecules and monolayers showed evidence of structural near-full coverage when deposited via the LB technique. The molecules and monolayers have been characterized and fabricated. The physical and electronic structures of hindrance or other molecule have been developed, in which a fraction of the monolayer is isomerized portion of the monolayer recovering to the trans state, and no additional recovery occurring as a result of blue photoisomerization, followed by a small fraction of the cis state, and no additional recovery occurring as a result of blue optical exposure. At this higher power and longer-duration exposure, XRR and UV−vis spectra not only exhibit an isomerization from the trans to the cis state but also indicate a suppression of the reverse cis-to-trans isomerization. The limited cis-to-trans photoisomerization is consistent with steric effects from either the bulkiness of the molecule or monolayer close-packing. Damage to the monolayer from UV/ozone is unlikely because the wavelength of UV light used in the experiment is reported to be generating extremely low concentrations of ozone.58

■ CONCLUSIONS

Molecular monolayers of a new molecule with electron-donating characteristics and externally reconfigurable structures have been fabricated. The physical and electronic structures of the molecules and monolayers have been characterized and show near-full coverage when deposited via the LB technique. The molecules and monolayers showed evidence of structural reconfiguration in response to optical exposure both in solution and when confined to a monolayer. A structural model for the photoisomerization and reconfiguration in the monolayer has been developed, in which a fraction of the monolayer is isomerized, depending on the intensity and duration of optical exposure. We also present evidence of limited reversibility of photoisomerization in monolayers, hypothesized to be steric hindrance or other molecule−surface interactions.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES


Figure 9. (a) XRR of a ReAzoC monolayer deposited at a surface pressure of 2S mN/m before illumination (black), after UV exposure (violet), and after subsequent blue exposure (blue). (b) Optical absorption spectra of the starting structure and before and after each XRR measurement.


