Tuning of Molecular Rectification in Donor/Acceptor Assemblies via Supramolecular Structures

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Tuning of molecular rectification has been demonstrated in donor/acceptor (D/A) assemblies. Electron flow was favorable from donor to acceptor in both D/A and A/D assemblies. A molecular layer of a D/A supramolecule was built via layer-by-layer electrostatic assembly of a monolayer of a donor and a monolayer of an acceptor in sequence. The advantages of D/A assemblies over D-σ-A molecules as a molecular rectifier have been discussed. The novelty of our approach opened up possibilities for selecting suitable D/A combinations and the separation between the donor and acceptor components in the assembly. In this article, we studied the effect of the substitution of fluorone (as acceptor), which tunes its molecular orbitals, on the rectification properties of the junction. The rectification of the molecular D/A assemblies has also been tuned by changing the spacing between the donor and acceptor moieties.

1. Introduction

The field of molecular electronics is becoming more fascinating than ever after a number of remarkable experiments showed that single molecules can be utilized in different electronic and optoelectronic components. A lot of research attempted to validate the early prediction by the Aviram and Ratner (AR) model.[1] They proposed that a D-σ-A molecule connecting an electron-donor moiety (D) to an electron-acceptor moiety (A) through a saturated σ bridge might act as a rectifier when sandwiched between two metallic contacts. Under forward bias, electron transfer from the cathode to the lowest unoccupied molecular orbital (LUMO) of the acceptor and from the highest occupied molecular orbital (HOMO) of the donor to the anode would occur favorably, resulting in A^- and D^+ species, respectively. Finally, the A^- and D^+ moieties would recombine to their ground states, resulting in a net transfer of charge carriers from one electrode (cathode) to the other (anode). Electron movement in the opposite direction would be forbidden by molecular orbitals of the components, resulting in molecular rectification or directionality in current flow through the molecule.

The AR model shows that for proper rectifier behavior, the electron affinity level of the acceptor is required to be either totally or partially empty and lie at or slightly above the Fermi level of the electrode and of course above the ionization potential of the donor.[1] Ellenbogen and Love argued that electron transfer would be favorable in the D to A direction,[2] because at a finite bias, the HOMO of the D component would be aligned with the LUMO of the A part. Localization of the electronic states in the D and A moieties of a molecule is well-known, except at particular biases where the voltage drop can align the two states and form a resonance state delocalized over the entire molecule. Such an event occurring in the bias window can also give rise to rectification.[3] The rectification can also depend on the profile of the electrostatic potential, which is extremely sensitive to where the electroactive part of the molecule lies in the monolayer. This effect can produce rectification in the direction opposite to the AR prediction.[4]

In general, experimental attempts to observe molecular rectification involved the synthesis of D-σ-A molecules with several constraints: (1) oriented films of the molecules have to be achieved; (2) molecular orbitals of the donor and acceptor components must be sufficiently localized so that they may form a charge-transfer complex; (3) the orbitals should not be too delocalized, so that electron transfer is possible between D^+ and A^-; and (4) additionally, metal contacts on molecularly thin layers are required for studying the electrical characteristics. Metal/molecule/metal sandwich structures based on Langmuir−Blodgett monolayers of a molecule with alkyl chains exhibited single-molecule properties and molecular rectification.[5−10] Hg drop electrodes as top contacts[11−13] or scanning tunneling microscopy with more-limited contact areas[9,10,14] was also used to characterize

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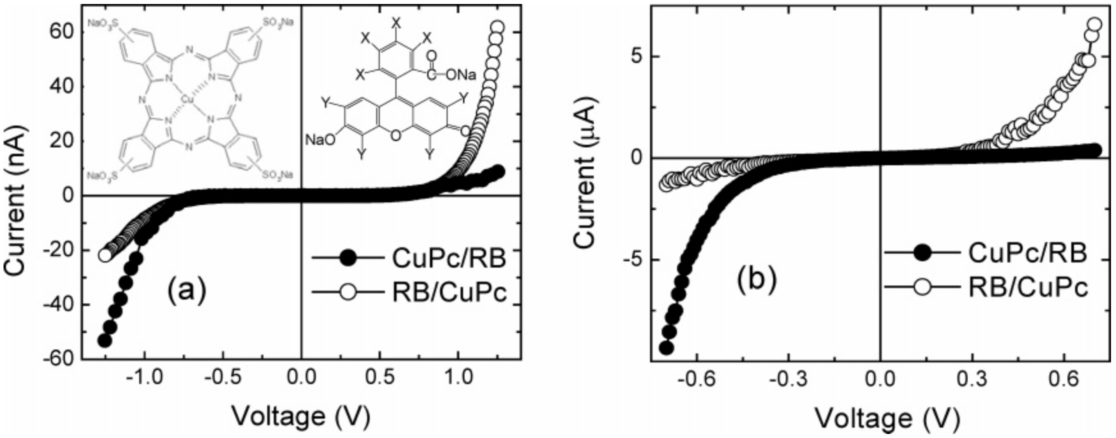

Figure 1. Asymmetric $I-V$ characteristics of CuPc/RB and RB/CuPc assemblies with (a) Si and Hg and (b) ITO and Hg electrode combinations. Inset of (a) shows the molecular structure of CuPc and fluorone. X = Cl and Y = I represent Rose Bengal (RB).

the current−voltage ($I-V$) characteristics of organic monolayers.

A radical approach to avoiding the complex chemical synthesis of D-σ-A molecules with an inherent possibility of orienting themselves is to build such molecules. Self-assembled monolayers (SAM) of two components on two metal electrodes were brought into contact to exhibit molecular rectification.[11,13,14] Recently, we built donor/acceptor (D/A) molecular assemblies via the layer-by-layer (LbL) electrostatic adsorption of a monolayer of a donor and a monolayer of an acceptor in sequence. Such D/A molecular assemblies exhibited electrical rectification.[15] In contrast to a unimolecular D-σ-A pair, a D/A supramolecular assembly has many advantages. A variety of D/A assemblies can be imagined and built via the LbL technique. Because the LbL deposition relies on surface charge reversal during the electrostatic adsorption of each layer,[16−18] the deposition of one molecular layer or monolayer is also assured. In a D-σ-A molecule, the donor and acceptor components are not always sufficiently isolated, so that their molecular orbitals may become delocalized over the entire molecule. In contrast, in a D/A assembly, the localization of molecular orbitals of the individual components can be kept in mind in building the assemblies by providing controlled isolation between them.

It is novel and important to control and tune molecular rectification. In this article, we demonstrate two approaches to controlling the directional flow of electrons through a molecular assembly: (1) molecular orbitals of an individual component of the D/A assembly can be tuned by introducing suitable functional groups, and (2) separation between the two components can be controlled in the submolecular scale. In this work, copper(II) phthalocyanine (CuPc) has been used as a donor, whereas five fluorone dyes in the xanthane class have been used as acceptor materials. Separation between the components has been tuned by controlling the pH of a polycation bath, in which the intermediate binder layer was deposited.

2. Experimental Section

Copper(II) phthalocyanine (CuPc), the fluorone dyes, and the polycation, namely poly(allylamine hydrochroride) (PAH), were purchased from Aldrich Chemical Co. and used without further purification. The molecular structure of CuPc and a general fluorone dye is shown in the inset of Figure 1a. LbL films of CuPc and fluorone dyes were deposited by electrostatic adsorption. Films were grown on precleaned indium tin oxide (ITO)-coated glass substrate and on silicon wafers. The polished Si(111) wafers were phosphorus doped (N-type) with a resistivity of 5−10 mΩ cm. To obtain LbL films, we used a PAH (mol wt = 70 000 g/mol) solution, 5×10^{-3} M on the basis of its repeat unit, as a polycation. Solutions of fluorone dyes and CuPc (5×10^{-3} M) in deionized water (Milli-Q, 18.2 MΩ·cm) were used as anionic baths. The pH levels of the cationic and anionic solutions were adjusted to 6.5. To deposit molecular D/A assemblies, i.e., a monolayer of the donor and a monolayer of an acceptor in sequence, we first dipped Si or ITO substrates in a polycationic bath for 15 min, followed by rinsing in three deionized water baths for 2, 2, and 1 min. The substrates were then dipped into the CuPc solution (anionic bath) for 15 min, followed by the same rinsing protocol in a separate set of water baths. This resulted in one molecular layer of the donor material. To complete a D/A assembly, on top of the donor monolayer, we deposited a layer of an acceptor material following the same protocol. Deposition of the outermost PAH layer resulted in symmetric structures (e.g., PAH/CuPc/PAH/fluorone/PAH) and also prevented Schottky barrier effects.[6] To vary the separation between the donor and the acceptor components, we varied the morphology of the intermediate PAH layer between the donor and acceptor monolayers. The pH of the PAH bath from which the intermediate PAH layer was deposited was varied between 5 and 10.5 in steps of 0.5. In all cases, the pH of the PAH bath, from which the two outermost PAH layers were deposited, was kept at 6.5, providing similar contacts with the electrodes in all the assemblies. Several control experiments were carried out with (1) CuPc and fluorone components individually, namely PAH/CuPc/PAH and PAH/fluorone/PAH films; (2) with only a PAH monolayer; and (3) in reverse structures, e.g., PAH/fluorone/PAH/CuPc/PAH films. The

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films for the control experiments were also deposited on both ITO and Si wafers.

Annealed D/A assemblies were kept in a vacuum chamber (1 × 10^{-3} Torr) at room temperature, with the film facing downward. A syringe with a Hg blob on the tip of a metal needle was slowly raised from outside the chamber by a micrometer screw until the blob just touched the film. The diameter of the blob was less than 0.5 mm. The contact between the film and the blob was monitored through a microscope. Bias was applied with respect to the Hg electrode, and $I-V$ characteristics were recorded at both sweep directions and in voltage loops. The voltage step was 0.01 V, with the scan speed varying between 5 and 20 mV/s. The $I-V$ characteristics were recorded with a Yokogawa 7651 dc source and a Keithley 486 picoammeter. The instruments were controlled by a personal computer via a general purpose interface bus (GPIB). To study the growth of film deposition, we repeated the deposition process on quartz substrates for 5−10 cycles, and UV−vis electronic absorption spectra were recorded after each cycle. The spectra confirmed uniform deposition of CuPc and the fluorone dyes. The thickness of the D/A assemblies was ∼5−6 nm for a particular pH of the intermediate PAH layer.

3. Results and Discussion

In all the D/A assemblies, a charge-transfer complex with a single pair of HOMO and LUMO levels did not form, as evidenced by electronic absorption spectra (of multilayer assemblies), which was an algebraic sum of the spectra of individual components. We have recorded $I-V$ characteristics of PAH/CuPc/PAH/fluorone/PAH and PAH/fluorone/PAH/CuPc/PAH assemblies. The pH of the PAH bath for the deposition of intermediate and outer layers of PAH was the same in all cases. Different halogen substitutions for fluorone resulted in different assemblies. X = Cl and Y = I represent Rose Bengal (RB). Figure 1 shows the $I-V$ characteristics of the assemblies with CuPc and RB. The $I-V$ characteristics of CuPc/RB (D/A case) and RB/CuPc (A/D case) assemblies with Si and Hg and ITO and Hg electrode combinations were asymmetric in nature. The figures show that both of the molecular assemblies act as rectifiers. The directionality of the electron flow is inverted when the order of the molecular components in the D/A assemblies is reversed. This confirmed the rectifying nature in the D/A assemblies. The inversion in the $I-V$ curve was, however, not exactly a mirror image. This might be due to the different metal-work functions that each component faced in the D/A and A/D cases. The overall current in assemblies on Si was two order of magnitude less than that on ITO. This could be due to the native SiO_2 on Si. The results in Figure 1 show that both the D/A and A/D assemblies favored electron flow in the donor-to-acceptor direction. This provides an experimental validation of the theory outlined by Ellenbogen and Love,[2] which allows for independent movement of molecular orbitals of the D and A components under bias. Electrostatic binding between the D and A components in D/A assemblies, in contrast to chemical bonding in the D-σ-A case, might have allowed for such an independent movement of the molecular orbitals and resulted in electron flow in the donor-to-acceptor direction in the D/A assembles. The experimental findings in this work are in contrast to those of the AR model, where electron flow is favorable in the acceptor-to-donor direction.

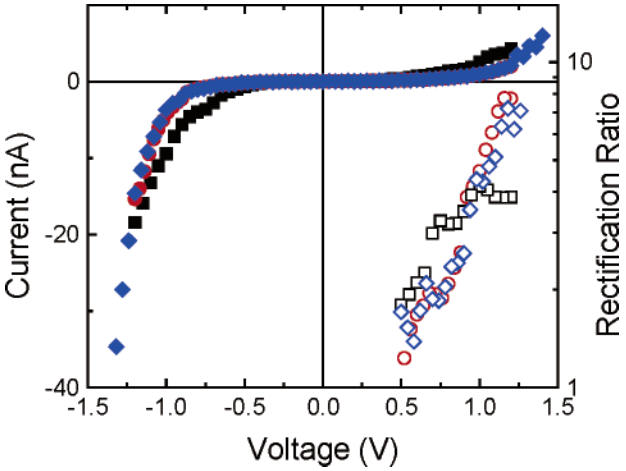


Figure 2. $I-V$ characteristics (filled symbols) and the corresponding rectification ratio above threshold voltage (open symbols) of a CuPc/Rose Bengal molecular assembly at three different points of the film (as represented by three types of symbols).

Figure 2 shows asymmetric $I-V$ characteristics of the CuPc/Rose Bengal molecular assembly at three different points of the film on Si wafer. The rectification ratio (RR) above the threshold voltage in each of the cases is also shown in the figure. The figure shows that molecular rectification was observed in the D/A assemblies with higher current in the reverse bias direction. The molecular orbitals of the donor and acceptor components favored electron flow in the donor to acceptor direction. Though the nature of $I-V$ characteristics remained mostly identical at different spots of the film, the current at a voltage varied to some extent. The RR at a voltage, however, did not vary from one spot to another. Because the current, not RR, should depend on the film/Hg contact area, the variation in current could be due to different sized Hg blobs being used in each of the cases.

To tune molecular rectification, we studied and compared $I-V$ characteristics from five different D/A assemblies. The halogen substitutes of the acceptor material were varied to tune the material's molecular orbitals. The five acceptors were chosen in such a way that they have the same basic structure but different substitutes. With the substitute groups in the aromatic system, which result in different energy levels of the molecule, it was possible to control the π-electron density in the backbone. In other words, the substitutes changed the ionization potential and electron affinity of the molecules, so that we could study their effect on the rectification of the molecular junctions. If different molecular structures were chosen, the total length of the D/A assembly and their interactions would have become different and hence a comparison would not have been possible.

For each of the assemblies, a range of $I-V$ characteristics were recorded with different maximum voltage (V_{max}). Typical $I-V$ characteristics for the other four D/A assemblies are shown in Figure 3. The figure shows that molecular rectification is observed in all the assemblies, but with a different rectification ratio. The substitutes of the acceptor material in the D/A assemblies controlled the directionality of electron flow and hence the RR. The maximum RR of the junctions varied between 1.3 and 45. With the addition of electronegative substitutes, both the HOMO and LUMO levels shift to lower energy. In addition, the band gap

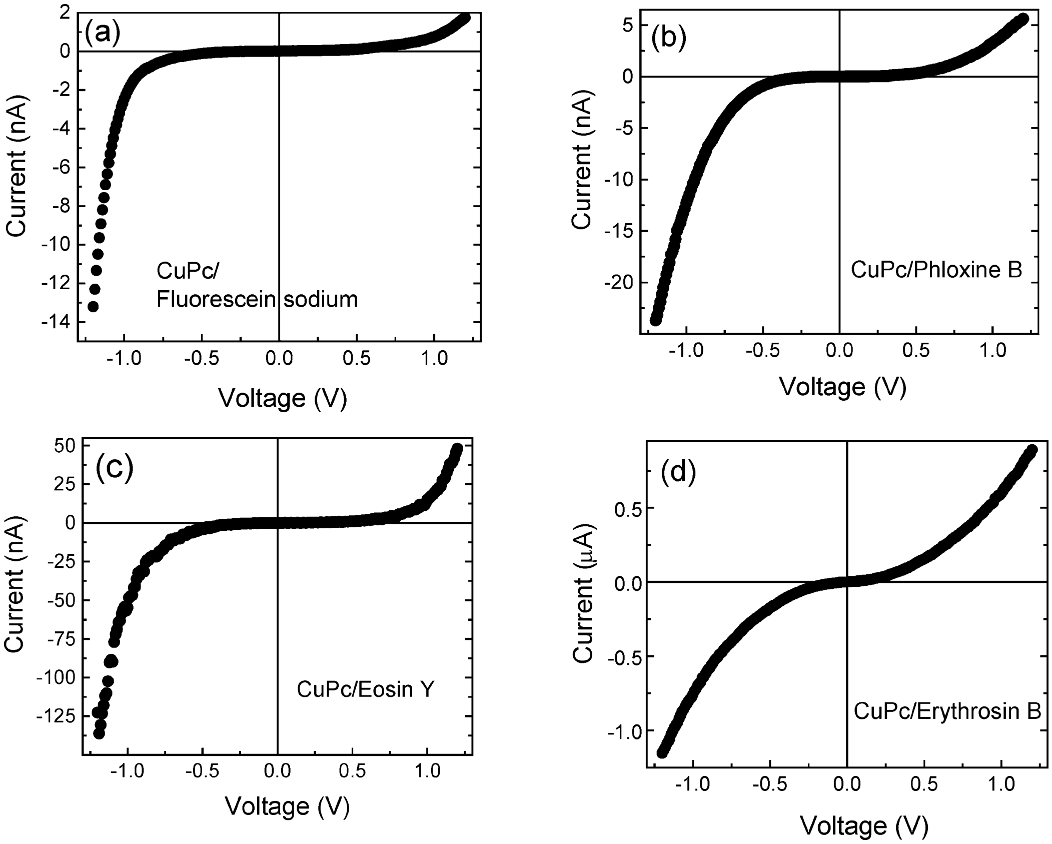
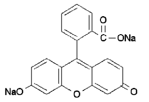
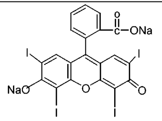
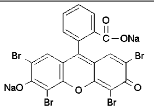
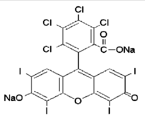
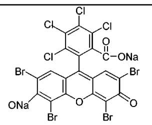


Figure 3. Asymmetric $I-V$ characteristics of four different molecular assemblies between Si and Hg electrodes, with a voltage scan rate of 10 mV/s. The pH of the PAH bath, from which intermediate and outermost PAH layers were deposited, was 6.5 in all cases.

decreases, suggesting that the shift of the LUMO is more than that of the HOMO level. Hence, with the addition of the substitutes in the acceptor molecule of the D/A assembly, the barrier with the Hg electrode changes in both bias modes and hence affects the directionality of current flow (or RR). One might question if electrode penetration may be the reason for having different RR for different junctions. It can simply be ruled out because of the fact that all the measurements were carried out at different points of the film (Figure 2, as an example). Had electrode penetration occurred, it would have been different from a spot to the other and would have resulted in different $I-V$ characteristics.

The tuning of molecular rectification by introducing substitution in the acceptor molecule of the CuPc/fluorone molecular rectifiers is summarized in Table 1. In all cases, electron flow was favored in the donor-to-acceptor direction. The RR depended on the substitutes of the acceptor. With fluorescein as an exception, the RR seemed to increase with the electron affinity of the substitutes of the acceptor. At a particular (low) voltage, RR was at a maximum for the assembly with fluorescein sodium. The D/A assembly with Rose Bengal as acceptor, however, withstood higher bias and consequently higher RR (up to 45 at 2.8 V). The values quoted here are for $V_{\max}$, for which reproducible results were obtained by applying voltage in several cycles. At still higher $V_{\max}$, many of the devices showed high current with signs of degradation. Only the results far below the breakdown point are presented in the manuscript. The results here show that the electron affinity and ionization potential levels of the D and A components can control molecular rectification in the D/A assemblies.

Table 1. Rectification Ratio (RR) for Different CuPc/Fluorone Molecular Assemblies with Si and Hg Electrodes (pH of intermediate PAH = 6.5)

name of acceptor molecule	functional groups	structure	RR at 1.2 V	maximum RR (at voltage)
fluorescein sodium	X=H, Y=H		7.5	14.0 (2.1 V)
erythrosin B	X=H, Y=I		1.3	3.0 (2 V)
eosin Y	X=H, Y=Br		2.6	10.0 (1.45 V)
rose bengal	X=Cl, Y=I		6	45.0 (2.8V)
phloxine B	X=Cl, Y=Br		4.2	5.0 (1.8 V)

To further tune the molecular rectifiers, we have varied the pH (from 5 to 10.5) of the PAH bath, from which the intermediate PAH layer was deposited. The pH of the PAH bath, from which the outermost PAH layers were deposited, was kept at 6.5 in all of the measurements. Here, the intermediate PAH layer binds the donor and the acceptor

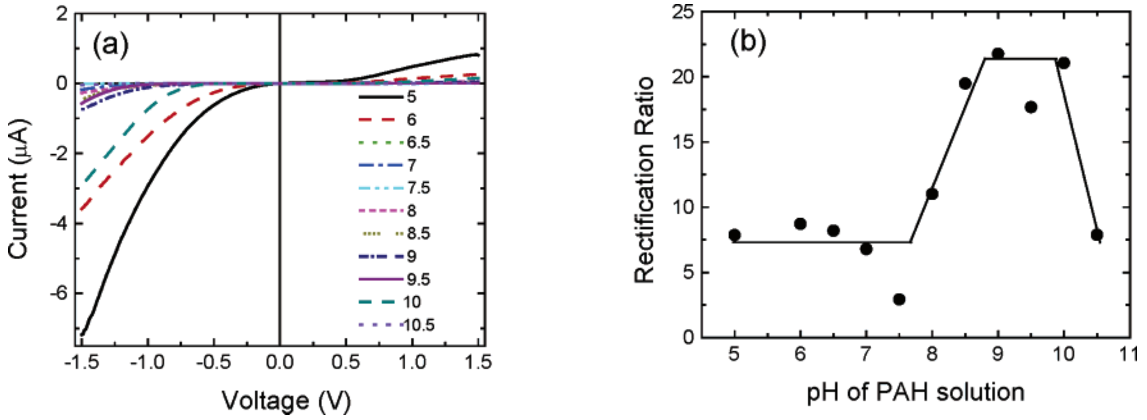


Figure 4. (a) $I-V$ characteristics of a CuPc/Rose Bengal assembly for different pH (as represented in the figure) levels of the intermediate PAH layer. (b) Rectification ratio at 1.5 V vs pH of the intermediate PAH layer of a CuPc/Rose Bengal assembly. The line is to guide the eye.

components and determines the separation between the two components. In LbL films, the pH controls the morphology of the polyions and hence its thickness.[19] As a result, the separation between the donor and acceptor components of the D/A supramolecules varies with the pH of intermediate PAH layer. The separation would control the localization/delocalization of the molecular orbitals of the individual components and should tune directional flow of electrons. We have characterized CuPc/RB assemblies with different pH levels of the intermediate PAH layer. The $I-V$ characteristics of the assemblies are shown in Figure 4a. The magnitude of current in both bias directions varied with the pH in a dissimilar fashion. The resulting RR for the D/A composites, as shown in Figure 4b, responded strongly to the pH of the intermediate PAH layer. The RR was at a maximum in the 9−10 pH range. Because the pK_a of PAH is around 7.5, the polycation was fully charged in solution at pH below 7.5. Hence the thickness of the intermediate PAH layer was not altered at pH below 7.5. Above 7.5, PAH become partially charged and thus the thickness of a monolayer increases with pH. Figure 4b shows that the RR goes through a maximum with pH of the intermediate layer. Here, with the pH, the separation between the donor and acceptor moieties also increases. The results show that at low pH levels of PAH, which result in the smallest separation between the D and A components, their molecular orbitals were delocalized. At higher pH (>10), loopy morphology of the PAH has the components widely separated so that their molecular orbitals become too localized. Electron transfer between the components hence ceased to occur. At both extremes, unidirectionality of current flow becomes unfavorable. At an optimum thickness of the intermediate PAH layer, the D/A assembly exhibited the highest rectification. The results presented in Figure 4 hence show novel methods for controlling molecular rectification.

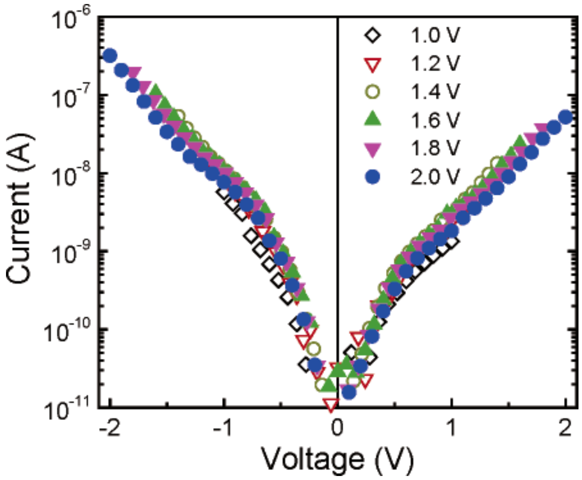


Figure 5. Asymmetric $I-V$ characteristics from a CuPc/Rose Bengal molecular assembly for different V_{max} (given in the figure). The pH of the PAH bath, from which the intermediate and outermost layers were deposited, was 6.5.

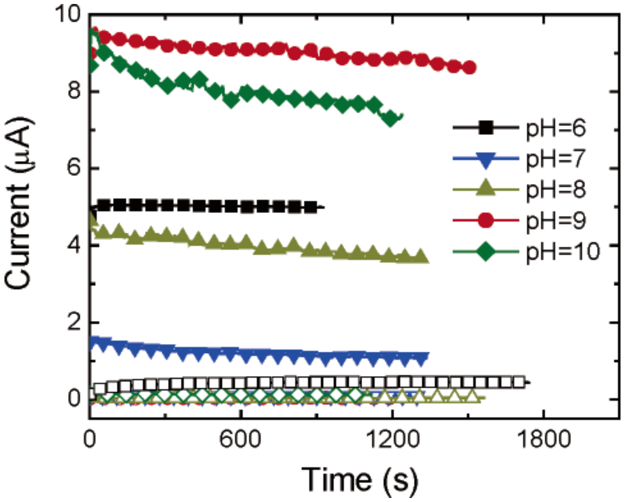


Figure 6. Current at +2 V (open symbols) and −2 V (filled symbols) pulses of a CuPc/Rose Bengal molecular assembly with five different pH levels of the intermediate PAH layer. Current values were recorded just before the end of a 1 s pulse. One voltage pulse was applied every 3 s (i.e., frequency = 0.33 Hz, duty cycle = 33%). Absolute values of the current at −2 V are plotted for comparison.

To study the stability and reproducibility of molecular rectification in different D/A assemblies, we have recorded $I-V$ characteristics (1) at different points on the film; (2) with increasing maximum sweep voltage, V_{max}; and (3) in loops; we have also (4) measured current at fixed ±V as a function of time. The log(I)−V plots for a CuPc/Rose Bengal assembly, with V_{max} ranging from 1.0 to 2.0 V, are shown in Figure 5. The plots, at the same position of the film, matched for different V_{max} values even in the low |V| region. With an increase in bias voltage, RR increased for all of the assemblies. A high degree of reproducibility and stability in

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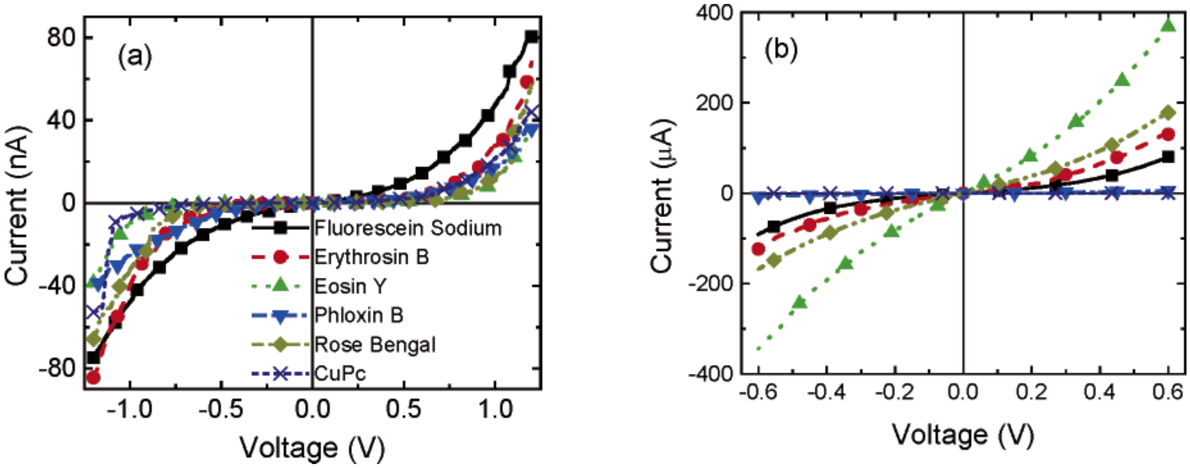

Figure 7. Near-symmetric *I*−*V* for individual components of D/A assemblies in (a) Si and Hg and (b) ITO and Hg electrode combinations. The pH of the PAH bath, from which the intermediate and outermost layers were deposited, was 6.5 in all cases.

molecular rectification from all the CuPc/fluorone assemblies was also observed when the *I*−*V* characteristics were recorded in continuous loops for 3−4 times. The RR above the threshold voltage in each of the cases matched.

The reproducibility and stability of molecular rectification has also been observed in *I*−*V* characteristics recorded in voltage pulse mode. The current was measured under a +2 or −2 V pulse (width = 1 s) for some time. Figure 6 shows the current at +2 and −2 V for CuPc/Rose Bengal assemblies with varied pH levels of the intermediate PAH layer (as has been presented in Figure 4). For all five of the assemblies, the current values at +2 V remained much lower than those at −2 V that exhibit rectification. The current at the forward bias remained steady, whereas that at the reverse bias direction showed a little decrease with time. The results hence show that the molecular rectification was sustained for a considerable period of time.

We have carried out some additional control experiments. To isolate and negate the effect of 1−1.5 nm native SiO_2 on Si, we recorded *I*−*V* characteristics without any organic film. The *I*−*V* plot for SiO_2 was symmetrical. The currents due to CuPc/fluorone assemblies were at least 3 orders of magnitude lower than the currents due to SiO_2 (Figure 1 of ref 15). The *I*−*V* curve of a monolayer of PAH, which binds CuPc and fluorone, was nonlinear and symmetrical. We also characterized a monolayer of the D and A components individually. In panels a and b of Figure 7, we present *I*−*V* characteristics from the monolayer of individual components of the D/A assemblies, i.e., CuPc and fluorone dyes, with Si and Hg and ITO and Hg electrode combinations, respectively. The *I*−*V* plots for the PAH/CuPc/PAH and PAH/fluorone/PAH films were mostly symmetrical in both electrode combinations. These control experiments show that the observed directionality in current flow in the molecular CuPc/fluorone assemblies was not due to any rectification arising out of the work functions of the two electrodes.

4. Conclusions

In conclusion, we have demonstrated tuning of molecular rectification in D/A assemblies or supramolecules. The directionality of the electron flow was maintained when D/A and A/D assemblies were compared. The advantages of the D/A assemblies over unimolecular D-σ-A as a molecular rectifier have been discussed. Instead of complex synthesis, it is now straightforward to build a molecular rectifier from suitable donor and acceptor moieties. We could study the effect of the acceptor's HOMO and LUMO levels on the RR. We showed that the rectification ratio depends strongly on the substitutes of the acceptor in the D/A assembly. We could also tune the rectification by varying the separation between the donor and acceptor moieties of the supramolecular assembly. We have shown that at an optimum spacing between D and A moieties, the rectification ratio reaches a maximum.

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