Rectification in Molecular Tunneling Junctions Based on Alkanethiolates with Bipyridine–Metal Complexes

Junwoo Park, Lee Belding, Li Yuan, Maral P. S. Mousavi, Samuel E. Root, Hyo Jae Yoon, and George M. Whitesides*

ABSTRACT: This paper addresses the mechanism for rectification in molecular tunneling junctions based on alkanethiolates terminated by a bipyridine group complexed with a metal ion, that is, having the structure AuTS-S(CH₂)₁₁BIPY-MCl₂ (where M = Co or Cu) with a eutectic indium–gallium alloy top contact (EGaIn, 75.5% Ga 24.5% In). Here, AuTS-S(CH₂)₁₁BIPY is a self-assembled monolayer (SAM) of an alkanethiolate with 4-methyl-2,2′-bipyridine (BIPY) head groups, on template-stripped gold (AuTS). When the SAM is exposed to cobalt(II) chloride, SAMs of the form AuTS-S(CH₂)₁₁BIPY-CoCl₂ rectify current with a rectification ratio of r⁺ = 82.0 at ±1.0 V. The rectification, however, disappears (r⁺ = 1.0) when the SAM is exposed to copper(II) chloride instead of cobalt. We draw the following conclusions from our experimental results: (i) AuTS-S(CH₂)₁₁BIPY-CoCl₂ junctions rectify current because only at positive bias (+1.0 V) is there an accessible molecular orbital (the LUMO) on the BIPY-CoCl₂ moiety, while at negative bias (−1.0 V), neither the energy level of the HOMO or the LUMO lies between the Fermi levels of the electrodes. (ii) AuTS-S(CH₂)₁₁BIPY-CuCl₂ junctions do not rectify current because there is an accessible molecular orbital on the BIPY-CuCl₂ moiety at both negative and positive bias (the HOMO is accessible at negative bias, and the LUMO is accessible at positive bias). The difference in accessibility of the HOMO levels at −1.0 V causes charge transfer—at negative bias—to take place via Fowler–Nordheim tunneling in BIPY-CoCl₂ junctions, and via direct tunneling in BIPY-CuCl₂ junctions. This difference in tunneling mechanism at negative bias is the origin of the difference in rectification ratio between BIPY-CoCl₂ and BIPY-CuCl₂ junctions.

INTRODUCTION

When charge passes through a molecule connected by two electrodes, if the rate of charge transport (CT) in one direction is different than in the opposite direction (at the same magnitude of applied voltage), the molecular junction rectifies current, and is relevant to the subject of molecular rectifiers. Rectification is especially useful in mechanistic studies of charge transport through molecular junctions because the same junction is used to measure tunneling currents at both positive and negative bias voltage. The commonality reduces errors due to junction-to-junction variability in the measurement of current.

We previously reported that molecular junctions composed of BIPY-terminated n-alkanethiol-based self-assembled monolayers (SAMs) on template-stripped metal surfaces rectify current. We have observed that the conductive properties (including rectification) of these BIPY junctions can change drastically upon exposure to metal ions. This paper describes the rectification of tunneling currents at ±1.0 V in junctions with the structure AuTS-S(CH₂)₁₁BIPY-M//GaOₓ/EGaIn, where M = Co or Cu (Figure 1). The objective of this paper is to understand why tunneling currents differ between BIPY-CoCl₂ junctions and BIPY-CuCl₂ junctions.

SAMs based on metal complexes of BIPY are an excellent model system to investigate molecular rectifiers classified as having an asymmetrically positioned chromophore in their molecular structure (e.g., molecules composed of an insulating alky chain terminated by a more conducting, aromatic moiety) for two reasons. First, the ability for BIPY to form complexes with transition metal ions makes it possible to modify the frontier energy levels of the BIPY-MCl₂ group. A survey of the effects of different metal ions (Cr, Mn, Fe, Co, Ni, or Cu) showed that BIPY-CoCl₂ and BIPY-CuCl₂ junctions exhibited pronounced differences in rectification. The differences in rectification between BIPY-CoCl₂ and BIPY-CuCl₂ junctions...
suggested that rectification is determined purely by the electronic structure of the molecular junction, as opposed to (a) asymmetry in the nature of the two electrodes (Au bottom-electrode and EGaIn top-electrode), (b) asymmetry in the top and bottom contacts (covalent Au–S bond at bottom-electrode and a van der Waals contact with the EGaIn), (c) redox reactions involving EGaIn, or (d) the oxide layer of EGaIn. Second, BIPY-MCl₂ junctions, in principle, have the same supramolecular structure, which eliminates the uncertainty associated with differences in packing density, orientation, and conformation.

### RESULTS AND DISCUSSION

**BIPY-CoCl₂ and BIPY-CuCl₂ SAMs both have 1:1 (M:BIPY) binding ratios.** X-ray photoelectron spectroscopy (XPS) was employed to characterize the elemental composition of the BIPY-MCl₂ SAMs, using a total of nine samples. The atomic ratio of nitrogen to sulfur in the SAMs was determined to 1.8 ± 0.04 for BIPY-CoCl₂ SAMs and 1.8 ± 0.05 for BIPY-CuCl₂ SAMs, after correcting for attenuation of the sulfur signal due to the SAM thickness (Table 1; see Supporting Information for details). These values agree with the ratio measured for BIPY-CoCl₂ and BIPY-CuCl₂ junctions which complexed with other halide anions, however, still showed no significant change in rectification (Figure S4).

**BIPY-CoCl₂ junctions rectify current while BIPY-CuCl₂ junctions do not.** Figures 2a and b show averaged $J(V)$ curves recorded on BIPY-CoCl₂ (548 traces on 26 junctions) and BIPY-CuCl₂ junctions (357 traces on 17 junctions) using the EGaIn measurement system. We report the rectification ratio, $r^\prime$, as the ratio of current density at a given positive and negative bias ($r^\prime = |J(+V)|/|J(−V)|$ at ±1 V). As shown in Figure 2c, BIPY-CoCl₂ junctions rectified tunneling current with a rectification ratio $(r^\prime)$ of 82.0. In BIPY-CuCl₂ junctions, however, we did not observe rectification $(r^\prime = 1.0$ at ±1.0 V).

The difference in rectification between BIPY-CoCl₂ and BIPY-CuCl₂ junctions is the result of a difference in their mechanisms of tunneling at negative bias. The largest difference in the magnitude of $J(V)$ occurs at negative bias, where BIPY-CuCl₂ junctions have a 3× larger tunneling current than BIPY-CoCl₂ junctions. At positive bias, the difference in the rate of charge tunneling between BIPY-CoCl₂ and BIPY-CuCl₂ is much smaller (the rate of tunneling is only ~2× larger in BIPY-CoCl₂ junctions). This observation—that complexation with copper increases the rate of tunneling at negative bias—led us to hypothesize that an additional conduction path (the HOMO) may be accessible at negative bias in BIPY-CoCl₂ but not in BIPY-CoCl₂ junctions. To assess this hypothesis, we measured the approximate HOMO energy levels of both the BIPY-CoCl₂ and BIPY-CuCl₂ junctions, using both cyclic voltammetry (CV) and ultraviolet photoelectron spectroscopy (UPS).

The HOMO of BIPY-CuCl₂, but not BIPY-CoCl₂, lies between the Fermi level of the two electrodes at ~1.0 V. We first characterized the S(CH₂)₁₁BIPY-CoCl₂ and S-(CH₂)₁₁BIPY-CuCl₂ SAMs on a AuTS surface with CV (Figure 3) in 0.1 M aqueous KClO₄ electrolyte solutions, using a Pt counter electrode, and an Ag/AgCl reference electrode. The scan rate was 0.1 V/s. For BIPY-CoCl₂ SAMs, no redox peak was observed, while BIPY-CuCl₂ SAMs showed a strong redox peak at ~1.0 V, consistent with the HOMO energy level determined by UPS.

### Table 1. Elemental Ratios in the AuTS-S(CH₂)₁₁BIPY-CoCl₂ and AuTS-S(CH₂)₁₁BIPY-CuCl₂ Junctions Characterized by XPS*

<table>
<thead>
<tr>
<th>Junctions</th>
<th>Sulfur:Nitrogen (corrected for thickness of SAMs)</th>
<th>Metal:Nitrogen</th>
<th>Metal:Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIPY-CoCl₂</td>
<td>1.27 ± 0.05</td>
<td>1.8 ± 0.04</td>
<td>1.8 ± 0.06</td>
</tr>
<tr>
<td>BIPY-CuCl₂</td>
<td>1.27 ± 0.08</td>
<td>1.8 ± 0.05</td>
<td>1.7 ± 0.12</td>
</tr>
</tbody>
</table>

*Raw data is in the Supporting Information. Experiments were replicated a total of nine times, and uncertainty values represent the standard deviation.

**Figure 1.** Schematic images of the molecular junction with the structures of AuTS-S(CH₂)₁₁BIPY-MCl₂//GaO₃/EGaIn. XPS results show a 1:1 ratio between the metal and the 2,2’-bipyridine group. In reality, interfaces at EGaIn are rough, and the Au surface is not perfectly flat. Detailed descriptions of molecular structure are summarized in the Supporting Information.
observed within the potential range of −0.2−1.0 V (vs Ag/AgCl in 1.0 M KCl (aq)). Outside of this potential window, new peaks appeared in the CV, which increased in peak height after each scan—and are thus assumed to be caused by damage to SAM (Figure S5). For this reason, we limited the voltage applied to the working electrode to −0.2 to +1.0 V. The BIPY-CuCl₂ SAMs, on the other hand, showed well-defined, reversible anodic (Eₚa = ∼470 mV) and cathodic (Eₚc = ∼350 mV) peaks within the −0.2 to +1.0 V window (Figure 3). We assume that these peaks are indicative of oxidation/reduction reactions between BIPY-Cu²⁺Cl₂ + e⁻ ↔ BIPY-Cu⁺Cl. We observed a peak separation of approximately ∼120 mV between the anodic and cathodic peaks. For an ideal, reversible redox reaction, the peak separation should be zero. Previous CV measurements on similar systems, however, are also characterized by finite values of peak separation. The redox process in the CV of the BIPY-CuCl₂ SAM is only partially reversible. We believe that a plausible origin of the irreversibility of the process is the dissociation of Cu²⁺ cations from the SAMs at rates comparable with the time scale of the CV experiments.

The energy level of the HOMO (E_HOMO) relative to vacuum can be estimated from the formal half-wave potential E₁/₂ obtained from the cyclic voltammogram (eq 1).

\[ E_{\text{HOMO}} = E_{\text{abs,NHE}} - eE_{1/2,NHE} \] (1)

where \( E_{\text{abs,NHE}} \) is the absolute potential energy (−4.5 eV) of the normal hydrogen electrode (NHE), and \( E_{1/2,NHE} \) is the \( E_{1/2} \) vs the NHE. The \( E_{1/2,NHE} \) of the S(CH₂)₁₁BIPY-CuCl₂ was 0.60 V, which gave a value for \( E_{\text{HOMO,BIPY,CuCl₂}} \) of −5.10 eV. This value of \( E_{\text{HOMO}} \) for BIPY-CuCl₂ is −0.80 eV with respect to the Fermi level of Au and is thus accessible when −1.0 V is applied to the junction.

We also characterized the HOMO levels of AuTS-S(CH₂)₁₁BIPY-CoCl₂ and AuTS-S(CH₂)₁₁BIPY-CuCl₂ SAMs using UPS (Figure S6). Based on the UPS results, the HOMO level of BIPY-CoCl₂ was −1.11 eV, and that of BIPY-CuCl₂ was −0.86 eV, with respect to the Fermi level of AuTS. The energy level of the HOMO for BIPY-CuCl₂ determined by UPS (−0.86 eV) was almost equal to the value obtained from CV (−0.80 eV). This result indicates that the HOMO level of the BIPY-CuCl₂ moiety is accessible (accessible) in the tunneling process at −1.0 V. Because the HOMO level of BIPY-CoCl₂, however, is more than 1.0 eV below the Fermi level of the Au electrode, it is not accessible (inaccessible) at −1.0 V. These results are consistent with our original hypothesis, that the accessibility of molecular orbitals at negative bias is directly correlated with the magnitude of current density at that bias and the overall rectification ratio.

**Temperature Dependence of Tunneling Rates.** Tunneling is a temperature-independent process, and evidence of temperature dependence in measurements of charge transport is generally associated with an electron hopping step. Electron hopping involves a formal redox process—however fleeting—and thus requires an energetically accessible molecular orbital. Thus, variable temperature measurements can be used to differentiate between a pure tunneling mechanism of charge transport and a mechanism that involves hopping. In these experiments, the EGaIn tip was gently brought into contact with the samples and the AuTS-S(CH₂)₁₁BIPY-MCl₂//GaO₉/EGaIn junction was encapsulated by a photocurable polymer (Norland Optical Adhesive 61, Norland Products). Then, we gently lifted the syringe containing EGaIn to form encapsulated BIPY-MCl₂.
junctons to allow for transfer to an environmentally controlled probe station (Lakeshore 1.5K Probe Station). Figure 4 shows the results of variable temperature measurements of charge transport across the BIPY-CoCl$_2$ and BIPY-CuCl$_2$ junctions. At $-1.0 \text{ V}$ and $+1.0 \text{ V}$, the values of current density in both BIPY-CuCl$_2$ and BIPY-CoCl$_2$ junctions change with temperature. This temperature dependence implies that there is an accessible molecular orbital at $+1.0 \text{ V}$ (see Supporting Information for details). At $-1.0 \text{ V}$, however, the current density in BIPY-CoCl$_2$ junctions does not change with temperature, while in BIPY-CuCl$_2$ junctions, it does. This result supports our previous CV and UPS data on the relative position of the HOMO levels of BIPY-CoCl$_2$ and BIPY-CuCl$_2$, as well as our mechanistic interpretation that the HOMO of BIPY-CuCl$_2$ is inaccessible at $-1.0 \text{ V}$, while the HOMO of BIPY-CoCl$_2$ is accessible. Interestingly, we observed a similar dependence on temperature for the current densities at both positive and negative biases for BIPY-CuCl$_2$. This symmetry suggests a similar activation energy for the hopping step at either bias. We do not believe that this symmetry must necessarily exist for all junctions of this type. Moreover, in comparison to the uncomplexed BIPY junction, we observed that the BIPY-CoCl$_2$ junction exhibited a difference in the dependence of current density on temperature (Figure S8).

Mechanism for Differences in Tunneling Currents between BIPY-MCl$_2$ Complexes. Figure 5a and 5b are schematic representations of the energy level diagrams of the BIPY-CoCl$_2$ and BIPY-CuCl$_2$ junctions at $-1.0 \text{ V}$ and $+1.0 \text{ V}$, based on the results of our experiments. The HOMO and LUMO are centered on the BIPY-MCl$_2$ complex, and are thus isolated from the alkyl chain (i.e., the rectangles representing these MOs do not span the entire width of the barrier) and are in close contact with the GaO$_x$/EGaIn electrode. As a result of their proximity to the GaO$_x$/EGaIn electrode, the HOMO and LUMO of the junction are coupled to the energy level of the GaO$_x$/EGaIn electrode, a phenomenon known as Fermi level pinning.

Our mechanistic proposal suggests that the inaccessible HOMO of BIPY-CoCl$_2$ at $-1.0 \text{ V}$ and the accessible LUMO at $+1.0 \text{ V}$ is the origin of the rectification in BIPY-CoCl$_2$ junctions. We believe that a MO that is energetically accessible, and is localized at one end of the molecule, reduces the width of the barrier by approximately the size of the MO (which in this system, is located on the BIPY-MCl$_2$ complex). This reduction in barrier width is concomitant with an increased rate of charge transport.

The Fowler–Nordheim (FN) plots in Figure 6 distinguish between direct tunneling and FN tunneling across the BIPY-MCl$_2$ junctions and support our mechanistic interpretation of charge transport in these systems. BIPY-CoCl$_2$ and BIPY-CuCl$_2$ show distinctly different graphical features in the FN plots. Most notably, while BIPY-CuCl$_2$ junctions show predominantly direct tunneling throughout the entire negative bias window, BIPY-CoCl$_2$ junctions have a transition in the conduction mechanism from direct tunneling to FN tunneling at both negative and positive bias. That is, above a threshold voltage (known as the transition voltage), they show a clear linear dependence of $\ln(J/V^2)$ on $1/V$.

For BIPY-CoCl$_2$ junctions, at $-1.0 \text{ V}$, the HOMO level ($-4.41 \text{ eV}$) is lower in energy than the Fermi level of the Au electrode ($-4.93 \text{ eV}$) and is thus not involved in the charge transfer process. The FN plot of the BIPY-CoCl$_2$ junctions shows that, at $-1.0 \text{ V}$, the conduction mechanism of BIPY-CoCl$_2$ junctions is FN tunneling (Figure 6a). These two results are consistent with the energy level diagram in Figure 5a. At positive bias ($+1.0 \text{ V}$), the conduction mechanism for BIPY-CoCl$_2$ is also FN tunneling. This result supports our interpretation of the variable temperature experiments, because conventional understanding of band structure (which admittedly may not be complete or accurate) suggests that, for a system in which the LUMO is localized adjacent to the ungrounded electrode, FN tunneling at $+1.0 \text{ V}$ is impossible without an accessible MO. That is, FN tunneling at $+1.0 \text{ V}$ strongly suggests that the LUMO of the BIPY-CoCl$_2$ moiety is energetically accessible for charge transfer at $+1.0 \text{ V}$ (Figure 6b).

For BIPY-CuCl$_2$ junctions, the results of our CV, UPS, and variable temperature experiments all suggest that the HOMO is energetically accessible at $-1.0 \text{ V}$. The FN plot in Figure 6b shows only direct tunneling between 0 and $-1.0 \text{ V}$, which is consistent with the energy diagram in Figure 5a involving an accessible HOMO. This mechanistic interpretation is also consistent with the higher rate of charge transport in BIPY-CuCl$_2$ junctions than in BIPY-CoCl$_2$ junctions, at $-1.0 \text{ V}$. Again, we believe that the accessible HOMO in the BIPY-CuCl$_2$ junction decreases the width of the barrier. At positive bias, the FN plot for the BIPY-CuCl$_2$ junctions (Figure 6b) shows a transition from direct tunneling to FN tunneling close to the $+1.0 \text{ V}$ region (the transition becomes clear when the applied bias is increased to $+1.5 \text{ V}$; see Supporting Information for details). This result is consistent with the energy diagram in Figure 5b, which involves an accessible LUMO at $+1.0 \text{ V}$. As is the case at negative bias, due to the accessible LUMO of BIPY-CuCl$_2$ at $+1.0 \text{ V}$, the barrier width across the junction is reduced.
and the rate of charge transport is nearly the same as that at −1.0 V. Thus, we suppose that the accessible HOMO at −1.0 V and the accessible LUMO at +1.0 V are why no rectification is observed in BIPY-CuCl2 junctions.30 These results, taken together, suggest that, at −1.0 V, the increased rate of tunneling (×33) of SAMs of BIPY-CuCl2 compared to BIPY-CoCl2 is the result of the presence of an accessible HOMO in the BIPY-CuCl2 junction (Figure 5a and 5b); the corresponding orbital is not accessible in the BIPY-CoCl2 junction. For BIPY-CuCl2 junctions, the mechanism consists of a hopping step to the BIPY-CuCl2 unit and then a direct tunneling step across the alkyl chain. By contrast, for BIPY-CoCl2 junctions, due to the inaccessibility of the HOMO level, the mechanism consists of FN tunneling across the entire molecule. At +1.0 V, the decreased rate of tunneling (×2) of SAMs of BIPY-CoCl2 compared to BIPY-CoCl2 arises principally from differences in the barrier height at the alkyl/BIPY-MCl2 interfaces. The mechanism of tunneling in the BIPY-CoCl2 junction consists of FN tunneling across the alkyl chain (therefore we infer a smaller width of the tunneling barrier), followed by a hopping step to the EGaIn electrode. The mechanism of tunneling in the BIPY-CuCl2 junction consists of direct tunneling across the alkyl chain followed by a hopping step to the EGaIn electrode.

Other BIPY-M complexes fit the trend. To support our hypothesis (i.e., the relative position of the HOMOs in BIPY-MCl2 junctions with respect to the Fermi level of Au electrode determines the occurrence of rectification and the mechanism of tunneling in BIPY-MCl2 junctions), using the EGaIn junction, we characterized the rectification ratio in BIPY-MCl2 junctions with other first row transition metals (M = Cr, Mn, Fe, Ni). According to our proposed mechanism, SAMs with a HOMO lower in energy than the Fermi level of Au electrode should rectify current because only at +1.0 V is there an accessible molecular orbital (the LUMO) on the BIPY-MCl2 moiety and the width of the tunneling barrier at +1.0 V is smaller than that at −1.0 V. Those with HOMOs higher in energy than the Fermi level of Au should not rectify current because there is an accessible molecular orbital on the BIPY-MCl2 moiety at both negative and positive bias and the widths of tunneling barriers at ±1.0 V are almost identical. In agreement with our proposed mechanism, the SAMs with HOMO energies that are lower than the Au surface—BIPY-CrCl2 (−0.96 eV) and BIPY-CuCl2 (−0.86 eV) junctions—rectified current (Figure 7), while the SAMs with HOMO energies that are lower than the Au surface—BIPY-CrCl2 (−0.96 eV) and BIPY-CuCl2 (−0.86 eV) junctions—did not rectify current (Figure 7).

Moreover, the junctions that rectified current displayed FN tunneling at −1.0 V (see Supporting Information, Figure S13), while the junctions that did not rectify current, displayed direct tunneling (Figure S13). These results show remarkable consistency with our analysis of the BIPY-CoCl2 and BIPY-CuCl2 junctions. The Supporting Information contains details.
CONCLUSIONS

In summary, this work describes the mechanism of charge tunneling for AuTS/S(CH$_2$)$_{11}$BIPY-MCl$_2$//GaO$_x$/EGaIn junctions, where M = Co or Cu. The complexation of metal with 2,2$'$-bipyridine-terminated SAMs changed the nature of rectification (e.g., rectifier or nonrectifier), and the mechanism of tunneling (FN tunneling or direct tunneling) at ±1.0 V. BIPY-CoCl$_2$ junctions rectify current ($r^+$ = 82.0) at ±1.0 V, while BIPY-CuCl$_2$ junctions do not ($r^+$ = 1.0). We assert that the rectification observed in BIPY-CoCl$_2$ junctions originates from the electronic structure of the molecules.

-Based on CV, UPS measurements, DFT calculations, electrical characterization, and variable temperature experiments, this study reaches four main conclusions:

(i) BIPY-CoCl$_2$ junctions rectify current because only at a positive bias (+1.0 V) is there an accessible molecular orbital (the LUMO) on the BIPY-CoCl$_2$ moiety, while at negative bias (−1.0 V) neither the energy level of the HOMO nor that of the LUMO lie between the Fermi levels of the electrodes.

(ii) BIPY-CuCl$_2$ junctions do not rectify current because there is an accessible molecular orbital on the BIPY-CuCl$_2$ moiety at both negative and positive bias (the HOMO is accessible at negative bias, and the LUMO is accessible at positive bias).

(iii) The difference in accessibility of the HOMO at −1.0 V causes charge transfer—at negative bias—to take place via Fowler–Nordheim tunneling in BIPY-CoCl$_2$ junctions, and via direct tunneling in BIPY-CuCl$_2$ junctions. This difference in tunneling mechanism at negative bias is the origin of the difference in rectification ratio between BIPY-CoCl$_2$ and BIPY-CuCl$_2$ junctions.

(iv) The mechanistic interpretation is also supported by expanding the types of metals in these BIPY-MCl$_2$ junctions, where M = Cr, Mn, Fe, and Ni. BIPY-M junctions with a low-lying HOMO with respect to the Fermi level of Au (M = Cr and Cu) rectified current, and those with high-lying HOMOs (M = Mn, Fe, Co, and Ni) did not rectify current.

Reliable rules or guidelines for relationships between molecular structure and charge transport are uncommon in the field of molecular electronics. Through a detailed mechanistic analysis of rectification and charge transport in BIPY-MCl$_2$ junctions, this work isolates the roles of molecular orbitals on the mechanisms of conductivity through molecular junctions. Furthermore, the mechanistic details described in this work are directly applicable to other molecular junctions, particularly those classified as having an insulating alkane chain terminated by a conductive moiety (i.e., conjugated aromatic group), and specifically how the frontier molecular orbitals influence the mechanism of conduction.

ASSOCIATED CONTENT

* Supporting Information
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c12641.
  Nomenclature, details of experimental methods, statistical analysis, mechanism of tunneling, and general information (PDF)

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Figure 6. (a) Fowler–Nordheim (FN) plots for BIPY-CoCl$_2$, derived from the current-density data in Figure 2a. A transition in conduction mechanism is observed, beginning with direct tunneling (DT) at lower voltages (logarithmic growth) to FN tunneling (FNT) at higher voltages (linear decay). (b) Fowler–Nordheim (FN) plots for BIPY-CuCl$_2$, derived from the current-density data in Figure 2b.

Figure 7. Rectification ratio versus energy of HOMO levels (measured by UPS) of BIPY-MCl$_2$ junctions.

Figure 8. (a) Fowler–Nordheim (FN) plots for BIPY-CoCl$_2$, derived from the current-density data in Figure 2a. A transition in conduction mechanism is observed, beginning with direct tunneling (DT) at lower voltages (logarithmic growth) to FN tunneling (FNT) at higher voltages (linear decay). (b) Fowler–Nordheim (FN) plots for BIPY-CuCl$_2$, derived from the current-density data in Figure 2b.
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Notes
The authors declare no competing financial interest.

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REFERENCES