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Author(s)
Horiguchi, Kazunori; Sagisaka, Takami; Kurokawa, Shu; Sakai, Akira

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Electron transport through Ni/1,4-benzenedithiol/Ni single-molecule junctions under magnetic field

Kazunori Horiguchi, Takami Sagisaka, Shu Kurokawa, and Akira Saka

Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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We have studied electron transport through Ni/1,4-benzenedithiol (BDT)/Ni single molecule junctions at cryogenic temperatures under magnetic field up to 250 mT. Instead of examining magnetoresistance (MR) of individual junctions, we measured the conductance of many junctions under a constant magnetic field and investigated how a single-molecule peak in a conductance histogram shifts with the field strength. We found that the single-molecule resistance at 77 K, deduced from the conductance peak position, shows a hysteresis against the field strength and takes a maximum around 50 mT when the magnetic field increases from 0 T to 150 mT. The observed resistance change yields a MR of ~80–90% for Ni/BDT/Ni single molecule junctions. This MR is higher than experimental MR reported for non-conjugating molecules but consistent with high theoretical MR predicted for π-conjugated molecules such as BDT. We have also investigated the nonlinearity of the current–voltage (I–V) characteristics of Ni/BDT/Ni junctions under 0 T and 150 mT and found that the nonlinearity changes its sign from negative at 0 T to positive at 150 mT. This result suggests that the junction transmission spectrum at 0 T should have a low-lying peak within 0.1 eV from the Fermi level, but the peak moves out of the bias window when the magnetic field increases to 150 mT. The observed field-induced change in the I–V nonlinearity is qualitatively consistent with theoretical I–V curves of Ni/BDT/Ni calculated for magnetized and non-magnetized Ni electrodes.

I. INTRODUCTION

Miniaturization of today’s silicon-based devices is approaching its physical and technological limits, and new concepts and structures of post-silicon devices have been intensively sought for in the past decades. Molecular devices are one of the promising candidates of such “beyond CMOS” devices, and much effort has been exercised on constructing various types of molecular devices. Many of such molecular devices contain single-molecule junctions as their central active element which primarily determines the device functionality and performance. As a result, understanding of single-molecule junctions becomes a critical issue for designing and optimizing molecular devices, and a number of theoretical and experimental investigations have been conducted for elucidating various properties of single-molecule junctions. In particular, electron transport through single-molecule junctions has been extensively worked out.

Single-molecule junctions also provide us a unique playground for spin manipulations because some organic molecules show a long spin relaxation time unattainable for inorganic materials. This makes single-molecule junctions a key element in molecular spintronics and a subject of extensive spin-transport studies. Rocha et al. have theoretically predicted that a nonmagnetic single-molecule sandwiched between a pair of ferromagnetic metal electrodes can function as a spin valve, and the junction magnetoresistance (MR) can be controlled by varying the magnetization direction of ferromagnetic electrodes. Because most molecules are insulators, such molecular spin-valves are basically not much different from tunneling magnetoresistance (TMR) devices. However, the presence of molecular levels in the tunneling gap makes molecular spin valves more varied in their characteristics than conventional TMR devices. An interesting example is a spin valve of π-conjugated molecules, where the molecular orbitals strongly couple to the spin-polarized electronic states of ferromagnetic electrodes and often lead to a large MR. In the case of non-conjugating molecular junctions such as Ni/octanedithiol/Ni, an octanedithiol molecule essentially acts as an insulator and the conduction is achieved by electron tunneling through the molecule. The bridging octanedithiol molecule, thus, makes little contribution to the junction MR. On the other hand, in Ni/triphenyldithiol(tricene)/Ni junctions, the tricene molecule differently couples to the spin-up and spin-down states of Ni electrodes and makes a tunneling probability dependent on the electrode spin polarization. According to the calculation by Rocha et al., the energy separation between the spin-up and spin-down transmission channels becomes significantly widened when a bridging molecule is replaced from octanedithiol to tricene. This yields a high MR (~600%) for Ni/tricene/Ni junctions compared to that of Ni/octanedithiol/Ni junctions (~100%). Similar MR enhancement has been theoretically predicted for other π-conjugated molecular spin valves, but experiments on molecular MR are still few in number, compared to ordinary conduction experiments.

In this study, we have fabricated Ni/benzenedithiol (BDT)/Ni single-molecule junctions and studied their spin dependent transport at cryogenic temperatures. Our bridging...
molecule is BDT, an archetypal \( \pi \)-conjugated molecule for which a high MR can be expected. For ferromagnetic electrodes, Co electrodes have been employed in some previous MR experiments, but we chose Ni electrodes in our experiment because a pair of nanogapped Ni electrodes can be readily prepared by exploiting the mechanically controllable break junction (MCBJ) method. Also, a good stock of theoretical and experimental information has been accumulated on Ni-based molecular junctions. With no bridging molecules, for example, the experimental TMR of Ni/vacuum/Ni junctions is \( \sim \)11\%\textsuperscript{,7} which slightly increases to \( \sim \)16\% when octanethiol is inserted between Ni electrodes.\textsuperscript{11} These values are in agreement with a theoretical TMR, \( \sim \)24\%, of Ni/vacuum/Ni junctions, calculated from the spin polarization of Ni electrodes.\textsuperscript{10} On the other hand, the MR of Ni/BDT/Ni junctions has been calculated to reach \( \sim \)40\%,\textsuperscript{12} and some authors predict even higher MR exceeding 400\%.\textsuperscript{13,14} Experimentally, Yamada \textit{et al.}\textsuperscript{15} have recently succeeded in measuring the MR of individual Ni/BDT/Ni junctions. They employed Ni-coated thin Au films for junction electrodes and, with increasing and decreasing magnetic field, observed a resistance loop that yields a negative MR of \( \sim \)(−30\%). They also found anisotropic MR (AMR) of nearly the same magnitude and suggested that the observed MR loop might be due to AMR caused by the magnetization rotation of the Ni electrodes. In this experiment, we took a different approach and, instead of applying a field ramp on each junction, measured the conductance and \( I−V \) characteristics of many Ni/BDT/Ni junctions under a static magnetic field. By varying the field strength, we could observe how the single-molecule conductance, in average, changes with field strength, and this allows us to estimate the MR of Ni/BDT/Ni single-molecule junctions. Furthermore, \( I−V \) characteristics under magnetic field provides us information on the junction transmission spectrum and its magnetic-field dependence.

II. EXPERIMENT

The MCBJ method is one of the standard techniques for preparing nano-gapped electrodes and has been widely used in experimental studies of atomic and molecular junctions. This method, however, encounters a serious difficulty when applied to MR measurements. That is magnetostriction of ferromagnetic electrodes which most likely crashes a junction and separated away the electrodes far enough for allowing magnetostriction. Then, we varied the field strength and re-established a junction under a new magnetic field. By repeating these procedures, we can obtain single-molecule conductance at different magnetic fields and acquire discrete data on junction MR. This method does not allow us to directly measure a MR of individual molecular junctions but yields the averaged MR sampled over many junctions. A similar approach has been used by Xiao \textit{et al.}\textsuperscript{17} to construct \( I−V \) characteristics of Au/BDT/Au junctions from a set of conductance data measured at different biases. Compared to conventional MR measurements using a field sweep, our method is more time consuming and yields discrete conductance data at a few field strengths. However, the use of static field enables us to avoid all troubles associated with a time-varying field, and measurements over many junctions are effective to suppress MR data scattering arising from fluctuations in junction configuration.

Our MCBJ substrate is a 0.3 mm-thick sheet of non-magnetic stainless-steel, one face of which is coated with a polyimide film. The sheet was cut into an 8 mm \( \times \) 30 mm rectangular strip, and a 0.3 mm-diameter Ni wire was glued on it with an adhesive. This MCBJ specimen was then set into a vacuum cell of a cryostat, and a droplet of BDT-ethanol solution was placed on a notch formed on the Ni wire. The BDT concentration was 0.5 mM. After breaking the Ni wire at the notch by bending the substrate, the cell was evacuated to \( <7 \times 10^{-4} \) Pa and backfilled with a purified He exchange gas of \( \approx 100 \) Pa. The specimen was cooled to 4 K and 77 K using liquid helium and nitrogen as a coolant, respectively. Magnetic field was applied from outside using an open-bore-type superconducting magnet. The direction of the magnetic field is perpendicular to the junction axis.

Coarse and fine bending of the MCBJ substrate was achieved by a linear stepping motor, placed on top of the cryostat, and a piezo actuator, respectively. The motor and the actuator are connected by a long driving shaft. For cutting off vibrations coming through the shaft, a gadget is incorporated between the shaft and the actuator, which mechanically decouple them during measurements. The entire cryostat was suspended by four springs for vibration isolation.

We made a field-cool of a junction under a constant magnetic field. After cooling, we relaxed the substrate bending using the linear motor and gradually decreased the junction gap distance while monitoring the junction current at 100 mV. Upon detecting the tunneling current, further gap control was made by the piezo actuator. The junction opening and closing was repeated many times, and the temporal change in junction conductance (referred to as a conductance trace) was measured at 20 mV. In order not to heavily damage the BDT-covered Ni electrodes, we adjusted the gap opening so that the conductance does not exceed 0.1G\textsubscript{0} at junction closure. All conductance and \( I−V \) measurements were made using Keithley 2635 source/meter as a bias source and a current meter.

III. RESULTS AND DISCUSSION

A. Field dependence of the conductance

Figure 1 shows examples of conductance traces observed during junction opening at 4 K with and without magnetic
field. At 0 T, the conductance exhibits a plateau-like structure around 0.02G₀ and, after showing the plateau, decreases to the tunneling regime. Similar plateaus were observed on other traces at 0 T. We carried out a control experiment with no BDT molecules and confirmed that the traces show no such plateaus and decrease nearly exponentially as illustrated by the leftmost trace in Fig. 1. The conductance of these plateaus is in good agreement with the reported single-molecule conductance of Ni/BDT/Ni (0.024G₀ (Ref. 15)) and also comparable to that of Pt/BDT/Pt (~0.03G₀ (Ref. 16)) and Au/BDT/Au (~0.01G₀ (Refs. 17 and 18)). We can, therefore, conclude that the observed 0.02G₀ plateaus correspond to the formation of Ni/BDT/Ni single-molecule junctions.

Under a magnetic field of 30 mT, the conductance trace depicted in Fig. 1 again exhibits the same plateau but at a position slightly below 0.02G₀. With further increasing the field to 250 mT, however, the plateau rises up to ~0.03G₀. This field-induced shift of the single-molecule conductance is not a single event but a robust phenomenon as seen in Fig. 2 where we compare conductance histograms obtained at different magnetic fields. In the zero-field histogram shown in Fig. 2(a), a peak at 0.019G₀ corresponds to the 0.02G₀ plateau observed in Fig. 1 and represents the single-molecule-conductance peak. When we apply a magnetic field, the peak first shifts to the lower conductance side and appears at 0.012G₀ at 30 mT in Fig. 2(b). Then, at 250 mT, the peak turns around and moves up to 0.030G₀ in Fig. 2(c). This field-induced shift of the conductance yields a high MR ΔR/R ~ 150% for Ni/BDT/Ni single-molecule junctions at 4 K. Three conductance values at zero and two field strengths are, however, too few in number for claiming a high MR, and more data must be acquired at various magnetic fields between 0 T and 250 mT. We, therefore, set out a series of conductance measurements with finer increments/decrements of the magnetic field. We, however, conducted these measurements not at 4 K but at 77 K. As we mentioned in Sec. II, we always opened the junction before varying the field strength to prevent junction crash by magnetostriction. At 4 K, we somehow had a very low chance of successfully re-bridging a BDT molecule after each junction opening. This made it too time consuming and impractical for carrying out many measurements under different magnetic fields at 4 K. We, therefore, raised the temperature to 77 K where the junction re-formation was found much easier. Higher temperatures, however, usually tend to reduce molecular MR and sometimes completely suppress it even below 77 K as reported for Ni/octanedithiol/Ni junctions.11

The temperature dependence of MR, however, differs for different materials,21 and the MR of Ni/BDT/Ni single-molecule junctions could hopefully be observed at 77 K. We, therefore, tried to measure the junction conductance at 77 K and examined how it changes with the magnetic field.

We first increased the field from 0 T to 150 mT by a 30 mT step and, at each field, measured the junction conductance. Out of five conductance histograms thus acquired, we show in Figs. 3(a)–3(c) three histograms measured at 0 T, 60 mT, and 150 mT, respectively. To save time and obtain as many histograms as possible under different fields, we recorded at each field fewer numbers of conductance traces than at 4 K. As a result, the histograms in Fig. 3 appear noisier than those in Fig. 2. Nevertheless, the single-molecule peak can be identified and indicated by an arrow in each panel in Fig. 3. At 0 T, the peak locates at 0.018G₀ in agreement with the peak position found at 4 K. In the histogram at 60 mT shown in Fig. 3(b), the peak goes down to 0.018G₀ but moves up to 0.034G₀ at 150 mT in Fig. 3(c). We repeated the same measurements on another specimen and observed the same peak shift. The position of the single-molecule peak obtained in these measurements is plotted in Fig. 4 as a function of the field strength. In the figure, the peak position is represented in resistance instead of conductance, and the results of two measurements are indicated by filled circles and squares, respectively. Error bars represent the standard deviation calculated from the peak width. For clarity, we put error bars only to one plot in the figure. Other plots including those that will be described below have error bars of similar magnitude. In both plots, the resistance first increases with the magnetic field, reaches a maximum around 50 mT, and then decreases at higher fields. Though the data points show
relatively large uncertainties, the variation of the junction resistance spans over approximately one standard deviation and should be a real effect. To confirm the appearance of resistance maximum, we reduced the field increment to 15 mT and closely examined the field dependence of the conductance from 0 T to 60 mT. The single-molecular resistance obtained from this auxiliary measurement is represented in Fig. 3 by filled triangles. Though the data points show some scatter, the results of three field-up measurements show reasonable agreement among them and unanimously indicate the existence of resistance maximum around 50 mT. The observed field dependence of the resistance yields a MR $\Delta R / R = (80–90)\%$ for Ni/BDT/Ni single-molecule junctions at 77 K. This MR is lower than that at 4 K as expected from the thermal reduction of MR at higher temperatures.

We next started from 150 mT and decreased the magnetic field by a 30 mT step. Three histograms obtained in this field-down measurement are displayed in Figs. 3(d)–3(f), and the position of the single-molecule peak, measured in resistance, is plotted in Fig. 4 by open circles. At 150 mT and 0 T, the resistance agrees with that obtained in the field-up measurements. At intermediate fields, the resistance exhibits small ups and downs but as a whole varies smoothly with the field. The plot indicates no maxima around 50 mT. We again closely examined the region 0–60 mT and finely decreased the magnetic field by a 15 mT step. The results are shown by open triangles in Fig. 4. As seen in the figure, the data points confirm the monotonous field dependence of the junction resistance. The MR of Ni/BDT/Ni thus exhibits hysteresis and follows different field dependence for increasing and decreasing the magnetic field. In particular, the resistance maximum only appears upon increasing the field strength.

Our results can be compared with previous theoretical and experimental studies. First, the observed hysteresis in MR suggests a spin valve behavior of Ni/BDT/Ni single-molecule junctions, and the junction resistance should vary with a relative alignment of the magnetization of Ni electrodes. In that case, the MR maximum would correspond to a threshold field at which the electrode magnetizations start to be aligned in parallel with each other. Because this field is solely determined by the coercivity of Ni electrodes and independent of bridging molecules, the same threshold should be observed for other molecular spin valves using Ni electrodes. Actually, the threshold field sensitively depends on the size and geometry of magnetic domains in electrodes and varies a lot among junctions. Nevertheless, previous MR experiments on various Ni-based junctions, e.g., Ni/octanedithiol/Ni,11 Ni/C60/Ni,19 Ni/carbon nanotube/Ni,20 and Ni/vacuum/Ni9 junctions, all indicate that a junction is in a high-resistance state at $<50$ mT and changes to a low-resistance state at $\approx 100$ mT. Thus, the threshold field of Ni-electrode junctions should be $\sim (50–100)$ mT, which is in reasonable agreement with the location of our MR maximum. This agreement suggests that Ni/BDT/Ni single-molecule junctions work as a spin valve and the observed MR change is due to the magnetization alignment of Ni electrodes.

We next point out that the observed MR, 150% at 4 K and (80–90)% at 77 K, is significantly larger than that of Ni/vacuum/Ni (11%)9 and Ni/octanedithiol/Ni (16%)11 junctions. This high MR confirms the predicted MR enhancement for $\pi$-conjugated molecules mentioned in Sec. I. Quantitatively, previous calculations12–14 on Ni/BDT/Ni junctions yield widely different MR values ranging from 40% to 400%. The observed MR values at 4 K and 77 K are within this range and hence consistent with theoretical calculations. Our results, however, are not in accord with the results of direct MR measurements conducted by Yamada.
who obtained a negative and smaller MR (−30%) for Ni/BDT/Ni junctions. As mentioned in Sec. I, their Ni electrodes are a thin overlayer and might have domain geometries much different from those of our wire electrodes. Also, their measurements were made at 300 K under a time-varying field applied parallel to a junction axis. On the other hand, we measured MR at cryogenic temperatures under a static magnetic field applied perpendicular to junctions. These differences in junction geometry and experimental conditions might lead to discrepancies in observed MR. Details are, however, yet unclarified and await further investigations.

**B. Field dependence of the I-V characteristics**

Electron transport through a molecular junction is basically characterized by \( T(E) \), a junction transmission spectrum which represents a probability of an electron of energy \( E \) transmitting through the junction. Specifically, a junction conductance can be derived from \( T(E) \) within the framework of the linear response theory. Experimentally, qualitative features of \( T(E) \) can be inferred from junction \( I-V \) characteristics. When \( T(E) \) has a peak inside a bias window \( E_F \leq E \leq 0.2V \), where \( E_F \) and \( V \) stand for Fermi energy and a bias voltage, respectively, the \( I-V \) curve shows a negative nonlinearity and bends convex upward. On the other hand, the curve rises up convex downward and exhibits positive nonlinearity if \( T(E) \) has no peaks in the bias window and monotonously increases with \( E \). Therefore, by measuring the \( I-V \) characteristics under different magnetic fields and examining their nonlinearity, we can investigate how the spectral features of \( T(E) \) change with the magnetic field.

We measured the \( I-V \) characteristics of Ni/BDT/Ni single-molecule junctions at 77 K by holding a junction in their single-molecule state and applying a bias ramp up to ±0.2 V. Measurements were made under zero field and a magnetic field of 150 mT. Similar to those of Au/BDT/Au junctions, the \( I-V \) curves of Ni/BDT/Ni junctions exhibit a linear behavior at low biases and become nonlinear at higher biases. To closely examine the nonlinearity of \( I-V \) characteristics, we differentiated \( I-V \) curves and converted them to the conductance-voltage (\( G-V \)) curves. Examples of \( I-V \) and \( G-V \) curves measured at 0 T are depicted in Figs. 5(a) and 5(b), respectively. In Fig. 5(a), the \( I-V \) curve exhibits a linear behavior near the origin but gradually bends down as the bias increases. Correspondingly, the \( G-V \) curve in Fig. 5(b) slightly decreases with increasing the bias for both positive and negative biases. A sharp dip at the origin is an artifact of numerical differentiation and of no physical significance. We collected 35 and 44 \( I-V \) curves at 0 T and 150 mT, respectively, and the resulting \( G-V \) curves are plotted in Figs. 5(c) and 5(d), respectively. The dip of each curve was not shown for clarity.

Because measurements were made on single-molecule junctions, \( G-V \) curves in Figs. 5(c) and 5(d) converge to the single-molecule conductances, \( \sim 0.02G_0 \) at 0 T and \( \sim 0.03G_0 \) at 150 mT, respectively. With increasing the bias, they show a variety of behaviors: some increase with the bias, some decrease, and a couple of them exhibit irregular behaviors. Such diversities in \( G-V \) curves are not unexpected for molecular junctions and generally attributed to fluctuations in junction configuration. Despite this diversity, a difference can be recognized between two groups of \( G-V \) curves shown in Figs. 5(c) and 5(d). In Fig. 5(c), majority of \( G-V \) curves slightly decrease with increasing the bias, while the \( G-V \) curves shown in Fig. 5(d) clearly tend to increase with the bias. To compare \( G-V \) curves more quantitatively, we calculated for each \( G-V \) curve a (normalized)
conductance change between 0.02 V and 0.2 V, \( \Delta G = (G(0.2 V) - G(0.02 V))/G(0.02 V) \). The distribution of \( \Delta G \) is shown in Figs. 6(a) and 6(b) for \( G - V \) curves at 0 T and 150 mT, respectively. A solid curve in each figure is a Gaussian fit to the distribution. Reflecting the diversity among \( G - V \) curves, \( \Delta G \) shows a broad distribution.

Nevertheless, we can see that the distribution center is slightly off to the negative side at 0 T but clearly locates in the positive side at 150 mT. This confirms that the nonlinearity of the \( I - V \) characteristics changes its sign from small negative to positive when the field increases from 0 T to 150 mT.

As we mentioned before, the nonlinearity of \( I - V \) characteristics can be related to the peak structure of \( T(E) \). The small negative nonlinearity at 0 T suggests that the zero-field \( T(E) \) should be nearly flat or have a low blunt maximum within our bias window \( E_F \pm 0.1 \text{ eV} \). On the other hand, the positive \( \Delta G \) in Fig. 6(b) indicates that the \( T(E) \) at 150 mT shows no peaks within that bias window and monotonously increases with \( E \). Presumably, the zero-field peak shifts to the higher energy side with applying the magnetic field and moves out of the bias window. As we discussed in the previous section, the magnetizations of our Ni electrodes would be aligned in parallel with each other at 150 mT. Our results, thus, suggest that the structure of \( T(E) \) changes with the relative orientation of electrode magnetizations and the low-lying peak of \( T(E) \) moves \( > 0.1 \text{ eV} \) away from \( E_F \) for a spin-parallel configuration.

These results on the \( T(E) \) of Ni/BDT/Ni single-molecule junctions can be compared with theoretical calculations. Seminario et al.\(^23\) calculated \( T(E) \) of various molecular junctions and found for non-magnetized Ni/BDT/Ni junctions a \( T(E) \) peak very close to the Fermi level. This peak is likely due to the hybridization of Ni and S orbitals.\(^12\) Because of this low-lying peak, their theoretical \( I - V \) curve shows a negative nonlinearity below 0.2 V, in agreement with our \( I - V \) curves at 0 T. For Ni/BDT/Ni junctions with magnetized Ni electrodes, previous calculations\(^12\) predicted a \( T(E) \) peak around 0.3 eV for a spin-parallel configuration. As a result, the theoretical \( I - V \) curve exhibits positive nonlinearity below 0.2 V, again in agreement with our experimental \( I - V \) curves at 150 mT. Thus, the theoretical calculations are consistent with the observed nonlinearity change in the \( I - V \) characteristics and support the assumed peak shift in \( T(E) \) spectrum for spin-parallel Ni electrodes. It should be noted, however, that the calculations of \( T(E) \) are made on idealized junctions with a straight molecule linking low-index planes of a perfect crystal. Geometry of real Ni/BDT/Ni junctions should be far from ideal, as suggested by varied \( G - V \) curves in Fig. 5, and \( T(E) \) would be largely different for different junctions. As a result, comparison between the theoretical and experimental \( T(E) \) remains qualitative at this time. For carrying out more quantitative comparison of the theoretical and experimental \( T(E) \) and its magnetization dependence, one would need more precise control over the geometry of a BDT molecule and also of Ni atoms at and near the molecule-anchoring point.

**IV. SUMMARY**

We have measured the conductance of Ni/BDT/Ni junctions under static magnetic fields up to 250 mT at cryogenic temperatures and statistically clarified the magnetic-field dependence of the single-molecule conductance. When the field strength is increased, the single-molecule resistance is found to take a maximum around 50 mT, leading to MR of 80%—90% at 77 K. Decreasing the magnetic field produces no resistance maximum, and the single-molecule resistance exhibits a hysteresis against the field strength. These results indicate a spin-valve behavior of Ni/BDT/Ni junctions. The observed MR is higher than that reported on non-conjugating molecules and confirms a predicted high MR for \( \pi \)-conjugated molecules. We have also investigated the \( I - V \) characteristics of Ni/BDT/Ni junctions under 0 T and 150 mT and found that the nonlinearity of the \( I - V \) curve is slightly negative at 0 T but changes to positive when the field increases to 150 mT. Our observations suggest that \( T(E) \) of Ni/BDT/Ni single-molecule junctions varies with the magnetization of Ni electrodes. For the energy range \( E_F \pm 0.1 \text{ eV} \), \( T(E) \) should show a blunt peak for non-magnetized Ni electrodes, but the spectrum changes to a monotonous behavior and increases with \( E \) when electrodes are magnetized in parallel. These magnetic-field-induced changes in the \( I - V \) nonlinearity and in the \( T(E) \) spectrum are consistent with the theoretical calculations made on magnetized and non-magnetized Ni/BDT/Ni junctions.

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