Chapter 5

Conductance Switching: Effect of Alignment of Magnetization-Vectors

In this chapter we have studied the effect of alignment of magnetization-vector on electrical bistability of nickel phthalocyanine (NiPc) and cobalt doped zinc oxide nanoparticles (Co-ZnO) in a monolayer. The planar nickel phthalocyanine molecules could be oriented parallel or perpendicular to the electrode substrate. The orientation of the molecules affects the electrical bistability, transport gap and density of states of the molecules. Electrical bistability of Co-ZnO nanoparticles also depends on the content of cobalt in the nanocrystals. With the use of such ferromagnetic nanocrystals, we align the magnetization vector of the nanocrystals in a monolayer in order to study the effect of alignment of their magnetic domains on the electrical bistability. We observe that the transport gap of the nanocrystals decreases upon conductance switching. The gap decreases also due to alignment of the magnetic domains of the cobalt-doped nanocrystals. When the magnetically-aligned nanocrystals undergo a conductance switching, the transport gap further decreases evidencing a correlation between the electrical bistability and the (change in) transport gap. Apart from alignment of domains, the effect of external magnetic field on electrical bistability of Fe$_3$O$_4$ quantum dots was also studied. Upon application of a magnetic field, the nature of electrical bistability changes
completely which conforms the occurrence of magnetization and conductance-switching to a high-state concurrently. The results show the viability of data-storage applications in quantum dots through a magnetic field.

5.1. Introduction

Over the years, a lot of attention has been put-forwarded on voltage-induced electrical bistability or resistive switching with an aim to obtain high-density, ultrafast, and less energy-consuming nonvolatile memory devices.\textsuperscript{1-6} In an electrical bistable device, more than one conducting-states are achieved through an application of a suitable voltage pulse.\textsuperscript{7} Presence of several conducting-states has also been established that has so far been explained in terms of electric-field-induced charge confinement/conformational change in the nanostructures/molecules or trap-state-assisted conduction process through the materials.\textsuperscript{3,8-11} A wide range of materials such as organic molecules, metal, and semiconducting nanoparticles have been characterized primarily to improve ratio between current values of high- and low-conducting states (On/Off ratio) and to study the mechanism of conductance switching or electrical bistability.\textsuperscript{12-16}

Several parameters have been found to affect the conductance switching, or more specifically the On/Off ratio. Functional groups of the material have been found to play a major role in determining the ratio.\textsuperscript{17-19} Concentration of active materials in a polymer matrix,\textsuperscript{20} capability to form a donor-acceptor composite,\textsuperscript{21-24} thickness of the active organic layer,\textsuperscript{25} etc are some of the parameters that have been found to play a role on the bistability or the On/Off ratio.

Use of magnetic elements in non-volatile memory applications may add a new dimension. Magnetic field could then be considered as another parameter in the “write” and “read” processes. With this in mind, we have fabricated devices based on nanoparticles of a magnetic material, namely an iron oxide,\textsuperscript{26,27} which is stable, so that magnetic-field effect of electrical bistable characteristics can be studied. Again, orientation of the magnetic-moments may have a role on their optical and electrical properties. That is, it would be motivating to
study if alignment of the magnetic domains of the nanocrystals in a monolayer influences certain device parameters. For this study, we have grown cobalt-doped ZnO nanoparticles and varied the content of the dopant that in turn controlled ferromagnetism of the oxide system. Monolayer of such doped-nanocrystals that could be probed with a STM tip provided us a unique system to study the effect of alignment of the magnetization vectors on current-voltage characteristics and electrical bistability. From the STS, we hence explored if the process of electrical bistability has any dependence on the alignment of magnetic domains of the ferromagnetic nanoparticles.

In another study, we have introduced the orientation of the organic molecules on a monolayer, which has been shown to have an impact on electrical bistability. The systems moreover provided a route to study the mechanism of electrical bistability. We first oriented such planer molecules (in a monolayer) in a chosen direction, such as, molecular plane parallel to the substrate or perpendicular to it, with an external magnetic field; here the magnetic moment of the molecules in the monolayer became aligned with the external field. The oriented (ionic) molecules were then immobilized with the polyion layer so that the active ionic organic molecules in the monolayer become electrostatically bound with a particular orientation. Such a monolayer with molecules oriented at a particular direction provided a possibility to study anisotropy of different physical parameters. In this direction, we have studied the effect of molecular orientation on electrical bistability of organic molecules in a monolayer through scanning tunneling microscopy (STM).

5.2. Experimental details

5.2.1. Molecules and polyions

The planar magnetic organic molecule that has been chosen to form a monolayer with a particular orientation of the molecules is tetrasulfonic acid tetrasodium salt of nickel(II) phthalocyanine (NiPc). Chemical structure of the molecule is shown in figure 5.1.(a). Suitably treated quartz or As-doped $n$-type Si $<111>$ (resistivity 3-10 m$\Omega$cm) substrates were used to
form a monolayer. Poly(allylamine hydrochloride) (PAH) was the polycation that immobilized the oriented ionic molecules through electrostatic binding.

5.2.2. Synthesis of ZnO and Co-doped ZnO nanocrystals

ZnO nanocrystals were grown following a standard procedure via decomposition of zinc acetate \([\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}]\) at room temperature by an addition of tetramethylammonium hydroxide \([\text{N(Me)}_4\text{OH} \cdot 5\text{H}_2\text{O}], \text{TMAH}\). In a typical synthesis, 5 mL (2.5 mM) TMAH in ethanol was added drop-wise (2 mL/min) to a 90 mL solution of 0.1 M \(\text{Zn(OAc)}_2\) in dimethyl sulfoxide (DMSO) under a constant stirring condition at room temperature. In 10 min, the solution became turbid, indicating formation of ZnO nanocrystals. The as-grown nanocrystals were precipitated from DMSO solution by an addition of ethyl acetate followed by centrifugation. Iterative washing in DMSO and precipitation with ethyl acetate ensured that excess reactants were removed from the final product.

To introduce cobalt as dopants, cobalt acetate \([\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}]\) was added to the reaction flask at a measured \([\text{Co}]:[\text{Zn}]\) concentration ratio. Upon addition of TMAH, the pink solution turned blue signifying formation of cobalt-doped ZnO nanocrystals. In this process, we controlled the ratio between \(\text{Co}^{2+}\) and \(\text{Zn}^{2+}\) ions in the reaction mixture up to 10 at. %. Since we would be forming a monolayer of the nanocrystals through a layer-by-layer electrostatic-assembly (LbL) approach, we formed trioctylphosphine oxide (TOPO) capped nanoparticles. Such a capping was done by carrying out the reaction at 180 °C under nitrogen environment by adding excess TOPO in the flask. After stirring continuously for 2 h, the solution was cooled down to 60 °C and 5 mL of ethanol was added to the flask. The nanoparticles were then separated from the unreacted components by the same process of washing and centrifugation in toluene and ethyl acetate, respectively.

5.2.3. Synthesis of Fe₃O₄ nanocrystals

\(\text{Fe}_3\text{O}_4\) nanoparticles were synthesized following standard methods. In brief, ferric acetylacetonate, 1-dodecanediol (DCD), oleic acid, oleylamine, and diphenyl ether (DPE) were
used. In 20 mL ferric acetylacetone solution (2 mM) in DPE, a mixture of 2.023 g DCD (10 mM), 1.605 g oleylamine (6 mM) and 1.694 g oleic acid (6 mM) were added. The solution was thoroughly degassed by purging N₂. Temperature of the solution was raised to 200 °C under vigorous stirring condition to allow the reaction to continue for 30 min. The solution was then refluxed for another 30 min at 250 °C. Color of the solution turned blackish indicating formation of Fe₃O₄ nanoparticles. The product was then cooled down to room temperature. It was repeatedly washed in n-hexane and centrifuged at 8000 rpm to separate out the nanoparticles, which was finally dried in vacuum.

5.2.4. Characterization of nanocrystals

The nanocrystals were characterized by recording their optical absorption spectrum in a colloidal solution and transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images with a Shimadzu model 2550 UV-Vis Spectrometer and a Jeol JSM 2010, respectively. Selected area electron diffraction (SAED) patterns and energy dispersive X-ray (EDX) analysis were carried out from the TEM analysis to determine the concentration of cobalt dopant in ZnO nanocrystals.

5.2.5. Pellet formation

In order to obtain homogeneous distribution of Fe₃O₄ nanoparticles in an active layer, they were mixed in TiO₂ nanostructures to form pellets so that the Fe₃O₄ nanoparticles may be characterized in an inert matrix. TiO₂ nanoparticles are commercially available and were purchased from Nanopowder Enterprises Inc., USA. The dried nanostructures were ground in a pestle and mortar to achieve homogeneous mixture of the nanostructures. Thorough mixture of the two nanostructures was placed in a dice and kept under a pressure of 5 ton for 15 min. The resulted pellet was annealed at 180 °C in ambient condition for 30 min to make the pellet harder. Concentration of Fe₃O₄ in TiO₂ remained ~ 0.7% by weight.
5.2.6. Monolayer formation

A monolayer of ionic molecules is generally formed through layer-by-layer (LbL) assembly process. The LbL films are formed by depositing alternating layers of oppositely charged ionic/polyions materials. Here, each monolayer of ionic molecules is adsorbed due to electrostatic binding followed by reversal of surface-charge. Growth of LbL film layer after layer is generally observed as an increase in optical absorption spectra. A monolayer of organic molecules is obtained when we stop LbL assembly process only after one cycle. In the present case, formation of a monolayer of NiPc was supported by measuring thickness of films after depositing different number of bilayers; extrapolated value of thickness at 1 bilayer matched the lateral dimension of the molecule. STM topography, as presented in figure 5.1.(b), also evidenced a monolayer of NiPc on a Si substrate. For comparison, topography of a bare Si is also shown in the same figure.

Formation of a monolayer of the ZnO and cobalt-doped ZnO nanocrystals was also a part of the LbL film deposition process. Monolayers were formed on an arsenic doped Si(111) substrates (conductivity = 3–10 mΩ cm). In practice, the Si substrates were first deprotonated, so that a monolayer of a polycation, namely poly(allylamine hydrochloride), PAH can be formed by dipping the substrate in a PAH solution (10 mM) for 15 min. The substrates were washed in deionized water thrice to remove loosely bound polycations. The substrates were then dipped in a colloidal solution of TOPO-capped cobalt-doped ZnO nanoparticles for 15 min followed by a similar washing protocol in toluene to remove loosely bound nanostructures from the substrate. This completed the formation of a monolayer of the nanocrystals.

5.2.7. To align magnetic domains of the nanocrystals in a monolayer

To align the magnetic domains of the nanocrystals adsorbed on a monolayer, we applied an external magnetic field (330 mT) to the substrate containing the monolayer. Direction of the external field was always perpendicular to the substrate so that the
magnetization vector of the oriented nanocrystals points outwards to the polished surface. We formed magnetic-field assisted multilayered LbL films to confirm that the magnetization vectors of ferromagnetic nanocrystals were truly aligned. That is, we continued with the conventional LbL absorption process without any external field after aligning the magnetization vectors of the preceding layer(s). We would show that the oriented magnetic domains assisted electrostatic adsorption process of the next monolayer. In a plot of absorbance of nanocrystals versus the number of layers of LbL multilayered films, the absorbance grew at a higher rate for the magnetic-field assisted LbL films as compared to the conventional LbL films.

Figure 5.1. (a) Chemical structure of tetrasulfonic acid tetrasodium salt of nickel(II) phthalocyanine (NiPc). (b) STM topography of a bare Si (left figure) and a monolayer of NiPc (right figure). The STM measurements were recorded in a constant current mode (0.5 nA at 1.2 V). The displayed scan area is 25.4 nm × 25.4 nm and 50.3 nm × 50.3 nm, respectively. (c) Schematic representations of a monolayer with parallel and perpendicular configurations of the molecules with the substrate, along with the LbL deposition process, are shown in upper and lower panels, respectively.
5.2.8. To orient NiPc molecules in a monolayer

Monolayer formation of NiPc with the molecules lying parallel or perpendicular to the substrate (depending on the direction of magnetic field being perpendicular or parallel with respect to the substrate, respectively) has been discussed in the previous chapter. Here, only a schematic representation of a monolayer with parallel and perpendicular configurations of the molecules with the substrate, along with the deposition protocol, is shown in figure 5.1(c).

5.2.9. Electrical bistability in a monolayer

We have characterized the monolayers of the nanocrystals with a scanning tunneling microscope (Nanosurf easyScan2) tip under an ambient condition. We have characterized both the types of monolayers: (i) pristine monolayer with magnetization vector randomized and (ii) vectors aligned along the perpendicular to the plane of the substrate and pointing outwards to the polished surface. To characterize the monolayer with magnetic moments being aligned, we used a magnetic substrate holder. The magnetic flux of the holder (75 mT), which pointed towards the direction of the aligned magnetization vectors of the nanocrystals, could assist in maintaining the alignment of the magnetic domains. That is, the oriented monolayer was mounted on the magnetic substrate holder in such a way that the magnetic flux exerted by the holder reinforces the alignment of magnetization vectors of the nanocrystals. To characterize the pristine monolayer without any preferred alignment of the magnetic moments, a nonmagnetic substrate holder was used so that the randomized magnetization vectors did not become aligned during the measurements.

Here, current-voltage (I-V) characteristics of nanocrystals in a monolayer were recorded with the doped Si substrate as a base electrode and Pt/Ir tip of the STM as the top one. The voltage was scanned in a small range (±2.0 V) to ensure that the scanning does not itself induce a higher conducting state. Apart from characterizing the pristine monolayers, I-V characteristics were recorded after application of a voltage pulse of suitable amplitudes and signs that were expected to induce a high-conducting state or restore the low-state. With the
bias being applied to the tip with respect to the base electrode, a negative voltage pulse induced a high-conducting state. A positive voltage pulse, on the other hand, reinstated the low-state. To determine the threshold voltage of conductance switching ($V_{Th}$) that induces the high-conducting state, we varied the magnitude of the voltage pulse from -3.0 to -8.0 V in steps of 0.2 V. The low-state was reinstated by applying a +8.0 V pulse before each measurement. Width of the voltage pulse was 10 or 100 ms. STM topography of the monolayer was captured to ensure the presence of the nanocrystals on the Si substrate. For each (cobalt) doping concentration, $I-V$ characteristics were recorded by selecting many different points on the topography of the monolayer.

Current-voltage ($I-V$) characteristics of the monolayers of NiPc were also recorded with scanning tunneling microscopy (STM) (Nanosurf easyScan2) under an ambient condition. $I-V$ characteristics through STM measurements were recorded at many different points on the films. To introduce different conducting states in molecules in a monolayer, a voltage pulse of suitable amplitude and direction was applied prior to recording $I-V$ characteristics.

5.3. Results and discussion

5.3.1. Characterization of nanocrystals

To determine the content of dopants in ZnO nanocrystals, we have carried out EDX analysis. A typical image for the 3 at. % case is shown in figure 5.2.(a). The analysis, as shown in the figure, returned a value (for the cobalt content) that matched well with the content that was added during the growth of the nanocrystals. Since the analyses for other dopant concentrations matched the at. % of cobalt added in the solution, in the rest of the manuscript we will refer the doped systems in terms of the measured [Co]:[Zn] concentration ratio in the reaction flask.
Figure 5.2. (a) Representative EDX analysis along with a table of atomic percent of the elements present in the nanocrystals. (b) TEM and HR-TEM images of cobalt-doped ZnO nanocrystals (3 at. %) showing the size distribution and lattice planes, respectively. (c) Distribution of the diameter of ZnO and cobalt-doped ZnO nanocrystals (5 at. %).

We have recorded TEM images of the nanocrystals. A typical image for a doped system (3 at. %) along with a HR-TEM image is shown in figure 5.2.(b). Crystalline nature of the nanostructures was clearly visible in the HR-TEM image. Lattice fringes of the nanocrystals had a spacing of 0.279 nm, which matched well with the lattice spacing of the <100> plane of ZnO crystals. Average diameter of ZnO nanocrystals as calculated from the TEM images was 3.6 nm. We have plotted the size distribution of the nanocrystals, as obtained from the TEM images, in figure 5.2.(c). When we compare the size distribution of ZnO and doped-ZnO nanocrystals, we find that the diameter decreased upon cobalt doping. The diameter of the nanoparticles became smaller upon doping, since the dopants inhibited the growth, as has been explained in terms of Gibbs-Thompson relationship between lattice strain and crystal solubility. Fe$_3$O$_4$ and TiO$_2$ nanoparticles were also characterized by transmission electron microscopy (TEM), and high-resolution TEM (HR-TEM) and Electron diffraction X-ray (EDX) analyses.
Figure 5.3 Optical absorption spectra of ZnO and cobalt-doped ZnO nanocrystals in dispersed solution.

We have recorded optical absorption spectra of ZnO and doped ZnO nanocrystals in dispersed solution (figure 5.3.). The spectra show that the band gap of the nanoparticles lies in the near-UV region. Upon an increase in the concentration of the dopant, the band shifted towards the short-wavelength region. The shift in the bandgap is due to a decrease in the diameter of the nanocrystals, as has been reflected in the TEM images (figure 5.2.(c)). With Co$^{2+}$ doping, a new band appeared in the lower wavelength region (around 600 nm) that has been assigned to be due to the ligand field transition, Co$^{2+}$ $^4A_{2g}^\rightarrow^4T_{2g}(P)$ and charge transfer band of Co$^{2+}$ in Co-ZnO quantum confined size regime.$^{28}$
5.3.2. Electrical bistability of nanocrystals in a monolayer

5.3.2.1. Threshold voltage determination

We have recorded characteristics of the nanocrystals in a monolayer with a Pt/Ir tip of a STM. Tip approaching current was kept low so that the tip did not influence the nanostructures. We first recorded I-V characteristics of the pristine monolayers. We then applied a suitable voltage pulse to switch the tunneling conductance of the nanocrystals to a high-state; I-V characteristics of the nanocrystals in their high-conducting state were then probed. In these materials, since a negative voltage pulse switches the nanocrystals to a high-state, we varied the magnitude of voltage pulse in the -3.0 to -6.8 V range. Pulse widths of 10 and 100 ms were chosen for each magnitude. Since a pulse of opposite magnitude reinstates the low-state, we applied a +8.0 V pulse before application of each negative voltage pulse. In figure 5.4.(a), we have plotted I-V characteristics in the -2.0 to +2.0 V range after application of different negative voltage pulse (width = 10 ms). The characteristics could be seen to have clubbed into two bunches. That is, a low-conducting state could be observed till the magnitude of voltage pulse was -5.2 V. When the magnitude was more negative, the I-V characteristics changed with a signature of conductance switching. Similar results were observed when the width of the voltage pulse was 100 ms. I-V characteristics of (a monolayer of) cobalt-doped ZnO nanocrystals (3 at. %) are shown in figure 5.4.(b). A typical STM topography is shown in the inset of the figure. The characteristics resembled the plot presented in figure 5.4.(a) apart from the voltage at which the "change-over" from the low to a high-state took place. The measurements enabled us to determine the threshold voltage (V_{th}) of conductance switching by plotting the current at a particular voltage versus the magnitude of voltage pulse (figure 5.4.(c)). The results show that there were two clear conducting-states. The current jumped to a high-value at the threshold-voltage of conductance switching. The |V_{th}| decreased upon the introduction of dopants. For 3 at. % cobalt doping, we have observed that a -4.4 V pulse was required to achieve a high-conducting state, as opposed to -5.4 V for the undoped ZnO.
Figure 5.4. Current-voltage characteristics of a monolayer of (a) ZnO and (b) cobalt-doped ZnO (3 at. %) in the ±2.0 V window after application of a 10 ms voltage pulse of a magnitude as specified in the legend. STM topography of a monolayer of cobalt-doped ZnO (3 at. %) is shown in the inset of (b). (c) Current at -1.5 V for the two monolayers as a function of the magnitude of voltage pulse that preceded the I-V characteristics.

5.3.2.2. Reproducibility and reversibility

To check reproducibility and reversibility of conductance switching, we carried out measurements at many different points and also in cycles at the same point. In figure 5.5.(a), we show I-V characteristics of a monolayer of ZnO nanoparticles; results carried out at 20
different points are shown along with their average characteristics. To introduce a high-state, we applied a voltage pulse of -5.4 V (width = 10 ms) which was higher than the $V_{th}$ that was required to switch the nanocrystals to a high-conducting state. That is, we recorded the tunneling current before and after application of a voltage pulse at the same points. $I$-$V$ characteristics of the nanocrystals in their low- and high-conducting states could be observed. The switching to the higher conducting state is reversible; by applying a voltage pulse of opposite magnitude (+5.4 V, 10 ms), the initial $I$-$V$ characteristics could be reinstated. As can be seen in figure 5.5(a), the two $I$-$V$ characteristics could be achieved reversibly over many cycles.

**Figure 5.5.** Current-voltage characteristics of a monolayer of (a) ZnO and (b) cobalt-doped ZnO (3 at.%) in the ±2.0 V window after application of a 10 ms voltage pulse of -5.4 V and -4.4 V, respectively. In each of the cases, measurements were carried out at many different points (as specified by dots of different colors) and also many different times (as specified by narrow lines). Average of the characteristics is shown as thick lines in each of the plots.

5.3.2.3. Effect of cobalt as dopants

Figure 5.5(b) shows $I$-$V$ characteristics of a monolayer of cobalt-doped ZnO nanoparticles (3 at.%) in their low and high-conducting states. All the $I$-$V$ characteristics were recorded in the same fashion. Here also, we present characteristics of the low and high-conducting states recorded at many different points to show the reproducibility of the results. We added characteristics after reversal of high- and low-states in cycles to show the
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reversibility of conductance switching. Here, since the magnitude of threshold voltage was low as compared to the undoped ZnO case, we applied a -4.4 V pulse (10 ms) to switch the doped nanoparticles to a high-state. The low-state was reinstated by applying a voltage pulse in the opposite direction (+4.4 V, 10 ms). While both the systems exhibited electrical bistability, the absolute value of current in the low- and high-states depended on the extent of cobalt-doping. Since we carried out measurements on nanocrystals having five different cobalt contents, we summed up the results as a plot of current in the low- and high-states at -1.5 V versus dopant concentration of the ZnO nanocrystals (figure 5.6.). We have added the ratio between the two currents, the On/Off ratio, in the figure. The results show that with an increase in the dopant-content, both low- and high-state currents steadily increase. Similar behavior was observed when current (of the low- and the high-states) measured at +1.5 V were plotted with respect to the content of cobalt. Due to an increase in the (modulus of) low-state current, the On/Off ratio decreased with an increase in the cobalt content in the nanocrystals. This is expected since, with conductance-switching occurring due to confinement of charge carriers, the diameter of the nanocrystals determines the extent of the increase of conductance or the On/Off ratio. Here, as stated earlier, with an increase in the cobalt-content in ZnO nanocrystals, the diameter of the nanocrystals shrunk to some extent thereby decreasing the On/Off ratio.

Figure 5.6. Current at -1.5 V of the high- and low-conducting states and their ratio (On/Off ratio) as a function of cobalt content in doped ZnO nanocrystals. The red diamond symbols representing the On/Off ratio refer to the axis on the right-hand side.
5.3.2.4. Effect of alignment of the magnetization vector

Since the rationale behind choosing cobalt-doped ZnO nanoparticles was their room-temperature ferromagnetism, we aimed to find if alignment of the magnetization vector of the nanocrystals in a monolayer has any effect on the tunneling current and electrical bistability. To do so, we choose a monolayer of doped nanoparticles. Apart from characterizing the pristine monolayer, we characterized the monolayer after aligning their magnetization vector perpendicular to the substrate and pointing outwards. We kept such a monolayer on a magnetic substrate holder of STM, so that the aligned magnetization vectors remained frozen during the measurements. We first determined the threshold voltage of conductance switching in these “oriented” monolayers. $I-V$ characteristics of such “oriented” nanocrystals in a monolayer were then measured at many different points before and after application of a voltage pulse (-4.4 V). For comparison, we have added characteristics of the two conducting states of the “unoriented” nanocrystals. Figure 5.7.(a) shows that while the nanocrystals with both “unoriented” and “oriented” magnetization vectors exhibited conductance switching, the oriented system yielded a higher current in the positive voltage region for both the conducting states. That is, upon an alignment of the magnetization vectors of the nanocrystals, the current in the positive voltage in both low- and high-conducting states increased with a consequent decrease in the On/Off ratio (inset of figure 5.7.(a)). The On/Off ratio remained unaffected in the negative voltage region. Such a dependence will be explained by considering transport gap of the nanocrystals in a monolayer.

5.3.2.5. Electrical bistability vis-à-vis change in transport gap

To analyze the electrical bistability in nanocrystals and how it is influenced by the alignment of magnetization vectors, we have plotted the characteristics in a log-linear scale. The characteristics for both types of monolayers in their low- and high-conducting states are shown in figure 5.7.(b). The voltage at which the magnitude of current rises from the background level points to an energy at which tip-metal’s Fermi level matches the conduction and valence band-edges of the nanocrystals. Here the bias being applied to the tip, the positive
voltage-onset signifies that electrons could be withdrawn from the nanoparticles and thus the location of the valence band-edge. Similarly, at the negative voltage-onset, electrons could be injected to the conduction band-edge. The difference between the two voltage-onsets would therefore denote the transport gap of the nanocrystals in a monolayer on the electrode. It may be added that the transport gap (sometimes referred to as an emission gap) is generally lower than the optical bandgap.

Figure 5.7. Effect of alignment of magnetization vectors of cobalt-doped ZnO nanoparticles on conductance switching. I-V characteristics of a monolayer of the doped ZnO nanoparticles (3 at. %) in their low- and high-conducting states. In both the figures, characteristics of the nanocrystals with their magnetization vector aligned or “oriented” and randomized or “unoriented” have been compared in (a) linear-linear and (b) log-linear scales. For each of the systems, results recorded at 20 different points on a monolayer are shown as dotted lines with the thick-line being the average of the 20 characteristics. In the inset of (a), the ratio between the currents in their high- and low-conducting states, the On/Off ratio, has been plotted for the “unoriented” and “oriented” monolayers.

When the nanocrystals undergo a conductance switching, we find that the valence band increases and the conduction band decreases ensuing a decrease in the transport gap. That is, a higher current (at any voltage) in the high-state is achieved due to the fact that the valence and conduction bands were closer to the Fermi energy of the tip. In other words, a
conductance switching that occurs upon application of a voltage pulse induces confinement of charge carriers in the nanocrystals leading to a decrease in the transport gap of the material on the electrode.

If we compare the change in transport gaps of the monolayers having oriented and unoriented magnetization vectors, we find that the transport gap decreased upon conductance switching in both the systems. The transport gap also decreased upon alignment of the magnetization vectors. In a monolayer with the vectors pointing outwards, aligned magnetic domains may have interacted with each other to yield a low transport gap of the (aligned) nanocrystals. The decrease in the transport gap however is due to an increase in the energy of the valence band-edge only leaving the conduction band-edge unchanged. This also led to the invariance of the tunneling current in the negative voltage region, at which electrons were injected to the conduction band, upon alignment of the magnetization vectors (figure 5.7.(a)). To sum up, both the alignment of magnetization vectors and the conductance switching result in a decrease in the transport gap of the nanocrystals in a monolayer.

**Figure 5.8.** Effect of dopant-concentration on bistability of aligned nanocrystals. Plots of transport gap of low- and high-conducting states of cobalt-doped ZnO nanocrystals in a monolayer. Results from monolayers with magnetization vectors (a) unoriented or randomized and (b) oriented or aligned perpendicular to the electrode are shown in the figures.
5.3.2.6. Effect of dopant-concentration on bistability of aligned nanocrystals

Since cobalt doping introduced ferromagnetism in ZnO nanocrystals, it is imperative to study the effect of cobalt content in the nanocrystals and alignment of the magnetization vector on electrical bistability and change in the transport gap. We have characterized monolayers of such nanocrystals having moments oriented and unoriented. For each system, we studied electrical bistability by recording STS before and after application of a voltage pulse of suitable magnitude that would switch the nanocrystals to their high-conducting state. The results have been summed up in figure 5.8. as plots of transport gap of the low- and high-conducting states of the monolayer of nanocrystals having "unoriented" or "oriented" magnetization vectors as a function of cobalt content in the nanocrystals. Here also, we characterized at many points on each monolayer and also many times at each point to confirm reproducibility and reversibility of the results. Such measurements have enabled us to add error bars in the transport gap. The figure shows that with an increase in the dopant content, the transport gap decreased. The gap decreased also upon conductance switching. For the “oriented” monolayer, the gap decreased with the increase in cobalt doping and also upon electrical bistability. Each of the values was lower in the “oriented” case (figure 5.8.(b)) as compared to that in the pristine monolayer when the magnetization vector was randomized or unaligned (figure 5.8.(a)).

5.3.3. Electrical bistability of organic molecules in a monolayer

5.3.3.1. Effect of orientation

We have recorded $I$-$V$ characteristics of pristine monolayers of NiPc with a STM tip. In figure 5.9.(a), we show a typical $I$-$V$ plot of a monolayer of NiPc molecules lying parallel to the electrode. To introduce a high-conducting state, we here applied a voltage pulse of -6.5 V (100 ms). $I$-$V$ characteristics of the film at the same point in a small voltage window (-3.0 to +3.0 V) after application of the voltage pulse, as presented in the same figure, show that the electrode/molecule/tip now returns a higher current at any voltage. The switching to a higher conducting-state is reproducible; by applying a reverse voltage pulse (+6.5 V, 100 ms), the initial $I$-$V$ can be reinstated. The two $I$-$V$ characteristics can be achieved reversibly over many
cycles. Characteristics of the pristine or low-state and the high-conducting state over five reversible cycles are shown in the figure. The electrically bistable characteristics with a monolayer of organic molecules characterized with Pt/Ir tip of a STM are itself of interest. It first of all rules out any possibility of filament formation and moreover evidences molecular nature of electrical bistability in a monolayer of this organic molecule.

Figure 5.9.(b) shows $I-V$ characteristics of a monolayer of NiPc with the molecules being perpendicular to the electrode surface. Here also, we show characteristics in low- and high-conducting states in cycles. While the high-state was introduced by applying a short voltage pulse of -6.5 V (100 ms), the low-state was reinstated by applying a voltage pulse in the opposite direction (+6.5 V, 100 ms). The molecules in this perpendicular configuration also show reversible electrical bistability over many cycles.

![Figure 5.9](image)

**Figure 5.9.** Current-voltage characteristics in a small voltage-window of a monolayer of NiPc with molecules (a) parallel and (b) perpendicular to the substrate. The low- and the high-state characteristics have been recorded after application of a voltage pulse of +6.5 V and -6.5 V, respectively; in cycles to show the reproducibility of electrical bistability. The low- and the high-state characteristics in five cycles are represented by black and blue (red) symbols, respectively. Each of five different symbols represents characteristics recorded after each cycle. (c) On/Off ratio of current in high- and low-states for the monolayers with molecules parallel and perpendicular to the substrate.
The degree of electrical bistability in these two orientations of molecules in a monolayer can be estimated by plotting the On/Off ratio versus voltage. Figure 5.9.(c) shows that the ratio was higher in a monolayer having molecules perpendicular to the substrate as compared to that having molecules parallel to the electrode. In the figure, we did not plot the ratio in the low voltage region where both low- and high-state current values were small leading to large errors in their ratio. The results show that when the planer molecules were perpendicular to the base electrode with its edge being probed, conductance switching of the molecules was enhanced as compared to the scenario when molecules were parallel to base electrode and faced the tip of the STM.

5.3.3.2. Transport gap and electrical bistability

To show reproducibility of the results, we carried out measurements at many different points on a monolayer. $I-V$ characteristics of the low- and high-conducting states in log-linear scale measured at 50 different points are shown in figures 5.10.(a) and 5.10.(b), respectively. Average of the characteristics in each of the two conducting-states has also been plotted in the respective figures. The measurements show homogeneity of the results. They further show that the variation in the characteristics is much smaller than the change in $I-V$ characteristics due to the conductance switching.

$I-V$ characteristics, when plotted in log-linear scale, can be used to measure the transport gap of molecules on the substrate. The voltages, where the amplitude in current starts to increase from its background value signify energies at which tip-metal's Fermi energy matches lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO). That is, at these positive and negative voltages, electrons can be injected by the tip and withdrawn from the molecule to the tip, respectively. The difference in the voltages or energies hence determines the transport gap of the molecules in a monolayer on the substrate. Figures 5.10.(a) and 5.10.(b) show that the electrical bistability is associated with a decrease in transport gap. That is, upon application of a voltage pulse of -6.5 V, transport gap of the molecules decreased leading to reducing barrier heights with the electrodes and hence
enabling higher carrier injection and consequently a higher tunneling current in the electrode/molecule/tip systems. As control experiments, we carried out measurements in (1) bare Si and (2) only polyelectrolyte layer (polyanion/polycation). In both the cases, no such $I$-$V$ and transport gap were observed. Since the latter system contained electrolytes with ionic groups, absence of a transport gap in such a system shows that the $I$-$V$s presented in figures 5.10.(a) and 5.10.(b) truly appeared due to the NiPc molecules in the monolayer instead of any polarization of the ionic groups.

![Graph](image)

**Figure 5.10.** Current-voltage characteristics of a monolayer on NiPc molecules lying perpendicular to the electrode (a) before and (b) after application of a voltage pulse that induces a high-state. Characteristics of measurements recorded at 50 different points on a monolayer are shown in the figures. Determination of transport gap is also shown in the figures. (c) A comparison of average $I$-$V$ characteristics of low- and high-states of NiPc molecules in their parallel and perpendicular orientations in a monolayer.
5.3.3.3 Transport gap and electrical bistability vis-à-vis orientation

We compared electrical bistability phenomenon in the two orientations of the molecules in the monolayers. $I-V$ characteristics of both low- and high-states, measured for parallel and perpendicular orientations of the molecules (with respect to the substrate electrode) in a monolayer are shown in figure 5.10.(c.) The results first of all show that the transport gap depended on the orientation of the molecules in a monolayer. The gap of the molecules parallel to the substrate (1.75 eV) was about 0.25 eV lower than that in molecules perpendicular to the electrode (2.00 eV). Upon application of a voltage pulse of -6.5 V (100 ms), transport gap of the molecules in both orientations decreased and reached a value of 1.05 eV. This decrease to 1.05 eV for both the orientations is in spite of the fact that in the low-state, the transport gap of the molecules in a monolayer was different for the two orientations of the molecules.

5.3.3.4. Density of states and electrical bistability

We have calculated density of states (DOS) of the molecules in their electrically bistable states. The DOS has been calculated for both orientations of the molecules in a monolayer. The results (figure 5.11.) show that with a conductance-switching, density of states increased along with a narrowing of bandgap. Peaks in the DOS spectrum evidencing LUMO and HOMO levels moved closer to each other. We can compare DOS spectra for the two orientations of molecules (in their low-state). It shows that the DOS for the molecules parallel to the substrate is not only higher than that of molecules in perpendicular configuration, the LUMO and HOMO levels in the former case are closer to each other. The results hence are in concurrence with the measurement of transport gap of the molecules in a monolayer.

5.3.3.5. Multilevel conductivity in monolayers

So far, in inducing a high-state, we applied a voltage pulse of -6.5 V; a +6.5 V reinstated the low-state. It can be intriguing to know if the amplitude of the pulse has any effect on electrical bistability and transport gap. That is, we aimed to find if there are any intermediate
conducting-states or $I$-$V$ characteristics. To do so, we varied the amplitude of voltage pulse that induces electrical bistability to the organic molecules in a monolayer. It may be reinstated that the voltage pulse was applied before recording $I$-$V$ characteristics in a small voltage-window of -3.0 to +3.0 V. To remove any reminiscent effect, we applied a +11.0 V pulse each time to induce the low-conducting state before applying a voltage pulse of amplitude ranging from -4.5 V to -11.0 V.

![Figure 5.11. Density of states of low- and high-states of NiPc molecules in a monolayer lying parallel or perpendicular to the electrode.](image)

$I$-$V$ characteristics of a monolayer of molecules parallel and perpendicular to the substrate are shown in figures 5.12.(a) and 5.12.(b), respectively. The results show that the $I$-$V$ plots depended on the amplitude of voltage-pulse applied prior to voltage-sweep. In fact, the $I$-$V$ characteristics in the small voltage window were bunched in three groups. That is, when the amplitude of voltage pulse ranged between -4.5 to -6.0 V, signature of a low-state of the molecules appeared. When the amplitude ranged between -6.5 to -8.5 V, the $I$-$V$ characteristics jumped showing a higher current value at each (magnitude of) applied voltage. This may be
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termed as 1\textsuperscript{st} high-state. The characteristics jumped again to a 2\textsuperscript{nd} high-state when voltage pulse’s amplitude was -9.0 V or more in magnitude. That is, the monolayer of the molecules evidenced three types of $I$-$V$ characteristics, namely, a low-one, a 1\textsuperscript{st} high-state, and a 2\textsuperscript{nd} high-state. The results hence display a clear example of multilevel conductance in an organic monolayer that has been reported earlier in other organic molecules.\textsuperscript{36-38} Retention time of the high-conducting states has been tested by recording $I$-$V$ characteristics (of the high-states) every 20 min for a couple of hours. We have observed that the current of 1\textsuperscript{st} and 2\textsuperscript{nd} high-states started to decrease after 1 h and 20 min, respectively.

**Figure 5.12.** $I$-$V$ characteristics in -3.0 to +3.0 V window after application of a voltage pulse of amplitude ranging from -4.5 to -11.0 V (as shown in legends). A +11.0 V pulse was applied each time to remove any reminiscent effect. Parts (a) and (b) represent monolayers with molecules parallel and perpendicular to the substrate, respectively.

5.3.3.6. Transport gap of multilevel high-states

It is interesting to look for transport gap of the molecules in their three conducting states. In figures 5.13.(a) and 5.13.(b), we have plotted the $I$-$V$ characteristics in log-linear scale for the two orientations of the molecules. The figures show that the transport gap of the molecules depends on the amplitude of voltage applied prior to recording $I$-$V$ characteristics. The transport gap is also bunched in groups for different amplitudes of voltage pulse. The low-
state had a larger transport gap. The 1st and the 2nd high-states have decreasingly lower gap. That is, in 1st and 2nd high-states, the gap progressively diminished leading to a decrease in barrier height with electrodes and hence an increase in tunneling current.

**Figure 5.13.** I-V characteristics, as shown in figure 5.12., in log-linear scale after application of a voltage pulse of amplitude ranging from -4.5 to -11.0 V (as shown in legends). Parts (a) and (b) represent monolayers with molecules parallel and perpendicular to the substrate, respectively.

A closer look of the transport gap of the two types of monolayer reveals further information. The bistability is related to both voltage pulse and orientation. While the off-state current depends on the orientation, the current and transport-gap of the high-states did not depend on the orientation of the molecules. In other words, even though the gap of the off-state was higher in the monolayer with molecules perpendicular to the substrate as compared to that with molecules parallel to the substrate, the gap of the 1st and also the 2nd high-state did not depend on the orientation of the molecules in the monolayer. Moreover, a comparison between figures 5.12. and 5.13. show that the I-V characteristics have a one-to-one correspondence with the transport gap. That is, tunneling current is dictated by the transport gap of the molecules. In other words, electrical bistability to a higher state occurs due to a change in transport gap of the molecules that in turn decreases the barrier height with the electrodes and correspondingly increases current in the electrode/molecule/tip systems.
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5.3.3.7. Conductance switching and molecular orientation

For the low-state, a high transport-gap and correspondingly a low-current in the monolayer with molecules perpendicular to the substrate as compared to those in the parallel orientation needs to be analyzed. For the low-state, the interaction between the molecules and the substrate plays a major role in determining $I-V$ characteristics. Hence, when the molecules are parallel to the substrate, they are electronically interacting with the electrode leading to a decrease in transport gap and a higher current. In a monolayer with molecules perpendicular to the substrate, no such interactions exists with the electrode; hence transport gap was wide and current was low. Application of a voltage pulse introduces space-charge in the molecules and thus decreases the gap further and correspondingly induces a high-state. That is, while the transport gap of the low-state depended on the orientation (and hence the interaction with the electrode), the current in the high-states depended mostly on the density of space-charges induced by the voltage pulse.

5.3.4. Electrical bistability of bulk devices

5.3.4.1 Electrical bistability

By inserting two silver electrodes (separation = 1 mm), electrical characteristics of the devices were measured. The devices were kept in a glass chamber under vacuum. Bias was applied in steps with a scan-speed of 50 mV/s. In order to observe electrical bistability, bias was applied in multiple loops between a positive and a negative value of voltage. Measurements were carried out also by applying a magnetic field in a direction perpendicular to that of the electric field and the plane of the pellet. Amplitude of magnetic field was varied in the 0 – 230 mT range.

The devices based on Fe$_3$O$_4$ nanoparticles have exhibited electrical bistability. Figure 5.14. shows $I-V$ characteristics of such a device under multiple voltage loops. When the (magnitude of) applied voltage exceeds 1.1-1.2 V, a transition in conductance from a low- to a high-state occurred. Threshold voltage of switching in both bias directions did not respond to
$V_{\text{Max}}$, which is the voltage up to which the bias was swept during the scan. The change in conductance is non-volatile, i.e., when the bias is withdrawn, the high-state is retained. The initial low-conducting state can be re-established only after application of a suitable low bias or short-circuiting the device. The transition between the two conducting states or electrical bistability is reproducible over many cycles; characteristics under three cycles are shown in the figure 5.14.

![Figure 5.14](image-url)

**Figure 5.14.** (a) Current-voltage characteristics of a Fe$_3$O$_4$:TiO$_2$ device under three voltage loops between $+1.5$ and $-1.5$ V. Plots “before applying any magnetic field”, “after application of 330 mT”, and “after removal of magnetic field” are shown in the figure. Control experiments from (b) ZnO:TiO$_2$ and (c) TiO$_2$ systems.

Such a nature of electrical-bistability in devices based on metal or semiconducting nanoparticles has been explained in terms of charge confinement in the nanoparticles. The
nanoparticles with higher carrier concentration form a percolating network that provides channels for conduction and hence a higher conducting-state. When probed under a “read voltage”, the high-state returned a higher current as compared to that from a device in its low-conducting state. Such an experiment to determine retention time of a memory device, commonly known as read-only memory (ROM) application\textsuperscript{3,5,39}, has been carried out for more than one hour. Under a prolonged period of operation, the difference between currents under the “read voltage” for the high- and low-states started to diminish. Similarly, if the voltage is looped for more than a hundred cycles, the device starts to exhibit a reminiscent effect with a closure of the hysteresis in $I$-$V$ characteristics. This could be due to accumulation of space change in the device. We have also measured switching time of the devices. Current under a sharp voltage pulse lagged by about 2.5 µs that may be considered as the switching time of these bistable devices.

### 5.3.4.2. Effect of external magnetic field on electrical bistability

We then applied a magnetic field and recorded $I$-$V$ characteristics under multiple voltage loops. We have plotted such characteristics in figure 5.14.(a). A comparison of the plots with the results obtained without any magnetic field reveals a couple of observations. First of all, the $I$-$V$ plot of the devices under a magnetic field is more close to that of a high-state without any magnetic field. This indicates a possible co-occurrence of magnetization and high-conducting state during electrical switching. That is, a high-conducting state may actually have originated due to orientation of magnetic domains of the nanoparticles.

Under a magnetic field, conductivity of the device actually decreases in the voltage scan towards 0 V. This nature of electrical-bistability is in contrast to the results without any magnetic field, where conductivity at a voltage was higher when bias was scanned to 0 V as compared to that during a voltage-sweep to a ±$V_{\text{Max}}$. In addition, overall conductivity of the device becomes higher under a magnetic field. The change in the nature of electrical-bistability under magnetic field is inherently interesting. The results show that magnetic field has a large influence on electrical-bistable properties of this type of devices. In a latter paragraph we will
show that the change in the nature of electrical bistability under magnetic field is a separate event as compared to the overall increase in conductivity or negative magnetoresistance.

$I$-$V$ characteristics under a magnetic field are reproducible over multiple voltage loops. Characteristics under three consecutive loops are shown in figure 5.14.(a). The effect of magnetic field is reversible in nature. That is, when the magnetic field was withdrawn, $I$-$V$ characteristics of the device returned to the “before applying a magnetic field” situation with the usual signature of a typical conductance-switching. This reversibility is instantaneous; that is $I$-$V$ characteristics recorded immediately after withdrawal of the magnetic field completely resembled the “before applying H” case. This could be due to superparamagnetic nature of Fe$_3$O$_4$:TiO$_2$ mixture (0.7% by weight). The magnetization studies of the mixture displayed superparamagnetic characteristics. This is may be due to very low concentration of the ferromagnetic nanoparticles in a nonmagnetic matrix. In other words, the system behaved as randomly oriented non-interacting ferromagnetic clusters.

$I$-$V$ characteristics of a control device based on ZnO nanoparticles (instead of Fe$_3$O$_4$ nanoparticles), as shown in figure 5.14.(b), did not respond to magnetic field of up to 400 mT. The devices based on ZnO nanoparticles exhibited a similar conductance switching. These devices however required a higher applied voltage to show signs of conductance-switching. Another control experiment in pellets of only TiO$_2$ did not exhibit any electrical bistability; magnetic field effect of bistability hence does not arise here. Characteristics from such control experiments are shown in figure 5.14.(c). The results presented in figure 5.14.(a), along with the control experiments, hence confirm that the observed change in the nature of electrical bistability in devices based on Fe$_3$O$_4$ nanoparticles is indeed due to orientation of magnetic domains under the application of a magnetic field.

The change in the nature of electrical bistability from “before applying magnetic field” to “after application of magnetic field”, as shown in figure 5.14.(a), can best be explored by recording $I$-$V$ characteristics under magnetic field of different magnitudes. Figure 5.15. shows $I$-$V$ plots of a device under a voltage loop with magnetic field ranging from 0 to 230 mT, which
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is higher than the field to achieve saturation in magnetization. The plot shows that with an increase in the magnetic field, the (amplitude of) threshold voltage of conductance-switching decreases in both bias directions. This has led to a situation so that the nanoparticles are already in a high-conducting state (even before application of a voltage that in general is needed for charge confinement to occur and consequently to yield a high-conducting state). In fact, under a critical magnetic field or higher, switching occurs to a low-conducting state instead of a high-one.

The current value at 1.5 V of a Fe$_3$O$_4$:TiO$_2$ device first increased with applied magnetic field followed by saturation at 150 mT. The monotonic increase in the value of current with magnetic field, as shown in the inset of figure 5.15, resembles the effect of negative magnetoresistance. Since we will restrict ourselves on the results pertaining to electrical-bistability, magnetoresistance has not been elaborated in this report.

![Figure 5.15](image)

Figure 5.15. Current-voltage characteristics of a Fe$_3$O$_4$:TiO$_2$ device under a voltage loop at different magnetic fields (as stated in the legends). Magnetic field variation of current value at 1.5 V is shown in the inset.
Figure 5.16(a) represents a plot of threshold voltage versus magnetic field. The (magnitude of) threshold voltage \( V_{Th} \) in both positive and negative voltages decreases with magnetic field. This decrease in threshold voltage of switching is associated with the changeover of electrical-bistability. That is, with little or no magnetic field the device switched to a higher-conducting state due to application of a bias. With a magnetic field of 110 mT or more, the effect is reversed; the device switched to a low-state due to application of a bias. In other words, if On/Off ratio is defined as the ratio between current values at a particular voltage during two sweep directions, i.e., voltage scans to a \(+V_{Max}\) and to 0 V, respectively, it crosses a value of unity at a magnetic field of 110 mT. (In principle, On/Off ratio is defined as the ratio between current values at a particular voltage during the voltage-sweep through a high- and a low-conducting state). This plot is shown in figure 5.16(b). The results show that electrical bistability of semiconducting quantum dots can be tuned by the application of magnetic field.

**Figure 5.16.** Magnetic field variation of (a) threshold voltage of conductance switching \( V_{Th} \) and (b) On/Off ratio (ratio between currents during voltage sweep to 0 V and to +1.5 V) at 0.6 V.
Dependence of electrical bistability on magnetic field is an interesting observation. As such it has been shown that an electric field on a device tends to orient the magnetic dipoles of the nanoparticles in a direction perpendicular to the electric field.\textsuperscript{40,41} Hence, in a “before applying magnetic field” case, application of bias (and correspondingly a flow of current) orients the magnetic domains. Such an oriented system has a higher conductivity and hence leads to a high-conducting state during voltage sweep from $+1.5\text{ V}$ (or $-1.5\text{ V}$) to $0\text{ V}$. Upon application of a suitably high magnetic field in a direction perpendicular to that of the electric potential and the plane of the pellet, the domains are oriented without the aid of any current flow. The initial conducting-state of a magnetized device is hence a high-conducting one. A bias of $1.5\text{ V}$ here has reduced the conductivity; this could be due to the heat generated in the device that may have disturbed the oriented domains.\textsuperscript{42,43}

5.4. Conclusions

In conclusion, we have studied electrical bistability of cobalt-doped ZnO nanocrystals and the effect alignment of their magnetic domains on electrical bistability in a monolayer by recording tunneling current through scanning tunneling spectroscopy. In a range of cobalt-doped ZnO nanocrystals, we have observed that the alignment of magnetization vectors and conductance switching both lead to a decrease in the transport gap. In studying electrical bistability of the monolayers of NiPc, oriented in parallel and perpendicular configurations on an electrode substrate, we have observed that the On/Off ratio and hence the electrical bistability is higher when molecules in the monolayer are oriented perpendicular to the substrate as compared to that with molecules parallel to the electrode. We have also observed that the electrical bistability is associated with a decrease in transport gap and an increase in the density of states. By varying the amplitude of voltage pulse, we could introduce multilevel conductance in the monolayer of NiPc molecules. The devices based on Fe$_3$O$_4$ nanoparticles exhibited switching to a high-conducting state under application of a bias. Under magnetic field, the nature of bistability has changed. With an increase in magnetic field, threshold-voltage of switching has decreased leading to a transition in the nature of electrical-bistability.
Thus we concluded that the conductance-switching (to a high-state) and orientation of magnetic domains of Fe₃O₄ nanoparticles occur concurrently.
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Reference


