Enhanced differential conductance through light induced current switching in Mn_{12} acetate molecular junctions

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The authors have observed through electrical transport measurements enhanced differential conductance ($\boldsymbol{G}=dI/dV$), up to $2e^2/h$ ($\sim 77\ \mu A/V$), through the $Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4 \cdot 2CH_3COOH \cdot 4H_2O$: "$Mn_{12}$–Ac" molecule. At room temperature, under optical illumination, electrical switching, accompanied by a 60-fold increase of $\boldsymbol{G}$ through Mn_{12}–Ac, was seen. The temperature dependence of $\boldsymbol{G}$ was used to determine the activation energy for molecular conduction to be $\sim$0.4 eV. Their results provide evidence for the possible use of Mn_{12}–Ac as a conducting wire, in addition to its proposed utility for information storage, for implementing multifunctional molecular electronics. © *2006 American Institute of Physics*.
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Molecular electronics, in addition to the possibilities of miniaturization, has the potential to extend the paradigm of obtaining functionality at the nanoscale. Consequently, several prototypical molecules have been proposed[1] for discrete components including wires, switches, rectifiers, and storage[2] in information processing. In this context, it would be especially interesting to harness a molecule's intrinsic synthetic tailorability[3] to construct a single molecule based multifunctional element. In this letter, we demonstrate enhanced differential conductance ($\boldsymbol{G}=dI/dV$) $\sim 77\ \mu A/V$ (close to $2e^2/h$) in the single molecular magnet: manganese acetate [$(Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4 \cdot 2CH_3COOH \cdot 4H_2O)$] "$Mn_{12}$–Ac" [Fig. 1(a)].

Several methods such as scanning probe microscopy,[4] crossed wire tunnel junctions,[5] mechanically controllable break junctions,[6] and hybrid approaches such as STM-break junctions[7] have been used to probe electrical transport at the single molecule level. In these molecular junctions, the observed peak $\boldsymbol{G}$ has generally[6,8–11] been less than 1 $\mu A/V$ (with one exception[12]—a $\boldsymbol{G}$ value of $\sim 50\ \mu A/V$ at 1.3 K in a ferrocene based organometallic molecule). Such low $\boldsymbol{G}$ values are attributed[13] to the molecule-electrode interactions.

In our work, we fabricated nanometer size gaps for probing molecular conduction in the Mn_{12}–Ac organometallic system, through electromigration induced breakage of thin Ti (7 nm)/Au (20 nm) wires[14] on both high temperature cured native oxide/Si and 100 nm evaporated SiO_2/Si substrates. This technique had been previously used to exquisitely probe single electron transport through single molecules[9,10] and is amenable to batch synthesis for large scale nanoelectronics. By regulating the voltage ramp rate (<30 mV/s) and temperature, we created a break junction with a very small gap[15] corresponding to nanometer separation[14] [Fig. 1(b)]. The breakage was monitored through electrical resistance measurement and the gap resistance was in the gigaohm range.

The break junctions were subsequently dipped into a solution of 3% 3-thiobenzoic acid [a linker molecule for hinging the Mn_{12}–Ac moiety to the electrodes, Fig. 1(a)] for 20 h. This treatment facilitates the formation of–S–Au bonds at the electrode interface, with dangling COO^- groups at the other end of the pendant acid. Any excess acid was then washed away, and the substrate was then treated, for 24 h, with a 0.1 mM solution of Mn_{12}–Ac dissolved in acetonitrile. The acetate groups ($-^-O_2CCH_3$) on the Mn_{12}–Ac then exchange rapidly with the COO^- groups.[16] It would then be reasonable to conclude, as assumed in other studies, that a single/few Mn_{12}–Ac molecule/s could span the electrode gap, if the $Mn_{12}O_{12}(O_2CCH_3)_{14}(O_2CR)_2(H_2O)_4$ (R=3-thiophenyl substitute) entity is of the appropriate size.

We then performed ac and dc electrical transport measurements to monitor the current (I)-voltage (V) characteristics on molecular junctions containing the Mn_{12}–Ac both in the dark and in the presence of illumination. The measurements were carried out in a helium gas ambient to minimize electrochemical interactions with the environment. The effects of the lead capacitance (and the interelectrode capacitance) were carefully calibrated out/subtracted. In five junctions, out of a total of 80, we obtained a significant enhancement in the magnitude of the currents under illumination from a halogen lamp white light source (peak wavelength $\sim$700 nm). Representative I-V characteristics are depicted in Fig. 2(a). By numerically differentiating the I-V curves [Fig. 2(a)] we obtained the differential conductance ($\boldsymbol{G}=dI/dV$)–voltage (V) curves [Fig. 2(b)]. Two features are noteworthy in the I-V and $\boldsymbol{G}$-V spectra: (a) an asymmetry, i.e., $I(V) \neq I(-V)$, and nonlinear behavior characteristic of molecular transport [see Fig. 2(a) inset], and (b) a dramatic change of the $\boldsymbol{G}$, on illumination, where a value of up to

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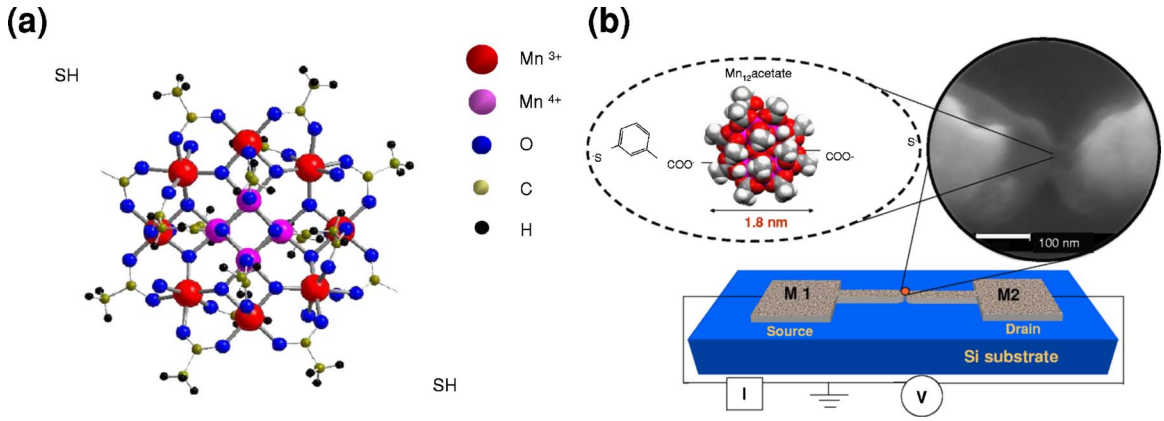

FIG. 1. (Color online) (a) Mn_{12}–Ac molecule showing the relative positions of the Mn^{3+} and the Mn^{4+} ions and the acetate/carboxylate (O_2CCH_3) groups. The linker molecule (3-thiobenzoic acid) is shown attached to either sides of the Mn_{12}–Ac. (b) The Mn_{12}–Ac molecule is laid across a nanojunction (inset shows a scanning electron microscope image), tethered to the electrodes M1 and M2 (source and drain), by the linker molecule, for electrical transport measurements.

77 μA/V was observed. (In the dark, $\boldsymbol{G}$ was ~4 μA/V—the same order as in measurements[6,12,17] on other molecules.) The unequal magnitudes of the peak $\boldsymbol{G}$ as a function of voltage polarity, as in Fig. 2(b), could arise from the unequal coupling of the molecule to the electrodes.[18–20]

While for any one particular Mn_{12}–Ac molecular junction, the *I-V* characteristics were stable and reproducible, we saw junction to junction variation in the maximum values of the differential conductance. While for two samples a peak $\boldsymbol{G}\sim 77$ μA/V was seen [Fig. 2(b)], for the other three samples $\boldsymbol{G}$ was in the range of 40–77 μA/V [Fig. 2(c)]. Possible explanations for variation of the peak $\boldsymbol{G}$ include a change of (i) molecular conformation and/or (ii) electrode coupling.[18,21–23] We think that the observed $\boldsymbol{G}$-*V* characteristics are unique and representative of the presence of

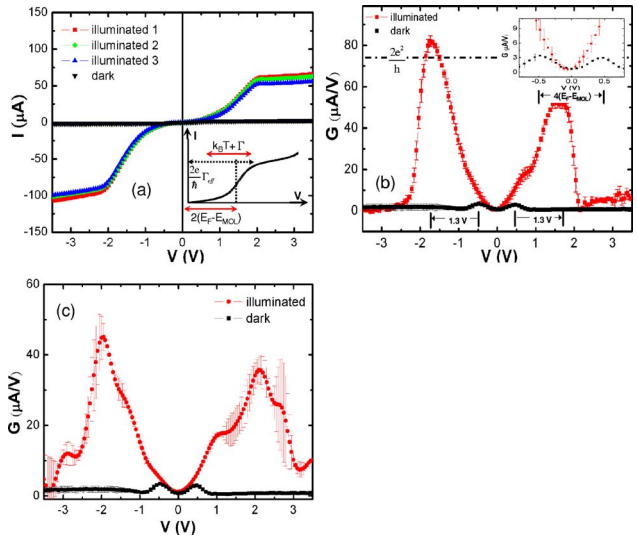

FIG. 2. (Color online) (a) Current (*I*)-voltage (*V*) characteristics of a Mn_{12}–Ac molecular junction. Three representative measurements are shown. The inset is a theoretical interpretation of the *I-V* characteristics of a single molecule (Ref. 19). (b) The differential conductance ($\boldsymbol{G}$)–voltage (*V*) graphs, obtained by differentiating (a), of the Mn_{12}–Ac molecule junction in the *dark* (black) and *under illumination* (red). A 60-fold increase in the $\boldsymbol{G}$, up to ~77 μA/V, is observed in the characteristics of the illuminated molecule. The inset shows a closeup of the $\boldsymbol{G}$-*V* spectra, for the dark/unilluminated molecule. The error bars were calculated from five consecutive voltage sweeps across the molecular junction. (c) $\boldsymbol{G}$-*V* plot for another Mn_{12}–Ac molecular junction is qualitatively similar to Fig. 2(b).

Mn_{12}–Ac molecule/s at the junction. We claim this on the basis of testing several (>200) control samples, viz., break junctions that are (a) molecule bare and (b) containing only the linker molecules. In the control samples, the *I-V* curves were nonreproducible, $\boldsymbol{G}$ was three to six orders of magnitude smaller, and illumination had negligible effect.

Other aspects of conduction through the Mn_{12}–Ac molecule/s were analyzed from the electrical transport characteristics. From the $\boldsymbol{G}$-*V* spectra of the molecule in the *dark* [Fig. 2(b) and inset], the distance between the differential conductance maxima was ~1 V which is in correspondence with the highest occupied molecular orbital–lowest unoccupied molecular orbital gap of 1.2 eV, inferred through electronic structure calculations.[24] When light was shone onto the molecular junction, there was an instantaneous (<0.1 s) increase in $\boldsymbol{G}$ from a low conductance, dark, state to a high conductance, illuminated, state with $\boldsymbol{G}_{\text{illuminated}}/\boldsymbol{G}_{\text{dark}}$ of 60, at 1.8 V. Additionally, the peak value of the $\boldsymbol{G}$ shifts by ~1.3 V [Fig. 2(b)], which was modeled in terms of a photoinduced voltage. By treating the molecule as a dielectric medium[25] ($\varepsilon\sim 3$) in between two parallel metal plates of area *A*, we derived a voltage change (ΔV) equal to ($e\Delta l/\varepsilon A$) due to a charge displacement of distance Δl [$e=1.602\times 10^{-19}$ C and $A\sim 3$ nm^2, Fig. 1(a)]. Such a charge rearrangement could occur in the Mn_{12}–Ac molecule, between the outer Mn^{3+} and the inner Mn^{4+} ions, with Δl of ~0.27 nm,[24] resulting in ΔV of ~0.5 V, of the same order as the measured 0.65 V (=1.3 V/2) shift.

Interpreted in terms of a molecular level model, energy level redistribution due to the impressed photovoltage causes charge transfer and modifies the $\boldsymbol{G}$-*V* characteristics. As the Mn_{12}–Ac molecule is intrinsically of mixed valence, it is likely[26] that this system can be readily and reversibly reduced, causing increased photoconductance. Further evidence for light induced charge transfer excitations arises from the optical absorption characteristics of Mn_{12}–Ac, in single crystalline and powder forms. It was seen[27] that charge transfer occurs from the inner Mn orbitals to the outer Mn orbitals at ~740 nm—wavelengths close to those used in our experiment. Enhanced photoconductance, for Mn_{12}–Ac, was also reported[28] in the 400–850 nm range.[29]

To probe the electrical transport mechanism further, we monitored the peak differential conductance ($\boldsymbol{G}_{\text{peak}}$) as a

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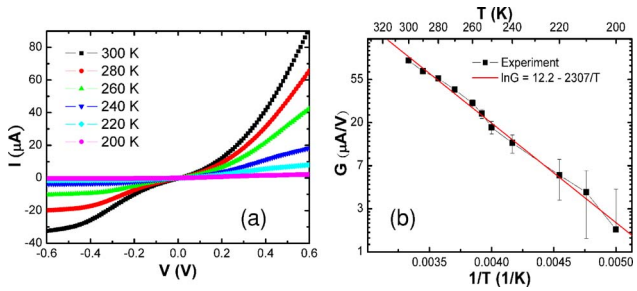

FIG. 3. (Color online) (a) Diodelike behavior and a decrease in $\boldsymbol{G}$ is seen for the Mn_{12}–Ac molecular junction with decreasing temperature. (b) $\boldsymbol{G}_{peak}$ decreases exponentially with the temperature, indicative of an activation-type behavior. From the slope of the straight line fit, we derive an activation energy $(E_a) \sim 0.4$ eV.

function of the temperature (T) [Fig. 3(a)] for the illuminated Mn_{12}–Ac molecule. An exponential decrease in $\boldsymbol{G}_{peak}$ was observed. From the slope of the $\boldsymbol{G}_{peak}$-T plot, we derived[24] an activation energy (E_a) for electrical conduction of $\sim$0.4 eV, which was close to the experimentally determined value for bulk Mn_{12}–Ac (Ref. 28) of 0.38 ($\pm$0.05) eV. Similar $\boldsymbol{G}(T)$ characteristics, at $T > 200$ K, have also been reported recently for other molecular junctions[30,31] with E_a being related to incoherent, intramolecular hopping processes[31] or T-dependent molecular conformation changes.[30]

The temperature variation of the $\boldsymbol{G}$ is additional proof that we were indeed measuring the Mn_{12}–Ac molecule/s and could rule out the possibility of conduction through clusters[32] or metal chains,[33] often present in break junctions. These characteristics also do not correspond to impurity or defect states in the oxide or the silicon substrate.[34] Preliminary experiments using a back and side gates[13] were not successful, possibly due to screening of the Mn_{12} cluster by the metal leads[32] or induced image charges.[17]

We conclude that our investigation, along with other recent studies,[35,36] could lay the foundation for integrating the nanoscale storage utility of Mn_{12}–Ac, with electrical transport at the single molecule level.

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