Nanoscale switch based on interacting molecular dipoles: Cooperativity can improve the device characteristics

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(Received 6 October 2010; accepted 14 December 2010; published online 18 February 2011)

We propose a nanoscale switch, giving a nonlinear function with two conductive states separated by a sharp transition region, on the basis of an array of molecular dipoles. We show theoretically that the local interactions between dipoles result in cooperative phenomena that can significantly improve the switching characteristics. We demonstrate the general validity of the concept in the cases of (*i*) an electrical switch robust to the finite size and variability effects inherent to the nanoscale and (*ii*) a sensing layer based on the voltage and ligand concentration dependence of the dipole array conductance. © *2011 American Institute of Physics*. [doi:10.1063/1.3549144]

I. INTRODUCTION

Digital computing requires switching between two (ON and OFF) conductive states separated by a sharp transition region. Molecular electronic switches based on redox centers,[1,2] metallic nanoparticles with ligand shells,[3–5] and molecular dipoles[6–13] have been demonstrated. Systems of experimental interest include metal clusters with redox addressable groups, gold nanoparticles functionalized with thiol chains, helical and cyclic β-peptides, and different nanostructures based on oligo(phenylene ethynylene) and ethynylbenzene molecules.

Designing a switch based on a finite number of nanoscale units assembled on an array can eliminate the need for reproducible access to each individual nanostructure. The control of single molecules and the connection to the external environment is difficult. In addition, nanoscale switches can show large variability in their individual physical properties.[14,15] On the contrary, small domains of moderately defective nanoscale units could still be used as reliable switches due tothe averaging effect of many nanostructures interacting cooperatively. Indeed, the cooperative effects should be enhanced at the nanoscale: the state of a given nanostructure in a small domain must be influenced by the states of the nearest neighbors because of the close proximity.[16] In particular, cooperative electronic phenomena are characteristic of two-dimensional molecular arrangements and allow electronic detection of different physical and chemical effects (see, e.g., Ref. 17).

Experimental systems of special relevance are nanomagnets[16,18] and nanodipoles[6–13,17] whose physical behavior is dictated by both the local field interactions between neighboring units and their individual coupling to an external field. Ideally, the local interactions should result in cooperative phenomena and sharp transitions between two well-defined conductance states. This behavior could be exploited to enhance the conductance modulation of the switches by the applied field, making reliable information processing possible even with nonidentical nanostructures.

We theoretically explore the properties of a switch based on an array of molecular dipoles acting cooperatively due tothe local interactions, assuming that the array as a whole has two states of significantly different electrical conductances G_L and G_H, with $G_L \ll G_H$. We also assume that the dipoles can be found in two states (that differ in their dipole moments) so that the conductance of the array is G_L (G_H) when all the dipoles are in the L (H) state. In general, however, the array has a conductance G intermediate between G_L and G_H which is determined by the states of the individual dipoles. Because these states can be tuned externally (by means of an applied voltage or by adsorbing a ligand from an external solution), electrically- and chemically-driven switching between the conductances G_L and G_H should be possible. The proposed concept is analyzed by using the statistical thermodynamics formalism as described by Hill[19,20] and Ben-Naim,[21] who have considered the effects of cooperativity and correlations in molecular dipoles for the cases of biological membranes and macromolecules in solution. This formalism allows one to obtain the average numbers of dipoles in the different individual states as a function of the array and the external conditions (e.g., temperature and applied voltage). From these average values, the conductance state of the array can be estimated. Because arrays of molecular dipoles are features of biophysical structures, the results could also be of importance for biological membranes and novel biosensors.[19–23] We do not attempt to model a particular system but rather to demonstrate the concept of a nanoscale switch which would be useful for information processing and chemical sensing.

II. PHYSICAL MODEL

The experimental motivation of the proposed nanoswitch is based on the following facts[6–11,17,22–24]: (*i*) a large number of externally tunable molecular dipoles of magnitude sufficient to interact with an applied electric field is available; (*ii*) molecular engineering of the dipole moments by selecting the appropriate chemical groups and their subsequent assembly into approximately defined architectures have been

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demonstrated; (*iii*) local interactions between dipoles are responsible for the observed cooperative phenomena; (*iv*) promotion or suppression of electron transfer in arrays of molecular dipoles has been reported and attributed to changes in the locally high dipolar electric field (in particular, the dipole moments in molecular junctions dictate the rectification phenomena in the current-voltage curves because it is the relative orientation of the internal dipole field and the externally applied field that controls the junction conductivity); and (*v*) moderately defective, locally imperfect molecular arrays could still be used in practical nanodevices because of the averaging effects produced by small domains of nanostructures acting cooperatively. In addition, previous theoretical studies have shown significant dipole moment variation[12,13,25] as well as conformational[7,12,26,27] and molecular orbital changes[13,28] that allow tuning the conduction state of molecules with the applied electric field.

The local interactions between dipolar moments are complicated because not only the electrical dipole-dipole interactions but also other effects, such as field-induced elastic deformations,[7,13] hydrogen bonding,[9,13] and the particular spatial packing of the dipoles[7,24] are important. In particular, while neighboring dipoles may be oriented in a stable antiparallel pair state canceling out the total dipole, other structures and dipole immobilization on metallic surfaces can also stabilize the parallel orientation.[7]

We propose a model that incorporates the basic features needed for a practical implementation while keeping the complexity to a minimum (Fig. 1). The local interactions between the dipoles in the array are restricted to nearest neighbors (see the lattice of Fig. 1; each dipole has c nearest neighbors). A number N of fixed dipoles on an approximately defined spatial arrangement can switch conformation between the L and H individual states of dipole moments p_L and $p_H \ll p_L$ because of the external field $E \approx -V/d$ (V is the applied voltage across the length d of the array). These dipole moments are effective values characteristic of the molecules forming the array in the L and H individual states. At low voltages V the L dipole state is stabilized (with respect to the H state) because of the attractive L-L interactions giving an interaction energy $\varepsilon_{LL} < 0$ for two neighboring dipoles in the L state and the effect of the external field [see Fig. 1(a)]. As the voltage V is increased, there is an electric field-driven transition of the dipoles from the L to the H state, provided that the exchange energy $\Delta\varepsilon \equiv 2\varepsilon_{LH} - \varepsilon_{LL} - \varepsilon_{HH}$ is positive [see Fig. 1(b)], where the interaction energies ε_{HH} and ε_{LH} correspond to a pair of neighboring dipoles in the H state and to the case of two dipoles in different states L and H, respectively. For realistic values of the system parameters, this transition may occur at low but close to ambient temperatures T. In fact, significant cooperative effects due to molecular dipole interactions have been observed in experiments conducted at ambient temperature for different arrangements (self-assembled organic monolayers on metallic surfaces,[29] mixed parallel and antiparallel dipole monolayers,[24] and molecular dipole sensing layers[17]; see also the reviews cited in Refs. 7 and 17). Interestingly, the microscopic details of the local interactions are not essential in the model and the only requirement is $\Delta\varepsilon > 0$. While this condition could be difficult to achieve with certain array geometries, the fact is that a variety of different approximately defined molecular architectures[7,17,24] are currently available. For instance, a relatively high value of ε_{LH} could result from the increased electrical and deformation energies associated with the charge and elastic mismatching in the lattice forming the dipole array when units in states of very different dipole moments coexist.[7,24]

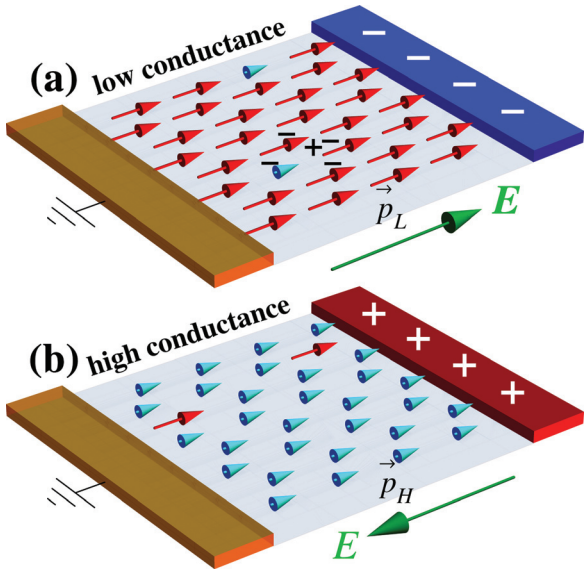

FIG. 1. (Color online) A lattice of N molecular dipoles with effective dipole moments p_L and $p_H (p_L \gg p_H)$ located between two electrodes. When a potential difference is externally applied to the electrodes, electron flow across the molecular dipoles is suppressed when it occurs in the direction opposite to a high dipole moment (a), and allowed in the reverse case (b) The external electric field triggers a conductance transition which is cooperative because of the local interactions between the dipoles. The distribution of charges around a central dipole is shown in (a).

The array of molecular dipoles is useful for implementing an electronic switch because the electron transfer should be determined by the direction of the dipole moments with respect to the high external field.[6,7] Electron flow across the dipole array should be suppressed when it occurs in the direction opposite to a high dipole moment [*low array conductance,* Fig. 1(a)], as observed experimentally in self-assembled monolayers[7] and molecular junctions,[6] while it should be allowed in the reverse case [*high array conductance*, Fig. 1(b)], even for a relatively low dipole moment. Note also that the molecule length could be decreased in the latter case [see Fig. 1(b)]. which could lead to an increased electronic conductance.[6,12,26] Because typical breakdown fields for thin films of self-assembled monolayers[17] should not be much higher than 10^8 V/m, we consider the maximum electric field $|E| = |V|/d \approx 1$ V/3 nm $= 3 \times 10^8$ V/m across the array.

While we restrict our analysis to the particular model of Fig. 1, some of the general effects to be described could also be exploited in other spatial architectures involving a dipole layer adsorbed on a substrate.[17] In particular, a sharp transition between the low and high conductance states of the array must occur at temperatures close to the critical temperature T_c characteristic of the system of interacting dipoles when V reaches a threshold voltage V_T. This fact should significantly improve the device characteristics, as we show later.

In the absence of an external electric field, the energy of a dipole lattice with $N_L = x_L N$ $(0 \le x_L \le 1)$ dipoles in the L state and $N_H = x_H N = N - N_L$ dipoles in the H state is $\varepsilon(0) = N_{LL}\varepsilon_{LL} + N_{HH}\varepsilon_{HH} + N_{LH}\varepsilon_{LH}$ where N_{ij} is the number of ij nearest-neighbors interactions and ε_{ij} their corresponding energies. Since $2N_{LL} = cN_L - N_{LH}$ and $2N_{HH} = cN_H - N_{LH}$, where c is the coordination number of the lattice, the total energy of the lattice is $\varepsilon(0) = \frac{c}{2}(N_L\varepsilon_{LL} + N_H\varepsilon_{HH}) + \frac{1}{2}N_{LH}\Delta\varepsilon$, where $\Delta\varepsilon \equiv 2\varepsilon_{LH} - \varepsilon_{LL} - \varepsilon_{HH}$ is the exchange energy. In the presence of an external electric field E, these dipole energies are shifted and the lattice energy is $\varepsilon(E) = \varepsilon(0) - (N_L p_L + N_H p_H)E$. The canonical partition sum of the lattice is

$$Z' = \sum_{N_L=0}^{N} (z_L)^{N_L}(z_H)^{N_H} \sum_{N_{LH}} e^{-\varepsilon(E)/k_B T} \tag{1}$$

where z_i is the internal partition function of a dipole in the i state (i = L, H). Taking the dipole layer in the H state as the reference state, $Z_H \equiv \left(z_H e^{-c\varepsilon_{HH}/2k_B T} e^{p_H E/k_B T}\right)^N$, and the partition sum becomes $Z \equiv Z'/Z_H$. This sum can be evaluated exactly in the case of a one-dimensional system using the transfer matrix formalism (see the Appendix). For other systems, the mean-field approximation,[19,20] $\varepsilon(0) \approx (c/2)(N_L\varepsilon_{LL} + N_H\varepsilon_{HH} + Nx_L x_H\Delta\varepsilon)$ transforms the sum into

$$Z = \sum_{N_L=0}^{N} s(E)^{N_L} \sum_{N_{LH}} \sigma^{N_{LH}} \approx \sum_{N_L=0}^{N} \binom{N}{N_L} [\sigma^c s(E)]^{N_L} \sigma^{-cN_L^2/N}$$
$$= \sum_{N_L=0}^{N} \binom{N}{N_L} s(E)^{N_L} \sigma^{cN_L(1-N_L/N)} \tag{2}$$

where $s(E) \equiv (z_L/z_H)e^{-c(\varepsilon_{LL}-\varepsilon_{HH})/2k_B T} e^{(p_L-p_H)E/k_B T}$ and $\sigma \equiv e^{-\Delta\varepsilon/2k_B T}$. This approximation predicts a phase transition with a critical temperature $T_c = c\Delta\varepsilon/4k_B$, so that $\sigma^c = e^{-2T_c/T}$.

The average fraction of dipoles in the L state is

$$\langle x_L \rangle = \frac{1}{N} \frac{\sum_{N_L=0}^{N} \binom{N}{N_L} N_L s(E)^{N_L} \sigma^{cN_L(1-N_L/N)}}{\sum_{N_L=0}^{N} \binom{N}{N_L} s(E)^{N_L} \sigma^{cN_L(1-N_L/N)}}. \tag{3}$$

The noncooperative behavior corresponds to $\sigma = 1$ $(T_c = 0)$ and is described by the Langmuir isotherm $\langle x_L \rangle = s(E)/[1 + s(E)]$.

While the results to be presented make use of Eq. (3), it is now worth introducing an approximation to better understand the behavior of the dipole array at different applied voltages. In the mean-field approximation the energy of the lattice can be presented as $\varepsilon = N_L\varepsilon_L + N_H\varepsilon_H$ where $\varepsilon_L \equiv (\varepsilon_{LL} + x_H^2\Delta\varepsilon)c/2$ and $\varepsilon_H \equiv (\varepsilon_{HH} + x_L^2\Delta\varepsilon)c/2$ are the effective energies of a dipole in the L and H states, respectively. If we approximate the lattice energy as $\varepsilon \approx N_L\langle\varepsilon_L\rangle + N_H\langle\varepsilon_H\rangle$, the partition function becomes $Z' \approx \left(z_L e^{-\langle\varepsilon_L\rangle/k_B T} + z_H e^{-\langle\varepsilon_H\rangle/k_B T}\right)^N$, and $\langle x_L \rangle$ can be evaluated from

$$\frac{\langle x_L \rangle}{1 - \langle x_L \rangle} \approx \frac{z_L e^{-\langle\varepsilon_L\rangle/k_B T}}{z_H e^{-\langle\varepsilon_H\rangle/k_B T}} = \sigma^{c(1-2\langle x_L\rangle)} s(E) \tag{4}$$

which resembles the Frumkin-Fowler-Guggenheim isotherm.[19] Because $s(E) \equiv s(0)e^{-(p_L-p_H)V/k_B T d}$ and $p_L > p_H$, an increase in the applied voltage leads to a decrease of both $s(E)$ and $\langle x_L \rangle$. Equation (4) predicts the first-order phase transition, shown in Fig. 1, from the low to the high conductance states of the array with increasing voltage, provided that $T < T_c$. This transition is continuous at the critical point, which is characterized by $(\partial s/\partial\langle x_L\rangle)_{T_c} = 0$ and $(\partial^2 s/\partial\langle x_L\rangle^2)_{T_c} = 0$, and corresponds to $\langle x_L \rangle_c = 1/2$ and $\sigma^{-c} = e^2$ (or, equivalently, $T = T_c \equiv c\Delta\varepsilon/4k_B$). A threshold voltage corresponding to the critical value $s(E)_c = 1$ can be defined as

$$V_T \equiv \frac{c\Delta\varepsilon}{4} \frac{\ln s(0)_c}{p_L - p_H} d = \frac{c}{4} \frac{\Delta\varepsilon \ln(z_L/z_H)_c - 2(\varepsilon_{LL} - \varepsilon_{HH})}{p_L - p_H} d. \tag{5}$$

Equations (3) and (4) allow the calculation of $\langle x_L \rangle$ as a function of the array characteristics (dipole moments, interaction energies, and the number of dipoles) and the external conditions (temperature and applied voltage). In the next section we show that, due to the cooperative nature of the transition, $\langle x_L \rangle$ can be switched sharply between the extreme values 0 and 1 by varying the external conditions, which allows the array to switch between G_L and G_H in Fig. 1. We introduce the simplifying assumption[26] that the relative array conductance roughly follows the average fraction of dipoles in the H state, $(G - G_L)/(G_H - G_L) = \langle x_H \rangle = 1 - \langle x_L \rangle$. In the case of a one-dimensional array, for instance, the conductance should be low when $\langle x_L \rangle > 0$ and increase rapidly when $\langle x_L \rangle$ switches to 0 but other geometries can give more complicated dependences. Nevertheless, if the array conductance G is dictated by the bistability of $\langle x_L \rangle$, intermediate conductances should only be observed over a narrow potential range. With this assumption, the voltage-induced transition for the average fraction of dipoles in the H state should be clearly shown in the conductance versus voltage curves. Finally, note that while we have used the conductance as the array output variable, relatively small reshapes of the molecular electron densities in the array, rather than net electron currents could also be used because of the concerted, cooperative behavior of many molecules acting together to give an enhanced electrical signal.[8,17] Clearly, these changes in the local electron density should correlate with the average fractions of dipoles in the different states, as it was assumed here.

III. RESULTS AND DISCUSSION

We solve Eq. (3) for $c = 4$, $d = 3$ nm, $p_L - p_H = 8$ D (1 D $= 3.3 \times 10^{-30}$ C m), and the dipole-dipole interaction energies $k_B T_c = -2\varepsilon_{LL} = 4\varepsilon_{LH} = \Delta\varepsilon$. The value of $p_L - p_H$ has been deliberately chosen in the high range of typical dipole moments[7–9,17,24,26] to better emphasize the concept involved [note also that the external electric field should act to increase this effective dipole moment difference; see Figs. 1(a) and (b) as well as Refs. 6 and 12]. Using the approximation $z_L \approx z_H$, the threshold voltage is $V_T = 0.47$ V when $T_c = 300$ K. Equivalently, the ratio between the energy due to the external field and the thermal energy at the critical temperature is $(p_L - p_H)|E|/k_B T_c \approx 2.1$ for $V = 1$ V (the higher voltage assumed later in Figs. 3 and 4, which can be

considered as a realistic value.[12,19] Note that the exchange energy $\Delta\varepsilon$ and the energy due to the external field $(p_L - p_H)E$ should be at least of the order of the thermal energy k_BT to overcome the dipole moment tendency to change randomly due tothermal fluctuations (stochastic switching should be avoided for the voltage-triggered switching to be efficient).[9,10]

Figure 2(a) shows the conductance ratio $(G - G_L)/(G_H - G_L) = \langle x_H \rangle$ of the dipole array at three different temperatures around the critical $T_c = \Delta\varepsilon/k_B = 300\,\mathrm{K}$. The case of noncooperative behavior ($\Delta\varepsilon/k_B = T_c = 0$, no sharp transition) is also shown for the sake of comparison. The results of Fig. 2(a) quantitatively demonstrate the concept described in Fig. 1, and clearly show how cooperativity enhances the switching response by significantly decreasing the width of the transition region between the ON (high conductance G_H) and the OFF (low conductance G_L) states of the array. This transition region can be narrowed further by increasing the dipole moment p_L and the critical temperature. Fig. 2(b) shows the slope of the conductance ratio $(G - G_L)/(G_H - G_L)$ as a function of the voltage at

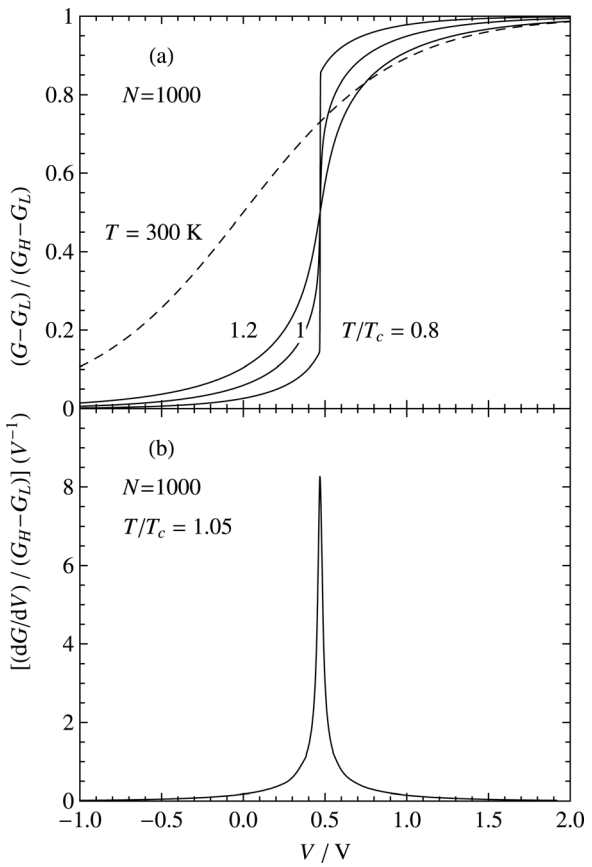

FIG. 2. (a) Cooperativity enhances the switching response by significantly decreasing the width of the applied voltage region characteristic of the transition between the ON (high conductance G_H) and the OFF (low conductance G_L) states of the array. The results shown correspond to $N = 1000$ dipoles at temperatures $T/T_c = 0.8$, 1.0, and 1.2 for $T_c = \Delta\varepsilon/k_B = 300$ K, giving a threshold voltage of $V_T = 2k_BT_cd/(p_L - p_H) = 0.47$V. The discontinuous curve shows the noncooperative behavior at 300 K for the same system parameters (except for $\epsilon_{ij} = 0$). (b) The slope of the conductance vs voltage curves shows a peak around the threshold voltage. The height of this peak is proportional to $(p_L - p_H)$ and inversely proportional to T_c, so that the switching can be enhanced by increasing the dipole moment p_L and the critical temperature.

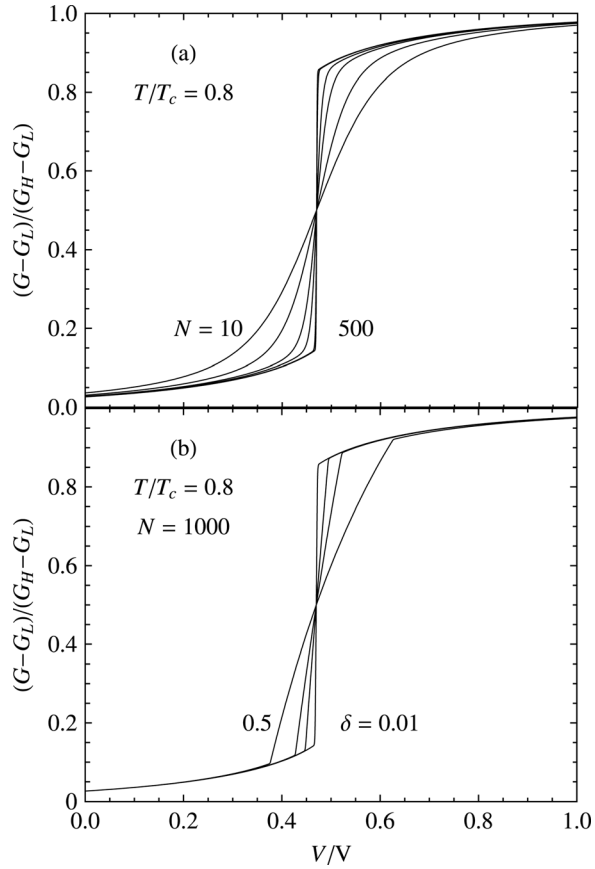

FIG. 3. (a) Finite-size effects widen the transition region between the high and low conductance states of the array, but the performance of the switch becomes practically independent of N for a few hundred dipoles in the array. The curves shown correspond to $T/T_c = 0.8$ and $N = 10$, 20, 50, 100, and 500 dipoles. (b) The switch is robust under moderate dipole moment variability δ. When the dipole difference $p_L - p_H$ is allowed to fluctuate around a mean value $\langle p_L - p_H \rangle = 8\,\mathrm{D}$ with a flat probability distribution of relative width $\delta \equiv \Delta(p_L - p_H)/\langle p_L - p_H \rangle$, the conductance vs voltage curves ($N = 1000$, $T/T_c = 0.8$) still show relatively narrow transition regions for moderate values of δ. The curves shown correspond to $\delta = 0.01$, 0.1, 0.2, and 0.5.

$T = 1.05T_c$ (note that the derivative diverges at the critical point for macroscopic systems). Clearly, this indicates that close to the critical temperature the dipole array should be highly sensitive to small voltage changes around the threshold voltage, showing a sharp transition between the two conductance states because of the local dipole interactions. Hence, cooperativity can significantly improve the switching characteristics.

One serious concern in the practical realization of the nanoswitch is the relatively small number of dipoles forming the array. These finite-size effects can also be analyzed with the help of Eq. (3) and the obtained results are shown in Fig. 3(a). The conductance ratio versus applied voltage of an array with 10 and 20 dipoles at $T/T_c = 0.8$ shows a transition region of a few tenths of a volt only, which is much sharper than that observed in the noncooperative case. Arrays with 100 and 200 dipoles have narrow transition regions, and arrays of 500 dipoles shows a transition that is practically discontinuous (i.e., an array of several hundred dipoles, for practical purposes, exhibits a macroscopic behavior).

Moreover, the switch appears to be robust under moderate dipole moment variability. Figure 3(b) shows the conductance ratio versus applied voltage of 1000 dipoles at

$T/T_c = 0.8$ when the dipole difference $p_L - p_H$ is allowed to fluctuate (because of the inherent fabrication uncertainties at the nanoscale) around a mean value $\langle p_L - p_H \rangle = 8\,\mathrm{D}$. For the sake of simplicity, a flat probability distribution with a relative width $\delta \equiv \Delta(p_L - p_H)/\langle p_L - p_H \rangle$ has been considered. It is observed that the width of the transition region is still lower than 0.05 V when the relative width of the dipole distribution is close to 10% ($\delta = 0.1$).

We note that, because the dipole array acts as an effective nanodiode [see Fig. 2(a)], the logical gates AND and OR could be readily implemented by a simple combination[5,25,30] of two dipole arrays in approximately defined architectures. In addition, the application of a time-dependent potential would permit the processing of an external signal from the resulting conductance modulation.[31]

The dipole array could also be used as the active layer for a sensor immersed in a solution of a ligand that binds to the molecular dipoles.[17,19,21,23] In this case, the ligand concentration (in addition to the applied voltage) could modulate the array conductance. The grand canonical partition function[19–21] of the system is

$$\Xi(T,N,\lambda_l) = \left(z_H e^{-c\varepsilon_{HH}/2k_BT} e^{p_H E/k_BT}\right)^N \sum_{N_L=0}^{N} \binom{N}{N_L} s(E)^{N_L} \times (1+\lambda_l z_{lL})^{N_L} (1+\lambda_l z_{lH})^{N_H} \sigma^{cN_L(1-N_L/N)} \quad (6)$$

where $\lambda_l \equiv e^{\mu_l/k_BT}$ is the absolute activity of the ligand (which is proportional to its concentration c_l in a dilute solution[20,32]), μ_l is the ligand chemical potential and z_{li} is the canonical partition function of the ligand bound to a dipole in the i state ($i = \mathrm{L}, \mathrm{H}$), including the Boltzmann factor for the adsorption energy. If $z_{lH} > z_{lL}$, an increase in λ_l gives an increase in the fraction of dipoles in the H state. Assuming that the ligand binds only to the dipoles in the H state ($z_{lL} = 0$), the average fraction of dipoles in the L state is given by Eq. (3) with $s(E)$ replaced by $s_l(E) \equiv s(E)/(1+\lambda_l z_{lH})$, which decreases with the ligand concentration. This occurs because the presence of the ligand shifts the equilibrium between the L and the H dipole states, favoring the H state, and then switching the array conductance from the low to the high value.

Figure 4 shows the conductance ratio as a function of $\lambda_l z_{lH} \equiv K c_l$, the product of the equilibrium binding constant and the ligand concentration,[20,32] for different applied voltages. The system parameters are those of Fig. 2 and the temperature is fixed at the critical value. Note that the transition region is not as narrow as in the case of the voltage-driven switch [see Fig. 2(a)] because $s_l(E)$ is (roughly) proportional to $(Kc_l)^{-1}$ in Fig. 4 while it changed exponentially with the voltage in Fig. 2(a). Clearly, the performance of the dipole array as the active layer of a sensor is enhanced by the cooperative effects (see the discontinuous curve in Fig. 4). By applying different voltages V, the ligand concentration range where the sensor could be operative can be significantly extended. Moreover, the active layer could also give a potentiometric signal (as opposed to the conductance-based output of Fig. 4) because the molecular dipole variations in the array should produce measurable electric potential changes (see Ref. 23 in this context). This may occur if the binding of the ligand to the molecular dipole occurs with local charge redistribution or transfer.[17]

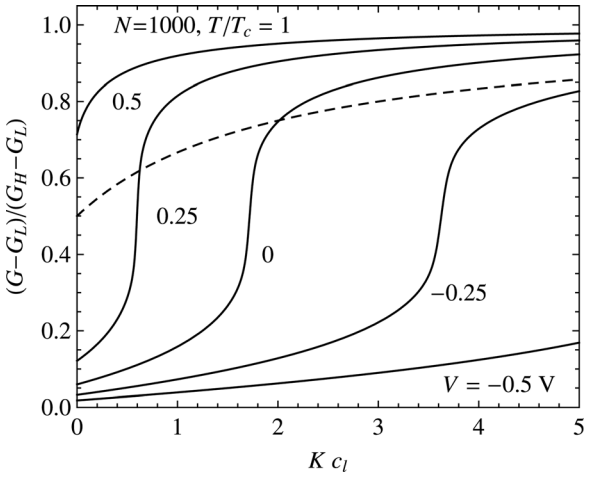

FIG. 4. The concentration of a ligand that binds to the molecular dipoles modulates the array conductance and allows for the implementation of a voltage-tunable sensor. The conductance ratio is represented as a function of the product of the equilibrium binding constant and the ligand concentration for $N = 1000$ dipoles, $T = T_c = 300$ K, and different applied voltages. The conductance transition occurs over a narrow concentration range and, remarkably, it can be shifted by changing the applied voltage V. The discontinuous curve shows the noncooperative behavior ($V = 0$ V, $T = 300$ K), thus providing evidence that the cooperative effects significantly improve the system performance.

IV. CONCLUSION

In conclusion, addressing a nanostructure formed by a small domain of molecular dipoles not only avoids the need for accessing single molecules in a reproducible manner[33] but also permits us to exploit the emerging cooperative properties in the design of switches robust against finite-size and variability effects inherent to the nanoscale. As a proof-of-concept, a nanoscale electrical switch and a sensing layer have been theoretically demonstrated on the basis of an ideal array of interacting dipoles. Finally we note that the reversible tuning of the dipole array between two approximately defined conductance states should also allow bit assignment and data storage modes.

ACKNOWLEDGMENTS

Financial support from the Ministry of Science and Innovation of Spain (project MAT2009-07747) and FEDER is acknowledged.

APPENDIX

The transfer matrix technique allows for the exact evaluation of the partition sum

$$Z = \sum_{N_L=0}^{N} s^{N_L} \sum_{N_{LH}} \sigma^{N_{LH}} \quad (A1)$$

in the case of one-dimensional systems. If $Z_{N,i}$ denotes the partition sum of a system of N dipoles where the last one is in state i ($i = \mathrm{L}, \mathrm{H}$), the following recurrence relations follow

directly from Eq. (A1): $Z_{N,H} = Z_{N-1,H} + \sigma Z_{N-1,L}$ and $Z_{N,L} = \sigma s Z_{N-1,H} + s Z_{N-1,L}$. The matrix $\mathbf{M} = \begin{pmatrix} 1 & \sigma \\ \sigma s & s \end{pmatrix}$ formed by the coefficients is known as the transfer matrix. Considering periodic boundary conditions (i.e., a ring of dipoles), the partition sum is[34,35]

$$Z = \mathrm{Tr}[\mathbf{M}^N] = \lambda_1^N + \lambda_2^N \tag{A2}$$

where the two eigenvalues of $\mathbf{M}$ are given by $2\lambda_i = (1+s) \pm [(1-s)^2 + 4\sigma^2 s]^{1/2}$ $(i = 1,2)$. The average fraction of dipoles in the L state is

$$\langle x_L \rangle = \frac{s}{N}\left(\frac{\partial \ln Z}{\partial s}\right)_{\sigma,N} \approx \frac{s}{\lambda_1^N + \lambda_2^N} \times \left[\lambda_1^{N-1}\left(\frac{\partial \lambda_1}{\partial s}\right)_\sigma + \lambda_2^{N-1}\left(\frac{\partial \lambda_2}{\partial s}\right)_\sigma\right]. \tag{A3}$$

In the thermodynamic limit $N \gg 1$, the Nth power of the smaller eigenvalue, λ_2^N, can be neglected in Eq. (A2) and

$$\langle x_L \rangle \approx \frac{s}{\lambda_1}\left(\frac{\partial \lambda_1}{\partial s}\right)_\sigma = \frac{s - 1 + [(1-s)^2 + 4\sigma^2 s]^{1/2}}{2[(1-s)^2 + 4\sigma^2 s]^{1/2}}. \tag{A4}$$

When $s \approx 1$ and $\langle x_L \rangle \approx 1/2$, Eq. (A4) can be approximated by $\langle x_L \rangle - 1/2 \approx (s-1)/4\sigma$, which implies that $\langle x_L \rangle$ changes from $\langle x_L \rangle \approx 0$ to $\langle x_L \rangle \approx 1$ over a region of thickness $\Delta s \approx 4\sigma$ around $s \approx 1$. Hence, the lower the value of the cooperativity factor σ, the sharper the transition. Because $\sigma = \mathrm{e}^{-T_c/T}$ in one-dimensional systems, the transition widens with increasing temperature (it has a width $\Delta s \approx 1.5$ at the critical temperature). Note, finally, that this is not a first-order phase transition because one-dimensional systems cannot exhibit a first order phase transition. Except for this fact, the results obtained with Eq. (A4) are qualitatively similar to those of Fig. 2. A direct extension of the above procedure also allows us to obtain the relevant equations for the case of the sensing layer (not shown here). Other problems concerning one-dimensional chains of dipoles are considered in Refs. 34 and 36.

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