Electric Field Control of Valence Tautomeric Interconversion in Cobalt Dioxolene

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We demonstrate that the critical temperature for valence tautomeric interconversion in cobalt dioxolene complexes can be significantly changed when a static electric field is applied to the molecule. This is achieved by effectively manipulating the redox potential of the metallic acceptor forming the molecule. Importantly, our accurate density functional theory calculations demonstrate that already a field of 0.1 V/nm, achievable in Stark spectroscopy experiments, can produce a change in the critical temperature for the interconversion of 20 K. Our results indicate a new way for switching on and off the magnetism in a magnetic molecule. This offers the unique chance of controlling magnetism at the atomic scale by electrical means.

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The integration of molecular electronics [1] with spintronics [2] has given birth to the new and fascinating field of molecular spintronics [3,4]. This encompasses a variety of phenomena, ranging from spin-injection and transport in organic semiconductors [4] to the engineering of magnetic surfaces by means of organic molecules [5]. One fascinating branch concerns electron transport in single magnetic molecules [6]. Here the aim is that of investigating the mutual influence between the spin state of the molecule and the electrical current that flows across it.

The detailed knowledge of the I-V curve of a two-terminal device may enable one to read the spin state of the molecule [7,8]. Much more challenging is the task of manipulating such a spin state. Magnetic fields do not have enough spatial resolution to address selectively single molecules; hence, the possibility of using electric fields instead appears particularly attractive. Recently it was proposed that spin crossover can be achieved electrically by exploiting the Stark effect [9,10]. The idea is that the high-spin (HS) and the low-spin (LS) states of a molecule in general have different polarizabilities and permanent electrical dipoles. Thus the energy Stark shift depends on the magnetic state and there may exist a particular condition where a HS to LS crossover is possible, with spectacular consequences on the molecule I-V curve [11].

Intriguingly there is an entire class of magnetic molecules, mainly incorporating Fe(II), known to exhibit temperature-induced LS to HS spin crossover (SC) [12]. Such entropy-driven transition is regulated by the relative Gibbs free energy between the HS and LS states,

$$\Delta G = G_{\mathrm{HS}} - G_{\mathrm{LS}} = \Delta H - T\Delta S, \qquad (1)$$

where $\Delta H = H_{\mathrm{HS}} - H_{\mathrm{LS}}$ and $\Delta S = S_{\mathrm{HS}} - S_{\mathrm{LS}}$ are, respectively, the enthalpy and the entropy variation ($\Delta G > 0$ means that the thermodynamically stable configuration is LS). In SC molecules $\Delta H > 0$ but $S_{\mathrm{HS}} > S_{\mathrm{LS}}$, so that as the temperatures increases the entropic term dominates over the enthalpic one and the molecules transit from a LS to a HS. The microscopic mechanism for the SC consists in moving an electron from a nonbonding to an antibonding state. The transfer produces the breathing of the metal ion coordination sphere with consequent phonon modes softening. Thus, both the spin and the vibrational entropy of the HS state dominate over those of the LS ones. Interestingly, it was recently demonstrated that the SC is strongly affected by electrostatic perturbations in the crystal environment [13].

An effect closely resembling the SC is observed in Co-dioxolene complexes, which exhibit an interconversion between redox isomers [14–16]. This is called valence tautomeric interconversion (VTI). The complex $[\mathrm{Co}(\mathrm{Me_2tpa})(\mathrm{DBCat})](\mathrm{PF_6})$ ($\mathrm{Me_2tpa}$ = methil derivatives of tris(2-pyridylmethyl)amine, DBCat = 3, 5-di-tert-butylcatecolato) [17,18], is an example of these compounds (see Fig. 1). This has two key ingredients: the Co

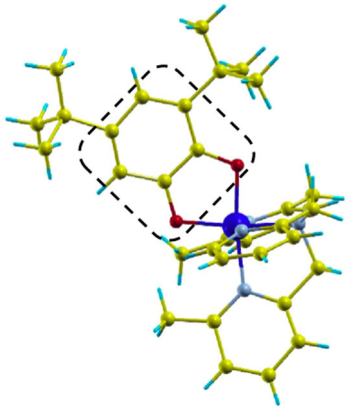

FIG. 1 (color online). Co-dioxolene investigated in this work. The cationic unit of the complex is $\mathrm{Me_2tpa}$ = methil derivatives of tris(2-pyridylmethyl)amine, DBCat = 3, 5-di-tert-butylcatecolato and o-dioxolene is enclosed in the dashed box. Color code: C = yellow (medium-light gray), O = red (medium gray), Co = blue (dark gray large sphere), N = grey (small sphere), H = light blue (light gray).

ion and the o-dioxolene group. In general, o-dioxolene binds to Co in three different oxidation states: di-negative catecholate (Cat), mononegative semiquinonate (SQ) and neutral quinone (Q). The low covalent character of the bond between o-dioxolene and Co allows charge and spin to be localized so that the molecule maintains well defined oxidation states and magnetic moments.

$[Co(Me_2tpa)(DBCat)](PF_6)$ is found in crystals as either diamagnetic Co(III)-catecholate (LS Co^{3+}-Cat) at low temperature, or as paramegnetic high-spin Co(II)-semiquinonate (HS Co^{2+}-SQ) at high temperature. The LS Co^{3+}-Cat $\rightarrow$ HS Co^{2+}-SQ transition is driven by an intramolecular electron transfer from Cat to Co. As for standard SC also, the VTI is entropy driven and can be understood with Eq. (1), where LS and HS now correspond, respectively, to LS Co^{3+}-Cat and HS Co^{2+}-SQ.

Much recent effort has been dedicated to increasing the cooperative nature of the VTI in crystals for data storage applications. Co-dioxolene complexes, however, may also find an interesting place in molecular spintronics as the strong interplay between charge transfer and spin transition suggests that electric fields may profoundly affect the molecule magnetic properties. This is demonstrated here. Our density functional theory (DFT) calculations show that charge transfer with consequent spin crossover can be induced by a static electric field. In particular we find that rather modest fields (~ 0.05 V/Å) are enough for changing the VTI critical temperature by as much as 100 K. This intriguingly new effect, which may allow one to fine-tune electrostatically the magnetic state of a molecule, can be readily verified experimentally.

Achieving an accurate quantitative description of the Co-dioxolene electronic structure is a difficult task. One in fact has to simultaneously assign the oxidation states of both Co and the dioxolene group, the Co spin state and also, for HS Co^{2+}-SQ, the magnetic exchange coupling between Co and SQ. Local and semilocal DFT approximations are inadequate since they largely overestimate the electronic coupling of the Co 3*d* shell with the SQ/Cat molecular orbitals. This is the same shortfall encountered when describing *F* centers in wide-gap semiconductors and it is rooted in the self-interaction error [19]. We overcome this limitation by means of two approaches: (1) the atomic self-interaction correction (ASIC) scheme [20], so far used for band structure [21] and electron transport [22] and (2) the B3LYP hybrid exchange correlation functional [23].

Calculations are performed with a development version of the SIESTA code [24] implementing the ASIC scheme. Norm-conserving Troullier-Martin pseudopotentials are employed together with a basis set of double-zeta plus polarization quality. GAMESS [25] and NWCHEM [26] are used for the B3LYP calculations (with the 6–31G* basis). We consider the experimental molecular geometries determined by standard x-ray data analysis for single crystals (Table I). This is the best computational strategy [27] since there is no crystallographic data for the molecule in the gas phase (the phase simulated here) and it is unclear whether DFT has enough accuracy to correctly describe the metal-to-ligand bond lengths across the VTI. Note that ASIC in its present formulation is not variational, so that we will use it only for calculating the single particle density of states (DOS), but not the total energy, for which we will employ B3LYP.

TABLE I. Co-O and Co-N bond lengths, *d*, for LS Co^{3+}-Cat and HS Co^{2+}-SQ as determined by x ray and used in our calculations. The last column reports the B3LYP total energy, calculated with respect to the total energy of LS Co^{3+}-Cat. LS Co^{2+}-SQ is a fixed spin configuration calculated at the molecular geometry of HS Co^{2+}-SQ.

Isomer	$d_{Co\text{-}O}$ (Å)	$d_{Co\text{-}N}$ (Å)	*E* (eV)
LS Co^{3+}-Cat	1.883, 1.898	2.0, 1.947, 2.011, 2.022	0
HS Co^{2+}-SQ	2.004, 2.083	2.169, 2.160, 2.1474, 2.151	2.229
LS Co^{2+}-SQ	1.883, 1.898	2.0, 1.947, 2.011, 2.022	2.789

Table I displays the energy difference between LS Co^{3+}-Cat, LS Co^{2+}-SQ and the HS Co^{2+}-SQ showing that B3LYP qualitatively reproduces the relative order of the states. The absolute values of the relative energies appear, however, drastically overestimated with respect to experimentally available enthalpies (a few hundreds meV) [28,29]. Such a quantitative disagreement between DFT and experiments, pathological to many SC compounds [13,27,30], cannot be attributed to having neglected the vibrational zero-point energies, which are much smaller than the electronic ones. Note that relaxing the molecule with B3LYP changes the Co-O and Co-N bond lengths by as little as 0.2% but reverses the states' order, with HS Co^{2+}-SQ becoming the lowest energy configuration (by 0.44 eV). This highlights the sensitivity of the total energy to the detailed molecule geometry (unknown for the gas phase) and to the DFT flavor utilized. In order to partially remove such an uncertainty we analyze a quantity, which depends on the slope of total energy difference with the electric field, and not on its absolute value.

The ASIC calculated DOS is displayed in Fig. 2. Although the details of the Kohn-Sham spectrum depend on the specific functional used, the position of the Co-3*d* shell relative to the Cat (SQ) molecular orbitals is returned consistently by both ASIC and B3LYP. Since there are no spectroscopic data for Co-dioxolene complexes to compare with, Fig. 2 should be interpreted as a schematic energy level diagram of the molecule. We notice that ASIC returns the expected weak hybridization between the Cat (SQ)-π^* and the Co-3*d* states. The Co-3*d* shell is clearly recognized in the DOS and it is filled according to the formal oxidation. The symmetry of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) can be appreciated by looking at the charge density contour plot. For instance for LS

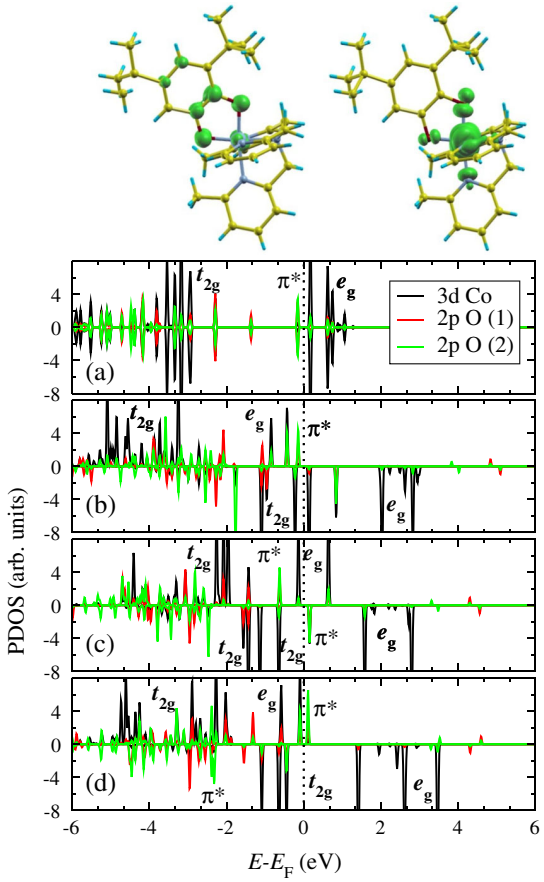

FIG. 2 (color online). Density of states projected over the $3d$ states of the Co and the $2p$ states of the two O atoms, as calculated with ASIC, for (a) LS Co^{3+}-Cat, (b) HS Co^{2+}-SQ, (c) LS Co^{2+}-SQ, and (d) HS Co^{2+}-SQ with antiferromagnetic coupling between the magnetic moment of the Co and the one of the SQ. The top panels display the charge density distribution (local DOS) for the HOMO (left) and LUMO (right) of LS Co^{3+}-Cat.

Co^{3+}-Cat the HOMO is the Cat-π^* state while the LUMO corresponds to the Co e_g.

After having demonstrated that DFT provides a satisfactory description of the electronic properties of the molecule, we now proceed to investigate the influence that an electric field, $\mathcal{E}$, has on the VTI. In particular we consider the situation where $\mathcal{E}$ is applied along the direction joining Co with Cat (SQ). Computational overheads are reduced by replacing the N ligands with ammonia molecules. This substitution does not bring any relevant modification to the electronic structure, but it has an effect on the energetics of the problem, since it decreases the energy difference between HS Co^{2+}-SQ and LS Co^{3+}-Cat to 1.591 eV. Note that in this case further geometrical relaxation has little effect on the electronic structure and the level ordering. Figure 3 shows the difference, $\Delta E = E_{\mathrm{HSCo^{2+}SQ}} - E_{\mathrm{LSCo^{3+}Cat}}$, between the ground state energies of LS Co^{3+}-Cat and HS Co^{2+}-SQ ($\Delta E > 0$ means $E_{\mathrm{HSCo^{2+}SQ}} > E_{\mathrm{LSCo^{3+}Cat}}$). Such a quantity is plotted as a

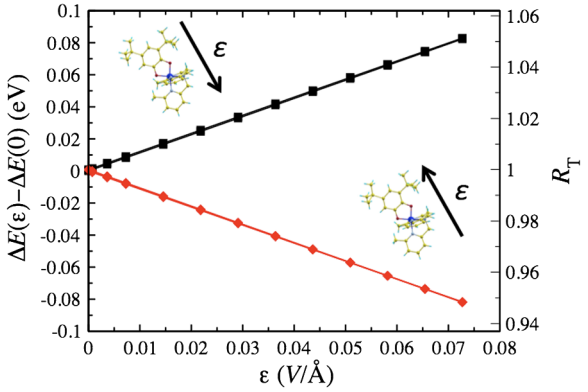

FIG. 3 (color online). Energy difference between HS Co^{2+}-SQ and LS Co^{3+}-Cat, ΔE, as a function of the electric field $\mathcal{E}$ (the energies are calculated with the B3LYP functional). The black line (square symbols) corresponds to the electric field pointing toward the quinone, while the red one (diamond symbols) to the electric field pointing toward the Co. The figure also reports R_T for the same molecule on the right-hand side of the y axis.

function of the electric field and with respect to the $\mathcal{E} = 0$ situation. The most important observation is that ΔE depends linearly on $\mathcal{E}$.

We recall here that the energy change of a quantum mechanical system under the influence of an external electric field is governed by the Stark effect, $\Delta E(\mathcal{E}) \propto \vec{p} \cdot \vec{\mathcal{E}} + \frac{1}{2}\sum_{ij}\mathcal{E}_i\alpha_{ij}\mathcal{E}_j$ where $\vec{p}$ is the permanent electrical dipole and α_{ij} the polarizability tensor. Thus the linear dependance found in Fig. 3 indicates that the first order Stark effect dominates the molecule response at these field intensities. Our DFT calculations confirm such a hypothesis and return a finite dipole moment at $\mathcal{E} = 0$ ($|\vec{p}|$ is 16.9 Debye for LS Co^{3+}-Cat and 26.3 Debye for HS Co^{2+}-SQ). Interestingly the energy decreases when $\mathcal{E}$ points from Co to the dioxolene and increases when it is along the opposite direction; i.e. ΔE is reduced for the field direction facilitating the VTI electron transfer. A linear fit of $\Delta E(\mathcal{E})$ gives us a slope of 1.12 eV/(V/Å). We can now extrapolate a critical electric field $\mathcal{E}_C = 1.4$ V/Å at which the states LS Co^{3+}-Cat and HS Co^{2+}-SQ become energetically degenerate. When $\mathcal{E}$ exceeds $\mathcal{E}_C$ a VTI occurs leading to SC and HS Co^{2+}-SQ becomes the new ground state of the molecule.

The calculated $\mathcal{E}_C$ unfortunately is quite large, so that in reality one cannot expect to observe an electric field induced VTI. Two important observations must be made. Firstly, such a large predicted $\mathcal{E}_C$ is the consequence of the large overestimation of $\Delta E(\mathcal{E} = 0)$, i.e., of the large DFT error over the energetics of the system in zero field. Secondly, our extrapolation assumes that the linear behavior will continue to high fields, a hypothesis certainly unrealistic as higher nonlinear contributions may become dominant in that limit. As such we have decided to investigate further a quantity much less sensitive to DFT uncertainties, i.e., the slope of $\Delta E(\mathcal{E})$. This depends only

on the molecule electrical dipole and polarizability (accurately described in DFT) and allows us to estimate with precision the relative change in the VTI crossover temperature, T_C, as a function of $\mathcal{E}$.

T_C is defined by the condition $\Delta G = 0$; i.e., it corresponds to the situation in which the Gibbs free energy of the two spin configurations become identical. This yields the equation

$$T_C = \Delta H/\Delta S = \Delta E/\Delta S, \quad (2)$$

where we have set the pressure to zero since we are considering the molecule "in vacuum," and we have approximated the enthalpy at T_C with the zero-temperature total electronic energy. In writing Eq. (2) we have also assumed that ΔS does not depend on the electric field, i.e $\Delta S(\mathcal{E}) \approx \Delta S(0)$, consistent with our computational strategy of not relaxing the atomic coordinates. We have verified in a few cases that the atomic relaxation under bias is much smaller then that due to the VTI, so that our assumption is well grounded in our own calculations.

Then the ratio between the critical temperature calculated in an electric field, $T_C(\mathcal{E})$, with that in zero field, $T_C(0)$, simply writes

$$R_T = T_C(\mathcal{E})/T_C(0) = \Delta E(\mathcal{E})/\Delta E(0). \quad (3)$$

Importantly R_T is expressed in terms of DFT total energies only, and in Fig. 3 we show that changes of T_C of the order of 5% can be obtained already at the much more modest field of 0.07 eV/Å. The uncertainty over such a value nevertheless remains quite large since the calculation still involves the determination of $\Delta E(0)$. A better estimate can be obtained by eliminating $\Delta E(0)$ completely and just using information about the slope of $\Delta E(\mathcal{E})$. This can be obtained by rewriting Eq. (2) as

$$[T_C(0) - T_C(\mathcal{E})]\Delta S(0) = \Delta E(0) - \Delta E(\mathcal{E}). \quad (4)$$

By taking the experimental estimate [29] $\Delta S(0) \approx 0.52$ meV/K we conclude that achievable electric fields can indeed induce large variations in T_C. In fact an electric field of 0.1 V/nm, typical of Stark spectroscopy [31], produces already a change in T_C of about 21 K. A field of 0.5 V/nm, obtainable in scanning tunnel microscopy experiments, can drift T_C by as much as 100 K.

In conclusion we have demonstrated that the critical temperature for the VTI in Co-dioxolene complexes can be drastically modified by a static electric field. Intriguingly, this represents a physical way to effectively modulate the redox potential of the metal acceptor, alternative to the chemical strategy of changing the radical groups of the molecule [29]. Such an external control of the magnetism of valence tautomeric compounds may open new avenues to the growing field of molecular spintronics.

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