Magnetic Properties

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Towards Molecular Magnetic Switching with an Electric Bias**

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Molecular spintronics[1–5] is an exciting concept for spin-based quantum computing. It is an extreme case of molecular electronics[6–12] in which individual spins are used as the smallest possible logical electronic switches. Electronic devices operate on logic states, which are represented either by dynamic transport of matter or by static configuration of states. In the latter, spin orientation is one property that may determine the configuration of a state, for example, in a molecule. Although, in principle, spin–orbit coupling forms the basis of the manipulation of electron spins by purely electric means (for example, the spin Hall effect), directly controlling this molecular property is generally only feasible by applying an external magnetic field. Manipulation and direct control of the spin state in a molecule by an *electric* field, however, has the potential to revolutionize computer technologies and would open a new pathway to spin-based quantum information processing.[13] For example, a logic device such as a molecular magnetic switch could be directly realized within an electronic circuit. Materials with such strongly correlated electron-state properties, for example, multiferroic systems that induce electric and magnetic coupling,[14–18] are among the most highly desired in semiconductor technologies.[19] To date, molecular systems with such properties are unknown.

Herein, we introduce such molecular systems that may serve as molecular magnetic switches. We predict the influence of an electric field on the spin states of a molecular system. We demonstrate this influence for a class of multistate molecules and thereby demonstrate a principle to control magnetic properties with an electric field. Apart from insight into magnetoelectronic properties in strongly correlated systems, studying the influence of an electric field on a molecule allows for a detailed investigation of the intrinsic effects of a molecular electronic device on molecular properties,[20] such as changes in orbital energies and shapes, band gaps, as well as electronic states and relative energies. To this end, we employ density functional calculations on two types of molecular systems, high-electron-density arenes which have been described previously[21] and square-planar gold dithiolate complexes.

An external electric field perturbs the electronic structure of a molecule. The effect of such a perturbation depends on the polarizability of the molecule and hence on the electronic configuration and the electronic state. The electron distribution in a molecule is readily distorted if the gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO–LUMO gap) is small. Because of the Stark effect, the energy of the system is shifted in the presence of an external electric field. For a system with no permanent electric dipole, the linear (first-order) Stark effect vanishes, and the correction to the energy is given by the second-order Stark effect, which is proportional to the polarizability α of the molecule and to the square of the electric field strength. The electric field $\mathbf{E}$ induces an electric dipole moment with the energy $E_{\mathrm{el}} = -\frac{1}{2}\boldsymbol{\alpha}\mathbf{E}^2$, where $\boldsymbol{\alpha}$ is the anisotropic polarizability tensor. This energy adds to that of the molecular electronic state.

This relation applies to the electronic (singlet) ground state as well as to (triplet or higher) excited spin states, whereby each electronic state responds differently to the perturbation. If a molecular system with appropriate electronic properties, such as the high-electron-density benzene complex[21] $Ba_2(C_6H_6)$, is employed, the effect of the electric field is quite intriguing. This complex consists of a benzene molecule sandwiched between two barium metal centers, each of which fully transfers their two valence electrons to the π electron cloud of the benzene fragment. The molecular complex thus features four excess π electrons on the benzene ring, such that it is a 10π benzene complex. Because of the extremely high π electron density, the electronic ground state of this molecule changes in the presence of an electric field from a nonmagnetic singlet to a magnetic triplet electromer with two unpaired electrons. The polarizabilities of the triplet state ($\alpha_{\parallel} = 501$ a.u., $\alpha_{\perp} = 1073$ a.u.) are higher than those of the singlet state ($\alpha_{\parallel} = 195$ a.u., $\alpha_{\perp} = 273$ a.u.). Thus, at high electric fields, the triplet state is more stabilized than the singlet state. Hence, a magnetic state switching occurs at a threshold of about 0.24 $\mathrm{V\,\AA^{-1}}$ for an electric field vector $\mathbf{E}_{\parallel}$ parallel to the benzene ring plane (Figure 1a), and at about 0.04 $\mathrm{V\,\AA^{-1}}$ for a perpendicular one ($\mathbf{E}_{\perp}$, Figure 1b). In the former (parallel) case, at a higher threshold voltage of about 0.32 $\mathrm{V\,\AA^{-1}}$, there is another transition from the nonmagnetic singlet to a magnetic quintet state ($\alpha_{\parallel} = 674$ a.u., $\alpha_{\perp} = 777$ a.u.) with a higher magnetic moment involving four

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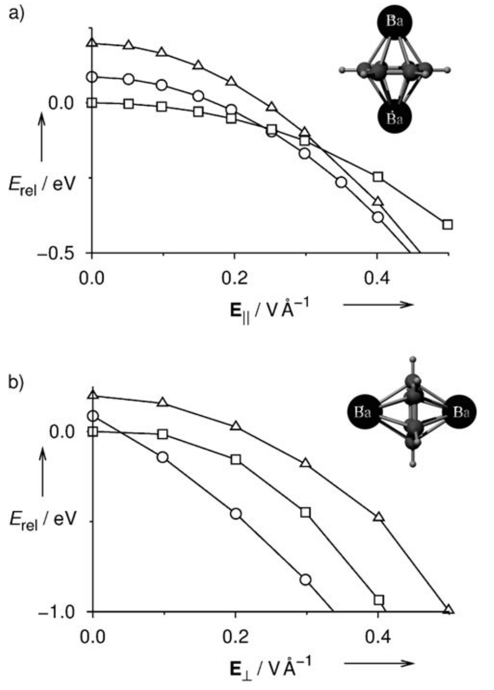


Figure 1. Stark effect on the relative energies of the singlet (□), triplet (○), and quintet (△) electronic spin states in high-electron-density benzene. a) The electric field $\mathbf{E}_{\parallel}$ is applied parallel to the benzene ring plane. b) The electric field $\mathbf{E}_{\perp}$ is applied perpendicular to the benzene ring plane.

unpaired electrons; both states are, however, energetically above the magnetic triplet state at this field strength.

This spin-state-crossing behavior under the influence of an electric field in the high-electron-density system lays the basis for the controlled manipulation of magnetism by electric means. The reason for this occurrence is quite straightforward. The three electronic states have different curvatures; the energetically higher ones react more strongly to the perturbation of the electric field. More importantly, however, the excited (magnetic) states are in the direct vicinity of the (nonmagnetic) singlet ground state, such that a state crossing is viable at low field strengths.

The high-electron-density benzene system may be further extended to molecular wires with alternating metal–benzene units (see Figure 2), that is, axially aligned metal–benzene substructures, in analogy to known structures of alkaline or alkaline earth metals and arenes[22,23] or to the multidecker transition-metal–arene wires previously synthesized by Kaya, Nakajima, and co-workers.[24–26] Such molecular wires thus bear more than one 10π benzene unit.[21] Tetravalent metal centers, for example thorium, act as four-electron donors and are π-bound to benzene. Hence, one or more $-\mathrm{Th}-(C_6H_6)-$ units insert into a benzene–barium bond. These extended molecular wire structures also exhibit spin-state crossing and thus corroborate the above switching phenomenon for $Ba_2(C_6H_6)$. Because of the increasing stabilization of the singlet ground state with increasing wire length, however, the threshold for spin-state crossing also increases (Table 1). The smallest of the 10π benzene congeners, bis(barium)benzene, therefore performs best.

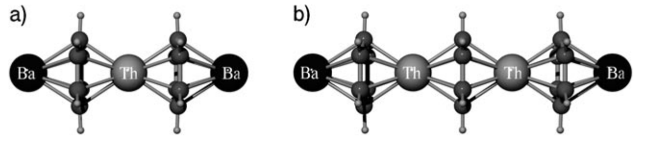


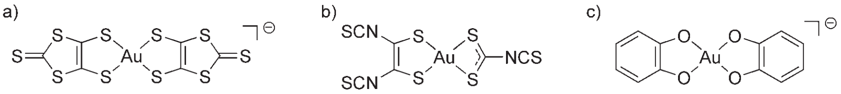
Figure 2. Molecular wires built from a) two and b) three 10π benzene units.

Table 1: Threshold field strengths $\mathbf{E}_{\perp,th}$ for singlet–triplet spin-state crossings in 10π benzene (bz) systems and singlet–triplet energy gaps ΔE_{S-T} at zero field strength.

	$\mathbf{E}_{\perp,th}$ [VÅ^{-1}]	ΔE_{S-T} [eV]
Ba-bz-Ba	0.04	0.1
Ba-bz-Th-bz-Ba	0.1	0.4
Ba-bz-Th-bz-Th-bz-Ba	0.2	0.7

A good candidate for a molecular magnetic switch must possess a high polarizability (i.e. a low HOMO–LUMO gap) as well as a nonmagnetic singlet electronic ground state with a very low singlet–triplet gap. The actual switching from a nonmagnetic state to a magnetic one (and vice versa) will in practice also depend on the transition probabilities from one spin state to another. An indication for this probability is given by the off-diagonal elements of the spin–orbit coupling matrix. In the special case of the D_{6h}-symmetric $Ba_2(C_6H_6)$ and larger multidecker 10π benzene complexes, these matrix elements are zero by definition, because the orbital angular momentum operators are of different symmetry than any of the molecular electronic state combinations. However, the spin–orbit coupling in such a complex is expected to be nonnegligible because of the presence of heavy metal centers (Ba or Th) and an overall symmetry breaking when such a molecule is embedded into a molecular device with bulk electrodes. Magnetic switches made from 10π benzene may then be obtained by flat deposition of benzene molecules onto the surfaces of two opposing Ba electrodes. This electrode material is also used in low workfunction cathodes for organic light-emitting diodes (OLED).[27]

The apparent difficulty to synthesize the elusive class of 10π benzene compounds motivates a quest for more readily accessible alternatives. One such alternative is given by salts of anionic square-planar gold dithiolate complexes such as $[\mathrm{Au(dmit)_2}]^-$ (Scheme 1 a, dmit = dimercaptoisotrithione). This complex can be prepared as highly oriented crystalline samples[28] and as well-ordered Langmuir–Blodgett (LB) molecular thin films.[29] The $[\mathrm{Au(dmit)_2}]^-$ complex is a closed-shell singlet species in which the gold metal center is formally in the (+III) oxidation state with a low-spin d^8 electron configuration. The unoccupied d orbital of gold is very low in energy, yielding a very small singlet–triplet gap of 0.6 eV and at the same time providing a low HOMO–LUMO gap of 2.2 eV with high polarizabilities in conjunction with the soft sulfur ligand sphere. Indeed, when subjecting a $[\mathrm{Au(dmit)_2}]^-$ complex to an electric field along the longitudinal axis, a spin-state crossing occurs at a threshold field



Scheme 1. Structural formulas of square-planar gold complexes. a) $[Au(dmit)_2]^-$, an anionic dithiolate complex with dmit ligands. b) $[Au(mnt')(CS'_2)]$, a neutral dithiolate complex; the divalent ligand is derived from maleonitriledithiolate (mnt) with isothiocyanate replacing the cyano groups; the monovalent ligand contains a dithiocarboxylate unit with another isothiocyanate group attached. c) $[Au(o\text{-}HQ)_2]^-$, an anionic diolate complex with *o*-hydroquinone ligands.

strength of about 0.43 V Å^{-1} (Figure 3). Spin-state transition is expected to be facile, with an ample spin–orbit-coupling matrix element of 717 cm^{-1} for a transition from the ^1A_g ground state to the first excited $^3B_{1g}$ state. The latter formally represents a single electron transfer from the delocalized cloud of the sulfur ligands to the gold-centered d_{yz} orbital, where the spin density is symmetrically distributed across the molecule. The polarizabilities of the two spin states are $\alpha_{long} =$ 689 a.u. for the singlet state and 1323 a.u. for the triplet state. The magnetic switching in square-planar gold complexes is not restricted to anionic structures, as a spin-state crossing also occurs for the neutral complex shown in Scheme 1 b at a threshold value of 0.21 V Å^{-1}. Furthermore, the square-planar gold diolate molecule in Scheme 1 c yields a spin-state transition at 0.37 V Å^{-1}, thus confirming that there is no restriction to sulfur-containing compounds.

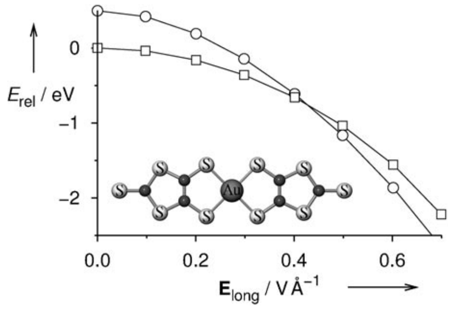


Figure 3. Stark effect on the relative energies of singlet (□) and triplet (○) spin states in $[Au(dmit)_2]^-$. The electric field $\mathbf{E}_{long}$ is applied parallel to the longitudinal axis of the molecule.

The above results imply that in principle any molecular system could be functional as a magnetic switch, provided it fulfills the necessary requirements. The polarizability of the molecule must be high, and the HOMO–LUMO gap must be small, such that the electronic structure of the molecular states are easily and distinctively perturbed by an external electric field. The molecule must possess a nonmagnetic ground state with a magnetic state in close proximity (a very low singlet–triplet gap). Finally, the probability for the formally forbidden transition between spin states must be nonzero. In the context of quantum computing, the main obstacles are related to phase decoherence of the magnetic moment. Along with phonon coupling, this phenomenon is a result of coupling with nuclear spins and intermolecular dipolar coupling. In the $[Au(dmit)_2]^-$ complex, nuclear spin coupling is minimized, because neither element present in the ligands has a nuclear spin, and the nuclear magnetic moment of gold is markedly small. Furthermore, intermolecular coupling is expected to be low even in the crystalline samples if the countercation is bulky enough to separate the $[Au(dmit)_2]^-$ units.

Compactness and high-density integration are among the most desired features in logic devices.[30] While molecular devices are generally compact owing to their small size, switches used in a conventional three-terminal setup with gate (input signal) and source/drain (output signal) electrodes are not high-density devices because of the gate electrode. Two-terminal molecular devices or switches with only source and drain electrodes, on the other hand, would allow for gateless switching and thus for high-density integrated configurations. The obvious challenge for the latter is decoupling of the input and output signals, since these go through the same terminals. An electrically controlled two-terminal molecular magnetic switch would show the twofold benefit of electric control over a magnetic property as well as input/output decoupling, since the input signal (bias voltage) would be decoupled from the output signal (spin state). This decoupling in turn permits low-power electrical write operations in connection with non-destructive magnetic readout.

Herein we have demonstrated a principle for the control of molecular spin state by an electric field. This method is based on the distinct difference in response of molecular electronic states upon perturbation with an external electric field. Molecular magnetic switching is generally conceivable in other molecular systems by tuning the electronic structure and thus the singlet–triplet gap to smaller values. Good examples are, in principle, phosphorescent emitting materials used in molecular OLEDs,[31] for which sufficient efficiency of the singlet–triplet spin-state transition has been demonstrated.[32] The above results may inspire future experimental efforts towards the synthesis and spectroscopic characterization of molecular magnetic switches to prove this switching concept fruitful.

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