Electrically controlled *g* factor and magnetism in conjugated metallorganic molecules

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Conjugated metallorganic molecules have localized spins at the central transition-metal ions and mobile π electrons in the surrounding ligands. Here we construct model Hamiltonians based on first-principles calculations to describe spins at the ions and π electrons in the ligands. It is shown that the *g* factor and magnetic susceptibility in such a molecule can be tuned to a great extent by an electrical voltage across one of the ligands. The underlying physics is that the voltage modifies the charge distribution of the ligand, which in turn changes the interplay of the ion's spin-orbit coupling and the energy splitting among its *d* orbitals. The capability of controlling the *g* factor and magnetism at the molecular level has great implications in quantum information storage and processing.

Organic molecules for charge transport, as in molecular wire junctions,[1–4] or for magnetism, as in nanomagnets,[5–7] are being extensively investigated. The stimulated quest for spintronics and quantum computing[8–10] renders it desirable to synthesize nanostructures with integrated spin and charge components, which can achieve sophisticated functions with much simpler circuitry and less demanding fabrication. Conjugated metallorganic molecules are one such type of material. The localized electron spins at central ions possess quantum information, and the π-conjugated ligand provides an efficient pathway for charge transport without spoiling the spins. For a free transition-metal ion, because of its spin-orbit (SO) interaction, the total angular momentum, j ($j=l+s$, $l+s-1$, …, $|l-s|$, with l and s being orbital and spin angular momenta), is a good quantum number to characterize an eigenstate, which will be split up into $2j+1$ sublevels with an equal spacing, $g\mu_B H$, upon the application of a magnetic field, H, where g is the Landé g factor,[11]

$$g = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}. \qquad (1)$$

The g factor determines the ion's magnetic properties including the magnetic moment of each sublevel, $-g\mu_B m_j$ ($m_j = -j, \ldots, j$), and the electron spin resonance frequency, $\omega = |g|\mu_B H/\hbar$. A metal ion in a compound, however, can exhibit multifarious magnetic behaviors because the magnetic moment and g factor can be strongly influenced by the local environment. In this Brief Report, we show that in a conjugated metallorganic molecule the magnetism and g factor can be electrically tuned to a great extent, by modifying the charge distribution in one of the ligands. Because the energy scale associated with the g-factor calculations, typically less than 10^{-4} eV, is much smaller than the energy uncertainty in common first-principles methods, we construct a spin Hamiltonian based on the lattice and electronic structures obtained from the first-principles calculations to study the g factor and magnetic susceptibility. In examining how an applied voltage affects charge distribution of π electrons in the conjugated ligand, we employ a tight-binding model, with model parameters obtained from first-principles results in literature, to make physics more transparent and computation more tractable. Electrically controlled g factor in semiconductor heterostructures are recently studied both experimentally and

theoretically.[12–14] The capability of controlling the g factor and magnetism at the molecular level will enable simple and versatile manipulation of individual electron spins.

Figure 1 shows a representative conjugated metallorganic molecule containing an ion, Fe (III). The surrounding ligands are phenanthroline, a strong ligand used in various complexes. One of the phenanthroline ligands is decorated by two dithiol (i.e., SH) groups at the ends for good contact with the electrodes. In this molecule the Fe ion, which has five 3*d* electrons, is surrounded by six N atoms, forming an octahedron. Such a molecule can be self-assembled because of its π conjugation.[15] The Cartesian coordinates throughout this Brief Report are set with the origin at the central ion and the six N atoms along the *x*, *y*, and *z* axes. The two N atoms in the ligand with the dithiol groups are in the *xy* plane. The ligand field due to the octahedral coordination breaks the fivefold degeneracy of the *d* orbitals in a free Fe ion into twofold-degenerate e_g states comprising d_{z^2} and $d_{x^2-y^2}$ and threefold-degenerate t_{2g} states comprising d_{xy}, d_{yz}, and d_{xz}, with an energy separation Δ. We carry out first-principles calculations (generalized gradient approximation) and obtain the accurate electronic structure and optimized lattice configuration of this molecule. In the ground state, the six N atoms are found to be at an equal distance $a=1.0$ Å from Fe (III) and $\Delta=3.2$ eV. The total spin of the ground state is found to be 1/2, with all five electrons occupying the t_{2g} levels, i.e., the ligand field is stronger than the exchange interaction that tends to align electron spins to achieve a high
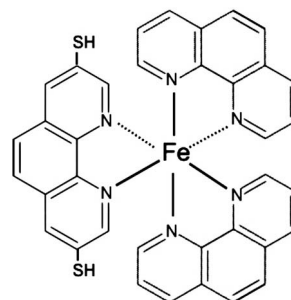

FIG. 1. A representative conjugated metallorganic molecule containing a transition-metal ion, Fe (III). The dithiol groups at the two ends of one ligand allow good contact between the molecule and electrodes.

spin of 5/2 (Hund's rule). This is consistent with the low-spin state observed in similar materials [Fe(phenanthroline)$_3$]I$_8$.[16] The large Δ suggests that the e_g states can be safely neglected in studying spin states in these molecules.[17] The electron spin in such a system would have a long lifetime, for all vibrational modes that couple with the central ion, according to our first-principles calculations, have an energy larger than 100 cm^{-1}, and the spin relaxation must resort to the two-phonon Raman process, as in N@C$_{60}$.[18]

Since five 3d electrons in the three t_{2g} orbitals is equivalent to one hole in a closed t_{2g} shell, we use the hole representation, where the SO coupling changes sign, becoming negative, and the energy order of the three orbitals is reversed, compared in the electron representation. In a perfect octahedral structure, the three t_{2g} orbitals are degenerate and behave like three p orbitals[19,20] since the states, $D_1 \equiv \frac{1}{\sqrt{2}}(d_{xz}$

$+id_{yz})$, $D_0 = id_{xy}$, and $D_{-1} \equiv \frac{1}{\sqrt{2}}(d_{xz} + id_{yz})$, have the same matrix elements of the orbital angular momentum l_k as the p orbitals except the sign: $\langle p_i|l_k|p_j\rangle = -\langle D_i|l_k|D_j\rangle$, where $p_1 = -\frac{1}{\sqrt{2}}(p_x + ip_y)$, $p_0 = p_z$, and $p_{-1} = \frac{1}{\sqrt{2}}(p_x - ip_y)$. Thus orbital $\boldsymbol{l}$ in t_{2g} is equivalent to $-\boldsymbol{l}$ within p orbitals and the magnetic moment, $\mu_B(\boldsymbol{l}+2\boldsymbol{s})$ in t_{2g} becomes $\mu_B(-\boldsymbol{l}+2\boldsymbol{s})$ in p, which leads to a different expression of the g factor, $g = -1 + 3\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$.[19] For a single particle in these t_{2g} states, j can be either 1/2 with $g=-2$ or $j=3/2$ with $g=0$.

We examine how the g factor and magnetism change when the three t_{2g} orbitals have slightly different energies. Denoting $d_1 = d_{xy}$, $d_2 = d_{xz}$, $d_3 = d_{yz}$, and $\langle d_i|V_T|d_i\rangle = E_i$ for electrons, where V_T is the potential due to the ligands, and using the basis of $(d_i\uparrow, d_i\downarrow)$, the Hamiltonian in the hole representation, which includes both the SO coupling and the Zeeman energy, reads

$$H = \begin{pmatrix} -E_1+\mu_B H_z & \mu_B(H_x-iH_y) & -i\mu_B H_x & -\frac{i}{2}\xi & i\mu_B H_y & \frac{1}{2}\xi \\ \mu_B(H_x+iH_y) & -E_1-\mu_B H_z & -\frac{i}{2}\xi & -i\mu_B H_x & -\frac{1}{2}\xi & i\mu_B H_y \\ i\mu_B H_x & \frac{i}{2}\xi & -E_2+\mu_B H_z & \mu_B(H_x-iH_y) & -\frac{i}{2}\xi-i\mu_B H_z & 0 \\ \frac{i}{2}\xi & i\mu_B H_x & \mu_B(H_x+iH_y) & -E_2-\mu_B H_z & 0 & \frac{i}{2}\xi-i\mu_B H_z \\ -i\mu_B H_y & -\frac{1}{2}\xi & \frac{i}{2}\xi+i\mu_B H_z & 0 & -E_3+\mu_B H_z & \mu_B(H_x-iH_y) \\ \frac{1}{2}\xi & -i\mu_B H_y & 0 & -\frac{i}{2}\xi+i\mu_B H_z & \mu_B(H_x+iH_y) & -E_3-\mu_B H_z \end{pmatrix}. \quad (2)$$

Here we assume that the applied magnetic field always coincides with one of the symmetry axes, i.e., x, y, or z axis. To see the interplay of the SO coupling and the energy splitting among t_{2g} states more clearly, for simplicity we assume that d_{xy} always resides at the middle of d_{xz} and d_{yz} in energy, $\delta = E_2 - E_1 = E_1 - E_3$. The SO coupling of Fe(III) is fixed $\xi = -300$ cm^{-1}.[21] We obtain the magnetic properties of the system by diagonalizing the Hamiltonian at a small magnetic field (linear response). Since the system has an odd number of electrons, according to Kramer's theorem, the six eigenstates in this system can be grouped into three Kramer's doublets, ψ_{2k-1} and ψ_{2k} ($k=1,2,3$), which is split upon the application of magnetic field H_ν along the ν axis ($\nu = x, y, z$) with an energy difference of $g_k^\nu \mu_B H_\nu$. The magnetic moments of each doublet, accordingly, have the same magnitude but are opposite in sign, $\mu_{2k-1}^\nu = -\mu_{2k}^\nu = g_k^\nu \mu_B/2$, where $\mu_k^\nu = \mu_B\langle\psi_k|l_\nu+2s_\nu|\psi_k\rangle$. In Fig. 2, we plot the energies and $|g_k^\nu|$ for the three doublets as a function of the energy splitting factor, δ. We see that when $\delta=0$, the SO coupling breaks the six t_{2g} states into a quartet and doublet. The doublet is the ground state with an isotropic g factor, $|g_1^\nu|=2$, and the g factors of the quartet are $g_2^\nu = g_3^\nu = 0$, in agreement with the

analysis by mapping t_{2g} to p states. As δ becomes finite, the quartet further splits into two doublets and the g factors become anisotropic. The g factor can be dramatically modified, from 0 to over 3, within a relatively small δ change of 0.1
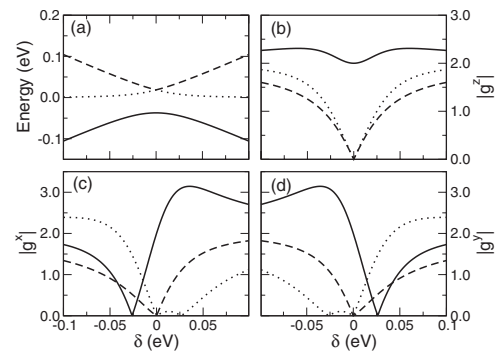

FIG. 2. (a) Energy, (b) $|g^z|$, (c) $|g^x|$, and (d) $|g^y|$ of the eigenstates as a function of energy splitting δ between t_{2g} levels. Solid, dotted, and dashed lines correspond to the ground state and the first and second excited states, respectively. The SO coupling is $\xi = -300$ cm^{-1}.
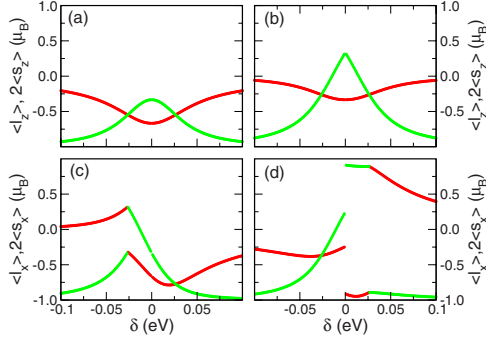
FIG. 3. (Color online) Magnetic-moment contributions from the orbital and spin angular momenta for the ground states (a) and (c) and for the first excited state (b) and (d). Red (dark gray) and green (light gray) lines represent the orbital and spin, respectively.

eV. In addition, g^x (g^y) becomes 0 at a finite δ for both the ground and excited states, as shown in Figs. 2(c) and 2(d), indicating that the system with that δ cannot be magnetized when the magnetic field is along the x (y) axis.

To further understand the g-factor change, we plot in Fig. 3 the contributions from the orbital and spin angular momenta to the magnetic momentum along the magnetic field direction for both the ground and excited states. When $|\delta| > |\xi| = 0.03$ eV, where the energy splitting dominates over the SO coupling, the increase of δ always diminishes the magnitude of the orbital, $|\langle l_\nu \rangle|$, which is the so-called orbital quenching due to the energy splittings.[19,20] Meanwhile the spin keeps increasing, approaching 1/2, its free-electron value. Consequently the g factor approaches 2 and becomes isotropic when δ is large. When $|\delta| < |\xi|$, however, the dependences of spin and orbital on δ become more complicated. In this regime, the SO interaction, which connects states with different orbitals and spins, can partially reinstate the orbital angular momentum and meanwhile suppress the spin from its free-electron value. For the ground state, as shown in Fig. 3(a), the magnitude of $\langle l_z \rangle$ increases and that of $\langle s_z \rangle$ decreases, while both remaining negative, as δ decreases. For the first excited state, as shown in Fig. 3(b), however, the SO coupling switches the direction of spin as δ decreases, and $\langle l_z \rangle$ and $2\langle s_z \rangle$ cancel each other when δ approaches 0.[22] Compared to $\langle l_z \rangle$ and $\langle s_z \rangle$, $\langle l_x \rangle$ and $\langle s_x \rangle$ change more dramatically as δ varies, as shown in Figs. 3(c) and 3(d). In particular, a discontinuity, where both the spin and the orbital change their signs, occurs when g^x or g^y becomes zero at the finite δ. At finite temperatures the magnetism is characterized by the magnetic susceptibility, χ^ν, $M^\nu = \chi^\nu H_\nu$, with M^ν being the averaged magnetic moment, $M^\nu = \frac{\sum_k \mu_k^\nu e^{-\varepsilon_k/k_B T}}{\sum_k e^{-\varepsilon_k/k_B T}}$, where ε_k is energy of the state $|\psi_k\rangle$, k_B is the Boltzmann constant, and T is temperature.

The energies of the t_{2g} orbitals, E_i, ultimately come from the interaction between the ion and ligands. Although the covalence bonding between the d orbitals and ligand molecular orbitals is important to quantitatively account for the splitting between e_g and t_{2g} states,[23] to elucidate the concept of electrically controlled magnetism and g factor, we use a simplified point charge model[24] to estimate E_i. In this model the energy levels in the ion are determined by the Coulomb potential caused by the six surrounding N atoms with negative excess charges

$$V_T(\mathbf{r}) = \sum_{i=1,6} \frac{q_i}{\sqrt{(x-x_i)^2 + (y-y_i)^2 + (z-z_i)^2}}, \quad (3)$$

where $\mathbf{r} \equiv (x, y, z)$, and (x_i, y_i, z_i) are the coordinates of the ith N atom and q_i its excess charge. Near the center, $r \equiv |\mathbf{r}| = \sqrt{x^2 + y^2 + z^2} \to 0$, where the Fe(III) is located, the potential can be expanded by using $(1 - 2qt + q^2)^{-1/2} = \sum_{l=0}^\infty P_l(t)q^l$, when P_l is the lth order Legendre polynomial. The wave functions of the 3d orbitals are $|3d_{pq}\rangle = \frac{1}{81}\sqrt{\frac{2}{\pi}}(\frac{Z}{a_0})^{7/2} e^{-(Z/3a_0)r} pq$, where $pq = xy, xz, yz$, a_0 is the Bohr radius, and Z is the effective nuclear charge. For Fe (III), $Z = 6.25$, according to Slater's formula.[25] We find

$$E_1 - E_2 = \eta(q^z - q^y), \quad E_1 - E_3 = \eta(q^z - q^x), \quad (4)$$

where $\eta = -(e^2/a)[-54(a_0/aZ)^2 + 6075(a_0/aZ)^4]$ and q^ν is the total charge of the two N atoms along the ν axis. From this model, the energy splitting between the centers of e_g and t_{2g} states would be

$$\Delta = \frac{14175}{2} \frac{e^2}{a} \left(\frac{a_0}{aZ}\right)^4 \sum_{i=1}^{6} q_i. \quad (5)$$

According to Eq. (4) and Fig. 2, the magnetism and g factor can be tuned by controlling the charges, q^ν, which can be achieved by applying a gate voltage across the ligand with the dithiol groups. To demonstrate this, we consider the following tight-binding model for the conjugated ligand, in which each C, N, and S atom contributes one π electron,[26,27]

$$H_L = -\sum_{\langle ij\rangle s} t_{ij}(c_{is}^\dagger c_{js} + \text{H.c.}) + \sum_i [\epsilon_i(V)c_{is}^\dagger c_{is} + U_i n_{i\uparrow} n_{i\downarrow}]$$
$$+ \sum_{\langle ij\rangle} \frac{K}{2}(u_i - u_j)^2. \quad (6)$$

Here $c_{is}^\dagger$ creates a π electron with spin s at atomic site i, t_{ij} is the electron hopping between nearest neighboring site i to site j. The electron-lattice coupling is included by assuming that the hopping integral across a bond depends on the bond length $t_{ij} = t_0[1 - \alpha(u_i - u_j)]$, where u_i is the displacement of the ith atom. The σ bond between two adjacent atoms in the ligand are described by a bond-stretching spring with an elastic constant K. This model is similar to the Su-Schrieffer-Heeger model widely used for conjugated polymers and molecules,[28] and the typical values of the electron-lattice coupling, elastic constant, and hopping, $\alpha = 5$ eV/Å, $K = 32$ eV/Å^2, and $t_0 = 1.7$ eV, are used. The Hubbard interaction is also taken into account, and for simplicity a common value $U_i = 1$ eV for C, N, and S atoms is adopted.[29] In this model the site energy, ϵ_i, is a function of the applied voltage, V. In the absence of voltage, the site energies, ϵ_i^0, for C, N, and S are set 0, −0.8, and 1.3 eV, respectively, which were extracted from systematic local-density functional studies of conjugated polymers.[30] The Hamiltonian is solved self-consistently by using the unrestricted Hartree-Fock approximation.[31] The excess charges in the two N atoms for $V = 0$ are found to be equal, −0.12|e|, where e is the electron charge, which results in $\Delta = 3.2$ eV from Eq. (5), consistent with the first-principles calculations. The four N atoms in the other two ligands also have this excess charge, which remains constant and independent to V. In Fig. 4, we plot the result for the case where the electrostatic potential in the
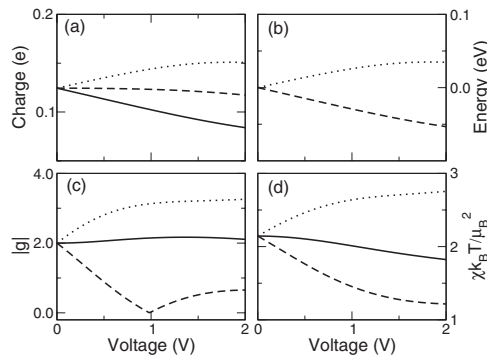
FIG. 4. Voltage-dependent charge of the two N atoms in the ligand with the (a) dithiol groups, (b) energy E_i of the t_{2g} orbitals, (c) $|g^\nu|$ of the ground state, and (d) magnetic susceptibility χ^ν. Solid and dotted lines in panel (a) plot the charge on individual N atoms, and the dashed line is the average. Dotted and dashed lines in panel (b) plot the energies of d_{xz} and d_{yz}, respectively. The energy of d_{xy} is fixed at 0. Solid, dotted, and dashed lines in panel (c) and (d) are for $\nu=z$, x, and y, respectively.

ligand depends on V in a simple linear form, $\epsilon_i(V)=\epsilon_i^0 +(z/L)V$, with L being the distance between the two electrodes attached to the S atoms and z the distance between the ith atom to the anode. Although the electrostatic potential profile inside a molecular junction can strongly deviate from the linear dependence,[32] it is shown that when a scatter center is in the middle of a molecule, as the N atoms in this case, the linear profile is quite reasonable.[33] We see from Fig. 4(a) that the applied voltage induces a change in excess charges of the two N atoms, which in turn gives rise to energy splittings among the t_{2g} orbitals, as shown in Fig. 4(b). Substituting the obtained E_i in Hamiltonian (1), we calculate the g factor of the ground state and the magnetic susceptibility at

room temperature as a function of the applied voltage and plot them in Figs. 4(c) and 4(d). The anisotropic g factors can be tuned between 0 and over 3 under a voltage less than 1 V, and the magnetic susceptibility can be significantly increased or decreased by the electric voltage, depending on the magnetic-field direction. Although the electric current through the ligand due to such a voltage may result in an additional magnetic field, δH, at the transition-metal ion, we estimate $\delta H \leq 0.1$ G,[34] which is much smaller than a typical external magnetic field H_0 in electron spin resonance, $H_0 \geq 10^3$ G, indicating that the electric-current effect on the local spin can be safely neglected. The tunability of g factor in such a molecule is extraordinary in terms of both range and responsivity. We emphasize that the electrically controlled g factor and magnetism can be achieved for electrostatic potentials other than the linear form, as long as the applied voltage can change the charge distribution in the ligand.

The electrically controlled g factor and magnetism in conjugated metallorganic molecules will allow electron spin resonance with a spatial resolution at the molecular level under a homogeneous magnetic field, which is important to coherently manipulate individual electron spins, a prerequisite to quantum computations. In addition, by controlling the magnetic moment and susceptibility, quantum information in individual spins can be selectively exposed, hidden, or processed, which can be used for quantum encryption, smart memory, and other spin logic devices.

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