

Spin-state tuning of decamethyl C₆₀ by an electric field

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Abstract

We study the electronic structure of decamethyl C₆₀ under an external electric field by investigating the radical spin arrangement using density functional theory. We find that antiparallel spin coupling (singlet state) is enhanced compared with parallel spin coupling (triplet state) by applying an electric field normal to the two isolated pentagonal rings surrounded by methyl groups. Furthermore, the electric field is found to change the relative stabilities of the spin states, leading to the possibility of spin state modulation of decamethyl C₆₀ by an electric field.

Keywords: Decaorgano C₆₀, Electronic structure, Electric field, Spin polarization

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1 Introduction

It is known that the electronic structure of carbon allotropes with three-fold coordination or sp^2 hybridization depends on their morphology, dimensionality, size, and boundary conditions [1]. The discovery [2] and mass production [3] of fullerenes allows such electronic structure variation to be confirmed. Because fullerenes have twelve pentagons embedded in graphene flakes with a zero-dimensional boundary condition [4], they have qualitatively different electronic structures [5, 6, 7, 8] from graphene [9], carbon nanotubes [10, 11], and other polycyclic hydrocarbon molecules consisting of only hexagonal rings [12, 13, 14]. Their hollow-cage structures approximately lead to a spherical harmonic (Y_{lm}) π -electron state. On the other hand, the detailed electronic structures of fullerenes show interesting diversity that sensitively depends on the cage size and symmetry [5, 6, 7, 8]. In addition to the molecular form of fullerene, fullerene can form condensed phases with various morphologies. The electronic structures of the fullerene solids exhibit further diversity depending on the forms of the condensed structures [15, 16].

In addition to the characteristic electronic structure of fullerenes, the twelve pentagons in fullerene lead to a large curvature of their sp^2 atomistic network, resulting in moderate chemical reactivity that allows the design of π -electron systems by chemically attaching atoms and molecules onto fullerene surfaces. It has been reported that chemical adsorption of halogen atoms, such as Br [17, 18] and F [19, 20], and various organic functional groups [21, 22] leads to an unusual electronic structure in the resultant chemically modified molecules. Because of the high controllability of the adsorption reaction of atoms and organic molecules, chemical modification of fullerenes is now considered to be promising procedures for controlling their electronic structure. Indeed, C_{60} derivatives with conical shapes have been synthesized under controlled modification of C_{60} by the attachment of

aromatic molecules [23, 24]. Such derivatives consist of C_{60} at the apex and five aromatic molecules attached to the five carbon atoms that surround one of the 12 pentagons in C_{60} , so that its shape is a nanometer-scale badminton shuttlecock. In our previous work, we demonstrated that penta-organo C_{60} exhibits spin polarization at the pentagonal ring surrounded by five aromatic molecules [25]. Further selective multiple addition of organic molecules onto penta-organo C_{60} results in deca-organo C_{60} [21, 26, 27], in which the organic groups attached to C_{60} divide the spherical π -electron system of C_{60} into two pentagonal π rings and a cyclic hexagonal π network. Our previous calculations have shown that decamethyl C_{60} possesses spin polarization at the pentagonal rings with antiparallel (singlet) and parallel (triplet) arrangements (Fig. 1) [28].

In this work, we investigate the modification of the stability of the spin states of decamethyl C_{60} by an external electric field based on first-principles total-energy calculations. Because of the three possible radical spin configurations, i.e., the singlet, triplet, and nonmagnetic states, in decamethyl C_{60} , possible procedures of spin-state tuning would allow the molecules to be a constituent unit for future spin electronic devices. Our density functional theory calculations show that the electronic structures of decamethyl C_{60} under an external electric field strongly depend on the mutual angle of the electric field with respect to the two pentagons possessing radical spins: By applying a normal electric field to the pentagons, the total energy of both singlet and triplet states monotonically increase with increasing electric field. Furthermore, the triplet spin state is less stable than the nonmagnetic state under the electric field of 0.26 V/\AA . In contrast, the relative stability of the spin state remains under an electric field parallel to the pentagons. Our findings clearly show a possible procedure for spin-state tuning of decamethyl C_{60} by applying an external electric field, which is an important technique for the practical application of the molecule in spin electronic devices in the near future.

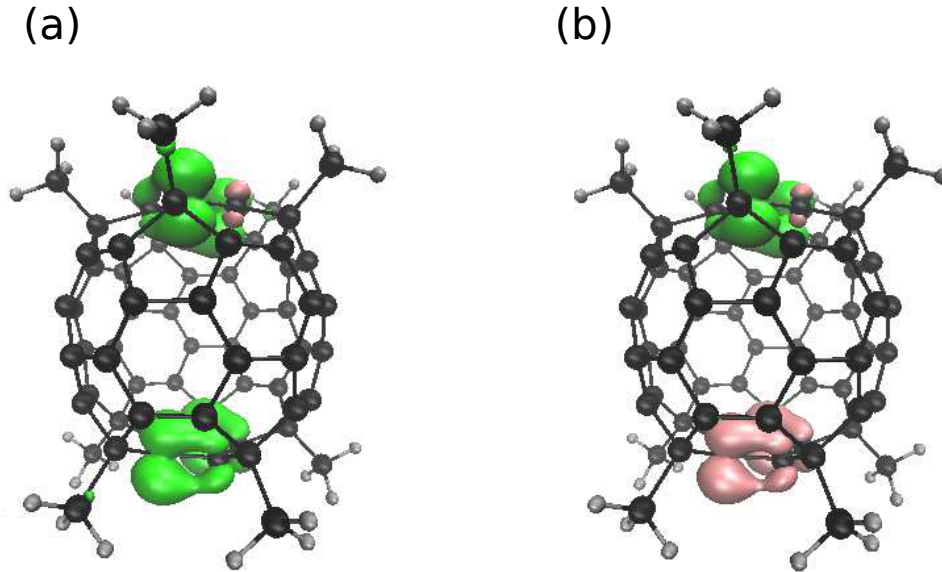


Figure 1: (Color online) Isosurface of the spin density of decamethyl C_{60} with (a) the triplet and (b) the singlet spin states. The colors of the isosurfaces correspond to the sign of the electron spin.

2 Calculation methods and structural model

All of the calculations were performed based on the framework of density functional theory [29, 30] using the Simulation Tool for Atom Technology (STATE) package [31]. We used the local spin density approximation with the Perdew–Zunger functional form for describing the exchange–correlation energy among the interacting electrons [32, 33]. Ultrasoft pseudopotentials generated using the Vanderbilt scheme were used to describe the interaction between electrons and ions [34]. The valence wave functions and charge density were expanded in terms of the plane-wave basis-set with cutoff energies of 25 and 225 Ry, respectively.

To simulate chemically decorated C_{60} under an electric field, we used an effective screening medium method (ESM) [35]. In the work, we used decamethyl C_{60} as a representative structure for decaorgano C_{60} , which is

sandwiched by two parallel metal electrodes simulated by an effective screening medium with 10 Å vacuum regions (Fig. 2). We applied an electric field between these two electrodes up to 0.26 V/Å. To investigate the molecule orientation dependence of the electronic structures of decamethyl C₆₀, we considered various molecule orientations, with the orientation defined as the angle (θ) between the pentagons surrounded by methyl groups and the electric field, from normal ($\theta = 0^\circ$) to parallel ($\theta = 90^\circ$). The atomic structures were fully optimized under zero electric fields. In the calculations under the condition of a finite electric field, the geometries were fixed to those under the condition of a zero electric field. Note that, the force acting on atoms under the electric field is less than about 5.1×10^{-3} eV/Å. Therefore, negligible atomic displacement due to the electric field is expected in this case.

3 Results and Discussion

Figure 3 shows the relative total energy as a function of the electric field for the triplet and singlet spin states of decamethyl C₆₀ for different orientations of the molecule with respect to the external electric field. In the case of $\theta = 0^\circ$, in which the electric field is normal to the pentagonal rings possessing radical spin, the energy monotonically increased with increasing electric field for both the triplet and singlet spin states. For electric fields greater than 0.26 V/Å, the triplet state has positive energy with respect to the nonmagnetic state, indicating that the triplet state is less stable than the nonmagnetic state. Furthermore, because the relative energy of the singlet state also monotonically increases with increasing external field, the singlet state would also be less stable than the nonmagnetic state under a high electric field. By extrapolating the energy with respect to the electric field, the singlet state is estimated to be less stable at an electric field of 0.6 V/Å. Therefore, the spin state of decamethyl C₆₀ is tunable by applying an electric field normal to the pentagonal rings possessing radical spins because of the different electrostatic potential between two pentagon radicals, inducing

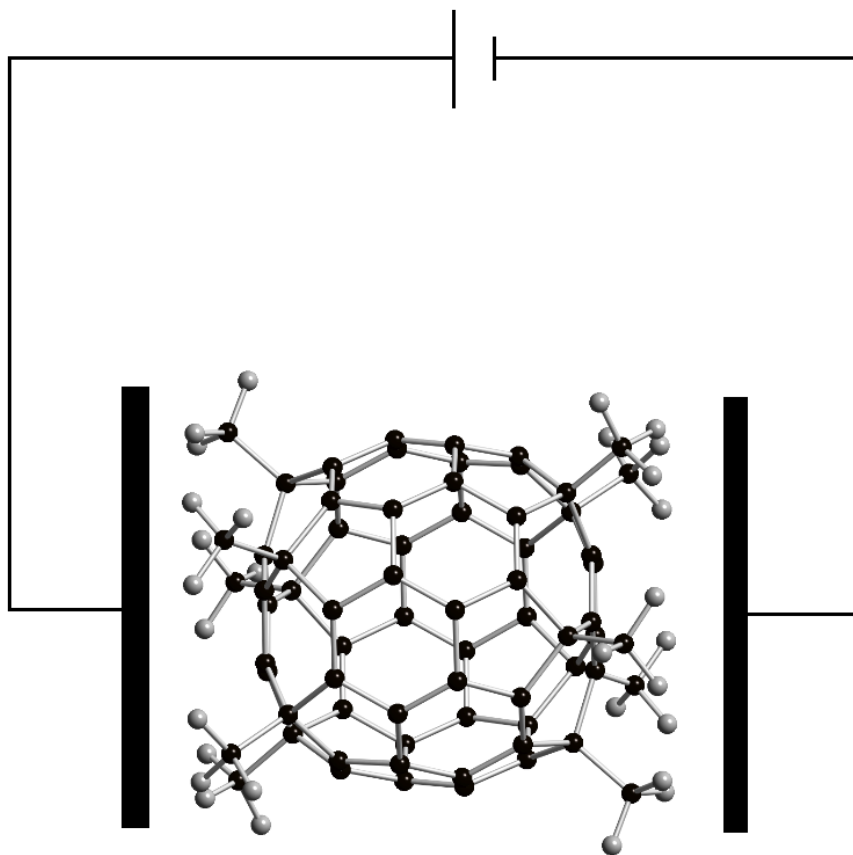


Figure 2: (Color online) Structural model of decamethyl C₆₀ under an electric field. Decamethyl C₆₀ is sandwiched between two parallel electrodes denoted by the thick black lines.

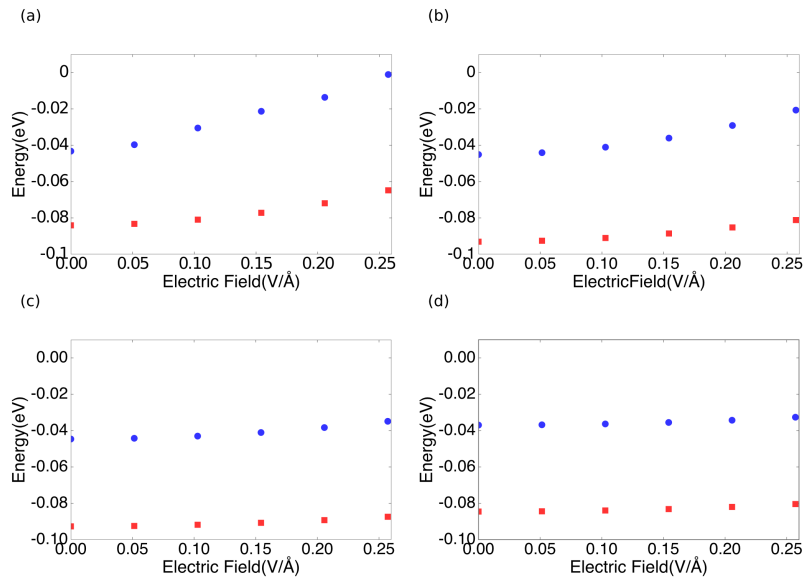


Figure 3: (Color online) Relative total energies of the triplet and singlet spin states of decamethyl C_{60} as a function of electric field with orientations (with respect to the pentagonal rings of molecules possessing radical spins) of (a) normal (0°), (b) 30° , (c) 60° , and (d) parallel (90°). Squares and circles denote the energies of singlet and triplet spin states, respectively. The energies are measured with respect to that of the nonmagnetic state.

spin state modification.

When tilting the molecule with respect to the electric field, the relative energies of the singlet and triplet spin states increased with increasing electric field. The energies of the triplet states increase more than those of the singlet states with increasing electric field, as in the case of the normal electric field. However, in contrast, the dependence of the energy with the electric field becomes weak with increasing tilt angle θ . Thus, for $\theta = 30^\circ$ and $\theta = 60^\circ$, we could not achieve a critical field that leads to a change of the relative stabilities of the triplet, singlet, and nonmagnetic spins states in the calculations.

We also investigate the energetics of decamethyl C_{60} with an electric field parallel to the pentagonal rings possessing radical spins (i.e., $\theta = 90^\circ$). In this case, the relative total energies of both the singlet and triplet states does not depend on the electric field and retain the relative stability among the three spin states. These results indicate the possibility that the spin state of decamethyl C_{60} is tunable by controlling both the electric field and the orientation of the molecule with respect to the electric field. Therefore, decamethyl C_{60} is a possible constituent for molecular spintronic devices that operate under an electric field.

We have demonstrated above that the relative stability of decamethyl C_{60} strongly depends on the radical spin state, molecule orientation, and external electric field. This indicates the possibility of tuning the exchange interaction between two radical spins, J , which can be evaluated by the total energy difference between the spin singlet and spin triplet states. Figure 4 shows the exchange interaction J between two radical spins of decamethyl C_{60} as functions of both the direction and strength of the electric field. Under a zero electric field, for all the field directions the total energy of the singlet state is lower than that of the triplet states, so the exchange interaction J is positive value. With increasing electric field, J strongly depends on the mutual molecule orientation with respect to the external electric field. We

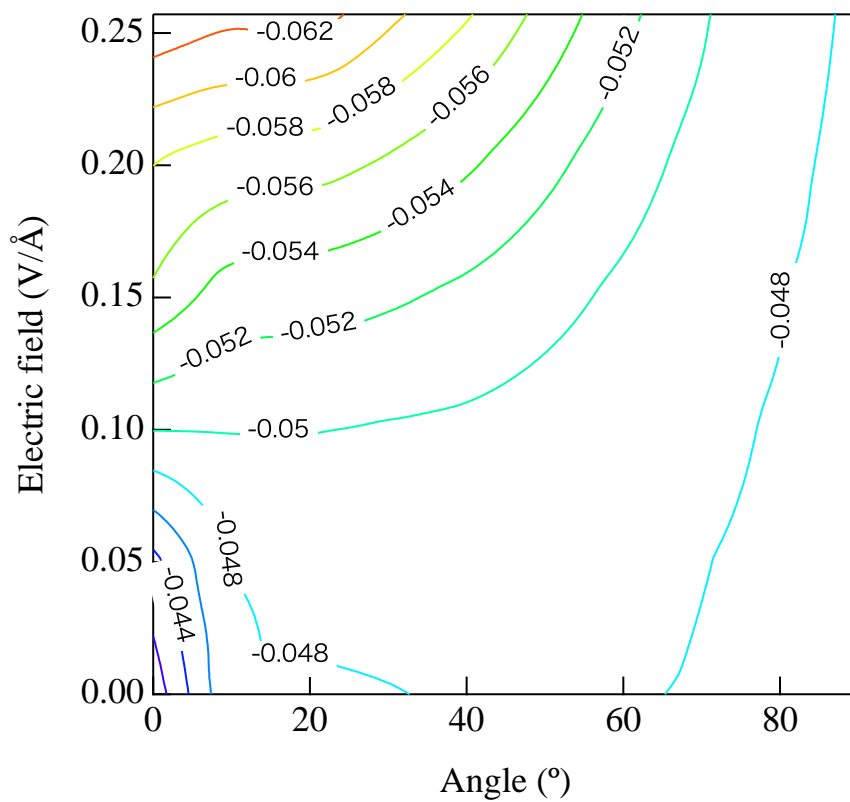


Figure 4: (Color online) Contour plot of the exchange interaction J between two radical spins of decamethyl C_{60} as functions of strength and direction of the electric field. The numerical values are in eV.

found that J monotonically decreases with increasing electric field for most of the molecule orientations. Thus, the electric field enhances the singlet spin coupling in the molecule and increases the relative stability of the triplet state around the normal field direction. In contrast, near the parallel field, the exchange interaction J retains its initial value under a zero electric field, because the electric field does not affect the relative stability of the spin state of decamethyl C_{60} . Thus, the electric field also tunes the exchange interaction J and causes unusual spin related phenomena of molecular solids consisting of decamethyl C_{60} .

Finally, we investigated the electronic structure of decamethyl C_{60} under an electric field to provide physical insight into the orientation dependence of the stability among the three spin states, because both the highest occupied (HO) and lowest unoccupied (LU) states of the singlet state and the HO state of the triplet state are localized on the pentagonal ring surrounded by the methyl groups. In the case of the triplet state, HO states of majority spin is doubly degenerated as in the case of the triplet state of O_2 molecule. While, in the case of singlet state, HO is a non-degenerated state with a lonepair of π electron. Figure 5 shows the energy gap between HO and LU states for each spin component of decamethyl C_{60} under an electric field. We found that the HO-LU gap of the triplet and singlet spin states are modulated by the normal electric field. The energy gap monotonically decreases with increasing electric field. This HO-LU gap modification is caused by the different electrostatic potentials of the three separate π electron systems, i.e., two pentagonal rings and the cyclic-phenanthrene, because the electric field between the two electrodes leads to a potential gradient inside the molecules (Fig. 6). The HO-LU gap modification in the triplet state by the electric field is larger than that of the singlet state. In contrast, in the case of the parallel electric field, the gap does not depend on the electric field because of the absence of the electrostatic potential difference among the separate π units [Fig. 5(b)].

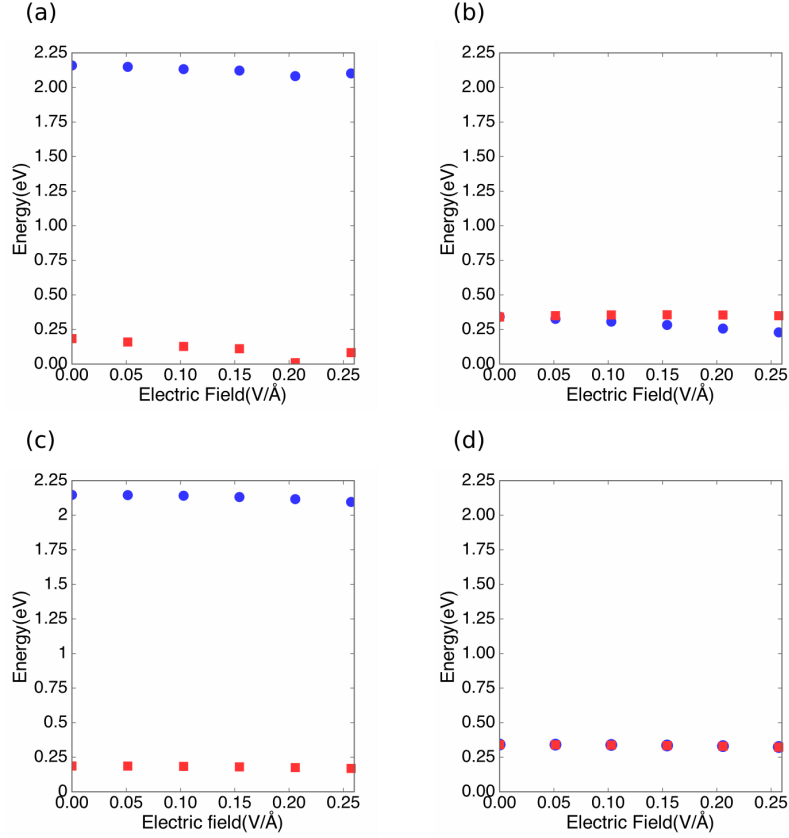


Figure 5: (Color online) HO-LU gap of decamethyl C₆₀ with (a) the triplet and (b) singlet spin states as a function of the external field normal to the pentagonal rings, and the HO-LU gap of decamethyl C₆₀ with (c) the triplet and (d) singlet spin states as a function of external field parallel to the pentagonal rings. In each panel, squares and circles denote the energy gap of the minority and majority spin states, respectively. Note that a minimum in panel (a) for the minority spin is ascribed to the numerical precision.

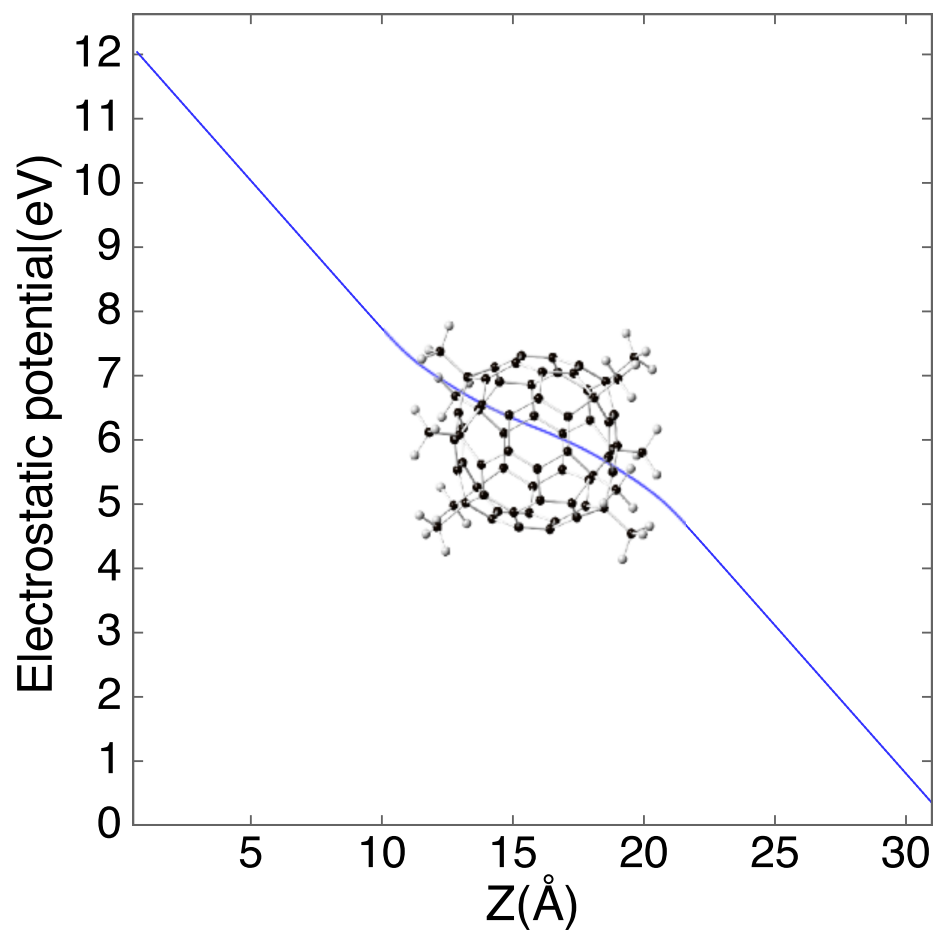


Figure 6: (Color online) Plane-averaged electrostatic potential of the decamethyl C_{60} along the z direction. The potential profile is calculated by the difference between the electrostatic potential with and without electric field to subtract the deep valley of atomic potential.

4 Conclusion

We have studied the electronic structures of decamethyl C_{60} under an external electric field based on first-principles total-energy calculations with the effective screening medium method. We find that the external electric field can modify the relative stabilities of the spin states of decamethyl C_{60} . Density functional theory calculations show that the electronic structures of decamethyl C_{60} under an external electronic field strongly depend on the angle of the electric field with respect to the two pentagons possessing radical spins in the decamethyl C_{60} molecule. By applying an electric field normal to the pentagons, the total energy of both the singlet and triplet states monotonically increased with increasing electric field. Furthermore, the triplet spin state is less stable than the nonmagnetic state under an electric field of 0.26 V/\AA . In contrast, the relative stabilities of the spin states retains for electric fields not normal to the pentagons. Our findings show a possible procedure for spin-state tuning of decamethyl C_{60} by an external electric field, which is an important technique for the practical application of the molecule in spin electronic devices in the near future.

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