Ligand-Driven Exchange Coupling in Graphene-Based Magnetic Materials

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Several forms of graphene-based magnetic materials have been investigated via density-functional theory utilizing dispersion correction and full geometry optimization. Our calculated results show that the perinaphthenyl radical (R1) has a spin of 1/2. However, in its [R1]2 dimer structure, the net spin becomes zero due to an antiferromagnetic spin-exchange between radicals. To avoid antiferromagnetic spin-exchange of identical face-to-face radicals, the alternating stack of composition R1/D25/R1 (with D25 = graphene-based diamagnetic molecule C15H13) has been designed and investigated. As expected, our calculated results confirm that the alternating stack R1/D25/R1 has a ferromagnetic spin-exchange between two R1 radicals with the spin-exchange coupling of J/kb = 277 K, and the spin moment of m = 2 μB (Bohr magneton unit). In order to explore ways to tailor spin-exchange coupling in stacks, five other R1/D25/R1-based alternating stacks with different ligand configurations of R1 have been designed and investigated. Interestingly, ferromagnetic spin-exchange in stacks can be enhanced by substituting ligands having a weak electron affinity for H atoms of a R1 molecule, while it can be weakened by substituting ligands having high electron affinity for H atoms of a R1 radical. These results can be explained in terms of the competitive hybridization between the HOMO (highest occupied molecular orbital) of radicals and the HOMO and LUMO (lowest unoccupied molecular orbital) of diamagnetic molecules. These results would give some indication for how the spin-exchange coupling in graphene-based alternating stacks can be tailored. [doi:10.2320/matertrans.M2016092]

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1. Introduction

Carbon is not only known as a biocompatible element, but also many advanced carbon-based materials with special functional and properties were synthesized, such as carbon nanotubes, fullerenes, graphene... Moreover, in the past twenty years metal-free magnets made from carbon-based compounds have been discovered and, more recently, there have been reports on the observation of magnetism in carbon1–14). Metal-free carbon structures exhibiting magnetic ordering represent a new class of materials and open a novel field of research that may lead to many new technologies1,2).

No physical law prohibits magnetic ordering in the structures containing only light elements like carbon. Bulk crystalline graphite is a strong diamagnet, with the magnetic susceptibility second only to superconductors. However, graphite containing certain defects can exhibit spontaneous magnetization2,5,7,8). Previous experimental studies also showed that long-range magnetic order in carbon-based materials can exist above room temperature2,5,7). It is greatly surprised that magnetism in carbon-based materials is determined by s- and p-electrons. However, the origin of magnetic order in pure carbon in only poorly understood2,4,5,7).

In this study, geometric structure, electronic structure, and magnetic properties of several forms of graphene-based magnetic materials, i.e. perinaphthenyl radicals C15H9 (R1)15–18), dimers [R1]2, and alternating stacks of R1 radicals and diamagnetic molecules, have been investigated using density-functional theory with dispersion correction and full geometry optimization. Our calculated results show that the R1 radical has a spin of 1/2. However, in its [R1]2 dimer structure, the net spin becomes zero due to antiferromagnetic spin-exchange between radicals. Understanding the magnetic interaction between radicals is one of the most fundamental and important subjects for developing high-spin radical stacks. The topological principle proposed is in line with the McConnell rule, stating that directly overlapping π-spin is antiferromagnetically coupling. Thus homo-radical stacks are likely to exhibit anti-parallel spin alignment and zero net collective spin.

To avoid antiferromagnetic spin-exchange due to directly overlapping π-spin, the graphene-based stack R1/D25/R1 has been designed and investigated. As expected, our calculated results confirm that the stack R1/D25/R1 has a ferromagnetic structure with the spin-exchange coupling of J/kb = 277 K. Moreover, to explore ways to tailor spin-exchange coupling in stacks, five other stacks R1-X/D25/R1-X with different ligand X have been designed and investigated. Interestingly, spin-exchange coupling in R1-X/D25/R1-X stacks varies as a function of electron affinity of R1-X radicals. These results can be explained in terms of competitive hybridizations between the HOMO (highest occupied molecular orbital) of radicals and the HOMO and LUMO (lowest unoccupied molecular orbital) of diamagnetic molecules. These results would give some hints for the design of new carbon-based magnetic materials.

2. Computational Method

In this study, graphene-based molecules were investigated using density functional theory with the double numerical ba-
sis sets plus polarization functional (DNP), as implemented in the DMol³ code[19]. All electrons were included in our calculations. The density functional was treated by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential[20]. The slab dipole correction was employed to correct exchange energy. The dispersion-corrected method proposed by Grimme[21] was used to describe for non-covalent forces such as Van Der Waals interactions. The hexadecapolar expansion scheme was adopted for resolving the charge density and Coulombic potential. The on-site charge and magnetic moment were evaluated via Mulliken population analysis[22,23]. For better accuracy, the real-space global cutoff radius was set to be 6.0 Å for all atoms. All structures of graphene-based molecules were fully optimized without any symmetry constraint. Spin-unrestricted self-consistent field (SCF) calculations were carried out with a convergence criterion of $10^{-6}$ a.u. for the total energies. In the optimization process, the convergence thresholds for the energy, energy gradient, and atomic displacement between optimization cycles were set at $10^{-6}$, $10^{-4}$ and $10^{-3}$ a.u., respectively.

In order to determine the ground state magnetic structure of each graphene-based stacks, we carried out total-energy calculations with full geometry optimization in triplet state and singlet state, allowing the relaxation of all atoms in stacks. The geometric structure of the ground state was employed for calculating the spin-exchange interaction. To evaluate the stability of the magnetic state for each molecular structure, the effective spin-exchange, $J$, of the molecular structures was estimated by the singlet-triplet separation[18,24,25] (See eq. (1)).

$$2J = \Delta E = E_S - E_T$$

where, $E_S$ and $E_T$ are the total electronic energy of the singlet and triplet states of a molecular structure, respectively.

The electron affinity ($E_a$) of a molecule was computed by using the formula in eq. (2).

$$E_a = E^- - E$$

where, $E$ and $E^-$ are the total electronic energy in the neutral state and the anionic state of a molecule, respectively.

3. Results and Discussion

The schematic geometric structure of the perinaphthyl radical C$_{13}$H$_9$ (R$_1$) is shown in Fig. 1(a). R$_1$ has a planar structure consisting of thirteen C atoms forming three aromatic rings with nine H atoms at the boundary. R$_1$ has the C$_{3v}$ symmetry with the C$_3$ axis through its central carbon atom (C0). Due to the C$_{3v}$ symmetry, C atoms can be classified in four sites C0, C1, C2, and C3, as labeled in Fig. 1(a). There is one C0 site, three C1 sites, six C2 sites, and three C3 sites. Depending on the C and H sites, the C-C and C-H bond lengths in R$_1$ vary slightly in the range of 1.396–1.434 Å and 1.091 Å, respectively. These results are consistent with the previous theoretical and experimental data reported in Refs. 18) and 17), as shown in Fig. 1(b). Our calculated results show that R$_1$ has one singly occupied molecular orbital (SOMO) resulting in a spin moment of 1 $\mu_B$, and its spin moment is distributed over nearly the entire radical, as depicted in Fig. 1(c). Previous studies demonstrate that two R$_1$ radicals can combine to form a dimer with strong antiferromagnetic (AFM) couplings resulting from direct $\pi-\pi$ stacking between their aromatic rings[26]. Due to antiferromagnetic coupling between R$_1$ radicals, the net spin of [R$_1$]$_2$ dimer becomes zero.

To avoid the typical AFM spin-exchange of identical face-to-face radicals, the alternating stack of composition R$_1$/D$_{25}$/R$_1$ (with D$_{25}$ = diamagnetic molecule C$_{34}$H$_{16}$ (Ref. 27) and references therein)) has been designed. D$_{25}$ is a planar diamagnetic molecule consisting of thirty-four C atoms forming ten aromatic rings with sixteen H atoms at the boundary, as displayed in Fig. 2(a). The schematic geometric structure of the R$_1$/D$_{25}$/R$_1$ stack is shown in Fig. 2(a). The intermolecular distance for R$_1$–D$_{25}$ in the R$_1$/D$_{25}$/R$_1$ stack is $d = 3.188$ Å. Our calculated results show that the planar structure of D$_{25}$
diamagnetic molecule is preserved in the R1/D25/R1 stack. To determine the ground state magnetic structure of the R1/D25/R1 stack, total energy calculations with full geometry optimization were carried out. Our calculated results showed that the ground state of the R1/D25/R1 stack is ferromagnetic (FM) with the spin moment of $2\mu_B$. To confirm this result, the spin polarization in the R1/D25/R1 stack was computed and depicted in Fig. 2(b). As shown in Fig. 2(b), the spin polarization for two R1 radicals is parallel. However, the spin polarization of D25 is an asymmetric structure, as depicted in Fig. 2(b), which can be attributed to the asymmetrically geometric structure of R1/D25/R1 stack, as shown in Fig. 2(c) and (d).

To evaluate the stability of the magnetic state of the R1/D25/R1 stack, the spin-exchange coupling (J) of the stack was estimated. Our calculated results confirm the ferromagnetic spin-exchange between two R1 radicals with $J/k_B = 277$ K. The FM spin-exchange in the R1/D25/R1 stack can be explained in terms of competitive hybridizations between the HOMO (highest occupied molecular orbital) of R1 radicals and the HOMO and LUMO (lowest unoccupied molecular orbital) of D25 diamagnetic molecule. Our calculated results show that the HOMO and LUMO of the aromatic molecules R1 and D25 are $\pi$-states resulting from hybridizations of the $p_z$ orbitals on carbon atoms, as shown in Fig. 3. The $\pi$-states can hybridize to form molecular orbitals for the R1 and D25 radicals, as shown in Fig. 4. The hybridization between the HOMO of R1 and the HOMO of D25 leads to an AFM structure of the R1/D25/R1 stack, as displayed in Fig. 4(a), while the hybridization between the HOMO of R1 and the LUMO of D25 leads to an FM structure of the R1/D25/R1 stack, as displayed in Fig. 4(b). However, the strength of these hybridizations depends on the difference in energy between the HOMO of R1 and the HOMO and LUMO of D25, the smaller the energy difference, the stronger the hybridization. The calculated energies of the HOMO of R1 and the HOMO and LUMO of D25 are $-4.205$, $-4.572$, and $-4.011$ eV, respectively. These results show that the energy of the R1 HOMO is closer to the D25 LUMO than the D25 HOMO. Hence, the hybridization between the R1 HOMO and the D25 LUMO dominates resulting in FM spin-exchange coupling in R1/D25/R1, as shown in Fig. 4(b). This result gives some hints for tailoring spin exchange in the R1/D25/R1 stack by variation in energy of HOMOs and LUMOs of R1 and D25.

Here, it is noted that, the HOMO energy of R1 is below the LUMO energy of D25. Therefore, it is expected that the ferromagnetic spin-exchange in the R1/D25/R1 stack will be enhanced as the HOMO energy of R1 increases. This can be done by substituting ligands having weak electron affinity for H atoms of R1. To confirm these expectations, more five R1-X/D25/R1-X stacks with different ligands X have been designed and investigated. The schematic geometric structure of R1-X radicals is displayed in Fig. 5. Our calculated bond lengths between carbon and X of R1-X radicals are tabulated in Table 2. As shown in Table 2, the R1-CN radical has the strongest electron affinity of $E_a = -3.09$ eV, and the R1-NH2 radical has the weakest electron affinity of $E_a = -1.13$ eV. As the expectation, the ferromagnetic spin-exchange of R1-X/D25/R1-X stacks increases...
es as the electron affinity of R1-X radicals is weakened, as shown in Table 1. Indeed, the spin-exchange coupling of R1-X/D25/R1-X stacks increases from $J/k_B = -340$ K to 654 K corresponding to the electron affinity of R1-X radicals weakened from $E_a = -3.09$ eV to $-1.13$ eV. These results also can be explained in terms of competitive hybridizations between the HOMO of R1-X radicals and the LUMO and HOMO of the D25 diamagnetic molecule. The strength of these hybridizations depends on the difference in their energy, the smaller the energy difference, the stronger the hybridization. The calculated energies of HOMOs and LUMOs for R1-X and D25 are listed in Table 2. Table 2 shows that the energy of the R1-CN HOMO is closer to the D25 HOMO than the D25 LUMO resulting in an AFM structure of the R1-CN/D25/R1-CN stack with $J/k_B = -340$ K. It is easy to see that the HOMO energy of R1-X radicals increases as $m$ increases. The HOMO energy of R1-X radicals increases from $-5.729$ eV for $m = 1$ to $-3.785$ eV for $m = 6$, as tabulated in Table 2. As $m$ increases, the HOMO energy of R1-X radicals tends to closer to the D25 LUMO than the D25 HOMO, as shown in Fig. 6. Hence, the hybridization between the R1 HOMO and the D25 LUMO tends to dominate in stacks with increase of $m$, leading to enhancement of FM spin-exchange coupling in stacks, as shown in Table 1.

To evaluate the stability of R1-X/D25/R1-X stacks, their formation energy, $E_f$, was calculated using eq. (3).

$$E_f = E_{\text{stack}} - (2E_{\text{radical}} + E_{\text{diamagnetic molecule}})$$

where, $E_{\text{stack}}$, $E_{\text{radical}}$, and $E_{\text{diamagnetic molecule}}$ are the total electronic energy of the stack, radical, and diamagnetic molecule, respectively.

The $E_f$ of R1-X/D25/R1-X stacks is tabulated in Table 1. $E_f$ is in the range of $-0.09$ eV to $-2.24$ eV. The $E_f$ of the R1-X/D25/R1-X stacks becomes more negative as $E_o$ increases. This result means that stacks become more stable with increasing $m$.

### Table 1

<table>
<thead>
<tr>
<th>$m$</th>
<th>Stacks</th>
<th>$J/k_B$ (K)</th>
<th>$d$ (Å)</th>
<th>$\Delta n$ (e)</th>
<th>$\Delta m$ (g)</th>
<th>$E_f$ (eV)</th>
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<tbody>
<tr>
<td>1</td>
<td>R1-CN/D25/R1-CN</td>
<td>-340</td>
<td>6.302</td>
<td>0.423</td>
<td>0.000</td>
<td>-0.09</td>
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<tr>
<td>2</td>
<td>R1-Cl/D25/R1-Cl</td>
<td>129</td>
<td>6.382</td>
<td>-0.007</td>
<td>0.390</td>
<td>-2.05</td>
</tr>
<tr>
<td>3</td>
<td>R1-OH/D25/R1-OH</td>
<td>248</td>
<td>6.454</td>
<td>-0.244</td>
<td>0.397</td>
<td>-2.00</td>
</tr>
<tr>
<td>4</td>
<td>R1/D25/R1</td>
<td>277</td>
<td>6.375</td>
<td>-0.194</td>
<td>0.389</td>
<td>-1.70</td>
</tr>
<tr>
<td>5</td>
<td>R1-S/D25/R1-S</td>
<td>603</td>
<td>6.359</td>
<td>-0.277</td>
<td>0.420</td>
<td>-2.00</td>
</tr>
<tr>
<td>6</td>
<td>R1-NH2/D25/R1-NH2</td>
<td>654</td>
<td>6.389</td>
<td>-0.411</td>
<td>0.490</td>
<td>-2.24</td>
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### Table 2

<table>
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<tr>
<th>$m$</th>
<th>$E_o$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$d_{\text{C-X}}$ (Å)</th>
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<tr>
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<td>-3.09</td>
<td>-2.26</td>
<td>1.432</td>
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<td>-3.609</td>
<td>-2.141</td>
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<tr>
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<td>-4.572</td>
<td>-5.729</td>
<td>-4.905</td>
<td>1.374</td>
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<tr>
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<td>-5.729</td>
<td>-4.257</td>
<td>-4.205</td>
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<td>-3.798</td>
<td>-3.785</td>
<td>1.768</td>
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<tr>
<td>6</td>
<td>-5.729</td>
<td>-3.798</td>
<td>-3.785</td>
<td>1.401</td>
</tr>
</tbody>
</table>

### Fig. 6

The HOMO and LUMO energy of D25, and the HOMO energy of R1-X radicals.

$E_f$ This trend can be explained in terms of $\pi-\pi$ stacking overlap between R1-X and D25. These results demonstrate the advantage of using radicals having high electron affinity as building blocks when designing stacks.

### 4. Conclusion

In order to explore ways to tailor spin exchange coupling in graphene-based alternating stacks, six stacks with different ligand configurations R1-X/D25/R1-X have been designed and investigated using density-functional theory with dispersion correction and full geometry optimization. Interestingly, ferromagnetic spin-exchange in stacks can be enhanced by using X ligands having weak electron affinity, while antiferromagnetic spin-exchange in stacks can be enhanced by using X ligands having high electron affinity. The spin-exchange coupling of R1-X/D25/R1-X stacks increases from $J/k_B = -340$ K to 654 K corresponding to the electron affinity of R1-X radicals weakened from $E_a = -3.09$ eV to $-1.13$ eV. These results can be explained in terms of competitive hybridizations between the HOMO of radicals R1-X and the HOMO and LUMO of diamagnetic molecules D25. These results would give some hints into how the spin-exchange coupling in carbon-based magnetic materials can be tailored.

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