Magnetic properties and quantum phase transitions of purely organic molecule-based ferrimagnets based on Green’s function theory

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Magnetic properties of a Heisenberg diamondlike spin chain model for purely organic molecule-based ferrimagnets are investigated by means of the many-body Green’s function method within random phase approximation. The molecule-based ferrimagnet is composed of $S=1/2$ monoradical molecules alternating with intermolecular antiferromagnetic (AF) interactions, and the $S=1$ site is composed of two $S=1/2$ spins by a finite intramolecular ferromagnetic ($F$) interaction. The numerical results reveal that occurrence of ferrimagnetic spin alignments along the chain is determined by the intermolecular AF interactions. Owing to the very small intermolecular AF interactions, the curves of the product of magnetic susceptibility and temperature ($\chi T$) against temperature display as a round peak at low temperatures, and the ferrimagnetic phase transition could only be detected at ultralow temperatures in practical organic compounds. Temperature- and magnetic-field-induced magnetic phase transitions are discussed, which are consistent with the experimental findings. The lower spatial symmetry of intermolecular interactions makes it easy to form spin pairs with a singlet ($S=0$) ground state along the chain and to reduce Curie temperature. The formations of molecular dimers and trimers along the chain have contributions to bring about $F$ alignments with effective $S=1/2$ magnetic supramolecules and to enhance Curie temperature. In addition, the experimental data of the magnetic susceptibility measurements for a molecule-based ferrimagnet are also fairly compared with our theoretical results. © 2008 American Institute of Physics. [DOI: 10.1063/1.2839274]

I. INTRODUCTION

Low-dimensional purely organic molecule-based ferrimagnets and other molecular functional magnets have attracted much attention both experimentally and theoretically in recent years.1–3 Many ferromagnets have been reported in genuinely organic molecule-based materials4 after the discovery of the first organic ferromagnet, p-NPNN.5 However, the magnetic phase transition temperature of most metal-free ferromagnets except for $\text{C}_{18}$ and its compounds6 is still below liquid helium temperature. In order to achieve stable organic magnets with high transition temperature $T_C$, ferrimagnetism has long been considered as an effective approach to present spontaneous magnetizations by the antiferromagnetic (AF) exchange couplings between two kinds of organic molecular radicals with different spin multiplicities. With the aid of this strategy, we can increase $T_C$ by elaborate controlling for intra- and intermolecular interactions and by enhancing the value of effective spins within a molecule as well.

Based on the theory of ferrimagnetism, a series of molecule-based organic ferromagnets have been designed and synthesized experimentally. Izuoka et al. synthesized a molecular complex of a ground state with a triplet $S=1$ biradical and an $S=1/2$ monoradical.7 However, they have not observed a phase transition to a bulk ferrimagnetic ordering state. Another work which should be mentioned is that of Hosokoshi et al.,8 who adopted a structure similar to that of Izuoka et al., and claimed to succeed in making for the first time a genuinely organic molecule-based ferrimagnet by using a single-component strategy. They utilized a triradical including $S=1$ and $S=1/2$ units within an organic molecule, connecting the $S=1$ and $S=1/2$ units by intramolecular ferromagnetic ($F$) and intermolecular AF interactions; nevertheless, the $T_C$ of the system is as low as about 0.28 K. It is worth noting that Takeda et al.,9 reported a new strategy to realize a higher $T_C$ organic $F$ compound by making use of intramolecular AF interactions between triradical “multispin” molecules, which makes $T_C$ increase up to 0.74 K. In recent years, Maekawa et al. have proposed the possible occurrence of the ferrimagnetic ordering in an alternating chain, which is composed of a ground-state singlet $S=0$ biradical and an $S=1/2$ monoradical. This strategy presents a new idea to obtain molecule-based ferrimagnets with high transition temperature. It is obvious that the low transition temperature $T_C$ of these organic magnetic materials makes them...
Therefore, the spin quantum number as the intermolecular interactions in crystalline solid states.

Far from practical applications. Thus, to search and synthesize genuinely organic ferromagnets with high $T_C$ is still a hard task for experimentalists, which has stimulated us to study the quantum magnetic transitions and spin alignment mechanism of organic molecule-based ferrimagnets from a theoretical point of view.

Compared with transition-metal-based molecular ferrimagnets, organic molecular-based magnets have two particular features. In organic molecule-based materials, spin density is distributed over many atomic sites in an open shell molecule, and hence, the intermolecular spin-spin interaction has a multicentered or multicontact nature. Furthermore, in most cases, intramolecular interactions in stable organic $S > 1/2$ molecules have the same order of magnitude as the intermolecular interactions in crystalline solid states. Therefore, the spin quantum number $S = 0$ for a single ground state and $S = 1$ for a triplet ground state might not be good quantum numbers for describing the biradical embedded in the molecular assemblages. Under the circumstances, the above-mentioned molecule-based ferrimagnets should be described as a spin-$1/2$ Heisenberg diamondlike chain model, as theoretically illustrated in Fig. 1. In the present paper, we will focus on the magnetic properties of the spin-$1/2$ Heisenberg diamondlike ferrimagnetic chain by means of the many-body Green’s function theory within random phase approximation (RPA). The remainder of the paper is organized as follows. The model Hamiltonian and theoretical method are introduced in Sec. II. In Sec. III, the sublattice magnetizations, the magnetic susceptibilities multiplied by temperature will be calculated, the temperature- and magnetic-field-induced phase diagrams will be explored, and a comparison to the experimental data for a genuinely organic molecule-based ferrimagnet will be made. Meanwhile, the influences of the spatial symmetry of magnetic interactions, molecular dimers, and trimers on the magnetic properties of the systems, in particular, on the magnetic transition temperature $T_C$ will be discussed. Finally, some conclusions will be given in Sec. IV.

II. MODEL AND THEORETICAL METHOD

The Hamiltonian of the spin-$1/2$ diamondlike ferrimagnetic chain in the presence of an external magnetic field $B$ can be written in the form

$$H = \sum_i^N \left\{ J_1 S_{i,a} \cdot S_{i,b} + J_2 S_{i,a} \cdot S_{i,c} + J_3 S_{i,b} \cdot S_{i,c} + \frac{1}{2} J_d(S_{i-1,b} \cdot S_{i,a} + S_{i,b} \cdot S_{i+1,a}) + \frac{1}{2} J_d(S_{i-1,c} \cdot S_{i,a} + S_{i,c} \cdot S_{i+1,a}) + B \cdot (S_{i,a}^z + S_{i,b}^z + S_{i,c}^z) \right\},$$

where $S_j$ is the spin operator at the $j$th site, and $S^z = S^+ \pm iS^-$. $N$ is the total number of spin repeating cells in the diamondlike chain. Throughout this paper, we consider only the case when the external field $B$ is along the $z$-axis direction, and for convenience, $g\mu_B = 1$ in the calculations. It should be noted that if the model compound is composed of single-component organic triradical molecules, the spin sites $S_{i,a}$, $S_{i,b}$, and $S_{i,c}$ denote the three radicals within a single organic molecule, respectively, and if the model is a biradical-monoradical alternating chain, the spin sites $S_{i,b}$ and $S_{i,c}$ denote the two radicals of a biradical molecule with an intramolecular $F$ interaction, $J_F(J_F < 0)$, and the biradical is coupled with the neighboring monoradical $S_{i,a}$ by intermolecular AF interactions $J_{AF}$ (e.g., $J_f > 0$, $i = 1, 2, 4, 5$).

The method we use is the many-body Green’s function theory which has long been applied to treat the Heisenberg exchange model. The retarded Green’s functions or double-time Green’s functions are, according to Bogolyubov and Tyablikov, as follows:

$$G_{ij}(t - \tau) = \langle \langle A_j; B_j(\tau) \rangle \rangle - i\theta(t - \tau)\langle [A_j B_j; A_j] \rangle,$$

where the subscripts $i$ and $j$ label lattice sites. The Green’s function is Fourier time transformed and then put into the equation of motion,

$$\omega\langle [A_j; B_j(\tau)] \rangle = \langle [A_j, B_j] \rangle + \langle [A_j H]; B_j \rangle \rangle.$$

Then the Green’s function is further Fourier transformed in one-dimensional real space,

$$G_{ij} = \frac{1}{N} \sum_k g(k)e^{ik(i-j)}.$$

The lower case letter $k$ represents wavevector. The integration of the wavevector $k$ is in one dimension. Now the Green’s function $g$ is a function of wavevector $k$ and frequency $\omega = \omega(k)$. According to the well-known spectral theorem, the statistical average of the product of the operators can be calculated as

$$\langle B_j A_i \rangle = \frac{i}{2\pi N} \sum_k e^{ik(i-j)} \int \frac{d\omega}{e^{\beta\omega} - 1} [g(k, \omega + \omega^*) - g(k, \omega - \omega^*)].$$

Where $\beta = 1/(k_B T)$, $k_B$ is being Boltzman’s constant, $T$ is the absolute temperature, and for convenience, $k_B = 1$ in...
calculation. The above formula helps us to calculate the magnetization of each sublattice. In our calculations, the RPA is employed.

Considering that there are three sublattices in every repeating unit, the operator A in the above formula is taken as \( S_{i,a}^+, S_{i,b}^+, \) and \( S_{i,c}^+ \), correspondingly, the operator B is taken as \( S_{i,a}^-, S_{i,b}^-, \) and \( S_{i,c}^- \). Then, a set of linear equations are obtained,

\[
\sum_{\lambda} (\omega_\lambda \delta_{\mu\lambda} - P_{\mu\lambda}(k)) g_{\lambda\beta}(\omega_\lambda) = \langle [S_{\mu}^+, B_{\beta}] \rangle,
\]

where \( P_{\mu\lambda}(k) \) is a parameter matrix as follows:

\[
P_{\mu\lambda}(k) = \begin{bmatrix}
- [B + (J_1 + J_4)(S_{i}^0) + (J_2 + J_3)(S_{i}^1)] & \langle S_{i}^0(J_1 + J_4 e^{ik}) \rangle & \langle S_{i}^0(J_2 + J_3 e^{ik}) \rangle \\
\langle S_{i}^1(J_2 + J_4 e^{-ik}) \rangle & - [B + (J_1 + J_4)(S_{i}^0) + J_3 (S_{i}^1)] & J_3 \langle S_{i}^1 \rangle \\
J_3 \langle S_{i}^1 \rangle & - [B + (J_2 + J_3)(S_{i}^0) + J_5 (S_{i}^1)] & 0
\end{bmatrix}.
\]

In Eq. (6), \( g_{\lambda\beta} \) is a Green’s function matrix corresponding to the operators \( S_{i,a}^+, S_{i,b}^+, S_{i,c}^+ \) and \( S_{i,a}^-, S_{i,b}^-, S_{i,c}^- \) in momentum space; it could be written as

\[
g_{\lambda\beta} = \begin{bmatrix}
\langle S_{i}^0(S_{i}^0) \rangle & \langle S_{i}^0(S_{i}^1) \rangle & \langle S_{i}^0(S_{i}^2) \rangle \\
\langle S_{i}^1(S_{i}^0) \rangle & \langle S_{i}^1(S_{i}^1) \rangle & \langle S_{i}^1(S_{i}^2) \rangle \\
\langle S_{i}^2(S_{i}^0) \rangle & \langle S_{i}^2(S_{i}^1) \rangle & \langle S_{i}^2(S_{i}^2) \rangle
\end{bmatrix}.
\]

To solve Eq. (6), one should first find the eigenvalues \( \omega_\lambda \) and the corresponding eigenvectors \( U_{\lambda\nu} \) of the matrix \( P \) by solving the following equations:

\[
\sum_{\lambda} (\omega_\lambda \delta_{\mu\lambda} - P_{\mu\lambda}(k)) U_{\lambda\nu} = 0.
\]

The solution of Eq. (6) is expressed by

\[
g_{\lambda\beta} = \sum_{\tau,\kappa} \frac{U_{\nu\tau} U_{\kappa\lambda}^{-1}}{\omega_\nu - \omega_\kappa} \langle S_{\kappa}^\nu, B_{\beta} \rangle,
\]

where \( U^{-1} \) is the inverse matrix of \( U \). Employing the spectral theorem equation (5), one obtains

\[
\langle B_{\beta} S_{\nu}^\nu \rangle = \sum_{\tau,\lambda} \frac{U_{\nu\tau} U_{\lambda\kappa}^{-1}}{\omega_\nu - \omega_\kappa} \langle S_{\kappa}^\nu, B_{\beta} \rangle.
\]

Considering spin value of \( S = 1/2 \) in the ferrimagnetic diamondlike chain, the statistical averages of sublattice magnetizations \( \langle S_{\nu}^\alpha \rangle (\alpha = a, b, c) \) can be evaluated by the following formula:

\[
\langle S_{\nu}^\alpha \rangle = \frac{1}{2} \langle S_{\nu,a}^+ S_{\nu,a}^- \rangle, \quad \alpha = a, b, c.
\]

Then the average magnetization in every repeating cell \( M_{\text{tot}} \) and the magnetic susceptibility \( \chi \) are defined as

\[
M_{\text{tot}} = \frac{1}{N} \sum_{i} \langle S_{i,a}^+ S_{i,a}^- \rangle + \langle S_{i,b}^+ S_{i,b}^- \rangle + \langle S_{i,c}^+ S_{i,c}^- \rangle, \quad \chi = \frac{\partial (M_{\text{tot}})}{\partial B}.
\]

The above equations can be solved self-consistently. In calculation, an initial state, composed by a set of magnetizations \( \{S_{\nu}^\alpha\} \), are put into the equations to produce the resultant magnetization. The iteration goes on until convergence is reached.

III. NUMERICAL RESULTS AND DISCUSSIONS

Considering the multicentered nature and the magnetic degrees of freedom within \( S > 1/2 \) molecules, there are four different cases particularly interesting, as displayed in Fig. 2, which will be considered in the present paper: (a) a symmetric ferrimagnetic diamondlike spin chain with \( J_1 = J_2 = J_4 = J_5 \), (b) a nonsymmetric ferrimagnetic diamondlike spin chain with \( J_1 = J_4 \neq J_2 = J_5 \), (c) a dimerized ferrimagnetic diamondlike spin chain with \( J_1 = J_2 \gg J_4 = J_5 \), and (d) a trimerized ferrimagnetic diamondlike spin chain with \( J_1 = J_5 \gg J_2 = J_4 \).

A. A symmetric ferrimagnetic diamondlike spin chain

We start our discussions with analysis of the sublattice magnetizations and the magnetic susceptibilities for case (a), where all AF interactions are uniform \( J_1 = J_2 = J_4 = J_5 \). In order to compare the results between intra- and intermolecular exchange interactions, \( J_5 \sim J_{\text{AF}} \) is considered first. Figure 3(a) manifests the temperature dependence of the sublattice magnetizations \( \langle S_{\nu}^\alpha \rangle (\alpha = a, b, c) \), where the parameter ratio \( \sigma \) is taken as 0.2, 0.4, 0.6, 0.8, and 1.0, and the numerical value of the external field \( B \) is set as 0.002/\( J_3 \). From the figure, we can find that, owing to the symmetry of intermolecular AF interactions, the sublattice magnetization \( \langle S_{\nu}^\alpha \rangle \neq 0 \), and \( \langle S_{\nu}^\alpha \rangle < 0 \), indicating that AF spin alignments occur along the chain; and with increasing \( \sigma \), the Curie temperature \( T_C \) (when \( T_C \sim 0 \), the magnetization approaches to zero) of the system ascends, which indicates that

\[
\text{FIG. 2. The four cases are considered. Case (a): a symmetric ferrimagnetic diamondlike spin chain, where all antiferromagnetic interactions are uniform (} J_1 = J_2 = J_4 = J_5 \text{); case (b): a nonsymmetric ferrimagnetic diamondlike spin chain with } J_1 = J_4 \neq J_2 = J_5 \text{; case (c): a dimerized ferrimagnetic diamondlike spin chain with } J_1 = J_2 \gg J_4 = J_5 \text{; and case (d): a trimerized ferrimagnetic diamondlike spin chain with } J_1 = J_5 \gg J_2 = J_4 .\)
\]
the intermolecular AF interactions play an important role in designing the organic molecule-based ferrimagnet with high Curie temperature $T_C$. The corresponding results for the temperature dependence of the magnetic susceptibility multiplied by temperature $\chi T$ are illustrated in Fig. 3(b). The minimum in the curves of the product $\chi T$ at temperature $T$ is indicative of the ferrimagnetic behavior in low-dimensional lattices. The low-temperature limit of $\chi T$ diverges, suggesting the possible occurrence of ferrimagnetism. We also find that, with increasing $\sigma$, the minimum of the curves, $\chi T_{\text{min}}$, decreases, while the corresponding temperature $T_{\text{min}}$ increases. At the same time, there exist two extreme cases. An extended chain with vanishing $J_3$, which is regarded as an array of vertex-sharing diamonds of exchange coupled spins, can also exhibit ferrimagnetic behavior, as illustrated in the inset of Fig. 3(b). With respect to the structure, an inorganic complex of Cu(II) (Ref. 19) with $S=1/2$ has a divergence in $\chi T$ at the low-temperature limit. So it is believed that only the topology of the AF interactions between the $S=1/2$ spins is responsible for the ferrimagnetic spin alignments. Another extreme case is that all AF interactions are much smaller than $J_3$ (e.g., $J_{\text{AF}} \ll J_F$), the calculated results for the $\chi T$ against temperature are depicted in Fig. 4, where the ratio $\sigma$ is set as 0.05, 0.1, and 0.15, and the value of the external field is taken as $B = 0.002|J_z|$. In this case, it is interesting that the curves of $\chi T$ exhibit a continuous increase as temperature decreases, followed by a round maximum. As the ratio $\sigma$ is much larger, the $\chi T$ drops to a minimum, and then increases with further decreasing temperature (see the curve labeled as $\sigma=0.15$ in Fig. 4 and its left inset), this behavior still indicates the occurrence of ferrimagnetic spin alignments in the diamondlike chain. However, when the ratio $\sigma$ is much smaller (see the curves for $\sigma=0.05$ and 0.1), as the temperature decreases, the $\chi T$ value monotonically decreases, but does not exhibit a minimum or display as an upturn-like ferrimagnetic behavior. This phenomenon is well consistent with the experimental observations in Ref. 20, where they designed and synthesized a triradical as a model compound for a single-component ferrimagnet, in which the intermolecular AF interactions are much smaller than the intramolecular $F$ ones. The experimental curves for the $\chi T$ are also copied in the right inset of Fig. 4. So it strongly indicates that the intermolecular AF interactions play an important role in the formation of ferrimagnetic ordering state in the magnetic systems.

To further investigate how the round peak in the curve of the $\chi T$ appears for the much smaller ratio $\sigma$ at low temperatures, the corresponding sublattice magnetizations $\langle S^z_\alpha \rangle$ ($\alpha=a,b,c$) against temperature for $\sigma=0.05$ and 0.20 are presented in Figs. 5(a) and 5(b), respectively. It is seen that, with increasing temperature, the expectation value $\langle S^z_\alpha \rangle$ changes its sign from negative to positive, giving rise to a compensation temperature $T_{\text{comp}}$, appearing in the curves of the sublattice magnetization $\langle S^z_\alpha \rangle$ against temperature. With increasing of the ratio $\sigma$, the compensation point moves towards higher temperatures. The changing of the sign of $\langle S^z_\alpha \rangle$ indicates that the spin alignments along the chain change from ferrimagnetic to ferromagnetic ones. So it can be believed that there exists an occurrence of temperature-induced phase transition. With further increasing temperature, the curve of $\langle S^z_\alpha \rangle$ shows a round peak, and then decreases, indicating that thermal fluctuations strengthen the sublattice magnetization $\langle S^z_\alpha \rangle$; nevertheless, with increasing of the ratio $\sigma$, this behavior becomes more and more weak. However, the
interesting characteristics are not found in \( \langle S^z_a \rangle \) and \( \langle S^z_c \rangle \). These phenomena can be explained as follows. In fact, the magnetic systems are applied to a small external field, and there obviously exists a competition between the external fields and the intermolecular AF interactions. The external field will open up an energy gap of the system. For a smaller intermolecular AF interaction, the energy gap due to the external field is larger than that of the AF excitations of the magnetic systems. Recalling Fig. 4, it is obvious that the temperature, corresponding to the maximum in the curves of the product \( \chi T \) against temperature for example, \( T_{\text{max}} = 0.294 \) for \( \sigma = 0.05 \), is just located in the \( J \) phase in Figs. 5(a) and 5(c), which indicates that appearance of the round peak in the \( \chi T \) for the much smaller intermolecular AF interactions origins from the \( F \) spin alignments for all spins along the chain. This clarifies the past explanations that the appearance of the round peak is only attributed to intramolecular \( F \) interactions. At the same time, from the phase diagrams, it is also uncovered that the rapid dropping in the curves of \( \chi T \) at low temperatures is attributed to the AF spin alignments of the systems. So it can be believed that the lower-temperature magnetic properties of the molecule-based ferrimagnets with much small intermolecular AF interactions are determined by that of the monoradical spin \( S_0 \). Similarly, the influence of the external fields on the sublattice magnetizations is also considered, and the corresponding field-induced phase diagram is illustrated as in Fig. 5(d). It can be seen that the ferrimagnetic ordering state only occurs in the lower external fields, because the stronger external fields will give rise to the \( F \) spin alignments for all spins along the chain. It should be pointed out that the field-induced phase diagram is well consistent with the \( T-H \) phase diagram from magnetic properties measurements for an organic molecule-based ferrimagnet in Ref. 3.

**B. A nonsymmetrical ferrimagnetic diamondlike spin chain**

Next, let us turn to discuss the nonsymmetrical ferrimagnetic diamondlike spin chain [case (b)]. As mentioned above, for an organic molecule-based magnet, the intermolecular interactions have a multicentered nature and low spatial symmetry. So it is essential to discuss the influence of spatial symmetry lowering of the intermolecular AF interactions on the spin distribution of the chain. In Fig. 6(a), we evaluate the temperature dependence of the sublattice magnetizations, where the parameters are set as \( J_1 = J_4 \), \( J_2 = J_5 = J_3 \), and \( \tau = J_1/|J_3| \). The ratio \( \tau = J_1/|J_3| \) signifies the spatial symmetry of the intermolecular exchange interactions and is set as 0.0, 0.4, 0.6, and 1.0. From the figure, we can see that, with increasing of the ratio \( \tau \), the Curie temperature \( T_C \) increases, which indicates that higher spatial symmetry of the intermolecular AF interactions has contribution to enhance the Curie temperature of...
the magnetic systems. Moreover, as the temperature approaches towards zero, with decreasing \( \tau \), the sublattice magnetization \( \langle S^z_l \rangle \) is reduced to the magnetic moment of \( \langle S^z_0 \rangle \) and has an obvious trend to form a single-pair state \( (S=0) \) with the spin \( S_0 \). This characteristic is consistent with the phenomenological analysis for the ground state of a molecule-based ferrimagnet by Shiomi and co-workers.\(^9,\!^11\) Nevertheless, with increasing \( \tau \), the sublattice magnetization \( \langle S^z_l \rangle \) increases, indicating that the reduced AF interactions with which enhance its spin density. Considering the whole-temperature region, the spin magnetic moment of the biradical is reduced by the quantum spin contraction. The spin contraction should occur in the metal-based ferrimagnetic chains. However, the contraction in the molecule-based ferrimagnetic chain is due to the asymmetric intermolecular AF interactions. This novel effect tells us that the spin state of a molecule is affected by the spatial symmetry of the intermolecular magnetic interactions, when the intermolecular interaction has a multicentered nature. The spin contraction can also be found in the corresponding curves of \( \chi T \), as illustrated in Fig. 6(b). It can be seen that, with increasing \( \tau \), owing to the strong intermolecular AF interactions, the minimum of \( \chi T \) decreases and shifts towards higher temperatures. This behavior is much similar to case (a). In particular, it is worth noting that, even when \( \tau=0 \), the curve \( \chi T \) still exhibits an obvious ferrimagnetic behavior. Its topology structure is just close to a typical model for designing purely organic magnets studied by Fang et al.,\(^2,\!^21\) who pointed out that the system has a stable high-spin ferrimagnetic ground state.

It should be mentioned that there exists a model organic compound based on nitronyl nitroxide radical on experiment for this case. Izuoka et al. have reported the crystal structure and the static magnetic susceptibility of a molecular complex, which consist of alternating chain of a doublet monoradical and a biradical molecule.\(^7\) The complex can be well described by the theoretical model as illustrated in Fig. 1. The molecular ground state of the biradical molecule has been found to be triplet \( (S=1) \) in a mixed crystal of biradical molecule diluted in a diamagnetic compound. The magnetic susceptibility multiplied by temperature \( \chi T \) measured at a certain external magnetic field is drawn through round circles in Fig. 7, which obviously exhibits a typical ferrimagnetic behavior. To our knowledge, the complex is the first model system for purely organic ferrimagnets with well-characterized molecular and crystal structure. In order to compare with experimental data, the external field \( B \) should be replaced by \( g\mu_B B \) in the calculations, where \( g \) is Landé factor and \( \mu_B \) is Bohr magneton. From the theoretical calculations, we can find that when the parameters are set as \( J_1 = J_4, J_3 = J_5 = 0.9 J_1, J_2 = 1.5 J_1 \), and the value of the external field \( B = 0.136 |J_1| / g\mu_B \), the curve for \( \chi T \) can be compared with the experimental results. The low-temperature maximum and intermediate-temperature minimum are both located at \( \sim 3 \) and \( 6 \) K, and our fitting results lead to \( J_1/k_B \sim (20 \pm 0.5) \) K, \( J_2/k_B \sim (18 \pm 0.5) \) K, and \( J_3/k_B \sim (30 \pm 0.5) \) K, which are well consistent with the experimental findings. At the same time, the results for \( \chi T \) against temperature in other different external fields are also drawn in the Fig. 7. From which, it can be seen that when the external field is much small (see \( B = 0.001 \)), the low-temperature limit of \( \chi T \) diverges which is similar to the discussions before; when the external field increases to a larger value, the curve for \( \chi T \) emerges a sharp peak at low temperatures, indicating that the external field opens up an energy gap, which makes \( \chi T \) go exponentially to zero for temperatures less than the gap in the applied field. With further increasing of the external field, the peak is suppressed and shifts towards high-temperature region. However, in a stronger external field, the low-temperature peak and minimum at the intermediate temperatures both vanish. It should be pointed out that those magnetic behaviors are well similar to ones of a spin-1 and spin-1/2 alternating ferrimagnetic spin chain in external magnetic fields.\(^7\)

C. Dimerized and trimerized ferrimagnetic diamondlike spin chain

Since there are no stable molecular or electrovalent bonds between two neighboring molecules, the molecular dimer of a biradical and a monoradical, and molecular trimer composed of a monoradical and the two nearest adjacent biradical molecules, are easily formed experimentally, indicating that the molecular dimers and trimers will play an important role in the magnetic properties of the molecule-based ferrimagnets. First, let us focus on the influence of the molecular dimers along the chain on the sublattice magnetizations, as illustrated in Fig. 8(a), where the parameters are taken as \( J_1 = J_2, J_4 = J_5 = 0.5 |J_3| \), and the ratio \( \nu = (|J_1| / |J_3|) \) denotes the dimerization degree of the intermolecular AF interactions. From Fig. 8(a), it can be seen that, with increasing of the ratio \( \nu \), the Curie temperature \( T_C \) increases to higher temperatures. This behavior could be well explained in terms of the spin polarization mechanism. In these situations, the alternating molecular chain of the biradical and monoradical can be regarded as an assembly of the biradical-monoradical pairs, which behaves as a magnetic supramolecule with an effective spin vaule \( S = 1/2 \). Thus, the spin polarization of the
magnetic supramolecules has been shown to bring about effectively \( F \) interactions along the chain. As a result, the ferrimagnetic spin alignments in the heteromolecular chains are shown to be equivalent to the \( F \) alignments of the effective \( S=1/2 \) spins. It should be pointed out that the equivalence has been examined in a real open-shell molecular system composed of the organic triradicals.\(^{22}\) In particular, for \( \nu = 0 \), the sublattice magnetizations drop to zero rapidly with increasing temperature, because the system reduces to \( N \) independent dimers for the adjacent radical and monoradical molecules, leading to the losing of the long-range magnetic ordering. However, from the calculated results, we can see that there exists a drawback for the spin polarization, because the sublattice and total magnetizations for the ground state are reduced by the strengthening of intermolecular AF interactions. Thus, the two opposite effects of the molecular dimers (e.g., to enhance Curie temperature \( T_C \), and to reduce the ground-state magnetizations) should be taken into account in designing and synthesizing of the molecule-based ferrimagnets. The corresponding results for the product \( \chi T \) are illustrated in Fig. 8(b). It can be seen that the curves of \( \chi T \) display as typical ferrimagnetic behaviors for all set parameters, and with increasing \( \nu \), the value \( \chi T_{\text{min}} \) decreases, the corresponding temperature \( T_{\text{min}} \) ascends to higher temperatures.

For the trimerized ferrimagnetic diamondlike spin chain [case (d)], the calculated results are shown in Figs. 8(c) and 8(d), where \( J_1 = J_5 \), \( J_2 = J_4 = 0.5 |J_3| \), and the ratio \( \gamma = J_1 / |J_3| \) denotes the trimerization degree. It is noted that, except for the curve for \( \gamma = 0 \), the main characteristics for this case are much similar to ones of the molecular dimerized case as discussed above. Because in the case \( \gamma = 0 \), the diamondlike chain reduces to a one-dimensional linear chain, which is much different from the case for \( \nu = 0 \) above. The magnetic behaviors in this case could also be explained in terms of the spin polarization mechanism. Nevertheless, what is different from above is that the trimerized unit, which can be regarded as an \( S=1/2 \) supramolecule, is composed of three nearest adjacent radicals, i.e., the radical \( S_{1-a} \) and \( S_{1-e} \), and \( S_{1-b} \) as illustrated in Fig. 2(d).

![FIG. 8. Magnetic properties of a dimerized and trimerized spin-1/2 ferrimagnetic diamondlike chain. (a) and (b) are drawn for case (c), e.g., \( J_4 = J_6 = 0.5 |J_3| \), \( J_1 = J_3 = \nu |J_3| \), where \( \nu \) indicates intermolecular dimerization; (c) and (d) are drawn for case (d), e.g., \( J_1 = J_5 = 0.5 |J_3| \), \( J_2 = J_4 = \gamma |J_3| \), where \( \gamma \) indicates trimerization among three nearest adjacent radicals; and (e) and (f) are drawn for different intramolecular ferromagnetic interactions \( J_4 \) in case (c), the parameters are set as \( J_1 = J_2 = J_3 = 0.5 J_4 \), \( J_1 = -\eta J_4 \), where \( \eta \) indicates the strengthening of the intramolecular interaction. In (a)-(d), the temperature is united by \( T / |J_3| \) and \( B = 0.002 |J_3| \); but in figures (e)-(f), the temperature is united by \( T / J_1 \) and \( B = 0.002 J_1 \).](image-url)
be stressed that with increasing of the ratio \( \eta \), the curves for the sublattice magnetization \( S^z \) and the product \( \chi T \) obviously approach to a limited case. This phenomenon should be understood that with stronger intramolecular \( F \) interactions within the biradical along the chain, there is a continual crossover from two independent doublet states in the biradical to a stable triplet ground state, such that the biradical having two \( S=1/2 \) spins becomes closer and closer to that of an effective \( S=1 \) monomolecule for the magnetic properties.

**IV. CONCLUSIONS**

In summary, the magnetic properties of purely organic molecule-based ferrimagnets are investigated in detail by means of the many-body Green’s function method within random phase approximation. Our results show that the intermolecular AF interactions play an important role in the ferrimagnetic spin alignments. The strengthening of the intermolecular AF interactions has contributions to enhance the Curie temperature \( T_C \) of the magnetic systems. By analysis of the sublattice magnetizations at finite temperatures, the magnetic phase transitions are obtained. From the phase diagrams, we have found that, owing to the very small intermolecular AF interactions, the spins along the diamond-like chain behave as \( F \) spin alignments even at very low temperatures, and the curves of the product \( \chi T \) against temperature display as a round peak at low temperatures. This magnetic behavior can be explored to explain the experimental observations. We have also got that, only when the temperature is cooled down to a ultralow temperature, the ferrimagnetic phase transition can occur, which makes it very difficult to observe an obvious ferrimagnetic phase transition in practical organic materials with small intermolecular AF interactions.

The spatial symmetry of the intermolecular AF interactions is important to stabilize the ferrimagnetic states of the magnetic systems. When the symmetry is lowered, it is easy to form an \( S=0 \) singlet ground state along the chain. This would make the Curie temperature \( T_C \) descend and reduce the sublattice magnetizations. Therefore, the magnetic degree of freedom within \( S>1/2 \) molecules and the spatial symmetry of intermolecular exchange interactions should be taken into account when to synthesize a purely molecular ferrimagnet containing \( S>1/2 \) molecules. In addition, our theoretical calculations could be fitted well to the experimental data.

The influences of the molecular dimer and trimer of a monoradical and a nearest adjacent biradical molecule on the magnetic properties of the molecule-based ferrimagnets are also discussed. It is concluded that the spin polarization of the magnetic supramolecules has shown to bring about effectively \( F \) interactions between the supramolecules, which is equivalent to the \( F \) alignments of the effective \( S=1/2 \) spins. As a result, the Curie temperature ascends. Meanwhile, compared to the influence of intramolecular \( F \) interactions on the magnetic properties of the magnetic systems, it is believed that the transition temperature to a possible ferrimagnetic ordering state should be governed by the AF interactions between the supramolecules.

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