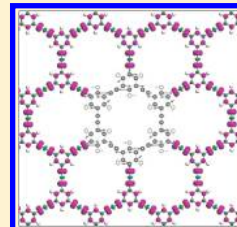


# Ferromagnetism in Two-Dimensional Carbon Chains Linked by 1,3,5-Benzenetriyl Units

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**ABSTRACT:** Development of organic materials with novel magnetic properties has been an important and challenging topic in organic chemistry. A useful paradigm in this direction is to have spin-containing (SC) components linked by ferromagnetic coupling (FC) units. Compared with the traditional SC components such as poly(1,3-phenylenecarbene)s and poly(1,3-phenylenephenylmethine)s, we show that the atomic carbon chains, due to their inherent magnetism and structural simplicity, can be promising magnetic building blocks of 2-D magnetic carbon structures. Using calculations based on density functional theory, we show that the structures constructed by the carbon chains with an odd number of C atoms linked by 1,3,5-benzenetriyl units are ferromagnetic. Independent of the chain length, each structural unit cell has a magnetic moment of  $6.0\mu_B$  and couples ferromagnetically in the 2-D lattice, although the energy difference between the ferromagnetic and antiferromagnetic coupling decreases with increasing chain length. The dynamic stability of the structures is confirmed by frequency calculations. The middle and high vibrational frequencies corresponding to the  $A_{1g}$  and  $E_{2g}$  modes of the structures with odd number carbon chains lie in the range of  $950\text{--}1470\text{ cm}^{-1}$ , which are lower than those ( $980$  and  $1555\text{ cm}^{-1}$ ) with even-numbered carbon chain structures. This suggests that Raman spectra can be used to identify the parity of carbon chains.



## 1. INTRODUCTION

Carbon is a unique element due to its flexibility of  $sp^3$ ,  $sp^2$ , and  $sp$  bonding features, which result in diverse structures such as diamond, graphite, fullerene cages, carbon nanotubes, graphene sheets, and atomic carbon chains. These carbon-based structures have been hotly pursued by researchers in chemistry, physics, and materials science because of their technological importance. Currently special attention has been paid to the magnetism of carbon-based materials because of their chemical tunability and weak spin-orbit and hyperfine couplings between the  $p$  electrons that are the main channels of relaxation and decoherence of electron spins.<sup>1</sup> Experimentally, magnetism of carbon-based systems such as hydrogenated nanographite ribbons,<sup>2,3</sup> activated carbon fibers,<sup>4</sup> and rhombohedral  $C_{60}$ ,<sup>5</sup> has been observed. Recently Chen et al.<sup>6</sup> observed intrinsic ferromagnetism of graphene-based materials at room temperature. Matte et al.<sup>7</sup> found that graphene samples show Curie-Weiss-type behavior, and the AC susceptibility data show the absence of spin-glass behavior. It has also been confirmed that zig-zag-edge states of graphene contribute to magnetism.<sup>8</sup> It is well known that ferromagnetism in carbon materials is a well-debated area. In the majority of the experiments, the signals are weak ( $<1\text{ emu}$ ), or in the case of stronger signals, there is ambiguity on the purity of the samples. Here we show that ferromagnetism does exist in the 2-D porous carbon-based structures composed of the carbon chains with an odd number ( $N$ ) of carbon atoms linked by the 1,3,5-benzenetriyl units.

Because of the inherent structural simplicity as well as the unique electronic, optical, and physicochemical properties, carbon chain is currently attracting tremendous attention from multidisciplinary areas ranging from organic chemistry,

nonlinear optics, and solid-state physics to astrophysics. The linear atomic carbon chains have been successfully carved out from a graphene sheet by using high-energy electron beam.<sup>9-11</sup> The carved carbon chains are longer and more stable than those previously synthesized using other methods.<sup>12-14</sup> It has been found that the HOMO-LUMO gap is strongly influenced by the number,  $N$  of carbon atoms constituting the chain.<sup>15</sup> Moreover, their third-order nonlinear optical properties and their nonresonant molecular second hyperpolarizabilities have been reported to increase as a function of the chain length.<sup>16,17</sup> For a free-standing finite carbon chain, the one with even  $N$  of C atoms has total magnetic moment of  $2\mu_B$ , whereas that with odd  $N$  has no net magnetic moment.<sup>18</sup> However, the situation is totally different when each end of the carbon chains is terminated with one H atom forming  $H-C_N-H$  structure. The carbon chains with odd  $N$  have magnetic moments of  $2\mu_B$ , whereas it is  $0\mu_B$  for the chains with even  $N$  of C atoms.<sup>19</sup> The observed magnetic behavior can be understood as follows:  $H-C_N-H$  polyynes have  $4N+2$  valence electrons,  $(N+1)$   $\sigma$  orbitals (each of them hosting two electrons), and  $(N-1)$  two-fold-degenerate  $p-p-\pi$  orbitals, which must accommodate the remaining  $2N$  electrons. Hence, when  $N$  is odd, the spin degeneracy must break to avoid a zero HOMO-LUMO gap. Even-numbered chains have an odd number of two-fold degenerate  $p-p-\pi$  orbitals, and hence there is no partially filled level in the unpolarized configuration: a singlet unpolarized ground state is favored. The resulting magnetic carbon chains are expected to be effective as

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spin filters, spin valves, and spin-transmitters.<sup>20,21</sup> Moreover, these carbon chains can be considered to be important structural building blocks for diverse composite structures. For example, they have been used as a linker to connect carbon nanotubes,<sup>22</sup> graphene flakes,<sup>9–11</sup> and functional groups.<sup>23</sup> Very recently, a novel 2-D periodic framework (graphdiyne) composed of carbon chains has been synthesized<sup>24</sup> through cross-coupling reaction using hexaethynylbenzene on copper surface. This novel structure is beyond graphene sheet and has been recently highlighted in *Nature Materials*.<sup>25</sup> However, it is not magnetic. Therefore, how to introduce magnetism to periodic structures composed of carbon chains has become one of the most challenging problems for chemists and physicists.

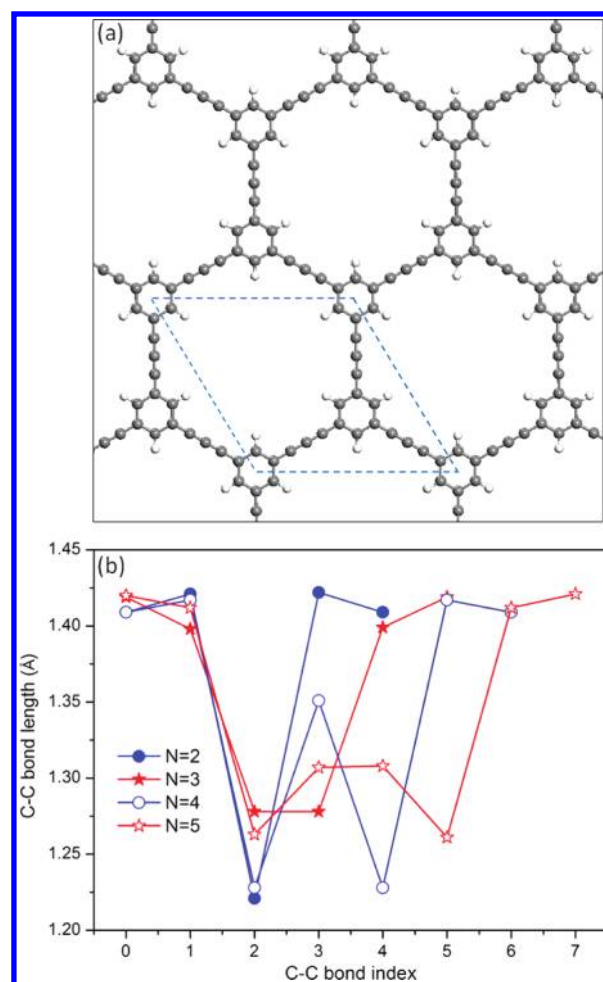
A well-known paradigm in pursuing organic magnetic materials is to have the SC components linked by ferromagnetic coupling units (FCUs).<sup>26</sup> To assemble the carbon chains with long-range magnetic coupling, we need to address the following questions: (1) How does one choose an effective FCU? (2) Is the assembled periodic structure thermodynamically stable? (3) Are the magnetic properties of the carbon chain segments retained when they are assembled to a 2-D periodic system? (4) Is the designed structure feasible in experiment? To date, the 1,3-benzenediyl and 1,3,5-benzenetriyl are well-known FCUs acting as strong and versatile ferromagnetic couplers in one and two dimensions.<sup>27</sup> When two SC components are connected by the 1,3-benzenediyl, the resulting diradical inevitably has two nearly degenerate nonbonding molecular orbitals (MOs) (for example, *m*-benzoquinodimethane). These nonbonding MOs distribute over the common atoms; therefore, strong exchange interactions are expected to occur between the two radical spins, leading to a high-spin configuration. This mechanism is closely related to Hund's rule in atomic physics.<sup>28,29</sup> In this Article, we report a first-principles study of magnetism of the new 2-D structures using the carbon chains as the SC components and the 1,3,5-benzenetriyls as FCUs.

## 2. COMPUTATIONAL METHOD

The numerical calculations have been performed using the spin-polarized density functional theory (DFT) with the Perdew–Burke–Ernzerhost (PBE)<sup>30</sup> form for the generalized gradient approximation (GGA) for exchange and correlation functional. The calculations of total energies, forces, and optimizations of geometries were carried out using a plane-wave basis set with the projector augmented plane wave (PAW) method,<sup>31</sup> as implemented in Vienna ab initio simulation package (VASP).<sup>32</sup> A kinetic energy cutoff of 400 eV was used. For the Brillouin zone sampling, a uniform grid of  $5 \times 5 \times 1$  Monkhorst-Pack *k*-point was used for the 2-D periodic frameworks. (The  $\Gamma$  point is included.) The supercell geometry for the images has been used, in which the adjacent distance is 12 Å, sufficient to prevent the interactions between them. All atoms are fully relaxed using a conjugate-gradient algorithm until the change in energy upon ionic displacement is  $<0.01$  meV and the magnitude of forces on each atom is  $<0.001$  eV/Å. The phonon frequencies at  $\Gamma$  point are obtained by the ab initio force constant method;<sup>33</sup> the nonresonant Raman spectrum is calculated simply using the empirical bond polarizability model.<sup>34,35</sup>

## 3. RESULTS AND DISCUSSION

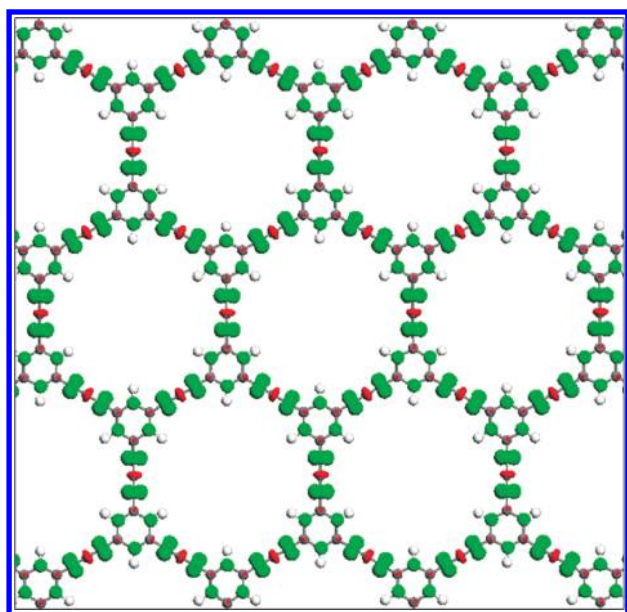
We start our discussion with the geometry that was assembled by using the carbon chains as SC components and the



**Figure 1.** (a) Optimized geometry of the  $C_6H_3-C_3-C_6H_3$  framework. The unit cell is marked by the rhombus. (b) Variation of C–C bond length with respect to C–C index for systems with even ( $N = 2, 4$ ) and odd ( $N = 3, 5$ ) numbered C chains.

1,3,5-benzenetriyl FCUs. A 2-D porous carbon-chain-based periodic structure was constructed, as shown in Figure 1a, where the  $C_3$  chain is chosen as an example. The unit cell contains three  $C_3$  chains and two FCUs (the  $C_6H_3$  rings). The optimized lattice parameters are  $a = b = 14.236$  Å. As stated above, a carbon chain  $C_N$  can be magnetic or nonmagnetic depending on its parity, that is, the size  $N$  and the end group. We have changed the size  $N$  of carbon chain from  $N = 1$  to 5 to generate different size periodic structures and to study the differences of their electronic and magnetic properties. In experiment, such kind of 2-D porous structure can be obtained by etching a graphdiyne sheet using electron beam irradiation and then using H atoms to passivate the dangling bonds of carbon rings.

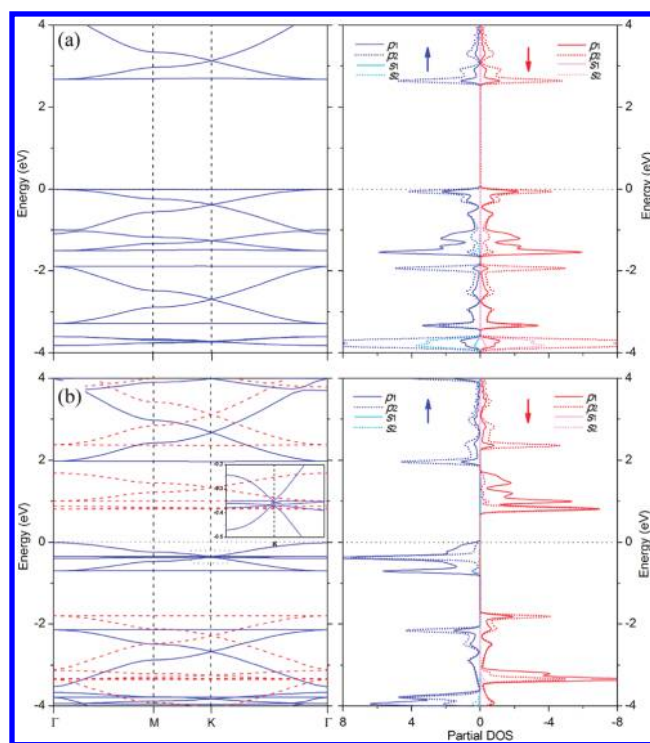
The geometry optimization was carried out for all 2-D periodic structures. The variation of C–C bond length with respect to the C–C bond index is plotted in Figure 1b. For a carbon chain,  $C_N$ , there are  $(N - 1)$  C–C bonds inside the chain, two C–C bonds that are connected with the  $C_6H_3$  rings on two ends of the chain, and one equivalent C–C bond for each of the two  $C_6H_3$  rings. Therefore, we have  $(N - 1) + 2 + 2 = N + 3$  bond indices (labeled starting from 0 to  $N + 2$  in Figure 1). The index 0 and index  $N + 2$  are for the C–C bond length ( $d_0$ ) in the two equivalent rings, the index 1 and index  $N + 1$  are for the bond



**Figure 2.** Iso-surface of the spin density at  $0.1 \mu_B \text{ \AA}^{-3}$  for the  $\text{C}_6\text{H}_3\text{-C}_3\text{-C}_6\text{H}_3$  framework. The green and red colors represent spin-up and spin-down electrons, respectively.

length ( $d_1$ ) between the carbon chain and the ring, and the others are for the bond length ( $d_i$ ) of the chain. We find that when  $N$  goes from 1 to 3 and to 5,  $d_0$  changes from 1.425 to 1.420 and to 1.418 Å, whereas  $d_1$  slightly increases from 1.393 to 1.398 and to 1.412 Å. For  $N = 3$ ,  $d_i$  is 1.278 Å. For  $N = 5$ ,  $d_i$  for the four C–C bonds is in the range of 1.261 to 1.308 Å. For  $N = 2$  and 4, these two structures have almost the same  $d_0$  (1.409 Å) and  $d_1$  (1.420 Å). For  $N = 4$ ,  $d_i$  oscillates significantly between 1.228 and 1.351 Å. In general, the length of single  $\sigma$  bond is  $\sim 1.47$  Å, whereas the double ( $\sigma + \pi$ ) and triple ( $\sigma + 2\pi$ ) bonds shrink to  $\sim 1.380$  and  $\sim 1.210$  Å, respectively. When a delocalized big  $\pi$  orbital takes part in bonding, the corresponding bond length will be slightly elongated. In the  $\text{C}_6\text{H}_3$  rings, the bond length is  $\sim 1.410$  to 1.420 Å, which lies between single and double bonds, corresponding to ( $\sigma + \text{big } \pi$ ) bonding, similar to that of a pristine graphene sheet, 1.42 Å. The bond in the inner  $\text{C}_N$  chains with odd  $N$  is close to a double bond, whereas for the even  $N$  carbon chains,  $\text{C}\equiv\text{C}$  triple bonds exist.

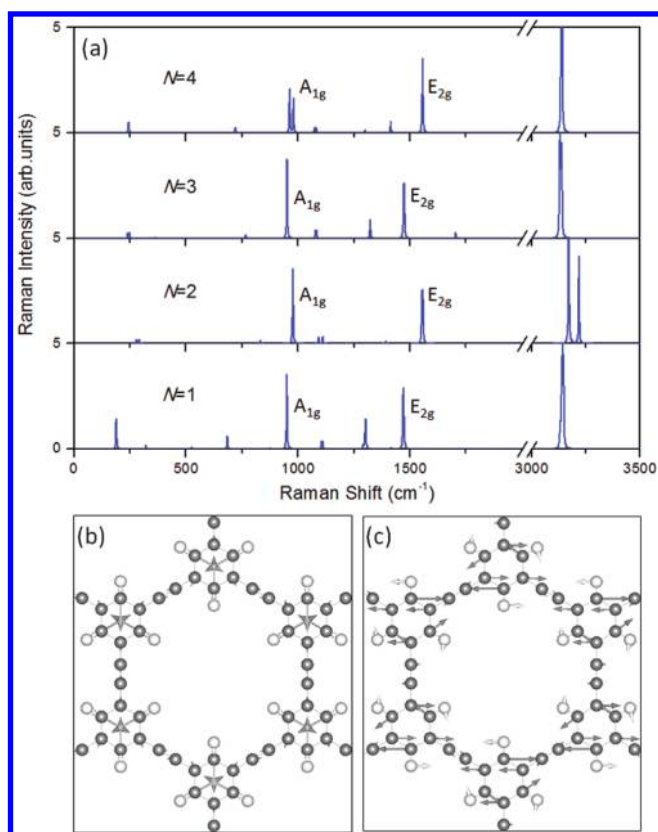
We next studied the magnetic properties of the carbon-chain-based 2-D structures. Extensive calculations were carried out for all systems ( $N = 1$  to 5) with different magnetic coupling between the unit cells, namely, ferromagnetic (FM) coupling, nonmagnetic (NM) coupling, and antiferromagnetic (AFM) coupling. For the AFM calculations, a supercell consisting of  $2 \times 2$  unit cells is used. It was found that the FM state is always lower in energy than either the AFM or NM states, and the magnetic moment per unit cell is  $6.0\mu_B$  for all odd  $N$  systems ( $N = 1, 3$ , and 5). The energy difference  $\Delta E$  between the FM and AFM (NM), defined as:  $\Delta E = E_{\text{FM}} - E_{\text{AFM(NM)}}$ , is calculated to be  $-0.20$  ( $-1.72$ ),  $-0.13$  ( $-1.55$ ), or  $-0.08$  ( $-1.32$ ) eV for  $N = 1, 3, 5$  respectively, indicating that these systems clearly favor the FM state. The NM state is found to be the ground state for the system when  $N$  is even. It is interesting to see that the carbon chains in the assembled 2-D structures behave like that in  $\text{H-C}_N\text{-H}$ , where the  $\text{C}_N$  chain is magnetic and each chain carries a moment of  $2\mu_B$  when  $N$  is odd, and it is nonmagnetic when  $N$  is even, regardless of the length of the chain.



**Figure 3.** Band structures of the 2-D periodic  $\text{C}_6\text{H}_3\text{-C}_N\text{-C}_6\text{H}_3$  frameworks along the high-symmetry points and the corresponding partial DOS. (a)  $N = 2$ . (b)  $N = 3$ . P1 (S1) and P2 (S2) lines in the partial DOSs represent the occupations of p (s) electrons from the carbon chains and the  $\text{C}_6\text{H}_3$  rings, respectively. The inserted figure in Figure 3b is the enlarged energy bands near the K point.

To understand further the magnetism exhibited in the new 2-D structures, we plot the iso-surface of the spin density for the system with  $N = 3$  carbon chains in Figure 2, which clearly shows that a net spin density is mainly localized on each of the C atoms in the chains, and the magnetic moment mainly comes from 2p electrons of the C atoms. More importantly, the spin couples ferrimagnetically [ $\uparrow\downarrow$ ] in the chains. Therefore, *antipattern rule* for magnetic coupling that is widely used in graphene nanoribbons<sup>36</sup> to explain the magnetism can be applied here; that is, the magnetic C atoms in the chain couple ferrimagnetically with their nearest neighbors, which leads to the C atoms at 1, 3, 5 sites in the 1,3,5-benzenetriyl FCUs couple ferromagnetically. In this way, a long-ranged magnetic ordering is established. The origin of the spin polarization is due to the presence of unsaturated carbon bonds in the odd  $N$  carbon chains. For the even  $N$  chains, all C atoms are saturated; therefore, no magnetism appears. For the odd  $N$  chains, the exact alternation of single and triple bonds cannot be achieved because of the even number of C–C bonds in the chains, and the magnetic C atom favors to couple ferrimagnetically with its nearest neighbor C atoms. Consequently, the chain with odd  $N$  carbon atoms displays a net spin with a uniform magnetic moment of  $2\mu_B$ . The FCU acts like a node to transfer magnetic coupling between the carbon chains. Therefore, we note that the new 2-D  $\text{C}_6\text{H}_3\text{-C}_N\text{-C}_6\text{H}_3$  framework can be considered to be a switch for controlling the transformation of magnetism from the FM to NM by changing the parity of the carbon atoms in the chain from odd  $N$  to even  $N$ .

The electronic structure of the new system was studied by performing band structure calculations. We note that the parity



**Figure 4.** (a) Nonresonant Raman spectra of the  $C_6H_3-C_N-C_6H_3$  ( $N = 1$  to 4) frameworks. (b,c)  $A_{1g}$  and  $E_{2g}$  modes, respectively, as labeled in Figure 4a. The solid arrows represent the vibrational vectors.

of  $N$  not only affects the bonding feature and magnetic properties but also changes the band structures. Although it was found that all assembled 2-D frameworks are direct-band gap semiconductors, the band gap for the structures with odd  $N$  carbon chains is much smaller than that for the even  $N$  carbon chains. For  $N = 1, 3$  and 5, the gap is 1.18, 0.82, and 0.77 eV, respectively, whereas for  $N = 2$  and 4, the corresponding values are 2.68 and 2.37 eV. The band gaps for both the odd and even  $N$  carbon chains containing frameworks decrease with increasing chain length. The band structures and the partial density of states (DOS) for  $N = 2$  and 3 are given in Figure 3, as examples. The difference between them is obvious. For  $N = 2$ , the system is a wide-gap nonmagnetic semiconductor. The bands near the Fermi level are dominated by the C 2p orbitals, but the contribution from the  $C_6H_3$  rings is larger than that from the chains. This is because 2p electrons in the carbon chains are all paired, which decreases their energy and makes them occupy the lower energy bands and be far away from the Fermi surface. This can be seen from the calculated partial DOS in Figure 3a, showing that the bands near the Fermi surface are mostly occupied by 2p electrons from the  $C_6H_3$  rings, and the spin-up and spin-down DOSs are totally identical. Therefore, the even  $N$  frameworks are nonmagnetic and nonmetallic. For  $N = 3$ , there are six spin-split bands near the Fermi level. Both the valence band maximum (VBM) and the conduction band minimum (CBM) arise from the C 2p orbitals in the chains. Actually, it was found that all calculated odd  $N$  frameworks have similar six-split bands. From the partial DOS in Figure 3b, we see that the contribution to the six-split bands from the C 2p orbitals in the chains is more than that from the rings. This is due to the higher

energy of the former ones induced by their imparity. Therefore, the unpaired 2p orbitals near the Fermi surface highly prefer to split, resulting in a total moment of  $6.0 \mu_B$  per unit cell. This is contributed mainly from the three carbon chains in the unit cell, namely, each chain contributes  $2.0 \mu_B$ . Therefore, the spin-polarized states make the system a narrow-band magnetic semiconductor.

Finally, we carried out frequency calculations for all new 2-D frameworks ( $N = 1$  to 5) to determine their dynamical stability. No imaginary frequencies were found. Consequently, all structures are dynamically stable. On the basis of the frequency calculations, we further calculated the Raman spectra. Note that Raman spectroscopy has been used to probe structural and electronic characteristics of graphite materials, providing useful information on in-plane vibration of  $sp^2$  carbon atoms (G-band), where graphite materials have a doubly degenerate (transverse optical (TO) and longitudinal optical (LO)) phonon mode with  $E_{2g}$  symmetry at the Brillouin zone center.<sup>37</sup> Recently, the carbon polyynic chains and cumulenic chains in free states were studied, and it was found that the different chains can be identified by means of Raman spectroscopy based on their intensity.<sup>38</sup> In our studied systems, the atomic carbon chains are not in free states but linked by 1,3,5-benzenetriyl units forming 2-D structures. So different behaviors can be expected, as the details of Raman spectra depend on the bonding environment and geometry. The calculated nonresonant Raman spectra for  $N = 1$  to 4 are plotted in Figure 4a. There are three strong peaks around 950, 1500, and 3140  $cm^{-1}$  for all frameworks corresponding to the middle, higher, and highest modes, respectively. The frequencies of the highest mode corresponding to the C–H stretching vibration are nearly the same for all the frameworks. The middle mode is labeled as  $A_{1g}$ , representing the movement of the 2,4,6 sites atoms in 1,3,5-benzenetriyl units along the carbon-chain directions, as shown in Figure 4b. The second peak, the higher mode, is labeled as  $E_{2g}$ , which has the same symmetry as that of the G-band ( $1582 \text{ cm}^{-1}$ ) of graphene. The corresponding vibrational directions of  $E_{2g}$  mode are given in Figure 4c. It shows that this mode is predominantly contributed by the vibrations of C atoms in the  $C_6H_3$  rings. Therefore, the frequencies of  $E_{2g}$  and  $A_{1g}$  modes mainly depend on the C–C bond length ( $d_0$ ) of the  $C_6H_3$  rings. On the basis of the calculated results, as given in Figure 1b, the bond length ( $d_0$ ) in the  $C_6H_3$  rings linked by even  $N$  carbon chains is shorter than that linked by odd  $N$  chains, which increases the force constant and results in higher frequencies. Consequently, we observed in the calculated Raman spectra, as shown in Figure 4a, that for the frameworks with even  $N$  carbon chains, the frequencies of  $A_{1g}$  and  $E_{2g}$  modes upshift by about 30 and 85  $cm^{-1}$ , respectively, as compared with those of about 950 and 1470  $cm^{-1}$  for the structures with odd  $N$ ; that is, they are dependent on parity of the carbon chains but not on the magnitude of  $N$ . Therefore, Raman spectra can be used to identify parity of the  $N$ .

#### 4. CONCLUSIONS

In summary, we have studied ferromagnetism and stability of novel organic magnetic materials based on the carbon chain 2-D porous structures. The following conclusions can be made: (1) 1,3,5-Benzenetriyl units can serve as effective ferromagnetic coupling units, and the *antipattern rule* of magnetic coupling in carbon structures makes the carbon chains with odd number of carbon atoms ferromagnetically coupled. The resulting magnetic

semiconductors have narrow band gaps. (2) The magnetic coupling strength and band gap can be further tuned by varying the carbon chain length. (3) When even  $N$  carbon chains are assembled, the systems become nonmagnetic semiconductors with wide band gaps and higher frequencies in  $A_{1g}$  and  $E_{2g}$  modes. (4) Because of the strong covalent bonding in carbon chains as well as in the 1,3,5-benzenetriyl units, the assembled structures are dynamically stable. Compared with the conventional organic magnetic materials composed of polyradicals or polymers, the inherent structural simplicity and flexible tunability of the atomic carbon chains make the studied 2-D porous carbon structures attractive candidates for magnetic applications. We hope our study will stimulate experimental effort in this direction.

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