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Xingxing Li, and Jinlong Yang

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# Realizing Two-Dimensional Magnetic Semiconductors with Enhanced Curie Temperature by Antiaromatic Rings Based Organometallic Frameworks

Xingxing Li<sup>†</sup> and Jinlong Yang<sup>†,\*</sup>

Department of Chemical Physics, Hefei National Laboratory for Physical Sciences at the Microscale, and Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China.

**ABSTRACT:** Two-dimensional (2D) magnetic semiconductors with room temperature ferromagnetism are very desirable. Despite the great progress made recently, the Curie temperature is still very low ( $\sim 45$  K), originated from the weak ferromagnetic superexchange interaction. Here, based on first principles calculations, we propose a general route to achieve 2D magnetic semiconductors with enhanced Curie temperature in organometallic frameworks by incorporating antiaromatic rings as organic linkers. Antiaromatic rings usually possess low-energy multiple spin states, which can be easily induced by adjacent magnetic moments of transition metals and subsequently coupled with them through the strong d-p direct exchange interaction, producing high temperature ferrimagnetic ordering. The design of 2D organometallic frameworks with typical antiaromatic rings such as pentalene, which show Curie temperatures above room temperature from classic Heisenberg model Monte Carlo (MC) simulations, confirms our proposal.

Two dimensional (2D) magnetic semiconductors, integrating semiconductivity, ferromagnetism and low dimensionality, serve as the cornerstone for high speed nanospintronic devices. However, due to the incompatibility between semiconductivity and ferromagnetism, the magnetic ordering temperature (Curie temperature) is usually significantly lower than room temperature, preventing any realist application. For example, the recently realized 2D CrGeTe<sub>3</sub> and CrI<sub>3</sub>, only present a Curie temperature about 45 K.<sup>1,2</sup> The underlying reason is the weak 90 ° d-p-d superexchange interaction. On the contrary, 2D metals with room temperature ferromagnetism are much easier to achieve, such as VSe<sub>2</sub> and gated Fe<sub>3</sub>GeTe<sub>2</sub>,<sup>3,4</sup> due to a completely different coupling mechanism, i.e. double exchange. Exploring room temperature magnetic semiconductors keeps challenging the physical chemistry world, and has been viewed as one of 125 big questions in science.<sup>5</sup> Note that a very recent theoretical work suggests the Curie temperature of 2D magnetic semiconductors could be largely enhanced by tuning the virtual exchange gap.<sup>6</sup>

In traditional inorganic magnetic semiconductors, the exchange interaction among transition metals is mediated by the closed shell p orbital of intervening main group element anions. In principle, changing the property of p orbital leads to tunable magnetic coupling. However, the limited control

degree of freedom (mainly the p orbital energy) hardly produces a high Curie temperature in reality. Fortunately, by virtue of the state-of-the-art metal organic framework (MOF),<sup>7</sup> the situation could be greatly improved. In MOF, magnetic transition metals are connected by organic linkers, whose frontier molecular orbitals (a coupled p orbital set) are responsible for the exchange interaction.<sup>8,9</sup> The orbital's energy, shape, phase and the spin state are all adjustable by choosing appropriate organic linkers, thus providing a versatile platform for magnetic semiconductors and the possibility to achieve high Curie temperature. Moreover, incorporating additional desirable properties, such as photomagnetism,<sup>10</sup> piezomagnetism,<sup>11</sup> chirality,<sup>12</sup> ferroelectricity,<sup>13</sup> luminescence and porosity is also feasible in MOF, offering an attractive way to generate multifunctional magnetic semiconductors, which is however difficult, or even impossible to achieve in a traditional inorganic material.

In this article, we propose to realize 2D magnetic semiconductors with enhanced Curie temperature by incorporating antiaromatic rings as organic linkers in MOF. Antiaromatic rings have at least three advantages for constructing magnetic MOFs: First, antiaromatic rings generally possess a low-energy multiple spin state, which is mostly lower than 10 kcal/mol above the ground state and may be easily induced by the chemical environment.<sup>14</sup> In other words, antiaromatic rings can be readily spin polarized or magnetized by the adjacent magnetic moments of transition metals. Then the magnetic moments of antiaromatic rings are expected to be antiparallel coupled with those of transition metals via the usually strong d-p direct exchange interaction, leading to high temperature ferrimagnetism. Second, antiaromatic rings (in its multiple spin state) have highly delocalized frontier molecular orbitals (coupled p orbitals), which are able to deliver the d-p direct exchange interaction effectively at a rather long distance. Last, compared to similar aromatic rings, antiaromatic rings often take a much strong potential to withdraw electrons from transition metals in order to make it aromatic. Such an enhanced charge transfer or hopping ability could result in an improved d-p direct exchange interaction, since the exchange energy for direct exchange is positively correlated with the electron hopping ( $t$ ) between magnetic orbitals as  $-4t^2/U$ , where  $U$  stands for Coulomb interaction parameter.<sup>15</sup> Based on the above potential advantages, antiaromatic rings are promising for building high temperature magnetic MOFs.

To validate our proposal, we first build a model system by employing the pentalene ring as organic linkers and transition metal Cr as nodes. With 8  $\pi$  electrons, pentalene is very reactive and can be synthesized in argon matrices by photocleavage of the corresponding dimer.<sup>16</sup> Pentalene commonly adopts two distinct structures: the localized closed-shell structure with  $C_{2h}$  symmetry and delocalized triplet state structure with  $D_{2h}$  symmetry (about 6 kcal/mol higher in energy).<sup>17</sup> The former is used to construct our initial structure. As shown in Figure 1(a), each pentalene is connected with two Cr atoms via the opposite C atoms in 2,5 position, while each Cr bonds to four pentalene rings and takes a nearly square planar coordination, forming a 2D orthorhombic lattice (Figure 1(b)). The pentalene rings are allowed to rotate freely along the Cr-C bonds to find their most stable conformation. Here, all pentalene rings are fluorinated to increase the Cr-C bond ionicity and induce semiconducting property (Figures S1 and S2). Note that the bonding mode where pentalene coordinates to transition metals with its five-membered rings<sup>18,19</sup> is not considered, since it is difficult to make 2D consecutive networks. We have tested other transition metals and the possibility of forming 2D hexagonal or triangular lattices, but failed to obtain a magnetic semiconductor property (Figures S3 and S4).

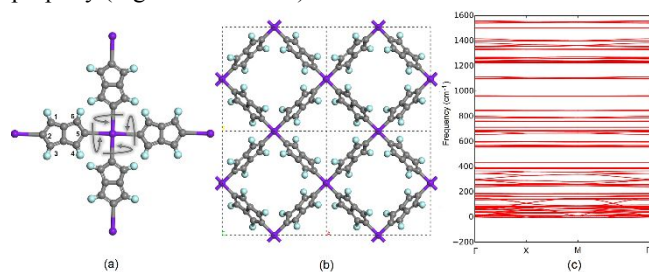


Figure 1. (a) Connectivity of pentalene-based 2D MOF. (b) optimized structure and (c) phonon band structure of 2D Cr-pentalene. Purple, grey and cyan balls represent Cr, C and F atoms, respectively.

To investigate the stability of designed 2D Cr-pentalene MOF, phonon band structure is calculated [Figure 1(c)]. We find no obvious imaginary frequency, indicating the structure is at least a local minimum on potential energy surface and expected to be stable dynamically. The dispersionless of phonon bands is ascribed to the rather big lattice constant (12.2 Å), while the existence of a crowd of soft phonons implies the flexibility feature of MOF. Ab initio molecular dynamics (AIMD) suggest that although 2D Cr-pentalene in the free-standing state is thermally stable only around 200 K, it can stabilize and work at room temperature when insulating dielectrics such as hexagonal BN sheets are integrated around (Figures S5 and S6).

The magnetic ground state of 2D Cr-pentalene MOF is determined to be ferrimagnetic coupling with a total magnetic moment of 4  $\mu_B$  per unit cell, which is energetically favored by 5.70 eV per unit cell compared to nonmagnetic state. Bader charge analysis reveals a local magnetic moment of 3.52  $\mu_B$  per Cr, and -0.76  $\mu_B$  per pentalene. Accordingly, Cr and pentalene possesses a formal spin of 2 and 1/2, respectively, which are aligned antiparallel to each other. It is clear a notable magnetic moment or spin has been induced on pentalene rings by the neighboring Cr atoms. The easiness of such magnetization is confirmed by the large spin polarization

energy of pentalene rings (0.70 eV per unit cell) (Figure S7). As shown in Figure 2(a) and Figure S8 (an enlarged and side-viewed plot), the pentalene magnetic moment is primarily contributed by the p orbitals of C atoms in 2,5 position and secondarily by the p orbitals of middle two C atoms. Exchange energy ( $E_{ex}$ ) defined as the energy difference between ferrimagnetic and ferromagnetic states is evaluated to be as large as -1.969 eV, indicating a robust ferrimagnetic coupling. To further estimate the Curie temperature, Monte Carlo (MC) simulation<sup>20</sup> has been performed based on the classic Heisenberg model. Counting in the nearest exchange interaction, the Hamiltonian can be written as eq 1, where  $J = -0.123$  eV (according to eq 2) is the nearest exchange parameter,  $S_i = 2$  and  $S_j = 1/2$  is the spin for Cr and pentalene, respectively. Here, higher order exchange interactions are not considered, since test calculations show they are at least one order of magnitude smaller than the nearest one.

$$H = -\sum_{ij} J \cdot S_i \cdot S_j \quad (1)$$

$$J = E_{ex}/16 = [E(\text{FIM}) - E(\text{FM})]/16 \quad (2)$$

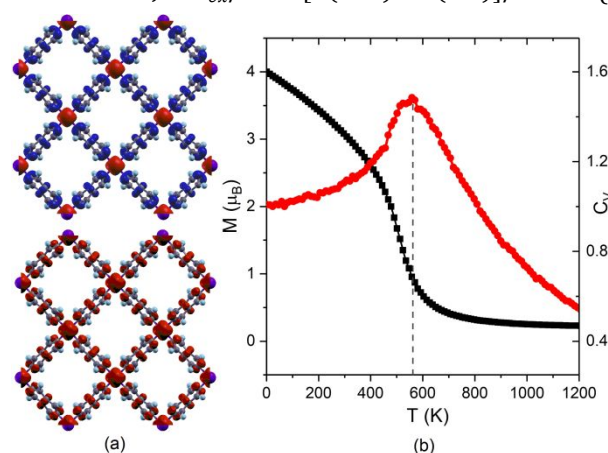


Figure 2. (a) Spin density of ferrimagnetic (top panel) and ferromagnetic (bottom panel) coupling for 2D Cr-pentalene with an isovalue of 0.05  $e/\text{\AA}^3$ . Red and blue indicate up and down spins, respectively. (b) Variation of magnetic moment ( $M$ ) per unit cell (black) and specific heat ( $C_V$ ) (red) with respect to temperature from classic Heisenberg model Monte Carlo (MC) simulation.

From the simulated curve of spin magnetic moment ( $M$ ) (Figure 2(b)), it is clear that when heated, magnetic moment gradually decreases from 4  $\mu_B$ , and becomes vanishingly small at high temperatures. Correspondingly, a sharp peak in the plot of specific heat ( $C_V$ ) is found around 560 K. This temperature is identified to be the Curie temperature of 2D Cr-pentalene. Further considering the underestimate trend of classic Heisenberg model,<sup>20</sup> the actual Curie temperature is expected to be much higher than room temperature.

In 2D Cr-pentalene, the magnetic coupling between transition metals (Figure S9) are mostly mediated by the strong direct exchange (-0.123 eV) between Cr and pentalene, with little contribution from the Cr-Cr superexchange (-0.003 eV). While for traditional ferromagnetic semiconductors like 2D CrGeTe<sub>3</sub>, the direct exchange is missing since the linkers are nonmagnetic and only the weak 90° superexchange (0.005 eV)<sup>21</sup> is presented, leading to significantly lower Curie temperature.

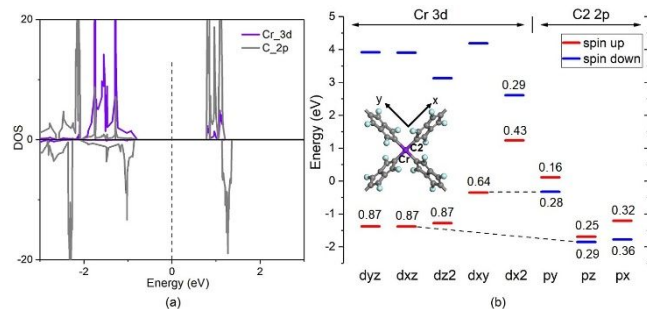


Figure 3. (a) Density of states (DOS) projected to Cr 3d and C 2p orbitals. (b) Band center energy diagram for Cr and adjacent C2 atom. The labelled numbers are occupation numbers for each partial orbital. The dotted line indicates the symmetry allowed and energy matched orbital interactions. All Fermi levels are set to zero.

After determining the magnetic ground state, the density of states is calculated to investigate the electronic property of 2D Cr-pentalene. As shown in Figure 3(a), a gap of 1.57 eV is found at HSE06 level, with its valence band maximum contributed mainly by Cr 3d states and conduction band minimum by C 2p orbitals. Around the Fermi level, the valence and conduction band edges are both spin-polarized in the same spin channel, indicating a half semiconductor character, which can be exploited for spin polarized carrier generation and injection.

To gain some insights into the strong Cr-pentalene exchange coupling, we calculate the band center and occupation number for five partial d orbitals of Cr atom and three partial p orbitals of C atom in the 2 position (labelled as C2). The band centers are evaluated as the first moment of the projected partial d orbital density of states referenced to the Fermi level, which are being commonly used in catalysis as an activity descriptor.<sup>22</sup> The obtained energy diagram in Figure 3(b) clearly indicates the Cr 3d orbitals are approximately split into four groups: (dyz, dxz), dz2, dxy and dx2, consistent with the square planar crystal field. Each group is further split into two spin-orbitals due to the Coulomb repulsion interaction. The total occupation number of Cr 3d orbitals is about 4.1, with the (dyz, dxz), dz2, dxy up-spin orbitals mostly occupied. Whereas, the p orbitals of C2 atom present no regular splitting, and the electrons are distributed to all partial p orbitals. It is worthy to note that the down-spin p orbital locates somewhat lower in energy than the up-spin one, and possesses a larger occupation number, indicating p orbitals are all down-spin polarized with respect to d orbitals, among which py orbital has the largest net spin ( $\sim -0.12$ ).

According to molecular orbital theory, strong orbital interaction only occurs when the two orbitals have a similar energy and matched symmetry. Based on the energy diagram, one can identify two significant orbital interactions: dxy-py and dxz-pz. In particular, the dxy and py orbitals present a very small energy difference ( $\sim 25$  meV), leading to notably enhanced orbital interaction. In terms of direct exchange, the electron hopping ( $t$ ) between dxy and py magnetic orbitals should be large since they match very well in both energy and space, thus resulting a high exchange energy ( $-4t^2/U$ ) and Curie temperature.

Based on the example of 2D Cr-pentalene, we have a great flexibility to design 2D magnetic semiconductors using different antiaromatic rings. We have calculated two other

systems built by cyclobutadiene with 4  $\pi$  electrons and s-indacene with 12  $\pi$  electrons (Figures S10 and S11). They all exhibit high temperature ferrimagnetism similar to 2D Cr-pentalene, with variable electronic structures: 2D-cyclobutadiene is a bipolar magnetic semiconductor with oppositely spin polarized valence and conduction band edges,<sup>23</sup> while 2D Cr-s-indacene becomes a near spin gapless semiconductor.<sup>24</sup> Moreover, benefited from organic synthesis, the structural, electronic and magnetic properties of these materials can be intentionally tuned by selective chemical modifications of antiaromatic rings,<sup>25-31</sup> or by inserting functional guests in the MOF's pores.

In conclusion, we have developed a promising method to achieve 2D magnetic semiconductors by employing antiaromatic rings as mediators of magnetic coupling between transition metals. Owing to the strong d-p direct exchange interactions, high temperature ferrimagnetic order is attainable. The method is verified by first principles calculations on several organometallic lattices with significantly enhanced Curie temperature compared to the up to date 2D magnetic semiconductors. This work is expected to stimulate researchers from areas of 2D magnetism, (anti-)aromaticity and MOFs to make 2D magnetic semiconductors towards room temperature application.

## ASSOCIATED CONTENT

**Supporting Information.** Computational method; test calculations on 2D Cr-pentalene organometallic lattice with pristine, fully fluorinated and hydroxylated pentalene rings; test calculations on 2D organometallic lattice with transition metals other than Cr; test calculations on 2D hexagonal and triangular organometallic lattices; the study of thermal stability of 2D Cr-pentalene; calculation of spin polarization energy of antiaromatic rings in 2D organometallic lattices; side-viewed plot of spin magnetic charge density of ferrimagnetic state for 2D Cr-pentalene; the scheme plot of magnetic coupling mechanism; the study of 2D organometallic lattice constructed by cyclobutadiene with 4  $\pi$  electrons and s-indacene with 12  $\pi$  electrons; the deduction of eq (2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\* jlyang@ustc.edu.cn

### Author Contributions

All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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