Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Assembling bi-coordinated Cr complex for ferromagnetic nanorings: insight from first-principles calculations

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Mean Field Theory Simulations of Quasi-1D Cr-CAAC Chain

Many quasi-1D organic ferromagnets have been reported both theoretically and experimentally.[1, 2] In physics, the 1D Ising model fails to show any spontaneous magnetic order, thus mean field theory (MFT) is often applied to estimate the magnetic phase transitions in quasi-1D spin systems.[3] In mean field approximation, we consider independently each lattice, while others as mean field effect. According to the Heisenberg model, the effective Hamitonian can be expressed as

$$H = -J\langle m\rangle m\gamma - \mu Bm,$$

where m corresponds to the magnetic moments (in μ_B) at each site (each unit cell is treated as one site). When the external magnetic field in z-direction is zero, the Zeeman term is excluded to the Hamiltonian. For each site five spin states are considered, namely, m=±4, m=±2 and m=0 since the calculated magnetic moment in the unit cell is 4 μ_B for the Cr-CAAC system. J refers to the Heisenberg direct exchange parameter, which can be obtained by

$$J = \frac{1}{2}\frac{E_{ex}}{2m^2},$$

where E_{ex} represents the exchange energy in the 2×1×1 supercell. Herein, we obtained the exchange parameter J to be 1.64 meV. The partition function Z was then computed by considering all possible spin configurations according to the spin multiplicity of Cr site,

$$\begin{aligned} Z &= \sum_m e^{-\frac{H}{k_B T}} \\ &= \sum_{m=0,\pm2,\pm4} e^{-\frac{-J\langle m\rangle m\gamma}{k_B T}} \\ &= 2\cosh\left(2p\langle m\rangle\right) + 2\cosh\left(4p\langle m\rangle\right) + 1, \end{aligned}$$

where $p = \frac{J\gamma}{k_B T}$, and $\gamma = 2$ (the coordination number of the Cr ions). Then the magnetic phase transition temperature was obtained by determining the bifurcation critical point of the ensemble-average magnetic moment <m>. According to MFT calculations, the phase transition of quasi-1D Cr-CAAC system from ferromagnetic to paramagnetic state occurs at the temperature of 304.23 K. Although mean field approximation might overestimate the phase transition temperature of magnetic systems, our simulated temperature of quasi-1D Cr-CAAC chain is 9% higher than that of previously reported theoretical result 279 K of low-dimensional organometallic system calculated with the same method.[4] Both the large magnetic moment on each Cr ion and strong exchange energy contribute to this high phase transition temperature of Cr-CAAC chain.

Complementary Information for Cr-CAAC Nanorings

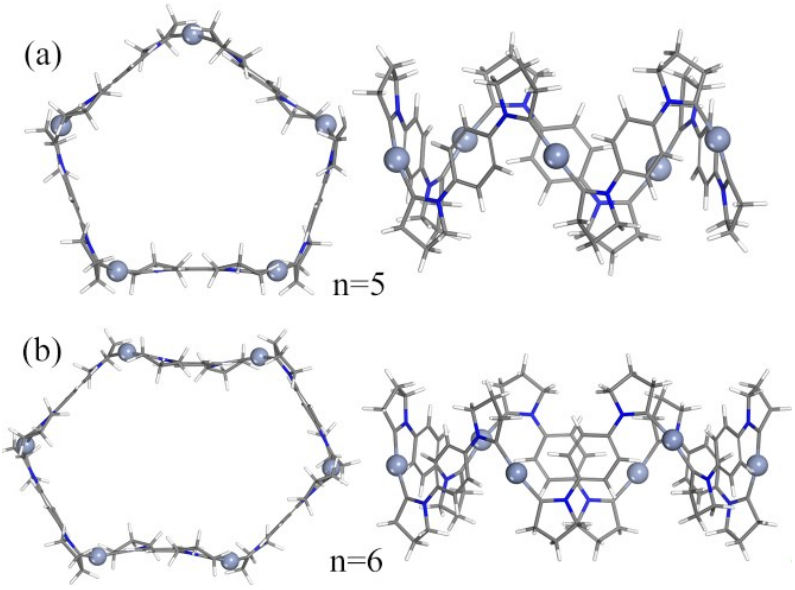

Fig. S1 The optimized ground state geometric structures of n-membered Cr-CAAC nanorings (n=5, 6). Top view and side view are shown from left to right.

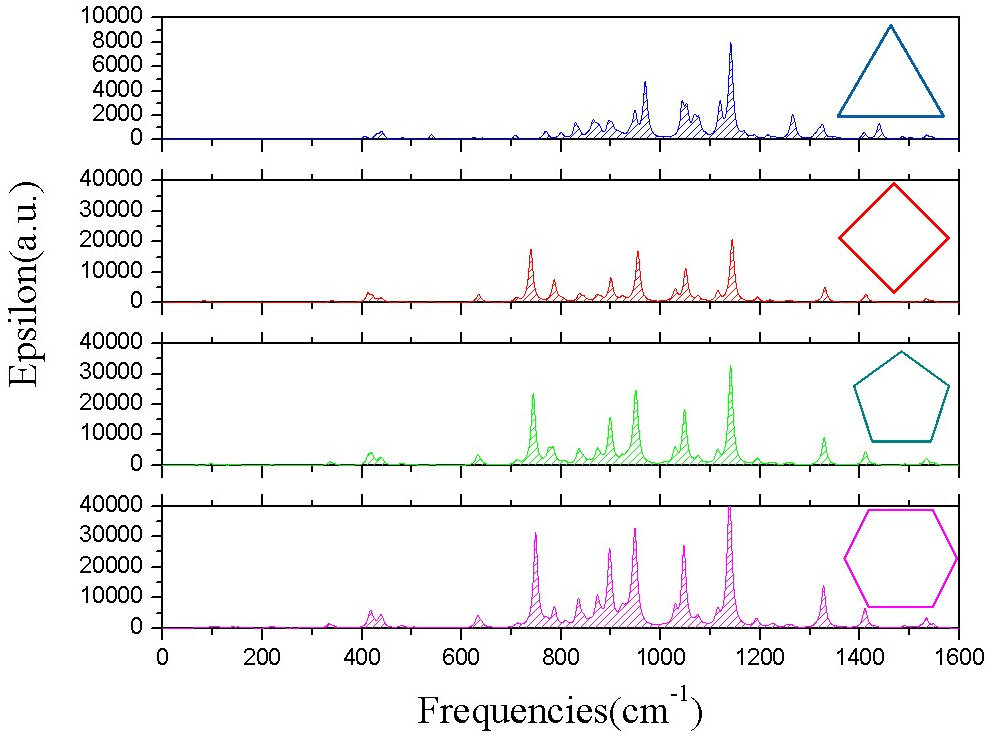

Fig. S2 Infrared spectra for n-membered Cr-CAAC nanorings (n=3- 6). Red, blue and magneta colour corresponds to four-membered, five-membered and six-membered ring, respectively. IR peak half-width at half height is set to be 5cm^{-1}.

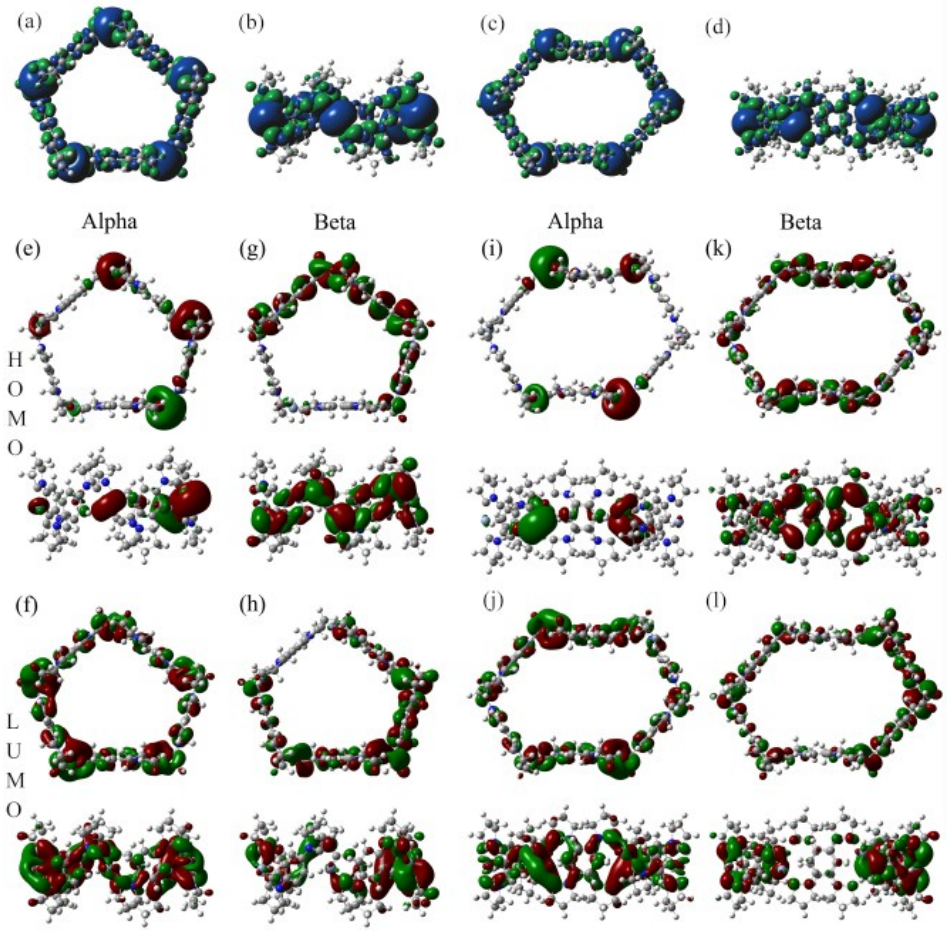

Fig. S3 The spin densities and frontier orbitals of n-membered Cr-CAAC nanorings. (a)-(d) From left to right corresponds to n=5 (a-b), n=6 (c-d), respectively. The isovalue of spin densities is set to be 0.001 a.u. (e)-(l) 3D contour plots of the calculated HOMOs and LUMOs of n-membered Cr-CAAC nanorings (n=5, 6). Alpha and beta orbitals are both exhibited for each HOMO and LUMO. The isovalue is set to be 0.015 a.u.

Notes and references

1 Y. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov and V. N. Spector, *Nature*, 1987, **326**, 370-372.

2 M. Takahashi, P. Turek, Y. Nakazawa, M. Tamura, K. Nozawa, D. Shiomi, M. Ishikawa and M. Kinoshita, *Physical Review Letters*, 1991, **67**, 746-748.

3 A. W. Sandvik, *Physical Review Letters*, 1999, **83**, 3069.

4 E. Kan, X. Wu, C. Lee, J. H. Shim, R. Lu, C. Xiao and K. Deng, *Nanoscale*, 2012, **4**, 5304-5307.