Two-dimensional bipolar magnetic semiconductors with high Curie-temperature and electrically controllable spin polarization realized in exfoliated Cr(pyrazine)$_2$ monolayers

Xiangyang Li$^1$, Haifeng Lv$^1$, Xiaofeng Liu$^1$, Tong Jin$^2$, Xiaojun Wu$^*$, Xingxing Li$^1$* & Jinlong Yang$^1$*

$^1$Hefei National Laboratory of Physical Science at the Microscale, Department of Chemical Physics, Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei 230026, China; $^2$Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei 230601, China

Received August 19, 2021; accepted November 10, 2021; published online November 12, 2021

Exploring two-dimensional (2D) magnetic semiconductors with room-temperature magnetic ordering and electrically controllable spin-polarization is a highly desirable but challenging task for nano-spintronics. Here, through first-principles calculations, we propose to realize such a material by exfoliating the recently synthesized organometallic layered crystal Li$_{0.7}$[Cr(pyz)$_2$]Cl$_{0.7}$·0.25(THF) (pyz=pyrazine, THF=tetrahydrofuran). The feasibility of exfoliation is confirmed by the rather low exfoliation energy of 0.27 J m$^{-2}$, even smaller than that of graphite. In exfoliated Cr(pyz)$_2$ monolayers, each pyrazine ring grabs one electron from the Cr atom to become a radical anion, and then a strong $d$–$p$ direct-exchange magnetic interaction emerges between Cr cations and pyrazine radicals, resulting in room-temperature ferrimagnetism with a Curie temperature of 342 K. Moreover, the Cr(pyz)$_2$ monolayer is revealed to be an intrinsic bipolar magnetic semiconductor where electrical doping can induce half-metallic conduction with controllable spin-polarization direction.

two-dimensional material, ferrimagnetism, bipolar magnetic semiconductor, half metal, first principles

Citation: Li X, Lv H, Liu X, Jin T, Wu X, Li X, Yang J. Two-dimensional bipolar magnetic semiconductors with high Curie-temperature and electrically controllable spin polarization realized in exfoliated Cr(pyrazine)$_2$ monolayers. Sci China Chem, 2021, 64: 2212–2217, https://doi.org/10.1007/s11426-021-1160-7

1 Introduction

Two-dimensional (2D) intrinsic ferromagnetic semiconductors, integrating semiconductivity, ferromagnetism, and low dimensionality, open up exciting opportunities for nanoscale-spintronic devices. Unfortunately, the usually weak ferromagnetic superexchange interaction makes their Curie temperature ($T_c$) far below room temperature, greatly limiting their practical applications. So far, the experimentally realized 2D ferromagnetic semiconductors, CrX$_3$ (X=Cl, Br, I) [1,2] and Cr$_3$Ge$_2$Te$_6$ [3], only retain their ferromagnetism below about 45 K. Theoretically, while a number of 2D ferromagnetic semiconductors have been predicted, such as CrOCl [4], CrSBr [5], GdI$_2$ [6], CrWI$_6$ [7], CrWG$_2$Te$_6$ [7] and K$_3$Co$_2$(PcCoO$_8$) [8], most of $T_c$ are still much lower than room temperature with a few exceptions, e.g., CrSeBr ($T_c$=500 K) [9], Fe$_3$P ($T_c$=420 K) [10] and CrMo$_2$S$_2$Br$_2$ ($T_c$=360 K) [11]. It still remains a challenge to search for 2D high-$T_c$ ferromagnetic semiconductors.

To solve the above issue, we have theoretically proposed a general scheme to realize room-temperature magnetic semiconductors in 2D metal-organic frameworks (MOFs) by introducing strong $d$–$p$ direct ferrimagnetic exchange inter-
actions between transition-metal cations and magnetic organic linker radical anions [12,13]. The applicable organic linkers are conjugated with electron acceptors such as pentalene ($T_c=560$ K) and diketopyrrolopyrrole (DPP) derivatives ($T_c=316$ K). Inheriting the high tunability of MOFs [14], the electrical and magnetic properties of such organo-metallic ferrimagnetic semiconductors are expected to be easily enriched and modulated by changing the transition metals, organic linkers, or framework geometries, thus enabling their versatile applications in the field of emergent magneto-electronics, magnetic sensing, and recording technologies [15,16]. Besides, it would also be fairly easy to integrate other functions, such as ferroelectricity [8], ferroelasticiy [17], quantum topology [18], photoelectricity [19] and chirality [20], to prepare multifunctional magnetic semiconductors. Despite the great potentials, the development of 2D organometallic ferrimagnetic semiconductors is still at an early stage and their experimental realization keeps an open question.

In addition to obtaining high-$T_c$, it is highly demanded to develop functional magnetic semiconductors with electrically controllable spin polarization. For this purpose, bipolar magnetic semiconductors (BMS) [21], characterized by oppositely and fully spin-polarized valence and conduction band edges, have been proposed by us previously, which can provide completely spin-polarized currents with the reversible spin-polarization direction by altering the polarity of applied gate-voltage [22,23]. Up to now, a number of BMS materials have been theoretically designed [6,24–29], but they are difficult to be realized in experiment, because most of them are extrinsic and require precisely-controlled chemical or physical modifications [24,25], or their magnetic orders are stable only at very low temperatures [6,27–29]. Therefore, it is urgent to find 2D BMS materials with both intrinsic magnetism and high-temperature magnetic stability.

Here, by marriage of our previously proposed $d$–$p$ direct ferrimagnetic exchange scheme [12,13] and the concept of BMS, we propose that 2D organometallic ferrimagnetic semiconductors, i.e., Cr(pyz)$_2$ monolayer, with high Curie-temperature and electrically controllable spin-polarization is experimentally accessible by exfoliating existing layered crystal of Li$_{0.7}$[Cr(pyz)$_2$]Cl$_{0.7}$·0.25(THF) (pyz=pyrazine, THF=tetrahydrofuran) [15]. The high Curie-temperature ($\sim342$ K) stems from the strong $d$–$p$ direct ferrimagnetic exchange interaction between Cr and magnetic pyz. The electrical control of spin-polarization originates from the 2D Cr(pyz)$_2$’s intrinsic BMS property, which can present half-metallicity with spin-polarization direction tuned by the type of electrical doping.

2 Computational details

First-principles calculations are carried out by using the density-functional theory (DFT) method within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) implemented in the Vienna Ab initio Simulation Package (VASP) [30]. The projector augmented wave (PAW) method [31] is used in the calculation. Specifically, the PAW_PBE pseudopotential is used for the C, H, and N elements, and the PAW_PBE Cr$_{pv}$ pseudopotential is used for the Cr element. The strong-correlated correction is considered with GGA+$U$ method [32] for structure optimization, phonon spectra calculation and ab initio molecular dynamic (AIMD) simulation. Here, the magnetic exchange energies, $\Delta E$, for [Cr(pyz)$_2$]$^-$ fragment are tested at different values of on-site Coulomb interaction parameter, $U$ (Table S1). It is found that when the $U$ value is set to 3 eV, $\Delta E$ is close to that in the literature (Figure S1) [15], and thus $U=3$ eV is adopted. The DFT-D3 method with Becke-Jonson damping [33] is adopted for the van der Waals (vdW) interactions. The energy cutoff employed for plane-wave expansion of electron wave-functions is set to 520 eV, which is sufficient for accurate computations by using the PAW pseudopotential method [34]. For sampling in the first Brillouin zone, the Monkhorst-Pack $k$-point mesh is set with a grid spacing less than 0.02 Å$^{-1}$. During the structural optimization, the residual force on each atom is set to less than 0.01 eV Å$^{-1}$. The energy convergence is set to $1 \times 10^{-6}$ eV. A vacuum region of about 15 Å is applied along the $z$-direction to avoid mirror interaction between neighboring slabs for the simulation of Cr(pyz)$_2$ monolayers. The phonon spectra are calculated using the finite displacement method implemented in PHONOPY code together with the VASP code [35]. To assess the thermal stability of Cr(pyz)$_2$ monolayers, the AIMD simulation is performed using a $3 \times 3 \times 1$ supercell at 400 K for 9 ps with a time step of 1 fs in the canonical (NVT) ensemble, where a Nosé-Hoover chain thermostat is used to control the temperature [36]. Besides, we use the Energy Decomposition Analysis (EDA) method [37] as implemented in the Amsterdam Density Functional (ADF) package [38] at the PBE-D3/TZ2P level to gain detailed insight into the different energetic contributions in the stability of the Cr(pyz)$_2$ monolayer. To simplify the calculation, we adopt a typical molecular fragment [Cr(pyz)$_2$]$^-$, as selected in the literature [15]. The energy barrier from the $C_{2h}$ to $D_{1h}$ structure is investigated with the climbing image nudged elastic band (CI-NEB) method [39]. To accurately describe the band structure and density of states, we further apply the screened hybrid HSE06 functional [40], which includes the accurate Fock exchange and usually performs much better than the GGA and GGA+$U$ methods [41–43]. It should be noted that the B3LYP functional widely used for isolated organic molecules is not chosen, because it is less accurate than the conventional GGA functionals for periodic solid-state materials [44].
3 Results and discussion

The bulk crystal Li$_{0.7}$[Cr(pyz)$_2$]Cl$_{0.7}$·0.25(THF) features a layered structure composed of alternating stacks of charge-neutral Cr(pyz)$_2$ and Li$_{0.7}$Cl$_{0.7}$ layers (Figure 1) [15]. For the Cr(pyz)$_2$ layer, each Cr$^{2+}$ ion is coordinated by four pyz units in a nearly square planar coordination pattern, and each pyz unit is coordinated by two adjacent Cr ions with a linear coordination geometry. Because the dihedral angle $\theta$ between the pyz and ab lattice planes has two possibilities (+45°, −45°), two stable rotational isomers ($C_{2h}$ and $D_{4h}$ symmetry) exist, and the exact crystal structure has not been determined in experiment. Figure 1a shows the detailed rotation operations to obtain the two isomers. For the $C_{2h}$ crystal (Figure 1b), the plane of pyz rings at the para-positions are inclined to the same side by about 45°. For the $D_{4h}$ crystal (Figure 1b), all the pyz rings around Cr ions are arranged obliquely clockwise or counterclockwise at the same time. The $C_{2h}$ structure can be easily transformed to the $D_{4h}$ structure with a small transition barrier of 0.08 eV per formula and an energy release of 0.69 eV per formula (Figure 1c). Note that the $D_{4h}$ structure is very similar to those of our previously proposed Cr(pentalene)$_2$ [12] and Cr(DPP)$_2$ [13]. Above all, we theoretically identify the $D_{4h}$ crystal as the most energetically favorable structure. Therefore, the $D_{4h}$ structure is used in the following studies.

Due to the relatively big interlayer distance (3.60 Å) between charge-neutral Cr(pyz)$_2$ and Li$_{0.7}$Cl$_{0.7}$ layers, the interlayer interaction is expected to be weak. Thus, a 2D Cr(pyz)$_2$ monolayer may be attained through the mechanical cleavage method. As shown in Figure 2a, by introducing two fractures above and below a Cr(pyz)$_2$ layer in the bulk structure and gradually increasing the distance from the equilibrium distance $d_0$ to $d$, the total energy differences ($E_{cl}$) as a function of ($d$−$d_0$) can be obtained from DFT calculations. $E_{cl}$ is defined as the total energy difference per unit surface area ($A$), $E_{cl}$=($E$−$E_0$)/2$A$, where $E_0$ and $E$ represent the total energy in the un-cleaved and cleaved state, respectively.

In the beginning, the total energy differences $E_{cl}$ increase quickly with ($d$−$d_0$), and then gradually converges to a constant value, which is known as the exfoliation energy. The predicted exfoliation energy for the Cr(pyz)$_2$ monolayers is only 0.27 J m$^{-2}$, which is even smaller than that of graphite (0.37 J m$^{-2}$) [45], directly indicating the monolayer can be easily prepared from the bulk crystal.

The stability of the exfoliated 2D Cr(pyz)$_2$ monolayers is further assessed by their phonon band structure and molecular dynamics simulation. In the calculated phonon dispersion curves (Figure 2b), no obvious imaginary frequency is observed, indicating that the 2D Cr(pyz)$_2$ monolayers are dynamically stable. The rather big lattice constant results in the dispersionlessness of phonon bands, while the existence of a large amount of soft phonon modes means the flexibility of the Cr(pyz)$_2$ monolayers [12]. To evaluate the thermal

![Figure 1](image-url)  (a) Schematic representation of the two rotational isomers ($C_{2h}$ and $D_{4h}$ symmetry) of Li$_{0.7}$[Cr(pyz)$_2$]Cl$_{0.7}$·0.25(THF) (pyz = pyrazine, THF = tetrahydrofuran). For the $C_{2h}$ crystal, the plane of pyz rings at the para-positions are inclined to the same side by about 45°, as indicated by the black arrows. For the $D_{4h}$ crystal, all the pyz rings around Cr ions are arranged obliquely clockwise or counterclockwise, as indicated by the red arrows. (b) Side view of optimized structures of $C_{2h}$ and $D_{4h}$ crystals. (c) Energy profile of the transition from $C_{2h}$ to $D_{4h}$ symmetry (color online).

![Figure 2](image-url)  (a) Exfoliation energy $E_{cl}$ as a function of separation distance ($d$−$d_0$) in the process of exfoliating one Cr(pyz)$_2$ layer from its bulk crystal. (b) Calculated phonon band structure of the exfoliated Cr(pyz)$_2$ monolayers. (c) Total potential energy fluctuation of a 3×3×1 supercell for the Cr(pyz)$_2$ monolayers during AIMD simulations at 400 K. The inset shows the snapshot at the end of the simulation of 9 ps (color online).
stability, AIMD simulations at 400 K lasting for 9 ps are performed (Figure 2c). The fluctuation of total potential energy for Cr(pyz)_2 monolayer gradually stabilizes after 1.5 ps, and then the evolution of energy with time fluctuates near its equilibrium value in a small range, indicating that the equilibrium of the system is achieved. The final structure is maintained well without any reconstruction after 9 ps, as shown in the insets of Figure 2c. Thus, 2D Cr(pyz)_2 monolayer is thermally stable at room temperature.

Besides, the total interaction energy between the Cr and pyz and its components are also analyzed and given in Table S2. Obviously, the total bonding energy is mainly contributed by the electrostatic (62.3%) and orbital (37.6%) components with negligible contribution from the dispersion (0.1%). Therefore, it can be concluded that the electrostatic and orbital interactions between the Cr and pyz ultimately make them form a stable MOF structure.

To determine the magnetic ground state of the Cr(pyz)_2 monolayers, five different magnetic states, namely one ferromagnetic (FM) state, one antiferromagnetic (AFM) state, and three ferrimagnetic (FiM) states (Figure S2), are calculated to compare their relative energies. It is found that the structure prefers the FiM1 state in which the Cr spins are all antiparallelly aligned with the pyz spins, maintaining the ferrimagnetism in its bulk crystal (Figure S3) [15]. For the metastable C_{2h} crystal, the magnetic ground state of the corresponding monolayer sheet remains ferrimagnetic (Table S3). In the FiM1 state, the total magnetic moment is 2.0 \mu_B per formula with a local magnetic moment of 3.4 \mu_B per Cr and −0.6 \mu_B per pyz. Accordingly, Cr and pyz possess a formal spin of 2 and 1/2, respectively. Figure 3a shows the spin density distribution in the ground FiM1 state. Obviously, the spin density on the pyz units is primarily contributed by the \( p \) orbitals of N atoms and only a small amount is distributed by the \( p \) orbitals of C atoms.

The ferrimagnetic coupling strength of Cr ions with pyz units is expected to be robust because of the large energy difference of 0.87 eV per formula between the FM and FiM1 states. To further estimate the Curie-temperature \( T_c \) of such ferrimagnetic coupling, we employ the Monte–Carlo (MC) simulations based on the classic Heisenberg model Hamiltonian [46],

\[
H = -\sum_{i,j} J_{ij} S_i \cdot S_j + \sum_i D_i S_i^2
\]

where \( J_{ij} \) are the exchange-coupling parameters displayed in Figure 3b, and \( S \) is the effective spin of Cr or pyz. \( D_i \) are the magnetic anisotropy parameters with a value of 0.05 meV for Cr and 0 meV for pyz, as deduced from the predicted magnetic anisotropy energy of 0.20 meV per Cr. The values of \( J_{ij} \) are calculated from the energy differences among the above five different magnetic states and illustrated in Table S4. Here, both the nearest neighbor and next-nearest neighbor spin exchange interactions are considered. It should be noted that the signs of exchange couplings \( J_1, J_2, J_3 \) and \( J_4 (J_4 > J_3, J_2, J_1) \) are all negative and antiferromagnetic, meaning that the next-nearest neighbor interactions \( J_2, J_3, \) and \( J_4 \) tend to frustrate the ferrimagnetic ordering dominated by the nearest neighbor interaction \( J_1 \). Similar situation is often observed in the literature, such as the next-nearest neighbor interaction \( J_3 \) for BiFeO_3 [47] and MnC_2 [48], and the fourth-nearest neighbor interaction \( J_4 \) for FeOX (X=F, Cl, Br, I) [49].

As shown in Figure 3c, the simulated curve of spin magnetic moment \( M \) decreases from 2 \mu_B to 0 with the increase of temperature. Correspondingly, the specific heat \( C_v(T) = \langle E^2 \rangle - \langle E \rangle^2 / T^2 \) is also calculated after the system reaches equilibrium at a given temperature. By locating the peak position of the \( C_v(T) \) plot, the ferrimagnetic Curie-temperature \( T_c \) is predicted to be 342 K, which is lower than that (510 K) of bulk crystal. Possible reasons including the unconsidered structural disorders are present in the experimentally synthesized bulk and the tendency of the classical Heisenberg model to underestimate \( T_c \). The influence of adopted functional on the estimation of Curie temperature is also tested. For example, when the more accurate HSE06 functional is used to calculate the magnetic exchange parameters, the simulated \( T_c \) will increase slightly from 342 to 386 K (Table S4 and Figure S4).

Note that the room-temperature ferrimagnetism in the Cr(pyz)_2 monolayers with a small magnetic anisotropy energy (0.20 meV per Cr) does not violate the Mermin–Wagner theorem, which predicts that, to achieve a 2D long-range magnetic order, we need to break the isotropic spin symmetry by magnetic anisotropy, but not predicts that the magnetic ordering temperature is totally determined by the magnetic anisotropy. Actually, according to the spin wave theory on typical 2D magnets such as CrI_3 [50], the magnetic Curie temperature \( T_c \) is correlated to both magnetic aniso-

![Figure 3](image)

(a) Spin density distribution of the ground ferrimagnetic state for the 2D Cr(pyz)_2 monolayers with an isovalue of 0.06 Å⁻³. Red and blue indicate up and down spins, respectively. (b) The nearest neighbor and next-nearest neighbor spin exchange paths for the Cr(pyz)_2 monolayers. The exchange-coupling parameter of \( J_k \) (\( k = 1-4 \)) is also marked. \( J_1 \) represents the coupling between Cr and the nearest neighbor pyz. \( J_2 \) represents the coupling between the nearest two Cr atoms. \( J_3 \) and \( J_4 \) represent the coupling between the nearest and next-nearest two pyz. (c) Magnetic moment \( M \) per formula (black) and specific heat \( C_v \) (red) as a function of temperature from a MC simulation of the classic Heisenberg model. Here, the magnetic exchange parameters calculated with the GGA+U functional are used (color online).
entropy and exchange coupling strength as

\[ k_B T_c = \frac{n|S|^2}{2\log(A_0 + 2n|S|)} \]  

(2)

where \( J \) is the exchange coupling strength, \( A_0 = 2DS + nS\lambda \) (\( n \) represents the number of the nearest coupling around each magnetic ion) is the spin-wave gap induced by the magnetic anisotropy (including easy-axis single-ion anisotropy \( D \) and anisotropic symmetric exchange \( \lambda \)). When the magnetic anisotropy is absent, \( A_0 \) is zero and equation (2) will give \( k_B T_c \approx 0 \), that is, no long-range magnetic order exists at finite temperatures, consistent with the Mermin-Wagner theorem. For the Cr(pyz)\(_2\) monolayer, by neglecting the anisotropic symmetric exchange \( \lambda \), we obtain \( A_0 = 2DS \times 2 \times 0.05 = 0.20 \) meV. By analyzing equation (2), we show that such a spin-wave gap \( A_0 \) is sufficient to stabilize room-temperature magnetic order. Because of the different spin values for Cr \( (S_C = 2) \) and pyz \( (S_{pyz} = 1/2) \), the equation (2) with only one spin parameter \( S \) cannot be directly applied to estimate the Curie temperature of the Cr(pyz)\(_2\) monolayer. However, considering that the \( S \) is treated as a classical vector in the spin Hamiltonian (equation (1)) [50], it is reasonable to normalize both the spin values of Cr and pyz to unity \( (S=1) \). Under such normalization, the nearest effective exchange strength \( J \) keeps as \(-108.4 \) meV, while other three next-nearest exchange couplings \( (J_2=J_4) \) are omitted. According to the above analysis, equation (2) is applied with \( S=1 \), \( J=J_1=108.4 \) meV. For the room-temperature magnetic order, \( i.e., T_c = 300 \) K, equation (2) will give a critical spin-wave gap \( A_0 = 1.8 \times 10^{-4} \) meV, which is three orders of magnitude smaller than the real \( A_0 \) of the Cr(pyz)\(_2\) monolayer, and therefore the room-temperature magnetic order in the Cr(pyz)\(_2\) monolayer should be feasible. In fact, using \( A_0=0.20 \) meV and \( J=108.4 \) meV, the Curie temperature within the spin-wave theory is predicted to be \( 559 \) K for the Cr(pyz)\(_2\) monolayers, significantly higher than room temperature. Above all, the room-temperature magnetic order for the Cr(pyz)\(_2\) monolayers is robust from both MC simulations and spin-wave theory.

To reveal the electronic properties of the 2D Cr(pyz)\(_2\) monolayers, the band structures and density of states are calculated with the HSE06 functional. The Cr(pyz)\(_2\) monolayer is found to be a direct semiconductor with a moderate band gap of \( 1.72 \) eV (Figure 4a). Particularly, the valence band maximum (VBM) state is 100% spin-polarized in the spin-up channel, whereas the conduction band minimum (CBM) state is 100% spin-polarized in the spin-down channel; that is, it belongs to an intrinsic BMS [21,23,26,27]. From the Kohn–Sham orbital distributions in Figure 4b, one can see that the VBM state is dominated by the \( p \) orbitals of N and C atoms, whereas the CBM state is built up by both the \( p \) orbitals of N and C atoms and 3\( d \) orbitals of Cr ions, which is also clear from the projected density of states in Figure S5.

The electronic structure of the BMS, Cr(pyz)\(_2\) monolayers, makes it promising for the control of spin polarization by electrical gating. Here, to simulate the carrier doping effect induced by applied gate voltage, the electronic structures of electron- and hole-doped Cr(pyz)\(_2\) monolayers, corresponding to positive and negative gate voltages, respectively, are studied at the doping concentration of \( 0.05 \) e/h per formula or \( 1.1 \times 10^{13} \) cm\(^{-2}\). As shown in Figure 4c and d, under electron doping (positive gate voltage), the Fermi level shifts up into CBM, presenting half-metallic conduction with a complete spin-down polarization; while the Fermi level shifts down into VBM under hole doping (negative gate voltage), half-metallicity with a full spin-up polarization is obtained. This property allows us to manipulate the carriers’ spin-polarization direction just by changing the sign of applied gate voltage.

4 Conclusions

To summarize, based on experimentally synthesized Li\(_{0.7} [\text{Cr(pyz)}\(_2\)] \text{Cl}_{0.7} \cdot 0.25(\text{THF})\), we propose to realize a 2D Cr(pyz)\(_2\) monolayer by using the mechanical cleavage method with a rather low exfoliation energy of \( 0.27 \) J m\(^{-2}\), which is even smaller than that of graphite. The exfoliated monolayer belongs to a 2D room-temperature ferrimagnetic semiconductor with a Curie temperature of \( 346 \) K, and possesses electrically controllable spin polarization. Such kind of organometallic ferrimagnetic semiconductors not only provide a new opportunity to achieve high-\( T_c \) 2D magnetic semiconductors, but also have great potential in the design of electrically controlled nanospintronic devices.

Acknowledgements This work is supported by the National Natural Science Foundation of China (21688102), by the National Key Research & Development Program of China (2016YFA0200604), by Anhui Initiative in Quantum Information Technologies (AHY090400), by the Youth Innova-
Conflict of interest  The authors declare no conflict of interest.

Supporting information  The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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