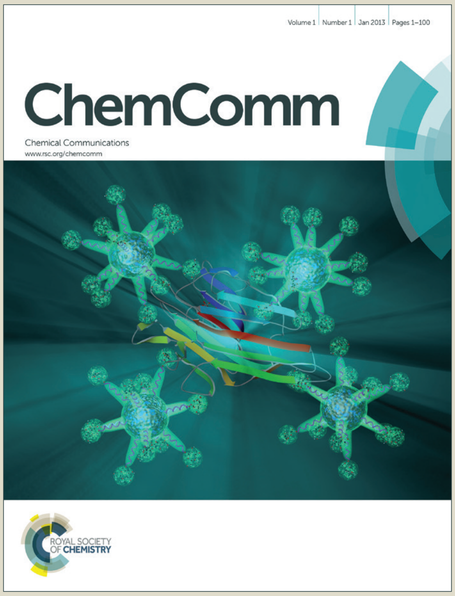

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COMMUNICATION

Chiral Tetrahedral Iron(II) Cages: Diastereoselective Subcomponent Self-Assembly, Structure Interconversion and Spin-Crossover Properties**

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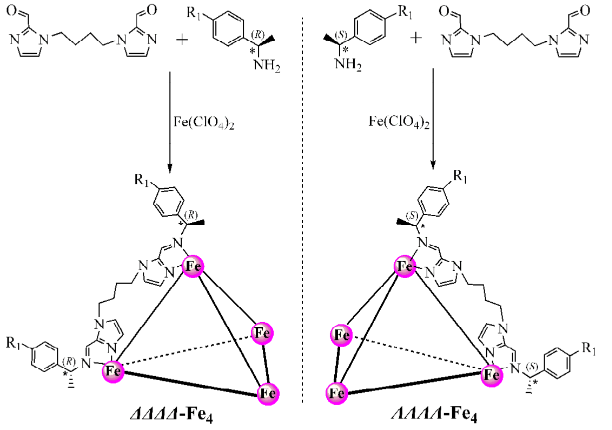
A new class of chiral tetrahedral iron(II) cages was prepared from subcomponent self-assembly with high diastereoselectivity. The cages can be interconvered through imine exchange. The chiral cages displayed spin transition close to room temperature, and the transition temperatures were affected by the substituent and uncoordination solvents.

The spin-crossover(SCO) phenomenon represents one of the most important examples of molecular bistability, in which the high-spin (HS) and low-spin (LS) states are interconvertible by external perturbations (such as temperature, pressure or light), thereby creating important expectations for the application in data storage, display technologies and chemosensors.[1] Whilst the majority of SCO compounds belong to mononuclear system, polynuclear 2×2 grids[2] and polyhedral cages[3] with multistability, magnetic interaction and gust dependent SCO properties have aroused particular interests in recent years. It has also been realized that multifunctional SCO materials can be generated through introducing additional functionalities, for instance, electrical conductivity,[4] liquid crystalline properties,[5] fluorescence[6] and non-linear optical properties.[7] In particular, enantiopure SCO compounds may offer wide new perspectives, for example, in magneto–chiral dichroism,[8] and ferroelectricity.[9] However, no homochiral polynuclear SCO cluster has been reported hitherto due to the enormous difficulty of simultaneously controlling the geometries of the cluster, the configuration of multiple metal centres and the extremely sensitive SCO behavior.

Recently, a series of enantiopure low-spin state iron(II) tetrahedral cages have been constructed by Nitschke et al. through subcomponent self-assembly for enantioselective guest recognition and stereoselective transformations.[10] To develop novel homochiral SCO cages, we focused our attention on subcomponent self-assembly of simple building blocks of flexible di(imidazole aldehyde), chiral phenylethylamine and iron(II) ions through the formation of coordinative (N→Fe) and covalent (C=N) bonds during the same self-assembly process (Fig. 1). The formed imidazole-imine (C=N) based ligands have the appropriate ligand-field strength for spin transition, and the SCO properties can be readily modulated by substituents, counteranions, and solvents. The optical phenylethylamine used here can induce an absolute configuration at the metal centre through chiral information transfer. As a result, the chiral cage is generated in a single reaction step from the commercially available chiral phenylethylamine and readily synthetically accessible 1,4-di(imidazole-2-carboxaldehyde)butane. Herein we describe the facile syntheses, structures and SCO properties of three couples of tetrahedral iron(II) chiral cages **1-3** $[Fe_4L_6](ClO_4)_8$·solvent (L = 1,4-di((imidazol-2-ylmethylene)-1-phenylethanamine)butane derivatives).



cage **1**: R_1 = H, cage **2**: R_1 = OCH_3, cage **3**: R_1 = Cl

Fig. 1 Synthesis of enantiopure tetrahedral cages **1-3** by subcomponent self-assembly of 1,4-di(imidazole-2-carboxaldehyde)butane chiral phenylethylamine and iron(II) ions.

1-3 were obtained in good yields by the self-assembly reactions of 1,4-di(imidazole-2-carboxaldehyde)butane, optical phenylethylamine and $Fe(ClO_4)_2·6H_2O$ in a molar ratio of 3:6:2 in CH_3CN. Dark purple crystals of **1-3** were obtained through slow diffusion of diethyl ether into the acetonitrile reaction sountion (see the Supporting information). The IR spectra at room temperature for cages **1-3** showed $\nu_{C=N}$ stretching absorption at 1609-1570 cm^{-1} corresponding to the low spin states of iron(II) centers, while peaks at 1098-1094 cm^{-1} revealed the existence of ClO_4^-. Remarkably, ^1H and ^{13}C NMR spectra of cages **1-3** showed only one set of coordinated ligand signals indicating that a single diastereoisomer with *T* point symmetry was formed in solution at room temperature (Fig. S3-S8).

Single-crystal X-ray diffraction study on **(*R*)-1**, **(*S*)-1**, **(*R*)-2**, **(*S*)-2**, and **(*S*)-3** unambiguously revealed the formation of homochiral tetrahedral iron(II) cages (Supporting information).

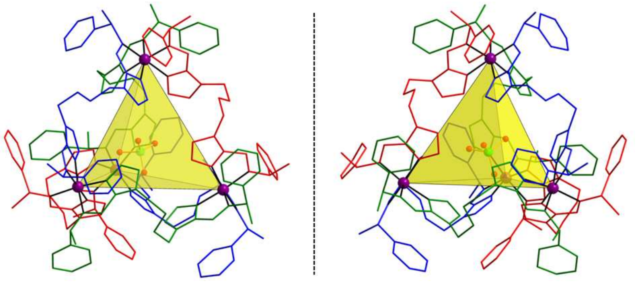


Fig. 2 X-ray crystal structures of enantiopure tetrahedral cages ***(R)*-1** (left) and ***(S)*-1** (left). All H atoms and the remaining seven anions have been removed for clarity.

Cages **1-3** show very similar structures except different substituent group on para-phenylethylamine (Fig. 2 and Fig. S9). Cages **1** and **3** crystallized in trigonal *R*3 chiral space group, while **2** crystallized in triclinic *P*1 chiral space group. The chiral structures of ***(R)*-1** and ***(S)*-1** are shown in Fig. 2. Each tetranuclear cage in **1-3** has noncrystallographic tetrahedral *T*-symmetry constructed from four C_3-symmetric metal centers occupied the vertices of tetrahedron, and six C_2-symmetric ligands situated the edges of tetrahedron. The iron(II) center coordinated with six nitrogen atoms from three different ligands form distorted octahedral geometries. Although the tris(bidentate) iron(II) coordination can present possible facial (*fac*) or meridional (*mer*) stereochemistry, in addition to *Δ* or *Λ* handedness, the *R*-phenylethylamine derivatives in **1-3** induced exclusively *fac-Δ* form for all the Fe(II) centers, whereas *S*-phenylethylamine derivatives induced *fac-Λ* chirality for the metal centers. In other words, the four metal centers in a tetrahedral cage lie in the same situation of either *ΔΔΔΔ* or *ΛΛΛΛ*. It seems that the stereochemically active groups of the ligands are oriented the configuration of the overall cage, where the ligands transfer their chirality to the metal centre and enable cooperative stereochemical coupling between the four metal centers.[11] All the di(imidazole-imine)butane linkers in **1-3** adopt *gauche-gauche* conformation with the dihedral angles of the two imidazole rings of 15.866-24.742°. The Fe–N bond lengths for **1-3** (1.916-2.06 Å) are typical for low spin-state Fe(II), which are in agreement with the reported SCO complexes.[12] The Fe···Fe separations within the tetrahedron are varying from 9.41 Å to 9.81 Å for cages **1-3**. One ClO_4^- anion is located at the centre of the internal cavity, and the remaining seven anions are decorated around the periphery of the cage. The terminal O atoms of the perchlorate anion in the central cavity interact with the hydrogen atoms of imidazole groups on cage superstructure via C-H···O hydrogen bonds implying that the anion may act as a template in the tetrahedral cage assembles.

The UV/Vis spectra of **1-3** are characterized by two π–π* transitions of imidazole and phenyl groups at 206-224 nm and 302 nm, respectively (Fig. S10). In addition, there are broad bands around 546 nm for **1-3**, which probably arise from metal-to-ligand charge transfer (MLCT) processes. The CD spectra contain intense split-type Cotton effects spanning the whole UV/visible region. The CD spectra of ***(R)*-1** and ***(S)*-1**, ***(R)*-2** and ***(S)*-2**, ***(R)*-3** and ***(S)*-3**, are mirror images of each other, thus demonstrating their absolute configuration and enantiopurity. In addition, CD spectra of the crude and recrystallized samples are almost identical, further confirming single diastereomer cage exists in solution (Fig. S11).

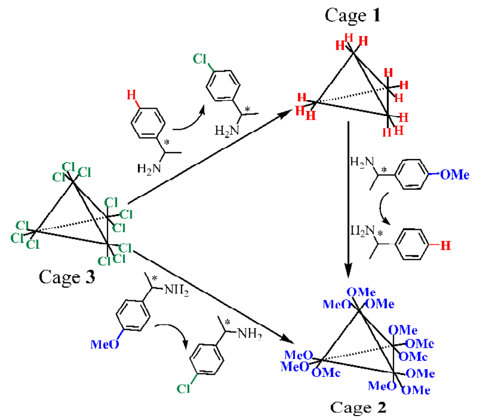


Fig. 3 Subcomponent substitution driven by electronic effects: more electron-rich chiral phenylethylamine are able to displace more electron-poor chiral phenylethylamine.

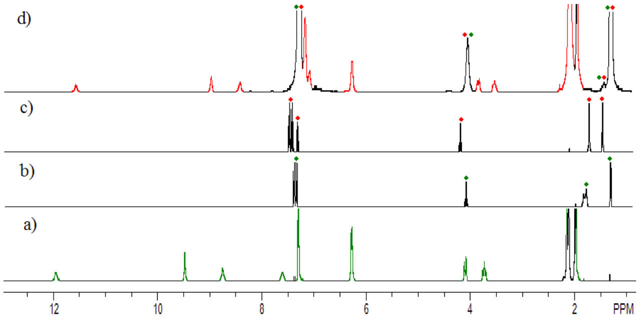


Fig. 4 ^{1}H NMR spectra: (a) ***(S)*-3**; (b) (*S*)-1-(4-chlorophenyl)ethylamine; (c) (*S*)-1-phenylethylamine; (d) ***(S)*-1** was formed through adding (*S*)-1-phenylethylamine into ***(S)*-3**. The signals from free subcomponents (*S*)-1-(4-chlorophenyl)ethylamine and (*S*)-1-phenylethylamine are marked by gree and red filled circles, respectively.

There is considerable interest in the dynamic structure interconversions through the application of external stimuli, such as light,[13] templates,[14] temperature,[15] solvent,[16] and so on. The substitution of electron-poor amines residues by more electron-rich amines within Schiff-base complexes has been investigated recently.[17] This phenomenon has also been demonstrated in our present chiral cage system. When the more electron-rich (*S*)-1-phenylethylamine (15 eq.) was added to a solution of ***(S)*-3** (1 eq.), the 12 electron-poor (*S*)-1-(4-chlorophenyl)ethylamine residues riding outside of the tetrahedral cage ***(S)*-3** were quantitatively displaced by (*S*)-1-phenylethylamine, and the analogous capsule ***(S)*-1** was formed (Fig. 3). This transformation was complete, which was clearly observed by ^{1}H NMR (Fig. 4) and CD spectra (Fig. S12). Similarly, ***(S)*-2** could also be prepared by substitution of the 12 electron-poor residues of (*S*)-1-(4-chlorophenyl)ethylamine in ***(S)*-3** and (*S*)-1-phenylethylamine in ***(S)*-1** by 15 equiv of the more electron-rich (*S*)-1-(4-methoxy-phenyl)ethylamine (Fig. S13-S14 and Fig. S16-S17). However, the substitution of electron-rich amines residues by excess electron-poor amines is incomplete in the present chiral cage system (Fig. S18-S19). As discussed above, the chiral cage to chiral cage transformation system involving the stereochemistry preference of metal centers was constructed, which may provide a unique example to understand the supramolecular dynamic transformation process.

The magnetic susceptibilities of polycrystalline samples of cages **1-3** were measured. Both enantiomers exhibit identical magnetic behaviors. The samples were quickly cooled from room temperature down to 2 K, and the magnetic susceptibility was first measured in the warming mode from 2 to 400 K. As shown in Figure. 5, the magnetic behaviors are similar for cages **1-3**. Upon heating, the $\chi_M T$ values increase continuously from 0.96, 0.81 and 0.11 $cm^3 K mol^{-1}$ at 2 K to 1.82, 1.46 and 0.28 $cm^3 K mol^{-1}$ at 20 K for **1-3**, respectively, due to the zero field splitting (ZFS) effect of the remaining high-spin Fe(II). Then $\chi_M T$ values remain nearly constant until 200 K suggesting that 17.5%, 14.6% and 2.9% of the Fe(II) ions are at the HS state at low temperatures for **1-3**, respectively. After 200K, $\chi_M T$ exhibit a gradual increase with the maximum of 9.36, 10.49 and 8.84 $cm^3 K mol^{-1}$ at 400 K, for **1-3**, respectively, which highlight the incomplete spin-crossover transition of four iron centers. As the expected spin-only $\chi_M T$ value of four HS Fe(II) ions is 12 $cm^3 K mol^{-1}$, the $\chi_M T$ values at 400 K indicate that about 78.0%, 87.4% and 73.7% of the four Fe(II) ions are in the HS state for **1-3**, respectively. Incomplete SCO behavior has been observed in previously studied of multinuclear SCO complexes.[2-3] Thermal gravimetry analysis of **1-3** reveals that the solvent molecules are removed when heated to 400 K (Fig. S20). The following magnetic data was again recorded in cooling mode from 400 to 2 K for the desolvated **1-3**. Upon cooling, the $\chi_M T$ values of moderately decreases to 4.22, 4.49 and 2.07 $cm^3 K mol^{-1}$ at 100 K for the desolvated cages **1-3**, respectively. The $\chi_M T$ values remain nearly constant until 30 K, and decrease further to 2.19, 2.36 and 0.92 $cm^3 K mol^{-1}$ at 2 K for the desolvated cages **1-3**. The desolvated cages **1-3** exhibits more gradual SCO behavior than the original solvated **1-3**. The distinct SCO properties are attributed to the guest effect in SCO compounds, which is consistent with the previous reports that the loss of solvent molecules stabilizes the HS state.[18] Magnetic studies reveal that ligand substituent, and lattice solvent exhibit great influences on SCO behaviors of cages **1-3**.

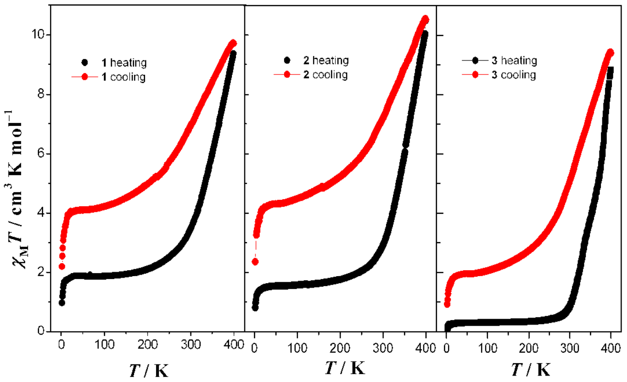


Fig. 5 Plots of $\chi_M T$ versus T for cages **1-3**.

In conclusion, unique chiral iron(II) tetrahedral cages with structure interconversion and spin-crossover close to room temperature, are present. It provides a possible facile entry for multifunctional materials by a novel synthetic strategy based on the subcomponent assembly of chirality into large discrete spin-crossover cages. These hitherto unexplored enantiopure SCO cages could be potentially applied in electronic switch and display device. Further efforts will be focused on the construction of diastereomerically pure metallo-supramolecular capsules with amazing structural motifs for spin switching, chiral separations, and diastereoselective catalysis.

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Notes and references

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† Electronic Supplementary Information (ESI) available: synthesis, structures, crystallography, NMR, TG, CD, UV, additional plot and discussion. CCDC 1025013-1025017. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

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