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ARTICLE TYPE

# Efficient optical resolution of water-soluble self-assembled tetrahedral $M_4L_6$ cages with 1,1'-bi-2-naphthol

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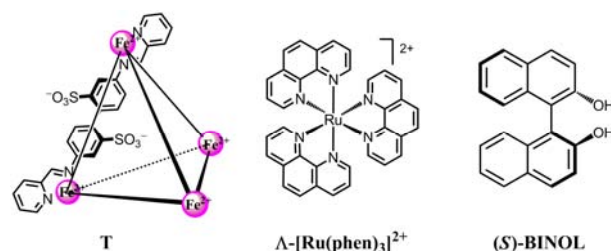
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In this paper, a water-soluble racemic self-assembled tetrahedral cage  $[Fe_4L_6]^{4+}$  was successfully resolved into their  $\Delta\Delta\Delta\Delta$  and  $\Lambda\Lambda\Lambda\Lambda$  enantiomers by (*R*)/(*S*)-1,1'-bi-2-naphthol. The enantiomeric excess of the resolved Fe(II) cage was 99%.

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The design and synthesis of tetrahedral, octahedral and other geometric configurations of self-assembled metal-organic cages using bridging ligands<sup>1</sup> is one of the most interesting fields in supramolecular chemistry.<sup>2</sup> Among the variety of cages, much attention has been paid to tetrahedral cages. Pioneering work for the synthesis and application of tetrahedral cages has been reported by Raymond,<sup>3</sup> Saalfrank,<sup>4</sup> Nitschke,<sup>5</sup> or several other groups.<sup>6</sup> Most of these self-assembled cages, with all metal centers having the same chiral configuration, are intrinsically chiral,<sup>7</sup> but they usually exist as racemic mixtures in solution or in the solid-state when achiral self-assembly components are used. In most cases, these cages have only been applied as hosts in host-guest chemistry. To explore the use of optically pure tetrahedral cages in chiral applications, such as chiral reaction vessels,<sup>8</sup> chiral separation agents,<sup>9</sup> and asymmetric catalysis,<sup>3c, 5c</sup> it is important to obtain a single enantiomer. Raymond *et al.* demonstrated that the chiral configurations of tetrahedral cages formed from rigid ligands and metal ions are more stable in solution than mononuclear and dinuclear complexes.<sup>10</sup> Thus, resolution for these racemic chiral-only-at-metal cages in solution is possible. However, little attention has been paid to the resolution of metal-organic polyhedral cages because resolution of these cages is very difficult and examples of such resolution are very rare. In 2001 Raymond successfully resolved a tetrahedral cage with labile metal centers,<sup>11</sup> although its chiral configurations required auxiliary encapsulated cations.<sup>10</sup>

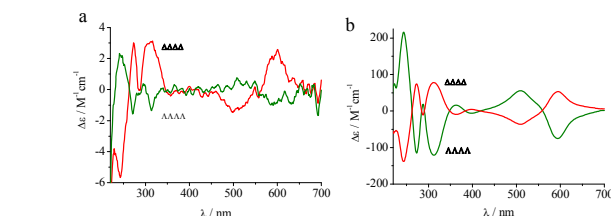
In 2008, Nitschke *et al.* reported the synthesis of the tetrahedral cage  $[Fe_4L_6]^{4+}$  (**T**) (Figure 1),<sup>5a</sup> which was assembled from the 4,4'-diaminobiphenyl-2,2'-disulfonic acid and 2-formylpyridine subcomponents with iron (II) and base. **T** has good solubility in water. They found that this tetrahedral cage exhibited high selectivity for encapsulating a hydrophobic guest molecule such as cyclopentane or cyclohexane. They also mentioned that a major practical advantage of this tetrahedral cage is its low cost from commercially available and inexpensive precursors. Tetrahedral cages, consisting of four metal centers (as vertices) and six ligands (as edges), can form all possible isomers in solution:  $\Delta\Delta\Delta\Delta/\Lambda\Lambda\Lambda\Lambda$  (*T*),  $\Delta\Delta\Delta\Lambda/\Lambda\Lambda\Lambda\Delta$  ( $C_3$ ),  $\Delta\Delta\Lambda\Lambda$  ( $S_4$ ).<sup>12</sup> For  $[Fe_4L_6]^{4+}$ , only the homochiral configurations ( $\Delta\Delta\Delta\Delta$  and  $\Lambda\Lambda\Lambda\Lambda$ ) exist in solution. However, it has not been reported if this tetrahedral cage is optically pure. The enantiopure cage will benefit its practical use in chiral applications. Herein, we attempt to resolve **T** using some simple chiral compounds (Figure 1).



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**Figure 1.** Molecular structures of cage **T**, resolving agents  $\Delta$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> and (*S*)-BINOL.

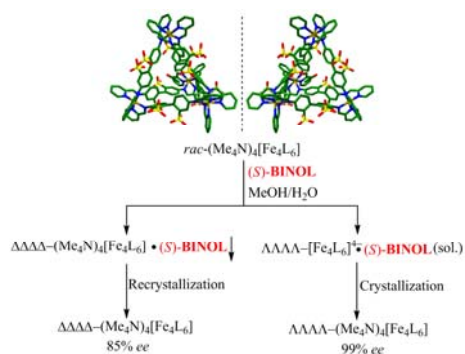
Optical resolution is usually based on the formation of diastereomeric ion pairs. Since **T** is an anion cluster, a cationic resolving agent must be needed. Two normally used cationic resolving agents, *L*-1-hydroxymethyl-3-methylbutyl (trimethyl)ammonium iodide (*Leu*<sup>+</sup>) and chiral *N*-benzylcinchoninium chloride (*Bcic*<sup>+</sup>), were selected to resolve *rac*-**T**. The resolution results show that **T** was only partially resolved (Figure S1). Thus, these two chiral cations were not suitable for the resolution of **T**. Subsequently,  $\Delta/\Lambda$ -[Ru(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (phen = 1,10-phenanthroline) (Figure 1), which has been used as a chiral induction agent for supramolecular self-assembly,<sup>13</sup> was selected as the resolving agent because its chiral configuration is stable in solution and there are three  $\pi$ -acidic ligands in its inner sphere. Therefore, we can conjecture that both the charge-charge and  $\pi$ - $\pi$  interactions may improve the chiral recognition during the resolution process. After stirring the methanol solution of **T** and  $\Delta/\Lambda$ -[Ru(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> at 50 °C for 1 h,  $\Delta/\Lambda$ -[Ru(phen)<sub>3</sub>]<sup>2+</sup> was exchanged with Me<sub>4</sub>N<sup>+</sup>. However, the CD spectra (Figure 2a) revealed that **T** was only partially resolved. This means that  $\Delta/\Lambda$ -[Ru(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> was not the best choice for the resolution of **T**, either.



**Figure 2.** CD spectra of enantio-enriched  $\Delta\Delta\Delta\Delta$ -**T** ( $\Delta\Delta\Delta\Delta$ , red) and  $\Lambda\Lambda\Lambda\Lambda$ -**T** ( $\Lambda\Lambda\Lambda\Lambda$ , green) for different resolving agents a:  $\Delta$ -[Ru(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and b: (*S*)-BINOL.

As mentioned above, using *Leu*<sup>+</sup>, *Bcic*<sup>+</sup> or  $\Delta/\Lambda$ -[Ru(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> as resolving agents, **T** was not completely resolved by the formation of diastereomeric salts. Accordingly,

we attempted to resolve **T** via the complex formation.<sup>14</sup> Commercially available chiral 1,1'-bi-2-naphthol (BINOL) (Figure 1), which is a neutral compound with two naphthyls and two hydroxyl groups, may interact with **T** via  $\pi$ -stacking and hydrogen-bonding interactions. Through the same resolution process by using  $\Delta$ -/ $\Lambda$ -[Ru(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> with (*R*)-/(*S*)-BINOL as the resolving agent, **T** could also be partially resolved, but the enantiopurity of the more soluble diastereomer and the less soluble diastereomer was still very low. When the diastereomers were redissolved in water/methanol for crystallization, we found that the samples did not dissolve completely. The dissolved portions of the more soluble diastereomer and the less soluble diastereomer had the same CD signals, and insoluble portions also had the same CD signals (Scheme S1). From this result, we speculate that water-methanol solution can be used as suitable resolution solvent.<sup>15</sup> Indeed, by stirring the water/methanol (vol:vol = 1:1) solution of **T** and (*S*)-BINOL at 50 °C for 1 h, after removal of (*S*)-BINOL, the CD spectra (Figure 2b) of the two enantiomers were nearly mirror images except for intensity, and their  $\Delta\epsilon$  intensity greatly increased. The high  $\Delta\epsilon$  value confirmed that **T** was successfully resolved. In this method, (*S*)-BINOL can be easily removed through crystallization by slow vapor diffusion of acetone into the H<sub>2</sub>O/MeOH solution of  $\Delta\Delta\Delta\Delta$ -**T** + (*S*)-BINOL or  $\Delta\Delta\Delta\Delta$ -**T** + (*S*)-BINOL (Scheme 1). In contrast to ionic resolving agents, this neutral resolving agent can be easily released from the related diastereomers without using any ion exchange technique.

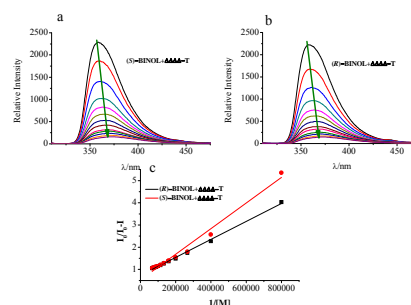


**Scheme 1.** Optical resolution of **T** using (*S*)-BINOL in 1:1 water-methanol solution followed by removal of (*S*)-BINOL during crystallization.

Based solely on the CD data, it is not possible to evaluate the enantiomeric excess (*ee*). However, the *ee* value of a chiral compound can be estimated by comparing the  $\Delta\epsilon$  intensity with a similar compound whose *ee* value is known. Raymond *et al.* suggested that if two compounds have the same chromophores located at the same configuration, the  $\Delta\epsilon$  intensity is proportional to the numbers of their chromophores.<sup>16</sup> In some cases, the CD signals of tetrahedral Fe(II) cages with schiff-base ligands at long wavelength that result from the metal-to-ligand charge-transfer transitions are used to estimate their *ee* or diastereomeric excess value.<sup>5b, 17</sup> Fortunately, we found that the chiral configuration at the metal centers of tetranuclear cage **T** is the same as a dinuclear triple-stranded Fe(II) helicate, which has been resolved by simple paper chromatograph.<sup>18</sup> Therefore, the  $\Delta\epsilon$  intensity of **T** at 593 nm should be twice that of the helicate. For cage **T** resolved by (*S*)-BINOL, the solution CD spectra (Figure 2b) of  $\Delta\Delta\Delta\Delta$ -**T** show  $\Delta\epsilon$  values of about  $-75 \text{ M}^{-1}\cdot\text{cm}^{-1}$  and  $65 \text{ M}^{-1}\cdot\text{cm}^{-1}$  at 593 nm compared with a  $\Delta\epsilon$  value of  $38 \text{ M}^{-1}\cdot\text{cm}^{-1}$  for the enantiopure  $[\text{Fe}_2\text{L}_3]^{4+}$  ( $\text{L}^1 = 4,4'$ -methylenebis(*N*-(pyridin-2-

ylmethylene)aniline)) helicate. From this analysis, we estimate the *ee* values of the  $\Delta\Delta\Delta\Delta$ -**T** and  $\Delta\Delta\Delta\Delta$ -**T** as 85% and 99%, respectively.

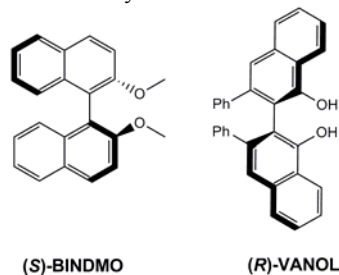
The absolute configuration of the resolved **T** cages can be determined by their CD spectra (Figure 2b). The  $\pi$ - $\pi^*$  transitions in the phenyl moiety of the ligands give rise to an atypical negative/positive exciton couplet at 283 nm, from which the chiral-at-metal configurations can be assigned to the  $\Delta/\Lambda$  form at each metal center.<sup>19</sup> The aqueous solution of  $\Delta\Delta\Delta\Delta$ -**T** or  $\Delta\Delta\Delta\Delta$ -**T** was stored under air for 30 days and then remeasured to reveal CD signals (311 nm) at least 78 % as intense as those initially measured (Figure S7). When excess cyclohexane was added to the aqueous solution of  $\Delta\Delta\Delta\Delta$ -**T**, the CD intensity did not decrease at room temperature after 24 h, and even at 323 K for 6 h, 90% of its CD intensity was retained (Figure S8 a). The little decrease of the CD intensity of the resolved cages upon complexation of cyclohexane mainly attributed to the dissociation of the resolved cages at high temperature since the CD intensity of the cages in the absence of cyclohexane also decreased a little at 323 K (Figure S8 b). This revealed that the chiral configuration of resolved cages is stable upon complexation of a guest and the resolved cage does not spontaneously open when acting as a host.



**Figure 3.** Fluorescence responses of (a) (*S*)-BINOL ( $2 \times 10^{-5} \text{ M}$ ) and (b) (*R*)-BINOL ( $2 \times 10^{-5} \text{ M}$ ) upon addition of the enantiopure  $\Delta\Delta\Delta\Delta$ -**T** at  $1.25 \times 10^{-6} \text{ M}$  intervals, (c) the Benesi-Hildebrand plots.

The fluorescence of BINOL in methanol showed a strong emission peak at  $\lambda = 358 \text{ nm}$ . When (*S*)-BINOL or (*R*)-BINOL was titrated with enantiopure  $\Delta\Delta\Delta\Delta$ -**T**, the fluorescence showed a red shift and gradually decreased with the increasing concentration of the chiral Fe(II) cage. The red shift of maximum wavelength and quenching of the fluorescence indicate that BINOL strongly interacts with the cage. Figure 3c shows good linear Benesi-Hildebrand plots for (*S*)-BINOL and (*R*)-BINOL ( $2.0 \times 10^{-5} \text{ M}$ ) in the presence of  $\Delta\Delta\Delta\Delta$ -**T** in methanol. The association constants  $K_{\text{BH}}$  were found to be  $3.2 \times 10^5 \text{ M}^{-1}$  with (*S*)-BINOL and  $1.6 \times 10^5 \text{ M}^{-1}$  with (*R*)-BINOL. The  $K_{\text{BH}}$  revealed that the binding of (*R*)-BINOL or (*S*)-BINOL with  $\Delta\Delta\Delta\Delta$ -**T** is very strong, but the decrease of fluorescence intensity of (*S*)-BINOL caused by  $\Delta\Delta\Delta\Delta$ -**T** was greater than that of (*R*)-BINOL, giving a chiralselectivity factor  $K_{\text{BH}}((\text{S})-\Delta\Delta\Delta\Delta)/K_{\text{BH}}((\text{R})-\Delta\Delta\Delta\Delta)$  of 2.0, indicating better chiral recognition between  $\Delta\Delta\Delta\Delta$ -**T** and (*S*)-BINOL. This result is identical to the fact that  $\Delta\Delta\Delta\Delta$ -**T** and (*S*)-BINOL form precipitates as the less soluble diastereomer (Scheme 1). The opposite trend in chiralselectivity between the substrate and the resolving agent was observed for the decrease of fluorescence intensity of (*R*)-BINOL and (*S*)-BINOL by  $\Delta\Delta\Delta\Delta$ -**T**, for which the chiralselectivity factor  $K_{\text{BH}}((\text{R})-\Delta\Delta\Delta\Delta)/K_{\text{BH}}((\text{S})-\Delta\Delta\Delta\Delta)$  was also 2.0, further confirming the better chiral discrimination between  $\Delta\Delta\Delta\Delta$ -**T** and (*R*)-BINOL (Figure S10).<sup>20</sup>

From the above fluorescence titration results, it can be assumed that the chiral BINOL interacts with **T** via  $\pi$ -stacking and/or hydrogen bonding. To further investigate how BINOL interacts with one of the enantiomers of cage **T**,  $^1\text{H}$  NMR titration experiments were carried out upon addition of  $\Delta\Delta\Delta\Delta$ -**T** into (*S*)-BINOL in the mixed deuterated methanol and water solution. However, no useful information was obtained because of the overlap of the NMR signals of **T** and BINOL. Therefore, another two binaphthol derivatives with the inherently chiral axis were selected to indirectly elucidate how BINOL interacts with **T** in the resolution process: (*S*)-2,2'-dimethoxy-1,1'-binaphthyl ((*S*)-BINDMO), which has a similar structure to that of BINOL but has no hydroxyl groups; and (*R*)-3,3'-diphenyl-2,2'-binaphthyl-1,1'-diol ((*R*)-VANOL), whose structure is quite different from that of BINOL (Figure 4). When these two chiral compounds were treated with **T**, respectively, silent CD spectra of the reaction solutions revealed that **T** was not resolved at all. Comparing the resolution results by (*S*)-BINDMO and (*R*)-VANOL with those using (*R*)-/(*S*)-BINOL as the resolving agents, it was suspected that the OH groups and the special chiral configuration of BINOL play a cooperative role in the molecular recognition of **T**. It is likely that the hydroxyl groups of BINOL interact with the sulfo groups of the bridging ligands in **T** through hydrogen bonds, and the appropriate  $\pi$ -stacking arrangement between the binaphthyls in BINOL and the phenyls of the edges in the cage **T** are responsible for the preferential formation of the less soluble diastereomers. In other words, the synergy of these two subtle noncovalent stereointeractions may lead to the successful resolution of **T** by the chiral BINOL.



**Figure 4.** Structures of (*S*)-BINDMO and (*R*)-VANOL.

In conclusion, four chiral compounds were selected as the resolving agents to resolve racemic **T**. **T** was partially resolved by  $\text{Leu}^+$ ,  $\text{Bcic}^+$ ,  $\Delta/\Lambda$ -[Ru(phen) $_3$ ](PF $_6$ ) $_2$  and (*R*)/(*S*)-BINOL in methanol, and successfully resolved by (*R*)/(*S*)-BINOL in 1:1 methanol-water solution. This is the first example of a self-assembled metal-organic tetrahedral cages being resolved by the neutral resolving agent through subtle noncovalent stereointeractions. We are currently interested in applying this method to other racemic metal-organic polyhedral cages, and investigating the application of the enantiopure chiral-only-at-metal cages in the related areas, such as asymmetric catalysis and chiral recognition.

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## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: [Supplemental figures and schemes, experimental details and characterizations]. See DOI: 10.1039/b000000x/

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