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# High Selectivity towards Small Copper Ions by a Preorganized Phenanthroline-Derived Tetradentate Ligand and New Insight into the Complexation Mechanism

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**A preorganized tetradentate phenanthroline-derived amide ligand, *N,N'*-diethyl-*N,N'*-ditolyl-2,9-dicarboxamide-1,10-phenanthroline (Et-Tol-DAPhen), was found to show high selectivity towards small copper ions, which might be due to the change of coordination mechanism from tetradentate to terdentate mode.**

Preorganization is an important factor to design ligands for selective complexation of one specific metal ion over another in aqueous solution[1]. A so-called preorganized ligand is the one that requires lowest energy to complex a target guest ion or molecule. Quantities of preorganized ligands, such as cyclodextrins[2], crown ethers[3], cryptands[4], calixarenes[5], and pillararenes[6] have been reported to possess excellent host-guest properties. Additionally, ligands with polypyridyl groups can be locked by fused benzo rings to obtain preorganization. Phenanthroline-derived ligands are the typical representatives. Harwood et al.[7] reported a series of preorganized ligands (2,9-bis(1,2,4-triazine-3-yl)-1,10-phenathroline, BTPhens) that replaced the bipyridine moiety with phenanthroline analogue, which led to the rapid and highly efficient separation of minor actinides from lanthanides. Hancock et al.[8] has performed deep and steady investigations on preorganized phenanthroline-derived ligands and harvested meaningful both experimental and theoretical results. Some ligand design rules (chelate ring size, hard/soft acid base theory, and preorganization) have been summarized[1]. One of the preorganized ligands, 1,10-phenanthroline-2,9-dicarboxamide, has been identified to fit best with large metal ions having an ionic radius of about 1.0 Å[9]. Molecular mechanics calculations showed that the optimum M-N bond length should be 2.52 Å, which was not favorable for small metal ions[9]. Other similar phenanthroline-derived ligands were found to have the strong ability to complex only relatively large metal ions[8]. On this purpose, metal ion size-based selectivity by the rigid phenanthroline ligands has been proposed.

Recently, we have reported a novel phenanthroline-derived tetradentate ligand, Et-Tol-DAPhen (**Fig. 1c**), which exhibited strong abilities and excellent selectivity towards large metal ions, especially actinides (U(VI), Th(IV), and Am(III))[10]. Incredibly, in present work, the extraction ability of Et-Tol-DAPhen towards small copper ions was also found to be extremely high at the acidity of 0.1-4.0 M (**Fig. 1a**). In 1.0 M $HNO_3$, the distribution ratio of Cu(II) between organic and aqueous phase is determined to be 1609 while those of other metal ions are below 10 except for Th(IV), Pb(II), and U(VI) (**Fig. 1b**). According to previous literatures[1], the five-membered chelate rings favor complexation with large metal ions having an ionic radius close to 1.0 Å. The copper ion ($r^+$ = 0.57 Å) is too small to well fit the cavity constructed by 1,10-phenathroline and its 2,9-dicarboxamide groups. Hence, it looks incredible that Et-Tol-DAPhen ligand shows such excellent selectivity towards copper ions. Here we provide some new insights into the complexation mechanism between preorganized phenanthroline tetradentate ligands and small copper ions.

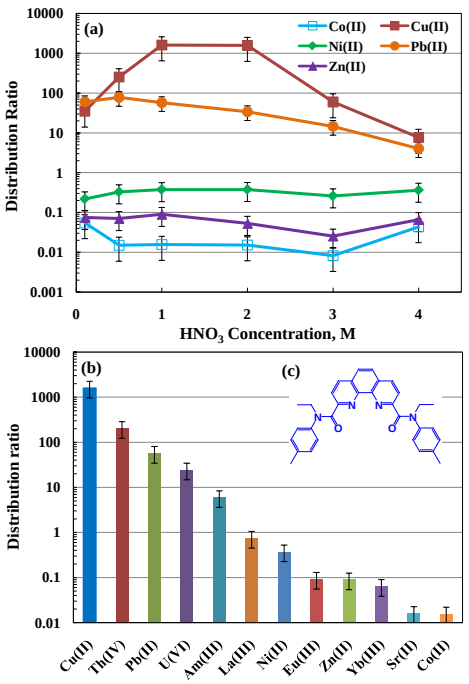


**Fig. 1** (a) Extraction properties of some transition metals by Et-Tol-DAPhen as a function of $HNO_3$ concentration in cyclohexanone. (b) Comparison of extraction ability of copper and other metal ions by Et-Tol-DAPhen in 1.0 M $HNO_3$ solution. (c) Structure of Et-Tol-DAPhen. The concentration of metal ions is 1 mM, except that of $^{241}$Am(III) is trace amount.

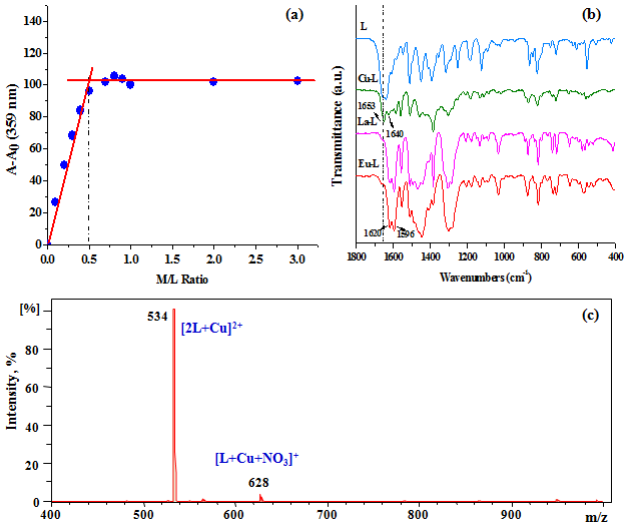


**Fig. 2** (a) Effect of Cu/L ratio on the fluorescence intensity at 359 nm of copper complexes with Et-Tol-DAPhen. (b) FT-IR spectra of Et-Tol-DAPhen, and its Cu(II), La(III), Eu(III) complexes. (c) ESI-MS spectra of Et-Tol-DAPhen and copper ion in $CH_3CN$ solvent at 1:1 ratio.

To investigate the complexation behaviors, the system of Et-Tol-DAPhen and copper ions were characterized by fluorescence, FT-IR, and mass spectrometry. The fluorescence intensity of Et-Tol-DAPhen increases with the decrease of pH values in $CH_3OH/H_2O$ solution (**Fig. S1**, ESI†), which is due to the strong protonation of the excited state[1,8a]. When adding metal ions into the methanol solution of Et-Tol-DAPhen, chelation enhanced fluorescence (CHEF) effect is not observed (**Fig. S2**, ESI†). All the fluorescences are quenched after the addition of metal ions. With respect to copper ion, we had expected distinctive quench of fluorescence on account of its highest distribution ratio. Unfortunately, copper ion leads to weaker quench of fluorescence than large metal ions such as La(III), Eu(III), U(VI), and Th(IV), which might be due to different complexation mechanisms. According to the results of fluorometric titration **(Fig. S3**, ESI†), we can determine the stable copper complex with Et-Tol-DAPhen to be 1:2 type (**Fig. 2a**). Furthermore, two ionic species at *m/z* 534 and 628 corresponding to $[CuL_2]^{2+}$ and $[CuL(NO_3)]^+$ (**Fig. S4**, ESI†), respectively, are observed in the electrospray mass spectrometry (ESI-MS) (**Fig. 2c**). Considering the relative abundance of these two species, the copper complex with stoichiometry of 1:2 seems to be the dominant species under the condition of ESI-MS. Additionally, from the FT-IR spectra (**Fig. 2b**), the peaks at 1653 and 1640 $cm^{-1}$ corresponding to the stretching vibration of amides in copper complex exhibit nearly no shift compared to those in Et-Tol-DAPhen ligand. In contrast, these two peaks in the spectra of La(III) and Eu(III) complexes have redshifts of 33 and 34 $cm^{-1}$, respectively. Comparing the spectroscopic properties of copper and lanthanide complexes can reach a conclusion that the two oxygen atoms of amide moieties in Et-Tol-DAPhen ligand may be both involved in the coordination with large lanthanide ions while no oxygen atom or only one single oxygen atom coordinates with small copper ions.

Yellow-green crystals of copper complex suitable for X-ray measurements were obtained by slow evaporation of the solution of $Cu(NO_3)_2$ and Et-Tol-DAPhen ligand in $CH_2Cl_2/CH_3OH$ (vol/vol, 1:1). The crystal structures of copper complex is shown in **Fig. 3** and X-ray crystallographic data are summarized in **Table S1**, ESI†.

The complex crystals are packed with multiple π-π stacking (**Fig. 3a**) and the π-π stacking distances between two neighboring phenanthroline moieties (**Fig. 3b**) are 3.440 Å. Compared to the ligand structure, the orientation of tolyl groups is changed[10]. The two tolyl groups are located in the opposite side of phenanthroline plane each other. Interestingly, one copper ion is bound with two Et-Tol-DAPhen ligands through two nitrogen atoms of phenanthroline moiety and one oxygen atom of amide moiety in each ligand, leaving another oxygen atom (O8 and O9) of amide moiety uncoordinated. This solid structure is quite consistent with the proposed one with the help of other auxiliary characterization methods. As shown in **Fig. 3c**, the bond lengths of Cu1-O2 and Cu1-O4 are 2.092(3) and 2.335(2) Å, respectively. The average Cu-N bond length is 2.104(3) Å. It is noteworthy that the Cu-O and Cu-N bond lengths are not equivalent, which leads to a distorted octahedral structure (**Fig. 3d**). Such a complexation mechanism in copper complex is quite different from those in lanthanide and actinide complexes. In uranyl and thorium complexes[10], two nitrogen atoms of phenanthroline moiety and two oxygen atoms of amide moieties are all involved in the coordination. However, in copper complex, the copper ion is so small that it is not well accommodated in the cavity constructed by these four oxygen and nitrogen donors. Copper ions are then liable to complex with only three donors of each ligand to decrease the strain energy. Additionally, it coordinates with two ligands to reach its maximum coordination number of six, which is benificial for its transfer from aqueous phase to organic phase.

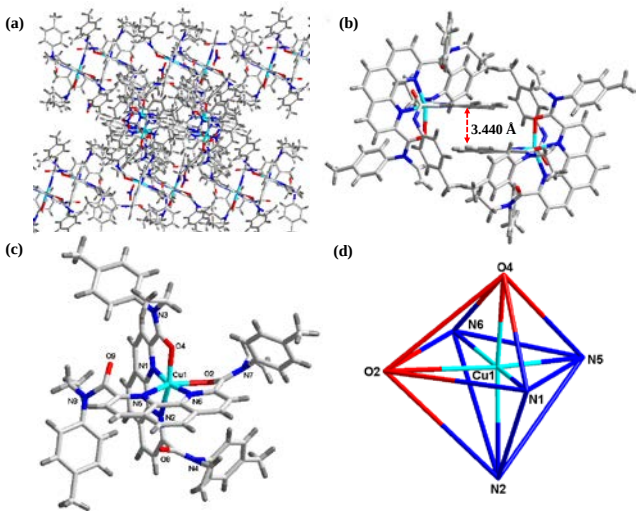


**Fig. 3** Crystal structure of copper complex with Et-Tol-DAPhen. (a) Packing pattern. (b) π-π stacking between phenanthroline and phenanthroline plane. (c) 1:2 complex structure. (d) Distorted octahedral structure. The anion and solvent molecules have been omitted for clarity. Selected bond lengths (Å): Cu1-N1 1.936(3), Cu1-O2 2.335(2), Cu1-N5 2.254(2), Cu1-N6 1.962(3), Cu1-O4 2.092(3), Cu1-N2 2.264(3).

In order to further investigate the electronic structure and the coordination modes, the copper complex was optimized and calculated at the B3LYP, BP86 and M06-2x level of theory using density functional theory (DFT) method. The predicted selective geometrical parameters concerning the copper atom and the

corresponding Wiberg bond indices (WBIs) are present in **Table S2**, ESI†. According to the calculated results (**Fig. S5**, **Table S3**, ESI†), copper ions coordinate with one oxygen atom and two nitrogen atoms in each ligand. The binding energy of copper ion and Et-Tol-DAPhen ligands is about -458 kcal/mol, which indicates that the formation of this complex is energetically favorable. It is clearly seen that the bond lengths at the BP86 level of theory are better in agreement with the X-ray crystallographic parameters, which suggests that the BP86 method is better suitable to this molecular system. The WBIs of the Cu-N and Cu-O are about 0.16-0.27, indicatve of weaker covalent character for these bonds[11]. In addition, the highest occupied molecular orbital (HOMO) and correlation occupied MO are provided in **Fig. S6**, ESI†. The relevant molecular orbitals to the lone pairs of N or O atoms and the d ortbital of Cu atom are shown in **Fig. 4**. These MO suggest that the binding of Et-Tol-DAPhen with copper ion could be attributed to the interactions between the lone pairs of N or O atoms and the unoccupied *d* orbital of copper ions.

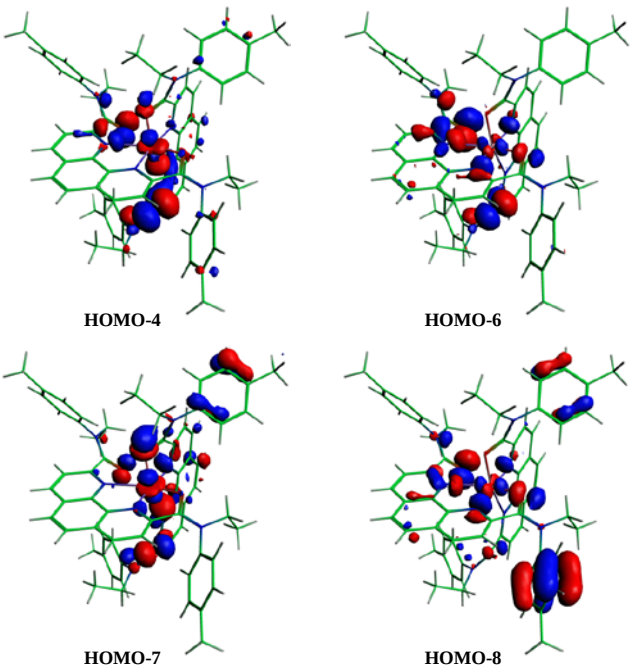


**Fig. 4** Selected α-spin frontier molecular orbitals of the copper complex. These molecular orbitals highlight the lone pairs of N or O atoms of Et-Tol-DAPhen and *d* orbital of Cu atom. The isosurface value of molecular orbitals is 0.03 au.

In summary, a preorganized tetradentate phenanthroline-derived amide ligand, Et-Tol-DAPhen, was found to show high selectivity towards small copper ions. Fluorescence, ESI-MS, and FT-IR spectra show that the copper ion is bound with two ligands. X-ray crystallographic structure and DFT calculations confirm that one copper ion is coordinated with two Et-Tol-DAPhen ligands through two nitrogen atoms of phenanthroline moiety and one oxygen atom of amide moiety in each ligand, leaving another oxygen atom of amide moiety uncoordinated. It is believed that the change of coordination mechanism from tetradentate to terdentate mode is quite beneficial for the complexation of small copper ion by preorganized phenanthroline-derived ligands. Our findings of this complexation mechanism may shed light on a new way to design metal-selective ligands and deeper understanding of the intriguing features of their complexes.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, fluorescence spectra, isotope patterns, crystal data, optimized structures, molecular orbital, and Cartesian coordinates of optimized structure. See DOI: 10.1039/b000000x/

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## Graphical Abstract