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Cu(II) assisted self-sorting towards pseudorotaxane formation†

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A new triamino macrocycle shows Cu(II) templated self-sorting of a pseudorotaxane out of sixteen such possibilities from the mixture of nine components of a tridentate, four bidentate ligands and four transition metal ions.

One of the most important aspects of self-assembly is the formation of interpenetrated molecules like rotaxanes, pseudorotaxanes, catenanes *etc.* for their potential applications in the area of molecular devices.[1–5] Self-assembly and self-sorting of more than two components demands selectivity.[6–10] It is challenging to develop an artificial set of molecules which can generate a self-assembled structure from a complex mixture of multiple components.[11] In a proof-of-concept experiment, we have demonstrated that a newly synthesized triamino macrocycle (**L**^{1}) and Cu^{2+} selectively form a pseudorotaxane with 1,10-phenanthroline (**L**^{2}) over 2,9-dimethyl-1,10-phenanthroline (**L**^{3}) 2,2′-bipyridine (**L**^{4}), and 6,6′-dimethylbipyridine (**L**^{5}) whereas the combination of **L**^{1} and **L**^{2} selectively bind with Cu^{2+} over Co^{2+}, Ni^{2+}, Zn^{2+}. Further, we show selective formation of the pseudorotaxane from a mixture of **L**^{1}–**L**^{5} and Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}. To the best of our knowledge this represents the first example of Cu(II) assisted self-sorting towards the formation of a pseudorotaxane from a mixture of multiple components.

A new macrocycle, **L**^{1} (Fig. 1a) having a tridentate amine chelating binding site and two amide functionalities was synthesized in good yield (ESI†). The UV/Vis spectrum of **L**^{1} with Cu^{2+} (1 : 1 complex) in methanol shows a distinguishable absorption band at 620 nm (ε = 127 M^{-1} cm^{-1}) corresponds to the d–d transition and titration of **L**^{1} with Cu^{2+} shows 1 : 1 binding in solution (Fig. 11S†). Crystals of the Cu^{2+} complex of **L**^{1} (**1**) suitable for single crystal X-ray study were obtained by slow evaporation of an acetonitrile (CH_3CN) solution of **L**^{1} and $Cu(ClO_4)_2\cdot6(H_2O)$. Detailed structural analysis of **1** reveals that Cu^{2+} is in penta coordination with the three –NH groups of **L**^{1} and two nitrogen atoms from CH_3CN (Fig. 1b and c).‡ The coordination geometry around copper(II) is distorted square pyramidal (τ = 0.2).[12] The N-atom of one of the two CH_3CN completes the square base with three –NH of **L**^{1} and the second CH_3CN occupies the apical position of the distorted square pyramid. The equatorial CH_3CN is bound to the metal ion more strongly [Cu1–N7, 1.980(12) Å] compared to the apical one [Cu1–N6, 2.232 (12) Å]. These coordinated solvent molecules could easily be replaced by other monodentate or bidentate ligands. In this context we have chosen four bidentate ligands, 1,10-phenanthroline (**L**^{2}), 2,9-dimethyl-1,10-phenanthroline (**L**^{3}) 2,2′-bipyridine (**L**^{4}) and 6,6′-dimethylbipyridine (**L**^{5}), for syntheses of Cu^{2+} templated ternary complexes possibly *via* pseudorotaxane formation. Complexes **2–5** were isolated in solid form upon reaction of **L**^{1}, Cu^{2+} and **L**^{2}/**L**^{3}/**L**^{4}/**L**^{5} respectively in a methanol/CH_2Cl_2 binary mixture. The electrospray ionisation mass spectrum (ESI-MS) of complexes **2–5** support the formulation of $[Cu(L^1)(X)(ClO_4)]^+$, X = **L**^{2}, **L**^{3}, **L**^{4} and **L**^{5} for complexes **2–5**, respectively (Fig. 2).

Solution state UV/Vis experiments were carried out to follow the formation of ternary complexes among **L**^{1}, Cu^{2+} and each one of **L**^{1}–**L**^{5} (Fig. 16S, ESI†). For these four combinations UV/Vis spectra showed broad absorption bands at 670, 632, 665 and 634 nm upon addition of 1 : 1 : 1 of equimolar solution of **L**^{1}, Cu^{2+} and **L**^{2}/**L**^{3}/**L**^{4}/**L**^{5} solution, respectively. In all four complexes red shifted absorption spectra are obtained compared to the absorption band at 620 nm for (1 : 1) **L**^{1} and Cu^{2+} under the same experimental conditions. Observed red shifts of the d–d bands in these complexes are in good agreement with the ligand field strengths. Additionally the X-band EPR spectra† in acetonitrile solution of all the complexes show very similar patterns with $g_\parallel > g_\perp$ indicating $d_{x^2-y^2}$ ground states with distorted square

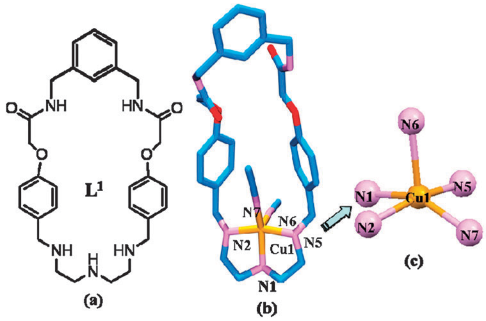

Fig. 1 (a) **L**^{1}, (b) single crystal X-ray structure of **1** and (c) distorted square pyramidal representation of Cu centre. H atoms in **1** are omitted for clarity.

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† Electronic supplementary information (ESI) available: Experimental details. CCDC 783143 (**1**) and 783144 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc10472a

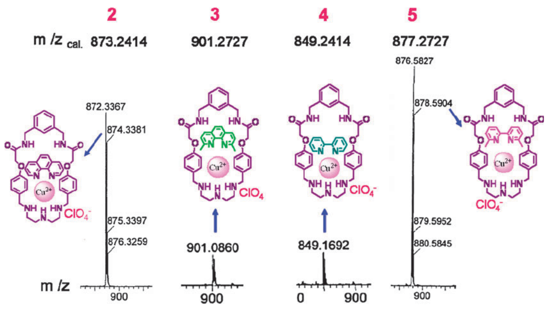
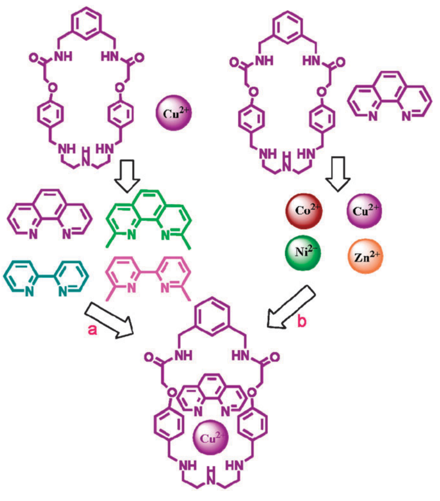


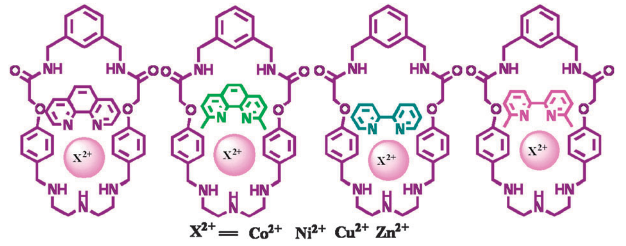
Fig. 2 ESI mass spectra of complexes **2–5**.

pyramidal geometry. All of these results suggest threading of bidentate ligands in the cavity of $\mathbf{L^1}$ to form ternary complexes of Cu^{2+}.

To investigate the selective formation of a ternary complex we carried out complexation studies of equimolar amounts of $\mathbf{L^1}$ and Cu^{2+} in a methanol/CH_2Cl_2 binary mixture in the presence of all bidentate ligands, $\mathbf{L^2}$–$\mathbf{L^5}$ (each at same molar amounts to that of $\mathbf{L^1}$) following path a (Scheme 1). The blue solid was isolated and characterized by ESI-MS as well as UV/Vis spectroscopic studies. Both studies support the formation of complex **2** from the mixtures. Thus this result reveals the preferential formation of ternary complex **2** from the mixture of six components. We performed another experiment to understand the selectivity toward Cu^{2+} by $\mathbf{L^1}$ and $\mathbf{L^2}$ over transition metal ions with common stable oxidation numbers (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) following path b (Scheme 1). Equimolar amounts of $\mathbf{L^1}$, $\mathbf{L^2}$ and all four metal ions were stirred for 4 h in a methanol/CH_2Cl_2 binary mixture at room temperature; the precipitate was characterized by UV/Vis, ESI-MS and energy dispersion X-ray (EDX) studies. The EDX spectrum (Fig. 27S)† shows only the presence of copper ions, and no peaks for other metal ions. Further spectroscopic studies confirm the formation of complex **2** in pure form. Considering paths a and b in Scheme 1, formation of a number of ternary complexes is possible which is shown in Scheme 2S†. Thus our studies clearly show the selective formation of ternary complex **2** out of these seven possible ternary complexes.



Scheme 1 Selective formation of one ternary complex from mixtures of analogous third components by path (a) and (b).



Scheme 2 Sixteen possible ternary complexes of $\mathbf{L^1}$ with all other components ($\mathbf{L^2}$–$\mathbf{L^5}$) and Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}.

When an equimolar solution of $\mathbf{L^2}$, $\mathbf{L^3}$, $\mathbf{L^4}$, $\mathbf{L^5}$ in a methanol/CH_2Cl_2 binary mixture was added to an equimolar mixture of $\mathbf{L^1}$, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} and stirred at RT, a blue precipitate developed after 4 h. ESI-MS of the collected precipitate shows a peak corresponding to $[Cu(\mathbf{L^1})(\mathbf{L^2})(ClO_4)]^+$ of the ternary complex **2** whereas no peaks corresponding to other possible ternary complexes involving macrocycle $\mathbf{L^1}$ are observed (Fig. 17S)†. It is important to mention that in the mixtures as many as 16 ternary complexes are possible with $\mathbf{L^1}$ (Scheme 2). Thus $\mathbf{L^1}$ selectively picks up Cu^{2+} and $\mathbf{L^2}$ from the mixture to form the ternary complex **2**.

Solution state selective formation of $[Cu(\mathbf{L^1})(\mathbf{L^2})(ClO_4)]^+$ is established by ESI-MS analysis of clear solutions obtained from all combinations described in the above three precipitate isolation processes by using low concentrations of ligands and metal ions in methanol. In all three cases, ESI-MS of the resulting clear solutions showed selective formation of the ternary complex that corresponds to $[\mathbf{L^1}\cdot\mathbf{L^2}\cdot Cu\cdot ClO_4]^+$ (Fig. 18S–20S)†.

The above studies show selective formation of ternary complex **2** from mixtures of different components. Thus we have carried out detailed studies on the formation of **2** in the solution and solid states. The UV/Vis titration of an equimolar mixture of $\mathbf{L^1}$, $\mathbf{L^2}$ with Cu^{2+} shows 1 : 1 : 1 ternary complexation (Fig. 28S)†. We also carried out ternary complexation studies in a step-wise manner. First we titrated $\mathbf{L^1}$ with Cu^{2+} which showed 1 : 1 complex formation (as shown in Fig. 11S)†; then we titrated the complex with $\mathbf{L^2}$ in methanol as shown in Fig. 3.

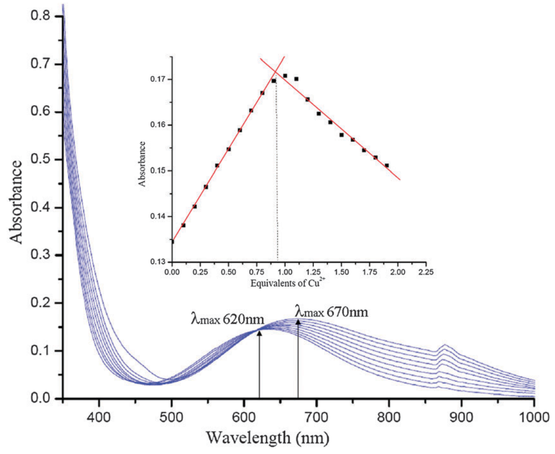


Fig. 3 UV/Vis titration profile of $\mathbf{L^1}$ + Cu^{2+} (5×10^{-3} M) with aliquots of $\mathbf{L^2}$ (5×10^{-3} M) in methanol. Selected UV-Vis spectra are shown for clarity whereas sigmoidal fits show more points.

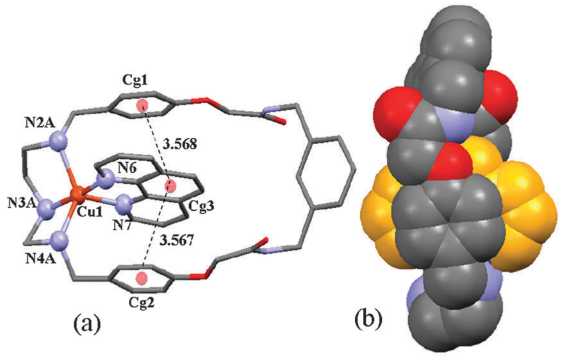


Fig. 4 (a) Single crystal X-ray structure of **2** with disordered diethylene triamine moieties in two positions. One set of disordered diethylene triamine is shown whereas H atoms and counter anions along with lattice water molecules are omitted for clarity. (b) Space-filling model of (a).

As a result the absorption band of the Cu^{2+}–$\mathbf{L^1}$ complex at 620 nm shifted to 670 nm, indicating the complexation of $\mathbf{L^2}$ with Cu^{2+}-$\mathbf{L^1}$ complex possibly *via* a threading mechanism to form a pseudorotaxane that supports 1 : 1 : 1 complexation of $\mathbf{L^1} : \mathbf{L^2} : Cu^{2+}$.

Single crystals of complex **2** suitable for X-ray analysis were obtained upon slow evaporation of acetonitrile solutions at RT. The single crystal X-ray structure of **2** shows involvement of $\mathbf{L^1}$, $\mathbf{L^2}$, and Cu^{2+} in the complex (Fig. 4) and confirms the coordination geometry where three of its coordination site are attached to –NH of $\mathbf{L^1}$ and the other two are coordinated with nitrogen centers of $\mathbf{L^2}$.‡ It is important to mention that $\mathbf{L^2}$ is coordinated to the metal center to satisfy the coordination number *via* threading of $\mathbf{L^1}$. This confirms the formation of a Cu^{2+} templated pseudorotaxane assembly from $\mathbf{L^1}$ and $\mathbf{L^2}$. Other than coordination number and geometry, the driving force for threading in complex **2** could be π–π stacking between the two phenyl rings of $\mathbf{L^1}$ and arene moiety of the $\mathbf{L^2}$ which is evident from the distance between Cg1···Cg3 (Cg1: centroid of ring C11–C15 and Cg3: centroid of ring C34–C49), and Cg2···Cg3 (Cg2: centroid of ring C22–C27) are 3.568 Å and 3.567 Å, respectively (Fig. 4a).

Thus, selective formation of **2** could be attributed to the suitable coordination sites and geometry of Cu^{2+} in the cavity of $\mathbf{L^1}$ over other metal ions whereas preferences of $\mathbf{L^2}$ over other bidentate ligands $\mathbf{L^3}$–$\mathbf{L^5}$ could be due to the resultant of the steric effect as well as π–π stacking interactions.

In summary, we have demonstrated a copper(II) templated co-ordination driven by self-sorting of a pseudorotaxane by a new triamino macrocycle and phenanthroline. This proof-of-concept strategy of selective formation of one complex from a common pool of other subcomponents could be extended in the area of self-sorting of complex mixtures in general. Selective formation of threaded complexes has an immense utility in the construction of new interlocked systems like rotaxanes and catenanes towards the development of metal driven molecular machines.

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Notes and references

‡ Crystallographic data for: **1**: $C_{34}H_{42}Cl_2CuN_7O_{13}$, M = 889.17, monoclinic, space group $P2(1)/c$, a = 9.328(2), b = 29.816(6), c = 15.503(3) Å, β = 109.638(10), V = 4061.0(14) Å^{-3}, ρ_{calcd} = 1.454 g cm^{-3}, Z = 4, ρ_{cal} = 1.454 g cm^{-3}, Z = 4, λ = 0.71073 Å, T = 100(2) K, 14 451 reflections, 2890 independent (R_{int} = 0.1059), and 1667 observed reflections [$I \geq 2\sigma(I)$], 516 refined parameters, R = 0.0609, $wR2$ = 0.1123. Crystallographic data for: **2**: $C_{42}H_{45}Cl_2$-CuN_7O_{14}, M = 991.17, monoclinic, space group $P2(1)/c$, a = 11.7929(9), b = 11.6986(9), c = 32.650(2) Å, β = 97.443(2), V = 4466.4(6) Å^3, ρ_{cal} = 1.474 g cm^{-3}, Z = 4, λ = 0.71073 Å, T = 100(2) K, 38 647 reflections, 7219 independent (R_{int} = 0.0363), and 5446 observed reflections [$I \geq 2\sigma(I)$], 589 refined parameters, R = 0.0591, $wR2$ = 0.1660.

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