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# Reversible anion-templated self-assembly of [2 + 2] and [3 + 3] metallomacrocycles containing a new dicopper(I) motif†‡

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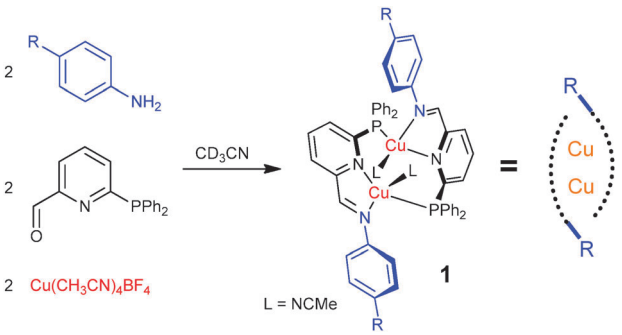
**A new dicopper(I) complex is reported that can be incorporated into extended architectures through multitopic carboxylate linkers; reversible carboxylate templation under pH control led to the formation of [2 + 2] and [3 + 3] metallomacrocycles.**

Recent years have seen major advances in the creation of complex self-assembled architectures from simple building blocks.[1] Subtle alterations in components' geometries[2] or the identities of metal ions[3] can result in major changes in a product's structure. The use of multiple 'chemically orthogonal' linkages has been exploited to generate structures in which each different kind of linkage contributes to the overall structure.[4] We have recently shown how subcomponent self-assembly,[5] the simultaneous formation of both dynamic covalent (C=N) and dative (ligand→M) bonds under thermodynamic control, can yield complex and functional dynamic systems.[6] Here we describe a new self-assembled dicopper(I) complex for use as a building block in the formation of extended multinuclear architectures including the anion templated assembly[7] of both a 52-membered [2 + 2] and a 78-membered [3 + 3] metallomacrocycle.

The reaction of 6-(diphenylphosphino)picolinaldehyde‡ with aniline and copper(I) yielded a dicopper(I) complex of the form $[Cu_2\mathbf{L^1}_2MeCN_2]\cdot 2BF_4$, **1** (Scheme 1).¶

The pyridyl imine ligands $\mathbf{L^1}$ each have three donor atoms, shared between the two copper centres, with the pyridyl and imine donors chelating the first $Cu^I$, while the diphenylphosphine moiety bridges to the second metal ion. Both copper(I) centres thus adopt a pseudotetrahedral coordination geometry with an $N_3P$ coordination sphere,[8] in which the third nitrogen donor is provided by an acetonitrile molecule. The metal centres are separated by 3.1698(14) Å, a distance greater than twice copper(I)'s van der Waals radius (2.80 Å).[9] The ligands are oriented in a head-to-tail arrangement, rendering this complex $C_2$-symmetric, as reflected both in the solution NMR spectra and the solid-state X-ray structure (Fig. 1).




**Scheme 1** Synthesis of $[Cu_2\mathbf{L^1}_2MeCN_2]$ **1** and its schematic representation (right).

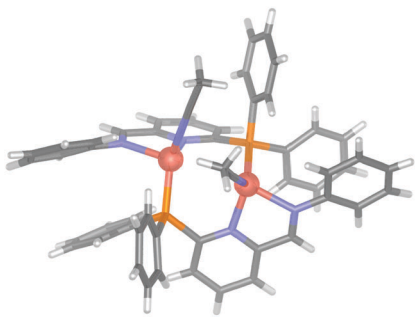


**Fig. 1** Schematic representation of the X-ray crystal structure of $\mathbf{1}\cdot 2HSO_4\cdot 2MeCN$, R = H. Counterions and solvent omitted for clarity.

Complex **1** has two modes of linkage for the formation of more complex structures. Firstly, the coordinated acetonitrile molecules can be replaced by multi-functional ligands capable of linking dimetallic units together.[10] Secondly, the dynamic-covalent imine bonds[11,12] can be exploited by substitution for a multi-functional amine.[5] These two types of modification can be carried out independently, increasing the diversity of structures available using this motif.

The reaction of **1** with disodium terephthalate ($Na_2\mathbf{L^2}$) yielded the terephthalate-linked tetranuclear species $[(Cu_2\mathbf{L^1})_2\mathbf{L^2}]$, **2** (Fig. 2). Its X-ray structure (Fig. 2) revealed

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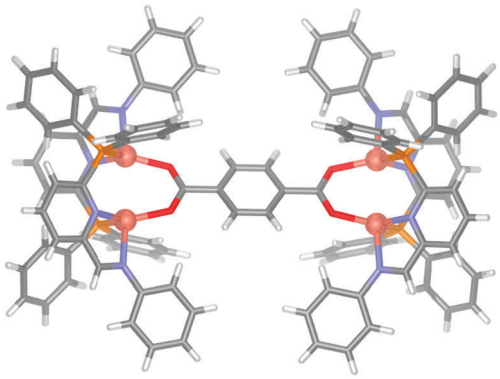
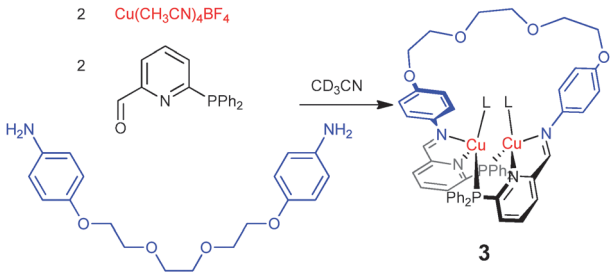


**Fig. 2** Schematic representation of the X-ray crystal structure of $2{\cdot}2BF_4{\cdot}1.5H_2O{\cdot}2C_4H_{10}O{\cdot}MeCN$ formed by the reaction of **1** with disodium terephthalate. Counter-ions and solvent omitted for clarity.




**Scheme 2** In the absence of templation, the reaction of aldehyde, diamine and Cu(I) gave 85% [1 + 1] metallomacrocycle $[Cu_2\mathbf{L}^3]{\cdot}2BF_4$, **3**.

dicarboxylate bridges between dicopper units.¶ The bridging mode also effected a shortening of the Cu···Cu distance by 0.31 Å to 2.8580(6) Å.

The ability to link more than one dicopper(I) domain together using diamines was investigated by the use of the dianiline triethyleneglycol bis(*p*-aminophenyl)ether in place of aniline in the synthesis of **1**. This reaction resulted in the formation of a 26 membered [1 + 1] metallomacrocycle **3**, whose ligand $\mathbf{L}^3$ is the Schiff-base condensation product of two phosphino-aldehyde residues with the dianiline (Scheme 2).

The flexible polyethylene glycol chain enables the ligand to encircle the dicopper motif of **1**, giving complex **3** (Scheme 2). The $^1$H NMR of **3** indicated that it exists as the majority product (85%) in a dynamic combinatorial library (DCL)[12] also containing higher oligomeric species. This library persisted even after repeated recrystallisations.

Employing both dianiline and terephthalate together resulted in the exclusive formation of the [2 + 2] metallomacrocyclic product $[Cu_4\mathbf{L}^3{}_2\mathbf{L}^2]{\cdot}2BF_4$, **4** (Scheme 3). Both the terephthalate ($\mathbf{L}^2$) and the dianiline ($\mathbf{L}^3$) link the two dicopper(I) domains forming a 52-membered metallomacrocyclic ring. Once again the Cu···Cu distances are reduced relative to those found in **1** with a separation of 2.9083(14) Å observed in the X-ray structure (Fig. 3).

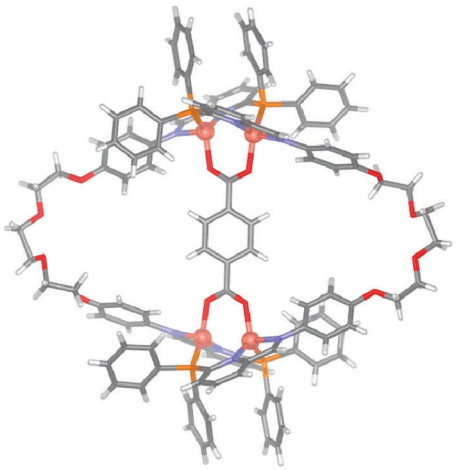
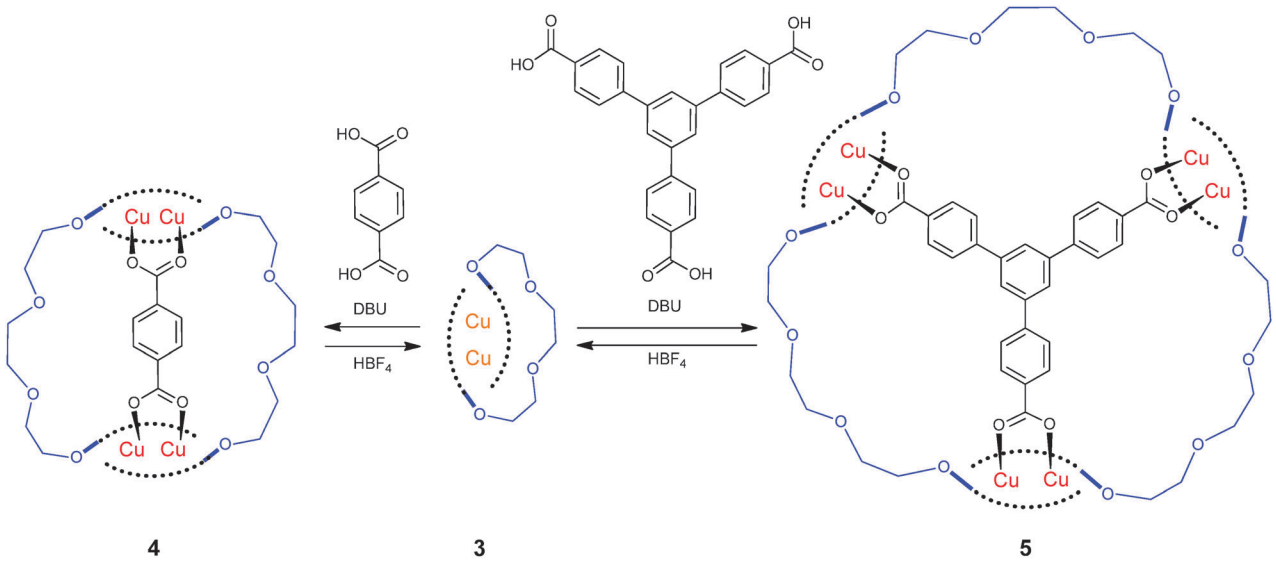


**Fig. 3** Schematic representation of the X-ray structure of $\mathbf{4}{\cdot}2BF_4{\cdot}4MeCN$. Counterions, solvent and disorder removed for clarity.




**Scheme 3** The addition of terephthalate to a solution of **3** yields [2 + 2] metallomacrocycle **4**; addition of 1,3,5-tris(4-carboxyphenyl)benzene yielded [3 + 3] metallomacrocycle **5**. Both **4** and **5** could be reversibly interconverted to **3** through acid/base cycling.

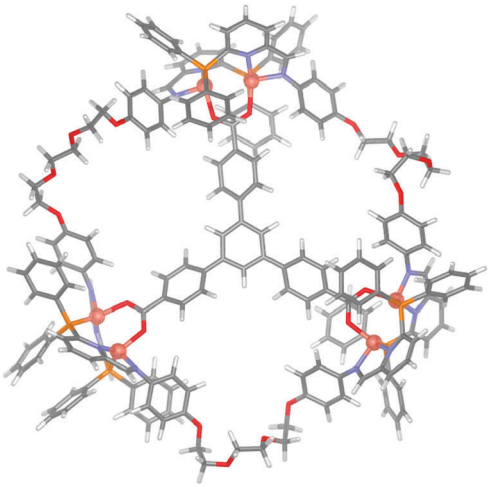


**Fig. 4** CAChe MM2[13] model of [3 + 3] metallomacrocycle **5**.

While in the solid state **4** crystallised in an achiral *meso* form, with the two coordinating domains of each $\mathbf{L^3}$ arranged on the same (*cis*) side of the molecule, in solution two species are observed in a ratio of 66 : 34. The second species occurs when the two binding domains are arranged mutually *trans* across the plane of the molecule forming a helix with two different enantiomers (*P vs. M*) present in a racemic (*rac*) mixture.

The *meso* and *rac* species exhibit different $^1$H NMR spectra (see Fig. S3–S5 in the ESI‡). Two-dimensional NMR experiments confirmed that both species were [2 + 2] metallomacrocycles, which interconvert slowly on the NMR timescale.

Substitution of $Na_2\mathbf{L^2}$ for 1,3,5-tris(4-carboxyphenyl) benzene ($H_3\mathbf{L^4}$) in the presence of DBU (1,8-diazabicycloundec-7-ene) yielded the [3 + 3] metallomacrocyclic product $[Cu_6\mathbf{L^3}_3\mathbf{L^4}]\cdot 3BF_4$, **5**. The product's identity was confirmed by ESI-MS and $^1$H NMR. Molecular modelling[13] confirmed the viability of such a structure (Fig. 4).

Each of **2**, **4** and **5** can be reversibly formed and destroyed under pH control.[14] The addition of $HBF_4$ to a solution of **4** or **5** yielded the untemplated DCL containing predominantly [1 + 1] metallomacrocycle **3**. Subsequent addition of DBU reformed the templated structures as detected by $^1$H NMR and ESI-MS. Such reversible pH switching between complex structures can provide the mechanisms that lend function to molecular machines.[15]

In conclusion, a new dicopper(I) complex has been synthesised, whose symmetrical structure incorporates dynamic covalent imine bonds and coordinatively unsaturated metal centres. Weakly coordinated solvent molecules can be displaced with anionic ligands to form extended structures, while the dynamic nature of the imine bonds can be exploited to form metallomacrocylic species incorporating dianiline groups. Employing both of these features has allowed for the anion templated synthesis of [2 + 2] and [3 + 3] metallomacrocycles. These metallomacrocycles can be readily and reversibly broken down and reformed by subsequent addition of an acid and a base. Other complex assemblies that are accessible by exploiting the dual functionality of this system are being investigated.

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## Notes and references

¶ **1**·2HSO$_4$·2MeCN: formula $C_{56}H_{52}Cu_2N_8O_8P_2S_2$, $M$ 1218.20, triclinic, $P\bar{1}$, $a$ 12.360(3), $b$ 14.495(3), $c$ 16.258(3) Å, $\alpha$ 95.16(3)°, $\beta$ 91.69(3)°, $\gamma$ 105.61(3)°, $V$ 2789.5(10) Å$^3$, $Z$ 2, $T$ 180(2) K, $N$ 60 657, $N_{ind}$ 12 532 ($R_{merge}$ 0.1261), $R_1(F)$ 0.0829, w$R_2(F^2)$ 0.2499. **2**·2BF$_4$·1.5H$_2$O·2C$_4$H$_{10}$O·MeCN: formula $C_{114}H_{106}B_2Cu_4F_8N_9O_{7.50}P_4$, $M$ 2273.74, orthorhombic, *pbam*, $a$ 12.147(2), $b$ 18.712(4), $c$ 23.253(5) Å, $V$ 5285.3(18) Å$^3$, $Z$ 2, $T$ 180(2) K, $N$ 51 480, $N_{ind}$ 6686($R_{merge}$ 0.0377), $R_1(F)$ 0.0372, w$R_2(F^2)$ 0.0967. **4**·2BF$_4$·4MeCN: formula $C_{124}H_{112}B_2Cu_4F_8N_{12}O_{12}P_4$, $M$ 2513.92, triclinic, $P\bar{1}$, $a$ 11.583(2), $b$ 16.843(3), $c$ 19.661(4) Å, $\alpha$ 66.03(3)°, $\beta$ 78.91(3)°, $\gamma$ 88.69(3)°, $V$ 3433.1(14) Å$^3$, $Z$ 1, $T$ 180(2) K, $N_{ind}$ 12 082($R_{merge}$ 0.0748), $R_1(F)$ 0.0812, w$R_2(F^2)$ 0.2437. SQUEEZE applied.


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