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Post-assembly guest oxidation in a metallo-supramolecular host and structural rearrangement to a coordination polymer;

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PTA hosted in a copper metallo-supramolecular triangle undergoes post-assembly oxidation to form PTAO in aerated solutions. The oxidation is triggered by selected co-solvents that also govern the formation of the final crystalline product leading to a discrete host-guest triangle {PTAO@[Cu(o-L)]_3} or to a 1D coordination polymer {(PTAO)_2@[Cu_8][Cu_2]}_{\infty} containing a {Cu_8} ring with a double hosting pocket.

Coordination driven metallo-supramolecular architectures where metal ions and polytopic ligands self-assemble to form discrete boxes and capsules represent intriguing host systems.¹ Impressive examples of their potentiality have been reported.² These metallo-supramolecular capsules can be used to safely store unstable and reactive compounds,^{2a} for space confined reactivity^{2b} or "enzyme-like" catalysis.^{2c} Moreover, they can be employed as nano-sized reactors by permitting in their cavities the synthesis of metal oxide nanoparticles with remarkable control of the nanoparticle size.^{2d} As recently demonstrated,³ the functional properties of such systems can be further tailored through post-functionalization of the metallo-supramolecular architecture. This approach is challenging and can be successfully adopted only in the presence of robust self-assembled architectures.

In this communication, we study the oxidation of PTA (1,3,5-triaza-7-phosphaadamantane) to PTAO (1,3,5-triaza-7-phosphaadamantane-7-oxide) in the environment of a coordination driven host. The reaction is performed in a post-assembled host-guest ensemble where PTA plays the role of a templating guest for the metallo-supramolecular host. Recently, we have reported that the self-assembly of Cu^{2+} ions with the *ortho* bis-(3-acetylacetone)benzene ligand (hereafter, *o*-LH₂) leads to formation

of a constitutional dynamic library (CDL) of metallo-supramolecular polygons where a dimeric rhomboid [Cu(o-L)]₂ and a trimeric triangle [Cu(o-L)]₃ are both accessible and in equilibrium.⁴ Selection toward the triangular species is thermodynamically driven in the presence of well-suited molecules acting as guests to form the $\{G(a)[Cu(o-L)]_3\}$ host-guest architectures, ^{4a,c} according to a molecular recognition mechanism with two possible paths (Fig. 1). Among the possible guests, PTA and its oxide PTAO are included. Both the host-guest species {PTA@[Cu(o-L)]₃} and {PTAO@[Cu(o-L)]₃} are accessible: they revealed to have quite strong and comparable host-guest association constants^{4c} (log K_{HG}^{PTA} = 3.39 (±2) and $\log K_{\mathrm{HG}}^{\mathrm{PTAO}}$ = 3.11 (±1) at 298 K) and a robust supramolecular motif. To the best of our knowledge, {PTA@[Cu(o-L)]₃} is one of the rare examples⁵ of a μ_3 -PTA molecule with three coordinating N atoms and a P atom not bonded to a metal centre. Therefore, the phosphorus atom is a free and available site to explore a series of well-known PTA derivatizations of practical interest.⁶ Firstly, we investigated the use of the [Cu(o-L)]₃ host as a scaffold for the post-assembly oxidation of the PTA molecule. PTA is an air-stable and water soluble phosphine, commonly used as a neutral P-donor ligand.⁶ It is usually oxidized with strong oxidation agents such as



Fig. 1 Representation of the two possible molecular recognition selection processes to give the $\{G@[Cu(o-L)]_3\}$ host-guest architecture developed in our previous studies.⁴

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30% H₂O₂,^{7a} nitrogen tetroxide^{7b} or with diluted H₂O₂ solutions in the presence of a rhenium based catalyst.7c Examples are also reported where PTA is partially oxidized in the presence of reduced metal ions $(Ni(\pi), {}^{8a} Co(\pi), {}^{8b,c} and Cu(\pi), {}^{8d})$. Herein, we report that oxidation can be successfully carried out under mild conditions using aerated solutions at room temperature, starting from the {PTA@[Cu(o-L)]₃} species. The reaction is triggered by selected co-solvents. Several co-solvents were tested such as methanol. ethanol, acetonitrile, ethyl acetate, tetrahydrofuran, 1,4-dioxane, acetone, n-hexane, cyclo-hexane and n-heptane. In three cases we succeeded in obtaining single crystals showing that the co-solvent also strongly affects the final crystalline product leading to: the starting host-guest motif {PTA@[Cu(o-L)]₃} from a CHCl₃*n*-hexane solution, the target oxidized species $\{PTAO(a)[Cu(o-L)]_{3}\}$ from a CHCl₃-CH₃CN solution, or an unpredictable oxidized species, a 1D coordination polymer, {[(PTAO)₂(H₂O)[Cu(o-L)]₈][Cu(o-L)]₂}_∞ (hereafter, $\{(PTAO)_2 @ [Cu_8] [Cu_2]\}_{\infty}$) from a CHCl₃-EtOH solution. The PTA host-guest species, $\{PTA@[Cu(o-L)]_3\}$, is very stable in air in the solid state as well as when dissolved in dichloromethane or chloroform solutions. Upon heating the supramolecular structure is not affected and the PTA guest is stable against oxidation. Interestingly, when {PTA@[Cu(o-L)]₃} is dissolved in a chloroform-acetonitrile solution and left in a closed vial, PTA spontaneously oxidizes (Fig. 2), as revealed from FT-IR spectra by monitoring the P=O stretching band at *ca.* 1160 cm⁻¹. Fig. 3 shows that after 6 hours the diagnostic P=O signal is clearly visible. The band intensity increases with time. Moreover, after one week, the formation of dark green cube shaped crystals of {PTAO(a)Cu₃} was observed and, after three weeks, a quantitative crop of single crystals was obtained from the CHCl3-CH3CN solution.



Fig. 2 Oxidation of $\{PTA@[Cu(o-L)]_3\}$ to $\{PTAO@[Cu(o-L)]_3\}$ in a CHCl₃-CH₃CN solution. Colour code: Cu purple, P orange, N blue, O red, C grey, H atoms are omitted for clarity.



Fig. 3 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in a CHCl₃-CH₃CN solution. The increase in the P=O band intensity with time.



Fig. 4 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in a CHCl₃-EtOH solution. The increase in the P=O band intensity with time.

Results obtained from FT-IR analysis showed a similar trend for {PTA@[Cu(o-L)]₃} dissolved in a chloroform–ethanol solution (Fig. 4). However, in this case a crystalline blue precipitate was obtained. Single crystal diffraction (SCD) and powder X-ray diffraction (PXRD) analyses revealed that this compound is a coordination polymer with a structure composed of two alternating subunits: a {Cu₂} dimer and a {Cu₈} ring (Fig. 5). The structure of the first subunit corresponds to the [Cu(o-L)]₂ dimer as it has been obtained from the CDL solution by constitutional crystallization^{4b} (see the ESI[†] for comparison). The main difference is that in the {Cu₂} subunit the Cu²⁺ ion is coordinated, in an apical position, by a nitrogen atom of a PTAO molecule.



Fig. 5 (a) Capped stick view of the crystal structure of $\{PTAO\}_{2} \otimes [Cu_{8}][Cu_{2}]\}_{\infty}$: a polymeric chain of alternating $\{Cu_{2}\}$ and $\{Cu_{8}\}$ units; (b) and (c) side and top views of the *double arrow* $\{Cu_{8}\}$ ring. Colour code: Cu purple, P orange, N blue, O red, C grey, H atoms are omitted for clarity.



Fig. 6 Structural correlation among the two CDL constituents and the $\{Cu_8\}$ ring. PTAO guests in the $\{Cu_8\}$ ring have been omitted for clarity.

Regarding the shape of the $\{Cu_8\}$ subunit, it can be described as a ring folded in a *double arrow* structure. This conformation is held up by the presence of two PTAO molecules hosted in two triangular cavities. The pockets are reminiscent of the [Cu(o-L)]₃ metallo-supramolecular triangular cavity. In fact, the $\{Cu_8\}$ ring can be described to be composed of "open triangles" (Fig. 6, blue part) connected by "open dimers" (Fig. 6, red part). SCD analysis indicates the existence of strong structural correlations between the $\{Cu_8\}$ ring and the CDL constituents. It can be hypothesized that {Cu₈} analogues are involved as transitory intermediates in the CDL self-assembly and in the equilibrium of the two constituents $(3[Cu(o-L)]_2 \rightleftharpoons 2[Cu(o-L)]_3)$. At variance with the $\{PTAO(a)[Cu(o-L)]_3\}$ species, in the coordination polymer PTAO interacts with the $\{Cu_8\}$ ring also through the P=O moiety. CCDC database research did not reveal any other example of P=O···Cu interaction involving the PTAO ligand (P=O···Cu 2.362(2) Å). In {(PTAO)₂@[Cu₈][Cu₂]}_{∞} there are two μ_4 -PTAO molecules with two nitrogen atoms coordinated to two Cu atoms of the $\{Cu_8\}$ ring, while the third nitrogen atom connects the alternating {Cu₂} and {Cu₈} subunits (see the ESI[†] for structural details). It is interesting to note that $\{(PTAO)_2 @ [Cu_8] [Cu_2]\}_{\infty}$ is obtained only as a consequence of PTA oxidation from chloroformethanol solutions of {PTA@[Cu(o-L)]3}. In fact, crystallization of the {PTAO@[Cu(o-L)]₃}⁹ species from the same solvents led to single crystals of the host-guest {PTAO@[Cu(o-L)]₃} supramolecular triangle with no evidence of the structural conversion to the $\{(PTAO)_2(a)[Cu_8][Cu_2]\}_{\infty}$ coordination polymer.

We found that the PTA oxidation rate can be significantly speeded up by bubbling air in $CHCl_3$ -co-solvent solutions (co-solvents = methanol, ethanol, acetonitrile, ethyl acetate, tetrahydrofuran, 1,4-dioxane, acetone, *n*-hexane, cyclo-hexane and *n*-heptane). In particular, THF, MeOH and EtOAc co-solvents gave the best oxidation results. FT-IR evidenced a significant increment of the P=O stretching band after few hours (ESI†). In contrast, chloroform–alkane solutions did not evidence any PTA oxidation. In particular, CHCl₃–*n*-hexane solutions yielded {PTA@[Cu(*o*-L)]₃}^{4c} single crystals. Finally, we found that {PTA@[Cu(*o*-L)]₃} did not



Fig. 7 UV-Vis spectroscopy. (i) PTA is oxidized by bubbling air in a $PTA@[Cu(o-L)]_3$ CHCl₃-CH₃CN solution. (ii) PTAO is recovered after guest exchange with HMT.

undergo oxidation when the CHCl₃-co-solvent solutions were stored under argon.

Air bubbling experiments were also used to quantitatively oxidize and then recover the PTAO molecule. In this case, the reaction was followed by UV-Vis spectroscopy. After bubbling air overnight in a {PTA@[Cu(*o*-L)]₃} CHCl₃–CH₃CN solution, the {PTA@[Cu(*o*-L)]₃} spectrum (red line, Fig. 7) changes to the characteristic {PTAO@[Cu(*o*-L)]₃} one (green line, Fig. 7).¹⁰ Subsequently, PTAO can be quantitatively recovered after guest-exchange with hexamethylenetetramine (HMT) to form the more stable {HMT@[Cu(*o*-L)]₃} species (log $K_{HG}^{HMT} = 6.28 (\pm 3)$ at 298 K).^{4c} The same experiment was repeated with a CHCl₃–THF solution, in this case a quantitative oxidation was achieved after six hours (ESI†) of air bubbling.

In conclusion, we have reported that a metallo-supramolecular host can be used as a suitable environment for PTA oxidation under mild conditions. The oxidation is triggered by several co-solvents, while it does not occur in pure chloroform or chloroform-alkane solutions. We found that the co-solvents strongly affect the final metallo-supramolecular crystalline product. In one case (CH₃CN), the desired {PTAO(a)[Cu(o-L)]₃} host-guest architecture was crystallized. In the other one (EtOH), the metallo-supramolecular motif underwent a deep structural rearrangement to a coordination polymer characterized by the presence of a {Cu₈} ring with two strained triangular pockets where two PTAO molecules are hosted. The experimental results clearly suggest that molecular oxygen is the oxidizing species, but the co-solvent trigger effect is still under investigation. Collected data evidence that apolar solvents, such as alkanes, do not promote PTA oxidation. On the other hand, a clear scale among the active co-solvents cannot be found when we consider their polarity¹¹ and their trigger ability in PTA oxidation. Another aspect to be taken into account is O2 solubility12 in the CHCl3-co-solvent system, but in this case also there is no correlation between the gas solubility and PTA oxidation. As a matter of fact, O₂ is much more soluble in apolar solvents than polar ones. For these reasons, further studies will be devoted to clarify the role of other possible actors in PTA oxidation including the metal centre as the possible catalytic active site, the supramolecular host as the reaction environment and their interplay with the chloroform–co-solvent system.

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