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Journal:	*ChemComm*
Manuscript ID:	CC-COM-07-2014-005422.R1
Article Type:	Communication
Date Submitted by the Author:	15-Sep-2014
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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

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

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

PTA hosted in a copper metallo-supramolecular triangle undergoes *post-assembly* oxidation to PTAO in aerated solutions. The oxidation is triggered by selected co-solvents that also rule 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] to perform space confined reactivity[2b] or "enzyme-like" catalysis.[2c] Moreover, they can be employed as nano-sized reactors by performing in their cavities the synthesis of metal oxide nanoparticles with a remarkable control of the nanoparticles 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 the *post-assembled* host-guest ensemble where PTA plays the role of 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*–LH$_2$) leads to 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@[Cu(*o*–L)]$_3$} host-guest architectures,[4a,4c] 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), log K_{HG}^{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 examples[5] of a μ_3-PTA molecule with three coordinating nitrogen atoms and the P atom not bonded to a metal centre. Therefore, the phosphorus atom is a free and avaible 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 neutral P-donor ligand.[6] It is usually oxidized with strong oxidation agents such as 30% H_2O_2,[7a] nitrogen tetraoxide[7b] or with diluted H_2O_2 solutions in the presence of a rhenium based catalyst.[7c] Examples are also reported where PTA is partially oxidized in the presence of metal ions that are reduced (Ni(II),[8a] Co(II)[8b,8c] and Cu(II)[8d]). Herein, we report that the oxidation can be successfully carried out under soft conditions through the use of aerated solution at room temperature, starting from the {PTA@[Cu(*o*–L)]$_3$} species. The reaction is triggered by selected co-solvents. Several co-solvents have been 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 $CHCl_3$/n-hexane solution, the target oxidized species {PTAO@[Cu(*o*–L)]$_3$} from a $CHCl_3$/CH_3CN solution or to an unpredictable oxidized species, a 1D coordination polymer {(PTAO)$_2$(H_2O)[Cu(*o*–L)]$_8$][Cu(*o*–L)]$_2$}$_\infty$ (hereafter, {[(PTAO)$_2$@[Cu$_8$][Cu$_2$]}$_\infty$) from a $CHCl_3$/EtOH solution. The PTA host-guest species,

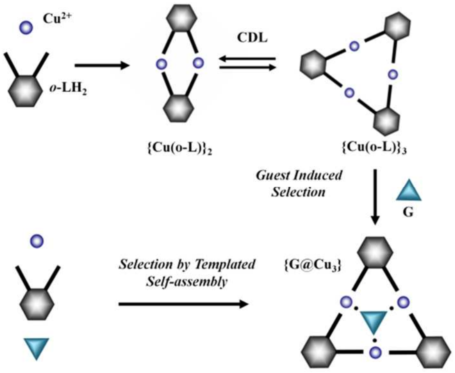

Fig. 1 Representation of the two possible *molecular recognition* selection processes to the {G@[Cu(*o*–L)]$_3$} host-guest architecture developped in our previous studies.[4]

{PTA@[Cu(*o*–L)]$_3$}, is very stable in air at 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 through FT-IR 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. At increasing times the band intensity increases. Moreover, after one week, the formation of dark green cubic shaped crystals of {PTAO@Cu$_3$} was observed and, after three weeks, a quantitative crop of single crystals was obtained from the CHCl$_3$/CH$_3$CN solution.

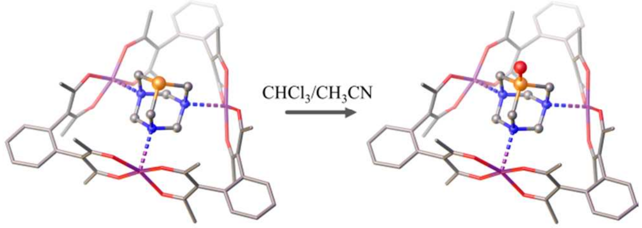

Fig. 2 Oxidation of {PTA@[Cu(*o*–L)]$_3$} to {PTAO@[Cu(*o*–L)]$_3$} in a CHCl$_3$/CH$_3$CN solution. Colour code: Cu purple, P orange, N blue, O red, C grey, H atoms are omitted for clarity.

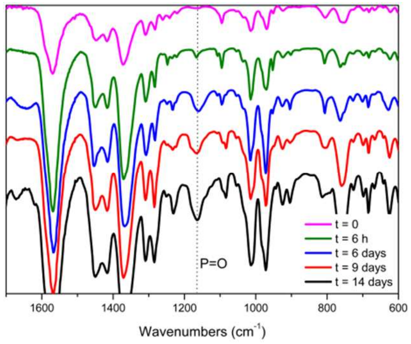

Fig. 3 Normalized FT-IR spectra of {PTA@[Cu(*o*–L)]$_3$} in a CHCl$_3$/CH$_3$CN solution. The P=O band intensity increments at increasing time.

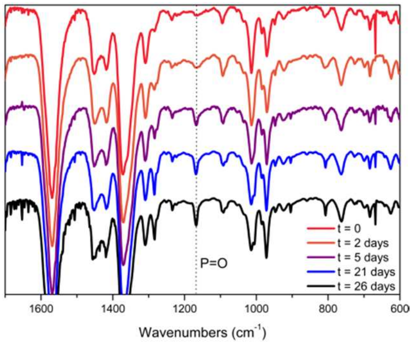

Fig. 4 Normalized FT-IR spectra of {PTA@[Cu(*o*–L)]$_3$} in a CHCl$_3$/EtOH solution. The P=O band intensity increments at increasing time.

FT-IR analysis showed a similar trend also for {PTA@[Cu(*o*–L)]$_3$} dissolved in a chloroform/ethanol solution (Fig. 4). However, in this case a cristalline blue precipitate was obtained. Single crystal and powder X-ray diffraction analyses (SCD, PXRD) revealed that this compound is a coordination polymer with a structure composed by two alternating subunits: a {Cu$_2$} dimer and a {Cu$_8$} 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 ESI for comparison). The main difference is that in the {Cu$_2$} subunit the Cu^{2+} ion is coordinated, in apical position, by a nitrogen atom of a PTAO molecule.

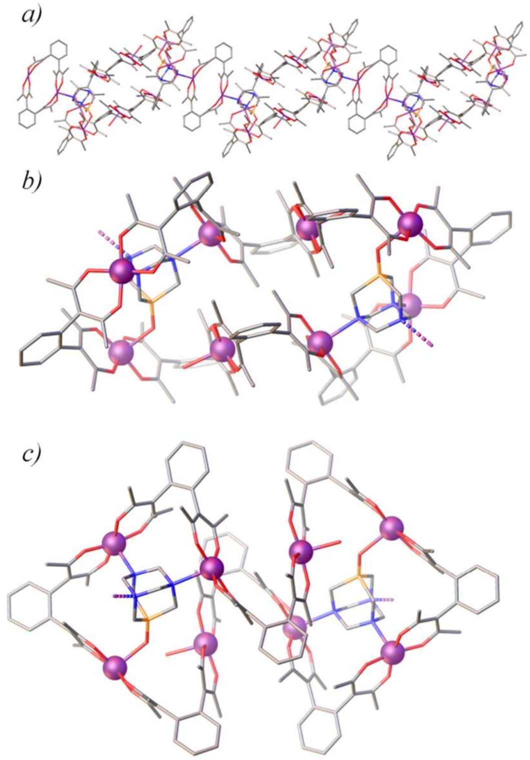

Fig. 5 *a)* Capped sticks view for the crystal structure of {[(PTAO)$_2$@[Cu$_8$]{Cu$_2$}}$_\infty$: polymeric chain of alternating {Cu$_2$} and {Cu$_8$} units; *b*) and *c*) side and top views of the *double arrow* {Cu$_8$} ring. Colour code: Cu purple, P orange, N blue, O red, C grey, H atoms are omitted for clarity.

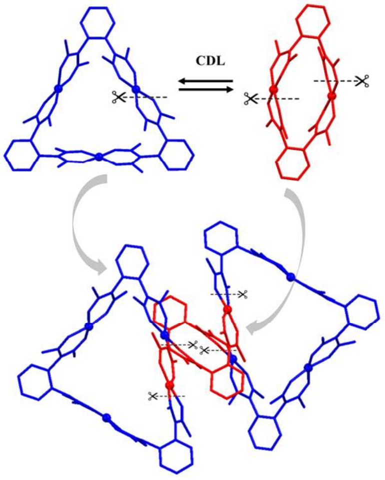

Fig. 6 Structural correlation among the two CDL constituents and the {Cu$_8$} ring. PTAO guests in the {Cu$_8$} ring have been omitted for clarity.

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-like cavities. The pockets are reminiscent of the [Cu(*o*–L)]$_3$ metallo-supramolecular triangle cavity. In fact, the {Cu$_8$} ring can be described as composed by "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 {Cu$_8$} analogues are involved as transitory intermediates in the CDL self-assembly and in the equilibrium of the two constituents (3[Cu(*o*–L)]$_2$ ⇌ 2[Cu(*o*–L)]$_3$). At variance of the {PTAO@[Cu(*o*–L)]$_3$} species, in the coordination polymer PTAO interacts with the {Cu$_8$} ring also through the P=O moiety. A CCDC database research did not revealed any other example of P=O···Cu interaction involving the PTAO ligand (P=O···Cu 2.362(2) Å). In {[(PTAO)$_2$@[Cu$_8$][Cu$_2$]}$_\infty$ 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 {Cu$_2$} and {Cu$_8$} subunits (see ESI for structural details). It is interesting to note as {(PTAO)$_2$@[Cu$_8$][Cu$_2$]}$_\infty$ is obtained only in consequence of PTA oxidation from chloroform/ethanol solutions of {PTA@[Cu(*o*–L)]$_3$}. In fact, crystallization experiments 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)$_2$@[Cu$_8$][Cu$_2$]}$_\infty$ coordination polymer.

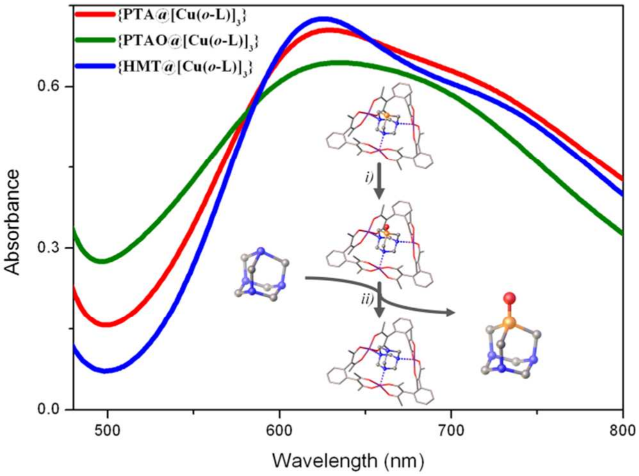

Fig. 7 UV-Vis spectroscopy. *i*) PTA is oxidized by bubbling air in a {PTA@[Cu(*o*–L)]$_3$} CHCl$_3$/CH$_3$CN solution. *ii*) PTAO is recovered after guest exchange with HMT.

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). On the contrary, chloroform/alkanes solutions did not evidence any PTA oxidation. In particular, CHCl$_3$/n-hexane solutions yield {PTA@[Cu(*o*–L)]$_3$}[4c] single crystals. Finally, we found that {PTA@[Cu(*o*–L)]$_3$} does not undergo oxidation when the CHCl$_3$/co-solvent solutions are stored under argon.

Air bubbling experiments have been also used to quantitatively oxidize and then recover the PTAO molecule. In this case, the reaction has been followed also *via* UV-Vis spectroscopy. After bubbling air overnight in a {PTA@[Cu(*o*–L)]$_3$} CHCl$_3$/CH$_3$CN 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 hexamethylentetramine (HMT) to form the more stable {HMT@[Cu(*o*–L)]$_3$} (log K_{HG}^{HMT} = 6.28 (± 3) at 298 K).[4c] The same experiment has been repeated with a CHCl$_3$/THF solution, in this case a quantitative oxidation has been 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 soft conditions. The oxidation is triggered by the employed co-solvents—while is not operating in pure chloroform or cloroform/alkane solutions. We have found that the co-solvent strongly affects the final metallo-supramolecular product. In one case (CH$_3$CN), the desired {PTAO@[Cu(*o*–L)]$_3$} host-guest architecture is obtained. In the other one (EtOH), the metallo-supramolecular motif undergoes a deep structural rearrangement towards a coordination polymer characterized by the presence of a {Cu$_8$} 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 polarity[11] and their trigger ability in the PTA oxidation. Another aspect to take into account is O$_2$ solubility[12] in the CHCl$_3$/co-solvent system, but also in this case there is not a correlation between the gas solubility and PTA oxidation. As a matter of fact, O$_2$ 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 the 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.

This work was supported by Italian MIUR through FIRB RBAP114AMK "RINAME". J. T. thanks the CaRiPaRo Foundation for a Ph.D. scholarship. M.R. thanks the University of Padova for a "Senior Research" fellowship and for a "Young Scholar" grant.

Notes and references

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† Electronic Supplementary Information (ESI) available: experimental, supplementary FT-IR, PXRD pattern and SCD data CCDC: 1013528. See DOI: 10.1039/b000000x/

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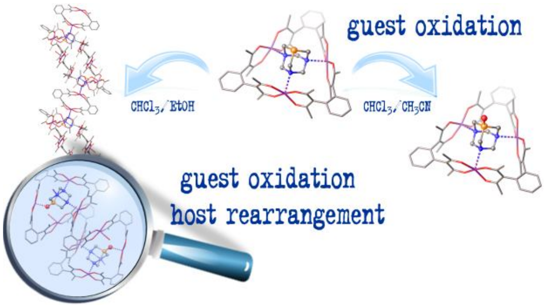

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