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

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Electronic Supplementary Information

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FT-IR Spectroscopy

FT-IR analysis was performed with a Nexus 870 FTIR (Nicolet), operating in the transmission range 500–4000 cm⁻¹, collecting 32 scans with a spectral resolution of 4 cm⁻¹. The samples were prepared by drop casting the solution on a NaCl round cell window.

Absorption spectroscopy

Absorption spectra were recorded on a CARY5E double-beam spectrophotometer with a spectral bandwidth of 2 nm. The contribution due to the solvent was subtracted.

Synthesis

Reagents were purchased from Aldrich and used as received. The ligand 1,2-bis-(3-acetylacetone)benzene (o-LH₂),^[1] PTA^[2] and PTAO^[2] have been prepared as reported in the literature. Single crystals of {PTA@[Cu(o-L)]₃} have been obtained from a chloroform-*n*-hexane solution by slow evaporation.^[3] The {G@[Cu(o-L)]₃} host-guest species have been prepared according to our previous procedures.^[3]

{PTA@[Cu(o-L)]3} oxidation to {PTAO@[Cu(o-L)]3}

A 10^{-3} M chloroform-acetonitrile (1:1) green solution of {PTA@[Cu(o-L)]₃} has been left in a closed vial. After one week, dark green cubic shaped crystals have been obtained. After three weeks, a quantitative crop of single crystals has been obtained. X-ray single crystal analysis on several crystals revealed that the unit cell corresponds to {PTAO@[Cu(o-L)]₃}^[3] (CCDC 971598). Elemental analysis: C 58.73 %, N 2.48%, H 5.33% (exp.); C 58.80%, N 2.54 %, H 5.48% (calc.). The same experiment repeated in a Schlenk tube under an argon atmosphere did not evidence PTA oxidation.

${PTA@[Cu(o-L)]_3}$ oxidation to ${[(PTAO)_2@[Cu_3]]_{\infty}}$

A 10^{-3} M chloroform-ethanol (1:1) green solution of {PTA@[Cu(o-L)]₃} has been left in a closed vial. After two weeks the solution turned gradually from green to blue. After three weeks, a crystalline blue precipitate with has been obtained. X-ray single crystal analysis revealed that this material is a

coordination polymer. Elemental analysis: C 54.15 %, N 2.36%, H 5.20% (exp.); C 55.23%, N 2.25 %, H 5.07% (calc.). The same experiment repeated in a Schlenk tube under an argon atmosphere did not evidence PTA oxidation. Moreover, the solution colour remained green and did not change toward blue.

Oxidation by air bubbling

 ${PTA@[Cu(o-L)]_3}$ (30 mg, 0.026 mmol) has been dissolved in a 1:1 chloroform-co-solvent (total volume 6 ml) solution. Co-solvents: methanol, ethanol, acetonitrile, ethyl acetate, tetrahydrofuran, 1,4-dioxane, acetone, *n*-hexane, cyclo-hexane and *n*-heptane. The solution has been air bubbled under continuous stirring and FT-IR spectra have been periodically collected.



Fig. S1 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in an air bubbled chloroform-acetonitrile solution. The increase in the P=O band intensity with time.



Fig. S2 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in an air bubbled chloroform-ethanol solution. The increase in the P=O band intensity with time.



Fig. S3 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in an air bubbled chloroform-1,4-dioxane solution. The increase in the P=O band intensity with time.



Fig. S4 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in an air bubbled chloroform-acetone solution. The increase in the P=O band intensity with time.



Fig. S5 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in an air bubbled chloroform-ethyl acetate solution. The increase in the P=O band intensity with time.



Fig. S6 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in an air bubbled chloroform-tetrahydrofuran solution. The increase in the P=O band intensity with time.



Fig. S7 Normalized FT-IR spectra of $\{PTA@[Cu(o-L)]_3\}$ in an air bubbled chloroform-methanol solution. The increase in the P=O band intensity with time.



Fig. S8 Normalized FT-IR spectra of {PTA@[Cu(*o*-L)]₃} in an air bubbled chloroform-cyclo-hexane solution.



Fig. S9 Normalized FT-IR spectra of {PTA@[Cu(o-L)]₃} in an air bubbled chloroform-*n*-hexane solution.



Fig. S10 Normalized FT-IR spectra of {PTA@[Cu(o-L)]₃} in an air bubbled chloroform-*n*-heptane solution.

Oxidation by air bubbling and guest exchange

a) {PTA@[Cu(o-L)]₃} (30 mg, 0.026 mmol) has been dissolved in 3 ml of chloroform and the UV-Vis spectrum of the solution has been collected (red line, Fig 7). Acetonitrile (3 ml) has been added and the solution has been air bubbled overnight under continuous stirring. FT-IR confirmed the PTA oxidation, the solvent has been evaporated and the green powder has been dissolved in 3 ml of chloroform (UV-Vis spectrum: green line, Fig. 7). HMT (3.6 mg, 0.026 mmol) has been added and the solution colour changed from green to turquoise indicating the formation of {HMT@[Cu(o-L)]₃} (UV-Vis spectrum: blue line, Fig. 7). The solvent has been removed and the solid dissolved in toluene (5 ml) at 50° C. A turquoise solution with a white solid has been obtained. After centrifugation, the solution has been removed and the white solid has been washed with three toluene aliquots (3 ml each) and vacuum dried. The white solid has been identified as PTAO through FT-IR and elemental analysis (C 45.78 %, N 26.80 %, H 7.65 % (exp.); C 45.86%, N 26.73 %, H 7.70% (calc.)). PTAO yield 4.5 mg (96 %).

b) Similar results (Fig S.8) have been obtained by bubbling air for 6 hours in a {PTA@[Cu(*o*-L)]₃} CHCl₃-THF solution. PTAO yield 98 %.



Fig. S11 UV-Vis spectroscopy. *i*) PTA is oxidized by bubbling air in a $\{PTA@[Cu(o-L)]_3\}$ CHCl₃-THF solution for 6 h. *ii*) PTAO is recovered after guest exchange with HMT.

Single crystal X-ray diffraction (SCD)

A single crystal of {[(PTAO)₂@[Cu₈][Cu₂]}_{∞} covered with Paratone-N oil was fastened on the top of a Lindemann glass capillary and centred on the head of a four–circle kappa goniometer Oxford Diffraction Gemini E diffractometer, equipped with a 2K × 2K EOS CCD area detector and sealed– tube Enhance (Mo) and (Cu) X–ray sources. Mo K α (λ = 0.71070 Å) radiation has been used for all the data collections. Data were collected at room temperature by means of the ω - scans technique using graphite–monochromated radiation, in a 1024 × 1024 pixel mode, using 2 × 2 pixel binning. The diffraction intensities were corrected for Lorentz and polarization effects and were also optimized with respect to absorption. Empirical multi–scan absorption corrections using equivalent reflections were performed with the scaling algorithm SCALE3 ABSPACK. Data collection, data reduction and finalization were carried out through the CrysAlisPro software.

Comments on {[(PTAO)₂@[Cu₈][Cu₂]}_∞ solution and refinement.

Despite several efforts to improve the crystals quality, the only useful specimens were not significantly diffracting at d < 0.85 Å. The data collection has been set to obtain a 100 % completeness

at d = 0.90 Å. Structures were solved by means of charge flipping method with OLEX2^[4] and refined by full–matrix least–squares methods based on F_o² with SHELXL^[5] in the framework of OLEX2 software. During the refinement, a phenyl ring and a methyl group have been splitted in two parts the occupancies of which were constrained to sum to 1.0 (SADI and FLAT restrains have been applied). Ordered non-hydrogen atoms were refined anisotropically whereas disordered non-hydrogen atoms with partial occupancy were refined isotropically. Hydrogen atoms connected to carbon atoms were included in idealised positions and a riding model was used for their refinement. DFIX and DANG instructions have been applied to better model the water molecule H atoms. The final difference Fourier map revealed the presence of non-negligible residual peaks. They could likely be assigned to four ethanol molecule but they could not be effectively modelled. The contribution of these peaks was removed using the mask routine of OLEX2. The program calculated a total solvent accessible volume/cell of 2207.6 Å³ (39 %), and a total electron-count/cell of 107 electrons. Such values closely fit four ethanol molecules.

Crystallization solvent	chloroform-ethanol
Chemical formula of the asymmetric unit	$C_{86}H_{94}Cu_5N_3O_{22}P$
Formula Mass of the asymmetric unit	1870.31
Crystal system	triclinic
$a/{ m \AA}$	17.0466(7)
b/Å	18.6805(7)
c/Å	21.1943(5)
$\alpha /^{\circ}$	72.532(3)
$\beta/^{\circ}$	66.428(3)
$\gamma/^{\circ}$	68.592(4)
Unit cell volume/Å ³	5664.3(3)
Temperature/K	295.9(5)
Space group	P-1
No. of formula units per unit cell, Z	2
Radiation type	MoKa ($\lambda = 0.71073$)
Absorption coefficient, μ/mm^{-1}	0.993
No. of reflections measured	37372
No. of independent reflections	18165
R _{int}	0.0368
Final R_I values $(I > 2\sigma(I))$	0.0528
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.1510
Final R_1 values (all data)	0.0703
Final $wR(F^2)$ values (all data)	0.1619
Goodness of fit on F^2	0.994
CCDC number	1013528

Table S1 Crystal data and structure refinement for	$\{[(PTAO)_2@[Cu_8][Cu_2]\}_{\infty}$

 $R_{1} = (\Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|); wR_{2} = \{\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2}; \text{ GOF} = \Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/(n - p)\}^{1/2} \text{ where } n \text{ is the number of data and } p \text{ is the number of parameters refined.}$

	{PTAO@[Cu(o-L)]3}	${[(PTAO)_2@[Cu_8][Cu_2]]_{\infty}}$
Cu-O min. and max. lengths (Å)	1.908(3) – 1.934(3) ^[3]	1.901(3) – 1.924(3)
Cu-N min. and max. lengths (Å)	2.474(3) ^[3]	2.386(3) - 2.499(3)
P=O length (Å)	1.486(5) ^[3]	1.486(3)

Table S2 Lengths comparison for the two compounds hosting PTAO.



Fig. S12 Asymmetric unit in the $\{[(PTAO)_2@[Cu_8][Cu_2]\}_{\infty}$ single crystal. Thermal ellipsoids drawn at the 30% probability level. Disordered parts are drawn as isotropic ball and stick. H atoms are omitted for clarity. H bond: O1…H 2.06 Å, O1…O1W 2.816(4) Å, O1…H…O1w 142°.



Fig. S13 Structure of $\{PTAO@Cu_3\}^{[3]}$ (CCDC 971598) with thermal ellipsoids drawn at the 30% probability level. Symmetry operations: * (1+y-x, 1-x, +z), # (1-y, +x-y, +z). H atoms are omitted for clarity.

	{Cu ₂ } subunit	[Cu(<i>o</i> -L)] ₂
Cu-O min. and max. lengths (Å)	1.906(3) - 1.922(3)	$1.861(10) - 1.883(9)^{[6]}$
Cu…Cu	4.968	4.551 ^[6]

Table S3 Lengths comparison in the $\{Cu_2\}$ subunit and the $[Cu(o-L)]_2$ dimer.



Fig. S14 *a*) {Cu₂} subunit in {[(PTAO)₂@[Cu₈][Cu₂]}_{∞} and *b*) [Cu(*o*-L)]₂ dimer^[6] crystallized from a chloroform/acetone mixture. H atoms are omitted for clarity.

Powder X-ray diffraction (PXRD)

PXRD measurements were carried out by means of a Bruker D8 Advance diffractometer equipped with a Göbel mirror and a Cu-Kα source (40 kV, 40 mA).



Fig. S15 Experimental and simulated $\{[(PTAO)_2@[Cu_3]]_{\infty} PXRD \text{ patterns (normalized intensity)}.$

References

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