Supplementary Material (ESI) for Chemical Communications

Supporting information for *Chemical Communications*

From discrete truncated octahedral nano-cages to 1D coordination polymer： Coordination-driven a single-crystal-to-single-crystal transformation via anion exchange

Ning Li,[ab] Feilong Jiang,[a] Lian Chen,[a] Xingjun Li[ab] Qihui Chen,[a] and Maochun Hong*[a]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese*

[b] *Academy of Sciences, Graduate School of the Chinese Academy of Sciences, Fujian, Fuzhou, 350002, China.*

E-mail: hmc@fjirsm.ac.cn

Contents

I. Physical measurements

Materials. $POCl_3$ pre-dried before use. Other reagents and solvents for syntheses were purchased from commercial sources and used no further purification. Elemental analyses were carried out by the Elemental Analysis Lab of our Institute. The FT-IR spectra were recorded as KBr pellets on a PerkinElmer Spectrum One FT-IR spectrometer. ^1H NMR spectra were measured on a Varian INOVA 400M spectrometer. ESI-MS spectra were recorded on Finnigan DECAX-30000 LCQ Deca XP ion trap mass spectrometer.

II. Syntheses

WARNING! Although we experienced no problems in handling the perchlorate compounds, they should be treated with great caution due to their potential for explosion.

Synthesis of *N*,*N*`,*N*``-tris(3-pyridinyl)phosphoric triamide, $(NC_5H_4NH)_3PO$. (tppa)

A 100ml three-necked flask was fitted with a mechanical stirrer and a reflux condenser. The 3-aminopyridine (3.1g, 0.033 mol) was placed in the three-necked flask, and pyridine (20 mL) was added in one portion. Then $POCl_3$ (1ml, 0.01mol) was dropwisely added. After addition of the $POCl_3$, the mixture began to boil. The reaction mixture was heated to 110℃ for 12 hr in a oil bath. The reaction mixture was cool to room temperature, and 50 ml water was added to three-necked flask. After filtration, 5 M NaOH solution was add to the filtrate, forming voluminous white precipitate. The precipitate was filtered out and washed with a small portion of water. The yield obtained was 2.8g or 78% theoretical yield. Melting point: 273-274℃. The crystals of the product were obtained from a mixture of ethanol and water (8:2) after slow evaporation at room temperature. Elemental analysis: found - C, 55.19 %; H, 4.63 %; N, 25.74 %; calc. for $C_{15}H_{15}N_6OP$ - C, 55.21 %; H, 4.63 %;N, 25.72 %. IR (KBr cm^{-1}) 3435(s), 1730(m), 1583(s), 1500(s), 1477(m), 1399(m), 1276(m)，

1264(m)，963(s), 803(m), 703(m), 630(m), 519(w). MS: *m*/*z* =326[TPPA+H^+].

Synthesis of $[Cu_6(TPPA)_8(H_2O)_6](ClO_4)_{12}(H_2O)_{24}$ (1)

A mixture of TPPA (1mmol 0.326g), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.6mmol 0.221g), H_2O (10 mL), and alcohol (2 mL) produced a clear, dark blue solution. The reaction solution was stirred at room temperature about 3h and then sealed in a 30-mL teflon-lined bomb at 80°C for seven days which was slowly cooled to room temperature. Dark blue block crystals of **1** suitable for X-ray analysis were obtained. (Yield: 83% based on Cu). IR (KBr cm^{-1}) 3408(s), 1730(m), 1637(s), 1614(s), 1455(m), 1337(m), 812(w), 750(m), 691(m), 617(m), 524(w). The above crystals of **1** were washed by 10ml ($EtOH/H_2O$ = 1:1(V:V)) and dried at 30ºC in vacuum for 48 hours until the weight was unchangeable (366mg). This pretreated sample was used for the elemental analyses. Found (%): C 38.67, H 4.58, N 0.00, S 12.52. These values are in good accordance with the complex $Cu_6(tppa)_8(ClO_4)_{12}(H_2O)_6$ in which the free water molecules in **1** have been removed in vacuum and only the coordination water molecules exist in the compound. Elemental analysis calcd (%) for $[Cu_6(TPPA)_8(H_2O)_6](ClO_4)_{12}$, $C_{120}H_{120}Cl_{12}Cu_6N_{48}O_{62}P_8$: calcd (%):C, 33.67; H, 2.83; N, 15.70; found: C, 32.33; H, 2.97; N, 15.61; The volatility of crystallization solvents in the samples contributes to the discrepancy in elemental analytical data.

Synthesis of $[Cu_6(TPPA)_8(\mu\text{-}Cl)Cl_{11}]_n \cdot 6nCl \bullet 22nH_2O$ (2)

When single crystals of **1** were immerged in NaCl aqueous solution (0.1mol/L) at room temperature for two days, the Cl^- ions were exchanged successfully in these single crystals resulting crystals **2** without noticeable loss of their crystallinity or diffracting power. IR (KBr cm^{-1}) 3423(s), 1585(s), 1396(s), 1336(m), 1274(m), 1215(w), 1194(s), 1112(m), 1066(m), 962(s), 807(m), 697(w), 624(w), 496(w). Take 100mg sample dried at 30ºC in vacuum for 48 hours until the weight was unchangeable. Elemental analysis calcd (%) for $[Cu_6Cl_5(tppa)_8(\mu\text{-}Cl)]n \cdot 6nCl$, $C_{120}H_{120}Cl12Cu_6N_{48}O_8P_8$: calcd (%) : C, 42.18; H, 3.54; N, 19.68; found: C 42.13, H

3.62; N, 19.53. The volatility of crystallization solvents in the samples contributes to the discrepancy in elemental analytical data.

III. Details of crystal data collection

Crystallographic data collection and structural refinement for compounds 1-2.

The diffraction data were measured with Mo Kα radiation (λ = 0.71073 Å) on a Rigaku AFC10 Saturn-70 CCD diffractometer at 293(2) K. The SMART and SAINT program packages [1] were used for data collection and integration, respectively. Collected data were corrected for absorbance using SADABS [2] based upon Laue symmetry using equivalent reflections. All structures were solved by direct methods and refined on F^2 by full-matrix least squares calculations with the using the SHELX-97 program package. [3] All of the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. Hydrogen of organic ligands were placed in the calculated positions, hydrogen atoms bound water molecules were found in the difference map, and the hydrogen atoms on the disordered water molecules were not treated during the structural refinements. Crystallographic data and structure refinement for compound **1 – 2** and **tppa** are summarized in the Table S1.

References

[1]. SMART and SAINT, Area Detector Software Package and SAX Area Detector Integration Program; Bruker Analytical X-Ray; Madison, WI, USA, 1997.

[2]. SADABS, Area Detector Absorption Correction Program; Bruker Analytical X-Ray; Madison, WI, USA, 1997.

[3]. Sheldrick, G. M. SHELXTL. Version 5.1; Bruker Analytical X-ray Systems Inc.: Madison, WI, USA, 1997.

Table S1. Crystal data and structure refinement parameters for compound **1 - 2.**

	1	**2**	**tppa**
CCDC deposit no.	CCDC- 764790	CCDC- 764791	CCDC- 765355
formula	$C_{60}H_{108}Cl_6Cu_3N_{24}O_{55}P_4$	$C_{60}H_{104}Cl_6Cu_3N_{24}O_{26}P_4$	$C_{15}H_{17}N_6O_2P$
fw	2572.90	2104.87	344.32
crystal system	Monoclinic	Monoclinic	Orthorhombic
space group	*C2/c*	*C2/c*	*P2(1)2(1)2(1)*
a, Å	33.419(6)	35.332(7)	8.689 (2)
b, Å	22.7212(5)	18.535(3)	12.097 (3)
c, Å	32.410(2)	35.992(7)	16.266 (4)
α, deg	90	90	90
β, deg	107.7120(10)	115.187(3)	90
γ, deg	90	90	90
V, Å^3	23443(4)	21330(7)	1709.7 (7)
Z	8	8	4
*D*c, g/cm^{-3}	1.423	1.224	1.338
μ, mm^{-1}	0.841	0.866	0.181
F(000)	14442	7976	720
crystal size, mm^3	0.45 × 0.40 × 0.35	0.43 × 0.40 × 0.34	0.76 × 0.50 × 0.16
θ range, deg	3.03 to 27.48	2.50 to 25.00	2.10 to 27.47
No. Of collected/unique reflns	90382 / 26786	65323 / 18630	3878 / 3681
GOOF	1.033	1.158	1.092
Final *R* indices ($I > 2\sigma(I)$)	0.0877	0.1209	0.0508
R indices (all data)	0.1195	0.1496	0.0531

IV. Figures

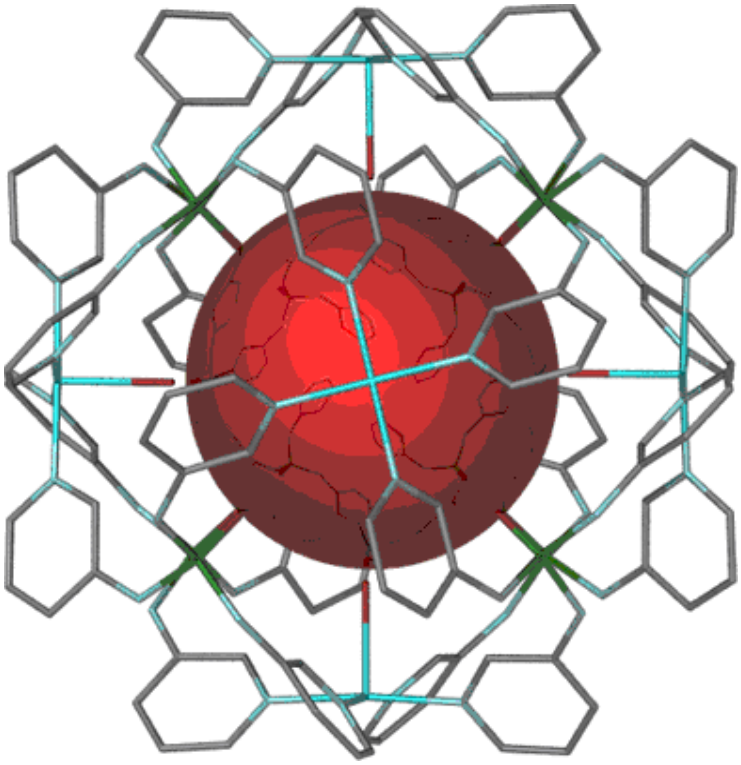

Figure S1. An **ORTEP** representation of compound **1** with 30% probability thermal ellipsoids (All the hydrogen atoms and solvent water molecules are omitted for clarity).

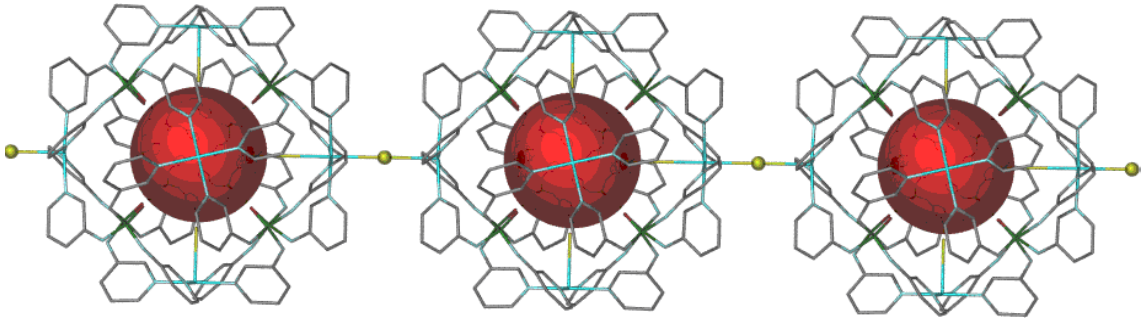

Figure S2. An **ORTEP** representation of compound **2** with 30% probability thermal ellipsoids (All the hydrogen atoms and solvent water molecules are omitted for clarity).

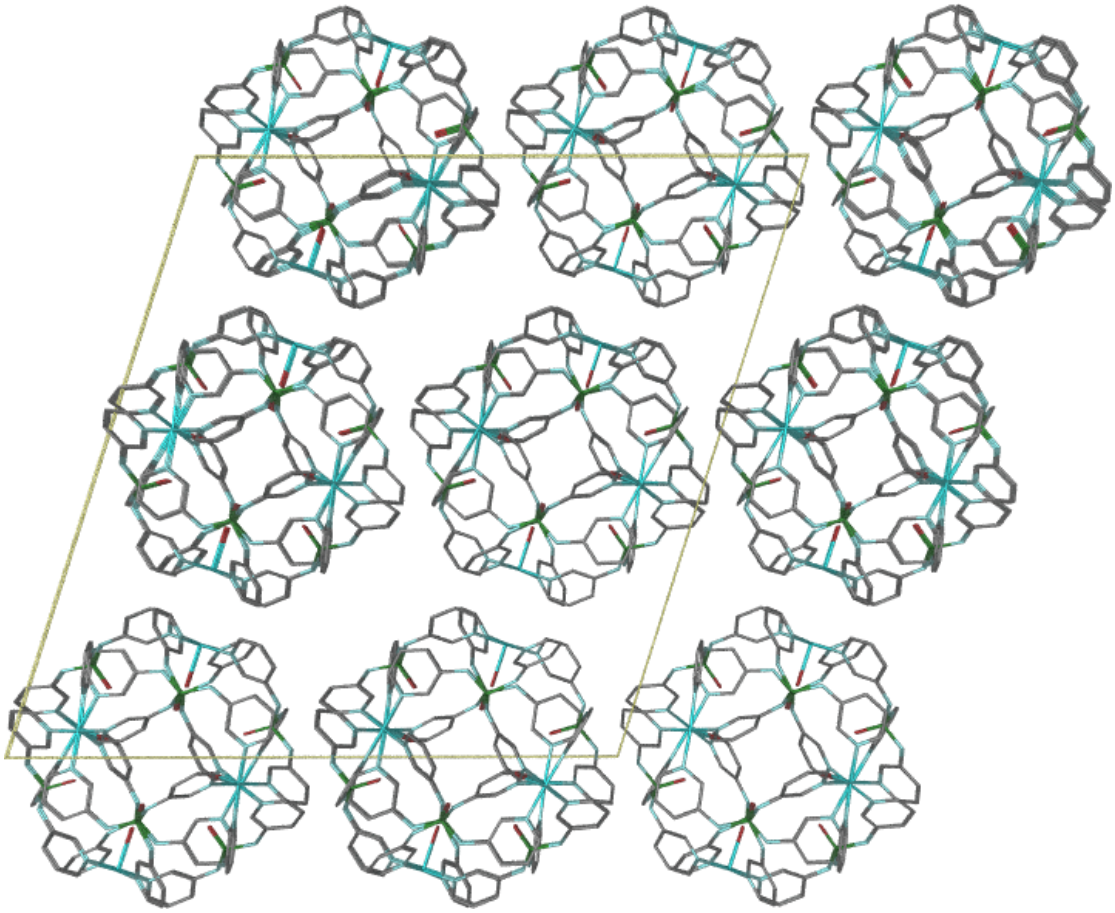

Figure S3. The packing model of compound **1** viewed from b axis.(H_2O molecules and perchloric acid anion are omitted for clarity

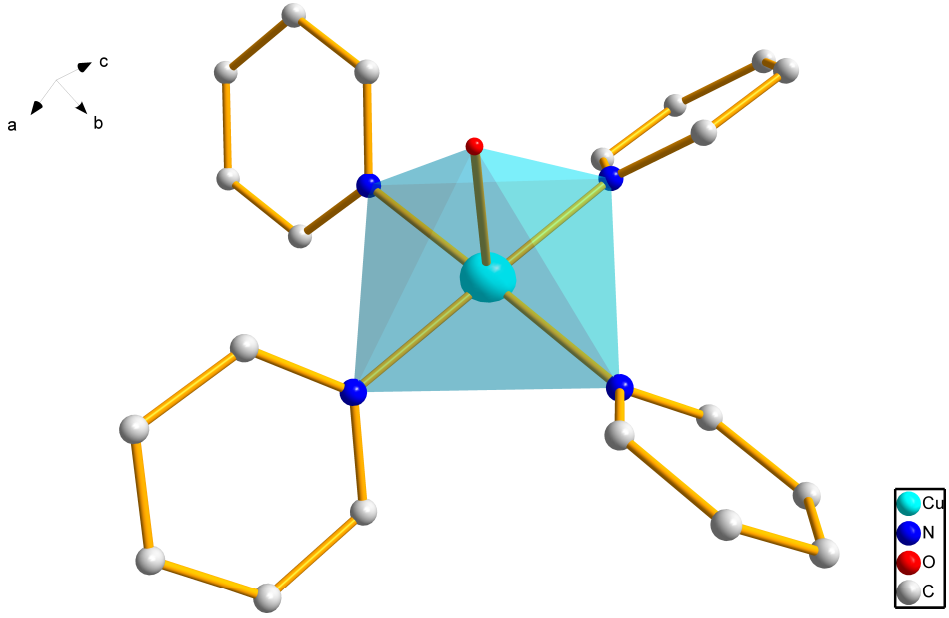

Figure S4. The tetragonal pyramid coordination model in **1**

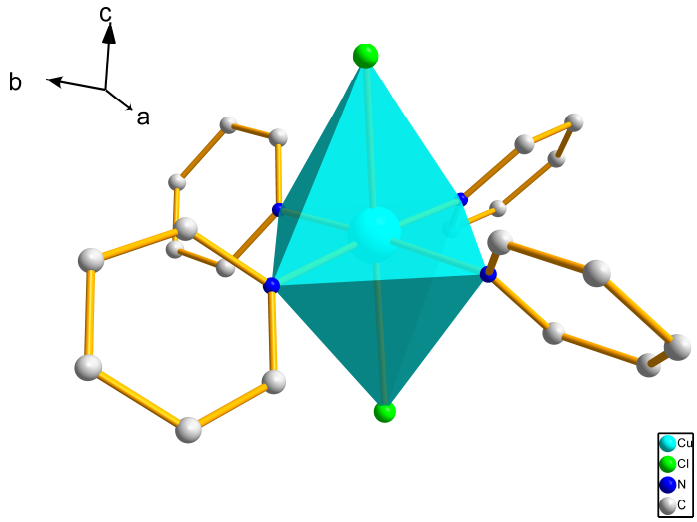

Figure S5a. The octahedron coordination models in **2**

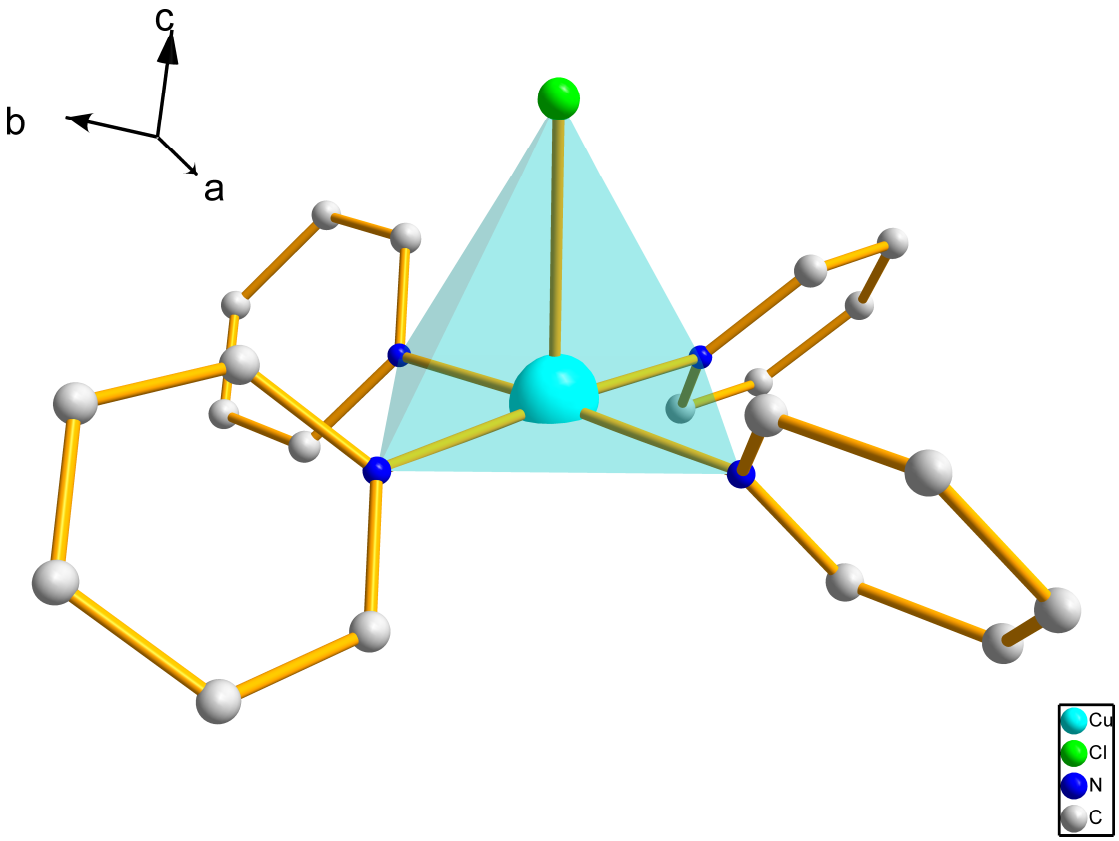

Figure S5b. The tetragonal pyramid coordination models in **2**

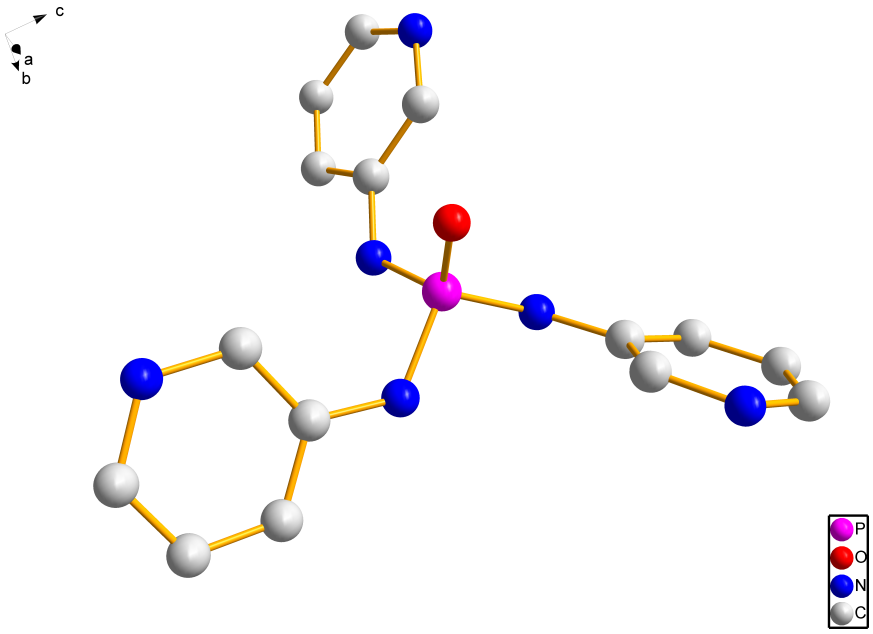

Figure S6. X-ray crystal structure of tppa

V. Characterization

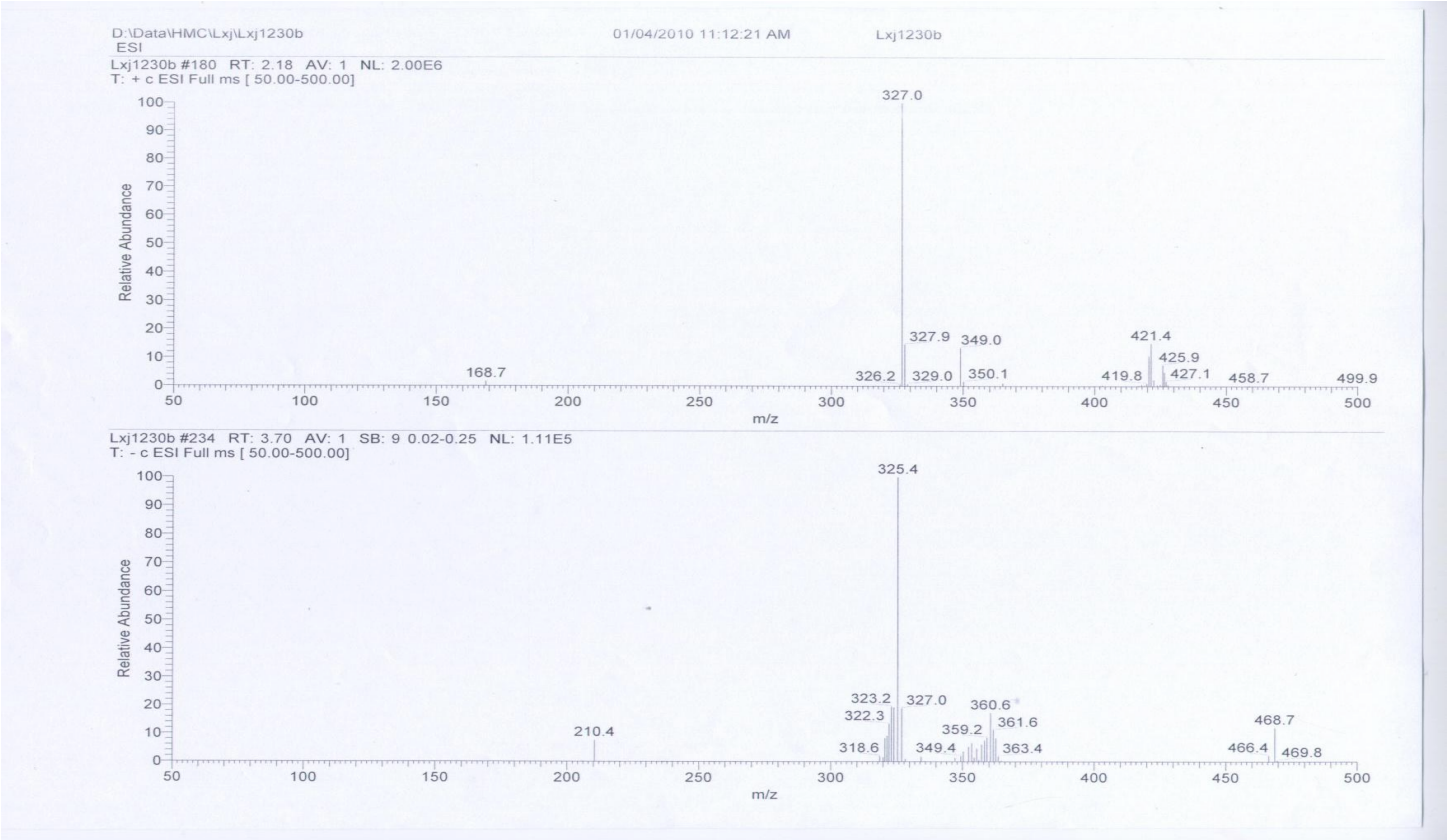

Figure S7. ESI-MS spectrum of tppa

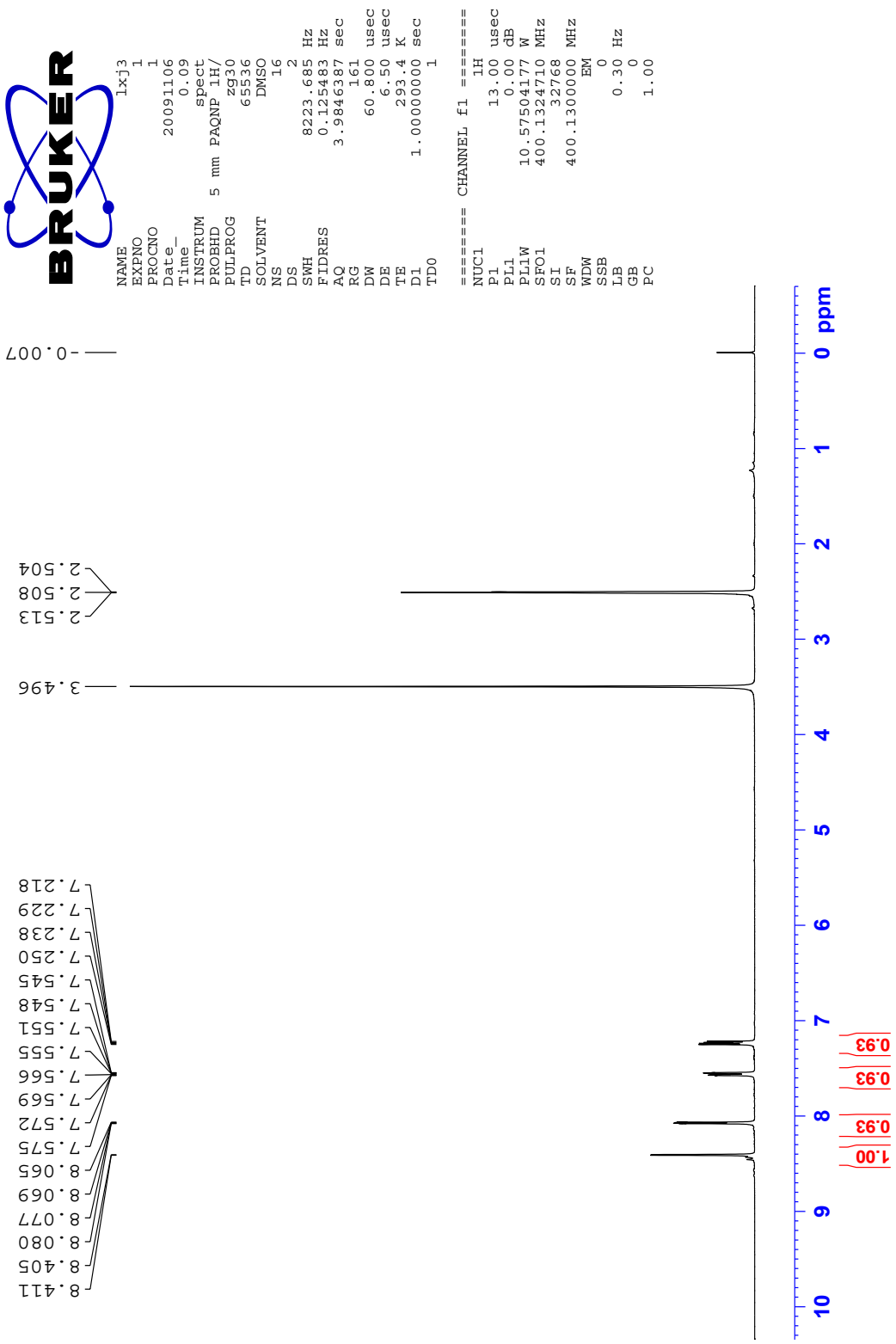

Figure S8. ^{1}H NMR spectrum of tppa

Cu^{2+}	Ligand ($C_{15}H_{15}N_6OP$)	(ClO_4^-)	Molecular formula.	Valency	Molecular weight	MS
6	8	0	$C_{120}H_{120}Cu_6N_{48}O_8P_8$	12	2991.41	249.20
6	8	1	$C_{120}H_{120}ClCu_6N_{48}O_{12}P_8$	11	3085.362	281.03
6	8	2	$C_{120}H_{120}Cl_2Cu_6N_{48}O_{16}P_8$	10	3184.310	319.03
6	8	3	$C_{120}H_{120}Cl_3Cu_6N_{48}O_{20}P_8$	9	3283.259	365.47
6	8	4	$C_{120}H_{120}Cl_4Cu_6N_{48}O_{24}P_8$	8	3382.207	423.52
6	8	5	$C_{120}H_{120}Cl_5Cu_6N_{48}O_{28}P_8$	7	3481.156	498.45
6	8	6	$C_{120}H_{120}Cl_6Cu_6N_{48}O_{32}P_8$	6	3580.104	598.01
6	8	7	$C_{120}H_{120}Cl_7Cu_6N_{48}O_{36}P_8$	5	3679.053	737.40
6	8	8	$C_{120}H_{120}Cl_8Cu_6N_{48}O_{40}P_8$	4	3778.00	946.49
6	8	9	$C_{120}H_{120}Cl_9Cu_6N_{48}O_{44}P_8$	3	3876.95	1295.64
6	**8**	**10**	**$C_{120}H_{120}Cl_{10}Cu_6N_{48}O_{48}P_8$**	**2**	**3975.898**	**1992.94**
6	8	11	$C_{120}H_{120}Cl_{11}Cu_6N_{48}O_{52}P_8$	1	4074.847	4074.847
6	8	12	$C_{120}H_{120}Cl_{12}Cu_6N_{48}O_{56}P_8$	0	4173.795	0

Table S2. m/z for complex **1** $[Cu_6[(C_5H_5N_2)_3PO]_8(ClO_4)_{12}\ nH_2O]$

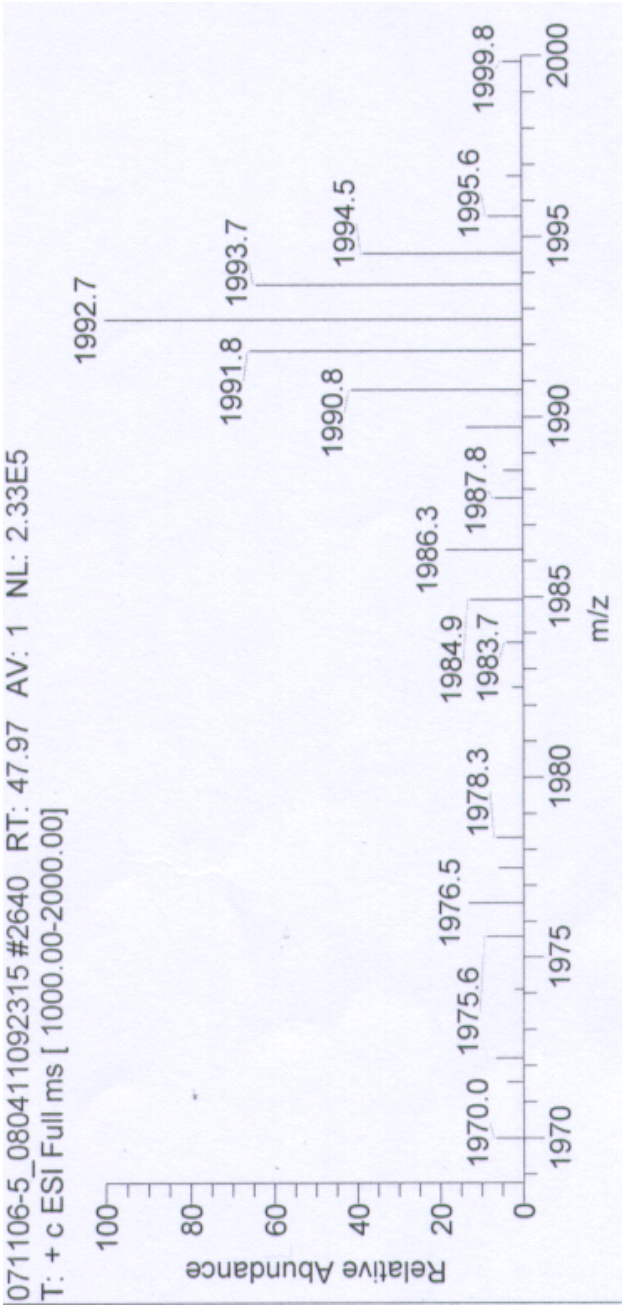

Figure S9. Mass spectrum for complex **1** in $MeOH/H_2O$.

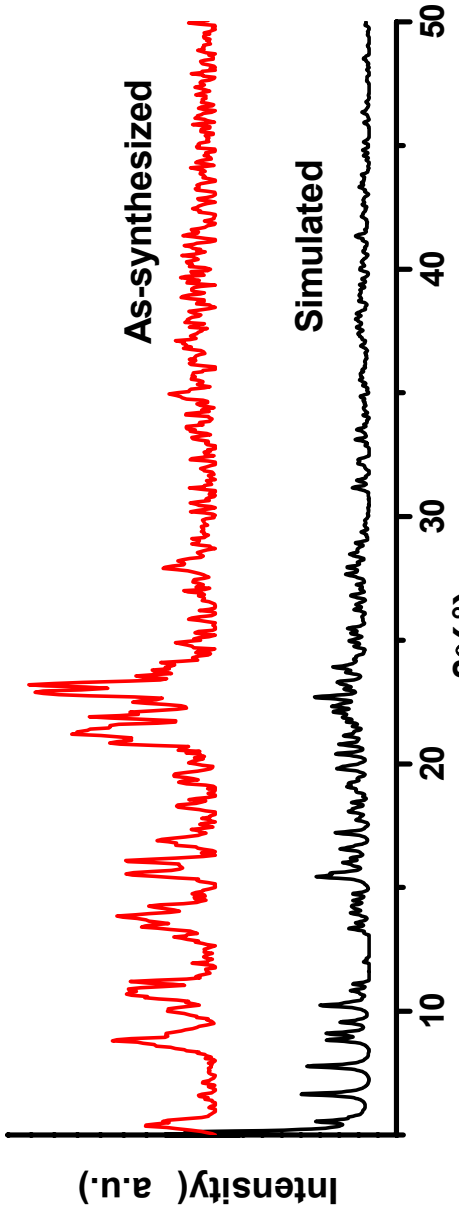

Figure S10. X-ray power diffraction pattern of **1.**

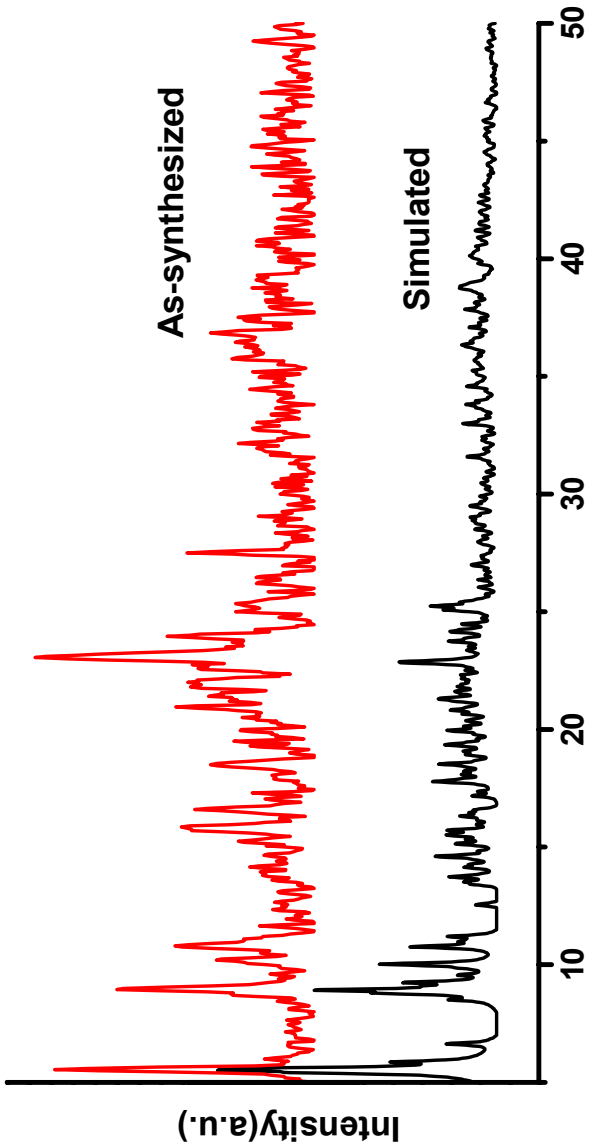

Figure S11. X-ray power diffraction pattern of **2.**

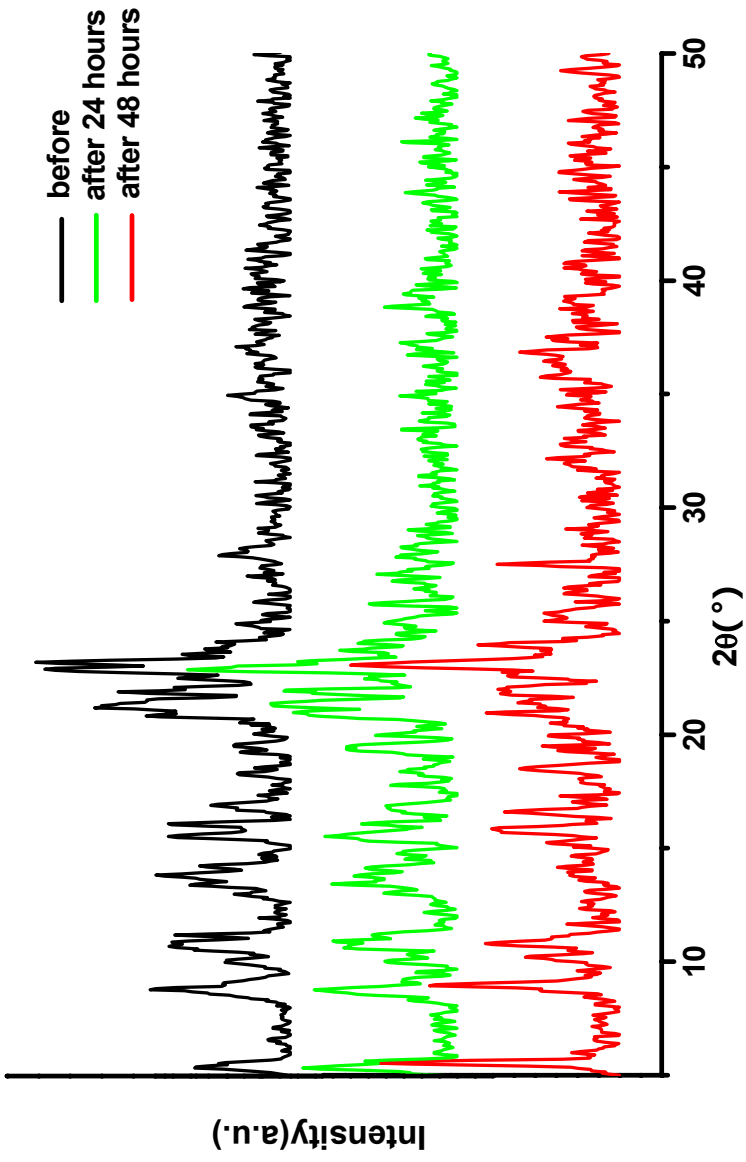

Figure S12. X-ray power diffraction patterns through the transformation