

Pyridazine-bridged copper(I) complexes of bis-bidentate ligands: tetranuclear [2x2] grid versus dinuclear side-by-side architectures as a function of ligand substituents

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Comments on crystal structure refinements

$[\text{Cu}^{\text{I}}_4(\text{L}^{p\text{-Me}})_4](\text{PF}_6)_4 \cdot 2(\text{CH}_3\text{CO})_2(\text{C}_2\text{H}_5)_2\text{O}$. Two of the four hexafluorophosphate anions are ‘twirl’ disordered with sof of 90:10 for one (F33 - F36 : F37 - F310) and 60:40 for the other one (F43 - F46 : F47 - F410). While the disorder of two acetone molecules of solvation could be readily modelled, the two diethyl ether molecules of solvation were severely disordered and could only be poorly modelled so they were removed using SQUEEZE.¹ SQUEEZE calculated an electron count/cell of 150 which matches well with the expected 2 diethyl ether molecules per asymmetric unit as this would account for 148 electrons/cell. Before SQUEEZE $R_1 = 0.0541$, afterwards $R_1 = 0.0408$.

$[\text{Cu}^{\text{I}}_4(\text{L}^{o,p\text{-Me}})_4](\text{PF}_6)_4 \cdot 7/2\text{C}_6\text{H}_6 \cdot 1/2\text{H}_2\text{O}$. Due to this being a weak data set, with a rapid drop off in intensity at moderate to higher angles [$R(\sigma) > 1$ at 1.05 - 1.00 Å], SHEL 7.0 1.05 was used to limit the reflections for refinement to $2.92 < \theta < 19.78^\circ$. Due to severe anisotropy (thin plates), restraints to anisotropic parameters (ISOR, SIMU, DELU) were applied to all atoms in the refinement. There are three full occupancy hexafluorophosphate anions, plus half a hexafluorophosphate anion (P4 F41 F42 F43 F44), which has F43 - P4 - F44 lying along a 2-fold axis, and a half occupancy hexafluorophosphate anion (P5 F51 F52 F53 F54 F55 F56, made SAME as P1 F11 F12 F13 F14 F15 F16), completing the charge balance for the four Cu(I) cations. One of the 2,4-dimethylanilino groups on one of the four independent ligand strands is disordered over two sites (C108 - C115 : C118 - C125) with an occupancy of 65:35, with a partial occupancy water molecule (O170) of solvation associated with the first part (65% occupancy). All of the 2,4-dimethylanilino groups were restrained to be similar by using DFIX with free variables on the similar C-C bond distances. There are three full occupancy and one

half occupancy (C161 - C166) benzene molecules of solvation, all of which were restrained with AFIX 66. Hydrogen atoms on the water molecule (H171 and H172) were found, HIMP'ed to 0.85Å and then the coordinates (xyz) were fixed whilst U rode on the attached oxygen atom, 1.2xU[O(170)].

[Cu^I₄(L^{m,m-F})₄](PF₆)₄·8(CH₃)₂CO. Due to this being a weak data set, with a rapid drop off in intensity at moderate to higher angles [$R(\sigma) > 1$ at 1.00 - 0.95 Å], SHEL 7.0 1.0 was used to limit the reflections for refinement to $2.92 < \theta < 20.82^\circ$. All of the aromatic rings were restrained to be FLAT. Restraints to anisotropic parameters (ISOR, SIMU, DELU) were applied to C, N, O and F atoms. Although this is a poorly resolved structure it is clear that the copper(I) complex of the 3,5-difluoro substituted ligand, L^{m,m-F}, forms a [2 x 2] grid in the solid state.

[Cu^I₄(L^{m,m-Cl})₄]⁴⁺. One half of the grid generates the other half by a 2-fold rotation. Initially the anions and solvent molecules in the asymmetric unit were tentatively modelled as two hexafluorophosphate anions, two and a half acetone molecules and one diethyl ether molecule. However, due to severe disorder, the anions and solvent molecules were subsequently removed by SQUEEZE.¹ SQUEEZE calculated an electron count/cell of 1111 which matches well with the expected 2 PF₆⁻, 2^{1/2} acetones and 1 diethylether in the asymmetric unit as this would account for 1048 electrons/cell. Before SQUEEZE $R_1 = 0.0657$, afterwards $R_1 = 0.0519$.

[Cu^I₂(L^{o-Ph})₂](PF₆)₂·6C₆H₆. The asymmetric unit of this structure consists of one copper cation coordinated by two half ligand strands (the side by side dicationic complex is generated by 2-fold rotation) and a total of three benzene molecules. The three benzene molecules per asymmetric unit are comprised of two half molecules which lie across 2-fold axes (one of these, C51-C53, comprises 3 full occupancy atoms as the 2-fold axis bisects the C-C bonds; the other one, C61-C64, comprises two full occupancy atoms, C62 and C63, and two half-occupancy atoms, C61 & C64, that lie on the 2-fold axis) and two full benzene molecules each of which is disordered 50:50 over two sites. That the structure was refined in the correct hand (chiral space group C222₁) was confirmed by a Flack parameter of 0.000(15).²

Comments on intermolecular interactions

Free ligand $L^{m,m-F}$. The intermolecular packing is diverse and complex as a range of different intermolecular interaction motifs are present. Hence it was not possible to prepare a single picture which clearly illustrates all of these interactions (instead the reader should use the cif file to visualise these). However, some of the interactions are shown in the perspective view down the a -axis (Figure S1). The C-H...N and C-F...H-C,^{3, 4} interactions are detailed in Table T1. The pyridazine ring shows offset π - π stacking^{5, 6} with one of the imine bonds (-C16=N4-) with the distances between the mean plane formed by the pyridazine ring and the atoms in the imine bond, C16 and N4, being 3.361 Å and 3.356 Å respectively. A C-F... π interaction⁷ can be seen between F4 and the π regions of the imine and the aromatic ring attached to N4, i.e. between F4 and -C16=N4-Ph, where Ph=C18-C23 and it is attached to N4 via C18 (C16...F4, 3.143 Å, N4...F4, 3.062 Å, C18...F4, 3.139 Å). Three C-F... π interactions,⁷ between the fluorine of one fluoro-substituted phenyl ring and the face of another fluoro-substituted phenyl ring, are also seen (C10...F1 3.073 Å; C10...F2 3.160 Å; C11...F1 3.156 Å).

Table T1 Short intermolecular contacts for $L^{m,m-F}$

	Distance D...A (Å)	Angle D-(H or F)...A (°)
C(4)#1 - H(4)#1...N(1)	2.609 (3.370)	137.43
C(19)#2 - H(19)#2...N(1)	2.610 (3.518)	159.98
C(10) - F(1)...H(21)#3	2.453	120.35
C(12) - F(2)...H(3)#4	2.702	158.66
C(12) - F(2)...H(4)#4	2.666	117.90
C(20) - F(3)...H(6)#2	2.661	132.24
C(20) - F(3)...H(9)#2	2.521	169.17
C(22) - F(4)...H(11)#5	2.440	123.11

Symmetry transformations used to generate equivalent atoms: #1 $x, y-1, z$; #2 $1-x, -y, 1-z$; #3 $x+1, 1/2-y, z-1/2$; #4 $2-x, 2-y, 1-z$; #5 $x-1, 3/2-y, 1/2+z$.

$[\text{Cu}^I_4(\text{L}^{p-\text{Me}})_4](\text{PF}_6)_4 \cdot 2(\text{CH}_3)\text{CO} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$. Figure S2 shows perspective views of the packing of the $[\text{Cu}^I_4(\text{L}^{p-\text{Me}})_4]^{4+}$ cations, with the hydrogen atoms, anions and solvent molecules removed in order to more clearly display the 2-dimensional sheets formed by the grids. The ‘gaps’ between these 2-D sheets are occupied by the solvent and anions. There are few intermolecular interactions between the grid complexes in this structure that fulfil the usual requirements, with most of the aromatic ring pairs being substantially offset from each other and outside the range expected for positive/stabilising interactions. The exceptions to this are the offset π - π interactions shown by the two ring pairs formed by the p -methyl substituted rings beginning at C18 and C38 and their respective symmetry generated equivalents in the neighbouring grids. These have: centroid to centroid distances of 3.992 and 4.123 Å, offset angles of 30.86 and

32.12°, and mean plane to centroid distances of 3.427 and 3.492 Å, respectively. The *p*-methyl substituted phenyl groups are arranged so as to maximise hydrophobic interactions.

[Cu^I₄(L^{*o,p*-Me})₄](PF₆)₄·⁷/₂C₆H₆·¹/₂H₂O. Figure S3 shows perspective views of the packing of the [Cu^I₄(L^{*o,p*-Me})₄]⁴⁺ cations, with the hydrogen atoms, anions and solvent molecules removed in order to display the 2-dimensional sheets formed by the grids. The ‘gaps’ between these 2-D sheets are occupied by the solvent molecules and anions. There are few intermolecular interactions between the grid complexes in this structure that fulfil the usual requirements, with most of the aromatic ring pairs being substantially offset from each other and outside the range expected for positive/stabilising interactions. The *o,p*-dimethyl substituted phenyl groups are arranged so as to maximise hydrophobic interactions.

[Cu^I₄(L^{*m,m*-F})₄](PF₆)₄·8(CH₃)₂CO. The two independent sets of parallel *m,m*-difluoro substituted phenyl ring pairs from two parallel ligand strands form intermolecular C - H...F - C hydrogen-bonds with their symmetry generated equivalents, leading to the formation of chains of grid complexes [Figure S4(a)]. One of these phenyl ring pairs forms two C - H...F - C hydrogen bonds [C(21)-H...F(34)-C(52): C - H...F distance 2.625 Å; H...F - C angle 134.7°; C(51)-H...F(3)-C(22): C - H...F distance 2.339 Å; H...F - C angle 132.5°]. The other phenyl ring pair only have one C - H...F - C interaction [C(11)-H...F(32)-C(42): C - H...F distance 2.461 Å; H...F - C angle 138.6°]. All three of these C - H...F - C interactions compare favourably with previously reported values specifically these lead to an expected mean distance of 2.648 Å ref³ [deconvoluted from mean (R_{HF})³ = 0.976, where $R_{\text{HF}} = d(\text{H...F})/(r_{\text{H}} + r_{\text{F}})$], and an expected bond angle range of 110 - 180°.³

The two dimensional sheets of grids are built up from the one dimensional chains of C - H...F - C hydrogen bonded grids by the interdigitation of the grids in neighbouring chains [Figure S4(b)]. These interdigitated grids show only one typical offset π - π stacking interaction.^{5,6} Specifically, the ring beginning C78 and its symmetry generated equivalent in the neighbouring grid have a centroid to centroid distance of 3.695 Å, an offset angle of 25.59° and mean plane to centroid distance of 3.360 Å. One of the fluorine atoms points into the centre of an aromatic ring of a neighbouring grid complex. The fluorine atom is 3.044 Å from the centroid of the ring, 3.043 Å from the ring mean plane and hence has a very small offset angle, of just 1.47°. Such aryl C-F... aryl face interactions have recently been highlighted by Boyd and co-workers in their studies of packing interactions in perfluorophenylporphyrin/fullerene systems.⁸

Figure S5 shows perspective views of the packing of the $[\text{Cu}_4(\text{L}^{m,m-\text{F}})_4]^{4+}$ cations with the hydrogen atoms, anions and solvent molecules removed in order to display the 2-dimensional sheets formed by the grids and the ‘gaps’ that are occupied by solvent and anions.

$[\text{Cu}_4(\text{L}^{m,m-\text{Cl}})_4]^{4+}$. Intermolecular offset π - π interactions^{5, 6} between the *m,m*-dichloroaniline groups are present (Figure 10), with the rings being parallel by symmetry, having a centroid to centroid distance of 4.176 Å, an offset angle 33.78° and a mean plane to centroid distance of 3.471 Å. There are three additional C-H - π intermolecular interactions⁵ between the phenyl rings, with centroid to centroid distances of 5.322, 5.500, 5.763 Å, hydrogen to acceptor mean plane distances of 2.661, 2.822, 2.350 Å, and angles between mean planes of 87.11, 87.48 and 81.40°. Additionally, there is a C - H...Cl - C interaction. It has a short H...Cl distance, C(51)-H...Cl(1) is 2.791 Å, in comparison to the expected deconvoluted mean distance of 2.945 Å ref³ [mean (R_{HCl})³ = 0.995, where $R_{\text{HCl}} = d(\text{H...Cl})/(r_{\text{H}} + r_{\text{Cl}})$], and a bond angle C-H...Cl of 104.3° which lies within the expected range of 90 - 130°.³

$[\text{Cu}_2(\text{L}^{o-\text{Ph}})_2](\text{PF}_6)_2 \cdot 6\text{C}_6\text{H}_6$. The hexafluorophosphate anions bridge the complexes by forming bifurcated C-H...F...H-C hydrogen bonds between two neighbouring pyridazine rings (F...H-C distance: 2.374, 2.382 Å; F...H-C angle: 167.04, 154.83°), leading to one dimensional chains which run along the *a*-axis (Figure S6). These chains are separated, with no apparent intermolecular interactions between them, by the solvent molecules which fill the “pores” that run alongside these one dimensional chains.

References

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Figure S1: Perspective view of the packing of the $\mathbf{L}^{m,m-F}$ molecule down the a -axis showing multiple intermolecular interactions (hydrogen atoms are shown).

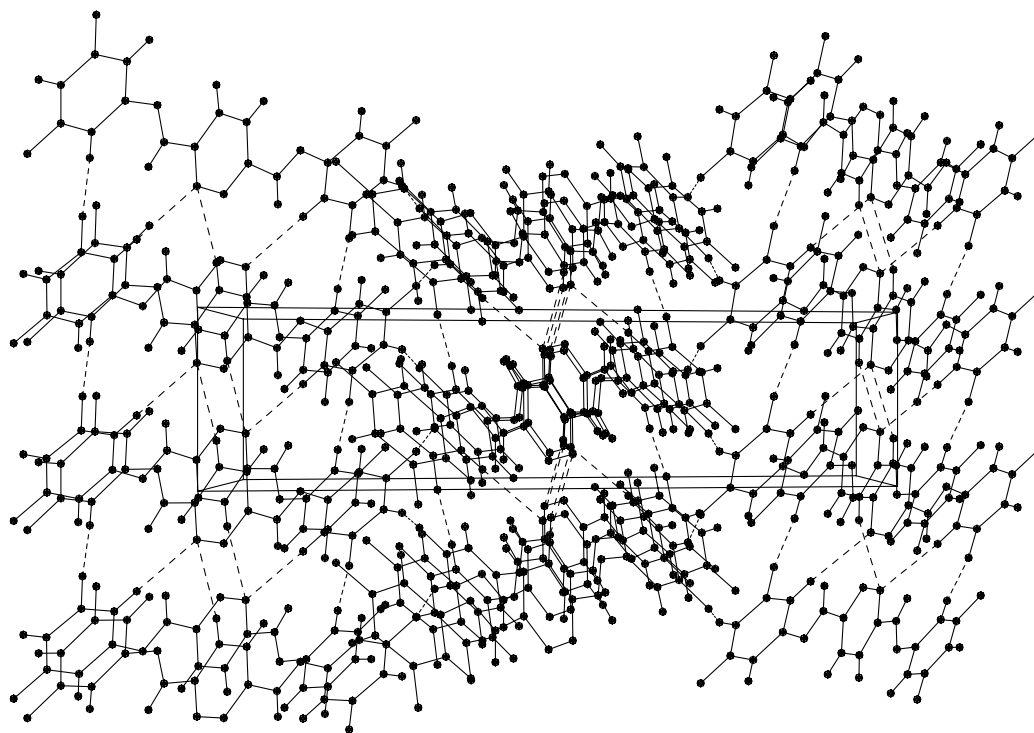


Figure S2: Perspective views of the packing of the $[\text{Cu}_4^{\text{I}}(\text{L}^{\text{p-Me}})_4]^{4+}$ cations with the hydrogen atoms, anions and solvent molecules removed for clarity (a) multiple layers viewed along the mean plane of the complexes, (b) a single layer viewed orthogonal to the mean plane of the complex.

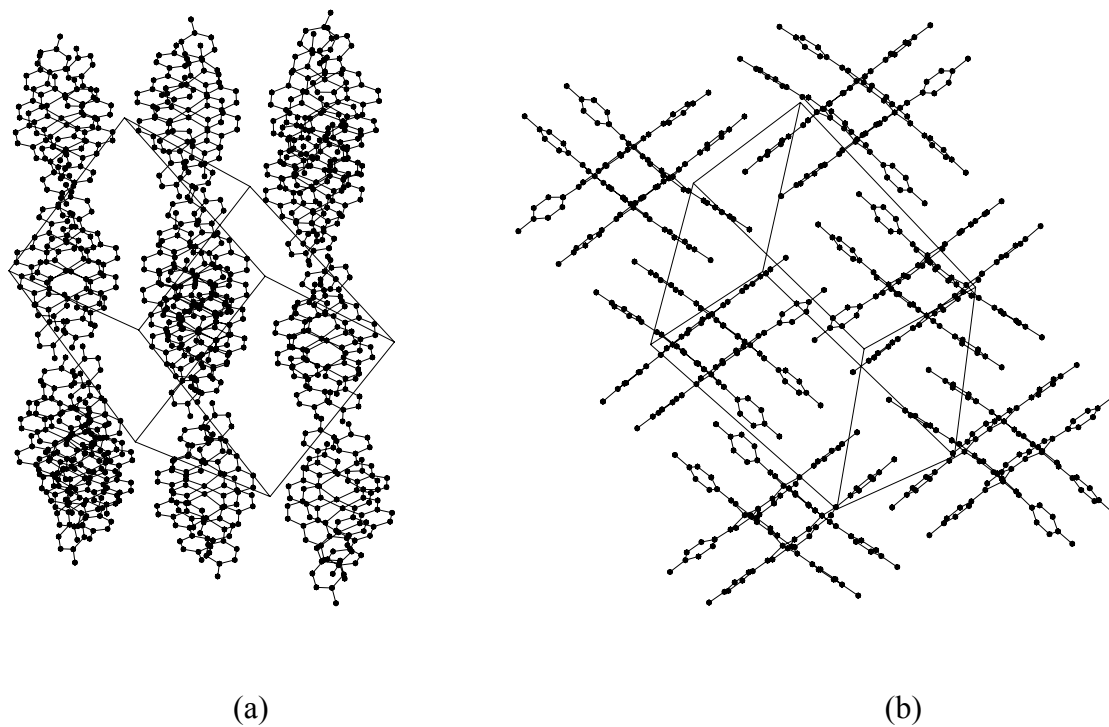


Figure S3: Perspective views of the packing of the $[\text{Cu}_4^{\text{I}}(\text{L}^{o,p\text{-Me}})_4]^{4+}$ cations with the hydrogen atoms, anions and solvent molecules removed for clarity (a) multiple layers viewed along the mean plane of the layer of complexes, (b) a single layer viewed orthogonal to the mean plane formed by the layer of the complexes.

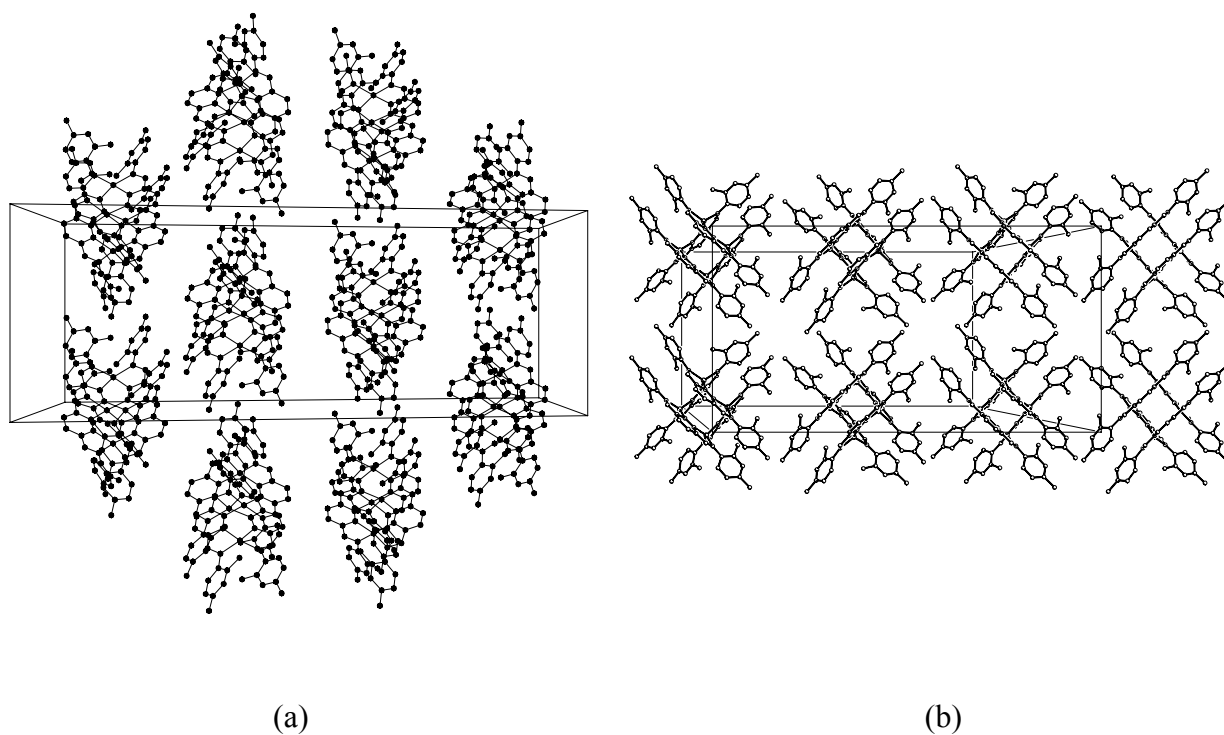
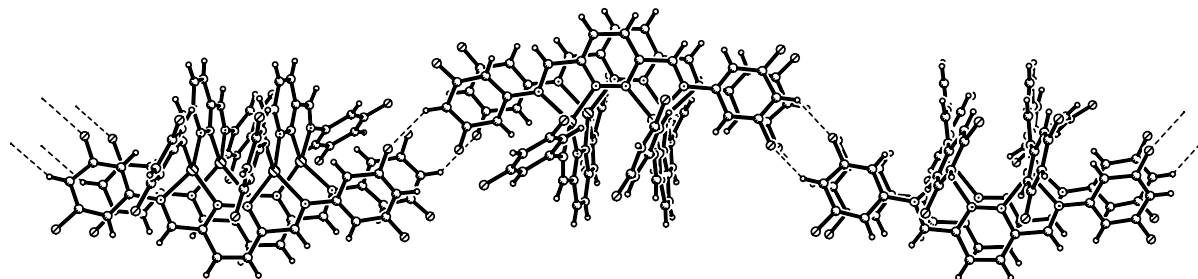
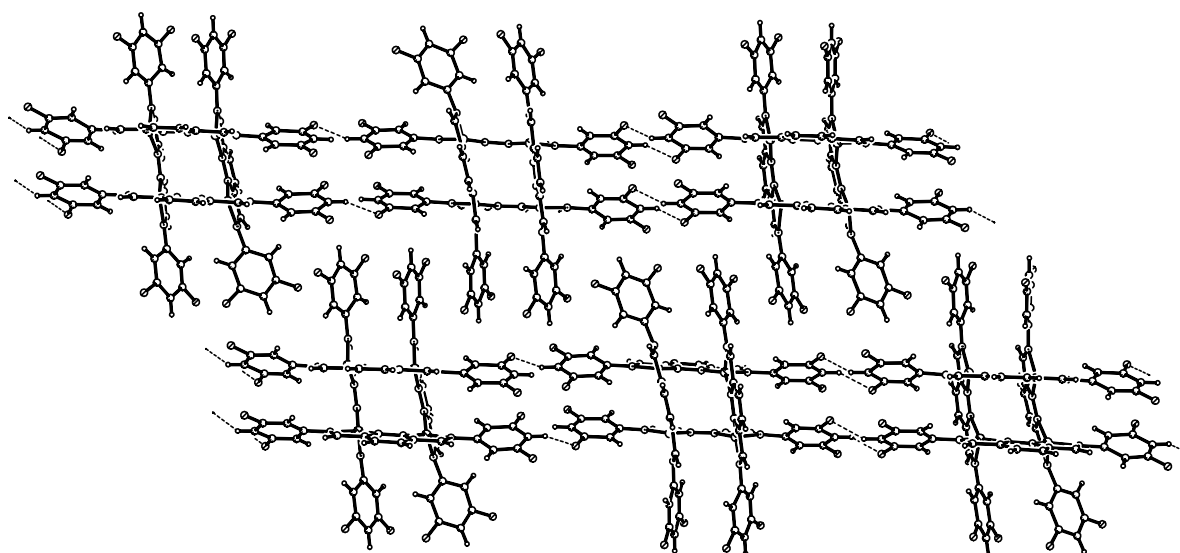


Figure S4: Perspective views of (a) the one-dimensional chain propagation of the $[\text{Cu}_4(\text{L}^{m,m-\text{F}})_4]^{4+}$ cations through C-F...H-C hydrogen bonding interactions, (b) the interdigitation of these one-dimensional chains to form two-dimensional sheets.



(a)



(b)

Figure S5: Perspective views of the packing of the $[\text{Cu}_4(\text{L}^{m,m-F})_4]^{4+}$ cations, with the hydrogen atoms, anions and solvent molecules removed for clarity (a) a single layer viewed orthogonal to the mean plane of the complex, (b) multiple layers viewed along the mean plane of the complexes.

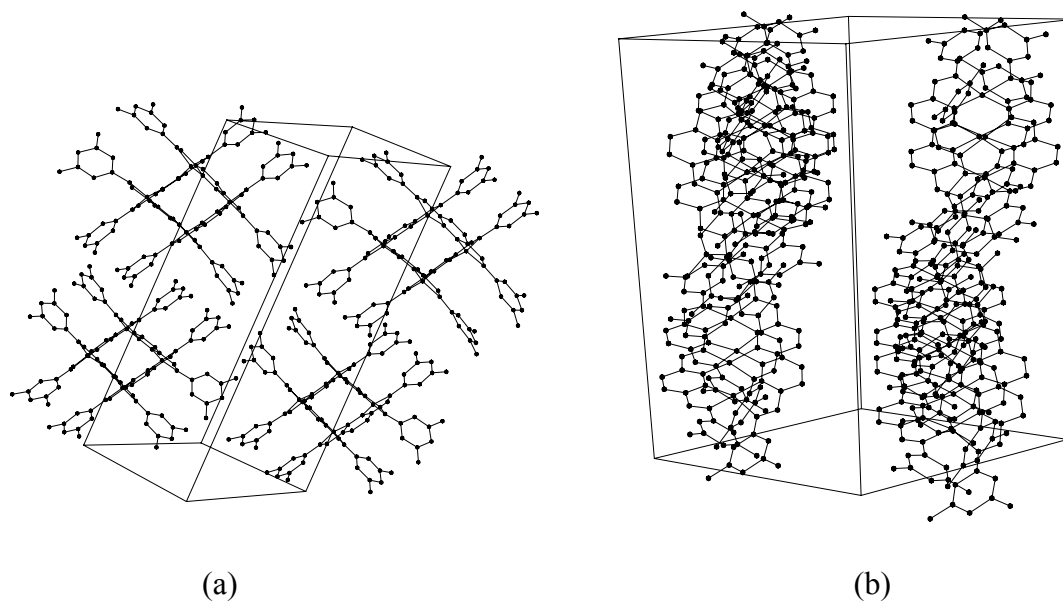
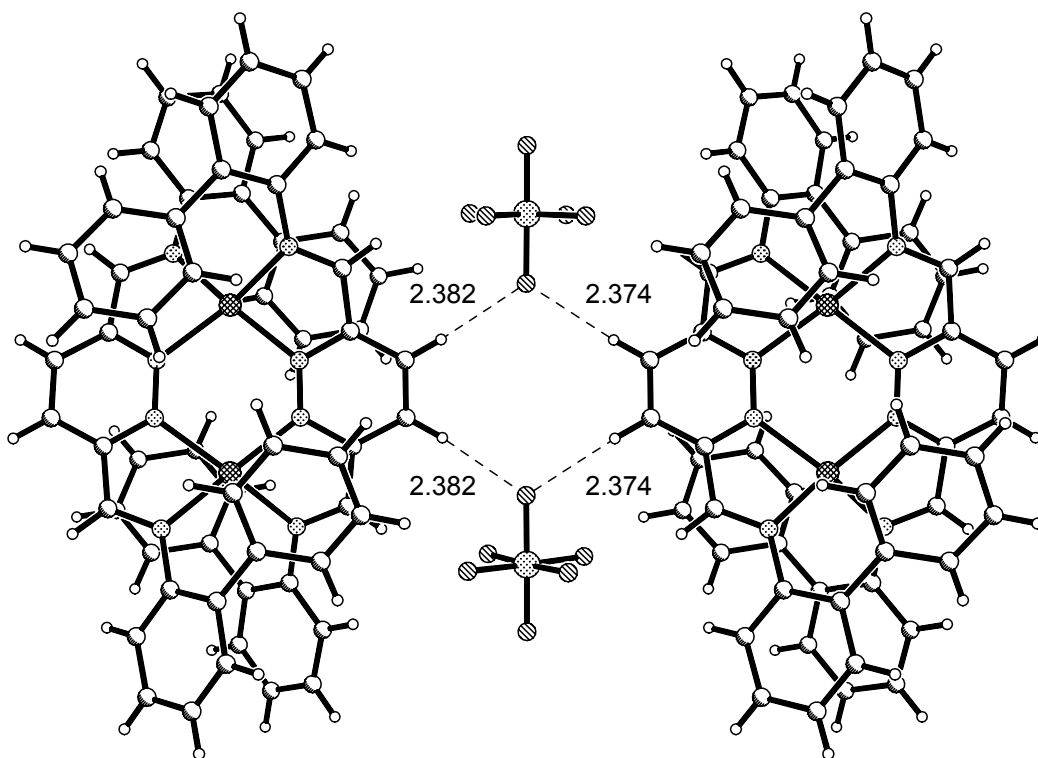
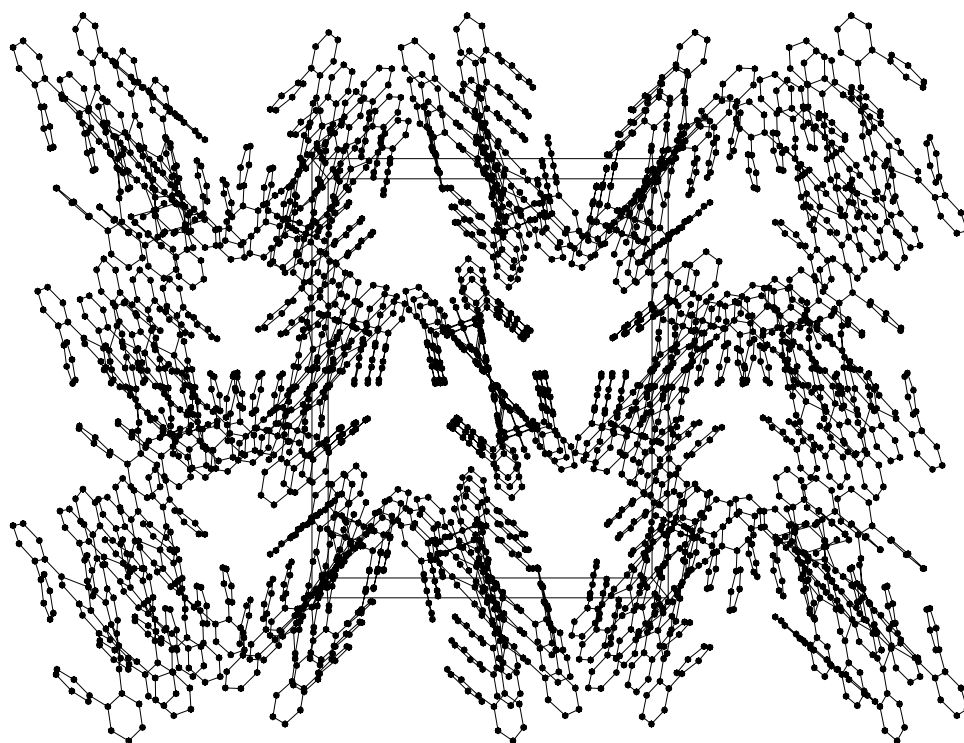


Figure S6: Perspective views of (a) the 1-dimensional propagation of the $[\text{Cu}_2(\text{L}^{o\text{-Ph}})_2]^{2+}$ cations by bridging hexafluorophosphate anions, (b) the 'pores' down the a -axis with solvent molecules and hydrogen atoms omitted for clarity.



(a)



(b)

Figure S7: Cyclic voltammogram of the free ligand $L^{m,m-Cl}$ in acetone run at 200 mVs^{-1} over the range of $+1.5 \text{ V}$ to -1.5 V vs. sat.AgCl/Ag, starting at $+0.4 \text{ V}$, scanning to the most negative potential, then to the most positive potential, then back to 0.4 V .

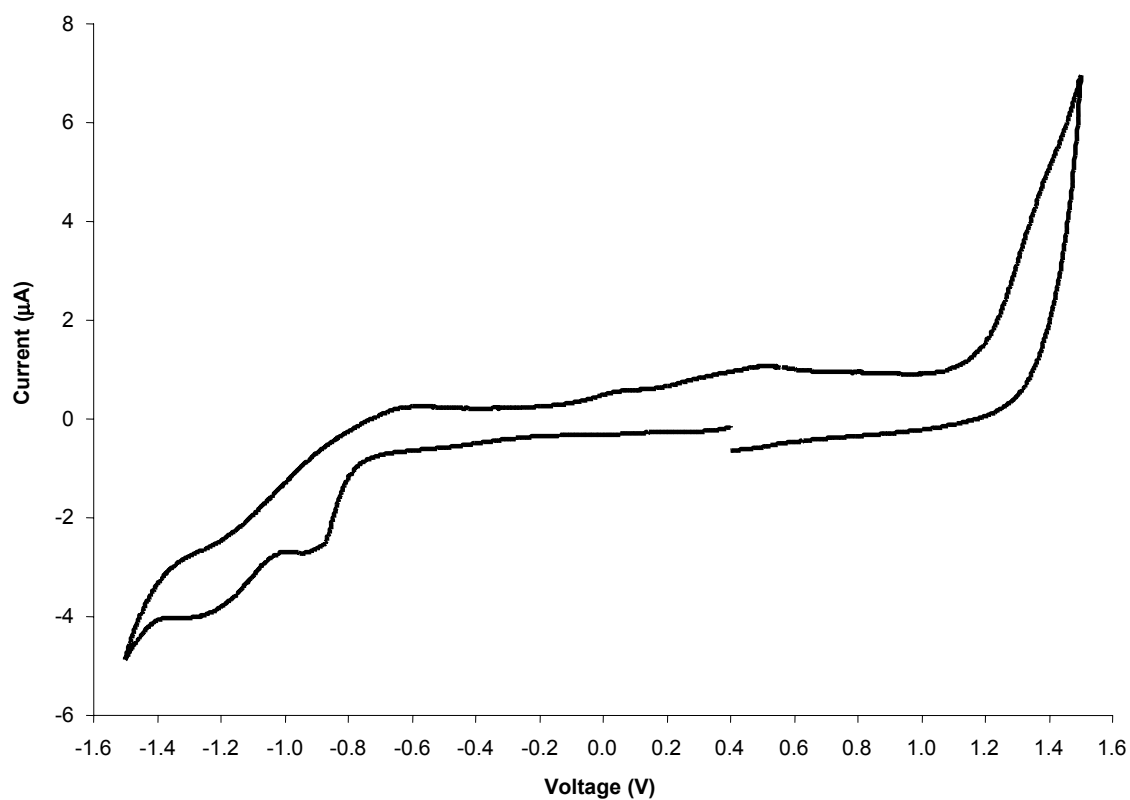


Figure S8: Cyclic voltammogram, run in acetone at 200 mVs^{-1} over the potential range of interest vs. sat.AgCl/Ag, showing the irreversible reduction process observed for the side-by-side complex $[\text{Cu}_2(\text{L}^{o-Ph})_2]^{2+}$.

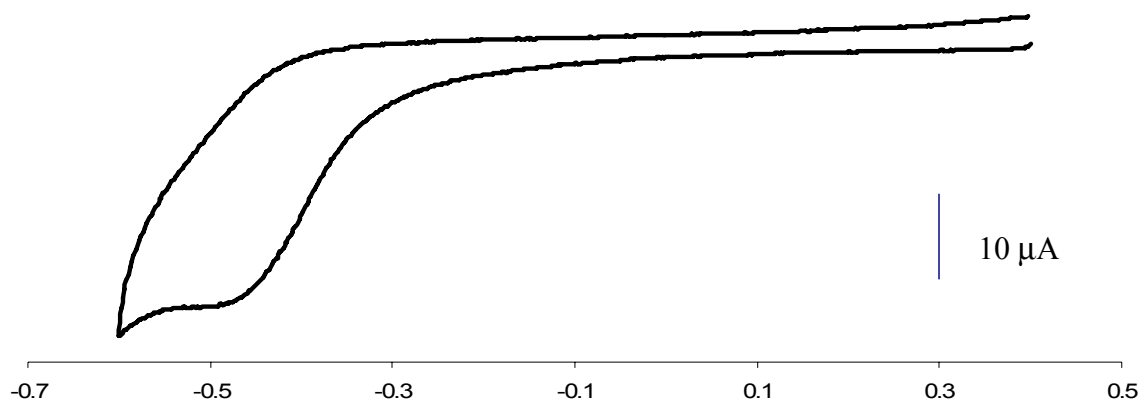


Figure S9: ^1H NMR spectra of the two complexes $[\text{Cu}^{\text{I}}_4(\text{L}^{m,m\text{-F}})_4]^{4+}$ and $[\text{Cu}^{\text{I}}_4(\text{L}^{p\text{-OMe}})_4]^{4+}$ in d_6 -acetone, along with the spectrum of a mixture of these two complexes which clearly shows that no ligand exchange has occurred.

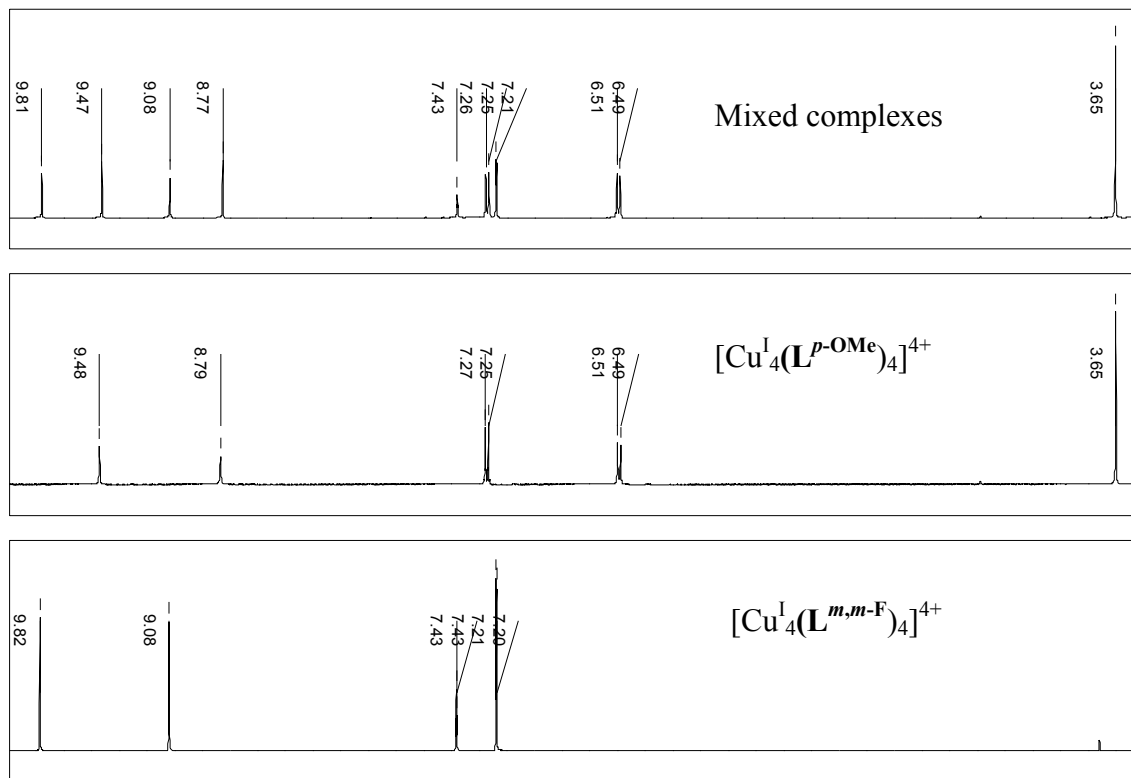


Figure S11: ^1H NMR spectrum, in d_6 -acetone, of the solid isolated from a 2:2:4 reaction of the free ligands $\text{L}^{m,m-\text{F}}$ and $\text{L}^{p-\text{OMe}}$ in one pot with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$.

