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Bis(4-pyridyl)mercury – a new linear tecton in crystal engineering: coordination polymers and co-crystallization processes

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Three new coordination polymers have been obtained using bis(4-pyridyl)mercury (py₂Hg) as a spacer: [Cu(Hmea)₂(py₂Hg)](ClO₄)₂·2(py₂Hg) **1**; [Cu₂(pa)₂(py₂Hg)(ClO₄)₂]·0.5(py₂Hg)·H₂O **2**, and [Cu₂(pa)₂(py₂Hg)₂](BF₄)₂ **3** (Hmea = monoethanolamine; Hpa = propanolamine). Compounds **1** and **2** are linear coordination polymers with mononuclear and binuclear alkoxo-bridged nodes, respectively. Compound **3** features a 3-D network with cadmium sulfate topology. The ability of py₂Hg to generate supramolecular solid-state architectures is illustrated by three systems resulted from co-crystallization processes: (4,4'-dihydroxybiphenyl)·(py₂Hg) **4**; (pyrogallol)·(py₂Hg) **5**; (phloroglucinol)·2(py₂Hg) **6**. The convolution of various supramolecular interactions (Hg···N, Hg···O, π···Hg, and π–π) in sustaining the architecture of the crystals is analyzed. A new synthetic method for bis(4-pyridyl)mercury was developed. It consists in a two-step reaction, starting from 4-iodopyridine and using ¹PrMgCl·LiCl and HgCl₂.

Introduction

Linear *exo*-bidentate ligands are among the most popular tectons in crystal engineering.¹ The archetype is 4,4'-bipyridyl, a molecule that has generated a huge number of coordination polymers with a rich structural diversity.² Numerous other bis(4-pyridyl) derivatives, with various lengths, are employed as well: 1,2-bis(4-pyridyl)ethylene,³ 1,2-bis(4-pyridyl)ethane,⁴ bis(4-pyridyl)acetylene,⁵ 1,4-bis(4-pyridyl)benzene,⁶ etc. The distance between the metallic nodes within a coordination polymer can be thus tuned by choosing the spacer with appropriate length.

The spacers with pyridyl groups connected by aliphatic chains can show various conformations (for example, *antiperiplanar* and *gauche* for the case of 1,2-bis(4-pyridyl)ethane), which play a crucial role in imposing a certain topology of the coordination polymers.⁷ Apart from their ability to connect two metal ions, these molecules can act as monodentate ligands or can be found uncoordinated, as guests, in the crystal. The nitrogen atom from the uncoordinated pyridyl moiety acts in such cases as a hydrogen bond acceptor.⁸ The pyridyl rings can be involved in π - π stacking interactions which also sustain the supramolecular solid state architectures.⁹

Most of the spacers employed in constructing coordination polymers are organic molecules. Several inorganic anions (e. g. azide,¹⁰ thiocyanate,¹¹ dicyanamide¹²) are also good linkers. The organometallic compounds containing functional groups that can coordinate to another metal ion have been also used as ligands in classical (Wernerian) coordination chemistry and crystal engineering, but to a lesser extent in comparison with organic molecules.¹³ Few organometallic species with ligands containing pyridyl groups were reported as tectons for homo- or heterometallic coordination compounds.^{13u-13x}

We recently enlarged the library of *exo*-bidentate ligands with 1,3-bis(4-pyridyl)azulene, which has an interesting potential in crystal engineering.¹⁴ Herein we present our first results on another bis(4-pyridyl) derivative, bis(4-pyridyl)mercury (py₂Hg), and its ability to generate coordination polymers, as well crystals resulting from co-crystallization processes. Although organomercurials represent already a quite large class of compounds, their use in crystal engineering was less explored.¹⁵ A new synthetic method for bis(4-pyridyl)mercury was developed.

Results and Discussion

The synthesis of bis(4-pyridyl)mercury was first reported by Partyka and Gray in 2009, with a yield of 12%.¹⁶ Their procedure, that is general for homoleptic diarylmercurials, consisted of reactions between mercury(II) acetate and arylboronic acids in the presence of cesium carbonate. We succeeded to increase the yield up to 40%, starting from 4-iodopyridine in a two-step reaction using ¹PrMgCl·LiCl and HgCl₂ (Scheme 1). The structure of py₂Hg was confirmed by the ¹H and ¹³C NMR spectra (See Experimental part).

Coordination polymers. The ability of py₂Hg to generate coordination polymers was checked

following a strategy developed by one of us, which is based on the formation of alkoxo-bridged binuclear species, when a copper(II) salt reacts with various aminoalcohols. These cationic species can act as nodes.¹⁷ The dimensionality of the resulting coordination polymers is strongly influenced by the denticity of the aminoalcohols. We employed for this study monoethanolamine (Hmea) and propanolamine (Hpa). Three new complexes have been obtained by reacting the solution containing the copper(II) salt and the aminoalcohol with py₂Hg, *i.e.* [Cu(Hmea)₂(py₂Hg)](ClO₄)₂·2(py₂Hg) **1**; [Cu₂(pa)₂(py₂Hg)(ClO₄)₂]-0.5(py₂Hg)·H₂O **2**, and [Cu₂(pa)₂(py₂Hg)₂](BF₄)₂ **3**, and their crystal structures have been solved.

The crystal structure of **1** is rather surprising, since the binuclear nodes are not formed, the aminoalcohol being not deprotonated. Consequently, the mononuclear [Cu(Hmea)₂]²⁺ species is formed instead of the expected binuclear alkoxo-bridged one. The structure of **1** consists of linear chains, constructed from {Cu(Hmea)₂} nodes connected by py₂Hg linkers, perchlorate ions and uncoordinated py₂Hg molecules (Figure 1a). Each copper(II) ion within the chain shows an elongated octahedral geometry: the equatorial plane is formed by the two Hmea nitrogen atoms (Cu1 – N3 = 2.057(9) Å), and pyridyl groups from two py₂Hg bridges (Cu1 – N1 = 2.033(8) Å); the axial positions are occupied by two Hmea oxygen atoms (Cu1 – O1 = 2.524(10) Å). The intrachain Cu...Cu distance is 13.906 Å, the length of the py₂Hg spacer (N1...N1^b; ^b = 1-*x*, 1-*y*, 1-*z*) being 9.844 Å. The values of the C – Hg – C angles are: C20 – Hg1 – C20^b = 180.0 and C14 – Hg2 – C15 = 178.5(5)°; ^b = 1-*x*, 1-*y*, 1-*z*. The packing diagram for crystal **1** is quite interesting, several supramolecular interactions being involved. First of all, we notice Hg...π interactions occurring between each mercury atom from the chain with one pyridyl ring arising from the uncoordinated py₂Hg molecule (Hg – centroid distance = 3.49 Å) – Figure 1b. This distance is within the range observed with other mercury...π arene interactions and within the sum of the van der Waals radii of mercury (1.72 – 2.00 Å) and of the carbon in aromatic systems (1.7 Å).¹⁸ The other pyridyl ring of the uncoordinated py₂Hg molecule is hydrogen bonded to the NH₂ group belonging to a neighbouring chain [N3...N4^c = 3.04(1) Å; N3 – H2N...N4^c = 171.5°] (^c = 2-*x*, -*y*, -*z*). Supramolecular layers are thus formed (Figure 1b).

The structure is expanded into the third direction by the hydrogen bonds established between the nitrogen atoms from the pyridyl rings interacting with the mercury atoms and the OH groups of the organic ligand [O1^d...N2 = 2.80(2) Å; O1^d – H1A...N2 = 153.7°] (^d = 2-*x*, 1-*y*, 1-*z*), and by the perchlorate ions. They form a triple bridge between two mercury atoms belonging to two

different uncoordinated py_2Hg molecules from adjacent layers and a mercury atom from a linear chain (Figure 1c). The distances associated to the $\text{Hg}\cdots\text{O}$ contacts are, respectively: $\text{Hg}2^e\cdots\text{O}3\text{P} = 3.038(14)$, $\text{Hg}2^f\cdots\text{O}3\text{P} = 3.134(13)$, $\text{Hg}1\cdots\text{O}1\text{P} = 3.125(2)$ Å ($^e = 1-x, -y, 1-z$; $^f = -1+x, y, z$), being in the range observed with other systems described in the literature.¹⁹

Compound **2** is a 1-D coordination polymer assembled from binuclear nodes, $\{\text{Cu}_2(\text{pa})_2\}$ built through deprotonated aminoalcohol units, and py_2Hg spacers (Figure 2a). Uncoordinated py_2Hg and water molecules are also found in the crystal. The two perchlorate ions are semi-coordinated to the two copper(II) ions within a node. The stereochemistry of the copper(II) ions is square pyramidal: the basal plane is formed by two oxygen atoms from the alkoxo bridges and by two nitrogen atoms, one arising from the amino group, the other one from the pyridyl group of the bridging py_2Hg molecule; for both copper(II) ions the apical position is occupied by the perchlorate ion ($\text{Cu}1 - \text{O}3^a = 2.713(10)$, $^a = 1+x, y, z$; $\text{Cu}2 - \text{O}7 = 2.598(13)$ Å). The basal copper-oxygen and copper-nitrogen distances, for the two copper(II) ions, vary between $\text{Cu}1 - \text{O}1 = 1.937(8)$, $\text{Cu}1 - \text{O}2 = 1.902(7)$ Å and $\text{Cu}2 - \text{O}1 = 1.915(7)$, $\text{Cu}2 - \text{O}2 = 1.918(8)$ Å, and, respectively, $\text{Cu}1 - \text{N}2 = 1.977(9)$, $\text{Cu}1 - \text{N}5 = 1.988(11)$ Å and $\text{Cu}2 - \text{N}1^b = 2.006(9)$, $\text{Cu}2 - \text{N}4\text{A} = 2.021(14)$ Å, $\text{Cu}2 - \text{N}4\text{B} = 2.014(17)$ Å; $^b = 1+x, 1+y, z$. The percentage of trigonal distortion from the square-pyramidal geometry is described by the τ parameter, defined as $[(\theta - \varphi)/60] \times 100$, where θ and φ are the angles between the donor atoms forming the plane in a square-pyramidal geometry.²⁰ The values of the τ parameter for the coordination polyhedron of copper(II) ions in **2** are: 13.33 % (Cu1) and 16% (Cu2). The intranode copper-copper distance is 2.981 Å. The value of the C10-Hg1-C1 angle for the bridging py_2Hg ligand is 174.9(5)°.

Pairs of chains are further connected by the uncoordinated py_2Hg molecules (Figure 2b), namely $\text{Hg}\cdots\pi$ interactions are established between each pyridyl moiety of one py_2Hg molecule and mercury atoms belonging to two different chains (the mercury-centroid distance is 3.49 Å). The stair-like supramolecular double chains are then interconnected by the perchlorate ions (Cl1), which act as bridges between the copper(II) ions from one double chain and the mercury atoms from the coordinated py_2Hg molecules belonging to another double chain ($\text{Hg}1\cdots\text{O}10^c = 3.029(18)$ Å; $^c = 1-x, 1-y, -z$). Supramolecular layers paralleling the crystallographic ab plane are thus assembled (Figure 2c). The crystallization water molecules connect these layers. Each water molecule is hydrogen bonded to the nitrogen atom of the amino group arising from the aminoalkoxo ligand ($\text{O}1\text{w}\cdots\text{N}5^d = 3.12(2)$ Å; $^d = 2-x, 1-y, 1-z$) and to another nitrogen atom

arising from the uncoordinated py_2Hg molecule ($\text{O1w}\cdots\text{N3} = 2.82(2) \text{ \AA}$) – (Figure 2d). The other crystallographically independent perchlorate ions (Cl2) from one supramolecular layer are semi-coordinated to the mercury atoms from the bridging py_2Hg molecules belonging to another supramolecular layer ($\text{Hg1}\cdots\text{O5}^e = 3.081(13) \text{ \AA}$; $e = 1-x, 1-y, 1-z$).

In previous papers we have shown that even if the aminoalcohol is bidentate, favouring in principle the formation of 2-D networks, the coordination of the anion, which blocks one site to the copper(II) ion, precludes the incorporation of a second spacer molecule.^{17c,d} Only 1-D coordination polymers are thus assembled.

In order to increase the dimensionality, using the same node, $\{\text{Cu}_2(\text{pa})_2\}$, we started from copper(II) tetrafluoroborate, the BF_4^- ion exhibiting lower coordinating potential. Indeed, the reaction between copper(II) tetrafluoroborate, propanolamine and bis(4-pyridyl)mercury affords a 3-D coordination polymer, $[\text{Cu}_2(\text{pa})_2(\text{py}_2\text{Hg})_2](\text{BF}_4)_2$ **3**. This is the first 3-D coordination polymer constructed from binuclear alkoxo-bridged nodes and linear spacers. Using other linear spacers (pyrazine, 4,4'-bipyridyl, bis(4-pyridyl)ethylene, 1,4-bis(4-pyridyl)benzene, bis(4-pyridyl)acetylene) and binuclear alkoxo-bridged nodes assembled by mea^- or pa^- ligands, we succeeded to obtain only 2-D coordination polymers.^{17a-d} Two py_2Hg linkers are connected to each copper(II) ion (Figure 3a), resulting in a cadmium sulphate topology (Figure 3b,c). The two copper(II) ions within the asymmetric unit are crystallographically nonequivalent and are pentacoordinated, with a square pyramidal geometry (Cu1: $\tau = 14.66\%$; Cu2: $\tau = 0.5\%$). For each copper(II) ion the basal plane is formed by two bridging alkoxo oxygen atoms, one nitrogen from the amino group, and one from a bridging py_2Hg (Cu1 – O1 = 1.913(8), Cu1 – O2 = 1.972(8), Cu2 – O1 = 1.952(8), Cu2 – O2 = 1.923(8), Cu1 – N2 = 2.013, Cu1 – N6 = 2.007 (11), Cu2 – N3 = 2.016(12), Cu2 – N5 = 1.987(12) \AA). The apical position is occupied by a nitrogen atom arising from the other py_2Hg spacer (Cu1 – N4^a = 2.292(10), Cu2 – N1 = 2.280(10); ^a = $x, 1.5-y, 0.5+z$). The intranode distance $\text{Cu}\cdots\text{Cu}$ is 3.038 \AA . The analysis of the packing diagram for crystal **3** reveals four interpenetrating nets (Figure 3d). Selected bond distances and angles for compounds **1** – **3** are collected in Table 1.

The diffuse reflectance spectra for compound **1** – **3** have been recorded (Figure 4). The electronic spectra of compounds **2** and **3** are very similar, in line with the square-pyramidal stereochemistry of the copper(II) ions: broad bands (maxima at 599 and, respectively, 637 nm) with tails at long wavelengths.

Co-crystallization processes. The ability of the nitrogen atoms of the py₂Hg molecule to act as a hydrogen bond acceptor prompted us to investigate the formation of crystals resulting from the interaction of a hydrogen bond donor with py₂Hg. As hydrogen bond donors we have chosen 4,4'-dihydroxy-biphenyl, 1,2,3-trihydroxybenzene (pyrogallol), and 1,3,5-trihydroxybenzene (phloroglucinol). We obtained single crystals with 1:1 molar ratio, *i.e.* (4,4'-dihydroxybiphenyl)·(py₂Hg) **4**; and (pyrogallol)·(py₂Hg) **5**, or 1:2 molar ratio, *i.e.* (phloroglucinol)·2(py₂Hg) **6**. The number and the orientation of the OH groups from the three phenols will definitely influence the supramolecular solid state architectures of the three crystals.

Let us discuss first the case of crystal **4**. As expected, hydrogen bonds are established between the two molecules ($O1^a \cdots N2 = 2.749(1) \text{ \AA}$, $O1^a - H1 \cdots N2 = 170.3^\circ$; $O2^b \cdots N1 = 2.741(1) \text{ \AA}$, $O2^b - H2 \cdots N1 = 166.1^\circ$; $^a = x, 1.5-y, 0.5+z$; $^b = -1+x, 0.5-y, -0.5+z$), resulting in infinite chains running in two different directions (Figure 5a). The py₂Hg molecules are almost linear ($C1 - Hg - C6 = 178.8^\circ$). Each mercury atom from one chain interacts with two oxygen atoms from two neighbouring parallel chains ($Hg1 \cdots O1 = 3.211(6)$, $Hg1 \cdots O2^c = 3.178(6) \text{ \AA}$; $^c = -1+x, y, z$), resulting in a 3-D supramolecular network (Figure 5b). Taking into account the semi-coordination of the oxygen atoms, the stereochemistry of the mercury atoms is distorted square planar. Two such independent networks interpenetrate (Figure 5c). The interpenetrating nets interact through $\pi-\pi$ contacts established between one pyridyl ring from one net and one phenyl ring arising from the 4,4'-dihydroxy-biphenyl molecule belonging to the other net (centroid-centroid distance = 3.66 \AA) – Figure 5d.

To obtain crystals **5** and **6** we employed two different trihydroxy-benzene molecules, *i.e.* pyrogallol and phloroglucinol, respectively. The crystals have grown from solutions containing the trihydroxy-benzene component and py₂Hg in 0.66 : 1 molar ratio. In spite of the similar crystallization conditions, the composition of crystals **5** and **6** is different. In crystal **5** the two components co-crystallize in 1 : 1 molar ratio, while in crystal **6** the molar ratio phloroglucinol : py₂Hg is 1 : 2.

There are two crystallographically independent mercury atoms in **5**. The corresponding py₂Hg molecules are involved in the assembling of two independent but similar layers, denoted **A** and **B** (Figure 6a): two vicinal OH groups from the pyrogallol molecule act as hydrogen bond donors towards two py₂Hg molecules (layer **A**, $O2 \cdots N4^a = 2.69(2) \text{ \AA}$, $O2 - H2 \cdots N4^a = 116.6^\circ$, $O3 \cdots N1^b$

= 2.68(2) Å, O3 – H3 \cdots N1^b = 148.4°; layer **B**, O4 \cdots N3^b = 2.74(2) Å, O4 – H7 \cdots N3^b = 161.1°, O6 \cdots N2^c = 2.68(2) Å, O6 – H6 \cdots N2^c = 147.4°; ^a = -0.5+x, 2-y, z; ^b = x, 1+y, z; ^c = 1-x, y, -0.5+z); the third OH group is weakly coordinated to the mercury atom from a third py₂Hg molecule (Hg1^c \cdots O1 = 3.026(1); Hg2^d \cdots O5 = 3.017(1) Å, ^c = -0.5+x, 1-y, z; ^d = -0.5+x, -y, z). Within each layer, the interacting pyrogallol and py₂Hg molecules describe a herringbone topology. The **A** and **B** layers, which are parallel to the crystallographic *ac* plane (Figure 6b), interact through π - π contacts established between pyridyl groups (centroid-centroid distance = 3.68 Å).

The supramolecular architecture of crystal **6** can be easily understood observing that: (a) the phloroglucinol molecules are interconnected by H-bonds involving two out of the three OH groups (Figure 7a), resulting in infinite supramolecular chains running along the crystallographic *c* axis (O3^a \cdots O2 = 2.66(2) Å, O3^a – H3^a \cdots O2 = 150.5°; ^a = 1.5-x, y, -0.5+z); (b) there are two crystallographically independent py₂Hg molecules; the py₂Hg1 molecules are coordinated to each other (one pyridinic nitrogen to mercury, Hg1 – N2^b = 2.995(3) Å, ^b = 1-x, -y, 0.5+z), resulting in zig-zag chains which also run along the *c* axis (Figure 7b); the py₂Hg2 molecules are coordinated through one pyridyl group to Hg1 atoms (Hg1 – N4 = 2.867(2) Å). Because of the interaction with the nitrogen atoms, the C21 – Hg1 – C17 angle deviates considerably from linearity (166.4(12)°), while the C29 – Hg2 – C11 angle is 175.8(14)°. The two types of chains are connected through H-bonds established between the third OH group of phloroglucinol and the nitrogen atom from a py₂Hg1 molecule (O1 \cdots N1 = 2.70(2) Å, O1 – H1 \cdots N1 = 144.4°). Each phloroglucinol supramolecular chain is connected to two py₂Hg-based chains, resulting in supramolecular layers which are parallel to the *ac* plane (Figure 7c). The structure is expanded into the third direction through the interaction of the Hg2 atom from one layer and the oxygen atom from one OH group belonging to another layer (Hg2 \cdots O2^c = 3.189(2) Å, ^c = 1-x, 2-y, 0.5+z) (Figure 7d). Two such supramolecular networks interpenetrate, as shown in Figure 7e.

The thermal analysis for compounds **3**, **4**, and **6** (Figure S1) reveal that they are stable, without any many losses, up to ca 200 °C.

Experimental part

Materials and physical measurements

The manipulation of air sensitive compounds was carried out under inert atmosphere, using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. 4-

Iodopyridine²¹ and ⁱPrMgCl·LiCl²² were obtained using literature methods. For the synthesis of compounds **1-6**, all reagents and solvents, purchased from commercial sources, were used as received, without any further purification.

The ¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker Avance III 400 instrument. The ¹H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (CHD₂OD, 3.31 ppm). The ¹³C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent (CD₃OD, 49.00 ppm).²³ ¹H and ¹³C resonances were assigned using 2D NMR experiments. The NMR spectra were processed using the *MestReC* and *MestReNova* software.²⁴ The HRMS APCI(+) spectrum was recorded on a Thermo Scientific Orbitrap XL spectrometer. Data analysis and calculations of the theoretical isotopic patterns were carried out with the Xcalibur software package.²⁵

IR spectra (KBr pellets) were recorded on a BIO-RAD FTS 135 spectrophotometer in 4000 to 400 cm⁻¹ frequencies range. Diffuse reflectance spectra were performed on a JASCO V-670 spectrophotometer, with standards of MgO. Elemental analysis was carried out on a EuroEa Elemental Analyser. Thermogravimetric analysis was carried out on a TA Q50 TGA instrument using alumina crucibles in nitrogen atmosphere. The heating rate was 10°C/min from room temperature (25°C) to 550°C.

X-ray crystallography

Single crystals for compounds **1-6** with proper shapes and dimensions were chosen for crystallographic data collection. X-ray measurements were performed on a STOE IPDS II single crystal diffractometer and on a Xcalibur E (compound **4**), using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F². The non-H atoms were refined with anisotropic displacement parameters. The BF₄⁻ anions in compound **3** are highly disordered which could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly disordered molecules were removed using the SQUEEZE procedure implemented in the PLATON package²⁶. The resulting new file was used to further refine the structure. Crystallographic data and structure refinement parameters for **1-6** are presented in Table 2. CCDC reference numbers: 1051164-1051169.

Hg(C₅H₄N-4)₂

A solution of 4-IC₅H₄N (3.61 g, 17.59 mmol) in anhydrous Et₂O (70 mL) was cooled to -5 °C and ¹PrMgCl·LiCl (19.35 mmol, 15 mL of 1.29 M solution in Et₂O) was added dropwise under argon and vigorous stirring, resulting in a brownish clay and a white suspension which was stirred for 2 h. Then a solution of HgCl₂ (2.39 g, 8.79 mmol) in anhydrous Et₂O (20 mL) was added and the reaction mixture was stirred overnight at r.t. The solvent was removed at reduced pressure and the remaining solid was dissolved in methanol, then filtered on a plug of alumina. The solvent was again removed *in vacuo* from the clear solution, the solid residue was treated with water (40 mL) and the suspension was extracted with chloroform (4x20 mL). The combined organic fractions were dried on anhydrous Na₂SO₄, filtered and the solvent was removed at reduced pressure. After washing with small amounts of acetone (4x2 mL) the title compound was obtained as colourless solid (1.25 g, 40%). M.p. 235°C (dec.). ¹H NMR (400 MHz, CD₃OD): δ 7.55 (4H, d, CCHCHN, ³J_{H,H} 5.3, ³J_{Hg,H} 107.8 Hz), 8.45 (4H, d, CCHCHN, ³J_{H,H} 5.0 Hz). ¹³C NMR (100.6 MHz, CD₃OD): δ 135.45 (s, CCHCHN), 148.60 (s, CCHCHN), 180.75 (s, CCHCHN). ¹⁹⁹Hg RMN (71.7 MHz, CD₃OD): δ -975.6 (s). MS (APCI+, MeCN): *m/z* (%) 359.05 (100) [M+H]⁺.

[Cu(Hmea)₂(py₂Hg)](ClO₄)₂·2py₂Hg **1**

0.008 g (0.021 mmol) Cu(ClO₄)₂·6H₂O solubilised in 5 mL dichloromethane and 3 mL methanol were mixed with 10 mL dichloromethane solution of monoethanolamine (Hmea) (0.0053 g, 0.086 mmol), resulting in a dark blue solution, left to stir at room temperature for few minutes until di(4-pyridyl)mercury (0.0077 g, 0.021 mmol) in 10 mL methanol was added and continued the stirring for another 2 hours. After few days, blue single crystals appeared from mother liquor by slow evaporation of the solvent at room temperature. IR (cm⁻¹, KBr): 3330(m), 3274(m), 293047(m), 2879(m), 1637(vs), 1617(vs), 1592(vs), 1523(m), 14895(m), 1456(m), 1417(m), 1109(vs), 1084(vs), 877(m), 816(m), 733(w), 692(w), 626(s). UV-VIS: 252, 208, 425, 577 nm. Elemental analysis: C 28.07, H 2.63, N 7.70% (calcd); C 27.10, H 3.07, N 6.88% (found).

[Cu₂(pa)₂(py₂Hg)(ClO₄)₂]-0.5py₂Hg·H₂O **2**

(0.0072 g, 0.019 mmol) $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 5 mL methanol were reacted with a methanolic solution of propanolamine (Hpa) (0.0058 g, 0.077 mmol) giving a green solution to which under continuously stirring was added 10 mL methanol solution of di(4-pyridyl)mercury (0.0069 g, 0.019 mmol). After two hours stirring, the mixture was filtered and left in air for slowly evaporation. In about a week violet single crystals of **2** resulted. IR (cm^{-1} , KBr): 3383(m), 3321(m), 2931(m), 2888(m), 2852(m), 1654(vs), 1592(s), 1527(s), 1501(s), 1415(s), 1343(s), 1221(m), 1109(vs), 1085(vs), 1066(vs), 934(m), 835(m), 750(w), 710(w), 692(w), 622(w). UV-VIS: 275, 373, 599 nm. Elemental analysis: C 24.62, H 2.66, N 6.84% (calcd); C 25.37, H 2.74, N 7.19% (found).

$[\text{Cu}_2(\text{pa})_2(\text{py}_2\text{Hg})_2](\text{BF}_4)_2$ **3**

Green single crystals of **3** were prepared in the same manner as for **2**, except that methanolic solutions of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0051 g, 0.021 mmol), Hpa (0.0065 g, 0.086 mmol) and di(4-pyridyl)mercury (0.0077 g, 0.021 mmol) were mixed and left to slowly evaporate. IR (cm^{-1} , KBr): 3386(m), 3324(m), 3274(m), 2951(m), 2913(m), 2892(m), 1519(vs), 1528(m), 1488(m), 1467(m), 1412(s), 1282(m), 1109(vs), 1083(vs), 1028(vs), 929(m), 805(m), 763(m), 734(m), 627(s), 584(m), 521(m). UV-VIS: 268, 334, 372, 637 nm. Elemental analysis: C 26.86, H 2.77, N 7.23% (calcd); C 27.20, H 3.24, N 7.26 % (found).

py_2Hg : 4,4'-dihydroxy-biphenyl (1:1) **4**

An ethanolic solution (5 mL) of 0.0024g (0.013 mmol) 4,4'-dihydroxy-biphenyl was added to a methanolic solution (5 mL) of 0.0047 g (0.013mmol) di(4-pyridyl)mercury and stirred for two hours. Left in air for slowly evaporation of the solvent, colorless single crystals of **4** appeared in few days. IR (cm^{-1} , KBr): 3391(m), 3062(m), 3042(m), 3004(m), 2977(m), 2927(m), 2874(m), 2855(m), 2734(m), 2650(m), 2581(m), 2481(m), 1655(s), 1606(vs), 1499(vs), 1437(s), 1406(s), 1384(s), 1294(vs), 1267(s), 1243(s), 1222(s), 1164(s), 1104(s), 1068(s), 1046(s), 1004(s), 880(vs), 821(vs), 792(s), 676(s), 513(s). Elemental analysis: C 48.66, H 3.34, N 5.16% (calcd); C 48.13, H 3.97, N 5.15% (found).

py_2Hg : 1,2,3-trihydroxybenzene (1:1) **5**

0.0016g (0.0126 mmol) 1,2,3-trihydroxybenzene in 5 mL ethanol were added to 0.0056g (0.0156 mmol) di(4-pyridyl)mercury in 3 mL methanol and the solution was continuously stirred for two hours at 60°C. The resulting orange solution was stored at 4°C until light orange single crystals of **5** appeared in a very low yield. IR (cm⁻¹, KBr): 3438(vs), 3047(m), 3016(m), 2923(m), 2853(m), 1624(s), 1572(vs), 1519(m), 1482(m), 1403(s), 1336(m), 1292(m), 1244(m), 1194(m), 1159(m), 1102(s), 1078(m), 1066(m), 1057(m), 1014(m), 795(vs), 735(w), 717(w), 665(w), 551(w).

py₂Hg : 1,3,5-trihydroxybenzene (2:1) **6**

Colorless single crystals of **6** were prepared in the same manner as **5**, except that 0.0033g (0.0092 mmol) di(4-pyridyl)mercury in methanol and 0.0008g (0.0063 mmol) 1,3,5-trihydroxybenzene in ethanol were mixed and stirred for 1.5 hours at 60°C. The solution was left to evaporate at 4°C. IR (cm⁻¹, KBr): 3434(vs), 3049(m), 2948(m), 2878(m), 1631(s), 1584(s), 1570(s), 1492(s), 1402(s), 1321(m), 1304(m), 1219(m), 1194(m), 1153(vs), 1101(s), 1088(m), 1066(m), 1007(s), 1014(m), 941(w), 879(m), 820(vs), 734(m), 682(m), 623(w), 555 (m), 518(s).

Conclusions

We have illustrated that bis(4-pyridyl)mercury can be a useful tecton in crystal engineering, with an excellent potential to generate novel coordination polymers and supramolecular solid state assemblies resulting from co-crystallization processes. Compound **3** represents the first 3-D coordination polymer constructed from binuclear alkoxo-bridged nodes and linear spacers. Apart from the similarities with the classical 4,4'-bipyridyl ligand and other linear bis(4-pyridyl) derivatives, py₂Hg has several peculiarities arising from the presence of the mercury atom, that can be involved in various supramolecular interactions. First of all, we observed that the mercury atom can be semi-coordinated by nitrogen and oxygen atoms. The interaction with these atoms causes a deviation from the linearity of the C – Hg – C fragment. Another supramolecular force that can intervene consists of $\pi \cdots \text{Hg}$ contacts, involving aromatic rings. The convolution of all these types of supramolecular interactions plays an important role in the three co-crystallization processes described here.

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Caption to the figures

Figure 1. Crystal structure of **1**: (a) View of chain along with the uncoordinated py_2Hg molecules; (b) Supramolecular layers resulting from $\text{Hg}\cdots\pi$ and $\text{N} - \text{H}\cdots\text{N}_{(\text{py})}$ interactions; (c) 3-D supramolecular architecture showing the bridging perchlorato ions (two interconnected layers are colored in green and violet).

Figure 2. Crystal structure of **2**: (a) View of the 1-D coordination polymer along with the uncoordinated py_2Hg molecules; (b) Supramolecular double chains; (c) Layers resulted by connecting the supramolecular chains by perchlorato ligands (green – bridging py_2Hg molecules; yellow – uncoordinated py_2Hg molecules); (d) View of the 3-D supramolecular architecture: the supramolecular layers represented in Figure 2c are interconnected through water molecules and semi-coordinated perchlorate ions (two interconnected layers are colored in green and violet).

Figure 3. Crystal structure of **3**: (a) Detail of the crystal structure showing the binuclear nodes connected by py_2Hg spacers; (b) Perspective view of the 3-D coordination polymer; (c) Cadmium sulphate topology of **3**; (d) Packing diagram showing the four-fold interpenetration.

Figure 4. Diffuse reflectance spectra for compounds **1** – **3**.

Figure 5. Crystal structure of **4**: (a) Supramolecular chains constructed from hydrogen-bonded 4,4'-dihydroxybiphenyl and py_2Hg molecules; (b) Perspective view of the 3-D supramolecular network; (c) Packing diagram showing the two-fold interpenetration of the supramolecular networks (green and grey); (d) π - π interactions between the interpenetrating nets.

Figure 6. Crystal structure of **5**: (a) Supramolecular layers constructed from hydrogen-bonded pyrogallol and py_2Hg molecules; (b) Interactions between **A** and **B** layers through π - π contacts involving pyridyl rings (black dotted lines).

Figure 7. Crystal structure **6**: (a) Supramolecular chains constructed by hydrogen-bonded phloroglucinol molecules; (b) Supramolecular chain constructed from py_2Hg molecules; (c) Top and lateral views of the supramolecular layers; (d) 3-D supramolecular net resulting from the interaction of the layer through $\text{Hg}\cdots\text{OH}$ contacts; (e) Packing diagram showing the two-fold interpenetration of the supramolecular nets.

Table 1. Selected bond distances (Å) and angles (°) for compounds **1** – **3**

	1		2		3
Cu1–N1	2.033(8)	Cu1 – O2	1.902(7)	Cu1 – O2	1.972(8)
Cu1–N3	2.057(9)	Cu1 – O1	1.937(8)	Cu1 – O1	1.913(8)
Cu1–O1	2.524(10)	Cu1 – N2	1.977(9)	Cu1 – N6	2.007(11)
		Cu1 – N5	1.988(11)	Cu1 – N2	2.013
		Cu1 – O3 ^a	2.713(10)	Cu1 – N4 ^a	2.292(10)
		Cu2 – O1	1.915(7)	Cu2 – O2	1.923(8)
		Cu2 – O2	1.918(8)	Cu2 – O1	1.952(8)
		Cu2 – N1 ^b	2.006(9)	Cu2 – N5	1.987(12)
		Cu2 – N4A	2.021(14)	Cu2 – N3	2.016(12)
		Cu2 – N4B	2.014(17)		
		Cu2 – O7	2.598(13)	Cu2 – N1	2.280(10)
Hg1 – C20	2.070(9)	Hg1 – C1	2.083(10)	Hg1 – C25	2.054(14)
Hg1 – C20 ^b	2.070(9)	Hg1 – C10	2.093(11)	Hg1 – C24	2.071(13)
Hg2 – C14	2.084(12)	Hg2 – C33	2.078(17)	Hg2 ^b – C26	2.010(15)
Hg2 – C15	2.087(12)			Hg2 – C14	2.070(18)
O1 Cu1 O1 ^a	180.0	O3 ^a Cu1 N2	102.9(4)	N4 ^a Cu1 O1	93.0(3)
N3 Cu1 N3 ^a	180.0	O3 ^a Cu1 O2	92.2(4)	N4 ^a Cu1 O2	94.7(4)
N1 Cu1 N1 ^a	180.0	O3 ^a Cu1 O1	87.9(3)	N4 Cu1 N6	97.1(4)
N1 Cu1 O1	94.2(3)	O3 ^a Cu1 N5	85.1(3)	N4 Cu1 N2	104.8(3)
N1 Cu1 N3	89.4(4)	O1 Cu1 O2	77.7(3)	O2 Cu1 O1	76.7(3)
N1 Cu1 O1 ^a	85.7(3)	O2 Cu1 N5	96.7(4)	O2 Cu1 N6	95.3(4)
N1 Cu1 N3 ^a	90.5(4)	O1 Cu1 N2	94.7(4)	N6 Cu1 N2	90.5(3)
O1a Cu1 N3	104.6(4)	N2 Cu1 N5	92.6(5)	N2 Cu1 O1	93.8(2)
O1 Cu1 N3	75.3(4)	O7 Cu2 O2	94.9(4)	N1 Cu2 O1	95.5(4)
C20 Hg1 C20 ^b	180.0	O7 Cu2 N4A	100.1(6)	N1 Cu2 O2	96.2(4)

C14 Hg2 C15	178.5(5)	O7 Cu2 N1 ^b	91.0(4)	N1 Cu2 N5	99.2(4)
		O7 Cu2 O1	91.8(4)	N1 Cu2 N3	98.7(5)
		O1 Cu2 O2	77.8(3)	O2 Cu2 O1	77.0(3)
		O1 Cu2 N4A	93.1(6)	O2 Cu2 N3	93.6(4)
		O1 Cu2 N4B	92.4(8)	N5 Cu2 O1	95.4(4)
		O2 Cu2 N1 ^b	94.8(4)	N3 Cu2 N5	90.1(5)
		N4A Cu2 N1 ^b	93.5(6)	Cu1 O2 Cu2	102.5(4)
		N4B Cu2 N1 ^b	95.1(8)	Cu1 O1 Cu2	103.6(4)
		Cu1 O1 Cu2	101.4(4)	C25 Hg1 C24	177.3(6)
		Cu1 O2 Cu2	102.6(4)	C14 ^b Hg2 ^b C26	176.3(7)
		C10 Hg1 C1	174.9(5)		
		C33 Hg2 C33 ^c	180.0(6)		

$$^a = 2-x, 1-y, -z$$

$$^b = 1-x, 1-y, 1-z$$

$$^a = 1+x, y, z$$

$$^b = 1+x, 1+y, z$$

$$^c = 1-x, -y, -z$$

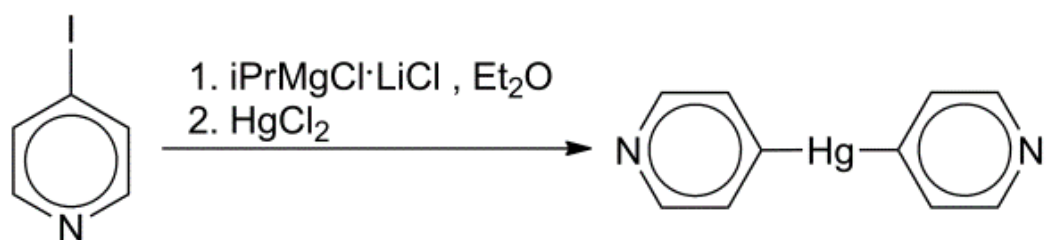
$$^a = x, 1.5-y, 0.5+z$$

$$^b = -1+x, 1+y, z$$

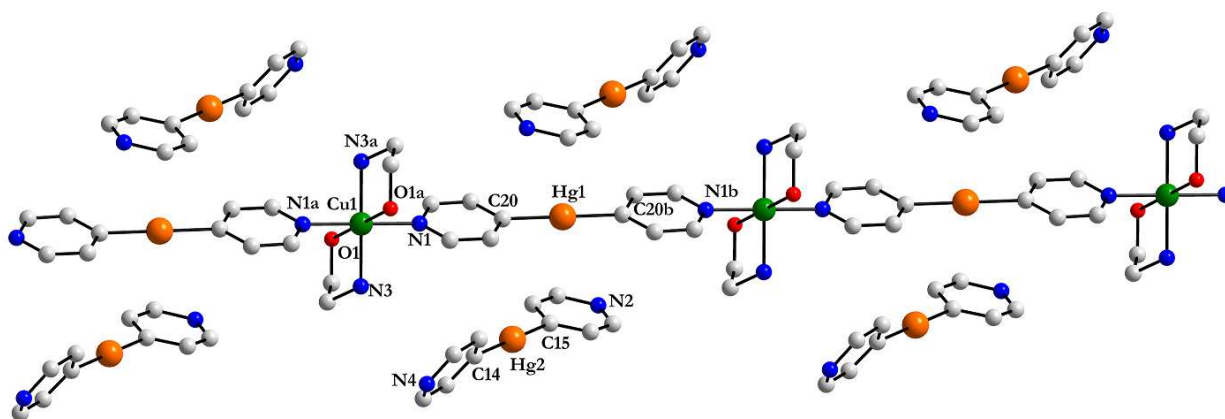
Table 2. Crystallographic data, details of data collection and structure refinement parameters for compounds **1 – 6**

	1	2	3	4	5	6
Formula sum	C ₃₄ H ₃₈ CuHg ₃ Cl ₂ N ₈ O ₁₀	C ₄₂ H ₆₀ Cu ₄ Hg ₃ Cl ₄ N ₁₀ O ₂₂	C ₂₆ H ₃₂ B ₂ Cu ₂ Hg ₂ F ₈ N ₆ O ₂	C ₂₂ H ₁₈ HgN ₂ O ₂	C ₁₆ H ₁₄ HgN ₂ O ₃	C ₂₆ H ₂₂ Hg ₂ N ₄ O ₃
Formula weight	1454.93	2054.73	1162.45	542.97	482.88	839.66
Crystal system	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pca</i> 2 ₁	<i>Pca</i> 2 ₁
<i>a</i> /Å	8.2953(2)	8.0200(5)	10.5149(11)	14.6075(13)	19.150(4)	26.220(5)
<i>b</i> /Å	10.6258(5)	14.2120(6)	12.0894(12)	8.1508(12)	10.919(2)	9.0815(18)
<i>c</i> /Å	12.4574(4)	14.6203(7)	29.347(3)	15.981(10)	14.603(3)	10.654(2)
α /°	83.389(6)	104.840(3)	90.0	90.0	90.0	90.0
β /°	81.479(3)	97.235(3)	92.74(8)	94.662(7)	90.0	90.0
γ /°	84.419(4)	93.608(5)	90.0	90.0	90.0	90.0
<i>V</i> /Å ³	1075.11(7)	1590.12(14)	3726.4(7)	1896.5(3)	3053.47(11)	2537.0(9)
<i>Z</i>	1	1	4	4	8	4
<i>D</i> _c /g cm ⁻³	2.247	2.146	2.072	1.902	2.101	2.198
T/K	293	293	293	293	293	293
μ /mm ⁻¹	11.351	8.771	9.413	8.135	10.095	12.123
Reflections collected	9831	18726	30824	8800	14934	21807
Independent reflection	3727 [<i>R</i> _{int} = 0.0645]	5572 [<i>R</i> _{int} = 0.1139]	6556 [<i>R</i> _{int} = 0.1267]	3833 [<i>R</i> _{int} = 0.1027]	5009 [<i>R</i> _{int} = 0.1153]	4344 [<i>R</i> _{int} = 0.2011]
<i>R</i> _{<i>I</i>} ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0371	0.0531	0.0564	0.0593	0.0505	0.0518
<i>wR</i> ₂ ^b (all data)	0.1087	0.1341	0.1156	0.1134	0.1148	0.1043
GOF	1.035	1.072	0.629	0.923	1.028	0.867
$\Delta\rho_{\min}/\Delta\rho_{\max}$ (e Å ⁻³)	-1.102/1.27	-1.301/1.140	-1.171/0.917	0.86/-1.02	-1.86/0.84	-1.185/0.773

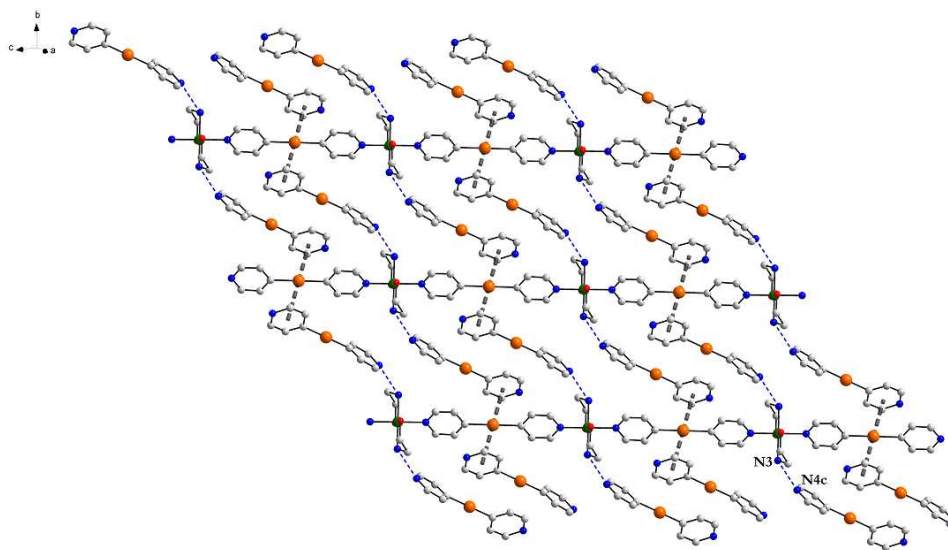
$$^a R_I = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; \quad w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP] \quad \text{where } P = [\max(F_o^2, 0) + 2F_c^2] / 3.$$



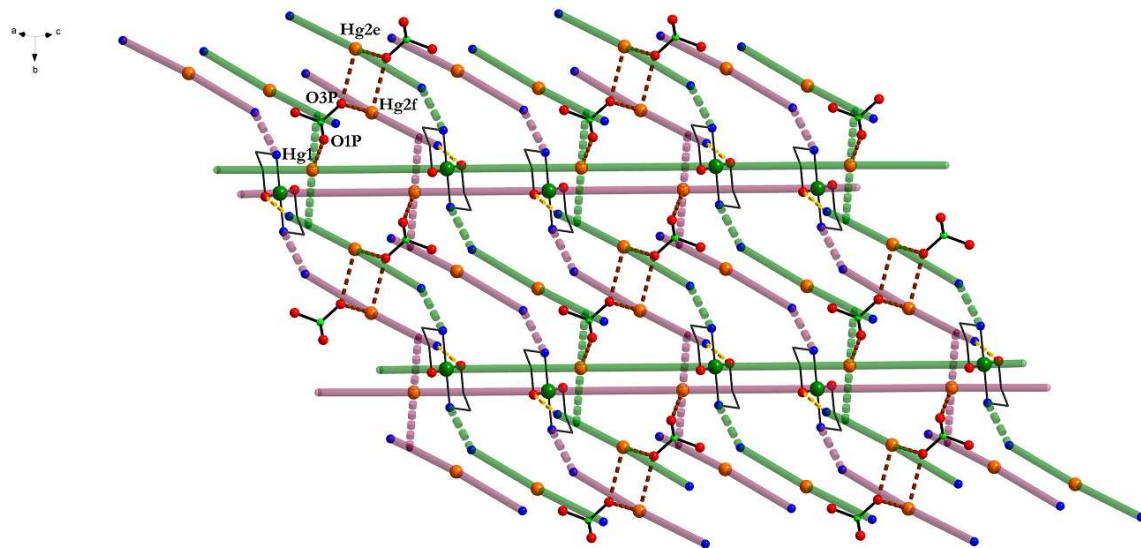
Scheme 1.



(a)

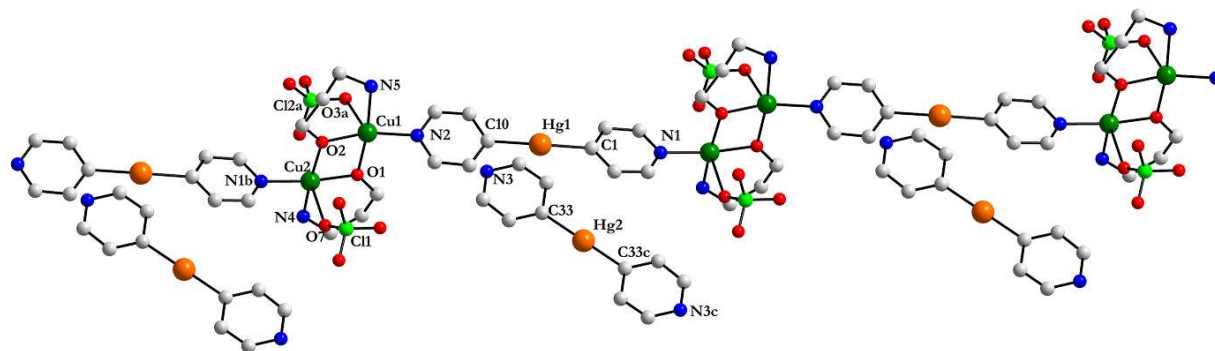


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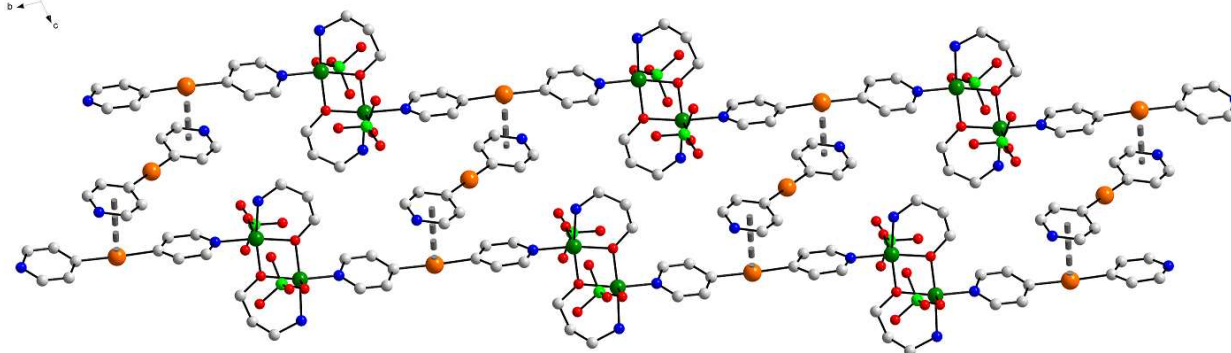


(c)

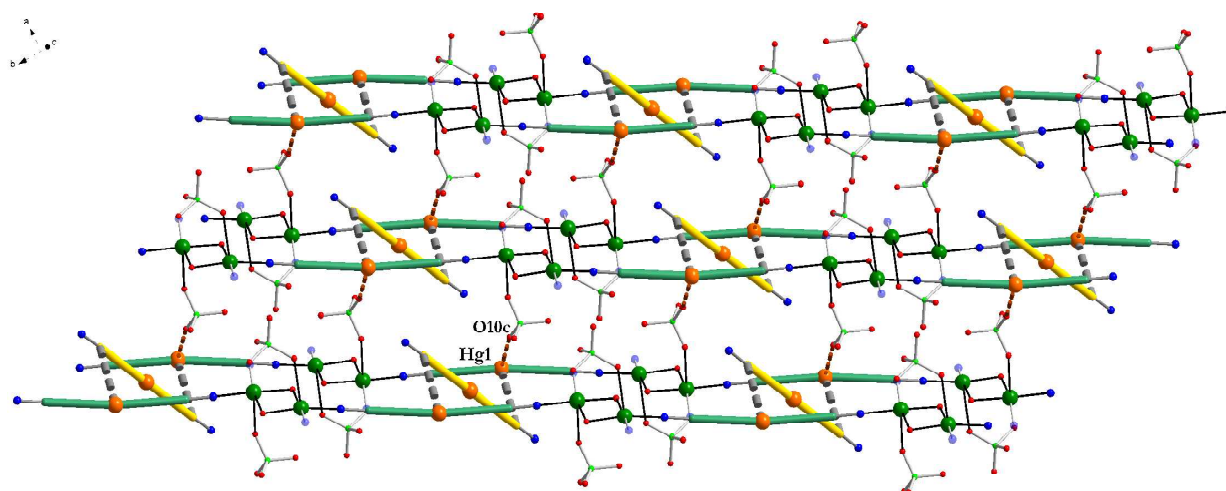
Figure 1.



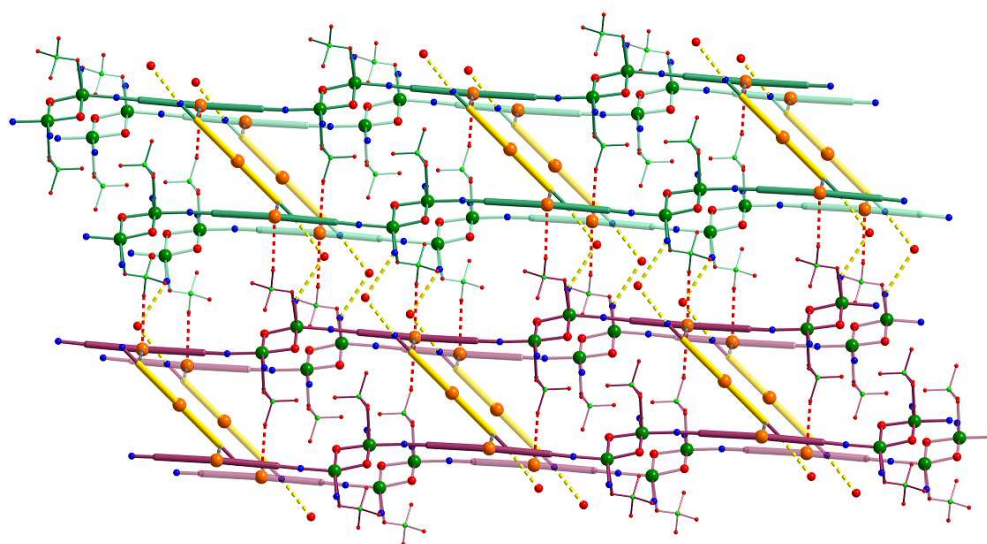
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(b)

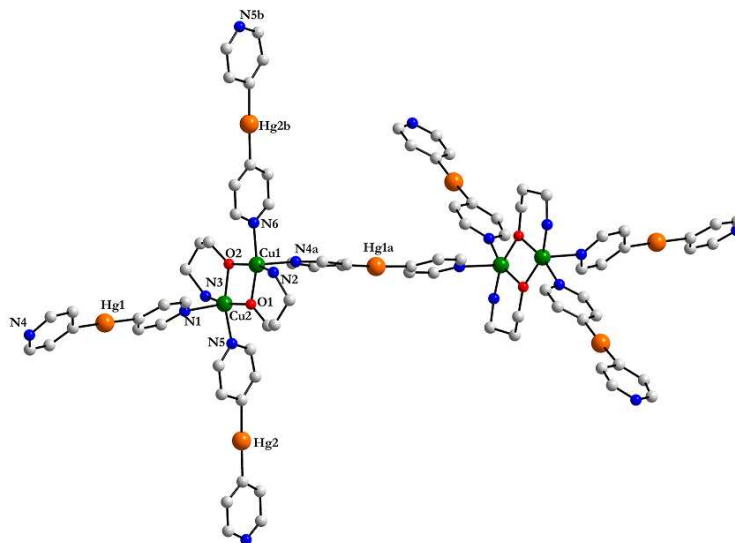


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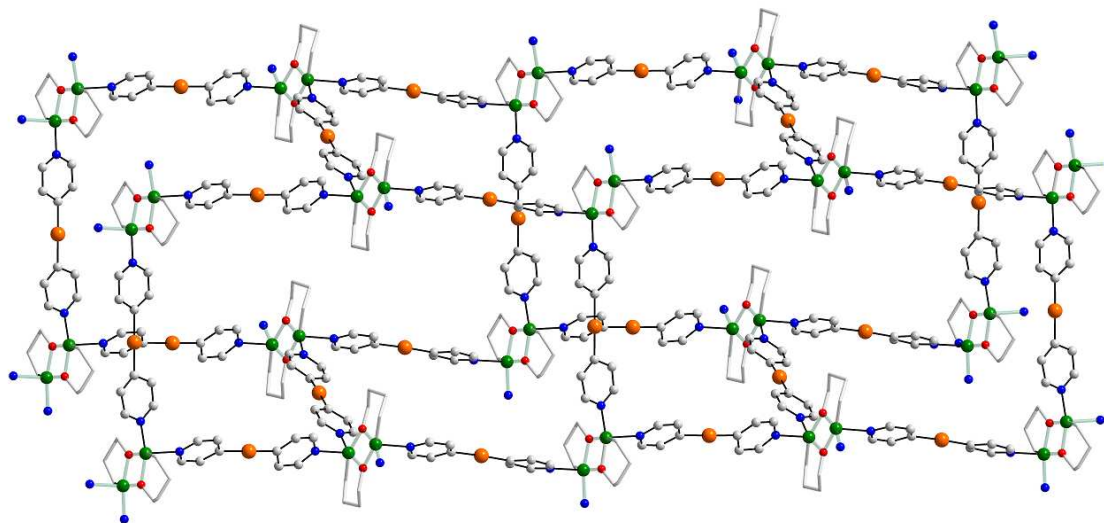


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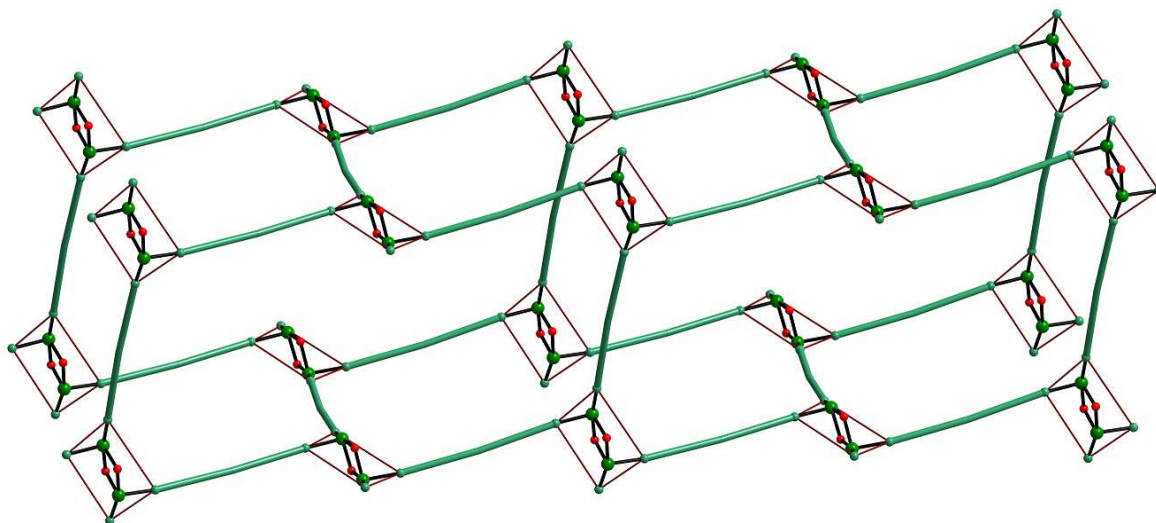
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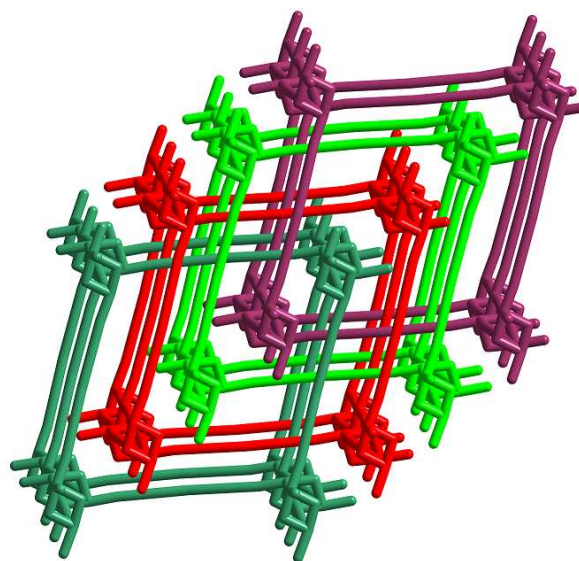
(a)



(b)



(c)



(c)

Figure 3.

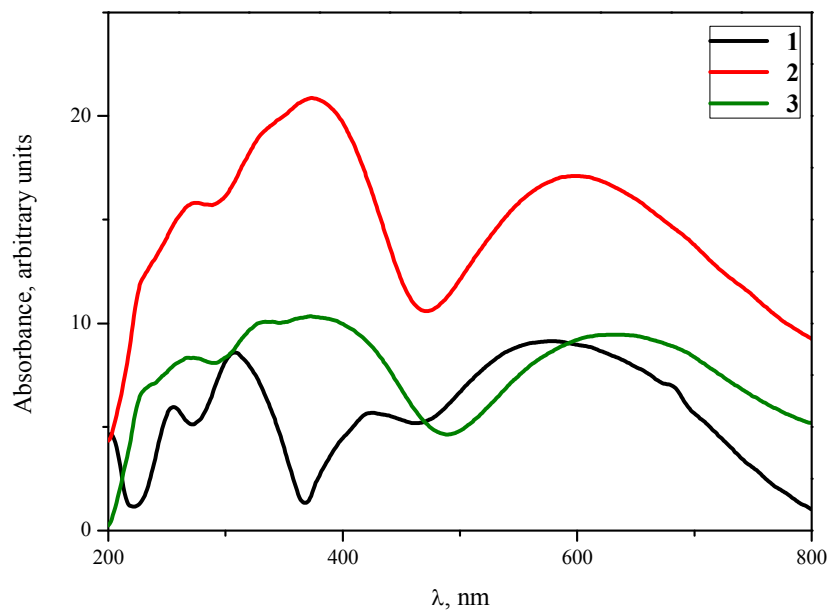
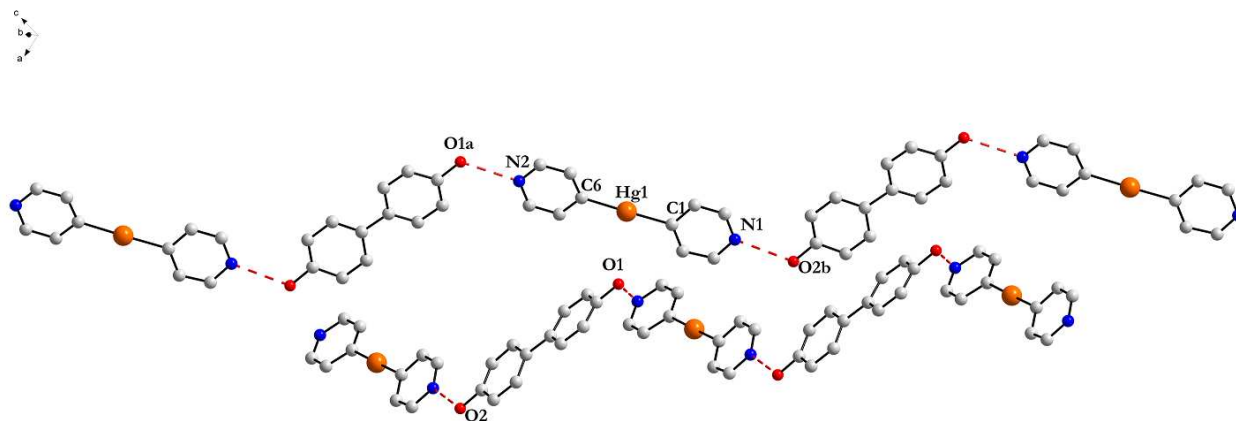
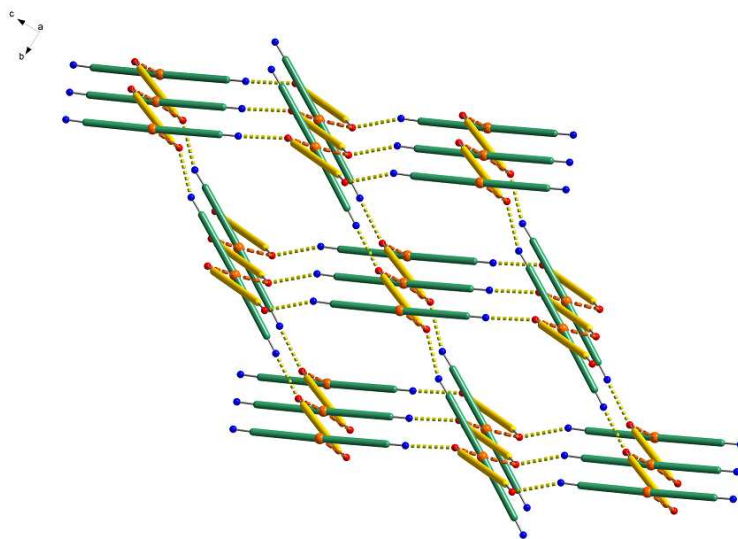


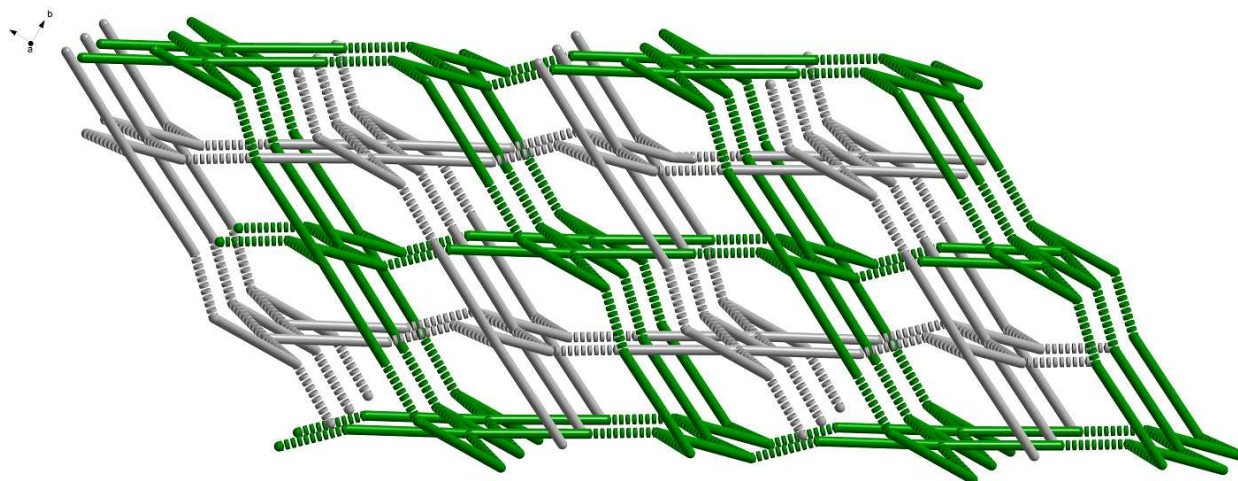
Figure 4.



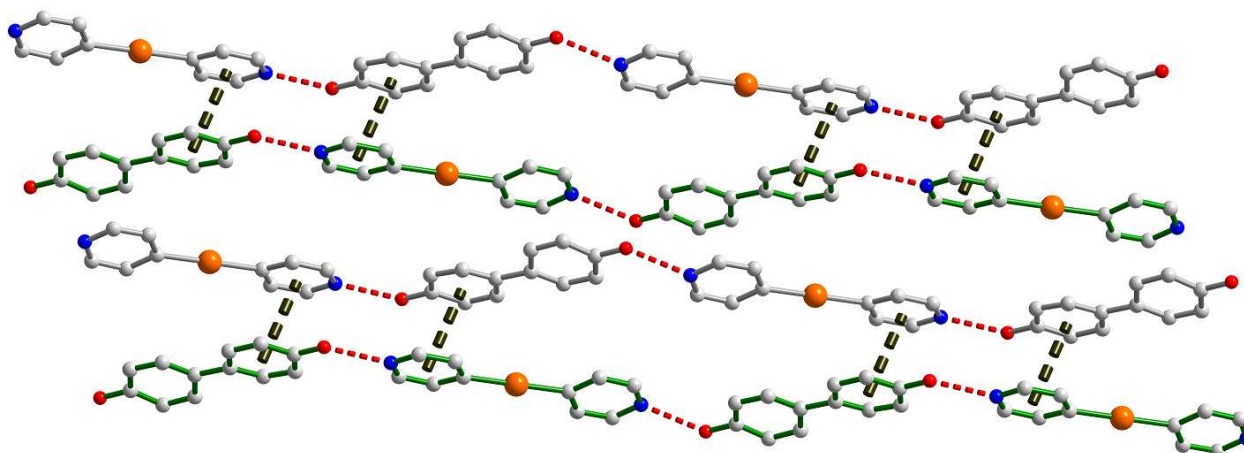
(a)



(b)

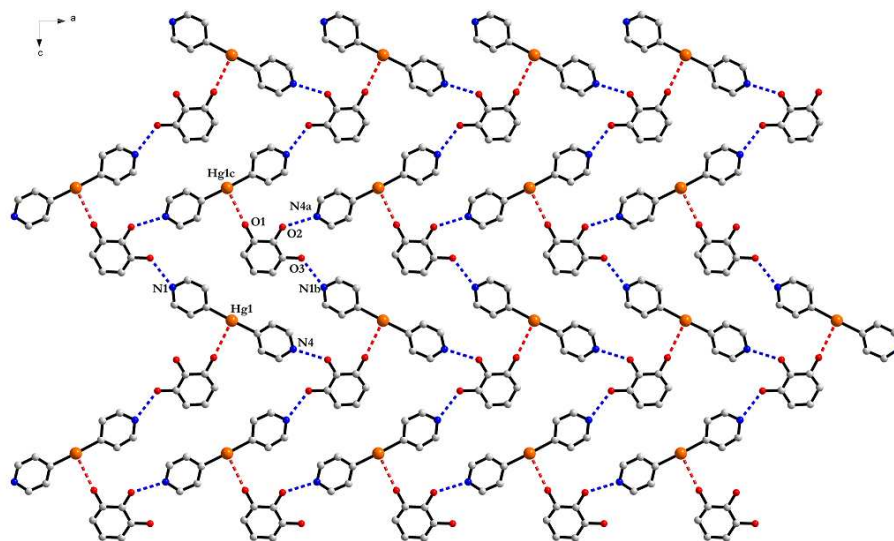


(c)

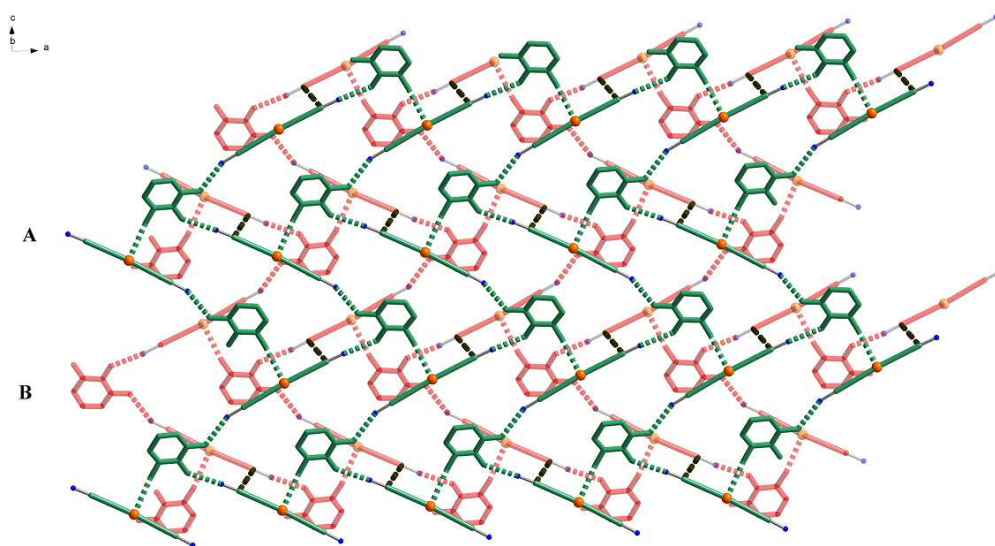


(d)

Figure 5.

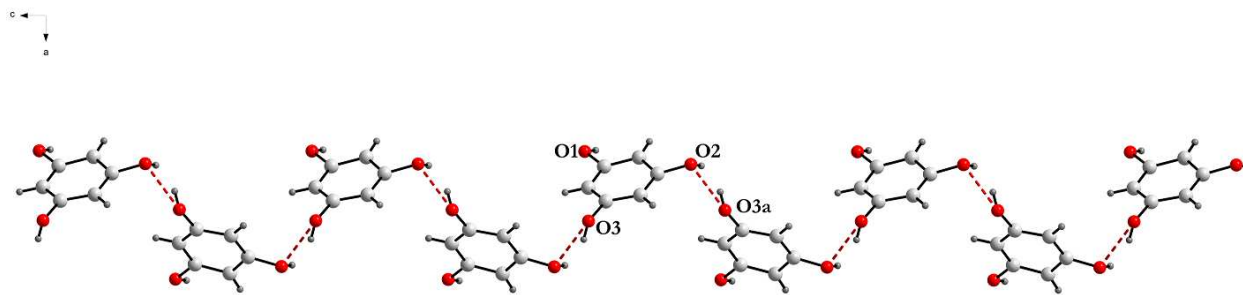


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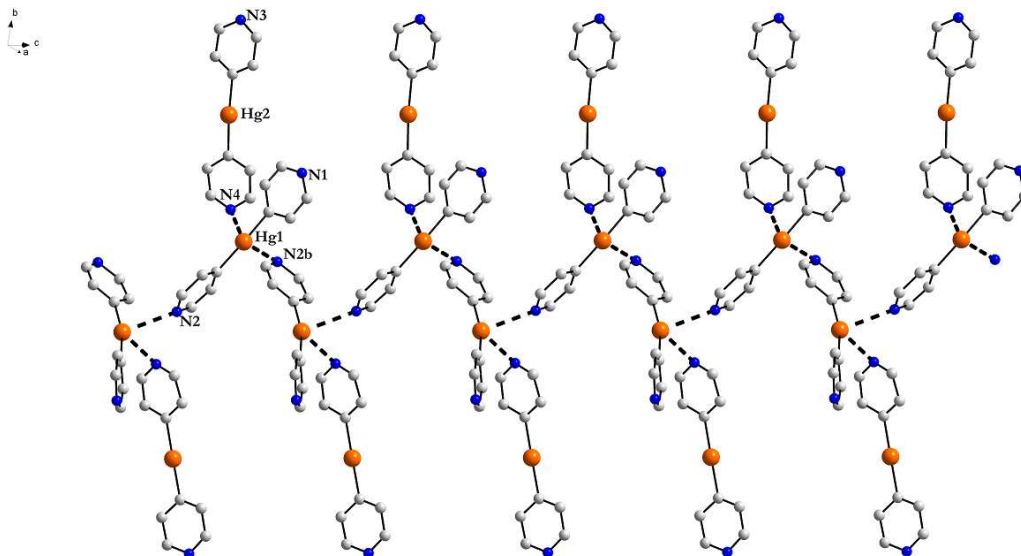


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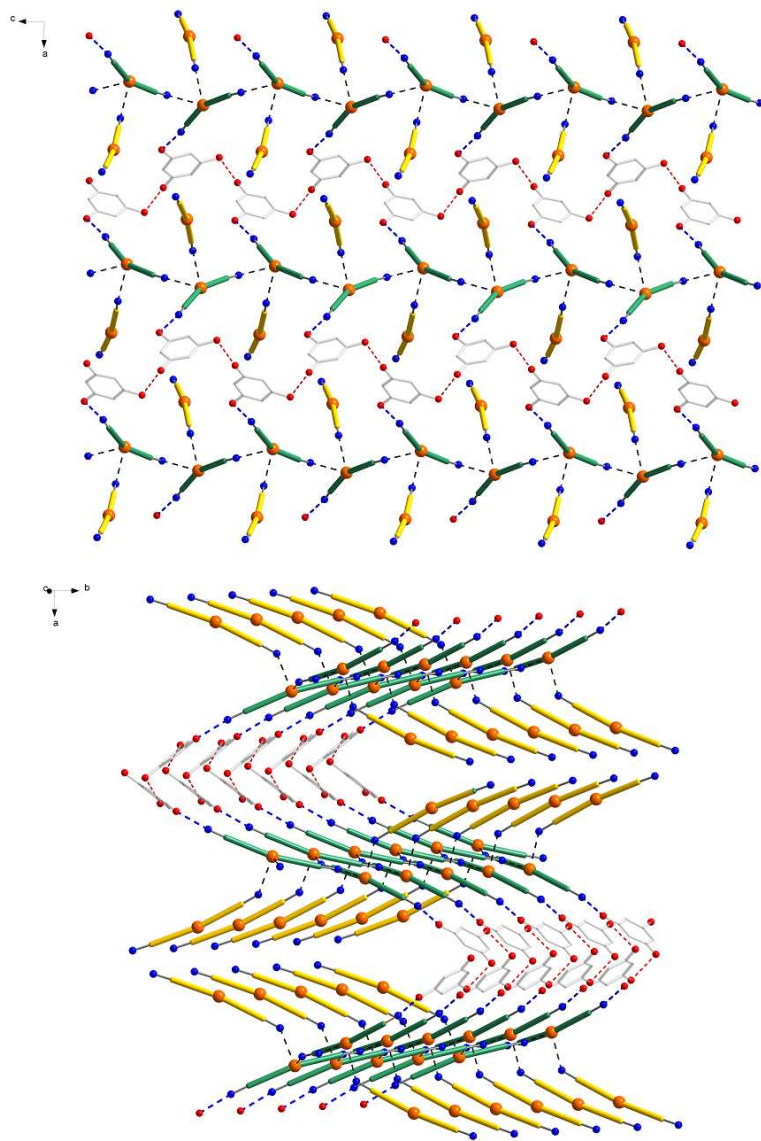
Figure 6.



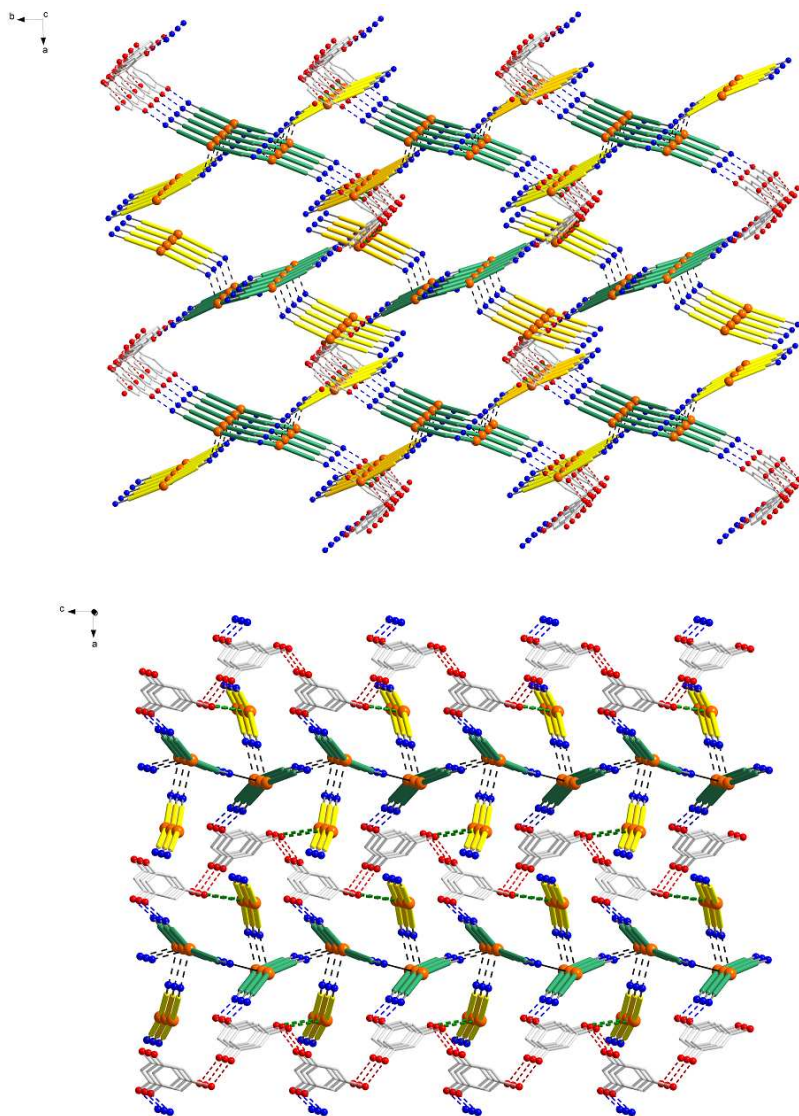
(a)



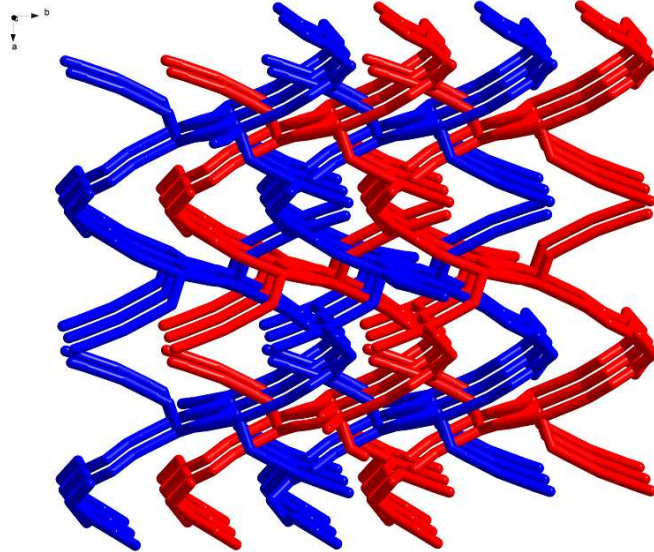
(b)



(c)



(d)



(e)

Figure 7.

Graphical Abstract

