Molecular tectonics: control of packing of luminescent networks formed upon combining bisamidinium tectons with dicyanometallates

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Abstract: The combination of bisamidinium dicationic tectons [X-2H^+] ($\text{X} = 2\text{-}4$) bearing four alkyl chains of variable lengths with linear $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Ag}$ or Au) anions leads to the formation of luminescent crystalline materials. The recognition mode, the connectivity patterns between cationic and anionic tectons leading to the formation of either 1- or 2-D networks as well as the packing of the latter are presented and discussed.

Introduction

Molecular tectonics¹, a branch of supramolecular chemistry² and supramolecular synthesis³ deals on one hand with the description of molecular crystals as periodic entities or networks⁴ resulting from specific interactions between molecular components⁵ and on the other hand, is concerned with the generation of periodic architectures in the crystalline phase through the design of tectons⁶ and molecular recognition patterns between tectons as nodes of the network. Concerning the latter, among various possible intermolecular interactions, H-bonding, owing to its rather directional nature,⁷ has been widely used. However, this type of interactions is rather weak and can be strengthened by addition of less directional electrostatic charge-charge interactions (charge-assisted H-bond).⁸ Another important characteristic defining molecular networks is their dimensionality which results from the number of translations of nodes in space. Indeed a single translation leads to a 1-D network whereas two and three translations in different space directions generate 2- and 3-D networks. For both 1- and 2-D networks, the control of their packing in the solid state leading to the formation of crystals is an important challenge. Another challenge in molecular tectonics is to design functional networks in the solid state displaying physical and/or chemical properties resulting from the specific interactions between tectons leading to their controlled arrangements. The design of crystalline solids displaying an induced property absent at the level of the individual tectons but expressed in the self-assembled architecture is of particular interest.

Here we report on the design and generation of a series of hybrid luminescent crystals resulting from combinations of dicyanometallate monoanions and bisamidinium dicationic tectons bearing four alkyl chains of variable length forming charge-assisted H-bonded networks and on the modulation of the distance between networks by the nature of the substituents localised on the organic tecton.

Results and discussion

We are involved for some time now in the design and formation of molecular network based on charge assisted H-bonding using bisamidinium type tectons.⁹ Using a variety of dicationic organic tectons, we have reported the formation of purely organic networks using carboxylates¹⁰ or sulfonates¹¹ as anionic partners. Furthermore, upon combining bisamidinium based tectons with polythiocyanatometallate,¹² polyoxalatometallate¹³ or polycyanometallate¹⁴, hybrid molecular networks have been obtained. Some of the reported crystals exhibit physical properties such as luminescence¹⁵ or porosity¹⁶ or liquid crystalline behaviour.¹⁷

We have demonstrated that the combination of the tecton 2-2H^+ (Scheme) with $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M} = \text{Ni}$, Pd or Pt)¹⁸ or $[\text{M}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Co}$, Fe or Cr)¹⁹ leads to the formation of 1- and 2-D H-bonded networks respectively with the same type of recognition patterns as for 1-2H^+ .^{14a} Importantly, by comparing the packing mode of 1-D networks obtained by associating tectons 1-2H^+ or 2-2H^+ with $[\text{M}(\text{CN})_4]^{2-}$, we have shown that the distance between 1-D networks in the crystal can be modulated by the nature of the substituents on the organic tecton (H for 1-2H^+ and propyl for 2-2H^+).¹⁸

Scheme

Furthermore, the combination of 1-2H^+ with $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Ag}$ or Au) leads also to the formation of 1-D networks however with a different connectivity pattern (Fig. 1a).¹⁵

For the latter case, it appeared interesting to investigate the role played by the alkyl substituents on the packing of 1-D networks in the crystalline phase and thus on the modulation of M-M distance (d) between metal centres belonging to consecutive networks (Fig. 1b).

Fig. 1: Schematic representation of the formation of 1-D networks and their packing in the solid state for combinations of dicyanometallate and tecton **1-2H⁺** (a) and its tetraalkylated analogues **X-2H⁺** ($X = 2-4$) (b).

Design of tectons X-2H⁺ ($X=1-4$): Bis-amidinium **X-2H⁺** ($X=1-4$) (Scheme 1) are analogous dicationic tetra H-bond donor tectons. They are based on two cyclic amidinium moieties connected by a phenyl spacer. The latter was introduced in order to impose the distance between the two acidic H atoms on the same face of the tecton and to restrain its conformational space. Furthermore, the presence of the aromatic spacer, owing to the electronic conjugation with the amidinium group, enhances considerably the stability of the tecton towards hydrolysis. Tectons **X-2H⁺** ($X=1-4$) diverge only by the nature of the substituents on the cyclic amidinium units. Indeed, whereas for the parent compound **1-2H⁺** no substituent is present, in the case of compound **X-2H⁺** ($X=2-4$), the position 3 of each cyclic amidine moiety bears two alkyl groups of different length (C3 for **2-2H⁺**, C6 for **3-2H⁺** and C12 for **4-2H⁺**). It is worth noting that these substituents are rather remote from the H-bond donor sites and thus should not interfere with the recognition processes with dicyanometallates.

Synthesis of tectons X-2H⁺ ($X=3-4$): The synthesis of **1-2H⁺**^{10,16} and **2-2H⁺**¹⁸ was previously reported. The preparation of compounds **3-2H⁺** and **4-2H⁺** (see experimental section) was achieved starting with malononitrile **5**, which was reacted, in anhydrous THF, with 1-bromoalkane (hexane for **3-2H⁺** and dodecane for **4-2H⁺**) in the presence of sodium hydride affording the dinitrile **6** and **7** in 27 and 74% yield respectively.²⁰ The dinitrile **6** and **7** were reduced upon treatment with borane in dry THF into the diamine **8** and **9** in 90 % yields in both cases. The condensation of **8** and **9** with 1,4-dicyanobenzene in the presence of P₂S₅²¹ afforded the desired compounds **3** and **4** in 21 and 15 % yields respectively.

Structural investigations

For all structural investigations by X-ray diffraction on single crystal, crystallographic data are given in table 1.

Structure of [3-2H⁺][Cl]₂ in the crystalline phase: The solid structure of the hydrochloride salt of **3** with the following formula C₃₈H₆₈N₄Cl₂•2H₂O was investigated by X-ray diffraction on a single crystal (Fig. 2, Table 1). The crystal is composed of **3-2H⁺**, two Cl⁻ anions and two water molecules. For the cationic part **3-2H⁺**, the C–N distances vary between 1.310(3) and 1.322(3) Å with the N–C–N angle of 121.0(2) and 121.1(2)°. These values are close to those observed for the analogous compounds [1-2H⁺][Cl]₂^{10,16} and [2-2H⁺][Cl]₂.¹⁸ Both six-member amidinium cycles adopt a half chair conformation and are almost parallel and tilted with respect to the phenyl ring with the NCCC dihedral angle varying between 38.53(27) and 42.51(38)°. The average distance of *ca.* 7.02 Å between nitrogen atoms belonging to two amidinium units **3-2H⁺** localised on the same side of the molecule is in accordance with what was observed for analogous compounds [1-2H⁺][Cl]₂^{10,16} and [2-2H⁺][Cl]₂.¹⁸ The four hexyl chains adopt an extended conformation (Fig. 2). Two H₂O molecules and Cl⁻ anions are located between consecutive dicationic units (Fig. 2). The two water molecules are interconnected through H-bonds ($d_{O-O} = 2.813(3)$ Å) and form a pair. They are further H-bonded with both the dicationic units ($d_{O-N} = 2.813(3)$ Å and 2.898(3) Å) and chloride anions ($d_{O-Cl} = 3.117(2)$ Å and 3.164(2) Å). The water pair, by bridging consecutive dicationic tectons, leads thus to the formation of a 1-D network (Fig. 2). The Cl⁻ anions also interact with the dication through H-bonds ($d_{N-Cl} = 3.095(2)$ and 3.136(2) Å).

The analogous hydrochloride salt [2-2H⁺][Cl]₂ also crystallises in the presence of water molecules (formula C₂₆H₄₄N₄Cl₂•2H₂O) and shows the same type of connectivity *i.e.* formation of a H-bonded water dimer interconnecting two chloride anions and interacting with the cationic unit.¹⁸

Figure 2: A portion of the crystal structure of [3-2H⁺][Cl]₂, showing the formation of a 1-D H-bonded network resulting from interconnection of consecutive salts [3-2H⁺][Cl]₂ by H-bonded water dimers. For distances and angles see text. H atoms, except those involved in H bonds are not represented for clarity.

Solid state Structure of H-bonded networks: For all networks obtained upon combining the dicationic tectons **X-2H⁺** ($X=2-4$) with [M(CN)₂]⁻ ($M = Ag$ or Au) anions, the geometry of the organic tecton remains almost identical and thus will not be described.

[2-2H⁺][Ag(CN)₂]: The combination of **2-2H⁺** with [Ag(CN)₂]⁻ anion leads to the formation of two different polymorphs α and β (Fig. 3) displaying the same morphology. In both cases, the crystal is exclusively composed of **2-2H⁺** cation and [Ag(CN)₂]⁻ anion. By using different crystallisation conditions (see experimental part), it was possible to obtain

both polymorphs in the monocrystalline state.

Figure 3: Schematic representation of the polymorph α (a) and β (b) observed for the combination of $\mathbf{X-2H}$ ($\mathbf{X=1-4}$) with $[\mathbf{M(CN)_2}]$ ($\mathbf{M=Ag}$ or $\mathbf{Au}$). Whereas for the polymorph α the connectivity mode leads to the formation of a 1-D H-bonded network, for the polymorph β , it generates a 2-D H-bonded network. For the latter, $[\mathbf{M(CN)_2}]$ rod-type anions and cations are differentiated by colour ((blue and green) and (grey and red) respectively) for clarity.

Figure 4: Portion of the crystal structure of $[\mathbf{Ag(CN)_2}].[2-2\mathbf{H}]$ for the polymorph α showing the formation of the 1D network along the c axis (a), the packing of the networks along the a axis (b) the tilt angle between two 1D network along the b axis. For distances and angles see text. H atoms are not represented for clarity, unless involved in H bonding.

The polymorph α (Fig. 3a) displays the same recognition pattern and connectivity as already observed for $\mathbf{1-2H}^+$.¹⁵ For the anionic unit $[\mathbf{Ag(CN)_2}]^-$, the coordination geometry around the Ag(I) centre is slightly bent with CAgC angle of $173.01(13)^\circ$ and NCAg angle of $174.1(3)^\circ$ and $175.9(3)^\circ$. The Ag-C and C $\equiv$ N distances are in the $2.066(3)$ and $2.069(2)$ Å and $1.139(3)$ and $1.144(3)$ Å ranges respectively.

All the dicationic and monoanionic tectons are interconnected through strong H-bonds and electrostatic charge-charge interactions, leading thus to a neutral 1-D H-bonded network.

As expected and previously observed for $[\mathbf{1-2H}^+][\mathbf{M(CN)_2}]$ ($\mathbf{M} = \mathbf{Ag}$ or $\mathbf{Au}$)¹⁵, the bridging of consecutive $\mathbf{2-2H}^+$ units by $[\mathbf{Ag(CN)_2}]^-$ anions takes place through a monohapto mode of H-bonding (one at each end of the anion) between N atoms of the anion acting as H-bond acceptor and acidic protons of $\mathbf{2-2H}^+$ (N–N distances varying between *ca* 2.87 and 2.88 Å) (Fig. 4a). Consequently, each $\mathbf{2-2H}^+$ is surrounded by four $[\mathbf{Ag(CN)_2}]^-$ anions. Owing to the length of the spacer (phenyl group) connecting the two cyclic amidinium units, the two $[\mathbf{Ag(CN)_2}]^-$ anions, disposed in a parallel fashion, located on the same side of the organic tecton are in close proximity with a Ag–Ag distance of *ca* 4.42 Å. The 1-D networks, running along the c axis, are packed in a parallel fashion along the a axis, with inter-network Ag–Ag distances of *ca* 6.80 Å (Fig. 4b). In marked contrast with the $\mathbf{1-2H}^+$ for which the 1-D networks pack in parallel fashion along both other axes, for $\mathbf{2-2H}^+$, although along a axis the networks are packed in parallel fashion however, along b axis, the 1D networks are tilted by 60.9° with respect to those along the a axis (Fig. 4c).

The second polymorph β displays a new type of connectivity pattern leading to a 2-D network (Fig. 3b). As for the polymorph α discussed above, the dicationic and monoanionic tectons are again interconnected through strong charge assisted H-bonds with the N–N distance varying between *ca* 2.85 and 2.96 Å (Fig. 5a). However, in marked contrast with the polymorph α for which each dianionic unit is connected to two (one on each side) tectons $\mathbf{2-2H}^+$, surrounded by four $[\mathbf{Ag(CN)_2}]^-$ anions (two on each side) disposed in parallel fashion leading thus to the formation of a 1-D neutral network (Fig. 3a and 4a), in the case of the polymorph β , although the connectivity between anionic and cationic tectons also takes place through a bis monohapto mode of H-bonding on each face of $\mathbf{2-2H}^+$ by two $[\mathbf{Ag(CN)_2}]^-$ anions, the latter are not parallel but twisted (twist angle of 61.8°) (Fig. 3b and 5a). Consequently, each dication $\mathbf{2-2H}^+$ is connected to four organic tectons by four anionic units leading to a neutral 2-D network (Fig. 5b). Within the 2-D network, the distance between two consecutive silver cations is 3.29 Å. For the anionic unit $[\mathbf{Ag(CN)_2}]^-$, the coordination geometry around the Ag(I) centre is linear (CAgC angle of $180.000(1)^\circ$ and NCAg angle varying between $174.14(17)^\circ$ and $178.7(2)^\circ$) with Ag–C and C $\equiv$ N distances varying between $2.066(2)$ and $2.0678(19)$ Å and $1.144(2)$ and $1.147(3)$ Å respectively). The Ag–Ag distance between two consecutive planes is equal to 11.34 Å.

Figure 5 : Portions of the crystal structure of $[\text{Ag}(\text{CN})_2] \cdot [\text{2-2H}^+]$ for the polymorph β showing the interconnection of consecutive cationic tectons by anionic units (a) and of the 2D network viewed in the (100) plane (b). For the view presented in a, the Ag atoms are eclipsed and consecutive $[\text{Ag}(\text{CN})_2]$ rod-type anions are located in consecutive planes (see figure 3b). Cationic tectons belonging to consecutive planes are differentiated by colour. For distances and angles, see text. H atoms are not represented for clarity, unless involved in H bonding.

Although the formation of the pure polymorph β could be established by PXRD which revealed a single crystalline phase (Fig. 6), the polymorph α could not be isolated as a pure polycrystalline material.

Figure 6: Comparison of the simulated (a) and recorded (b) PXRD patterns for the polymorph β obtained upon combining $[\text{Ag}(\text{CN})_2]$ anion with tecton 2-2H^+ .

$[\text{M}(\text{CN})_2]_2[\text{3-2H}^+]$ ($\text{M} = \text{Ag or Au}$): For combinations of tecton 3-2H^+ , with $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Ag or Au}$), we were only able to generate a 1-D H bonded network analogous to the polymorph obtained with 2-2H^+ combined with $[\text{Ag}(\text{CN})_2]$. Crystals were exclusively composed of 3-2H^+ and $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Ag or Au}$) and *isostructural* (see table 1). Despite many attempts, the 2D network could not be generated.

The coordination geometry around the Ag(I) or Au(I) centre is almost linear (CMC angle of $178.26(12)^\circ$ for $\text{M} = \text{Ag}$ and of $179.63(16)^\circ$ for $\text{M} = \text{Au}$). The NCM angle is in the $177.5(3) - 177.9(3)^\circ$ range for $\text{M} = \text{Ag}$ and $178.1(4) - 178.2(4)^\circ$ for $\text{M} = \text{Au}$. The M-C distance varies between $2.053(3)$ and $2.061(3)$ Å for $\text{M} = \text{Ag}$ and between $1.969(4)$ and $1.971(4)$ Å for $\text{M} = \text{Au}$. The $\text{C}\equiv\text{N}$ distance vary between $1.138(4)$ and $1.140(4)$ Å for $\text{M} = \text{Ag}$ and between $1.131(5)$ and $1.144(5)$ Å for $\text{M} = \text{Au}$ (Fig. 7). The 1-D network is formed by H-bonds between the anionic and cationic tectons with the N-N distance of *ca* 2.84

and 2.86 Å for $\text{M} = \text{Ag}$ and *ca* 2.82 and 2.85 Å for $\text{M} = \text{Au}$. The M-M distance of *ca* 4.92 Å for $\text{M} = \text{Ag}$ and *ca* 4.44 Å for $\text{M} = \text{Au}$ is rather long. As observed for $[\text{M}(\text{CN})_2]_2[\text{1-2H}^+]$ ($\text{M} = \text{Ag, Au}$)¹⁵, the 1-D networks, running along the *c* axis, are packed in a parallel fashion along the *a* and *c* axis, with Ag-Ag and Au-Au distances of *ca* 6.49 Å and 6.53 Å respectively along *a* and *ca* 13.80 Å and 13.75 Å respectively along *c*.

Figure 7: A portion of the structure of $[\text{Ag}(\text{CN})_2] \cdot [\text{3-2H}^+]$ showing the parallel packing of consecutive H-bonded 1-D networks in the (100) plane (a) and perpendicular to the *c* axis (b). C atoms of consecutive networks are differentiated by colour for clarity (pink and green, and pink and blue). For distances and angles see text. H atoms are omitted for clarity.

$[\text{M}(\text{CN})_2]_2[\text{4-2H}^+]$ ($\text{M} = \text{Ag or Au}$): The combination of 4-2H^+ with $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Ag or Au}$) leads, as in the case of tecton **2**, to two different connectivity patterns corresponding to polymorphs α and β obtained with 2-2H^+ combined with $[\text{Ag}(\text{CN})_2]^-$ anion. Whereas for $[\text{Ag}(\text{CN})_2]^-$ anion a 2-D network is obtained, for $[\text{Au}(\text{CN})_2]^-$ anion a 1-D network is formed. Attempts to generate the polymorph 1-D with $[\text{Ag}(\text{CN})_2]^-$ and polymorph 2-D with $[\text{Au}(\text{CN})_2]^-$ were unsuccessful.

For the 1D network formed with $[\text{Au}(\text{CN})_2]^-$, the connectivity pattern is identical to the one observed for 2-2H^+ and 3-2H^+ combined with the same anion (polymorph α) (Fig. 3a). For the latter, an almost linear coordination geometry around the Au(I) centre was observed with CAuC angle varying between $177.3(4)^\circ$ and NCAu angles of $176.4(9)^\circ$ and $176.8(9)^\circ$. The Au-C and $\text{C}\equiv\text{N}$ distances are in the $2.012(9) - 2.015(9)$ Å and $1.115(9) - 1.119(9)$ Å ranges respectively. As for the other cases discussed above, anionic and cationic tectons are hydrogen bonded with the N-N distance varying between *ca* 2.82 and 2.84 Å. Within the 1-D network, the Au-Au distance of *ca* 4.63 Å is rather long (Fig. 8a). The 1-D networks, running along the *b* axis, are packed in a parallel fashion along the *a* axis with a Au-Au distance of *ca* 8.42 Å (Fig. 8b).

As for the $2\text{-}2\text{H}^+$ analogue, for $4\text{-}2\text{H}^+$, although along a axis the networks are packed in parallel fashion, they are not parallel along the c axis with a tilt of 42.7° with respect to those along the b axis (Fig. 8c). Along the c axis, the Au-Au distance is *ca* 19.48 Å.

The dodecadecyl alkyl chains are interdigitated along both a and c axis (Fig. 8b and c).

Figure 8 : Portions of the structure obtained upon combining $4\text{-}2\text{H}^+$ with $[\text{Au}(\text{CN})_2]^-$ showing the connectivity pattern between the anionic and cationic tectons forming a 1-D H-bonded network running along the b axis (a), the parallel packing of the 1-D networks along the a axis (b) and along the c axis (c). For distances and angles see text. For the representation of packing (a and b, the consecutive networks are differentiated by colour and H atoms are omitted for clarity.

For the 2D organisation obtained with $[\text{Ag}(\text{CN})_2]^-$, two of the four alkyl chains of $4\text{-}2\text{H}^+$ are disordered. For the anionic partner, coordination geometry around the Ag(I) centre is linear (C-Ag-C angle of $180.000(1)^\circ$). N-Ag angles of $175.4(5)^\circ$ and $179.0(5)^\circ$ and Ag-C and C $\equiv$ N distances in the 2.062(6)-2.065(5) Å and 1.120(5)-1.136(6) Å ranges are observed respectively. All dicationic and mono anionic units are interconnected through strong charge assisted H-bonds with N-N distance varying between *ca* 2.83 and 2.89 Å (Fig. 9a). The connectivity mode is analogous to the one observed for the polymorph β obtained upon combining $2\text{-}2\text{H}^+$ with $[\text{Ag}(\text{CN})_2]^-$ (Fig. 3b). Consecutive $[\text{Ag}(\text{CN})_2]^-$ anions twisted with an angle of 64.0° (Fig. 9a). Within the 2-D network, a rather short Ag-Ag distance of *ca* 3.32 Å is observed (Fig. 9b). The shortest Ag-Ag distance between consecutive planes is equal to *ca* 22.31 Å.

Figure 9 : Portions of the structure of the 2-D network formed between $4\text{-}2\text{H}^+$ and $[\text{Ag}(\text{CN})_2]^-$ showing views along (a) and perpendicular (b) to Ag-axis. For distances and angles see text. H atoms are not represented for clarity.

The purity of both $[\text{Ag}(\text{CN})_2]_2[4\text{-}2\text{H}^+]$ and $[\text{Au}(\text{CN})_2]_2[4\text{-}2\text{H}^+]$ crystalline materials was investigated by PXRD which revealed a good fit between the simulated and observed patterns (Fig. 10).

Figure 10: Powder X-ray diffraction study showing the comparison between simulated (a for $[\text{Au}(\text{CN})_2]_2[4\text{-}2\text{H}^+]$ (1D) and d for $[\text{Ag}(\text{CN})_2]_2[4\text{-}2\text{H}^+]$ (2D)) and recorded (b for $[\text{Au}(\text{CN})_2]_2[4\text{-}2\text{H}^+]$ and c for $[\text{Ag}(\text{CN})_2]_2[4\text{-}2\text{H}^+]$) patterns. Differences in peaks intensities are due to preferential orientations of the microcrystalline powders.

Effects of alkyl chain length on the packing: For all networks obtained upon combining $\text{X-}2\text{H}^+$ ($\text{X} = 1\text{-}4$) with $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Ag}$ or Au) anions, the M-M distance within the network (4.42 Å for $[\text{Ag}(\text{CN})_2]_2[2\text{-}2\text{H}^+]$ (1D), 3.29 Å for $[\text{Ag}(\text{CN})_2]_2[2\text{-}2\text{H}^+]$ (2D), 4.92 Å for $[\text{Ag}(\text{CN})_2]_2[3\text{-}2\text{H}^+]$ (1D), 4.44 Å for $[\text{Au}(\text{CN})_2]_2[3\text{-}2\text{H}^+]$ (1D), 4.62 Å for $[\text{Au}(\text{CN})_2]_2[4\text{-}2\text{H}^+]$ (1D) and 3.32 Å $[\text{Ag}(\text{CN})_2]_2[2\text{-}2\text{H}^+]$ (2D)) is almost not affected by the length of the alkyl chain. This is not surprising and expected since this distance is imposed to a certain degree by the nature of the rigid aryl spacer connecting the two cyclic amidinium cations.

For the $[M(CN)_2]_2[X-2H^+]$ ($M = Ag$ or Au and $X = 1^{15-3}$) systems for which 1-D arrays are packed in a parallel mode along both other axes, whereas the M-M distance between consecutive networks along a axis does not reflect the difference in size between H for $1-2H^+$ and hexyl chains for $3-2H^+$, along the c axis, the M-M distance increases with the size of the substituent (7.15 Å and 7.37 Å for $M = Ag$, and Au respectively for $1-2H^+$ and 13.80 and 13.75 Å for $M = Ag$, and Au respectively for $3-2H^+$). For $[Ag(CN)_2]_2[2-2H^+]$ and $[Au(CN)_2]_2[4-2H^+]$, since the packing mode is different, this comparison can not be made.

It is worth noting that for both $[Ag(CN)_2]_2[2-2H^+]$ (1D) and $[M(CN)_2]_2[3-2H^+]$ (1D), among the four alkyl chains, two (one on each extremity) are roughly within the main plane of the unit whereas the other two, in *trans* configuration, are pointing almost perpendicular to the main plan of the tecton (tilt angles of 66.6°, 66.5° and 66.5° for $[Ag(CN)_2]_2[2-2H^+]$, $[Ag(CN)_2]_2[3-2H^+]$ and $[Au(CN)_2]_2[3-2H^+]$ respectively). This orientation of the chains is responsible for the increase of the distance between consecutive 1-D networks along the c axis. In marked contrast with $[M(CN)_2]_2[2-2H^+]$ and $[M(CN)_2]_2[3-2H^+]$, in the case of the centrosymmetric $[Au(CN)_2]_2[4-2H^+]$, the two alkyl chains located on each extremity of the tecton are *syn* oriented and almost perpendicular to the main plane of the unit. This peculiar orientation of the C12 chains is probably responsible for the different packing mode observed.

Luminescent properties: All the obtained crystalline materials exhibits blue luminescence upon irradiation at 370 nm (Fig. 11). The fluorescence may be due to both metal centred transitions (closed-shell $d^{10}-d^{10}$ interactions)²² resulting from rather short the M-M distance and metal to ligand charge transfer. Indeed, for the 1-D networks the M-M distance is in the 4.42-4.92 Å range. Even for the 2-D networks obtained with $2-2H^+$ and $4-2H^+$, owing to their peculiar connectivity pattern, a M-M distance in the 3.29-3.32 Å range is observed. It is worth noting that, for the 1-D systems, the blue luminescence observed is probably due to intermetallic interactions within networks imposed by the design of tectons $[X-2H^+]$ ($X = 1-4$). Indeed, the M-M distance between 1-D networks is too long to allow any interaction.

Figure 11 : Photomicrograph showing the blue luminescence of the $[M(CN)_2]_2[X-2H^+]$ crystals ($M = Ag$ or Au and $X = 2-4$) when irradiated in the 370 nm region for a) $[Ag(CN)_2]_2[2-2H^+]$ (1D), b) $[Ag(CN)_2]_2[3-2H^+]$ (1D), c) $[Au(CN)_2]_2[3-2H^+]$ and d) $[Ag(CN)_2]_2[4-2H^+]$

Conclusions

We have shown that combinations of bisamidinium dicationic tectons $[X-2H^+]$ ($X = 2-4$) with $[M(CN)_2]^-$ ($M = Ag$ or Au) anions leads to the formation of crystalline materials resulting from the interconnection of the cationic and anionic tectons by strong charge-assisted H-bonds. Whereas in the case of $2-2H^+$ two polymorphs corresponding to 1- and 2-D H-bonded networks (polymorphs α and β) differing by the connectivity patterns between tectons have been obtained, for $3-2H^+$, only a 1-D network was observed in the presence of $[M(CN)_2]^-$ ($M = Ag$ or Au) anions. For $4-2H^+$, whereas with $[Au(CN)_2]^-$ anion a 1-D network was obtained, with $[Ag(CN)_2]^-$ anion the formation of a 2-D network was observed. The study of the role played by the size of substituents on the extremities of cationic tectons (H for $1-2H^+$, propyl for $2-2H^+$, hexyl for $3-2H^+$ and dodecyl for $4-2H^+$) on the packing of 1-D networks revealed, as expected no effect on the M-M distance for metal centres located within the 1-D networks. Owing to the orientation of the alkyl chains for $2-2H^+$ and $3-2H^+$, whereas for the packing of 1-D networks along a axis, the M-M distance was not reflecting the size of the substituent, along the c axis, a correlation was observed. The M-M distance is imposed in the case of the analogous 1-D networks by the aryl spacer connecting the two cyclic amidinium units. In the case of 1-D networks, it is worth noting that the luminescence property observed for both metal centres ($Ag(I)$ and $Au(I)$) is probably due to the controlled disposition of $[M(CN)_2]^-$ anions in close proximity resulting from specific recognition events taking place between anionic and cationic tectons. The combination of other dicationic tectons with cyanometallate anions is currently under investigation.

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Experimental

Single-Crystal Studies.

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-K α ($\lambda = 0.71073$) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using the APEX (1.022) package. The hydrogen atoms were introduced at calculated positions and not refined (riding model).²³

Powder diffraction studies (PXRD)

Diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-K α radiation with a scanning range between 3.8 and 30° using a scan step size of 2°/mn.

Luminescent images

Luminescence images have been obtained using the Zeiss

Axioplan 2 microscope equipped with a Filter Set 02488002-9901-000 G 365 FT 395 LP 420 (G = excitation, LP = dichroic mirror).

Synthesis

The synthesis of $[2\text{-}2\text{H}^+][\text{Cl}^-]_2$ has been already described.¹⁸

The chemicals purchased from commercial sources were used without further purification.

The synthesis of $[3\text{-}2\text{H}^+][\text{Cl}^-]_2$ and $[4\text{-}2\text{H}^+][\text{Cl}^-]_2$ have been achieved following the already described procedure^{18, 24} for

$[2\text{-}2\text{H}^+][\text{Cl}^-]_2$ (scheme 1).

Synthesis of the dinitrile 6²⁴: A solution of malononitrile **5** (5 g, 75.7 mmol) in anhydrous THF (100 ml) was added dropwise to a suspension of NaH (4.5 g, 189 mmol) in THF (80 ml) at 0°C and the mixture was stirred for 2 hrs before 1-bromohexane (31.2 g, 189 mmol) dissolved in 40 ml of dry THF was added. The mixture was refluxed for 26 hrs under argon. The excess of sodium hydride was quenched with MeOH (15 ml) and solvents were evaporated. The product was extracted with CH_2Cl_2 (160 ml) and the organic layer was washed with H_2O (200 ml) and a saturated solution of NaCl (200 ml) before it was dried over MgSO_4 and evaporated. The residue was purified by column chromatography (SiO_2 , cyclohexane) affording the desired dinitrile **6** as a yellowish oil in 27 % yield. ¹H-NMR (CDCl_3 , δ ppm): 0.89 (t, 6H, ³J = 6.3 Hz, CH_3), 1.31 (m, 12H, CH_2), 1.68 (m, 4H, $\text{CH}_2\text{-CH}_2\text{-C}$), 1.91 (m, 4H, $\text{CH}_2\text{-C}$) ; ¹³C-NMR (CDCl_3 , δ ppm): 13.96 (CH_3), 22.40, 25.50, 28.48, 31.27, 37.77 (CH_2 *n*-hexyle + C quat.), 115.82 ($\text{C}\equiv\text{N}$).

Synthesis of the dinitrile 7²⁴: A solution of malonitrile **5** (5.4 g, 82 mmol) in anhydrous THF (60 ml) was added dropwise to a suspension of NaH (4.3 g, 181 mmol) in THF (80 ml) at 0 °C and the mixture stirred for 30 min. 1-bromododecane (41 g, 164 mmol) dissolved in dry THF (40 ml) was added and the mixture was first stirred during 2 hrs at room temperature and then refluxed for 17 hrs under argon. The excess of sodium hydride was quenched with MeOH (15 ml) and the solvents were evaporated. The residue was suspended in water and the pH was adjusted to 1 with an HCl solution. The product was extracted with Et_2O (3 x 100 ml) and the organic layer washed with H_2O (100 ml) and a saturated solution of NaCl (100 ml) before it was dried over MgSO_4 and evaporated. The residue was further washed with CH_2Cl_2 (100 ml) and water (100 ml) before it was dried over MgSO_4 and evaporated. The residue was purified by column chromatography (SiO_2 , cyclohexane $\rightarrow$ CH_2Cl_2) affording the desired dinitrile **7** as a white solid in 74 % yield. ¹H-NMR (CDCl_3 , δ ppm): 0.88 (t, 6H, ³J = 6.3 Hz, CH_3), 1.26 (m, 36H, CH_2), 1.65 (m, 4H, $\text{CH}_2\text{-CH}_2\text{-C}$), 1.90 (m, 4H, $\text{CH}_2\text{-C}$). ¹³C-NMR (CDCl_3 , δ ppm): 14.18 (CH_3), 22.77, 25.63, 28.95, 29.24, 29.46, 29.61, 29.68, 31.99, 37.90 (CH_2 *n*-dodecyle + C quat.), 115.91 ($\text{C}\equiv\text{N}$).

Synthesis of the diamine 8²⁴: A BH_3 solution in THF (1N, 50 ml) was added dropwise to a solution of the dinitrile **6** (2.0 g, 8.5 mmol) in anhydrous THF (50 ml). The reaction mixture was refluxed for 24 hrs under argon. The excess of BH_3 was quenched carefully with water (10 ml) and the solvents were evaporated. To the residue thus obtained, 100 ml of a solution (MeOH 50%, H_2O 25%, HCl (12N) 25%) was added and the

mixture refluxed overnight. After evaporating the solvents, an aqueous solution of NaOH was added dropwise until the pH 13 was reached. The product was extracted several times with CH_2Cl_2 (3 x 80 ml). The organic layer was further washed with H_2O (80 ml), dried over MgSO_4 and evaporated to dryness affording the diamine **8** as a colourless oil in ca 90 % yield. The latter was directly used in the next step. ¹H-NMR (CDCl_3 , δ ppm): 0.87 (t, 6H, ³J = 6.5Hz, CH_3), 1.15, 1.30 (m, 20H, CH_2 *n*-hexyle), 2.51 (s, 4H, $\text{CH}_2\text{-NH}_2$). ¹³C-NMR (CDCl_3 , δ ppm): 14.00 (CH_3), 22.62, 22.82, 30.24, 31.82, 32.49, 40.27 (CH_2 *n*-hexyle + C quat.), 46.13 ($\text{CH}_2\text{-NH}_2$).

Synthesis of the diamine 9²⁴: A BH_3 solution in THF (1N, 110 ml) was added dropwise to a solution of the dinitrile **7** (6 g, 15.8 mmol) in anhydrous THF (50 ml). The reaction mixture was refluxed for 24 hrs under argon. The excess of BH_3 was quenched carefully with water (20 ml) and the solvents were evaporated. To the residue was added to 200 ml of a mixture of MeOH (50%), H_2O (25%) and HCl (12N, 25%) and the mixture was refluxed 22 hrs. After evaporating the solvents, an aqueous solution of NaOH was added dropwise until the pH = 13 was reached. The product was extracted several times into CH_2Cl_2 (3 x 100 ml). The organic layer was further washed with H_2O (10 ml), dried over MgSO_4 and evaporated to dryness affording the diamine **9** as a colourless oil in ca 90 % yield. The latter was directly used in the next step. ¹H-NMR (CDCl_3 , δ ppm): 0.83 (t, 6H, ³J = 6.5 Hz, CH_3), 1.21 (m, 44H, CH_2 *n*-dodecyle), 2.50 (s, 4H, $\text{CH}_2\text{-NH}_2$). ¹³C-NMR (CDCl_3 , δ ppm): 14.13 (CH_3), 22.72, 22.92, 29.39, 29.71, 30.57, 31.96, 32.60, 39.31 (CH_2 *n*-dodecyle + C quat.), 47.03 ($\text{CH}_2\text{-NH}_2$).

Synthesis $[3\text{-}2\text{H}^+][\text{Cl}^-]_2$: Diamine **8** (5.0 g, 21.3 mmol) and 1,4-dicyanobenzene (1.35g, 10.5 mmol) and P_2S_5 (100 mg) as catalyst were mixed under argon and the temperature was first raised to 120 °C for 30 min and then to 180 °C for another 30 min. The mixture was dissolved in CH_2Cl_2 (100 ml) and acidified with 100 ml of an aqueous 10% HCl solution. The mixture was stirred vigorously and Et_2O (150 ml) was added. The solvents were evaporated and $[3\text{-}2\text{H}^+][\text{Cl}^-]_2$ was obtained as a white solid with an overall yield of 21 %. Mp: decomposition at 240 °C. ¹H-NMR (CD_3OD , δ ppm) : 0.90 (t, 12H, ³J = 6.5 Hz, CH_3), 1.33 (m, 88H, CH_2 *n*-hexyle), 3.38 (s, 8H, $\text{CH}_2\text{-NH}_2$), 7.97 (s, 4H, CH arom.); ¹³C-NMR (CD_3OD , δ ppm): 19.97 (CH_3), 22.2, 29.5, 30.6, 31.4, 32.7 (CH_2 *n*-hexyle + C quat.), 47.7 ($\text{CH}_2\text{-NH}_2$), 128.3 (CH arom.), 159.0 (N-C=N). Elemental analysis: $\text{C}_{38}\text{H}_{68}\text{N}_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, calculated: C = 66.35 %, H = 10.55 %, N = 8.14 %, found: C = 66.56 %, H = 10.70 %, N = 7.88 %. IR (cm^{-1}): 2954, 2932, 2862, 1516, 1469, 1350, 1328, 1298, 1187, 984, 853, 832, 723, 799. ES MS : m/z : 290.29, calculated 290.27 ($[3\text{-}2\text{H}^+]$, $\text{C}_{38}\text{H}_{68}\text{N}_4$), 579.54, calculated 579.54 ($[3\text{-H}^+]$, $\text{C}_{38}\text{H}_{67}\text{N}_4$). Decomposition at 240 °C.

Synthesis $[4\text{-}2\text{H}^+][\text{Cl}^-]_2$: Diamine **9** (3.0 g, 7.32 mmol) and 1,4-dicyanobenzene (469 mg, 3.66 mmol) and P_2S_5 (15 mg) as catalyst were mixed under argon and the temperature was first raised to 180 °C for 1 hr and then to 230 °C during 1.5 hr. The mixture was dissolved in CH_2Cl_2 (80 ml) and acidified with 80 ml of an aqueous solution of HCl (5%). The mixture was stirred vigorously and Et_2O (150 ml) was added. The solvents

were evaporated and $[4\text{-}2\text{H}^+][\text{Cl}^-]_2$ was obtained as a white solid with an overall yield of 15 %. Mp: decomposition at 235 °C. $^1\text{H-NMR}$ (CDCl_3 , δ ppm) : 0.87 (t, 12H, $^3\text{J} = 6.5$ Hz, CH_3), 1.21 (m, 88H, CH_2 *n*-dodecyle), 3.34 (s, 8H, $\text{CH}_2\text{-NH}_2$), 8.46 (s, 4H, CH arom.), 10.67 (br, 4H, NH) ; $^{13}\text{C-NMR}$ (CD_3OD , δ ppm) : 13.0 (CH_3), 22.3, 29.1, 29.3, 29.7, 30.6, 31.6, 32.6 (CH_2 *n*-dodecyle); 128.3 (CH arom.). Elemental analysis: $\text{C}_{62}\text{H}_{116}\text{N}_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ calculated: C = 73.98 %, H = 11.82 %, N = 5.57 %, found: C = 74.20 %, H = 11.70 %, N = 5.13 %. IR (cm^{-1}): 2957, 2929, 2852, 1464, 1331, 1293, 1188, 1100, 1023, 990, 858, 841, 698. ES MS : m/z : 458.46, calculated 456.46 ($[4\text{-}2\text{H}^+]$, $\text{C}_{62}\text{H}_{116}\text{N}_4$), 915.91, calculated 915.91 ($[4\text{-}2\text{H}^+]$, $\text{C}_{62}\text{H}_{115}\text{N}_4$). Decomposition at 235 °C.

Crystallisation

Crystallisation of $[3\text{-}2\text{H}^+][\text{Cl}^-]_2$: Colourless crystals of $[3\text{-}2\text{H}^+][\text{Cl}^-]_2$ of molecular formula $\text{C}_{38}\text{H}_{68}\text{N}_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ were obtained by slow evaporation of a solution of $[3\text{-}2\text{H}^+][\text{Cl}^-]_2$ (4 mg) dissolved in EtOH (5 ml).

Formation of crystals of $[2\text{-}2\text{H}^+][\text{Ag}(\text{CN})_2]_2$ (polymorph α): Colourless crystals were obtained upon slow evaporation of a solution of $[2\text{-}2\text{H}^+][\text{Cl}^-]_2$ (4 mg) and $\text{KAg}(\text{CN})_2$ (3 mg) dissolved in EtOH (5 ml). Yield: ca. 65%. IR: $\nu_{\text{C}\equiv\text{N}} = 2134$ cm^{-1} . Decomposition above 280 °C.

Formation of crystals of $[2\text{-}2\text{H}^+][\text{Ag}(\text{CN})_2]_2$ (polymorph β): In a crystallization tube (4 mm diameter) equipped with a stopper, upon slow diffusion at 4 °C, through a layer of distilled H_2O (0.6 ml), of a MeOH solution (0.4 ml) of $[2\text{-}2\text{H}^+][\text{Cl}^-]_2$ (4 mg) into an aqueous solution (0.6 ml) of $\text{KAg}(\text{CN})_2$ (4 mg), colourless crystals of $[2\text{-}2\text{H}^+][\text{Ag}(\text{CN})_2]_2$ were obtained after two weeks. Yield: ca. 75%. IR: $\nu_{\text{C}\equiv\text{N}} = 2137$ cm^{-1} . Decomposition above 280 °C.

Formation of crystals of $[3\text{-}2\text{H}^+][\text{Au}(\text{CN})_2]_2$: A saturated MeOH solution (5 ml) of $\text{KAu}(\text{CN})_2$ (12 mg) was added to a saturated MeOH solution (5 ml) of $[3\text{-}2\text{H}^+][\text{Cl}^-]_2$ (10 mg). The white precipitate thus obtained was filtered after one hour and redissolved in a minimum of *i*Pr-OH. Colourless crystals of $[3\text{-}2\text{H}^+][\text{Au}(\text{CN})_2]_2$ appeared after several days upon slow evaporation at room temperature. Yield: ca. 45%. Elemental analysis: $\text{C}_{42}\text{H}_{68}\text{Au}_2\text{N}_4$, calculated: C = 49.31 %, H = 6.70 %, N = 5.48 %, found: C = 50.11 %, H = 6.54 %, N = 4.9 %. IR: $\nu_{\text{C}\equiv\text{N}} = 2156$ cm^{-1} . Decomposition above 300 °C.

Formation of crystals of $[3\text{-}2\text{H}^+][\text{Ag}(\text{CN})_2]_2$: The same procedure as for $[3\text{-}2\text{H}^+][\text{Au}(\text{CN})_2]_2$ was applied using 12 mg of $\text{KAg}(\text{CN})_2$. Yield ca. 70%. IR: $\nu_{\text{C}\equiv\text{N}} = 2138$ cm^{-1} .

Decomposition above 300 °C.

Formation of crystals of $[4\text{-}2\text{H}^+][\text{Au}(\text{CN})_2]_2$ (polymorph α): A saturated MeOH solution (5 ml) of $\text{KAu}(\text{CN})_2$ (10 mg) was added to a saturated MeOH solution (5 ml) of $[4\text{-}2\text{H}^+][\text{Cl}^-]_2$ (10 mg). The white precipitate thus formed was filtered after one hour and redissolved in a minimum of MeOH. Colourless crystals of $[4\text{-}2\text{H}^+][\text{Au}(\text{CN})_2]_2$ appeared after ca 2 weeks upon evaporation at room temperature. Yield: ca. 55%. Elemental analysis: $\text{C}_{66}\text{H}_{116}\text{Au}_2\text{N}_8$, calculated: C = 56.00 %, H = 8.26 %, N = 7.92 %, found: C = 56.41 %, H = 7.97 %, N = 7.28 %. IR: $\nu_{\text{C}\equiv\text{N}} = 2154$ cm^{-1} . Decomposition above 300 °C.

Formation of crystals of $[4\text{-}2\text{H}^+][\text{Ag}(\text{CN})_2]_2$ (polymorph β): The same procedure as for $[4\text{-}2\text{H}^+][\text{Au}(\text{CN})_2]_2$ was

applied using 10 mg of $\text{KAg}(\text{CN})_2$. Yield: ca. 55%. Elemental analysis: $\text{C}_{66}\text{H}_{116}\text{Ag}_2\text{N}_8$, calculated: C = 64.06 %, H = 9.45 %, N = 9.06 %, found: C = 63.26 %, H = 8.86 %, N = 8.91 %. Yield : ca. 75% . IR: $\nu_{\text{C}\equiv\text{N}} = 2135$ cm^{-1} . Decomposes above 300 °C.

Notes and references

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Table 1. Crystallographic Parameters (wavelength = 0.71073 Å, at 173K) for [X-2H⁺](X= 2-4) combined with Cl⁻, Au(CN)₂⁻ or Ag(CN)₂⁻.

Formula	[3-2H ⁺][Cl ⁻] ₂ (1D) C ₃₈ H ₆₈ N ₄ Cl ₂ , 2(H ₂ O)	[2-2H ⁺][Ag(CN) ₂ ⁻] ₂ (1D) C ₃₀ H ₄₄ Ag ₂ N ₈	[2-2H ⁺][Ag(CN) ₂ ⁻] ₂ (2D) C ₃₀ H ₄₄ Ag ₂ N ₈	[3-2H ⁺][Ag(CN) ₂ ⁻] ₂ (1D) C ₄₂ H ₆₈ Ag ₂ N ₄	[3-2H ⁺][Au(CN) ₂ ⁻] ₂ (1D) C ₄₂ H ₆₈ Au ₂ N ₄	[4-2H ⁺][Au(CN) ₂ ⁻] ₂ (1D) C ₄₂ H ₆₈ Au ₂ N ₄
Molecular weight	687.90	732.47	732.47	900.78	1078.98	1078.98
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P2(1)/c	P-1	P-1	P-1	P-1
a(Å)	9.2183(7)	6.7993(4)	6.5879(2)	6.4924(4)	6.5286(13)	6.5286(13)
b(Å)	9.5015(7)	19.1350(10)	11.3381(4)	13.0691(8)	12.843(3)	12.843(3)
c(Å)	24.6412(18)	12.7204(6)	12.2853(4)	13.8015(7)	13.746(3)	13.746(3)
α(deg)	83.832(3)	90	112.8290(10)	90.224(2)	89.31(3)	89.31(3)
β(deg)	81.225(2)	94.261(2)	91.8580(10)	95.777(2)	83.39(3)	83.39(3)
γ(deg)	76.505(3)	90	104.2740(10)	98.978(2)	81.26(3)	81.26(3)
V(Å ³)	2068.3(3)	1650.41(15)	811.18(5)	1150.60(12)	1131.6(4)	1131.6(4)
Z	2	2	1	1	1	1
Colour	colourless	colourless	colourless	colourless	colourless	colourless
Crystal dim (mm)	0.20 x 0.15 x 0.15	0.20 x 0.06 x 0.05	0.08 x 0.04 x 0.01	0.04 x 0.04 x 0.03	0.06 x 0.06 x 0.05	0.06 x 0.06 x 0.05
D _{calc} (gcm ⁻³)	1.105	1.474	1.499	1.300	1.583	1.583
F(000)	756	748	374	470	534	534
μ (mm ⁻¹)	0.192	1.218	1.239	0.887	6.512	6.512
Number of data meas.	17654	9385	11943	9194	12977	12977
Number of data with I > 2σ(I)	8857 [R(int) = 0.0433]	3700 [R(int) = 0.0381]	3686 [R(int) = 0.0282]	5244 [R(int) = 0.0322]	6275 [R(int) = 0.0353]	7666 [R(int) = 0.0353]
R	R ₁ = 0.0562, wR ₂ = 0.1197	R ₁ = 0.0315, wR ₂ = 0.0511	R ₁ = 0.0225, wR ₂ = 0.0552	R ₁ = 0.0393, wR ₂ = 0.0959	R ₁ = 0.0340, wR ₂ = 0.0690	R ₁ = 0.0340, wR ₂ = 0.0690
R _w	R ₁ = 0.1236, wR ₂ = 0.1466	R ₁ = 0.0566, wR ₂ = 0.0540	R ₁ = 0.0303, wR ₂ = 0.0587	R ₁ = 0.0594, wR ₂ = 0.1032	R ₁ = 0.0512, wR ₂ = 0.0733	R ₁ = 0.0512, wR ₂ = 0.0733
GOF	1.025	1.065	1.020	1.028	1.021	1.021
Largest peak in final difference (eÅ ⁻³)	0.542 and -0.547	0.989 and -0.604	0.416 and -0.404	0.702 and -0.401	1.981 and -1.224	1.981 and -1.224