Molecular tectonics: design of luminescent H-bonded molecular networks†

Carmen Paraschiv,[a,b] Sylvie Ferlay,[a] Mir Wais Hosseini,*[a] Véronique Bulach[a] and Jean-Marc Planeix[a]

[a] Laboratoire de Chimie de Coordination Organique, UMR CNRS 7140, Université Louis Pasteur, F-67000 Strasbourg, France. E-mail: hosseini@chimie.u-strasbg.fr
[b] Inorganic Chemistry Laboratory, University of Bucharest, 020464-Bucharest, Romania

Using bis-amidinium dications as tetra H-bond donor tectons and Au(CN)$_2$⁻ anion, neutral 1-D networks based on a bis monohapto mode of H-bonding are obtained. Owing to the short metal–metal distance within the network, luminescent crystals are obtained. The emission phenomena may be tuned by the nature of the spacer connecting the two cyclic amidinium groups.

Molecular tectonics[1] deals with the design of tectons[2] and their self-assembly in the crystalline phase into molecular networks. The latter are infinite periodic structures generated by interconnection of tectons based on molecular recognition processes. The understanding of the relationship between tectons features (geometry and energy) and networks characteristics (connectivity, geometry and topology) is a subject of current interest. So far the vast majority of reported studies deals with structural features. However, the design of functional networks remains an important and challenging step. Here we report not only on the design of luminescent networks but also on the tuning of the emission phenomena.

Although the design of molecular networks may be based on a variety of reversible intermolecular interactions such as van der Waals interactions, H- and/or coordination- bonding, let us focus here on the H-bond. The latter is the most used attractive interaction for the formation of molecular networks.[3]

Dicationic bis-amidiniums possessing two sets of two acidic hydrogen atoms on each face are tetra H-bond donors. These molecules are interesting tectons since one may easily control the distance between acidic protons on each face. The analysis of the recognition pattern on each face of these tectons reveals two possible modes of H-bonding (mono- and di-hapto). We have previously demonstrated the generation of H-bonded networks between such tectons and a variety of anionic species.[4] In particular, by tuning the distance between the two cyclic moieties through the choice of appropriate spacers, one can impose a dihapto mode of H-bonding with carboxylates[5] (Fig. 1a), tetra-[6] (Fig. 1b) or hexacyanometallates.[7] A further possibility, based on the monohapto mode of H-bonding, may be explored through the use of bis monodentate linear anions (Fig. 1c). Rather interestingly, in that case, one must be able to control the distance between the two anionic units on the same face of the tecton through the choice of the spacer connecting the two amidinium rings.

As linear bis-monodentate anion, Au(CN)$_2$⁻ complex was chosen because of its chemical stability and optical properties. Indeed, because of aurophilic interactions,[8] these species show distance dependent luminescence both in solution and in the solid state.[9] The control of Au–Au distance by combining Au(CN)$_2$⁻ anion with mono ammonium[10] and mono amidinium[11] cations has already been reported.

Dealing with the amidinium type tecton, both dications 1[12] and 2[13] (Scheme 1) were used. For these two tectons, because of the difference between ethyl and phenyl spacers connecting the two amidinium rings, the distances between the two N atoms located on the same face are *ca.* 5.2 Å and 7 Å.

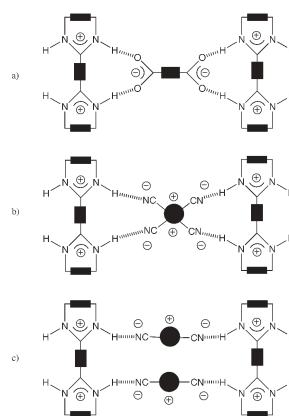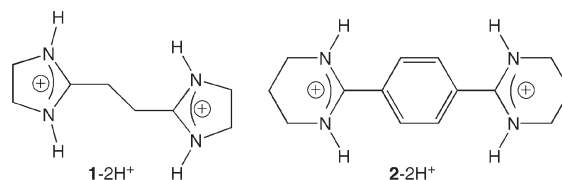In an 8 mm diameter crystallisation tube, at r.t., upon slow

Fig. 1 Schematic representation of portions of H-bonded 1-D networks formed between bis amidinium tectons and carboxylates (a), tetracyanometallates (b) and dicyanometallate (c).

1-2H⁺   **2**-2H⁺

Scheme 1

diffusion through an EtOH layer (1 ml) of an aqueous solution (1 ml) of compound **1** (0.05 M, 13.2 mg) into an aqueous solution (1 ml) of K[Au(CN)$_2$] (0.1 M, 28.8 mg), colourless single-crystals were obtained after several days. The X-ray diffraction study‡ revealed that the crystal (monoclinic system, with *C*2/*c* as the space group) is exclusively composed of **1** dication and Au(CN)$_2$⁻ anion (Fig. 2a).

For the tecton **1**, possessing a crystallographic inversion centre of symmetry, all four acidic protons are localised on the nitrogen atoms of **1**. Within each NCN fragment, the C–N distance and N–C–N angle are in the range of 1.29–1.32 Å and 112.5° respectively. Both five-membered amidinium rings are parallel and
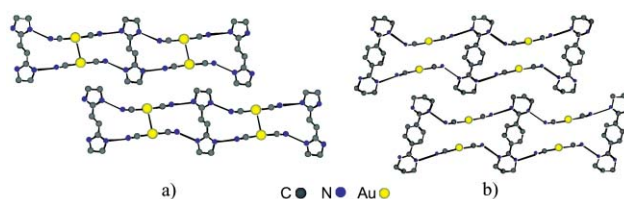

Fig. 2 Portions of X-ray structures showing the formation and packing of consecutive 1-D H-bonded network obtained between Au(CN)$_2$⁻ and tectons **1** (a) and **2** (b). For bond distances and angles see text. H atoms are omitted for clarity.

† Dedicated to J.-P. Sauvage on the occasion of his 60th birthday.

coplanar (NCCC dihedral angles of –52.0° and 51.9°). The ethyl fragment connecting the two amidinium rings is in the *trans* conformation (CCCC dihedral angle of −180°). The nitrogen atoms localised on the same side of the molecule are distant by 5.23 Å.

For the anionic unit $Au(CN)_2^-$, the coordination geometry around the Au(I) centre is almost linear (CAuC angle of 175.3° and NCAu angle of 175.5° and 177.3°) with Au–C and CN distances varying between 1.982 and 1.990 Å and 1.151 and 1.157 Å respectively.

All the dicationic and mono anionic units are interconnected through strong H-bonds and electrostatic charge–charge interactions leading to a neutral 1-D network. As expected (Fig. 1c), the bridging of consecutive tectons **1** is ensured by $Au(CN)_2^-$ anions 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 **1** (N–N distance varying between 2.863 and 2.889 Å). Consequently, each face of the tecton **1** is connected to two $Au(CN)_2^-$ anions with Au–Au distance of 3.33 Å. The 1-D networks are packed in a parallel fashion. The shortest Au–Au distance between consecutive networks in one plane and between consecutive planes are 7.8 Å and 5.4 Å respectively.

In an 8 mm diameter crystallisation tube, at r.t., upon slow diffusion through an EtOH layer (1 ml) of an aqueous solution (1 ml) of compound **2** (0.015 M, 10 mg) into an aqueous solution (1 ml) of K[Au(CN)$_2$] (0.030 M, 10 mg), colourless single-crystals were obtained after several days. The X-ray diffraction study‡ revealed that the crystal (triclinic system, with *P*-1 as the space group) is again exclusively composed of **2** dication and $Au(CN)_2^-$ anion (Fig. 2b).

Again, all four acidic protons are localised on the nitrogen atoms of **2**. For the NCN (angle of 121.5°) fragment, the C–N distance is in the range of 1.311–1.319 Å. Both six-membered amidinium rings adopt a half chair conformation and are almost parallel and coplanar but tilted with respect to the phenyl ring with NCCC dihedral angle varying between −37.2° and 37.0°. The distance between nitrogen atoms localised on the same face of the tecton is 7.03 Å.

The characteristics for anionic unit $Au(CN)_2^-$ are almost identical to the above-mentioned case (CAuC angle of 175.4°; NCAu angle of 175.8° and 176.8°; Au–C and CN distances varying between 1.986 and 1.990 Å and 1.147 and 1.148 Å respectively).

As in the previous case, an analogous neutral 1-D network is formed (Fig. 1c), the bridging between cationic and anionic tectons is identical to the above mentioned case using the tecton **1** (N–N distance varying between 2.900 and 2.927 Å). However, because of the longer distance between H-bond donor atoms localised on the same face of the molecule (7.03 Å) with respect to the case using the tecton **1** (5.23 Å), a Au–Au distance of 4.22 Å is observed. The 1-D networks are again packed in a parallel fashion, shortest Au–Au distances between consecutive networks in one plane and between consecutive planes of 9.52 Å and 6.75 Å respectively.

Tectons **1** and **2** were not only designed for the formation of H-bonded networks in the presence of anions such as $Au(CN)_2^-$, but also for the generation of photoluminescence through the control of Au–Au distance within the recognition pattern. As expected, for combinations of **1** and **2** with $Au(CN)_2^-$ rather short and long Au–Au distances of 3.3 Å and 4.2 Å are observed respectively.

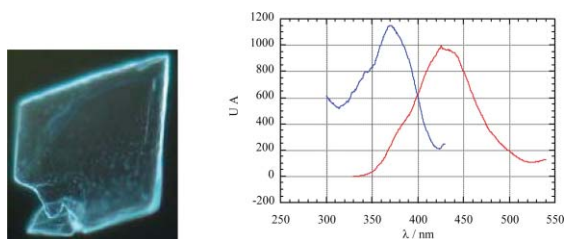Interestingly, colourless crystals obtained using the tecton **1** are

strongly luminescent at room temperature (Fig. 3 left). Their excitation at 370 nm generates a blue emission ($\lambda_{max} = 430$ nm) (Fig. 3 right). This photoluminescence may be attributed to aurophilic interactions. Indeed, the short Au–Au distance of 3.3 Å is perfectly compatible with such interactions.

Although, in the case of **2**, the Au–Au distance of 4.2 Å is much longer than 3.6 Å which is commonly accepted as an upper limit for aurophilic interactions,[14] nevertheless, crystals formed in the presence of **2** were also weakly luminescent.

In conclusion, we have demonstrated that dicationic tectons **1** and **2** lead in the presence of $Au(CN)_2^-$ linear anion to the formation of 1-D H-bonded networks which are formed by bridging of consecutive dicationic tectons by anions through a monohapto mode of H-bonding. It was also demonstrated that the Au–Au distance within the network can be finely "tuned" by the nature of the spacer connecting the amidinium cyclic moieties. Interestingly, in both cases the crystals formed are photoluminescent. The formation of other functional photonic networks using silver complexes as well as chiral analogues of **1** and **2** is under current investigation.

Notes and references

‡ (**1**–2H$^+$–2AuCN$_2^-$)$_n$: (Colourless, 173 K), C$_{12}$H$_{16}$Au$_2$N$_8$, M = 666.26, monoclinic, a = 20.4496(13), b = 6.5736(4), c = 13.0371(7) Å, β = 109.790(5)°, U = 1649.04(17) Å^3, Z = 4, space group C2/c, D_C = 2.68 g cm^{-3}, Mo-Kα, μ = 17.781 mm^{-1}, 2407 independent data with $I > 2\sigma(I)$, R = 0.025, Rw = 0.067. (**2**–2H$^+$–2AuCN$_2^-$)$_n$: (Colourless, 173 K), C$_{18}$H$_{20}$Au$_2$N$_8$, M = 742.36, triclinic, a = 6.7502(2), b = 7.3697(2), c = 11.2137(4) Å, α = 87.514(2), β = 85.612(2), γ = 67.274(2)°, U = 512.97(3) Å^3, Z = 1, space group P$\bar{1}$, D_C = 2.403 g cm^{-3}, Mo-Kα, μ = 14.304 mm^{-1}, 3062 independent data with $I > 2\sigma(I)$, R = 0.021, Rw = 0.052. Data were collected on a Bruker SMART CCD Diffractometer and structural determination was achieved using the SHELXS-97. CCDC 243551 & 243552. See http://www.rsc.org/suppdata/cc/b4/b410459p/ for crystallographic data in .cif or other electronic format.

1 S. Mann, *Nature*, 1993, **365**, 499.
2 M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696.
3 G. D. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York, 1989; M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; G. M. Whitesides, J. P. Mathias and T. Seto, *Science*, 1991, **254**, 1312; F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 1993, **115**, 5991; D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229; J. F. Stoddart and D. Philip, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1155; C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, **22**, 397; S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357; V. A. Russell and M. D. Ward, *Chem. Mater.*, 1996, **8**, 1654.
4 M. W. Hosseini, *Coord. Chem. Rev.*, 2003, **240**, 157.
5 M. W. Hosseini, R. Ruppert, P. Schaeffer, A. De Cian, N. Kyritsakas and J. Fischer, *Chem. Commun.*, 1994, 2135; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 102.
6 S. Ferlay, V. Bulach, O. Felix, M. W. Hosseini, J.-M. Planeix and N. Kyritsakas, *Cryst. Eng. Commun.*, 2002, **4**, 447.
7 S. Ferlay, O. Félix, M. W. Hosseini, J.-M. Planeix and N. Kyritsakas, *Chem. Commun.*, 2002, 702; S. Ferlay, R. Holakovski, M. W. Hosseini, J.-M. Planeix and N. Kyritsakas, *Chem. Commun.*, 2003, 1224; S. Ferlay and M. W. Hosseini, *Chem. Commun.*, 2004, 787.
8 H. Schmidbaur, *Chem. Soc. Rev.*, 1995, **24**, 391; P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.
9 M. A. Rawashdeh-Omary, M. A. Omary and H. H. Patterson, *J. Am. Chem. Soc.*, 2000, **122**, 10371.
10 M. Stender, M. M. Olmstead, A. L. Balch, D. Rios and S. Attar, *J. Chem. Soc., Dalton Trans.*, 2003, 4282.
11 A. H. Schwellnus, L. Denner and J. C. A. Boeyens, *Polyhedron*, 1990, **9**, 975.
12 G. Brand, M. W. Hosseini, R. Ruppert, A. De Cian, J. Fischer and N. Kyritsakas, *New J. Chem.*, 1995, **19**, 9.
13 O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *New J. Chem.*, 1997, **21**, 285.
14 S. S. Pathaneni and G. R. Desiraju, *J. Chem. Soc., Dalton Trans.*, 1993, 319.

Fig. 3 An image under fluorescent microscope of a luminescent crystal obtained upon combining the dicationic tecton **1** with $Au(CN)_2^-$ anion (left) and its excitation and emission spectra at 298 K (right).