Molecular tectonics: generation of 2-D molecular networks by combination of coordination and hydrogen bonds

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The combination of two organic tectons **1** and **2**, based on a 1,4-phenylenediamine backbone functionalised with two pyridine units through amide junctions with $HgCl_2$, leads to the formation of two types of 2-D networks, one of the purely metallo-organic type, based on only coordination bonds, and the other combining both coordination and hydrogen bonds.

Introduction

Molecular tectonics[1–3] is a branch of chemistry dealing with the design, formation and description of molecular networks.[4] This approach is based on individual molecular building blocks or tectons[2] bearing in their structure complementary interaction sites defining recognition patterns. By repetitive processes, these tectons generate molecular networks by translation of recognition patterns. In the crystalline phase, molecular networks are infinite periodic architectures formed upon mutual interconnection between complementary or self-complementary building tectons. Thus, molecular networks are defined by the nature of tectons composing the architecture (shape, interaction sites, and their localisation in space), the type of interaction involved in the interconnection of consecutive tectons and finally, the number of independent translations operating on the recognition patterns.[4] The latter aspect defines the dimensionality of the network (1-, 2- or 3-D). With that respect, the definition of recognition patterns also called supramolecular synthons[5] which upon translation become structural nodes of the network is an important issue. The nature of the recognition pattern is related to the type of interaction taking place between complementary or self-complementary tectons. Various types of attractive interactions (van der Waals contacts, hydrogen bond, coordination bond, π–π, π–cation and electrostatic interactions) have been used to generate a huge variety of molecular networks. Among them, three categories of networks, namely H-bonded,[6] coordination[7] and inclusion[8] networks, are the most commonly reported. However, it is of interest to notice that the formation of the crystal imposes tridimensional packing of networks, which also requires a variety of interactions. In other words, when taking into account all possible interactions, a crystal by definition is a 3-D network. Thus defining a network in the crystalline phase is a subjective issue and requires a hierarchical scale allowing the ranking of recognition patterns. The most appropriate scale would be based on the energy of interactions. For the sake of demonstration, let us restrict ourselves on one hand to a combination of hydrogen and coordination bonds and on the other hand to the formation of 1- and 2-D networks (Fig. 1).

In the case of a bidentate tecton bearing one H-bond and one coordination bond generator (Fig. 1a), clearly two different interaction patterns will take place and, since both patterns are only translated in one direction of space, such a tecton will lead to a 1-D network (Fig. 1d). If considering the pattern based on the H-bond formation (Fig. 1b) as dominant, the network would be qualified as H-bonded network. However, if the coordination bond interconnecting consecutive tectons (Fig. 1c) was considered as dominant, the network would be described as a coordination network. The case of the tetradentate tecton (Fig. 1e) is even more demonstrative. Indeed, the 2-D network formed (Fig. 1h) may either be described as resulting from the interconnection of consecutive 1-D H-bonded networks (Fig. 1f) through coordination bonds (Fig. 1g) or as resulting from the bridging of 1-D coordination networks by H-bonding. However, based on the difference in the energy of interactions, since a coordination bond is stronger than an H-bond, one may consider the recognition pattern based on the coordination bond as primary and the other based on H-bond as secondary. Consequently both networks would be qualified as metallo-organic coordination networks.

Examples of simultaneous use of coordination bonds associated with hydrogen bonds of the amide type have been reported.[9–11]

Let us illustrate the above discussion by two real cases in which the two isomeric tectons **1** and **2** (Scheme 1) are combined with $HgCl_2$. Both combinations lead to the formation of two different types of 2-D networks.

Results and discussion

The design of the organic tectons **1** and **2** (for preparation see experimental section) is based on the aryl group bearing two pyridine moieties as coordinating sites. The junction between the two parts is effected by an amide group. The two tectons, differing only by the position of connection of the amide group to the pyridyl group (position 4 for **1** and 3 for **2**), are structural isomers. It worth noting that the amide junction

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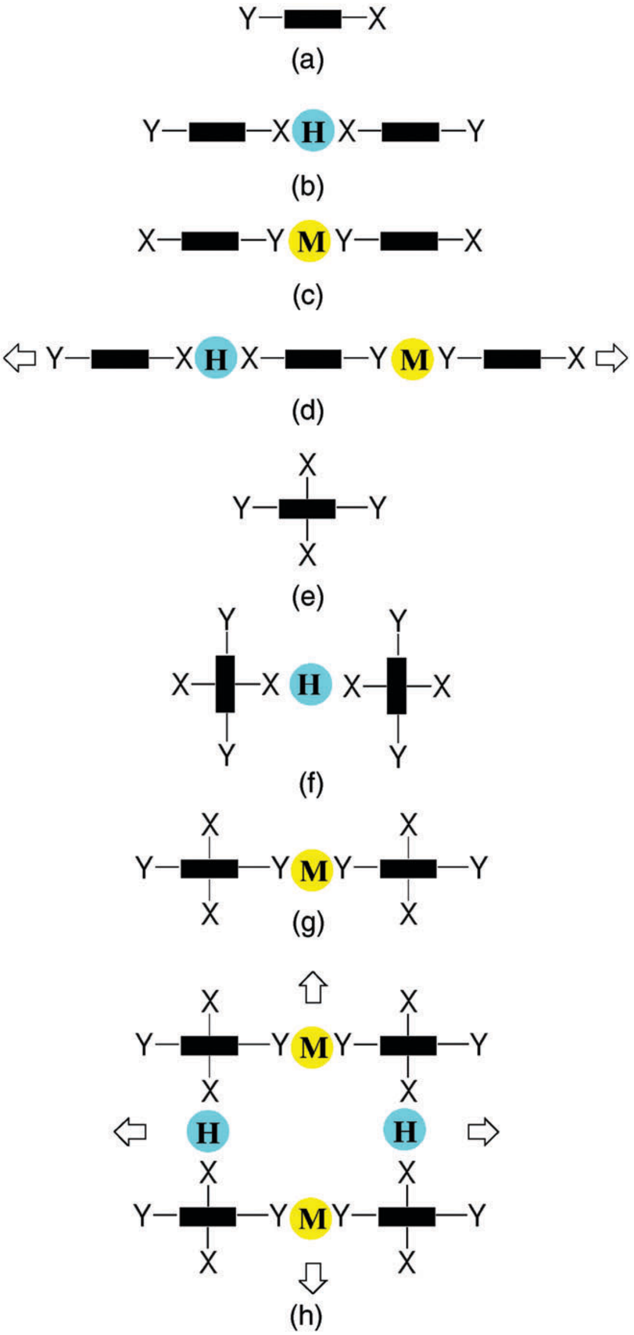
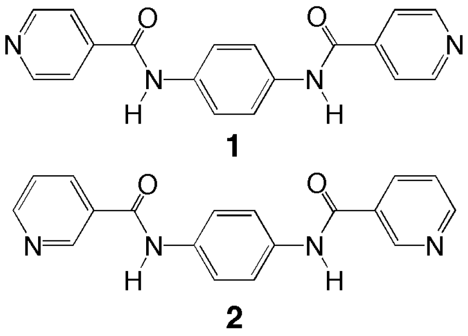


Fig. 1 Schematic representation of 1- and 2-D networks based on tectons bearing different interaction sites. Bidentate (a) or tetradentate (e) tectons bearing X and Y sites able to establish H-bonds (b and f) and coordination bonds (c and g) lead, upon combination of both modes of interactions, to the formation of 1-D (d) or 2-D (h) networks.

might not be an innocent connecting group since it may either be involved in the binding of the metal centre through the oxygen atom of its C=O moiety or establish a hydrogen bond of NH···O type. Although all three components (aryl moiety, pyridine and HNCO group) of both tectons **1** and **2** are rigid units, both possess rotational flexibility and may adopt a variety of conformations and configurations due to the rotational barrier of the amide group (Fig. 2).



Scheme 1

Structural isomers of **1** and **2** based on 1,2-phenylenediamine and 1,3-phenylenediamine have been reported and were shown to generate networks in the presence of a variety of metal centres.[11,12] The formation of a 1-D network based on the use of the tecton **2** and HgI_2 was also previously reported.[13]

Since both tectons **1** and **2** are neutral units, in order to avoid the presence of unbound anions, $HgCl_2$ was chosen as a neutral metallatecton. Furthermore, Hg(II) appeared to us as an interesting cation since it presents rather loose coordination demands. Indeed, it offers a variety of coordination numbers (between 2 and 6) and geometries (linear, tetrahedral, octahedral). Mercury halides have been previously used as metallatectons by others[11–14] and by us.[15]

At room temperature, upon slow diffusion of an EtOH solution of $HgCl_2$ into a DMSO solution of **1**, colourless crystals were obtained after *ca.* one week. X-Ray diffraction on a single crystal (Table 1) revealed that the crystal (monoclinic, $P2/c$) is exclusively composed of **1** and $HgCl_2$. For the organic moiety, presenting a centre of symmetry, among various possible conformations and configurations (Fig. 2), both amide groups ($d_{C=O} = 1.23$ Å, $d_{N-CO} = 1.35$ Å, $d_{C-CO} = 1.49$ Å) of the tecton **1** adopt the *trans* configuration (HNCO dihedral angles of $-172.4°$ and $+172.5°$). The amide groups are neither coplanar with the aryl ring nor the pyridine unit but tilted by 37.5° and 31.0°, respectively. Interestingly, the oxygen atom of the C=O group is located at 2.55 and 2.70 Å from the nearest hydrogen atoms of the aryl group and pyridine, respectively.

When considering only the formation of coordination bonds, the crystal may be described as a neutral 1-D network resulting from the bridging of organic tectons **1** by $HgCl_2$ units. The interconnection takes place through the coordination of Hg(II) by the nitrogen atoms of the pyridine group belonging to consecutive tectons **1** (Fig. 3). The mercury cation is surrounded by two Cl anions ($d_{Hg-Cl} = 2.35$ Å) and two N atoms ($d_{Hg-N} = 2.44$ Å) belonging to two consecutive tectons **1**. The metal centre adopts a distorted tetrahedral coordination geometry (NHgN angle of 96.5°, ClHgCl angle of 152.5° and NHgCl angle of 95.0 and 103.2°).

However, the analysis of the packing of 1-D networks in a plane allowed us to spot another type of specific interaction between consecutive 1-D networks. Indeed, due to the *trans* configuration of both amide groups (*anti–anti*, see Fig. 2) and antiparallel orientation of the C=O groups (see Fig. 2), consecutive 1-D networks are interconnected through H bonds

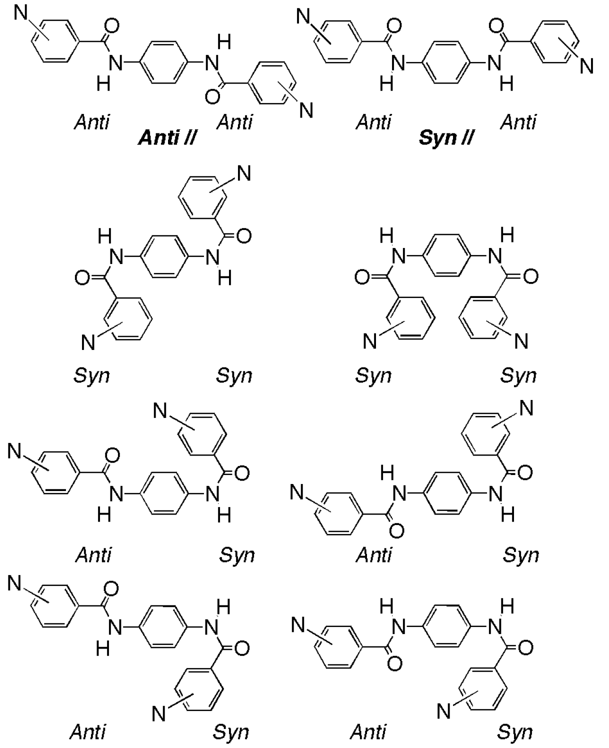


Fig. 2 Representation of some of the different conformations and configurations which may be adopted by tectons **1** and **2** supposing that the aryl ring, the pyridine and the amide group are in the same plane.

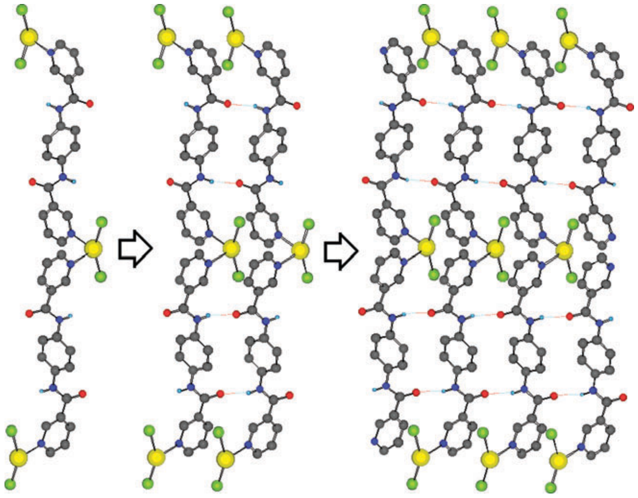


Fig. 3 Portions of the structure of the 2-D coordination networks formed between **1** and $HgCl_2$. The 2-D network is generated by both coordination (Hg–Npy) and H bonds (NH···O=C). The arrows represent the gradual construction of the network. For the sake of clarity, H atoms, except those involved in H-bonding, are not represented. For bond distances and angles see text.

($d_{NH\cdots O}$ = 2.04 Å, NHO angle of 163.0°) between the C=O groups belonging to one strand and the NH moieties belonging to the consecutive strand (Fig. 4). Both aryl and pyridine rings belonging to consecutive 1-D networks are parallel, however the distance of *ca.* 5.0 Å clearly shows the absence of direct interactions. When taking into account all specific interactions, the structure may be described as a 2-D network based on two types of recognition pattern, one of the coordination type and the other of H-bonding type. As discussed in the introduction of this contribution (Fig. 1), when taking into account energetic factors, the coordination pattern may be considered as primary and the H-bond pattern as secondary. The network may then be considered as a coordination network. The same type of arrangement has been previously observed for the combination of the *ortho* isomer of **2** based on 1,2-phenylenediamine with $HgCl_2$.[11]

At room temperature, upon slow diffusion of an EtOH solution of $HgCl_2$ into a DMSO solution of **2**, colourless

Table 1 Data collection and refinements for $\mathbf{1}\cdot HgCl_2$ and $\mathbf{2}\cdot HgCl_2$

	$\mathbf{1}\cdot HgCl_2$	$\mathbf{2}\cdot HgCl_2$
Formula	$C_{18}H_{14}N_4O_2\cdot HgCl_2$	$C_{18}H_{14}N_4O_2\cdot HgCl_2$
Molecular weight [g mol^{-1}]	589.84	589.84
Crystal system	Monoclinic	Monoclinic
Space group	$P2/c$	$P2_1/n$
a [Å]	13.0454(5)	8.3336(2)
b [Å]	5.0255(10)	9.2373(2)
c [Å]	13.777(2)	11.4459(3)
β [°]	96.005(9)	94.207(5)
V [Å^3]	898.2(2)	878.73(4)
Z	2	2
Colour	Colorless	Colorless
Crystal size [mm]	0.26 × 0.10 × 0.05	0.10 × 0.10 × 0.08
ρ_{calcd} [g cm^{-3}]	2.181	2.23
$F(000)$	560	560
μ [mm^{-1}]	8.888	9.085
Temperature [K]	173	173
λ [Å]	0.71073	0.71073
Radiation	MoKα	MoKα
Diffractometer	KappaCCD	KappaCCD
Scan mode	Phi scans	CCD
φ range for collection [°]	2.97/32.99	2.5/30.03
Number of reflections	3354	4717
Number of data with $I > 3\,\sigma(I)$	2557	1928
Number of variables	123	124
R	0.0328	0.017
wR	0.0912	0.022
GOF	1.081	0.976

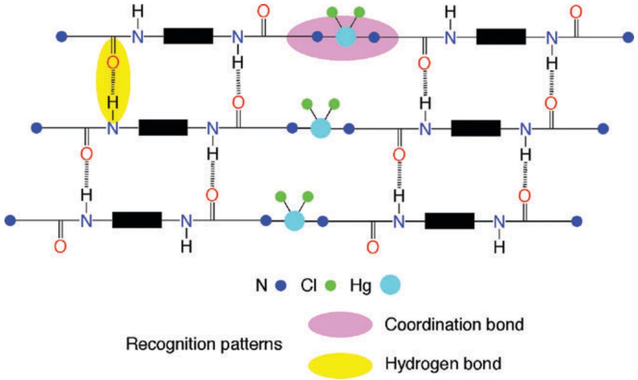


Fig. 4 Schematic representation of the 2-D network formed upon combining both coordination and H-bonds. The 2-D network may be regarded as 1-D coordination networks, obtained upon mutual bridging between metal centres and organic tectons **1**, interconnected through H-bonds taking place between amide groups.

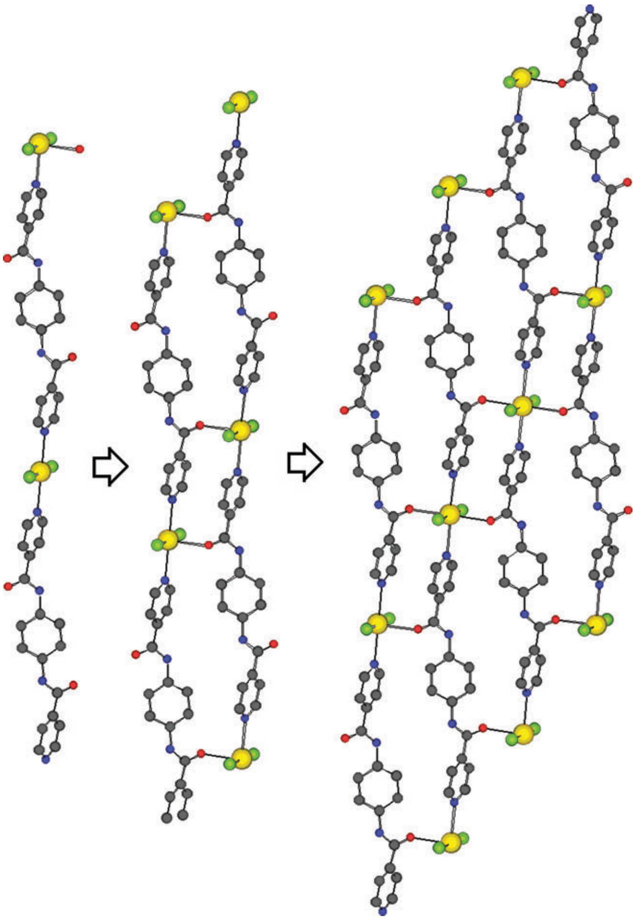


Fig. 5 Portions of the structure of the 2-D coordination networks formed between **2** and $HgCl_2$. The 2-D network is exclusively generated through coordination bonds (Hg–Npy and Hg–O=C) between **2** and the mercury cation adopting the octahedral coordination geometry. The arrows represent the gradual construction of the network. For the sake of clarity, H atoms are not represented. For bond distances and angles see text.

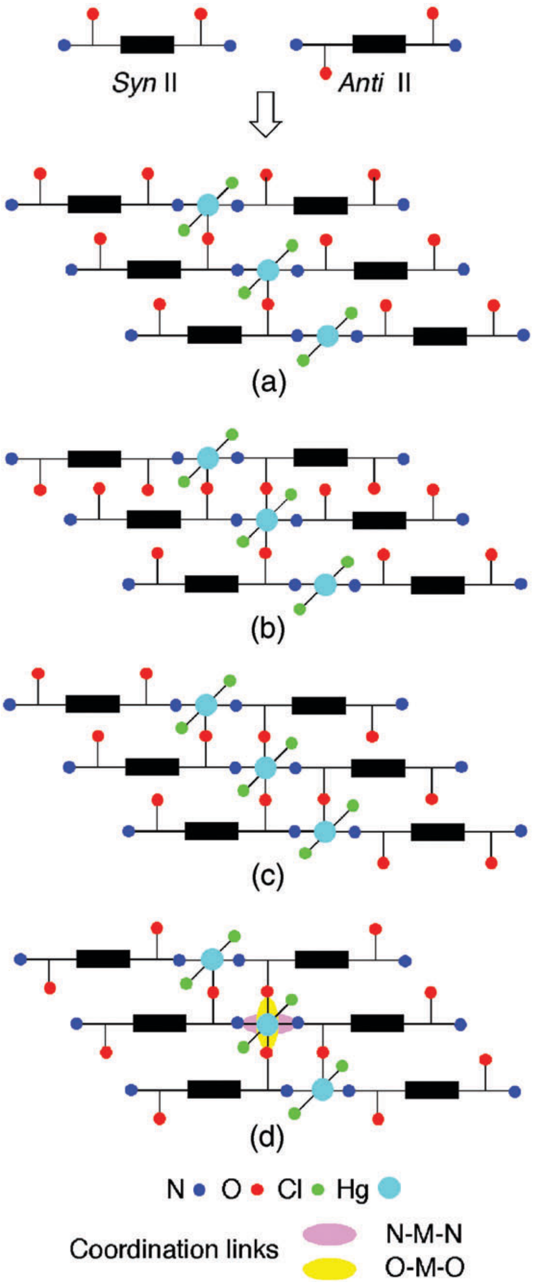


Fig. 6 Schematic representation of a systematic analysis of the possible modes of connection between the tecton **2**, adopting *syn* and *anti* arrangements of the CO groups, and the mercury cation adopting the octahedral coordination geometry. Only the arrangement depicted in d (bottom) leads to the absence of coordination frustration (for the description of the four cases represented see text).

crystals were again obtained after *ca.* one week and analysed by X-ray diffraction on a single crystal (Table 1). The crystal (monoclinic, $P2_1/n$) was again exclusively composed of **2** and $HgCl_2$. Again, the tecton **2** possesses a centre of symmetry and adopts the *anti* configuration (antiparallel orientation of the C=O groups) as in the case of **1** mentioned above. Both amide groups ($d_{C=O}$ = 1.22 Å, $d_{N\text{–}CO}$ = 1.36 Å, $d_{C\text{–}CO}$ = 1.50 Å) of the tecton **2** adopt the *trans* configuration (HNCO dihedral angles of −166.5° and +166.4°). The amide groups are again neither coplanar with the aryl ring nor with the pyridine unit but tilted by 36.0° and 33.2°, respectively. As in the case of **1**, the oxygen atom of the C=O group is located at 2.35 and 2.54 Å from the nearest hydrogen atoms of the aryl group and pyridine, respectively.

The interconnection between the tecton **2** and $HgCl_2$ leads to the formation of a neutral 2-D network. The coordination sphere around Hg(II) is composed of two chloride anions ($d_{Hg\text{–}Cl}$ = 2.38 Å), two nitrogen ($d_{Hg\text{–}N}$ = 2.62 Å) and two oxygen ($d_{Hg\text{–}O}$ = 2.70 Å) atoms. In marked contrast with the above mentioned case in which, in the presence of the tecton **1**, Hg(II) adopts the rather common tetrahedral coordination geometry, in the case of **2**, the donor centres are arranged in the rather less common octahedral geometry (NHgN, OHgO and ClHgCl angles of 180.0°, OHgCl angles of 92.9° and 87.0° and NHgCl angles of 91.2 and 88.8°). The 2-D network may be described as 1-D coordination networks, formed upon bridging of consecutive tectons **2** by $HgCl_2$ complexes through coordination bonds established between pyridine type nitrogen atoms and Hg(II) centres. The resulting 1-D networks are further connected through coordination bonds between the carbonyl groups of **2** and mercury centres (Fig. 5).

In order to better understand the formation of the 2-D network, we analysed, in a systematic way, different possibilities based on the combination of two conformations (*syn* parallel and antiparallel) of the tecton **2** with a metal centre adopting the octahedral coordination geometry. In order to simplify the analysis, we supposed that both amide junctions adopt the *trans* configuration as observed both in the case of **1** and **2** and that only the nitrogen atom of the pyridine ring and oxygen atom of the carbonyl moiety take part in the coordination (Fig. 6). It is worth noting that when the tecton **2** is combined with HgI_2, only a 1-D network is observed.[13] Indeed, the coordination between **2** and Hg(II) takes place only with the nitrogen atoms of the pyridine units and the C=O groups do not participate in the binding of metal centres.

In the case of **2** adopting the *syn* parallel conformation (Fig. 2) for which the two C=O groups are oriented towards the same face of the tecton (Fig. 6 a, b and c), all arrangements lead to frustration in the coordination pattern. Indeed, in all three cases, all C=O groups cannot be coordinated to metal centres. Interestingly, only in the case of the antiparallel conformation, no frustration is obtained (Fig. 6d). This is indeed what is observed in the case of **2** which adopts indeed the antiparallel arrangement.

Conclusion

Upon combining two structural isomeric organic tectons **1** and **2**, based on the aryl group bearing two pyridine units connected through amide junctions, with $HgCl_2$ acting as a metallatecton, two different bidimensional networks have been generated. Whereas for the tecton **2** the combination leads to a 2-D network exclusively based on two types of coordination bonds (Hg–Npy and Hg–O=C), in the case of **1**, the network is generated through both coordination bonding (Hg–Npy) and H-bonding (NH···O=C) taking place between amide groups. With the aim of increasing the dimensionality of molecular networks, we are currently exploring other possibilities of combining different types of interactions.

Experimental section

Synthesis

Although the straightforward synthesis of **2** was described previously,[13] we report here our own procedure for the preparation of both **1** and **2**.

At room temperature, 1 g of 1,4-phenylenediamine (9.2 mmol) was dissolved in 50 ml of dry THF. To this solution was added 5 g of the commercially available hydrochloride salt of nicotinoyl or isonicotinoyl chloride. After stirring for 30 min, 10 ml of triethylamine was added and the mixture was stirred overnight. After evaporation to dryness, the yellow residue was poured into an aqueous solution (50 ml) of K_2CO_3 (1.2 M). The solid was filtered and the pure compounds **1** and **2** were obtained in *ca.* 75% yield as white solids upon crystallisation from a DMSO–EtOH mixture.

Compound 1. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 7.58 (m, 2H, *H*-Py); 7.77 (s, 4H, *H*-Ar); 8.30 (m, 2H, *H*-Py); 8.76 (m, 2H, *H*-Py); 9.12 (d, J = 1.73 Hz, 2H, *H*-Py); 10.46 (s, 2H, N*H*); ^{13}C (75.48 MHz, $CDCl_3$, 25 °C), δ (ppm): 121.2; 124.0; 131.0; 135.2; 135.9; 149.0; 152.5; 164.4. Anal. for $C_{18}H_{14}N_4O_2$ (318.34 g mol^{-1}), calcd: C: 67.9%, H: 4.4%, N: 17.6%; found: C: 65.8%, H: 4.3%, N: 16.8%.

Compound 2. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 7.78 (s, 4H, *H*-Ar); 7.88 (d, J = 6 Hz, 4H, *H*-Py); 8.79 (d, J = 6 Hz, 4H, *H*-Py); 10.52 (s, 2H, N*H*); ^{13}C (75.48 MHz, $CDCl_3$, 25 °C), δ (ppm): 121.2; 122.0; 135.2; 142.3; 150.7; 164.4. Anal. for $C_{18}H_{14}N_4O_2$ (318.34 g mol^{-1}), calcd: C: 67.9%, H: 4.4%, N: 17.6%; found: C: 67.3%, H: 4.4%, N: 17.5%.

Crystallisation conditions

In a crystallisation tube (height = 15 cm, diameter = 0.4 cm), at room temperature upon slow diffusion of an EtOH solution (1 ml) of $HgCl_2$ (6×10^{-6} moles) into a DMSO solution (1 ml) of **1** or **2** (6×10^{-6} moles), colourless crystals were obtained after *ca.* one week.

Crystallography

Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα (λ = 0.71073) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using the APEX (1.022) package. All hydrogen atoms have been calculated except those connected to disordered atoms. CCDC reference numbers 284053–284054. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512569n

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References

1 S. Mann, *Nature*, 1993, **365**, 499.
2 M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696.
3 M. W. Hosseini, *Acc. Chem. Res.*, 2005, **38**, 313.
4 M. W. Hosseini, *CrystEngComm*, 2004, **6**, 318.
5 G. D. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York, 1989.
6 (*a*) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; (*b*) G. M. Whitesides, J. P. Mathias and T. Seto, *Science*, 1991, **254**, 1312; (*c*) F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 1993, **115**, 5991; (*d*) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, **22**, 397; (*e*) S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357; (*f*) D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229; (*g*) J. F. Stoddart and D. Philip, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1155; (*h*) J. R. Fredericks and A. D. Hamilton, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. Davis, D. D. Macnico, F. Vögtle, J. P. Sauvage and M. W. Hosseini, Elsevier, Oxford, 1996, vol. 9, p. 565; (*i*) V. A. Russell and M. D. Ward, *Chem. Mater.*, 1996, **8**, 1654; (*j*) D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, **33**, 601; (*k*) K. T. Holman, A. M. Pivovar, J. A. Swift and M. D. Ward, *Acc. Chem. Res.*, 2001, **34**, 107; (*l*) L. Brammer, in *Perspectives in Supramolecular Chemistry*, ed. G. Desiraju, Wiley, Chichester, 2003, vol. 7, p. 1; (*m*) M. W. Hosseini, *Coord. Chem. Rev.*, 2003, **240**, 157; (*n*) C. B. Aakeroy and A. M. Beatty, in *Comprehensive*

Coordination Chemistry II, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Amsterdam, 2004, vol. 1, p. 679; (*o*) E. Demers, T. Maris and J. D. Wuest, *Cryst. Growth Des.*, 2005, **5**, 1227.

7 (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*b*) M. W. Hosseini, *NATO ASI Ser., Ser. C*, ed. D. Braga, F. Grepioni and A. G. Orpen, Kluwer, Dordrecht, The Netherlands, 1999, **538**, 181; (*c*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **193**, 117; (*d*) G. F. Swiergers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; (*e*) B. Moulton and M. J. Zawortko, *Chem. Rev.*, 2001, **101**, 1629; (*f*) M. Eddaoui, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*g*) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247; (*h*) C. Janiak, *Dalton Trans.*, 2003, 2781; (*i*) S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2434.

8 (*a*) M. W. Hosseini and A. De Cian, *Chem. Commun.*, 1998, 727; (*b*) J. Martz, E. Graf, A. Decian and M. W. Hosseini, in *Perspectives in Supramolecular Chemistry*, ed. G. Desiraju, Wiley, Chichester, 2003, vol. 7, p. 177.

9 (*a*) C. B. Aaekeröy and A. M. Beatty, *Chem. Commun.*, 1998, 1067; (*b*) A. M. Beatty, *CrystEngComm*, 2001, **51**, 243; (*c*) A. M. Beatty, *Coord. Chem. Rev.*, 2003, **246**, 131; (*d*) C. B. Aaekeröy, A. M. Beatty, J. Desper, M. O'Shea and J. Valdes-Martinez, *Dalton Trans.*, 2003, 3956.

10 (*a*) Z. Quin, M. C. Jennings and R. J. Puddephatt, *Inorg. Chem.*, 2001, **40**, 6220; (*b*) Z. Quin, M. C. Jennings and R. J. Puddephatt, *Chem.–Eur. J.*, 2002, **8**, 735; (*c*) Z. Quin, M. C. Jennings and R. J. Puddephatt, *Inorg. Chem.*, 2003, **42**, 1956; (*d*) T. J. Burchell, D. J. Eisler, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2003, 2228; (*e*) T. J. Burchell, D. J. Eisler and R. J. Puddephatt, *Chem. Commun.*, 2004, 944.

11 J. Burchell, D. J. Eisler and R. J. Puddephatt, *Inorg. Chem.*, 2004, **43**, 5550.

12 (*a*) S. Muthu, J. H. K. Yip and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 2001, 3577; (*b*) S. Muthu, J. H. K. Yip and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 2002, 4561.

13 Y.-Y. Niu, Y.-L. Song, J. Wu, H. Hou, Y. Zhu and X. Wang, *Inorg. Chem. Commun.*, 2004, 471.

14 (*a*) D. M. Ciurtin, N. G. Pshirer, M. D. Smith, U. H. F. Bunz and H.-C. zur Loye, *Chem. Mater.*, 2001, **13**, 2743; (*b*) N. D. Draper, R. J. Batchelor and D. B. Leznoff, *Cryst. Growth Des.*, 2004, **4**, 621; (*c*) L. Li, Y. Song, H. Hou, Z. Liu, Y. Fan and Y. Zhu, *Inorg. Chim. Acta*, 2005, **358**, 3259; (*d*) T. J. Burchell and R. J. Puddephatt, *Inorg. Chem.*, 2005, **44**, 3718.

15 (*a*) P. Grosshans, A. Jouaiti, M. W. Hosseini and N. Kyritsakas, *New J. Chem.*, 2003, **27**, 793; (*b*) P. Grosshans, A. Jouaiti, V. Bulach, J.-M. Planeix, M. W. Hosseini and J.-F. Nicoud, *Chem. Commun.*, 2003, 1336; (*c*) P. Grosshans, A. Jouaiti, N. Kardouh, M. W. Hosseini and N. Kyritsakas, *New J. Chem.*, 2003, **27**, 1806; (*d*) M. Henry and M. W. Hosseini, *New J. Chem.*, 2004, **28**, 897; (*e*) P. Grosshans, A. Jouaiti, V. Bulach, J.-M. Planeix, M. W. Hosseini and N. Kyritsakas, *Eur. J. Inorg. Chem.*, 2004, 453; (*f*) C. Klein, E. Graf, M. W. Hosseini and N. Kyritsakas, *ACA Transactions*, 2004, **39**, 1.