Molecular tectonics: design of coordinating tectons based on fluorene bearing pyridines and structural analysis of their coordination networks generated in the presence of mercury and cobalt salts

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A series of six new bis-monodentate tectons based on the fluorene skeleton and bearing two pyridine derivatives as coordinating sites have been designed and prepared. The ability of two of them presenting a "V" type geometry to generate coordination networks in the presence of $HgCl_2$ or $CoCl_2$ acting as metallatectons and offering either a "V" or a square type geometry respectively was structurally studied by X-ray diffraction on single crystals. Whereas a combination of "V" shaped organic and metallic tectons leads to a 1-D coordination network, when combining a "V" shaped organic tecton with a metallatecton presenting four available coordination sites occupying the corners of a square, a 2-D neutral coordination network was obtained. In the latter case, a two-fold homo interpenetrating architecture was obtained.

The design of organic tectons leading in the presence of metallic centres to the generation of coordination networks in the crystalline phase is a subject of current interest.[1–18] These infinite molecular architectures are formed upon mutual bridging of organic and metallic tectons and possess translational symmetry, *i.e.* translation of coordination patterns, which defines their dimensionality (1-, 2- or 3-D). Because the combination of organic tectons and metallic centres offers a large number of structural possibilities and furthermore, since metal centres may present a variety of physical properties (redox, optical, magnetic), the formation of coordination networks or polymers may be of interest in the area of material sciences.

For some time now, we have been engaged in the design and characterisation of coordination networks in the crystalline phase.[19–36] In continuation of our systematic investigation, we have designed new "V" shaped organic tectons based on a fluorene backbone and investigated their ability to generate coordination networks when combined with metallatectons possessing two or four available coordination sites and adopting "V" or square type geometries.

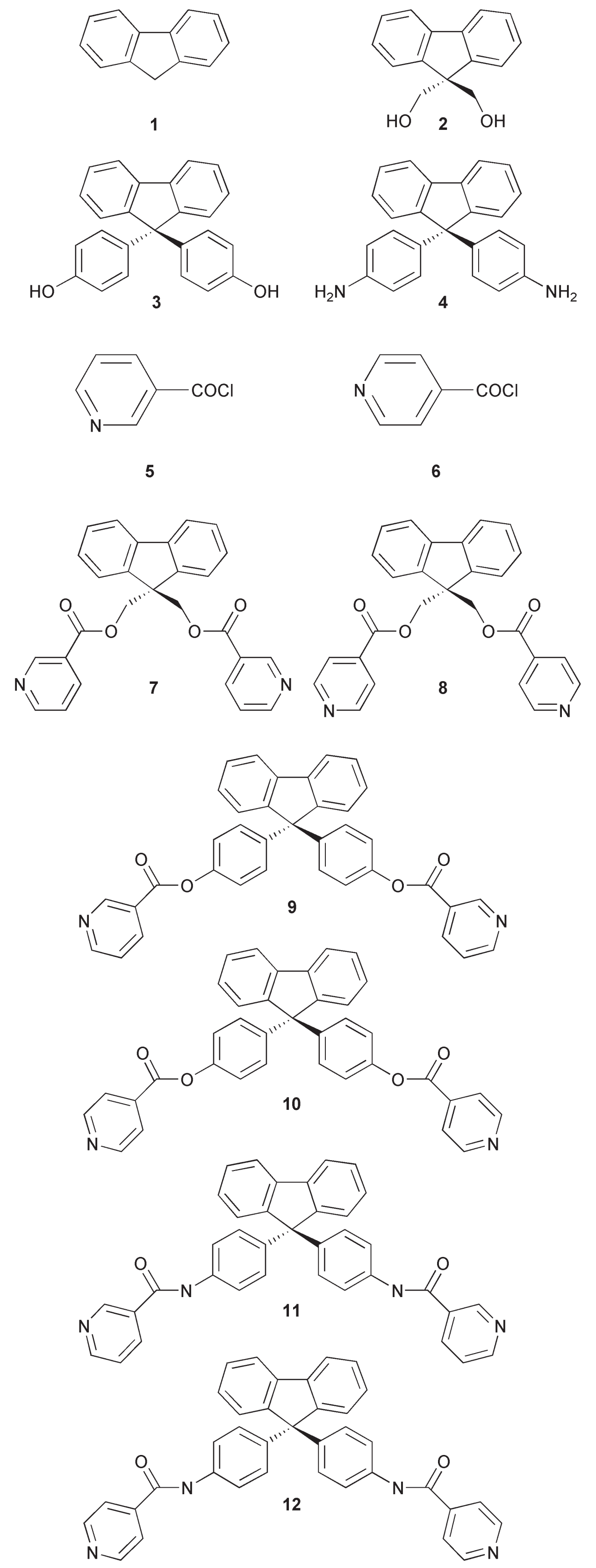
Here we report the synthesis of six new tectons **7**–**12** (Scheme 1) and the formation of two new coordination networks formed upon crystallisation of tectons **8** and **9** in the presence of $HgCl_2$ and $CoCl_2$ respectively.

Fluorene **1** (Scheme 1) is an interesting rigid backbone for the design of tectons since it offers the possibility of introducing in a symmetrical fashion 2 (Fig. 1a and b) or 4 (Fig. 1c) coordination sites. The connection of two coordinating units may either be at positions 2 and 7 (Fig. 1a) or 9 (Fig. 1b). Although few examples of fluorene bearing two pyridine units at positions 2 and 7 have been reported,[15,37,38] the tectons presented in this study are based on double functionalisation of fluorene **1** backbone at position 9.

All six tectons **7**–**12** are based on the fluorene **1** skeleton and bear two pyridine moieties as monodentate coordinating sites. Based on the junction between the fluorene moiety and pyridine units, these tectons may be described as two classes, one based on an ester group connecting the pyridine to the fluorene (**7**–**10**) and the other one on an amide junction (**11**–**12**). Tectons **7**–**10** differ either by the nature of the spacer between the fluorene unit and pyridine moiety ($CH_2C(O)O$ for **7** and **8** or PhC(O)O for **9** and **10**) or on the connecting position of the pyridinoyl moiety to the backbone (position 3 for **7** and **9** and position 4 for **8** and **10**). For the other class, the difference between the two tectons results only from the connecting position of the pyridinoyl moiety (position 3 for **11** and 4 for **12**).

For the synthesis of **7**–**12**, all starting materials **2**–**6** were commercially available. The synthesis of **7**–**12** was achieved upon condensing the hydrochloride salt of nicotinoyl chloride **5** or of isonicotinoyl chloride **6** with fluorene derivatives **2**–**4** (see experimental section).

For the design of a coordination network which results from mutual interconnection of an organic tecton and a metallic centre, one must consider the specificity of both partners in terms of coordinating sites and their location offered by the organic moiety and coordination sites and geometry required by the metal centre. For the latter, one may differentiate two possibilities. Either the metal acts as an atomic centre or as a complex unit which may be called metallatecton. Since tectons **7**–**12** are neutral units, our strategy, as previously demonstrated,[22,25,27,32,35] was to use dicationic metal centres such as Hg^{2+} and Co^{2+} as their chloride salts. Indeed, due to the coordinating nature of Cl^- anion, whereas $HgCl_2$ should act as a neutral metallatecton offering two available coordination sites located at the extremities of a "V", $CoCl_2$, again a neutral metallatecton, should offer four unoccupied coordination sites located at the corners of a square (Fig. 2). As the continuation of our previous study on the possibilities of combining organic and metallic tectons with different geometries,[35] a combination



Scheme 1

of tectons **7**–**12** and $HgCl_2$ both possessing a "V" type shape should in principle lead to the formation of 1-D neutral coordination networks (Fig. 2a), whereas in the case of $CoCl_2$ (square planar), among several possibilities related to the orientation of the organic tecton presenting a "V" type geometry, one may expect 2-D coordination networks (Fig. 2b).

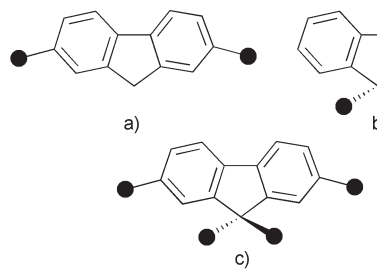


Fig. 1 Schematic representation of fluorene based tectons bearing two monodentate coordination site at positions 2 and 7 (a) or 9 (b) and four coordination sites at positions 2, 7 and 9 (c).

Among several trials dealing with the formation of coordination networks using tectons **7**–**12** and $HgCl_2$ or $CoCl_2$ salts, so far, only in the case of tectons **8** and **9** have single crystals of suitable quality for X-ray diffraction been obtained (see experimental section) and structurally characterised in the solid state.

At room temperature, upon slow diffusion of a $CHCl_3$ solution of **8** or **9** into an EtOH solution of $HgCl_2$ or $CoCl_2 \cdot 6H_2O$, colourless and pink single crystals were obtained respectively after *ca.* 48 hours and studied by X-ray diffraction (see experimental part).

For the combination of **8** offering two coordinating sites occupying the extremities of a "V" with $HgCl_2$ possessing

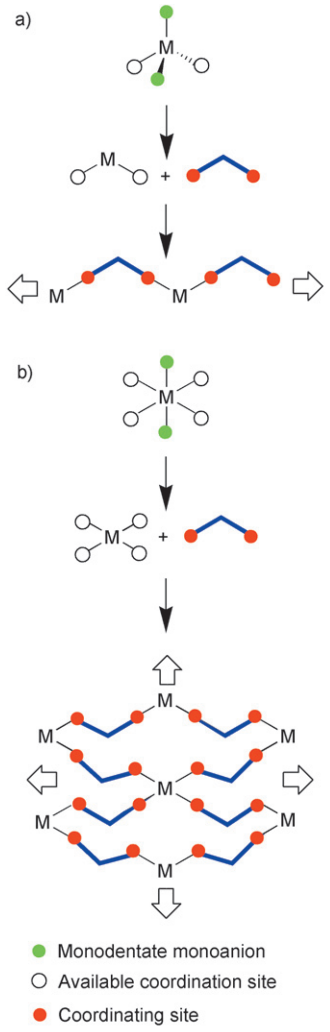


Fig. 2 Schematic representation of the formation of 1- and 2-D neutral coordination networks based on the mutual bridging between a bis monodentate tecton possessing a "V" shaped geometry and metallatectons offering two (a) or four (b) available coordination sites occupying the extremities of a V or the corners of a square.

two available coordination sites in "V" type disposition, the formation of a "zigzag" type 1-D neutral coordination network resulting from the mutual bridging between **8** and $HgCl_2$ was observed (Fig. 3a). The crystal (triclinic system, space group $P\bar{1}$, $Z = 2$) is composed of neutral networks and $CHCl_3$ solvent molecules.

For the organic tecton **8**, the plane of the ester group (C–O distance varying between 1.326 Å and 1.341 Å and C=O 1.197 Å and 1.211 Å, OCO angle of *ca* 125.0°) is tilted with respect to the pyridine ring (CCCO dihedral angles of 15.2° and 16.5°).

The coordination sphere around Hg^{2+} cations is composed of two Cl^- anions with Hg–Cl distances of 2.34 and 2.37 Å and two N atoms (Hg–N distances of 2.43 and 2.45 Å) belonging to two consecutive tectons **8**. The coordination geometry around the metal is a distorted tetrahedron (Cl–Hg–Cl and N–Hg–N angles of *ca.* 153.5° and *ca.* 98.9° respectively). The distance between two consecutive mercury centres within the 1-D network is 14.00 Å. The 1-D networks are packed in parallel and eclipsed fashion generating cavities which are occupied by $CHCl_3$ solvent molecules with no specific interactions between them and the network portions of the structure (Fig. 3b). The shortest distance between two mercury centres belonging to two consecutive 1-D network is 14.52 Å.

Dealing with the combination of "V" shape tecton **9** and $CoCl_2$ possessing four available coordination sites located within the square base of the octahedron, the generation of a 2-D networks (Fig. 4a) of the (4,4) sheet type (Fig. 4b) was observed. The puckered 2-D neutral coordination network results from the mutual bridging between **9** and $CoCl_2$. The crystal (monoclinic system, space group $P\,2/n$, $Z = 2$) is composed of tecton **9**, $CoCl_2$, $CHCl_3$ and 3 H_2O solvent molecules.

For the organic tecton **9**, the plane of the ester group (C–O and C=O distances of 1.360 Å and 1.200 Å, OCO angle of 124.0°) is almost parallel to the pyridine ring (CCCO dihedral angles of −3.4° and −3.5°). The plane of the ester groups is tilted with respect to the connecting phenyl moiety (CCOC dihedral angles of 61.3° and −83.0°).

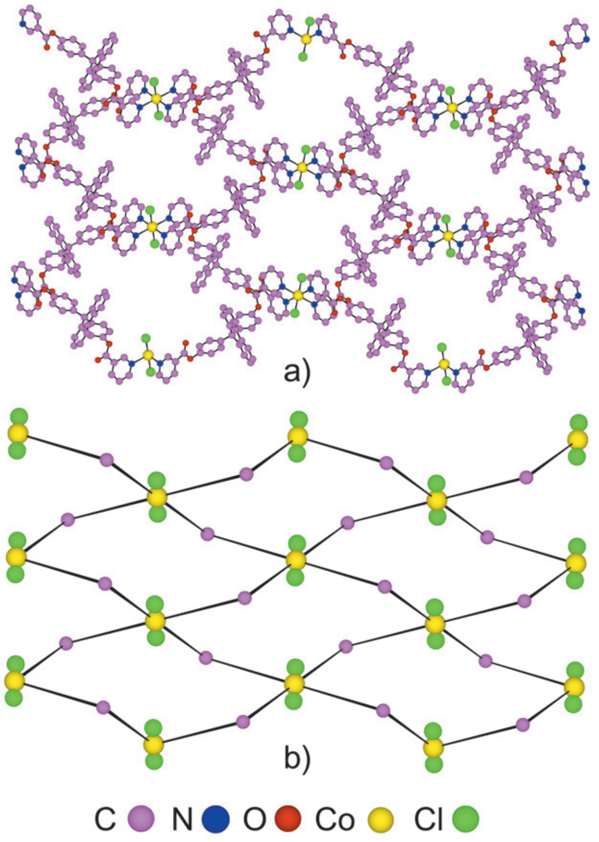


Fig. 4 A portion of the neutral 2-D network obtained upon self-assembly of the tecton **9** with $CoCl_2$ (a) and the topological simplification made by connecting the central C atom of the tecton to cobalt atoms (b). Solvent molecules and H atoms are not represented for clarity. For bond distances and angles see text.

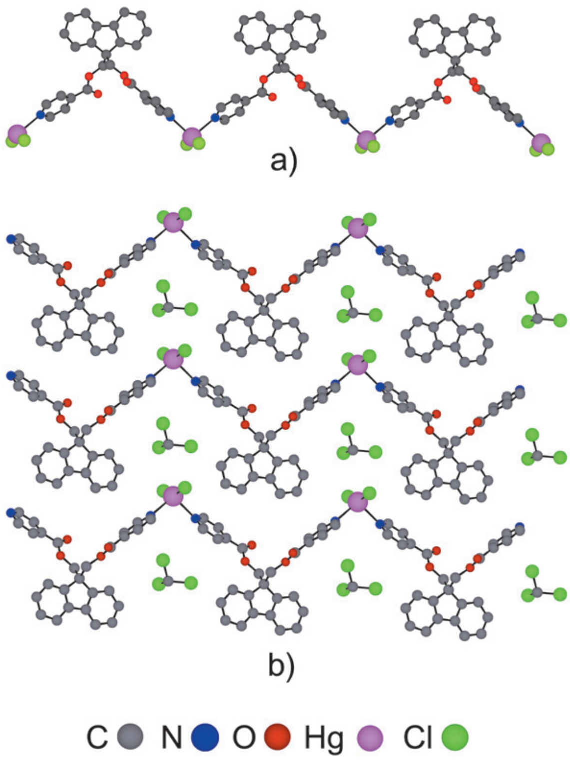


Fig. 3 A portion of the neutral 1-D network obtained upon self-assembly of the tecton **8** with $HgCl_2$ (a) and the packing of 1-D networks as well as occupation of empty space by chloroform molecules (b). H atoms are not represented for clarity. For bond distances and angles see text.

The coordination sphere around Co^{2+} cations is composed of two Cl^- anions with Co–Cl distance of 2.387 Å and four N atoms (Co–N distance varying between of 2.191 and 2.269 Å) belonging to four different tectons **9**. The coordination geometry around the metal is a distorted octahedron (Cl–Co–Cl angles of 180.0° and N–Co–N *trans* angle of 180.0° and N–Co–N *cis* angle varying between 87.8° and 92.2°).

Probably as result of better packing,[1,39] a two-fold homo interpenetrating architecture is obtained (Fig. 5a). The parallel interpenetration for which the mean planes of the two sheets are parallel, takes place with no increase in the dimensionality (Fig. 5b). Examples of interpenetrated 2-D networks have been previously reported.[40,41]

The packing of interpenetrated 2-D networks in the crystal generates channels which are filled with solvent molecules with no specific interactions between theme and the neutral coordination networks (Fig. 5b). However, the H_2O molecules are interconnected through H-bonds (O–O distance of 2.93 and 2.98 Å). Furthermore, one of the three H_2O units present in the channel bridges consecutive $CHCl_3$ molecules in a non symmetrical fashion (O–Cl distance of *ca.* 2.13 and 2.53 Å) thus leading to a 1-D network composed of H_2O and $CHCl_3$ molecules.

In summary, the synthesis of six new neutral coordinating tectons **7**–**12** based on the fluorene backbone bearing two pyridine units and adopting a "V" shape geometry was achieved. Upon combining one of the reported tectons (**8**) with $HgCl_2$ behaving as a metallatecton and offering two available coordination sites occupying the extremities of a "V" (V, V combination), a neutral 1-D coordination network is generated. For the (V, square) type combination, obtained upon combining the

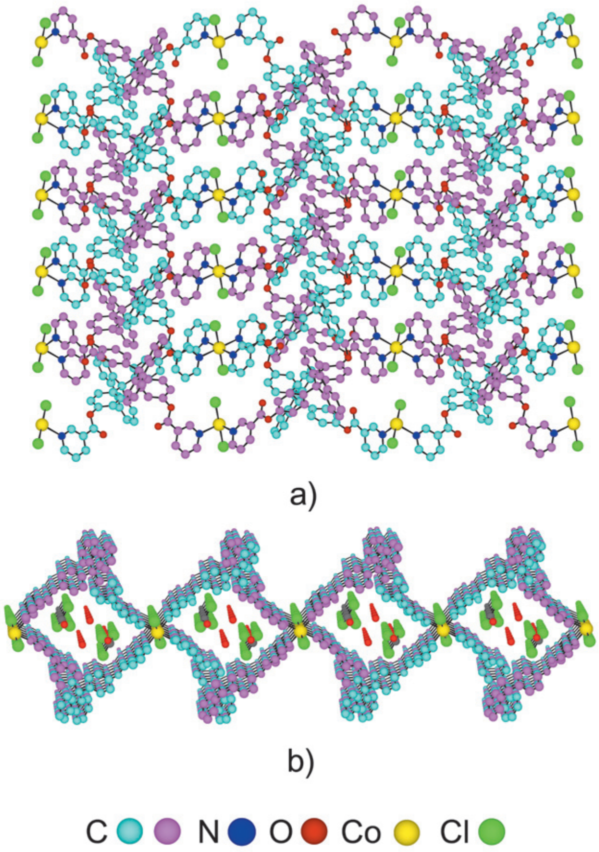


Fig. 5 A portion of the neutral 2-D network obtained upon self-assembly of the tecton **9** with $CoCl_2$ showing the homo interpenetration of two 2-D networks (a) and a perpendicular view showing the formation of channels and their occupation by solvent molecules (b). In order to illustrate the interpenetration of the two 2-D networks, the C atoms of the two independent networks are differentiated by colour. For bond distances and angles see text.

"V" shaped organic tecton **9** and $CoCl_2$ metallatecton offering four coordination sites occupying the corners of a square, a neutral 2-D coordination network is obtained. In the latter case, a two-fold homo parallel interpentration with no increase in dimensionality is observed. The packing of 2-D networks leads to channels which are filled with solvent molecules. Among the three H_2O molecules present, one of them bridges consecutive $CHCl_3$ molecules generating thus a 1-D H-bonded network composed of H_2O and $CHCl_3$ molecules. The generation of coordination networks and discrete metallamacrocycles based on other reported tectons and metal centres is currently under investigation.

Experimental section

Synthesis of tectons 7–12

General. All commercially available reagents were purchased and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker spectrometers at 400 and 300 MHz and at 50 MHz, respectively. Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université Louis Pasteur, Strasbourg.

General procedure for the preparation of compounds 7 and 9. Under argon, to a solution of **2** or **3** in dry pyridine (30 ml), the hydrochloride salt of *iso*nicotinoyl chloride **5** was added and the mixture refluxed for 3 hours. The solvent was removed under reduced pressure and to the solid thus obtained 100 ml of a saturated K_2CO_3 aqueous solution was added and the mixture extracted with CH_2Cl_2 (3 × 50 ml). The organic layer was dried ($MgSO_4$) and the solvent removed affording the pure compounds **7** and **9** as colourless solids.

General procedure for the preparation of compounds 8 and 10. Under argon, to a solution of **2** or **3** in dry THF (120 ml), the hydrochloride salt of nicotinoyl chloride **6** was added and the mixture stirred for 15 minutes before Et_3N (5 ml) was added and the mixture further stirred at room temperature for 48 hours. Volatiles were removed under reduced pressure and to the solid thus obtained 100 ml of a saturated K_2CO_3 aqueous solution was added and the mixture extracted with CH_2Cl_2 (3 × 50 ml). The organic layer was dried ($MgSO_4$) and the solvent removed affording the pure compounds **7** and **9** as colourless solids.

General procedure for the preparation of compounds 11 and 12. Under argon, to a solution of **4** in dry THF (120 ml), the hydrochloride salt of *iso*nicotinoyl chloride **5** or nicotinoyl chloride **6** was added and the mixture stirred for 15 minutes before Et_3N (5 ml) was added and the mixture further stirred at room temperature for 48 hours. Volatiles were removed under reduced pressure and to the solid thus obtained 100 ml of a saturated K_2CO_3 aqueous solution was added and the mixture extracted with CH_2Cl_2 (3 × 50 ml). The organic layer was dried ($MgSO_4$) and the solvent removed affording a yellowish solid. The pure compounds **11** and **12** were obtained as colourless solids after chromatography (Al_2O_3, CH_2Cl_2–2.5% MeOH).

Compound 7 (1.64 g, 73% yield): 2 (1 g, 4.42 mmol), 5 (1.96 g, 11 mmol). ^1H-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 4.77 (s, 4H), 7.40 (m, 6H), 7.68 (d, 2H, $J = 7.5$ Hz), 7.82 (d, 2H, $J = 7.5$ Hz), 8.22 (dt, 2H, $J = 7.9$ Hz and 2 Hz, 8.78 (dd, 2H, $J = 7.8$ Hz and 1, 8 Hz), 9.16 (d, 2H, $J = 1.9$ Hz); ^{13}C-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 53.3, 66.9, 120.5, 123.5, 124.6, 125.7, 127.7, 128.9, 137.1, 140.9, 144.1, 150.7, 153.6, 164.8. mp = 125 °C, $C_{27}H_{20}N_2O_4$ calc. C 74.30%, H 4.62%, N 6.42%, found C 74.49%, H 4.73%, N 6.47%.

Compound 8 (1.77 g, 79% yield): 2 (1 g, 4.42 mmol), 6 (1.96 g, 11 mmol). ^1H-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 4.76 (s, 4H), 7.35 (t, 2H, $J = 7.5$ Hz), 7.48 (t, 2H, $J = 7.5$ Hz), 7.66 (d, 2H, $J = 7.5$ Hz), 7.76 (d, $J = 4.6$ Hz), 7.82 (d, 2H, $J = 7.7$ Hz), 8.79 (d, 4H, $J = 4.6$ Hz); ^{13}C-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 53.4, 67.1, 120.6, 122.7, 124.6, 127.7, 129.0, 136.8, 140.9, 143.9, 150.8, 164.7. mp = 143 °C, $C_{27}H_{20}N_2O_4$ calc. C 74.30%, H 4.62%, N 6.42%, found C 74.10%, H 4.77%, N 6.35%.

Compound 9 (1.2 g, 75% yield): 3 (1 g, 2.85 mmol), 5 (1.5 g, 8.6 mmol). ^1H-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 7.10 (dd, $J = 6,6$ Hz and 2,9 Hz), 7.30 (m, 6H), 7.45 (m, 6H), 7.79 (d, 2H, $J = 7,5$ Hz), 8.41 (dt, 2H, $J = 8$ Hz and 1,8 Hz), 8.84 (dd, 2H, $J = 3,1$ Hz and 1,8 Hz), 9.36 (d, 2H, $J = 0,7$ Hz); ^{13}C-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 64.6, 120.3, 121.3, 123.5, 125.5, 126.1, 127.8, 127.9, 129.3, 137.6, 140.1, 143.7, 149.3, 150.6, 151.3, 154.0, 163.8. mp = 234 °C, $C_{37}H_{24}O_4N_2$ calc.C 79.27%, H 4.32%, N 5.10%, found C 78.81%, H 4.30%, N 5.34%.

Compound 10 (1.2 g, 75% yield): 3 (1 g, 2.85 mmol), 6 (1.5 g, 8.6 mmol). ^1H-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 7.10 (d, $J = 6.8$ Hz), 7.32 (m, 6H), 7.40 (m, 4H), 7.79 (d, 2H, $J = 7.3$ Hz), 7,96 (d, 4H, $J = 6.0$ Hz), 8.85 (dd, 4H, $J = 6$ Hz and 1,4 Hz); ^{13}C-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 64.6, 120.4, 121.2, 123.2, 126.1, 127.8, 128.0, 129.3, 136.7, 140.1, 143.8, 149.3, 150.6, 150.8, 163.7. mp 284 °C, $C_{37}H_{24}O_4N_2$, calc. C 79.27%, H 4.32%, N 5.10%, found C 77.58%, H 4.35%, N 5.10%.

Compound 11 (1.0 g, 66% yield): 4 (1 g, 2.87 mmol), 5 (1.5 g, 8.6 mmol). ^{1}H-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 7.27 (m, 6H), 7.42 (m, 6H), 7.50 (d, 4H, $J = 7.5$ Hz), 7.77 (s, 2H, NH), 7.79 (d, 2H, $J = 7.5$ Hz), 8.18 (dt, 2H, $J = 8.0$ Hz and 2.0 Hz), 8.76 (dd, 2H, $J = 3.1$ Hz and 1.7 Hz), 9.05 (d, 2H, $J = 1.7$ Hz); ^{13}C-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 64.6, 120.7, 121.0, 123.9, 126.4, 128.1, 128.4, 130.9, 135.8, 137.9, 139.9, 141.5, 149.1, 151.1, 152.5,164.4. mp = 315 °C, $C_{37}H_{26}N_4O_2$, calc. C 79.55%, H 4.69%, N 10.03%, found C 74.42%, H 4.73%, N 10.14%.

Compound 12 (0.8 g, 52% yield): 4 (1 g, 2.87 mmol), 6 (1.5 g, 8.6 mmol). ^{1}H-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 7.25 (m, 8H), 7.37 (t, 2H, $J = 7.2$ Hz), 7,48 (d, 4H, $J = 8.6$ Hz), 7,66 (dd, 4H, $J = 6.0$ Hz and 1,4 Hz), 7,77 (d, 2H, $J = 8.2$ Hz), 7.83 (s, 2H, N–H), 8.78 (dd, 4H, $J = 6.0$ Hz and 1,3 Hz); ^{13}C-NMR ($CDCl_3$; 300 MHz; 25 °C): δ (ppm): 64.6, 101.8, 120.3, 120.5, 120.9, 126.0, 127.7, 127.9, 128.8, 135.9, 140.0, 142.0, 142.7, 150.7, 163.9. mp = 179 °C, $C_{37}H_{26}N_4O_2$, calc. C 79.55%, H 4.69%, N 10.03%, found C 79.46%, H 4.77%, N 9.86%.

Crystallisation conditions

In a crystallising tube, upon slow liquid–liquid diffusion at room temperature of a solution of the tecton **8** or **9** (5 mg) in chloroform (1 ml) into a solution of $HgCl_2$ or $CoCl_2 .6H_2O$ salts (1.5 mg) in EtOH (1.5 ml) colourless and pinkish single crystals respectively were obtained after *ca.* 48 hours.

Crystal structure characterisation. X-ray diffraction data collection was carried out on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα radiation. For all structures, diffraction data were corrected for absorption and analysed using OpenMolen package.[42] All non-H atoms were refined anisotropically.

Crystal data for: (**8**·$HgCl_2$) (colourless crystals, 173 K): $C_{27}H_{20}Cl_2HgN_2O_4{\cdot}CHCl_3$, M = 827.35, triclinic, space group $P\bar{1}$, $a = 10.5204(2)$, $b = 11.2241(2)$, $c = 14.0039(3)$ Å, $\alpha = 109.398(5)°$, $\beta = 91.023(5)°$, $\gamma = 103.730(5)°$, $V = 1506.71(8)$ Å^3, $Z = 2$, $D_c = 1.82$ g cm^{-3}, $\mu = 5.588$ mm^{-1}, 6863 data with $I > 3\sigma(I)$, $R = 0.036$, $Rw = 0.045$.

Crystal data for: (**9**·$CoCl_2$) (Pink crystals, 173 K): $C_{74}H_{48}Cl_2CoN_4O_8{\cdot}CHCl_3{\cdot}3H_2O$, M = 1424.49, monoclinic, space group $P\ 2/n$, $a = 17.6763(2)$, $b = 7.1511(1)$, $c = 28.2492(3)$ Å, $\beta = 91.544(5)°$, $V = 3569.54(7)$ Å^3, $Z = 2$, $D_c = 1.33$ g cm^{-3}, $\mu = 0.489$ mm^{-1}, 7678 data with $I > 3\sigma(I)$, $R = 0.075$, $Rw = 0.100$. CCDC reference numbers 216090 and 216091. See http://www.rsc.org/suppdata/nj/b3/b308947a/ for crystallographic data in .cif or other electronic format.

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