

Crystal engineering: molecular networks based on inclusion phenomena

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Inclusion processes based on molecular recognition processes may be used as a design principle for the generation of molecular networks in the solid state. Hollow tuneable molecular modules (koilands) based on fusion of pre-organised cavities were shown to be assembled in the solid state into one-dimensional molecular arrays (koilates) either by self-inclusion or by interconnection using connector molecules. The formation of the molecular networks in the crystalline phase was established by X-ray studies.

Introduction

Molecular solids are defined by the chemical nature of their molecular components and by their interactions with respect to each other in the crystalline phase. With our present level of knowledge, the complete understanding and therefore prediction of all intermolecular interactions in the crystalline phase seems unreachable. Therefore, it appears that crystal structures are not predictable.¹ However, following the statement by Jack Dunitz:² 'A crystal is, in a sense, the supramolecule *par excellence*', using appropriate molecular modules, one may predict some of the intermotive interactions. Molecular networks are defined as supramolecular structures, theoretically composed of infinite number of molecules, possessing translational symmetry.³ Whereas molecules are described as assemblies of atoms interconnected by covalent bonds, by analogy, one may describe molecular networks as hypermolecules in which the connectivity between the elementary components (molecular modules) is ensured by non-covalent intermotive interactions.

The construction of large molecular networks (10^{-6} – 10^{-3} m scale) with predicted and programmed structure may hardly be envisaged through step by step type strategy. However, the preparation of such higher-order materials may be reached through iterative self-assembling processes engaging individual modules. This strategy relies on a double analysis. One is at the molecular level, dealing with the individual modules composing the solid, and the other is at the supramolecular level, dealing with the intermotive or intermolecular interactions.^{4,5} Obviously the latter type of analysis is more subtle. For the design and synthesis of molecular networks, the approach called molecular tectonics,⁶ which is based on the self-assembly⁷ of structurally defined and energetically programmed complementary tectons⁸ (from Greek *tektōn*: builder), seems to be the most viable one. The synthesis of solids based on iterative assembling of individual complementary tectons still remains a challenge. A strict control of the self-assembly of molecular modules in the solid state should lead to structurally strictly controlled molecular networks (one-, two- and three-dimensional solids).

Dealing with design, whereas an endo molecular receptor forms discrete molecular complexes with a selected exo-substrate, an exo-receptor may form either discrete species with substrates acting as stoppers or molecular networks in the presence of appropriate connectors (Fig. 1). Thus, in order to achieve an iterative assembling process, the building blocks or

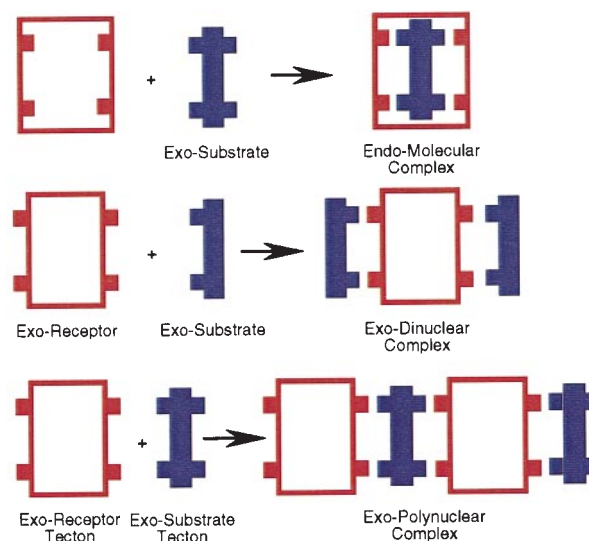


Fig. 1 Schematic representation of the formation of discrete molecular complexes by an endo-receptor and a substrate (top), by an exo-receptor and two stoppers (middle) or of a linear molecular network by an exo-receptor and a connector (bottom)

tectons must fulfil both structural and energy criteria. In particular, the complementary tectons must recognise each other (molecular recognition) and furthermore should allow the repetition of the recognition patterns which may be designed as assembling cores. These two requirements lead to molecular modules possessing connecting points or interaction sites located in a divergent fashion. We have previously reported exo-ligands based on mercaptocalix[4]arenes,^{9a} calix[4]arene,^{9b} tetraarylporphyrin^{9c} bearing bidentate catechol units and macrocyclic frameworks containing bipyridine units.^{9d}

Thus, the most important operational concepts in molecular tectonics are molecular recognition between tectons and geometrical features, encoded within their frameworks, allowing the iteration of the recognition processes. Molecular networks may be obtained by an iterative assembling process of either self-complementary, or of several complementary tectons.

In terms of interaction energy between molecular modules governing the recognition and assembling processes, hydrogen¹⁰ and coordination¹¹ bonds have been almost exclusively used for the formation of molecular networks. However, some time ago, we proposed the use of rather weak van der Waals interactions responsible for the inclusion processes between concave and convex molecules.^{12,13} Although, based on the above mentioned approach, molecular networks were obtained using all three types of interactions, *i.e.* hydrogen bond,¹⁴ coordination bond¹⁵ and van der Waals interactions^{12,13} the present article shall be mainly devoted to molecular networks based on inclusion phenomena in the solid state.

Design of koilands

The chemistry of inclusion complexes based on concave and convex molecules, *i.e.* the inclusion of a substrate within the cavity of a receptor molecule, is an established area. One may extend the concept of inclusion in solution to the construction of new networks in the solid state. Koilands^{12,13} (from Greek *koilos*: hollow) were defined as multicavity receptor molecules composed of at least two cavities arranged in a divergent fashion. Since each individual cavity offers the possibility of forming inclusion complexes with a convex molecules, fusing, in a rigid framework, two or more of such cavities may lead in the presence of an appropriate connector to a non-covalently assembled polymeric species which may be called a koilate. For example, linear koilates (one dimensional linear molecular arrays or α -networks) may be assembled in the solid state using non-covalent van der Waals interactions between a rigid and compact direceptor possessing two divergent cavities with an angle of 180° between them (linear koiland) and a linear connector, possessing two extremities each capable of being included within the cavities of the direceptor (Fig. 2).

For the design of koilands, calix[4]arene derivatives¹⁶ appeared to be candidates of choice (Fig. 3). Indeed, these compounds offer a preorganised and tuneable hydrophobic pocket surrounded by four aryl moieties as well as four hydroxy groups for further functionalisation. Furthermore, both the entrance and the depth of the preorganised cavity of calixarenes may be controlled by the nature of the substituent R at the *para* position (Fig. 4), *i.e.* Bu^t (**1**), H (**2**), Me (**3**), Ph (**4**). Whereas for the parent compounds **1**, **2** and **4** the cone conformation was established in the solid state by X-ray studies, to our knowledge, for compound **3** no X-ray data are available so far. The basket-type cavity of calix[4]arene derivatives such as **1** resulting from the cone conformation has been shown to accommodate in the solid state a variety of neutral guests.¹⁷

The design of koilands was based on the fusion of two calix[4]arenes derivatives in the cone conformation by two silicon atoms (Fig. 4).¹² Examples of fused calix[4]arenes using titanium(IV), niobium(V), aluminium(IV) and more recently zinc have been reported.¹⁸ Two calix[4]arenes have also been interconnected by organic¹⁹ and organometallic bridges.²⁰

Tuning the cavity

The general strategy for the synthesis of koilands was based on treatment of the calix derivatives by NaH in dry THF followed by addition of SiCl₄. The desired compounds were usually obtained after chromatography on silica or by crystallisation. The starting material for the synthesis of all koilands reported

was the *p*-*tert*-butylcalix[4]arene **1** prepared according to the published procedure.²¹ The calix[4]arene **2** was obtained by aluminium chloride *de-tert*-butylation of **1**.²² The latter was the common starting material for the synthesis of both *p*-methylcalix[4]arene **3** and *p*-phenylcalix[4]arene **4**. Although the syntheses of **3**²³ and **4**²⁴ were first reported by Gutsche *et al.*, the procedures by Ungaro and coworkers²⁵ and by Atwood and coworkers²⁶ respectively were found to be more convenient. The koilands **9**²⁷ (42%), **12**¹² (60%) and **14**²⁷ (17%) based on the double fusion of two *p*-methylcalix[4]arenes **3**, *p*-*tert*-butylcalix[4]arene **1** and *p*-phenylcalix[4]arenes **4**, respectively

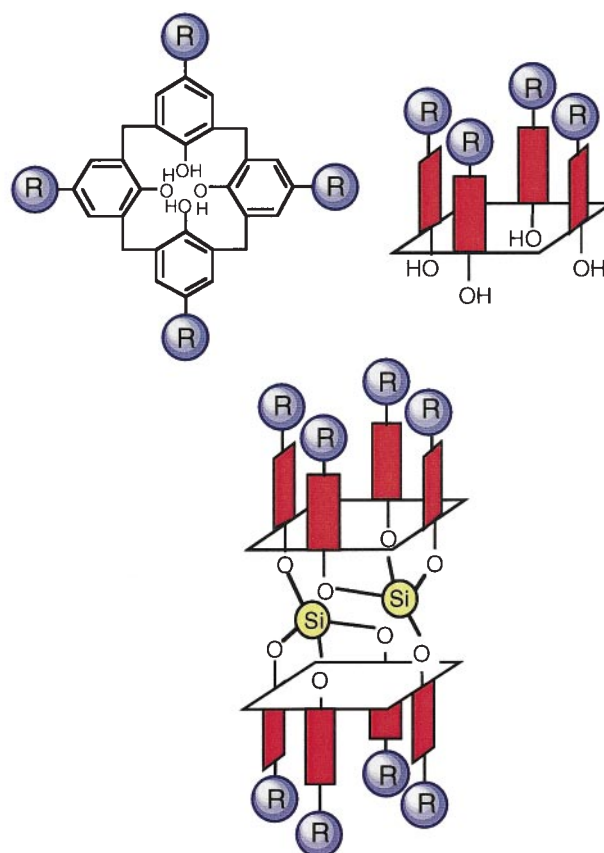


Fig. 3 Calix[4]arene derivatives (top left) and schematic representations of its cone conformation (top right) and of linear koilands obtained by fusion of two such units by two silicon atoms (bottom)

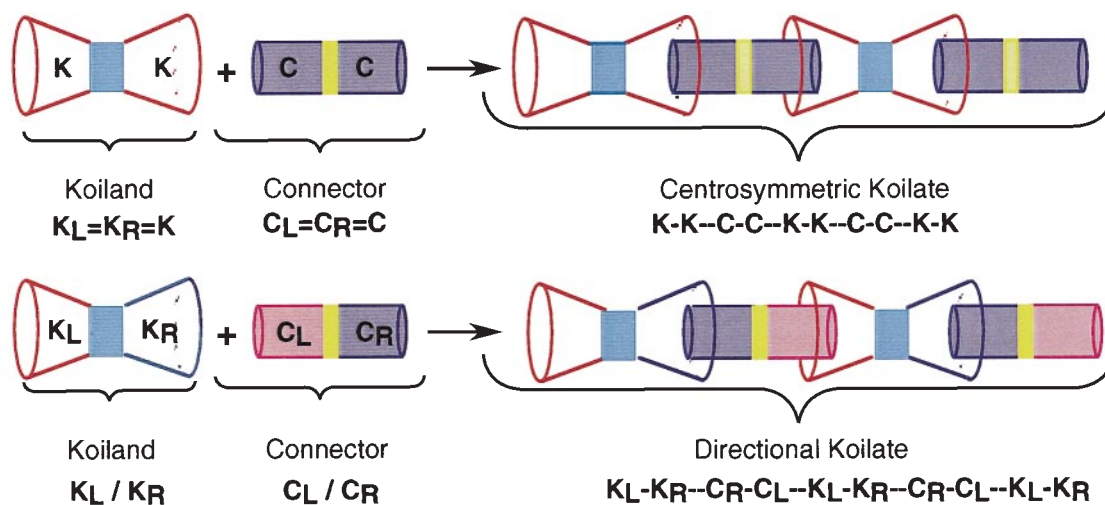


Fig. 2 Schematic representation of the formation of centrosymmetric (top) and directional (bottom) koilates (linear molecular network) by centrosymmetric (top) or non-centrosymmetric (bottom) linear koilands and connectors

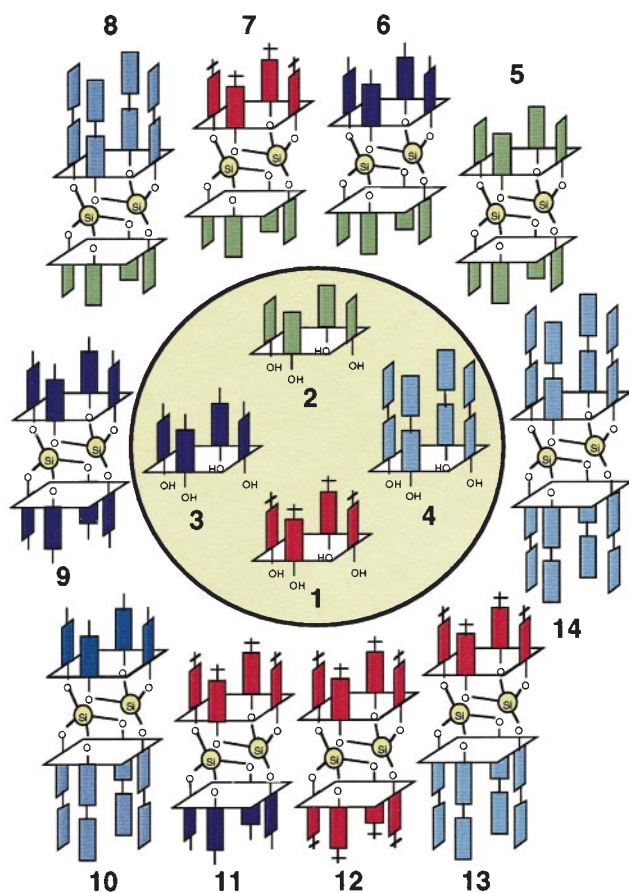


Fig. 4 Schematic representation of parent calix[4]arene derivatives **1–4** used as preorganised cavities and of centro-symmetric (**5, 9, 12, 14**) and non-centrosymmetric (**6–8, 10, 11, 13**) koilands formed by fusion of two calix units by two silicon atoms

with two silicon atoms were obtained as colourless stable crystalline solids.

The solid state structures of **9**²⁷ and **12**¹² were confirmed by X-ray studies which revealed that both compounds were indeed centrosymmetric aryloxy dimers consisting of two Si and two calixarenes. Both calixarene units were in cone conformation, thus presenting two divergent cavities (Fig. 5).

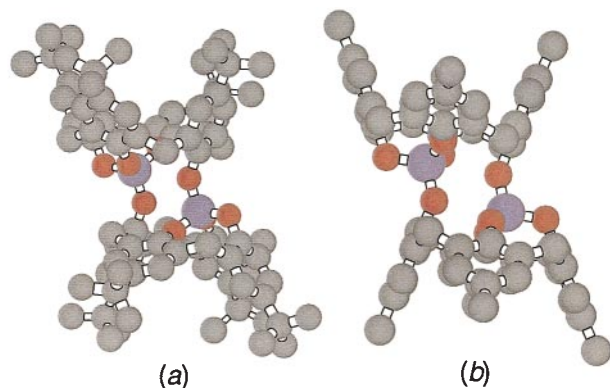


Fig. 5 X-Ray structures of linear koilands **9** (a) and **12** (b) showing the interconnection of two cavities in a linear fashion. For the sake of clarity, solvent molecules and hydrogen atoms are not presented.

Formation of discrete binuclear inclusion complexes

In order to ascertain the possibility of double inclusion, discrete binuclear complexes composed of koiland **12** and CHCl_3 ,¹² anisol²⁸ and *p*-xylene²⁸ were prepared (Fig. 6). The crystal study showed that in all three cases, each cavity accommodates,

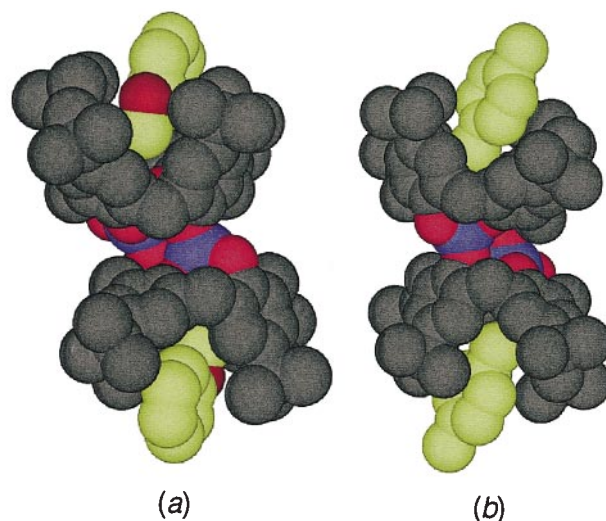


Fig. 6 X-Ray structures of discrete binuclear inclusion complexes formed by the linear koiland **12** and anisol (a) and *p*-xylene (b). For the sake of clarity, the carbon atoms of the substrate are coloured in green and the hydrogen atoms are not presented.

in a inclusive fashion, a solvent molecule. For the anisol co-crystals, amongst the four anisol molecules present in the lattice, only two of them, one at each side, were deeply inserted through their Me groups into the cavities of the hollow module [Fig. 6(a)]. In the case of *p*-xylene, although a sandwich complex composed of the parent compound **1** and the solvent with a 1 : 1 ratio was reported in the solid state,²⁹ with the koiland **12**, again a discrete binuclear inclusion complex in the solid state was obtained [Fig. 6(b)]. Again, amongst the three *p*-xylene molecules present, two of them penetrate deeply into the cavities of **12** through one of their Me groups. Whereas the formation of discrete binuclear complexes with CHCl_3 and anisol may be explained by their restricted dimension and unfavourable geometry, in the case of *p*-xylene possessing the right topology, one could, *a priori*, expect the formation of a koilate. However, it appeared from the X-ray study that the distance between the two Me groups ($d_{\text{C-C}} = 5.83 \text{ \AA}$) was too short to allow the interconnection of two consecutive units and thus the formation of the koilate.

Formation of koilates

Hexadiyne, a rod type molecule, possessing both the requested linear geometry and distance between its two terminal Me groups ($d_{\text{C-C}} = 6.65 \text{ \AA}$) leads indeed to the formation of the desired koilate (Fig. 7). The latter crystallises out from either

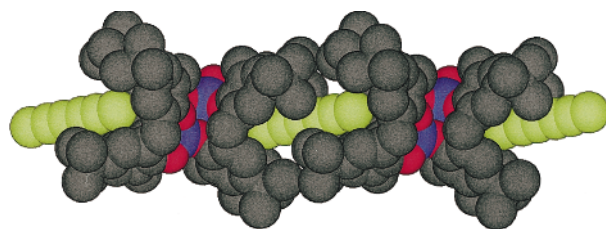


Fig. 7 A portion of the X-ray structure of the koilate formed between the koiland **12** and hexadiyne as the connector. The one-dimensional network is obtained by a single translation of the assembling core defined by the inclusion of the connector into the cavity of the receptor. For the sake of clarity, the carbon atoms of the connector are coloured in green and the hydrogen atoms are not presented.

CHCl_3 -MeOH or CHCl_3 -hexane mixtures of koiland **12** and hexadiyne in large excess.²⁸ The X-ray analysis revealed that in the crystal, in addition to **12** and hexadiyne present in 1 : 1 ratio, two CHCl_3 molecules were also present. The lattice is indeed composed of molecular linear arrays of koilates formed between

koilands **12** and hexadiyne as connectors. Each connector bridges two consecutive hollow bricks by penetrating their cavities through its terminal Me groups. The methyl groups of hexadiyne are deeply inserted into the cavity of the koiland. Indeed, the shortest distance between the Me group of the connector and the aromatic carbon atom (CO) of the koiland is 3.64 Å. It is worth noting that the hexadiyne molecules are extremely well encapsulated by two consecutive koilands **12** forming a sandwich, the shortest distance between the Me groups of the *tert*-butyl moieties of **12** being 3.51 Å.

Functionalisation of koilands

Calix[4]arene, in addition to the features stated above, presents further advantages by being readily modified at the *para* position by a large variety of substituents bearing functionalities. In particular, one may introduce at the *para* position functional groups such as allyl moieties.³⁰ It has been shown previously that although the compound **15** shows temperature-dependent conformational mobility, below room temperature it adopts a cone conformation.³⁰ The design of the new koiland **16** [Fig. 8(a)] possessing functional groups at both faces of the

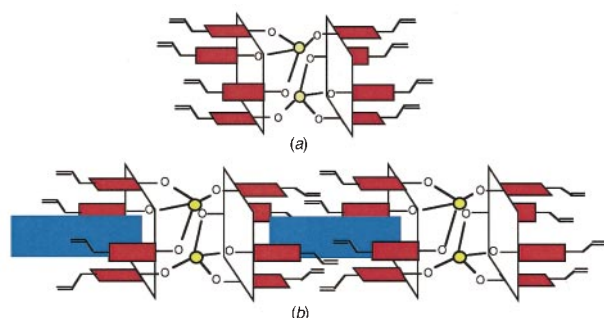


Fig. 8 Schematic representations of the doubly fused tetraallylcalix[4]arene **16** (a) and of the linear koilate formed in the presence of connector molecules (b)

molecule was based on the double fusion of the parent compound **15** with two silicon atoms.³¹ Compound **15** was prepared according to published procedures³⁰ starting from compound **12**¹ which was dealkylated leading thus to the compound **2** and the latter was first converted into the allyl ether and then, by a Claisen rearrangement, to the desired compound **15**. The doubly fused compound **16** was obtained after column chromatography in 53% yield upon treatment of compound **15** in dry THF by NaH followed by addition of SiCl₄.³¹

Since it has been previously observed that *p*-xylene, a rigid, compact and ditopic molecule, forms in the solid mononuclear and binuclear inclusion complexes with *p*-*tert*-butylcalix[4]arene^{17,29} **1** and with the koiland **12**²⁸ respectively, the formation of a one-dimensional network using compound **16** as the koiland and *p*-xylene as the connector was investigated [Fig. 8(b)]. Suitable crystals were obtained from a mixture of compound **16** and *p*-xylene in excess and PrⁱOH at room temperature. The X-ray analysis³¹ showed the following features (Fig. 9). The crystals were composed exclusively of **16** and *p*-xylene disposed in an alternate fashion. Both the connector and the koiland were centrosymmetric, the latter offering two divergent cavities. The coordination geometry around the silicon atoms was tetrahedral. As predicted, a linear koilate was formed through the interconnection of two cavities belonging to consecutive koilands **16** with the *p*-xylene molecule. In the crystal one could identify an assembling core which could be defined as the inclusion of a Me group of the connector within a cavity of **16**. The shortest C–C distance of 3.63 Å between the Me groups of the connector and one of the carbon atoms belonging to one of the phenolic group at the bottom of the cavity indicated a high degree of inclusion. The formation of the α -network resulted from a single translation of the assembling core.

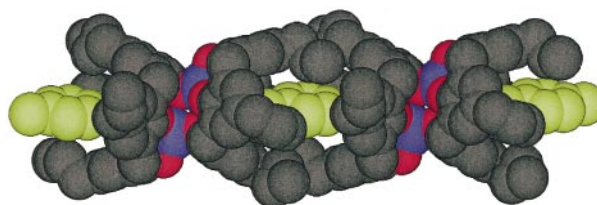


Fig. 9 A portion of the X-ray structure of the koilate formed between the koiland **16** and *p*-xylene as the connector. The one-dimensional network is obtained by a single translation of the assembling core defined by the inclusion of the connector into the cavity of the receptor. For the sake of clarity, the carbon atoms of the connector are coloured in green and the hydrogen atoms are not presented.

Although the formation of the α -network was predicted, the X-ray analysis revealed another unexpected feature. Due to the large number of rotations available for the allyl moieties, one cannot in fact predict their conformations in the crystal lattice. Interestingly, when looking at lateral packing of consecutive linear koilates, it was observed that among the eight allyl groups present in each koiland **16**, two of them were oriented centrosymmetrically in a peculiar manner (Fig. 10). Indeed, two

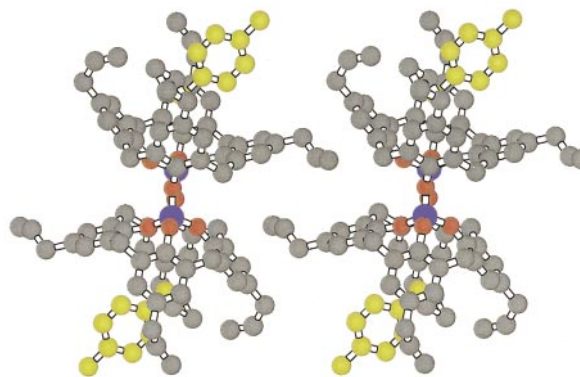


Fig. 10 A portion of the X-ray structure of the koilate formed between the koiland **16** and *p*-xylene as the connector showing the lateral packing of linear koilates leading to parallel disposition of the allyl moieties

alkene moieties belonging to two consecutive koilands were located perfectly parallel to each other with an alkene-to-alkene distance of 4.52 Å between them. Although the observed distance seems slightly too long, the proximity of the two double bonds suggests the possibility to interconnect covalently the koilates by performing a [2 + 2] cycloaddition reaction in the solid state.

It is interesting to notice that although, using compound **12** and hexadiyne, the first fully characterised linear koilate was obtained in the solid state,²⁸ one could nevertheless argue that, owing to the presence of CHCl₃ molecules in the lattice, the formation of the koilate was governed by solvent molecules. The formation of the koilate with compound **16** and *p*-xylene precludes this objection since in that case the linear koilate was formed in the solid without the presence of any solvent molecules in the lattice.

Formation of koilates by self-inclusion

As demonstrated above, koilands may lead in the solid state either to discrete molecular complexes in the presence of molecules acting as stoppers [Fig. 11(a)] or to linear molecular networks in the presence of appropriate connectors [Fig. 11(b)]. Another alternative route to the formation of linear koilate may be based on the use of self-complementary koilands possessing simultaneously two divergent cavities and connecting moieties [Fig. 11(c)]. Compound **16** fulfils these requirements. Indeed, the latter possesses two preorganised cavities resulting from the fusion of two calix units in cone conformation, as well as allyl groups at both faces of the molecule which may act as connectors.³²

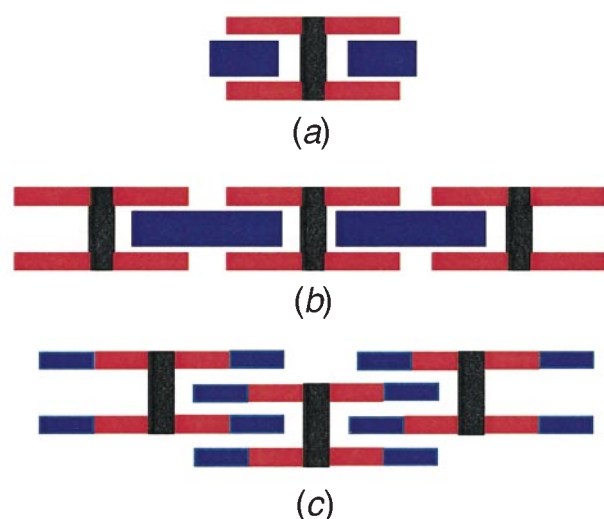


Fig. 11 Schematic representation of discrete binuclear inclusion complexes formed between koilands and stopper molecules (a) or of infinite linear molecular networks formed by koilands in the presence (b) and absence (c) of connector molecules

A study based on X-ray diffraction on single crystals obtained under various conditions for the compound **16** revealed indeed the formation of an α -network in the solid state. Upon slow liquid–liquid diffusion at room temperature of EtOH into a CHCl_3 solution of compound **16**, suitable large, colourless, air stable at room temperature, mono-crystals of the same morphology (rhombic) were obtained. The X-ray analysis revealed that the crystal was exclusively composed of compound **16**. The latter, offering two divergent cavities, was centrosymmetric. As in the case of other koilands presented above, the coordination geometry around the silicon atoms was tetrahedral. In the crystalline phase, the self-complementary koiland **16** formed a linear koilate (Fig. 12) through the

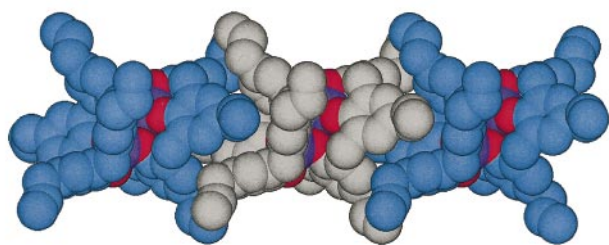


Fig. 12 A portion of the X-ray structure of the koilate formed by self-inclusion of the koiland **16**. The one-dimensional network is obtained by a single translation of the assembling core defined by the inclusion of the allyl moieties acting as internal connector into the cavity of the consecutive koiland **16**. For the sake of clarity, the carbon atoms of the consecutive koilands are differentiated by colour and the hydrogen atoms are not presented.

interconnection of two cavities belonging to consecutive koilands **16** by van der Waals interactions. The assembling core leading by a single translation to the α -network, could be identified as the inclusion of one of the four allyl groups located at one of the two faces of the molecule **16** by one of the two cavities of the consecutive self-complementary compound **16**. The shortest C–C distance between the terminal CH_2 of the allyl group acting as connector and carbon atoms of one of the aromatic moieties of the cavity belonging to the next unit varied from 3.63 to 3.92 Å, including a rather high degree of inclusion. Interestingly, when crystals of compound **16** were grown from other solvent systems such as toluene–EtOH, CHCl_3 –PrⁱOH and toluene–PrⁱOH, in all cases, crystals of the same morphology and stability were obtained and their investigation by X-ray (lattice parameters) confirmed that they were the same. However, when crystals of **16** were grown by the same technique from a CH_2Cl_2 –EtOH mixture, two types of crystals,

one with a rod-type morphology and the other with rhombic shape, were observed. Whereas the crystals with rhombic morphology were stable at room temperature and proved by X-ray analysis to be of the same type as those mentioned above, the rod-shape crystals were unstable outside the solution. Their analysis by X-ray diffraction revealed the presence of **16** and three molecules of CH_2Cl_2 . In the lattice two types of discrete inclusion complexes were present and therefore no network based on inclusion processes could be identified (Fig. 13). The

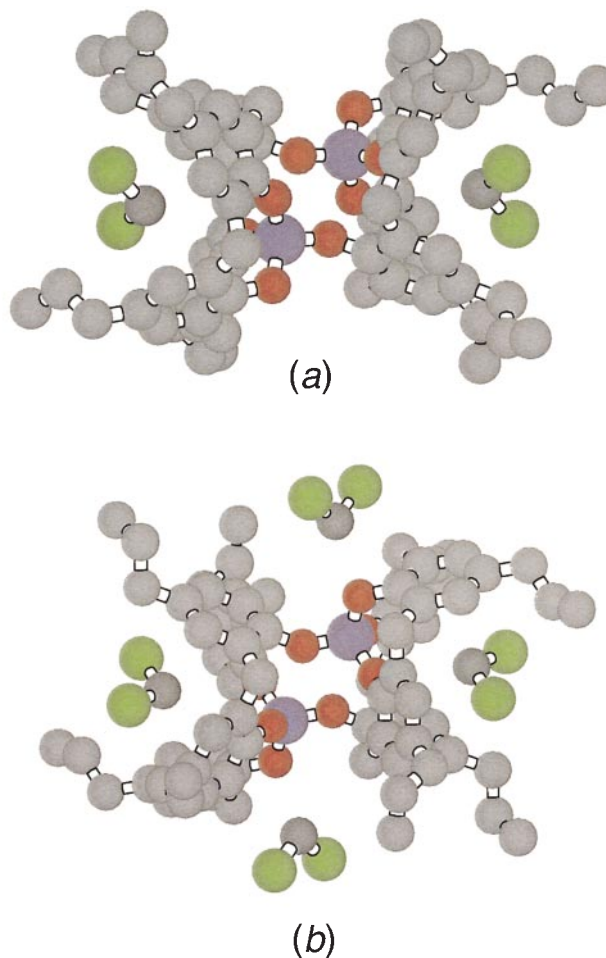


Fig. 13 X-Ray structures of the discrete bi- (a) and tetra-nuclear (b) inclusion complexes formed by the linear koiland **16** and CH_2Cl_2 . For the sake of clarity, the hydrogen atoms are not presented.

two types of units were a binuclear [Fig. 13(a)] and a tetranuclear [Fig. 13(b)] CH_2Cl_2 inclusion complex. For the binuclear complex, both cavities of compound **16** were occupied by a CH_2Cl_2 molecule. For the tetranuclear species, among the four CH_2Cl_2 present, as in the case of the binuclear complex, two of them occupied the two preorganised cavities, whereas the remaining solvent molecules were located within the two ‘pockets’ resulting from the positioning of the allyl groups. The difference between the two discrete complexes observed in the lattice may be assigned to two different conformations adopted by the allyl groups.

It is worth noting that in the case of the self-complementary compound **16** depending on composition of the solution, all three situations (Fig. 11), *i.e.* discrete inclusion complexes and one-dimensional networks formed either by interconnection of consecutive units by connectors or by self-interconnection, were obtained.

Towards directional koilates

In dealing with one-dimensional networks, the control of the directionality of the assembly remains an important and

challenging issue. In all cases of koilates mentioned above, although the dimensionality of the molecular assembly could be controlled (α -network) by the geometrical features of the building blocks, due to their centrosymmetric nature, no particular directionality could be obtained (Fig. 1). In order to control both the dimensionality and the directionality of koilates, one may use non-symmetric koilands (Fig. 14). The design of non-centrosymmetric koilands may be based either on electronic or on geometric differentiation.

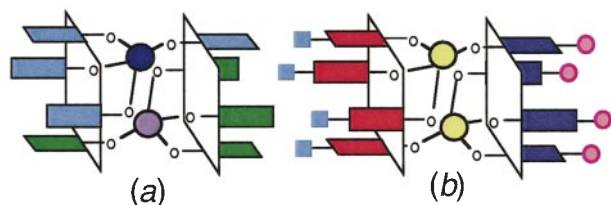


Fig. 14 Schematic representation of non-centrosymmetric koiland based either on electronic (a) or geometric (b) differentiation of the two cavities

Electronic differentiation [Fig. 14(a)] may be achieved by using two different fusing atoms with the same oxidation state IV such as Si and Ti or with different oxidation states III and IV such as B and Si. The non-symmetric nature of the Si–Ti heterobinuclear koiland is based on the induced difference between the two calix units by their coordination to two different metals with different electronegativity. Indeed, one of the calixes is triply coordinated to a Si atom whereas the other unit is triply coordinated to a Ti atom. The synthesis of the Si–Ti heterobinuclear koiland **17** [Fig. 15(a)] was achieved.³³ The stepwise strategy used was based on the preparation of the mono-fused compound **18** [Fig. 15(b)] which was shown by NMR ROESY experiments to adopt a face to face ‘syn’ conformation. Upon treatment of the latter by TiCl_4 the desired compound **17** was obtained in high yield.

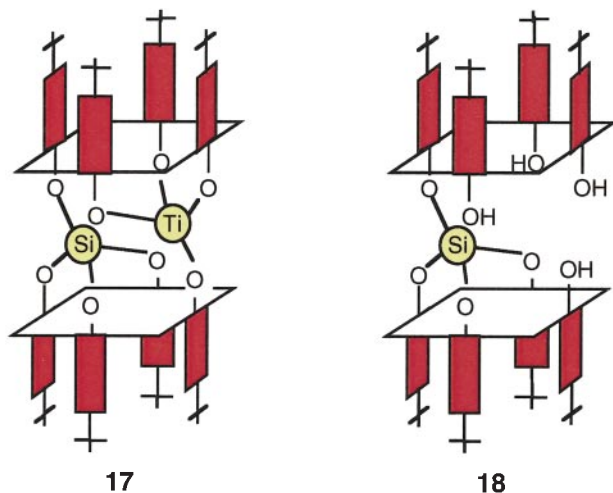


Fig. 15 Schematic representation of the koiland obtained by double fusion of two *p*-*tert*-butylcalix[4]arenes by silicon and titanium atoms **17** and of the mono-fused compound **18**

Geometric differentiation [Fig. 14(b)] may be accomplished, while keeping the same fusing element such as Si, by connecting two different calix units. Mixed compounds based on the double fusion of two different calix units by two Si atoms have been prepared. The general strategy for the preparation of non-symmetric koilands **6–8**, **10**, **11** and **13** (Fig. 4) was based on a combinatorial approach. Upon treatment of a combination of two different calix[4]arenes [X,Y] ($X = Y = 1-4$) with base, followed by reaction with SiCl_4 , as expected, three different koilands [X–X], [Y–Y] of the homo type (centrosymmetric) and [X–Y] of the hetero type (non-centrosymmetric) were obtained.³⁴

In solution, as expected, ^{29}Si NMR studies revealed the presence of two signals for the non-centrosymmetric heterodimers, whereas for the centrosymmetric koilands a unique signal was observed. In the solid state structures of compounds **6** and **7** were confirmed by X-ray analysis (Fig. 16). For both

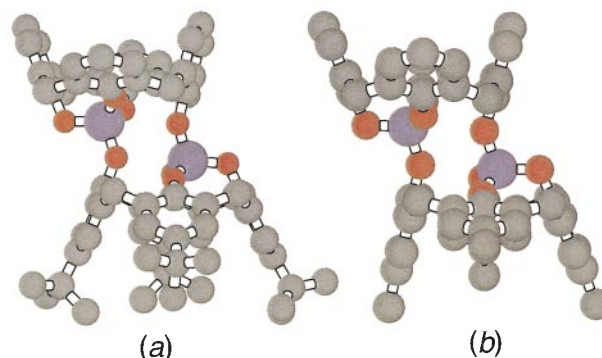


Fig. 16 X-Ray structures of linear koilands **6** (a) and **7** (b) showing the interconnection of two different calix units by two silicon atoms. For the sake of clarity, solvent molecules and hydrogen atoms are not presented.

compounds, the coordination geometry around the silicon atoms was tetrahedral. The Si–Si distance varied only slightly from 3.84 Å for **6** to 3.77 Å for **7**. These values are similar to those previously observed for compounds **9** and **12**.

Formation of directional koilates using the non-centrosymmetric koilands mentioned above is under current investigation.

Conclusions

In conclusion, it has been demonstrated that hollow molecular modules may be assembled in the solid state into one-dimensional molecular arrays either by self inclusion or by interconnection using connector molecules. Thus, inclusion processes based on van der Waals interactions may be used as a design principle for the generation of molecular networks in the solid state. Although at the present state of affairs, this approach remains essentially structural, by using molecular building blocks possessing specific magnetic, photonic or electric properties, one may extend this strategy to the preparation of functional solids. Work along these lines is in progress.

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Notes and References

- 1 A. Gavezzotti, *Acc. Chem. Res.*, 1994, **27**, 309.
- 2 J. D. Dunitz, *Pure Appl. Chem.*, 1991, **63**, 177.
- 3 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. X. Delaigue, E. Graf, F. Hajek, M. W. Hosseini and J.-M. Planeix, in *Crystallography of Supramolecular Compounds*, ed. G. Tsoucaris, J. L. Atwood and J. Lipkowski, NATO ASI, Kluwer, 1996, **C480**, 159; G. Brand, M. W. Hosseini, O. Félix, P. Schaeffer and R. Ruppert, in *Magnetism a Supramolecular Function*, ed. O. Kahn, NATO ASI, Kluwer, 1996, **C484**, 129.
- 4 J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995.
- 5 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
- 6 S. Mann, *Nature*, 1993, **365**, 499.
- 7 J. S. Lindsey, *New J. Chem.*, 1991, **15**, 153; D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229; D. Philip and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1155.
- 8 M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696.
- 9 (a) X. Delaigue, J. McB. Harrowfield, M. W. Hosseini, A. De Cian, J. Fischer and N. Kyritsakas, *J. Chem. Soc., Chem. Commun.*, 1994, 1579; X. Delaigue, M. W. Hosseini, A. De Cian, N. Kyritsakas and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1995, 609 (b) G. Mislin, E. Graf and M. W. Hosseini, *Tetrahedron Lett.*, 1996, **37**, 4503; (c) C. Drexler, M. W. Hosseini, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1997, **38**, 2993; (d) C. Kaes, M. W. Hosseini, R. Ruppert, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1994, **35**, 7233; C. Kaes, M. W. Hosseini, R. Ruppert, A. De Cian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1995, 1445; C. Kaes, M. W. Hosseini, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1997, **38**, 3901; 4389; *Chem. Commun.*, 1997, 2229.
- 10 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; D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1994, **27**, 51; V. A. Russell and M. D. Ward, *Chem. Mater.*, 1996, **8**, 1654.
- 11 R. Robson, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. Macnicol and F. Vögtle, Pergamon, New York, vol. 6 (ed. D. D. Macnicol, F. Toda and R. Bishop), 1996, p. 733.
- 12 X. Delaigue, M. W. Hosseini, A. De Cian, J. Fischer, E. Leize, S. Kieffer and A. Van Dorsselaer, *Tetrahedron Lett.*, 1993, **34**, 3285.
- 13 X. Delaigue, M. W. Hosseini, R. Graff, J.-P. Kintzinger and J. Raya, *Tetrahedron Lett.*, 1994, **35**, 1711.
- 14 G. Brand, M. W. Hosseini, R. Rupert, A. De Cian, J. Fischer and N. Kyritsakas, *New J. Chem.*, 1995, **19**, 9; M. W. Hosseini, R. Rupert, P. Schaeffer, A. De Cian, N. Kyritsakas and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1994, 2135; M. W. Hosseini, G. Brand, P. Schaeffer, R. Ruppert, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1996, **37**, 1405; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 102; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1997, **38**, 1755; 1933; *New J. Chem.*, 1997, **21**, 285.
- 15 C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. H. White, *Angew. Chem.*, 1998, in press.
- 16 C. D. Gutsche, *Calixarenes, Monographs in Supramolecular Chemistry*, ed. J. F. Stoddart, Royal Society of Chemistry, London, 1989; *Calixarenes. A Versatile Class of Macrocyclic Compounds*, ed. J. Vicens and V. Böhmer, Kluwer Academic, Dordrecht, 1991; V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713.
- 17 C., D. Gutsche, B. Dhawan, K. H. No and R. Muthukrishnan, *J. Am. Chem. Soc.*, 1981, **103**, 3782; G. D. Andreetti, R. Ungaro and A. Pochini, *J. Chem. Soc., Chem. Commun.*, 1979, 1005; R. Ungaro, A. Pochini, G. D. Andreetti and P. Domiano, *J. Chem. Soc., Perkin Trans. 2*, 1985, 197; M. Coruzzi, G. D. Andreetti, V. Bocchi, A. Pochini and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1133.
- 18 M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087; F. Corazza, C. Floriani, A. Chiesti-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1990, 1083; J. L. Atwood, S. G. Bott, C. Jones and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1992, 1349; J. L. Atwood, P. C. Junk, S. M. Lawrence and C. L. Raston, *Supramol. Chem.*, 1996, **7**, 15.
- 19 D. Kraft, J.-D. van Loon, M. Owens, W. Verboom, W. Vogt, M. A. McKervey, V. Böhmer and D. N. Reinhoudt, *Tetrahedron Lett.*, 1990, **31**, 4941; J.-D. van Loon, D. Kraft, M. J. K. Ankoné, W. Verboom, S. Harkema, V. Böhmer and D. N. Reinhoudt, *J. Org. Chem.*, 1990, **55**, 5176.
- 20 P. D. Beer, A. D. Keefe, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1990, 3675.
- 21 C. D. Gutsche and M. Iqbal, *Org. Synth.*, 1989, **68**, 234.
- 22 C. D. Gutsche and J. A. Levine, *J. Am. Chem. Soc.*, 1982, **104**, 2652.
- 23 C. D. Gutsche and K. C. Nam, *J. Am. Chem. Soc.*, 1988, **110**, 6153.
- 24 C. D. Gutsche and K. H. No, *J. Org. Chem.*, 1982, **47**, 2708; K. H. No and C. D. Gutsche, *J. Org. Chem.*, 1982, **47**, 2713.
- 25 M. Almi, A. Arduini, A. Casnati, A. Pochini and R. Ungaro, *Tetrahedron*, 1989, **45**, 2177.
- 26 R. K. Juneja, K. D. Robinson, C. P. Johnson and J. L. Atwood, *J. Am. Chem. Soc.*, 1993, **115**, 3818.
- 27 F. Hajek, E. Graf and M. W. Hosseini, *Tetrahedron Lett.*, 1996, **37**, 1409.
- 28 F. Hajek, E. Graf, M. W. Hosseini, X. Delaigue, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1996, **37**, 1401.
- 29 M. Perrin, F. Gharnati, D. Oehler, R. Perrin and S. Lecocq, *J. Inclusion Phenom.*, 1992, **14**, 257.
- 30 C. D. Gutsche and J. A. Levine, *J. Am. Chem. Soc.*, 1982, **104**, 2653.
- 31 F. Hajek, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1760.
- 32 F. Hajek, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Mater. Res. Bull.*, 1998, in press.
- 33 X. Delaigue, M. W. Hosseini, E. Leize, S. Kieffer and A. Van Dorsselaer, *Tetrahedron Lett.*, 1993, **34**, 7561.
- 34 F. Hajek, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1997, **38**, 4555.

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