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Locking high energy 1D chain of dichloromethane molecules containing abnormally short Cl···Cl contacts of 2.524 Å inside organic crystals†

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1D helical channels can be created by "sticky" end-mediated formation of 1D helical stacks composed of short cavity-containing helices and are able to host 1D chains of dichloromethane molecules containing extraordinarily short intermolecular Cl···Cl contacts of 2.524 Å in length that computationally destabilize the host–guest complex by 14.94 kcal mol^{-1}.

Recently, we reported a series of crescent-shaped internally H-bonded foldamer molecules[1] with their aromatic backbones enforced by internally placed continuous H-bonding networks and with their repeating monomeric units respectively derived from methoxybenzene,[2] fluorobenzene,[3] pyridone,[4] and pyridine[5] motifs. With a further backbone confinement *via* a covalent macrocyclization, the appropriately sized pentamers can become circularly folded to arrive at a unique pentagon shape.[2c–j,3,4] Otherwise, the closely related folding oligomers take up a helical shape instead.

More recently, by introducing "sticky ends" into the two ends of helically folded pyridine-based foldamers[5] such as **1** (Fig. 1a), we succeeded in demonstrating, for the first time, a spontaneous resolution of racemic aromatic helices into their enantiopure single-handed helical forms *via* chiral crystallization without resorting to chiral auxiliary or external stimuli.[6] A key to the successful chiral crystallization is the "sticky end"-mediated formation of 1D chiral stacks of the same handed helices (Fig. 1b) that subsequently associate intercolumnarly to form 3D ordered chiral crystal lattices. Concurrent with the formation of the 1D chiral stacks is the creation of a 1D hollow cavity of ~2.5 Å in radius whose interior is decorated by both H-bond donors (amide protons) and acceptors (pyridine N-atoms and ester O-atoms), making these cavity-containing 1D stacks suitable for accommodating small guest molecules[5b,c] or functional groups.[5d] Indeed, slow diffusion of methanol (MeOH) into **1**-containing dichloromethane(CH_2Cl_2) solution led to crystals containing 1D chains of MeOH molecules inside their chiral cavity while slow diffusion of acetone or ethyl acetate into **1**-containing CH_2Cl_2 solution resulted in CH_2Cl_2-containing crystals (Fig. 1c). Surprisingly, even after re-growing the crystals of **1** in water-containing solvents, no water molecules can be found in **1** while other pyridine-derived analogous oligomers of the same length can accommodate up to two water molecules in their cavity.[5b,c] This suggests that the 1D hollow cavity formed by stacking oligomers of **1** on top of each other is functionally quite selective and displays higher binding affinities toward CH_2Cl_2 molecules than water molecules.

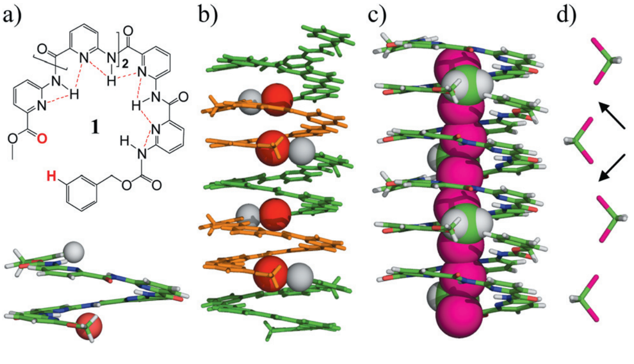

Fig. 1 (a) Chemical structure of a pyridine-based helical oligoamide **1** (top) and its crystallographically determined helical structure (bottom). The two "sticky" end groups, *i.e.*, ester and benzene group, contain a partially charged O-atom (red ball) and aromatic proton (gray ball) that form a weak intermolecular H-bond of 1.50 kcal mol^{-1} in strength. (b) The formation of 1D chiral packing and 1D helical channel by **1** *via* complementary "sticky" end groups and aromatic π–π stacking forces. (c) Encapsulation of 1D chain of dichloromethane molecules in 1D helical channel formed by **1**. (d) Crystallographic observation of abnormally short intermolecular Cl···Cl contacts of 2.524 Å. In the CPK model, H = gray, O = red, C = green and Cl = hot pink.

In the crystal structure, each CH_2Cl_2 molecule is at most associated with three helically folded pentamer molecules of **1** but predominantly wrapped around and stabilized by just one pentamer molecule in the middle (Fig. 2a). The top pentamer

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† Electronic Supplementary Information (ESI) available: Synthetic route for **1**, X-ray crystal data sheet of **1**·CH_2Cl_2 with CCDC number, CIF file, and details of the computational methods are given in the Supporting Information. CCDC 838392 and 838393. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25888a

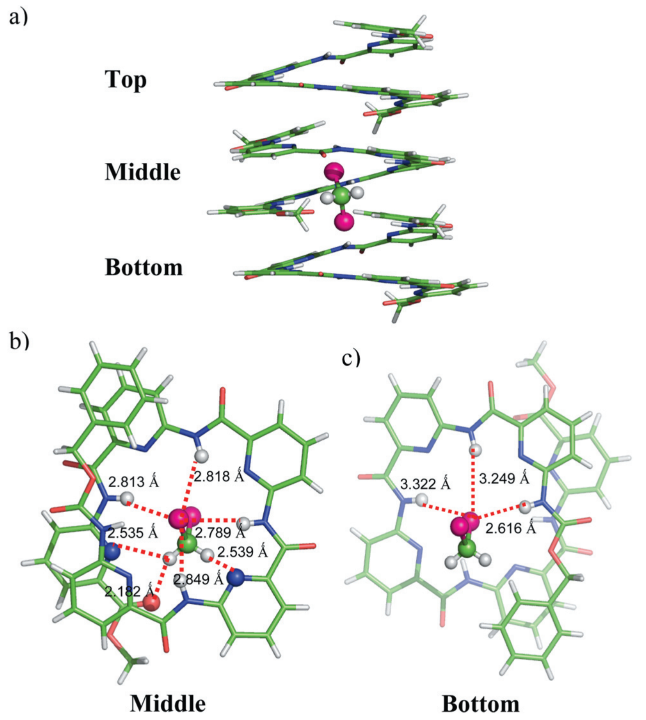

Fig. 2 (a) A CH_2Cl_2 molecule trapped inside the cavity formed by three molecules of **1**. (b) Middle complex, illustrating intermolecular H-bonds (dotted lines) of varying lengths found among the trapped CH_2Cl_2 molecule, amide protons, and ester carbonyl O-atom in **1**. (c) Bottom complex, illustrating intermolecular H-bond of 2.616 Å formed between bottom Cl-atom from CH_2Cl_2 and an amide proton in **1**. In both (b) and (c), atoms participating in H-bonds of within 3.0 Å are represented by small balls of varying colours: H = gray, O = red and Cl = hot pink. H-bonds are shown as dotted red lines.

Table 1 The intermolecular Cl⋯Cl distances (Å) in varying molecular crystals

In crystals of Cl_2 molecules at 0.1 MPa[a,7a]			
22 K 3.258 Å	55 K 3.273 Å	100 K 3.296 Å	160 K 3.330 Å
In crystals of CH_2Cl_2 molecules[7b]			
293 K/1.63 GPa 3.324 Å	293 K/1.33 GPa 3.360 Å	153 K/0.1 MPa 3.492 Å	
In crystals containing 1D chains of CH_2Cl_2 molecules			
3.284 Å[7c]	3.438 Å[7d]	3.498 Å[7e]	3.635 Å[7f]

[a] 0.1 MPa = one atmospheric pressure.

molecule interacts very weakly with a CH_2Cl_2 molecule through van der Waals forces. In the middle complex (Fig. 2b), four amide protons (gray balls), two pyridine N-atoms (blue balls) and one carbonyl O-atom (red ball) in **1** provide an anchor point to fix the spatial orientation of the CH_2Cl_2 molecule by respectively forming four weak intermolecular H-bonds of 2.789–2.849 Å with the top Cl-atom from CH_2Cl_2, two H-bonds of 2.535 Å and 2.539 Å with the two protons from CH_2Cl_2, and one H-bond of 2.182 Å with a proton from CH_2Cl_2. In the bottom complex (Fig. 2c), the bottom Cl-atom from CH_2Cl_2 forms only one weak intermolecular H-bond of 2.616 Å with an amide proton in **1**.

A more careful examination of one dimensionally aligned CH_2Cl_2 molecules lying within the hollow cavity of **1** reveals very short intermolecular Cl⋯Cl contacts of 2.524 Å in length among the immediately adjacent CH_2Cl_2 molecules at a temperature of 100 K (Fig. 1d). An intermolecular Cl⋯Cl distance of as short as 2.524 Å in regularly arrayed CH_2Cl_2 molecules is very unusual particularly with respect to those found in the molecular crystals of chlorine[7a] or CH_2Cl_2[7b] molecules or 1D chains of CH_2Cl_2 molecules trapped in other types of organic frameworks.[7c–f]

Experimentally as compiled in Table 1, the intermolecular Cl⋯Cl distance in the solid chlorines varies from 3.258 to 3.330 Å within a temperature range of 22–160 K at one atmospheric pressure (0.1 MPa),[7a] and those chlorine contacts found in the crystal structure of CH_2Cl_2 molecules fall within 3.324–3.492 Å at varying temperatures and pressures. In a few other limited examples where 1D chains of CH_2Cl_2 molecules are trapped within the organic crystal lattices made up of non-porous organic molecules, the chlorine contacts range from 3.284 to 3.635 Å. Similarly, the shortest Cl⋯Cl intermolecular contacts observed in other chlorine-containing organic molecules such as 1,1,2,2-tetrachloroethane at 0.5 GPa[7g] and 1,2-dichloroethane at 0.7 GPa[7h] are 3.478 and 3.587 Å, respectively. It is very interesting to note that an increase in pressure by 3000 atmospheric pressure at 298 K results in an experimentally observable very marginal compression of the intermolecular Cl⋯Cl contact length by 0.036 Å (Table 1). As a further comparison, the covalent bond length of Cl–Cl bond in Cl_2 measures at 1.98 Å at 160 K/0.1 MPa.

The Dreiding force field[8a] has been successfully used to calculate the structure of organic crystals with a very high hole mobility.[8b] The interacting energies between the two non-covalently interacting chlorine atoms at varying distances ($d_{\text{Cl}\cdots\text{Cl}}$ = 2.4–4.5 Å) hence were computed using the Dreiding force field with the Gasteiger charge method[8c] (Fig. 3). Our calculation shows that the intermolecular forces between the two Cl-atoms are attractive when $d_{\text{Cl}\cdots\text{Cl}} > 3.134$ Å, become zero when $d_{\text{Cl}\cdots\text{Cl}} = 3.134$ Å, and turn out to be repulsive when $d_{\text{Cl}\cdots\text{Cl}} < 3.134$ Å. Such repulsive energies increase rapidly upon a further shortening of Cl⋯Cl distance. In particular, for $d_{\text{Cl}\cdots\text{Cl}} = 2.524$ Å, the repulsion energy amounts to as large as 15.06 kcal mol^{-1}, suggesting a great difficulty for the intermolecular Cl⋯Cl contact length to be as short as 2.5 Å in 1D chains of CH_2Cl_2 molecules.

The observed abnormally short Cl⋯Cl intermolecular distance of 2.524 Å with high repulsion energy of 15.06 kcal mol^{-1} therefore invokes us to further study this remarkable phenomenon and stabilization mechanism by theoretical calculations using the Dreiding force field. To derive binding energies that dictate the formation of a high energy 1D chain of CH_2Cl_2 molecules, the crystallographically determined structural motifs of varying types were used directly for all the energy computations without further geometric optimizations (Fig. 4a–c). The calculations were first carried out to obtain the energetic profiles related to the formation of 1D helical stack by **1** without (Fig. 4a) and with (Fig. 4b) the guests in it, and of a 1D chain of

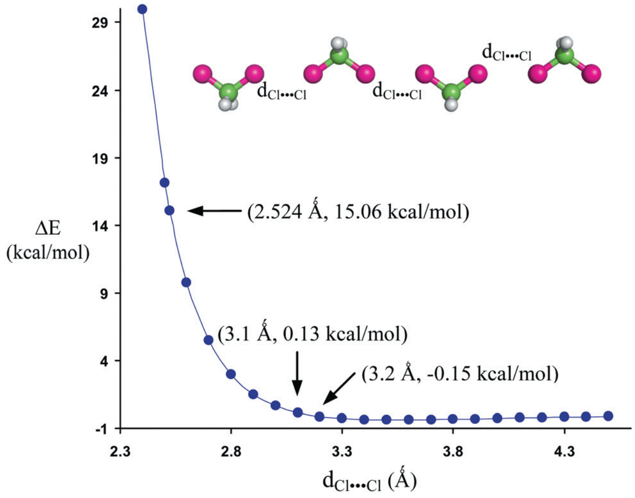

Fig. 3 Structural model of 1D chain of dichloromethane molecules where all the chlorine atoms are coplanar and aligned in a linear fashion as well as the calculated interacting energy (Δ*E*, kcal mol^{-1}) *vs.* intermolecular Cl···Cl distance ($d_{Cl\cdots Cl}$, Å). The energies were obtained by using the Dreiding force field under periodic conditions and differ insignificantly from the energy values calculated on the basis of 1D chain of dichloromethane molecules directly taken from crystal structure where chlorine atoms are roughly coplanar and aligned in a linear fashion (Fig. 1c and d).

CH_2Cl_2 molecules (Fig. 4c). Computationally, inclusion of a 1D chain of CH_2Cl_2 molecules into the 1D helical channel formed by **1** is an energetically favored process, leading to an energy gain of 32.81 kcal mol^{-1} (Fig. 4b). This is a result of the efficient aromatic stacking that seems to be the major driving force, contributing 31.86 kcal mol^{-1} per helical pentamer into the 1D columnar stack, and that, with additional energy gains from H-bonding networks formed between host **1** and CH_2Cl_2 molecules (Fig. 2), can more than compensate for the energetic penalty of 14.94 kcal mol^{-1} per short Cl···Cl contact of 2.524 Å in length (Fig. 4c).

Calculations were then carried out to provide more detailed insight into the formation of the host–guest complex and its varying fragments (Fig. 4d–g). From the computed energies, it can be seen that a one dimensionally aligned tripartite ensemble made up of three pentamer molecules provides a net stabilizing energy of 9.92 kcal mol^{-1} for one CH_2Cl_2 molecule (Fig. 2a and 4d). A deconvolution of this net energy reveals the largest contribution of 5.99 kcal mol^{-1} (Fig. 4e) from the middle pentamer that forms H-bonds of varying strengths with the CH_2Cl_2 molecule while the top and bottom pentamers contribute a respective binding energy of 0.65 kcal mol^{-1} (Fig. 4f) and 3.36 kcal mol^{-1} (Fig. 4g) to the stabilization of the CH_2Cl_2 molecule inside the helical channel. By using the deconvoluted energies of ΔE_{4a} and ΔE_{4c} along with ΔE_1 and ΔE_3, the binding energy underlying the dimerization of two **1**·CH_2Cl_2 complexes (Fig. 4h) can be estimated to be 20.93 kcal mol^{-1} by means of equation of $\Delta E_5 = \Delta E_1 + \Delta E_{4a} + \Delta E_{4c} - \Delta E_3$, a value that is very close to the calculated binding energy of 20.75 kcal mol^{-1} (Fig. 4h). This suggests to us that the two strongly repulsive Cl-atoms from the two neighbouring CH_2Cl_2 molecules are held together in a close proximity of 2.524 Å by the aromatic π–π stacking (ΔE_1, Fig. 4a) and attractive forces between "top" CH_2Cl_2 molecule and "bottom" pentamer (ΔE_{4c}, Fig. 4g) and between "bottom" CH_2Cl_2 molecule and "top" pentamer (ΔE_{4a}, Fig. 4e), which override the strongly repulsive interactions between two Cl-atoms.

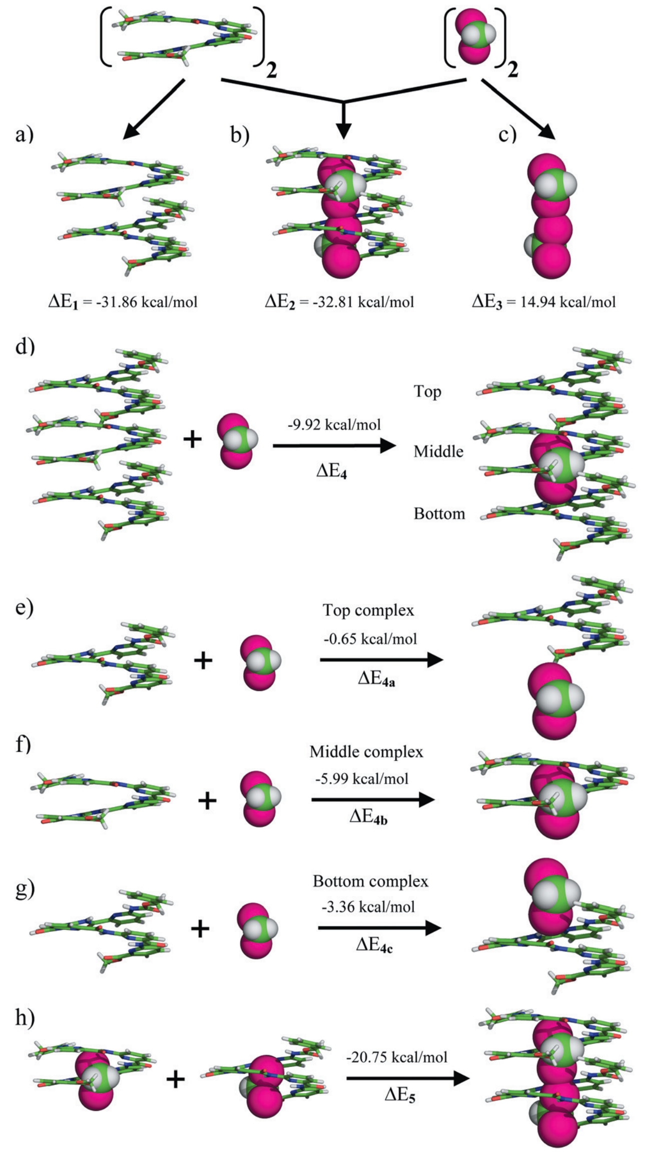

Fig. 4 Structural models of **1**·CH_2Cl_2 complex and its varying fragments used for deriving the corresponding energies in kcal mol^{-1} by using the Dreiding force field. All the models were taken directly from the crystal structure without further geometric optimizations.

By further calculating Mulliken charge distributions of the bound CH_2Cl_2 molecule and around the interior of **1** at the B3LYP/6-31G(d,p) level, it becomes readily comprehensible why the CH_2Cl_2 molecules can stably sit inside the channel's cavity despite the existence of non-covalently interacting strongly repulsive Cl-atoms. The estimated partial atomic charges show that the top Cl-atom from CH_2Cl_2 acquires a partial negative charge of −0.045 (Fig. 5) and is surrounded by four amide protons that carry partial positive charges of 0.274–0.281 (Fig. 5) and that are within the H-bonding distances

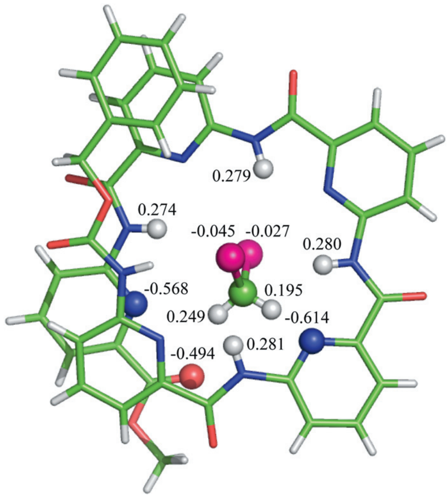

Fig. 5 The calculated Mulliken charge distributions around the interior of **1** and a CH_2Cl_2 molecule at the B3LYP/6-31G(d,p) level. The partially positively and negatively charged protons and Cl-atom in CH_2Cl_2 are stabilized by opposite charges from pyridine N-atoms, ester O-atom and amide protons in the nearby areas, fixing the position of CH_2Cl_2 molecules and allowing them to sit comfortably inside the 1D channel formed by **1**. For the side view and H-bonds, see Fig. 2a and b.

of 2.789–2.849 Å (Fig. 2a). In addition, the two protons from CH_2Cl_2 possess partial positive charges of 0.249 and 0.195 and are stabilized by adjacent negatively charged pyridine N-atoms (−0.568 and −0.614) and carbonyl O-atom (−0.494). It is worth mentioning that the repulsive interactions among Cl-atoms from CH_2Cl_2 and N- or O-atoms in **1** are insignificant since all the distances among them are invariably larger than 3.49 Å.[9]

In summary, we report here for the first time a crystallographic observation of 1D chains of CH_2Cl_2 molecules containing an abnormally short highly unstable Cl⋯Cl contact of 2.524 Å in length trapped in 1D organic helical channels. An energetic penalty of 14.94 kcal mol^{-1} associated with this short contact is compensated by aromatic π–π stacking forces involving a full overlap of helical backbones of **1** (31.86 kcal mol^{-1}), and attractive forces between CH_2Cl_2 molecule and its vertically adjacent pentamer molecules of **1** that are worth about 4.01 kcal mol^{-1} in total. Additionally, every CH_2Cl_2 molecule is further stabilized by one pentamer molecule of **1** *via* the formation of weak intramolecular H-bonds of varying strengths, giving a stabilizing energy of 5.99 kcal mol^{-1} to the host–guest complex. Straightforwardly, the appropriately charged interiorly arrayed amide protons, pyridine N-atom and carbonyl O-atom in **1** provide critically important stabilizations to the partially charged protons and Cl-atoms from CH_2Cl_2 molecule, allowing the CH_2Cl_2 molecules to sit inside the channel's interior, be aligned one-dimensionally, and comfortably stay in contact with each other *via* short highly unstable Cl⋯Cl contacts of 2.524 Å.

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9 Compared to the unbound CH_2Cl_2 that has a respective partial charge of 0.205 and −0.022 on its H- and Cl-atoms, formation of the H-bonds between the foldamer host and CH_2Cl_2 promotes the charge transfer from protons to more electronegative atoms, resulting in the bound CH_2Cl_2 being more negatively charged on its two Cl-atoms (−0.045 and −0.027) and more positively charged on one of its two H-atoms (0.249). These increases in partial charges further enhance the interactions between the foldamer host **1** and CH_2Cl_2 molecules, providing sufficient energetic gains to overcome the intermolecular repulsion between the Cl-atoms in close contacts.