Multiphase self-assembly of 5-alkoxyisophthalic acid and its applications

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A summary of our recent studies on multiphase self-assembly of 5-alkoxyisophthalic acid (C_nISA) as a versatile molecular building block is described. An interplay of weak interactions such as hydrogen bonding and van der Waals forces (alkyl chain crystallization) is the key factor in achieving and controlling the multiphase self-assembly of C_nISAs. Self-assembly of pure acids and its stoichiometric mixtures with bifunctional diazines in the solid state is described with typical examples. Supramolecular structures observed at the solid–solution interface (2D crystals) show characteristic similarities and differences with the structures observed in the 3D crystal lattices. C_nISAs with $n > 16$ exhibit thermotropic behavior. An overview of the important features of the mesophase is also discussed. The self-assembly in solution leads to a cyclic structure similar to the one observed in the single crystal lattice of C_nISAs with shorter alkyl chains ($n = 6$–10). Towards designing a functional supramolecular system, properly functionalized C_nISAs are used and the analysis of the results from their photophysical studies at the solid–solution interface is discussed.

The self-assembly process is very common in biological systems.[1] However, the reproducibility and consistency observed in natural systems for the synthesis of functional macroarchitectures such as proteins and enzymes are difficult to mimic in non-natural systems. Weak intermolecular forces such as electrostatic or van der Waals interactions play an important role in self-assembly processes.[2] Understanding and controlling these interactions may allow the design of new building blocks for the synthesis of novel functional supramolecular materials.[3]

The controlled formation of supramolecular structures in the solid state, in the mesophase and in solution from molecular building blocks using the self-assembly process has been an active area of research in recent years.[4,5] However, due to the lack of a single molecular model which can be studied in all the above mentioned phases, a systematic comparison of the self-assembly process has not been feasible. This is very important in designing new materials with the same structure under various conditions.[6]

Our goal in this area is to combine more than one intermolecular interaction, mainly strong hydrogen bonding and weak alkyl chain crystallization, to control the self-assembly process of both molecular and macromolecular systems.[7,8] This approach explores the synthesis of molecular and macromolecular building blocks and investigates controlled self-assembly in multiple phases.

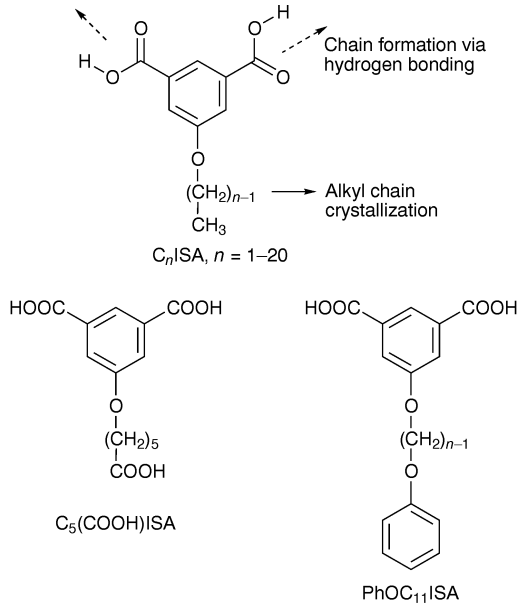
We are interested in understanding the role of a substituent—an alkyl chain—at the C5-position of isophthalic acid (ISA) in influencing the multiphase self-assembly process of C_nISAs (Scheme 1).[7–9] We can also explore the interplay of hydrogen bonding—acid dimer formation—and alkyl chain crystallization towards the formation of superstructures in multiple phases. In this paper, the similarities and differences of supramolecular structures formed from 5-alkoxyisophthalic acids (C_nISAs) in the solid lattice, in the mesophase, in solution and at the interface are discussed with examples.

Self-assembly in the Crystal Lattice

The synthesis of C_nISA has been described elsewhere.[10] Single crystals suitable for crystal structure analyses were grown by slow evaporation of tetrahydrofuran (THF) solutions. Crystal structure analyses were performed on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated CuKα radiation.

5-Hexadecyloxyisophthalic acid (C_{16}ISA), on crystallization from a dry THF solution, self-assembles into a lamella-type structure where the dimer formation of the acid groups is the main hydrogen-bonding motif.[8] The alkyl groups from the adjacent hydrogen-bonded chains interdigitate to form an extended sheet-type lattice (Fig. 1). This is true for all C_nISAs where $n > 12$. All aromatic rings in the hydrogen-bonded chain lie in one plane (plane of the page in Fig. 1), whereas the alkyl chains interact and pack in a three-dimensional lattice. Neighboring phenylene rings along the hydrogen-bonded chain are coplanar with a distance of 2.62 Å between the H-bonded oxygen atoms of the carboxyl groups.

C_nISAs with a chain length $n = 6$–10, show a cyclic structural organization. Here, six isophthalic acid molecules form a



Scheme 1 Design strategy and molecular structures of C_nISA and its derivatives

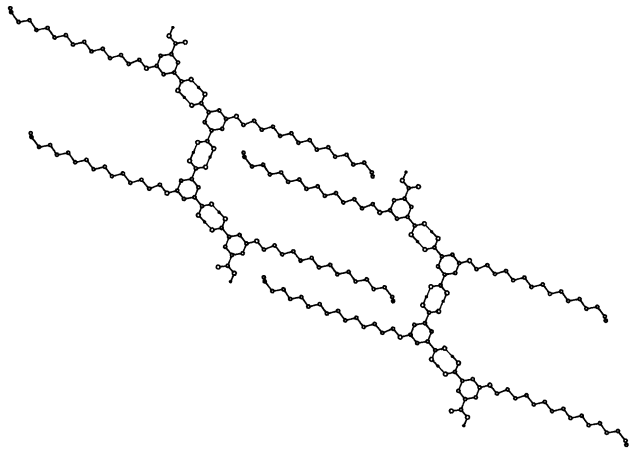


Fig. 1 Crystal structure of C_{16}ISA

ring with 12 hydrogen bonds. These rings pack one on top of the other to give a channel-type architecture (Fig. 2). A closer look at the packing of the crystal lattice reveals that each hexameric ring structure is connected to six of its neighbors *via* the alkyl groups. One C–C bond along the alkyl chain (usually 3–4 carbon atoms from the end of the chain) is in a *gauche* conformation. This creates a bend along the alkyl chain, by which the terminal 3–4 carbon atoms are inserted into the middle of the adjacent channels. It also permits the interior of each channel to be filled with the alkyl groups from the neighboring channels. A complete analysis of the structure is given in our recent paper.[11]

After establishing the self-assembly of C_nISAs in the crystal lattice, investigation of the tolerance limit of the lattices towards both polar and bulky non-polar substituents is important in understanding the dominance of weak interactions in the self-assembly process. Towards understanding this factor, C_nISA derivatives are synthezised with polar and non-polar, but sterically demanding, functional groups at the end of the alkyl chain far away from the isophthalic acid head group. From the initial results, it appears that both channel-type and sheet-type structures can accommodate various substituents.[12]

The structure of the C_6ISA lattice is maintained even when another carboxyl group is incorporated at the end of the alkyl chain [C_5(COOH)ISA, Fig. 3]. The aliphatic carboxyl group

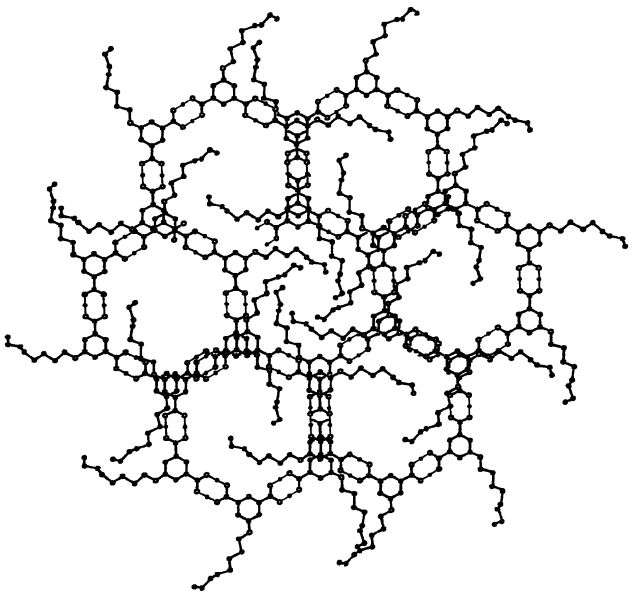


Fig. 2 Crystal structure of C_8ISA, showing the packing motif in the crystal lattice (projection along the *c* axis of the hexagonal unit cell)

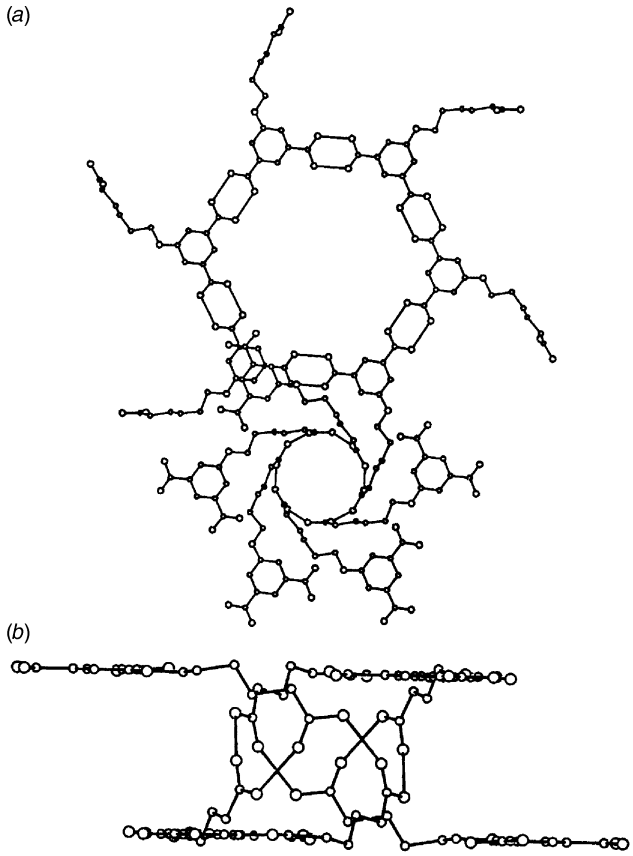


Fig. 3 Crystal structure of C_5(COOH)ISA (*a*) plot perpendicular and (*b*) parallel to the plane of the hydrogen-bonded hexamers of the isophthalic acids

does not interfere with the hydrogen-bonding motif of the isophthalic acid unit, but forms another ring in the lattice, where six acid groups at the end of the alkyl chain, from the six adjacent ISA channels, are involved. There are no symmetric acid dimers present in the second ring structure. Each COOH group interacts with two other ones, thus generating a ring-type structure. This lattice is isostructural with the crystal structure of C_6ISA. The details of the crystallographic parameters will be published elsewhere.[13]

A similar tolerance is seen in PhOC_{11}ISA (Fig. 4), where the bulky phenoxy group is accommodated in the lattice similar to C_{16}ISA. Here also, the hydrogen bonded chain is planar and the alkyl chains interact in a three-dimensional fashion as seen in for C_{16}ISA (Fig. 1).[14]

The other area of interest is the self-assembly of C_nISAs in the presence of an added bifunctional hydrogen-bonded acceptor. Diazines were chosen as suitable partners mainly owing to the strong acid–base interaction and thereby the strong hydrogen-bond formation. So far, the self-assembly of C_nISAs in the crystal lattice has been examined in the presence of diazines such as pyridazines (Pyz), pyrimidines (Pym), pyrazines (Pyr) and 4,4′-bipyridine (Bipy) (Scheme 2). Both Pyz and Pym are included in one class where the hydrogen-bond

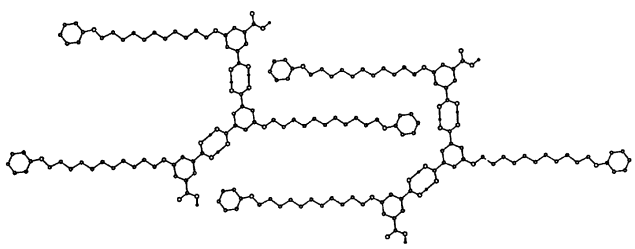
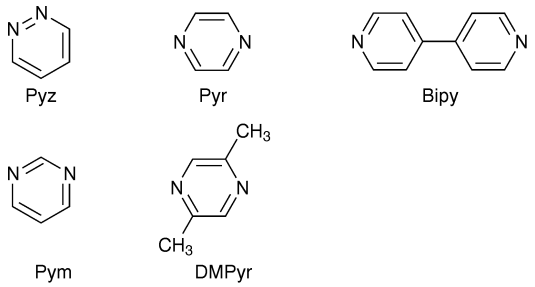


Fig. 4 Crystal structure of PhOC_{11}ISA



Scheme 2 Molecular structures of the hydrogen-bond acceptors studied

acceptor sites (N-atoms) are located within an angle of less than 180° to each other. As a typical example, a cocrystal of $C_{16}ISA \cdot Pym$ shows an alternating array of acid and base molecules.[8,15] Each of the carboxyl groups hydrogen bonds to one nitrogen atom of the pyrimidine molecule. This hydrogen-bonding motif in conjunction with the alkyl chain crystallisation gives rise to a ribbon-type structure. These ribbons are packed with a herring-bone type arrangement in the crystal lattice (Fig. 5).

The other diazines of interest involve 'linear molecules' such as Pyr and Bipy. Here the hydrogen bond acceptor sites are organized in a linear fashion with an angle of 180° between the nitrogen atoms. The crystal structure of $C_{12}ISA \cdot Pyr$ is particularly interesting. First, when a stoichiometric mixture was crystallized from the THF solution, crystals of $C_{12}ISA \cdot Pyr$ with a 2 : 1 component ratio were obtained. Many repeated attempts to grow a stoichiometric crystal were unsuccessful. In the crystal lattice, each of the acid molecule forms hydrogen bonds with two adjacent acid molecules on either side of it along the hydrogen bonded chain and to one nitrogen atom of a Pyr molecule (Fig. 6). The alkyl chains from the adjacent hydrogen-bonded chain interdigitate and crystallize to form a ribbon-type structure. The Pyr molecule crosslinks the adjacent hydrogen-bonded acid ribbons. All phenylene rings of the acid molecules in one hydrogen bonded chain are coplanar, however, the Pyr molecules form an angle with the plane of the acid ribbons. Since a large number of the above mentioned structures are layer-type and the hydrogen bonded strands are planar and stable, it is anticipated that these structures can be deposited from a solution onto a substrate at the liquid–solid interface.

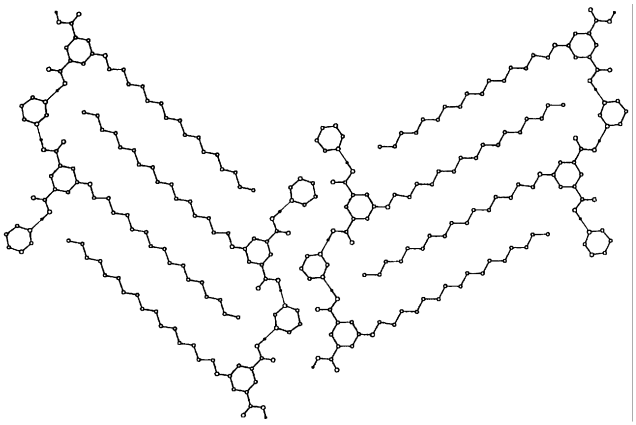


Fig. 5 Crystal structure of $C_{16}ISA \cdot Pym$

Self-assembly at the Interface

It has been shown that a wide variety of organic compounds can be deposited from solution as two-dimensional (2D) crystals on the basal plane of highly oriented pyrolytic graphite (HOPG) and imaged *in situ* by scanning tunneling microscopy (STM).[16] The interplay of hydrogen bonding and alkyl-chain packing on the 2D-organization of fatty acids and alcohols has been studied.[17] Small disturbances in the packing of long alkyl chains can have an appreciable effect on the 2D crystal lattice of a molecule.[18] Having explored the influence of the alkyl-chain length and the effect of adding H-bond acceptors on the self-assembly of C_nISAs in bulk,[7–9,11] the self-assembly of C_nISAs on a flat substrate is discussed in this section. In

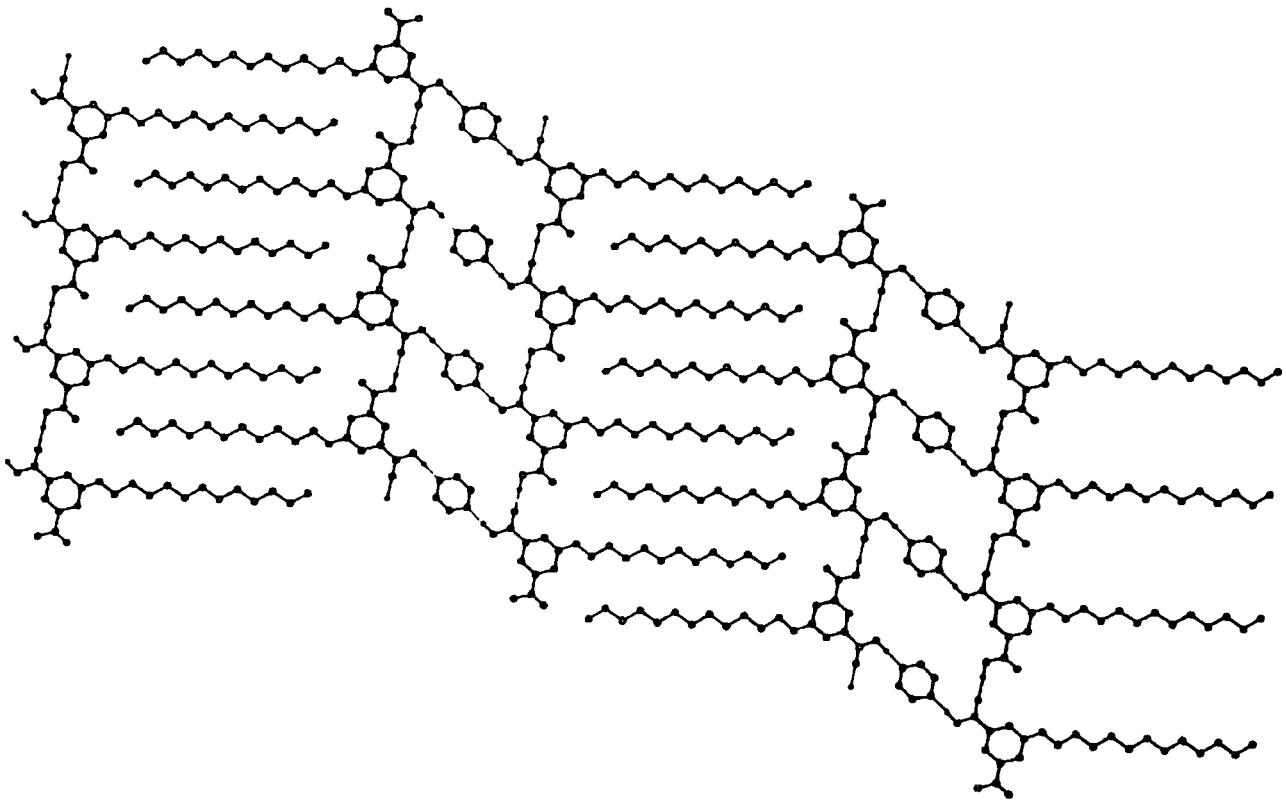


Fig. 6 Crystal structure of $C_{12}ISA \cdot Pyr$

order to demonstrate the concept, STM images of C_{16}ISA and its 2 : 1 stoichiometric donor–acceptor complexes with the bifunctional bases Pyr and DMPyr (Scheme 2) with submolecular resolution are discussed in detail.[19]

The experiments were carried out as follows. A drop of solution (2 mM) of C_nISA in phenyloctane was applied to a vertically placed slab of freshly cleaved HOPG (Advanced Ceramics, Cleveland, USA) by means of a Pasteur pipette. The drop slipped off the substrate leaving an approximately 20 μm thick liquid film on the surface, into which the tunneling tip was immersed. The physisorbed two-dimensional crystals were investigated *in situ* at the solid–liquid interface using a home-built scanning tunneling microscope (STM).[20] Once the investigation of the pure C_nISA solution was completed, a drop of pure Pyr or DMPyr was added to the same monolayer of C_nISA on the graphite substrate. After a few minutes, images of the stoichiometric compound could be recorded. This is only possible for two reasons: one involves the greater strength of the hydrogen bonds with Pyr and C_nISA which allows the molecules to form a stable structure. The other is the dynamic equilibrium between the monolayer and the solution on top of it, which then corrects any defect in the 2D structure formed *via* the self-assembly process. The STM images were obtained in constant height mode under ambient conditions. Two-dimensional-lattice constants for the monolayer were calculated by *in situ* comparison with the known values of the underlying graphite lattice. Refinement of the data was achieved by evaluating the Moiré pattern.[21] STM images of highly ordered monolayers of C_{16}ISA (Fig. 7), C_{16}ISA · $\frac{1}{2}$DMPyr (Fig. 8) were obtained with submolecular resolution. In both the 2D and the 3D structure the pure acid (C_{16}ISA) forms closely packed arrays of interdigitating hydrogen-bonded ribbons. In 3D, two sets of planes have to be considered: one, which is defined by the H-bonded strands and a second one, in which the close packing of the alkyl chains is observed. However in 2D both H-bonded strands and alkyl chains must lie in one plane. As a result, the hydrogen-bonding pattern in the 2D structure is different from the one in the 3D crystal lattice. A proposal for the 2D hydrogen-bonding pattern is depicted in Scheme 3.

Introducing a bifunctional aromatic base such as Pyr or DMPyr leads to strong hydrogen bonding between the COOH group and the N atom of the diazine,[22] which in turn changes the self-assembly pattern. The structure (see Fig. 8) again consists of hydrogen-bonded strands of acid molecules. The alkyl side chains of two neighboring strands interdigitate and the resulting lamellae are cross-linked by diazine mol-

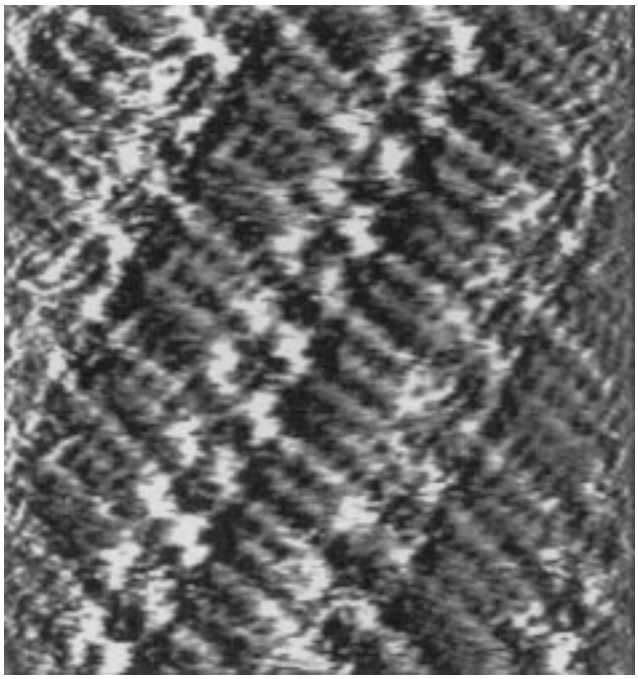


Fig. 7 STM image of C_{16}ISA

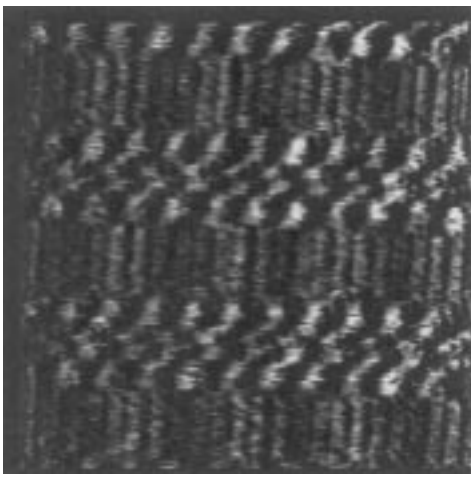
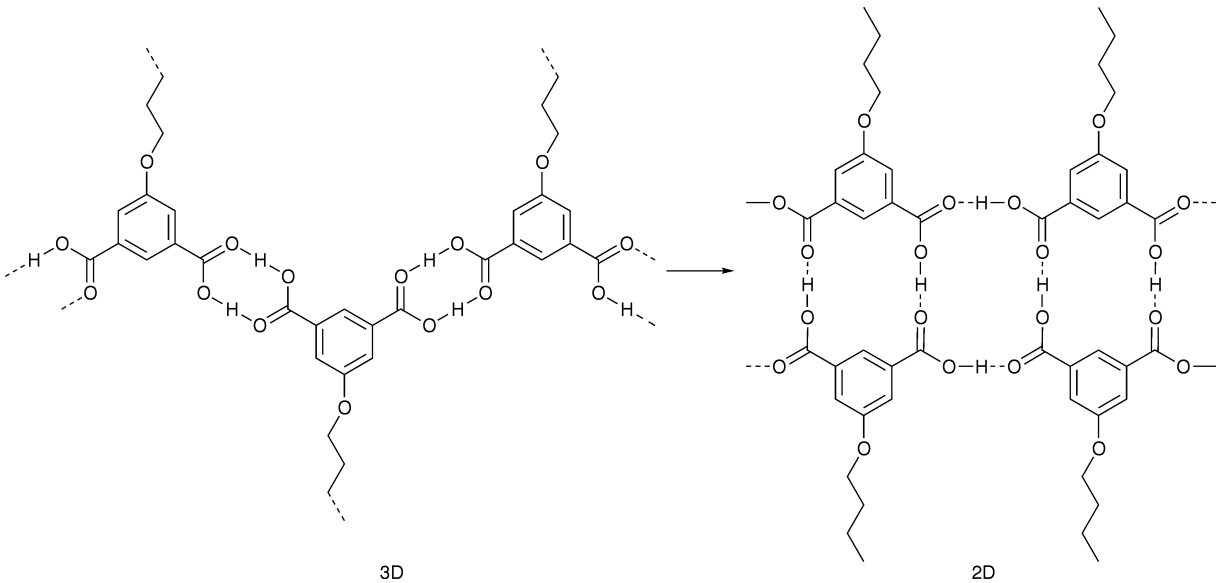


Fig. 8 STM image of the C_{16}ISA · $\frac{1}{2}$DMPyr complex



Scheme 3 Hydrogen-bonding motif in 3D and 2D lattices

ecules. In contrast to the structure of the pure acid, the 3D crystal lattice of these complexes consists of almost flat molecular sheets (see Fig. 6) which closely resemble the monolayer structure. The complex $C_{16}ISA \cdot \frac{1}{2}DMPyr$ displayed a much greater monolayer stability than the similar complex $C_{16}ISA \cdot \frac{1}{2}Pyr$. An increase in the alkyl chain length and the presence of two additional methyl groups at the base led to a more closely packed structure. It was also observed that the addition of DMPyr stabilized the $C_{16}ISA$ monolayer considerably. We attribute this phenomenon to the greater strength of the acid–base hydrogen bond as compared to the acid–acid hydrogen bond, which it substitutes.[22]

Once the self-assembly of C_nISAs and their derivatives in 2D- and 3D-crystal lattices is established, the next step is to explore the self-assembly of C_nISAs in the mesophase. Here the stability and temperature-dependent dynamic nature of the lattice are of major interest towards designing functional materials with mesomorphic properties. The induced liquid crystallinity would also increase the desired processibility.

Self-assembly of C_nISAs in Mesophase

The C_nISAs with $n > 16$ show thermotropic LC behavior.[23] The mesophase has been characterized using polarization microscopy, differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS) measurements and solid-state NMR spectroscopy.[24] $C_{18}ISA$ exhibits a mosaic texture of a highly fluid smectic phase on heating in a small temperature range and on cooling between 418 and 370 K.[23] The molecules can be oriented by shearing and form lamellar structures perpendicular to the shearing direction. On cooling, the material supercools to a large extent and no crystallization or interdigitation of alkyl chains is observed (Fig. 9). However, the alkyl chains interdigitate and crystallize during heating. The structure observed after the recrystallization resembles its 3D structure with a sheet-type lattice. A similar phenomenum can be observed for stoichiometric mixtures of the acids and bifunctional diamines such as 4,4′-bipyridine (Bipy, Scheme 2). For example, a premelted sample of the mixture $C_{18}ISA \cdot Bipy$

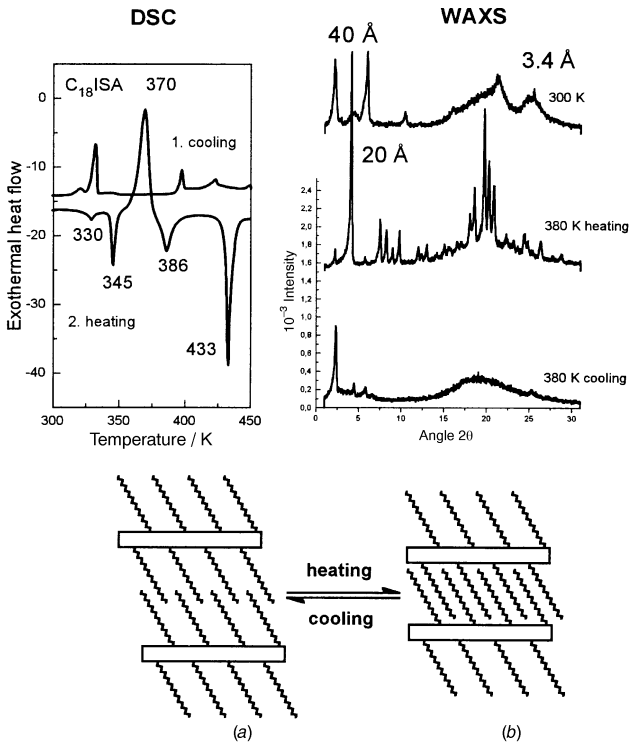


Fig. 9 DSC and WAXS data of $C_{18}ISA$ and a schematic representation of its molecular organization in a premelted sample before (*a*) and after recrystallization (*b*)

shows a strong reflection in the WAXS spectrum at 23.8 Å (at 300 K), which indicates an interdigitated layer structure. The complex with lower Bipy content has a layer distance of 44.9 Å at 300 K, corresponding to the non-interdigitated structure. As seen for pure $C_{18}ISA$, a reversible transition from non-interdigitated structures to interdigitated ones is observed on heating. These transitions are also confirmed by solid-state NMR studies.

The nature of the intermolecular interaction of the complementary building blocks in the mesophase was characterized from an infrared spectrum of the sample.[23] The broad absorption bands at 3080 and 2650 cm^{-1} in the IR spectrum of $C_{18}ISA$ indicates the existence of strong hydrogen bonds between the carboxylic acid groups. The absorption bands of the carbonyl group at 1696 and 915 cm^{-1} are also characteristic of strong acid dimer formation in the lattice. In case of the $C_{18}ISA \cdot Bipy$ mixture, the broad bands seen in the IR spectrum of the pure acid are shifted to 2440 and 1920 cm^{-1}, which are characteristic of acid–amine-type hydrogen bonds. The absence of the bands at 2650 and 960–875 cm^{-1} prove that all acid groups are hydrogen bonded to the nitrogen atoms of Bipy and no acid dimers are present in the mesophase. The characteristic absorption band due to the carbonyl group at 1702 cm^{-1} indicates the presence of COOH···N hydrogen bonds and not an ionic mixture (due to proton transfer from acid to the basic nitrogen) or acid dimer.

Since the supramolecular organization of C_nISAs in the mesophase is similar to that observed in the single crystal lattice and at the interface, it is a challenge to self-assemble these building blocks in solution and to achieve similar supramolecular architectures.

Self-assembly of C_nISAs in Solution

One of the major problems in studying the self-assembly of molecules in solution using hydrogen bonding as a major secondary interaction is that the molecules need to be soluble in non-polar solvents.[25] All C_nISAs described so far are not soluble in non-protic solvents such as benzene or toluene. Introduction of two alkyl chains on a single molecule increases the solubility in non-polar solvents (*e.g.* toluene) in which a cyclic hexamer is observed.[26] The structural characterization in solution is achieved by ^1H NMR spectroscopy (at room temperature, Fig. 10) and vapor pressure osmometry (VPO, at 40 °C) measurements.

The chemical shift of the proton at the C2 position of ISA shows a characteristic concentration dependent behavior, with a maximum change at 15 mM concentration. After this concentration limit, the chemical shift remains essentially constant. The molar mass of the complex formed at concentrations above this limit (15 mM) is obtained from VPO measurements and has a value of 2800 *vs.* a benzil standard. The calculated mass of the hexameric aggregate is 2856.

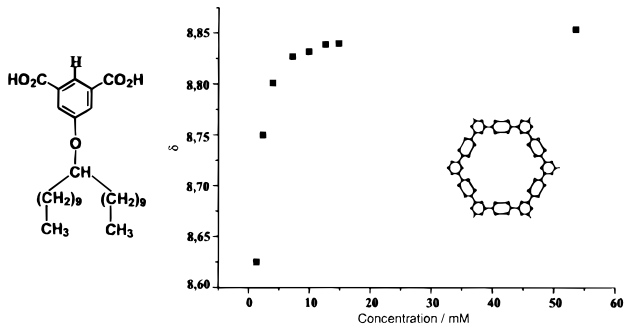
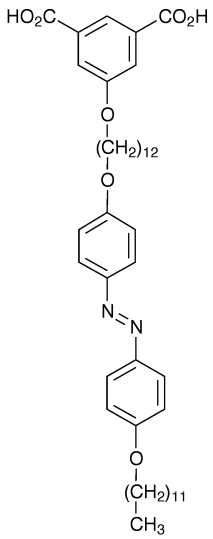


Fig. 10 Concentration dependence on the chemical shift of the proton at the C2-position of an ISA derivative, in toluene at room temperature



$C_{12}AZOC_{12}ISA$

Scheme 4 Molecular structure of an azo-functionalized C_nISA

Both NMR and VPO results are consistent with a hexameric aggregate formation in toluene. Similar aggregates are also seen in the crystal lattices of C_nISAs where $n = 6$–10 (Fig. 3). However, the packing requirements necessary for a solid lattice do not apply for the structures in solution, where the alkyl chains are solvated by the solvent.

Since the alkali-metal salts of C_nISAs are amphiphilic, self-assembly of these molecules can be studied in aqueous solution. Macroscopic fibers are formed from the micellar solutions of potassium salts of C_nISAs ($n > 16$).[27] In a typical procedure, the molecules are dissolved in potassium hydroxide (2 equivalents) solution at 80 °C. Upon cooling, fibers are formed in mass quantities which can be filtered and analyzed. Menger and Lee[27] proposed that the molecule first organizes into a disc-type structure, which then self-assembles to form a fiber. Detailed analysis of the structure of the fiber obtained from our experiments will be published elsewhere.[28] It is also possible to draw fibers from the mesophase of neutral C_nISAs. Preliminary structural characterization reveals that the molecules are organised in such a way that the molecular axis is parallel to the fiber axis.[29]

Strategy towards the Design of a Functional Supramolecular Architecture

Since the 2D structures are most easily characterized by high-resolution STM imaging, we proceeded with the fabrication of 2D monolayers from functionalized C_nISA derivatives and the investigation of photophysical and chemical characteristics. Moreover, the large amount of structural information available from the self-assembly studies of C_nISAs in 3D lattices are useful to control the structure and thereby properties of the 2D crystals at the interface. A systematic investigation of the effect of chemical modification of the single molecule on its 2D structure is still in its infancy. For the aim of designing a functional self-assembly, C_nISA derivatives are synthesised with photochemically active functional groups in the middle of the alkyl chain. Using this approach, it is possible to incorporate various functional groups such as polymerizable groups (*e.g.* acrylate), dimerizable groups (*e.g.* activated double bonds) and isomerizable groups (*e.g. cis–trans* isomerisation of a double bond, Scheme 4).

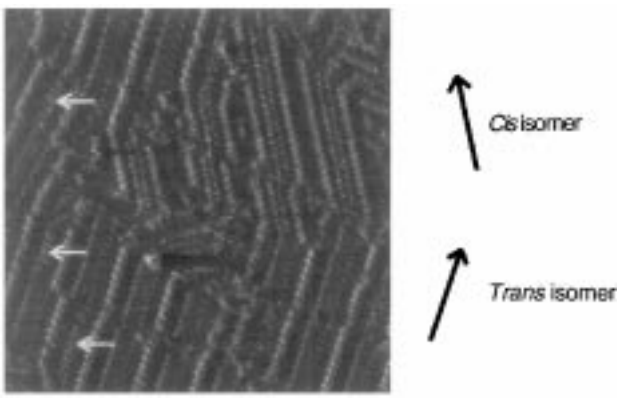


Fig. 11 STM image of the *cis–trans* isomerization of $C_{12}AZOC_{12}ISA$

The first example in this category involves imaging the *cis–trans* isomerization of an azo group incorporated into the C_nISA monolayer. The compound $C_{12}AZOC_{12}ISA$ forms a stable monolayer, when codeposited with octan-1-ol.[30] The *trans* isomer is stable on the surface and packs well. After irradiation, some percentage of the molecules undergo isomerization to give *cis* isomers and this results in domain formation on the substrate (Fig. 11). So far, attempts to achieve 100% isomerization of $C_{12}AZOC_{12}ISA$ at the interface have been unsuccessful.

Our future interest is to explore the reactivity of various activated functional groups at the interface towards stabilizing the self-assembly, changing the morphology of the monolayer and to store and process information at the interface. Moreover, the reactivity of a functional group at a small domain can be investigated in real time using STM, which may help to identify the structure of various intermediates, which are otherwise difficult to characterize.[31]

We have demonstrated that with a simple molecular building block (C_nISA) various supramolecular architectures such as molecular ribbons, layers and channels can be created in the solid lattice. Furthermore, it is possible to incorporate both polar and non-polar functional groups in the molecular structure of C_nISAs, and still obtain a self-assembly comparable to the parent acids. We have also presented STM images with submolecular resolution of monolayers of pure C_nISAs and a donor–acceptor complex of the latter. The 2D structure of the pure acid shows some resemblance to its 3D structure, while the molecular sheet of the supramolecular assembly from a 2 : 1 mixture of the diacid and diazine is identical to a projection plane of the corresponding 3D crystal. Supramolecular architectures observed from the self-assembly of C_nISAs in the mesophase and in solution exhibit a very close resemblance to the ones observed in the solid lattice.

In conclusion, the self-assembly of C_nISAs in all of the above mentioned phases indicates that the supramolecular organization of these molecules is dictated both by hydrogen bonding and alkyl chain crystallization. By tuning these two interactions, it is possible to study C_nISAs in the solid state, in the mesophase, in solution, and at an interface and to obtain comparable structural information. Preliminary results reported in the last section indicate that properly functionalised derivatives of C_nISAs are suitable for designing functional supramolecular materials.

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