Interdigitated supramolecular laminates

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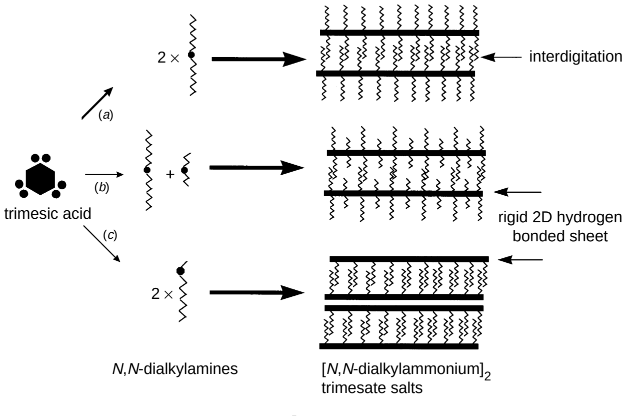
Secondary ammonium salts of trimesic acid form robust interdigitated lamellar structures which are sustained by a combination of strong hydrogen bonds in two dimensions and hydrophobic interactions in the third dimension.

Various types of lamellar, bilayer and monolayer architectures have been investigated for applications in membranes, mesogens, surfactants and Langmuir–Blodgett (LB) films.[1] A better understanding of the structural details of these systems and their relationship to specific chemical processes and functions requires structural information from the crystalline state. Rational design of such organized molecular assemblies in the solid state is also a fundamental and contemporary problem of crystal engineering[2,3] and the use of hydrogen bonds to impart dimensional control over network structures is now well established.[4] We report herein a novel two-dimensional hydrogen bonded motif which forms lamellar crystal structures because of strong hydrogen bonds between complementary organic cations and anions. Furthermore, the entire three-dimensional molecular arrangement is predictable with reasonable accuracy as a consequence of hydrophobic interactions between interdigitated alkyl or aryl groups in the third dimension.

Partially or fully deprotonated salts of 1,3,5-benzenetricarboxylic acid (trimesic acid, H_3TMA) invariably react with amines to afford salts with flat hydrogen-bonded sheet structures.[5] These rigid hydrogen-bonding patterns are robust and the presence of ammonium cations in the sheet makes such structures ideal for designing interdigitated supramolecular lamellar structures since long-chain alkyl groups can be substituted at the ammonium moiety. Scheme 1 depicts various possible layered structures that one might design using secondary alkylammonium salts of $HTMA^{2-}$. The series of dialkylammonium salts, $[NHPr_2]_2[HTMA]$ **1**, $[NH(C_6H_{13})_2]_2[HTMA]$ **2**, $[NH(C_8H_{17})_2]_2[HTMA]$ **3** and $[NH(C_{10}H_{21})_2]_2[HTMA]$ **4**, were synthesized by slow addition of 2 equiv. of the appropriate amine to 1 equiv. of H_3TMA in MeOH and, in order to prevent precipitation of non-stoichiometric products, refluxing for 2 h. Quantitative yields of the colourless solids **1–4** were obtained by slow evaporation of MeOH. Crystals of **1** and **2–4** suitable for single-crystal X-ray crystallography were obtained from butan-1-ol and MeOH, respectively (**1**, mp > 300 °C; **2**, mp 243 °C; **3**, mp 248 °C; **4**, mp 265 °C).



Scheme 1

The crystal structures† of **1–4** exhibit identical two-dimensional hydrogen-bonding networks stabilized by $N^+–H\cdots O^-$ and $O–H\cdots O^-$ hydrogen bonds as shown in Fig. 1. Table 1 is a compilation of hydrogen bond lengths of **1–4** and indicates that the relevant hydrogen bond lengths are almost identical. The ammonium protons in the sheet are engaged in a robust hydrogen-bonding network and are arranged in alternating columns (Fig. 1). The hydrophobic alkyl substituents of the ammonium cations project above and below the sheet and the space between the protruding columns of alkyl groups facilitates interdigitation or close-packing of the adjacent layers (Fig. 2). The geometrical arrangement of the cations in the layer is

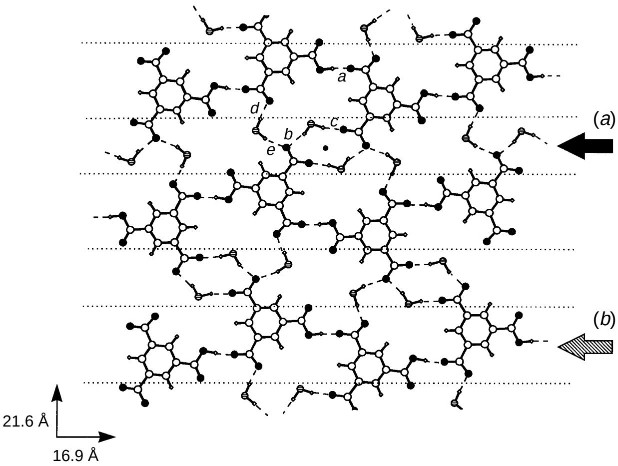


Fig. 1 The two-dimensional hydrogen bonding network observed in **1**–**4**. Five different hydrogen bonds are marked (shown as dashed lines, *a*–*e*, Table 1). The alkyl substituents of the ammonium cations are omitted for clarity. N and O atoms are shown as hatched and filled circles, respectively. The dotted lines are marked on the sheet to show the alternating columns of alkyl subsituents. (*a*) Substituents of the ammonium cation project perpendicular to this plane; (*b*) space suitable for interdigitation of alkyl groups from neighbouring layers.

Table 1 Hydrogen bonding distances (Å) in the two-dimensional layers of **1–5**

	O···O	N···O			
	a	*b*	*c*	*d*	*e*
1	2.540(6)	2.773(8)	2.732(6)	2.887(8)	2.654(8)
2	2.511(10)	2.765(12)	2.728(11)	2.834(12)	2.635(15)
3	2.543(4)	2.772(5)	2.701(4)	2.829(4)	2.654(4)
4	2.524(12)	2.766(13)	2.696(11)	2.818(13)	2.690(13)
5[a]	2.567(7)	2.751(8) 2.777(8)	2.709(8) 2.769(7)	2.809(8)	2.687(7)

[a] **5** crystallizes in a non-centrosymmetric space group ($P2_1$). Consequently, unlike **1–4**, there is no crystallographic inversion center across *b* and *c*.

critical and controls the stacking in the third direction. The interlayer separations of **1**–**4** are *ca*. 7.0, 10.3, 12.4, 14.6 Å, respectively, and are directly related to the alkyl chain lengths and the interdigitation of the alkyl groups that facilitates close packing. There is a recognizable tilt in the octyl and decyl chains of **3** and **4** with respect to the surface of the sheet (77.2, 73.9°), especially when compared to that seen for the propyl and hexyl groups in **1** and **2**, respectively (87.4, 89.0°). Such an observation is to be expected.[6] The dimensions of the repeating unit of the plane are *ca*. 16.9 × 21.6 Å in all five compounds, but only correspond to unit-cell parameters, *i.e*. the *bc* plane, in **3**–**5**.

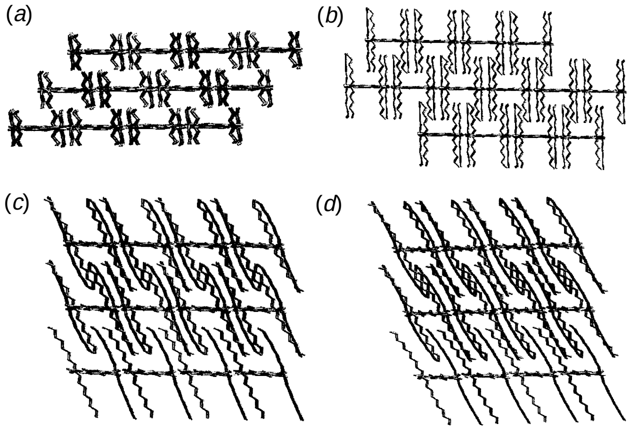


Fig. 2 Perspective views of the supramolecular laminates **1**–**4** [(*a*)–(*d*)]. Note that interdigitation and tilt of the alkyl groups occurs as the chain length increases.

We have also been able to synthesize a mixed-cation supramolecular laminate of HTMA^{2-} with *N*,*N*-dibenyzlammonium and *N*,*N*-dipropylammonium, **5** [Scheme 1(*b*)].[6] **5** is a doubly deprotonated salt and the asymmetric unit contains four HTMA^{2-} anions, six *N*,*N*-dibenzylammonium cations, two *N*,*N*-dipropylammonium cations and one molecule of MeOH. The crystal structure reveals an interdigitated supramolecular laminate architecture with alternating layers of different composition (Fig. 3). The hydrogen-bonding pattern of layer A, a mixed-cation supramolecular laminate, is similar to **1**–**4** (Fig. 1, Table 1). However, layer B, which contains dibenzylammonium cations, has a slightly different hydrogen-bonding pattern as the MeOH molecule is also involved in the hydrogen-bonding scheme. This observation suggests that a wide range of new supramolecular laminates is at hand, possibly with interesting properties such as liquid crystallinity and the ability to intercalate guest molecules.[7]

In conclusion, **1**–**5** serve as good examples of rationally designed solids and should be of help for the general study and understanding of laminate packing arrangements. The results reported herein further suggest that the complex problem of controlling three-dimensional architecture in solids can successfully be reduced to a simple one-dimensional problem by using the strategy of choosing a suitably substituted rigid two-dimensional layer as a starting point.[4]

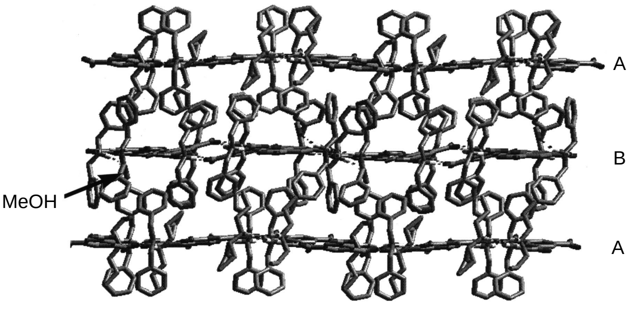


Fig. 3 The interdigitated mixed supramolecular laminate structure of **5**. Layer A contains *N*,*N*-dibenzylammonium and *N*,*N*-dipropylammonium cations. Layer B contains dibenzylammonium cations only. Note that MeOH is involved in the hydrogen bonding in layer B.

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Footnotes and References

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† *Crystal data* for **1**–**5**: $C_{21}H_{36}N_2O_6$ **1**, M_w = 412.5, monoclinic, space group $P2_1/c$, a = 8.734(3), b = 16.951(7), c = 17.811(7), β = 103.99(4)°, U = 2558.70(14) Å^3, Z = 4, D_c = 1.07 Mg m^{-3}, T = 290 K, μ = 0.07 mm^{-1}. 1427 reflections out of 3349 unique reflections with $I > 2.5\sigma(I)$ were considered, R_f = 0.083, R_w = 0.068. $C_{33}H_{60}N_2O_6$ **2**, M_w = 580.9, monoclinic, space group $P2_1/n$, a = 11.531(3), b = 16.942(2), c = 19.952(6), β = 98.07(3)°, U = 3859.2(16) Å^3, Z = 4, D_c = 1.00 Mg m^{-3}, T = 290 K, μ = 0.06 mm^{-1}. 1339 reflections out of 5042 unique reflections with $I > 2.5\sigma(I)$ were considered, R_f = 0.090, R_w = 0.086. The data for **1** and **2** were measured on an Enraf-Nonius CAD-4 diffractometer at 290 K using the ω scan mode. $C_{41}H_{76}N_2O_6$, **3**, M_w = 693.1, monoclinic, space group $P2_1/c$, a = 12.4771(7), b = 16.8788(9), c = 21.5789(11), β = 91.992(1)°, U = 4541.7(4) Å^3, Z = 4, D_c = 1.01 Mg m^{-3}, T = 173 K, μ = 0.06 mm^{-1}. 4222 reflections out of 6333 unique reflections with $I > 3.0\sigma(I)$ were considered, R_f = 0.114, R_w = 0.101. $C_{49}H_{92}N_2O_6$ **4**, M_w = 805.3, monoclinic, space group $P2_1/c$, a = 14.6856(8), b = 16.8941(11), c = 21.5929(13), β = 97.970(2)°, U = 5305.5(6) Å^3, Z = 4, D_c = 1.01 Mg m^{-3}, T = 173 K, μ = 0.06 mm^{-1}. 2064 reflections out of 4291 unique reflections with $I > 3.0\sigma(I)$ were considered, R_f = 0.117, R_w = 0.115 $C_{133}H_{148}N_8O_{25}$ **5**, M_w = 2256.2, monoclinic, space group $P2_1$, a = 16.7901(3), b = 16.8905(2), c = 21.9464(2), β = 96.384(1), U = 6185.3(4), Z = 2, D_c = 1.211 Mg m^{-3}, T = 173 K, μ = 0.08 mm^{-1}. 18350 reflections out of 20 242 unique reflections with $I > 4.0\sigma(I)$ were considered, R_f = 0.083, R_w = 0.086. The intensity data for **3**–**5** were collected on a Siemens SMART/CCD diffractometer at 173 K using the θ scan mode. The thermal parameters for the terminal C atoms in the alkyl chains of **1-5** are high, probably a manifestation of unresolvable disorder, and account for the relatively high R values. CCDC 182/518.

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