Supramolecular mesomorphic structures based on 2,5-dialkoxyterephthalic acid derivatives

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Self-assembly of 2,5-di-*n*-alkoxyterephthalic acids (C_nOTpA) and 2,5-di-*n*-hexylterephthalic acid (C_6TpA) as bifunctional hydrogen bond donors with bifunctional acceptors 1,3-diaminopropane (Dap), piperazine (Pip) and 4,4′-bipyridine (Bipy) has been investigated, both in the crystal lattice and in the mesophase. Stoichiometric mixtures of compounds C_nOTpA with diamine Dap form mesophases with a lamellar-type structure and constitute, to the best of our knowledge, the first examples of the generation of mesophases from 2,5-di-*n*-alkoxyterephthalic acids and bifunctional diamines. The liquid crystalline behaviour of these mixtures was characterized using X-ray scattering, DSC and polarizing microscopy. The self-assembly of complexes C_6TpA·Bipy and C_6TpA·Pip in the crystal lattice was characterized using single crystal X-ray structural analysis. In the crystal lattice of C_6TpA·Bipy, only hydrogen bonding interactions between the neutral acid and the base were observed. However, in the crystal structure of cocrystals of C_6TpA with Pip, an ionic interaction was observed due to proton transfer from the acid group to the basic nitrogen atoms of the base.

Recently, much attention has been paid to the self-assembly of complementary building blocks.[1] The assembly of the components is effected and controlled by intermolecular forces such as hydrogen bonding,[2] ionic[3] and charge transfer interactions[4] and metal complexation.[5] The induction of thermotropic liquid crystalline phases by hydrogen bonded molecules, possessing amphiphilic character, has been the subject of a recent review.[2] Mesophase generation in amphiphilic systems is ascribed to hydrogen bonding interactions between the polar head groups and to the spatial separation of polar and apolar groups.[2] The generation of molecular mesomorphic complexes from hydrogen bond donor and acceptor molecules, including the formation of chiral smectics, has been reported.[6,7] Supramolecular polymeric structures, based on non-covalent bonding of complementary components, have been synthesized by various groups.[8–12] Most of the structures involve bifunctional[13] hydrogen-bonded molecular building blocks.[9–12] Amongst them, the tartaric acid derivatives are known to give helical chiral supramolecular structures in the mesophase.[9a]

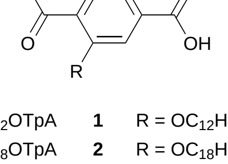
Our goal is to design and synthesize molecular building blocks, suitable for the investigation of self-assembly processes in multiple phases. With the aim of understanding the role of weak interactions such as hydrogen bonding and van der Waals interactions, multiphase self-assembly of bifunctional molecular building blocks has been investigated by our group. Recently, we reported the self-assembly of 5-alkoxyisophthalic acids (C_nISA) in the crystal lattice,[14] in the mesophase,[15] at the interface[16] and in solution.[17] Depending upon the length of the alkyl chains (*n*), channel-type or sheet-type crystal lattices are formed.[14] Moreover, we have shown that plausible relationships exist between the single crystal structures and the two-dimensional organization of C_nISAs and their complexes with bifunctional amines on a graphite substrate.[16a] The supramolecular organization and molecular dynamics of the amphiphilic C_{12}ISA, C_{18}ISA, and their complexes with bifunctional bases have been investigated by ^{2}H NMR spectroscopy.[15] The mesophases of C_{12}ISA, C_{18}ISA and C_{18}ISA·Pip complex are mainly stabilized by both hydrogen bonding and strong apolar (van der Waals) interactions of the alkyl groups.

To extend the concept of the interplay of weak interactions in the self-assembly process, we here discuss 2,5-di-*n*-alkoxyterephthalic acids (C_nOTpA), 2,5-di-*n*-hexylterephthalic acid (C_6TpA) and their complexes with bifunctional bases as new building blocks. The effect of the length of alkyl groups of the terephthalic acid plus the conformational rigidity and basicity of the hydrogen bond acceptors on the structure generation are examined.

In this context, we discuss the formation of a novel class of mesomorphic materials, whose hydrogen bonding can also be investigated using data from single crystal X-ray structural analysis of model complexes C_6TpA·Pip and C_6TpA·Bipy. C_6TpA was chosen in those model complexes as an analogue of C_nOTpA for the quality of crystals (suitable for single crystal X-ray structural analyses) obtained from THF solutions of its mixtures with bifunctional bases. Hydrogen bond donors (carboxy groups), their directionality, the substitution pattern on the aromatic core, and the parent compound (terephthalic acid) are identical for C_6TpA and C_nOTpA. We were not able to obtain suitable crystals for X-ray structure determination from mixtures of C_nOTPA and bifunctional bases (solubility of the stoichiometric complexes in THF is rather poor). So far, the conformational freedom and the increased basicity of the bifunctional amine component (Dap) have not been studied in relation to the formation of mesomorphic layer structures in combination with rigid dicarboxylic acids. Here, we show that these factors are important in controlling the self-assembly of molecular components and inducing mesomorphic behaviour.

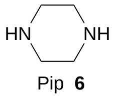
Results and Discussion

Hydrogen bond donor–acceptor complexes and their structural characteristics are examined in the following section.

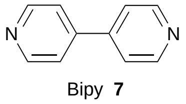


C_{12}OTpA **1** R = $OC_{12}H_{25}$
C_{18}OTpA **2** R = $OC_{18}H_{37}$
C_{20}OTpA **3** R = $OC_{20}H_{41}$
C_6TpA **4** R = C_6H_{13}

Dap **5**



Pip **6**



Bipy **7**

Mixtures were prepared from THF solutions of the terephthalic acid derivatives by addition of solutions of the appropriate base in THF and subsequent solvent evaporation. Hydrogen bonding between the complementary components in the mesophase was established using infrared (IR) spectroscopy and in the solid lattice by IR and single crystal X-ray structural analysis.

First, the structural characteristics of $C_nOTpA{\cdot}Dap$ mixtures will be discussed. In the IR spectrum of the mixture of, for example, $C_{12}OTpA$ with Dap, the band corresponding to the dimeric carboxylic C=O vibration at 1710 cm^{-1} is absent. Furthermore, the fingerprint band of —COOH dimers, corresponding to the OH···O oop vibration (expected in the range 960–875 cm^{-1}) is not observed.[18] On the other hand, two broad shoulders present in the IR spectrum of this mixture, with maxima at 2671 and 2175 cm^{-1} (25 °C), indicate the formation of ammonium–carboxylate species.[19] Generally, samples were not exposed to temperatures higher than 165 °C, in order to avoid condensation reactions. Samples were analysed by ^1H NMR and IR spectroscopy after characterization of the mesophase in order to verify the absence of condensation reactions. The equimolar mixture of $C_{12}OTpA$ and Dap was examined by X-ray scattering measurements at temperatures between 25 and 165 °C. The X-ray diffraction (XRD) patterns at temperatures up to 135 °C show reflections in the wide-angle region which correspond to a crystalline arrangement of the alkyl chains. Starting at 145 °C (mesophase), no alkyl chain crystallinity is observed in the diffraction patterns of the mixture. The diffractograms in the mesophase exhibit a characteristic Bragg reflection in the small-angle region, which prove the formation of a layer structure. Between 145 and 165 °C, the XRD patterns are in accord with the ones of smectic A mesophases. Endothermal transitions at 89 and 125 °C are detected by differential scanning calorimetry (DSC) in the first heating cycle, which can be ascribed to the crystal–crystal transitions. The crystal-to-mesophase transition is observed at 141 °C. Optical examination under crossed polarizers shows that a ductile, birefringent melt is formed above this temperature, giving evidence of the formation of a mesomorphic phase. Analyses of the mixture by optical microscopy, DSC and XRD show that the mixture isotropizes at 172 °C. In the same way, the equimolar mixture of $C_{18}OTpA$ and Dap exhibits crystalline alkyl chain order up to 130 °C, as shown by X-ray scattering studies. At this temperature, the interlayer distance amounts to 31.5 Å, according to the first order Bragg reflection in the small-angle region. At 150 °C, only an amorphous halo is observed in the wide-angle region, indicating a liquid-like random organization of the alkyl chains. In the small-angle region, a layer reflection and its second and third order are observed (layer-spacing 32.3 Å). Again, the XRD patterns obtained between 150 and 165 °C are characteristic of smectic A mesophases. For this mixture, two endothermal crystal–crystal transitions at 58 and 86 °C are detected in the first heating cycle by DSC. The crystal-to-mesophase transition occurs at 150 °C. As in the case of $C_{12}OTpA{\cdot}Dap$, here also a ductile, birefringent melt is seen through crossed polarizers above the melting temperature. Oily streaks and focal conic fan textures, characteristic of a smectic A mesophase, are observed (Fig. 1).

The mesophase exists up to the highest temperature of examination (165 °C). From the DSC and X-ray scattering studies, an equimolar mixture of $C_{20}OTpA$ and Dap undergoes two crystal–crystal transitions at 69 and 119 °C and a crystal-to-mesophase transition at 149 °C (first heating cycle). Above this temperature the material exists as an anisotropic, viscous melt, showing oily streaks and focal conic fan textures. Fig. 2(*a*) displays the X-ray diffraction pattern of $C_{20}OTpA{\cdot}Dap$ in the crystalline state at 90 °C (layer-spacing 32.9 Å), while Fig. 2(*b*) shows the corresponding diffractogram in the mesophase at 150 °C (layer-spacing 34.7 Å). Again, the mesophase is stable up to the highest temperature of examination (165 °C).

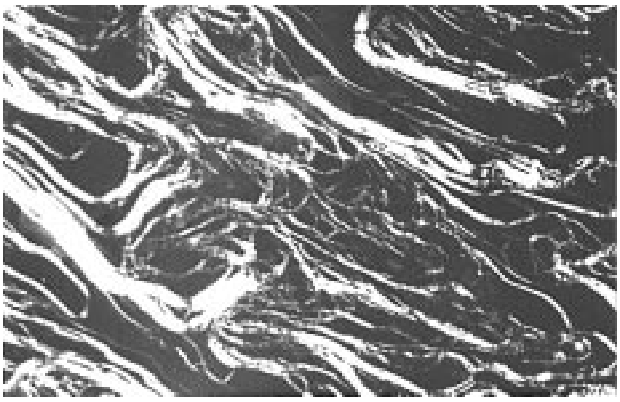


Fig. 1 Optical texture of compound **2·5** in the mesophase (crossed polarizers, 165 °C, on heating)

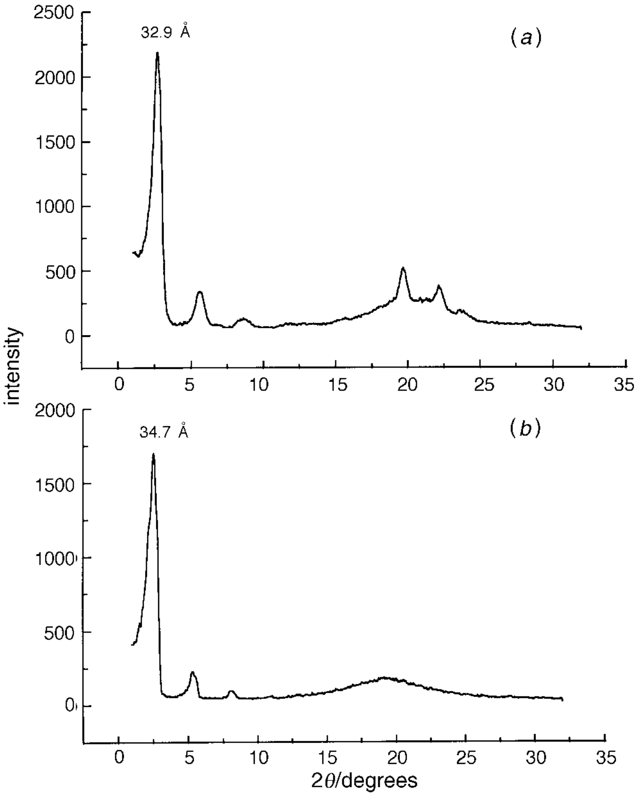
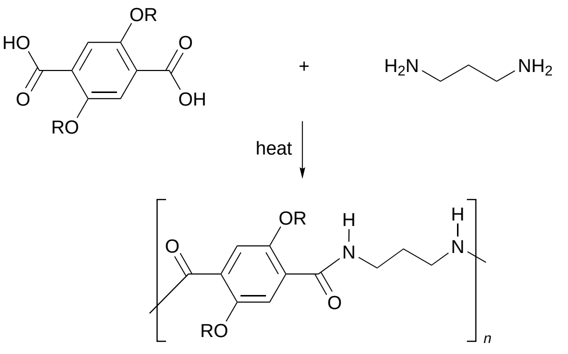


Fig. 2 X-Ray diffraction patterns of **3·5** at (*a*) 90 °C (crystalline state) and (*b*) 150 °C (mesophase)

The plot of the layer-spacing in the mesophase at 150 °C *versus* the length of the alkyl chain for all mixtures discussed above gives a straight line with an intercept at 6 Å. This value is similar to that observed for the width of the aromatic core of polyamides and polyesters.[20] The presence of a linear relationship between alkyl chain length and the layer-spacing indicates the isostructural nature of the mesomorphic mixtures from the homologous series of $C_nOTpA{\cdot}Dap$ ($n = 12$, 18, 20). The observed layer-spacings in the mesophase can be explained, assuming partial interdigitation of the alkyl side chains. The analysis of $C_{12}OTpA{\cdot}Dap$ and $C_{18}OTpA{\cdot}Dap$ mixtures after X-ray measurements indicated that no chemical reaction occurred during the WAXS heating cycle, since ^1H NMR and IR spectra were identical to those of the initial samples. In contrast to this, a chemical condensation reaction occurs at a higher temperature (above 170 °C),[21] generating oligoamides **8**–**10**, as detected by MALDI–TOF–MS (Scheme 1).

The amount of products formed during the condensation reaction was monitored by ^1H NMR spectroscopy. A sample



8 R = $C_{12}H_{25}$
9 R = $C_{18}H_{37}$
10 R = $C_{20}H_{41}$

Scheme 1

of complex C_{18}OTpA·Dap showed *ca.* 60% starting material, after heating to a temperature of 220 °C for 3 min. When the sample was exposed to this temperature for 30 min, no starting complex could be detected. Oligoamides **9** with molecular masses corresponding to $n = 1$–4 were observed in the MALDI–TOF spectra.

Elucidation of the self-assembly characteristics of 2,5-di-*n*-alkylterephthalic acids (C_nTpA) and their complexes with bifunctional hydrogen bond acceptors in the crystal lattice is of interest. We were able to obtain single crystals of high quality from an equimolar solution of C_6TpA with Pip. The structure of the cocrystal, grown from an equimolar solution of the mixture of C_6TpA and Pip was determined by single crystal X-ray structural analysis (Figs. 3 and 4).

The asymmetric unit contains 1.5 molecules of C_6TpA and one molecule of Pip. One of the terephthalic acids (acid 1) is located at a centre of symmetry. Piperazine and the other acid molecule (acid 2) are located at general positions. A projection of the crystal structure, showing the full H-bonding network, is shown in Fig. 3. A closer analysis of the bond lengths reveals that the acid 2 is a dianion (C—O bond length 1.24 Å), whereas in the acid 1, typical bond lengths of a free acid are observed (C=O: 1.21, C—O: 1.30 Å). Thus, the composition of the crystallized complex is $(C_6TpA^{2-}\cdot Pip^{2+})\cdot(C_6TpA)_{1/2}$. The hydrogen bonding motif in the crystal lattice is very complex: each diprotonated piperazine is hydrogen-bonded to four terephthalic acid molecules, of which three (acid type 2) are carboxylates. The fourth hydrogen bond is directed to the carbonyl oxygen [O(11″)] of an acid type 1. The hydrogen bonding geometry around the piperazinium ion and around O(11″) (acid type 1) is displayed in more detail in Fig. 4(*a*) and (*b*), respectively. Since each nitrogen atom of the Pip is involved in two hydrogen bonds, a three-dimensional organization of the molecules is observed in the lattice: there are no acid dimers seen in the crystal lattice. The relevant crystal data, hydrogen bonding distances, bond lengths and angles of C_6TpA·Pip are listed in Tables 1 and 2. The hexyl side groups in acid 1 and one of the side groups of acid 2 are disordered, *i.e.* for some of the atoms, more than one partially occupied site is detected. These side chains fill the space between the hydrogen-bonded strands. At room temperature, there apparently already exists a fairly large mobility in these regions of the lattice, as seen by the large anisotropic temperature factors, visible in Fig. 4(*a*) and 4(*b*). The comparatively large *R* index of the refinement of the X-ray diffraction data results from this disorder. Nevertheless, the lengths of the rigidly hydrogen-bonded atoms are determined with an accuracy of approximately 0.01 Å. Since the length of the alkyl chain is too short for effective interdigitation, the hydrogen bonding is the

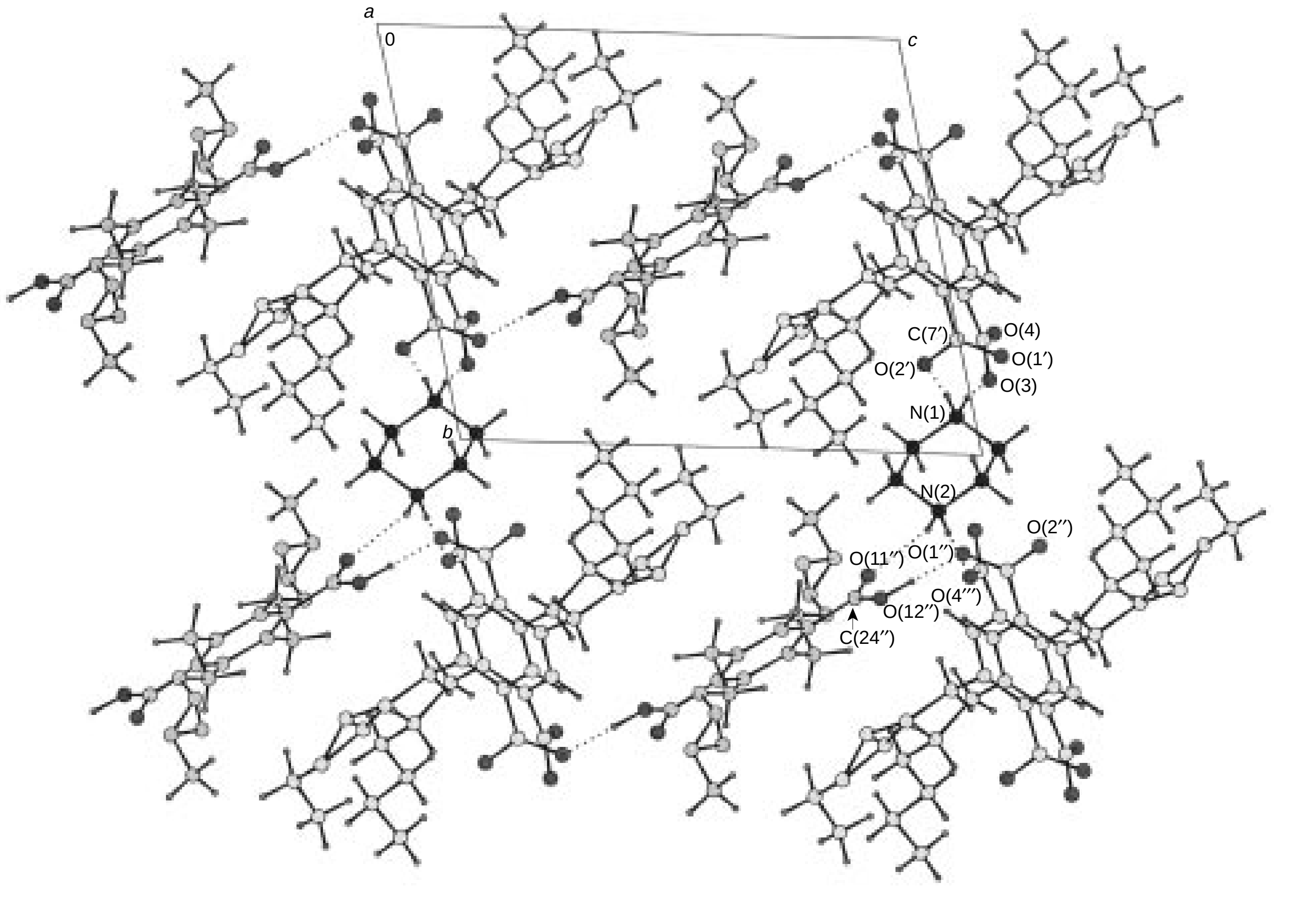


Fig. 3 Crystal structure of **4·6** (overview)

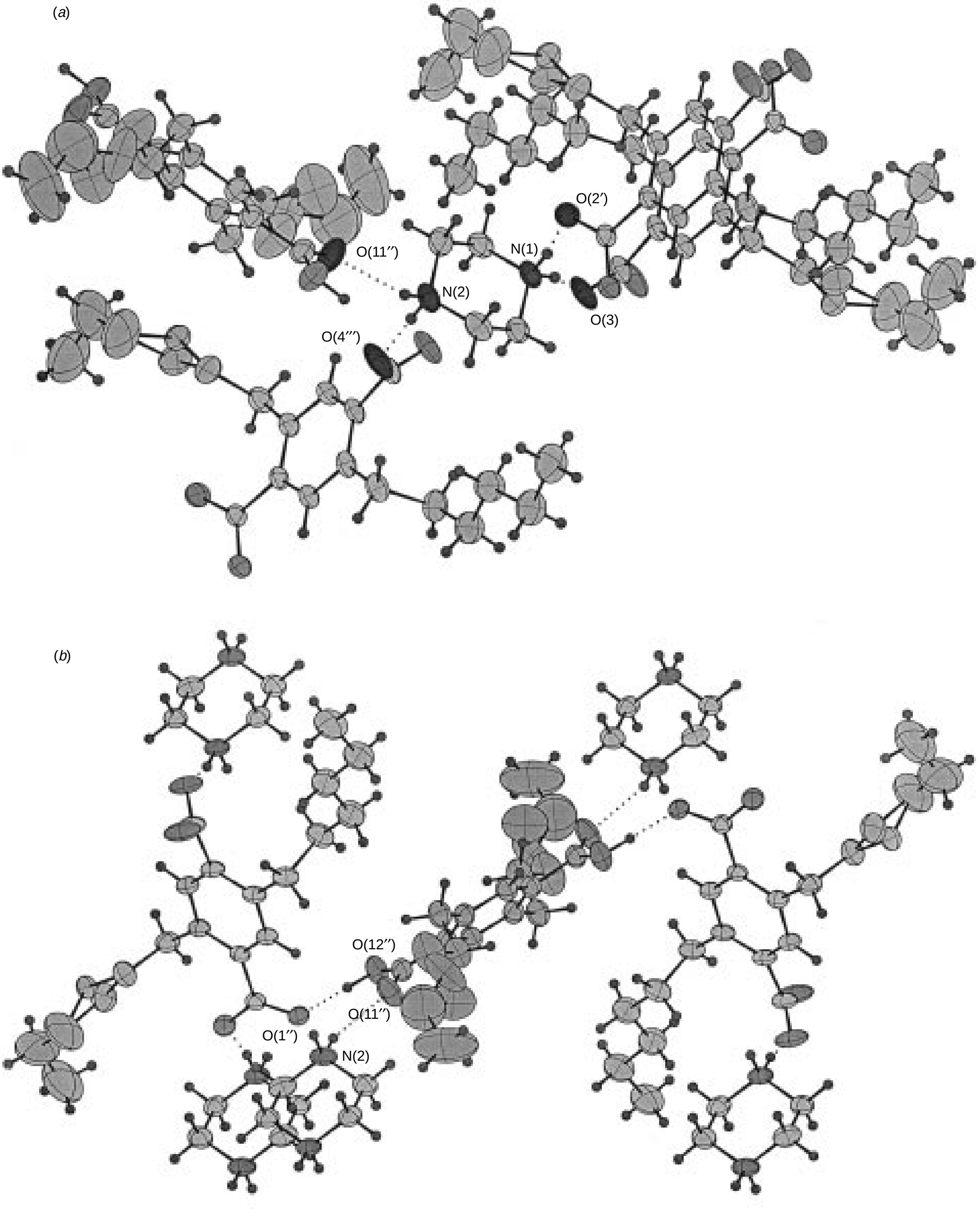


Fig. 4 Crystal structure of **4**·**6**. (*a*) The hydrogen bonding geometry around the piperazinium ions. (*b*) The hydrogen bonding geometry around O(11″) of acid type 1.

dominant interaction towards controlling the self-assembly in the crystal lattice.

Our preliminary attempts to crystallize mixtures from long chain C_nOTpA and bifunctional amines have not been successful. The effect of the length of alkyl chains in the self-assembly of C_nTpA plus C_nOTpA has already been studied.[22] In order to investigate the impact of a semi-rigid bifunctional strong base on the phase-formation behaviour of C_nOTpA, we substituted the flexible strong base Dap with piperazine. However, the studied complex C_{12}OTpA·Pip forms no mesophase, and instead undergoes a broad melting transition between 140 and 160 °C with decomposition of the material, according to polarizing microscopy, TGA, and XRD.

As a further variation of the nature of the added bifunctional base with C_nOTpA and C_nTpA mixtures, we used the weaker, rigid base 4,4′-bipyridine as the hydrogen bond acceptor. Stochiometric mixtures of C_6TpA and C_{18}OTpA with Bipy show a melting point at 189 °C (decomposition of the complex)

Table 1 Crystallographic data for **4·6** and **4·7**

compound	**4·6**	**4·7**
crystal data		
empirical formula	$1.5\,(C_{20}H_{30}O_4)\cdot C_4H_{10}N_2$	$C_{20}H_{30}O_4\cdot C_{10}H_8N_2$
formula mass	587.82	490.64
crystal colour	colourless	colourless
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a/Å	11.536(2)	11.427(3)
b/Å	12.131(1)	16.201(4)
c/Å	14.624(1)	16.195(3)
α(°)	71.874(6)	90
β(°)	72.422(9)	109.855(20)
γ(°)	68.255(9)	90
V/Å^3	1765.7(4)	2819.9(13)
Z	2	4
D/g cm^{-3}	1.106	1.156
μ/cm^{-1}	5.650	5.750
F(000)	642	1056
structure solution and refinement		
no. of total reflections	6761	4397
no. of unique reflections	6761	4397
no. of observed reflections	5431	3523
absorption correction type	empirical, ψ scans	empirical, ψ scans
no. of refined parameters	379	343
final R	0.075	0.064
final R_W	0.082	0.071
data collection parameters		
T/K	300	300
$2\theta_{max}$ (°)	130	126

Table 2 Bond length for **4·6** and **4·7**, and dihedral angles for **4·7**

Bond lengths/Å			
4·6		**4·7**	
C(7′)–O(1′)	1.264(3)	C(4)–O(1)	1.206(4)
C(7′)–O(2′)	1.242(3)	C(4)–O(2)	1.324(5)
C(8)–O(3)	1.242(3)	C(14)–O(11)	1.211(6)
C(8)–O(4)	1.243(3)	C(14)–O(12)	1.313(5)
C(24″)–O(11″)	1.212(3)	N(1)···O(2)	2.61(1)
C(24″)–O(12″)	1.297(3)	N(2)···O(12)	2.61(1)
N(1)···O(2′)	2.65		
N(1)···O(3)	2.64		
N(2)···O(4‴)	2.58		
N(2)···O(11″)	2.79		
O(1″)···O(12″)	2.52		

Dihedral angles of **4·7** (°)

	acid 2 [C(11),C(12),C(13)]	pyridyl 1 [N(1),C(21–25)]	pyridyl 2 [N(2),C(26–30)]
acid 1 [C(1),C(2),C(3)]	168(1)	92.6(2)	78.0(2)
acid 2 [C(11),C(12),C(13)]	—	75.1(2)	89.7(2)
pyridyl 1 [N(1),C(21–25)]	—	—	14.6(1)
pyridyl 2 [N(2),C(26–30)]	—	—	—

and 126 °C, respectively, but no thermotropic mesophase. However, single crystals of C_6TpA·Bipy suitable for X-ray structural analysis were obtained from the THF solution of the mixture.

The structure contains infinite chains with an alternating sequence of hydrogen-bonded donors and acceptors, thus giving rise to a supramolecular polymer, based on electrostatic hydrogen bonding (Fig. 5). The acid molecules are located at centres of symmetry and the bipyridine molecules at a general site. There are two crystallographically independent acids present in the crystal lattice. The projection of the crystal structure reveals that the plane of the aromatic rings of the C_6TpA molecules are approximately parallel to each other and perpendicular to the ones of the bipyridyl acceptor. O—H···N distances between adjacent carboxylic acid groups and bipyridine nitrogen atoms amount to 2.59 Å. This distance is in good agreement with a literature value of 2.6 Å for similar hydrogen bonded N—O contacts.[23] In contrast to the hydrogen bonding situation seen in the crystal lattice of the complex C_6TpA·Pip, the hydrogen bonds in complex C_6TpA·Bipy are not of an ionic nature as proved by the different lengths for the C(4)—O(1) and C(4)—O(2) bonds [1.206(4) and 1.324(5) Å, respectively]. The different findings for **4·6** (proton transfer) and **4·7** (no proton transfer) in the crystal lattice can be accounted by the different basicities of **6** (pK_α of protonated secondary amines about 11, relative to water)[24] and **7** (pK_α of protonated pyridine about 5.2).[25] Due to the unshared pair of electrons in the sp^3-orbital of the piperazine nitrogen atoms in hosting it, compared with the unshared pair in the sp^2-orbitals of the bipyridine nitrogen atoms, basicity is higher in the case of piperazine: the sp^3-orbitals possess less s-orbital character than the sp^2-orbitals, causing the increased reactivity of the

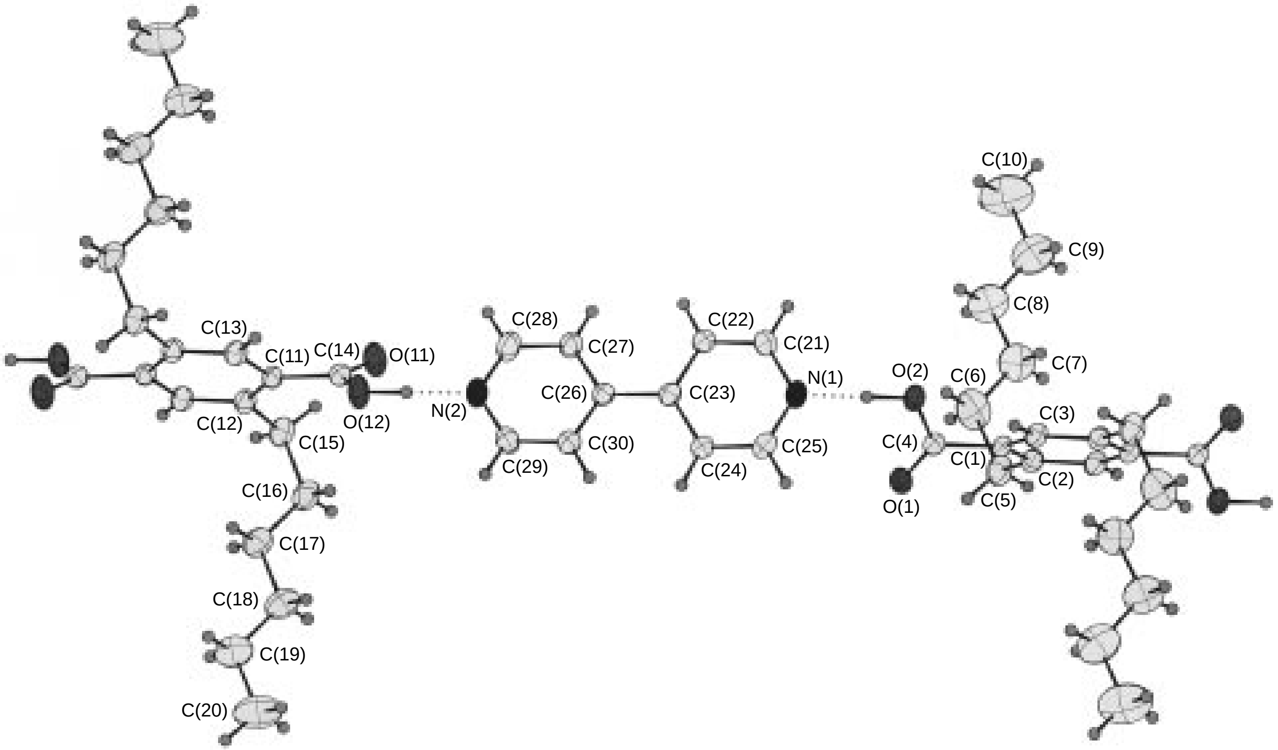


Fig. 5 Molecular structure of **4·7** in the crystal

electron pair in the sp^3-orbitals.[25] Crystallographic data for C_6TpA·Bipy are listed in Table 1, selected bond lengths and dihedral angles are listed in Table 2.

Conclusion

In this study, we present the characterization of supramolecular complexes formed from equimolar amounts of 2,5-di-*n*-alkoxyterephthalic acids (C_nOTpA) with 1,3-diaminopropane (Dap). Above the melting temperatures of the complexes mesomorphic phases are formed whose structures are in accordance with liquid crystalline phases of the smectic A type up to 165 °C. The evidence for this conclusion is provided by the characteristic textures (for **2·5** and **3·5**) and X-ray diffraction patterns (for all mixtures) obtained. The linear relationship between the layer-spacing and the alkyl chain length in the mesophases reveals that the phases are isostructural and that the thickness of the smectic layers is determined by the length of the alkyl side chains of the terephthalic acids. The observed layer-spacings indicate that the alkyl chains from adjacent smectic layers interdigitate partially. Interaction of complementary components in complexes C_nOTpA·Dap has an ionic character, as established by the IR data and deduced from the single crystal X-ray structural analysis of the model compound C_6TpA·Pip. In the case of the weaker proton acceptor 4,4′-bipyridine, only hydrogen bonding interactions are observed between the neutral carboxylic acid groups and the basic nitrogen atoms along the supramolecular strands, as seen in the crystal lattice of C_6TpA·Bipy.

Focusing on the structural variation of the base, we observe that the rigid bifunctional hydrogen bond acceptor with low basicity 4,4′-bipyridine and the conformationally restrained, semi-rigid, cycloaliphatic strong base piperazine are not able to induce mesomorphic properties in their studied complexes with C_nOTpA. In contrast, the conformationally flexible strong aliphatic base Dap forms ionic complexes with strong hydrogen bonding, which then gives rise to a stable mesophase in all complexes investigated. It is important to point out that the mesomorphic complexes formed by the strong flexible base Dap with C_nOTpAs have no precedence in the literature.

For hydrogen-bonded supramolecular polymers,[9–12] consisting of stoichiometric amounts of complementary building blocks or self-complementary units, systematic variation of the basicity and flexibility of the hydrogen bond acceptors, together with introduction of side chains in the donor molecules, has—to the best of our knowledge—not yet been studied. These three factors determine the phase formation characteristics of the molecular building blocks.

In the area of crystal engineering, the self-assembly of various bifunctional molecular building blocks has been revealed.[9b–f,12] No thermotropic liquid crystalline properties are reported for these complexes.

The formation of liquid crystalline association polymers, based on the self-assembly of bifunctional complementary building blocks, was reported.[19a] *meso*-, D- and L-2,3-Didodecyloxytartaric acid was endowed with uracil and 2,6-diacylaminopyridine units. Mixtures of the complementary building blocks form hexagonal columnar mesophases. The study focuses on the impact of chirality on the formation of overstructures.

4,4′-Bipyridine[10a,b] or *trans*-1,2-bis(4-pyridyl)ethylene[10c] and carboxylic diacids, containing flexible aliphatic spacers, have been shown to form smectic mesophases. The structures were not examined by X-ray scattering. The generation of nematic LC phases from bis pyridyls and an α,ω-bis(benzoic acid)-substituted tetraethylene glycol was observed.[11a] Finally, a study on smectic mesophases of ionic mixtures of aliphatic dicarboxylic acids and aliphatic diamines is documented.[1h] The formation of association polymers was discarded by the authors. The materials could not be structurally characterized in the mesophase by X-ray scattering due to amide formation at temperatures above 170 °C.

All studies besides the report[9f] using carboxylic diacids as H-bonding donors in the cited literature deal with flexible diacids. None of these studies explores the systematic alkyl chain length variation of pendant side groups, grafted on the self-assembling constituents (only materials described in references[9a,d] contain side chains). As reported for covalently bonded thermotropic main chain rigid rod polymers, in our study we found a linear correlation between smectic layer spacings and alkyl side chain length.[20]

All complexes presented (including ours) forming mesomorphic phases, possess at least one flexible section in one of the constituents. This section seems to be essential to increase the molecular dynamics and to reduce crystallization tendency. We are currently designing supramolecular mesomorphic ammonium complexes based on terephthalic acids, carrying chiral substituents for the generation of ferroelectric materials. The interplay of hydrogen bonding and van der Waals interactions in the systems should help to increase the phase stability, despite the increased steric demand of chiral moieties, orientated perpendicularly to the director. In the same way, the aforementioned interactions should increase the alignment in the mesophase strongly in comparison with conventional liquid crystals, based merely on lipophilic and charge-transfer interactions.

Experimental

Instruments

MALDI–TOF MS: Bruker Reflex. ^{1}H and ^{13}C NMR: Varian Gemini (50.3 and 200 MHz), Bruker AMX 300 (75.5 and 300 MHz), AMX-500 (125.8 and 500 MHz). *J* Values are given in Hz. IR: Nicolet 320 FT-IR spectrometer and Nicolet 60 SX FT-IR spectrometer, equipped with a hot-stage. X-Ray diffraction measurements: 1-D WAXS: Siemens Kristalloflex diffractometer D 500 equipped with a scintillation detector and a hot-stage (graphite crystal monochromator, slit collimation, beam divergence 0.3 °, Cu-Kα radiation, $\lambda = 1.541$ Å, temperatures corrected); 2-D WAXS: Rigaku rotating Cu anode RU-300 with an area detector with 4 bar Xe-filled multiwire proportional chamber (operated at 10 kW, pinhole-collimation, $2\theta = 0$–30 °, $\Delta 2\theta = 0.8$ °, graphite-monochromated Cu-Kα radiation, $\lambda = 1.541$ Å, temperatures uncorrected). All measurements were done in sealed glass capillaries. DSC: Mettler D 30. TGA: Mettler TG 50. Polarizing microscopy: Leitz Axiophot microscope equipped with a Linkam TMS 90 hotstage.

Materials

Diethyl 2,5-dihydroxyterephthalate (98%), 1-bromododecane (95%), 1-bromooctadecane (96%), 1-bromoicosane (98%), 4,4′-bipyridine (98%), piperazine (99%) and 1,3-diaminopropane (99%) were purchased from Aldrich, *N,N*-Dimethylformamide (DMF) was used without further purification for the preparation of C$_n$OTpA **1**–**3** (Fluka), potassium carbonate (>99%) and potassium hydroxide (85%) were obtained from Riedel-de Haen. 4,4′-Bipyridine and piperazine were purified by recrystallization from acetone–light petroleum. 1,3-Diaminopropane was purified by distillation under reduced pressure. All syntheses were performed under inert gas atmosphere. All synthesised compounds and mixtures gave sufficient elementary analyses (error $\leqslant \pm 0.4\%$).

2,5-Di-*n*-alkoxyterephthalic acids (1–3). The acids **1**–**3** were prepared as described for the synthesis of C$_{12}$OTpA (**1**). Bromododecane (20.63 g, 79 mmol), ethyl 2,5-dihydroxyterephthalate (10.2 g, 39 mmol) and potassium carbonate (21.3 g, 154 mmol) were suspended in 270 ml of DMF and stirred overnight at 80 °C. The solvent was evaporated *in vacuo*, and 50 ml of water was added. The mixture was extracted with 250 ml of dichloromethane (DCM) after acidification of the aqueous phase with concentrated hydrochloric acid. The organic phase was washed twice with 50 ml of water, followed by the evaporation of DCM to give a brown oil. The brown oil was dissolved in 70 ml of DCM and precipitated by dropwise addition to 800 ml of methanol, within 1 h. The white precipitate was again dissolved in 60 ml of DCM and reprecipitated from 400 ml of methanol, yielding 15 g (65%) of a white powder of diethyl 2,5-di-*n*-dodecyloxyterephthalate as first crop. 9.81 g (16.6 mmol) of this material was saponified in 60 ml of ethanol, 60 ml of water plus 4.38 g (66 mmol) of KOH under reflux. Upon acidification of the reaction mixture with concentrated hydrochloric acid, crude product **1** precipitated immediately. The material was filtered and washed with water (5×20 ml). Residual water was removed by azeotropic evaporation after addition of 100 ml of ethanol. Recrystallization from THF yielded 8.29 g of colourless needles (93%). δ_H (300 MHz, 80 °C, [^{2}H$_6$]DMSO): 7.27 (s, 2 H, Ar-H), 3.99 (t, *J* 6.4, 4 H, OCH$_2$), 1.69 (m, 4 H, CH$_2$), 1.44–1.18 (m, 36 H, CH$_2$), 0.85 (t, *J* 6, 6 H, CH$_3$); δ_C (75.5 MHz, 80 °C, [^{2}H$_6$]DMSO) 166.01, 150.47, 125.58, 115.97, 69.48, 30.83, 28.57, 28.53, 28.34, 28.25, 28.20, 24.91, 21.56, 13.29; mp 138.6 °C (DSC, second heating).

2: δ_H (300 MHz, 80 °C, [^{2}H$_6$]DMSO): 7.23 (s, 2 H, Ar-H), 3.97 (t, *J* 6.3, 4 H, OCH$_2$), 1.68 (m, 4 H, CH$_2$), 1.43–1.18 (m, 60 H, CH$_2$), 0.85 (t, *J* 6, 6 H, CH$_3$); mp 136.5 °C (DSC, second heating).

3: δ_H (200 MHz, 25 °C, CDCl$_3$) 7.88 (s, 2 H, Ar-H), 4.3 (t, *J* 6.5, 4 H, OCH$_2$), 1.9 (m, 4 H, CH$_2$), 1.6–1.05 (m, 68 H, CH$_2$), 0.89 (t, *J* 6, 6 H, CH$_3$); mp 134.4 °C (DSC, second heating).

2,5-Di-*n*-hexyl terephthalic acid (4). The acid **4** was prepared analogously to the general procedure in ref. 26. δ_H (200 MHz, 25 °C, [^{2}H$_6$]DMSO) 7.63 (s, 2 H, Ar-H), 2.88 (t, *J* 7, 4 H, CH$_2$), 1.52 (m, 4 H, CH$_2$), 1.29 (m, 12 H, CH$_2$), 0.86 (t, *J* 6.6 CH$_3$); δ_C (50.3 MHz, 25 °C, [^{2}H$_6$]DMSO) 168.77, 140.58, 133.50, 132.18, 33.09, 31.42, 31.25, 28.89, 22.25, 14.14; mp 243 °C (DSC, second heating).

Mixtures

All mixtures were obtained by preparation of a concentrated solution of the terephthalic acids in tetrahydrofuran and subsequent equimolar addition of the base dissolved in a few ml of tetrahydrofuran (10 mass% solutions). Evaporation of the solvent to dryness *in vacuo* delivered the complexes. The materials were ground to fine powders in an agate mortar and dried further under vacuum (50 °C, 10^{-2} mbar).

1·5: δ_H (300 MHz, 120 °C, [^{2}H$_6$]DMSO) 7.12 (s, 2 H, Ar-H), 3.98 (t, *J* 6.6, 4 H, OCH$_2$), 2.75 (t, *J* 7, 4 H, NCH$_2$), 1.77–1.57 (m, 6 H, CH$_2$), 1.43–1.14 (m, 36 H, CH$_2$), 0.87 (t, *J* 6.7, 6 H, CH$_3$). δ_C (75.5 MHz, 80 °C, [^{2}H$_6$]DMSO) 167.86, 149.94, 129.15, 115.72, 69.57, 37.19, 30.81, 28.84, 28.62, 28.53, 28.37, 28.19, 25.02, 21.55, 13.31.

2·5: δ_H (300 MHz, 120 °C, [^{2}H$_6$]DMSO) 7.12 (s, 2 H, Ar-H), 3.98 (t, *J* 7, 4 H, OCH$_2$), 2.78 (t, *J* 7, 4 H, NCH$_2$), 1.68 (m, 4 H, CH$_2$), 1.56 (m, 2 H, CH$_2$), 1.49–1.17 (m, 60 H, CH$_2$), 0.87 (t, *J* 6, 6 H, CH$_3$).

3·5: δ_H (300 MHz, 120 °C, [^{2}H$_6$]DMSO) 7.14 (s, 2 H, Ar-H), 3.98 (t, *J* 6.6, 4 H, OCH$_2$), 2.73 (t, *J* 7, 4 H, NCH$_2$), 1.75–1.5 (m, 6 H, CH$_2$), 1.45–1.2 (m, 68 H, CH$_2$), 0.87 (t, *J* 6.7, 6 H, CH$_3$).

1·6: δ_H (300 MHz, 80 °C, [^{2}H$_6$]DMSO) 7.11 (s, 2 H, Ar-H), 3.95 (t, *J* 6.6, 4 H, OCH$_2$), 2.85 (m, 8 H, NCH$_2$), 1.67 (m, 4 H, CH$_2$), 1.5–1.2 (m, 36 H, CH$_2$), 0.86 (m, 6 H, CH$_3$); δ_C (75.5 MHz, 80 °C, [^{2}H$_6$]DMSO) 167.17, 150.12, 127.92, 115.74, 69.51, 43.40, 30.78, 28.49, 28.28, 28.15, 24.95, 21.51, 13.28.

4·6: δ_H (300 MHz, 80 °C, [^{2}H$_6$]DMSO) 7.44 (s, 2 H, Ar-H), 2.85 (m, 12 H, NCH$_2$, CH$_2$), 1.52 (m, 4 H, aliph. CH$_2$), 1.4–1.2 (m, 12 H, CH$_2$), 0.86 (t, *J* 7 Hz, 6 H, CH$_3$); δ_C (75.5 MHz, 80 °C, [^{2}H$_6$]DMSO) 169.69, 138.34, 135.52, 130.33, 43.57, 32.50, 30.64, 28.22, 21.49, 13.29.

2·7: δ_H (300 MHz, 100 °C, [^{2}H$_6$]DMSO) 8.71 (d, *J* 4.4, 4 H, Ar-H), 7.75 (d, *J* 4.4, 4 H, Ar-H), 7.27 (s, 2 H, Ar-H), 4.0 (t, *J*

6.6, 4 H, CH_2), 1.70 (m, 4 H, CH_2), 1.5–1.19 (m, 60 H, CH_2), 0.86 (t, J 6.6, 6 H, CH_3); δ_C (75.5 MHz, 100 °C, $[^2H_6]$DMSO) 165.76, 150.41, 149.95, 144.02, 125.67, 120.61, 116.05, 69.56, 30.63, 28.35, 28.24, 28.06, 28.0, 24.75, 21.34, 13.06.

4·7: δ_H (300 MHz, 80 °C, $[^2H_6]$DMSO) 8.71 (d, J 4.4, 4 H, Ar-H), 7.77 (d, J 4.4, 4 H, Ar-H), 7.6 (s, 2 H, Ar-H), 2.87 (t, J 7.6, 4 H, CH_2), 1.53 (m, 4 H, CH_2), 1.29 (m, 12 H, CH_2), 0.85 (t, J 7, 6 H, CH_3). δ_C (75.5 MHz, 80 °C, $[^2H_6]$DMSO) 168.02, 150.10, 144.08, 139.71, 133.05, 131.21, 120.77, 32.32, 30.51, 28.04, 21.43, 13.25.

X-Ray structural analyses of 4·6 and 4·7

Suitable crystals of the compounds were obtained by slow isothermal evaporation of the solvents from concentrated THF solutions of the substances. Data were collected at room temperature on a Nonius CAD 4 diffractometer with graphite-monochromated Cu-Kα radiation ($\lambda = 1.5418$ Å) in the range $\theta < 65°$ with the θ–2θ scan mode. Reflections having $F > 3\sigma(F)$ were used in the structure refinement. The structures were solved by direct methods (SHELXS) and refined on F by full-matrix least-squares analyses with anisotropic thermal parameters for C, N, O. The hydrogen atoms were refined in the riding mode with fixed isotropic temperature factors. An empirical absorption correction was applied to the data. Pertinent crystallographic data are summarized in Table 1, selected bond lengths and dihedral angles are shown in Table 2. Tables of the atomic coordinates, the anisotropic and isotropic thermal parameters, and the full list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/52.

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