Conformation and orientation of alkyl chains in the layered organic–inorganic hybrids: $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$)

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Layered organic–inorganic hybrids based on perovskite-derived alkylammonium lead halides have been demonstrated as important new materials in the construction of molecular electronic devices. Typical of this class of materials are the single-perovskite slab lead iodides of the general formula $(C_nH_{2n+1}NH_3)_2PbI_4$. While for small n, these compounds are amenable to single-crystal structure determination, the increasing degree of disorder in the long chain ($n = 12,14\ldots$) compounds makes such an analysis difficult. In this study, we use powder X-ray diffraction, and vibrational and ^{13}C NMR spectroscopies to establish the conformation, orientation and organization of hydrocarbon chains in the series of layered alkylammonium lead iodides $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$). We find that the alkyl chains adopt a tilted bilayer arrangement, while the structure of the inorganic layer remains invariant with respect to the value of n. Conformation-sensitive methylene stretching modes in the infrared and Raman spectra, as well as the ^{13}C NMR spectra indicate that bonds in the methylene chain are in *trans* configuration. The skeletal modes of the alkyl chain in the Raman spectra establish that there is a high degree of all-*trans* conformational registry for the values of n studied here. From the orientation dependence of the infrared spectra of crystals of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16$), we find that the molecular axis of the all-*trans* alkyl chains are tilted away from the interlayer normal by an angle of 55°. This value of this tilt angle is consistent with the dependence of the c lattice expansion as a function of n, as determined from powder X-ray diffraction.

Introduction

Layered organic–inorganic compounds formed by cooperative assembly from organic and inorganic precursors have been widely studied.[1] In these molecular hybrids or composites, organic groups are interleaved between inorganic sheets and held in place either by covalent or ionic bonding.[2] These hybrids may be distinguished from intercalated layered compounds[3] for example, of graphite or of transition metal dichalcogenides, since unlike the latter they do not exist independently of the organic moiety. Interest in these compounds may be attributed to the fact that they can in principle, combine properties of the inorganic and organic parts within a single system. The nature of bonding allows for a variety of differing combinations of organic and inorganic parts and hence properties may be tuned simply by an appropriate selection of the inorganic and organic precursor.

A majority of the organic–inorganic molecular composites studied have been derived from the layered perovskite structure and comprise inorganic perovskite sheets alternating with either a double-layer of organic primary ammonium cations or a layer of organic diammonium cations.[4] The properties of these systems may not only be tuned by substitution of the organic and inorganic layers but also by modulating the thickness of the inorganic perovskite slab.[5] Applications of such layered perovskite materials include development of functional magnetic,[2] electronic[6] and optoelectronic[7] materials. Molecular hybrids of Pb(II) and Sn(II) iodides have been regarded as semiconductor/insulator 'natural' quantum-well structures.[4,8–10] Strong exciton absorption as well as sharp excitonic photoluminescence have been observed in these materials even at room temperature. The significant enhancement of excitonic binding energies is a consequence of the smaller dielectric constant of the alkylammonium insulating barrier layer as compared to the inorganic 'well' layer. The resulting dielectric confinement strengthens Coulombic interaction between electron and hole leading to stable excitons with large binding energies.[11] The exciton binding energies and hence the photoluminescence properties can therefore be tuned by varying the dielectric constant of the organic barrier layer and this has been successfully demonstrated in the layered Pb(II) iodides.[12]

While details of the ordering of the Pb–I inorganic backbone structure of the $(C_nH_{2n+1}NH_3)_2PbI_4$ compounds are reasonably well understood, direct characterization of the alkyl chain assemblies, especially for larger n, is lacking. Previous structural (X-ray diffraction) studies[13] on $(C_nH_{2n+1}NH_3)_2PbI_4$ have focused mostly on the shorter chain analogues ($n < 8$) in which the alkyl chains have limited conformational freedom. For larger values of n (10 and 12), Ishihara and coworkers reported crystal structure data as a part of a detailed study of the optical properties of these compounds.[11] However, their results were limited to reporting lattice parameters and the structure of the inorganic PbI4 layer. They showed that there are two PbI4 layers in the unit cell, perhaps related by a centre of inversion and that the in-plane lattice parameters are invariant with respect to the value of n. In view of the above, a detailed characterization of the conformation and organization of alkyl chains, especially for longer chains, in $(C_nH_{2n+1}NH_3)_2PbI_4$ is relevant. There exists one complete study of the $n = 9$ compound, $(C_9H_{19}NH_3)_2PbI_4$,[14] but this compound is

characterized by the complete interdigitation of the carbon chains and therefore a very compact inter-PbI_4 slab separation. As we find no evidence for interdigitation in the present compounds, we are led to suspect that the class of compounds described by these authors belongs to a distinct polymorphic group, different from the compounds discussed here.

Here we report a complete study of alkyl chain conformation in a series of long chain alkylammonium lead iodides $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$), using X-ray diffraction and vibrational (FT-IR, FT-Raman) and NMR spectroscopies. Vibrational[15] and NMR[16] spectroscopies are sensitive probes of local molecular conformation in alkyl chain assemblies. An analysis of the interlayer structure using X-ray diffraction data in conjunction with spectroscopic measurements has allowed for a comprehensive characterization of the conformation and orientation of alkyl chains in the organic–inorganic molecular hybrids $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$). Since our characterization of the compounds is based on powders and is largely by spectroscopy (*i.e.* using *local* probes) we expect that the ensuing structures would cast light on the kind of materials that are obtained by techniques such as spin casting.

Experimental

$(C_nH_{2n+1}NH_3)_2PbI_4$ compounds were prepared by mixing stoichiometric quantities of PbI_2 and $C_nH_{2n+1}NH_2$ in hydroiodic acid and refluxing to obtain a clear yellow solution. The solution was then cooled slowly to precipitate the $(C_nH_{2n+1}NH_3)_2$-PbI_4 compounds. The colour of the precipitated compounds varied from orange in the case of shorter chains ($n = 6,8$) to yellow ($n = 12,16,18$). The compounds were washed with distilled water till the filtrate showed complete absence of acid. Single crystals of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16$) were grown by slow cooling ($1° \text{ min}^{-1}$). Typical size of the crystals was $2 \times 2 \times 0.1$ mm. These crystals have been screened by single crystal X-ray diffraction, but we find that they are too micaceous for a complete X-ray structure solution. The chemical composition of the organic part was established by C, H, N analysis. $n = 12$: C – 26.63% (26.5%); N – 2.56% (2.58%); H – 5.73% (4.98%); $n = 16$: C – 33.56% (32.2%); N – 2.39% (2.35%); H – 6.51% (5.53%). Calculated values are given in parenthesis.

Powder X-ray diffraction patterns were recorded in the θ–2θ Bragg–Brentano geometry on a Siemens D5005 diffractometer employing Cu-Kα radiation. The powders were mounted by pressing them onto a glass substrate. Data were collected at a typical scan rate of $1°$ 2θ per minute and rebinned into $0.02°$ steps. The one-dimensional projected electron densities along the c-axis were calculated from the Fourier transform of the 00l intensities.[17] The intensities of these 00l reflections were extracted by fitting individual peaks in the pattern using the XND Rietveld code.[18] One-dimensional Fourier maps (projections of the electron densities along the c axis) were generated using standard proceedures[17] using the following formula:

$$\rho(z) = 1/L[F_0 + 2 \sum F_l \cos(2\pi l z)]$$

where $\rho(z)$ is the electron density at the point z along the c direction in crystallographic coordinates, F_0 is arbitrary and set to zero, and F_l is given by $\sqrt{I_{00l}}$; the intensity of the 00l reflection. L is the repeat distance along the c direction.

FT-IR spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ compounds were recorded as KBr pellets on a Bruker IFS55 spectrometer at 4 cm^{-1} resolution. Infrared spectra of crystals of $(C_nH_{2n+1}$-$NH_3)_2PbI_4$ ($n = 12,16$) were recorded in the spectral range 400–4000 cm^{-1} on a Bruker IFS55 spectrometer equipped with a polarizer accessory. The spectra for different orientations of
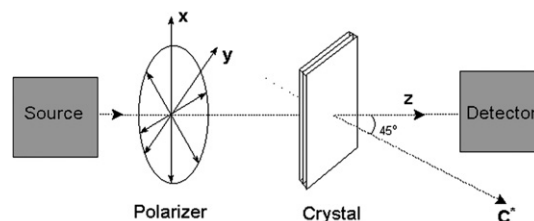

Fig. 1 Schematic representation of the experimental set-up for measuring the infrared spectra for different orientations of the electric field vector, E, of the incident IR beam with respect to the interlamellar normal, C^*. The crystals were held on the spectrometer such that the C^* axis makes an angle of $45°$ with respect to the direction of propagation of the IR beam z.

the electric field vector, E of the incident IR with respect to the C^* axis of the crystals (the axis normal to the layers) were obtained using the arrangement shown in Fig. 1. The lamellar crystals, sandwiched between two KBr pellets, were mounted in the spectrometer such that the axis normal to the crystal layers, C^*, was at an angle of $45°$ with respect to the direction of propagation of the incident IR beam z, and lying in the y–z plane (Fig. 1). Spectra for various angles of polarization of the electric field vector in the x–y plane were recorded using the polarizing accessory (Bruker Polarizing accessory I6798) placed between the source and the sample. The angle of polarization in the x–y plane was software controlled.

In the above scheme for an 'x' polarization of the IR beam $E \perp C^*$ a spectrum is obtained whereas, for the 'y' polarization the spectrum is a combination of the $E \| C^*$ and $E \perp C^*$ spectra. Since the angle between C^* and z, the propagation vector, is known ($45°$), the individual contributions may be obtained.[19,20] The intensity for 'x' polarization, I_x is given by:

$$I_x = I(E \perp C^*)$$

while for 'y' polarization

$$I_y = \cos^2 45 \, I(E \perp C^*) + \cos^2 45 \, I(E \| C^*)$$

For any angle, θ, of the polarization of E in the x–y plane:

$$I_\theta = \cos\theta I_x + \sin\theta I_y = \cos\theta I(E \perp C^*)$$
$$+ \sin\theta[\cos^2 45 \, I(E \perp C^*) + \cos^2 45 \, I(E \| C^*)]$$

From a measurement of the IR spectrum at two different angles of polarization of the electric field vector, E, in the x–y plane, the spectra for $E \perp C^*$ and $E \| C^*$ could be recovered and subsequently, the spectrum for any orientation, ϕ, of E with respect to C^* can be calculated.[19,20]

FT-Raman spectra were recorded on a Bruker IFS FT-Raman Spectrometer, using a Nd:YAG (wavelength 1.064 μm) laser as exciting radiation. All spectra were recorded at 4 cm^{-1} resolution with an unpolarized beam, using aluminium sample holders. Laser power was kept at 100 mW and typically around 400 spectra were summed to improve the signal to noise ratio. ^{13}C CP-MAS NMR were recorded on a Bruker DSX-300 solid state spectrometer at a Larmor frequency of 75.46 MHz with a contact time of 1 ms. The spectra were externally referenced to tetramethylsilane (TMS).

Results and discussion

X-ray diffraction

Fig. 2(a) shows the low angle region of the X-ray diffraction patterns of the various $(C_nH_{2n+1}NH_3)_2PbI_4$ compounds (with n indicated). Only 00l lines are observed due to the extremely high degree of preferred orientation arising from the manner in which the sample was mounted. The interlayer spacing for the $n = 10$ and 12 compounds are identical to the values
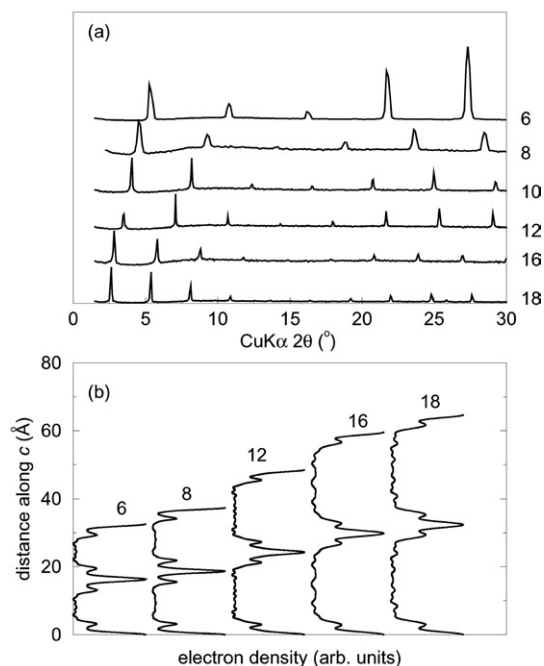
Fig. 2 (a) X-ray diffraction patterns showing $00l$ reflections of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 6,8,12,16,18$). (b) Projected one dimensional electron density, along the interlayer c axis, of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 6,8,12,16,18$) obtained by a Fourier transform of the X-ray $00l$ intensities.

reported in the literature. The $00l$ reflections can be counted as corresponding to $l = 1,2,3…$ or $l = 2,4,6….$. We have chosen the latter based on the established structure of some $(C_nH_{2n+1}NH_3)_2MX_4$ species.[11] General hkl reflections were generally not observed in the XRD patterns as a result of the micaceous nature of the sample, so it was not possible to obtain the in-plane structural parameters. Neither was it possible to perform a complete Rietveld type analysis of the data.

The one-dimensional projections of electron densities along the c-axis, calculated from a Fourier transform of the $00l$ intensities, are displayed in Fig. 2(b) Typically $00l$ reflections up to $l = 30$ were observed for the different compounds on going up to $100°$ in 2θ. Because the chains between the PbI_4 slabs scatter only weakly, we are unable to resolve the nature of the organic portion in these composite structures. The I–(PbI_2)–I slabs in the structure (traversing the c axis) are however well defined. It is seen that the metric of the inorganic part of the structure is unchanged on modifying the organic portion through changing the number of carbon atoms in the chain. The distance between the peaks corresponding to the apical I and the corner shared PbI_2 planes is uniformly about 3.0(1) Å. This should be compared with the Pb–I distance of 3.2 Å in PbI_2[21] and the distribution of Pb–I distances from 3.0 Å to 3.3 Å in some ternary compounds of Pb and I.[22] The X-ray diffraction results indicate that the structure of the PbI_4 layers remain unaltered as n varies from 6 to 18 in the $(C_nH_{2n+1}NH_3)_2PbI_4$ compounds. A similar observation had been reported by Ishihara and coworkers for the $n < 12$ compounds. In the following sections the characterization of the structure and conformation of the alkyl chains in the $n = 12,16,18$ compounds by vibrational and NMR spectroscopies is discussed. It may be recalled that detailed crystallographic structures have been reported only for the shorter chain analogues of $(C_nH_{2n+1}NH_3)_2PbI_4$.[13]

Vibrational spectroscopy

Vibrational spectroscopy has been extensively used for probing conformation in alkyl chain assemblies.[23] Infrared and
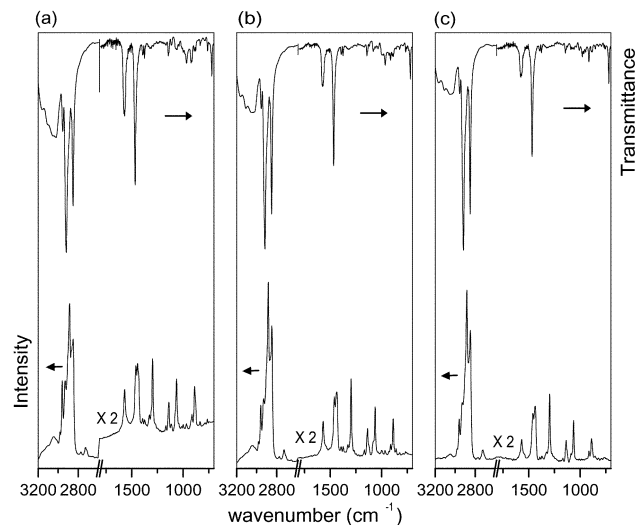

Fig. 3 FT-IR and FT-Raman spectra of $(C_nH_{2n+1}NH_3)_2PbI_2$ (a) $n = 12$ (b) $n = 16$ (c) $n = 18$.

Raman spectroscopic studies of n-alkanes have led to detailed correlation of the spectra with structural features such as chain conformation, chain packing and even specific conformational sequences. The position, line shape, and splitting of the methylene stretching and bending modes have been used to determine the conformation of methylene units in various phases of n-alkanes.[24–26] These results have been extensively used in the study of alkyl chain assemblies in systems like phospholipids,[27] micelles[28] and self-assembled monolayers.[29]

The infrared and Raman spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$) are shown in Fig. 3(a–c) respectively. The spectral features for the three compounds appear at almost identical frequencies in both the IR and Raman spectra. A detailed assignment of the observed peak positions for the $n = 18$ compound is given in Table 1. The IR spectra shows two strong bands at 2850 cm^{-1} and 2919 cm^{-1} assignable to the symmetric and anti-symmetric stretching modes of the $-(CH_2)_n-$ methylene group. The intense band at 1467 cm^{-1} may be assigned to the CH_2 scissoring mode and the strong band at 720 cm^{-1} to the methylene rocking mode. It is interesting to note that neither of these bands are split. These methylene rocking and scissoring modes are known to split into two components in closely packed alkyl chain systems, where more than one chain is present per unit cell due to interchain

Table 1 Observed peak positions in the infrared and Raman spectra of $(C_{18}H_{37}NH_3)_2PbI_4$ and their assignments

IR/cm^{-1}	Assignment	Raman/cm^{-1}	Assignment
3160 (br)	NH$_3^+$ 'head' group	2980 (w)	
3110 (br)	NH$_3^+$ 'head' group	2960 (m)	CH$_3$ asym stretch
3050 (br)	NH$_3^+$ 'head' group	2929 (m)	CH$_3$ sym stretch
3020 (br)	NH$_3^+$ 'head' group	2882 (vs)	CH$_2$ anti sym stretch
2952 (m)	CH$_3$ asym stretch	2848 (s)	CH$_2$ sym stretch
2918 (vs)	CH$_2$ anti sym stretch	1569 (s)	
2867 (w)	CH$_3$ sym stretch	1461 (vs)	CH$_2$ bending
2850 (vs)	CH$_2$ sym stretch	1436 (s)	CH$_2$ bending
1565 (br)		1297 (vs)	CH$_2$ twisting
1467 (s)	CH$_2$ scissoring	1137 (m)	C–C stretch
1393 (m)		1064 (m)	C–C stretch
1375 (m)	CH$_3$ sym bending	888 (s)	
967 (s)	C–N stretch		
914 (s)	C–N stretch		
720 (vs)	CH$_2$ rocking		

interactions.[30] The absence of splitting of the 1467 cm^{-1} and 720 cm^{-1} modes in the IR spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ indicates that the intermolecular interactions between alkyl chains are weak in these compounds. Apart from the bands due to the methylene groups, the stretching and bending modes of the terminal methyl groups can also be identified. The symmetric and asymmetric stretching modes of the methyl group appear at 2867 cm^{-1} and 2952 cm^{-1} while the symmetric bending mode appears at 1375 cm^{-1}. Stretching modes of the NH_3^+ 'head' group are seen as a broad band between 3200–3000 cm^{-1} and the C–N stretching modes are seen at 965 cm^{-1} and 912 cm^{-1}.

The Raman spectra of these compounds show two strong bands at 2882 cm^{-1} and 2848 cm^{-1} assignable to the antisymmetric and symmetric stretching modes of the methylene groups. The bands at 1431 cm^{-1} and 1297 cm^{-1} are assigned to the methylene scissoring and twisting modes. The C–C skeletal stretching modes appear at 1137 cm^{-1} and 1064 cm^{-1}. Regions of the vibrational spectra sensitive to the methylene chain conformation are discussed in greater detail in the subsequent sections.

C–H stretching region *Infrared.* The C–H stretching region of the IR spectrum of alkyl chain assemblies is sensitive to the conformation of the methylene chains.[24,25] For an all-*trans* alkyl chain, as in the case of crystalline *n*-alkanes, the symmetric and antisymmetric stretching modes of the methylene $[–(CH_2)_n–]$ groups appear in the range 2846–2849 cm^{-1} and 2916–2918 cm^{-1} respectively.[24] With increasing number of *gauche* conformers, as in the high temperature disordered liquid phases of *n*-alkanes, the positions of these peaks shift to higher wavenumbers, typically 2856–2858 cm^{-1} for the symmetric stretching mode and 2924–2928 cm^{-1} for the antisymmetric stretching modes.[25] The increased number of *gauche* conformers in the chain is also reflected by an increased line width for these bands.

The observed peak positions of the symmetric (2850 cm^{-1}) and anti-symmetric (2918 cm^{-1}) C–H stretching modes of the methylene groups in $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$) [Fig. 4(a)] are close to those observed in crystalline *n*-alkanes having all-*trans* conformation. This indicates that the majority of the methylene units of the alkyl chains in these layered perovskites adopt the *trans* conformation.

Raman. The C–H stretching region in the Raman spectrum of alkyl chain assemblies is dominated by two prominent bands, centered at 2880 cm^{-1} and 2850 cm^{-1}. These have been assigned to the methylene antisymmetric and symmetric stretching modes. The ratio of the intensities of the band at ~2880 cm^{-1} to that at ~2850 cm^{-1} (I_{2880}/I_{2850}) is known to be sensitive to both conformational disorder of the alkyl chains as well as their packing and has been widely used to characterize alkyl chain assemblies.[23] The reported values of (I_{2880}/I_{2850}) vary from ~2 in crystalline *n*-alkanes to ~0.7 in the corresponding liquid-phase. It has been shown that the intensity of the methylene symmetric stretching mode, I_{2850}, is sensitive to lateral interactions and hence to the packing arrangement.[31] Differences in lateral packing are also reflected as changes in the line width of the 2850 cm^{-1} band. The intensity I_{2880} is, however, unaffected by such interactions but is sensitive to the conformation of the methylene chain, decreasing in the liquid-phase as compared to the solid.[32] The intensity ratio I_{2880}/I_{2850} is thus sensitive to both conformational order as well as lateral interactions.

The Raman spectrum in the region of C–H stretching is shown in Fig. 4(b). The intensity ratio I_{2880}/I_{2850} as calculated from the peak heights for the compounds $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$) are 1.59, 1.33 and 1.32 respectively. Thus the methylene stretching modes in the infrared as well as the Raman spectra indicate that a majority of the methylene units in these compounds, irrespective of the alkyl chain length, are in the *trans* conformation.

C–C skeletal stretch (Raman). The C–C skeletal stretching region in the Raman spectra from 1050 to 1150 cm^{-1} has been shown to be sensitive to the relative amounts of *gauche* and *trans* conformers present in an alkyl chain.[23,32] An all-*trans* alkyl chain normally shows two strong bands at 1130 cm^{-1} and 1065 cm^{-1}. The presence of a central band at 1080 cm^{-1} is characteristic of randomization (interruption of all-*trans* conformation) of the chain due to presence of *gauche* conformers. The ratio of the peak heights of the band at 1130 cm^{-1} to the band at approximately 1080 cm^{-1} has been considered a qualitative measure of the amount of *gauche* conformer present in the methylene chain.[32] This ratio has, for example, been extensively used for studying the order–disorder transitions in phospholipids.[23]

The Raman spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$) in the region of 1500–800 cm^{-1} are shown in Fig. 5. Spectra of all these compounds show two intense bands at 1135 cm^{-1} and 1064 cm^{-1}. The band at 1080 cm^{-1} due to *gauche* conformers appears as a small peak for the $n = 18$ compound but for the $n = 12,16$ compounds it is seen only as a shoulder to the 1130 cm^{-1} band. The Raman spectra indicate that a majority of the bonds of the methylene chains in these compounds adopt a *trans* conformation and are in registry.
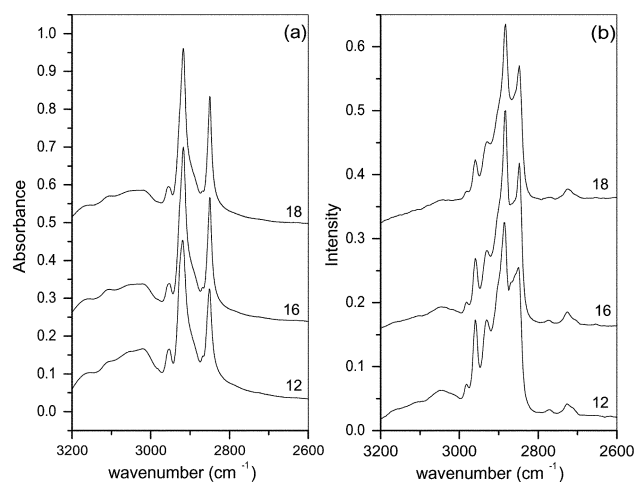

Fig. 4 (a) FT-IR and (b) FT-Raman spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$) in the region of the methylene stretch.
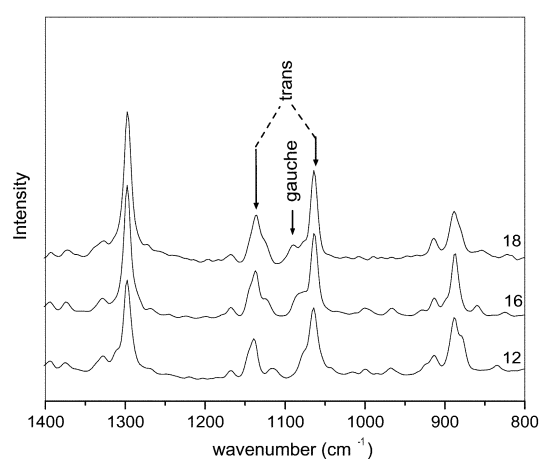

Fig. 5 FT-Raman spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$) in the region of 1500–800 cm^{-1} showing the C–C skeletal stretching bands.

Corroborative evidence for the above observation is also found in the infrared spectra. In the infrared spectrum of alkyl chain systems, the presence of end-*gauche* defects is known to result in a peak at ~1341 cm^{-1},[33] whereas kinks formed by *gtg'* sequences between all-*trans* segments is known to yield a broad band at 1366 cm^{-1} and a double-*gauche* (*gg'*) sequence results in a peak at 1355 cm^{-1}. The fact that we find no evidence for the existence of any of these bands in the infrared spectra of these compounds, further supports the above inference.

NMR spectroscopy

NMR spectroscopy is widely used in the study of alkyl chain system like micelles, liquid crystals,[34] *etc*. In particular, ^{13}C NMR chemical shift differences have been used to characterize the conformation of methylene chains.[35] It has been shown that the degree of shielding of a carbon atom in a methylene chain depends on the relative population of *trans* and *gauche* conformers, with the *trans* conformer giving rise to a downfield shift.[36] The ^{13}C CP-MAS NMR spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ (n = 12,16,18) are shown in Fig. 6. The spectra show eight carbon resonances which, in order of increasing downfield shift, can be assigned to C_1, C_{n-2}, C_5–C_{n-3}, C_4, C_2, C_3, C_{n-1}, C_n carbon atoms respectively. Carbon atoms are numbered successively starting from the methylene carbon closest to the NH_3^+ group.

It may be seen from the figure that the resonance for C_5–C_{n-3} atoms shows a single peak at 34.6 ppm. In alkyl chain systems where a section of the methylene chains are present in a disordered *gauche* conformation, two resonances are observed. The one appearing down-field has been assigned to an 'all-*trans*' ordered conformation and the accompanying up-field resonance to a disordered conformation. The presence of a single resonance for the C_5–C_{n-3} carbon atoms in $(C_nH_{2n+1}NH_3)_2PbI_4$ (n = 12,16,18) implies either that methylene units of the alkyl chain adopt an all-*trans* structure or a majority of the methylene units are in a disordered conformation, either would give rise to a single resonance. The latter possibility may however be ruled out since the observed positions and intensity ratios of the C–H stretching frequencies in the IR and Raman and the 1130 cm^{-1} C–C skeletal stretch in the Raman spectrum indicate the contrary. Thus the observed single resonance for the C_5–C_{n-3} carbons in $(C_nH_{2n+1}NH_3)_2PbI_4$ (n = 12,16,18) is attributed to an ordered *trans* conformation of the methylene chains.

The results of the vibrational and ^{13}C NMR spectra clearly indicate that a majority of the methylene units in the alkyl chain assembly of $(C_nH_{2n+1}NH_3)_2PbI_4$ (n = 12,16,18) adopt the *trans* conformation.

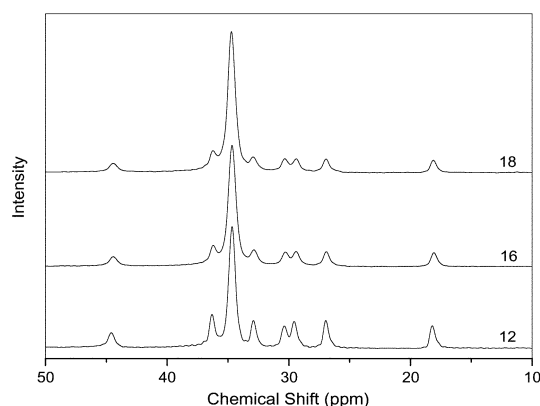**Fig. 6** ^{13}C CP-MAS NMR spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ (n = 12,16,18).

Orientation of the alkyl chains. The orientation of the all-*trans* alkyl chain was determined from the orientation dependent IR spectra in the C–H stretching region of crystals of $(C_nH_{2n+1}NH_3)_2PbI_4$ (n = 12,16) and independently from the observed lattice expansion as a function of n. The tilt angle of the alkyl chains was estimated from the dichroic ratio of the symmetric and antisymmetric methylene stretching modes.[37] The tilt angle is the angle the molecular axis of the all-*trans* methylene chain makes with the interlayer normal. The spectra in the methylene stretching region for the two orientations $E \perp C^*$ and $E \| C^*$ on crystals of $(C_nH_{2n+1}NH_3)_2$-PbI$_4$ (n = 12,16) recorded by the arrangement mentioned in the experimental section are shown in Fig. 7(a) and 7(c). From the two spectra, the spectrum for different angles, ϕ, of the electric field vector of the incident IR radiation (E) with respect to the interlayer normal (C^*), may be calculated. The dichroic ratios $I_\phi/I_{\phi+90}$ for the symmetric (2850 cm^{-1}) and antisymmetric (2918 cm^{-1}) methylene stretching modes of $(C_nH_{2n+1}NH_3)_2PbI_4$ (n = 12,16) have been plotted as a function of ϕ in Fig. 7(b) and 7(d). $I(\phi)$ is the intensity of the vibrational mode for an angle ϕ. The dichroic ratio for the symmetric and antisymmetric methylene C–H stretching modes peak at 33° for the n = 12 and at 38°and 36°for the n = 16 compound, respectively.

The dichroic ratio for a vibrational mode will peak at a value ϕ for which the electric field vector of the incident IR beam is parallel to the transition dipole moment of that mode. For an all-*trans* methylene chain the transition dipole moment of the methylene symmetric stretching modes (μ_s) are orthogonal to the molecular axis but lie in the molecular plane of the *trans* methylene chain, whereas that of the antisymmetric stretching modes (μ_{as}) are orthogonal to the molecular axis and also to the molecular plane. The fact that the dichroic ratio for these two modes in $(C_nH_{2n+1}NH_3)_2PbI_4$ (n = 12,16) peak at approximately the same values of ϕ implies that the molecular plane of the all-*trans* methylene chain has no fixed orientation with respect to the C^* axis. The transition dipole
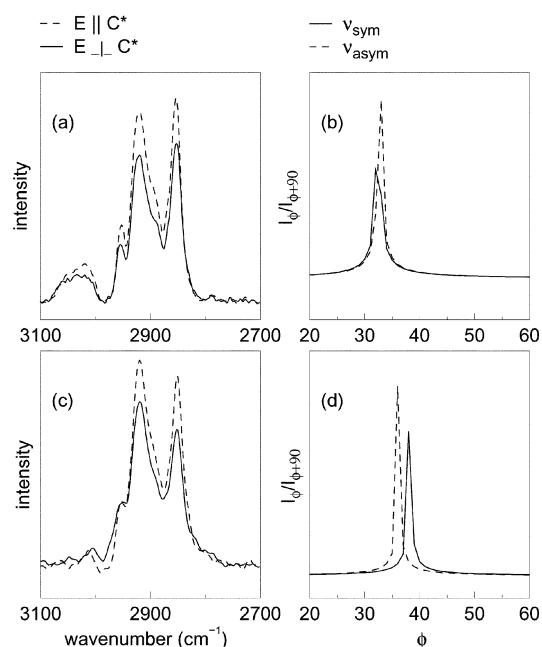

Fig. 7 IR spectra in the C–H stretching region of a crystal of $(C_nH_{2n+1}NH_3)_2PbI_4$ recorded for the two orientations of the electric field vector (E) of the incident IR beam with respect to the interlayer normal (C^*), $E\|C^*$ (dotted line) and $E\perp C^*$ (solid line), for the (a) n = 12 and (c) n = 16 compounds. The plot of the corresponding dichroic ratios ($I_\phi/I_{\phi+90}$) as a function of ϕ for the methylene symmetric (dotted line) and antisymmetric (solid line) stretching modes for the (b) n = 12 and (d) n = 16 compounds.
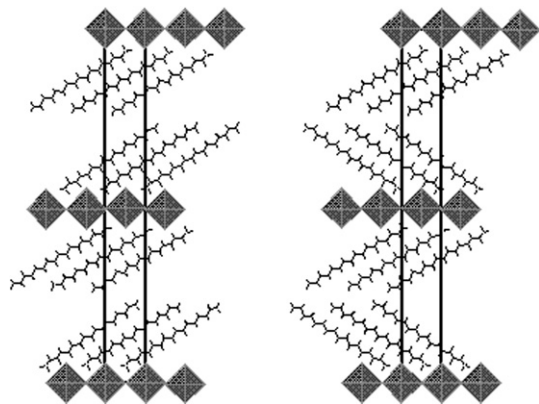
Fig. 8 A schematic depicting the structure and orientation of the alkyl chains in the layered $(C_nH_{2n+1}NH_3)_2PbI_4$ compounds. Either of the two arrangements shown would satisfy the observations of the present study.

moment of the symmetric and antisymmetric stretching modes of the methylene groups lie in a plane perpendicular to the molecular axis. The angle at which the dichroic ratio peaks is therefore the angle this plane makes with the interlayer normal[38] and the tilt angle is 90° minus this value. From Fig. 7(b) and 7(d), the tilt angle of the alkyl chains with respect to the interlayer normal is 57° for the $n = 12$ and 53° for the $n = 16$ compound.

The tilt angle may also be estimated from the observed changes in the lattice spacing as a function of the alkyl chain length. For an all-*trans* methylene chain, addition of a methylene unit would increment the length of the chain by 1.25 Å. Thus an increase in the c lattice spacing of 2.5 Å per additional methylene unit would have been observed if the all-*trans* chain of the bilayer were normal to the PbI_4 layer. From the X-ray determined c spacing for the $n = 12$, 16 and 18 compound, we obtain a value of 1.36 Å as the increment in the spacing for each additional methylene unit. This would be realized if the all-*trans* chain were tilted away from the interlayer normal by an angle of 57°. This value is almost identical to that determined from the dichroic measurements. The present results indicate that in the organic–inorganic layered hybrids $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12,16,18$) the alkyl chains adopt an all-*trans* conformation with the molecular axis of the chain tilted away from the interlayer normal by an average of 55° (Fig. 8).

Conclusions

We have described the disposition of alkyl chains (conformation and orientation) in the layered hybrids $(C_nH_{2n+1}NH_3)_2$-PbI_4 ($n = 12,16,18$) by developing a model that is consistent with the results of powder X-ray diffraction analysis of the 00*l* reflections as well as vibrational and NMR spectroscopies. In future work, we expect to be able to quantify the precise extent of the all-*trans* registry of the alkyl chains, and the temperature dependence of the structure. As pointed out in the introduction, the optical properties of these materials are strongly modulated by the dielectric organic layer that controls the communication of excitons from one inorganic layer to the next. We believe that the detailed understanding of the disposition of alkyl chains presented here will assist in the design of new optical materials.

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