

# Hydrogen bonding, alkyl chain crystallization and constitutional isomerism in solid-state self-assembly of dodecyloxyisophthalic acid complexes

Balasubramaniam Venkataramanan, Zu Ning, Jagadees J. Vittal and Suresh Valiyaveetil\*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, S 173543, Singapore. E-mail: chmsv@nus.edu.sg

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Self-assembly of the molecular complexes of *O*-alkoxy isophthalic acid (**5-C<sub>12</sub>** and **4-C<sub>12</sub>**) with 4,4'-bipyridine (bipy) in the crystal lattice is described. Complexes **5-C<sub>12</sub>ISA·bipy** and **4-C<sub>12</sub>ISA·bipy** exhibit 3-D supramolecular structures through and interplay of H-bonding, alkyl chain interdigitation,  $\pi\cdots\pi$  and C-H $\cdots\pi$  interactions. The former forms a unique triple helix which further assembles into a 2D network stabilized via  $\pi\cdots\pi$  stacking interactions. The latter forms hydrogen bonded supramolecular sheets.

## Introduction

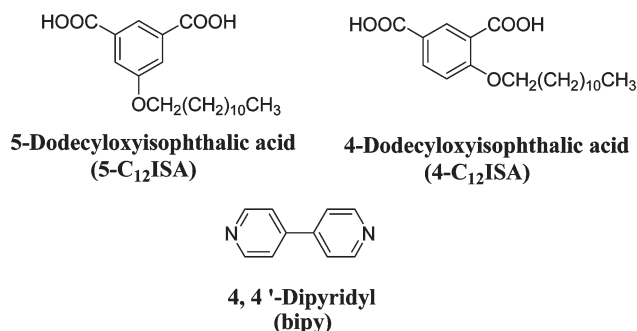
Self-assembly of small molecular components into a complex macromolecular architecture is an interesting phenomenon with many examples in biotic and abiotic systems.<sup>1</sup> Weak forces such as hydrogen bonds and van der Waals forces play an important role in the formation of supramolecular architectures in the crystal lattice.<sup>2</sup> Self-assembly of molecular building blocks assisted by non-covalent interactions such as electrostatic (*e.g.*, hydrogen bonding, dipole-dipole, donor-acceptor interactions) and van der Waals forces (*e.g.*, alkyl chain crystallization,<sup>3</sup>  $\pi\cdots\pi$  stacking) allows us to design interesting supramolecular architectures such as boxes,<sup>4</sup> squares,<sup>5</sup> figure eight,<sup>6</sup> grids,<sup>7</sup> tapes,<sup>8</sup> rosettes,<sup>9</sup> macrocycles,<sup>10</sup> capsules,<sup>11</sup> dendritic species,<sup>12</sup> helicates<sup>13,14</sup>. Mimicking helical topology has gained immense attention due to their biological importance.<sup>15</sup> A hydrogen-bonded helical system comprising of single chemical components has been observed.<sup>13,14</sup> However, self-assembly assisted formation of triple-helicates in non-metallic compounds are rare in literature.

Recently, isophthalic acid and its derivatives have been used to form interesting supramolecular architectures in the crystal lattice,<sup>16a-d</sup> in solution,<sup>16c,d</sup> in the mesophase<sup>16e</sup> and at the interface.<sup>16f</sup> We have previously reported that crystallization of a 1 : 1 mixture of 5-dodecyloxyisophthalic acid and pyrazine produced a sheet-type crystal lattice with 2 : 1 stoichiometry.<sup>17</sup> Our repeated failure in getting single crystals with a 1 : 1 stoichiometry of this complex was explained using the fact that close packing of alkyl chains in the layer-type lattice was only possible with 2 : 1 stoichiometry.<sup>17</sup> This paper describes the interplay of hydrogen bonding, alkyl chain crystallization, weak interactions and constitutional isomerism in the solid-state self-assembly of dodecyloxyisophthalic acid complexes with 4,4'-bipy.

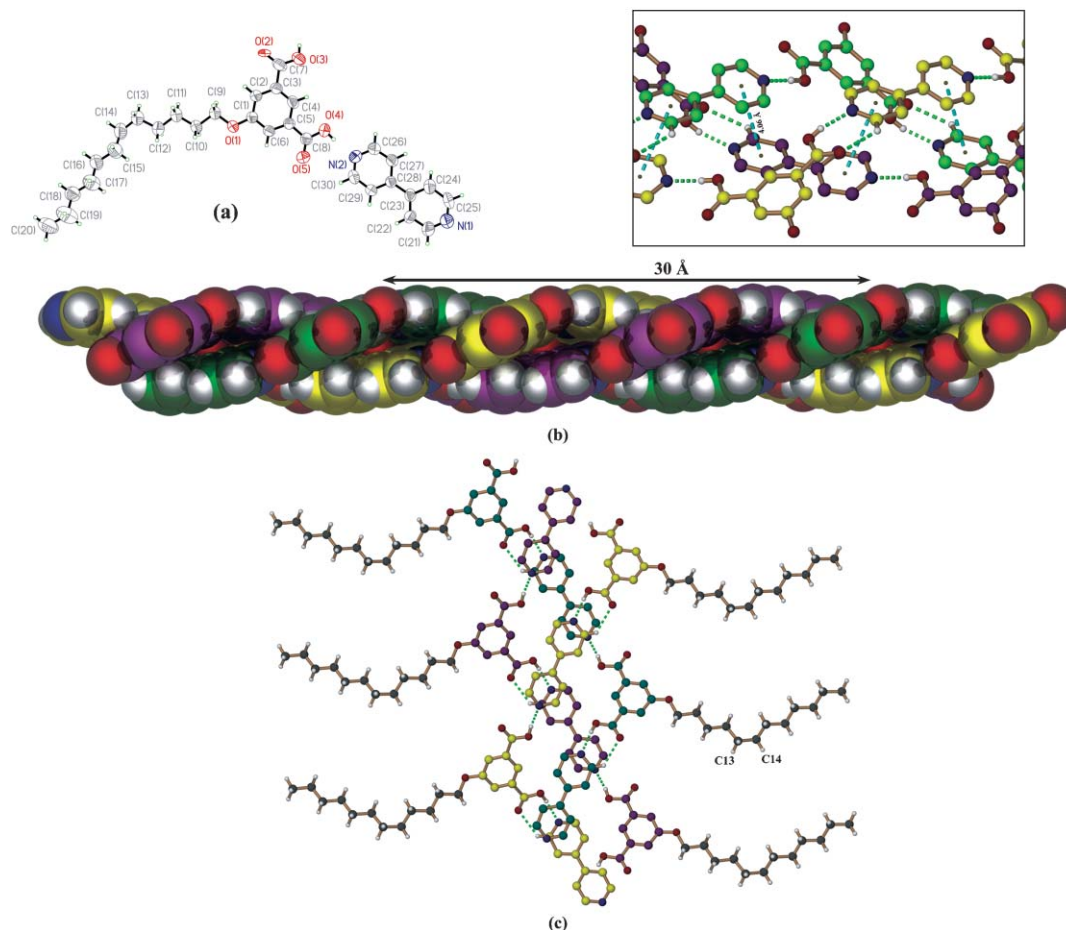
## Solid state self-assembly of 5-C<sub>12</sub>ISA·bipy

Good quality single crystals from a 1 : 1 stoichiometric mixture of 4,4'-bipyridyl (bipy) with 5-dodecyloxyisophthalic acid (**5-C<sub>12</sub>ISA**)<sup>18</sup> (Scheme 1) were obtained and characterized by single-crystal X-ray crystallography. Single crystals of the 5-C<sub>12</sub>ISA·bipy complex were obtained from ethanol/dimethylsulfoxide solution *via* slow evaporation of the solvent.

ORTEP representation of the complex is shown in Fig. 1a. X-ray analysis of the single crystals indicated the formation of triple helices with strong hydrogen bonds (O-H $\cdots$ N) and alkyl chain interdigitation along the helical axis. In the crystal lattice (monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*), carboxyl groups are hydrogen bonded to the nitrogen atom of the bipyridyl molecules to form a linear chain (O-H $\cdots$ N, 1.95 and 1.84 Å, respectively). Crystallographic data are given in Table 1. CCD reference numbers 146451 and 146452. See <http://www.rsc.org/suppdata/ce/b4/b417663d> for crystallographic data in CIF or other electronic format. Three such molecular chains are twisted together to give a triple helix along the *b*-axis (Fig. 1b). The helical complexes pack together through a combination of several intermolecular interactions. Firstly, the pyridyl rings (bipy) from the interpenetrating layers stack on each other through offset  $\pi$ - $\pi$  interactions, forming an unusually compact, ordered and stable molecular solid. The distance between the centroids of stacked aromatic rings is 4.06 Å (Fig. 1, enclosed box). The pitch of the helix is 30 Å (Fig. 1a). Both right-handed and left-handed helices are observed in the crystal lattice due to the centrosymmetric space group *P*<sub>2</sub><sub>1</sub>/*c*. Secondly, C-H(alkyl) $\cdots\pi$ <sub>arene</sub> (2.9–3.3)Å interactions occur between an alkyl proton (H9A, H14B and H17A) and an aromatic ring (C<sub>1</sub>–C<sub>6</sub>, N<sub>2</sub>–C<sub>26</sub>–C<sub>30</sub> and N<sub>1</sub>–C<sub>21</sub>–C<sub>25</sub>, respectively) from an adjacent molecule. Alkyl chains from the neighbouring helices are interdigitated and close packed in a plane parallel to the *b*-axis (Fig. 1c). All C–C bonds in the alkyl chain are in



**Scheme 1** Molecular structure of dodecyloxyisophthalic acid and 4,4'-bipyridine.



**Fig. 1** (a) ORTEP representation of **5-C<sub>12</sub>ISA·bipy** complex with atom numbering. Thermal ellipsoids are drawn at 50% probability level. Colour codes: C, grey; H, white; O, red; N, blue (b) A portion of the triple helix formed between three single stranded helices generated upon self-assembly between **5-C<sub>12</sub>ISA** and bipy. Also indicated are the  $\pi\cdots\pi$  interactions between the helices (enclosed box). Alkyl chains and certain H-atoms are eliminated for clarity; the C atoms belonging to three different strands composing the triple helices are differentiated by colours for clarity. (c) Alkyl chain packing between the helices, indicating the *gauche* conformation at C<sub>13</sub>–C<sub>14</sub>. Click here to access a 3-D representation of Fig. 1c.

*anti*-conformation except one bond in the middle (C<sub>13</sub>–C<sub>14</sub>) with a *gauche* conformation (Fig. 1c). This facilitated a better interdigitation of alkyl chains from the neighbouring helices. The distance between the carbon atoms in the adjacent interdigitated alkyl chains from the neighbouring helices is *ca.* 4 Å and that of the alkyl chains of the same helix is 9 Å. All atomic positions are well resolved and no noticeable disorder is seen inside the lattice. The hydrogen bond parameters of the complex **5-C<sub>12</sub>ISA·bipy** are shown in Table 2. Also, these helices pack parallel to each other (at the corners of the unit cell, Fig. 2a) in the crystal lattice and are stabilized by weak C–H $\cdots$ O interactions. [ $d(\text{H}\cdots\text{O})$  2.49, 2.58 Å, Fig. 2b].

#### Solid state self-assembly of **4-C<sub>12</sub>ISA·bipy**

Single crystals of **4-C<sub>12</sub>ISA·bipy** complex were obtained from a solution of reactant in acetonitrile/dimethylsulfoxide mixture.<sup>18</sup> X-ray analysis of single crystals of complex **4-C<sub>12</sub>ISA·bipy** (triclinic,  $P\bar{1}$ ) shows that the acid groups are hydrogen bonded to the basic nitrogen atom (O–H $\cdots$ N, 1.85 and 1.86 Å, respectively) of the 4,4'-bipyridyl molecules to form linear hydrogen bonded steps in the crystal lattice. ORTEP representation of the complex is shown in Fig. 3a. Unlike **5-C<sub>12</sub>ISA·bipy** complex, helical structures are not formed in the crystal lattice, but linear hydrogen bonded molecular tapes that are arranged parallel to each other are observed (Fig. 3b, *a*-axis).

However, the two bipyridyl molecules hydrogen bonded to the acid groups of a single **4-C<sub>12</sub>ISA** molecule are not crystallographically equivalent. Interdigitated alkyl chains

are packed parallel to one of the dipyrindyl molecule and repeated throughout the lattice (Fig. 3b). The other bipyridyl unit organizes in a staggered manner in the crystal lattice. Due to this organization, there are two distinct domains in the crystal lattice, one involves the hydrogen bonded acids and bipyridyl molecules and the other one involves alternatively packed alkyl chains and bipyridyl molecules. The angle between the two crystallographically independent dipyrindyl units is *ca.* 40°. A 2D-arrangement of the molecules in the co-crystals is shown in Fig. 4. It is interesting to note that each 4,4'-bipy molecule interacts with four acid molecules through the formation of O–H $\cdots$ N and C–H $\cdots$ O pairwise hydrogen bonds [H $\cdots$ N, 1.86 Å and H $\cdots$ O, (2.44–2.58) Å, respectively] to construct molecular tapes. The C–H $\cdots$ O hydrogen bonds link parallel tapes to create supramolecular sheets (Fig. 4a). Usually 4,4'-bipy hydrogen atoms take part in such interactions. The distance between the parallel molecular sheets (Fig. 4b) and bipyridyl molecules involved in the construction of tapes (Fig. 4a) is 8.97 and 8.65 Å, respectively. Details of O–H $\cdots$ N/C–H $\cdots$ O are provided in Table 3. These supermolecules organize to yield a 2D sheet structure comprised of cavities that are being filled by acetonitrile molecules. Disordered acetonitrile solvent molecules run along the crystal axis and thus stabilize the bridging bipy through weak interactions (C22–H22 $\cdots$ N1s: 2.59 Å, 163°), Fig. 4b. The bridged 4,4'-bipy is further stabilized *via* offset  $\pi\cdots\pi$  interactions. The distance between the centroids of (bipy: **4-C<sub>12</sub>ISA**) is 4.40 Å. C–H $\cdots\pi$  interactions occur between the 4,4'-bipy (C–H, donor) and **4-C<sub>12</sub>ISA** ( $\pi$ -ring, acceptor). In addition to alkyl chain

**Table 1** Crystal data and details of structure determination<sup>11</sup> Single crystals suitable for X-ray diffraction studies for complexes **5-C<sub>12</sub>ISA·bipy** and **4-C<sub>12</sub>ISA·bipy** were grown from the appropriate solvent mixture by slow evaporation of solvents at room temperature in air. The crystals were sealed in a quartz capillary and data collection was carried out on a Bruker SMART CCD system. The software used was SMART<sup>20</sup> for collecting frames of data, indexing reflections and determining lattice parameters; SAINT<sup>20</sup> for integration of intensity, reflections and scaling; SADABS<sup>21</sup> for absorption corrections; and SHELXTL<sup>22</sup> for space group determination, structure solution and least squares refinements on  $F^2$ . The structure of the complex was solved by direct methods and remaining non-hydrogen atoms located in Fourier difference maps. Full-matrix least-squares refinements were carried out with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were placed on calculated positions (C–H 0.96 Å) and assigned isotropic thermal parameters riding on their parent atoms.

	<b>5-C<sub>12</sub>ISA·bipy<sup>a</sup></b>	<b>4-C<sub>12</sub>ISA·bipy<sup>b</sup></b>
Formula	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub> ·C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub> ·C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> ·MeCN
<i>M</i>	506.62	544.65
Crystal system	monoclinic	Triclinic
Space group	P2 <sub>1</sub> /c	P1̄
<i>a</i> /Å	14.207(3)	8.6519(2)
<i>b</i> /Å	10.2673(2)	8.9745(2)
<i>c</i> /Å	20.4022(2)	20.2624(1)
$\alpha$ /°	90	97.423(10)
$\beta$ /°	105.5349(10)	92.7270(10)
$\gamma$ /°	90	92.6650(10)
<i>V</i> /Å <sup>3</sup>	2849.89(9)	1556.15(5)
<i>Z</i>	4	2
<i>D<sub>c</sub></i> /g cm <sup>−3</sup>	1.181	1.162
$\mu$ /mm <sup>−1</sup>	0.080	0.079
<i>T</i> /K	293	293
$\lambda$ /Å	0.71073	0.71073
Measured reflections	13287	11009
Independent reflections	2558	3959
<i>R</i> <sub>1</sub> , <i>I</i> > 2σ( <i>I</i> )	0.0708	0.0662
<i>wR</i> <sub>2</sub> , <i>I</i> > 2σ( <i>I</i> )	0.2046	0.1653

A crystal of appropriate dimensions<sup>a</sup> 0.10 × 0.50 × 0.50 Å; <sup>b</sup> and 0.30 × 0.30 × 0.32 Å was mounted on a Bruker AXS SMART CCD 3-circle diffractometer with Mo Kα radiations.

**Table 2** Significant intermolecular interactions (interatomic distances in Å and bond angles in °) found in the X-ray structures of **5-C<sub>12</sub>ISA·bipy**

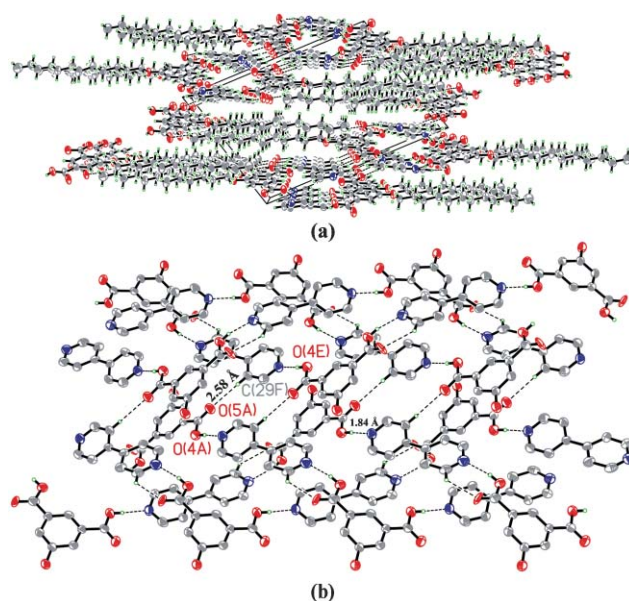
D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(D–H...A)
O3–H3...N1 <sup>i</sup>	0.82	1.95	2.748(4)	166
O4–H4...N2	0.82	1.84	2.656(3)	172
C20–H20A...O2 <sup>ii</sup>	0.96	2.49	3.352(13)	149
C25–H25...O2 <sup>iii</sup>	0.93	2.49	3.159(13)	129
C29–H29...O5 <sup>iv</sup>	0.93	2.58	3.502(4)	174

<sup>a</sup> Symmetry codes: (i)  $-x, -3/2 + y, 3/2 - z$ ; (ii)  $1 - x, 1/2 + y, 1/2 - z$ ; (iii)  $-x, 3/2 + y, 3/2 - z$ ; (iv)  $-x, 2 - y, 1 - z$ .

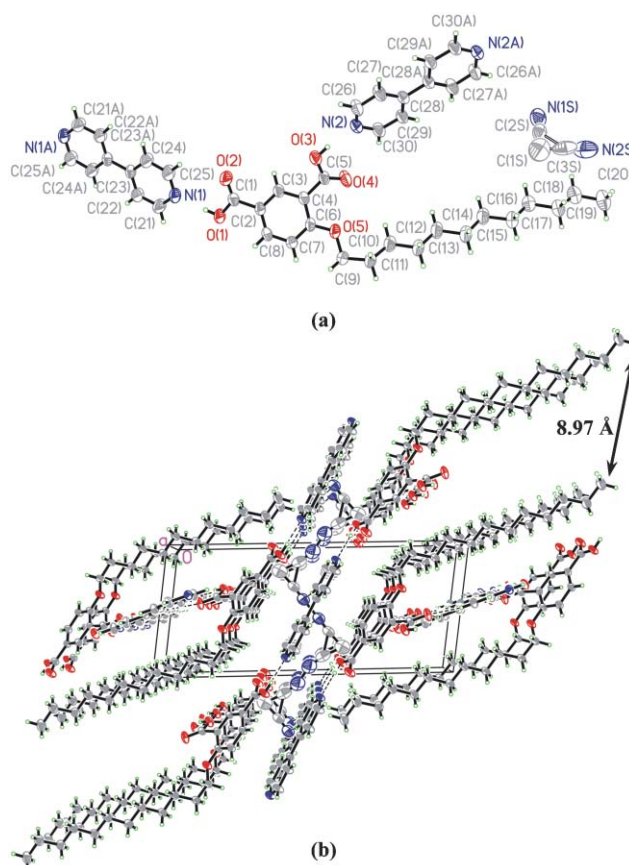
interdigitation, C–H... $\pi$  interactions were also observed between alkyl chain hydrogen atoms (C16–H16B, donor) and bipy ( $\pi$ -ring, acceptor) molecules.

## Conclusion

In conclusion, an interesting triple helix from achiral building blocks, **5-C<sub>12</sub>ISA** and bipy, is achieved as a result of interplay of hydrogen bonding, alkyl chain crystallization and weak interactions. Even though the chemical constituents are the same, complex **4-C<sub>12</sub>ISA·bipy** failed to show such a helical structure; instead, a step-type lattice was formed. The co-crystallization of 4,4' bipyridine with various di-, and tri-, carboxylic acids resulted in hydrogen bonded tape or sheet-type arrangements depending on the geometry of the acids.<sup>19</sup> By



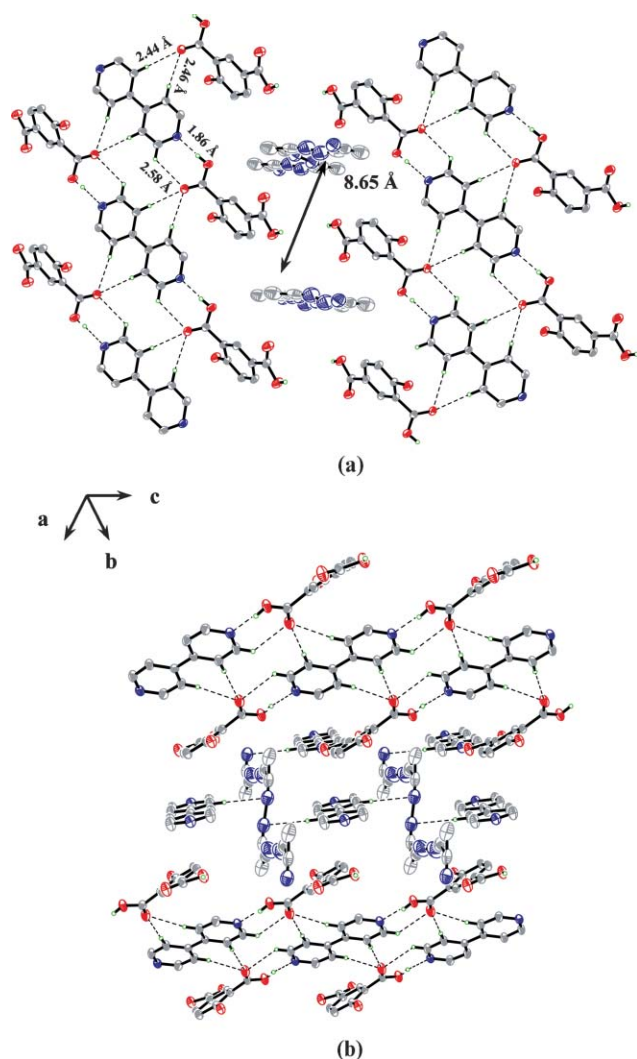
**Fig. 2** (a) Tube-like cavity generated within triple helices as viewed along the *b*-axis. (b) Annotation of interactions (C–H...O) between the neighbouring helices.



**Fig. 3** Crystal structure of **4-C<sub>12</sub>ISA·bipy** complex. (a) Molecular structure with atom numbering. Colour codes: C, grey; H, white; O, red; N, blue. (b) Hydrogen bonding and alkyl chain packing motif in the crystal lattice, note the alternate packing of dipyrindyl and alkyl chains and a layer of solvent molecules (*a*-axis). Click here to access a 3-D representation of Fig. 3b.

considering the similar nature and strength of the hydrogen bonding in both complexes, it appears that close-packing requirements of constitutional isomers play a significant role in deciding the topology of the lattice. To our knowledge, this is a unique example in which optimization of multiple weak interactions such as electrostatic (hydrogen bonding), van





**Fig. 4** Interaction between the molecules of acid, 4-C<sub>12</sub>ISA and bipy in the molecular complex. Notice the formation of molecular tapes through pairwise hydrogen bonds (a) in absence of bridging 4,4'-bipy (b) showing the interaction of bridging 4,4'-bipy with acetonitrile.

**Table 3** Significant intermolecular interactions (interatomic distances in Å and bond angles in °) found in the X-ray structures of 4-C<sub>12</sub>ISA-bipy

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(D-H...A)
O1-H1...N1	0.82	1.85	2.664(3)	177
O3-H3...N2	0.82	1.86	2.671(3)	169
C22-H22...N1s <sup>i</sup>	0.93	2.59	3.487(8)	163
C25-H25...O2	0.93	2.58	3.226(3)	127
C27-H27...O4 <sup>ii</sup>	0.93	2.46	3.383(3)	171
C29-H29...O4 <sup>iii</sup>	0.93	2.44	3.360(3)	172
C30-H30...O4	0.93	2.58	3.205(3)	125

<sup>a</sup> Symmetry codes: (i)  $-x, 1-y, -z$ ; (ii)  $1+x, -1+y, 1+z$ ; (iii)  $-1+x, y, z$ .

der Waals interaction (alkyl chain packing), weak interactions and constitutional isomerism is involved in the solid-state self-assembly of *O*-alkoxyisophthalic acid complexes.

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  - 18 Both **5**-alkoxyisophthalic acid and **4**-alkoxyisophthalic acid were synthesized according to reported procedure.<sup>15e,16</sup> Both compounds were characterized using analytical techniques. The spectroscopic data for both compounds are given below. **5**-C<sub>12</sub>ISA: Yield: 8.7 g (45.0%) <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, δ ppm): 0.9 (t, 3H), 1.2 (m, 18H), 1.7 (m, 2H), 4.0 (t, 2H), 7.6 (s, 2H), 8.1 (s, 1H); <sup>13</sup>C NMR (300 MHz, DMSO-d<sub>6</sub>, δ ppm): 13.8, 22.0, 25.2, 28.4, 28.6, 28.9, 31.2, 67.9, 118.8, 121.9, 122.0, 132.6, 158.7, 166.3; MS *m/z* 349.2 (M-1). **4**-C<sub>12</sub>ISA: Yield: 9.0 g (46.80%) <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, δ ppm): 0.90 (t, 3H), 1.20 (m, 18H), 1.7 (m, 2H), 4.15 (t, 2H), 7.2 (d, 1H), 8.0 (d, 1H), 8.2 (s, 1H); <sup>13</sup>C NMR (300 MHz, DMSO-d<sub>6</sub>, δ ppm): 13.8, 22.0, 25.2, 28.4, 28.5, 28.6, 28.9, 31.2, 68.4, 113.0, 121.4, 122.2, 132.0, 134.0, 160.8, 166.3, 166.6; MS *m/z* 349.2 (M-1).
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