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Nanostaircase formation in the solid state from self-assembling synthetic terephthalamides with a common molecular scaffold

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Abstract—The design and construction of nanostructured materials using proper self-assembling molecular building blocks is a real challenge to scientists. Here, we present the formation of a new nano-architecture, i.e., nanostaircase in the solid state by using molecular building blocks, which are amenable to self-assembly in a directed manner to form the specific nanostructure. The molecular building blocks are terephthalamides **1**–**4**, which are bis-terephthalamides of methyl esters of various α-amino acids including L-leucine **1**, D-leucine **2**, L-isoleucine **3**, and α-aminoisobutyric acid (Aib) **4**. All terephthalamides presented here, irrespective of their different side chain residues or stereochemistry, self-assemble to form supramolecular nanostaircase structures in crystals. Each terephthalamide contains two good hydrogen-bond donors and two hydrogen-bond acceptors. Two N–H···O hydrogen bonds and C–H···π interactions are responsible for the formation and stabilization of the nanostaircase structures in crystals. The molecular building blocks are packed orthogonally to each other in crystals and this arrangement can help the formation of nanostaircase structure upon self-assembly.
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1. Introduction

Fabrication of various nanomaterials can be achieved by mainly two approaches: one approach is photolithography and the other is the 'bottom-up' approach. Using photolithography only two-dimensional nano-scaled materials can be prepared. However, using 'bottom-up' approach, where molecular self-assembly plays a key role, three-dimensional nanostructured materials can be constructed.[1] Another advantage of using a bottom-up approach is that well-defined nanostructured materials can be prepared by using suitable molecular building blocks and the property of the nanomaterials can be tuned by designing appropriate, self-assembling, molecular building blocks. The design and construction of various nanostructured materials using molecular self-assembly is a very active area of current research.[2] Nanotubes obtained from various, suitable, self-assembling, organic compounds based molecular building blocks have been well studied.[3] Similarly peptide based nanorods have been constructed using oligopeptide scaffolds.[4] Peptide nanotubes have been used in many applications such as structure directed synthesis of silver nanowires,[5] electrochemical applications.[6] There are also numerous examples of self-assembling peptide based nanofibers.[7]

There are several examples of metal ion directed supramolecular staircase formation.[8] Several structures of terephthalamides have also been reported using either single crystal X-ray diffraction studies or neutron fiber diffraction studies. However, in all previously mentioned bis-terephthalamide structures only intermolecularly hydrogen-bonded supramolecular β-sheets,[9] ribbon[10] or helix[11] are reported, but not a supramolecular nanostaircase. We decided it would be interesting to use a conformationally rigid molecular scaffold, which can pack at about right angles to each other using intermolecular hydrogen bonding and other noncovalent interactions like C–H···π, π···π interactions to form a specific, well-defined, supramolecular nano-architecture.

In the course of our continuing interest in constructing various supramolecular nano-architectures including nanorod[4] and nanotube,[12] we have synthesized and characterized four compounds **1**–**4**, which are bis-terephthalamides of methyl esters of α-amino acids L-leucine, D-leucine, L-isoleucine, and α-aminoisobutyric acid (Aib), respectively. A schematic representation of all four terephthalamides is shown in Figure 1. In this paper, we present the formation of nanostaircase structures in crystals from a series of self-assembling terephthalamides with a common molecular scaffold.

Keywords: C–H···π interactions; Nanostaircase; Terephthalamide; Self-assembly; Hydrogen bonds.
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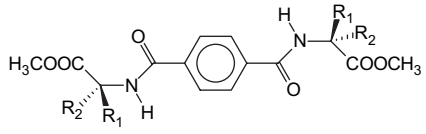

1: R_1 = -$CH_2CH(CH_3)_2$, R_2 = H
2: R_1 = H, R_2 = -$CH_2CH(CH_3)_2$
3: R_1 = -$CH(CH_3)(CH_2CH_3)$, R_2 = H
4: R_1 = R_2 = -CH_3

Figure 1. Schematic representation of terephthalamides **1**, **2**, **3**, and **4**.

These supramolecular nanostaircase structures are formed and stabilized by various noncovalent interactions including intermolecular hydrogen bonding and C–H$\cdots\pi$ interactions.

2. Results and discussion

Colorless single crystals of terephthalamides **1**–**4** were grown from methanol–water solution by slow evaporation. The crystal structure data for four terephthalamides are given in Table 1. Terephthalamides **1**–**3** crystallize in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit. The monoclinic crystals of terephthalamide **4** crystallize in the centrosymmetric space group $P2_1/c$ with 1/2 molecule in the asymmetric unit. Selected backbone torsion angles of all terephthalamides are listed in Table 2. In terephthalamides **1** and **2** the isobutyl groups have large atomic displacement parameters (ADPs). In residues with long side chains, the side chains are more flexible, hence large ADPs are observed for these groups. From the crystal structure of terephthalamide **1**, it is evident that there is no intramolecular

Table 1. Crystallographic data for terephthalamides **1**, **2**, **3**, and **4**

	1	**2**	**3**	**4**
Formula	$C_{22}H_{32}N_2O_6$	$C_{22}H_{32}N_2O_6$	$C_{22}H_{32}N_2O_6$	$C_{18}H_{24}N_2O_6$
Formula weight	420.5	420.5	420.5	364.39
Crystallizing solvent	Methanol–water	Methanol–water	Methanol–water	Methanol–water
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Temperature [K]	293	293	293	293
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1/c$
a [Å]	10.022 (6)	9.9970 (12)	10.148 (7)	11.288 (5)
b [Å]	10.094 (6)	10.1066 (13)	10.645 (7)	9.657 (4)
c [Å]	12.626 (7)	12.6432 (16)	11.592 (8)	9.601 (4)
β [°]	108.719 (9)	108.679 (2)	109.795 (10)	110.008 (7)
V [Å^3]	1209.7 (12)	1210.1 (3)	1178.2 (14)	983.3 (7)
Z	2	2	2	2
ρ_{calcd} [g cm^{-3}]	1.154	1.154	1.185	1.231
λ [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.084	0.084	0.086	0.093
$2\theta_{max}$	46.6	46.6	53	53.2
F(000)	452	452	452	388
Total reflns	7458	7471	8599	7173
Unique reflns	1831	1834	2344	1925
Reflns used	1610	1630	2065	1654
Parameters	271	271	303	166
$R1$ [$I>2\sigma(I)$]	0.0884	0.0925	0.0480	0.0665
$wR2$	0.2586	0.2742	0.1376	0.1984
Max. and min. electron density [e/Å^3]	0.31, −0.20	0.35, −0.25	0.19, −0.14	0.50, −0.25

Table 2. Selected backbone torsional angles (°) of terephthalamides **1**, **2**, **3**, and **4**

Terephthalamide **1**			
C2M–O2M–C2′–C2A	174.6 (14)	C1M–O1M–C1′–C1A	−170.3 (16)
O2M–C2′–C2A–N2	167.8 (8)	O1M–C1′–C1A–N1	−45.5 (13)
C2′–C2A–N2–C8	−110.6 (8)	C1′–C1A–N1–C1	−82.0 (9)
C2A–N2–C8–C5	−179.8 (6)	C1A–N1–C1–C2	179.5 (7)
Terephthalamide **2**			
C2M–O2M–C2′–C2A	167.8 (16)	C1M–O1M–C1′–C1A	−176.1 (14)
O2M–C2′–C2A–N2	45.9 (12)	O1M–C1′–C1A–N1	−167.9 (8)
C2′–C2A–N2–C8	83.4 (8)	C1′–C1A–N1–C1	110.3 (8)
C2A–N2–C8–C5	179.0 (6)	C1A–N1–C1–C2	179.4 (6)
Terephthalamide **3**			
C2M–O2M–C2′–C2A	177.2 (4)	C1M–O1M–C1′–C1A	−179.2 (4)
O2M–C2′–C2A–N2	168.4 (3)	O1M–C1′–C1A–N1	169.6 (3)
C2′–C2A–N2–C8	−133.6 (3)	C1′–C1A–N1–C1	−103.7 (3)
C2A–N2–C8–C5	178.0 (2)	C1A–N1–C1–C2	175.6 (3)
Terephthalamide **4** (the atom names with a terminating 'a' belong to the second half of the molecule related by a inversion center)			
C1M–O1M–C1′–C1A	−174.8 (3)	C1Ma–O1Ma–C1′a–C1Aa	174.8 (3)
O1M–C1′–C1A–N1	−49.6 (3)	O1Ma–C1′a–C1Aa–N1a	49.6 (3)
C1′–C1A–N1–C4	−47.6 (3)	C1′a–C1Aa–N1a–C4a	47.6 (3)
C1A–N1–C4–C2	−175.36 (16)	C1Aa–N1a–C4a–C2a	175.36 (16)

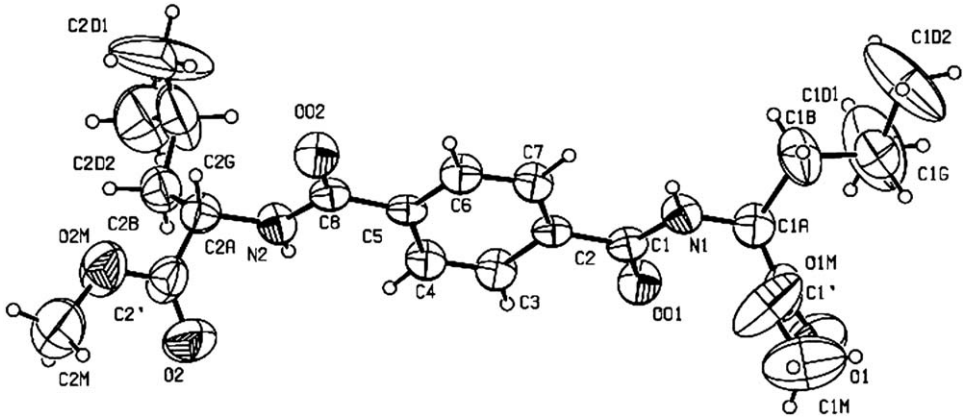

Figure 2. ORTEP diagram of terephthalamide **1** with atomic numbering scheme. Ellipsoids at 30% probability.

hydrogen bond and the molecule possesses an overall extended backbone conformation (Fig. 2). Terephthalamide **1** self-assembles to form a supramolecular nanostaircase structure in crystals with various noncovalent interactions being present including intermolecular hydrogen bonding and CH···π interactions (Fig. 3). There are two intermolecular hydrogen bonds (N1–H1···O02, 2.058 (5) Å, 2.882 (7) Å, 160.03 (35)°, symmetry equivalent $-x+1$, $y+0.5$, $-z+2$ and N2–H2···O01, 2.141 (5) Å, 2.945 (7) Å, 155.35 (36)°, symmetry equivalent $-x$, $y-0.5$, $-z+2$) that connect the individual molecules of terephthalamide **1** to form supramolecular nanostaircase structure in which the length of the steps is 7.5 Å (0.75 nm) and the height of the steps of the staircases is also 7.5 Å (0.75 nm). In crystals, individual molecules are stacked orthogonally to each other using N–H···O hydrogen bonding and C–H···π interactions and this particular arrangement helps to form the supramolecular nanostaircase structure. There is a C–H···π interaction[13] between C2D2–H2D6 with the centroid of the phenyl ring of terephthalamide moiety (C2D2–H2D6···π, 3.26 Å, 4.047 Å, 140.97°) (Fig. 6a) in supramolecular nanostaircase of the terephthalamide **1**.

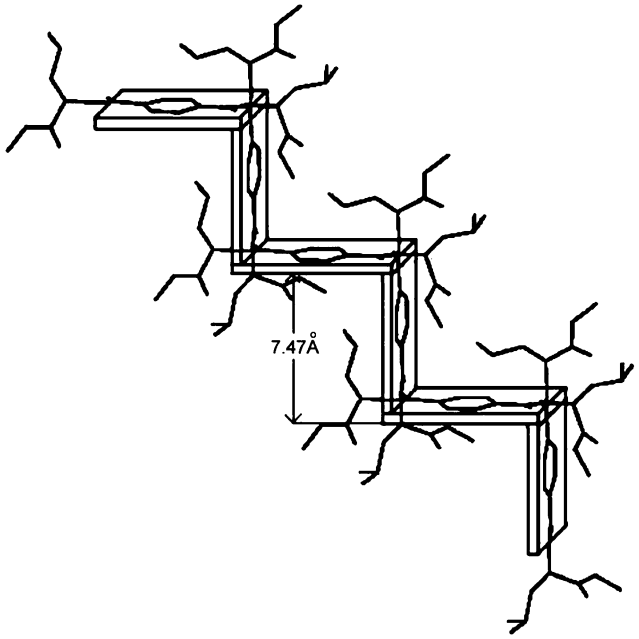

Figure 3. Crystal packing diagram of the terephthalamide **1** illustrating the supramolecular nanostaircase structure.

Terephthalamide **2** contains two D-leucine residues and adopts a molecular structure, which is a mirror image of terephthalamide **1** (Fig. 4). The only difference between them is the reversal of sign of the comparable backbone torsion angles (O2M–C2′–C2A–N2 and O1M–C1′–C1A–N1; C2′–C2A–N2–C8 and C1′–C1A–N1–C1) of terephthalamide **2** with respect to terephthalamide **1** (Table 2). Terephthalamide **2** also self-assembles to form a supramolecular nanostaircase (Fig. 5) in crystals through various noncovalent interactions including intermolecular hydrogen bonding (N1–H1···O02, 2.144 (5) Å, 2.946 (8) Å, 154.90 (39)°, symmetry equivalent $-x+2$, $y+0.5$, $-z+2$ and N2–H2···O01,

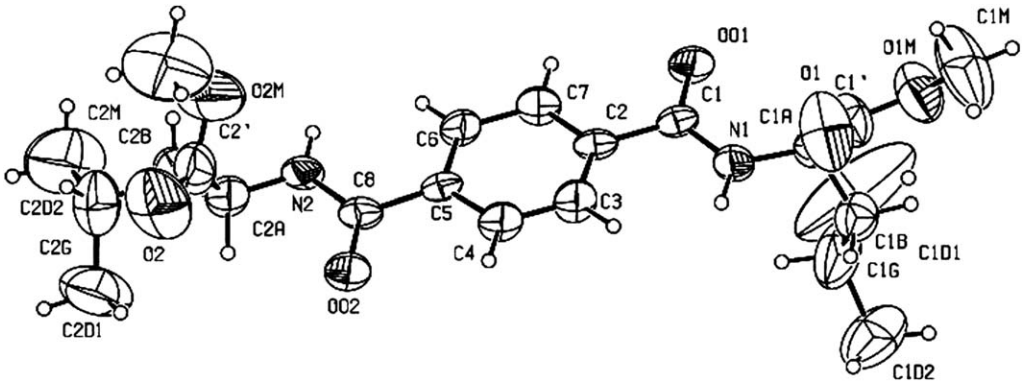

Figure 4. ORTEP representation of terephthalamide **2** with atomic numbering scheme. Ellipsoids at 30% probability.

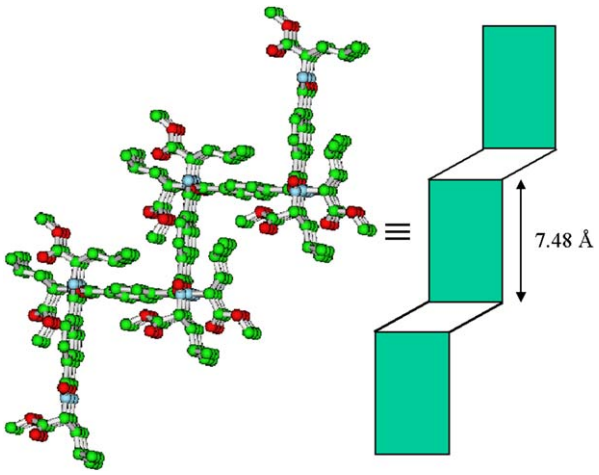

Figure 5. Nanostaircase arrangement of terephthalamide **2** in crystals and its schematic representation.

2.050 (5) Å, 2.877 (7) Å, 160.84 (35)°, symmetry equivalent $-x+1$, $y-0.5$, $-z+2$). There is a C–H···π interaction between C1D2–H1D5 with centroid of the phenyl ring of terephthalamide moiety (C1D2–H1D5···π, 3.18 Å, 3.982 Å, 142.66°) (Fig. 6b) in supramolecular nanostaircase of the terephthalamide **2**.

Both L-leucine residues of terephthalamide **1** have been substituted by L-isoleucine residues in terephthalamide **3** (Fig. 7). However, the inherent characteristic feature of terephthalamide **3** is similar to that of terephthalamide **1**. The only difference between them is the difference among numerical values of the comparable backbone torsion angles (O2M–C2′–C2A–N2 and O1M–C1′–C1A–N1; C2′–C2A–N2–C8 and C1′–C1A–N1–C1) of terephthalamide **3** (Table 2). Terephthalamide **3** also self-associates to form a supramolecular nanostaircase architecture utilizing two intermolecular hydrogen bonds (N1–H1···O02, 2.211 (36) Å, 2.999 (4) Å, 166.88 (341)°, symmetry equivalent $-x+1$, $y+0.5$, $-z+1$ and N2–H2···O01, 2.337 (42) Å, 3.089 (5) Å, 163.16 (387)°, symmetry equivalent $-x$, $y-0.5$, $-z+1$) (Fig. 8). There is a C–H···π interaction between C2D1–H2D2 with centroid of the phenyl ring of terephthalamide moiety (C2D1–H2D2···π, 3.378 Å, 4.009 Å, 125.2°) in the supramolecular nanostaircase of terephthalamide **3**.

The achiral terephthalamide **4** also adopts an extended backbone molecular conformation (Fig. 9). The comparable backbone torsion angles of the symmetric terephthalamide **4** (O1M–C1′–C1A–N2 and O1Ma–C1′a–C1Aa–N1a; C1′–C1A–N1–C4 and C1′a–C1Aa–N1a–C4a) have the same numerical values but are opposite in sign (Table 2). Utilizing two intermolecular hydrogen bonds (N1–H3···O01, 2.022 (25) Å, 2.856 (3) Å, 174.10 (221)°, symmetry equivalent x, $-y+0.5$, $z-0.5$ and N1a–H3a···O01, 2.022 (25) Å, 2.856 (3) Å, 174.10 (221)°, symmetry equivalent $-x+1$, $y+0.5$, $-z+0.5$, the 'a' after atom name indicates that the second half of the molecule is related by an inversion center), terephthalamide **4** forms a supramolecular nanostaircase architecture (Fig. 10). The nanostaircase structure is also stabilized by C–H···π interaction between C1B2–H1B5 with centroid of the phenyl ring of terephthalamide

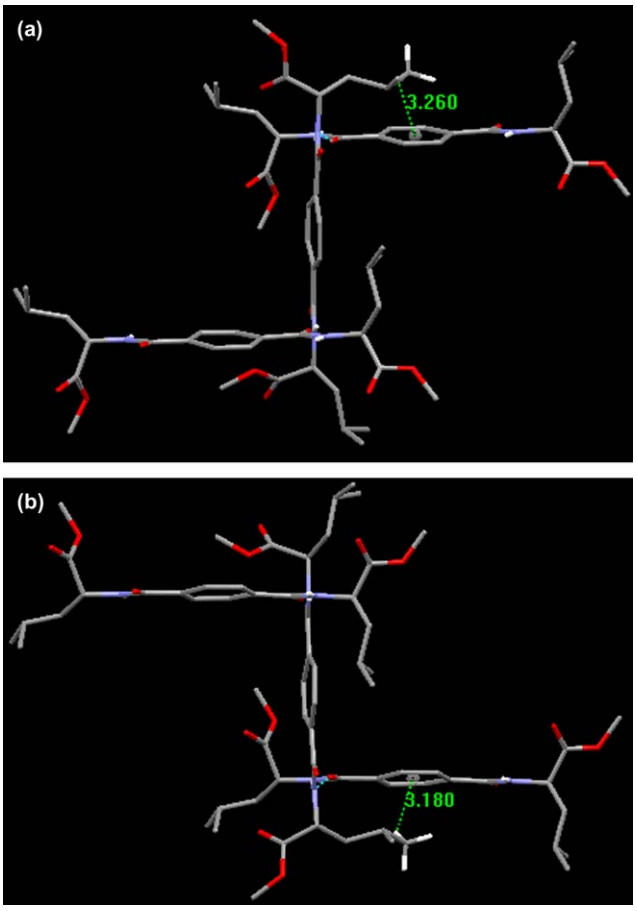

Figure 6. Packing modes of nanostaircase structures by C–H···π interactions in (a) terephthalamide **1** and (b) terephthalamide **2** in crystals.

moiety (C1B2–H1B5···π, 3.427 Å, 4.355 Å, 162.54°) (Fig. 11) of the terephthalamide **4**.

All four terephthalamides with different amino acid side chains or stereochemistry self-assemble in a similar manner in which the molecular building blocks are packed against each other orthogonally to form a nanostaircase structure utilizing N–H···O hydrogen bonding and C–H···π interactions. It is interesting to note that the previously reported crystal structure of *N*,*N*′-bis(methoxycarbonylmethyl)-terephthalamide[10] (molecule **A**), reveals that the molecule **A** self-assembles through two intermolecular hydrogen bonds along the crystallographic *b* axis to form a supramolecular ribbon or sheet-like structure (Fig. 12). In this molecular packing, the aromatic rings of these adjacent molecules are close to perpendicular direction with a distance of 5.13 Å between the centers of the two aromatic rings. In the formation of the above mentioned ribbon or sheet-like structure, the self-assembling molecules are stacked atop one another and they are interconnected by only N–H···O hydrogen bonding. However, in our case molecular building blocks are stacked almost orthogonally to each other in all four terephthalamides and they are associated with intermolecular –C═O···H–N– hydrogen bonding as well as C–H···π interactions. This helps to form supramolecular nanostaircase structures. The step-length of the nanostaircase is ~7.5 Å and the height of the steps is ~7.5 Å. Here, the reported terephthalamides **1**–**4** fail to stack atop one another to

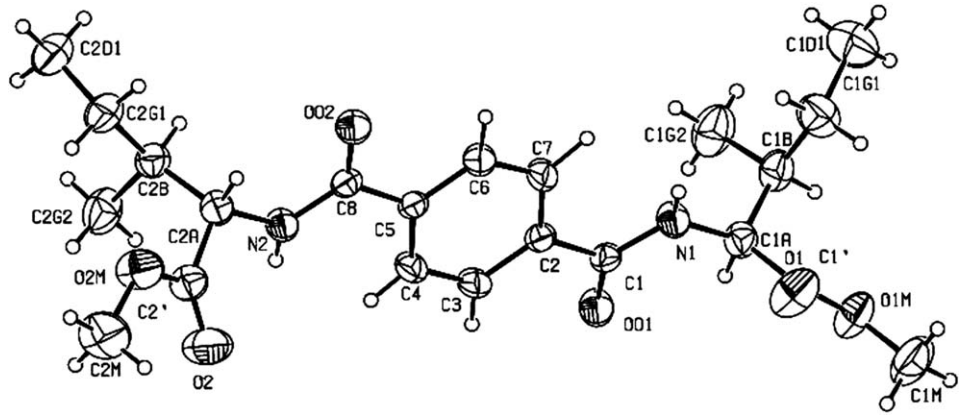

Figure 7. Molecular conformation of terephthalamide **3** with atomic numbering scheme. Thermal ellipsoids are shown at 30% probability level.

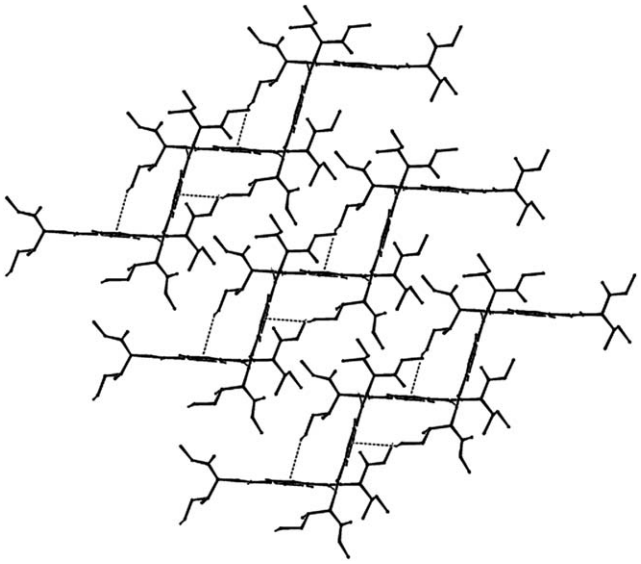

Figure 8. Supramolecular staircase structure obtained from the higher order self-assembly of the terephthalamide **3** in crystals. The C–H$\cdots\pi$ interactions are shown as dotted line.

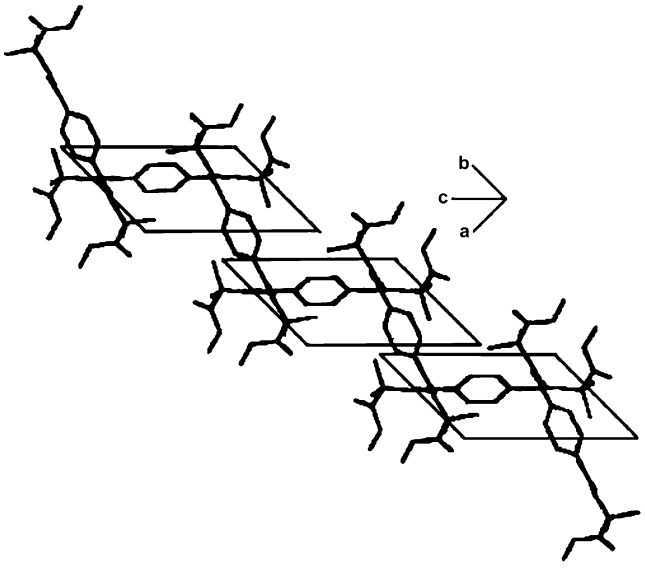

Figure 10. Packing diagram of the terephthalamide **4** showing the supramolecular staircase architecture in crystals stabilized by multiple intermolecular hydrogen bonds.

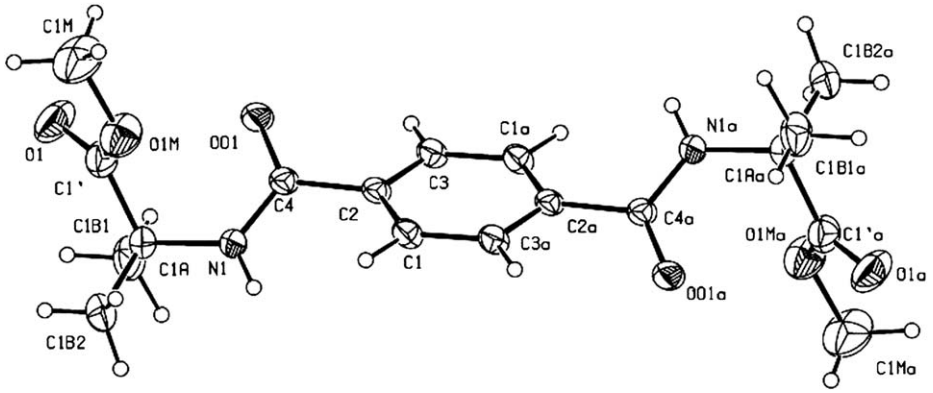

Figure 9. The molecular structure of terephthalamide **4** with atomic numbering scheme. Ellipsoids at 30% probability.

form supramolecular sheet- or ribbon-like structure, which might be due to the steric hindrances associated with the bulky amino acid side chains. Orthogonal packing between the self-associating molecular building blocks (terephthalamides **1**–**4**) may be favored by the presence of C–H$\cdots\pi$ interactions between the amino acid side chain H-atoms and the centrally located aromatic moiety, which was absent in the molecular packing of the molecule **A**.

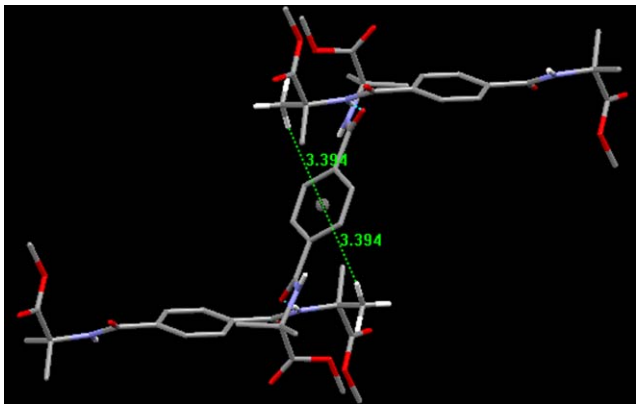

Figure 11. A view of interconnected C–H···π interactions in terephthalamide **4**.

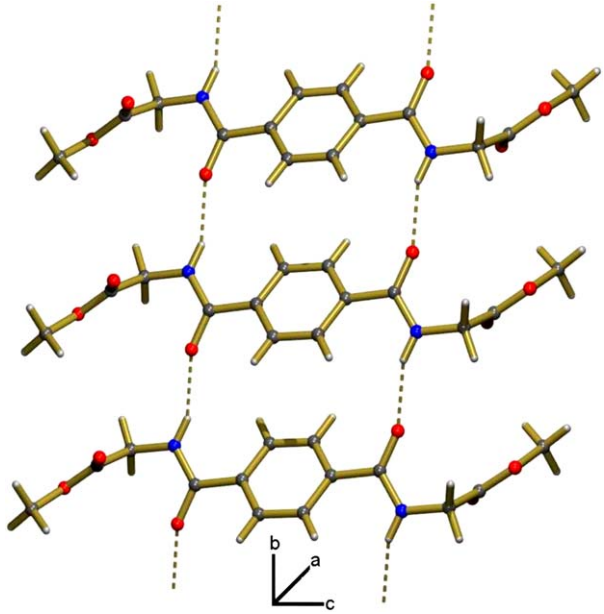

Figure 12. Crystal packing of terephthalamide **A** showing the formation of intermolecularly hydrogen-bonded ribbon-like structure. Intermolecular hydrogen bonds are shown as dotted lines.

3. Conclusion

This paper clearly demonstrates the formation and stabilization of supramolecular nanostaircase structures in crystals using suitable self-assembling synthetic terephthalamides with a common molecular scaffold. Here, the self-assembly of molecular building blocks is guided in such a way that individual molecules can pack at about right angles to each other using various noncovalent interactions including C═O···H–N hydrogen bonding and CH···π interactions to form nanostaircase structures. We have identified here a common structural unit (i.e., bis-terephthalamide based methyl esters of various α-amino acids containing different side chains or stereochemistry), which self-assembles in similar fashion to form a well-defined nanostructure, namely, a nanostaircase. This result may open up a new field of constructing new supramolecular nano-structures (using appropriate molecular building blocks), which has some useful implications in supramolecular chemistry and as well as in crystal engineering.[14]

4. Experimental

4.1. General

Reagent or analytical grade material was obtained from commercial suppliers and used without further purification. Terephthalamides **1**, **2**, **3**, and **4** were synthesized by the conventional solution phase methodology.[15] A solution of terephthalic acid (0.83 g, 5 mmol) in 10 mL of DMF was cooled in an ice-water bath. The H–Xxx–OMe (Xxx=Leu, D-Leu, Ile, and Aib) was isolated from the corresponding methyl ester hydrochloride (20 mmol) by neutralization, subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 10 mL. This was then added to the reaction mixture, followed immediately by DCC (2.06 g, 10 mmol) and HOBt (1.35 g, 10 mmol). The reaction mixture was stirred for three days. The residue was taken in ethyl acetate (60 mL) and the DCU was filtered off. The organic layer was washed with 2 M HCl (3×50 mL), brine (2×50 mL), 1 M sodium carbonate (3×50 mL), and brine (2×50 mL), then dried over anhydrous sodium sulfate and evaporated in vacuo to yield terephthalamides **1**–**4** as white solid. Purification was done by silica gel column (100–200 mesh) using ethyl acetate as eluent. The final compounds were fully characterized by IR spectroscopy, 300 MHz ^{1}H NMR spectroscopy, and mass spectrometry. Optical rotations were measured on a Perkin–Elmer 341LC polarimeter. IR spectra were recorded on a Shimadzu (Japan) model FTIR spectrophotometer with KBr pellets. ^{1}H NMR spectra were recorded with a Brüker DPX 300 MHz spectrometer. Mass spectra were recorded on a Hewlett Packard Series 1100MSD spectrometer.

4.1.1. Terephthalamide 1. Yield=1.68 g (4 mmol, 80%); R_f=0.72 (EtOAc); $[\alpha]_D^{20}$ +42.3 (c=0.7 in chloroform); mp 144–146 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 7.85 (s, 4H; Aromatic ring Hs), 6.65 (d, J=8.1 Hz, 2H; Leu NH), 4.9–4.83 (m, 2H; Leu C$^{\alpha}$H), 3.78 (s, 6H; –OCH_3), 1.79–1.65 (m, 6H; Leu C$^{\beta}$H & C$^{\gamma}$H), 1.01–0.97 ppm (m, 12H; Leu C$^{\delta}$H); IR (KBr): $\bar{\nu}$=3325, 1747, 1635, 1550 cm^{-1}; MS (ESI): m/z (%): 421.3 (48) $[M+H]^+$, 841.5 (100) $[2M+H]^+$; elemental analysis calcd (%) for $C_{22}H_{32}N_2O_6$ (420): C 62.85, H 7.6, N 6.66; found: C 63.1, H 7.8, N 7.03.

4.1.2. Terephthalamide 2. Yield=1.50 g (3.5 mmol, 71%); R_f=0.75 (EtOAc); $[\alpha]_D^{20}$ −42.9 (c=0.7 in chloroform); mp 138–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 7.85 (s, 4H, Aromatic ring Hs), 6.69 (d, J=8.4 Hz, 2H; D-Leu NH), 4.87–4.83 (m, 2H; D-Leu C$^{\alpha}$H), 3.79 (s, 6H; –OCH_3), 1.78–1.65 (m, 6H; D-Leu C$^{\beta}$H & C$^{\gamma}$H), 1.01–0.93 ppm (m, 12H; D-Leu C$^{\delta}$H); IR (KBr): $\bar{\nu}$=3325, 1746, 1636, 1548, 1500 cm^{-1}; MS (ESI): m/z (%): 421.3 (33) $[M+H]^+$; 863.3 (100) $[2M+Na]^+$; elemental analysis calcd (%) for $C_{22}H_{32}N_2O_6$ (420): C 62.85, H 7.6, N 6.66; found: C 62.51, H 7.92, N 7.15.

4.1.3. Terephthalamide 3. Yield=1.6 g (3.8 mmol, 76%); R_f=0.6 (EtOAc); $[\alpha]_D^{20}$ +46.4 (c=0.7 in chloroform); mp 82–84 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 7.87 (s, 4H, Aromatic ring H), 6.70 (d, J=8.4 Hz, 2H; Ile NH), 4.84–4.8 (m, 2H; Ile C$^{\alpha}$H), 3.79 (s, 6H; –OCH_3), 2.17–2.0 (m, 2H; Ile C$^{\beta}$H), 1.16–1.5 (m, 10H; Ile C$^{\gamma}$H),

0.99–0.97 ppm (m, 6H; Ile $C^{\delta}H$); IR (KBr): $\bar{\nu}$=3411, 3345, 1744, 1636, 1548, 1503 cm^{-1}; MS (ESI): *m/z* (%): 421.3 (55) $[M+H]^+$; 841.5 (100) $[2M+H]^+$; elemental analysis calcd (%) for $C_{22}H_{32}N_2O_6$ (420): C 62.85, H 7.6, N 6.66; found: C 63.21, H 7.52, N 6.95.

4.1.4. Terephthalamide 4. Yield=1.3 g (3.5 mmol, 72%); R_f=0.7 (EtOAc); $[\alpha]_D^{20}$ 0.01 (*c*=0.7 in chloroform); mp 220–222 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.84 (s, 4H; Aromatic ring H), 6.84 (s, 2H; Aib NH), 3.80 (s, 6H; $-OCH_3$), 1.7 ppm (s, 12H; Aib $C^{\beta}H$); IR (KBr): $\bar{\nu}$=3322, 3226, 1741, 1631, 1560 cm^{-1}; MS (ESI): *m/z* (%): 388.0 (100) $[M+Na+H]^+$; 366.0 (52) $[M+2H]^+$; elemental analysis calcd (%) for $C_{18}H_{24}N_2O_6$ (364): C 59.34, H 6.59, N 7.69; found: C 60.01, H 6.98, N 7.75.

4.2. X-ray crystallography

All crystal data were measured on a Bruker AXS Smart Apex CCD diffractometer with Mo K_α (λ=0.71073 Å) radiation at 20 °C. The structure was obtained by direct methods using SHELXS-97.[16] Refinement was carried out with a full matrix least squares method against F^2 using SHELXL97.[17] CCDC-229937 (**1**), CCDC-600050 (**2**), CCDC-229938 (**3**), and CCDC-229939 (**4**) contain the supplementary crystallographic data for the paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).

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References and notes

1. (a) Seeman, N. C.; Belcher, A. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 6451–6455; (b) Zhang, S. *Nat. Biotechnol.* **2003**, *21*, 1171–1178; (c) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312–1319.
2. (a) Gao, X.; Matsui, H. *Adv. Mater.* **2005**, *17*, 2037–2050; (b) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 988–1011.
3. (a) Reches, M.; Gazit, E. *Nano Lett.* **2004**, *4*, 581–585; (b) Ghadiri, M. R.; Granja, J. R.; Buehler, L. K. *Nature* **1994**, *369*, 301–304.
4. Haldar, D.; Banerjee, A.; Drew, M. G. B.; Das, A. K.; Banerjee, A. *Chem. Commun.* **2003**, 1406–1407.
5. Reches, M.; Gazit, E. *Science* **2003**, *300*, 625–627.
6. Yemini, M.; Reches, M.; Rishpon, J.; Gazit, E. *Nano Lett.* **2005**, *5*, 183–186.
7. (a) Yokoi, H.; Kinoshita, T.; Zhang, S. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8414–8419; (b) Guler, M. O.; Soukasene, S.; Hulvat, J. F.; Stupp, S. I. *Nano Lett.* **2005**, *5*, 249–252; (c) Sone, E. D.; Stupp, S. I. *J. Am. Chem. Soc.* **2004**, *126*, 12756–12757.
8. (a) Ghosh, S. K.; Bharadwaj, P. K. *Eur. J. Inorg. Chem.* **2005**, 4886–4889; (b) Gabbai, F. P.; Schier, A.; Riede, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 622–624; (c) Fortin, D.; Drouin, M.; Harvey, P. D. *J. Am. Chem. Soc.* **1998**, *120*, 5351–5352; (d) Nagata, N.; Kugimiya, S.; Fujiwara, E.; Kobuke, Y. *New J. Chem.* **2003**, *27*, 743–747; (e) Ren, C.-X.; Zhu, H.-L.; Yang, G.; Chen, X.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 85–90; (f) Alexakis, A.; Tomassini, A.; Chouillet, C.; Roland, S.; Mangeney, P.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4093–4095.
9. (a) Cobbledick, R. E.; Small, R. W. H. *Acta Crystallogr., Sect. B* **1972**, *28*, 2893–2896; (b) Gardner, K. H.; English, A. D.; Forsyth, V. T. *Macromolecules* **2004**, *37*, 9654–9656.
10. Armelin, E.; Escudero, E.; Campos, L.; Puiggali, J. *Acta Crystallogr., Sect. C* **2001**, *57*, 172–173.
11. Yin, H.; Lee, G.; Sedey, K. A.; Rodriguez, J. M.; Wang, H.-G.; Sebti, S. M.; Hamilton, A. D. *J. Am. Chem. Soc.* **2005**, *127*, 5463–5468.
12. Ray, S.; Haldar, D.; Drew, M. G. B.; Banerjee, A. *Org. Lett.* **2004**, *6*, 4463–4465.
13. Brandl, M.; Weiss, M. S.; Jabs, A.; Sühnel, J.; Hilgenfeld, R. *J. Mol. Biol.* **2001**, *307*, 357–377.
14. (a) Arora, K. K.; Pedireddi, V. R. *J. Org. Chem.* **2003**, *68*, 9177–9185; (b) Varughese, S.; Pedireddi, V. R. *Chem.—Eur. J.* **2006**, *12*, 1597–1609; (c) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311–2327; (d) Aitipamula, S.; Thallapally, P. K.; Thaimattam, R.; Jaskolski, M.; Desiraju, G. R. *Org. Lett.* **2002**, *4*, 921–924.
15. Bodanszky, M.; Bodanszky, A. *The Practice of Peptide Synthesis*; Springer: New York, NY, 1984; pp 1–282.
16. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
17. Sheldrick, G. M. *SHELXL97 Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.