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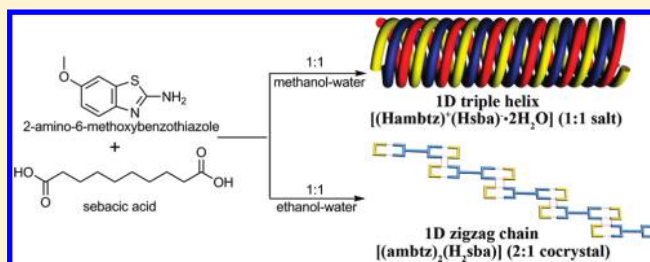
Solvent-Controlled Rare Case of a Triple Helical Molecular Braid Assembled from Proton-Transferred Sebacic Acid

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S Supporting Information

ABSTRACT: A novel triple helix based on proton-transferred sebacic acid was observed in a 1:1 organic salt of [(Hambtz)⁺(Hsba)[−]·2H₂O] (**1**, ambtz = 2-amino-6-methoxybenzothiazole, H₂sba = sebacic acid) incorporating a zigzag water chain. Changing the solvent system, another simple 1D zigzag chain, cocrystal [(ambtz)₂(H₂sba)] (**2**), was obtained. The structural dissimilarity between them was dependent on different conformations of ambtz and H₂sba modulated by solvent systems. The photoluminescence behaviors of **1** and **2** were also discussed.



Helices are ubiquitous and have been recognized as an extremely valuable shape not only in nature but also in biological macromolecules such as the single α -helix in protein, double helix in DNA, and triple helix in polynucleotide molecules.¹ Inspired by such sophisticated biological helices, crystal engineers have exerted great effort into the design and synthesis of artificial multiple-stranded helical structures due to their aesthetically pleasing structures as well as their significance in biomimics or functional chiral materials.² As we know, the ever-increasing number of helical structures, including single-, double-, and multiple-stranded helices, are usually constituted of multidentate ligand strands that intertwine around and ligate to a metal center,³ but their counterparts assembled through solely noncovalent interactions (e.g., hydrogen bond and $\pi \cdots \pi$ stacking) are much less common.⁴ The metal-free helices are more suitable models than the metal-containing ones to mimic these biomacromolecules both structurally and functionally, due to the fact that helical chains in biomacromolecules are mainly constructed through the cooperative interaction of several noncovalent interactions instead of strong metal coordination. To the best of our knowledge, in spite of a number of organic polymers and oligomers assembled into single helices or double-stranded helices in the absence of metal ions have been documented to date,⁵ only limited preparative methodologies are available for building multiple-stranded helical structures without the assistance of coordinating metal ions,⁶ which is perhaps due to the relatively weak directing effect of the hydrogen bond and the intricacy of the self-assembly process for these systems.

On the other hand, cocrystals are the subject of intense research in crystal engineering.⁷ It has long been known that when combinations of certain organic species are mixed together for crystallization, the crystals that are formed contain both the species in a structure that is quite different from those of the

parent species.⁸ As one of the excellent supramolecular synthons, aminobenzothiazole and its derivatives incorporating multiple hydrogen-bonding sites and metal ion binding donors have been extensively utilized in the new materials, biochemistry and agriculture chemistry, due to the high biological activity, lower toxicity, as well as excellent chemical reactivity.⁹ The long aliphatic dicarboxylic acid with adaptable deprotonated forms and conformations has also exhibited novel functions such as dianion templating^{10a} and heterosynthons with nitrogen-containing compounds in the realms of metal–organic coordination network and molecular cocrystal.¹⁰

Bearing in mind all of the points mentioned above, recently, in the course of the cocrystallization of 2-amino-6-methoxybenzothiazole and a flexible aliphatic dicarboxylic acid for searching novel intertwined structures, we astonishingly disclosed a triple helix, [(Hambtz)⁺(Hsba)[−]·2H₂O] (**1**), assembled from proton-transferred sebacic acid. For comparison, another 1D zigzag hydrogen-bonded chain, [(ambtz)₂(H₂sba)] (**2**), was obtained in the same process just by changing solvent systems (Scheme 1).

Complexes **1** and **2** were obtained using a “one-pot” method by ultrasonic treatment of equimolar amounts of ambtz and H₂sba in methanol–water for **1** and ethanol–water for **2**. Phase purities of **1** and **2** are sustained by the powder X-ray diffraction patterns (Figure S1, see Supporting Information). The solid FT-IR spectra (Figure S2) of **1** and **2** show characteristic absorption bands for amino and carboxyl groups.¹¹ Both complexes are air stable, and their thermal stability was explored by thermogravimetric analysis (TGA, Figure S3). The TGA curve of **1** shows the first weight loss of 7.88% in the temperature range 30–105 °C,

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Scheme 1. Preparation Route of the 1D Triple Helix and Zigzag Chain

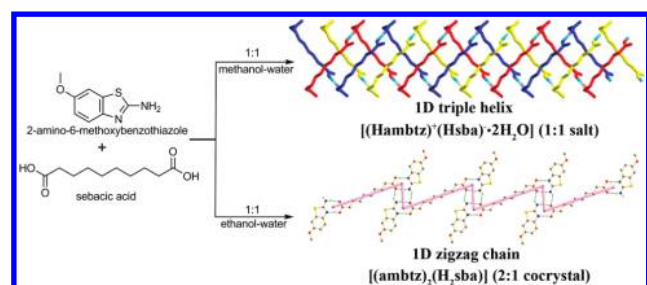


Table 1. Crystallographic Data for 1 and 2

complex	1	2
empirical formula	C ₁₈ H ₃₀ N ₂ O ₇ S	C ₂₆ H ₃₄ N ₄ O ₆ S ₂
formula weight	418.50	562.69
crystal system	orthorhombic	triclinic
space group	<i>Fdd2</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	19.323(5)	7.283(3)
<i>b</i> (Å)	84.57(2)	10.528(4)
<i>c</i> (Å)	5.0562(13)	10.592(4)
α (deg)	90	108.699(6)
β (deg)	90	103.443(6)
γ (deg)	90	107.806(5)
<i>V</i> (Å ³)	8263(4)	681.5(4)
<i>T</i> (K)	173(2)	173(2)
<i>Z</i> , <i>D</i> _{calcd} (mg/m ³)	16, 1.346	1, 1.371
<i>F</i> (000)	3584	298
μ (mm ⁻¹)	0.198	0.243
ref collected/unique	9634/3593	4896/2375
<i>R</i> _{int}	0.0476	0.0215
parameters	255	172
^a <i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0519	0.0453
^b <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1261	0.1249
GOF	1.043	1.034
max./min., Δρ (e·Å ⁻³)	0.466/−0.224	0.403/−0.216

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

corresponding to the exclusion of two lattice water molecules (calcd: 8.61%), and the residual component collapses upon further heating to 175 °C. Complex 2 is solvent free and thermally stable to 168 °C. These results are in good agreement with solid state crystal structures.

The molecular structure of 1 was determined by single-crystal X-ray diffraction analysis (Table 1). Complex 1 crystallizes in the orthorhombic noncentrosymmetric space group *Fdd2* with an asymmetric unit that contains one cation Hambtz^+ , one mono-anion Hsba^- , and two lattice water molecules (Figure 1a). The nature of complex 1 is an organic salt, as a consequence of proton transfer between one of the carboxyl groups in H_2sba and the nitrogen atom on the thiazole ring of ambtz leading to a charge assisted $\text{N}-\text{H}^+\cdots\text{O}^-$ hydrogen bond ($\text{N2}\cdots\text{O3} = 2.657(3)$ Å). Of course, this interaction will also maximize the Coulombic energy in this structure due to the interactive anion and cation. Another hydrogen bond ($\text{N1}\cdots\text{O2} = 2.803(4)$ Å) combines with the charge assisted $\text{N}-\text{H}^+\cdots\text{O}^-$ hydrogen bond to form a

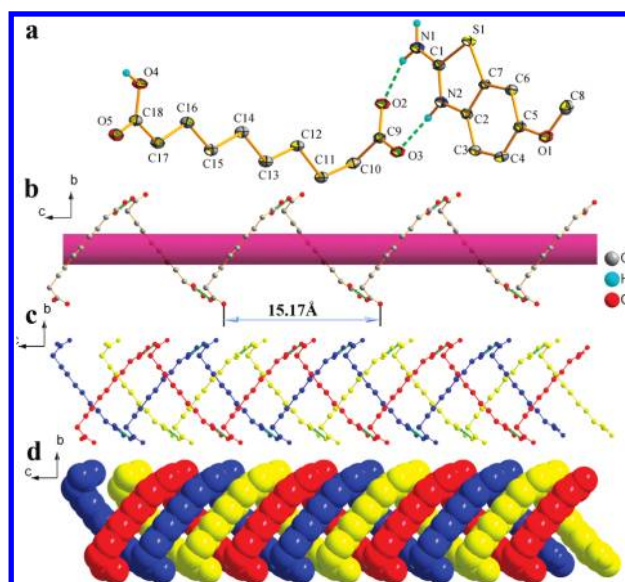


Figure 1. (a) ORTEP representation of the asymmetric part of the unit cell in the 1:1 cocrystal of Hambtz^+ and Hsba^- with 30% thermal ellipsoids; all water molecules are omitted for clarity. (b) Ball and stick view of the single 1D helical chain constructed by $\text{O}\cdots\text{O}$ hydrogen bonds highlighted by green dashed lines. (c and d) Ball and stick (c) and space-filling (d) views of the triple helical 1D braid; each strand of the triple helix is color coded in red, blue, and yellow.

heteromeric $R_2^2(8)$ motif, according to graph-set analysis nomenclature.¹² Notably, the $\text{C18}-\text{O4}$ bond length (1.305(4) Å) is nearly 0.1 Å longer than the $\text{C18}-\text{O5}$ bond length (1.208(4) Å), while another carboxyl group shows nearly identical $\text{C}-\text{O}$ bond lengths ($\text{C9}-\text{O2} = 1.245(4)$ and $\text{C9}-\text{O3} = 1.254(4)$ Å), which enables us to unambiguously determine the deprotonated carboxyl group.

In complex 1, the conformations of ambtz and H_2sba should be noted. The potentially different conformers of ambtz are caused by the freedom of rotation about the $\text{C}-\text{O}$ σ -bond. According to the relative positions of the methyl group and the S atom on the thiazole ring, we assigned the Hambtz in 1 to the *cis* conformation because the methyl group and the S atom located on the same side with respect to the $\text{C5}-\text{O1}$ bond. The methyl group is approximately coplanar with the phenyl ring, deviating it from ca. 0.12 Å. On the other hand, the H_2sba possesses a ten carbon aliphatic backbone and there exist seven different torsion angles. In 1, Hsba^- shows one small torsion angle of $59.3(4)^\circ$ and six large ones ranging from $171.0(3)$ to $-179.9(3)^\circ$, indicating a *gauche-anti-anti-anti-anti-anti-anti-anti* conformation according to the stereochemistry terminology.¹³ As demonstrated by a CSD (Cambridge Structure Database) survey with the help of ConQuest version 1.3,¹⁴ there are 32 structures containing the uncoordinated H_2sba , of which 23 (71.9%) exhibit the *anti-anti-anti-anti-anti-anti-anti-anti* conformation, 5 (15.6%) the *gauche-anti-anti-anti-anti-anti-anti-anti-anti*, 2 (0.06%) the *gauche-anti-anti-anti-anti-anti-anti-anti-anti*, 1 (0.03%) the *anti-gauche-anti-anti-anti-anti-anti-anti-anti*, and 1 (0.03%) the *anti-gauche-anti-anti-anti-anti-anti-anti-anti* conformation, while the *gauche-anti-anti-anti-anti-anti-anti-anti* conformation in 1 may not be the lowest energy one for H_2sba and has not been encountered until now.

The monodeprotonated H_2sba in 1 acts as hydrogen bond donor as well as acceptor. The dihedral angle formed between the plane of one deprotonated carboxyl group ($\text{O2}-\text{C9}-\text{O3}$) of

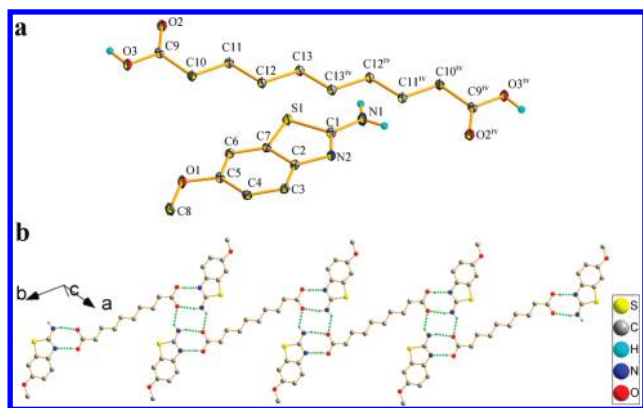






Figure 2. (a) ORTEP representation of the molecule of **2** with 30% thermal ellipsoids. (Symmetry code: (iv) $-x + 1, -y + 1, -z$.) (b) Ball and stick view of the 1D zigzag chain incorporating $R_2^2(8)$ and $R_4^2(8)$ hydrogen bond motifs.

Hsba⁻ and the plane determined by the rest of Hsba⁻ is nearly 90°. The Hsba⁻ is bound to its neighbor through one strong hydrogen bond of 2.522(3) Å (O4⁻⋯O2^{iv}) involving a *syn* proton on O4 and an *anti* lone pair of electrons on O2, resulting in an approximately orthogonal arrangement of the interactive Hsba⁻ with respect to the aliphatic carbon backbone, which is responsible for the formation of the single-stranded helix along the 2₁ screw axis (Figure 1b). The helical pitch, defined by the distance between equivalent atoms generated by one full rotation of the 2₁ screw axis, is 15.17 Å, which is thrice the crystallographic *b*-axis length. To fill the large unoccupied void in the single helix, every three concentric chains with the same handedness entwined with the other to generate a triple helix. A close inspection of the packing of the triple helix shows that there are no obvious hydrogen-bonding and π -stacking interactions between the three strands. Therefore, the three strands in this triple helix are connected by virtue of attractive intermolecular forces, van der Waals interactions (Figure 1c).

Remarkably, a 1D zigzag water chain (Figure S4) comprised of crystallographically independent O1W and O2W exists between the adjacent 1D triple helices. As we know, the hydrogen bonded water chains are closely relevant to many biological processes and also exist in a confined environment of metal–organic coordination networks or hydrogen bonded supramolecular networks.¹⁵ Within this water chain, the O1W acts as double hydrogen bond donors and single hydrogen bond acceptor, while O2W acts as double hydrogen bond donor and acceptor. The $\text{O1W} \cdots \text{O2W}$ and $\text{O1W} \cdots \text{O2W}^i$ separations are 2.883(4) and 2.799(4) Å, respectively, which are longer than the 2.758 Å generated from the ab initio calculations¹⁶ and comparable to the distances found in a similar 1D water chain residing in the void of 3D $[\text{Ag}_2(4,4'\text{-bipyridine})_2(\text{oxalate}) \cdot 7\text{H}_2\text{O}]_n$.¹⁷ The $\text{O2W} \cdots \text{O1W} \cdots \text{O2W}^i$ bond angle is $125.67(12)^\circ$, which is different from the tetrahedral angle found in ice I_h and I_c .¹⁸ The 1D water chains link adjacent 1D triple helices to form a 2D sheet (Figure S5) through $\text{O2W} \cdots \text{O3}^{\text{ii}}$ (2.692(3) Å) and $\text{O2W} \cdots \text{O5}^{\text{iii}}$ (2.737(3) Å) hydrogen bonds. (Symmetry codes: (i) $x, y, z + 1$; (ii) $x + \frac{1}{2}, y, z - \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + 1, z - \frac{3}{2}$.)

When the solvent system was changed from methanol–water to the comparatively less polar ethanol–water in the same synthesis procedure, we obtained complex **2** as a 1D zigzag

Table 2. Comparison Conformations of ambtz and H₂sba in 1 and 2^a

ambtz	1	2
	 <i>cis-</i>	 <i>trans-</i>
H ₂ Sba	 <i>gauche-anti-anti-anti-anti-anti-anti-anti</i>	 <i>anti-anti-anti-anti-anti-anti-anti</i>

^a yellow: S; red: O; blue: N; grey: C; cyan: H

^a yellow, S; red, O; blue, N; gray, C; cyan, H.

hydrogen-bonded chain with 2:1 stoichiometry of ambtz and H₂sba, excluding any solvent molecule. No proton transfer between ambtz and H₂sba was observed in **2**. Single-crystal X-ray diffraction analysis reveals that complex **2** crystallizes in the triclinic $P\bar{1}$ space group, and one ambtz and half a H₂sba exist in the asymmetric unit of **2** (Figure 2a). The H₂sba lies on the inversion center, and its carboxyl group and carbon backbone are roughly coplanar. The dihedral angle of two planes defined by ambtz and H₂sba is 10.8°. The ambtz is hydrogen bonded to H₂sba, yielding a heteromeric R₂²(8) motif (N1...O2ⁱ = 2.862(2) and N1...O2ⁱⁱ = 2.842(2) Å). The adjacent hydrogen bonded [ambtz·H₂sba] units are further linked by centrosymmetric R₄²(8) motifs (O3...N2ⁱⁱⁱ = 2.658(2) Å) to form the resulting 1D zigzag chain (Figure 2b). The R₂²(8) and R₄²(8) motifs have also been observed in aminopyrimidinium/carboxylate salts,¹⁹ carboxylic acid/amide cocrystals,²⁰ and similar 2-amino-6-methylbenzothiazole/dicarboxylic acid cocrystals.²¹ (Symmetry codes: (i) $x, y - 1, z$; (ii) $-x, -y + 1, -z$; (iii) $x, y + 1, z$.)

The conformations of ambtz and H₂sba in **2** are evidently different from those in **1** (Table 2). The methyl group and the S atom locate at the opposite sides with respect to the C5–O1 bond, indicating a *trans* conformation. Significantly, the centrosymmetric H₂sba shows four large torsion angles falling in the range 170.37(17)–180.0°, suggesting an usual *anti-anti-anti-anti-anti-anti* conformation. The different conformations play an important role in avoiding the helical structure in **2**.

As described above, the crystalline products **1** and **2** depend on the synthetic surroundings, and interestingly, the solvent systems serve as a structure-directing factor during cocrystallization to result in different hydrogen-bonded motifs. As we know, solvent molecules with different sizes, polarities, and coordination abilities present in the coordination spheres of the metal ions usually exert their impact on the formation of metal–organic coordination networks;²² however, it is still sparse that the solvent system modulates the hydrogen bonded structures through changing the conformations of building modules. Customarily, solvent-dependent self-assembly could be classified as two categories depending on a variety of factors, such as the composition of the reactants: (i) solvents control structures, without being encapsulated by the host networks; (ii) intercalation of solvent guests in the host adjusts the supramolecular arrays.²³ Complexes **1** and **2** are synthesized with the same reactants and the same reaction conditions but using

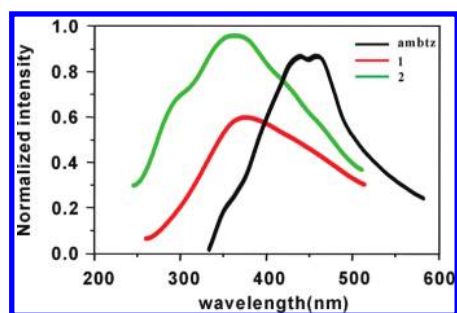


Figure 3. Photoluminescence of ambtz and complexes **1** and **2** in the solid state.

methanol–water and ethanol–water as solvent systems, respectively. The methanol or ethanol molecule, though in the absence of the products, insensibly regulates the formation of different conformations of ambtz and H₂sba for **1** and **2**. We also should note that the different stoichiometries were observed in the structures of **1** (Hambtz⁺/Hsba[−] 1:1 salt) and **2** (ambtz/H₂sba 2:1 cocrystal), which could be attributed to the fact that the dicarboxylic acid with a long aliphatic chain could be more soluble in a comparatively less polar ethanol–water solvent system; consequently, the lower ratio of the H₂sba in the crystal structure of **2** was found.

The solid-state photoluminescent emission spectra of **1**, **2**, H₂sba, and ambtz were studied at room temperature. The emission of H₂sba is very weak and can be negligible. This is due to the presence of low-lying excited states of $n \rightarrow \pi^*$ character that predominantly decay via nonradiative pathways such as efficient intersystem crossing and/or internal conversion.²⁴ Under the excitation of 280 nm, the maximum emissive peaks for **1** and **2** were around 371 and 368 nm, respectively (Figure 3). Compared to the emission of ambtz ($\lambda_{\text{em}} = 440$ nm, $\lambda_{\text{ex}} = 280$ nm), the emissions of organic salt **1** and cocrystal **2** were blue-shifted, which indicated that the emission of photons from the $\pi^* \rightarrow \pi$ transition occurring in ambtz was affected by the different types of hydrogen bonding environment in the solid-state.²⁵ The different emissive behaviors between **1** and **2** may be related to the proton transfer from H₂sba to ambtz in **1**, which was not the same case in **2**.

In summary, we synthesized and characterized a novel hydrogen bonded triple helical structure based on proton-transferred sebacic acid. Changing solvent systems, we obtained a 1D zigzag hydrogen bonded chain. Structural comparison suggests that both ambtz and H₂sba were induced by different solvent systems to exhibit obviously distinct conformations which are responsible for the different hydrogen bonded motifs in **1** and **2**. The photoluminescence behaviors of **1** and **2** were also discussed.

■ ASSOCIATED CONTENT

Supporting Information. Preparation of complexes **1** and **2**, tables S1–S3, and IR and powder XRD patterns. X-ray crystallographic files in cif format for complexes **1** (CCDC 827639) and **2** (827640). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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