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U-Shaped Aromatic Ureadicarboxylic Acids as Versatile Building Blocks: Construction of Ladder and Zigzag Networks and Channels

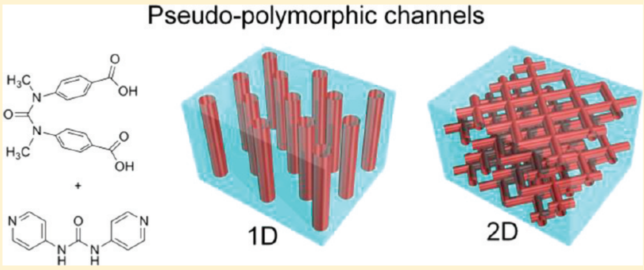
Shugo Hisamatsu,[†] Hyuma Masu,[‡] Isao Azumaya,[§] Masahiro Takahashi,[†] Keiki Kishikawa,[†] and Shigeo Kohmoto*,[†]

[†]Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

[‡]Chemical Analysis Center, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

[§]Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan

S *Supporting Information*



ABSTRACT: In order to examine versatility of ureadicarboxylic acids as U-shaped building blocks for crystal engineering, their crystal structures and cocrystals with pyridine derivatives were investigated. H-bonding networks created by a sequential linking of H-bonded carboxylic acid dimers resulted in the formation of ladder-type networks in the crystals of *N*,*N*′-diethyl-*N*,*N*′-diphenylureadicarboxylic acid (**2**) and *N*,*N*′-diallyl-*N*,*N*′-diphenylureadicarboxylic acid (**3**). A zigzag type H-bonding network with wedging of water molecules into carboxy—carboxy H-bonding was observed for *N*,*N*′-dibenzyl-*N*,*N*′-diphenylureadicarboxylic acid (**4**). Cocrystals of *N*,*N*′-dimethyl-*N*,*N*′-diphenylureadicarboxylic acid (**1**) with 2,5-di(pyridine-4-yl)thiazolo[5,4-*d*]thiazole (**5**) and **2** with 4,4′-dipyridyl (**6**) afforded zigzag-type assembled structures. Two types of channel structures were created in the cocrystals of **1** and dipyridylurea (**7**) by inclusion of water molecules together with either methanol or ethanol. The former afforded a straight-type one-dimensional channel, while the latter afforded a fishnet-type two-dimensional channel.

INTRODUCTION

Development of simple and unique building blocks and an appropriate choice of intermolecular interactions are essential for the progress of crystal engineering.[1] They can be utilized as key elements to design crystal lattice structure. Metal coordination has a strong power to regulate crystal lattices because of their rigidity and the controllable direction of coordination. Therefore, intensive studies on metal—organic frameworks (MOFs) have been carried out to design tailor-made functional materials, such as nanoporous materials.[2] Organic crystals without metal coordination lack these advantages. However, diversity of weak intermolecular interactions operating in there is attractive, which generates a variety of crystal structures including polymorphs.[3] We are interested in building blocks to create aromatic architectures with folding,[4] especially a column of zigzag-type aromatic networks[5] in a supramolecular way. Piling of aromatics can create potential electrically conductive molecular wires.[6] Among the known aromatic folded building blocks, ureas,[7] guanidines,[8] and imides,[9] we employed ureas. For this purpose we developed *N*,*N*′-dimethyl-*N*,*N*′-diphenylureadicarboxylic acid **1** and applied it to the fabrication of triple helices by inclusion of dipyridyl aromatic compounds.[10] In this paper, we report on further studies on the versatility of aromatic ureadicarboxylic acids as U-shaped building blocks for the creation of diversified aromatic architectures.

It is known that conformation of arylureas has a characteristic feature. Depending on the substituents at the nitrogen atom, they adopt two distinctive conformations, either a linear *trans*,*trans*- or a folding *cis*,*cis*-conformation. Substitution of the hydrogen atom to other groups at the urea nitrogen atom causes a drastic change in the conformation of aromatic urea compounds from the linear to the folding one (Chart 1a).[11] As the intermolecular interaction for supramolecular assembling, we chose carboxy—carboxy H-bonding.[12] It can roughly be classified into two types, dimeric and catemeric.[13] It is interesting that the same building block can take dual types of H-bonding patterns, which results in the creation of differing H-bonding networks and polymorphs. Our preliminary results showed that ureadicarboxylic acid **1** afforded double catemeric H-bonding networks in its crystal structure[10] (Chart 1b). Two sets of H-bonding networks were created independently among the carboxys of the upper and among those of the bottom of the U-shaped **1**. There will be two patterns of networks in dimeric H-bonding depending on the orientation of ureadicarboxylic acids. The first type is the dimeric H-bonding created among the upper carboxys and the bottom carboxys of the neighboring ureadicarboxylic acids depicted as dimeric type A in Chart 1c. The second type, dimeric type B, involves H-bonding among upper carboxys or bottom carboxys (Chart 1d). In the dimeric type A, utilization of one of the carboxys for

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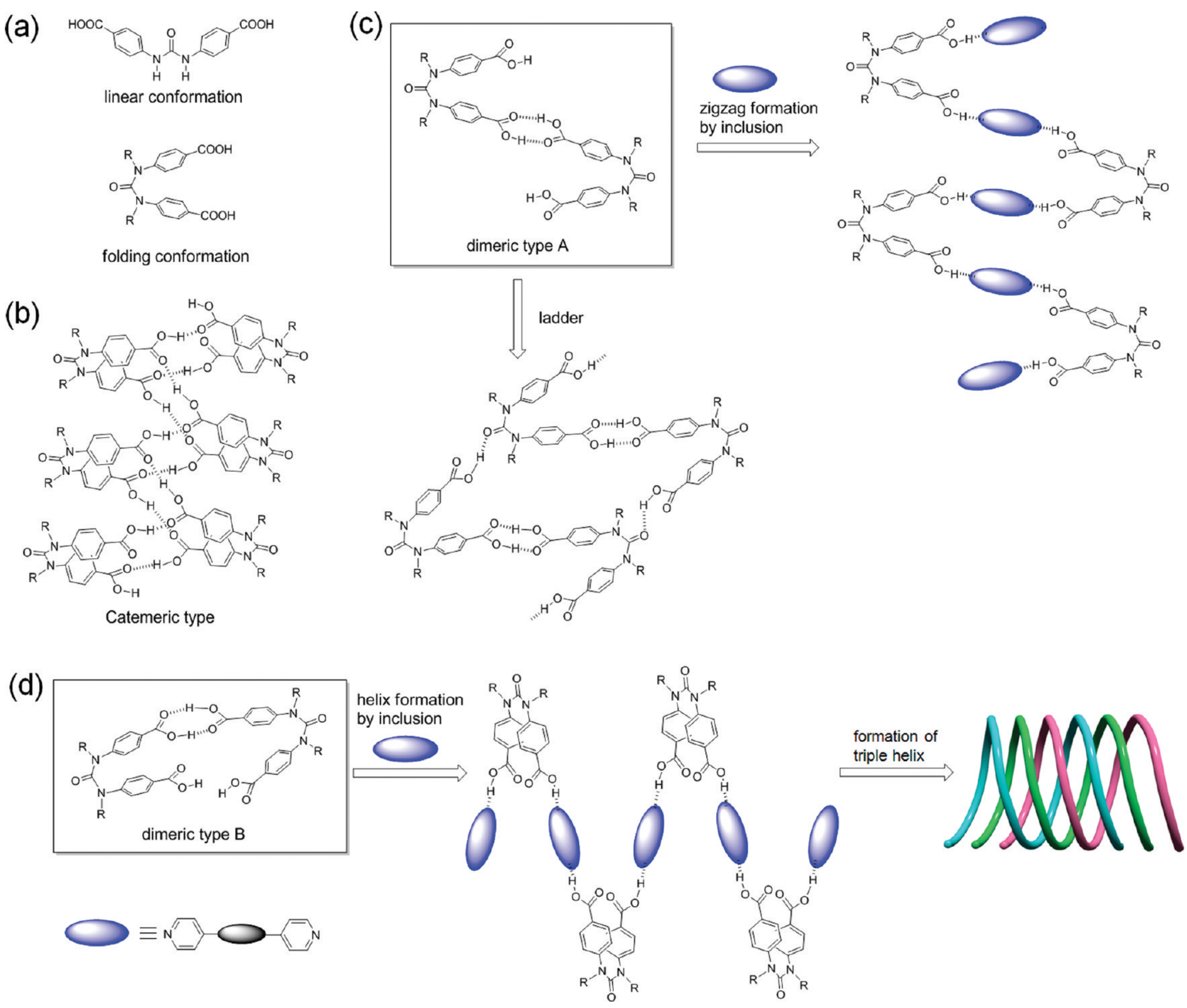
Chart 1. Conformations of Aromatic Ureadicarboxylic-Acids (a) and Their H-Bonding Networks, Catemeric (b) and Two Types of Dimeric, Type A (c) and Type B (d)



H-bonding with the carbonyl of the ureylene moiety affords a ladder-type H-bonding network. Inclusion of linear spacer molecules by pinching with two carboxys results in the formation of an extended zigzag H-bonding network. We have chosen bipyridyl derivatives as spacer molecules since carboxy-pyridine H-bonding is a well-known and reliable intermolecular interaction in crystal engineering.[14] Inclusion of a fluorescent spacer is especially interesting from the viewpoint of the construction of a fluorescent column with tuning of fluorescent color.[15] In the dimeric-type B, inclusion of such spacer molecules by pinching gives a helical H-bonding network which leads the formation of triple helices as we have reported preliminarily.

EXPERIMENTAL SECTION

Materials and Methods. All the reagents and solvents employed were commercially available and used as received without further purification. ^{1}H and ^{13}C NMR spectra were recorded for samples in $CDCl_3$ with Me_4Si as an internal standard.

Synthesis. Ureadicarboxylic acid **1**[10] and dipyridylurea **7**[16] were prepared according to the literature.

4,4′-(Carbonylbis(ethylazanediyl))dibenzoic Acid (2). The compound was prepared by saponification of 4,4′-(carbonylbis-(ethylazanediyl))dibenzoate (^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 8.7 Hz, 4H), 6.84 (d, J = 8.6 Hz, 4H), 4.32 (q, J = 7.1 Hz, 4H), 3.72 (q, J = 7.1 Hz, 4H), 1.36 (t, J = 7.1 Hz, 6H), 1.17 (t, J = 6.8 Hz, 6H)) which was synthesized by ethylation of 4,4′-(carbonylbis-(azanediyl))dibenzoate in 80% yield. To a solution of diethyl 4,4′-(carbonylbis(ethylazanediyl))-dibenzoate (133 mg, 0.32 mmol) in EtOH (10 mL) was added a solution of KOH (108 mg, 1.9 mmol) in water (1 mL). The resulting mixture was refluxed for 8 h. After the reaction, the solvent was evaporated and to the residue was added water and aqueous 1 M HCl solution. The precipitate formed was filtered off and dried to give **2** (65 mg, 57%). Mp 276–280 °C; IR (KBr) 2971 (w), 2935 (w), 1715 (s), 1692 (s), 1589 (s), 1244 (s) cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.75 (d, J = 8.7 Hz, 4H), 7.04 (d, J = 8.6 Hz, 4H), 3.78 (q, J = 7.1 Hz, 4H),1.17 (t, J = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.3, 158.8, 147.7, 130.4, 126.7, 125.3, 45.7, 13.8; HRMS (ESI), calcd for $C_{19}H_{19}N_2O_5$ [M − H]$^-$ 355.1299, found 355.1303.

4,4′-(Carbonylbis(allylazanediyl))dibenzoic Acid (3). In a similar manner as for the synthesis of **2**, saponification of the corresponding diethyl ester gave **3** in a yield of 84%. Mp 272−274 °C; IR (KBr) 3078 (w), 2983 (w), 1711 (s), 1684 (s), 1591 (s) cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.75 (d, J = 8.4 Hz, 4H), 7.08 (d, J = 8.7 Hz, 4H), 5.99 (ddt, J = 17.3 Hz, J = 9.9 Hz, J = 6.3 Hz, 2H), 5.14 (dd, J = 1.5 Hz, J = 17.1 Hz, 2H), 5.09 (dd, J = 1.5 Hz, J = 10.2 Hz), 4.35 (d, J = 6.0 Hz, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.6, 159.1, 149.3, 147.6, 134.5, 130.3, 126.8, 125.3, 118.5, 53.2; HRMS (ESI), calcd for $C_{21}H_{19}N_2O_5$ [M − H]$^-$ 379.1299, found 379.1300.

4,4′-(Carbonylbis(benzylazanediyl))dibenzoic Acid (4). In a similar manner as for the synthesis of **2**, saponification of the corresponding ditethyl ester gave **4** in a yield of 90%. Mp 225−229 °C; IR (KBr) 3248 (br. w), 3032(w), 2944 (m), 2905(m), 1689 (s), 1603 (s), 1425(m), 1280 (m) cm^{-1}; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.63 (d, J = 8.7 Hz, 4H), 7.39−7.35 (m, 4H), 7.28−7.19 (m, 4H), 7.00 (d, J = 8.7 Hz, 4H), 4.99 (s, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.5, 160.4, 147.5, 138.5, 130.5, 129.1, 128.0, 127.0, 125.6, 53.9; HRMS(ESI), calcd for $C_{29}H_{25}N_2O_5$ [M + H]$^+$ 481.1769, found 481.1748.

2,5-Di(pyridine-4-yl)thiazolo[5,4-*d*]thiazole (5)[17]. A solution of rubeanic acid (100 mg, 0.83 mmol) and 4-pyridinecarboxaldehyde (0.20 mL, 2.2 mmol) in anhydrous DMF (5 mL) was refluxed for 2.5 h at 153 °C. Upon cooling, the product was recrystallized out from the resulting solution. Filtration and washing with water afforded **5** as yellow needles (174 mg, 71%). Mp over 300 °C; IR (KBr) 3426 (s), 3038 (w), 2923 (w), 2853 (w), 1591 (s), 1442 (s), 1234 (s), 815 (s), 696 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, J = 6.0 Hz, 2H), 7.88 (d, J = 6.4 Hz, 4H); HRMS (ESI), calcd for $C_{14}H_9N_4S_2$ [M + H]$^+$ 297.0263, found 297.0261.

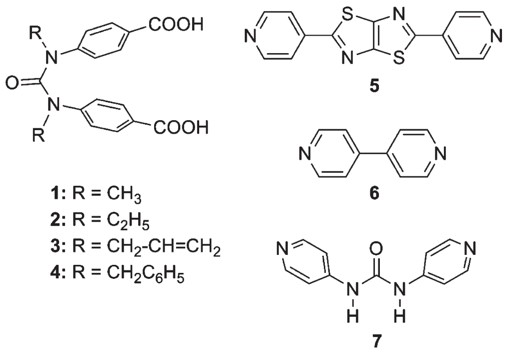
Recrystallization. Recrystallization was carried out at room temperature by a vapor diffusion method. A vessel containing 3−10 mg of sample dissolved in 3−6 mL of solvent was placed in a jar in which solvent to be vaporized was added. After the sample stood for several days, single crystals of compounds **2**, **3**, and **4**, and cocrystals **2·6** and **1·7**·MeOH (containing **1**, **7**, methanol, and water in a ratio, 2:3:4:9.5, respectively) were obtained from methanol with diffusion of water vapor. Single crystals of **1·5** were obtained from chloroform/ethanol with diffusion of hexane vapor. Cocrystals **1·7**·EtOH (containing **1**, **7**, ethanol, and water in a ratio, 2:3:3:5.5, respectively) were recrystallized from ethanol with diffusion of water vapor.

X-ray Crystallography. X-ray diffraction data for the crystals were measured on CCD diffractometers. Data collections were carried out at low temperature by using liquid nitrogen. All structures were solved by direct methods SHELXS-97,[18] and the non-hydrogen atoms were refined anisotropically against F^2, with full-matrix least-squares methods SHELXL-97.[18] All hydrogen atoms except that in water molecules were positioned geometrically and refined as riding. The positions of hydrogen atoms in water molecules were determined based on the electron density distribution. Other details of refinements of the crystal structures are described in Supporting Information.

RESULTS AND DISCUSSION

Ureadicarboxylic acids **2**, **3**, and **4** (Chart 2) were prepared by ethylation, allylation, and benzylation of 4,4′-(carbonylbis(azanediyl))dibenzoic acid ethyl ester, respectively, followed by hydrolysis. All of them gave single crystals suitable for crystallographic analysis. Cocrystals **1·5**, **2·6**, **1·7**·MeOH (containing **1**, **7**, methanol, and water in a ratio, 2:3:4:9.5, respectively), and **1·7**·EtOH (containing **1**, **7**, ethanol, and water in a ratio, 2:3:3:5.5, respectively) were obtained by recrystallization of **1** or **2** with the corresponding bipyridyl derivatives (Chart 2). Their crystal data including angles (θ) and torsion angles (φ) between the planes of two phenyl rings of aromatic ureadicarboxylic acids are summarized in Table 1. All of them have U-shaped molecular structures with *cis,cis*-conformation. Cocystals **1·7**·MeOH and **1·7**·EtOH contained *trans,cis*-conformation together with *cis,cis*-conformation. Conformations of their U-shaped molecular structures are very different. The degree of distortion is ranged with θ and φ of 18−37° and 12−50°, respectively. This could be originated in the flexible molecular structures of aromatic ureadicarboxylic acids. The values of φ are smaller than that observed in the previously reported **1** (φ = 58°), which showed a zipper-type double catemeric network as depicted in Chart 1b.[10] In contrast, ureas **2**, **3**, and **4** gave crystal structures based on H-bonding of the dimeric type A as shown in Chart 1c. The O−H···O═C H-bonding between the carboxy and ureylene moieties, together with this dimeric type A carboxy−carboxy H-bonding, creates ladder-type H-bonding networks in the crystal structures of **2** and **3** (Figure 1). They have almost identical network structures.

Chart 2. *N,N′*-Disubstituted Aromatic Ureadicarboxylic Acids for Crystallographic Study and Dipyridyl Derivatives Examined for the Preparation of Cocrystals with Them



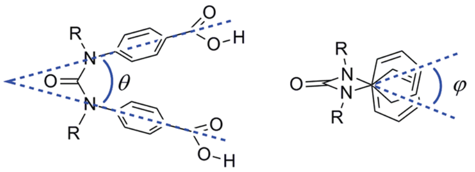
One of the carboxy moieties participates in the dimeric type H-bonding with the neighboring carboxy moiety with the oxygen−oxygen atomic distance of 2.64 Å. The other carboxy moiety interacts with the neighboring carbonyl oxygen atom of the ureylene moiety via H-bonding with the oxygen−oxygen atomic distance of 2.62 Å. Sequential interactions of these furnish a ladder-type structure. Figure 1b,e shows the packing structures for **2** and **3**, respectively, viewed from the direction of the *c*-axis. A gear-like structure is created by gathering of the ladders as shown in the space-filling models (Figure 1c,f). The cavities of the ladders are filled with the ethyl or allyl groups of the ureylene moieties of the neighboring ladders. It is interesting that a slight difference in the size of the substituents at the urea nitrogen atom, either methyl or ethyl, could change their crystal structures from the double catemeric to the ladder structure. The oxygen−oxygen atomic distances for H-bonding of the carboxylic acid dimers for **2** and **3** are 2.64 and 2.63 Å, respectively, and those for C═O···H interaction between the carboxy moiety and the carbonyl oxygen atom are 2.62 Å for both ureadicarboxylic acids.

A zigzag-type assembling is created in the crystal structure of **4**·H_2O by applying a modified H-bonding (dimeric type A). Two molecules of water are wedged into one of the dimeric type H-bonding of carboxys (Figure 2a). The O−O atomic distances

Table 1. Crystallographic Data for Aromatic Ureadicarboxylic Acids and Their Complexes with Pyridine Derivatives

compound	**2**	**3**	**4**·H_2O	**1**·**5**	**2**·**6**	**1**·**7**·MeOH	**1**·**7**·EtOH
formula	$C_{19}H_{20}N_2O_5$	$C_{21}H_{20}N_2O_5$	$C_{29} H_{27} N_2 O_5$	$C_{31} H_{24} N_6 O_5S_2$	$C_{29}H_{28}N_4O_5$	$C_{71}H_{97}N_{16}O_{26.5}$	$C_{73}H_{91}N_{16}O_{21.5}$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/c$	$C2/c$	$Pbca$
a (Å)	9.5177(7)	9.4088(2)	9.9661(1)	8.3904(1)	11.842(3)	22.746(3)	25.6980(4)
b (Å)	17.235(3)	18.474(2)	18.3254(2)	15.0050(2)	16.252(3)	31.072(4)	19.7165(4)
c (Å)	10.909(2)	10.940(1)	14.3623(2)	22.5231(3)	14.325(4)	25.140(4)	30.1786(6)
α (°)	90	90	90	90	90	90	90
β (°)	93.011(3)	95.535(1)	101.586(1)	96.430(1)	109.151(2)	115.475(1)	90
γ (°)	90	90	90	90	90	90	90
V (Å^3)	1787.05(5)	1892.7(4)	2569.58(5)	2817.77(6)	2604.2(11)	16041(4)	15290.7(5)
D_c (Mg m^{-3})	1.325	1.335	1.250	1.473	1.307	1.301	1.335
Z	4	4	4	4	4	8	8
T (K)	150	120	173	173	150	150	173
R_1 [$I > 2\sigma(I)$]	0.0377	0.0375	0.0415	0.0492	0.0465	0.0668	0.0630
wR_2 [$I > 2\sigma(I)$]	0.0907	0.0867	0.1120	0.1213	0.1045	0.1867	0.1801
angle θ (°)[a]	32	35	26	33	18	37	23
torsion angle φ (°)[b]	46	42	50	30	41	34	12

[a] Angles (θ) between the planes of two phenyl rings of ureadicarboxylic acids. [b] Torsion angles (φ) between the planes of two phenyl rings of ureadicarboxylic acids.



for the dimeric type H-bonding of carboxys are 2.59 Å and those between the carboxys and the wedged water molecules are 2.57 and 2.71 Å. The H-shaped packing of the three zigzag networks is observed from the direction of [101] (Figure 2b). A similar type of hydrate of carboxylic acid was reported in the crystal structure of 2-chloro-4-nitrobenzoic acid.[19] Tetrameric motif involving two molecules each of 2-chloro-4-nitrobenzoic acid and water created 2D sheet structure.

We have found that the size of the substituents at the urea nitrogen atom is sensitive to the type of H-bonding network to be created, the double catemeric or dimeric structure. The latter affords the ladder or the zigzag-type folding. The results prompted us to examine the effect of the substituent and the spacer molecule to be pinched on the supramolecular assembly. In order to explore further this zigzag-type assembling, we have prepared cocrystals of **1** and **5**, and also **2** and **6**. Single crystal X-ray structural analysis of these showed that the composite ratios of ureadicarboxylic acids and dipyridyl derivatives are 1:1 for both cocrystals. Zigzag-type H-bonding networks were formed in both cases. The H-bonding between the carboxy and the nitrogen atom of the pyridyl works well to sandwich dipyridyl derivatives with ureadicarboxylic acids via the dimeric type A pattern. They did not give triple helices observed in the cocrystals of **1** and dipyridyl derivatives (the dimeric type B pattern).

Figure 3a shows the zigzag-type H-bonding network observed in **1**·**5**. The O−N atomic distance for H-bonding between the carboxy and the pyridyl moieties is 2.66 Å. The torsion angle φ in the cocrystal **1**·**5** is 41°. Zigzag strands are stacked in the direction of the a-axis with sliding (Figure 3b). The layer distances between the adjacent thiazole derivative **5** is 3.67 Å and the distance between the centroids of **1** and **5** is 3.74 Å. The zigzag pitch, 23.1 Å, is slightly longer than that (ca. 20 Å) observed in the cocrystals of **1** and 4,4′-bipyridyl derivatives (1:1).[10] It is interesting that even the inclusion of the longer dipyridyl derivative affects a little on the zigzag pitch. As we referred to previously in the formation of triple helices, the zigzag pitch should remain almost the same independent of the length of dipyridyl derivatives employed as spacers. Since the widths of the linear aromatic spacers are nearly the same, the zigzag with nearly the same pitch will be generated but with different widths of the zigzag depending on the length of the spacer molecules. The present case is a similar situation as in the formation of triple helices.

The crystal structure of cocrystal **2**·**6** afforded a zigzag-type H-bonding network (Figure 4a). However, the pattern of zigzag folding is different from that of **1**·**5** even though the way of pinching is the same (the dimeric type A pattern). The distance between the carboxy oxygen atom and the pyridyl nitrogen atom is 2.67 Å. As shown in Figure 4b, a cross-patterned H-bonding network is created, which results in the formation of a eight-shaped-type zigzag-sequence with the zigzag pitch of 14.3 Å. The pitch is fairly smaller than that of **1**·**5**. We observed the formation of a triple helix in the cocrystal **1**·**6**.[10] It is interesting that a small

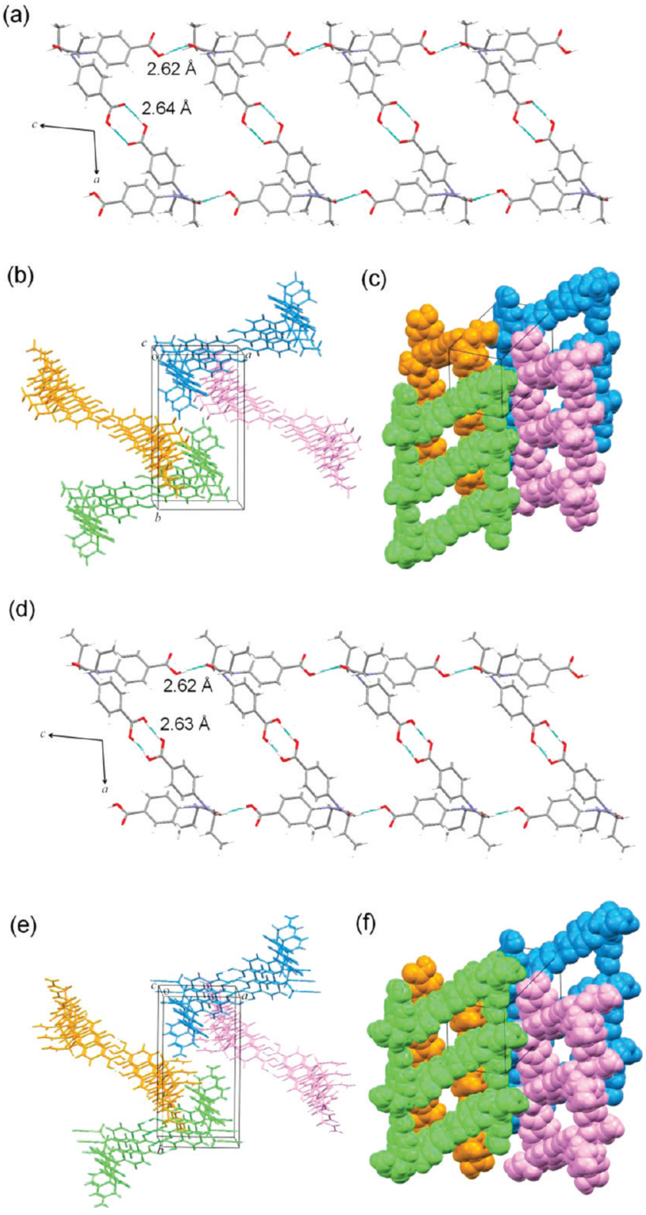


Figure 1. Crystal structures of **2** and **3**. Ladder-type H-bonding networks of **2** (a) and **3** (d) in which H-bonds are indicated with blue lines together with the O−O atomic distances. Packing diagrams of **2** (b) and **3** (e) viewing along the *c*-axis and side views of **2** (c) and **3** (f) indicated by a space-filling model in which each ladder is colored differently.

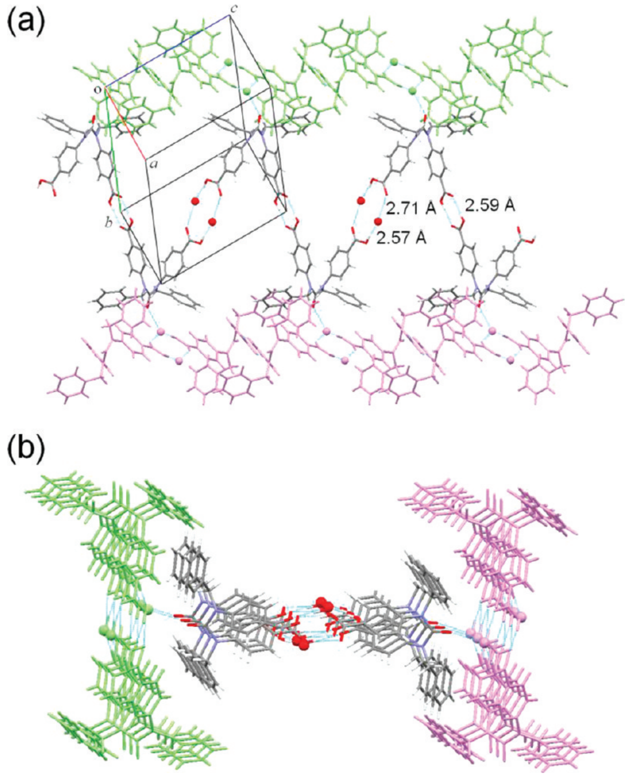


Figure 2. Crystal structures of $\mathbf{4}\cdot H_2O$. Packing diagram showing (a) the zigzag-type H-bonding network and (b) the front view along the [101] direction. Oxygen atoms of the wedged water molecules are indicated by spheres of arbitrary size. H-bonds are indicated with blue lines together with the O−O atomic distances.

difference in the size of the substituent at the urea nitrogen atom, either methyl or ethyl, causes a significant difference in the creation of zigzag architecture. The zigzag strands are stacked together to cover their zigzag gaps (Figure 4c,d).

In order to demonstrate the versatility of the ureadicarboxylic acid as a potential U-shaped building block, we applied it to the construction of channel structures. The folding shape of the building block could be favorable to prepare space for channels. Our design of a channel structure is as follows. The first step is the creation of a straight scaffold arranged with hydrogen bonding sites at a constant interval. The second step is the insertion of the U-shaped units between the straight scaffolds by two-point H-bonding to furnish channels. The interval between the U-shaped building blocks could be available as a vacancy for the channel. For a candidate of the straight scaffold, we employed bipyridylurea **7**. Bipyridylureas were utilized as diverse structural scaffolds in crystal engineering.[20] It was reported that **7** could assemble linearly in the presence of dicarboxylic acids.[21] Protonation of one of the pyridyl moieties of **7** by carboxylic acids generates pyridinium which creates a H-bond with the remaining pyridyl moiety. The sequential H-bonding affords the linear array of **7**. Carboxylates generated after protonation interacts with the urea moiety by H-bonding resulting in the formation of channels. Two carboxylates of the U-shaped building block connect the two straight scaffolds.

Recrystallization of **1** in the presence of **7** from methanol with diffusion of water vapor gave solvated cocrystals $\mathbf{1}\cdot\mathbf{7}\cdot$MeOH with a large unit cell volume. Molar ratio of **1**, **7**, and methanol was 2:3:4, which was also observed by ^{1}H NMR analysis. Crystal structure of the complex showed a channel structure in which methanol and water molecules were included. Figure 5a shows nanometer-size channels viewed along the *c*-axis in which included methanol and water molecules are omitted for clarity. Two conformations of **1**, *cis,cis*- and *trans,cis*-confromations, exist in the cocrystals. In Figure 5, they are colored light green (*cis,cis*) and pink (*trans,cis*), respectively. DFT calculations (B3LYP/6-31(G)d) of three possible conformations of **1**, *cis,cis*-, *trans,cis*-, and *trans,trans*-conformations, were carried out. Urea *cis,cis*-**1** is slightly more stable than *trans,cis*-**1** and *trans,trans*-**1** is least stable one. Their relative energies are 0.90 and 1.55 kcal/mol for *trans*,

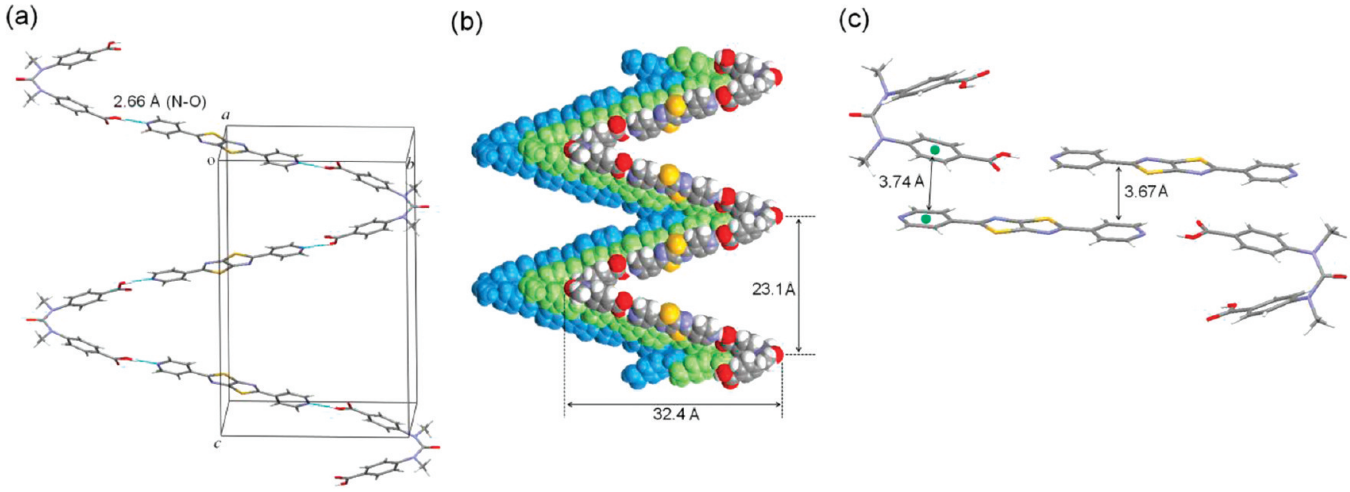


Figure 3. Crystal structure of **1**·**5**. (a) Zigzag-type H-bonding network. (b) Packing diagram viewed from the direction of the *a*-axis. (c) The layer distance between the adjacent **5** and the distance between the centroids of **1** and **5**.

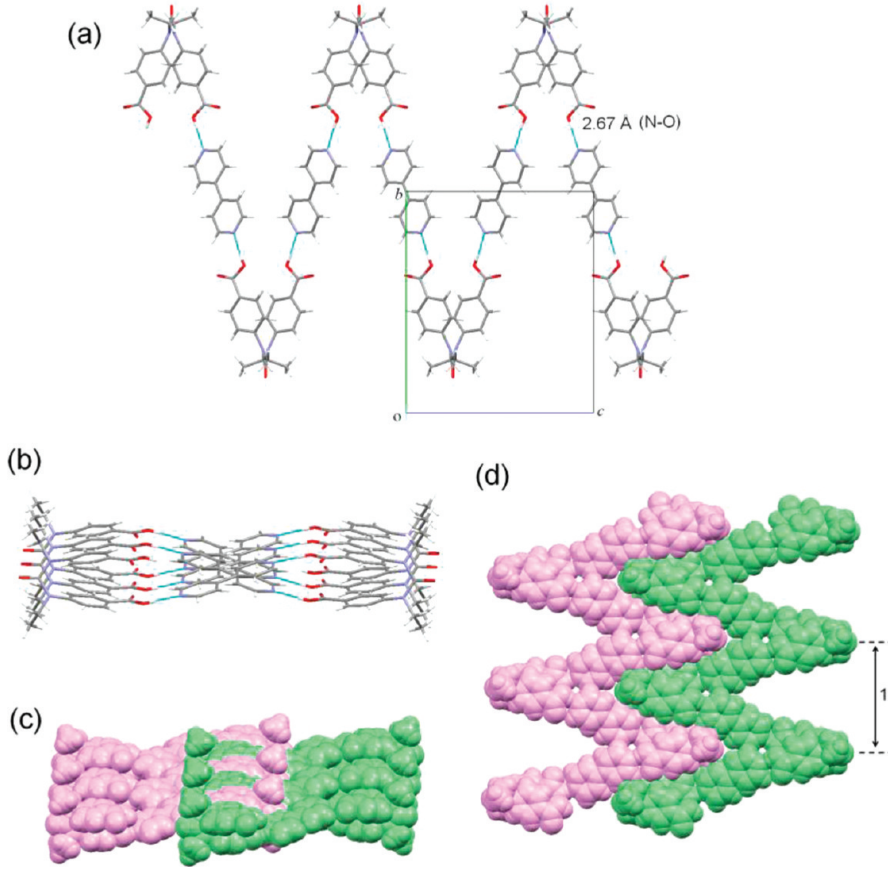


Figure 4. Crystal structure of **2**·**6**. (a) Supramolecularly assembled zigzag H-bonding network. (b) A cross-patterned network viewed along the *c*-axis. Packing diagrams, (c) a side view and (d) a front view in which strands are colored bright pink and green for clarity.

cis-**1** and *trans*,*trans*-**1**, respectively, in comparison with *cis*,*cis*-**1** as 0 kcal/mol.

Pyridinium derived from the protonation of 7 by **1** creates a linear array of 7 via H-bonding between the pyridinium and pyridine moieties of protonated 7. Figure 5b shows the 2D sheet generated on the *ac* plane by assembling of the linear array of protonated 7. Between these arrays the carboxylates derived from **1** possessing *cis*,*cis*-conformation are located as binders to connect the arrays. Figure 5c,d shows the way of H-bonding between the arrays of protonated 7 and the carboxylate of **1** viewed from the direction of [101] and the *c*-axis, respectively. The first and the third rows and also

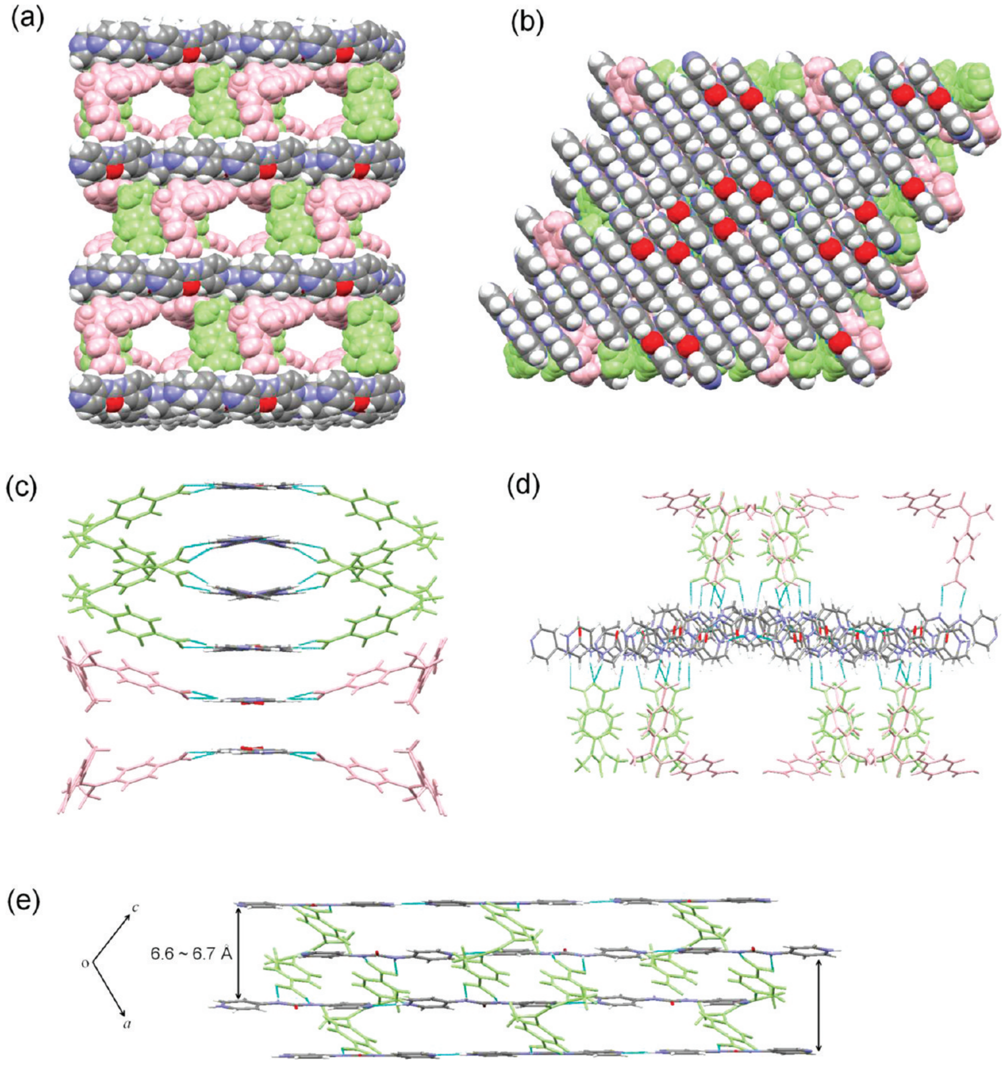


Figure 5. Single crystal X-ray structure of **1**·**7**·MeOH. *cis,cis*- and *trans,cis*-conformations of **1** are indicated with light green and pink colors, respectively. (a) The channel structure viewed along the *c*-axis in which methanol and water molecules included in the channels are omitted for clarity. (b) A view along the *b*-axis to show the 2D sheet of **7**. H-bonding networks viewed from (c) the direction of [101], (d) the *c*-axis, and (e) the *b*-axis. H-bonds are indicated with blue lines.

the second and the fourth rows of the array of protonated **7** are connected by the two-point-H-bonding with the carboxylates of *cis,cis*-**1**. The layer distance between the alternate arrays is 6.6−6.7 Å, which is twice the thickness of the pyridine ring (Figure 5e). The results indicate that efficient stacking is taking place between the arrays. The angle θ and torsion angle φ between the planes of two phenyl rings in *cis,cis*-**1** are 36.6 and 33.4°, respectively. The remaining fifth and sixth rows are H-bonded with the carboxylates possessing *trans,cis*-conformation.

When the solvent of recrystallization of **1** and **7** was changed from methanol to ethanol with diffusion of water vapor, we obtained a different type of channel structure. In a sense, a pseudopolymorphic channel was created. In contrast to a straight 1D channel obtained from methanol with diffusion of water vapor, an unusual fishnet-type 2D channel was furnished. Figure 6a,b shows packing structures of **1**·**7**·EtOH viewed from the direction of (a) [110] and (b) $[\bar{1}\bar{1}0]$ in which ethanol and water molecules included in the channels are omitted for clarity. Fishnet-type 2D channels are created on the *ab* plane (Figure 6c). The crossing angle of channels is about 75°. Each sheet of 2D channels was separated by the wall of assembled arrays of protonated **7**. Figure 6d shows a schematic representation of fishnet-type 2D channels. The difference between the 1D and the 2D channels originates in the way of H-bonding of the carboxylate to the ureylene moiety of protonated **7**. The carboxylates pinch the neighboring two arrays of protonated **7** by H-bonding in the 2D channels while they pinch the two alternate arrays of protonated **7** in the 1D channels (Figure 6e). The layer distance between the two neighboring arrays of protonated **7** in the 2D channels is 3.2−3.3 Å, which is equivalent to the thickness of the pyridine ring. The angle θ and torsion angle φ in the *cis,cis*-conformation of carboxylate **1** are 23.2 and 12.1°, respectively. These values are fairly small compared to those of other aromatic ureadicarboxylic acids. Owing to its flexible molecular structure, **1** can adapt its conformation to the desirable one for channels, which results in unusual pseudopolymorphic channels.

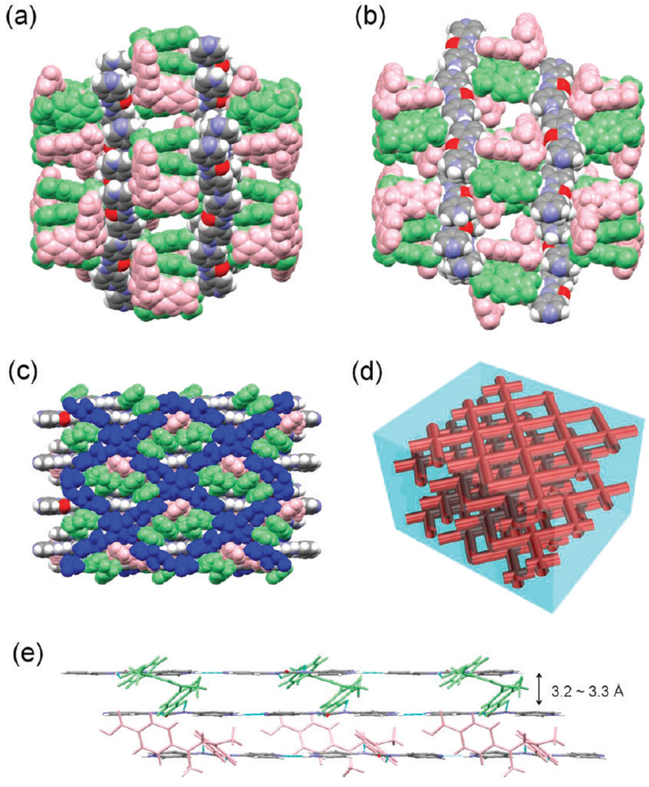


Figure 6. Single crystal X-ray structure of **1**·**7**·EtOH. *cis,cis*- and *trans,cis*-conformations of **1** are indicated with light green and pink colors, respectively. (a) The channel structure presented by space-filling model viewed from the direction of (a) [110] and (b) $[\bar{1}10]$ in which ethanol and water molecules included in the channels are omitted for clarity. (c) A view along the *c*-axis showing fishnet-type 2D channels created on the *ab* plane in which ethanol and water molecules are colored blue. Hydrogen atoms of water molecules are not included. (d) Schematic representation of fishnet-type channels in a crystal. (e) The layer structure viewed along the *c*-axis.

CONCLUSION

We have demonstrated the usefulness and versatility of aromatic ureadicarboxylic acids as U-shaped building blocks for crystal engineering. Self-assembled ladder-type and zigzag-type structures can be generated depending on the choice of the substituents on the urea nitrogen atom. Supramolecularly assembled zigzag architectures are created in cocrystals of them with dipyridyl derivatives. Especially interesting is the creation of pseudopolymorphic channels by assembling with dipyridilyurea. Two types of channels, straight-type 1D and fishnet-type 2D channels, were obtained by inclusion of methanol and ethanol, respectively.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** The crystallographic information files (CIF) and crystal data of compounds **2**, **3**, and **4**·H_2O and cocrystals, **1**·**5**, **2**·**6**, **1**·**7**·MeOH, and **1**·**7**·EtOH. This information is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*Phone: +81-43-290-3420. Fax: +81-290-3422. E-mail: kohmoto@faculty.chiba-u.jp.

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