Self-Assembly of Organometallic−Organic Hybrid Supramolecular Arrays from Ferrocenyl Dipyridines and Aromatic Carboxylic Acids

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ABSTRACT: The ferrocenyl bipyridines, 1,1′-bis[2-(4-pyridyl)vinyl]ferrocene (**1a**) and 1,1′-bis[2-(3-methyl-4-pyridyl)vinyl]ferrocene (**1b**), were cocrystallized with aromatic acids such as 4-alkoxybenzoic acids (**2**), terephthalic acid (**3a**), isophthalic acid (**3b**), phthalic acid (**3c**), and trimesic acid (**4**). Eight complexes were obtained as single crystals, and their crystal structures were successfully determined by X-ray analysis. When **1a** was assembled with **2**, a [1 + 2] self-assembly occurred, to generate supramolecular arrays in which one molecule of **1a** and two molecules of **2** were held together through hydrogen bonding. In the cocrystallization of ferrocenyl bipyridines with benzene dicarboxylic acid (**3a**, **3b**, and **3c**), proton transfer occurred depending on the kind of benzene dicarboxylic acid. Thus, the cocrystals of **1a**$^{+}$·**3b**$^{-}$, **1b**$^{+}$·**3b**$^{-}$, and **1b**$^{+}$·**3c**$^{-}$ consist of proton-transferred ionic supramolecular species, whereas that of **1b**·**3a** are composed of [2 + 2] assembled cyclic supramolecular structures. Complexation of **1a** with **4** afforded the [2 + 3] self-assembly with an intriguing prismatic cagelike structure.

Introduction

Noncovalent synthesis represents a powerful strategy for the spontaneous and programmed generation of supramolecular architectures on the basis of the instructions stored in the building components and of the interactive algorithms that bind these components together.[1,2] In recent years, the technique has provided direct and predictable access to remarkably discrete supramolecular aggregates of well-defined structures with combined properties via complementary intermolecular interactions, such as hydrogen bonding and aromatic $\pi-\pi$ stacking interactions.[3] Most studies described so far are based on organic motifs. Moreover, compared with this, relatively few reports deal with the use of organometallic components.[4,5] In this respect, our interests lie in the use of organometallic component molecules that can form robust supramolecule with organic molecular components through directed noncovalent interactions. Employing organometallic molecules to form crystalline architectures seems to be an attractive idea for an approach to crystal engineering. Simple association of two complementary compounds can be used to combine the unique properties of inorganic components with well-established aspects of a supramolecular organic chemistry. Therefore, it can create a new class of crystalline materials with new and remarkable physical properties and potential applications in optical and electronic devices, which are not possessed by either of the components alone.

Our research has been concentrated on the exploitation of ferrocenyl bipyridine in the rational development of organic−organometallic hybrid supramolecular systems.[6] The ferrocenyl bipyridines used in our study contain two pyridine rings conjugated with ferrocenyl moiety through a rigid spacer unit. Their use for an assembly with organic components has several attractive features. First, the rotation barrier of cyclopentadienyl rings about the iron is low and the ferrocene moiety acts as an atomic ball bearing. Thus, they can change their conformations and adopt the optimal one during complexation with organic components.[7] Second, the interring spacing in ferrocene is around 3.3 Å, or approximately two aromatic thickness.[6a,8] Thus, the binding of aromatic organic molecules can, in principle, be augmented by $\pi-\pi$ stacking interactions. Third, the conjugation with ferrocenyl moiety should make pyridyl N atoms more basic compared with simple organic derivatives. Moreover, they should act as better acceptors constructing robust hydrogen bonding motifs. An additional consideration is that ferrocene shows useful optical and electronic properties such as a strong charge transition and reversible redox behavior.[9] It is thought that their self-assembled adduct can have potential applications in optical and electronic devices.

In our previous works, we assembled ferrocenyl bipyridine, 1,1′-bis[2-(4-pyridyl)vinyl]ferrocene, with aromatic diols into crystalline supramolecular aggregates. We also demonstrated a simple crystal engineering strategy for achieving NLO active crystalline materials.[6a,b] In this paper, we turn our attention to the extension of our strategy to carboxylic acids. The complexation of ferrocenyl bipyridines with mono-, bi-, and tricarboxylic aromatic acids readily affords new binary cocrystals. Molecular components used in this study are shown in Chart 1. Most of them contain the organic−organometallic hybrid supramolecular arrays assembled through the robust hydrogen bonding motif between COOH and pyridine. In other hand, the adducts of their assembly with phthalic or isophthalic acid show the occurrence of an acid−base reaction and formation of proton transferred ionic supramolecular species. Herein, we report the details of their assemblies.

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Chart 1. Molecular Components Used in This Work
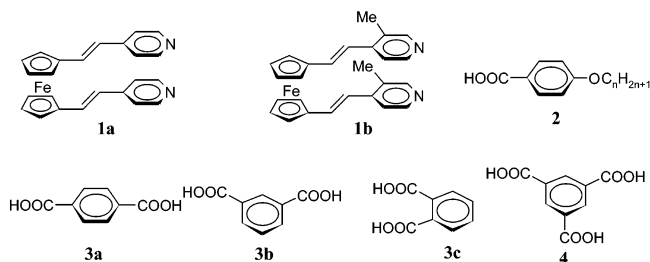
Experimental Section

General Considerations. The reactions for synthesis of 1,1′-bis[2-(4-pyridyl)vinyl]ferrocene (**1a**) and 1,1′-bis[2-(3-methyl-4-pyridyl)vinyl]ferrocene (**1b**) were carried out under nitrogen using standard Schlenk techniques. Distilled, dry, and oxygen-free solvents were used throughout. Routine ^{1}H NMR spectra were recorded with a Bruker 300 or 500 spectrometer. Elemental analyses were performed by the Analytical Center, College of Engineering, Seoul National University. **1a** was previously reported and prepared according to the reported procedure.[6c] Thermotropic properties of **1a·2** were studied by heat stage polarizing microscopy using a Nikon Optiphot-2 polarizing microscope equipped with a Mettler FP 82 HT hot stage and control unit and were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7).

Preparation of 1,1′-bis[2-(3-methyl-4-pyridyl)vinyl]ferrocene (1b). To the solution of LDA (generated in situ by the reaction of diisopropylamine (2.3 mL, 16.4 mmol) in 30 mL of THF with *n*-BuLi (10.0 mL, 16.0 mmol) at −78 °C) was added 4-picoline (1.7 mL, 15.1 mmol) at −78 °C. While the solution was stirred at room temperature for 30 min, the solution turned to reddish. To the reddish solution was added 1,1′-ferrocenedicarboxaldehyde (1.56 g, 6.20 mmol) at room temperature. While the resulting reaction mixture was stirred at room temperature for 4 h, brown solids were precipitated. To the solution were added excess water (30 mL) and methylene dichloride (30 mL). The methylene dichloride layer was collected, evaporated to dryness, and dissolved in 15 mL of pyridine. The pyridine solution was cooled to 0 °C. Excess POCl$_3$ (3 mL) was added dropwise to the pyridine solution. While the solution was stirred at room temperature for 1.5 h, the color of the solution turned to violet. To the violet solution was added ice to quench excess POCl$_3$. After evaporation of pyridine, the residue was dissolved in water (100 mL) and basified to precipitate reddish solids by aqueous 4 M NaOH. Filtration of the solution gave red solids. Purification of the red solids by chromatography on a silica gel column eluting with Et$_2$O/MeOH (v/v, 1:1) gave 1.70 g of **1** (70%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.29 (s, 2 H), 8.25 (d, 5.0 Hz, 2 H), 7.19 (d, 5.0 Hz, 2 H), 6.86 (d, 16.0 Hz, 2 H), 6.67 (d, 16.0 Hz, 2 H), 4.49 (t, 1.7 Hz, 4 H, Cp), 4.35 (t, 1.7 Hz, 4 H, Cp), 2.16 (s, 6 H) ppm; Anal. Calcd. for C$_{26}$H$_{24}$FeN$_2$: C, 74.29; H, 5.76; N, 6.66. Found: C, 74.38; H, 5.54; N, 6.64.

Preparation of Cocrystals of 1a·2. 1a (0.025 mg, 0.064 mmol) and 4-alkoxybenzoic acid **2** (2 equiv) were dissolved in 5 mL of boiling ethanol. The solution was allowed to cool to room temperature and evaporated in air for a week. The precipitate was washed with cold ethanol and dried under vacuum. All of **1a·2** except for **1a·2g** were obtained quantitatively. For **1a·2g**, cocrystallization had to be done in 24 h due to the crystallization of 4-dodecylbenzoic acid itself, and the yield was rather poor (30.8%).

1a·2a: Anal. Calcd. for C$_{48}$H$_{52}$FeN$_2$O$_6$: C, 71.28; H, 6.48; N, 3.46. Found: C, 71.36; H, 6.57; N, 3.44.

1a·2b: Anal. Calcd. for C$_{50}$H$_{56}$FeN$_2$O$_6$: C, 71.76; H, 6.74; N, 3.35. Found: C, 71.37; H, 6.42; N, 3.36.

1a·2c: Anal. Calcd. for C$_{52}$H$_{60}$FeN$_2$O$_6$: C, 72.21; H, 6.99; N, 3.24. Found: C, 71.76; H, 6.53; N, 3.25.

1a·2d: Anal. Calcd. for C$_{54}$H$_{64}$FeN$_2$O$_6$: C, 72.63; H, 7.22; N, 3.14. Found: C, 72.38; H, 6.89; N, 3.21.

Table 1. Crystal Data and Structure Refinement for 1a·2a, 1a·2b, and 1a·2c

	1a·2a	1a·2b	1a·2c
empirical form	C$_{50}$H$_{56}$FeN$_2$O$_6$	C$_{26}$H$_{30}$Fe$_{0.5}$NO$_3$	C$_{54}$H$_{64}$FeN$_2$O$_6$
formula weight	836.82	432.43	892.92
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	10.8013(12)	8.0056(9)	10.6119(8)
b, Å	15.060(2)	10.0879(12)	16.010(2)
c, Å	26.755(3)	28.566(2)	16.438(2)
α, °	90	90	64.011(12)
β, °	96.707(9)	91.989(8)	76.227(8)
γ, °	90	90	74.387(8)
volume, Å^3	4322.4(9)	2305.6(4)	2394.3(5)
Z	4	4	2
d(calcd), Mg/m^3	1.286	1.246	1.239
θ range, °	1.53−24.99	2.14−24.97	1.55−24.97
no. tot. collection	8009	4350	8917
no. unique data	7575	4042	8420
no. params refined	534	404	570
R1	0.1201	0.0428	0.0574
wR2	0.2389	0.1045	0.1174
gof	0.815	1.110	1.036

1a·2e: Anal. Calcd. for C$_{56}$H$_{68}$FeN$_2$O$_6$: C, 73.03; H, 7.44; N, 3.04. Found: C, 72.72; H, 7.68; N, 3.08.

1a·2f: Anal. Calcd. for C$_{58}$H$_{72}$FeN$_2$O$_6$: C, 73.40; H, 7.65; N, 2.95. Found: C, 73.26; H, 8.07; N, 2.85.

1a·2g: Anal. Calcd. for C$_{60}$H$_{74}$FeN$_2$O$_6$: C, 73.75; H, 7.84; N, 2.87. Found: C, 73.58; H, 7.62; N, 2.90.

Preparation of Cocrystals of 1·3. A total of 0.25 mmol of **1** and **3** (1 equiv.) was dissolved in hot EtOH and allowed to stand for several days to give cocrystals of **1·3**.

1a·3b (70% yield): Anal. Calcd. for C$_{32}$H$_{26}$FeN$_2$O$_4$·2H$_2$O: C, 64.66; H, 5.09; N, 4.71. Found: C, 64.35; H, 5.06; N, 4.61.

1b·3a (61% yield): Anal. Calcd. for C$_{34}$H$_{30}$FeN$_2$O$_4$: C, 69.63; H, 5.16; N, 4.78. Found: C, 69.54; H, 5.42; N, 4.65.

1b·3b (64% yield): Anal. Calcd. for C$_{34}$H$_{30}$FeN$_2$O$_4$·H$_2$O: C, 67.56; H, 5.34; N, 4.63. Found: C, 67.61; H, 5.45; N, 4.62.

1b·3c (89% yield): Anal. Calcd. for C$_{34}$H$_{30}$FeN$_2$O$_4$: C, 69.63; H, 5.16; N, 4.78. Found: C, 69.47; H, 5.32; N, 4.78.

Preparation of Cocrystals of 1a·4. A total of 0.10 g (0.24 mmol) of **1a** and 40 mg (0.19 mmol) of **4** were dissolved in hot 1,4-dioxane and allowed to stand for several days to give 0.13 g (0.066 mmol) of **1a·4** (80% based on **1a**). Anal. Calcd. for C$_{90}$H$_{72}$Fe$_3$N$_6$O$_{12}$·2C$_4$H$_8$O$_2$: C, 66.38; H, 5.00; N, 4.64. Found: C, 66.01; H, 4.69; N, 4.32.

X-ray Data Collection, Structure Determination, and Refinement. The diffraction data for **1a·2a**, **1a·2b**, **1a·2c**, and **1a·3b** were collected on an Enraf-Nonius CAD4 automated diffractometer at room temperature using graphite-monochromated Mo Kα radiation (α = 0.71073 Å). Unit cells were determined by centering 25 reflections in the appropriate theta range. In the cases of **1b·3a**, **1b·3b**, **1b·3c**, and **1a·4**, diffractions were measured by an Enraf-Nonius CCD single-crystal X-ray diffractometer. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares with SHELXL-97.[10] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in **1a·2a**, **1a·2c** were located on an ideal position using a riding model with 1.2 or 1.5 equivalent isotropic temperature factors of the atoms to which they are attached. In case of **1a·2b**, all hydrogen atoms except for those attached to the methyl group [H(26A), H(26B), and H(26C)] were found in different Fourier maps and refined. H(1) and H(03) in **1a·3b**, H(101) and (H102) in **1b·3a**, H(01), H(03), H(101), H(102), H(103), and H(104) in **1b·3b**, H(101) and H(102) in **1b·3c**, and H(B1), H(B2), and H(B3) in **1a·4** were located from difference Fourier maps. All hydrogen atoms on the water molecules in **1a·3b** and one hydrogen atom of each water molecule in **1a·3b** were not located. The rest of the hydrogen atoms were located on the ideal position using a riding model with 1.2 or 1.5 equivalent isotropic temperature factors of the atoms to which they are attached.

Table 2.   Measured Phase Transition Temperatures of 1a·2

	during first heating	during first cooling
1a·2a	Cry − 139.9 °C − Iso	Iso − 122.4 °C − Cry
1a·2b	Cry − 144.1 °C − Iso	Iso − 112.2 °C − Cry
1a·2c	Cry − 138.4 °C − Iso	Iso − 115.2 °C − SmA − 102.8 °C − Cry
1a·2d	Cry − 127.7 °C − Iso	Iso − 114.9 °C − SmA − 78.8 °C − Cry
1a·2e	Cry − 135.6 °C − Iso	Iso − 120.7 °C − SmA − 93.63 °C − Cry
1a·2f	Cry − 132.3 °C − Iso	Iso − 122.2 °C − SmA − 98.7 °C − Cry

Table 3.   Crystal Data and Structure Refinement for 1a·3b, 1b·3a, 1b·3b, and 1b·3c

	1a·3b	1b·3a	1b·3b	1b·3c
empirical form	$C_{32}H_{30}FeN_2O_6$	$C_{34}H_{30}FeN_2O_4$	$C_{68}H_{64}Fe_2N_4O_{10}$	$C_{34}H_{30}FeN_2O_4$
formula weight	594.43	586.45	1208.93	586.45
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P1$	$P\bar{1}$
a, Å	9.4041(18)	9.4294(5)	9.3960(10)	10.238(1)
b, Å	9.801(3)	11.1365(5)	10.2460(10)	10.514(1)
c, Å	16.376(5)	14.5979(8)	16.1260(10)	14.621 (1)
α, °	91.80(2)	71.618(3)	99.329(4)	76.225(2)
β, °	102.506(19)	76.482(3)	101.505(5)	85.982(2)
γ, °	106.834(19)	82.086(3)	106.720(5)	63.954(2)
volume, Å³	1403.2(6)	1411.01(12)	1416.6(2)	1372.26(9)
Z	2	2	1	2
D(calcd), Mg/m³	1.407	1.380	1.417	1.419
θ range, °	2.18−24.97	2.93−27.52	3.81−27.42	1.44−27.46
no. tot. collection	5236	12098	8923	9678
no. unique data	4919	6461	8923	6229
no. params refined	378	381	782	380
R1	0.0753	0.0546	0.0780	0.0456
wR2	0.1881	0.1334	0.1816	0.1298
gof	1.066	1.073	1.075	1.168

Table 4.   Crystal Data and Structure Refinement for 1a·4

	1a·4
empirical formula	$C_{98}H_{88}Fe_3N_6O_{16}$
formula weight	1773.29
crystal system	monoclinic
space group	$C2/c$
a, Å	27.9720(10)
b, Å	19.6220(10)
c, Å	17.2750(10)
β, °	112.206(2)
volume, Å³	8778.4(7)
Z	4
d(calcd), Mg/m³	1.342
θ range, °	2.08−22.60
no. tot. collection	19930
no. unique data	5757
no. params refined	558
R1	0.0475
wR2	0.0782
gof	0.827

All hydrogen atoms in **1a·2a** not involving hydrogen bonding were treated as idealized contributions. Crystal data and refinement results are summarized in Table 1, Table 3, and Table 4. Selected bond length and angles are listed in S1, S2, and S3 in Supporting Information.

Results and Discussion

Cocrystallization of Ferrocenyl Dipyridine with 4-Alkoxybenzoic Acids. When 1,1′-bis[2-(4-pyridyl)-vinyl]ferrocene (**1a**) and 4-alkyloxybenzoic acids, 4-C_nH_{2n+1}-OC_6H_4COOH (n = 6 (**2a**), 7 (**2b**), 8 (**2c**), 9(**2d**), 10 (**2f**), 11(**2g**)) were dissolved together in hot EtOH and then the solutions were allowed to slowly evaporate, deep red solids of **1a·2** were precipitated from the solution, respectively. The formation of 1:2 complexes was confirmed by elemental analysis. In case of **1a·2a**, **1a·2b**, and **1a·2c**, high quality single crystals were obtained and the X-ray crystallographic analyses were carried out. Their X-ray structural analyses revealed the oc-

currence of [1 + 2] self-assemblies. All of them contain the supramolecular arrays in which one molecule of **1a** and two molecules of **2** are held together through hydrogen bonding.

In the crystal of **1a·2a**, the two cyclopentadienyl rings on **1a** adopt an eclipsed conformation while the two substituents adopt an 1,1′-orientation, i.e., a *syn*-fashion. Two pyridine rings are stacked by each other through intramolecular π−π interactions and face in almost the same direction. Pyridine moieties of **1a** and carboxylic acids of **2a** form robust hydrogen-bonded motifs in which a primary O−H···N interaction and a secondary C−H···O force involving an α-hydrogen atom of the pyridine group participate (Figure 1). Indeed, this type of supramolecular synthon between carboxylic acids and pyridines has been previously established in organic solids.[11] A pair of **2a** participating in hydrogen bonds are stacked and pendant hexyl chains weakly contact each other via van der Waals interaction. While the hydrogen bonded motifs in their assemblies are alike, molecular conformation of **1a** in **1a·2b** is quite different from that found in **1a·2a**. In the crystal of **1a·2b**, **1a** consists of a crystallographically imposed inversion center at the iron. Thus, two cyclopentadienyl rings on **1a** adopt a staggered conformation and the two substituents adopt a typical 1,3′-orientation, i.e., an *anti*-fashion. The overall supramolecular structure is a fully extended "S" geometry, and there is no interaction between **2b** molecules in the supramolecular unit (Figure 2). In the crystal of **1a·2c**, the molecular conformation of **1a** is similar to that found in **1a·2a** (*syn*-fashion). However, the arrangement between two **2c** molecules in a supramolecular unit differs from that found in **1a·2a**. One of **2c** is laid almost perpendicular to pyridine rings of **1a** (Figure 3). As a result, the carboxylic acid group is inclined to point away from the corresponding pyridine rings, and thus no secondary
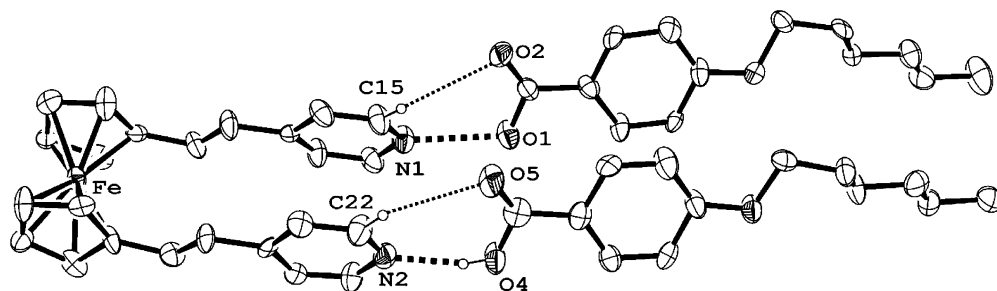
Figure 1. An ORTEP drawing of the supramolecular unit found in the cocrystal of **1a·2a**.
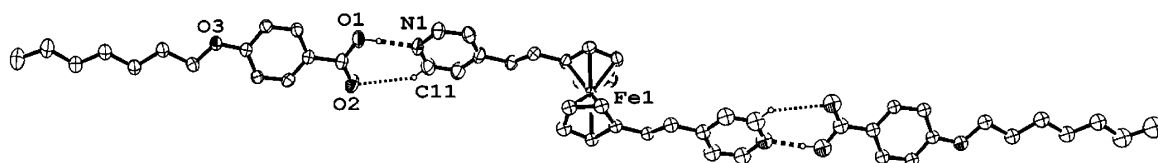

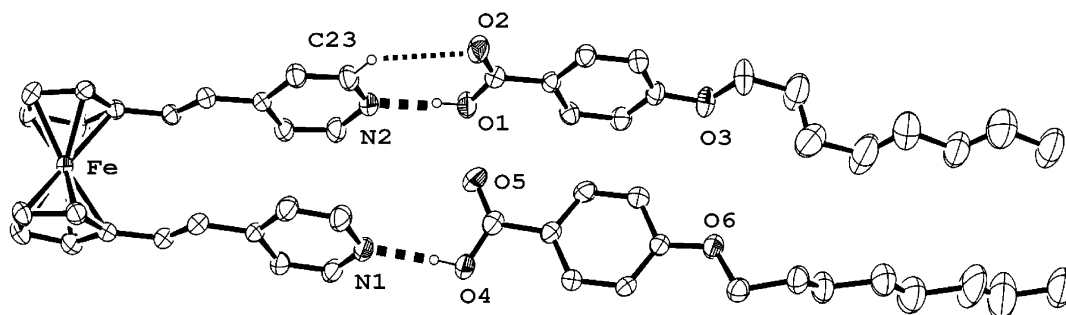**Figure 2.** An ORTEP drawing of the supramolecular unit found in the cocrystal of **1a·2b**.

Figure 3. An ORTEP drawing of the supramolecular unit found in the cocrystal of **1a·2c**.

C−H···O interactions are observed. The conformation of **1a** in the cocrystals is largely dependent on the number of the methylene unit in alkyl tails of **2**, such that cis conformation is found in hexyl and octyl homologues and trans- in heptyl homologue. The origin of this odd/even alternation is difficult to clarify at this stage. However, it is plausible that this phenomenon is related to the change in the inter- and intramolecular packing of the hydrophobic alkyl chains on varying the even−odd parity.[12]

Analyses of their crystal packing mode show that the principal axes of the rod like supramolecules are approximately parallel to each other and these arrangements allow favorable intermolecular attractions (Figure 4). This observation suggests that the cocrystals can be considered to have the required characteristics to show liquid crystalline behavior. Thus, their thermotropic properties were primitively observed using a polarizing microscope equipped with a hot stage and DSC. Upon cooling **1a·2c** from its isotropic phase, the focal conical texture, a characteristic of smetic A phase, was observed under a polarizing microscope (Figure 5). Their phase transition temperatures were confirmed by exothermic peaks in a DSC thermogram and are listed in Table 2. Their thermotropic properties are quite different from either of their single components, which suggests these liquid crystalline characteristics come from the association of components.

This kind of self-assembly process via hydrogen bond formation has been widely established for organic liquid crystals.[13] However, its application to the preparation of metal-containing liquid crystals is rare so far.[14] Since it creates a step in the overall structure leading to a lack of coplanarity between the substitution, 1,1′-substituted ferrocenyl moiety is generally regarded as a poor component to incorporate into a mesogenic system.[15] In these cocrystals, the hydrogen bonding motif between pyridine and carboxylic acids acts as dangling long alkyl tails to **1a** and, at the same time, serves itself as a mesognenic core. As a consequence, it compensates the reduction of mesogenic properties by ferrocenyl moiety, therefore stabilizing mesophases. This result demonstrates the simple crystal engineering route for preparing metal containing liquid crystalline materials.[16]

Cocrystallization of Ferrocenyl Bipyridines with Benzene Dicarboxylic Acids. Recently, we have published the formation of a thermodynamically most favorable discrete cyclic array of **1a·3a** from the cocrystallization of its molecular components.[17] In its supramolecular unit, **1a** and **3a** are held together by the combination of O−H···N and four C−H···O hydrogen-bonding forces as well as inter- and intramolecular $\pi-\pi$ stacking forces between aromatic moieties. As our continuing study on the self-assembly with benzene dicarboxylic acids, cocrystallization of **1a** with isophthalic (**3b**), and phthalic acids (**3c**) were attempted, respectively. Cocrystals containing **1a** and **3** in 2:2 ratio were afforded by allowing a solution to slowly evaporate. Their formulations were confirmed by elemental analysis. We envisioned that if all potential proton donors and acceptors were involved in the hydrogen bonding,
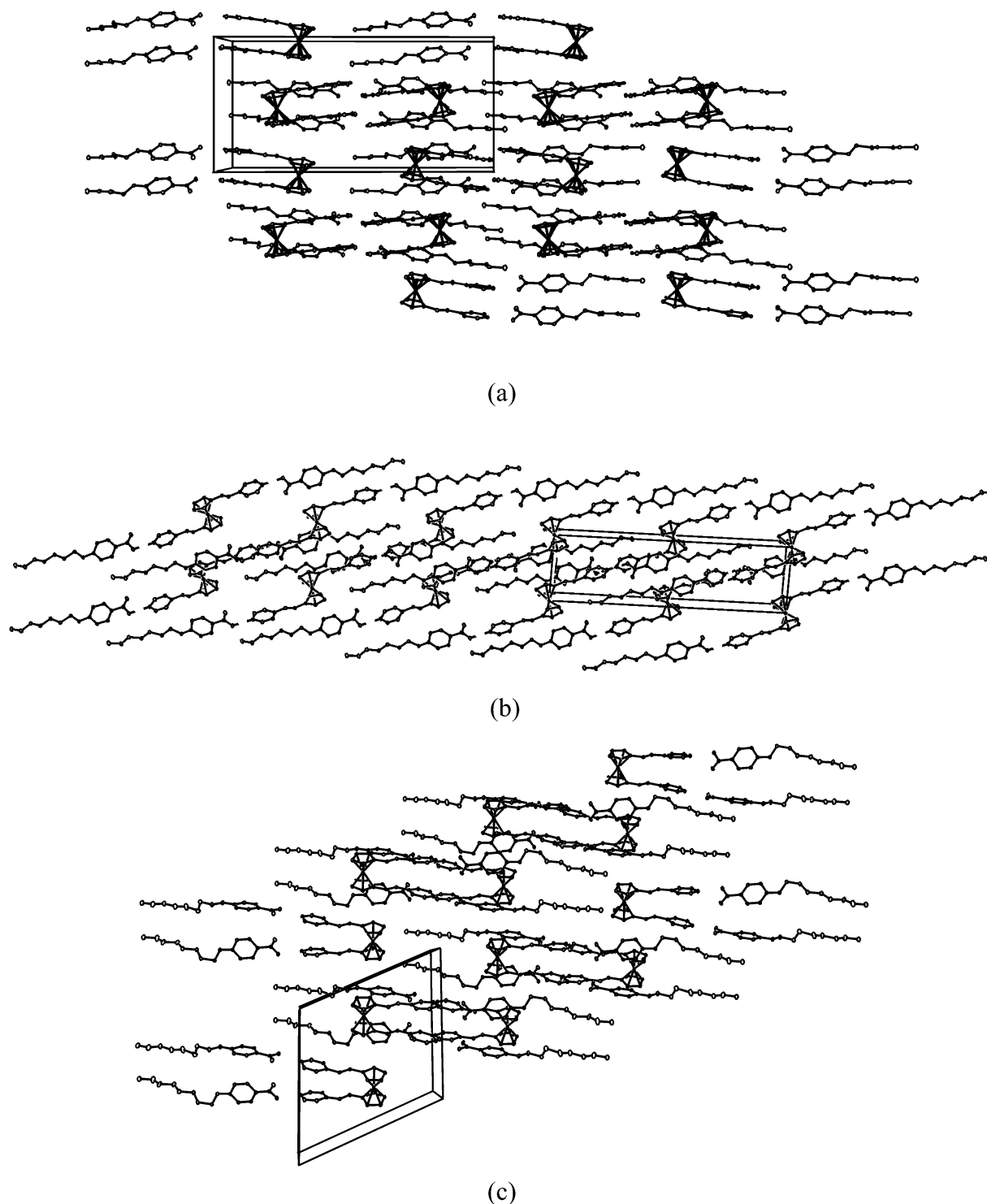
(a)

(b)

(c)

Figure 4. Packing diagrams for **1a·2a** (a), **1a·2b** (b), and **1a·2c** (c).

discrete closed structure like **1a·3a** would result. Single crystals of **1a$^+$·3b$^-$** with high quality were isolated from the solutions and X-ray crystallographic studies were carried out.

However, beyond our expectation, the X-ray structure analysis of the cocrystal between **1a** and **3b** shows a quite different supramolecular assembly from **1a·3a**. The major difference is the absence of hydrogen bonding between the pyridine and carboxylic acid groups. More-over, a proton is transferred from one carboxylic group of **3b** to one of the nitrogen atoms of **1a** and, conse-quently, leads to the monoprotonated cation, **1a$^+$**, with simultaneous formation of the monodeprotonated isoph-thalate anion of **3b$^-$**. Two **1a$^+$** ions are assembled through two N–H···N hydrogen bridges between pro-tonated and nonprotonated pyridine groups and form a dicationic cyclic unit in which two pyridines are stacked by the π–π interaction. These supramolecular units are piled up by the way of aromatic stacking interactions, thus leading to a columnar structure. Anions of **3b$^-$** form O–H···O hydrogen bonds in a head-to-tail arrangement that give a polyanionic chain. This type of hydrogen bond is ubiquitous and has been classified by Gilli et al. as a negative charge assisted hydrogen bond.[18] The

Figure 5. A microphotograph of a focal conical texture of smetic A phase of the cocrystal **1a·2c**.

packing manner is worthy of note in that cationic columns from **1a⁺** and anionic chains from **3b⁻** are alternatively disposed in a crystallographic *ac* plane (Figure 6).

To investigate the ramifications arising from the modification of basicity of the proton acceptor component, we studied similar self-assembly reactions using **1b** instead of **1a** and compared their adducts with cocrystals derived from **1a**. While **1a** and **1b** have a very similar molecular skeleton, pyridines in **1b** are supposed to be more basic due to the possession of electron donating methyl substituents. Single crystals of **1b·3a**, **1b⁺·3b⁻**, and **1b⁺·3c⁻** were obtained from assemblies of **1b** with **3a**, **3b**, and **3c** under the same reaction conditions as applied to the reaction with **1a**. X-ray

crystallographic analyses showed that their assembly manner bears a significant similarity to that found in the assemblies involving **1a**.

During the cocrystalliztion of **1b** with **3a**, a proton transfer does not arise and [2 + 2] self-assembly occurs. The supramolecular structural motif constituting **1b·3a** is almost identical with that of **1a·3a** except for the protruding methyl groups, such that two **1b** molecules form a cyclic array with two **3a** molecules around a pseudo-inversion center by means of hydrogen bonding interactions between neutral pyridnes and carboxylic acids (Figure 7). When **1b** and **3b** were assembled, the proton-transferred cocrystals of **1b⁺·3b⁻** were isolated. No hydrogen bonding between pyridine and carboxylic acid is observed. The crystal structure of **1b⁺·3b⁻** has quite a strong resemblance to that of **1a⁺·3b⁻**, which includes the formation of cationic dimeric structures and anionic chains and the inclusion of water molecules, and their alternative alignment manner (Figure 8). In the case of the assembly between **1a** and **3c**, a proton transfer from carboxylic acid to pyridine occurs. Therefore, the resulting cocrystal **1b⁺·3c⁻** consists of mono-protonated **1b⁺** and phthalate monoanion of **3c⁻**: **1b⁺** exists in the form of a dimeric supramolecular unit and the **3c⁻** ion subsists as a discrete ion form (Figure 9). The **3c⁻** ions stabilize themselves by forming intra-molecular O−H···O hydrogen bonds, and there are no significant interactions between them.

How can we explain the different behaviors of **3a**, **3b**, and **3c** toward **1**? The carboxylic acid of **3c** with the pK_a value of 2.95 is considered to be quite acidic compared with either of **3a** (pK_a 3.49) or **3b** (pK_a 3.53), respectively. While the proton transferred species of **1a⁺** and **3c⁻** were readily detected in a solution NMR study, no evidence for the proton transfer was found in a solution
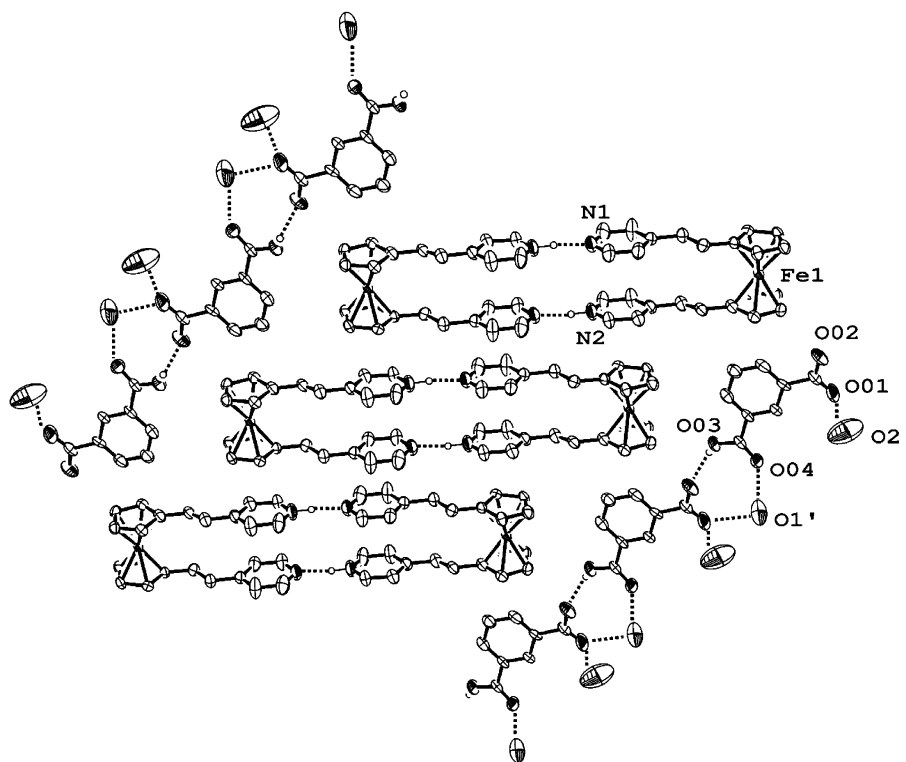

Figure 6. The dimeric supramolecular unit of **1a⁺** and the anionic chain of **3b⁻** and their alternative arrangement in the cocrystal of **1a⁺·3b⁻**.
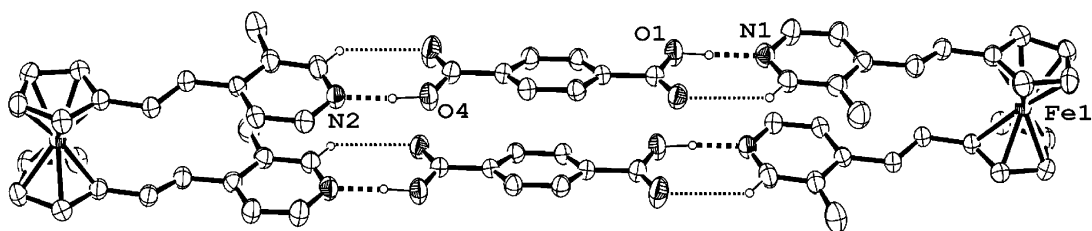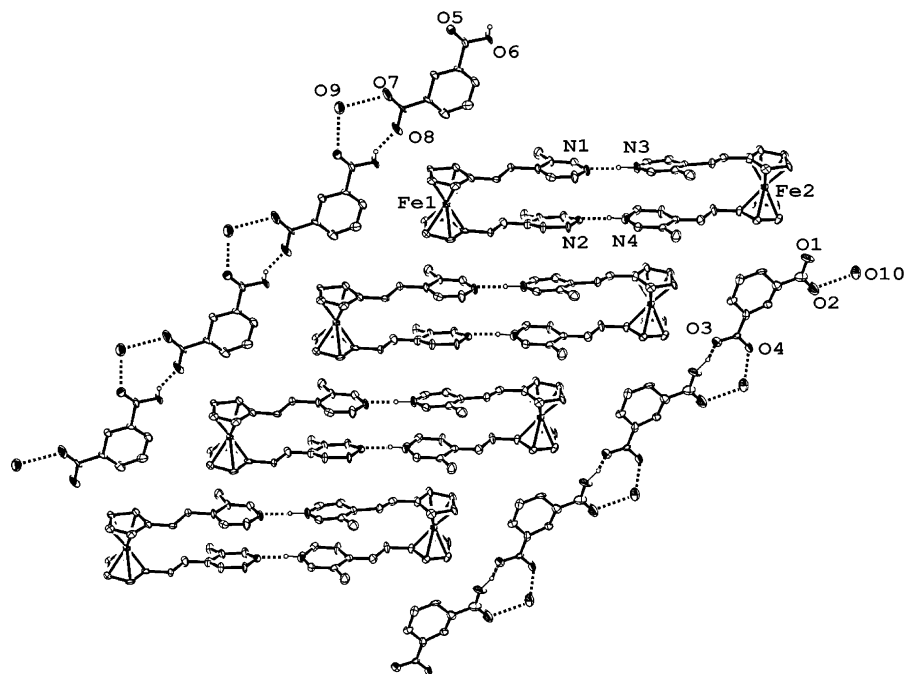
Figure 7. An ORTEP drawing of the supramolecular unit found in the cocrystal of **1b·3a**.

Figure 8. The dimeric supramolecular unit of **1b**$^+$ and the anionic chain of **3b**$^-$ and their alternative arrangement in the cocrystal of **1b**$^+$·**3b**$^-$.
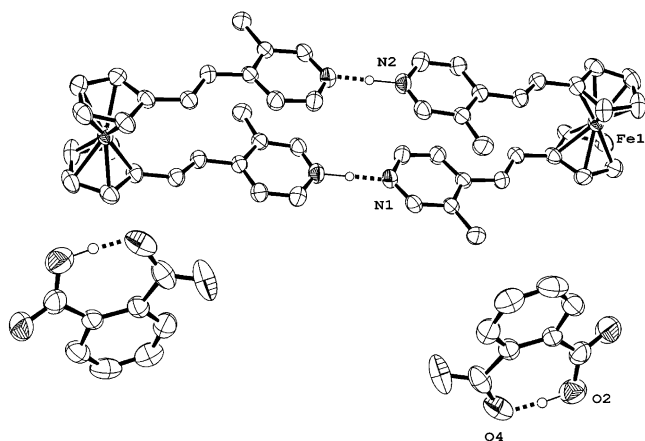

Figure 9. The dimeric supramolecular unit of **1b**$^+$ and the discrete anion of **3c**$^-$ in the cocrystal of **1b**$^+$·**3c**$^-$.

containing **1a** and **3a** and **1a** and **3b**.[19] Therefore, the proton transferred species of **1b**$^+$·**3c**$^-$ is presumed to be from a solution based acid−base reaction and be attributed to the strong proton-donating ability of **3c**.[20] Owing to their moderate acidity, the proton in either of **3a** or **3b** does not seem to be transferred to **1a** or **1b**. Thus, the formation of **1a·3a** and **1b·3a** can be regarded as the crystallization of the solution-based species. On the other hand, it is reasonable to assume that the proton transfer in the formation of **1a**$^+$·**3b**$^-$ and **1b**$^+$·**3b**$^-$

occurs during the crystallization or just before the crystallization. The differences arising between the formation of **1a·3a** and **1a**$^+$·**3b**$^-$ or between **1b·3a** and **1b**$^+$·**3b**$^-$ may come from the difference in the crystallization process. It is presumed that several phenomena arising during the crystallization of **1a**$^+$·**3b**$^-$ or **1b**$^+$·**3b**$^-$ such as formation of an anionic chain, a close molecular packing, and an inclusion of water largely contribute the formation of proton transferred crystals.

Cocrystallization of Ferrocenyl Bipyridine with Benzene Tricarboxylic Acid. In the hope of expanding our strategy to higher dimensional structures, self-assembly between **1a** and trimesic acid (**4**) was also attempted. We anticipate that if a proton transfer does not arise, [2 + 3] assembly would occur and afford a prismatic cage structure that has attracted much attention in this field and been relatively undeveloped.[21]

Due to the poor solubility of **4** in alcohol, their assembly was carried out in a different solvent from that applied to the previous assemblies. When **1a** and **4** were dissolved together in hot dioxane and the solution was allowed to slowly evaporate, crystals of **1a·4** were isolated from the solution. The formation of cocrystals containing **1a** and **4** in the ratio of 2:3 was confirmed by elemental analysis of their adduct. Crystallographic analysis reveals the occurrence of [2 + 3] assembly in the solid state and the gratifying formation of a cage-like supramolecular array. Figure 10 shows an ORTEP
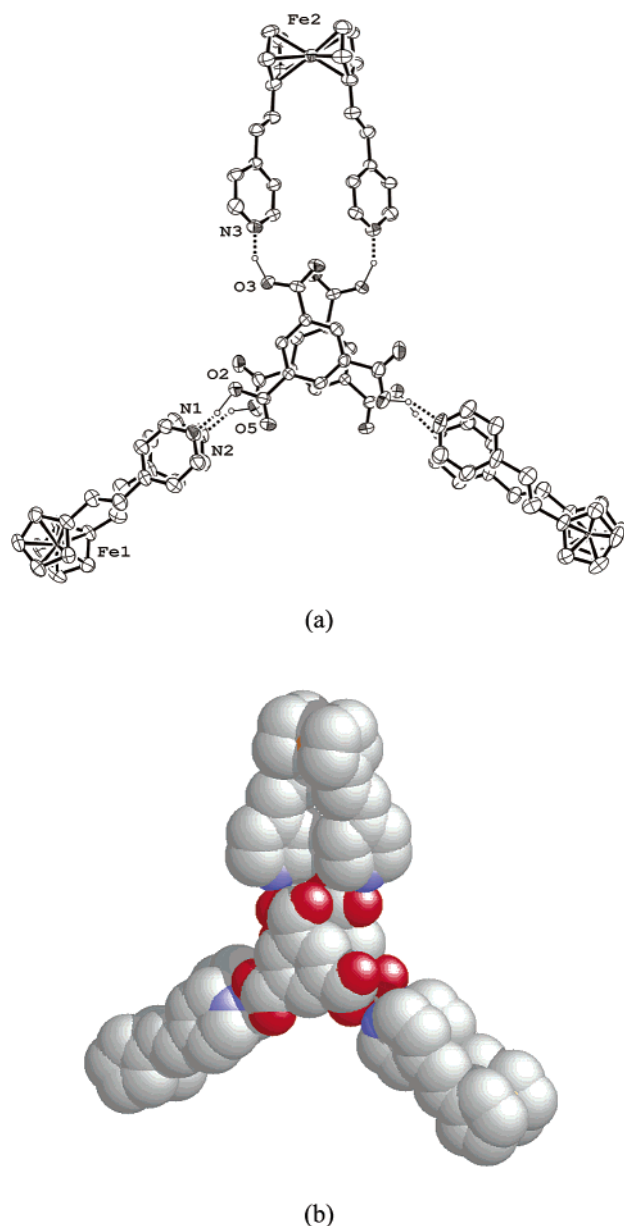
(a)

(b)

Figure 10. The [2 + 3] assembled supramolecular unit found in the cocrystal of **1a·4**: (a) An ORTEP perspective, (b) A space filling representation.

drawing and space-filling model of the supramolecular structure, which is generated by the symmetry operation around the C_2 rotational axis. Three molecules of **1a** in a supramolecular unit recognize two molecules of **4** through six of hydrogen bondings between pyridine and carboxylic acids. The arrangement of **1a** and **4** is reminiscent of the structure found in **1a·3a**, such that pyridines of **1a** with a *syn*-conformation form coplanar hydrogen-bonded motifs with carboxylic acids of a $\pi-\pi$ stacked trimesic acid dimer. One of three molecules of **1a** is tilted by almost 90° from a parallel alignment and its substituents are situated at the 1- and 2′-positions, which permits linear hydrogen bonding with the $\pi-\pi$ stacked **4** dimer. As a result, the supramolecular structure is stabilized by cooperative interactions involving six hydrogen bonding motifs formed between pyridine and carboxylic acid as well as inter- and intramolecular $\pi-\pi$ stacking forces present between pyridine rings and benzene rings. This structure rep-

resents the rational construction of a discrete supramolecular aggregate through predetermined algorithms based on hydrogen bonds and $\pi-\pi$ stacking interactions, which are preprogrammed in the structures of their molecular precursors.

Conclusion

In this study, we have shown that a simple combination of ferrocenyl dipyridines and aromatic carboxylic acids can create a variety of supramolecular architectures by self-assembly. The complexation of ferrocenyl bipyridine with alkoxybenzoic acids afforded binary cocrystals composed of supramolecular arrays assembled through the hydrogen-bonding motif between COOH and pyridine. Their thermal studies demonstrated that this convenient cocrystallization process could be adopted for the generation of metal-containing liquid crystalline materials. In the cocrystallization of ferrocenyl bipyridine with isophthalic acid and phthalic acid, the proton transfer occurred and cocrystals containing ionic supramolecular species were generated, respectively. Moreover, complexation with terephthalic acids and trimesic acids afforded [2 + 2] and [2 + 3] assembled discrete cyclic arrays, which are sustained by the cooperative interactions of hydrogen bonding and $\pi-\pi$ stacking forces. These structures may be a fundamental example for the rational design of a novel supramolecular structure by a noncovalent synthesis strategy based on an understanding of the noncovalent intermolecular forces between molecular components. In the context of crystal engineering, we believe that this result offers considerable potential for rational design of inorganic−organic hybrid crystalline structure and composition with specific solid-state properties.

Supporting Information Available: Tables of selected bond lengths and angles, and X-ray crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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