Organometallic−Organic Hybrid Crystals from Ferrocenyl Dipyridine and Binaphthol: Different Crystal Structures and Nonlinear Optical Properties Depending upon the Reaction Medium and Optical Purity of Binaphthol

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The hydrogen bond directed molecular recognition between 1,1′-bis(ethenyl-4-pyridyl)-ferrocene (**1**) and (±)-1,1′-binaphthol (**2**)/(−)-1,1′- binaphthol ((−)-**2**) has been studied by cocrystallization in different solvents. Single-crystal X-ray structures reveal that 3:2, 2:1, and 1:1 complexes (**3**, **4**, and **5**, respectively) of 1,1′-bis(ethenyl-4-pyridyl)ferrocene (**1**) and (±)-1,1-binaphthol (**2**) are formed in tetrahydrofuran, methanol, and ethanol, respectively. **5** has a noncentrosymmetric packing arrangement, and an efficiency of 0.3 times that of urea in second-harmonic generation has been measured at 1295 nm. An X-ray crystal structure of **6**, 1:1 complex of **1** with (−)-**2** in ethanol, reveals that all the molecular dipoles are aligned in the same direction (i.e, a polar crystal), but **6** has modest nonlinear optical properties (ca. 0.4 times that of urea).

Introduction

Crystal engineering is a powerful technique that allows one to design crystals with specific solid-state properties.[1] The possibility of utilizing hydrogen bonds as a means of engineering novel materials with desired structural characteristics is currently a topic of intense investigation.[2] Most studies described so far are based on organic motifs. Recently, it has been recognized[1c,3] that the structural and chemical versatility of organometallic molecules can be utilized to prepare solids with predefined physical and chemical properties.

We have synthesized conformationally flexible 1,1′-bis(ethenyl-4-pyridyl)ferrocene (**1**) to use as an assembler and studied the cocrystallization of **1** with racemic (±)-1,1′-binaphthol (**2**) in MeOH, THF, and EtOH. Unexpectedly, the supermolecule obtained from the cocrystallization of **1** and **2** in EtOH belongs to the non-centrosymmetric space group. This result has stimulated our curiosity to study the cocrystallization of **1** with (−)-1,1′-binaphthol ((−)-**2**) in EtOH. Herein we describe our study on the cocrystallization of **1** with **2** in MeOH, THF, and EtOH and with (−)-**2** in EtOH.

Experimental Section

General Considerations. (±)-1,1-Binaphthol (**2**) and (−)-1,1′-binaphthol ((−)-**2**) (Aldrich) were used as received. Cocrystallization was carried out under air. ^{1}H NMR spectra were recorded with a Bruker 300 spectrometer. Elemental analysis was performed by the Analytical Center, College of Engineering, Seoul National University. Melting points were measured on a Thomas-Hoover capillary melting point apparatus 6427-H10 and not corrected. The synthesis of **1** has been reported[4] very recently.

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Table 1. Crystal Data and Structure Refinement for 1, 3, 4, 5, and 6

	1	3	4	5	6
formula	$C_{24}H_{20}FeN_2$	$C_{64}H_{60}Fe_{1.5}N_3O_4$	$C_{68}H_{56}Fe_2N_4O_3$	$C_{46}H_{40}FeN_2O_3$	$C_{44}H_{34}FeN_2O_2$
fw	392.27	1018.93	1088.87	724.65	678.58
temp, K	293(2)	293(2)	293(2)	293(2)	293(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	triclinic	triclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	Cc	$C2$
a, Å	7.5712(9)	11.2617(9)	11.4016(11)	14.4953(11)	14.6369(13)
b, Å	10.6230(6)	16.039(2)	15.6189(12)	10.7993(11)	10.9368(13)
c, Å	23.313(3)	17.762(2)	17.638(2)	23.770(2)	11.6928(13)
α, deg	90	113.245(9)	70.461(8)	90	90
β, deg	90	107.599(7)	75.708(9)	91.457(6)	114.769(8)
γ, deg	90	95.433(8)	69.481(7)	90	90
V, Å^3	1875.0(3)	2724.7(5)	2742.2(5)	3719.7(5)	1699.6(3)
Z	4	2	2	4	2
R1	0.0605	0.087	0.078	0.0413	0.0337
wR2	0.2279	0.298	0.205	0.0701	0.0597

Synthesis of 1. To the solution of lithium diisoproylamide (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 (1.5 mL, 15.4 mmol) at −78 °C. While the solution was stirred at room temperature for 30 min, the solution turned 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 $POCl_3$ (1 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 (30 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_2O/MeOH (v/v, 1:1) gave 1.70 g of **1** (70%). Single crystals suitable for X-ray study were grown by slow evaporation of the THF solution of **1**. Mp: 215 °C dec. ^1H NMR (C_6D_6, 300 MHz): δ 8.49 (d, 6.0 Hz, 4 H), 6.68 (d, 6.0 Hz, 4 H), 6.61 (d, 16.2 Hz, 2 H), 6.25 (d, 16.2 Hz, 2 H), 4.21 (t, 1.7 Hz, 4 H, Cp), 4.07 (t, 1.7 Hz, 4 H, Cp) ppm. Anal. Calcd for $C_{24}H_{20}FeN_2$: C, 73.48; H, 5.14; N, 7.14. Found: C, 73.48; H, 5.14; N, 7.34.

Cocrystallization. 3. Compounds **1** (20 mg, 0.051 mmol) and **2** (14.6 mg, 0.051 mmol) were dissolved in 3 mL of THF. The solution was allowed to evaporate at room temperature for 4−5 days. Red lamellar crystals were isolated in 72% yield (based on **1**). IR (KBr pellet): ν_{O-H} 3405 cm^{-1} (very weak). Anal. Calcd for $C_{128}H_{120}Fe_3N_6O_8$: C, 75.44; H, 5.93; N, 4.12. Found: C, 75.43; H, 5.55; N, 4.48.

4. The red needle-shaped crystals of **4** were obtained in the same way as **3**, using MeOH instead of THF as the reaction medium. Yield based on **1**: 58%. IR (KBr pellet): ν_{O-H} 3421 cm^{-1} (very broad and weak). Anal. Calcd for $C_{68}H_{56}Fe_2N_4O_3$: C, 75.07; H, 5.19; N, 5.15. Found: C, 74.95; H, 5.25; N, 5.13.

5. The red lamellar crystals of **5** were obtained in the same way as **3**, using EtOH instead of THF as the reaction medium. Yield based on **1**: 88%. IR (KBr pellet): ν_{O-H} 3500 cm^{-1} (very broad). Anal. Calcd for $C_{46}H_{39}FeN_2O_3$: C, 76.35; H, 5.43; N, 3.87. Found: C, 76.13; H, 5.12; N, 4.08.

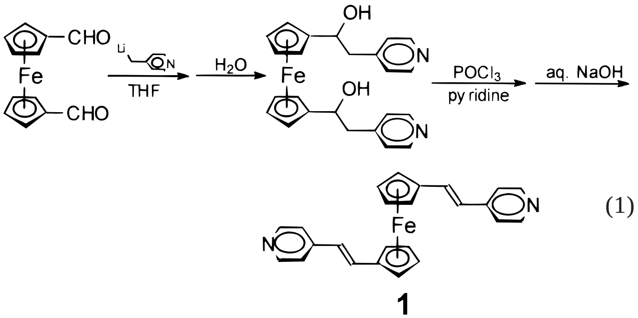
6. Compounds **1** (80.7 mg, 0.20 mmol) and ((−)-**2**) (58.9 mg, 0.20) were dissolved in 10 mL of EtOH. After evaporation of the solvent at room temperature for 7 days, long block-shaped crystals of **6** were obtained in 91% yield. Mp: 180 °C. IR (KBr pellet): ν_{O-H} 3438 cm^{-1}. Anal. Calcd for $C_{44}H_{34}FeN_2O_2$: C, 77.88; H, 5.05; N, 4.13. Found: C, 78.07; H, 5.03; N, 4.30.

Crystal Structure Determination of 1, 3, 4, 5, and 6. Crystals of **1** was grown by THF, crystals of **3** and **4** were grown by slow evaporation of the solvent in THF and methanol, respectively, and **5** and **6** were grown by slow evaporation of the solvent in ethanol. Diffraction was measured by an Enraf-Nonius CAD4 automated diffractometer. Unit cells were determined by centering 25 reflections in the appropriate 2θ range. Other relevant experimental details are listed in Table 1. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically; H1″ and H2″ in **3**, H1 and H1′ in **4**, H(01) and H(02) in **5**, and H(1) and H(9) in **6** were found in the Fourier map and refined isotropically. The thermal ellipsoids at C18 and C19 in **5** showed high positional and thermal parameters due to the two positions of the double bond[5] in fragment **1**. Final occupancy ratio converged to 56.8(3.8):43.2(3.8) for C18/C19 and C18′/C19′. The same thing happened to **6**. The final occupancy ratio in **6** converged to 65.7(3.7):34.3(3.7) for C6/C7 and C6′/C7′.

SHG Measurements. The measurements of second harmonic generation (SHG) intensity were carried out by the Kurtz−Perry powder technique,[6] using the beam of $\lambda = 1.295$ μm and $I = 5$ MW/cm^2 generated by a BBO optical parametric oscillator pumped by a Nd:YAG laser. Samples in the range 75−150 μm were used, and the thickness of the samples was 270 μm.

Results

Synthesis and Crystal Structure of 1. Ferrocenes adopt various conformations depending upon the magnitude of the rotational barrier[7] and can be considered in a sense as nonrigid molecules that have variable structures. Thus, compound **1** was prepared from 1,1′-ferrocenedicarboxaldehyde, which is readily accessible from ferrocene (eq 1).



(1)

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Treatment of 1,1′-ferrocenedicarboxaldehyde with the lithium carbanion of 4-picoline followed by protonation

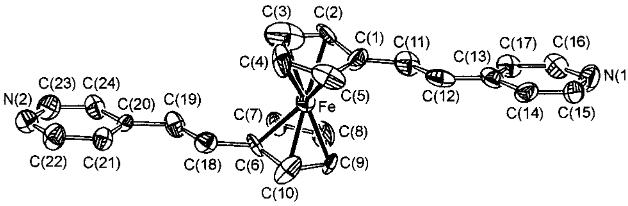

Figure 1. An ORTEP drawing of **1**.

and dehydration gave **1** in 70% yield. Very recently, Beck et al. reported[4] the preparation of **1** and studied its application in the synthesis of nonlinear optical material. They used the Wittig−Horner reaction of aldehydes with diphenyl(4-picolyl)phosphane oxide to obtain ferrocenyl dipyridine derivatives. Single crystals of **1** suitable for an X-ray study were grown by slow evaporation of the THF solution of **1**. Crystal data and details of refinement are given in Table 1, and Figure 1 shows the view of molecule **1**, which belongs to noncentrosymmetric $P2_12_12_1$. For the structure of **1**, bonding parameters fall in the expected range.[8] The Cp rings are planar and nearly parallel, the angle between the planes being 1.30°. The torsion angles between the cyclopentadienyl ring and pyridine ring are 13.12° and 15.56°. The two cyclopentadienyl rings on **1** adopt a staggered conformation, while the two substituents of **1** adopt a typical 1,3′-orientation,[9] i.e., an anti-fashion.

Cocrystallization of 1 with 2 and Crystal Structures of 3, 4, and 5. The use of (±)-1,1-binaphthol in the preparation of inclusion compounds through hydrogen bonding with alcohols, amines, and amides is quite popular.[10] Thus, we expect that changing the reaction medium in the crystal engineering of (±)-1,1-naphthol-related compounds may allow one to obtain different supramolecular architectures. Cocrystallization of **1** with **2** has been carried out in several solvents including THF, MeOH, and EtOH.

Cocrystallization of **1** with **2** in THF at room temperature led to the isolation of **3**. The supermolecule **3**, belonging to the space group $P\bar{1}$, contains **1** and **2** in the ratio of 3:2, along with solvent molecules (Figure 2). Selected intra- and intermolecular bond lengths and angles are given in Table 2. The asymmetric unit was chosen to contain one and a half molecules of **1**, one molecule of **2**, and two molecules of THF. The supermolecule consists of a crystallographically imposed inversion center at the iron of *anti*-**1**. Thus, through the symmetry operation, (*S*)-(−)- and (*R*)-(+)-**2** are bridged by a symmetric bridging group, *anti*-**1**, with the ferrocene moiety being staggered via hydrogen bonding (N1−O2″, 2.667 Å; ∠N1−H2″−O2″, 147.4°). (*S*)-(−)- and (*R*)-(+)-**2** are also hydrogen bonded to two *syn*-**1** (N2−O1″, 2.713 Å; ∠N2−H1″−O1″, 169.3°) with ferrocene being eclipsed groups and with the dihedral angle between the two naphthalene rings in **2** being 83.6°. Thus, *syn*- and *anti*-**1** coexist in the same supermolecule. Through a symmetrical bridging group *anti*-**1**, two enantiomeric components, (*S*)-(−)- and (*R*)-(+)-**2**, associate to give an achiral supermolecule **3** of meso type. Two molecules of THF are in an asymmetric unit, presumably arising from difficulties in close-packing of **1** and **2**.

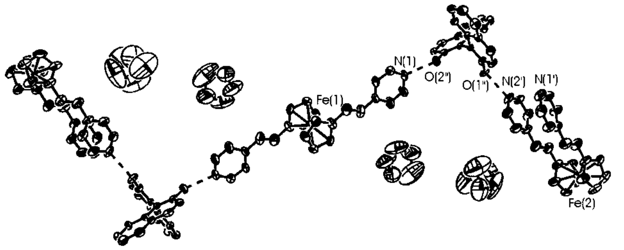

Figure 2. Structure of **3** with some hydrogen-bonding contacts indicated (broken lines).

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3, 4, 5, and 6[a]

		3	
Fe(1)−C(3)	1.992(11)	C(6)−C(7)	1.194(13)
Fe(1)−C(5)	2.044(9)	C(11′)−C(12′)	1.288(13)
Fe(2)−C(9′)	1.996(12)	C(18′)−C(19′)	1.271(14)
Fe(2)−C(10′)	2.038(10)	C(2″)−O(1″)	1.342(10)
C(16′)−N(1′)	1.301(14)	C(12″)−O(2″)	1.368(9)
C(15′)−N(1′)	1.321(13)	C(11″)−C(12″)	1.369(11)
C(1)−Fe(1)−C(1)#1	180.00(3)	C(1″)−C(2″)−O(1″)	119.4(8)
C(1′)−Fe(2)−C(6′)	110.4(4)	C(11″)−C(12″)−O(2″)	117.7(9)
		4	
Fe(1)−C(1)	2.042(8)	C(22″)−N(2′)	1.30(2)
Fe(1)−C(6)	2.054(8)	C(01)−O(1)	1.357(9)
Fe(2)−C(1′)	2.055(7)	C(01′)−O(1′)	1.365(8)
Fe(2)−C(6′)	2.069(7)	C(02)−C(02′)	1.486(10)
C(23)−N(2)	1.334(10)		
C(1)−Fe(1)−C(6)	110.3(3)	C(02)−C(01)−O(1)	117.1(7)
C(1′)−Fe(2)−C(6′)	108.2(3)	C(02′)−C(01′)−O(1′)	117.8(7)
		5	
Fe−C(5)	2.014(7)	C(02)−O(01)	1.354(7)
Fe−C(6)	2.057(7)	C(012)−O(02)	1.366(8)
C(22)−N(2)	1.318(9)	C(01)−C(011)	1.479(7)
C(16)−N(1)	1.332(9)		
C(1)−Fe−C(6)	110.4(3)	C(O11)−C(012)−O(02)	118.2(5)
C(01)−C(02)−O(01)	117.3(5)		
		6	
Fe−C(2)	2.024(5)	C(11)−N(1)	1.323(8)
Fe−C(3)	2.038(5)	C(14)−O(1)	1.357(5)
C(10)−N(1)	1.322(8)	C(13)−C(13)#3	1.488(7)
C(1)−Fe−C(1)#2	117.0(4)	C(13)−C(14)−O(1)	118.9(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z+1$; #2 $-x, y, -z+1$; #3 $-x, y, -z$.

Cocrystallization of **1** and **2** in methanol at room temperature gave the crystalline supermolecule **4**, which belongs to the space group $P\bar{1}$ as **3**. An asymmetric unit in **4** consisting of two molecules of **1**, one molecule of **2**, and one molecule of water is shown in Figure 3. Selected intra- and intermolecular bond lengths and angles are given in Table 2. Each asymmetric unit contains (*S*)-(−)-**2** or (*R*)-(+)-**2** and is chiral. The asymmetric units are packed in a centrosymmetric

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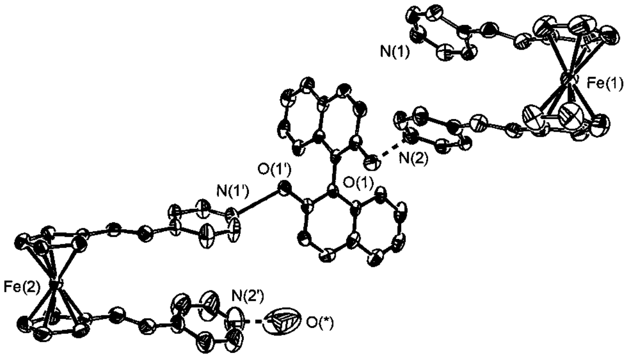

Figure 3. Structure of **4** with some hydrogen-bonding contacts indicated (broken lines).

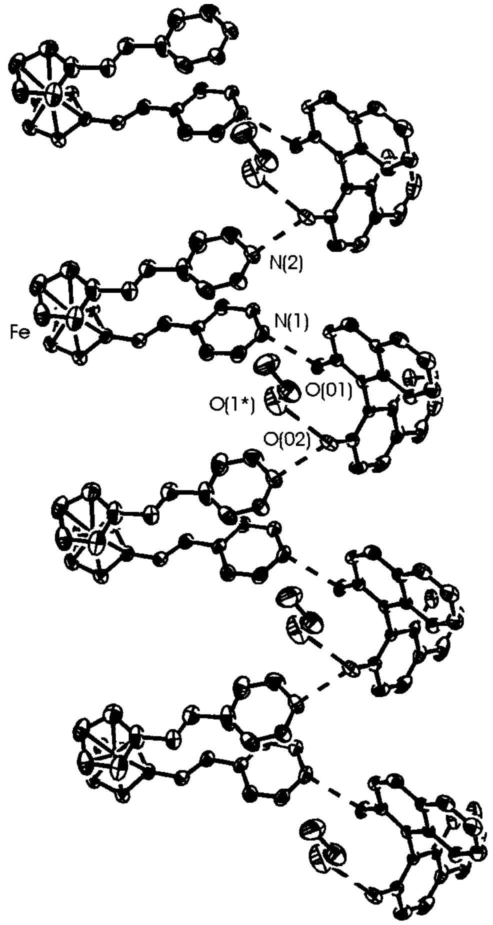

Figure 4. Structure of **5** with some hydrogen-bonding contacts indicated (broken lines).

fashion. Figure 3 shows that the ferrocene unit is of an almost perfectly eclipsed conformation. The two hydroxy groups in **2** are hydrogen bonded to a pyridyl group of *syn*-**1** and a pyridyl group of another *syn*-**1**, with the dihedral angle between the two naphthalene rings in **2** being 79.1° and bond distances of O1···N2, 2.712 Å, and O1′···N1′, 2.681 Å, and bond angles of ∠N2−H1−O1, 161.1°, and ∠N1′−H1′−O1′, 164.0°. Water molecules are included in **5** and bonded to one of the free pyridyl groups with a bond distance of N2′···O*, 2.8278 Å.

Cocrystallizion of **1** and **2** in ethanol at room temperature resulted in the supermolecule **5** with **1**, **2**, and ethanol in the ratio of 1:1:1. The crystal structure of **5** (Figure 4), belonging to the space group *Cc*, looks like a stairlike chain structure. Selected intra- and intermolecular bond lengths and angles are given in Table 2. Each chain consists of **1** and **2** in the ratio of 1:1 with hydrogen bonds (bond distances N1−O01, 2.694 Å, and N2···O02, 2.698 Å, and bond angles of ∠N1−H01−O01, 160.6°, and ∠N2−H02−O02, 166.0°), and the dihedral angle between the two naphthalene rings in **2** is 85.2°. Each chain consists of the same enantiomers (*RRRR*-**2** or *SSSS*-**2**) and is chiral. Each chain is connected to each other through the C−H···π interaction[11] between the Cp ring in one chain and the aromatic ring of naphthalene in another chain: the Cp ring and naphthalene ring are almost perpendicular to each other, with a dihedral angle of 81.0°, the distance (3.598 Å) between the centroid of the closest aromatic ring of **2** and the nearest C atoms of Cp is shorter than the shortest distance (3.787 Å) between the C atoms of the closest aromatic ring of **2** and the nearest C atoms of Cp, and the angle C−H···centroid is 160.0°. Thus, each chain is connected to each other, and the chains are packed in a non-centrosymmetric manner, i.e., a polar crystal. Strands are cross-linked to form a two-dimensional network through aromatic C−H···π interactions and act like threadlike molecules eventually to form a three-dimensional interwoven system.

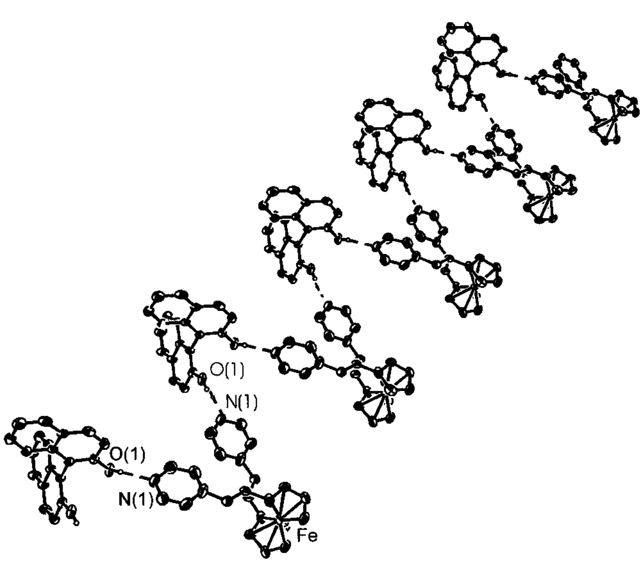

Figure 5. Single stranded helical structure of **6** maintained by hydrogen bonding.

Cocrystallization of 1 with (−)-2 and Crystal Structure of 6. Cocrystallization of **1** with (−)-**2** was carried out in THF, methanol, and ethanol, respectively. However, cocrystallization of **1** and (−)-**2** in THF and methanol, respectively, gave powdered materials. Cocrystallization of **1** with (−)-**2** from ethanol in a molar ratio 1:1 resulted in the formation of supramolecular complex **6**. X-ray analysis (Figure 5) of **6**, belonging to the space group *C*2, revealed tubular-helical 1:1 assemblies of circular structures linked by hydrogen bonds, $\pi-\pi$ interactions, and aromatic C−H···π interactions. Selected intra- and intermolecular bond lengths

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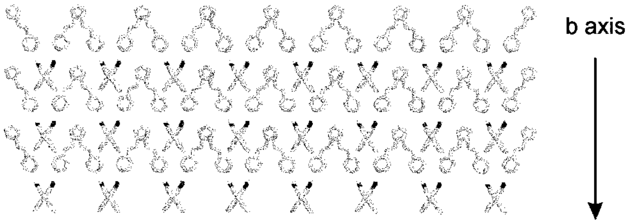

Figure 6. Two-dimensional layered structure of **6** assembled through the CH···π interaction (view down the *a* axis); note the perfect alignment of molecular dipole moments along the *b* axis.

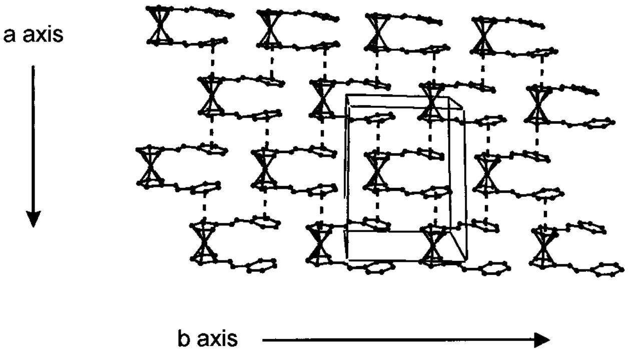

Figure 7. Molecular packing diagram of **6** illustrating the π-stacking between Cp and pyridyl rings (view down the *c* axis); note the perfect arrangement of molecules along the *b* axis. Molecules of (−)-1,1′-binaphthol are omitted for clarity.

and angles of **6** are given in Table 2. Supermolecule **6** forms a well-defined supramolecular structure. The two substituents on the cyclopentadienyl groups of the ferrocene are situated at 1- and 2′-positions (a dihedral angle of 36.6°), and the interplanar angle between the two pyridyl rings is 22.0°, which allows nearly linear hydrogen bonds to be formed. The bond distance between heteroatoms in the hydrogen bond is 2.706 Å, the bond distance of H−O in the hydrogen bond is 0.811 Å, and that of H···N is 1.917 Å. The bond angle of ∠O−H−N is 164.0°. One of C−H bonds of the pyridyl rings interacts with one of the aromatic rings of binaphthol in an edge-to-face manner, eventually to align all the molecular dipoles in the same direction (i.e., a polar crystal) (*b* axis). The distance between the centroid of the closest aromatic ring of the binaphthol and the nearest C atom of pyridyl is 3.840 Å (H−centroid 2.970 Å; C−H···centroid 157.2°), and the interplanar angle is 88.0°. Thus, each strand is cross-linked to form a two-dimensional layer through aromatic C−H···π interactions (Figure 6). A self-assembly of layers develops, in which the two cyclopentadienyl rings of ferrocene are π-stacked to two pyridine rings of another discrete complex. All of the cyclopentadienyl rings and pyridine rings are π−π stacked with each other (Figure 7). Such π−π stacking appears to play an important role in the formation of three-dimensional aggregates.[10a,12]

Discussion

The hydrogen-bonding patterns observed in **3**, **4**, and **5** are quite different; supermolecule **3** consists of three molecules of **1** (two molecules of *syn*-**1** and one molecule of *anti*-**1**) and (*S*)-(−)- and (*R*)-(+)-**2** with four hydrogen bonds, **4** consists of *syn*-**1** and **2** in the ratio of 2:1 with two hydrogen bonds, and **5** consists of *syn*-**1** and **2** in the ratio of 1:1 with hydrogen bonds. The X-ray crystal structure of free **1** (Figure 1) shows an anti-conformation. However, to achieve good hydrogen bonding *anti*- and *syn*-**1** coexist in **3**, while in **4** and **5** only *syn*-**1** is observed. Thus, the versatility observed in the recognition of chiral components in **3**, **4**, and **5** seems to be closely related to the flexibility of **1**.[7] In **3** and **5**, solvent molecule(s) was (were) included and in **4** water molecules instead of methanol. The water molecules in **4** might come from air during the cocrystallization. When the cocrystallization of **1** with **2** was carried out in wet ethanol, no water molecules were included in the crystal: **5** was obtained. The inclusion of water molecule in **4** was presumably due to the methanol itself. The change of reaction medium affects greatly the crystal structure.

Recently, crystal engineering targeted at crystals exhibiting large optical nonlinearities has attracted much interest because supramolecular effects[13] can be applied to prevent antiparallel stacking of nonliner chromophores and to favor a polar order. It has been also reported[14] that it is possible to induce preferential crystallization of non-centrosymmetric polymorphs by using polar solvents. However, results obtained thus far for guest−host inclusion complexes are not impressive. Fortunately, **5** belongs to a non-centrosymmetric space group *Cc* even though we use racemic **2** as a component. Thus, **5** has a nonzero dipole moment and has an efficiency in SHG 0.3 times that of urea at 1295 nm.

Encouraged by the result of **5**, we tried to find materials possessing high nonlinear optical properties by using enantiomerically pure (−)-**2** instead of racemic **2**. Thus, cocrystallization of **1** with (−)-**2** has been carried out in THF, MeOH, and EtOH, respectively. As already mentioned, the choice of the solvent in the cocrystallization of **1** and (−)-**2** was critical. Supermolecule **6** was obtained in EtOH. The crystal structure of **6** belongs to the noncentrosymmetric space group *C*2. Compared to the crystal structure of free **1**, the ferrocene fragment in **6** is deformed and should have a nonzero dipole moment. At first, we expected that the hydrogen bonding would enhance the molecular hyperpolarizability. The electronic absorption spectrum of **6** in the solid state shows a strong band at 518 nm, which is 56 nm red-shifted compared to that of free **1**: the hydrogen bonding causes the electron-acceptibility of pyridyl groups to be higher and, consequently, the 1,1′-bis(ethenyl-4-pyridyl)ferrocenyl moiety to have an enhanced dipole moment. As shown in Figure 6, all the molecular dipoles align in the same direction (i.e., a polar crystal). Thus, a large second-harmonic generation was expected. However, contrary to our expectation, an efficiency 0.4 times that of urea has been measured at 1295 nm presumably due to the phase mismatching. The reason for the poor efficiency has not been solved yet and will be the topic to resolve in the near future.

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Conclusion

We have demonstrated the ease of assembly of ferrocenyl dipyridine (**1**) and binaphthol (**2** or (−)-**2**) into crystalline supramolecular aggregates. Crystal structures and solid-state properties are quite sensitive to the change of the reaction medium: cocrystallization of **1** and **2** in THF forms a 3:2 complex (**3**), in MeOH a 2:1 complex (**4**), and in EtOH a 1:1 complex (**5**). Supermolecules **3** and **4** belong to the centrosymmetric space group $P\bar{1}$, while for **5** hydrogen bonding leads to noncentrosymmetric packing arrangement (*Cc*) with modest nonlinear optical properties. Supermolecule **6**, obtained by the cocrystallization of **1** with (−)-**2** in EtOH, is a polar crystal with a perfect dipole alignment. However, the efficiency of **6** in the second-harmonic generation was not high as expected, but was only 0.4 times that of urea.

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Supporting Information Available: Herringbone interactions in crystal **5** and the network of C−H⋯π interactions of neighboring helicates in **6**, and tables of atomic coordinates, complete bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1**, **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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