Crystal Engineering with Structurally Flexible 1,1′-Substituted Ferrocenes for Nonlinear Optical Materials

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Cocrystals derived from 1,1′-bis(ethenyl-4-pyridyl)ferrocene (**1**) and resorcinol/phloroglucinol and a crystal of 1,1′-bis-(ethenyl-4-quinolinyl)ferrocene (**5**) have been studied with the aim of engineering crystalline NLO materials. X-ray structure analyses revealed a NLO active *syn*-type molecular conformation of **1** and **5** via hydrogen bonding with resorcinol/phloroglucinol and π-π interaction between quinoline rings, respectively. For **5**, all molecular dipoles are aligned in the same direction and the SHG efficiency is about 4 times that of urea.

Introduction

Crystal engineering, based on an understanding of physical phenomena such as charge transfer, electrostatic interaction, hydrogen bonding, van der Waals interaction, and π−π stacking, is a powerful technique for the production of functionalized solid materials with optimized properties.[1,2] It has been applied to various organometallic compounds.[3,4] Flexible π-bonds between metal and ligands produce highly variable organometallic structures (and packing modes), depending on the solid-state intra- and intermolecular nonbonding interactions.

Because of the significant electron-donating strength of the ferrocenyl group it is regarded as a good donor part of a donor−π-acceptor system for chromophores with high NLO responses.[5−10] Thus far, most efforts to synthesize NLO materials have concentrated on mono-acceptor conjugated ferrocenyl compounds, with little work on bis-substituted systems.[11] During an investigation into the preparation of chromophores with high NLO responses, we reported the crystal structures of 1,1′-bis(ethenyl-4-pyridyl)-ferrocene, **1**, and its cocrystals with 1,1′-binaphthol.[12] The two substituents on the cyclopentadienyl group of **1** adopt a typical 1,3′-orientation, i.e., in *anti*-fashion. Cocrystals of **1** with 1,1′-binaphthol in methanol and ethanol have the two substituents of the ferrocene at the 1- and 1′-positions, respectively. The use of optically pure 1,1′-binaphthol led to a noncentrosymmetric packing arrangement. Thus, the moiety **1** in cocrystals was quite flexible and its conformation appears to be sensitive to the hydrogen-bonding patterns with 1,1′-binaphthol molecules or incorporated solvent molecules. Consequently, we sought to establish a simple and transferable crystal engineering strategy for achieving the NLO active molecular conformation of the bis-substituted ferrocenyl molecule with readily available aromatic alcohols such as 1,3-dihydroxybenzene (resorcinol) and 1,3,5-trihydroxybenzene (phloroglucinol).[13,14] In addition, an analogue, 1,1′-bis(ethenyl-4-quinolyl)ferrocene, **5**, containing additional aromatic rings was synthesized to induce a π−π interaction between the aromatic rings, eventually leading to a *syn*-type molecular conformation. We report here the results of our investigation of the cocrystallization of **1** with resorcinol and phloroglucinol as well as the synthesis and crystal structure of **5**.

Results and Discussion

Cocrystallization of 1 with Resorcinol and Phloroglucinol: Crystal Structures of 2, 3, and 4

Resorcinol and phloroglucinol function as multifunctional hydrogen bond donors in the crystal engineering of one- or two-dimensional structures.[15,16]

When equimolar amounts of **1** and resorcinol were dissolved in THF and the resultant solution allowed to evaporate at room temperature, long block-shaped crystals of **2** were isolated in quantitative yield. X-ray crystallographic analysis reveals the formation of supramolecule **2** that contain **1** and resorcinol in the ratio 1:1 (Figure 1). A molecule of **1** and resorcinol are coupled via two hydrogen bonds between the pyridines of **1** and the hydroxy groups of **2**. The two cyclopentadienyl rings on **1** adopt an eclipsed con-

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formation while the two substituents of **1** adopt a 1,1′ -orientation, i.e., a *syn*-fashion. For simultaneous hydrogen bonds with two widely separated oxygen atoms [O01−O02, 4.797(6) Å], the separation of the two pendant ligands smoothly increases from 3.398(7) (C11−C18) to 4.172(6) Å (N1−N2), which makes **1** appear to stretch its arms toward a resorcinol molecule. The two pyridine ring centers are 3.967 Å apart and the two ring planes make a torsion angle of 12.5(3)°. The phenyl ring of resorcinol in **2** is slightly inclined to make an angle of 64.1(2)°−83.8(2)° with the cyclopentadienyl rings and the pyridine rings of **1**. Compared with the symmetric molecular structure of free ligand **1**, the ferrocene fragment in **2** is largely deformed into an asymmetric structure, which is expected to have a nonzero molecular dipole moment. However, supramolecules **2** are packed in a centrosymmetric manner (space group: $P2_1/n$) and the net molecular dipole moments in the crystal should be zero.

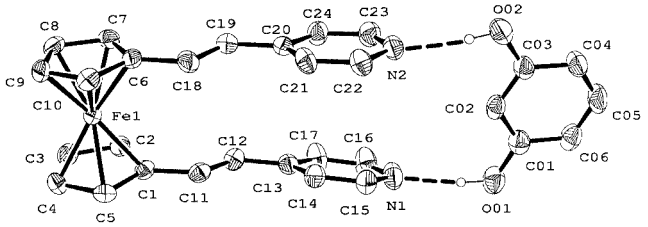


Figure 1. ORTEP drawing of **2** with 30% thermal ellipsoids

Cocrystallization of **1** with phloroglucinol was carried out in THF and EtOH, respectively. In THF at room temperature supramolecule **3** was formed, a unit of which consists of one molecule of **1**, one of phloroglucinol, and one solvent molecule of THF (Figure 2). The molecular structure of **1** (*syn*-type) and the hydrogen-bonding pattern are very similar to those in **2**. Of the three hydroxy groups of phloroglucinol, two make hydrogen bonds with pyridines of **1**, and the third is interconnected with a THF molecule. The conformation of phloroglucinol and the hydrogen bonds with the two pyridines are very similar to what is found in its cocrystal with 2,4-dimethylpyridine.[16] Supramolecules of **3** are packed in a centrosymmetric manner (Space group: $P2_1/n$) in the same way as **2**.

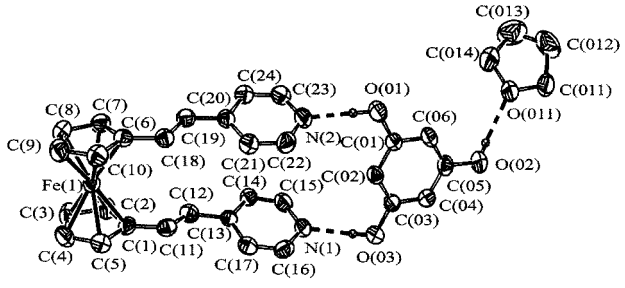


Figure 2. ORTEP drawing of **3** with 50% thermal ellipsoids

Cocrystallizion of **1** and phloroglucinol in EtOH at room temperature resulted in a supramolecule **4**, which consists of three components of **1**, phloroglucinol, and EtOH in the ratio 1:1:1. The crystal structure of **4** is a stair-like chain structure (Figure 3). A molecule of **1** in crystal **4** also makes double hydrogen bonds with a phloroglucinol molecule and shows a *syn*-type conformation, as it does in **2** and **3**. The incorporated EtOH molecule acts as a paste that connects components in the construction of a hydrogen-bonded supramolecular chain structure. It serves as a hydrogen donor to a phloroglucinol and also as a hydrogen acceptor to another phloroglucinol molecule. Every molecule of **1** within a supramolecular unit is fixed, facing the same direction, and their molecular dipole moments accumulate in a supramolecular unit. Crystal **4** belongs to the noncentrosymmetric space group, *Pc*. However, its asymmetric unit is composed of two triads of molecules with a pseudoinversion relation and two kinds of supramolecular chain face in opposite directions in a crystal (Figure 4). Therefore, the net dipole moment of the crystal **4** is expected to be close to zero.

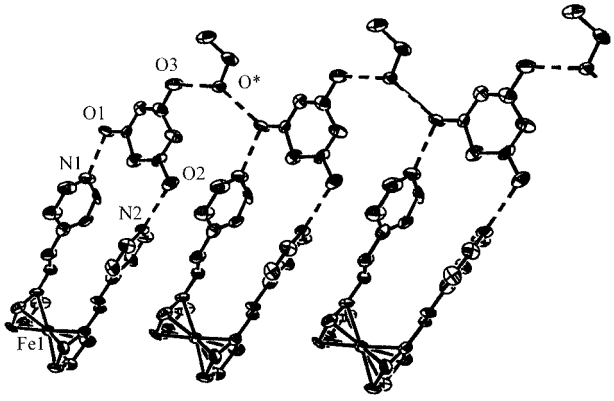


Figure 3. ORTEP drawing of **4** with 50% thermal ellipsoids

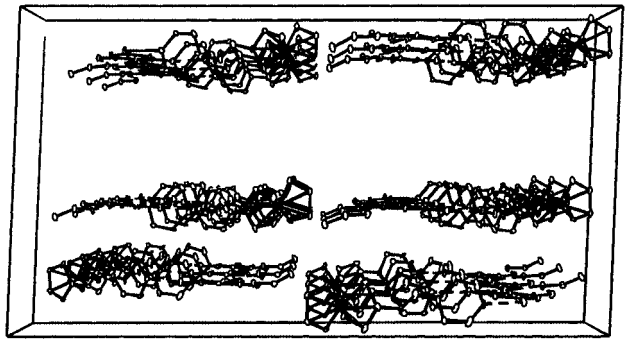
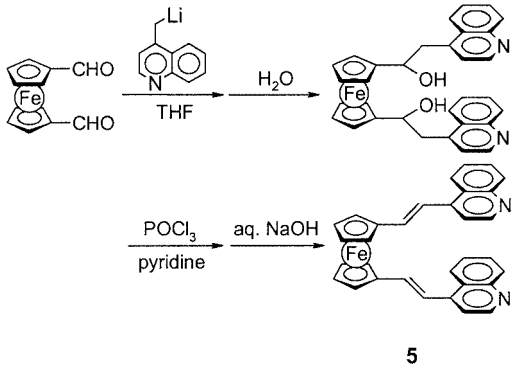


Figure 4. Cell packing diagram of **4**

Synthesis and Crystal Structure of 5

Compound **5**, an analogue of **1**, containing an additional aromatic ring for intramolecular stacking was prepared by treatment of 1,1′-ferrocenedicarboxaldehyde with the lithium carbanion of lepidine followed by protonation and dehydration (73% yield) (Scheme 1).



5

Scheme 1. Synthesis of **5**

Single crystals of **5** suitable for an X-ray study were grown by slow evaporation of an MeOH solution of **5**. Figure 5 shows a view of **5**, which belongs to the noncentrosymmetric space group, *Cc*.

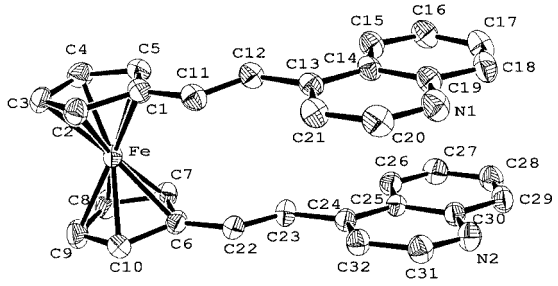


Figure 5. ORTEP drawing of **5** with 30% thermal ellipsoids

The molecular structure of **5** displays a polar conformation with a nonzero dipole moment. Two substituents of **5** adopt a 1,1′-orientation with an eclipsed conformation. The torsion angles of C(1)−C(11)−C(6)−C(22) and C(12)−C(13)−C(23)−C(24) are 8.6° and 8.0°, respectively, and the twist angle between two Cp rings is 7.5°. Two quinoline-bearing substituents lie on top of each other, indicating intramolecular stacking. The pyridine ring centers and the benzene ring centers are 3.657 and 3.876 Å apart, respectively. The tilt angle between two quinoline planes is 6.1(1)°, which quantitatively expresses the occurrence of π−π interactions between the two rings. Previously, Togni et al.[17] reported a similar eclipsed molecular structure for 1,1′-disubstituted ferrocene by virtue of the attractive interaction between two sulfur-containing fragments. However, in contrast to the highly tilted molecular structure in Togni's result, the Cp and quinoline rings of **5** are roughly coplanar with dihedral angles of 7.6(2)° and 11.2(2)°. A coplanar arrangement of Cp and substituents of **5** may allow maximum orbital mixing and effective electronic communication between an electron-donating ferrocene and electron-withdrawing quinoline groups, i.e., effective delocalization along the conjugated chains. Two N atoms of quinolines of **5** make contacts with quinoline and Cp rings in neighboring molecules (Figure 6). The CH···N distances of 2.59(4) and 2.78(4) Å and the C−H···N angles of 160(3)° and 167(3)° indicate weak C−H···N hydrogen-bonding interactions. The distances and angles fall in the range of reported interactions between $C(sp^2)$−H and N in a heterocyclic group.[18b−18d] Both intermolecular C−H···N interactions are arranged in almost the same direction and, eventually, cause all of the molecular dipoles in crystal **5** to align along the A axis (i.e., a polar crystal) (Figure 7). Such C−H···N interaction appears to be important in determining the crystal packing.[18]

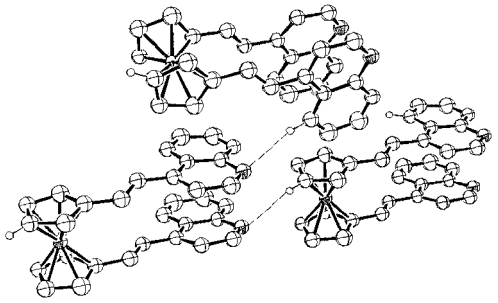


Figure 6. CH···N interactions of **5**

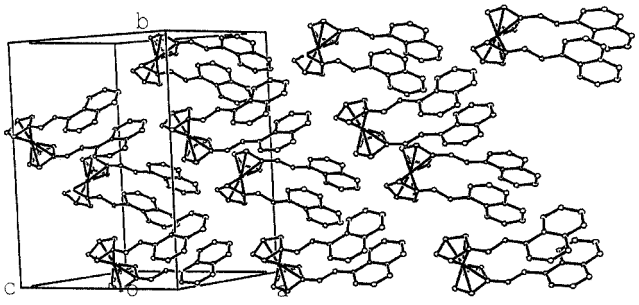


Figure 7. Cell packing diagram of **5**

Discussion

Ferrocenes adopt various conformations, depending on the magnitude of the rotational barrier, and are considered, in a sense, as nonrigid molecules that have a variable structure.[19] Free **1** crystallizes in the symmetric *anti*-conformation, which should possess a zero molecular dipole moment and hyperpolarizability.[12] However, in cocrystals of **2**, **3**, and **4**, the two substituents on the cyclopentadienyl groups of the ferrocene are situated at 1- and 1′-positions, and **1** shows a *syn*-type geometry. Resorcinol and phloroglucinol molecules act like molecular clips to create simultaneous double hydrogen bonds with a molecule of **1** and fix its conformation as a dipolar one − a prerequisite for a nonlinear optical molecule. Unlike the symmetric molecule of free **1**, asymmetric supramolecules of **2**, **3**, and **4** should possess nonzero molecular hyperpolarizabilities. However, the crystal arrangements of **2**, **3**, and **4** reveal an anti-parallel alignment of molecular dipoles, therefore no second-harmonic generations (SHG) are expected for the bulk materials. In the crystals **3** and **4**, solvent molecules of THF and EtOH are incorporated through hydrogen bonding with phloroglucinol. EtOH molecules of **4** serve as molecular

pastes to construct a supramolecular chain and align all dipoles in a supramolecular unit in the same direction.

Compound **5** crystallizes in a dipolar *syn*-type conformation due to the significant π−π interaction between two pendent arms.[20] Moreover, an almost perfect dipole alignment is realized in crystal **5** through weak intermolecular C−H···N interactions. Thus, an effective SHG was expected. When Kurtz powder measurements were performed at 1.36 μm, **5** shows an SHG efficiency of about 4 times that of urea.[21] This is quite low compared with the highest bulk susceptibility (χ^2 up to 220 times the value for urea) reported for ferrocenyl derivatives,[10c] presumably due to the weak electron-accepting ability of the quinoline group.

Conclusion

We have demonstrated two crystal engineering approaches for achieving the NLO active molecular conformation of structurally flexible disubstituted ferrocenyl compounds. An X-ray crystal structure analysis of **5** shows that it crystallizes in a NLO active conformation. The efficiency of **5** in the second harmonic generation is 4 times that of urea. This is not a high value compared with the known bulk susceptibilities for ferrocenyl derivatives. We anticipate that the introduction of more electron-withdrawing groups into the skeleton of **5** will give more efficient NLO materials. Further related research will continue to be pursued.

Experimental Section

General Remarks: Resorcinol (Aldrich), phloroglucinol dihydrate (Aldrich), and lepidine (Lancaster) were used as received. The synthesis of **5** was carried out under nitrogen by using standard Schlenk techniques. Freshly distilled, dried, and oxygen-free solvents were used throughout. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 300 spectrometer. Elemental analysis was performed by the Analytical Center, College of Engineering, Seoul National University. High-resolution mass spectroscopy was carried out at the Korea Basic Science Institute (Daegu). 1,1′-Ferrocenedicarboxaldehyde and 1,1′-bis(ethenyl-4-pyridyl)ferrocene, **1**, were prepared according to published procedures.[22,23]

Cocrystallization of 1 with Resorcinol (Synthesis of 2): Compound **1** (20 mg, 0.051 mmol) and resorcinol (5.6 mg, 0.051 mmol) were dissolved in EtOH (5 mL). The resultant solution was allowed to evaporate at room temperature for 7 days. Long block-shaped crystals of **2** were isolated in quantitative yield. $C_{30}H_{26}FeN_2O_2$ (502.40): calcd. C 71.72, H 5.22, N 5.58; found C, 71.26, H 5.34, N 5.71.

Cocrystallization of 1 with Phloroglucinol (Syntheses of 3 and 4): Compound **1** (20 mg, 0.051 mmol) and phloroglucinol dihydrate (8.3 mg, 0.051 mmol) were dissolved in THF (5 mL). The resultant solution was allowed to evaporate at room temperature for about 7 days. Red needle-shaped crystals of **3** were then isolated in quantitative yield. $C_{34}H_{34}FeN_2O_4$ (590.50): calcd. C 69.16, H 5.80, N 4.74; found C, 68.99, H 5.46, N 4.83. Red cubic crystals of **4** were obtained quantitatively in the same way as **3**, using EtOH instead of THF as the reaction medium. $C_{32}H_{32}FeN_2O_4$ (564.46): calcd. C 69.16, H 5.80, N 4.74; found C, 68.99, H 5.46, N 4.83.

Synthesis of 5: Lepidine (1.2 mL, 9.1 mmol) was added at −78 °C to a solution of LDA (generated in situ by the reaction of diisopropylamine (1.3 mL, 9.3 mmol) in THF (30 mL) with *n*BuLi (4.0 mL, 10.0 mmol) at −78 °C). The resultant solution turned reddish during stirring at room temperature for 30 min. 1,1′-Ferrocenedicarboxaldehyde (0.66 g, 2.7 mmol) was then added at room temperature. This reaction mixture turned brownish as it was stirred at room temperature for 4 h, after which excess water (30 mL) and methylene dichloride (30 mL) were added. The methylene dichloride layer was collected, evaporated to dryness, and dissolved in pyridine (15 mL). The pyridine solution was cooled to 0 °C and excess $POCl_3$ (2 mL) was added dropwise. The resultant solution turned dark green during stirring at room temperature for 1 h, after

Table 1. Crystal data and structure refinement for **2**, **3**, **4**, and **5**

	2	**3**	**4**	**5**
Empirical formula	$C_{30}H_{26}FeN_2O_2$	$C_{34}H_{34}FeN_2O_4$	$C_{65}H_{64}Fe_2N_3O_8$	$C_{32}H_{24}FeN_2$
Molecular mass	502.38	590.48	1126.89	492.38
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	Pc	Cc
a, Å	9.199(4)	9.3745(7)	18.523(3)	13.031(1)
b, Å	23.122(4)	28.2106(12)	8.8577(14)	18.937(3)
c, Å	11.671(3)	11.0040(9)	33.919(5)	10.679(1)
α, deg.	90	90	90	90
β, deg.	98.868(2)	95.666(6)	92.354(12)	116.313(8)
γ, deg.	90	90	90	90
Volume, Å^3	2452.5(12)	2895.9(3)	5560.3(15)	2362.2(5)
Z	4	4	4	4
d(calcd.), Mg/m^3	1.361	1.354	1.349	1.385
θ range, deg	1.76-24.97	1.99-24.97	2.20-24.98	3.84−27.41
No. tot. Collection	4580	5398	5059	4484
No. unique data	4299	5075	5059	4484
No. params refined	420	474	711	412
$R1$	0.0480	0.0466	0.0439	0.0389
$wR2$	0.0913	0.0885	0.1165	0.0809
Gof	0.944	1.019	1.099	1.096

Table 2. Selected intra- and intermolecular bond lengths (Å) and angles (°) for **1**,[12] **2**, **3**, **4**, and **5**

1					
C(1)−C(11)	1.46(2)	C(11)−C(12)	1.27(2)	C(12)−C(13)	1.49(2)
C(6)−C(18)	1.495(14)	C(18)−C(19)	1.32(2)	C(19)−C(20)	1.469(13)
2					
Fe(1)−C(7)	2.021(5)	Fe(1)−C(1)	2.053(4)	Fe(1)−C(6)	2.056(5)
C(1)−C(11)	1.455(6)	C(11)−C(12)	1.307(7)	C(12)−C(13)	1.458(7)
C(6)−C(18)	1.463(7)	C(18)−C(19)	1.307(7)	C(19)−C(20)	1.460(7)
C(16)−N(1)	1.321(8)	C(22)−N(2)	1.344(6)	C(01)−O(01)	1.346(6)
C(03)−O(02)	1.354(7)	N(1)−O(01)	2.733(6)	N(2)−O(02)	2.738(6)
C(1)−Fe(1)−C(6)	108.8(2)			O(01)−C(01)−C(02)	122.7(5)
O(02)−C(03)−C(02)	122.4(5)			N(1)−H(001)−O(01)	169(6)
N(2)−H(002)- O(02)	172(6)				
3					
Fe(1)−C(2)	2.032(4)	Fe(1)−C(6)	2.058(4)	C(01)−O(01)	1.361(4)
C(1)−C(11)	1.452(5)	C(11)−C(12)	1.304(6)	C(12)−C(13)	1.483(5)
C(6)−C(18)	1.453(5)	C(18)−C(19)	1.315(5)	C(19)−C(20)	1.458(5)
C(03)−O(03)	1.364(5)	C(05)−O(02)	1.371(5)	C(02)−C(03)	1.379(5)
N1−O03	2.795(5)	N2−O01	2.761(5)	O011−O02	2.772(5)
C(1)−Fe(1)−C(6)	109.14(16)			O(01)−C(01)−C(02)	122.1(4)
O(03)−C(03)−C(04)	118.0(4)			O(02)−C(05)−C(06)	122.7(4)
C(15)−N(1)−C(16)	114.1(4)			C(23)−N(2)−C(22)	114.6(4)
O011−H02−O02	172(6)			N2−H01−O01	173(4)
N1−H03−O03	176(6)				
4					
Fe(1)−C(8)	1.993(12)	Fe(1)−C(6)	2.074(10)	N(1)−C(16)	1.305(17)
C(1)−C(11)	1.488(12)	C(11)−C(12)	1.307(14)	C(12)−C(13)	1.477(12)
C(6)−C(18)	1.452(13)	C(18)−C(19)	1.215(14)	C(19)−C(20)	1.498(14)
C(22)−N(2)	1.312(19)	C(01)−O(1)	1.392(14)	C(03)−O(2)	1.256(13)
C(05)−O(3)	1.404(14)	Fe(2)−C(9′)	2.048(10)	Fe(2)−C(4′)	2.084(13)
C(01′)−O(1′)	1.358(15)	C(03′)−O(2′)	1.346.(13)	C(05′)−O(3′)	1.457(13)
C(1′)−C(11′)	1.478(14)	C(11′)−C(12′)	1.207(15)	C(12′)−C(13′)	1.459(11)
C(6′)−C(18′)	1.441(14)	C(18′)−C(19′)	1.313(13)	C(19′)−C(20′)	1.487(13)
N1−O2	2.779(13)	N2−O1	2.719(14)	N2′−O3′	2.748(13)
N1′−O1′	2.566(13)	O1*−O2′	2.769(11)	O1*−O1′	2.772(12)
O2*−O3	2.745(13)	O2*−O1	2.764(13)		
C(1)−Fe(1)−C(6)	109.4(4)			C(16)−N(1)−C(15)	114.9(10)
C(23)−N(2)−C(22)	118.4(12)			O(1)−C(01)−C(02)	117.0(9)
O(2)−C(03)−C(04)	118.4(10)			C(06)−C(05)−O(3)	118.3(11)
C(1′)−Fe(2)−C(6′)	110.3(4)			C(16′)−N(1′)−C(15′)	114.7(10)
C(23′)−N(2′)−C(22′)	116.8(11)			O(1′)−C(01′)−C(02′)	116.3(10)
O(2′)−C(03′)−C(04′)	125.8(9)			O(3′)−C(05′)−C(06′)	118.3(10)
5					
Fe−C(6)	2.055(3)	Fe−C(1)	2.060(3)	N(1)−C(20)	1.316(5)
C(1)−C(11)	1.452(4)	C(11)−C(12)	1.336(5)	C(12)−C(13)	1.466(4)
C(6)−C(22)	1.446(4)	C(22)−C(23)	1.328(4)	C(23)−C(24)	1.455(4)
N(1)−C(19)	1.375(4)	N(2)−C(31)	1.320(4)	N(2)−C(30)	1.373(4)
C(6)−Fe−C(1)	108.50(12)			C(20)−N(1)−C(19)	116.0(3)
C(31)−N(2)−C(30)	116.1(3)				

which ice was added to quench the excess $POCl_3$. After evaporation of pyridine, the residue was then dissolved in water (30 mL) and basified by aqueous 4 M NaOH. Extraction with methylene dichloride (100 mL) followed by chromatography on a silica gel column eluting with Et_2O/MeOH (v/v, 5:1) gave 1.70 g of **5** (73%). Single crystals suitable for X-ray study were grown by slow evaporation of a methanol solution of **5**. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.42 (t, $^3J_{H,H}$ = 1.8 Hz, 4 H), 4.61 (t, $^3J_{H,H}$ = 1.8 Hz, 4 H), 7.03 (d, $^3J_{H,H}$ = 15.9 Hz, 2 H), 7.26~7.36 (m, 6 H), 7.61 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H), 7.93 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 8.01 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 8.54 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 68.98, 77.14, 83.58, 115.87, 120.58, 123.04, 126.08, 126.28, 129.25, 130.26, 133.06, 142.59, 148.87, 150.04, ppm. HRMS (EI) for $C_{32}H_{24}FeN_2$: calcd. 492.1289, obsd. 492.1284. $C_{32}H_{24}FeN_2$ (492.40): calcd. C 78.06, H 4.91, N 5.69; found C, 78.24, H 4.81, N 5.50.

Crystal Structure Determinations of 2, 3, 4, and 5: Diffractions for **2**, **3**, and **4** were 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 structures for **2**, **3**, and **4** were solved by direct methods using SHELXS-86 and refined by full-matrix least-squares with SHELXL-93.[24] For **5**, the diffraction data were collected on an Enraf−Nonius CCD single crystal X-ray diffractometer and the structure solved by direct methods using SHELXS-97 and refined against all F^2 data (SHELXS-97).[25] All non-hydrogen atoms were refined anisotropically. All hydrogen

atoms in **2**, **3**, and **5** and H(01*), H(02*), H(01), H(03), and H(01′) in **4** were found in the Fourier map and refined. The rest of the hydrogen atoms were located in ideal positions using a riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they were attached. The absolute structures of **4** and **5** could not be defined as insufficient data were collected.

CCDC-196212 to -196215 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

SHG Measurements: The measurements of second harmonic generation (SHG) intensity were carried out by the Kurtz−Perry powder technique,[21] using a beam with $\lambda = 1.360$ μm and $I = 5$ MW/cm^2 generated by a BBO optical parametric oscillator pumped by a Nd:YAG laser. Samples were in the range 75−150 μm, and were 270 μm thick.

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