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2D Molecular Square Grid with Strong Blue Fluorescent Emission: A Complex of Norfloxacin with Zinc(II)

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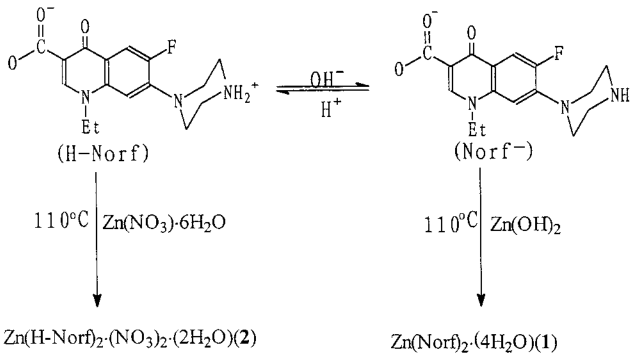
Introduction

The elegant, pioneering works of self-assembly of molecular squares (or rectangles and rhombohedra) containing metal ions by Lehn, Robson, Stang, and Fujita in the past decade[1] demonstrated novel and functional molecular architectures with many special functional properties such as luminescence,[2] redox activity,[3] molecular recognition (or enantioselectivity),[1,4] second-harmonic generation,[5] and magnetism[6] as well as catalysis.[1d] The self-assembling approach has since been at the frontiers of molecular science. Blue luminescent chelating compounds or coordination polymers in particular have been of intense interest in part because they are one of the key color components required for full-color EL displays and are still rare. Wang and co-workers recently reported several new types of blue luminescent coordination and organometallic compounds.[7] We have also prepared several blue luminescent organic−inorganic hybrid coordination polymers.[8] To this end, we have performed the two hydrothermal reactions of norfloxacin (H-Norf) with Zn(OH)$_2$ and Zn(NO$_3$)$_2$•6H$_2$O, respectively. To our surprise, the reaction affords two different products, Zn(Norf)$_2$•4H$_2$O (**1**) and Zn(H-Norf)$_2$•(NO$_3$)$_2$•2H$_2$O (**2**) (Scheme 1) in which **1** represents an unprecedented neutral metal-based molecular square grid with strong blue fluorescent emission in comparison to the free ligand. H-Norf is widely used for the treatment of many infections[9,10] and its metal complexes have also received much more attention.[11] Here we report syntheses of **1** and **2** and their X-ray crystal structures and fluorescent properties.

Scheme 1



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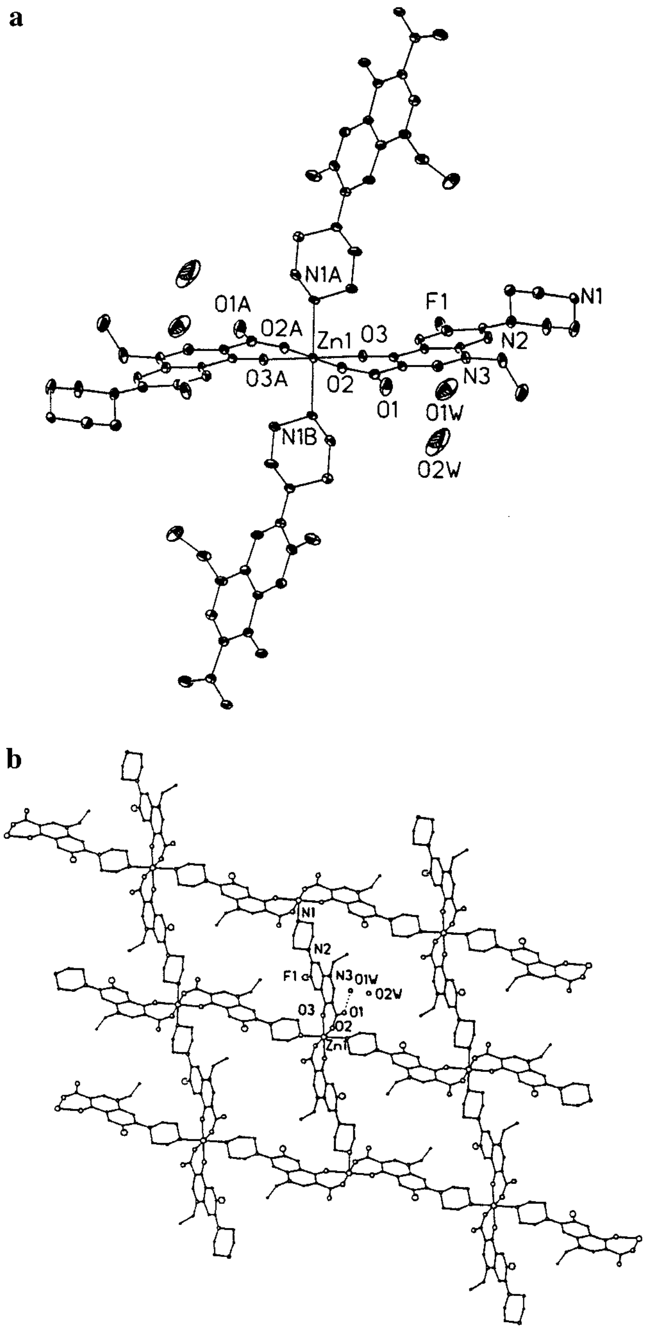

Figure 1. (a) ORTEP view of $Zn(Norf)_2{\cdot}4H_2O$ (**1**). The thermal ellipsoids are drawn at the 30% probability level. (b) An extended 2D network perspective view of $Zn(Norf)_2{\cdot}4H_2O$ (**1**).

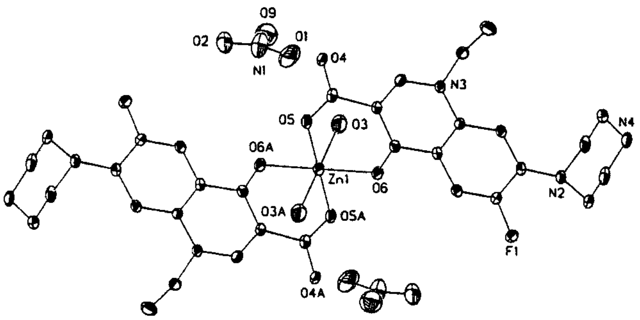

Figure 2. ORTEP view of $Zn(H\text{-}Norf)_2{\cdot}(NO_3)_2{\cdot}2H_2O$(**2**).The thermal ellipsoids are drawn at the 30% probability level.

Results and Discussion

The pale-yellow block crystalline **1** and the colorless block crystalline **2** containing neutral H-Norf were harvested by the hydrothermal reactions of H-Norf with $Zn(OH)_2$ at pH ca. 7−8 and $Zn(NO_3)_2{\cdot}6H_2O$ at pH ca. 6.5, respectively. While the difference in pH here is small, the formation of **1** and **2** containing $Norf^-$ anion and H-Norf, respectively, suggests that coordination of H-Norf with Zn(II) ion mainly depends on the pH of the solution. In a neutral or weakly basic solution, the N atom of the piperidyl ring can take part in the coordination to the metal ion, while in the weak acidic solution, the N atom of the piperidyl ring is protonated and fails to bind to the metal ion as evidenced by their crystal structure determination later.

The X-ray crystal analysis of **1** revealed that the Zn(II) ion is coordinated in a distorted octahedral geometry (Figure 1a), with an equatorial plane composed of four oxygen atoms [O(2), O(3), O(2A), and O(3A)]. Two of the oxygen atoms are from the quinoline ring and the other from carboxylate, which form a stable six-membered chelating ring. The apical positions are occupied by two N atoms [N(1B) and N(1C)] of piperidyl rings, resulting in the formation of a 2D square grid with a cavity dimension of 13.481×13.481 Å^2 (Figure 1b). The carboxylate group of Norf in **1** acts as a monodentate ligand with one oxygen of the carboxylate group uncoordinated. The uncoordinated carbonyl oxygen atom of carboxylate in Norf is strongly hydrogen bonded to water molecules (2.839 Å). The position of the uncoordinated carbonyl oxygen atom points up and is perpendicular to the molecular square cavity; water molecules are thus not enclathrated in the cavity but intercalated between two adjacent layers. The adjacent layers almost perfectly overlap together so that the cavity looks like a non-interpenetrating open channel. Furthermore, the nanosized squares are interlinked together by the intercalated water molecules, which are bonded through hydrogen bonding (O−H···O length at 2.797 Å), and uncoordinated carbonyl oxygen by a strong hydrogen bonding, resulting in the formation of a nanosized hydrophobic tube (or tunnel). The 2D nanosized neutral cavity without any interpenetrations is to our knowledge rare and appears to be very useful for host−guest chemistry.[1,4] On the other hand, the coordination mode of Norf in **1** is the first observed in the known H-Norf and quinolone complexes.[9] **1** is almost insoluble in most common solvents such as ethanol, chloroform, ethyl acetate, acetone, acetonitrile, benzene, and water.

The environment around Zn(II) in **2** is also slightly distorted octahedral (Figure 2). Unlike in **1**, the apical positions are occupied by two water molecules, resulting in the formation of a monomer perhaps because the protonated N atom of the piperidyl ring has lost its coordination capacity. Thus, H-Norf is a typical zwitterion in **2**.

To study the thermal stability of compound **1**, thermogravimetric analysis (TGA) was performed on the polycrystalline sample. One strikingly clean weight loss step occurred at ca. 50−125 °C (9.15% loss) and corresponds to the removal of four water molecules per formula unit (9.42%). It is interesting to note that no weight loss was recorded between the temperatures 125 and 300 °C, probably suggesting the formation of a stable nanosized molecular square.

The most important feature of the structure of **1** is the 2D condensed polymeric structure, and this unique structure perhaps leads to significant enhancement of fluorescent intensity which is almost 2−3 times larger than that of free H-Norf, probably due to coordination of H-Norf to Zn(II) increasing the ligand conformational rigidity, thereby reducing the nonradiative decay of the intraligand $^1(\pi-\pi^*)$ excited state. Similar enhancement of the intraligand fluorescence has also been reported for [Zn-

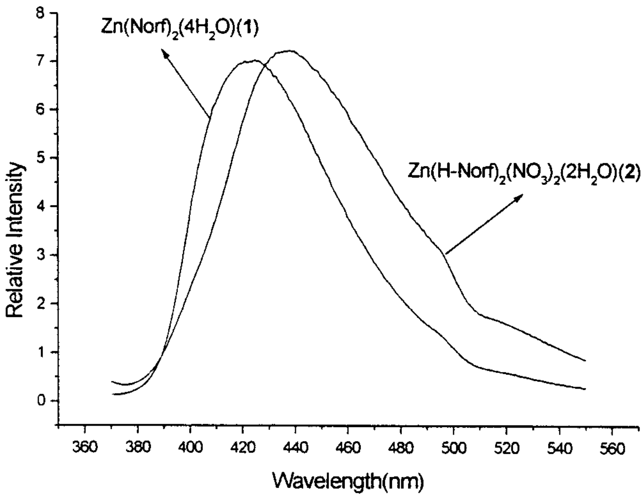

Figure 3. Fluorescent emission spectra of $Zn(Norf)_2 \cdot 4H_2O$ (**1**) and $Zn(H\text{-}Norf)_2 \cdot (NO_3)_2 \cdot 2H_2O$ (**2**) in the solid state at room temperature ($\lambda_{ex} = 350$ nm).

$(terpyridine)_2]^{2+}$ and $[Zn(L)_2(OAc)_2]$ (L = *N*,*N*′-bisbenzyl-2,7-diamino-1,8-naphthyridine).[8] The solid state diffuse reflectance UV−vis spectra of **1** and **2** show two intense bands at 339.8 and 281.5 nm for **1** and 344.3 and 272.5 nm for **2**, respectively, which are assigned to the intraligand $\pi-\pi^*$ transition of H-Norf (329.9 and 278.1 nm) and match well with excitation spectra of **1**, **2**, and free ligand ($\lambda_{max} = 350$ nm). The emission of **1** [$\lambda_{max} = 420$ nm ($\tau = 1.2$ ns, $\Phi_{em} \approx 0.26$)] (τ = lifetime, Φ = quantum efficiency; the short lifetime suggests that luminescence should be assigned to fluorescence) and **2** [$\lambda_{max} = 440$ nm ($\tau = 2.0$ ns, $\Phi_{em} \approx 0.23$)] (Figure 3) is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature, and can probably be assigned to the intraligand fluorescent emission since a weak similar emission [$\lambda_{max} = 440$ nm ($\tau = 1.0$ ns, $\Phi_{em} \approx 0.11$)] is also observed for free H-Norf. It is noteworthy that the emission wavelength in **1** is slightly shorter than those found in **2** and H-Norf, probably as a result of decreased $\pi-\pi$ stacking interactions.

In conclusion, both **1** and **2** show strong blue fluorescent emission, and they may be used as an advanced material for blue-light emitting diode devices. The 2D polymeric structure of **1** may make it a candidate for thermally stable and solvent-resistant blue fluorescent material for its low solubility in most common solvents.

Experimental Section

Synthesis of 1 and 2. Compound 1. $Zn(OH)_2$ (1 mmol) and H-Norf (2 mmol) were thoroughly mixed in a mortar with pestle and placed in a thick-walled Pyrex tube (ca. 20 cm long). After 0.5 mL of EtOH and 1.5 mL of H_2O were added, the tube was frozen with liquid N_2, evacuated under vacuum, and flame-sealed. The tube was heated at 110 °C for 1 day to give pale yellow block crystals (only one phase) in 65% yield based on H-Norf. Anal. Calcd for $C_{32}H_{42}F_2ZnN_6O_{10}$: C, 49.65; H, 5.47; N, 10.86. Found: C, 49.72; H, 5.60; N, 10.97. Solid reflectance UV−vis (nm): 339.8, 281.5. IR (KBr, cm^{-1}): 3400 (m), 3206 (m), 2941 (w), 1621 (s, ν_{COO-}), 580 (w), 1530 (w), 1490 (s, ν_{COO-}), 1386 (m), 1343 (m), 1264 (m), 1190 (m), 1120 (w), 1040 (w), 1112 (m), 940 (m), 891 (w), 831 (w), 790 (w), 751 (w), and 640 (w).

Compound 2. The procedures are similar to those of **1** except that $Zn(NO_3)_2 \cdot 6H_2O$ was used. The colorless block crystals (one phase) were harvested, with a yield of 85% based on H-Norf. Anal. Calcd for $C_{32}H_{40}F_2N_8O_{14}Zn$: C, 44.08; H, 4.67; N, 12.97. Found: C, 44.18; H, 4.59; N, 13.07. Solid reflectance UV−vis (nm): 344.3, 272.5. IR (KBr, cm^{-1}): 3404 (m), 3002 (vw), 1621 (s, ν_{COO-}), 1561 (m), 1482 (s, ν_{COO-}), 1380 (vs, ν_{NOOO-}), 1262 (s), 1201 (w), 1035 (w), 924 (w), 821 (w), 791 (w), and 759 (m).

Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
empirical formula	$C_{32}H_{42}F_2N_6O_{10}Zn$	$C_{32}H_{40}F_2N_8O_{14}Zn$
fw	774.09	864.09
T, K	293(2)	293(2)
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$ (No. 2)
a, Å	5.8190(12)	8.9800(18)
b, Å	21.660(4)	9.0140(18)
c, Å	13.289(3)	12.726(3)
α, deg	90.00	69.37(3)
β, deg	100.10(3)	72.05(3)
γ, deg	90.00	68.87(3)
V, Å^3	1649.0(6)	879.7(3)
Z	2	1
ρ(calcd), g/cm^3	1.559	1.631
μ(Mo Kα), cm^{-1}	8.25	7.92
F(000)	808	448
GOF	0.972	1.436
R1, wR2^a		
$I > 2\sigma(I)$	0.0456, 0.1221	0.0578, 0.1734
all data	0.1119, 0.1551	0.0849, 0.1871

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) in **1** and **2**

1		**2**	
Distances (Å)			
Zn(1)−O(2)	2.070(3)	Zn(1)−O(5)	2.028(3)
Zn(1)−O(3)	2.095(3)	Zn(1)−O(6)	2.057(3)
Zn(1)−N(1A)	2.253(3)	Zn(1)−O(3)	2.160(4)
Angles (deg)			
O(2)−Zn(1)−O(2A)	180.000(1)	O(5)−Zn(1)−O(5A)	180.0(3)
O(2)−Zn(1)−O(3)	87.00(11)	O(6)−Zn(1)−O(6A)	180.0
O(2A)−Zn(1)−O(3)	93.00(12)	O(5)−Zn(1)−O(6)	88.58(12)
O(2)−Zn(1)−N(1A)	90.93(13)	O(5)−Zn(1)−O(3)	87.97(18)
O(2)−Zn(1)−N(1B)	89.07(13)	O(6)−Zn(1)−O(3)	91.74(16)
O(3)−Zn(1)−N(1A)	87.19(13)	O(5A)−Zn(1)−O(3)	92.03(18)
O(3)−Zn(1)−N(1B)	92.81(13)	O(6A)−Zn(1)−O(3)	88.26(16)
N(1A)−Zn(1)−N(1B)	180.000(1)		

X-ray Crystallographic Determinations of 1 and 2. Data were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied in each case.[12] Selected bond lengths and angles are given Table 1, and relevant crystallographic data are presented in Table 2. The structure was solved with direct methods using the program SHELXTL (Sheldrick, 1997).[13] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless.

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Supporting Information Available: Crystallographic data, in CIF format, for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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