Inorganic Chemistry
· Communication

Self-Assembly of a Luminescent Zinc(II) Complex: a Supramolecular Host–Guest Fluorescence Signaling System for Selective Nitrobenzene Inclusion

Sanjib Das and Parimal K. Bharadwaj*

Department of Chemistry, Indian Institute of Technology Kanpur, 208016, India

A luminescent Zn(II) complex, [Zn(bpy)(aba)$_2$] (**1**) {bpy = 2,2′-bipyridyl and aba = 4-dimethylaminobenzoate} has been synthesized as a white solid. Complex **1** shows unusually high selectivity toward nitrobenzene in the presence of other organic guests in solution, as well as in the vapor phase, resulting in both a dramatic color change and a concomitant quenching of luminescence. When crystallized from nitrobenzene, **1** affords deep red crystals with the composition [Zn(bpy)(aba)$_2$]·C$_6$H$_5$NO$_2$ (**2**) as a hydrogen-bonded channel structure via unusual intermolecular C–H···C(sp^3) and H···H interactions. Inside the channels, nitrobenzene molecules form infinite polar linear tapes through strong C–H···O interactions in a head-to-tail fashion. The desorption and resorption of nitrobenzene can be achieved in a thermally reversible manner that can be monitored by X-ray powder diffraction patterns.

Supramolecular self-assembly of molecular solids is a potentially important area of contemporary research for designing a variety of functional materials with specific properties[1] such as optical nonlinearity, magnetism, conductivity, supramolecular storage of molecules, catalytic activity, selective adsorption, and so on. In this context, self-assembly of luminescent metal complexes triggered by specific organic guest molecules to design supramolecular functional architectures can be very useful in emerging optoelectronic and photonic technologies because analytical methods based on the emission phenomena are among the most sensitive available. Few reports are available on the guest-specific solid-state fluorescence modulation and photochromism in organic crystalline inclusion complexes.[2] However, lumi-nescent metal complexes are gaining significant attention as sensors and probes in view of their applications in light emitting diode[3] (LED), biomedical analyses,[4] fluorescence imaging,[5] and possibly, cancer phototherapy.[6] In a recent report, Wang and co-workers showed that the solid-state fluorescence intensity of a Zn(II) complex could be partially quenched upon benzene inclusion.[7] Eisenberg et al. showed that the linear chain of stacked Au(I) dimers become luminescent upon exposure to vapors of aprotic solvents such as acetone, CH$_3$CN, CH$_2$Cl$_2$, or CHCl$_3$ where as Balch et al. have reported, solvent-stimulated luminescence of Au(I) organometallic complexes is quite important from the perspectives of sensor applications for the detection of volatile organic compounds in environmental and public safety control.[8] In this communication, we report the synthesis of a luminescent compound, [Zn(bpy)(aba)$_2$] (**1**), which shows remarkable selectivity toward nitrobenzene, in solution as well as in vapor states, resulting in a sharp color change with concomitant quenching of luminescence due to supramolecular self-assembly in a thermally reversible manner (Scheme 1). Nitrobenzene is highly toxic and causes vomiting, skin and eye irritation, and headache. Continuous exposure to this compound leads to liver damage and anemia.[9]

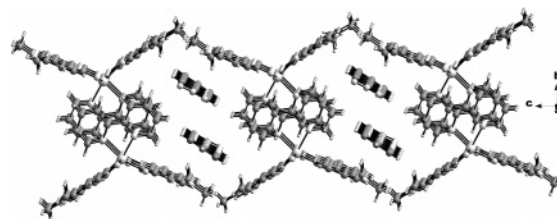* To whom correspondence should be addressed. E-mail: pkb@iitk.ac.in.

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Scheme 1. Schematic Representation of Nitrobenzene Inclusion by Compound **1**
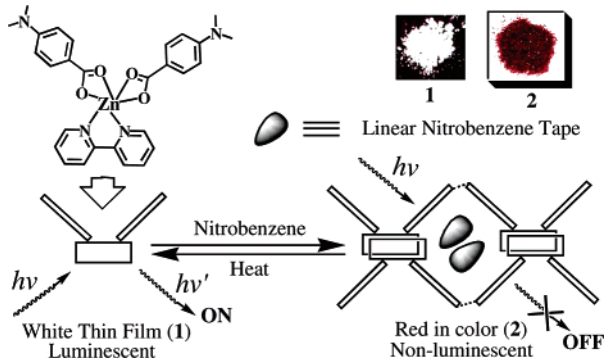
Complex **1** is synthesized[10] by reacting $Zn(OAc)_2 \cdot 2H_2O$, 2,2′-bipyridyl, and 4-(dimethylamino)benzoic acid in 1:1:2 molar ratio at room temperature and crystallizes with a metal-bound water molecule, $[Zn(bpy)(aba)_2(H_2O)]$ (**1′**), from DMF solvent. When **1** is dissolved with stirring in nitrobenzene ($\sim 1 \times 10^{-1}$ M), a red solid is precipitated in about 10 min. Elemental analysis gives the composition of the red solid as $[Zn(bpy)(aba)_2] \cdot C_6H_5NO_2$ (**2**). The filtrate, on slow evaporation at room temperature, affords deep red crystals after 1 week with the same composition as **2**. The powder patterns of **2** and the red solid are also identical.

X-ray crystallographic analyses shows that the structure[11] of **2** consists of neutral $[Zn(bpy)(aba)_2]$ units where carboxylate groups are asymmetrically bound to the metal, showing a large difference in the Zn−O bond distances (2.08, 2.18 Å) due to the mismatch between the size of the metal ion and the bite angle of the carboxylate group. Each *aba* unit in the complex is involved in an intricate array of strong C−H···O hydrogen bonding with its neighbor thus forming a hydrogen-bonded polymeric chain along the crystallographic *a* axis. The bipyridyl groups are oriented perpendicular to this chain structure and are involved in π···π stacking interactions with each other at 3.937 Å besides forming strong C−H···O interactions with the neighboring carboxylate O atoms. When viewed down the *a* axis, it looks like a pillar with four extensions. This structure exhibits two rare noncovalent interactions: One of them is the C−H··· $C(sp^3)$ interactions between the methyl terminals of two pillar structures[10] showing a wide range of distances [2.729−3.565 Å] where the methyl group acts as a H-bond acceptor.[12] The second unusual feature is the existence of short intermolecular H···H contacts[10] of 2.07 Å that are only slightly greater than the shortest reported value (1.96 Å) to date.[13]

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(10) See Supporting Information.
(11) Crystal data for **2**: deep red, rectangular, crystal dimensions 0.17 × 0.15 × 0.13 mm³, monoclinic, $P2_1/c$, Z = 4, a = 8.180(5) Å, b = 27.217(5) Å, c = 13.890(5) Å, β = 95.04(5)°, V = 3080(2) Å³, ρ_{cald} = 1.45 g cm⁻³, T = 100(2) K, μ = 0.852 mm⁻¹, θ_{max} = 28.32°, 7579 reflections collected of which 5496 were unique. R1 = 0.0540, wR2 = 0.1200 with a GOF of 1.027 for I > 2σ(I); residual electron density: 0.575 and −0.377 e Å⁻³.
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Figure 1. Packing diagram of **2** viewed down the crystallographic *a* axis showing the H-bonded channels occupied by nitrobenzene tapes.
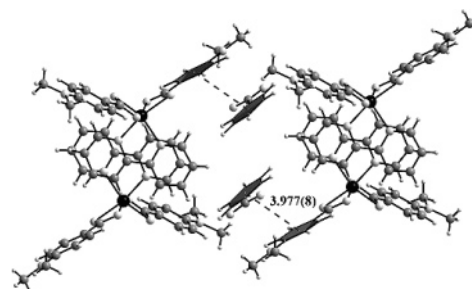
Figure 2. Perspective view of **2** showing π···π interactions between the *aba* units and nitrobenzene.

These intermolecular noncovalent interactions lead to a large H-bonded channel structure along the crystallographic *a* axis. The channels are not empty but are occupied by nitrobenzene molecules that are bound to the $[Zn(bpy)(aba)_2]$ units via C−H···O and C−H···π interactions with the *aba* moieties. There are also considerable π···π stacking interactions between the *aba* units and nitrobenzene molecules with a distance of 3.977 Å inside the channels (Figure 2). The nitrobenzene molecules themselves form infinite polar linear tapes through strong C−H···O interactions in a head-to-tail fashion along the crystallographic *a* axis.[10] Two such tapes are paired via C−H···O interactions in an antiparallel fashion. Thus, the stability of the solid-state structure of **2** is derived from the large number of noncovalent interactions present.

In the solid state, **1** exhibits a single absorption band at 370 nm while **2** shows bands at 370 and 550 nm.[10] The red color of **2** is derived from the charge-transfer transition between aromatic moieties of electron rich *aba* unit and electron-poor nitrobenzene unit.[14] Complex **1** exhibits a broad intense emission at λ_{max} = 520 nm, while **2** is nonemissive. The emission in **1** is due to a strong intraligand charge transfer (ILCT) from the donor *N,N*-dimethylamino group to the acceptor carboxylate end of the *aba* units.[15] Existence of strong C−H···π [3.821, 3.649 Å], as well as π···π [3.977 Å] stacking interactions involving nitrobenzene and *aba* units, readily converts the emissive intramolecular charge transfer (ICT) state to nonemissive ligand-to-ligand CT state. Because of this, **2** does not show any emission behavior. Fluorescence quenching by C−H···π and π···π stacking interactions are well documented in the literature.[16]

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Compound **1** exhibits high selectivity toward nitrobenzene over other organic aromatic guests such as benzene, toluene, chlorobenzene, xylene, etc. or aliphatic guests, such as alcohols, amines, etc. in solution. All efforts to crystallize **1** from different organic solvents other than nitrobenzene remain unsuccessful. However, when a small amount of nitrobenzene is added to these solutions, deep red crystals of **2** are obtained after a few weeks in each case as the sole product. To probe further the emission behavior of **1** toward nitrobenzene vapor, a thin film is prepared by spin-coating a CH_2Cl_2 solution of the complex onto a quartz plate. When the plate-supported film is exposed to nitrobenzene vapor, the white color changes to red within 10 min and the resulting red film becomes nonemissive.

The spectral characteristics of **1** in the solution phase are consistent with its solid-state behavior. In dichloromethane, **1** exhibits an absorption band at $\lambda_{max} = 307$ nm attributable to an ILCT transition that is solvatochromic in nature.[10] It exhibits dual fluorescence in dichloromethane and can be assigned[15] as the locally excited (LE) and the ICT transition from the donor *N,N*-dimethyl amino group to the acceptor carboxylate end of the *aba* units, respectively. The ICT emission, located at $\lambda_{max} = 442$ nm ($\lambda_{ex} = 307$ nm), is solvatochromic in nature, while LE emission remains virtually unchanged with respect to solvent polarity. Upon gradual addition of nitrobenzene to the dichloromethane solution of **1**, the intensity of the emission bands decreases. The linear Stern–Volmer response[10] with nitrobenzene as quencher is consistent with well-behaved fluorescence quenching systems.[17] To demonstrate the selectivity of **1** toward nitrobenzene, we have monitored the change in fluorescence quantum yields in the presence of different guests structurally similar or otherwise to nitrobenzene in dichloromehane solution. Figure 3 clearly shows that compound **1** has a remarkably high selectivity toward nitrobenzene in terms of change of fluorescence quantum yield. The X-ray crystal structure of **1** clearly revels that the linear nitrobenzene tapes strongly interact to each other, as well as with the *aba* units of **1** via C–H···π(*aba* unit) and π(nitrobenzene tape)···π(*aba* unit) interactions inside the H-bonded cavity that leads to fluorescence quenching. Thus, we speculate that this may be the possible reason in solution also. To support this fact, we further carry out the effect of *p*-nitrotoluene in the fluorescence intensity of **1** in dichloromethane. Interestingly, we do not find any significant lowering of quantum yield of **1**. This supports the fact that the methyl group in *p*-nitrotoluene inhibits interaction in a head-to-tail fashion like nitrobenzene to form linear tapes and hence cannot be incorporated inside
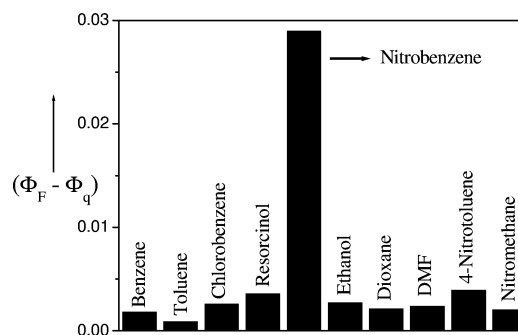
Figure 3. Schematic representation showing the change of fluorescence quantum yield ($\Phi_F - \Phi_q$) of compound **1** in dichloromethane (1×10^{-6} M) upon addition of the selected guest molecules with $\lambda_{ex} = 307$ nm. Φ_F and Φ_q are quantum yields of compound **1** in absence and presence of a guest, respectively.

the open channels to interact with the chromophoric units (*aba* moiety) of **1** to induce fluorescence quenching, although a very precise nature of interactions between nitrobenzene molecules and **1** in solution cannot be established at this time.

Thermogravimetric investigation[10] of **2** clearly shows that all nitrobenzene is completely lost at 148 °C. With the escape of nitrobenzene, the solid-state structure of **2** breaks down and the fluorescence is recovered completely. To show thermal reversibility of nitrobenzene inclusion, we have recorded X-ray powder diffraction (XRD) patterns of **1** in solvated, desolvated, and resolvated conditions.[10] It shows that, after removal of nitrobenzene from the solvated compound at 150 °C followed by resolvation, the initial spectral pattern can be restored and the cycle of solvation followed by desolvation can be repeated several times without destroying the complex. Similar behavior is observed in the case of a quartz-supported thin film of **1** upon exposure to nitrobenzene vapor. Thus, the reversible solvation and desolvation leads to reversible on/off switching of solid-state luminescence (Scheme 1).

In conclusion, a luminescent Zn(II) complex is reported that can selectively capture nitrobenzene in solution, as well as detect nitrobenzene vapor through both sharp color change and luminescence quenching in a thermally reversible manner. The self-assembled structures exhibit a number of unusual rare noncovalent interactions in addition to conventional hydrogen bonding. Designing of supramolecular host–guest fluorescence signaling systems for other toxic guests is in progress in our laboratory.

Supporting Information Available: X-ray crystallographic data for **1'** and **2**; TGA; fluorescence/UV−vis spectra; XRD pattern; and synthetic details of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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