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Water Clusters Gather Luminescent Zinc(II) Complexes around Hydrogen-Bonded Framework Structures and Associated Fluorescence Modulation

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ABSTRACT: Luminescent complexes $[\text{Zn}(\text{phen})(\text{dca})_2]$ (**1**) and $[\text{Zn}(\text{bpy})(\text{aba})_2]$ (**2**) (phen = 1,10-phenanthroline, dca = 4-dimethylamino cinnamate, bpy = 2,2'-bipyridyl, aba = 4-dimethylamino benzoate) are formed readily at room temperature when the reactants are allowed to react in a 1:1:2 molar ratio. Complex **1** self-assembles into a hydrogen-bonded framework structure in aqueous ethanol to form $\{[\text{Zn}(\text{phen})(\text{dca})_2] \cdot 3\text{H}_2\text{O} \cdot \text{EtOH}\}_n$ (**3**), in which four complex units gather around tetrameric water clusters. Similarly, complex **2** forms a different hydrogen-bonded framework structure with the empirical formula $\{[\text{Zn}(\text{bpy})(\text{aba})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**4**), in which octameric water clusters assemble $[\text{Zn}(\text{bpy})(\text{aba})_2]$ complex units. Compounds **3** and **4** exhibit significant red shifts of the emission bands with respect to **1** and **2**, respectively. On heating, compound **3** loses water to form **1** and then later upon recrystallization from aqueous ethanol forms **3** as monitored by X-ray powder patterns. Similarly, the transformation between **2** and **4** is also reversible.

Introduction

Hydrogen-bonding interactions and their fluctuations are responsible for the anomalous properties of bulk water. Recent years have witnessed both theoretical^{1–3} and experimental^{4–10} scrutiny of a number of small water clusters in different surroundings to investigate the development of properties of the condensed phase in a stepwise manner. For biological molecules, the energetic optimization of hydrogen-bonded networks involving enzyme, water, and substrate is an intrinsic part of the molecular recognition process, while in chemical systems the design of molecular solids with specific properties can make use of directional and complementary intermolecular noncovalent interactions involving water molecules. The degree of structuring of the water cluster that can be imposed by its environment and vice versa can be of importance in shaping the final structure. Herein, we describe the synthesis of two highly luminescent compounds, $[\text{Zn}(\text{phen})(\text{dca})_2]$ (**1**) and $[\text{Zn}(\text{bpy})(\text{aba})_2]$ (**2**) (phen = 1,10-phenanthroline, dca = 4-dimethylamino cinnamate, bpy = 2,2'-bipyridyl, aba = 4-dimethylamino benzoate), that can be engineered by a collection of octameric and tetrameric water clusters, respectively, to two-dimensional (2D) hydrogen-bonded frameworks with significant changes in their emission characteristics. Luminescent metal complexes are potentially important as sensors and probes¹¹ in view of their application in many biomedical analyses.¹² In these contexts, the present study points to the importance of hydrogen-bonding interactions between water and an emitting chromophore on its emission characteristics. Several recent reports are available^{13,14} on the effects of organic solvents on luminescent properties of transition metal complexes without providing any direct correlation between structure and luminescent properties. We show here that the water clusters not only trigger self-assembly with concomitant changes in the emission characteristics, but the process of forming hydrogen-bonded framework structures and their decomposition into the parent complexes are also thermally reversible (Scheme 1).

Experimental Section

Materials. 1,10-Phenanthroline, 2,2'-bipyridyl, 4-dimethylamino cinnamic acid, and 4-dimethylamino benzoic acid were purchased from Aldrich Chem. Co., while Zn(II) acetate dihydrate was from SD Fine Chemicals, India, and was used as received without further purification. All solvents were freshly distilled prior to use.

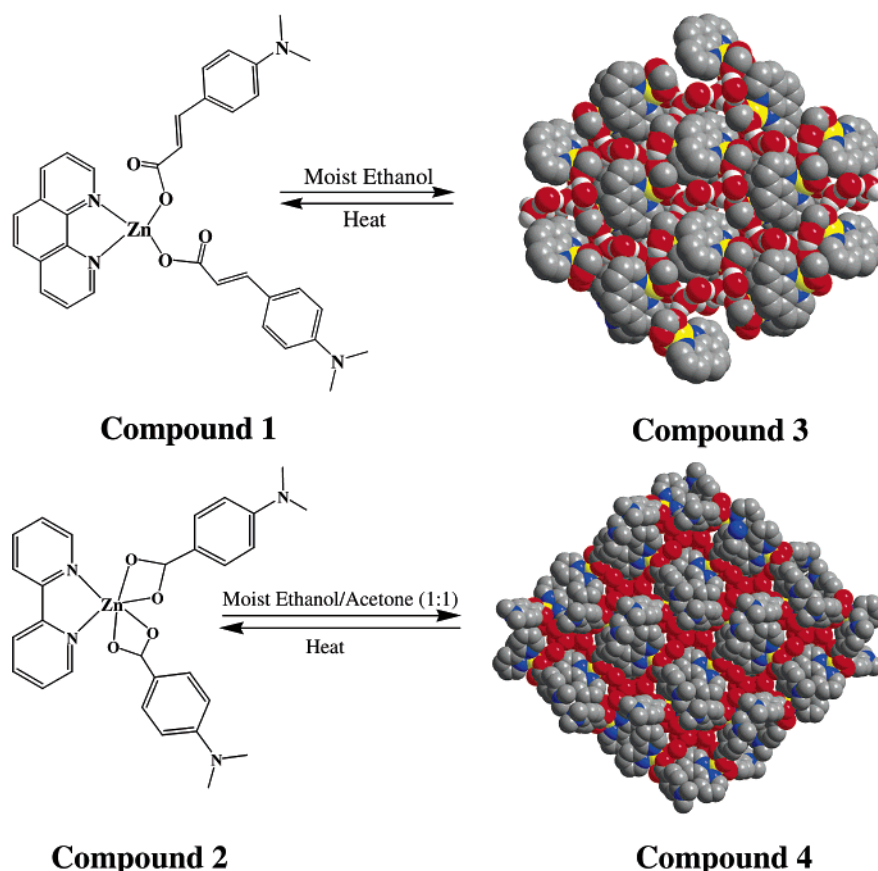
Physical Measurements. Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin-Elmer model 1320; X-ray powder pattern (Cu K α radiation at a scan rate of 3°/min, 293 K) Siefert ISODEBYEFLEX-2002 X-ray generator; thermogravimetric analysis (heating rate of 5° C/min) Perkin-Elmer Pyris 6. Microanalyses for the compounds were obtained from CDRI, Lucknow. UV–vis spectra in solution phase were recorded on a JASCO V-570 spectrophotometer at 298 K. Fluorescence spectra in solution phase were recorded on a Perkin-Elmer LS50B, Luminescence spectrometer at 298 K. Solid-state emission as well as excitation spectra of compounds **1–4** were collected using SPEX Fluorolog 3, model FL3-22 spectrometer.

Synthesis of $[\text{Zn}(\text{phen})(\text{dca})_2]$, (1**).** The complex $[\text{Zn}(\text{phen})(\text{dca})_2]$ (**1**) was synthesized by treating a methanolic solution (15 mL) containing 1,10-phenanthroline (198 mg, 1 mmol) and 4-dimethylamino cinnamic acid (382 mg, 2 mmol) to an aqueous solution (10 mL) of zinc acetate dihydrate (219 mg, 1 mmol) at room temperature. After the solution was stirred for 24 h, a light yellow solid that precipitated out was collected by filtration, washed thoroughly with methanol, and finally dried under vacuum. Yield 80%. Anal. Calcd. for $\text{C}_{34}\text{H}_{32}\text{N}_4\text{O}_4\text{Zn}$: C, 65.23; H, 5.15; N, 8.94%. Found: C, 65.16; H, 5.20; N, 9.05%. The light yellow solid upon crystallization from moist ethanol at room temperature afforded orange crystals of $\{[\text{Zn}(\text{phen})(\text{dca})_2] \cdot 3\text{H}_2\text{O} \cdot \text{EtOH}\}_n$ (**3**) in 63% yield, suitable for X-ray crystallography. However, no crystals could be isolated when methanol or any other alcohol was used in place of ethanol.

Synthesis of $[\text{Zn}(\text{bpy})(\text{aba})_2]$, (2**).** A methanolic solution (10 mL) containing 2,2'-bipyridyl (156 mg, 1 mmol) and 4-dimethylamino benzoic acid (330 mg, 2 mmol) was added to an aqueous solution (10 mL) of zinc(II) acetate dihydrate (219 mg, 1 mmol) at room temperature. After the solution was stirred for 6 h, an off-white solid precipitated out that was collected by filtration, washed thoroughly with methanol, and finally dried under vacuum. Yield 70%. Anal. Calcd. for $\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_8\text{Zn}$: C, 54.06; H, 5.83; N, 9.0%. Found: C, 54.15; H, 5.91; N, 9.09%. The off-white solid was crystallized at room temperature from a mixture of ethanol/acetone (50% v/v ratio) to obtain yellow rectangular parallelepipeds of $\{[\text{Zn}(\text{bpy})(\text{aba})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**4**) in 56% yield, suitable for X-ray crystallography. Use of methanol or any other alcohol in place of ethanol did not afford any crystals.

X-ray Structural Studies. Single-crystal X-ray data on **3–4** were collected at 100 K on a Bruker SMART APEX CCD diffractometer

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Scheme 1. Schematic Representation of Reversible Modulation of Emission Properties by Water Clusters in the Solid State

using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT¹⁵ software. An empirical absorption correction was applied to the collected reflections with SADABS¹⁶ using XPREF.¹⁷ The structure was solved by the direct method using SHELXTL¹⁸ and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97¹⁹ program package. Non-hydrogen atoms were refined anisotropically. For **3**, all hydrogen atoms were located in successive difference Fourier maps, whereas for **4** hydrogen atoms of the water molecules could not be located. In the refinement, hydrogens were treated as riding atoms using SHELXL default parameters. The crystal and refinement data are collected in Table 1 while selected bond distances and angles are collected in Table 2.

Results and Discussion

All four compounds are air-stable and moderately soluble in water as well as alcohol.

The asymmetric unit of **3** consists of neutral $[\text{Zn}(\text{phen})(\text{dca})_2]$, one ethanol, and three water molecules. Each Zn(II) ion is bonded to two N atoms of the phen and two O atoms from two carboxylate groups of dca in a pseudotetrahedral fashion. The Zn–N (2.093, 2.090 Å) and Zn–O (1.96 Å) distances are found to be normal compared²⁰ to other Zn(II) complexes. The second O atom of each carboxylate group makes only a semi-bond (~ 2.53 Å) with the metal.

Two water molecules (O1w, O2w) in the asymmetric unit are connected to another two centrosymmetrically related water molecules (O1w', O2w') forming a cyclic planar tetrameric water cluster. This cluster is connected on two sides by one ethanol molecule $[\text{O1w} \cdots \text{O}(\text{ethanol})]$, 2.836 Å].

A closer look at the water cluster (Figure 1) reveals that O1w acts as a double hydrogen-bond donor to O2w and O2w' and a

Table 1. Crystal Data and Details of Structure Refinements for 3 and 4

compound	3	4
empirical formula	$\text{C}_{36}\text{H}_{44}\text{N}_4\text{O}_8\text{Zn}$	$\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_8\text{Zn}$
formula weight	726.12	621.98
radiation, wavelength	Mo K α , 0.71073 Å	Mo K α , 0.71073 Å
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	17.438(5)	12.904(5)
b (Å)	11.626(5)	14.885(5)
c (Å)	17.477(5)	16.565(5)
β (°)	104.66(5)	106.161(5)
V (Å ³)	3428(2)	3056.0(18)
Z	4	4
$F(000)$	1528	1304
D_{calc} (g cm ^{−3})	1.407	1.352
crystal size (mm ³)	$0.13 \times 0.11 \times 0.09$	$0.13 \times 0.11 \times 0.09$
T (K)	100 (2)	100 (2)
μ (Mo K α) (mm ^{−1})	0.775	0.856
reflections measured	8498	7540
unique reflections	5195	5270
used $[I > 2\sigma(I)]$		
parameters (N)	431	370
GOF	1.071	1.043
final R indices	$R1 = 0.0833$	$R1 = 0.0695$
$[I \geq 2\sigma(I)]$	$wR2 = 0.2047$	$wR2 = 0.2000$
R indices (all data)	$R1 = 0.1398$	$R1 = 0.1002$
	$wR2 = 0.2333$	$wR2 = 0.2203$
max/min residual (e Å ^{−3})	0.944/−0.750	1.327/−0.617
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2

single acceptor from ethanol, while O2w acts as a double hydrogen-bond donor to nearby metal-bound carboxylate O atoms assembling four $[\text{Zn}(\text{phen})(\text{dca})_2]$ units around each tetrameric water cluster. Thus, the tetramer and ethanol together fit very well in the cavity and at the same time interact strongly

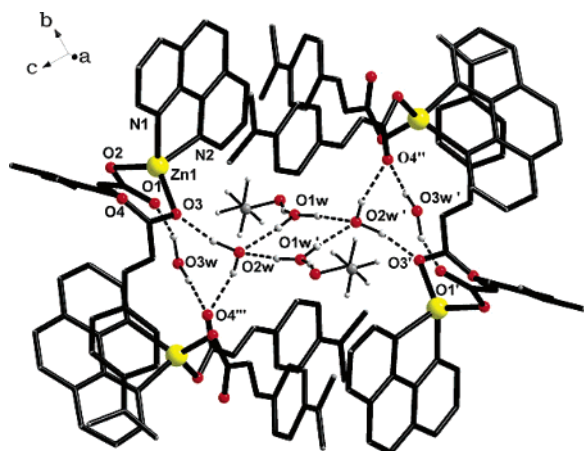
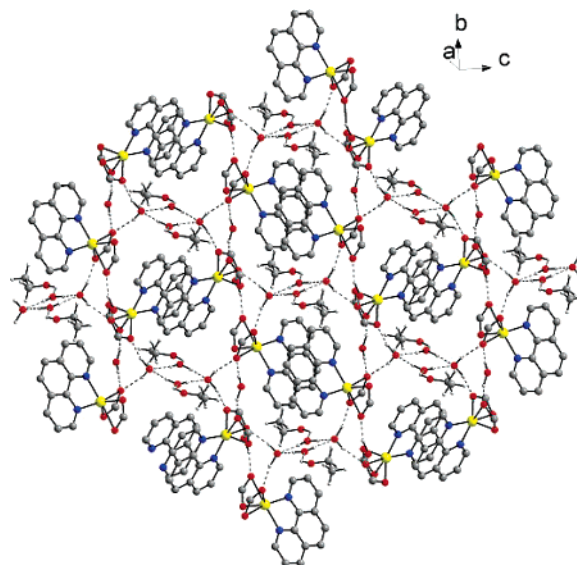
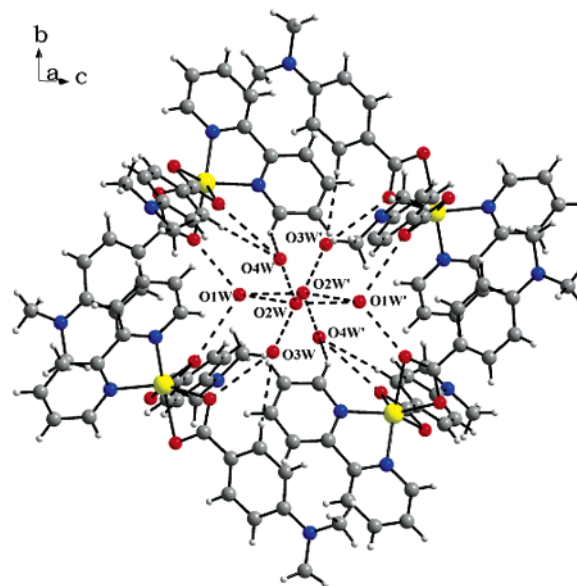
Table 2. Bond Lengths (Å) and Angles (°) of Compound 3 and 4

Compound 3			
Zn1–N1	2.093(4)	N1–Zn1–N2	80.05(16)
Zn1–N2	2.090(4)	N1–Zn1–O2	108.92(14)
Zn1–O1	2.532(5)	N1–Zn1–O3	120.56(15)
Zn1–O2	1.988(3)	N2–Zn1–O2	106.93(16)
Zn1–O3	1.969(3)	N2–Zn1–O3	114.23(15)
Zn1–O4	2.525(5)	O2–Zn1–O3	119.07(14)
Compound 4			
Zn1–N1	2.067(3)	N1–Zn1–N2	78.22(13)
Zn1–N2	2.086(3)	N1–Zn1–O1	92.30(19)
Zn1–O1	2.186(5)	N1–Zn1–O3	92.79(15)
Zn1–O2	2.165(5)	N2–Zn1–O2	97.60(17)
Zn1–O3	2.267(5)	N2–Zn1–O4	92.69(16)
Zn1–O4	2.148(5)	O1–Zn1–O2	59.9(2)
		O1–Zn1–O3	89.88(17)
		O2–Zn1–O4	94.32(15)
		O3–Zn1–O4	59.5(2)

with the environment. This explains why **1** readily crystallizes in aqueous ethanol, and no crystals are formed when other alcohols are used in place of ethanol. Another two centrosymmetrically related water molecules (O3w, O3w') act as double hydrogen-bond donors to nearby carboxylate O atoms further reinforcing the 2D structure approximately in the *bc* crystallographic plane (Figure 2). The nonbonding distance between O1w...O2w is 2.948 and between O1w...O2w' is 2.863 Å. Other distances of interest are collected in Table 2. The overall structure is further stabilized by intermolecular π – π interactions between the aromatic rings of phenanthroline and one of the dca molecules with an interplanar spacing of 3.74 Å. The bond distances and bond angles in the ligand moieties and those involving the metal ion and the ligands lie within normal ranges.

The structure of **4** consists of neutral [Zn(bpy)(aba)₂] and four water molecules in the asymmetric unit. Each Zn(II) ion is bonded to two N atoms of a 2,2'-bipyridyl and four O atoms from two carboxylate group of aba moieties in an octahedral fashion (Figure 3). The Zn–N distances (Table 2) are found to be normal compared²⁰ to other Zn(II) complexes. One of the carboxylate groups is asymmetrically bound to metal showing a big difference in the Zn–O bond distances (Table 2). The four water molecules are connected to four other centrosymmetrically related water molecules to form an octamer.

Theoretical calculations³ show two minima in the potential energy surface corresponding to two isomers of nearly identical energy with *S*₄ and *D*_{2d} symmetries for the (H₂O)₈ cluster. In these structures, O atoms occupy the corners and hydrogen bonds along the edges. Similar structures have been detected

**Figure 1.** X-ray structure of complex 3. Only water and ethanol hydrogen atoms are shown for clarity.**Figure 2.** Complex 3 viewed in the crystallographic *bc* plane. Some hydrogen atoms are omitted, and only carboxylate parts of the dca moieties are shown for clarity.**Figure 3.** X-ray structure of complex 4, viewed down the crystallographic *a* axis showing the octameric water cluster inside the four units of complex 2.

in the molecular beam²¹ and in gas-phase C₆H₆(H₂O)₈ clusters.²² In crystal hosts, cubane,²³ opened-cubane,²⁴ cyclic octamer²⁵ resembling ice *I*_h, and cyclic octamer consisting of a hexamer and two dangling water molecules²⁶ have been identified. In **4**, a different type of octameric cluster is present. Here, atoms O1w and O2w are hydrogen bonded to O1w' and O2w' forming a cyclic quasi-planar tetrameric unit. Two water molecules (O3w, O4w) are hydrogen bonded to one corner of the tetramer, while the other two (O3w', O4w') are hydrogen bonded to the opposite corner (Figure 4). The shape of the cluster is commensurate with the overall structure of **4** whose stability is derived from water–water and water–carboxylate hydrogen-bonding interactions (Table 2).

However, hydrogen atoms bound to the water molecules could not be located in the difference maps. Compound **4** also shows strong C–H...O intermolecular interactions between bipyridyl or benzene H and carboxylate O atoms that further cement the

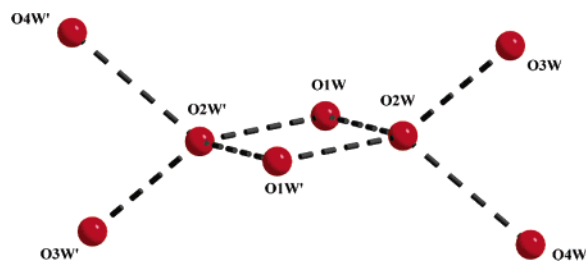


Figure 4. A perspective of the octameric water cluster inside the 2D structure of compound **4**.

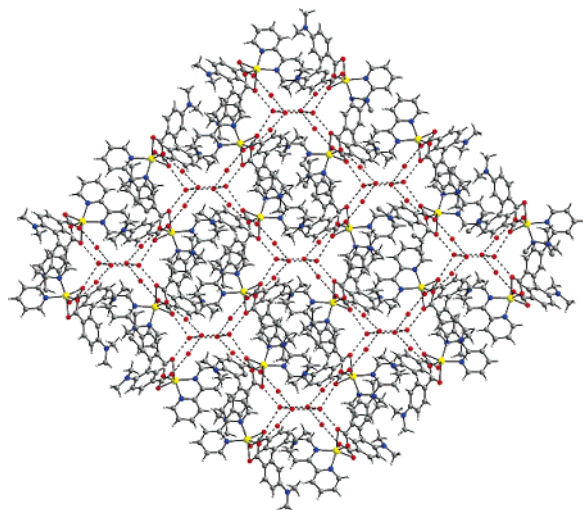


Figure 5. Crystal packing of **4**, approximately in the crystallographic *bc* plane. The interactions within the octamer as well as among the water molecules and carboxylate oxygen atoms are shown with broken lines.

structure (Figure 5). The importance of C—H...O interactions has attracted much attention in biochemistry because of its potential capacity in stabilizing particular structures of biomolecules such as nucleic acids,²⁷ proteins,²⁸ and carbohydrates.²⁹ Although this type of hydrogen-bonding was found decades earlier in organic systems, this interaction was accepted widespread only recently as a result of theoretical³⁰ efforts.

Thermal gravimetric analysis of **3** shows³¹ that the compound decomposes only above 300 °C showing its robustness. It gives a (9.71 mg sample in air) loss of 13.8 wt % at 102 °C corresponding to one ethanol and three water molecules (calculated 13.5%). In the case of **4** with a 11.74 mg sample in air, 11.4% (calculated 11.6%) weight loss occurs³¹ at 110 °C corresponding to four water molecules. In this case also, the decomposition temperature is above 200 °C. The FTIR spectra³¹ of **3** and **4** exhibit broad absorption centered at 3416 and 3437 cm⁻¹, respectively, attributable⁷ to the O—H stretching frequency pertaining to the water cluster.

Compound **1** shows an unusually high affinity toward water. Its solubility in common organic solvents increases significantly when a small amount of water is present. All attempts to crystallize the molecule in different protic and aprotic organic solvents in dry conditions remained unsuccessful. Only in aqueous ethanol crystals of **3** can be obtained as the sole product. This suggests that in **3**, water and ethanol together play a significant role in stabilizing the crystal structure via hydrogen bonding among water molecules themselves and with that of the complex molecular units. Compound **2** shows a similar behavior in the presence of water.

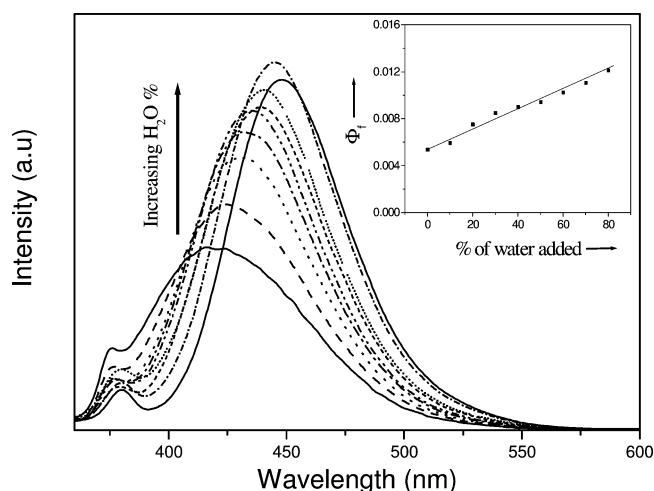


Figure 6. Fluorescence spectra of **1** (conc 1×10^{-6} M) in different ratios (v/v) of water/ethanol mixture. Inset: Corresponding plot of ϕ_f vs % of water added to the ethanolic solution of **1**.

The emission spectra of **1** and **2** are recorded in several solvents with different polarity.³¹ The dual fluorescence observed in highly polar solvents could be readily assigned³² as the locally excited (LE) and the intramolecular charge transfer (ICT) transitions, respectively. The quantum yield (referenced to quinine sulfate³³ in 1 N sulfuric acid as standard, $\lambda_{\text{ex}} = 350$ nm, $\phi_0 = 0.54$) is found to be 0.01 in a highly polar aprotic solvent like acetonitrile, while in a protic solvent like absolute ethanol, it is only 0.005. To demonstrate the important role of water molecules to the emission characteristics of **1**, we have studied the change of fluorescence quantum yield in the presence of different amounts of water in an absolute ethanolic solution of **1**. Figure 6 clearly shows that the intensity of the ICT band increases with a pronounced red shift ($\lambda_{\text{max}} = 419$ and 448 nm in absolute ethanol and 1:8 (v/v) EtOH/H₂O mixture, respectively), while the position of the absorption bands³¹ remain virtually unchanged although with lowering of intensity. This suggests that there is an important role of water in establishing a hydrogen-bonded contribution to the stability of the excited state as well as the dipole moment change from the ground to the excited state.³⁴

Excitation spectra of **1** and **2** in the solid state can be located in the range, 350–450 nm (Figures 7 and 8, inset) assignable to the intraligand transitions. In the solid state, **1** and **2** exhibit a broad emission at λ_{max} of 535 and 520 nm, respectively, assignable³⁵ to a charge transfer from the donor *N,N*-dimethyl amino group to the acceptor carboxylate end (ICT). In comparison, solid-state emission spectra of **3** and **4** show two distinct emission bands—an ICT and a TICT band. The ICT band for **3** is located at 595 nm that is red shifted by 60 nm with respect to the band shown by **1**. For **4**, this band appears at 565 nm, which is also red shifted by 45 nm. This drastic shift in the ICT can be attributed to the strong hydrogen-bonding interactions between the water molecules and the nearby carboxylate O atoms that change the donor–acceptor character of the dca and aba moieties. The TICT band³⁶ in **3** and **4** is located at 661 nm that arises from restricted rotation of the *N,N*-dimethyl amino group with respect to the phenyl moiety due to formation of 2D hydrogen-bonded open framework structures assisted by the water clusters.

Once water molecules are removed from **3** and **4** by heating at 110 °C for 1 h under vacuum, the emission peaks shown by the product coincide with that of **1** and **2**. Compounds **3** and **4** can be obtained upon further crystallization from the heated

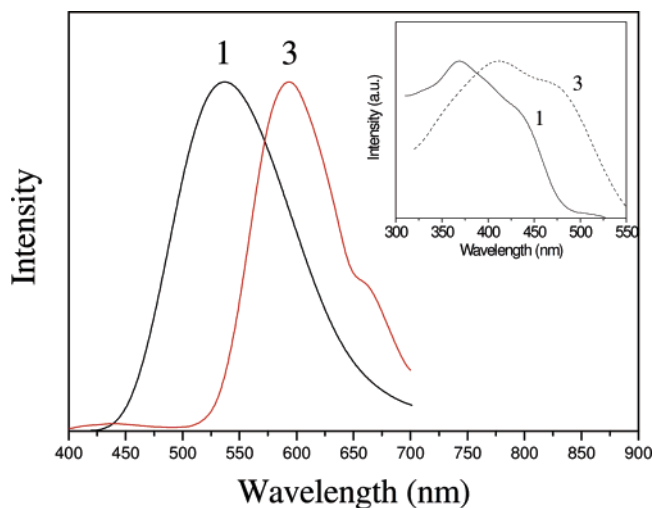


Figure 7. Normalized solid-state fluorescence spectra for compound **1** and **3**. Inset: Excitation spectra of compound **1** and **3** in solid state.

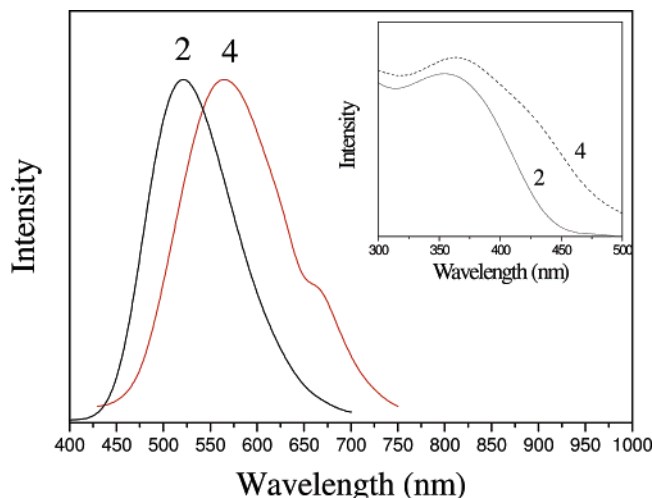


Figure 8. Normalized solid-state fluorescence spectra for compound **2** and **4**. Inset: Excitation spectra of compound **2** and **4** in solid state.

Table 3. Luminescent Data for **1–4**

compound	solid-state		$\Delta\lambda$
	$\lambda_{\text{max}}(\text{ex})$	$\lambda_{\text{max}}(\text{em})$	
[Zn(phen)(dca) ₂] (1)	370	535	60
{[Zn(phen)(dca) ₂]·3H ₂ O·EtOH} _n (3)	415	595	
[Zn(bipy)(aba) ₂] (2)	370	520	45
{[Zn(bpy)(aba) ₂]·4H ₂ O} _n (4)	370	565	

sample in moist ethanol and ethanol/acetone mixture. This transformation between the two compounds was studied several times without any decomposition of the Zn(II) complex as monitored by X-ray powder diffraction.³¹ In conclusion, modulation of emission properties in the presence of different externally added stimuli³⁷ has been restricted mostly in solution so far. In contrast, tuning of emission properties in the solid state has attracted intensive interest because it could be more potentially useful in electronic and photonic devices.³⁸ Herein, we reported reversible solid-state modulation of emission characteristics of a luminescent Zn(II) complex where water clusters are capable of not only constructing well-defined molecular arrangements but also tuning the emission properties to the resulting bulk assembly. The luminescent characteristics of the complexes can be directly correlated with the X-ray structure. Compounds **3** and **4** obtained via supramolecular

chemistry exhibit red fluorescence that could be promising as a probe in many potential applications such as high-resolution imaging of biological cells with less photodamage. The structure and dynamics of these water molecules can be studied by the large Stokes shift. In this context, the present study points to the important effects of hydrogen-bonding interactions between water and an emitting chromophore on its emission characteristics.

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Supporting Information Available: Crystallographic data (CIF), building mode of octameric and tetrameric water clusters into a 2D polymeric structure, and thermograms of **3** and **4**, X-ray powder diffraction patterns for **1** and **2** in hydrated and dehydrated conditions, fluorescence spectra of **1** and **2** in solution phase, FTIR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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