Pd^{II}, Zn^{II} and Ag^{I} Complexes of Tetrakis(*N*-7-azaindolyl)benzene: Variation of Bonding Modes, Extended Structures and Luminescence

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Pd^{II}, Ag^{I} and Zn^{II} complexes of tetrakis(7-azaindolyl)benzene (ttab), $[(PdCl_2)_2(ttab)]$ (**1**), $[(ZnCl_2)_2(ttab)]$ (**2**), $[Ag(NO_3)]_2(ttab)$ (**3a**) and $[Ag(NO_3)(DMSO)]_2(ttab)$ (**3b**) were synthesized and fully characterized by NMR spectroscopy, single-crystal X-ray diffraction and elemental analyses. The ttab ligand in these complexes displays two different bonding modes. In the Pd^{II} and Zn^{II} complexes, the ttab ligand chelates to the metal center via two *ortho* 7-azaindolyl groups (the *ortho* mode). In contrast, in the Ag^{I} complex, it chelates to the Ag^{I} ion via two *meta* 7-azaindolyl groups (the *meta* mode). In the solid state, molecules of **1** and **2** form grid-like extended structures that host solvent molecules such as DMSO and CH_2Cl_2. Compound **3a** appears to be a coordination polymer and can be converted into compound **3b** when dissolved in DMSO. A hydrogen bonded complex $[Zn(O_2CCF_3)_2(H_2O)_2](ttab)$ (**4**), which displays an unusual hydrogen bonded helical chain structure in the solid state, was also characterized. Except for compound **1**, these new compounds all emit blue light when irradiated by UV radiation.
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Introduction

Luminescent transition metal complexes are of great interest because of their potential application in chemical optical sensors, photosensitization and electroluminescent devices.[1,2] We have previously demonstrated that Pt^{II} and Pd^{II} complexes of 7-azaindole based organic ligands can emit green and orange light, either in frozen solutions or in the solid state, when irradiated by UV light.[2f,3a] In addition to luminescent properties, the coordination chemistry displayed by transition metal complexes of the 7-azaindole-based ligands is also interesting. As we reported previously, the coordination mode displayed by ligands involving 7-azaindolyl groups varies drastically according to the geometry of the ligand. For example, as shown in Scheme 1, the 1,3-bis(7-azaindolyl)benzene ligand has been found to bind to Pd^{II} or Pt^{II} centers as a tridentate NCN-type ligand through cyclometallation[3] (bonding mode **A**). In contrast, the 1,2-bis(7-azaindolyl)benzene ligand usually acts as a bidentate chelate ligand through the two 7-azaindolyl groups (bonding mode **B** in Scheme 1).[3b] The 1,3,5-tris(7-azaindolyl)benzene ligand, on the other hand, uses two of the 7-azaindolyl groups to chelate to the metal center with the NCN type of binding similar to that in **A**, and uses the remaining 7-azaindolyl group as a bridging ligand to form a trinuclear complex (**C**).[2f] Recently we reported the synthesis of the new ligand 1,2,4,5-tetrakis(7-azaindolyl)benzene (ttab),[4] which is a bright blue luminescent emitter. The organoplatinum complexes of ttab have been found to display unusual structural features and chemical reactivity.[4] In the previously reported organoplatinum complexes, the ttab ligand chelates to the Pt^{II} center in the *ortho* bonding mode (**D**) as shown in Scheme 1. Further investigation revealed that the ttab ligand also displays a second bonding mode (**E**), the *meta* mode. The third bonding mode (**F**), the cyclometallation mode, was not observed for the ttab ligand.

The metal ion and the ligands surrounding the metal ion appear to play a key role in the bonding mode of the ttab ligand. We report herein the results of our investigation on Pd^{II}, Ag^{I} and Zn^{II} complexes of the ttab ligand.

Results and Discussion

Syntheses of Complexes

The ttab ligand reacts readily with K_2PdCl_4 and $ZnCl_2$ in solution to afford complexes $[(PdCl_2)_2(ttab)]$ (**1**) and $[(ZnCl_2)_2(ttab)]$ (**2**), respectively, in nearly quantitative yields. When ttab was reacted with $AgNO_3$, we obtained a white solid of **3a**, which displays blue luminescence at ambient temperature and is insoluble in most organic solvents. Based on elemental analysis results, **3a** has the formula $[Ag(NO_3)]_2(ttab)$. Compound **3a** can be dissolved in DMSO under sonication to form a dinuclear complex $[Ag(NO_3)(DMSO)]_2(ttab)$ (**3b**), in which the DMSO molecules coordinate to the Ag^{I} center through the oxygen atom, as

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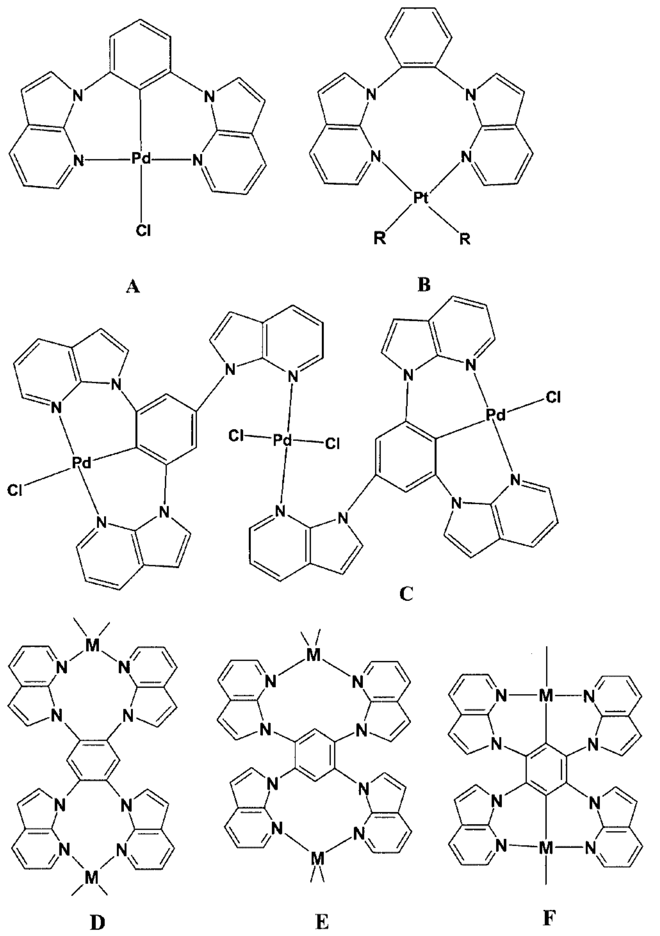

Scheme 1

confirmed by X-ray diffraction analysis. Anhydrous $ZnCl_2$ reacts with ttab in a THF solution, resulting in a blue luminescent white solid of **2**. Attempts to synthesize the complex $[Zn(O_2CCF_3)_2]_2$(ttab) by reacting $Zn(O_2CCF_3)_2$ hydrate with ttab were unsuccessful. Every attempt led to the isolation of crystals of $[Zn(O_2CCF_3)_2(H_2O)_2]$(ttab) (**4**), where the $Zn(O_2CCF_3)_2(H_2O)_2$ molecule is not coordinated to the ttab ligand but hydrogen bonded with the ttab ligand in the crystal lattice as confirmed by the X-ray diffraction study. The structures of ttab, **1**, **2**, **3b** and **4** were determined by X-ray diffraction analyses. Selected bond lengths and angles for **1**, **2**, **3b** and **4** are provided in Table 1.

Structures of ttab and of the Complexes

There are 1.5 independent molecules in each asymmetric unit of the crystal lattice of ttab, with one of the ttab molecules being located at the inversion center of symmetry. The structure of one of the independent molecules in the crystal lattice of ttab is shown in Figure 1. The ttab ligand has a non-planar structure. The 7-azaindolyl groups do not have significant conjugation with the central benzene ring as indicated by the dihedral angle between the central benzene plane and the 7-azaindolyl plane that ranges from 46.6° to 76.7°. Unlike 1,2-bis(7-azaindolyl)benzene or 1,3-bis(7-azaindolyl)benzene, which have only one way of chelating to the metal center, ttab has four nitrogen donor atoms available, which can chelate to the metal center either with two *ortho* 7-azaindole moieties (*ortho* fashion, **D**) or with two *meta* 7-azaindole moieties (*meta* fashion, **E**). In addition, it is conceivable that the ttab ligand could also form cyclometallated complexes (**F**), especially with the Pd^{II}

Table 1. Selected bond lengths [Å] and angles [°]

		1	
Pd(1)−N(2)	2.022(4)	N(2)−Pd(1)−N(4)	87.25(15)
Pd(1)−N(4)	2.032(4)	N(2)−Pd(1)−Cl(2)	176.34(13)
Pd(1)−Cl(2)	2.2852(15)	N(4)−Pd(1)−Cl(2)	90.46(11)
Pd(1)−Cl(1)	2.2900(14)	N(2)−Pd(1)−Cl(1)	90.51(12)
		N(4)−Pd(1)−Cl(1)	177.76(11)
		Cl(2)−Pd(1)−Cl(1)	91.78(6)
		C(7)−N(2)−Pd(1)	123.7(4)
		C(14)−N(4)−Pd(1)	124.0(3)
		2	
Zn(1)−N(2)	2.053(10)	N(2)−Zn(1)−N(4)	97.2(3)
Zn(1)−N(4)	2.068(9)	N(2)−Zn(1)−Cl(1)	116.7(2)
Zn(1)−Cl(1)	2.196(3)	N(4)−Zn(1)−Cl(1)	123.9(3)
Zn(1)−Cl(2)	2.246(3)	N(2)−Zn(1)−Cl(2)	105.6(3)
		N(4)−Zn(1)−Cl(2)	104.6(3)
		Cl(1)−Zn(1)−Cl(2)	107.05(12)
		C(7)−N(2)−Zn(1)	131.1(8)
		C(14)−N(4)−Zn(1)	129.4(7)
		3b	
Ag(1)−N(1)	2.300(7)	N(1)−Ag(1)−N(3)	136.3(2)
Ag(1)−N(3)	2.335(9)	N(1)−Ag(1)−O(1)	128.9(3)
Ag(1)−O(1)	2.403(7)	N(3)−Ag(1)−O(1)	88.3(3)
Ag(1)−O(3A)	2.53(3)	N(1)−Ag(1)−O(3A)	106.4(13)
		N(3)−Ag(1)−O(3A)	80.9(8)
		O(1)−Ag(1)−O(3A)	103.8(15)
		4	
Zn(1)−O(6)	1.930(12)	O(6)−Zn(1)−O(5)	103.0(4)
Zn(1)−O(5)	1.943(10)	O(6)−Zn(1)−O(3)	98.9(6)
Zn(1)−O(3)	2.04(2)	O(5)−Zn(1)−O(3)	135.7(7)
Zn(1)−O(1)	2.066(17)	O(6)−Zn(1)−O(1)	96.0(6)
Zn(1)−O(4)	2.467(16)	O(5)−Zn(1)−O(1)	101.1(6)
Zn(1)−O(2)	2.557(16)	O(3)−Zn(1)−O(1)	114.4(9)

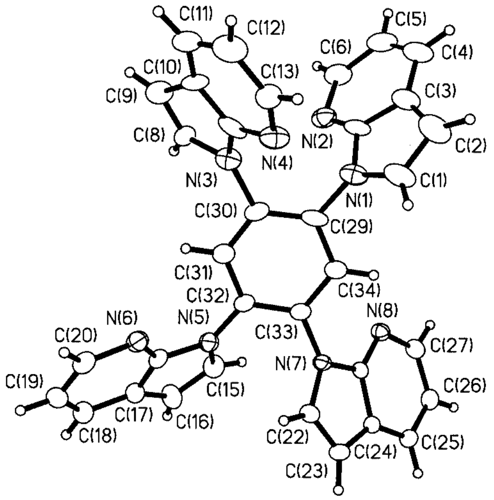

Figure 1. A diagram showing the structure of one of the independent ttab molecules in the crystal lattice with labeling schemes

and Pt^{II} centers, in the same manner as 1,3-bis(7-azaindolyl)benzene and 1,3,5-tris(7-azaindolyl)benzene, as shown in Scheme 1. However, despite our repeated attempts to react Pd^{II} and Pt^{II} ions with ttab under various conditions, no cyclometallated products were obtained. For the Pd^{II} ion, the *ortho* chelated complex **1** was isolated, instead.

The structure of **1**, as shown in Figure 2, has a crystallographically imposed inversion center of symmetry. Each Pd^{II} ion in **1** is chelated by two *ortho* 7-azaindolyl groups via the nitrogen atoms, resulting in a dinuclear complex. Each Pd^{II} center adopts a typical square-planar geometry, with the two nitrogen donor atoms *cis* to each other and two chloride ligands *trans* to each nitrogen atom. The Pd−N and Pd−Cl bonds in **1** show typical bond lengths with averages of 2.027(4) Å and 2.2876(14) Å, respectively, which are close to those reported previously.[2f,3a] The four 7-azaindolyl planes are nearly perpendicular to the central benzene ring as indicated by the dihedral angles between the 7-azaindolyl plane and the benzene ring (100.2° and 102.6°, respectively). The central benzene ring of the ttab ligand is "sandwiched" midway between the two $PdCl_2N_2$ planes. The $PdCl_2N_2$ plane is approximately parallel to the central benzene plane as indicated by the dihedral angle of 25.5° between these two planes. The separation distance between the two Pd^{II} centers in **1** is 6.660(2) Å. As a result, the distance between the center of the benzene ring and the Pd atom is 3.33(1) Å. The shortest contact distances between the Pd atom and the carbon atoms of the benzene ring are 2.99(1) Å [Pd(1)−C(16)] and 3.01(1) Å [Pd(1)−C(15)]. These distances are considerably shorter than the sum (≈3.22 Å) of the van der Waals radii of Pd and C, indicating the presence of some interactions between the Pd atom and the benzene ring. The structure of **1** resembles that of $[(PtR_2)_2(ttab)]$, where R equals methyl or

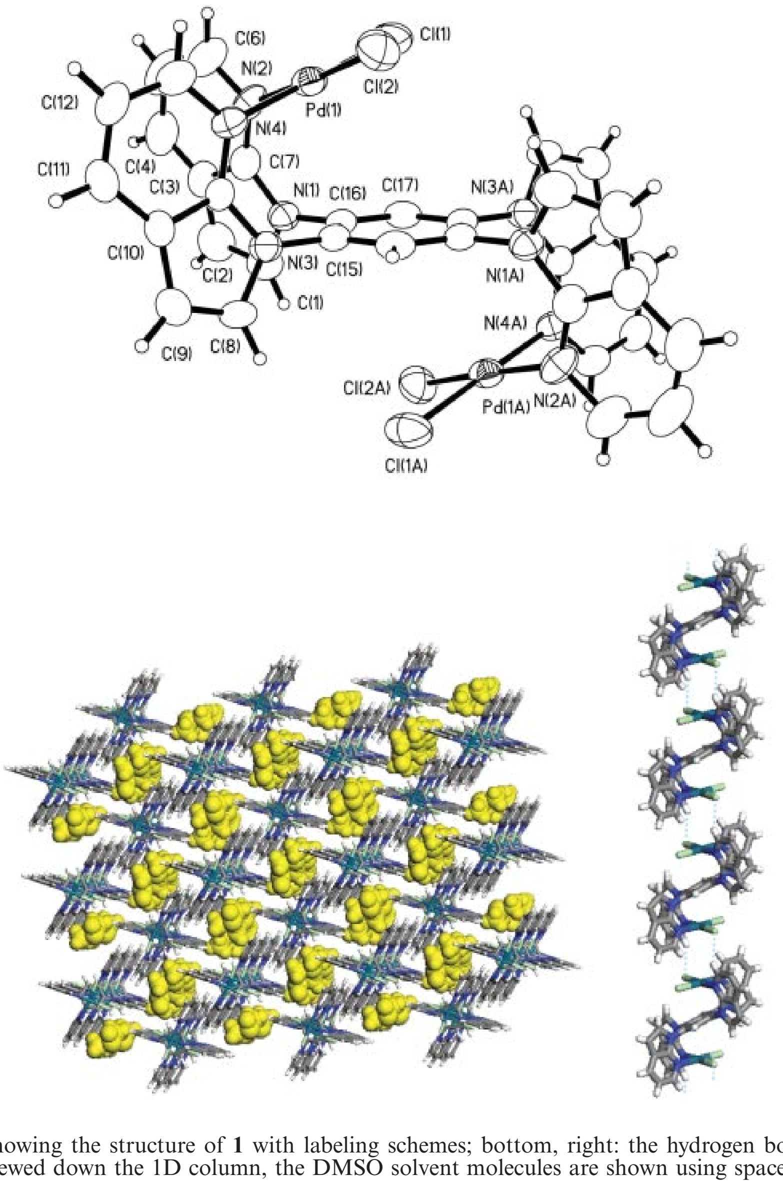

Figure 2. Top: a diagram showing the structure of **1** with labeling schemes; bottom, right: the hydrogen bond-linked 1D column; left: unit cell packing diagram viewed down the 1D column, the DMSO solvent molecules are shown using space-filling models

phenyl, reported previously, where substantial interactions between the Pt atom and the central benzene ring were also observed.[4]

Molecules of **1** stack along the *b* axis as shown in Figure 2. There are weak intermolecular hydrogen bonding interactions between the chloride ligands and the protons on the 7-azaindole rings of the neighboring molecules [Cl(1)···C(13) = 3.62 Å, Cl(2)···C(6) = 3.70 Å], leading to the formation of a 1D column. The shortest intermolecular Pd···Pd distance along the 1D column is 4.800(2) Å. The void space between the 1D columns forms extended channels in the crystal lattice. DMSO solvent molecules are located in these channels, as shown in Figure 2. There are hydrogen bonding interactions between the oxygen atom of the DMSO molecule and a proton on the central phenyl ring of the ttab ligand as indicated by the O···C distance of 3.10 Å. Crystals of **1** are stable at ambient temperature and no loss of DMSO solvent molecules was observed, as evident by the elemental analysis results.

Earlier we postulated that a "sandwich" structure similar to **1** is only possible for metal ions that have a square-planar geometry,[4] based on the assumption that if the metal ion has a tetrahedral geometry, it would bring the ligands bound to the metal center into close contact with the central benzene ring of the ttab ligand and as a result, the *ortho* coordination mode would not be possible. To prove this postulation, we examined the structure of **2**. As shown in Figure 3, the molecule of **2** has a crystallographically imposed inversion center. One surprising finding is that the ttab ligand adopts the *ortho* coordination mode with the Zn^{II} ion in the same manner as that observed in **1**. The common coordination geometry for a four-coordinate Zn^{II} ion is tetrahedral. The *ortho* bonding mode displayed by the ttab ligand in **2** is therefore totally unexpected. Each Zn^{II} center in **2** has a distorted tetrahedral geometry, with two nitrogen donor atoms from the ttab ligand occupying two coordination sites and two chloride ligands occupying the other two sites. The bond angles of N(2)−Zn(1)−N(4), N(2)−Zn(1)−Cl(1), and N(4)−Zn(1)−Cl(1), which are 97.2(3)°, 116.7(2) °, and 123.9(3) °, respectively, deviate significantly from a typical tetrahedral geometry. To minimize steric interactions between the chloride ligand Cl(1) and the central phenyl ring of the ttab ligand, the Zn(1)−Cl(1) bond is almost parallel to the central phenyl ring of ttab. The Zn(1)−Zn(1A) separation distance is 7.538(2) Å, much longer than the Pd(1)−Pd(1A) distance in **1**. The distance between Cl(1) and the center of the central phenyl ring of ttab is 3.19 Å. The distances between the Cl(1) atom and C(15), C(16), C(17) atoms of the phenyl ring are in the range of 3.42 to 3.50 Å, much shorter than the corresponding Cl−C separation distances in **1** [the shortest Cl−C distance in **1**, 3.76 Å, is between Cl(1) and C(16)]. The Zn(1)−Cl(2) bond is considerably longer than the Zn(1)−Cl(1) bond (by 0.05 Å). The Zn−N and Zn−Cl bond lengths in **2** [av. 2.060(9) Å and 2.221(3)Å, respectively] are typical.[5] The orientation of the 7-azaindolyl groups in **2** is similar to their orientation in **1**, with the dihedral angles between the 7-azaindolyl planes and the central benzene plane being 82.7° and 82.4°, respectively. However, the bond angles of C(7)−N(2)−Zn(1) [131.1(8)°] and C(14)−N(4)−Zn(1) [129.4(7)°] are considerably larger than the corresponding ones in **1** [C(7)−N(2)−Pd(1) = 123.7(4)°, C(14)−N(4)−Pd(1) = 124.0(3)°]. The geometry distortion around the metal ions and the nitrogen donor atoms in **2** is clearly a consequence of steric interactions between the chloride ligands and the central phenyl group. Nonetheless, the structure of **2** demonstrates that the *ortho* bonding mode is possible and favorable for a tetrahedrally coordinated Zn^{II} ion. In solution, only one set of chemical shifts for the ttab ligand was observed in the ^1H NMR spectrum of **2**. Therefore, we believe that only one bonding mode, most likely the *ortho* mode, exists in solution for complex **2**. In coordinating solvents such as DMSO, the $ZnCl_2$ units appear to dissociate from the ttab ligand as indicated by the ^1H NMR spectrum of **2** in [D_6]DMSO, which is exactly identical to that of the free ttab ligand in [D_6]DMSO. We believe that the DMSO solvent molecules are coordinated to the $ZnCl_2$ unit in solution, replacing the nitrogen donor atoms of the ttab ligand and resulting in the dissociation of the complex **2**.

In the crystal lattice, molecules of **2** (Figure 3) form one-dimensional chains through intermolecular hydrogen bonding interactions between the chloride ligands of one molecule and the protons on the 7-azaindole rings of the neighboring molecules in a similar manner as observed in **1**. The intermolecular Cl(1)···C(2′) separation distance is 3.67 Å. An interesting feature is that the 1D columns of **2** are arranged in such a way that rhombohedral-shaped channels are formed. Disordered CH_2Cl_2 solvent molecules occupy these channels. The crystals of **2** lose the trapped solvent molecules rapidly at ambient temperature, causing the collapse of the crystal lattice. The structure of the dinuclear silver complex **3b** is shown in Figure 4. In contrast to the structures of **1** and **2**, the ttab ligand in **3b** adopts the *meta* bonding mode. The molecule of **3b** has a crystallographically imposed center of inversion symmetry. Each Ag^{I} ion is coordinated to two 7-azaindolyl groups at the 1,3 positions of the ttab ligand. The Ag^{I} center is also coordinated to two oxygen atoms, one from the DMSO molecule and the other from a disordered nitrate anion. Coordination to a metal center via the oxygen atom of the DMSO ligand has previously been observed.[6] The bond angles around the Ag(1) atom range from 80.9(8) to 136.3(2)°. The geometry of the Ag(1) center can therefore be best described as a highly distorted tetrahedron. The dihedral angles between the 7-azaindolyl plane and the central benzene ring are 123.7° and 115.9°, respectively, much greater than those of **1** and **2**. The preference for the "*meta*" bonding mode shown by the ttab ligand in **3b** could be attributed to the relative bulkiness of the DMSO and NO_3^- ligands compared to the chloride ligands. The *meta* mode appears to minimize the interactions between the oxygen donor ligands and the central phenyl ring as well as satisfy the geometric preference of the Ag(1) ion. The distance between the two Ag(1) centers in **3b** is 6.594(2) Å, similar to the Pd−Pd distance observed in **1**. The distances between the

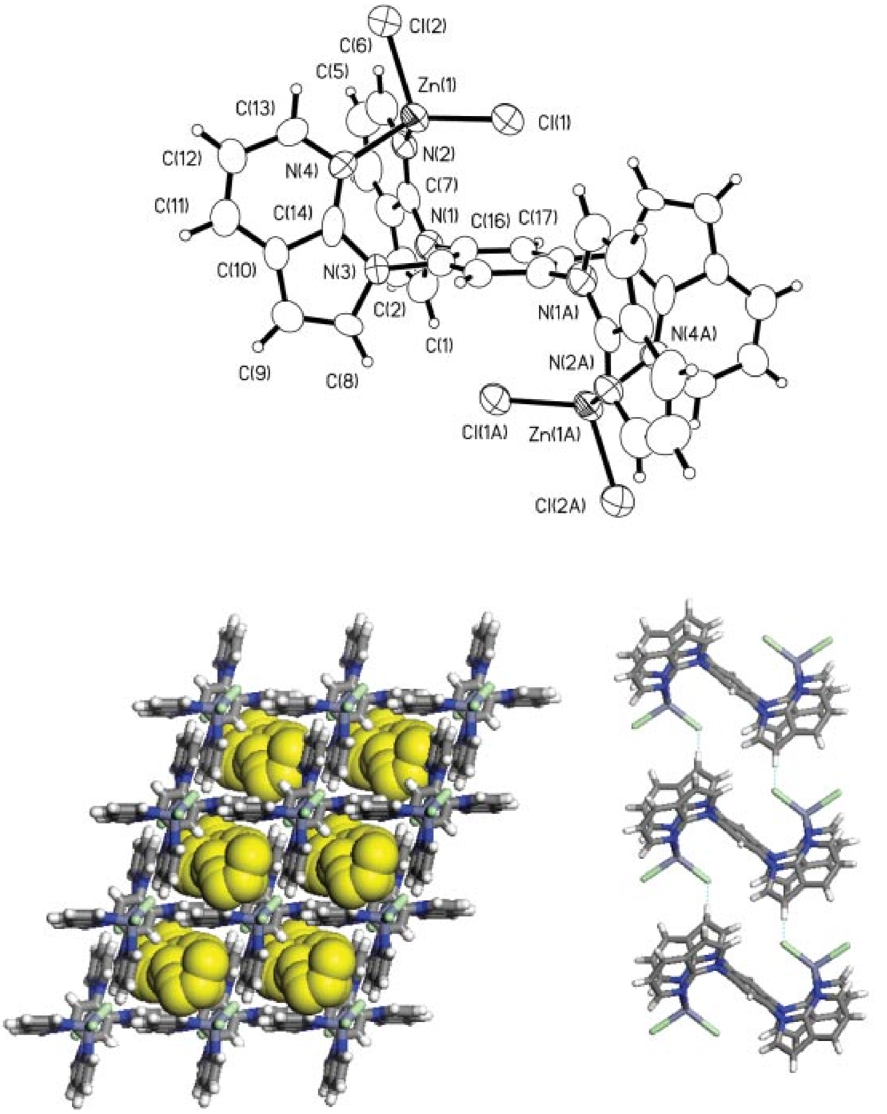

Figure 3. Top: a diagram showing the structure of **2** with labeling schemes; bottom, right: the hydrogen bond-linked 1D column; left: unit cell packing diagram viewed down from the 1D column, the disordered CH_2Cl_2 solvent molecules are shown using space-filling models

Ag(1) center and the carbon atoms C(15), C(16) and C(17) of the central phenyl ring, which are 3.20 Å, 2.72 Å and 3.17 Å, respectively, are either close to or less than the van der Waals contact distance of Ag−C (literature C−Ag bond length: ≈2.58 Å).[7b] Therefore, some weak bonding interactions between the Ag centers and the central phenyl ring appear to be present. The Ag(1)−O(1) and Ag(1)−O(3A) bond lengths are similar to those reported previously.[7]

The extended structure of **3b** is shown in Figure 4. Each molecule of **3b** is bonded to four neighboring molecules through hydrogen bonding between the oxygen atom of the nitrate ion and a proton (H14′) on the 7-azaindole ring of the neighboring molecule, as indicated by the O(4)···C(12′) distance of 3.33 Å, to form a two-dimensional layered network. In the crystal lattice, these layers stack on top of one another in an *ABAB* fashion, with toluene molecules filling the gaps. Compound **3b** slowly loses the DMSO ligands and reverts back to **3a** upon standing at ambient temperature. Due to the poor solubility of **3a**, NMR and X-ray diffraction experiments could not be carried out. Based on the poor solubility, the elemental analysis and the structure of **3b**, we believe that **3a** is likely to be a one-dimensional coordination polymer, where the nitrate anions function as bridging ligands, linking the dinuclear silver units together (in a similar way as that observed in **3b)** to form a coordination polymer chain.

Because the *meta* structure displayed by complex **3b** appears to be the consequence of the relatively large ligands DMSO and nitrate, we decided to examine the reaction of $Zn(O_2CCF_3)_2$ with the ttab ligand, anticipating a *meta* structure similar to that of **3b**. However, surprisingly, the product we isolated does not contain any coordination bonds between the Zn^{II} ion and the ttab ligand. Instead, the ttab ligand and the $Zn(O_2CCF_3)_2(H_2O)_2$ molecule located in the crystal lattice are linked together via hydrogen bonds, as shown in Figure 5. The H_2O ligands are from the starting material. Repeated efforts to synthesize the water-

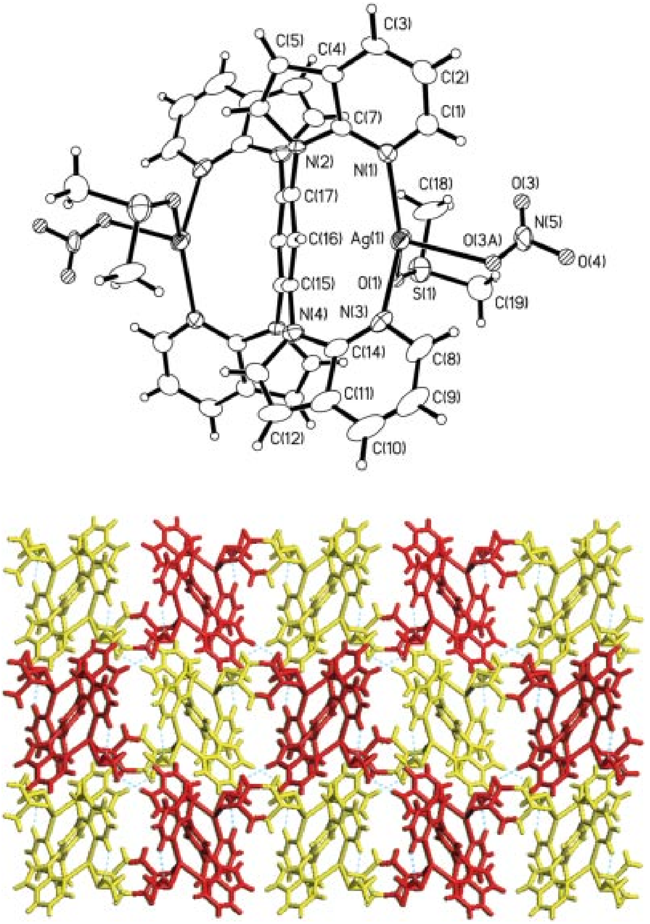

Figure 4. Top: a diagram showing the structure of **3b** with labeling schemes; for clarity, the oxygen atoms on DMSO and the NO_3^- are shown as ideal spheres; one of the disordered oxygen atoms [O(4A)] is not shown; bottom: unit cell diagram showing two layers (red and yellow) of hydrogen bond-linked 2D sheets

free complex $[Zn(O_2CCF_3)_2]_2$(ttab) were unsuccessful. Despite the poor quality of the crystal of **4**, the crystal data established unambiguously that the Zn^{II} ion is coordinated to two trifluoroacetate ligands and two H_2O ligands with an irregular geometry: four normal Zn−O bonds and two long Zn−O bonds [Zn(1)−O(2) = 2.557(16) Å, Zn(1)−O(4) = 2.467(16) Å]. The four non-coordinating nitrogen atoms of the ttab ligands form hydrogen bonds with the coordinated H_2O ligands. The N(8) and N(6) atoms are hydrogen-bonded to the O(6) atom while the N(2) and N(4) atoms are bonded to the O(5A) atom from a neighboring $Zn(O_2CCF_3)_2$ $(H_2O)_2$ group, as indicated by the distances of O(5A)···N(2), 2.73(2) Å; O(5A)···N(4), 2.74(2) Å; O(6)···N(6), 2.70(2) Å; O(6)···N(8), 2.71(2) Å. The $[Zn(O_2CCF_3)_2$ $(H_2O)_2]$ unit therefore functions as a linker for the ttab ligands through hydrogen bonds, leading to the formation of an unusual hydrogen-bond linked 1D chain (Figure 5). Extended structures involving metal complexes and organic molecules linked by hydrogen bonds have been reported previously.[8] One important feature of **4** is that the hydrogen-bonded 1D chains are helical and rotate in the same direction in the crystal lattice, resulting in the formation of a chiral lattice as shown in Figure 5. Interestingly, the hydrogen-bonding interactions between the zinc(II) complex and the ttab molecule are apparently retained in non-coordinating solvents such as CH_2Cl_2, as confirmed by the ^1H NMR study, which shows that the chemical shifts of the ttab molecule in **4** are drastically different from those of the free ttab molecule. In coordinating solvents such as DMSO, the NMR spectrum of **4** is identical to that of the free ttab ligand, indicating the Zn^{II} complex is no longer interacting with the ttab ligand through hydrogen bonds. It is very likely that the DMSO molecules coordinate to the Zn^{II} center and saturate the coordination sphere of the Zn^{II} ion, which may or may not lead to the replacement of the H_2O ligands at the zinc center. Due to the presence of an excess of DMSO molecules, the H_2O ligands are very likely to form hydrogen bonds with the DMSO solvent molecules instead of the ttab molecule, thus resulting in the free ligand-like behavior of the ttab molecule in DMSO. Toluene solvent molecules were also found in the lattice of **4** (one toluene per molecule of **4**), which do not escape from the crystal lattice at ambient temperature, as indicated by elemental analysis results.

Luminescent Properties

When irradiated by UV light, ttab emits a bright blue light both in solution and in the solid state. The emission maximum of ttab in a CH_2Cl_2 solution is at 377 nm when the concentration of the solution is approximately 10^{-4} M, while at high concentrations a significant red shift is observed (e.g. 0.10 M solution, emission maximum at approximately 463 nm), which can be attributed to intermolecular interactions or excimer emission. Compound **1** shows no detectable luminescence in solution or in the solid state, attributable to the quenching by the Pd^{II} ion. Compound **2** is blue luminescent in solution and in the solid state (λ_{max} = 380 nm). Compound **3a** is blue luminescent in the solid state with the emission maximum at 432 nm. The substantial red shift of the emission band of **3a**, compared to that of free ttab in solution, is clearly caused by intermolecular interactions in the solid state. Due to the insolubility of **3a** in most solvents, no spectrum was recorded in solution. Compound **3b** does not display any significant luminescence in the solid state, weak blue luminescence from **3b** in solution was observed (λ_{max} = 375 nm). The emission spectra of ttab, **2**, **3a**, **3b** and **4** are shown in Figure 6. The emission maximum of **2** (375 nm) in a CH_2Cl_2 solution (approx. 10^{-4} M) is essentially the same as that of the free ligand ttab. The emission bands of **2** and **3b** in solution at the same concentration resemble that of the free ttab ligand in solution, indicating that they are all ttab-based emissions. However, the intensity of the emission bands of **2** and **3b** is much weaker than that of the free ttab under the same conditions, indicating that the Zn^{II} ion and the Ag^{I} ion partially quench the emission from the ttab ligand. Compound **4** displays blue luminescence in solution. However, the emission spectrum of **4** recorded in CH_2Cl_2 is blue-shifted by about 20 nm, compared to that of the free ttab ligand recorded under the same conditions. Furthermore, the emis-

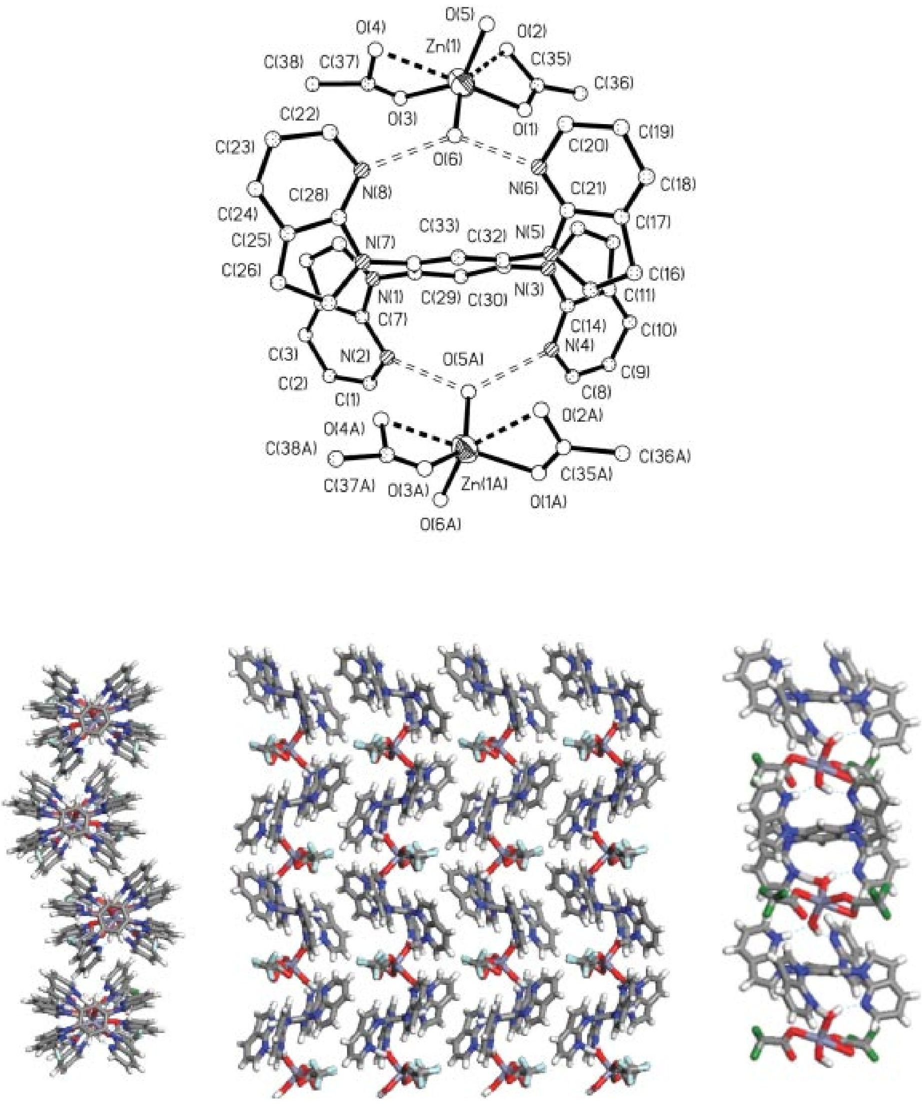

Figure 5. Top: a diagram showing the structure of **4** with labeling schemes (a second [$Zn(O_2CCF_3)_2(H_2O)_2$] unit from a neighboring molecule is also shown to demonstrate the hydrogen bond pattern.); for clarity, the disordered fluorine atoms are omitted and all atoms except zinc are shown as ideal spheres; bottom, right: the hydrogen bond linked 1D chain; left: the view projected down the 1D chain; middle: the packing of the 1D chains in the lattice

sion intensity of **4** is about 1% of the intensity of the free ttab ligand. These experimental observations provide further support for the presence of hydrogen-bonding interactions between the [$Zn(O_2CCF_3)_2(H_2O)_2$] group and the ttab ligand in solution. This appears to partially quench the emission of the ttab ligand.

In summary, both the *meta* and *ortho* coordination modes of the ttab ligand were established. The cyclometallated bonding mode was not observed for the ttab ligand. Both the coordination geometry of the metal ion and the nature of the surrounding ligands appear to influence the bonding mode of the ttab ligand. The unusual extended structures displayed by the complexes of the ttab ligand and its hydrogen-bonded compound were demonstrated. The fact that these extended structures have the tendency to host solvent molecules makes these compounds potentially useful for applications in host-guest chemistry. The Pd^{II} ion appears to be capable of completely quenching the lumi-

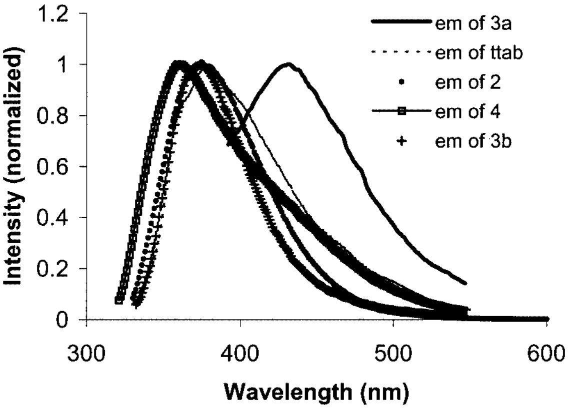

Figure 6. The emission spectra of ttab (1.0×10^{-4} M, CH_2Cl_2), **2** (1.0×10^{-4} M, CH_2Cl_2), **3a** (solid), **3b** (1.0×10^{-4} M, DMSO) and **4** (1.0×10^{-4} M, CH_2Cl_2)

nescence of the ttab ligand while the Zn^{II} and Ag^{I} ions partially quench the emission of the ttab ligand. Hydrogen-bonding interactions also lead to the significant quenching of the ttab luminescence. The sensitivity of the ttab luminescence toward various metal ions and hydrogen-bonding interactions makes it potentially useful as a fluorescent sensor for certain metal ions and molecules, which are being investigated in our laboratory.

Experimental Section

All the starting materials were purchased from Aldrich Chemical Co. THF was dried by refluxing over sodium and was freshly distilled prior to use. All the other reagent-grade solvents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 300 or 500 MHz spectrometer. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model 2 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Ltd, Delta, British Columbia.

Synthesis of $[(PdCl_2)_2(ttab)]$ (1): A solution of ttab (0.20 mmol, 0.108 g) in 20 mL of CH_3CN was added to a solution of K_2PdCl_4 (0.40 mmol, 0.130 g) in a minimum amount of water. The mixture was stirred at room temperature for 0.5 h, and the yellow precipitate was collected by filtration and washed with CH_3OH and diethyl ether. Recrystallization of the crude product from DMSO yielded orange crystals of **1** (0.204 g 97%). ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 8.93 (d, *J* = 5.0 Hz, 4 H, 7-aza), 8.17 (s, 2 H, phenyl), 8.14 (d, *J* = 7.0 Hz, 4 H, 7-aza), 7.70 (d, *J* = 3.5 Hz, 4 H, 7-aza), 7.29 (dd, *J* = 7.0, *J* = 5.0, 4 H, 7-aza), 6.76 (d, *J* = 3.5 Hz, 4 H, 7-aza) ppm. ^{13}C NMR: δ = 147.4, 145.6, 137.7, 136.7, 132.3, 131.3, 122.3, 117.7, 103.4 ppm. $C_{34}H_{22}Cl_4N_8Pd_2\cdot 2DMSO$ (1053.52): calcd. C 43.32, H 3.25, N 10.64; found C 42.85, H 3.20, N 10.48.

Synthesis of $[(ZnCl_2)_2(ttab)]$ (2): Anhydrous $ZnCl_2$ (0.054 g, 0.4 mmol) and ttab (0.108 g, 0.2 mmol) were mixed in 20 mL of THF and stirred overnight under nitrogen. The white precipitate formed was collected by decanting the solution, it was washed with THF and dried under vacuum to afford a white powder of **2** (0.148 g, 91%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 9.14 (dd, *J* = 5.5, *J* = 1.5 Hz, 4 H, 7-aza), 8.16 (dd, *J* = 8.0, *J* = 1.5 Hz, 4 H, 7-aza), 7.74 (d, *J* = 4.0 Hz, 4 H, 7-aza), 7.55 (s, 2 H, phenyl), 7.30 (dd, *J* = 8.0, *J* = 5.5 Hz, 4 H, 7-aza), 6.72 (d, *J* = 4.0 Hz, 4 H, 7-aza) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 147.9, 145.2, 139.3, 136.1, 134.3, 131.7, 124.7, 117.5, 104.1 ppm. $C_{34}H_{22}Cl_4N_8Zn_2\cdot 0.5CH_2Cl_2$ (857.66): calcd. C 48.32, H 2.70, N 13.07; found C 48.56, H 2.73, N 13.02.

Synthesis of $[Ag_2(NO_3)_2(ttab)]_n$ (3a): A solution of $AgNO_3$ (0.50 mmol, 0.085 g) in 5 mL of H_2O was layered on top of a solution of ttab (0.10 mmol, 0.0542 g) in 5 mL of CH_2Cl_2. After 12 days standing at ambient temperature, the white precipitate formed was collected and washed with H_2O, ethanol and then CH_2Cl_2, and dried under vacuum to afford **3a** (0.064 g, 73%). Compound **3a** is not soluble in non-coordinating solvents. As a result, NMR spectra were not recorded. $C_{34}H_{22}Ag_2N_{10}O_6$ (882.32): calcd. C 46.28, H 2.51, N 15.87; found C 46.91, H 2.65, N 15.75.

Synthesis of $[Ag_2(NO_3)_2(ttab)(DMSO)_2]$ (3b): Upon dissolution in DMSO under sonication, **3a** was converted into **3b** quantitatively. ^{1}H NMR (300 MHz, DMSO, 25 °C): δ = 8.50 (s, 2 H, phenyl), 8.24 (d, *J* = 4.5 Hz, 4 H, 7-aza), 8.08 (d, *J* = 7.5 Hz, 4 H, 7-aza), 7.24 (dd, *J* = 7.8, *J* = 4.8 Hz, 4 H, 7-aza), 7.10 (d, *J* = 3.0 Hz, 4 H, 7-aza), 6.52 (d, *J* = 3.6 Hz, 4 H, 7-aza) ppm. ^{13}C NMR: δ = 146.6, 143.6, 132.4, 129.7, 128.6, 128.1, 121.3, 117.0, 102.2 ppm. The CHN analysis results for **3b** are identical to those of **3a**, due to the loss of DMSO ligands prior to the analysis.

Table 2. Crystallographic data

Compound	1	2	3b	4
Formula	$C_{34}H_{22}Cl_4N_8Pd_2\cdot 2DMSO$	$C_{38}H_{34}N_8Zn_2Cl_4\cdot 4CH_2Cl_2$	$C_{38}H_{34}Ag_2N_{10}O_8S_2\cdot 2C_7H_8$	$C_{38}H_{24}N_8O_6F_6Zn\cdot C_7H_8$
FW	1053.45	1154.79	1222.88	962.13
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$Pca2_1$
a, Å	12.072(3)	9.553(5)	10.032(4)	18.853(11)
b, Å	11.333(3)	9.753(5)	19.692(9)	12.279(7)
c, Å	15.538(4)	14.156(7)	13.866(6)	19.603(11)
α, °	90	85.300(13)	90	90
β, °	93.693(4)	89.561(11)	106.307(10)	90
γ, °	90	63.010(9)	90	90
V, Å^3	2121.4(8)	1170.8(11)	2628.9(19)	2628.9(19)
Z	2	1	2	4
$D_{calc,}$ g cm^{-3}	1.649	1.638	1.545	1.408
T, K	297	296	298	298
μ, cm^{-1}	12.42	17.48	8.88	6.22
2θ, max, °	56.66	56.80	56.70	56.80
Reflns measured	14855	8374	17597	29882
Reflns used	5043	5373	6286	8729
Parameters	253	265	317	559
Final *R* [$I > 2θ(I)$]	R_1 [a] = 0.0459	R_1 [a] = 0.0948	R_1 [a] = 0.0625	R_1 [a] = 0.0893
	wR_2 [b] = 0.0694	wR_2 [b] = 0.1961	wR_2 [b] = 0.1262	wR_2 [b] = 0.1871
R (all data)	R_1 = 0.1362	R_1 = 0.2833	R_1 = 0.2822	R_1 = 0.3045
	wR_2 = 0.0823	wR_2 = 0.2458	wR_2 = 0.1682	wR_2 = 0.2440
Goodness-of-fit on F^2	0.769	0.745	0.685	0.777

[a] $R_1 = \Sigma|F_0| - |F_c|/\Sigma|F_0|$. [b] $wR_2 = [\Sigma w\,[(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_0^2) + (0.075P)^2]$, where $P = [\mathrm{Max}(F_0^2,0) + 2F_c^2]/3$.

Synthesis of $[Zn(O_2CCF_3)_2(H_2O)_2](ttab)$ (4): $Zn(CF_3COO)_2{\cdot}3H_2O$ (0.079 g, 0.23 mmol) and ttab (0.070 g, 0.13 mmol) were dissolved in 20 mL of THF at ambient temperature. Slow diffusion of toluene into the solution afforded colorless crystals of **4**. (0.114 g, 91%). ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 8.49$ (br. s, 4 H, H_2O), 8.17 (s, 2 H, phenyl), 8.10 (d, $J = 4.2$ Hz, 4 H, 7-aza), 7.25 (m, 8 H, 7-aza), 7.11 (d, $J = 3.6$ Hz, 4 H, 7-aza), 6.56 (d, $J = 3.6$ Hz, 4 H, 7-aza) ppm. For comparison purposes, the ttab free ligand ^1H NMR spectroscopic data are also included here (CD_2Cl_2, 25 °C): $\delta = 8.25$ (s, 2 H, phenyl), 8.16 (dd, $^3J = 5.0$, $^4J = 1.5$ Hz, 4 H, 7-aza), 7.85 (dd, $^3J = 7.5$, $^4J = 1.5$ Hz, 4 H, 7-aza), 7.05 (dd, $^3J_1 = 7.5$, $^3J_2 = 5.0$ Hz, 4 H, 7-aza), 6.98 (d, $^3J = 3.5$ Hz, 4 H, 7-aza), 6.37 (d, $^3J = 3.5$ Hz, 4 H, 7-aza) ppm. $C_{38}H_{26}F_6N_8O_6Zn{\cdot}C_7H_8$ (962.20): calcd. C 56.17, H 3.56, N 11.65; found C 55.94, H 3.44, N 11.98.

X-ray Crystallographic Analysis: Single crystals of ttab were obtained by slow diffusion of hexanes into a CH_2Cl_2 solution. Single crystals of **1** were obtained from a saturated DMSO solution. Single crystals of **2** were obtained from a CH_2Cl_2 solution. Single crystals of **3b** were obtained by slow diffusion of toluene and ethanol into a DMSO solution. Single crystals of **4** were obtained from a toluene/THF solution. All crystals were mounted on glass fibers. All data were collected on a Bruker P4 X-ray diffractometer with a SMART CCD 1000 detector, with monochromated Mo-K_α radiation, operating at 50 kV, 30 mA and ambient temperature. No significant decay was observed during the data collection. Data were processed on a Pentium PC using Bruker Axs Windows NT SHELXTL software package (version 5.10).[9] Neutral atom scattering factors were taken from Cromer and Waber.[10] Empirical absorption correction was applied to all crystals. The crystals of ttab and **2** belong to the triclinic space group $P\bar{1}$. The crystals of **1** and **3b** belong to the monoclinic space groups $P2_1/n$ and $P2_1/c$, respectively. The crystals of **4** belong to the orthorhombic space group $Pca2_1$. All structures were solved by direct methods. DMSO molecules were located in the lattice of **1** (2 DMSO per molecule of **1**). Disordered CH_2Cl_2 molecules were located in the lattice of **2** (4 CH_2Cl_2 per molecule of **2**). Toluene molecules were located in the lattice of **3b** and **4** (2 toluene per molecule of **3b**, 1 toluene per molecule of **4**). There are 1.5 independent molecules in the asymmetric unit of ttab. The disordered nitrate ions of **3b** and the CH_2Cl_2 molecules that co-crystallized with **2** were modeled successfully. All non-hydrogen atoms in **1−3b** were refined anisotropically except for the disordered nitrate ion, the co-crystallized toluene and CH_2Cl_2 molecules. The quality of the crystals of **4** is poor and partially twin. The CF_3 groups in **4** are all disordered. As a result, not all non-hydrogen atoms in **4** can be refined anisotropically. The positions of the hydrogen atoms were calculated and their contributions in structural factor calculations were included. The crystal data are summarized in Table 2. (The crystal data for the free ttab ligand are provided in the supporting information).

CCDC-213370 (**1**), -213371 (**3b**), -213372 (**4**), and -213374 (**2**) 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].

Supporting Information Available (see footnote on the first page of this article): A complete drawing of compound **3b** and the excitation and emission spectra.

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