



# Solvent effect on 3D topology of hybrid fluorides: Synthesis, structure and luminescent properties of Zn(II) coordination compounds



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## ABSTRACT

The mixture  $\text{ZnF}_2/\text{HF}_{\text{aq}}/\text{Hamtetraz}$  (*Hamtetraz* = 5-aminotetrazole) with the molar ratio 10/80/10 reacts at 160 °C in different solvents (methanol/water and water respectively) to give two new 3D compounds:  $(\text{Zn}_4\text{F}_4(\text{amtetraz})_4)\cdot\text{H}_2\text{O}$  (1) and  $(\text{Zn}_4\text{F}_4(\text{H}_2\text{O})(\text{amtetraz})_4)\cdot\text{H}_2\text{O}$  (2). The structures, determined by single crystal X-ray diffraction, exhibit neutral 3D-frameworks with narrow cavities that contain water molecules. Each network is built up from two types of parallel chains connected by aminotetrazolate ligands. The comparison of 1 and 2 with literature compounds shows that the nature of the polar solvent, aprotic or protic, influences the network characteristics, as well as the condensation of inorganic species or the bridging mode of the organic moieties. The luminescence properties of the zinc fluoro-aminotetrazolates are discussed.

## 1. Introduction

Porous coordination compounds, also known as Metal-Organic Frameworks (MOFs), have emerged during the last two decades. These hybrid compounds are nowadays considered as a new generation of multifunctional materials for potential applications in several fields, such as gas storage, health, catalysis or luminescent devices [1–4]. The desired properties can be tuned by combining the inorganic units, commonly built up from 3d metals or lanthanides [5–8] and the organic linkers, mainly carboxylic acids or azoles [9,10]. Azole ligands are extremely versatile linkers due to their heterocyclic character, in particular tetrazole derivatives [11]. Four nitrogen atoms, available in tetrazole rings, allow a broad range of bridging modes, opening the way to the design of new porous crystalline buildings with a remarkable structural diversity [10].

Whether the nature of the organic and inorganic entities plays a key role [12–15], it has been demonstrated that reaction conditions such as the synthesis temperature, the solvent or the pH [16–18] can strongly influence on framework design. Although very numerous examples of MOFs based on carboxylic acid linkers are available [19,20], fewer studies are reported for azole based networks [21,22], and those on fluorinated being downright scarce [23].

Our recent work has been focused on the deep understanding of the

influence of the synthesis parameters in azole based fluorinated networks, for instance, the molar ratio between the starting reactants and the synthesis temperature. We have shown that for fluorine rich compositions, hybrids with covalent bonds between the organic and inorganic entities and with high dimensionalities are favoured [24,25]. Moreover we have demonstrated the key role of the synthesis temperature on the topology of fluorinated MOFs [26]. At high temperatures and in solvothermal conditions, dimethylformamide solvent (DMF) hydrolyses into dimethylammonium cation  $[\text{Hdma}]^+$  and formate anion  $(\text{HCOO})^-$  [27,28]. The fragments produced by the DMF decomposition can either enter into the coordination sphere of the metal cation or act as a template. The network dimensionality can also be tuned by increasing the synthesis temperature, as demonstrated for hybrid fluorozincates prepared in acetonitrile (MeCN) [29].

Herein, we highlight the determining role of the solvent in the crystallization of zinc fluoro-aminotetrazolates. The solvothermal reaction of identical starting mixtures of  $\text{ZnF}_2/\text{HF}_{\text{aq}}/\text{Hamtetraz}$  was explored in different solvents. Two new hybrid fluorides  $(\text{Zn}_4\text{F}_4(\text{amtetraz})_4)\cdot\text{H}_2\text{O}$  (1) and  $(\text{Zn}_4\text{F}_4(\text{H}_2\text{O})(\text{amtetraz})_4)\cdot\text{H}_2\text{O}$  (2) were identified in methanol/water and water, respectively. Their structures are compared to the previously reported networks  $[\text{Hdma}]\cdot(\text{Zn}_4\text{F}_5(\text{amtetraz})_4)$  and  $[\text{NH}_4]\cdot(\text{Zn}_4\text{F}_5(\text{amtetraz})_4)\cdot 3\text{H}_2\text{O}$ , respectively prepared in dimethylformamide and acetonitrile [24,29]. Lastly

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**Table 1**Selected inter-atomic distances of zincate groups in  $(\text{Zn}_4\text{F}_4(\text{amtetraz}))\cdot\text{H}_2\text{O}$  (1) and  $(\text{Zn}_4\text{F}_4(\text{H}_2\text{O})(\text{amtetraz})_4)\cdot\text{H}_2\text{O}$  (2).

	1			2		
	Zn-(F/N)	d, Å	Cluster, Geometry	Zn-(F/N/O)	d, Å	Cluster, Geometry
Layer B	Zn(1)-F(2)	1.981 (6)	$\text{ZnF}_2\text{N}_3$ trigonal bipyramid	Zn(1)-F(1)	1.979 (3)	$\text{ZnF}_2\text{N}_3$ trigonal bipyramid
	Zn(1)-F(1)	1.988 (6)		Zn(1)-F(2)	1.982 (3)	
	Zn(1)-N(6)	2.019 (8)		Zn(1)-N(6)	2.011 (4)	
	Zn(1)-N(12)	2.103 (7)		Zn(1)-N(21)	2.091 (4)	
	Zn(1)-N(15)	2.154 (8)		Zn(1)-N(18)	2.126 (4)	
	< Zn-F > = 1.985 Å < Zn-N > = 2.092 Å			< Zn-F > = 1.981 Å < Zn-N > = 2.076 Å		
	Zn(2)-F(2)	1.979 (5)	$\text{ZnF}_2\text{N}_3$ trigonal bipyramid	Zn(2)-F(2)	1.982 (3)	$\text{ZnF}_2\text{N}_3\text{O}$ octahedron
	Zn(2)-F(1)	2.019 (5)		Zn(2)-F(1)	2.014 (3)	
	Zn(2)-N(1)	1.963 (9)		Zn(2)-N(1)	2.054 (4)	
	Zn(2)-N(14)	2.079 (8)		Zn(2)-N(17)	2.137 (4)	
	Zn(2)-N(11)	2.127 (7)		Zn(2)-N(20)	2.141 (4)	
	< Zn-F > = 1.999 Å < Zn-N > = 2.056 Å			< Zn-F > = 1.998 Å < Zn-N > = 2.111 Å		
	Layer A	Zn(3)-F(4)	2.033 (5)	$\text{ZnF}_2\text{N}_4$ octahedron	Zn(3)-F(4)	2.027 (3)
Zn(3)-F(3)		2.060 (5)	Zn(3)-F(3)		2.077 (3)	
Zn(3)-N(17)		2.083 (8)	Zn(3)-N(15)		2.094 (4)	
Zn(3)-N(20)		2.114 (8)	Zn(3)-N(11)		2.110 (4)	
Zn(3)-N(9)		2.137 (8)	Zn(3)-N(4)		2.120 (4)	
Zn(3)-N(3)		2.186 (8)	Zn(3)-N(8)	2.195 (4)		
< Zn-F > = 2.046 Å < Zn-N > = 2.130 Å				< Zn-F > = 2.052 Å < Zn-N > = 2.130 Å		
Zn(4)-F(4)		2.015 (5)	$\text{ZnF}_2\text{N}_4$ octahedron	Zn(4)-F(3)	2.019 (3)	$\text{ZnF}_2\text{N}_4$ octahedron
Zn(4)-F(3)		2.021 (5)		Zn(4)-F(4)	2.049 (3)	
Zn(4)-N(4)		2.114 (9)		Zn(4)-N(9)	2.116 (4)	
Zn(4)-N(8)		2.156 (8)		Zn(4)-N(3)	2.147 (4)	
Zn(4)-N(18)		2.183 (7)		Zn(4)-N(14)	2.203 (4)	
Zn(4)-N(21)		2.234 (8)	Zn(4)-N(12)	2.252 (4)		
< Zn-F > = 2.018 Å < Zn-N > = 2.172 Å			< Zn-F > = 2.034 Å < Zn-N > = 2.180 Å			

the photoluminescent properties of the compounds prepared in methanol (2), in DMF and MeCN were investigated, since coordination polymers based on  $\text{Zn}^{2+}$  and azole ligands have been reported as promising candidates for potential applications as photoactive materials: chemical sensors or light emitting diodes (LEDs) [30,31].

## 2. Results and discussion

### 2.1. Crystal structure description and comparison with other known structures

Compounds 1 and 2 crystallize in the orthorhombic and monoclinic systems, respectively; both phases show a 3D neutral framework in which disordered water molecules are inserted. 1 and 2, with non-centrosymmetric space groups, exhibit roughly similar structures that are confirmed by the examination of inter-atomic distances (Table 1), at the exception of one oxygen atom. The 3D frameworks can be described from two types of (001) layers connected along the *c* axis by anionic ligands *amtetraz*<sup>-</sup> in the connection mode N1,N2,N4 as defined in [24] (Fig. 1(a) and (b)).

The first type of layer (A), located at *z* = 0 and 1/2 for 1 and at *z* = 0 for 2, results from the association of  $\infty[\text{ZnFN}_4]$  chains by tetrazolate anions in N1,N2,N3,N4 bridging modes (Fig. 2(a)). The zinc atoms, Zn (3) and Zn(4), adopt an octahedral coordination and are surrounded by two fluorine atoms and four nitrogen atoms from independent organic anions.  $\text{Zn}(3)\text{F}_2\text{N}_4$  and  $\text{Zn}(4)\text{F}_2\text{N}_4$  entities, linked by fluorine corners with *trans* or *cis* orientation, respectively, alternate in these original chains. At *z* = 1/4 and *z* = 3/4 for 1 (B layer) and at *z* = 1/2 for 2 (B' layer), the second type of layers is observed, in which the tetrazolate linkers connect the chains of zinc polyhedra in N1,N2,N3,N4 bridging mode (Fig. 2(b)).

In 1, evidenced in a mixture of methanol and water, the  $\text{ZnF}_2\text{N}_3$  (Zn (1) and Zn(2)) units share adjacent and opposite fluorine corners to form  $\infty[\text{ZnFN}_3]$  *cis-trans* chains. In 2, obtained with water only, a similar condensation is observed but the metal cations adopt a trigonal bipyramidal geometry in  $\text{Zn}(1)\text{F}_2\text{N}_3$  and an octahedral geometry in  $\text{Zn}(2)\text{F}_2\text{N}_3\text{O}$ . Therefore, in absence of methanol, water molecules complete the immediate coordination sphere of Zn(2) cations. If water molecules are mentally ignored in 1 and 2, both structures present a same architecture with a calculated porosity of 19% (PLATON software [32]). It must be noted that both structures 1 and 2 can also be described as inorganic chains connected by *amtetraz* anions along two other perpendicular directions. A similar construction is observed for two other compounds,  $[\text{NH}_4]\cdot(\text{Zn}_4\text{F}_5(\text{amtetraz})_4)\cdot 3\text{H}_2\text{O}$  and  $[\text{Hdma}]\cdot(\text{Zn}_4\text{F}_5(\text{amtetraz})_4)$ , also prepared in identical reaction mixtures but in different solvents, respectively acetonitrile (MeCN) and dimethylformamide (DMF) (Fig. 3) [24,29].

In  $[\text{NH}_4]\cdot(\text{Zn}_4\text{F}_5(\text{amtetraz})_4)\cdot 3\text{H}_2\text{O}$  and  $[\text{Hdma}]\cdot(\text{Zn}_4\text{F}_5(\text{amtetraz})_4)$ , two types of [100] chains are distinguished (Fig. 4). These chains, in which zinc cations adopt octahedral or trigonal bipyramidal coordinations, are linked by tetrazolate anions in the N1,N2,N4 bridging mode as observed in (1) and (2). The first *trans*-chain  $\infty[\text{ZnFN}_4]$  results from the connection of  $\text{ZnF}_2\text{N}_4$  octahedra by two opposite F<sup>-</sup> vertices while the second *trans*-chain  $\infty[\text{Zn}_2\text{F}_3\text{N}_4]$  results from the condensation of two  $\text{ZnF}_3\text{N}_2$  polyhedra by one (F-F) edge, to give dimeric units that are further connected by opposite F<sup>-</sup> corners. The difference between both structures is the relative orientation of chains (Fig. 3), governed by the symmetry elements ( $P2_1/c$  for  $[\text{NH}_4]\cdot(\text{Zn}_4\text{F}_5(\text{amtetraz})_4)\cdot 3\text{H}_2\text{O}$  and  $P2/m$  for  $[\text{Hdma}]\cdot(\text{Zn}_4\text{F}_5(\text{amtetraz})_4)$ ).

Interestingly, the formation of *trans*-chains linked by organic ligands in N1-N2-N4 bridging mode is formed in aprotic polar solvents (DMF, MeCN), whereas with protic polar solvents (methanol, water), both

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