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ARTICLE

Photoluminescence of the First Examples of Metal-Organic-Frameworks with Two Novel Tetrazolatephenyl Acetic Acid Derivatives. An Experimental and Theoretical Study.

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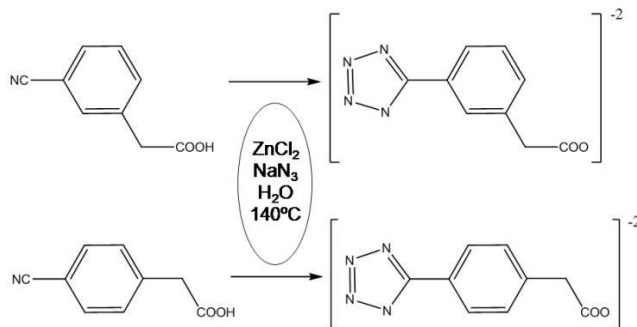
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We report on the synthesis of two new Zn Metal-Organic-Frameworks with 1,3-tetrazolatephenyl-acetic and 1,4-tetrazolatephenyl-acetic spacers obtained *in situ* by hydrothermal routes. These three-dimensional structures exhibit an intense blue-green long lifetime photoluminescence emissions at room temperature in the solid state. To the best of our knowledge, this is the first time that coordination compounds have been synthesized with these ligands.

1. Introduction.

The Metal-Organic Framework materials currently represent an area of enormous interest owing not only to the need of developing new functional materials but also of elucidating their topologies and their potential applications.¹ Recently, the design and study of Zn-based MOF has evolved enormously² because of their interesting structures and in particular their potential applications in areas such as luminescence,³ gas adsorption,⁴ sensing, and optical storage.⁵ These materials are commonly prepared through a bottom-up approach, using solvothermal methods, connecting ions with the appropriate bridging ligands. Still, there is a great interest in the design of new bridging ligands that will allow the preparation of novel MOFs. In the last years, we and others have described different metal coordination polymers based on tetrazolate with interesting topologies synthesized by *in situ* Demko-Sharpless cycloaddition reactions of organonitriles and sodium azide.⁶ Moreover, we have shown the use of hydrothermal syntheses to generate *in situ* new ligands and construct novel three-dimensional coordination polymers.⁷ Following our previous studies, we have designed, by hydrothermal routes, two new multidentate bridging anionic ligands derivatives of tetrazolatephenyl-acetic acid (H₂tzbaa), 3-tetrazolatephenyl acetic and 4-tetrazolatephenyl acetic linkers (Scheme I), which contain one carboxylate group and one tetrazolate ring with a methylene-benzene group in the middle of the spacer. Thanks to its extended aromaticity and to the presence of poly-

heterosubstituted penta- and hexa-atomic rings, H₂tzbaa is a good candidate for enhanced emissive properties tunable, in principle, by coordination to different metals or environments.

Scheme I. Spacers obtained *in situ* by hydrothermal routes.

Here, we report on the synthesis, the crystal structure and the luminescence properties of the first examples of 3D-MOFs [Zn(1,3-tzbaa)]_n (**1**) and [Zn(1,4-tzbaa)]_n (**2**) with the new multidentate derivative anionic tzbaa²⁻ ligands, demonstrating the potential of this new linkers to construct novel MOFs. To the best of our knowledge, these are the first examples of MOFs with these derivative ligands, investigated here for the first time. There is only one biological study on 1,4-H₂tzbaa, used as

inhibitor for the Syk C-Terminal SH2 Domain in biomedical area.⁸

2. Experimental.

General Procedures: Unless stated otherwise, all reactions were conducted by hydrothermal conditions, with the reagents purchased commercially and used without further purification.

2.1. Preparation of complexes.

Preparation of [Zn(1,3-tzbaa)]_n (1). A mixture of ZnCl₂ (0.136 g, 1 mmol), 3-cyanophenyl acetic acid (0.161 g, 1 mmol), sodium azide (0.195 mg, 3 mmol) and distilled water (10 mL) was sealed in a Teflon-lined acid digestion autoclave and heated at 160 °C under autogenous pressure. After 12 h of heating, the reaction vessel was slowly cooled down to room temperature during a period of about 3 h. Yellow crystals of the compound under study were obtained. Yield: 65%, based on Zn. Anal. calcd C₉H₆N₄O₂Zn: C 40.37, H 2.24, N 20.93. Found: C 40.78, H 2.81, N 21.29. IR/cm⁻¹: 3421 (s), 2921 (m), 2850 (w), 1536 (s), 1385 (s), 1209 (m), 1077 (m), 813 (m), 773 (m), 742 (s), 684 (s).

Preparation of [Zn(1,4-tzbaa)]_n (2). A mixture of ZnCl₂ (0.136 g, 1 mmol), 4-cyanophenyl acetic acid (0.161 g, 1 mmol), sodium azide (0.195 mg, 3 mmol) and distilled water (10 mL) was sealed in a Teflon-lined acid digestion autoclave and heated at 160 °C under autogenous pressure. After 12 h of heating, the reaction vessel was slowly cooled down to room temperature during a period of about 3 h. Colourless crystals of the compound under study were obtained. Yield: 39%, based on Zn. Anal. calcd C₉H₆N₄O₂Zn: C 40.37, H 2.24, N 20.93. Found: C 40.49, H 2.92, N 21.11. IR/cm⁻¹: 3440 (m), 2957 (w), 2910 (w), 1541 (s), 1382 (s), 1212 (m), 1018 (m), 832 (m), 743 (m), 710 (m).

2.2. Physical measurements.

Elemental analyses were carried out at the “Centro de Instrumentación Científica” (University of Granada) on a Fisons-Carlo Erba analyser model EA 1108. IR spectra on powdered samples were recorded with a Thermo Nicolet IR200FTIR using KBr pellets.

2.3. Single-Crystal Structure Determination.

Suitable crystals of **1** and **2** were mounted on a glass fibre and used for data collection on a Agilent Supernova diffractometer, equipped with CCD area detector and using microfocused monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by applying the ω -scan method. Lorentz-polarization and empirical absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares calculations on F^2 using the program SHELXS97.⁹ Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. Final

$R(F)$, $wR(F^2)$ and goodness of fit agreement factors, details on the data collection and analysis can be found in Table 1. Selected bond lengths and angles are given in Tables S1 and S2 (ESI). CCDC reference numbers for the structures of **1** and **2** were 930950 and 930951. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336-033; e-mail, deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic Data and Structural Refinement Details.

Compound	1	2
Formula	C ₉ H ₆ N ₄ O ₂ Zn	C ₉ H ₆ N ₄ O ₂ Zn
M_r	267.55	267.55
Crystalsystem	Orthorhombic	Orthorhombic
Space group (no.)	$Pna2_1$	$Pca2_1$
a (Å)	10.4858(3)	18.5081(5)
b (Å)	18.8309(6)	4.8230(1)
c (Å)	4.8130(2)	10.9635(4)
V (Å ³)	950.36(6)	978.65(5)
Z	4	4
D_c (g cm ⁻³)	1.87	1.816
μ (MoK α) (mm ⁻¹)	2.572	2.498
T (K)	293	293
Observed reflections	2031 (1835)	1955 (1510)
R_{int}	0.0303	0.0429
Parameters	145	145
GOF	1.08	1.049
R_I for $I > 0$ (and for $I > 2 \sigma(I)$)	0.0386 (0.0319)	0.0536 (0.0347)
wR_2 for $I > 0$ (and for $I > 2 \sigma(I)$)	0.0784 (0.0731)	0.0677 (0.0580)
Flack parameter	-0.04(2)	-0.01(2)
Largest peak and hole (e Å ⁻³) of residual density	0.543 and -0.389	0.402 and 0.-348

$$^a R_I = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$$

2.4. Luminescence measurement.

A Varian Cary-Eclipse Fluorescence Spectrofluorimeter was used to obtain the fluorescence spectra. The spectrofluorimeter was equipped with a xenon discharge lamp (peak power equivalent to 75 kW), Czerny-Turner monochromators, R-928 photomultiplier tube which is red sensitive (even 900 nm) with manual or automatic voltage controlled using the Cary Eclipse software for Windows 95/98/NT system. The photomultiplier detector voltage was 700 V and the instrument excitation and emission slits were set at 5 and 5 nm, respectively.

3. Results and Discussion.

Hydrothermal reactions of zinc chloride (1 mmol) with the appropriate 3-cyanophenyl acetic acid or 4-cyanophenyl acetic acid (1 mmol) and sodium azide (3 mmol) in water (10 ml) at 160 °C for 12 h followed by cooling to room temperature over 3 h yields prismatic yellow and colourless crystals of **1** (in 65% yield) and **2** (in 39% yield), respectively.

3.1. Description of the structures.

The crystal structures were determined by single crystal X-ray diffraction.

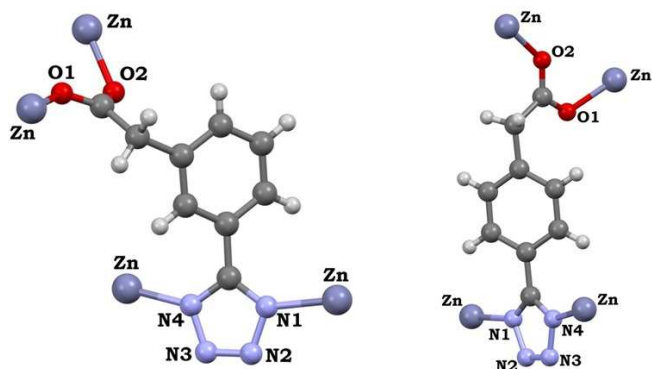


Figure 1. A view of the coordination mode of the ligands (1,3-tzbaa)²⁻ and (1,4-tzbaa)²⁻ for **1** (left) and **2** (right), respectively. Selected bond distances for **1** and **2** respectively: Zn-N1 2.001(3), 1.991(5); Zn-N4 1.965(3), 1.973(6); O(1)-Zn(1) 1.972(3), 1.965(2); O(2)-Zn(1) 1.962(3), 1.976(2); N(1)-N(2) 1.361(4), 1.379(6); N(2)-N(3) 1.287(4), 1.285(5); N(3)-N(4) 1.348(4), 1.352(6).

Both MOFs crystallize in the orthorhombic system and in the crystal class *mm2*, though in two different space groups (*Pna2₁* and *Pca2₁* for **1** and **2**, respectively). Both form three-dimensional networks, originated from tetrahedral Zn²⁺ connectors coordinated to four (tzbaa)²⁻ linkers. The binding sites of the (tzbaa)²⁻ ligands are the two oxygens of the carboxylate group and two nitrogen atoms (N1 and N4) of the tetrazole ring. (1,3-tzbaa)²⁻ and (1,4-tzbaa)²⁻ are structural isomers, therefore the coordination polymers are different. This depends on the distance between the carboxylic and the tetrazole groups in the two ligands, on their mutual orientation and on their conformations. In (1,3-tzbaa)²⁻, the tetrazole and the carboxylic group are inclined with respect to the phenyl ring by ca 44° and 67°, respectively, whereas in (1,4-tzbaa)²⁻ the planes are less inclined (32° and 60°, respectively). Details of the principal bonding distances are given in caption to Figure 1. For **2**, the Zn1 atom has a ZnN₂O₂ environment in which is coordinated with two oxygen atom pertaining to the carboxylate group and two nitrogen atoms from the tetrazole ring. The network of **2** is characterized by large 6-member rings, made of 3 linkers and 3 connectors, producing apparent channels (though, not sufficiently large to host extra-framework molecules). These channels are parallel to *b* and therefore perpendicular to the 2₁ helix (Figure 2, bottom). The rings are formed by two long and one short edges. Long edges interconnect one Zn atom coordinated to the carboxylate group with another Zn coordinated to the tetrazole group. Short edges

interconnect two Zn atoms linked to O1 and O2 or two Zn atoms linked to N1 and N4. This network has the topological type of Lonsdaleite (the so-called hexagonal diamond).

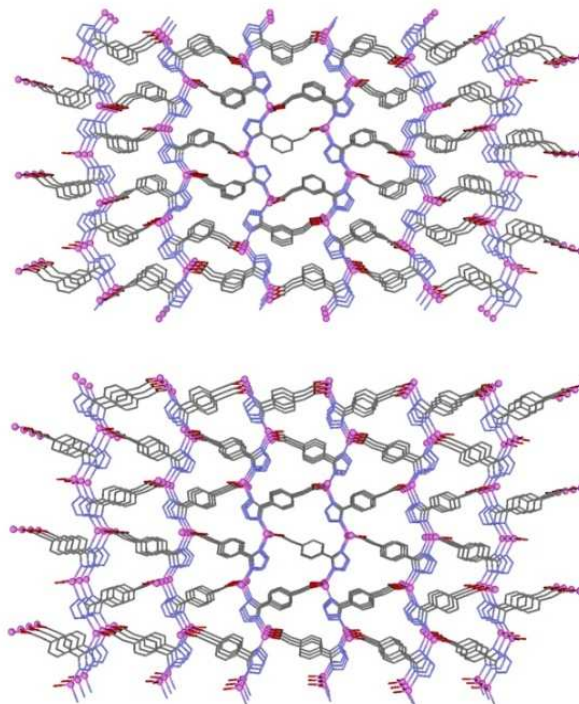


Figure 2. Packings of **1** (top) and **2** (bottom) along *c* and *b* axes, respectively.

The Zn1 atom in **1** has a tetrahedral ZnN₂O₂ geometry in which two positions are occupied by two oxygen atoms pertaining to carboxylate groups of different (1,4-tzbaa)²⁻ ligands, and the other positions are nitrogen atoms from tetrazolate rings. In this case, the structure of **1** is more complex (Figure 2, top), having three different types of cycles: one 8-member rings (4 connectors + 4 linkers); three 6-member rings (4 connectors + 2 linkers); two 4-member rings (2 connectors + 2 linkers). 4- and 8-member rings form apparent channels along the helical axis *c*., visible in Figure 2 (top), whereas the 6-member ones form channels perpendicular to the plane of the plot and parallel to *a*. The network has the topology of SrAl₂, which is quite frequent for MOFs.

3.2. Luminescence Studies.

The emission spectra of **1** and **2** in the solid state at room temperature are shown in Figure 3. Broad intense emission bands are observed, centred about $\lambda = 449$ and 479 nm, respectively, upon excitation at $\lambda = 350$ nm. The emissions in complexes **1** and **2** are assigned to intraligand $\pi \rightarrow \pi^*$ transitions.

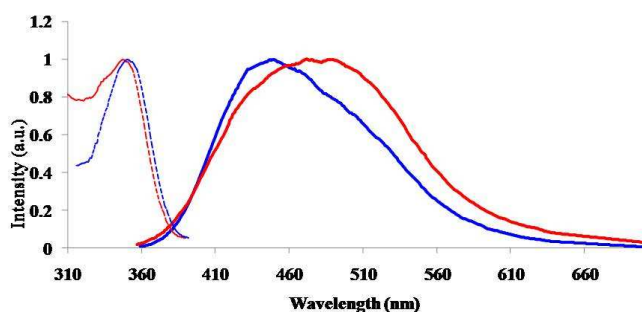


Figure 3. The emission spectra of **1** (blue) and **2** (red) after excitation at 350 nm in solid state at room temperature.

Emission spectra of **1** and **2**, as well as free 1,3-tzbaa²⁻ and 1,4-tzbaa²⁻ ligands were also calculated computationally. All theoretical calculations were performed using the Gaussian 09 package¹⁰. Atomic coordinates of **1** and **2** were obtained from their corresponding crystal structures, being both systems reduced to their minimum possible size (models 1 and 2 hereafter), i.e. the first coordination sphere of a Zn²⁺ cation (see Figure 4). The energy calculation and geometry optimization of the first six vertical excited singlet and triplet states was carried out using time-dependent density functional theory (TD-DFT), the B3LYP functional¹¹ and 6-31G+(d,p) basis set for all atoms. The molecular orbitals were visualized using gMolden¹² and emission spectra data were processed using Microsoft Excell (2007).

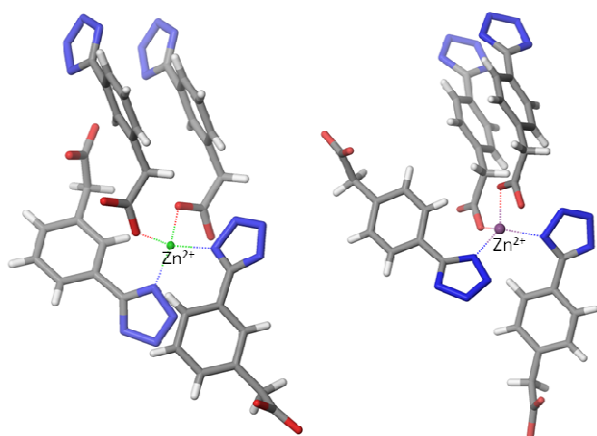


Figure 4. Models 1 and 2 generated from crystal structures of **1** and **2**, respectively.

Theoretical TD-DFT studies revealed that absorption and emission spectra of compounds **1** and **2** (Table 1) are related to intrinsic electronic properties of ligands 1,3-tzbaa²⁻ and 1,4-tzbaa²⁻ (Table S3 and Figure S6), respectively, which are generated *in-situ* in the reaction path of compounds **1** and **2**.

Compound	Exp. Emis.(nm)	Calc. Emis. (nm)	Calc. Transitions
1	449	474	HOMO←LUMO
2	479	417 504	HOMO←LUMO+1 HOMO←LUMO

Table 1. Experimental and calculated emission maxima and corresponding transitions for models 1 and 2.

Interestingly, theoretical TDDFT calculations estimated a 30nm shift between the emission maxima of models 1 and 2 (474nm vs 504nm), respectively, which agrees with the 30nm shift observed experimentally (449nm vs 479nm) (Figure 5). Model 1 shows a LUMO→HOMO transition at 474 nm (Table 1 and Figure 5), 25nm red shifted as compared to the experimental results (449nm). Model 2 shows a LUMO+1→HOMO and a LUMO→HOMO relaxation at 417 and 504 nm, respectively, slightly red shifted as compared to experimental results (479nm).

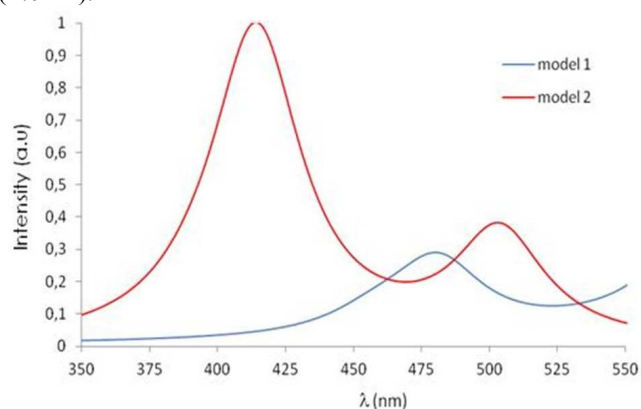


Figure 5. Calculated emission spectra of models **1** and **2**.

As observed from the shape of the orbitals depicted in Figure 5, the emission spectra observed experimentally are related to π*→π transitions between the aromatic ring and the carboxylic group of the ligands (Figure 6) present in the described MOFs.

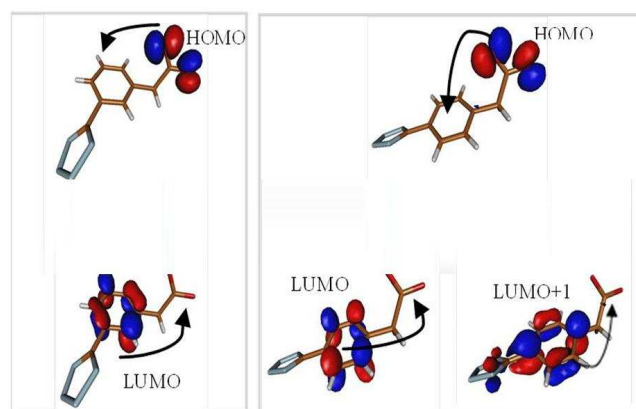


Figure 6. Representation of the molecular orbitals involved in absorption (top) and emission (bottom) spectra of compounds **1** and **2**.

The similarity of emissions for **1** and **2** is in agreement with the explanation, which indicates that ligand-centered π - π^* excitation is responsible for emissions. In contrast with Zn complexes of 5-aliphatic tetrazolates that usually show emissions in the range of 390–420 nm,¹³ energetic emissions in **1** and **2** possibly come from the conjugation of tetrazolate and phenyl-carboxylate groups. The decay curves were fitted to mono exponential function: $I = I_0 + A_1 \exp(-t/\tau)$, where I and I_0 are the luminescent intensities at time t and 0, τ is defined as the luminescent lifetime. For this function, the best fit of the experimental luminescence intensities to the above equation led to the lifetimes of 0.084 ms and 0.098 ms for **1** and **2**, respectively.

Conclusions

We have succeeded in synthesising the first metal-organic-frameworks with the 1,3-tetrazolatephenyl-acetic and 1,4-tetrazolatephenyl-acetic spacer ligands. These compounds show fascinating structures with intense blue-green photoluminescence emission at room temperature in the solid state. To the best of our knowledge, this is the first time that coordination compounds have been synthesized with these new multidentate ligands.

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Notes and references

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† CCDC 930950 and 930951 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Photoluminescence of the First Examples of Metal-Organic-Frameworks with Two Novel Tetrazolatephenyl Acetic Acid Derivatives. An Experimental and Theoretical Study.

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We report on the synthesis of two new Zn Metal-Organic-Frameworks with 1,3-tetrazolatephenyl-acetic and 1,4-tetrazolatephenyl-acetic spacers obtained *in situ* by hydrothermal routes. These three-dimensional structures exhibit an intense blue-green long lifetime photoluminescence emissions at room temperature in the solid state. To the best of our knowledge, this is the first time that coordination compounds have been synthesized with these ligands.

