Benzoate substituents effects on the structure of Zn(II) complexes and 1D 4,4’-bipyridine derived coordination polymers

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Keywords: Zn(II) complexes; *N*-heterocyclic ligands; coordination polymer; supramolecular network; photoluminescence properties.

Abstract

The aim of this work is to study the influence of different substituents in two closely related ligands, 3,5-dihydroxybenzoate (3,5-$(HO)_2Bz$) and 3,5-dimethoxybenzoate (3,5-$(MeO)_2Bz$), in the structure of zinc complexes. The compound $[Zn(3,5\text{-}(MeO)_2Bz)_2(CH_3OH)]_2$ (**2**) has been synthesized, characterized and its crystal structure elucidated, showing a *paddle wheel* type dinuclear molecule, with four bridging carboxylate ligands in a *syn-syn* coordination mode and methanol molecules in the apical positions. This discrete structural array is different than the polymeric structure observed in $\{[Zn(\mu\text{-}3,5\text{-}(HO)_2Bz)(\mu\text{-}OH_2)(H_2O)_2]\cdot 3,5\text{-}(HO)_2Bz\cdot 4H_2O\}_n$, previously reported in our group. These two Zinc complexes were used as precursor for the synthesis of coordination polymers (CPs) with the 4,4'-bipyridine (4,4'-bpy) linker. The solvent used in their synthesis influences the chemical composition of this CPs. Thus, $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-bpy})]\cdot 2DMSO\}_n$ (**3**) was achieved in dimethylsulfoxide (DMSO) while $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-bpy})]\cdot 4,4'\text{-bpy}\cdot 1/2CH_3OH\}_n$ (**4**) was formed in methanol (MeOH) as solvent. The reaction of **2** with 4,4'-bpy yielded $[Zn_2(\mu\text{-}3,5\text{-}(MeO)_2Bz)_4(\mu\text{-}4,4'\text{-bpy})]_n$ (**5**) in methanol, while after recrystallization in boiling water, complex $\{[Zn(3,5\text{-}(MeO)_2Bz)_2(\mu\text{-}4,4'\text{-bpy})]\cdot H_2O\}_n$ (**6**) was isolated in low yield. This compound **6** can also be synthesized by a mechanochemical approach, using water in a liquid assisted grinding. The crystal structures of complexes **3**, **4** and **6** were elucidated, all three showing *zigzag* polymeric arrays. Both polymers containing 3,5-$(MeO)_2Bz$ (**5** and **6**), showed solid state luminescence.

1. Introduction

Coordination polymers (CPs) have attracted an enormous interest among chemists due to their interesting physical and chemical properties [1,2]. The 4,4’-bipyridine (4,4’-bpy) is an *exo*-bidentate ligand which acts as an ideal linker between transition metals and could be considered as a prototypical rigid ligand for the formation of coordination polymers. The structure of the polymers constructed by 4,4’-bpy are strongly dependent on the geometric preference of the metal ions and on the metal-to-ligand molar ratio [1,3]. It can promote the formation of a great variety of frameworks, varying from 1D to 3D nets [4]. A 1:1 metal-to-ligand molar ratio usually generates linear or *zigzag* chains while the 1:2 metal-to-ligand molar ratio tends to form square grid [5,6] or diamond-like structures [7], among others. Besides, the final network could be highly influenced by other factors (anionic ligands that complete the metal coordination, pH value and solvent used in the synthesis, solubility of products). In some cases, a subtle alteration in any of these factors can lead to complexes with different structure and/or dimensionality [1]. It must be considered that 4,4’-bpy can also act as a terminal ligand or as an uncoordinated guest molecule, which may be further involved in hydrogen bonding and/or π-π stacking interactions [8-12]. The supramolecular structures made from the aggregation of 1D polymers can exhibit cavities/channels of molecular dimensions and thus include different guest molecules [1,2]. All these possibilities explain the difficulty to define the suitable experimental conditions for the formation of a coordination polymer with a desired structure. Therefore, systematic investigation is still necessary for the better understanding of the relationships between the structures of the coordination polymers and the experimental parameters for their preparation.

The carboxylate ligands constitute an important class of ligands in the formation of CPs and concretely one of the most used in the construction of CPs in combination with 4,4′-bpy [13-15]. The presence of hydroxyl groups in carboxylate ligands determine the arrangement of the polymer chains, as hydroxyl groups can be involved in the formation of hydrogen bond intermolecular interactions [16] and even in metal coordination [17]. As part of our research in compounds formed by carboxylate ligands and Zn(II) as metal node, recently we have reported the synthesis of complex $[Zn(3,5\text{-}(HO)_2Bz)_2(H_2O)_2]_n$ (**1**), which by recrystallization in water gives the coordination polymer $\{[Zn(\mu\text{-}3,5\text{-}(HO)_2Bz)(\mu\text{-}OH_2)(H_2O)_2]\cdot 3,5\text{-}(HO)_2Bz\cdot 4H_2O\}_n$. Moreover, its reaction with monodentate pyridine ligand leads to the formation of monomeric compounds [18]. As a continuation of this study, we first synthesized a Zn complex including a closely related ligand, $3,5\text{-}(MeO)_2Bz$. The properties as electron donating groups are very similar for hydroxyl and methoxy groups and thus both benzoic acid derivatives have a very similar pK_a value ($H(3,5\text{-}HO)_2Bz$, 4.04; $H(3,5\text{-}MeO)_2Bz$, 3.96) [19]. The most important difference between both ligands is the capacity of hydroxyl groups of being a hydrogen bond donor, that not only determines the supramolecular interactions but also indirectly determines the coordination sphere around Zn(II) cations. Further, we used both complexes as precursors to prepare one-dimensional coordination polymers with 4,4'-bpy as linker, and different solvents were used for each precursor combination. These new materials are fully characterized, including the elucidation of four crystal structures and their solid-state luminescence analyzed.

2. Experimental

2.1 Materials and general details

Zinc oxide nanopowder (<100 nm particle size), Zinc acetate dihydrate ($Zn(MeCO_2)_2 \cdot 2H_2O$), 3,5-dihydroxybenzoic acid ($3,5\text{-}H(HO)_2Bz$), 3,5-dimethoxybenzoic acid ($3,5\text{-}H(MeO)_2Bz$), 4,4'-bipyridine (4,4'-bpy), and methanol (MeOH) and dimethylsulfoxide (DMSO) as solvents, were purchased from Sigma-Aldrich and used without further purification. All reactions and manipulations were carried out in air. The synthesis of $[Zn(\mu\text{-}3,5\text{-}(HO)_2Bz)_2(H_2O)_2]_n$ (**1**) has been previously described in the literature [18]. Elemental analyses (C, H, N) were carried out on a Euro Vector 3100 instrument. FTIR-ATR spectra were recorded on a Tensor 27 (Bruker) spectrometer, equipped with an attenuated total reflectance (ATR) accessory model MKII Golden Gate with a diamond window in the range 4000-600 cm^{-1}. ^1H NMR spectra were recorded on an NMR-FT Bruker 250 MHz or an NMR-FT Bruker 400 MHz spectrometer in DMSO-d_6 solution at room temperature (r.t.). All chemical shifts (δ) are given in ppm. The photoluminescence properties of Zn(II) complexes were studied by confocal scanning laser microscopy (CSLM, Leica TCS SP5). Approx. 20 mg of each complex were mounted on Ibidi culture dishes (Ibidi GmbH, Martinsried, Germany), excited with a blue diode laser (405 nm) and the fluorescence intensity was recorded generating a lambda stack with emission wavelength ranging from 415 to 750 nm.

*2.2 Synthesis of $[Zn(\mu\text{-}3,5\text{-}(MeO)_2Bz)_2(CH_3OH)]_2$ (**2**)*

A solution containing $3,5\text{-}H(MeO)_2Bz$ (364 mg, 2.00 mmol) in MeOH (40 mL) was added to a solution of $Zn(MeCO_2)_2 \cdot 2H_2O$ (219 mg, 1.00 mmol) in MeOH (30 mL) at r.t. The resulting colorless solution was allowed to concentrate at r.t. until colorless crystals precipitated. The obtained crystals were filtered and washed with cold methanol

(5 mL) and dried in air. Suitable crystals for X-ray diffraction method were grown by slow evaporation of mother liquors for 24 h.

Yield: 284 mg (61.8%) (with respect to $Zn(MeCO_2)_2{\cdot}2H_2O$) Elemental Analysis: Calc. for $C_{38}H_{44}O_{18}Zn_2$ (919.56 g·mol^{-1}): C 49.63; H 4.82. Found: C 49.59; H 4.78%. FTIR-ATR (wavenumber, cm^{-1}): 3191(w) [ν(O-H)], 3098-3010(br) [ν(C-H)$_{ar}$], 2977(w) [ν(C-H)$_{al}$], 2946(w) [ν(C-H)$_{al}$], 1629(w), 1586(s) [ν$_{as}$(COO)], 1554(m), 1450(m) [ν$_s$(COO)], 1424(m), 1381(s), 1326(m), 1303(w), 1249(w), 1194(m), 1151(s), 1059(m) [δ(C-H)$_{ip}$], 1015(m) [δ(C-H)$_{ip}$], 854(m), 788(w), 759(s) [δ(C-H)$_{oop}$], 678(w), 649(w). ^{1}H NMR (250 MHz; DMSO-d_6; 298 K): δ = 3.16 [6H, d, ^3J = 5.2 Hz, CH_3-OH], 3.76 [24H, s, CH_3-OR], 4.09 [2H, q, ^3J = 5.2 Hz, CH$_3$-OH], 6.60 [4H, t, ^4J = 2.5 Hz, *p*-C*H*], 7.08 [8H, d, ^4J = 2.4 Hz, *o*-C*H*].

*2.3 Synthesis of $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]{\cdot}2DMSO\}_n$ (**3**)*

A solution containing 4,4'-bpy (93 mg, 0.60 mmol) in DMSO (10 mL) was added to a solution of compound **1** (234 mg, 0.57 mmol) in DMSO (10 mL) at r. t. The resulting yellow solution was allowed to concentrate at r.t. until a white powder precipitated. The obtained solid was filtered and washed with cold ethanol (5 mL) and dried in air. Suitable crystals for X-ray diffraction method were grown by slow evaporation of mother liquors for 50 h.

Yield: 288 mg (73.3%) (with respect to compound **1**). Elemental Analysis: Calc. for $C_{28}H_{30}N_2O_{10}S_2Zn$ (684.09 g·mol^{-1}): C 49.16; H 4.42, N 4.10. Found: C 49.43; H 4.39; N 4.03%. FTIR-ATR (wavenumber, cm^{-1}): 3190(m) [ν(O-H)], 3101-3004(br) [ν(C-H)$_{ar}$], 2991-2830 [ν(C-H)$_{al}$], 1611(w) [ν(C=N)$_{4,4'\text{-}bpy}$], 1577(s) [ν$_{as}$(COO)], 1496(w), 1420(w), 1386(s) [ν$_s$(COO)], 1357(s), 1284(m), 1226(w), 1162(m), 1078(w), 989(s) [δ(C-H)$_{ip}$], 946(s), 862(w), 849(w), 823(m), 777(s) [δ(C-H)$_{oop}$], 642(m). ^{1}H

NMR (250 MHz; DMSO-d_6; 298 K): δ = 6.30 [2H, t, ^4J = 2.2 Hz, *p*-C*H*], 6.85 [4H, d, ^4J = 2.3 Hz, *o*-C*H*], 7.87 [4H, d, ^3J = 5.9 Hz, $(m\text{-}CH)_{4,4'\text{-bpy}}$], 8.76 [4H, br, $(o\text{-CH})_{4,4'\text{-bpy}}$], 9.24 [4H, s, Ar-O*H*].

2.4 Synthesis of $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-bpy})]\cdot 4,4'\text{-bpy}\cdot 1/2\ CH_3OH\}_n$ (**4**)

A solution containing 4,4'-bpy (186 mg, 1.20 mmol) in MeOH (10 mL) was added to a solution of compound **1** (234 mg, 0.57 mmol) in MeOH (10 mL) at room temperature. The resulting yellow solution was allowed to concentrate at r.t., until a white powder precipitated. The solid was filtered and washed with cold MeOH (5 mL) and dried in air.

Single crystals suitable for X-ray diffraction structure elucidation were obtained after 48 h by layering a solution of compound **1** (115 mg, 0.28 mmol) in MeOH (10 mL) over a solution containing 4,4'-bpy (87 mg, 0.56 mmol) in $CHCl_3$ (10 mL).

Yield: 320 mg (79.6%) (with respect to compound **1**). Elemental Analysis: Calc. for $C_{34.5}H_{28}N_4O_{8.5}Zn$ (700.03 g·mol^{-1}): C 59.19; H 4.03; N 8.00. Found: C 59.32; H 3.95; N 8.01%. FTIR-ATR (wavenumber, cm^{-1}): 3106-3055(br) [$\nu(C\text{-}H)_{ar}$], 2991-2830 [$\nu(C\text{-}H)_{al}$], 1610(w) [$\nu(C{=}N)_{4,4'\text{-bpy}}$], 1594(m) [$\nu_{as}(COO)$], 1554(s) [$\nu(C{=}N)_{4,4'\text{-bpy}}$], 1443(w), 1409(s), 1388(s) [$\nu_s(COO)$], 1326(w), 1227(w), 1148(s), 1061(m) [$\delta(C\text{-}H)_{ip}$], 1004(m), 851(w), 809(m), 793(s) [$\delta(C\text{-}H)_{oop}$], 772(s) [$\delta(C\text{-}H)_{oop}$], 726 (w), 643(m), 615(m). ^{1}H NMR (250 MHz; DMSO-d_6; 298 K): δ = 6.29 [2H, t, ^4J = 2.4 Hz, *p*-C*H*], 6.85 [4H, d, ^4J = 2.3 Hz, *o*-C*H*], 7.85 [8H, dd, ^3J = 4.6 Hz, ^4J = 1.8 Hz $(m\text{-}CH)_{4,4'\text{-bpy}}$], 8.74 [8H, d, ^3J = 4.6 Hz, $(o\text{-CH})_{4,4'\text{-bpy}}$], 9.24 [4H, s, Ar-O*H*].

2.5 Synthesis of $[Zn_2(\mu\text{-}3,5\text{-}(MeO)_2Bz)_4(\mu\text{-}4,4'\text{-bpy})]_n$ (**5**)

A solution containing 4,4'-bpy (150 mg, 0.96 mmol) in MeOH (40 mL) was added to a solution of compound **2** (440 mg, 0.48 mmol) in MeOH (50 mL) at r.t. The resulting solution was allowed to concentrate at r.t, until light yellow crystals precipitated out of solution. The obtained crystals were filtered and washed with cold methanol (5 mL) and dried in air. All the assays to obtain suitable crystals for structure elucidation yielded samples of bad quality.

Yield: 248 mg (51%) (with respect to compound **2**). Elemental Analysis: Calc. for $C_{46}H_{44}N_2O_{16}Zn_2$ (1011.67 g·mol^{-1}): C 54.61; H 4.38, N 2.77. Found: C 54.40; H 4.18; N 2.80%. FTIR-ATR (wavenumber, cm^{-1}): 3094-3013(br) [$\nu(C\text{-}H)_{ar}$], 2937(w) [$\nu(C\text{-}H)_{al}$], 2835(w) [$\nu(C\text{-}H)_{al}$], 1613(w) [$\nu(C{=}N)_{4,4'\text{-bpy}}$], 1580 (s) [$\nu_{as}(COO)$], 1453(w), 1423(w), 1368(s) [$\nu_s(COO)$], 1330(w), 1220(m), 1152(s), 1046(m) [$\delta(C\text{-}H)_{ip}$], 831(w), 788(s) [$\delta(C\text{-}H)_{oop}$], 758(s) [$\delta(C\text{-}H)_{oop}$], 640(m). ^{1}H NMR (400 MHz; DMSO-d_6; 298 K): δ = 3.77 [24H, s, C*H*$_3$-OR], 6.61 [4H, t, ^4J = 2.5 Hz, *p*-C*H*], 7.08 [8H, d, ^4J = 2.4 Hz, *o*-C*H*], 7.85 [4H, dd, ^3J = 4.2 Hz, ^4J = 1.7 Hz, (*m*-C*H*)$_{4,4'\text{-bpy}}$], 8.74 [4H, br, (*o*-CH)$_{4,4'\text{-bpy}}$].

*2.6 Synthesis of $\{[Zn(3,5\text{-}(MeO)_2Bz)_2(\mu\text{-}4,4'\text{-bpy})]\ H_2O\}_n$ (**6**)*

A single crystal of compound **6** suitable for X-ray diffraction structural elucidation was obtained by recrystallization of compound **5** in boiling water for 6 h with low yield. Owing to obtain the compound **6** with high yield the mechanochemical method was used. Reaction between **2** (264 mg, 0.57 mmol) and 4,4'-bpy (90.0 mg, 0.58 mmol) in 1:1 proportion was performed, by manual grinding in an agate mortar using some drops of water in a liquid assisted grinding process and posterior thermal treatment at 60 ºC for 12 hours. This method leads to quantitative transformation of the initial reagents, although their elemental analysis denotes that the compound obtained by this route contains only 0.25 molecules of water instead of one. The presence of water was confirmed by FTIR-ATR spectrum (*vide infra*).

Elemental Analysis: Calc. for $C_{28}H_{26.5}N_2O_{8.25}Zn$ (588.40 g·mol^{-1}): C 57.15; H 4.54; N 4.76. Found: C 57.43; H 4.32; N 4.58%. FTIR-ATR (wavenumber, cm^{-1}): 3644(w) [ν(O-H)], 3423(w) [ν(O-H)], 3097-3017(br) [ν(C-H)$_{ar}$], 2962(w) [ν(C-H)$_{al}$], 2840(w) [ν(C-H)$_{al}$], 1607(m) [ν(C=N)$_{4,4'\text{-bpy}}$], 1577 (s) [ν$_{as}$(COO)], 1450(m), 1420(w), 1370(s) [ν$_s$(COO)], 1332(m), 1209(m), 1149(s), 1060(m) [δ(C-H)$_{ip}$], 1048(m) [δ(C-H)$_{ip}$], 924(w), 828(m), 785(s) [δ(C-H)$_{oop}$], 760(s) [δ(C-H)$_{oop}$], 642(m). ^{1}H NMR (400 MHz; DMSO-d_6; 298 K): δ = 3.78 [12H, s, CH_3-OR], 6.70 [2H, br, *p*-C*H*], 7.07 [4H, d, ^4J = 2.6 Hz, *o*-C*H*], 7.86 [4H, d, ^3J = 5.3 Hz, (*m*-C*H*)$_{4,4'\text{-bpy}}$], 8.75 [4H, br, (*o*-CH)$_{4,4'\text{-bpy}}$].

2.7 X-ray crystallography

For **2**, from a total of 28510 reflections, 4969 were independent (average redundancy 5.738, completeness = 99.5%, R$_{int}$ = 4.83%, R$_{sig}$ = 3.29%) and 4243 (85.39%) were greater than 2σ(|F|^2). For **3**, from a total of 51755 reflections, 8393 were independent (average redundancy 6.166, completeness = 99.7%, R$_{int}$ = 7.96%, R$_{sig}$ = 6.47%) and 6456 (76.92%) were greater than 2σ(|F|^2). For **4**, from a total of 75712 reflections, 9069 were independent (average redundancy 8.348, completeness = 99.8%, R$_{int}$ = 4.76%, R$_{sig}$ = 2.83%) and 7659 (84.45%) were greater than 2σ(|F|^2). For **6**, from a total of 79570 reflections, 8446 were independent (average redundancy 9.421, completeness = 99.1%, R$_{int}$= 5.88%, R$_{sig}$ = 3.64%) and 6311 (74.72%) were greater than 2σ(|F|^2).

The structures were solved using the Bruker SHELXTL Software, package and refined using SHELX [20]. Crystal data and relevant details of structure refinement for compounds **2-4** and **6** are reported in Table 1.

[Insert table 1]

Molecular graphics were generated with the Mercury 3.6 software [21, 22]. Color codes for all molecular graphics: dark grey (Zn), blue (N), red (O), yellow (S), grey (C), white (H).

3. Results and discussion

3.1 Synthesis and general characterization

The displacement of the acetate ions present in the $Zn(MeCO_2)_2$ salt by 3,5-$H(MeO)_2Bz$ acid in MeOH, yielded complex $[Zn(3,5\text{-}(MeO)_2Bz)_2(CH_3OH)]_2$ (**2**). This compound and the previously reported $[Zn(3,5\text{-}(HO)_2Bz)_2(H_2O)_2]_n$ (**1**), containing a closely related ligand, were used as starting materials to synthesize CPs using 4,4'-bpy as a linker. The solvent used in the synthesis has a great influence on the nature of the final product; here are presented the pure and crystalline products. All these new compounds (**2-6**) were characterized by elemental analysis, FTIR-ATR and ^1H NMR spectroscopies and powder X-ray diffraction (S.I: Figure S1-S4). Besides the crystal structure of compounds **2-4** and **6** has been elucidated.

*3.2 Crystal and extended structure of compound **2***

Compound **2** crystallizes in the triclinic P-1 space group. It has a paddle-wheel binuclear Zn(II) structure, with four bridging carboxylate ligands in a *syn-syn* coordination mode (Figure 1a). Selected bond lengths and angles are provided in Table 2. The asymmetric unit contains one Zn(II) center, two bidentate anionic 3,5-$(MeO)_2Bz$ ligands and a coordinated MeOH molecule. Each Zn(II) cation presents a square pyramidal structure ($\tau = 0.002$) [23], with four oxygen atoms from different 3,5-$(MeO)_2Bz$ ligands in the equatorial plane and the oxygen of the methanol molecule in the axial position (Figure 1a). The Zn-O bond lengths are in the 2.00-2.03 Å interval for the carboxylate ligand, and 1.978(10) Å for the oxygen of the methanol. All these distances are of the same order as described in literature [24-26]. Zn(II) cations are displaced 0.35 Å from the basal plane towards the apex.

[Insert Table 2]

The more significant intermolecular interaction is a bifurcated hydrogen bond between the hydrogen of each methanol and two oxygen atoms of different carboxylate groups of a closer molecule. The expansion of these interactions defines supramolecular chains in [100] (Figure 1b).

[Insert Figure 1]

The comparison between **2** and $\{[Zn(\mu\text{-}3,5\text{-}(HO)_2Bz)(\mu\text{-}OH_2)(H_2O)_2]\cdot(3,5\text{-}(HO)_2Bz)\cdot 4H_2O\}_n$ [18] is remarkable. In the latter case, a polymeric cationic compound was formed, and only half of the carboxylate ligands are coordinated to the Zn(II) cations. Thus, replacement of the hydroxyl groups of 3,5-$(HO)_2$Bz by methoxy groups, indirectly conditions the coordination sphere around Zn(II) centers and also reduces the possibility of supramolecular hydrogen bond interactions.

*3.3 Crystal and extended structures of compounds **3**, **4** and **6***

The asymmetric units of compounds **3**, **4** and **6** contain one Zn(II) center, two carboxylate ligands (3,5-$(HO)_2$Bz for **3** and **4** and 3,5-$(MeO)_2$Bz for **6**) and one coordinated 4,4'-bpy linker. In addition, all of them contain uncoordinated guest molecules: two DMSO (**3**), one MeOH and one 4,4'-bpy (**4**) and one water molecule (**6**). Other Zn(II) compounds described in literature showing 1D coordination polymers with *zigzag* disposition of the 4,4'-bpy are $\{[Zn(L_1)(4,4'\text{-bpy})]\cdot 0.52CH_3OH\}_n$ (L_1 = *N*-(1,3-diphenyl-4-propylene-5-pyrazolone) [27], $\{[Zn(L_2)(4,4'\text{-bpy})]\cdot CH_3OH\}_n$ (L_2 = *N*-(1-phenyl-3-benzyl-4-propilene-5-pyrazolone) [27] {Zn(4,4'-

bpy)$_2$(O_2CFeCO_2)$_2$]·0.5H_2O}$_n$ [28]. All these compounds include solvent molecules (CH_3OH, H_2O) in their structures.

In the three compounds the zinc centers present a distorted tetrahedral structure, in which each Zn(II) is coordinated to two nitrogen atoms from two 4,4'-bpy and two oxygen atoms from two monodentate carboxylate ligands (Figures 2a-2c).

[Insert Figure 2]

The Zn-O$_{carbox}$ and Zn-N bond lengths (Table 3) are comparable to those described in literature: {Zn_2(4,4'-bpy)$_2$(4-aba)$_4$]·5H_2O}$_n$ (4,4'-bpy = 4,4'-bipyridine; aba = 4-aminobenzoato) (Zn-O: 2.079(6) and 1.955(6) Å; Zn-N: 2.079(6) and 2.077(6) Å) [29]; [Zn(bpy)$_2$(4,3-ahba)$_2$]$_2$ (4,3-ahba = 4-amino-3-hydroxycarboxylic acid) (Zn-O: 1.955-2.006 Å; Zn-N: 2.174(4) and 2.264(3) Å) [30]; {[Zn(4,4'-bpy)($MeCO_2$)$_2$]}$_n$ (Zn-O: 2-016-2.298 Å; Zn-N: 2.173(3) and 2.180(3) Å) [14].

[Insert Table 3]

The three compounds are 1D coordination polymers in which zinc centers are bridged *via* 4,4'-bpy ligand. The N-Zn-N angles are 95.28(10)º (**3**), 100.78(5)º (**4**) and 106.02(6)º (**6**), which determine that 4,4'-bpy ligand directs the formation of *zigzag* chains. These chains propagate along the [001] axis for **3**, along the [1-21] axis for **4** and along the [-110] axis for **6** (Figures 3a-3c). In each polymer the 4,4'-bpy presents different orientation respect to the plane that contains all the Zn atoms of the chain, and also respect to the plane of the aromatic ring of the carboxylate ligand. In **6,** consecutive 4,4'-bpy and 3,5-$(MeO)_2$Bz ligands are almost planar (6º) (Figure 3c).

[Insert Figure 3]

In **3**, each DMSO molecule accepts two hydrogen bonds with two hydroxyl groups from two 3,5-$(HO)_2$Bz ligand from adjacent chains (O8-H8O···O10: 1.86 Å, 169º; O3-H3O···O10: 1.88 Å, 172º and O4-H4O···O9: 1.95 Å, 156º). All hydroxyl groups are involved in these interactions and establish 2D supramolecular networks parallel to the *ac* plane (Figure 4, Table 4).

[Insert Figure 4]

In **4**, the hydroxyl groups interacts with shorter hydrogen bonds with the non-coordinated oxygen atom of the carboxylate group (O4-H4A···O6: 1.82 Å, 167º; O7-H7A···O2: 1.94 Å, 170º) or with other hydroxyl groups of a neighboring chain (O3-H3A···O8: 1.92 Å, 160º). Other weak π-π stacking interactions between 4,4'-bpy and 3,5-$(HO)_2$Bz ligands at a Cg1···Cg2 distance of 3.571(1) Å (Cg1:N1-C15-C16-C17-C18-C19; Cg2: C9-C10-C11-C12-C13-C14) are also present. All this set of interactions promotes the formation of the 3D supramolecular structure. Interestingly, the non-coordinated 4,4'-bpy ligand does not have any strong direct interaction with this network, but interacts *via* the methanol solvent, that is connected with a nitrogen atom of this additional 4,4'-bpy and also with a hydroxyl groups of a 3,5-$(HO)_2$Bz ligand (O8-H8A···O1W: 1.81 Å, 172º and O1W-H1WO···N3: 1.92 Å, 163º). In **6**, the water molecule forms a hydrogen bond interaction with one uncoordinated oxygen atom of a carboxylate group (Table 4).

[Insert Table 4]

It can be observed that DMSO molecules in **3** (Figure 5a) and MeOH and uncoordinated 4,4'-bpy ligand in **4** (Figure 5b), occupy potential channels in the crystal structures. However, all the essays to selectively remove these neutral molecules, using different solvent treatment or moderate heating under vacuum, leads to the collapse of the structure instead of producing porous materials. Meanwhile, polymer chains in **6** form a close packed structure, leaving only the appropriate volume to accommodate one water molecule.

[Insert Figure 5]

3.3 Photoluminescence

When solid samples of compound **1-6** were observed under black-light (commercially available 8 W black light tube with a spectral peak centered around 365 nm) only compounds **5** and **6** show an intense blue photoluminescence visible to naked eye. The response to black light irradiation is only observed in solid state, after dissolution of **5** or **6** in hot water, photoluminescence disappears (and after solvent evaporation the recovered precipitates show blue photoluminescence again). The solid state fluorescence was measured at room temperature, using λ_{ex} = 405 nm in both cases (Figure 6) and showed emission peaks at 490 and 480 nm for **5** and **6**, respectively. The emission peaks could be explained using ligand centered transitions, as Zn(II) ion belongs to d^{10} electronic configurations and is difficult to oxidize/ reduce [18, 31, 32].

[Insert Figure 6]

It seems that the combination of 4,4'-bpy and 3,5-$(MeO)_2$Bz ligands is key to produce luminescent compounds, while the crystal structure has low influence, considering that both coordination polymers must probably have different structures, in **5** 4,4'-bpy connects binuclear clusters while in **6** it connects single Zn atoms. However, both compound show luminescence peaks, which are only 10 nm shifted with similar intensities and shapes. Luminescence is probably due to the increased rigidity of ligands in the polymeric structure, with concomitant decrease of radiation, the minor decay process of the intraligand ($\pi \rightarrow \pi^*$) excited state and the reduced energy loss between intramolecular or intermolecular interactions of organic linkers. The strong fluorescent emission of **5** and **6** may make them potentially useful photoactive materials.

3.4 FTIR-ATR and ^1H NMR spectroscopies

IR spectra of the compounds **2-6** confirm the presence of 3,5-$(HO)_2$Bz, 3,5-$(MeO)_2$Bz and 4,4'-bpy ligands. The five IR spectra displayed the characteristic carboxylate bands between 1586 and 1368 cm^{-1}, attributable to $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$. For compounds **3-6**, the difference between these bands is 198 (**3**), 206 (**4**), 212 (**5**) and 207 (**6**) cm^{-1}, indicating that in these compounds the carboxylate shows a monodentate coordination mode; whereas, for compound **2** the difference is 136 cm^{-1} indicating a bridged coordination mode [33, 34]. The absence of a band between 1720 and 1690 cm^{-1} in the five compounds indicates that the carboxylic acid is deprotonated.

In these spectra, the bands belonging to the 4,4'-bpy ligand which are assigned to the $\nu(C=N)$, appear between 1629 and 1607 cm^{-1}. Moreover, compound **3** exhibits a band at 1554 cm^{-1}, which can be assigned to $\nu(C=N)$ of the free 4,4'-bpy molecule [35]. The bands attributable to the aromatic groups $\nu(C=N)$, $\nu(C=C)$, $\delta(C=N)$, $\delta(C=C)$, $\delta(C\text{-}H)_{ip,}$ $\delta(C\text{-}H)_{oop}$ are also assigned (S.I: Figure S5-S9) [36, 37].

The ^1H NMR spectra of the complexes **2-6** were recorded in DMSO-d_6 and clearly show the signals of the 3,5-$(HO)_2$Bz, 3,5-$(MeO)_2$Bz and 4,4'-bpy ligands. Compounds **2-6** present two signals attributable to *p*-H and *o*-H of 3,5-$(HO)_2$Bz and (3,5-$(MeO)_2$Bz ligands between 7.08 and 6.29 ppm. For **3** and **4** other signal attributable to O*H* groups of the aromatic ring are also present. The integral value of the signals attributable to *o*-H and *m*-H are consistent with the presence of one 4,4'-bpy in compound **2, 5** and **6** and two 4,4'-bpy in compound **4**. These signals appear between 8.76 and 7.07 ppm (S.I: Figure S10-S14) [36, 37]

4. Conclusions

The crystal structure elucidation of $[Zn(\mu\text{-}3,5\text{-}(MeO)_2Bz)_2(CH_3OH)]_2$ (**2**) allowed to ascertain that the replacement of the hydroxyl groups in $3,5\text{-}(HO)_2Bz$ ligand by methoxy groups has a noticeable influence in both the coordination of the carboxylate to the Zn(II) center and the supramolecular structure. The reaction of both zinc benzoates with 4,4'-bpy resulted in four CPs. It is remarkable that, independent of the carboxylate ligand, 4,4'-bpy formed polymeric *zigzag* chains in which Zn(II) ions adopt a tetrahedral structure and the $3,5\text{-}(HO)_2Bz$ or $3,5\text{-}(MeO)_2Bz$ acts as a monodentate carboxylate ligand. The addition of 4,4'-bpy linker displaced the bridging coordination of both carboxylate ligands. The chemical composition of the CPs depends on the experimental conditions, especially the solvent used in their synthesis.. Moreover, the substituents of the benzoate derivatives as well as the solvent occluded molecules (DMSO, **3** and MeOH, **4**), played an important role in the formation of the supramolecular networks based on hydrogen bond interactions directing the final packing. Interestingly, the neutral guest molecules (DMSO in **3**; MeOH and non-coordinated 4,4'-bpy in **4**) occupy potential channels. Both CPs including $3,5\text{-}(MeO)_2Bz$ and 4,4'-bpy (**5** and **6**) demonstrated blue-green emission in the solid state, in spite of their different bpy:benzoate ratio.

Declaration of Competing Interest

The are no conflicts to declare

Acknowledgement

This work was financed by CB615921 project, the Spanish National Plan of Research MAT2015-65756R, and 2017SGR1687 project from the Generalitat de Catalunya. The authors also acknowledge “Fundació La Caixa” for CB616406 endowment, and this work also was partially financed by the Spanish National Plan of Research CTQ2017-83632-CO2-P1. F. S. acknowledges the PIF pre-doctoral fellowship from the Universitat Autònoma de Barcelona.

Appendix A. Supplementary data

Complete ^{1}H NMR and FTIR-ATR spectra and PXRD data is available as Supporting Information. CCDC 1942915 (**2**), 1856041 (**3**), 1856042 (**4**) and 1942916 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1Ez, UK; fax:(+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Figure captions

Figure 1. Crystal structure of [Zn(μ-3,5-(MeO)$_2$Bz)$_2$(CH$_3$OH)]$_2$ (**2**). **a.** Molecule detail; **b.** Supramolecular chains formed by expansion of hydrogen bond interactions. Hydrogen atoms are omitted for clarity, except those which participate in the intermolecular interactions.

Figure 2. Coordination environment of Zn in **a.** {[Zn(3,5-(HO)$_2$Bz)$_2$(μ-4,4'-bpy)]·2DMSO}$_n$ (**3**); **b.** {[Zn(3,5-(HO)$_2$Bz)$_2$(μ-4,4'-bpy)]·4,4'-bpy·1/2CH$_3$OH}$_n$ (**4**) and **c.** {[Zn(3,5-(MeO)$_2$Bz)$_2$(μ-4,4'-bpy)]·H$_2$O}$_n$ (**6**) (*bottom*). Hydrogen atoms, solvent molecules and non-coordinated 4-4'-bpy are omitted for clarity

Figure 3. Different perspective views of chains in **a.** {[Zn(3,5-(HO)$_2$Bz)$_2$(μ-4,4'-bpy)]·2DMSO}$_n$ (**3**); **b.** {[Zn(3,5-(HO)$_2$Bz)$_2$(μ-4,4'-bpy)]·4,4'-bpy·1/2CH$_3$OH}$_n$ (**4**) and **c.** {[Zn(3,5-(MeO)$_2$Bz)$_2$(μ-4,4'-bpy)]·H$_2$O}$_n$ (**6**). Hydrogen atoms, solvent molecules and non-coordinated 4-4'-bpy are omitted for clarity

Figure 4. Views of the 2D supramolecular expansion in **3** formed by O-H···O hydrogen bond interactions. Only hydrogen atoms which participate in the intermolecular interactions are shown.

Figure 5. View of **a.** compound **3** (*c* axis) and **b.** compound **4** (*b* axis). Hydrogen atoms are omitted for clarity. DMSO in **3** and non-coordinated 4-4'-bpy in **4** are depicted in yellow and green color, respectively.

Figure 6. Spectral profiles representing photoluminescence intensity versus emission wavelength in the 415–750 nm range for [Zn$_2$(μ-3,5-DMB)$_4$(μ-4,4'-bpy)]$_n$ (**5**, *red line*) and {[Zn(3,5-DMB)$_2$(μ-4,4'-bpy)]·H$_2$O}$_n$ (**6**, *blue line*)

Table 1. Crystallographic data for compounds **2**, **3**, **4** and **6**

	2	**3**	**4**	**6**
Empirical formula	$C_{38}H_{44}O_{18}Zn_2$	$C_{28}H_{30}N_2O_{10}S_2Zn$	$C_{69}H_{56}N_8O_{17}Zn_2$	$C_{28}H_{28}N_2O_9Zn$
Formula weight	919.47	684.03	1399.95	601.89
T (K)	100(2) K	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073 Å	0.71073	0.71073	0.71073
System, space group	Triclinic, P -1	Monoclinic, Pc	Triclinic, P -1	Monoclinic , C 2/c
Unit cell dimensions				
a (Å)	6.8291(4)	13.2419(7)	10.6316(6)	23.0160(14)
b (Å)	11.7622(7)	7.7558(4)	11.6986(7)	27.8171(15)
c (Å)	12.6198(7)	15.6016(7)	14.0895(8)	8.7942(5)
α (º)	98.886(3)	90	96.653(2)	90
β (º)	94.647(3)	108.253(2)	102.794(2)	102.896(2)
γ (º)	93.081(3)	90	111.997(2)	90
V (Å^3)	995.97(10)	1521.68(13)	1545.70(16)	5488.4(5)
Z	1	2	1	8
Dcalc (g cm^3)	1.533	1.493	1.504	1.457
μ (mm^{-1})	1.282	1.003	0.858	0.952
F(000)	476	718	722	2496
Crystal size (mm^3)	0.22 x 0.061 x 0.044 mm^3	0.172x0.099x0.033	0.329x0.091x0.075	0.244 x 0.101 x 0.090
hkl ranges	-9<=h<=9, -15<=k<=15, -16<=l<=16	-18≤h≤18, -11≤k≤11, -18≤l≤22	-14≤h≤14, -16≤k≤16, -19≤l≤19	-32<=h<=32, -39<=k<=39, 12<=l<=12
2θ range (º)	2.588 to 28.378 (0.75Å resolution)	2.626 to 30.583 (0.70Å resolution)	1.925 to 30.097 (0.71Å resolution)	2.332 to 30.675 (0.70Å resolution)
Reflections collected/ unique/[Rint]	28510/4969 [R_{int} = 0.0483]	51755/8393/[R_{int} = 0.0796]	75712/9069/[R_{int} = 0.0476]	79557/8444 [R_{int} = 0.0588]
Completeness to θ = 25.240	99.7 %	99.9%	99.8%	99.8 %
Absorption Correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6774	0.7461 and 0.7051	0.7460 and 0.6566	0.7460 and 0.6930
Refinement method	Full-matrix least-squares on $\|F\|^2$	Full matrix least-squares on $\|F\|^2$	Full matrix least-squares on $\|F\|^2$	Full-matrix least-squares on $\|F\|^2$
Data/restrains/parameters	4969/5/267	8393/2/393	9069/5/438	8444 / 3 / 371
Goodness of fit (GOF) on $\|F\|^2$	1.022	1.097	1.064	1.049
Final R indices [I>2σ(I)]	R1 = 0.0248, wR2 = 0.0557	R1 = 0.0376, wR2 = 0.0612	R1 = 0.0371, wR2 = 0.0990	R1 = 0.0406, wR2 = 0.0868
R indices (all data)	R1 = 0.0352, wR2 = 0.0596	R1 = 0.0765 wR2 = 0.0759	R1 = 0.0458 wR2 = 0.1038	R1 = 0.0686, wR2 = 0.0958
Extinction coefficient	n/a	n/a	n/a	n/a
Largest. Diff. peak and hole (e Å^{-3})	0.581 and -0.691	0.430 and -0.652	2.449 and -1.420	0.365 and -0.558

Table 2. Selected bond lengths (Å) and bond angles (º) for compound **2**, and lengths (Å) and angles (º) related to hydrogen bond interactions

<table>
<tr><td>2</td><td></td><td colspan="2"></td><td></td></tr>
<tr><td colspan="2"><i>Bond length (Å)</i></td><td colspan="3"><i>Bond angles (º)</i></td></tr>
<tr><td>Zn(1)-O(9)</td><td>1.9718(10)</td><td>O(9)-Zn(1)-O(5)</td><td colspan="2">101.46(5)</td></tr>
<tr><td>Zn(1)-O(5)</td><td>2.0009(12)</td><td>O(9)-Zn(1)-O(1)</td><td colspan="2">101.61(5)</td></tr>
<tr><td>Zn(1)-O(1)</td><td>2.0107(13)</td><td>O(5)-Zn(1)-O(1)</td><td colspan="2">89.10(6)</td></tr>
<tr><td>Zn(1)-O(6)#1</td><td>2.0234(13)</td><td>O(9)-Zn(1)-O(6)#1</td><td colspan="2">98.72(5)</td></tr>
<tr><td>Zn(1)-O(2)#1</td><td>2.0305(15)</td><td>O(5)-Zn(1)-O(6)#1</td><td colspan="2">159.67(5)</td></tr>
<tr><td>Zn(1)-Zn(1)#1</td><td>2.8726(3)</td><td>O(1)-Zn(1)-O(6)#1</td><td colspan="2">89.27(7)</td></tr>
<tr><td></td><td></td><td>O(9)-Zn(1)-O(2)#1</td><td colspan="2">98.52(5)</td></tr>
<tr><td></td><td></td><td>O(5)-Zn(1)-O(2)#1</td><td colspan="2">88.53(7)</td></tr>
<tr><td></td><td></td><td>O(1)-Zn(1)-O(2)#1</td><td colspan="2">159.79(5)</td></tr>
<tr><td></td><td></td><td>O(6)#1-Zn(1)-O(2)#1</td><td colspan="2">86.05(8)</td></tr>
<tr><td colspan="5">Intermolecular interactions</td></tr>
<tr><td>D-H···A</td><td>D-H (Å)</td><td>H···A (Å)</td><td>D···A (Å)</td><td>>D-H···A(º)</td></tr>
<tr><td>O(9)-H(9O)···O(2)</td><td>0.84</td><td>2.31</td><td>2.9897(19)</td><td>138</td></tr>
<tr><td>O(9)-H(90)···O(6)</td><td>0.84</td><td>2.31</td><td>3.0227(18)</td><td>143</td></tr>
</table>

#1 -x+1,-y+2,-z+1

Table 3. Selected bond lengths (Å) and bond angles (º) for compounds **3, 4** and **6**

3			
Bond length (Å)		*Bond angles (º)*	
Zn(1)-O(1)	1.940(3)	O(1)-Zn(1)-O(5)	111.25(10)
Zn(1)-O(5)	1.957(3)	O(1)-Zn(1)-N(1)	126.44(15)
Zn(1)-N(1)	2.049(3)	O(5)-Zn(1)-N(1)	97.74(14)
Zn(1)-N(2)#1	2.060(4)	O(1)-Zn(1)-N(2)#1	97.32(14)
Zn(1)···Zn(1)	11.1388(7)	O(5)-Zn(1)-N(2)#1	131.48(15)
		N(1)-Zn(1)-N(2)#1	95.28(10)
4			
Bond length (Å)		*Bond angles (º)*	
Zn(1)-O(1)	1.9630(11)	O(1)-Zn(1)-O(5)	103.78(4)
Zn(1)-O(5)	1.9771(11)	O(1)-Zn(1)-N(1)	118.00(5)
Zn(1)-N(1)	2.0410(12)	O(5)-Zn(1)-N(1)	100.25(5)
Zn(1)-N(2)#1	2.0292(13)	O(1)-Zn(1)-N(2)	121.25(5)
Zn(1)···Zn(1)	11.1334(7)	O(5)-Zn(1)-N(2)	110.99(5)
		N(1)-Zn(1)-N(2)	100.78(5)
6			
Bond length (Å)		*Bond angles (º)*	
Zn(1)-O(5)	1.9316(13)	O(5)-Zn(1)-O(1)	128.00(6)
Zn(1)-O(1)	1.9379(14)	O(5)-Zn(1)-N(1)	109.55(6)
Zn(1)-N(1)	2.0333(15)	O(1)-Zn(1)-N(1)	103.28(6)
Zn(1)-N(2)	2.0386(15)	O(5)-Zn(1)-N(2)	99.57(6)
Zn(1)···Zn(1)	11.1417(7)	O(1)-Zn(1)-N(2)	108.83(6)
		N(1)-Zn(1)-N(2)	106.02(6)

3 #1:x,-y,z-1/2

Table 4. Lengths (Å) and angles (º) related to hydrogen bond interaction in compounds **3**, **4** and **6**

3				
D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	>D-H···A(º)
O(3)-H(3A)···O(10)	0.84	1.88	2.716(5)	172
O(4)-H(4O)···S(1)	0.84	2.86	3.601(3)	149
O(4)-H(4O)···O(9)	0.84	1.95	2.742(5)	156
O(7)-H(7O)···O(9)	0.84	1.91	2.746(5)	178
O(8)-H(8O)···S(2)	0.84	2.86	3.631(4)	154
O(8)-H(8O)···O(10)	0.84	1.86	2.694(5)	169
4				
O1W-H1WO···N3	0.84	1.92	2.7334(5)	163
O3-H3A···O8	0.84	1.92	2.722(2)	160
O4-H4A···O6	0.84	1.82	2.647(2)	167
O7-H7A···O2	0.84	1.94	2.770(2)	170
O8-H8A···O1W	0.84	1.81	2.646(3)	172
6				
O1W-H1WB···O6	0.85(3)	1.96(3)	2.807(3)	173(2)

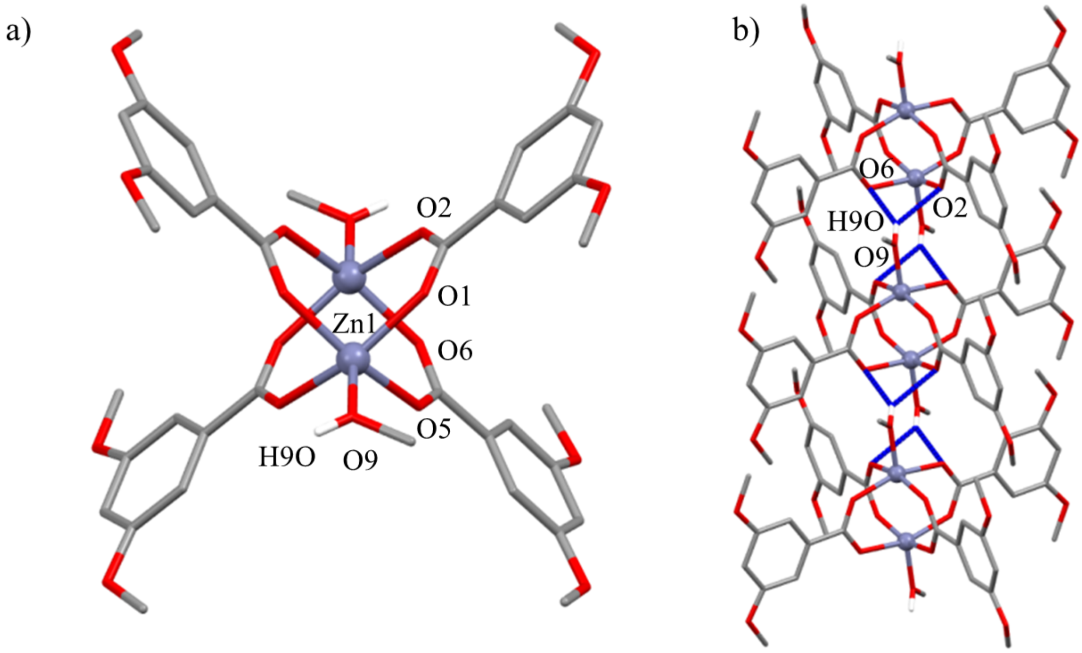

Figure 1. Crystal structure of $[Zn(\mu\text{-}3,5\text{-}(MeO)_2Bz)_2(CH_3OH)]_2$ (**2**). **a.** Molecule detail; **b.** Supramolecular chains formed by expansion of hydrogen bond interactions. Hydrogen atoms are omitted for clarity, except those which participate in the intermolecular interactions.

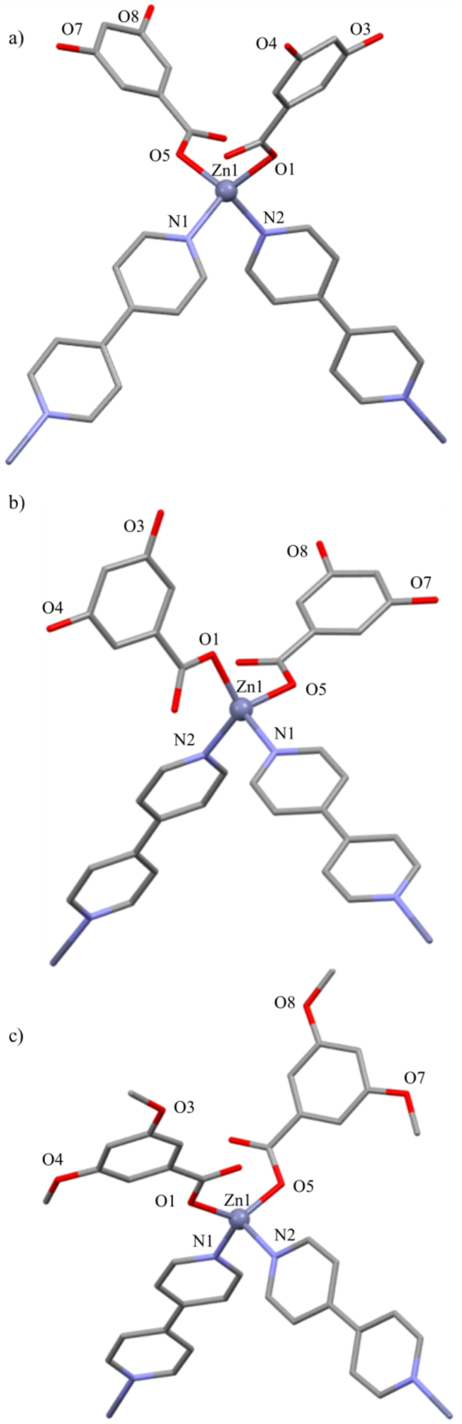

Figure 2. Coordination environment of Zn in **a.** $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 2DMSO\}_n$ (**3**); **b.** $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 4,4'\text{-}bpy\cdot 1/2CH_3OH\}_n$ (**4**) and **c.** $\{[Zn(3,5\text{-}(MeO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot H_2O\}_n$ (**6)** (*bottom*). Hydrogen atoms, solvent molecules and non-coordinated 4-4'-bpy are omitted for clarity

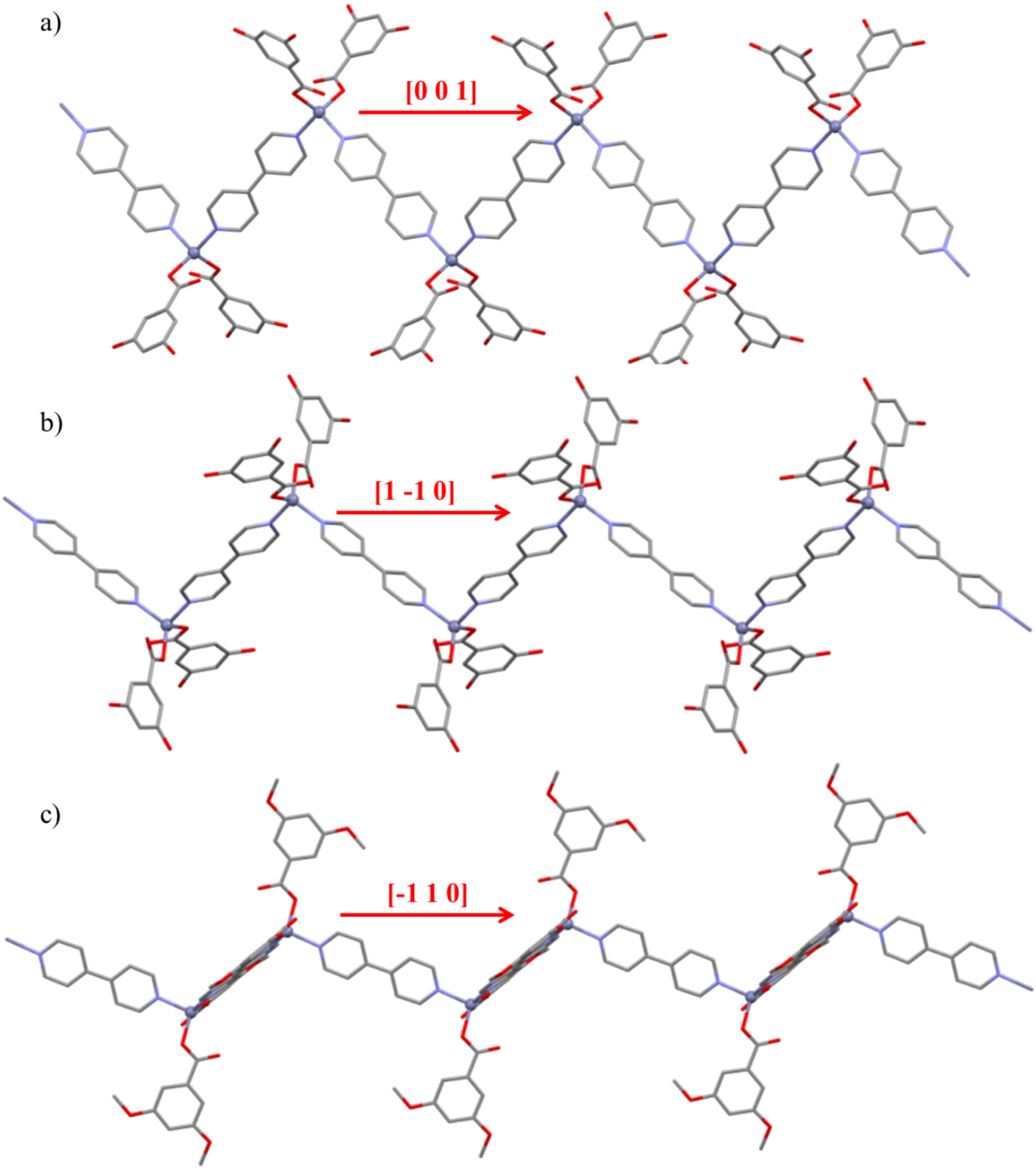

Figure 3. Different perspective views of chains in **a.** $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 2DMSO\}_n$ (**3**); **b.** $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 4,4'\text{-}bpy\cdot 1/2CH_3OH\}_n$ (**4**) and **c.** $\{[Zn(3,5\text{-}(MeO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot H_2O\}_n$ (**6**). Hydrogen atoms, solvent molecules and non-coordinated 4-4'-bpy are omitted for clarity

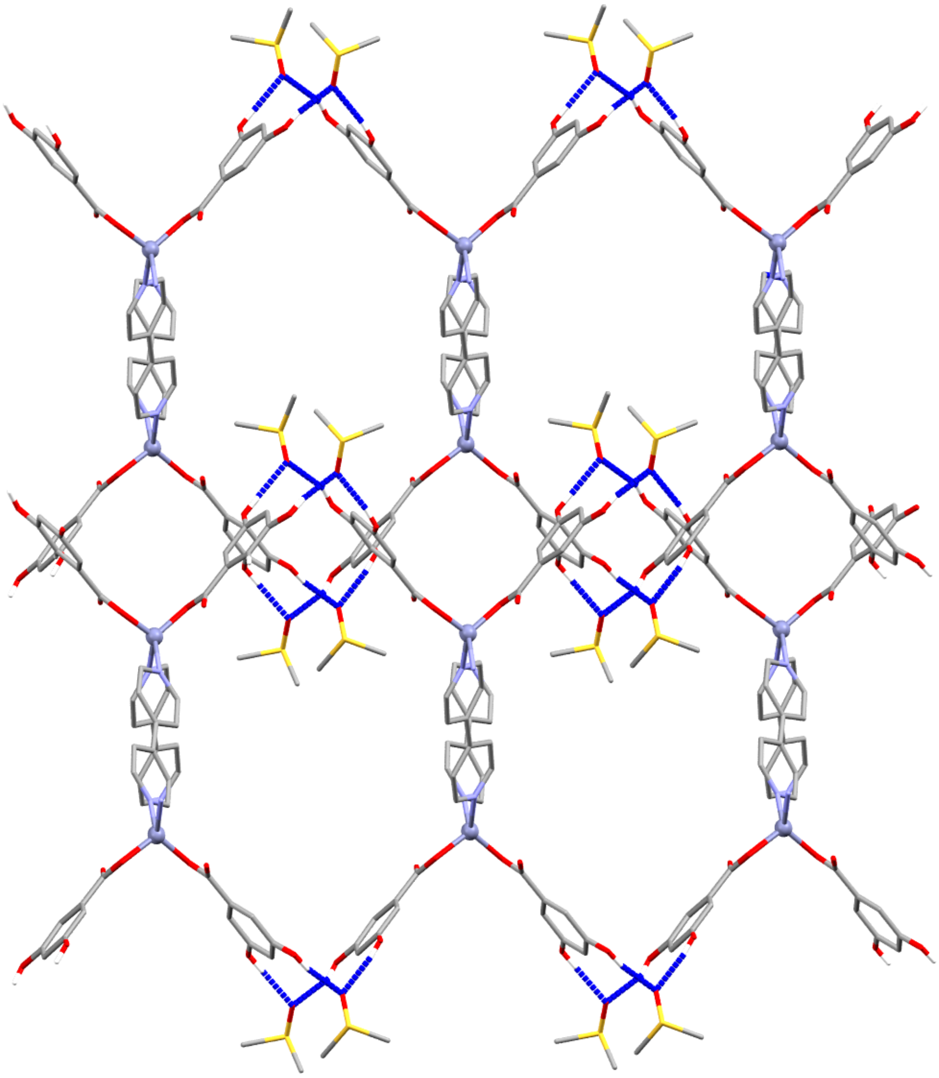

Figure 4. Views of the 2D supramolecular expansion in **3** formed by O-H···O hydrogen bond interactions. Only hydrogen atoms which participate in the intermolecular interactions are shown.

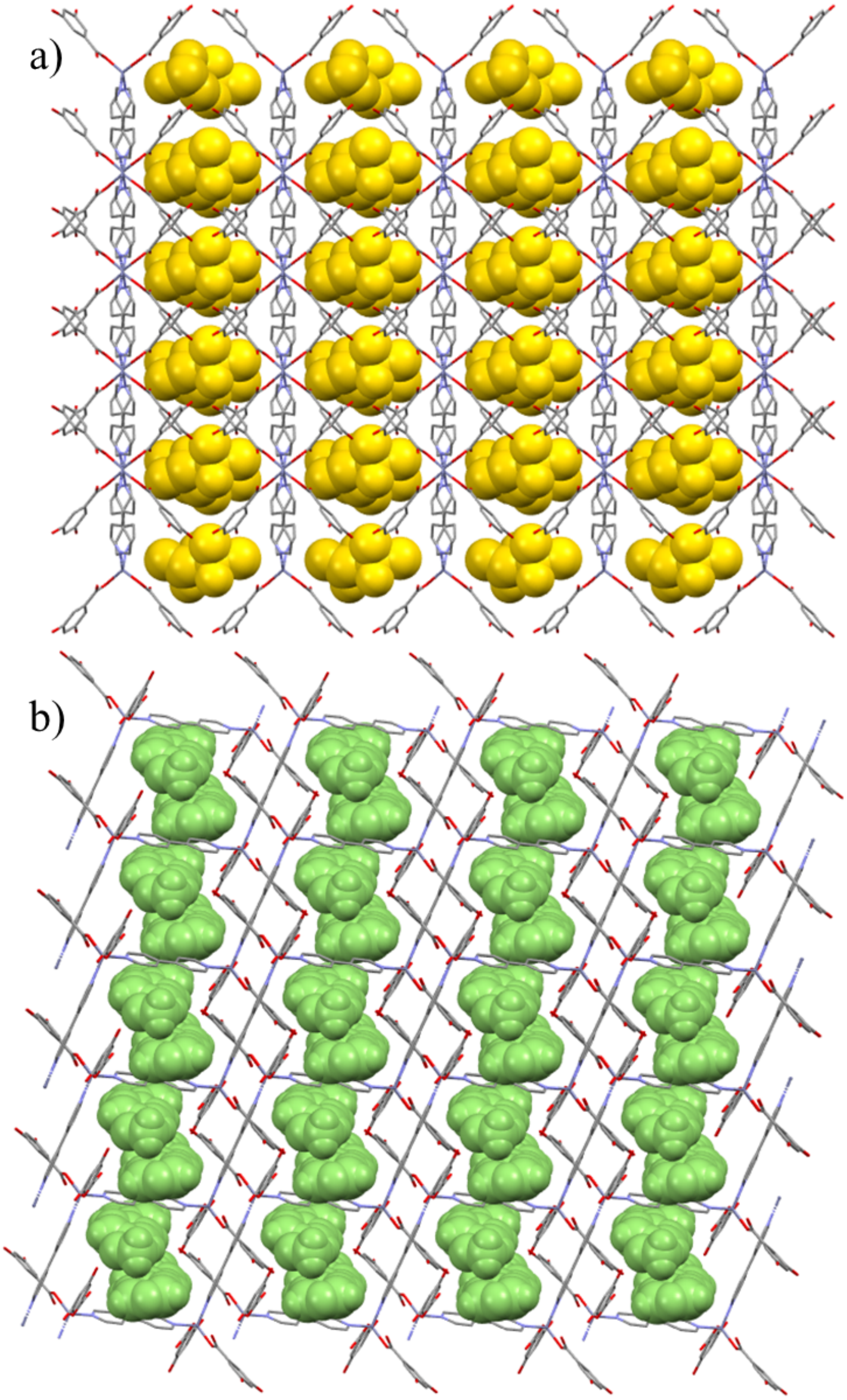

Figure 5. View of **a.** compound **3** (*c* axis) and **b.** compound **4** (*b* axis). Hydrogen atoms are omitted for clarity. DMSO in **3** and non-coordinated 4-4'-bpy in **4** are depicted in yellow and green color, respectively.

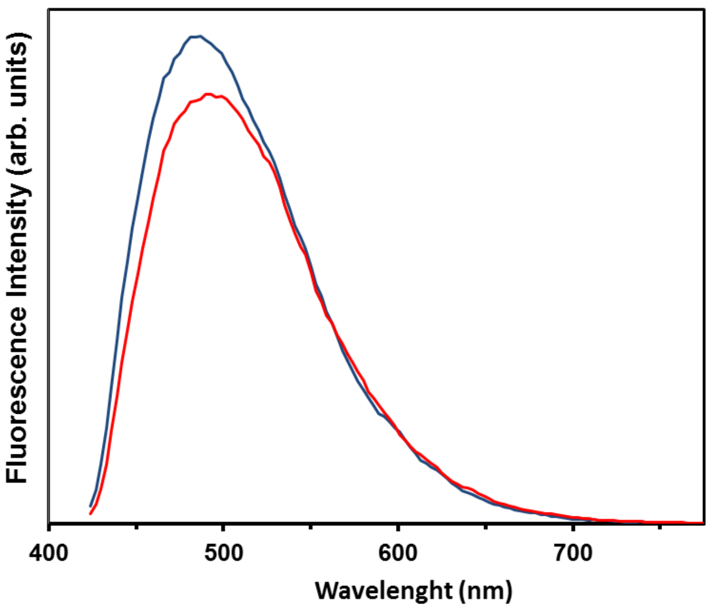

Figure 6. Spectral profiles representing photoluminescence intensity versus emission wavelength in the 415–750 nm range for $[Zn_2(\mu\text{-}3,5\text{-DMB})_4(\mu\text{-}4,4'\text{-bpy})]_n$ (**5**, *red line*) and $\{[Zn(3,5\text{-DMB})_2(\mu\text{-}4,4'\text{-bpy})]\cdot H_2O\}_n$ (**6**, *blue line*)

From: Dr. Josefina Pons
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Spain

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To: Professor Bernhard Lippert
Inorganica Chimica Acta

September 23th, 2019

Dear Professor Bernhard Lippert,

the authors declare there are no conflicts of interest.

Yours sincerely,

Josefina Pons Picart

E-mail: Josefina.Pons@uab.es

Fax: +34-935812477

Supporting Information

Benzoate substituents effects on the structure of zinc complexes and 1D 4,4’-bipyridine derived coordination polymers

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[b]*Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona, Martí i Franquès s/n, 08028-Barcelona, Spain.*

[c]*Unitat de Difracció de Raig-X, Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB), Universitat de Barcelona, Solé i Sabarís, 1-3, 08028-Barcelona, Spain.*

Powder X-Ray diffraction patterns

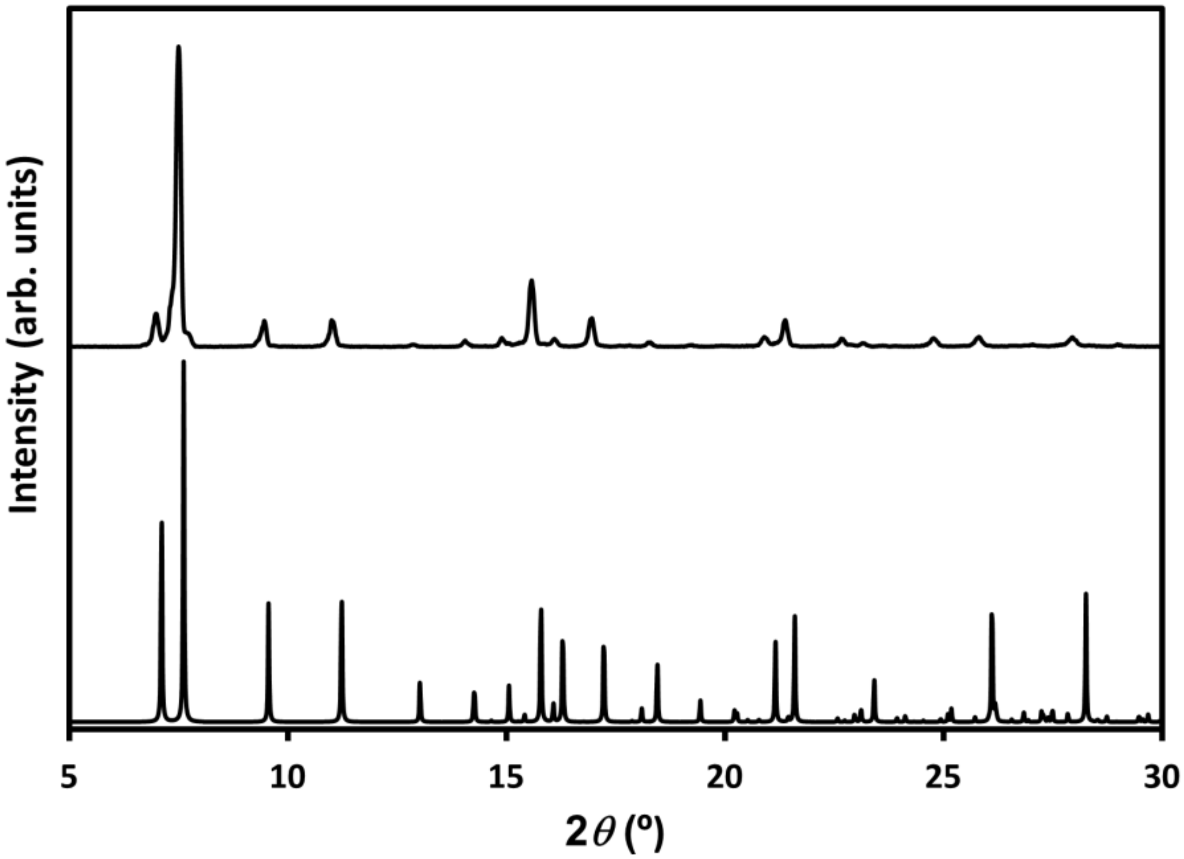

Figure S1. Comparison between the powder XRD pattern simulated from the crystal structure data of [Zn(μ-3,5-$(MeO)_2Bz)_2(CH_3OH)]_2$ (**2**), determined at 100 K (*bottom*) and the experimental pattern measured at room temperature (*top*).

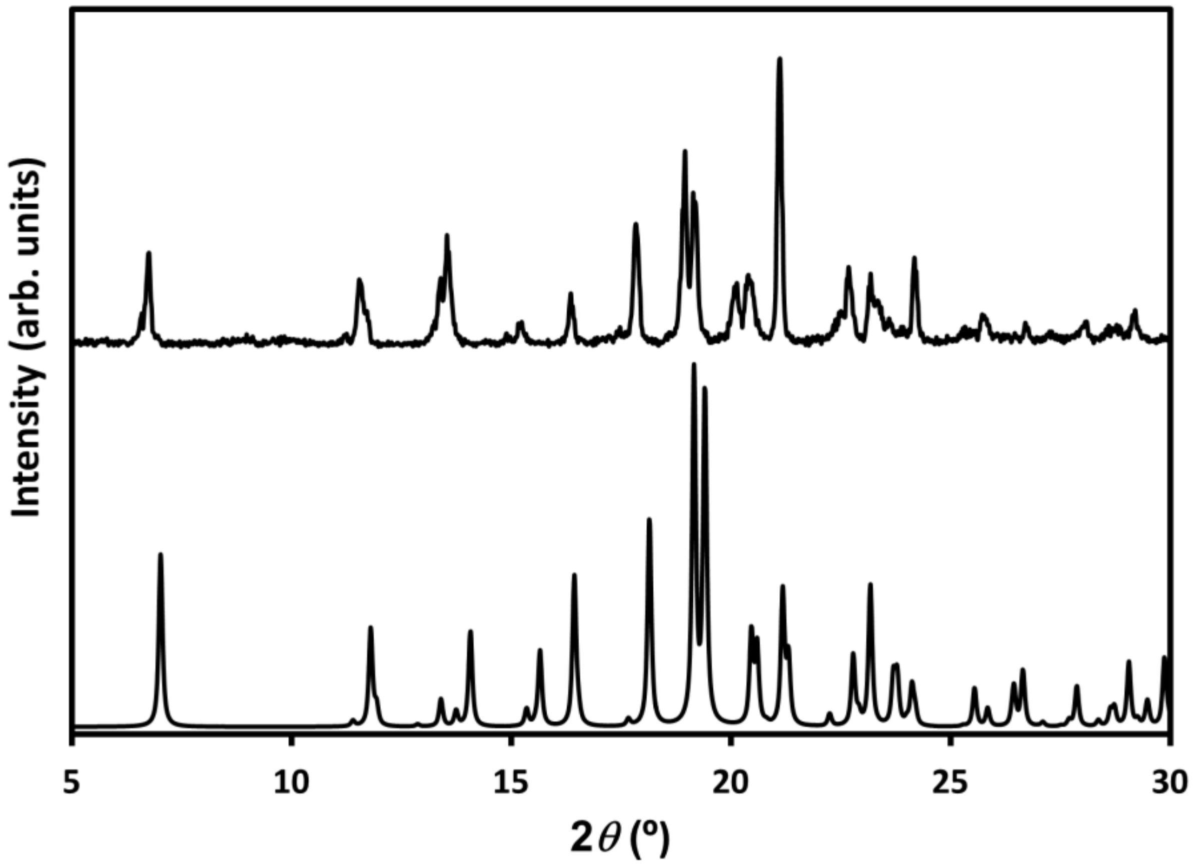

Figure S2. Comparison between the powder XRD pattern simulated from the crystal structure data of $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 2DMSO\}_n$ (**3**), determined at 100 K (*bottom*) and the experimental pattern measured at room temperature (*top*).

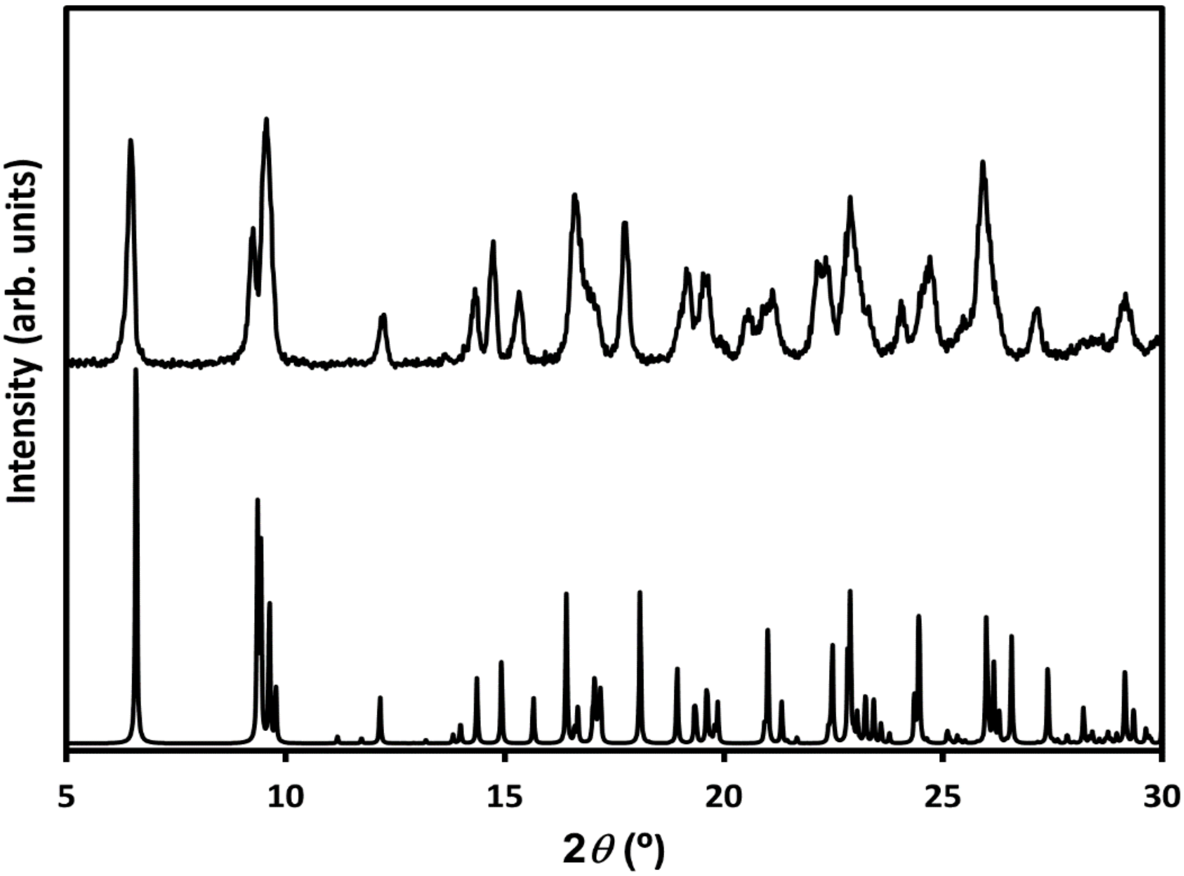

Figure S3. Comparison between the powder XRD pattern simulated from the crystal structure data of {[Zn(3,5-$(HO)_2Bz)_2$(μ-4,4’-bpy)]·4,4’-bpy·1/2CH_3OH}$_n$ (**4**), determined at 100 K (*bottom*) and the experimental pattern measured at room temperature (*top*). Small displacement of the peaks was due to the different characterization temperature of the powder (room temperature) and the single crystal (100 K).

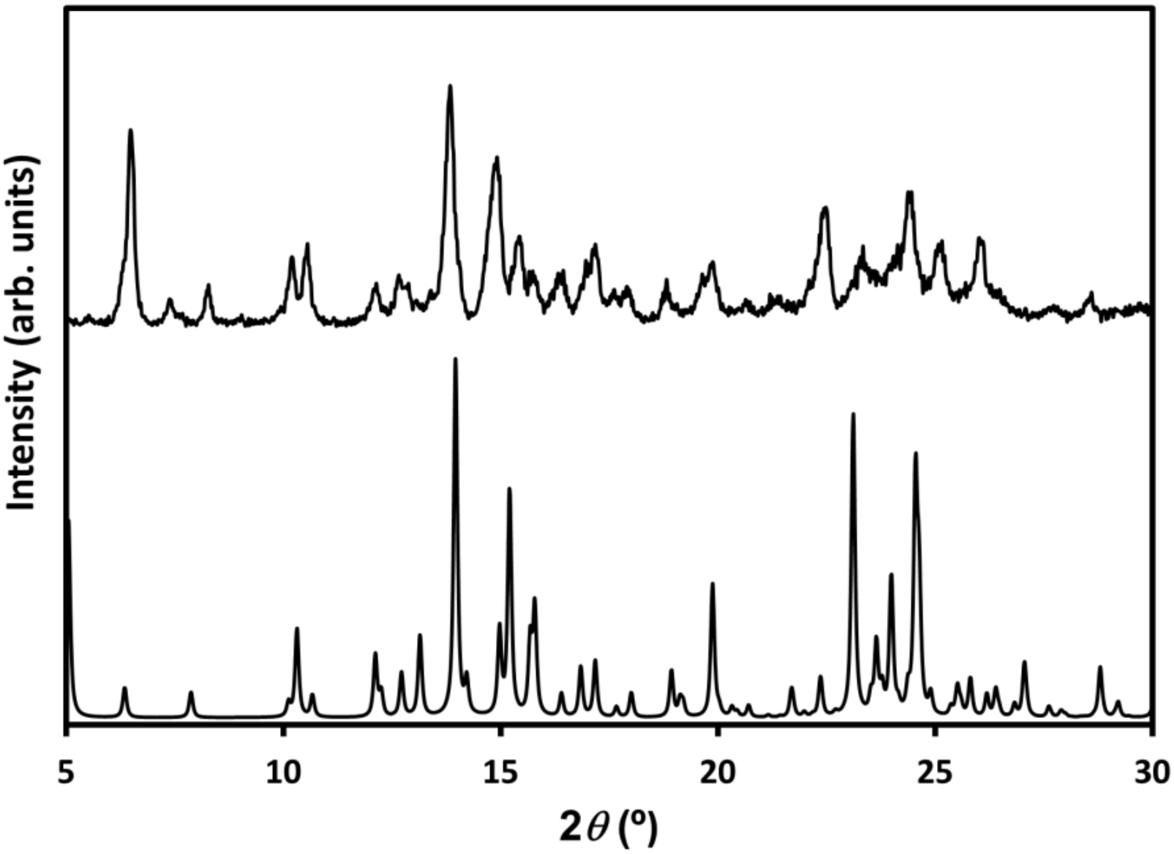

Figure S4. Comparison between the powder XRD pattern simulated from the crystal structure data of {[Zn(3,5-(MeO)$_2$Bz)$_2$(μ-4,4'-bpy)]·H_2O}$_n$ (**6**), determined at 100 K (*bottom*) and the experimental pattern measured at room temperature (*top)*. Small displacement of the peaks was due to the different characterization temperature of the powder (room temperature) and the single crystal (100 K) and also possibly be the loss of some water content.

ATR-FTIR and ^{1}H-NMR spectroscopic data

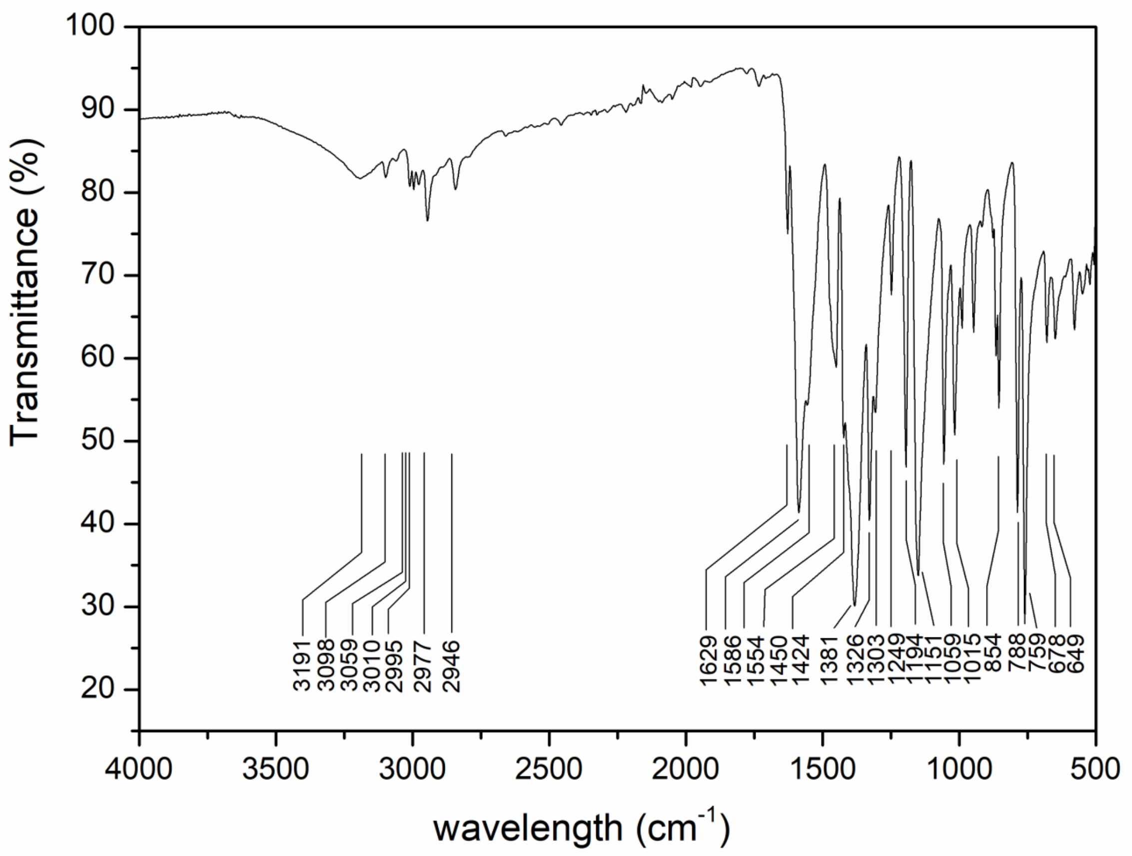

Figure S5. FTIR-ATR spectrum of $[Zn(\mu\text{-}3,5\text{-}(MeO)_2Bz)_2(CH_3OH)]_2$ (**2**)

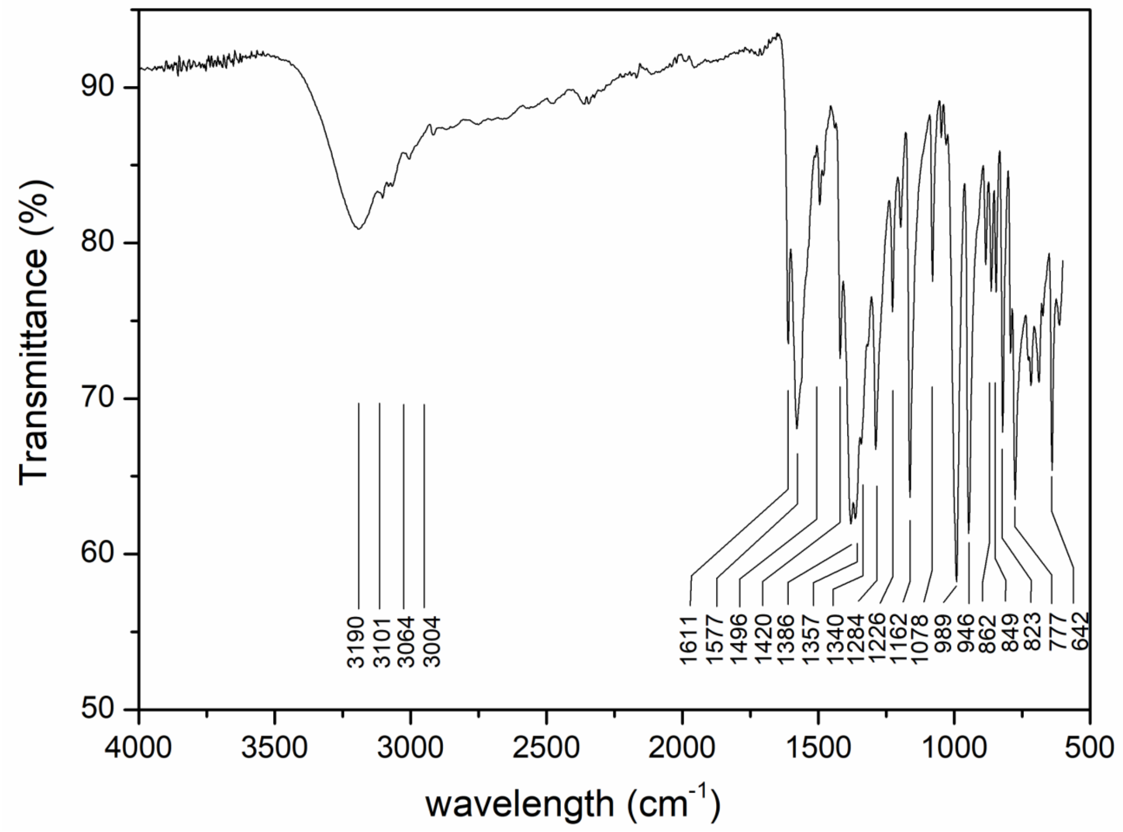

Figure S6. FTIR-ATR spectrum of {[Zn(3,5-$(HO)_2$Bz$)_2$(μ-4,4’-bpy)]·2DMSO}$_n$ (**3**)

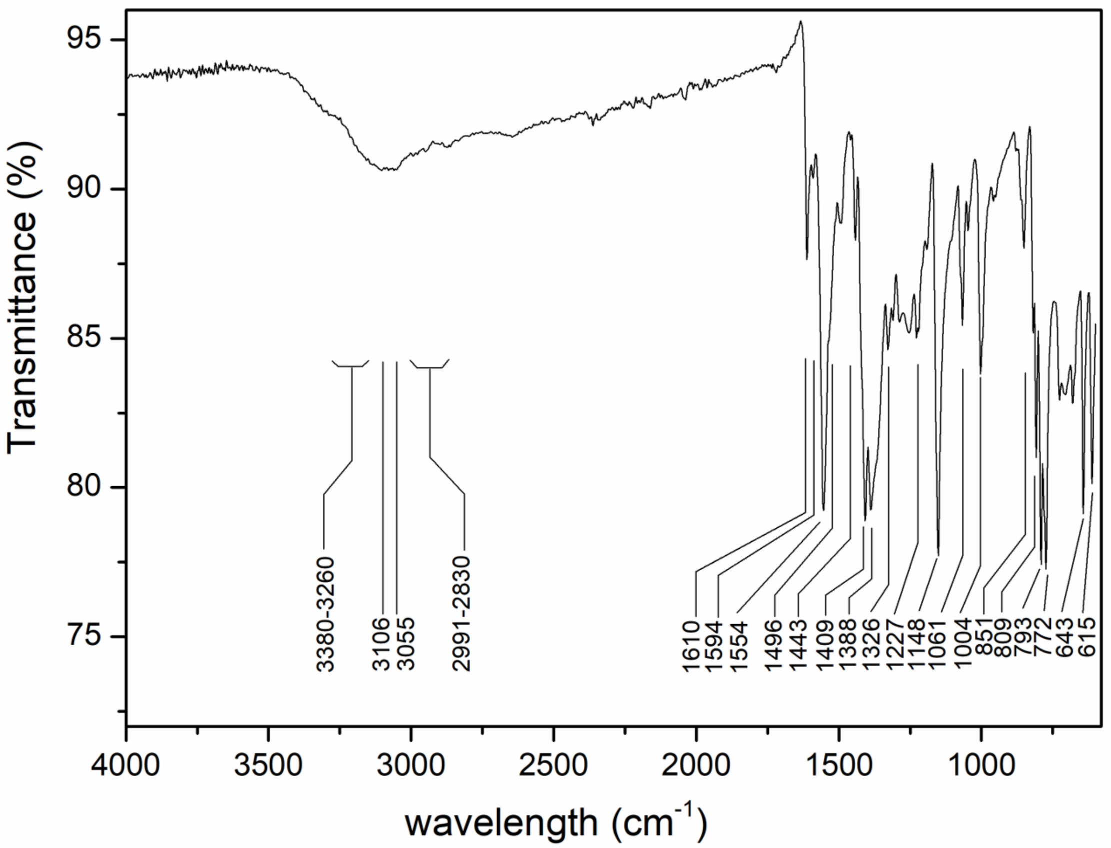

Figure S7. FTIR-ATR spectrum of $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 4,4'\text{-}bpy\cdot 1/2CH_3OH\}_n$ (**4**)

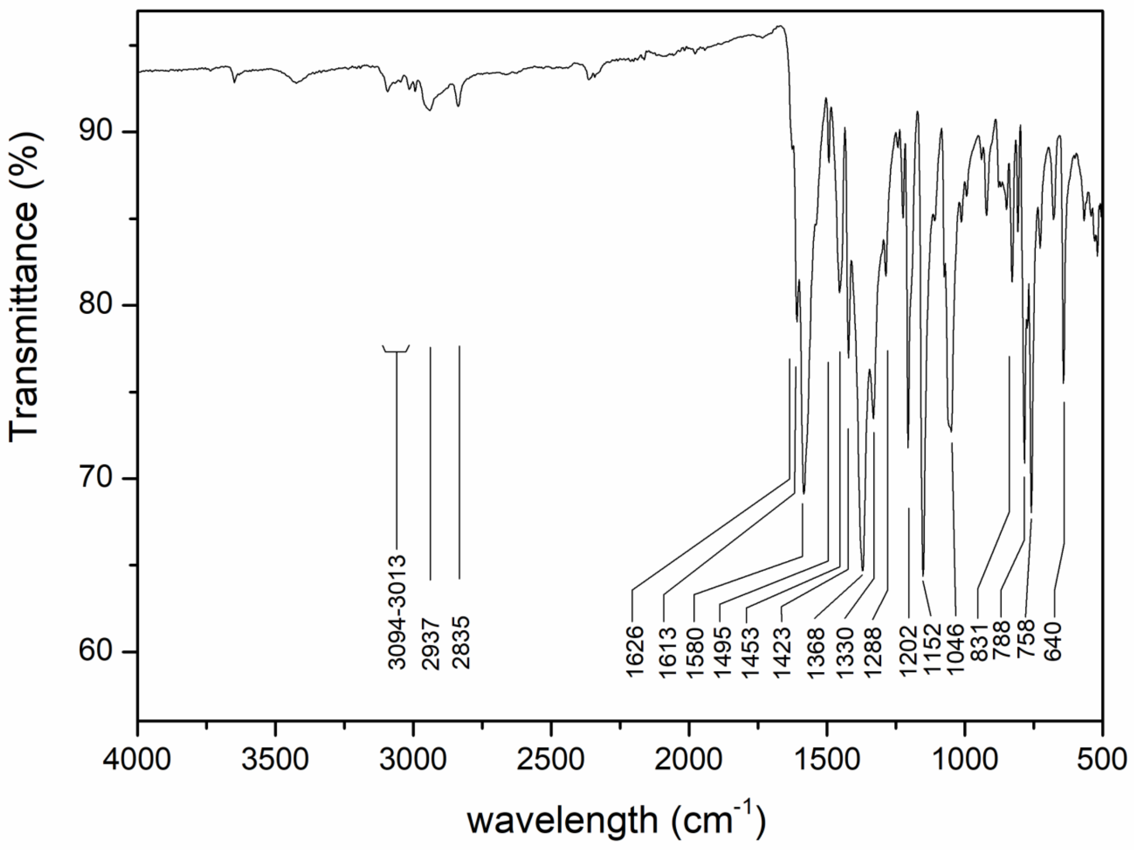

Figure S8. FTIR-ATR spectrum of $[Zn_2(\mu\text{-}3,5\text{-}(MeO)_2Bz)_4(\mu\text{-}4,4'\text{-}bpy)]_n$ (**5**)

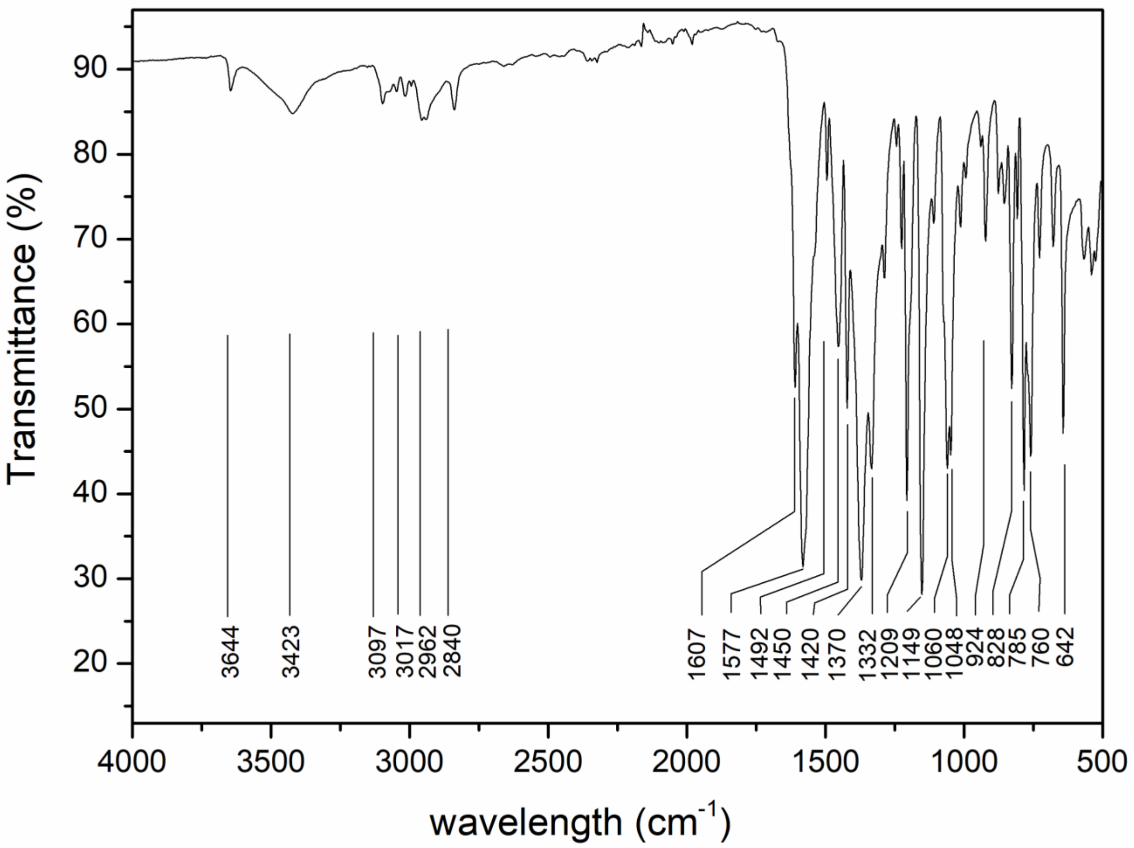

Figure S9. FTIR-ATR spectrum of $\{[Zn(3,5\text{-}(MeO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot H_2O\}_n$ (**6**)

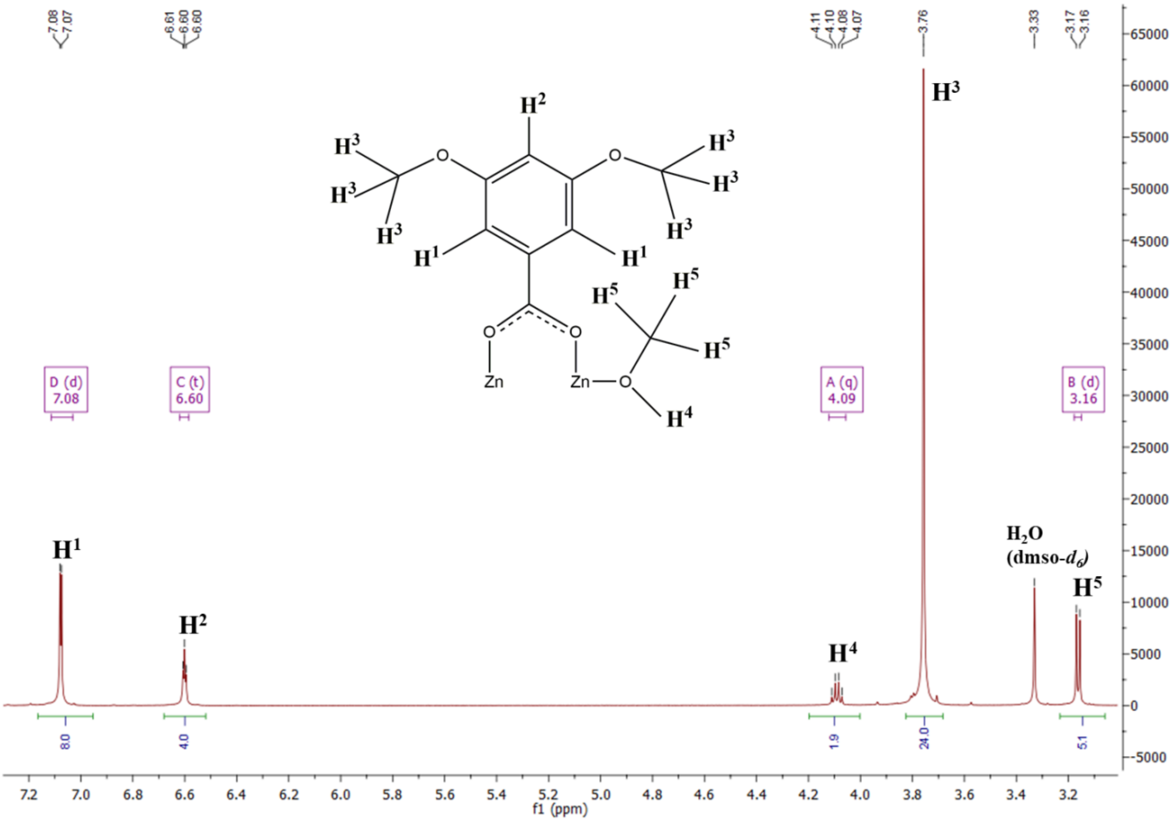

Figure S10. ^{1}H-NMR spectrum of [Zn(μ-3,5-(MeO)$_2$Bz)$_2$(CH$_3$OH)]$_2$ (**2**)

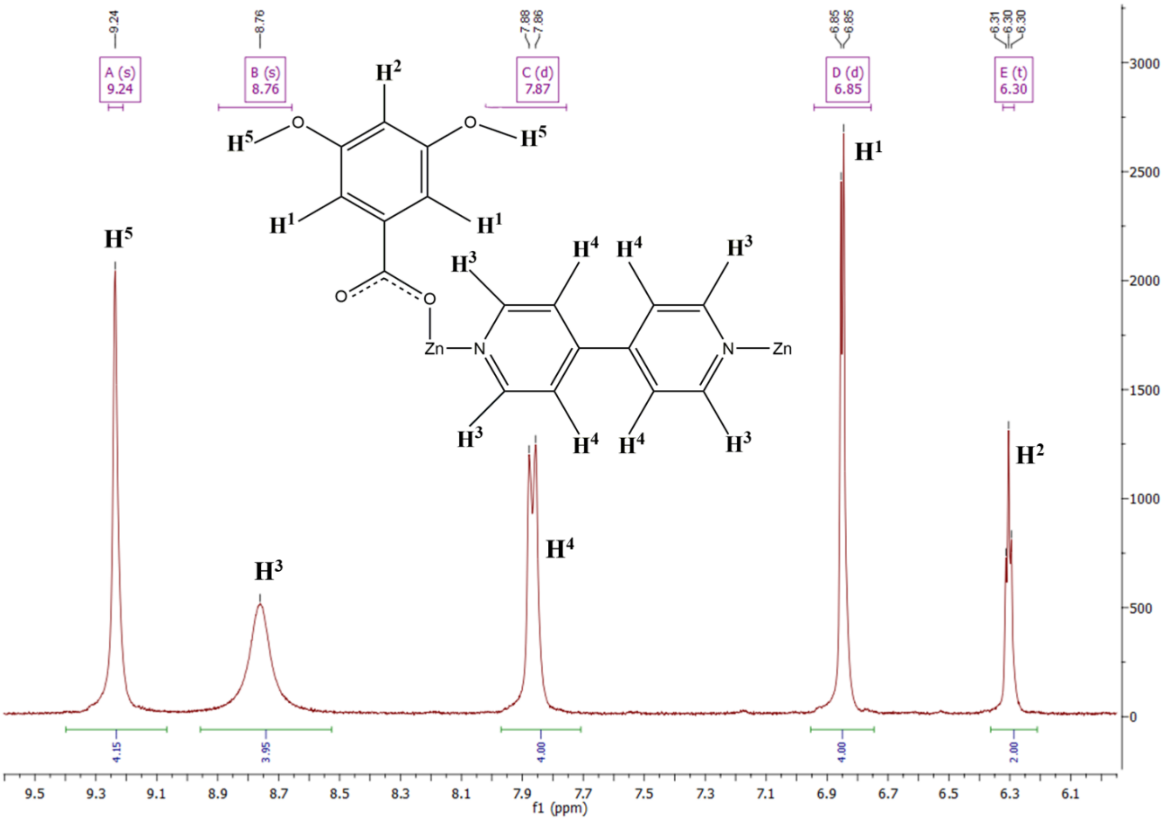

Figure S11. ^{1}H-NMR spectrum of {[Zn(3,5-(HO)$_2$Bz)$_2$(μ-4,4'-bpy)]·2DMSO}$_n$ (**3**)

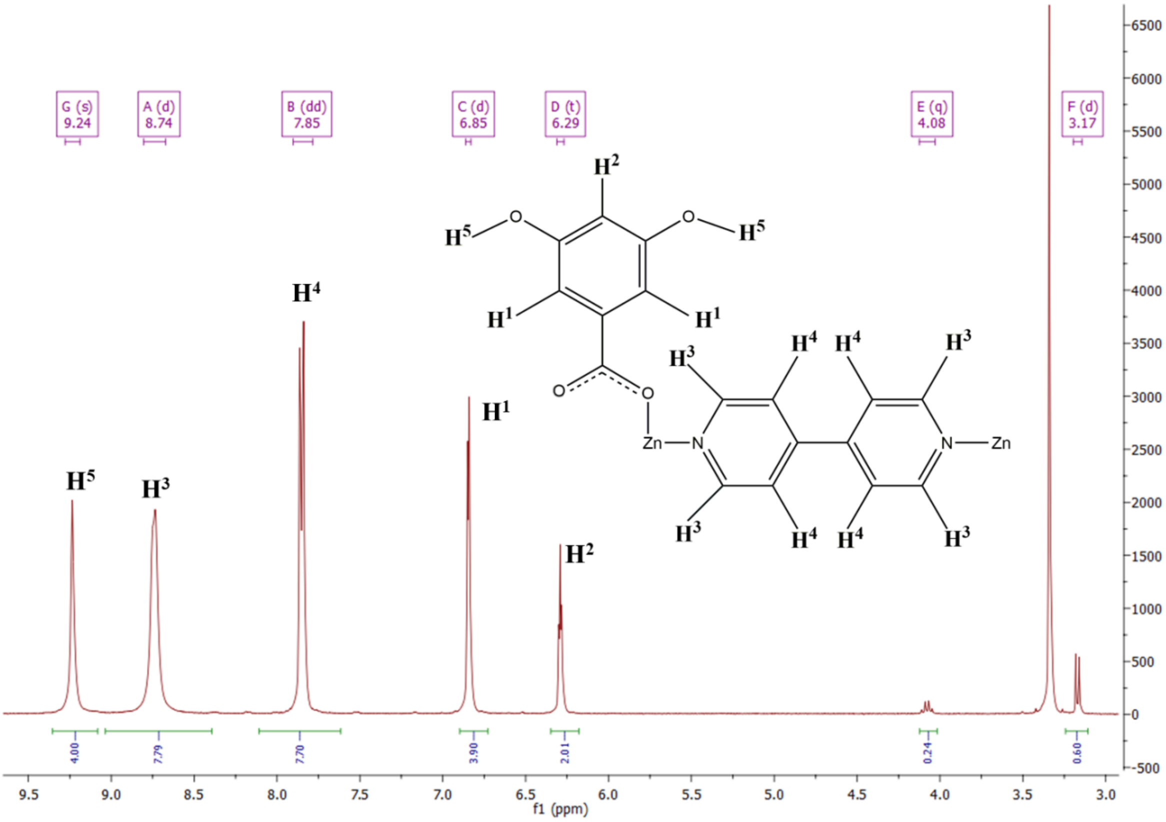

Figure S12. ^{1}H-NMR spectrum of $\{[Zn(3,5\text{-}(HO)_2Bz)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 4,4'\text{-}bpy\cdot 1/2CH_3OH\}_n$ (**4**)

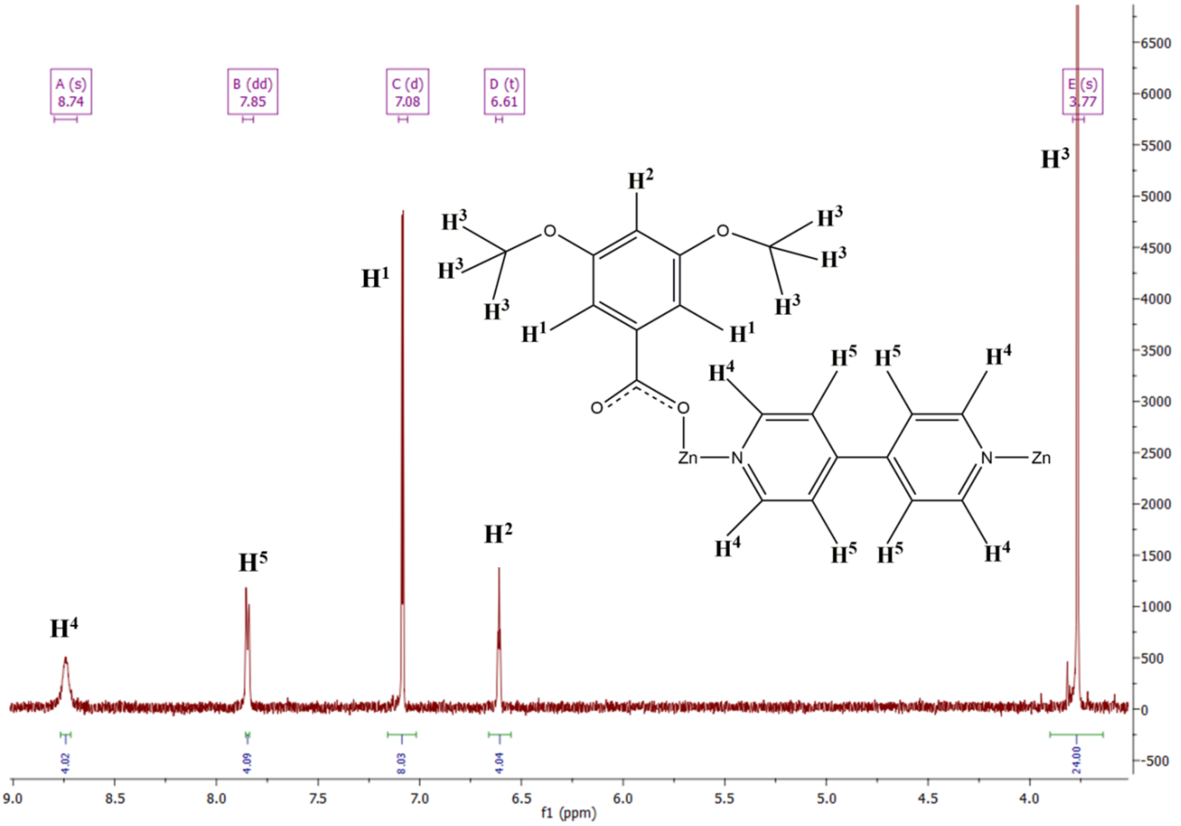

Figure S13. ^{1}H-NMR spectrum of [Zn$_2$(μ-3,5-(MeO)$_2$Bz)$_4$(μ-4,4'-bpy)]$_n$ (**5**)

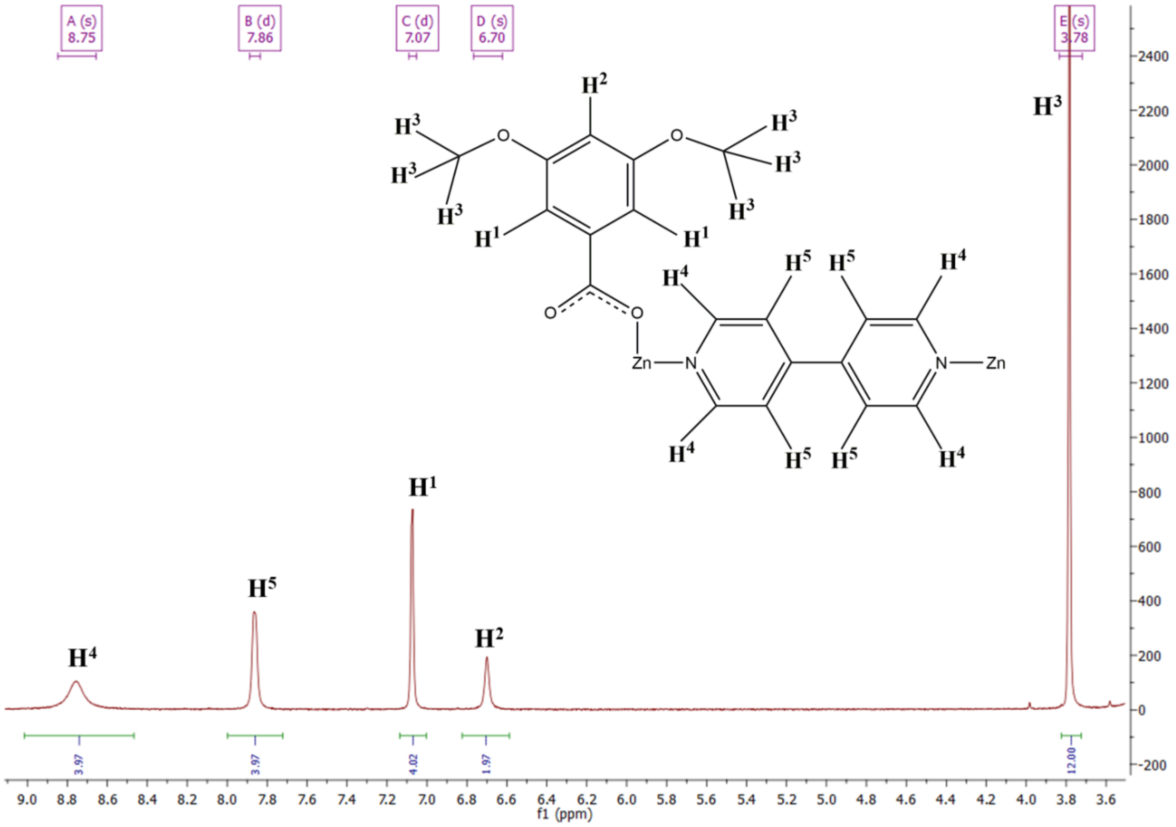

Figure S1. ^{1}H-NMR spectrum of {[Zn(3,5-(MeO)$_2$Bz)$_2$(μ-4,4'-bpy)]·H$_2$O}$_n$ (**6**)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_c20wb185_0m_aa

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: mo_c20wb185_0m_aa

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Bond precision:  C-C = 0.0020 A          Wavelength=0.71073

Cell:           a=6.8291(4)       b=11.7622(7)     c=12.6198(7)
                alpha=98.886(3)   beta=94.647(3)   gamma=93.081(3)
Temperature:    100 K

                 Calculated                Reported
Volume           995.97(10)                995.97(10)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C38 H44 O18 Zn2           C38 H44 O18 Zn2
Sum formula      C38 H44 O18 Zn2           C38 H44 O18 Zn2
Mr               919.51                    919.47
Dx,g cm-3        1.533                     1.533
Z                1                         1
Mu (mm-1)        1.282                     1.282
F000             476.0                     476.0
F000'            476.82
h,k,lmax         9,15,16                   9,15,16
Nref             4992                      4969
Tmin,Tmax        0.910,0.945               0.677,0.746
Tmin'            0.754

Correction method= # Reported T Limits: Tmin=0.677 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.995          Theta(max)= 28.378

R(reflections)= 0.0248( 4243)     wR2(reflections)= 0.0596( 4969)

S = 1.022                 Npar= 267
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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PLAT220_ALERT_2_C Non-Solvent  Resd 1  O   Ueq(max)/Ueq(min) Range        4.0 Ratio
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         O1 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         O5 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        Zn1 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         C1 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C10 Check
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          8 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          1 Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.003 Degree
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          5 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn1      --O1       .       16.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn1      --O5       .       17.7 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn1      --O9       .        5.4 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn1      --O2_a     .       15.7 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn1      --O6_a     .       15.9 s.u.
PLAT794_ALERT_5_G Tentative Bond Valency for Zn1       (II)      .       2.21 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............          5 Note
PLAT883_ALERT_1_G No Info for _atom_sites_solution_primary .......    Please Do !
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  13 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

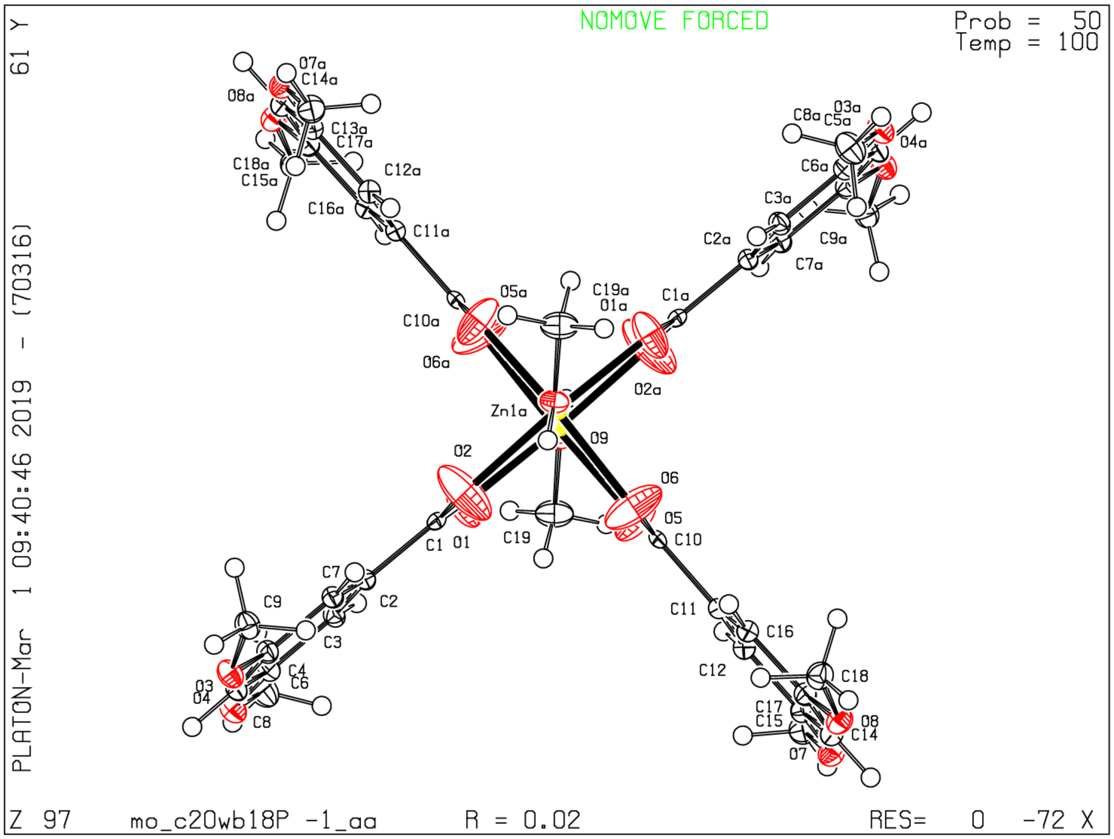
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/02/2019; check.def file version of 18/02/2019

Datablock mo_c20wb185_0m_aa - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: mo_C20VB108A_0m_b

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Bond precision:  C-C = 0.0067 A          Wavelength=0.71073

Cell:           a=13.2419(7)    b=7.7558(4)        c=15.6016(7)
                alpha=90        beta=108.253(2)    gamma=90
Temperature:    100 K

                Calculated                Reported
Volume          1521.68(13)               1521.68(13)
Space group     P c                       P c
Hall group      P -2yc                    P -2yc
Moiety formula  C24 H18 N2 O8 Zn, 2(C2 H6 C24 H18 N2 O8 Zn, 2(C2 H6
                O S)                      O S)
Sum formula     C28 H30 N2 O10 S2 Zn      C28 H30 N2 O10 S2 Zn
Mr              684.05                    684.03
Dx,g cm-3       1.493                     1.493
Z               2                         2
Mu (mm-1)       1.003                     1.003
F000            708.0                     708.0
F000’           709.39
h,k,lmax        18,11,22                  18,11,22
Nref            9329[ 4670]               8393
Tmin,Tmax       0.888,0.967               0.705,0.746
Tmin’           0.842

Correction method= # Reported T Limits: Tmin=0.705 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.80/0.90      Theta(max)= 30.583

R(reflections)= 0.0376( 6456)     wR2(reflections)= 0.0759( 8393)

S = 1.097                  Npar= 393
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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STRVA01_ALERT_4_C           Flack test results are ambiguous.
           From the CIF: _refine_ls_abs_structure_Flack    0.481
           From the CIF: _refine_ls_abs_structure_Flack_su    0.013
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0067 Ang.
```

Alert level G

```
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension          1 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............           4 Report
PLAT111_ALERT_2_G ADDSYM Detects New (Pseudo) Centre of Symmetry .         95 %Fit
PLAT113_ALERT_2_G ADDSYM Suggests Possible Pseudo/New  Space Group       P2/c Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

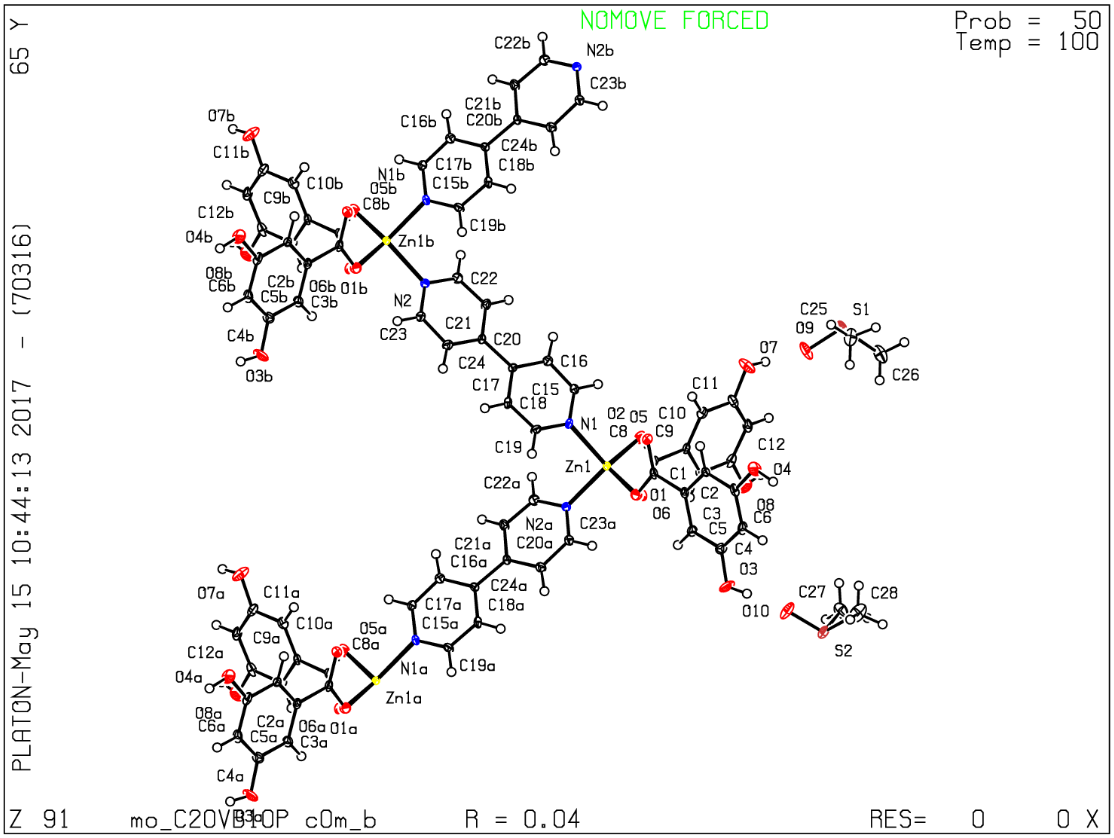
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/03/2017; check.def file version of 24/03/2017

Datablock mo_C20VB108A_0m_b - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_C20VB231_0m_aa

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: mo_C20VB231_0m_aa

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Bond precision:  C-C = 0.0029 A          Wavelength=0.71073

Cell:          a=10.6316(6)      b=11.6986(7)      c=14.0895(8)
               alpha=96.653(2)   beta=102.794(2)   gamma=111.997(2)
Temperature:   100 K

                Calculated                 Reported
Volume          1545.70(16)                1545.70(16)
Space group     P -1                       P -1
Hall group      -P 1                       -P 1
Moiety formula  2(C24 H18 N2 O8 Zn), 2(C10 2(C24 H18 N2 O8 Zn), 2(C10
                H8 N2), C H4 O             H8 N2), C H4 O
Sum formula     C69 H56 N8 O17 Zn2         C69 H56 N8 O17 Zn2
Mr              1400.00                    1399.95
Dx,g cm-3       1.504                      1.504
Z               1                          1
Mu (mm-1)       0.858                      0.858
F000            722.0                      722.0
F000'           722.89
h,k,lmax        14,16,19                   14,16,19
Nref            9089                       9067
Tmin,Tmax       0.911,0.938                0.657,0.746
Tmin'           0.754

Correction method= # Reported T Limits: Tmin=0.657 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 30.097

R(reflections)= 0.0371( 7698)     wR2(reflections)= 0.1038( 9067)

S = 1.064                 Npar= 438
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.9 Note
PLAT369_ALERT_2_C Long   C(sp2)-C(sp2) Bond  C25      - C26      .       1.54 Ang.
PLAT369_ALERT_2_C Long   C(sp2)-C(sp2) Bond  C27      - C30      .       1.55 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         11 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          3 Check
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  0.76A   From O1W             1.19 eA-3
```

Alert level G

```
ABSTY01_ALERT_1_G  Extra text has been found in the _exptl_absorpt_correction_type
            field, which should be only a single keyword. A literature
            citation should be included in the _exptl_absorpt_process_details
            field.
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          4 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          7 Report
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension          1 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............           5 Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.002 Degree
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          1 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          3 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          4 Report
PLAT300_ALERT_4_G Atom Site Occupancy of O1W        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C1W        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1WO       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1WA       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1WB       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H1WC       Constrained at        0.5 Check
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT432_ALERT_2_G Short Inter X...Y Contact  C32      ..C32              3.07 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........           4 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #          6 Check
PLAT794_ALERT_5_G Tentative Bond Valency for Zn1       (II)      .       1.83 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............           7 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         10 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          5 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
```

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
26 **ALERT level G** = General information/check it is not something unexpected

```
 2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 9 ALERT type 2 Indicator that the structure model may be wrong or deficient
 5 ALERT type 3 Indicator that the structure quality may be low
13 ALERT type 4 Improvement, methodology, query or suggestion
 3 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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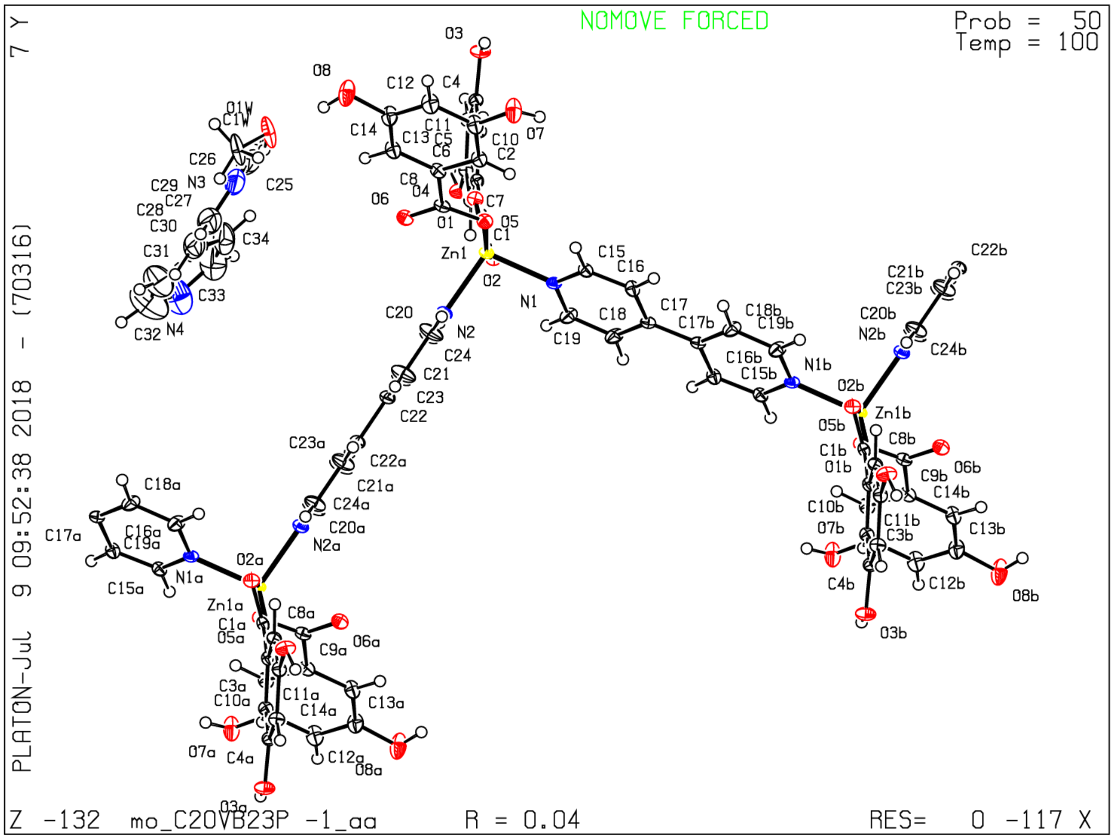
PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock mo_C20VB231_0m_aa - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_C20XB34A_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: mo_C20XB34A_0m_a

```
Bond precision:  C-C = 0.0025 A          Wavelength=0.71073

Cell:            a=23.0160(14)     b=27.8171(15)       c=8.7942(5)
                 alpha=90          beta=102.896(2)     gamma=90
Temperature:     100 K

                Calculated                Reported
Volume          5488.4(5)                 5488.4(5)
Space group     C 2/c                     C 2/c
Hall group      -C 2yc                    -C 2yc
Moiety formula  C28 H26 N2 O8 Zn, H2 O    C28 H26 N2 O8 Zn , H2 O
Sum formula     C28 H28 N2 O9 Zn          C28 H28 N2 O9 Zn
Mr              601.91                    601.89
Dx,g cm-3       1.457                     1.457
Z               8                         8
Mu (mm-1)       0.952                     0.952
F000            2496.0                    2496.0
F000'           2499.46
h,k,lmax        33,39,12                  32,39,12
Nref            8519                      8444
Tmin,Tmax       0.891,0.918               0.693,0.746
Tmin'           0.793

Correction method= # Reported T Limits: Tmin=0.693 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.991          Theta(max)= 30.675

R(reflections)= 0.0406( 6309)     wR2(reflections)= 0.0958( 8444)

S = 1.049                  Npar= 371
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

```
PLAT420_ALERT_2_B D-H Without Acceptor       O1W      --H1WA     .     Please Check
```

Alert level C

```
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.3 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          6 Report
PLAT976_ALERT_2_C Check Calcd Resid. Dens.  0.55A   From O1W            -0.56 eA-3
PLAT976_ALERT_2_C Check Calcd Resid. Dens.  0.54A   From O1W            -0.55 eA-3
PLAT976_ALERT_2_C Check Calcd Resid. Dens.  0.47A   From O1W            -0.48 eA-3
PLAT976_ALERT_2_C Check Calcd Resid. Dens.  0.45A   From O1W            -0.47 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H1WA             -0.38 eA-3
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          3 Note
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension          1 Info
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large       8.25 Why ?
PLAT128_ALERT_4_G Alternate Setting for Input Space Group     C2/c       I2/a Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          3 Report
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          2 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Zn1       (II)      .       1.92 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          3 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         66 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          2 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         16 Info
```

```
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```

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PLATON version of 03/05/2019; check.def file version of 29/04/2019

Datablock mo_C20XB34A_0m_a - ellipsoid plot