Novel Zn-CPs based on the biocompatible molecule
bisdemethoxycurcumin (BDMC)

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Abstract

This article introduces a new family of coordination polymers (CPs) that contains a natural biocompatible curcumin derivative, the bisdemethoxycurcumin (BDMC), coordinated to Zn(II) centers. The reaction between BDMC and zinc acetate, performed under mild conditions in ethanol, provides a new 1D phase termed BDMCZn-1. In addition, dimensionality and porosity of this network have been expanded by studying the reaction occurring between three species, the BDMC, the Zn(II) and a ditopic co-linker: 1,2-bis(4-pyridyl)ethylene, 1,3-bis(4-pyridyl)propane or 4,4’-bipyridine. In total, seven new CPs are presented, named as BDMCZn-x. The structures of five of them could be elucidated by single crystal X-ray diffraction. Moreover, we show that the combination of the latest technique with solid-state $^{13}$C nuclear magnetic resonance is a powerful tool set to analyze the coordination modes of the BDMC, providing insight into the two unresolved structures. In the achievement of the new CPs, we further discuss the coordination capacity of BDMC, the relevance of solvents and supramolecular interactions.

Keywords: Coordination polymers, curcuminoids, dipyridine co-linker, bisdemethoxycurcumin, solid-state $^{13}$C NMR.
**Introduction**

In the field of coordination polymers (CPs), the use of natural molecules with health benefits or therapeutic effect as the main component/s of the skeleton is gaining attention.¹ Research in this subject focus on the controlled delivery of such species as active ingredients (AIs), thus minimizing the necessity of carriers and the existence of potential pollutant agents. CPs have multiple potential applications, depending on their physical and chemical properties, and the use of biocompatible molecules would facilitate medical purposes, for example, as drug delivery systems or in diagnosis by imaging.²,³ Actually, for these CPs the porosity is not mandatory, considering that the biolinkers when are released act themselves as AIs.⁴ Examples of employed biolinkers for CPs building are peptides, oligopeptides, carbohydrates, amino acids, nucleobases and porphyrins.⁵-¹¹ In the studied natural linkers, frequent drawbacks are the lack of symmetry factors in the molecule and the presence of considerable flexibility, which make challenging the crystallization of CPs with high dimensionality.¹² In a more extended picture, a pro-active approach to sustainability would involve the consistent addition of new polytopic natural and biorenewable linkers in the creation of 1D-3D polymeric architectures for all kind of purposes aside biomedical applications.¹

Connected with the above, curcuminoids (CCMoids, Fig. 1a) are diarylheptanoids bioderived molecules firstly extracted from the rhizomes of the plant *curcuma longa*,¹³ which can also be synthetized using the synthetic methods described by Pabon and others.¹⁴-¹⁶ These species, and particularly curcumin (CCM), the prevalent CCMoid in the turmeric root, have been used since ancient times in food, medicine and as a natural dye. Its effect as anti-inflammatory, anti-angiogenic, anti-oxidant, anti-cancer agent has been extensively studied.¹⁷-¹⁹ From a structural point of view, natural CCMoids have three potential sites toward metal-ligand coordination, consisting in one β-diketone/enol group and two phenolic rings with different substituents.²⁰ As polytopic linkers, CCMoids are perfect candidates for the synthesis
of CPs, since they retain specific symmetry in the molecule, and possess certain flexibility. These molecules can exhibit numerous coordination modes with metal ions, giving place to a high structural diversity in the crystallized products. There are many examples of the coordination of CCM and 3d/4f/5d metal centers. However, reported reactions regarding the coordination of metals with the rest of CCMoids from the turmeric root, i.e., bisdemethoxycurcumin (BDMC) and demethoxycurcumin (DMC) (Fig. 1a), are less common.

Interestingly, the number of biomedical studies involving BDMC has increased due to its higher stability vs. CCM, for instance regarding in-vivo degradation.

Figure 1. Molecular structures of: (a) main CCMoids (CCM=curcumin, DMC=Demethoxycurcumin, BDMC=Bisdemethoxycurcumin) present in the turmeric root (central image), and (b) used dipyridine co-linkers (bpy=4,4’-bipyridine, bpe=1,2-bis(4-pyridyl)ethylene, bpp=1,3-bis(4-pyridyl)propane)
Beside the CCM bioMOFs described in the literature by Su et al.\textsuperscript{12} and us,\textsuperscript{27} to the best of our knowledge, there are only few CCMoid CPs reported involving transition metals (Co(II) and Ni(II)), also by some of us.\textsuperscript{28} In this respect, this work presents the first examples of a series of CPs synthetized with a Zn(II) source and the natural CCMoid BDMC. The significant symmetry and conjugated nature of this polytopic biomolecule confer attractive characteristics for CPs synthesis. In relation to the metal, the encouraging results of Zn(II) in studies of biocompatibility\textsuperscript{29} and the low toxicity of this cation in different tissues\textsuperscript{30} have triggered its use in combination with the biolinker BDMC. The investigated reactions of BDMC with Zn(II), performed in EtOH under solvothermal conditions, resulted in a dense 1D CP (BDMCZn-1).

In addition, as a way to increase the dimensionality and porosity of the network, the use of ancillary linkers, chosen from the family of the dipyridines (1,2-bis(4-pyridyl)ethylene (bpe), 1,3-bis(4-pyridyl)propane (bpp) and 4,4'-bipyridine (bpy)) in Fig. 1b), was studied.\textsuperscript{31,32} With this procedure, seven new CPs, with 1D and 3D dimensionalities, were crystallized (BDMCZn1, -2a, 2b, 3, 4a, 4b and 4c). The structures of five of the newly synthetized compounds could be elucidated by single crystal X-ray diffraction. Solid-state $^{13}$C nuclear magnetic resonance (NMR) measurements were performed as a complementary technique to ascertain the different coordination modes of the BDMC molecule within the compounds. This technique is sensible to little changes in the disposition, environment and conformation of the analyzed molecules.\textsuperscript{33} Obtained spectral data from the unresolved crystalline materials were correlated to potential crystal topology and composition to outline the structures. This work shows a rich variety of crystallographic structures using a CCMoid aside from CCM, and solid-state $^{13}$C NMR as a handy characterization tool to discern coordination of such type of species. Our results aim to show CCMoids as purposeful polytopic building units toward the creation of future extended structures in CPs.
Experimental section

Materials

Zn(OAc)$_2$·2H$_2$O and the ancillary linkers (bpy, bpe and bpe) were provided by Sigma Aldrich.

BDMC was synthetized using a modification of Pabon method.$^{14}$ EtOH was supplied by Scharlab.

Synthetic method

Synthetized CPs were obtained using a solvothermal methodology and EtOH as a solvent. Reactions were carried out in 10 mL Pyrex vials with hermetic closures, which were placed in an oven at 80 ºC for three days. The end products were collected after cooling down the vials to room temperature. Crystals, placed on the walls and at the bottom of the vials, were recovered directly from the mother solution and washed with fresh solvent before drying.

**BDMCZn-1.** 30.00 mg (0.097 mmol) of BDMC and 21.36 mg (0.097 mmol) of Zn(OAc)$_2$·2H$_2$O were mixed in 2 mL of EtOH. The vial was stirred ultrasonically up to the complete solubilization of all reagents to proceed with the solvothermal treatment. Yield 56-60 wt.%. ATR-FTIR data (cm$^{-1}$): 1603 (νC=C aromatic), 1591 (C=O st,β-diketone), 1487 (νC=C aromatic), 1382 (δCCH), 1297 and 1234 (C-Ost phenolic), 1157 (opp CCH aromatic and CCH skeletal), 970 (=CH$_8$ opp). EA (wt.%) data for [Zn(BDMC)(EtOH)] or ZnC$_{21}$H$_{19}$O$_5$ (416.74 g·mol$^{-1}$) calculated C: 60.37, H: 4.89; found C: 60.30, H: 5.16.

**BDMCZn-2a and 2b.** Both were synthetized as 1 but adding an extra reagent consisting on either 8.86 mg (0.048 mmol) or 17.73 mg (0.097 mmol) of bpe. Yields 52-70 wt.%. ATR-FTIR data of **BDMCZn-2a (cm$^{-1}$):** 1603 (νC=C aromatic), 1537 (C=O st,β-diketone), 1494(νC=C aromatic), 1407, 1240 (C-Ost phenolic), 1158 (opp CCH aromatic and CCH skeletal), 968 (=CH$_8$ opp). EA (wt.%) for [Zn(BDMC)(bpe)(OAc)$_n$·2nH$_2$O or ZnC$_{33}$H$_{28}$O$_6$N$_2$·2H$_2$O (649.47 g·mol$^{-1}$) calculated C: 60.98, H: 4.96, N: 4.31. found C: 61.05, H: 4.76, N: 4.54.
ATR-FTIR data of **BDMCZn-2b** (cm$^{-1}$): 1602 (νC=C aromatic), 1587 (C=Oβ-diketone), 1483, 1442 (υC=N), 1394 (δCCH), 1298, 1243 (C-Ostphenolic), 1154 (opp CCH aromatic and CCH skeletal), 981 (=CHð opp). EA, the best fit of the found data (C: 64.41, H: 4.42 and N: 2.91 wt.%), obtained by using a molar ratio for Zn:BDCM:bpe of 1:1:0.5 (C: 64.88, H: 4.14, N: 3.03 wt.%), therefore resulting in the formulae [Zn(BDMC)(bpe)$_{0.5}$] or ZnC$_{25}$H$_{19}$O$_{4}$N (462.79 g·mol$^{-1}$).

**BDMCZn-3.** The system was synthetized as -1 but adding either 19.29 mg (0.048 mmol) or 38.58 mg (0.097 mmol) of bpp. Yield 75-80 wt.%. ATR-FTIR data (cm$^{-1}$): 1599 (νC=C aromatic), 1590 (C=Oβ-diketone), 1482 (νC=C aromatic), 1439 (υC=N), 1384 (δCCH), 1262 (C-Ostphenolic), 1157 (oppCCH aromatic and CCH skeletal), 968 (=CHð opp). EA (wt.%) for [Zn(BDMC)(bpp)$_{1/2}$]$_{n}$·n/2EtOH or Zn$_{2}$C$_{51}$H$_{42}$O$_{8}$N$_{2}$·C$_{2}$H$_{6}$O (987.68 g·mol$^{-1}$) calculated C: 64.45, H: 4.9, N: 2.84, found C: 64.03, H: 5.21, N: 2.91.

**BDMCZn-4a, 4b and 4c.** The three systems were synthetized as BDMCZn-1 but adding either 15.19 mg (0.048 mmol) or 30.38 mg (0.097 mmol) of bpy. **BDMCZn-4c** was the only compound obtained in significant quantity, with a yield of 38-54 wt.%. ATR-FTIR data (cm$^{-1}$): 1614 (νC=C ring), 1590 (C=Oβ-diketone), 1483(νC=C aromatic), 1382 (δCCH), 1261(C-Ostphenolic), 1155 (opp CCH aromatic and CCH skeletal), 965 (=CHð opp). EA, the best fit of the found data (C: 58.71, H: 4.07, N: 3.4 wt.%), obtained by using a molar ratio for Zn:BDCM:bpy of 1:1:0.5 (C: 59.33, H: 4.56, N: 2.88 wt.%) with 2 H$_{2}$O molecules in the structure, therefore resulting in the formulae [Zn(BDMC)(bpy)$_{0.5}$]$_{n}$·2nH$_{2}$O or ZnC$_{24}$H$_{18}$O$_{4}$N·2H$_{2}$O (485.8 g·mol$^{-1}$).

**Characterization.** Prepared samples were characterized first by routine powder X-ray diffraction (PXRD) by recording the patterns on a Siemens D-5000 diffractometer with Cu Kα radiation. Single-crystal X-ray diffraction (SCXRD) data for **BDMCZn-1** were collected on a Bruker APEXII Qazar CCD diffractometer equipped (Grup de Magnetisme i Molècules Funcionals, Universitat de Barcelona) at Mo-k-α wavelength using phi and omega scans at 100 K. The structures were solved by intrinsic phasing methods (SHELXT)$^{34}$ and refined on F$^{2}$.
Hydrogen atoms were included on calculated positions, riding on their carrier atoms. Data for the rest of characterized species (BDMCZn-2a,-3,-4a,-4b) were collected at XALOC beamline at ALBA synchrotron (Spain) with a 0.72931 Å wavelength using the Dectris Pilatus 6M detector at 100 K. The phi scan was repeated at three different κ angles (0, 45 and 90º), and merged afterwards to increase the completeness and redundancy when possible. Data were indexed, integrated and scaled using the XDS software. Crystallographic data for all compounds are summarized in Tables S1 in the SI, and the corresponding CIF files have been deposited in the Cambridge Crystallographic Data Centre and can be accessed free of charge at https://www.ccdc.cam.ac.uk/structures/ (CCDC deposition numbers 1991279 - 1991283).

Samples chemical composition (C, H and N) were assessed by elemental analysis (EA, Thermo Carlo Erba Flash 2000). Thermogravimetric analysis (TGA, NETZSCH -STA 449 F1 Jupiter), performed up to 600 °C in air or Ar, was used to determine the thermal stability and composition of some samples. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were obtained in a in FTIR JASCO 4700LE equipment using the ATR accessory with a resolution of 4 cm⁻¹ and 32 scans. For the measurements, ca. 5 mg of the powdered samples were deposited covering the crystal of the ATR accessory and pressed with the pressure tip.

The solid-state ¹³C NMR experiments were performed on a Bruker Avance III at a magnetic field of 9.4 T, equipped with a double channel 4.0 mm MAS probe. Sample spinning was set to 10 kHz. A contact time of 2500 us (63 KHz), a recycle delay of 1 s, 27 k scans (overall experimental time 8 h) and a decoupling power of 83.3 KHz were used in all experiments. Pure adamantane was used as external chemical shift reference (CH signal at 29.5 ppm).
Results and Discussion

The combination of solvothermal conditions and EtOH provides seven new CPs with BDMC as the principal linker and Zn(II) as the metallic node. **BDMCZn-1** could be resolved by SCXRD using a conventional radiation source. Nevertheless, **BDMCZn-2a, -3, -4a and -4b** compounds precipitated as spherulitic crystals, in which each crystal was composed by small subunits of only few microns. Consequently, for the SCXRD analysis a synchrotron source was necessary. Unfortunately, the obtained crystals for **BDMCZn-2b and 4c** did not present enough quality for SCXRD structural elucidation. Solid-state $^{13}$C NMR spectral analysis, together with TGA, ATR-FTIR and EA data, were then used to provide further inside in their structures regarding main formulae, coordination mode and dimensionality.

Crystal structures

**BDMCZn-1**, with stoichiometry [Zn(BDMC)(EtOH)]$_n$, crystallizes in the monoclinic P2$_1$/c space group. Crystallographic parameters for this structure are detailed in Table S1. In the asymmetric unit, one Zn(II) atom appears tetracoordinated, having the basal plane occupied by the β-diketone of one BDMC linker and one EtOH molecule, meanwhile in the apical position the metallic center coordinates to the phenolic ring of a neighboring BDMC linker (Fig. 2a). The pseudo-tetrahedral geometry of the Zn(II) is imposed by the coordination with the two oxygens in the β–diketone (angles O-Zn-O between 99-120º). Each BDMC is coordinated to two different Zn(II) atoms by the β-diketone and one phenolic ring, while the second phenol remains protonated. As a consequence, the system presents a 1D zig-zag chain where successive BDMC molecules form angles of 85.50º (Fig. 2b). The chains are held together in a 3D structure by hydrogen bonds established through the coordinated ethanol molecules (Fig 2c). The result is a compact packing with negligible structural porosity. The PXRD pattern obtained for **BDMCZn-1** indicates high purity for the precipitated powder (Fig. S1).
**Figure 2.** Schematic representation of the crystal structure of compound BDMCZn-1: (a) repeating unit showing the coordination mode of Zn(II) and BDMC, (b) zig-zag chain in the 1D structure, and (c) extended 3D framework through H-bonding projected in the $a$ and $c$ directions. Color code: C grey, O red and Zn blue.

**BDMCZn-2a** presents a $[\text{Zn(BDMC)(bpe)(OAc)}]_{n}\cdot 2n\text{H}_2\text{O}$ stoichiometry. This compound crystallizes in the monoclinic $P2_1/c$ space group (Table S1), as well as BDMCZn-1, but its structure involves bpe molecules as co-linkers. The asymmetric unit contains a single pentacoordinate Zn(II) atom bonded to the β-diketone of one BDMC, two pyridine N atoms of two additional bpe co-linkers and one oxygen from the acetate ligand. The Zn(II) ion adopts a square based pyramidal geometry with the β–diketone, the acetate and one of the bpe co-linkers on the basal plane and the second bpe at the apical position (Fig. 3a). Overall, the geometry is slightly distorted ($\tau = 0.43$), with angles smaller than 90° in the bonds that implicate the oxygen
atoms of the β–diketone (between 85.4-88.1°) and larger in the angle between the two N-donor linkers (94.88°). A similar coordination number has been observed in the past in CPs and MOFs, as well as when Zn(II) coordinate to a synthetic CCMoid. In this structure, both phenol groups of the BDMC molecule remain protonated and do not participate in the coordination to the metal, which is exclusively established through the β–diketone. Therefore, a new 1D zig-zag array is formed by coordinative bonds established exclusively between the Zn(II) metal centers and the ditopic bpe molecules (with an angle of 64.58°, Fig. 3b). In the supramolecular structure, the chains are held together by hydrogen bonds established between the remaining protonated phenol groups in the BDMC molecules and the acetate groups of different chains, having half of those through water bridges (Fig. 3c). Again, the result is a dense structure with a negligible porosity (calculated using Mercury). Although the general disposition of Zn(BDMC)(OAc) units attached through the bpe is similar to other CCMoid-CPs published with CoII and NiII using bpy, the molecular blocks of BDMCZn-2a are unique in the sense that each Zn unit coordinates to BDMC and acetate ligands instead of coordinating only to CCMoid molecules. The comparison between the PXRD of BDMCZn-2a and the pattern calculated from the single crystal structure indicates contamination with a different phase (see peaks at 2θ=5.96 and 8.62°) (Fig. S1). Such fact could be related to the low stability of the crystals in the absence of solvent (Fig. S2), which produces changes in the structure during the PXRD measurement. Actually, the mixture Zn:BDMC:bpe has a complex crystallization behavior, since the reduction of the molar ratio of bpe (from 1 to 0.5 with respect to Zn(II)) provides the new compound BDMCZn-2b, with a different PXRD pattern (Fig. S1) of BDMCZn-2a. Unfortunately, further characterization of the new compound was hampered by poor quality of the crystals found. Its composition was estimated using EA data and corroborated by solid-state 13C NMR and ATR-FTIR.
Figure 3. Schematic representation of the crystal structure of compound BDMCZn-2a: (a) repeating unit showing the coordination mode of Zn(II) and BDMC, (b) zig-zag chain in the 1D structure, and (c) extended 3D framework through H-bonding in the b and c projections. Color code: C grey, O red, N blue and Zn light blue.

BDMCZn-3. This system presents a [Zn(BDMC)(bpp)$_{0.5}$]$_n$·n/2EtOH stoichiometry and crystallizes in the orthorhombic P2$_1$ space group (Table S1). The repeating unit has a similar composition as BDMCZn-1, but now EtOH groups are replaced with bpp co-linkers. As a result, a 3D architecture is found in contrast to the 1D observed for BDMCZn-1. The structure of BDMCZn-3 is highly complex, with four crystallographically different Zn(II) atoms, all of them tetracoordinated (Fig. 4a) and four independent BDMC units. Each pseudo-tetrahedral Zn(II) is bonded on the basal plane to the β-diketone of one BDMC linker and to one phenolic ring of a neighbor. The apical position is occupied by the pyridinic moiety of a bpp co-linker. Hence, as described in BDMCZn-1, each BDMC is coordinated to two different Zn(II) atoms,
through the β-diketone and one phenol ring, while the second phenol group remains protonated. The basic unit is constituted by zig-zag \([\text{Zn(BDMC)}]_n\) chains extended in two perpendicular directions with an angle of 86.81° (Fig. 4b). These units are attached by the co-linker bpp (Fig. 4c) that adopts a L-shaped conformation, reducing in a great manner its length. The dense packing of this basic construction leads to interpenetration of the elements within the 3D structure (Fig. 4d), giving place to a dense material with null porosity (calculated by Mercury).

Figure 4. Schematic representation of the crystal structure of compound BDMCZn-3: (a) repeating unit showing the coordination mode of Zn(II) and BDMC, (b) projections of the zig-zag basic unit chain, (c) projection of the 3D structures in the \(b\) and \(a\) directions, and (d) views of the interpenetrated structure, without and with space filling function in Mercury. Color code: C grey, O red, N blue and Zn light blue.
BDMCZn-4a, -4b and -4c. The three compounds display similar stability and precipitate simultaneously from the reagent’s mixture. Nevertheless, single crystals of BDMCZn-4a and BDMCZn-4b could be resolved isolating them by hand from the bulk constituted mainly by unresolved powdered BDMCZn-4c phase. Both compounds (BDMCZn-4a and BDMCZn-4b) are rather similar and have alike stoichiometry, with formula \([\text{Zn}_2(\text{BDMC})_2(\text{bpy})]_n\cdot n\text{H}_2\text{O}\cdot n\text{EtOH}\) and \([\text{Zn}_2(\text{BDMC})_2(\text{bpy})]_n\cdot 2n\text{EtOH}\), respectively, differentiating themselves in the nature and number of adsorbed solvent molecules. Even though these two systems have similar stoichiometry, they crystallize in different space groups, C2/c and P2_1/n (Table S1), for BDMCZn-4a and BDMCZn-4b, respectively.

Both structures are formed by dinuclear units connected through the ligands. Each dimer displays a Zn_2O_6 core formed by two pentacoordinate crystallographically equivalent Zn(II) atoms (Figs. 5a,b)\(^{37-39}\) coordinated each to a β-diketone moiety from one BDMC unit and one pyridinic group, from the 4,4'-bpy, in addition to two phenolate groups from neighboring CCMoids molecules that act as the bridging ligands within the dimeric cluster. Therefore, the coordination sphere of the metallic centers in BDMCZn-4a and BDMCZn-4b is the same; however, the geometry of the Zn(II) ions differ between structures. In BDMCZn-4a, each Zn(II) center adopts a square based pyramidal geometry (τ = 0.28) with four oxygen atoms from three different BDMC linkers on the basal plane (depicted in Fig. 5a, in which β-diketone is shown in red and phenolate in black) and one N atom from a pyridine moiety in the apical position (Fig. 5a displayed in green). In BDMCZn-4a, the angles O-Zn-N are between 96.1-108.2° and the angles O-Zn-O are in the range 76.8-93.4°. In contrast, the Zn(II) centers in BDMCZn-4b display a bipyramidal trigonal geometry (τ = 0.79) having at the apical positions a phenolate group (Fig. 5b, in black) from a CCMoids and half coordinated β-diketone moiety from another (Fig. 5b, in red). The equatorial positions contain similar fragments and include a pyridinic moiety (Fig. 5b, in green). In BDMCZn-4b, the angles are smaller for O-Zn-N (86.8-
129.3°) and larger for O-Zn-O (79.1-98.1°). Again BDMCZn-4a and BDMCZn-4b present general similar trends in the way of expanding and connecting the dimers through the phenolate bridges and the bpy. Both structures display all the BDMC units coordinated through the β-diketone moiety to one Zn(II) ion and one phenolate ring to another center, remaining protonated the second phenolate in the CCMoid unit and giving an overall 3D structure (Fig. 5c,d).

Another important difference between these two products resides in the incorporated solvents, H₂O and EtOH in BDMCZn-4a, and exclusively EtOH in BDMCZn-4b, whose intermolecular interactions add disparity between the two 3D structures (Fig. 6a,b). The void space in BDMCZn-4a take up 20.2 v% of the unit cell volume. The porosity is organized in 1D channels extended in the b axis. The EtOH/H₂O molecules fill up such porous and are distributed in pairs, relating through an inversion center, having strong hydrogen bonds between one EtOH and one H₂O molecule within the sets (with a O-H···H-O_EtOH distance of 2.630 Å and angle of 164.9°). Also, each one of these molecules presents several interactions with the surroundings, displaying O_bk-diketone-O_H₂O, C-H_py···O_H₂O and C-H_CCMoid···O_EtOH distances of 2.793, 2.874 and 3.636 Å (showing the latest an angle of 169.64°). This crowded supramolecular network allows the interrelation of separated BDMC linkers through the solvent molecules (Fig. S3). For BDMCZn-4b, the structural porosity is reduced to 12.6 v%, constituted by isolated non-connected pores where the EtOH molecules are placed. The adsorbed EtOH units are disordered, displaying, in the solved structure, the same probability for two opposite positions at the same location. Now, the EtOH is confined in a smaller void, surrounded by pyridinic and CCMoid segments, with not as effective hydrogen bonding as in the former, presenting short O_Phenol···H-O_EtOH distances (2.941 Å) but small angles; such poor interactions allow the dual disposition of the molecule in the crystal (Fig. 6c,d).
In the case of BDMCZn-4c, its structure could not be resolved even though it was the major phase obtained in the solvothermal treatment of Zn:BDMC:bpy mixtures. For this compound, knowledge of the composition and formulae were acquired using EA and TGA (SI) data together with solid-state $^{13}$C NMR studies and ATR-FTIR spectrum.

**Figure 5.** Schematic representation of the crystal structure of compounds BDMCZn-4a and BDMCZn-4b: (a) and (b) repeating units showing the coordination modes of Zn(II) and BDMC, and (c) and (d) two different projections of the 3D structures. Color code: C grey, O red, and Zn light blue; bipyridine molecules in green and BDMC forming bridges in black.
Figure 6. Schematic representation of the crystal and pore structures of compounds BDMCZn-4a and BDMCZn-4b: (a) and (b) established H-bonding (arrows indicate the solvent molecules), and (c) and (d) void maps generated by Mercury showing 1D channels in BDMCZn-4a and isolated pores in BDMCZn-4b. Color code: C grey, O red, N blue and Zn light blue.

Solid-state $^{13}$C NMR

BDMCZn-1, -2a, -2b, -3 and -4c crystalline phases were further analyzed by solid-state $^{13}$C NMR. This technique has been successfully used in the characterization of CCM in solid state,$^{40-42}$ and it is of great assistance in the case of microcrystalline materials, such as MOFs and COFs.$^{43,44}$ Here, the analysis of the free BDMC linker, together with the correlation with the previously elucidated crystal structures by single crystal XRD, were used to provide insight
on the unresolved structures (BDMCZn-2b and 4c phases). The solid-state $^{13}$C NMR spectra of the mentioned species are shown in Fig. 7. The assignment of the signals relates by comparison to previous reports on curcumin and solid-state $^{13}$C NMR studies of the neat BDMC in solution.\textsuperscript{40}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Solid-state $^{13}$C NMR of pristine BDMC and compounds BDMCZn-1, BDMCZn-2a, BDMCZn-3, BDMCZn-2b and BDMCZn-4c, showing also peaks assignment.}
\end{figure}
For pristine BDMC, the signal related to the methine carbon (at the center of the CCMoid skeleton, C₁) at 103.7 ppm, together with the two highly separated β-diketone shifts, C₂ and C₂', at 191.9 and 176.8 ppm, proves the stabilization of the keto-enol form vs. the diketone. In addition, the signals of the C₈ and C₈' (connected to the hydroxyl groups) appear differentiated, at 160.8 and 157.3 ppm, probably due to effect of the keto-enol form and different surroundings for both endings of the molecule. The rest of signals, from the diarylheptanoid skeleton and additional aromatic groups, fall in the 115-145 ppm region, where it is feasible to discriminate among them, split in their majority. Taking into account the literature and simulations, they follow a C7(C7') – C6(C6') – C3(C3') – C5(C5') – C4(C4') order, from highest to lowest field, in the above mentioned range.⁴⁰

In BDMCZN-1 and BDMCZN-3, the chemical shifts of C₂ and C₂' appear closer now and at lower fields than pristine BDMC (184.6 and 183.5 ppm for BDMCZN-1 and 186.1 and 182.9 ppm for BDMCZN-3, respectively). This alignment is a consequence of the coordination with Zn(II), having C₂ and C₂' similar displacements. For BDMCZN-2a happens the same, thus appearing the signals at 182.5 and 179.9 ppm, respectively, although here the spectrum displays an additional signal coming from the C=O group in the acetate ligand coordinated to the metallic center (at 178.6 ppm, Fig. 7). In addition, the C₈ chemical displacement for BDMCZN-1 and -3 remain similar as the free BDMC, as this linker also remains free in these structures, while the analogous (C₈) in each system displays shifts to lower fields than BDMC, due to the coordination of this phenol group to a Zn(II) center. If the two phenol groups in the phenyl rings remain free, as it happens in BDMCZN-2a, the displacement values of C₈ and C₈' are very similar among them and closer to pristine BDMC.

Additional features, such as the chemical shifts of the coordinated EtOH (18.10 and 60.96 ppm) in BDMCZN-1 can also be discriminated, as well as the signals of the coordinated acetate moiety in BDMCZN-2a (178.6 and 18.4 ppm). In a similar manner, chemical shifts of the
pyridinic co-linkers for BDMCZn-2a and BDMCZn-3 appear in the range of 120 to 160 ppm (aromatic groups of bpe and bpp together with the double bond from the bpe system) and between 30 to 60 ppm in the case of the aliphatic groups of BDMCZn-3. Their assignment was possible by comparing with the solid-state $^{13}$C NMR spectra of the free co-linkers, measured in the same conditions than the CPs.

The knowledge acquired on solid-state $^{13}$C NMR from the direct comparison of BDMCZn-1, -2a and -3, related to their respective crystallographic structures, was used towards the analysis of the spectra of the unresolved systems BDMCZn-2b and -4c. Unfortunately, the necessity of a substantial amount of sample (ca. 100 mg) limited the use of the technique towards the analysis of the minor phases, such as BDMCZn-4a and -4b. However, for BDMCZn-4c, general trends from the co-linkers observed in BDMCZn-2a and BDMCZn-3 (Table S2) were applicable for the case of the bpy bridges. In addition, the displacements in the solid-state $^{13}$C NMR spectra of BDMCZn-2b and BDMCZn-4c are similar and point to the coordination of their respective BDMC linkers through the keto/enol moiety and one phenolic ring. In both cases, the displacements of C$_2$ - C$_{2'}$ and C$_8$ - C$_{8'}$ were similar to those found for BDMCZn-1 and BDMCZn-3. Furthermore, both spectra suggest exclusive coordination of the Zn(II) centers with BDMC and bpe or bpy, excluding the possibility of extra coordinated ethanol or acetate molecules. Having into account all the above, and the additional characterization data for composition obtained from TGA (Fig. S3) and EA, it is presumed the formation, in BDMCZn-2b, of a more extended structure than that found for BDMCZn-2a, due to the double coordination of the BDMC linker and the displacements of the bpe together with the estimated stoichiometry found by EA ($[\text{Zn(BDMC)(bpe)}_{0.5}]$). Similarly, for BDMCZn-4c, the derived formulae, $[\text{Zn(BDMC)(bpy)}_{0.5}]_n\cdot2\text{H}_2\text{O}$, agrees with the TGA analysis that provides similar BDMC weight percentages and shows the existence of solvent within the structure together with coordinated bpy. Hence, the solid-state $^{13}$C NMR spectrum
suggests also the formation of a structure similar to that found for BDMCZn-3 (Fig. 7), which includes the possibility of a different coordination number for the Zn(II) units (e.g.: tetra- instead of pentacoordinate) within the structure comparing with BDMCZn-4a and -4b.

These results are in concordance with the observed in the ATR-FTIR spectra. In the spectra of the CPs, a reduction of the band related with the νOH (3493-2890 cm\(^{-1}\)) is observed in comparison with that of the free BDMC, due to the coordination of the β-diketone and one of the phenol groups (Fig. S5a). This also agrees well with the absence of bands around 1560 cm\(^{-1}\) (Fig. S5b) in the CPs, due to the δCOH in the enol and the hydroxy groups according with the work of Kolev et al.\(^{45}\) Also related, the peculiar coordination of BDMCZn-2a (which preserves the two phenols protonated and an acetate coordinated to the metal center) presents a broad band in the carboxylic region (around 1600 cm\(^{-1}\)), related to the acetate, overlap some of CCMoid nature appearing the bands related to the δCOH vibrational mode with a similar intensity than in the pristine CCMoid.

**Comparative analysis and general trends**

Due to the variety of coordination numbers, metal geometries and coordination modes of the ligand that can be observed in the structures of this work (table 1), a more in-depth analysis of them has been carried out. As mentioned previously, BDMC has three positions for metals to coordinate displayed in Table 2, through the O\(_2\)-O\(_3\) in the keto/enol group and through the oxygens O\(_1\) and O\(_4\) in the phenyl rings. However, full BDMC coordination has not been observed in this work (with or without the use of co-linkers). Indeed, triple coordination has only been described for CPs based on the pair Zn(II)/CCM precipitated in alcoholic media using solvents with rather basic nature, such as dimethylacetamide (DMA) or dimethylformamide (DMF).\(^{46}\) Our first trials indicated that the pair Zn(II)/BDMC was not crystallized in any of these basic solvents.
Table 1. Metal coordination, metal geometry and coordination mode of the BDMC in the CPs.

<table>
<thead>
<tr>
<th>CPs</th>
<th>Metal coordination</th>
<th>Metal geometry</th>
<th>Coordination modes of the BDMC</th>
</tr>
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<tr>
<td>BDMCZn-1</td>
<td>Tetracoordinate</td>
<td>Pseudo-tetrahedral</td>
<td>A</td>
</tr>
<tr>
<td>BDMCZn-2a</td>
<td>Pentacoordinate</td>
<td>Square based pyramidal</td>
<td>B</td>
</tr>
<tr>
<td>BDMCZn-3</td>
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<td>A</td>
</tr>
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<td>BDMCZn-4a</td>
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<td>Square based pyramidal</td>
<td>A</td>
</tr>
<tr>
<td>BDMCZn-4b</td>
<td>Pentacoordinate</td>
<td>Bipyramidal trigonal</td>
<td>A</td>
</tr>
</tbody>
</table>

Remarkably, coordination reactions worked well by using exclusively EtOH and proof of that is the formation of BDMCZn-1. However, in EtOH the number of coordinated sites for the BDMC molecule never reached its maximum, displaying one binding position in BDMCZn-2a and two in BDMCZn-1, -3 and the -4 series, independently of the use of additional co-linkers in the reactions. As expected, in all cases, the most reactive group is the central keto/enol moiety which always appears coordinated.

Our structures can be categorized using two features: (i) the absence or use of a dipyridinic co-linker (taking into account its length and flexibility) and (ii) the adsorbed/coordinated solvent molecules. We observed that both factors affect significantly the coordination and conformation adopted by the main linker, BDMC. The analysis of the results indicates that, as expected, the addition of a dipyridine based co-linker increased the dimensionality of the system with respect to BDMCZn-1, going from 1D to 3D. Only for BDMCZn-2a a 1D network was obtained, which seems to be favored by the inclusion of the large bpe molecule (distance N1-N2 of 9.37 Å) with a limited degree of flexibility. This co-linker confers to the Zn(II) metal...
centers the possibility of being located far away (distance Zn-Zn of 13.49 Å), thus restricting potential interactions between BDMC molecules and Zn(II) atoms, hindering in this way the coordination of the ligand through more than one site. Certainly, in BDMCZn-2a, the BDMC did not act as a linker extending the network of the CP, but rather it is essentially a ligand that completes the coordination of Zn(II) center. BDMCZn-3 and the BDMCZn-4 series, involving bpp (with an L-shape due to its flexible aliphatic skeleton) and bpy, respectively, had shorter N1-N2 distances than BDMCZn-2a (6.87 and 7.06 Å, respectively). The length of these co-linkers is short enough to allow the BDMC molecules to coordinate through two points (the keto/enol moiety and one phenolate group) to two neighboring Zn(II) atoms. These CPs are extended simultaneously by means of the BDMC and dipyridinic co-linker, resulting in 3D structures with variable complexity.

For the analysis of the crystal structures based on the BDMC linker, it should be considered the different disposition of the phenolic rings promoted by the conformations originated within the CCMoids skeleton (Fig. 8). For that, it is worthwhile to pay attention to the networks described for the pristine and solvated BDMC ligand. Free BDMC prefers to crystalize together with solvent molecules to lower the crystal free energy, in which the solvent species fill voids and bind efficiently the host molecules providing an extended network with multipoint hydrogen bonding. Typically, adsorbed protic solvents are involved in the formation of the network by acting as bridges between consecutive BDMC units. Therefore, BDMC molecules appear separate enough to adopt a non-tensioned near-flat equilibrium conformation. Previous works had shown that the asymmetric units of BDMC·H₂O and BDMC·MeOH are composed by one molecule of BDMC with O₁-O₄ distances of 17.79 Å and to 17.73 Å, respectively. On the contrary, non-solvated BDMC structures develop a compact packing in which the molecules present strong and direct interactions among them. To achieve this, the BDMC adopts highly distorted conformations presenting curvy forms or segmented molecular
backbones not fully extended, presenting in both cases shorter O$_1$-O$_4$ phenolate distances between 16.41 and 17.06 Å.$^{48}$

**Figure 8.** Superimposition of the BDMC moieties in the asymmetric units of the different precipitated compounds, compared to pristine BDMC conformations: (a) BDMC.H$_2$O (grey), BDMCZn-1 (blue), BDMCZn-2a (purple), BDMCZn-3 (orange), BDMCZn-4a (green), and (b) BDMC (grey), BDMCZn-4b (yellow).

Similarly, the different BDMC conformations found in our CPs can be classified analyzing the established short interactions and hydrogen bonding created with the solvent or even additional molecules. These interactions affect the overall BDMC architecture, with one side of the molecule remaining planar (typically the one containing the phenolic ring coordinated to the metal), being this fully extended and defining here the reference plane P1 (which includes C$_3$ to C$_8$, Fig. 7). The other side of the CCMoid molecule defines the plane P2 (from C$_3'$ to C$_8'$, Fig. 7), which displays a high degree of possible conformations based on non-extended versions of the CCMoid skeleton adopted to promote improvements in the packing. Significant atomic distances between O$_1$-O$_4$ for the coordinated BDMC linkers and P1-P2 angles are shown in Table for each resolved CP.
In BDMCZn-1, the CCMoid linker has a quasi-flat conformation with a P1-P2 angle of 10.32° and one of the O1-O4 highest lengths (17.32 Å). Here, the BDMC molecules interact through the coordinated EtOH molecule. The context for BDMCZn-2a is quite different, since the BDMC coordinates the Zn(II) center through the keto/enol moiety and the network is exclusively extended by the bpe co-linker. Hence, the co-linker establishes the 3D structure, allowing extra structural degrees of freedom for the BDMC ligand. Therefore, the latest remains interacting with the surrounding and creates hydrogen bonding through both phenol groups that finally restrain the ligand. As a result, the BDMC displayed a curved geometry with a marked P1-P2 angle of 38.26°, which bring together the O1-O4 atoms to a distance of 16.57 Å. On the other hand, compound BDMCZn-3 has an elaborated 3D structure with four independent BDMC molecules that interact through bridges of EtOH and H2O molecules. The result is a low distorted and almost flat conformation for all the BDMC molecules, with O1-O4 distances of 17.05-17.30 Å and P1-P2 angles of 8.76-11.9°. Finally, the BDMCZn-4 series, involving the bpy co-linker, exhibits the strongest influence of the adsorbed solvent in the resulting structure. Note that BDMCZn-4a and BDMCZn-4b had the same network stoichiometry, [Zn2(BDMC)2(bpy)]n, differing in the composition only in the adsorbed solvent molecules (H2O or EtOH). In BDMCZn-4a, strong hydrogen bonds are established through H2O and EtOH bridges and here the BDMC adopts a near planar geometry with a O1-O4 distance of 17.42 Å and a P1-P2 angle of 17.75°. In a totally different scenario, the adsorbed EtOH molecules in BDMCZn-4b interact weakly with the crystal network. The lack of interaction of the BDMC linkers through solvent bridges results in a highly tensioned molecule with a distorted conformation. As a result, the O1-O4 distance is of 15.98 Å and the P1-P2 angle of 44.10°. Again, the main reason of such a large stretching is the approximation between BDMC molecules to allow short interactions that stabilize the structure with the corresponding higher distortion of the CCMoid skeleton (through the site that remains uncoordinated).
In Fig. 8, the structures of the BDMCZn-1/4b systems are compared with the conformation of pristine BDMC in either solvated crystal either involving H₂O or unsolvated. Superimposition of the BDMC molecules in the asymmetric unit of each solved structure in this work shows the flexibility of the CCMoid molecule that adopt different conformations. The BDMC disposition in BDMCZn-1, -2, -3 and -4b is similar to that found in solvated BDMC (Fig. 8a), while BDMCZn-4c has a conformation similar to unsolvated BDMC (Fig. 8b).

Table 2. BDMC distances O₁-O₄ and angles P₁-P₂ in the different compounds. The schematic draw shows the linker conformation in each compound. Color code: C grey, O red N blue and Zn light blue.

<table>
<thead>
<tr>
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<th>O₁-O₄ [Å]</th>
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<td>38.26</td>
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<td>8.76-11.19</td>
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<tr>
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<td>15.98</td>
<td>44.10</td>
<td><img src="image5" alt="Schematic 4b" /></td>
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</table>
Conclusions

The reaction between BDMC and Zn(OAc)$_2$ in EtOH produced a 1D structure with formula [Zn(BDMC)(EtOH)]$_n$ (BDMCZn-1). The reaction among BDMC, Zn(II) and the secondary linker bpe formed either a 1D compound with stoichiometry [Zn(BDMC)(bpe)(OAc)]$_n$·nH$_2$O (BDMCZn-2a) or an unresolved phase with an estimated [Zn(BDMC)(bpe)$_{0.5}$]$_n$ stoichiometry (BDMCZn-2b). On the contrary, the use of either bpp or bpy co-linker induced the crystallization of 3D structures with formulae [Zn(BDMC)(bpp)$_{0.5}$]$_n$·n/2EtOH (BDMCZn-3) and [Zn(BDMC)(bpy)$_{0.5}$]$_n$·nSolv (Solv = H$_2$O and EtOH in BDMCZn-4a, EtOH in -4b and 2 H$_2$O in the estimation of -4c), respectively. The BDMC in these structures is coordinated to Zn(II) by the β-diketone and one phenolic ring (BDMCZn-1, -2b, -3, -4a, -4b and -4c) or only through the β-diketone group (BDMCZn-2a). From the seven crystallized new CPs, five could be structurally elucidated by single crystal XRD. By compiling the results achieved in the solid state characterization performed by XRD, EA, TGA, ATR-FTIR and solid-state $^{13}$C NMR it can be concluded that: (i) BDMCZn-2b incorporated only half of the bpe co-linker present in BDMCZn-2a, with [Zn(BDMC)(bpe)$_{0.5}$]$_n$ as a feasible formula; (ii) BDMCZn-4a and-4b have similar network units of [Zn(BDCM)(bpy)$_{0.5}$], but differ in the coordination geometry of the Zn(II) and also present different adsorbed H$_2$O/EtOH solvent molecules, and (iii) BDMCZn-4c shows lots of similarities with the corresponding minor phases (BDMCZn-4a and -4b) but also shares features with BDMCZn-3. The high mobility present in the arms of the BDMC molecule originates a myriad of possible conformations, giving place to the new family of CPs here presented. The existence of hydrogen bonding stabilizes near-equilibrium conformations, while the absence of these bridges forces the molecule to adopt curved/shrank conformations. In all cases, the presence of free phenol groups in the structures opens the possibility of post-synthetic reactions that can modify the properties of these CPs. This factor becomes especially important in a compound like BDMCZn-4a, in which these phenol groups may be easily
accessible, resulting in new potential applications. Moreover, the reported materials are
constituted by Zn(II) and a biologically compatible curcumin derivative. Therefore, they can be
included in the sub-class of biological metal-organic CPs and the potential activity and stability
under biological conditions would be examined in a future work.

Associated Content

Supporting Information.

Additional figures of the structures and crystals, powder X-ray diffraction, thermal
characterization, ATR-FTIR spectrum, values of the solid-state $^{13}$C NMR and the
crystallographic details.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Acknowledgement

This work has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 R&D programme (ERC-724981). We also acknowledge the Spanish Government, Ministerio de Ciencia e Innovación (projects CTQ2017-83632, CTQ2015-68370-P and PGC2018-098630-B-I00 - MAT2016-77852-C2-1-R, and Ramon y Cajal grant RYC-2017-22910) and the Generalitat de Catalunya for the grant 2017SGR1277. C.D., N.A.A., A.L.P., A.G.C, an L.R.C. acknowledge the financial support through the “Severo Ochoa” program for Centres of Excellence in R&D (SEV-2015-0496) under the FUNMAT-FIP-2016 fellowship. Special thanks to the Alba synchrotron for the possibility of carrying out the measurements of the crystals in the experiments AV-2017042211, AV-2018052864, AV-2018072912, AV-2019023285 at beam line BL13–XALOC. This work (L.R.C.) has been done in the framework of the doctoral program “Chemistry” of the Universitat Autònoma de Barcelona.
Abbreviations

AI, active ingredients; BDMC, bisdemetoxycurcumin; CP, coordination polymers; bpe, 1,2-bis(4-pyridyl)ethylene; bpp, 1,3-bis(4-pyridyl)propane; bpy, 4,4'-bipyridine; CCM, curcumin; CCMoid, curcuminoid; DMC, demethoxycurcumin; EA, elemental analysis; EtOH, ethanol; ATR-FTIR, attenuated total reflectance Fourier transform infrared; MOF, metal organic framework; OAc, acetate; PXRD, powder crystal X-ray diffraction; SCXRD, single crystal X-ray diffraction; solid-state $^{13}$C NMR, solid state $^{13}$C nuclear magnetic resonance; TGA, thermal gravimetric analysis.

References


Novel Zn-CPs based on the biocompatible molecule bisdemethoxycurcumin (BDMC)

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Briefs

A new family of coordination polymers (CPs) have been synthetized having the biomolecule bisdemethoxycurcumin (BDMC) as the principal linker; here this natural molecule coordinates to Zn(II) centers. The use of co-linkers has been also explored. We discuss structural details, dimensionality, porosity, coordination capacity of the polytopic ligands, solvent effect and supramolecular interactions to gain insight into this new CPs.

Synopsis