



A 2D metal–organic framework based on dizinc coordination units bridged through both flexible and rigid ligands



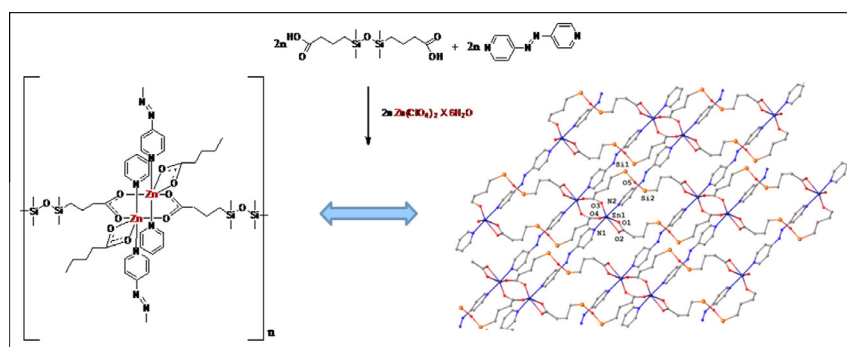
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HIGHLIGHTS

- A new 2D metal–organic framework with flexible siloxane bridges was obtained.
- Polymeric nature is manifested through glass transition evidenced by DSC.
- Due to the dimethylsiloxane units, the polymer shows low water vapor sorption.
- The compound shows different sorption capacity for H₂ and N₂ at low pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

A new coordination polymer has been obtained by reacting 1,3-bis(3-carboxypropyl)tetramethyldisiloxane and 4,4'-azopyridine with Zinc(II) perchlorate in excess. The structure of the crystalline compound separated in good yield was identified by spectral and X-ray diffraction analysis proving to be a 2D metal–organic framework. The thermal behavior was investigated by thermogravimetry and differential scanning calorimetry. The presence of the tetramethyldisiloxane moiety confers increased hydrophobic character to the metallo–organic structure as was emphasized by water vapour sorption measurements performed at different temperatures in dynamic regime. The suitability of the polymer for the gas sorption was tested for hydrogen and nitrogen as guest molecules at 77 K and 0–1 atm pressure range.

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1. Introduction

The self-assembly of polydentate ligands and transition metal ions into coordination polymers and networks constitutes a field of high interest from both point of view of the basic structural chemistry and application potential of these compounds in hot areas such as gas storage and separation, catalysis, luminescence, magnetism, sensors, and drug delivery [1–7]. A high diversity of topologies can be obtained in dependence on many factors, such

as the coordination geometry preferred by the metal, the chemical structure of the chosen ligands, the counterions, the guest molecules and the experimental conditions (reaction temperature, pH, solvent system). The configuration and the connection mode of the ligands are very important for the final structure of the coordination polymers [8]. The carboxylate- and pyridine-based ligands, as well as the combination of them have been widely used [9–11]. The organic aromatic polycarboxylate ligands have attracted intensive research interest due to their various coordination modes to metal ions [12]. The most frequent chosen are the aromatic dicarboxylic acids, which can bridge metal cations [3,13]. On the other hand, 4,4'-bipyridyl as bifunctional ligand proved to be

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highly suitable for the construction of the porous organic–inorganic hybrid solids [14]. Different more or less flexible derivatives such as, dipyridylamine, 2,2'-bipyrimidine, 1,2-bis(4-pyridyl)ethane [15], ethylene-bipyridyl or azopyridine are also currently used. The flexible bis(N-containing heterocyclic ring) ligands containing substitutedazole rings tethered by an alkyl spacer have been extensively used [3,12,13]. Coordination polymers based on flexible ligands usually exhibit unexpected architectures and interesting properties due to the variable conformations of these ligands [8].

Zn^{2+} , a d^{10} metal ion, is particularly suitable for the construction of coordination polymers and networks. The spherical d^{10} configuration is associated with a flexible coordination environment so that the geometries of Zn complexes can vary from tetrahedral through trigonal bipyramidal and square pyramidal to octahedral. Severe distortions of the ideal polyhedron have also been observed [2,16,17]. Polymeric Zn complexes have been proved to possess photoluminescent and nonlinear optical (NLO) properties or robust and thermally stable open-framework structures with permanent porosity useful for sorption or selective inclusion of guest molecules [2,13].

A lot of flexible porous zinc coordination polymers were constructed on the basis of carboxylic acids and pyridine derivatives considered as flexible components. Thus, by reacting 1,4-benzenedicarboxylic acid with 4,4'-azopyridine and $Zn(NO_3)_2$, it has been found that 4,4'-azopyridine was *in situ* reduced to 1,2-bis(4-pyridyl)hydrazine resulting two polymeric structures that showed gas sorption properties [18]. Complexes generated by a flexible dicarboxylic ligand, 1,3-adamantanediic acid, with different pyridyl-containing co-ligands and Zn(II) salts, showed diverse structures from 1D zig-zag chains, 2D grids to 3D pillar-layer networks. It has been concluded that diverse coordination modes and the conformation of dicarboxylic ligand have a significant effect on the formation and dimensionality of the resulting structures [19]. Reactions of $Zn(NO_3)_2$ with tetrakis(4-pyridyl)cyclobutane and 1,4-benzenedicarboxylic acid, 4,4'-biphenyldicarboxylic acid, 5-methyl-1,3-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, 5-amino-1,3-benzenedicarboxylic acid or 4,4'-benzophenonedicarboxylic acid under solvothermal conditions led to the formation of coordination polymers having different twofold interpenetrating 3D (4,4)- or 2D (3,4)-connected structures [9].

In this paper we reacted Zinc(II) perchlorate with 1,3-bis(3-carboxypropyl)tetramethyldisiloxane in presence of 4,4'-azopyridine as co-ligand resulting a polymeric structure as X-ray diffraction analysis revealed. The choice of this dicarboxylic acid, unusual for such structures was based on the premise that the presence of the tetramethyldisiloxane moiety could confer hydrophobicity to the formed complex structure and protection of the metal ions against attack of water molecules [20]. In addition, its large and flexible Si–O–Si bond angle ranging between 135° and 180° [21] might induce low glass and melt transitions or self-assembling ability. The structural flexibility induces desorption in a hysteretic profile that can be exploited for controlled delivery or release of drugs and gases [22].

The compound was structurally characterized and the thermal and sorption behaviors were investigated.

2. Experimental

2.1. Materials

1,3-Bis(3-carboxypropyl)tetramethyldisiloxane, $[HOOC(CH_2)_3(CH_3)_2Si]_2O$, Cx, was synthesized by using the method described in Ref. [23,24]. The other reactants, 4,4'-azopyridine, AzPy, 2,6-dimethylpyridine, and Zinc(II) perchlorate hexahydrate,

$Zn(ClO_4)_2 \cdot 6H_2O$ were purchased from Sigma Aldrich while the solvents (methanol and ethanol) were acquired from Chimopar S.A. and were used as received.

2.2. Measurements

Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vertex 70 FTIR spectrometer. Measurements were performed in the transmission mode in the range $400\text{--}4000\text{ cm}^{-1}$.

ATR-FTIR spectra were recorded using a Bruker Vertex 70 FTIR spectrometer equipped with a ZnSe crystal. Measurements were performed in ATR (Attenuated Total Reflectance) mode in the $600\text{--}4000\text{ cm}^{-1}$ range at room temperature with a resolution of 4 cm^{-1} and accumulation of 32 scans.

The proton magnetic resonance (1H NMR) spectra were acquired in DMSO at $25^\circ C$ with a Bruker Avance DRX 400 MHz spectrometer operating at 400.13 MHz for 1H .

UV–VIS absorption spectra were recorded on spectrophotometer Shimadzu UV-1700 using quartz cuvettes of 1 cm width.

Fluorescence spectra were obtained by using a Perkin Elmer LS55 luminescence spectrometer in solution.

The thermogravimetric analysis of the sample dried for 24 h in vacuum at $60^\circ C$ was performed on STA 449F1 Jupiter NETZSCH (Germany) equipment. The measurements were made in the temperature range $20\text{--}700^\circ C$ under a nitrogen flow (50 mL/min) using a heating rate of $10^\circ C/min$. An alumina crucible was used as a sample holder.

Differential scanning calorimetry (DSC) measurements were conducted on the sample without any previous thermal treatment by using a DSC 200 F3 Maia (Netzsch, Germany). Nitrogen was used as inert atmosphere at a flow rate of 100 mL/min. A heating and cooling rate of $10^\circ C/min$ was applied.

Dynamic water vapor sorption (DVS) capacity of the samples was determined in the relative humidity (RH) range 0–90% by using the fully automated gravimetric analyzer IGAsorp produced by Hiden Analytical, Warrington (UK).

Hydrogen and nitrogen adsorption/desorption isotherms at 77 K were registered with a Quantachrome Autosorb 1-MP automated gas adsorption system. The cryogenic temperatures were controlled using liquid nitrogen at 77 K. The isotherms were measured after the outgassing of the samples under vacuum for 24 h at $60^\circ C$. The total analysis times were 549 min for hydrogen and 637 min for nitrogen. The Brunauer–Emmet–Teller (BET) method was used to calculate the specific surface area.

2.2.1. X-ray crystallography

Crystallographic measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo-K radiation. The crystal was placed 40 mm from the CCD detector. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [25]. The structure was solved by direct methods using SHELXS-97 [26] and refined by full-matrix least-squares on F^2 with SHELXL-97 [26]. All atomic displacements for non-hydrogen were refined using an anisotropic model. Hydrogen atoms were placed in fixed, idealized positions and refined as rigidly bonded to the corresponding atom. Hydrogen atoms for OH-groups and water molecule have been placed by Fourier Difference accounting for the hybridization of the supporting atoms and of hydrogen bonds parameters. The main crystallographic data together with refinement details are summarized in Table 1.

2.3. Procedure

In a 50 mL round bottom flask equipped with magnetic stirrer, and reflux condenser were mixed a solution consisting of

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