

*Dedicated to the memory of
Acad. Bogdan C. Simionescu (1948–2024)*

ONE-DIMENSIONAL Zn(II) COORDINATION POLYMER BASED ON 1,3-BIS(3-CARBOXYPROPYL)TETRAMETHYLDISILOXANE AND 1,4-BIS((1H-IMIDAZOL-1-YL)METHYL)BENZENE: SYNTHESIS, STRUCTURAL CHARACTERIZATION AND APPLICATIONS

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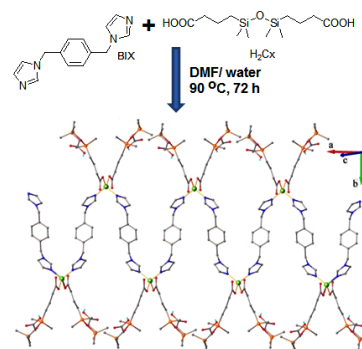
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A new one-dimensional coordination polymer, $\{[Zn(HC_x)_2(BIX)]\}_n$ CP, has been obtained by reacting 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (H_2C_x) and 1,4-bis((1H-imidazol-1-yl)methyl)benzene (BIX) with zinc(II) nitrate in solvothermal conditions. The structure of the coordination polymer was confirmed by single-crystal X-Ray diffraction analysis and IR spectroscopy. Zn(II) coordination polymer exhibited fluorescence properties and has proved efficient sensing of Fe^{3+} through fluorescence quenching effect. The Stern-Volmer constant was $1.95 \times 10^5 M^{-1}$ and the limit of detection of Fe^{3+} was $3.63 \mu M$.



INTRODUCTION

Coordination polymers have been developed as a new class of hybrid materials built up with organic linkers and inorganic salts or clusters having 1D, 2D or 3D architectures and proven applicability in gas storage,¹ catalysis², luminescent

detection of analytes,³ magnetism,⁴ drug delivery,⁵ or tissue engineering.⁶ While the most commonly used ligands are carboxylic acids (aliphatic and aromatic ones), the neutral N- donor compounds have been employed in the construction of coordination polymers to promote both structural flexibility and functionality. The main advantage

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of these structures arises from the variety of the structural and chemical compositions, which facilitate the design and optimization of properties. Recently, luminescent coordination polymers have been explored as sensors.⁷ The luminescence may originate from organic ligands, metal cations or guest solvent molecules. d^{10} metal ions such as Zn(II) or Cd(II) demonstrated photoluminescent properties, in combination with carboxylic acids and ancillary N-donors promoting efficient sensing,⁸ as well as catalytic activity.⁹ Sensing of Zn(II) coordination polymers was addressed by quenching mechanisms of various analytes: cations, anions, antibiotics, nitro-aromatic compounds.^{10,11}

In this paper, we report the first 1D coordination polymer, $\{[Zn(HCx)_2(BIX)]\}_n$, built based on Zn(II) ions with 1,4-bis((1H-imidazol-1-yl)methyl)benzene (BIX) and a highly flexible carboxylic acid having a disiloxane unit in the structure, in solvothermal conditions. The utilization of BIX co-ligand in

construction of 1D, 2D or 3D coordination networks has already been reported in combination with rigid di- or tricarboxylic ligands,^{12,13} while with aliphatic carboxylic acids is less addressed. The compound was structurally characterized, and its luminescence and selective sensing behaviors were investigated.

RESULTS AND DISCUSSION

Solvothermal method was used to prepare an 1D coordination polymer by mixing DMF solutions of a dicarboxylic acid, 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (H_2Cx), as a ligand, and a bis(imidazole) derivative, 1,4-bis((1H-imidazol-1-yl)methyl)benzene (BIX), as co-ligand, with addition of Zn(II) ions (Scheme 1). Single crystals separated by controlled cooling at $1^\circ/\text{min}$ were suitable for single-crystal X-Ray analysis.

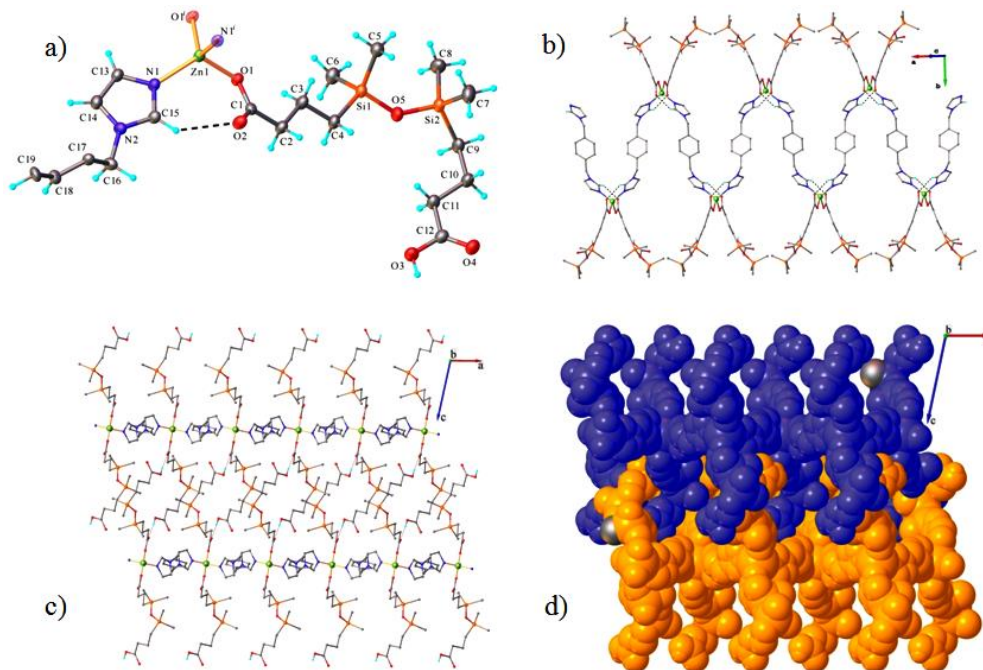
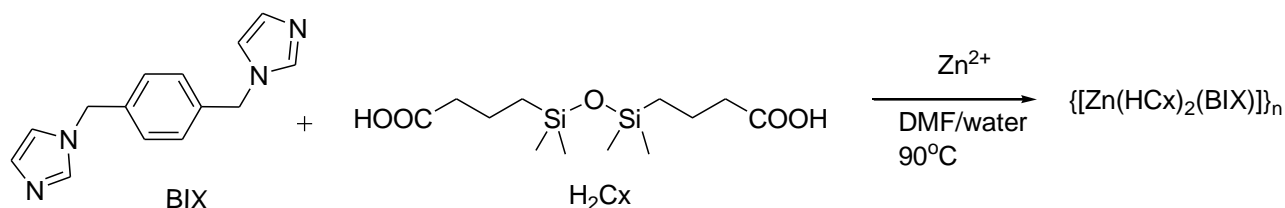


Fig. 1 – The crystal structure of CP: a) View of the asymmetric unit showing the metal coordination with atom labelling scheme and thermal ellipsoids at 40 % level. Symmetry generated atoms are shown with faded colours; b) View of 1D coordination polymer; c) Partial view of the crystal packing along b axis showing the role of H-bonds; d) Sphere packing representation.

Symmetry codes: $i) 1.5 - x, y, 1 - z$.

According to the results of the single crystal X-ray diffraction study (Fig. 1), the Zn(II) complex is a one-dimensional coordination polymer consisting of tetrahedral $\{ZnO_2N_2\}$ metal nodes and bidentate-bridged BIX ligands playing the role of linkers. The asymmetric part of the unit cell (Fig. 1a) comprises one Zn^{2+} cation, which occupies a special position on the two-fold axis, one mono-deprotonated HCx^- residue and half of the BIX neutral molecule. There are no co-crystallized solvent molecules in the crystal. The metal atom is four coordinated in a slightly distorted N_2O_2 tetrahedral geometry. BIX molecule behaves as a bidentate-bridging ligand with Zn1-N1

distance of 1.998(2) Å, while the HCx^- ligand fulfils a monodentate function with Zn1-O1 distance of 1.982(1) Å. The second non-deprotonated carboxylic group is not coordinated to the metal being involved as donor towards adjacent coordinated carboxylate group as acceptor of proton. All the components of the structure are linked to form a strip-like coordination polymer (CP) running along 101 direction, as shown in Fig. 1b. In turn, the CPs are interconnected *via* strong O-H...O and also weak C-H...H hydrogen bonds (Table 1), which determine the formation of a dense and complex 3D supramolecular network (Fig. 1c, d) showing the lack of solvent accessible voids.

Table 1

Hydrogen bonds parameters in the crystal structure of CP

D-H...A	$d_{(D-H)}/\text{Å}$	$d_{(H-A)}/\text{Å}$	$d_{(D-A)}/\text{Å}$	D-H-A/ $^\circ$	Symmetry codes for A
O3-H...O2	0.84	1.75	2.591(2)	176.0	1.5 - x, 0.5 - y, 0.5 - z
C15-H...O2	0.95	2.47	3.172(2)	130.2	-
C15-H...O4	0.95	2.42	3.200(2)	139.2	1.5 - x, 0.5 - y, 0.5 - z
C16-H...O4	0.99	2.43	3.317(3)	149.1	1.5 - x, 0.5 - y, 0.5 - z
C16-H...O1	0.99	2.52	3.469(2)	159.5	0.5 + x, 1 - y, z

The IR spectrum of Zn(II) complex is shown in Fig. 2. The main spectral changes from the starting compounds consist in the appearance of the carboxylate groups highlighted by the asymmetric and symmetric stretches at 1583 cm^{-1} and 1402 cm^{-1} , respectively. The difference between the asymmetric and symmetric stretching vibrations in complex, ($\Delta (v_{as} - v_s) = 181 \text{ cm}^{-1}$), compared to those the sodium salt of the dicarboxylic acid,¹⁴ whose value is 139 cm^{-1} , confirms the monodentate coordination of the carboxylate group in the complex. The non-

deprotonated carboxylic group is evidenced by the band at 1711 cm^{-1} . The characteristic vibrations for the tetramethyldisiloxane units in the structure are present at 1042 cm^{-1} (Si-O-Si bond), 1256 and 840 cm^{-1} (Si-CH₃ groups). The bands at 1531, 1236 and 1173 cm^{-1} are assigned to -C=N-, C-N stretching and C-H deformation vibrations in the imidazole ring. At lower wavenumbers (550–455 cm^{-1}) there are visible weak bands attributed to newly formed Zn-O and Zn-N bonds in the complex (Fig. 2).

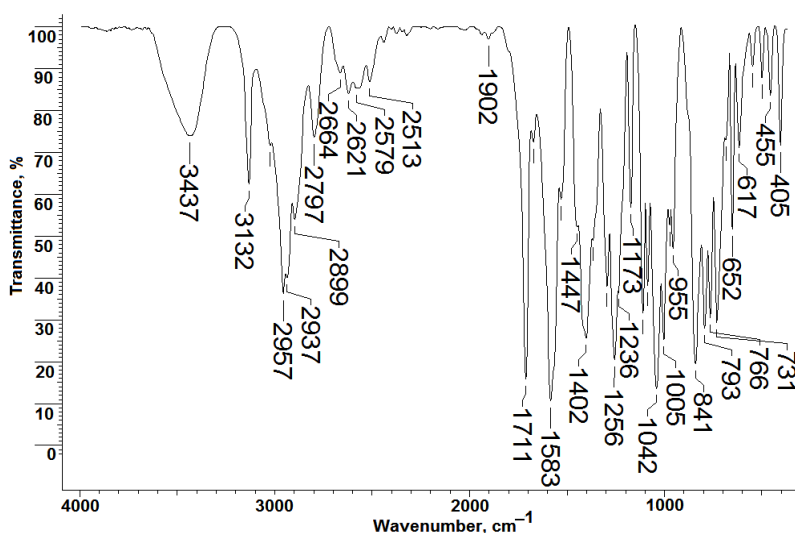


Fig. 2 – IR spectrum of Zn(II) coordination polymer, CP.

In order to prove the excited-state processes and the involvement of the higher energy electronic states ($S_n > 1$), transient absorption (TA) was used. The positive ΔOD component at shorter wavelengths (290, 300 and 345 nm), which decrease in time, are assigned to the $\pi \rightarrow \pi^*$ transitions in Zn(II) complex

(absorption in excited state (ESA)). The negative component at 315 nm corresponds to the absorption of the ground state S_0 (ground state bleaching band (GBS)). The large negative component at longer wavelengths (395, 450 and 505 nm) corresponds to the stimulated emission (SE) (Fig. 3).

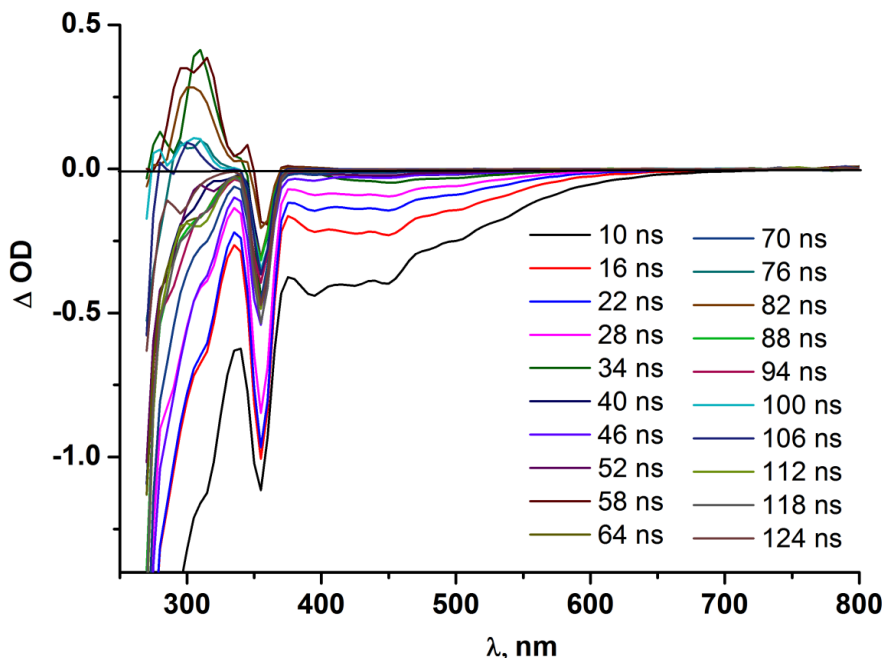


Fig. 3 – Transient absorption of the Zn(II) coordination polymer, CP.

Zn(II) coordination polymer was tested in fluorescence detection of Fe^{3+} by fluorescence quenching mechanism. The poor water stability of coordination polymers in moisture conditions has been identified as one of the key limitations for such applications. Most of them, among which MOF-5 (containing tetrahedral Zn(II) terephthalate clusters)¹⁵ or HKUST-1 (Cu(II) nodes connected by 1,3,5-benzenetricarboxylate units)¹⁶ are prone to degradation in moisture media, where the hydrolysis of weak metal-oxo coordination bonds, that results in linker replacement with water, often occurs. This problem can be solved by direct synthesis of hydrophobic metal-organic frameworks¹⁷ or by endowing the framework with stronger coordination bonds for more robust secondary-building units by using basic N-donor ligands or highly charged metals such as Zr(IV) or Ti(IV). Preparation of coordination networks with ligands containing tetramethyldisiloxane units in their structure demonstrated hydrophobic properties and stability in moist media.¹⁴ The fluorescence spectrum of Zn(II) complex in water, registered at room temperature, showed emission peak at 356 nm under excitation with $\lambda_{ex} = 315$ nm. Considering the d^{10}

electron configuration of Zn(II), which does not allow oxidation/reduction reactions and electronic excited leaps for fluorescence emission, the emission at 356 nm is assigned to the $\pi \rightarrow \pi^*$ or $\pi^* \rightarrow n$ charge transfer in BIX ligand.

The fluorescence intensity of Zn(II) complex remained stable in water during 24 h indicating its hydrolytic stability.

During the titration of Zn(II) suspension with Fe^{3+} solution, the fluorescence intensity gradually decreases and redshifts from 356 to 390 nm as the concentration of Fe^{3+} increases from 8.75 to 350 μM , when the fluorescence intensity vanishes completely (Fig. 4). The fluorescence quenching can occur by a static or dynamic process or by a combination of these two processes. The linearity of the plots obtained from state-steady determinations indicates that the quenching process can take place by a single mechanism, either static or dynamic. The value of K_{SV} constant was $1.95 \times 10^5 M^{-1}$. The limit of detection (LOD) value of Fe^{3+} was 3.63 μM for Zn(II) complex, which indicates the effectiveness in luminescent sensor detection of low concentrations of Fe^{3+} similar to other Zn(II) coordination polymers.¹⁸

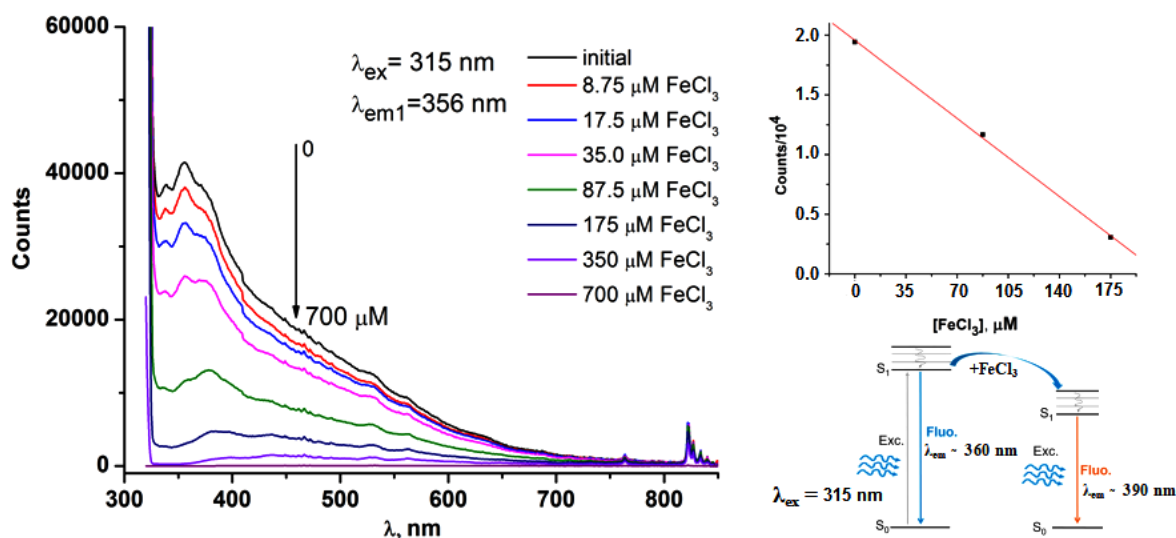


Fig. 4 – Fluorescence spectra of CP after adding different amounts of FeCl_3 ; Stern-Volmer plotting data and Perrin-Jablonski diagram for fluorescence quenching of Zn(II) with FeCl_3 .

EXPERIMENTAL

Materials and methods

1,3-Bis(3-carboxypropyl)tetramethyldisiloxane, H_2Cx , was prepared according to reference,¹⁹ 1,4-bis((1H-imidazol-1-yl)methyl)benzene, BIX, was synthesized according to reference,²⁰ zinc(II) nitrate hexahydrate, ferric chloride and dimethylformamide were purchased from Sigma Aldrich.

IR spectra were registered in transmittance mode (KBr pellets) using an FT-IR VERTEX 70 spectrometer (Bruker Optics, Ettlingen, Germany), in the 400–4000 cm^{-1} spectral range, with a resolution of 4 cm^{-1} and 32 scans. The spectra were processed in OPUS 6.5 software using water and CO_2 compensation, baseline correction and normalization manipulation tools. Transient absorption spectra were measured with LP980, Edinburgh Instruments by using Nd YAG Laser, maxim output 500 mJ, pulse duration 4–6 ns at excitation wavelength 355 nm. LP980 is a fully integrated and sophisticated transient absorption spectrometer that used the pump-probe technique for measuring transient kinetics, and spectra. In kinetic mode, a single point detector is used to measure the transient kinetics at a single wavelength, and spectra can be built up by automated scanning over a wavelength range and slicing the data.

Emission spectra and fluorescence quenching tests were obtained using an FS5 Edinburgh Instruments spectrofluorometer. To assess the sensing detection of Fe^{3+} , Zn(II) complex was

suspended in water 3mg/ mL and the concentration of Fe^{3+} (stock solution of concentration $6.5 \times 10^{-3} \text{ M}$ in water) was varied between 1.75 μM to 700 μM . The dependence of concentration of FeCl_3 to the intensity of fluorescence of Zn(II) complex and the quenching constant (K_{SV}) were calculated by plotting the experimental results with Stern-Volmer equation: $I_0/I = 1 + K_{\text{SV}} \times [\text{C}]$, where I_0 and I are the fluorescence intensity of Zn(II) complex before and after the addition of FeCl_3 , $[\text{C}]$ is the molar concentration of FeCl_3 . The standard deviation and K_{SV} were used to calculate the limit of detection (LOD) of Fe^{3+} ions by formulae $\text{LOD} = 3.3 \times (\sigma/K_{\text{SV}})$, where σ is the standard deviation of the emission intensity data.

Single-crystal X-ray diffraction data were collected on an Rigaku Oxford-Diffraction XtaLAB Synergy, Dualflex, HyPix diffractometer using $\text{Cu K}\alpha$ radiation. The unit cell determination and data integration were carried out using the CrysAlisPro package from Oxford Diffraction.²¹ The multi-scan correction for absorption was applied. The structure was solved with program SHELXT using the intrinsic phasing method and refined by the full-matrix least-squares method on F^2 with SHELXL.^{22,23} Olex2 was used as an interface to the SHELX programs.²⁴ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon were added in idealized positions and refined using a riding model, while that attached to O were obtained from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds. Selected crystallographic data and structure

refinement details are provided in Table 2 and the corresponding CIF-files. The supplementary crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or

from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.ca.ac.uk), for CCDC 2426078.

Table 2

Crystal data and details of structure refinement for Zn(II) coordination polymer

Empirical formula	C ₃₈ H ₆₄ N ₄ O ₁₀ Si ₄ Zn
Formula weight	914.66
Temperature/ K	100
Space group	<i>I</i> 2/a
<i>a</i> /Å	13.9625(4)
<i>b</i> /Å	11.2441(3)
<i>c</i> /Å	30.4894(9)
α /°	90
β /°	101.844(3)
γ /°	90
Volume/Å ³	4684.8(2)
<i>Z</i>	4
ρ_{calc} g/cm ³	1.297
μ /mm ⁻¹	2.165
Crystal size/mm ³	0.25×0.15×0.02
2 θ range/°	5.924 to 133.17
Reflections collected	14697
Independent reflections	4147 [R _{int} =0.0306]
Data/restraints/parameters	4147/0/263
GOF on <i>F</i> ²	1.059
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0348, 0.0961

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

$$\text{GOF} = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$$

where *n* is the number of reflections and *p* is the total number of parameters refined.

Preparation of Zn(II) coordination polymer

In a 50 mL round bottom flask a solution of 1,3-bis(3-carboxypropyl)tetramethyldisiloxane, H₂Cx, (0.100 g, 0.32 mmol) in DMF (5 mL) was mixed with a solution of 1,4-bis((imidazol-1-yl)methyl)benzene, BIX, (0.073 g, 0.32 mmol) in DMF (3 mL). The mixture was stirred at room temperature for 10 min and then transferred into a glass tube containing a solution of zinc(II) nitrate (0.191 g, 0.64 mmol) in Millipore water (2 mL). The mixture was ultrasonicated for a good homogenization and was then introduced into solvothermal oven for 72 h at 90 °C. By controlled cooling at 1°/min, colourless crystals were obtained which were filtered, washed with DMF/water mixture and dried at room temperature. Yield: 0.072 g (70 %).

IR (KBr), cm⁻¹: 3437w, 3132m, 3024m, 2957s, 2937s, 2899m, 2797w, 2621w, 2513w, 1711vs, 1672m, 1583vs, 1531m, 1447m, 1402s, 1367m, 1294s, 1256s, 1236s, 1173m, 1111s, 1086s, 1042vs, 1005s, 972m, 955m, 841vs, 793s, 766s, 731s, 685m, 652m, 617m, 550w, 498w, 455w, 405m.

CONCLUSIONS

Treatment of zinc(II) nitrate with the ligands mixture, consisting in 1,3-bis(3-carboxypropyl)tetramethyldisiloxane and 1,4-bis((imidazol-1-yl)methyl)benzene, under solvothermal conditions led to a one-dimensional CP. In the crystal structure, Zn(II) exhibited a tetrahedral geometry involving two monodentate carboxylate groups and bidentate-bridging BIX molecules. The structure extended into 3D supramolecular network through strong O-H...O interactions of the non-deprotonated carboxylic groups and weak C-H...O hydrogen bonding. The ground and excited absorption and emission states of Zn(II) complex were highlighted by transient absorption analysis. This study provides a feasible approach for obtaining new luminescent coordination polymers and highlights the potential application of Zn-CP in luminescence sensing, which is of significant importance for environmental protection.

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