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Highlights

- Synthesis of a new Mg(II) porphyrin polymer with the pyrazine ligand: (I).
- UV-visible and fluorescence spectroscopic characterization of (I).
- Cyclic voltammetry investigation of (I).
- X-ray molecular structure of (I) showing C-H... π intermolecular interactions.
- exhibits promising antibacterial activity for Gram-(+) and (-) bacteria.

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Synthesis, Molecular Structure, Spectroscopic Characterization and Antibacterial Activity of the Pyrazine Magnesium Porphyrin Coordination Polymer

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Abstract

A new material of magnesium(II) polymer compound with the formula $\{Mg^{II}(TPP)(pz)\}$. $0.5[Mg^{II}(TPP)]\cdot CH_2Cl_2_n$ (I), (TPP) = meso-tetraphenylporphyrinato and pz = pyrazine) was synthetized and characterized by IR, UV-visible, PL photoluminescence and ¹H NMR spectroscopy studies, single-crystal XRD analyses and cyclic voltammetry. The crystal structure of (I) is made by the 1D {[Mg(TPP)(pz)]} polymeric chains (molecules I(A)) where the tetracoordinated magnesium(II) complexes [Mg(TPP)] (molecules I(B)) are located as well as the dichloromethane solvent molecules. The crystal packing of (I) is stabilized by intermolecular C-H···Cg π interactions where Cg is the centroid of phenyl and pyrrole rings. Additionally, the photophysical properties have been evaluated by UV-visible absorption and fluorescence emission spectroscopies. The UV-visible spectrum of (I) shows a redshift Soret band value (428 nm) compared to that of the free base H₂TPP porphyrin while the λ_{max} values of the O bands are in the range 560 - 610 nm. The optical gap of (I) was estimated at 1.99 eV. The cyclic voltammogram of the title compound presents two reversible oxidation waves and one reversible reduction wave. The HOMO and LUMO energy values were deduced from the voltammogram which are -4.96 and -2.85 eV respectively. Furthermore, bioactivity investigations revealed that the free porphyrin, the starting material [Mg^{II}(TPP)] and complex (I) could be used as potential antibacterial agents.

KEYWORDS: Magnesium porphyrin complexes, Coordination polymer, X-ray molecular structure, cyclic voltammetry, Antibacterial agents.

Introduction

Porphyrins are naturally occurring species such as the protoporphyrin IX presents in hemes, in cytochromes P450 and in chlorophylls. Porphyrins and metalloporphyrins have very interesting physicochemical properties (UV-visible, fluorescence, redox, etc.) which make them particularly attractive in a large number of areas.[1–4] These fields of application require more complex molecular architectures and more elaborate porphyrinic nucleus substitution schemes. And seeing that porphyrinic units are remarkable precursors in supramolecular chemistry as excellent components in the design of efficient molecular materials with improved electrochemical and photo-physical properties.[5] Indeed, these porphyrinic macrocycles are used in several projects, such as photo-induced electron transfer [6,7], semiconductors [8], chemical sensors [9], and photovoltaic solar cells.[10] Recently studies have shown that porphyrins are also effective against viruses and yeasts.[11,12] Likewise, the porphyrin nucleus presents an efficient source for the synthesis of a large number of active antimicrobial and antioxidant agents.[13–15] In addition, several porphyrin compounds have been developed as photosensitizers for photodynamic therapy.[16,17] During the last decades, many crystal structures of porphyrins and metalloporphyrins have

been reported whose physicochemical properties and crystal stacking are governed by axial ligands coordination modes.[18] Furthermore, much effort has been directed toward the creation of organized self-assemblies that result in microporous crystalline solids based on meso-tetraarylmetalloportphyrins. [19,20] These species are known as building blocks, which have interesting applications.[21] Among M(II) porphyrins, magnesium(II) porphyrins are the least studied compounds. Our research group has extensive experience in the design and characterization of new materials based on metalloporphyrins with several metals such as iron, cobalt, cadmium, manganese and magnesium. [22-26] Notably, the increasing number of polymers based on metalloporphyrins [27] where different synthetic methods are employed to obtain such type of polymers. One of these methods adopts the central metal coordination strategy of a metalloporphyrin through the nitrogen atoms of a bidentate ligand.[28] The present work is a continuation of our investigation on magnesium (II) metalloporphyrins [26,29-30] where the pyrazine *meso*-tetraphenylporphyrin magnesium(II) coordination complex (complex (I)) is synthesized and characterized by single crystal X-ray diffraction. The UV-visible, fluorescence, cyclic voltammetry investigations of the complex (I) are reported. The antibacterial activity of our Mg(II) porphyrin compounds were tested against some Gram (+) (Staphylococcus aureus, Enterococcus faecalis) and Gram (-) (Pseudomonas aeruginosa and Escherichia coli) bacteria.

Experimental section

Materials and methods

All chemicals/reagents used were of analytical grade and were used as received without any purification. The dichloromethane (DCM), hexane, magnesium chloride (MgCl₂), dimethylformamide (DMF), pyrrole, pyrazine, propionic acid, ethanol and benzaldehyde were purchased from Sigma-Aldrich. The meso-tetraphenylporphyrin (H₂TPP) and the (mesotetraphenylporphyrinato)- magnesium(II) ([Mg(TPP)], was synthesized according to the reported methods. Electronic absorption spectra were taken in a SPECORD 200 (analytikjena) UV-Visible spectrophotometer. Luminescence properties of the complexes were analyzed using an Horiba Scientific Fluoromax-4 Fluorescence spectrophotometer. IR. And ¹H NMR spectra were obtained using, successively, a Shimadzu FTIR-8400 spectrophotometer in the 4000–400 cm⁻¹ range and a Bruker 300 MHz Spectrometer. For single crystal X-ray diffraction studies, the diffracted crystal was glued to a glass fibre and mounted on Bruker XSCANS diffractometer. The instrument has CCD area detector and data intensity has been collected at 153 K using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The unitcell parameters were calculated and refined from the full data set. The reflections were scaled and corrected for absorption effects by using SADABS. [31] The structure is solved by direct methods using SIR-2004 program [31] and refined using the SHELXL-2015 program.[32] The hydrogen atoms were placed in calculated positions and refined by using a riding model. The crystallographic data and structural refinement details of (I) is shown in Table 1. The electrochemical measurements were performed in an electrochemical workstation CH instrument CHI600E using glassy carbon electrode as the working electrode, Pt electrode as an auxiliary electrode and Ag/AgCl electrode as a reference electrode.

Synthesis

Synthesis of the meso-tetraphenylporphyrin (H_2TPP)

The *meso*-tetraphenylporphyrin (H_2TPP) was synthesized from the acid catalyzed condensation of pyrolle (4 mol eq.) and benzaldehyde (4 mol eq.) in the presence of propionic acid.[33] Benzaldehyde (1.62 mL, 16 mmol) and pyrrole (1.11 mL, 16 mmol) were combined

and heated under reflux for 1 h in the presence of propionic acid (100 mL). The product was filtered off, then washed with hot water and methanol until the filtrate was colorless, affording purple glistering crystals.

Synthesis of the (meso-tetraphenylporphyrinato)magnesium(II) complex $[(Mg^{II}(TPP)]]$

A sample of 1 g (1.02 mmol) H_2 TPP and 0.554 g (4.07 mmol) of magnesium chloride was refluxed in 120 mL DMF for 6 h. After removing the solvent, the solid product was dissolved in dichloromethane (DCM), filtered and dried under vacuum.[34] The crystals ware obtained from a mixture of dichloromethane-ethanol-hexane solvent.

Synthesis of complex the catena-poly{(pyrazine)(meso-tetraphenylporphyrinato) magnesium(II)}(meso-tetraphenylpor-phyrinato)magnesium(II) dichloromethane monosolvate

[Mg^{II}(TPP)] (15 mg, 0.023 mmol) was dissolved in 5 mL of distilled dichloromethane. Pyrazine (15 mg, 0.09 mmol) was then added and the solution was stirred at room temperature for 10 hours. Crystals of the title complex (I) were obtained by slow diffusion of n-hexane through the dichloromethane solution. Anal. Calcd (found) for C₁₄₂H₉₆N₁₆Mg_{2.25}Cl₄ (2222.84 g/mol): C, 76.94; H, 4.36; N, 10.11%. Found: C, 76.80; H, 4.25; N, 10.05%. **UV– vis** [CH₂Cl₂: λ_{max} in nm (logɛ)]: 428 (5.96), 568 (4.60), 608 (4.35). **IR** (solid, cm⁻¹): 3000-2850, 932-536, 998, 1240, 1506, 1463, 1355, 1132, 1585, 2950, 2843. ¹**H NMR** (300 MHz, CDCl₃, 298 K): δ = 8.85 ppm (s, 8 H, pyrrole β-H), 8.15 ppm (dd, 8 H, (J= 8.2, 7.8 Hz), TPP *o*-H), 7.62-7.83 ppm (m, 12 H, TPP *m-*, *p*-H), 6.34 ppm (dd, 4 H, (J=8.6, 4.8 Hz pyrazine).

 Table 1. Crystal parameters of compound (I).

Chemical formula	C142H96N16Mg2.25Cl4
Formula Weight M_r (g.mol ⁻¹)	2222.84
Crystal size/mm ³	0.45 imes 0.39 imes 0.36
Crystal System	Triclinic
Space Group	P-1
a (Å)	13.189 (3)
b (Å)	14.877 (3)
c (Å)	15.996 (3)
α (°)	110.48 (3)
β (°)	102.32 (3)
γ (°)	92.18 (3)
$V(Å^3)$	2850.6 (12)
Z	2
Reflections collected	33620
Independent / observed reflections	11018, 8060
R _{int}	0.047
d_{calc} ./ g cm ⁻³	1.29
$\mu/ \text{ mm}^{-1}$	0.179
T(K)	293(2)
<i>F</i> (000)	1155
R_I^{a} , $wR2^{b}$	0.063, 0.209
GooF (S)	1.04
Δ_{ρ} (max, min) (e/Å ³)	0.98, -0.47

 $\overline{{}^{a}: R_{1} = \Sigma ||F_{0}| - |F_{c}|| / \Sigma |F_{0}|}.$

^b: $wR_2 = \{\Sigma[w(|F_0|^2 - |F_c|^2)^2]/\Sigma[w(|F_0|^2)^2]\}^{1/2}.$

Antibacterial screening

Pathogenic strains were cultivated on nutrient agar at 37 °C for 24 h. Then, pure colonies were suspended in 10 mL of physiological medium, mixed during 5 min and suspensions were adjusted to 0.5 McFarland standard turbidity. The milliliter of bacterial suspension was spread over Muller Hinton Agar medium plates and incubated for 30 min at 37 °C. Then, 6 mm diameters wells were dug in agar medium using sterile glassy borer. The Mg(II) complexes were –dissolved in DMSO (1 mg/mL) and were introduced into the respective wells, leading to a final concentration of 10⁻⁵ M, one of the wells was supplemented with DMSO as control. These plates were placed in a 37 °C incubator for 24 h to allow bacterial growth. After 24 h, the diameters of the clear zone of inhibition surrounding the sample were measured in millimeters by digital caliper.

Results and discussion

Spectroscopic studies

UV-vis absorption spectroscopy

The electronic spectra of porphyrins and metalloporphyrins manifest high sensitivity toward structural modifications. Figure 1 shows the UV-visible absorption spectra in dichloromethane solvent of the free-base porphyrin H₂TPP, [Mg^{II}(TPP)] starting material and complex (I). The absorption spectra of the free bae porphyrin consists of one strong B band, known as the Soret band, in the near UV region located at 420 nm followed by four weaker Q bands in the visible region between 500 and 700 nm. The starting material display one higher intensity Soret band located at 425 nm followed by two lower intensity Q bands between 500 and 700 nm. The Soret and Q bands are assigned to $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ (π - π *) transitions within the highly π conjugated macro-rings. it is noted that the number of Q bands reduced for the metallic porphyrins is due to the increase in symmetry (from D_{2h} to D_{4h}). The lower symmetry (D_{2h}) of free base porphyrin is ascribed to the presence of two diagonally positioned hydrogen atoms in its N4 core [35]. The coordination of magnesium(II) ion with the ligand (pyrazine) induces bathochromic shift of the Soret and the Q bands as illustrated by Figure 1. This phenomenon is usually attributed to the porphyrinic ring deformation due to coordination of magnesium(II) ion.



Figure 1. UV-visible absorption spectra of H_2 TPP, Mg^{II} (TPP), and compound (I), in dichloromethane solution at concentrations around 10^{-6} mol.L⁻¹.

The energy difference between the levels of the HOMO and LUMO (optical band gap) [36] is obtained from the UV-visible spectrum. The optical gap energy (Eg-op) is calculated from the Tauc plot method as shown in Figure 2. The Eg-op value of (I) is 1.99 eV, which is in the normal range of *meso*-arylporphyrins and *meso*-metalloporphyrin. This is an indication that complex (I) exhibits semiconductor properties.



Figure 2. Plots of $(\alpha h \upsilon)^2$ versus the photon energy (E) of H₂TPP, [Mg^{II}(TPP)] and compound (I), α is the absorption coefficient.

Table 2. UV-visible data of H ₂ TPP,	he starting material [Mg ^{II} (TP	P)], compound (I) and a selection of related
compounds.		

Compound S	oret band (m (logɛ)	m) Q band (logɛ)	s (nm)	Eg-op. (eV)	[ref]
H ₂ TPP	418 (6.92)	515 (5.73) 550(4.33)	588(4.42) 648(4.20)	1.86	t.w. ^a
H ₂ TPP	416 (6.10)	513 (5.70) 550(4.36)	590(4.24) 646(4.19)	1.86	[37]
H ₂ TPP	-			1.83	[38]
[Mg ^{II} (TPP)]	425 (5.97)	564 (4.70)	604 (4.48)	2.00	t.w.
[Mg(TPP)]	424 (5.87)	563 (4.52)	603 (4.39)	-	[39]
Complex (I)	428 (5.96)	568(4.60)	608(4.35)	1.99	t.w.
$[Mg(TPP)(HMTA)_2]^b$ (II	() 434 (6.22)	575 (4.97)	617 (4.98)	1.96	[26]
[Mg(TPP)(THF) ₂]	426 (5.75)	564 (4.25)	604 (3.95)	-	[40]

^a: t.w.: this work, ^b: HMTA = hexamethylenetetramine.

Steady-state emission spectroscopy

Luminescence properties of compound (I) was studied at room temperature in dichloromethane solution. The spectrum of (I) exhibits two well defined fluorescence peaks at 616 and 670 nm (Figure 3) assigned as Q(0,1) and Q(0,0) respectively, upon in the excitation of 617 nm. The luminescence quantum yields of the synthesized compounds are calculated by the approach of relative method of measurement [41], in which the integrated luminescence intensities are measured using magnesium porphyrin complex [Mg(TPP)] as the standard (Φ = 0.15). We measured the fluorescent lifetime (τ _f) in dichloromethane solution, By means of a time-correlated single photon counting technique. The photoluminescent lifetime

of compound (I) is 4.5 ns. The fluorescence wavelengths of the fluorescence bands, the fluorescence quantum yields (ϕ_f), and the fluorescence lifetimes (τ_f) values of the starting material [Mg^{II}(TPP)], complex (I) and some related porphyrin species are summarized in Table 3.



Figure 3. Emission spectra of H_2 TPP, $[Mg^{II}(TPP)]$ and compound (I) in dichloromethane solution at 10⁻⁶ mol.L⁻¹ concentration.

Table 3. Emission characteristics of H_2TPP , $[Mg^{II}(TPP)]$, complex (I) and a selection of other magnesium mesotetraporphyrins compounds.

Compound	Q(0,0) [nm]	Q(0,1) [nm]	ϕ_{f}	$\tau_f[ns]$	ref.
H ₂ TPP	650	713	0.11	8.0	t.w. ^a
H ₂ TPP	653	722	0.12	9.6	[42]
[Mg ^{II} (TPP)]	608	663	0.13	5.0	t.w.
[Mg ^{II} (TPP)]	608	661	0.15	9.2	[43]
Complex (I)	616	670	0.12	4.5	t.w.
$[Mg(TPP)(HMTA)_2]^b$ (II)	620	665	0.14	4.7	[26]
[Mg(TPP)(THF) ₂]	609	660	0.16	8.9	[44]

^a: t.w. = This work, ^b: HMTA = Hexamethylenetetramine.

Cyclic voltammetry investigation

We have studied the electrochemistry properties of our Mg-TPP-pz derivative using the cyclic voltammetry technique. This investigation was in DCM using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte (0.2 M). As shown in Figure 4, our synthesized compound (I) exhibits two reversible oxidation waves and one reversible reduction wave. These oxidation and reduction waves are attributed to the porphyrin macrocycle.



Figure 4. Cyclic voltammogram of complex (I). The solvent is CH2Cl2, and the concentration is ca. 10-3 M in 0.2 M TBAP, 50 mV/s, vitreous carbon working electrode ($\emptyset = 3$ mm).

Figure 4 illustrates the cyclic voltammogram of the compound (I). The two first successive anodic waves (O1/R1) and (O2/R2) are reversible and correspond to one-electron transfers involving the porphyrin cores. The correspondent potential values of these waves are 0.34 V / 0.59 V. In the negative potential region, the cyclic voltammograms of (I) exhibits reversible one-electron porphyrin-ring-centered cathodic waves (O3/R3) at $E_d(1/2)$ at ca. -1.78 V. In that way, the response of (I) is representative of the classical behavior of metalloporphyrins with a no electroactive metal (such as Zn Mg and Cd), which undergoes two reversible one electron transfers, both in oxidation and reduction. For (I), the second reduction of the porphyrin is not observed since it falls beyond the solvent reduction. A summary of the half-wave potentials of porphyrin ligands and Mg complexes is listed in Table 4.

From the voltammogram of (I) we determined the HOMO and LUMO energy levels and the electrochemical gap (Eg-el) can be calculated by the following relations [45]:

$$E_{HOMO}$$
 (IP: ionization potential) = - ($V_{onset-ox} - V_{ref} + 4.8$) eV
 E_{LUMO} (EA: electron affinity) = - ($V_{onset-red} - V_{ref} + 4.8$) eV
 $E_{ref} = (E_{LUMO} - E_{HOMO})$ eV

where $V_{onset-red}$ is the reduction onset, $V_{onset-ox}$ is the oxidation onset and V_{ref} is the ferrocene half-wave potential (0.42 V). The energy level of the Fc /Fc⁺ is assumed to be 4.8 eV below the vacuum level.

Compound Reduction Ref. Oxidation E_{onset-ox} E_{onset-red} E_{HOMO} E_{LUMO} E_{g-el} O1/R1 O2/R2 O3/R3 O4/R4 H_2TPP^a 1.07 1.31 -1.47 -1.15 0.65 -1.36 -5.50 -3.49 2.01 [46] $[Mg^{II}(TPP)]^{b}$ 0.59 0.34 -1.92 0.23 -1.61 -4.88-3.04 1.84 [26] [Mg^{II}(TPP)(THF)₂] 0.94 2.22 0.65 -1.57 [44] _ ---_ 1.90 $[Mg^{II}(TPP)(HMTA)_2]^{c} 0.73$ 0.99 -1.45 _ 0.57 -1.33 -4.93 -3.03 [26] 0.65 0.95 -1.65 0.58 -1.53 -4.96 -2.85 2.11 Complex (I) t.w.^d

Table 4. Redox potential data (in V) for the H_2 TPP porphyrin, complex (I) and a selection of magnesium metalloporphyrins compound. All data are obtained from voltammograms recorded in dichloromethane and the potentials are reported versus SCE.

^a: 0.1 M NBu₄PF₆ in CH₃CN; ^b: 0.2 M TBAP in CH₂Cl₂; ^c: HMTA = Hexamethylenetetramine; ^d: t.w.: this work,.

X-ray diffraction

Crystal of (I) suitable for X-ray diffraction study were obtained by slow diffusion of n-hexane through the DCM solution containing complex (I). Complex (I) crystallizes in a triclinic system with the space group P-1. The crystallographic data and the structural refinement details are reported in Table 1. The single crystal X-ray diffraction study shows that in the crystal lattice of complex (I) two types of molecules are presents. Indeed, a one dimensional chain made by [Mg(TPP)(pz)] monomer (molecule IA) coexists with the tetracoordinated [Mg(TPP)] complex (molecule IB) and a dichloromethane solvent molecule. This means that the asymmetric unit of (I) is by one [Mg(TPP)(pz)] moiety, a half [Mg(TPP)] molecule and one DCM solvent molecule. The ORTEP diagrams of the crystallographically independent molecules (A and B) and the dichmoroethane molecule of (I) are shown in Figure 5.



Figure 5. ORTEP diagram of complex (I). The hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level.

The coordination sphere of Mg(II) cation for molecule IA is described as octahedron, in which equatorial positions are occupied by the four pyrrole nitrogen atoms and the apical positions are occupied by N-donor atoms of the pyrazine molecules. Structural arrangement along the a-axis is shown in Figure 6.



Figure 6. Representation of the 1D Mg-porphyrin chains (molecules IA) and molecules IB.

The framework of (I) consists of a 1D polymer chain extending along the (a) axis in which the magnesium centers are bridged by pyrazine ligands, forming a Mg-pyrazine-Mg linear polymer. This chain is twisted to minimize the steric hindrance due to the presence of the [Mg(TPP)] (molecules IB) and the DCM solvent molecules between these chains. Figure 7 is an illustration of the crystal packing of (I).



Figure 7. Representation of the crystal packing of (I).

The values of the mean equatorial distance between the central metal and the four nitrogens of the porphyrin (Mg–Np) are respectively 2.072 (2) Å and 2.112 (2) Å for (IA) and (IB). The Mg__Np of the {[Mg(TPP)(pz)]} coordination polymer b(molecule IA) is very close to those of the related hexacoordinated Mg(II) metalloporphyrins (Table 5) which is not the case of the [Mg(TPP)] complex (molecule IB). For this later species, the Mg–Np is quite high (2.112 (2) Å) which is due to the disordered Mg atom located in the inversion center.

In the molecule (IA), the magnesium-nitrogen bond length value of the axial ligand (Mg-N(pz) is 2.341 (2) Å. This value is comparable to those of related Mg(II)-porphyrins

with N-donor cyclic axial ligand such as 4,4'-bipyridine, 4-picoline, piperazine and pyridine (Table 5).

Compound	$Mg - N_L^a$ (Å)	$Mg - N_p^{b}(A)$	ref
Molecule (IA)	2.341(2)	2.068(2)	t.w.
		2.077(2)	t.w.
Molecule (IB)		2.112(2)	t.w.
$[Mg(tn-OEP)(4,4'-bpy)]^{c}$	2.259(3)	2.087(2)	[47]
[Mg(TBrPP)(HIm)] ^{d,e}	2.121(2)	2.095(2)	[48]
$[Mg(TPBP)(4,4'-bpy)_2]^f$	2.319-2.290	2.065	[49]
$[Mg(TPP)(py)_2]$	2.3764(2)	2.071(5)	[50]
$[Mg(TPP)(1-MeIm)_2]^g$	2.297(8)	2.078(10)	[51]
$[Mg(TPP)(4-pic)_2]^h$	2.386(2)	2.071(4)	[51]
$[Mg(TPP)(pip)_2]^i$	2.419(4)	2.072(5)	[51]
$[Mg(TPP)(py)_2]$	2.369(2)	2.063(3)	[52]
$[Mg^{II}(OEP)_{2}(4.4'-dipy)_{2}]$	2.259(3)	2.087(2)	[53]
-	2.272(3)	2.100(2)	[53]

Table 5. Selected bond lengths in several hexacoordinate magnesium metalloporphyrins.

^a: Mg—N_L = distance between the metal and the nitrogen of the N-donor axial ligand, ^b: Mg—N_p = average equatorial metal–nitrogen pyrrole distance, ^c: tn-OEP = octaethyl-tetranitroporphyrinato, ^d: TBrPP = *meso*-bromophenyl)porphyrinato, ^e: Him = imidazole, ^f: TPBP *meso*-tetrabenzoyloxyphenylporphyrinato, ^g: 1-MeIm = 1-methylmidazole, ^h: 4-pic = 4-picoline, ⁱ: pip = piperidine.

The coordinating compound (I) consists of one-dimensional polymeric chains along axis a (molecule IA). These chains define cavities containing the Mg(II) porphyrin complexes (molecule IB) (Figure 7). The two planes containing the porphyrin macrocycles of one Mg(TPP)-py-Mg(TPP) dimer of the polymer (molecules IA) presents a angle value equal to 21 ° (Figure 8) This tilte is fore probably due, as was already mentioned, to the presence of the [Mg(TPP) (molecules IB) and the DCM solvents molecules. The crystal lattice of (I) is stabilized by intermolecular interactions type C-H…Cg where Cg is the center of gravity of the nucleus (centroid) of a pyrrole or a phenyl ring (Figure 9). The intra molecular and the intermolecular distances C-H…Cg are summarized in Table 6.

$\overline{D-H\cdots A^a}$	Symmetry of A	D····A (Å)	$D - H \cdots A$ (°)
C12A–H12A····Cg2	X,V,Z	3,750(3)	142
C14A–H14A····Cg11	-1+x,y,z	3,858(3)	160
C15A–H15A····Cg4	1-x,-y,1-z	3,468(4)	138
C19A–H19A····Cg1	2-x,1-y,1-z	3,592(5)	161
C22–H22····Cg5	X,V,Z	3,318(4)	107
C23–H23····Cg1	X,Y,Z	3,445(3)	129
C25–H25····Cg3	X,Y,Z	3,739(3)	143
C48–H48•••Cg5	1-x,-y,1-z	3,840(4)	159

Table 6. Intermolecular and intramolecular interactions for complex (I).

^a: D = donor atom and A = accepter atom.

Cg1 is the centroid of the N1-C1-C2-C3-C4 pyrrole five membered ring.

Cg2 is the centroid of the N2-C6-C7-C8-C9 pyrrole five membered ring.

Cg3 is the centroid of the N6-C27-C28-C29-C30 pyrrole five membered ring.

Cg4 is the centroid of the N7-C32-C33-C34-C35 pyrrole five membered ring.

Cg5 is the centroid of the N8A-C1A-C2A-C3A-C4A pyrrole five membered ring.

Cg11 is the centroid of the C17A-C18A-C19A-C20A-C21A-C22A phenyl six membered ring.



Figure 8. Drawing showing the angle between the two planes of the two successive porphyrins that constitute the polymer (IA).



Figure 9. Schematic representation of the intermolecular C–H···Cg, π interactions.

Antibacterial activity

Porphyrins appeal large attention because of their significant antibacterial activity.[54-58] In the present work, we evaluated the antibacterial activity of the free base porphyrin H₂TPP, the starting material [Mg(TPP)] and complex (I) which were tested at the concentration of 100 μ g/mL against two Gram-negative bacteria (Pseudomonas aeruginosa (ATCC 27853) and Escherichia coli (ATCC35218)) and two Gram-positive bacteria (Staphylococcus aureus

(ATCC 25923) and Enterococcus faecalis (ATCC 29212)) using well agar diffusion assay as described by Mahdhi et al. [59]



Figure 10. In vitro antimicrobial activity of H₂TPP, Mg^{II}(TPP) and compound (I).

Analysis of the results shows that the *meso*-phenylporphyrin H_2TPP has moderate activity against E. faecalis with an inhibition zone of 11 mm and low activity against S. aureus with an inhibition zone of 4 mm. However, this inhibition zone was not observed on the two bacteria P. aeruginosa and E. coli. For the metallated porphyrin [Mg(TPP)] and [Mg(TPP)(pz)] After insertion of the metal Mg(II) in(I) complexes we noticed a slight increase in the activity for E. faecalis (13 mm) and E. coli (3 mm), and improved antibacterial activity against S. aureus with an inhibition zone of 16 mm. Furthermore, complex (I) is the most effective against all strains tested with the highest antibacterial activity. This pyrazine magnesium derivative shows an inhibition zone diameter of 11 mm and 12 mm against P. aeruginosa and E. coli, respectively. It also inhibites E. faecalis by 14 mm and S. aureus by 15 mm. These values are higher than those obtained with the standard drug tetracycline which has ~ 12 mm diameter inhibition zone against P. aeruginosa and E. coli. [59] If we look closely at the results we can see that the metal insertion has an effect on the inhibition zone. The improved antimicrobial performance of the complexes can be attributed to the Overtone's concept and Tweedy's chelation theory. [60, 61] Chelation reduces the polarity of the metal ion, mainly because of the partial sharing of its positive charge with the donor groups of ligands and possibly the π electron delocalization within the whole chelate ring system thus formed during coordination. This process of chelation thus strengthens the lipophilic character of the central atom, which in turn favors its permeation through the lipoid layer of the membrane [62-68], and hence enhances the biological utilization ratio and activity of the compounds. The literature survey revealed that antibacterial activity of magnesium porphyrinic compounds are comparable.

Conclusion

In summary, we have prepared and characterized a new polymer magnesium(II) porphyrin coordination compound (I). The UV-visible and fluorescence spectra of (I) show results

similar to those of the already known Mg(II) porphyrins, the quantum yield value and the usual fluorescent lifetime are in the ranges reported for mesotetraphenylporphyrinato)magnesium(II) species. The cyclic voltammetry investigation on complex (I) are also reported and the electrochemical gap values of these porphyrin species were determined from the voltammograms which are slightly higher than those of the optical gap. The X-ray investigation shows that the crystal lattice of (I) is made by {[Mg^{II}(TPP)(pz)]· $0.5[Mg^{II}(TPP)] \cdot CH_2Cl_2\}_n$ (I), (TPP = meso-tetraphenylporphyrinato and Py = pyrazine) complex aligned in one dimensional chain along to the a axis. The supramolecular structure of (I) is made by the polymer chains (molecules A), are sustained by weak C-H... π involving Cg pyrrole and phenyl centroids rings intermolecular interactions, with the magnesium porphyrin molecules uncoordinated (molecules B). Furthermore, the antibacterial studies shows that there tested porphyrin species have significant antibacterial activity and that complex (I) exhibits a better activity and could be a promising species to design antibacterial activity molecule against bacterial strains. Improvement to enhance activity against other strains will be investigated.

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Appendix A. Supplementary data

CCDC 2023484 contain the supplementary crystallographic data of complex (I). These data can be obtained free of charge via http://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 e-mail: deposit@ccdc.cam.ac.uk.

CRediT author statement

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Authorship contributions

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DECLARATION OF INTEREST

I declare that we as authors have a responsibility to disclose any interests that may appear to influence the presentation of data objectively

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