A Mixed-ligand Zn(II)-based Coordination Polymer for Selectively Detect 2,4,6-Trinitrophenol (TNP) and Treatment Effect on Periodontal Diseases via Inhibition Effect on P. gingivalis Growth

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Abstract: A new difunctional Zn(II) coordination polymer (CP) with the chemical formula of [Zn(TBTA) (L)₁.⁵]ₙ (I) has been synthesized hydrothermally from tetrabromoterephthalic acid (H₂TBTA) and 4,4′-bis(imidazole-1-yl)-biphenyl (L) ligands. Furthermore, due to its strong intense emission and open N donor sites, complex 1 could be used as a light-emitting sensor to determine 2,4,6-trinitrophenol (TNP) which has high selectivity and sensitivity. Furthermore, the anti-bacterial effect of the compound against P. gingivalis in vitro was evaluated by measuring the P. gingivalis growth curves after compound treatment. And the RT-PCR assay was performed to detect the relative expression of ragA and ragB, which are important for the P. gingivalis growth. The potential anti-infectious mechanism was further studied by using molecular docking technique.

Key words: Zn(II)-complex, mixed-ligand, TNP sensing, periodontal diseases, molecular docking

1 Introduction

Recent reports issued by the World Health Organization (WHO) indicated that periodontal diseases influence about 10-15% of adults all over the world, which serious damaged people’s quality of life¹. Periodontal diseases are polymicrobial inflammatory diseases, which are usually caused by different factors combined with the character of periodontal support tissues destruction². Thus, it is urgent for us to study new strategy for periodontitis treatment. Porphyromonas gingivalis (P. gingivalis) is a kind of anaerobic bacteria, playing a vital important role in the pathogenic of periodontal microbes, which is also reported having closely relationship with chronic periodontitis, invasive periodontitis, periodontal abscess and pulp infection, and concomitant systemic diseases³-⁴. ragA and ragB are the most important gene involved in the growth procession of P. gingivalis, so ragA and ragB may be the target candidates for the disease therapy⁵.

In recent years, metal-organic frameworks (MOFs) or coordination polymers (CPs) have attracted much attention owing to their applications in sensing, catalysis and gas storage/separation as well as other fields⁶-⁹. Because of the functionality and porosity of CPs, it can maintain the supramolecular interaction between CP host and selective guest analyte, which can be transformed into measurable luminescence response, so it has invested a lot of efforts in the application of chemical sensing¹⁰-¹². The explosive components of commercial explosives and mines are nitroaromatic hydrocarbons, such as TNP, DNT, DNB, TNB, TNT and so on. Aliphatic nitro compounds along with aromatic are dangerous or and explosive in nature. TNP is often utilized in dyestuff, leather, glass industries as well as pyrotechnics, it exposure to TNP vapor can cause adverse effects on health. Organic compounds improper disposal can lead to environmental pollution in soils and systems of aquatic¹³-¹⁷. To enhance the sensing performance of the CPs toward the TNP, one of the most effective approaches is to introduce the binding sites to form the host-guest interaction. Recent literatures have revealed that the mixed ligand approach is a feasible approach for the construction.
of CPs with specific binding sites. Furthermore, the concept of mixed-ligand synthesis has been applied to generate multiple-component coordination polymers that exhibit distinct properties with respect to the pure form. In this study, a new difunctional Zn(II) coordination polymer (CP) with the chemical formula of [Zn(TBTA)](L)_{1.5}·(1) has been synthesized hydrothermally from tetrabromomethane-phthalic acid (H₂TBTA) and 4,4'-bis(imidazole-1-yl)-biphenyl ligands. Furthermore, due to its strong intense emission and open N donor sites, complex 1 could be used as a light-emitting sensor to determine 2,4,6-trinitrophenol (TNP) which has high selectivity and sensitivity. In the biological research, to evaluate the anti-bacterial activity of the synthetic compound after treatment at indicated condition, the P. gingivalis growth was measured firstly. The results indicated the excellent anti-bacterial activity of the compound in vitro. Besides, the RT-PCR results of the ragA and ragB genes in P. gingivalis was measured, and the data suggested that the compound could inhibit the ragA and ragB genes expression and then inhibit the P. gingivalis growth during periodontal diseases. The results of potential binding models were acquired from posture scoring software along with molecular docking assay, which exhibits possible binding pattern of compound to target protein, and offered a latent regulation mechanism of compound to modulate the DNA binding process to the protein.

2 Experimental
2.1 Chemicals and measurements
The solvents used in this work are obtained from the Tianjin FuChen Chemical Reagents Company and used without further treatment. The metal salts and organic ligands were purchased from the Jinan Henghua Chemical Reagent Factory and were used as received. The results of element content of C, H and N were acquired by using Perkin-Elmer EA 2400 elemental analyzer. Infrared spectra of KBr pellets between 4000 and 400 cm⁻¹ were analyzed via Nicolet 6700 infrared spectrometer. With Bruker D8 Advance instrument we collected the data of X-ray powder diffraction (XRPD) under the room temperature by Cu Kα radiation (λ = 1.54056 Å). The emission along with excitation spectra of solid/liquid fluorescence were measured via fluorescence spectrometer (Edinburgh, FS5).

2.2 Preparation for coordination polymer [Zn(TBTA)](L)_{1.5}·(1)
We mixed Zn(NO₃)₂·6H₂O which is 56 mg and 0.2 mmol, L of 28 mg and 0.1 mmol, H₂TBTA which is 48 mg and 0.1 mmol, NaOH of 8 mg and 0.2 mmol, as well as 10 mL H₂O to form a mixture, it was placed in 25 mL container of Teflon-lined stainless steel and heated it for three days to 140°C under the autogenous pressure. We acquired colorless crystal 1 with bulk-shape via cooling it to the room temperature at 5°C·h⁻¹ rate with a yield of 38.4% on the basis of ligands. Elemental analysis caled (%) for C₃₅H₂₁Br₄N₆O₄Zn: C, 43.13; H, 2.17; N, 8.62; Found: C, 43.52; N, 8.54; H, 2.33. IR spectra of KBr pellet, cm⁻¹: 3135(s); 1597(s); 1515(s); 1385(m); 1306(s); 1063(s); 822(s); 740(w); 653(w).

Diffraction data for single crystals of 1 were obtained around room temperature on an automated Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator, λ(MoKα) = 0.71073 Å, o-scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package. The structures were solved by dual space algorithm (SHELXT) and refined by the full-matrix least squares technique (SHELXL) in the anisotropic approximation (except hydrogen atoms). Since solvent molecules are randomly dispersed in the structure, their position cannot be accurately located with conventional discrete atom models. Table 1 shows 1’s refinement index along with crystal data.

### Table 1: Complexes 1's crystallographic parameters along with refinement details.

| Parameter | Value |
|-----------|-------|
| Empirical formula | C₃₅H₂₁Br₄N₆O₄Zn |
| Formula weight | 974.59 |
| Temperature/K | 293(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.9362(3) |
| b/Å | 11.4563(5) |
| c/Å | 15.5439(2) |
| a° | 84.221(2) |
| β° | 71.962(3) |
| γ° | 83.987(2) |
| Volume/Å³ | 1668.81(10) |
| Z | 2 |
| ρcal/cm³ | 1.940 |
| μ/mm⁻¹ | 5.576 |
| Data/restraints/parameters | 5888/0/451 |
| Goodness-of-fit on F² | 1.133 |
| Final R indexes [I>2σ(I)] | R₁ = 0.0440, wR₂ = 0.1327 |
| Final R indexes [all data] | R₁ = 0.0561, wR₂ = 0.1509 |
| Largest diff. peak/hole / e Å⁻³ | 3.31/-1.96 |
| CCDC | 1958957 |

2.3 P. gingivalis growth curves
To detect the anti-bacterial activity of the synthetic
compound, the growth curves of \textit{P. gingivalis} was measured firstly. This experiment was conducted under the guidance of the manufactures’ instructions: in brief, the \textit{P. gingivalis} cells cultured in BBL medium added with 10 \(\mu\)g/mL hemin and vitamin K (THB-HK) at 37°C anaerobic (80% N\(_2\)/10% H\(_2\)/10% CO\(_2\)) condition. When the optical values reached 0.2 at 660 nm (OD\(_{660}\)), the \textit{P. gingivalis} suspension was added in wells of 96-well plates (100 \(\mu\)L/well), and then serious dilutions of the compound was added into wells for co-culture. Wells supplemented with fresh medium and \textit{P. gingivalis} suspension without tested compound were utilized as a control group. The bacterial cells were incubated at anaerobic conditions at 37°C for 24 h, the growth of bacterial was monitored every 60 min by measuring and recording the OD\(_{660}\) values of each well using Multi-Mode Microplate Reader. The growth curves were calculated utilizing Prism software on the basis of three biological and techniques replications.

### 2.4 RT-PCR

RT-PCR detection was carried out to evaluate the relative expression of the genes take part in the \textit{P. gingivalis} bacterial growth, such as \textit{ragA} and \textit{ragB}. This measurement was conducted in accordance with the protocols with some modifications. Briefly, the \textit{P. gingivalis} in the BBL broth were cultured in an incubator at 37°C anaerobic conditions to the OD\(_{660}\) value of 0.2. Then, the bacteria cells were inoculated to the plates with 96-well and compound was added at the specified concentration for treatment. After that, the bacteria were collected, washed with PBS for three times and the total RNA in the cells were extracted with TRIzol kit (Invitrogen, USA). The total extracted RNA was then quantified and transcribed into the DNA utilizing cDNA Synthesis Kit (Thermo Fisher 20 Science, USA). Finally, StepOnePlus Real-Time PCR System was carried out for relative genes detection. The genes related with the growth ability of \textit{P. gingivalis} were determined using \textit{ropD} as the internal reference. The data were expressed as mean ± SD. The sequences of primers used in the detection were showed in Table 2.

### 2.5 Molecular Docking

Discovery studio 3.0 is an extensive utilized software. We choose it as a platform for the simulation of molecular docking, which can realize molecular docking of proteins with small molecules. Its advantage is that it is customized at the aim of better supporting the development of high-precision scoring function. The structure of ligand was derived from the structure of crystal acquired by measuring X-ray and downloaded from the protein date bank (PDB), using ligand preparation tools before the docking program was performed. The receptor protein was 4QJU (PDB ID) which has been widely utilized for the simulation of molecular docking along with the screening of drug since it has protein residues and double helix structure at the same time. The Libdock, CDOCKER and ligand pose scoring Tools have been utilized to generate the structures of receptor along with ligand for the simulation of molecular docking, grid box length is set at 40, it is enough large to cover all the docking bag and involve double helix chains as well as protein moieties.

| Genes | Sequences |
|-------|-----------|
| \textit{ragA} | TGCAAAATCGTGAAGCTGACG |
| ATGGCTAATAAACGCGCAA |
| \textit{ragB} | ATGAAGCAATAATTTATTG |
| TTATATCCGAGTCCTTTAT |
| \textit{ropD} | GAGATGGGACATACACACGT |
| ACCTTCTCCAGCCGCATCATC |

### 3 Results and Discussion

#### 3.1 Molecular structures

The title complex \(\text{I}\) was obtained through H\(_2\)TBTA, L as well as \textit{Zn(NO}_\text{3})\text{·6H}_2\text{O} hydrothermal reaction with NaOH as the pH modulator. Structural decomposition and refinement on the basis of crystal data collected under the room temperature reveals complex \(\text{I}\) crystallizes within triclinic system with P\(_1\) space group, its asymmetric unit contains a \(\text{Zn(II)}\) ion, TBTA\(^{2-}\) ligands two halves, as well as one and a half L ligands, all of them contribute to the formation of neutral framework (Fig 1a). Every \(\text{Zn(II)}\) ion exhibits five-coordinated with three oxygen atoms (O3, O2 and O1) of two TBTA\(^{2-}\) ligands carboxylate groups along with two nitrogen atoms (N3 and N2) of distinct L ligands, forming a geometry [ZnN2O3] with trigonal pyramidal, and its \(\tau\) value was 0.86 (Fig. 1a). The lengths of \textit{Zn–O} are 1.972(3) Å along with 2.470(3) Å, and \textit{Zn–N} distances are 2.015(4) Å along with 2.032(4) Å. The coordination angles of \(\text{Zn}^{2+}\) centers ranged from 94.90(16) to 126.98(17)°. Compared CPs based on \(\text{Zn(II)}\) reported in the past, bond distances along with bond angles are within a normal range. According to Fig 1b, bridged L ligands have two kinds of coordination pattern, i. e., L-II and L-I, and L-I ligands have two kinds of anticonformational coordination bridging, and the separation distance between two \(\text{Zn(II)}\) atoms and \(\text{Zn}^{2+}\)-Zn is 17.72(3) Å. L-I two imidazole rings are mutual to each other. However, the L-II ligand is cis-conformed to link a neighbouring \(\text{Zn(II)}\) center, and dihedral angle of two imidazole rings is 42.11(2)°. Hence, the formation of the [\text{Zn}_2L_3]\(^{2+}\), binuclear secondary building unit is along axis b. At the same time, the TBTA\(^{2-}\) ligand with complete dephosphorization extended[\text{Zn}_2L_3] further by \((\kappa_1\cdot\kappa_0)-(\kappa_1\cdot\kappa_0)\cdot\mu_2\) coordination, forming two-dimensional layered
structures, and the distances of Zn are 10.842 Å along with 11.165 Å on bc plane, respectively (Fig. 1b). The two-dimensional network is deep interconnected to the three-dimensional supramolecular skeleton through the interactions of π⋯π stacking with the imidazole and benzene rings of the adjacent L ligands, and the planar distance is 3.821 Å (Fig. 1c). Topologically, the two-dimensional layer could be simplified to the three-linked hcb topology with [6^3] point symbol (Fig. 1d).

To confirm that the crystal structure is truly representative of the bulk material, PXRD experiments were carried out for the as-prepared complex 1. The PXRD experimental and computer-simulated patterns of the corresponding compound in the Fig. 2 show that the PXRD patterns of the bulk synthesized materials are comparable with those of simulated from the measured single crystals, indicating the as-prepared crystalline samples are in high phase purity.

3.2 Selective luminescent detection of TNP

1 and L ligand solid-state luminescence spectra under the room temperature were studied via utilizing strong luminescence properties of electron-rich π-conjugated ligands and CPs of d^{10} metal ions as well as their latent applications as the chemical sensors. The observation of 1’s strong emission at 502 nm, and observation of L strong emission at 500 nm under excitation at 390 nm (Fig. 3a). The coordination of L ligand and Zn will increase L rigidity in 1, and reduce the energy loss, so that 1 exhibits stronger emission than L ligand. Owing to similarity of the luminescence spectra of free L ligand and 1, 1’s luminescence is due to the electron excitation centered on ligands. 1’s strong emission strength encouraged us to discuss its latent ability as the small molecules sensor. 1’s luminescence preformances as the suspension within distinct solvents were studied. Emission strengthes depend strongly on dispersants. 1’s NB suspension exhibited the lowest strength relative to other solvent suspensions, and showed almost complete luminescence quenching. 1’s quenching effect on NB stimulated us to deep study sensing other
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NACs solution (5 micron, 1,3-DNB, NB, TNP, 4-NP, 4-NT as well as 2,4-DNT) was added to 1’s DMF suspension for luminescence titration. According to Fig. 3b, the whole NACs can extinguish 1’s emission to varying degrees. After adding TNP, 1’s emission strength reduced steadily. After adding 100 μL TNP solution, 1’s emission strength decreased by nearly 97.23%, which is higher than that of other NACs solutions (4-NP, 4-NT, 2,4-DNT, 1,3-DNB and NB are 24.75%, 13.49%, 18.10%, 10.20% and 3.94%, respectively), as shown in Fig. 2c. Stern-Volmer equation was used to quantitatively analyze luminescence quenching efficiency: \( I_0/I_1 = 1 + K_{sv} \times [M] \), in which \( I_0 \) and \( I_1 \) are the largest 1’s luminescent strength before and after adding analyte, \([M]\) is the molar analyte consistence, while \( K_{sv} \) is the constant of quenching. Under low consistences, the Stern-Volmer curve of NACs almost linear (Fig. 3d). From low consistence region linear fitting, TNP quenching constant was \( 4.3 \times 10^4 \text{ M}^{-1} \) (Fig. 3b), that was several times larger than other NACs solutions (4-NP, 4-NT, 2,4-DNT, 1,3-DNB and NB are \( 5.7 \times 10^6 \text{ M}^{-1} \), \( 1.7 \times 10^6 \text{ M}^{-1} \), \( 3.27 \times 10^5 \text{ M}^{-1} \), \( 1.7 \times 10^4 \text{ M}^{-1} \), and \( 3.9 \times 10^3 \text{ M}^{-1} \), respectively). Furthermore, 1’s \( K_{sw} \) of TNP was also larger than most reported TNP sensors based on CP. In addition, the framework stability of 1 after the TNP detection has been determined via the PXRD measurements, which indicates that the PXRD patterns of the samples after the TNP detection are similar to those of the as-prepared samples, showing its good framework stability in the TNP detection process.

3.3 Compound suppresses the growth rate of P. gingivalis

Chronic periodontitis is usually caused by the pathogens, in which P. gingivalis is recognized as the most common one. After the synthesis of the new compound, its anti-bacterial activity was evaluated in this experiment. To explore the effective killing ability of bacteria by, the inhibitory function of the compound on the P. gingivalis growth was measured firstly. The P. gingivalis cells were planted to plate of 96-well and co-incubated with compound, the absorbance of each well was measured every 60 min. From the results showed in Fig. 4, we can see the bacteria in positive group (P. gingivalis suspension without compound treatment) has a similar growth rate with the control group, which could reach to about 0.5 absorbance after 24 h cultivation. However, After treated with the synthetic compound, the OD values were significantly reduced, suggesting the inhibition of compound on P. gingivalis growth in vitro.

3.4 Compound inhibits ragA and ragB genes expression in P. gingivalis

The anaerobic bacteria P. gingivalis is known to be closely related to the development of chronic periodontitis,
invasive periodontitis, periodontal abscess and pulp infection, and concomitant systemic diseases. As reported, *ragA* and *ragB* are the most important gene involved in the growth procession of *P. gingivalis*. So, in the experiment, in order to evaluate compound protective function in *P. gingivalis* infection induced chronic periodontitis, the *ragA* and *ragB* genes relative expression was determined via RT-PCR assay. According to the results in Fig. 5, we can see the compound treatment obviously reduced the level of *ragA* and *ragB*, which is obvious distinct from control group. This gene expression results showed that new compound has a good anti-bacterial activity, which was due to the inhibition of *ragA* and *ragB* gene expression.

### 3.5 Molecular Docking

The molecular docking helps us to exhibit how the ligand interacts with receptor protein at level of molecular. At the aim of understanding the phenomenon among the experiment discovered in above results, we chose the target protein (PDB: 4QJU) to explore possible interactions of the synthesized compound and the target protein. According to Fig. 6A and B, because of the interaction activity with receptor protein, the complex can be utilized as the protective activity which has strong confidence. It depicts a general view of encapsulating the compound into the binding bag offered via the target protein. The molecular docking results which showed the most favorable binding modes had been found through cross docking and ligand scoring module. It could be conducted that the synthesized compound had latent binding pattern with the complex, indicating a possible regulation mechanism. In Fig. 6C and D, we showed a surface binding mode of the complex to reveal the potential binding mode and mechanism. When functional group oxygen-containing interacts with receptor, the disadvantageous binding pattern of energy indicates that the binding stability is weak. The results are in good agreement with the experimental observations.

### 4 Conclusion

In summary, we have successfully prepared a novel di-functional Zn(II) coordination polymer (CP) via tetrabromoterephthalic acid (H$_2$TBTA) ligands and 4,4'-bis(imidazole-1-yl)-biphenyl reaction. The X-ray of single crystal diffraction study shows that complex 1 reveals a two-di-
mensional(3)-linked hcb net which was deep extended to the 3D supramolecular structure via interactions of π⋯π stacking. Furthermore, due to its strong intense emission and open N donor sites, complex 1 could be used as a light-emitting sensor to determine 2,4,6-trinitrophenol (TNP) which has high selectivity and sensitivity. In the present biological study, the bacterial growth curves of *P. gingivalis* was detected to evaluate the anti-bacterial activity of compound *in vitro*. The results indicated that the compound has the excellent inhibitory effect against *P. gingivalis* growth *in vitro*. Next, the RT-PCR results showed that compound could decrease *ragA* and *ragB* relative expression and then inhibit the growth of pathogen. In conclusion, the compound showed excellent treatment on *P. gingivalis* induced periodontal diseases by suppressing the *ragA* and *ragB* genes expression in bacteria. The results of ligand posture scoring module along with molecular docking offered a latent binding pattern of targeted protein and the compound, and offered a possible mechanism for this compound to bind the target protein.

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