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TIMPZ: An exquisite building block for metal/hydrogen coordination polymers

Carolina B. P. Ligiéro, Thiago V. Oliveira, Chárbel C. F. Fontes, José T. C. Barragan, Fernanda W. Y. So, Lauro T. Kubota, René A. Nome, and Paulo C. M. L. Miranda*[a]

Abstract: *The novel polynitrogenated ligand* tetra-[4(5)-imidazoyl]pyrazine (TIMPZ, ***1***) *and its pincer complex of Fe(II) are described. This ligand has an outstanding ability to aggregate in 1D-superstructures by means of hydrogen bonding or metal chelation. TIMPZ shows an unprecedented conformational control over the supramolecular assembly. Metal or hydrogen coordination switches the conformation of peripheral rings driving the assembly preferences. For* $[Fe_n(TIMPZ)_{n+1}]^{2n+}$ *complexes, UV-Vis spectroscopy shows a bathochromic shift of the main visible absorption band with higher "n" values. TIMPZ also has hydrogen-bond triggered* excited-state intramolecular proton transfer (ESIPT) *fluorescence, which is completely inhibited by chelation with transition metals.*

Introduction

Coordination polymers have caught the attention of the scientific community due to their electronic, magnetic, and optical properties.[1] Structural queuing to form one-dimensional supramolecular assemblies can lead to the emergence of band-like electrical transport and tailored chemical properties. Thus, cooperative interactions between discrete molecules allow the appearance of molecular-based ferromagnets, ferroelectric materials, electrical conductors and non-linear optical materials using coordination polymers.[2] A major drawback for coordination polymers involving highly charged cations is the charge accumulation due to metal summoning.[3] Many different bridging ligands have been used to construct such 1D superstructures, some of them bearing bipyridine or terpyridine subunits.[1-2] In this work, we introduce the new ligand tetra-[4(5)-imidazoyl]pyrazine (TIMPZ, **1**) capable of promoting 1D assemblage. The presence of imidazole nuclei avoids excessive charge accumulation in heterocyclic nuclei due N-H polarization and allows higher one-dimensional elongation of the aggregates. Nevertheless, conformational change of peripheral imidazole rings due to hydrogen or metal coordination drives the assembly preferences allowing two different superstructures.

To achieve a multimodal ligand capable of selectively self-assembling by hydrogen bonding or by metal chelation to form 1D-superstructures depending on applied conditions, we envisaged the construction of heterocycle bearing two different conformations: the first favoring a linear array of hydrogen bonds, and a second one having a preference for metal chelation (TIMPZ, **1**, Figure 1).

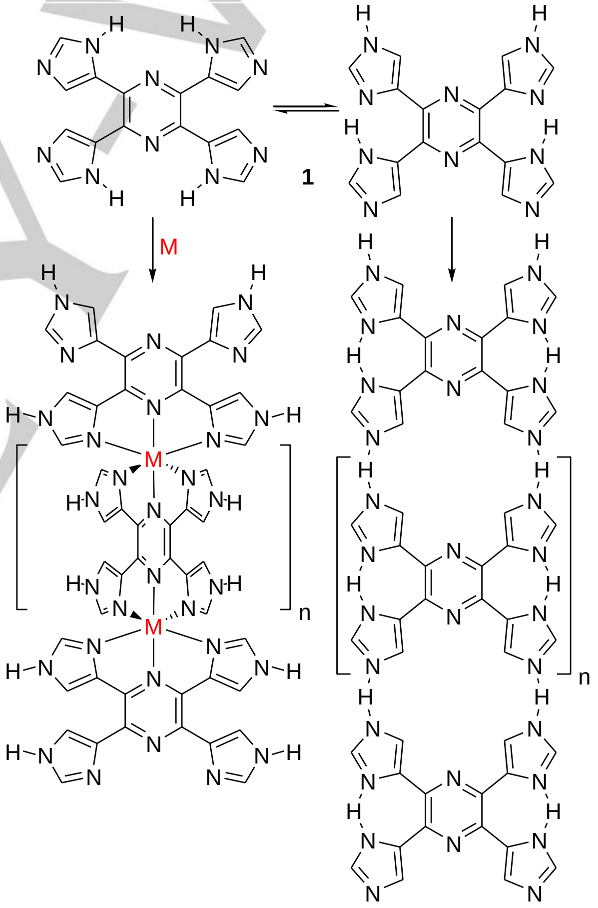

Figure 1. Tetra-[4(5)imidazoyl]pyrazine (TIMPZ, 1) and conformation preferences for hydrogen bonding 1D-superstructures (right) and 1D-coordination polymers (left).

An extended array of hydrogen bonds could be formed in neutral media due to imidazole ring association. Conversely, in the presence of metallic cations it would be possible to change the conformation of the imidazole rings to perform 1D-coordination polymers into an octahedral environment.

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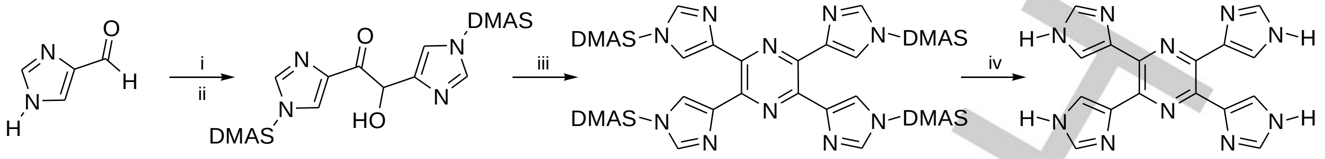

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Scheme 1. Reagents and conditions for preparation of TIMPZ (**1**): i) (a) NaH, acetonitrile, rt, 1.5h, (b) DMAS-Cl, acetonitrile, rt, 18h, 91%; ii) MeOH, TEA, 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride, 50°C, 30min, 96%; iii) NH_4OAc, pyridine, 80°C, 2h, 65%; iv) (a) HBr_{aq}, 100°C, 2h, (b) NH4OH$_{aq}$, 88%.

In order to investigate this hypothesis TIMPZ (**1**) was promptly prepared from 4(5)-imidazolecarbaldehyde (**2**) in 4 steps as described at Scheme 1.

Results and Discussion

DMAS protecting group proved to be essential to promote the acyloin coupling and it was easily removed from the pyrazine derivative **4** by diluted acid aqueous solutions or by heating. The acyloin coupling was successfully promoted by thiazolium carbene catalysts. Pyrazine nucleus was achieved by the condensation of acyloin **3** with ammonium acetate in pyridine at 80°C.[4] Two different TIMPZ salts were crystallized depending on the applied conditions: a diprotonated salt (**A**), and a tetraprotonated salt (**B**) as shown in Figure 2.

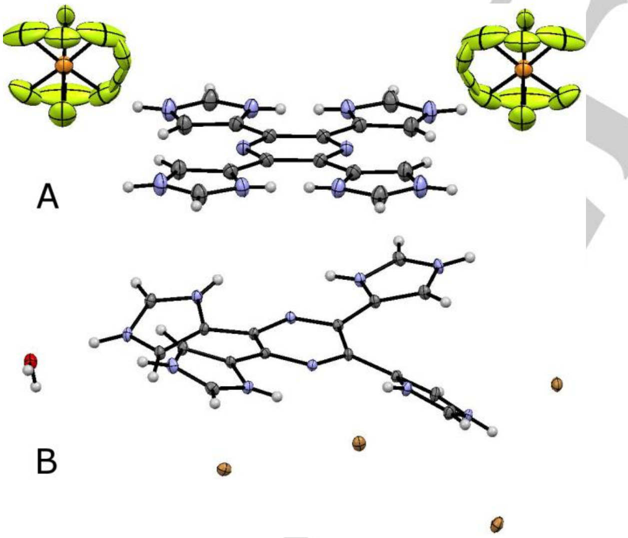


Figure 2. ORTEP representation of (**A**) [(TIMPZ·2H)$(PF_6)_2$], and (**B**) [(TIMPZ·4H)Br_4·H_2O]. Ellipsoids displayed at 50% probability. Crystallographic data about compounds **A** and **B** were deposited in Cambridge Crystallographic Data Centre with numbers CCDC-1868584 and CCDC-1583381, respectively.

Fluorescence spectra of TIMPZ shows a Stokes shift of 3854.5 cm^{-1}, even in DMSO solution, and can be described by a two-state system with $pK_a^* = 2$ showing an excited-state intramolecular proton transfer (ESIPT) mechanism.[5] Fluorescence was inhibited by strongly acidic or basic media, as well as metal coordination.[6] In the case of metal coordination, ESIPT fluorescence suppression is due to conformational exchange avoiding intramolecular hydrogen-bonding (Figure 1) and consequently the proton transfer in the excited-state.

DRX data clearly indicate that all rings in diprotonated TIMPZ (**A**) are in a planar configuration owing to the formation of a seven-membered ring. N···N distance was observed to be as short as 2.543 Å and calculated N–H···N angle was about 159.7°. Similar chemical structures bearing strong intramolecular H-bond qualitatively correlates with the more downfield shift in ^{1}H-NMR.[6] Experimentally, the $\delta > 10$ downfield shift and sharp N-H peak for weak acidic hydrogen supports the intramolecular H-bond formation.[6] Therefore, in the case of the neutral TIMPZ, the N(2)–H···N(1) TIMPZ H-NMR signals in THF-d8 located at δ = 18.10 ppm suggests a low barrier N–H···N hydrogen bond.[7] This can also be evidenced by the infrared frequencies of the N–H stretching observed at $\sim$1000-600 cm^{-1}.[8]

HRMS analyses of a diluted aqueous solution of TIMPZ revealed the presence of oligomers bearing as many as 22 monomer units in four different degrees of protonation (Figure 3). We observed an exponential relationship between the HRMS signal intensity and the number of monomer units in the supramolecular structure for each protonation state. These findings suggest a double hydrogen-bond superstructure by means of resonance-assisted hydrogen bond (RAHB) in a synergistic cooperation between hydrogen-bond strengthening and π-delocalization as shown in Figure 1.[9] Increasing of protonation at the supramolecular aggregate reinforces the intramolecular N–H···N hydrogen bond due to RAHB improvement. This phenomenon seems to be confined for each monomer, which causes a slight lowering of intermolecular N-H···N bonds.

We fitted the HRMS intensities with a linear supramolecular model based on an array of monomer units in which the binding energy between units is constant. The supramolecular assembly is formed by hydrogen bonding between adjacent TIMPZ molecules. As a result, each configuration is singly degenerate. Since the hydrogen bonding pattern between adjacent TIMPZ molecules is assumed to remain the same throughout the structure, the energy levels are equally spaced. Thus, the HRMS signal intensities are associated with Boltzmann probabilities of finding the linear supramolecular system microstate with a given length, and the slope of each curve shown in Figure 4 directly gives the average binding energy (in k_BT units) between monomer units for each group.

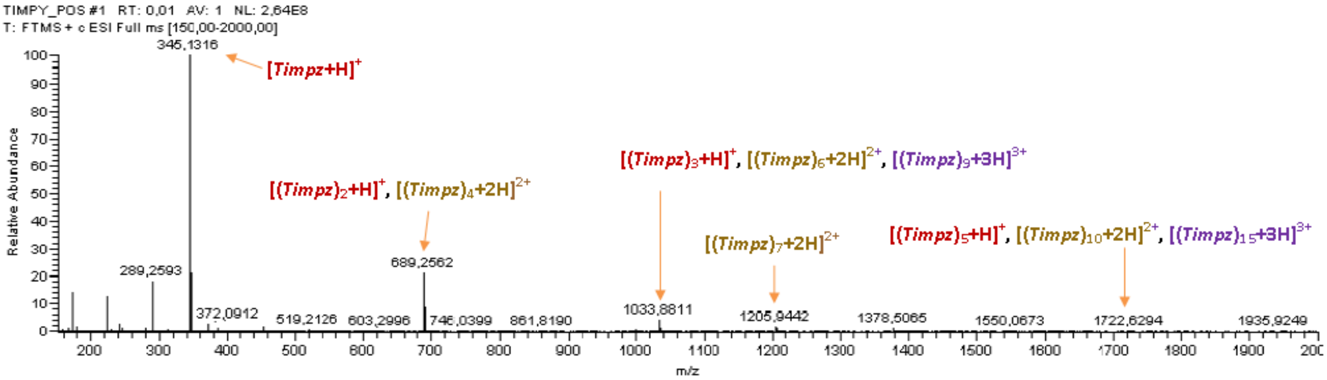


Figure 3. HRMS (ESI) of TIMPZ supramolecular arrays showing the coexistence four different degrees of protonation ($TIMPZ_n$+H^+, $TIMPZ_n$+$2H^+$, $TIMPZ_n$+$3H^+$, and $TIMPZ_n$+$4H^+$). Ion intensity profile at diluted aqueous solution.

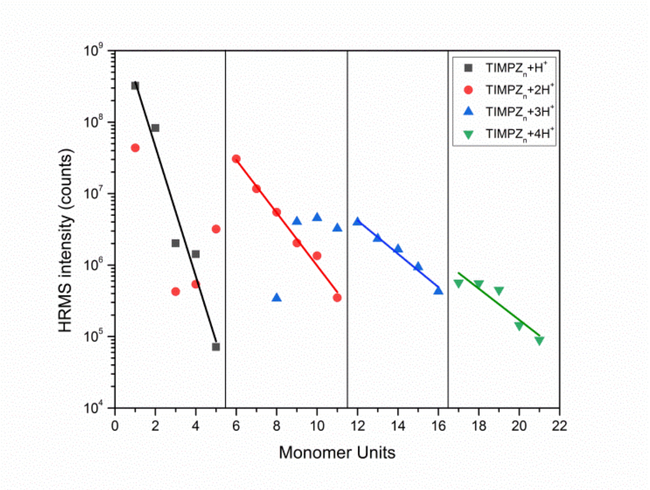


Figure 4. Linearized plot of ion intensities for each protonated state: $TIMPZ_n$+H^+ (black), $TIMPZ_n$+$2H^+$ (red), $TIMPZ_n$+$3H^+$ (blue), and $TIMPZ_n$+$4H^+$ (green).

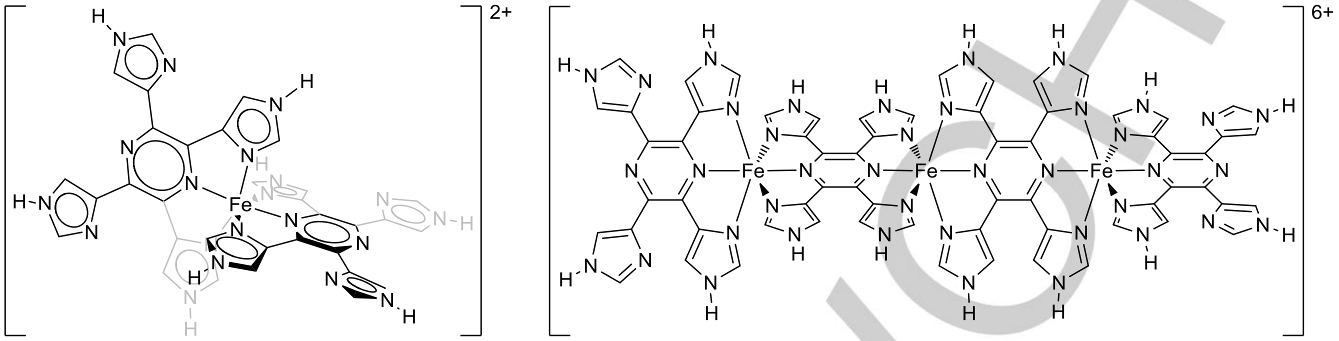
Linear fit of the natural logarithm of HRMS intensities as a function of number of monomers gave average binding energies of -2.48(R^2=0.94), -1.01(R^2=0.98), -0.64(R^2=0.98), and -0.48(R^2=0.91) kcal/mol respectively for $TIMPZ_n$+H^+, $TIMPZ_n$+$2H^+$, $TIMPZ_n$+$3H^+$, and $TIMPZ_n$+$4H^+$, consistent with weak (relative to the thermal energy) hydrogen bonding between units, as expected. Since the sample size and thus the number of monomer units is finite, the model also predicts that the probability of finding the system with a given length is inversely proportional to the polymer length (Figure 4).

In comparing binding energies, the larger negative slope for +1 assemblies in relation to +2, +3, +4 aggregates means a stronger decay for higher protonated assemblies (Figure 4). Extrapolation of the retrieved binding energies as a function of charge gives an intercept of -7.66 kcal/mol (R^2=0.99) for the neutral aggregate, a value consistent with medium hydrogen bonding strength. On the other hand, with increasing charges, the length of the observed assemblies also increases, such that the larger number of units is 5(+1), 11(+2), 16(+3) and 22(+4). Thus, the interplay of electrostatics, hydrogen bonding, and finite system size gives the observed results shown in Figure 4.

$[Fe(TIMPZ)_2](PF_6)_2$ (**6**, Figure 5) was easily prepared by addition of an aqueous solution of Fe(II) perchlorate into an ethylene glycol solution of TIMPZ (1:2 ratio). Interestingly, the same complex was obtained when Fe(III) was used as reagent, even under ordinary conditions. In the last case, we detected a complex mixture of oxidized byproducts of TIMPZ containing quinonoid derivatives of the ligand. In both cases the complexes were prepared in good to excellent yields (60-90%) and they were silent into EPR analyses. They also furnished identical HRMS, ^1H and ^{13}C-NMR, UV-Vis, CV, IR, and conductimetry results. The signals in the UV-Vis absorbance spectra (200-400 nm) correspond to the ligand charge transfer (LCT), $\pi \rightarrow \pi^*$ transition. TIMPZ complex of Fe(II) has a strong absorption at 569 nm (ε=1.156·10^4 L·cm^{-1}·M^{-1}) due to a metal-to-ligand charge transfer (MLCT) which is red-shifted in comparison to the analogous complexes where the bands is observed at 350-450 nm.[10]

HRMS analyses of a diluted aqueous solution of **6** shown the presence of the ion *m/z* 372.09167 (0.296 ppm error considering $[Fe(TIMPZ)_2]^{2+}$ and a matched isotopic pattern to the expected complex. We also detected small amounts of 1D coordination polymers as large as 3 cations and 4 TIMPZ by HRMS (ESI), even when an excess of the ligand was used. In this case, the UV-Vis spectra of the aqueous solutions show additional absorptions bands whose positions undergoes a bathochromic shift upon increasing the length of the coordination polymers. We observed λ_{max} at 620 for n=2 and 720 nm for n=3, which are compatible to the metal-to-metal plus ligand charge transfer (MMLCT) transitions.[1,11]

Cyclic voltammetry of **6** in glassy carbon, using Ag/AgCl electrode as reference, shows only one quasi-reversible redox process. Observed anodic peak potential and its current were respectively 0.516 V and 49 μA. Conversely, observed cathodic peak potential and its current were respectively 0.333 V and 21μA. Observed conductivity of **6** in methanol (203 $S\cdot cm^{2}\cdot mol^{-1}$) for a $1 mmol\cdot L^{-1}$ solution also indicated a 2:1 anion/cation ratio.[12]



6

$[Fe_3(TIMPZ)_4]^{6+}$

Figure 5. Structures of observed $Fe_n(TIMPZ)_{n+1}]^{2n+}$ complexes: $[Fe(TIMPZ)_2]^{2+}$ (left) and $[Fe_3(TIMPZ)_4]^{6+}$ (right)..

Conclusion

In summary, starting from 4(5)-imidazolecarbaldehyde a new bis N^3 ligand, TIMPZ (**1**), was synthesized in 4 steps with 46% global yield. TIMPZ has an outstanding ability to aggregate to form 1D-superstructures and has a high affinity for several metals. Both protonated and metal coordinated TIMPZ are able to form 1D-supramolecular arrays as large as 22 units. Additionally, an intriguing intramolecular low barrier hydrogen bond (LBHB) was observed and it is associated to an excited-state intramolecular proton transfer (ESIPT) mechanisms which causes a Stokes shift of 3854.5 cm^{-1}. The fluorescence was observed even in DMSO solution, but it was inhibited by strong acidic or basic media, as well as metal coordination. $[Fe(TIMPZ)_2]^{2+}$ showed a quasi-reversible redox process involving only one electron and a HOMO-LUMO energy gap of 2.179 eV and a high molar absorptivity ($11.555\cdot 10^3$ $L\cdot cm^{-1}\cdot M^{-1}$) at 569 nm suggesting its application in optoelectronic devices. The ability of TIMPZ to perform 1D coordination polymers could be proved by the observation of $[Fe_n(TIMPZ)_{n+1}]^{2n+}$ ions as large as 3 cations and 4 ligands by HRMS (ESI), even when an excess of the ligand was used.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: coordination polymers · metal–organic frameworks · hydrogen bonds · conformation driven assembling · supramolecular chemistry

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Layout 1:

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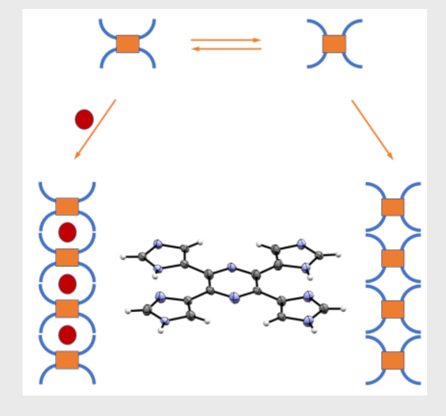

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TIMPZ: An exquisite building block for metal/hydrogen coordination polymers

Layout 2:

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