

# A rare binuclear metallocyclic planar 20, 26 and 34 membered zinc-organic rings



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## ABSTRACT

A rare discrete binuclear twenty, twenty-six and thirty-four membered zinc-organic metallocyclic compounds were synthesized and structurally characterized. The twenty membered metallocyclic molecule is arranged in a three-dimensional supramolecular network through hydrogen bonding, while the twenty-six membered metallocyclic ring is packed in a well define three dimensional framework. The thirty-four membered metallocyclic ring is closely packed through a weak interaction.

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## 1. Introduction

The design and synthesis of metal–organic assemblies (MOAs) such as discrete metal–organic metallocyclics (MOMs) and metal–organic frameworks (MOFs) have drawn much attention in materials chemistry [1–3]. The construction of MOAs are mainly directed by several parameters like metal, organic spacer, solvent,  $P^H$  and temperature [4,5]. Notably, N donor azolium organic spacers can be a useful tool to construct the MOAs with extended dimensions and porosity. Despite the wide range of MOFs, very few late transition metal MOMs are known. Barbour and co-workers reported the different discrete flexible azolium based discrete MOMs for adsorption of  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO$ ,  $CH_4$ ,  $CO_2$  and iodine and single-crystal (SC) to single crystal–single crystal (SC–SC) transformation [6–11]. Interestingly,  $[Cu_2Cl_4(\mathbf{bia})]$  ( $\mathbf{bia}$  = 9,10-bis(imidazol-1-ylmethyl)anthracene) probe was used as a tool to recognize the guanosine 5'-monophosphate [12], while  $[Pd_2(\mathbf{bbb})_2Cl_4] \cdot 1.5CH_2Cl_2$  ( $\mathbf{bbb}$  = 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene) was employed for Suzuki coupling reactions [13]. Notably, few structurally characterized zinc-metallocyclic compounds,  $[Zn_2X_4(\mathbf{bim})_2]$  ( $X = Cl$  or  $Br$ ;  $\mathbf{bim}$  = ditopic bis(1-imidazolyl)methane) [14],  $[Zn_2X_4(\mathbf{btre})_2]$  ( $X = Cl$ ,  $Br$ ;  $\mathbf{btre}$  = 1,2-bis(1,2,4-triazol-4-yl)ethane) [15] are known. However, the metallocyclic planar zinc-organic rings are limited [16–28].

Herein, we reported the first metallocyclic planar 20, 26 and 34 membered zinc-organic rings,  $\{[ZnBr_2(\mathbf{L}^1)]_2 \cdot 2HBF_4\}$ ,  $\mathbf{L}^1$  = 1,3,5-tris(1-imidazolyl)benzene (**1**),  $\{[ZnBr_2(\mathbf{L}^2)] \cdot DMF\}$ ,  $\mathbf{L}^2$  = 1,4-bis(imidazol-1-ylmethyl)benzene (**2**) and  $\{[ZnBr_2(\mathbf{L}^3)]_2 \cdot 2MeOH\}$ ,  $\mathbf{L}^3$  = 4,4'-bis(imidazol-1-ylmethyl)biphenyl (**3**), respectively (see Chart 1).

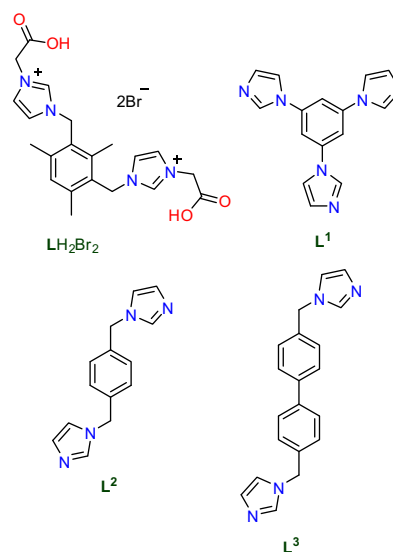


Chart 1. Molecules  $LH_2Br_2$ ,  $L^1$ ,  $L^2$ , and  $L^3$ .

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## 2. Experimental

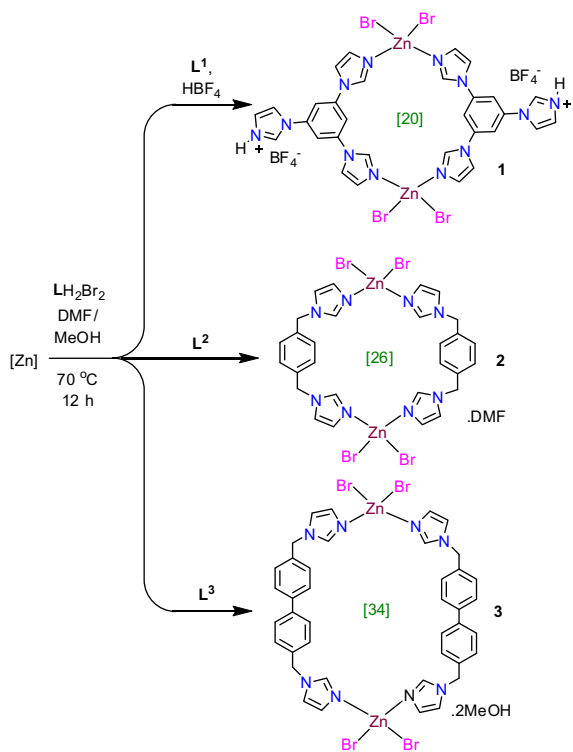
### 2.1. General considerations

The solvents were purchased from commercial sources and purified according to standard procedures [29]. Unless otherwise stated, the chemicals were purchased from commercial sources. The compounds  $\text{LH}_2\text{Br}_2$  [30,31], 1,3,5-tris(1-imidazolyl)benzene ( $\text{L}^1$ ) [32], 1,4-bis(imidazol-1-ylmethyl)benzene ( $\text{L}^2$ ) [33] and 4,4'-bis(imidazol-1-ylmethyl)biphenyl ( $\text{L}^3$ ) [34] were prepared accordingly to the previously reported methods. FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV–Vis spectra were measured on a T90+ UV–Vis spectrophotometer. Elemental analyses were performed by the Euro Vector EA-300 elemental analyzer. The crystal structures of **1–3** were measured on an Oxford Xcalibur 2 diffractometer with a standard 4-circle kappa-goniometer, Eos detector (Active area 92 mm diagonal) and two X-ray sources, one of which is a Supernova Cu source (wavelength 1.5418 Å) with focusing mirrors. A suitable crystal was selected and mounted on a Gemini E goniometer. Data were collected at 150 or 298 K using an Oxford Cryojet Low-Temperature device. The structures of **1–3** were solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss–Newton minimization [35]. Absorption corrections were performed on the basis of multi-scans. Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint has been made for any of the compounds. The function minimized was  $[\sum w(F_o^2 - F_c^2)^2]$  ( $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ), where  $P = (\max(F_o^2, 0) + 2F_c^2)/3$  with  $\sigma^2(F_o^2)$  from counting statistics. The functions  $R_1$  and  $wR_2$  were  $(\sum ||F_o| - |F_c||)/\sum |F_o|$  and  $[\sum w(F_o^2 - F_c^2)^2/\sum (wF_o^4)]^{1/2}$ , respectively. In molecule **1**, the fluorine atoms of  $\text{BF}_4^-$

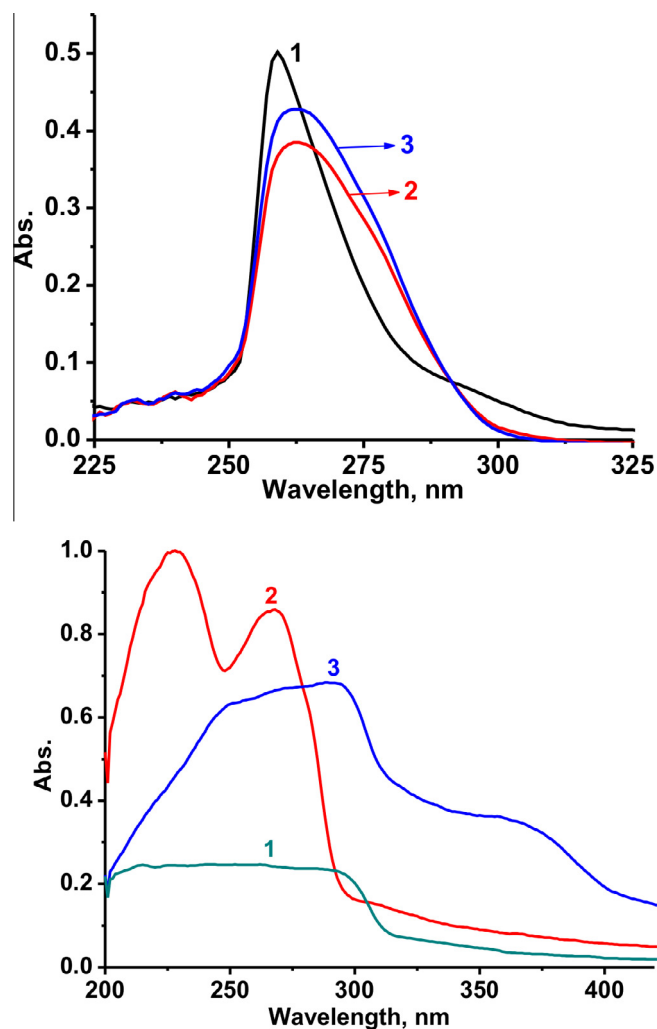
anion shows high thermal parameters. Attempts to fix the disordered F1 and F2 did not improve the data quality. In molecule **2**, the ring cavity is filled with a disordered DMF solvent molecule. The estimated the volume of each of the two voids at 217 Å<sup>3</sup> with electron count of 57 in each, which is nearly comparable with DMF electron count. Thus, one DMF molecule is occupied in each ring cavity, which is further confirmed by TGA. The initial weight loss till 450 °C is about 9%, which is nearly comparable with the calculated weight loss (7.3%) of one DMF molecule. Thus, two voids in total give two molecules of DMF per unit cell. The disordered DMF molecule is squeezed out for the final refinement.

### 2.2. Synthesis of $\{\{\text{ZnBr}_2(\text{L}^1)\}_2 \cdot 2\text{HBF}_4\}$ (**1**)

A mixture of  $\text{LH}_2\text{Br}_2$  (0.1 g, 0.179 mmol),  $\text{L}^1$  (0.050 g, 0.180 mmol) and  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.067 g, 0.180 mmol) in DMF/MeOH (2 mL) was heated at 70 °C for 12 h then the reaction mixture was allowed reach at room temperature, resultant solid was dissolved in  $\text{HBF}_4$  (0.5 mL) and the solution was slowly evaporated at room temperature. After 20 days the colorless crystals of **1** were formed, washed with water, methanol and dried under high vacuum. Yield: 36% (based on  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ). M.p. 312–314 °C (Dec.). Anal. Calc. for  $\text{C}_{30}\text{H}_{26}\text{N}_{12}\text{Br}_4\text{B}_2\text{F}_8\text{Zn}_2$  (1178.66): C, 33.57; H, 2.22; N, 14.26. Found: C, 33.5; H, 2.2; N, 14.3%. <sup>1</sup>H NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 9.07$  (s, 6H, 1mH), 8.25 (s, 6H, 1mH and



**Scheme 1.** Synthesis of **1–3**.  $[\text{Zn}] = \text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{L} = [1,3,5\text{-Me}_3\text{-C}_6\text{H}(\text{2,4}\text{-}\{\text{CH}_2\text{N}(\text{CH}_2\text{NCH}_2\text{CO}_2)_2\text{CH}_2\}_2)^2]$ ;  $\text{L}^1 = 1,3,5\text{-tris}(1\text{-imidazolyl})\text{benzene}$ ;  $\text{L}^2 = 1,4\text{-bis}(\text{imidazol-1-ylmethyl})\text{benzene}$ ;  $\text{L}^3 = 4,4'\text{-bis}(\text{imidazol-1-ylmethyl})\text{biphenyl}$ .



**Fig. 1.** Top: The UV-Vis absorption spectra of **1–3** in DMSO at room temperature ( $8 \times 10^{-6}$  M). Bottom: The solid-state UV-Vis absorption spectra of **1–3**.

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