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1. Dhrubajyoti Majumdar—Main author, research concept, contributed synthesis, total manuscript preparation and main research work carried out.

2. Tapan Pal contributed only X-ray crystallographic section

3. Dheeraj kumar Singh and Deepak K. Pandey contributed DFT section

4. Debaprasad Parai contributed only Molecular docking section

5. Dipankar Mishra Research guide and Supervisor

6.Kalipada Bankura contributed research proposal guide, fluorescence analysis, stokes shift and preparation of different Molecular graphics.

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# **GRAPHICAL ABSTRACT**



DFT investigations of linear Zn<sub>3</sub>-type complex with compartmental N/O-donor Schiff base: Synthesis, characterizations, crystal structure, fluorescence and molecular docking

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## ABSTRACT

A linear Zn(II) complex,  $[Zn_3(L^{OMe-pn})_2(\eta^1-NCS)_2]$  (1) containing a N<sub>2</sub>O<sub>2</sub>O'<sub>2</sub> donor Schiff base, (H<sub>2</sub>L<sup>OMe-pn</sup> =N, N-bis(3-methoxysalicylidene)-2, 2-dimethylpropane-1, 3 diamine) has been synthesized and structurally well characterized. SCXRD study reveals that in 1, the asymmetric section contains two identical discrete unit and each discrete unit contains three zinc metal ions (Zn1, Zn2 and Zn3) which are crystallographic independent, two deprotonated ligands [L<sup>OMe-pn</sup>]<sup>2-</sup> and [SCN<sup>-</sup>] ions which are linked with only terminal zinc ion in a  $\eta^1$  mode where terminal zinc atoms (Zn1/Zn3) are distorted square pyramidal while Zn2 is square antiprismatic. All computational calculations were performed by the DFT/M06 functional and the 6-31G \* basis set in the ground state. Complex optimized structure, HOMO-LUMO energy gap, Hirshfeld surface, MEP and NLO property was nicely explained with the help of DFT. Total dipole moment, average polarizability and first hyperpolarizability were calculated where  $\alpha$  and  $\beta^{hyp}$  values are well demonstrate the NLO property of complex (1). In addition, Bader's "atoms-in-molecules" was analysed to delineate complex non-covalent interactions using the same level of theory. Experimental electronic spectra were explained using TD-DFT level of calculations with an IEFPCM solvent model. DMF solvent explore complex (1) is a fluorescent material with maximum emission at 479 nm at an excitation wavelength of 300 nm. Finally, molecular docking was executed with cytochrome P450 from *B. megaterium* and *M. tuberculosis*. Results of molecular docking and HOMO-LUMO energy gap can provide new insights in the development of antimycobacterial drugs and next-generation semiconductor devices.

Keywords: Schiff base, Zn(II), DFT, Molecular docking, Luminescence

## 1. Introduction

During (1834-1915) Prof. H. Schiff opened an unheard multidisciplinary research window after his successful discovery of Schiff bases and other imines [1] and was responsible for research into aldehydes. Now Schiff base ligands are ubiquitous in coordination chemistry of transition metals due to its availability, easy synthetic approach, exhibit various denticities and functional behaviours [2,3]. In recent decades, complexes derived from such privilege ligands have become prime research area due to their attracting molecular structures and interesting properties [4-6] which are utilized as fluorescent material, non-linear optics, catalysis, magnetism, molecular recognition, biomedicine [7-12], optoelectronics [13-16], involvement of many catalytic functions for biological and non-biological processes [17,18], metallomesogens [19] and so forth. Spurred by the catalytic activity of various mono/dinuclear zinc complexes [20-24], usually heterometallic Zn<sub>2</sub>Cu calixarene complex have greater catalytic efficiency than usual Zn<sub>3</sub>-type complexes [25-28]. In this juncture, compartmental N<sub>2</sub>O<sub>2</sub>O'<sub>2</sub> donor Schiff bases derived from salicylaldehyde derivatives (ortho vanillin) and specific diamines, readily coordinate to d-block transition metal ions in a tetradentate (N<sub>2</sub>O<sub>2</sub>) fashion to afford d-block mono/di-nuclear/homometallic/tri- and tetranuclear complexes consisting of two molecules of parent salen ligands [29-31]. Herein  $\mu_2$ -phenoxo bridging plays an important role in assembling metal ions and also two salentype ligands. The presence of alkoxy groups (-OR, R=Me, Et) at position 3 of salicylidene moieties, an additional O<sub>4</sub> coordination site and phenoxo oxygen is readily available in conjunction with  $N_2O_2$  site (Scheme 3). In fact,  $O_4$  site is particularly suitable for heterometallic 3d-4f complex formation with interesting magnetic and photochemical

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properties [32-34]. Similarly, introduction of hydroxyl groups at 3 position of salicylidene moieties, reinforced the formations of mono/di/tri/heteronuclear complexes [35-38]. Such common trimetallic structural motif has already portrayed by A. Mustapha et. al. (Scheme S1B) [39]. Therefore, novel complex formations using hexadentate ( $N_2O_2O'_2$ ) Schiff base and pseudo-halide [SCN<sup>-</sup>] ions are common synthetic strategy over many years where versatile bridging mode of [SCN<sup>-</sup>] ions [40-42] were nicely explored (Scheme S2) without exception. Herein the stereochemistry and coordination number attainment governed not only the pseudo-halide spacers but also the steric requirements of the Schiff bases [43, 44]. The unique selection of zinc metal ions is due to its zero-crystal field stabilization energy (CFSE) and d<sup>10</sup> configuration which permits favourable architecting with flexible coordination environments [45].

Our motivated research group has already reported a number of pseudo-halide bridged Zn(II)/Cd(II) discrete/polynuclear complexes with different compartmental N/O-donor Schiff bases and explore their photoluminescence, DFT/TD-DFT, cytotoxic effect, apoptosis, autophagy, necrosis type classical cell death, *in vitro* antibacterial and anti-biofilm properties vividly [46-51]. Meanwhile, the outcome of previous works is the progressive response of photoluminescence, cytotoxicity, antibacterial and anti-biofilm properties [52-54]. Although till date various Zn<sub>3</sub>-salen type complexes [35-38] nicely explore their molecular architectures but it is worth to mention here that always small amount of research efforts were devoted for the synthesis of trinuclear zinc metal complex with current Schiff base ligand and [SCN<sup>-</sup>] spacers followed by novel scientific analyses of DFT/TD-DFT, Hirshfeld surface (HS), Bader's "atoms-in-molecules" (AIM), Molecular electrostatic potential (MEP), Frontier molecular orbital (FMO), Non-linear optics (NLO) and molecular docking with cytochrome P450 from *B. megaterium* and *M. tuberculosis* as a representative model.

In this article, we report successfully synthesis, spectral characterizations including SEM-EDAX analysis, single-crystal structure, DFT/TD-DFT, photophysical and molecular docking with cytochrome P450 from *B. megaterium* and *M. tuberculosis* in favour of complex  $[Zn_3(L^{OMe-pn})_2(\eta^1-NCS)_2]$  (1).

## 2. Experimental section

## 2.1. Starting materials

All research chemicals were of analytical grade and used as received without any purification. Zn(OAc)<sub>2</sub>.2H<sub>2</sub>O, KSCN, *ortho* vanillin, and 2, 2-dimethyl-1, 3-propanediamine were directly purchased from Sigma Aldrich Company, USA. High grade solvents such as CH<sub>3</sub>OH, CH<sub>3</sub>CN and DMF were purchased from Merck company.

## 2.2. Physical measurements

Elemental (CHN) analysis for ligand and the complex was carried out on a Perkin-Elmer 2400 elemental analyzer. FT-IR and Raman spectra were recorded as KBr pellets (4000–400 cm<sup>-1</sup>) using Perkin–Elmer spectrum RX 1 and BRUKER RFS 27 in the range 4000-50 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra was recorded on a Bruker 300MHz FT-NMR spectrometer using trimethyl silane as internal standard in DMSO-d<sub>6</sub> solvent. EDAX and SEM experiments was performed on EDAX OXFORD XMX N (model) using Tungsten filament and JEOL Model JSM-6390LV. UV-Visible spectra (200-1100 nm) were determined using Hitachi model U-3501 spectrophotometer. Fluorescence spectra in DMF solvent were measured at room temperature using Perkin-Elmer LS50B Spectrofluorometer model. Phase purity of the trinuclear complex (1) is carried out using Powder X-ray diffraction measurement by BRUKER AXS, GERMANY X-ray diffractometer model using Cu K $\alpha$ -1 radiation. Ligand and trinuclear Zn(II) complex quantum yield ( $\Phi$ ) were determined using very popular equation (1) where quinine sulphate used as secondary standard ( $\Phi = 0.57$  in water) [55].

$$\frac{\Phi_s}{\Phi_R} = \frac{A_s}{A_R} \times \frac{(Abs)_R}{(Abs)_S} \times \frac{n_s^2}{n_R^2}$$
(1)

The meaning of each terms according to equation (1): A terms denote the fluorescence area under the curve; Abs denotes absorbance; n is the refractive index of the medium;  $\Phi$  is the fluorescence quantum yield; and subscripts S and R denote parameters for the studied sample and reference respectively.

## 2.3. X-ray crystallography

Crystals were grown by slow evaporation of CH<sub>3</sub>OH and few drops (1:1) mixture of CH<sub>3</sub>CN+DMF at room temperature. Good quality crystals data was collected on a Bruker SMART CCD [56] diffractometer using Mo K<sub>a</sub> radiation at  $\lambda = 0.71073$  Å. Judicious crystal data collection purpose we have operated different popular programs such as SMART program for collecting frames of data, indexing reflections and determining lattice parameters, SAINT [57] for integration of the intensity of reflections and scaling, SADAB [58] for absorption correction and SHELXTL for space group, structure determination and least-squares refinements on  $F^2$ . Crystal structure of complex (1) was fully solved after refining by full-matrix least-squares methods against  $F^2$  using the program SHELXL-2014 [59] and Olex-2 software [60]. It is worth to mention here that the A-Level Alert in the checkCIF (1) is related only to the ADP max/min Ratio ....7.1 oblate since examined single crystal was a small-sized, brittle, weakly diffracting (despite using Mo  $K_{\alpha}$  radiation) and presence of atoms disorder. Herein data reported is the best one among the collected. Crystal structure solving purpose all non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen positions were fixed at calculated positions which is refined isotropically. Different crystallographic figures were designed using latest version of Diamond

software [61]. The crystallographic data and full structure refinement parameters for complex (1) is submitted in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1904939.

Formula	$C_{44}H_{48}N_6O_8S_2Zn_3$
M/g	1049.11
Crystal system	Monoclinic
Space group	$P2_{1}/c$
a/Å	24.371(3)
b/Å	19.435(2)
c/Å	19.8118(19)
α (°)	90
β (°)	93.833(3)
γ (°)	90
V/Å <sup>3</sup>	9363.2(17)
Z	8
$ ho_{ m c}/ m g\ cm^{-3}$	1.488
$\mu/\mathrm{mm}^{-1}$	1.671
F(000)	4320
Cryst size (mm <sup>3</sup> )	$0.045 \times 0.031 \times 0.022$
$\theta$ range (deg)	0.997
Limiting indices	$-26 \le h \le 29$
	$-23 \le k \le 23$
	$-23 \le l \le 24$
Reflns collected	84684
Ind reflns	$17391[R_{\text{int}} = 0.1790, R_{\text{sigma}} = 0.1789]$
Completeness to $\theta$ (%)	0.997
Refinement method	Full-matrix-block least-squares on F <sup>2</sup>
Data/restraints/ parameters	17391/0/1151
Goodness-of-fit on $F^2$	1.034
Final <i>R</i> indices	$R_1 = 0.0990$

**Table 1** Crystal data and structure refinement parameters of complex (1)

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$[I > 2\theta(I)]$	$wR_2 = 0.2050$
R indices (all data)	$R_1 = 0.2076$
	$wR_2 = 0.2563$
Largest diff. peak and hole ( $e \cdot Å^{-3}$ )	0.964 and -2.486

## 2.4. Computational methodologies

Modelled complex (1) density functional theory (DFT) was implemented in GAUSSIAN 16 suite of programs [62]. Ground state energy of all the system is optimized in DMSO (Dimethyl Sulfoxide) and the integral equation formalism Polarizable Continuum Model (IEFPCM) was used to estimate the solvent effect [62]. The new highly parameterized estimated exchange-correlation energy functional M06 (Meta-generalized gradient approximation (GGA) functional exchange) chosen for the complete calculations within the framework of the DFT method [62, 63] where over all the atoms, a valence double-zeta polarized basis array 6-31 G\* was applied. The vibrational analysis was performed based on the second derivatives to confirm the existence of the minima of the potential surface which confirms the absence of imaginary frequency. To obtain electronic absorption spectra, vertical transition energies, oscillator strength, the time-dependent density functional theory (TD-DFT) was employed at M06/6-31G\* level of theory in DMSO by using same IEFPCM model [62]. The GaussView 6 software was used to visualize optimized structures, molecular electrostatic potential (MESP) map, frontier molecular orbital graphics and theoretically calculated UV-Vis spectra [64]. Gauss sum [65] was utilized at the finale phase of calculations to compute the fractional contribution of the various individual components in the crystal to each molecular orbital. The first hyperpolarizability ( $\beta^{hyp}$ ) and its components

were theoretically calculated at M06/6-31G\* level of theory by adopting the finite field (FF) approach. The FF approach, which provides very constant results in accordance with the experimental results, was used to calculate the first hyperpolarizability ( $\beta^{hyp}$ ) of a variety of chemical systems. [66a] The total static dipole moment is determined by using equation (1) as

$$\mu = \mu_x^2 + \mu_y^2 + \mu_z^2$$

(1)

The isotropic polarizability calculated by using equation (2) as:

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

(2)

The first-order hyperpolarizability  $(\beta^{hyp})$  is:

$$\beta^{\text{hyp}} = \left[ \left( \beta_{xxx}^{\text{hyp}} + \beta_{xyy}^{\text{hyp}} + \beta_{xzz}^{\text{hyp}} \right)^2 + \left( \beta_{yyy}^{\text{hyp}} + \beta_{yzz}^{\text{hyp}} + \beta_{yxx}^{\text{hyp}} \right)^2 + \left( \beta_{zzz}^{\text{hyp}} + \beta_{zxx}^{\text{hyp}} + \beta_{zyy}^{\text{hyp}} \right)^2 \right]^{\frac{1}{2}}$$
(3)

The Hirshfeld surfaces and the 2D fingerprint plots were calculated using the Crystal Explorer [66b] software, which accepts a CIF-format structure input file obtained as a result of single-crystal X-ray diffraction. HS is the external contour of the space consumed in a crystalline environment by a molecule or an atom. The normalized contact distance  $d_{norm}$  is a function of distances to the surface from nuclei (atoms) inside (d<sub>i</sub>) and outside (d<sub>e</sub>) the Hirshfeld surface, compared with their respective van der Waals radii ( $r_i^{vwd}$  and  $r_e^{vwd}$ ) and expressed as:

$$d_{norm} = \frac{d_i - r_i^{vwd}}{r_i^{vwd}} + \frac{d_e - r_e^{vwd}}{r_e^{vwd}}$$

(4)

The combination of  $d_e$  and  $d_i$  as a 2D fingerprint plot summarizes intermolecular contacts in the crystal. The 2D fingerprint plots were displayed in the 0.5 – 3.0 Å range. The topological analyses were performed by the Bader's "atoms-in-molecules" theory by means of Multiwfn software [66c].

## 2.5. Molecular docking

The bacterial cytochromes P450 are cytosolic heme-thiolate proteins from a superfamily of heme-containing monooxygenases and analogous to eukaryotic mitochondrial P450 system. These enzymes are involved in several important physiological processes like metabolism of fatty acids and xenobiotics, catabolism of compounds used as carbon source and the production of biologically active secondary metabolites such as antibiotics or antifungals [67]. Bacillus and Mycobacteriam are two clinically significant bacterial genera due to their deleterious roles in various human diseases [68-69]. Moreover, emergence of new drug resistant strains from these genera has worsen the scenario nowadays and it needs new alternatives of conventional treatment strategies. Bacterial cytochrome P450 can be a novel therapeutic target as it coordinates many metabolically essential pathways [69-70]. In this study, we selected cytochrome P450 from B. megaterium and M. tuberculosis as representative model for docking analysis. Molecular docking was performed using cytochrome P450 of *B. megaterium* (PDB ID: 1FAG; resolution=2.7 Å) and *M. tuberculosis* (PDB ID: 3G5H; resolution=1.4 Å). The crystallographic structures of the protein with their downloaded native ligands were from RCSB Protein Data Bank (PDB) [https://www.rcsb.org/pdb]. The active site of the enzymes was defined using a radius of 5 Å around natural ligand which was extracted from the PDB.

2.6. Synthesis of Schiff base

Schiff base  $(H_2L^{OMe-pn})$  has been synthesized in our laboratory following the common literature method (Scheme 1) [71]. Briefly, ligand was obtained by refluxing 2, 2-dimethyl-1, 3-propanediamine (0.0511 g, 0.5 mmol) with 3-methoxy-2-hydroxybenzaldehyde (0.152 g, 1 mmol) in (50 mL) in methanol at 70°C for 3 h. Vacuum evaporation of this yellow solution gave the desired ligand in semisolid form. Ligand solution was evaporated to (15 mL) and the concentrated solution used for complex preparation without further purification.

N, N-bis(3-methoxysalicylidene)-2, 2-dimethylpropane-1, 3diamine: Yield: (68%), elemental analysis calcd (%) for C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>: C 68.09, H 7.07, N 7.56; Found: C 68.07, H 7.03, N 7.52. IR (KBr cm<sup>-1</sup>): v=1652 (vs), 1252 (s), 3378 (s), <sup>1</sup>H NMR (DMSO-d6, 300 MHz):  $\delta$  (ppm): 3.3 (s, 3H<sup>1</sup>), 6.7-7.0 (m, 1H<sup>2</sup>, 1H<sup>3</sup>, 1H<sup>4</sup>), 8.5 (m, 1H<sup>5</sup>), 13.86 (1H<sup>6</sup>) (Scheme S3, Fig. S2A),UV-Vis  $\lambda_{max}$  (MeOH): 219 and 266 nm.



Scheme 1 Synthesis of compartmental Schiff base ligand  $(H_2L^{OMe-pn})$ 

# 2.7. Synthesis of $[Zn_3(L^{OMe-pn})_2(\eta^1-NCS)_2]$ (1)

To the methanolic solution (15 mL) of zinc acetate dihydrate (0.2195 g, 1 mmol), (15 mL) concentrated ligand (H<sub>2</sub>L<sup>OMe-pn</sup>) solution was added drop wise and the resulting solution was stirred for 1 h. Then (10 mL) methanolic solution of KSCN (0.097 g, 1 mmol) was added to it. The overall reaction mixture was refluxed for 25 min at 80  $^{0}$ C followed by addition of few drops (1:1) mixture of (CH<sub>3</sub>CN+DMF). Further, stirring was continued for about 1 h. Finally, colourless filtrate was kept for crystallization by slow evaporation at room temperature. Single colourless crystals, suitable for X-ray diffraction were obtained after 7 days on slow evaporation of the solution in open atmospheric condition. Crystals were isolated by filtration and air dried. Yield: 0.290 g, Anal. Calc. for C<sub>44</sub>H<sub>48</sub>N<sub>6</sub>O<sub>8</sub>S<sub>2</sub>Zn<sub>3</sub>: C, 50.37; H, 4.61; N, 8.01. Found: C, 50.40; H, 4.63; N, 8.04 %. IR (KBr cm<sup>-1</sup>) selected bands: v(C=N), 1622 vs, v(C-O<sub>Phenolic</sub>) 1219 s, v(SCN) 2086 vs, v (Zn-N) 467 s, FT-Raman (cm<sup>-1</sup>) selected bands: v(C=N), 1632 vs, v(SCN) 2109 vs, UV-Vis  $\lambda_{max}$  (DMF): 280 and 362 nm.

## 3. Results and discussion

## 3.1. Synthesis

The present study is based upon the employment of one N<sub>2</sub>O<sub>2</sub>O'<sub>2</sub> donor compartmental Schiff base which was synthesized by the condensation of 2, 2-dimethyl-1, 3-propanediamine with ortho vanillin in MeOH at (1:2 M) ratio [71]. Complex (1) was derived from compartmental ligand in moderate yield by taking the following procedure where (1:1:1 M) ratio of Zn(II) acetate dihydrate, Schiff base and KSCN in minimum volume methanolic solution under stirred and refluxing condition followed by few drops of (1:1) mixture (CH<sub>3</sub>CN+DMF) (Scheme 1). Colourless block shaped crystals of complex (1) appeared at the junction of the solutions after few days. Complex (1) possess trinuclear building blocks where two terminal zinc metal centres (Zn1 & Zn2) presence in crystallographic asymmetric unit that are placed at the inner N<sub>2</sub>O<sub>2</sub> cavities. Further, [SCN<sup>-</sup>] ions function as  $\eta^1$  coordination mode (Scheme S2, ESI) allowing distorted square pyramidal environment while terminal Zn(II) ion (Zn2) in the outer  $O_2O_2$  compartment fulfilled octa coordination with square antiprismatic geometry. The above stereochemical occupancy of zinc metal ions are similar with other reported salentype compartmental Zn<sub>3</sub>-Schiff base complexes [72-76]. Structural skeleton of Schiff base (Scheme S1, ESM) completely divulges its compartmental hexadentate nature since it comprises two pockets (Scheme 2) and such pocketing nature is identical with other reported salen-type compartmental ligands (Scheme S1A, ESM). Meanwhile, Table 2 further highlighted few examples of Zn<sub>3</sub>-type Schiff base complexes basic structural motif where most of the reported complexes are normal trinuclear Zn(II) without exception  $\{Zn(DMF)[Zn(L^3)(H_2O)(SCN)]\}_2$  [73]. Therefore, judicious literature survey received some basic knowledge of current Schiff base compartment utilization (N2O2 vs O2O2) during homo/heterometallic complex formations. Synthesized complex stoichiometry was confirmed from different microanalytical results and characterized by FT-IR, Raman, UV-Vis, <sup>1</sup>H NMR, SEM-EDAX, PXRD, single X-ray crystal diffraction as well as fluorescence spectroscopy.



Scheme 2 Synthetic route for  $Zn_3$ -nuclear metal complex (1)



Scheme 3 Existing compartmental ligand showing N<sub>2</sub>O<sub>2</sub> vs O<sub>2</sub>O<sub>2</sub> pocket

Zn <sub>3</sub> -Schiff base complexes	[SCN <sup>-</sup> ] ion bridging	Pockets (N <sub>2</sub> O <sub>2</sub> vs	Ref
		$O_2O_2$ ) used	
$\{Zn(DMF)[Zn(L^3)(H_2O)(SCN)]\}_2$	$n^1$ -NCS bonded only	Ves	73
	reported	<b>y</b> 08	15
	reported		
$\frac{1}{2\pi \left[\frac{7}{2} \left(\frac{1}{2}\right) \left(\frac{3}{2}\right) \left(\frac{1}{2}\right) \left(\frac{1}{2}\right$			72
$Zn[Zn(L^{-})(\mu_2-HCOO)(DMF)]_2.H_2O$	-	yes	13
$Zn[Zn(L^3)(\mu_2-HCOO)]_2$	-		
2			
$Zn[Zn(L^3)(\mu_2-OAC)]_2$	-		
$Zn[Zn(L^{3})(\mu_{2}-NO_{2})(EtOH)]_{2}.2H_{2}O$	-		
		C.	
$[Zn(Saldmen)_3(OH)](ClO_4)_20.25H_2O$	-	yes	75
$[Zn_{3}(H_{2}L_{1})_{2}(OAc)_{2}]$	-	ves	74
		<b>J U</b>	, -
$[7n_{2}(H_{2}I_{2})_{2}(OA_{1})]$ EtOH DME			
$[\mathbf{Z}_{\mathbf{n}}(\mathbf{I})(\mathbf{OA}_{\mathbf{n}})]$			76
$[ZII_3(L)_2(OAC)_2]$		yes	70
$[Zn_3(L^{OWPPH})_2(\eta^*-NCS)_2]$	$\eta$ -NCS coordinated	yes	This
	with terminal Zn		work

# 3.2. Spectral characterizations

Common spectroscopic tools (FT-IR, Raman, UV-Vis) have been used for Schiff base and complex (1) characterizations purpose (Fig.S1, Fig.S2, Fig. S3, Fig. S4). The different FT-IR stretching values are properly listed in Table 3. The characteristic imines (C=N) stretching vibration of synthesized ligand was found nearly to be 1652 cm<sup>-1</sup> [77]. The absence of the N-H stretching band from trinuclear complex (at 3150 cm<sup>-1</sup>) conclusively confirmed the condensation of all the primary amine groups [77]. FT-IR stretching value at 3378 cm<sup>-1</sup> of Schiff base is due to O-H stretching which is completely vanished from 1. In 1, FT-IR and FT-Raman (C=N) stretching vibration bands are shifted to 1622 cm<sup>-1</sup> (for IR) (Fig. S2) and 1632 cm<sup>-1</sup> (for Raman) respectively (Fig.S3). These spectral data directly reflect the coordination mode of the imine nitrogen atom to the zinc metal ion centre [78]. 1 displayed strong bands at 2086 cm<sup>-1</sup> (for FT-IR) and 2109 cm<sup>-1</sup> (for FT-Raman) [79,80] which are

directly attributable to v(SCN) binding mode (Fig.S2). Aliphatic C-H stretching resonance in **1** observed at 2932-2964 cm<sup>-1</sup> (for FT-IR) and 2916 cm<sup>-1</sup> (for FT-Raman) respectively. Also, Ar-O stretching frequency observed at 1219 and 1221 cm<sup>-1</sup> (for FT-IR and Raman) nearly identical with previously reported salen-based ligands [81]. Herein the bridging fashion of [SCN<sup>-</sup>] ions were compared thoroughly with previously reported pseudo-halide linked Zn(II)-Schiff base complexes (Table S2 and Table S2A) to support the existence of [SCN<sup>-</sup>] spacers in complex (**1**).

Compounds	$\nu$ (C=N)	$v(C-O_{Phenolic})$	v(O-H)/H <sub>2</sub> O	ν(N-H)	v(Zn-N)	$v(SCN^{-})$
(H <sub>2</sub> L <sup>OMe-pn</sup> )	1652	1252	3378	3150-3450 absence	-	-
1	1622	1219	2	-	467	2086 vs

Table 3 FT-IR spectral data (cm<sup>-1</sup>) of Schiff base and complex (1)

## 3.3. UV-Vis spectra

The complexing behaviour of zinc metal ion on the absorption property of the compartmental Schiff base ligand was explained using UV-Vis absorption spectra after measuring the same experiment in DMF. Free Schiff base ligand in MeOH exhibit band near at 219 nm and 266 nm which can be attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  type of transitions within the Schiff base ligand while for Zn<sub>3</sub>-nuclear metal complex in DMF exhibit ligand-based bathochromic shifts UV-Vis spectra at 280 nm and 362 nm respectively (Fig. S4). This is mainly attributed to  $L \rightarrow M$  charge transfer  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  type transitions [78,82]. Fig.S4 confirmed the shape and intensity of the absorption spectrum are typical of bis (iminophenolato) ligands [83]. Moreover, the UV-Vis absorption spectrum of Schiff base ligand and complex are almost unchanged in presence of triethylamine base (TEA) but changes broadening peak by the presence of HCl into the solution (Fig. S4A-S4B). This absorption behaviour is typically

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observed for salen ligands when complexed with Zn [84,85]. Further, UV-Vis spectra divulge the coordination mode of the ligand with zinc metal ions in  $\mathbf{1}$  which are red shifted. Herein the metal centric broad d-d absorption band was unexpected since  $d^{10}$  configuration zinc metal ion is diamagnetic.

## 3.4. <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR spectroscopy is one of the essential tool to justify the Schiff base formation and its effective binding ability with Zn(II) metal ion. At the same time, we have considered standard *ortho* vanillin <sup>1</sup>H NMR spectral data to explain the changes of reaction occur between the aldehyde group (-CHO) in ortho vanillin and diamines during Schiff base formation. The <sup>1</sup>H NMR proton numbering scheme of synthesized Schiff base and Zn<sub>3</sub>nuclear metal complex are submitted in Scheme S3 and Fig. S2A-Fig.S2B. <sup>1</sup>H NMR spectra of ligand clarified that no broad peak was identified in the region  $\delta$  5.0-8.0 ppm that further confirmed the absence of free -NH<sub>2</sub> group function. Moreover, the formation of Schiff base ligand was confirmed by the appearance of azomethine (-CH=N-) proton signal (<sup>5</sup>H) near  $\delta$ 8.5 ppm [86]. Schiff base Ligand exhibit proton NMR signals specially for aromatic, OCH<sub>3</sub> (<sup>1</sup>H) and phenolic OH (OH<sup>6</sup>) protons near at  $\delta$  6.7-7.0 ppm,  $\delta$  3.3-3.7 ppm and  $\delta$  13.86 ppm respectively [87]. Now after comparison of the ligand chemical shift value with that of Zn<sub>3</sub>type metal complex, it confirms that phenolic proton (OH<sup>6</sup>) signals is totally vanished in the synthesized Zn(II) complex suggesting coordination mode of the phenolic oxygen with Zn(II)metal ion after deprotonating function of the Schiff base [88]. Apart from, the azomethine (-CH=N-) proton (<sup>5</sup>H) undergoes a significant chemical shift further confirmed the coordination motif of azomethine nitrogen to the zinc metal ion during formation of Zn<sub>3</sub>nuclear metal complex [86].

## 4. X-ray single crystal structure

## 4.1. Crystal structure of $[Zn_3(L^{OMe-pn})_2(\eta^1-NCS)_2]$ (1)

The single crystal of homo-trinuclear complex (1) has been grown in the mixture of solvent CH<sub>3</sub>OH and few drops of (1:1) mixture of CH<sub>3</sub>CN+DMF in the ratio of metal ion (Zn<sup>2+</sup>): ligand (H<sub>2</sub>L<sup>OMe-pn</sup>): co-ligand (KSCN) is 1:1:1. When the block shape colorless crystal was subjected to the X-ray crystal diffraction, it reveals that the asymmetric unit contains two identical discrete unit and each discrete unit contains three zinc metal ions which are crystallographic independent, two deprotonated form of Schiff base  $[L^{OMe-pn}]^{2-}$  and two co-ligands, [SCN] ions. Thus, the formula of each discrete unit is  $[Zn_3(L^{OMe-pn})_2(\eta^1-NCS)_2]$ . The complex crystallizes in the monoclinic space group P121/c1 with Z=8 and further crystallographic studies divulge that all the metal ions are full occupancy and the charge of the complex is balanced by the co-ligand [SCN<sup>-</sup>] ions and the Schiff base  $[L^{OMe-pn}]^{2-}$ . The ORTEP and the perspective view of asymmetric unit of complex (1) is shown in Fig.1 and Fig.2. The selected some important bond lengths and bond angles are given in Table S1.



Fig.1. ORTEP diagram of complex (1) (30 % ellipsoid probability)



**Fig.2**. The perspective view of the asymmetric unit of **1** (Hydrogen atoms are omitted for clarity)

From the design point of view, ligand ( $H_2L^{OMe-pn}$ ) is having two tetradentate pockets and the binding atoms of one pocket is O2N2 whereas in another pocket is 40 (Fig.3a). Additionally, the ligand having two hydroxyl (-OH) groups which are deprotonated during complex formation consequent to binding with the zinc metal ions. Further close inspection of the crystal structure, it is found that each ligand ( $H_2L^{OMe-pn}$ ) binds with the two zinc metal ions and in each discrete unit the middle zinc metal ion having octa coordinated which is actually the outer zinc metal ion (green circle in Fig. 3b), of each ligand ( $H_2L^{OMe-pn}$ ) is symmetrically shared by the these two ligands ( $H_2L^{OMe-pn}$ ) leading to the linear homo-trinuclear zinc metal cluster of formula [ $Zn_3O_8N_4$ ]<sup>2+</sup>. The octa coordinated stereochemical environment of zinc metal ions (Zn2 & Zn5) is already identical with previously reported Zn(II)-Schiff base complexes [72]. To avoid steric interaction between –OMe groups at each end of ( $H_2L^{OMe-pn}$ ) the position of the two ligands [ $L^{OMe-pn}$ ]<sup>2-</sup>in each discrete unit is almost perpendicular with each other in order to attain maximum stability (Fig. 3b). Aside from, the coordination activity afforded by the ligand [ $L^{OMe-pn}$ ]<sup>2-</sup>, two [SCN<sup>-</sup>] anions further attack on the linear trimeric zinc metal

cluster with the formula  $[Zn_3O_8N_6]$  (Fig. 3c). The position of the each  $[SCN^-]$  anion is perpendicular with respect to the ligand  $[L^{OMe-pn}]^{2-}$  and looks like an insect trunk (Fig.3d).



**Fig. 3**. (a) The tetradentate pocket in the ligands  $(H_2L^{OMe-pn})$ ,  $[Zn_3O_8N_6]$  in complex (1), (b) the position of the two ligands  $[L^{OMe-pn}]^{2-}$  unit (almost perpendicular to each other, green and blue circle represent the presence of zinc metal ions.) (c) trimeric zinc metal cluster and (d) the perpendicular position of the [SCN<sup>-</sup>] anion with respect to ligand  $(H_2L^{OMe-pn})$ 

Moreover, further analysis of the crystal structure discloses the number of non-covalent interaction (C-H···· $\pi$ ,  $\pi$  ·· $\pi$  and hydrogen bonding interactions) (Fig. S7A) exist between the two discrete part in the asymmetric unit (Fig. 4).



Fig.4. The non-covalent interaction in complex (1)

The binding fashion of each ligand  $[L^{OMe-pn}]^{2}$  to the zinc metal ions in each discrete unit are same and Fig.S6A represents the binding platform of the coordinating atoms and their patterns are  $\eta$ 1-oxygen,  $\eta$ 2-oxygen and  $\eta$ 1-nitrogen of the ligand  $[L^{OMe-pn}]^{2}$ . The two [SCN<sup>-</sup>] anions in each discrete unit acts as a monodentate fashion ( $\eta$ 1-nitrogen) and binds to the at each end on the metal center in the trimeric metal core. This bridging modes of [SCN<sup>-</sup>] ion as well as bond lengths (Zn-NCS) (~1.981–2.091 Å) are similar to the previously reported Zn(II)-Schiff base complexes (Table S3). Meanwhile using compartmental N/O-donor Schiff base, we have successfully synthesized only homo trimetallic complex (1) while major preferential encapsulation of metals by the reference ligand leads to heterometallic complex formations (Table S6). To the best of our knowledge this is the first homo trimetallic system where two compartments are solely occupied by zinc metal ions with  $\eta^1$ -NCS coordination mode of terminal zinc only.

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The structural environment for five coordination number zinc metal centres (Zn1 and Zn3) were calculated from Addison parameter Tau (r), (r = $|\beta - \alpha|/60^\circ$  where  $\beta$ ,  $\alpha$  are the two largest angles around zinc metal atom; r =0 for a perfect square pyramidal and 1 for a perfect trigonal bipyramidal geometry [89]. Thus, coordination number of metals Zn1, Zn2 and Zn3 are five, eight and five respectively and these coordination numbers are fulfilled by 2O, 3N for Zn1, 8O for Zn2 and 2O, 3N for Zn3, afforded distorted square pyramidal, square antiprismatic and distorted square pyramidal respectively (Fig. S7C). The Addison tau ( $\tau$ ) parameters are 0.611, 0.150 for Zn1 and Zn3 respectively (ideal value of tau for square pyramidal geometry is 0). Similar geometry around the metal centers are shown by metals (Zn4, Zn5 and Zn6) in the other discrete unit (Fig. S7B). As a result, it's generated a homo trimetallic system. The average distances between two Zn atoms is 3.531Å {Zn1-Zn2 = 3.525, Zn2-Zn3 = 3.530, Zn4-Zn5 = 3.552, Zn5-Zn6 = 3.520} and the average angle between them is 106.33 ° {Zn1-O11-Zn21 = 105.4(3) °, Zn1-O10-Zn2 = 105.1(2)°, Zn3-O14-Zn2 = 106.7(3)°, Zn3-O15-Zn2 = 107.1(3)°, Zn6-O2-Zn = 106.1(3)°, Zn6-O3-Zn5 = 105.9(3)°, Zn4-O6-Zn5 = 107.3)°, Zn4-O7-Zn5 = 107.5(3)°}. In fact, the Zn-Zn bond distances (Å) are

comparable to other trinuclear zinc metal complexes (Table S4).

## 4.2. SEM-EDAX

The chemical composition of the trinuclear complex (1) was analysed with the help of SEM-EDAX profile analysis. Further, the chemical composition of the complex was confirmed from EDAX profile. The weight percentage (%) contribution of the elements is shown in Table S5 and their EDAX profile in Fig.S5A. The calculated and EDAX values of essential elements in Zn<sub>3</sub> complex are nearly good agreement. Preferably EDAX profile contained only predictable elements and no impurity of other elements are present. Therefore, the empirical formula of **1** is formulated as  $C_{44}H_{48}N_6O_8S_2Zn_3$ . Interestingly, the EDAX profile of trinuclear complex reflects the highest peak of C followed by O, N, Zn which further agreed

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the empirical formula. Besides, the important structural morphological features are supported by SEM (scanning electron microscope) analysis. SEM images characterized the size and morphological structure of the trinuclear zinc metal complex. Herein, micrograph of SEM (Fig.S5B) clearly explores that the morphology of the complex (1) is plate shape up to 2  $\mu$ m.

4.3. X-ray powder diffraction

Powder X-ray diffraction patterns for complex (1) were recorded at room temperature. The PXRD patterns were recorded experimentally by scanning the compound in the range  $(2\theta=4^{0}-50^{0})$ . According to Fig.S6 the well-defined sharp PXRD peaks is due to crystalline nature of the complex. The experimental PXRD patterns (Fig.S6) of the bulk materials of the complex are similar with the patterns simulated from single X-ray crystal diffraction data (CIF for 1) which is obtained from CCDC Mercury software consisting that single crystals and bulk material are the same. The results of PXRD analysis can provide the additional confirmation of the phase purity of each bulk samples of the complex.

## 5. DFT analyses

### 5.1. Hirshfeld Surface

The non-covalent supramolecular interactions in complex (1) were explained on the basis of HS and 2D fingerprint analysis where Fig.5 provides the details of  $d_{norm}$ , shape index, curved index, fragment patch and 2D finger print plots for complex (1). In 1, the total volume of the surface was 2323.70 Å<sup>3</sup>, globularity is 0.635 and asphericity 0.285. 2D finger plots provide information on various forms of interactions between these complexes and other atoms of the surround molecules. The close inspection of Table 4 reveals that for complex (1), the major contribution to the crystal packing is interactions H…H (56.8%) followed by 10% of interaction is between the C-H and H-C (8.8%), 6.6% between the nearby hydrogen atom and sulfur atoms, and 0.5% between oxygen and hydrogen atoms. Remaining contacts which are less than 0.5% are negligible.

SL. No.	Type of interactions	<b>Contribution (%)</b>
1.	C····C (i.e. $\pi$ ···· $\pi$ )	0.6
2.	C····H (i.e. C-H··· $\pi$ )	10
3.	$S \cdots H$ (i.e. C- $S \cdots H$ )	6.6
4.	N····H	1.9
5.	C-H··· O	0.5
6.	Н…С	8.8
7.	H···H	56.8

Table 4 Different type of interactions on HS in complex (1)





Curvedness



Shape Index





Fig. 5. Hirshfeld surfaces analysis for complex (1):  $d_{norm}$ , Shape index, curvedness and different 2D fingerprint plots

## 5.2. Energy and HOMO-LUMO analysis

Complex (1) was optimized in DMSO using a PCM model for including solvent effect at M06/6-31G\* level of theory. Fig. 6 portrays the ground state geometry of discrete unit of complex (1). Theoretically calculated structure is in accordance with the crystal structures where it depicts it is a trinuclear homometallic Zn(II) complex. In this structure peripherals Zn pentacoordinate while Zn-atoms is atoms are central eightcoordinated. Also, both the  $[SCN^{-}]$  co-ligands and nitrogen atoms of  $[L^{OMe-pn}]^{2-}$  ligands are

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attached with the peripheral Zn-atoms where central zinc attached atom is with nearby oxygen atoms. The distance between two Zn-atoms are 3.23 Å which is almost similar to crystal structure data (3.51 Å). Interesting outcome has been drawn on the basis of mapping of the frontier molecular orbitals (FMOs) for complex (1). HOMO (highest occupied molecular orbital) value dictates the electron donating ability of (1) and LUMO (lowest unoccupied molecular orbital) indicates the electron accepting nature of the molecule. It is also well known that information of the delocalization of the  $\pi$  let electron cloud is necessary to derive the non-linear optical properties of  $\pi \Box$  conjugated complexes [90]. From the close inspection of the HOMO-LUMO density plot, HOMO of 1 is largely contributed by the Schiff base ligand (H<sub>2</sub>L<sup>OMe-pn</sup>) and its deprotonated hydroxyl group which coordinated with the central Zn-atom of the one discrete unit of 1. Whereas in LUMO, the electron density is mainly distributed over both the ligand (H<sub>2</sub>L<sup>OMe-pn</sup>) and on one co-ligand [SCN<sup>-</sup>]. Bridging is found to be strong and stable as it does not contribute much to HOMO or LUMO in the bridging process and affects the stability of the complex.



Fig. 6. Ground state geometry of a discrete unit of 1 (black colour balls represent carbon

atoms)

Investigation of FMOs reveals that HOMO has energy of -5.63 eV and LUMO has -1.56 eV and HOMO LUMO density plot (Fig.7) was used for the probing of FMOs of the complex (1). HOMO-LUMO energy gap ( $\Delta E = E_{LUMO} - E_{HOMO}$ ) is 4.07 eV which makes the complex stable and can be associated with the band gap of the compound. Theoretical UV-Vis spectra were also calculated to further confirm the semiconducting properties of 1 within 200-600 nm region of the wavelength (Fig.S9). The theoretical band gap here is within the range of 3-6 ev described for the wide bandgap semiconductors [91, 92]. From this point of view complex (1) possess the semiconducting property also since its bandgap is around ~4.07 eV (wide-bandgap semiconductor), its use in different devices will allow devices to work at much higher voltages, frequencies and temperatures than traditional semiconductor-based products. Recently Zn(II)-based 1-D CP observed similar theoretical bandgap so that CP can behave as semiconducting property [92]. Complex (1) can be well used next-generation devices for general semiconductor based on these wide-bandgap.



**Fig.7.** Frontier molecular orbitals of complex (1) ( $\Delta$ : Energy gap between HOMO and LUMO)

## 5.3. MEP

To understand the relationship between molecular structure and behaviour, molecular electrostatic potential (MESP) was calculated. The MEP is defined as the potential experienced by a unit positive charge near the molecule due to the distribution of electron density. MEP indicates the relative polarity of the molecule as the positive potential of electrophilic attack sites can be predicted while the adverse potential indicates nucleophilic

attack sites. The expression for the MEP is given at any point in the space close to the molecule

$$V(r) = \sum \frac{z_A}{|R_A - r|} - \int \frac{\rho_{(r')dr'}}{|r' - r|}$$

(5)

Where,  $z_A$  is the charge on nucleus *A* that was studied at  $R_A$ ,  $\rho(r^{*})$  is the electron density. *V* (*r*) defines the net electrostatic effect of the total charge distribution (electrons + nuclei) of the molecule at point r. MEP mapping has recently played a significant role in analysing the geometric structure and polarity of different molecular systems also in charge density analysis [93]. To visualize electrophilic and nucleophilic regions in complex (1), MEP was generated on DFT optimized structures at M06/6-31G\* level of theory (Fig.S7D). In 1, nitrogen, oxygen and sulphur are the electronegative atoms and two [SCN] co-ligands, hence, these regions indicate the most negative MEP while rest of the area has blue colour which indicate the positive MEP (electrophilic). The potential on MEP surface of complex (1) is following the order as; red < yellow < orange < green < blue. In the discrete unit of 1, highest negative potential between [SCN<sup>-</sup>] ion and metal centre (Zn) leads to the formation of asymmetric unit of complex (1) via hydrogen bonding which consist two symmetric discrete units and provides the stability to their strong structure (Fig.4, single-crystal X-ray structure).

### 5.4. TD-DFT

In DMSO, additional TD-DFT computations were performed to quantify the contributions to absorption spectra from different frontier orbitals (Table S9). It is evident from the results that HOMO-LUMO is the main molecular orbital contributor in the area responsible for transfer (CT) in complex (1) (Table S9). Figure S10 displays the TD-DFT predicted UV – Vis spectra of complex (1). The analyses indicated two major electronic transitions with

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oscillator strength of 0.071, 0.018, and 0.039 at 368 nm, 365 nm and 347 nm (Experimental ~362 nm for 1). Herein, the oscillator strength is higher for the vertical transition at 368 nm which can be correlated to experimentally  $\lambda_{max}$  362 nm. The first electronic transition is mainly due to the transition of electron from the HOMO to LUMO (72%) and HOMO $\rightarrow$ L+2 (16%). The second transition is from HOMO $\rightarrow$ L+1 (68%) and HOMO $\rightarrow$ L+3 (17%). The third transition is mainly from HOMO $\rightarrow$ L+2 (52%) and HOMO $\rightarrow$ L+1 (14%). HOMO of complex (1) consists primarily of  $\pi$ -orbitals, while LUMO consists of  $\pi$ \*-orbitals.

## 5.5. NLO property

 $\Delta E$  is correlated with the transfer of electron density from the HOMO to the LUMO and its value is important for determining NLO properties of the molecular systems. Nonlinear optics deals with the interactions between various materials and applied electromagnetic (EMT) fields applied which generates a new EMT field with change in frequency, phase or other physical properties. For a device to be useful in a device must exhibit a high degree of nonlinearity at a reasonable power level. In complex (1), the values for different parameters such as electric dipole moment ( $\mu$ ), polarizability ( $\alpha$ ) and first hyperpolarizability ( $\beta^{hyp}$ ) were calculated at the M06/6 $\square$ 31G\* level of theory (Table 5). The first hyperpolarizability ( $\beta^{hyp}$ ) value for complex (1) was calculated to be 39.55 × 10<sup>-31</sup> esu. The activity shown by complex (1) is may be due to the increased distribution of  $\pi$ -electronic charge at the ground state by donor and acceptor moieties under the impact of an electrical field. Furthermore,  $\beta^{hyp}$  is often associated with charge transfer bands arising from the movement of the electron cloud through the donor to the acceptor moieties through the  $\pi$ -electronic framework, and such electronic clouds interact with external fields, resulting in an increase in  $\beta^{hyp}$ . The ( $\alpha$  and  $\beta^{hyp}$ ) values are well demonstrate the NLO behaviour of complex (1) [93d].

**Table 5** DFT calculated dipole moment ( $\mu$ ), average polarizability ( $\alpha$ ) and first hyperpolarizability ( $\beta^{hyp}$ ) obtained at M06/6-31G\* level of theory

Complex	μ (Debye)	$\alpha$ (10 <sup>-22</sup> esu)	$\beta^{\text{hyp}}$ (10 <sup>-31</sup> esu)
1	11.53	0.37	39.55

## 5.6. AIM analysis

For determining the existence of long-range interactions in 1, the Bader's theory of "atoms in molecules" (AIM) have been used, which provides a clear description of chemical bonding by the topological analysis of it. For characterizing and understanding a variety of interactions in molecules the AIM theory has been successfully used. From Fig.S11, the AIM analysis shows the distribution of bond, ring critical points (RCPs) and bond paths in discrete unit of 1. According to Fig.S11, the presence of several bond (orange small spheres) and ring (small yellow sphere) critical points and bond paths (dark yellow lines) can be confirmed which is interconnecting several atoms thus confirming the existence of longrange interactions. Here, the presence of bond critical points (BCPs) and bond paths connecting two atoms are a clear and unambiguous evidence for the existence of an interaction. For all predicted chemical bonds, the CPs (3, -1) are located. During the analysis 'Poincare-Hopf' relationship was satisfied which confirms that all the CPs may have been found. It can be noticed that each C-H $\cdots\pi$ , C-H $\cdots$ S and C-H interactions are characterized by the bond critical points and bond paths that connects the hydrogen atoms with the C, O, S atoms. The AIM analysis also confirms the interaction between the central Zn-atom and oxygen of methoxy group of ligands. Here, it is also confirmed that both the [SCN] co-ligand is also interacting with methoxy group of Schiff base ligand by analysing the BCPs and bond paths. Consequently, ring CPs (yellow sphere) are also generated upon complexation due to the formation of the supramolecular ring in both the ligands. The yellow colour lines show the bond paths between ring critical point. The main CPs (3, -1) were located for both the [SCN<sup>-</sup>] co-ligand with Zn-atoms and between methoxy hydrogens and oxygen atoms (weak hydrogen bonds). Topological parameters for CPs (3, -1) for Zn-N and C-H...O bonds

(labelled in the Fig.S11) are listed in Table 6 that characterizes the noncovalent interactions. The critical points (3, -1) analogous to Zn-N and C-H...O bonds are depicted by positive values of  $\nabla 2\rho$  (Laplacian of  $\rho$  (r)) and negative value of total energy densities  $(H(\mathbf{r}))$ . It is an indication that bonds formed by Zn atoms are of intermediate types (interatomic interactions) and it shows these bonds are highly polar with significant ionic contribution. In addition, all intermolecular interactions lead to closed-shell interactions with  $\nabla 2\rho(\mathbf{r}) > 0$  and  $H(\mathbf{r}) < 0$  at CPs (3, -1). For assuring the presence of the intermolecular contacts, topological characteristics such as  $\rho(\mathbf{r})$  at CPs (3, -1) for Zn-N and C-H...O bonds are very crucial. This case is in accordance with the fact that  $\nabla 2\rho(\mathbf{r})$  values must be higher for Zn-N bonds. The value of  $\rho(\mathbf{r})$  at CPs (3, -1) is very useful for deciding the strength of the interactions. Here, the largest value of  $\rho(\mathbf{r})$  found for Zn-N type interactions for complex (1) is varying from 0.0883 to 0.006 a.u. The analysis of  $\rho(\mathbf{r})$  at CPs (3, -1) indicates that Zn-N type interactions are stronger than hydrogen bonds which will be further cleared by the analysis of bond energies. As clear from the crystal structure that the two outer zinc metal ions are shared by the two ligands (H<sub>2</sub>L<sup>OMe-pn</sup>) which leads to the linear homotrinuclear zinc metal cluster of formula  $[Zn_3O_8N_4]^{2+}$ . From the topological parameters, the bond energies of these Zn-N bonds including [SCN] co-ligands are of the range of ~15-18 kcal/mol which is comparatively higher in comparison with the bond energies of C-H...O bonds which are due to the interaction between methoxy hydrogen and oxygen atoms.

**Table 6.** Topological Parameters for complex (1) where  $\rho$ ,  $\nabla 2\rho$ , G(r), V(r) and H(r) are the electron density (a.u.), Laplacian density value (a.u.), Langangian kinetic energy (Hartree), potential energy (Hartree) and total energy density at critical points and bond energy |-E bond| respectively (in kcal/mol)

<mark>Bonds</mark>	<mark>ρ (r)</mark>	<mark>∇2ρ(r)</mark>	G(r)	V(r)	H(r)	-G(r)/V(r)	<mark> –E bond </mark>
(Zn-N)	0.0883	0.30544	<mark>0.1150</mark>	-0.1537	-0.0387	0.7482	18.9557
(Zn-N)	0.0733	0.2385	0.0855	<mark>-0.1114</mark>	-0.0258	0.7675	15.6095
(Zn-N)	0.0811	0.2577	<mark>0.0971</mark>	-0.1299	-0.0327	0.7474	17.3495
(C-H•••O)	0.0060	0.0268	0.0054	-0.0042	0.0012	1.2857	0.59618
(C-H•••O)	0.0110	0.0413	0.0093	<mark>-0.0083</mark>	0.0009	1.1204	1.71158
(Zn-N)	0.0879	<mark>0.3033</mark>	0.1142	-0.1525	-0.0383	<mark>0.7488</mark>	18.8664
(Zn-N)	0.0742	<mark>0.2410</mark>	<mark>0.0869</mark>	<mark>-0.1136</mark>	<mark>-0.0266</mark>	<mark>0.7649</mark>	15.8102
(Zn-N)	0.0811	0.2578	0.0971	-0.1298	-0.0326	0.748	<mark>17.3494</mark>

## 6. Fluorescence

Schiff base ligand is sufficiently soluble in methanol whereas complex (1) is soluble in DMF solvent. Therefore, to keep constancy about correct absorption and emission spectral studies we were undertaken reference spectra in MeOH and DMF solvent at room temperature (Table 7). Fluorescence spectra (Fig.8) revealing that the free Schiff base is practically shows fluorescence peak at *ca* 353 nm upon excitation at *ca* 300 nm which could be attributed to intra-ligand ( $\pi \rightarrow \pi^*$ ) type transition while for complex (1) photo excitation at the same wavelength shows bathochromic red shifted fluorescence maxima with the major emission peak at *ca* 479 nm. Moreover, the emission intensity of 1 is stronger than free ligand which also observed in similar complexes [94]. We have thoroughly checked the changes of fluorescence emission intensity (if any) after addition of triethylamine base (TEA) and HCl [Fig.S8-Fig.S9]. Interestingly, while the addition of TEA has almost no impact on the fluorescence emission of 1 but bathochromic red shift observed in case of ligand. In contrast,

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after addition of HCl on both ligand and Zn(II) complex fluorescence emission bathochromically shifted. This is common feature for other salen-type Zn(II) complexes. Apart from, it is notice for acidic solution fluorescence emission peak is maximum broadening [94]. Herein, emission arising from a protonated species of the ligand which is a common feature for salicylaldehyde [95] and salicylideneaniline [96] derivatives. Surprisingly, here emission arising from keto-enol tautomerism in the excited state common for ortho substituted several phenolic compounds for which a H-bond is formed between -OH and the ortho position substituent [97]. Complex (1) also demonstrated very large stokes shifts up to 179 nm which were calculated by considering the difference between absorption and emission wavelengths [98]. Synthesized Zn(II) complex observed stokes shifts 125 nm, 126, and 179 nm only in DMF, DMF+TEA (triethylamine) and DMF+ HCl. The large stokes shifts of Schiff base ligand over complex is due to solvent polarity [98]. The large stokes shifts are mainly attributed to the presence of bulky substituents reducing the intermolecular  $\pi$ - $\pi$  stacking [99]. The incremental enhancement of fluorescence emission intensity of 1 over free ligand may due to effective coordination via N, O-donor with Zn(II) metal ion, consequently increased the conformational rigidity via chelation effect [CHEF] and subsequently loss of energy by radiation less thermal vibration. In fact, the active fluorescence emission compared to free ligand may be due to d<sup>10</sup> configuration Zn metal ion is really difficult or hard to oxidize or reduce. This type fluorescence behaviour may be attributed due to the intra-ligand  $(\pi \rightarrow \pi^*)$  type transition or L $\rightarrow$ M charge transfer referred as CHEF (Chelation enhanced fluorescence) [100-108] The low quantum yield of ligand is due to fast Photoinduced electron transfer (PET) from nitrogen lone pair to the conjugated phenolic moiety in the reference Schiff base. Ligand-Metal effective complexation mode prevents PET process, thereby enhances the quantum yield ( $\phi$ ) of trinuclear Zn(II) complex

[109-111]. Fluorescence enhancement through  $Zn_3$ -type Schiff base complex formation opens up the opportunity for next generation photochemical applications.



Fig.8. Ligand-centred emission spectra for complex (1)

Table 7 Summary of steady-stat	e fluorescence of Schiff	base and complex (1)
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Schiff base	Abs	λ <sub>ex</sub> (nm)	$\lambda_{em}(nm)$		Stokes	Quantum Yield
	λmax				shifts	( <b>þ</b> )
	(nm)				(nm)	
$(H_2L^{OMe-pn})$ in	219,266	300	353		87	0.0346
MeOH						
$(H_2L^{OMe-pn})$ in	225,276	300	443		167	
MeOH + TEA						
$(H_2L^{OMe-pn})$ in	219,274	300	500		226	
MeOH + HCl						
Complex		A la a	2	2	Stoker	Quantum Viald
Complex		ADS	$\lambda_{ex}$	$\lambda_{em}$	SIUKES	Qualituin Tielu
Complex		Abs λmax	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	shifts	(¢)
Complex		Abs λmax (nm)	λ <sub>ex</sub> (nm)	$\lambda_{em}$ (nm)	shifts (nm)	Quantum Tield (φ)
Complex		Ads λmax (nm)	λ <sub>ex</sub> (nm)	λ <sub>em</sub> (nm)	shifts (nm)	Quantum Tield (φ)
$= [Zn_3(L^{OMe-pn})_2(\eta^1-NC)]$	CS) <sub>2</sub> ] (1)	Abs λmax (nm) 280,354	λ <sub>ex</sub> (nm) 300	λ <sub>em</sub> (nm) 479	shifts (nm) 125	Quantum Tield (φ) 0.0363
[Zn <sub>3</sub> (L <sup>OMe-pn</sup> ) <sub>2</sub> (η <sup>1</sup> -NC in DMF	CS) <sub>2</sub> ] (1)	Ads λmax (nm) 280,354	λ <sub>ex</sub> (nm) 300	λ <sub>em</sub> (nm) 479	stokes shifts (nm) 125	(φ) 0.0363
$\frac{[Zn_3(L^{OMe-pn})_2(\eta^1-NC)]}{[Zn_3(L^{OMe-pn})_2(\eta^1-NC)]}$	$CS_{2}(1)$ $CS_{2}(1)$	Abs λmax (nm) 280,354 280,359	λ <sub>ex</sub> (nm) 300	λ <sub>em</sub> (nm) 479 485	shifts (nm) 125 126	(φ) 0.0363
$[Zn_{3}(L^{OMe-pn})_{2}(\eta^{1}-NC)]$ in DMF $[Zn_{3}(L^{OMe-pn})_{2}(\eta^{1}-NC)]$ in DMF+TEA	$\frac{[S]_{2}(1)}{[S]_{2}(1)}$	Abs λmax (nm) 280,354 280,359	λ <sub>ex</sub> (nm) 300 300	λ <sub>em</sub> (nm) 479 485	stokes shifts (nm) 125 126	Quantum Tield (φ) 0.0363
$[Zn_{3}(L^{OMe-pn})_{2}(\eta^{1}-NC)$ in DMF $[Zn_{3}(L^{OMe-pn})_{2}(\eta^{1}-NC)$ in DMF+TEA $[Zn_{3}(L^{OMe-pn})_{2}(\eta^{1}-NC)]$	$\frac{[S]_{2}(1)}{[S]_{2}(1)}$	Abs λmax (nm) 280,354 280,359 300,347	λ <sub>ex</sub> (nm) 300 300 300	λ <sub>em</sub> (nm) 479 485 526	stokes shifts (nm) 125 126 179	Quantum Tield (φ) 0.0363
$[Zn_{3}(L^{OMe-pn})_{2}(\eta^{1}-NC)$ in DMF $[Zn_{3}(L^{OMe-pn})_{2}(\eta^{1}-NC)$ in DMF+TEA $[Zn_{3}(L^{OMe-pn})_{2}(\eta^{1}-NC)$ in DMF+TEA	$\frac{[S]_{2}(1)}{[S]_{2}(1)}$	Abs           λmax           (nm)           280,354           280,359           300,347	λ <sub>ex</sub> (nm) 300 300 300	λ <sub>em</sub> (nm) 479 485 526	stokes shifts (nm) 125 126 179	Quantum Tield (φ) 0.0363

## 7. Molecular docking

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The crystal structure of complex (1) was found to bind with Bacillus cytochrome P450 through stable hydrogen bonds with Ala264, Thr268, Ala330. Other amino acids like Ala74, Leu75, Thr88, Ala264, Ala328, Pro329 and Cys400 are involved in the formation of various types of hydrophobic interactions, whereas Lys69 could generate a weak electrostatic bond with the trinuclear Zn(II) complex (Fig.9 and Table S8). The de-solvation energy for this docking complex was -862.26 kcal mol<sup>-1</sup> having a geometric score of 6534. Other docking study with Mycobacteria cytochrome P450 also resulted to a favorable docked complex with a de-solvation energy and geometric score of -563.29 kcal mol<sup>-1</sup> and 7770, respectively (Table S7). Docking showed that the test crystal might be anchored into active site of the protein through H-bonds with His343, Gln385 and Arg386. Residues like Leu76, Val78, Val83, Ile102, Phe168, Phe230, Ala233 and Pro346 were the other amino acids found in this complex forming  $\pi - \pi$  and  $\pi$  – alkyl interactions (Fig.9 and Table S8). Bacterial cytochrome P450 was found to be very essential for their viability and thus inhibition of this enzyme could exhibit a potent antibacterial activity against a broad range of bacteria. The primary interactions found in the native substrate binding site of the *B. megaterium* cytochrome P450 were Pro329, Ala330 and Met354 which were also noticed in cytochrome P450-Zn<sub>3</sub> complex [68]. Additional regions of the native protein crystal structure involved in substrate contacts were Leu29, Leu75, Val78, Ile263, Ala264, Leu437 and Thr438. In this study, Zn<sub>3</sub>-type complex can form interactions with most of these residues as observed in our docking study. So, it can be predicted that complex (1) has the potentiality to inhibit the lipid metabolism activity of this cytochrome P450 by blocking the binding site for its actual substrate. The catalytic site of *M. tuberculosis* cytochrome P450 consisted of five vital residues viz. Ser237, Cys345, Pro346, Gln385 and Arg386, and Zn<sub>3</sub> crystal established strong H-bonding networks with His343, Gln385, Arg386 [70, 112] (Fig.9). Binding of Zn<sub>3</sub>-type complex to this cytochrome P450 involved numerous van der Waals contacts with hydrophobic side chains of

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Val78, Val83, Phe168, Ala233 and Phe280. Interestingly the same amino acids were found with the native ligand YTT ((3S,6S)-3,6-bis(4-hydroxybenzyl) piperazine-2,5-dione) which suggested us about the potentiality of Zn<sub>3</sub>-type complex as a lead to the development of antimycobacterial drugs (Table S8).



**Fig.9.** Molecular docking analysis of *B. megaterium* cytochrome P450 (A1 & A2) and *M. tuberculosis* cytochrome P450 (B1 & B2) with complex (1). In A1 and B1, complex is represented in green color and binding site is highlighted by purple colored solid surface. A2 and B2 show the illustration of crystal-amino acid interactions found within the respective docked complexes

## 8. Concluding remarks

The synthesis and characterization of one new trinuclear Zn(II) complex,  $[Zn_3(L^{OMe-pn})_2(\eta^1 - \eta^2)]$  $NCS_{2}$  (1) with compartmental N/O-donor Schiff base are described in this paper. Complex structure has been characterized by various spectroscopic protocols, PXRD, SEM-EDAX, fluorescence as well as single-crystal X-ray diffraction study. SCXRD study revealed that the stereochemical environment of zinc centres (Zn1/Zn3) are distorted square pyramidal while for central Zn2 attained octacoordinated square antiprism. Such stereochemical environment has been facilitated due to combine occupancy of N<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>O<sub>2</sub> compartments by unique zinc metal ions. Complex structure is optimized by DFT/M06 functional method using 6-31G\* basis set. The non-covalent supramolecular interactions were nicely explained in terms of HS and 2D fingerprint plots analyses. Herein the result reported primarily stress on the importance of HOMO-LUMO energy gap, MEP, TD-DFT, NLO and topological analyses using Bader's "atoms-in-molecules" concept. Complex (1) exhibit fluorescence emission in DMF solvent due to CHEF effect. Meanwhile, ligand and complex fluorescence spectral emission changes have been checked thoroughly in presence of DMF, DMF+TEA (triethylamine) and DMF+ HCl using stokes shifts. Finally, molecular docking was executed with cytochrome P450 from *B. megaterium* and *M. tuberculosis* as a representative model. Thus, the prospective study in the present manuscript deals a new insight in the development of antimycobacterial drugs as well as next-generation semiconductor devices.

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## Appendix A. Supplementary material

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Details supplementary data related to this article can be associated in ESM\_J MOL STRUC. CCDC number 1904939 contain the supplementary crystallographic data (excluding structure factors) in CIF format for the structure reported of complexes. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: <u>http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi</u>, e-mail: data\_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

## References

[1] H. Schiff, Ann. Suppl. 343(3)1864-1865.

[2] R. Hernandez-Molina, A. Mederos A, J. McCleeverty, T. J. Meyer, Comprehensive Coordination Chemistry II, vol 1, Elsevier, Amsterdam, p 411, 2004.

[3] A. Andruh, F. Tuna, M. A. Cato (Ed), Focus on Organometallic Chemistry Research, Nova Publishers, Hauppauge, p 144, 2005.

[4] B. K. Seth, A. Ray, A. Saha, P. Saha, S. Basu, Potency of photoinduced electron transfer and antioxidant efficacy of pyrrole and pyridine based Cu(II)-Schiff base complexes while binding with CT-DNA, J. Photochem. Photobiol. B 132 (2014) 72-84.

[5] M. Dehkhodaei, M. Khorshidifard, H. A. Rudbari, M. Sahihi, G. Azimi, N. Habibi, S. Taheri, G. Bruno, R. Azadbakht, Synthesis, characterization, crystal structure and DNA, HAS-binding studies of four Schiff base complexes derived from salicylaldehyde and isopropylamine, Inorg. Chim. Acta. 466 (2017) 48–60.

[6] A. Rauf, A. Shah, K. S. Munawar, A. A. Khan, R. Abbasi, M. A. Yameen, A. M. Khan,
A. R. Khan, I. Z. Qureshi, H. B. Kraatz, Z. Rehman, Synthesis, spectroscopic characterization, DFT optimization and biological activities of Schiff bases and their metal (II) complexes, J. Mol. Struct. 1145 (2017) 132–140.

[7] S. Jain, T. A. Khana, Y. P. Patilb, D. Pagariyac, N. Kishorec, S. Tapryald, A. D. Naike, S. G. Naik, Bio-affinity of copper(II) complexes with nitrogen and oxygen donor ligands: Synthesis, structural studies and in vitro DNA and HAS interaction of copper(II) complexes, J. Photochem. Photobiol. B 174 (2017) 35–43.

[8] P. Roy, M. Manassero, K. Dhara, P. Banerjee, Synthesis, characterization and fluorescence properties of hexanuclear zinc(II) complexes, Polyhedron 28 (2009)1133–1137.

[9] S. S. Bhat, A. A. Kumbhar, H. Heptullah, A. A. Khan, V.V. Gobre, S. P. Gejji, V. G. Puranik, Synthesis, Electronic Structure, DNA and Protein Binding, DNA Cleavage and Anticancer Activity of Fluorophore Labelled Copper(II) Complexes, Inorg. Chem. 50 (2011) 545–558.

[10] S. Dhar, M. Nethaji, A. R. Chakravarty, Synthesis, crystal structure and photo-induced DNA cleavage activity of ternary copper(II) complexes of NSO-donor Schiff bases and NN-donor heterocylic ligands, Inorg. Chim. Acta. 358 (2005) 2437–2444.

[11] M. F. Primik, S. Goschl, M. A. Jakupec, A. Roller, B. K. Keppler, V. B. Arion, Structure–Activity Relationships of Highly Cytotoxic Copper(II) Complexes with Modified Indolo[3,2-*c*]quinoline Ligands, Inorg. Chem. 49 (2010) 11084–11095.

[12] J. H. Li, J. F. Dong, H. Cui, T. Xu, L. Z. Li, A copper(II) complex of the Schiff base from L-valine and 2-hydroxy-1-naphthalidene plus 1,10-phenanthroline: synthesis, crystal structure, and DNA interaction, Transit. Met. Chem. 37 (2012) 175–182.
[13] G. Consiglio, S. Failla, P. Finocchiaro, I. P. Oliveri, R. Purrello, S. D. Bella, Supramolecular Aggregation/Deaggregation in Amphiphilic Dipolar Schiff-Base Zinc(II) Complexes, Inorg. Chem. 49 (2010) 5134–5142.

[14] T. D. Pasatoiu, C. Tiseanu, A. M. Madalan, B. Jurca, C. Duhayon, J. P. Sutter, M. Andruh, Study of the Luminescent and Magnetic Properties of a Series of Heterodinuclear
 [Zn<sup>II</sup>Ln<sup>III</sup>] Complexes, Inorg. Chem. 50 (2011) 5879–5889.

[15] J. H. Wen, C.Y. Li, Z. R. G. Geng, X.Y. Ma, Z. L. Wang, A potent antitumor  $Zn^{2+}$  tetraazamacrocycle complex targeting DNA: the fluorescent recognition, interaction and apoptosis studies, Chem. Commun. 47 (2011) 11330–11332.

[16] T. Kawamoto, M. Nishiwaki, Y. Tsunekawa, K. Nozaki, T. Konno, Synthesis and Characterization of Luminescent Zinc(II) and Cadmium(II) Complexes with N,S-Chelating Schiff Base Ligands, Inorg. Chem. 47 (2008) 3095–3104.

[17] R. Beckett, B.F. Hoskins, The structure of the cobalt(II) derivative of the sulphur chelate, dithioacetylacetone, Chem. Commun. (1967) 909-910.

[18] R. Beckett, B.F. Hoskins, Square-planar complexes of pentane-2,4-dithione (dithioacetylacetone): crystal structures of the cobalt(II) and nickel(II) derivatives, J. Chem. Soc., Dalton Trans. (1974) 622-625.

[19] N. Hoshino, Liquid crystal properties of metal–salicylaldimine complexes.: Chemical modifications towards lower symmetry, Coord. Chem. Rev. 174 (1998) 77-108.

[20] (a) H. Ed. Sigel, Zinc and its role in Biology and Nutrition; Marcel Dekker: New York, 1983,

(b) B. L. Vallee, D. S. Auld, New perspective on zinc biochemistry: Cocatalytic sites in multi-zinc enzymes, Biochemistry 32 (1993) 6493-6500,

(c) S. Hikichi, M. Tanaka, Y. Moro-oka, N. Kitajima, Phosphate ester cleavage with a zinc hydroxide complex. Formation and crystal structure of a dinuclear zinc complex bridged with a phosphate monoester, J. Chem. Soc., Chem. Commun. (1992) 814-815.

[21] M. Ruf, K. Weis, H. Vahrenkamp, J A new pyrazolylborate zinc hydroxide complex capable of cleaving esters, amides and phosphates, J. Chem. Soc., Chem. Commun. (1994) 135-136.

[22] S. Uhlenbrock, B. Krebs, A Phenoxy□Bridged Homodinuclear Zn Complex with an Unusual Coordination Sphere; Model Compound for the Active Site of Phospholipase C<sup>+</sup>, Angew. Chem., Int. Ed. Engl. 31 (1992)1647-1648.

[23] C. He, S. J. Lippard, Modeling Carboxylate-Bridged Dinuclear Active Sites in Metalloenzymes Using a Novel Naphthyridine-Based Dinucleating Ligand, J. Am. Chem. Soc. 122 (2000) 184-185.

[24] M. Ruf, K. Weis, H. Vahrenkamp,  $Zn-O_2H_3-Zn$ : a Coordination Mode of the Hydrolytic Zinc-Aqua Function and a Possible Structural Motif for Oligozinc Enzymes, J. Am. Chem. Soc. 118 (1996) 9288-9294.

[25] (a) S. E. Denmark, S. P. D. Connor, S. R. Wilson, Solution and Solid-State Studies of a Chiral Zinc-Sulfonamide Complex Relevant to Enantioselective Cyclopropanations, Angew. Chem. Int. Ed. Engl. 37 (1998) 1149-1151,

(b) E. Kikuta, S. Aoki, E. Kimura, A New Type of Potent Inhibitors of HIV-1 TAR RNA-Tat Peptide Binding by Zinc(II)-Macrocyclic Tetraamine Complexes, J. Am. Chem. Soc. 123 (2001)7911-7912.

[26] (a) E. C. Fusch, B. Lippert, [Zn3(OH)2(1-MeC-N3)5(1-MeC-O2)3]4+ (1-MeC =1-Methylcytosine): Structural Model for DNA Crosslinking and DNA Rewinding by Zn(II)? J.
Am. Chem. Soc. 116 (1994) 7204-7209,

(b) A. Neels, H. Stoeckli-Evans, Trinuclear Zinc(II) Complexes and Polymeric Cadmium(II) Complexes with the Ligand 2,5-Bis(2-pyridyl)pyrazine: Synthesis, Spectral Analysis, and Single-Crystal and Powder X-ray Analyses, Inorg. Chem. 38 (1999) 6164-6170, (c) R. L. Paul, A. J. Amoroso, P. L. Jones, S. M. Couchman, Z. R. Reeves, L. H. Rees, J. C. Jeffery, J. A. McCleverty, M. D. Ward, Effects of metal co-ordination geometry on self-assembly: a monomeric complex with trigonal prismatic metal co-ordination *vs.* tetrameric complexes with octahedral metal co-ordination, J. Chem. Soc., Dalton Trans. (1999) 1563-1568,

(d) M. Gembicky, P. Baran, R. Boca, H. Fuess, I. Svoboda, M. Valko, Zinc(II) trinuclear complexes involving pyridine *N*-oxide ligands: distortion isomerism and magnetic properties of copper(II) analogues, Inorg. Chim. Acta. 305 (2000) 75-82.

[27] (a) P. Molenveld, W. M. G. Stikvoort, H. Koojiman, A. L. Spek, J. F. J. Engbersen, D.
N. Reinhoudt, Dinuclear and Trinuclear Zn(II) Calix[4]arene Complexes as Models for Hydrolytic Metallo-Enzymes. Synthesis and Catalytic Activity in Phosphate Diester Transesterification, J. Org. Chem. 64 (1999) 3896-3906,

(b) P. Molenveld, J. F. J. Engbersen, D. N. Reinhoudt, Specific RNA Dinucleotide Cleavage by a Synthetic Calix, Angew. Chem. Int. Ed. Engl. 38 (1999) 3189-3192,

[28] A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. Mislin, B. W. Skelton, C. Taylor, A. H. White, Linear, Divergent Molecular Receptors – Subtle Effects of Transition Metal Coordination Geometry, Eur. J. Inorg. Chem. (2000) 823-826.

[29] (a) P. Pfeiffer, E. Breith, E. Lu<sup>--</sup>bbe, T. Tsumaki, Tricyclische orthokondensierte Nebenvalenzringe, Ann. Chem. 503 (1933) 84-130,

(b) P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, H. Thielert, Innere Komplexsalze der Aldimin□ und Azoreihe, J. Prakt. Chem. 149 (1937) 217-296.

[30] (a) S. J. Gruber, C. M. Harris, E. Sinn, Metal complexes as ligands—IV [1,2,3]: Bi- and Tri- nuclear complexes derived from metal complexes of tetradentate salicylaldimines, J. Inorg. Nucl. Chem. 30 (1968) 1805-1830,

(b) C. A. Bear, J. M. Waters, T. N. Waters, Crystal and molecular structure of the tetranuclear copper complex di-µchlorobis{chloro[NN'ethylenebis(salicylideneiminato)copper(II)]copper(II)}, J. Chem. Soc., Dalton Trans. (1974)1059-1062,

(c) J. M. Epstein, B. N. Figgis, A. H. White, A. C. Willis, Crystal structures of two trinuclear Schiff-base copper(II) complexes, J. Chem. Soc., Dalton Trans. (1974) 1954-1961,

(d) I. Cacelli, L. Carbonaro, P. La Pegna, Kinetics and Equilibria of Nickel(II)–Schiff Base Adducts Formation, Eur. J. Inorg. Chem. (2002) 1703-1710.

[31] (a) C. Fukuhara, E. Asato, T. Shimoji, K. Katsura, M. Mori, K. Matsumoto, S. Ooi, Mixed oxidation state trinuclear cobalt complexes with bridging sulphito and Schiff-base ligands. Part 1. Preparation of the complexes  $[Co^{II}(\mu-SO_3)_2(\mu-L)_2CO^{III}_2(ROH)_2](L = Schiff base anion, R = alkyl)$  and structure determination of  $[Co^{II}(\mu-SO_3)_2(\mu-\alpha,\alpha'-Me_2-salpd)_2Co^{III}_2(Pr^nOH)_2] \cdot 2Pr^nOH$ , J. Chem. Soc., Dalton Trans. (1987) 1305-1311,

(b) C. Fukuhara, K. Tsuneyoshi, K. Katsura, N. Matsumoto, S. Kida, M. Mori, Linear Tetranuclear Copper(II) Complexes with Bridging Methoxide and a Schiff-Base Ligand: The Preparation and Magnetic Study of the [Cu(salpd- $\mu$ -O,O')( $\mu$ -L)Cu( $\mu$ -CH<sub>3</sub>O)<sub>2</sub>Cu( $\mu$ -L)(sapd- $\mu$ -O,O')Cu] Complexes (and L=Acetate or Formate Ions) and the Structure Determination of the Complex with L=Acetate, Bull. Chem. Soc. Jpn. 62 (1989) 3939-3943,

(c) A. Gerli, K. S. Hagen, L. G. Marzilli, Nuclearity and formulation of SALPN2- complexes formed from M(O2CCH3)2: resolution of longstanding problems by x-ray crystallography, Inorg. Chem. 30 (1991) 4673-4676,

(d) D. U¬ lku<sup>¬</sup>, F. Ercan, O. Atakol, F. N. Dincüer, Bis{(#-acetato)[#-bis(salicylidene)-1,3-propanediaminato](dimethyl sulfoxide)nickel(II)}nickel(II), Acta Crystallogr. Sect. C 53 (1997) 1056-1057,

(e) O. Atakol, C. Arici, F. Ercan, D. U¬ lku<sup>¬</sup>, Bis{(#-acetato)[#-bis(salicylidene)-1,3propanediaminato]copper(II)}copper(II) dioxane solvate, Acta Crystallogr. Sect. C 55 (1999) 511-513,

(f) O. Atakol, M. Aksu, F. Ercan, C. Arici, M. N. Tahir, D. U $\neg$  lku<sup>"</sup>, A linear trinuclear Cd<sup>II</sup>-Cd<sup>II</sup> complex with a #-acetato bridge: bis{(#-acetato)[#-bis(salicylidene)-1,3-propanediaminato]cadmium(II)} cadmium(II), Acta Crystallogr. Sect. C 55 (1999) 1072-1075,

(g) J. Reglinski, S. Morris, D. E. Stevenson, Supporting conformational change at metal centres. Part 1: octahedral systems, Polyhedron 21 (2002) 2167-2174.

[32] (a) J. -P. Costes, F. Dahan, A. Dupuis, J. -P. Laurent, A Genuine Example of a Discrete Bimetallic (Cu, Gd) Complex: Structural Determination and Magnetic Properties, Inorg. Chem. 35 (1996) 2400-2402,

(b) J. -P. Costes, F. Dahan, A. Dupuis, J. -P. Laurent, A General Route to Strictly Dinuclear Cu(II)/Ln(III) Complexes. Structural Determination and Magnetic Behavior of Two Cu(II)/Gd(III) Complexes, Inorg. Chem. 36 (1997) 3429-3433,

(c) J. -P. Costes, F. Dahan, A. Dupuis, J. -P. Laurent, Experimental Evidence of a Ferromagnetic Ground State ( $S = \frac{9}{2}$ ) for a Dinuclear Gd(III)–Ni(II) Complex, Inorg. Chem. 36 (1997) 4284-4286,

(d) J. -P. Costes, F. Dahan, A. Dupuis, J. -P. Laurent, Structural studies of a dinuclear (Cu, Gd) and two trinuclear (Cu<sub>2</sub>, Ln) complexes (Ln=Ce, Er). Magnetic properties of two original (Cu, Gd) complexes, New J. Chem.22 (1998) 1525-1529,

(e) J. -P. Costes, F. Dahan, A. Dupuis, J. -P. Laurent, Nature of the Magnetic Interaction in the  $(Cu^{2+}, Ln^{3+})$  Pairs: An Empirical Approach Based on the Comparison Between Homologous  $(Cu^{2+}, Ln^{3+})$  and  $(Ni_{LS}^{2+}, Ln^{3+})$  Complexes, Chem. Eur. J. 4 (1998) 1616-1620,

(f) J. -P. Costes, F. Dahan, A. Dupuis, Influence of Anionic Ligands (X) on the Nature and Magnetic Properties of Dinuclear LCuGdX<sub>3</sub>·nH<sub>2</sub>O Complexes (LH<sub>2</sub> Standing for Tetradentate Schiff Base Ligands Deriving from 2-Hydroxy-3-methoxybenzaldehyde and X Being Cl, N<sub>3</sub>C<sub>2</sub>, and CF<sub>3</sub>COO), Inorg. Chem. 39 (2000) 165-168,

(g) J. -P. Costes, F. Dahan, B. Donnadieu, J. Garcia-Tojal, J. -P. Laurent, Versatility of the Nature of the Magnetic Gadolinium(III)–Vanadium(IV) Interaction – Structure and Magnetic Properties of Two Heterobinuclear [Gd, V(O)] Complexes, Eur. J. Inorg. Chem. (2001) 363-365,

(h) J. -P. Costes, J. M. Clemente-Juan, F. Dahan, F. Dumestre, J. -P. Tuchagues, Dinuclear (Fe<sup>II</sup>, Gd<sup>III</sup>) Complexes Deriving from Hexadentate Schiff Bases: Synthesis, Structure, and Mössbauer and Magnetic Properties, Inorg. Chem. 41 (2002) 2886-2891,

(i) R. Gheorghe, M. Andruh, J. -P. Costes, B. Donnadieu, A rational synthetic route leading to 3d–3d'–4f heterospin systems: self-assembly processes involving heterobinuclear 3d–4f complexes and hexacyanometallates, Chem. Commun. (2003) 2778-2779,

(j) R. Koner, H. -H. Lin, H. -H. Wei, S. Mohanta, Syntheses, Structures, and Magnetic Properties of Diphenoxo-Bridged  $M^{II}Ln^{III}$  Complexes Derived from *N*,*N*<sup>4</sup>-Ethylenebis(3-ethoxysalicylaldiimine) (M = Cu or Ni; Ln = Ce–Yb): Observation of Surprisingly Strong Exchange Interactions, Inorg. Chem. 44 (2005) 3524-3536.

[33] (a) W. -K. Wong, H. Liang, W. -Y. Wong, Z. Cai, K. -F. Li, K. -W. Cheah, Synthesis and near-infrared luminescence of 3d-4f bi-metallic Schiff base complexes, New J. Chem. 26 (2002) 275-278,

(b) O. Margeat, P. G. Lacroix, J. -P. Costes, B. Donnadieu, C. Lepetit, K. Nakatani, Synthesis, Structures, and Physical Properties of Copper (II)–Gadolinium (III) Complexes Combining Ferromagnetic Coupling and Quadratic Nonlinear Optical Properties, Inorg. Chem. 43 (2004) 4743-4750,

(c) W. -K. Lo, W. -K. Wong, J. Guo, W. -Y. Wong, K. -F. Li, K. -W. Cheah, Synthesis, structures and luminescent properties of new heterobimetallic Zn-4f Schiff base complexes, Inorg. Chim. Acta. 357(2004) 4510-4521,

(d) X. Yang, R. A. Jones, V. Lynch, M. M. Oye, A. L. Holmes, Synthesis and near infrared luminescence of a tetrametallic Zn<sub>2</sub>Yb<sub>2</sub> architecture from a trinuclear Zn<sub>3</sub>L<sub>2</sub>Schiff base complex, Dalton Trans. (2005) 849-851.

[34] J. P. Costes, J. -P. Laussac, F. Nicode`me, Complexation of a Schiff baseligand having two coordination sites ( $N_2O_2$  and  $O_2O_2$ ) with lanthanide ions (Ln = La, Pr): an NMR study, J. Chem. Soc., Dalton Trans. (2002) 2731-2736.

[35] (a) E. Lamour, S. Routier, J. -L. Bernier, J. -P. Catteau, C. Bailly, H. Vezin, Oxidation of Cu<sup>II</sup> to Cu<sup>III</sup>, Free Radical Production, and DNA Cleavage by Hydroxy-salen–Copper Complexes. Isomeric Effects Studied by ESR and Electrochemistry, J. Am. Chem. Soc. 121 (1999) 1862-1869,

(b) N. F. Choudhary, N. G. Connelly, P. B. Hitchcock, G. J. Leigh, New compounds of tetradentate Schiff bases with vanadium (IV) and vanadium (V), J. Chem. Soc. Dalton Trans. (1999) 4437-4446,

(c) G. Verquin, G. Fontaine, M. Bria, E. Zhilinskaya, E. Abi-Aad, A. Aboukai<sup>°</sup>s, B. Baldeyrou, C. Bailly, J. -L. Bernier, DNA modification by oxovanadium (IV) complexes of salen derivatives, J. Biol. Inorg. Chem. 9 (2004) 345-353,

(d) M. R. Bermejo, M. I. Ferna´ndez, A. M. Gonza´lez-Noya, M. Maneiro, R. Pedrido, M. J. Rodri´guez, M. Va´zquez, Chloride as Supramolecular Glue: Anion □ Directed Assembly of a 2D Network of Mn<sup>III</sup> Complexes, Eur. J. Inorg. Chem. (2004) 2769-2774.

[36] P. Guerriero, S. Tamburini, P. A. Vigato, U. Russo, C. Benelli, Mössbauer and magnetic properties of mononuclear, homo- and hetero-dinuclear complexes, Inorg. Chim. Acta. 213 (1993) 279-287.

[37] (a) U. Casellato, P. Guerriero, S. Tamburini, S. Sitran, P. A. Vigato, From compounds to materials: heterodinuclear complexes as precursors in the synthesis of mixed oxides; crystal structures of  $[Cu(H_2L_A)]$  and  $[{CuY(L_A)(NO_3)(dmso)}_2]\cdot 2dmso$   $[H_4L_A=N,N'-ethylenebis(3-hydroxysalicylideneimine), dmso = dimethyl sulphoxide], J. Chem. Soc., Dalton Trans. (1991) 2145-2152,$ 

(b) A. Aguiari, E. Bullita, U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, Macrocyclic and macroacyclic compartmental Schiff bases: synthesis, characterization, X-ray structure and interaction with metal ions, Inorg. Chim. Acta. 202 (1992) 157-171,

(c) U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, C. Benelli, Mononuclear, homoand heteropolynuclear complexes with acyclic compartmental Schiff bases, Inorg. Chim. Acta. 207 (1993) 39-58, (d) M. Sakamoto, Y. Nishida, K. Ohhara, Y. Sadaoka, A. Matsumoto, H. Okawa, Copper(II)lanthanide(III) complexes of compartmental ligand, N,N'-bis(3hydroxysalicylidene)ethylenediamine, Polyhedron 14 (1995) 2505-2509,

(e) M. Sakamoto, T. Ishikawa, Y. Nishida, Y. Sadaoka, A. Matsumoto, Y. Fukuda, M. Sakai, M. Ohba, H. Sakiyama, H. Okawa,  $V(IV)O \Box Ln(III)$  complexes (Ln  $\Box$  La, Eu or Gd) of the compartmental ligand N,N'-bis(3-hydroxysalicylidene)ethylenediamine, J. Alloys Compd. 238 (1996) 23-27,

(f) H. Aono, M. Tsuzaki, A. Kawaura, M. Sakamoto, E. Traversa, Y. Sadaoka, LaMnO<sub>3</sub> Fine Powder Prepared by the Thermal Decomposition of a Heteronuclear Complex, LaMn(dhbaen)(OH)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub>, Chem. Lett. (1999)1175-1176,

(g) T. Le Borgne, E. Rivie`re, J. Marrot, P. Thue´ry, J. -J. Girerd, M. Ephritikhine, Syntheses, X $\square$ Ray Crystal Structures, and Magnetic Properties of Novel Linear  $M^{\blacksquare}_{=}$  U<sup>IV</sup> Complexes (M=Co, Ni, Cu, Zn), Chem. Eur. J. 8 (2002) 773-783,

(h) R. Miyamoto, T. Sugai, S. Sudoh, Spectroscopic study of the coordination sphere of Gd(III) in  $Gd(III) \square M(II)$  complexes with a compartmental ligand, where the local environment around Gd(III) is controlled by (M(II) M(II)=Ni(II), Zn(II) and a vacancy), Polyhedron 21 (2002) 2127-2135,

(i) H. Aono, N. Kondo, M. Sakamoto, E. Traversa, Y. J. Sadaoka, Thermal decomposition products of the heteronuclear complex,  $LaNi(dhbaen)(NO_3)(H_2O)_n$ , Eur. Ceram. Soc. 23 (2003) 1375-1381,

(j) L. Salmon, P. Thue'ry, E. Rivie're, J. -J. Girerd, M. Ephritikhine, Versatility of the nature of the magnetic Cu(II)-U(IV) interaction. Syntheses, crystal structures and magnetic properties of  $Cu_2U$  and CuU compounds, Dalton Trans. (2003) 2872-2880,

(k) C. T. Zeyrek, A. Elmali, Y. Elerman, Magnetic characterization, synthesis and crystal structure of a heterodinuclear Cu<sup>II</sup>Gd<sup>III</sup> Schiff base complex bridged by the two phenolic oxygen atoms, J. Mol. Struct. 740 (2005) 47-52.

[38] J. Sanmartı'n, M. R. Bermejo, A. M. Garcı'a-Deibe, O. Piro, E. E. Castellano, An unusual [4 + 4 + 4] bishelical complex, Cu3(H2L)(L)·2H2O [H4LA = N,NA-bis(3-hydroxysalicylidene)-1,4-diaminobutane]: synthesis and crystal structure, Chem. Commun. (1999) 1953-1954.

[39] A. Mustapha, K. Busch, M. Patykiewicz, A. Apedaile, J. Reglinski, A. R. Kennedy, T. J.Prior, Multidentate ligands for the synthesis of multi-metallic complexes, Polyhedron 27 (2008) 868-878.

[40] H. Zhang, X. Wang, K. Zhang, B. K. Teo, Molecular and crystal engineering of a new class of inorganic cadmium-thiocyanate polymers with host–guest complexes as organic spacers, controllers, and templates, Coord. Chem. Rev. 183 (1999) 157-195.

[41] P. Orioli, B. Bruni, M. D. Vaira, L. Messori, F. Piccioli, Decomposition of Ascorbic Acid in the Presence of Cadmium Ions Leads to Formation of a Polymeric Cadmium Oxalate Species with Peculiar Structural Features, Inorg. Chem. 41 (2002) 4312-4314.

[42] H. D. Bian, W. Gu, J. -Y. Xu, F. Bian, S. -P. Yan S, D. -Z. Liao, Z. -H. Jiang, P. Cheng, The First  $\mu_3$ -Oxalato-Bridged Copper Complex with Tridentate Schiff Base Ligand *N*-Ethyl-*N*'-Salicylidene-1,2-diaminoethane: Synthesis, Structure, and Magnetic Properties, Inorg. Chem. 42 (2003) 4265-4280.

[43] J. L. Burmeister, Linkage isomerism in metal complexes, Coord. Chem. Rev. 3 (1968)225-245.

[44] A. H. Norbury, A. I. P. Sinha, The co-ordination of ambidentate ligands, Q. Rev. Chem.Soc. 24 (1970) 69-94.

[45] D. J. Majumdar, D. Das, S. S. Sreejith, S. Nag, S. Dey, S. Mondal, K. Bankura, D. Mishra, Synthesis, characterizations and single crystal structure of di-nuclear azido-bridged Cd(II) coordination polymer with Schiff base precursor ( $H_2L_{pent}^{OMe}$ ): DFT, fluorescence, solvatochromism and *in vitro* antimicrobial assay, Inorg. Chim. Acta. 496 (2019) 119069.

[46] D. J. Majumdar, M. S. Surendra Babu, S. Das, J. K. Biswas, M. Mondal, S. Hazra, Synthesis, X-ray crystal structure, photo luminescent property, antimicrobial activities and DFT computational study of Zn(II) coordination polymer derived from multisite N,O donor Schiff base ligand ( $H_2L^1$ ), J. Mol. Struct. 1138 (2017) 161-171.

[47] D. J. Majumdar, J. K. Biswas, M. Mondal, M. S. Surendra Babu, R. K. Metre, S. Das, K. Bankura, D. Mishra, Coordination of N,O-donor appended Schiff base ligand  $(H_2L^1)$  towards Zinc(II) in presence of pseudohalides: Syntheses, crystal structures, photoluminescence, antimicrobial activities and Hirshfeld surfaces, J. Mol. Struct. 1155 (2018) 745-757.

[48] D. J. Majumdar, J. K. Biswas, M. Mondal, M. S. Surendra Babu, S. Das, R. K. Metre, S.
S. SreeKumar, K. Bankura, D. Mishra, Cd(II) Pseudohalide Complexes with N, N'□Bis(3□ ethoxysalicylidenimino) 1,3□Diaminopropane: Crystal Structures, Hirshfeld Surface, Antibacterial and Anti□Biofilm Properties, ChemistrySelect 3 (2018) 2912-2925.

[49] D. J. Majumdar, S. Dey, S. S. Sreekumar, S. Das, D. Das, R. K. Metre, K. Bankura, D. Mishra, Nitrato, Pseudohalo□Linked Zn(II)/Cd(II) Schiff□Base Complexes with 1,3□ Diimine Spacer Group: Syntheses, Crystal Structures, DFT, TD□DFT and Fluorescence Studies, ChemistrySelect 3 (2018) 12371-12382.

#### Journal Pre-proo

[50] D. J. Majumdar, D. Das, S. S. Sreejith, S. Das, J. K. Biswas, M. Mondal, D. Ghosh, K. Bankura, D. Mishra, Dicyanamide-interlaced assembly of Zn(II)-schiff-base complexes derived from salicylaldimino type compartmental ligands: Syntheses, crystal structures, FMO, ESP, TD-DFT, fluorescence lifetime, *in vitro* antibacterial and anti-biofilm properties, Inorg. Chim. Acta. 489 (2019) 244-254.

[51] D. J. Majumdar, S. Das, R. Thomas, Z. Ullah, S. S. Sreejith, D. Das, Pooja Shukla, K. P.
 Bankura, D. Mishra, Syntheses, X-ray crystal structures of two new Zn(II)-dicyanamide complexes derived from H<sub>2</sub>vanen-type compartmental ligands: Investigation of thermal, photoluminescence, *in vitro* cytotoxic effect and DFT-TDDFT studies, Inorg. Chim. Acta.
 (2019)221-234.

[52] D. J. Majumdar, M. S. Surendra Babu, S. Das, C. Mohapatra, J. K. Biswas, M. Mondal, Syntheses, X-ray Crystal Structures, Photoluminescence Properties, Antimicrobial Activities and Hirshfeld Surface of Two New Cd(II) Azide/Thiocyanate Linked Coordination Polymers, ChemistrySelect 2 (2017) 4811-4822.

[53] D. J. Majumdar, S. Dey, S. S. Sreekumar, S. Das, D. Das, J. K. Biswas, M. Mondal, P. Shukla, T. Pal, K. Bankura, D. Mishra, Syntheses, crystal structures and photo physical aspects of azido-bridged tetranuclear cadmium (II) complexes: DFT/TD-DFT, thermal, antibacterial and *anti*-biofilm properties, J. Mol. Struct. 1179 (2019) 694-708.

[54] (a) D. J. Majumdar, S. Das, J. K. Biswas, M. Mondal, Synthesis, structure, fluorescent property, and antibacterial activity of new Cd(II) metal complex based on multidentate Schiff base ligand *N*,*N*'-Bis(3-methoxysalicylidenimino)-1,3-diaminopropane, J. Mol. Struct. 1134 (2017) 617-624,

(b) D. J. Majumdar, Y. Agrawal, R. Thomas, Z. Ullah, M. K. Santra, S. Das, T. K. Pal, K. Bankura, D. Mishra, Syntheses, characterizations, crystal structures, DFT/TD□DFT, luminescence behaviors and cytotoxic effect of bicompartmental Zn (II)□dicyanamide Schiff base coordination polymers: An approach to apoptosis, autophagy and necrosis type classical cell death, Appl. Organomet. Chem. 34 (2020) e5269.

[55] B. Valeur, Molecular Fluorescence, Principles and Applications, fifth ed. Wiley-VCH, Wienheim, pp. 161, 2009.

[56] G. M. Sheldrick, SADABS, a software for empirical absorption correction, Ver. 2.05;

University of Göttingen: Göttingen, Germany, 2002.

[57] SMART & SAINT Software Reference manuals Version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003.

[58] SHELXTL Reference Manual Ver. 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

[59] G. M. Sheldrick, SHELXTL, a software for empirical absorption correction Ver.6.12; Bruker AXS Inc.: WI. Madison, 2001.

[60] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2, *OLEX2*: a complete structure solution, refinement and analysis program, J. Appl. Crystallog. 42 (2009) 339-341.

[61] K. Bradenburg, Diamond, Ver. 3.1eM; Crystal Impact GbR: Bonn, Germany, 2005.

[62] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N.

#### Journal Pre-proo

Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M.
Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A.
Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N.
Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P.
Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo,
R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J.
Fox, Gaussian 16, revision B.01; Gaussian, Inc., Wallingford CT, 2016.

[63] A. G. Ioannou, S. M. Colwell, R. D. Amos, The calculation of frequency-dependent polarizabilities using current density functional theory, Chem. Phys. Lett. 278 (1997) 278-284.

[64] Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor. Chem. Acc. 120 (2008) 215-241.

[65] (a) R. Dennington, T. Keith, J. Millam, K. Eppinnett, L. W. Hovell, R. Gilliland, *GaussView*, version 6; Semichem Inc.: Shawnee Mission, KS, 2016,

(b) N. M. O'Boyle, A. L. Tenderholt, K. M. Langner, cclib: A library for package independent computational chemistry algorithms, J. Comput. Chem. 29 (2008) 839-845.

[66] (a) M. Shkir, S. Muhammad, S. AlFaify, A. Irfan, P. S. Patil, M. Arora, H. Algarni, Z. Jingping, An investigation on the key features of a D– $\pi$ –A type novel chalcone derivative for opto-electronic applications, RSC Adv. 5 (2015) 87320-87332,

(b) M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka, M. A. Spackman, Crystal Explorer *17* (**2017**). University of Western Australia. http:// hirshfeldsurface.net. (c)T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyser, J. Comput. Chem. 33 (2012) 580-592.

[67] (a) A. Greule, J. E. Stok, J. J. De Voss, M. J. Cryle, Unrivalled diversity: the many roles and reactions of bacterial cytochromes P450 in secondary metabolism, Natural Product Reports. 35 (2018)757-791,

(b) I. N. A. Van Bogaert, S. Groeneboer, K. Saerens, W. Soetaert, The role of cytochrome P450 monooxygenases in microbial fatty acid metabolism, FEBS journal. 278 (2011) 206-221,

(c) F. Hannemann, A. Bichet, K. M. Ewen, R. Bernhardt, Cytochrome P450 systems—
biological variations of electron transport chains, Biochimica et Biophysica Acta. 1770
(2006) 330-344.

[68] H. Li, T. L. Poulo, The structure of the cytochrome p450BM-3 haem domain complexed with the fatty acid substrate, palmitoleic acid, Nature Structural Biology. 4 (1997) 140-146.

[69] P. Belin, M. H. Le Du, A. Fielding, O. Lequin, M. Jacquet, J. -B. Charbonnier, A. Lecoq, R. Thai, M. Courçon, C. Masson, C. Dugave, R. Genet, J. -L. Pernodet, M. Gondry, Identification and structural basis of the reaction catalyzed by CYP121, an essential cytochrome P450 in *Mycobacterium tuberculosis*. PNAS. 106 (2009) 7426-7431.

[70] I. Schuster, R. Bernhardt, Inhibition of Cytochromes P450: Existing and New Promising Therapeutic Targets, Drug Metabolism Reviews. 39 (2007) 481-499.

[71] S. Mirdya, S. Roy, S. Chatterjee, A. Bauza, A. Frontera, S. Chattopadhyay, Bonds in Crystal Engineering: A Combined Experimental and Theoretical Study on a Series of Hemiand Holodirected Nickel(II)/Lead(II) Complexes, Cryst. Growth Des. 19 (2019) 5869-5881. [72] S. Akine, W. Dong, T. Nabeshima, Octanuclear Zinc(II) and Cobalt(II) ClustersProduced by Cooperative Tetrameric Assembling of Oxime Chelate Ligands, Inorg. Chem.45 (2006) 4677-4684.

[73] X. -X. Zhou, H. -C. Fang, Y. -Y. Ge, Z. -Y. Zhou, Z. -G. Gu, X. Gong, G. Zhao, Q. -G. Zhan, R. -H. Zeng, Y. -P. Cai, Assembly of a Series of Trinuclear Zinc(II) Compounds with N<sub>2</sub>O<sub>2</sub> Donor Tetradentate Symmetrical Schiff Base Ligand, Cryts. Growth Des. 10 (2010) 4014-4022.

[74] Y. Zhao, Z. Li, H. Li, S. Wang, M. Niu, Synthesis, crystal structure, DNA binding and in vitro cytotoxicity studies of Zn(II) complexes derived from amino-alcohol Schiff-bases, Inorg. Chim. Acta. 482 (2018) 136-143.

[75] C. Maxim, T. D. Pasatoiu, V. Ch. Kravtsov, S. Shova, C. A. Muryn, R. E.P. Winpenny, F. Tuna, M. Andruh, Copper(II) and zinc(II) complexes with Schiff-base ligands derived from salicylaldehyde and 3-methoxysalicylaldehyde: Synthesis, crystal structures, magnetic and luminescence properties, Inorg. Chim. Acta. 361 (2008) 3903-3911.

[76] D. Dey, G. Kaur, M. Patra, A. R. Choudhury, N. Kole, B. Biswas, A perfectly linear trinuclear zinc–Schiff base complex: Synthesis, luminescence property and photocatalytic activity of zinc oxide nanoparticle, Inorg. Chim. Acta. 421 (2014) 335-341.

[77] M. Maiti, D. Sadhukhan, S. Thakuta, S. Roy, G. Pilet, R. J. Butcher, L. J. Charbonniere,
S. Mitra, Series of Dicyanamide-Interlaced Assembly of Zinc-Schiff-Base Complexes:
Crystal Structure and Photophysical and Thermal Studies, Inorg. Chem. 51 (2012)1217612187.

[78] A. B. P. Lever, Inorganic Spectroscopy, second ed., Elsevier, New York, 1984.

[79] J. E. Pate, P. K. Ross, T. J. Thamann, C. A. Reed, K. D. Karlin, T. N. Sorrell, N. E. I. Solomon, Spectroscopic studies of the charge transfer and vibrational features of binuclear copper(II) azide complexes: comparison to the coupled binuclear copper active site in met azide hemocyanin and tyrosinase, J. Am. Chem. Soc. 111 (1989) 5198-5209.

[80] D. A. Dows, E. Whittle, G. C. Pimentel, Infrared Spectrum of Solid Ammonium Azide : A Vibrational Assignment, J. Chem. Phys. 23 (1955) 1475.

[81] W. K. Dong, K. Y. X. Sun, C. Y. Zhao, X. Y. Dong, L. Xu, Synthesis, structure and properties of supramolecular Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup> and Zn<sup>II</sup> complexes containing Salen-type bisoxime ligands, Polyhedron 29 (2010) 2087-2097.

[82] G. J. Sole, L. E. Bausa, D. Jaque, An Introduction to the Optical Spectroscopy of Inorganic Solids, John Wiley & Sons, New York, 2005.

[83] J. Chakraborty, S. Thakurta, G. Pilet, R. Z. Ziessel, L. J. Charbonniere, S. Mitra, Syntheses, Crystal Structures and Photophysical Properties of Two Doubly  $\mu$  Phenoxo Bridged Ln<sup>III</sup> (Ln = Pr, Nd) Homodinuclear Schiff Base Complexes, Eur. J. Inorg. Chem. (2009), 3993-4000.

[84] T. Yu, W. Wu, W. Li, Z. Hong, R. Hua, M. Li, B. Chu, B. Li, Z. Zhang, Z. Z. Hu, Synthesis, crystal structure and electroluminescent properties of a Schiff base zinc complex, Inorg. Chim. Acta. 359 (2006) 2246-2251.

[85] F. Gao, W. -J. Ruan, J. -M. Chen, Y. -H. Zhang, Z. -A. Zhu, Spectroscopy, NMR and DFT studies on molecular recognition of crown ether bridged chiral heterotrinuclear salen Zn(II) complex, Spectrochim. Acta. Part A 62 (2005) 886-895.

[86] B. V. Agarwala, S. Hingorani, Structural elucidation of *o*-vanillin isonicotinoyl hydrazone and its metal complexes, Transit. Met. Chem. 18 (1993) 576-578.

[87] B.V. Agarwala, S. Hingorani, V. Puri, G. A. Naganagowda, Synthetic and physicochemical studies of uranium complexes with semicarbazone and hydrazine, Inorg. Chim. Acta. 176 (1990) 149-154.

[88]. R. C. Maurya, P. Patel, S. Rajput, Synthesis and Characterization of  $N \square (o \square$  Vanillinidene) $\square p \square$  anisidine and  $N, N' \square bis(o \square$  Vanillinidene)ethylenediamine and Their Metal Complexes, Inorg. Nano-Met. Chem. 33 (2003) 817-836.

[89] A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn, G. C. Verschoor, Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) perchlorate, J. Chem. Soc. Dalton Trans. (1984)1349–1356.
[90] S. Pearton, F. Ren, M. Mastro, Gallium Oxide Technology, Devices and application,

Elsevier, 2019 (DOI: 10.1016/C2017-0-01768-8).

[91] H. Li, H. Xu, X. Shen, K. Han, Z. Bi, R. Xu, Size-, electric-field- and frequencydependent third-order nonlinear optical properties of hydrogenated silicon nanoclusters, Sci. Rep. 6 (2016) 28067-28075.

[92] (a) P. Sanchora, D. K. Pandey, D. Rana, A. Materny, D. K. Singh, Impact of Size and Electronegativity of Halide Anions on Hydrogen Bonds and Properties of 1-Ethyl-3-methylimidazolium-Based Ionic Liquids, J. Phys. Chem. A 123 (2019) 4948-4963,

(b) B. Dutta, D. Das, J. Datta, A. Chandra, S. Jana, C. R. Sinha, P. P. Ray, M. H. Mir, Synthesis of a Zn(II)-based 1D zigzag coordination polymer for the fabrication of optoelectronic devices with remarkably high photosensitivity, Inorg. Chem. Front. 6 (2019) 1245-1252.

#### Journal Pre-proo

[93] (a) A. Bharti, P. Bharati, R. Dulare, M. K. Bharty, D. K. Singh, N. K. Singh, Studies on phenylmercury(II) complexes of nitrogen–sulfur ligands: Synthesis, spectral, structural characterization, TD-DFT and photoluminescent properties, Polyhedron 65 (2013) 170-180,

(b) P. Khandelwal, D. K. Singh, S. Sadhu, P. Poddar, Study of the nucleation and growth of antibiotic labeled Au NPs and blue luminescent Au<sub>8</sub> quantum clusters for  $Hg^{2+}$  ion sensing, cellular imaging and antibacterial applications, Nanoscale 7 (47) (2015) 19985-20002,

(c) D. Majumdar, S. Dey, D. Das, D. K. Singh, S. Das, K. Bankura, D. Mishra, Heterometallic Zn(II)-K(I) complex with salen-type Schiff-base ligand: Synthesis, crystal structure, solid-state photoluminescent property and theoretical study, J. Mol. Struct. 1185 (2019) 112-120,

(d) P. G. Lacroix, Synthesis and Second-Order Nonlinear Optical Properties of New Copper(II), Nickel(II), and Zinc(II) Schiff-Base Complexes. Toward a Role of Inorganic Chromophores for Second Harmonic Generation, Chem. Mater. 8 (1996) 541-545.

[94] D. Sadhukhan, A. Ray, G. Rosair, L. Charbonniere, S. Mitra, A Two-Dimensional Zinc(II)–Schiff Base Coordination Polymer Formed by Six-Membered Metallacyclic Repeating Motif: Structural Aspects, Thermal and Photophysical Properties, Bull. Chem. Soc. Jpn. 84 (2011) 211-217.

[95] L. Rodriguez-Santiago, M. Sodupe, A. Olivia, J. Bertran, Hydrogen Atom or Proton Transfer in Neutral and Single Positive Ions of Salicylic Acid and Related Compounds, J. Am. Chem. Soc. 121 (1999) 8882-8890.

[96] S. Mitra, N. Tamai, Femtosecond spectroscopic study on photochromic salicylideneaniline, Chem. Phys. Lett. 282 (1998) 391-397.

[97] J. Catalan, F. Toribio, A. U. Acuna, Intramolecular hydrogen bonding and fluorescence of salicylaldehyde, salicylamide, and o-hydroxyacetophenone in gas and condensed phase, J. Phys. Chem. 86 (1982) 303-306.

[98] P. Sen, A highly fluorescent tri-nuclear boron complex with large Stokes shifts based on tripodal Schiff base: synthesis and photophysical properties, J. Chem. Sci. 131 (2019) 63.

[99] D. Zhang, Y. Wen, Y. Xiao, G. Yu, Y. Liu, X. Qian, Bulky 4-tritylphenylethynyl substituted boradiazaindacene: pure red emission, relatively large Stokes shift and inhibition of self-quenching,

Chem. Commun. 39 (2008) 4777-4779.

[100] J. R. Lakowicz, Topics in Flourescence Spectroscopy, Plenum Press, New York, 1994.

[101] S. Ray, S. Konar, A. Jana, S. Patra, S. Chatterjee, J. A. Golen, A. L. Rheingold, S. Mandal, S. K. Kar, Three new pseudohalide bridged dinuclear Zn(II), Cd(II) complexes of pyrimidine derived Schiff base ligands: Synthesis, crystal structures and fluorescence studies, Polyhedron 33 (2012) 82-89.

[102] Y. Li, L. Shi, L. -X. Qin, L. -L. Qu, C. Jing, M. Lan, T. D. James, Y. -T. Long, An OFF–ON fluorescent probe for  $Zn^{2+}$  based on a GFP-inspired imidazolone derivative attached to a 1,10-phenanthroline moiety, Chem Commun. 47 (2011) 4361-4363.

[103] Jr. A. ValeK, The life and times of excited states of organometallic and coordination compounds, Coord. Chem. Rev. 200 (2000) 933-978.

[104] D. -W. Fu, H. -L. Cai, Y. Liu, Q. Ye, W. Zhang, Y. Zhang, X. -Y. Chen, G. Giovannetti, M. Capone, J. Li, R. -G. Xiong, Diisopropylammonium Bromide Is a High-Temperature Molecular Ferroelectric Crystal, Science 339 (2013) 425-428.

[105] D. -W. Fu, W. Zhang, H. -L. Cai, Y. Zhang, J. -Z. Ge, R. -G. Xiong, S. D. Huang, Supramolecular Bola-Like Ferroelectric: 4-Methoxyanilinium Tetrafluoroborate-18-crown-6, J. Am. Chem. Soc.133 (2011)12780-12786.

[106] D. -W. Fu, W. Zhang, H. -L. Cai, J. -Z. Ge, Y. Zhang, R. -G. Xiong, Diisopropylammonium Chloride: A Ferroelectric Organic Salt with a High Phase Transition Temperature and Practical Utilization Level of Spontaneous Polarization, Adv Mater. 23 (2011) 5658-5662.

[107] D. -W. Fu, H. -L. Cai, S. -H. Li, Q. Ye, L. Zhou, Y. Zhang, F. Deng, R. -G. Xiong, 4-Methoxyanilinium Perrhenate 18-Crown-6: A New Ferroelectric with Order Originating in Swinglike Motion Slowing Down, Phys. Rev. Lett. 110 (2013) 257601.

[108] W. -Y. Zhang, Y. -Y. Tang, P. -F. Li, P. -P. Shi, W. -Q. Liao, D. -W. Fu, H. -Y. Ye, Y. Zhang, R. -G. Xiong, Precise Molecular Design of High- $T_c$  3D Organic–Inorganic Perovskite Ferroelectric: [MeHdabco]RbI<sub>3</sub> (MeHdabco = *N*-Methyl-1,4-diazoniabicyclo[2.2.2]octane), J. Am. Chem. Soc. 139 (2017)10897-10902.

[109] Z. Wang, J. Wang, J. Li, M. Feng, G. Zou, X. Huang, [Bmim]<sub>2</sub>SbCl<sub>5</sub>: a main group metal-containing ionic liquid exhibiting tunable photoluminescence and white-light emission, Chem Commun. 51 (2015) 3094-3097.

[110] K. Takahashi, Y. Hasegawa, R. Sakamoto, M. Nishikawa, S. Kume, E. Nishibori, H. Nishihara, Solid-State Ligand-Driven Light-Induced Spin Change at Ambient Temperatures in Bis(dipyrazolylstyrylpyridine)iron(II) Complexes, Inorg. Chem. 51 (2012) 5188-5198.

[111] P. Ghosh, P. K. Bharadwaj, J. S. Roy, S. Ghosh, Transition Metal (II)/(III), Eu(III), and Tb(III) Ions Induced Molecular Photonic OR Gates Using Trianthryl Cryptands of Varying Cavity Dimension, J. Am. Chem. Soc. 119 (1997) 11903–11909.

[112] D. Leys, C. G. Mowat, K. J. McLean, A. Richmond, S. K. Chapman, M. D. Walkinshaw A. W. Munro, Atomic Structure of Mycobacterium tuberculosis CYP121 to 1.06 Å Reveals Novel Features of Cytochrome P450, J. Biochem. 278 (2003) 5141-5147.

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## **RESEARCH HIGHLIGHTS**

- A linear Zn\_3-type complex was synthesized from N/O-donor Schiff base (H\_2L^{OMe-pn}) •
- Characterized by various spectroscopic protocols, PXRD, SEM-EDAX and SCXRD •
- DFT based analysis of HS, FMO, MEP, NLO and AIM •
- DMF solvent explore fluorescent behavior based on stokes shifts •
- Molecular docking was executed with cytochrome P450 from B. megaterium and M. • tuberculosis

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## **Decleration of Interest of Statement**

DFT investigations of linear Zn<sub>3</sub>-type complex with compartmental N/O-donor Schiff

base: Synthesis, characterizations, crystal structure, fluorescence and molecular

## docking

Author contributions of the above article will be mentioned as follows----

1. Dhrubajyoti Majumdar—Main author, contributed synthesis, total manuscript preparation and main research work carried out.

- 2. Tapan Pal contributed X-ray crystallographic section
- 3. Dheeraj kumar Singh and Deepak K. Pandey contributed only DFT section
- 4. Debaprasad Parai contributed Molecular docking section

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- 5. Dipankar Mishra Research guide and Supervisor
- 6. Kalipada Bankura contributed different Molecular graphics preparation