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#### Research paper

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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

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#### ABSTRACT

Two new dicyanamide modulated zinc metal complexes  $[Zn_4(L^{OMe})_2(\mu_1-dca)_2(\mu_{1.5}-dca)_2]$  (1) and  $[Zn_3(L^{OEt})_2(H_2O)(\mu_1-dca)(\mu_1-dca)](2)$ have been synthesized using H<sub>2</sub>vanen-type compartmental ligands. Schiff base ligands and the complexes were characterized by means of elemental analyses, FT-IR, FT-Raman, UV-Visible, powder X-ray diffraction, TGA and fluorescence spectroscopy. Dicyanamide modulated Zn<sub>4</sub>/Zn<sub>3</sub>-nuclear metal complexes were structurally characterized by single crystal X-ray diffraction studies. In 1, the asymmetric Zn<sub>2</sub>nuclear unit was ensembled with one fully deprotonated Schiff base ligand [L<sup>OMe</sup>]<sup>2-</sup> along with two dicyanamide ions where two structurally independent Zn(II) metal centers are found in the X-ray crystal structure. Single X-ray crystal structure confirmed the environment of Zn1 is distorted square pyramidal whereas Zn2 acquires distorted tetrahedral geometry. Unlike 1, in 2 three independent zinc metal centers have been identified as square pyramidal (Zn1), distorted trigonal bipyramidal (Zn2) and distorted tetrahedral (Zn3). 1 and 2 geometry were optimized using hybrid B3LYP functional with DGDZVP basis set to explain frontier molecular orbitals, molecular electrostatic potential and Hirshfeld surface (d<sub>norm</sub> surfaces and 2D fingerprint plots). The electronic UV-Vis properties were determined by TD-DFT approach. The steady state and time-resolved fluorescence properties have been explored in DMSO solution. 1 and 2 exhibit biexponential decay and intra-ligand  $(\pi \rightarrow \pi^*)$  fluorescence behaviors with lifetimes in the range (2.45-5.71 ns). In addition, complexes solid-state and different solvent-dependent absorption and fluorescence spectra have been reported. Finally, the cytotoxic effect of the investigated dicyanamide complexes against breast cancer cell line (MCF7) shows promising results which makes them prospective complexes for anticancer medicament studies.

Keywords: Schiff base, Zn(II), Dicyanamide, DFT, Cytotoxic, Photoluminescence, TGA

#### 1. Introduction

 $\Omega$ -shape H<sub>2</sub>vanen-type compartmental ligands [1] on account of its tunable design [2] are capable of forming complexes with different transition metal ions, which can exhibit high thermodynamic stability, good photoluminescence and biological properties [3-8]. In this juncture, coordination chemistry of d<sup>10</sup> metal ions under the influence of identical ligands is always flourishing and well-studied research area since such ligands have preparative accessibilities, varied denticity, forming complexes with interesting molecular architectures and topologies [9-19]. However, systematic investigation of common counter anion effect involving pseudo-halide like dicyanamide anion  $[N(CN)_2]$ , coordination chemistry of group 12 metal ions with salen-type motifs is still unveiled of research. Salen-type complexes are employed as catalysts for organic reactions, supramolecular building blocks, nonlinear optical materials, interesting magnetic properties etc. [20-32]. Unlike other metals, zinc function as innumerable important role in chemical and biological field e.g. constructive active site of many hydrolytic enzymes, act as Lewis acid catalysts [33a-b], immune system, as a vital cofactor in many biological processes [33c-d]. Pseudo-halides and conjugated Schiff base platforms having interesting binding properties with zinc or other transition metal complexes always exhibit significant bioactivity owing to the presence of azomethine linkage, heteroatoms and presence of active metal centers [33e]. Moreover, research of cytotoxicity against breast cancer cell lines of Zn(II)-Schiff base complexes have irrefutably been growing exponentially because of their proven effectiveness as attractive frontrunner complex structures [34, 35]. This enhanced bioactivity may be explained with the help of 'Overton's concept' or 'Chelation theory' [36]. During the last few years, we have been exploring the photoluminescence, DFT, thermal, *in vitro* 

antibacterial and anti-biofilm properties of Zn(II)/Cd(II) metal complexes derived from N,O-rich *ortho* vanillin Schiff base platform especially in presence of pseudo-halide anions [SCN]<sup>-</sup>/[N<sub>3</sub>]<sup>-</sup>/[N(CN)<sub>2</sub><sup>-</sup>].Therefore, the only outcome of previous works is that common pseudo-halides linked metal complexes exhibit strong photoluminescence, antimicrobial and anti-biofilm properties [37a-h].To search further photoluminescence properties in solid-state as well as different solvent-dependent absorption and fluorescence spectra, complexation was carried out with Zn(II) metal ion and H<sub>2</sub>vanen-type ligands in presence of dicyanamide anion.

The unique d<sup>10</sup> candid nature, zero CFSE value always favor zinc metal ion to attain different molecular architectures [38a-f]. Hence the key factors for syntheses of zinc metal complexes are always careful selection of organic ligands along with effect of pseudo-halide anions such as dicyanamide or other common pseudo-halides [39]. Dicyanamide, a larger pseudo-halide ion-rod is under active consideration of complexation since it exhibits versatile coordination motifs with different metal ions [40-44]. Till date different dimensional molecular architectures and topologies of dicyanamide pseudo-halide involving complexes have been emerged in literature [45-60]. The  $\mu_{1,5}$ -bridging mode of dicyanamide is always expected but terminal coordination mode is rare due to its long chain length and negative charge delocalization over the symmetrical molecule [61]. In our dicyanamide complexes, a rare combination of terminal as well as  $\mu_{1,5}$ -bridging mode have been observed.

Herein, we report syntheses, X-ray crystal structures, DFT/TDDFT, cytotoxic effect, different solvent-dependent absorption and fluorescence spectra, steady state and time-resolved fluorescence properties of  $Zn_4/Zn_3$ -nuclear metal complexes viz.,  $[Zn_4(L^{OMe})_2(\mu_1-dca)_2(\mu_{1,5}-dca)_2]$  (1) and  $[Zn_3(L^{OEt})_2(H_2O)(\mu_1-dca)(\mu_{1,5}-dca)]$  (2) respectively.

#### 2.1. Materials and physical measurements

All the research chemicals were of analytical grade and used as purchased without further purification. All synthetic reactions were done in open air. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. IR and Raman spectra were recorded as KBr pellets (4000-400 cm<sup>-1</sup>) by using Perkin-Elmer spectrum RX 1 and BRUKER RFS 27 (4000-50 cm<sup>-1</sup>). UV-Visible spectra (200-1100 nm) were determined by using Hitachi model U-3501 spectrophotometer. Fluorescence spectra in DMSO solvent (spectroscopic grade) were measured by using Perkin-Elmer LS50B Spectrofluorometer model at room temperature (298K). Fluorescence lifetime measurements were recorded by using JOBIN-VYON M/S Fluorimeter. Thermo-gravimetric analyses (TGA) were carried out on a TGA-5OH analyzer from ambient temperature to 700°C at a temperature rate of 10°C/min in a flowing 30ml/min under environment of nitrogen atmosphere using a platinum cell. Powder diffraction measurements were carried out using BRUKER AXS, GERMANY X-ray diffractometer model using radiation Cu K $\alpha$ -1. Using equation (1), quantum yield ( $\Phi$ ) for dicyanamide bridged Zn(II)-complexes have been determined where quinine sulfate is preferentially used as the secondary standard ( $\Phi = 0.57$ in water) [62]

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

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.

#### 2.2. X-ray crystallography

Crystal data of dicyanamide complexes were collected on a Bruker SMART CCD [63] diffractometer using Mo K<sub>a</sub> radiation at  $\lambda = 0.71073$  Å. For collection of crystal data different common popular programs were operated e.g. SMART program used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT [64] for integration of the intensity of reflections and scaling, SADAB [65] for absorption correction, and popular SHELXTL for space group and structure determination and least-squares refinements on  $F^2$ . The crystal structure of 1-2 were fully solved and refined by full-matrix least-squares methods against  $F^2$  by using the common program SHELXL-2014 [66] and Olex-2 software [67]. It is worth mentioning that the Alert Level A in the checkCIF of 2 is related only to the Rint value is greater than 0.25 since examined single crystal was a small-sized, brittle and weakly diffracting. All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen positions were fixed at calculated positions and refined isotropically. Different crystallographic diagrams were constructed for two complexes by using latest Diamond software [68]. The crystallographic data and full crystal structure refinement parameters for 1-2 are submitted in Table 1. Crystallographic data (excluding structure factors) of both complexes have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1887056-1887057. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: http://www.ccdc.cam.ac.uk/cgibin/catreq.cgi, e-mail:data request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Formula	$C_{44}H_{36}N_{16}O_8Zn_4$	$C_{88}H_{88}N_{20}O_{19}Zn_6$
M/g	1178.45	2122.00
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	C2/c
a/Å	9.626(4)	27.467(3)
b/Å	11.345(4)	17.906(2)
c/Å	108.821(4)	19.190(2)
α (°)	108.821(4)	90.00
$\beta$ (°)	94.207(5)	95.518(7)
γ (°)	101.057(5)	90.00
V/Å <sup>3</sup>	1294.7(9)	9394.4(18)
Ζ	2	4
$ ho_{ m c}/ m g\ cm^{-3}$	1.511	1.500
$\mu/\mathrm{mm}^{-1}$	1.896	1.585
F(000)	596	4352
Cryst size (mm <sup>3</sup> )	$0.280 \times 0.220 \times 0.180$	$0.2 \times 0.2 \times 0.1$
$\theta$ range (deg)	0.963	0.988
Limiting indices	$-12 \le h \le 13$	$-32 \le h \le 32$
	$-15 \le k \le 15$	$-21 \le k \le 19$
	-17≤1≤17	$-22 \le 1 \le 22$
Reflns collected	39885	48010
Ind reflns	$6706 [R_{int} = 0.0756, R_{sigma} =$	$8002 [R_{int} = 0.5605, R_{sigma} =$
	0.0594]	0.3608]
Completeness to $\theta$ (%)	0.963	0.998
Refinement method	Full-matrix-block least-	Full-matrix-block least-squares on
	squares on F <sup>2</sup>	F <sup>2</sup>
Data/restraints/	6706/657/327	8002/0/604
parameters		
Goodness-of-fit on $F^2$	1.002	0.926
Final <i>R</i> indices	$R_1 = 0.0738$	$R_1 = 0.0995$
$[I > 2\theta(I)]$	$wR_2 = 0.2110$	$wR_2 = 0.1127$
R indices (all data)	$R_1 = 0.1516$	$R_1 = 0.2674$
\`, ``,	$wR_2 = 0.2666$	$wR_2 = 0.1435$
Largest diff. peak and hole(e·Å <sup>-3</sup> )	1.324 and -0.590	0.091 and -1.002

# Table 1 Crystal data and full structure refinement parameters of $1 \mbox{ and } 2$

#### 2.3. Computational methodologies

All DFT calculations are performed on the optimized geometry using hybrid B3LYP functional with DGDZVP basis set. Frequency calculations are performed for the absence of imaginary frequencies, such that a geometry minimum is obtained. All calculations were performed using Gaussian 09W software [69] and visualized using Gauss View 5.0 [70]. Hirshfeld surface analysis and 2D fingerprint plots were generated using Crystal Explorer 17 via cif files obtained as a result of single crystal X-ray diffraction. The Hirshfeld surface were calculated with DFT using B3LYP functional and 6-31G(d) basis set using the TONTO *Abinitio* and DFT code fixed within the Crystal Explorer 17 [71]. The TD-DFT calculations for (1-2) are performed using CAM-B3LYP functional using DGDZVP basis set with methanol as solvent using the PCM model to incorporate the solvent effects.

#### 2.4. Cell culture and growth inhibition

Breast cancer cell line MCF7 was grown in DMEM (Dulbecco's Modified Eagle Medium) as monolayer supplemented with 10 % FBS (Foetal Bovine Serum), 100 U/ml penicillin and 100  $\mu$ g/ml streptomycin at 37°C in a humid, 5% CO<sub>2</sub> atmosphere. The cytotoxic effect of Zn(II)dicyanamide complexes are evaluated by MTT (3-(4, 5 dimethylthiazol-2-yl)-2,5diphenyltetrazolium bromide) assay. Cells (5 X 10<sup>3</sup> per well of 96 well plate) were seeded 24 hours prior to the treatment. The cells were treated with different concentrations of the compounds (0 – 100  $\mu$ M) for 48 hours in triplicate. After 48 hours of drug treatment, MTT solution (20  $\mu$ M of 5 mg/ml stock for each well) was added to the media and cells were further allowed to be incubated for 4 hours in humid 5% CO2 incubator. Then, media containing MTT solution was replaced by MTT solvent (isopropanol, 4 mM HCl and 0.01% Triton X-100) and

incubated for 15 min at room temperature with gentle rocking to ensure the complete dissolution of Formazan. Finally, the absorbance was measured at 590 nm using a Thermo Pierce Elisa plate reader. All experiments were carried out at least three biological triplicates. The percentage of viable cells was calculated in comparison with the growth of vehicle treated cells and it was taking as 100%.

#### 2.5. Syntheses of Schiff base ligands

Schiff base ligands were synthesized by the common condensation process of 1 mmol (0.152 g) 3-methoxysalicylaldehyde or (0.1662 g) 3-ethoxysalicylaldehyde with 0.5 mmol (0.0301 g) ethylenediamine (en) in (30 mL) of methanol for ca. 2 h (Scheme 1). The orange yellow solution was used for dicyanamide complex formation.



Scheme 1. Synthetic Scheme for H<sub>2</sub>vanen-type ligands

#### 2.6. Synthesis of $[Zn_4(L^{OMe})_2(\mu_1-dca)_2(\mu_{1,5}-dca)_2]$ (1)

To the methanolic solution (20 mL) of zinc acetate dihydrate (0.2195 g, 1 mmol), yellow colored solution of Schiff base ligand (H<sub>2</sub>L<sup>OMe</sup>) was added directly followed by mixing an aqueous methanolic solution (5 mL) of sodium dicyanamide (0.0891 g, 1 mmol). The overall reaction mixture was then refluxed for 30 min at 60 °C. Then few drops of Dichloromethane (DCM) were added. Solution was cooled at room temperature and constant stirring continued for 3 h. Finally, the light yellow filtrate was kept for crystallization by slow evaporation at room temperature. After 15 days yellow colored single crystal suitable for X-ray crystallography was obtained. Crystals were isolated by filtration and air dried. Yield: 0.467g, Anal. Calc. for C<sub>44</sub>H<sub>36</sub>N<sub>16</sub>O<sub>8</sub>Zn<sub>4</sub>: C, 44.85; H, 3.08; N, 19.02. Found: C, 44.78; H, 3.00; N, 19.00 %. IR (KBr cm<sup>-1</sup>) selected bands: v(C=N), 2286 m, 2220 m, 2170 vs, v(C=N), 1643 vs, FT-Raman (cm<sup>-1</sup>) selected bands: v(C=N), 1640 vs, v(C=N), 2276 m, 2208 s, 2128 s, UV-Vis  $\lambda_{max}$  (DMSO): 285 nm, 363 nm.

#### 2.7. Synthesis of $[Zn_3(L^{OEt})_2(H_2O)(\mu_1-dca)(\mu_{1,5}-dca)]$ (2)

Complex **2** was prepared by adopting the similar procedure as **1** except Schiff base solution used is (H<sub>2</sub>L<sup>OEt</sup>). Yield: 0.459g, Anal. Calc. for C<sub>88</sub>H<sub>88</sub>N<sub>20</sub>O<sub>19</sub>Zn<sub>6</sub>: C, 49.81; H, 4.18; N, 13.20 Found: C, 49.75; H, 4.13; N, 13.14 %. IR (KBr cm<sup>-1</sup>) selected bands: v(C=N), 2280 m, 2217 m, 2180 vs, v(C=N), 1638 vs, FT-Raman (cm<sup>-1</sup>) selected bands: v(C=N), 1654 vs, v(C=N), 2281 s, 2227 m, 2172 w, UV-Vis  $\lambda_{max}$  (DMSO): 279 nm, 368 nm.

#### 3. Results and discussion

#### 3.1. Syntheses

Schiff base ligands were synthesized by the condensation of ethylenediamine (en) with 3methoxysalicyldehyde or 3-ethoxysalicyldehyde in MeOH at 1:2 molar ratio [72]. Complexes (1-2), derived from two identical ligands were prepared in good yields by taking the following

procedure where 1:1:1 molar ratio of zinc acetate dihydrate, Schiff base ligands (H<sub>2</sub>L<sup>OMe</sup>/H<sub>2</sub>L<sup>OEt</sup>) and sodium dicyanamide in methanolic solution under stirred condition (Scheme 2). The versatile binding ability of H<sub>2</sub>vanen-type ligands and dicyanamide anions with metal ions ( $M^{2+}$ ) are presented in Scheme S1-S2. The crystal complexes were isolated only from slow evaporation of mixed solvent (CH<sub>3</sub>OH-DCM) medium at room temperature. H<sub>2</sub>vanen-type ligands comprises two imines, two phenols and methoxy or ethoxy groups. After de-protonation action of [L<sup>OMe</sup>]<sup>2-</sup> /[L<sup>OEt</sup>]<sup>2-</sup> the N<sub>2</sub>O<sub>2</sub> imine-based chelating site of ligand has the novel property to bind perfectly with several transition metal ions whereas pseudo-halide preferentially dicyanamide anions assisted complexation with zinc metal ion is still now unveiled of research. Such compartmental ligands have additional coordination moiety  $(N_2O_2)$  to a transition metal ion that reorganizes the ligand in a  $\Omega$ -shape generating a second potential recognition site  $O_2O_2$  which are further able to accept several metal ions [1] (Scheme 3). Air stable yellow coloured neutral zinc metal complexes are successfully characterized by elemental analyses, UV-Vis, FT-IR, FT-Raman, powder X-ray diffraction, TGA, X-ray crystallography and fluorescence spectroscopy. According to Scheme 2, two Schiff base ligands are behaving as 'pendant' character on account of its additional donor groups attached to its periphery. In modern coordination chemistry, such pendant ligands are used in a variety of different chemical application. Till date Mitra et al. reported different salen-type ligands involving Zn(II)-dicyanamide complexes [73]. To the best of our knowledge H<sub>2</sub>vanen-type ligands have never been utilized to synthesize neutral dicyanamide modulated  $Zn_4/Zn_3$ -nuclear metal complexes (1 or 2).



Scheme 3:  $H_2$  vanen-type ligand showing  $\Omega$ -shape of  $O_2O_2$  potential site

#### 3.2. Spectral characterizations

H<sub>2</sub>vanen-type Schiff base formations are well characterized by IR, and UV-Vis spectroscopic studies (Fig.S1, Fig.S2). The characteristic imines v(C=N) of two symmetric ligands are found to be 1633, 1631 cm<sup>-1</sup> respectively [74a-b] (Fig.S1). In complexes (1-2), these stretching vibration bands are shifted to 1643, 1638 cm<sup>-1</sup> [74c] (Fig.S1). Pseudo-halide dicyanamide anion [N(CN)<sub>2</sub>]<sup>-</sup> showed three sharp strong characteristic band preferably in the region 2300-2170 cm<sup>-1</sup> [75]. Two medium intensity bands (at 2286, 2220 cm<sup>-1</sup> in 1 and 2280, 2217 cm<sup>-1</sup> in 2) and effective strong intensity band (at 2170 cm<sup>-1</sup> in 1 and 2180 cm<sup>-1</sup> in 2) are indicative of the presence of dicyanamide in these two complexes. In this context, IR spectra with other reported Zn(II)-dicyanamide complexes were further consider to established the bridging propensity of pseudo-halide [N(CN)<sub>2</sub>]<sup>-</sup> anions (Table 3) [77]. Aliphatic C-H stretching bands for dicyanamide complexes, Ar-O stretching frequencies observed near at 1243-1217 cm<sup>-1</sup> and 1242-1217 cm<sup>-1</sup> which is similar to the other reported salen-type ligands [78].

**Table 2** Comparison of asymmetric stretching frequency [FT-IR],  $v_{as}(dca)$ , of the dicyanamideanion with other reported dicyanamide complexes

Complexes	ν(		Ref	
	$v_{as+}v_s(C\equiv N)$	$v_{as}(C\equiv N)$	$\nu_{s}(C\equiv N)$	
$[Zn_4(L^{OMe})_2(\mu_1-dca)_2(\mu_{1,5}-dca)_2]$	2286	2220	2170	This work
$[Zn_3(L^{OEt})_2(H_2O)(\mu_1-dca)(\mu_{1,5}-dca)]$	2280	2217	2180	This work
Free $[N(CN)_2]^-$ anion	2300-2170	2232	2179	a
$[Zn_2(L)(\mu_{1,5}-dca)_2]_n$	2370	2345-2323	2253-2190	b

$\{Zn_2(L^1)(\mu_{1,5}-dca)_2dca.CH_3OH\}_2$	2357-2345	2295	2223	73
$[Zn_2(L^2)(\mu_{1,5}-dca)dca]_n$	2371-2345	2244	2134	73
$[Zn_3(L^3_2)(\mu_{1,5}-dca)_2]_n$	2379-2360	2277	2213	73
[(HL2)Zn2(L2)(dca)2]ClO4	2292	2226	2173	с
${Zn_2(L^1)(\mu_{1,5}-dca)_2dca](H_2O)}_n$	2345	-	2193	39
$\{[Zn_2(L)(\mu_{1,5}-dca)](ClO_4)\}_n$	2377	-	2188	
$\{[Na(CuIIL3)2](\mu 1, 5-dca)\}n$	2244	2189	2134	d
$[Zn(dca)_2]$	2298-2209	1417-1408	964	e
$[Cu_2(\mu_{1,5}\text{-}dca)(\mu\text{-}L)_2ClO_4]_n$	2286	2232	2179	f
[Zn(LH)(OAc)(dca)]	2170	-		g
[Cd(LH)(OAc)(dca)]	2157	-	-	
$[CuL^{1}(\mu_{1,5}-dca)]_{n}$	2343-2123	-	<b></b>	h
$[CuL^2(\mu_{1,5}-dca)]_n$				
$[CuL(\mu_{1,5}\text{-}dca)_n].nH_2O$	2293	2240	2174	i
[ZnL(dca)] <sub>n</sub>	2380-2230	-	-	j
[BN(CN) <sub>2</sub> ]	-	2287	2170	k
$[(Cu(II)L)_2M(II)(\mu_{1,5}-dca)_2]_n$	-	2288	2165	1

 Table 3 Raman spectra of different stretching vibration v(CN) bands for M(II)-dicyanamide

 complexes

M(II)-	Different Raman spectral bands [cm <sup>-1</sup> ]						Ref	
dicyanamide								
complexes	$v_{s}(C \equiv N)$	$v_{as}(C \equiv$	v <sub>s</sub> (C	CNC)	δ(CNC)/	$v(MN)_{amide}$	$v(MN_{CN})$	
		N)			δ(NCN)			
KN(CN) <sub>2</sub>	2219	2195	9	82	669	-	-	a
	2209				546			
$Fe{[N(CN)_2]_2}$	2260	2194	9	63	682	291	256	a
		2176			523		213	
$Co\{[N(CN)_2]_2\}$	2265	2198	9	72	746	300	266	a
					683		236	
$Ni\{[N(CN)_2]_2\}$	2276	2207	1(	)45	690	317	288	a
		2185	9	80	533			
$Cu{[N(CN)_2]_2}$	2294	2174	9	50	665	318	310	a
	2272				533		278	
$Zn\{[N(CN)_2]_2\}$	2289	2217	9	80	670	333	238	a
		2190					206	
				v(de	ca) cm <sup>-1</sup>			
		$v_{as+}v_s(C\equiv N)$ $v_{as}(C\equiv N)$ $v_s(C\equiv N)$ -			-			

[Cu(dca) <sub>2</sub> ]	2272	2174	2294	-	b
Li{N(CN) <sub>2</sub> ]	2236 2246	2168	2105	-	c
${\rm LiCs_2[dca]_3}$	2288	2133	-	-	c
$[Zn_4(L^{OMe})_2(\mu_1-dca)_2(\mu_{1,5}-dca)_2]$	2276	2208	2128		This wor k
$[Zn_3(L^{OEt})_2(H_2O)(\mu_1-dca)(\mu_{1,5}-$	2281	2227	2172		This
dca)]					wor
					k

#### 3.3. UV-Vis spectra

The UV-Vis spectroscopic study of Schiff base ligands along with the dicyanamide complexes was done in the wavelength region (200-1100 nm) using spectroscopic grade DMSO as solvent (Fig.S2). Free Schiff base ligands exhibit bands at 332 nm and 336 nm which are assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. Dicyanamide complexes exhibit ligand-based transition at 285 nm, 363 nm (for 1) and 279 nm, 368 nm (for 2) respectively due to  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  type of transitions [79, 80]. No characteristic broad d-d absorption band was assigned in the UV-Vis spectra of either complex 1 or 2.

3.4. X-ray powder diffraction studies

The crystalline phase purity of two dicyanamide complexes was confirmed by X-ray powder diffraction pattern. The X-ray powder diffraction patterns for both dicyanamide complexes were recorded experimentally after considering  $2\theta$  scan from  $4^{0}$  to  $50^{0}$ . As clearly observed in the experimental PXRD patterns (Fig.S4), most of the major peak positions of the bulk solids of both dicyanamide complexes agree very well with the patterns simulated from single-crystal diffraction data (CIF for **1** & **2**) obtained from CCDC Mercury software consisting that single crystals and bulk material are the same. It also further confirms phase purity of the bulk crystal sample.

 $\mathbf{\mathbf{\mathbf{\mathbf{5}}}}$ 

#### 4. Description of X-ray crystal structure

4.1. Crystal structure of  $[Zn_4(L^{OMe})_2(\mu_1-dca)_2(\mu_{1,5}-dca)_2]$  (1)

Single crystal X-ray analysis reveals that complex 1 crystallizes in triclinic space group *P*-1 (Z = 2). As depicted in Fig.1, the asymmetric unit comprises one half the overall molecule, i.e  $[Zn_2(L^{OMe})(dca)_2]$ . The selected important bond angles (°) and bond length (Å) are given in Table S1.



**Fig.1.** Perspective view of asymmetric unit of **1** where hydrogen atoms are omitted for clarity Asymmetric di-nuclear unit was ensembled with one fully deprotonated ligand  $[L^{OMe}]^{2-}$  along with two cyanamide ions. In the formation of di-nuclear assembly a fully deprotonated ligand grasps two Zn(II) ions in  $\mu_2-\eta^2:\eta^1:\eta^1:\eta^2$  mode (Fig.2). In this binding mode, the fully

deprotonated hexadentate ligand utilizes only four coordination sites i.e. two phenolate oxygen atoms (O1, O2) and two imine nitrogen atoms (N1, N2). Interestingly, tetradentate pocket (O<sub>2</sub>N<sub>2</sub>) has been used to accommodate Zn(1) metal center. On contrary, tetradentate pocket (O<sub>4</sub>) accommodate Zn(2) metal center where only two phenolate  $\mu_2$ -oxygen atoms have been utilized in binding of Zn(2) metal center. Coordination number of Zn(2) metal center is fulfilled by binding of two dca anions. One of the dca anion shows  $\mu_1$  coordination mode acts as a terminal ligand. On the other hand, another dca anion shows  $\mu_{1,5}$  coordination mode (Fig.2) to connect Zn(2) and Zn(1) centers of subunits. So, this bridging coordination mode has connected the two di-nuclear asymmetric units to form overall tetranuclear assembly (Fig.3). The tetranuclear unit possesses a 16-member macrocycle ring (Zn<sub>4</sub>O<sub>4</sub>N<sub>8</sub>C<sub>2</sub>) between two connected di-nuclear motifs through  $\mu_{1,5}$  coordination mode of dicyanamide anion (Fig.4).



Fig.2. Binding mode of the ligand [L<sup>OMe</sup>]<sup>2-</sup> and anionic dca in 1



Fig.4. 16-member macrocycle ring (Zn<sub>4</sub>O<sub>4</sub>N<sub>8</sub>C<sub>2</sub>) between two connected di-nuclear motifs

Two structurally independent Zn(II) centers are found in the single X-ray crystal structure. Zn(1) displays 5-coordination geometry with distorted square pyramidal shape with a r value 0.16 [81] (ideal value of tau (r) for square pyramidal geometry is 0) which is consists of one apical N atom from bridging dicyanamide anion and basal  $N_2O_2$  donors from fully deprotonated ligand (Fig.5). Zn(2) shows four coordination in a distorted tetrahedral geometry (Fig.5) which is composed by two N atoms from dca anion, two phenolate oxygen atoms from deprotonated coordinating ligand [L<sup>OMe</sup>]<sup>2-</sup>.



Fig.5. Coordination geometry around Zn centers (a) Zn1 acquires a distorted square pyramidal shape (b) Zn2 acquires distorted tetrahedral shape

The bond lengths of metal coordinated phenoxy atom are of range 1.984- 2.040 Å while the metal coordinated nitrogen atoms are of range 1.935- 2.062Å. The bond angle Zn1-O2-Zn2 and Zn1-O1-Zn2 are 101.8° and 99.66° respectively (Fig.3). The distance between Zn 1 and Zn 2 metal centers is 3.100 Å that is totally comparable to other Zn—Zn separation of double phenoxo-bridged Zn<sub>2</sub> complexes [82a-b]. The bond distances in **1** are totally comparable to other reported Zn(II)-dicyanamide complexes (Table 4) [76]. Complex **1** shows 2D supramolecular assembly formation owing to the presence of N--H secondary interactions in the solid-state

structure (Fig.S5). The formation of 2-D polymeric structure is felicitated by N4 and N5 of terminal dca anion bonding with C-H groups (Fig.S5).

4.2. Crystal structure of  $[Zn_3(L^{OEt})_2(H_2O)(\mu_1-dca)(\mu_{1,5}-dca)]$  (2)

Single X-ray data analysis reveals that the compound crystallizes in the monoclinic system in the C2/c space group (Z=4). The structure of complex 2 is detailed in Fig.6. The selected bond distances (Å) and angles (°) are given in Table S1.



**Fig.6.** Molecular structure of **2** where hydrogen atoms are omitted for clarity The crystal structure of complex **2** consists of a neutral and trinuclear unit  $[Zn_3(L^{OEt})_2(H_2O)(\mu_1 - dca)(\mu_{1,5}-dca)]$  with a water of crystallization. The homometallic trinuclear complex **2** was assembled with the help of two fully deprotonated ligands  $[L^{OEt}]^{2-}$ . As discussed in previous structure, the fully deprotonated hexadentate ligand utilizes tetra cordination to accommodate the

Zn(II) ions. Two ligands has been utilzed in the complex formation which has shown different coordination behaviour. One of the deprotonated ligand shows coordination behaviour in  $\mu_2$ - $\eta^2$ : $\eta^1$ : $\eta^1$ : $\eta^2$  mode (Fig.2) which accommodate two Zn(II) centers where phenolate oxygen atom functions as a bridging ligand to form a four-membered Zn<sub>2</sub>O<sub>2</sub> motif. On the other hand, other deprotonated ligand display  $\mu_1$ - $\eta^1$ : $\eta^1$ : $\eta^1$ : $\eta^1$  coordination mode (Fig.7) to accommodate only one Zn(II) center. Futhermore, one of the dca anion shows  $\mu_{1,5}$  coordination mode (Fig.2) to connect Zn(3) and Zn(1) centers of different subunits to construct the trinuclear assembly. Another dca anion displays  $\mu_1$  coordination mode to coordinate the Zn(3) metal center in order to fulfil charge and coordination number. Besides, coordination number of Zn(2) metal center is fulfilled by coordination of water molecule.



Fig.7. Binding mode of the ligand  $[L^{OEt}]^{2-}$  in 2

The zinc atom in mono-nuclear moiety is five-coordinated with square pyramidal geometry. The Zn2 atom in di-nuclear moiety is also five-coordinated with distorted trigonal bipyramidal geometry. Here, Zn3 atom present shows distorted tetrahedral structure being four-coordinated (Fig.8). In the vicinity of all the Zn atoms both oxygen and nitrogen coordination geometry are found. The bond length of metal coordinated phenolate oxygen is in the range of 1.978 - 2.732 Å. The Zn-N bond lengths are of range 1.922 – 2.090 Å. The bond angle of Zn2-O5<sub>phenoxy</sub>-Zn3

and Zn2-O7<sub>phenoxy</sub>-Zn3 are 99.4 and 99.2° respectively. The distance between Zn 2 and Zn 3 metal centers is 3.082 Å that is comparable to other Zn—Zn separation of double phenoxobridged Zn<sub>2</sub> complexes [82a-b]. The bond distances of **1** and **2** are totally comparable to other reported Zn(II)-dicyanamide Schiff base complexes (Table 4) [76]. The complex **2** displays rich supramolecular interaction through C-H...N and C-H...Π interaction to generate a 2D assembly (Figure S6). The structural aspect, architectures and bridging propensity of dicyanamide anion involving complex **1** & **2** has been compared with different dicyanamide complexes coordinated to closely identical salen-type ligands (Table 5) [83]. Complex **1** & **2**, some selected important bond distances (Å) and angles (°) values are shown in Table 6.



**Fig. 8** Local coordination assembly of (a) Zn1 having square pyramidal (b) Zn2 having distorted trigonal bipyramidal (c) Zn3 having distorted tetrahedral

Complexes	Bond distances (Å)	Ref
$[Zn_4(L^{OMe})_2(\mu_1\text{-}dca)_2(\mu_{1,5}\text{-}dca)_2]$	1.943-2.043	This work
$[Zn_3(L^{OEt})_2(H_2O)(\mu_1-dca)(\mu_{1,5}-dca)]$	1.922-2.080	This work
Free $[N(CN)_2]^-$ anion	1.220-1.280	a
$[Zn_2(L)(\mu_{1,5}-dca)_2]_n$	1.986-2.074	b
$\{Zn_2(L^1)(\mu_{1,5}\text{-}dca)_2dca.CH_3OH\}$	2.036-2.073	73
$[Zn_2(L^2)(\mu_{1,5}\text{-}dca)_2dca]_n$	1.988-2.080	73
$[Zn_3(L^3_2)(\mu_{1,5}-dca)_2]_n$	2.005-2.119	73
$[(HL^2)Zn_2(L^2)(dca)_2]ClO_4$	1.954-2.094	с
$\{Zn_2(L^1)(\mu_{1,5}\text{-}dca)_2dca](H_2O)\}_n$	1.984-2.068	39
$\{[Zn_2(L)(\mu_{1,5}\text{-}dca)](ClO_4)\}_n$	2.102-2.180	
$\{[Na(Cu(II)(L3)2](\mu 1,5-dca)\}n$	1.980-2.644	d
$[Zn(dca)_2]$	1.980-2450	e
$[Cu_2(\mu_{1,5}-dca)(\mu-L)_2ClO_4]_n$	1.970-1.988	f
[Zn(LH)(OAc)(dca)]	1.907-1.987	g
[Cd(LH)(OAc)(dca)]	1.987-2.346	
$[CuL^1(\mu_{1,5}-dca)]_n$	1.948-2.463	h
$[CuL^2(\mu_{1,5}\text{-}dca)]_n$	1.958-2.373	
$[CuL(\mu_{1,5}\text{-}dca)_n].nH_2O$	1.973-2.258	i
[ZnL(dca)] <sub>n</sub>	2.046-2.154	j
[BN(CN) <sub>2</sub> ]	2.002-2.207	k
$[(Cu(II)L)_2M(II)(\mu_{1,5}-dca)_2]_n$	2.017-2.064	1

**Table 4** Bond distances (Å) comparison of Zn(II)-dicyanamide complexes with other reported dicyanamide complexes

**Table 5** Structurally characterization of M(II)-dicyanamide Schiff base complexes of the anionic forms of present investigated ligand ( $H_2L^{OMe}/H_2L^{OEt}$ ) with closely resemblance ligand ( $H_2L^{OMe1}$ )

Complexes	Closely identical	Present	Bridging	Complex	Ref
	salen-type ligands	investigated	nature of	nature	
	$(H_2L^{OMe1}/H_2L^{OEt})$	salen-type	[N(CN) <sub>2</sub> ] <sup>-</sup>		
	anionic donor forms	ligands	anion		
$[Zn_4(L^{OMe})_2(\mu_1-dca)_2(\mu_{1.5}-$	-	In <b>1</b> ,	$\mu_{1.5}$ as	$Zn_4/Zn_3$ -	This
dca) <sub>2</sub> ]		diphenoxido	well as	nuclear	work
		N(iminne) <sub>2</sub> O(	terminal	metal dca	
		phenoxo) <sub>2</sub>	bridging	complexes	
		Zn(II) metal	of dca		
		occupation.	observed.		
		-OMe also	Two		
		coordinated	complexes		
$[Zn_3(L^{OEt})_2(H_2O)(\mu_1-dca)(\mu_{1,5}-$	-	with Zn(II)	are neutral		This
dca)]					work
		For <b>2</b> , water			
		is			
		additionally			
		coordinated			
		with zinc			
		metalOEt			
		also			
		with $Z_{n}(\mathbf{II})$			
$1$ (i) [Cu(II) $Z_{p}(II)(dop)$ (u	(i)Dinhanavida di	with Zh(11)	u daa	Hotoro	0
1. (1) [ $Cu(11)ZII(11)(UCa)_2(\mu_{1,5})$	(I)Diplicitoxido di-	-	$\mu_{1,5}$ -uca	metallic	a
	N(iminne). O(nhenovo).			di-nuclear	
(ii)[(Cu(II)] Cd(II)(dea))(Cu(I))	$\Gamma_{\rm U}({\rm III})$ metal		udca	ui-nucicai	
DI Cd(II) {Cu(II)(MeCN)I Cd	occupation		μ1,5-αθα	1D	
$(II)(u_1 - dca)]_{-}$				polymer	
(II)(µ1,5 ded)]n	(ii) Diphenoxido poly-			porymer	
	nuclear moiety.				
	O(phenoxo) <sub>2</sub> O(ethoxy)				
	2 Zn(II) or Cd(II) metal				
v	occupation.				
2. $[Zn_2(L)(\mu_{1,5}-dca)_2]_n$	Diphenoxido	-	$\mu_{1,5}$ -dca	2D	76b
	moiety.		• 7-	hexagonal	
	$N(\text{iminne})_2 O(\text{phenoxo})_2$			helical	
	Zn(II) metal			chains	
	occupation.				
$3 \{Zn_2(L^1)(u_1, dea)\}$	Dinhenoxido		u, -dca	Discrete	73
H}	moiety.		μ1,5 ανα	1D	

	N(iminne) <sub>2</sub> O(phenoxo) <sub>2</sub>			polymer	
$[Zn_2(L^2)(\mu_{1,5}\text{-}dca)_2dca]_n$	Zn(II) metal			and 1D	
	occupation.			loop like	
$[Zn_3(L^3_2)(\mu_{1,5}-dca)_2]_n$				polymer	
4 [(HI 2)7n (I 2)(dan) - 1C10	Dinhanavida		u. daa	Di nuclear	760
4. $[(\Pi L^{-})Z\Pi_{2}(L^{-})(UCa)_{2}]CIO_{4}$	Diplielloxido	-	$\mu_{1,1}$ -uca	DI-IIucieai	700
	N(iminna) O(nhanaya)				
	along with O(Mathoxy)				
	Zn(II) metal				
5 (7n (I))(u daa) daa](H O)	Dhanavida		u daa	1D	20
$5.{2 \Pi_2(L^2)(\mu_{1,5}uca)_2uca](\Pi_2O)}$	Flielloxido	-	$\mu_{1,5}$ -dea	nolymor	39
∫n	N(iminna) O(nhanaya)			porymer	
([7n (I)(u - doo)](C(O)))	$N(\text{Infinite})_2O(\text{phenox}0)$ $N(\text{Dr}) Z_{\text{P}}(\text{II}) \text{ model}$				
$\{[ZII_2(L)(\mu_{1,5}-uca)](CIO_4)\}_n$	N(Fy) ZII(II) Inetal				
$f_{\rm c}$ (ENa(Cu(U)(L2)2)(1.5	Dinhenewide		daa	1D	764
$0.{[INa(Cu(II)(L3)2](\mu 1,3-$	Dipnenoxido	-	$\mu_{1,5}$ -dca	ID Delaman	/60
dca) n	$\frac{\text{molety.}}{\text{N(inviews)}}$			Polymer	
	$N(\text{Iminne})_2 O(\text{pnenoxo})_2$				
	Cu(II) metal				
	occupation. Na metal				
	also occupied in the				
	O(methoxy)				
			1	20	$\overline{7}$ (1)
$/. [(Cu(II)L)_2MI(II)(\mu_{1,5}-$	Phenoxido	-	$\mu_{1,5}$ -aca	2D	76 (I)
$dca)_2]_n$	Molety.			polymer	
	$N(1minne)_2O(pnenoxo)$				
	of M(II) metal				
			1	1D	766
$8.[Cu_2(\mu_{1,5}-dca)(\mu-L)_2CIO_4]_n$	$N(\text{Iminne})_2 O(\text{pnenoxo})_2$	-	$\mu_{1,5}$ -dca		/01
	Cu(II) metal			Polymer	
$[(\mathbf{A}_{\mathbf{A}})(\mathbf{A}_{\mathbf{A}})(\mathbf{A}_{\mathbf{A}})]$	Occupation.			Mana	76-
9.[Zn(LH)(OAc)(dca)]	N(1minne)O(phenoxo)	-	$\mu_{1,5}$ -dca	Mono-	/6g
[Cd(LH)(OAC)(dca)]	of Zn(II)/Cd(II) metal			nuclear	
10 [CyJ] ( dae)]	N(iming a) Q(nh an awa)/		daa	Dalar	761
$[10.[CuL^{2}(\mu_{1,5}-aca)]_{n}$	N(Iminne)O(pnenoxo)/	-	$\mu_{1,5}$ -dca	Poly-	/011
$[CuL^{2}(\mu_{1,5}-uca)]_{n}$	NMe <sub>2</sub> /NEt <sub>2</sub> , Cu(II)			nuclear	
	Minimum a)Q(ah an arra)/			1 D D - 1	7(:
11.[CuL( $\mu_{1,5}$ -dca) <sub>n</sub> ].nH <sub>2</sub> O	N(iminne)O(pnenoxo)/	-	$\mu_{1,5}$ -dca	ID Poly-	/01
	NMe <sub>2</sub> , Cu(II) metal			nuclear	
$\frac{12 [Cy (L_3)(dec)]}{12 [Cy (L_3)(dec)]}$	V(iminno)O(nhonowe)/			Dolyman	<u> </u>
$12.[Cu_2(L^2/(uca)_2]_n.H_2O.1.5Me]$	N(Imme)(pnenoxo)/	-	$\mu_{1,5}$ -aca	Polymer	D
	in-motphonine of Cu(II)				

25

Bond lengths (Å)	Value (Å)	Bond angles (°)	Value (°)
1			
Zn1-N1	2.662(6)	N1-Zn1-N2	81.4(3)
Zn1-N2	2.049(9)	O1-Zn1-O2	78.4(2)
Zn1-N6	1.943(6)	O2-Zn2-O1	79.4(2)
Zn1-O1	2040(5)	N3-Zn2-N6	116.00(3)
Zn1-O2	2.010(6)	N3-Zn2-O1	110.5(2)
Zn2-N3	1.935(7)	O2-Zn1-N8	105.1(2)
Zn2-O2	1.984(6)	O1-Zn1-N8	104.2(2)
Zn2-O1	2.016(5)	N1-Zn1-O1	89.00(3)
		N1-Zn1-O2	145.8(3)
		N1-Zn1-N8	108.8(3)
		N2-Zn1-N8	112.9(3)
2			
Zn1-N1	2.080(9)	N1-Zn1-N2	78.9(3)
Zn1-N2	2.09(9)	O1-Zn1-O3	91.8(2)
Zn1-O3	2.010(6)	O3-Zn1-N5	103.4(3)
Zn1-O1	1.978(6)	N5-Zn1-N1	99.3(3)
Zn1-N5	2.014(8)	N5-Zn1-N2	104.2(3)
Zn2-N4	2.043(8)	N3-Zn2-N4	81.10(3)
Zn2-N3	2.010(8)	O5-Zn2-O7	78.5(2)
Zn2-O5	2.019(6)	N7-Zn3-N8	123.6(3)
Zn2-O7	2.012(6)	O5-Zn3-O7	77.9(2)
Zn3-O5	2.022(6)	N7-Zn3-O5	111.00(30
Zn3-07	2.034(6)		
Zn3-N7	1.922(8)		
Zn3-N8	1.968(6)		

### Table 6 Selected some important bond distances (Å) and angles (°) for 1 and 2 $\,$

#### 4.3. Hirshfeld surface

Hirshfeld surface analysis is generally used to study the intermolecular between different molecules and intra molecular interaction within a molecule in a crystal lattice. It's size and

shape of the complex is used as tool for qualitative and quantitative interpretation of close contacts within the crystal system of the complex. Hirshfeld surface of a particular complex is explained as a set of points in the 3D region where the contribution to the density of electron is same to the total contribution from all other molecules. MESP mapping on the Hirshfeld surface acts as a tool to study electrostatic complementarily between nearby molecules, which provides basic knowledge about the crystal packing. Total electrostatic interactions are determined as a sum of electrostatic interaction, polarization, dispersion and exchange repulsion which all are calibrated against dispersion corrected DFT [84]. HS summarizes the complex information present in a molecule into a color plot, which is a finger print of the various types of intermolecular interactions in the unit cell. Details of  $d_{norm}$ , shape Index and curved Index are provided for 1 and 2 in Fig. 9 and Fig. 10.

For 1, the globularity value is 0.568 and a sphericity value if 0.042. This shows that 1 deviate from perfect spherical shape. For 2, the globularity value is 0.695 and a sphericity value is 0.02. These values suggest that 1 is more deviate from the sphericity than 2. 2D finger plots provides information about different types of interactions between these complexes and other atom of the surround molecules. The HS study shows that for 1, the maximum interaction is between the complex and hydrogen atoms from the surrounding molecules (67.3%). 15.2 % of interaction is between the molecule and surrounding carbon atoms, 8.5% between the nearby nitrogen atoms, 8.8% between the oxygen atoms and 0.2% between zinc atoms. In case of 2, the maximum interaction is observed between the complex and outside hydrogen atoms, from the surrounding complex molecules (57.3%). It was followed by interaction with carbon (19.2%), with nitrogen (18.9%), with oxygen (2.7%) and finally least with zinc (1.7%). Unlike 1, we can see that interaction with zinc, nitrogen and carbon is more for complex 2.



Fig.9. Hirshfeld surface analysis of 1: d<sub>norm</sub>, Shape index, curvedness and different 2D plots



**Fig.10.** Hirshfeld surface analysis of **2**: d<sub>norm</sub>, Shape index, curvedness and different 2D plots

#### 4.4. FMO analysis

Mapping of the frontier molecular orbitals released interesting results for **1** and **2**. HOMO of the complex is found to lie primarily on the zinc atoms, while LUMO is found to be present more on the ligand atoms of one fragment. The bridging system is neither having HOMO or LUMO, which makes the bridging very strong and stable. This is having effect on the overall stability of the complex. The frontier molecular orbitals of **1** and **2** are represented in Fig.S7 and Fig.S8. The energy of HOMO for **1** is -7.2608 eV, while that of LUMO is -1.1058 eV. The HOMO-LUMO gap is -6.1550 eV, which is very high which makes the complex stable and unreactive. These data can be used to find other frontier orbital data as follows, ionization potential: I=-E<sub>HOMO</sub>, electron affinity A=-E<sub>LUMO</sub>, hardness  $\eta$ = (I-A)/2, and electrophilicity index  $\omega = \mu^2/2\eta$ . For this complex, the ionization energy is 7.2608 eV and electron affinity are 1.1058 eV. The hardness is

found to be 3.0775 and the inverse of the hardness is termed as softness which is a measure of degree of chemical reactivity and for this complex it is low (0.3249). The overall electrophilicity index of the molecule is found to be 2.8432. This index is very important for predicting the interaction between the substrate and the system of study in different chemical and biological systems. The chemical potential value is -4.1833 eV, which is a comparatively low value, makes the overall system less prone to any further chemical reaction, which is in consistent with the energy gap data.

In case of **2**, HOMO lies more on the ligand moiety on the one side, while LUMO is found to be spread over the metal and ligand moieties on the other side (Fig.S8). This can give rise to interesting charge transfer phenomena between the ligands and metal atoms on either side, which may lead to some novel properties and requires further studies. The bridge ligand is not with any frontier orbital. The HOMO is this complex is with energy -6.6496 eV and LUMO -0.9587. The energy gap is 5.6909 eV, which is less than that of **1**, which indicates that the electronic excitations are easier in **2**. The ionization potential is 6.6496 EV, less than **1**; electron gain enthalpy 0.9587 eV, which is also comparatively low. The chemical potential value is -3.804, which is also comparatively less, which suggests that over all reactivity of this complex is less than that of the previously discussed complex. Hardness value is 2.8454; while softness value is 0.3514, which is comparatively high.

#### 4.5. MESP analysis

Molecular electrostatic potential provides the groups or atoms in the complex are more susceptible to electrophilic and nucleophilic attack. The color code used in generic visualization programs helps us to identify the reactivity centers. The red and yellow areas are designated as electrophilic and blue area is nucleophilic [85]. MESP plot of **1** indicates that nitrogen atoms

from the free ligand, Schiff's base on the either sides of complex fragments show red color, suggesting that the area is more electrophilic when compared to others (Fig S9). No specific blue colored region is found in the complex, which suggests that there are no specific nucleophilic centers in the region. The bridging ligands, which is a dicyanamide linker doesn't give any red or blue color suggesting they are neither nucleophilic nor electrophilic, hence not susceptible to any sort of attack from an electrophilic or nucleophilic reagent, which suggests the stability of the complex. MESP plot of complex 2 is showing some interesting results. It can be found that there is no much red shaded part in the molecular surface, indicating that there are no specific electrophilic points in the surface. Nucleophilic centers in blue color are present at the ends of the Schiff's base ligands and near other nitrogen atoms. Another blue region is observed in the nitrogen atom of the linking dicyanamide ligand, suggesting a nucleophilic center there, prompting attack from an electrophile. It can be concluded that the stability and reactivity of **1** and **2** are entirely different from each other.

#### 4.6. TD-DFT analysis

The computational TD-DFT study of dicyanamide modulated zinc metal complexes exhibits electronic transitions that are mainly due to intra-ligand charge transfer transition. All the HOMOs in Zn(II)-dicyanamide complexes are mainly consist of  $\pi$ -orbitals only and the LUMOs are consist of ligand  $\pi$ \*-orbitals only. The TD-DFT simulated UV-Vis spectra of 1 and 2 is represented in Fig.S10 and all details of calculated HOMO-LUMOs are lucidly presented in Table S2. The analyses revealed that there are two major electronic transitions at 321.47 nm and 270.57 nm with oscillator strength 0.2119 and 0.260 (Experimental ~363 nm and ~285 nm for 1). The first electronic transition is mainly due to the transition of electron from the HOMO-2 to LUMO+1 (47%) and HOMO-2 to LUMO+3 (17%) and HOMO to LUMO+3 (18%). The second

transition is from HOMO-15 to LUMO (25%), HOMO-7 to LUMO (25%) and HOMO-6 to LUMO+1 (13%). Further, the TD-DFT analysis of **2** observed two major electronic transitions at 325 nm and 321 nm (Experimental ~368 nm for **2**). In case of **2**, there are 12 theoretically possible electronic transitions, but only 4 of them are with significant oscillator strength having numbers 7,8,9 and 10 (Table S2). The oscillator strength of transition 9 is 0.1663 and it is due to transitions from HOMO-1 to LUMO+2 (50%), HOMO-1 to LUMO+3(10%) and HOMO to LUMO+3(32%). The second major transition is number 10 with an oscillator strength 0.1472 which is contributed by transitions between HOMO-2 to LUMO (38%) and HOMO-2 to LUMO+1 (42%).

#### 5. Photoluminescence studies

Metal Schiff base complexes fluorescence properties are extremely important due to their versatile application in chemical sensors, in photochemistry and also in electroluminescent displays [86]. Schiff base ligands and Zn(II)-dicyanamide Zn<sub>4</sub>/Zn<sub>3</sub>-type complexes are highly soluble in DMSO, hence photoluminescence properties are monitored in DMSO solution at room temperature followed by solid-state condition (Table 7). Unlike other salen-type ligands, synthesized H<sub>2</sub>vanen-type ligands are intrinsic fluorophores due to the presence of azomethine-conjugated aromatic nuclei [87]. In DMSO solution, upon photo excitation at 333 nm, both Schiff base ligands exhibit fluorescent emission maxima centered at 459 nm and 461 nm. Similarly, Zn<sub>4</sub>/Zn<sub>3</sub>-nuclear metal complexes upon photo excitation at wavelength 370 nm shows fluorescence maxima with the major emission peak near at 476 nm and 481 nm (Fig. 11). Hence in DMSO solution dicyanamide complexes are fluorescent active with respect to free Schiff base ligands. Under solid-state, complexes upon photo excitation at wavelength 368 nm, 367 nm shows photoluminescence with the main emission moderately weak intense peak at 409 nm and

463 nm respectively (Fig.12). Similarly, Schiff bases upon photo excitation at 325 nm shows two peaks at 366 nm, 458 nm respectively. Thus, in solid-state small spectral emission intensity of Schiff base compounds may be due to the occurrence of PET processes in the presence donor atoms lone pair within it [88]. The quenching of solid-state fluorescence upon L-M complexation can be explained on the basis of some important processes like magnetic perturbation, redox activity and electrons [89]. The higher fluorescence intensity of Zn(II)-dicyanamide complexes in comparison to free Schiff base ligands probably due to effective coordination of ligand donor centers to the zinc metal ion thus increased the conformational rigidity of molecular complex via chelation enhanced fluorescence [CHEF] and subsequently loss of energy by radiation less thermal vibration. Besides, this may be due to the reason that d<sup>10</sup> configuration zinc metal ion is difficult or hard to oxidize or reduce. Hence these types of fluorescence behavior may be assigned predominantly due to the intra-ligand  $(\pi \rightarrow \pi^*)$  transition or L $\rightarrow$ M charge transfer. This type of fluorescence emission is popularly referred as chelation enhanced fluorescence [CHEF] [90-92] whereas for quenching of fluorescence concept, the same is referred as 'Chelation enhancement of Quenching effect' (CHEQ) [90]. The nature of emission spectra of complexes and ligands are identical with other reported ligands [73, 93] and Zn(II)-dicyanamide complexes (Table S3). Therefore, two dicyanamide modulated Zn<sub>4</sub>/Zn<sub>3</sub>-nuclear metal complexes exhibit good photoluminescence behavior in DMSO solution over solid-state. The reason is that in DMSO, the fluorescence behaviors are mainly ligand centered whereas in solid-state it is totally packing dependent [94]. To get a better understanding on emitting Zn(II)-dicyanamide complexes, time-resolved fluorescence spectroscopic studies have been undertaken and described below. The decay profiles of 1-2 have been clearly submitted in Fig.S11. The fluorescence lifetime for two dicyanamide complexes have been measured upon excitation at 370

nm. The nature of decay profile of zinc metal complexes will be best fitted to bi-exponential nature (with acceptable comparable  $\chi^2$  values) which are comparable to other salen-based ligand Zn(II) complexes [93, 95a-b]. **1** and **2** exhibit lifetimes within the range (2.41-5.71 ns) and strictly there is no definite trend observed in solution state fluorescence lifetimes (Table 7). The calculated average fluorescence lifetime value further divulges that importance of excited states stabilities of complex **2** are greater than **1**. The bi-exponential decay profiles are best explained as due to competition of different excited states that is  $\pi \rightarrow \pi^*$  excited states involved in the emission features for (**1-2**) and preferably CT character that quenches the fluorescence [96].



Fig.11. Ligand-centered Fluorescence emission spectra of 1 and 2



Fig. 12. Solid-state Fluorescence of ligands and Zn(II)-dicyanamide complexes

Compounds	$\lambda_{ex}$ (nm)	$\lambda_{em}$	$\lambda_{em}$ (nm)	Quantum	$\tau_{l}[ns]$	$\tau_2[ns]$	<\cap\$\tag{r}[ns]	$\chi^2$
		(nm)	[Solid-	Yield				
			state]	(φ)				
1	370	476	409	0.01791	0.974	3.7%	2.45	
					(76%)	(24%)		1.13
2	370	481	463	0.01056	2.70	7.81	5.71	
					(67%)	(33%)		1.37
$(H_2L^{OMe})$	333	459	366	0.04801				
$(H_2L^{OEt})$	333	461	458	0.04889				

Table 7 Photoluminescence properties and time-resolved photoluminescence decay of 1-2

#### 5.1. Solvent-dependent absorption and fluorescence spectra

To gain more insights into the photoluminescence properties of **1** and **2**, different solventdependent absorption and fluorescence emission spectra can be analyzed. Thus, the absorption and fluorescence spectra of both dicyanamide complexes were taken in different solvents such as DMF, CHCl<sub>3</sub>, CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CN, CH<sub>3</sub>CN.H<sub>2</sub>O etc. It is noteworthy to mention here that in **1**, on passing from less polar to highly polar solvent no remarkable changes of absorption spectra [97a-b] whereas in **2** non-protic DMF solvent appreciably changes the absorption spectra (Fig.S12-S13). Therefore in **2**, solvent-dependent absorption spectrum variation is slightly higher

than 1. As a general overview of solvent effects on the electronic absorption and fluorescence spectra is that large differences are observed in the fluorescence emission spectra between polar and non-polar solvents [97c]. Therefore in 1, we observed that in protic solvent ( $CH_3CN.H_2O$ ) fluorescence emission maxima at 484 nm (Fig.S12). For complex 2 situation is reversed where less polar DMF solvent fluorescence emission maxima at 471 nm (Fig.S13). With increasing solvent polarity zinc metal complexes fluorescence band maxima are largely red shifted compared to absorption band. Thus, it has been readily observed that effect of solvent polarity on the emission maxima has more profound than absorption maxima [98]. This fact positively indicates an increase of dipole moment of excited state compared to ground state. Hence polarity of a particular solvent will largely influence the spectral shifts. On passing from less polar solvent to highly polar solvent fluorescence spectral bands are more structurally organized.

#### 6. Thermal behavior

Thermal characteristics of the two dicyanamide complexes were studied using TG-DTG techniques under nitrogen atmosphere (Fig.S14). Complex **1**, loss the two sets of  $\mu_{1,5}$ -dicyanamide linkers *via* a twostep thermal disintegration. This can be seen from the figure in the region 200-294 °C, where an initial disintegration unit occurs which corresponds to a mass loss of about 7.12 % (calculated value 7.58 %) (Fig. S14(a)). The is immediately followed by another mass loss (6.82 %, calculated value 7.58 %) in the region 298-313 °C which corresponds to the loss of the second set of dicyanamide linkers associated with two binuclear zinc complexes. This is followed by a continues decomposition of the binuclear complex (95.21 %) in the temperature range 322-404 °C. In complex **2**, below a temperature of 200 °C, a mass loss of about 2.79% (calculated 3.22%) is observed which due to the loss of the water molecules present (Fig.S14(b)). The second decomposition occurs in the temperature range 200-456 °C, where there is a mass

loss of about 18.27% (calculated value 17.85%) which may be due to the loss of the two  $\mu_{1,5}$ -dicyanamide linker units. Third dissociation occurs in the temperature range 456-548 °C corresponds to a mass loss of about 55.93% which may be due to the dissociation of the major part of the ligand units.

#### 7. Cytotoxic effect

We assessed the cytotoxic effect of two dicyanamide complexes in breast cancer cell line (MCF7) using MTT assay (Fig.13). Results strongly revealed that there will be no remarkable changes of cytotoxic effect in between two complexes against breast cancer cell line MCF7. **1** and **2** inhibits the growth of MCF7 cells in a dose dependent manner with 50% growth inhibition IC<sub>50</sub> at 46.6 ± 10.69 and 47.8 ±10.78  $\mu$ M, respectively. This result further suggests that **1** or **2** has moderate cytotoxic effect on growth of breast cancer MCF7 cells. Thus, Zn<sub>4</sub>/Zn<sub>3</sub>-nuclear metal complexes may lead to identification of potent anti-cancer agent. This observation further discloses that since both complexes are zinc metal-dependent, hence their anti-cancerous potency is nearly identical. A details systematic comparison of cytotoxic effect of **1-2** with other reported M(II)-complexes/cis-platin/Pt-analogous complexes were nicely presented in Table S4. Unlike cis-platin complexes, our dicyanamide modulated zinc metal complexes viz., [Zn<sub>4</sub>(L<sup>OMe</sup>)<sub>2</sub>( $\mu$ <sub>1</sub>-dca)<sub>2</sub>( $\mu$ <sub>1,5</sub>-dca)<sub>2</sub>] (**1**) and [Zn<sub>3</sub>(L<sup>OEt</sup>)<sub>2</sub>(H<sub>2</sub>O)( $\mu$ <sub>1</sub>-dca)( $\mu$ <sub>1,5</sub>-dca)] (**2**) exhibit strong cytotoxic effect towards breast cancer cell line (MCF7).



Fig.13. Cytotoxic effect in breast cancer cell line (MCF7) of 1 and 2

#### 8. Conclusion

This paper primarily describes the syntheses and structural aspects of two new dicyanamide modulated Zn<sub>4</sub>/Zn<sub>3</sub>-nuclear neutral metal complexes with  $\Omega$ -shape compartmental ligands. Single X-ray crystal study completely divulges that in **1** and **2** structurally independent different geometries zinc metal centers are present. Though most of the activities of the complexes are associated with zinc metal ion and Schiff base ligand fragment, pseudo-halide dicyanamide anions also plays crucial role to form tetra and trinuclear zinc metal framework having marvelous terminal and  $\mu_{1,5}$  bridging features. Different solvent-dependent absorption and fluorescence spectra of dicyanamide complexes have been reported. The steady state and timeresolved fluorescence properties have been explored in DMSO solution. Fluorescence lifetime study further revealed the importance of excited state stabilities of **2** is higher than **1**. Theoretical FMO, MESP concepts were successfully applied in two complexes to substantiate the experimental results. Non-covalent supramolecular interactions in the crystal structure were

quantified by means of Hirshfeld surface ( $d_{norm}$  surfaces and 2D fingerprint plots). TD-DFT methods were employed to explain the electronic properties of dicyanamide complexes. Cytotoxic effect of 1-2 against human breast cancer cell line (MCF7) revealed that  $Zn_4/Zn_3$ -nuclear metal complexes in near future function as anti-cancerous agent.

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#### Appendix A. Supplementary material

Details supplementary data related to this article can be associated in ESM\_ICA. CCDC number 1887056-1887057 contains 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.: http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail: data\_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

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# Acceleration

- Two new Zn(II)-dicyanamide neutral complexes were synthesized and characterized
- X-ray crystal structure divulges that complexes are  $Zn_4/Zn_3$ -nuclear metal core involving  $\mu_{1,5}$  and terminal dicyanamide bridging propensity
- Hirshfeld surface, FMO, MESP and TD-DFT calculations were carried out successfully
- Steady state and time-resolved fluorescence properties have been reported. 1 and 2 exhibit intra-ligand  $(\pi \rightarrow \pi^*)$  fluorescence in DMSO solvent with lifetimes in the range (2.41-5.71 ns)

MAS

• Cytotoxic effect of 1 and 2 was evaluated against breast cancer cell line (MCF7)

