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Synthesis and characterization of three new photo-luminescent cadmium(II) complexes with azide: Variation in molecular structures with changes in the denticity of blocking ligands

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- Synthesis and characterization of three new photoluminescent cadmium(II) complexes with azide: Variation in
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  blocking ligands
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- 11 Abstract

Three new cadmium(II) coordination complexes,  $[Cd(dede)(\mu-1,3-N_3)(\mu-1,1-N_3)]_n$  (1), 12 13  $(1,1,1-N_3)/(ClO_4)_4 H_2O$  (3) {dede = N,N-diethyl-1,2-diaminoethane,  $HL^1$  = 2-(2-14 (diethylamino)ethylimino)methyl)phenol and  $HL^2 = 2-(2-(diethylamino)ethylimino)methyl)-6-$ 15 methoxyphenol}, have been prepared and characterized by elemental and spectral analysis. The 16 structures of the complexes have been confirmed by single crystal X-ray diffraction studies. 17 Complex 1 contains alternating double  $\mu$ -1,1- and  $\mu$ -1,3-azide bridges and creates two-18 dimensional sheet with  $6^3$ -hcb topology. Complex 2 consists of  $\mu$ -1,1- azide bridged chain and 19 forms three-dimensional architecture via hydrogen bonding interactions. Complex 3 has a partial 20

cubane [Cd<sub>3</sub>O<sub>4</sub>] core consisting of trinulear cadmium(II) moieties. The variation in the denticity
of the ligands causes changes in the molecular and crystalline architectures of the complexes. All
the three complexes show fluorescence.

24 **Keywords**: Cadmium(II); crystal structure; azide, octahedral;  $6^{3-}$ hcb.

#### 25 1. Introduction

The potential applications of the coordination polymers in catalysis, optics, magnetism, 26 molecular architectures, materials chemistry etc have attracted the attention of the synthetic 27 inorganic chemists for their rational design and synthesis [1-6]. These materials consist of 28 metallic centers assembled by multifunctional organic or inorganic linkers, such as 29 pseudohalides, dicyanamide, carboxylates etc [7-9]. Among them, azide is widely used to build 30 various polynuclear transition metal complexes with fascinating structural diversities and 31 promising potential applications in functional materials [10-12]. It is to be noted here, azide 32 serves as a very good ligand in propagating magnetic interaction among the paramagnetic centers 33 and as a result, huge numbers of azide bridged transition complexes have been prepared in order 34 to examine the magnetic exchange interaction in these species [13-15]. Focusing to cadmium(II) 35 with d<sup>10</sup> configuration, the azide bridged polynuclear complexes did not receive considerable 36 attention till date, possibly because of the lack of magnetic exchange interaction in it. In this 37 context, it is noteworthy that the importance of the cadmium(II) complexes lies in their strong 38 luminescence properties. 39

In the present work, we have used N,N-diethyl-1,2-diaminoethane as a bidentate blocking ligand and its condensation products with salicylaldehyde and 3-methoxysalicylaldehyde respectively to form tridentate (HL<sup>1</sup>) and tetradentate (HL<sup>2</sup>) Schiff base blocking ligands. The

43 ligands are then made to react with cadmium(II) in presence of azide. Our intension was to examine the changes, if any, in the crystalline and supra-molecular architecture of the complexes 44 with the change in the denticity of the ligands. N,N-diethyl-1,2-diaminoethane forms alternating 45 double  $\mu$ -1,1- and  $\mu$ -1,3-azide bridged neutral two-dimensional sheet with 6<sup>3</sup>-hcb topology. On 46 the other hand, the use of the tridentate Schiff base (HL<sup>1</sup>) as the blocking ligand, an one-47 dimensional chain of azide bridged cadmium(II) complex is formed. The complex forms three-48 dimensional architecture via hydrogen bonding interactions. The use of tetratendate Schiff base 49  $(HL^2)$  leads to produce a trinuclear cadmium(II) complex having a partial cubane  $[Cd_3O_4]$  core. 50 The variation in the blocking ligands changes the molecular and crystalline architectures of 51 cadmium(II) azide complexes. Herein, we like to report the synthesis, characterization, crystal 52 structures, supramolecular architectures and fluorescence properties of three new cadmium(II) 53 azide complexes. 54

#### 55 **2. Experimental**

All starting materials and solvents were commercially available, reagent grade, and used
as purchased from Sigma-Aldrich without further purification.

#### 58 Caution!!!

59 The azide complexes are potentially explosive. Although no problem was encountered in 60 the present study, only small amounts of the materials should be prepared and they must be 61 handled with care.

62 2.1. Preparations

#### 63 2.1.1. Synthesis of $[Cd(dede)(\mu-1,3-N_3)(\mu-1,1-N_3)]_n(1)$

A methanol solution of N,N-diethyl-1,2-diaminoethane (dede) (1 mmol, 0.140 ml) was added to a methanol solution of cadmium(II) acetate dihydrate (1 mmol, 0.266 g) drop wise with constant stirring, followed by the addition of an aqueous methanol solution of sodium azide (1 mmol, 0.065 g). The stirring was continued for 1 h. Diffraction quality single crystals were obtained after few days on slow evaporation of the solution in open atmosphere.

69 Yield: 0.21 g (69 %). Anal. Calc. for C<sub>6</sub>H<sub>16</sub>CdN<sub>8</sub> (312.67): C, 23.05; H, 5.16; N, 35.84 %. 70 Found: C, 23.01; H, 5.07; N, 35.91 %. IR (KBr, cm<sup>-1</sup>): 3444 ( $\nu_{NH2}$ ), 2051 ( $\nu_{N3}$ ); UV–Vis,  $\lambda_{max}$ 71 (nm), ( $\epsilon_{max}$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)) (DMSO), 260 (6.9 × 10<sup>2</sup>).

72 2.1.2. Synthesis of  $[{Cd_3(L^1)_2(\mu-1,1-N_3)_4(CH_3OH)_2} \cdot 2CH_3OH \cdot 2H_2O]_n(2)$ 

A methanol solution of salicylaldehyde (1 mmol, 0.104 ml) and N,N-diethyl-1,2diaminoethane (1 mmol, 0.140 ml) was refluxed for 1 h to prepare the tridentate Schiff base, 2-(2-(diethylamino)ethylimino)methyl)phenol (HL<sup>1</sup>). A methanol solution cadmium(II) acetate dihydrate (1 mmol, 0.266 g) was added drop wise to the methanol solution of the Schiff base followed by addition of aqueous methanol solution of sodium azide (1 mmol, 0.065 g) with constant stirring. The stirring was continued for an additional 20 min. Diffraction quality single crystals were obtained after few days on slow evaporation of the solution in open atmosphere.

80 Yield: 1.55 g (74%). Anal. Calc.  $C_{58}H_{102}Cd_6N_{32}O_{11}$  (2098.11): C, 40.18; H, 5.93; N, 4.85 81 %. Found: C, 40.13; H, 5.87; N, 4.92 %. IR (KBr, cm<sup>-1</sup>):1634 ( $\nu_{C=N}$ ), 2071 ( $\nu_{N3}$ ), 3382 ( $\nu_{OH}$ ); 82 UV–Vis,  $\lambda_{max}$  (nm), ( $\epsilon_{max}$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)) (DMSO), 377 (3.1 × 10<sup>4</sup>).

83 2.1.3. Synthesis of  $[(CdL^2)_3(\mu-1,1,1-OH)][(CdL^2)_3(\mu-1,1,1-N_3)](ClO_4)_4 \cdot H_2O(3)$ 

A methanol solution of 3-methoxysalicylaldehyde (1 mmol, 0.152 g) and N,N-diethyl-84 1,2-diaminoethane (1 mmol, 0.140 ml) was refluxed for 1 h to prepare a tetradentate Schiff base, 85 2-(2-(diethylamino)) ethylimino) methyl)-6-methoxyphenol (HL<sup>2</sup>). A methanol solution of 86 cadmium(II) perchlorate hexahydrate (1 mmol, 0.419 g) was added drop wise to the methanol 87 solution of the Schiff base followed by addition of aqueous methanol solution of sodium azide (1 88 mmol, 0.065 g) with constant stirring. The stirring was continued for additional 30 min. Single 89 crystals, suitable for X-ray diffraction, were obtained after few days on slow evaporation of the 90 solution in open atmosphere. 91

92 Yield: 1.66 g (63%). Anal. Calc. for  $C_{84}H_{129}Cd_6N_{15}O_{30}Cl_4$  (2645.21) : C, 38.14; H, 4.92; 93 N, 7.94 Found: C, 38.05; H, 4.86; N, 8.01. IR (KBr, cm<sup>-1</sup>): 1088 ( $v_{CIO4}$ ), 1633 ( $v_{C=N}$ ), 2058 ( $v_{N3}$ ), 94 3468 ( $v_{OH}$ ), 2975 ( $v_{CH}$ ); UV–Vis,  $\lambda_{max}$  (nm), ( $\epsilon_{max}$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)) (DMSO), 394 (3.1 × 10<sup>3</sup>), 95 348 (3.6 × 10<sup>3</sup>), 272 (3.2 × 10<sup>3</sup>).

#### 96 2.2. *Physical measurements*

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 97 240C elemental analyzer. Infrared spectra in KBr (4500-500 cm<sup>-1</sup>) were recorded using a 98 PerkinElmer FT-IR spectrum two spectrometer. Electronic spectra in DMSO (800-200 nm) 99 were recorded on a Jasco V-630 UV-Vis spectrophotometer. Fluorescence spectra in DMSO 100 101 were obtained on a Hitachi F-7000 Fluorescence spectrophotometer at room temperature. Lifetime measurements were recorded using Hamamatsu MCP photomultiplier (R3809) and 102 were analyzed by using IBHDAS6 software. The powder XRD spectra were recorded in a  $2\theta$ 103 104 range of 2–50° using a 1D Lynxeye detector under ambient conditions.

105

#### 106 **2.3. X-ray crystallography**

107 Single crystals of the complexes were used for data collection using a Bruker D8 OUEST area detector diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$ = 108 0.71073 Å) at 100 K. The X-ray intensity data were measured. The frames were integrated with 109 the Bruker SAINT Software package using a wide-frame algorithm. The molecular structure was 110 solved by direct method and refined by full-matrix least squares on  $F^2$  using SHELXS-97 and 111 SHELXL-2013 [16]. Non-hydrogen atoms were refined with anisotropic thermal parameters. 112 The hydrogen atoms attached to oxygen were located by difference Fourier maps and were kept 113 at fixed positions. All other hydrogen atoms were placed in their geometrically idealized 114 positions and constrained to ride on their parent atoms. Data were corrected for absorption 115 effects using the multi-scan method (SADABS) [17]. Data collection software = BRUKER 116 117 APEX II [18]; Cell refinement software = SAINT V8.34A (Bruker AXS Inc., 2013); Data reduction software = SAINT V8.34A (Bruker AXS Inc., 2013). The crystallographic and 118 refinement data of the complexes are summarized in Table 1. Selected bond lengths are gathered 119 120 in Table 2. Selected bond angles are summarized in Tables S1, S2 and S3.

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#### 122 3. Results and discussions

123 3.1. Synthesis

A bidentate chelating ligand (dede), a tridentate Schiff base ( $HL^1$ ) and a tetradentate Schiff base ( $HL^2$ ) were used in the present work to prepare cadmium(II) azide complexes. The Schiff base ligands,  $HL^1$  and  $HL^2$ , had been prepared by 1:1 condensation of N,N-diethyl-1,2diaminoethane with salicylaldehyde and 3-methoxysalicylaldehyde, respectively, in methanol,

following the literature method [19]. The ligands were not isolated and their methanol solutions 128 were used directly to prepare the complexes. 129

Complex 1 was synthesized by stirring N.N-diethyl-1.3-diaminoethane (dede) with 130 cadmium(II) acetate dihydrate and sodium azide in methanol. The bidentate ligand blocked two 131 132 sites of the octahedral cadmium(II). The remaining sites were occupied by azides. Exploiting the  $\mu$ -1,1- and  $\mu$ -1,3-bridging capacity of azides, a two-dimensional coordination polymer, 133 (1) was formed. Complex 2 was prepared on adding  $[Cd(dede)(\mu-1,3-N_3)(\mu-1,1-N_3)]_n$ 134 cadmium(II) acetate dihydrate and sodium azide into the methanol solution of HL<sup>1</sup>. The 135 tridentate Schiff base occupied three coordinating sites of octahedral cadmium(II). Exploiting 136 bridging capacity of phenoxo oxygen atoms and azides, a one-dimensional coordination 137 polymer,  $[{Cd_3(L^1)_2(\mu-1,1-N_3)_4(CH_3OH)_2} \cdot 2CH_3OH \cdot 2H_2O]_n$  (2), was formed. On the other 138 hand,  $[(CdL^2)_3(\mu-1,1,1-OH)][(CdL^2)_3(\mu-1,1,1-N_3)](ClO_4)_4 \cdot H_2O(3)$ , was produced on stirring the 139 tetradentate Schiff base, HL<sup>2</sup> with cadmium(II) perchlorate hexahydrate and sodium azide. X-140 ray quality single crystals of all the three complexes were obtained from methanol solution by 141 slow evaporation at room temperature. The formation of the complexes is shown in Scheme 1. 142 X CF

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Scheme 1: Preparation of complexes 1, 2 and 3.

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#### 153 *3.2. Description of structures*

#### 154 $3.2.1. [Cd(dede)(\mu-1,3-N_3)(\mu-1,1-N_3)]_n(1)$

The complex crystallizes in the monoclinic space group  $P2_1/c$ . The structure 155 156 determination reveals that the cadmium(II) is coordinated by two amine nitrogen atoms, N(1)and N(4), of the chelating ligand, dede and two nitrogen atoms, N(1Z) and N(4Z), from two 157 azides. A symmetry related nitrogen atom,  $N(1Z)^{b}$ , from a  $\mu$ -1,1-azide coordinate cadmium(II) to 158 form a centrosymmetric dimer. Another nitrogen atom, N(6Z)<sup>a</sup> from a symmetry related µ-1,3-159 azide ( $^{a} = 1-x, -1/2+y, 1/2-z$ ) coordinate Cd(1) to complete its octahedral geometry {Figure 1(a)} 160 and thereby connects the above mentioned dimers to form a two-dimensional sheet along 161 crystallographic ab plane {Figure 1(b)}. Cadmuim(II)-nitrogen bond lengths are ranging from 162 2.3172(13) to 2.4054(13) Å, as was also observed in similar systems [20-22]. The closest 163 conformation of the saturated five member ring, Cd(1)-N(1)-C(2)-C(3)-N(4) is half chair with 164 puckering parameters Q(2) = 0.4716(16) Å and  $\varphi = 275.48(14)^{\circ}$  [23]. The Cd…Cd separation 165 (3.5146(4) Å)across double u-1,1-azide bridge is much shorter than that (5.6774(3) Å) for single 166  $\mu$ -1,3-azide bridge, as expected. End-on ( $\mu$ -1,1) azide bridges are asymmetric with N–N 167 distances in the range 1.207(2)-1.154(2) Å, whereas end-to-end ( $\mu$ -1,3) bridges are practically 168 169 symmetric with N–N distances of 1.180(2) Å, as were also observed in similar systems [24] Topology analysis reveals a  $6^3$ -hcb topology (Figure 2) with cadmium(II) occupying the nodes, 170 where end-to-end and end-on azide connectors take part in the formation of edges. 171

The hydrogen atom, H(3A), attached to the nitrogen atom, N(4), is participated in weak hydrogen bonding with an azide nitrogen atom,  $N(12)^c$ , related by an inversion centre. Another hydrogen atom, H(3B), attached to N(4), is also involved in hydrogen bonding (Table 3) with the

symmetry related (x,-1+y,z) nitrogen atom, N(6Z)<sup>d</sup> (Figure S1) to form a 2D sheet along 175 crystallographic ab plane. There is no other supra-molecular interaction present in the complex. 176 The neighbouring layers are packed along the crystallographic c axis and no hydrogen bonding 177 interactions are observed between the layers. The nearest interlayer Cd(II)...Cd(II) distance is 178 9.0503(4) Å. 179

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#### 3.2.2. $[{Cd_3(L^1)_2(\mu-1,1-N_3)_4(CH_3OH)_2} \cdot 2CH_3OH \cdot 2H_2O]_n(2)$

182 The molecular structure of 2 with selected atom numbering scheme is shown in Figure 3. The complex crystallizes in the orthorhombic space group Fdd2. The complex assumes chain 183 structure having trinuclear cadmium(II) moieties as the building blocks, in which all the 184 cadmium(II) {Cd(1), Cd(2) and Cd(3)} possess distorted octahedral geometries. Two nitrogen 185 atoms, N(4Z) and N(10Z), from two µ-1,1-bridged azides and two oxygen atoms, O(7) and 186 O(7A), from two deprotonated Schiff base molecules and two more oxygen atoms, O(100) and 187 O(200), from two methanol molecules coordinate Cd(2) to complete its distorted octahedral 188 189 geometry. The environment around Cd(3) centre is very similar to that of the Cd(1) centre. Cd(1)is coordinated by two nitrogen atoms, N(1) and N(4), and an oxygen atom, O(7), of a tridentate 190 deprotonated Schiff base and two  $\mu$ -1,1-bridging azide nitrogen atoms, N(1Z) and N(4Z). On the 191 other hand, Cd(3) is coordinated by two nitrogen atoms, N(1A) and N(4A), and an oxygen atom, 192 O(7A), of a second molecule of the tridentate deprotonated Schiff base, and two  $\mu$ -1,1-bridged 193 azide nitrogen atoms, N(7Z) and N(10Z). Symmetry related nitrogen atoms, N(7Z)<sup>e</sup>, and N(1Z)<sup>f</sup>, 194 from two different  $\mu$ -1,1-bridged azide coordinate Cd(1) and Cd(3) respectively to grow the 195 196 polymer along the crystallographic screw axis.

The angles between Cd(1)N(4Z)O(7)Cd(2) and Cd(2)N(10Z)O(7A)Cd(3) rhombohedral 197 planes are  $83.87^{\circ}$  and that between Cd(2)N(4Z)O(7)Cd(1) and Cd(1)N(7Z)N(1Z)Cd(3) 198 rhombohedral planes are 64.29<sup>0</sup>. The saturated five membered chelate rings, Cd(1)-N(1)-C(2)-199 200 C(3)-N(4) and Cd(3)-N(1A)-C(2A)-C(3A)-N(4A) assume envelope conformation with puckeing parameters q = 0.508(3) Å,  $\varphi = 56.7(3)^{\circ}$  and q = 0.487(3) Å,  $\varphi = 57.1(3)^{\circ}$  respectively. The N(1)– 201 Cd(1)-N(4) and N(1A)-Cd(3)-N(4A) angles are 76.17(8)° and 76.12(8)° respectively and are 202 typical of five-membered chelates [25,26]. Cd–N<sub>imine</sub> distances [2.298(2)–2.307(2) Å] are shorter 203 than the Cd–N<sub>amine</sub> [2.375(2)–2.378(2) Å] distances, as was also observed in similar systems [24, 204 27-30]. The Cd(2)···Cd(1), Cd(2)···Cd(3) and Cd(1)···Cd(3) distances are 3.525(1), 3.625(1) and 205 6.165(1) Å respectively. The bridging azides are quasi-linear; the N–N–N angles are 178.0(3)°, 206 179.7(3)°, 178.6(3)° and 178.3(3)°, as was observed in similar systems [25]. 207

The hydrogen atom, H(400), attached with the oxygen atom, O(400), of the non-208 coordinating lattice water molecule participates in hydrogen bond formation with the azide 209 nitrogen atom, N(12Z). The oxygen atom, O(400), of the same water molecule forms another 210 hydrogen bond with the hydrogen atom, H(300), attached with the oxygen atom, O(300), of the 211 non-coordinated methanol molecule. Again, the hydrogen atoms, H(100) and H(200), attached 212 respectively with the oxygen atoms, O(100) and O(200), of the coordinated methanol molecules 213 involve in hydrogen bonding interactions with the symmetry related nitrogen atom,  $N(9Z)^g$  {<sup>g</sup> = 214 1-x,1-y,z} of a neighbouring molecule. These hydrogen bonding interactions lead to the 215 formation of three-dimensional supramolecular network (Figure S2). The details of hydrogen 216 bonding interactions are given in Table 3. The complex shows intra-chain C–H $\cdot\cdot\cdot\pi$  interactions 217 with C...centroid distances being in the range 3.6-3.8 A. 218

#### 220 $3.2.3. [(CdL^2)_3(\mu-1,1,1-OH)][(CdL^2)_3(\mu-1,1,1-N_3)](ClO_4)_4 \cdot H_2O(3)$

221 Complex **3** contains two independent cations,  $[(CdL^2)_3(\mu-1,1,1-OH)]^{2+}$  (A) and 222  $[(CdL^2)_3(\mu-1,1,1-N_3)]^{2+}$  (B), and four non-coordinated perchlorate anions together with a lattice 223 water molecule. The structures of both independent cations (A and B) have crystallographic 3-224 fold symmetry. A perspective view of  $[(CdL^2)_3(\mu-1,1,1-OH)]^{2+}$  (A) with selected atom 225 numbering scheme is shown in Figure 4.  $[(CdL^2)_3(\mu-1,1,1-N_3)]^{2+}$  (B) has a very similar structure, 226 as shown in Figure 5.

The trinuclear cationic parts are comprised of three  $CdL^2$  subunits in which each 227 cadmium(II) is coordinated to a deprotonated tetradentate monoanionic ligand  $(L^2)^{-}$ . The subunits 228 are held together by two distinct bridging systems: (i) an oxygen atom (O500) of a triply 229 bridging hydroxo group (in A) or a nitrogen atom ( $\overline{N1AZ}$ ) of a triply bridging azide group (in B), 230 which is coordinated to each of three cadmium(II) centers, and (ii) three hydroxo oxygen atoms, 231 each of them from three different ligand molecules. The three cadmium(II) and the bridging 232 233 hydroxo group (in A) {or the bridging azide group (in B)} form a flattened trigonal pyramid, with the cadmium(II) falling at the corners of equilateral sides (3.536(1) Å in A and 3.628(1) Å 234 in B) and angles  $(60.00(2)^0)$ . The face-capping oxygen atom O(500) is located at 1.020 Å above 235 the plane defined by the Cd<sub>3</sub> triangle in A. On the other hand, the face-capping nitrogen atom 236 (N1AZ) is located at 1.301 Å above the plane defined by the  $Cd_3$  triangle in B. 237

The presence of  $Cd_3OH$  in A is confirmed by (a) the location of the hydrogen atom at the expected position in the final difference Fourier map, (b) the electroneutrality of the crystal, and (c) the refined Cd–O(H) distances and Cd–O(H)–Cd angles, which agree well with a roughly tetrahedral or pseudo-tetrahedral sphere of Cd, Cd, Cd, H species around the oxygen atom. The

average bond lengths in the square-pyramidal coordination sphere both in A and B are close tothose in other related Cd(II) complexes [20].

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#### 245 *3.3. IR, electronic and fluorescence spectra and powder X-ray diffraction study*

In the IR spectrum of complex 1, the sharp band due to the amino NH2 group appears at 3444 cm<sup>-1</sup> [31]. In the IR spectra of complexes 2 and 3, band corresponding to the azomethine (C=N) stretching vibration appear at around 1634 and 1633 cm<sup>-1</sup> respectively. Very strong bands around 2050 cm<sup>-1</sup> are assigned to the vibration of the bridging azide ligands [32-33]. In the IR spectra of complexes 2 and 3, broad bands at ~ 3382 and 3468 cm<sup>-1</sup> may be assigned as OH stretching vibrations.

The electronic spectra for all the complexes were recorded in DMSO solution in the 252 range 200–800 nm. In case of complexes 1 and 2, the intense absorption bands are observed 253 around 260 and 377 nm respectively. For complex 3, three bands around 272, 348 and 394 nm 254 are noticed. All the bands are assigned as intra ligand charge transfer transitions [34]. The 255 complexes exhibit luminescence in DMSO medium. On exciting at 260, 377 and 348 nm, 256 emissions are observed at 418, 422, and 421 nm for complexes 1, 2, and 3 respectively. The 257 fluorescence lifetimes of the complexes are investigated in DMSO solution at room temperature. 258 The lifetimes of 1, 2 and 3 are about 12.21, 11.17 and 12.25 ns respectively (Table 4), which are 259 similar to other cadmium(II) complexes [35]. Decay profiles (Figure S3, Supplementary 260 Information) were fitted following the literature method [34]. The relative fluorescence quantum 261 yields for the complexes were measured in DMSO using quinine sulfate (in 0.5 (M) H<sub>2</sub>SO<sub>4</sub>,  $\Phi =$ 262 0.54) as the quantum yield standard [36]. The fluorescence quantum yields of complexes 1, 2 and 263

264 **3** are 0.0047, 0.178 and 0.1624 respectively. Quantum yields were calculated following the literature method [37] 265

The experimental powder XRD patterns of the bulk product of all the complexes 266 are in good agreement with the simulated XRD patterns from single crystal X-ray diffraction, 267 268 confirming purity of the bulk samples (Figure S4). SCR

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#### 4. Summary 270

The synthesis and characterization of three cadmium(II) azide complexes with N,N-271 diethyl-1,2-diaminoethane have been described in the present paper. Cadmium(II) centres 272 assume octahedral geometries in all three complexes. Complex 1 features alternating double µ-273 1,1- and  $\mu$ -1,3- azide bridges and forms two-dimensional sheet with 6<sup>3</sup>-hcb topology. Hydrogen 274 bonding interaction in complex 2 leads to three-dimensional supramolecular network. Complex 3 275 contains two independent trinuclear cations with partial cubane [Cd<sub>3</sub>O<sub>3</sub>X] cores, in which 276 cadmium(II) centres are bridged by  $\mu$ -1,1,1-OH or  $\mu$ -1,1,1-N<sub>3</sub>. The use of three different 277 278 blocking ligands can effectively change the molecular and crystalline architectures of the complexes. All the complexes show fluorescence with fluorescence lifetime ~ 12 ns. 279

280

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#### 286 Appendix A. Supplementary data

CCDC 996855, 1000620 and 1005615 contain the supplementary crystallographic data 287 for the complexes 1, 2 and 3 respectively. These data can be obtained free of charge via 288 http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data 289 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: 290 SCK deposit@ccdc.cam.ac.uk. 291

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366	Table 1: Crystal	data and refinement details	of complexes 1, 2 and 3.
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	1	2	3
Formula	C <sub>6</sub> H <sub>16</sub> CdN <sub>8</sub>	$C_{58}H_{102}Cd_6N_{32}O_{11}$	$C_{84}H_{129}Cd_6Cl_4N_{15}O_{30}$
Formula Weight	312.67	2098.11	2645.21
Temperature (K)	100	100	100
Crystal system	Monoclinic	Orthorhombic	Trigonal
Space group	$P2_{l}/c$	Fdd2	P31c
a(Å)	10.4729(3)	35.4193(15)	13.0841(10)
b(Å)	8.2775(2)	35.9490(13)	13.0841(10)
c(Å)	13.7414(4)	12.7424(5)	34.980(3)
β	100.1363(12)	90	90
Z	4	8	2
$d_{\rm calc} ({\rm g \ cm}^{-3})$	1.771	1.718	1.694
μ (mm <sup>-1</sup> )	1.847	1.617	1.392
F(000)	624	8400	2668
Total Reflections	18604	59966	40479
Unique Reflections	2179	10871	7921
Observed data[ $I > 2 \sigma(I)$ ]	2044	10255	6904
No. of parameters	146	499	424
R(int)	0.023	0.025	0.050
R1, wR2 ( all data)	0.0144, 0.0324	0.0235, 0.0379	0.0456, 0.0760
R1, wR2 $[I > 2 \sigma (I)]$	0.0127, 0.0307	0.0197, 0.0371	0.0343, 0.0727

	Cd(1)–N(1)	2.4054(13)	Cd(1)–N(1Z)	2.3528(12)
1	Cd(1)–N(4)	2.3172(13)	Cd(1)–N(6Z) <sup>a</sup>	2.3688(13)
	Cd(1)–N(4Z)	2.3363(13)	$Cd(1)-N(1Z)^b$	2.3618(12)
	Cd(1)–O(7)	2.272(2)	Cd(1)–N(1)	2.375(2)
	Cd(1)–N(1Z)	2.268(2)	Cd(1)–N(4)	2.307(2)
	Cd(1)–N(4Z)	2.310(3)	Cd(1)–N(7Z) <sup>e</sup>	2.515(3)
	Cd(2)–O(7)	2.249(2)	Cd(2)–O(7A)	2.2799(19)
	Cd(2)–O(100)	2.392(3)	Cd(2)-O(200)	2.340(2)
2	Cd(2)–N(4Z)	2.280(3)	Cd(2)–N(10Z)	2.283(2)
	Cd(3)–O(7A)	2.2774(19)	Cd(3)–N(7Z)	2.333(3)
	Cd(3)–N(1A)	2.379(2)	Cd(3)–N(4A)	2.298(2)
	Cd(3)–N(10Z)	2.327(2)	$Cd(3)-N(1Z)^{f}$	2.400(2)
	Cd(1)–O(8)	2.601(5)	$Cd(1)-N(1)^{h}$	2.362(9)
	Cd(1)–O(500)	2.282(3)	$Cd(1)-O(7)^{h}$	2.234(7)
	Cd(1)–O(7)	2.205(5)	$Cd(1)-N(4)^{h}$	2.272(7)
3	Cd(2)–O(7A)	2.211(5)	Cd(2)–N(1A)	2.364(7)
6	Cd(2)–N(1AZ)	2.466(6)	Cd(2)–N(4A)	2.252(9)
	Cd(2)–O(7A) <sup>i</sup>	2.183(8)	Cd(2)–O(8A) <sup>i</sup>	2.504(5)

**Table 2:** Selected bond lengths (Å) of complexes **1**, **2** and **3**.

370 Symmetry transformations <sup>a</sup> = 
$$1-x, -1/2+y, 1/2-z$$
; <sup>b</sup> =  $1-x, 1-y, -z$ , <sup>e</sup> =  $3/4-x, -1/4+y, 1/4+z$ , <sup>f</sup> =  $3/4-x$ 

371 
$$x, 1/4+y, -1/4+z, h = -x+y, 1-x, z; i = 1-x+y, 1-x, z.$$

Complex	D–H···A	D–H	Н…А	D····A	∠D–H…A
	$N(4)-H(3A)\cdots N(12)^{c}$	0.91	2.47	3.3023(18)	152
1	$N(4)-H(3B)\cdots N(6Z)^d$	0.91	2.23	3.1183(18)	166
	O(100)-H(100)···N(9Z) <sup>g</sup>	0.77(4)	2.10(4)	2.838(3)	163(4)
	O(200)–H(200)…N(9Z) <sup>g</sup>	0.93(4)	1.86(4)	2.785(3)	176(2)
2	O(400)–H(400)…N(12Z)	0.8700	2.1100	2.873(5)	146.00
	O(300)–H(300)…O(400)	0.8400	1.9800	2.809(6)	168.00

**Table 3**: Hydrogen bond distances (Å) and bond angles (°) in complexes 1 and 2.

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374 Symmetry transformations  $^{c} = 1-x, 1-y, -z, ^{d} = x, -1+y, z, ^{g} = 1-x, 1-y, z.$ 

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**Table 4:** Photo-physical data for the complexes **1-3**.

	Samples	$\lambda_{ex}(nm)$	$\lambda_{em}(nm)$	$\tau_{av}(ns)$	$\chi^2$
		260	418	12.21	1.020891
	2	377	422	11.17	1.1531
.0	3	348	421	12.25	1.063163
P					

378



Figure 1: (a) Perspective view of the complex 1 with selective atom-numbering scheme. Hydrogen atoms are not shown for clarity. Symmetry transformations,  $^{a} = 1-x,-1/2+y,1/2-z; ^{b} = 1-x,1/2+y,1/2-z$ . (b) Two-dimensional sheet of the complex 1. Only the relevant atoms are shown.







Figure 3: Perspective view of complex 2 with selective atom numbering scheme. Hydrogen 389 atoms, alkyl groups, non-coordinated methanol and water molecules are omitted for clarity. 390 Symmetry transformations e = 3/4-x, -1/4+y, 1/4+z; f = 3/4-x, 1/4+y, -1/4+z. 391 MAS

392



Figure 4: Perspective view of the trinuclear cation  $[(CdL^2)_3(\mu-1,1,1-OH)]^{2+}$  (A) of complex 3 with selective atom-numbering scheme. The hydrogen atoms (except OH) are not shown for clarity. Symmetry transformation, <sup>h</sup> = -x+y,1-x,z.



Figure 5: Perspective view of the trinuclear cation  $[(CdL^2)_3(\mu-1,1,1-N_3)]^{2+}$  (B) of complex 3 with selective atom-numbering scheme. Hydrogen atoms are not shown for clarity. Symmetry transformation <sup>i</sup> = 1-x+y,1-x,z.

# **Highlights**

Synthesis and characterization of three new photoluminescent cadmium(II) complexes with azide: Variation in molecular structures with changes in the denticity of blocking ligands

Sumit Roy, Prasanta Kumar Bhaumik, Klaus Harms, Shouvik Chattopadhyay

• Synthesis and characterization of three cadmium(II) azide complexes

•Presence of alternating double  $\mu$ -1,1- and  $\mu$ -1,3-azide bridges

• Formation of two-dimensional sheet with 6<sup>3</sup>-hcb topology

• Formation of partial cubane [Cd<sub>3</sub>O<sub>4</sub>] core consisting of trinulear cadmium(II) moieties

# **Graphical Abstract (Pictogram)**

Synthesis and characterization of three new photoluminescent cadmium(II) complexes with azide: Variation in molecular structures with changes in the denticity of blocking ligands

Sumit Roy, Prasanta Kumar Bhaumik, Klaus Harms, Shouvik Chattopadhyay



# **Graphical Abstract (Synopsis)**

Synthesis and characterization of three new photoluminescent cadmium(II) complexes with azide: Variation in molecular structures with changes in the denticity of blocking ligands

Sumit Roy, Prasanta Kumar Bhaumik, Klaus Harms, Shouvik Chattopadhyay

Three new photo-luminescent cadmium(II) azide complexes have been synthesized and the structures have been confirmed by X-ray crystal structure analysis. Bidentate, tridentate and tetradentate ligands have been used as the blocking ligands in preparing the complexes. The structures of the complexes were drastically varied with the variation in the denticity of the blocking ligands.