Electronic Supporting Information

Coordination Induced Fluorescence Enhancement and Construction of a Zn_3 Constellation through Hydrolysis of Ligand Imine Arms

Avijit Sarkar[a], Aloke Kumar Ghosh[a], Valerio Bertolasi[b] and Debashis Ray *[a]

Synthesis

2,6-Bis-[(2-hydroxy ethylimino)methyl]-4-methylphenol (H_3bemp). A methanolic solution of 2,6-diformyl-4-methylphenol (1.0 g, 6.1 mmol) and 2-aminoethanol (0.74 g, 12.2 mmol) was refluxed for 1 h. A yellow solution was obtained and kept for solvent evaporation. A light yellow crystalline product was collected by filtration, washed with a minimum volume of methanol, and dried in vacuum over P_4O_{10}. Yield: 1.35 g (89%), m.p. 145 °C; Anal. for $C_{13}H_{18}N_2O_3$ (MW = 250.1 g mol^{-1}): calcd. C, 62.42; H, 7.19; N, 11.20; found C, 62.11; H, 7.24; N, 11.32%. Infrared spectrum (cm^{-1}, KBr disk): 3346(s), 1639(s), 1610(m), 1445(m), 1254(m), 1071(s), 1057(m), 905(m), 883(s), 574(m). 1H NMR (DMSO-d6, ppm): *d* 8.54 (2H, s, imine H), 7.50 (2H, s, ArH), 3.62 (4H, t, CH2), 3.52 (4H, t, CH2), 2.49 (3H, s, CH3). ^{13}C NMR (DMSO-d6, ppm): *d* (C9,12) 161.64; (C1) 160.39; (C4,7) 32.34; (C5) 126.00; (C3,8) 121.01; (C11,14) 61.88; (C10,13) 60.70; (C6) 19.93.

2,6-Bis-[(3-hydroxy propylimino)-methyl]-4-methylphenol (H_3bpmp). To the methanolic solution of 2,6-diformyl-4-methylphenol (1.0 g, 6.1 mmol), 3-amino-1-propanol (0.91 g, 12.2 mmol) was added under air at room temperature (28 °C) and stirred for 2 h to give a orange semi-solid after complete evaporation of solvent in air for 12 h. The semi-solid product thus obtained was used directly for complexation reaction without further characterization. Yield: 1.32g (78%).

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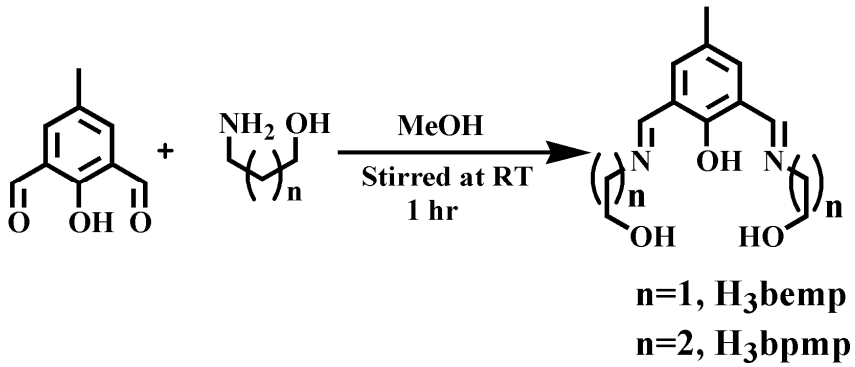

Scheme S1. Synthesis of H_3bemp and H_3bpmp.

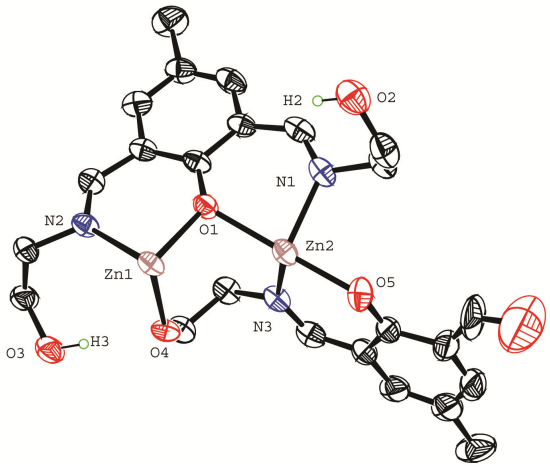

Figure S1. The asymmetric unit of complex **1** shows binding of two Zn atoms and one each of H_2bemp^- and emp^{2-}.

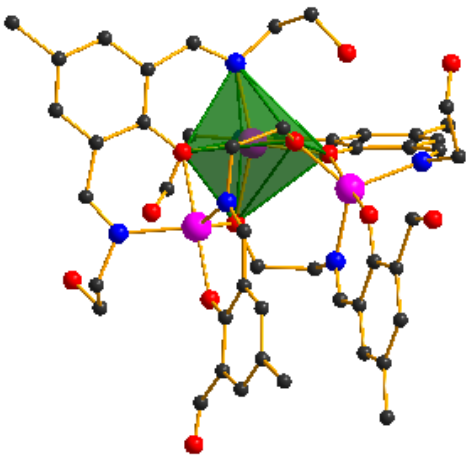

Figure S2. Distorted octahedral arrangement around central Zn1 atom in **1**.

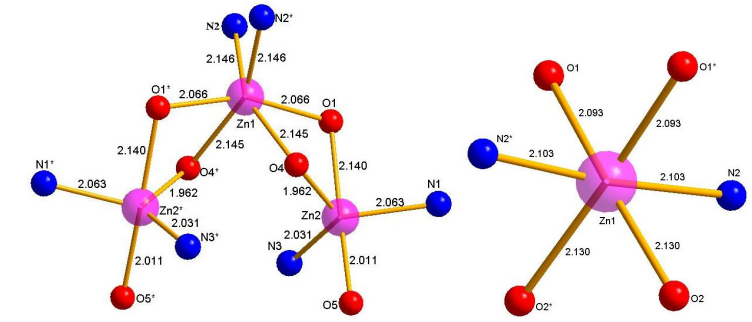

Figure S3. Metric parameters in close-up views for **1** and **2·2H$_2$O**.

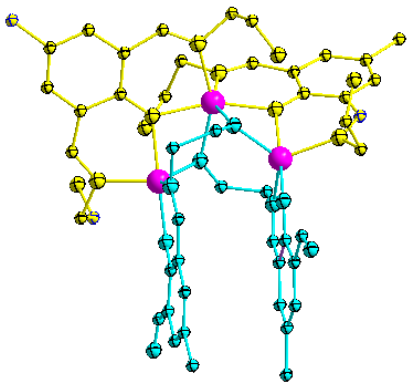

Figure S4. Two different coordination environments around the Zn_3 complex originate from binding of two lignads H_2bemp^- (yellow) and emp^{2-}(sky blue).

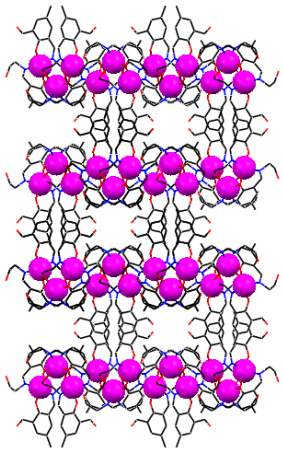

Figure S5. Layered zig-zag arrangement of Zn_3 motifs in the corresponding packing arrangement of 1.

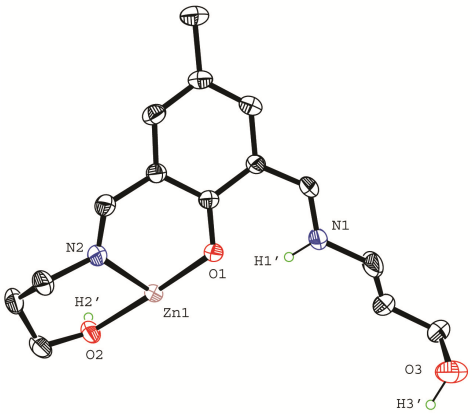

Figure S6. The asymmetric unit of **2**·2H_2O consists of one Zn^{2+} ions and one neutral H_2bpmpH^N.

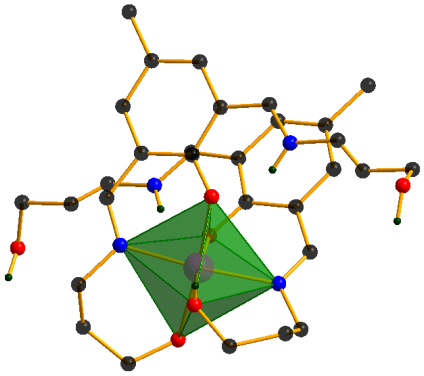

Figure S7. Mononuclear coordination leads to less distorted octahedral (green colored polyhedron) arrangement around the Zn atom of **2·2H_2O**.

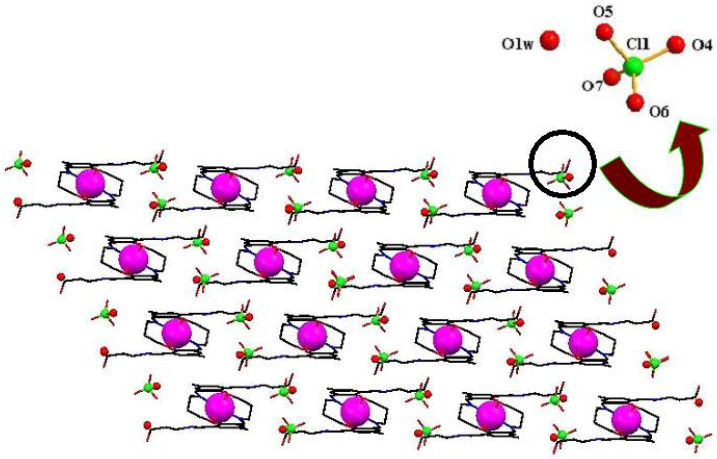

Figure S8. The *b*-axis crystal packing diagram of **2**·2H_2O showing individual mononuclear units separated by dangling iminium-alcohol arms surrounded by perchlorate anions and water of crystallization.

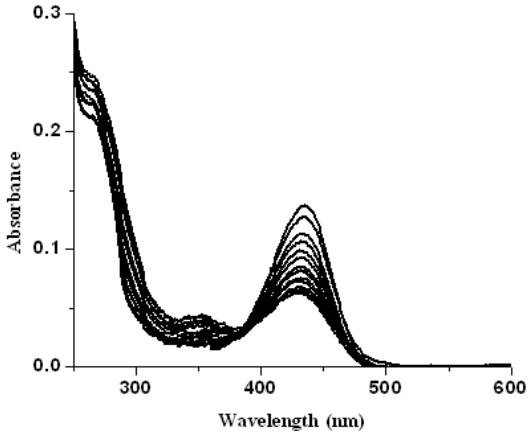

Figure S9. Spectrophotometric titrations of H_3bemp (1.0×10^{-5} M) with various numbers of equivalents of $Zn(ClO_4)_2\cdot6H_2O$ in 10mM HEPES buffer (pH 7.4) at room temperature

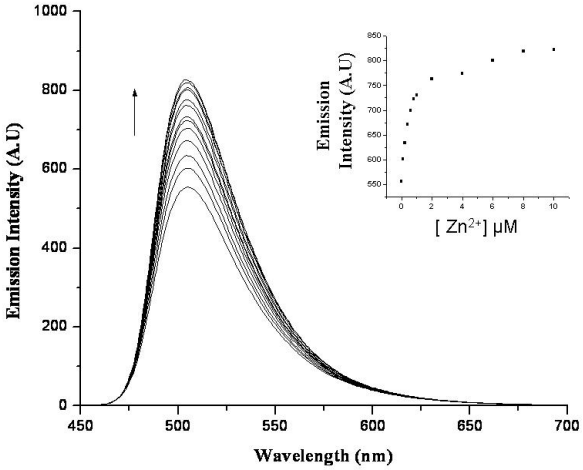

Figure S10. Emission spectra of 10 μM of H_3bpmp in the presence of 0, 0.1, 0.4, 0.6, 0.8, 1, 2, 4, 5, 8, 9, 11, 12 μM of free Zn^{2+} ions in 10mM HEPES buffer (pH 7.4) at room temperature (excitation 348 nm, emission 504 nm). Inset: Fluorescent enhancement versus different concentrations of Zn^{2+} emission intensity at 504 nm.

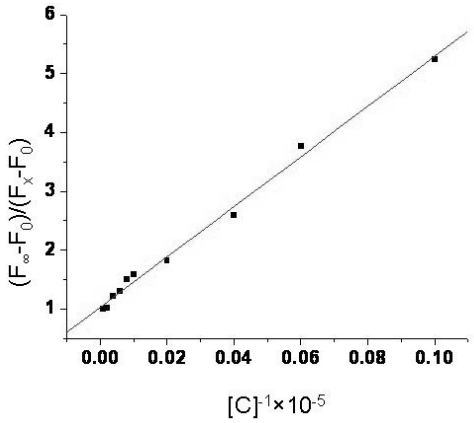

Figure S11. Determination of binding constant, *K*, from the slope of a modified Benesi-Hildebrand plot.

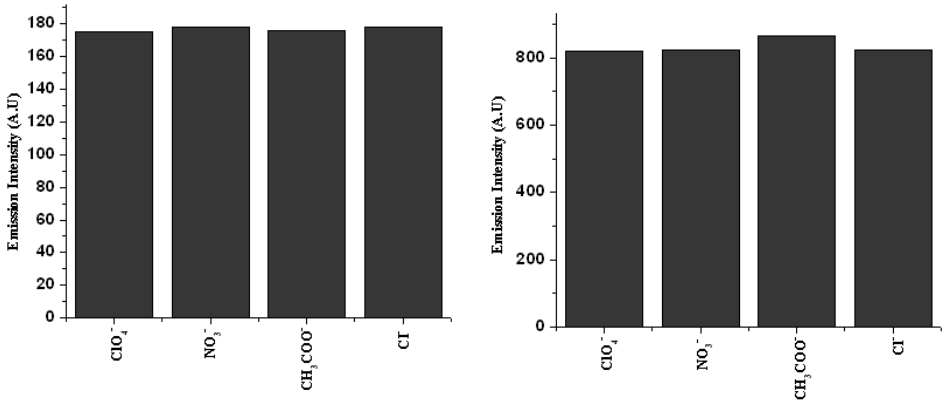

Figure S12. Anion independent emission behaviour of H_3bemp (left) and H_3bpmp (right) in presence of various Zn^{2+} salts ($ZnCl_2$, $Zn(NO_3)_2$, $Zn(CH_3COO)_2$, and $Zn(ClO_4)_2$) at the excitation wavelength of 350 nm**.**

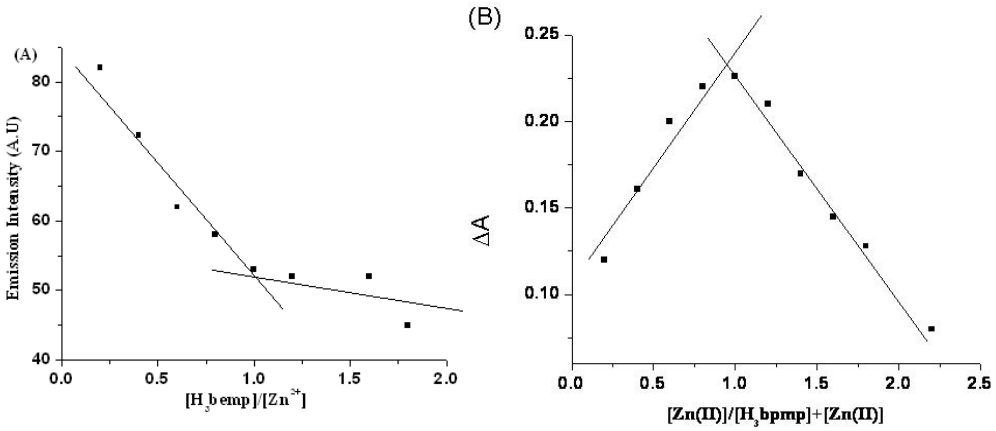

Figure S13. Job's plot analysis illustrating (A) 1:1 stoichiometry for H_3bemp and Zn^{2+} ion. (B) 1:1 stoichiometry between H_3bpmp and Zn^{2+} ion.

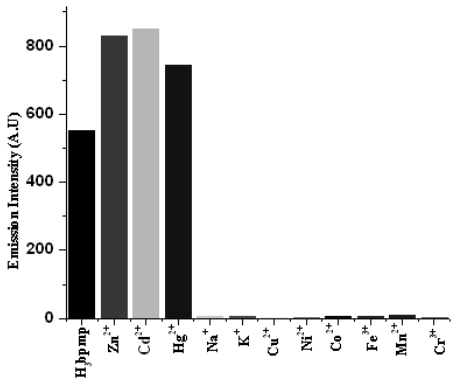

Figure S14. Relative fluorescence intensity change profile of H_3bemp (1.0×10^{-5} M) in the presence of various metal ions at room temperature (excitation 348 nm)

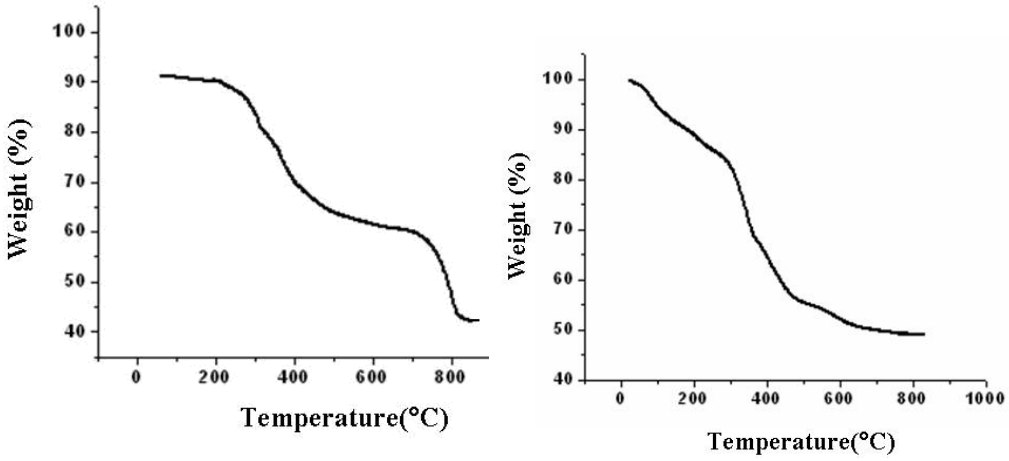

Figure S15. Thermo gravimetric plots for 1 (left) and $2{\cdot}2H_2O$ (right)**.**