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A green polymeric zinc(II) complex: Synthesis, structural characterization, and theoretical studies

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Synthesis and X-ray structural characterization of a Zn(II) polymer $[Zn(NCS)_2(L)]_n$ (**1**) [L = 4,4′-bipyridine] have been reported. The compound, having a metal [Zn(II)] with d^{10} electronic configuration at the centre of each monomeric unit, shows green colour (absorption band at 648 nm). Molecular orbital energy calculations (and the theoretical spectra obtained therefrom) using GAUSSIAN-09 program package show that HOMO-LUMO energy difference gradually decreases from monomeric to tetrameric units. On considering λ_{max} to be 648 nm in the non-linear fit equation (λ_{max} versus molecular units), it is found that 13 molecular units are responsible for the experimentally observed green color of **1**.

Keywords: Coordination chemistry, Coordination polymers, Polymeric complexes, Molecular orbital energy calculations, Density functional calculations, Zinc, 4,4′-Bipyridine

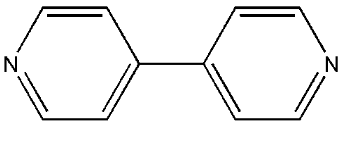
Most of the d^{10} metal complexes are colourless because of the absence of *d-d* transitions. Often they have the colour of their coordinated ligand(s). For this very reason no absorption methods can be used for determination of the metal-ligand binding and other interactions. Instead, fluorimetric methods are used[1]. Color in the d^{10} metal complexes can originate only if there is some kind of charge transfer transition(s). First account of the d^{10} metal complexes in the lower energy part of the visible region was reported by Ogawa *et al.*[2] Subsequently, blue metal complexes of Zn(II), Cd(II), Hg(II) and In(III) by were reported by Goswami *et al.*[3] In this present study, we have synthesized and X-ray crystallographically characterized one polymeric Zn(II) complex $[Zn(NCS)_2(L)]_n$ (**1**) [L = 4,4′-bipyridine] which is of green color and exhibits a sharp band in the visible region.

Experimental

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. UV-vis and IR spectra (KBr discs, 4000-300 cm^{-1}) were recorded using a Shimadzu UV-vis 2450 spectrophotometer and Perkin-Elmer FT-IR (model RX1) spectrometer, respectively.

For the synthesis of $[Zn(NCS)_2(L)]_n$ (1), zinc(II) nitrate hexahydrate (1 mmol, 0.29 g) was dissolved in aqueous methanol and stirred over magnetic stirrer for about 30 min. The ligand, L (1 mmol, 0.15 g), in solid form was added to the solution of zinc nitrate pinch by pinch. This mixture was again stirred slowly for about an hour. The aqueous solution of ammonium thiocyanate (2 mmol, 0.15 g) was then added and the entire reaction mixture was kept in open air for slow evaporation. Green coloured transparent block shaped crystals appeared after a week or so. Yield, 1.72 g (35%). Anal. (%) Calcd. for $C_{22}H_{16}N_6S_2Zn$: C, 53.51; H, 3.24; N, 17.02; Found, C, 53.29; H, 3.12; N, 17.01; IR (KBr, cm^{-1}), 1625, 2150. UV-vis (MeOH, nm), 648.

The GAUSSIAN-09 Revision C.01 program package was employed for all geometries and energies calculations[4]. The geometries of the molecular units of **1** in the gas phase were optimized without restrictions of symmetry in singlet ground state for **1** along with the gradient-corrected density functional theory (DFT) level with three-parameter fit of the exchange and correlation functional of Becke (B3LYP)[5], which includes the correlation functional of Lee *et al.* (LYP)[6]. The basis set LANL2DZ was employed for the all atoms of **1** following the related valence double ζ basis set of Hay and Wadt[7]. The molecular orbital energy levels and electronic spectra of **1** were calculated with the time-dependent density functional theory (TD-DFT) method. The solvent effect was simulated for molecular units of **1** using the polarizing continuum model with the integral equation formalism (C-PCM) in methanol[8].



4,4′-Bipyridine (L)

Table 1 — Crystallographic data and structure refinement parameters of **1**

Empirical formula	$C_{12}H_8N_4S_2Zn$	D_{calc} (g cm^{-3})	1.519
Formula weight	337.73	Absorption coefficient (mm^{-1})	1.936
T (K)	293(3)	h, k, l	-21, 21/-6, 6/-20, 20
Wavelength (Å)	0.71073	F(000)	680
Crystal system	Monoclinic	θ range (°)	$2.49 < \theta < 21.01$
Space group	C2/c	T_{max} and T_{min}	0.760 and 0.827
Unit cell dimensions		Data completeness	0.998
a (Å)	18.181(8)	Total reflection	6606
b (Å)	5.268(2)	Reflection independent (R_{int})	1308 (0.028)
c (Å)	17.163(8)	Reflection observed ($I > 2\sigma$)	1059
α (°)	90	R_1	0.052
β (°)	116.07(2)	wR_2	0.1617
γ (°)	90	Goodness of fit	1.061
V(Å^3)	1476.6(11)	Largest difference peak and hole (e Å^{-3})	0.62, -0.44
Z	4		

$R_1 = \Sigma||F_o| - |Fc||/ \Sigma |F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$,
calcd. $w = 1/[\sigma^2(F_o^2) + (0.0927P)^2 + 2.4559P]$ where $P = (F_o^2 + 2F_c^2)/3$.

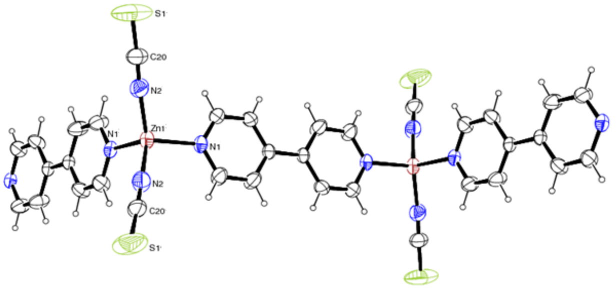


Fig. 1 – ORTEP of **1** with 30% ellipsoid probability plot.

Table 2 — Selected experimental and optimized bond distances and bond angles for **1**

	Expt.	Optimized
Bond lengths (Å)		
Zn(1)-N(1)	2.033(4)	2.01305
Zn(1)-N(1)	2.034(4)	2.04924
Zn(1)-N(2)	1.898(6)	1.86796
Zn(1)- N(2)	1.898(6)	1.94012
Bond angles (deg.)		
N(2)-Zn(1)-N(2)	123.0(4)	121.58071
N(2)-Zn(1)-N(1)	105.7(2)	105.07486
N(2)-Zn(1)-N(1)	107.1(2)	107.65058
N(1)-Zn(1)-N(1)	107.3(2)	107.32029

Table 3 — Energy of HOMO and LUMO for different units of **1**

Orbitals	Energy (eV)			
	Monomer	Dimer	Trimer	Tetramer
LUMO	-2.58	-2.93	-2.96	-2.97
HOMO	-6.27	-6.29	-6.28	-6.27

Single crystals of **1,** suitable for X-ray crystallographic analysis, were selected following examination under a microscope. Diffraction data at 293(3) K for **1** were collected on a Bruker P4 CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). All calculations were carried out using SHELXL-97[9] and ORTEP-32[10].

Results and discussion

Green colored crystalline tetracoordinated polymeric complex **1** was obtained in good yield through a single pot reaction of 1:1 molar ratio of the zinc nitrate hexahydrate and L in methanol-water solution. Ammonium thiocyanatre (2 equiv.) was added from outside to the reaction mixture. The synthetic procedure is summarized as follows:

$$\mathrm{Zn(NO_3)2.6H_2O + 2NH_4NCS + L \xrightarrow[298\ K]{MeOH} [Zn(NCS)2(L)]n + 2NH4NO3 + 6H_2O}$$

The complex was quite stable in air as well as in presence of moisture. It was characterized by elemental analysis, IR and UV-vis spectroscopy and finally by single crystal X-ray diffraction. The moisture insensitive complex is soluble in methanol.

The thermal ellipsoid plot of compound **1** is represented in Fig. 1. The crystallographic parameters and bond angle-bond distance data are listed in Tables 1 and 2, respectively. **1** crystallizes in monoclinic crystal system with *C*2/*c* space group. From the bond angle-bond distance data, the Zn(II) site in each unit of the polymeric structure is assumed to have tetracoordination with distorted tetrahedral molecular geometry. The bond angles at metal centers are slightly less than the ideal tetrahedral bond angle 109°28′. The bond distance ranges from 2.034(4) Å to 1.898(6) Å [Δ (difference between maximum and minimum bond distance) = 0.136 Å].

The geometry of **1** was optimized in the singlet state using the DFT method with the B3LYP

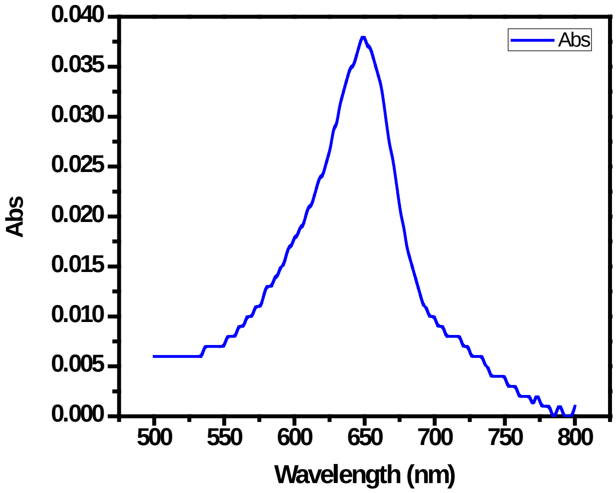


Fig. 2 — UV–vis spectrum of **1** in methanol at room temperature. The concentration of **1** was 2×10^{-3} *M*.

functional. The optimized geometry parameters are given in Table 3. Calculated bond lengths and angles are in good agreement with values observed from X-ray crystal structure data. The general trends observed in the experimental data are well reproduced in the calculations. The largest difference is 0.03 Å for the Zn-N(2) bond distance and largest difference of bond angle is 1.41° for N(2)-Zn(1)-N(2).

In IR spectra, sharp bands at 1625 and 2150 cm^{-1} for **1** are attributed to the imine and thiocyanate functions, respectively[11]. UV-vis absorption studies were carried out with a methanol solution of **1** (2×10^{-3} *M*). The light green colored solution showed a sharp band at 648 nm ($\varepsilon = 30\ M^{-1}cm^{-1}$) (Fig. 2).

Theoretical spectra of the mono-, di-, tri- and tetramer of the $[Zn(NCS)_2(4,4'\text{-bipyridine})]_n$ are shown in Fig. 3. A gradual movement of the spectra from higher to lower energy (i.e., towards visible range) was observed for mono- to tetrameric units in 1D coordination polymer of **1**. Further calculations of higher units were not possible because of the limitations of the computational facilities available with the authors. However, the experimentally observed data of λ_{max} value was put in the non-linear fit of first order exponential equation (1) which shows that ~13 molecular units can give the absorption at 648 nm (Fig. 4).

$$y = y_0 + A_1e^{-x/t1} \qquad \text{... (1)}$$

The calculated electronic spectra extrapolated to 13 or more units formed a plateau and were in agreement

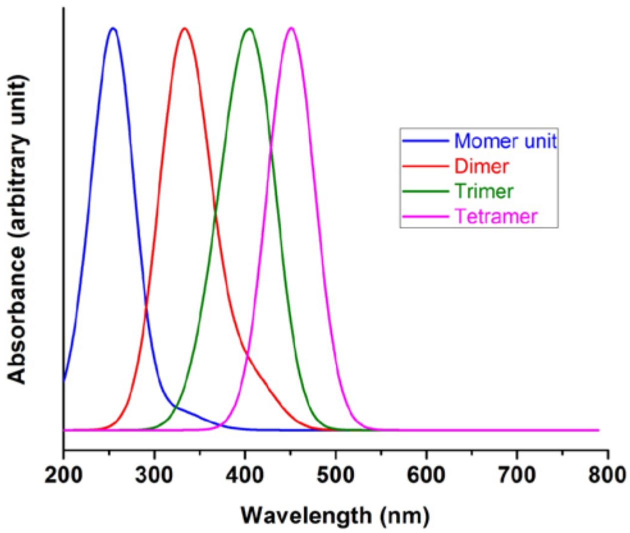


Fig. 3 — Calculated UV-vis spectra of mono-, di-, tri- and tetrameric unit(s) for $[Zn(NCS)_2(4,4'\text{-bipyridine})]_n$ complex using C-PCM model in methanol.

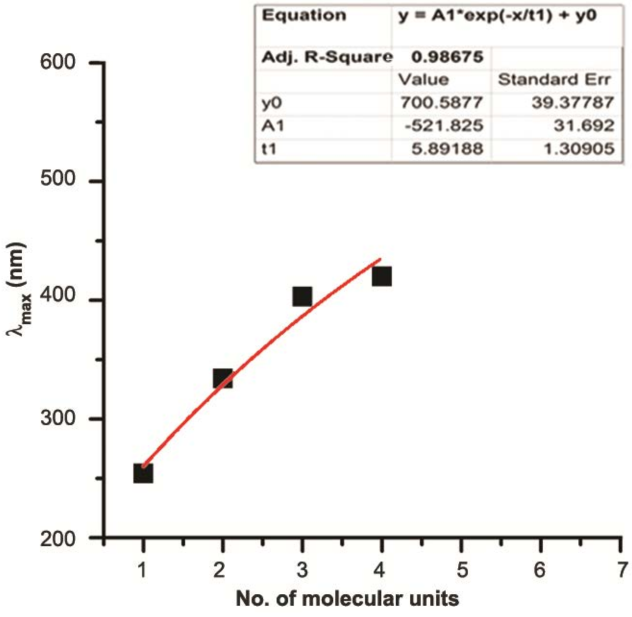


Fig. 4 — Non-Linear fit for the absorption maximum of different units versus molecular units.

with the experimentally observed wavelength of **1**. The HOMO and LUMO energies and their contour diagrams of molecular units are presented in Fig. 5. Also, HOMO and LUMO energies of different units of **1** are tabulated in Table 3. Thus, the calculated results indicate that the origin of green color is the inherent properties of polymerization of monomeric units in **1**.

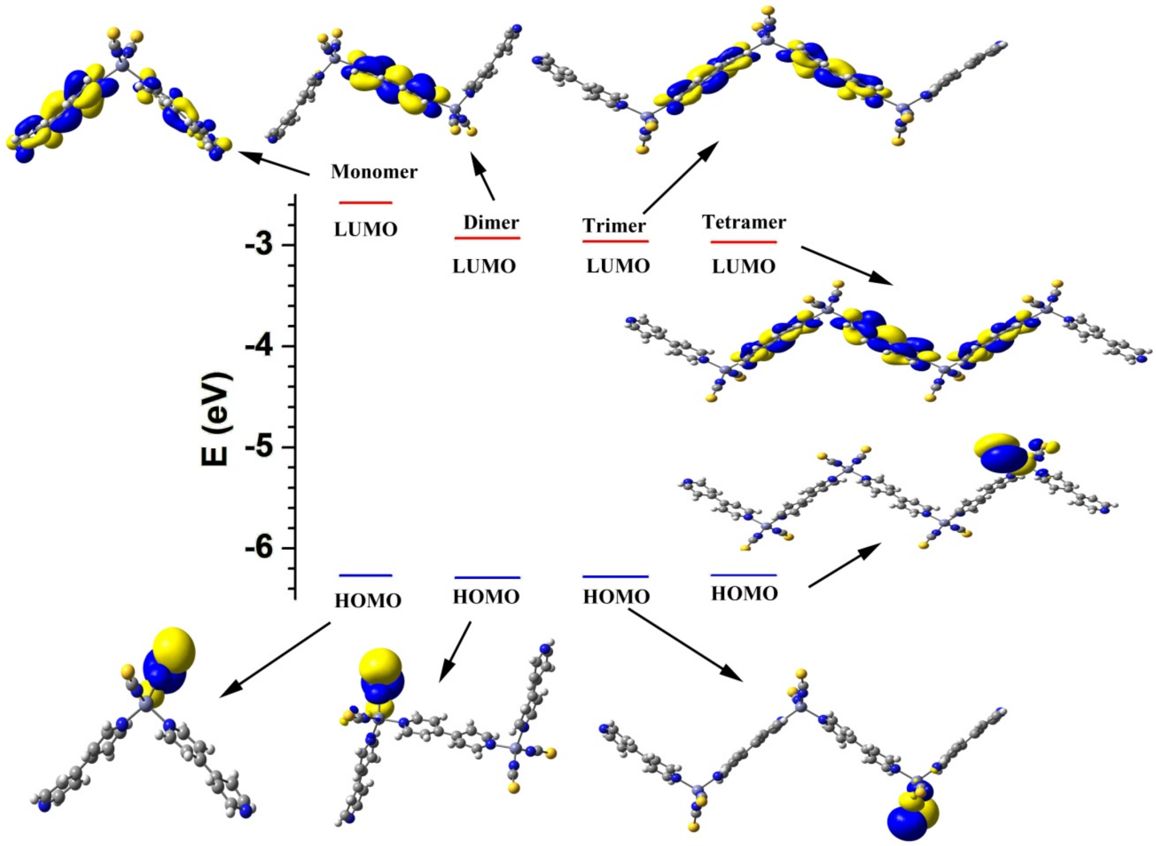


Fig. 5 — HOMO and LUMO energies with contour diagram of different molecular units of **1**.

In summary, we have synthesized and X-ray crystallographically characterized a Zn(II) polymer (**1**) which is, interestingly, green in color. The color is explained by the calculated molecular orbital energies. From the calculations it is proposed that ~13 molecular units in the polymer can give absorption in the visible range.

Supplementary data

CCDC 1567134 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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