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Synthesis and Spectroscopic Properties of a Fluorosensor for Zn^{2+} ions

Nawal K. Al-Rasbi*, Bushra Al-Wihibi and Nada Al-Nofali

*Department of Chemistry, College of Science, Sultan Qaboos University, P.O. Box: 36, PC 123, Al-Khod, Muscat, Sultanate of Oman. *Email: nrasbi@squ.edu.om.*

ABSTRACT: The new Schiff base ligand **L**: (E)-N'-(pyridin-2-ylmethylene)acetohydrazide, was synthesized, and its reaction with Zn(II) ions form the complex: $[ZnL_2](ClO_4)_2$, as confirmed by X-ray crystallography. This complex is stable in polar and non-polar solvents as proven by NMR. A significant enhancement in the fluorescence was observed from **L** upon coordination to Zn(II) ions over other transition metals such as Fe(II), Co(II), Ni(II), Cu(II), Cd(II) and Ag(I). These results suggest that **L** can be used as a selective flourosensor for the detection of Zn(II) ions.

Keywords: Schiff base; Zinc(II); Crystal structure; Flourosensor.

التركيب والخصائص الضوئية لحساس طيفي لأيونات الزنك

نوال الراسبي، بشرى الوهيبي و ندى النوفلي

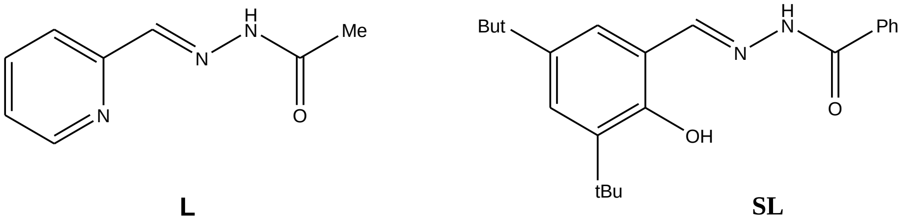
ملخص: تم تركيب شيفليجند **L** ودراسة تفاعله مع أيونات الزنك لتكوين المركب: $[ZnL_2](ClO_4)_2$ كما ثبت من التركيب البلوري. ولقد دل الرنين المغناطيسي الهيدروجيني بأن المركب ثابت في المحاليل القطبية وغير القطبية. هذا وقد لاحظنا زيادة في الطيف الضوئي للمانح في مركب الزنك مقارنة بمركبات فلزية أخرى تتكون من الحديد، الكوبالت، النيكل، النحاس والفضة. هذه النتائج ترشح الليجند **L** كحساس ضوئي متخصص لاستكشاف أيونات الزنك.

مفتاح الكلمات: شيفليجند، زنك(II)، تركيب بلوري، الطيف الضوئي.

1. Introduction

In recent years, there was a great interest in Schiff base ligands for their unusual photophysical properties. Their compounds have potential significance in light emitting diodes [1], as models in bioinorganic chemistry [2] and as chemical sensors [3]. The Schiff base ligands with polydentate donors such as imine are known for their selective detection of metal ions and other anions [4]. Many research groups have designed extensive Schiff base derivatives by incorporating fluorescent units. Sensing of transition metal ions has become an important goal in chemistry because of their important biological and environmental roles [5]. Zinc is an essential co-factor in many biological processes like brain function and pathology [6]. The main challenge in the design of an effective fluorescent probe for Zn^{2+} is to create a probe that responds selectively to Zn^{2+} over other metal ions such as Ca^{2+}, Mg^{2+} and Cd^{2+} [7]. A variety of Zn^{2+} sensors have been reported based on quinoline, [8] coumarin [9] and Schiff base ligands [7].

In this paper, we describe the synthesis and spectroscopic characterization of a tridentate Schiff base ligand **L** (Scheme 1). The ligand was designed by incorporating pyridyl and acetyl groups that have a strong affinity for metal ions. The ligand is poorly fluorescent due to excited state electron transfer in the C=N bond. Upon complexation with metal ions, the structure's rigidity inhibits the excited-state electron transfer process, and hence the fluorescence is produced. Our work also includes an investigation of the selectivity of **L** to Zn^{2+} ions by exploring the fluorescence properties in solution.

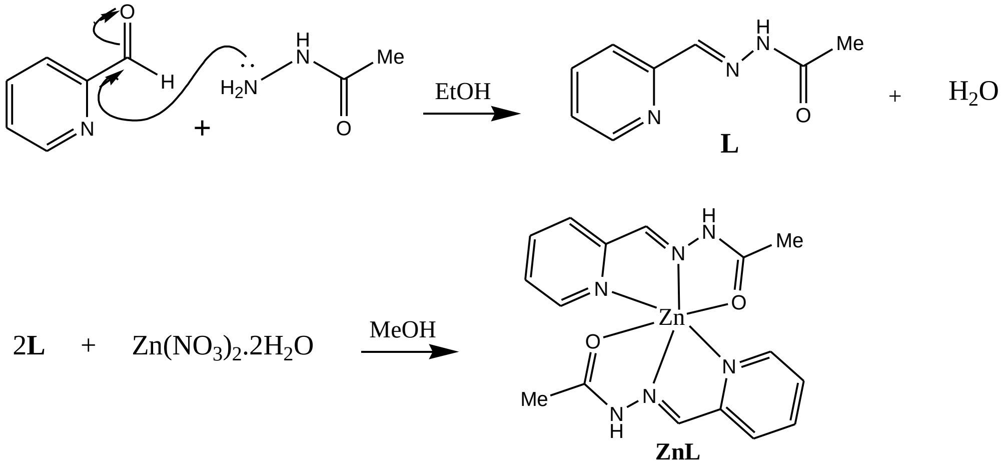


Scheme 1. A presentation of the Schiff base ligand **L** used in this work.

2. Results and discussion

2.1 Synthesis and crystal structure studies

The Schiff base ligand used, **L**, was generated by the condensation reaction of stoichiometric amounts of acetic hydrazide with picolinaldehyde according to the standard method used for the synthesis of Schiff base ligands [10]. All of the spectroscopic and analytical data were consistent with the correct formulation of the ligand. The IR spectrum of **L** showed a strong imine absorption, $\nu_{C=N}$ at 1627 cm^{-1}. The reaction of **L** with $Zn(ClO_4)_2$ in 1:2 molar ratio afforded colorless crystals with the general empirical formula $[ZnL_2](ClO_4)_2$ by elemental analysis (Scheme 2). The X-ray structure showed the simple mononuclear Zn(II) complex: $[ZnL_2](ClO_4)_2{\cdot}MeOH$ (**ZnL**) that is presented in Figure 1 and Table 1. Initially, we thought that **ZnL** may adapt a dimeric structure similar to other related Schiff base systems such as $[Zn_2SL_2(CH_3CO_2)(C_2H_6OH)]$ reported by Peng *et al.*[11] because the acetyl oxygen atoms are not basic enough to coordinate to two metal centers.



Scheme 2. Schematic presentation of the synthetic routes for **L** and its Zn(II) complex **ZnL**.

However, the Zn(II) ion was found to be in a 6-coordinate N_4O_2 environment, coordinating to two ligands in a meridional fashion. The bond distances to the Zn(II) ion were comparable to related Zn(II) compounds. The Zn–N bonds to the imine donor (2.073(4) Å) were slightly shorter than to the pyridyl donor (2.153(4) Å). The Zn–O_{ac} bond distances were the longest, 2.164(3) and 2.222(3) Å. The angle between the two $Zn(NNO)_2$ planes was 92.78°. The crystal packing for **ZnL** exhibited intermolecular $\pi\cdots\pi$ interactions between the alternating pyridine rings forming parallel chains of alternating molecules. The remaining perchlorate ions and methanol molecules exhibited a combination of O···HC and NH•••O hydrogen contacts within the molecules (Figure 1 (b)). These have very important consequences on the emission properties of the complex.

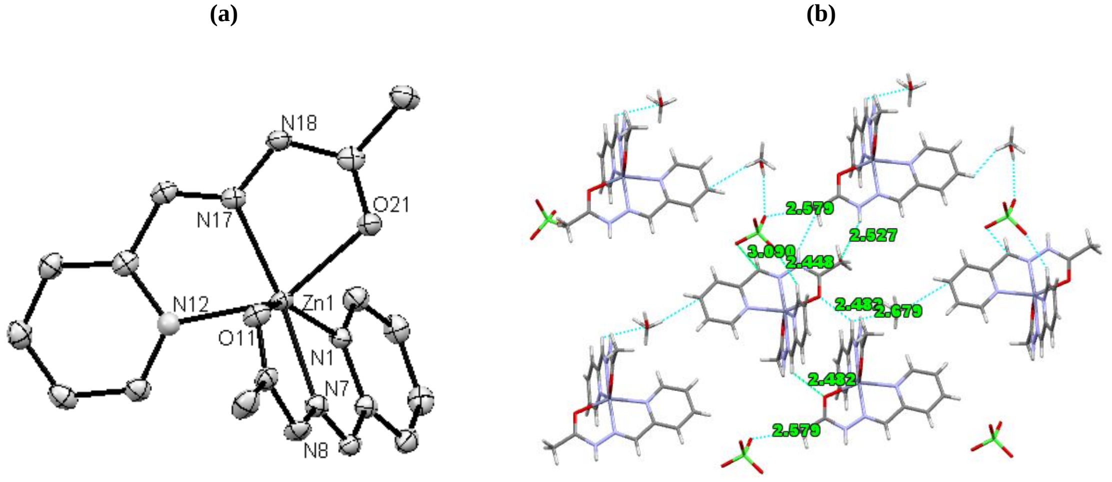

(a) (b)

Figure 1. (a) View of the complex cation of **ZnL**. The counter ions and solvent molecules are omitted for clarity. (b) The crystal packing of **ZnL,** showing the packing of molecules into parallel chains by hydrogen contacts of O···HC in the range 2.448–3.090 Å and NH•••O in the range of 2.482–2.527 Å.

Table 1. Bond lengths [Å] and angles [°] for **ZnL**.

Zn(1)-N(17)	2.071(4)
Zn(1)-N(7)	2.077(4)
Zn(1)-N(1)	2.148(4)
Zn(1)-N(12)	2.158(4)
Zn(1)-O(21)	2.164(3)
Zn(1)-O(11)	2.222(3)
N(17)-Zn(1)-N(7)	165.89(15)
N(17)-Zn(1)-N(1)	118.00(15)
N(7)-Zn(1)-N(1)	76.05(15)
N(17)-Zn(1)-N(12)	76.35(15)
N(7)-Zn(1)-N(12)	99.95(14)
N(1)-Zn(1)-N(12)	103.06(14)
O(21)-Zn(1)-O(11)	92.80(12)
N(7)-Zn(1)-O(21)	108.85(14)
N(17)-Zn(1)-O(11)	92.79(13)
N(1)-Zn(1)-O(21)	88.63(13)
N(12)-Zn(1)-O(21)	150.82(14)

Table 2. Crystallographic data for **ZnL**.

Formula	$C_{17}H_{22}N_6Cl_2O_{11}Zn$
Formula weight	622.68
T (K)	100(2) K
Crystal system	Triclinic, P–1
a (Å)	9.6126(11)
b (Å)	11.8491(13)
c (Å)	12.7991(15)
α (°)	112.255(4)
β (°)	111.853(4)
γ (°)	96.455(4)
V(Å^3), Z	1196.5(2), 2
D_{calc}/μ (mm^{-1})	1.728/ 1.321
Crystal size (mm)	0.16 x 0.15 x 0.15
Reflections collected	15386
Data / restraints/ parameters	5857 / 0 / 283
Goodness-of-fit on F^2	1.050
Final R indices	R1 = 0.0725 wR2 = 0.1886
Largest diff. peak and hole (e.Å^{-3})	2.012 and -1.526

2.2 ^{1}H NMR studies

The ^{1}H NMR spectra of re-dissolved crystals of Zn(II) complex **ZnL**, were investigated in $CDCl_3$ and DMSO-*d*$_6$ (Figure 2). The spectra exhibited the number of peaks expected for the molecular structure and confirmed the stability of **ZnL** in solution. In general, it was found that the complex **ZnL** exhibits a 2-fold symmetry, such that the two coordinating ligands are equivalent to one another. It was noticed in the ^{1}H NMR spectrum of **ZnL** in DMSO-*d*$_6$, that the N–H and CH_3 signals are strongly downfield shifted to 11.50 and 3.40 ppm indicating that these protons are under a rich electronic zone *via* H-bonding with DMSO molecules. The pyridine and CH=N protons are slightly down-field shifted when compared to those in $CDCl_3$. These results suggest that the pyridine and CH=N protons of **ZnL** are under the shielding zone of π-electrons of a conjugated system due to aggregation of molecules in non-polar solvents *via* π–π stacking interactions as referred from the crystal packing [12].

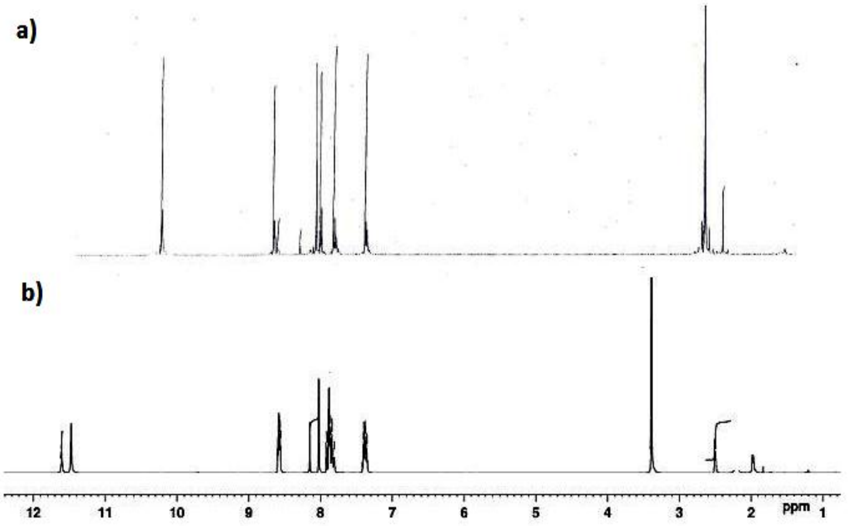


Figure 2. The ^{1}HNMR spectra of re-dissolved crystals of **ZnL** a) in $CDCl_3$ and b) DMSO-*d*$_6$ at ambient temperature.

2.3 Luminescence properties

The UV/Vis absorption spectra of the ligand and its Zn(II) complex are shown in Figure 3a. The ligand exhibited strong absorption in the UV region at 304 nm (ε ~38,100 M^{-1} cm^{-1}) and a shoulder at ca. 318 nm. These transitions could be attributed to π–π* transitions of the aromatic rings and the imine bonds present in the molecules [13]. Upon complexation to Zn(II) ion, a distinct red shift of the high energetic band was observed at 313 nm (ε ~47,500 M^{-1} cm^{-1}). The band was highly intense and unresolved. However, a new weak band observed at 363 nm (ε ~13,000 M^{-1} cm^{-1}) contributed to the formation of the lowest-energy excited state of ligand centered π–π* transitions in **L**–Zn(II) bonds [14].

The ligand, **L** has no emissive chromophores and hence, is not luminescent. Excitation of the complex **ZnL** in DCM at 363 nm, exhibited an enhanced emission centered at 468 nm (Figure 3b). Excitation at the highest energy absorption band, 313 nm, revealed very weak emission. Normally in the presence of coordinating Zn(II) ions, the fluorescence of a ligand is enhanced by preventing the photo induced electron transfer (PET) process in the ligand [15]. This explains the intense emission of the complex at an excitation wavelength of 368 nm as this absorption is based on **L**–Zn(II) transition.

In switching to more polar solvents such as THF, the effect of polarity is much more pronounced in the emission of **ZnL** (Figure 3b). The emission spectrum showed an intense band with a large red-shift to 480 nm with respect to those in DCM. The ^{1}H NMR results suggest that **ZnL** molecules can form aggregates in a less polar DCM solution. In switching to a polar THF solution, the molecules of **ZnL** are under the influence of

H-bonding with THF molecules. This would cause random aggregates of **ZnL** in THF, and hence the emission energy of **ZnL** is red shifted [16-17].

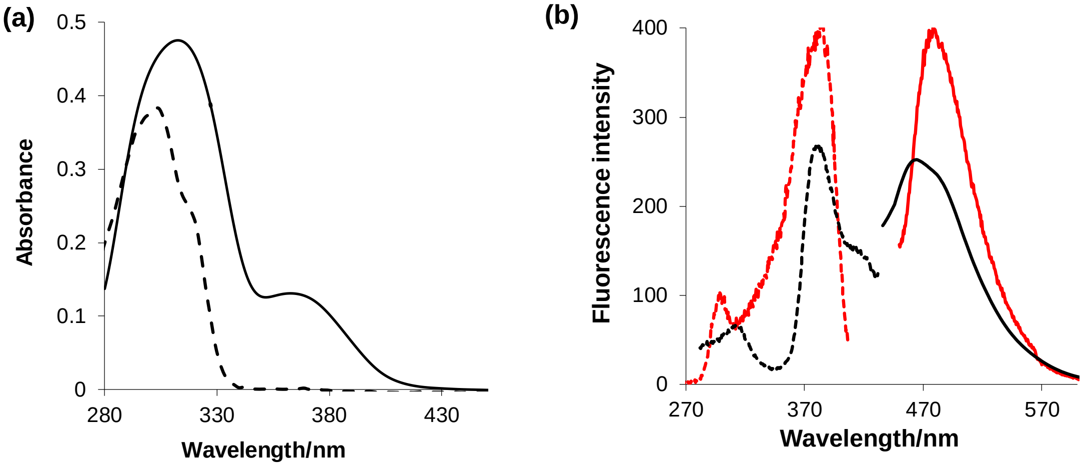


Figure 3. (a) The absorption spectra of **L** (dashed line) and **ZnL** (solid line) in DCM at RT. (b) Emission (solid line) and excitation (dashed line) spectra of **ZnL** in 1.0 x 10^{-5} M DCM (black) and THF (red) solutions at RT.

The selectivity of **L** towards Zn(II) ions was also investigated by the titration of the solution of **L** in DCM with a methanoic solution of $Zn(ClO_4)_2$ (0–1.5 equiv.). The bands of these spectra showed systematic enhancement in fluorescence which was very similar to that of **ZnL** complex after the addition of few equivalents of Zn(II) ions. The maximum fluorescence intensity was observed at a molar stoichiometry of 1:2 between Zn(II) ions and **L**. This is the point where all **L** molecules coordinate to Zn(II) ions to form the complex **ZnL** (1:2 molar ratio). Further addition of Zn(II) ions revealed no enhanced emission. However, in switching to a polar THF solvent, addition of Zn(II) to **L** enhanced the emission in a similar manner to the complex **ZnL**, as the emission was red-shifted.

The emission behavior of **L** upon titration with other *d*-metals such as Fe(II), Co(II), Ni(II) and Cu(II) was also investigated. The emission of their complexes did not enhance the emission of **L**. These metals exhibited electronic *d-d* transitions that caused the quenching of emission in their complexes. For Zn(II), the metal has a fully filled *d*-shell, d^{10} and exhibits no such *d-d* transitions. Instead, coordination to a Zn(II) center would enhance emission from the coordinating ligand. However, the emission of **L** was also studied with other d^{10} metals such as Cd(II) and Ag(I). These metals failed to induce the fluorescence from **L**, probably because these metals failed to form a suitable coordination environment around **L** to inhibit the PET process for their larger ionic radii. The high selectivity of **L** towards Zn(II) ions over other metal ions suggests that the ligand **L** can act as a fluorosensor for Zn(II).

3. Conclusions

The synthesis and crystal structure of the Zn(II) complex with a new tridentate Schiff base ligand '**L**' has been investigated and fully characterized. The structure of the complex: $[ZnL_2](ClO_4)_2$ is retained in polar and non-polar solvents as confirmed by NMR. It has been found that the emission of **L** is induced upon coordination to Zn(II) over other metal ions such as Fe(II), Co(II), Ni(II), Cu(II), Cd(II) and Ag(I). These results suggest that **L** can be used as a selective fluorsensor for the detection of Zn(II) ions.

4. Experimental

4.1 General details

All organic reagents, metal salts and solvents were purchased from Sigma-Aldrich and were used as received without further purification. Infrared spectra were recorded as KBr pellets on a Perkin Elmer FT-IR spectrometer BX in the range of 4000-400 cm^{-1}. Electrospray (ES) mass spectra were recorded on a VG Autospec magnetic sector instrument. Proton magnetic resonance (^{1}H-NMR) spectra were recorded using a 500 MHz AVANCE Bruker NMR spectrometer. Chemical shifts (δ_{ppm}) were recorded in parts per million (ppm) downfield from TMS (assigned as zero ppm). Elemental analyses for carbon, hydrogen and nitrogen were performed using a Perkin Elmer 2400 CHNS/ O Series II Elemental Analyser.

4.2 Preparation of ligand

The ligand **L** was prepared according to the general method for preparation of Schiff bases. A solution of pyridine-2-aldehyde (1.1 g; 10 mmol) in EtOH (20 mL) was added dropwise to a solution of acetic hydrazide (0.65 g; 10 mmol) in EtOH (20 mL) and refluxed at 85 °C for four hours. The reaction mixture was concentrated under vacuum and cooled in the fridge to yield 1.40 g (86 %) of L. ES-MS: *m/z*= 164.0 [M^+] 186.0 [$Na+M^+$]. IR (KBr, cm^{-1}) 3450, 3010, 2944, 1627, 1394-1600. ^1H NMR ($CDCl_3$): 10.20 (1H, s, NH), 8.61 (1H, d, CH), 8.05 (1H, s, py H^6), 7.93 (1H, d, py H^3), 7.73 (1H, t, py H^5), 7.28 (1H, t, py H^4) and 2.40 (3H, s, Me). $C_8H_9N_3O$ (163.01): calcd. C 58.88, H 5.56, N 25.75; found C 58.94, H 5.62, N 25.69%.

4.3 Preparation of [ZnL_2](ClO_4)$_2$·MeOH, ZnL

To a solution of **L** (0.27 g; 1.66 mmol) in MeOH (10 mL) was added dropwise a solution of $Zn(ClO_4)_2$ (0.22 g; 0.83 mmol) dissolved in MeOH (5 mL) at room temperature. The yellowish solution which formed was left for the solvent to slowly evaporate off. Colorless needles formed within few days. Yield 88%. ES-MS: *m/z* 393.77. IR (KBr, cm^{-1}) 1623.^1H NMR (DMSO-d_6): 11.50 (1H, s, NH), 8.58 (1H, s, CH), 8.14 (1H, d, J= 9 Hz py H^6), 7.80-7.93 (2H, m, py H^3,H^5), 7.35 (1H, dt, py H^4) and 3.28 (3H, s, Me). $ZnC_{16}H_{18}N_6O_{10}Cl_2$ (590.64): calcd. C 32.54, H 3.07, N 14.23; found C 32.63, H 3.11, N 14.21%.

4.4 Spectrofluorimetric measurements

UV-visible spectra were recorded on a Varian Cary 50 conc UV-visible spectrophotometer in the range 250-800 nm. Quartz cuvettes of 1 cm path length were used and solvent background corrections were applied. Steady state luminescence spectra were recorded on a Perkin-Elmer LS50B fluorimeter. Solution spectra were measured using 1 cm quartz cuvettes. The spectrofluorimetric titrations were performed as follows. Stock solutions of the ligands (*ca.* 1.0 x 10^{-5} M) were prepared by dissolving an appropriate amount of the ligand in a 50 mL volumetric flask and diluting it to the mark with DCM or THF. Titrations were carried out by the addition of µL amounts of standard solutions of $Zn(ClO_4)_2$, $Fe(ClO_4)_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, $Cd(SO_4)_2$ and $AgBF_4$ in MeOH to a solution of **L** in DCM or THF.

4.5 Crystallography

Single crystals of the complex were obtained as detailed above. The crystal structure of **ZnL**, [ZnL_2](ClO_4)$_2$·MeOH, was carried out at the University of Sheffield. Data was collected at 100 K, using a Bruker APEX-II CCD diffractometer equipped with Mo-Kα radiation. Absorption corrections were applied in each case using SADABS [18]. The structures were solved by direct methods and refined by full matrix least squares methods on F^2 using SHELXL-97 [19,20]. The hydrogen atoms were generated geometrically with isotropic thermal parameters. Some oxygen atoms in perchlorates were disordered and refined with isotropic displacement parameters. The MeOH molecule was refined with isotropic displacement parameters to keep the refinement stable.

Crystallography data (excluding the structure factors) for the reported structure have been deposited with the Cambridge Crystallographic Data Centre CCDC 943597.

5. Acknowledgements

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