Asian Journal of Chemistry; Vol. 32, No. 4 (2020), 945-951

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22525

New Zn(II) Complexes of Substituted *bis*(Salicylidene)phenyl-1,2-diamino Based Organic Ligands: Synthesis, Photoluminescence, Applications in Forensic Fingerprint and Dye Sensitized Solar Cells

M. SRINIVAS[1,*], N. SULOCHANA[1], G.R.YOGESH KUMAR[2], K.M. MAHADEVAN[3,*] and H.S. BHOJYA NAIK[4]

[1]State Forensic Science Laboratory, Madivala, Bengaluru-560068, India
[2]Department of Studies in Chemistry, Bengaluru University, Jnana Bharathi Campus, Bengaluru-560056, India
[3]Department of P.G. Studies & Research in Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta-577451, India
[4]Department of Studies and Research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta-577451, India

*Corresponding authors: E-mail: srinivas1885@gmail.com; mahadevan.kmm@gmail.com

Received: 7 November 2019; *Accepted*: 24 December 2019; *Published online*: 25 February 2020; AJC-19817

New azomethine-Zn(II) complexes of *bis*(salicylidene)phenyl-1,2-diamino organic ligand derivatives were synthesized by the reaction of salicylaldehyde, substituted phenyl-1,2-diamine with zinc acetate. The synthesized complexes were characterized by FTIR, ^{1}H NMR and EDS. Their photophysical and electrochemical properties were studied and their applicability for dye-sensitized solar cells (DSSCs) and forensic finger print developments have been demonstrated. Photoluminescence studies revealed that the emission peaks of the complexes in solution state appeared at 372-406 nm and emitted blue light. Latent fingerprint detection study indicated that the powder compounds show good adhesion and finger ridge details without back ground staining. Based on these results, it was ascertained that these Zn(II) complexes can serve as a suitable non-dopant blue light emitting compound for flat panel display applications and applied to detect fingerprints on all types of smooth surfaces.

Keywords: Schiff base, Zinc(II), Complexes, Photoluminescence, Cyclic voltammetry, Latent finger print, Dye sensitized solar cells.

INTRODUCTION

Organo metal complexes are synthesized in recent years mainly because of their applications in organic light emitting diodes (OLEDs) [1-3]. Organo polymers with copper and zinc metal complexes exhibits good fluorescent spectra and displayed blue luminescence in solution state. Hence, these complexes have received much attention in OLED applications [4].

Ligands having Schiff bases possesses potential multidentate capabilities and presence of phenolic hydroxyl group, complexes formed by phenolate oxygen had shown good luminescent property at room temperature [5]. Several salicylaldiminato ligands of zinc(II) complexes exhibits thermally stable photoluminescent properties and they were used in the construction of OLEDs because of their considerable variation in electrical properties [6,7]. Since their discovery in 1991, dye sensitized solar cells (DSSCs) have been broadly studied as a substitute to silicon-based solar cells, due to their simple structure, flexibility, low production cost, and wide range of application. Hence low efficiency of DSSCs compared to that of silicon-based cells has limited their commercial implementation [9,10]. Fingerprints are important clue material as they have unique ridges skin pattern for fingers of individual persons, which gives the evidence about presence/involvement of suspected persons either in crime or crime scene. Hence it is used as one of the important physical evidence in criminal justices' system. However, these finger prints are invisible to naked eyes. Hence to enhance the visibility of fingerprints several techniques are being used. In recent years, many developments have reported to enhance the visibility of ridges, such as metal nano particles, which showed fluorescent latent finger print on various surfaces [11-17]. Nanoparticles prepared by natural products such as green tea leaf extract having metal complex used as a good fluorescent marker for the enhancement of the latent finger print [18]. A series of organic ligand-based metal complexes shown a good latent finger print mark over the conventional method which was reported in the earlier report [19]. In continuation, the present work reports the synthesis and characterization of Schiff base based Zn(II) complexes and the same have been explored for their applications as OLEDs, DSSCs and latent finger printmarkers having better enhancement of the visibility.

EXPERIMENTAL

4-Nitro/carboxylphenyl-1,2-diamine, salicylaldehydes and zinc acetate were purchased from Sigma-Aldrich India Ltd. The common reagents were purchased from Spectrochem India Pvt. Ltd. and used as received. Analytical thin layer chromatography (TLC) were conducted on Merck-60 F_{254} silica gel precoated on aluminum sheets. TLC plates were viewed under UV-light. Melting points were determined in capillary tubes closed at one-end and are reported uncorrected. Infrared spectra were recorded by a scanning method on a Thermo Fisher iS 10 Nicolet FT-IR spectrometer (Thermo Fisher Scientific Inc. Germany) instrument in the wavenumber range of 4000-500 cm^{-1}. ^{1}H NMR spectra were recorded at 400 MHz in DMSO-d_6 with TMS as an internal standard on Varian 400 NMR Autosampler (Varian, California, USA) spectrophotometer and the chemical shifts are given in δ ppm. The photoluminescence (PL) measurement was performed on a Jobin Yvon Spectrofluorometer Fluorolog-3 (Jobin Yvon Inc. 3880 Park Avenue, Edison, NJ 08820, USA) equipped with a 450 W Xenon lamp as an excitation source, Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) measurements were performed on a VEGA3LMUVG13171475 of TESCAN, Brno, Kohoutovice, CZ.

Synthesis of N,N′-*bis*(salicylidene)-(4-nitro-1,2-phenylenediamine) (L^1H_2): To a stirred solution of 4-nitrobenzene-1,2-diamine (0.306 g, 2.0 mmol) in dry methanol (10 mL) added a solution of salicylaldehyde (0.488 g, 4.0 mmol) in dry methanol (20 mL) at room temperature. The resulted yellow solution was refluxed for 3 h. The reaction was monitored by TLC (petroleum ether:ethyl acetate, 7:3). After completion of the reaction, solvent was distilled off under reduced pressure on a rotary evaporator to afford **L^1H_2**. The resulted yellow coloured solid was recrystallized from methanol. Yield: 0.70 g, 97 %; m.p.: 112-114 ºC; m.f.: $C_{20}H_{15}N_3O_4$; FT-IR (ν_{max}, cm^{-1}, ATR): 3369 (phenolic O-H), 1612 (C=N), 1488-1429 (NO_2); ^{1}H NMR: (DMSO-d_6, 399.64 MHz), δ ppm: 8.126 (3H, m, 3-H, 17-H, 13-H), 7.049-7.094 (2H, m, 5-H, 19-H), 7.384-7.454 (2H, m, 4-H, 18-H), 7.795-7.856 (2H, m, 6-H, 20-H), 8.601 (1H, s, 10-H), 8.448-8.464 (1H, d, *J* = 6.4 Hz, 12-H), 7.031 (2H, s, 7-H, 14-H), 5.435 (2H, s, -OH).

Synthesis of 3,4-*bis*((salicylidene)amino)benzoic acid (L^2H_2): To a stirred solution of 3,4-diaminobenzoic acid (0.304 g, 2.0 mmol) in dry methanol (10 mL) added a solution of salicylaldehyde (0.488 g, 4.0 mmol) in dry methanol (20 mL) at room temperature. The resulted yellow solution was refluxed for 3 h. The reaction was monitored by TLC (petroleum ether:ethyl acetate, 7:3). After completion of the reaction, the solvent was distilled off under reduced pressure on a rotary evaporator to afford **L^2H_2**. The resulted yellow coloured solid was recrystallized from methanol. Yield: 0.691 g, 96 %); m.p.: 97-98 ºC; m.f.: $C_{21}H_{16}N_2O_4$; FT-IR (ν_{max}, cm^{-1}, ATR): 3067 (phenolic O-H), 2360 (carboxylic O-H), 1610 (C=N); ^{1}H NMR: (DMSO-d_6, 399.64 MHz), δ ppm: 8.902 (1H, s, 10-H), 8.250-8.281 (1H, d, *J* = 12.4 Hz, 12-H), 7.809-7.863 (1H, m, 13-H), 7.352-7.397 (1H, m, 6-H), 7.070-7.173 (1H, m, 20-H), 6.093-7.049 (2H, m, 9-H, 5-H), 6.843-6.886 (1H, m, 4-H), 6.661-6.682 (1H, d, *J* = 8.4 Hz, 3-H), 6.549-6.567 (1H, d, *J* = 7.2 Hz, 17-H), 6.433 (1H, s, 7-H), 6.3364 (1H, s, 14-H), 5.360 (2H, s, -OH).

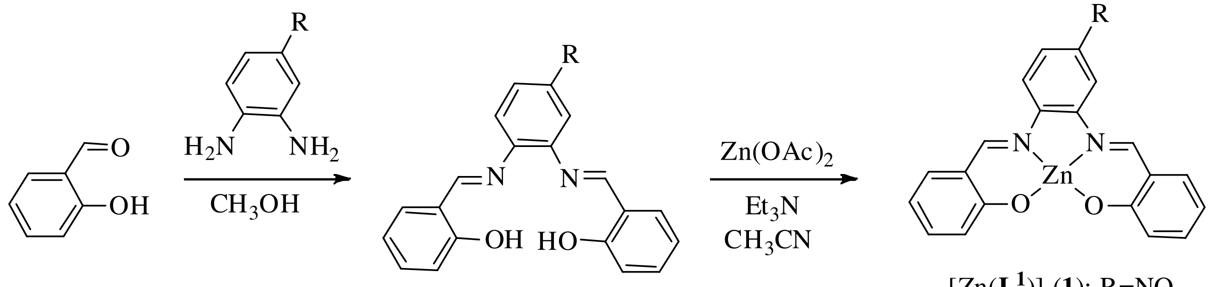
Synthesis of Zn(II) complexes: To a stirred acetonitrile solution (15 mL) of zinc acetate (1 mmol, 0.183 g), a solution of corresponding ligand (**L^1H_2** & **L^2H_2**) (1 mmol, 0.361/0.360 g) in acetonitrile (10 mL). The resulting mixture was refluxed for about 4 h. The completion of the reaction was regularly monitored by TLC. The reaction mixture was cooled to room temperature resulted a precipitate of complex. The solid was filtered and dried to get zinc(II) complex (**Scheme-I**).

[Zn(L^1)] (1): Yield: 0.378 g, 89 %; m.p.: 96-98 ºC; m.f.: $C_{20}H_{13}N_3O_4Zn$; FT-IR (KBr, ν_{max}, cm^{-1}): 1592 (C=N), 1458 (N-O); ^{1}H NMR: (DMSO-d_6, 300.13 MHz), δ ppm: 6.528-6.576 (2H, t, 3-H, 17-H), 6.722-6.752 (2H, d, 5-H, 19-H), 7.271-7.317 (2H, t, 4-H, 18-H), 7.443-7.544 (2H, d, 6-H, 20-H), 8.773 (1H, s, 13-H), 8.113-8.143 (1H, d, 10-H), 8.203-8.223 (1H, d, 12-H), 9.135 (1H, s, 7-H), 9.206 (1H, s, 14-H)

[Zn(L^2)] (2): Yield: 0.358 g, 85 %; m.p.: 97-98 ºC; m.f.: $C_{21}H_{14}N_2O_4Zn$; FT-IR (KBr, ν_{max}, cm^{-1}): 2359 (carboxylic O-H), 1599 (C=N); ^{1}H NMR: (DMSO-d_6, 300.13 MHz), δ ppm: 6.782-6.898 (4H, q, 3-H, 5-H, 17-H, 19-H), 6.999-7.083 (2H, t, 4-H, 18-H), 7.294-7.317 (2H, t, 6-H, 20-H), 7.657-7.687 (1H, d, 13-H), 8.101-8.182 (4H, q, 7-H, 10-H, 12-H, 14-H), 9.727 (1H, bs, COOH).

RESULTS AND DISCUSSION

A new substituted Schiff base ligands, N,N′-bis(salicylidene)-(4-nitro-1,2-phenylenediamine) (**L^1H_2**) and 3,4-bis((salicylidene)amino) benzoic acid (**L^2H_2**) have been synthesized



L^1H_2; R=NO_2
L^2H_2; R=COOH

[Zn(**L^1**)] (**1**); R=NO_2
[Zn(**L^2**)] (**2**); R=COOH

Scheme-I: Synthesis of new Schiff's base ligands, **L^1H_2** and **L^2H_2** and their complexes (**1** and **2**) by the condensation of respective 1,2-phenylenediamine derivative with salicylaldehyde in methanol. Ligands, $\mathbf{L^1H_2}$ and $\mathbf{L^2H_2}$ obtained were yellow crystalline solid in nature and soluble in polar organic solvents *viz*. methanol, ethyl acetate, chloroform, dichloromethane, acetonitrile, DMF and DMSO but insoluble in non-polar or less polar solvents like benzene, toluene, hexane, heptane, THF and diethyl ether.

The complexation of $\mathbf{L^1H_2}$ and $\mathbf{L^2H_2}$ with zinc acetate in reflux condition using acetonitrile as a solvent gave solid Zn(II) (**1** and **2**) complexes. These complexes were found to be highly soluble in DMSO and DMF, partially soluble in methanol, chloroform, dichloromethane and ethanol but insoluble in less/non-polar solvents like hexane, heptane, diethyl ether, THF and toluene.

FT-IR analysis: In the IR spectra of $\mathbf{L^1H_2}$ and $\mathbf{L^2H_2}$, phenolic O-H and C=N stretching bands were appeared at 3369, 3067 and 1612, 1610 cm^{-1}, respectively. The NO_2 stretching vibrational band in $\mathbf{L^1H_2}$ was appeared at around 1488-1429 cm^{-1}. The carboxylic O-H stretching bands in $\mathbf{L^2H_2}$ were appeared at around 2360 cm^{-1}.

The C=N stretching band in complexes **1** & **2** was appeared red shift of about 20-11 cm^{-1}, when compared to those bands in respective ligands as expected in the reported similar complexes [19,20]. An absence of phenolic OH stretching band in complexes **1** & **2** indicated the coordination of imine nitrogen (C=N) and phenolic oxygen (Ar-O) with central metal ions (Zn^{2+}) in the metal complexes **1 & 2**. Since both zinc(II) complexes were able to record ^{1}H NMR spectra, a diamagnetic characteristic can be attributed to the tetrahedral structure of both Zn(II) complexes.

SEM-EDX analysis: Obtained SEM images (Fig. 1) shows a cotton bulbs shape for complex **1** (size 100 µm length, HV-20kV), a spider nest form for complex **2** (size 50 µm length, HV-12kV). The EDS of Zn(II) complexes **1** & **2** further confirms the presence of elemental profile such as zinc, carbon and oxygen.

Photoluminescence: The excitation, emission spectra and Commission International de I'Eclairage (CIE) spectra of Zn(II) complexes are shown in Fig. 2. Excitation spectra of Zn(II) complexes were obtained by monitoring the emission at the wavelength of 448 nm and 435 nm, respectively. Excitation spectrum involves different emission broad peaks at range 300 -500 nm. Photoluminescence emission spectra were recorded in the range of 400-600 nm under UV excitation at 378 nm (**1**) and 360 nm (**2**) wavelengths (Table-1).

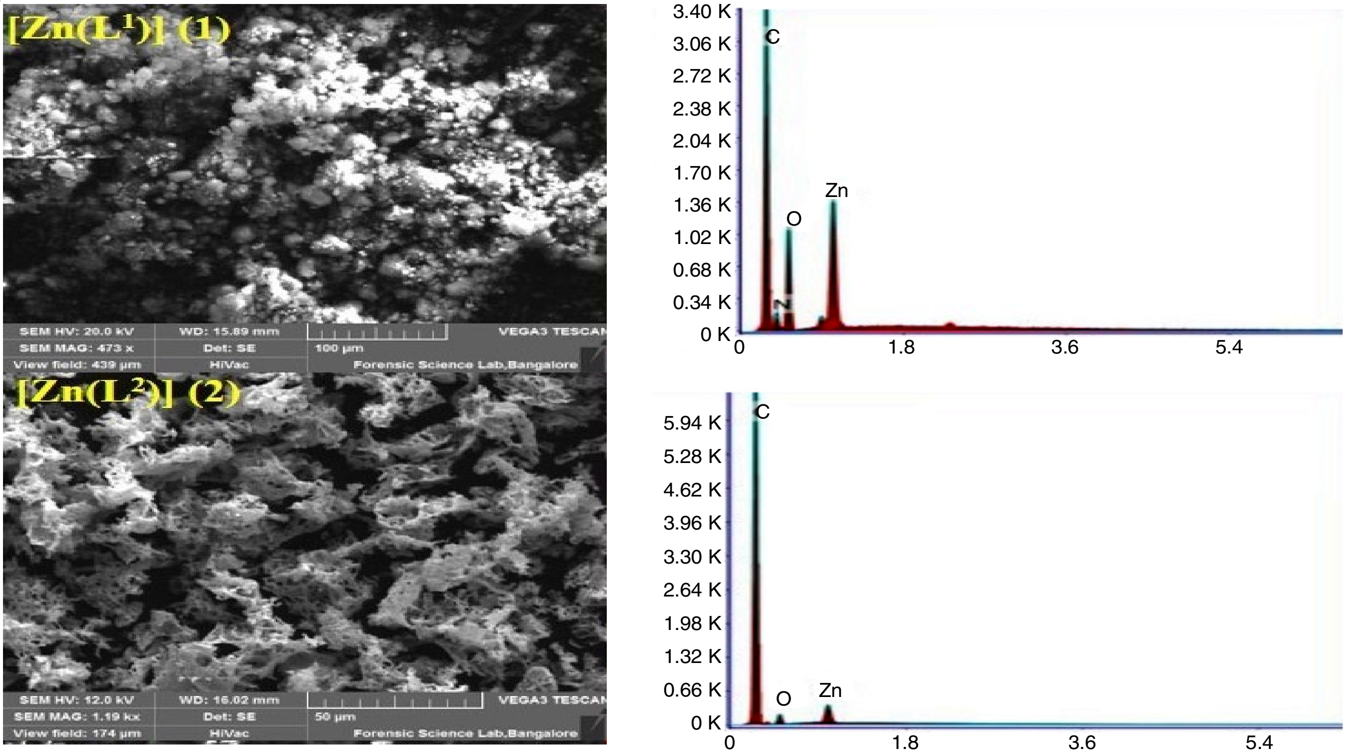


Fig. 1. SEM images and EDS elemental profile of the Zn(II) complexes **1** and **2**

TABLE-1
PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES OF ZINC(II) COMPLEXES **1** AND **2**

Complexes	$^a\lambda_{max}$ (nm) / ε (M^{-1} cm^{-1})		$^b\lambda_{em}$ (nm) (from PLI graph)	E_{ox} (eV)	E_{red} (eV)	$^cE_{0-0}$ (eV) or E_{gap}
	π–π*	CT				
1	264.0	378.0	448	1.24	2.76	2.76
2	234.5	292.5	435	1.48	2.85	2.85

^{a}Maximum absorption in dry ACN solution (0.1 M) at 25 °C. ^{b}Maximum emission in ACN solution (0.1 M) at 25 °C, ^{c}Maximum absorption in ACN solution (0.1 M) at 25 °C. E_{0-0} or E_{gap} was calculated by $1240/\lambda_{em}$. E_{red} was calculated from $E_{ox} - E_{0-0}$. E_{ox} was obtained from cyclic voltammogram.

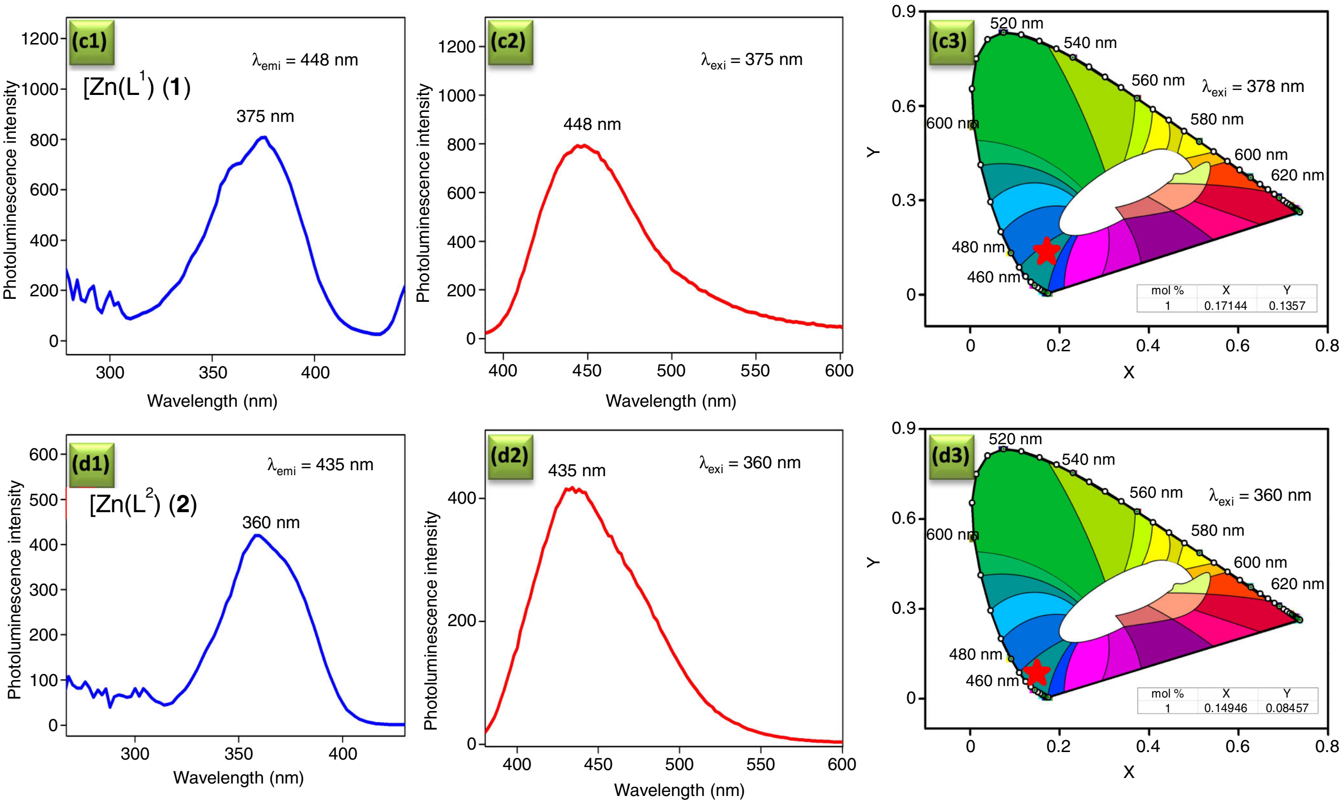


Fig. 2. Photoluminescence spectra of the ligands and their Zn(II) complexes (**1** and **2**), excitation spectra, emission spectra and CIE diagram

Commission International de I'Eclairage (CIE) 1931 x-y chromaticity diagrams of Zn(II) complexes are also depicted in Fig. 2. The CIE chromaticity coordinates were located in the light blue region for Zn(II) complexes. To identify technical applicability of blue emissions, the CCT was determined from CIE coordinates. Zn(II) complexes also displayed blue emission in solution state and images were captured under UV light (Fig. 3).

Electrochemical studies: Cyclic voltammetric method have been adopted to study the electrochemical properties of synthesized ligands and metal complexes. The cyclic voltammograms were recorded in dry acetonitrile (10 mL) with Bu_4NPF_6 as supporting electrolyte and glassy carbon as working electrode, platinum wire as counter and Ag/AgCl as reference electrodes. The cyclic voltammograms at different scan rate (50, 100 and 200 mV s^{-1}) were recorded for ligands and metal complexes. In Fig. 4, ligands $\mathbf{L^1H_2}$ and $\mathbf{L^2H_2}$ exhibited a pair of redox couple in the applied potential range of -1.5 V to +2.0 V. Whereas, the metal complexes marked as Zn(II) complex **1** & **2** exhibited two oxidation and a reduction peak in the applied potential range of -2.0 to +2.0 V during forward and reverse scans. The metal complexes showed distinct oxidation peaks at a higher scan rate of 200 mV s^{-1}, since the electropolymerization of metal complexes were observed to be minimum. Hence, fast-scan rate of 200 mV s^{-1} has been considered for calculation of energy levels of complexes. The oxidation potentials for complexes **1** & **2** were found to be 1.24 and 1.48 V, respectively. The results stated that E_{ox} values are higher than that of iodide/triiodide (I^-/I_3^-) redox couple (0.4 V *vs.* NHE), which provides sufficient driving force for regeneration of exited state complexes to ground state by taking electrons from (I^-/I_3^-) redox couple. Equally, the $E_{o\text{-}o}$ energies or E_{gap} of complexes **1** & **2** were determined from emission spectra of the complexes and found to be 2.76 and 2.85 eV, respectively. Similarly, reduction potentials (E_{red}) of the complexes **1** & **2** were determined by using the empirical formulae $E_{ox} - E_{o\text{-}o}$, and calculated as -1.52 and -1.35 V, respectively. Therefore, newly syntheiszed Zn(II) complexes based DSSCs could be expected and would conduct more effective electron injection from excited sate complexes into conductive band of TiO_2.

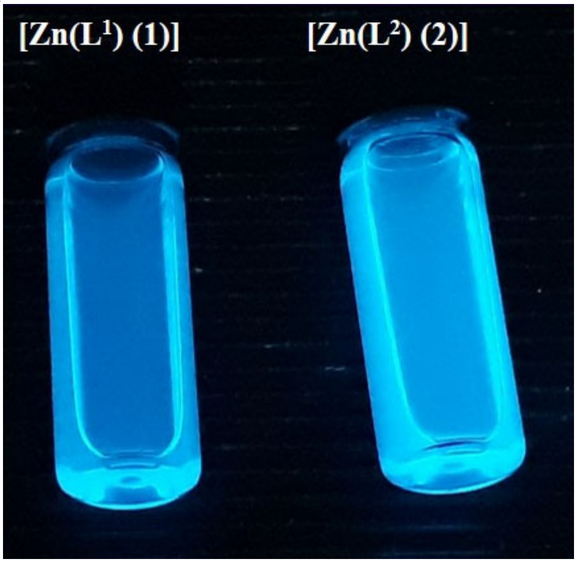


Fig. 3. Photography of Zn(II) complexes **1** and **2** in ethanol under UV light at longer wave length (366 nm)

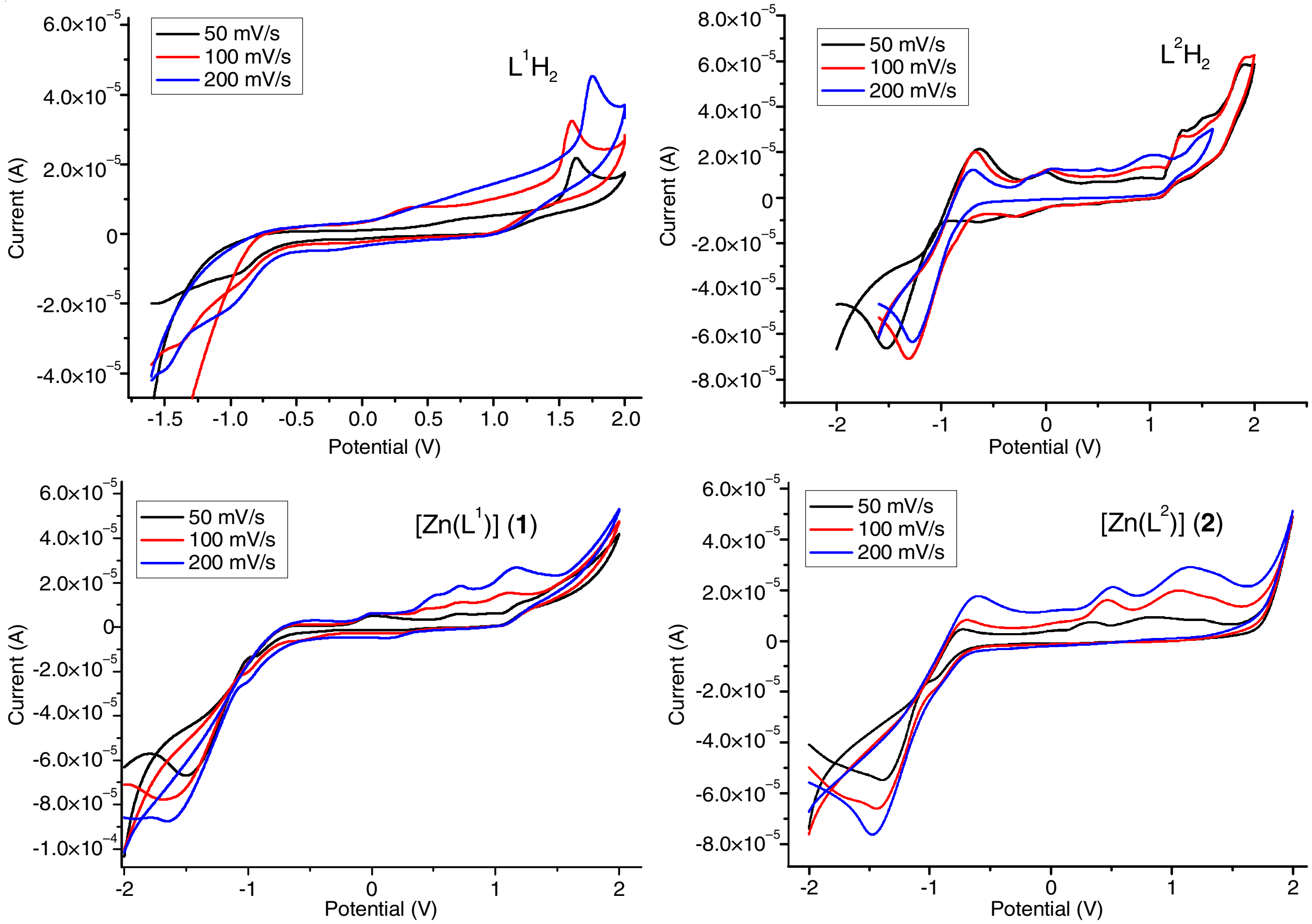


Fig. 4. Cyclic voltammogram of Schiff's base ligands, L^1H_2 and L^2H_2 and their Zn(II) complexes **1** and **2**

DSSCs application: The synthesized complexes **1** and **2** were subjected to DSSCs fabrication. Chander and Komarala [21] reported the fabrication and characterization of DSSCs on TiO_2 film by doctor blade method and the detailed procedure for the preparation of a DSSC photoanode and the assembly of DSSC. The same procedure was adopted during the fabrication of complexes **1** and **2**, which shows a good performance towards DSSCs. Hence, these complexes can be effectively used for the fabrication of dye sensitized solar cell application to convert light energy into electric. The plots of photo-current density (I) *versus* voltage (V) are shown in Fig. 5. The values of V_{oc}, I_{sc}, FF and η are given in Table-2. The photovoltaic conversion efficiency (η) of DSSCs sensitized with complexes **1** and **2** were found to be 0.08 and 0.36 % under AM 1.5 irradiation (1000 W/m^2).

Fingerprint development: Method for development of fingerprint was already discussed in earlier report [19]. The fingerprint analysis was carried out for synthesized Zn(II) complexes **1** & **2**. Comparison of class and individual characteristic marks of fingerprint on the surface of different materials marked as a-f (Fig. 6), are comparatively enhanced with that of the fingerprints developed through commercial powders (black and white powder) [19]. Hence, Zn(II) complexes **1** & **2** can be effectively used as a forensic fingerprint marker in the identification of individual and detection of latent fingerprints.

Conclusion

In this work, zinc(II) complexes of Schiff base were synthesized and characterized by means of ^{1}H NMR, FT-IR, SEM-EDS, cyclic voltammetric and photoluminescence analysis. Photoluminescence studies revealed that the emission peaks of zinc(II) complexes in both solution and solid states appeared at 360-448 nm and emitted a blue light. Conjugated Zn(II) complexes has electron acceptor, showed performance as photo-

TABLE-2
DSSCs PERFORMANCE DATA OF ZINC(II) COMPLEXES **1** AND **2**

Complex	V_{oc} (mV)	$I_{sc} \times 10^{-4}$ (mA)	$P_{max} \times 10^{-4}$ (mW)	$V_{mp} \times 10^{-4}$ (mV)	$I_{mp} \times 10^{-4}$ (mA)	P_{max} (mW)	FF (%)	η (%)
1	246	1.830	0.168	146	1.150	0.168	37	0.08
2	351	6.247	0.724	225	3.219	0.7422	33	0.36

$P_{max} = I_{mp} \times V_{mp} \times 10^{-4}$; $P_{the} = I_{sc} \times V_{oc} \times 10^{-4}$; $FF = P_{max}/P_{the}$; η (%) = P_{max}/100 mW/sX (19.63); open circuit voltage (V_{oc}), fill factor (FF) and efficiency (η)

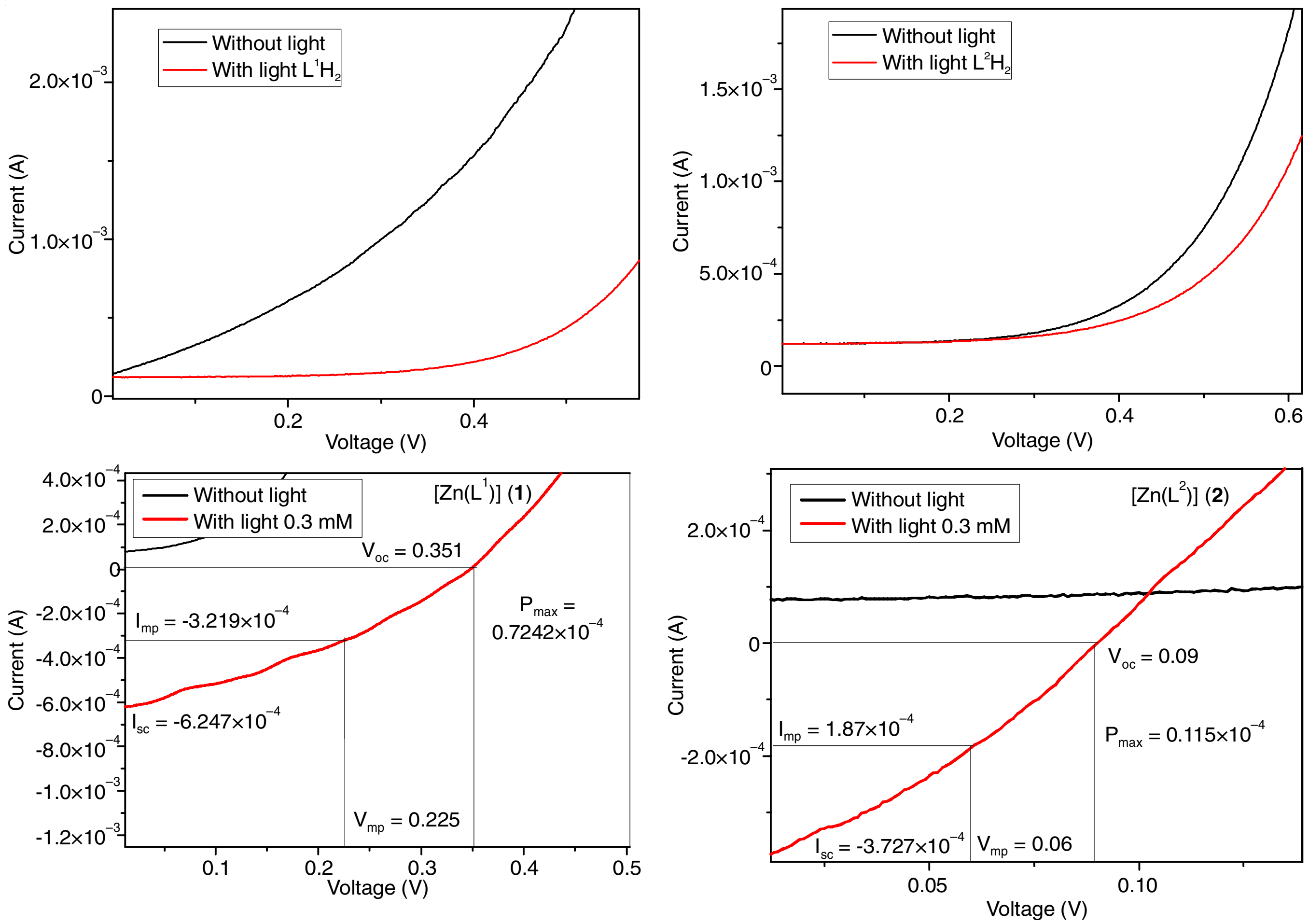


Fig. 5. I/V characteristics DSSCs of small area (0.5 cm^2) sensitized by different concentrations (0.3 mM) of complexes **1** and **2**

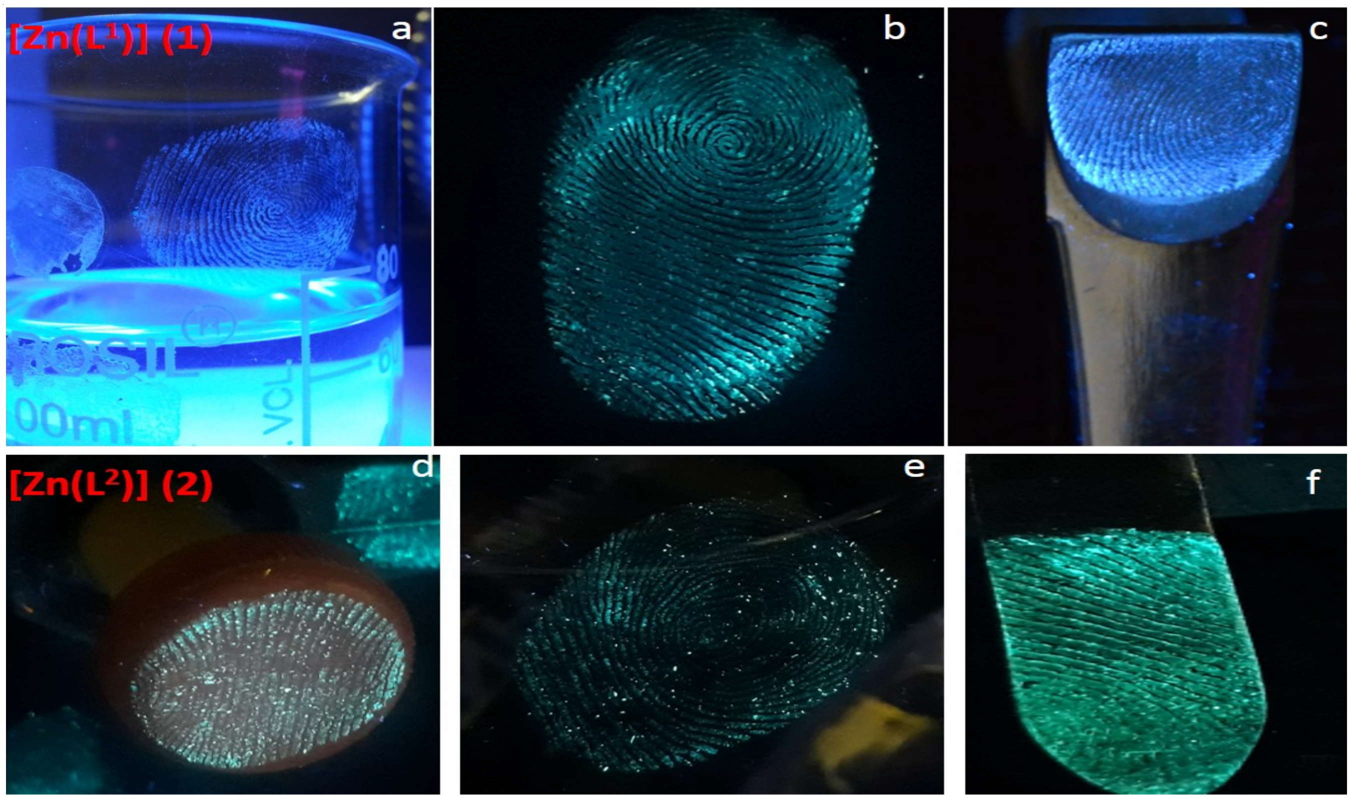


Fig. 6. Finger prints were developed from the complexes **1** and **2** on the surfaces of different materials. The photographs were captured under UV light (~365 nm), (a) glass beaker, (b) outer surface of laptop, (c) stapler, (d) micro pipette, (e) petri dish, (f) forceps tip

sensitizers in DSSCs. These Zn(II) complexes can be effectively used as a forensic tool marker in the detection of latent fingerprints. These development procedures are facile and exhibits excellent performance and high efficiency.

ACKNOWLEDGEMENTS

The authors thank the Directorate of Forensic Science Laboratory, Bengaluru, India for SEM-EDS analysis; Tumkur University, Tumakuru, India for cyclic voltammetric and photoluminescence analyses.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. Z. Shahedi, M.R. Jafari and A.A. Zolanvari, *J. Mater. Sci. Mater. Electron.*, **28**, 7313 (2017); https://doi.org/10.1007/s10854-017-6417-5
2. Z. Onal, H. Zengin and M. Sonmez, *Turk. J. Chem.*, **35**, 905 (2011).
3. R. Kumar, A. Dvivedi and P. Bhargava, *AIP Conf. Proced*., **1728**, 020025 (2016); https://doi.org/10.1063/1.4946075
4. Y. He, C. Zhong, Y. Zhou and H. Zhang, *J. Chem. Sci.*, **121**, 407 (2009); https://doi.org/10.1007/s12039-009-0047-2
5. X. Qin, Y. Ji, Y. Gao, L. Yan, S. Ding, Y. Wang and Z. Liu, *Z. Anorg. Allg. Chem.*, **640**, 462 (2014); https://doi.org/10.1002/zaac.201300279
6. Z. Q. Feng and X. L. Y. Feang Ye, *The Scientific World J.*, **2013**, 956840, (2013); https://doi.org/10.1155/2013/956840
7. Z. Li, A. Dellali, J. Malik, M. Motevalli, R.M. Nix, T. Olukoya, Y. Peng, H. Ye, W.P. Gillin, I. Hernández and P.B. Wyatt, *Inorg. Chem.*, **52**, 1379 (2013); https://doi.org/10.1021/ic302063u
8. E. Nosova, T. Stupina, A. Chupakhin, G. Lipunova, M. Valova, P. Slepukhin and V. Charushin, *Open Chem.*, **13**, 61 (2015); https://doi.org/10.1515/chem-2015-0005
9. B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991); https://doi.org/10.1038/353737a0
10. M. Durr, M. Schmid, M. Obermaier, S. Rosselli, A. Yasuda and G. Nelles, *Nature*, **4**, 607 (2005); https://doi.org/10.1038/nmat1433
11. L.R. Xu, Y. Li, S.Z. Wu, X.H. Liu and B. Su, *Angew. Chem. Int. Ed.*, **51**, 8068 (2012); https://doi.org/10.1002/anie.201203815
12. L. Feng, X. Sun, C. Liu and W. Xing, *Chem. Commun.*, **48**, 419 (2012); https://doi.org/10.1039/C1CC16522D
13. Y. Li, L.R. Xu, Y.Y. He and B. Su, *Electrochem. Commun.*, **33**, 92 (2013); https://doi.org/10.1016/j.elecom.2013.04.033
14. K. Li, W.W. Qin, F. Li, X.C. Zhao, B.W. Jiang, K. Wang, S.H. Deng, C.H. Fan and D. Li, *Angew. Chem. Int. Ed.*, **52**, 11542 (2013); https://doi.org/10.1002/anie.201305980
15. L.R. Xu, Z.Y. Zhou, C.Z. Zhang, Y.Y. He and B. Su, *Chem. Commun.*, **50**, 9097 (2014); https://doi.org/10.1039/C4CC03466J
16. J. Tan, L. Xu, T. Li, B. Su and J. Wu, *Angew. Chem. Int. Ed.*, **53**, 9822 (2014); https://doi.org/10.1002/anie.201404948
17. M. Wang, M. Li, M. Yang, X. Zhang, A. Yu, Y. Zhu, P. Qiu and C. Mao, *Nano Res.*, **8**, 1800 (2015); https://doi.org/10.1007/s12274-014-0686-6
18. G.P. Darshan, H.B. Premkumar, H. Nagabhushana, S.C. Sharma, S.C. Prashanth and B.D. Prasad, *J. Colloid Interface Sci.*, **464**, 206 (2016); https://doi.org/10.1016/j.jcis.2015.11.025
19. M. Srinivas, G.R. Vijayakumar, K.M. Mahadevan, H. Nagabhushana and H.S. Bhojya Naik, *J. Sci. Adv. Mater. Devices*, **2**, 156 (2017); https://doi.org/10.1016/j.jsamd.2017.02.008
20. M. Srinivas, T.O. Shrungesh Kumar, K.M. Mahadevan, S. Naveen, G.R. Vijayakumar, H. Nagabhushana, M.N. Kumara and N.K. Lokanath, *J. Sci. Adv. Mater. Devices*, **1**, 324 (2016); https://doi.org/10.1016/j.jsamd.2016.07.002
21. N. Chander and V.K. Komarala, *Indian J. Pure Appl. Phys.*, **55**, 737 (2017).