

Synthesis, Characterization, Photoluminescence Property of Al(III) Schiff Base Complexes and Their Applications in Forensic Fingerprint and Dye Sensitized Solar Cells

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Aluminium(III)-Schiff base complexes of *bis*(salicylidene)phenyl-1,2-diamino organic ligand derivatives were synthesized by condensation reaction with salicylaldehyde, substituted phenyl-1,2-diamine with aluminum trichloride and characterized by ¹H NMR, FTIR, EDS and ICP-AAS. Photophysical properties like photoluminescence (PL) and IV characteristics were studied for the dye-sensitized solar cells (DSSCs) performance. The latent forensic finger print developments have also been demonstrated from the synthesized complexes. Photoluminescence studies revealed that emission peaks of the complexes in solution state appeared at 418- 572 nm and emitted blue and pale-yellow light. Latent fingerprint detection study indicated that the powder compounds show a good adhesion and finger ridge details without back ground staining. Based on these results, these Al(III) complexes can serve as a suitable non-dopant blue light as well as pale yellow light emitting compound for flat panel display applications and applied to detect latent fingerprints on variable substrates.

Keywords: Schiff base, Photoluminescence, Cyclic voltammetry, Latent finger print, dye-sensitized solar cells.

INTRODUCTION

Schiff base metal complexes are most interesting in practical applications because of the ease of synthesis of salicylaldiminato Schiff base ligands, strong chemical nature, scaling up for bulk production and readily forms highly stable metal complexes by coordination affinity with metal ions [1]. As the dye-sensitized solar cells are important class of components, which can convert the naturally occurring sun light in to electric energy by capturing photons to enhance the efficiency of solar cell, which is eco-friendly, cost effective, easy fabrication, flexibility, low weight, colour option and transparency [2-4]. Hence, the study on these materials were carried extensively. It is most essential to increase the photocurrent by increasing molar extinction coefficient and an extinction of solar absorption spectra of the present studied compounds from the visible to near infrared region [5,6].

There are many experiments have been confirmed that Schiff base dyes having π -conjugated bridge and richer electron

donors of the dyes are found to be shown good photovoltaic performance of dye-sensitized solar cells (DSSCs) [7-10]. Schiff base ligands exhibit multidentate capabilities in the presence of phenolic hydroxyl group and nitrogen atom of the imine moiety participated in Al(III) stable complexes by showing good luminescent property at room temperature in solution state [11,12].

In present work, the synthesis and characterization of Schiff base Al(III) complexes were carried out and also explored for their applications as DSSCs and latent finger print markers with better enhancement of the visibility.

EXPERIMENTAL

4-Nitro/carboxylphenyl-1,2-diamine, salicylaldehydes and aluminum trichloride were purchased from Sigma-Aldrich India, Ltd. Thin layer chromatography (TLC) were conducted on Merck-60 F₂₅₄ silica gel precoated on aluminum sheets. TLC plates were viewed under UV chamber. Melting points

were determined in capillary tubes and are uncorrected. Infra-red 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} . ^1H NMR spectra were recorded at 400 MHz in $\text{DMSO}-d_6$ 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., USA) equipped with a 450 W Xenon lamp as an excitation source, ICP-AAS analysis were recorded on HORIBA JOBIN Yvon Inc., USA. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) measurements were performed on a VEGA3LMUVG13171475 of TESCAN.

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 and the reaction was monitored by TLC (petroleum ether:ethyl acetate, 7:3). After completion of the reaction, a 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 $^\circ\text{C}$; m.f.: $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}_4$; FT-IR (ν_{max} , cm^{-1} , ATR): 3369 (phenolic O-H), 1612 (C=N), 1488-1429 (NO_2); ^1H NMR: ($\text{DMSO}-d_6$, 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, $J = 6.4\text{ Hz}$, 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, a 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 $^\circ\text{C}$; m.f.: $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_4$; FT-IR (ν_{max} , cm^{-1} , ATR): 3067 (phenolic O-H), 2360 (carboxylic O-H), 1610 (C=N); ^1H NMR: ($\text{DMSO}-d_6$, 399.64 MHz), δ ppm: 8.902 (1H, s, 10-H), 8.250-8.281 (1H,

d, $J = 12.4\text{ Hz}$, 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, $J = 8.4\text{ Hz}$, 3-H), 6.549-6.567 (1H, d, $J = 7.2\text{ Hz}$, 17-H), 6.433 (1H, s, 7-H), 6.3364 (1H, s, 14-H), 5.360 (2H, s, -OH).

Synthesis of complexes: A solution (10 mL) of L^1H_2 / L^2H_2 (1 mmol, 0.361/0.360 g) in acetonitrile was added to a stirred solution of aluminum trichloride (1 mmol, 0.078 g) in acetonitrile (10 mL). The reaction mixture was refluxed for 4 h and monitored by TLC. After completion of the reaction the reaction mixture was bring to room temperature, obtained precipitate was filtered and dried to afford complex **1** and **2** respectively.

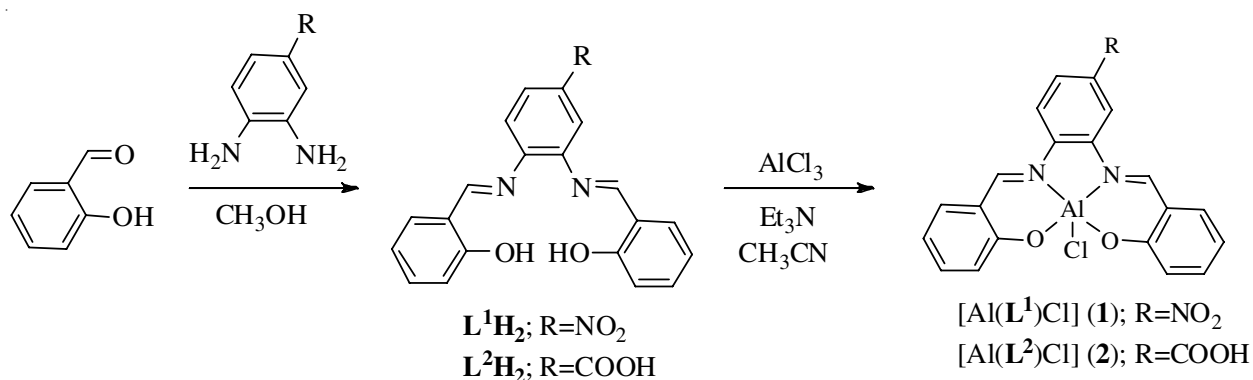
[Al(L^1)Cl] (1**):** Yield: 0.358 g, 85%; m.p.: 96-98 $^\circ\text{C}$; m.f.: $\text{C}_{20}\text{H}_{13}\text{N}_3\text{O}_4\text{ClAl}$; Elemental analysis %: Found (calcd.): C, 57.06 (56.95); H, 3.09 (3.11); N, 9.82 (9.96); FT-IR (ν_{max} , cm^{-1} , KBr): 1594 (C=N), 1488 (N-O); ^1H NMR: ($\text{DMSO}-d_6$, 300.13 MHz), δ ppm: 6.759-6.898 (2H, m, 3-H, 17-H), 6.978-7.061 (2H, q, 5-H, 19-H), 7.293-7.341 (2H, t, 4-H, 18-H), 7.639-7.687 (2H, t, 6-H, 20-H), 8.10-8.186 (3H, m, 13-H, 10-H, 12-H), 9.154 (1H, s, 7-H), 9.224 (1H, s, 14-H).

[Al(L^2)Cl] (2**):** Yield: 0.345 g, 82%; m.p.: 97-99 $^\circ\text{C}$; m.p.: $\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_4\text{ClAl}$; Elemental analysis: Found (calcd.): C, 59.68 (59.94); H, 3.51 (3.35); N, 6.52 (6.66); FT-IR (ν_{max} , cm^{-1} , KBr): 2359 (carboxylic O-H), 1540 (C=N); ^1H NMR: ($\text{DMSO}-d_6$, 300.13 MHz), δ ppm: 6.790-6.811 (2H, q, 3-H, 17-H), 7.005-7.032 (2H, q, 5-H, 19-H), 7.302-7.322 (2H, t, 4-H, 18-H), 7.666-7.693 (2H, q, 6-H, 20-H), 8.108-8.189 (5H, m, 13-H, 7-H, 10-H, 12-H, 14-H), 9.732 (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) were synthesized from condensation of respective 1,2-phenylenediamine derivative with salicylaldehyde in methanol (**Scheme-I**). The obtained yellow coloured solid L^1H_2 and L^2H_2 ligands were soluble in polar organic solvents *viz.*, chloroform, dichloromethane, ethyl acetate, methanol, acetonitrile, DMF and DMSO but insoluble in non-polar solvents like benzene, toluene, hexane, heptane, THF and diethyl ether.

The ligands L^1H_2 and L^2H_2 and aluminum trichloride in reflux condition using acetonitrile as a solvent afforded yellow coloured solid complexes **1** and **2**, respectively. The complexes were found to be highly soluble in DMSO and DMF, partially



Scheme-I: Synthesis of metal complexes (**1** and **2**) through Schiff base ligands (L^1H_2 & L^2H_2)

soluble in chloroform, dichloromethane, methanol 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 L^1H_2 and L^1H_2 , the 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 L^1H_2 appeared at around 1488-1429 cm^{-1} . The carboxylic O-H stretching bands in L^2H_2 were appeared at 2360 cm^{-1} .

The C=N stretching band in complexes **1** & **2** appeared red shift when compared to those bands in respective ligands as expected in the reported similar complexes [13,14]. Also, the 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 (Al^{3+}) in metal complexes, **1** & **2**.

Photoluminescence: The excitation, emission spectra and Commission International de l'Eclairage (CIE) spectra of metal complexes **1** & **2** as shown in Fig. 1 (a1), (a2), (a3) and (b1), (b2), (b3) respectively. Excitation spectra of complexes **1** & **2** were obtained by monitoring the emission at the wavelength of 455 and 572 nm, respectively. Photoluminescence emission spectra were recorded in the range of 400-600 nm under UV excitation at 317 nm (**1**) and 449 nm (**2**) wavelength. Commission International de l'Eclairage (CIE) 1931 x-y chromaticity diagrams of complexes **1** & **2** are depicted in Fig. 1.

Electrochemical studies: Cyclic voltammetric (CV) were recorded to study the electrochemical properties of obtained metal complexes **1** & **2**. The CV were recorded in dry acetonitrile (10 mL), at different scan rates (50, 100 and 200 $mV s^{-1}$) with Bu_4NPF_6 as supporting electrolyte and glassy carbon as working, platinum wire as counter and Ag/AgCl as reference

electrodes. In Fig. 2, metal complexes **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 electro-polymerization 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 1.62 and 1.37 V, respectively (Table-1). The obtained 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 excited state complexes to ground state by taking electrons from (I^-/I_3^-) redox couple. Equally, the E_{o-o} energies or E_{gap} of complexes **1** & **2** were determined from emission spectra of the complexes and which are found to be 2.96 & 2.16 eV, respectively. Similarly, the reduction potentials (E_{red}) of complexes **1** & **2** were determined by using the empirical formulae $E_{ox} - E_{o-o}$, and calculated as -0.34 and -0.79 V, respectively. Therefore, it was expected that Al (III) complexes **1** & **2** would performed DSSCs.

DSSCs application: The synthesized complexes **1** and **2** were subjected to DSSCs fabrication. Chander and Komarala [15] reported the fabrication and characterization of DSSCs on TiO_2 film by doctor blade method and the procedure for the preparation of a DSSC photoanode. The same procedure was adopted during the fabrication of complex **1** and **2**. The complexes **1** and **2** show 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. 3. The values of V_{oc} , I_{sc} , FF

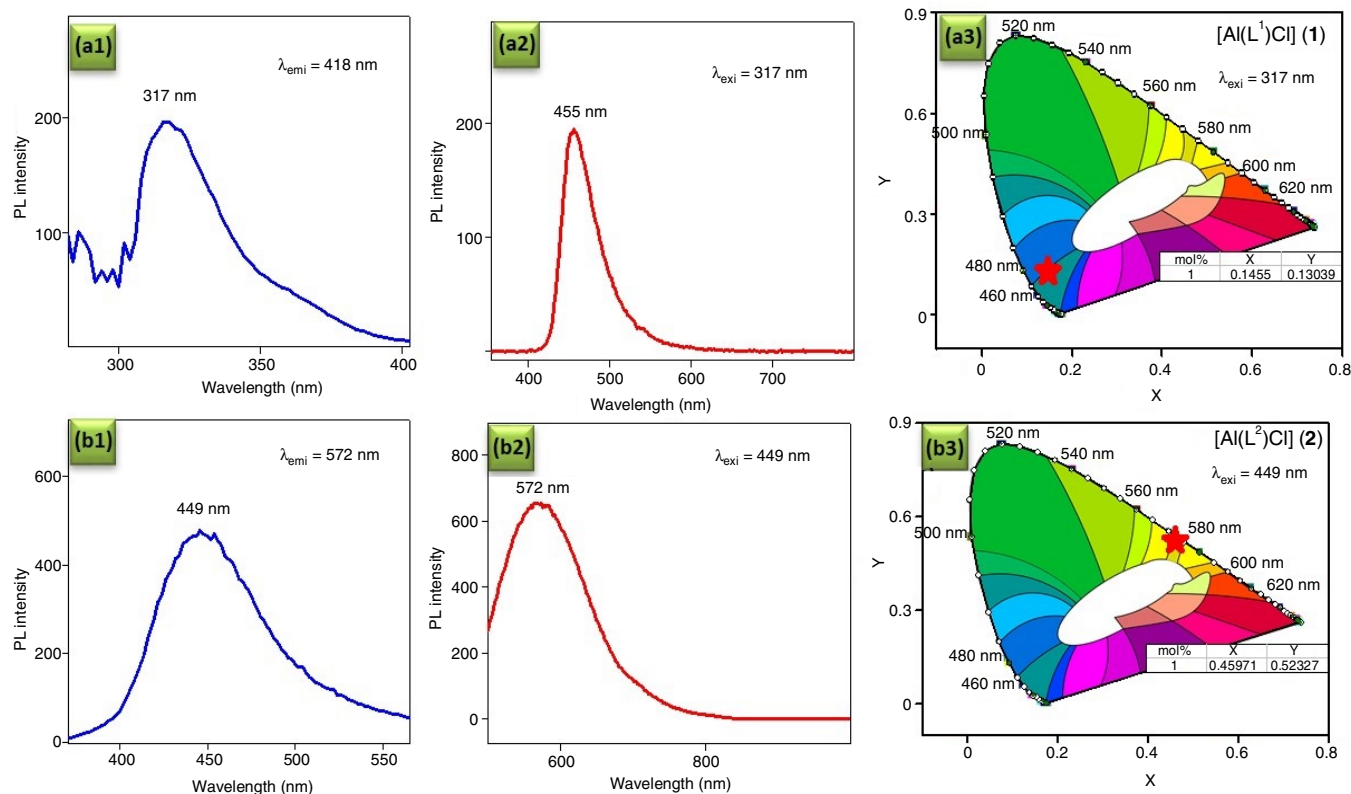
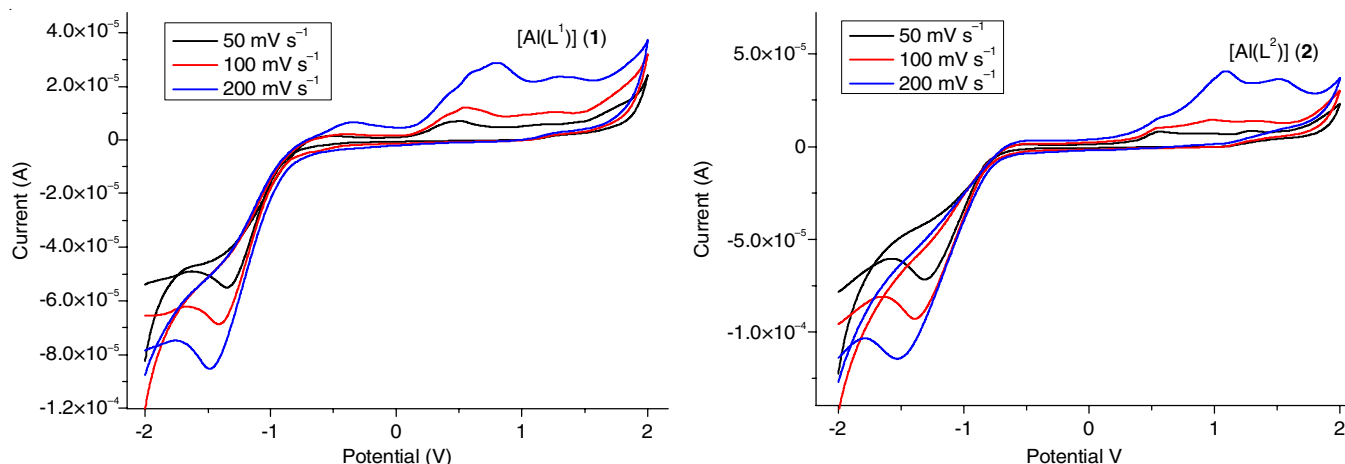
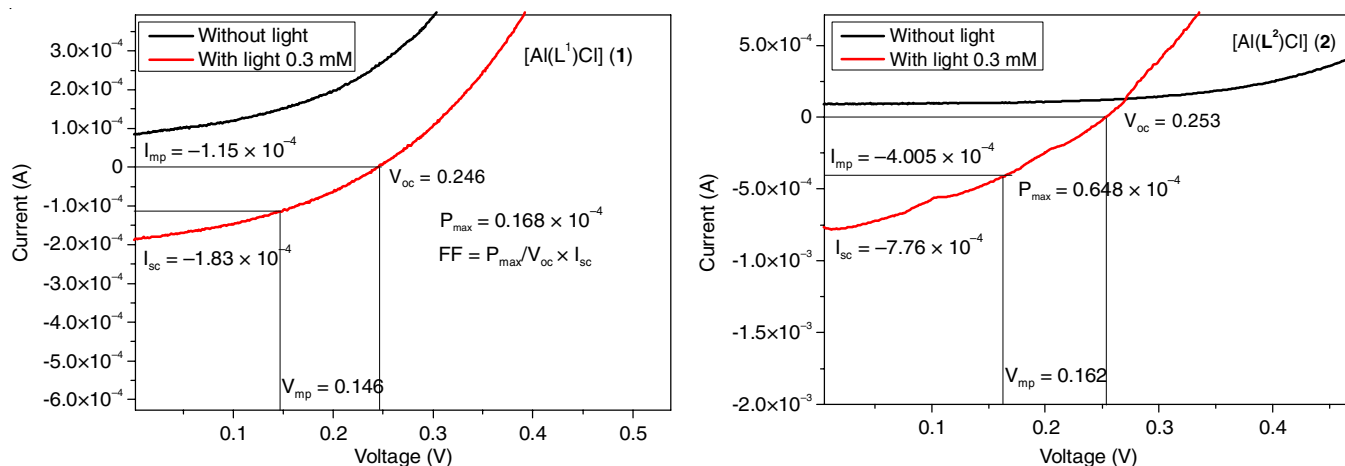


Fig. 1. Excitation spectra, emission spectra and CIE diagram of Al(III) complexes (**1** and **2**)

Fig. 2. Cyclic voltammogram of Schiff's based Al(III) complexes **1** and **2**TABLE-1
PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES OF METAL COMPLEXES **1** AND **2**

Complexes	^a λ_{abs} (nm) ϵ (M ⁻¹ cm ⁻¹)		^b λ_{em} (nm) (from PLI graph)	E_{ox} (eV)	E_{red} (eV)	^c E_{0-0} (eV) or E_{gap} of C1 to C4
	π - π	CT				
1	264.0	342.0	418	1.62	2.96	2.96
2	233.5	335.0	572	1.37	2.16	2.16

^aMaximum absorption in dry ACN solution (0.1 M) at 25 °C. ^bMaximum emission in acetonitrile solution (0.1 M) at 25 °C, ^cMaximum absorption in ACN solution (0.1 M) at 25 °C. E_{070} or E_{gap} was calculated by $1240/\lambda_{\text{em}}$. ^d E_{red} was calculated from $E_{\text{ox}} - E_{070}$. ^e E_{ox} was obtained from cyclic voltammogram.

Fig. 3. I/V characteristics DSSCs of small area (0.5 cm²) sensitized by different concentrations (0.3 mM) complexes **1** and **2**TABLE-2
DSSCs PERFORMANCE DATA OF METAL COMPLEXES **1** AND **2**

Complexes	V_{oc} (mV)	$I_{\text{sc}} \times 10^{-4}$ (mA)	$P_{\text{max}} \times 10^{-4}$ (mW)	V_{mp} (mV)	$I_{\text{mp}} \times 10^{-4}$ (mA)	P_{max} (mW)	FF (%)	η (%)
1	91	-3.720	0.115	60	1.870	0.115	34	0.05
2	253	-7.760	0.648	162	4.005	0.648	33	0.33

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

and η are given in Table-2. The photovoltaic conversion efficiency (η) of DSSCs sensitized with complexes **1** and **2** are found to be 0.05 and 0.33 % under AM 1.5 irradiation (1000 W/m²).

Fingerprint development: The development procedure of fingerprint was already discussed in earlier report [13]. The

synthesized complexes **1** & **2** showed a good performance as a novel fingerprint powder for the development of latent fingerprints on various substrates (Fig. 4). The development of fingerprints by using complexes **1** & **2** exhibited a outstanding performance compared to existing methods which were followed by the fingerprint bueros [13].

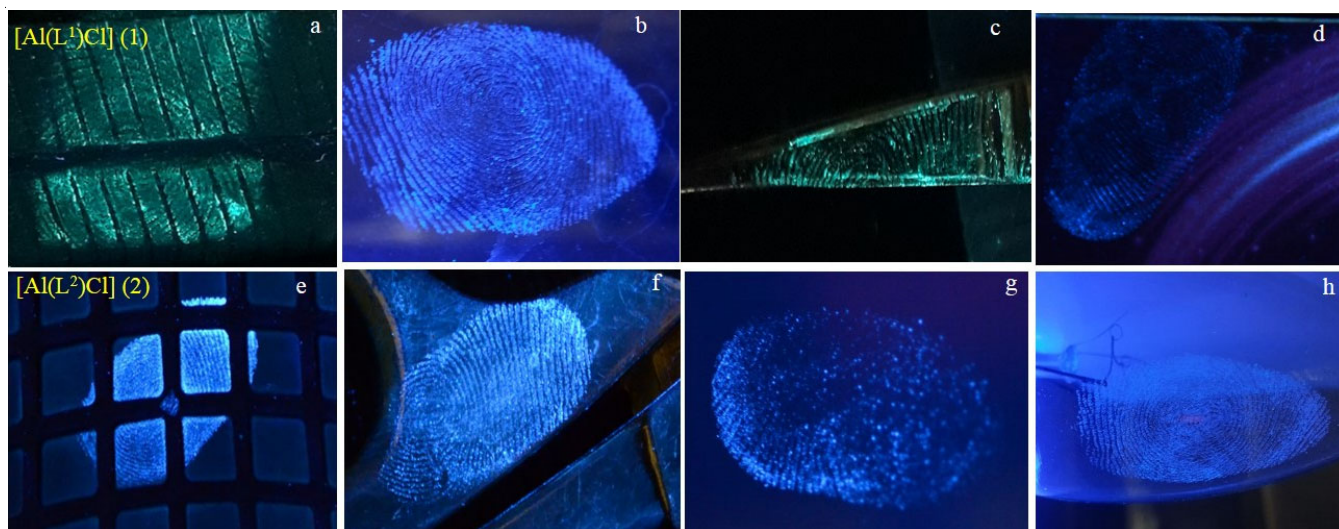


Fig. 4. Finger prints were developed from the complexes **1** and **2** on the surfaces of different materials. The photographs were captured under UV light (~ 365 nm), (a) micro pipette holder, (b) petri dish, (c) forceps tip, (d) match box, (e) cell phone back case, (f) scissor, (g) outer surface of laptop, (h) bulb

The morphology and elemental composition of the metal complexes have been illustrated by SEM and EDS. The SEM micrographs and EDS elemental profile of metal complexes **1** & **2** are shown in Fig. 5. The micrograph of complex **1** shows small cut rods like morphology and complex **2** shows cauliflower like morphology (View field ~ 300 , size of 50 and 100 μm length). The EDS elemental profile of complexes **1** & **2** confirmed the presence aluminium, carbon, chlorine, nitrogen and oxygen.

An ICP-AAS was used to analyze aluminum content in the synthesized complexes after acid digestion and treatment. A certified reference material was purchased from inorganic

ventures for the calibration of aluminum. The required quantity of complexes **1** & **2** were digested with 5% nitric acid and make up to 25 mL in calibrated standard flasks separately. The prepared samples were subjected to ICP-AAS analysis for the presence of aluminium. Presence of aluminium was detected in the metal complexes **1** & **2** and the results are shown in Fig. 6.

Conclusion

Schiff base Al(III) complexes **1** & **2** were synthesized and characterized by ^1H NMR, FT-IR and ICP-AAS. The properties of Al(III) complexes were studied by means of cyclic voltammetric, SEM-EDS, DSSCs and photoluminescence analysis.

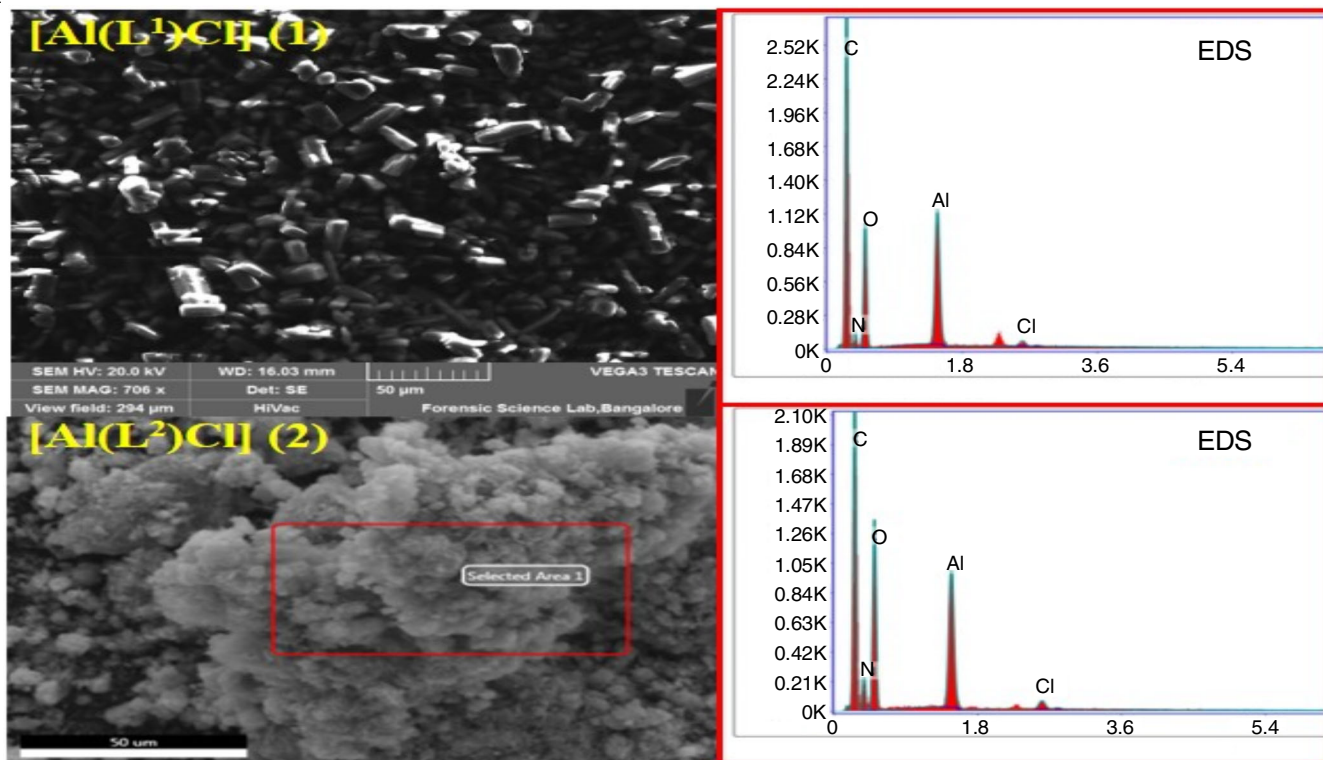
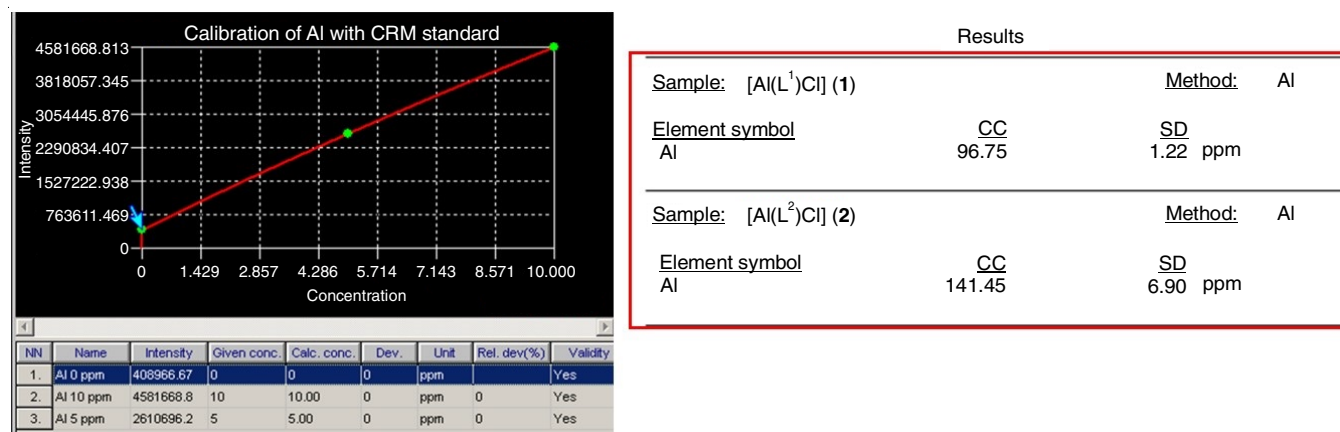


Fig. 5. SEM images and elemental profile of complexes **1** and **2**

Fig. 6. ICP AAS calibration of aluminum with certified standard and obtained results of complexes **1** and **2**

The photoluminescence studies showed that the emission peaks of Al(III) complexes in both solution and solid states appeared at 418–572 nm and emitted blue light. Conjugated Al(III) complexes has electron acceptor and showed DSSCs performance as photosensitizers. These Al(III) complexes can be effectively used as good adhesive powder in the development of latent fingerprints in order to identify the individual.

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CONFLICT OF INTEREST

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

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