

Manganese(III) Complexes with Tetradentate Schiff Base Ligands: IR, UV/Vis, Electrochemistry and Fluorescence Properties

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Abstract: Three trivalent manganese complexes have been synthesized, isolated, and characterized, namely, $[MnCl(OH_2)(Lx)] \cdot nH_2O$ (**I-III**). *Lx* is a tetradentate Schiff base ligand, where *Lx* = **LI**, 2,2'-{1,2-phenylenebis[nitrilomethylidene]}bis(phenolate), **LII**, 2,2'-{1,2-phenylenebis[nitrilomethylidene]}bis(5-methoxyphenolate), and **LIII**, 2,2'-{1,2-phenylenebis[nitrilomethylidene]}bis(4-methoxyphenolate), *n* = 1, 1.5 and 0 for **I**, **II** and **III**, respectively. These complexes were characterized using IR, elemental analysis and UV-Vis spectroscopy. In addition, the fluorescence, photoluminescence (PL), electrochemistry and thermal stability of these complexes were studied.

Keywords: manganese; Schiff base; electrochemistry; photoluminescence

■ INTRODUCTION

Schiff base ligands attracted the attention of researchers for many decades because of their unique properties and their ease of synthesis and tailoring [1-5]. The coordination of Schiff base ligands with transition metals results in complexes with better properties in term of solubility, biological and catalytic activity [1-7]. Thus, organic-metal chelate complexes, in particular, have attracted a lot of attention. Manganese-Schiff base complexes are actively used as catalysts due to their ability to epoxidize unfunctionalized alkenes with high stereoselectivity [8]. The structural characterization of the manganese-Schiff base complexes used to improve enantioselectivity has been reported [9-10]. The Mn-Schiff base compounds exhibit the subtle changes to its property due to the nature of the axial ligands. Therefore, solvents used for crystallization give a significant impact to the crystal structure of the complex [11-12]. Organic-metal complexes of salicylaldehyde Schiff base ligands are expected to show good luminescent properties because its hydroxyl group and a coordinating nitrogen atom and a delocalized π -system [13-14].

In this paper, three ligands formed from the reaction of salicylaldehyde and its alkoxy substituents with *o*-phenylenediamine namely **LI**, 2,2'-{1,2-phenylenebis[nitrilomethylidene]}bis(phenolate), **LII**, 2,2'-{1,2-pheny-

lenebis[nitrilomethylidene]}bis(6-methoxyphenolate), **LIII**, 2,2'-{1,2-phenylenebis[nitrilomethylidene]}bis(5-methoxyphenolate), and their respective complexes with Mn(III) ion as well as their electrochemical and photoluminescent properties are presented.

■ EXPERIMENTAL SECTION

Materials

All the chemicals and solvents used for the synthesis were reagent grade. Manganese chloride tetrahydrate, $[MnCl_2 \cdot 4H_2O]$ (Acros), Salicylaldehyde (Acros), *o*-phenylenediamine (Merck), Triethylamine (Merck), 4-methoxysalicylaldehyde (Acros), and 5-methoxysalicylaldehyde (Acros) were used as received.

Procedure

Physical measurements

Microanalyses (CHN) were performed on a Perkin-Elmer 2400II elemental analyzer. Electronic spectra were obtained using a JASCO V-500 spectrophotometer for UV/VIS in solution and Perkin-Elmer lambda 35 for solid state. FT-IR spectra were recorded on Perkin-Elmer 2000 FT-IR with samples were prepared as KBr pellets. Electrochemical experiments were carried out using an Epsilon potentiostat with three-electrode configuration consisting of a platinum working electrode, a Pt wire as

auxiliary electrode and Ag/AgCl as the reference electrode and 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate as supporting electrolyte in DMF solution under dry nitrogen atmosphere with a scan rate of 0.1 V s^{-1} . Data were collected using Epsilon EC-V160 software supplied by Bioanalytical. Fluorescence spectra were obtained using JASCO spectrofluorometer FP-750. Photoluminescence (PL) spectra were executed at room temperature by using Jobin Yvon HR800UV system. Thermal investigations (TGA/DGA) were carried out on a Perkin Elmer thermogravimetric analyzer TGA7 under nitrogen environment on heating rate $10 \text{ }^\circ\text{C min}^{-1}$.

Synthesis

General method: using our previous method [15-16], the complexes I-III were prepared by refluxing a mixture of the corresponding aldehyde (4 mmol) [I, salicylaldehyde; II, 4-methoxysalicylaldehyde and III, 5-methoxysalicylaldehyde], and *o*-phenylenediamine (2 mmol), in ethanol (20 mL) in a 50 mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser for 30 min. Then $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (2 mmol) in 10 mL ethanol was added, followed by the addition of 0.5 mL triethylamine. The mixture was stirred for three hours at room temperature. The brown precipitate obtained by filtration was washed with ethanol about 5 mL, then washed by copious amount of diethyl ether, and dried at room temperature. The general scheme of chemical equations is illustrated in Fig. 1.

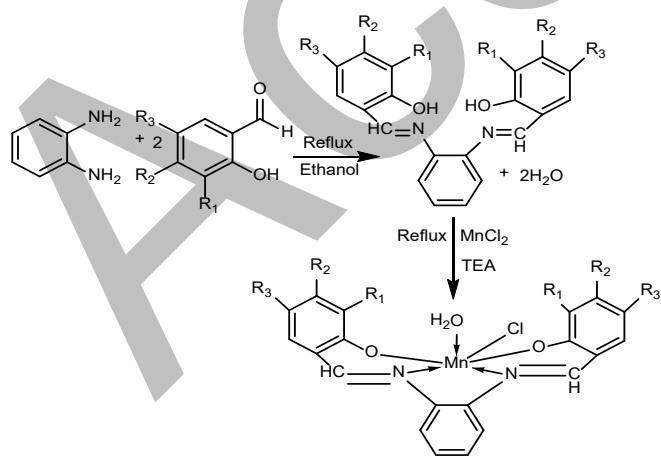


Fig 1. General scheme of synthesis of complexes I, II and III

Synthesis of aquachloro-2,2'-{1,2-phenylenebis[nitrilomethylidene]}bis(phenolate)manganese(III) H_2O , I. The complex was prepared by the general method, using salicylaldehyde, (yield: 0.519 g, 58.87%, m.p. > $300 \text{ }^\circ\text{C}$). IR spectroscopy (KBr, cm^{-1}): $\nu(\text{O-H}) \text{H}_2\text{O}$ 3413, $\nu(\text{C-H})$ aromatic 3016, $\nu(\text{C=N})$ 1604, $\nu(\text{C=C})$ 1578, 1537, 1494. UV/Vis spectroscopy (in acetonitrile, λ_{max} nm, ϵ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 246 (41.9×10^3), 336 (27.6×10^3), 434 (10.2×10^3). UV/Vis spectroscopy (solid, λ_{max} nm): 214, 245, 327. Anal. Calc. For $\text{C}_{20}\text{H}_{16}\text{ClMnN}_2\text{O}_3 \cdot \text{H}_2\text{O}$: C, 54.50; H, 4.12; N, 6.36, Mn, 12.46%. Found: C, 54.27; H, 3.65; N, 6.53; Mn, 12.94%.

Synthesis of aquachloro-2,2'-{1,2-phenylenebis[nitrilomethylidene]}bis(5-methoxyphenolate)manganese(III) $\cdot 1.5\text{H}_2\text{O}$, II. The complex was prepared by the general method, using 4-methoxysalicylaldehyde, (yield: 0.773 g, 75.81%, m.p. > $300 \text{ }^\circ\text{C}$). IR spectroscopy (KBr, cm^{-1}): $\nu(\text{O-H}) \text{H}_2\text{O}$ 3411, $\nu(\text{C-H})$ aromatic 3007, $\nu(\text{C-H}) \text{CH}_3$ 2938, 2837, $\nu(\text{C=N})$ 1619, $\nu(\text{C=C})$ 1598, 1573, 1522. UV/Vis spectroscopy (in acetonitrile, λ_{max} nm, ϵ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 254 (30.58×10^3), 347 (28.43×10^3), 436 (14.70×10^3). UV/Vis spectroscopy (solid, λ_{max} nm): 238, 252, 318, 361, 401. Anal. Calc. For $\text{C}_{22}\text{H}_{20}\text{ClMnN}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$: C, 51.83; H, 3.53; N, 5.49, Mn, 10.78%. Found: C, 52.04; H, 3.64; N, 5.46; Mn, 11.11%.

Synthesis of aquachloro-2,2'-{1,2-phenylenebis[nitrilomethylidene]}bis(4-methoxyphenol)manganese(III), III. The complex was prepared by the general method, using 5-methoxysalicylaldehyde (yield: 0.517 g, 53.54%, m.p. > $300 \text{ }^\circ\text{C}$). IR spectroscopy (KBr, cm^{-1}): $\nu(\text{O-H}) \text{H}_2\text{O}$ 3475, 3412, $\nu(\text{C-H})$ aromatic 3023, $\nu(\text{C-H}) \text{CH}_3$ 2939, 2833, $\nu(\text{C=N})$ 1618, $\nu(\text{C=C})$ 1601, 1580, 1534. UV/Vis spectroscopy (in acetonitrile, λ_{max} nm, ϵ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 249 (39.91×10^3), 299 (22.26×10^3), 335 (23.10×10^3), 460 (8.82×10^3). UV/Vis spectroscopy (solid, λ_{max} nm): 236, 253, 311, 359, 402, 480. Anal. Calc. For $\text{C}_{22}\text{H}_{20}\text{ClMnN}_2\text{O}_5$: C, 54.73; H, 4.18; N, 5.80, Mn, 11.38%. Found: C, 54.75; H, 3.63; N, 5.76; Mn, 10.91%.

RESULTS AND DISCUSSION

Infrared Spectrum

All the complexes show a broad band between $3424\text{--}3411 \text{ cm}^{-1}$ in their infrared spectra, attributed to

O-H stretching of coordinate/lattice water. Aromatic C-H band appears between 3058–3007 cm^{-1} , C=N band appears between 1640–1604 cm^{-1} [17], and for all complexes, the C=N band was shifted to higher wavenumbers than in free ligands, except I which may be due to the alkoxy substituent effect. Aromatic C=C bands appear at their normal position between 1601–1494 cm^{-1} , as shown in Fig. 2.

Electronic Spectrum

The electronic spectra of Mn(III) complexes in acetonitrile have mostly similar features, consisting of an intense band at 204–250 nm (49019.6–40000.0 cm^{-1}), bands of moderate-intensity at ca. 300–360 nm (33333.3–27777.8 cm^{-1}) and one band or shoulder at 430–460 nm (23255.8–21739.1 cm^{-1}) (Fig. 2). The first two bands can be assigned as π to π^* azomethane intraligand transition, while the third one can be assigned to phenolate O ($p\pi$) to Mn ($d\pi$) ligand to metal charge transfer [18]. No d-d bands observed due to the presence of strong tail of the charge transfer band at lower energy. Electronic spectra of all the Mn(III) complexes in solid state show similar spectra to those obtained in acetonitrile except that the shoulder appearing in the region of 525–644 nm

(19047.62–15528.0 cm^{-1}), is either reduced or shifted to lower wavelength in acetonitrile (Fig. 3).

Electrochemical Properties

The electrochemical properties of I–III investigated by cyclic voltammetry (CV) in DMF solution, containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte, using an Ag/AgCl reference electrode under a dry nitrogen atmosphere with a scan

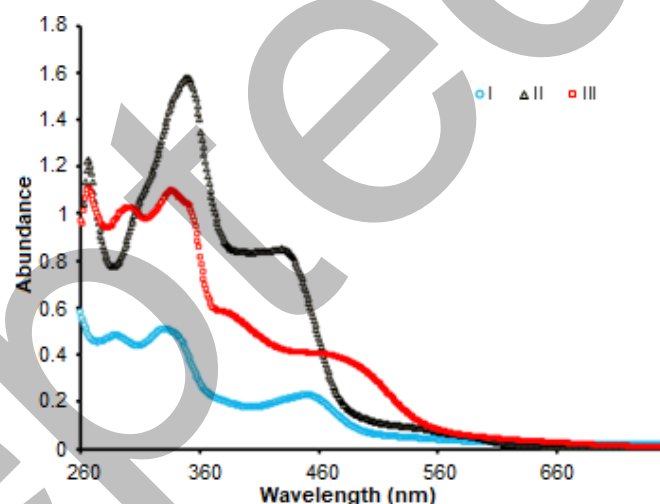


Fig 3. Electronic spectra of I, II and III (in acetonitrile, 1.0×10^{-6} M)

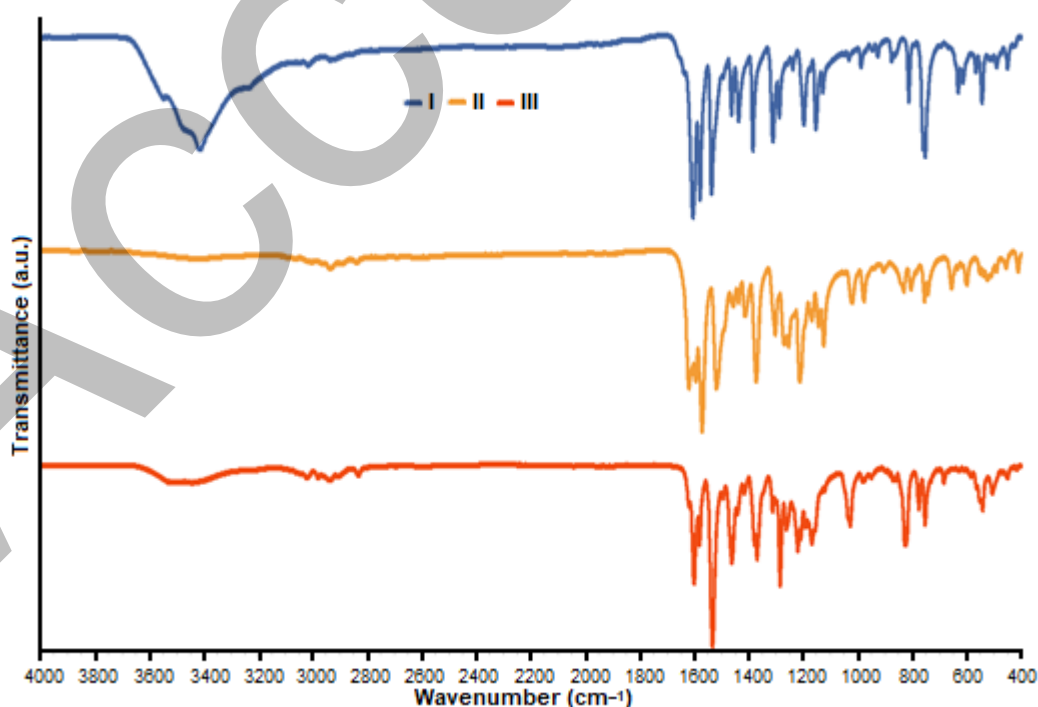


Fig 2. IR spectra of complexes I, II and III

rate of 0.1 V s^{-1} . Compounds **I-III** exhibit quasi-reversible reduction-oxidation wave, all the reduction peaks are observed at negative potentials (**I** -0.217, **II** -0.353 and **III** -0.325), and all the oxidation peaks are observed at positive potential (**I** 0.061, **II** 0.096 and **III** 0.066) (Fig. 4 and Table 1). The quasi-reversible reduction-oxidation due to $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple has been observed for previously reported complexes with similar ligand environment [18-20].

Fluorescence Properties

The fluorescence and photoluminescence spectra of

compounds **I-III**, and their ligands **LI-LIII** are characterized by broad bands, in the region between 400–600 nm, typical of the intramolecular charge-transfer bands [21]. The photophysical data of the present systems in DMF are listed in Table 2 and showed in Fig. 5. The general feature, the blue shift in the range (18–65 nm) is observed in the fluorescence spectra in DMF compared with the photoluminescence spectra in the solid state, attributable to the DMF dielectric constant [22]. The other feature observed is the blue shift in the range 13–20 nm in compounds **I**, and **II**, in the fluorescence spectra, compare with their ligands. This blue shift may

Table 1. The electrochemical properties of **I-III** were investigated by cyclic voltammetry in acetonitrile

Compound	E_{red} (V)	E_{ox} (V)	$E_{1/2}$ (V)	$\Delta E_{\text{ox-red}}$
I	-0.217	0.061	-0.078	0.278
II	-0.353	0.096	-0.128	0.449
III	-0.325	0.066	-0.129	0.391

Note: $E_{1/2} = (E_{\text{ox}} + E_{\text{red}})/2$

$\Delta E_{\text{ox-red}} = E_{\text{pa}} - E_{\text{pc}}$, V, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively

Table 2. The fluorescence and photoluminescence (PL) of compounds **I-III** and their respective ligands **LI-LIII**

Compound	λ_{max} excitation	λ_{max} fluorescence	λ_{max} PL*
I	330	480	529
LI	396	500	534
II	330	472	537
LII	383	485	537
III	346	518	528
LIII	342	520	553

Note: * all photoluminescence was obtained by excitation at 325 nm

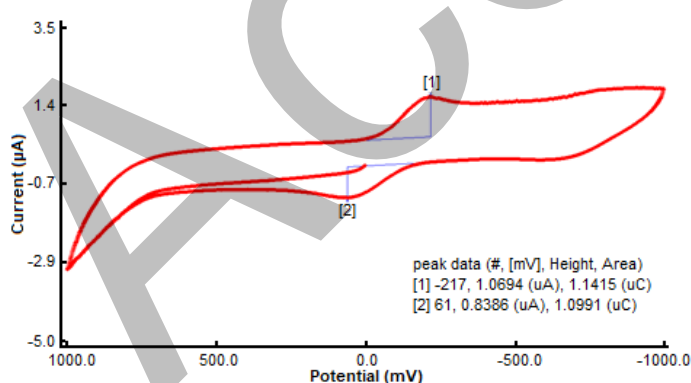


Fig 4. Cyclic voltammetry of compound **I**, in DMF with 0.1 mol dm^{-1} tetrabutylammonium tetrafluoroborate as supporting electrolyte (working electrode, platinum; reference electrode, Ag/AgCl; Scan rate 100 mV s^{-1})

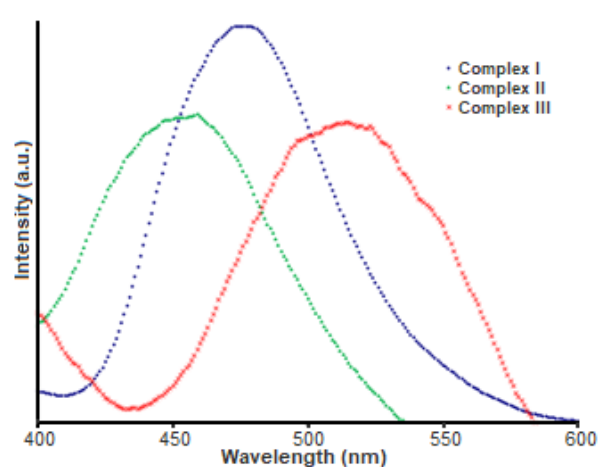


Fig 5. Fluorescence emission spectra of manganese complexes in solution

be due to the effect of the coordination of Mn(III) with the ligands. This shift was not observed in the rest of the complexes because of high emission intensity of their ligands and its broaden band.

Thermogravimetric Analysis

The thermogravimetric analyses (TGA) of compounds

I-III were performed in the temperature range of 30–900 °C and under N₂ atmosphere. All the complexes exhibited remarkable thermal stability and had an onset temperature for decomposition at about 260 °C, after release of solvated and coordinated water. The results indicate that these complexes are thermally stable, and the details can be seen in Fig. 6.

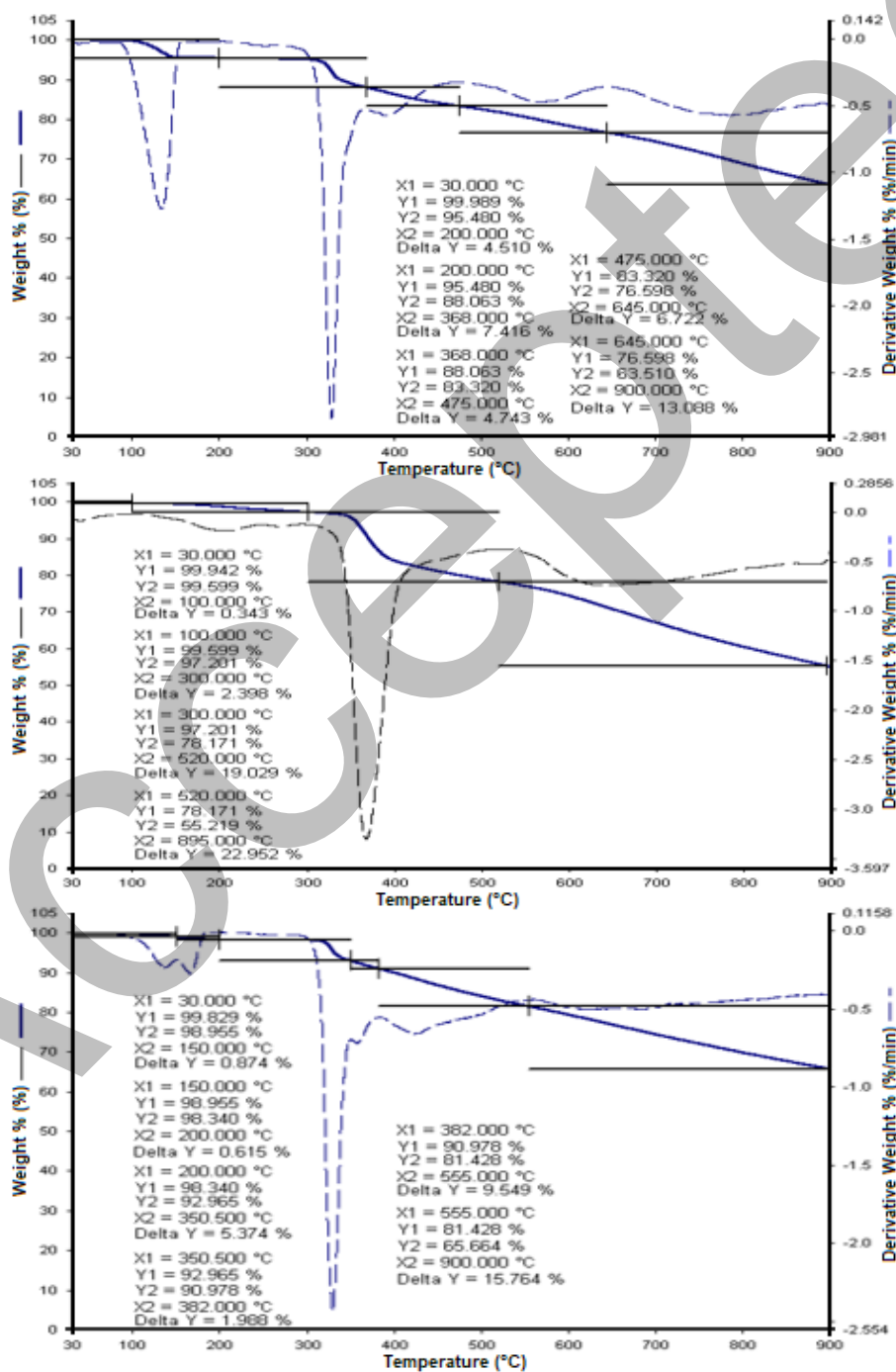


Fig 6. Thermogram of complexes I-III under nitrogen environment on heating rate 10 °C/min

■ CONCLUSION

In this paper, three tetradentate Schiff base ligands and their Mn(III) complexes, namely, **I**, **II** and **III**, were successfully prepared through the coordination of Mn(III) to NONO in the ligand center. These complexes have been isolated and characterized using infrared spectroscopy (IR), elemental analysis (CHN), atomic absorption spectroscopy (AAS), and UV-Vis spectroscopy. In addition, the fluorescence, photoluminescence (PL), electrochemistry and thermal stability of these complexes were studied. The results showed that these complexes display fluorescence emission, reversible redox properties, and good thermal stability. From these studies, it can be concluded that the substitution position of the methoxy group affects the properties of these complexes and can be used to tune the optical properties of these complexes.

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