

Synthesis, Crystal Structure, Electrochemical and Fluorescence Studies of a Novel Zn(II)-Fluorophore, 1,10-Phenanthroline-5,6-dione (Phen-dione)

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The crystal structure of 1,10-phenanthroline-5,6-dione ligand with Zn(II), tris(1,10-phenanthroline-5,6-dione)zinc(II) hexafluorophosphate, [Zn(phen-dione)₃](PF₆)₂, is reported. The complex was characterized by elemental analysis, IR, ¹H NMR, electronic absorption spectroscopies, cyclic voltammetry and X-ray crystallography. Yellow crystals of [Zn(phen-dione)₃](PF₆)₂ were formed by ether diffusion into an acetonitrile solution of the complex. The title complex crystallized in monoclinic crystal system (*Z* = 2) with space groups of *P*2₁, *a* = 12.0299(15) Å, *b* = 14.5306(19) Å, *c* = 13.1879(17) Å, β = 94.058(2)° and *V* = 2299.5(5) Å³. The structure was refined by using 10048 independent reflections, with *I* > 2σ(*I*) to an *R* factor of 0.0490. Single-crystal structure showed that the coordination geometry around the Zn(II) was a distorted octahedron. The complex showed an intense fluorescence band at visible region (690 nm) in CH₃CN with an excitation wavelength of 310 nm at 25.0 ± 0.1 °C.

Cyclic voltammogram of the title complex showed two quasi-reversible reduction couples at negative potential, which were assigned to the consecutive reduction of phen-dione ligand to phen-semiquinonate and phen-diolate respectively by analogy to other phen-dione complexes at scan rate 200 mV s⁻¹.

Keywords: Zn(II) complex, 1,10-Phenanthroline-5,6-dione, Zn(II)-Fluorophore, Phen-semiquinonate, Fluorescence

INTRODUCTION

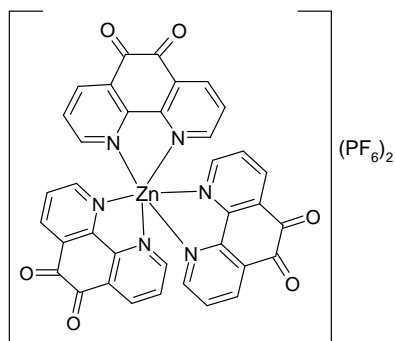
Complexes of 1,10-Phenanthroline-5,6-dione (phen-dione) ligand have been extensively studied. Phen-dione is a well-known N∩N chelating agent with a rigid planar structure. The phen-dione complexes, similar to other polypyridine complexes, exhibit optical and electrochemical properties, metal-to-ligand charge transfer (MLCT) in the visible light region, reversible reduction and oxidation, and fairly intense luminescence. Regarding these properties, however, slight differences exist between phen-dione complexes and bipyridine complexes. Phen-dione ligand plays important roles

as molecular scaffolding for supramolecular assemblies, building block for the synthesis of metallo-dendrimers and thin films of luminescent complexes [1-12].

Metal complexes of the type [M(LL)₃]ⁿ⁺, where LL is either phen-dione or 1,10-Phenanthroline ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA. The ligand or the metal in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing an easy access to the details involved in DNA-binding and cleavage [13-20].

Herein, we report the synthesis, characterization, electrochemical and fluorescence properties, and crystal structure of [Zn(phen-dione)₃](PF₆)₂ (Scheme 1).

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Scheme 1

EXPERIMENTAL

Materials and Measurements

All reagents and solvents used were reagent grade. 1,10-Phenanthroline-5,6-dione was synthesized according to the literature procedure [4,21-22].

Elemental analyses were performed by Heraeus CHN-O-Rapid elemental analyzer. IR spectra were recorded as KBr pellets on a FTIR JASCO 460 spectrophotometer and electronic spectra on a JASCO 7850 spectrophotometer. ^1H NMR spectra were recorded on a Bruker DRX-500 MHz, Avance spectrometer at ambient temperature in DMSO-d_6 . Cyclic voltammograms were recorded by using a Metrohm 694 apparatus. Three electrodes were utilized in this system, a platinum disk working electrode (RDE), a platinum wire auxiliary electrode and Ag/AgCl reference electrode. The platinum disk working electrode was manually cleaned with 1- μm diamond polish prior to each scan. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH), was recrystallized twice from ethanol-water (1/1) and vacuum-dried at 110 $^\circ\text{C}$ overnight. Acetonitrile was distilled over alumina and degassed under vacuum prior to use in cyclic voltammetry. The solutions were deoxygenated by bubbling with Ar for 15 min. Fluorescence spectra were taken on a CARY ECLIPS spectrophotometer. The spectra were measured in acetonitrile solution at room temperature. Solutions were taken in a 1 cm path length fused silica cell. The band pass for the excitation and emission monochromators was set at 5 nm each.

Synthesis of $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2 \cdot 3\text{CH}_3\text{CN}$

To a solution of ZnCl_2 (137 mg, 1 mmol) in water was added 1,10-phenanthroline-5,6-dione (630 mg, 3 mmol) dissolved in 50 ml ethanol. The resulting solution was stirred at room temperature for 24 h. The complex was precipitated as a light yellow solid by addition of ammonium hexafluorophosphate (NH_4PF_6) (652 mg, 4 mmol). The product, $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2$, was collected by suction filtration, washed with cold water and diethylether, and then air dried. Diffusion of diethylether into an acetonitrile solution of the complex yielded yellow crystals suitable for crystallography. Yield: 230 mg, 92%. Anal. Calcd. for $\text{C}_{42}\text{H}_{27}\text{F}_{12}\text{N}_9\text{O}_6\text{P}_2\text{Zn}$: C, 45.49; H, 2.45; N, 11.37. Found: C, 45.08; H, 2.47; N, 11.50.

X-Ray Crystallographic Study of $[\text{Zn}(\text{Phen-dione})_3](\text{PF}_6)_2 \cdot 3\text{CH}_3\text{CN}$

Single-crystal X-ray diffraction measurements were carried out on a Bruker Apex II, using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, $2\theta < 55^\circ$) at 100(2) K. Unit cell parameters were determined by the least-squares calculation with θ angle ranging from 2.09 to 27.10 $^\circ$. Intensities of 23786 reflections were measured using Bruker Apex II CCD Area detector giving 10048 unique reflections. The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were located from the difference-Fourier syntheses and placed in geometrically calculated positions. All hydrogen atom positions were refined in isotropic approximation in riding model with the Uiso(H) parameters equal to 1.5 Ueq(Ci) for methyl groups and 1.2 Ueq(Ci) for other carbon atoms, where U(Ci)s are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. All calculations were made on an IBM PC/AT using the SHELXTL version 5.1 software [24] giving a final $R_1 = 0.0601$, $WR_2 = 0.1409$ (for 7434 reflections with $I > 2\sigma(I)$). The largest diffraction peak and hole on the final difference-Fourier map were 0.649 and $-0.610 \text{ e \AA}^{-3}$.

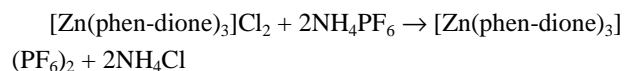
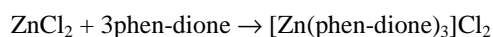
Further details of the structural analyses are given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Table 1. Crystallographic Data and Structure Refinement Summary for [Zn(phen-dione)₃](PF₆)₂.3CH₃CN

Empirical Formula	C ₄₂ H ₂₇ F ₁₂ N ₉ O ₆ P ₂ Zn
Formula weight	1109.04
Temperature	100(2) K
Wavelength	0.71073 Å (Cu K α)
Crystal system, Space group	Monoclinic, <i>P2₁</i>
Unit cell dimension	<i>a</i> = 12.0299(15) Å α = 90.00 deg <i>b</i> = 14.5306(19) Å β = 94.058(2) deg <i>c</i> = 13.1879(17) Å γ = 90.00 deg
Volume	2299.5(5) Å ³
<i>Z</i>	2
Density	1.602 (g cm ⁻³)
Absorption coefficient	0.711 (mm ⁻¹)
<i>F</i> (000)	1116
Crystal shape	Plate
Crystal color	Yellow
Crystal size	0.05 × 0.02 × 0.02 mm
Theta rang for data collection	2.09-27.10 deg
Reflections collected/unique	23786/10048 [<i>R</i> (int) = 0.0490]
Goodness-of-fit on <i>F</i> ²	1.018
Data/restraints/parameters	10048/16/638
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0601, <i>WR</i> ₂ = 0.1409
<i>R</i> indices (all data)	<i>R</i> ₂ = 0.0900, <i>WR</i> ₂ = 0.1575
Limiting indices	-15 ≤ <i>h</i> ≤ 15, -18 ≤ <i>k</i> ≤ 18, -16 ≤ <i>l</i> ≤ 16

RESULTS AND DISCUSSION

The title complex was synthesized in good yield at room temperature according to the following reactions:



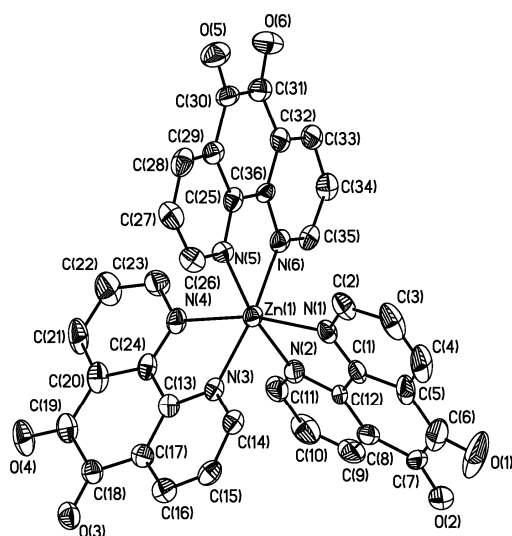
Under these conditions, the phen-dione ligands preferentially bind to Zn(II) through the nitrogen atoms instead of the carbonyl groups. Due to the poor solubility of [Zn(phen-dione)₃]Cl₂ in common organic solvents such as acetone and acetonitrile, the chloride salt of the complex was replaced by hexafluorophosphate salt. The complex [Zn(phen-

dione)₃](PF₆)₂ is air-stable and can be readily recrystallized. The elemental analysis of the complex was consistent with C₄₂H₂₇F₁₂N₉O₆P₂Zn formula. However, it is worth mentioning that the perchlorate salt of this complex was obtained by a mixture of zinc perchlorate and phendione in the sealed Teflon-line bomb at 160 °C [26].

Figure 1 shows the coordination geometry around the Zn(II). The three independent bidentate phen-dione ligands are coordinated to the Zn(II) atom solely *via* the two N atoms, whereas in the *M*(O,O'-phen-dione)₃ (*M* = Ti and V) complexes, the phen-dione ligands are coordinated *via* the C=O moieties to the metal centers [1]. As shown in Fig. 1, the coordination geometry around the Zn(II) is distorted-octahedron, with bite angles of 76.27-77.34° for all three bidentate ligands. However, in perchlorate salt, the *cis* bond angles fall within the range of 76.2-98.1°. The Zn(II)-N bond

Table 2. Selected Bond Lengths (Å) and Angles (°) for $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2 \cdot 3\text{CH}_3\text{CN}$

Bond lengths			
Zn(1)-N(1)	2.129(4)	O(2)-C(7)	1.216(9)
Zn(1)-N(5)	2.146(4)	O(3)-C(18)	1.211(6)
Zn(1)-N(3)	2.150(4)	O(4)-C(19)	1.212(6)
Zn(1)-N(6)	2.151(4)	O(5)-C(30)	1.211(6)
Zn(1)-N(2)	2.158(4)	O(6)-C(31)	1.219(7)
Zn(1)-N(4)	2.191(4)	N(1)-C(1)	1.326(7)
O(1)-C(6)	1.186(8)	N(1)-C(2)	1.348(7)
N(2)-C(11)	1.328(7)	N(3)-C(13)	1.355(6)
N(2)-C(12)	1.349(7)	N(3)-C(14)	1.355(6)
N(4)-C(23)	1.317(7)	N(5)-C(26)	1.340(7)
N(4)-C(24)	1.335(7)	N(5)-C(25)	1.342(7)
N(6)-C(35)	1.337(7)	N(6)-C(36)	1.358(6)
Bond angle			
N(1)-Zn(1)-N(5)	98.47(16)	N(3)-Zn(1)-N(6)	171.51(14)
N(1)-Zn(1)-N(3)	94.20(15)	N(1)-Zn(1)-N(2)	76.75(17)
N(5)-Zn(1)-N(3)	100.19(15)	N(5)-Zn(1)-N(2)	170.13(16)
N(1)-Zn(1)-N(6)	94.20(15)	N(3)-Zn(1)-N(2)	88.84(15)
N(5)-Zn(1)-N(6)	77.34(16)	N(6)-Zn(1)-N(2)	94.27(16)
N(1)-Zn(1)-N(4)	167.19(15)	N(3)-Zn(1)-N(4)	76.27(15)
N(5)-Zn(1)-N(4)	91.72(15)	N(6)-Zn(1)-N(4)	95.61(15)
N(2)-Zn(1)-N(4)	94.29(16)	C(1)-N(1)-C(2)	118.8(4)
C(1)-N(1)-Zn(1)	115.5(3)	C(2)-N(1)-Zn(1)	125.5(4)
C(11)-N(2)-C(12)	118.7(5)	C(11)-N(2)-Zn(1)	126.6(4)
C(12)-N(2)-Zn(1)	114.3(4)	C(13)-N(3)-C(14)	117.3(4)
C(13)-N(3)-Zn(1)	115.4(3)	C(14)-N(3)-Zn(1)	127.0(3)
C(23)-N(4)-C(24)	118.8(4)	C(23)-N(4)-Zn(1)	126.7(4)
C(24)-N(4)-Zn(1)	114.6(3)	C(26)-N(5)-C(25)	118.9(4)
C(26)-N(5)-Zn(1)	126.3(4)	C(25)-N(5)-Zn(1)	114.6(3)
C(35)-N(6)-C(36)	119.2(4)	C(35)-N(6)-Zn(1)	126.3(4)

**Fig. 1.** ORTEP diagram of the $[\text{Zn}(\text{phen-dione})_3]^{2+}$ cation. Hydrogen atoms are deleted for clarity.

lengths range from 2.129(4) to 2.191(4) Å, with an average of 2.154(5) Å while, in perchlorate salt, the average Zn(II)-N bond length is 2.167 Å [26], that is, longer than those in PF₆ salt. As shown in Fig. 2, there is no strong hydrogen bond in the crystal of the complex. The counter ions (PF₆⁻ anions) are not close enough to interact with hydrogen atoms of phen-dione ligands. The two counter ions PF₆⁻ are distorted octahedron, with P-F bond lengths ranging from 1.584(4) to 1.621(4) Å. On the other hand, in the perchlorate salt, the complex molecules are assembled by hydrogen bonding interaction into 2D layers parallel to (101), where the phen-dione donor hydrogen atoms to the perchlorate anion oxygen atoms and the π-π stacking interactions play important role in the stabilization of the crystal structure. This complex in perchlorate salt crystallized in monoclinic crystal system (*Z* = 4) with space group of *P12₁1/n*, *a* = 10.4974(9) Å, *b* = 18.048(2) Å, *c* = 18.807(2) Å, β = 94.547(1)°, *V* = 3552.0 Å³ and an *R* factor of 0.0490 [26].

The ¹H NMR spectra of the free phen-dione and Zn(II) complex showed three signals in 7.5-8.9 ppm range. The

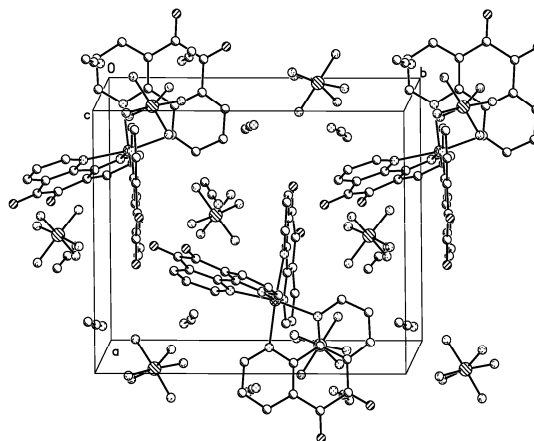


Fig. 2. Unit cell of [Zn(phen-dione)₃](PF₆)₂.3CH₃CN.

relative intensities of these signals were congruent with the proposed structure. Due to high liability of Zn(II) complex and exchange of ligand, the ¹H NMR signals were broad, making it difficult to see the splitting of each peak (Fig. 3) [25].

The IR spectrum of the free phen-dione showed a sharp

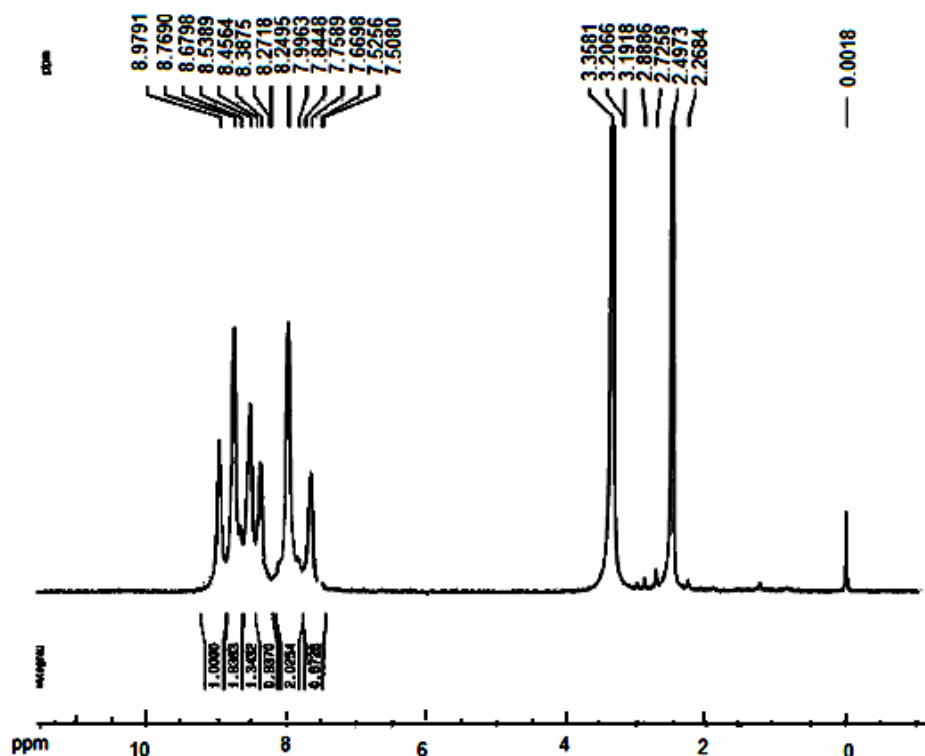


Fig. 3. The ¹H NMR spectrum of [Zn(phen-dione)₃](PF₆)₂ in DMSO-d₆.

band at 1675 cm^{-1} , which associated with the stretching frequency of the C=O band of the ligand [17,27]. The observed band did not shift significantly in comparison with the corresponding complexes. This was reasonable since the C=O moieties were far from the coordination site of the ligand with the metal ion [4,28-31]. The IR spectrum of the complex showed a band around 1695 cm^{-1} , which was assigned to the $\nu(\text{C}=\text{O})$ band of an *o*-quinoid group of the phen-dione ligand. In general, the carbonyl stretching frequency was relatively insensitive to change in the metal center, a reflection of the fact that the effect of the metal center and its coordination environment on the carbonyl stretch was a secondary one. In the $\text{M}(\text{O},\text{O}'\text{-phen-dione})_3$ ($\text{M} = \text{V}$ and Ti) and $\text{M}(\text{O},\text{O}'\text{-phen-dione})_3(\text{M}'\text{L}_n)_3$ ($\text{M} = \text{V}$, $\text{M}'\text{L}_n = \text{TiCl}_4$, $\text{M} = \text{Ti}$, $\text{M}'\text{L}_n = \text{TiCp}_2$ and $\text{M} = \text{V}$, $\text{M}'\text{L}_n = \text{TiCp}_2$), phen-dione ligand was coordinated to metal ion as a phen-semiquinonate or phen-diolate *via* oxygen atoms. In these complexes, the carbon-oxygen stretching vibration of about $200\text{-}300\text{ cm}^{-1}$ shifted to the lower wave number [1]. The strong absorption band at 840 cm^{-1} was assigned to $\nu(\text{P-F})$ and demonstrated the existence of PF_6^- as a counter ion [29].

The electronic spectrum of the complex that was recorded in acetonitrile solution (Fig. 4) exhibited three absorption bands in the UV region and one band in the visible region. These bands centered at 253, 293 and 314 nm and were assigned to ligand-centered ($\pi \rightarrow \pi^*$) transitions [28,30-32]. The strong absorption band centered at 487 nm was assigned to $n \rightarrow \pi^*$ of the C=O group of phen-dione ligand. The solvent dependency of $n \rightarrow \pi^*$ energy on the solvent polarity, which is a well-known phenomenon, was the reason behind such an assignment [25,32]. The $n \rightarrow \pi^*$ transition of the complex showed a blue shift by changing the solvent from CH_2Cl_2 to DMSO. This behavior is consistent with ground-state stabilization of the complex's permanent dipole by the solvent.

The fluorescence spectrum of $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2$ was obtained in CH_3CN at $25.0 \pm 0.1\text{ }^\circ\text{C}$ (Fig. 5) with excitation at 310 nm. The band structures of the absorption and fluorescence spectra of this complex were essentially the same as those of phen-dione. In previous studies [32], the lowest excited singlet states of $\text{Zn}(\text{II})$ -polypyridyl complexes were assigned as mainly polypyridyl ligand localized $^1(\pi, \pi^*)$. This assignment was consistent with that of the $\text{S}_0 \rightarrow \text{S}_1$ absorption. The lowest excited singlet states of $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2$

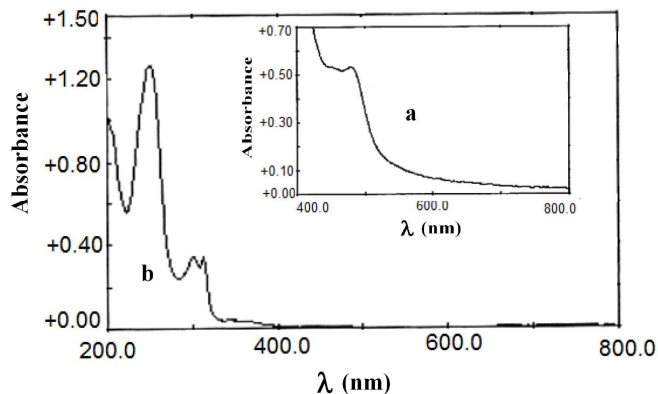


Fig. 4. UV-Vis absorption spectra of $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2$ in CH_3CN ($a = 10^{-3}\text{ M}$, $b = 10^{-5}\text{ M}$).

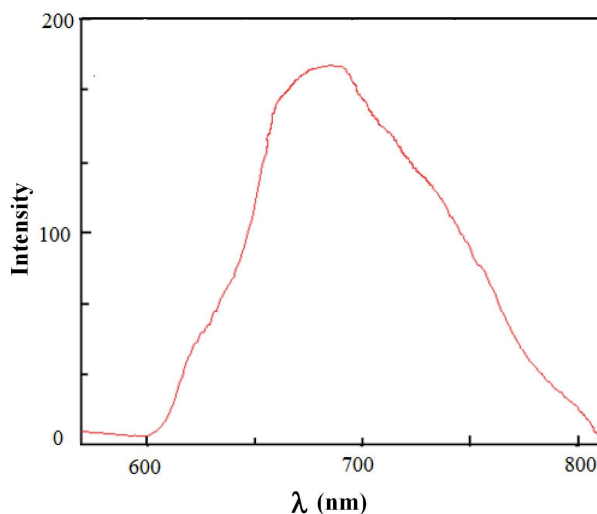


Fig. 5. Fluorescence spectrum of $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2$ in CH_3CN at $25.0 \pm 0.1\text{ }^\circ\text{C}$; Excitation wavelength = 310 nm.

can be assigned as mainly phen-dione localized $^1\text{L}_b(\pi, \pi^*)$ ($= \text{A}_{1g}(\pi, \pi^*)$ in the O_h point group and $\text{A}_1(\pi, \pi^*)$ in the D_3 point group).

In $\text{ZnX}_2(\text{phen})$ (where phen = 1,10-phenanthroline and $\text{X} = \text{Cl}$, Br and I), the $\text{S}_0 \rightarrow \text{S}_1$ absorption and fluorescence spectra were red-shifted from those of phen. This means that the π conjugated system of $\text{ZnX}_2(\text{phen})$ was not completely localized on the phen moiety but was somewhat extended to

the halogen atoms [33].

It is shown in previous studies [17] that the free phen-dione has a very weak fluorescence at 543 nm. The intense fluorescence band of $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2$ at 690 nm, as was described above, could be assigned as intraligand emission of phen-dione ligand. When phen-dione coordinated to Zn(II) and tris(1,10-phenanthroline-5,6-dione)zinc(II) cation formed, the intensity of Zn(II)-fluorophore emission increased. As expected, the structure rigidity of the complex was larger than free ligand.

Cyclic voltammetry was used to examine the electrochemical behavior of this complex. In the beginning, for a better understanding of the observed behavior, the electrochemical behavior of free phen-dione was described, followed by a discussion of the electrochemical behavior of the complex. Previous studies have shown that the phen-dione ligand is electrochemically active due to the presence of the *o*-quinone moiety [28,30,31,34]. It should be mentioned that the 1,10-phenanthroline (starting material for synthesis of phen-dione ligand) is also electro-active. As with quinines in general, the electrochemical behavior is strongly dependent on whether an aprotic solvent such as acetonitrile or an aqueous solvent is employed. In acetonitrile, the free ligand shows two reversible one-electron-reduction waves. The formal potentials for the processes are -0.45 and -1.25 V, and they represent formation of the ion radical and dianion of the free phen-dione ligand. In an aqueous solvent, the process is the "two-electron/two-proton" reduction of the quinone to the hydroquinone [27,34].

In the light of what was said, the electrochemical behavior of phen-dione complexes can be explained. The presence of metal centers such as Fe(II), Ru(II) and Os(II) suggests that a metal-localized oxidation should be expected, and in aprotic solvents, the phen-dione ligand would show two reduction waves. In comparison with 1,10-phenanthroline complexes as described in an earlier report [26], the potential of each reduction wave of phen-dione would shift to more positive potential. This behavior indicates the higher acidity of the phen-dione ligand. Cyclic voltammograms of the tris(phenanthroline-dione) complexes, $\text{M}(\text{phen-dione})_3^{n+}$, indicate that all phen-dione ligands are electro-active at the same potential [27,35-36].

Cyclic voltammetry was performed in an acetonitrile

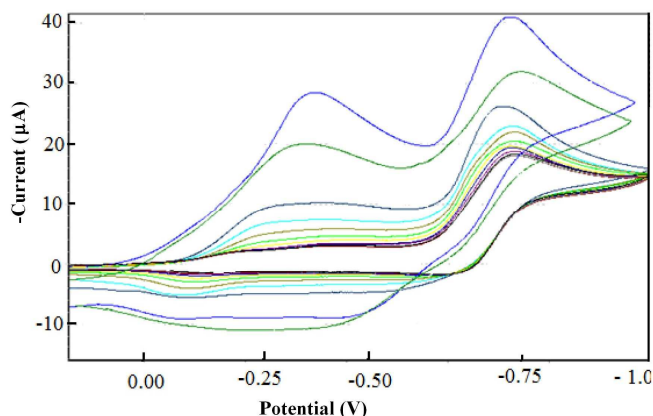
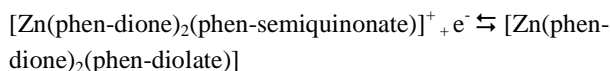
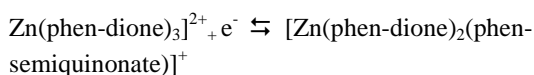
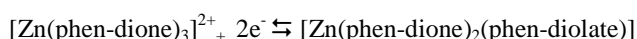


Fig. 6. Cyclic voltammogram of $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2$ in CH_3CN at scan rates of 25-375 mV s^{-1} ; 0.1 M TBAH as a supporting electrolyte.

solution of $[\text{Zn}(\text{phen-dione})_3](\text{PF}_6)_2$ with 0.1 M TBAH as a supporting electrolyte at scan rate 25-200 mV s^{-1} (Fig. 6). In this voltammogram, two quasi-reversible reduction couples at -0.450 and -0.740 V are assigned to the reduction of phen-dione ligand to phen-semiquinonate and phen-diolate, respectively, by analogy to other phen-dione complexes [27,30]. In comparison with free phen-dione, the reduction couples shift to more positive potentials due to the coordination of phen-dione ligand to the zinc(II) center.



However, by decreasing the scan rate to 50 mV s^{-1} , the reduction of phen-dione to phen-diolate occurs in one step [27,30-32].



Due to the electrochemically innocent behavior of the Zn(II) ion in comparison to other phen-dione transition metal complexes, there is not any reduction couple associated with metal center [38-39].

SUPPLEMENTARY MATERIALS

Crystallographic data for the structure reported in this work have been deposited with the Cambridge Crystallographic Data Center as supplementary materials (CCDC No 692176).

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