THE SUBSTITUENT EFFECT ON THE VARIATION OF PHOTOPHYSICAL PROPERTIES OF 1,10-PHENANTHROLINE IN THE ANALYSIS OF Fe(II)

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1INTRODUCTION

1,10-Phenanthroline is known to be the parent molecule of an important class of weakly fluorescent chelating agents with remarkable structural and chemical properties like planarity, rigidity, aromaticity, and basicity. Chelation of Fe(II) with 1,10-phenanthroline forms a non-fluorescent metal-ligand complex in 1:3 ratio. The $\pi \rightarrow \pi^*$ electronic transition of 1,10-phenanthroline, which accounts for its fluorescence emission, is polarised along the molecular plane of the phenanthroline skeleton. The substitution of different functional groups to pristine 1,10-phenanthroline will alter its electronic delocalization.[1] This property of 1,10-phenanthroline could be exploited to design novel fluorescent sensors with enhanced sensitivity and selectivity for Fe(II) trace detection in environmental and biological samples.[1] In this study, 5-nitro-1,10-phenanthroline and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline were used as the two main derivatives of pristine 1,10-phenanthroline to determine and improve the variation of photophysical properties in the analysis of Fe(II). The Nitro group acts as an electron-withdrawing group (EWG) through negative resonance and inductive effects, while the oxygen bound to the aromatic ring in 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline act as an electron-donating group (EDG) through the positive resonance effect and negative inductive effect. These juxtaposed electronic effects were utilized to enhance the detection capabilities of pristine 1,10-phenanthroline in the analysis of Fe(II).

2 METHODOLOGY

2.1 The investigation of the spectral characteristics of 1,10-phenanthroline and its derivatives

Absorption and fluorescence emission spectra were obtained for 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline in methanol/water 1:1 (v/v) solution at 25 ^{0}C. The magnitudes of absorption and emission spectral shifts were determined for all three compounds. (Note: wavelengths corresponding to the absorption peak maxima obtained were used as the excitation wavelengths for the three compounds.)

2.2 The substituent effect on the variations of the fluorescence quenching of 1,10-phenanthroline and its derivatives by Fe(II) with temperature

Fluorescence emission intensities corresponding to each of the three probe molecules were recorded in methanol/water/aqueous buffer 5:4:1 (v/v) solution at the optimum pH range of 3.50-3.70. Upon the addition of Fe(II) ions at each spike, Stern-Volmer plots for the three probe molecules were generated at temperature values: 278 K, 288 K, 298 K, and 308 K . The quenching mechanisms of 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline with Fe(II) were determined based on the Stern-Volmer quenching constants.

2.3 Determination of the limit of detection and limit of quantification of 1,10-phenanthroline and its derivatives in the analysis of Fe(II)

Stern-Volmer plots were obtained for 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline in methanol/water/aqueous buffer 1:1 (v/v) solution, upon quenching with Fe(II).The pH of the medium was maintained in the range of 3.50 to 3.70 at 25 °C. The limit of detection (LOD) and limit of quantification (LOQ) were determined for the quenching of the three fluorophores by Fe(II) through linear regression analysis.

3 RESULTS AND DISCUSSIONS

3.1 The investigation of the spectral characteristics of 1,10-phenanthroline and its derivatives

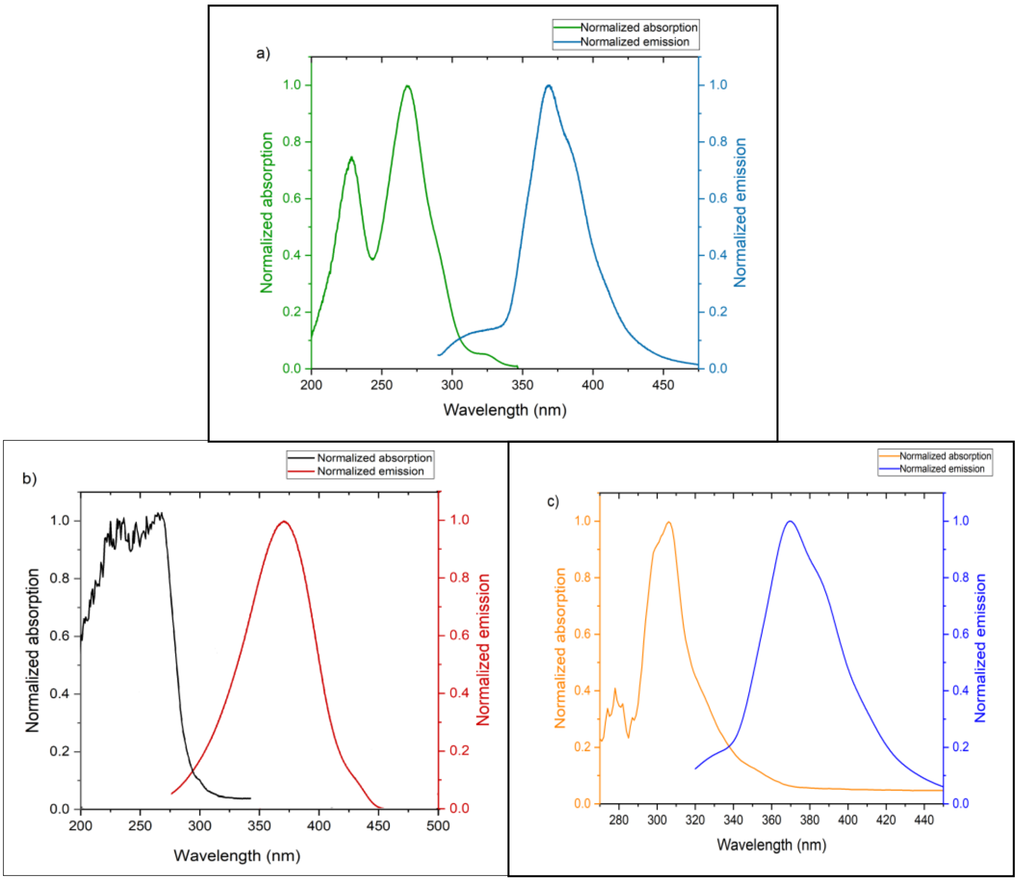

Figure 3.1: Graphical representation of the normalised absorption and fluorescence emission spectra of a) pristine 1,10-phenanthroline at λ_{ex} 268 nm b) 5-nitro-1,10-phenanthroline at λ_{ex} 265 nm, and c) 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline at λ_{ex} 303 nm in methanol/water 1:1 (v/v) system at 25 °C.

According to Figure 3.1, the absorption and emission peak maxima and corresponding stokes shifts for 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline were determined and summarized as given in the table below.

Table 3.1: Excitation, emission wavelengths, and the Stokes shifts of 1,10-phenanthroline and its nitro and epoxy derivatives in methanol/water 1:1 (v/v) system at 25 °C.

Compound	Absorption/excitation wavelength (nm)	Emission wavelength (nm)	Stokes shift (nm)
1,10-Phenanthroline	268	367	99
5-Nitro-1,10-phenanthroline	265	366	101
5,6-Epoxy-5,6-dihydro-[1,10]phenanthroline	303	373	70

It could be observed that absorption and emission spectra show a blueshift and a higher Stokes shift value for the nitro derivative; and a redshift with a lower Stokes shift value for the epoxy derivative of the 1,10-phenanthroline. Thus, this indicates that the presence of either an EWG or an EDG on 1,10-phenanthroline alters the spectral behaviour considerably. Asymmetric derivatives of 1,10-phenanthroline like 5-nitro-1,10-phenanthroline has a higher dipole moment than symmetric derivatives like 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline and pristine 1,10-phenanthroline.Thus asymmetric excited-state fluorophores will be more stabilized than symmetric fluorophores in polar solvents like methanol/water 1:1 (v/v).[1] Thus, only a slight blueshift for the nitro derivative is observed despite being a strong deactivating group. Epoxy derivative gets extensively stabilized, which gives rise to a prominent redshift in the absorption and emission spectra.

3.3 The substituent effect on the variations of the fluorescence quenching of 1,10-phenanthroline and its derivatives by Fe(II) with temperature

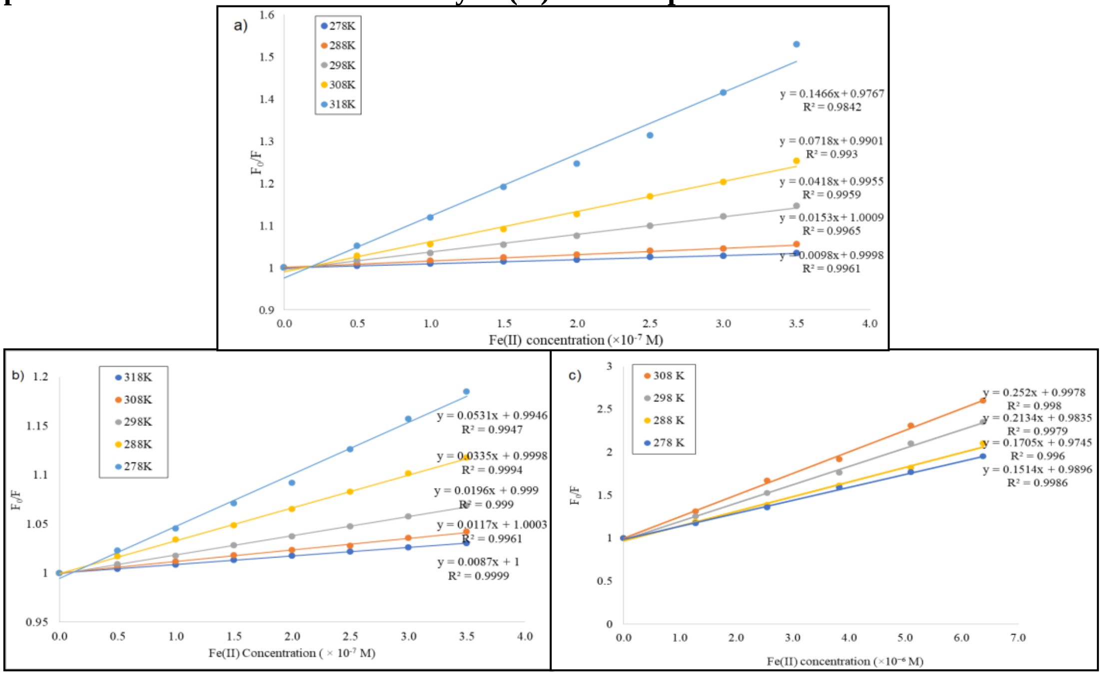

Figure 3.3: Stern-Volmer plots for the fluorescence quenching of a) 1,10-phenanthroline at λ_{ex} 268 nm b) 5-nitro-1,10-phenanthroline at λ_{ex} 265 nm, and c) 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline at λ_{ex} 303 nm with Fe(II) in methanol/water/aqueous buffer 5:4:1 (v/v) system in the optimum pH range of 3.50-3.70.

Table 3.2: The summary of the Stern-Volmer quenching constants for 1,10-phenanthroline and its nitro and epoxy derivatives with Fe^{2+} at different temperatures.

Temperature	Stern-Volmer quenching constant ($\times 10^6$ M^{-1})		
	1,10-phenanthroline	5-nitro-1,10-phenanthroline	5,6-epoxy-5,6-dihydro-[1,10]phenanthroline
278 K	1.466	0.531	0.151
288 K	0.718	0.335	0.170
298 K	0.418	0.196	0.213
308 K	0.153	0.117	0.252

Intercepts of Stern-Volmer plots have approach unity for 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline at all temperatures, as shown in Figure 3.3. Intercept at unity indicates that only one type of quenching mechanism has been involved in each system; either static quenching or dynamic quenching. Upon the increase of temperature, the Stern-Volmer quenching constants for both 1,10-phenanthroline and 5-nitro-1,10-phenanthroline have decreased. For 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline, an increase in the magnitude of the Stern-Volmer quenching constant was observed upon the temperature rise. Typically, with the temperature rise, dissociation of metal-ligand complexes occurs, leading to a reduction of static quenching, decreasing the Stern-Volmer quenching constant. Concurrently, dynamic quenching increases with the increase of molecular and metal ion collisions with the rise of temperature. Thus, it could be concluded that pristine 1,10-phenanthroline and its nitro derivative show static quenching while the epoxy derivative predominantly shows dynamic quenching with Fe(II) with increasing temperature.[2] The deviation of the quenching mechanism in an epoxy derivative could be attributed to its molecular properties that facilitate the collisional effect more than the metal-ligand complex dissociation rates leading to the overpowering of dynamic quenching effect from the static quenching mechanism.

3.3 The determination of limit of detection and limit of quantification of 1,10-phenanthroline and its derivatives in the analysis of Fe(II)

Linear regression analysis was conducted for the Stern-Volmer plots generated for 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline in methanol/water/aqueous buffer 1:1 (v/v) in the range of 3.50 to 3.70 at 25 ^{0}C. Statistical data obtained within the 95% confidence limit is as shown in the table below.

Table 3.3: The summary of the reported analytical parameter values of 1,10-phenanthroline and its nitro and epoxy derivatives with Fe2+ under optimized conditions.

Analytical parameter	1,10-phenanthroline	5-nitro-1,10-phenanthroline	5,6-epoxy-5,6-dihydro-[1,10]phenanthroline
Slope ($\times 10^7 M^{-1}$)	0.1089	0.0113	0.0292
Intercept	0.8984	0.9980	0.9183
Standard deviation of the intercept (σ)	0.1437	0.0030	0.0016
Correlation coefficient (r^2)	0.9697	0.9987	0.9986
LOD (µM)	0.4350	0.0880	0.1320
LOQ (µM)	1.3190	0.2670	0.5510

A better correlation is observed for 5-nitro-1,10-phenanthroline and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline than for the pristine 1,10-phenanthroline.The detection limits and quantification limits for both the derivatives of 1,10-phenanthroline show a significant improvement over their parent molecule. The detection sensitivity for Fe(II) by 5-Nitro-1,10-phenanthroline and 5,6-epoxy-5,6-dihydro-[1,10]phenanthroline has improved from their parent molecule in a significant level.

CONCLUSIONS/RECOMMENDATIONS

Nitro and epoxy derivatives of the 1,10-phenanthroline show improved photophysical properties than their parent molecule and could be used as turn-off fluorescent probes to quantify trace amounts of Fe(II).

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