

Synthesis and Photophysical Behaviours of Novel Phenanthro[9,10-*d*]imidazole Substituted Azo Dyes in Solvent Media

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Abstract

In this study, three novel phenanthroimidazole derivatives containing azo group were synthesized and their photophysical properties were investigated. For this purpose, 2-(4-nitrophenyl)1*H*-phenanthro[9,10-*d*]imidazole structure obtained from 9,10-phenanthroquinone and 4-nitrobenzaldehyde was reduced with palladium on activated charcoal 10 % and hydrazine hydrate. Phenanthro[9,10-*d*]imidazole-2-yl)aniline obtained in this way was converted to phenanthroimidazole-azo derivatives containing different aromatic groups. Structural analyses were performed by FT-IR, NMR, LC-MS spectroscopic techniques. Spectral characterizations and photostability studies of phenanthroimidazole derivatives were performed by UV-vis and fluorescence spectroscopy in solvent media. The maximum absorption and emission wavelengths, molar extinction coefficients, singlet energy levels, Stokes' shift values of phenanthroimidazole-azo derivatives were obtained.

Keywords: Phenanthroimidazole, azo group, fluorescence spectroscopy, dye-solvent interaction.

1. Introduction

Azo dyes are one of the most important commercial colorants with their favorable properties separated from other dye classes such as wide color ranges, high fastness and color intensities [1-2]. They are also used for the coloring paper, nonlinear optic materials and textile [3-5]. Numerous different molecules can be connected with each other by means of the azo bridge (-N=N-). In this way, the color properties (color intensity, wavelength etc.) of the organic dyes can be changed by extending the conjugation. Five membered heterocycles, especially imidazoles, have been used in the synthesis of many dyes as conjugated π systems. Phenanthroimidazoles have a larger conjugate system than the imidazole ring. Phenanthroimidazole based compounds have a wide application area and can be used as a dye-sensitizer in solar cells, organic light emitting diodes, solid state fluorescence applications, organic emitters in blue-light emitting materials and optic chemosensors [6-10].

Synthetic studies on phenanthroimidazole derivatives gain significant interest since early 1970s [11-12]. There

are several studies in literature about the synthesis of azo dyes containing imidazole and benzimidazole rings [13-14]. Phenanthroimidazole ring is a newer unit for azo dyes and phenanthroimidazole-azo structure can be used at various applications addition to the other azo classes.

In this study, three novel phenanthroimidazole substituted azo dyes (PA) were synthesized (Figure 1). The most general synthesis procedure is the condensation reaction of 9,10-phenanthrenequinone with 4-nitrobenzaldehyde in the presence of ammonium acetate and acetic acid [15]. The nitro group of the phenanthroimidazole compound was first reduced to the amino group [16], afterwards azo coupling reaction was carried out with aromatic rings which have different electron donating groups [17, 18]. Absorption, fluorescence and photostability measurements were performed in the solvent media.

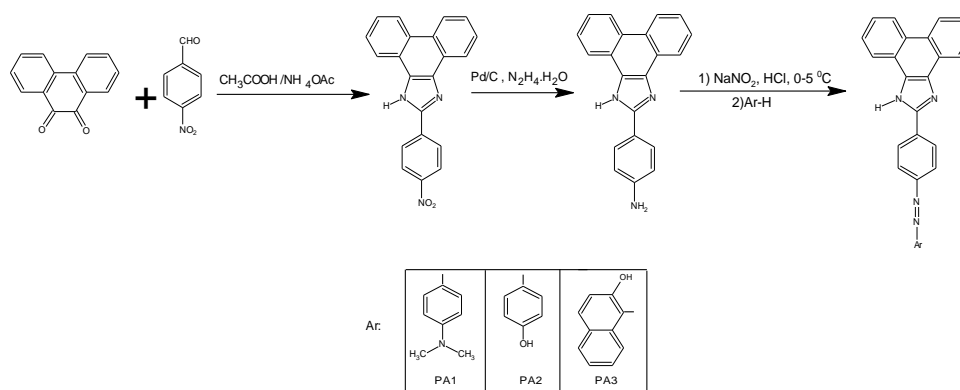


Figure 1. Synthetic pathways of phenanthroimidazole-azo derivatives.

In the literature, there are azo dyes which have imidazole and benzimidazole rings but synthesis of phenanthroimidazole based azo dyes are limited. The new long conjugated phenanthroimidazole azo dyes which have electron donor groups were obtained with this study. It is thought that these dyes can be used for sensor and luminescence applications due to their longer conjugation and photostability behaviours.

2. Materials and Methods

All reagents were obtained from Sigma Aldrich and Merck. Solvents used in spectroscopic studies were of analytical grade and used without a purification process.

FT-IR spectra were recorded on a Perkin Elmer-Spectrum BX spectrophotometer. NMR spectra were determined with a Varian 400 MHz spectrometer. LC-MS analyses were performed with an Agilent Technologies 1260 Infinity liquid chromatography system hyphenated to a 6420 Triple Quad mass spectrometer. UV-vis spectra were measured on a Shimadzu UV-1800 spectrophotometer. Fluorescence measurements were performed using a Perkin Elmer LS55 spectrophotometer.

¹H NMR spectra for all derivatives were measured in d₆-DMSO solvent, ¹³C NMR spectrum was measured for only PA1. ¹³C NMR for PA2 and PA3 couldn't obtained in different solvents even if measurement is carried out overnight.

2.1 Synthesis and Characterization of PA Derivatives

2.1.1 Synthesis of N,N-dimethyl-4-[[4-(1H-phenanthro[9,10-d]imidazole-2-yl)phenyl]diazanyl]aniline (PA1)

An aqueous solution of NaNO₂ (0.246 g, 3.56 mmol) were added dropwise to the cooled mixture of 1:10 HCl-water (11 ml) and 4-(1H-phenanthro[9,10-d]imidazole-2-yl)aniline (1 g, 3.24 mmol). The mixture was stirred between 0-5 °C for 30 min. N,N-dimethyl aniline (0.4 ml, 3.24 mmol) and sodium acetate (0.089 g, 1.08 mmol) were added separately to the diazonium salt which composed. The mixture was stirred for 1 more hour at 0 °C and neutralized with 2 N NaOH solution. It was

extracted with ethyl acetate and the organic fraction was dried over anhydrous MgSO₄. The solvent was evaporated with a rotary evaporator. Recrystallization was performed from ethyl acetate. FT-IR [KBr, ν max (cm⁻¹): 3072 (aromatic C-H stretch), 2902 (aliphatic C-H stretch), 1600 (N=N stretch), 1518 (ring vib.), 1362 (C-N stretch). ¹H-NMR (d₆-DMSO, 400 MHz) δ (ppm): 3.05 (s, 6H, 2 x CH₃-N), 6.82-6.84 (m, 2H, aromatic), 7.62-7.64 (m, 2H, aromatic), 7.74 (t, 2H, aromatic, j=8Hz), 7.82-7.84 (m, 2H, aromatic), 7.97-7.99 (m, 2H, aromatic), 8.44-8.47 (m, 2H, aromatic), 8.59 (d, 2H, aromatic j=8Hz), 8.85 (d, 2H, aromatic j=8Hz). ¹³C-NMR (d₆-DMSO, 400 MHz) δ (ppm): 40.28 (2C), 112.06 (4C), 122.45 (1C), 122.91 (4C), 125.36 (4C), 127.38 (4C), 127.62 (2C), 131.40 (2C), 144.22 (2C), 148.95 (2C), 153 (2C). LC-MS (ESI) m/z=441.9 [M⁺].

2.1.2 Synthesis of 4-[[4-(1H-phenanthro[9,10-d]imidazol-2-yl)phenyl]diazanyl]phenol (PA2)

An aqueous solution of NaNO₂ (0.06 g, 0.89 mmol) were added dropwise to the cooled mixture of 1:10 HCl-water (11 ml) and 4-(1H-phenanthro[9,10-d]imidazole-2-yl)aniline (0.25 g, 0.81 mmol). The mixture was stirred between 0-5 °C for 30 min. Phenol (0.076 g, 0.81 mmol) in 5 ml 10% NaOH were cooled to 0 °C and then added slowly to the diazonium salt which composed. The mixture was stirred for 1 more hour at 0 °C and it was brought to pH 8 with 2 N NaOH solution. It was extracted with ethyl acetate and the organic fraction was dried over anhydrous MgSO₄. The solvent was evaporated. Recrystallization was performed from acetone. FT-IR [KBr, ν max (cm⁻¹): 3421 (O-H stretch), 3229 (N-H stretch), 3056 (aromatic C-H stretch), 1595 (N=N stretch), 1248 (C-O stretch). ¹H-NMR (d₆-DMSO, 400 MHz) δ (ppm): 6.96 (d, 2H, aromatic, j=8Hz), 7.60-7.64 (m, 2H, aromatic), 7.71-7.73 (m, 2H, aromatic), 7.85 (d, 2H, aromatic, j=8Hz), 8.02 (d, 2H, aromatic, j=8Hz), 8.48 (d, 2H, aromatic, j=8Hz), 8.58 (d, 2H, aromatic, j=8Hz), 8.83 (d, 2H, aromatic, j=8Hz), 10.37 (bs, N-H and O-H). LC-MS (ESI) m/z=414.8 [M⁺].

2.1.3 Synthesis of 1-[[4-(1H-phenanthro[9,10-d]imidazol-2-yl)phenyl]diazanyl]-2-naphthol (PA3)

PA3 was prepared by the same procedure for PA2 using the 2-naphthol instead of phenol. FT-IR [KBr, ν max (cm^{-1}): 3050 (aromatic C-H stretch), 1614 (N=N stretch), 1494 (ring vib.), 1209 (C-O stretch). $^1\text{H-NMR}$ (d_6 -DMSO, 400 MHz) δ (ppm): 6.88 (d, 1H, aromatic, $j=8\text{Hz}$), 7.43-7.47 (m, 1H, aromatic), 7.60-7.64 (m, 3H, aromatic), 7.71-7.75 (m, 3H, aromatic), 7.92 (d, 1H, aromatic, $j=8\text{Hz}$), 8.02 (d, 2H, aromatic, $j=12\text{Hz}$), 8.44 (d, 2H, aromatic, $j=12\text{Hz}$), 8.55-8.59 (m, 3H, aromatic), 8.82 (d, 2H, aromatic, $j=8\text{Hz}$). LC-MS (ESI) $m/z=464.8$ [M^+].

3. Results and Discussion

The photophysical properties of the PA derivatives were characterized in dimethylformamide (DMF), dichloromethane (DCM), chloroform (CHCl_3), tetrahydrofuran (THF) solvents by means of UV-vis absorption and emission spectroscopy. The spectroscopic studies of PA2 were made in DMF and THF solvents because it is only soluble in them.

Maximum absorption, emission and excitation wavelengths (λ_{max} ; $\lambda_{\text{max}}^{\text{f}}$; λ_{ex} in nm), molar extinction coefficients (ϵ ; in $\text{L mol}^{-1} \text{cm}^{-1}$), singlet energy levels (E_s , kJ/mol), Stokes' shifts of PA derivatives for all solvents used are shown in Tables 1, 2, 3.

Stokes' shift is the wavelength difference between the band maxima of the excitation and emission spectra of the same electronic transition.

Es calculations were estimated by $E = h \cdot \frac{c}{\lambda}$ formula.

(h: Planck constant, c: speed of light, λ : maximum absorption wavelength)

3.1 Absorption and Emission Studies of PA Derivatives in Different Solvents

Spectroscopic studies for PA derivatives were carried out in the concentration of 1.0×10^{-5} M. These derivatives exhibited maximum absorption wavelengths between 407-555 nm in all solvents used. The bands observed at UV-vis spectra below 400 nm can be attributed to the π - π^* transitions. These bands can be seen in Figure 2 for all derivatives in THF. The peaks above 400 nm are related to the low energy n - π^* transition.

For all derivatives, the emission band was obtained when excited nearly $\lambda_{\text{max}1}$. When PA derivatives were excited at values close to $\lambda_{\text{max}2}$, the emission band wasn't observed.

$n \rightarrow \pi^*$ transition undergoes bathochromic shift with increasing polarity of solvent (Table 1,2 and 3) [19]. DMF has the highest polarity index in the solvents used.

All absorption spectra of PA derivatives were analyzed, bathochromic shift was observed for $n \rightarrow \pi^*$ transition in DMF between 38-49 nm compared to the other solvents.

When $\lambda_{\text{max}2}$ values of PA derivatives are examined, it is seen that PA3 has the longest absorption wavelengths. This situation is probably due to the increasing electron donating effect of donor groups attached to the aromatic rings (Figure 2).

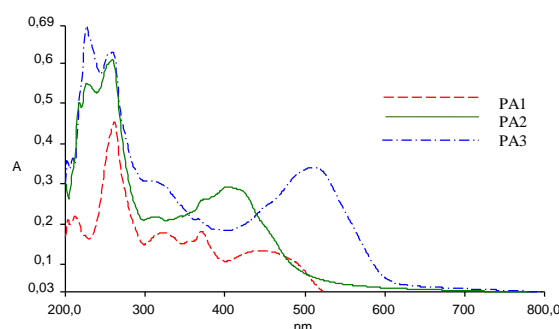


Figure 2. Absorption spectrum of PA derivatives in THF

The molar extinction coefficients of all PA derivatives were found to be enough for sensitizer cell applications [20]. It has varied between 8000 - 53000 $\text{Lmol}^{-1}\text{cm}^{-1}$ for ϵ_1 and 12000 - 37000 $\text{Lmol}^{-1}\text{cm}^{-1}$ for ϵ_2 in this study. The emission wavelengths were observed between 380-428 nm for all derivatives. Figure 3 shows the emission and excitation spectrum of PA3 in all solvents used. This derivative showed a bathochromic shift approximately between 8-28 nm compared to the other derivatives (Table 1, 2 and 3). This situation can be explained by the enhancement of electron-charge transfer due to longer conjugation.

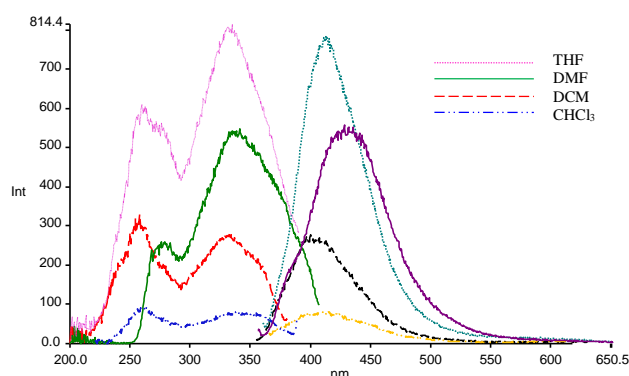


Figure 3. Emission and excitation spectrum of PA3 in all solvents used.

The singlet energy levels (E_s) of all derivatives were estimated to be about 87.25-92.63 for E_{s1} and 51.41-70.09 kcal/mol for E_{s2} in solutions. A large Stokes' shift is often highly desirable for fluorescence measurements in sensor studies. In this study, Stokes' shift values were found in the range of 60-92 nm in solutions. These values are acceptable for many fluorescence applications.

Table 1. UV–vis spectroscopic data (λ /nm, ϵ /Lmol⁻¹ cm⁻¹) and emission spectroscopic data (Es, kcal/mol) of PA1 in different solvents.

Solvent	C (M)	$\lambda_{\max 1}$ (nm)	$\lambda_{\max 2}$ (nm)	$\lambda_{\text{ex.}}$ (nm)	$\lambda_{\text{f max}}$ (nm)	ϵ_1 Lmol ⁻¹ cm ⁻¹	ϵ_2 Lmol ⁻¹ cm ⁻¹	$\Delta\lambda$	Es ₁ kcal/mol	Es ₂ kcal/mol
DCM	1.0x10 ⁻⁵	321	455	320	380	11000	20000	60	88.88	62.70
DMF		315	500	323	400	53000	18000	77	90.57	57.06
CHCl ₃		319	451	325	389	8000	15000	64	89.44	63.30
THF		319	451	325	394	18000	13000	69	89.44	63.30

Table 2. UV–vis spectroscopic data (λ /nm, ϵ /Lmol⁻¹ cm⁻¹) and emission spectroscopic data (Es, kcal/mol) of PA2 in different solvents.

Solvent	C (M)	$\lambda_{\max 1}$ (nm)	$\lambda_{\max 2}$ (nm)	$\lambda_{\text{ex.}}$ (nm)	$\lambda_{\text{f max}}$ (nm)	ϵ_1 Lmol ⁻¹ cm ⁻¹	ϵ_2 Lmol ⁻¹ cm ⁻¹	$\Delta\lambda$	Es ₁ kcal/mol	Es ₂ kcal/mol
DMF	1.0x10 ⁻⁵	308	456	325	401	39000	37000	76	92.63	62.57
THF		309	407	328	404	17000	24000	76	92.33	70.09

Table 3. UV–vis spectroscopic data (λ /nm, ϵ /Lmol⁻¹ cm⁻¹) and emission spectroscopic data (Es, kcal/mol) of PA3 in different solvents.

Solvent	C (M)	$\lambda_{\max 1}$ (nm)	$\lambda_{\max 2}$ (nm)	$\lambda_{\text{ex.}}$ (nm)	$\lambda_{\text{f max}}$ (nm)	ϵ_1 Lmol ⁻¹ cm ⁻¹	ϵ_2 Lmol ⁻¹ cm ⁻¹	$\Delta\lambda$	Es ₁ kcal/mol	Es ₂ kcal/mol
DCM	1.0x10 ⁻⁵	327	516	331	403	9000	12000	72	87.25	55.30
DMF		309	555	336	428	50000	34000	92	92.33	51.41
CHCl ₃		320	517	341	408	12000	21000	67	89.16	55.18
THF		309	510	332	412	31000	34000	80	92.33	55.94

3.2 Photostability Studies

Photostability studies of PA derivatives were performed by using a steady state spectrofluorimeter in the mode of “Time Based Measurements” employing a xenon arc lamp. All of the fluorophores were excited at around 370 nm, the data were obtained at their maximum emission wavelengths for one hour monitoring.

The steady results were obtained for all derivatives. The photostability results of PA3 in solvent media can be seen in Figure 4.

4. Conclusions

New compounds containing phenanthroimidazole ring were added to the azo dye classes by means of this study. These derivatives can be used in many different application fields with their fluorescence properties. Spectroscopic characterizations for synthesized PA derivatives were performed in different solvents. When the maximum absorption wavelengths were examined in

studied solvents, the bathochromic shift was observed in DMF for all derivatives for n- π^* transition. Depending on the increased conjugation, PA3 exhibits a bathochromic shift in emission spectra relative to other derivatives. The photostability tests were performed in solvent media. Results showed that all derivatives were photostable for one hour in different solvents.

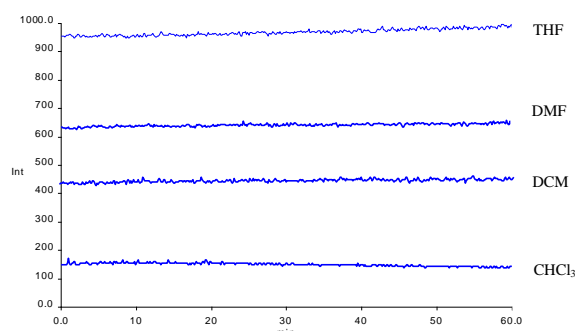


Figure 4. Photostability results of PA3 in all studied solvents.

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