

Synthesis and Spectrophotometric P^H Sensing Applications of Poly-2-[4-(diethylaminophenyl)imino]-5-nitro-phenol and its Schiff Base Monomer for Two Different P^H Ranges

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Abstract Poly-2-[4-(diethylaminophenyl)imino]-5-nitro-phenol (PEAPINP) and 2-[4-(diethylaminophenyl)imino]-5-nitro-phenol (EAPINP) were prepared as new pH sensors. Spectrophotometric and spectrofluorometric response of the novel sensors in various p^H values were investigated. EAPINP has the ability to respond linearly at alkaline P^H values, 8 to 9, and can be utilized in absorption and wavelength radiometric methods. PEAPINP has the ability to respond linearly at lower pH values, 6 to 7, and can be used as an alternative pH sensor in this range. The new sensors are yellow-colored in acidic and neutral media and red-colored in alkaline P^Hs. With their colorimetric responses at different pH ranges EAPINP and PEAPINP can be used to develop color-tunable P^H sensors.

Keywords Polyazomethine · P^H sensor · Fluorescence · Schiff base · Differential scanning calorimetry

Introduction

During the last 20 years, global research and development (R&D) on the field of sensors has expanded exponentially in terms of financial investment, the published literature, and the number of active researchers [1]. Glass P^H electrodes are unsuitable for certain applications such as determination of intracellular P^H, microscopy studies as well as measurement of extreme P^H values (<1 or >9). In contrast to the electrochemical methods, optical P^H sensors based on absorbent and fluorescent probes without such drawbacks

have been applied in a variety of industrial, environmental, and medicinal areas [2–4]. With the development of wavelength-radiometric techniques, the design of molecular structure with dual absorption and emission which depends on the P^H value has been an attractive challenge [3, 5, 6]. Despite these advantages, only a few examples of such systems have been reported so far [5, 7–9]. Arshak et al. were reviewed the current state-of-the-art methods to measure P^H levels using polymer based materials [10]. Most common fluorescent P^H sensors are suitable for P^H from 4 to 9. They are promising to be applied in biological applications, determining neutral P^H values of normal body fluids [3]. One advantage of P^H sensors over the P^H electrodes is their wide P^H scales. There are, however, only a few optical P^H sensors for use at high or low P^Hs [11–16]. There is still need for developing of P^H sensors available in different P^H ranges.

Polyazomethines (PAMs), with their useful properties have attracted much attention of researchers so far [17, 18]. PAMs and their oligophenol derivatives have been widely investigated with their optical, electrochemical, thermal, and conductivity measurements [19–21]. Some chelate derivatives of PAMs were also developed as alternative gas sensing materials [22]. Additionally, Schiff base substituted oligophenols could be used as antimicrobial agents [23]. Schiff base substituted oligophenols have been studied by Kaya and co-workers for the last decade. This class of the polymers was mainly found to be electroactive as well as semi-conductive materials [24, 25]. Their conductivities were increased by doping with iodine [26]. Coupling selectivity of the Schiff base substituted oligophenols were also studied and two coupling mechanisms were reported including C-O-C and C-C couplings [19, 25]. The formation of C-O-C coupling in the polymer structure decreases the phenolic –OH proton numbers and consequently acidity of the polymer. This results in lower acidity of the oligophenol than the Schiff base

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monomer model. Resultantly, the Schiff bases containing phenol units that can response towards different P^H s could work in different P^H range than their oligophenol derivatives. For this reason, in this study, we declare development of new spectrophotometric P^H sensors for both alkaline (P^H 8.0–9.0) and acidic (P^H 6.0–7.0) conditions based on 2-[4-(diethylaminophenyl)imino]-5-nitro-phenol (EAPINP) and its oligophenol derivative. In the range of P^H 6–10, EAPINP and PEAPINP cause color changes and allow the production of color-tunable P^H sensors. A linearly response in the P^H range of 8–9 was obtained for EAPINP and in the range of P^H 6–7 for PEAPINP using spectrophotometric measurements. Herein, we report the design and syntheses of novel P^H sensors those are sensitive in acidic-basic environments. The sensing mechanism of the novel sensors is also suggested that clarifying the different available P^H ranges for the monomer and polymer.

Experimental

Materials

4-diethylaminobenzaldehyde, 2-amino-5-nitro-phenol, methanol, ethanol, acetone, dioxane, ethyl acetate, toluene, n-hexane, dichloromethane, $CHCl_3$, THF, DMF, and KOH were supplied by Merck Chemical Co. and used as received. 30% aqueous solution of sodium hypo chlorite, NaOCl was supplied from Paksoy Chemical Co. (Turkey).

Preparation of 2-[4-(diethylaminophenyl)imino]-5-nitro-phenol (EAPINP)

EAPINP was prepared by the condensation of 4-diethylaminobenzaldehyde (0,177 g, 0.001 mol) with 2-amino-5-nitro phenol (0,154 g, 0.001 mol) in methanol (30 ml) achieved by boiling the mixture under reflux for 5 h at 70 °C (Scheme 1). The precipitated 2-[4-(diethylamino-phenyl)imino]-5-nitro-phenol (EAPINP) was filtered, recrystallized from methanol and dried in a vacuum desiccator (yield, 70%) [27].

Synthesis of Poly-2-[4-(diethylaminophenyl)imino]-5-nitro-phenol (PEAPINP)

PEAPINP was synthesized through oxidative polycondensation of 2-[4-(diethylaminophenyl)imino]-5-nitro-phenol using

NaOCl as the oxidant [24–26]. EAPINP (0.313 g, 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.001 mol) and placed into a 50 ml three-necked round-bottom flask which was fitted with a condenser, thermometer, stirrer, and an addition funnel containing 2 ml of NaOCl aqueous solution (30% by weight). After heating up to 60 °C, NaOCl was added drop by drop over about 20 min. Reaction was maintained for 5 h. Then, the reaction mixture was cooled at the room temperature, 0.001 mol HCl (37%) added for neutralization, and kept for 24 h at the room temperature for precipitation of the polymer. The mixture was filtered, washed with hot water (3×25 ml) and methanol (2×20 ml) to separate the mineral salts and unreacted monomers, respectively. The obtained polymer was dried in a vacuum oven at 60 °C for 24 h. The reaction design is given in Scheme 2.

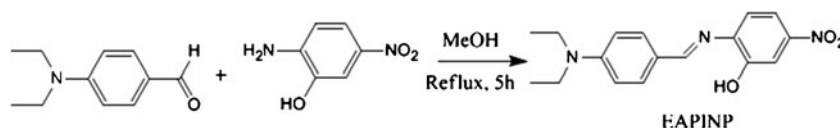
Characterization Techniques

The solubility tests were done using 1 mg sample and 1 ml solvent at 25 °C. The infrared spectra were measured by Perkin Elmer Spectrum One FT-IR system. The FT-IR spectra were recorded using universal ATR sampling accessory within the wave numbers of 4,000–550 cm^{-1} . The synthesized compounds were also characterized using 1H - and ^{13}C -NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded by using deuterated DMSO- d_6 as a solvent at 25 °C. Tetramethylsilane was used as internal standard. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) techniques of Shimadzu Co. For SEC investigations, an SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. \times 300 mm columns was used; eluent: DMF (0.4 ml/min), polystyrene standards were used. A refractive index detector (RID) was used to analyze the products at 25 °C.

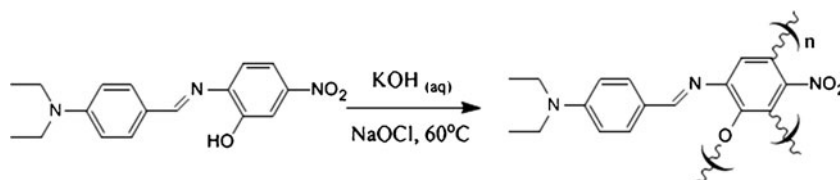
Optical Measurements

Fluorescence and absorption spectra were recorded by Shimadzu RF-5301PC spectrofluorophotometer and Perkin Elmer Lambda 25, respectively. Measurements were carried out in ethanol-water (2/1, v/v) solutions in the P^H range of 6–10. P^H s of the solutions were adjusted by 0.1 mol L^{-1} concentrated buffer solutions of Na_2HPO_4 - NaH_2PO_4 . Excitation wavelength for emission measurements and emission wavelength for excitation measurements were 510 and

Scheme 1 Synthesis of 2-[4-(diethylaminophenyl)imino]-5-nitro-phenol (EAPINP)



Scheme 2 Synthesis of poly-2-[4-(diethylaminophenyl)imino]-5-nitro-phenol (PEAPINP)



574 nm; and 246 and 306 nm for EAPINP and PEAPINP, respectively.

Results and Discussion

Solubilities and Structures of the Compounds

EAPINP have red colored-powder forms whereas its polyphenol derivative, PEAPINP, is black colored. EAPINP is completely soluble in many organic solvents such as acetone, THF, DMF, dichloromethane, and CHCl_3 . However it's partially soluble in methanol, ethanol, n-hexane, toluene, ethyl acetate, and dioxane. PEAPINP was completely soluble in DMF, DMSO, and H_2SO_4 while it is

partially soluble in acetone, THF, dichloromethane, CHCl_3 , and ethyl acetate. Also it was insoluble in apolar solvents like n-hexane and toluene.

According to the FT-IR spectra the structure of EAPINP is confirmed by growing imine ($\text{CH} = \text{N}$) peak at $1,605 \text{ cm}^{-1}$ with disappearing of the $\text{C} = \text{O}$ and $-\text{NH}_2$ peaks of 4-diethylaminobenzaldehyde and 2-amino-5-nitro-phenol, respectively. O-H stretch of phenolic hydroxy is also observed at $3,281 \text{ cm}^{-1}$. Additionally, at the FT-IR spectrum of PEAPINP imine ($\text{HC} = \text{N}$) and O-H stretch peaks shift up to $1,625$ and $3,355 \text{ cm}^{-1}$, respectively. This is because of the polyconjugated structure of the polymer. Polymer structure of PEAPINP is also confirmed by broad peaks as the result of the polymerization. Other characteristic FT-IR values are also shown below.

Fig. 1 a ^1H -NMR and b ^{13}C -NMR spectra of EAPINP

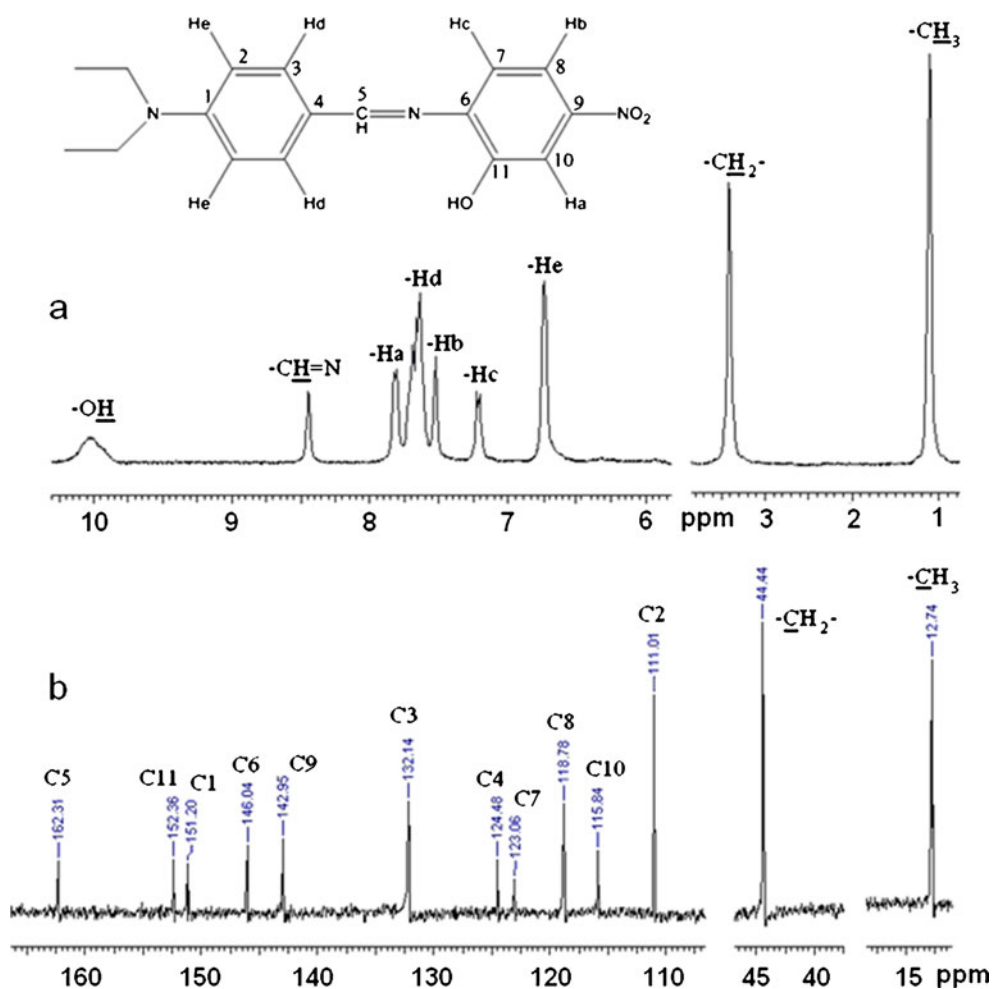
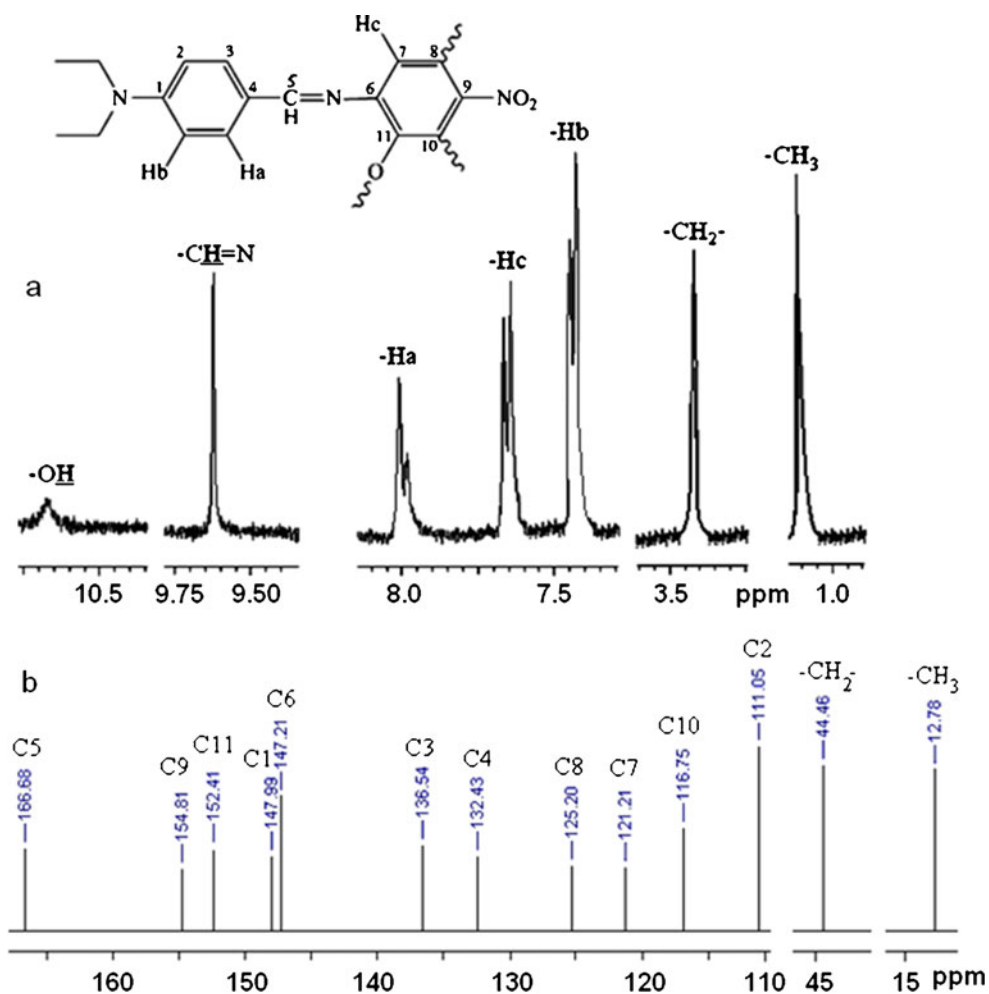


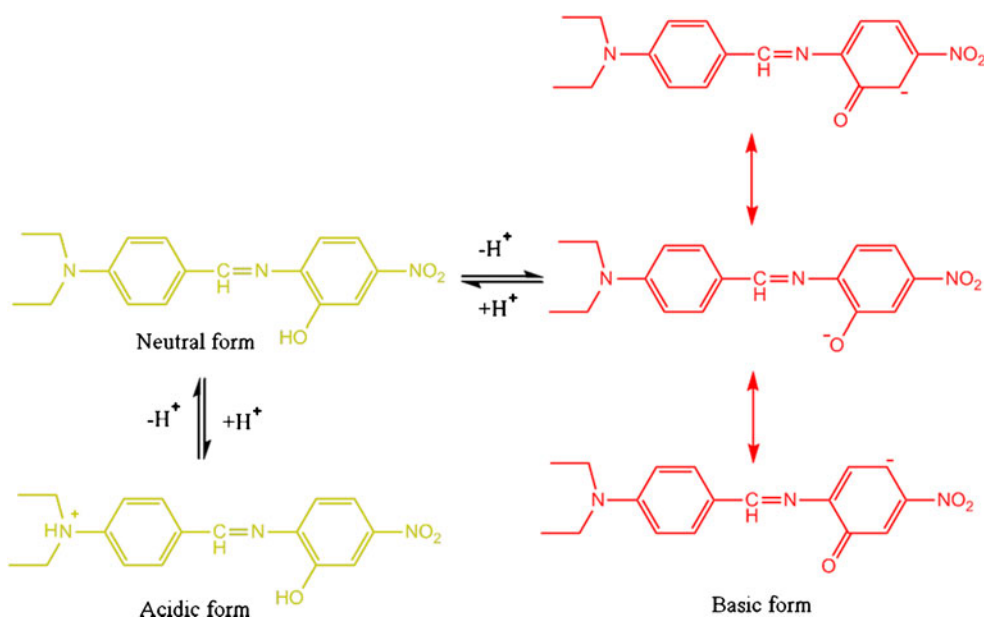
Fig. 2 **a** ^1H -NMR and **b** ^{13}C -NMR spectra of PEAPINP



^1H and ^{13}C -NMR analyses results of the synthesized compounds are given below. The ^1H and ^{13}C -NMR spectra of EAPINP and PEAPINP are also shown in Figs. 1 and 2,

respectively. According to the ^1H -NMR results of the compounds the structures of EAPINP and PEAPINP are confirmed by specific -OH and CH=N peaks observed at

Scheme 3 Protonation–deprotonation equilibria of EAPINP

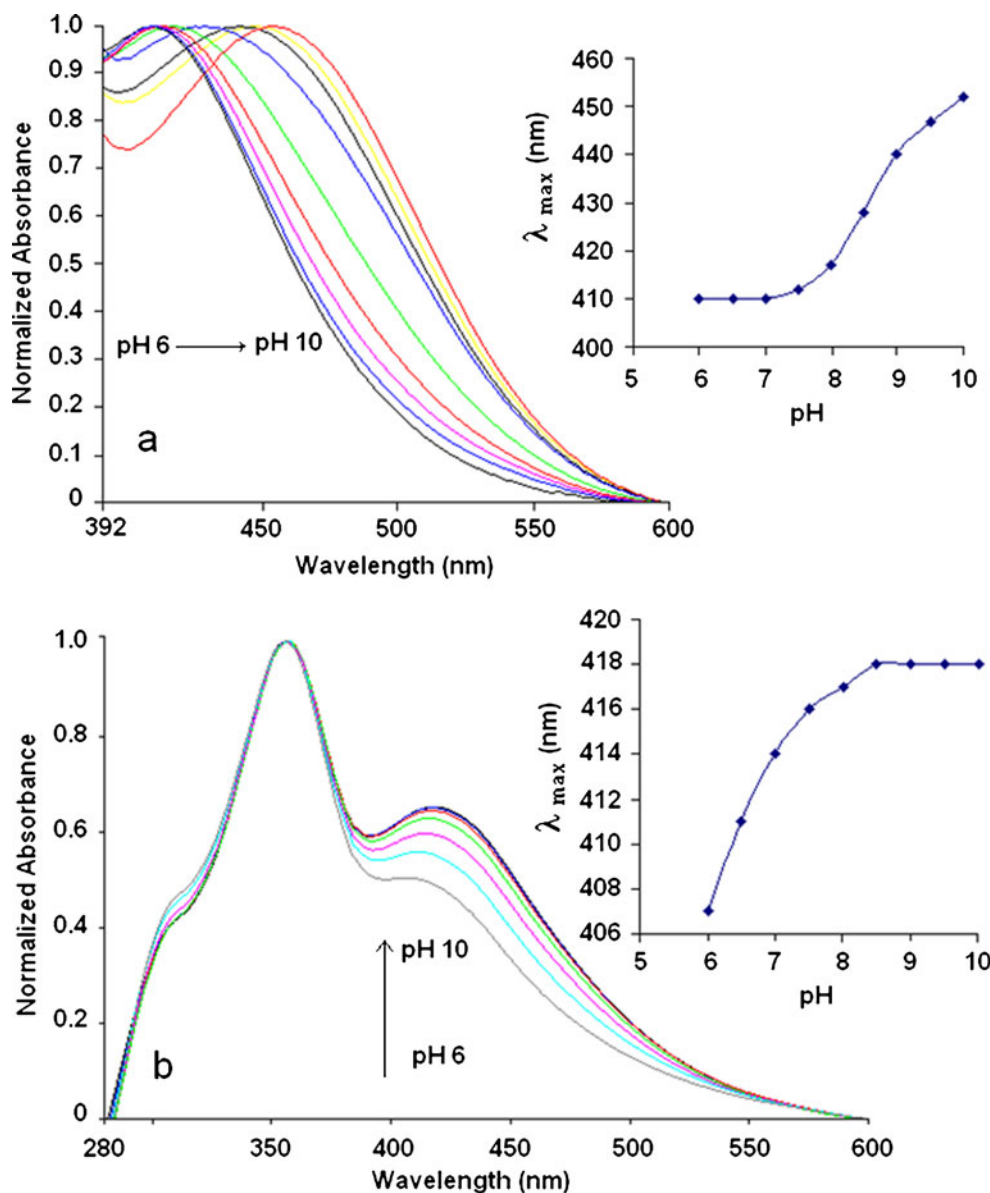


10.02 and 8.44; and 10.67 and 9.62 ppm, respectively. However, it's clearly observed that the –OH peak integration of PEAPINP is lower than that of EAPINP. This is probably because of the C–O–C coupling of the monomer units. Kaya et al. have previously studied the radical polymerization mechanism of polyphenols [19]. This mechanism suggests that phenol-based monomers can be polymerized by C–C and C–O–C coupling of monomer units. The C–C coupling mechanism proceeds by intermolecular combination of the monomer units at the *ortho* and *para* positions of phenolic –OH. However, C–O–C coupling occurs by combination of a phenoxy radical with an *ortho* or *para* position of another monomer unit. Also, Kaya and co-workers calculated the C–C/C–O–C coupling rates by comparison of phenolic –OH integrations of oligophenols

and corresponding monomers using ¹H-NMR spectra [25]. As a result of Figs. 1 and 2, PEAPINP is obtained with forming of both coupling mechanisms. Other NMR results are also given below.

EAPINP: FT-IR (cm⁻¹): ν(O–H) 3,281 s, ν(C–H Phenyl) 3,105 m, ν(C–H Aliphatic) 2981, 2940, 2,900 m, ν(C = N) 1,605 s, ν(C = C phenyl) 1574, 1544, 1,505 s, ν(C–O) 1267 s. ¹H-NMR (DMSO): δ ppm, 10.02 (s, 1H, –OH), 8.44 (s, 1H, –CH = N–), 7.81(s, 1H, Ar–Ha), 7.64 (d, 2H, Ar–Hd), 7.52 (d, 1H, Ar–Hb), 7.23 (d, 1H, Ar–Hc), 6.74 (d, 2H, Ar–He), 3.42 (s, 4H, –CH₂–), 1.11 (s, 6H, –CH₃). ¹³C-NMR (DMSO): δ ppm, 162.31 (C5–H), 152.36 (C11–ipso), 151.20 (C1–ipso), 146.04 (C6–ipso), 142.95 (C9–ipso), 132.14 (C3–H), 124.48 (C4–ipso), 123.06 (C7–H), 118.78 (C8–H), 115.84 (C10–H), 111.01 (C2–H), 44.44 (–CH₂–), 12.74 (–CH₃).

Fig. 3 Spectrophotometric response of EAPINP (a) and PEAPINP (b) related to different pH values



PEAPINP: FT-IR (cm^{-1}): $\nu(\text{O-H})$ 3,355 s, $\nu(\text{C-H Phenyl})$ 3,099 m, $\nu(\text{C-H Aliphatic})$ 2,975 m, $\nu(\text{C}=\text{N})$ 1,625 s, $\nu(\text{C}=\text{C phenyl})$ 1587, 1552, 1,523 s, $\nu(\text{C-O})$ 1,272 s. $^1\text{H-NMR}$ (DMSO): δ ppm, 10.67 (s, $-\text{OH}$), 9.62 (s, $-\text{CH}=\text{N}-$), 8.01 (d, Ar-Ha), 7.64 (d, Ar-Hc), 7.44 (d, Ar-Hb), 3.42 (s, $-\text{CH}_2-$), 1.12 (s, $-\text{CH}_3$). $^{13}\text{C-NMR}$ (DMSO): δ ppm, 166.68 (C5-H), 154.81 (C9-*ipso*), 152.41 (C11-*ipso*), 147.99 (C1-*ipso*), 147.21 (C6-*ipso*), 136.54 (C3-H), 132.43 (C4-*ipso*), 125.20 (C8-*ipso*), 121.21 (C7-H), 116.75 (C10-*ipso*), 111.05 (C2-H), 44.46 ($-\text{CH}_2-$), 12.78 ($-\text{CH}_3$).

According to the SEC chromatogram PEAPINP has two fractions. The number-average molecular weight (M_n), weight average molecular weight (M_w), polydispersity index (PDI), and fraction percentage values are calculated as 6,400, 8,400 g mol^{-1} , 1.310, and 58%; and 3760, 3,790 g mol^{-1} , 1.008, and 42%, respectively. Totally; M_n , M_w , and PDI values of PEAPINP is obtained as 5,290, 6,460 g mol^{-1} , and 1.221, respectively. According to these results PEAPINP contains approximately 17–21 repeated units.

Optical Characteristics

Diethylamino group of EAPINP is the corresponding site from stable spectral change depending on the P^{H} values [28]. Diethylamino is an electro-donating group in neutral and basic conditions. However, in the acidic conditions this group becomes an electron withdrawing site, which causes decreasing in conjugation of the molecule and inhibition of the photoinduced electron transfer (PET) between the electro-donor phenolic $-\text{OH}$ and electro-acceptor $-\text{NO}_2$ groups [28, 29]. At the high P^{H} values, diethylamino group donates electrons into the molecule which increases the conjugation of the molecule. Consequently, in the basic conditions the molecule is in the red-colored form due to high conjugation whereas in the yellow-colored form in the acidic media. Schematic illustration of protonation/deprotonation mechanism of EAPINP is shown in Scheme 3.

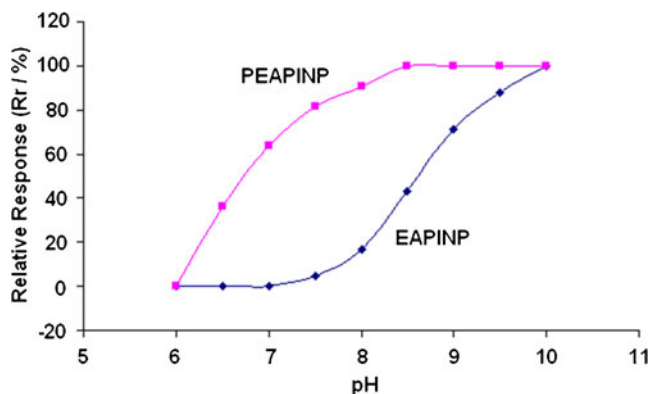


Fig. 4 Relative spectrophotometric response (Rr) of EAPINP and PEAPINP in the P^{H} range of 6–10

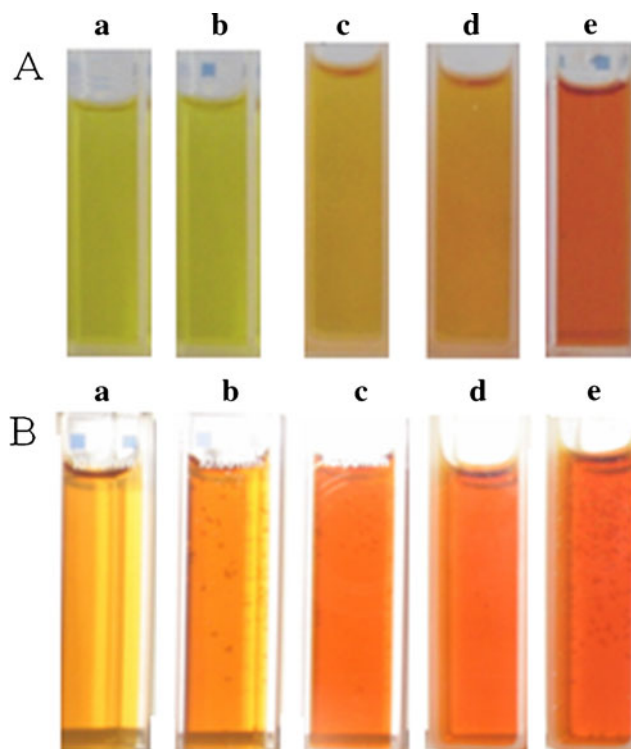


Fig. 5 Color changes of EAPINP (a) and PEAPINP (b) at various P^{H} values: (a) 6.0, (b) 7.0, (c) 8.0, (d) 9.0, and (e) 10.0

The normalized absorption spectra of EAPINP in different P^{H} values are given in Fig. 3a. At the absorption spectra specific spectral changes are obtained as shifting of

Table 1 Spectral response of EAPINP at various P^{H} values

P^{H}	UV ($\lambda_{\text{max}}/\text{nm}$)		Fluorescence			
	EAPINP	PEAPINP	EAPINP		PEAPINP	
			$^{\text{a}}\text{I}_{\text{Ex}}$	$^{\text{b}}\text{I}_{\text{Em}}$	$^{\text{c}}\text{I}_{\text{Ex}}$	$^{\text{d}}\text{I}_{\text{Em}}$
6.0	410	407	300	292	885	867
6.5	410	411	1072	1128	664	624
7.0	410	414	344	344	842	836
7.5	412	416	279	268	918	887
8.0	417	417	136	112	902	868
8.5	428	418	132	102	905	873
9.0	440	418	120	95	924	891
9.5	447	418	110	86	937	891
10.0	452	418	110	86	902	886

^a Maximum excitation intensity of EAPINP at 510 nm, emission wavelength for excitation: 574 nm

^b Maximum emission intensity of EAPINP at 574 nm, excitation wavelength for emission: 510 nm

^c Maximum excitation intensity of PEAPINP at 248 nm, emission wavelength for excitation: 306 nm

^d Maximum emission intensity of PEAPINP at 305 nm, excitation wavelength for emission: 247 nm

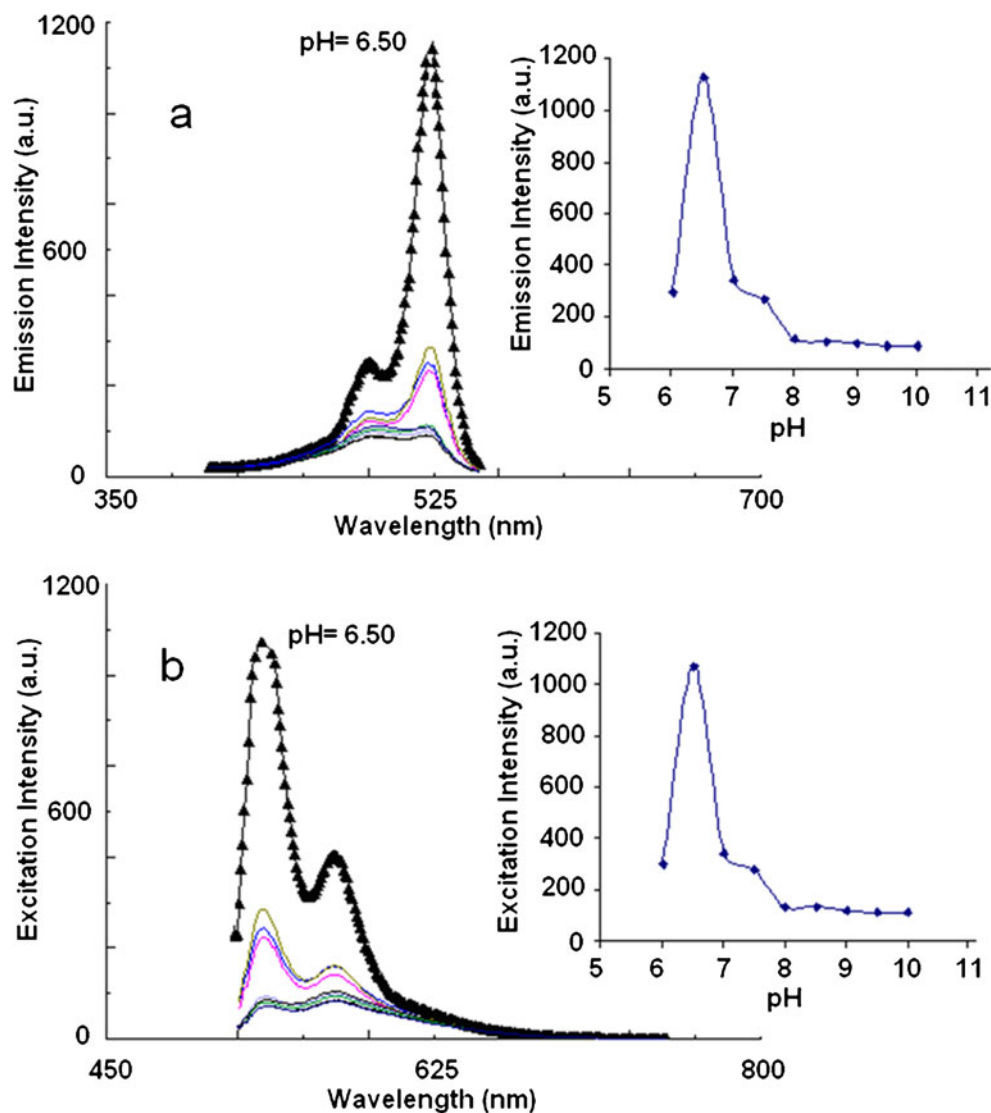
absorption edges. Figure 3a shows the red shifts in the edge of the absorption spectrum of EAPINP when the P^H increases. Maximum absorbance wavelengths (λ_{max}) are also plotted on the right side of Fig. 3a. This region is also corresponding from the color change between yellow-red colors. However, the spectral changes of that region are limited in the range of P^H 7–10. Also, linearly response of this area is limited in the range of P^H 8 to 9. This indicates that the use of EAPINP as a spectrophotometric P^H sensor is useful in the P^H range of 8–9. The regression coefficient of EAPINP obtained in the range of P^H 8 to 9 is 0.9997. As a result the following equation (Eq. 1) derived from spectral response of EAPINP in the range of $P^H=8-9$ could be used in P^H measurements:

$$pH = \frac{\lambda_{max} - 232.83}{23} \quad (1)$$

The normalized absorbance spectra of PEAPINP in different P^H values are also given in Fig. 3b. Similarly,

when P^H of the media is increased the absorption edge of the spectrum clearly shifts up to the higher wavelengths. λ_{max} values of PEAPINP are also plotted on the right side of Fig. 3b. However, on the contrary of spectral response of EAPINP, PEAPINP has linearly response limited in the range of $P^H=6-7$. As seen in Fig. 3, EAPINP and PEAPINP have nearly opposite responses in different P^H s. Scheme 3 presents the protonation/deprotonation of EAPINP which mainly occurred at phenolic $-OH$ during conversion in neutral and basic media. However, as mentioned above the polycondensation reaction of EAPINP proceeds by C-O-C and C-C couplings. As a result of C-O-C coupling of the monomer units phenolic hydroxy group numbers of PEAPINP decrease which also causes decreasing of acidity of the oligomer. Due to lower number of $-OH$ protons the polymer doesn't present clear spectral change in the basic conditions. Resultantly, PEAPINP could be used as a spectrophotometric sensor at higher acidic conditions

Fig. 6 PL spectra of EAPINP at various P^H values: **a** Emission spectra, λ_{Ex} 510 nm, inset; the changes of PL intensities at 532 nm, **b** excitation spectra, λ_{Em} 574 nm, inset; the changes of PL intensities at 522 nm. Slit: λ_{Ex} 5 nm, λ_{Em} 5 nm



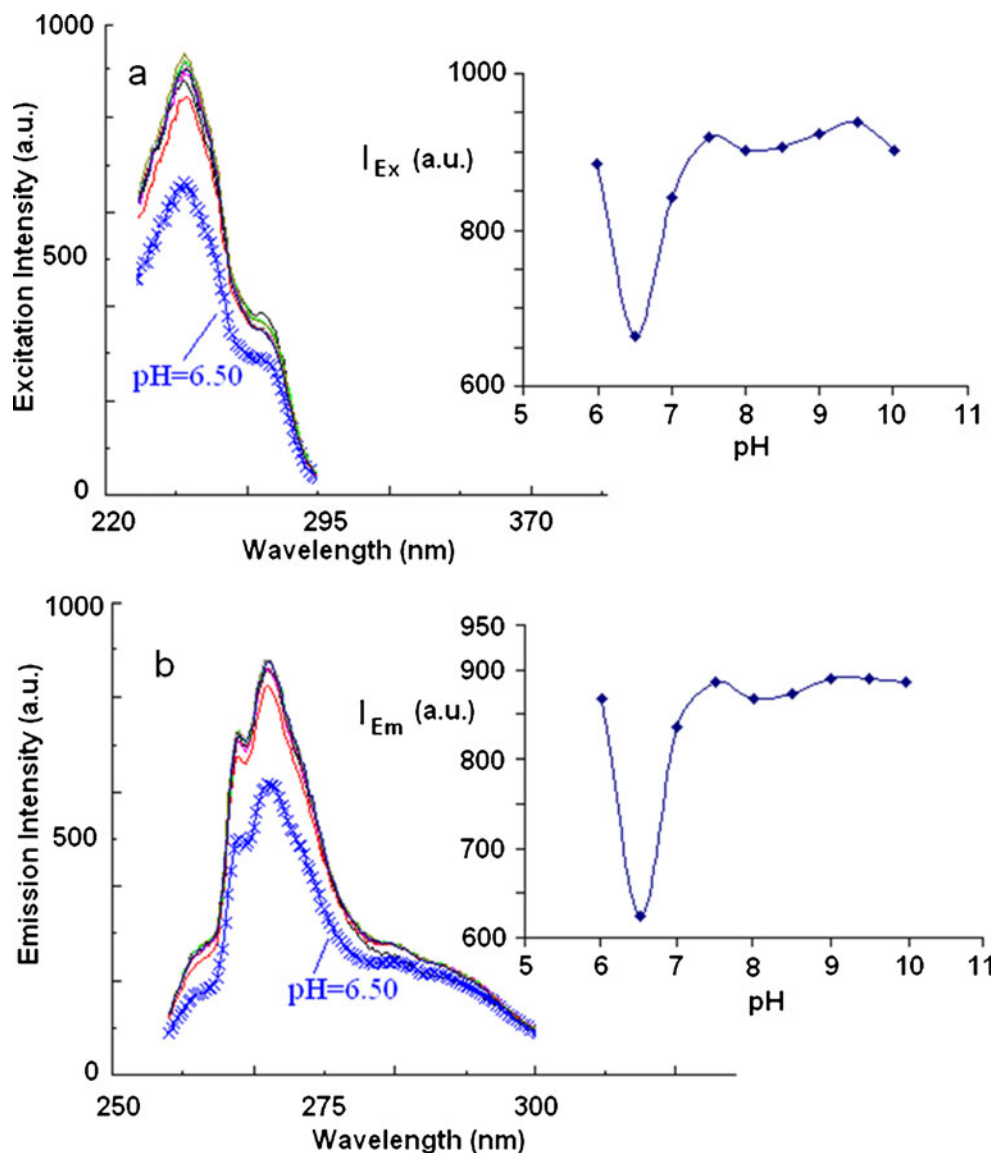
than that of EAPINP. According to the obtained results PEAPINP could be used as a spectrophotometric P^H sensor in the pH range of 6–7. The regression coefficient of PEAPINP obtained in this range is 0.9966. The following equation (Eq. 2) derived from spectral response of PEAPINP in the range of $P^H=6-7$ could be used in P^H measurements:

$$\text{pH} = \frac{\lambda_{\max} - 365.17}{7} \quad (2)$$

According to the obtained results the relative spectrophotometric responses (R_r) of the synthesized compounds are determined using the following equation (Eq. 3) and shown in Fig. 4.

$$R_r = \frac{\lambda_x - \lambda_{\min}}{\lambda_{\max} - \lambda_{\min}} \times 100 \quad (3)$$

Fig. 7 PL spectra of PEAPINP at various P^H values: **a** Excitation spectra, λ_{Em} 306 nm, inset; the changes of PL intensities at 305 nm, **b** emission spectra, λ_{Ex} 247 nm, inset; the changes of PL intensities at 248 nm. Slit: λ_{Ex} 5 nm, λ_{Em} 5 nm



where λ_{\max} is the maximum absorption wavelength at P^H of 10, λ_{\min} is the maximum absorption wavelength at P^H of 6, and λ_x is the maximum absorption wavelength at the test P^H . Figure 4 clearly indicates that EAPINP and its polyphenol derivative have opposite response towards different P^H s. In lower P^H s the response of PEAPINP sharply increases while EAPINP has nearly no response. An opposite behaviour is observed at the higher P^H s; the response of EAPINP increases while the response of PEAPINP is stable.

The color changes of EAPINP and PEAPINP at various P^H s are also shown in Fig. 5. As seen in Fig. 5a at P^H of 7 EAPINP is in the yellow-colored form. When the P^H is increased up to 10 the color changes from yellow to red. That agrees with the spectrophotometric measurements; in the range of P^H 7–10 the absorption edge shifts from 410 nm until 460 nm, which causes color changes and

allows the production of a color-tunable P^H sensor. However, the novel sensor can be used as a color-tunable P^H sensor for only limited P^H values which is suitable in the range of $P^H=7-10$. Some other Schiff base derivatives have been also synthesized as colorimetric sensors in presence of different ions like fluoride [30]. PEAPINP has also similar colors with darker forms in both acidic and basic conditions as seen in Fig. 5b. However, at the lower P^H s, when P^H increased from 6.0 to 7.0 a clearly color change could be observed for PEAPINP while no change is observed for EAPINP. Similarly, in the range of $P^H=8-10$ the color of EAPINP clearly changes while the color of PEAPINP doesn't change, agreed with the spectrophotometric measurements as mentioned above.

Different Schiff base compounds have been previously studied as emission/excitation based P^H probes [31]. Emission and excitation based spectral characteristics of EAPINP are also determined in the P^H range of 6.0–10.0. The results are given in Table 1. The signal changes of emission-excitation spectra of EAPINP are also monitored at different P^H ranges in Fig. 6. EAPINP exhibited the best response between P^H 6.5 and 10.0 in the direction of a decrease in signal intensity at 574 nm and 510 nm in emission and excitation spectra, respectively. Upon exposure to the solutions between P^H 6.5 and 10.0, EAPINP exhibited 92% and 90% relative signal changes in direction of decrease in emission and excitation intensities, respectively. However, fluorescence based spectral changes of EAPINP could not be useful in P^H sensor applications due to its irregular intensity changes.

Emission and excitation based spectral characteristics of PEAPINP are also given in Fig. 7. According to the obtained results, PEAPINP has also opposite response of EAPINP when exposed to different P^H s. For example, PEAPINP has the minimum PL intensities at $P^H=6.5$ while EAPINP has the maximum. Upon exposure to the solutions between P^H 6.5 and 10.0, PEAPINP exhibited 43% and 41% relative signal changes in direction of decrease in emission and excitation intensities, respectively. However, the absence of the linear spectrofluorometric response upon different P^H s makes the polymer un-useful to use as a spectrofluorometric P^H sensor.

Conclusion

A novel Schiff base and its polyphenol derivative (EAPINP and PEAPINP) were synthesized and characterized. Spectrophotometric and spectrofluorometric behaviors of the synthesized compounds were investigated in different P^H values in the range of $P^H=6-10$. Obtained results showed that EAPINP could be used as a sensitive spectrophotometric pH sensor in the range of $P^H=8-9$

while PEAPINP could be used in the range of $P^H=6-7$ depending on their linearly spectral responses. PEAPINP was found to have lower acidity than its monomer compound because of the C-O-C coupling which decreases the phenolic -OH numbers. Resultantly, we demonstrate that due to their available active centers for proton attacks the novel Schiff base and its polyphenol derivative can be used as alternative spectrophotometric P^H sensors for different P^H ranges including 6–7 and 8–9. EAPINP and PEAPINP can be also used as color-tunable P^H sensors in practice. As a result, EAPINP and PEAPINP with their easily and inexpensive productions could be alternative P^H probes.

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