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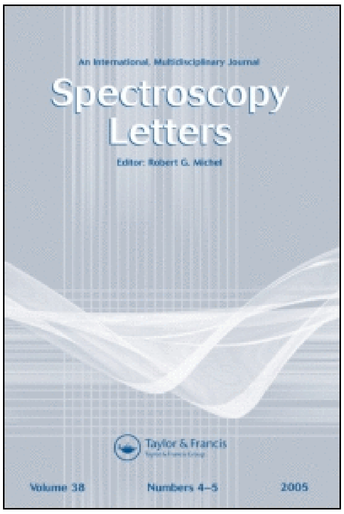

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pH-Driven Fluorescent Switch Behavior of Azometine Dyes in Solid Matrix Materials

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ABSTRACT Photoinduced switch behaviors of two dimethylamino-bearing azometine derivatives (AZM-I and AZM-II) were investigated in conventional solvents, polyvinyl chloride (PVC) and ethyl cellulose (EC) by means of absorption and emission spectroscopy. The fluorescence modulation of the molecular switches arises from increasing response of the exploited molecules to pH between $pH = 6.00$ and 11.00 in emission intensity at 590 and 582 nm. In the employed systems optical or chemical inputs are transduced into detectable spectroscopic outputs after the controlled exchange of protons between solution and membrane phases. In immobilized phases the attained reversible relative signal changes were very good; 97% and 99% for AZM-I and AZM-II respectively. Sensitivities of the molecular switches to most abundant anions and metal cations were also investigated. Except that of bicarbonate, Hg^{2+} and Ag^{+}, presence of anions and metal cations in test medium did not restrict the proton sensing ability of the molecules.

KEYWORDS fluorescence, molecular switch, pH, proton

INTRODUCTION

Studies on molecules that can behave as molecular devices, switches, logic gates, sensors, and molecular level machines have increased rapidly over the past two decades. According to Fu and coworkers molecular scale systems and molecular materials are very promising for electronic, optoelectronic applications and for intelligent materials. The goals of the field are dual. First, is to provide molecular materials for a multitude of electronic applications. Second, is to utilize single molecular scale systems, e.g., a molecule, supermolecule, molecular aggregate or cluster, as electronic devices for the processing of optical, electrical, magnetic, chemical, or biological signals.[1]

Interest of chemists has been focused on second goal. Raymo and co-workers explained the photoinduced proton exchange between molecular switches, which is based on the photoinduced ring closing of a merocyanine to produce a spiropyran with the release of a proton. In this design the liberated proton is captured by either one of two pyridine derivatives with the formation of their conjugate acids. This transformation induced a significant increase in chemical shift for the resonances of the pyridyl protons and also a pronounced color change. The overall process was fully reversible.

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Relying on this mechanism, an optical input is transduced into a detectable spectroscopic output after the controlled intermolecular exchange of protons in solution phase.[2]

Silva et al.[3] employed fluorescent 'off–on–off' proton switches derived from natural products in methanol–water mixtures. Xiao et al. defined a proton-triggered fluorescent switch through direct connection of a proton sponge, 1,8-bis(dimethylamino)naphthalene to a fluorophore; 4-aminonaphthalimide. The molecular fluorescent switch was based on a photoinduced electron transfer (PET) mechanism and exhibited significant fluorescence enhancement upon binding the low concentration protons in water.[4] Tang and Cheng introduced a novel trinuclear Ru(II) polypyridyl complex as a pH-induced molecular switch. Their molecule was functional in acetonitrile-Briton-Robinson buffer (1:1) solution.[5] Delattre and working group characterized photophysical properties of a pH dependent molecular switch; pyridin-4-yl indolizin β-cyclodextrin, in water. They clarified the protonation–deprotonation effects in aqueous solution by absorption, fluorescence, circular dichroism, and NMR spectroscopy experiments at neutral and acidic pH.[6] Shi and coworkers[7] reported synthesis and photophysical properties of "on and off" switchable proton sensors in different organic solvents. Shiraishi and coworkers investigated pH induced spectral response of solvent polarity driven multiply configurable on/off fluorescent indicator; diethylenetriamine bearing pyrene fragments into detail.[8] Röhr et al. reported thiophenyl-substituted boron–dipyrromethene dyes as proton- and redox-controlled switching molecular probes in a variety of solvents.[9]

Results of these studies performed in liquid phase provided valuable information for researchers; however, they remain far from applications in information technology at this stage. The integration of liquid components with solid state optics is not practical and molecule-based solid state approaches employing polymeric media should be developed. In this context, recently, Shiraishi et al.[10] published temperature-driven on/off fluorescent behavior and pH sensing ability of anthracene-conjugated thermo responsive polymer. They attributed the temperature-driven switching of the pH dependent fluorescence intensity profile to the heat-induced phase transition of the polymer from coil to globule.[10]

In another work, Brown and coworkers immobilized anthracene-based, H^+-driven, 'off–on–off' fluorescent switches on organic and inorganic polymeric solids; tentagel and silica. The environment of the organic bead displaced apparent switching thresholds towards lower pH values. These switches were ternary logic gate tags, and are expected to be useful in strengthening molecular computational identification (MCID) of small solid objects.[11] It is obvious that, in photo-electronics, and biomedical or electric engineering**,** production in solid state is advantageous over liquid systems. The outputs of the experimental results acquired from solid-state systems will be more helpful. In this work, we aimed to acquire comparative spectral data from both solvent phase and solid state employing dimethylamino-bearing fluorescent azometine derivatives as pH-driven fluorescent switches.

To our knowledge, the AZM-I and AZM-II were used for the first time as logic gates in plasticized PVC and EC matrices. These dyes have the advantages of long term photostability, high relative signal change, long wavelength absorption/emission capability and high fluorescence quantum yield values in immobilized forms.

Offered azometine dyes are appropriate for use as pH driven fluorescent switches for pH 6.00 and 11.00. Acidity constants of 7.45 and 7.72 (in ethanol) also make them proper for sensing of bicarbonate.

EXPERIMENTAL

Reagents

The polymer membrane components, polyvinyl chloride (PVC) (high molecular weight) and plasticizer, bis(2-ethylhexyl)phthalate (DOP) were obtained from Merck and Fluka. Ethyl cellulose (with an ethoxy content of 46%) and potassium tetrakis(4-chlorophenyl)borate (PTCPB) were from Aldrich. Tetraoctylammonium hydroxide (TOAOH); in the form of 20% solution in methanol was supplied from Fluka.

Absolute ethanol (EtOH), tetrahydrofuran, (THF), dichloromethane (DCM), toluene/ethanol mixture (To:EtOH, 80:20) were of analytical grade. Solvents for the spectroscopic studies were used without further purification. Acid solutions were prepared with hydrochloric acid and potassium chloride (for around pH = 2.0), disodium hydrogen phosphate/citric acid (for around pH = 5.0), potassium dihydrogen phosphate/sodium hydroxide (for around pH = 7.0), and boric acid (H_3BO_3)/potassium chloride (KCl) for alkaline pH in carbon dioxide-free water. Titrations in non-aqueous media were performed with tetrabutylammonium hydroxide (TBAOH) and perchloric acid. Millipore water was used throughout the studies. Solutions of metal cations were prepared from respective metal nitrates, sulphates or chlorides and diluted with 5.0×10^{-3} M buffers of demanded pH. The pH values of the solutions were checked using a digital pH meter (Orion) calibrated with standard buffer solutions of Merck. All the experiments were carried out at room temperature; 25 ± 1°C. Rose Bengal was used as reference standard for quantum yield calculations. The molecules; 4(dimethylamino)-benzaldehyde2-[[4(dimethylamino)phenyl]methylene] hydrazone (AZM-I) and 4-(dimethylamino)benzaldehyde2-[[4-cyanophenyl]methylene]hydrazone (AZM-II) were synthesized in our laboratories according to the literature method and characterized with ^{1}H NMR and IR based data.[12–14]

Schematic structures of the employed molecules, AZM-I and AZM-II were shown in Fig. 1.

AZM-I: IR (KBr): 2909 (C-H), 1598 (C=N) cm^{-1}. ^{1}H-NMR (400 MHz, d_6-DMSO): δ 2.97 (s, 12H, $4 \times CH_3$), 6.66 (d, 4H, J = 8.4 Hz, $4 \times ArH'$), 7.57 (d, 4H, J = 8.8 Hz, $4 \times ArH''$), 8.41 (s, 2H, −N=CH), GC-MS $[M]^+ = 294.3$, mp = 265.2°C.

AZM-II: IR (KBr): 2912 (C-H), 2226 (CN), 1604 (C=N) cm^{-1}. ^{1}H-NMR (400 MHz, d^6-DMSO): δ 2.95 (s, 6H, $2 \times CH_3$), 6.62 (d, 2H, J = 7.6 Hz, $2 \times ArH_1$), 7.56 (d, 2H, J = 8.0 Hz, $2 \times ArH_2$), 7.66 (d, 2H, J = 8.1 Hz, $2 \times ArH_3$), 8.41 (d, 2H, J = 8.2 Hz, $2 \times ArH_4$), 8.47 (s, 1H, −N=CH), 8.54 (s, 1H, −N=CH), GC-MS $[M]^+ = 276.3$, mp = 269.1°C.

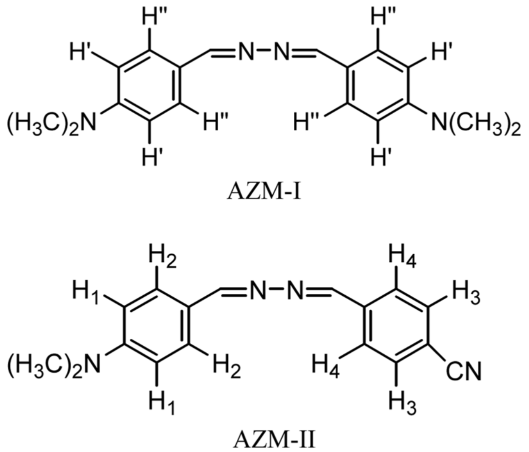

FIGURE 1 Chemical structures of AZM-I and AZM-II dyes.

Instrumentation

Absorption spectra were recorded using a Shimadzu 1601 UV-visible spectrophotometer. Steady state fluorescence emission and excitation spectra were measured using Varian Cary Eclipse Spectrofluorometer with a Xenon flash lamp as the light source.

pH measurements were carried out with fiber optic probe (2 m long) and solid sample tip accessories constructed on the spectrofluorometer. For instrumental control, data acquisition and processing the software package of the spectrofluorometer was used. The tip of the bifurcated fiber optic probe was interfaced with a sensing film in a buffer containing homemade 300 µL flow cell. The flow cell was equipped with a four channel Ismatec Reglo Analog peristaltic pump. Flow rate of the peristaltic pump was kept at 2.2 mL min^{-1}. Analyte solutions or buffers were transported with the peristaltic pump via tygon tubing of 2.06 mm i.d. Schematic structure of the instrumental set-up was published earlier.[15]

Thin Film Preparation Protocols

PVC based thin membranes were prepared to contain 120 mg of PVC, 240 mg of plasticizer (DOP), 1.2 mg of AZM-I or AZM-II (2.5 mmol dye/kg polymer), stoichiometric amount of potassium tetrakis (4-chlorophenyl) borate and 1.5 mL of THF. The prepared cocktails contained 33% PVC and 66% plasticizer by weight.

Ethyl cellulose based cocktails were prepared from 1.0 g of a 5% ethyl cellulose solution in ethanol/toluene (20/80, v/v) and by addition of 2.0 mg of the AZM-I or AZM-II dyes. During bicarbonate sensing studies this solution was mixed with 100 µL of the methanolic TOA-hydroxide solution. The TOA-OH solution was previously equilibrated with a CO_2/N_2 gas mixture (CO_2 content 3%) in order to form a lipophilic hydrogen carbonate buffer.

In all cases, the resulting cocktails were spread onto a 125 µm polyester support (MylarTM). The film thicknesses of the dried sensing slides were measured with Tencor Alpha Step 500 prophylometer and found to be 5.72 ± 0.12 µm ($n = 15$). The employed polyester support was optically fully transparent, ion impermeable and exhibited good adhesion to PVC and EC. Each sensing film was cut to 1.2 cm × 3.0 cm size, fixed diagonally into the

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sample cuvette and the excitation and fluorescence emission spectra were recorded. For flow through measurements, the sensor films of 30 mm diameter were cut, placed into the buffer containing 300 μL black-Teflon flow cell and interfaced with the fiber tip (6 mm diameter). The contact between the sensor membrane and the buffer provided a constant fluorescence signal. pH determinations were carried out pumping buffer solutions of desired pH.

RESULTS AND DISCUSSION

Spectral Characterization

Absorption spectra of the AZM-I and AZM-II dyes were recorded in the solvents of ethanol, DCM, THF, toluene/ethanol (To:EtOH; 80:20) mixture and in solid phases of PVC and EC. The absorption spectra and absorbance related data of the employed compounds were shown in Fig. 2, Fig. 3, and Table 1.

The AZM-I dye exhibited one intensive absorption maximum around 391 nm in ethanol, DCM, THF and in To:ETOH mixture. When doped into PVC and EC, the basic form of AZM-I yielded absorption maxima of 392 nm and 398 nm, respectively. In acidic environments the absorption maxima were shifted to 500 nm and 488 nm for PVC and EC, respectively.

The UV-vis spectra of AZM-II dye exhibited double efficient absorbance bands and high molar extinction coefficients around 311 and 394 nm in the employed solvents (see Table 1). In PVC and EC, absorption bands of AZM-II appeared at 394/496 and 390/494 nm, respectively.

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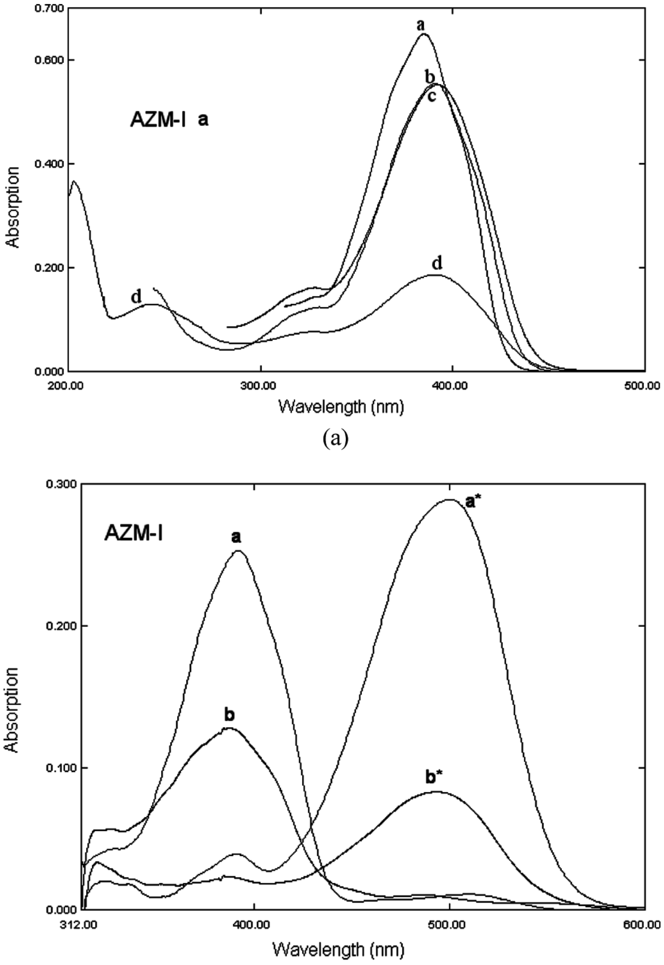
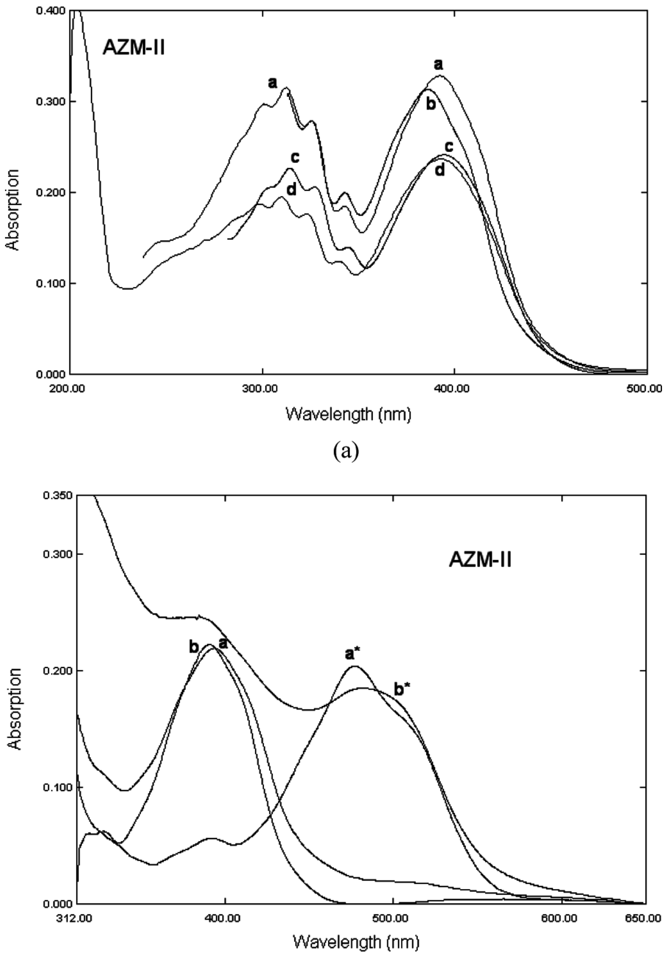


(a)

(b)

FIGURE 2 Absorption spectra of the AZM-I dye (10^{-6} M dye or 2 mM dye/kg polymer). AZM I-a a) THF b) DCM c) To:EtOH d) EtOH; AZM I-b a) PVC (basic) a*) PVC (acidic) b) EC (basic) b*) EC (acidic).



(a)

(b)

FIGURE 3 AZM-II a: a) DCM b) THF c) To:EtOH d) EtOH; AZM-II b: a) PVC (basic) a*) PVC (acidic) b) EC (basic) b*) EC (acidic).

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TABLE 1 **UV-Vis Spectra Related Data of AZM-I and AZM-II in the Solvents of EtOH, DCM, THF and Toluene/Ethanol Mixture (80:20) and in Solid Matrices of PVC and EC**

Compound	Matrix	λ^1_{abs}	λ^2_{abs}	$\epsilon_{\max}$ (λ^1_{abs})	$\epsilon_{\max}$ (λ^2_{abs})
AZM I	EtOH	243	391	12900	18600
AZM I	DCM	244	391	15800	55200
AZM I	THF		385		65000
AZM I	To:EtOH		391		55200
AZM I	PVC	392 (basic)	500 (acidic)	107000	108544
AZM I	EC	388 (basic)	488 (acidic)	96045	84100
AZM II	EtOH	310	394	19500	23600
AZM II	DCM	312	393	31500	32800
AZM II	THF		387		38300
AZM II	To:EtOH	314	395	22600	24100
AZM II	PVC	394 (basic)	496 (acidic)	41030	40846
AZM II	EC	390 (basic)	494 (acidic)	32165	26372

Differences between the absorption bands of AZM-I and AZM-II can be attributed to the structural properties of the dyes. While AZM-I having a symmetrical structure with two electron-donating $-N(CH_3)_2$ groups at both ends, the AZM-II has one electron-donating $-N(CH_3)_2$ group at one end and one electron-withdrawing group; $-CN$ at the other side which enhances electronic shift in a conjugated electron-rich system.

Fluorescence Quantum Yield Calculations

The azomethine dyes; AZM-I and AZM-II were excited at 505/590 and 510/582 nm in PVC and EC respectively (see Table 2). Fluorescence quantum yield values (φF) of the AZM-I and AZM-II were calculated employing comparative William's method in ethanol and PVC, which involves the use of well-characterized standards with known (φF) values.[16] For this purpose, the absorbance and corrected emission spectra of different concentrations of reference standard Rose Bengal ($\lambda_{ex} = 525$ nm, quantum yield (φF) = 0.11 in alkaline ethanol) and the employed molecules were recorded, and, the integrated fluorescence intensities were plotted versus corresponding absorbances. The gradients of the plots were proportional to the quantum yield of the studied molecules. Quantum yield (φF) values were calculated according to the following equation

TABLE 2 **Spectral Characterization of AZM-I and AZM-II dyes**

Compound	Matrix	λ^{ex}_{ex}	λ^{em}_{ex}	$\Delta\lambda_{ST}$ (Stoke's shift)	f_F (Quantum yield)
AZM I	EtOH	422	473	53	4.2×10^{-3} in EtOH
AZM I	DCM				
AZM I	THF	422	466	44	
AZM I	To:EtOH	422	469	47	
AZM I	PVC	505	590	85	0.4290
AZM I	EC	505	580	75	0.2336
AZM II	EtOH	415	473	58	1.9×10^{-3} in EtOH
AZM II	DCM	400	454	54	
AZM II	THF	420	480	60	
AZM II	To:EtOH	410	468	58	
AZM II	PVC	510	582	72	0.4153
AZM II	EC	500	572	72	0.3805

$\lambda^{ex}_{\max}$ = maximum excitation wavelength in nm; $\lambda^{em}_{\max}$ = maximum emission wavelength in nm; $\Delta\lambda_{ST}$ = Stoke's shift and $(_F$ = Quantum yield.

where ST and X denote standard and sample, respectively. Grad is the gradient from the plot and n is the refractive index of the solvent or polymer matrix material.[16]

$$\phi_X = \phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right) \times \left(\frac{n_x^2}{n_{ST}^2}\right) \qquad (1)$$

The AZM-I dye displayed enhanced fluorescence emission quantum yield (φF); 0.4290 and longer excitation wavelength $\lambda_{ex} = 505$ nm in immobilized PVC with respect to (φF) of 4.2×10^{-3} and $\lambda_{ex} = 422$ nm, in ethanol (see Table 2). The comparatively small ΦF values reported in ethanol can be attributed to the internal charge transfer (ICT) state by rotation of the central N–N bond and a following radiationless deactivation. The enhancement observed in fluorescence emission quantum yield of AZM-II can be explained in the same way. In all of the employed matrices, Stokes' shift values were high enough and extended from 47 to 85 nm. Stokes' shift is an important parameter for fluorescence and optical sensor studies because the high Stokes' shift value allows the emitted fluorescence photons to be easily distinguished from the excitation photons. Stokes' shift exceeding 30 nm is recommended for easy visualization and sensitive detection. The Stokes' shifts of AZM-I and AZM-II which are 85 nm and 72 nm in PVC matrix, respectively, permit the usage of azometine dyes in together with solid-state optic components such as LEDs or fiber optics.

Acid–Base Behavior of the AZM Derivatives in Ethanol

The AZM derivatives contain available active centers for proton attacks. Possible protonation-deprotonation route and following electronic shifts of the AZM derivatives were shown in Fig. 4. On the other hand the knowledge of acidity constants (pKa) of AZM derivatives is of fundamental importance in order to provide information on chemical reactivity range of the dyes. For this reason, the absorption and emission based pH induced response of AZM-I and AZM-II were investigated in ethanol.

Fluorescence spectra of **AZM-I** in ethanol between pH 4.7 and 8.9 and related emission based sigmoidal response (pH versus $(I - I\mathrm{o})/I\mathrm{o}$) were shown in Fig. 5. pH measurements were performed with commercially available pH electrodes for non-aqueous media.

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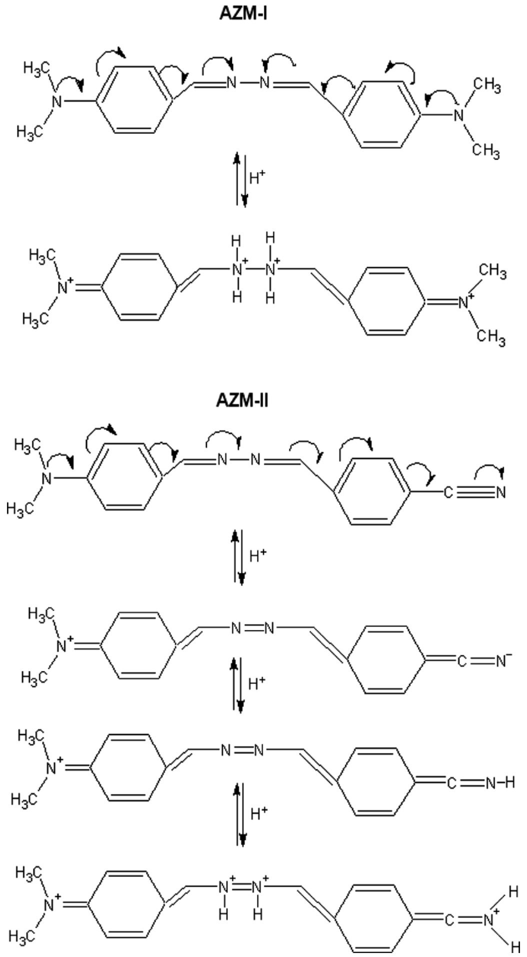

FIGURE 4 Protonation–deprotonation equilibria of azometine dyes; AZM-I: 4(dimethylamino)benzaldehyde2-[[4(dimethylamino) phenyl]methylene]hydrazone and AZM-II: 4-(dimethylamino) benzaldehyde2-[[4-cyanophenyl]methylene]hydrazone.

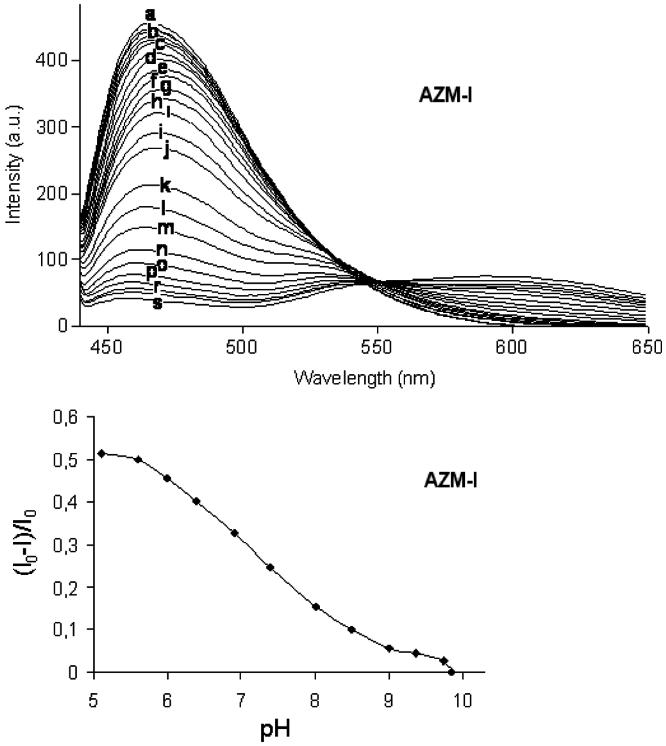

FIGURE 5 pH dependent emission spectra of 10^{-5} M AZM-I in EtOH between pH 8.9 and 4.7 a: pH = 8.98, b:8.62, c:8.27, d:8.12, e:7.80, f:7.67, g:7.47, h:7.18, I:7.02, I: 6.75, J; 6.38, k: 6.17, l: 6.04, m:5.88, n:5.62, p:5.4 s: 4.7) Excitation wavelength; 422 nm emission wavelength; 473 nm.

The acidity constants were calculated via the following equation;

$$\mathrm{p}K_\mathrm{a} = \mathrm{pH} + \log[(I_x - I_\mathrm{b})/(I_\mathrm{a} - I_x)] \qquad (2)$$

where I_a and I_b are the signal intensities of the dyes in their acid and conjugate base form respectively.[17] The pKa values were found to be 7.45 and 7.72 for AZM-I and AZM-II in ethanol, respectively. Since the emloyed dyes are nonsoluble in water, it is nearly impossible to assess their acid-base characteristics in known water-solvent systems and a known pH scale. It is a well known fact that, the pH scale in non-aqueous media is governed by the autoprotolysis or autodissociation constant of the solvent.

Ethanol provides a pH scale between 0–20 ($K_0 = 10^{-19.8}$) where a pH less than 10 is acidic and a pH greater than 10 is basic. The calculated pKa values ranging from 7.45 to 7.42 reveal that the AZM dyes can measure the pH with a high resolution in near neutral region in ethanol. Both of the AZM dyes exhibited a ratiometric but irreversible response to H^+ ions in the ethanol. Due to the observed irreversible response, the potential of AZM molecules as optical switches for the potential realization of artificial functions at the molecular level was not explained in the solution phase.

Acid–Base and Molecular Switch Behavior of the AZM Derivatives in PVC Matrix

Understanding of the switching behavior and indicator chemistry in solid-state is important to transfer the switching mechanisms to miniaturized molecule-based solid-state devices.

The AZM derivatives become reversibly working H^+ selective molecular probes when doped into plasticized PVC together with the anionic additive; potassium tetrakis-(4-chlorophenyl) borate. In these systems, H^+ ions are extracted into the optode membrane by the anionic additive, meanwhile, potassium ions diffuse from the membrane into the aqueous phase according to the mechanism of ion-exchange. The first-step of response mechanism of AZM derivatives can be explained by the following ion-exchange pathways. Following this; successive and fast protonation steps occur (see Fig. 4).

$$\begin{aligned} &\mathrm{AZM(org)} + \mathrm{K^+(org)} + \mathrm{TpClPB^-(org)} + \mathrm{H^+(aq)} \\ &\quad \leftrightarrow \mathrm{AZMH(org)^+} + \mathrm{TpClPB^-(org)} + \mathrm{K^+(aq)} \qquad (3) \end{aligned}$$

Figures 6 and 7 reveal pH dependent absorption and emission response of PVC doped AZM-I and AZM-II upon exposure to solutions between pH 6.00 and 11.00.

Both of the dyes exhibited "S" shaped spectrophotometric titration curves with one inflection point. The p*K*a values of AZM-I and AZM-II were found to be 9.08 and 9.11 in PVC, respectively. Stepwise protonation of inner azometine nitrogens are likely very close so one pKa value found belong to these. Similarly, competing protonation of azometine and nitrile nitrogens of AZM-II, results with one well shaped distinct inflection point (see Fig. 7). The lack of a second observable inflection point for AZM dyes is attributable to rapid protonation-deprotonation equilibria.

Due to the observed reversible response, the potential of AZM molecules as optical switches at the molecular level was evaluated. The optical and chemical inputs addressing the AZM derivatives modulate the absorption and emission intensities of the molecules. Relying on these operating principles, we have reproduced the functions of regarding logic circuits. Figures 8 and 9 reveal the optical and chemical inputs and absorption/emission based switching principles of PVC doped AZM dyes.

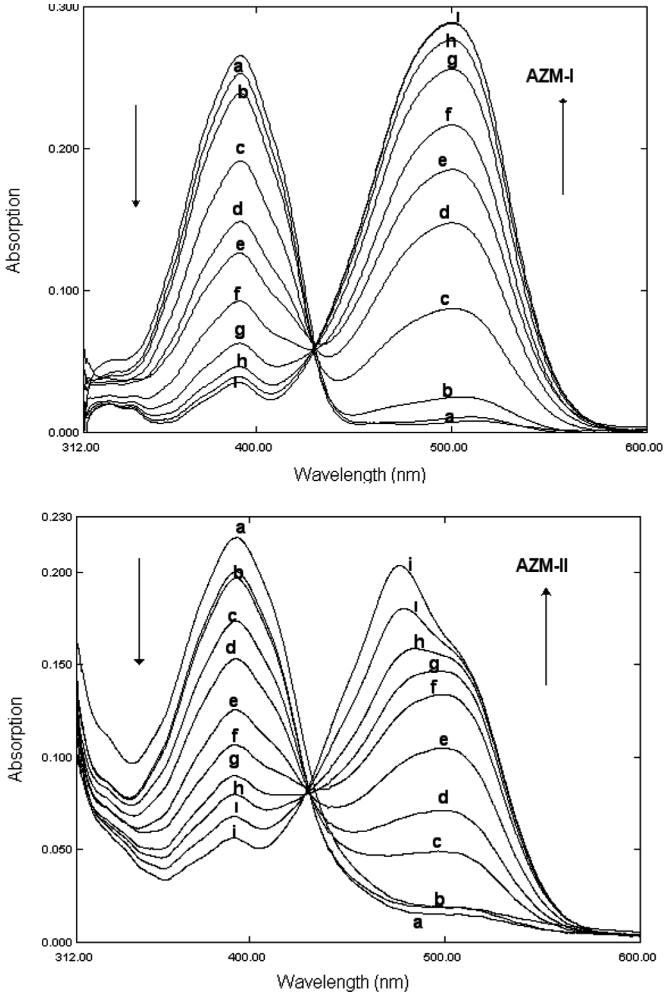

FIGURE 6 **Absorption spectra of AZM-I and AZM-II (2 m mol dye/kg polymer) in PVC after addition of acid solutions in the pH range of 6.00 to 11.00 pH: a) 11.00, 10.50, b) 10.00, c) 9.50, d) 9.00, e) 8.50, f) 8.00, g) 7.50, h) 7.00, ı) 6.50, 6.00.**

Under the influence of a chemical input (varying pH between 6.00 and 11.00) AZM-I yielded two different optical outputs; an increasing absorption intensity upon protonation at 500 nm and a decreasing absorption intensity at 392 nm. The spectroscopic output at 500 nm switches to a high value when the concentration of H^+ (chemical input) is high (**1**) (See Fig. 8a). It reverts to a low value when the concentration of H^+ is low (**0**). In a contrast manner,

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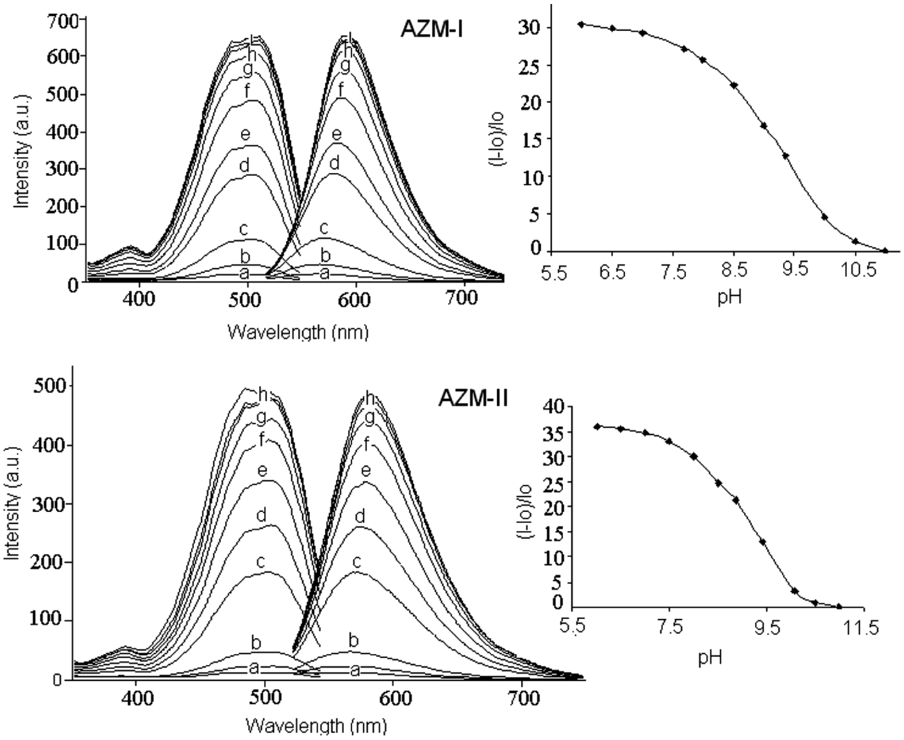

FIGURE 7 pH induced emission based spectral response of the thin film form of PVC doped *AZM-I* in the pH range of 11.00 to 6.00. pH: a) 11.00, b) 10.50, c) 10.00, d) 9.50, e) 9.00, f) 8.50, g) 8.00, h) 7.50, ı) 7.00, 6.50, 6.0 and *AZM-II* in the pH range of 11.00 to 6.00. pH: a) 11.00, 10.50 b) 10.00 c) 9.50 d) 9.00 e) 8.50 f) 8.00 g) 7.50 h) 7.00, 6.50, 6.00. Excitation/emission wavelengths; 505/590 nm, and, 510/582 nm for AZM-I and AZM-II, respectively. Inset: pH dependent titration curves of AZM-I and AZM-II.

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the spectroscopic output at 392 nm switches to a high value when the concentration of H^+ is low (**1**) and a low value when the H^+ is high (**0**).

Molecular switch behavior of AZM-II is very similar (see Fig. 8b) and the both logic gates shown in Fig. 8 can be concluded as "NOT" gates or "inverter" gates.

Figures 9a and b, reveal excitation-emission based molecular switch behavior of PVC doped AZM-I and AZM-II respectively. Under the influence of two different inputs (a chemical input; varying pH between 6.00 and 11.00 and an optical input; excitation at 505 nm) AZM-I exhibited two different optical outputs; a varying emission intensity at 590 nm and an excitation intensity at 505 nm (see Figs. 7 and 9). The spectroscopic output at 590 nm switches to a high value when the pH is in the range of 6.0 to 7.5 (**1**). (see Fig. 9a). It reverts to a low value when the pH is in the rage of 10.00 to 11.00 (**0**). The 0 and 1 positions of the spectroscopic output observed at 505 nm were parallel to the responses of the output of 590 nm. (see Fig. 9a). Except that of slight changes observed in the excitation/emission wavelengths or relative signal changes, the switch behavior of the AZM-II in PVC was parallel to the AZM-I. Both logic gates shown in Fig. 9 can be concluded as "NOT AND" gates.

As a result, a chemical input or a combination of chemical and optical inputs can modulate an optical output on the basis of ion exchange dependent protonation–deprotonation equilibrium. These processes can be monitored by visible absorption or emission spectroscopy, following the absorbance/emission changes associated with the bands of the protonated and deprotonated forms. Furthermore, photoinduced protonation–deprotonation reactions, are fast enough and equilibrium state can be established within minutes in the employed solid matrices. These results demonstrate that such simple reactions can be coupled with solid state optics and with microfludics to transduce incoming chemical inputs to well defined spectroscopic outputs.

Acid–Base and Molecular Switch Behavior of the AZM Derivatives in EC Matrix

The AZM dyes exhibited very similar absorption and emission based spectral response to proton ions

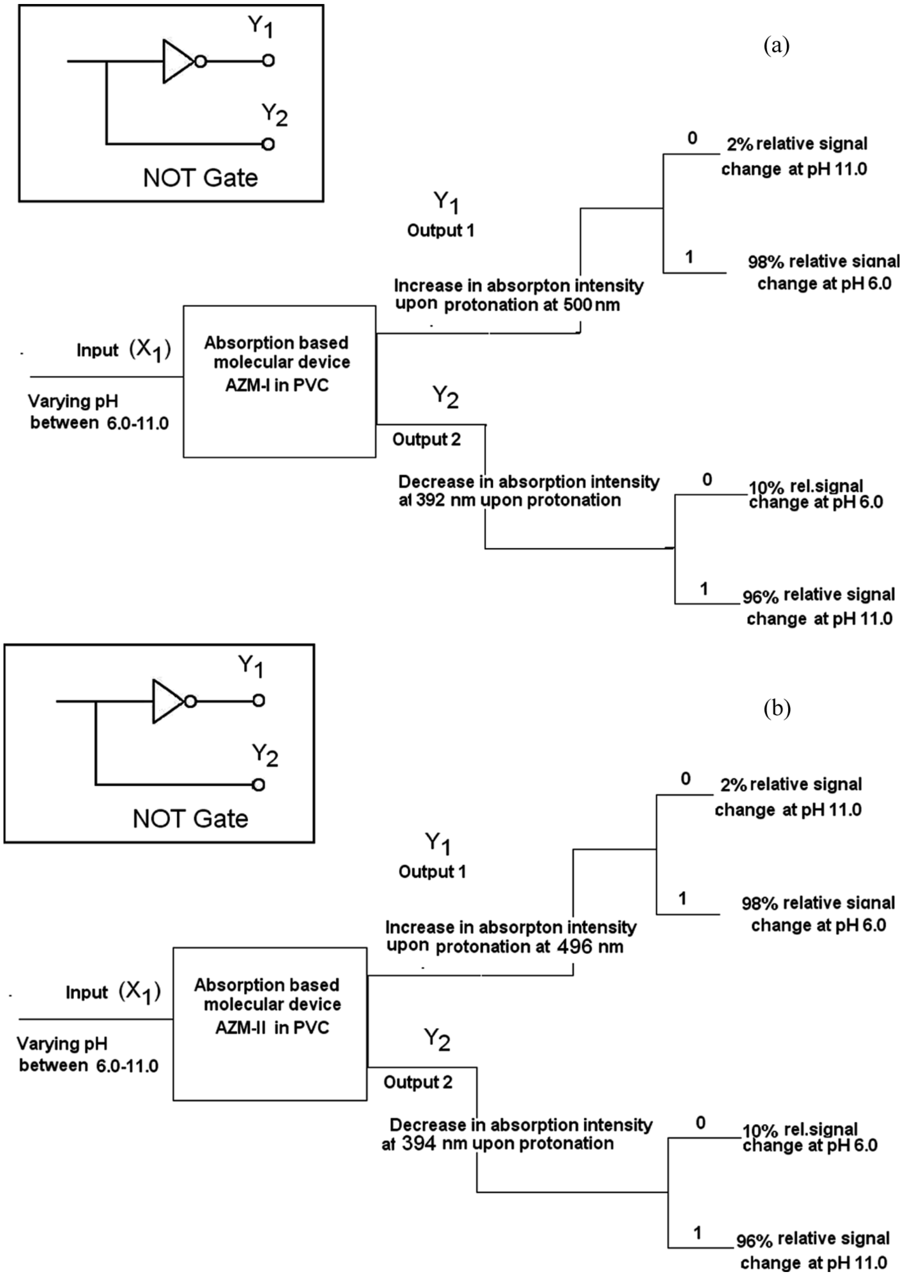

FIGURE 8 Modulation of the absorption intensities of PVC doped molecular devices; AZM-I and AZM-II by chemical inputs and their operating principles.

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when doped into EC matrix. The EC doped AZM-I and AZM-II exhibited a parallel increase both in emission and excitation intensity after exposure to different concentrations of solutions in the pH range of pH = 6.00 to 11.00. In EC doped films the pK_a values of AZM-I and AZM-II were found to be 7.74 and 7.51, respectively. Figure 10 shows pH induced emission/excitation based spectral response of the EC doped AZM dyes in the pH range of 6.00 to 11.00. The similarities of spectral response of AZM dyes to pH in PVC and EC can easily be understood from a comparison of Figs. 7 and 10. Molecular switch behaviors of AZM-I and AZM-II in EC are very close to the behaviors observed in PVC. Same logic gate schemes were obtained for EC doped AZMs. However, they are not shown in this article.

Reproducibility of the Response

The sensing slides were found to give reversible and reproducible results on absorption and fluorescence emission measurements when pH was varied

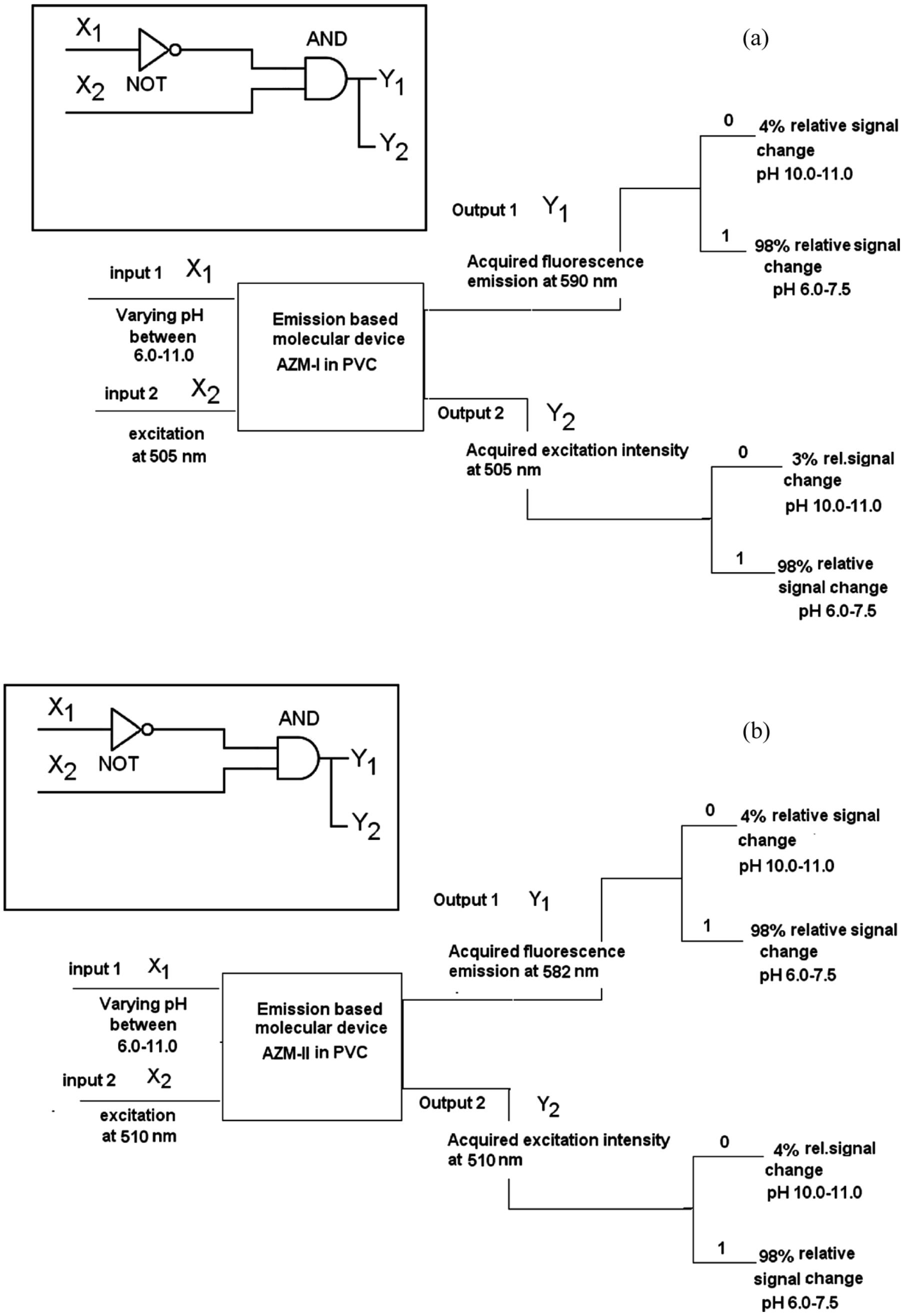

FIGURE 9 **Modulation of the emission intensities of PVC doped molecular devices; AZM-I and AZM-II by chemical and optical inputs and their operating principles.**

within the dynamic working range. The response of PVC and EC doped AZM-I and AZM-II to pH was investigated in buffered solutions. Regeneration was accomplished with concentrated buffer solutions at opposite pH values. Figure 11 shows the relative signal change, and reversibility performance of the PVC doped AZM-I and AZM-II. The EC doped dyes exhibited very similar response to pH.

The reproducibility of the AZM-I was assessed by repeatedly introducing a sample of pH 11.00 and 6.00. The AZM-I was found to reach 90% of the signal intensity (τ_{90}) within 1.0 to 3.0 min. between the first and third cycles, the level of reproducibility of the upper signal level was quite good with a S.D. of 280 ± 2. The reproducibility performance of AZM-II was also quite good except that the relatively longer response times in the alkaline region (see Fig. 11). The response time can be improved by adjusting the film thickness of sensing slides and flow rate of buffer solutions. In our case, film thickness was

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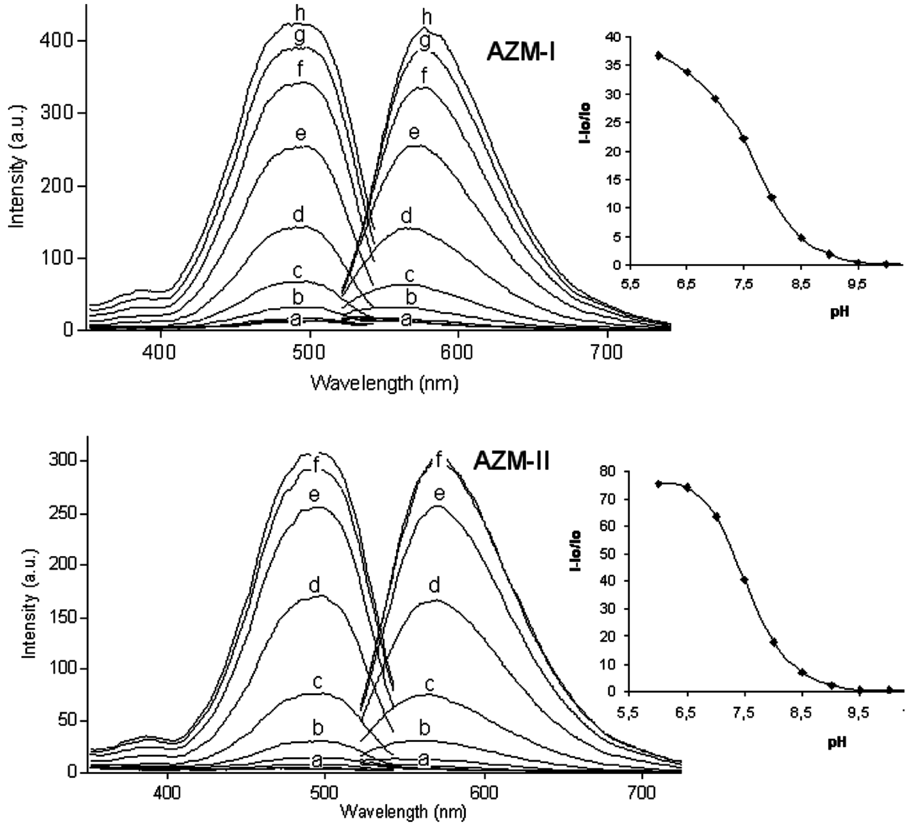

FIGURE 10 pH induced emission based spectral response of the EC doped AZM-I and AZM-II in the pH range of 6.00 to 11.00. pH: a) 11.00, 10.50, 10.00, 9.50 b) 9.00 c) 8.50 d) 8.00 e) 7.50 f) 7.00 g) 6.50 h) 6.00. Excitation/emission wavelengths; 505/580 nm, and, 500/572 nm for AZM-I and AZM-II, respectively. Inset: emission based sigmoidal response of AZM-I and AZM-II to pH.

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found to be approximately 5 μm. The film thickness can be reduced and shorter response times can be reached.

Cross Sensitivity to Anions, Metal Cations and Effect of Ionic Strength

The variations in fluorescence intensities at 590 and 582 nm in the presence of NO_3^-, ClO_4^-, AcO^-, $C_2O_4^{2-}$, HCO_3^-, and SO_4^{2-} were tested with 10^{-3} M solutions of the anions in separate solutions for both of the dyes. The cross-sensitivities of the AZM dyes to Na^+, K^+ and many polyvalent metal ions (Zn^{2+}, Hg^+, Hg^{2+}, Sn^{2+}, Ca^{2+}, Bi^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+} and Fe^{3+}) were also investigated in phosphate or acetic acid/acetate buffered solutions at pH 7.00 or pH 5.50.

Results were evaluated in terms of relative signal changes (RSC); $(I-I_o)/I_o$, where I was the fluorescence intensity of the sensing membrane after exposure to ion-containing solutions and I_o is the fluorescence intensity of the sensing slide in ion-free buffer solution. Only the HCO_3^-, induced fluorescence bands of AZM dyes exhibiting a RSC ratio of 80%.

The fluorescence was dramatically quenched in presence of Hg^{2+} and Ag^+ at 590 nm exhibiting a RSC ratio of 76% and 70%. Other alkali, alkaline earth, and transition metal ions produced insignificant responses where RSCs ranged from 0.02 to 0.28.

The effect of ionic strength on the PVC doped AZM derivatives was tested in 135 mM NaCl containing 5.0×10^{-3} M phosphate buffer which covers the physiologically important salinity level. The p*K*a values of PVC doped AZM-I and AZM-II were found to be 9.35 ± 0.07 and 9.17 ± 0.04, respectively. In clinically important salinity levels, the p*K*a of AZM-I exhibited an increase of 0.27 p*K*a units with respect to its original value but the p*K*a of AZM-II was not affected.

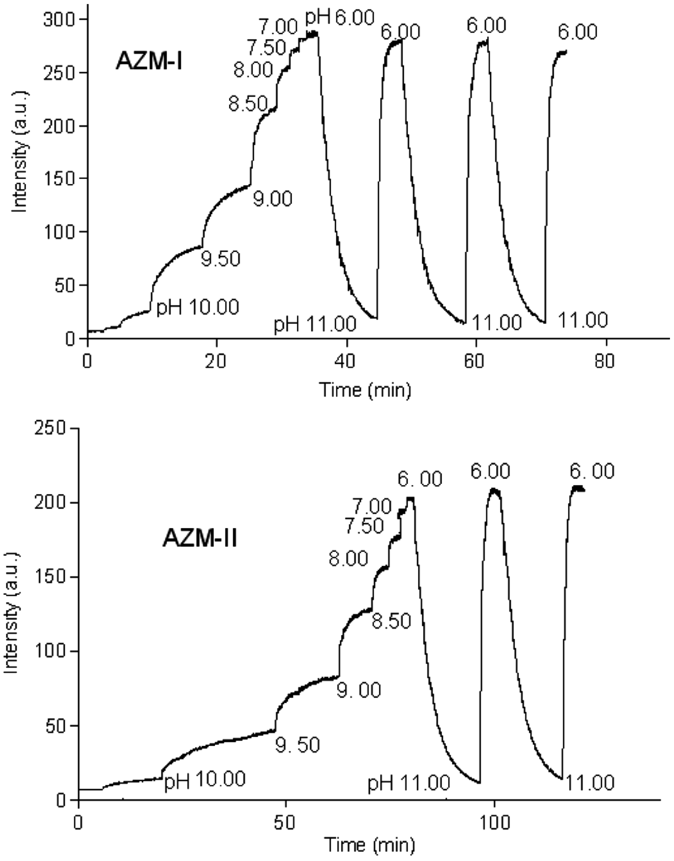

FIGURE 11 **Response curve and regeneration performance of PVC doped AZM-I and AZM-II. Data were acquired with fiber optic probe which is in contact with flow system.**

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CONCLUSION

There are only a limited number of fluorescent "proton-driven" molecular switches available covering the neutral-alkaline pH region. We demonstrate that, the AZM derivatives; with fast switching speeds; contain available active centers for proton attacks and are appropriate for use as fluorescent pH probes between pH 6.00 and 11.00. The p*K*a values of 7.74 and 7.51 and large dynamic working range make the EC-doped AZM molecules promising indicators for dissolved CO_2 sensing in environmental and physiological samples. The compatibility of the employed molecules with the solid-state optical components (in particular LED's emitting in the wavelength range of 500 to 510 nm) and fiber optics can be useful in construction of inexpensive and miniaturized field available instrumentation. The most notable source of interference to the pH sensitivity of AZM-I and AZM-II is the quenching of the excited state by the cations of Hg^{2+}, Bi^{3+} and Ag^{+} at neutral or slightly acidic pHs.

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