

Optical Sensor for Aliphatic Amines Based on the Simultaneous Colorimetric and Fluorescence Responses of Smart Textile

Desislava Staneva,¹ Rositza Betcheva,¹ Jean-Marc Chovelon²

¹Department of Textile, University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

²Laboratoire d'Application de la Chimie à l'Environnement, University of Claude Bernard—Lyon 1, CNRS-UMR 5634, 69622 Villeurbanne Cedex, France

DOI 10.1002/app.26724

Published online 20 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The pH indicator proposed is a water-soluble dye based on benzo[de]anthracen-7-one. Dissolving in buffered aqueous solution, it changes color from yellow to orange and in the mean time decreases its fluorescence emission as a function of the amine concentration. Viscose fabric, dyed with the same dye has been investigated as a new reversible colorimetric and fluorescent sensor material for ammonia and aliphatic amines in buffered solution. The high value of the dye pK_a and the influence of the textile matrix on the selective detection of dimethylamine compared to ammonia, trimethylamine, and methylamine have been studied. The different response of the solution

and textile matrix as well as the optical analyses both as a color change and a fluorescence emission have been discussed. The advantage of this sensor is the fact that depending on the analytical problem to be solved and the available instrumentation it can be used either as a fluorogenic or as a chromogenic chemosensor. In addition, the textile sensor is characterized by facile fabrication, low cost, sensibility, and reproducibility. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1950–1956, 2007

Key words: optical sensor; amines; benzo[de]anthracen-7-one dye; smart textile; stimuli-sensitive polymer

INTRODUCTION

Amines and ammonia are used for the preparation of colorants, medicines, surfactants, catalysts, pesticides, polymers, etc. They are toxic both in the gas phase and dissolved in liquids. A variety of sensors have been developed for their determination in environmental, industrial, food, biological, and clinical samples. One of the sensing principles for the detection of ammonia and aliphatic amines is the optical-sensing method, which is based on the pH indicator dyes, solvatochromic dye,¹ metal complexes,² chromo- and fluororeactants,³ the hydrogen bond generation,⁴ ligand exchange,⁵ Berthelot indophenol reaction,⁶ etc. An indicator displays changes in its optical properties, such as absorbance or fluorescence intensity, upon interacting chemically or physically with the analyte of interest.

In the case of the pH indicator ammonia or amines react with the protonated dye and give an ammonium ion and the deprotonated dye.⁷ The pK_a values of the dyes are important for the sensor characteristics as sensitivity, response time, and the position of the dynamic measuring range.^{8,9}

Immobilizations of dyes on the different matrices^{2,4,9,10} are used for developing reusable and relatively stable materials for highly sensitive and real-time analyses. In most cases, this deposition is long, multistage, and expensive. However, dyeing of textile with suitable indicator dyes is a very simple and cheap process to produce an optical sensor for amines. Textile is flexible, soft, lightweight, breathable, robust, and washable. In our previous studies, we have already used textiles as solid-state carriers of smart dyes as sensors for metal ions and protons.^{11,12}

There are data showing that the matrix sets a certain microenvironment and polarity for the dye and influences the sensing process.^{4,10,13} Textile can also play an active role in the detection of amine and ammonia. The dyed fabric responding to external factors (pH value, moisture or solvents content, electromagnetic radiation, etc.) by changing or producing a color belongs to chromic materials.¹⁴ Combination between the traditional properties of textile and sensors ones leads to a next generation of smart (intelligent) materials with new application opportunities. These colored active textiles can be used as sanitary textiles, indicating the presence of various substances in urine, etc.¹⁵ Solvatochromic chameleon clothing for public safety officials or workers in the chemical industry¹⁶ is capable of environmental monitoring and detecting a nearby spillage.^{17,18}

Correspondence to: D. Staneva (stanevagr@yahoo.com).

Recently, we have reported the synthesis of a novel pH indicator dye based on benzo[de]anthracen-7-one. This dye has been investigated as a colorimetric¹⁹ or fluorescent²⁰ pH sensor in aqueous solution and immobilized on a textile viscose matrix. The new dye possesses as an advantage a higher pK_a value than other pH dyes (aminofluorescein,¹³ bromocresol green,²¹ acridine orange,²² and naphtholsulphonate²²) used for the detection of ammonia and aliphatic amines and has good spectral properties (the absorption and fluorescence maxima in the visible range). The combination of changes in both fluorescence and color of the indicator dye in the same pH region can be used for the investigation of colored solutions such as wine, beer, synthetic resin, essential oils, surfactants, plant, and soil extract.²³

The choice of a textile material as an active matrix is important for the sensing process. Viscose fibers compared to the other cellulose fibers possess a higher degree of swelling in aqueous solution. Thus, dissolved in water ammonia and amines diffuse easier to receptor of the dye.

The aim of this work is to study a viscose fabric dyed with a pH indicator dye based on benzo[de]anthracen-7-one as a sensor material for ammonia and aliphatic amines in aqueous solution. The detected substances are ammonia, trimethylamine (TMA), methylamine (MA), and dimethylamine (DMA) because pK_a of the benzo[de]anthracen-7-one dye is between the pK_a values of their corresponding acids. This allows their selective detection. The comparison between the response of the solution and textile matrix as well as between the two optical analyses as color change and fluorescence emission also deserves studying.

EXPERIMENTAL

Chemicals and sensor fabrication

Ammonium chloride and amines (MA, DMA, and TMA) were used as obtained from Aldrich. Amine and ammonia solutions 0.1 mol L^{-1} were prepared by dissolving the appropriate amount of the respective amine and ammonium chloride in distilled water. All measurements are accomplished in 0.1 mol L^{-1} sodium phosphate buffer of pH 8.0. Distilled water was used for all measurements and solutions.

1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbonyl)-methyl]-pyridinium chloride (BD) (Fig. 1) and the dyeing of the commercial viscose fabric were prepared according to previously described procedures.¹⁹

Analysis

All solution absorption measurements were performed using a UV-vis Double Beam Spectrophotom-

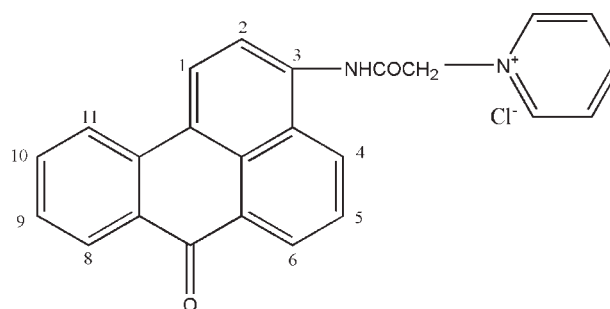


Figure 1 Chemical structure of 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbonyl)-methyl]-pyridinium chloride (BD).

eter Uvikon 930 at $10^{-5} \text{ mol L}^{-1}$. The fluorescence spectra were taken on a FP-6500 Jasco Spectrofluorometer at $10^{-5} \text{ mol L}^{-1}$. The viscose fabric sample was placed diagonally into the quartz cuvette (filled with buffer solution at known concentration of ammonia or amine) to improve the reproducibility of the fluorescence measurements.

The color characteristics of the fabrics were determined on a Texflach ACS/DATACOLOR with a Spectraflash 600 spectrophotometer.

The FTIR spectra were recorded on a Bruker IFS-113v spectrometer at a 2 cm^{-1} resolution using KBr pellets.

The pH values of the solutions were measured with a pH-meter LPH33OT, Solea-Tacussel electronics.

The equilibrium constants K for the reaction of amines and ammonia with BD in the textile matrix were calculated, using the equation³:

$$I = (K I_{\min} c_{\text{amine}} + I_{\max}) / (1 + K c_{\text{amine}}) \quad (1)$$

where I is the fluorescence intensity at defined amine concentration c_{amine} , while I_{\min} and I_{\max} are the fluorescence intensities of the deprotonated and the protonated form of BD.

RESULTS AND DISCUSSION

Optical properties of the indicator dye, exposed to different concentration of aqueous DMA solutions

BD is a pH sensitive water-soluble dye, which responds to alkaline medium (pH > 10.0) with a simultaneous color change from yellow to orange-red-dish and quenching of the fluorescent emission.^{19,20} These properties enable it to sense bases such as amines and ammonia. pH 8.0 of the aqueous solution has been selected as the optimum pH value for monitoring the amount of amines and ammonia in unknown sample. At this pH, the spectrum of BD in its protonated form has an absorbance maximum at 412 nm and fluorescence emission at 553 nm, both of

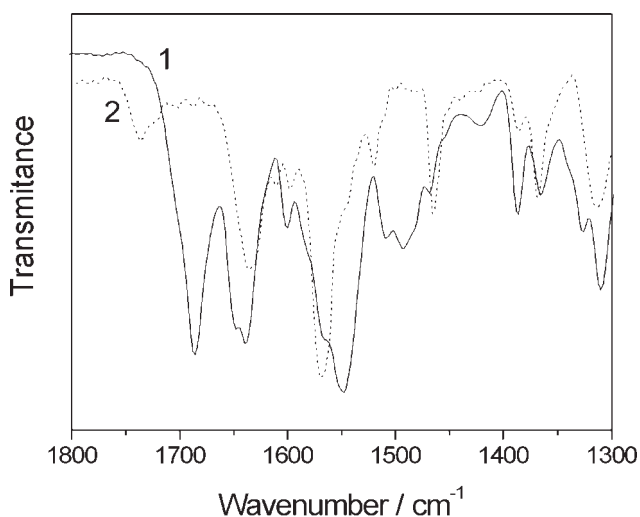


Figure 2 Infrared spectra of the BD in protonated (1) and deprotonated (2) form.

high intensity. Amines and ammonia are presented in their electrically neutral form along with the ammonium form. The correct amine and ammonia concentrations have been calculated using the Henderson–Hasselbach equation and the pK_a value of each amine, at pH 8.0 and 25°C.⁸

The deprotonation of dye amide group in the presence of DMA is confirmed by IR spectra of BD (Fig. 2). Indeed in the presence of the DMA two characteristic amide bands are affected: the first one at 1687 cm^{-1} , which is assigned to the carbonyl group and another one at 1493 cm^{-1} assigned to N–H in the amide group. These bands disappear during the reaction.

The different concentrations of DMA have been added to BD solution at a concentration $10^{-5} \text{ mol L}^{-1}$ in a sodium phosphate buffer of pH 8.0. Figure 3 illustrates changes in the absorption maxima and the fluorescence intensity of BD. The band in the absorption spectra at 412 nm disappears, while a new one appears at 452 nm. The intensity of absorption at 452 nm grows steadily with increasing the amine concentration. The above process is naked eye visible: the yellow solution of BD became orange. The fluorescence emission at 553 nm quenches under the same conditions.

Color measurement of dyed textile sensor, exposed to different concentration of aqueous DMA solutions

The color of dyed viscose fabric changes significantly after dipping into preliminary prepared solutions at different concentration of DMA in a pH 8.0 sodium phosphate buffer. The measurements have been carried out at a 10:1 liquor ratio at room temperature. The time for exposure is 3 min. The increase in DMA

concentration leads to a deeper color and a faster response. Color changes have been characterized by VIS reflectance spectra of the wet material at D_{65} light source and $D/10^\circ$ illumination–observer geometry. That spectra have been used for calculating CIE $L^*a^*b^*$ coordinates.

The changes in the fabric color from yellow to orange lead to displacement of position in the color space, defined by a^* and b^* axes. Decreasing of L^* (lightness) is related both to the color change and fluorescence quenching.

The response of the dyed fabric to different concentration of DMA has been estimated quantitatively by the color differences (ΔE^*). Viscose fabric treated with an aqueous sodium phosphate buffer at pH 8.0 is

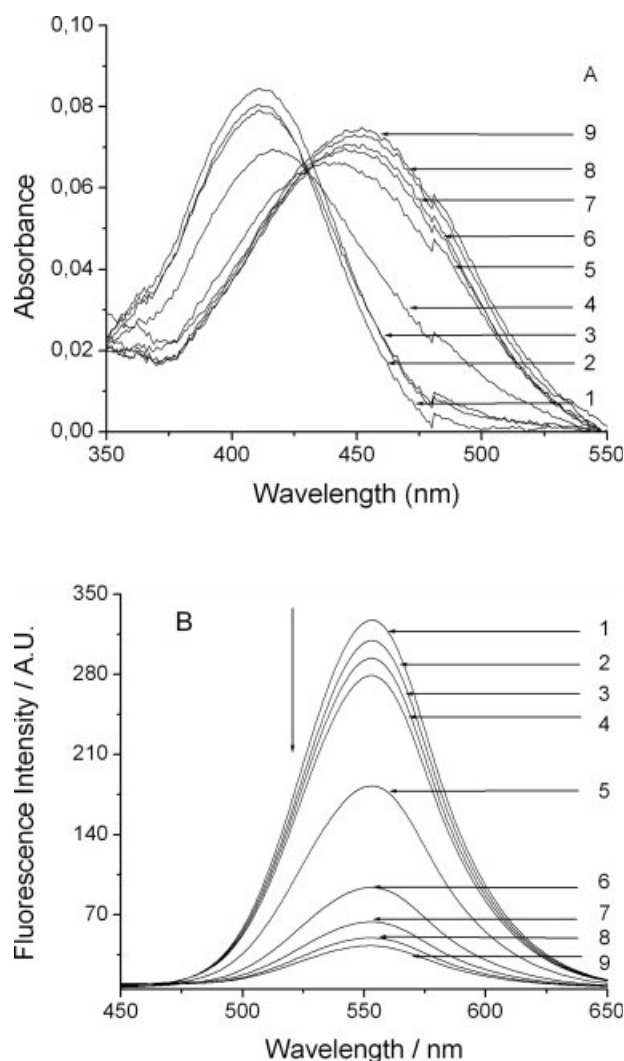


Figure 3 The changes in solution of BD at pH 8.0, sodium phosphate buffer after the addition of DMA. A: absorbance spectra (1) 0, (2) 0.16, (3) 0.32, (4) 0.63, (5) 0.95, (6) 1.27, (7) 1.58, (8) 1.90, (9) $2.22 \times 10^{-5} \text{ mol L}^{-1}$; B: fluorescence spectra ($\lambda_{\text{exc}} = 412 \text{ nm}$) (1) 0, (2) 0.08, (3) 0.16, (4) 0.32, (5) 0.63, (6) 0.95, (7) 1.27, (8) 1.58, and (9) $1.90 \times 10^{-5} \text{ mol L}^{-1}$.

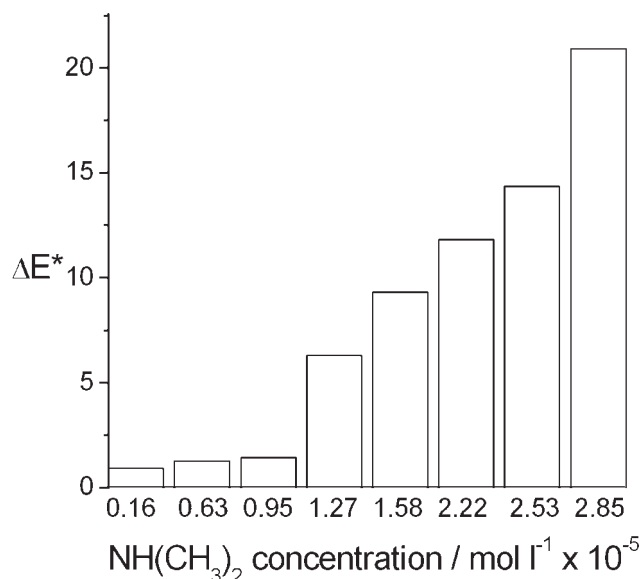


Figure 4 Colour difference ΔE^* as a function of DMA concentration.

taken as a reference ($\Delta E^* = 0$). Figure 4 reveals the differences between the color of this particular fabric sample and those obtained at different concentrations of DMA. As seen clearly ΔE^* in $1.27 \times 10^{-5} \text{ mol L}^{-1}$ is considerably greater than that at the lower concentrations.

Influence of aliphatic amine and ammonia on the fluorescence properties of BD immobilized onto the viscose textile matrix

The fact that the fluorescence emission of the BD also decreases upon addition of aliphatic amines and ammonia gives the opportunity for a more detailed analysis of the textile sensor behavior.

The dynamic response of the dyed viscose textile to DMA in buffer solution has been monitored as a change in fluorescence emission intensity at the emission wavelength $\lambda_F = 543 \text{ nm}$ (the excitation wavelength $\lambda_{\text{ext}} = 412 \text{ nm}$). Characteristic response curves obtained for different concentration of DMA are shown in Figure 5. An exposure time of 3 min is sufficient for the determination of DMA in the $0.32\text{--}2.38 \times 10^{-5} \text{ mol L}^{-1}$ range, although the dynamic range can be shifted to higher or lower concentration by varying the exposure time.

The same experiments have been performed with ammonia, MA, and TMA with dissolved and immobilized BD to investigate how immobilization of the indicator dye can change some characteristics, such as pK_a , dynamic range, working wavelengths, or selectivity.²⁴ In our previous study, it has been found out that the nature of organic solvents or textile material could affect the position of the emission maximum of BD. Emission spectra recorded for BD in methanol so-

lution ($\lambda_F = 546 \text{ nm}$) or BD-dyed viscose fabric ($\lambda_F = 543 \text{ nm}$) have shown that they have approximately the same maximum and these values are hypsochromically shifted compared to that observed in aqueous solution where $\lambda_F = 553 \text{ nm}$. In addition, the values of BD ($pK_a = 10.8$ and 10.1) are quite similar for both its states—immobilized and dissolved in aqueous solution respectively, which indicates insignificant influence of the immobilization on the sensor properties.²⁰ However, the situation is more complex when electrically neutral analytes, such as amine have to be detected. The response of the sensor is governed by three parameters (lipophilicity, nucleophilicity/basicity, and bulkiness) of the analyzed molecule.²⁵

The response of textile sensor to different ammonia and amines concentrations is shown in Figure 6. Apparently, the influence of MA and DMA in this concentration range upon fluorescence emission of the textile sensor is greater than that of TMA and ammonia.

DMA, TMA, and ammonia are products of microbial degradation and associated with seafood spoilage. However, each of them appears due to different reasons. The investigated textile sensor gives opportunity for their selective detection.

The equilibrium constants of BD in aqueous solution and in viscose fabric for ammonia and amines are shown in Table I. Equation (1) has been used for the calculation.

Table I shows BD to be the most sensitive compared to DMA, followed by MA, ammonia, and TMA, which is in agreement with the order of the proton-acceptor abilities of the alkyl amines in aqueous solution ($\text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH} > \text{R}_3\text{N}$).²⁶

In the case of the sensor immobilized on textile, the reactions with ammonia and MA are more efficient than those with BD in solution. Whereas, in the cases

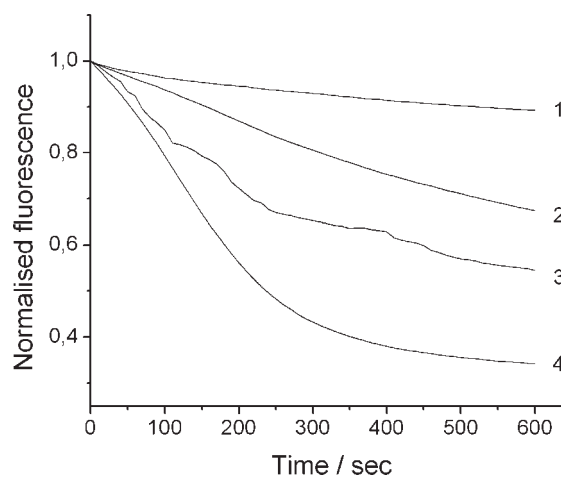


Figure 5 Typical dynamic response fluorescence curves of the dyed viscose textile recorded as a result of exposure to different concentrations of DMA (1) 0.32 , (2) 1.27 , (3) 1.58 , and (4) $2.38 \times 10^{-5} \text{ mol L}^{-1}$ for 600 s.

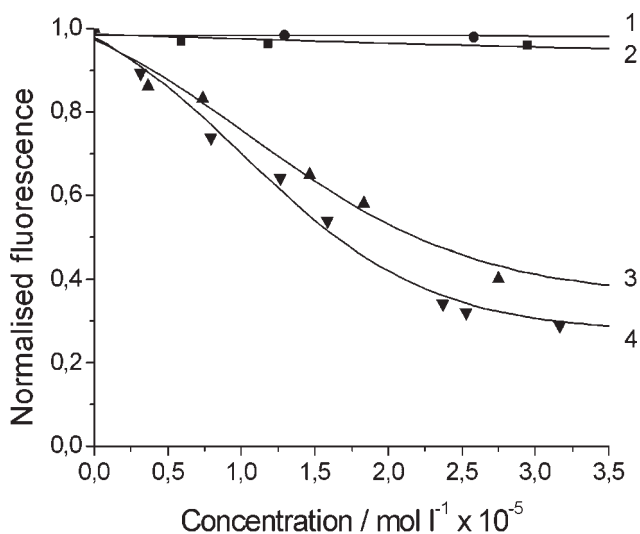


Figure 6 Response function of dyed textile fabric on exposure to (1) TMA, (2) ammonia, (3) MA, and (4) DMA in an aqueous sodium phosphate buffer, pH 8.0.

of detecting DMA and TMA, the textile sensor is less sensitive than that in solution.

The sensor properties of BD are not significantly influenced by the textile immobilization. However, the optical detection by means of a BD is supposed to be due to the deprotonation rate of the dye, which is influenced by the base strength of amines, the time for approaching the reaction center of the analyzed molecules, and the solvation of the end product (the positively charged ammonium ion). Solvents having large dielectric constants favor charge formation and separation, e.g., deprotonation is easier in water ($\epsilon = 78.4$) than in methanol ($\epsilon = 32.7$).

As an example, Figure 7 presents the evolution of the fluorescence quenching of BD either in aqueous solution as a function of the concentration of MA (1) and DMA (4) or in textile matrix—as a dependence on the concentration of MA (2) and DMA (3). Since DMA is more alkylated than MA, its basic properties increase, but in the same time it hinders the approach of the amide group and decreases the solvation of the

TABLE I
Equilibrium Constant of Dissolved BD and of an Immobilized on Textile Sensor for Ammonia and Amines in a Sodium Phosphate Buffer, pH 8.0

Amine	$K_{\text{eq.}} (M^{-1})$
Solution	
Ammonia	13,700
MA	66,700
DMA	160,300
TMA	9,200
Textile sensor	
Ammonia	19,700
MA	83,300
DMA	90,900
TMA	4,100

ammonium ion. The same reasoning can be applied for the detection of ammonia and TMA in the case of viscose fabric.

It is well known that the main advantage of fluorescence over other light-based methods such as absorbance is its high sensitivity.²⁷ The combination of changes in both fluorescence and color of the indicator BD gives an opportunity to evaluate its behavior as a fluorogenic and chromogenic chemosensor.

Some data from fluorescence and absorbance experiment of diluted or immobilized BD are given in Table II. The immobilization of BD shifts the lower limit of detected DMA concentration to a higher value. The color of BD solution changes at the concentration of DMA lower than those at which the textile does. The lowest detection limit can be measured by the fluorescence of the dissolved BD. The linear range is also shifted depending on the type of analysis.

Interference study

All measurements have been performed in 0.1 mol L⁻¹ sodium phosphate buffer of pH 8.0 and the interaction of the dye with other strong bases, such as OH⁻ is governed to some extent by the buffer capacity. The changes in the emission maxima by large concentration of sodium hydroxide compare with aliphatic amine gives the opportunity to distinguish the amine from sodium hydroxide for example. Also, when adding aliphatic amines no shifts of the emission maxima occur in the spectra of the textile material unlike the case of high hydroxyl ion concentrations. The fact is a reliable tool to identify the amines added. There is no interference both in color and fluorescence emission due to pH variation in the range of pH 4.6–9.5.^{19,20}

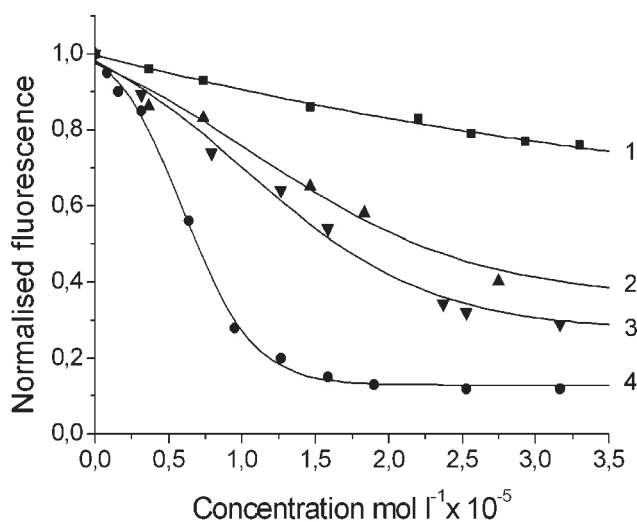


Figure 7 Evolution of the fluorescence quenching of BD either in aqueous solution as a function of (1) MA and (4) DMA concentrations or in textile matrix as a function of (2) MA and (3) DMA concentrations.

TABLE II
Sensing Characteristics of Dissolved BD and Immobilized on Textile Sensor Toward DMA

BD	Analytical approach	Limit of detection (10^{-5} mol L $^{-1}$)	Color change (10^{-5} mol L $^{-1}$)	Linear range (10^{-5} mol L $^{-1}$)
Solution	Absorbance	0.16	0.95	0.32–0.95
	Fluorescence	0.08	–	0.08–0.95
Textile	Color difference	1.27	1.27	0.95–2.85
	Fluorescence	0.32	–	0.32–2.53

The color readily changes back from orange to yellow, if the sample is not in contact with amine under carbon dioxide from the air. This is also valid for fluorescence emission. However, the effect on the aqueous measurements remains negligible for the experiment time. With increasing pH of the sample, all gaseous carbon dioxide are conveniently converted to the nondetectable hydrogencarbonate and carbonate anions.²⁸

One of the advantages of the used dye as a sensor of amines is its pK_a value, which is higher than that of other pH dyes used for the detection of ammonia and aliphatic amines. This means that the dye is deprotonated more difficultly and very few more basic substances could affect its sensor response. The amide group is successfully used as a receptor for fluoride ion in acetonitrile²⁹; however, in aqueous solution, halide ions are highly solvated and deactivated. No interference effect is observed from F^- , Cl^- , CH_3COO^- , HCO_3^- , and metal cations as Cu^{2+} , Zn^{2+} , Ni^{2+} , and Na^+ .

Reversibility

The sample of dyed fabric has been consecutively dipped in preliminary prepared solutions of distilled water (pH 5.9) then into DMA (with concentration 1.58×10^{-5} mol L $^{-1}$) and vice versa for 3 min. A fast and full reversibility of the color and fluorescence emission can be easily achieved by dipping the textile into distilled water.

The reproducibility of the color change has been determined by the color difference ΔE^* . The relative standard deviations for distilled water and DMA ($n = 5$) determined are 4.6 and 3.6%, respectively.

The same conditions have been used to measure the reversibility of the fluorescence intensity of the dyed viscose fabric (Fig. 8). The relative standard deviations are 3.0% for both distilled water and DMA ($n = 5$).

CONCLUSIONS

A new pH indicator dye BD for the detection of amines is proposed. It changes its color from yellow to orange and in the mean time decreases its fluores-

cence emission as a function of the amine concentration in aqueous solution. The sensitivity of the proposed dye is in the range achieved with the other well-known reaction between primary amines, *o*-phthalic dialdehyde (OPA), and β -mercaptoethanol in solution, which offers great sensitivity and selectivity.^{30–34} The necessity to use a multicomponent mixture for the analysis and the limitation for monitoring of the primary amino compounds in solution by OPA method have been overcome. In this study, BD, containing an amide group as receptor, in solution, is more selective to dimethylamine than to trimethylamine and ammonia. However, another substituent in the dye molecule, which can influence the amide group reactivity, can change its selectivity as well. Investigations on such alternations are being performed at the moment.

The immobilization on the textile matrix is the other factor determining the sensor properties. It has been found that the viscose fabric changes the selectivity and sensitivity of the dye to a certain degree. The advantages of the textile sensor are its simple production, low cost, sensibility, and reproducibility. It also allows a very quick and easy detection of chemical or bioprocesses leading to emission of

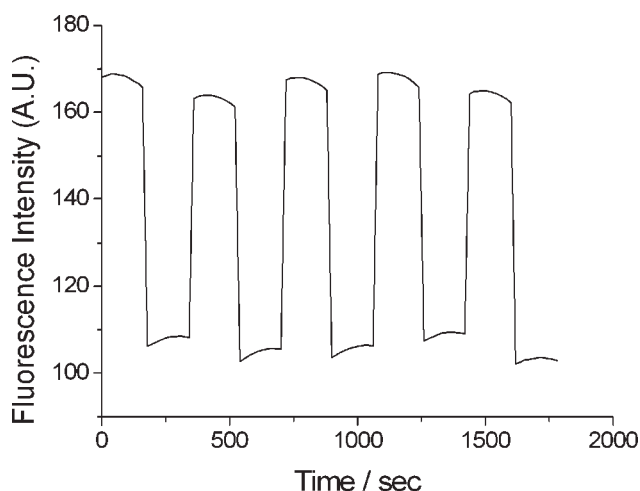


Figure 8 Reproducibility of the fluorescent intensity of the textile viscose fabric response from DMA 1.58×10^{-5} mol L $^{-1}$ to distilled water pH = 5.9 and vice versa for 3 min.

amines in the environment (chemical leaks, protein denaturation, etc.).

References

1. Fiorilli, S.; Onida, B.; Macquarrie, D.; Garrone, E. *Sens Actuators B* 2004, 100, 103.
2. Absalan, G.; Soleimani, M.; Asadi, M.; Ahmadi, M. *Anal Sci* 2004, 20, 1433.
3. Mohr, G.; Demuth, G.; Spichiger-Keller, U. *Anal Chem* 1998, 70, 3868.
4. Chen, X.; Lin, L.; Li, P.; Dai, Y.; Wang, X. *Anal Chim Acta* 2004, 506, 9.
5. Malins, C.; Landl, M.; Simon, P.; MacCraith, B. *Sens Actuators B* 1998, 51, 359.
6. Lau, K.; Edwards, S.; Diamond, D. *Sens Actuators B* 2004, 98, 12.
7. Wolfbeis, O. *Molecular Luminescence Spectroscopy: Methods and Application, Part 2*; Schulman, S., Ed.; Wiley: New York, 1987.
8. Trinkel, M.; Trettnak, W.; Reininger, F.; Benes, R.; O'Leary, P.; Wolfbeis, O. *Anal Chim Acta* 1996, 320, 235.
9. Ozawa, S.; Hauser, P.; Seiler, K.; Tan, S.; Morf, W.; Simon, W. *Anal Chem* 1991, 63, 640.
10. Grafe, A.; Haupt, K.; Mohr, G. *Anal Chim Acta* 2006, 565, 42.
11. Grabchev, I.; Betscheva, R.; Bojinov, V.; Staneva, D. *Eur Polym J* 2004, 40, 1249.
12. Grabchev, I.; Staneva, D.; Betscheva, R. *Polym Degrad Stab* 2006, 91, 2257.
13. Lobnik, A.; Wolfbeis, O. *Sens Actuators B* 1998, 51, 203.
14. Rijavec, T. *Tekstilec* 2005, 48, 7.
15. Engin, M.; Demirel, A.; Engin, E.; Fedakar, M. *Measurement* 2005, 37, 173.
16. Singh, M. *Pakistan Text J* 2004.
17. Khalil, S.; Yuan, J. M.; El-Sherif, M. A. *Environ Monit Remed* 2003, 12, 38.
18. Bradock, S. E.; Mohony, M. *Thomes Hudson Ann Rep* 1999, 34, 141.
19. Staneva, D.; Betscheva, R. *Dyes Pigments* 2007, 74, 148.
20. Staneva, D.; Betscheva, R.; Chovelon, J.-M. *J Photochem Photobiol A* 2006, 183, 159.
21. Pacquit, A.; Lau, K.; McLaughlin, H.; Frisby, J.; Quillty, B.; Diamond, D. *Talanta* 2006, 69, 515.
22. Wolfbeis, O.; Posch, H. *Anal Chim Acta* 1986, 185, 321.
23. Krunjatz, I., Ed. *Chemical Encyclopaedia, Vol. II: Moscow*, 1988; p. 1216.
24. Koller, E.; Wolfbeis, O. *Fiber Optic Chemical Sensors and Biosensors*; CRC Press: Boca Raton, 1991; Chapter 7.
25. Mohr, G.; Citterio, D.; Demuth, C.; Fehlmann, M.; Jenny, L.; Lohse, C.; Moradian, A.; Nezel, T.; Rothmaier, M.; Spichiger, U. *J Mater Chem* 1999, 9, 2259.
26. Reichard, C. *Solvent Effects in Organic Chemistry*; Ebel, H. F., Ed.; Verlag Chemie: New York, 1979.
27. Martinez-Manez, R.; Sancenon, F. *Chem Rev* 2003, 103, 4419.
28. Rhines, T.; Arnold, M. A. *Anal Chim Acta* 1990, 231, 231.
29. Liu, B.; Tian, H. *J Mater Chem* 2005, 15, 2681.
30. Simons, J.; Johnson, D. *J Org Chem* 1978, 43, 2886.
31. Dai, F.; Burkert, V.; Singh, H.; Hinze, W. *Microchem J* 1997, 57, 166.
32. Lindroth, P.; Mopper, K. *Anal Chem* 1979, 51, 1667.
33. Chem, R.; Scott, C.; Trepman, E. *Biochim Biophys Acta* 1979, 576, 440.
34. Piletska, E.; Piletsky, S.; Subrahmanyam, S.; Karim, K.; Turner, A. *Polymer* 2001, 42, 3603.