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Synthesis and functional properties of new optical pH sensor based on benzo[de]anthracen-7-one immobilized on the viscose

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Abstract

The synthesis of a new pH sensor based on the fluorescent water-soluble 1-[(7-oxo-7*H*-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride is described. The molecule displays colour change from yellow to orange-reddish as a function of pH in aqueous solution. Viscose fabric could be used as a planar sensor for the visualization of pH gradients via imaging in two dimensions over large surfaces with highly local resolution. The results from colour measurement showed that the dyed viscose fabric is suitable for ‘‘naked eye’’, on-line, reversible solid-state pH sensor in the alkaline region.

Keywords: Optical pH sensor; Smart textile; Benzo[de]anthracen-7-one; Dye

1. Introduction

pH is one of the key parameters that can be used to describe many processes and it provides valuable information about the progress of such processes. Molecular spectroscopy presents the possibility of the immediate detection and determination of pH in aqueous solution [1]. Recent years have witnessed the growing interest in the investigation of systems that are capable of changing their functional characteristic under certain conditions. Colorimetric pH sensors are very simple to operate and permit detection with the ‘‘naked eye’’ which makes them particularly attractive. On the other hand, fluorescence pH sensors are widely used in a more precise and sensitive manner than their colorimetric counterparts.

Internal charge transfer (ICT) is an important design principle and a push–pull π-electron system is usually required to separate substantial charges in order to perturb the receptor [2]. The most widely used indicator dyes in the alkaline pH region are triarylmethane types (phenolphthalein, thymolphthalein) and variously substituted azo and stilbene dyes [3,4]. For example, they can be used for the detection of basic substances (ammonia, amines) or for the early and precise diagnostic of the processes occurring in concrete, the pH of which is in the range of 11–13. Sensor dyes, which undergo changes in both their fluorescence and colour in the same pH region, can be used for the investigation of coloured solutions such as wine, beer, synthetic resin, essential oils, surfactants, plant and soil extract [5].

The choice of receptor defines the pH range wherein the dyes can be used as sensors. Hydroxyl groups, different amine substituted derivatives and the trifluoroacetyl group [3] each have found application as receptors in the design of pH-sensing molecules. The amide group (peptide) occurs widely in nature and possesses interesting chemical properties which have not, until now, been investigated as a receptor in the design of pH sensors.

Low and high molecular mass compounds are two types of pH chemosensors, which are already available for pH detection in aqueous media. The synthesis of different polymers with appropriate properties provides conditions not only for detecting a minor pollutant concentration but also for developing reusable, flexible and relatively stable materials for highly

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sensitive sensors as well [6,7]. However, very often immobilization of the pH-sensitive dye into a polymer matrix affects its sensing behavior [4,8,9].

Textile materials possess a number of specific surfaces, as well as both mechanical and operational properties that could be very useful in applying them as solid-state carriers of different chemosensors. The large contact surface of textiles in general enables efficient contact with the detected substances compared to other polymer materials used for the same purpose. Recently, different textile materials have been studied as solid-state support of sensors [10]. Chromic or chameleon materials, which can change their colour according to external conditions (light, heat, electricity, pressure, liquid, electron beam) [11], are a representative of intelligent textiles. Overall some applications of this material are that they are capable of detecting a nearby spillage and environmental monitoring for public safety officials or workers in the chemical industry [12,13]. pH-sensitive sensors have been developed and woven into the fabric of a soldier's clothing [14].

To our knowledge, benzo[de]anthracen-7-one derivatives have not been investigated as optical sensors. They were chosen in this work because they combine excellent colour characteristics, fluorescence intensity and high thermo- and photo-stability [15–20]. In addition, they have an internal charge transfer excited state in the visible region and the respective colour ranges from yellow to reddish; they also emit in the visible spectrum, having an intense fluorescence emission band at 500–600 nm and can act as dual fluorescent-colorimetric sensor.

This paper concerns the synthesis and functional properties of a new 1-[(7-oxo-7*H*-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride dye as potential pH sensor. Its molecular structure has been designed to combine pH-dependent colour and fluorescence properties in the alkaline pH range. For the first time, the viscose fibers have been used as a solid matrix so as to obtain a reusable, mechanically stable and flexible optical pH sensor.

2. Experimental

2.1. Synthesis of 3-amino-benzo[de]anthracen-7-one

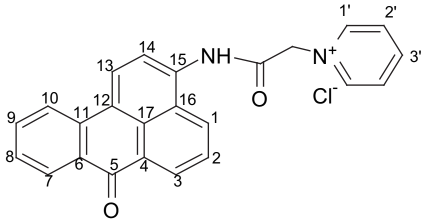
3-Amino-benzo[de]anthracen-7-one was prepared [21] by nitration of benzo[de]anthracen with fuming nitric acid and subsequent reduction of the nitro group from the 3-nitro-benzo[de]anthracen by Na_2S. M.p. = 245–246 °C (cc. [21] 246 °C).

2.2. Synthesis of 2-chloro-N-(7-oxo-7H-benzo[de]anthracen-3-yl)-acetamide (*B1*)

3-Amino-benzo[de]anthracen-7-one (2.45 g, 0.01 mol) was dissolved in 50 ml of dioxan and to this solution at 50 °C 2 ml of chloracetylchloride was added drop wise. The mixture was stirred at this temperature, and after 2 h by pouring into water, filtering and drying in vacuum the product was isolated.

Yield: 85%. FT-IR (KBr) cm^{-1}: 3056, 2956, 1674, 1650, 1598, 1544, 1320, 776; ^1H NMR (ppm): 9.01 (br s, 1H, NH), 8.81 (dd, $J = 7.3$, 1.1 Hz, 1H), 8.50 (m, 2H), 8.30 (m, 3H), 7.87 (dd, $J = 8.2$, 7.3 Hz, 1H), 7.77 (dd, $J = 8.1$, 7.3, 1.5 Hz, 1H), 7.56 (dd, $J = 7.8$, 7.3 Hz, 1H), 4.42 (s, 2H, $OCCH_2Cl$). Elemental analysis: $C_{19}H_{12}O_2NCl$ (321.69): Calcd. C 70.93, H 3.73, N 4.35; Found C 70.81, H 3.72, N 4.26.

2.3. Synthesis of 1-[(7-oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride (*B2*)

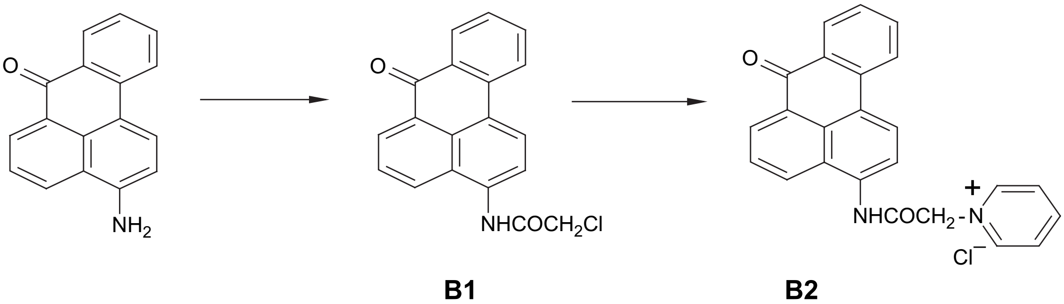


2-Chloro-*N*-(7-oxo-7*H*-benzo[de]anthracen-3-yl)-acetamide (3.21 g, 0.01 mol) was dissolved in 50 ml *N*,*N*-dimethylformamide and 2.4 ml of pyridine was added. After that the solution was stirred for 4 h at 80 °C. After cooling to room temperature and the precipitate was filtered off, washed with acetone and dried in vacuum at 50 °C.

Yield: 73%. FT-IR (KBr) cm^{-1}: 3015, 2976, 1686, 1640, 1600, 1548, 1309, 774, 678; ^1H NMR (DMSO-d_6, ppm): δ 11.30 (br s, 1H, NH), 9.16 (d, $J = 5.8$ Hz, 2H), 8.89 (d, $J = 8.2$ Hz, 1H), 8.78 (d, $J = 8.3$ Hz, 1H), 8.70 (m, 2H), 8.59 (d, $J = 8.2$ Hz, 1H,), 8.31 (dd, $J = 7.8$, 1.3 Hz, 1H), 8.25 (dd, $J = 5.8$, 7.4 Hz, 2H), 8.07 (d, $J = 8.3$ Hz, 1H), 8.00 (t, $J = 7.8$ Hz, 1H), 7.86 (dd, $J = 8.2$, 7.0 Hz, 1H), 7.62 (t, $J = 7.5$ Hz, 1H), 5.95 (s, 2H, $N^+{-}CH_2$). ^{13}C NMR: 183.8 (C5), 164.7 (HNCO), 146.5 (C1′), 146.3 (C3′), 135.5 (C), 134.1 (C8), 130.6 (C9), 129.7 (C1), 128.4 (C3), 127.9 (C), 127.6 (2C, C10+C2′), 127.3 (CH), 126.5 (C2), 125.5 (C13), 123.9 (C7), 123.2 (C), 121.4 (C14), 62.3 (OC*C*H_2N). Elemental analysis: $C_{24}H_{17}N_2O_2Cl$ (400.74): Calcd. C 71.92, H 4.24, N 6.99; Found C 71.80, H 4.19, N 6.89.

2.4. Analysis

All solution absorption measurements were performed using a UV–Vis Double Beam Spectrophotometer (Uvikon 930) at 10^{-5} M l^{-1}; the fluorescence spectra were taken on a FP-6500 Jasco spectrofluorometer at 10^{-5} M l^{-1}. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra; fluorescein was used as a reference ($\Phi_F = 0.86$) [22]. The IR spectra of new dyes were recorded on a Bruker IFS-113v spectrometer at a 2 cm^{-1} resolution using KBr pellets. The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^1H and ^{13}C, respectively, using a dual 5 mm probe head. The measurements were carried out in D_2O solution at ambient temperature. The chemical shift was referenced to tetramethylsilane (TMS), standard



Scheme 1. Synthesis of 1-[(7-oxo-7*H*-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride (**B2**).

experiments with 30° pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortion less enhancement by polarization transfer (DEPT) spectra was recorded under the same conditions as the ^{13}C NMR spectra and $\tau = (2\ ^1J_{CH})^{-1} = 3.45$ μs was used. The colour characteristics of the fabrics were determined on a Texflach ACS/DATACOLOR with spectrophotometer Spectraflash 600. The colour at different pH of samples has been measured in order to quantify this response for the dyed viscose fabric. The pH values of the solutions were measured with a pH-meter LPH33OT, Tacussel electronics.

3. Results and discussion

3.1. Synthesis of 1-[(7-oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride (B2)

The synthetic route used for the preparation of water-soluble 1-[(7-oxo-7*H*-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride (**B2**) is outlined in Scheme 1.

The initial 3-amino-benzo[de]anthracen-7-one was prepared by the nitration of the benzo[de]anthracen-7-one and reduction of the nitro group with sodium sulphide following a method described previously [21]. Acylation of the primary amino group with chloracetylchloride was carried out (at 50 °C during 2 h in dioxan solution) to give product **B1**, which was isolated by pouring the reaction mixture into ice water and filtering the precipitate. Dye **B1** has an activated chlorine atom, which can be attacked by pyridine. The final product **B2** was obtained by the reaction of **B1** with pyridine in *N*,*N*-dimethylformamide at 80 °C for 4 h. The resulting yellow precipitate of dye **B2** is water soluble due to the ionic nature of the pyridine quaternary. It was filtrated and washed by acetone and dried under vacuum.

The reaction and purity of products **B1** and **B2** were monitored by thin-layer chromatography (acetone–*n*-heptane, 1:1). FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopic studies and elemental analysis confirmed the chemical structures of new products **B1** and **B2**.

Dye **B2** is a typical cationic dye, which is suitable for dyeing polyacrilonithrile or polyamide fibers. On the other hand, the structure of dye **B2** can give some options for covalent bonding with cellulose in slightly alkaline medium [23]. The pyridine hydrochloride could be applied as a catalyst to promote the reaction of dye **B2** with cellulose.

Commercial fabric made of viscose fibers has been used for studying the dyeing with **B2** and the behavior of dyed material as a pH sensor. It is well known that viscose fibers compared to the other cellulose fibers possess a higher degree of swelling in aqueous solution and a higher dye ability due to the faster diffusion of dye into fibers. Same diffusion phenomenon is typical for the hydroxyl anions and protons and it is supposed to be a very favorable condition for a quick response of dyed textile to the pH changes occurred.

3.2. Functional characteristics of the monomeric dye B2

The functional photophysical properties of dye **B2** were investigated in aqueous and methanol solutions at a concentration of 10^{-5} mol l^{-1}. Table 1 summarizes the basic spectral characteristics of **B2** in aqueous and methanol solutions: the values of absorption (λ_A) and fluorescence (λ_F) maxima, molar extinction coefficient (ε), Stokes shift ($\nu_A - \nu_F$) and quantum yield of fluorescence (Φ_F). The dye **B2** studied was of yellow colour and displayed yellow-green fluorescence. In UV–visible spectra of both solvents a broad absorption was observed between 350

Table 1
Photophysical characteristics of dye **B2** in aqueous and methanol solution

Solution	λ_A (nm)	ε (l mol^{-1} cm^{-1})	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
Water	413	10 500	553	6129	0.090
Methanol	410	10 000	546	6075	0.087

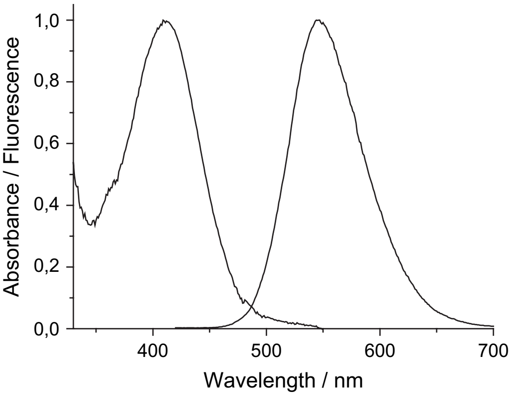


Fig. 1. Normalized absorption and fluorescence spectra of dye **B2** in aqueous solution.

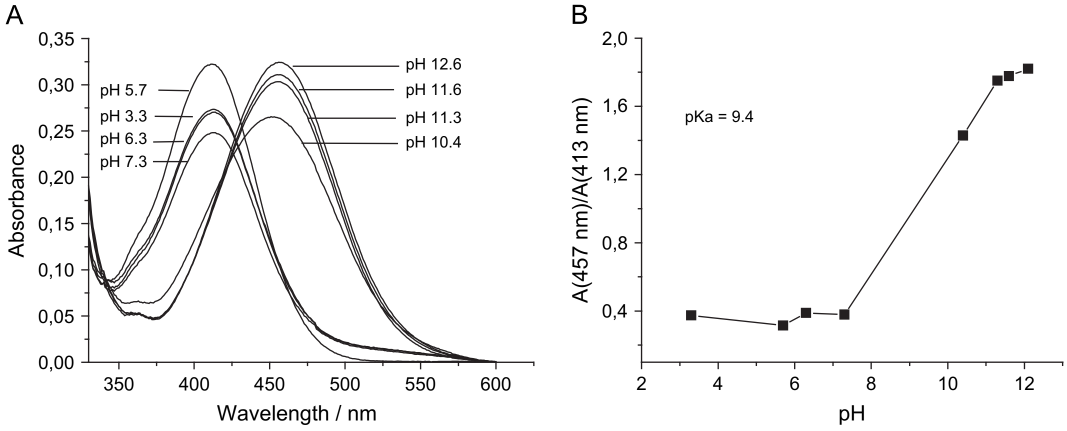


Fig. 2. Absorption spectra of dye **B2** as function of pH (A), and the wavelength-ratiometric plot, constructed from the *A* (457 nm)/*A* (413 nm) absorption values vs solution pH (B).

and 500 nm with λ_A maximum at 413 nm (water) and at 410 nm (methanol). The molar extinction coefficients ε (at λ_{max}) are $10\,500\ \text{l mol}^{-1}\ \text{cm}^{-1}$ in water and $10\,000\ \text{l mol}^{-1}\ \text{cm}^{-1}$ in methanol solutions, respectively. The amide group of dye **B2** has weaker electron donation properties than the amino group in 3-amino-benzo[de]anthracen-7-one. The absorption maximum of dye **B2** is shifted hypsochromically if compared to that of 3-amino-benzo[de]anthracen-7-one, due to the weaker electron donating ability of the amide group than the amino group.

In the absorption spectra of dye **B2**, the long-wave band in the visible region has a charge transfer (CT) character, due to $\pi\pi^*$ electron transfer during the $S_0 \rightarrow S_1$ transition of the dye molecule. Emitting fluorescence light it is deactivated and passes from the S_1 to the basic S_0 state. At room temperature, a week emission is observed between 450 and 700 nm with λ_F at 553 nm (water) and at 546 nm (methanol), corresponding to a $S_1 \rightarrow S_0$ transition.

Fig. 1 presents the normalized absorption and fluorescence spectra of **B2** dye in aqueous solution as an example. As seen from Fig. 1, the absorption and fluorescence spectra have bands with a single maximum, without vibrational structure. The fluorescence curve is an approximately equal mirror image of the absorption curve which is the indicative of the molecular structure of dye **B2** in excited state and prevailing fluorescence emission. The overlap between absorption and fluorescence spectra is low and an aggregation effect for the concentration at about $10^{-5}\ \text{mol l}^{-1}$ has not been observed.

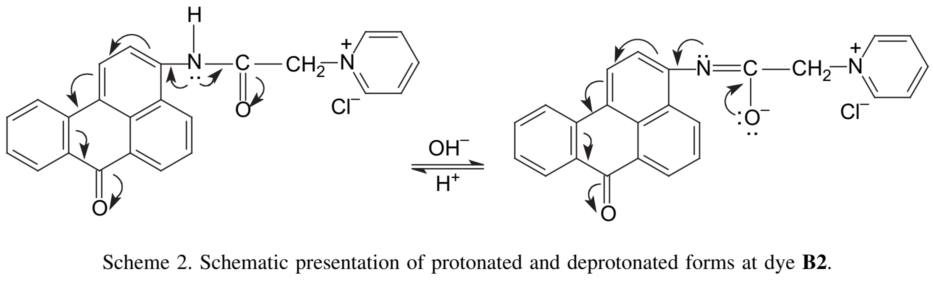
*3.3. The pH influence on the absorption spectra of dye **B2** in aqueous solution*

With regard to the practical application of dye **B2** as a pH sensor, absorption spectra in different pH have been investigated. As can be seen in Fig. 2A, dye **B2** shows pH dependence in absorbance. In the pH range from 3.3 to 7.3, **B2** has a yellow colour and gives an absorption maximum at 413 nm. With increasing of the alkalinity (pH = 10.4–12.6), the absorption maximum is shifted bathochromically to $\lambda = 457$ nm and corresponding colour of the solution becomes orange-reddish. Fig. 2B plots the dependence of *A* (457 nm)/*A* (413 nm) on pH. The calculated pKa ≈ 9.4 is determinate from the absorption spectra.

We propose that deprotonation of the imino group (Scheme 2) restores the internal charge transfer (ICT) as it is in 3-amino-alkyl-benzo[de]anthracen-7-one, which leads to this significant red shift $\Delta\lambda_A = 34$ nm of the absorption maximum.

Scheme 2 shows the option for a significant interaction between benzo[de]anthracen-7-one chromophor and the amide group as receptor via nitrogen atom existing in the molecule of dye **B2**. In this case the unshared electron pair of nitrogen atom interacts with π-electron system of the carbonyl from the amide group, which leads to a partial double character of the C–N bond.

The amide group atoms are located on the same plane and the wide-angle rotation around the C–N amide bond is hindered. In contrast, the unshared electron pair of nitrogen



Scheme 2. Schematic presentation of protonated and deprotonated forms at dye **B2**.

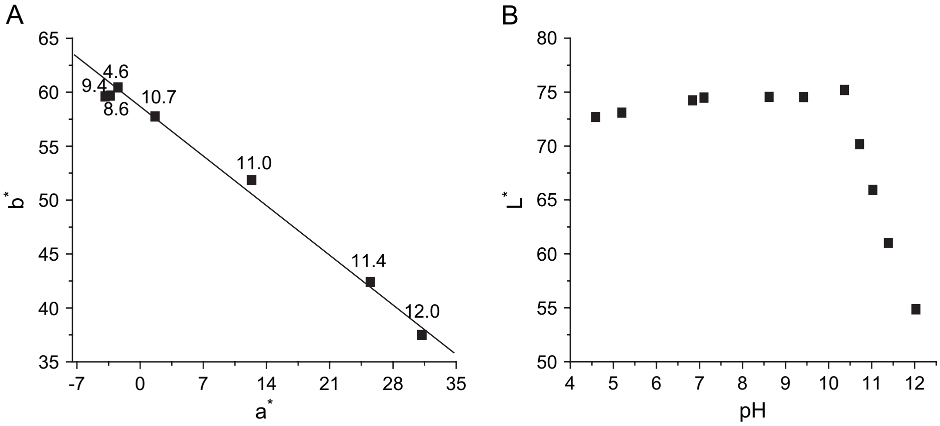


Fig. 3. The influence of pH on the textile colour: (A) a^* and b^* chromaticity coordinates, (B) lightness.

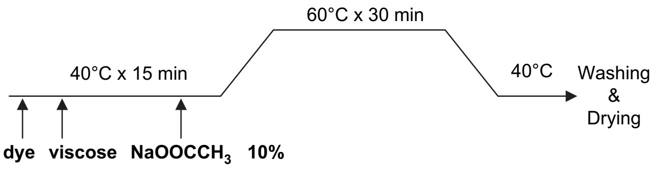
atom interacts with π-electron system of the aromatic chromophore. It is a proof that planar structure of N-atom in the molecule of 3-amino-benzo[de]anthracen-7-one is rather sp^2 than a pyramidal one [24]. The increase in the pH of the aqueous solution leads to change in the chromophoric system shown in Scheme 2. Dye **B2** exhibits NH-acidity in alkaline medium over pH = 10.4. Separation of the amide group proton sets free the other electron pair at N-atom. As presented in Scheme 2, one unshared electron pair of nitrogen atom interacts with π-electron system of benzo[de]anthracen-7-one molecule while the other one does the same with the carbonyl group. This leads to an increase in the electron donating properties of the substituent at 3 position of the chromophore molecule and to an increase in the conjugated chromophoric system. As a result, the bathochromic shift in absorption spectra is observed (Fig. 2A). The chemical reaction is fast and reversible and gives a colour change from yellow to orange-reddish.

3.4. Dyeing procedure of viscose fabrics

In order to transfer pH sensor properties of dye **B2** to the viscose material it was necessary to perform a dyeing procedure. Viscose fabric with 170 g/m^2 mass, scoured and ready for dyeing has been used for our experiments.

The viscose fabric was dyed using a liquor ratio of 1:25 with 0.5% omf dye; 10% aqueous sodium acetate pH = 8–8.5 was used to control the application pH (Scheme 3).

After dyeing, the fabric was rinsed in cold water followed by soaping in a bath at liquor ratio 50:1, temperature 50 °C for 20 min with 5.0 g/l detergent and finally rinsed thoroughly in water before being allowed to dry in the open air. There was not any change of colour after the drying.



Scheme 3. Dyeing procedure.

3.5. Colour measurement of dyed textile sensor

A "naked" eye colour sensor has to show a strong colour change response for a particular parameter. The colour of dyed viscose fabric changed significantly after dipping in preliminary prepared solutions at different pH. The measurements were carried out at room temperature and a 10:1 liquor ratio. In the pH range from acidic (pH = 4.6) up to pH 10.0, the observed colour is bright yellow; while after exposure at pH higher than 10.7, the colour changes to orange-reddish immediately. Colour changes were characterized by VIS reflectance spectra of the wet material at D_{65} light source and D/10° illumination–observer geometry. That spectra were obtained by spectrophotometer Spectraflash 600 and they were used for calculating CIE $L^*a^*b^*$ coordinates. Visually, a drastic change of colour from yellow to orange-reddish as a function of pH was observed. Fig. 3 shows that the dyed fabric exposed to alkalis has a significant decrease of L^* (lightness) and simultaneous change of a^* and b^* chromaticity coordinates at pH over 10 due to the above mentioned change of colour.

Viscose fabric at pH = 4.6 of the solution $\Delta E^* = 0$ was taken as a reference. The colour difference between this particular fabric sample and those obtained at different pH values are presented in Fig. 4. It can be clearly seen that ΔE^*, in alkaline medium (pH = 12) was considerably greater than that

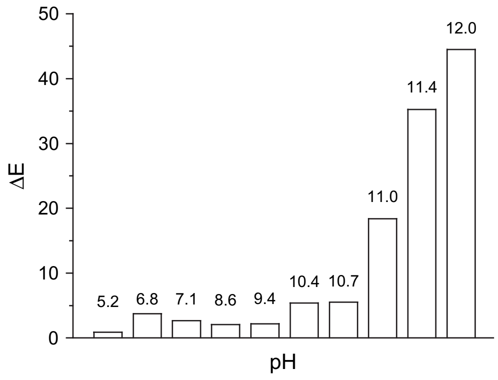


Fig. 4. Colour difference as a function of pH.

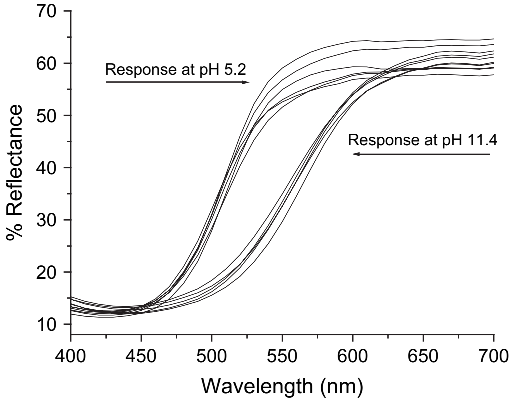


Fig. 5. Reproducibility of the textile viscose fabric response from pH 5.2 to 11.4 and vice versa.

in the pH range 7.1–9.4. The magnitude of the colour differences obtained is several times greater than the average human sensitivity to colour changes.

The repeatability of the dyed viscose fabric response to consecutive changes of pH from 5.2 to 11.4 and vice versa is shown in Fig. 5. The time for exposure to pH 11.4 was 1 min with visible change in the colour from yellow to orange. The return to yellow colour at pH 5.2 required a longer time (3 min).

4. Conclusions

The synthesis and characterization of new water-soluble 1-[(7-oxo-7*H*-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride, has been described. Dye colour changes at different pH due to a deprotonation of the imino group followed by restoring the internal charge transfer and significant red shift $\Delta\lambda_A = 34$ nm of the absorption maximum in alkaline medium. The colour of viscose fiber material treated with this dye changes considerably at different pH as well. It has been found out that there is a good repeatability of colours appeared at consecutive pH changes from 5.2 to 11.4 and vice versa which is a necessary condition for a continuous use and on-line application. This novel type of textile pH-indicator for optical detection could be used for measurement of pH values above 10.50. It has a potential to be applied in sensor strips for precise evaluation of small changes in the range of pH 10.50–12.50. It is suitable for monitoring of aggressive environment, e.g., in concrete and industrial pollutants. Further investigations into this phenomenon led to the development of simple colorimetric sensors for both dissolved and gaseous ammonia and amines.

Acknowledgment

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