

# Fluorescent benzo[de]anthracen-7-one pH-sensor in aqueous solution and immobilized on viscose fabrics

Desislava Staneva<sup>a,\*</sup>, Rositza Betcheva<sup>a</sup>, Jean-Marc Chovelon<sup>b</sup>

<sup>a</sup> University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

<sup>b</sup> University of Claude Bernard, Lyon 1, Laboratoire d'Application de la Chimie à l'Environnement (LACE), CNRS-UMR 5634, boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France

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## Abstract

The photophysical characteristics of a new water-soluble fluorescent pH sensitive 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride based on ICT (internal charge transfer) are described. “On-off” switching of fluorescence as a function of pH in aqueous solution of the above substance has been observed. For the first time the viscose textile fabric has been investigated as a solid matrix for immobilizing the sensor molecules. The fluorescent behaviour of dyed viscose fabric in pH 2.0–12.1 range is discussed.

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**Keywords:** Fluorescent sensor; pH; Smart textile; Benzo[de]anthracen-7-one

## 1. Introduction

Fluorescent pH-sensors are analytical tools widely used in chemistry, biology, medicine and the environment protection. Some new developments in this area are related to the synthesis and application of fluorescent organic compounds with spectral characteristics highly sensitive to the different environmental changes. Some derivatives of 4-dimethylamino phthalimide, 1,8-naphthalimide and anthracen have been reported as quite effective for that purpose [1,2]. Generally these compounds have low quantum fluorescent yields in polar organic solvents and aqueous solution. Searching for new fluorophores with improved photostability, large Stokes Shift and specific spectral characteristics for optical pH-sensing are still a focus of research interest [3]. In the recent years derivatives of benzo[de]anthracen-7-one have been intensively studied, as far as they possess excellent colour characteristics, high fluorescence intensity together with good thermal and photostability [4]. They can be used for dyeing synthetic and natural textile fibers [5] as well as for daylight fluorescent pigments [6], laser dyes [7] and

as polymerizable dyes for structural colouration of polymer materials [8]. The use of this chromophoric system in liquid crystalline systems for colour displays is another option for their application [9]. Some benzo[de]anthracen-7-one derivatives have been investigated as ligands in charge-transfer complexes with iodine [10] or for analysis of thiols by liquid chromatography [11]. To our knowledge the benzo[de]anthracen-7-one derivatives have not been investigated as fluorescent sensors.

The choice of the receptor defines the pH range, wherein the sensor can be used. Hydroxyl group, amine group and different amine substituted derivatives have found application in the design of pH-sensing molecules. On the other hand the amide (peptide) group is widely spread in nature. This group has interesting chemical properties and has not been investigated as a receptor in pH-sensors.

Polymeric materials can be applied as reusable [12] and mechanically stable sensor films for non-invasive pH measurements [13,14] and for planar solid supports coated with a sensor layer enabling the mapping of 2D pH profiles [13,15]. It has been shown that the response time and the photophysical properties of a solid-state device might be affected by decreasing of fluorescent effectiveness [16,17] that could be avoided by appropriate immobilization of pH dye on a solid-

\* Corresponding author. Tel.: +359 2 8163263.

E-mail address: [grabcheva@mail.bg](mailto:grabcheva@mail.bg) (D. Staneva).

state carrier. Different textile materials have been studied as solid-state carriers of sensors [18]. The main advantage of such composite materials is the possibility for developing flexible sensors with surface, mechanical and operational properties suitable for repeated measurements in different media. Recently we have reported the synthesis, absorption and colorimetric properties of a novel water-soluble 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride dye (BD) [19] in aqueous solution and immobilized on a textile viscose matrix. It has been found that the immobilization does not affect the properties of the dye as a colorimetric pH-sensor.

The aim of this paper is to investigate the influence of pH on the fluorescence characteristics of BD in aqueous solution and in viscose textile matrix in order to reveal its behaviour as homogeneous and heterogeneous pH fluorescent chemosensor.

## 2. Experimental

### 2.1. Materials and methods

The synthesis and characterization of BD have been described recently [19]. As an initial product was used 3-amino-benzo[de]anthracen-7-one. The acylation of the primary amino group with chloroacetylchloride gives product having an activated chlorine atom, which can be attacked by pyridine in *N,N*-dimethylformamide at 80 °C for 4 h. The final 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride BD was obtained as yellow precipitate. It was filtrated and washed by acetone and dried under vacuum.

Commercial viscose fabric (production of Svilozha Ltd., Svishtov, Bulgaria) with 170 g m<sup>-2</sup> mass, scoured and ready for dyeing was used as a polymer matrix. The viscose fabric was dyed at 60 °C for 30 min, using a liquor ratio of 1:25 with 0.5% omf dye. A 10% aqueous sodium acetate pH 8–8.5 was used to control the application pH. 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<sup>-1</sup> detergent and finally rinsed thoroughly in water before being allowed to dry in the open air [19]. There was not any change of colour after the drying. Deionised water was used for all procedures and measurements.

### 2.2. Analysis

All solution absorption measurements were performed using a UV-vis Double Beam Spectrophotometer Uvikon 930 at 10<sup>-5</sup> mol l<sup>-1</sup>. The fluorescence spectra were taken on a FP-6500 Jasco spectrofluorometer at 10<sup>-5</sup> mol l<sup>-1</sup>. For the fluorescence measurements the viscose composite material was placed diagonally into the sample quartz cuvette to improve the reproducibility of measurement. Fluorescence quantum yield was determined on the basis of the absorption and fluorescence spectra. Fluorescein was used as a reference ( $\Phi_F = 0.86$ ) [20]. The pH values of the solutions were measured with a pH-meter LPH330T, Solea-Tacussel electronics.

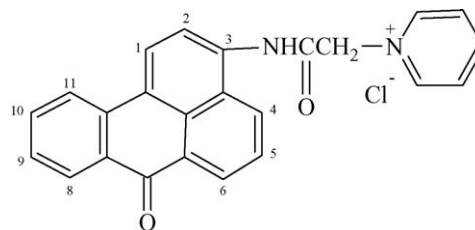
## 3. Results and discussion

### 3.1. Functional photophysical properties of the 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride (BD)

Chemical structure of BD [19] is shown in Scheme 1.

BD is yellow and displays yellow-green fluorescence in solution. It has been synthesized as a new fluorescence pH-sensor, based on ICT (internal charge transfer), where a push-pull  $\pi$ -electron system is required to separate substantial charges perturbed by the guest (in our case proton or hydroxide anion) [21].

Fig. 1 presents the normalized absorption and fluorescence spectra of BD in aqueous solution. When detecting the fluorescence intensity at the individual emission maximum, the excitation spectrum appears to be identical to the corresponding recorded absorption spectrum. A long-wave band in the visible region of the absorption spectrum of BD ( $\lambda_A = 413$  nm,  $\epsilon = 10,500$  l mol<sup>-1</sup> cm<sup>-1</sup>) 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 weak emission is observed between 450 and 700 nm with fluorescence maximum at 553 nm in water, corresponding to a  $S_1 \rightarrow S_0$  transition. The absorption and fluorescence spectra have bands with a single maximum, without vibrational structure. The fluorescence curve could be considered as an approximately equal mirror image of the absorption curve



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

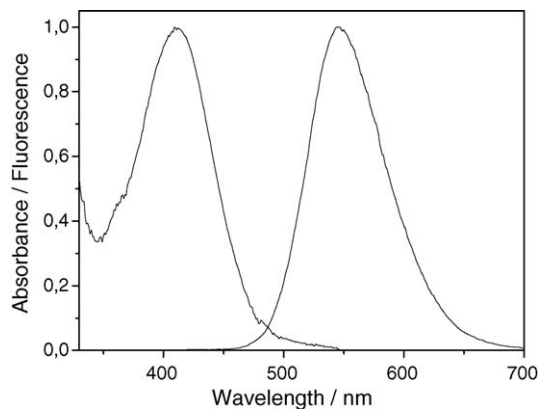


Fig. 1. Normalized absorption and fluorescence spectra of 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride in aqueous solution at 10<sup>-5</sup> mol l<sup>-1</sup>. The excitation wavelength is 413 nm.

and it is indicative for a dye molecular structure 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  $10^{-5} \text{ mol l}^{-1}$  is not observed.

The acylation of 3-amino-benzo[de]anthracen-7-one leads to decrease the electron-donor properties of the substitute and as a result the BD absorption maximum shifts hypsochromically compared to that of 3-amino-benzo[de]anthracen-7-one. The fluorescent emission of BD is also effected. The unshared electron pair of nitrogen atom interacts with  $\pi$ -electron system of the amide carbonyl group and with  $\pi$ -electron system of the benzo[de]anthracen-7-one. The wide-angle rotation around the N–C amide bond and N–C<sub>3</sub> in benzo[de]anthracen-7-one is hindered (Scheme 1). The structure becomes more rigid and excludes the possibility of conformation isomerisation as a result fluorescent emission enhances. However, the possible tautomerism of the amide group by solvent or external effects can change this. It is important to know all factors, which could alter the chemical nature of the chromophore molecules. This gives useful information for fluorescent pH-sensing behaviour of the BD. The other investigations upon photophysical properties of the benzo[de]anthracen-7-one derivatives are already proved their dependence on the nature of the environment (the polarity, viscosity, intermolecular interaction and the possible formation of hydrogen bonds) [22–24]. The charge redistribution is the main photophysical process taking place at excitation and the property of a substitute on position C-3 in benzo[de]anthracen-7-one controls this process [25]. Two mutually incompatible factors decrease the fluorescent intensity of 3-amino-benzo[de]anthracen-7-one and its derivatives [26]: (i) the donor–acceptor interaction between the carbonyl group of benzo[de]anthracen-7-one and substitutes along  $\pi$ -conjugated system and (ii) the formation of intermolecular hydrogen bonds. The evidence for above is the effect of the different organic solvents on the absorption and fluorescent maxima of BD, presented in Fig. 2. The polarity of the media is characterized by the empir-

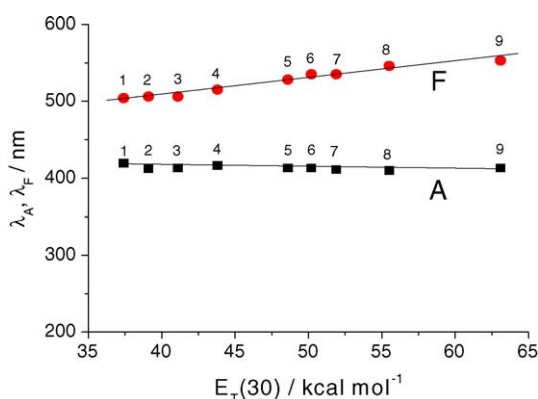


Fig. 2. Dependence of absorption (A) and fluorescence (F) maxima of 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride on the empirical parameters of solvent polarity  $E_T(30)$  [27]: solvent used: (1) tetrahydrofuran; (2) chloroform; (3) dichloromethane; (4) *N,N*-dimethylformamide; (5) 1-butanol; (6) propanol-2; (7) ethanol; (8) methanol; (9) water.

ical polarity parameter  $E_T(30) \text{ kcal mol}^{-1}$ , which is sensitive to both dipolar interactions and the interaction between solute and hydrogen-bond donor solvents [27].

Solvent or external effects can show up in emission even when they are hardly visible in absorption. The solvent dipolar effects can influence better on the excited-state dipole for the longer time scale of the emission experiment than the absorption one [1,27].

When absorption spectra are measured in different solvents it is found a negligible blue shift of the absorption maxima with increasing the polarity of solvents ( $\Delta\lambda_A = 6 \text{ nm}$ ). This means, that ground state is more dipolar than the excited state. Thus, with increasing solvent polarity, the energy of the ground state is lowered more than that of the excited state.

The fluorescent maxima of BD are significantly red shifted with increasing solvent polarity ( $\Delta\lambda_F = 47 \text{ nm}$ ). Thus, the fluorescence of BD exhibits a positive solvatochromism. This effect can be explained by the enhanced polarization of chromophoric system in the excited state, large dipole–dipole interactions and by possible formation of intermolecular hydrogen bonds between BD and solvent molecules.

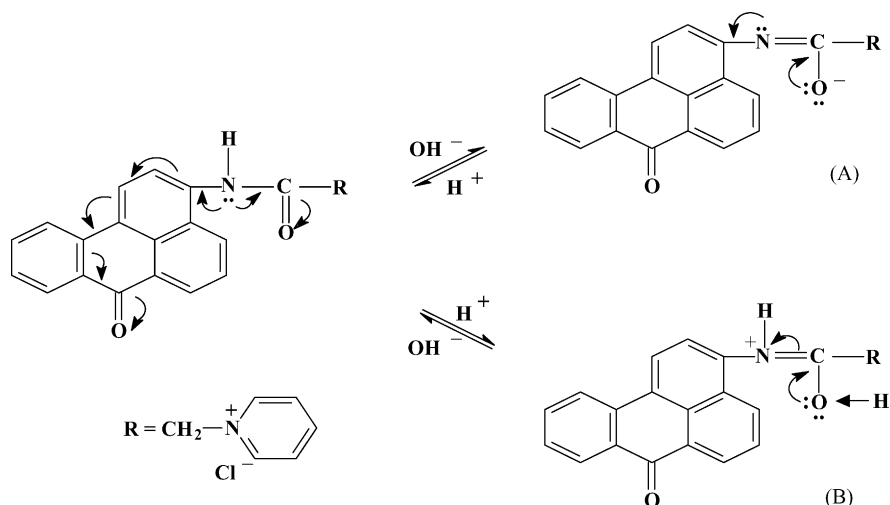
The opposite solvatochromism, observed in the absorption and fluorescent spectra of BD is due to the ground-state geometry of the molecule provides the amide substitute with a significant dipole moment, partly opposite to the benzo[de]anthracen-7-one dipole. The dipole on the excited  $\pi\pi^*$  state is larger, than the ground-state dipole, but is displaced from the direction of the ground-state dipole [25]. The solvent molecules influence on these dipoles in different way at absorption and emission experiments. Upon photon absorption the solvent dipoles are not correctly oriented to stabilize efficiently the excited state. The longer time of the emission experiment enables the solvent dipoles to reorientate and a new relaxed excited state is obtained. It is from this equilibrium state that fluorescence occurs at room temperature. This is applied also to ground state after emission. All this shows the important role of the nitrogen atom as mediator between the benzo[de]anthracen-7-one as fluorophore and amide group as receptor in response of the fluorescent chemosensor BD in pH change.

The ability of BD to emit absorbed light energy is characterized quantitatively by the fluorescence quantum yield  $\Phi_F$ . It has been calculated on the basis of absorption and fluorescence spectra by Eq. (1):

$$\Phi_F = \Phi_{st} \frac{S_u A_{st} n_{Du}^2}{S_{st} A_u n_{Dst}^2} \quad (1)$$

where  $\Phi_F$  is the emission quantum yield of the sample,  $\Phi_{st}$  is the emission quantum yield of the standard,  $A_{st}$  and  $A_u$  represent the absorbance of standard and sample at the excited wavelength, respectively.  $S_{st}$  and  $S_u$  are the integrated emission band areas of the standard and sample respectively,  $n_{Dst}$  and  $n_{Du}$  are the solvent refractive indexes of standard and sample, the subscript indexes u and st refer to the BD and standard, respectively.

The quantum yields of dye BD in both proton donating aqueous and methanol solutions are:  $\Phi_F = 0.087$  and  $\Phi_F = 0.090$ , respectively. These values are not high but they are quite higher



Scheme 2. Schematic presentation of (A) deprotonated and (B) protonated forms at 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride.

compared to the quantum yield of 3-amino-benzo[de]anthracen-7-one in methanol ( $\Phi_F = 0.002$ ) [8]. Again, important role have the influence of the amide group ( $-\text{NHC}=\text{O}$ ) on the polarization of BD molecule and the probable hydrogen bonds formation with solvent.

Stokes Shift ( $\nu_A - \nu_F$ ) indicating the difference in properties and structure of fluorescent compounds between the ground  $S_0$  state, and the first excited  $S_1$  state is calculated by Eq. (2):

$$\nu_A - \nu_F = \left( \frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \quad (2)$$

The calculated Stokes Shift is  $6129 \text{ cm}^{-1}$  in water and  $6075 \text{ cm}^{-1}$  in methanol solutions. These values are higher compared to those of some other amino and alkoxy benzo[de]anthracen-7-one derivatives [25,28]. Upon increasing the solvent polarity both the absorption and fluorescent maxima of the other derivatives are shifted bathochromically. In the case of BD such a shift has been observed only of the fluorescent maxima, as the absorption maxima are shifted slightly hypsochromically.

### 3.2. Influence of pH on the fluorescence properties of 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbamoyl)-methyl]-pyridinium chloride dye in aqueous solution

Schematic presentation of the influence that protons and hydroxyl ions have on BD chromophoric system is shown in Scheme 2. As it can be seen, pH increase in aqueous solution changes BD chromophoric system (Scheme 2A). Detached proton from the amide group sets free the other electron pair at nitrogen atom. One unshared electron pair of nitrogen atom interacts with  $\pi$ -electron system of benzo[de]anthracen-7-one molecule, while the other one does the same with the carbonyl group. This leads to more pronounced electron donating properties of the nitrogen atom at C-3 position of the chromophore molecule. The significant bathochromic shift in the absorption

spectra is observed ( $\Delta\lambda_A = 34 \text{ nm}$ ) [19] and the fluorescence emission decreases strongly. The emission is ‘switched on’ prior to the recognition of the hydroxide anion. After that the reduction potential of the receptor increases, which enhances the quenching followed by a fluorescence ‘switching off’.

In acidic medium (pH < 4.0) proton joins the amide oxygen atom and that changes the chromophore system (Scheme 2B). In this case the change of electron donating properties of the amide group is insignificant which is due to the positive charge at the nitrogen atom. No change at the position of absorption maximum has been observed [19] but the fluorescence intensity decreases without being quenched totally (Fig. 3A). Deactivation of the excited BD in this case most probably is due to more hindered formation of intermolecular hydrogen bonds as well as to conformational isomerisation occurred. Regarding the sensor properties in general it should be pointed out that the above-mentioned transformations causing fluorescent quenching and enhancement are reversible.

The fluorescence properties of BD in aqueous solution in the 3.3–12.6 pH range have been investigated. Fig. 3A shows the fluorescence spectra of BD at different pH. It is seen, that there is not any change in the position of fluorescent maxima ( $\lambda_F = 553 \text{ nm}$ ). Fig. 3B presents the pH response of BD as a function of  $I/I_{\text{max}}$  versus pH, where  $I$  is the measured fluorescence intensity at a given pH and  $I_{\text{max}}$  is the maximum fluorescence intensity. The emission is ‘switched on-off’ between pH 9.4 and 11.6.

The  $\text{p}K_a$  of BD has been determined from the changes of fluorescence intensity as a function of pH by Eq. (3):

$$\text{pH} - \text{p}K_a = \log \frac{I_{\text{Fmax}} - I_{\text{F}}}{I_{\text{F}} - I_{\text{Fmin}}} \quad (3)$$

The calculated  $\text{p}K_a$  value is  $10.1 (\pm 0.1)$ .

Fig. 4 shows the change of fluorescence quantum yield ( $\Phi_F$ ) in aqueous solution at different pH values. The highest quantum yield has been obtained at pH 5.7 ( $\Phi_F = 0.09$ ). At low pH values,  $\Phi_F$  decreases most likely due to the interaction of protons with the carbonyl amide group ( $-\text{NHC}=\text{O}$ ).

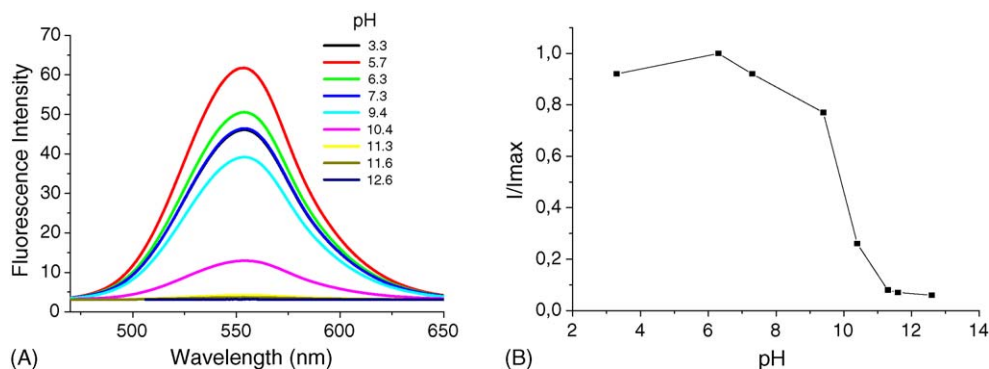


Fig. 3. (A) The changes in the fluorescence emission spectra of dye BD as a function of pH in aqueous solution at pH range 3.3–12.6. (B) Dependence of ( $I/I_{\max}$  at  $\lambda_F = 553$  nm) at different pH range ( $\lambda_{\text{exc}} = 413$  nm).

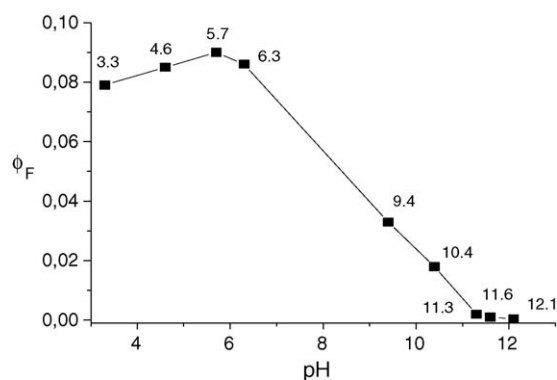


Fig. 4. Fluorescence quantum yield ( $\phi_F$ )–pH profiles for dye BD.

### 3.3. Influence of pH on the fluorescence properties of BD immobilized on the viscose textile matrix in aqueous solution

The fluorescence intensity of BD immobilized on textile matrix has been investigated in 2.0–12.1 pH range. The emission maximum in 2.0–10.2 pH range occurs at 543 nm. It is hypsochromically shifted compared to that observed in aqueous solution ( $\lambda_F = 553$  nm) and is approximately as in methanol solution ( $\lambda_F = 546$  nm) [19]. In alkaline medium at  $\text{pH} \geq 10.2$  the emission maximum shows a gradual bathochromic shift to 564 nm (Fig. 5A). The difference is attributed to the intermolec-

ular forces and to the hydrogen bonds between BD and the hydroxyl groups of viscose fibers. These interactions destabilize additionally the polar excited state. It is well known that viscose fibers swell in alkaline solution as far as the hydroxyl groups interact with sodium hydroxide. As a result the fluorophore response to the changes in its environment is quite fast and reversible.

As discussed for aqueous solution measurements taken in acidic medium lower than pH 4.0 the fluorescence emission decreases as a result from the addition of a proton to the oxygen atom of amide group. Nevertheless, total quenching has not been observed (Fig. 5B). It is seen that the emission is ‘switched on-off’ in a narrow pH range between pH 10.2 and 12.1.

The pH dependence of fluorescence intensity in this region has been analyzed and  $\text{p}K_a$  has been determined ( $\text{p}K_a = 10.8 (\pm 0.1)$ ). It is interesting to note that this value is close as this in aqueous solution, which indicates that the immobilized BD molecules save their sensor properties. The fluorescence intensity of the solution and immobilized BD decreases both in strong acidic and basic medium. Though, the change in the emission maxima only of the immobilized BD gives the opportunity to distinguish the pH region (Figs. 3A and 5A).

Fig. 6 plots the repeatability and reversibility of the pH induced fluorescence signal change of BD immobilized on viscose fabric. The sample of dyed viscose was alternatively dipped in preliminary prepared solutions with pH 5.2 and pH 11.4 for 3 min and for 1 min, respectively. The difference in

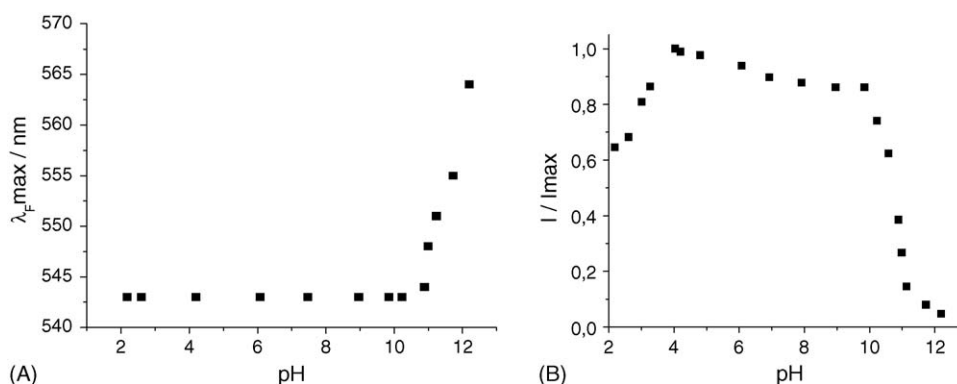


Fig. 5. (A) Changes in the fluorescence maxima of viscose fabrics as a function of pH in aqueous solution. (B) Dependence of ( $I/I_{\max}$  at  $\lambda_F = 543$  nm) at different pH ( $\lambda_{\text{exc}} = 413$  nm).

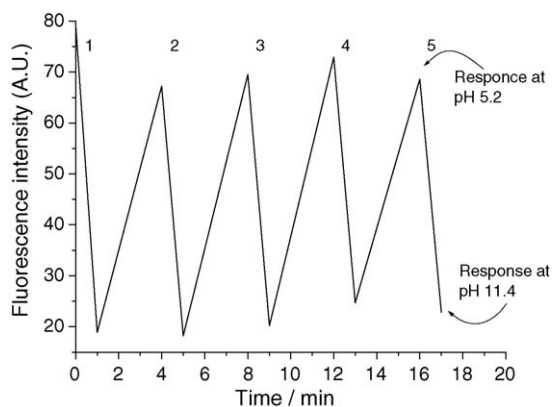


Fig. 6. Reproducibility of the fluorescence response of viscose fabric dyed with BD at pH 5.2 for 3 min and at pH 11.4 for 1 min.

the time necessary for the reproduction of the fluorescence response can be explained by the fact that the reaction occurring between the amide group and the protons has a different nature from the one between the amide group and hydroxyl ions (Scheme 2). In alkaline medium the reaction is probably more rapid.

#### 4. Conclusions

The investigations carried out have shown that functional properties of the newly synthesized water-soluble 1-[(7-Oxo-7H-benzo[de]anthracen-3-ylcarbonyl)-methyl]-pyridinium chloride depend on pH changes in aqueous media. The BD has been immobilized on textile viscose fabric and has been studied for the first time as a potential heterogeneous pH sensitive material. It has been proved that the solid matrix in this case does not impair the sensor properties of the BD. The immobilized fluorophore exhibits good reversibility, repeatability and satisfactory response of the pH induced fluorescence signal change.

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