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Colorimetric sensing of cyanide anions in aqueous media based on functional surface modification of natural cellulose materials

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ABSTRACT

The synthesis of two new water soluble azo dyes and their optical response to different anions is reported herein. Solution studies in water indicate that cyanide induces a colour change in these dyes, whereas no changes are observed in the presence of other anions, such as CH_3COOH^-, HSO_4^-, ClO_3^-, ClO_4^-, Cl^-, Br^-, $H_2PO_4^-$, $S_2O_3^-$, F^-, NO_3^-, I^-, NO_2^-, SO_3^{2-}, S^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, N_3^-, SCN^-, F^-, CO_3^{2-}, HCO_3^{2-}. In the second part of the paper, we report the incorporation of one of these dyes onto cellulosic fibres. The dye-sensitized cellulose materials were immersed in solutions of different anions and their response studied. The material is able to detect cyanide about 0.01–0.07 μM in aqueous solution with high selectivity over other anions.

1. Introduction

Due to the important roles of the anions played in the biological processes, the recognition and sensing of anions has received considerable attention over recent years.[1–12] In addition, there is interest in finding better and more efficient ways of detecting anions that can be potentially harmful to the environment or human health. One such anion is cyanide, which is lethal to humans at concentrations of 0.5–3.5 mg per kg of body weight.[13] Consequently, the presence of this anion in drinking water (1.9 μM as maximum concentration)[13] can pose a very serious risk to human health. It is therefore evident that reliable and efficient ways of detecting the presence of cyanide in water are needed. Although highly effective experimental protocols and detection techniques cyanide ions have been reported,[14,15] aqueous media, which are common in biological systems, often collapse their sensing functions. Because these anions are relatively small and are strongly solvated in protic solvents, interaction between these anions and anion sensors is hampered.[16,17] Therefore, much more powerful host–guest interactions are required to develop anion sensors that work in aqueous media. In this sense, many optical chemosensors have been developed to perform selective anion detection visually and, in addition, to allow the quantification of such species.[18–21] of the strategies used for the development of anionic chemosensors, the most simple involves the design of molecules that change colour following an alteration in their molecular structure due to their contact with anions. In this case, the selectivity of the chemosensor towards an anion is related to the fact that anionic species have differentiated capabilities to interact with the receptor site in the chemosensor, for instance, through hydrogen bonding. In spite of these developments there are still relatively few examples of selective probes for cyanide owing to high interference from other anions, in particular, fluorides.[22,23] Another drawback with most of the current methods is that the detection needs to be carried out in organic solvents (or mixtures of organic solvents and water), which limits their application to the analysis of 'real' samples that are often aqueous solutions. Therefore, the development of selective and efficient methodologies for detecting cyanide from aqueous media is in great demand. Recently we are developed a new generation of water soluble chemosensor able to detect the cyanide anion in pure water.[24] The water solubility of this new chemosensor generation was obtained by glyco conjugation of the starting organic chemodosimeter with the usual carbohydrates[23] following the general structure of the water soluble colouring agents reported previously.[25] Other various methods based on the functional modification of nanocrystalline TiO_2 films or membrane anchored with azo dye,[26] quantum dots,[27] supported materials[28] or polymers[29] to specifically react with cyanide have been reported. However, the development of facile, low-cost, highly sensitive and practical cyanide chemosensors that function in aqueous media

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still remains a challenge. Practical heavy anion sensors that allow on-site, real time detection without using any spectroscopic instruments have received a great deal of attention. In particular, colorimetric sensors[26–28] are extremely attractive because of the ease of observation with the naked eye. The colour change of these sensitizer materials in the presence of parts per million concentrations of cyanide salt was observed. However, the naked-eye detection of parts per billion level of cyanide in aqueous solution has not been achieved without the use of spectrophotometers due to the low surface area of flat TiO_2 film used for anchoring dye molecules.[26] In order to develop a simple material able to detect the cyanide anions in pure aqueous media, our idea consist of the incorporation of the adequate cyanide chemodosimeter into the natural fibres. For this purpose, our attention was focused to the cellulose as a support to incorporate the chemosensors that are not soluble in water via chemical grafting (Fig. 1). The final functionalized cellulose was then exposed to the aqueous solutions of various anions to investigate its selectivity and sensitivity towards cyanide anions.

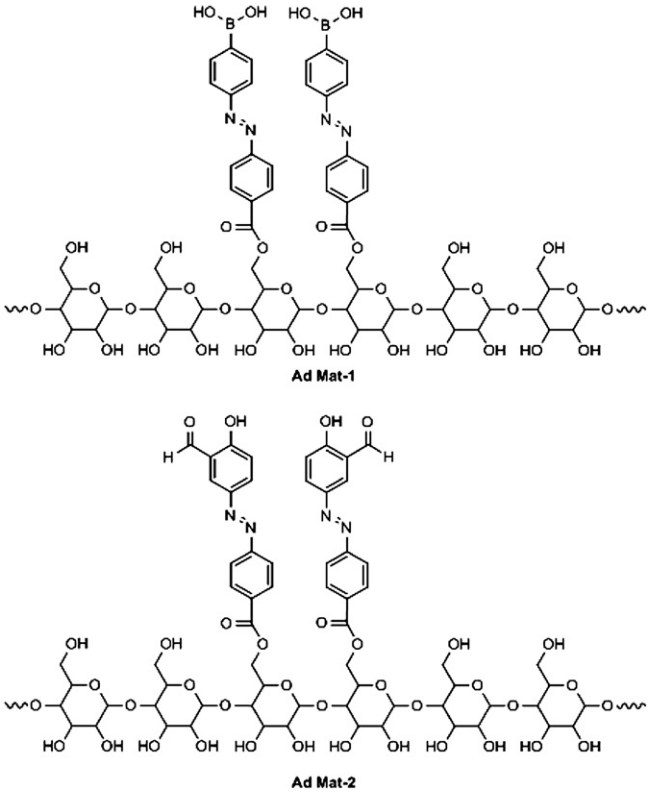


Fig. 1. Schematic representation of cyanide sensing using functionalized natural cellulose substance.

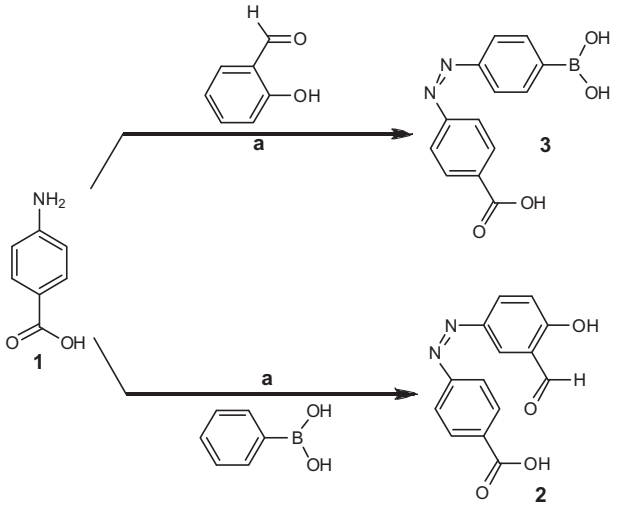
2. Results and discussions

2.1. Syntheses of chemosensors 2 and 3

The synthesis of the azoic dyes **2** and **3** is shown in Scheme 1.

The treatment of 4-amino-benzoic acid **1** with $NaNO_2$ in acidic medium afford its corresponding diazonium salt, which treated by phenyl boronic acid or salicylaldehyde to afford the azo dyes **2** and **3**, respectively in high yield.

In order to investigate and compare the chemosensing properties and the detection limit of the synthesized chromogenic probes **2** and **3** in pure water solution and when these chemosensors are supported on the cellulose material, these organic compounds are



Scheme 1. Synthesis of chemosensors **2** and **3**. Reagent and conditions: (a) $NaNO_2$, HCl 1 N, water, 0 °C to rt, 3 h.

firstly chemically modified by coupling with glucose and glycerol, to make them water soluble, as reported in our previous studies.[24] The chemical modification of the dyes **2** and **3** is carried by an esterification coupling of the carboxylic group (*COOH*) of the dyes **2**, **3** and the primary alcohol group (*−OH*) of the protected glucose **4** and the protected glycerol **5**[30] to afford the protected azo dyes **6** and **7**, respectively. Finally, a simple deprotection of **6** and **7** by TFA 90% solution at room temperature affords the water soluble chemosensors **8** and **9** (Scheme 2).

The Table 1 reports the UV–vis data and the measured water solubility of all synthesized dyes.

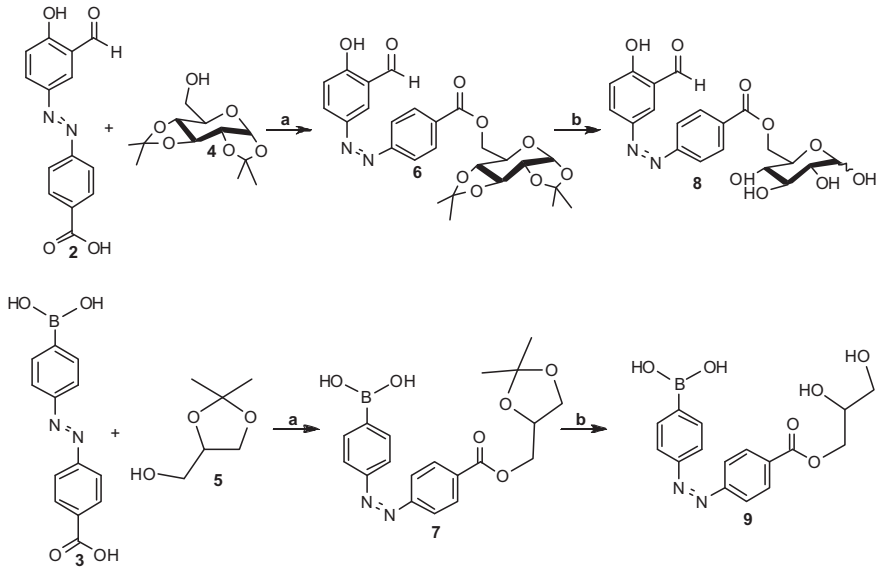
The results reported in Table 1 show that λ_{max} does not exhibit any significant shift after the chemical modification of the starting dyes **2** and **3**, by glyco conjugation with glucose or glycerylation with glycerol moiety. Also, molar extinction coefficient values can be considered almost constant, only very small differences being detected. Thus, derivatization of the carboxylic function in prepared dyes **2** and **3** does not affect the UV–vis spectrum as these groups are far from the chromophore.

2.2. Absorption spectral characteristics of chromogenic probes 8 and 9 in water

The ability of **8** and **9** to complex with anions was explored with UV–vis absorption spectrometry in pure water. Among the eleven anions tested in water solution CH_3COOH^-, HSO_4^-, ClO_3^-, ClO_4^-, Cl^-, Br^-, $H_2PO_4^-$, $S_2O_3^-$, F^-, NO_3^-, I^-, NO_2^-, SO_3^{2-}, S^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, N_3^-, SCN^-, F^-, CO_3^{2-}, HCO_3^{2-} and CN^- as their sodium salts, **8** and **9** responded to only CN^- resulting in a colour change from colourless to yellow for **8** and from green/yellow to colourless for **9** (Fig. 2), indicating that probes **8** and **9** can serve as a 'naked-eye' cyanide indicators in pure water. The absorption profiles of the sensors showed a remarkably higher selectivity for cyanide over the other anions in water. This colour change was also confirmed by UV–vis spectroscopy study. The treatment of the dyes **8** and **9** with a solution of cyanide caused a λ_{max} shift of the chromogenic probes from 357 nm to 432 nm for **8** and from 412 nm to 351 nm for **9**.

The strong nucleophilicity of cyanide in water seems to be the major contributor to the high selectivity of **8** and **9** for cyanide in water (Scheme 3).

However, anion, such as F^- and AcO^- should interact with the aqueous medium through H-bonding, and this solvation leads to a decrease in their basicity, thus, resulting in the poor deprotonation reaction as reported in our previous studies.[24]



Scheme 2. Synthesis of the water soluble chemosensors **8** and **9**. Reagent and conditions: (a) $SOCl_2$, DCM, rt, 2 h (b) TFA 90%, rt, 3 h.

Table 1
Spectroscopic solubility data of the synthesized dyes

Dyes	λ_{max} (MeOH) [nm]	Log ε_{max} (M^{-1} cm^{-1})	Solubility[a] [g/L]
2	357	4.3921	Insoluble
3	411	4.3222	Poorly soluble at 60 °C
6	357	4.3951	Insoluble
7	412	4.3254	Insoluble
8	358	4.3991	67.54
9	422	4.3287	70.45

[a] The solubility was measured at room temperature.

2.3. Sensitivity and detection limit in solution

Once the anion selectivity of **8** and **9** in water was established, it was of interest to determine the sensitivity and the detection limit of these two chromogenic probes. The detection limit[31] was calculated by measuring the absorbance changes by increasing the amount of cyanides (from 0 to 1 equiv). To determine the binding stoichiometry, a Job's plot of $(A-A_0)$ versus equivalent of the cyanide ion was established. Fig. 3 show a near linear correlation between intensity difference absorption $(A-A_0)$ and CN^- concentration in water at

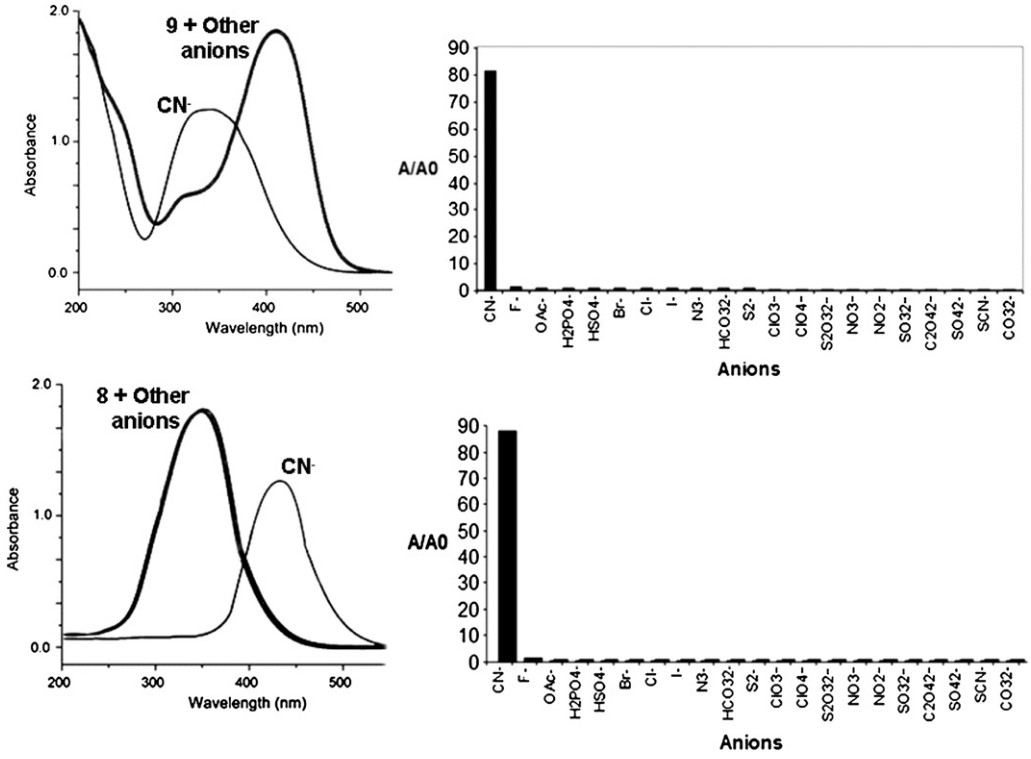
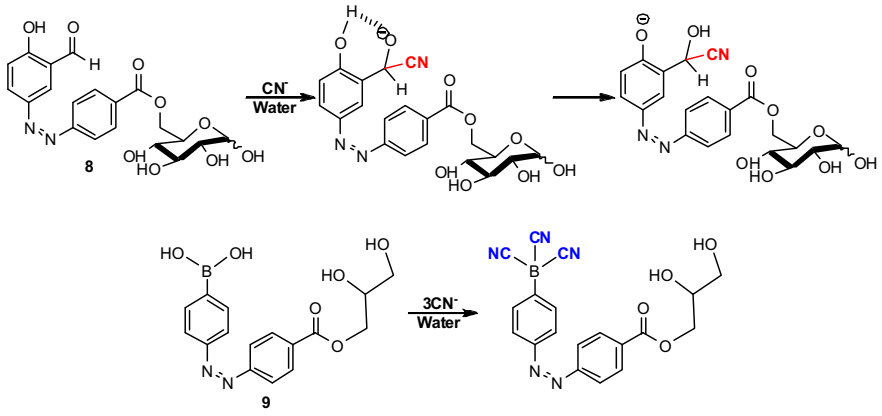


Fig. 2. (a) The absorbance response of the solution containing chemosensor **8** and **9** in pure water (10^{-4} M) at room temperature and at pH=7 in the presence of 3.10^{-4} M various anions.



Scheme 3. Proposal mechanism for **8** and **9** towards CN^-.

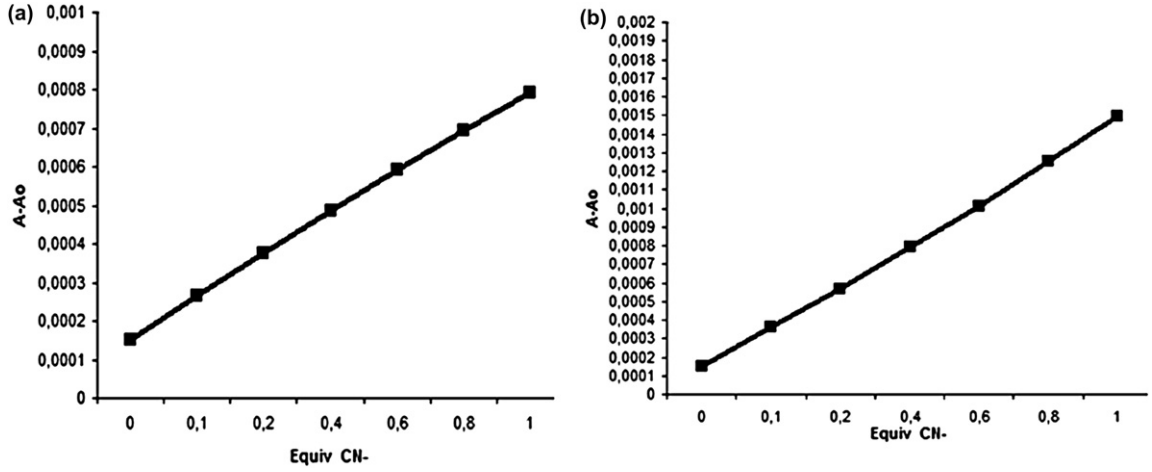


Fig. 3. The plot of $A-A_0$ versus equivalent of [CN^-] for the titration of **8** (a) and **9** (b) (10^{-5} M) with CN^- (0–1 equiv) in water at 25 °C and at pH=7.

room temperature, which indicates one to one binding between the probe and cyanide.

The Table 2 reports the detection limit[31] of chromogenic probes **8** and **9**.

Table 2
Detection limit of chromogenic probes **8** and **9**

Chromogenic probes	Detection limit
8	0.39 μM
9	0.37 μM

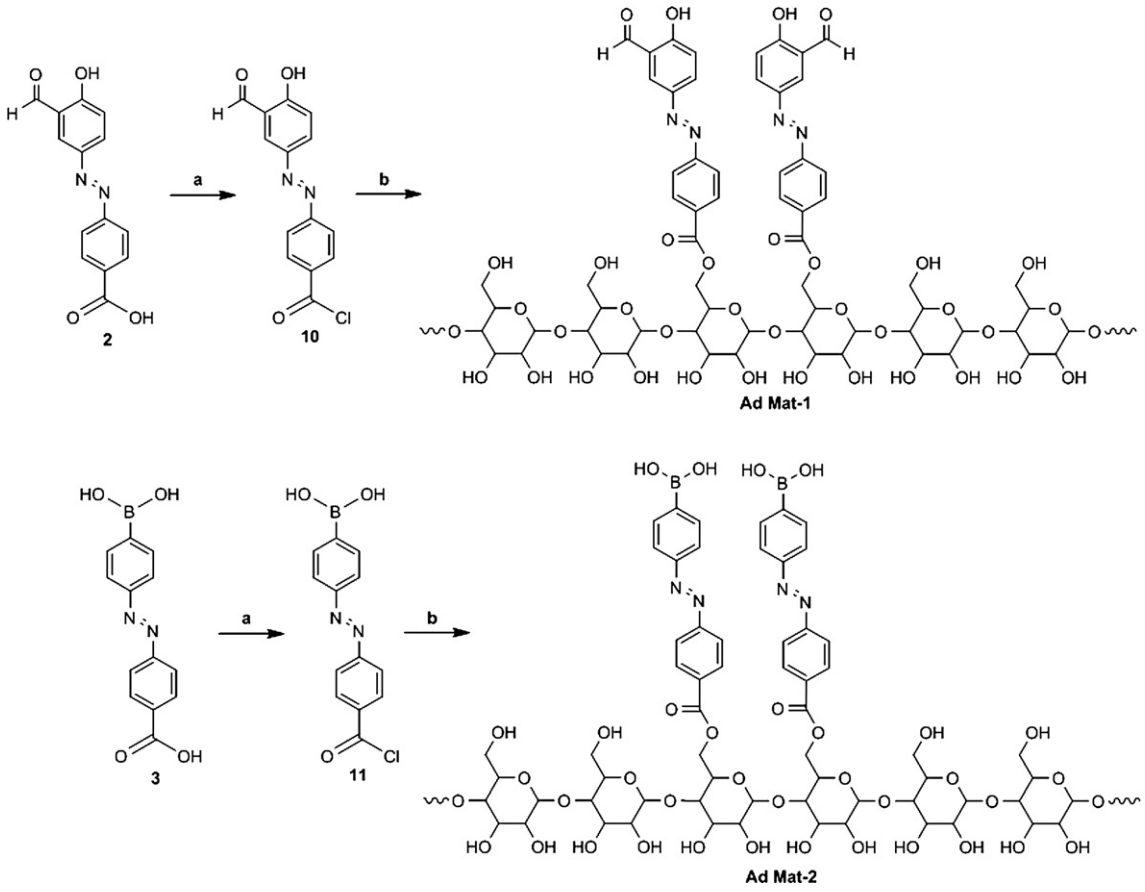
According to the World Health Organization (WHO), cyanide concentrations lower than 1.9 μM are acceptable in drinking water,[13] which meant that our water soluble chemosensors **8** and **9** based colorimetric method are sensitive enough to monitor cyanide concentration in drinking water.

2.4. Functional surface modification of natural cellulose

Once the anion-sensing properties of **8** and **9** were established in solution, it was of interest to incorporate these dyes onto nano structured natural cellulose fibre. The resulting functionalized cellulose by organic dyes can be exposed to aqueous solutions of the cyanide anions to be detected. Scheme 4 shows the synthesis strategy to functionalize the cellulose fabrics by the chromogenic probes **2** and **3**. Compounds **2** and **3** are first treated with $SOCl_2$ to afford its corresponding acyl chlorides **10** and **11**. Then, a simple esterification of **10** or **11** and the hydroxyl groups of cellulose fibre in DMSO as solvent at 100 °C allows the incorporation of the dyes **10** or **11** on the cellulose materials.

The presence of graft dyes on the surface of the treated cotton fabric samples has been also identified by IR(ATR) spectroscopy. The FTIR spectra of the biosourced and grafted cellulose are shown in Fig. 4. The $-OH$ stretching vibration of the biosourced cellulose occurs at 3397.07 cm^{-1} and the broad $C-H$ stretching band appears from 2800 to 3000 cm^{-1} region, these $-OH$ and $-CH$ are common in the spectrum a, b and c in Fig. 4. In the grafted cotton, the $-OH$ band has undergone a shift towards 3411.08 cm^{-1}. It can also be observed that the hydroxyl band intensity of the grafted cellulose was considerably less than that of the pure cellulose. This may be an indication of the possible participation of the hydroxyl groups in the chemical modification. This can be further supported by the decreased peak about 1163 cm^{-1}, which can be assigned to the $C-O$ stretching vibration of the $-CH_2OH$ group. However, if the cellulose fabric was exposed to the treatment by the dyes **2** and **3**, a new peak appeared at around 1750 cm^{-1}, these are from the esterification reaction of the hydroxyl group of the cellulose material and the carboxylic group of the dyes **2** and **3** via the formation of ester group. Therefore the peaks appeared at 1732.54 cm^{-1} (in the case of **Ad Mat-1**) and at 1731.33 cm^{-1} (in the case of **Ad Mat-2**) corresponds to the $C=O$ stretching of ester group.

The functionalized cellulose materials are then exposed to aqueous solutions of various anions (the same as those used in solution) and the optical changes of the modified textile are investigated. An initial qualitative naked-eye study indicated that the



Scheme 4. Functionalization of the cellulose fabrics. Reagents and conditions: (a) $SOCl_2$, DCM, rt, 2 h (b) DMSO, 100 °C, 1.5 h.

chemosensor materials only changed colour in the presence of cyanide anions (Fig. 5). The colour change of the sensor material is due to the selective coordination of cyanide with the chromogenic probes receptors of dye **2** and **3**. Depending on the concentrations of the CN^- solutions, the sensor material showed an obvious colour change within 1–10 min. However, a closer inspection of the system showed that in the presence of cyanide, not only does the adsorbed dye change colour, but it also desorbs from the cellulose chemosensors. This was confirmed by measuring the UV–vis absorption spectrum of the sensitized cellulose materials in the presence of increasing amounts of cyanide (Fig. 6c).

As displayed in Fig. 6a, the chemosensor modified cellulose materials underwent an obvious colour change from green/yellow to yellow/orange for **8** after being dipped into cyanide aqueous solutions. Because of the high surface areas of functionalized cellulose material, as expected, the colour change could be clearly seen by naked eye inspection. Also, λ_{max} shift of the sensitized **Ad Mat-1** from 351 to 426 nm (Fig. 6b). The 75 nm hypsochromic shift indicates that cyanide anions react via nucleophilic substitution with its aldehyde receptor on the chromogenic group **8**. However, no colour change was observed for **Ad Mat-1** upon exposing it to aqueous solutions of other anions, such as CH_3COOH^-, HSO_4^-, ClO_3^-, ClO_4^-, Cl^-, Br^-, $H_2PO_4^-$, $S_2O_3^-$, F^-, NO_3^-, I^-, NO_2^-, SO_3^{2-}, S^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, N_3^-, SCN^-, F^-, CO_3^{2-}, HCO_3^{2-} in a large excess as shown in Fig. 6a. These anions did not cause any hypsochromic shift of the initial 351 nm adsorption band of the chemosensor functionalized filter textile (Fig. 6b). Furthermore, the colouration response in the presence of CN^- is not influenced by addition of other anions. Upon exposing the **Ad Mat-1** or **Ad Mat-2** to aqueous solutions of CN^- (10 mM) mixed with CH_3COOH^-, HSO_4^-, ClO_3^-, ClO_4^-, Cl^-, Br^-, $H_2PO_4^-$, $S_2O_3^-$, F^-, NO_3^-, I^-, NO_2^-, SO_3^{2-}, S^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, N_3^-, SCN^-, F^-, CO_3^{2-}, HCO_3^{2-} (1 mM), it showed the same colour change as well as the band shift in the absorption spectra (from 351 nm to 426 nm for **Ad Mat-1** and from 412 nm to 351 nm for **Ad Mat-2**). These results indicate the high selectivity of the chemosensor modified filter paper for the detection of CN^- from mixed aqueous solutions of various anions.

To establish the sensitivity of **Ad Mat-1** and **Ad Mat-2** to cyanide and the detection limit of the system, the absorbance of the functionalized cellulose materials at different cyanide concentrations was recorded (Fig. 7). Plotting ΔA versus [CN^-] allowed us to calculate the detection limit to be 0.011 μM for **Ad Mat-1** and 0.075 μM for **Ad Mat-2** (see Supplementary data). The difference between the detection limit of cyanide anions in solution and on solid support may be explained by the large surface area of the solid support, which facilitates the contact between the receptor site and the cyanide anions. The choice of the textile support is crucial to develop a functional material able to detect cyanide in pure water, in this sense; this support must be hydrophilic material to facilitate the reaction between cyanide and chemosensor incorporated on the fabric. The cotton is a very interesting choice because of its hydrophilic character and its natural availability.

To investigate the pH effect in the sensing ability of the sensitised materials, **Ad Mat-1** and **Ad Mat-2** are immersed in aqueous solutions of different acidity (namely, pH 5, 9 and 11) and left in such solutions for some time. As shown in Fig. 8, a constant decrease in the intensity of the λ_{max} of the materials was observed at pH 11 with time.

The decrease in the intensity of the λ_{max} of the **Ad Mat-1** and **Ad Mat-2** materials observed at pH 11 can be explained by the desorption of the dyes from the materials due to the saponification of

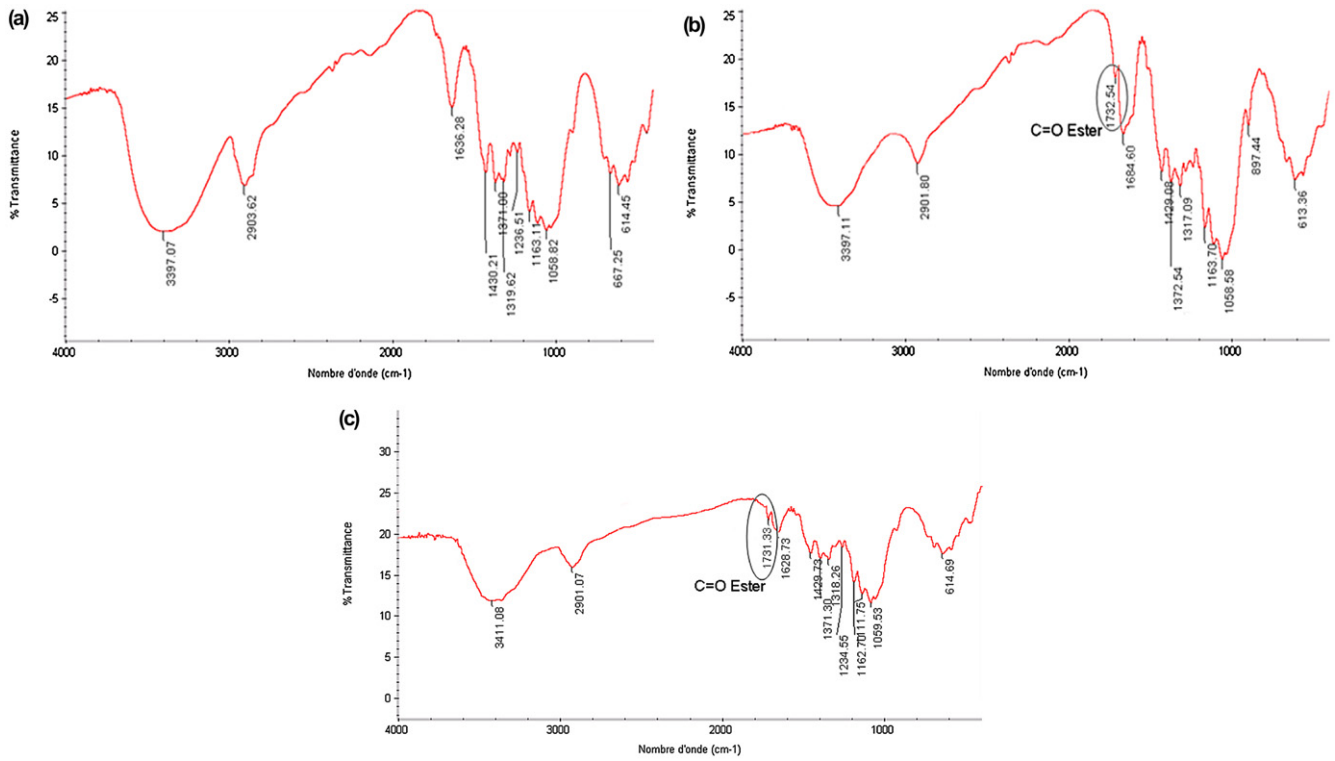


Fig. 4. FTIR transmission spectra of (a) the scoured cotton fabric and (b) the functionalized cotton fabric **Ad Mat-1** (c) the functionalized cotton fabric **Ad Mat-2**.

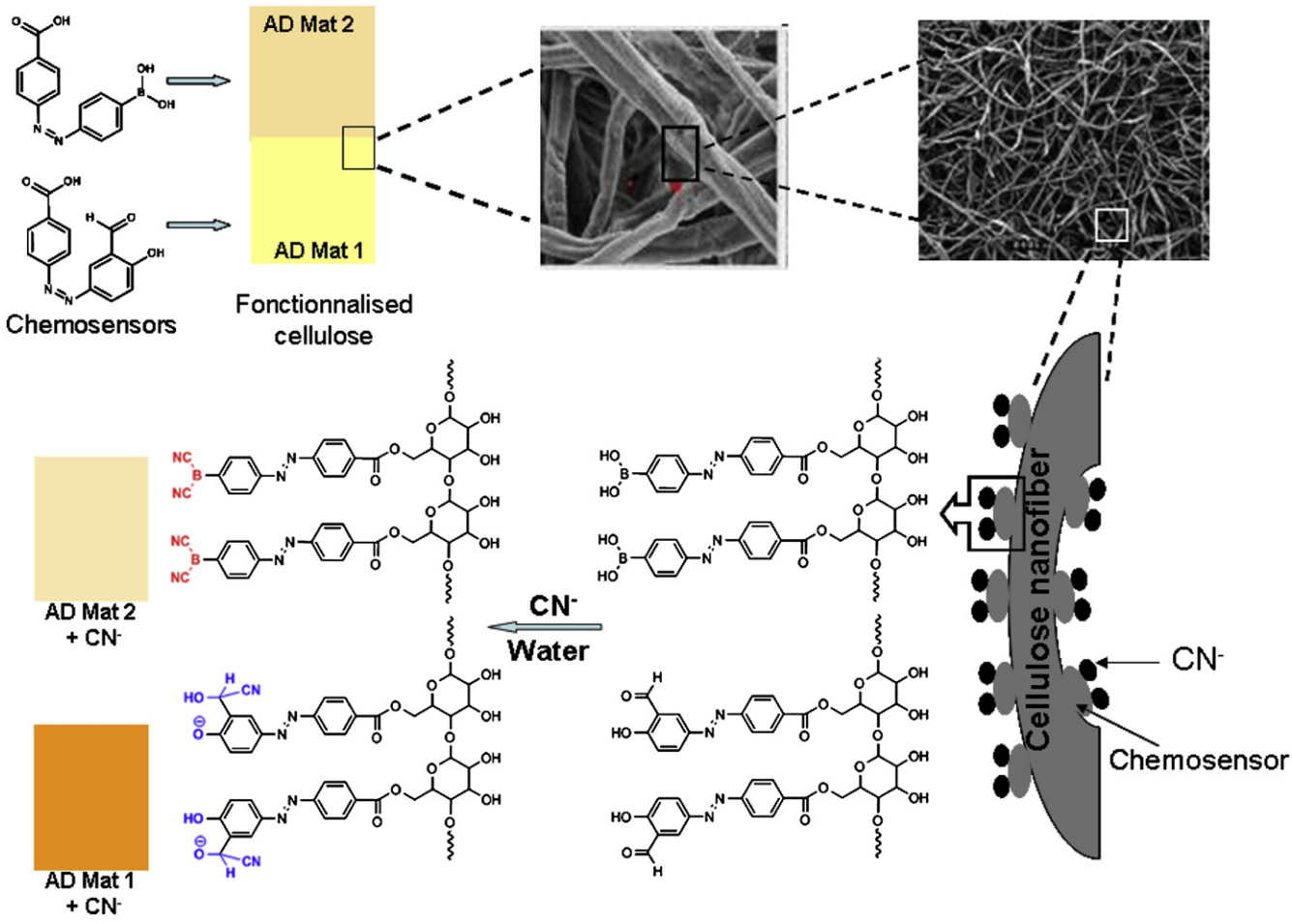


Fig. 5. Schematic representation of CN^- sensing using dyes modified natural cellulose substance.

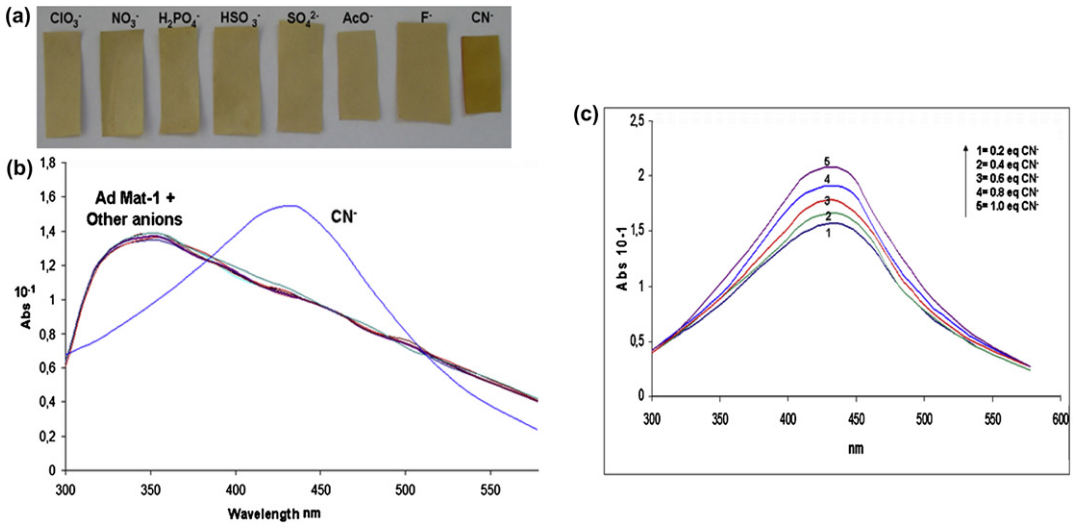


Fig. 6. Colour change of the chemosensor-modified cellulose fibre upon exposure to aqueous solutions of different anions –1 mM (a). Solid UV–vis spectra of the chemosensors –2-modified cellulose fibre after dipping in aqueous solutions at pH=7 of different anions (b). Absorption spectra of the chemosensor –2-modified cellulose fibre upon contact with increase amount of aqueous solution of CN^-.

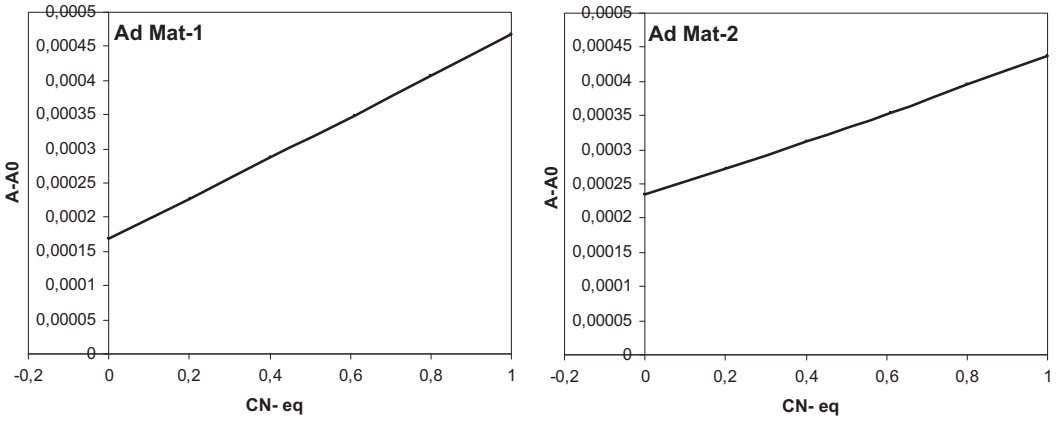


Fig. 7. Normalised absorption spectra of **Ad Mat-1** and **Ad Mat-2** immersed in aqueous solutions of cyanide at different concentrations.

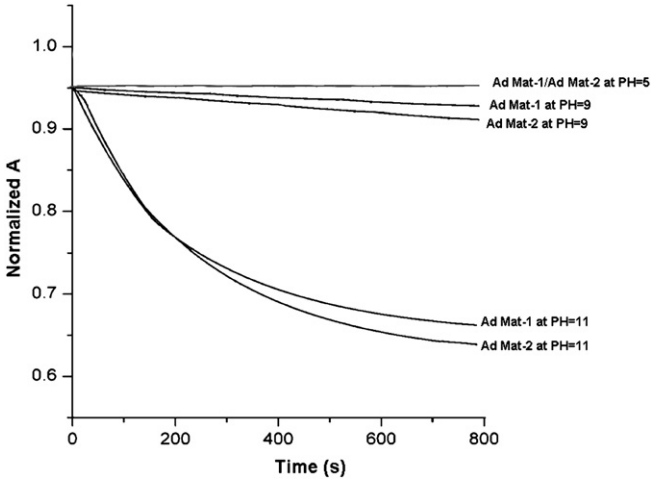


Fig. 8. Plot showing the reduction in intensity of the λ_{max} absorption for the **Ad Mat-1** and **Ad Mat-2** materials as a function of pH.

the esteric groups at pH=11. Therefore, the sensitised materials, **Ad Mat-1** and **Ad Mat-2** can be used for cyanide detection in water at 5<pH<11.

3. Conclusions

Two new water-soluble dyes (**8** and **9**) are prepared, and their optical responses to anions are studied both in pure water. The water solubility is obtained by the incorporation of the water soluble molecules (glucose end glycerol) on the starting organic dyes and its corresponding water soluble derivatives present very high chemo selectivity towards cyanide anions in water. Organic compounds **2** and **3** were then grafted on natural cellulose fibres and its optical properties studied. Immersion of these functionalized textiles in an aqueous solution of cyanide induced a colour change that can be used for the detection of cyanide down to 0.01–0.07 μM. These easy-to-use materials also showed also a high degree of cyanide selectivity in aqueous medium.

4. Experimental section

4.1. Materials and instrumentations

TLC was carried out on silica gel pre-coated plates (Merck; 60 Å F_{254}) and spots located with (a) UV light (254 and 366 nm), (b) ninhydrin (solution in acetone), (c) fluorescamine, (d) I2 or (e) a basic solution of permanganate [$KMnO_4$ (3 g), K_2CO_3 (20 g) and NaOH (0.25 g) in water (300 mL)]. Flash column chromatography (FCC) was carried out on Merck silica gel 60 (230–400 mesh) according to Still et al.[32] ^1H and ^{13}C NMR spectra were recorded at 200 MHz with Varian spectrometers in deuteriated solvents and are reported in parts per million (ppm) with the solvent resonance used as the internal reference. Mass spectra were recorded with a Thermo Fisher LCQ fleet ion-trap instrument (the spectra reported were also using the ESI+*c* technique). Elemental analysis was carried out with a Perkin–Elmer 240C Elemental Analyzer. Transmission mode spectra (32 scans, 4 cm^{-1} resolution) were measured with KBr pellets of finely cut and ground fabrics. FTIR ATR spectra (216 scans, 4 cm^{-1} resolution) were collected with a MIRacle, single reflection horizontal ATR accessory (PIKE instruments) having a diamond ATR crystal fixed at incident angle of 45°. UV–vis spectra were recorded with a Cary-4000 Varian spectrophotometer. The compound **5** was prepared following the procedures reported in the literatures.[30]

4.2. Preparation of chromogenic probes titration solutions

Stock solutions (1 mM) of the tetrabutylammonium salts of CH_3COOH^-, HSO_4^-, ClO_3^-, ClO_4^-, Cl^-, Br^-, $H_2PO_4^-$, $S_2O_3^-$, F^-, NO_3^-, I^-, NO_2^-, SO_3^{2-}, S^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, N_3^-, SCN^-, F^-, CO_3^{2-}, HCO_3^{2-} in water were prepared. Stock solutions of chemodosimeter (0.1 mM) were prepared in water. Test solutions were prepared by placing 4–40 μL of the probe stock solution into a test tube, adding an appropriate aliquot of each anion, and diluting the solution to 4 mL with water. In the case of **Ad Mat-1** and **Ad Mat-2** titration, a fragment of these textiles were immersed in stock solutions of each anions for 1–10 min (1 mM) and dried under air flux. All the experiments were carried out at 20±2 °C.

4.3. General procedure A: synthesis compounds 2 and 3

To a solution 4-amino benozoic acid (1 mol) in 15 mL of water/HCl 1 N: 15/1.5, a solution of $NaNO_2$ (1.4 mmol) in water (2 mL) was added dropwise at 0 °C and the resulting mixture was stirred for 30 min. The diazonium salt solution previously prepared was added dropwise to the solution of salicaldehyde or phenyl boronic acid (1 mol) in methanol (3 ml) and the combined solutions were maintained at 0 °C for 6 h with stirring. After this time, the pH was adjusted to 8 and the resulting mixture was diluted with chloroform (20 ml), the formed product was isolated by filtration and washed with chloroform to afford the corresponding azo dyes **2** or **3**.

*4.3.1. Synthesis 4-((3-formyl-4-hydroxyphenyl)diazenyl)benzoic acid (**2**).* The product **2** was prepared according to the general procedure ***A*** using the following quantities: 4-amino benzoic acid (1.00 g, 7.29 mmol), salicaldehyde (0.89 g, 7.29 mmol), $NaNO_2$ (0.56 g, 8.74 mmol), in HCl 1 N/water (10 mL), to afford **2** (1.24 g, 62%). ^1H NMR (200 MHz, DMSO-d_6): δ=10.28 (s, 1H), 8.37–8.22 (AA'XX' system, 4H), 8.09 (m, 2H), 7.29 (m, 1H), 5.31 (s, 1H) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): δ=193.9, 169.4, 164.3, 157.3, 145.6, 132.9, 130.9, 130.2, 124.5, 122.7, 118.4, 116.3 ppm. MS (ESI): m/z=271.21 $[M+1]^+$. $C_{14}H_{10}N_2O_4$ (270.06): calcd C, 62.22; H, 3.73; N, 10.37, found, C, 62.31; H, 3.79; N, 10.42.

*4.3.2. Synthesis of 4-((4-boronophenyl)diazenyl)benzoic acid (**3**).* The product **3** was prepared according to the general procedure ***A*** using the following quantities: 4-amino benzoic acid (1.00 g, 7.29 mmol), phenyl boronic acid (0.88 g, 7.29 mmol), $NaNO_2$ (0.56 g, 8.74 mmol), in HCl 1 N/water (10 mL), to afford **3** (1.51 g, 77%). ^1H NMR (200 MHz, DMSO-d_6): δ=8.40–8.21 (AA'XX' system, 4H), 8.12 (s, 2H), 8.02–7.94 (AA'XX' system, 4H) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): δ=169.7, 157.5, 152.9, 133.5, 132.6, 130.4, 123.7, 122.8, 108.9, ppm. MS (ESI): m/z=271.17 $[M+1]^+$. $C_{13}H_{11}BN_2O_4$ (270.08): calcd C, 57.82; H, 4.11; N, 10.37, found, C, 57.89; H, 4.17; N, 10.41.

4.4. General procedure B: synthesis compounds 6 and 7

A mixture **2** or **3** (1 mol) and $SOCl_2$ (1 mol) in dry DCM (2 mL) was stirred under a hydrogen atmosphere at room temperature for 1 h. The solvent evaporated in vacuo to give the crude product, which was coupled, without purification, with the protected glucose **4** or the protected glycerol **5** (1 mol) in THF as solvent. The formed products are isolated by flash chromatography to afford the corresponding dyes **6** or **7**.

*4.4.1. Synthesis of compound **6**.* The product **6** was prepared according to the general procedure ***B*** using the following quantities: dye **2** (1.00 g, 3.70 mmol), $SOCl_2$ (0.44 g, 3.70 mmol), **4** (0.96 g, 3.70 mmol), in THF (10 mL), to afford **6** (1.53 g, 81%). R_f 0.53 (EtOAc/PE: 2/3). ^1H NMR (200 MHz, DMSO-d_6): δ=10.27 (s, 1H), 8.36–8.22 (AA'XX' system, 4H), 8.10 (m, 2H), 7.23 (m, 1H), 5.53 (d, 1H, $J_{1,2}$=5.1 Hz, H-1), 5.31 (s, 1H, PhO*H*), 4.62 (dd, 1H, $J_{2,3}$=2.4 Hz, $J_{3,4}$=7.8 Hz, H-3), 4.33 (dd, 1H, H-2), 4.22 (dd, 2H, $J_{4,5}$=1.8 Hz,H-4), 4.19 (m, 2H, H-6a, H-6b), 4.01 (ddd, 2H, $J_{5,6a}$=6.6 Hz, $J_{5,6b}$=4.4 Hz, H-5), 1.46, 1.41, 1.34, 1.33 [4s, each 3H, 2× C(CH_3)2] ppm. ^{13}C NMR (50 MHz, DMSO-d_6): δ=193.4, 165.5, 164.2, 157.3, 145.8, 132.7, 130.9, 130.4, 124.2, 122.6, 118.4, 116.6, 96.1 (C-1), 70.9 (C-2), 70.5 (C-4), 70.3 (C-3), 65.8 (C-5), 63.7 (C-6), 25.8, 25.7, 24.8, 24.3 [4× C(CH_3)2] ppm. MS (ESI): m/z=513.28 $[M+1]^+$. $C_{26}H_{28}N_2O_9$ (512.18): calcd C, 60.93; H, 5.51; N, 5.47, found, C, 60.97; H, 5.56; N, 5.51.

*4.4.2. Synthesis of compound **7**.* The product **7** was prepared according to the general procedure ***B*** using the following quantities: dye **3** (1.00 g, 3.71 mmol), $SOCl_2$ (0.45 g, 3.70 mmol), **4** (0.97 g, 3.70 mmol), in THF (10 mL), to afford **6** (1.61 g, 87%). R_f 0.49 (EtOAc/PE: 2/3). ^1H NMR (200 MHz, DMSO-d_6): δ=8.41–8.22 (AA'XX' system, 4H), 8.12 (s, 2H), 8.03–7.93 (AA'XX' system, 4H), 4; 51–4.30 (m, 3H), 3.94–3.89 (m, 2H), 1.25 (s, 6H) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): δ=166.6, 157.4, 152.6, 133.7, 132.6, 130.8, 123.5, 122.7, 118.5, 108.8, 75.7, 67.9, 64.6, 26.1 ppm. MS (ESI): m/z=385.23 $[M+1]^+$. $C_{19}H_{21}BN_2O_6$ (384.15): calcd C, 59.40; H, 5.51; N, 7.29; found, C, 59.45; H, 5.56; N, 7.32.

4.5. General procedure C: deprotection of compounds 6 and 7

A solution of **6** or **7** (1 mol) in 90% aqueous CF_3COOH (18 mL) was stirred at room temperature for 2 h and the red-violet reaction mixture was concentrated under diminished pressure and repeatedly co-evaporated with toluene (4×30 mL) to afford the water-soluble dyes **8** and **9**.

*4.5.1. Synthesis of compound **8**.* The product **8** was prepared according to the general procedure ***C*** using the following quantities: dye **6** (1.00 g, 1.96 mmol), to afford **8** (0.79 g, 95%). ^1H NMR (200 MHz, DMSO-d_6): δ=10.26 (s, 1H), 8.36–8.23 (AA'XX' system, 4H), 8.11 (m, 2H), 7.22 (m, 1H), 5.82 (d, 1H, J=9.3 Hz), 5.76 (m, 1H), 5.56 (m, 2H),

5.33 (s, 1H, PhO*H*), 5.24 (dd, 1H, *J*=10.2, 3.3 Hz), 4.2 (m, 2H) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): see Table 3 for glycidic moiety and δ=193.7, 165.6, 164.2, 157.6, 145.6, 132.7, 130.8, 130.6, 124.4, 122.5, 118.6, 116.9 ppm. MS (ESI): m/z=433.25 $[M+1]^+$. $C_{20}H_{20}N_2O_9$ (432.12): calcd C, 55.56; H, 4.66; N, 6.48, found, C, 55.61; H, 4.69; N, 6.52.

Table 3
^{13}C NMR spectroscopic data (δ, ppm) for the glycide portions for deprotected 3-*O*-D-glucoyl derivatives

Dyes	C-1	C-2	C-3	C-4	C-5	C-6
8-α**p**	92.4	72.1	81.9	72.1	70.0	61.2
8-α**p**	92.4	72.1	82.0	72.1	70.0	61.3

*4.5.2. Synthesis of compound **9**.* The product **9** was prepared according to the general procedure C using the following quantities: dye **7** (1.00 g, 2.60 mmol), to afford **9** (0.83 g, 92%). ^{1}H NMR (200 MHz, DMSO-d_6): δ=8.42–8.22 (AA'XX' system, 4H), 8.12 (s, 2H), 8.01–7.91 (AA'XX' system, 4H), 4.52–4.29 (m, 2H), 3.91–3.61 (m, 3H), 3.56 (s, 2H) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): δ=166.5, 157.3, 152.6, 133.8, 132.5, 130.7, 123.6, 122.7, 118.6, 108.9, 70.6, 65.9, 63.6 ppm. MS (ESI): m/z=345.22 $[M+1]^+$. $C_{16}H_{17}BN_2O_6$ (344.12): calcd C, 55.84; H, 4.98; N, 8.14; found, C, 55.88; H, 5.03; N, 8.19.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.04.061.

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