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Halochromic properties of sulfonphthaleine dyes in a textile environment: The influence of substituents

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ABSTRACT

The application of pH-sensitive dye molecules onto textile materials is a promising method for the development of sensor materials. Ten commonly used pH-indicators, namely sulfonphthaleine dyes, are applied onto polyamide 6 using two distinct methods: conventional dyeing of fabrics and dye-doping of nanofibres. The influence of the substituents of each dye on their interaction with polyamide, as well as the difference between both application methods is investigated. For the conventionally dyed fabrics, halogen substituents are needed to result in a pH-sensitive fabric. This can be traced back to halogen bonding and is supported by theoretical simulations. Dye-doped nanofibrous non-wovens show significant dye leaching, which can be understood based on the very acidic electrospinning solution. The use of a complexing agent improves the leaching properties, especially for dyes containing four bromine substituents. These findings indicate the importance of halogen substituents on sulfonphthaleines for further research in the development of pH-sensitive sensors.

1. Introduction

The colouring of textile materials is a widely applied and well-known process, wherein the focus is mainly on the development of dyes resulting in textile materials with constant colour [1,2]. Recently however, in the light of stimuli-responsive polymeric materials [3–7], an increasing interest is shown in the development of colour-changing materials such as pH-sensitive textiles [8–15]. These halochromic textiles can show an easily visible output signal in a non-destructive way. They also maintain all advantages of their parent materials: a textile sensor shows a high flexibility in contrast to conventional sensor systems. Furthermore, their applicability on large surfaces and the ability to give a local signal are great benefits [16–30]. Possible applications include wound bandages and detection of acid vapours [13,31].

Herein, we focus on the application of sulfonphthaleine dyes on polyamide 6 (PA6). Sulfonphthaleine dyes form a relatively small dye class, but are widely used as acid–base indicators because they show a clear colour transition in function of pH. Therefore they find application in various other areas, such as detection of pesticides and CO_2, but also in biological and medical fields [32–51]. To utilise these dyes in textile sensors, a thorough understanding of their behaviour in aqueous solution is a prerequisite. Following our experience in studying a dye molecule in aqueous solution [14], a systematic study of ten commercially available sulfonphthaleine dyes was performed [15], wherein a clear influence of the substituents was found on the pH-sensitive behaviour (Fig. 1).

The colour changing mechanism of sulfonphthaleine dyes can be ascribed to a protonation/deprotonation reaction, as illustrated in Scheme 1. The dyes can exist in a neutral form (**x**) in powder or in very acidic media. The most interesting molecular change (and thus colour change), however, is the deprotonation of a single anion ($\mathbf{x}_a$) to a resonance stabilised double anion ($\mathbf{x}_b$). The pK_a values given in

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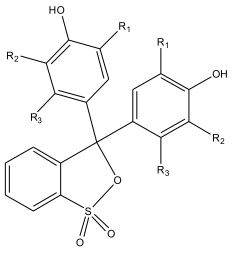


	R_1	R_2	R_3	pK_a
(1) Phenol Red	H	H	H	8.0
(2) Cresol Red	CH_3	H	H	8.3
(3) m-Cresol Purple	H	H	CH_3	8.5
(4) Xylenol Blue	CH_3	H	CH_3	9.1
(5) Thymol Blue	i-Pr	H	CH_3	8.9
(6) Chlorophenol Red	Cl	H	H	6.7
(7) Bromophenol Blue	Br	Br	H	4.1
(8) Bromocresol Purple	Br	CH_3	H	6.3
(9) Bromocresol Green	Br	Br	CH_3	4.8
(10) Bromothymol Blue	i-Pr	Br	CH_3	7.4

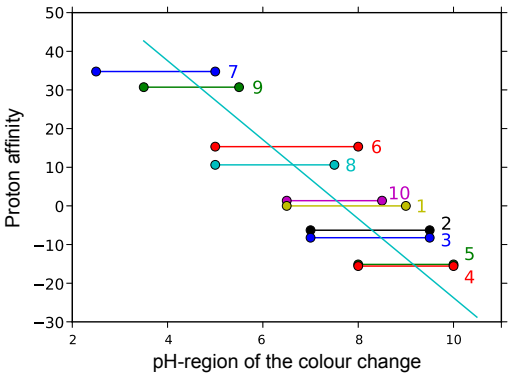
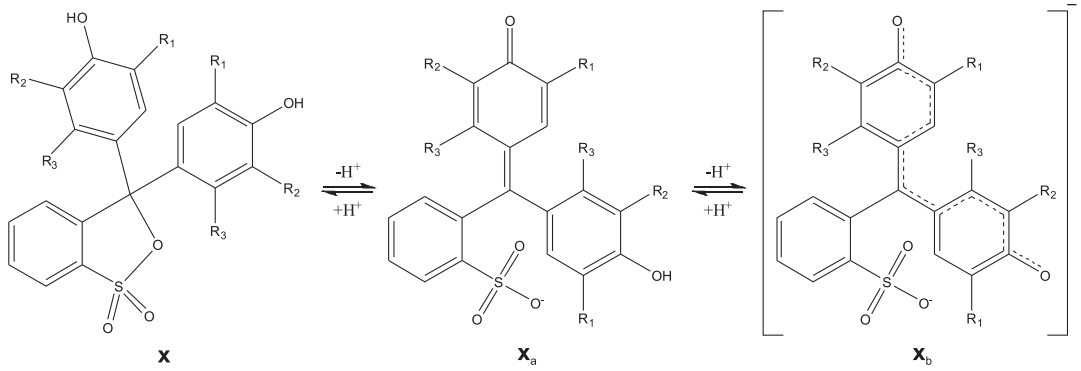


Fig. 1. Basic structure of sulfonphthaleine dyes and substituents of all studied molecules. The linear correlation between theoretical proton affinities and experimental pK_a's on the right hand side illustrates the large influence of substituents on the halochromic behaviour (adapted with permission from Ref. [15]).



Scheme 1. General colour changing mechanism for sulfonphthaleine dyes. While the neutral structure **x** is observed only in very acidic solutions or in powder, the relevant colour change originates from a deprotonation from the single anionic form $\mathbf{x}_a$ to a double anion $\mathbf{x}_b$.

Fig. 1 are those of the deprotonation reaction from $\mathbf{x}_a$ to $\mathbf{x}_b$ and it can clearly be seen that the substituents have a large influence on the pH-region where this reaction happens. The molecular structure of these dyes is not only important for the observed colour transition, but also for the behaviour during the different dye application processes, as will be shown in this contribution.

Sulfonphthaleine dyes are applied onto PA6 in this work using two methods: conventional dyeing of fabrics and dye-doping of nanofibres. Nanofibres have a very small fibre diameter (and thus high specific surface area) [52], which results in very fast reaction times. This makes them very suitable as basis to develop halochromic sensors for wound healing and other optical applications [24,28,53–67]. Conventional fabrics have a slower reaction time because of their larger fibre diameter, but are ubiquitous, which is why they are also investigated here.

For the development of nanofibres, polyamide 6 and dye molecules are dissolved into a formic acid/acetic acid solution, which is then electrospun. During this very fast process (which occurs at room temperature), the solvent evaporates, forcing entrapment of the dye molecules in the fibres (see top of Fig. 2). Conventional dyeing of fabrics on the other hand is a diffusion process: during a relative long time (one hour) and at elevated temperature (100 °C) [68], the dye molecules are allowed to diffuse into the micro fibres from an aqueous solution at pH 5 (in the form of a fabric, see bottom of Fig. 2). Dye-fibre interactions are therefore the driving force for this dyeing process. The pH of both dyeing processes determines in which state the dye molecules will be (neutral, anion or dianion, see Scheme 1). This, combined with other differences such as fibre diameter, will greatly influence the interactions between the dye and PA6. These will be analysed using UV/Vis spectroscopy and by performing dye leaching tests.

Further insight will be gained by applying molecular modelling, which is increasingly applied when studying dye molecules [69–71]. These simulations will provide insight on a molecular scale and help to understand the cause of a colour change [14,15]. The theoretical calculations in this work, which are all performed using Density Functional Theory (DFT), are utilised to gain a better understanding of the interaction of sulfonphthaleine dyes with the PA6 environment. This was previously successful to understand the experimentally observed pH-sensitive behaviour [28]. It has also been shown that M06-2X provides a good agreement with experiment when studying interactions, especially halogen bonding [72,73].

In a previous study, it was shown that the substituents of sulfonphthaleine dyes have a large influence on the pH-sensitive behaviour in aqueous solution [15]. The same ten molecules will now be applied onto PA6 to analyse the influence of these substituents on the interaction with PA6 and to study changes in pH-sensitive behaviour. Moreover, the dyeing will be performed in two different ways: conventional dyeing of fabrics (Section 4.1) and by dye-doping nanofibres (Section 4.2). The difference between these two methods is expected to have a large influence on the interaction, which is analysed by UV/Vis spectroscopy and dye leaching tests and will be further discussed in Section 4.3. As in our previous work, a combined experimental and theoretical approach is used to unravel the halochromic behaviour.

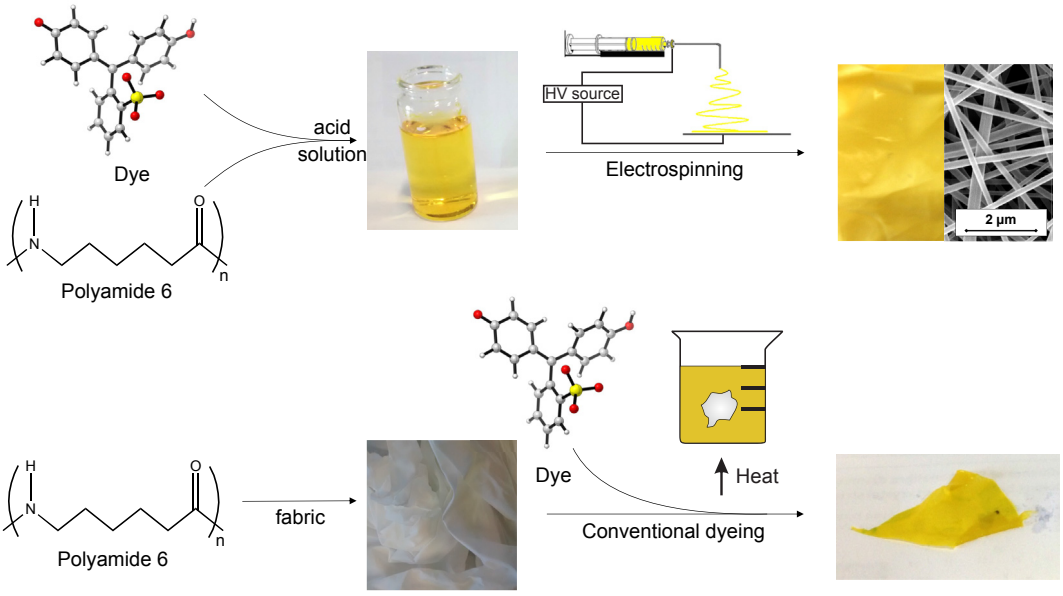


Fig. 2. For the fabrication of nanofibres (top), polyamide 6 and dye molecules are dissolved into a formic acid/acetic acid solution, which is then electrospun. During the conventional fabric dyeing process (bottom), dye molecules are allowed to diffuse from an aqueous solution at pH 5 into the polyamide 6 fabric at elevated temperature (100 °C).

2. Materials and methods

All dye molecules were supplied by Sigma–Aldrich and used as received, together with hydrochloric acid (1 mol/L), acetic acid (1 M) and sodium hydroxide (50 m%) for pH regulation. Measurement of the pH values was executed with a Hamilton glass electrode and a SympHony pH meter. UV/Vis spectra of a 10 mg/L solution were measured on the Lambda 900 spectrophotometer from PerkinElmer in the interval 300–800 nm (with a resolution of 1 nm). The transmission measurements in solution were recalculated to absorbance; reflection measurements on the fabrics/non-wovens were recalculated to Kubelka–Munk.

Conventional dyeing was performed on white PA6 fabrics provided by Concordia Textiles, Belgium. Each fabric is submerged at a liquid ratio of 100:1 in a 0.3% on mass fibre (%omf) dye solution; buffered at pH 5. The mixture was subsequently heated to 100 °C in a Matis Labomat for one hour, allowing for diffusion of the dye molecules into the fabric.

The nanofibrous PA6 non-wovens were produced by solvent electrospinning using a 50/50 acetic acid/formic acid (AA/FA) solvent system and a PA6 concentration of 16 wt% [74]. Prior to electrospinning, the solutions were characterised to determine their viscosity (Brookfield LVDV-II), conductivity (Radiometer Analytical CDM210) and surface tension (Wilhelmy plate method). For electrospinning, 18 gauge needles and a grounded aluminium collector were used. Process parameters were adapted to result in a stable process; a flow rate of 2 mL/h, a tip-to-collector distance of 6 cm and an applied voltage between 20 and 25 kV were used. All electrospinning trials were performed at ambient humidity and temperature (45 ± 10%RH, 18 ± 3 °C). The obtained nanofibre morphology was examined by scanning electron microscopy (FEI Quanta 200 F) at an accelerating voltage of 20 kV. Sample preparation was done using a gold sputter coater (Balzers Union SKD 030).

Pure PA6 solutions were electrospun as reference, dye-doped samples were obtained by adding sulfonphthaleine dyes directly to the PA6 electrospinning solution. All coloured nanofibrous PA6 non-wovens contained a dye concentration of 0.3%omf. The effect of the complexing agent poly-(diallyldimethylammonium chloride) (PDADMAC) was tested for a concentration of 4%omf, also added directly to the electrospinning solution. For electrospinning, PA6 (M_w 51,000 g/mol, PDI 1.82), PDADMAC (M_w 100,000–200,000, 20 wt% aqueous solution), AA (99.8 v%) and FA (98–100 v%) were supplied by Sigma–Aldrich and used as received. No significant differences in solution properties or nanofibre morphology were seen between blank PA6 nanofibres and dye-doped or PDADMAC-containing nanofibres.

Analysis of the dye migration/immobilisation was done in two different ways. Firstly, the leaching in an aqueous solution with controlled pH was tested by introducing 10 mg of fabric in 10 mL of the aqueous solution. After 24 h, the samples are removed and the solution was measured by UV/Vis spectroscopy. The absorbance gives an effective measure of the dye migration to the water bath of known pH. Secondly, the dye transfer to a PA6 reference fabric was tested based on the standard ISO 105-E01:1994. The fabric was placed between two adjacent reference fabrics showing affinity for the dye, in our case PA6 on one side and wool on the other. While in contact with these reference fabrics, the sample was immersed in an aqueous solution with controlled pH for 30 min and subsequently placed in an oven (37 °C) under a calibrated load for 4 h. The staining of the adjacent PA6 reference fabric was characterised by UV/Vis spectroscopy, obtaining the Lab-values (OptLab-SPX, 10° observer, D65 illuminant). Based on these values, a colour difference (ΔE) could be calculated between the unstained and the stained reference, giving an effective measure of the dye migration to the PA6 adjacent fabrics. A detailed description of the calculation of a colour difference (ΔE) can be found in the Supporting Information (SI) of Ref. [31].

3. Theory and calculation

All calculations were carried out in Gaussian09 [75] using Density Functional Theory (DFT), as this method is both computationally efficient and sufficiently accurate for examining large dye molecules. Geometries were optimised using the M06-2X electronic structure method in combination with the 6-31G(d,p) basis set [76]. M06-2X is a meta hybrid functional, using 54% exact exchange. Conformational analysis and frequency calculations were performed to find the absolute minimum for each system.

4. Discussion

4.1. Conventional dyeing of fabrics

All ten sulfonphthaleine molecules were conventionally dyed onto PA6. In Fig. 3, the UV/Vis spectra of Phenol Red (**1**) are shown for the dye in solution and dyed onto PA6 at different pH values. The UV/Vis spectra of Xylenol Blue (**4**) and Bromophenol Blue (**7**) are also depicted, as examples of dyes with electron donating and withdrawing substituents respectively. The spectra obtained with all dyes are shown in Section S1 of the SI.

It is clear that a distinction can be made between the effect of electron donating groups (**2**–**5**) and electron withdrawing groups (**6**–**10**). Fabrics dyed with Phenol Red (**1**) and dyes with electron donating substituted dyes (**2**–**5**) do not show any halochromic behaviour, while those containing dyes with electron withdrawing groups (**6**–**10**) on the other hand do. The colour change was noticed to be rather slow, however, which is why the spectra for fabrics with dyes **6**–**10** are recorded after 24 h immersion in a pH bath. It is emphasised that dyes **1**–**5** did not show a halochromic behaviour in the fabric, but did in aqueous solution. Upon deprotonation of the dye molecules, however, a high amount of leaching occurred (see further below). This indicates a weak interaction that is confirmed by the absorption peaks of these dyed fabrics (around 430 nm), which is almost equal to the one in solution around neutral pH. The fabrics dyed with **6**–**10** maintain their halochromic behaviour, which suggests that the halogen substituents allow for a different kind of stronger interaction with the textile material, which will be analysed by the leaching tests. To gain more insight into the pH-range where the colour change happens, the maximum absorption wavelengths are plotted in function of pH for dyes **1**, **4** and **7** in Fig. 3; plots obtained with all dyes are shown in Section S1 of the SI. It is clear that for dyes **6**–**10** the pH-sensitive behaviour is very similar in solution as dyed onto PA6 fabrics: both the absorption wavelengths and pH where the colour change happens are almost the same, albeit the latter is sometimes shifted slightly more towards acidic environment.

To gain more insight into the difference in halochromicity, dye leaching tests are performed. These tests give a quantitative measure for the dye–polymer interaction and two different leaching techniques are applied (see Section 2). The first is dye leaching to an aqueous solution, where the fabric is submerged in a water bath at three different pH values: 2, 7 and 12. The amount of dye leached into the water bath is a measure for the interaction strength between the dye and the environment, in which a higher value represents weaker interactions. The second method used is a staining test, in which the dye leaching to another blanc fabric is studied. The colour change of this blanc fabric (measured as ΔE) serves as a measure of the amount of dye leached. The advantage of this method is that water solubility has a lower influence compared to standard leaching tests. All data can be found in Section S2 of the SI, the leaching at pH 12 to an aqueous solution is given in Table 1.

For all dyes, the leaching was found to be much higher at pH 12 than at lower pH values, as can be seen in Section S2 of the SI, which is why only the results for pH 12 are given in Table 1. At high pH, the dye molecules get a double-anionic structure. This suggest that the

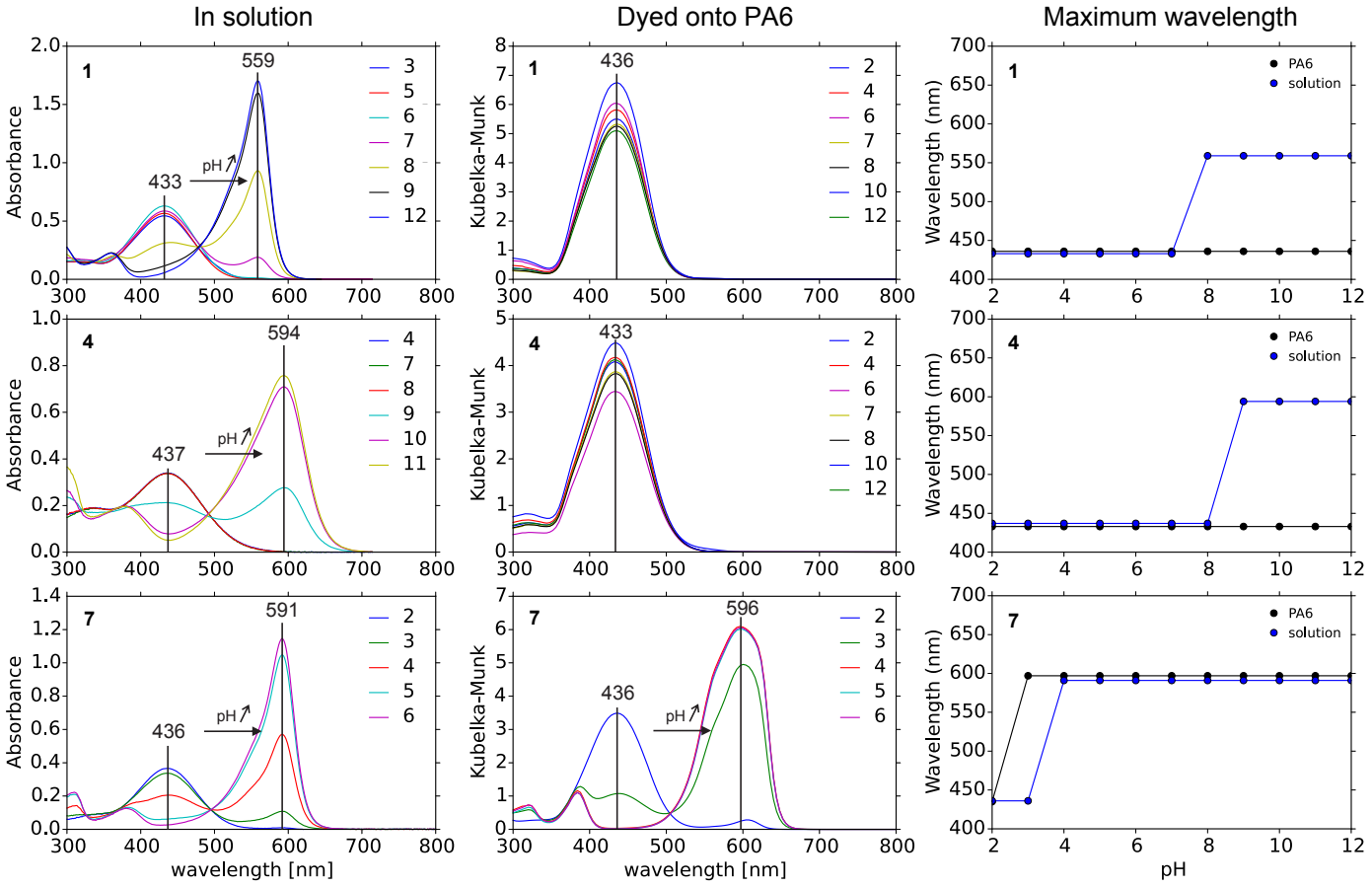


Fig. 3. UV/Vis spectra of dyes **1**, **4** and **7** in solution (left hand side) and conventionally dyed onto PA6 fabrics (centre) at different pH-values. On the right hand side, the maximum absorption wavelength of the dyes is plotted in function of pH both in solution and dyed onto PA6 fabrics.

Table 1
Leaching results for all dyes at pH 12 of the conventional dyed PA6 fabrics (% leached to aqueous solution and ΔE of reference fabric) and the dye-doped PA6 nanofibres (with and without complexing agent PDADMAC).

		Conventional dyeing of PA6 fabrics	Dye doping of PA6 nanofibres	
		% Leached	% Leached	
Dye	pK_a		Without PDADMAC	With PDADMAC
1	8.0	66	84	68
2	8.3	76	98	–
3	8.5	53	80	–
4	9.1	58	100	75
5	8.9	42	86	–
6	6.7	62	88	–
7	4.1	16	48	13
8	6.3	35	76	–
9	4.8	13	5	7
10	7.4	13	74	–

higher solubility of the dye in aquatic environment causes a larger driving force for breaking the interactions with the fibre and enhanced dissolution of the dye into the leaching bath. It is noticed that dyes exhibiting a high water leaching, also result in a high colour change (ΔE) of the reference fabric. Therefore, only the results of leaching to an aqueous solution are given in Table 1, all other data can be found in Section S2 of the SI. This indicates that the solubility of the dye molecules have a lesser effect on the leaching data.

Dyes **1**–**5** show rather high leaching, which confirms the results of the UV/Vis analysis: the dyes get deprotonated and leach out of the fabric. Dyes **7**–**10**, containing bromine substituents, show much lower leaching, which further confirms the pH-sensitive behaviour discussed above. Moreover, as can be seen from Table S1 in the SI, they leach even less in more acidic environment, which is also the pH-region where these dyes change colour. Dye **7** for example has a colour change below pH 4 and leaches only 0% and 3% at pH 2 and 7 respectively, making it an ideal sensor for acid vapours. Dye **6**, which has a chlorine substituent, shows rather high leaching, but still shows halochromic behaviour in the fabric. This indicates that halogen substituents must allow for different interaction(s) with PA6 compared to dyes without halogens, which can be maintained upon (de)protonation. This will be further discussed in Section 4.3. It is also noted that only dyes **7** and **9** have their pK_a below pH 5, the pH of the dyeing process, meaning they will be mainly in the dianionic form and the others in the anionic form, which could explain their very low leaching as they are entrapped in their most soluble state. When comparing dyes **8** and **10**, however, one can see that this is not the only parameter influencing the leaching behaviour: their pK_a's differ only one unit (both above pH 5) and there is still a factor 3 difference in percentage of dye leached. Dye **10** is much bulkier than **8**, which indicates that the molecular weight of the dye molecules also has an influence and this will also be examined in Section 4.3.

4.2. Dye-doping of nanofibres

In contrast to the conventional dyeing process, direct electrospinning of coloured nanofibres is not based on diffusion processes of a dye into a polymer matrix, but the dyes are forced into the fibres as the solvent evaporates. As mentioned in the introduction, this is expected to have an influence on the possible interactions. When trying to perform a UV/Vis spectroscopy analysis at different pH-values, very high leaching was observed. Therefore, leaching tests were performed first and the results at pH 12 are given in Table 1. Data at pH 2 and 7 can be found in Section S1 of the SI. Given the similar results between both leaching tests for the conventionally dyed fabrics, only dye leaching to the aqueous pH bath was recorded here.

It can clearly be seen that most dyes have a rather poor interaction with the PA6 nanofibres. Compared to the results of the conventional dyeing process, it can be concluded that the interactions with the non-wovens is much lower. Taking into account the very acidic electrospin solution, dyes will be in the neutral or anionic form (**x** or $\mathbf{x}_a$), meaning they are entrapped in their least water-soluble form, which can partly explain the high leaching observed here. It is also noted that the differences between the different dye molecules are much smaller. This indicates less effect of the molecule itself on the leaching properties, which is discussed in Section 4.3.

To try and improve upon this result, electrospinning of dye-doped nanofibres was repeated for dyes **1**, **4**, **7** and **9** with the addition of a complexing agent, PDADMAC. This polycationic agent is often used to suppress dye leaching [24], the results of which are also given in Table 1 (full data in Table S2 of the SI). PDADMAC has a beneficial effect for all dyes, which means that the ionic interactions with the complexing agent indeed limit the migration of the dye molecules out of the matrix. The effect of PDADMAC is more pronounced for dyes **7** and **9** as compared to dyes **1** and **4**, which will be discussed further on.

Recording UV/Vis spectra with changing pH for non-wovens that show very high (pH-dependent) leaching is quite error-prone. Therefore, only dye-doped samples with PDADMAC are analysed using UV/Vis spectroscopy (Fig. 4). The most important observation is that all dye-doped nanofibres, including those with **1** and **4**, are halochromic, in contrast to conventionally dyed fabrics. This is probably due to the fact that the combination of PA6 and PDADMAC allows for stronger interaction with the dye molecules than only PA6. It must, however, be kept in mind that the leaching is still relatively high. Samples dye-doped with **7** and **9** on the other hand also show a clear colour change. Combined with their much better leaching results, they are suitable candidates to be used as sensor materials. It is also noted that the colour change is on the time scale of minutes and is thus much faster than the conventionally dyed fabrics. This is due to the much smaller fibre diameter and increased specific surface area, which enhances contact to the aqueous environment.

The peaks in acidic environment are almost the same as in solution (see also Fig. 3 and Section S1 of the SI); in alkalic environment the difference is in the range of 10–15 nm. It can clearly be seen from Fig. 4 that the alkalic peak for the nanofabric dye-doped with **4** is composed of two smaller peaks. One is around 570 nm, which is about the same as in solution, which is why this peak can be ascribed to non-bonded dye. Similar to the conventionally dyed fabrics, the maximum absorption wavelength is plotted in function of pH in Section S3 of the SI. It is again seen that the pH-sensitivity is similar compared to solution, although it is noticed for dye **1** that the colour change happens in more acidic environment (around pH 6 compared to around pH 8 in aqueous solution).

4.3. Study of interactions

As indicated in Sections 4.1 and 4.2, the molecular weight of the dye has a clear influence on the leaching properties. To gain more insight, the percentage of dye leached at pH 12 (taken from Table 1) for conventional fabrics and dye-doped fibres (with and without PDADMAC) are plotted vs the molecular weight of each dye in Fig. 5.

For both dyeing processes, a clear influence of the molecular weight on dye leaching is seen. A higher molecular weight results in lower leaching, which indicates the leaching process is (at least

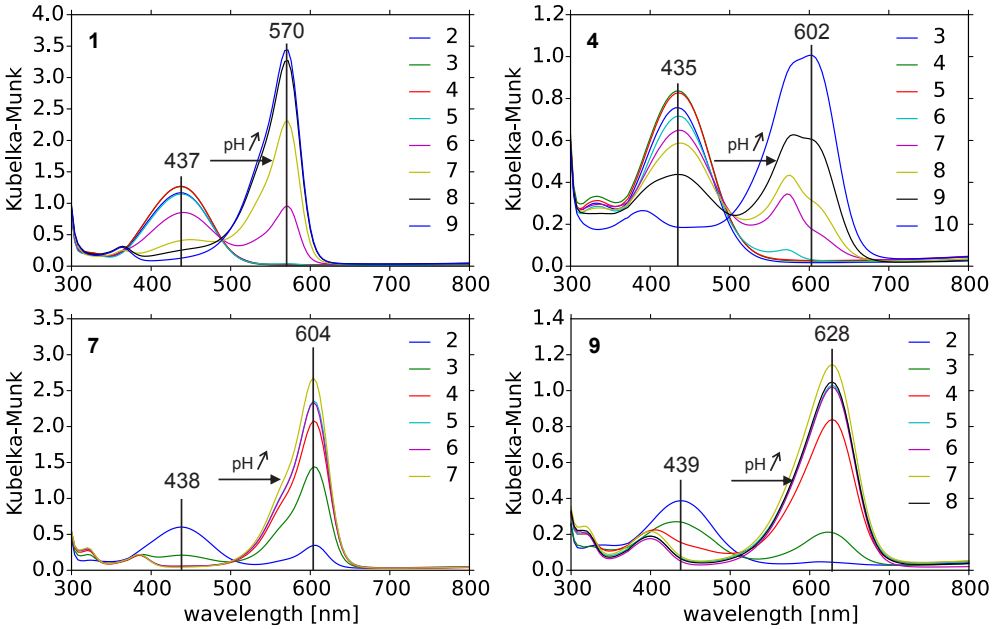


Fig. 4. UV/Vis spectra of nanofibre samples dye-doped with **1**, **4**, **7** and **9** at different pH values.

partially) diffusion driven. This effect is most pronounced for the conventionally dyed fabrics, where the R^2 of a linear regression is more than 0.90. This indicates that diffusion is indeed the predominant factor for leaching, which can be understood from the large fibre diameter.

For the dye-doped samples, however, the slope of the linear regression is lower, indicating a lower influence of the molecular weight on the leaching properties. Combined with the R^2 value of only around 0.75, this suggests there are other factors also influencing the leaching behaviour. This can partially be ascribed to the small fibre diameter and large specific surface area, although this still does not explain why the complexing agent PDADMAC has such a large effect on **7** and **9** and to lesser extent on **1** and **4**, as can clearly be seen from Fig. 5.

Therefore, it was examined if the acidic nature of the electrospinning solution (ESS) plays a role in this. The ESS consists of 50% formic acid and 50% acidic acid. This is a very acidic medium and it is thus not unlikely that some dye molecules undergo another protonation (and thus go to form **x** in Scheme 1). This molecular change should cause a colour change and therefore the UV/Vis spectra of all dyes in the ESS are measured and compared to the spectra in aqueous solution as we had measured before [15]. The spectra for dyes **1**, **4**, **7** and **9** are given in Fig. 6, the others can be found in Section S4 of the SI.

In the ESS, the dyes without halogen substituents (**1**–**5**) show a colour change, which translates in a new absorption peak in the UV/Vis spectrum. This colour change indicates that these molecules indeed undergo complete protonation in the ESS resulting in the neutral form **x** in Fig. 1. Similarly, dye **6**, with a chloride substituent, also shows a new absorption peak. Dyes **7**–**10** show an equilibrium between **x** and $\mathbf{x}_a$. For **7** and **9** only a small extra peak is observed, meaning that the equilibrium is mostly shifted to the single anionic form ($\mathbf{x}_a$). This can be understood from the high electron withdrawing properties of the four bromine substituents on each dye molecule. The remainder of the negative charge on the bulk of these molecules allows for Coulomb interactions with the polycationic complexing agent PDADMAC, which explains the lower tendency for leaching of these dyes. Dyes **6** and **8** have only two bromine substituents. The electron withdrawing effect is thus smaller, which is why the equilibrium is mostly shifted to the neutral form **x**. This shows that the substituents have an indirect effect on the interaction of the dye with PA6 + PDADMAC.

Besides the actual leaching values, it was observed that for the conventionally dyed fabrics, only dyes with halogen substituents

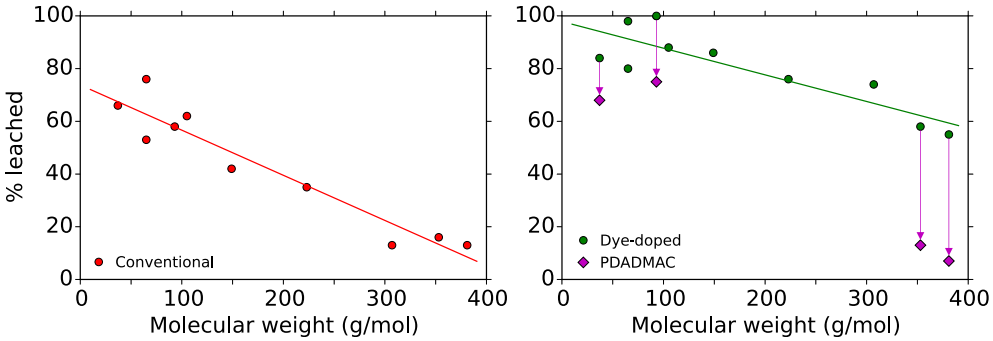


Fig. 5. Leaching of all dyes with both dyeing methods in function of dye molecular weight: conventional dyeing on the left hand side and dye-doping of nanofibres on the right hand side. For the latter, the improvement upon adding of PDADMAC is indicated.

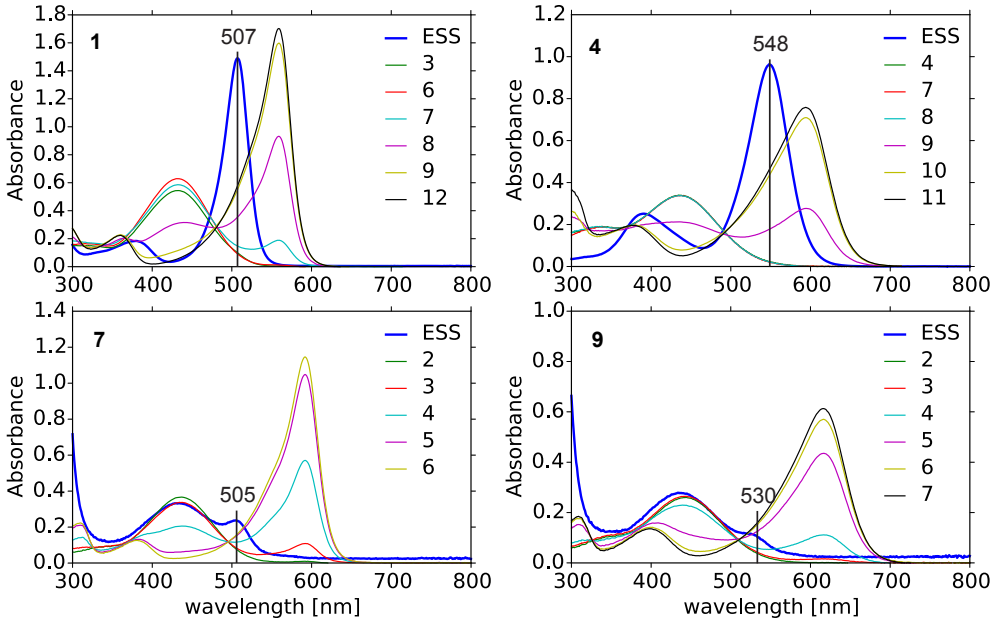


Fig. 6. UV/Vis spectra of dyes **1**, **4**, **7** and **9** in aqueous solution at different pH values and in the electrospin solution (ESS).

change colour and maintain their interaction with the textile matrix (Fig. 3). To obtain more insight into the interaction of the dye molecules with PA6, we studied interaction energies. An in-depth study of the polymeric structure of PA6 would require MD sampling of the configuration space and simulations at high length and time scale, which are beyond the scope of this paper. Therefore, a relatively simple molecule, methylacetamide (Fig. 7), which has the same amide group in a comparative molecular environment, is used to evaluate the interactions. These interactions occur at several positions on the dye molecules, of which the only sites that differ between the dyes are on the phenolic rings. Hence these phenolic rings, which are either neutral or anionic, are taken as model systems (Fig. 7). We only report electronic interaction energies (ΔE_{el}), as our small model system does not give a realistic representation of the entropies of the molecules entrapped in a textile matrix.

Two types of interactions between the methylacetamide molecule and the phenolic rings are possible: hydrogen bonds and halogen bonds. Both interactions are considered in Fig. 8. The hydrogen-bonded structures (A, B, C and D) clearly exhibit the highest interaction energies. The hydrogen bonds for the negatively charged systems (B and D) are roughly twice as strong as for the neutral ones (A and C). The negatively charged system is stabilised by the methylacetamide molecule, which explains this high ΔE_{el}. If an explicit interaction with the halogen substituents is considered (E and F), the interaction energies are substantially lower. The halogen bond with bromine (E) is stronger than the one with chlorine (F), which can be understood from the size of both substituents. The length of the halogen bonds indicated in Fig. 8 is

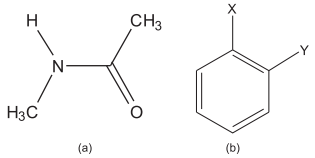


Fig. 7. Schematic structure of methylacetamide (a) and phenolic ring (b), used to mimic the interaction with polyamide.

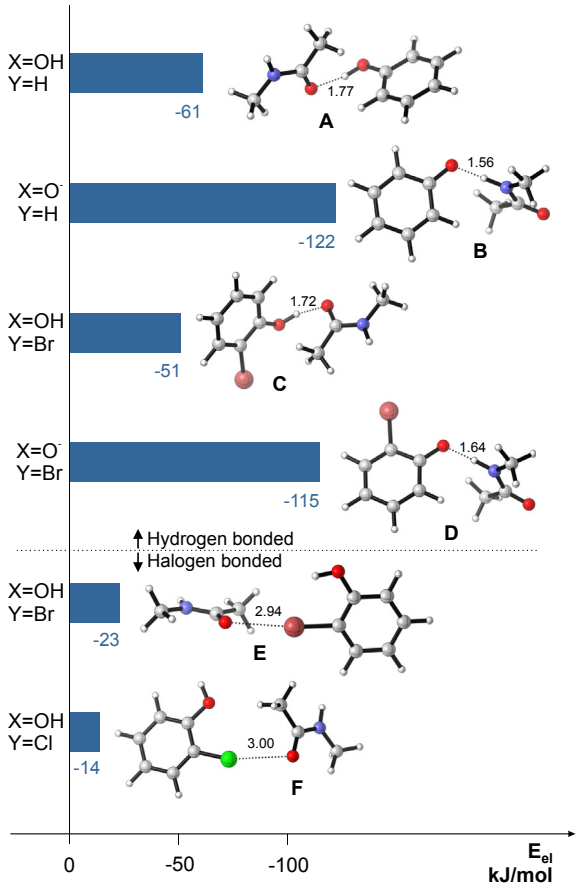


Fig. 8. Interaction ΔE_{el} of methylacetamide with several aromatic rings representative for the dye molecules (see also Fig. 7). The hydrogen bonds are possible for each dye and are not influenced by the presence of a halogen substituent. The halogen bonds, however, are only possible for dyes with halogen substituents. Since hydrogen bonds are easily broken in aqueous solution, this indicates why dyes with halogen substituents maintain interaction upon deprotonation. All structures are optimised with M06-2X/6-31G(d,p) and distances are in given Å.

consistent with values found in literature [72]. Even though only one methylacetamide molecule is considered in these halogen bonds, chlorine and especially bromine are large atoms, allowing for multiple halogen bonds. Moreover, since the bond distances are about double in length, these bonds are expected to be easier to form.

Based on the results above, hydrogen bonds between the dyes and PA6 are the dominant interaction. These interactions are possible for each dye in this set, so no distinction can be made hereupon. Moreover, hydrogen bonds are easily broken in an aqueous environment in favour of hydrogen bonds with the water solvent. This is certainly feasible for a dianionic structure, where multiple water molecules can stabilise the system. This can explain why in alkalic environment the dianions leach out of the textile matrix more substantially. Halogen bonds on the other hand are only possible for dyes **6**–**10** and are, as shown above, an important contribution to the overall interaction of sulfonphthaleine dyes with polyamide. These halogen bonds are much less affected by the anionic/dianionic form of the dye, nor the aqueous solvent, so it can be assumed that these interactions can be maintained. It is, therefore, proposed that these halogen bonds allow the dyes to stay fixed in the polyamide matrix upon deprotonation, allowing for halochromic textile fabrics for dyes **6**–**10**. This also explains why the fabric dyed with **6**, even though it showed high leaching, is still pH-sensitive. This is a direct effect of the substituents, which is in contrast to the nanofibrous samples, where an indirect effect of the substituents determined the charge of the dye molecules in the ESS and therefore possible interactions with PA6 with PDADMAC. This emphasises the importance of the solution parameters, and more specifically the pH, on the final interactions.

5. Conclusions

In this paper, a set of ten pH-sensitive sulfonphthaleine dyes was dyed onto polyamide 6 using two different application methods. Using conventional dyeing, a large influence of the substituents was found both on the leaching properties and the halochromicity. A linear trend between the molecular weight of each dye and the amount of dye leached was found, explaining why dyes with bromine substituents showed much lower leaching. It was also observed that only dyes with halogen substituents still exhibited pH-sensitive behaviour. Hydrogen bonds are possible for each dye molecule and, with the aid of molecular modelling, it was seen that the hydrogen bond interaction energy is about the same for each dye. Hydrogen bonds are, however, more easily broken in aqueous environment. Dyes with halogen substituents can also show halogen bonding, which was proposed to be an important contribution to the overall interaction. Halogen bonds are less affected by the aqueous environment, explaining why these dyes can maintain their interaction with the fibres after discolouration. In conclusion, the substituents have both an indirect effect (molecular weight) and direct effect (halogen bonding) on the possible interactions with PA6.

For the dye-doped nanofibrous non-wovens, the importance of the very acidic electrospinning solution was shown. Most dyes are in the neutral state during electrospinning form a formic acid/acetic acid mixture, meaning they have little to no tendency to interact with the polyamide chains. Moreover, the dye solubility will be enhanced when placed into an aqueous environment. This explains the very high leaching for all dyes. When adding a polycationic complexing agent, however, it was seen that the leaching properties of two dye molecules with four bromine substituents greatly improved. By using UV/Vis spectroscopy, it was seen that these dyes are still mostly in the anionic form, allowing for interaction with the positively charged complexing agent. This could be understood from the high electron withdrawing effect of bromine. The substituents have therefore an indirect effect on the interaction with PA6 nanofibres, namely the (de)protonation state of the molecule in the electrospinning solution.

These findings show the important role of substituents for the development of halochromic textile materials. Not only do they greatly influence the pH-sensitive properties themselves, as was shown before, but they also directly affect possible interactions with the textile environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.09.007.

References

[1] Zollinger H. Color chemistry: synthesis, properties, and applications of organic dyes and pigments. VHCA en WILEY-VCH; 2003.
[2] Kim S. Functional dyes. Elsevier; 2006.
[3] Bamfield P. Chromic phenomena, technological applications of colour chemistry. Royal Society of Chemistry; 2001.
[4] Kirschning A, Monenschein H, Wittenberg R. Angew Chem Int Ed 2001;40:650–79.
[5] Vancoillie G, Pelz S, Holder E, Hoogenboom R. Polym Chem 2012;3:1726–9.
[6] Pietsch C, Schubert U, Hoogenboom R. Chem Commun 2011;47:8750–65.
[7] Fournier D, Du Prez F. Macromolecules 2008;41:4622–30.
[8] Roy D, Cambre JN, Sumerlin BS. Prog Polym Sci 2010;35:278–301.
[9] Emond M, Sun J, Gregoire J, Maurin S, Tribet C, Jullien L. Phys Chem Chem Phys 2011;13:6493–9.
[10] Mohr GJ, Wolfbeis OS. Anal Chim Acta 1994;292:41–8.
[11] Trupp S, Alberti M, Carofiglio T, Lubian E, Lehmann H, Heuermann R, et al. Sens Actuators B 2010;150:206–10.
[12] Kuwabara T, Nakajima H, Nanasawa M, Ueno A. Anal Chem 1999;71:2844–9.
[13] Van der Schueren L, De Clerck K. Text Res J 2009;80:590–603.
[14] De Meyer T, Hemelsoet K, Van Der Schueren L, Pauwels E, De Clerck K, Van Speybroeck V. Chem Eur J 2012;18:8120–9.
[15] De Meyer T, Hemelsoet K, Van Speybroeck V, De Clerck K. Dyes Pigm 2014;102:241–50.
[16] Egawa Y, Hayashida R, Anzai J. Anal Sci 2006;22:1117–9.
[17] Wang H, Callahan PM. J Chromatogr A 1998;828:121–34.
[18] Canamares MV, Garcia-Ramos JV, Domingo C, Sanchez-Cortes S. J Raman Spectrosc 2004;35:921–7.
[19] Fabbri P, Pilati F, Rovati L, McKenzie R, Mijovic J. Opt Mat 2011;33:1362–9.
[20] Capel-Cuevas S, Cuellar MP, de Orbe-Paya I, Pegalajar MC, Capitan-Vallvey LF. Anal Chim Acta 2010;681:71–81.
[21] Tao X, Li J, Möhwald H. Chem Eur J 2004;10:3397–403.
[22] Staneva D, Betcheva R, Chovelon JM. J Photochem Photobiol A 2006;183:159–64.
[23] Ertekin K, Cinar S, Aydemir T, Alp S. Dyes Pigm 2005;67:133–8.
[24] Van der Schueren L, Mollet T, Ceylan O, De Clerck K. Eur Polym J 2010;46:2229–39.
[25] Van der Schueren L, De Clerck K. Int J Cloth Sci Tech 2011;23:269. 274274.
[26] Van der Schueren L, De Clerck K. Color Technol 2012;128:82–90.
[27] Van der Schueren L, Hemelsoet K, Van Speybroeck V, De Clerck K. Dyes Pigm 2012;94:443–51.
[28] Van Der Schueren L, De Meyer T, Steyaert I, Ceylan O, Hemelsoet K, Van Speybroeck V, et al. Carbohydr Polym 2013;91:284–93.
[29] Staneva D, Betcheva R, Chovelon JM. J Appl Polym Sci 2007;106:1950–6.
[30] Li G, Xiao J, Zhang W. Dyes Pigm 2012;92:1091–9.
[31] Steyaert I, Vancoillie G, Hoogenboom R, De Clerck K. Polym Chem 2015;6:2685–94.
[32] Machida K, Lee H, Uno T. J Raman Spectrosc 1979;8:172–6.
[33] Macka M, Andersson P, Haddad PR. Anal Chem 1998;70:743–9.

[34] Fujii T, Toriumi K. J Chem Soc Faraday Trans 1993;1(89):3437–41.
[35] Flores R. Anal Biochem 1978;88:605–11.
[36] You L, Wu Z, Kim T, Lee K. J Colloid Interface Sci 2006;300:526–35.
[37] Ghaedi M, Khajesharifi H. Spectrochim Acta Part A 2012;86:62–8.
[38] Drummond C, Grieser F, Healy T. J Chem Soc Faraday Trans 1989;1(85):537–50.
[39] Buvári A, Barcza L, Kajtár M. J Chem Soc Perkin Trans 1988;2:1687–90.
[40] Burford G, Pickering B. Biochem J 1972;128:941.
[41] Kurzweilová H, Sigler K. Yeast 1993;9:1207–11.
[42] Webster D. Clin Chim Acta 1974;53:109–15.
[43] Marona H, Schapoval E. J Pharm Biomed Anal 2001;26:501–4.
[44] Robertson J. J Clin Microbiol 1978;7:127–32.
[45] Baylor SM, Hollingworth S. J Gen Physiol 1990;96:449–71.
[46] Berthois Y, Katzenellenbogen JA, Katzenellenbogen BS. Proc Natl Acad Sci U S A 1986;83:2496–500.
[47] Byrne RH, Breland JA. Deep-Sea Res Oceanogr A 1989;36:803–10.
[48] Bellerby RGJ, Olsen A, Johannessen T, Croot P. Talanta 2002;56:61–9.
[49] Clayton TD, Byrne RH. Deep-Sea Res Oceanogr A 1993;40:2115–29.
[50] Zhang H, Byrne RRH. Mar Chem 1996;52:17–25.
[51] Yao W, Byrne R. Environ Sci Technol 2001;35:1197–201.
[52] Wendorff JH, Agarwal S, Greiner A. Electrospinning: materials, processing and applications. Wiley-VCH Verlag; 2012.
[53] Chigome S, Torto N. Anal Chim Acta 2011;706:25–36.
[54] Bhardwaj N, Kundu SC. Biotechnol Adv 2010;28:325–47.
[55] Thavasi V, Singh G, Ramakrishna S. Energy Environ Sci 2008;1:205.
[56] Ding B, Wang M, Yu J, Sun G. Sensors 2009;9:1609–24.
[57] Wang X, Drew C, Lee S-H, Senecal K, Kumar J, Samuelson L. J Macromol Sci Part A 2002;39:1251–8.
[58] Matlock-Colangelo L, Baeumner AJ. Lab Chip 2012;12:2612.
[59] Goh Y-F, Shakir I, Hussain R. J Mat Sci 2013;48:3027–54.
[60] Agarwal A, Raheja A, Natarajan TS, Chandra TS. Sens Actuators B Chem 2012;161:1097–101.
[61] Lee EM, Gwon SY, Ji BC, Wang S, Kim SH. Dyes Pigm 2012;92:542–7.
[62] Liang X, Li Y, Peng W, Bai J, Zhang C, Yang Q. Eur Polym J 2008;44:3156–62.
[63] Di Benedetto F, Mele E, Camposeo A, Athanassiou A, Cingolani R, Pisignano D. Adv Mater 2008;20:314–8.
[64] Camposeo A, Di Benedetto F, Stabile R, Cingolani R, Pisignano D. Appl Phys Lett 2007;90:1–4.
[65] Camposeo A, Benedetto FD, Stabile R, Neves AAR, Cingolani R, Pisignano D. Small 2009;5:562–6.
[66] Fantini D, Costa L. Polym Adv Technol 2009;20:111–21.
[67] Wolfbeis OS. Anal Chem 2008;80:4269–83.
[68] Waring DR, Hallas G. Topics in applied chemistry: the chemistry and application of dyes. Plenum Press; 1990.
[69] Guillaumont D, Nakamura S. Dyes Pigm 2000;46:85–92.
[70] Adamo C, Jacquemin D. Chem Soc Rev 2013;42:845–56.
[71] Charaf-Eddin A, Planchat A, Mennucci B, Adamo C, Jacquemin D. J Chem Theory Comput 2013;9:2749–60.
[72] Kozuch S, Martin JML. J Chem Theory Comput 2013;9:1918–31.
[73] Forni A, Pieraccini S, Rendine S, Sironi M. J Comput Chem 2014;35:386–94.
[74] De Vrieze S, De Schoenmaker B, Ceylan z, Depuydt J, Van Landuyt L, Rahier H, et al. J Appl Polym Sci 2011;119:2984–90.
[75] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian09 revision D.01. Wallingford CT: Gaussian Inc.; 2009.
[76] Zhao Y, Schultz NE, Truhlar DG. J Chem Theory Comput 2006;2:364–82.