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Luminescent hybrid materials which contain fluorene and stilbene based fluorophores were coated onto cotton fabrics to design textile-based pH sensors.
Luminescent hybrid coatings prepared by the sol-gel process for textile-based pH sensor

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Fluorene and Stilbene based fluorophores were synthesized and characterized by NMR, IR and mass spectroscopy (ESI-MS). These fluorescent dyes were coated onto cotton fabrics by the sol-gel method using Tetraethylorthosilicate (TEOS) and Propyltriethoxysilane (PTES) as silica precursors. Herein, the optical properties of the synthesized compounds and the elaborated fabrics were studied. The luminescent properties of the fluorophores were examined in three forms, as a powder, dissolved in ethanol, and grafted onto the fabric by the sol-gel method. Furthermore, the effect of the fluorophore’s concentrations in sol-gel solution on the fluorescence properties of the elaborated hybrid coatings was investigated. The synthesized fluorophores exhibited a good pH sensitivity and a strong wavelength shift in acidic or basic media, ascribed to the protonation-deprotonation of the phenolic groups and pyridine of the fluorophores molecules. Along, we have successfully developed pH-sensitive fluorescent textiles and tested their efficiency in different pH media.

Introduction

In the last two decades, fluorescent dyes or fluorophores have received much considerable attention because of their potential applications including traceability, sensing, detection, and labeling targeting molecules.1-3 These dyes were used for the detection of toxic metals,4,5 traces of explosives,6,7 and bio-imaging for the detection of cancer cells or the visualization of living organisms.8,9 These compounds have shown their ability to be employed as pH sensors and pH probes, due to their high fluorescence quantum yield, and for their better sensitivity than conventional ones such as phenolphthalein and Thymol blue.10 They are therefore widely used in analytical and bio-analytical chemistry,11 in cell biology12,13 and medicine.14

The fluorophores grafted on textiles have been used for different applications such as design, fashion materials, and cloths. Several works have been reported for the immobilization of fluorophores on textiles.15-17 Indeed, the deposition of fluorescein into cotton yarns using the impregnation method was reported for anti-counterfeiting applications.18 F. khan et al.19 provided a new strategy for the applications of dye molecules on textiles by coating fluorescein isothiocyanate labeled poly(allylamine hydrochloride) and poly(acrylic acid) on cotton fabric by the layer-by-layer (LBL) assembled films method. Y. Luo et al.20 have reported the use of the dip-dyeing process to immobilize the fluorescent material onto cotton fibers to detect and separate the Cd2+ in water. The luminescent carbon nanoparticles were prepared by in situ hydrothermal synthesis, then applied directly to obtain fluorescent cotton fibers. Upon photonic excitation with different wavelengths, the prepared fibers emit bright and colorful photoluminescence.21 The application of lanthanide metal-organic framework to prepare the photoluminescent viscose fabrics,22 and to develop the photoluminescence cotton fabrics with a traffic safety employing spray-coat approach were also reported.23 The sol-gel method is a technique that can be used to trap molecules such as fluoresphore in a 2D or 3D silica-based systems, it is a well-known technique for its low-temperature conditions and its ability to achieve different shapes.24-28 This process requires hydro-alcoholic solutions of an organometallic precursor, most of the time an hybrid film onto the textile surface to confer it new functionalities, depending on the entrapped molecules, such as flame retardancy,29 water repellency30 or anti-microbial.31,32 Besides, when a chromic dye is incorporated inside the sol-gel coating, the surface of textile materials can be used as pH probes, which leads to flexible sensors that offer the possibility of controlling continuously the pH of large volume systems.33 Fluorescent dyes could play a similar role with emission spectra which are pH-dependent upon UV excitation. Additionally, these fluorophores must be able to provide a first accurate pH value so that they can be used as very sensitive pH sensors in strips for medical and paramedical uses for example. The preparation of a textile-based, highly sensitive pH sensor can be also used to determine the pH of human sweat, which provides information for patient monitoring and athletes.34

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textile pH-sensor can be prepared by the use of branched polymer
fabrics by the sol-gel process. An efficient pH-induced fluorescence
of these smart textiles is expected to be observed.  

As it is well known, the fluorescence of quadripolar dyes is strongly
sensitive to pH values in aqueous solution. In this work, we have
grafted some of these fluorophores based on fluorene and stilbene
bearing at their extremities a phenolic hydroxyl group onto cotton
fabrics by the sol-gel process. An efficient pH-induced fluorescence
of these smart textiles is expected to be observed.  

For this purpose, we have synthesized and characterized four
fluorophores: 2-(N-(4-acetoxystyryl) phenyl)-N-ethylamino) ethanol
(P1), 2-(N-(4-(2-pyridin-4-yl) vinyl) phenyl) amino) ethane-1-ol (P2),
Synthesis of 4-(2-(7-(2-(4-hydroxy-phenyl))-vinyl)-9,9-diethyl-9H-
fluoren-2-yl)-vinyl) -phenyl ester (P3) and 4-(2-(7-(2-(pyridine)-
vinyl)-9,9-diethyl-9H-fluoren-2-yl)-vinyl) -phenylester (P4). All
the products were analyzed by infrared spectroscopy (IR), nuclear
magnetic resonance (NMR) and Electrospray ionization-mass
spectroscopy (ESI-MS). The optical properties of the synthesized
compounds were recorded and discussed. Then, the fluorescent dyes
were applied on cotton fabrics by the sol-gel method using the
tetraethyloholsilicate (TEOS) and the propytriethoxysilane (PTES)
as silica precursors, employing the pad-dry-cure technique. The
morphology of coated cotton fabrics by the fluorophore via the sol-
gel process was observed by scanning electron microscopy (SEM)
and the optical properties of the elaborated fabrics were also
investigated. The pH sensitivity of the synthesized fluorophores was
studied and pH sensors grafted onto textile materials have been
designed.  

Experimental
Materials and Method
Cotton (CO) woven fabric weighing 168 g/m² was used.
tetraethyloholsilicate (TEOS, Mw = 208.33 g.mol⁻¹). Propyl
triethoxysilane (PTES, Mw = 206.35 g.mol⁻¹), ethanol (EtOH, 99 %)
and HCl (37%) were purchased from Sigma-Aldrich and Merck
Chemical companies. All the chemicals are analytically pure and used
without further purification.

2.1.2. ¹H NMR and ¹³C NMR spectra
¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance (300
MHz) apparel using TMS as an internal reference. Splitting patterns
recorded in this work are: s (singlet), d (doublet), dd (double-of-
doublet), t (triplet), p (pentet), and m (multiplet).

2.1.3. Fourier-Transform Infrared spectroscopy FTIR-ATR
The infrared spectra were recorded on a Nicolet 550 FTIR-ATR
spectrophotometer. The source type is Mid-infrared Ever-Glo and
Tungsten/halogen. The spectral range for the device is 4000 - 750 cm⁻¹
optimized, mid-infrared beamsplitter, and its resolution is better
than 0.4 wavenumbers.

2.1.4. Scanning Electron Microscopy (SEM)
The SEM micrographs were recorded using a ZEISS Supra 55VP
scanning electron microscope operating under a high vacuum at 3 kV
and using a secondary electron detector (Everhart-Thornley
detector).

2.1.5. Photoluminescence measurements
The fluorescence spectra were recorded in a dilute solution, using a
spectrofluorometer (HAMAMATSU Photonics Multi-Channel
Analyzer PMA-12) in scan mode from 250 to 500nm with a step of
5nm. The excitation source is a 400W xenon lamp whose wavelength
is selected using a Jobin-Yvon TRIF 180 monochromator equipped
with two 600 rpm and 1400 rpm gratings. The fluorescence emitted
by the sample is focused on a bundle of optical fibers connected to a
Jobin-Yvon TRIAX 550 monochromator equipped with three gratings
(150 rpm, 1200 rpm, and 2400 rpm) and a CCD camera. SYMPHONY
1024 × 256 pixels cooled with liquid nitrogen. The entire device is,
therefore, suitable for excitation between 200 and 800 nm and
detection in emission between 250 and 1000 nm. Quantum yield efficiencies were measured using the C9920-02G PL-
QY measurement system from Hamamatsu. The set-up consisting of a
150W monochromatized Xe lamp, an integrating sphere
(SpectraCoating, φ = 3.3 in.) and a high sensitivity CCD camera.

2.2. Synthesis and characterization of the compounds
2.2.1. Synthesis of 2-(N-(4-acetoxystyryl) phenyl)-N-ethylamino)
ethanol (P1)
In a flask surmounted by a condenser, a g (0.103 mmol) of 2-[ethyl
(4-iiodophenyl)-amino] ethanol are dissolved in 90 ml of acetonitrile
and deaerated by bubbling under argon for 30 minutes at room
temperature. Subsequently, 4.41 g (0.271 mmol) of acetoxystyrene,
39.9 mg (1.77 mmol) of palladium diacetate, 36.4 mg (1.19 mmol) of
tri-o-polyphosphine and 2.77 g (0.274 mmol) of triethylamine are
added. The solution is heated at 95°C and left under stirring for 24
hours. The residue is purified by chromatographic column of silica
eluting with a mixture of ethyl acetate / cyclohexane (1:1). Solid
brown, yield 86.8%, FT-IR (KBr) ν cm⁻¹: 3351 cm⁻¹ (OH), 2965 -
2877 cm⁻¹ (C=H alkane), 1747 cm⁻¹ (C=O), 1600-1500 cm⁻¹ (phenyl,
1.1747 cm⁻¹ (O, C = O), 1600-1500 cm⁻¹ (u, aromatic C = C), 1535 cm⁻¹ (O, CN), 960 (u,=C-H). 1H NMR (400 MHz,
#C13, 298 K): δ ppm) 1.19(t, 3H), 2.31(s, 1H), 3.47(q, 2H), 3.51(t,
7.40-7.42(d,2H, ArH). 13C NMR (100 MHz, CDCl3, 298 K): δ ppm)
2.26 (s, 3H), 6.80(d, 2H, ArH), 6.88-6.92 (d, 1H, CH=CH), 6.97-
7.01(d,1H,CH=CH), 7.05-7.08(d, 2H, ArH), 7.40-7.42(d,2H, ArH),
7.47-7.49(d, 2H, ArH). 13C NMR (400 MHz, CDCl3, 298 K): δ ppm)
169.55, 149.24, 135.78, 128.65, 127.69, 126.75, 121.54, 59.78, 21.02,
11.76. ESI-MS: m/z Cald for C20H23NO3 326 and Found 325.
2.2.2. Synthesis of 2-((N-(4-(2-(pyridin-4-yl) vinyl) phenyl) amino) ethane-1-ol (P2)

In a flask surmounted by a condenser, 3 g (0.103 mmol) of 2-ethyl (4-iodophenyl) amino) ethanol, in 90 ml of acetonitrile is deaerated by bubbling under argon for 30 min at room temperature. 2.48 g (0.235 mmol) of vinylpyridine, 34.2 mg (1.52 mmol) of palladium diacetate, 31.42 mg (1.02 mmol) of tri-o-polyporphine and 2.38 g (0.008 mmol) of diethylamine are added, the solution is heated at 95°C and left under stirring for 24 h. The product is purified by crystallization from acetonitrile. Solid yellowish green, yield 72%, FT-IR, 1H NMR, and 13C NMR analysis and Mass. ESI-MS: m/z Cald for C39H44N2O 540.79 and Found 541.

2.2.3. Synthesis of 4-((2-(7-[[2-(4-hydroxyphenyl)-vinyl]-9-dihexyl-9H-fluoren-2-yl]-vinyl)-phenyl ester (P3)

In a flask surmounted by a condenser, 3 g (5.11 mmol) of 9,9-dihexyl-2,7-diido-9H Fluorene in 90 ml of acetonitrile is deaerated by bubbling under argon for 30 min at 25 °C. 1.65 g (1.022 mmol) of triethylamine are added. The solution is heated at 95°C and left under stirring for 24 hours, solvent are then removed under vacuum (0.235 mmol) of the triethylamine are added, the solution is heated at 94°C and left under stirring for 24 h. The product is purified by column of silica using CH2Cl2 / cyclohexane (1/1) as eluent and then the column is terminated with ethyl acetate. The residue is purified by column of silica using CH2Cl2 / heptane (1/1) as eluent. Solid brown, yield 73%, 1H NMR (400 MHz, CDCl3, 298 K): δ (ppm) 0.68 (s, 4H, CH2 ), 0.77(t, 6H, CH3), 1.13-1.06(m, 12H, CH3), 2(m, 4H, CH2), 6.85-6.87(d, 4H), 7.10-7.08 (d, 2H), 7.44-7.46 (d, 8H), 7.48 (s, 2H) 7.66-7.64 (d, 2H).13C NMR (400 MHz, CDCl3, 298 K): δ (ppm) 155.05, 151.09, 143.03, 139.94, 136.09, 132.02, 129.90, 127.45, 126.77, 120.08, 115.37, 110.29, 108.93, 54.55, 40.20, 31.12, 29.38, 23.39, 22.23, 21.65, 13.65 ESI -MS: m/z Cald for C41H46O2 570.82 and Found 571.

2.2.4. Synthesis of 4-((2-((7-[[2-(pyridine)-vinyl]-9-dihexyl-9H-fluoren-2-yl]-vinyl)-phenyl ester (P4)

In a flask surmounted by a condenser, 1 g (1.7 mmol) of 9,9-dihexyl-2,7-diido-9H Fluorene in 30 ml of acetonitrile is deaerated by bubbling under argon for 30 min at room temperature. 0.358 g (3.41 mmol) of vinylpyridine, 57.2 mg (0.085 mmol) of palladium diacetate, 51.7 mg (0.17 mmol) of tri-o-polyporphine and 34.5 mg (3.41 mmol) of triethylamine are added, the solution is heated at 95°C and left under stirring for 24 h. The residue is purified by column of silica using CH2Cl2 / heptane (1/1) as eluent. Solid green, yield 90%, 1H NMR (400 MHz, CDCl3, 298 K): δ (ppm) 0.65 (s, 4H, CH2 ), 0.75 (t, 6H, CH3), 1.02-1.08 (m, 12H, CH3)2, 1.04 (m, 4H, CH2), 7.07-7.11 (d, 2H),7.10-7.08 (d, 2H),7.40-7.44(d, 4H),7.52-7.56(d, 6H), 7.71-7.72(d, 2H). 8.5-8.60 (d, 4H).13C NMR (400 MHz, CDCl3, 298 K): δ (ppm) 151.84, 149.86, 145.13, 141.52, 135.38, 133.99, 126.46, 125.27, 121.35, 120.88, 120.34, 55.17, 40.50, 31.52, 29.72, 23.79, 22.60, and 14.03. ESI-Ms: m/z Calcd for C39H44N2O 540, 79 and Found 541.

2.3. Preparation of hybrid coatings by the sol-gel process

Cotton fabrics were coated using the sol-gel process combined with the pad-dry-cure technique. TEOS (50 %)/PTES (50%), HCl (0.01 M), distilled water and EtOH were mixed with a molar ratio of 10/0.008/60/55 to obtain the sol-gel solution. The fluorescent dyes were added to have a concentration corresponding to 1.05 mmol.L-1. The solution was agitated for 3 h at 70°C. Then, the cotton fabrics were impregnated in the solution and padded to give 80 % weight pick-up. The samples were dried for 30 min at 80°C and cured for 1 h at 120°C. The resulting fabrics coated with the fluorophores via the sol-gel process were respectively labeled T1, T2, T3, and T4.

Results and discussion

3.1. Fluorophores synthesis

In this study, four organic fluorophores were obtained via the Mizoroki-Heck coupling between Fluorene and Stilbene cores substituted with two different arms as depicted in Scheme 1. The fluorophores were characterized and their molecular structures were confirmed by FT-IR, 1H NMR, and 13C NMR analysis and Mass.

Scheme 1. Synthetic routes to P1, P2, P3 and P4 fluorophores

3.2. Optical properties of fluorophores in solution

The fluorophores were characterized and their molecular structures were confirmed by FT-IR, 1H NMR, and 13C NMR analysis and Mass.
The internal quantum yield curves as a function of the excitation wavelength of the synthesized fluorophores (P1, P2, P3, and P4) are gathered in Fig 1. These measurements were carried out with dilute solutions of ethanol. The fluorescent dyes concentrations were about 1.05 mmol.L⁻¹. We note, the internal quantum yields by Φi (number of photons emitted) and the absolute quantum yields by Φa (Φa = Φi * absorbance).

According to this figure, the maximum excitation wavelength of P1 and P2 based stilbene fluorophores is respectively 340 nm and 410 nm, whereas it is 400 nm for the quadripolar fluorophores P3 and P4. The emission spectra of the four fluorescent dyes were recorded upon excitation at these different wavelengths at 300 K. Table 1 summarizes all the fluorescence data for each of them. The absolute quantum yields were added in this table, considering that the absorption is nearly 100 % for each fluorophore at their maximum excitation.

| Fluorophore | λ max ex (nm) | λ max em (nm) | Φi [%] | Φa [%] |
|-------------|---------------|---------------|--------|--------|
| P1          | 340           | 438           | 8.7    | 8.5    |
| P2          | 410           | 495           | 5.0    | 4.9    |
| P3          | 400           | 446           | 10.6   | 10.4   |
| P4          | 400           | 479           | 32.0   | 31.6   |

Table 1. Fluorescence data for P1, P2, P3, and P4 fluorophores

3.3. Characterization of treated fabrics

3.3.1. SEM characterization

Fig 3 shows the SEM images of samples T3 and T4. The coating with the TEOS/PTES mixture is very homogeneous. It can, therefore, be deduced that the dispersion of the fluorophores in the TEOS/PTES mixture did not affect the polymerization of the alkoxysilanes to achieve high-quality hybrid coatings. Indeed, for all the fluorophores the coatings are very homogeneous and cover well the surface of the fibers.

3.3.2. Optical characterization of fabrics coated with fluorescent hybrid materials

The internal quantum yield curves as a function of the excitation wavelength of the fabrics (T1, T2, T3, and T4) coated with the sols containing the P1, P2, P3, and P4 fluorophores are shown in Fig 4.

According to this figure, the maximum excitation wavelength of the fabrics T1, T2, T3, and T4 is 385, 500 and 405 nm, respectively. The emission spectra of the fabrics keep the same profile as those of the solutions previously reported, except for the sample T2 which exhibits a significant bathochromic shift of 95 nm (Fig 5).
bathochromic displacement is mainly due to the presence of HCl traces used as a catalyst for the preparation of the sol-gel solution. These results were visually confirmed by comparing the luminescent hybrid coated fabrics upon daylight and upon 365 nm with an UV lamp as shown in the pictures in Fig. 6. For all the fabrics except T2, the fluorophores are colourless upon daylight (Fig 6-a), whereas upon UV excitation, the fabrics emit fluorescence with different colors (Fig 6-b).

![Fluorescence emission spectrum of (a) T1 and T2 and (b) T3 and T4 fabrics](image)

**Figure 5.** Fluorescence emission spectrum of (a) T1 and T2 and (b) T3 and T4 fabrics

In order to investigate the effect of the sol-gel coating on the luminescent properties of the fluorophores, these latter were examined in three forms, as a powder, dissolved in ethanol, and grafted onto the fabric by the sol-gel method. The quantum yields of fluorophores in different forms were presented in Fig. 7. The fluorophores powder does not emit fluorescence, which can be explained by the absence of the dispersive medium and thus by a concentration quenching effect since the molecules are too close to each other. When they are grafted to the surface of textiles, their quantum efficiency is even higher than dissolved in the solution. This is certainly due to the presence of silica which disperses the fluorophore molecules thus playing the role of solid solvent. The bathochromic effect observed for the fluorophore P2 is attributed to the protonation of pyridine by HCl used during the sol-gel synthesis.

**3.3.3. Effect of fluorescent dyes concentration on optical properties**

We have only performed this study for the P3 and P4 fluorophores since they exhibit a higher quantum yield. We started by preparing several solutions with different fluorophore concentrations in the aim to measure their quantum yield. Similarly, we prepared several sol-gel solutions (50%TEOS / 50% PTES) with different concentrations in the purpose to coat them on cotton fabrics. All pieces of information are gathered in Table 2.

![Graph showing absolute quantum yield](image)

**Figure 7.** Absolute quantum yields in different types of samples for (a) P1, P2 fluorophores and (b) P3, P4 fluorophores

| Fluorophore | Concentration in solution (mol.L⁻¹) | Concentration in sol (mol.L⁻¹) |
|-------------|-----------------------------------|-------------------------------|
| P3, P4      | C1 1.05x10⁻³                      | 1.05x10⁻³                     |
| P3, P4      | C2 2.1x10⁻⁴                       | 2.1x10⁻⁴                     |
| P3, P4      | C3 1.48x10⁻⁴                     | 1.48x10⁻⁴                    |
| P3, P4      | C4 1.05x10⁻⁴                     | 1.05x10⁻⁴                    |
| P3, P4      | C5 2.79x10⁻⁵                     | 2.79x10⁻⁵                    |
| P3, P4      | C6 9.32x10⁻⁶                     | 9.32x10⁻⁶                    |
| P3, P4      | C7 1.05x10⁻⁶                     | 1.05x10⁻⁶                    |

From Fig 8, it is observed that the absolute quantum yield of fluorescence goes to a maximum. Also, it is noticeable that the emission intensity decreases when the concentration of the solutions increases. The maximum absolute quantum yields of the P3 and P4 fluorophores is 52% in the solution for the concentrations between C5 and C6. The same trend was observed in the case of grafted fabrics, the maximum absolute quantum yield is 37% for P3 and 31% for P4 for concentrations between C2 and C3. We can conclude that with a small quantity of fluorophore dispersed on the surface of the textile we can achieve suitable luminescent properties allowing us to develop tracer or pH-sensitive textile strip.
3.4. Development of pH sensor

3.4.1. pH-sensitive properties in aqueous solution

To exploit the pH sensory abilities of the synthesized fluorophores, we have studied the peculiar optical properties associated with their protonated (acidic) and deprotonated (basic) form. The protonation and deprotonation form of the synthesized fluorophores P2, P3 and P4 by HCl and NaOH solutions are shown in Scheme 2. It is worth indicating that P1 does not exhibit protonated and deprotonated species.

The absorption properties of these fluorophores are modified with the modification of the concentration of hydronium ions (pH). As shown in Fig 9, the P2 and P4 fluorophores go through a bathochromic shift, over 95 nm for the fluorophore P2 and more than 40 nm for the fluorophore P4 that is observed when the pH value decreases while the P3 fluorophore leads to a slight bathochromic shift along with an increase of the absorbance intensity when the pH value rises from 6.8 to 13. We assume that pH dependence of the absorption intensities on the UV-visible spectra is directly linked to the protonation-deprotonation of the fluorophores and thus the presence in solution of their acidic or basic species.

To evidence their pH sensitivity, the emission spectra of each fluorescent dyes were recorded in solution at different pH upon excitation at their optimal wavelength. The results, shown in Fig 10, evidenced undoubtedly their ability to be used as pH sensors.

Figure 8. Absolute quantum yield as a function of the concentration (a) in solution and (b) on the coated CO fabrics for P3 and P4 fluorophores

Figure 9. Absorption spectrum of the protonated and deprotonated form of (a) P2, (b) P3 and (c) P4 fluorophores in solution

Figure 10. Emission spectra as a function of pH for the (a) P2, (b) P3 and (c) P4 fluorophores in solution
3.4.2. pH-sensor properties on cotton fabrics

Textile-based pH sensors T2, T3, and T4 were prepared using the previous P2, P3, and P4 fluorescent dyes incorporated in sol-gel solutions and coated onto cotton fabrics by the pad-dry-cure technique. In the aim to demonstrate the effectiveness of these sensors, the samples were immersed separately in solutions with an experimentally measured pH of 0.5, 6.8, 10.0 and 13.0, and then their optical properties were recorded and compared.

For the T2 sample, the main emission band shifts from the orange wavelength range to the yellow-green one while turning the pH from neutral to basic (Fig 11,12), which may be explained by the change from the protonated form to the deprotonated form. The orange fluorescence of the textile is due to the protonation of the pyridine arm by HCl added during the preparation of the sol. The passage to the basic medium is also accompanied by the change of color from orange to yellow and a decrease in fluorescence, as shown in the Fig 11,12.

As shown in Fig 13,14, the fluorescence spectrum of the T3 fabric changes from an emitting band in the blue range to weak green emission when the pH changes from neutral to basic, which corresponds to the protonation-deprotonation mechanism of the fluorophore molecule. The transition to the base medium is also accompanied by changes in color from transparent to yellow.

In Fig 15, a decrease of the fluorescence intensity is also observed when the pH values increase. In the case of the T4 fabric, the emission spectrum switches from a broad blue light to an emission in the green range when the fabric is immersed in the acidic medium. The immersion of the fabric in the basic medium causes no shift in the emission spectrum. We understand that the acid added during the synthesis of the sols was not sufficient enough to carry out the total protonation of the two pyridine arms.
Conclusion

Regarding this work, we started by the synthesis of different organic fluorophores using the Heck coupling of Stilbene and Fluorene cores. All the obtained compounds have excellent solubility in organic and inorganic solvents, especially in ethanol. Their photoluminescence properties were recorded, notably, the excitation and emission spectra. These fluorophores were grafted onto textile surfaces using the sol-gel process and employing the pad-dry-cure method. Emission spectra confirm their grafting on textile surfaces with relatively high absolute fluorescence yields. The optical properties of fluorophores in powder form, in solution and grafted onto the fabric were discussed. The effect of fluorophore concentrations, used for the sol-gel method, on the photoluminescence properties of the elaborated fabrics was also investigated in this work. Finally, we have successfully developed a pH-sensitive fluorescent textiles sensor by protonation and deprotonation of phenolic groups and pyridine of the synthesized fluorophores and we evidenced its effectiveness.

Conflicts of interest

There are no conflicts to declare.

References

1. Y.-Y. Guo, L.-Z. Yang, J.-X. Ru, X. Yao, J. Wu, W. Dou, W.-W. Qin, G.-L. Zhang, X.-L. Tang and W.-S. Liu, Dyes and Pigments, 2013, 99, 693–698.
2. L. Yang, W. Yang, D. Xu, Z. Zhang and A. Liu, Dyes and Pigments, 2013, 97, 168–174.
3. N. Fu, Y. Chen, J. Fan, G. Wang and S. Lin, Sensors and Actuators B: Chemical, 2014, 203, 435–443.
4. I. Leray and B. Valeur, European Journal of Inorganic Chemistry, 2009, 2009, 3525–3535.
5. T. Balaji, S. A. El-Safty, H. Matsunaga, T. Hanaoka and F. Mizukami, Angewandte Chemie International Edition, 2006, 45, 7202–7208.
6. R. Tu, B. Liu, Z. Wang, D. Gao, F. Wang, Q. Fang and Z. Zhang, Anal. Chem., 2008, 80, 3458–3465.
7. X. Wang, Y. Guo, D. Li, H. Chen and R. Sun, Chem. Commun., 2012, 48, 5569–5571.
8. T. R. Krishna, M. Parent, M. H. V. Werts, L. Moreaux, S. Gmouh, S. Charpak, A.-M. Caminade, J.-P. Majoral and M. Blanchard-Desce, Angewandte Chemie International Edition, 2006, 45, 4645–4648.
9. Y. Kimura, A. Momotake, N. Takahashi, H. Kasai and T. Arai, Chem. Lett., 2012, 41, 528–530.
10. D. Staneva and R. Betcheva, Dyes and Pigments, 2007, 74, 148–153.
11. M. F. Frasco and N. Chaniotakis, Anal Bioanal Chem, 2010, 396, 229–240.
12. I. Zhang, R. E. Campbell, A. Y. Ting and R. Y. Tsien, Nat Rev Mol Cell Biol, 2002, 3, 906–918.
13. D. W. Domaille, E. L. Que and C. J. Chang, Nat Chem Biol, 2008, 4, 168–175.
14. W. W. Miller, M. Yafuso, C. F. Yan, H. K. Hui and S. Arick, Clinical Chemistry, 1987, 33, 1538–1542.
15. G. J. Mohr, Sensors and Actuators B: Chemical, 2018, 275, 439–445.
16. D. Staneva, E. Vasileva-Tonkova and I. Grabchev, Journal of Photochemistry and Photobiology A: Chemistry, 2019, 375, 24–29.
17. D. Staneva, R. Betcheva and J.-M. Chevelon, Journal of Applied Polymer Science, 2007, 106, 1950–1956.
18. K. Baatout, F. Saad, A. Baffoun, B. Mahlig, D. Kreher, N. Jaballah and M. Majdoub, Materials Chemistry and Physics, 2019, 234, 304–310.
19. F. Khan, P. Liu, S. Yang, Y. Ma and Y. Qiu, Dyes and Pigments, 2017, 142, 358–364.
20. Y. Luo, D. Tang, W. Zhu, Y. Xu and X. Qian, J. Mater. Chem. C, 2015, 3, 8485–8489.
21. Y. Yu, J. Wang, J. Wang, J. Li, Y. Zhu, X. Li, X. Song and M. Ge, Cellulose, 2017, 24, 1669–1677.
22. H. E. Emam, H. N. Abdelhamid and R. M. Abdelhameed, Dyes and Pigments, 2018, 159, 491–498.
23. T. A. Khattab, M. M. G. Fouda, M. S. Abdelrahman, S. I. Othman, M. Bin-Jumah, M. A. Alqaraawi, H. Al Fassam and A. A. Allam, J Fluoresc, 2019, 29, 703–710.
24. A. Bentis, A. Boukhriess, A. Grancaric, M. El Bouchi, M. El Achaby and S. Gmouh, Cellulose, DOI: 10.1007/s10570-018-2206-4.
25. A. Boukhriess, D. Boyer, H. Hannache, J.-P. Robin, R. Mahiou, O. Cherkaoui, S. Therias and S. Gmouh, Cellulose, 2015, 22, 1415–1425.
26. A. Boukhriess, S. Gmouh, H. Hannache, J.-P. Robin, O. Cherkaoui and D. Boyer, Cellulose, 2016, 3355–3364.
27. A. Bentis, A. Boukhriess, D. Boyer and S. Gmouh, IOP Conf. Ser.: Mater. Sci. Eng., 2017, 254, 122001.
28. M. El messoudi, A. Boukhriess, O. Cherkaoui, M. El Kouali and S. Gmouh, J Coat Technol Res, 2019, 1–10.
29. D. Lin, X. Zeng, H. Li, X. Lai and T. Wu, Journal of Colloid and Interface Science, 2019, 533, 198–206.
30. B. Wang, B. Lei, Y. Tang, D. Xiang, H. Li, Q. Ma, C. Zhao and Y. Li, J Coat Technol Res, 2018, 15, 611–621.
31. A. Vilčnik, I. Jerman, A. Šurca Vuk, M. Koželj, B. Orel, B. Tomšič, B. Simončič and J. Kovač, Langmuir, 2009, 25, 5869–5880.
32. J. Jia, K. Chen, T. Zeng, D. Yao and C. Wang, Ind. Eng. Chem. Res., 2012, 51, 4541–4548.
33. A. Boukhriess, H. Hannache, J.-P. Robin, O. Cherkaoui and D. Boyer, Cellulose, 2016, 3355–3364.
34. D. W. Domaille, E. L. Que and C. J. Chang, Nat Chem Biol, 2008, 4, 168–175.
35. M. L. Zamora, J. M. Dominguez, R. M. Trujillo, C. B. Goy, M. A. Sánchez and R. E. Madrid, Sensors and Actuators B: Chemical, 2018, 260, 601–608.
36. J. Jia, K. Chen, T. Zeng, D. Yao and C. Wang, Ind. Eng. Chem. Res., 2020, 59, 2899–2907.
37. J. Van der Schueren, K. de Clerck, G. Brancatelli, G. Rosace, E. Van Damme and W. De Vos, Sensors and Actuators B: Chemical, 2012, 162, 27–34.
38. M. L. Zamarra, J. M. Dominguez, R. M. Trujillo, C. B. Goy, M. A. Sánchez and R. E. Madrid, Sensors and Actuators B: Chemical, 2018, 260, 601–608.
39. J. Jia, K. Chen, T. Zeng, D. Yao and C. Wang, Ind. Eng. Chem. Res., 2020, 59, 2899–2907.
40. J. Van der Schueren and K. De Clerck, International Journal of Clothing Science and Technology, 2011, 23, 269–274.
41. F. Vatansever, R. Burtovyy, B. Zdyrko, K. Ramaratnam, T. Andrukh, S. Minko, J. R. Owens, K. G. Kornev and I. Luzinov, ACS Appl. Mater. Interfaces, 2012, 4, 4541–4548.
42. B. Valeur: Invitation à la fluorescence moléculaire. De Boeck supérieur; ISBN 2804145972. 2004 Sep 6.