Dyes and Pigments 214 (2023) 111208

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

# Reversible thermochromic systems based on a new library of flavylium spirolactone leuco dyes

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ARTICLE INFO

*Keywords:*
Chromogenic dyes
Spirolactone dyes
Leuco dyes
Flavylium
Reversibility
Thermochromism

ABSTRACT

The aim of this work was the design, synthesis, and characterization of new chromogenic spirolactone dyes based on a 2-phenyl-1-benzopyrylium (flavylium) backbone for further development of thermochromic smart labels. The influence of electron-donating and electron-withdrawing groups on the five synthesized dyes was studied in terms of color modification, acid-base behavior and thermochromic properties. By using UV–Vis absorption and emission spectroscopies, molar absorptivity, oscillator strength, Stokes shift, and fluorescence quantum yield were determined for each dye to evaluate the impact on color and excited state properties of the designed structures. The acid-base behavior and the ability to evolve towards leuco species was assessed by titrations with triethylamine and *N,N*-diisopropylethylamine in non-polar and polar aprotic solvents such as acetonitrile and octan-1-ol. In addition, the reversibility of the color was also evaluated by titrations with polar protic solvents (water and ethanol) and Lewis acids (gallic acid and iron(III) chloride). The number of equivalents of base/acid required to reach the leuco product and then to reverse the color were determined by representing the absorption maximum as a function of added base/acid in acetonitrile (water content less than 0.01-v/v). Finally, the thermochromic properties were evaluated in the presence of long-chain organic amines and water-insoluble solvents with melting points close to room temperature. The synthesized compounds can switch between two species if the appropriate conditions are used. Moreover, the tests carried out to assess their thermochromic behavior concluded that all dyes display thermochromism to some extent. The dyes that have electron-withdrawing groups attached, such as cyano, display stronger chromogenic effects useful for future applications.

## 1. Introduction

Thermochromism is defined as the ability of a material to change color in a reversible or irreversible manner upon heating/cooling cycles. The change may be a transition between two colored states or between a colored state and an uncolored one and can be gradual or abrupt (at a certain temperature threshold) [1,2]. Thermochromism was found in organic and inorganic compounds, polymers, and hybrid materials, and the most frequently used are liquid crystals and spirolactone (leuco) dyes [3–8].

Spirolactone dyes are organic compounds that are well-known for their thermochromic properties and are widely used in industry because of their low-cost manufacturing process. They are generally used for displaying applications due to their high color contrast on different surfaces, and their availability in a broad range of colors [9]. These dyes are often used to produce dynamic colors in products such as mugs, t-shirts, magazines, or toys, but not only. They are also used as sensors (if the temperature accuracy is not so crucial), warning messages, security elements for tickets, smart cards, erasable pens, and documents, or as temperature indicators for products such as beverages, ice-cream, and others [1,10,11]. The most common thermochromic dyes of spirolactone type are fluorans, crystal violet lactone, spiropyrans and fulgides (Fig. 1), and are the color formers in a multi-component system [12].

Materials and pigments based on thermochromic spirolactone dyes usually consist of at least three components: a color former (the leuco dye), a color developer (usually a weak acid) and a solvent (a long-chain alkyl alcohol, ester, ketone, ether, or acid), which are micro-encapsulated and after ink formulation printed directly on the surface of

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https://doi.org/10.1016/j.dyepig.2023.111208
Received 4 November 2022; Received in revised form 30 January 2023; Accepted 1 March 2023
Available online 3 March 2023

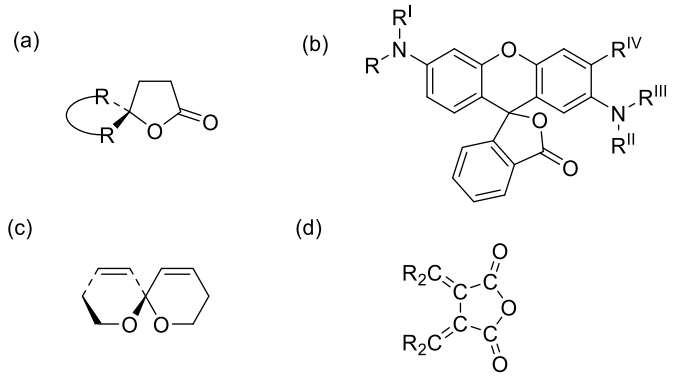



**Fig. 1.** Typical leuco dyes; (a) spirolactones, (b) fluorans, (c) spiropyrans, and (d) fulgides.

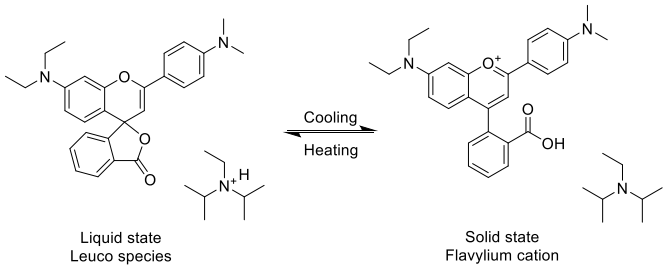
a display, Fig. 2 [13–17].

Sensitive to the changes in pH, the leuco dye molecules are alternating between two chemical species, where one is colored and the other one colorless. The reversible coloration/discoloration of a leuco dye system results from the alternate predominance of two competing interactions: one between the leuco dye and the color developer (acid-base reaction), and the other between the color developer and the solvent (non-covalent interactions). The former usually predominates at lower temperatures, when the solvent solidifies, and the latter in the liquid state, when the color developer is interacting with the solvent. Typically, the melting point of the solvent controls the temperature at which the color of the thermochromic composite changes [1,15,18–21].

Specifically, spirolactone dyes do not undergo these reactions by themselves, they rather change color because of a change in pH. In solution, the colored (protonated) species exists when the pH is more acidic (usually around 4), and the uncolored (deprotonated) species predominates when the pH is more alkaline. The temperature is only used to shift the equilibrium [22].

A thermochromic material based on a three-component system capable to change color after a phase transition was reported by Raquel Gavara *et al.* in 2010. The system was developed by introducing a flavylium cation with a 2-carboxyphenyl group in position 4 as a new family of leuco dyes (as color former), an organic amine and a suitable solvent (acetonitrile or *n*-pentadecanonitrile). The color change effect was taking place due to protonation/deprotonation of the carboxylic group upon changing from liquid to solid state, Scheme 1. The deprotonation reaction was favored in the liquid state because the solvation entropy increases, making the proton transfer process to the amine easier. This was a reversible process because once the solid state was reached, the proton returns to the carboxylic moiety stabilizing the colored flavylium cation [25,28].

As can be seen in Scheme 1, the above studies were carried out with a flavylium cation having 2 amino substituents attached which developed a blue color. To our knowledge, it was a first system where a weak base color developer was used. Yet there were some barriers that hamper applications, namely: a) solvents used are not water insoluble or are




**Scheme 1.** Phase-change thermochromic system based on a flavylium dye [25].

rather expensive; b) the study was done only with one compound, limiting greatly the color palette; c) it remained unanswered of other flavylium dyes could be used in 3 component thermochromic systems.

Therefore, inspired by the example mentioned above, we have proposed to further study this system by designing a small library of flavylium dyes with electron-donating and electron-withdrawing substituents to evaluate their impact on colors. In addition, we have also proposed to evaluate their thermochromic behavior in water-insoluble solvents and long-chain organic amines, commonly used in industry [23], that can be further encapsulated and used in the development of thermochromic smart labels.

Here we show that materials composed of dyes with electron-withdrawing groups, such as cyano, exhibited most pronounced color change effect with a clear transition from colorless to colored state in other organic solvents, and not restricted to nitriles [25]. For those containing electron-donating groups, such dimethylamine, the switch was not so obvious outside nitrile solvents, as the transition was between two colored states that exhibited almost the same hue.

## 2. Experimental

### 2.1. Materials and methods

All solvents and chemicals were reagent grade and used as received. Ultrapure Millipore grade water was used, and acetonitrile was dried over molecular sieves, 4 Å. Thin-layer chromatography was run on pre-coated TLC sheets ALUGRAM® Xtra SIL G/$UV_{254}$ or pre-coated TLC sheets ALUGRAM® RP-18W/$UV_{254}$, purchased from Macherey-Nagel. The reverse phase column was run by using a LiChroprep® RP-18 silica gel (40–63 μm) from Merck. The deuterated solvents ($CD_3CN$, DMSO-$d_6$ and DCl) were purchased from Eurisotop. The NMR spectra at 298 K were obtained on a Bruker AMX400 operating at 400 MHz ($^1H$) and 100 MHz ($^{13}C$), deuterated solvent signals were used as an internal reference. HR ESI MS analyses were performed on a Bruker maXis UHR ESI-Qq-TOF mass spectrometer in the positive ion mode. FT-IR spectra were recorded with a PerkinElmer plug-and-play UATR accessory, for powders analysis, and the spectra were collected in transmission mode. Absorption spectra were recorded with a Shimadzu UV-2501PC/Varian Cary 100 Bio spectrophotometer, and fluorescence spectra on a HORIBA iHR320 SPEX Fluorolog 3–22. As for the thermochromic studies, the

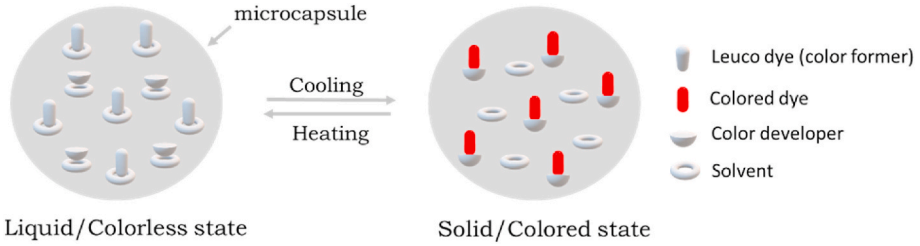



**Fig. 2.** Schematic description of a typical thermochromic multi-component pigment, where the molecular interactions between the solvent, the color developer and the leuco dye are described for the case in which the color is developed in the solid state.

spectra were recorded on a Cary 5000i coupled to a Varian Peltier temperature controller. A quartz cuvette with a 2 mm optical pathway was used to obtain suitable absorptions from the solid samples. For the thermochromic systems with the transition temperature/color below room temperature, an DankamHT E995F (DTU6005-0027-SN) with an aluminum plate was used.

### 2.2. Synthesis

#### 2.2.1. General experimental procedure of compounds I–V

Syntheses of compounds **I–V** were carried out by heating a solution of 2-[4-(dibutylamin)-2- hydroxybenzoyl] benzoic acid (2.5 mmol) with a corresponding acetophenone (2.5 mmol) in concentrated sulfuric acid (7 mL), at 100 °C. The reactions were kept under stirring between 4 and 8 h, and the conversion of the reagents was checked by TLC (DCM: MeOH = 9:1). After cooling, the acidic mixture was poured onto an ice bath, and the raw material was isolated by filtration. The final products were obtained either by recrystallization from mineral acids or separation through reverse phase chromatography (MeOH:$H_2O$ = 1:1) in an overall yield of 25–89%.

#### 2.2.2. 4-(2-Carboxyphenyl)-7-(dibutylamino)-2-(4-(dimethylamino) phenyl) chromenylium perchlorate (I)

$^1$H NMR 400 MHz, DMSO-$d_6$, $\delta$ (ppm): 88.33 (2H, d, $J$ = 8.9 Hz), 8.16 (1H, d, $J$ = 7.8 Hz), 7.94 (1H, s), 7.84 (1H, t, $J$ = 7.7 Hz), 7.75 (1H, t, $J$ = 7.8 Hz), 7.53 (1H, d, $J$ = 7.5 Hz),7.28 (1H, d, J ~ 2 Hz), 7.15 (1H, dd, $J$ = 7.2 Hz, J ~2 Hz), 7.10 (1H, d, $J$ = 7.2 Hz), 6.93 (2H, bt, $J$ = 9.0 Hz), 3.56 (4H, d, $J$ = 8.4 Hz), 3.19 (6H, s), 1.59 (4H, m), 1.38 (4H, m), 0.94 (6H, t, $J$ = 7.4 Hz). $^{13}$C NMR 126 MHz, DMSO-$d_6$, $\delta$ (ppm): 166.76, 166.19, 161.07, 157.33, 154.79, 154.38, 135.96, 132.54, 131.12, 130.63, 130.43, 130.18, 129.88, 128.74, 115.94, 114.87, 114.24, 112.48, 108.88, 96.42, 50.56, 39.53, 29.01, 19.50, 13.81. HRMS: calcd. for $C_{32}H_{37}N_2O_3^+$: 497.2799; found: 497.2796. Yield: (1.24 g), 86%.

#### 2.2.3. 4-(2-Carboxyphenyl)-7-(dibutylamino)-2-(p-tolyl) chromenylium chloride (II)

$^1$H NMR 400 MHz, DMSO-$d_6$ plus DCl, $\delta$ (ppm): 8.82 (1H, d, $J$ = 7.7 Hz), 8.71 (2H, d, $J$ = 8.0 Hz), 8.38 (1H, t, $J$ = 7.6 Hz), 8.31 (2H, t, $J$ = 7.6 Hz), 8.28 (1H, s), 8.04 (2H, d, $J$ = 8.0 Hz), 7.97 (1H, d, $J$ = 7.5 Hz), 7.88 (1H, d, $J$ = 9.4 Hz), 7.78 (1H, dd, $J$ = 9.4 Hz, J ~2 Hz),7.75 (1H, bs, J ~2 Hz), 4.15 (4H, t, $J$ = 7.9 Hz), 3.02 (3H, s), 2.31–2.18 (4H, m), 1.98 (4H, m), 1.53 (6H, t, $J$ = 7.4 Hz). $^{13}$C NMR 126 MHz, $CD_3CN$ plus DCl, $\delta$ (ppm): 180.33, 167.21, 165.80, 164.57, 160.25, 157.47, 146.70, 136.90, 133.68, 132.16, 131.27, 130.76, 130.46, 128.60, 127.94, 111.13, 97.21, 52.47, 29.93, 21.73, 20.52, 13.96. HRMS: calcd. for $C_{31}H_{34}NO_3^+$: 468.2533; found: 468.2534. Yield: (0.35 g), 25%.

#### 2.2.4. 4-(2-Carboxyphenyl)-7-(dibutylamino)-2-(4-nitrophenyl) chromenylium perchlorate (III)

$^1$H NMR 400 MHz, $CD_3CN$ plus DCl, $\delta$ (ppm): 8.44 (2H, d, $J$ = 8.8 Hz), 8.38 (2H, d, $J$ = 8.9 Hz), 8.26 (1H, d, $J$ = 7.8 Hz), 7.84 (1H, t, $J$ = 7.5 Hz), 7.77 (1H, t, $J$ = 7.6 Hz), 7.71 (1H, s), 7.42 (1H, d, $J$ = 7.5 Hz), 7.33 (1H, d, $J$ = 9.6 Hz), 7.25 (1H, dd, $J$ = 9.5 Hz, $J$ = 2.4 Hz), 7.19 (1H, d, $J$ = 2.4 Hz), 3.62 (4H, t, $J$ = 9.4 Hz), 1.69 (4H, m), 1.44 (4H, m), 0.99 (6H, t, $J$ = 7.3 Hz). $^{13}$C NMR 126 MHz, $CD_3CN$ plus DCl, $\delta$ (ppm): 167.09, 160.94, 160.33, 157.93, 151.18, 136.64, 134.16, 132.07, 131.68, 131.17, 130.44, 129.81, 129.30, 125.50, 120.33, 112.59, 97.53, 52.79, 29.99, 20.63, 14.08. HRMS: calcd. for $C_{30}H_{31}N_2O_5^+$: 499.2227; found: 499.2229. Yield: (0.70 g) 47%.

#### 2.2.5. 4-(2-Carboxyphenyl)-2-(4-cyanophenyl)-7-(dibutylamino) chromenylium perchlorate (IV)

$^1$H NMR 400 MHz, $CD_3CN$ plus DCl $\delta$ (ppm): 8.29 (2H, d, $J$ = 8.4 Hz), 8.27 (2H, d, $J$ = 7.8 Hz), 8.04 (2H, d, $J$ = 8.3 Hz), 7.84 (1H, t, $J$ = 7.6 Hz), 7.77 (1H, t, $J$ = 7.6 Hz), 7.74 (1H, s), 7.42 (1H, d, $J$ = 7.5 Hz), 7.33 (1H, d, $J$ = 9.6 Hz), 7.24 (1H, dd, $J$ = 9.5 Hz, $J$ = 2.4 Hz), 7.20 (1H, d, $J$ = 2.4 Hz), 3.62 (4H, t, $J$ = 6.5 Hz), 1.70 (4H, m), 1.44 (4H, m), 0.98 (6H, t, $J$ = 7.3 Hz). $^{13}$C NMR 126 MHz, $CD_3CN$ plus DCl, $\delta$ (ppm): 168.42, 167.20, 163.20, 160.28, 157.65, 138.80, 133.72, 133.31, 132.01, 131.40, 130.89, 130.32, 130.15, 129.36, 128.27, 119.88, 118.26, 111.81, 97.19, 52.49, 29.75, 20.45, 13.90. HRMS: calcd. for $C_{31}H_{31}N_2O_3^+.H_2O$: 497.2435; found: 497.2432. Yield: (1.29 g), 89%.

#### 2.2.5.1. 4-(2-Carboxyphenyl)-7-(dibutylamino)-2-(4-fluorophenyl) chromenylium hydrogensulfate (V).

$^1$H NMR 400 MHz, $CD_3CN$ plus DCl, $\delta$ (ppm): 8.30 (2H, m), 8.26 (1H, d, $J$ = 7.9 Hz), 7.82 (1H, t, $J$ = 7.6 Hz), 7.76 (1H, t, $J$ = 7.6 Hz), 7.71 (1H, s), 7.40 (3H, m), 7.33 (1H, d, $J$ = 9.6 Hz), 7.23 (1H, bd, $J$ = 9.8 Hz), 7.20 (1H, bs), 3.60 (4H, t, $J$ = 8.0 Hz), 1.68 (4H, m), 1.42 (4H, m), 0.97 (6H, t, $J$ = 7.3 Hz). $^{13}$C NMR 126 MHz, $CD_3CN$ plus DCl, $\delta$ (ppm): 179.33, 173.11, 167.90, 167.26, 165.88, 164.17, 160.37, 157.70, 136.81, 133.70, 132.20, 131.45, 131.39, 131.32, 130.91, 130.48, 130.43, 127.32, 127.30, 119.81, 111.39, 97.27, 52.55, 20.53, 13.96. HRMS: calcd. for $C_{30}H_{31}FNO_3^+$: 472.2282; found: 472.2283. Yield: (0.76 g), 64%.

## 3. Results and discussions

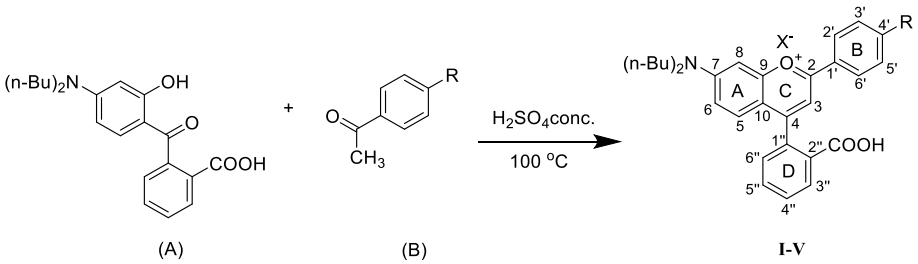
*Synthesis:* The synthesis of compounds **I–V** was adapted after reference [24], and the general experimental pathway is described in Scheme 2. The dyes were synthetized by carrying out different condensation reactions using an equimolar ratio between the corresponding benzophenone (A) and acetophenone (B). The reactions were run between 4 and 8 h in the presence of concentrated sulfuric acid, at 100 °C. The final products were isolated either by recrystallization or by purification through reverse phase chromatography in an overall yield of 25–89%.

Different colors were achieved by attaching to the R position of the B-ring, electron-donating or electron-withdrawing groups, Table 1. Strong and weak activating/deactivating groups, such as dimethylamine, methyl, nitro, cyano and fluorine were used. Furthermore, various anions like perchlorate (compound I, III and IV), chloride (compound II) and hydrogensulfate (compound V) ensured the neutrality of the molecules, the anion's nature was defined by the synthetic and purification procedures.

*Spectrophotometric data:* Spectrophotometric characterization was performed by using absorption and emission spectrophotometry. The data were collected in acidic methanolic solutions at room temperature, for both absorption (Fig. 3) and emission (Supplementary Information, SI). Methanol was selected for these measurements because all dyes showed good solubility in polar protic solvents. And the acid was added to ensure that all carboxylic moieties were protonated, and the dyes were in their colored (cationic) form. The spectra show a blue shift of *circa* 70 nm on going from strong (compound I) to weak (compound II) donor groups attached on ring B, Fig. 3a. This shift has a visible impact on the color, as it changes from blue (compound I) to magenta (compound II). On the other hand, when strong electron-withdrawing groups like nitro and cyano (compounds III and IV) were replaced by a weaker electron-withdrawing group like fluorine (compound V) the blue shift was smaller, *circa* 14 nm, Fig. 3b. And in this case, the color changed from purple (compound III) to various shades of magenta (compounds IV and V).

In terms of photophysical parameters, Table 2, there are substantial differences across the five dyes. Fluorescence quantum yield is high for compound **I**, but low for the other compounds. It is also remarkable that the presence of the amino group at position 4′ drastically increases the oscillator strength, making the color more intense.

Compounds **III** and **IV** display a large Stokes shift, highlighting a high variation of the dipole moment during the electronic transition, expected for a push-pull compound. This is compatible with a charge transfer from ring A (with the amine donor group) to ring B (with an electron acceptor group) during the electronic transition. The oscillator strengths are higher when compared with compound **II** (mainly a typical




**Scheme 2.** General experimental pathway used to obtain the spirolactone dyes based on flavylium backbone, compounds **I–V**.

**Table 1**
The attached substituents, compounds **I–V**.

| Compound | R | $X^-$ | Color |
|---|---|---|---|
| ***I*** | $N(CH_3)_2$ | $ClO_4^-$ | blue |
| ***II*** | $CH_3$ | $Cl^-$ | light magenta |
| ***III*** | $NO_2$ | $ClO_4^-$ | purple |
| ***IV*** | CN | $ClO_4^-$ | dark magenta |
| ***V*** | F | $HSO_4^-$ | light magenta |

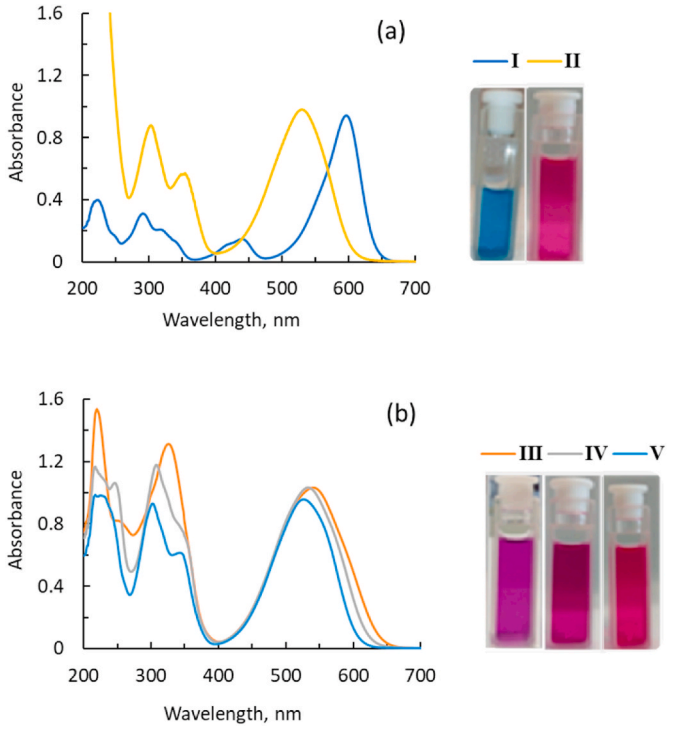



**Fig. 3.** Absorption spectra recorded in acidic methanolic solutions, compounds **I–V**. Molar concentration: [**I**] = 1.5 × $10^{-5}$ mol $dm^{-3}$; [**II**] = 7.3 × $10^{-5}$ mol $dm^{-3}$; [**III**] = 6.51 × $10^{-5}$ mol $dm^{-3}$; [**IV**] = 6.3 × $10^{-5}$ mol $dm^{-3}$; [**V**] = 6.43 × $10^{-5}$ mol $dm^{-3}$.

**Table 2**
Molar absorptivity coefficient (Ɛ), oscillator strength (f), Stokes' shift (SS) and fluorescence quantum yields (Φ) in acidic methanolic solutions, compounds **I–V**.

| Compound | R | $\lambda_{abs}^{max}$ (nm) | ϵ ($M^{-1}$ $cm^{-1}$) | f | $\lambda_{em}^{max}$ (nm) | SS ($cm^{-1}$) | Φ (%) |
|---|---|---|---|---|---|---|---|
| **I** | N $(CH_3)_2$ | 597 | 83006 | 0.70 | 640 | 1154 | 88.5 |
| **II** | $CH_3$ | 532 | 13448 | 0.21 | 595 | 2061 | 0.7 |
| **III** | $NO_2$ | 540 | 21568 | 0.39 | 698 | 4192 | 2.8 |
| **IV** | CN | 533 | 22675 | 0.39 | 682 | 4099 | 12.4 |
| **V** | F | 526 | 22778 | 0.37 | – | – | – |

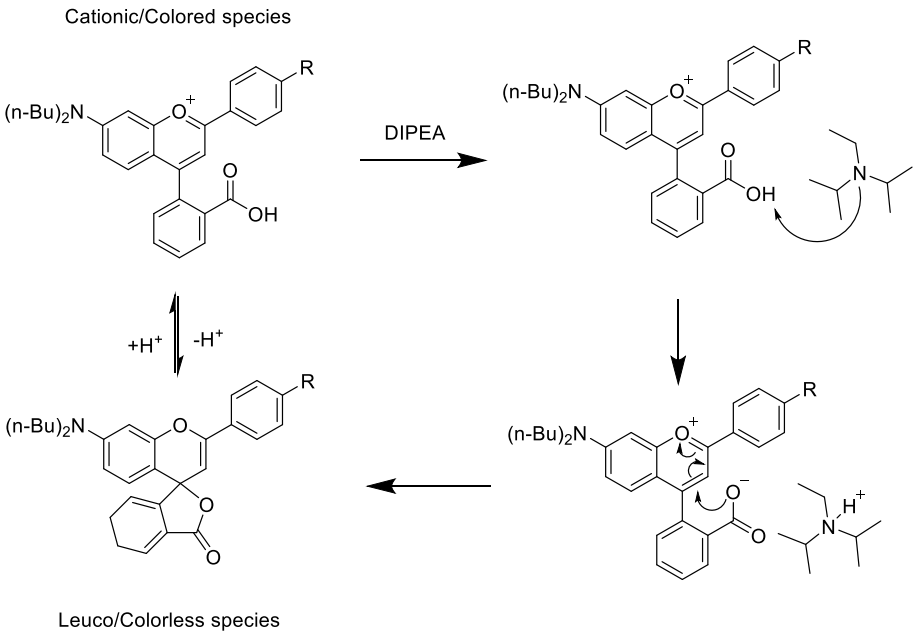
π,π* transition with no particular CT character). Furthermore, the absorption band is rather broad. For compound **V** a similar trend was noticed, but it was not fluorescent, and the Stokes shift could not be measured.

We observed that amino groups, due their electron donating properties, increase the oscillator strength and shift the absorption spectra into the red decreasing the HOMO-LUMO energy difference. This also gives rise to high fluorescent quantum yields, since the impact of non-radiative processes is smaller due to the high oscillator strength (which impacts the radiative rate constant as well) [25]. Electron withdrawing groups gives rise to charge-transfer states and resemble the so-called TICT states [28]. TICT molecules are known for their low fluorescence quantum yields in polar solvents such as methanol since the charge transfer excited state is non-fluorescent. The HOMO-LUMO energy difference will be due to a local excited-state (LE), and is essentially π,π* transition that undergoes charge-transfer in the excited state explaining the large Stokes shift [28]. The final result is that compounds **III**, **IV** and **V** have basically the same color and extinction coefficients due to the local π,π* transition, and large Stokes shift and low fluorescent quantum yields due to charge transfer processes in the excited states (absent on compound I). Compound **II** displays only π,π* transitions, small Stokes shifts and low fluorescent quantum yields since the absence of an electron donor/acceptor ring B leads to negligible resonance between ring A and B increasing non-radiative twisting processes in the excited state.

*Acid-basic behavior*: To evaluate the ability of the synthetized spirolactone dyes to switch between two species (e.g., to move from cationic/colored species to leuco/colorless species) by deprotonation or protonation of carboxylic group [25], Scheme 3, titrations were performed under various conditions.

In particular, the acid-basic behavior of dye **I** was checked by performing titrations with different organic bases such as triethylamine (TEA) and *N,N*-diisopropylethylamine (DIPEA) in non-polar protic solvent (octan-1-ol) and polar aprotic solvent (acetonitrile, water content 0.01-v/v). Therefore, when titrations were performed in acetonitrile as a function of added TEA, the dye was completely decolorized, Fig. 4a. In contrast, when acetonitrile was replaced with a non-polar protic solvent such as octan-1-ol, the cationic species are strongly stabilized, Fig. 4b. This behavior may be due to physical interactions through the formation of hydrogen bonds between the carboxyl group of the dye and the hydroxyl group of the solvent or between the hydroxyl group of the solvent and the nitrogen atom of the amine, which prevent the transfer of protons to the amine and thus the formation of the lactone.

When TEA was replaced by DIPEA keeping acetonitrile as solvent, the same discoloration effect was observed and, in addition, the presence of a clear isosbestic point appears, Fig. 5a. This point highlights a process involving two species in equilibrium, possibly between the cationic and leuco species. By using the data collected in acetonitrile and DIPEA the number of equivalents of base required to fully reach the leuco species were determined by representing the maximum absorption of the lowest energy transition as a function of added DIPEA, Fig. 5b. The number of equivalents required to reach the leuco species was less than one, Table 3. This behavior can be assigned to the slightly basic nature of




**Scheme 3.** Proposed acid-basic mechanism of newly flavylium-based dyes in the presence of an organic amine.

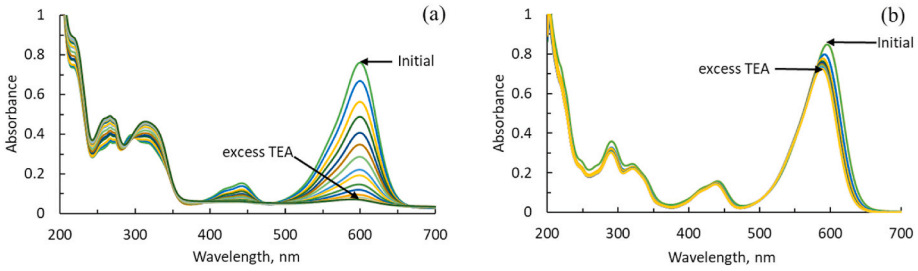



**Fig. 4.** Absorption spectra recorded in acetonitrile (a) and octan-1-ol (b) as a function of added TEA, compound **I**.

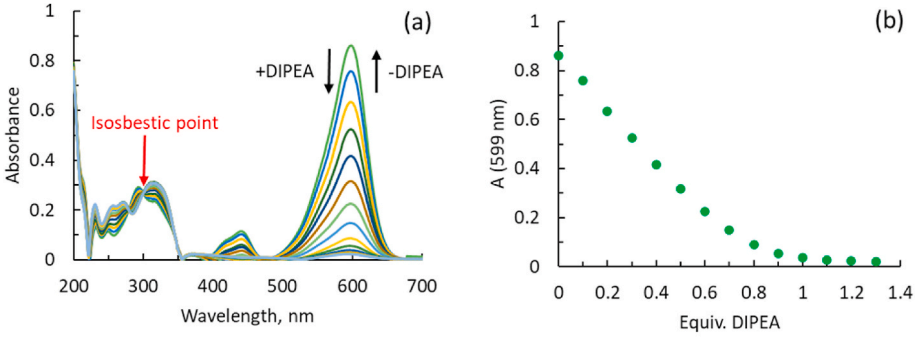



**Fig. 5.** Absorption spectra of compound **I** in acetonitrile as a function of added DIPEA (a); Absorption at $\lambda_{max}$ as a function of the number of equivalents of added DIPEA (b).

**Table 3**
Equivalents of added DIPEA in acetonitrile, compounds **I-VII**.

| Compound | R | Absorption (nm) | Equiv. DIPEA |
|---|---|---|---|
| **I** | $N(CH_3)_2$ | 599 | 1.1 |
| **II** | $CH_3$ | 531 | 0.7 |
| **III** | $NO_2$ | 542 | 0.9 |
| **IV** | CN | 534 | 0.8 |
| **V** | F | 528 | 0.8 |

acetonitrile [26] and therefore, to its ability to behave as a proton acceptor to some extent, therefore an equilibrium between leuco and color species already exists. These results also show the influence of substituents on the lactonization process, because by having a methyl group as substituent it is much easier to reach the leuco species. An amount of 0.7 equivalents of base (compound II) was enough for a complete conversion process to the uncolored form.

After reaching the colorless species, various tests were performed to assess the reversibility of the color changes. Polar protic solvents such as water and ethanol, and acids such as gallic acid and iron(III) chloride

(Lewis acid) have been tested, Fig. 6. The color was reversed completely in the presence of water (Fig. 6a) and partially in the presence of ethanol (6b). This behavior is compatible with the higher acidity of water when compared to ethanol. On the other hand, Lewis acids such as iron(III) chloride are also capable to fully reverse the color (6c), while weak acids such as gallic acid only partially revert color (6d). Therefore, Lewis acids are suitable to be used as color developers for further development of thermochromic systems. As well, for this study by using the data recorded in the presence of iron(III) chloride, Fig. 7a, the equivalents of acid used to fully reverse the color were determined as an example of a Lewis acid color developer. The equivalents of used acid were determined by representing the absorption maximum as a function of added iron(III) chloride, Fig. 7b. And according to the data, all dyes required an excess of iron(III) chloride to completely reverse the color, see Table 4. This highlights the fact that association equilibrium constants between Fe(III) and these dyes are not high. Previously it was shown that for Crystal Violet Lactone there is a two-step mechanism in which $FeCl_3$ must first dissociate to form $FeCl_2^+$ [27]. This step has a rather unfavorable equilibrium constant, which hinders the interaction with the dye to give rise to colored species. Still, the association constant in the second step is high, and we can effectively use $FeCl_3$ as a color developer even if we need a molar excess of this reagent.

*Thermochromic behavior*: The thermochromic behavior of dyes **I–V** was evaluated by developing a three-component system containing the spirolactone dye, an organic amine, and a suitable solvent. Color switching was gradual, with an initial color transition at −11 °C and a stronger color contrast at −20 °C when the cooling rate was kept constant at 1 °C/min. And as can be seen in Fig. 8, all dyes exhibited to some extent reversible thermochromic behavior.

The initial assessment of thermochromism was performed by using acetophenone (m.p. 20.2 °C) as solvent and *N,N*-dimethyldodecylamine as a base, and then, to cover a broad range of switching temperature, other solvents with melting points close to room temperature such as nitrobenzene (5.7 °C), acetonaphthone (55–56 °C), cinnamonitrile (19–22 °C) and benzoyl cyanide (28–31 °C) were also used. In the second case, the most balanced properties were obtained for compound **IV** when the ratio dye:base was 1:0.5, Fig. 9. Also, for these systems the color switching was gradual, and the temperatures displayed for the solid state (Fig. 9, bottom side) show the temperature at which the strongest color contrast was observed. In all the cases the color transition started with 2,3 °C before the full contrast was displayed. The thermochromic effect took place, because once the solid state is reached, the thermodynamic equilibrium favors the transfer of the proton from the conjugated acid of the amine to the lactone, yielding the colored opened form, Scheme 4 [28]. Since **IV** has the cyano group, this finally points out that thermochromic materials are easier to achieve with the presence of electron-withdrawing groups (push-pull effect), that favor a more labile equilibria between leuco and colored forms. It is also worth noting that the thermochromic behavior of leuco dye system is a complex phenomenon and depends on various factors such as the chemical structure, solvent and developer used. Acetonitrile has already shown similar thermochromic behavior for all dyes when tested, but this experiment was not presented in the paper as it was not part of the objective of the work. As for compound **IV**, we have also tried to explain this peculiar behavior by comparing the Hammett constants and Kamlet-Taft parameters between nitrobenzene and benzonitrile, but since the differences were insignificant, we could not draw a clear conclusion. However, we can point out that these small details can make the difference in a such complex system.

Furthermore, by using transmittance spectrophotometry the transition temperature and response time were determined for the thermochromic system formulated by compound **IV** (0.05%-w/w), *N,N*-dimethyldodecylamine (0.5 equivalents) and acetonaphthone. To determine the transition temperature, the absorption spectra were acquired as a function of temperature (Supplementary information) on cooling cycle when going from 60 °C to 15 °C and the stabilization time was 5 min for every degree. Then, by representing the ΔA:

$$\Delta A = A_{\lambda=550nm} - A_{\lambda=750nm}$$

which accounts for the amount of color developed subtracting the baseline measured at 750 nm as a function of temperature, the transition point was displayed, Fig. 10.

As for the response time, the transmittance was acquired as a function of time at 530 and 750 nm on both freezing and melting when the temperature was hold at 20 °C and 60 °C (Supplementary information). At 750 nm we can detect the solvent phase transition (which occurs at

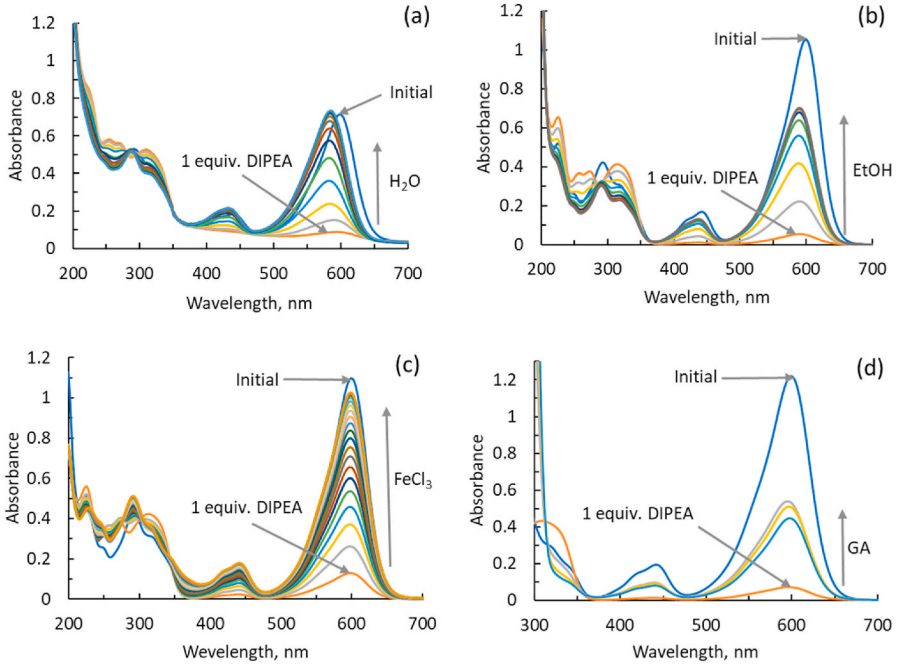



**Fig. 6.** Absorption spectra of compound **I** in acetonitrile and DIPEA, as a function of added water (a), ethanol (b), iron(III) chloride (c), and gallic acid (d).

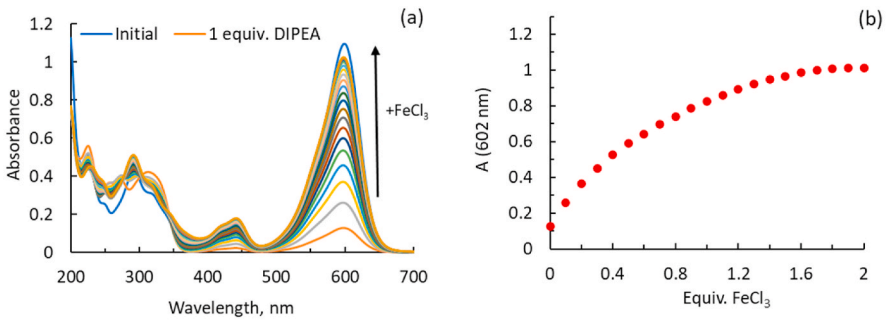



**Fig. 7.** Absorption spectra of compound **I** in acetonitrile and DIPEA (1 Equiv.), as a function of added $FeCl_3$ (a); Absorption at $\lambda_{max}$ as a function of the number of equivalents of added $FeCl_3$ (b).

**Table 4**
Equivalents of added acid in acetonitrile, compounds **I-VII**.

| Compound | R | Absorption (nm) | Equiv. $FeCl_3$ |
|---|---|---|---|
| **I** | $N(CH_3)_2$ | 602 | 1.6 |
| **II** | $CH_3$ | 529 | 2.25 |
| **III** | $NO_2$ | 552 | 3.25 |
| **IV** | CN | 529 | 2.25 |
| **V** | F | 552 | 3.25 |

39 °C) while at 530 nm we also detect the color change. The time difference between these two effects was determined to be *circa* 2 min for cooling and 0.5 min for heating. We give an estimative value for the response time because it is highly dependent of the working conditions. And in our case, it is important mentioning that 1 cm quartz cuvette with a volume of 0.7 mL was used for data collection.

Finally, we can point out that the above results showed the advantage of easily adjusting the transition temperature only by changing the solvent, without the need of any structural modification as for other thermochromic systems such as polydiacetylene [29–31], Schiff bases [32,33], bianthrones [34,35], and others [36]. Both solvents with melting points close to room temperature or well below 0 °C are suitable to be used, as the color contrast it does not shows to be affected in either case. In addition, the results also showed that, if appropriate conditions are used, the thermochromic effect can be quite strong, with a clear transition from colorless to colored state. These results compare well with classical thermochromic systems [13–15] and have a huge potential to be used in industry, since affordable components were used in the design of the experiments. As for the switching time, it occurred in a narrow time range, but it should be pointed out that it highly depends of heat transfer processes not discussed in this work.

## 4. Conclusion

Five chromogenic dyes of spirolactone type based on flavylium backbone have been successfully synthesized, structurally and spectrophotometric characterized. The influence of substituents in position 4′ of the flavylium skeleton was studied in terms of color modification, acid-basic behavior and thermochromic properties.

The compounds displayed distinct colors in acidic methanolic

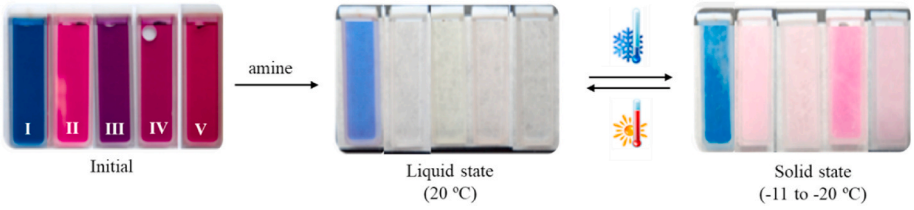



**Fig. 8.** Reversible thermochromic behavior of compounds **I–V** (~0.07%-w/w) in acetophenone and *N*,*N*-dimethyldodecylamine (1 equivalent).

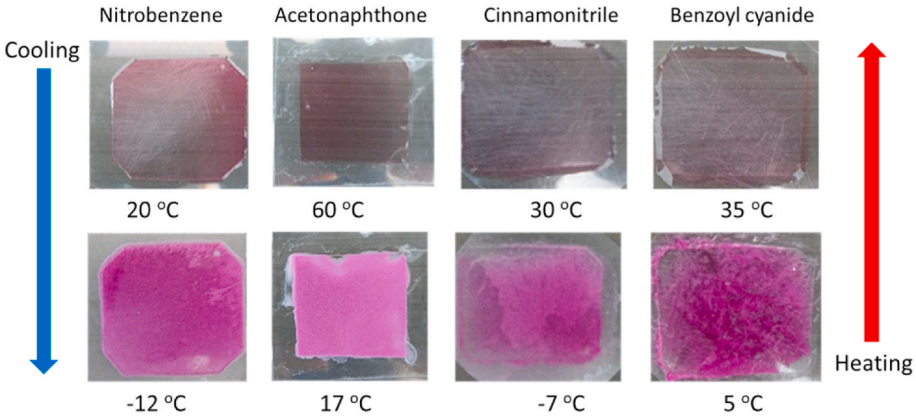
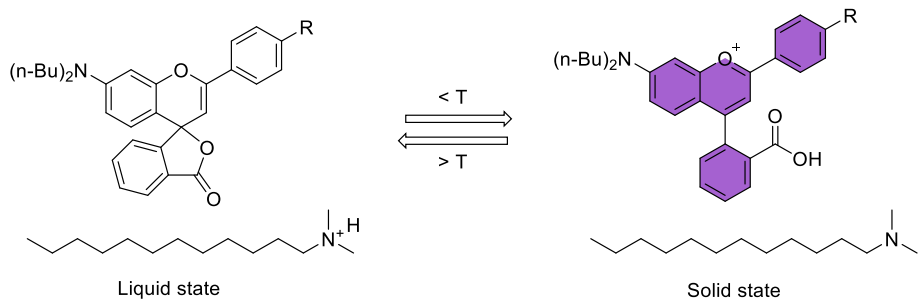



**Fig. 9.** The reversible thermochromic behavior of compound **IV** (~0.05%-w/w) in nitrobenzene, acetonaphthone, cinnamonitrile and benzoyl cyanide plus *N*,*N*-dimethyldodecylamine (0.5 equivalents).




**Scheme 4.** Schematic molecular representation of the thermochromic spirolactone system based on phase transition.

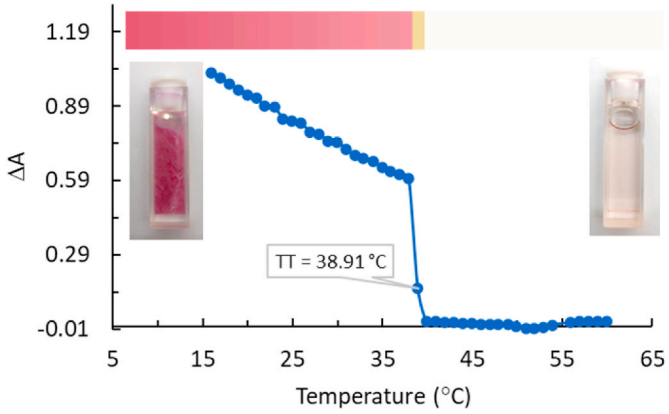



**Fig. 10.** The transition temperature (TT) of thermochromic system formulated by compound **IV** (0.05%-w/w), *N*,*N*-dimethyldodecylamine (0.5 equivalents) and acetonaphthone. The photos show the material at 20 °C and 60 °C while the color bar are the colors calculated from the absorption spectra converted to CIE L*a*b color coordinates.

solutions, going from blue (compound I)/purple (compound III) to various shades of magenta (compound II, IV and V). In addition, the photophysical parameters show that amino group, due their electron donor properties, raise the oscillator strength and shift the absorption spectra into the red. Electron-withdrawing groups give rise to charge-transfer states, but their impact on the final color is much smaller. Furthermore, the spectrophotometric studies showed that all the dyes were able to switch to the leuco species when acetonitrile was used as a solvent and DIPEA as a base. Moreover, these results also showed the influence of substituents on the lactonization process, since by attaching methyl groups it is much easier to reach the leuco species, with only 0.7 base equivalents (compound II) required for a complete conversion process. Furthermore, the thermochromic studies pointed out that thermochromic materials are easier to achieve with the presence of electron-withdrawing groups (push-pull effect), that favor a more labile equilibria between leuco and colored forms.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

The authors do not have permission to share data.

## Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 814299 - CHARISMA. This work also received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the project UIDB/50006/2020 (LAQV-REQUIMTE).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2023.111208.

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