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Optical properties of new fluorescent iminocoumarins: Part 1

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Abstract

The optical properties of 10 new iminocoumarin dyes, bearing a cyano group at the 3-position, were studied in CH_2Cl_2 by UV/vis absorption and fluorescence spectroscopy. Five of the dyes bear a free imino group, and differ by the nature and position of their electron-donor group. Among them, the dye bearing a diethylamino group at the 7-position displayed the most interesting optical properties. All the compounds were compared to analogues containing an ethoxycarbonyl group on the imino function. The presence of the ethoxycarbonyl group systematically induced a shift of the absorption and emission spectra towards long wavelengths. For the three dyes where charge transfer is weak, substitution reduced fluorescence efficiency. In contrast, the fluorescence quantum yield and lifetime were slightly increased for the compounds with strong charge transfer, and especially for that bearing a diethylamino group at the 7-position. This shows that substitution on the imino group can be a convenient way to obtain good fluorescent probes designed for various purposes.

Keywords: Iminocoumarin; Fluorescence

1. Introduction

For many decades, coumarin derivatives have been one of the most widely studied classes of fluorescent dyes, and probably one of the most frequently used [1–3]. These dyes find applications in fields as varied as the colouring of textile fibres and other materials, cell biology, medical analysis, lasers, sensors and advanced photophysical systems. In contrast, very few comparable investigations have been carried out on the neighbouring series of iminocoumarins, although interesting optical properties can be expected too. Those authors who have studied the optical properties of iminocoumarin derivatives have focused on compounds that bear an electron-releasing group in the 7-position, and an electron-acceptor group in the 3-position, a choice probably justified by the fact that this substitution pattern leads to enhanced absorption and fluorescence efficiency in the closely related coumarin series. In the iminocoumarin derivatives reported, the role of the electron donor in the 7-position is classically played by the efficient *N*,*N*-dialkylamino group, while the nature of the electron-withdrawing group in the 3-position is more frequently allowed to vary. For instance, the introduction of a benzimidazole fragment has been reported to contribute to enhanced fluorescence efficiency [4,5]. This type of molecule has been incorporated as a fluorescent signalling unit in a Ca^{2+} indicator [6,7]. In this case, the advantage of using an iminocoumarin instead of a coumarin is that the former allows nitrogen substitution with a lipophilic chain, bestowing on the sensor strong affinity for cell membranes. The attachment of an ester or amido group in the 3-position has also led to a dye with interesting lasing properties and high sensitivity to solvent effects [8]. As for the compounds bearing a cyano group in the 3-position, they have been investigated as colour formers for heat-sensitive recording sheets [9] and, after substitution of the imino group by a $CH{=}C(CN)_2$ residue, as fluorescent dyes for laser or dyeing applications [10,11].

Recently, we reported the synthesis of new iminocoumarin derivatives [12]. They were obtained by condensation

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of *O*-hydroxybenzaldehydes with an equimolecular amount of malononitrile in the presence of piperidine as the catalyst. Malononitrile was used for synthesis because the presence of two nitrile groups on this reactant makes the methylenic protons very acidic and allows the iminocoumarins to be obtained in high yields. Consequently, all our compounds bear a cyano group at the 3-position. They can be divided into two series. The dyes of series **1** (**1a**–**1e**, Scheme 1) bear a free imino group. They differ by the nature (diethylamino or methoxy) and position of their electron-donor group. The dyes of series **2** are the corresponding *N*-ethoxycarbonyl derivatives (**2a**–**2e**). The substitution of the imino group was achieved by reacting the compounds of the first series with ethyl chloroformate. Regarding the electron-donor group, the substitution pattern is similar to that of the dyes of series **1**, so a systematic comparison can be carried out. We report here the spectroscopic and photophysical properties of these compounds. All the dyes were studied in dichloromethane by UV/vis absorption spectroscopy, then by steady-state and dynamic fluorescence spectroscopy. For the sake of comparison, the spectroscopic properties of the coumarins **3** and **4** were studied too. The iminocoumarin dyes that display the best optical properties will be the topic of a second paper, where they will be studied more thoroughly in a wide number of solvents.

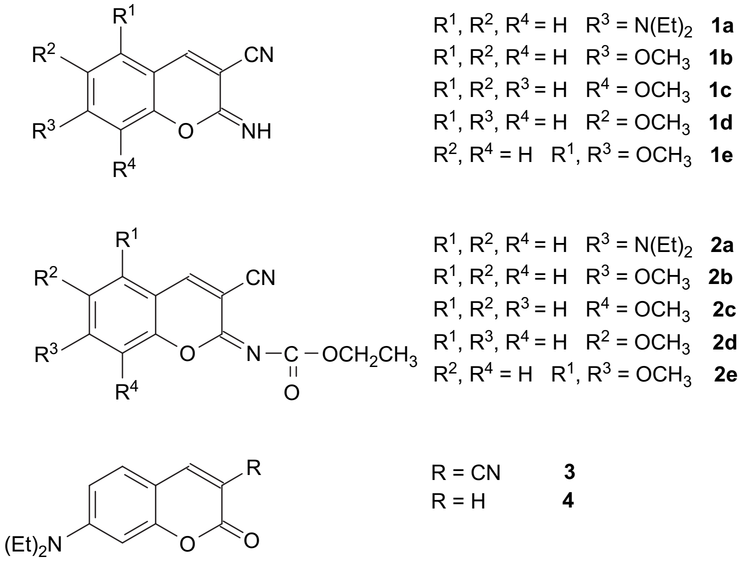
2. Experimental

2.1. Materials

The dyes of series **1** and **2** were synthesized as previously described [12]. Some were obtained pure after recrystallization in ethanol (**1a**), acetonitrile (**1e**) and methanol (**2a** and **2e**). Dye **1b** was purified by thin layer chromatography on silica plates using a mixture of chloroform and ethanol (95:5, v/v) as the eluent. Dyes **1c**, **1d**, **2b**, **2c** and **2d** were purified by HPLC using a C18 column and a water/acetonitrile (50:50, v/v) mixture as the mobile phase. To prepare dye **3**, compound **1a** was dissolved in a mixture of 70% ethanol and 30% acetic acid and heated at reflux during 1 h. Crystals of compound **3** that precipitated upon cooling were filtrated and dried. Their structure and purity were checked by conventional methods. Dye **4** (7-diethylaminocoumarin or Coumarin 110) was purchased from Aldrich and used as received. For spectroscopic measurements, analytical grade dichloromethane from Prolabo was used without further purification.

2.2. Apparatus

A Waters 510 high performance liquid chromatograph equipped with a Waters 991 UV/vis photodiode array detector was used to purify the compounds. UV/vis absorption spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer. The estimated experimental error was 2 nm on the band maximum and 5% on the molar extinction coefficient. Steady-state fluorescence work was performed on a Photon Technology International (PTI) Quanta Master 1 spectrofluorometer. All excitation and emission spectra were corrected. The fluorescence quantum yields (Φ) were determined using the classical formula: $\Phi_x = (A_s F_x n_x^2 \Phi_s)/(A_x F_s n_s^2)$ where A is the absorbance at the excitation wavelength, F is the area under the fluorescence curve, and n is the refractive index. Subscripts s and x refer to the standard and to the sample of unknown quantum yield, respectively. Coumarin 6 in ethanol ($\Phi = 0.78$) was taken as the standard [13]. For poorly emissive dyes, 4-diethylamino-7-nitrobenzoxadiazole in dichloromethane was taken as a reference, its quantum yield (0.10 [14]) having been previously determined with respect to that of Coumarin 6 in ethanol. Fluorescence decay was measured with the stroboscopic technique utilising a Strobe Master fluorescence lifetime spectrometer from PTI. The excitation source was a flash lamp filled with a mixture of nitrogen



R^1, R^2, R^4 = H R^3 = N(Et)$_2$ **1a**
R^1, R^2, R^4 = H R^3 = OCH$_3$ **1b**
R^1, R^2, R^3 = H R^4 = OCH$_3$ **1c**
R^1, R^3, R^4 = H R^2 = OCH$_3$ **1d**
R^2, R^4 = H R^1, R^3 = OCH$_3$ **1e**

R^1, R^2, R^4 = H R^3 = N(Et)$_2$ **2a**
R^1, R^2, R^4 = H R^3 = OCH$_3$ **2b**
R^1, R^2, R^3 = H R^4 = OCH$_3$ **2c**
R^1, R^3, R^4 = H R^2 = OCH$_3$ **2d**
R^2, R^4 = H R^1, R^3 = OCH$_3$ **2e**

R = CN **3**
R = H **4**

Scheme 1. Chemical structure of the iminocoumarin and coumarin dyes.

and helium (30/70). Data were collected over 200 channels with a time-base of 0.1 ns per channel. Analysis of fluorescence decay was performed using the multiexponential method software from PTI. All spectrophotometric measurements were conducted in a thermostated cell at 25 °C.

3. Results and discussion

3.1. UV/vis absorption spectra

The concentration of the dyes dissolved in dichloromethane was in the 10^{-5} M range. The compounds of series **1** were analysed first. Among them, dyes **1a**, **1b** and **1e**, which bear an electron-donor group in the 7-position, showed a strong low-energy band. This band is particularly intense ($\varepsilon = 41{,}200\ \mathrm{M^{-1}\,cm^{-1}}$) and situated at long wavelengths (414 nm) for **1a** (Fig. 1), which contains a diethylamino group, i.e. a strong electron-donor group. It is weaker and less red-shifted for the two other compounds that bear a methoxy group, which is only a moderate electron donor. Consequently, this band was attributed to charge transfer occurring between the electron-donor group in the 7-position and the electron-withdrawing groups. Analogy with coumarin dyes suggests that the imino group is the main electron-withdrawing group in these molecules. However, its effect may be enhanced by the presence of the cyano group, as illustrated by the resonance structures (Scheme 2), both groups forming the electronegative pole of the molecule. On looking more precisely at dye **1e**, it appears that adding a second donor group at the 5-position did not modify the shape of the absorption band, but slightly increased its intensity, as shown by the molar absorption coefficient (ε).

The UV/vis absorption spectrum of dyes **1c** and **1d** (Fig. 2), whose methoxy substituents are borne at the 8 and 6-positions, respectively, was markedly different. It displayed a rather intense band at around 310 nm, followed by a weak band at longer wavelengths (364 nm for **1c** and 388 nm for **1d**). In the case of **1d**, the long-wavelength band is well distinct, and it is stronger than for **1c**. We were surprised by the presence of these bands at long wavelengths. We checked that they did not result from a specific solvent effect. To do so, the absorption spectrum of dyes **3** and **4** in ethyl acetate and in ethanol was recorded. It exhibited exactly the same shape than in dichloromethane, with only small wavelength shifts due to solvatochromic effect. We also verified on compound **3** that the long-wavelength band did not arise from self-association. By using cells of different optical path-lengths, the absorption spectra were recorded for concentrations ranging from 1×10^{-3} M to 5×10^{-6} M, and they appeared to be strictly superimposable after normalization. Therefore, it was concluded that the long-wavelength bands were normally part of the spectrum. According to their molar absorption coefficients, they were assigned to π–π* transitions.

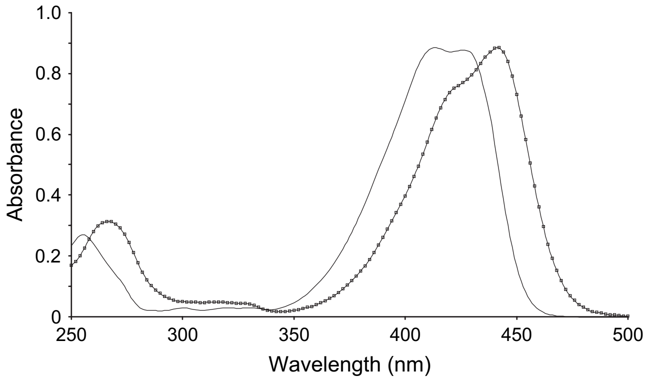


Fig. 1. UV/vis absorption spectrum of compounds **1a** (2.16×10^{-5} M, plain line) and **2a** (2.26×10^{-5} M, dotted line) in CH_2Cl_2.

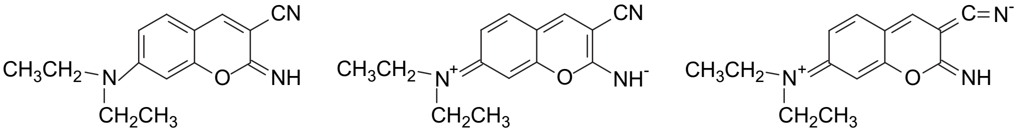
Let us now turn our attention towards the compounds of series **2**. Each was compared to its analogue in series **1**. Substitution of the imino group by an ethoxycarbonyl group influenced more or less strongly the UV/vis absorption spectrum, according to the molecule considered. For compounds **2a**, **2b** and **2e**, the absorption maximum underwent a shift to longer wavelengths, reaching 24 nm in the case of **2a**. Some differences in the shape of the spectrum were also noticeable, and seemed to result from intensity variations of the vibrational bands (Fig. 1). Concerning compounds **2c** and **2d**, the presence of the *N*-ethoxycarbonyl group led to no change at all in spectrum shape. Only the absorption maximum wavelength was slightly red-shifted for **2c** compared to **1c**. A slight increase of the molar absorption coefficient was also noted for most of the compounds of series **2**. The spectral characteristics are gathered in Table 1.

3.2. Excitation spectra

For fluorescence spectroscopy, the dye concentration was in the 10^{-6} M range, so absorbance at the excitation wavelength was kept around 0.05. For all compounds from series **1** and **2**, the excitation spectrum was similar to the absorption spectrum (Table 1), and did not vary with the emission wavelength. This indicates that the species visible on the absorption spectrum is also responsible for fluorescence emission.

3.3. Steady-state emission spectra

For all the compounds, the shape and position of the emission spectra were independent of the excitation wavelength, which confirms that only one species emits in each solution. In particular, exciting compounds **1c** and **1d** on either of the bands led to the same emission spectrum. This confirms the π–π* nature of the transition that corresponds to the long-wavelength band, because when the transition at lowest energy is of the n–π* type, this usually leads to a non-fluorescent excited state. The emission spectrum of all the compounds showed one structureless emission band, where some shoulders could occasionally be distinguished (Fig. 3). Its maximum varies in the order: **1d** > **1c** ≈ **1a** > **1e** > **1b**. For the molecules that bear a substituent in the 7-position, this order follows the magnitude of the electron-donor effect. But, it is very surprising to see that, of the five compounds considered, **1d** and **1c** emit at the longest wavelengths.



Scheme 2. Resonance structure of compound **1a**.

Looking now at the compounds of series **2**, substitution by an ethoxycarbonyl group induced a red shift of the emission spectrum for all the compounds. The shift was strong (26 and 28 nm, respectively) for **2a** and **2b**, if considering the emission maximum. However, it must be mentioned that the spectrum shape varied for these compounds after substitution, which suggests that the bands responsible for the absorption maximum are not issued from the same vibrational levels. For compound **2e**, the spectrum shape was unchanged and the shift was 14 nm. The shift was weak for molecules **2c** and **2d**. It seems that the ethoxycarbonyl group enhances the electron attracting effect of the imino group and reinforces intramolecular charge transfer. This effect is significant for the molecules that bear the electron-donor group in the 7-position, and it depends on the strength of the donor group.

3.4. Fluorescence quantum yields and lifetimes

The fluorescence quantum yield was determined by excitation at the absorption maximum for each dye. Molecule **1a** showed an excellent quantum yield of 0.84. It was only one quarter of this value for **1b**, then decreased drastically for **1e**. The fluorescence efficiency of compounds **1c** and **1d** was poor. It seems that the substitution by the ethoxycarbonyl group slightly enhanced the quantum yield of **2a** and **2e**. In contrast, the quantum yield of the other molecules was markedly decreased.

The fluorescence lifetimes were measured by excitation at 337 nm, collecting the signal at the maximum emission wavelength for each compound. The decays were found to be monoexponential in every case and it was checked that using two exponentials did not improve the fit. For most of the compounds bearing a free imino group, the lifetimes were above the nanosecond scale. Only compound **1c** showed a lifetime well below this value. For compounds where the imino group has been substituted, the lifetime was increased for **2a** and **2e**, and markedly decreased for the other compounds. It must be underlined that below 0.7 ns, the lifetimes obtained must be considered with circumspection, since our apparatus lacks precision in this range of values.

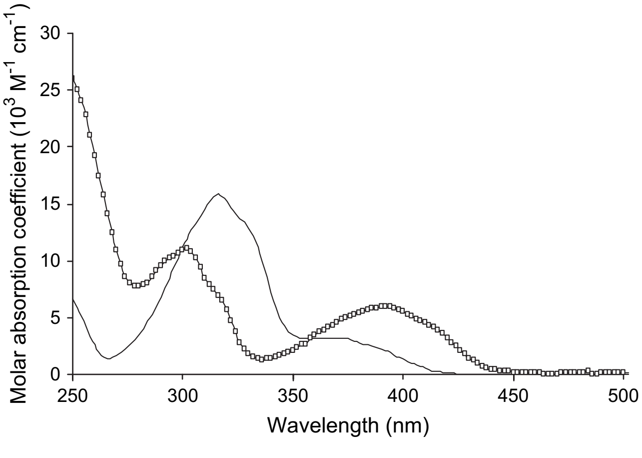


Fig. 2. UV/vis absorption spectrum of compounds **1c** (plain line) and **1d** (squares) in CH_2Cl_2.

3.5. Deactivation constants

The values of the fluorescence quantum yield and lifetime give access to the calculation of the radiative (k_r) and non-radiative (k_{nr}) deactivation constants, classically defined as $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$. Let us recall that, very schematically, a high value for k_r indicates that the energy levels of the molecule favour high fluorescence efficiency, whereas a high value for k_{nr} indicates that non-radiative deactivations, such as rotations, vibrations, or hydrogen bonding, take place in the molecule and offer deactivation channels that compete with fluorescence.

The values of k_r and k_{nr} are reported in Table 1. The two of them vary by a factor of about 35 according to the compound considered. For compounds of series **1**, the k_r value was particularly high for **1a**, as could be expected, the presence of strong charge transfer being favourable to fluorescence. This value decreased for **1b**, and then collapsed for the other members of the series. It can be noted that for **1e**, the k_r value was particularly low, compared to that of **1b**. Therefore, the presence of two methoxy groups is not compatible with good fluorescence efficiency. The k_{nr} value roughly follows the reverse order. It was low for **1a**, and higher for the other molecules.

Let us now look at the effect of substitution of the imino group by an ethoxycarbonyl group. It appears that the radiative and non-radiative deactivations remain in the same order of magnitude for molecules where internal charge transfer is strong (namely **2a** and **2e**). In contrast, molecule **2b** is intrinsically less emissive than its analogue **1b**, and also loses excitation energy via non-radiative deactivation pathways that have been opened by the presence of the *N*-ethoxycarbonyl group.

*3.6. Comparison of **1a** with its coumarin analogue*

It appears from this study that compound **1a** is of particular interest for fluorescence use. The comparison with a coumarin analogue (compound **3**) could tell us if the introduction of the imino group in the coumarin structure has led to an

Table 1
Spectroscopic and photophysical characteristics of the iminocoumarin derivatives

Compound	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{ex} (nm)	λ_{em} (nm)	Φ	τ (ns)	k_r (10^8 s^{-1})	k_{nr} (10^8 s^{-1})
1a	256	14,000	258	460	0.84 ± 0.02	2.9 ± 0.5	2.90 ± 0.68	0.55 ± 0.20
	414	41,200	414	482 (sh)		$\chi^2 = 2.81$		
	428	41,000	429					
1b	254	7900	250	387 (sh)	0.21 ± 0.02	2.5 ± 0.2	0.84 ± 0.16	3.16 ± 0.36
	358	15,500	354	406		$\chi^2 = 3.88$		
1c	316	15,800	325	462	$1.3 (\pm 0.2) \times 10^{-2}$	0.4 ± 0.2[a]	–	–
	364	3800	370 (sh)			$\chi^2 = 1.88$		
1d	242	16,700	–	468	$6.2 (\pm 0.5) \times 10^{-2}$	1.6 ± 0.2	0.38 ± 0.09	5.86 ± 0.87
	306	11,000	304			$\chi^2 = 1.01$		
	388	4800	390					
1e	252	9100	257	428	$4.7 (\pm 0.2) \times 10^{-2}$	2.4 ± 0.1	0.19 ± 0.02	3.97 ± 0.18
	360	21,900	361			$\chi^2 = 2.03$		
	372	20,700	373					
	394 (sh)	10,000	–					
2a	266	14,800	270	486	0.85 ± 0.04	3.6 ± 0.1	2.36 ± 0.18	0.42 ± 0.12
	423 (sh)	34,000	422 (sh)			$\chi^2 = 3.51$		
	440	39,400	443					
2b	316 (sh)	6700	310 (sh)	414 (sh)	$6.5 (\pm 1.0) \times 10^{-3}$	0.8 ± 0.2	0.08 ± 0.04	14.2 ± 4.3
	357	19,400	354	434		$\chi^2 = 1.14$		
	370	20,100	368	462 (sh)				
	390 (sh)	1300	390 (sh)					
2c	322	17,100	325	465	$3.4 (\pm 1.2) \times 10^{-3}$	0.3 ± 0.2[a]	–	–
	374 (sh)	2400	375 (sh)			$\chi^2 = 1.51$		
2d	244	22,700	242	470	$4.7 (\pm 0.5) \times 10^{-2}$	0.3 ± 0.1[a]	–	–
	306	12,800	303			$\chi^2 = 1.10$		
	388	6100	384					
2e	244	16,200	–	442	$5.9 (\pm 0.2) \times 10^{-2}$	2.6 ± 0.3	0.23 ± 0.02	3.62 ± 0.48
	364 (sh)	22,000	364			$\chi^2 = 2.38$		
	376	24,100	376					
	396 (sh)	16,200	396 (sh)					
3	260	14,300	260	460	0.82 ± 0.02	2.7 ± 0.3	3.04 ± 0.46	0.66 ± 0.17
	428	46,600	427			$\chi^2 = 1.73$		
4	256	10,500	256	433	0.90 ± 0.02	3.3 ± 0.3	2.73 ± 0.33	0.30 ± 0.04
	376	29,600	376			$\chi^2 = 3.97$		

λ_{abs}: maximum absorption wavelength for peaks and shoulders (sh) above 240 nm; ε: corresponding molar absorption coefficient; λ_{ex}: maximum excitation wavelength and shoulders. λ_{em}: maximum emission wavelength and shoulders; Φ_f: fluorescence quantum yield with excitation at the maximum absorption wavelength; τ: fluorescence lifetime; k_r and k_{nr}: radiative and non-radiative deactivation constants, respectively.

[a] The τ value must be considered with circumspection, since our apparatus lacks precision below 0.7 ns.

improvement or not. Concerning absorption, the spectrum of **3** was slightly narrow when compared to that of **1a**, with only one maximum instead of two, and its molar absorption coefficient was slightly higher. In emission, the two compounds share many common spectroscopic features, with identical maximum wavelengths, and very close quantum yield and lifetime, with a very small advantage for **1a**. Thus, it appears that the replacement of the oxygen atom by an NH group as the electron-withdrawing centre leads to very small changes of the spectroscopic behaviour, at least in dichloromethane.

3.7. Influence of the cyano group on the spectroscopic properties

As explained in Section 1, all the compounds studied here bear a cyano group in the 3-position because of synthesis convenience. However, it was interesting to see the influence of the cyano group on the spectroscopic properties. To do so, a comparison was made between compounds **3** and **4**, which both are coumarins. It appeared that the presence of the cyano group on **3** markedly influences the spectrum position, making the absorption and emission spectra shift to the red by 52 and 27 nm, respectively (Table 1). In contrast, the coumarin deprived of the cyano group has higher quantum yield and longer fluorescence lifetime. This suggests that the cyano group, which is rotating freely, induces some deactivation pathways.

4. Conclusions

This study, based on the comparison of a series of iminocoumarin derivatives, highlights the structures that are more

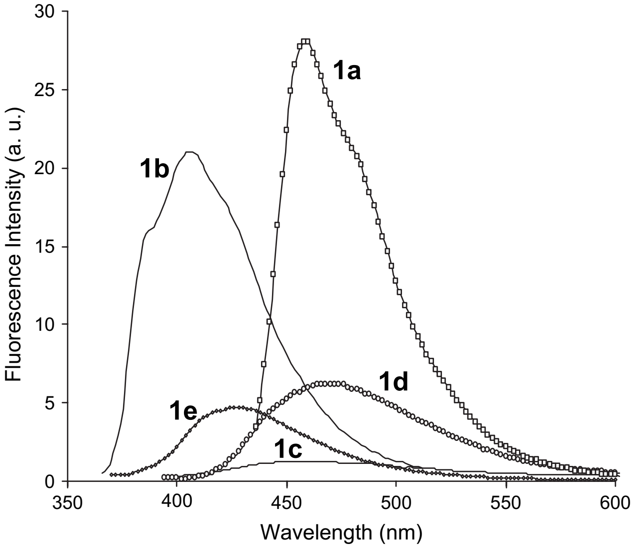


Fig. 3. Emission spectrum (λ_{ex} = maximum λ_{abs}) of the five dyes of series **1** in CH_2Cl_2. The intensity is proportional to the quantum yield, except for **1a** where it was divided by 3.

efficient for the application researched, that is, the preparation of fluorescent dyes designed for biological labelling and imaging. It confirms that the intramolecular charge transfer allowed by the presence of a strong electron-donor group at the 7-position favours fluorescence properties, as is the case for the coumarin series. However, it was interesting to note here that the double substitution by a moderate donor group in the 7 and 5-positions did not improve the system, compared to mono-substitution.

It appeared that some iminocoumarins such as **1a** display fluorescence properties as good as those of coumarins. The quantum yield is high and the lifetime of several nanoseconds allows measurements to be carried out without ultra-fast equipment. On this compound, the substitution of a hydrogen of the free imino group by an ethoxycarbonyl group induces a red shift of the absorption and emission spectra, and the fluorescence efficiency is maintained, and even improved. This type of substitution allows interesting possibilities to fix the fluorescent moiety to a substrate, so the compound could advantageously be used as a fluorescent label. It will now be very interesting to see what happens in other solvents, closer to biological medium, and this will be the topic of our forthcoming paper.

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