



Solid-state fluorescence properties of small iminocoumarin derivatives and their analogues in the coumarin series



Nihel Abid-Jarraya^a, Kacem Khemakhem^a, Hamida Turki-Guermazi^a, Souhir Abid^a,
Nathalie Saffon^b, Suzanne Fery-Forgues^{c,d,*}

^a Laboratory of Applied Chemistry HCGP, Faculty of Science, University of Sfax, 3038 Sfax, Tunisia

^b Service Commun RX, Institut de Chimie de Toulouse, ICT- FR2599, Université Paul Sabatier, 31062 Toulouse Cedex 9, France

^c CNRS, SPCMIB-UMR 5068, F31062 Toulouse, France

^d Université de Toulouse, SPCMIB-UMR 5068, F31062 Toulouse, France

ARTICLE INFO

Article history:

Received 14 March 2016

Received in revised form

22 April 2016

Accepted 24 April 2016

Available online 25 April 2016

Keywords:

Coumarin

Iminocoumarin

Solid-state fluorescence

Photoluminescence

Crystal

ABSTRACT

Considering the many potential applications of fluorescent materials, dyes that exhibit emission in the solid state are in high demand, especially if they are easy to prepare and inexpensive. In this respect, exploring the behaviour of basic iminocoumarins seemed relevant. The spectroscopic properties of 3-cyano-7-diethylamino-2-iminocoumarin and a derivative bearing an ethoxycarbonyl group were therefore studied in the solid state, and a comparison was made with the corresponding coumarin. The three compounds had very close fluorescence properties in solution. In contrast, the coumarin derivative was much more emissive in the solid state than the iminocoumarins. This discrepancy was tentatively related to the crystal packing modes. A comparison was made with 7-diethylaminocoumarin to clarify the role of the cyano group, which may not be advantageous from a spectroscopic viewpoint. Using a solvent-exchange method, the three cyano compounds generated elongated microparticles, the substituted iminocoumarin derivative even led to flat microfibers. This work shows that small coumarins are valuable solid-state fluorescent dyes while small iminocoumarins should be used as building blocks to access more elaborated compounds if solid-state applications are envisaged.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Fluorescent dyes that emit efficiently in the solid-state are of recent and increasing interest. Whether used as thin layer or micro/nanoparticles, they find more and more applications in the fields of optoelectronics, chemical sensing and biological imaging [1–5]. Such molecules are still a few and their design is delicate. Actually, providing the molecules with a rigid, conjugated electron system and judiciously located auxochrome groups is not enough to ensure good solid-state emission properties. The molecular arrangement in the solid state is also of primary importance. If this arrangement is not appropriate, emission is quenched upon aggregation, as frequently encountered for the great majority of fluorophores whose head-to-head stacking leads to virtual extinction of

fluorescence [6,7].

Some families of dyes have been relatively unexplored in the solid state. This is the case for coumarins, which paradoxically constitute the most popular class of fluorescent dyes for use in solution and in polymers. These dyes generally emit in the blue-green region and they have been widely used as fluorescent tracers and sensors for a very long time [7–10]. Their synthesis is quite easy, so that various substitution patterns are available, and their spectroscopic and photophysical properties in solution have been extensively investigated. Curiously, the solid-state fluorescence properties of coumarins and coumarin-based fluorophores only began to attract interest less than a decade ago [11–25]. These studies have mainly been conducted with the purpose of developing materials for organic light-emitting diodes (OLEDs) [12–18] and non-linear optics [19]. It is now well acknowledged that many coumarins are fluorescent in the solid state. A few authors, including us, have considered the solid-state fluorescence properties of these dyes with respect to the molecular arrangement in the crystals [20–23]. This approach is still in its early stages, but it is

* Corresponding author. Laboratoire de Synthèse et Physico-Chimie des Molécules d'Intérêt Biologique (SPCMIB), Université de Toulouse III, Bât.2R1, 118 route de Narbonne, 31062 Toulouse Cedex 9, France.

E-mail address: sff@chimie.ups-tlse.fr (S. Fery-Forgues).

beginning to provide some useful information for future research. To the best of our knowledge, no comparable investigation has been undertaken for iminocoumarins that constitute a close family of dyes. Their solid-state emission properties have hardly been reported [26–28]. The main drawback of iminocoumarins is certainly that they are prone to hydrolysis and this may explain why these compounds are much less known and used than coumarins. But, dyes of the two families often display very close spectroscopic properties in solution. The advantage of iminocoumarins is that substitution of the imino function allows easy access to elaborated compounds. We observed that some derivatives were emissive in the solid state and we recently showed their value to prepare fluorescent nanofibers and microparticles [26–28]. Therefore, it seemed instructive to gain more information about these compounds and to see whether the similarity with coumarins is also true for emission in the solid state.

The aim of the present paper was to compare the photoluminescence properties of closely related iminocoumarin and coumarin dyes (Fig. 1). Our choice was to investigate very simple dye molecules that could lead to cheap materials. 3-Cyano-7-diethylamino-2-iminocoumarin (**1**) is the basis of various derivatives synthesized and studied in our team [26–34]. Compound **2** was obtained by grafting an ethoxycarbonyl group on the imino function of **1** and it is a good model of substituted iminocoumarin. Compound **3** is the corresponding coumarin analogue. For the purpose of comparison, the well-known laser dye, 7-diethylaminocoumarin (**4**), was also studied in the solid state. All these compounds are archetypes of good fluorophores in solution. According to the popular substitution pattern, the diethylamino group in the 7-position acts as a strong electron donor group, involved in a favourable resonance structure with the electron acceptor at the 2-position [7,8]. In compounds **1** to **3**, the cyano group was introduced at the 3-position both for synthesis conveniences and for shifting the fluorescence spectrum to the red [29,30]. A previous study showed that all these compounds were indeed valuable as fluorescent markers in solution [31]. In the following work, the photoluminescence properties were examined on powder compounds and tentatively interpreted in the light of the crystal packing modes obtained by X-ray analysis. To get information about the self-association properties of compounds **1** to **3**, the type of microstructures spontaneously obtained using a simple solvent-exchange process was regarded.

2. Experimental

2.1. Materials

Ethylacetate was from Sigma Aldrich and dimethylsulphoxide (DMSO) from Fisher Scientific. Absolute ethanol was from VWR. High-pressure demineralized water (resistivity 18.3 MΩ cm) was prepared with a Milli-Q apparatus (Millipore). 7-Diethylaminocoumarin (Coumarin 110, laser grade 99%) was purchased from Sigma Aldrich and used as received. Compounds **1–3** were synthesized as previously described [35]. In a first step, the

iminocoumarin (**1**) was obtained by condensation of 2-hydroxy-4-diethylamino-benzaldehyde with stoichiometric amount of malonitrile and piperidine. To prepare compound **2**, *N*-ethoxycarbonylation of **1** was performed with ethylchloroformate. Coumarin **3** was prepared by hydrolysis of **1** in a mixture of acetic acid and ethanol (30:70 v/v). The three compounds were recrystallized twice in ethanol. The yields were higher than 70%. The compounds were checked for quality by ¹H and ¹³C NMR (attributions were made using 2D NMR), HPLC/MS, HRMS and microanalysis.

2.1.1. 3-Cyano-7-diethylamino-2-iminocoumarin (3-cyano-7-diethylamino-2*H*-1-benzopyran-2-ylidene) (**1**)

¹H NMR (300 MHz, DMSO-d₆): δ = 1.12 (t, J = 7.5 Hz, 6H, CH₃), 3.43 (q, J = 7.5 Hz, 4H, CH₂), 6.31 (s, 1H, H8), 6.59 (dd, J = 9 and 3 Hz, 1H, H6), 7.31 (d, J = 9 Hz, 1H, H5), 8.05 (s, 1H, H4), 8.20 (s, 1H, NH). ¹³C NMR (75.4 MHz, DMSO-d₆): δ = 12.30 (CH₃), 44.25 (CH₂), 94.17 (C3), 96.15 (C8), 106.00 (C10), 108.17 (C6), 116.67 (C≡N), 130.66 (C5), 146.35 (C4), 152.11 (C7), 153.28 (C2), 156.30 (C9). ESI+/HRMS *m/z* calcd for C₁₄H₁₆N₃O: 242.1293; found: 242.1298 (MH⁺); elemental analysis calcd (%) for C₁₄H₁₅N₃O: C 69.69, H 6.27, N 17.41; found: C 69.55, H 6.68, N 17.44.

2.1.2. 3-Cyano-7-diethylamino-2-(*N*-ethoxycarbonyl)iminocoumarin (Carbamic acid, *N*-(3-cyano-7-diethylamino-2*H*-1-benzopyran-2-ylidene)-, ethyl ester) (**2**)

¹H NMR (300 MHz, DMSO-d₆): δ = 1.12 (t, J = 6 Hz, 6H, CH₃), 1.27 (t, J = 6 Hz, 3H, CH₃), 3.47 (q, J = 6 Hz, 4H, CH₂), 4.20 (q, J = 6 Hz, 2H, CH₂O), 6.42 (d, J = 3 Hz, 1H, H8), 6.75 (dd, J = 9 Hz and 3 Hz, 1H, H6), 7.43 (d, J = 9 Hz, 1H, H5), 8.34 (s, 1H, H4). ¹³C NMR (75.4 MHz, DMSO-d₆): δ = 12.28 (CH₃), 14.18 (CH₃), 44.41 (CH₂), 61.71 (OCH₂), 91.70 (C3), 96.24 (C8), 106.39 (C10), 110.04 (C6), 115.63 (C≡N), 131.29 (C5), 148.97 (C4), 151.06 (C2), 152.95 (C7), 155.70 (C9), 158.53 (C=O). ESI+/HRMS *m/z* calcd for C₁₇H₂₀N₃O₃: 314.1505; found: 314.1504 (MH⁺); C₁₇H₁₉N₃O₃Na: 336.1324; found: 336.1321 (MNa⁺); elemental analysis calcd (%) for C₁₇H₁₉N₃O₃: C 65.16, H 6.11, N 13.41; found: C 64.89, H 6.29, N 13.17.

2.1.3. 3-Cyano-7-diethylamino-2-coumarin (3-cyano-7-diethylamino-2*H*-1-benzopyran-2-one) (**3**)

¹H NMR (500 MHz, DMSO-d₆): δ = 1.15 (t, J = 6 Hz, 6H, CH₃), 3.51 (q, J = 6 Hz, 4H, CH₂), 6.62 (d, J = 3 Hz, 1H, H8), 6.84 (dd, J = 9 Hz and 3 Hz, 1H, H6), 7.52 (d, J = 9 Hz, 1H, H5), 8.55 (s, 1H, H4). ¹³C NMR (125 MHz, DMSO-d₆): δ = 12.30 (CH₃), 44.97 (CH₂), 90.41 (C3), 96.53 (C8), 107.00 (C10), 110.35 (C6), 116.22 (C≡N), 131.35 (C5), 151.98 (C4), 153.29 (C7), 157.50 (C9), 158.51 (C2). ESI+/HRMS *m/z* calcd for C₁₄H₁₅N₂O₂: 243.1134; found: 243.1143 (MH⁺); elemental analysis calcd (%) for C₁₄H₁₄N₂O₂: C 69.41, H 5.82, N 11.56; found: C 69.15, H 5.62, N 11.38.

2.2. Apparatus

High resolution mass spectra were obtained at the 'Service Commun de Spectrométrie de masse de l'Institut de Chimie de

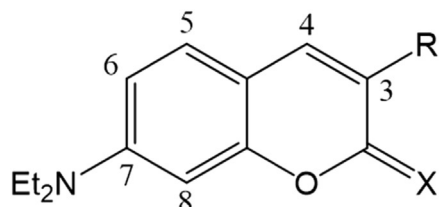


Fig. 1. Chemical structures of the coumarin and iminocoumarin derivatives **1–4**.

- X = NH, R = CN (**1**)
 X = NC(O)OEt, R = CN (**2**)
 X = O, R = CN (**3**)
 X = O, R = H (**4**)

Download English Version:

<https://daneshyari.com/en/article/175332>

Download Persian Version:

<https://daneshyari.com/article/175332>

[Daneshyari.com](https://daneshyari.com)