Dyes and Pigments 94 (2012) 81–87

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

Fluorescent nanofibers and microcrystals obtained by reprecipitation of a long-chain iminocoumarin derivative

Hamida Turki [a], Souhir Abid [a], Nathalie Saffon [b], Suzanne Fery-Forgues [c,*]

[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] Laboratoire des Interactions Moléculaires Réactivité Chimique et Photochimique, CNRS UMR 5623, Université Paul Sabatier, 31062 Toulouse Cedex 9, France

ARTICLE INFO

Article history:
Received 7 October 2011
Received in revised form
26 October 2011
Accepted 27 October 2011
Available online 13 November 2011

Keywords:
Coumarin
Iminocoumarin
Fluorescence
Microcrystal
Nanofiber
Reprecipitation

ABSTRACT

An iminocoumarin derivative bearing a fatty chain, specifically N-palmitoyl-3-cyano-7-diethylamino-2-iminocoumarin, was synthesized and used to prepare particles owing to a solvent exchange process (reprecipitation method). The composition of the reprecipitation medium was allowed to vary. In all cases, very thin particles that emitted yellow–orange light were obtained. In water alone, they looked like nanofibers or nanoribbons. Addition of surfactants at concentrations lower than the CMC favored the formation of bladed microcrystals. In the presence of acetonitrile, elongated microcrystals with good wave-guiding properties were obtained. The fluorescence properties were discussed on the basis of the crystal packing mode. It appears that the flexibility of the imino function leads to an original crystal structure, which is compatible with solid-state fluorescence. This property, together with the ease of synthesis, makes this family of compounds interesting for subsequent use as optically-active nanomaterials.

1. Introduction

In the rapidly expanding field of organic nano- to micrometer-sized materials, fluorescent nanofibers and nanocrystals occupy a very special position. Both of them find potential use in new technology devices [1–7], as well as in the field of chemical and biochemical sensors [8–13]. As a matter of fact, specific applications closely depend on the nature and size of these nano-objects. For instance, the particular shape of nanofibers makes them unique candidates for individual insertion in miniaturized systems where they act as active component to generate or transmit light [6,7]. When they display wave-guiding properties, they can also find original applications such as the authentication of precious documents [7]. In contrast, small round-shaped nanocrystals are particularly useful as fluorescent emitters in living cells for biological studies [14], as well as for medical imaging [15].

The ideal would be that molecules assemble spontaneously to give the desired particles. This would allow easy and cheap preparation of materials using bottom–up approaches. Unfortunately, we miss data to know which chemical modifications must be brought to molecules to favor the formation of a given type of particle. This field has hardly been explored and the task is particularly difficult, since many limitations associated to solid-state fluorescence must simultaneously be taken into account [16,17]. For example, the frequently encountered molecular arrangement where strong head-to-head stacking interactions take place is not compatible with fluorescence emission and must absolutely be avoided.

In this context, our team recently investigated the formation of fluorescent nanoparticles from some coumarin derivatives, using a solvent exchange process called reprecipitation method. Although the studied coumarin derivatives only differed by very small structural changes, an evolution was noted in the shape of the obtained particles. For instance, Coumarin 6 (i.e. 3-(2′-benzothiazolyl)-7-diethylaminocoumarin) and Coumarin 7 (i.e. 3-(2′-benzimidazolyl)-7-diethylaminocoumarin) spontaneously gave microrods [18,19] while the analogs bearing a methyl and a butyl group on the benzimidazolyl group lead to straight and entangled nanofibers, respectively [18]. Obviously, all these molecules show a tendency to give elongated structures, but the formation of nanofibers was unexpected. Actually, the driving force being quite weak, these particles rarely form in a spontaneous way from small molecules, although a few compounds have been reported to give nanofibers via simple solvent-exchange or drop-casting methods

* Corresponding author. Tel.: +33 5 61 55 68 05; fax: +33 5 61 55 81 55.
E-mail address: sff@chimie.ups-tlse.fr (S. Fery-Forgues).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.10.018

[11,20–27]. At this stage of the work, increasing significantly the length of the alkyl chain seemed interesting to us. In fact, it is known that the van der Waals interactions that take place between aliphatic groups contribute to stabilize the fibers, together with the π–π interactions due to aromatic groups [6,28]. Unfortunately, long-chain derivatives of Coumarin 7 were tedious to synthesize. Moreover, making a correlation between the spectroscopic behavior and the packing arrangement in the crystal is essential for understanding the emission properties in the solid-state, and our substituted coumarins were quite reluctant to form single crystals of macroscopic size, usable for standard X-ray crystallographic analysis. For these reasons, no further investigation was carried out on this series of dyes and our attention was turned toward closely related structures.

A new work was therefore undertaken in the 3-cyano-7-diethylamino-2-iminocoumarin series. These dyes have been studied by our team for six years [29–33]. Some of them display excellent spectroscopic properties, similar to those of the corresponding coumarins, and their fluorescence behavior can be widely modulated by varying the chemical structure in view of different applications. Another distinct advantage of iminocoumarins is that they lend themselves well to substitution on the imino function, so a large variety of structures can be obtained easily. Moreover, most of these compounds readily crystallize. In the present work, the iminocoumarin derivative **1** (Fig. 1) bearing a fatty chain on the imino function was synthesized and used to prepare particles by the reprecipitation method. The shape and size of the formed particles were studied, as well as the optical properties, which were discussed on the basis of the molecular arrangement obtained by X-ray diffraction analysis.

2. Experimental section

2.1. Materials

Acetone (Carlo Erba) and high-pressure demineralized water (resistivity 18 MΩ cm) prepared with a Milli-Q apparatus (Millipore) were used as solvents. Palmitoyl chloride and Triton TX100 were purchased from Aldrich. Sodium dodecylsulfate and cetyltrimethylammonium bromide were from Acros.

2.2. Preparation of N-palmitoyl-3-cyano-7-diethylamino-2-iminocoumarin (*1*)

Palmitoyl chloride (10 mmol) diluted in 2 mL of chloroform was added dropwise, for 30 min, to a stirred solution of 10 mmol of 3-cyano-7-diethylamino-iminocoumarin [29] in 30 mL of chloroform containing 10 mmol of pyridine, while keeping the mixture at 0 °C. The basic medium was then allowed to reach room temperature and was stirred for 3–4 h. A triple extraction with water was realized. The organic phase was then dried, the solvent was evaporated off and the crude product was precipitated in cyclohexane, filtered and dried. It was purified by TLC chromatography on silica plates using toluene/ethyl acetate 2:1 as the eluent, and extracted with ethylacetate. After solvent evaporation, compound **1** was obtained as a light ochre powder with a yield of 30%. IR (KBr): C≡N (2224 cm^{-1}), C=O (1700 cm^{-1}), C=N (1652 cm^{-1}), C=C (1611 cm^{-1}). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm = 7.73 (s, 1H, H4), 7.20 (d, J = 9 Hz, 1H, H5), 6.55 (dd, J = 9 Hz, J = 3 Hz, 1H, H6), 6.31 (d, J = 3 Hz, 1H, H8), 3.44 (q, J = 9 Hz, 4H, CH_2–N), 2.57 (t, J = 9 Hz, 2H, CH_2–CO), 1.74 (qn, 9 Hz, 2H, CH_2–CH_2–CO), 1.27 (broad signal, 24H, $(CH_2)_{12}$), 1.23 (q, J = 9 Hz, 6H, CH_3–CH_2–N), 0.90 (t, J = 9 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm = 185.91 (C=O), 156.32 (C9), 152.86 (C4), 150.58 (C2), 146.89 (C7), 130.43 (C5), 115.50 (C≡N), 109.27 (C10), 106.55 (C6), 97.17 (C8), 94.82 (C3), 45.25 (CH_2N), 39.07 (CH_2–CO), 31.93 (CH_2–CH_2–CO), 29.70, 29.66, 29.58, 29.46, 29.36, 29.32, 24.53, 22.69 $(CH_2)_{12}$, 14.12 (CH_3–CH_2–N), 12.39 (CH_3). Anal. calc. for $C_{30}H_{45}N_3O_2$: C, 75.11; H, 9.46; N, 8.76. Found: C, 74.89; H, 9.83; N, 8.64 MS: 480 (M + H^+); 497 (M + NH_4^+).

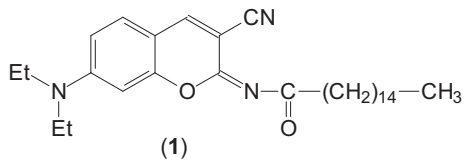
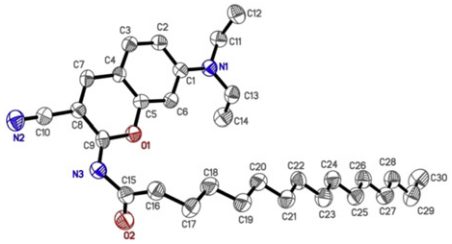


Fig. 1. Chemical structure of the iminocoumarin derivative **1**.

2.3. Crystallographic data for N-palmitoyl-3-cyano-7-diethylamino-2-iminocoumarin (*1*)

Data were collected at low temperature T = 193(2) K on a Bruker-AXS APEX II diffractometer with MoKα radiation (λ = 0.71073 Å) by using phi- and omega-scans. Semi-empirical absorption corrections were employed. The structure was solved by direct methods (SHELXS 97) [34] and all non-hydrogen atoms were refined anisotropically using the least-square method on F^2 [35].

Crystal data for **1**: $C_{30}H_{45}N_3O_2$ M = 479.69, monoclinic, P 2_1/c, a = 23.407(2) Å, b = 13.6876(11) Å, c = 9.0658(7) Å, α = γ = 90°, β = 98.918(5)°, V = 2869.5(4) $Å^3$, Z = 4. In all, 21,215 reflections (4684 independent, R_{int} = 0.1651) were collected. 320 Parameters, 0 restraints, R_1 [$I > 2\sigma(I)$] = 0.0617, $wR2$ [all data] = 0.1879, largest diff. peak and hole: 0.196 and −0.177 e $Å^{-3}$.



CCDC 854483 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or for the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033; e-mail: deposit@ccdc.cam.ac.uk).

2.4. Apparatus

Mass spectra were obtained at the "Service Commun de Spectrométrie de masse de l'Université Paul Sabatier de Toulouse" with a ThermoQuest spectrometer using DCI/NH_3 as the ionization mode. The ^{1}H NMR spectra were recorded on a Bruker AC300 spectrometer operating at 300.13 MHz. The microanalysis was obtained with a Perkin Elmer 2400 series II elemental analyzer in the "Service d'Analyse Chimique du Laboratoire de Chimie de Coordination de Toulouse". Spectroscopic measurements were conducted at 20 °C in a temperature-controlled cell. UV–vis absorption spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer. Corrected steady state fluorescence spectra on solutions and suspensions were recorded with a Photon Technology International (PTI) Quanta Master 1 spectrofluorometer. The fluorescence quantum yields (Φ) on solutions and suspensions were determined using the classical formula: $\Phi_x = (A_s \times F_x \times n_x^2 \times \Phi_s)/(A_x \times F_s \times n_s^2)$ where A is the absorbance at the excitation wavelength, F the area under the fluorescence curve