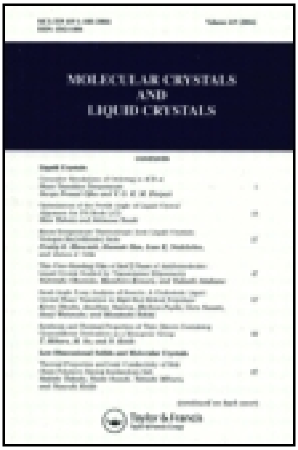

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Morphology Control of Organic Luminescent Microcrystals Grown in the Presence of Ionic and Nonionic PAMAM Dendrimers

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Morphology Control of Organic Luminescent Microcrystals Grown in the Presence of Ionic and Nonionic PAMAM Dendrimers

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Poly(amidoamine)dendrimers bearing different terminating groups were used as additives in the reprecipitation of a fluorescent nitrobenzoxadiazole (NBD) derivative and directed the formation of thin plates or needle-like microcrystals. The optical properties of the microcrystals were investigated.

Keywords: dendrimer; luminescence; microcrystals; reprecipitation method

INTRODUCTION

Because of the diversity of their chemical and physical properties, microcrystals of organic molecules promise interesting technological applications in the fields of photonics, nonlinear optics, and electronics [1]. However, very little is known yet about their preparation; a major requirement for practical use is the ability to grow microcrystals of controllable structure, size, and morphology.

Organic compounds often show thermal instability, so that the methods used to prepare ultrafine particles of metals and semiconductors cannot generally be applied. Vapor-deposition methods may only occasionally be used [2,3]. Alternatively, microcrystallization can be carried out in spatially restricted environments, such as those afforded by microemulsions [4], polymer matrices [5], and sol-gel glasses [6],

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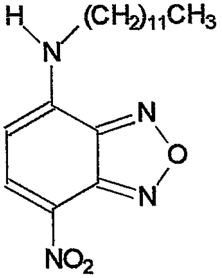
although the two first methods have not allowed until now homogeneous populations of microcrystals to be produced.

Besides the cited methods, a simple and still convenient way for the fabrication of organic microcrystals, called the reprecipitation method, has been recently developed by Nakanishi's team. The compound is dissolved in a hydrophilic organic solvent, and this concentrated solution is poured into a large volume of water, which acts as a nonsolvent for the compound. Precipitation occurs, which can lead to microcrystal dispersion [1,7]. It has been shown that different factors influence the size and morphology of the microcrystals. The first one is the concentration of the injected organic solution [8,9]. The lower it is, the smaller the size of the microcrystals obtained. A second critical factor is temperature, which directly influences the rate of crystallization [9,10]. The two factors can of course be combined [11]. Subsequent freeze and thaw cycles [12], microwave irradiation [13], sonication [14], and aging of the microcrystal suspension [15] can also affect the crystals' size. Besides, some additives, such as surfactants, can be placed into the medium [9,16]. They act as inhibitors, preventing crystal growth along one or many directions, and it is also possible that micelles form around the small particles, interfering with the aggregation process.

As far as we know, macromolecules have scarcely been used as additives in the reprecipitation method. However, some observations relative to the fields of biomineralization and inorganic chemistry suggest that they could play an interesting role. In fact, it is now widely acknowledged that anionic proteins direct crystallization of minerals in living creatures [17]. Naka and coworkers have also shown in vitro that the crystallization mode of $CaCO_3$ was modified in the presence of an anionic dendrimer [18]. These reports recently prompted us to investigate the influence of a poly(amidoamine) (PAMAM) dendrimer, terminated by 64 carboxylate groups, upon the reprecipitation process of an organic fluorescent dye [19]. Unexpectedly, a drastic acceleration of the microcrystallization rate was observed in the presence of the dendrimer. The question that arises now is whether the dendrimer charge has an influence upon the microcrystallization process. So, in the present paper, the effect of differently terminated dendrimers was compared. Anionic, cationic, and neutral dendrimers were successively used. We show here that the shape and size of dye microcrystals can be nicely tuned by the presence of these additives. The dye chosen belongs to the well-known nitrobenzoxadiazole (NBD) series [20,21]. It is very close to the dye that was used in our previous work, and which provided useful information on the different steps of the crystallization process. The difference is that compound **1**, used in the present work, bears 12 carbon atoms on the alkyl chain instead of 8. This little increase in chain length makes the change in the crystal shape more spectacular for **1**, according to the dendrimer used as additive.



(1)

EXPERIMENTAL

Materials

Compound **1** was prepared as previously described [22]. Absolute ethanol was from Carlo Erba Reagenti. High-pressure demineralized water (resistivity 16 MΩ cm) was used. Anionic and cationic PAMAM starburst dendrimers were purchased from Aldrich and used without further purification. The glucose-persubstituted dendrimer was synthesized in the laboratory [23]. Sodium acetate was from Prolabo, 1,6-hexanediamine and glucose were from Acros.

Apparatus

Ultra-violet visible (UV/vis) absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. The measurements were conducted at 25°C in a thermostatted cell. Corrected steady-state fluorescence spectra were registered on a Photon Technology International (PTI) Quanta Master 1 spectrofluorometer. The fluorescence quantum yields (Φ) 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, and n the refraction 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 [24].

The size and shape of the microcrystals were observed with a Zeiss MC80DX fluorescence microscope.

RESULTS AND DISCUSSION

Fluorescent derivative 4-*n*-dodecylamino-7-nitrobenz-2-oxa-l,3-diazole (**1**) was synthesized as previously described [22]. To obtain microcrystals, a concentrated solution of the dye in ethanol was prepared, then micro amounts of this solution were rapidly injected into water, which is a poor solvent for the dye. The dye concentration in the recrystallization medium was 2×10^{-5} M, a value almost 300 times higher than the solubility threshold. The proportion of ethanol in water was 2% v/v. Just after injection of the dye, the solution was yellow. Then, it discolored, and the organic compound precipitated and crystallized as red agglomerated, irregular microcrystals. This process was monitored by UV/vis absorption spectroscopy. Just after the dye injection, the UV/vis absorption spectrum displayed the characteristic features of dispersed amino-NBD dye, that is a π–π^* band around 336 nm and an intense charge-transfer band peaking at 464 nm. This spectrum underwent strong modifications during the reprecipitation process. The bands were shifted to the red and their intensity was markedly reduced. Completion was considered to be attained when no evolution of the UV/vis absorption spectrum was detected any longer. In the absence of additives, the whole reprecipitation process took about 17 h.

In a second experiment, anionic carboxylate-terminated dendrimer of the PAMAM family, generation 3.5 (G3.5), was placed into the aqueous crystallization medium at a concentration of 5×10^{-5} M, then the dye solution was injected. In this case, the crystallization process was achieved within 1 h. The suspension was pink, with a yellow glint, and particles were invisible to the naked eye. The UV/vis absorption spectrum showed a strong red-shift of the bands, accompanied by a moderate decrease in intensity. The size and shape of the microcrystals were analyzed by fluorescence microscopy; all the crystals were emitting above 580 nm. They were rectangular. The biggest ones measured $6 \times 3\,\mu$m, and were extremely thin (Fig. 1, left). Contrary to what was observed in water alone, the crystals grown in the presence of dendrimer were not agglomerated.

The anionic dendrimer was then replaced by a cationic PAMAM dendrimer, generation G4, bearing 64 primary amino groups at the periphery. In water, at neutral pH, all the amino groups are protonated [25]. The recrystallization experiment was repeated with **1** in these conditions. Results very similar to those observed with the

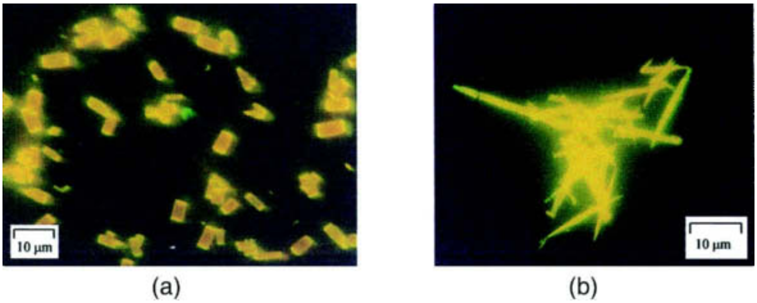


FIGURE 1 Fluorescence microscopy image of microcrystals of **1** grown in the presence of anionic G3.5 dendrimer (left) and in the presence of an equimolar mixture of G3.5 and G4 dendrimers (right). Total dye concentration: 2×10^{-5} M; total dendrimer concentration: 5×10^{-5} M.

anionic dendrimer were obtained with regard to the crystallization rate and the morphology of the microcrystals.

Because both anionic and cationic dendrimers had an influence upon the reprecipitation process, the influence of an equimolar mixture of these dendrimers (each at 2.5×10^{-5} M) was also considered. The crystallization rate was close to that obtained with only one of the dendrimers at 5×10^{-5} M. But, a drastic change in the crystals shape was noted. The presence of the dendrimer mixture induced the formation of thin needles, 10 to 20 µm long, with narrow extremities (Fig. 1, right).

Finally, this work was extended to a neutral dendrimer, carrying out reprecipitation in the same conditions as above. A PAMAM dendrimer persubstituted by 64 glucose groups (G4 glu), previously synthesized in the laboratory [23], was dissolved in water at a concentration of 5×10^{-5} M. Again, the crystallization process was drastically accelerated as compared with water, but it was significantly slower than with charged dendrimers. It took about 2 h to reach completion. In the presence of the glucose-persubstituted dendrimer, large needles appeared, very close to those obtained with the dendrimer mixture. Small amounts of rectangular crystals were also observed. Some of them resemble the microcrystals obtained with each of the charged dendrimer, others are smaller and probably result from the breaking of the needles.

Blanks were performed using aqueous solutions of sodium acetate at a concentration of 3.2×10^{-3} M and 1,6-hexanediamine at 1.6×10^{-3} M, which corresponds to the concentration of terminal groups in the dendrimer solutions. The crystallization rate was only slightly enhanced. In both cases, agglomerated microcrystals were produced. This indicates that the increase in ionic strength of the medium because of the presence of the terminal groups cannot fully account for the effect observed in the presence of charged dendrimers. Besides, the same experiment was performed in the presence of glucose (3.2×10^{-3} M), and reprecipitation was found to be unchanged compared to water alone. Consequently, the fact that the functional groups are borne by a macromolecule seems to be necessary for a strong effect to be observed upon reprecipitation.

The role played by the dendrimer seems to be quite complex. It seems to be different from that generally reported for small molecules that only inhibit the growth rate of one or many crystal faces and that induce a slowing down of the crystallization process. Herein, the presence of dendrimer leads to a strong acceleration, whatever the nature of the peripheral groups. Evidence was given previously that some interactions, probably of electrostatic nature, take place between NBD groups and carboxylate groups [19]. Moreover, it is known that the NBD groups have an affinity for the hydroxyl groups [20]. However, we still do not know to what extent these specific interactions affect the reprecipitation process. It must also be kept in mind that a small amount of anionic PAMAM dendrimer (17% in weight) was detected by elemental analysis in the dried microcrystals of the NBD dye used in our previous work [19]. Several hypotheses are presently explored. For example, a possibility is that the dendrimer surface offers sites of nucleation or increases the local concentration in dye. The dendrimer could also act as a surface stabilizer for the colloids of the NBD dye, preventing them from coalescing.

The optical properties of the different microcrystals in suspension in their native medium were investigated. The UV-visible absorption spectra were deconvoluted, as pictured in Fig. 2. They were composed of five bands. Bands A and C are quite close, respectively, from the π–π^* and charge-transfer bands of amino-NBD molecules dissolved in water [20]. By comparison, bands B and D are markedly red-shifted. It seems that the UV/vis absorption spectrum arises from distinct populations of molecules, which interact differently with their crystalline environment. From one load of microcrystal to another, these four bands underwent only slight shifts in wavelength (Table 1). In contrast, some differences were observed in their relative intensities. In particular, band C was particularly intense for the microcrystals grown with the dendrimer mixture and with the neutral dendrimer; that is, when needle-like microcrystals are present in the suspension. As for the wide band E, its nature is stilll unclear.

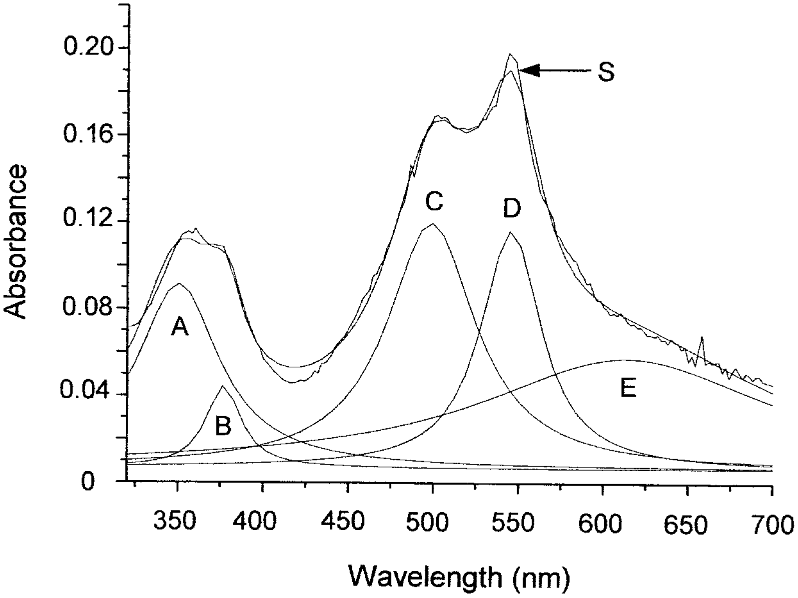


FIGURE 2 UV/vis absorption spectrum of microcrystals of **1** grown in the presence of G3.5 PAMAM dendrimer (top full line). Bands A to E were obtained by deconvolution, using five Lorentzian functions. Spectrum S is the sum of the calculated bands. Total dye concentration in the suspension: 2×10^{-5} M; Dendrimer concentration: 5×10^{-5} M.

With regard to the emission spectra recorded by exciting at 480 nm, the deconvolution showed the existence of two bands, centered at around 580 and 646 nm. This suggests the existence of at least two types of emissive molecules in the microcrystal suspension. It can be noted that the first band is close to the emission of dye molecules dissolved in water. It was relatively less intense for the rectangular microcrystals obtained in the presence of G3.5 dendrimer. The emission quantum yield was measured on the suspensions, by exciting at 482 nm. It was found to be around 1×10^{-3} in every case.

The optical properties of the different microcrystals are therefore quite close. Some authors have reported drastic variations in the optical properties when the microcrystal size was allowed to change in the submicrometer range [2,5,10,11,26]. The small differences observed here are probably better explained by the presence of imperfections at the microcrystal surface [5,27]. It must be noted that all the measurements were performed on microcrystal suspensions, so they give average values. More information is expected from near field spectroscopy[28], which considers only one microcrystal at a time.

TABLE 1 Spectroscopic Characteristics of the Microcrystals of **1** Grown in the Presence of the Various Dendrimers: Maximum Wavelength and Area of the Bands of the Deconvoluted Absorption and Emission Spectra ($\lambda_{ex} = 480$ nm)

	Absorption										Emission			
	A		B		C		D		E		A′		B′	
	λ, nm	Area, %	λ, nm	Area, %	λ, nm	Area, %	λ, nm	Area, %	λ, nm	Area, %	λ, nm	Area, %	λ, nm	Area, %
G3.5	350	17.4	376	3.3	498	25.3	545	16.5	613	37.5	580	46	652	54
G4	356	15.5	379	4.8	499	28.1	544	21.6	612	30.0	580	60	646	40
G3.5 + G4	354	14.4	376	4.5	501	41.8	544	14.5	604	24.8	580	65	645	35
G4 glu	355	15.3	376	4.2	504	53.7	543	18.1	678	8.7	579	65	645	35

CONCLUSION

This work confirms our hypothesis that macromolecules can be used as additives in the reprecipitation process of organic compounds. By using different dendrimers, the size and shape of the microcrystals can be modulated in a reproducible way. Quite homogeneous populations of microcrystals were obtained. Investigations are now underway to explain how the presence of dendrimers can induce the morphology change observed in the dye microcrystals. In particular, it would be interesting to know if the different crystal shapes observed correspond to different crystal structures, that is, whether polymorphs are formed. To our knowledge, the effect of polyelectrolytes upon the microcrystallization of organic compounds has not been thoroughly studied yet. The present work shows that it raises many questions of fundamental and practical interest.

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