PHOTOPHYSICS OF CYANINE DYES ON SURFACES: LASER-INDUCED PHOTOISOMER EMISSION OF 3,3′-DIALKYLTHIACARBOCYANINES ADSORBED ON MICROCRYSTALLINE CELLULOSE

Anabela S. OLIVEIRA[a1,*], Paulo ALMEIDA[b] and Luis Filipe VIEIRA FERREIRA[a2]

[a] *Centro de Química Física Molecular – Complexo Interdisciplinar, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal; e-mail: [1] pcd739@alfa.ist.utl.pt, [2] pcd748@alfa.ist.utl.pt*

[b] *Departamento de Química da Universidade da Beira Interior, Rua Marques d'Ávila e Bolama, 6200 Covilhã, Portugal; e-mail: palmeida@alfa.ubi.pt*

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The photophysics of three thiacarbocyanine dyes, 3,3′-dimethylthiacarbocyanine iodide (DMTCC), 3,3′-diethylthiacarbocyanine iodide (DETCC), and 3,3′-dipropylthiacarbocyanine iodide (DPTCC) was studied when adsorbed on microcrystalline cellulose in the concentration range from $5.0 \cdot 10^{-4}$ to 10.0 μmol g^{-1}. Using ground-state diffuse reflectance absorption technique, only H aggregate formation was detected for all the probes. The amount of aggregate formed depends on the hydration degree of the sample, always decreasing with sample dryness. The fluorescence quantum yields for all the adsorbed dyes are one order of magnitude higher than those observed in nonviscous solvents, being 0.98 for DMTCC, 0.96 for DETCC, and 0.63 for DPTCC. Laser-induced fluorescence emissions were recorded (using an intensified-charge-coupled-device detection system) as a function of the laser power, showing that for dry concentrated samples irradiated with high laser intensity, a second fluorescence emission band (bathochromically shifted relative to the monomer emission) was detected. This emission shows a supralinear dependence on laser power. The new emissions here detected arise from fluorescent photoisomers formed *via* singlet monomers, by a two-photon absorption process.

Key words: Cyanine dyes; H and J aggregates; Microcrystalline cellulose; Diffuse reflectance; Laser-induced luminescence; Photoisomers; Two-photon absorption processes.

In the last few years, we have been studying surface photochemical and photophysical processes of several probes, namely cyanine dyes, adsorbed on various opaque heterogeneous powdered supports, particularly microcrystalline cellulose[1–9].

These studies were possible due to the recent development of diffuse reflectance techniques and fluorescence emission experiments in front surface geometry combined with powerful laser excitation sources[1b,10–12].

The above-mentioned processes are extremely dependent on the interaction of the probes with solid supports, especially with the powdered microcrystalline cellulose matrix, which in some conditions may provide a particularly rigid environment strongly affecting the photophysics of the probes[1–6].

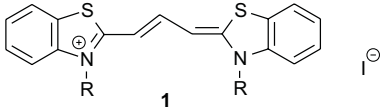
Microcrystalline cellulose is a very pure form of cellulose obtained by chemical treatment, where its amorphous regions are attacked and transformed into a highly crystalline residue[13]. It is constituted of glucose units joined by β-1,4-glycosidic links[13], the hydroxy groups of which have a strong affinity for polar protic (alcohols) and aprotic (*e.g.* acetonitrile, acetone) solvents or probes which can reach them[5]. If a solution of the probe in one of these swelling solvents is added to microcrystalline cellulose, the cellulose-to-cellulose hydrogen bonds are replaced by cellulose-to-solvent bonds and the matrix swells to a degree which depends on the solvent used for sample preparation[5]. Probes can then penetrate into submicroscopic pores of the solid substrate and remain strongly entrapped within the cellulose polymer chains after solvent removal[1–6].

Cyanine dyes are currently used as sensitizers in photography and photodynamic therapy, in dye lasers and optical storage of data[14,15]. Such a wide range of relevant applications supports and justifies the increasing interest in the study of their photophysical and photochemical properties in heterogeneous media[15b].

In recent works[1–3] we verified that the deposition of several cyanines within the microcrystalline cellulose chains[1a,2] using good swelling solvents, slows down the nonradiative deactivation processes that generally determine the cyanine solution photophysics[16], leading to an increase in the fluorescence quantum yields and lifetimes. As a result of entrapment into cellulose, 2,2′-cyanine, 2,2′-carbocyanine[1,3], oxacarbocyanines, and oxadicarbocyanine[2] exhibit fluorescence quantum yields in some cases more than one order of magnitude higher than those observed in ethanolic solutions. The same behaviour was observed by rigidifying the chemical structure of the cyanine dye molecule through its inclusion in rigid hosts such as micelles and Langmuir–Blodgett films[17] or using cyanines with a rigid chemical structure in solution[16b]. Ground-state diffuse-reflectance studies revealed that on cellulose samples the amount of aggregation is always greater in wet samples when compared with the dry ones[1–3].

In this paper, we extend our recent studies with 2,2′-cyanines[1,3] and several oxacyanines[2] adsorbed on microcrystalline cellulose to three 3,3′-dialkylthiacarbocyanines with the following structure.

Samples were compared using UV-VIS ground-state diffuse-reflectance measurements as well as steady-state and laser excitation luminescence in order to get a close insight into the influence of the size of alkyl substituents on their photophysics and on the trends of their photoisomer emission.



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1a, R = Me 3,3'-Dimethylthiacarbocyanine iodide (DMTCC)
1b, R = Et 3,3'-Diethylthiacarbocyanine iodide (DETCC)
1c, R = Pr 3,3'-Dipropylthiacarbocyanine iodide (DPTCC)

With these studies we hope to extend our knowledge on the nature of interactions of these cyanines with polymer chains and on the influence of the structure of the guest cyanine dye molecule in the immobilization process.

EXPERIMENTAL

Dyes Synthesis, Materials and Sample Preparation

3,3′-Dialkylthiacarbocyanine iodides were synthesized using the following procedure[18].

A mixture of equimolar proportions of 2-methylbenzothiazole and of the appropriate alkyl 4-methylbenzenesulfonate was heated at 100 °C for 1–3 h until an almost quantitative conversion into the quaternary salt was obtained (TLC check, Kieselgel 60F254, Merck). The resulting solid salt was condensed with triethyl orthoformate in boiling pyridine (10 ml of pyridine per mol of the salt); the boiling period ranging from 1 to 3 h (TLC check).

The dyes were isolated by addition of diethyl ether to this mixture, redissolving the precipitate in the minimum amount of hot methanol and converting it into the iodide by treatment with an excess of aqueous potassium iodide (1.4 g/10 ml). Generally, we used two volumes of the KI solution per one volume of the methanolic solution.

The products were crystallized from methanol or ethanol until TLC-pure dyes were obtained. All the dyes were characterized by ^{1}H NMR, ^{13}C NMR, IR, and UV-VIS spectra.

3,3′-Diethylthiacarbocyanine iodide and 3,3′-dipropylthiacarbocyanine iodide were also purchased from Aldrich in the highest purity available and, after checking its purity by UV-VIS spectroscopy and TLC, were used without further purification. The commercial cyanines produced the same results as those synthesized.

2-Methylbenzothiazole, methyl and ethyl 4-methylbenzenesulfonate, triethyl orthoformate, pyridine, and potassium iodide were purchased from Aldrich in the highest purity available. All the solvents used for synthesis were of analytical grade. Pyridine was dried before use. Propyl 4-methylbenzenesulfonate was prepared from 4-methylbenzene-

sulfonyl chloride and propan-1-ol in pyridine at 0 °C, and isolated as an oil by adding an excess of dilute hydrochloric acid. Extraction was done with diethyl ether, followed by drying, filtering and solvent evaporation, and distillation of the ester under reduced pressure[19].

Ethanol for sample preparation (Merck, Uvasol grade) was used as received. Molecular sieves (3 and 4 Å, 4–8 mesh, Aldrich, activated by slow heating up to 250 °C under vacuum) were used since very well dried ethanol was required for sample preparation.

Microcrystalline cellulose[13] (Fluka DSO) with 50 μm average particle size was dried under vacuum (*ca* 10^{-1} Pa) at 60 °C for at least 24 h before sample preparation.

The sample preparation method involved deposition of probes on the microcrystalline cellulose substrate by slow solvent evaporation and is described in detail in refs[1–6]. Ethanol was used as a solvent. The samples were analyzed under dry (totally moisture-free samples) or wet conditions (air-equilibrated samples, containing some moisture).

Ground-State Absorption Experiments in the UV-VIS Regions

Ground-state absorption studies of the 3,3′-dialkylthiacarbocyanines adsorbed on microcrystalline cellulose were performed using an OLIS 14 UV/VIS/NIR spectrophotometer with a diffuse reflectance attachment. The integrating sphere is 90 mm in diameter coated inside with a standard white coating. The standard apparatus was modified to include the possibility of using short-wave pass filters (Corion 550-S) which exclude luminescence of thiacarbocyanines from reaching the detector (Hamamatsu, Model R955). Further experimental details and description of the system calibration used to obtain accurate reflectance measurements are given in ref.[6]. Solution measurements were made using the same apparatus in the normal transmission mode.

The reflectance, R, from each sample was obtained by scanning the excitation monochromator in the adequate wavelength region; the remission function, $F(R)$, was calculated using the Kubelka–Munk equation, defined by Eq. (*1*):

$$F(R) = (1 - R)^2/(2R) = K/S \quad . \tag{1}$$

The Kubelka–Munk equation applies to optically thick samples, *i.e.*, those where any further increase in thickness does not affect the experimentally determined reflectance R. Symbols K and S stand for the absorption and scattering coefficients with dimensions $(\text{length})^{-1}$ (ref.[10]). For an ideal diffuser, where the radiation has the same intensity in all directions, $K = 2\varepsilon C$ (ε is the Naperian absorption coefficient, C is the concentration)[10]. Since the substrate usually absorbs at the excitation wavelength, λ_e,

$$F(R)_{\text{dye}} = F(R)_{\text{tot}} - F(R)_{\text{cell}} = \Sigma_i 2\varepsilon_i C_i/S \quad , \tag{2}$$

where $F(R)_{\text{cell}}$ is the blank obtained with a cell containing only microcrystalline cellulose. This equation predicts a linear relation for the remission function of the probe as a function of concentration (for a constant scattering coefficient) whenever the probe is in the form of a monomer.

Steady-State and Laser-Induced Fluorescence Emission Experiments

Corrected steady-state fluorescence emission spectra of the cyanines under study adsorbed on microcrystalline cellulose were obtained using a home-made fluorimeter specifically designed for front surface measurements, which has been previously described in detail[11].

On a solid substrate, the fluorescence intensity, I_F, is related to the concentration of the adsorbed dye through the reflectance at the excitation wavelength, according to Eq. (*3*):

$$I_F = GI_0(1 - R)f_{dye}\phi_F \ , \qquad (3)$$

where G is a constant which depends on the apparatus geometry, I_0 is the intensity of the excitation light at the excitation wavelength, R is the reflectance measured at the excitation wavelength, f_{dye} is the fraction of the excitation light absorbed by the dye at the excitation wavelength (defined as $f_{dye} = F(R)_{dye}/F(R)_{tot}$) and ϕ_F is the fluorescence quantum yield.

The fluorescence quantum yields, ϕ_F, of the thiocarbocyanines adsorbed on microcrystalline cellulose were determined by the method reported in ref.[6] for probes adsorbed in powdered solids. The methods uses Eq. (*4*):

$$\phi_F^u = \phi_F^s \frac{I_F^u}{I_F^s} \frac{(1 - R_s^{\lambda e}) f^s}{(1 - R_u^{\lambda e}) f^u} \frac{I_0^s(\lambda_e)}{I_0^u(\lambda_e)} \ , \qquad (4)$$

where u and s refer, respectively, to unknown and standard samples; $I_0^s(\lambda_e)/I_0^u(\lambda_e)$ is easily obtained provided that the energy profile of the system is accurately known. Rhodamine 101 was used as a reference compound ($\phi_F^s = 1.0$).

Fluorescence emission spectra of powdered samples were also measured in our laser-induced time-resolved emission system. The excitation source is the 337.1 nm pulse of a nitrogen laser (model PL2300, Photon Technology Instruments) that gives 1.6 mJ/pulse and has a pulse width of 600 ps. The light emitted from the powdered samples was measured in a front-surface arrangement by a gated intensified-charge-coupled-device (ICCD, model Instaspec V, Oriel). Neutral density filters were placed between the laser and the sample to reduce tha laser excitation intensity that hits the sample (enabling the use of different excitation intensities) and also in front of the ICCD camera to prevent intense emission light for saturating it.

RESULTS AND DISCUSSION

Ground-State Absorption Spectra of Thiacarbocyanines Adsorbed on Microcrystalline Cellulose

Figure 1 displays ground-state absorption spectra for diferent loadings of DMTCC adsorbed from ethanol on microcrystalline cellulose. Figure 1a shows the variation of the percentage reflectance as a function of the wavelength. Figures 1b and 1c show the correspondent remission functions normalized at the absorption maximum of the dye. Figures 1a and 1b present

the results for air-equilibrated samples, containing some moisture, while Fig. 1c refers to dry samples.

For low concentrations of the DMTCC deposited on microcrystalline cellulose, the dye absorbs from 400 to 650 nm, with the maximum at 564 nm and a vibrational shoulder at 532 nm, independently of the sample dryness. In spite of a bathochromic shift of 5 to 7 nm, this spectrum resembles very much the one reported previously for this dye in ethanol[16d] and for

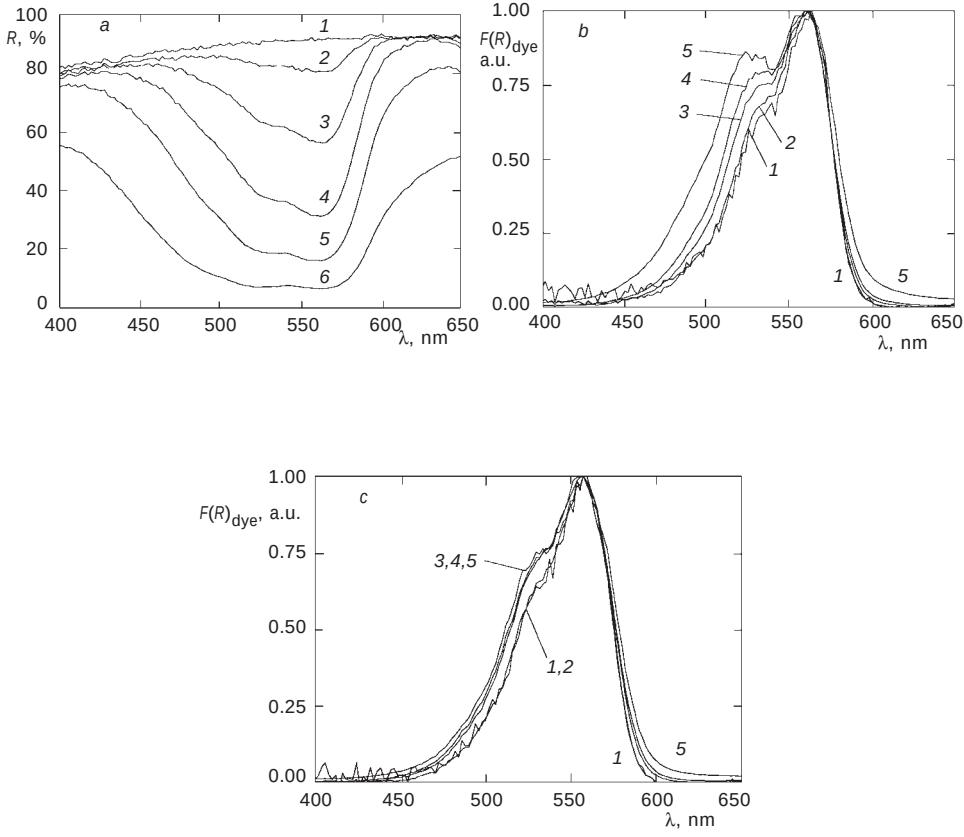

FIG. 1

Reflectance spectra (a) and remission function values (normalized at the maximum of the monomer) (b) and (c) of 3,3′-dimethylthiacarbocyanine iodide adsorbed on microcrystalline cellulose. a Air-equilibrated samples: *1* 0, *2* $2.3 \cdot 10^{-8}$, *3* $1.0 \cdot 10^{-7}$, *4* $5.8 \cdot 10^{-7}$, *5* $1.0 \cdot 10^{-6}$, *6* $4.7 \cdot 10^{-6}$ mol of dye per gram of the substrate; b air-equilibrated samples: *1* $2.3 \cdot 10^{-8}$, *2* $1.0 \cdot 10^{-7}$, *3* $5.8 \cdot 10^{-7}$, *4* $1.0 \cdot 10^{-6}$, *5* $4.7 \cdot 10^{-6}$ mol of dye per gram of the substrate; c dry samples showing monomers of H aggregates, concentrations corresponding to b

DETCC in alcohols (λ_{max} = 557 nm in methanol[16b]; λ_{max} = 559 nm in ethanol[20a] with a vibrational shoulder at 525 nm) or in very dilute aqueous solutions[20b]. This similarity makes it possible to interpret this absorption band as the characteristic absorption of the monomer molecules adsorbed on the microcrystalline cellulose substrate. As shown in Fig. 1, the increase in the DMTCC loading on microcrystalline cellulose above 0.1 μmol g^{-1} clearly produces a neat increase in the absorption intensity at 532 nm, relative to the monomer absorption maximum. A similar behaviour was already observed for DETCC in water[20b] or adsorbed on TiO_2 (ref.[20c]). The new band is due to the presence of H aggregates (sandwich dimers)[21]. As described for other cyanine dyes adsorbed on microcrystalline cellulose, the dye aggregation is extremely dependent on the moisture content of the sample, being strongly favoured by its presence[1–3]. As can be seen in Fig. 1, absorption spectra are similar for wet (Figs 1a and 1b) and dry (Fig. 1c) samples but for the same dye loading, dry samples always show smaller amounts of aggregates than the wet samples.

We also studied ground-state absorption of DETCC and DPTCC on microcrystalline cellulose and we verified that both of them behave similarly to the methyl derivative (see above). On cellulose, for the range of concentrations under study, there is no evidence for the formation of 3,3′-dialkylthiacarbocyanine H aggregates larger than dimers, contrary to what was observed on the TiO_2 surface[20c] or in water[20b] where the H aggregate formation process progresses beyond aggregates with two species.

Steady-State Fluorescence Spectra of Thiacarbocyanines Adsorbed on Microcrystalline Cellulose

Figure 2 shows the corrected steady-state fluorescence emission spectra of increasing loadings of DMTCC adsorbed on microcrystalline cellulose. The experiments were performed at 20 ± 1 °C, irradiating the sample with a xenon lamp at 500 nm.

These results were obtained with dry cellulose samples, but they are very similar to those obtained with wet samples in the overall concentration range. When adsorbed on microcrystalline cellulose, DMTCC fluoresces intensely in contrast to the generally weak fluorescence of carbocyanines in nonviscous solvents[16]. The fluorescence intensity increases with the dye loading on the substrate up to 0.2 μmol g^{-1}. For higher concentrations, the fluorescence emission intensity decreases. A comparison of curves *4* and *5* in Fig. 2 clearly shows an extinction process starting at about 0.2–0.4 μmol g^{-1}, which is the concentration range where H aggregates start to be formed. In

fact, it is the presence of aggregates that promotes the observed fluorescence extinction process: as their concentration grows, the fraction of the incident light that is absorbed by the emissive monomers decreases.

The changes in the fluorescence intensity of DMTCC on microcrystalline cellulose with a concentration parameter clearly illustrate the above-explained behaviour; they are presented in Fig. 3.

The fluorescence emission dependence on the concentration of the adsorbed dye was also investigated for DETCC and DPTCC deposited on cellulose; the experiments were performed under identical conditions. The obtained results are very similar to those with DMTCC, presenting the same fluorescence intensity dependence with increasing of the dye loading. In spite of the fact that DETCC fluoresces with approximately the same intensity as DMTCC, we found that for DPTCC, fluorescence intensity is clearly smaller. The variation in the fluorescence intensity of DETCC and DPTCC on microcrystalline cellulose as a function of concentration parameter is also plotted in Fig. 3.

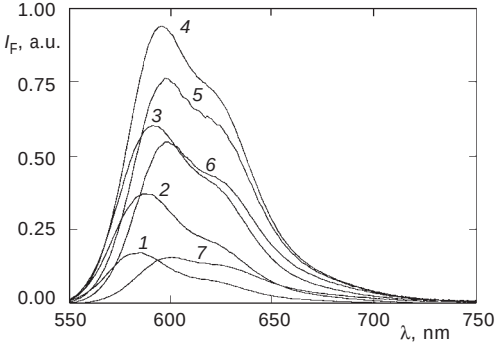

FIG. 2
Corrected steady-state fluorescence emission spectra of 3,3′-dimethylthiacarbocyanine iodide adsorbed on microcrystalline cellulose (dry samples excited at 500 nm). The concentrations: *1* $5.0 \cdot 10^{-9}$, *2* $2.3 \cdot 10^{-8}$, *3* $1.0 \cdot 10^{-7}$, *4* $5.8 \cdot 10^{-7}$, *5* $1.0 \cdot 10^{-6}$, *6* $2.3 \cdot 10^{-6}$, *7* $4.7 \cdot 10^{-6}$ mol of dye per gram of the substrate

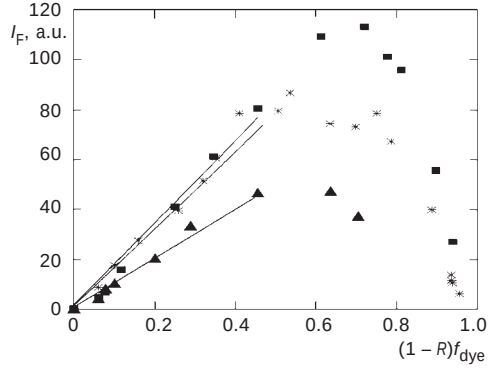

FIG. 3
Fluorescence intensity of 3,3′-dimethylthiacarbocyanine iodide (■), 3,3′-diethylthiacarbocyanine iodide (✳), and 3,3′-dipropylthiacarbocyanine iodide (▲) adsorbed on microcrystalline cellulose, excited at 500 nm and measured as the total area under the corrected emission spectra as a function of $(1 - R)f_{dye}$

Fluorescence Quantum Yield of Thiacarbocyanines Adsorbed on Microcrystalline Cellulose

Using the method previously described in ref.[6], we determined the fluorescence quantum yield, ϕ_F, for the 3,3′-dialkylthiacarbocyanines on microcrystalline cellulose. The obtained results are shown in Fig. 3. Values of 0.98 ± 0.02, 0.96 ± 0.02, and 0.62 ± 0.02 were found, respectively, for the fluorescence quantum yield of the methyl, ethyl, and propyl derivatives of 3,3′-dialkylthiacarbocyanine on cellulose. The quantum yields refer to the monomer emission and are determined for low loadings. Wet, dry or argon--purged samples gave the same ϕ_F within the experimental error. These values show an increase in the fluorescence quantum yield for these adsorbed dyes of about one order of magnitude higher than that determined for the same dyes in ethanolic solutions, where ϕ_F never exceeds 0.02–0.05 (refs[16b,20a]).

Although DMTCC and DETCC reach approximately a value of the quantum yield, $\phi_F \cong 1$, DPTCC shows a considerably lower quantum yield. This behaviour is attributed to the influence of the volume of the alkyl substituents at the 3 and 3′ positions of the thiacarbocyanine structure; the results make clear its important role on the fluorescence emission properties of these thiacarbocyanines, even when dyes are adsorbed on substrates that can induce an increase in the rigidity of the chromophoric structures, as in the case of the adsorption on microcrystalline cellulose. If the 3 and 3′ substituents are small, as it is the case of methyl and ethyl, the inclusion of the dye in the cellulose matrix imports the dye molecule high rigidity and planarity, which secures a high fluorescence quantum yield. The nonradiative deactivation processes, usually dominated by the photoisomerization process which prevails in nonviscous media, are almost completely elimininated, as indicates the nearly unit fluorescence quantum yields. This also shows that DMTCC and DETCC on microcrystalline cellulose are adsorbed mainly as the all-*trans* conformer, considered to be responsible for the fluorescence emission of this dye[16b,22]. However, the presence of a slightly bulkier substituent, such as propyl, already promotes a stereochemical hindrance which leads to a distortion of the planar, strongly emissive form of thiacarbocyanine derivatives. The observed decrease in the fluorescence quantum yield of the DPTCC shows that in this case, inclusion in a rigid medium such as microcrystalline cellulose, is not sufficient to prevent the large departure from planarity of the chromophoric chain, induced by the presence of bulky substituents on the nitrogen atoms of terminal heterocyclic rings.

It is important to compare these results with those obtained with an analogue of thiacarbocyanine, structurally rigidified by the inclusion of the polymethine chain in fused heterocyclic rings which link both the nitrogen atoms, thus inhibiting the rotation about the conjugated chain. The quantum yield of the rigid analogue in methanol is only 0.52 (ref.[16b]). Carbocyanines structurally rigidified usually exhibit high fluorescence quantum yields which depend on the increase in rigidity and planarity. From this comparison it can be seen that the large increase in the fluorescence quantum yield for the cyanine dyes on cellulose is related to the decrease in mobility of the polymethine chains within microcrystalline cellulose. In the specific case of the 3,3′-dialkylthiacarbocyanine dyes, it can be concluded that the decrease in the participation of nonradiative deactivation mechanisms is more efficient by inclusion of the nonrigidified dye within the microcrystalline cellulose substrate than by structural rigidification of the compound. In fact, the value of 0.52 exhibited by the rigidified thiacarbocyanine in methanol shows that its structure still experiences a high degree of torsion which is larger than that in the 3,3′-dipropyl derivative within microcrystalline cellulose.

Laser-Induced Fluorescence Spectra of Thiacarbocyanines Adsorbed on Microcrystalline Cellulose

Figure 4 presents the corrected laser-induced fluorescence emission spectra for increasing loadings of DMTCC (dry samples) on microcrystalline cellulose. The spectra were produced using a pulsed N_2 laser as excitation source (337 nm and 1.6 mJ per pulse, 600 ps pulse width).

For dilute samples down to 0.1 μmol g^{-1}, a single emission band was recorded, which coincides with the typical emission of the monomeric form of the dye adsorbed on cellulose, obtained previously with a conventional xenon excitation lamp (*cf.* Fig. 2 and curves *1–3* of Fig. 4a). However, for more concentrated samples, a second emission band, not detected for steady-state fluorescence measurements, appears at wavelengths higher than the monomer emission wavelengths. This second emission, which peaks at 630–632 nm, is especially intense for 1.0 μmol g^{-1} and decreases considerably for higher concentrations, being produced only if high excitation intensities per unit of area are used (full laser power beam of 1.6 mJ, focused to a spot with an area of 2–3 mm^2). For wet samples, the second emission is considerably smaller.

We further investigated the laser-induced fluorescence of different loadings of DETCC and DPTCC adsorbed on microcrystalline cellulose; a similar

dual fluorescence emission was observed. In parallel with the above reported fluorescence quantum yield results for the monomeric form of these dyes, DMTCC and DETCC, have approximately the same dual fluorescence emission intensity, while for DPTCC it is considerably smaller. This suggests that the volume of the alkyl group also affects the yield of the second emission.

The dual fluorescence emissions are similar to those already reported for other cyanines on cellulose, *viz*. for 2,2′-carbocyanine[1a] and for the 3,3′-diethyloxadicarbocyanine[2], their origin being the emissive photoisomers. These isomers can be already formed in the ground state (as is the case of the 3,3′-diethyloxadicarbocyanine)[2] and/or be formed under high intensity laser excitation (like for the 2,2′-carbocyanine)[1a]. Although a careful analysis of the ground-state absorption and steady-state emission results from the three 3,3′-dialkylthiacarbocyanines on microcrystalline cellulose did not reveal the presence of ground-state conformer and/or photoisomer emission band. Its existence cannot be disregarded, since for the DETCC in solution, both the all-*trans* isomer absorbing at 560 nm (ref.[23]) and the *cis* metastable photoisomer absorbing at 545 nm (refs[16c,24]) were reported. For the wet samples, the observation of a considerably lower photoisomer emission is associated with the existence of a high concentration of aggregated species which determines the decrease in the amount of free monomers which can undergo photoisomerization.

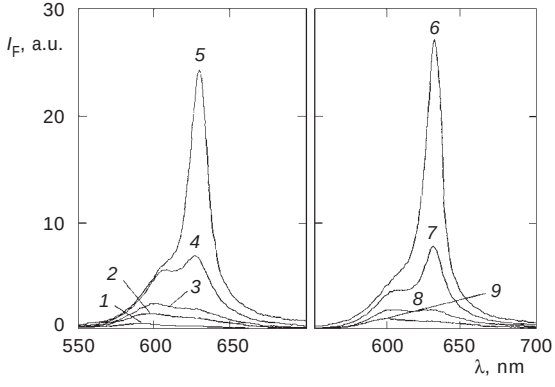

FIG. 4

Corrected fluorescence emission spectra of 3,3′-dimethylthiacarbocyanine iodide adsorbed on microcrystalline cellulose, obtained after pulsed laser excitation (337 nm, 1.6 mJ per pulse) and recorded with an ICCD. The concentrations: *1* $5.0 \cdot 10^{-9}$, *2* $5.0 \cdot 10^{-8}$, *3* $1.0 \cdot 10^{-7}$, *4* $2.5 \cdot 10^{-7}$, *5* $7.5 \cdot 10^{-7}$, *6* $1.0 \cdot 10^{-6}$, *7* $2.5 \cdot 10^{-6}$, *8* $5.0 \cdot 10^{-6}$, *9* $10.0 \cdot 10^{-6}$ mol of dye per gram of the substrate

The dependence of the intensity of both fluorescence emission bands with the intensity of the excitation source for DMTCC, DETCC and DPTCC adsorbed on microcrystalline cellulose was further studied. Figure 5 presents the laser-induced corrected emission spectra of 0.5 μmol g^{-1} of DMTCC on microcrystalline cellulose obtained after several laser excitation intensities. These results are similar to those obtained for the other two dialkylthiacarbocyanines on cellulose in the same concentration range. For dilute samples, which simply show monomer emission, the spectra are independent of the laser intensity. In this case, the results were identical to those obtained with these samples using a xenon lamp or a pulsed laser as excitation sources. On the contrary, for more concentrated samples, where the presence of both emission bands is revealed for full laser excitation intensity (see Fig. 5), a progressive decrease in the laser intensity leads to a parallel decrease in the intensity of the second emission band. For sufficiently low laser intensities, fluorescence emission spectra are similar to those obtained with stationary excitation. The changes in the photoisomer emission intensity as function of the laser excitation intensity were quantified. In the inset of Fig. 5, for 0.5 μmol g^{-1} of DMTCC on microcrystalline cellulose, the intensity of the photoisomer emission, I_{N^*}, was plotted as

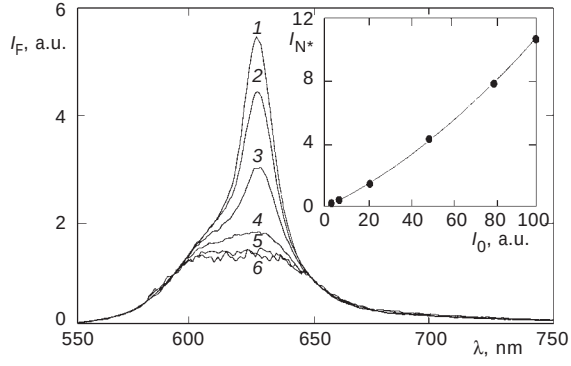

FIG. 5

Corrected fluorescence emission spectra of 3,3′-dimethylthiacarbocyanine iodide adsorbed on microcrystalline cellulose, obtained after pulsed laser excitation (337 nm, 1.6 mJ per pulse) and recorded with an ICCD. The spectra are normalized at the maximum of the monomer emission. The concentration of the sample is $5.0 \cdot 10^{-7}$ mol of dye per gram of the substrate. *1* 100% is the maximum laser excitation energy, *i.e.*, 1.6 mJ per pulse; *2* 79.8%, *3* 49.2%, *4* 20.8%, *5* 5.9%, *6* 2.2%. Inset: Intensity of the photoisomer emission as function of the laser excitation intensity for $5.0 \cdot 10^{-7}$ mol of 3,3′-dimethylthiacarbocyanine iodide per gram of microcrystalline cellulose

function of the laser excitation intensity, I_0. I_{N^*} was measured through subtraction of the monomer emission intensity from the total laser-induced emission intensity at the maximum photoisomer emission wavelength. A supralinear dependence on laser excitation intensity was observed. For DETCC and DPTCC, the same nonlinear dependence of the photoisomer emission on the excitation intensity was found. This result is consistent with photoisomer emission arising from isomers formed after and/or before laser excitation. If the isomers are formed after laser excitation, they are originated in a two-photon absorption process, the first photon being needed to create the isomer and the second one to excite it; if they are already formed before laser excitation, a single photon is needed for the photoisomer emission to occur.

CONCLUSIONS

For the three 3,3′-dialkylthiacarbocyanine dyes adsorbed on microcrystalline cellulose (alkyl = methyl, ethyl, propyl), H dimers are the only aggregates formed with the increase in dye loading. As observed previously for other cyanines on this natural polymer, the decrease in the humidity content of the samples reduces the amount of the H aggregates.

DMTCC and DETCC exhibit high fluorescence quantum yields on cellulose, showing that the inclusion of these molecules within the polymer chains by the use of ethanol leads to an almost complete elimination of the nonradiative deactivation mechanisms.

The presence of a bulky substituent such as propyl in the 3 and 3′ positions of the thiacarbocyanine promotes a clear increase in the nonradiative deactivation processes, inhibiting the molecule to become entrapped within the polymer chains, and in this way, to have a planar structure.

Fluorescence emission studies of wet and dry cellulose samples of the three thiacarbocyanines using a xenon lamp as an excitation source produced only monomer emission in the whole range of concentrations under study. However, under intense laser excitation, dry samples exhibit a second emission band located at higher wavelengths than the normal monomer emission. This second emission is very intense and yields a supralinear dependence on excitation intensity. In fact, after intense laser excitation, photoisomerization of non-aggregated monomers occurs and they may reach a higher electronic state by absorption of a second photon. This excited photoisomer is responsible for the above-mentioned second emission. With wet samples, aggreagate formation greatly inhibits the photoisomerization process.

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