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Spectroscopic characterization of red perylimide/surfactant nanocomposites

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Abstract Novel photoluminescent materials formed by some selected surfactants, metal derivatives of bis(2-ethylhexyl) sulfosuccinate ($M(AOT)_n$; M = Na^+, Co^{2+}, Er^{3+} and Yb^{3+}), bis(2-ethylhexyl) amine (BEEA), bis(2-ethylhexy1) phosphoric acid (HDEHP) and a 1:1 BEEA/HDEHP mixture, doped with the red perylimide (ROT-300) have been prepared, and their optical properties have been tested by absorption spectroscopy and steady state and time-resolved fluorescence. Experimental results show spectral shifts of the typical ROT-300 absorption and fluorescence bands with respect to that in apolar solvent medium. Data analysis leads consistently to attribute this feature mainly to the freezing of the diffusive movement of the dye molecules confined in the nanodomains of the surfactant liquid crystals, whilst minor effects can be due to interaction with the surfactant polar groups. Potentialities of these novel luminescent nanostructured composites as dye lasers, optical amplifiers and solar concentrators have been highlighted. In particular, under optical pumping using a pulse laser, amplified spontaneous fluorescence emission of the ROT-300/HDEHP system above an excitation energy threshold value of about 725 mJ cm^{-2} was observed.

Introduction

Surfactant-based systems are characterized by the coexistence of locally ordered polar and apolar domains of nanometric size, separated by a large interface surface. This structural feature allows for the solubilization of a large variety of hydrophilic, hydrophobic and amphiphilic species. The basic mechanism consists of the confinement of the solute, with suitable orientation, within the spatially separated regions mentioned above. Moreover, specific solute–surfactant interactions are likely to occur in many cases, and effects on the physico-chemical properties of the solubilized species due to their specific surroundings and orientational/positional order can be thus expected. This feature makes the surfactant-based systems of considerable technological interest as solubilizing and reaction media for specialized applications [1, 2].

In the ambit of our investigations in this field, we explored the possibility of modulating the optical properties of a well-known fluorescent dye, red perylimide (ROT 300, see Fig. 1 for molecular structure), by confining this compound in some representative surfactant media. It is worth to note that ROT-300 is characterized by a high heat and chemical stability, strong luminosity and a fluorescence quantum yield close to 1. Given these properties, ROT-300 has been included in several liquid and solid matrices to produce active lasing media or solar concentrators [3, 4].

However, to the best of our knowledge, no attempt to investigate its optical properties when confined in surfactant-based systems has been performed.

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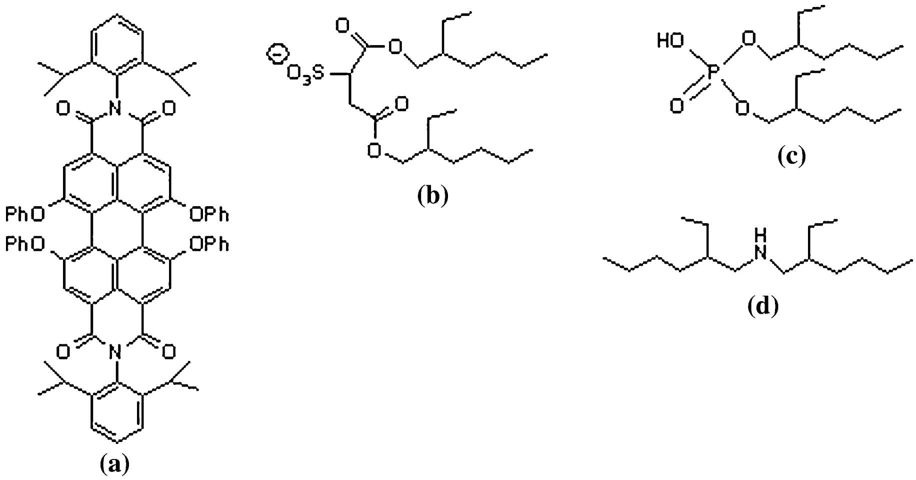

Fig. 1 Molecular structures of **a** ROT-300, **b** bis(2-ethylhexyl) sulfosuccinate (AOT) anion (for positive counterion see text), **c** bis(2-ethylhexy1) phosphoric acid (HDEHP) and **d** bis (2-ethylhexyl) amine (BEEA)

In this article, we report on the optical properties of ROT-300 solubilized in metal derivatives of bis(2-ethylhexyl) sulfosuccinate (M(AOT)$_n$; M = Na$^+$, Co^{2+}, Er^{3+}, Yb^{3+}), bis(2-ethylhexyl) amine (BEEA), bis(2-ethylhexy1) phosphoric acid (HDEHP), and a 1:1 HDEHP/BEEA mixture. The molecular structures are displayed in Fig. 1. These surfactants, characterized by the same apolar moiety and different polar groups, have been selected to work out the possible role played by the head group on the electronic properties of the solute confined within the micelle. Further, the replacement of the sodium counterion of the well-known surfactant NaAOT with transition metal and lanthanides could confer tailored functionalities to the resulting micellar aggregates and liquid crystalline phases such as enhanced luminescence and selective entrapment.

Starting from microemulsions in apolar solvents (typically *n*-heptane) containing the dye solubilized in the reverse micelles of the surfactant, a composite material with liquid crystalline features can be easily obtained by simple evaporation of the organic solvent. In many cases, hexagonal phases have been obtained and characterized [5].

Thus, keeping in mind that surfactant-based systems generate easy processable and low-cost materials, any structural information on the type and number of intermolecular interactions between the dye and the surfactant can be exploited in view of potential applications of the composites in devices for light concentration, solar energy conversion, lighting and dye lasing.

Materials and methods

Materials

Sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT, Sigma, 99%) has been dried for several days and stored under vacuum before use. Bis(2-ethylhexyl) amine (BEEA, Sigma 97%), bis(2-ethylhexyl) phosphoric acid (HDEHP, Sigma 97%) and *n*-heptane (Aldrich, 99%) were used as received. ROT-300 (BASF, Ludwigshafen) was a generous gift of the Prof. M. Catellani.

Methods

The preparation procedure of M(AOT)$_n$ derivatives (M = Co^{2+}, Er^{3+}, Yb^{3+}) from NaAOT has been reported elsewhere [6].

The ROT-300/M(AOT)$_n$/*n*-heptane solutions were prepared by adding, to a weighted amount of surfactant, a $0.6*10^{-4}$ M ROT-300/*n*-heptane stock solution, to obtain a 0.1 M surfactant concentration.

The ROT-300/M(AOT)$_n$ composites have been obtained by gentle evaporation at room temperature of the volatile component (*n*-heptane) of drops of these solutions deposited on quartz suprasil windows. Coloured and highly transparent films of selected thickness and surface shape can be obtained by controlling the evaporation process.

The other samples have been obtained by dissolving weighted amounts of ROT-300 in pure HDEHP, BEEA and in a 1:1 BEEA/HDEHP mixture. The resulting materials appear highly viscous but homogeneous liquid phases which can be easily confined in appropriate devices to exploit their photoluminescence.

For spectroscopic analysis, liquid samples were contained in standard 1 mm pathlength quartz cuvettes (1 cm pathlength for steady state and time-resolved fluorescence spectra), whilst solid samples were deposited as transparent films on quartz suprasil windows.

UV–Vis spectra were recorded in the range 200–1000 nm with a Perkin Elmer (Lambda 900) UV–Vis spectrometer with a spectral resolution of 0.5 nm.

Steady-state fluorescence measurements were made at 25 °C using a Horiba Jobin–Yvon spectrofluorimeter (Fluoromax-4) with excitation at 455 nm, using a 90°

geometry for liquid samples and a 60° reflection geometry for solid samples.

Time-correlated single photon counting (TCSPC) measurements were carried out using the Fluoromax-4 apparatus equipped with a single photon counting controller (FluoroHub, Horiba Jobin–Yvon) and a pulsed diode light source (Nanoled, repetition rate 1 MHz, pulse duration 1.27 ns, 368 nm), collecting the radiation at 586 nm. Data fitting was accomplished using least-squares methods with DAS6 Fluorescence Decay Analysis Software.

Steady-state fluorescence measurements as a function of the excitation energy were made using as light source the second harmonic of a 1064 nm pulsed Nd:YAG laser (Quanta System) with a pulse duration of 5 ns and a repetition rate of 10 Hz. The emission has been collected with a Hamamatsu Mini Spectrometer C10083CA TM-VIS/NIR-CCD coupled with an optical fibre Thorlabs QMMJ-55-UVVIS-25/125-3-1). The set up has a bandpass of 2 nm. Excitation laser light has been removed using a proper notch filter (Edmund Optics).

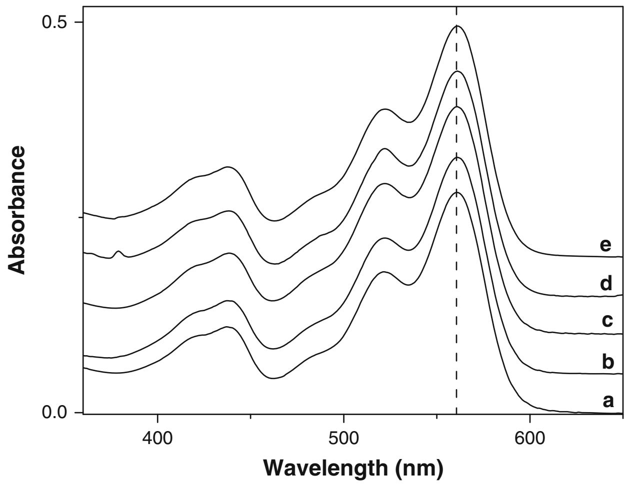

Fig. 2 Absorption spectra of 0.6*10^{-4} M ROT-300 in pure *n*-heptane, (*a*) and in various 0.1 M M(AOT)$_n$/*n*-heptane micellar solutions: Na(AOT)/*n*-heptane, (*b*); Co(AOT)$_2$/*n*-heptane, (*c*); Er(AOT)$_3$/*n*-heptane, (*d*) and Yb(AOT)$_3$/*n*-heptane, (*e*)

Results and discussion

UV–Vis spectra

The absorption spectrum of 0.6*10^{-4} M ROT-300 in pure *n*-heptane is reported in Fig. 2. It shows two main features due to the S_0–S_1 and S_0–S_2 electronic transitions occurring in 460–600 and 380–460 nm spectral ranges, respectively. The band shape of the S_0–S_1 transition reflects the skeletal movements of the perylene [4].

The position (λ_{max}) and the molar extinction coefficient (ε_s) at the maximum of these two bands are reported in Table 1a. These values are in good agreement with those reported in the literature for ROT-300 in an analogous organic apolar solvent (cyclohexane: S_0–S_1: 47100 M^{-1} cm^{-1}, 556.0 nm; S_0–S_2: 16900 M^{-1} cm^{-1}, 439.0 nm) [4].

Figure 2 shows the absorption spectra of ROT-300 dissolved in the 0.1 M surfactant solutions. No detectable band shift of these spectra with respect to that of ROT-300

Table 1 Position (λ_{max}) and molar extinction coefficient (ε_s) at the band maximum of ROT-300 in the (a) micellar solutions, (b) surfactant-based composites and (c) HDEHP, BEEA and BEEA/HDEHP systems for the S_0–S_1 and S_0–S_2 transitions

Sample	S_0–S_1		S_0–S_2	
	ε_s (M^{-1} cm^{-1})	λ_{max} (nm)	ε_s (M^{-1} cm^{-1})	λ_{max} (nm)
a				
ROT-300/*n*-heptane	47000	560.8	18333	437.2
ROT-300/NaAOT/*n*-heptane	46167	561.1	15500	437.9
ROT-300/Co(AOT)$_2$/*n*-heptane	48667	560.9	17333	438.8
ROT-300/Er(AOT)$_3$/*n*-heptane	47833	561.0	18000	438.2
ROT-300/Yb(AOT)$_3$/*n*-heptane	49167	561.3	19167	437.4
b				
ROT-300/NaAOT	–	571.0	–	440.5
ROT-300/Co(AOT)$_2$	–	571.1	–	441.0
ROT-300/Er(AOT)$_3$	–	571.2	–	442.2
ROT-300/Yb(AOT)$_3$	–	571.6	–	440.6
c				
ROT-300/HDEHP	–	567.6	–	438.8
ROT-300/BEEA	–	565.7	–	440.3
ROT-300/BEEA/HDEHP	–	569.0	–	439.3

in pure *n*-heptane is observed, with only some changes in the band intensity. We are inclined to interpret this behaviour hypothesizing that, given the hydrophobic character of ROT-300 molecule, it is always preferentially dissolved in the apolar bulk medium.

Figure 3 shows the absorption spectra of the corresponding composite materials obtained from the solutions described above by evaporation of *n*-heptane. When ROT-300 is confined in such environments, a red shift of the absorption band is observed. This is shown in Fig. 3a and b where the spectra, normalized to the same height of the more intense peak, are collected. For comparison purpose, also the normalized spectrum of ROT-300 in pure *n*-heptane is shown. The positions at the maximum of the two typical bands are collected in Table 1b.

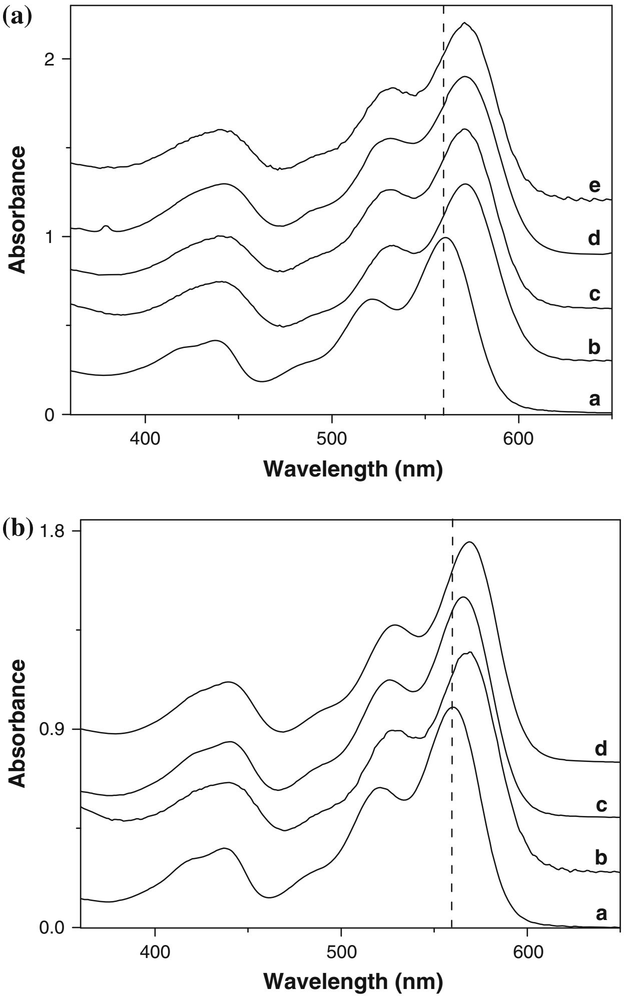

Fig. 3 **a** Normalized absorption spectrum of ROT-300 in pure *n*-heptane (*a*), and in composite materials obtained from NaAOT (*b*), $Co(AOT)_2$ (*c*), $Er(AOT)_3$ (*d*) and $Yb(AOT)_3$ (*e*), respectively. **b** Normalized absorption spectrum of ROT-300 in pure *n*-heptane (*a*), HDEHP (*b*), BEEA (*c*) and a 1:1 mixture of HDEHP + BEEA (*d*)

It is also worth to note that, in the cases of the ROT-300/$M(AOT)_n$ composites, the confinement in the surfactant matrix involves a nearly constant red shift of about 10 nm of the S_0–S_1 electronic transition and of about 4 nm of the S_0–S_2. The absence of specific effects due to the nature of the counterion indicates that the ROT-300 is preferentially localized in the apolar domains of the typical two-dimensional hexagonal structure of these surfactants [5, 7].

Thus, the occurrence of the red shift could be reasonably attributed to the changes involved on passing from the liquid to the solid state consisting in the freezing of the translational degrees of freedom of the ROT-300 due to its entrapment in the surfactant liquid crystals, i.e. the so-called rigidochromism effect.

The entries of Table 1c refer to the cases of the ROT-300 confined in HDEHP, BEEA and 1:1 mixture of BEEA/HDEHP. In such samples, a system-specific red shift can be observed. This behaviour can be attributed to some additional effect due to the acidic or basic nature of HDEHP and BEEA, respectively [8, 9].

Fluorescence spectra

The fluorescence spectra of ROT-300 in *n*-heptane and in the surfactant/*n*-heptane solutions are shown in Fig. 4. The fluorescence band shows a mirror image relationship with respect to the S_0–S_1 electronic transition. Moreover, it can be observed that the position of the fluorescence band is negligibly affected by the presence of surfactant reverse micelles. This finding, consistently with the analysis of the absorption spectra, confirms that ROT-300 is mainly dispersed in the apolar medium.

In Fig. 5a, we compare the fluorescence spectra of ROT-300 in *n*-heptane with those in the $M(AOT)_n$ composites,

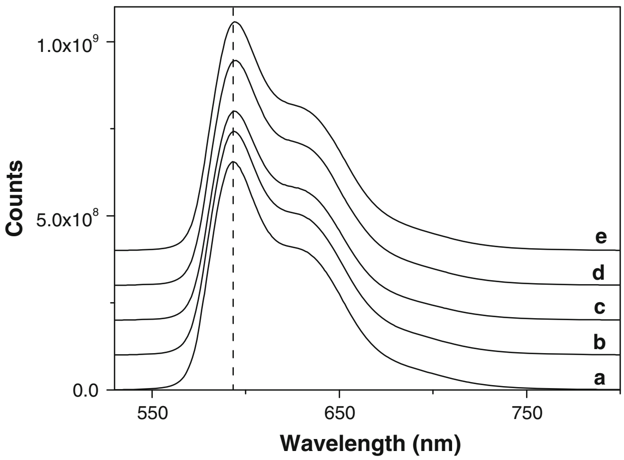

Fig. 4 Fluorescence spectra of ROT-300 in *n*-heptane (*a*), Na(AOT)/*n*-heptane (*b*), $Co(AOT)_2$/*n*-heptane (*c*), $Er(AOT)_3$/*n*-heptane (*d*) and $Yb(AOT)_3$/*n*-heptane (*e*) solutions

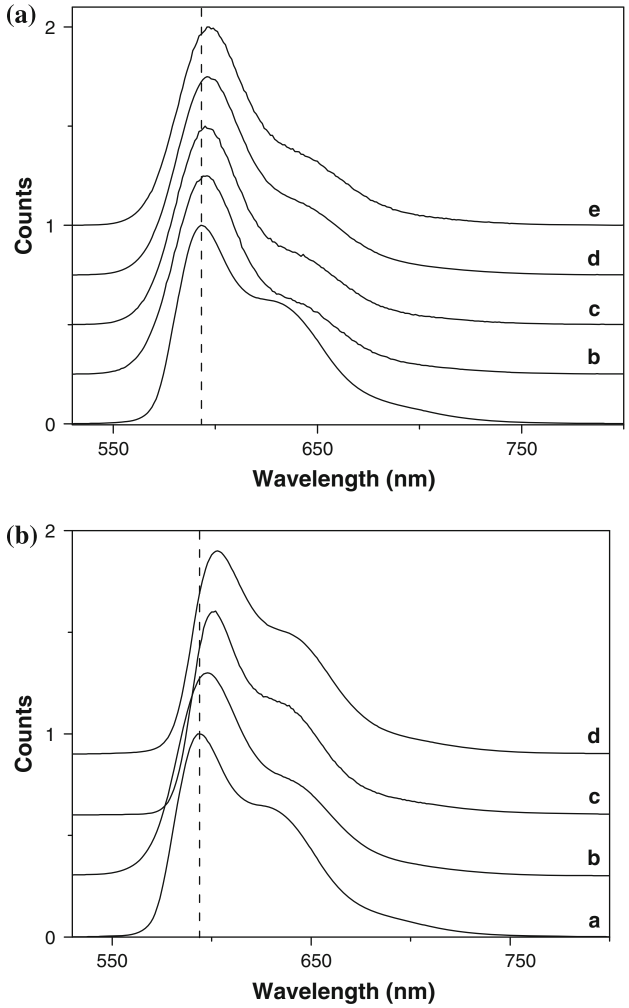

Fig. 5 **a** Fluorescence spectra of ROT-300 in *n*-heptane (*a*) and in the composites obtained from Na(AOT) (*b*), Co(AOT)$_2$ (*c*), Er(AOT)$_3$ (*d*) and Yb(AOT)$_3$ (*e*) respectively. **b** Fluorescence spectra of ROT-300 in *n*-heptane (*a*) and in pure HDEHP (*b*), pure BEEA (*c*) and a 1:1 mixture of HDEHP + BEEA (*d*)

whilst in Fig. 5b with those in HDEHP, BEEA and a 1:1 mixture of HDEHP + BEEA.

In the cases of the ROT-300/M(AOT)$_n$ composites, the most striking effect is the depression of the shoulder occurring at about 620 nm accompanied by a red shift of about 3 nm of the main peak attributable to the rigidochromism effect. When considering the fluorescence response of these samples, the absence of specific effects due to the nature of the counterion indicates that the ROT-300 is localized in the apolar domains of the surfactant matrix. Moreover, the depression of the shoulder implies that the confinement in the surfactant matrix should involve the opening of a nonradiative disexcitation channel of the dye.

As to the cases of the ROT-300 confined in HDEHP, BEEA and 1:1 mixture of HDEHP + BEEA, it can be noted a system-specific red shift in the 4–9 nm range without depression of the 620 nm shoulder.

Further insights on the environment sensed by ROT-300 were searched by monitoring the time-resolved fluorescence spectra. We have found that these spectra can be consistently described in terms of two exponential decay functions where, according to literature, the faster component—characterized by a quite constant relaxation time of about 0.2 ns—can be attributed to the sample scattering [10–12].

The second decay, attributable to the excited ROT-300, gives the relaxation times collected in Table 2.

The relaxation time of ROT-300 in pure *n*-heptane (6.94 ns) compares favourably with the literature value in cyclohexane (7.55 ns) [4].

Moreover, it is negligibly affected by the presence of the reverse micelles. Conversely, some system specific changes, generally leading to lower lifetimes, are observed in the M(AOT)$_n$ composites and in HDEHP, BEEA and 1:1 mixture of HDEHP + BEEA. Finally, the existence of a single decay time points towards nearly homogeneous binding sites.

Amplified spontaneous emission experiments and results

A preliminary scrutiny of the potential application of the investigated systems as active laser media has been carried out. In particular, the fluorescence spectra of the ROT-300/HDEHP system under optical pumping at 532 nm at increasing excitation energy have been collected (Fig. 6).

As highlighted by Fig. 7, by plotting the fluorescence intensity at the band maximum (598 nm) as a function of the excitation energy, it is of interest to note a dramatic slope change, concomitant with an emission spectrum narrowing, above an excitation threshold of 725 ± 10 mJ cm^{-2} revealing the occurrence of amplified spontaneous emission

Table 2 Fluorescence lifetime τ (ns) for ROT-300 in surfactant-based systems

Sample	τ (ns)
ROT 300/*n*-heptane	6.94 ± 0.02
ROT 300/NaAOT/*n*-heptane	6.81 ± 0.02
ROT 300/Co(AOT)$_2$/*n*-heptane	6.72 ± 0.02
ROT 300/Er(AOT)$_3$/*n*-heptane	6.83 ± 0.02
ROT 300/Yb(AOT)$_3$/*n*-heptane	6.86 ± 0.02
ROT 300/NaAOT	6.15 ± 0.02
ROT 300/Co(AOT)$_2$	1.27 ± 0.01
ROT 300/Er(AOT)$_3$	4.40 ± 0.01
ROT 300/Yb(AOT)$_3$	6.96 ± 0.01
ROT 300/HDEHP	6.40 ± 0.02
ROT 300/BEEA	3.90 ± 0.12
ROT 300/HDEHP/BEEA 1:1	5.10 ± 0.01

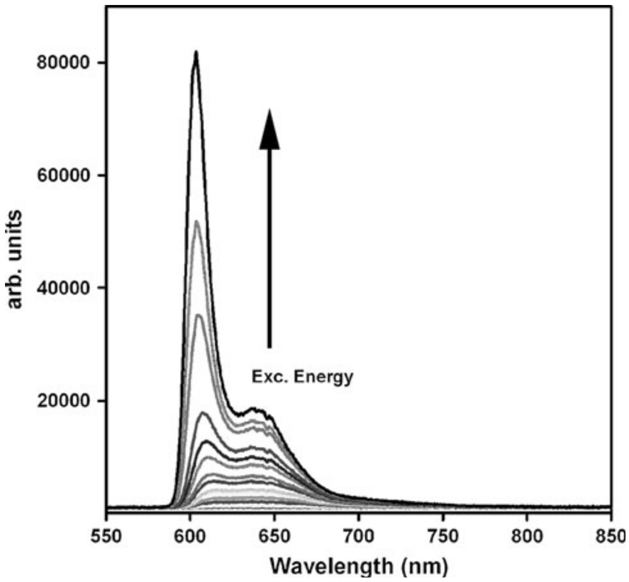

Fig. 6 Fluorescence spectra of the ROT-300/HDEHP system at increasing excitation energy

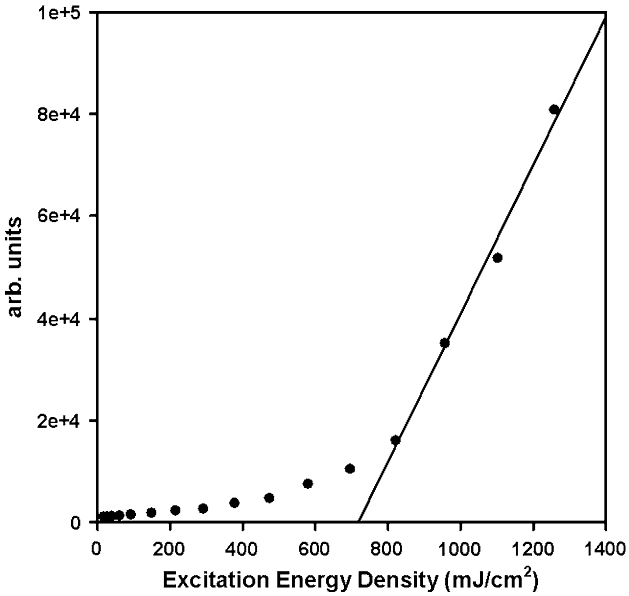

Fig. 7 Fluorescence intensity at the band maximum as a function of the excitation energy

(ASE), which makes this system an interesting candidate as active laser medium.

Conclusions

A detailed study of the optical properties by absorption spectroscopy and fluorescence of the red perylimide (ROT-300) dye in some surfactant-based systems formed by some metal derivatives of bis(2-ethylhexyl) sulfosuccinate, bis(2-ethylhexyl) amine and bis(2-ethylhexy1) phosphoric acid has been carried out.

Whilst negligible spectral effects are observed when ROT-300 is solubilized in the reverse micelle solutions with respect to pure *n*-heptane, significant red shifts of the band positions are observed when ROT-300 is confined in the pure surfactant matrix, namely in the composite liquid crystalline material obtained after slow evaporation of the organic solvent. This behaviour has been attributed to the freezing of the translational degrees of freedom of dye molecules, whilst some effects could arise from the interactions with the polar head group, especially in the case of acid or basic surfactants. The dye molecules preserve their optical properties in the matrix, and, in particular, they show optical gain, as seen through ASE measurements [13]. Given that the surfactant-based systems are able to organize the spatial distribution of the dye in their nanodomains and the resulting material can be easily processed forming transparent films on appropriate support, it can be proposed that they are potentially interesting media for designing novel luminescent materials as dye lasers, optical amplifiers or solar concentrators [14].

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