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LETTERS

Energy Transfer in Dye-Doped Mesostructured Composites

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Energy transfer between the organic laser dyes coumarin 485 and pyrromethene 567 was investigated in mesostructured silica/block copolymer thin films. The 2-D hexagonal mesostructured silica thin films were made using acidic sol−gel synthesis with poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), ($EO_{20}PO_{70}EO_{20}$) as the structure-directing agent. The dyes were doped into the film synthesis solutions so that they underwent co-assembly with the silica and block copolymer. At a very low concentration of acceptor, one acceptor molecule for every 20 donor molecules, the donor's emission was drastically quenched, suggesting efficient energy transfer. Investigations into amplified spontaneous emission revealed that the donor/acceptor system resulted in full gain narrowing at significantly lower concentrations than systems without a donor.

Introduction

Photosynthetic organisms provide the best examples of efficient energy transfer through highly efficient light-harvesting complexes that channel energy to a reaction center.[1] However, several other systems have been developed that successfully use energy transfer. Recently, energy transfer has been investigated for the production of optical devices such as organic light-emitting diodes (OLEDs) and for extending the wavelength emission range of polymers and sol−gel optical materials.[2−5] Employing energy transfer has made more efficient devices. For example, significantly lower lasing thresholds are obtained in polymeric systems by using energy transfer to reduce self-absorption at the emission wavelength while maintaining a strong absorption at the pump wavelength.[2,3] An interesting approach to investigate energy transfer has been used in biphasic micellular systems, in which the dye is confined to one phase or the other to increase the efficiency of energy transfer.[6] From the viewpoint of composite materials as host matrixes that possess hydrophobic/hydrophilic domains, the study of energy transfer in composite materials offers similar potential interest.

Among composite materials, mesostructured silica/block copolymer composites are emerging as a class of materials that are well-suited as host media for optical dye species.[7] Mesoscopic integration of the block-copolymer and silica components yields structures that combine the mechanical strength of the inorganic framework with the desirable processing and solubility properties of the organic polymer. Further, these materials offer new opportunities for controlling the local environments of occluded species since they possess adjustable inorganic/organic compositions and mesoscopic structures with a variety of symmetries. These multiple environments permit mesostructured materials to be readily doped with organometallic complexes,[8] semiconducting nanocrystals,[9,10] semiconducting polymers,[11] and dyes.[12,13] Extensive synthetic work enables processing into optically important structures such as thin films,[14−17] fibers,[18] monoliths,[19,20] hierarchical ordering,[21] and micropatterns produced by soft lithography.[13,22,23] Not only do these materials offer a wide range of dopants and morphologies but also they have demonstrated their utility by controlling energy transfer in conjugated polymers,[11] reducing aggregation in organic

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dyes,[13,24] forming lasing materials,[13,24−26] and successfully working as chemical sensors.[23,27]

The host system chosen for this study is mesostructured silica/block copolymer composite thin films. A poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer ($EO_{20}PO_{70}EO_{20,}$) was used as the structure-directing agent. This system has been shown previously to form well-organized mesostructured materials over a wide range of synthetic conditions. Here, we report the study of energy transfer and amplified spontaneous emission (ASE) in mesostructured silica thin films doped with coumarin 485 as a donor dye and pyrromethene 567 as the acceptor dye.

Experimental Section

Sample Preparation. In a typical preparation, 5.02 g of tetraethyl orthosilicate (TEOS) [Aldrich] was hydrolyzed by reaction with 1.8 g of water (pH ~ 2.0 with HCl) until the solution was homogeneous. Separately, 1.37 g of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), ($EO_{20}PO_{70}EO_{20}$) [P123 Pluronic, BASF USA, Mount Olive, NJ] was dissolved in 10 g of THF. The solutions were mixed and 27.7 mg of 7-(dimethylamino)-4-(trifluoromethyl)coumarin (coumarin 485) [Exciton] and 0−6.6 mg of boron [3-ethyl-5-[1-(4-ethyl-3,5-dimethyl-2H-pyrrol-2-ylidene-κ*N*)ethyl]-2,4-dimethyl-1-H-pyrrolato-κ*N*]difluoro-, (T-4)- (9CI) (pyrromethene 567) [Exciton] were added and stirred for an additional hour prior to use. The final molar composition TEOS:THF:H_2O:HCl:P123:coumarin 485:pyrromethene 567 was 1:5.8:4.2:0.00078:0.009:0.0044:0−0.00089. Thin films were prepared by dip coating at 10 cm/min, resulting in ~900-nm-thick films on freshly cleaned glass slides over an area of 1.5 × 2.5 cm^2. Alternatively, mesostructured silica films were prepared on freshly cleaned glass slides by spin coating at 3000 rpm for 20 s. All films were allowed to dry overnight before further characterization. For ASE measurements, where optimized waveguiding is critical to thresholds, silicon wafers with 2D hexagonal mesoporous thin films on their surface were used as supports. The mesoporous films were prepared by spin-coating solutions of similar composition as described previously, only without the addition of the laser dye. After drying for 24 h, the films were calcined at 400 °C for 4 h.

Characterization Measurements. X-ray diffraction (XRD) patterns were obtained on a Scintag PAD X^2 diffractometer employing Cu Kα radiation. Transmission electron microscopy (TEM) was performed using a JEOL 2000 FX microscope and the samples were prepared by scraping off the films after calcination at 400 °C for 4 h. UV−Vis absorption measurements were made using a Shimadzu UV-1610 spectrometer. Photoluminescence spectra were recorded in a 45° setup and excited with the 351 nm line from a Spectra-Physics 2065 argon ion laser. ASE measurements were performed by excitation at a 90° angle using light from the third harmonic of a Q-switched Nd:YAG laser (355 nm, about 10 ns pulse width, 10 Hz repetition rate). Regions of the laser beam were selected by using an adjustable slit and focused by a rectangular lens onto the sample (typically to an area of 8 mm × 0.4 mm). Incident laser power was measured with a power meter (Molectron). Light emerging from the end of the waveguides was collected by a set of two lenses and focused on the entrance slit of a 0.25 m monochromator (150 groves/mm). For signal detection, a liquid-nitrogen-cooled CCD detector was used. Quantum efficiency measurements were made using an integrating sphere configuration similarly to that described previously.[28] The excitation source was the 351 nm line of an argon laser, which was separated from the other UV lines using a prism.

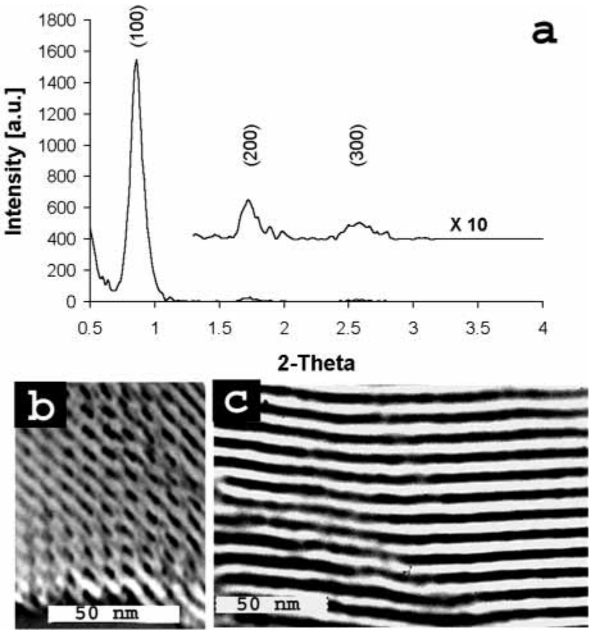

Figure 1. (a) X-ray diffraction pattern of mesostuctured silica thin films. (b) TEM micrograph of the characteristic hexagonal structure in a calcined sample. (c) TEM micrograph of the channel structure in a calcined sample.

Results and Discussion

It has been previously demonstrated that 2D hexagonal mesostructured silica films prepared using block copolymers and dip-coating give optically clear films with highly aligned mesostructural ordering.[15] This is demonstrated in our films by X-ray diffraction (Figure 1a). The X-ray diffraction pattern shows only *h*00 reflections, indicative of hexagonally arranged channels aligned parallel to the substrate plane, as commonly found for mesostructured silica films prepared by P123 block-copolymer templating under weakly acidic conditions (SBA-15 type materials). To confirm the ordering, TEMs were made using calcined samples. Figures 1b and 1c, respectively, show typical TEM micrographs of both the characteristic hexagonal structure and channels. Although long-range mesostructural ordering might be interesting for certain applications, in our case the organic−inorganic separation, which defines the mesostructure itself, is more important. The biphasic nature on the nanometer scale provides chemically different environments for the dyes. In other words, the chemical surrounding of the occluded species can be tuned, depending on its preference for either of the two nanoseparated phases. Furthermore, it has been demonstrated that dyes that preferentially segregate into the organic phase are less prone to aggregation and therefore have higher quantum efficiencies.[24]

An important consideration in energy transfer systems is the choice of donors and acceptors. The donor should have a stronger absorption at the pump wavelength, and its emission should overlap the absorption of the acceptor. In Figure 2, the emission from coumarin 485 is shown (maximum 515 nm) with the absorption band of pyrromethene 567 (maximum ~ 520 nm). The shaded section in the figure clearly shows the significant overlap that indicates an overlap in energy gaps for the transitions of the emitting coumarin 485 and the absorbing pyrromethene 567, thus permitting efficient energy transfer from the coumarin 485 to the pyrromethene 567.

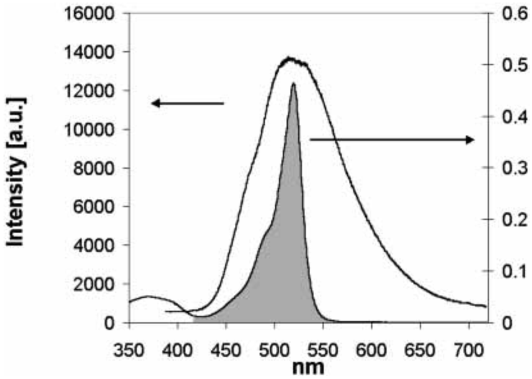

Figure 2. Emission spectra for coumarin 485 doped mesostructured silica thin films and absorption spectrum of pyrromethene 567 doped mesostructured thin films. The region where spectral overlap occurs is shaded.

The efficiency of the energy transfer was investigated by measuring the photoluminescence (PL) spectra in a series of samples with different ratios of donor to acceptor. Typical spectra for the donor/acceptor series are presented in Figure 3a. Emission from mesostructured silica thin films doped with 1 wt % coumarin 485 is broad with its maximum at 515 nm. As pyrromethene 567 (acceptor) is added to the synthesis while maintaining a constant 1 wt % coumarin 485, coumarin's (donor) emission is drastically quenched. At low concentrations, 0.06 wt % pyrromethene 567 [1 pyrromethene for every 20 coumarin molecules (1:20)], virtually no emission from the coumarin is evident. A very weak luminescence from coumarin is observed as a small rise starting at around 450 and continuing to 500 nm. However, a strong emission from the pyrromethene 567 with its maximum at 545 nm is present. As the concentration of acceptor is increased to 0.11 wt % (1:10 by molecules), the donor emission reduces to merely a slight rise before the intense pyrromethene 567. Finally, at 0.24 wt % pyrromethene 567 (1:5 by molecules), no donor emission is observable while the acceptor's emission is readily seen. Furthermore, no wavelength shifts occur for pyrromethene's emission peak as its concentration is increased, or compared to its emission without the presence of donor. The strong quenching at low concentrations of acceptor indicates that the energy transfer is highly efficient.

To better quantify the energy transfer, the total efficiency of the system was investigated by measuring the quantum efficiencies of the films using an integrating sphere technique.[28] The quantum efficiency for the mesostructured silica thin film with 1 wt % coumarin 485 donor is 48%. Upon doping with a small amount of pyrromethene 567, 1:20, the quantum efficiency for the multiple dye composite jumps to 74%. As the concentration of pyrromethene 567 is increased to 1:10, the quantum efficiency drops to 58% and finally falls to 35% for 1:5. This observation supports our photoluminescence data that energy transfer is very efficient. The decrease in overall quantum efficiency as the pyrromethene concentration is increased can be explained by an increase in self-absorption in combination with dye aggregation, which probably occurs at these high concentrations. For example, in the 1:5 sample the total weight percent of dye is ~1.24 wt %. Another way to investigate the overall effect of the donor can best be seen by comparing the emission of pyrromethene 567 in films with and without coumarin 485. The maximum emission intensity is more than five times greater for all systems where the coumarin 485 in present, Figure 3b.

The ability of the energy transfer to enhance stimulated emission was probed by studying the possibility of amplified spontaneous emission (ASE). The phenomenon of ASE can be explained as a result of very high-gain amplification of the spontaneously emitted light by stimulated emission. The typical signature for ASE is a gain narrowing effect of the emission peak width when the pump power exceeds a certain threshold.[29] When the energy transfer samples are pumped with the third harmonic of an Nd:YAG laser (355 nm) in a 90° geometry, at low pump intensities a typical broad photoluminescence spectrum is observed full width half-maximum (fwhm) 50 nm, Figure 4a. As the pump power is increased, the pyrromethene 567 emission begins to narrow until a fully gain-narrowed spectrum fwhm ~ 8 to 10 nm is observed (Figure 4b). Thresholds for the series of donor/acceptors are 100 kW/cm^2 for 1:5, 127 kW/cm^2 for 1:10, and 175 kW/cm^2 for 1:20. In all samples, a small fluorescence background was observed around 520 to 540 nm. Investigations into photostabilities showed the samples to be stable for a few thousand pulses at low pulse rates slightly above threshold, but no efforts have been made at optimization.[24]

For comparison purposes, stimulated emission was investigated in samples with no donor present, only pyrromethene 567, and for pure donor, coumarin, systems. The only sample that underwent full gain narrowing was the 0.24 wt % pyrromethene 567 sample (1:5 blank) and its threshold was over twice as high in comparison to the donor/acceptor system. For the 1 wt % coumarin (donor), 0.06 wt % and 0.11 wt % pyrromethene 567 samples no gain narrowing was observed at the highest measured pump intensities, ~ 350 kW/cm^2.

Conclusions

We have demonstrated energy transfer between coumarin 485 and pyrromethene 567 in mesostructured silica thin films. Even at low concentrations, one pyrromethene for every twenty coumarins, the dominant emission peak is from the pyrromethene. As the concentration of pyrromethene increases, the luminescence from the coumarin progresses from partially to

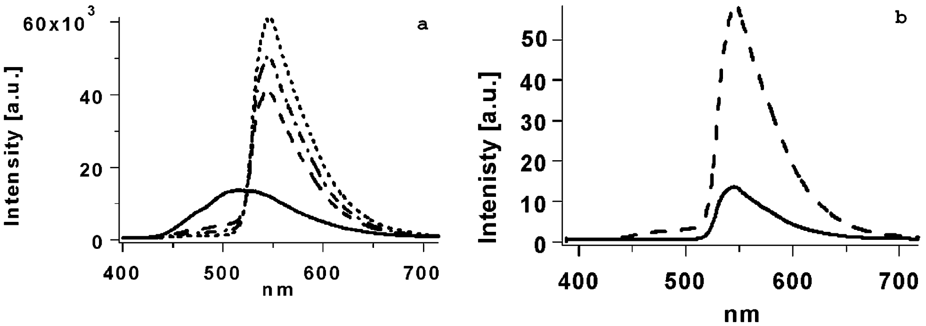

Figure 3. (a) Photoluminescence spectra for coumarin (—), pyrromethene:coumarin 1:20(– –), 1:10(– · –), 1:5(···), in mesostructured silica thin films. (b) Photoluminescence spectra for 0.24 wt % Pyromethene 567-doped mesostructured silica films with 1 wt % coumarin 485 (– –) and without coumarin 485(—).

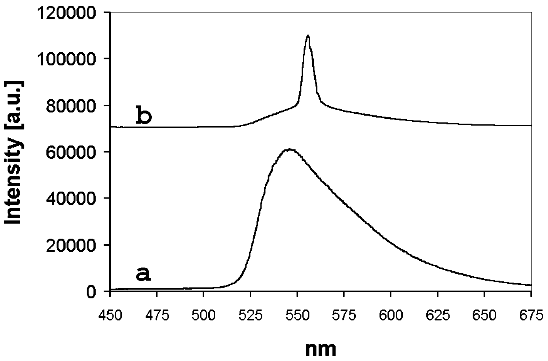

Figure 4. Photoluminescence spectrum for 1:5 sample (a) below ASE threshold, and (b) above ASE threshold.

fully quenched while the peak position of the pyrromethene remains constant. Investigations into amplified spontaneous emission showed moderate thresholds and significant reductions in thresholds compared to systems where no donor was present. Energy transfer within mesostructured materials can be used to enhance the luminescence and lasing wavelength range for a single excitation wavelength. This makes it possible to use emissive dyes with lower solubility, and to create more efficient luminescent sensors.

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References and Notes

(1) Orrit, M. *Science* **1999**, *285*, 349−350.

(2) Berggren, M.; Dodabalapur, A.; Slusher, R. E.; Bao, Z. *Nature* **1997**, *389*, 466−469.

(3) Gupta, R.; Stevenson, M.; Dogariu, A.; McGehee, M. D.; Park, J. Y.; Srdanov, V.; Heeger, A. J.; Wang, H. *Appl. Physics Lett.* **1998**, *73*, 3492−3494.

(4) Law, H. K.; Tou, T. Y.; Ng, S. W. *Appl. Opt.* **1998**, *37*, 5694−5696.

(5) Baldo, M. A.; Obrien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151−154.

(6) Kenney-Wallace, G. A.; Flint, J. H.; Wallace, S. C. *Chem. Phys. Lett.* **1945**, *32*, 71−75.

(7) Scott, B. J.; Wirnsberger, G.; Stucky, G. D. *Chem. Mater.* **2001**, *13*, 3140−3150.

(8) Ogawa, M.; Nakamura, T.; Mori, J.; Kuroda, K. *J. Phys. Chem. B* **2000**, *104*, 8554−8556.

(9) Dag, O.; Ozin, G. A.; Yang, H.; Reber, C.; Bussiere, G. *Adv. Mater.* **1999**, *11*, 474−480, 429.

(10) Srdanov, V. I.; Alxneit, I.; Stucky, G. D.; Reaves, C. M.; DenBaars, S. P. *J. Phys. Chem. B* **1998**, *102*, 3341−3344.

(11) Nguyen, T. Q.; Wu, J. J.; Doan, V.; Schwartz, B. J.; Tolbert, S. H. *Science* **2000**, *288*, 652−656.

(12) Marlow, F.; McGehee, M. D.; Zhao, D. Y.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1999**, *11*, 632−636, 596.

(13) Yang, P. D.; Wirnsberger, G.; Huang, H. C.; Cordero, S. R.; McGehee, M. D.; Scott, B.; Deng, T.; Whitesides, G. M.; Chmelka, B. F.; Buratto, S. K.; Stucky, G. D. *Science* **2000**, *287*, 465−467.

(14) Yang, H.; Coombs, N.; Sokolov, I.; Ozin, G. A. *Nature* **1996**, *381*, 589−592.

(15) Zhao, D. Y.; Yang, P. D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Chem. Commun.* **1998**, 2499−2500.

(16) Ogawa, M. *Chem. Commun.* **1996**, 1149−1150.

(17) Brinker, C. J.; Lu, Y. F.; Sellinger, A.; Fan, H. Y. *Adv. Mater.* **1999**, *11*, 579−585, 514.

(18) Huo, Q. S.; Zhao, D. Y.; Feng, J. L.; Weston, K.; Buratto, S. K.; Stucky, G. D.; Schacht, S.; Schuth, F. *Adv. Mater.* **1997**, *9*, 974−978.

(19) Melosh, N. A.; Lipic, P.; Bates, F. S.; Wudl, F.; Stucky, G. D.; Fredrickson, G. H.; Chmelka, B. F. *Macromolecules* **1999**, *32*, 4332−4342.

(20) Attard, G. S.; Glyde, J. C.; Goltner, C. G. *Nature* **1995**, *378*, 366−368.

(21) Yang, P. D.; Deng, T.; Zhao, D. Y.; Feng, P. Y.; Pine, D.; Chmelka, B. F.; Whitesides, G. M.; Stucky, G. D. *Science* **1998**, *282*, 2244−2246.

(22) Trau, M.; Yao, N.; Kim, E.; Xia, Y.; Whitesides, G. M.; Aksay, I. A. *Nature* **1997**, *390*, 674−676.

(23) Fan, H. Y.; Lu, Y. F.; Stump, A.; Reed, S. T.; Baer, T.; Schunk, R.; Perez-Luna, V.; Lopez, G. P.; Brinker, C. J. *Nature* **2000**, *405*, 56−60.

(24) Wirnsberger, G.; Yang, P. D.; Huang, H. C.; Scott, B.; Deng, T.; Whitesides, G. M.; Chmelka, B. F.; Stucky, G. D. *J. Phys. Chem. B* **2001**, *105*, 6307−6313.

(25) Wirnsberger, G.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2525−2527.

(26) Scott, B. J.; Wirnsberger, G.; McGehee, M. D.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **2001**, *13*, 1231−1234.

(27) Wirnsberger, G.; Scott, B. J.; Stucky, G. D. *Chem. Commun.* **2001**, 119−120.

(28) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89−96.

(29) Siegman, A. E. *Lasers*; University Science Books: Mill Valley, CA, 1986.