

Time-Resolved Fluorescence Quenching Studies in Nanocomposite Materials Made of Silica and Cetyltrimethylammonium Bromide

Vlasoula Bekiari, Maria-Luisa Ferrer, and Panagiotis Lianos*

Engineering Science Department, University of Patras, 26500 Patras, Greece

Received: January 15, 1999; In Final Form: April 1, 1999

Fluorescence quenching studies have been performed in silica/cetyltrimethylammonium bromide nanocomposite materials made by the sol–gel method and by mixing prehydrolyzed tetramethoxysilane with aqueous surfactant micelles. Hydrophobic probes incorporated in these materials are solubilized in the surfactant subphase where they can diffuse. Pyrene forms diffusion-controlled excimers there. The subphase is organized, providing a polar hydrocarbon interface and a hydrophobic interior, and it most probably consists of percolating surfactant clusters, each formed by fusion of several micelles. Hydrophilic molecules are incorporated in the embedding silica phase, and they are immobilized. Quenching is much more restricted in films than in bulk matrices, even though films support a large number of molecular layers. This result is consistent with the existence of alternating surfactant bilayer/silica layer structure, previously proposed.

1. Introduction

Composite silica/surfactant materials have recently attracted large interest mainly because surfactant organization is exploited as a template to fabricate ordered mesoporous structures.^{1–7} Silica/surfactant composites are, however, interesting nanophase materials themselves, even though not much attention has been paid to them so far. Surfactants in silica matrices or thin films are organized, and they seem to create an organic nanophase that keeps several characteristics of a surfactant subphase in solution or at interfaces; e.g., they provide a hydrophobic environment and a polar/hydrocarbon interface.^{8,9} The mobility of molecular species incorporated in silica/surfactant xerogels and the kinetics of interactions between them are expected to be very much influenced by the nature of the microenvironment where the species are solubilized. In fact, pure silica matrices slow down molecular motion or dictate total immobilization.¹⁰ A substantial mobility is then expected only in a “fluid” subphase, which surfactants can successfully provide. The existence of the surfactant subphase can be useful for incorporating and dispersing photoactive species that may be otherwise insoluble in the precursor solutions making the gels. The presence of surfactant will also affect the rate of leaching of hydrophobic or hydrophilic molecules incorporated in such composite materials.¹¹ Silica matrices and films used as hosts of photoactive species may then benefit from the functionality provided by the presence of amphiphilic species. In addition, the presence of surfactants or other organic material in a silica matrix may be exploited to modify its mechanical, electrical, and optical (i.e., refractive index) properties,¹² and this fact adds to the importance of these materials.

In the present work we have performed fluorescence quenching studies, both steady-state and time-resolved but with emphasis to the latter, in silica/surfactant composite materials by using some different probes, both hydrophobic and hydrophilic. Our principal goal was to study the kinetics of a bimolecular interaction in such a complex environment, since

not much work has been done in that direction. Fluorescence quenching is a powerful tool that has been repeatedly used to study organized microheterogeneous phases,^{13–16} and we believe that it may be equally successful in composite nanophase materials. We have thus adopted such methods to study both bulk matrices and thin films made by the sol–gel method. Tetramethoxysilane is used as precursor of silica, and cetyltrimethylammonium bromide (CTAB) aqueous micelles are used as precursors of the surfactant subphase. The choice of CTAB was simply based on the fact that it is the most popular for making composite organic/inorganic materials. It must be emphasized that the surfactant concentration range studied in this work is the one where spherical aqueous micelles are formed, i.e., much lower than the usual concentration used to obtain highly ordered mesoporous structures.^{2,7} The choice of relative concentrations was dictated by an effort to obtain transparent composite matrices, necessary for photophysical studies.

2. Experimental Section

Cetyltrimethylammonium bromide (CTAB, Fluka), tetramethoxysilane (TMOS, Aldrich), tris(2,2'-bipyridine)ruthenous dichloride hexahydrate (Ru(bpy)₃²⁺, Aldrich), methyl viologen (MV²⁺, Aldrich), pyrene (Fluka), and coumarin-153 (C-153, Aldrich) were of the best quality available and used as received. Millipore water was used in all experiments.

Composite silica-surfactant matrices and thin films were made as previously.¹⁷ The whole procedure was carried out at ambient conditions. TMOS was partially hydrolyzed by mixing it with acidified water (pH 3.0) at a molar ratio of TMOS/water = 1:2. The mixture was continuously stirred for 1 h. At the beginning it was turbid, but in the course of the proceeding hydrolysis it became clear. Then to 1 mL of this original sol, we added 5.4 mL of 0.1 M aqueous CTAB solution under vigorous stirring. The obtained sol was transparent and homogeneous. Immediately after preparation, a glass slide, previously cleaned in sulfochromic solution, was dipped in the sol and withdrawn at a speed of 44 mm/min. The obtained film was left to dry in air. Probes and quenchers were introduced in the film by solubilization in the original aqueous micellar solution. All films were

* To whom correspondence should be addressed. Phone: 30-61-997587. Fax: 30-61-997803. E-mail: lianos@upatras.gr.

transparent. Transparent matrices (xerogels) were also obtained by slowly drying the original colloidal solution at 40 °C. The solutions were dried in plastic cuvettes covered with perforated aluminum foil.

Measurements were performed at ambient conditions. Steady-state fluorescence measurements were made with a home-assembled spectrofluorometer using Oriel parts. Time-resolved fluorescence decay profiles were recorded with the single-photon-counting technique using a homemade nanosecond hydrogen flash lamp and ORTEC electronics. The installation has been tested by recording decay profiles of the present (pyrene) and other fluorophores in different environments and comparing our results with those found in the literature.

3. Model for Time-Resolved Analysis

The fluorescence decay profiles of pyrene in the presence of excimers or in the presence of C-153 and of Ru(bpy)₃²⁺ in the presence of MV²⁺ were analyzed by a model of stretched exponentials given by the following equation:^{15,16,18}

$$I(t) = I_0 \exp(-t/\tau_0) \exp[-C_1(t/\tau_0)^f + C_2(t/\tau_0)^{2f}] \quad 0 < f < 1 \quad (1)$$

while the first-order quenching rate constant was calculated by

$$K(t) = \frac{1}{\tau_0} [fC_1(t/\tau_0)^{f-1} - 2fC_2(t/\tau_0)^{2f-1}] \quad (2)$$

C_1 , C_2 , and f are parameters calculated by fitting eq 1 to the experimental decay profile and used to calculate the values of $K(t)$. τ_0 is the decay time in the absence of quencher, and it is measured in separate experiments.

The model of eq 1 applies to any quenching reaction where an excited luminophore can, in principle, be quenched by any quencher present. Thus, it applies to electron- or energy-transfer as well as to diffusion-controlled quenching. It is particularly fit to complex systems with unknown but, certainly, restricted geometry. It is also particularly fit to the present system where information on molecular diffusion is sought by analysis of the luminescence decay profiles. The model is based on the fundamental kinetics of restricted reactions where a reactant behaves as a random walker. In a restricted environment, the number of distinct sites visited by the random walker within a time interval t is not proportional to t but to t^f , where $0 < f < 1$, hence, the noninteger power of time in eq 1. Obviously, the restrictions imposed by the reaction domain reflect on the value of f , f being smaller in more restricted reactions. In the development of the decay law for quenching in restricted geometries,¹⁹ it is found that the second exponential of eq 1 should actually contain an infinite number of terms. The first two terms in the series have a specific meaning.^{15,19} The first is proportional to the number of distinct sites visited within a time interval and the second to its variance. In theoretically produced luminescence decay profiles or for data recorded without noise, fitting with eq 1 is impossible.¹⁸ When the decay profile is recorded with a large number of data, with Gaussian distribution, as with the single-photon-counting technique presently used, only the number of distinct sites visited and its variance are quantities different from zero.¹⁵ For this reason, the two terms of the second exponential in eq 1 suffice to fit the experimental decay profile. This approximation gives very satisfactory results. Figure 1a presents an example of fitting eq 1 to an experimental decay profile of pyrene incorporated, together with C-153, in a composite SiO₂/CTAB matrix.

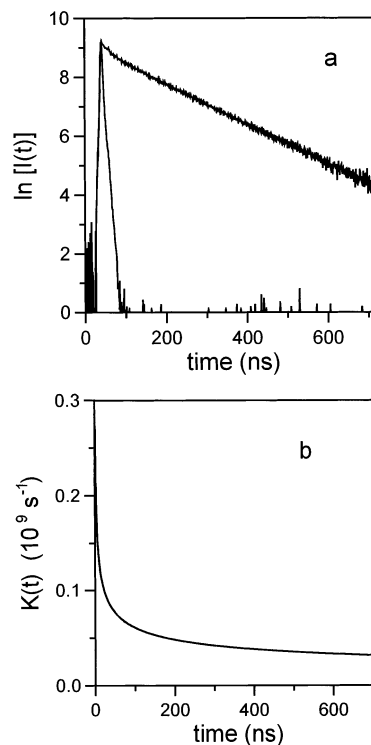


Figure 1. (a) Plots of the experimental decay curve, the fitted curve, and the exciting flash profile for a composite SiO₂/CTAB matrix containing pyrene and C-153. The pyrene/surfactant and the C-153/surfactant ratio was 1/5000 and 1/20,000, respectively. (b) Plot of the corresponding decay constant $K(t)$ vs time.

The rate constant is time-dependent in all cases where the model of eq 1 applies, since it then depends on the distance between the reacting species. Distance dependence creates time dependence, which becomes even more intense in the case of restricted geometries. Thus, the value of K in eq 2 is time-dependent. Figure 1b shows a typical example of the time evolution of $K(t)$. Since it is difficult to tabulate any $K(t)$ value for any value of time, we usually choose to tabulate only its value K_1 at the first time channel and its value K_L at the last recorded time channel (i.e., at a time approximately equal to the decay time of the free luminophore multiplied by 4, e.g., at about 720 ns in the case of pyrene, cf. Figure 1). Then K_1 represents the rate constant at short times and K_L the rate constant at long times. Both K_1 and K_L are, of course, first-order rate constants; i.e., they increase with quencher concentration.

Variants of the above model of stretched exponentials have been systematically used in the past by various authors to study, in particular, interactions in solid-state materials. The donor decay model for resonance energy-transfer quenching is the best known model of stretched exponentials.²⁰ The exponent f in that model is 0.5, when the reaction occurs between homogeneously and isotropically distributed donors and acceptors. Blumen et al. have then showed that in restricted environments f depends on the dimensionality of the reaction configuration.^{19,21} Argyrakis and Kopelman have demonstrated the scaling laws that apply to diffusion in percolating clusters.^{22,23} The presently used model, based on these previous studies, takes advantage of time-resolved analysis to follow molecular diffusion and interaction in complex systems with nonspecific geometry.

4. Results and Discussion

In the results presented hereafter, the luminophore and quencher concentrations are given as molar ratios over surfactant

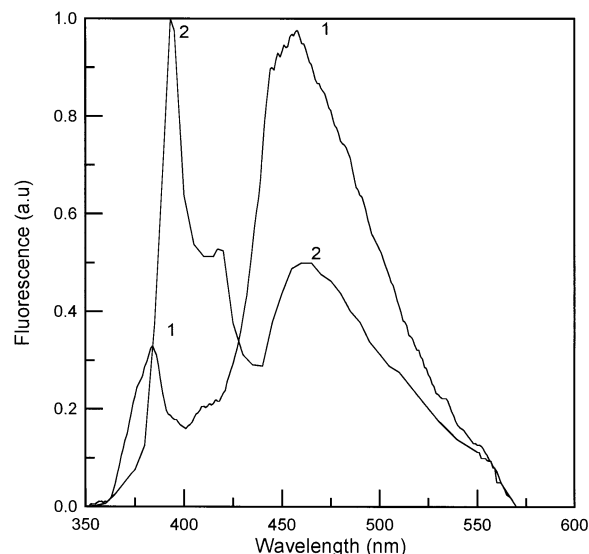
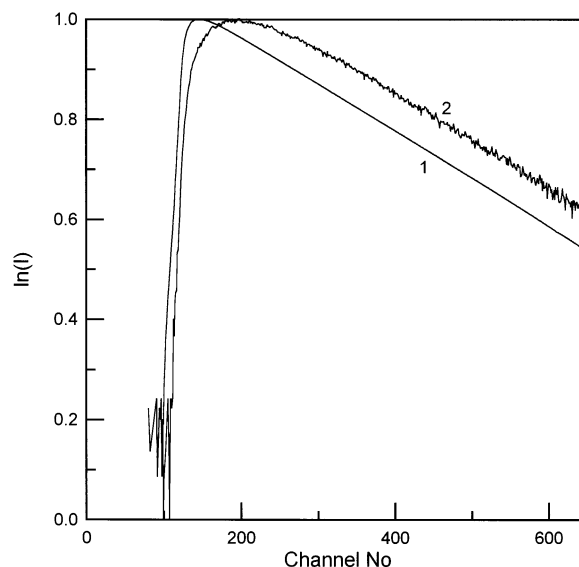
TABLE 1: Analysis of the Fluorescence Decay Profiles of Pyrene in the Presence of C-153 in Silica/CTAB Xerogel Matrices According to the Model of Eqs 1 and 2^a

[C-153]/[CTAB]	<i>f</i>	<i>K</i> ₁ (10 ⁶ s ⁻¹)	<i>K</i> _L (10 ⁶ s ⁻¹)	<i>K</i> ₁ / <i>K</i> _L
1/40000	0.71	15	1.0	16
1/20000	0.69	21	1.4	15
1/10000	0.69	24	1.7	14
1/5000	0.69	28	2.0	14
1/2000	0.71	37	2.4	15
1/1000	0.69	41	2.7	15

^a Pyrene over surfactant concentration ratio was 1/5000. [CTAB] concentration was in all cases 0.1 M (as measured in the original solution).

concentration. The surfactant concentration in the original solution was 0.1 M, and it was chosen in order to produce transparent xerogels. Such transparent materials have been obtained in the surfactant concentration range up to 0.2 M.¹⁷

4.1. Study of Silica/CTAB Xerogel Matrices with the Pyrene/C-153 Pair and with Pyrene Excimer. C-153 quenches pyrene fluorescence by resonance energy transfer.^{17,24} This is verified by steady-state fluorescence quenching measurements. The decay time of the donor pyrene in silica/CTAB xerogels in the absence of the acceptor C-153 was found to be 188 ns. The decay time of pyrene in an inert environment may be as high as 400 ns. The lower decay time in the present case is due to quenching by the bromide counterions, while a limited quenching also comes from a weak interaction with the quaternary ammonium group.²⁵ Experience from the study of aqueous CTAB micelles with pyrene has shown that this global quenching affects only the value of the above decay time but has no effect on the analysis of the interaction of pyrene with a quencher. $\tau_0 = 188$ ns is already a higher value than the one obtained in aqueous CTAB micelles.²⁵ The rigidity of the environment provided by a xerogel slows down both bromide and other quenching mechanisms, such as rotational and vibrational interactions and oxygen quenching. The above value is a result of all these opposing trends, which, fortunately, do not affect the analysis of fluorescence quenching data. Table 1 shows the results of the analysis of fluorescence decay profiles of donor pyrene in the presence of increasing amounts of quencher (acceptor) C-153 by using the model of eqs 1 and 2. Figure 1 also shows a typical example of curve fitting and of the time evolution of the rate constant. The values of the noninteger constant exponent *f*, given in column 2, were independent of quencher concentration, within experimental error, and were equal to about 0.70. This value is much higher than the typical exponent found in purely energy-transfer quenching (i.e., 0.50). It means that quenching is facilitated by an additional mechanism, which, in the present case, is nothing else but diffusion of the reactants within the reaction domain. That the reactants diffuse in the xerogel is supported by the fact that pyrene forms excimers in a dynamic manner there. Indeed, for pyrene concentrations of $\geq 1/100$ (i.e., $\geq 10^{-3}$ M in the original solution) a large quantity of excimer was formed that decreased as the solution gelled but never disappeared, as seen in Figure 2. This is not the case for pure silica matrices.¹⁰ The remaining excimer is formed by excited-state interaction and not by aggregation. This is seen by the data of Figure 3 where the decay profile of the excimer emission is parallel to that of the monomer emission. The decay time of the excimer is much shorter than the decay time of the monomer. The isochronous decays of Figure 3 obviously reveal that the excimer is only formed through monomer. The curved rising part of the excimer decay profile also points to the fact that the excimer is formed through a dynamic process and it is not due to direct

**Figure 2.** Fluorescence spectra of 10⁻² M pyrene in 0.1 M aqueous CTAB (1) and in the ensuing xerogel (2). The monomer pyrene spectrum has been deformed by self-absorption because of the high concentration of the fluorophore.**Figure 3.** Pyrene monomer (1) and excimer (2) fluorescence decay profile in a SiO₂/CTAB xerogel recorded at 380 nm (monomer) and 450 nm (excimer).**TABLE 2: Analysis of the Fluorescence Decay Profiles of Pyrene Monomer in the Presence of Excimers in Silica/CTAB Xerogel Matrices According to the Models of Eqs 1 and 2^a**

[pyrene]/[CTAB]	<i>f</i>	<i>K</i> ₁ (10 ⁶ s ⁻¹)	<i>K</i> _L (10 ⁶ s ⁻¹)	<i>K</i> ₁ / <i>K</i> _L
1/100	0.71	18	2.1	9
1/33	0.72	22	2.6	9
1/14	0.71	28	3.4	8
1/10	0.69	36	3.5	9

^a [CTAB] concentration was in all cases 0.1 M (as measured in the original solution).

excitation of a ground-state dimer. Time-resolved analysis of pyrene monomer in the presence of excimers also showed that excimer formation is a diffusion-controlled process. The analysis was again made by the model of eqs 1 and 2, and the results are presented in Table 2. Interestingly, *f* was constant again and practically equal to the value obtained with the resonance-energy-transfer-quenching pair. It is clear that the efficiency of

TABLE 3: Analysis of the Luminescence Decay Profiles of Ru(bpy)₃²⁺ in the Presence of MV²⁺ in Silica/CTAB Xerogel Matrices According to the Model of Eqs 1 and 2^a

[MV ²⁺]/[CTAB]	<i>f</i>	<i>K</i> ₁ (10 ⁶ s ⁻¹)	<i>K</i> _L (10 ⁶ s ⁻¹)	<i>K</i> ₁ / <i>K</i> _L
1/33	0.50	23	0.1	328
1/20	0.49	34	0.1	283
1/5	0.49	58	0.2	276

^a The luminophore over surfactant concentration ratio was 1/100. [CTAB] concentration was in all cases 0.1 M (as measured in the original solution).

quenching in the studied microenvironment mainly depends on a common factor that exists in both these two very different quenching mechanisms. This common factor could be nothing else but the capacity of diffusion within the reaction domain. This fact is also seen from the values of *K*_L (i.e., the long-time quenching rate constant; column 4 of Table 2). *K*_L was different from zero. It naturally increased with pyrene concentration, since it is a first-order rate constant. However, *K*_L is zero in CTAB aqueous micelles where no exchange of pyrene molecules between micelles, i.e., no long-time diffusion, is allowed. Once more then, the above data make obvious the existence of diffusion in the studied microenvironment. As for the rest of the data of Tables 1 and 2, column 3 gives the short time rate constant *K*₁ and column 5 the ratio *K*₁/*K*_L. This last ratio gives the importance of the short-time quenching efficiency with respect to the long-time quenching efficiency, which mainly depends on diffusion. *K*₁/*K*_L is higher in the case of the pyrene-C-153 pair, since energy transfer facilitates quenching from a distance while excimer formation necessitates close contact. Pyrene and C-153 are solubilized at the polar/hydrocarbon interface.¹⁷ Nevertheless, they remain probes of the surfactant subphase and not of its surrounding environment. We may then safely conclude that CTAB does form a subphase within the silica xerogel. It is natural to admit that the surfactant heads are on the surface of the subphase in contact with silica. We believe that original micelles found in the precursor solution do not remain intact in the xerogel, but they rather fuse to produce a bilayer structure, as previously proposed.^{8,9} This conclusion is based on the following data: (1) pyrene excimers are much less in the xerogel than in the original micellar solution; (2) *K*_L for pyrene excimer formation is zero in CTAB aqueous micelles, but it obtains a substantial value in xerogels (cf. Table 2). This means that there exists a substantial long-distance diffusion within the matrix. Such long-distance displacement is possible in a percolating surfactant bilayer. Such a conclusion is in accordance with the value of *f*, which satisfies the limit set for percolating clusters.²²

4.2. Study of Silica/CTAB Xerogel Matrices with the Ru(bpy)₃²⁺/MV²⁺ Pair. MV²⁺ is a typical quencher of Ru(bpy)₃²⁺ luminescence.²⁶ Because they are charged, they are both probes of hydrophilic environments. Time-resolved analysis of luminescence decay profiles could be performed at various probe and quencher concentrations with similar results. Table 3 presents data obtained in the same concentration range as that used to make films, for reasons of comparison. Both luminophore and quencher are positively charged and repelled by the similarly charged CTAB micelles. They then find themselves in the continuous phase of the original micellar solution, i.e., in water, and they are expected to be solubilized in the silica subphase when they are in the xerogel. Inspection of the data of Table 3 reveals that quenching is very efficient at short times (cf. *K*₁ values), but it is almost zero at long times (cf. *K*_L values). Also the value *f* is much lower in the present case than it was for pyrene excimer formation and for pyrene/C-153 resonance

TABLE 4: Analysis of the Luminescence Decay Profiles of Ru(bpy)₃²⁺ in the Presence of MV²⁺ in Silica/CTAB Films According to the Model of Eqs 1 and 2^a

[MV ²⁺]/[CTAB]	<i>f</i>	<i>K</i> ₁ (10 ⁶ s ⁻¹)	<i>K</i> _L (10 ⁶ s ⁻¹)	<i>K</i> ₁ / <i>K</i> _L
1/33	0.23	23	0.13	177
1/20	0.25	27	0.15	180
1/10	0.28	33	0.19	174
1/5	0.33	46	0.27	170
1/2	0.36	76	0.48	158

^a The luminophore over surfactant concentration ratio was 1/100. [CTAB] concentration was in all cases 0.1 M (as measured in the original solution).

energy transfer. It is obvious that the hydrophilic probes are immobilized and only close-lying pairs can interact. In this respect, *K*₁/*K*_L values, which are more than an order of magnitude higher here than in the case of the hydrophobic probes, underline the importance of the short-range with respect to the long-range quenching. The present results highlight the existence of two different subphases in the composite matrix with different properties, i.e., the embedding silica subphase providing a polar rigid environment and the embedded surfactant subphase providing a polar/hydrocarbon interface and a rather fluid interior.

4.3. Comparison with Similar Data Obtained with Thin Composite Silica/Surfactant Films. SiO₂/CTAB composite films, which are deposited on glass slides by dip-coating, are about 200 nm thick.¹⁷ If they were homogeneous, they would essentially constitute a material with bulk properties, since they consist of hundreds of molecular layers. However, time-resolved analysis of luminescence quenching data revealed that the dimensionality of the quenching process is in fact very low. Indeed, as seen in Table 4, which shows the analysis of Ru(bpy)₃²⁺ luminescence decay profiles in the presence of MV²⁺, the *f* value was very low, much lower than the value obtained in bulk matrices (cf. Table 3). The value *f*, which reflects the restrictions imposed on quenching, is smaller in reaction domains of lower dimensionality. To explain this finding, we have adopted¹⁷ a structural model proposed by Ogawa.²⁷ The composite material organizes itself in alternating layers consisting of a surfactant bilayer followed by a much thinner silica layer. The reacting probes, both hydrophilic and hydrophobic, are then confined in essentially two-dimensional layers. Therefore, the dimensionality of their interactions appears much lower than in bulk matrices. Indeed, we have previously found¹⁷ that the *f* values obtained with the pyrene/C-153 pair in SiO₂/CTAB films are about 0.45, i.e., also much lower than 0.70 observed in the corresponding bulk matrices.

5. Conclusion

When organic molecular species are solubilized in composite nanophase silica/CTAB matrices and films, made by mixing prehydrolyzed silica and aqueous CTAB micelles, they seem to have a preference for one subphase or the other according to their hydrophilicity or oleophilicity. Hydrophilic probes, which in the precursor solution are found in the aqueous continuous phase, when incorporated in the composite matrix, they find themselves in the silica subphase where they are immobilized. Hydrophobic probes, which in the original precursor solution are solubilized in the dispersed micellar environment, find themselves solubilized in the organic subphase, when they are incorporated in the composite matrix or film. In this subenvironment they have the capacity to displace themselves, albeit slowly, in a percolating subphase.

Acknowledgment. We acknowledge financial aid from the program ΠΕΝΕΔ of ΓΓΕΤ.

References and Notes

- (1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, 359, 710.
- (2) Raman, N. K.; Anderson, M. T.; Brinker, C. J. *Chem. Mater.* **1996**, 8, 1682.
- (3) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, 8, 1147.
- (4) Yang, H.; Kuperman, A.; Coombs, N.; Mamiche-Afara, S.; Ozin, G. A. *Nature* **1996**, 379, 703.
- (5) Steel, A.; Caw, S. W.; Anderson, M. W. *J. Chem. Soc., Chem. Commun.* **1994**, 1571.
- (6) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, 267, 865.
- (7) Goltner, C. G.; Antonietti, M. *Adv. Mater.* **1997**, 9, 431.
- (8) Ogawa, M.; Kikuchi, T. *Adv. Mater.* **1998**, 10, 1077.
- (9) Firouzi, A.; Kumar, D.; Bull, L. M.; Besier, T.; Sieger, P.; Huo, Q.; Walker, S. A.; Zasadzinski, J. A.; Glinka, C.; Nicol, J.; Margolese, D.; Stucky, G. D.; Chmelka, B. F. *Science* **1995**, 267, 1138.
- (10) Brusilovsky, D.; Reisfeld, R. *Chem. Phys. Lett.* **1987**, 141, 119.
- (11) Ferrer, M.-L.; Bekiari, V.; Lianos, P. *Chem. Mater.* **1997**, 9, 2552.
- (12) Yamada, N.; Yoshinaga, I.; Katayama, S. *J. Mater. Chem.* **1997**, 7, 1491.
- (13) Zana, R. In *Surfactant Solutions: New Methods of Investigation*, *Surfactant Science Series*; Zana, R., Ed.; Marcel Dekker: New York, 1987; Vol. 22, p 241.
- (14) Duportail, G.; Lianos, P. In *Vesicles*, *Surfactant Science Series*; Rosoff, M., Ed.; Marcel Dekker: New York, 1996; Vol. 62, p 295.
- (15) Lianos, P. *Heterog. Chem. Rev.* **1996**, 3, 53.
- (16) Bekiari, V.; Lianos, P. *J. Colloid Interface Sci.* **1996**, 183, 552.
- (17) Ferrer, M.; Lianos, P. *Langmuir* **1996**, 12, 5620.
- (18) Lianos, P.; Argyrakis, P. *J. Phys. Chem.* **1994**, 98, 7278.
- (19) Klafter, J.; Blumen, A. *J. Chem. Phys.* **1984**, 80, 875.
- (20) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983.
- (21) Klafter, J.; Blumen, A.; Zumofen, G. *J. Lumin.* **1984**, 31&32, 627.
- (22) Argyrakis, P.; Kopelman, R. *J. Chem. Phys.* **1986**, 84, 1047.
- (23) Lindenberg, K.; Sheu, W.-S.; Kopelman, R. *J. Stat. Phys.* **1991**, 65, 1269.
- (24) Tummino, P. J.; Gafni, A. *Biophys. J.* **1993**, 64, 1580.
- (25) Lianos, P.; Viriot, M. L.; Zana, R. *J. Phys. Chem.* **1984**, 88, 1098.
- (26) Milosavljevic, B. H.; Thomas, J. K. *J. Phys. Chem.* **1985**, 89, 1830.
- (27) Ogawa, M. *J. Am. Chem. Soc.* **1994**, 116, 7941.