

Absorption and Exciton Emission by an Aggregated Cyanine Dye Occluded within Mesoporous SBA-15

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We report the formation of monomeric and J-aggregated 1,1'-diethyl-3,3'-di(4-sulfobutyl)-5,5',6,6'-tetrachlorobenzimidazolocarbocyanine (referred to as TDBC) encapsulated within a silicate mesostructure, specifically SBA-15, under different pH conditions. To facilitate incorporation of TDBC, it was necessary to functionalize the interface of the synthesized SBA-15 for proper guest–host electrostatic interaction between the anionic dye and the inner core surface charge, through use of a silylation reagent, (aminopropyl)triethoxysilane, which at high pH values results in formation of $-\text{NH}_3^+$ surface species. XRD, UV-vis absorption and fluorescence measurements are used as spectroscopic tools to characterize SBA-15 host samples as well as composites consisting of the host and encapsulated molecules. J-aggregated TDBC occluded within SBA-15 represents a robust, new superradiant fluorescent nanomaterial.

I. Introduction

We report in this paper efforts in our laboratory to form cyanine aggregates within one-dimensional mesoporous silicates. Our aim is to create an encapsulated species where constraints in aggregate length and orientation, associated with the spatially constricted and directional character of the cavity, as well as controls available in the synthesis process, result in a nanocomposite that is a new material, possessing the unique spectroscopic and other optical properties generally associated with cyanine dye aggregates, while assuming a more robust and manipulable physical form. These composites are being examined as potential new nanostructural materials with useful optical properties, including, in some cases, high luminescence cross-section (resulting from superradiance), controllable strong attenuation of incident radiation, and their chemical sensors prospects. The focus of our present study with the occluded, aggregated cyanine dye is quite distinct from that of other investigators, whose efforts have focused on occluded molecules or atoms, with the aim to exploit their evinced catalytic, environmentally remunerative, or optoelectronic properties.^{1–10}

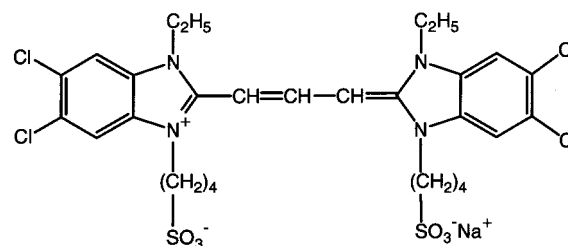
Recently, studies from this laboratory have been reported on techniques for forming aggregated molecules within MCM-14 aluminosilicate structures.^{11,12} In one study we encapsulated tetrakis(*p*-sulfonatophenyl)porphyrin, also referred to hereinafter as TSPP, within aluminum-incorporated MCM-41, and provided spectroscopic evidence that confirmed the encapsulation—in particular, the dramatic changes in absorption and emission spectra that occur upon formation of the occluded aggregate.¹¹ However, this system has reduced prospect for exploitation of the composite material for device or new materials applications, because exciton emission, which is indicative of aggregate formation, is weak. The weakness of the emission is due to the resultant emission from the Q-state, following internal conversion from the initially excited B-state of the porphyrin and the low emission cross section between the Q-state and the ground state. In a second study, we have encapsulated monomeric and

aggregated 1,1',3,3'-tetraethyl-5,5',6,6'-tetrachlorobenzimidazolocarbocyanine (hereinafter referred to as TTBC) within MCM-41 and found strong excitonic emission from the aggregated composite.¹² But, for this latter case, the amount of aggregated TTBC formed within the channels of MCM-41, as a result of the synthetic approach used, did not dominate the emission from the sample, since a substantial amount of monomer remained within the mesoporous channels. Moreover, from XRD studies we ascertained that the structural integrity of the aluminosilicate was somewhat compromised upon forming the occluded aggregate. Consequently, this sample also had diminished promise as regards applications.

In the present study, we have replaced MCM-41 with SBA-15, which has a thicker wall structure—which can be varied in the range 31 to 64 Å—than the 10 to 15 Å wall thickness range commonly found for MCM-41. We have additionally developed an encapsulation strategy as well as used a cyanine dye that leads, mainly, to the formation of the aggregated species within the core of the mesoporous silicate.

SBA-15 was first synthesized in 1998,¹³ and is similar to MCM-41 in structure (viz., one-dimensional uniform tubular pores that are hexagonally arranged), composition, and pore size; the latter, of which, can be varied in the range from 46 to 300 Å by choice of template (vide infra) and hydrothermal treatment.

In the present paper, we report the preparation and optically excited luminescence of a nanocomposite consisting of the cyanine dye 1,1'-diethyl-3,3'-di(4-sulfobutyl)-5,5',6,6'-tetrachlorobenzimidazolocarbocyanine (TDBC), occluded within modi-



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fied mesoporous SBA-15 (*vide infra*). Both monomeric and J-aggregated TDBC were encapsulated within modified SBA-15 by host–guest interaction. J-aggregated TDBC was formed from TDBC monomers within the channels by changing the pH of the microenvironment within the cavity. As detailed in our recent publications regarding composites derived from aluminosilicates and aggregated molecules,^{11,12} luminescence results from coherent emission from the excitonic state derived from coupled, aligned monomeric species within such quantum confinement systems.

II. Experimental Section

Synthesis of Siliceous SBA-15. Polycrystalline powders of the mesostructural siliceous SBA-15 were prepared by using triblock copolymer as the template.^{13,14} Briefly, 6.0 g of triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO₂₀PO₇₀EO₂₀, also referred to as Pluronic 123, Aldrich) was dissolved in 170 mL of 2 M aqueous HCl with stirring. Next, 13.5 mL of tetraethyl orthosilicate (TEOS, Aldrich) was added dropwise to the resultant solution at room temperature. The mixture was stirred for 24 h at ca. 313 K. Then the temperature was raised to ca. 373 K, and the reaction allowed to stand for 48 h in a Teflon-lined autoclave. The resulting precipitate was filtered, dried, and calcined in air at ca. 773 K to obtain the final product, SBA-15 (see discussion below of XRD patterns).

To functionalize the synthesized SBA-15, to promote monomeric TDBC incorporation as well as formation of aggregated TDBC from the occluded monomers—by satisfying guest–host intermolecular and/or electrostatic interactions, we modified the surface of the SBA-15 through use of a silylation reagent, (aminopropyl)triethoxysilane (APTES; NH₂–(CH₂)₃–Si–(C₂H₅O)₃), which links oxygen atoms on the silicate surface.

For our studies, the modified SBA-15 was prepared by using an approach similar to the one we used in the modification of MCM-41.¹¹ Briefly, about 0.5 g of the calcined SBA-15 was mixed with a chloroform solution of APTES (25 mL, 0.2 M) and stirred overnight at room temperature. The precipitate was filtered and washed with chloroform and dichloromethane.

Various TDBC/SBA-15 assemblies were obtained through mixing of the modified SBA-15 with TDBC monomer in different ratios. Upon basifying filtered residues containing various assemblies in a programmed way, thereby changing the pH of the microenvironment within the cavity of the silicate, conditions were attained where the J-aggregated TDBC were formed from occluded monomers. Specifics of the chemical and spectroscopic techniques are provided below.

Formation of TDBC/SBA-15 Composites. A typical preparation of a TDBC/SBA-15 composite involved stirring a mixture of 300 mg of modified SBA-15 in 15 mL of TDBC solution (derived from 3.0 mg TDBC dissolved in 15 mL of water: methanol mixed solvent of 9:1 volume ratio (H₂O:CH₃OH) for at least 24 h at room temperature, with the pH held at ca. 4.5 using 2 M H₂SO₄. The suspension was then centrifuged, and the transparent aqueous solution decanted. The residue was washed at least 3 times with distilled water to remove TDBC monomers from the external surface and then dried in air. The product is here designated TDBC-M/SBA-15, where TDBC-M indicates that monomeric TDBC is encapsulated within the modified SBA-15.

The formation of occluded, aggregated TDBC involved adding 2 M NaOH to the solid occluded monomer residue described above. An immediate color change of the residue

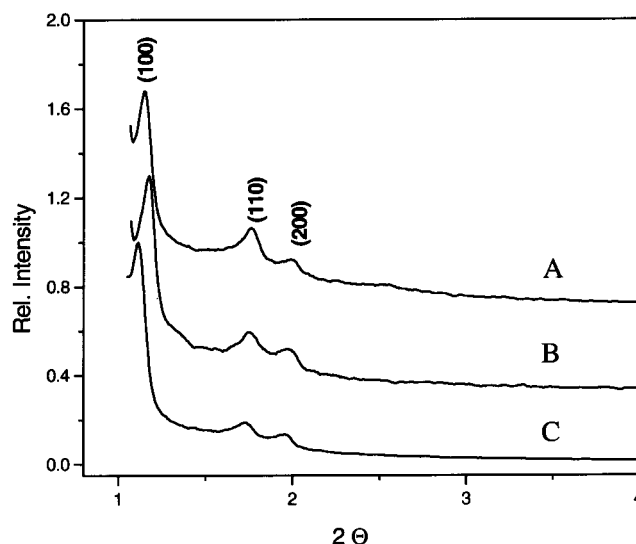


Figure 1. XRD patterns of (A) calcined SBA-15, (B) modified SBA-15, and (C) TDBC-A/SBA-15.

occurred from white to dark pink. The absorption spectrum of the powdered residue (section III below) is interpreted as indicating the presence of occluded J-aggregated TDBC, here designated TDBC-A/SBA-15.

Instrumentation. Absorption spectra were recorded using a Perkin-Elmer, Lambda 18, UV-vis-NIR spectrometer. Steady-state fluorescence spectra were acquired using a SPEX, Fluorolog-τ2 spectrofluorometer. The X-ray diffraction (XRD) instrument used was a Rigaku diffractometer using Cu K_{α1} (0.154 nm) X-rays: typically run at a voltage of 40 kV and current of 30 mA.

III. Results and Discussion

XRD patterns of pristine calcined SBA-15, modified SBA-15, and the aggregate-incorporated composite (TDBC-A/SBA-15) are shown in Figure 1. Using Bragg's equation and comparison with reference studies,¹³ an interplanar spacing $d_{100} \approx 77$ Å for calcined SBA-15 was calculated. Additionally, since we followed a published synthetic approach (in which a pore size was determined through a nitrogen adsorption–desorption isotherm), and the same d_{100} spacing was found in that study, we assumed the same 50 Å pore size, and used d_{100} to calculate the wall thickness of 40 Å. Additionally, we estimated (by geometrical approximation) that upon attachment of the (putative) monolayer of silylation product the pore size was narrowed to ca. 42 Å, which we anticipate to be more than sufficient to allow TDBC to be incorporated into the modified SBA-15.

The XRD patterns of modified SBA-15 and TDBC-A/SBA-15 show strong (100) peaks, suggesting that framework stability of the mesoporous material is well maintained for modified SBA-15 when aggregated TDBC is formed in its interior. It is to be noted that there is almost no change in relative intensities of (110) and (200) scattering reflections for the composite consisting of aggregated TDBC and SBA-15 when compared to the same bands for both calcined SBA-15 and modified SBA-15. In our prior work,^{11,12} when an aggregated cyanine dye (TTBC) or an aggregated porphyrin (TSPP) was formed within modified MCM-41, although the MCM-41 ordered structure was maintained, the relative intensities of (110) and (200) reflections were dramatically decreased. Our observation for SBA-15 is interpreted as indicating that the thicker wall aids in maintaining structural integrity when occluded, aggregated TDBC is formed.

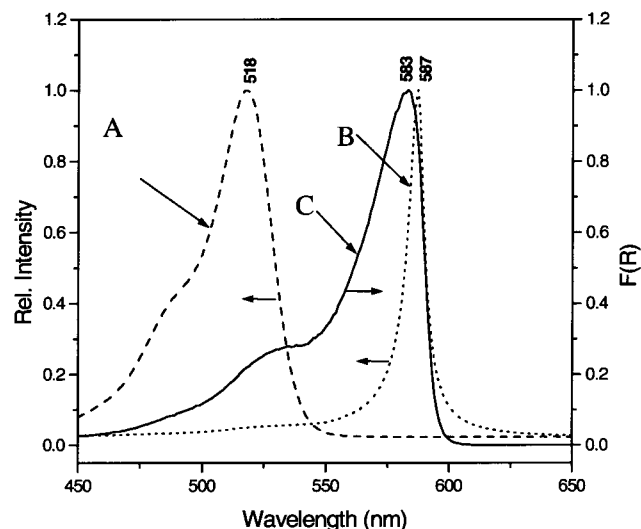


Figure 2. UV-vis spectra of TDBC in various environments. (A) Homogeneous solution-phase monomeric TDBC at 5×10^{-5} M in methanol solvent (dashed line). (B) Solution-phase aggregated TDBC, formed from monomer concentration of 5×10^{-5} M at pH = 11 in aqueous solvent (dotted line). (C) Aggregated TDBC encapsulated in SBA-15 that was modified by surface silylation using (aminopropyl)-triethoxysilane, designation TDBC-A/SBA-15 (solid line). $F(R)$, the right-hand-side label refers to the so-called remission function (a linear function of the concentration of homogeneous absorbers) for diffuse reflection measurements and is calculated from $F(R) = (1 - R)^2/2R$. In this expression, R is the diffuse reflectance, given by $R = J_0/I_0$, where I_0 is the incident intensity at the surface and J_0 is the intensity of the reflected light [see, for example, Kubelka, P. J. *Opt. Soc. Am.* **1948**, 38, 448.].

Moreover, a greater stability of SBA-15 compared to MCM-41 has been demonstrated through its stability in boiling water,¹³ in which MCM-41 does not survive. For the present study, silylation is mainly used to functionalize SBA-15 so as to satisfy the requirement for host-guest interaction, while, in our earlier studies, silylation of MCM-41 was used both to rigidify the framework upon incorporation of the aggregated species and to functionalize the interface for appropriate guest-host interaction.^{11,12}

It is also to be noted that direct encapsulation of aggregated TDBC into the MCM-41 channels was not possible, and the "ship-in-bottle" approach, as used in our earlier studies,^{11,12} was used here also. Thus, to meet the host-guest requirement, it is necessary to first encapsulate the monomers in the modified SBA-15 and then to form aggregated TDBC within the pores of SBA-15.

The diffuse reflectance (DR), UV-vis spectrum of the sample designated TDBC-A/SBA-15 is shown in Figure 2. Also included in this figure, for comparison purposes, are transmission UV-vis spectra of TDBC in methanol solution (where monomer exists) and in aqueous solution (at a pH where aggregated TDBC forms). The prominent absorption bands near 590 nm in the figure are attributable to excitonic absorption bands (i.e., J-aggregate bands; see refs 15,16) of the respective systems, and are diagnostic for the presence of aggregated molecules. The band at ca. 518 nm is attributed to the solution monomeric species. The lack of a spectrum for the TDBC-M/SBA-15 composite in Figure 2 is due to the colorless nature of the sample for the pH (i.e., 4.5) at which individual molecules become occluded within the aluminosilicate, ostensibly due to a change of the chemical form of monomer to, possibly, a protonated form of the dye, which characteristically does not absorb light in the visible region. In this latter case, the protonation would

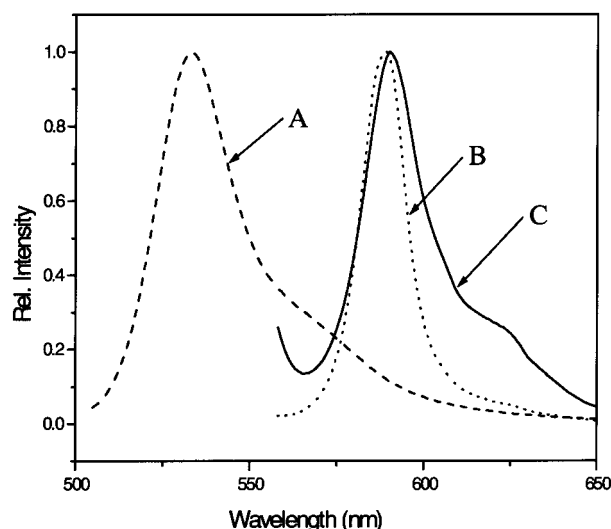


Figure 3. Fluorescence spectra of TDBC: (A) 5×10^{-5} M monomeric TDBC in methanol, excited at 490 nm (dashed line); (B) aggregated TDBC at 5×10^{-5} M and pH = 11.0 using water as solvent, excited at 550 nm (dotted line); and (C) TDBC-A/SBA-15, excited at 550 nm (solid line).

be expected to involve the proton associated with the $-\text{NH}_3^+$ groups on the surface.

We further note that in Figure 2 a blue shift is found for the occluded J-aggregate when compared to the solution aggregate, 583 nm versus 587 nm, respectively. Such a shift can be rationalized in terms of charge-transfer caused by host-guest interaction, which is connected to steric effects associated with the pore structure within modified SBA-15. In addition, the size of the blue shift (ca. 4 nm) is sufficiently small as to suggest that upon formation of the aggregate the molecules couple to one another and realign from their original locations, such that site-specific perturbations to the exciton absorption energy are diminished, in line with our assertions for the system consisting of encapsulated tetrakis(*p*-sulfonatophenyl)porphyrin aggregate within MCM-41.¹¹ The presence of sites with different interaction strengths that interact with the occluded aggregate is expected to lead to a broadened absorption spectrum of the occluded aggregate relative to that of the solution aggregate. This latter prospect, we believe, is borne out upon comparing parts C and B of Figure 2.

It is also found in Figure 2 (part C) that the intensity of the aggregate absorption band (with peak position at ca. 583 nm) is substantially greater than that of the absorption band attributable to the monomer (represented by the shoulder at ca. 525 nm). We interpret this finding as indicating that the majority of TDBC molecules within the composite designated TDBC-A/SBA-15, indeed, is sequestered within the aggregate structure. It might be noted that our prior work with occluded TTBC suggested that only about half of the occluded TTBC molecules existed in the aggregated state in the channels of MCM-41,¹² thus the present system represents a better fit to our initial goal of constructing a system in which the aggregated form of the cyanine dye is the majority species present within the channels of the nanoporous silicate.

Fluorescence spectra for solution phase and composite systems are contained in Figure 3. As shown in parts B and C of Figure 3, which were acquired with excitation at 550 nm, the emissions from aggregated TDBC in solution and the composite TDBC-A/SBA-15 reflect their molecular exciton origins by exhibiting very small Stokes shifts in relation to their respective absorption bands shown in Figure 2. The essentially

zero shift between the absorption and emission peaks for the aggregate in solution (part B of Figure 2 and part C of Figure 3, respectively) indicates that the individual molecules of the aggregate are essentially "identical" as regards movement of the exciton along the chain of coupled molecules for the solution phase system. On the other hand, the nonzero but small shift between the peaks in parts B and C of Figure 3 can be interpreted as indicating that site effects on the exciton energy, though averaged for the aggregate within the composite structure, are not completely eliminated. Motional averaging, also, would rationalize the fact that the emission bandwidth in parts B and C of Figure 3 more closely match than do the absorption bands in parts B and C of Figure 2. Stated in a slightly different way, the above-mentioned similarity between the exciton emission band of the aggregate in solution and in the composite, both in terms of band positions and widths, can be interpreted as indicating that upon formation of the aggregate the molecules are coupled and realigned such that site specific perturbations to the exciton absorption energy, line width, and possibly other properties are diminished.

The emission band, as represented by the shoulder band at ca. 625 nm, to the red of that attributable to the peak of the exciton emission for the composite system is likely attributable to a vibroexcitonic transition. In support of this assertion, it is to be noted that we have observed bands on the shoulders of the main exciton emissions in other composite systems that we have studied (including spectra reported in ref 12), and, in particular, we have acquired excitation spectra for the system involving the cyanine dye 1,1',3,3'-tetraethyl-5,5',6,6'-tetrachlorobenzimidazolocarbo-cyanine (referred to as TTBC; the same system studied in ref 12) encapsulated within mesoporous aluminosilicate and shown that they derive from the ground aggregate species.¹⁷

IV. Conclusion

The combination of XRD, UV-vis absorption and fluorescence measurements of TDBC in solution and post-formation addition to SBA-15 silicate indicates that we are able to form aggregated TDBC occluded in the core. Upon basifying the monomeric TDBC/SBA-15 composite, aggregated TDBC is

formed from occluded monomers. To facilitate formation of incorporated J-aggregated TDBC, surface silylation, using an alkoxysilane reagent, was performed to functionalize the walls of the silicate. The composite consisting of J-aggregated TDBC and the modified SBA-15 represents a new nanomaterial whose spectroscopic properties emanate from quantum confinement over several coherently responding molecules, associated with the coherence length, and whose structural form is further dictated by the restricted growth region defined by the one-dimensional nanoporous structure of the silicate.

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