Aggregation and Exciton Emission of a Cyanine Dye Encapsulated within Mesoporous MCM-41

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We report the formation of monomeric and J-aggregated 1,1′,3,3′-tetraethyl-5,5′,6,6′-tetrachlorobenzimidazolocarbocyanine (referred to as TTBC) encapsulated within an aluminosilicate mesostructure, specifically MCM-41, under different pH conditions. It was necessary to stabilize the synthesized MCM-41 through use of a silylation reagent, (aminopropyl)triethoxysilane, which cross-links oxygen on the surface (thus thickening the walls of the mesoporous material) and functionalizes the interface for proper guest–host interaction. XRD, UV–vis absorption and fluorescence measurements are used as spectroscopic tools to characterize the various products. The composite consisting of J-aggregated TTBC and the aluminosilicate represents a new fluorescent nanomaterial that possesses the properties of the aggregate, yet avoids the essentially unfettered topography and physical length accompanying the formation of an aggregate in solution or adsorbed onto an interface.

I. Introduction

Spectroscopic and optical dynamics properties of aggregated cyanine dyes in homogeneous systems[1,2] and as adsorbates in heterogeneous systems[3–14] have been widely investigated in the author's laboratory. A natural extension of our interest is to examine the formation of cyanine aggregates within a mesoporous cage compound. The aim in this case would be 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, whereas assuming a more robust and manipulable physical form. Our ultimate goal is to exploit such new materials for optical and optoelectronic applications.

In terms of research activities described in the literature involving an occluded species, most efforts exploit the one-dimensional uniform pore sizes and thermal stability of mesoporous siliceous materials as hosts to organize either guest atoms,[15] polymers,[16–18] or organic and inorganic compounds,[19–21] with the aims of creating composite materials with catalytic,[22] environmentally remunerative,[23] or optoelectronic properties.[24] Also, recently, dye-doped microstructures and mesostructures have been advanced as novel microlasers and optoelectronic devices.[25]

The focus of our present study with the occluded aggregated cyanine dye is quite distinct from that of the other investigators referenced above. We draw upon prior studies in our laboratory on several aggregated cyanine dyes in heterogeneous systems; in particular, with aggregation of cyanine dyes on electrode surfaces[3–14] as well as on the surfaces of different colloidal particles.[26,27] In the latter case, we have studied 1,1′,3,3′-tetraethyl-5,5′,6,6′-tetrachlorobenzimidazolocarbocyanine (referred to as TTBC) adsorbed onto colloidal silica[26] as well as 1,1′-diethyl-3,3′-di(3-sulfopropyl)-5,5′,6,6′-tetrachlorobenzimidazolocarbocyanine (referred to as BIC) adsorbed onto colloidal
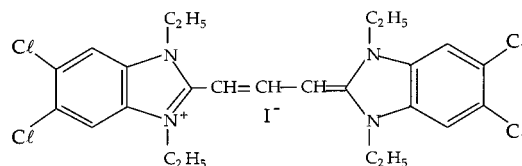
Figure 1. Structure of 1,1′,3,3′-tetraethyl-5,5′,6,6′-tetrachlorobenzimidazolocarbocyanine (TTBC) iodide.

silver.[27] We found, for both systems, that a form of lasing occurs, defined by us as superradiant lasing, at phenomenally low optical pumping thresholds.

Moreover, in a recent paper,[28] we reported a technique for encapsulating tetrakis(*p*-sulfonatophenyl)porphyrin, also referred to as TSPP, within an aluminosilicate, specifically, an aluminum incorporated MCM-41, and the spectroscopic evidence confirming the encapsulation; in particular, the dramatic changes in absorption and emission spectra upon formation of the occluded aggregate. This composite system has enormous value as regards proof-of-concept and possibly in regards to its unique absorption property. But because exciton emission from aggregated porphyrin B-state (i.e., S_2) molecules to their ground state, is dipolar forbidden, the weak emission to the ground S_0 state arises from individual Q-state (i.e., S_1) molecules that are formed through internal conversion of B-state molecules. Such weak emission greatly diminishes the prospect of exploiting the composite for materials or device applications. Aggregated cyanine dyes, on the other hand, typically fluoresce very intensely, and when incorporated within the pores of mesoporous materials, may represent systems with wide utility.

In recognition of the aforementioned prospect, our focus in the present paper is on optically excited luminescence of a composite system consisting of an aggregated cyanine dye—specifically, TTBC, see Figure 1—occluded within mesoporous aluminosiliceous MCM-41. The luminescence results from coherent emission from the excitonic state derived from coupled, aligned monomeric species. Such a composite evinces enhanced

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emission with a shortened radiative lifetime and may have specific utility in such applications as the active element in a flat-panel display device, as the secondary emitter at a near-field optical microscope (NSOM) fiber tip, and as a monochromatic emitting component in coatings for identification of objects in robotic vision and search-and-rescue endeavors.

II. Experimental Section

Synthesis of Modified Al Containing MCM-41. Polycrystalline powders of the mesostructural aluminosilicate MCM-41 were prepared by using cetyltrimethylammonium bromide (CTAB) as the template.[29,30] Briefly, Na_2SiO_3 (Aldrich, $\sim$27% SiO_2) solution and a calculated amount of $NaAlO_2$ (Alfa) solution (Si/Al = 20) were added to CTAB (Aldrich) solution according to the molar composition ratio $5SiO_2$:$0.4Al_2O_3$:CTAB: $610H_2O$. The pH was lowered to 11 with 2 M H_2SO_4 and the mixture was stirred for more than 3 h at about 318 K. Then the temperature was raised to 373 K, and the reaction allowed for 72 h in a Teflon-lined autoclave. The resulting precipitate was filtered, washed thoroughly with distilled water, and calcined in air at 773 K to obtain the final product, MCM-41 (see discussions below of XRD patterns).

To stabilize the synthesized MCM-41 and allow monomeric TTBC incorporation as well as formation of aggregated TTBC from the occluded monomers, we found it necessary to modify its interior structure through use of a silylation reagent, (aminopropyl)triethoxysilane (APTES; $NH_2-(CH_2)_3-Si-(C_2H_5O)_3$), thus linking oxygen atoms on the aluminosilicate surface and rigidifying the mesoporous framework, and satisfying guest-host intermolecular and/or electrostatic interactions as well. For our studies, the modified MCM-41 was prepared according to ref 31. Briefly, about 1.5 g of the calcined MCM-41 was mixed with a chloroform solution of APTES (100 mL, 0.2 M) and stirred overnight at room temperature. The precipitate was filtered and washed with chloroform and dichloromethane.

Various MCM-41/TTBC assemblies were obtained through mixing of the modified MCM-41 with TTBC 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 aluminosilicate, conditions were attained where the J-aggregated TTBC were formed from occluded monomers. Specifics of the chemical and spectroscopic techniques are provided below.

Formation of TTBC/MCM-41 Composites. A typical preparation of a TTBC/MCM-41 composite involved stirring a mixture of 300 mg of modified MCM-41, 4.5 mg TTBC, and 15 mL of distilled water for over 24 h at room temperature with the pH held at ca. 7.0 using 2 M NaOH. The solution was then centrifuged, and the transparent aqueous solution decanted. The residue was washed ca. 3 times with distilled water to remove TTBC monomers from the external surface, and then dried in air. The product is here designated TTBC-M/MCM-41, where TTBC-M indicates that monomeric TTBC is encapsulated within the modified MCM-41: absorption and emission studies (see below, section III) have confirmed the presence of monomer under the above conditions.

The formation of occluded, aggregated TTBC involves adding 2 M NaOH to the solid residue above. An immediate color change of the residue occurred from light red to dark pink. Absorption spectra of the powdered residue (see below, section III) indicated the presence of occluded J-aggregated TTBC, here designated TTBC-A/MCM-41.

Instrumentation. Absorption spectra were recorded using a Perkin-Elmer, Lambda 18, UV−vis−NIR spectrometer. Steady-
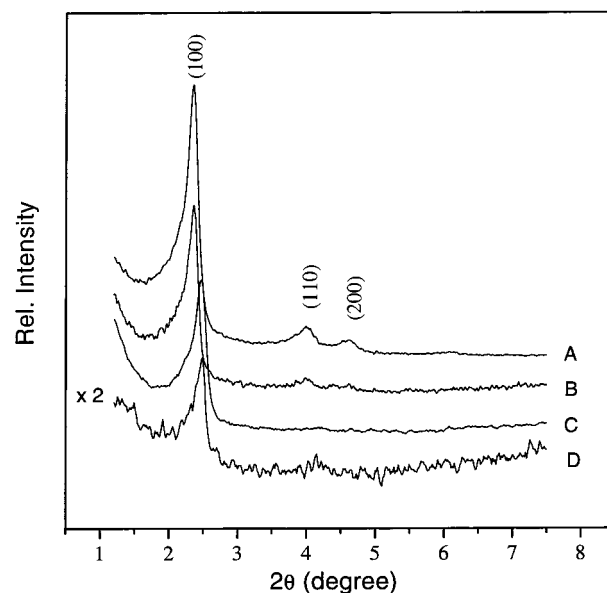

Figure 2. XRD patterns of (A) calcined MCM-41, (B) modified MCM-41, (C) TTBC-M/MCM-41, and (D) TTBC-A/MCM-41.

state fluorescence spectra were acquired using a SPEX, Fluorolog-τ2 spectrofluorometer. The X-ray diffraction (XRD) instrument used was a Rigaku diffractometer using Cu $K_{\alpha 1}$ (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 MCM-41, modified MCM-41, the monomer-incorporated composite (TTBC-M/MCM-41), and the aggregate-incorporated composite (TTBC-A/MCM-41) are shown in Figure 2. Using Bragg's equation and comparison with reference studies,[32−34] the pore size of calcined MCM-41 is estimated to be ca. 33 Å. Additionally, we find, upon attachment of the (putative) monolayer of silylation product to the internal channels of the calcined MCM-41, that the pore size is narrowed to ca. 24 Å, which is sufficiently large to allow TTBC, of approximate dimensions ca. (8×17) Å^2, to be incorporated into the modified MCM-41.

The XRD patterns of TTBC-M/MCM-41 and TTBC-A/MCM-41 show strong (100) peaks, suggesting that framework stability is still maintained for the modified MCM-41 when either monomeric or aggregated TTBC is incorporated. What difference in relative intensities that occur likely is attributable to electrostatic interaction between positive-charged TTBC and the interior walls of the cage as well as with the aggregate's transverse dimension as it grows along the channel length of the aluminosilicate.

We found that monomeric TTBC could be occluded into either calcined or modified MCM-41. However, upon formation of aggregated TTBC from monomers, the (100) peak intensity for the calcined MCM-41 loses significant intensity (not shown), indicating that the framework was not sufficiently strong to allow aggregation, thus resulting in disintegration of the structure. Rigidification of the calcined MCM-41 was a prerequisite to allowing occluded aggregate formation. It is also to be noted that direct encapsulation of aggregated TTBC into the MCM-41 channels was not possible, and the "ship-in-bottle" approach, as used in our study dealing with encapsulation of TSPP into MCM-41,[28] was used here also.

Diffuse reflectance (DR) UV−vis spectra of the samples designated TTBC-M/MCM-41 and TTBC-A/MCM-41 are shown
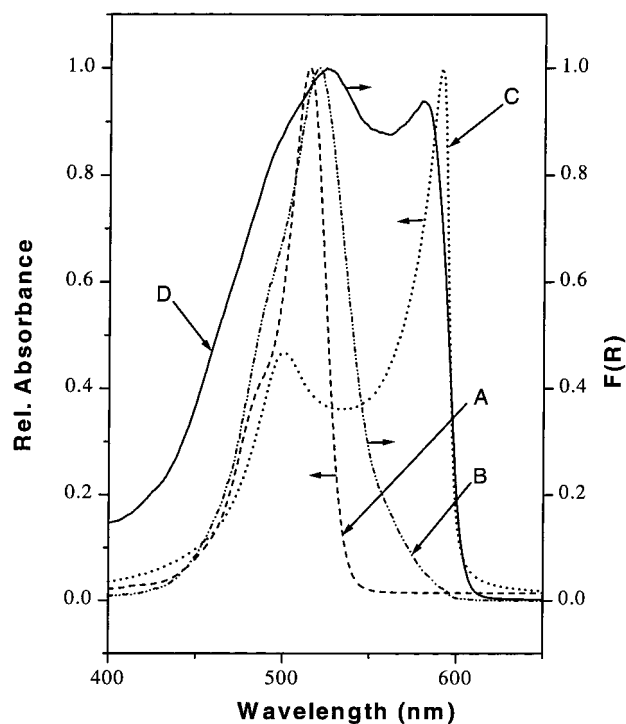
Figure 3. UV−vis spectra of TTBC in various environments. (A) Homogeneous solution phase monomeric TTBC at 5×10^{-5} M and pH = 8.0 in methanol solvent (dashed line). (B) Monomeric TTBC encapsulated in MCM-41 that was modified by surface silylation using (aminopropyl)triethoxysilane (APTES). The composite is designated TTBC-M/MCM-41 (dot-dot−dashed line) and was formed from a aqueous suspension of the aluminosilicate and TTBC at a pH of ca. 7. (C) Solution phase aggregated TTBC formed from monomer concentration of 5×10^{-5} M at pH = 11.5 in aqueous solvent (dotted line). (D) Aggregated TTBC encapsulated in MCM-41 that was modified by surface silylation using (aminopropyl)triethoxysilane, designation TTBC-A/MCM-41 (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.].

in Figure 3. Also included in this figure, for comparison purposes, are transmission UV−vis spectra of TTBC in methanol solution (where monomer exists) and in aqueous solution (at a pH concentration where aggregated TTBC forms). The prominent absorption band at 590 nm in part C of this figure is termed the J-band and is indicative of aggregate formation. It is to be noted that we have also found, as will be detailed in a subsequent report, that resonance excitation of Raman scattering at 590 nm results in resonantly enhanced low-frequency bands (below ca. 300 cm^{-1}) that we have shown to also be diagnostic for aggregate formation.[3,34]

Continuing with Figure 3, it is observed that the occluded monomer exhibits a red shift for its absorption band (520 nm) when compared to the band of the solution monomeric species (514 nm). A blue shift is found for the encapsulated J-aggregate when compared to the solution aggregate, 580 and 592 nm, respectively. Such shifts can be rationalized in terms of intramolecular charge-transfer caused by host−guest interaction, which is connected to steric effects associated with the pore structure within modified MCM-41. The formation of the occluded monomer is rationalized by the fact that at pH = 7 the surface amino groups are not protonated, which makes it possible for positively charged TTBC to experience a favorable
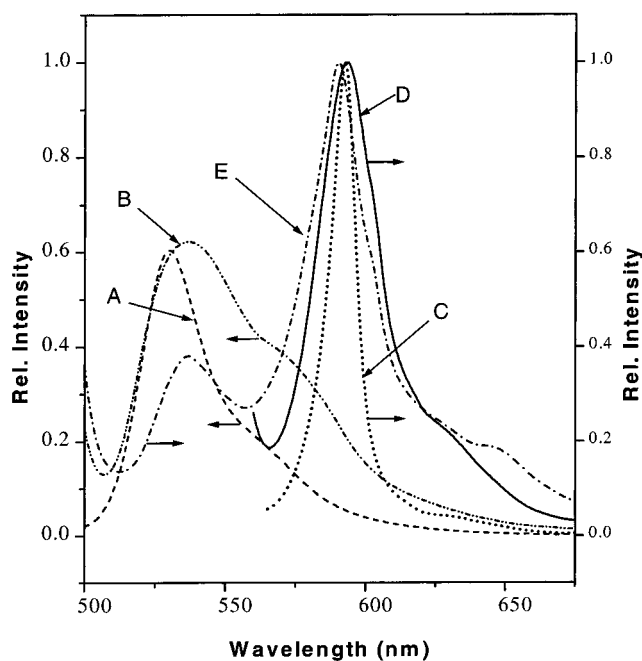

Figure 4. Fluorescence spectra of TTBC: (A) 5×10^{-5} M monomeric TTBC at pH = 8.0 in methanol, excited at 490 nm (dashed line); (B) TTBC-M/MCM-41, excited at 490 nm (dot-dot−dashed line); (C) aggregated TTBC at 5×10^{-5} M and pH = 11.0 using water as solvent, excited at 550 nm (dotted line); (D) TTBC-A/MCM-41, excited at 550 nm (solid line); and (E) TTBC-A/MCM-41, excited by 490 nm radiation (dash−dotted line).

interaction with the lone pair electrons, thus facilitating monomer incorporation. The broaden structure for the monomeric band (part D) relative to that for the solution monomer (part C) can be attributed to site specific adsorption of encapsulated TTBC; suggesting that the monomer is distributed at various positions within the cage and experience, as a result, a range of perturbations.

Fluorescence spectra for solution phase and composite systems were also acquired (see Figure 4). Fluorescence measurements entailed front-surface illumination of the samples, using the aforementioned spectrofluorometer. Both solid samples and solution samples were excited with essentially the same cross section of radiation, however the granularity of the composite likely leads to fewer absorbing entities in the excitation region. We found, as shown in parts A and B of Figure 4, acquired with excitation at 490 nm, that the emissions from monomeric TTBC in solution and the composite TTBC-M/MCM-41 possess about equal Stokes shifts to their respective absorption bands shown in Figure 3. However, the width of the composite's emission band suggests a greater dephasing of excitonic energy than for the aggregate formed in homogeneous solution. By the same argument, the similarity between the fluorescence spectra of the aggregate in solution and in the composite (parts C and D, respectively; excited at 550 nm with peak positions at ca. 594 nm), 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. We also note that the actual intensity at the fluorescence peak for the encapsulated aggregate is, on an absolute scale, about a factor of 2 greater than that for the solution species. Also, for TTBC-A/MCM-41, upon excitation at 490 nm (part E of Figure 4), the emission at ca. 590 nm is found to be significantly larger than that corresponding to the monomer at ca. 537 nm,

suggesting that a substantial fraction of the available monomers has been incorporated into the aggregated species.

IV. Conclusion

The combination of XRD, UV−vis absorption and fluorescence measurements of TTBC in solution and post-formation addition to an MCM-41 aluminosilicate indicates that we are able to form both monomeric and aggregated TTBC occluded in the core. To facilitate formation of incorporated J-aggregated TTBC, surface silylation, using an alkoxysilane reagent, was performed to thicken and functionalize the walls of the aluminosilicate. The composite consisting of J-aggregated TTBC and the modified MCM-41 represents a new nanomaterial whose properties derive from exciton energies and dynamics that result from quantum confinement. On the basis of a conflation of the present and other studies from this laboratory, we conclude that the quantum confinement is associated with both the restricted growth region available to the spontaneously self-assembled molecular aggregate, which forms when TTBC monomers are exposed to a sufficiently basic microenvironment, and the intrinsic confinement (characterized in terms of a coherence length[36,37]) of the exciton's movement among a subset of coherently responding molecules within the physical aggregate.

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