

Anisotropic Optical Properties and Structures of Block Copolymer/Silica Thin Films Containing Aligned Porphyrin *J*-Aggregates

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Mesostructured silica–block copolymer thin films are demonstrated to provide orientationally ordered host matrixes for stable alignment of coassembled porphyrin *J*-aggregates with anisotropic optical properties. Visible light at 490 nm was absorbed anisotropically ($A_{\parallel}/A_{\perp} = 1.35$) by aligned, hexagonally ordered (ethylene oxide)₂₀–(propylene oxide)₇₀–(ethylene oxide)₂₀ (P123) triblock copolymer/silica nanocomposite films containing 1–5 wt % tetrakis(4-sulfonatophenyl)porphyrin (TPPS₄) guest species in the form of *J*-aggregates. Amorphous silica prepared similarly and containing TPPS₄ *J*-aggregates, but without structure-directing block copolymer species, absorbed light isotropically ($A_{\parallel}/A_{\perp} = 1.00$). The porphyrin guest species were determined to be preferentially associated with the hydrophilic ethylene oxide moieties of the triblock copolymer, by using two-dimensional (2D) solid-state ¹H{¹H} and ¹³C{¹H} NMR correlation experiments, including under conditions of fast (45 kHz) magic-angle spinning. Interrelationships are shown and established among synthesis conditions, the molecular, mesoscopic, and orientational structural ordering in the porphyrin-containing nanocomposite thin films, and their macroscopic optical properties.

Introduction

Mesostructured silica–block copolymer composites are attractive host materials for a variety of optically responsive guest species, including inorganic dopants, small organic dye molecules, and large conjugated polymers.^{1–8} The mesostructured host provides a number of benefits, including high compatibilities of organic agents in the hydrophobic polymer components or of inorganic species in the relatively hydrophilic silica network. In addition, the strongly cross-linked silica network yields enhanced mechanical and thermal stabilities, compared to wholly organic polymers. Mesostructured silica–block copolymer materials can furthermore be processed into macroscopic fibers,⁹ films,^{10–12} and monoliths,^{13–16} for subsequent integration into a range of devices for optical applications.

Many of the desirable properties of inorganic–organic composite materials often arise from mesoscopic organization of the dissimilar inorganic and organic components and their high interfacial contact. At sufficient concentrations, amphiphilic block copolymers locally separate into distinct hydrophilic and hydrophobic regions with uniform dimensions and periodicities in the range 5–50 nm, according to the composition, structure, and lengths of the copolymer blocks.¹⁷ Selective incorporation and polymerization of soluble inorganic precursor species within the hydrophilic regions of the self-assembled copolymer blocks yield composite mesostructured materials into which optically responsive agents can be simultaneously incorporated.^{1,2,4–8,18–21} High dye concentrations and material stabilities have been demonstrated, leading to desirable combinations of properties that are often difficult to achieve in wholly inorganic or wholly organic materials alone. These include low thresholds of

amplified spontaneous emission,⁶ optical limiting properties,⁷ fast/adjustable response times,⁴ improved resistance to mechanical and photophysical damage,⁷ enhanced processability, etc.

One useful property of mesostructured inorganic–organic composites that has not been significantly exploited for optical applications is the inherent anisotropies of certain mesophase structures. Templated silica has been synthesized with high extents of hexagonal or lamellar mesostructural ordering that has also resulted in materials with significant extents of long-range orientational ordering.^{1,2,6,11,16,22–28} Thin film processing techniques, such as spin or dip coating, often rely on rapid evaporation-induced self-assembly,²⁹ which is however difficult to control and often leads to films lacking long-range anisotropy. Nevertheless, mesostructured inorganic–organic films with high extents of orientational ordering have been obtained by using anisotropic substrates, for example rubbed layers of polyimides^{25,26} or photoaligned layers of polymers,²³ or orienting fields, e.g., mechanical (surface or flow)^{16,24} or magnetic.^{22,27,28} Such orientational ordering can, in principle, be exploited to produce materials with anisotropic optical properties, including polarized or nonlinear absorption or emission.

In practice, however, the incorporation of guest agents to impart anisotropic optical properties to inorganic–organic hybrid materials has been challenging. Among the reasons are the combined needs to select guest species (1) with optical absorption/emission or other photophysical properties that are intrinsically anisotropic, (2) that can be easily introduced into the orientationally ordered mesochannels, and (3) that have sufficiently long lengths and high aspect ratios that they can be aligned within the relatively large (5–50 nm) diameter mesochannels. In particular, the latter two are often difficult to achieve in combination.

One approach involves removal of the block copolymer species (e.g., by calcination or solvent extraction), after which

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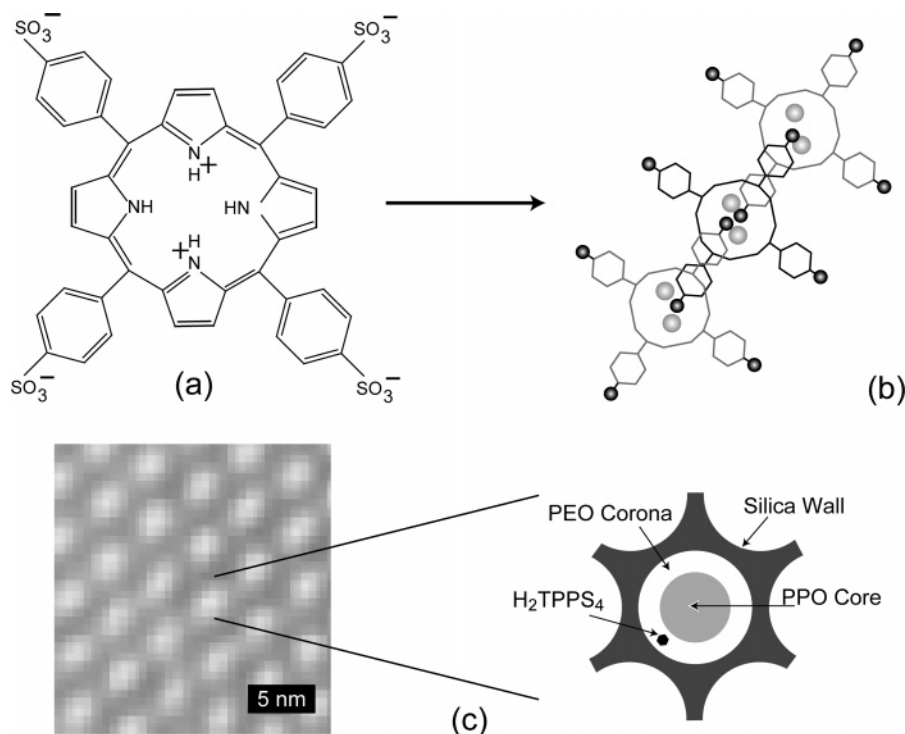


Figure 1. (a) Molecular structure of tetrakis(4-sulfonatophenyl)porphyrin ($\text{H}_2\text{TPPS}_4^{2-}$). (b) Schematic diagram of a supramolecular J -aggregate, resulting from the self-assembly of the charged building blocks. J -aggregates form under acidic conditions as a result of intermolecular electrostatic interactions between the negatively charged sulfonate groups (black spheres) on the phenyl rings and positively charged hydrogen atoms (gray spheres) associated with the pyrrole nitrogen atoms of the central porphyrin macrocycle. (c) TEM image of a highly ordered hexagonal mesostructured silica/EO₂₀PO₇₀EO₂₀ block copolymer composite and a schematic diagram showing the locus of J -aggregate solubilization principally within the hydrophilic PEO corona regions surrounding the relatively hydrophobic PPO cores.

guest species may be infiltrated into the aligned mesopores. Such postsynthesis introduction of guest species into preformed mesochannels may be limited by diffusion limitations, pore blockages, and/or incompatibility with interior channel surfaces. Nevertheless, the inclusion of conjugated macromolecules has yielded materials exhibiting anisotropic optical responses.^{3,30,31} The inclusion of small cyanine dye species also led to materials exhibiting optical anisotropy, presumably as a result of specific interactions with the aligned silica walls.¹ By comparison, incorporation of optical guest species during syntheses of the mesostructured silica hosts is frequently limited by the low solubilities of hydrophobic macromolecular guests or surfactant-passivated nanoparticles in polar solvents and/or their poor stabilities under the highly acidic or alkaline conditions generally used. Consequently, to our knowledge there have been no reports of the inclusion of large conjugated polymers directly during syntheses of orientationally ordered mesostructured composite materials.

Self-assembling porphyrin dye species present an interesting alternative to the use of large high-molecular-weight conjugated polymers, because they form extended ribbonlike J -aggregates under the acidic aqueous conditions used in the synthesis of mesostructured silicas. Though single porphyrin molecules are relatively small, the extended J -aggregates that they form possess many of the same or similar optical properties associated with large conjugated systems, including electron delocalization and the corresponding delocalization of excitons following photoexcitation. For example, it has been shown that tetrakis(4-sulfonatophenyl)porphyrin ($\text{H}_2\text{TPPS}_4^{2-}$) species form J -aggregates of between 10^1 and 10^5 molecules as a result of intermolecular π - π interactions between stacked aromatic groups and electrostatic interactions among oppositely charged moieties.³²⁻³⁴ For the case of TPPS₄ under acidic conditions, two pyrrole moieties in the central porphyrin macrocycle become

protonated to positively charged $-\text{NH}^+$ groups that interact with negatively charged terminal SO_4^- groups of two adjacent $\text{H}_2\text{TPPS}_4^{2-}$ molecules, as illustrated in Figure 1a,b.^{33,35,36} The mean length of such J -aggregates depends critically on the solution conditions, especially on pH and ionic strength.^{32,37} The resulting J -aggregates are of interest as models for photosynthesis and because of potential applications in nano-optoelectronics. By synthesizing mesostructured materials under conditions in which the host matrix and the porphyrin J -aggregates simultaneously self-assemble, it is possible to circumvent several of the difficulties associated with the incorporation of large chromophores with anisotropic optical properties.

Here, mesostructured inorganic-organic materials containing aligned coassembled J -aggregates of porphyrin dyes are described, including the measurement and control of J -aggregate distributions in orientationally ordered thin films. Rather than infiltrating the dye guest species into a previously calcined mesostructured host powder,^{38,39} however, the TPPS₄ J -aggregates are incorporated by direct coassembly from acidic solution in the presence of amphiphilic mesostructure-directing block copolymer species and network-forming silica species. This leads to the formation of mesostructured block copolymer/silica composite materials containing coassembled and co-orientationally ordered porphyrin J -aggregates. Moreover, by using a combination of two-dimensional (2D) solid-state NMR spectroscopy correlation techniques, the locations of the self-assembled J -aggregates within the PEO corona regions of the silica-block copolymer mesostructures are established [Figure 1c].

Experimental Section

Sample Preparation. Transparent mesostructured block copolymer/silica composites were synthesized by using acidic

silica sol–gel solutions containing nonionic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO₂₀PO₇₀–EO₂₀, Pluronic P123, BASF USA) amphiphilic triblock copolymers. In a typical synthesis, 1.7 g of tetraethoxysilane (TEOS, Aldrich, St. Louis, MO) was hydrolyzed in an acidic solution (pH 2.0, 1.0 g of ethanol, 0.9 g of water) containing the desired amount of *meso*-tetra(4-sulfonatophenyl)porphyrin dihydrochloride (H₄TPPS₄H₂Cl₂, Frontier Scientific, Logan, UT) previously dissolved in slightly basic solution (pH ~8) to create predominantly monomeric dye species. To this solution was added 0.47 g of EO₂₀PO₇₀EO₂₀ (corresponding to a volume fraction of ~47%) dissolved in 2.3 g of ethanol. Prior to the formation of the *J*-aggregates, the porphyrin molecules are highly soluble in aqueous solutions and small enough (~2 nm) to be easily accommodated in the ca. 8-nm-diameter mesochannels. Alternatively, the dye–silica solution was used without addition of the block copolymer to produce an amorphous silica glass host matrix. Under acidic conditions, the porphyrin molecules are predominantly protonated at the two macrocycle pyrrole sites [Figure 1a] and the sulfonated groups are ionized, as represented by the shorthand notation “H₂TPPS₄²⁻”. The resulting solutions were spin-cast onto glass slides by using an apparatus based upon a design by Kobayashi,^{40,41} in which the spinning axis was perpendicular to the plane of the substrate, producing linear (as opposed to radial) outward flow. This resulted in mesostructured nanocomposite films with linear macroscopic orientational order, which after drying, were transparent and approximately 1 μm thick. By comparison, the radial flow pattern produced by a conventional spin coater led to dye–nanocomposite films that did not exhibit significant anisotropic optical absorption properties.

Sample Characterization. Small-angle X-ray scattering (SAXS) measurements were performed to determine the mesostructural ordering of the synthesized films. One-dimensional (1D) SAXS patterns were acquired using a Scintag X2 (Cu K_α radiation) powder diffractometer. Transmission 2D SAXS experiments were also performed using Cu K_α radiation (1.54 Å), generated with a fine focus (0.2 mm) Rigaku rotating-anode generator and detected by a Bruker HI-STAR multiwire area detector (11-cm-diameter active area). Mesostructural ordering of the materials was confirmed using a FEI Tecnai G2 Sphera transmission electron microscope (TEM) operating at 200 kV.

The degrees of alignment of the included TPPS₄ *J*-aggregates in the thin films were determined by comparing the absorption of light polarized perpendicular to the spin-coating direction to that of light polarized parallel. These anisotropic optical measurements were conducted on a home-built spectrometer consisting of a broad-band light source and a CCD detector with an integrated grating to allow observation of wavelengths between 200 and 850 nm. The light was collected by using an optical fiber and, for linear dichroism measurements, passed through a linear polarizer before being focused onto the sample. The transmitted light was then focused into a second optical fiber connected to the CCD camera. For the optical studies, a dye loading of 1 wt % H₂TPPS₄²⁻ was used to compare mesostructured composites and amorphous silica glass as host matrices; films of the latter tended to phase-separate macroscopically and produce large dye aggregates when concentrations above 1 wt % H₂TPPS₄²⁻ were used.

Molecular-level compositions and structures of the composite materials were characterized by 1D and 2D solid-state nuclear magnetic resonance (NMR) spectroscopy under conditions of magic-angle spinning (MAS) at room temperature. All NMR experiments were carried out on a Varian Infinity Plus spec-

trometer operating at 499.67 MHz for ¹H and 125.66 MHz for ¹³C, with proton field strengths of 100 kHz. ¹H and ¹³C chemical shifts were referenced according to previous experiments on mesostructured block copolymer silica powders.¹⁵ A dye loading of 5 wt % H₂TPPS₄²⁻ was used for the NMR studies to increase ¹H and ¹³C NMR signal intensities. The amount of dye incorporated over the loading range used in this study (1–5 wt %) did not affect the hexagonal mesostructure nor significantly influence the optical properties of the silica–block copolymer–H₂TPPS₄²⁻ composite, as evidenced by X-ray diffraction and optical absorption measurements. For fast ¹H MAS studies, polycrystalline acidic H₄TPPS₄H₂Cl₂ was used as received.

To determine the locations of the included porphyrin guest species with respect to the poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) components of the composite host matrix, it was necessary to remove the mesostructured thin films from their glass substrates mechanically. This was not anticipated to have any effect on molecular-level structures, compositions, or the distributions of guest species within the mesostructured composites. The resulting powders were packed into 4-mm MAS rotors for the ¹³C{¹H} heteronuclear correlation experiments or 1.8-mm MAS rotors for the double-quantum ¹H–{¹H} homonuclear correlation experiments under fast (45 kHz) MAS conditions. Because of the large homonuclear ¹H–¹H dipole–dipole couplings present in TPPS₄ *J*-aggregates, fast sample spinning (45 kHz) was necessary to obtain resolved 2D ¹H{¹H} double-quantum correlation spectra. This was achieved by using a home-built 1.8 mm MAS probe head⁴² and a pulsed multiple-quantum recoupling sequence.⁴³ ¹³C{¹H} heteronuclear chemical-shift correlation (HETCOR) NMR experiments could not be carried out at these fast spinning rates, because of insufficient ¹³C signal intensity at natural abundance (1.1% ¹³C), due to the limited sample volume associated with the small-diameter rotors required to achieve such high rotation frequencies. Instead, the ¹³C{¹H} HETCOR experiments were performed using a 4-mm MAS probe head, which provided larger sample volumes and adequate sensitivity for the dilute ¹³C spins, though it required slower MAS spinning frequencies (12 kHz). Homonuclear phase-modulated Lee–Goldberg decoupling⁴⁴ (100 kHz) on the protons was applied during the evolution period of the ¹³C{¹H} heteronuclear correlation (HETCOR)^{45,46} experiments to achieve well-resolved 2D spectra and enable observation of the ¹H resonances associated with the TPPS₄ dye species.

Results and Discussion

Anisotropic Optical Properties of H₂TPPS₄²⁻ *J*-Aggregates in Mesostructured Host Films. Confinement of ribbonlike *J*-aggregates formed by intermolecular self-assembly of H₂TPPS₄²⁻ porphyrin dye species under acidic conditions within the channels of an aligned mesostructured block copolymer/silica composite is expected to result in a material with anisotropic optical properties. In the absence of included dye guest species, lamellar, hexagonal, and cubic films can be synthesized by varying the volume ratio between the block copolymer component and the silica precursor in the spin-coating solution.¹² The range of block copolymer-to-silica volume ratios for which hexagonal films have been obtained in the absence of included guest species is relatively wide (0.40–0.55). By choosing a block copolymer volume fraction in the center of this relative concentration regime (~0.47), the addition of up to 5 wt %⁴⁷ H₂TPPS₄²⁻ was not expected to affect the phase behavior sufficiently to prevent the formation of a hexagonal mesostructure. This was confirmed by the 1D SAXS measurements shown

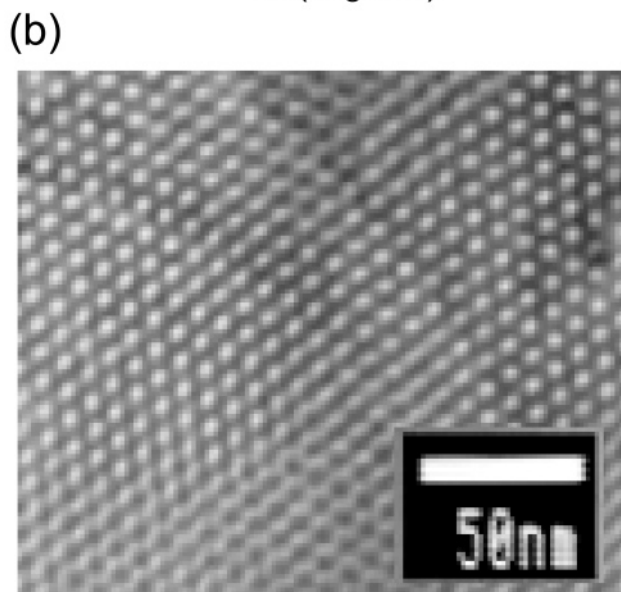
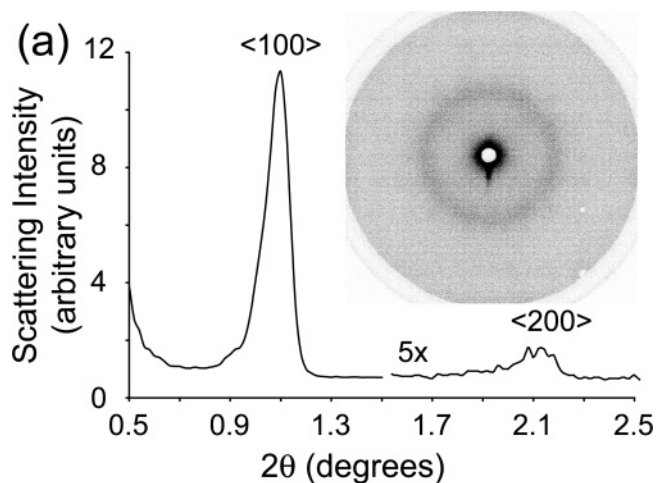


Figure 2. (a) One-dimensional small-angle X-ray scattering pattern obtained from a spin-cast 1- μm -thick 47 vol % (46 wt %) P123 triblock copolymer/silica thin film containing 5 wt % $\text{H}_2\text{TPPS}_4^{2-}$. The observed 2θ reflections at 1.05° and 2.10° correspond to d -spacings of 8.4 and 4.2 nm, respectively, consistent with a hexagonal phase in which the hydrophobic PPO cylinders lie in the plane of the substrate. The inset shows a 2D SAXS pattern obtained from the film prior to removal from the glass substrate. (b) Representative transmission electron micrograph showing the high extent of hexagonal ordering present in the composite film.

in Figure 2a. Both the $\langle 100 \rangle$ and $\langle 200 \rangle$ reflections are clearly observed, with a d_{100} -spacing of approximately 8.4 nm that corresponds well with previous reports in the literature.¹² The formation of a highly ordered hexagonal mesophase was confirmed by transmission electron microscopy, as shown in Figure 2b. The absence of a $\langle 110 \rangle$ reflection in the 1D SAXS pattern is indicative of alignment of the hexagonally ordered PPO cylinders within the plane of the film, although the distributions of cylinder orientations within this plane may be transversely isotropic. This is confirmed by 2D SAXS measurements of the films conducted in transmission mode, a representative diffraction pattern of which is shown as an inset in Figure 2a, which reveals diffuse rings (rather than distinct spots) with the same d_{100} - and d_{200} -spacings as in the 1D SAXS pattern above.

The optical properties of dye species are a sensitive probe of their environment, and in the case of the porphyrin TPPS_4 , UV–vis absorption spectra are sensitive to the formation of extended

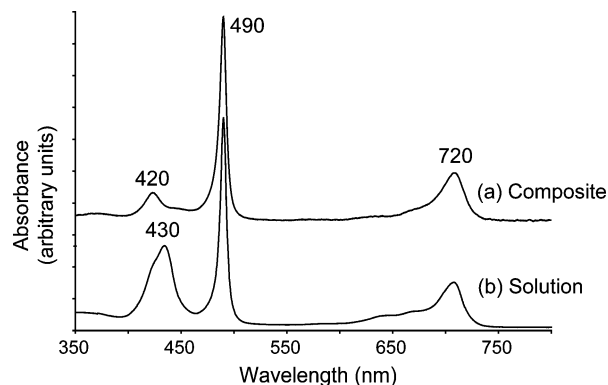


Figure 3. UV–visible light absorption spectra obtained for (a) 1 wt % $\text{H}_2\text{TPPS}_4^{2-}$ in a hexagonally mesostructured silica–block copolymer thin film ($\sim 1 \mu\text{m}$ thick) containing 47 vol % P123 and (b) 10 mM TPPS_4 (as $\text{H}_2\text{TPPS}_4^{2-}$) in aqueous acidic solution (pH 2) at room temperature. The narrow peaks observed for the composite film in (a) suggest well-formed J -aggregates that are stabilized against further aggregation by the mesostructured host matrix.

J -aggregates.^{33,36,48} Figure 3 shows optical absorption spectra acquired from a 1 wt % $\text{H}_2\text{TPPS}_4^{2-}$ -doped mesostructured silica–block copolymer composite film (47 vol % P123) [Figure 3a] and for a comparable concentration (10 mM) of $\text{H}_2\text{TPPS}_4^{2-}$ dissolved in an aqueous acidic (pH 2) solution [Figure 3b]. For both samples, a peak associated with the electronic transition of $\text{H}_2\text{TPPS}_4^{2-}$ to its first excited state is observed at 720 nm. More interestingly, a sharp J -band is also clearly seen at 490 nm for both the $\text{H}_2\text{TPPS}_4^{2-}$ -containing solution and composite film. This band arises from excitonic coupling between transition dipoles aligned longitudinally along the axes of the J -aggregates formed from the self-assembly of the $\text{H}_2\text{TPPS}_4^{2-}$ molecules.^{33,48} The additional band observed at 420 nm in the film most likely arises from the second transition dipole present in the chromophore, which is aligned perpendicular to the first dipole.³³ In solution, a set of overlapping absorption bands is observed between approximately 420 and 430 nm. These bands contain contributions from the transition dipoles oriented perpendicular to the long axes of individual J -aggregates, along with face-to-face (H -aggregate-like) stacking of J -aggregate bundles.^{34,48–50}

The relative intensities of the different optical absorption bands at 420, 430, and 490 nm in Figure 3 yield insight into the interactions among different J -aggregate species. Specifically, the much higher relative intensity of the 420–430 nm band versus that at 490 nm in the solution-state optical absorption spectrum [Figure 3b], compared to that for the composite film [Figure 3a], suggests that larger bundles of mutually interacting J -aggregates form in aqueous acidic solution under otherwise equivalent pH 2 conditions. This is consistent with our observations and previous reports,⁴⁸ that this and similar $\text{H}_2\text{TPPS}_4^{2-}$ solutions (in the absence of any codissolved polymer species) form gel-like states after standing for several days, even at concentrations of only 5 mM $\text{H}_2\text{TPPS}_4^{2-}$. In contrast, the presence of mesostructural ordering in the composite film allows J -aggregates to be formed, but apparently prevents their (generally undesirable) further aggregation into larger multiaggregate bundles. Furthermore, the narrow absorption peaks observed in Figure 3a for the film suggest a relatively homogeneous distribution of aggregate sizes and environments that remain stable for at least 3 months. These findings are similar to previous reports of the enhanced stabilities and optical properties of unaggregated, unaligned nonionic tetraphenylporphyrin molecules incorporated into mesostructured block copolymer/silica composites.⁷

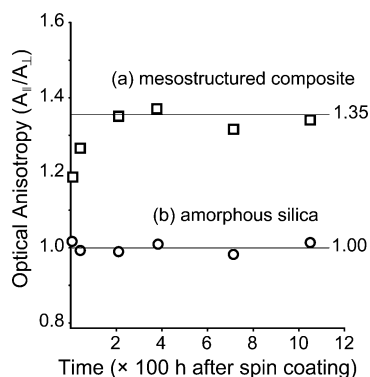


Figure 4. Anisotropic optical absorption measured for the 490 nm band for 1 wt % $\text{H}_2\text{TPPS}_4^{2-}$ *J*-aggregates incorporated into (a) a $\sim 1\text{-}\mu\text{m}$ -thick hexagonally mesostructured silica/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (47 wt % P123) composite film [Figure 3a] and (b) an amorphous silica glass film. Optical anisotropy is defined as the ratio of absorption of light polarized parallel to the spin-coating direction ($A_{||}$) versus that polarized perpendicular (A_{\perp}). The solid lines represent the mean optical anisotropy observed for the two different materials between 200 and 1200 h after spin coating. The dye-doped mesostructured film exhibits substantial optical anisotropy, unlike the silica glass film, which does not.

As mentioned above, the 490-nm band observed in the UV–vis absorption spectra arises from a transition dipole moment that is aligned with the long axes of the *J*-aggregates formed from the self-assembly of the $\text{H}_2\text{TPPS}_4^{2-}$ molecules.³³ It thus can serve as a good indicator of the degree to which the *J*-aggregates are aligned in different host media. To determine the influence of the mesostructured composite host on the formation and stability of orientationally ordered $\text{H}_2\text{TPPS}_4^{2-}$ *J*-aggregates, the absorption of light polarized parallel ($A_{||}$) and perpendicular (A_{\perp}) to the spin-coating direction were measured and compared for $\text{H}_2\text{TPPS}_4^{2-}$ incorporated into an orientationally ordered block copolymer/silica composite film and into an amorphous silica glass film [Figure 4]. For films containing aligned *J*-aggregates, the absorption of light polarized parallel to the long axis of the *J*-aggregates is expected to be greater than that of light polarized perpendicular to this axis,⁴¹ yielding an optical anisotropy (defined as $A_{||}/A_{\perp}$) greater than unity. As shown in Figure 4 for an amorphous 1 wt % $\text{H}_2\text{TPPS}_4^{2-}$ -doped silica glass film containing no mesostructure-directing block copolymer species, a mean optical anisotropy value of unity (i.e., isotropic optical absorption) was observed for the 490-nm band at all times after the spin-coating process. This indicates that the *J*-aggregates present in this amorphous silica host are oriented stably and (at least transversely) isotropically in the plane of the non-mesostructured film.⁵¹

By comparison, for the same hexagonally mesostructured $\text{H}_2\text{TPPS}_4^{2-}$ -containing composite films as discussed above, an initial optical anisotropy value of 1.2 was measured for the 490-nm absorption band immediately after spin coating. After 200 h, the optical anisotropy was moreover observed to increase to a higher mean value of 1.35, reflecting further aggregation of the porphyrin dyes molecules to produce longer and/or additional *J*-aggregates. In aqueous solutions, the aggregation of TPPS_4 has been shown to occur on time scales of several hours,³⁷ and the mobility of the dye species solubilized in the mesostructured composite film is expected to be lower, leading to even slower aggregation kinetics. It is interesting to note that the band at 490 nm shows preferential absorption of light polarized parallel to the spin-coating direction, while the 420-nm bands shows preferential absorption of light with perpendicular polarization. This is consistent with the 420-nm band arising from transition dipoles that are oriented perpendicular to those associated with

the 490-nm band, which are oriented along the long axes of the included *J*-aggregates. Furthermore, the optical anisotropy value measured at 420 nm was 0.85, close to the reciprocal value ($1/0.85 = 1.18$) of that measured at 490 nm (1.35) and consistent with two orthogonal transition dipoles associated with the same aligned *J*-aggregates. Similar optical anisotropy values were measured for identically processed films containing up to 5 wt % $\text{H}_2\text{TPPS}_4^{2-}$, which also displayed substantially higher optical absorbances, consistent with similar *J*-aggregate alignment at higher porphyrin loadings. The observed anisotropic optical absorption compares well to previous studies using calcined mesostructures as alignment media for postsynthetically incorporated and unaggregated cyanine dyes.¹ The mesostructured *J*-aggregate-containing composite films and their orientational ordering are stable over prolonged periods of time, with no loss of alignment detected over a period of at least 3 months, within the sensitivity limits of the optical anisotropy measurements.

The bulk anisotropy observed ($A_{||}/A_{\perp} = 1.35$) is expected to be limited by molecular disorder of unaggregated porphyrin molecules or within individual *J*-aggregates, distributions of *J*-aggregate alignments within their ordered host mesochannels, or imperfect alignments of the mesochannels themselves. The use of aligned substrates, for example rubbed polyimide films,^{25,26} may present additional opportunities for increasing the extent of orientational ordering achievable for mesostructured silica films and consequently also for included $\text{H}_2\text{TPPS}_4^{2-}$ *J*-aggregates. This may facilitate the preparation of films with optical anisotropies approaching the high values (~ 10) reported for highly aligned polymer films containing pseudo-isocyanine *J*-aggregates.⁵²

Dye Interactions and Locations in a Mesostructured Composite Host. The alignment, stability, and photophysical response properties of dye-containing composite materials depend crucially on the molecular interactions among the dye species, block copolymer components, solvent(s), and silica network. The importance of acidic solution conditions for the formation of $\text{H}_2\text{TPPS}_4^{2-}$ *J*-aggregates has been previously discussed above. In addition, the balance of interactions are expected to differ between different *J*-aggregate guests and between the *J*-aggregates and the different PEO (more hydrophilic) and PPO (more hydrophobic) moieties of the structure-directing block copolymer species⁷ or the silica framework. Such interactions establish whether and to what extent the dye species coassemble into *J*-aggregates within the mesostructured composite hosts and, if they do, with which host components they may preferentially associate within the mesoscale channels. Such considerations are known to affect the optical properties of dye guest species incorporated in nanostructured composite host matrixes, but have been challenging to establish in solid-state materials.^{7,18,19,53,54}

Speculations about where guest molecules may preferentially reside in mesostructured composites can be made by considering their relative hydrophilicities and hydrophobicities with respect to the block copolymer and silica network components. However, for amphiphilic guest molecules such as the porphyrins used here, establishing species location(s) is difficult without direct spectroscopic evidence, for which there are unfortunately few suitable methods. Such difficulties have been principally due to often severe sensitivity (low dye concentrations) and/or resolution limitations (overlapping signals) for many spectroscopic characterization methods, including optical and magnetic resonance techniques. Differences in the optical absorption spectra of dye species in block copolymer/silica composites may

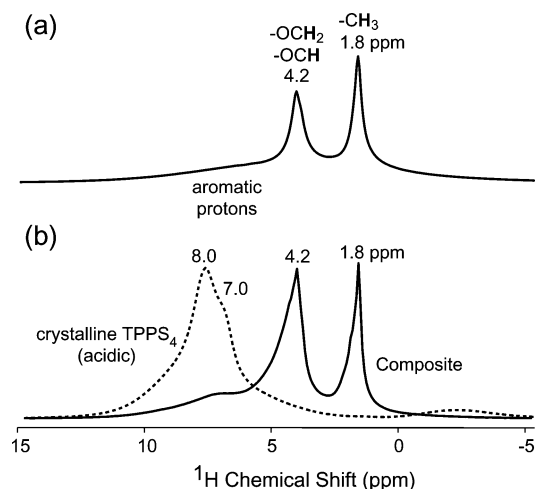


Figure 5. Single-pulse ^1H MAS spectra obtained at room temperature for powders of hexagonally mesostructured silica/EO₂₀PO₇₀EO₂₀ (47 wt % P123) composite films containing 5 wt % H₂TPPS₄²⁻ acquired at different sample spinning frequencies: (a) 12 and (b) 45 kHz. The samples were obtained by mechanically removing $\sim 1\text{-}\mu\text{m}$ -thick films [Figure 2] from their glass substrates. For comparison, a single-pulse ^1H MAS spectrum obtained for crystalline acidic H₄TPPS₄H₂Cl₂ at a spinning frequency of 45 kHz under identical conditions is shown as a dotted line in (b).

in favorable cases allow solubilization in one component to be distinguished from other local environments, when compared to spectra obtained from homopolymer solutions or films. However, for relatively similar polymer components, such as PEO and PPO, this is unfortunately often not possible.⁷

NMR spectroscopy is a powerful tool for probing molecular-level interactions that can be used to distinguish the locations of guest molecules with respect to the components of their heterogeneous host matrix. In practice, both signal sensitivity and resolution challenges are frequently present, though these can often be surmounted with sufficiently high concentrations of NMR-active species of interest and using powerful multidimensional NMR correlation methods. This includes signals that can be observed for NMR-active nuclei associated with the self-assembling host components, along with the optically responsive guest species of direct interest, in solutions^{55,56} or solid-state materials. As a result, it is possible to correlate signals arising from the host matrix, e.g., the block copolymer or silica species, with those arising from the included dye guest species.

Specifically, two-dimensional $^1\text{H}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR correlation techniques allow interactions to be measured between the porphyrin *J*-aggregates and the block copolymer components of the mesostructured composite host matrix. Because homonuclear dipole–dipole couplings between protons in the ring structures of the porphyrin *J*-aggregates [Figure 1] are large (ca. 40–50 kHz), even previous solution-state studies of H₂TPPS₄²⁻ *J*-aggregates have yielded at best poorly resolved proton spectra.⁵⁷ One means of reducing the broadening influence from such large homonuclear dipolar couplings in solid-state NMR is the use of magic-angle sample spinning at sufficiently high spinning speeds to average these spatially dependent interactions. For systems like the H₂TPPS₄²⁻ *J*-aggregates with strong ^1H – ^1H couplings, this typically requires much higher MAS frequencies than are conventionally used. Figure 5 shows, for example, ^1H MAS spectra obtained at different spinning rates for a powder sample prepared from a hexagonally mesostructured silica/EO₂₀PO₇₀EO₂₀ (47 vol % P123) composite film containing 5 wt % H₂TPPS₄²⁻.⁵⁸ At spinning rates of 12 kHz, two distinct ^1H signals are observed [Figure 5a], one at 1.8 ppm corresponding

to the $-\text{CH}_3$ protons associated with the PPO moieties of the P123 triblock copolymer species and one at 4.2 ppm corresponding to overlapping and unresolved signals of the $-\text{OCH}_2-$ protons of the PEO moieties and the $-\text{OCH}_2-$ and $-\text{OCH}-$ protons of the PPO moieties also of the triblock copolymer. A very broad peak is discernible between 5 and 9 ppm, attributed to the aromatic protons of the H₂TPPS₄²⁻ dye species. At this moderate MAS spinning rate (12 kHz), line broadening from dipole–dipole interactions between the various proton moieties of the self-assembled porphyrin dye molecules is insufficiently reduced to distinguish their signals from those of hydroxyl species (associated with adsorbed water or framework silanol groups) that are expected in this region of the spectrum.¹⁵

Under fast MAS conditions, however, substantially improved spectral resolution is achieved, especially for strongly dipole–dipole-coupled proton species. For example, at a sample spinning frequency of 45 kHz, a reduction of the line width associated with the aromatic moieties of the TPPS₄¹H species is observed. The effectiveness of high MAS spinning rates (45 kHz) for narrowing the ^1H line widths in the region 5–9 ppm establishes the existence of large ^1H – ^1H dipolar couplings associated with these moieties, consistent with those expected for aromatic species and atypical of those associated with isolated surface silanol groups, which are generally much smaller. As shown in Figure 5b, in addition to the same signals at 1.8 and 4.2 ppm from the P123 proton moieties (whose line shapes reflect heterogeneous distributions of local structural and dynamical environments¹⁵), a distinct, but still broad, peak is clearly observed at ~ 7 ppm. This signal is similar to that present in the ^1H MAS spectrum [Figure 5b, dotted line] of pure crystalline acidic H₄TPPS₄H₂Cl₂ obtained under the same conditions (45 kHz, room temperature), which shows a broad peak at 8 ppm with a distinct shoulder at ~ 7 ppm. The additional spectral features arise at least in part from the greater extent of protonation of the sulfonated groups in the crystalline H₄TPPS₄H₂Cl₂ solid, compared to the H₂TPPS₄²⁻ guests in the mesostructured composite. However, even with the improved resolution obtained at 45 kHz MAS, on the basis of these 1D ^1H spectra alone, it is not possible to determine where the dye species are localized with respect to the PEO or PPO triblock copolymer components.

Nevertheless, the use of fast MAS conditions, in combination with 2D double-quantum (DQ) NMR correlation methods, yields crucial resolution enhancements that allow correlated nuclear spin interactions to be measured and identified and thus important intermolecular interactions to be established. Since both the excitation and subsequent reconversion periods of 2D double-quantum MAS experiments rely on the presence of through-space dipole–dipole couplings between spins, mutually correlated signal intensity is only observed for species that are in close spatial proximity (ca. ≤ 0.35 nm for ^1H).⁵⁹ The $^1\text{H}\{^1\text{H}\}$ DQ-MAS spectrum acquired at 45 kHz for the 5 wt % H₂TPPS₄²⁻-containing mesostructured silica/block copolymer composite is shown in Figure 6. The signals along the dotted diagonal line shown in the spectrum correspond to ^1H spins correlated to other identical nearby ^1H spins via their mutual dipole–dipole couplings. In these cases, each spin has the same isotropic chemical shift as its coupled partner, with the double-quantum shift in the vertical dimension corresponding to the sum of the individual single-quantum shifts of the two dipolar-coupled sites. For example, in the 2D $^1\text{H}\{^1\text{H}\}$ DQ-MAS spectrum of Figure 6, correlated intensity along the diagonal is observed for signals associated with the $-\text{CH}_3$ protons (1.8 ppm single-quantum chemical shift) of the PPO and those (unre-

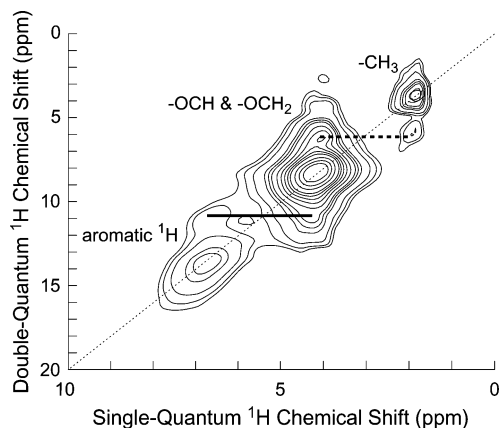


Figure 6. Solid-state double-quantum $^1\text{H}\{^1\text{H}\}$ correlation NMR spectrum acquired at room temperature under fast MAS conditions at 45 kHz for a powder obtained from hexagonally mesostructured silica/ $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (47 wt % P123) thin films containing 5 wt % $\text{H}_2\text{TPPS}_4^{2-}$ [Figures 2 and 5b]. Intensity correlations that arise from dipole–dipole interactions between the $-\text{CH}_3$ and alkylene oxide $-\text{OCH}_2-$ or $-\text{OCH}-$ moieties of the P123 triblock copolymer species are indicated by the dotted line, while correlations corresponding to interactions between the aromatic protons of the TPPS₄ dye species and the alkylene oxide protons of the P123 are indicated by the solid line.

solved) from the alkylene oxide $-\text{OCH}_2-$ protons of the PEO and the $-\text{OCH}_2-$ and $-\text{OCH}-$ protons of the PPO moieties (4.2 ppm single-quantum chemical shift). Such intensity correlations are consistent with the close spatial proximities of these moieties to other identical groups along the extended PPO and PEO segments of the structure-directing P123 triblock copolymer species.

By comparison, signals that appear symmetrically and horizontally on either side of the diagonal line in 2D $^1\text{H}\{^1\text{H}\}$ double-quantum MAS spectra correspond to dipole–dipole couplings between nuclei with different single-quantum shifts, which are thus associated with chemically and/or structurally distinct sites. In Figure 6, for example, such *off*-diagonal correlated intensity is observed (horizontal dashed line) between the $-\text{CH}_3$ PPO protons (1.8 ppm, single-quantum shift) and unresolved signals associated with the $-\text{OCH}_2-$ and $-\text{OCH}-$ protons of the PPO moieties and the $-\text{OCH}_2-$ PEO protons (4.2 ppm, single-quantum shift), both with 2D intensity maxima at double-quantum shifts⁶⁰ of 6.0 ppm. Such intensity correlations are again consistent with the close mutual spatial proximities of these different covalently bonded PPO moieties associated with the P123 triblock copolymer species.

More importantly, however, correlated intensity in the 2D $^1\text{H}\{^1\text{H}\}$ DQ-MAS spectrum of Figure 6 is also observed between the alkylene oxide proton signals and protons associated with the porphyrin dye species. Specifically, significant and symmetric *off*-diagonal 2D intensity is observed along the solid line at a double-quantum shift of 11.1 ppm and corresponding single-quantum signals at 4.2 ppm ($-\text{OCH}_2-$, $-\text{OCH}-$ P123 moieties) and 6.9 ppm, associated with the aromatic protons of the included $\text{H}_2\text{TPPS}_4^{2-}$ dye species. These single-quantum-shift projections correspond well with those observed for the triblock copolymer and porphyrin species in the accompanying single-pulse ^1H MAS spectra discussed in Figure 5b above. Their corresponding intensity correlations establish the close spatial proximity of a significant fraction of the $\text{H}_2\text{TPPS}_4^{2-}$ dye molecules to the P123 triblock copolymer species. Furthermore, the dye species appear to associate principally with the PEO $-\text{OCH}_2-$ moieties and not the more hydrophobic PPO blocks, as can be concluded from the absence of correlated 2D signal

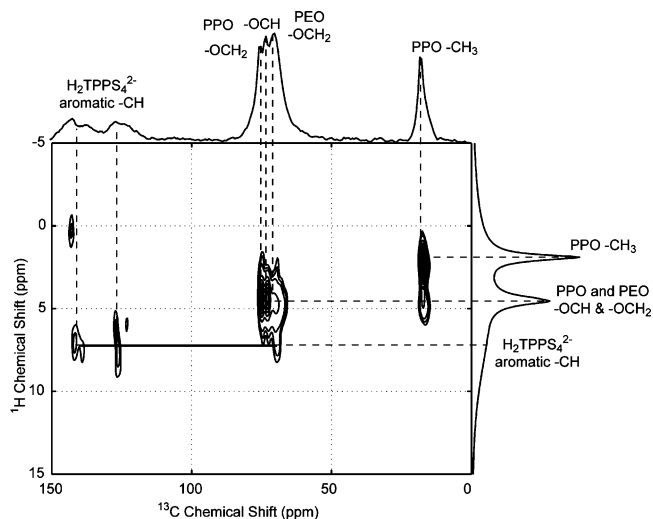


Figure 7. Solid-state $^{13}\text{C}\{^1\text{H}\}$ heteronuclear chemical-shift correlation NMR spectrum acquired under conditions of MAS (12 kHz), proton decoupling (100 kHz), and at room temperature for the same powder obtained from hexagonally mesostructured $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ /silica thin films containing 5 wt % $\text{H}_2\text{TPPS}_4^{2-}$ as used in Figures 2, 5, and 6. For the mixing time used (5 ms), all of the ^{13}C and ^1H resonances are clearly resolved and assigned as indicated in the accompanying single-pulse 1D MAS spectra along their respective axes. Most importantly, a clear $^{13}\text{C}\{^1\text{H}\}$ intensity correlation (solid line) is observed between the aromatic ^1H signals associated with the $\text{H}_2\text{TPPS}_4^{2-}$ dye species and the ^{13}C signals from the $-\text{OCH}_2-$ groups associated with the PEO moieties of the block copolymer.

intensity involving the well-resolved PPO $-\text{CH}_3$ groups: no correlated signal intensity is detected in Figure 6 at single- and double-quantum-shift values of 1.8 and 8.7 ppm, respectively, as would otherwise be the case. Consequently, the 2D $^1\text{H}\{^1\text{H}\}$ DQ-MAS correlation data thus suggest that the $\text{H}_2\text{TPPS}_4^{2-}$ *J*-aggregates interact more strongly with the more hydrophilic PEO blocks.

To determine unambiguously whether the $\text{H}_2\text{TPPS}_4^{2-}$ dye molecules associate with the PEO and/or PPO moieties of the P123 triblock copolymer species, homonuclear-decoupled 2D $^{13}\text{C}\{^1\text{H}\}$ heteronuclear chemical-shift correlation (HETCOR) experiments were conducted to exploit the superior resolution of ^{13}C signals. The substantially larger ^{13}C chemical shift range, compared to ^1H , allows overlapping ^1H signals associated with the different $-\text{OCH}-$ and $-\text{OCH}_2-$ moieties of the PEO and PPO P123 blocks to be distinguished by correlating their respective isotropic ^1H and ^{13}C chemical shifts under conditions of magic-angle spinning. For sufficiently long $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization (CP) contact times, correlated $^{13}\text{C}\{^1\text{H}\}$ signal intensity would be expected not only from covalently bonded $^1\text{H}-^{13}\text{C}$ spin pairs, but also from spatially proximate though noncovalently bonded ^1H and ^{13}C nuclei, including those involved in interactions between porphyrin guests and the P123 host species.

In the 2D $^{13}\text{C}\{^1\text{H}\}$ HETCOR spectrum shown in Figure 7, it is possible to resolve clearly the four different proton moieties associated with the P123 triblock copolymer, along with the extents to which they each interact with the $\text{H}_2\text{TPPS}_4^{2-}$ dye species. For example, the $-\text{OCH}_2-$ moieties of the PEO blocks give rise to 2D signal intensity at 4.2 ppm in the ^1H dimension and 72 ppm in the ^{13}C dimension, which is distinct from those associated with the PPO blocks. By comparison for the PPO moieties, correlated 2D signal intensities are observed for the $-\text{OCH}_2-$ groups at 4.2 ppm ^1H and 76 ppm ^{13}C , for the $-\text{OCH}-$ groups at 4.2 ppm ^1H and 74 ppm ^{13}C , and for the

—CH₃ groups at 1.8 ppm ¹H and 17 ppm ¹³C. In addition to the signals associated with the triblock copolymer species, the H₂TPPS₄²⁻ dye molecules give rise to broad, partially resolved signals in the aromatic regions of the respective ¹H and ¹³C spectral dimensions, with 2D intensity correlations near 7 ppm ¹H and between 110 and 150 ppm ¹³C, which were not observed in 2D ¹³C{¹H} HETCOR spectra of similar, but undoped, mesostructured silica.¹⁵ The additional signal intensity observed at approximately 0.5 ppm in the ¹H dimension and 145 ppm in the ¹³C dimension likely results from protons associated with the phenyl groups that are positioned above the neighboring central porphyrin ring systems in the *J*-aggregates [Figure 1b]. Because the central porphyrin ring presents a large aromatic system, ring-current effects are anticipated that could account for the observed upfield shift.⁶¹ For the relatively long 5-ms CP contact time used here, 2D intensity correlations are observed between the —CH₃ groups and the —OCH₂— and —OCH— moieties of the PPO blocks, because of their close mutual spatial proximities. Specifically, 2D correlated intensity is observed in Figure 7 at a ¹H chemical shift of 4.2 ppm, corresponding to the —OCH— and —OCH₂— PPO protons, and a ¹³C chemical shift of 17 ppm, corresponding to the PPO —CH₃ carbon atoms, respectively. In addition, correlated signal intensities are resolved at 1.8 ppm ¹H, corresponding to the PPO —CH₃ protons, and 74 and 76 ppm ¹³C, corresponding to the PPO —OCH— and —OCH₂— carbon atoms. Consistent with this, no intensity correlations are observed between any of the PPO moieties and the H₂TPPS₄²⁻ dye species. In contrast, for the —OCH₂— moieties of the PEO blocks (72 ppm ¹³C), correlated 2D signal intensity is clearly measured with respect to the aromatic protons of the H₂TPPS₄²⁻ dye species (7 ppm ¹H), as indicated by the solid line in Figure 7. Taken together with the ¹H{¹H} DQ NMR experiments [Figure 6] discussed above, these results confirm and unambiguously establish that the H₂TPPS₄²⁻ porphyrin *J*-aggregates associate principally with the hydrophilic PEO blocks of the P123 triblock copolymer species. These structural results are summarized schematically in Figure 1c, which shows the locus of *J*-aggregate solubilization to be principally within the PEO corona regions of the mesostructured silica/PEO—PPO—PEO block copolymer composite, consistent with the ionicity of the H₂TPPS₄²⁻ guest species.

Conclusions

Orientationally ordered mesostructured block copolymer/silica thin films are shown to be suitable host matrixes for coassembling and aligning supramolecular porphyrin *J*-aggregates. Under acidic solution conditions and using a linear spin coater, 1- μ m-thick EO₂₀PO₇₀EO₂₀/silica composite films containing ~1–5 wt % H₂TPPS₄²⁻ porphyrin dye species were produced with high extents of long-range orientational and hexagonal mesostructural order. The mesostructured composite films provide high porphyrin solubilities (up to at least 5 wt %), allowing *J*-aggregates to coassemble within the mesoscale channels, while reducing the formation of undesirable *J*-aggregate bundles or agglomerations. In addition, the orientational ordering of the mesostructured silica host is also imparted on the included porphyrin *J*-aggregates. Overall optical anisotropies of ca. 1.35 were measured and found to be stable on time scales greater than several months.

The location of the included porphyrin dye species within the mesostructured composite host matrix is determined unambiguously by solid-state 2D ¹H{¹H} and ¹³C{¹H} NMR correlation methods. The location(s) of the dye guest species within such heterogeneous host matrixes is expected to play an

important role in their optical responses and stabilities, by influencing the local electronic environment, mobility, and anisotropy of the chromophore aggregates. The combination of ¹H{¹H} double-quantum NMR measurements under fast (45 kHz) MAS conditions and homonuclear-decoupled ¹³C{¹H} heteronuclear correlation NMR experiments establishes that the self-assembled H₂TPPS₄²⁻ *J*-aggregates preferentially associate with the hydrophilic PEO blocks of the structure-directing PEO—PPO—PEO triblock copolymer species. Such insights provide molecular-level design criteria for the rational modification of the host matrix and/or dye selection to direct the guest species into the local environment(s) desired and thus to optimize optical performance of the functionalized composite materials. Such approaches and methods are expected to be applicable generally to the preparation of mesostructured thin films with anisotropic optical properties and the characterization of optically responsive guest species within heterogeneous host matrixes. Greater control over the synthesis, processing, and photophysical properties of dye-containing mesostructured optical materials and devices, including higher dye loadings, improved stabilities, and anisotropic optical responses, are anticipated to result.

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References and Notes

- (1) Fukuoka, A.; Miyata, H.; Kuroda, K. *Chem. Commun.* **2003**, 284–285.
- (2) Marlow, F.; McGehee, M. D.; Zhao, D. Y.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1999**, *11*, 632–636.
- (3) Molenkamp, W. C.; Watanabe, M.; Miyata, H.; Tolbert, S. H. *J. Am. Chem. Soc.* **2004**, *126*, 4476–4477.
- (4) Wirnsberger, G.; Scott, B. J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **2000**, *12*, 1450–1454.
- (5) Wirnsberger, G.; Scott, B. J.; Stucky, G. D. *Chem. Commun.* **2001**, 119–120.
- (6) 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.
- (7) Melosh, N. A.; Steinbeck, C. A.; Scott, B. J.; Hayward, R. C.; Davidson, P.; Stucky, G. D.; Chmelka, B. F. *J. Phys. Chem. B* **2004**, *108*, 11909–11914.
- (8) Scott, B. J.; Wirnsberger, G.; Stucky, G. D. *Chem. Mater.* **2001**, *13*, 3140–3150.
- (9) Huo, Q. S.; Zhao, D. Y.; Feng, J. L.; Weston, K.; Buratto, S. K.; Stucky, G. D.; Schacht, S.; Schüth, F. *Adv. Mater.* **1997**, *9*, 974–978.
- (10) Lu, Y. F.; Ganguli, R.; Drewien, C. A.; Anderson, M. T.; Brinker, C. J.; Gong, W. L.; Guo, Y. X.; Soyez, H.; Dunn, B.; Huang, M. H.; Zink, J. I. *Nature* **1997**, *389*, 364–368.
- (11) Zhao, D.; Yang, P.; Melosh, N.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1998**, *10*, 1380–1385.
- (12) Alberius, P. C. A.; Frindell, K. L.; Hayward, R. C.; Kramer, E. J.; Stucky, G. D.; Chmelka, B. F. *Chem. Mater.* **2002**, *14*, 3284–3294.
- (13) Feng, P. Y.; Bu, X. H.; Stucky, G. D.; Pine, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 994–995.
- (14) Attard, G. S.; Glyde, J. C.; Goltner, C. G. *Nature* **1995**, *378*, 366–368.
- (15) Melosh, N. A.; Lipic, P.; Bates, F. S.; Wudl, F.; Stucky, G. D.; Fredrickson, G. H.; Chmelka, B. F. *Macromolecules* **1999**, *32*, 4332–4342.

- (16) Melosh, N. A.; Davidson, P.; Chmelka, B. F. *J. Am. Chem. Soc.* **2000**, *122*, 823–829.
- (17) Klok, H. A.; Lecommandoux, S. *Adv. Mater.* **2001**, *13*, 1217–1229.
- (18) Minoofar, P. N.; Dunn, B. S.; Zink, J. I. *J. Am. Chem. Soc.* **2005**, *127*, 2656–2665.
- (19) Minoofar, P. N.; Hernandez, R.; Chia, S.; Dunn, B.; Zink, J. I.; Franville, A. C. *J. Am. Chem. Soc.* **2002**, *124*, 14388–14396.
- (20) Onida, B.; Borello, L.; Fiorilli, S.; Bonelli, B.; Areat, C. O.; Garrone, E. *Chem. Commun.* **2004**, 2496–2497.
- (21) 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.
- (22) Firouzi, A.; Schaefer, D. J.; Tolbert, S. H.; Stucky, G. D.; Chmelka, B. F. *J. Am. Chem. Soc.* **1997**, *119*, 9466–9477.
- (23) Fukumoto, H.; Nagano, S.; Kawatsuki, N.; Seki, T. *Adv. Mater.* **2005**, *17*, 1035–1039.
- (24) Melosh, N. A.; Davidson, P.; Feng, P.; Pine, D. J.; Chmelka, B. F. *J. Am. Chem. Soc.* **2001**, *123*, 1240–1241.
- (25) Miyata, H.; Kuroda, K. *Chem. Mater.* **2000**, *12*, 49–54.
- (26) Miyata, H.; Noma, T.; Watanabe, M.; Kuroda, K. *Chem. Mater.* **2002**, *14*, 766–772.
- (27) Tolbert, S. H.; Firouzi, A.; Stucky, G. D.; Chmelka, B. F. *Science* **1997**, *278*, 264–268.
- (28) Yamauchi, Y.; Sawada, M.; Noma, T.; Ito, H.; Furumi, S.; Sakka, Y.; Kuroda, K. *J. Mater. Chem.* **2005**, *15*, 1137–1140.
- (29) Brinker, C. J.; Lu, Y. F.; Sellinger, A.; Fan, H. Y. *Adv. Mater.* **1999**, *11*, 579–585.
- (30) Schwartz, B. J.; Nguyen, T. Q.; Wu, J. J.; Tolbert, S. H. *Synth. Met.* **2001**, *116*, 35–40.
- (31) Tolbert, S. H.; Wu, J. J.; Gross, A. F.; Nguyen, T. Q.; Schwartz, B. J. *Microporous Mesoporous Mater.* **2001**, *44*, 445–451.
- (32) Koti, A. S. R.; Taneja, J.; Periasamy, N. *Chem. Phys. Lett.* **2003**, *375*, 171–176.
- (33) Ohno, O.; Kaizu, Y.; Kobayashi, H. *J. Chem. Phys.* **1993**, *99*, 4128–4139.
- (34) Pasternack, R. F.; Schaefer, K. F.; Hambright, P. *Inorg. Chem.* **1994**, *33*, 2062–2065.
- (35) Ribo, J. M.; Crusats, J.; Sagues, F.; Claret, J.; Rubires, R. *Science* **2001**, *292*, 2063–2066.
- (36) Sutter, T. P. G.; Rahimi, R.; Hambright, P.; Bommer, J. C.; Kumar, M.; Neta, P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 495–502.
- (37) Pasternack, R. F.; Fleming, C.; Herring, S.; Collings, P. J.; dePaula, J.; DeCastro, G.; Gibbs, E. J. *Biophys. J.* **2000**, *79*, 550–560.
- (38) Xu, W.; Guo, H. Q.; Akins, D. L. *J. Phys. Chem. B* **2001**, *105*, 7686–7689.
- (39) Xu, W.; Guo, H. Q.; Akins, D. L. *J. Phys. Chem. B* **2001**, *105*, 1543–1546.
- (40) Kobayashi, T. *J-Aggregates*; World Scientific Publishing: Singapore, 1996.
- (41) Misawa, K.; Ono, H.; Minoshima, K.; Kobayashi, T. *Appl. Phys. Lett.* **1993**, *63*, 577–579.
- (42) Samoson, A.; Tuhern, T.; Past, J. *J. Magn. Reson.* **2001**, *149*, 264–267.
- (43) Feike, M.; Demco, D. E.; Graf, R.; Gottwald, J.; Hafner, S.; Spiess, H. W. *J. Magn. Reson. Ser. A* **1996**, *122*, 214–221.
- (44) Vinogradov, E.; Madhu, P. K.; Vega, S. *Chem. Phys. Lett.* **1999**, *314*, 443–450.
- (45) Caravatti, P.; Braunschweiler, L.; Ernst, R. R. *Chem. Phys. Lett.* **1983**, *100*, 305–310.
- (46) Metz, G.; Wu, X. L.; Smith, S. O. *J. Magn. Reson. Ser. A* **1994**, *110*, 219–227.
- (47) The weight fraction of dye molecules in the final material was estimated based on the assumption of full condensation of the silica framework and evaporation of any solvent.
- (48) Ribo, J. M.; Crusats, J.; Farrera, J. A.; Valero, M. L. *J. Chem. Soc., Chem. Commun.* **1994**, 681–682.
- (49) Gandini, S. C. M.; Gelamo, E. L.; Itri, R.; Tabak, M. *Biophys. J.* **2003**, *85*, 1259–1268.
- (50) Maiti, N. C.; Mazumdar, S.; Periasamy, N. *J. Phys. Chem. B* **1998**, *102*, 1528–1538.
- (51) Optical anisotropy measurements on *J*-aggregate-containing thin films do not provide sufficient information to distinguish full 3D isotropy (*J*-aggregates oriented randomly even with in the plane of the substrate) from 2D isotropy (*J*-aggregates aligned parallel to the substrate, but randomly oriented within the plane of the substrate), because the probing light beam only carries polarization perpendicular to the direction of the beam.
- (52) Kobayashi, T.; Misawa, K. *J. Lumin.* **1997**, *72–74*, 38–40.
- (53) Fu, Y.; Ye, F. M.; Sanders, W. G.; Collinson, M. M.; Higgins, D. A. *J. Phys. Chem. B* **2006**, *110*, 9164–9170.
- (54) Hernandez, R.; Franville, A. C.; Minoofar, P.; Dunn, B.; Zink, J. I. *J. Am. Chem. Soc.* **2001**, *123*, 1248–1249.
- (55) Steinbeck, C. A.; Hedin, N.; Chmelka, B. F. *Langmuir* **2004**, *20*, 10399–10412.
- (56) Steinbeck, C. A.; Chmelka, B. F. *J. Am. Chem. Soc.* **2005**, *127*, 11624–11635.
- (57) Rubires, R.; Crusats, J.; El-Hachemi, Z.; Jaramillo, T.; Lopez, M.; Valls, E.; Farrera, J. A.; Ribo, J. M. *New J. Chem.* **1999**, *23*, 189–198.
- (58) The higher dye loading (5 wt %) was necessary to obtain a sufficient signal from the dye species to make these NMR studies feasible. In order to carry out the optical studies discussed above, a lower dye loading (1 wt %) was chosen to allow better comparison with non-mesostructured sol-gel silica in which concentrations above 1 wt % tended to lead to large (visible) dye aggregates. The amount of dye incorporated over the range 1–5 wt % did not affect the mesostructure of the silica-block copolymer composite as evidenced by X-ray diffraction.
- (59) Brown, S. P.; Emsley, L. Solid-State NMR. In *Handbook of Spectroscopy*; Gauglitz, G., Vo-Dinh, T., Eds.; Wiley: Weinheim, 2003.
- (60) Double-quantum coherences appear with a chemical shift in the double-quantum dimension that is the sum of the single-quantum chemical shifts of the two species involved.
- (61) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349–1383.