Light Harvesting by a Periodic Mesoporous Organosilica Chromophore**

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Light-harvesting antenna materials have received increased attention in recent years for use in the design of highly efficient photocatalysts, solar cells, and light-emitting devices.[1] A range of supramolecular materials, such as dendrimers,[2] organogels,[3] porphyrin arrays,[4] and photoactive polymers,[5] have been reported to display efficient light-harvesting and/or energy-transfer properties. However, the actual construction of devices and systems based on these materials has proven to be difficult owing to the limited degree of macroscale organization typically exhibited by these molecular systems. Calzaferri et al. recently reported a novel approach to construct devices with the desired light-harvesting antenna properties by designing a host–guest antenna system based on microparticulate single-crystal zeolite.[6] The macroscopic ordered porosity of zeolite causes the dye molecules to be aligned according to the one-dimensional pore channels, and the excitation energy of light absorbed by the zeolite crystals is transported by the dye molecules through the channels or from the injector molecules fixed at the entrances. The macroscopic organization of dye molecules using an ordered porous solid therefore represents a promising approach for attaining the desired macroscopic properties.[6, 7]

Periodic mesoporous organosilica (PMO), synthesized from up to 100 % organic-bridged alkoxysilane precursors ((R′O)$_3$Si−R−Si(OR′)$_3$) by surfactant-assisted supramolecular assembly, is a new class of hybrid organic–inorganic porous material in which the organic groups (R) are densely and covalently embedded within the framework forming the pore walls.[8] A number of PMOs with interactive bridging organic groups such as benzene,[9] biphenyl,[10] naphthalene,[11] and divinylbenzene,[12] have been found to exhibit crystal-like molecular-scale periodicity of the organic groups in the framework. PMOs can also be obtained as a transparent

film[13] or monolith[14] in addition to particle morphologies, presenting considerable advantages for device fabrication. Recently, the synthesis and optical properties of luminescent PMOs prepared from 100 % chromophore precursors were reported.[11,15–19] These fluorescent materials exhibit efficient light absorption owing to the dense packing of chromophores in the framework. The placement of chromophores within the PMO framework appears to be advantageous, as such luminescent PMOs allow chromophores to be located in two spatially separated regions, that is, in the framework and in the mesochannels.[19, 20] This configuration could potentially be exploited to promote the transfer of excitation energy from the framework donors to acceptors in the mesochannels (Figure 1). Such a scheme has great potential for enhancing
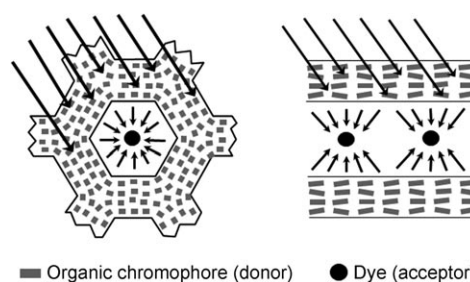

Figure 1. Schematic illustration of energy transfer from organic chromophores in the framework to dye in the mesochannels of PMO.

the luminescence of the dye doped in the channels through efficient energy transfer from the PMO framework. However, there have been very few reports on energy transfer from the framework to mesochannels in PMO materials. Mesostructured silica films bearing lanthanide complexes have been investigated, although the energy-transfer efficiency was found to be relatively poor.[21] Herein, highly efficient energy transfer from biphenyl in the PMO framework to a small amount of coumarin 1 dye doped in the mesochannels is demonstrated. In this configuration, light energy absorbed by approximately 125 biphenyl groups in the framework is funneled to a single coumarin 1 molecule in the channel with almost 100 % quantum efficiency, resulting in significant enhancement of emission from the coumarin 1 dye. This result demonstrates the potential of PMO as a light-harvesting scaffold for light-emitting devices and photoreaction systems.

The biphenyl-bearing PMO powder examined herein has a two-dimensional hexagonal lattice with a lattice constant of $a = 5.4$ nm and pore diameter of $d_a = 3.5$ nm (obtained from

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DFT calculations), and the biphenyl groups are aligned periodically (1.19 nm) in the framework.[10] The pore wall thickness $(a-d_a)$ is estimated to be 1.9 nm, corresponding to four layers of biphenyl groups, and the Brunauer-Emmet-Teller (BET) surface area is 802 m^{2}g^{-1}. The powder consists of primary particles of approximately 300–500 nm in size (Figure 2a). Uniform mesochannels in a hexagonal arrangement can be clearly observed by transmission electron microscopy (Figure 2b). Films of biphenyl-PMO were pre-

pared using three different template surfactants (C$_{18}$TMACl, Brij76, P123) through evaporation-induced self-assembly after dip-coating (C$_{18}$TMACl, P123) or spin-coating (Brij76). The biphenyl-PMO films thus obtained are transparent and highly uniform, with a thickness of (400 ± 50) nm and a wormhole-like disorder ($d = 9.4$ nm; P123) or lamellar ($d = 4.6$, 6.2 nm; C$_{18}$TMACl, Brij76)[16] structure (see Supporting Information). The PMO framework does not exhibit the molecular-scale periodicity, which is different from that of the biphenyl-PMO powder. The coumarin 1 dye was chosen as the energy acceptor due to the almost complete overlap of the absorption band of the dye with the emission band of biphenyl-PMO, which is desirable for efficient fluorescence resonance energy transfer.[22] The biphenyl-PMO powder was doped with coumarin 1 dye by adsorption from an aqueous biphenyl-PMO suspension containing the dye and a surfactant (C$_{18}$TMACl). The biphenyl-PMO films were doped with the coumarin 1 by adding the dye to the sol used for dip- or spin-coating. Doping in both cases resulted in the molecular dispersion of coumarin 1 molecules in the channels (Figure 3a).

The UV/Vis absorption spectrum of the coumarin 1/biphenyl-PMO film (1.2 mol% coumarin 1/biphenyl) shows a strong absorption band at a peak wavelength (λ_{max}) of 264 nm (absorption coefficient, $(73\,000 \pm 9000)$ cm^{-1}), which is assigned to densely packed biphenyl groups in the framework, and a weak band at 374 nm (absorption coefficient, (1600 ± 200) cm^{-1}) due to the coumarin 1 dye in the channels
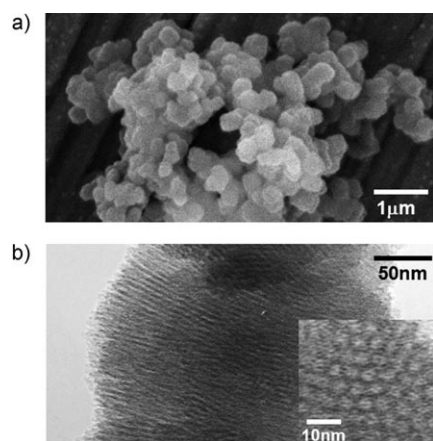

Figure 2. a) Scanning and b) transmission electron micrographs of biphenyl-PMO powder. (Inset) Hexagonal cross-section of one-dimensional channels in the two-dimensional hexagonal lattice.
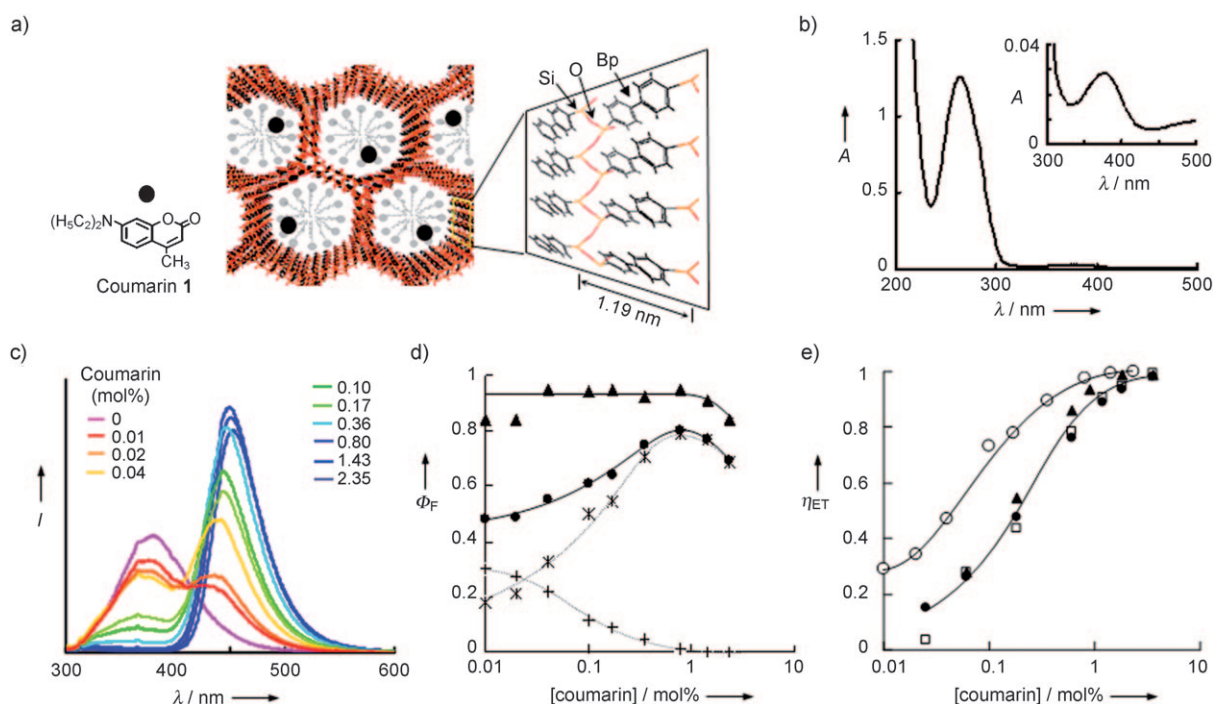

Figure 3. Energy-transfer properties of coumarin 1 dye-doped biphenyl-PMO. a) Schematic representation of coumarin 1/biphenyl-PMO. Bp = biphenyl. b) UV/Vis absorption spectrum of coumarin 1/biphenyl-PMO film (1.2 mol% coumarin 1/biphenyl, C18TMACl, ca. (400 ± 50) nm thickness) and detail of spectrum at 300–500 nm (inset). c) Fluorescence spectra for coumarin 1/biphenyl-PMO powders with 0–2.35 mol% coumarin 1 (excitation wavelength, 270 nm; normalized by absorption rate). d) Fluorescence quantum yield (Φ_F) of coumarin 1/biphenyl-PMO under excitation at 270 nm (●) and 380 nm (▲) as a function of coumarin 1 concentration, showing biphenyl (+) and coumarin 1 (*) components contributing to Φ_F (270 nm). e) Energy-transfer efficiency of biphenyl-PMO powder (○), and biphenyl-PMO films prepared using P123 (wormhole; ▲), C18TMACl (lamellar; ●), and Brij76 (lamellar; □).

(Figure 3b). The absorption band of coumarin 1 appears at a similar wavelength to that of coumarin 1 dissolved in a polar solvent, which differs from that in a nonpolar solvent (see Supporting Information), suggesting that the coumarin 1 molecules are located in the vicinity of the hydrophilic interfaces of the micelles rather than in the hydrophobic interior (Figure 3a).[23] Figure 3c shows the change in the fluorescence spectrum of the coumarin 1/biphenyl-PMO powder according to coumarin 1 concentration (0–2.35 mol%). The biphenyl emission at 380 nm weakens with increasing coumarin 1 concentration, and is accompanied by strengthening of the coumarin 1 emission at 440–450 nm. This result indicates that the excitation energy of the biphenyl groups is transferred to the coumarin 1 dye, as direct excitation of the coumarin 1 at 270 nm is negligible (<0.5%). A quantitative study of the energy transfer process was conducted by measurement of the fluorescence quantum yield (Φ_F). Interestingly, the total Φ_F given by the two emission components (biphenyl and coumarin 1) under excitation at 270 nm increases with coumarin 1 concentration from $\Phi_F = 0.42 \pm 0.02$ (0 mol%) to $\Phi_F = 0.80 \pm 0.04$ (0.80 mol%; Figure 3d). This finding represents direct evidence that energy transfer occurs directly from biphenyl in the framework to the coumarin 1 dye in the channels without a radiation–reabsorption process. The quantum yield of the coumarin 1 dye under direct excitation at 380 nm is constant at $\Phi_F = 0.93 \pm 0.05$ up to a coumarin 1 concentration of 0.80 mol% (Figure 3d), above which Φ_F decreases slightly due to self-quenching by coumarin 1 molecules in the channels. The energy-transfer efficiency (η_{ET}) estimated from the quenching rate of biphenyl emission ($= 1 - \Phi_F(c)/\Phi_F(0)$, where c is coumarin 1 concentration)[22] is close to 100% even at low coumarin 1 concentrations of 0.80 mol% (powder) and 1.80 mol% (film; Figure 3e). This result indicates that light energy absorbed by approximately 125 and 56 biphenyl groups (calculated by 100/0.80 and 100/1.80) in the biphenyl-PMO powder and film, respectively, are funneled to a single coumarin 1 molecule with almost 100% quantum efficiency, representing an excellent light-harvesting antenna property. The emission from the coumarin 1 dye in biphenyl-PMO is strongly enhanced by energy transfer from biphenyl in the framework under excitation at 270 nm compared to direct excitation of the coumarin 1 dye at 380 nm (Figure 4).

The estimated coumarin 1 concentrations achieving η_{ET} of 50% are 0.044 and 0.17 mol% for the biphenyl-PMO powder and film (Figure 3e), which are relatively low compared to those for reported previously for solid-state energy transfer systems, such as dye-doped mesoporous silica containing lanthanide complexes in the framework (6.7 mol% for $\eta_{ET} = 29.5\%$)[21] and pentacene-doped tris(quinolin-8-olate)aluminum(III) (Alq$_3$) amorphous films (0.23 mol% for $\eta_{ET} = 51\%$).[24] The Förster radius (R_0),[22] defined as the theoretical donor–acceptor distance at $\eta_{ET} = 50\%$ assuming direct resonance energy transfer, is 3.2 nm for the coumarin 1/biphenyl-PMO system (see Supporting Information). The average biphenyl (donor) to coumarin 1 (acceptor) distance estimated experimentally in the present study is around 5.9 nm for the powder and around 3.8 nm for the film. This calculation is based on the coumarin 1 concentration at $\eta_{ET} =$
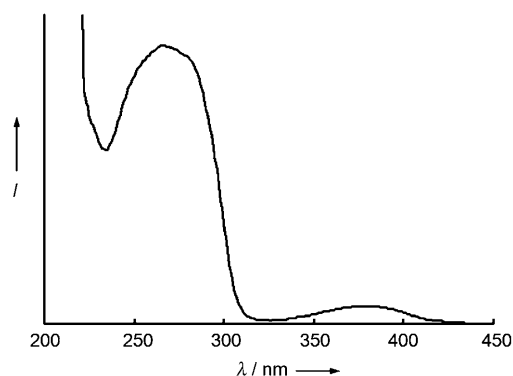

Figure 4. Excitation spectrum of coumarin 1/biphenyl-PMO film (1.2 mol%, C$_{18}$TMACl, (400 ± 50) nm thickness). The emission was detected at 440 nm.

50% and assumes a homogeneous distribution of coumarin 1 molecules in a biphenyl-silica with the biphenyl density of the present biphenyl-PMO, and a sphere of volume $(4/3)\pi R^3$ for each biphenyl (see Supporting Information). The longer biphenyl–dye distance obtained in the present study compared to R_0 suggests that another mechanism may, in part, contribute to the efficient energy transfer in coumarin 1/biphenyl-PMO (particularly for the powder sample), in addition to Förster-type direct energy transfer.

The time-resolved fluorescence decay of the undoped biphenyl-PMO is characterized by a multiple exponential profile (Figure 5A), as commonly observed in condensed matter systems such as organic crystals.[25] The average fluorescence lifetimes estimated assuming a quadruple-exponential fitting are 20 ns for the powder and 14 ns for the film. The decay of the biphenyl emission is shortened by dye doping, accompanied by a fast rise in the decay profile of coumarin 1 emission (Figure 5B,C), again indicating resonance energy transfer without a radiation process. Further study on the efficient energy transfer is currently being conducted through detailed analysis of the decay profiles and transient absorption measurements.
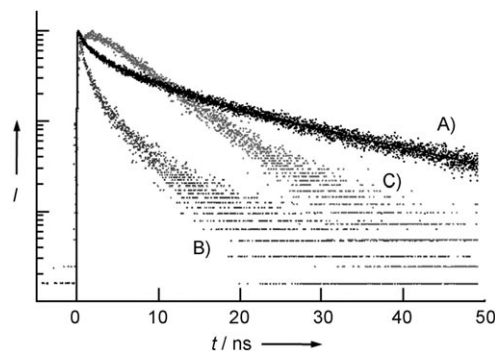

Figure 5. Fluorescence decay profiles of biphenyl-PMO powder monitored at 370 nm (A), and coumarin 1/biphenyl-PMO powder (0.66 mol%) monitored at 370 nm (B), and 500 nm (C) (excitation wavelength, 266 nm). The solid line for biphenyl-PMO is fitted by convolution of the instrument response function and quadruple-exponential function.

PMO-based light-harvesting materials, such as those prepared herein, have considerable advantages for the design of a range of applications. These applications, such as the light-emitting and photoreaction systems, are possible owing to the ability to incorporate a variety of photoactive materials in the mesochannels. There have been many reports on the incorporation of photoactive materials, such as organic dyes,[26] metal complexes,[27] conjugated polymers,[28] and metal and semiconductor nanoparticles[29] in mesoporous silica. The results herein suggest that the physical and chemical properties of these photoactive materials could be enhanced by the use of a light-harvesting PMO. Furthermore, the absorption wavelength of PMO can be tuned by appropriate selection of framework organic groups. For example, PMOs bearing anthracene[16,17] or oligo(phenylenevinylene)[30] have been shown to exhibit strong absorption bands near 400 nm, which may prove to be very important for solar energy applications. The robustness of the framework structure and the easy and flexibility of processing film and particle morphologies are also notable advantages of PMOs for a range of practical applications.

Experimental Section

All reagents and solvents were of the highest commercial quality and used without further purification. The organosilane precursor of 1,4-bis(triethoxysilyl)biphenyl (BTEBP, $(C_2H_5O)_3Si-C_6H_4C_6H_4-Si-(OC_2H_5)_3$, MW = 478.73) was obtained from Nard Institute, Ltd., Japan. The cationic surfactant, octadecyltrimethylammonium chloride (C_{18}TMACl, $C_{18}H_{37}N(CH_3)_3Cl$, MW = 348.05), was purchased from TCI. The surfactants P123 ($HO(CH_2CH_2O)_{20}(CH_2CH-(CH_3)O)_{70}(CH_2CH_2O)_{20}H$) and Brij76 ($C_{18}H_{37}(OCH_2CH_2)_{10}OH$), and the coumarin 1 dye (7-diethylamino-4-methylcoumarin, $C_{14}H_{17}NO_2$, MW = 231.79), were purchased from Aldrich.

Biphenyl-PMO powder: The biphenyl-PMO powder was synthesized according to the method reported in the literature[10] under slightly modified conditions (Supporting Information).

Coumarin 1/biphenyl-PMO powder: Biphenyl-PMO powder (0.1 g) was suspended in 100 g of an aqueous solution of 0.038 M C_{18}TMACl surfactant and mixed with coumarin 1 dye at appropriate amounts (0.01–4.00 mg). The suspensions were stirred at room temperature for 12 h and filtered, and the recovered powders were air-dried to obtain the coumarin 1/biphenyl-PMO powder. The concentration of adsorbed coumarin 1 dye was determined from the coumarin 1 concentrations in the filtrates by UV/Vis absorption spectroscopy using an appropriate calibration curve. The initial solutions of 0.01, 0.02, 0.04, 0.10, 0.20, 0.40, 1.00, 2.00, and 4.00 mg coumarin 1 per 0.1 g of biphenyl-PMO were thus determined to afford powders of 0.01, 0.02, 0.04, 0.10, 0.17, 0.36, 0.80, 1.43, and 2.35 mol% coumarin 1 with respect to biphenyl, respectively. The concentration of biphenyl groups in the biphenyl-PMO powder based on the chemical unit ($SiO_{1.5}-C_6H_4C_6H_4-SiO_2H$) is 3.77 mmol g^{-1}.

Coumarin 1/biphenyl-PMO films: A surfactant solution was first prepared by dissolving an optimized molar ratio of surfactant in a mixture of ethanol (EtOH), deionized water (H_2O), and hydrochloric acid (HCl). An EtOH solution of coumarin 1 was then added to the surfactant solution, followed by addition of BTEBP under vigorous stirring. After stirring at room temperature for 2 h, the sol was coated onto quartz glass substrates by dip-coating (P123 and C_{18}TMACl) or spin-coating (Brij76), and the coated film was dried at room temperature. The mixture were optimized for each surfactant as follows: 1 BTEBP/0–0.036 coumarin 1/0.055 P123/86.6 EtOH/0.012 H_2O/0.064 HCl, 1 BTEBP/0–0.036 coumarin 1/0.48 Brij76/104 EtOH/0.013 H_2O/0.016 HCl, and 1 BTEBP/0–0.036 coumarin 1/

0.92 C_{18}TMACl/104 EtOH/0.012 H_2O/0.016 HCl. Dip-coating was performed at a dipping speed of 2 cm min^{-1}, and spin-coating was conducted at a spinning speed of 4000 min^{-1} for 30 s.

Measurements: The UV/Vis absorption spectra of the film samples were recorded using a spectrophotometer (V-670, JASCO). The fluorescence spectra and quantum yields were evaluated using an absolute photoluminescence quantum yield measurement system equipped with a calibrated integrating sphere and a multi-channel spectrometer (C9920–02, Hamamatsu Photonics). Prior to measurements, the quantum yields of naphthalene (7.6×10^{-5} M in cyclohexane) and anthracene (1.0×10^{-5} M in ethanol) solutions under argon gas bubbling were evaluated as standard samples, and the results were confirmed to be identical to reported values within ± 0.01: 0.23 at 270 nm for naphthalene, and 0.27 at 355 nm for anthracene. The excitation spectrum was measured using a spectrofluorometer (FP6500, JASCO). Film thickness was measured using a DEK-TAK 3ST surface profiler measuring system (ULVAC Japan) with a needle force weight of 1 mg. Fluorescence decay curves were measured using a time-correlated single photon counting system (SPC-730, Becker & Hickl) (Supporting Information).

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