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Transparent and visible-light harvesting acridone-bridged mesostructured organosilica film†

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Transparent and visible light-harvesting acridone-bridged periodic mesoporous organosilica (PMO) films were prepared by acidic sol–gel polycondensation of non-methylated and *N*-methylated acridone-bridged bis-triethoxysilane precursors in the presence of a template surfactant *via* evaporation-induced self-assembly (EISA). A muddy film containing small aggregates was obtained from the non-methylated precursor. The aggregate was formed by strong intermolecular hydrogen bonds between N–H and C=O of the acridone groups during EISA. However, a transparent PMO film was successfully formed from the *N*-methylated precursor. Capping of the amine group hindered the intermolecular hydrogen bonds and effectively suppressed aggregate formation. The obtained acridone-bridged PMO film showed a visible light absorption band with an edge at 430 nm and fluorescence emission centered at 500 nm. Furthermore, doping of a fluorescent dye into the mesochannels of the acridone–PMO promoted efficient energy funneling from the framework acridone groups into the dye, resulting in a strong fluorescence emission centered at 600 nm from the dye.

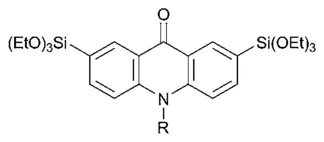
Introduction

Periodic mesoporous organosilicas (PMOs),[1–3] synthesized from up to 100% organic-bridged alkoxysilane precursors [$(R'O)_3Si$–R–$Si(OR')_3$, R = organic group, $R' = CH_3, C_2H_5$] by surfactant-templated supramolecular assembly, are a new class of functional hybrid materials in which the organic groups are densely and covalently embedded within the silica framework forming ordered mesochannels. A broad spectrum of functionalities can be introduced into the frameworks by the design of organosilane precursors with specific functional organic groups (R). A large number of PMOs bearing various bridging organic groups have been reported.[3] Some PMOs with interactive bridging organic groups, such as benzene,[4] biphenyl,[5] naphthalene,[6] and divinylbenzene,[7] have been found to exhibit crystal-like molecular-scale periodicity of the organic groups in the frameworks. As a result of these unique features, PMOs have attracted much attention for use in various applications such as catalysts,[8] adsorbents,[9] and optical devices.[10]

We have found unique optical functionalities of biphenyl-bridged PMO, such as efficient fluorescence emission[11] and light-harvesting antenna properties, that is, the funneling of light energy absorbed in the framework into dyes in the mesochannels.[12] The latter indicates the significant potential of PMOs as light-harvesting scaffolds in light-emitting devices and photoreaction systems.

Recently, visible-light absorptive PMOs containing diacetylene,[13] diimine,[14] diphenylvinylene,[15] anthracene[16] and oligo(phenylenevinylene) groups[17] have been reported, which would be important for application to visible-light responsive optical devices. However, these PMOs are unstable, because they contain chemically reactive vinylene, imine and acene units, which can result in degradation with light-irradiation. On the other hand, the recently reported acridone-bridged PMO powder[18] is expected to exhibit high chemical stability, because acridone derivatives are known to show high stability as luminescence probes.[19] However, there have been no reports on the synthesis of an acridone-bridged PMO films. PMO films are preferably utilized for optical applications (*e.g.* lighting), due to lack of light scattering loss and their flexibility for shaping.[20]

Here, we focus on the synthesis of a transparent and visible-light harvesting acridone-bridged PMO film *via* evaporation-induced self-assembly (EISA). Using the conventional acridone-bridged organosilane precursor **1** (Fig. 1) resulted in the



1 : R = H
2 : R = CH_3

Fig. 1 Acridone-bridged organosilane precursors **1** and **2**.

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† Electronic supplementary information (ESI) available: Synthetic route of precursor **2**, ^1H NMR and ^{13}C NMR spectra of **2**, FT-IR spectrum of precursor **1**, UV-vis absorption spectra of sol solution of **1** before and after filtration, optical micrograph of **F-2** after extraction of the surfactant, FT-IR spectra of methylacridone-bridged PMO film before and after surfactant extraction, UV-vis absorption and fluorescence emission spectra of **F-1** and aggregates of precursor **1**, excitation spectra of **F-1** and **F-2**, and fluorescence emission spectra and quantum yields of **F-2** before and after extraction of the surfactant. See DOI: 10.1039/c0jm00275e

formation of a muddy film containing aggregates. These aggregates were generated by intermolecular hydrogen bonds between N–H and C═O of the acridone group during EISA. For the suppression of aggregate formation, we designed a new precursor **2** (Fig. 1) in which the nitrogen atom is capped with a methyl substituent. The capping hindered intermolecular hydrogen bonding, and this allowed the successful formation of a transparent PMO film. The obtained film exhibited visible light absorption and efficient light-harvesting antenna properties.

Results and discussion

Synthesis of precursors

Two types of acridone-bridged organosilane precursors, 2,7-bis(triethoxysilyl)acridone **1**[18] and 2,7-bis(triethoxysilyl)-9-methylacridone **2** (with nitrogen atom capped by a methyl substituent), were synthesized by rhodium-catalyzed triethoxysilylation[21] of the corresponding 2,7-dibrominated acridone derivatives in 60% and 99% yield, respectively (Scheme S1 and Fig. S1 and S2 in ESI†). The infrared absorption (IR) spectrum of **1** showed absorption bands at 3260 and 1621 cm^{-1} corresponding to the stretching mode of hydrogen-bonded N–H and C═O groups, respectively (Fig. S3 in ESI†). Precursor **1** showed relatively low solubility in ethanol and THF, which are typically used as solvents for acidic sol–gel polycondensation, due to strong interaction between the acridone groups by hydrogen bonding. In contrast, precursor **2** was quite soluble, due to the hindering of intermolecular hydrogen bonds by capping of the nitrogen atom.

Preparation of mesoporous organosilica films

Acridone-bridged PMO films were prepared by spin-coating of sol solutions containing precursors **1** or **2**, a template surfactant P123, hydrochloric acid and water in ethanol. While the sol solution of **1** formed a small amount of precipitates within 3 h, possibly due to low solubility of the oligomers of **1**, the sol solution of **2** did not form any precipitates for at least 3 days, and a transparent sol solution containing the oligomers of **2** was obtained. These sol solutions were filtered using a membrane filter (0.20 μm) prior to spin-coating to remove the precipitates. The ultraviolet-visible (UV-vis) absorption measurement of the sol solution of **1** showed that >93% of **1** was still remained after filtration (Fig. S4 in ESI†).

Fig. 2 shows a photograph and optical micrographs of the spin-coated films prepared from the filtered sol solutions of **1** and **2** (denoted as **F-1** and **F-2**, respectively). **F-1** was muddy yellow and contained small aggregates of approximately 1 μm in size (Fig. 2a and b). The transmittance of **F-1** was 96% at 500 nm due to light scattering by the aggregates. These aggregates were formed during EISA, because >0.20 μm particles were removed by filtration prior to spin-coating. In contrast, **F-2** was obtained as a transparent yellow film without aggregates (Fig. 2c) that exhibited high transmittance of >99% at 500 nm, due to the lack of light scattering loss. **F-2** was stable without cracking in air and its transparency was mostly retained even after extraction of the surfactant (Fig. S5 in ESI†).

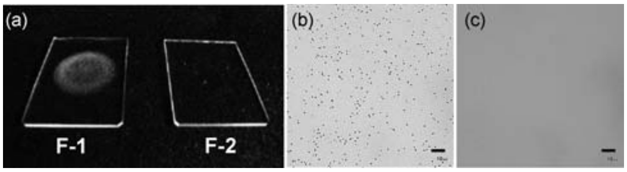

Fig. 2 (a) Photograph of **F-1** (left) and **F-2** (right), and optical micrographs of (b) **F-1** and (c) **F-2** (scale bar represents 10 μm).

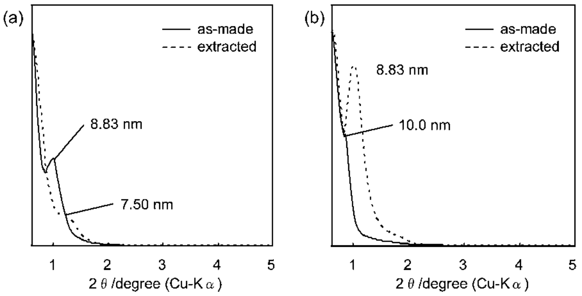

Fig. 3 XRD patterns of (a) **F-1** and (b) **F-2**.

Fig. 3 shows X-ray diffraction (XRD) patterns of **F-1** (a) and **F-2** (b) before and after extraction of the template surfactant. Complete removal of the surfactant was confirmed by IR measurements (Fig. S6 in ESI†). **F-1** and **F-2** show diffraction peaks with *d*-spacings of 8.83 and 10.0 nm, respectively, which indicates the formation of periodic mesostructures before extraction of the surfactant. For **F-1**, the diffraction peak was significantly broadened after the extraction, which suggests partial collapse of the periodic mesostructure, even after treatment with ammonia vapor for reinforcing of the framework structure. The collapse may be attributed to a low degree of condensation in the organosilica framework, which could possibly be due to a small fraction of the oligomers in the sol solution and preferential aggregate formation by strong intermolecular hydrogen bonding. In contrast, **F-2** shows an intense diffraction peak (8.83 nm) after the surfactant extraction, which suggests formation of the periodic mesoporous structure with shrinkage (from 10.0 to 8.83 nm), but without collapse. This result indicates that the framework structure of **F-2** is well-condensed, due to hindering of the intermolecular hydrogen bonds. Both films showed no peaks at $2\theta > 4.4°$ (*d*-spacing < 2 nm), which indicates no molecular-scale periodicity of the acridone groups in the frameworks.

Optical properties of mesoporous organosilica films

UV-vis absorption and fluorescence emission measurements were carried out to characterize the optical properties of the obtained films and to elucidate details of the aggregates in **F-1**. Fig. 4 depicts UV-vis absorption and fluorescence emission spectra of **F-1**, **F-2** and their precursors (2-propanol solution). **F-2** showed absorption bands at 385 and 399 nm. The absorption spectrum was primarily similar to that for the **2** solution, which has been typically observed in PMO films[11] and suggests weak interaction between the acridone groups in the ground state. However, **F-1** showed a strong absorption band at 416 nm and a weak absorption band at 392 nm. The absorption spectrum was quite different from that of the **1** solution, but was similar to that

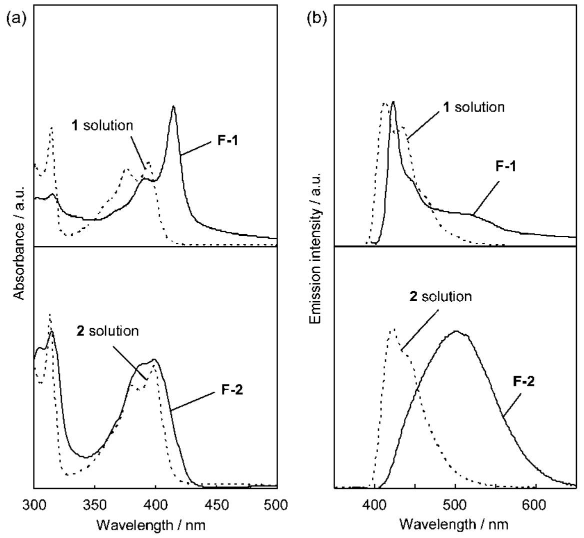

Fig. 4 (a) UV-vis absorption and (b) fluorescence emission spectra of mesostructured organosilica films (solid lines) and 2-propanol solutions of the corresponding acridone-bridged precursors (dashed lines). The excitation wavelength was 380 nm for all samples.

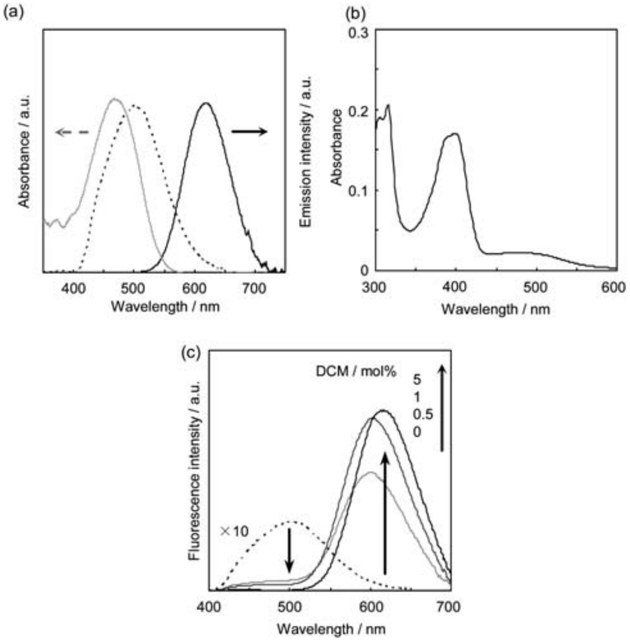

Fig. 5 (a) Fluorescence emission spectrum (dashed line) of **F-2** and UV-vis absorption (grey) and fluorescence emission (solid line) spectra of DCM (10^{-5} M in 2-propanol). (b) UV-vis absorption spectrum of 1 mol% DCM doped **F-2**. (c) Fluorescence emission spectra of DCM doped **F-2** with 0–5 mol% DCM (excitation wavelength of 380 nm).

of the aggregates of precursor **1** prepared by spin-coating an ethanol solution (Fig. S7a in ESI†). This suggests that the conformation of most of the acridone groups in **F-1** is similar to that of the aggregates of precursor **1**.

The fluorescence band of **F-2** was red-shifted and broadened from that of the **2** solution, due to formation of the excimer, which suggests strong interaction between the acridone groups in the excited state, as typically observed in PMO films.[11] In addition, the excitation spectrum at the band maximum (500 nm) was primarily identical to the UV-vis absorption spectrum, which indicates that the fluorescence emission is originated from one component, which indicates the formation of a homogeneous film of **F-2** (Fig. 2c). In contrast, **F-1** showed fluorescence emissions from at least two components, with a sharp emission band at 422 nm and two broad emission bands at 450 and 520 nm. The two former bands could result from emission of the aggregates in the film, because the band positions are similar to those for the aggregates of precursor **1** (Fig. S7b in ESI†) and the excitation spectrum at 450 nm showed a sharp peak attributable to the aggregates at 416 nm (Fig. S8a in ESI†).[22] The latter band at 520 nm is attributed to the excimer emission from the homogeneous organosilica phase, due to the similar band position and excitation spectrum (520 nm: Fig. S8a in ESI†) to those of **F-2** (Fig. S8b in ESI†). The fluorescence quantum yields were 0.03 and 0.06 for **F-1** and **F-2**, respectively. Both films showed a significant decrease in their fluorescence quantum yields from the corresponding precursor solutions (**1**: 0.75, **2**: 0.60), possibly due to solid state quenching.

Finally, the light-harvesting antenna properties of the transparent acridone-bridged PMO film (**F-2**) were investigated. The DCM dye (4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran) was chosen as an energy acceptor, due to good overlap of its absorption band and the emission band of **F-2** (Fig. 5a), which would promote efficient excitation energy transfer. The UV-vis absorption spectrum of the dye-doped **F-2** (1 mol%) showed a weak band at 478 nm, due to the dye in the mesochannels, in addition to a strong band at 399 nm due to the acridone groups (Fig. 5b). The band position of the dye in **F-2** was similar to that in polar solvents such as dimethyl sulfoxide,[23] which suggests that the dye molecules are likely to be present at the hydrophilic interface of the surfactant micelles and the framework, rather than at the hydrophobic cores. Fig. 5c shows fluorescence emission spectra for dye-doped **F-2** at various dye concentrations (0, 0.5, 1 and 5 mol%) upon excitation at 380 nm. 0.5 mol% dye-doping significantly quenched the emission from the acridone groups, while promoting a strong emission from the dye at 600 nm. 1 mol% dye-doping further decreased and increased the emission from the acridone groups and the dye, respectively, and the fluorescence quantum yield reached 0.36. This value is much higher than that of non-doped **F-2** (0.06), which suggests that the emission from the dye results not from a radiation–reabsorption process, but from direct excitation energy transfer from the acridone groups to the dye, as also observed in the acridone-bridged PMO powder.[18] On the other hand, 5 mol% dye-doping resulted in a slight red-shift of the dye emission band, due to aggregation of the dye.

Conclusion

A transparent and visible-light absorptive acridone-bridged PMO film was successfully prepared from the newly designed acridone-bridged organosilane precursor **2**. Compared with the conventional precursor **1**, capping of the nitrogen atom with a methyl substituent improved the solubility of the precursor and its oligomers, due to the hindering of intermolecular hydrogen bonds, which suppressed the formation of precipitates in the sol solution and aggregates during EISA, allowing successful formation of a transparent PMO film. The film exhibited monomeric absorption and an excimer fluorescence emission, which is a typical behavior for PMO films. Dye-doping of the film resulted in quenching of the emission from the framework, while strong emission from the dye was promoted, which confirmed light-harvesting antenna properties.

Experimental

Materials and general methods

All reagents and solvents were purchased from Aldrich, Tokyo Chemical Industry, Wako Pure Chemical Industries, and Nacalai Tesque and used without further purification. A poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (EO_{20}–PO_{70}–EO_{20}, P123) (Aldrich) was used as a nonionic template surfactant. Precursor **1** was synthesized according to the literature.[18] Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-EXC400P spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-*d* (δ 77.0) for ^{13}C NMR. Infrared (IR) absorption measurements were conducted on a Thermo Nicolet Avatar 360 FT-IR spectrometer using an attenuated total reflection (ATR) attachment. Mass spectra were recorded on a Bruker Daltonics Autoflex mass spectrometer (MALDI: matrix-assisted laser desorption ionization). Optical microscopy observations were performed using an Olympus BX51 microscope. X-Ray diffraction (XRD) measurements were performed on a Rigaku RINT-TTR diffractometer with Cu-Kα radiation (50 kV, 300 mA). Ultraviolet-visible (UV-vis) absorption spectra were measured using a Jasco V-670 spectrometer. Fluorescence emission spectra were obtained using a Jasco FP-6500 spectrometer. Fluorescence quantum yields were determined using a photoluminescence quantum yield measurement system equipped with a calibrated integrating sphere (Hamamatsu Photonics, C9920-02). Optical measurements were carried out for the films without extraction of the surfactant to suppress fluorescence quenching by oxygen[11] (Fig. S9 in ESI†) and aggregation of dye molecules in the mesochannels.[17]

Synthesis

Precursor **2** was synthesized according to the synthetic route shown in Scheme S1†.

9-Methylacridone. To a mixture of 9(10*H*)-acridone (6.00 g, 30.7 mmol) in distilled DMF (240 mL) was added NaH (3.07 g, 60% oil dispersion, 76.7 mmol) at 0 °C. The reaction mixture was stirred at 60 °C for 30 min, then iodomethane (4.80 mL, 77.0 mmol) was added, and stirring was continued at 60 °C for 18 h. The reaction mixture was quenched with H_2O. The resulting solid was collected by filtration and thoroughly washed with ethanol to give title compound as light-yellow solid (4.77 g, 74%). The filtrated water phase was extracted with chloroform, them washed with brine, dried over magnesium sulfate, and concentrated to give the title compound (1.31 g, total yield is 95%). δ_H (400 MHz, $CDCl_3$, Me_4Si), 3.89 (3H, s, CH_3), 7.29 (2H, dt, *J* 1.8 and 7.3 Hz, aromatic), 7.51 (2H, d, *J* 7.7 Hz, aromatic), 7.72 (2H, dt, *J* 1.8 and 7.3 Hz, aromatic), 8.56 (2H, dd, *J* 1.8 and 7.7 Hz, aromatic).

2,7-Dibromo-9-methylacridone. To a mixture of 9-methylacridone (6.00 g, 28.7 mmol) in distilled DMF (280 mL) was added dropwise a solution of *N*-bromosuccinimide (10.8 g, 60.7 mmol) in distilled DMF (80 mL) at 0 °C. The reaction mixture was stirred at 80 °C for 18 h, and quenched with H_2O. The resulting solid was collected by filtration and thoroughly washed with hexane to give the title compound as yellow solid (6.57 g, 62%). The filtrated water phase was extracted with chloroform, then washed with brine, dried over sodium sulfate, and concentrated. The residue was washed with hexane to give the title compound (3.80 g, total yield is 98%). δ_H (400 MHz, $CDCl_3$, Me_4Si), 3.87 (3H, s, CH_3), 7.41 (2H, d, *J* 9.2 Hz, aromatic), 7.79 (2H, dd, *J* 2.6 and 9.2 Hz, aromatic), 8.62 (2H, d, *J* 2.6 Hz, aromatic).

2,7-Bis(triethoxysilyl)-9-methylacridone (2). To a mixture of $[Rh(CH_3CN)_2(cod)]BF_4$ (74.4 mg, 0.20 mmol), 2,7-dibromo-9-methylacridone (1.20 g, 3.27 mmol), and *n*-Bu_4NI (2.41 g, 6.52 mmol) were added distilled DMF (48 mL) and triethylamine (2.74 mL, 19.7 mmol). After addition of triethoxysilane (2.41 mL, 13.1 mmol), the reaction mixture was stirred at 80 °C for 2 h, then concentrated under vacuum to remove DMF. The resulting mixture was treated with Et_2O to give a solution of the title compound in Et_2O, which was filtered through a Celite plug and charcoal, and the filter cake was rinsed with Et_2O. The combined filtrates were concentrated under vacuum to give the title compound as yellow crystalline solid (1.72 g, 99%). λ_{max}(*i*-PrOH)/nm 314 (ε/dm^3 mol^{-1} cm^{-1} 10 800), 381 (6400) and 398 (7600); ν_{max}(neat)/cm^{-1} 2971, 2925, 2887, 1641(C=O), 1599, 1479, 1176 and 958; δ_H (400 MHz, $CDCl_3$, Me_4Si), 1.28 (18H, t, *J* 7.2 Hz, 6 × OCH_2CH_3), 3.92 (3H, s, CH_3), 3.93 (12H, q, *J* 7.2 Hz, 6 × OCH_2CH_3), 7.55 (2H, d, *J* 8.7 Hz, aromatic), 8.02 (2H, dd, *J* 1.4 and 8.7 Hz, aromatic), 8.91 (2H, d, *J* 1.4 Hz, aromatic); δ_C (100 MHz, $CDCl_3$, $CDCl_3$) 18.3, 33.6, 58.9, 114.3, 122.3, 123.4, 135.5, 139.7, 143.9, 178.0 (C=O); *m*/*z* (ESI) 533.2250 (M$^+$. $C_{26}H_{39}NO_7Si_2$ requires 533.2265).

Preparation of organosilica films. The acridone- or 9-methylacridone-bridged organosilane precursors (**1** or **2**, 60 mg) and P123 (60 mg) were dissolved in EtOH (2.0 g), and then deionized water (12.0 μL) and 2 M HCl aqueous solution (4.0 μL) were added to the solution. The mixture was stirred at room temperature for 3 h (for **1**) or 24 h (for **2**) to form the sol solution. After passing through a membrane filter (0.20 μm), the sol solution was coated on a quartz glass plate by spin-coating (4000 rpm, 30 s) and dried under reduced pressure to give an organosilica film. In case of the dye doping, the DCM dye (ethanol solution) was added to the sol solution (the molar DCM/**2** ratios of 0.5, 1 and 5 mol%) and then stirred for a few minutes at room temperature just prior to spin-coating.

Removal of the template surfactant from organosilica films

In order to remove the template surfactant, the organosilica films were exposed to the vapor of a 28% NH_3 aqueous solution at 60 °C for 12 h, and then immersed in ethanol for 12 h at 60 °C to provide a surfactant-free sample. Complete removal of the surfactant was confirmed by IR measurements (Fig. S4 in ESI†).

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