Mesostructured organosilica with a 9-mesityl-10-methylacridinium bridging unit: photoinduced charge separation in the organosilica framework†

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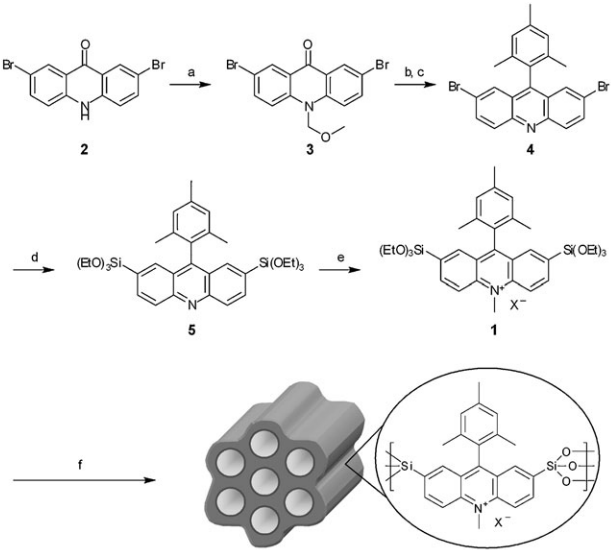
Polycondensation of 9-mesityl-10-methylacridinium-bridged organosilane in the presence of a nonionic surfactant yielded a mesostructured organosilica solid with a functional framework that exhibited long-lived photoinduced charge separation.

Photoexcitation of electroactive chromophores can induce a variety of chemical reactions. Of particular interest for photocatalysis or energy conversion applications is photoinduced electron transfer in donor–acceptor systems.[1,2] While photoinduced charge separation in charge transfer complexes consisting of donor and acceptor molecules has been widely studied, increasing attention has been focused on covalently-linked donor–acceptor dyads for the construction of more efficient photoreaction systems.[2]

Recently, 9-mesityl-10-methylacridinium (Mes–Acr$^+$) salts, in which the donor (Mes) and acceptor (Acr$^+$) moieties are directly connected, have been reported to exhibit prominent photocatalytic behavior and electronic activities in solutions or polymer matrices.[3–6] The mechanism of Mes–Acr$^+$-mediated photoreaction has been examined intensively[4,5] with the Mes–Acr$^+$ cation reported to serve as a dual sensitizer, with the capacity for efficient singlet oxygen formation and electron-transfer reaction.[5d] In practical terms, immobilization of the Mes–Acr$^+$ unit in a solid porous framework is important due to the wide range of potential applications, including as solid-state photocatalysts and in electrical devices. Furthermore, dense packing of the Mes–Acr$^+$ unit may also lead to the induction of unique photochemical and electrical properties through the specific intermolecular interactions.

Periodic mesoporous organosilicas (PMOs) prepared by surfactant-directed self-assembly of bridged organosilane precursors ($(R'O)_3Si–R–Si(OR')_3$, R: organic bridging group) are promising candidates as solid-state functional materials because their function can be well tailored by appropriate selection of organic bridges (–R–) within the framework, control of the meso-scale porous structure, which provides a high surface area,[7–9] and precise morphology control.[10] Recently, unique and significant optical and electrical properties have been demonstrated for systems in which π-conjugated organic bridges are dispersed or densely accumulated within the pore walls of PMOs, providing efficient photoluminescence, hole transport within pore walls and light-harvesting antenna properties.[9] Moreover, systems capable of photocatalytic hydrogen evolution and CO_2 reduction have been constructed; in the case of hydrogen evolution, charge transfer complexes were included within the PMO framework,[9h] while in CO_2 reduction, a rhenium complex was located among the mesochannels.[9i] Expansion of the framework organics to include photochemically and electronically active species is thus of great importance for PMO-based optical, photocatalytic and electronic applications.

In this communication, we report on the preparation of mesostructured organosilica materials consisting of a 9-mesityl-10-methylacridinium (Mes–Acr$^+$)–silica hybrid framework, and describe their photoinduced charge separation behavior. The mesostructured materials were successfully obtained from the newly designed precursor **1** (Scheme 1) without dilution of the scaffold silica sources (*e.g.*, tetraethoxysilane),



Scheme 1 Synthetic route for preparation of Mes–Acr$^+$ organosilane precursor **1** and mesostructured organosilica. (a) NaH, MOMCl, DMF; (b) MesMgBr, THF; (c) HCl aq.; (d) $HSi(OEt)_3$, NEt_3, n-Bu_4NI, $[Rh(cod)(CH_3CN)_2]BF_4$, DMF; (e) MeOTf, CH_2Cl_2 (X = OTf); (f) Brij76, HCl aq., EtOH.

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which resulted in an organosilica framework with a high density of Mes–Acr$^+$ units. Time-resolved absorption spectroscopy of the Mes–Acr$^+$–silica hybrid films suggested that the photoinduced charge separation state can be retained over a microsecond time scale through 'intermolecular' charge migration in the framework.

The Mes–Acr$^+$-bridged precursor **1** was prepared starting from commercially available 2,7-dibromoacridone **2** in 74% overall yield (five steps) (Scheme 1). Protection of **2** with methoxymethyl chloride (MOMCl) followed by treatment with 2-mesitylmagnesium bromide and deprotection by hydrochloric acid afforded the desired 2,7-dibromo-9-mesitylacridine **4** in 75% yield (three steps). The resulting dibromide **4** was successfully transformed to bis(triethoxysilyl)-mesitylacridine **5** in 98% yield according to a previously reported method, giving 3,6-bis(triethoxysilyl)carbazole.[11] For subsequent methylation of **5**, screening of several methylating reagents (MeI, MeOTf and Me_3OBF_4) and solvents (PhMe, n-C_6H_{14}, MeCN, Et_2O and CH_2Cl_2) identified MeOTf and CH_2Cl_2 as the optimal methylating reagent and solvent, respectively, to give Mes–Acr$^+$-bridged precursor **1** in quantitative yield.

Mesostructured Mes–Acr$^+$–silica hybrid materials were successfully obtained by evaporation-induced self-assembly from an acidic sol solution containing **1** and the template nonionic surfactant Brij76 ($C_{18}H_{37}(OCH_2CH_2)_{10}OH$) (molar ratio of **1**/Brij76/EtOH/H_2O/HCl = 1.0/0.74/855/8.7/0.052). Fig. 1 shows an X-ray diffraction (XRD) pattern of the cast film prepared at room temperature. An intense peak corresponding to d = 6.50 nm and weak diffraction peaks of d = 3.81, 3.32, 2.50, 2.30 nm are observed, which can be indexed as the (100), (110), (200), (210) and (300) planes of a 2D hexagonal mesostructure.‡ It is noteworthy that a mesostructured film containing a relatively large organic bridge was successfully prepared from 100% organosilane precursor **1** without the addition of pure silica precursors. The mesostructure formation is expected to occur by the interaction of the hydrophilic poly(ethylene oxide) chain of Brij76 with the polar ionic organic bridge and the hydrophilic silanol groups of the hydrolyzed **1**. The periodic mesostructure was maintained after extraction of the template surfactant by immersing the organosilica hybrid film in ethanol (50 °C, 12 h). After extraction, the XRD peak corresponding to meso-scale periodicity was broadened, but its d-spacing value was almost the same as that for the surfactant-templated film (Fig. 1).

In order to examine the photochemical functionality of the organosilica hybrid framework, transient absorption spectra were measured for the mesostructured Mes–Acr$^+$–silica hybrid film prepared at a thickness of *ca.* 4 μm, for which sufficient signal intensity was expected to be obtained. The transient spectra, obtained by laser irradiation (λ = 355 nm, 7 ns pulse), showed absorption bands at *ca.* 380 nm and 420–550 nm (Fig. 2a), although the spectral shapes were somewhat disturbed, possibly due to a haze effect in the thick sample. These peaks were observed over a microsecond time scale as shown in Fig. 2a and b. The transient absorption band at 420–550 nm can be attributed to one or more of various chemical species such as the acridinyl radical (Acr$^\bullet$), mesityl radical cation (Mes$^{\bullet +}$) and triplet state of Mes–Acr$^+$.[5] On the other hand, the sharp absorption band at 380 nm is characteristic of Acr$^\bullet$, which is usually observed at 370 nm for Mes–Acr$^+$ ions in acetonitrile.[5] The present results indicate that photoinduced charge separation of Acr$^\bullet$ and its counterpart Mes$^{\bullet +}$ occurs in the organosilica framework over a microsecond time scale. The half-life as estimated from the absorbance decay at 380 nm is 3.5 μs (Fig. 2b). For a Mes–Acr$^+$ ion in benzonitrile solution, the transient absorption spectrum was reported to exhibit decay of microsecond[3] or nanosecond order[5b] with first-order kinetics consistent with an intramolecular process.

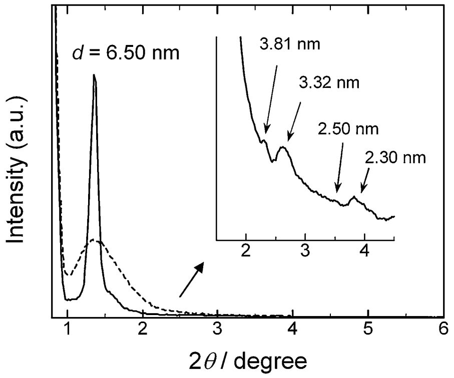

Fig. 1 XRD patterns of the organosilica film prepared from **1** and Brij76 before (solid line) and after extraction (broken line) of the template surfactant.

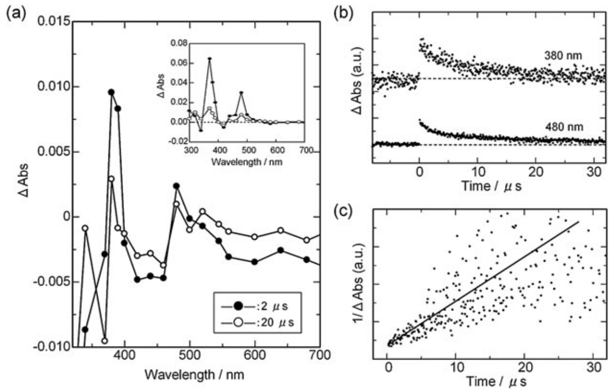

Fig. 2 (a) Transient absorption spectra of the mesostructured organosilica film prepared from **1** after laser excitation at 355 nm. (b) Time profiles of absorbance decay at 380 and 480 nm. (c) Time profile of the reciprocal of the absorbance decay at 380 nm. Inset of (a) shows transient absorption spectra of a transparent polycondensed film of **1** without surfactant.

The signal intensities of the organosilica film at 380 and 480 nm exhibited similar decay time profiles (Fig. 2b), which suggests that the Mes$^{\bullet +}$ and Acr$^\bullet$ species underwent charge recombination. The decay curves of the change in absorbance, ΔAbs, at 380 and 480 nm were not well-fitted by single exponential functions, in contrast with those for a Mes–Acr$^+$ solution, indicating that the mechanism for intramolecular charge recombination is not as straightforward in the present case. However, plotting the inverted ΔAbs values over time gives a linear relation as shown in Fig. 2c. These results indicate that the decay process obeys second-order kinetics, *i.e.*, $1/[\mathrm{Acr}^\bullet] = kt + 1/[\mathrm{Acr}^\bullet]_0$, where [Acr$^\bullet$] is the concentration of

Acr$^\bullet$, supporting a collision model for two diffusive radical species with the same concentrations (*i.e.*, [Acr$^\bullet$] = [Mes$^{\bullet +}$]). Thus it is likely that the two radical species Mes$^{\bullet +}$ and Acr$^\bullet$ generated by photoexcitation of the Mes–Acr$^+$ unit separately migrate in the organosilica framework, resulting in a charge separation state with a microsecond-order lifetime and subsequent charge recombination as a second-order process. Weak electrostatic attractive forces between the cationic (Mes$^{\bullet +}$) and neutral (Acr$^\bullet$) species may also play an important role in the induction of such long-lived charge separation states in this condensed matter system. Photoinduced charge separation behavior was also evaluated for a haze-free non-structured Mes–Acr$^+$–silica film prepared without surfactants by time-resolved spectroscopic analysis (Fig. 2a, inset), which showed clear absorption spectral profiles and similar static and dynamic optical behavior to that of the mesostructured film (see ESI†).

The formation of mesoporous structure in the Mes–Acr$^+$–silica has a great merit for application to solid catalyst because reactant molecules can easily access the charge-separated sites generated on the high-surface area organosilica framework. Photocatalytic ability of the mesoporous Mes–Acr$^+$–silica was evaluated in photooxidation reactions, which were previously reported in homogeneous Mes–Acr$^+$ systems.[4d,e] Briefly, after extraction of Brij76, the mesostructured Mes–Acr$^+$–silica hybrid was ground and dispersed in a dichloromethane solution of benzyl alcohol or triphenylphosphine. After visible light irradiation (xenon lamp, >385 nm, 12 h) of the suspensions under O_2 bubbling, benzaldehyde or triphenylphosphine oxide, respectively, was produced as confirmed by ^{1}H NMR spectroscopy (see ESI†). These results indicate that the photocatalytic ability of the Mes–Acr$^+$ unit is retained when covalently fixed within the solid silica matrices. The NMR spectra also confirmed that no leaching of the Mes–Acr$^+$ unit from the organosilica hybrid had taken place during reaction.

In conclusion, mesostructured organosilica hybrids with a Mes–Acr$^+$ bridging unit were prepared from a newly designed organosilane precursor **1** without dilution. Photoinduced charge separation within the Mes–Acr$^+$–silica hybrid framework was demonstrated over a microsecond time scale. PMOs containing a high density of photochemically active organic bridges have great potential for photovoltaic materials and recyclable photocatalytic systems.

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Notes and references

‡ Electron microscopy observation of the mesostructures was difficult because the organosilica hybrids were rapidly damaged by electron beam irradiation.

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