Special Feature: Recent Research Developments on Periodic Mesoporous Organosilicas

Research Report

Arrangement of Functional Organic Groups in Mesostructured and Mesoporous Organosilica Frameworks

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∎**ABSTRACT**∥ Periodic mesoporous organosilica (PMO) materials that have been prepared by surfactant-directed hydrolysis and polycondensation of bridged organosilane precursors are applicable to various functional systems because of their structural diversity on both the molecular scale and mesoscale. This report highlights recent developments in functional mesostructured and mesoporous organosilica materials by the controlled arrangement of organic groups fixed within and/or onto the frameworks of PMOs. Promotion of excimer formation within the pore walls is presented as a new approach to the preparation of highly fluorescent mesostructured films. Hydrogen-bonded PMOs that exhibit molecular-scale order within the pore walls can be a useful platform for photoinduced electron transfer systems. Controlled arrangement of functional organic groups in PMO frameworks will significantly contribute to improvements in the optical and electronic properties as well as the further development of potential applications.

∎**KEYWORDS**∥ Inorganic–organic Hybrid, Self-assembly, Organosilica, Mesostructures, Mesoporous Materials

1. Introduction

Hydrolysis and polycondensation of bridged organosilane precursors ($R[Si(OR')_3]_n$; $n \geq 2$, R' = Me, Et, etc.) in the presence of surfactant templates leads to the preparation of periodic mesoporous organosilicas (PMOs) that consist of covalent inorganic–organic hybrid frameworks (**Fig. 1**).[1-4] In contrast to conventional mesoporous silica materials, it is possible to functionalize the framework itself by densely embedding photofunctional, electroactive, and reactive organic groups (R) within the pore walls of PMOs. Various challenging applications that employ the periodic mesostructures and functions derived from organic moieties are expected for PMOs.

To date, efficient fluorescence emission,[5-8] long-range charge transport,[9-11] and the development of solid catalysts[12-16] have been realized in mesostructured
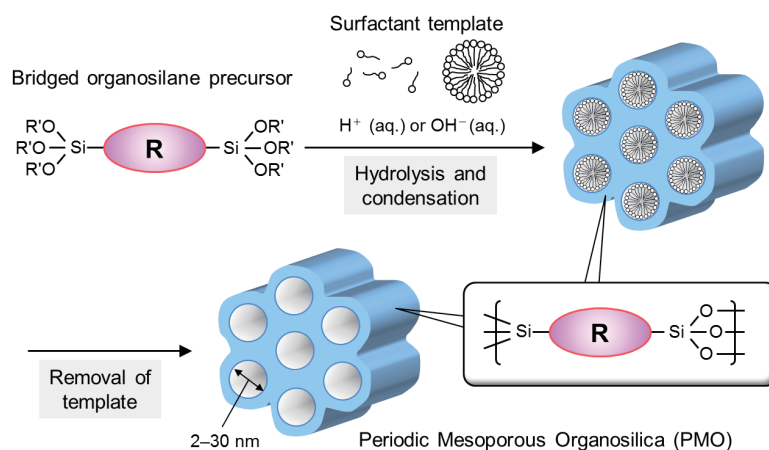

Fig. 1 Synthesis of periodic mesoporous organosilica (PMO) by surfactant-directed polycondensation of a bridged organosilane precursor.

and mesoporous organosilicas by the incorporation of a variety of organic and organometallic species into the pore walls and by control of the densities and locations of these species in the materials (**Fig. 2**). Control of the density of organic groups is critical for tuning the optical and electronic properties of PMOs (Fig. 2(a)). Increasing the density of functional π-conjugated organic groups is advantageous for the formation of electron conducting paths,[9-11] while highly fluorescent organosilica films have been prepared by diluting the chromophores within the pore walls.[6,7] Chemical modification of porous frameworks and their surfaces with multiple functional components is essential to construct solid catalysts and reaction fields (Fig. 2(b)).[12-16] On the other hand, molecular-scale ordering of the organic bridging groups within the pore walls, which is one of the most remarkable structural features of PMOs, may be a key for functionalization (Fig. 2(c)).[17-22] Lamellar structures that consist of alternating organic–silica layers have been found for the pore walls of PMOs prepared

(a) Functional organic group

(b) Surface modifier

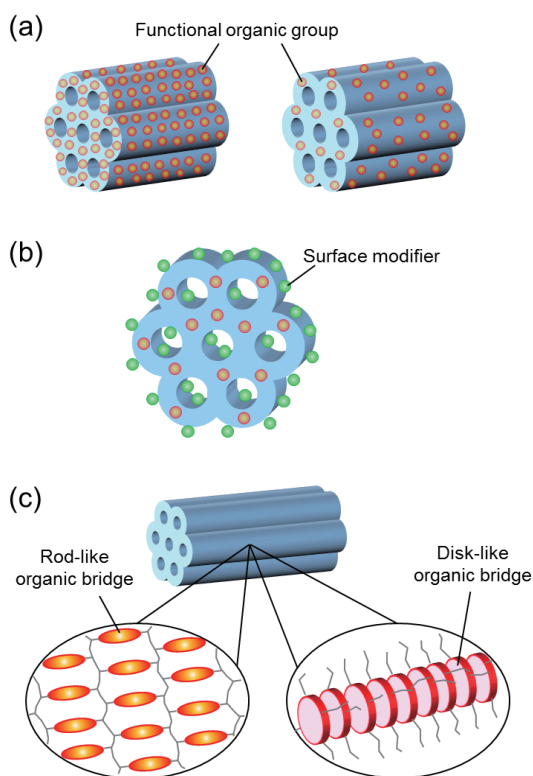(c) Rod-like organic bridge   Disk-like organic bridge

Fig. 2 Arrangement of organic groups in a PMO framework: (a) density control of functional organic groups inside the pore walls; (b) surface modification of organosilica pore walls; (c) molecular-scale ordering of organic bridging groups within pore walls.

from rod-like bifunctional organosilanes, such as benzene, biphenyl, naphthalene, and 1,4-divinylbenzene derivatives.[17-21] These rod-like organic bridges with large free volume and unhindered rotational motion are shown to behave as a molecular rotor, which may lead to the development of dielectric and ferroelectric materials that are responsive to external fields.[23] The introduction of disk-like perylene bisimide moieties has led to the formation of π-stacked columnar structures within the pore walls of PMOs.[22] The perylene bisimide-based PMO after electron doping is reported to exhibit stabilization of the resultant anionic radicals and charge delocalization in the π-stacked organosilica columns.

This report highlights the recent developments in the functionalization of mesostructured and mesoporous organosilicas by controlled arrangement of the organic groups. In Sec. 2, it is shown that a dense accumulation of fluorescent chromophores within the framework of mesostructured organosilica films can lead to an enhancement of fluorescence emission through excimer formation.[24] A new class of molecular-scale order found for pore walls of a hydrogen-bonded PMO and its potential are discussed in Sec. 3.[25] In Sec. 4, photoinduced charge separation in a multifunctionalized framework of the hydrogen-bonded PMOs is described.[26]

2. Fixation of a High Density of Fluorescent Chromophores

Significant photoluminescence properties have been reported for mesostructured organosilica films.[6-8] These films are prepared by acidic sol–gel polycondensation of bridged organosilane precursors based on fluorescent chromophores in the presence of template materials. For fluorescent mesostructured films that incorporate guest dyes into the mesopores, Förster resonance energy transfer from the organosilica framework to the guest dyes has been observed, which leads to the tuning of emission colors.[7,8,27]

The density of the fluorescent chromophores in the pore walls has a significant effect on the optical properties of the films. Fixation of a high density of chromophores is advantageous to achieve high light absorptivity. However, a dense accumulation of chromophores generally results in concentration quenching of fluorescence, presumably due to exciton migration or energy transfer from photoexcited species

to quenching sites. Therefore, appropriate dilution of chromophores within the pore wall using pure silica precursors (e.g. tetraethoxysilane (TEOS)) has been required for the preparation of highly fluorescent organosilica films.[6,7]

A material design that promotes the formation of excimers has enabled the achievement of both high light absorptivity and efficient fluorescence emission in mesostructured organosilica films.[24] Pyrene derivatives, which are typical fluorescent chromophores, are known to exhibit a strong excimer band emission. The excimer state of a pristine pyrene is theoretically described as an exciton-resonance state, and is reported to form a sandwich geometry with a distance of ca. 3.3 Å and a slight displacement.[28] To achieve a configuration of pyrenes suitable for the formation of highly emissive excimers in an organosilica framework, the 1,6-diphenylpyrene (DPPy)-derived precursor DPPy-Si was used to prepare fluorescent mesostructured films (D-Fn; n indicates the weight ratio (%) of the DPPy-Si to the total framework precursor weight (DPPy-Si + TEOS)) and their optical properties were compared with those of 1,3,6,8-tetraphenylpyrene (TPPy)-bridged mesostructured organosilica films (T-Fn) (**Fig. 3**).[7]

Figure 4 shows fluorescence spectra for D-Fn and T-Fn. The fluorescence spectra for D-Fn are broad and show no vibrational structure. The fluorescence wavelengths of D-Fn are longer than that of a solution of DPPy-Si in CH_2Cl_2 and those of T-Fn. These results indicate that the D-Fn films efficiently form excimers. In contrast, the fluorescence spectra of the T-Fn films mainly exhibit monomer band emission, probably due to the isolation of TPPy chromophores by the steric hindrance of four phenyl substituents (Fig. 3). **Figure 5** compares the fluorescence quantum yields of D-Fn and T-Fn. The D-Fn films exhibit higher quantum yields with an increase in the concentration of the DPPy chromophore, which shows a striking contrast to the T-Fn films. It should be noted that D-F100 prepared without dilution using TEOS, which can absorb light most strongly, shows the highest quantum yield (0.79) due to the efficient formation of highly emissive excimers. The promotion of excimer formation in organosilica frameworks can thus be a new material design concept to achieve both strong light absorption and efficient fluorescence emission.
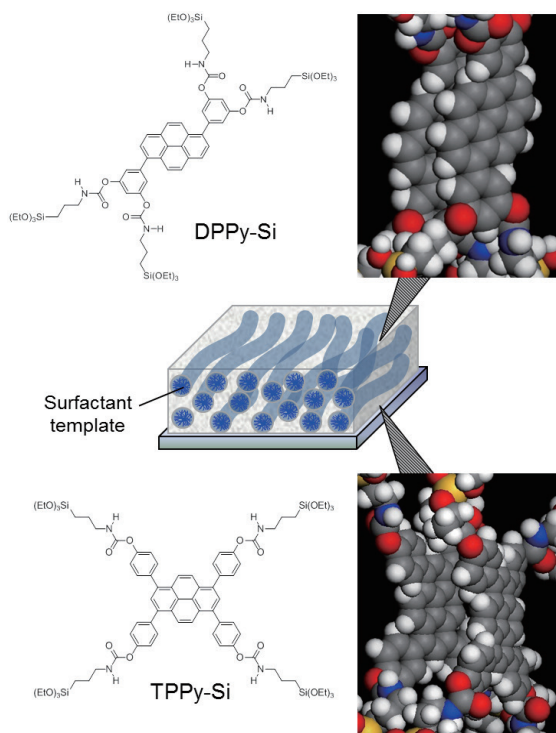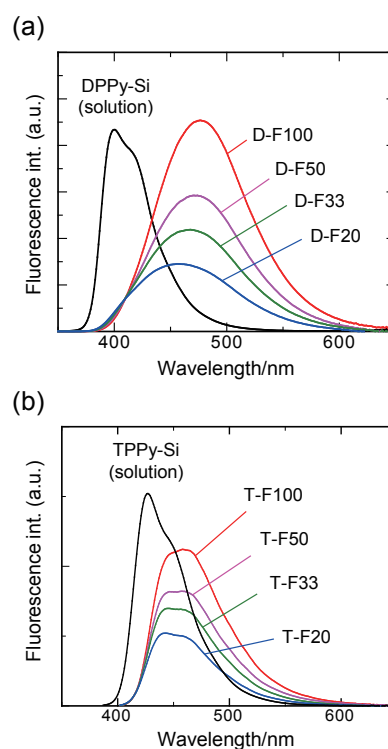

Fig. 3 Chemical structure of pyrene-derived organosilane precursors and aggregation models of the adjacent chromophores in the frameworks of mesostructured films.

Fig. 4 Fluorescence spectra for mesostructured organosilica films and solutions of the precursor compounds in CH_2Cl_2 upon excitation at λ = 340 nm: (a) DPPy-silica films and a solution of DPPy-Si; (b) TPPy-silica films and a solution of TPPy-Si.

3. Molecular-scale Order in a Hydrogen-bonded PMO

Molecular-scale ordering of organic bridging groups within the pore walls of PMOs has attracted much attention because functional organic species are fixed at a high density and with controlled orientation and arrangement.[17-22] Lamellar structures resulting from bifunctional rod-like precursors[17-21] and π-stacked columnar structures formed using disk-like precursors[22] have been reported as a molecular-scale order of the pore walls of PMOs (Fig. 2(c)). These ordered structures are constructed through hydrophilic and hydrophobic interactions of the hydrolyzed precursors ($R[Si(OH)_3]_n$). Here, if specific and strong intermolecular interactions are introduced into the organosilane precursors, then a new class of molecular-scale order is expected to be induced in the framework of PMOs.

The use of a hydrogen-bonding cyclohexane triamide precursor, Cy-Si, led to the formation of PMO with a new molecular-scale order (**Fig. 6**). The hydrogen-bonded PMO (Cy-PMO) was prepared by basic hydrolysis and polycondensation of Cy-Si in the presence of a cationic template surfactant. The formation of mesopores was confirmed by transmission electron microscopy (TEM) observation (Fig. 6(b)) and nitrogen adsorption–desorption isotherm measurement. Figure 6(c) shows an X-ray diffraction pattern of the PMO. In addition to a strong diffraction peak at $d = 5.36$ nm, which corresponds to the formation of a periodic mesostructure, small diffraction peaks are observed at $2\theta = 6$–22°. These peaks are attributed to molecular-scale order in the pore walls. The d-spacing values (1.43, 0.84, 0.70, 0.54, 0.47, and 0.41 nm) are in the ratios of $1:1/\sqrt{3}:1/2:1/\sqrt{7}:1/3:1/\sqrt{12}$, which indicates that a 2D hexagonal structure with a lattice constant of 1.65 nm is formed within the pore walls. Considering the molecular size of the precursor and the formation of hydrogen bond chains, the PMO framework is constructed with the hydrogen-bonded organosilica columns packed in a 2D hexagonal
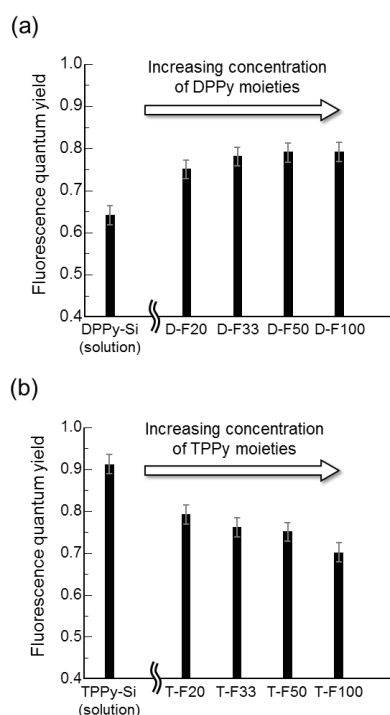
(a)

(b)

Fig. 5 Comparison of fluorescence quantum yields for mesostructured organosilica films and solutions of the precursor compounds in CH_2Cl_2 upon excitation at $\lambda = 340$ nm: (a) DPPy-silica films and a solution of DPPy-Si; (b) TPPy-silica films and a solution of TPPy-Si.
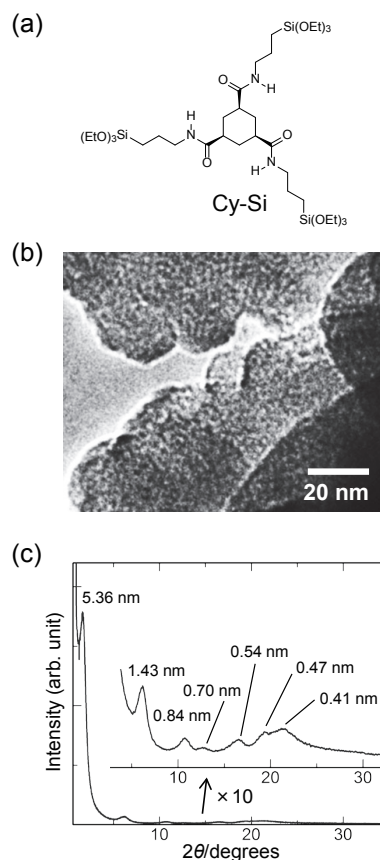
(a)

Cy-Si

(b)

20 nm

(c)

Fig. 6 (a) Chemical structure of hydrogen-bonding organosilane precursor Cy-Si. (b) TEM image of Cy-PMO. (c) XRD pattern of Cy-PMO.

lattice, as shown in **Fig. 7**. The introduction of strong and directional hydrogen-bonding interactions contributes to the formation of the new molecular-scale order. The hydrogen-bonded Cy-PMO was also found to intercalate guest molecules with the same triamide moiety into the pore walls. This intercalation behavior can be utilized for modification of the PMO framework. The preparation of a functional PMO using the hydrogen-bonded intercalation is described in the next section.

4. Charge Separation in a Multifunctionalized PMO Framework

A large number of studies have been devoted to chemical modification of the framework of mesoporous materials to construct highly functional solid materials applicable to adsorption, separation, sensing, and catalysis.[1-4] In these applications, the physical and chemical properties of the porous frameworks are strongly dependent on the density, relative distance, and location of the incorporated functional species.

Charge separation on a pore wall functionalized with three electroactive compounds has recently been achieved using the hydrogen-bonded Cy-PMO and by site-selective modification of the framework.[26] **Figure 8** shows a schematic illustration of surface modification of the PMO framework (Fig. 8(a)) and photoinduced charge transfer on the multifunctionalized pore wall (Fig. 8(b)). Cy-PMO can incorporate hydrogen-bonding guest molecules into the pore walls. The combination of hydrogen-bonded
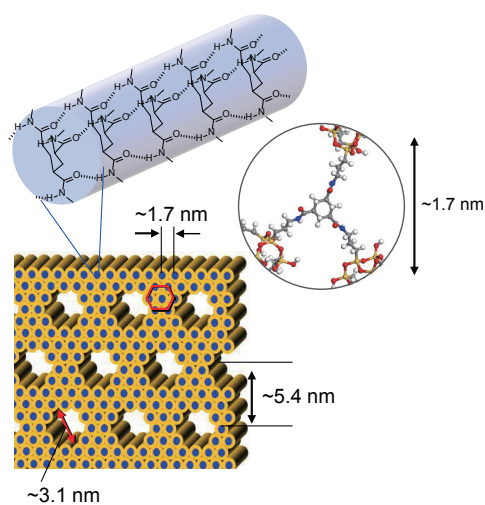
intercalation with surface modification using silane coupling agents realizes site-selective multifunctionalization of the organosilica framework (Fig. 8(a)).

The site-selective modification has been performed step-by-step for nanoparticulate Cy-PMO containing a naphthalimide-derived guest (**N**) within the pore walls and a surfactant template in the mesopores, as shown in **Fig. 9**. Naphthalene derivative **D** and viologen derivative **A**, which have higher electron-donating and electron-accepting properties than **N**, respectively, were fixed onto the external surface of the particles, and onto the surfaces of the mesopores (Fig. 8(b)).

Photoinduced electron transfer on the pore walls was confirmed by spectroscopic measurements. Fluorescence emission from **N** was quenched step-by-step by the modification with **D** and **A** (**Fig. 10**(a)). The fluorescence quantum yields decreased from 0.098 to 0.044 and 0.026. This quenching behavior is attributed not to excitation energy transfer but to photoinduced electron transfer because the fluorescence emission band of **N** has no overlap with the absorption bands of **D** and **A**. A cationic radical species of **A** was detected for the UV-irradiated Cy-PMO-**D**/**N**/**A** by UV-vis absorption spectroscopy

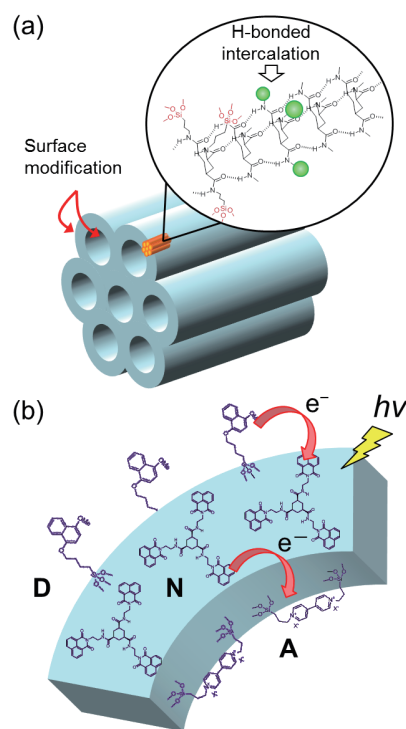**Fig. 7** Schematic illustration of the hierarchical structure of Cy-PMO.

Fig. 8 (a) Multifunctionalization of PMO framework with surface modification and hydrogen-bonded intercalation. (b) Schematic illustration of photoinduced electron transfer on a multifunctionalized pore wall.
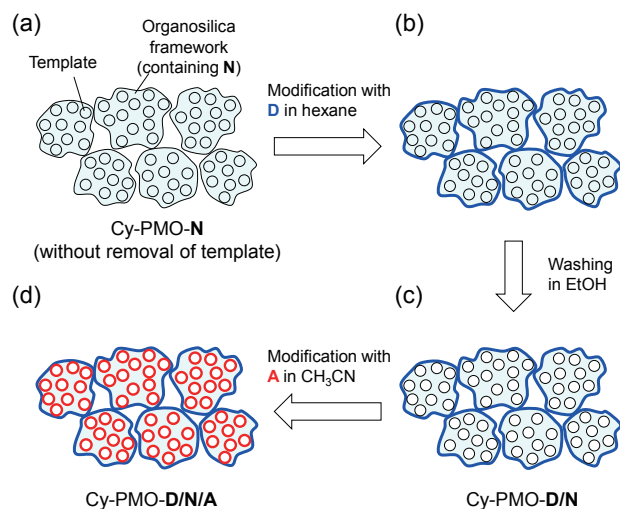
Fig. 9 Step-by-step modification of Cy-PMO with **N**, **D** and **A**: (a) Cy-PMO-**N**; (b) modification of the outer surface with **D**; (c) removal of templates in mesopores; (d) modification of the inner surface with **A**.
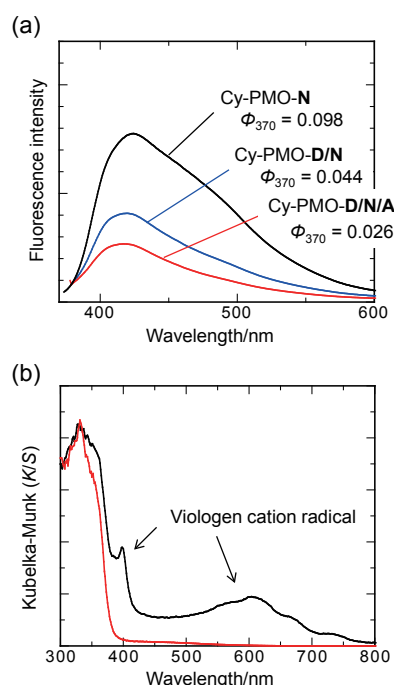

Fig. 10 (a) Fluorescence spectra and fluorescence quantum yields for modified Cy-PMO nanoparticles. (b) UV-vis spectra for Cy-PMO-**D/N/A** before (red) and after (black) UV irradiation.

(Fig. 10(b)). The present results indicate that two photoinduced electron-transfer processes from **D** to **N** and from **N** to **A** occur on the pore walls of Cy-PMO-**D/N/A** (Fig. 8(b)). However, radical species of **N** and **D** were not detected within the same timescale, which indicates that the two electron-transfer processes are not coupled, but are independent. This is probably due to the low concentration of **N** and the thick pore walls (3–4 nm) of the Cy-PMO. If efficient electron transfer across the pore walls is realized, then site-selective multifunctionalization of PMOs could be a promising approach to the construction of solid-state reaction fields.

5. Conclusions

The author has focused on the functionalization of mesostructured and mesoporous organosilica materials through the controlled arrangement of organic groups. Fluorescence emission enhanced by excimer formation within the pore walls suggests a new approach to the preparation of highly fluorescent mesostructured materials with high light absorptivity. Molecularly ordered hydrogen-bonded PMOs can be a useful platform for the construction of solid-state reaction fields. In addition to the diversity in the chemical structures of the organic components, spatial arrangement and density control of the organic groups will lead to further improvement of the functions of mesoporous organosilica materials that have significant potential for light-harvesting, electron transportation, adsorption, separation, sensing, and reaction catalysis.

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