Asymmetric Photoreaction in Peptide Assemblies Confined in Mesoporous Silica Nanopores

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We have developed novel mesoporous silica films whose pores are densely packed with chiral peptide assemblies. In this research, two asymmetric photoreactions in the chiral peptide environment demonstrated the first examples of chiroptical function in mesoporous silica films. Photochromism of a spiropyran dye doped in mesoporous silica containing an L-alanylalanine derivative was examined. Conversion between the spiropyran form and merocyanine form was reversibly repeated upon alternate irradiation of UV and visible light. Negative circular dichroism (CD) signals observed for the spiropyran form were erased in the merocyanine form. In the second example, photocyclization of a diarylethene derivative was similarly investigated. Upon UV irradiation, the photocyclization of the diarylethene occurred reversibly and CD spectra assigned to the closed form were observed in the hexagonal structured silica containing L-alanylalanine residues. The sign of the CD spectrum was reversed when a D-alanylalanine amphiphile was used as the host. However, the CD signals were significantly depressed in amorphous silica, indicating the importance of a regular arrangement of the host peptide and guest dye for an efficient chiroptical response. Chiral HPLC analyses on extracted products confirmed that the observed CD behavior was based on net asymmetric photocyclization.

Key words: Mesoporous Silica, Peptide, Asymmetric Photoreaction, Spiropyran, Diarylethene

1. INTRODUCTION

Transparent films of mesoporous silica are attracting great interest for photonic applications,[1-14] because they are mechanically robust and have high surface area for good dispersal of optically functional molecules. In particular, the chiroptical function of such materials may lead to memory devices with a non-destructive reading property.[15,16] However, the chiroptocal functions of mesoporous silica films have not been fully developed, although several observations of simple photocromism of dye molecules doped in mesoporous silica have been reported. The main difficulty on the chiroptical property probably exists in lack of mesoporous silica materials with appropriate chiral medium. Recently, we have successfully prepared mesoporous silica films densely packed with chiral peptide assemblies in their pores.[17-19] Here, we report preliminary results on photochromism and chiroptical responses from spiropyran and diarylethene derivatives that were doped into the peptide assemblies of the mesoporous silica films.

2. EXPERIMENTAL

The molecules used in this research are summarized in Fig.1. A typical procedure for the fabrication of spiropyran-doped mesostructured silica films is as follows. A mixed solution containing 0.0053 g of *conc*-HCl, 0.204 g of H_2O, 1.684 g of MeOH, and 1.00 g of tetramethyl orthosilicate (TMOS) was stirred for 10 min at room temperature. Amphiphilic peptide (0.1 mmol) and spiropyran derivatives (5 μmol) were dissolved in the above-mentioned sol-gel solution (0.434 g) followed by stirring for an additional 20 min at room temperature. A transparent film was obtained by spin-coating the resulting sol-gel solution (final mixing molar ratio: peptide / spiropyran / H_2O / HCl / TMOS / MeOH = 0.1 / 0.005 / 1.7 / 0.0076 / 1 / 8). Mesoporous silica films doped with the diarylethene derivative were prepared by a similar procedure. Electronic absorption spectra, circular dichroism (CD) spectra, FT-IR spectra, and X-ray diffraction (XRD) patterns were recorded on JASCO V-570 spectrophotometer, JASCO model J-820 spectrophotometer, JASCO FT/IR-660 plus spectrophotometer, and Rigaku model RINT2500PC small and wide-angle XRD diffractometers, respectively. The transmission electron microscopic (TEM) images were obtained on a JEOL JEM-2010 transmission electron microscope at Mitsui Chemical Analysis and Consulting Service Inc. Profiles of thermogravimetric analysis (TGA) were recorded on a Mettler Toledo TGA/SDTA851 thermogravimetric analyser. Resolution of **DE-c** was achieved by analytical chiral column stationary phase HPLC using a 25 cm x 4.6 mm i.d. Daicel AD-H column (6:4 hexane/2-propanol v/v,
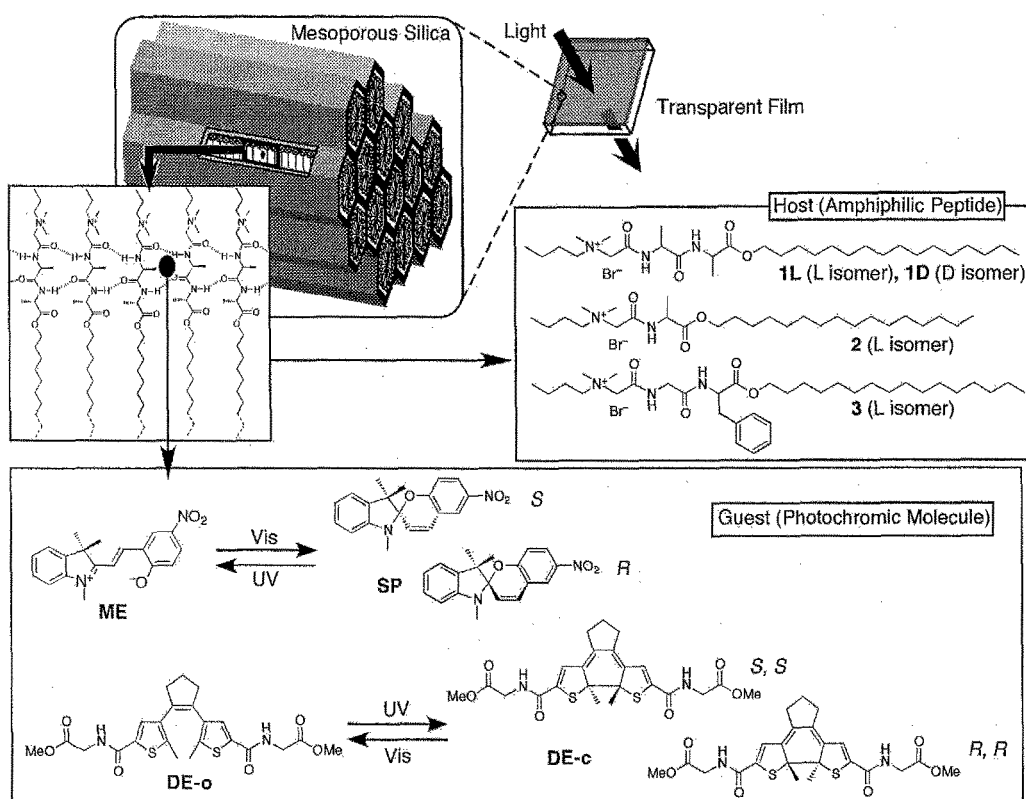
Fig. 1 Outline of this study was illustrated with formulae of host peptides and guest molecules.

0.4 mL min⁻¹).

3. RESULTS AND DISCUSSION

3.1 Spiropyran photoreaction in mesopore films.

The XRD pattern of the film was characteristic of a hexagonal silicate structure, with (100) and (200) diffraction peaks and with the d spacing of the former being 4.5 nm (Fig. 2A(a)). A diffraction peak remained after calcination at 450 °C for 3h (Fig. 2A(b)),
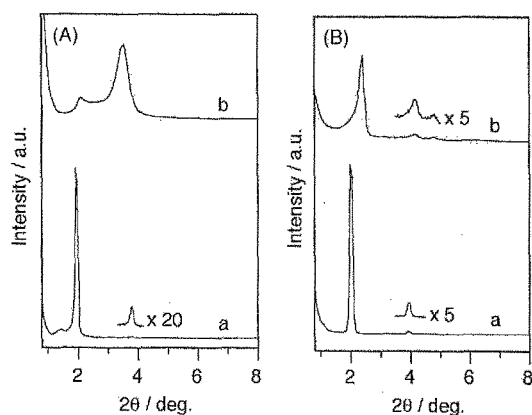

Fig. 2 XRD profiles of the spiropyran-doped mesoporous silica film (A) and the diarylethene-doped mesoporous silica film (B): a, before calcination; b, after calcination. Host peptide is 1L.

although the d spacing decreased and the peak was somewhat broadened. The hexagonal structure was also confirmed by a TEM image (Fig. 3A) showing the hexagonally packed channels with a diameter of approximately 4.3 nm. Thermal analysis based on TGA measurement showed that the composite silica film underwent a weight loss of 47.9% at 180–550 °C.

UV/visible light irradiation is known to cause reversible photoisomerization between the closed spiropyran form (SP) and the open merocyanine form (ME).[15] The obtained silica films were transparent and exhibited reversible photochromism upon light
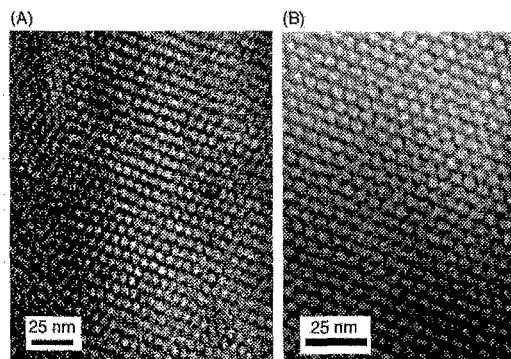

Fig. 3 TEM images of the spiropyran-doped mesoporous silica film (A) and the diarylethene-doped mesoporous silica film (B). Host peptide is 1L.

irradiation. The freshly prepared film was red-colored, reflecting the presence of the **ME** form. The electronic absorption spectrum of the UV-irradiated hexagonal film showed an intense peak at 410 nm indicating that part of the **ME** was protonated (Fig. 4A(b)).[20,21] The film color was lost upon visible light irradiation (420 nm) and the resulting film gave a spectrum having peaks at 270 nm and 340 nm, which are typical characteristics of the closed **SP** form (Fig. 4A(a)).[20,21] Alternate irradiation by visible light and UV light (280 nm) converted the spiropyran reversibly to **SP** and **ME**, respectively.

In the **SP** form, the presence of a chiral center can induce a chiroptical response. Circular dichroism (CD) spectra of the spiropyran-doped hexagonal film were simultaneously measured. The CD signal from the film containing the **ME** guest in 1L-filled film was almost negligible (Fig. 4B(b)). Therefore, the induced CD of the achiral **ME** is not significant even in the chiral peptide assembly. In contrast, the 1L film containing the closed **SP** guest showed clear CD signals (Fig. 4B(a)). A mirror image of the CD spectrum was observed when the chirality of the host was reversed to 1D (Fig. 4B(c)). Spectral shapes of these films are similar to those of solutions of chirally resolved **SP**
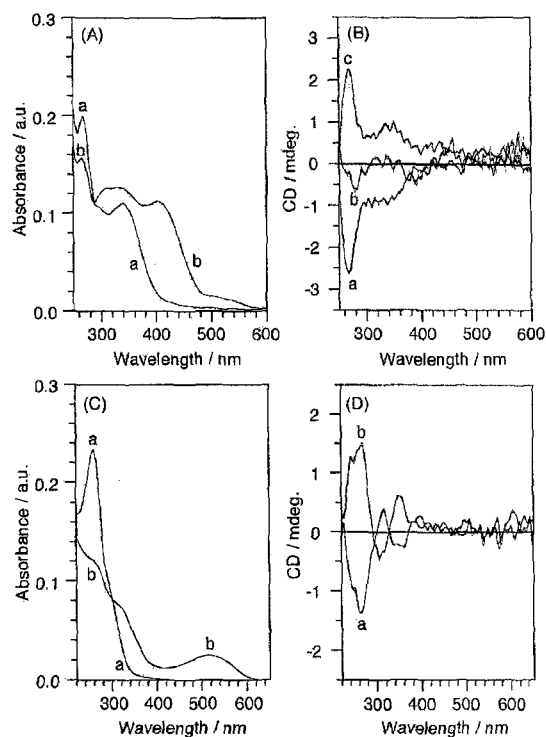
molecules although slight red-shifts were observed.[15] Alternate irradiation of the UV light and visible light induced a repeatable change of CD signals with near-zero response from the **ME** form. This switching ability implies availability of this mesoporous film for reversible recording, reading and erasing of the chiroptical signals.

3.2 Diarylethene photoreaction in mesopore films.

As the second example, photocyclization of the diarylethene derivative (see Fig. 1) in the chiral peptide assemblies filled in a mesoporous silica film was similarly investigated. Diarylethenes are known to show excellent thermal irreversibility and fatigue resistance that are indispensable characteristics for optoelectronic applications such as memory and switching devices.[22-26] Their closed forms have chiral centers and, therefore, its application to non-destructive memory reading is expected. Mesoporous silica films containing host peptide and the diarylethene derivative were prepared by a procedure silmilar to the spriropyran-doped films. Formation of a regular hexagonal structure was indicated by sharp peaks in the XRD pattern (Fig. 2B(a)) that remained after the calcination process (Fig. 2B(b)). Its TEM image also confirmed a hexagonal pore arrangement (Fig. 3B).

Irradiation of UV right (313 nm) induced conversion of the open form of the diarylethene (**DE-o**) to the closed one (**DE-c**) accompanied by a color change (from colorless to red). Electronic absorption spectra of the corresponding species (Fig. 4C) agreed with the previously reported spectra.[25] The spectral change can be reversibly repeated upon alternate irradiation of UV light (313 nm) and visible light (> 500 nm). As shown in Fig. 4D, clear CD signals were observed for **DE-c** in 1L-filled film. The spectral shape and intensity were qualitatively reversed when the host peptide was changed to 1D. In order to confirm asymmetric photoreaction of the diarylethene derivative, the UV-irradiated film was dissolved in aqueous HF. The resulting material after HF evaporation was analyzed by
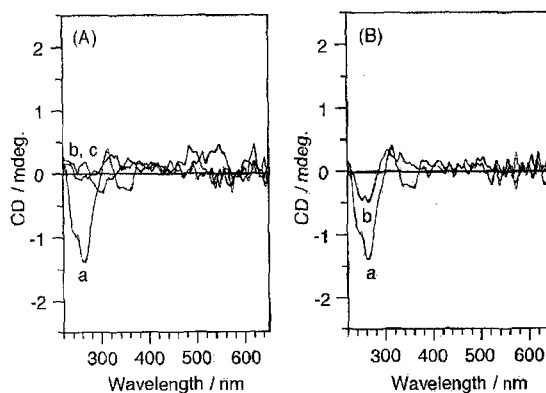
Fig. 4 (A) Electronic absorption spectra of the spiropyran-doped mesoporous silica film with 1L: a, **SP** form; b, **ME** form. (B) CD spectra of the spiropyran-doped mesoporous silica film: a, **SP** form in 1L; b, **ME** form in 1L; c, **SP** form in 1D. (C) Electronic absorption spectra of the diarylethene-doped mesoporous silica film with 1L: a, **DE-o** form; b, **DE-c** form. (D) CD spectra of the diarylethene-doped mesoporous silica film: a, **DE-c** form in 1L; b, **DE-c** form in 1D. In all the spectra, spectrum of the corresponding non-guest film was subtracted.

Fig. 5 (A) CD spectra of the **DE-c**-doped mesoporous silica film: a, in 1L; b, in 2; c, in 3. (B) CD spectra of the 1L-containing silica film doped with **DE-c**: a, in regular hexagonal geometry; b, in amorphous geometry. In all the spectra, spectrum of the corresponding non-guest film was subtracted.

chiral HPLC. The HPLC analysis indicated enantiomeric excess of 1.0 ± 0.2% and –0.9 ± 0.2% in the 1L-filled film and the 1D-filled film, respectively. This result confirmed that net asymmetric photoreaction of the diarylethene derivative occurred in the chiral peptide environment formed within the silica mesopores, although the enatiomeric excess value still remained low because conditions were not optimized.

The importance of interaction with the host peptide on the chiroptical response was suggested in control experiments using silica films containing other amphiphilic peptides. CD signals from **DE-c** in **2**-filled film or **3**-filled film were almost absent (Fig. 5A), although photoreaction from **DE-o** to **DE-c** was clearly observed in the corresponding electronic absorption spectra. The reason for the difference between 1 (AlaAla), **2** (Ala), and **3** (GlyPhe) are not clear, but specific interaction between the AlaAla residue and the guest diarylethene derivative is undoubtedly influential on the net asymmetric reaction. The effect of mesostructure type on the chiroptical response was similarly investigated through modifying the preparation conditions of the silica films. Intentional elongation of the so-gel reaction prior to the spin-coating process caused extensive formation of silica network resulting in an amorphous silica structure. This amorphous film showed very small chiroptical CD signals (Fig. 5B) even though the film composition (1L, **DE-c**, and silica) was almost the same as that of the hexagonally arranged film. Random mixing of the diarylethene derivative with the amphiphilic peptide should lead to an inefficient chiral interaction. The host peptide and the guest dye should be confined in well-organized nanospace for efficient chiral control of the asymmetric photoreaction.

4. CONCLUSIONS

In conclusion, we have successfully demonstrated the first examples of the chiroptical response from spiropyran-doped and diarylethene-doped peptide assemblies in mesoporous silica films. There is a notable difference in chiroptical response of the diarylethene derivative between hexagonal and amorphous films. In the present case, a successful chiroptical output was obtained only when the regular hexagonal silica matrix was used. This is a striking indicator that structure control of the host chiral environment is an indispensable factor for an improved response. This knowledge is important for the development of practical applications.

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