

Immobilization of One-Dimensional Charge-Transfer Assemblies in Mesoporous Silica Films through Discotic Molecule Templating

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In this research, we have successfully immobilized one-dimensional columns of charge-transfer (CT) complexes within the cylindrical pores of mesoporous silica films. The mesoporous composite films were prepared by use of amphiphilic CT columns composed of a discotic electron donor, a triphenylene derivative, and various acceptors as templates rather than conventional surfactants. XRD analysis of these films revealed formation of a 2D-hexagonal structure that was confirmed by honeycomb-like patterns in its TEM image. A pore diameter comparable to the molecular dimension of the donor molecule with folded side chains indicates that each CT column was stably segregated into an individual mesopore. The films have a transparent appearance with colors specific to the CT adsorption band. The immobilized CT columns displayed neither solvatochromism nor guest exchange behavior, while the interlayer CT columns were easily leached out from lamellar structured films upon exposure to organic solvent. Red-shifts observed for the CT bands of the complexes confined in the cylindrical mesopores imply long-range ordering of the column.

Key words: Mesoporous silica, Charge-transfer complex, Discotic molecule, Film, Triphenylene

1. INTRODUCTION

Mesoporous silica materials have been attracted much attention with respect to use of their uniform and regular mesopore arrays for catalysis and adsorption.¹ The organized pore structures also provide media suitable for

stabilization of quantum structures.²⁻³ Several kinds of macroscopic morphologies, such as powder,⁴ fiber,⁵⁻⁶ and film,⁷⁻¹⁰ can be fabricated. In particular the film form of the mesoporous silica has high potential due to transparency, uniformity, and micron-level thickness.^{2,11-}

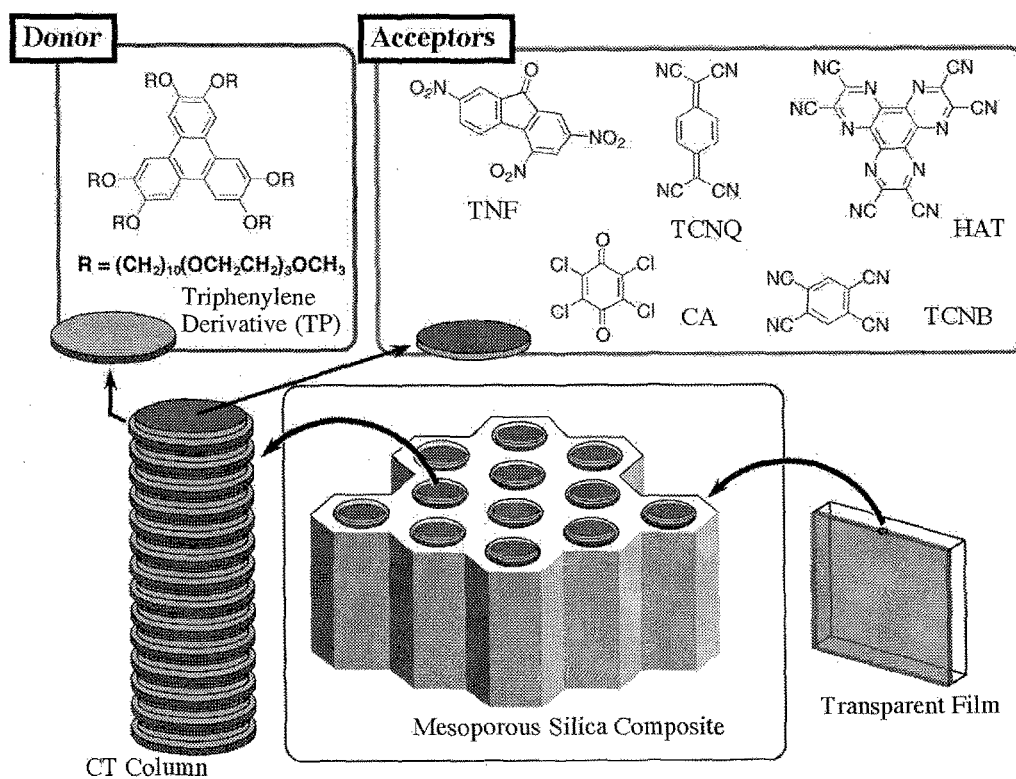


Fig. 1. Schematic representation of mesoporous silica films templated by CT columns.

¹⁴ If we use functional materials as templates for the characteristic mesopores, unique assemblies could be densely confined in size-defined pores. Unfortunately, this strategy has not been developed, because conventional surfactants are usually used as templates.

Here, we propose use of an amphiphilic discotic molecule that has a triphenylene core as a template for mesoporous silica films. This is because stacking columns of the discotic molecule show assembling behavior similar to surfactant micelles.¹⁵⁻¹⁶ Triphenylene-type donor molecules are known to form columnar CT complexes with various acceptor molecules,¹⁷⁻¹⁹ possibly leading to various functions²⁰⁻²³ such as photoconductivity. In this research, the triphenylene-type CT columns were successfully immobilized into cylindrical pores of mesoporous silica films and the confined CT column showed superior stability as well as long-range ordering (Fig. 1).²⁴⁻²⁵

2. EXPERIMENTAL

CT complexes were prepared by mixing an amphiphilic triphenylene derivative TP (Fig. 1) with electron acceptor molecules such as 2,4,7-trinitro-9-fluorenone (TNF), 2,3,6,7,10,11-hexacyano-hexaazatriphenylene (HAT), 7,7,8,8-tetracyanoquinodimethane (TCNQ) chloranil (CA), and 1,2,4,5-tetracyanobenzene (TCNB) in benzene solution followed by solvent evaporation. The donor TP²⁴ and one of these acceptors HAT²⁶ were synthesized according to the literature method, while the other acceptor molecules were obtained from commercial sources.

Mesostructured silica films were prepared as follows. Tetrabutoxy orthosilicate (TBOS) was partially hydrolyzed and oligomerized in the presence of the

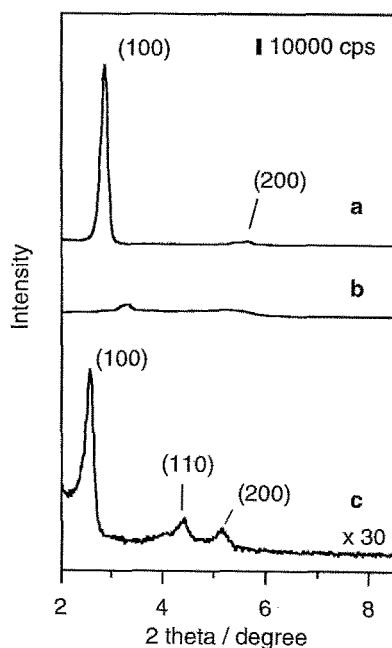


Fig. 2. XRD patterns of mesoporous silica film prepared from TP: a, before calcination; b, after calcination; c, powder scraped from the film of a.

template, the CT complexes or TP alone, with the aid of small amount of H₂O in HCl/EtOH solution. Final compositions of the precursor solutions for 2D-hexagonal and lamellar films were TP+acceptor/TBOS/H₂O/EtOH = 1/1/60/300/1500 and 1/1/20/100/4600 in molar ratio, respectively. After aging the precursor solution at room temperature for 2-48 h, it was deposited on glass substrates by spin-coating, dip-coating, or casting followed by drying at room temperature for 12 h. The films were dried at 373 K for 12 h and then calcined at 723 K for 3 h. The mesostructures of the films were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The CT columns immobilized in mesostructured silica films were characterized by electronic absorption spectroscopy.

3. RESULT AND DISCUSSION

3.1 Mesoporous silica films from the acceptor-free template.

A mesostructured silica film was successfully prepared from TP alone in the absence of an electron acceptor, although TP itself did not form any structure in the bulk phase. The formation of a regular assembly of the TP stacking columns was evidently assisted by interaction with the silica frameworks. An XRD pattern of this uncalcined film showed both a strong peak and weak peak assignable to (100) and (200) reflection of a 2D-hexagonal structure, respectively (Fig. 2a). Appearance of the (110) peak in the XRD pattern

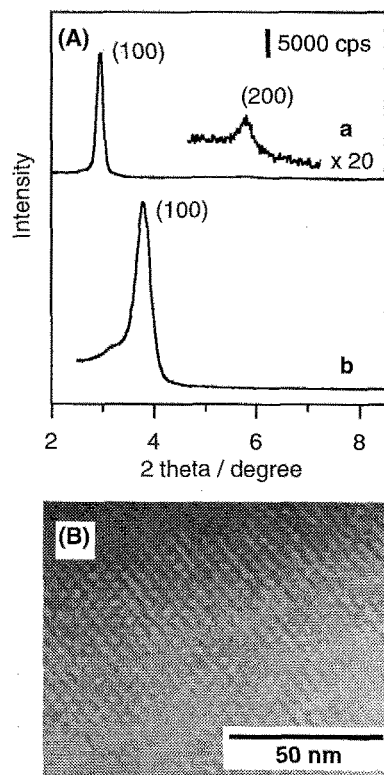


Fig. 3. (A) XRD patterns of hexagonal mesoporous films templated by a TP/TNF complex: a, before calcination; b, after calcination. (B) A TEM image of (A)-a.

of powder scraped from the film indicates the 2D-hexagonal structure of the original film (Fig. 2c), because the (110) peak is known to be absent in oriented hexagonal films.^{10,27} Pore diameter estimated from the d_{100} -spacing (3.1 nm) of the uncalcined film is comparable to the molecular dimensions of TP with folded side chains, which indicates that each TP column fills an individual mesopore. However, the XRD peaks became weak and broad after template removal by calcination (Fig. 2b). The silica frameworks are not thermally stable enough to maintain the hexagonal mesopore structure.

3.2 Mesoporous silica films from the CT complex template.

A CT complex column of TP with TNF was also successfully immobilized within the 2D-hexagonal mesopore by the templating method. This was confirmed by XRD patterns of the film (Fig. 3(A)a) and powder from the films. The TEM image of the film cross-section clearly shows a honeycomb-like structure (Fig. 3(B)), which strongly supports the hexagonal structural assignment. Pore diameter estimated from the d_{100} -spacing (3.0 nm) is comparable with the TP molecular dimension and again indicates that each CT column fills an individual cylindrical pore. Furthermore, this sharp and strong XRD peak remained after template removal by calcination (Fig. 3(A)b), which suggests that thermal stability of the silica framework was improved. The silica framework is probably stabilized by suppressing the distortion of TP column by acceptor intercalation. A similar

stabilization effect was observed for the non-silica triphenylene mesophase.^{19,28} A stabilized mesopore framework after calcination was also observed at decreased TNF/TP molar ratio (~ 0.1), which indicates that only a small amount of the acceptor is necessary for the structural stabilization. Mesoporous silica films in 2D-hexagonal geometry were similarly obtained from CT complexes of TP with the other acceptors.

Lamellar structured films confining the CT complexes were also obtained by use of the precursor solution modified with a decreasing TBOS:TP ratio and diluting with EtOH. A reduction in the molar ratio of mediating silicate to the template induced mesophase transition of the CT column/silica system to form the lamellar phase.²⁹ The strong and sharp peaks of the film were removed completely by calcination (Fig. 4A), and the (110) peak was not observed even for powdered films. These XRD characteristics clearly indicate formation of the lamellar phase. The lamellar layered structure was also confirmed by a clear striped pattern in a TEM image (Fig. 4B). The CT column is estimated to lie between silica layers that cannot completely segregate each CT column.

3.3 Electronic properties.

All the composite films are highly transparent, and stained with blue to red colors. Their absorption maxima are in order similarly to those observed in the MeCN solutions of the corresponding CT complexes (Table 1) and thus are recognized as CT bands specific

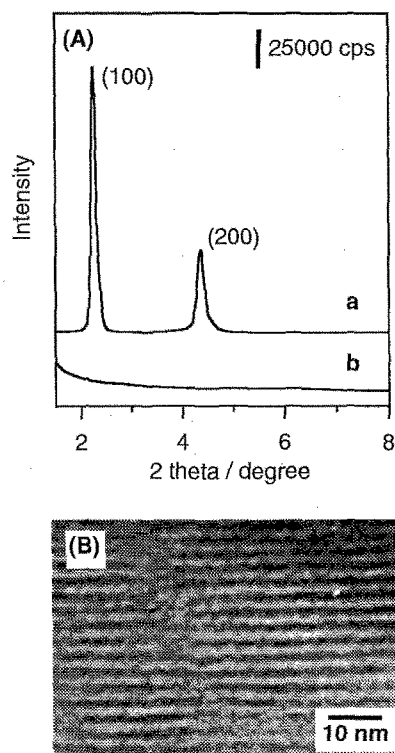


Fig. 4. (A) XRD patterns of lamellar mesoporous films templated by a TP/TNF complex: a, before calcination; b, after calcination. (B) A TEM image of (A)-a.

Table 1. Absorption maxima (nm) of hexagonal mesoporous films containing CT columns.

TNF	TCNB	HAT	CA	TCNQ
490	548	615	700	890, 410

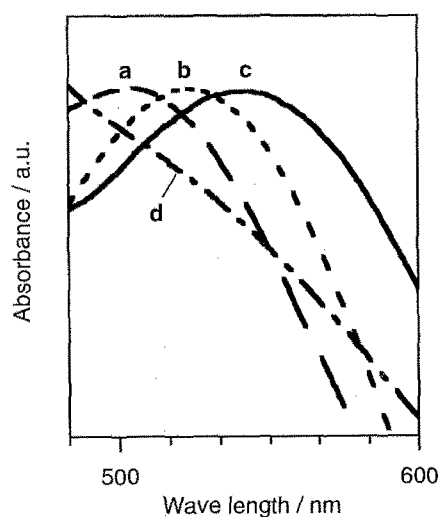


Fig. 5. Electronic absorption spectra of CT complexes, TP/TCNB, in various media: a, MeCN solution; b, cast film without silica; c, silica film with hexagonal phase; d, silica film with lamellar phase.

to paired acceptors, which indicates that CT interaction is maintained within the silica frameworks. Interestingly, these absorption maxima of the films were apparently red-shifted compared to the corresponding MeCN solutions and cast films. In Fig. 5, the CT bands of the TP/TCNB complex in various environments are summarized as typical examples. Intra- and inter-columnar packing of a triphenylene assembly has been reported to be influenced by such nano-confined space.³⁰ The shifts observed in the hexagonal mesoporous silica may arise from long-range structural ordering of densely packed columnar stacks induced by constriction within rigid silica frameworks. Effective confinement of the CT column was also apparent from its superior stability. The CT column confined in the one-dimensional pore of the hexagonal mesoporous silica was not influenced upon exposure of the film to organic solvent containing a stronger acceptor. In contrast, the CT column in the lamellar phase exhibited unclear CT bands and the complex was immediately leached out upon exposure to organic solvent.

4. CONCLUSION

We have successfully demonstrated the first example of immobilization of one-dimensional CT columns within the cylindrical pores of mesoporous silica films through discotic molecule templating. The CT interaction between the discotic donor and an acceptor was maintained inside the mesopore accompanied by a significant stabilization of the silica framework. Furthermore, the confinement of the CT complex in the nanospace probably induced long-range structural ordering of the columns. Such mesoporous composite films can be obtained from various CT complexes even in non-stoichiometric ratios. We believe that the silica films prepared in this research have considerable potential in nano-fabrication and electro-optical applications.

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