$Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\theta/2\theta$ scans, $2\theta < 56°$) at 163 K. A total of 3466 refelctions were measured, 2908 ($R_{int} = 0.0364$) independent reflections were used in further calculations and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic (for non-hydrogen atoms) and isotropic (for H atoms) approximation. The refinement converged to $R1 = 0.0632$ (from 1914 unique reflections with $I > 2\sigma(I)$) and w$R2 = 0.1591$ (from all 2795 unique reflections), the number of the refined parameters is 388, GOF = 1.022. All calculations were performed on an IBM PC/AT using the SHELXTL software (G. M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI, 53719, USA). CCDC-182770 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Color-Tunable Transparent Mesoporous Silica Films: Immobilization of One-Dimensional Columnar Charge-Transfer Assemblies in Aligned Silicate Nanochannels**

Akihiro Okabe, Takanori Fukushima, Katsuhiko Ariga, and Takuzo Aida*

Charge-transfer (CT) complexes in solution and in the crystalline state have attracted much attention in the fields of organic chemistry, photochemistry, solid-state physics, and so forth.[1] For a variety of applications utilizing CT complexes, long-range structural ordering of donor/acceptor assemblies would be important. From this point of view, disclike molecules that form columnar phases are potential candidates for the formation of infinite, one-dimensional CT assemblies, which may be useful for optoelectronic applications including photoconductive materials, solar cells, and thin-film transistors.[2] Triphenylene derivatives are representative of those molecules whose columnar phase is known to be stabilized upon complexation with suitable acceptors.[3] Immobilization of such columnar CT assemblies in optically transparent solid supports would be of great interest for materials science and device fabrication. Mesoporous silicates are particularly interesting[4] because they can provide highly ordered, unidirectional channels that are optimal for the long-range structural ordering of CT assemblies. Here we report the fabrication of novel mesostructured silica films by using triphenylene-based CT complexes as templates for sol–gel synthesis. The films were highly transparent and color-tunable from blue to red depending on the nature of the intercalating electron acceptor, and showed red-shifted CT absorption bands in the aligned silica nanochannels.

Amphiphilic triphenylene derivatives **1** and **2** were found to form CT complexes with electron acceptor molecules such as 2,4,7-trinitro-9-fluorenone (TNF), 2,3,6,7,10,11-hexacyanohexaazatriphenylene (HAT), 7,7,8,8-tetracyanoquinodimethane (TCNQ), chloranil (CA), and 1,2,4,5-tetracyanobenzene (TCNB, Figure 1). A typical procedure for the fabrication of mesostructured silica films is as follows: **1** (35.8 mg, 16.8 μmol) was added to a solution of TNF (5.28 mg, 16.8 μmol) in benzene, and the mixture was evaporated to leave a brown residue, which was then dissolved in a mixture of EtOH (1.18 g), 12 N hydrochloric acid (6.18 mg), and water (81 mg). Tetrabutoxysilane (TBOS; 324 mg, 1.01 mmol) was

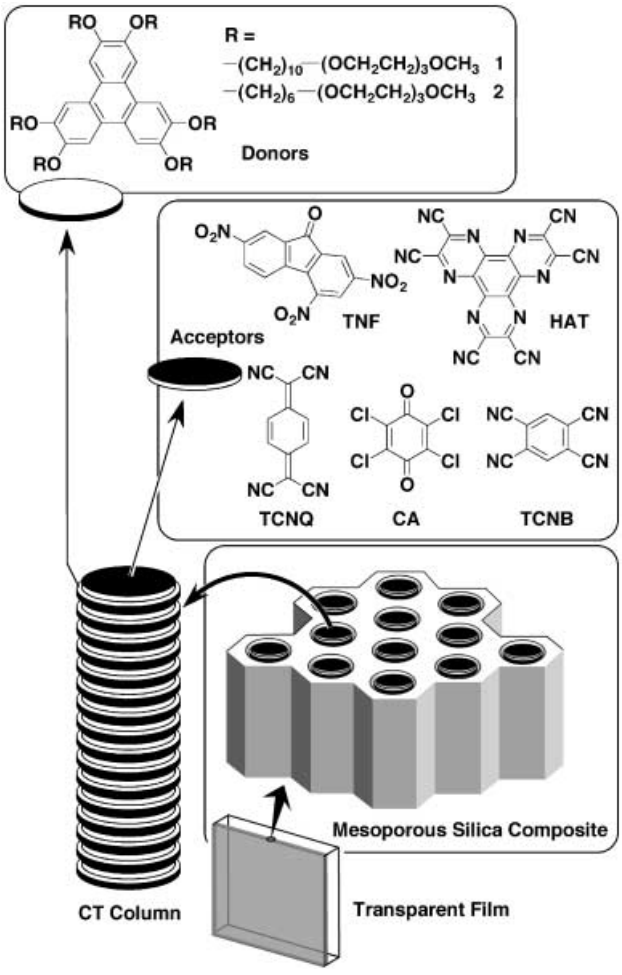

Figure 1. Formulas of donors **1**, **2**, and acceptor species, and a schematic representation of a mesoporous silica film containing one-dimensional columnar charge-transfer (CT) assemblies immobilized in a hexagonal array of nanoscopic channels.

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added to this solution, and the mixture was allowed to stand for 12 h at room temperature (approximately 25 °C), whereupon partial polymerization of TBOS took place. The resulting solution (a few drops) was cast on a cover glass to give a brown transparent film (see Figure 5a (A)), which was dried in air for 24 h at room temperature and then for an additional 12 h at 100 °C. The X-ray diffraction (XRD) pattern of the film was characteristic of hexagonal silicate structures, with (100) and (200) diffraction peaks, and with the *d* spacing of the former being 2.98 nm (Figure 2a (A)).[5] The

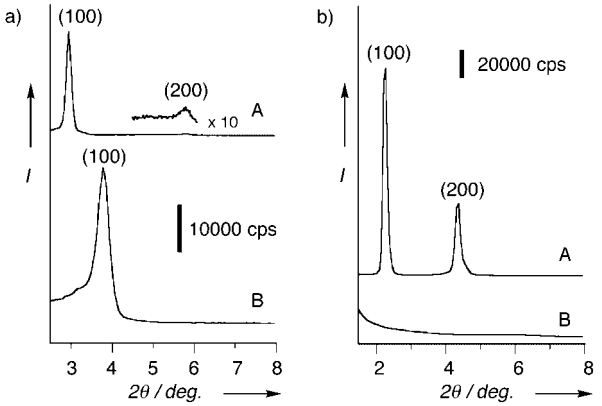

Figure 2. X-ray diffraction (XRD) patterns (A, uncalcined; B, calcined) of composite silica films prepared with an equimolar mixture of **1** and TNF, with molar ratios of TBOS and **1** of a) 60:1 and b) 20:1. Diffraction peaks (100) and (200) are at 2.98 and 1.52 nm, respectively, in Figure 2a (A); (100) at 2.34 nm in Figure 2a (B); (100) and (200) at 3.91 and 2.02 nm, respectively, in Figure 2b (A).

d spacing decreased to 2.34 nm upon calcination at 450 °C for 3 h (Figure 2a (B)). The hexagonal structure was confirmed by a very clear transmission electron microscopy (TEM) image of the film (Figure 3a). Magnified TEM images of the film (Figure 3b and 3c) indicate that hexagonally packed channels with a diameter of approximately 3 nm are regularly aligned, parallel to the substrate surface. The observed pore

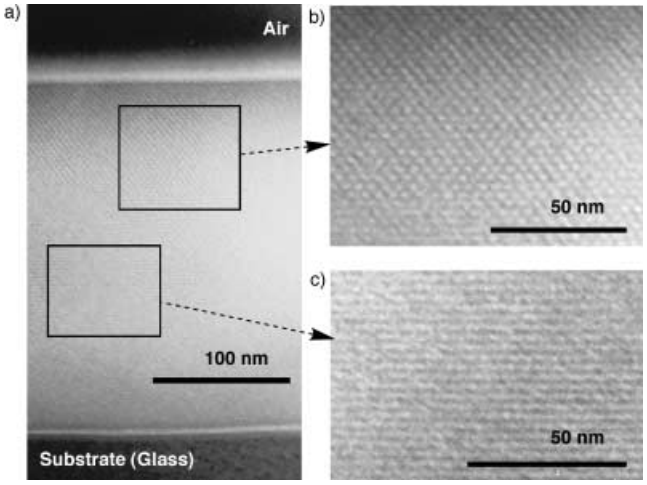

Figure 3. Transmission electron micrographs of a composite silica film (hexagonal geometry) prepared from an equimolar mixture of **1** and TNF at a TBOS/**1** molar ratio of 60:1; a) a cross-section of the whole film; b) and c) magnified for imaging the direction of the mesoporous channels with respect to the glass substrate surface. Estimated pore diameter is 2.7 nm.

diameter is comparable to the molecular dimensions of **1** with shrunken side chains, which indicates that each silicate channel contains only one CT column. Examination of the film by thermogravimetric analysis (TGA) showed that the composite silica film underwent a weight loss of 49 % at 175–600 °C, which is comparable to results reported previously.[6]

Transparent silica films with characteristic colors were successfully obtained from **1**, by a procedure similar to that described above, with all of the other acceptors listed in Figure 1, and also from **2** with TNF. Dip-coating and spin-coating, in addition to casting, were all effective for the fabrication of mesoporous composite silica films. Here, the molar ratio of TBOS to template is one of the most important factors for hexagonal structuring. A high TBOS:**1** molar ratio (for example, 60:1) resulted in a hexagonal structure, whereas silica films with a lamellar structure were obtained when the TBOS:**1** molar ratio was as low as 20:1 (Figures 2b and 4). In

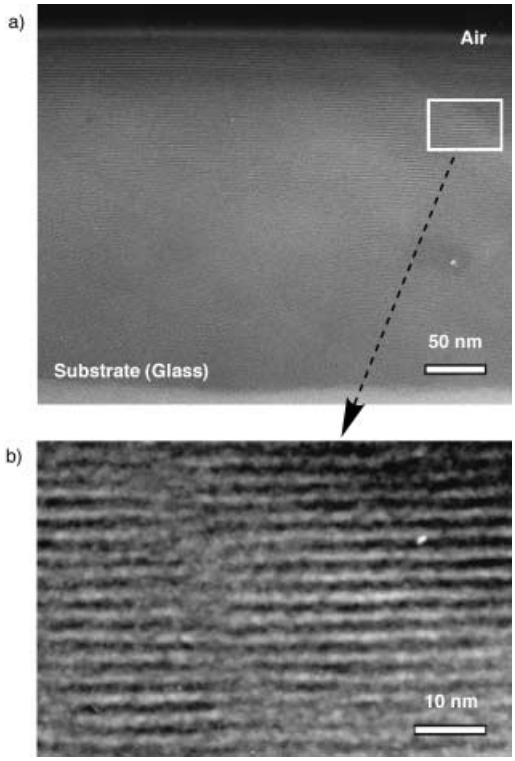

Figure 4. Transmission electron micrographs of a composite silica film (lamellar structure) prepared from an equimolar mixture of **1** and TNF at a TBOS/**1** molar ratio of 20:1; a) a cross-section of the whole film; b) magnified for imaging the direction of silica layers with respect to the glass substrate surface. The estimated thickness of the sum of the silica and the organic layers is 3.8 nm.

addition, CT interactions are crucial for the fabrication of thermally robust composite silica films. A cast silica film prepared from **1** without an acceptor displayed clear XRD peaks, which became less clear upon calcination of the film at 450 °C.[7] However, when using a CT acceptor, such as TNF, the composite silica films that were deposited maintained a clear XRD pattern, even after calcination, and at various **1**:TNF molar ratios ranging from 1:1 to 9:1. In the case where the **1**:TNF molar ratio was 9:1, it was necessary to use

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tetramethoxysilane (TMOS) instead of TBOS as the silica source and MeOH instead of EtOH as the solvent for the sol–gel process.[7] Although CT interactions contribute to the thermal stability of the composite silica films, neither **1** alone nor its CT complexes with acceptors such as TNF did not display, in the bulk phase, any liquid-crystalline textures in polarized microscopy.

The silica films were all highly transparent and exhibited a range of coloration from blue to red, characteristic of CT interactions (Figure 5a).[8] CT absorption spectra of the silica

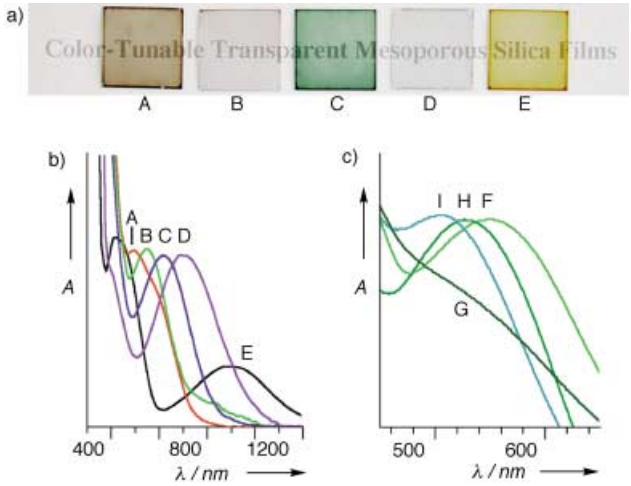

Figure 5. a) Images and b) CT absorption spectra of composite silica films prepared with equimolar mixtures of **1** and (A) TNF, (B) TCNB, (C) HAT, (D) CA, and (E) TCNQ as acceptors. c) CT absorption bands (450–650 nm) of **1**/TCNB complexes in a mesoporous silica film (F), a silica film with a lamellar structure (G), bulk phase (a cast film) without silica (H), and an acetonitrile solution (I).

films prepared with equimolar mixtures of **1** and TNF (A), TCNB (B), HAT (C), CA (D), and TCNQ (E) showed absorption maxima at 490, 548, 615, 700, and 890 nm (with another absorption at 410 nm), respectively (Figure 5b), which are red-shifted from those observed for the reference CT complexes without silica (Figure 5c). For example, the CT absorption band of the composite silica film prepared from an equimolar mixture of **1** and TCNB (Figure 5c(F); 548 nm) was red-shifted by 43 and 22 nm from those of the CT complexes in acetonitrile (2.0 mM, Figure 5c(I); 505 nm) and from the bulk phase (a cast film on a cover glass, Figure 5c(H); 526 nm), respectively. The spectral profile of the composite silica film prepared **1** and TCNB (1:1) remained unchanged when immersed for 12 h in acetonitrile and even in a solution of HAT in acetonitrile; HAT is a stronger electron acceptor than TCNB.[9] These observations suggest that the structure of the composite silica films are defect-free, in which the included CT complex is highly stabilized within nanoscopic channels and isolated from outer environments. The red shifts of the absorption maxima for the silica-immobilized CT complexes (for example, Figure 5c(F)) may be as a result of an enhanced, long-range structural ordering of densely packed donor/acceptor assemblies within the nanoscopic silicate channels. In relation to this, a silica film with a lamellar structure, prepared from **1** and TCNB (1:1 molar ratio) and used as a reference material, showed a very broad CT band (Figure 5c(G)), which was apparently blue-shifted from that of the composite silica film with a hexagonal geometry (Figure 5c(F)). Furthermore, the composite lamellar film, when immersed in acetonitrile, was immediately decolorized because of the release of the included CT complex.

In conclusion, we have demonstrated the first example of the immobilization of one-dimensional columnar charge-transfer (CT) assemblies in mesoporous silica films consisting of a hexagonal array of nanoscopic channels. The films are highly transparent and color-tunable by the appropriate choice of the intercalating acceptor, and therefore have potential for a variety of optical applications. The silica wall segregates the individual CT columns, which display neither solvatochromism nor guest-exchange activity, and exhibit red-shifted absorption bands, possibly as a consequence of a long-range structural ordering. Furthermore, the donor/acceptor molar ratio, which is related to photoconductive properties, can be varied over a wide range from 1:1 to 9:1. The present work may be the basis for new research on nanoscopic composite materials. In particular, the fabrication of anisotropic composite silica films with mesoscopic channels aligned vertically to the film surface is worthy of further investigation.

Experimental Section

HAT was synthesized according to a literature method,[10] while other acceptors were obtained from commercial sources. Donor molecules **1** and **2** were synthesized as follows: A mixture of 2,3,6,7,10,11-hexahydroxytriphenylene (80.0 mg, 0.247 mmol), 1-bromo-10-(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)decane (970 mg, 2.53 mmol),[4f] and potassium carbonate (600 mg, 4.35 mmol) in dry DMF (8 mL) was heated at 90 °C under Ar. After 66 h, the reaction mixture was poured into water, the organic layer separated, and extracted with CH_2Cl_2. The combined extract was evaporated to dryness, and the residue was purified by chromatography on silica gel with CH_2Cl_2/MeOH as eluent to give **1** as a pale-yellow oil (464 mg, 88%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.83$ (s, 6H), 4.22 (t, $J = 6.8$ Hz, 12H), 3.67–3.53 (m, 72H), 3.44 (t, $J = 6.8$ Hz, 12H), 3.37 (s, 18H), 1.97–1.89 (m, 12H), 1.61–1.52 (m, 24H), 1.45–1.27 ppm (m, 60H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 148.83$, 123.49, 107.34, 71.88, 71.46, 70.57, 70.53, 70.46, 70.00, 69.70, 58.96, 29.68, 29.64, 29.62, 29.55, 26.22, 26.14 ppm; MALDI-TOF-MS: 2138.48 ($[M+H]^+$ calcd for $C_{120}H_{217}O_{30}$: 2138.55). **2** (1.39 g, 86%) was obtained as a pale-yellow oil by a procedure similar to that for the preparation of **1**. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.82$ (s, 6H), 4.22 (t, $J = 6.8$ Hz, 12H), 3.67–3.52 (m, 72H), 3.49 (t, $J = 6.8$ Hz 12H), 3.37 (s, 18H), 1.98–1.90 (m, 12H), 1.70–1.56 (m, 24H), 1.52–1.44 ppm (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 148.83$, 123.53, 107.35, 71.89, 71.35, 70.58, 70.55, 70.47, 70.08, 69.58, 58.99, 29.70, 29.52, 26.09, 26.06 ppm; MALDI-TOF-MS: 1802.10 ($[M+H]^+$ calcd for $C_{96}H_{169}O_{30}$: 1802.17). Composite silica films with hexagonally aligned mesoporous channels were prepared in a manner described in the previous section. Composite silica films containing **1**/TNF (1:1) and **1**/TCNB (1:1) with a lamellar structure were prepared according to a method described below: Typically, an equimolar mixture of **1** (15.0 mg, 7.0 μmol) and TNF (2.2 mg, 7.0 μmol) was dissolved in EtOH (1.48 g) containing 12 N hydrochloric acid (7.77 mg). Tetrabutoxysilane (TBOS, 45 mg, 140 μmol) was added to this solution, and the mixture was allowed to stand for 12 h at room temperature (approximately 25 °C) for partial polymerization of TBOS. A viscous solution was obtained, which was cast, dip-coated, or spin-coated onto a cover glass, and dried in air for 24 h at room temperature and then an additional 12 h at 100 °C. Electronic absorption spectra and XRD patterns were recorded on a JASCO V-570 spectrophotometer and a Rigaku RINT2500PC small- and wide-angle X-ray diffractometer, respectively. The TEM images were obtained on a JEOL JEM-2010 transmission electron microscope at Mitsui Chemical Analysis and Consulting Service Inc. TGA profiles were recorded on a Shimadzu TGA 50 thermogravimetric analyzer. Calcination

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of composite silica films was carried out by initially heating for 12 h at 100 °C, followed by heating for 3 h at 450 °C in a Yamato F0810 muffle furnace.

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Characterization of a Planar Cyclic Form of Water Hexamer in an Organic Supramolecular Complex: An Unusual Self-Assembly of Bimesityl-3,3′-Dicarboxylic Acid**

J. Narasimha Moorthy,* R. Natarajan, and P. Venugopalan*

Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday

There is an upsurge of interest in contemporary theoretical and experimental research to unravel the structural details of water clusters.[1–8] The clusters are believed to be the perfect means for characterizing the structural changes and bonding mechanisms in passing from isolated molecules to a macroscopic collection, namely, bulk water, whose anomalous properties still remain mysteries.[1,2,9] A variety of modern theoretical and experimental methods have been employed to characterize the clusters. Both experiment and theory strongly suggest that the water trimer, tetramer, and pentamer have cyclic and quasiplanar minimum-energy structures. The larger clusters are expected to have 3D geometries, with the hexamer behaving as the transition from 2D to 3D structures.[1,2] The X-ray structural characterization of a decamer[10] and an octamer water cluster (cubic[11] and cyclic[12] forms) have been reported recently. Theoretical calculations for the hexamer have revealed the existence of several energy minima corresponding to "ring", "book", "bag", "cage", and "prism" topologies within 0.7 kcal mol^{-1}.[13–15] The lowest energy conformer is the "cage" followed by the "book" and "prism" structures, which are less than 0.1 and 0.2 kcal mol^{-1} higher in energy, respectively.[13–15] The "ring" and "bag" structures have been shown to be 0.5 and 0.7 kcal mol^{-1} higher in energy than the "cage". To date, "chair"[16,17] and "boat"[18] cyclic hexamers included in host lattices have been characterized by X-ray crystallographic analysis. While Saykally and co-workers characterized the cage form of the hexamer,[15] Nauta and Miller reported the detection of a "quasiplanar" hexamer in a helium droplet.[19] Herein, we report the first X-ray structural characterization of the high-energy cyclic form of the water hexamer trapped in an organic supramolecular complex with the bimesityl dicarboxylic acid **4**. The planar ring constitutes the basic structural motif of the high-pressure Ice II modification,[20] and is also one of the prominent morphologies found in the computer simulation of liquid water.[21]

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