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Photoluminescent Silicate Microsticks Containing Aligned Nanodomains of Conjugated Polymers by Sol–Gel-Based In Situ Polymerization**

Takuzo Aida* and Keisuke Tajima

Polymeric materials with unidirectionally aligned nanodomains of conjugated polymers are expected to have potential for novel electroconductive and optoelectronic devices.^[1] In this respect, template-assisted polymerizations in organized media have attracted much attention.^[2, 3] An attractive approach is to utilize mesoporous inorganic materials with ordered hexagonal arrays of uniformly sized nanoscale channels.^[4] Bein et al. reported the synthesis of a graphite-type conducting carbon nanowire by free-radical polymerization of acrylonitrile within the silicate channels of MCM-41, followed by pyrolysis of the resulting polymer.^[5] More recently, Cardin et al. reported Ni^{II}-catalyzed polymerization of alkynes inside the silicate channels of MCM-41 to give polyyne/silica hybrid composites.^[6] On the other hand, Tolbert et al. reported the synthesis of photoluminescent polymer/silica hybrids by loading poly(phenylene vinylene) derivatives into pre-formed mesoporous silicate channels.^[7] However, because of adsorption, such post-loading approaches may not always guarantee complete filling of the nanoscopic channels with functional guests. Hence, new strategies are required for the synthesis of well-defined composite materials from conjugated polymers and nanostructured silicates.

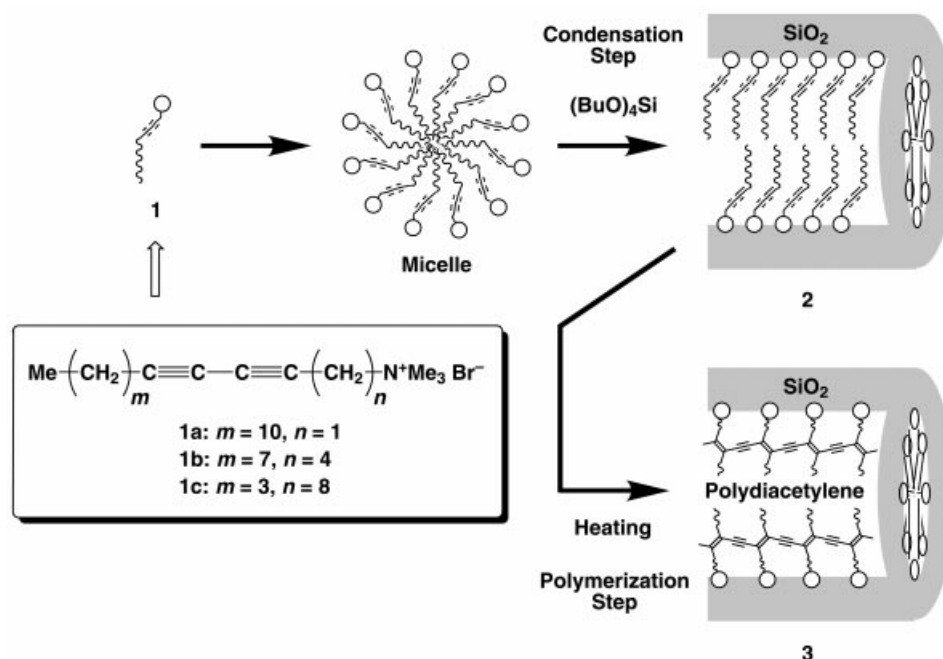
We have reported some unique approaches toward controlled macromolecular synthesis using mesoporous silicate materials.^[8–10] Here we report on the fabrication of novel micrometer-scale photoluminescent silicate sticks with segregated nanodomains of conjugated polymers by sol–gel-based in situ polymerization of diacetylenic surfactant monomers **1**, which were then used as templates for the formation of mesostructured silicates (Scheme 1). This method is expected to allow complete filling of the silicate channels with ordered diacetylenic monomers **2**. Such a dense packing of the monomer is essential for the polymerization of **1** within the silicate channel, since diacetylene derivatives can only be polymerized topochemically in condensed crystalline and semi-crystalline phases.^[11]

The template surfactant monomers 2,4-, 5,7-, and 9,11-hexadecadiynyltrimethylammonium bromides **1a–1c** were synthesized by a Cadiot–Chodkiewicz coupling reaction of

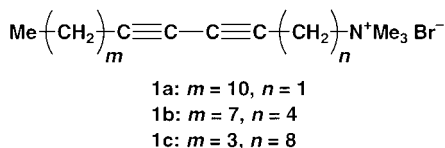
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[**] K.T. thanks the Japan Society for the Promotion of Science (JSPS) for a Young Scientist Fellowship.

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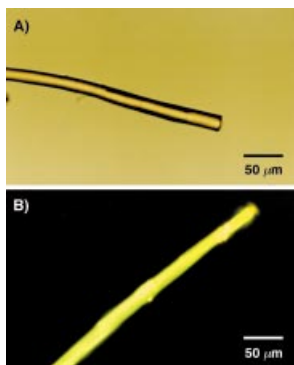


Scheme 1.

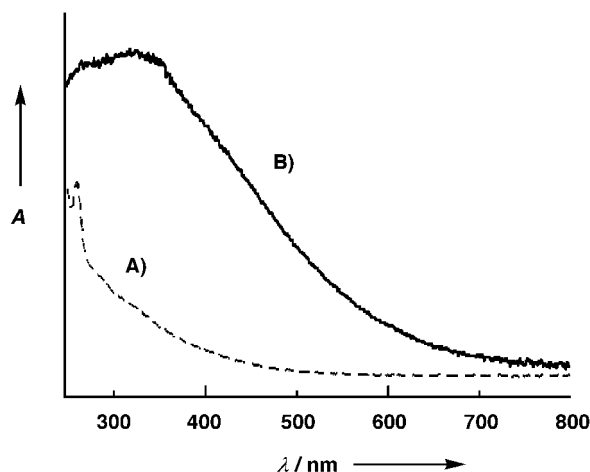
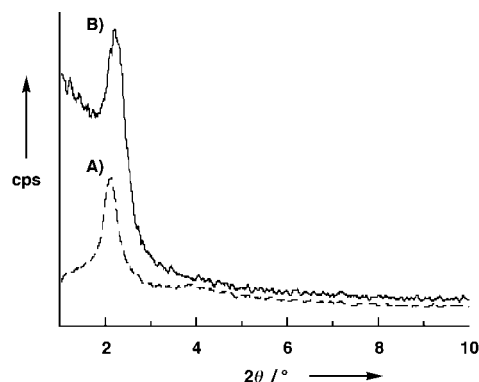


the corresponding 1-bromo-1-alkynes with alkynic alcohols, followed by subsequent transformation of the terminal hydroxy groups of the products into ammonium salts. Mesostructured silicates **2a** and **2b** were synthesized by a method reported by Stucky et al. for the preparation of mesoporous silica fiber.^[12] Typically, **1** (0.5 g) and tetrabutyl orthosilicate (0.98 g) were successively added to aqueous hydrochloric acid (6 wt %) with stirring, and the resulting phase-separated system was allowed to stand for 5 d at 20 °C. When **1a** and **1b** were used as templates, white fibrous precipitates were formed, which were collected by filtration and dried in vacuo. In contrast, when **1c** was used which has eight methylene units between the diacetylenic moiety and the ammonium ion, no precipitation resulted.

Optical microscopy showed that precipitates **2a** (Figure 1 A) and **2b** both have a sticklike morphology with a diameter of approximately 15–25 μm.^[12] The IR spectrum of **2a** showed a stretching band due to C≡C at 2260 cm⁻¹, and the electronic absorption spectrum showed a band at 260 nm and essentially no absorption bands in the visible region (Figure 2 A). These spectral profiles indi-

Figure 1. A) Optical micrograph of **2a** and B) fluorescence micrograph of **3a**.

cate that the fibrous silica contains template surfactant monomer **1a**. X-ray diffraction (XRD) on **2a** showed a peak with a d spacing of 37.7 Å, which is characteristic of a (100) diffraction originating from the hexagonal structure of the silicate.^[12, 13] Fibrous silicate **2b**, prepared from surfactant monomer **1b**, showed a smaller d spacing of 34.9 Å (Figure 3). Compared with the d spacing of 39.9 Å for a fibrous mesostructured silica prepared with a saturated template such as hexadecyltrimethylammonium bromide,^[12] these d spacings are clearly smaller and suggest a tilted orientation of the diacetylenic moiety of the monomer in the nanoscale silicate channel (Scheme 1). Thermogravimetric analysis (TGA) of **2b** showed a content of surfactant monomer of 41 wt %, which is as high as those reported for conventional mesoporous silicates con-

Figure 2. Electronic absorption spectra of A) **2a** and B) **3a**.Figure 3. X-ray diffraction (XRD) patterns of A) **2b** and B) **3b**.

taining template surfactants.^[4a, 6] Therefore, the silicate channels of **2b** are likely filled with densely packed **1b**.

Exposure of **2a** and **2b** to UV light ($\lambda_{\text{max}} = 254 \text{ nm}$) from a high-pressure mercury lamp for 2 h did not result in any color change associated with the polymerization of the included monomers. In contrast, upon heating at 170°C for 2 h under N_2 ,^[14] **2a** and **2b** both showed a marked color change from white to orange. Infrared spectroscopy on the colored material formed from **2a**, for example, showed a complete disappearance of the $\text{C}\equiv\text{C}$ vibrational band at 2260 cm^{-1} , which indicates that included monomer **1a** has polymerized to form an IR-silent $-\text{C}=\text{C}-\text{C}\equiv\text{C}-\text{C}=\text{C}-$ sequence (**3a**). Electronic absorption spectroscopy on **3a** in the solid state showed a broad band centered at 350 nm with an upper threshold around 650 nm (Figure 2B), assignable to a $\pi-\pi^*$ electronic transition of the conjugated polymer backbone. Differential scanning calorimetry (DSC) on **2b** showed a broad exothermic peak at $150-280^\circ\text{C}$, originating from the polymerization of included **1b**, while no exothermic peak was observed for a mesoporous silica reference prepared with hexadecyltrimethylammonium bromide as a nonpolymerizable template.^[13] Colored material **3b** was found to retain essentially the same XRD characteristics as those of **2b**, although the diffraction peaks were slightly less intense (Figure 3). Transmission electron microscopy (TEM) on **3b** indicated that the honeycomb array of the hexagonal silicate channels is maintained during the thermally induced polymerization of included **1b**.^[13] Fluorescence microscopy on **3a** and **3b** (Figure 1B) showed that the entire silicate sticks emit a yellowish green fluorescence. The emission spectrum of **3a** showed a broad fluorescence band centered at 550 nm , while the excitation spectrum, monitored at 550 nm , displayed a band centered at 450 nm ,^[13] which corresponds to the long-wavelength part of the absorption band of **3a** (Figure 2). Absorption and emission profiles of polydiacetylene derivatives are known to be influenced by the effective conjugation length along the polymer chain.^[15-17] In general, polymerization of diacetylenes in highly ordered, crystalline states gives nonemissive, blue polymeric materials having a long conjugation length. At lower degrees of molecular ordering, red, photoluminescent materials with a relatively short conjugation length are usually formed.

Interestingly, when the conjugated polymer was isolated from **3b**, by destroying the silicate framework with HF, and cast on a quartz plate, the emission spectrum showed two fluorescence maxima at 470 and 510 nm (Figure 4B), which are considerably blue-shifted from that of **3b** at 550 nm (Figure 4A). Similarly, the excitation spectrum of the cast film, monitored at 510 nm , also showed a peak (400 nm) with a notable blue shift relative to that of **3b** (470 nm). For comparison, when microcrystalline **1b** was thermally polymerized, the resulting polymeric material, cast on a quartz plate, showed quite similar emission (Figure 4C) and excitation spectral profiles to those of the cast film of the polymer extracted from **3b** (Figure 4B). Since these two polymers showed almost identical emission profiles in CHCl_3 ($\lambda_{\text{em}} = 470$ and 500 nm), the red-shifted spectral profiles of **3b** indicate a possible effect of confinement in the nanoscale silicate channel on the effective conjugation length of the polymer

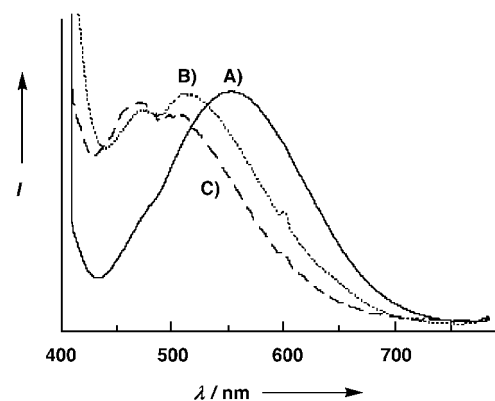


Figure 4. Fluorescence spectra upon excitation at 400 nm of A) **3b**, B) a cast film of the polymer extracted from **3b**, and C) a cast film of a polymer obtained by thermally induced polymerization of **1b**.

chain. To investigate whether the polymer extracted from **3b** can be reloaded into the nanoscale silicate channels, calcined mesoporous silica fibers^[12] were dispersed in a solution of the extracted polymer in CHCl_3 , and the resulting suspension was subjected to several freeze–pump–thaw cycles and allowed to stand overnight. Filtration of the suspension left a yellow powder, whose emission profile did not reproduce that of **3b** but was quite similar to that of the cast film of the extracted polymer. Therefore, **3b** can not be prepared by post-loading.

In conclusion, template-assisted in situ polymerization gave the first micrometer-scale photoluminescent silicate sticks with nanodomains of conjugated polymers segregated by ordered silicate channels. These silicate microsticks with a diameter of $15-25 \mu\text{m}$ are easily manipulated under the optical microscope to give a particular alignment for investigating optical and electronic properties. The present sol–gel-based approach could possibly be useful for the development of nanostructured optoelectronic and electroconductive materials.^[18]

Experimental Section

Propargyl alcohol (0.84 g , 15.0 mmol) was added at room temperature to a mixture of CuCl (90 mg), MeOH (6 mL), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.6 g), water (2.1 mL), and a $70 \text{ wt}\%$ aqueous solution of EtNH_2 (4.8 mL) under N_2 to give a yellow suspension. 1-Bromotridecyne (3.0 g , 11.6 mmol) was then added dropwise at 35°C , and the mixture was heated at 40°C for 1 h . The reaction mixture was extracted three times with diethyl ether, and the combined extract was dried over MgSO_4 and subjected to column chromatography with hexane/ethyl acetate ($10/1$) as eluent. The second fraction was collected and the solvent evaporated to give 2,4-hexadecadiynol in 68% yield. 2,4-Hexadecadiynol (0.6 g , 2.6 mmol) was treated with CBr_4 (1.1 g , 3.3 mmol) in the presence of Ph_3P (1 g , 3.8 mmol) in CH_2Cl_2 (20 mL) at 0°C for 5 min , and the reaction mixture was subjected to chromatography on silica gel with hexane as eluent. The second fraction was collected and the solvent evaporated to give 1-bromo-2,4-hexadecadiyne in 92% yield. 1-Bromo-2,4-hexadecadiyne (0.25 g , 0.83 mmol) was then treated with an excess of Me_3N (28% aqueous solution, 5 mL) at room temperature overnight, and the reaction mixture was evaporated to dryness and freeze-dried to give **1a** in quantitative yield. $^1\text{H NMR}$ (270 Hz , CDCl_3): $\delta = 0.90$ (t, 3H, CH_3), 1.28 (16H, CH_2), 1.57 (2H, CH_2), 2.30 (t, 2H, CH_2), 3.56 (s, 9H, NCH_3), 4.94 (s, 2H, CH_2); FAB-MS: m/z : 277 [$M^+ - \text{Br}$] (calcd: 276), 633 [$2M^+ - \text{Br}$] (calcd: 633). Surfactant monomers **1b** and **1c** were obtained in comparable yields in a manner similar to that for the preparation of **1a**. **1b**: $^1\text{H NMR}$ (CDCl_3): $\delta = 0.90$ (t, 3H, CH_3), 1.27 (10H, CH_2), 1.52 (2H, CH_2), 1.65 (2H, CH_2), 1.96 (2H, CH_2), 2.26 (t, 2H,

CH₂), 2.42 (t, 2H, CH₂), 3.48 (s, 9H, NCH₃), 3.72 (2H, NCH₂); FAB-MS: 276 ([M – Br]⁺ calcd 276). **1c**: ¹H NMR (CDCl₃): δ = 0.90 (t, 3H, CH₃), 1.37 (14H, CH₂), 1.77 (2H, CH₂), 2.26 (4H, CH₂), 3.48 (s, 9H, NCH₃), 3.60 (2H, NCH₂); FAB-MS: 276 [M⁺ – Br] (calcd 276), 634 [2M⁺ – Br] (calcd 633).

Thermally induced polymerization of **1b**, **2a**, and **2b** was carried out by heating a N₂-purged glass tube containing a powder sample in a Kugelrohr apparatus at 170 °C for 2 h. For extraction of the included polymer from **3b**, the composite powder was suspended in aqueous hydrofluoric acid (55 wt %) at room temperature for 1 h, and N₂ was bubbled into the resulting clear solution to flush out volatile fractions.

Absorption and fluorescence spectra were recorded in reflection mode on JASCO U-best V-560 and FL-777W spectrophotometers, respectively, with attachments for powder samples. Infrared spectra of KBr pellet samples were recorded on a JASCO FTIR-610 spectrophotometer. X-ray diffraction patterns were recorded on a Rigaku RINT 2400 diffractometer with CuK_α radiation (20 kV, 50 mA) and a step size of 0.004° at a scan speed of 1° min^{–1}. Optical and fluorescence micrographs were taken by an Olympus VANOX AH2-FL microscope, and excitation (395–415 nm) and emission filters (>455 nm) were used for fluorescence microscopy. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 at a heating rate of 10 °C min^{–1}. Transmission electron microscopy (TEM) was performed on a Hitachi H-9000UHR electron microscope operated at 300 kV.

Received: April 13, 2001

Revised: August 1, 2001 [Z16942]

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Design and Evolution of a Miniature Bcl-2 Binding Protein**

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The design of molecules that bind protein surfaces with nanomolar affinity and high specificity presents a major challenge for chemical biologists.^[1] Molecules that possess these properties have potential as therapeutic leads for protein targets^[2] and new tools for proteome research.^[3] We have described a general strategy for the design of miniature α -helical proteins^[4] that bind DNA with high affinity and selectivity.^[5] This protein grafting strategy involves identifying the α -helical residues used for DNA recognition by a natural DNA-binding protein and substituting them on the small, stable protein scaffold avian pancreatic polypeptide (aPP).^[6] Grafting of the DNA contact residues of the bZIP protein GCN4^[7] followed by functional selection generated a folded miniature protein that bound DNA with exceptional affinity and specificity.^[8] Here we demonstrate the versatility of protein grafting for the design of selective miniature protein-binding proteins (Figure 1) and report highly potent and specific ligands for human Bcl-2 and Bcl-X_L.^[9]

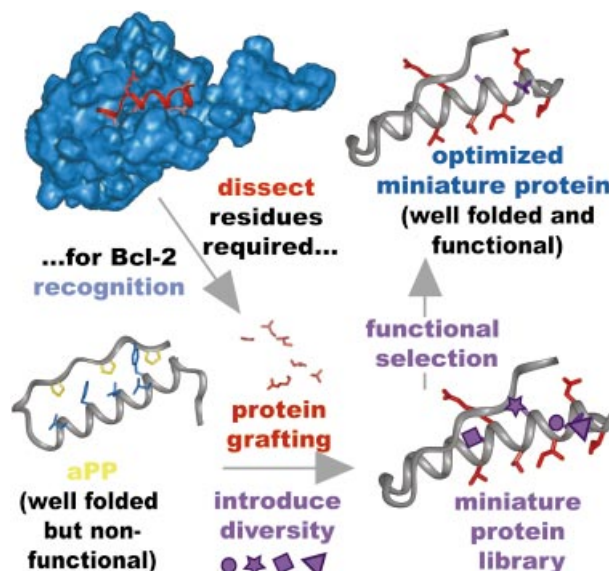


Figure 1. Protein grafting and evolution of high affinity miniature protein ligands for Bcl-2 and Bcl-X_L.

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[**] We thank the HHMI Biopolymer/Keck Foundation Biotechnology Resource Laboratory (Yale University School of Medicine, New Haven, CT) for oligonucleotide and peptide synthesis and amino acid analysis and Professor Jennifer Doudna (Yale University) for use of a Perseptive Voyager-DE (MALDI-TOF) mass spectrometer. We are grateful also to Dr. Junying Yuan and Dr. Alexi Degterev (Harvard Medical School) for a generous gift of Bcl-X_L-His₆ and Stacey E. Rutledge for helpful comments. This work was supported by the National Institutes of Health.

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