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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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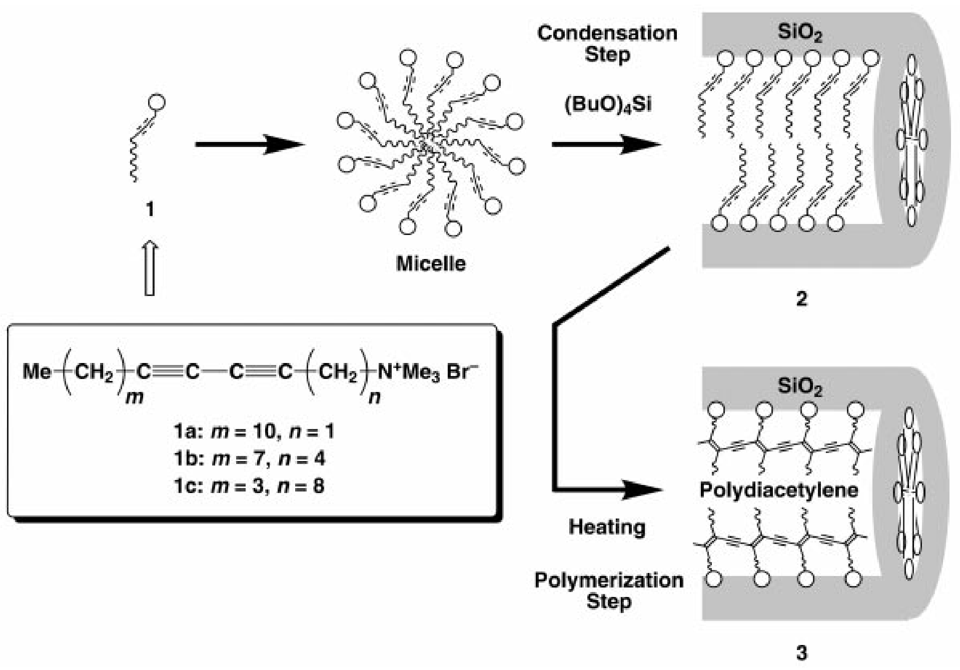

Scheme 1.

$$\mathrm{Me}\left(\mathrm{CH_2}\right)_m\mathrm{C{\equiv}C{-}C{\equiv}C}\left(\mathrm{CH_2}\right)_n\mathrm{N^+Me_3\,Br^-}$$

1a: $m = 10$, $n = 1$
1b: $m = 7$, $n = 4$
1c: $m = 3$, $n = 8$

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.

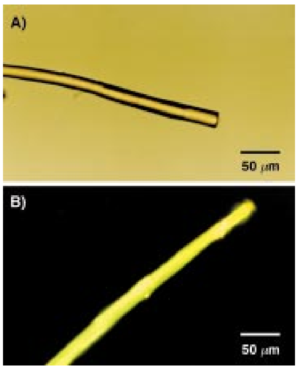

Figure 1. A) Optical micrograph of **2a** and B) fluorescence micrograph of **3a**.

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 indicate 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-

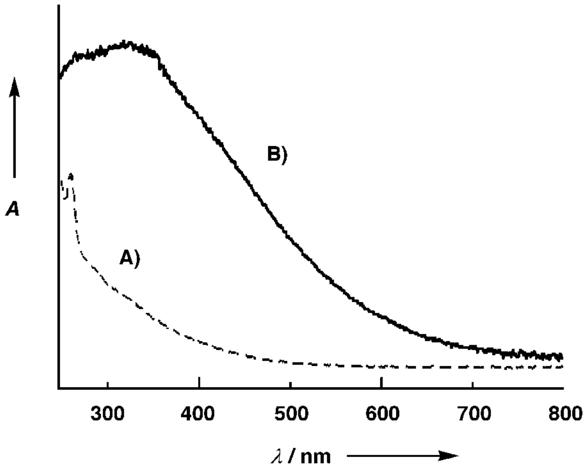

Figure 2. Electronic absorption spectra of A) **2a** and B) **3a**.

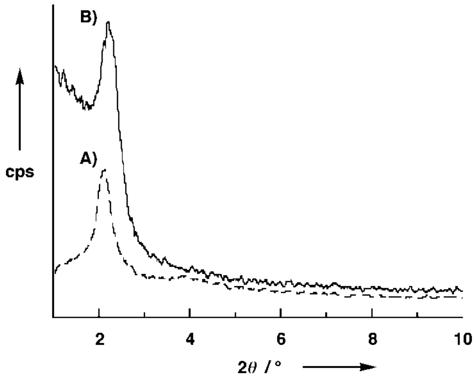

Figure 3. X-ray diffraction (XRD) patterns of A) **2b** and B) **3b**.

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 ($\lambda_{max} = 254$ 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 C≡C vibrational band at 2260 cm^{-1}, which indicates that included monomer **1a** has polymerized to form an IR-silent −C=C−C≡C−C=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 °C, originating from the polymerization of included **1b**, while no exothermic peak was observed for a mesoporous silicate 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 $CHCl_3$ ($\lambda_{em} = 470$ 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 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.

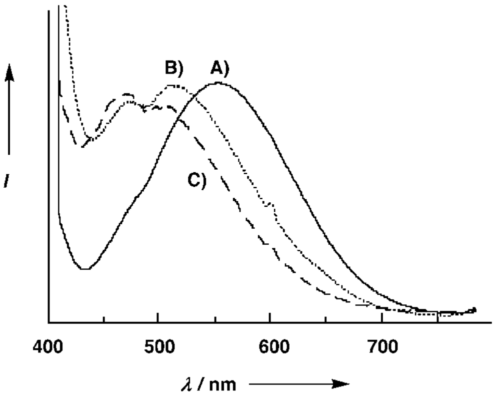

Figure 4. Fluorescence spectra upon excitation at 400 nm of A) **3b**, B) a cast film of the polymer extracted from **3b**, and C) a cast film of a polymer obtained by thermally induced polymerization of **1b**.

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 µm 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), $NH_2OH \cdot HCl$ (0.6 g), water (2.1 mL), and a 70 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. ^1H 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 [$M^+ - Br$] (calcd: 276), 633 [$2M^+ - Br$] (calcd: 633). Surfactant monomers **1b** and **1c** were obtained in comparable yields in a manner similar to that for the preparation of **1a**. **1b**: ^1H 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, CH$_2$), 2.42 (t, 2H, CH$_2$), 3.48 (s, 9H, NCH$_3$), 3.72 (2H, NCH$_2$); FAB-MS: 276 ([M − Br]$^+$ calcd 276). **1c**: ^{1}H NMR (CDCl$_3$): $\delta = 0.90$ (t, 3H, CH$_3$), 1.37 (14H, CH$_2$), 1.77 (2H, CH$_2$), 2.26 (4H, CH$_2$), 3.48 (s, 9H, NCH$_3$), 3.60 (2H, NCH$_2$); 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 N$_2$-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 N$_2$ 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 Cu$_{K\alpha}$ 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.

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

Jason W. Chin and Alanna Schepartz*

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]

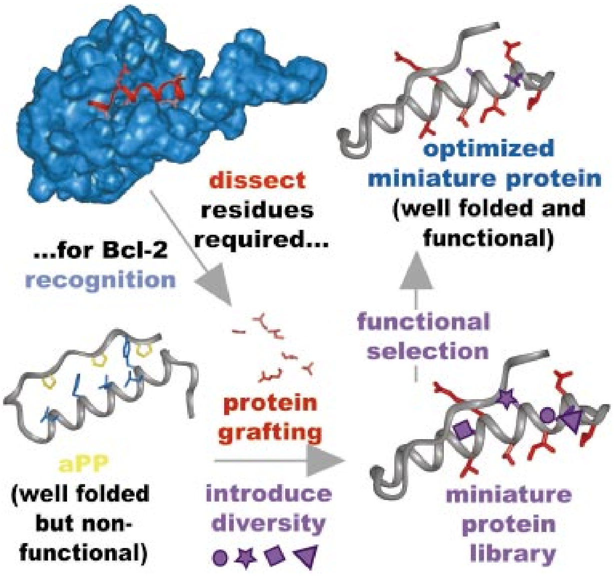

Figure 1. Protein grafting and evolution of high affinity miniature protein ligands for Bcl-2 and Bcl-X$_L$.

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