Nonionic fluorescent oligomeric surfactant for ordered mesoporous silica structure

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A fluorescent oligomeric surfactant prepared by multi-step synthesis was used as a template to obtain ordered mesostructured silica, the fluorescent surfactant completely fills the nano-channels and the emission spectrum shows that the composite is red-shifted 32 nm when compared with the surfactant in aqueous solution.

Controlling the nanoscale structure of rodlike conjugated oligomers can give optical materials of high luminescent efficiency and stability. Of particular recent interest are rod–coil block copolymers composed of π-conjugated polymer chains as the rod-like component. The incorporation of conjugated oligomers into block copolymer structures affords one the tuning of molecular organization and thus the optical and electric properties of these materials.[1–3] Recently, Yu's group[1a,b] and Stupp's groups[1c,d] have independently synthesized a series of amphiphilic molecules consisting of oligo(phenylene vinylene) end-substituted with a hydrophilic poly(ethylene glycol) segment and an alkyl chain. Such a kind of rod–coil amphiphilic structure can self-assembly into various mesostructural organizations which give improved optoelectronic properties. This is due to either isolation or alignment of the fluorophores in the mesostructure.[1] An alternative approach for achieving a similar goal is through the incorporation of the fluorescent molecules inside the nanopores of mesoporous silica materials.[4] There has been several approaches for the pore filling. However, in most of them, the degree of loading of fluorophores is not high because it is not so easy for the guest molecules to completely fill a pre-formed nanopore system.

A mesoporous solid with complete pore-filling by fluorescent molecules would be interesting since such hybrid materials would provide greater control over the molecular alignment and stability. They have great potential for optoelectronic applications.[5] To achieve this purpose, the use of functionalized template surfactants is more desirable than the post-synthesis loading approaches, since the post-synthesis loading procedures often do not provide high filling of the channels by the fluorophores.[6] It has been reported that mesoporous silica containing diacetylenic surfactants can be polymerized by photo- or thermal treatment to give fluorescent polydiacetylenes which highly filled the nano-channels.[7,8] Polypyrrole and polythiophene were formed by oxidative coupling of the corresponding surfactants in the mesostructures.[9,10] A better strategy would be combining the self-assembly approach[5–7] directly with the synthesis of mesostructured fluorophore/silica nanocomposites. In this communication, we report a preparation of fluorescent surfactants for the mesoporous silica structure. The main advantages of this approach are that the chromophores can be arranged in an ordered way in the nano-channels, and the emission of the surfactants can be controlled. Here we prepare a novel diblock co-oligomer with a fluorescent hydrophobic portion and use it as the template to synthesize an ordered mesostructured organic/silica hybrid.

Diblock copolymers with poly(ethylene oxide) as the hydrophilic portion for the synthesis of mesoporous silica were first reported by Stucky *et al.*[11] The advantage of using poly(ethylene oxide) block is that the hydrophilic and hydrophobic ratio can be fine-tuned easily, the hydrophobic tails could be of various functional groups such as alkyl chains,[11] diacetylenes,[7] and poly(methyl acrylate).[12] We can then adjust the length of conjugation in the hydrophobic portion while keeping the hydrophilic–hydrophobic balance within the formation limit for mesostructures. In this communication, we present a synthesis of the coil–rod–coil triblock copolymer, hexyl-oligo(*p*-phenyleneethynylene)-poly(ethylene oxide) (Hex-OPE-PEO) and then use it as a template for making the ordered fluorophore/silica nanocomposite.

The commercially available poly(ethylene glycol) monomethyl ether, $Me(OCH_2CH_2)_nOH$ (n = 16), was deprotonated by sodium hydride in dried THF and then treated with 4-iodobenzylbromide at room temperature to give the modified $Me(OCH_2CH_2)_nOCH_2C_6H_4I$, **1**. The hydrophobic portion **2** was prepared by a multi-step synthesis including Sonogashira reaction and desilylation starting from 1-bromo-4-iodobenzene.[13] The reaction of **1** with **2** using the Sonogashira catalytic system gave our fluorescent surfactant **3** (Hex-OPE-PEO as shown in Scheme 1).

A typical procedure for the preparation of **3** is described as follows: **1** (9.66 g, 10.0 mmol), **2** (2.52 g, 12.0 mmol), $Pd(PPh_3)_4$ (0.231 g, 0.20 mmol) and CuI (0.076 g, 0.40 mmol) were placed in a Schlenk tube, then dried THF (20 mL) and Et_3N (20 mL) were charged into the reactor. The mixture was stirred at 40 °C under N_2. It is easy to monitor the reaction by ^1H NMR, the singlet signal at 4.46 ppm is assigned as the benzylic protons of **1**. After 12 h, the signal at 4.46 ppm completely vanished and a new singlet appeared at 4.56 ppm due to the benzylic protons of **3**. After cooling the reaction mixture to room temperature, the resulting solution was passed through a short silica gel column with THF as eluent. The solution was evaporated to dryness and then redissolved in MeOH with a small amount of water. The alcoholic solution was extracted with hexane twice to remove excess **2**. The

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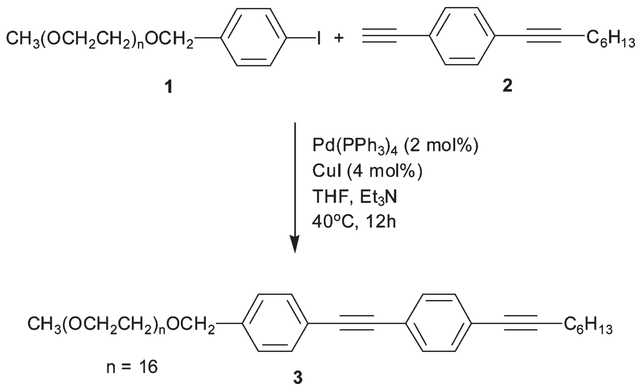

Scheme 1 Preparation of oligomeric fluorescent surfactant Hex-OPE-PEO.

methanol was evaporated and Et_2O was added and the solution containing **3** was dried over $MgSO_4$. After filtration and evaporation of Et_2O, **3** was obtained as a deep yellow viscous oil in 87% yield.† **3** is highly soluble in water, so that it can be used directly as template without addition of any co-surfactant for the preparation of organic/silica composites.

The fluorescent template–silica hybrid was synthesized according to well-known procedures for mesoporous silica.[11,12] HCl (6 g) and tetraethyl orthosilicate (1.5 g) were successively added with stirring to a solution of **3** (0.5 g) in H_2O (25 g). The clear solution turned opaque after 30 min at 30 °C and the resulting phase-separated system was allowed to stir for an additional 24 h under these conditions. The precipitate was combined with H_2O and treated hydrothermally at 100 °C for 24 h.[12,14] A yellow powder, **4**, was obtained after filtration and removal of water *in vacuo* at room temperature for 12 h.

The powder X-ray diffraction (PXRD) pattern of **4** showed a peak with a *d* spacing of 5.7 nm. The transmission electron microscopy (TEM) images showed that the composites possess an ordered mesostructure (Fig. 1). Thermogravimetric analysis (TGA) data showed the content of fluorescent surfactants of 43 wt% for **4**, which is as high as those published mesoporous silicates containing nonionic diblock copolymeric surfactants.[11]

A colorless powder was obtained after calcination of **4** at 560 °C for 6 h, the sample presented a typical type IV N_2 adsorption–desorption isotherm with sharp capillary condensation at P/P_0 around 0.4 (Fig. 2). The pore size estimated by the Barrett–Joyner–Halenda method is 3.0 nm, the pore volume of the calcined sample is at 0.76 $cm^3\ g^{-1}$, and the BET surface area is about 1028 $m^2\ g^{-1}$.

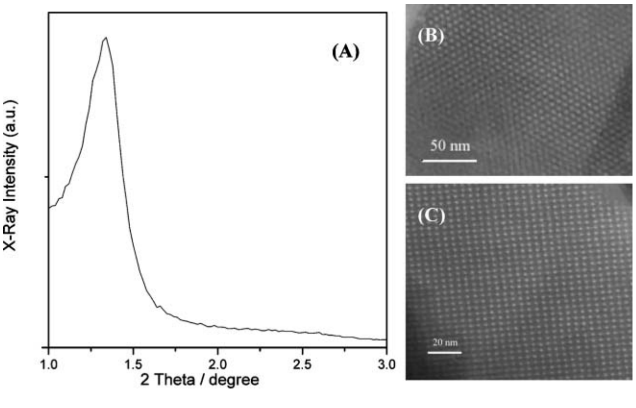

Fig. 1 (A) Powder X-ray diffraction (XRD) pattern of the as-synthesized **4**; (B) and (C) are representative TEM images of **4**.

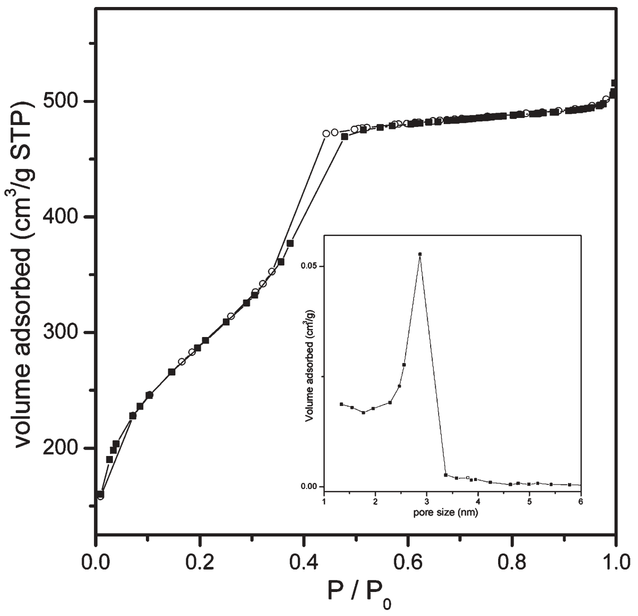

Fig. 2 Nitrogen adsorption–desorption isotherm plots and size distribution curve of the calcined **4**.

The fluorescent brightness of **3** (neat Hex-OPE-PEO) and its silica nanocomposite **4** (powder) under UV lamp light (λ = 365 nm) are compared in Fig. 3. The brightness of **4** is much higher than that of surfactant **3**. This is probably because the surfactant molecules are well-aligned unidirectionally and separated by an inorganic framework for **4**. Radiationless quenching is thus much reduced. The fluorescence spectrum of **3** (Hex-OPE-PEO) in aqueous solution shows an emission maximum at 408 nm while the emission spectrum of **4** showed a broad fluorescence band centered at 440 nm, it is 32 nm red-shifted from that of free surfactant (Fig. 4). The fluorescent red-shift of **4** may be due to either the unidirectional alignment of **3** in the nano-channels or its nonpolar environment. To make sure, an aqueous solution of **3** was also treated at 100 °C for 24 h; its fluorescent spectrum showed the emission maximum of this sample was very close to that of the untreated surfactant. Another experiment was done to demonstrate the confinement effect that a blending of surfactant **3** with commercially available silica gel did not show any shift of the emission maximum when compared with pure Hex-OPE-PEO even though the blend was hydrothermally treated at 100 °C for 24 h. There are previous reports showing that red-shifted

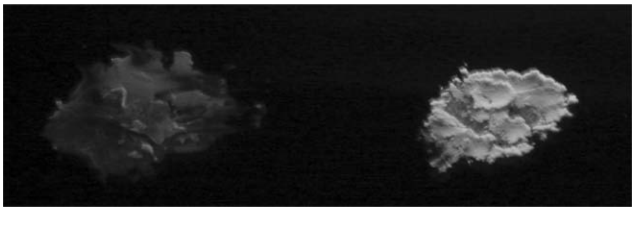

Fig. 3 Fluorescent photo image of **3** (neat, left) and **4** (powder, right) under UV light (λ = 365 nm).

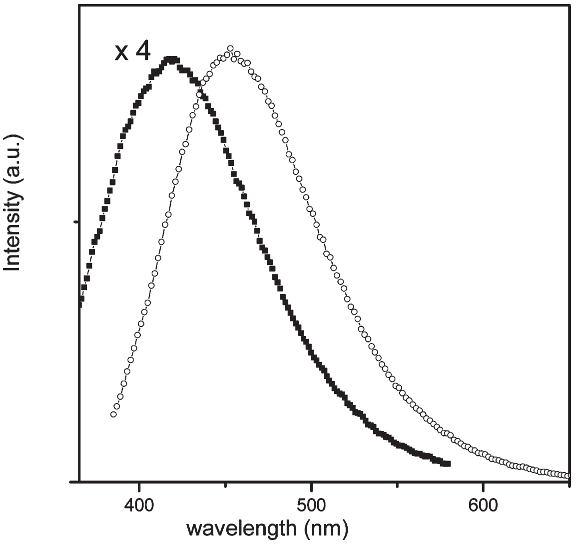

Fig. 4 Fluorescence spectra of fluorescent surfactant **3** (-■-, aqueous solution), and **4** (-○-, powder).

fluorescence of conjugated polymers is observed in a confined space or under a rigid environment.[8,15]

In conclusion, this is the first report that a complete pore-filling of fluorescent molecules inside mesopores is achieved. We have prepared a novel water-soluble fluorescent oligomeric surfactant and used it to synthesize ordered mesostructured organic/inorganic composites. Recently, Tolbert and coworkers have used CTAB as the major surfactant in order to solubilize an amphiphilic fluorescent surfactant to make mesoporous silica.[4] The loadings of the fluorophores were thus much lower. In this work, the strategy of using a block copolymer containing the rod component of fluorophores as a template for mesoporous silica is demonstrated. As a consequence, the brightness of the nanocomposites is higher and the emission wavelength is red-shifted as compared to that of the free surfactant. By varying the host–guest interactions and orientations in the nanochannels, the luminescence of the chromophore–surfactant may be judiciously controlled which is under study in our group. Furthermore, with the ease of casting the materials into films, optoelectronic applications can be envisioned.

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Notes and references

† Spectral data of **1**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, J = 7.6 Hz, 2H), 7.04 (d, J = 7.6 Hz, 2H), 4.46 (s, 2H, benzylic-*H*), 3.60 (br, OCH_2CH_2), 3.33 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.4 (2C), 136.8 (2C), 129.0, 92.7, 72.4 (benzylic-*C*), 69.5–71.8 (OCH_2CH_2), 59.0 (OCH_3). FAB-MS: *m*/*z*: 975.4 $[M + Na]^+$ (Calcd. 975.5). Spectral data of **3**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 4.56 (s, 2H, benzylic-*H*,), 3.59 (br, OCH_2CH_2), 3.32 (s, 3H, OCH_3), 2.36 (t, J = 6.9 Hz, 2H), 1.53–1.58 (m, 2H), 1.37–1.42 (m, 2H), 1.27–1.29 (m, 4H), 0.85 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 138.6, 131.9 (2C), 131.3 (2C), 131.2 (2C), 128.3, 127.4 (2C), 123.9, 122.1, 92.5, 90.5, 89.0, 80.2, 72.7 (benzylic-*C*), 69.5–71.8 (OCH_2CH_2), 58.9 (OCH_3), 31.2, 28.7, 28.5, 22.4, 19.4, 13.9. FAB-MS: *m*/*z*: 1057.6 $[M + Na]^+$ (Calcd. 1057.6).

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