been discussed in detail previously.[11, 12] Here, only the current analysis method used to monitor a titration will be elucidated:

The following considerations apply to 1:1 complexes with a stability constant K defined by [Eq. (1)], in which [C], [M], [MC] represent the concentrations of crown ether, metal ion and complex, respectively.

$$K = \frac{[\mathrm{MC}]}{[\mathrm{C}][\mathrm{M}]} \tag{1}$$

In our experiment, as well as the solvent and the crown ether as in a common HRS experiment (binary systems), the complex and the thiocyanide salt have also to be taken into account. Fortunately, no contribution of the salt could be observed; so the new HRS equation simplifies to [Eq. (2)], in which $I_{2\omega}$ (I_ω) is the harmonic (fundamental) intensity, g is a calibration constant, and $[i](\beta_i)$ are the actual concentrations (hyperpolarizability) of solvent ($i = \mathrm{S}$) crown ($i = \mathrm{C}$) and complex ($i = \mathrm{MC}$).

$$\left(\frac{I_{2\omega}}{I_\omega^2}\right) = g\,[\mathrm{S}]\beta_\mathrm{S}^2 + g\,[\mathrm{C}]\beta_\mathrm{C}^2 + g\,[\mathrm{MC}]\beta_\mathrm{MC}^2 \tag{2}$$

Further, if we could assume that $[\mathrm{M}] \approx [\mathrm{M}]_0$, we can derive [Eq. (3)].

$$\left(\frac{I_{2\omega}}{I_\omega^2}\right) = g\,[\mathrm{S}]\beta_\mathrm{S}^2 + g\,[\mathrm{C}]_0\left\{\frac{\beta_\mathrm{C}^2 + K\beta_\mathrm{MC}^2}{1 + K\,[\mathrm{M}]_0}\right\} \tag{3}$$

Here, the HRS signal is represented as a function of the initial concentrations of crown ether $[\mathrm{C}]_0$ and salt $[\mathrm{M}]_0$. Therefore, if the hyperpolarizability of the crown ether is known, one can obtain the hyperpolarizability of the complex *and* the stability constant by plotting the HRS signal as a function of the initial concentration of added metal ion.

However, as the efficiency of complexation of the studied crown ether is too high, [M] cannot be approximated by $[\mathrm{M}]_0$. Consequently, the full HRS equation is given by [Eq. (4)].

$$\left(\frac{I_{2\omega}}{I_\omega^2}\right) = g\,[\mathrm{S}]\beta_\mathrm{S}^2 + g\,[\mathrm{C}]_0\beta_\mathrm{C}^2 + g(\beta_\mathrm{MC}^2 - \beta_\mathrm{C}^2) \frac{[\mathrm{C}]_0 + [\mathrm{M}]_0 + 1/K - \sqrt{([\mathrm{C}]_0 + [\mathrm{M}]_0 + 1/K)^2 - 4\,[\mathrm{C}]_0 + [\mathrm{M}]_0}}{2} \tag{4}$$

Again, a nonlinear least-squares analysis of the HRS signal versus $[\mathrm{M}]_0$ delivers K and β_MC. A similar relation can be derived for the spectrophotometric analysis.[14]

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Self-Assembled Organometallic Block Copolymer Nanotubes[**]

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Nanostructured materials offer exciting new possibilities in science and technology because of their unique characteristics.[1] Since the discovery of carbon-based nanotubes,[2] the prospect of using such structures as components in nanotechnology has led researchers to explore the design and fabrication of nanotubules using various other materials.[3] The self-assembly of amphiphilic block copolymers in block-selective solvents has been shown to result in a myriad of nanoscale morphologies including spheres, cylinders, vesicles, and layers.[4] In addition, bilayer tubule formation was recently reported for crew-cut polystyrene-*b*-poly(ethylene oxide) in water by Yu and Eisenberg,[5] while Stewart and Liu [6] have constructed monolayer nanotubes from a triblock copolymer which forms cylindrical micelles by sequential corona cross-linking and selective core degradation. Jenekhe and Chen have also formed monolayer tubules from rod–coil block copolymers and have examined the encapsulation of fullerenes.[7]

The self-assembly of block copolymers clearly offers a potentially powerful route for the generation of nanostructured materials however, to date, virtually all the studies have focussed on organic block polymers. As a result of the discovery of the living anionic ring-opening polymerization (ROP) of strained silicon-bridged [1]ferrocenophanes, it has become possible to access polyferrocene block copolymers which combine organometallic segments with inorganic or organic coblocks.[8, 9] The incorporation of the polyferrocene block offers the opportunity to access self-assembled materials with redox-active, semiconducting or preceramic nanodomains, or with large periodic variations in the refractive index suitable for optical and photonic applications.[10, 11] We have previously reported the self-assembly of poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS, block ratio of 1:6) to form PFS cylinders within a PDMS matrix in the solid state and novel "wormlike" micelles with a PFS core and a PDMS corona in hexane. As a result of the presence of a PFS core such phase separated structures are of interest as

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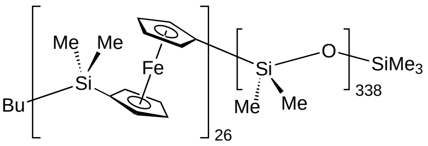
possible semiconductive or magnetic nanowires.[12] Herein, we report the surprising and facile formation of the first organometallic nanotubes using a PFS-*b*-PDMS block copolymer with a different block ratio of 1:13.

The synthesis of PFS_{26}-*b*-PDMS_{338} (**1**) was accomplished by using a sequential anionic ROP procedure analogous to that described previously.[12] In a block selective solvent for PDMS such a block ratio would be expected to promote the formation of spherical "starlike" micelles with a PFS core. However, a remarkable self-assembly process to form tubules was achieved simply by the direct dissolution of block copolymer **1** in hexanes, a good solvent for PDMS and a precipitant for PFS. Micellar solutions with various initial concentrations of polymer **1** were prepared and the formation of the tubes was confirmed by transmission electron microscopy (TEM) after solvent evaporation. As the ferrocene units are electron rich and TEM relies on differences in electron density for contrast, the poly(ferrocene) regions were imaged selectively without staining. The PDMS corona is not apparent in the TEM images unless the entire micelle is shadowed with Pt atoms (see below).



PFS-*b*-PDMS, **1**

Figure 1a illustrates the network of nanotubes produced at a polymer concentration of 2.1 mg mL^{-1} (in hexanes). The width of the tubules is 29 nm, and remains constant along the entire length. The width of the PFS shell is about 9 nm, which corresponds to the average PFS block length in a distribution of lengths, and thus leaves a cavity width of 11 nm. Tubules formed at a concentration of 1 mg mL^{-1} or greater have the same width. The length of these nanotubes ranges from 360 to 930 nm. One can also observe the presence of monodisperse spherical aggregates or hollow spheres, among the tubules. These spheres have a diameter of 29 nm, the same as the width of the nanotubes. As discussed below, these spheres appear to fuse over time.

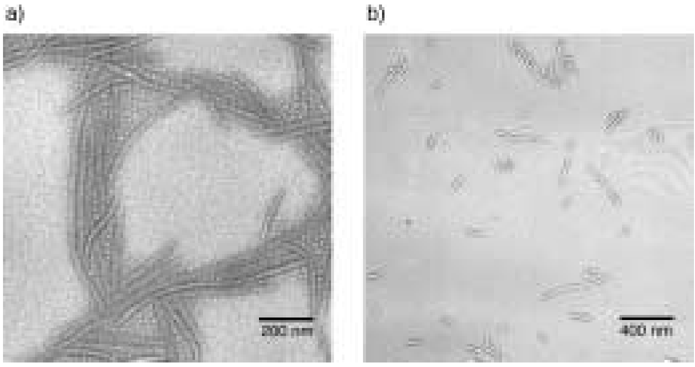


Figure 1. TEM micrographs of PFS-*b*-PDMS miscelles in hexanes taken after three days of self-assembly at concentrations of: a) 2.1 mg mL^{-1} and b) 0.55 mg mL^{-1}.

At a lower concentration of 0.55 mg mL^{-1} (Figure 1b), hollow spheres and tubes of various lengths form, which provided further interesting data. The tubes are 40 nm wide, with a cavity of 22 nm width and lengths ranging from 50 to 500 nm. Hollow spheres are also observed in the image, with a diameter that is close to the thickness of the tubes. Even though the width of the tubes is larger than that formed at higher concentration, the width of the PFS layer remains constant at approximately 9 nm.

Based on the crystal structure of a linear pentameric oligo(ferrocenyldimethylsilane), the distance between monomers in a fully extended chain would be 6.91 Å.[13, 14] Thus, the theoretical length of a fully stretched block with 26 PFS units in the shell is 18 nm, twice as long as the measured thickness of the PFS layer. Therefore, the PFS block does not appear to be fully extended. A similar result has been observed in PFS-*b*-PDMS wormlike micelles, where the PFS core has a diameter of 20 nm, which represents a maximum PFS block length of 10 nm.[9] As 33 ferrocene units are present in the PFS block of that particular block copolymer, the theoretical fully stretched length is 22 nm, which is also twice the actual length. This observation suggests that the packing of the PFS chains in the cylindrical micelles is similar to that in the nanotubes.

Valuable information can also be extracted from Figure 1b to suggest how the organometallic tubules may form. Nanotube assembly appears to arise from the fusion of smaller "subunits", such as spherical aggregates and shorter tubes. Although no intermediate has been trapped thus far and no vesicles have been found to pinch together as Yu and Eisenberg have observed,[5] the increase of tubule length as a function of concentration suggests the fusion of smaller structures to form longer ones. A detailed time-dependence study is desirable, and we have performed some preliminary experiments. Figure 2a shows a sample taken from the 2.1 mg mL^{-1} micellar solution in hexanes after three weeks, where the length of the tubes reaches 1.50 µm, and the number of spheres has dramatically decreased. Figure 2b shows a sample taken from the 0.55 mg mL^{-1} solution after six weeks, where the spherical aggregates are also no longer present and the tubes have increased in length. These results imply that the hollow spheres are precursors of the tubules.

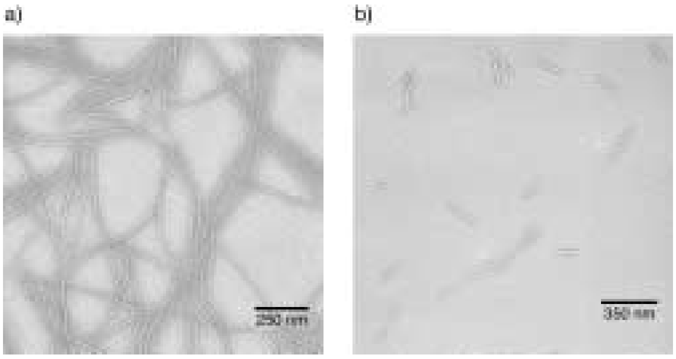


Figure 2. TEM micrographs of PFS-*b*-PDMS miscelles in hexanes: a) 2.1 mg mL^{-1} taken after three weeks, b) 0.55 mg mL^{-1} taken after six weeks.

Although there is no theory explaining the formation of cavities in systems such as ours, de Gennes predicted the formation of bilayer tubules from vesicles for a rod–coil system.[15, 16]

Noteworthy is that optical effects can make it difficult to distinguish between hollow tubes and solid cylinders by TEM a result of misfocussing. To address this issue we deposited the aggregates derived from **1** in hexanes onto a TEM grid already covered with solid cylindrical micelles of PFS_{42}-*b*-PI_{188} (PI = polyisoprene). Reexamination of the grid showed the presence of both nanotubes and cylinders.

Based on the analysis of the TEM micrographs we propose the structure for these tubules shown schematically in Figure 3a. Although we have shown evidence to indicate that these structures are single walled, it is possible that some of the PDMS chains are inverted, pointing towards the tubular cavity (Figure 3b). Thus some PDMS blocks may be trapped within the cavities during the self-assembly process. Because of the curvature, which leads to the formation of spherical and, eventually, tubular morphologies, we imagine that the number of PDMS chains in the exterior corona is much larger than the number inside the cavity.

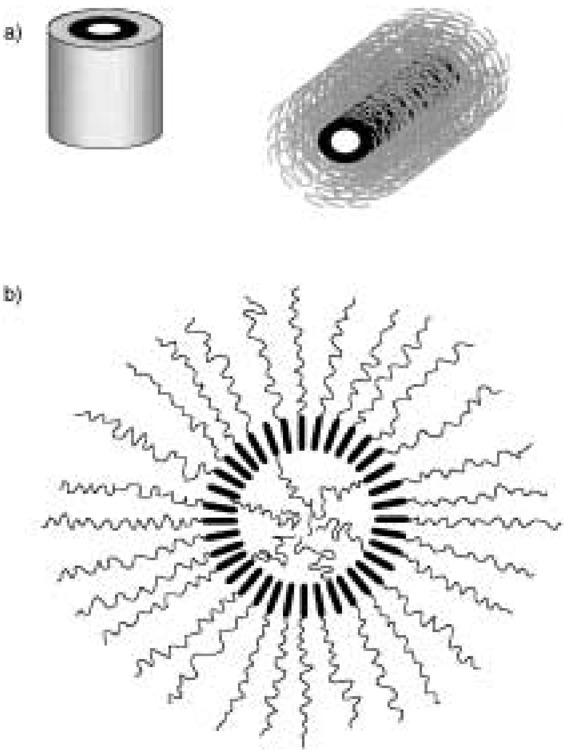


Figure 3. a) Schematic representation of a PFS-*b*-PDMS tubule. The PDMS block is the corona (gray region or coils), and the PFS block is the shell in the tube (black). The cavity is located in the middle (white). The schematic tubule is not drawn to scale. b) Schematic cross section of a tubule. PFS blocks are represented by rods and the PDMS blocks are represented by coils.

Although the images in Figure 1 and 2 indicate that the micelles formed are hollow, we attempted to obtain additional evidence to support this proposition by trying to fill the cavity with a substance that could be detected in TEM experiments. This encapsulant chosen was *n*-butylferrocene (BuFc) as this species is sufficiently volatile that material not encapsulated by the tubes would evaporate under the vacuum present in the TEM sample chamber. At the same time we hoped that loss of material by leakage through the tube ends would be relatively slow. Encapsulation was achieved by dissolving **1** in a solution of BuFc in hexanes. This procedure caused the tubules to assemble while trapping BuFc within their cavities (Figure 4).

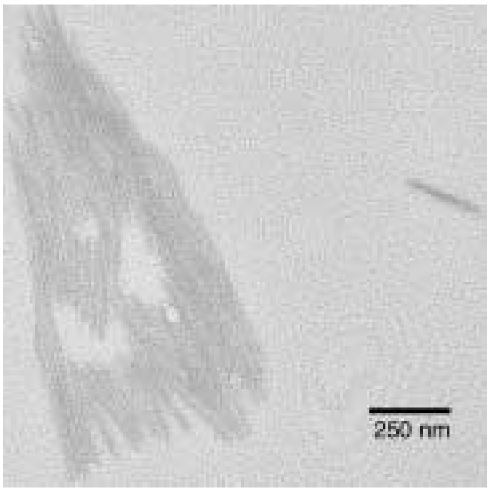


Figure 4. TEM micrograph of PFS-*b*-PDMS tubules with *n*-butylferrocene encapsulated within the cavities.

Two important pieces of information can be extracted from the Figure. First, since BuFc is electron rich it is dark under TEM relative to the background. Such contrast can be seen in the middle region of the tube, which appears clear in tubules without added BuFc, and supports the premise that these tubules are indeed hollow and that they have been "filled" with BuFc. Second, encapsulation of BuFc did not distort the morphology or dimensions (still 29 nm in width) of the self-assembled tubules.[17] As shown previously, the PFS blocks can crystallize (melting temperature (T_m) ca. 122–143 °C) and lock a structure in place.[11, 14] It would then be unlikely that facile distortion of the nanotubes would occur, and it appears that these structures are indeed stable to the addition of small molecules.

We attempted to take advantage of the hydrophobicity of the PDMS corona and added water to see if the tubules would fuse together. Four weeks after the self-assembly of tubules in a 1 $mg\,mL^{-1}$ micellar solution in hexanes twice the volume of water was added, and the mixture was agitated. TEM images showed that this treatment resulted in the organization of tubules into bundles (Figure 5). This process also increased the tubule length to 7 μm whereas the tubule width was unaffected. The fusion of these tubes in the presence of water provides further evidence for the formation of long tubes from smaller tubes and hollow spheres.

As TEM selectively images the PFS regions, the TEM-derived dimensions exclude the width of the PDMS corona. We therefore performed Pt shadow-casting TEM on the 1 $mg\,mL^{-1}$ sample to estimate the width of the corona in the solid state. Figure 6 reveals the nanostructure with a Pt coating; the hollow cavity of the tube is no longer apparent as

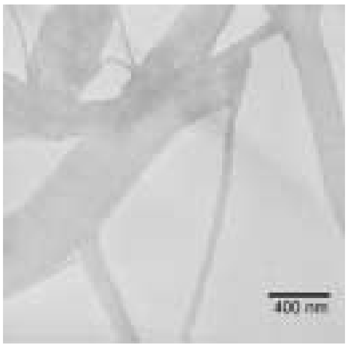


Figure 5. TEM micrograph of PFS-*b*-PDMS tubules after the addition of water.

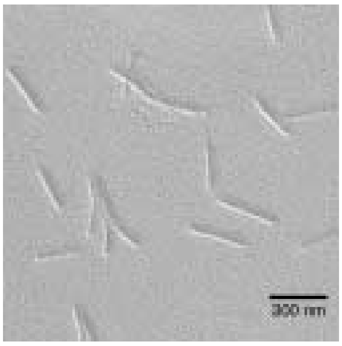


Figure 6. Platinum shadow-casting TEM micrograph of PFS-*b*-PDMS tubules performed at a 20° angle.

the dense Pt atoms cover the entire micelle. By performing some basic geometric calculations based on the angle at which this procedure was carried out (20°) and the length of the shadow, we determined the height of the tube to be between about 10–20 nm and the overall width to be around 40–50 nm. It appears that the Pt coating used partially buried the tubes, thus leading to a smaller apparent height than expected, and the geometry of the cross section therefore cannot be confirmed to be a perfect circle.

In summary, we have demonstrated the facile and unexpected formation of novel organometallic nanotubes by the self-assembly of PFS-*b*-PDMS block copolymer **1** in hexanes. Encapsulation of BuFc also showed the presence of a cavity within the tubes and the ability to insert small molecules inside the structures.

Experimental Section

The synthesis of polymer **1** was performed by a published procedure,[9, 12] the only difference was the amount of monomer used so as to obtain a 1:13 PFS:PDMS ratio. A solution of the block copolymer **1** in THF was analyzed by gel permeation chromatography (GPC) versus polystyrene standards, which revealed an estimated M_n of 36300 $\text{g}\,\text{mol}^{-1}$, polydispersity index (PDI) = 1.04. ^{1}H NMR spectroscopic analysis was used to determine the ratio of PFS to PDMS (1:13). The number of repeat units for the PFS block was determined by GPC ($M_n = 6360\,\text{g}\,\text{mol}^{-1}$) for a homopolymer sample which was removed prior to block copolymer formation. ^{1}H NMR (200 MHz, C_6D_6): $\delta = 0.28$ (s, 78H, $SiO(CH_3)_2$), 0.55 (s, 6H, $FcSi(CH_3)_2$), 4.10 (s, 4H, C_5H_4), 4.26 (s, 4H, C_5H_4). The sample of PFS_{42}-*b*-PI_{188} was prepared as part of a separate study.[17]

Encapsulation of *n*-butylferrocene (BuFc) was performed by diluting BuFc (100 mg; purchased from Aldrich Co.) with hexanes (10 mL), followed by the addition of PFS-*b*-PDMS (10 mg) to the mixture. Excess BuFc spontaneously evaporated inside the microscope.

Samples for TEM were prepared by aerosol spraying a micellar solution (ca. 50 μL) with a specific polymer concentration onto a carbon film (ca. 10 Å) grown on mica and then floated off the mica and placed on 300-mesh gilder copper TEM grids. For the samples mixed with water, a micellar solution (20 μL of a 1 $\text{mg}\,\text{mL}^{-1}$ solution) was mixed with water (40 μL). The mixture was briefly agitated and then the two-phase mixture (15 μL) was placed on a 300-mesh gilder copper grid for 2 min. The excess fluid was removed by touching the droplet with a piece of filter paper. Transmission electron micrographs were obtained on a Hitachi model 600 electron microscope.

For platinum shadow casting, a micellar solution (1 $\text{mg}\,\text{mL}^{-1}$) was sprayed on a carbon-coated mica and then placed in a high vacuum chamber coater (Edwards, model E12E4) above a 5 mm spherical platinum source at a 20° angle. Pt atoms were sprayed onto the mica by inducing high voltage at 10^{-5} Torr. The sample was then floated onto a 300-mesh copper grid.

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