

of kanemite. The resulting square pore system has not been observed among reported mesoporous materials^[1–11, 16, 18, 19] and is not defined by the geometrical packing of surfactant molecules.^[4, 10] Although the frameworks are not fully retained after calcination, this approach provides a way to incorporate inorganic structural units into mesostructured materials, which will lead to the development of novel mesoporous materials with crystalline inorganic frameworks.

Experimental Section

A layered C₁₆TMA–kanemite complex was prepared by mixing a layered polysilicate kanemite (NaHSi₂O₅·3H₂O (1.05 g) derived from δ-Na₂Si₂O₅ (1.00 g)) and a 0.1M C₁₆TMACl aqueous solution (200 mL) at room temperature; the C₁₆TMA/Si ratio was 2. The resulting C₁₆TMA–kanemite complex is a layered material, which was confirmed by the powder XRD pattern of the product (Figure 6a). The peak at a *d* spacing of 2.9 nm and the higher ordered diffraction peaks were observed, and the spacings increased when *n*-decyl alcohol was further intercalated into the product. The resulting layered complex (1.01 g) was dispersed in distilled water (150 mL; pH ca. 9.6). The pH value of this suspension was decreased by the addition of acetic acid (1M); the addition procedure was conducted slowly over 30 min. The as-synthesized KSW-2 powders were air-dried and calcined at 550 °C with a heating rate of 10 K min^{−1} in ambient air for 6 h to remove organic fractions. Although the acid species are not significant for the synthesis of KSW-2, the concentration of acids must be carefully chosen, depending on the acid species used. The amount of distilled water and the adjusted pH value are also important because the solubility of C_nTMA ions is one of the key conditions for the formation of KSW-2.

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- [1] T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* **1990**, 63, 988–992.
- [2] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, 359, 710–712.
- [3] Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gler, P. Sieger, R. Leon, P. M. Petroff, F. Schüth, G. D. Stucky, *Nature* **1994**, 368, 317–321.
- [4] Q. Huo, R. Leon, P. M. Petroff, G. D. Stucky, *Science* **1995**, 268, 1324–1327.
- [5] A. Corma, *Chem. Rev.* **1997**, 97, 2373–2419.
- [6] H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara, G. A. Ozin, *Nature* **1996**, 379, 703–705; H. Yang, N. Coombs, I. Sokolov, G. A. Ozin, *Nature* **1996**, 381, 589–592.
- [7] Y. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, M. H. Huang, J. I. Zink, *Nature* **1997**, 389, 364–368.
- [8] A. Sayari, P. Liu, *Microporous Mater.* **1997**, 12, 149–177.
- [9] T. Kimura, Y. Sugahara, K. Kuroda, *Chem. Lett.* **1997**, 983–984; T. Kimura, Y. Sugahara, K. Kuroda, *Chem. Commun.* **1998**, 559–550; T. Kimura, Y. Sugahara, K. Kuroda, *Microporous Mesoporous Mater.* **1998**, 22, 115–126; T. Kimura, Y. Sugahara, K. Kuroda, *Chem. Mater.* **1999**, 11, 508–518.
- [10] Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **1996**, 8, 1147–1160.
- [11] A. Firouzi, D. Kumar, L. M. Bull, T. Besier, P. Sieger, Q. Huo, S. A. Walker, J. A. Zasadzinski, C. Glinka, J. Nicol, D. Margolese, G. D. Stucky, B. F. Chmelka, *Science* **1995**, 267, 1138–1143.
- [12] F. Liebau, *Structural Chemistry of Silicates*, Springer, Heidelberg, **1985**, and the references therein. The variation in the chemical shifts is probably due to the changes in the various bond angles among SiO₄ tetrahedra in the single layered silicate sheets owing to the difference in the ionic radii between Na⁺ and the head group of C₁₆TMA⁺.
- [13] H. Gies, B. Marler, S. Vortmann, U. Oberhagemann, P. Bayat, K. Krink, J. Rius, I. Wolf, C. Fyfe, *Microporous Mesoporous Mater.* **1998**, 21, 183–197; S. Vortmann, J. Rius, B. Marler, H. Gies, *Eur. J. Mineral.* **1999**, 11, 125–134.

- [14] L. A. J. Garvie, B. Devouard, T. L. Groy, F. Camara, P. R. Buseck, *Am. Mineral.* **1999**, 84, 1170–1175.
- [15] K. Beneke, G. Lagaly, *Am. Mineral.* **1977**, 62, 763–771.
- [16] S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima, K. Kuroda, *Bull. Chem. Soc. Jpn.* **1996**, 69, 1449–1457. The obtained mesoporous silica in the paper was denoted as FSM-16.
- [17] G. Horváth, K. Kawazoe, *J. Chem. Eng. Jpn.* **1983**, 16, 470–475. The pore size was calculated from the adsorption branch by the Horváth–Kawazoe method.
- [18] A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B. F. Chmelka, *Science* **1993**, 261, 1299–1303.
- [19] C. A. Fyfe, G. Fu, *J. Am. Chem. Soc.* **1995**, 117, 9709–9714.

Second-Order Nonlinear Optical Properties of Functionalized Ionophores: Cation-Steered Modulation of the First Hyperpolarizability**

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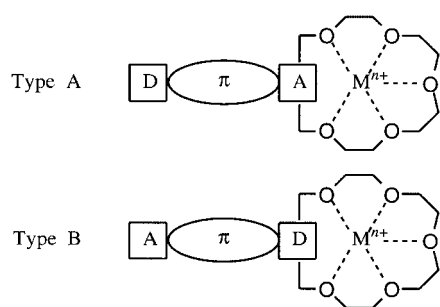
Functionalized ionophores are of major interest for their ability to complex various ionic species. As complex formation generally induces severe changes in their photophysical properties, they are widely used as a tool for ion recognition. Accordingly, the influence of cation binding on the intramolecular charge-transfer (ICT) transition has been studied intensively, mostly on donor–acceptor substituted aromatic chromoionophores.^[1–3] Among them, two classes of ionophores can be distinguished (Scheme 1): type A chromophores that interact with the ion through the acceptor site of the chromophore, which enhances the ICT and induces a bathochromic shift of the charge transfer band; and type B chromophores that interact via the donor site and reduce the ICT (hypsochromic shift).

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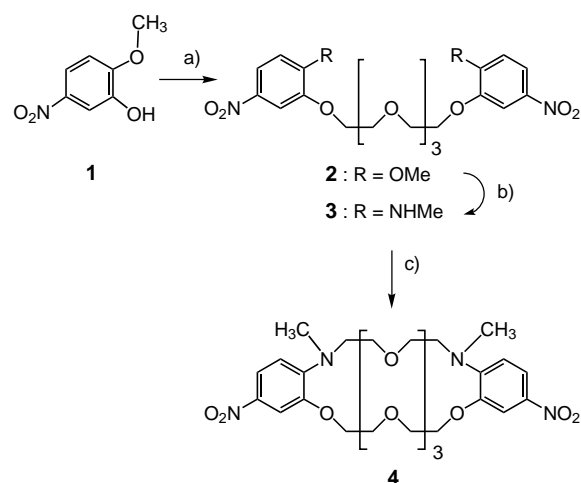
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Scheme 1. Types of interaction between chromoionophores (composed of a donor D, acceptor A, and bridging moiety) and ions.

Nonlinear optics (NLO) have received attention for its applications in the domain of optoelectronics and photonics. Organic and, more recently, organometallic materials have been the subject of elaborate studies. Their versatile synthesis, combined with large and rapid NLO properties, makes them preeminent materials of choice.^[4–6] Until recently, the optimization of their second-order NLO properties has merely focused on the synthesis of compounds with improved donor, acceptor, or bridging moieties in typical D- π -A derivatives and octopoles (noncentrosymmetry is a prerequisite for second-order NLO). Parallel to this “synthetic” approach, a new route to tailor the molecular NLO response is now being explored, namely the modification of the optical nonlinearity “after synthesis”, using the photo- or electrochemical properties of the NLO compound.^[7–9] As for the chromoionophores, the changes induced by these processes on the ICT properties are in fact responsible for the modulation of the second-order NLO efficiencies.^[10] In this regard, the influence of cation binding on the molecular hyperpolarizability of a NLO functionalized crown ether (**4**; Scheme 2) is examined.

The functionalized crown shows an intense absorption band in the visible region attributed to ICT from the amine donor to the nitro acceptor moieties. Addition of alkaline(earth) ions induces antiauxochromic (hypsochromic and hypochromic effect) shifts in the absorption spectra (Table 1), as



Scheme 2. Synthesis of NLO functionalized crown ether. a) 3,6,9-trioxaundecane-1,11-diyl bistosylate, K_2CO_3 , dry acetone, reflux, quant.; b) methanolic $MeNH_2$ solution (40% v/v), in a sealed tube, 100 °C, quant.; c) 3,6,9-trioxaundecane-1,11-diyl bistosylate, NaH, dry DMF, 80 °C, 22%.

Table 1. Experimental results for the crown ether.

	$\Delta\lambda^{[a]}$ [nm]	$\beta_{\text{excess}}^{[b]}$ [10^{-30} esu]	$\beta_{\text{titr}}^{[c]}$ [10^{-30} esu]	$\log K_{\text{HRS}}^{[d]}$	$\log K_A^{[d]}$
Crown		38			
+ Na^+	– 12	32	28	1.6 ± 0.1	1.20 ± 0.02
+ K^+	– 14	27	28	2.5 ± 0.1	2.23 ± 0.02
+ Ba^{2+}	– 13	24	26	$3 \pm 2^{[e]}$	$6 \pm 3^{[e]}$

[a] λ_{max} of the crown ether is 406 nm. [b] Hyperpolarizability obtained using an excess of cation. [c] Hyperpolarizability obtained by titration. [b,c] *p*-nitroaniline was used as an external reference (29×10^{-30} esu), relative error on $\beta = 5\%$, except for $Ba^{2+} = 10\%$. [d] Stability constant K obtained by hyper-Rayleigh scattering (HRS) or absorption (A) measurements. [e] A slight increase of the signal at high concentrations prohibits a more accurate determination of K . This increment most likely originates from a weak type A interaction.

expected for type B interactions. Moreover, upon gradual addition of the cation, the spectra show a well defined isosbestic point (Figure 1), which suggests a 1:1 stoichiometry for the crown ether–ion complex formed. Although the observed blue shift is rather small, it does indicate that the interaction between the nitrogen lone pair and the alkaline(earth) ion hinders the ICT from the amine donor to the nitro acceptor within the conjugated NLO-phore. In other words, interaction with the cation reduces the electron donor strength of the amine. As such, a reduction of the nonlinear response may be expected.

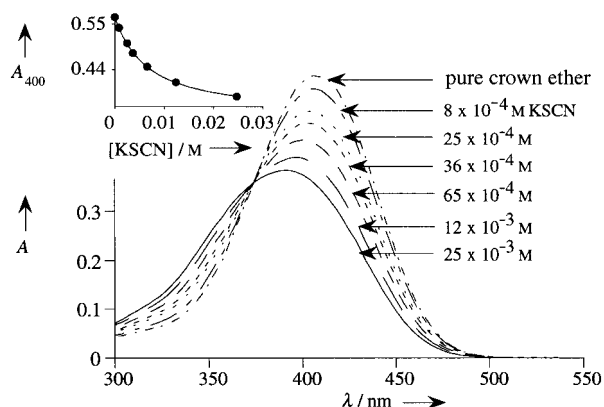


Figure 1. Effect of KSCN addition upon the absorption spectra of the crown ether **4**. Inset: Absorption at 400 nm versus the concentration of KSCN.

The molecular hyperpolarizability β of crown ether and complexes are determined by hyper-Rayleigh scattering (HRS).^[11, 12] As the induced hypsochromic shifts are rather modest and as the CT band is far from the second-harmonic wavelength (532 nm), variations in resonance enhancement are kept to a minimum. Therefore, the differences in β can be entirely attributed to the effect of the ion on the electronic structure of the NLO-active functionality.

HRS reveals a reduction of β by 25–35% upon addition of an excess amounts of cation (β_{excess} in Table 1). The largest reduction is obtained for Ba^{2+} , affirming that the bivalent ion is more efficient in attenuating the electron-donor character of the crown nitrogen atom. Further, both alkaline metal ions diminish the NLO response evenly. Hence, whereas both

diameter and charge of alkaline(earth) ions are known to influence the extent of complexation with crown ethers,^[1-3] the hyperpolarizability seems to be modulated only by their charge. Next, the NLO response has been monitored while gradually increasing the ion concentration. A progressive decrease of the HRS signal was observed (Figure 2). Utilizing

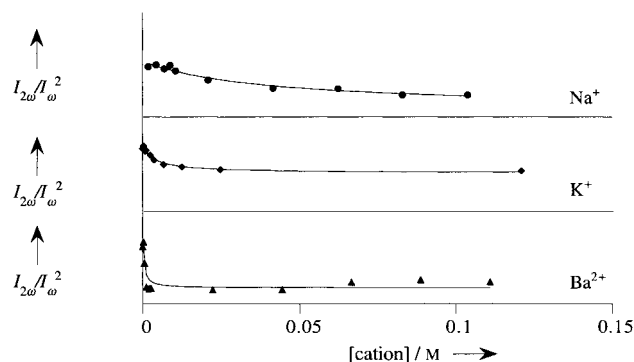


Figure 2. HRS signal ($I_{2\omega}/I_{\omega}^2$) as a function of the cation concentration. Solid lines represent the best fits according to Equation (4).

a modified HRS equation [Eq. (4)], we were able to describe this HRS signal as a function of the concentration of the added cation. The hyperpolarizabilities, as determined in the titration experiment, confirm the values found with an excess of cation. Again, the largest decrease is observed for complexation with the bivalent alkaline-earth ion. In addition, the modified HRS equation not only allowed for the assessment of β but also of the stability constant K (Table 1). The latter is shown to be in good agreement with the stability constant obtained with absorption titrimetry. In contrast to the NLO parameter, the stability constant does depend on both charge ($K_{\text{Ba}^{2+}} > K_{\text{K}^+}, K_{\text{Na}^+}$) and diameter of the cation ($K_{\text{Na}^+} < K_{\text{K}^+}$). This indicates that the match between the ionophore topology and the cation characteristics (for example, crown cavity versus ion radius) acts upon the ion affinity.^[1-3]

The results presented above demonstrate that the first hyperpolarizability of a NLO-functionalized ionophore can be reduced through cation binding. Correspondingly, they suggest that tuning can also be accomplished using type A interactions (that is, with the acceptor). To examine this route, we have studied the effect of binding K^+ on a 1,3-*cone* functionalized calixarene (**5**).^[13] For this system, the ICT band displays a significant bathochromic shift (40 nm) with an enhanced extinction coefficient upon cation binding (Figure 3), in accordance with type A interactions. As such, cation binding improves the ICT and the nonlinear response may be enhanced. The latter is again verified by HRS. In contrast to what was observed for the crown ether, the resonant enhanced hyperpolarizability of the calixarene indeed increases upon binding of the cation (Figure 4). However, no well defined isosbestic point was observed in the spectra

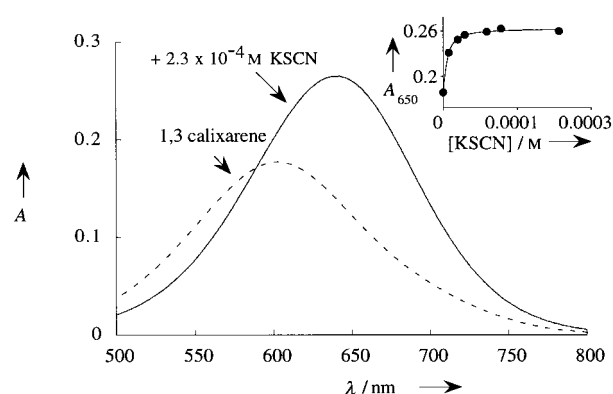
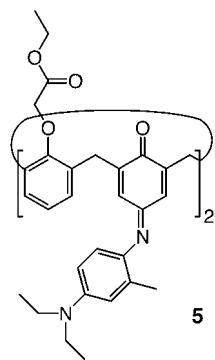


Figure 3. Effect of KSCN addition upon the absorption spectra of the indole calixarene **5**. Inset: Absorption at 650 nm versus the concentration of KSCN.

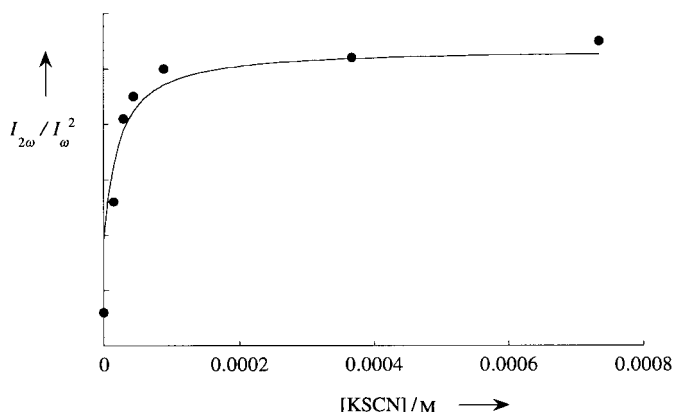


Figure 4. HRS signal of the calixarene in function of the added KSCN concentration. Solid lines represent the best fit with Equation (4).

during complex formation (no 1:1 complex), which precludes a correct determination of K , and β in the case of HRS, by titration. The study of the limiting structures revealed an increase in β of 70 % ($\beta_{\text{free calixarene}} = (170 \pm 10) \times 10^{-30}$ esu).

In conclusion, we have demonstrated that the molecular first hyperpolarizability of NLO-functionalized ionophores can be modulated through direct interaction of cations with the ionophore donor and acceptor moieties. Unprecedented, the difference in NLO response of crown ether and complex allowed us to monitor the cation binding and to determine the stability constant using hyper-Rayleigh scattering. As such, this technique offers a good alternative to study cation binding.

Experimental Section

Compound **1** was treated with 3,6,9-trioxaundecane-1,11-diyl bistosylate in the presence of K_2CO_3 to produce podand **2**, then a nucleophilic reaction with MeNH_2 afforded **3** in a quantitative yield (Scheme 2). Again, the Williamson synthesis with 3,6,9-trioxaundecane-1,11-diyl bistosylate was performed to give dibenzo-diaza[30]crown-10 derivative **4** in 22% yield after column chromatography. The synthesis of **5** has been reported elsewhere.^[13]

For the NLO experiments, acetonitrile was used as a solvent. Alkaline and alkaline-earth thiocyanides were of the highest quality available. HRS has

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.

$$K = \frac{[MC]}{[C][M]} \quad (1)$$

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 ($i = S$) crown ($i = C$) and complex ($i = MC$).

$$\left(\frac{I_{2\omega}}{I_\omega^2}\right) = g[S]\beta_S^2 + g[C]\beta_C^2 + g[MC]\beta_{MC}^2 \quad (2)$$

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

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

Here, the HRS signal is represented as a function of the initial concentrations of crown ether $[C]_0$ and salt $[M]_0$. 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 $[M]_0$. Consequently, the full HRS equation is given by [Eq. (4)].

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

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

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- [1] H. G. Löhr, F. Vögtle, *Acc. Chem. Res.* **1985**, *18*, 65.
- [2] B. Valeur in *Topics in Fluorescence Spectroscopy: Probe Design and Chemical Sensing*, Vol. 4 (Eds.: J. R. Lakowicz), Plenum, New York, **1994**, p. 21.
- [3] T. Hayashita, M. Takagi in *Molecular Recognition: Receptors for Cationic Guests*, Vol. 1 (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, G. W. Gokel), Elsevier Science, Oxford, **1996**, p. 635.
- [4] P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley-Interscience, New York, **1991**.
- [5] T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, A. Persoons, *J. Mater. Chem.* **1997**, *7*, 2175.
- [6] I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **1998**, *42*, 291.
- [7] P. C. Ray, P. K. Das, *Chem. Phys. Lett.* **1997**, *281*, 243.
- [8] B. J. Coe, *Chem. Eur. J.* **1999**, *5*, 2464.
- [9] S. Yitzchaik, T. J. Marks, *Acc. Chem. Res.* **1996**, *29*, 197.
- [10] J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664.
- [11] K. Clays, A. Persoons, *Rev. Sci. Instrum.* **1992**, *63*, 3285.
- [12] I. D. Morrison, R. G. Denning, W. M. Laidlaw, M. A. Stammers, *Rev. Sci. Instrum.* **1996**, *67*, 1445.
- [13] Y. Kubo, S. Tokita, Y. Kojima, Y. T. Osano, T. Matsuzaki, *J. Org. Chem.* **1996**, *61*, 3758.
- [14] J. Bourson, J. Pouget, B. Valeur, *J. Phys. Chem.* **1993**, *97*, 4552.

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 nano-domains, 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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