

Experimental

The textures and the growth kinetics of the hexagons were analyzed using a polarizing microscope equipped with a Mettler hot stage and a Leica image analyzing system. AFM investigations were performed with a Digital Instruments setup and fluorescence microscopy investigations were performed on the discotic host materials containing fluorescent dyes as guest molecules.

Received: July 31, 1998

- [1] S. Chandrasekhar, *Liquid Crystals*, Cambridge University Press, Cambridge **1992**.
- [2] G. Blasse, G. J. Dirksen, A. Meijerink, J. F. Van der Pol, E. Neeleman, W. Drenth, *Chem. Phys. Lett.* **1989**, *154*, 420.
- [3] D. Markovitsi, I. Lecuyer, P. Lianos, J. Malthête, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1785.
- [4] D. Markovitsi, F. Rigaut, M. Mouallem, J. Malthête, *Chem. Phys. Lett.* **1987**, *135*, 236.
- [5] D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, K. Siemensmeyer, *Phys. Rev. Lett.* **1993**, *70*, 457.
- [6] D. Adam, P. Schuhmacher, J. Simmerer, L. Häußling, K. Siemensmeyer, K. H. Etbach, H. Ringsdorf, D. Haarer, *Nature* **1994**, *371*, 141.
- [7] D. Adam, P. Schuhmacher, J. Simmerer, L. Häußling, K. Paulus, K. Siemensmeyer, K. H. Etbach, H. Ringsdorf, D. Haarer, *Adv. Mater.* **1995**, *7*, 276.
- [8] J. Simmerer, B. Glösen, W. Paulus, A. Kettner, P. Schuhmacher, A. Adam, K.-H. Etbach, K. Siemensmeyer, J. H. Wendorff, H. Ringsdorf, D. Haarer, *Adv. Mater.* **1996**, *8*, 815.
- [9] T. Christ, B. Glösen, A. Greiner, A. Kettner, R. Sander, V. Stümpflen, V. Tsukruk, J. H. Wendorff, *Adv. Mater.* **1997**, *9*, 48.
- [10] T. Christ, V. Stümpflen, J. H. Wendorff, *Macromol. Chem. Rapid Commun.* **1997**, *18*, 93.
- [11] I. H. Stapff, V. Stümpflen, J. H. Wendorff, D. B. Spohn, D. Möbius, *Liq. Cryst.* **1997**, *23*, 613.
- [12] G. Lüssem, J. H. Wendorff, *Polym. Adv. Technol.* **1998**, *9*, 443.
- [13] B. Glösen, W. Heitz, A. Kettner, J. H. Wendorff, *Liq. Cryst.* **1996**, *20*, 627.
- [14] B. Glösen, A. Kettner, J. Kopitzke, J. H. Wendorff, *J. Non-Cryst. Solids* **1998**, *241*, 113.
- [15] B. Glösen, *Ordnung und Beweglichkeit: Untersuchungen zur Struktur und Dynamik diskotischer Flüssigkristalle*, Görlich & Weiershäuser, Marburg, Germany **1997**.
- [16] T. Christ, F. Geffarth, B. Glösen, A. Kettner, G. Lüssem, O. Schäfer, V. Stümpflen, J. H. Wendorff, V. V. Tsukruk, *Thin Solid Films* **1997**, *302*, 214.
- [17] C. Baehr, M. Ebert, G. Frick, J. H. Wendorff, *Liq. Cryst.* **1990**, *7*, 601.
- [18] G. Strobl, *The Physics of Polymers*, Springer, Berlin **1996**, p. 157.
- [19] W. L. Winterbottom, *Acta Metall.* **1967**, *15*, 303.
- [20] H. Sato, S. Shinozaki, *Surf. Sci.* **1970**, *22*, 229.
- [21] B. Kevenhörster, *Diploma Thesis*, Universität Marburg, Germany **1998**.



See page 187 for ordering details.

A Simple Method to Prepare Head-to-Tail Coupled, Regioregular Poly(3-alkylthiophenes) Using Grignard Metathesis**

By Robert S. Loewe, Sonya M. Khersonsky, and Richard D. McCullough*

Poly((3-substituted)thiophenes) (PTs) represent a class of polymer that are environmentally stable, highly processable, and exhibit high electrical conductivity. These materials are promising candidates for field-effect transistors, optical and electronic sensors, light-emitting diodes (LEDs), and nonlinear optical materials, to name a few.^[1] However, the polymerization of the non-symmetrical 3-substituted thiophene leads to a mixture of PT structures containing three regiochemical linkages between repeat units (2,2', 2,5', 5,5'). The 2,2' and 5,5' couplings are considered defects in the polymer structure since they diminish conjugation and prevent ideal solid-state packing, thus impairing these materials' electronic and photonic properties. However, the synthesis of the pure 2,5' (or head-to-tail (HT) coupled) regioregular PTs was first accomplished by our group by employing Kumada cross-coupling methods to regiospecifically polymerize 2-bromo-3-alkyl-5-magnesiobromothiophene.^[2] Other methods have employed organozinc^[3] reagents with nickel(II) catalysts. We have also shown that regioregular PTs can be made using Stille cross-coupling procedures,^[4,5] while others have employed Suzuki cross-coupling.^[6] Despite these new advances, the above synthetic procedures have some drawbacks. The method developed in our laboratory^[2] requires highly purified starting materials, most important of which is the monomer, 2-bromo-3-alkylthiophene. In addition, this method requires cryogenic temperatures and long polymerization times ranging from 12 to 24 h or longer. The Rieke method starts with the easy-to-purify 2,5-dibromo-3-alkylthiophene (since the compound is the highest boiling fraction in the crude mixture in its preparation), however, it requires the non-trivial preparation of Rieke zinc via alkali metal reduction of zinc halides, employs cryogenic temperatures, and necessitates long reaction times. Both Suzuki and Stille coupling methods also suffer from many of the above drawbacks. In addition, there have been no reports of using the above methods for the large-scale synthesis of HT-PTs. This communication will describe a new method for the preparation of HT-poly(3-alkylthiophenes) (HT-PATs) that is simple, efficient, fast, and economical.

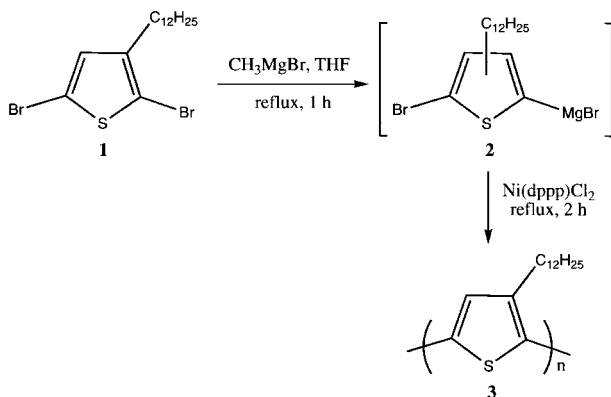
[*] Prof. R. D. McCullough, R. S. Loewe, S. M. Khersonsky
Department of Chemistry, Carnegie Mellon University
4400 Fifth Avenue, Pittsburgh, PA 15213-2683 (USA)

** We are grateful to the NSF (CHE-9509959) for financial support. We also thank Lubrizol for providing a research fellowship for RSL and Eric van Inwegen for help with syntheses.

Scheme 1 presents the new synthesis of HT-PATs. Treatment of the easily prepared and purified 2,5-dibromo-3-alkylthiophene (**1**) with one equivalent of commercially available methylmagnesium bromide in refluxing tetrahydrofuran (THF) affords intermediate **2** (as a 4:1 mixture of regiochemical isomers), which, when treated with 0.5 mol-% Ni(dppp)Cl₂, where dppp is 1,3-diphenylphosphinopropane, produces HT-coupled, regioregular poly(3-alkylthiophene) (HT-PAT). The yield of the analytically pure CHCl₃-soluble fraction is 60–70 % in 1–3 h. Regiochemical polymerization can also be achieved with vinylmagnesium bromide or dodecylmagnesium bromide in high yields (>70 %). The large-scale preparation of HT-PATs is also trivial. When 13 g of **1** (R = dodecyl) was polymerized in 3 h, 4 g of pure HT-polydodecylthiophene (HT-PDDT) was produced. All of the polymers have reasonable molecular weights (by gel permeation chromatography, GPC), low polydispersities ($M_n = 20\text{--}35$ kDa, polydispersity index = 1.20–1.47), and $\geq 99\%$ HT–HT couplings. In addition, thiophene monomers bearing polyether side chains^[7] can be polymerized by this new method as well.

The physical data on HT-PDDT prepared by Scheme 1 are identical to HT-PDDT prepared by methods previously developed in our laboratory.^[2b] It has been shown that it is possible to determine the regioregularity of PATs using ¹³C and ¹H NMR.^[3b] Figure 1 shows both the ¹H and ¹³C NMR spectra of HT-PDDT as prepared in Scheme 1. The high degree of regioregularity can be seen by the appearance of only one singlet in the aromatic region as well as a clean triplet in the methylene region of the ¹H NMR spectrum. ¹³C NMR shows only four distinct thiophene carbon resonances. The solid-state UV-vis behavior of this material is typical of HT-PDDT, with a λ_{max} of 565 nm with shoulders at 530 and 615 nm. The band edge occurs at 710 nm. Solution UV-vis spectroscopy shows a λ_{max} of 448 nm. Similar results are seen with HT-polyhexylthiophene (HT-PHT).

The above findings were a consequence of an observation made in the reaction shown in Scheme 2. Compound **1** was reacted with vinylmagnesium bromide and Ni(dppp)Cl₂ in order to produce 2-bromo-3-alkyl-5-



Scheme 1. Synthesis of HT-coupled, regioregular poly(3-dodecylthiophene).

vinylthiophene (and its isomer) (**4**). Instead, the products recovered were unreacted **1** (90 %) and regioregular HT-PDDT (10 %). The NMR of the crude mixture did not show any vinyl group resonances, suggesting that the reaction failed in its original capacity.

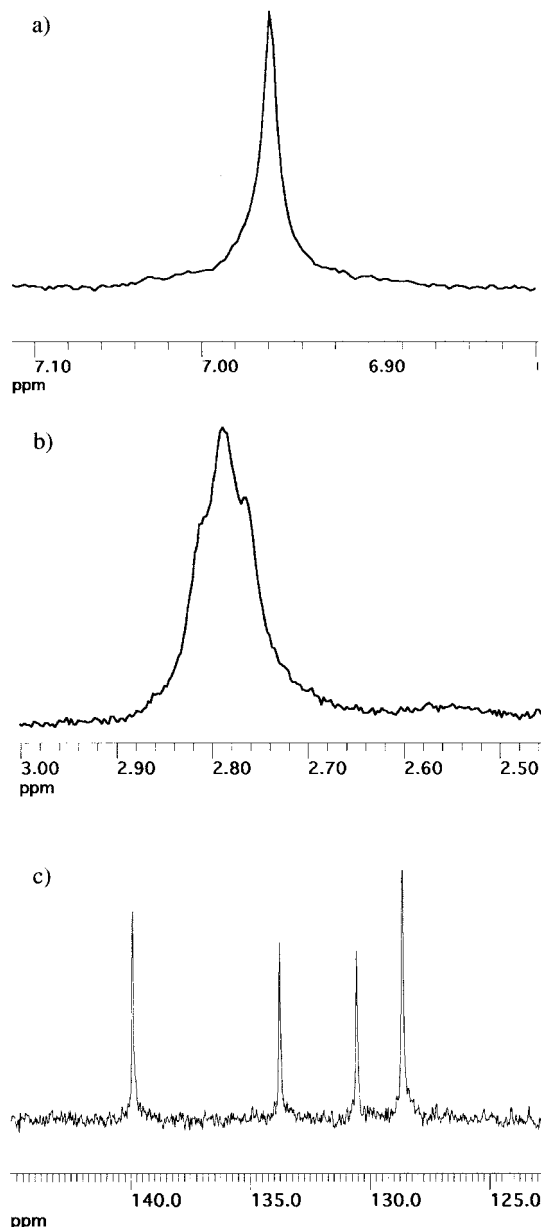
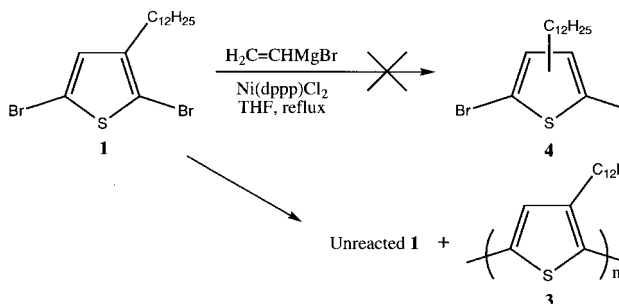
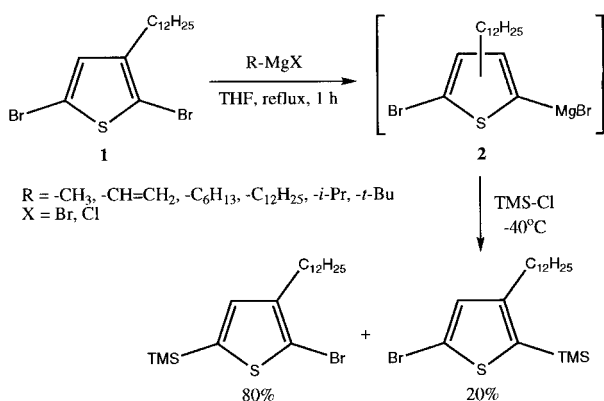


Fig. 1. ¹H and ¹³C NMR spectra of HT-PDDT: a) aromatic region (¹H), b) methylene region (¹H), c) aromatic region (¹³C).

Mechanistically, it appeared that a Grignard metathesis occurred, leading to the formation of a thienyl Grignard reagent (a more stable Grignard reagent) (Scheme 3). To test this hypothesis, compound **1** was treated with a variety of Grignard reagents and quenched with trimethylsilyl chloride. The quenching results strongly suggest that a magnesium–bromine exchange reaction is taking place. This was most clearly shown when the Grignard reagent employed



Scheme 2. Anticipated (A) and actual (B) reaction pathways.



Scheme 3. Quenching of Grignard metathesis reaction.

in the quenching study was dodecylmagnesium bromide. Quenched products consisted of a mixture of regiochemical thiophene isomers as well as dodecylmagnesium bromide (the byproduct of metathesis). These results also show (quite surprisingly) that this exchange occurs with a large degree of regiocontrol (80:20 distribution of isomers, regardless of the Grignard reagent employed, Scheme 3). Recent results on the usefulness of a similar magnesium-halogen exchange reaction^[8] led us to optimize Scheme 1 in order to provide an easy method to prepare HT-PATs. Initially, we have found that use of methylmagnesium bromide leads to the best results for polymerization. The formation of the gaseous byproduct of Grignard metathesis (methyl bromide) appears to aid the clean and complete formation of intermediate **2**.

Despite the regioselectivity of the metathesis reaction (80:20 mixture of isomers), the degree of regioselectivity displayed in the resulting polymer is even higher (99% HT-HT). It appears that we are observing the same type of catalyst selectivity as reported in earlier publications.^[3b] Catalyst selectivities of up to 20:1 have also been noted in some Stille couplings of isomers.^[9] We are currently exploring the mechanism of this reaction in further detail.

In summary, the advantages of this new method are many. Preparation and purification of the thiophene monomers are quick and easy (one or two steps from readily available starting materials) and the corresponding Grignard reagents are cheap and easy to handle. This reac-

tion does not require the use of cryogenic temperatures like other methods^[2,3] and can be carried out on very large scales, making this method potentially applicable industrially. This method produces regioregular HT-poly(3-alkylthiophenes) very quickly, economically (avoiding expensive MgBr₂^[2] and ZnCl₂^[3] reagents), and in high yields. The unexpected regiocontrol displayed in the Grignard metathesis step makes this reaction very promising. Further studies on this reaction are currently being performed.

Experimental

Preparation of 2,5-Dibromo-3-dodecylthiophene (1): 3-Dodecylthiophene [2b] (19.41 g, 77.06 mmol) was dissolved in 100 mL of THF. *N*-Bromosuccinimide (27.43 g, 154 mmol) was added to the solution over a period of 5 min. The solution was stirred at room temperature for 2 h. The solvent was removed in vacuo and 250 mL of hexane was added (to precipitate all the succinimide). The mixture was filtered through a silica plug (to remove the succinimide) and the solvent was removed in vacuo. A simple Kugelrohr distillation (120 °C, 0.02 torr) afforded the title compound (26.26 g, 83.3%) (the highest boiling fraction) as a clear, colorless oil. ¹H NMR (CDCl₃): δ [ppm] 6.76 (s, 1H), 2.49 (t, 2H), 1.52 (m, 2H), 1.25 (m, 18H), 0.87 (t, 3H). ¹³C NMR (CDCl₃): δ [ppm] 143.0, 130.9, 110.3, 107.9, 31.9, 29.7, 29.6, 29.4, 29.1, 25.4, 22.7, 14.1. (Calcd. for C₁₆H₂₆Br₂S: C 46.84%, H 6.39%, Br 38.95%; found: C 46.51%, H 6.47%, Br 38.69%.)

Preparation of HT-PDDT (3): 2,5-Dibromo-3-dodecylthiophene (1.28 g, 3.12 mmol) (**1**) was dissolved in 18 mL of dry THF. Methylmagnesium bromide (3.15 mL, 1.0 M solution in butyl ether) was added and the mixture was heated to reflux for 1 h. Ni(dppp)Cl₂ (16.9 mg) was added and the solution was stirred at reflux for 2 h. The mixture was poured into 150 mL of methanol and filtered into a Soxhlet thimble. Soxhlet extractions were performed with methanol (to remove monomer and salts), hexanes (to remove catalyst and oligomers), and chloroform. The chloroform fraction was reduced and dried in vacuo to afford 0.510 g (65% yield) of the title polymer as a violet film. ¹H NMR (CDCl₃): δ [ppm] 6.96 (s, 1H), 2.79 (t, 2H), 1.69 (m, 2H), 1.25 (m, 18H), 0.86 (t, 3H). ¹³C NMR (CDCl₃): δ [ppm] 139.89, 133.74, 130.52, 128.61, 31.94, 30.56, 29.69, 29.53, 29.38, 22.70, 14.10. (Calcd. for (C₁₆H₂₆S)_n: C 76.79%, H 10.47%; found: C 76.41%, H 10.43%.)

Large Scale Preparation of HT-PDDT (3): The procedure is the same as above with **1** (13.9 g, 33.8 mmol), 250 mL of dry THF, and 34 mL of CH₃MgBr (1.0 M solution in butyl ether) being refluxed for 50 min, followed by the addition of 196 mg of Ni(dppp)Cl₂. After the mixture has been refluxed for another 100 min, the reaction is worked up as above with 1.4 L of MeOH, and extraction leads to a 40% yield (3.4 g) of pure HT-PDDT.

Fast Preparation of HT-PDDT (3): The procedure is the same as above with **1** (1.8 g, 4.4 mmol), 25 mL of dry THF, and 4.4 mL of CH₃MgBr (1.0 M solution in butyl ether) being refluxed for 20 min, followed by the addition of 12 mg of Ni(dppp)Cl₂. After the mixture has been refluxed for another 20 min, the reaction is worked up as above with 100 mL of MeOH, and extraction leads to a 68% yield (750 mg) of pure HT-PDDT.

Received: August 10, 1998
Final version: October 9, 1998

- a) R. D. McCullough, P. C. Ewbank, in *Handbook of Conducting Polymers*, 2nd ed. (Eds: T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds), Marcel Dekker, New York **1998**, p. 225. b) Z. Bao, A. Dodabalapur, A. J. Lovinger, *Appl. Phys. Lett.* **1996**, *69*, 4108. c) H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741.
- a) R. D. McCullough, R. D. Lowe, *J. Chem. Soc., Chem. Commun.* **1992**, 70. b) R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, *J. Org. Chem.* **1993**, *58*, 904. Some 3-alkylthiophenes can be purchased from, e.g., Lancaster Synthesis.
- a) T.-A. Chen, R. D. Rieke, *J. Am. Chem. Soc.* **1992**, *114*, 10087. b) T.-A. Chen, X. Wu, R. D. Rieke, *J. Am. Chem. Soc.* **1995**, *117*, 233.
- R. D. McCullough, P. C. Ewbank, R. S. Loewe, *J. Am. Chem. Soc.* **1997**, *119*, 633.
- A. Iraqi, G. W. Barker, *J. Mater. Chem.* **1998**, *8*, 25.
- S. Guillerez, G. Bidan, *Synth. Met.* **1998**, *93*, 123.
- R. D. McCullough, S. P. Williams, *J. Am. Chem. Soc.* **1993**, *115*, 11608.

- [8] L. Boymond, M. Rottländer, G. Cahiez, P. Knochel, *Angew. Chem. Int. Ed.* **1998**, *37*, 1701.
 [9] V. Farina, B. Krishnan, D. R. Marshall, G. P. Roth, *J. Org. Chem.* **1993**, *58*, 5434.

Inorganic–Organic Nanotube Composites from Template Mineralization of Tobacco Mosaic Virus**

By Wayne Shenton, Trevor Douglas, Mark Young, Gerald Stubbs, and Stephen Mann*

The use of biological molecules, assemblies and systems in the development of inorganic materials synthesis continues to offer new and exciting alternatives to conventional synthetic strategies.^[1] Biological templates, such as protein cages,^[2,3] viroid capsules,^[4] bacterial rhabdosomes,^[5] S-layers,^[6] multicellular superstructures,^[7] biolipid cylinders,^[8,9] and DNA,^[10–13] have been utilized to direct the deposition, assembly, and patterning of inorganic nanoparticles and microstructures. In this paper, we report a new approach to the template-directed synthesis of inorganic–organic nanotubes using tobacco mosaic virus (TMV).

TMV is a remarkably stable virion, remaining intact at temperatures up to 60 °C and at pH values between 2 and 10. Each viral particle consists of 2130 identical protein subunits arranged in a helical motif around a single strand of RNA to produce a hollow protein tube, 300 × 18 nm in size, with a 4 nm-wide central channel.^[14,15] The internal and external surfaces of the protein consist of repeated patterns of charged amino acid residues, such as glutamate, aspartate, arginine, and lysine.^[16] In principle, these functionalities should offer a wide variety of nucleation sites for surface-controlled inorganic deposition, which, in association with the high thermal and pH stability, could be exploited in the synthesis of unusual materials such as high-aspect-ratio composites and protein-confined inorgan-

ic nanowires. Here we show that TMV is a suitable template for reactions such as co-crystallization (CdS and PbS), oxidative hydrolysis (iron oxides), and sol-gel condensation (SiO₂) (Fig. 1).

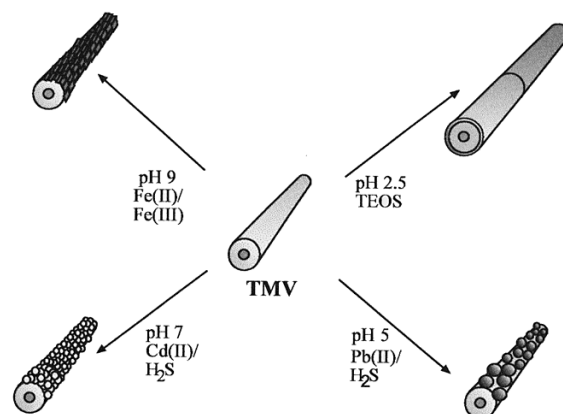


Fig. 1. Scheme showing routes for the synthesis of nanotube composites using TMV templates. Clockwise from top right: sol-gel condensation (silica); coprecipitation (PbS and CdS nanocrystals); oxidative hydrolysis (iron oxide).

Specific nucleation of CdS on the surface of dispersed particles of TMV was achieved by exposing a buffered suspension of the virions in 10 mM CdCl₂ to H₂S gas for up to 6 h. Transmission electron microscopy (TEM) revealed the presence of mineralized tubular structures, approximately 50 nm in width, which consisted of a 16 nm thick electron-dense outer crust and a 18 nm diameter internal core (Fig. 2a). Energy dispersive X-ray (EDX) analysis confirmed the presence of cadmium and sulfur in individual filaments, and high resolution lattice images indicated that the inorganic coating consisted of disordered aggregates of crystalline CdS particles 5 nm in size (Fig. 2b). The lattice spacings were in agreement with those obtained by selected area electron diffraction (SAED) of individual mineralized tubules, which showed powder patterns (*d*-spacings 0.336 nm (111), 0.206 nm (220), 0.176 nm (311), 0.133 nm (331), 0.118 nm (422)), corresponding to CdS nanoparticles with the zinc-blende crystal structure. The results were therefore consistent with a relatively uniform coating of CdS nanocrystals on the external surface of the TMV template. Although nucleation of CdS within the 4 nm diameter internal cavity of the protein structure could not be completely ruled out, most of the sample appeared to consist of hollow CdS–virion nanotubules.

Similar results were obtained when dispersions of TMV in buffered Pb(NO₃)₂ were exposed to H₂S gas. TEM and EDX analysis indicated that the black precipitate consisted of heavily mineralized TMV particles, approximately 40 nm in width (Fig. 3). Individual virions were completely coated with a densely packed layer of PbS crystallites, which were up to 30 nm in size and either prismatic or irregular in shape. Lattice images (Fig. 3, inset) and SAED data were consistent with single-domain PbS nanocrystals

[*] Prof. S. Mann,^[+] W. Shenton^[+]
 Department of Chemistry
 University of Bath
 Bath BA2 7AY (UK)
 Dr. T. Douglas
 Department of Chemistry, Temple University
 Philadelphia, PA 19122-2585 (USA)
 Prof. M. Young
 Department of Plant Sciences
 Montana State University
 Bozeman, MT 59101 USA (USA)
 Prof. G. Stubbs
 Department of Molecular Biology
 Vanderbilt University
 Nashville, TN 37235 (USA)

[+] Present address: School of Chemistry, University of Bristol, Bristol BS8 1TS, UK.

**] We gratefully acknowledge Giuseppe Ruggiero for work on computer-generated images of TMV.