c) E. M. Carreira, R. A. Singer, *Tetrahedron Lett.* **1994**, *35*, 4323; d) T. K. Hollis, B. Bosnich, *J. Am. Chem. Soc.* **1995**, *117*, 4570; e) M. Oishi, S. Aratake, H. Yamamoto, *J. Am. Chem. Soc.* **1998**, *120*, 8271; f) A. Yanagisawa, K. Kimura, Y. nakatsuka, H. Yamamoto, *Synlett* **1998**, 958.

[6] The structure was unambiguously determined by X-ray crystallographic analysis and by chemical masking of the hydroxy or amino group by acetylation. CCDC-187438 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[7] D. A. Dieterich, I. C. Paul, D. Y. Curtin, *J. Am. Chem. Soc.* **1974**, *96*, 6372.

[8] To elucidate the mechanism of this reaction, in situ infrared spectroscopy[10] and ESI mass spectra[11] of the trimethylsilyl triflate–nitrosobenzene complex were measured; detailed results will be published in due course.

[9] For examples of C-nitroso–metal complexes, see: a) D. Mansuy, M. Drem, J. C. Chottard, J. P. Girault, J. Guilhem, *J. Am. Chem. Soc.* **1980**, *102*, 844; b) M. A. Andres, C. F. Cheng, *J. Am. Chem. Soc.* **1982**, *104*, 4268; c) E. R. Møller, K. R. Jørgensen, *J. Am. Chem. Soc.* **1993**, *115*, 11814; d) R. S. Strivastava, K. M. Nicholas, *J. Org. Chem.* **1994**, *59*, 5365; e) M. Johannsen, K. R. Jørgensen, *J. Org. Chem.* **1995**, *60*, 5979; f) R. S. Strivastava, M. A. Khan, K. M. Nicholas, *J. Am. Chem. Soc.* **1996**, *118*, 3311; g) R. S. Strivastava, K. M. Nicholas, *J. Am. Chem. Soc.* **1997**, *119*, 3302; h) J. R. Bleeke, J. M. B. Blanchard, *J. Am. Chem. Soc.* **1997**, *119*, 5443; i) K. R. Flower, A. P. Lightfoot, H. Wan, A. Whiting, *Chem. Commun.* **2001**, 1812.

[10] In situ IR spectra were recorded on a ReactIR 1000 instrument from ASI Applied Systems. Trimethylsilyl triflate (1 equiv) was added to a solution of nitrosobenzene (1 equiv) in 1,2-dichloropropane; as trimethylsilyl triflate was added, the absorption at 1505 cm^{-1} (nitrosobenzene N=O stretch) decreased in intensity while the absorption at 1264 cm^{-1} (*trans* azoxybenzene N−O stretch) simultaneously increased in intensity.

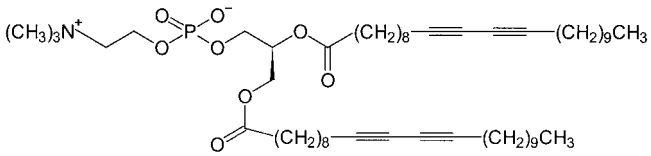
[11] ESI mass spectra of the trimethylsilyl triflate–nitrosobenzene complex showed peaks at *m/z* 214 ($Ph_2N_2O_2^+$) and *m/z* 329 [$Et_3Si(PhNO)_2^+$], thus confirming the presence of the dimer.

Chiral Templating of Silica–Lipid Lamellar Mesophase with Helical Tubular Architecture**

Annela M. Seddon, Harish M. Patel, Sandra L. Burkett, and Stephen Mann*

The use of amphiphilic surfactants and polymers in the template-directed synthesis of periodically ordered hybrid mesophases has produced a diverse range of new inorganic-based materials with controlled mesoporosity and functionality.[1] A key challenge for the future lies with the reproducible processing of mesostructured materials, and specifically with the control of higher order properties such as structural hierarchy and macroscopic shape. Although mesostructured nanoparticles,[2] colloids,[3] tubes,[4] fibers,[5] hollow shells,[6] gyroids, and helicoids[7] have been prepared, these rely on the subtle interplay of extrinsic factors associated with the growth mechanism, which are often difficult to control. An alternative strategy is to use molecular structure to direct the expression of form so that increased levels of morphological control can be achieved through the transcription of internal information. In this respect, chiral organic molecules known to be efficient gelators of organic solvents have been used recently to prepare helical tapes of silica by in situ coating of gel filaments.[8] However, although these molecules are capable of self-assembly and directing the surface deposition of silica, they show no propensity to coassemble with the inorganic phase at the mesostructural level.

Herein we demonstrate that the diacetylenic-containing chiral lipid, 1,2-bis(10,12-tricosadiyonyl)-*sn*-glycero-3-phosphatidylcholine ($DC_{8,9}PC$, Scheme 1) can be used simultaneously as a structure-directing template, "morphogen" and photoactive monomer to synthesize high aspect ratio helical



Scheme 1. Molecular structure of $DC_{8,9}PC$. The polar lipid headgroup is zwitterionic over the pH range 3 to 13.[19]

tubules and ribbons that consist of polymerizable periodic mesostructured silica–lipid walls with a twisted lamellar architecture. Although organic tubules formed from $DC_{8,9}PC$ have been extensively investigated,[9] and studies on silica[10] and metallic coatings,[11] and surface decoration with gold nanoparticles[12] or polypyrrole threads[13] have been carried out, there are to the best of our knowledge no reports on the coassembly of periodic hybrid mesostructures using this or other chiral lipids.

Addition of aqueous HBr to a solution of $DC_{8,9}PC$ and tetraethylorthosilicate (TEOS) in ethanol at room temperature at a TEOS:$DC_{8,9}PC$ molar ratio of 8.3:1 resulted in instantaneous formation of a white precipitate. Transmission electron microscopy (TEM) studies revealed that over 90% of the sample was in the form of open-ended silicified helical tubules and ribbons with diameters, lengths, and wall thickness of 0.5–1.5 μm, >5 μm, and 50–150 nm, respectively (Figure 1a). The hybrid microstructures consisted of smooth external and internal surfaces, which, along with the general absence of colloidal silica precipitation, suggested that TEOS acid hydrolysis and condensation were specifically associated and coupled with self-assembly of the lipid molecules. This was confirmed by high-resolution TEM images of areas of the helical tubules in which the lipid bilayers were fortuitously oriented approximately parallel to the electron beam. Under such conditions, continuous lattice fringes were observed with

[*] Prof. S. Mann, A. M. Seddon, Dr. H. M. Patel
School of Chemistry
University of Bristol
Bristol BS8 1TS (UK)
Fax: (+44) 117-929-0509
E-mail: s.mann@bristol.ac.uk
Dr. S. L. Burkett
Department of Chemistry
Amherst College
Amherst, MA 01002-5000 (USA)

[**] We thank the University of Bristol and EPSRC for financial support, and Dr. S. A. Davis and Dr. C. Göltner for helpful discussions.

  0044-8249/02/4116-2988 $ 20.00+.50/0

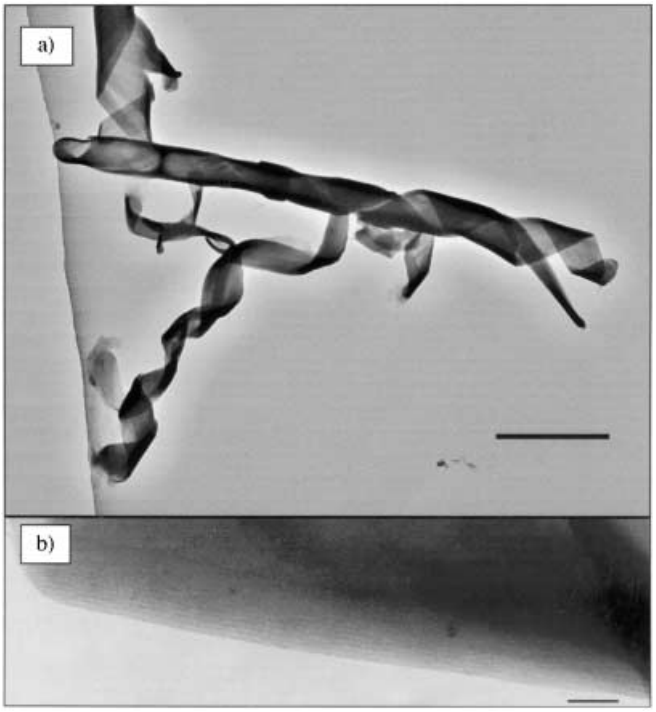


Figure 1. TEM images of a) silica–lipid helical tubules and ribbons, scale bar = 2 μm, b) tubule edge showing lattice fringes corresponding to a lamellar hybrid mesostructure. Scale bar = 50 nm.

spacings of about 4.5 nm (Figure 1b) that were consistent with a twisted multilamellar hybrid mesophase in which the lipid bilayers were intercalated with thin sheets of amorphous silica. Energy-dispersive X-ray (EDX) analysis showed the presence of Si, P, and Br associated with the mineralized tubules, and thermogravimetric analysis (TGA) indicated that they contained about 70 wt% lipid. Significantly, calcination at 410 °C produced inorganic replicas that consisted of intact tubes and twisted ribbons of amorphous silica.

Powder X-ray diffraction (XRD) patterns showed three broad low-angle peaks with d spacings of 4.0, 1.4, and 0.84 nm, corresponding to the (002), (006), and (00$\underline{1}$0) reflections of a partially ordered lamellar mesophase with an interlayer spacing of about 8.4 nm (Figure 2a). A very broad high-angle peak centered at $2\theta = 22°$, attributed to amorphous silica was also observed. In contrast, XRD data from a sample of unmineralized lipid tubules/ribbons (Figure 2b) showed sharp

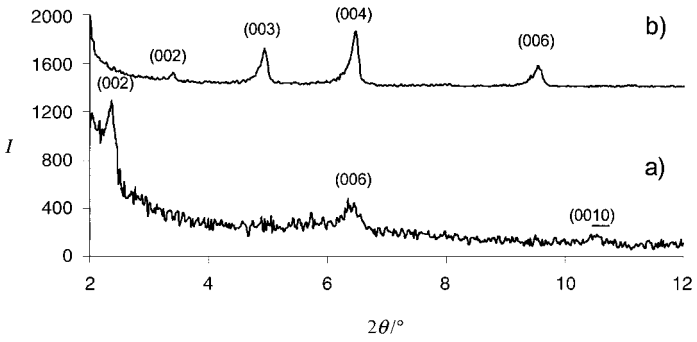


Figure 2. XRD data; a) silica–lipid mesophase, b) unmineralized lipid tubules. I = intensity.

(002), (003), (004), (006), (008), (00$\underline{1}$0), and (00$\underline{1}$2) reflections corresponding to a lamellar L_c mesostructure with 5.6 nm interlayer spacing and noninterdigitated crystalline chain packing.[14] Similar data were obtained for a sample of silica-coated lipid microstructures produced by adding TEOS to dispersions of preformed tubules, except that the diffraction lines were broadened. The results indicate therefore that in situ acid hydrolysis of TEOS during lipid self-assembly results in an expansion of the interlayer spacing by about 3 nm due to intercalation of silica between the $DC_{8,9}PC$ bilayers. Given a wall thickness of 50 to 150 nm, this corresponds to a stack of five to 15 hybrid sheets, which must be sufficiently flexible to undergo twisting in response to the stress field associated with intralayer crystalline packing of the chiral lipid molecules.

FTIR and Raman spectra were consistent with previous observations on unmineralized tubules[15] and indicated that the crystalline packing of the lipid molecules was not significantly changed by silica intercalation. For example, FTIR spectra showed $DC_{8,9}PC$ bands at 718 (CH_2 rock), 1469 (CH_2 scissors), 2849 (CH_2 str), and 1725 cm^{-1} (C=O str) in both the unmineralized and mineralized samples. The former also showed bands between 1175 and 1345 cm^{-1} corresponding to the P–O stretch but these were masked to some extent in the mineralized tubules/ribbons by additional Si-O-Si framework vibrations at 1050 cm^{-1} (large band) and 1200 cm^{-1} (shoulder). Raman spectra of the silica–lipid lamellar mesophase showed a peak at 2263 cm^{-1} corresponding to the monomer C≡C stretch of the diacetylene groups.

Dried samples of the white silicified tubules turned blue due to diacetylene polymerization when left for two days in the light under ambient conditions. No changes in the FTIR spectra were observed, but corresponding Raman spectra showed a characteristic shift in the C≡C stretch from 2263 to 2086 cm^{-1} and the appearance of a new band at 1454 cm^{-1},

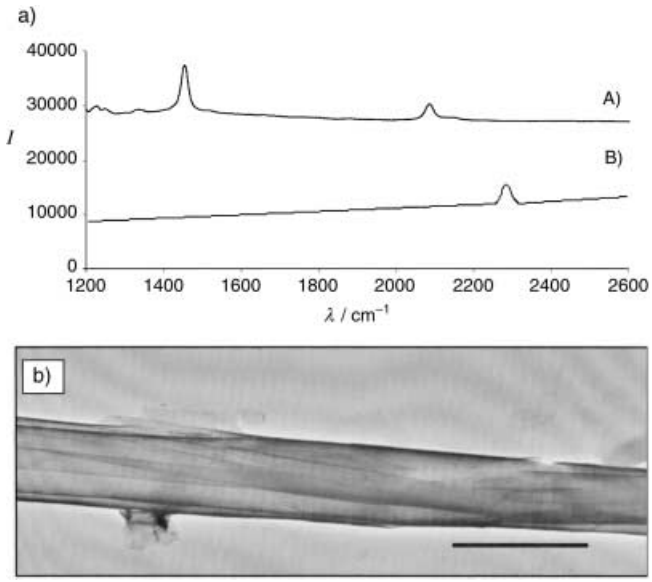


Figure 3. a) Raman spectra of silica–lipid tubules; A) before and B) after diacetylenic polymerization by exposure to light for two days. I = intensity. b) TEM image of polymerized silica–lipid tubule showing absence of helical architecture. Scale bar = 2 μm.

  0044-8249/02/4116-2989 $ 20.00+.50/0

corresponding to the C=C stretch (Figure 3a). This is consistent with the polymerization of the diacetylenic monomer backbone and the formation of conjugated ene–yne linkages[16] in the self-assembled lipid–silica architecture (Figure 4). Corresponding TEM images showed that the silica–lipid tubules were preserved after polymerization but usually without the helical surface patterning (Figure 3b), indicating that the side edges of the helical seam become fused into a continuous wall structure during polymerization. Diacetylene polymerization in surfactant and lipid bilayers occurs below the chain melting temperature (T_m) and involves a topotactic reaction in which the adjacent monomers are fixed at appropriate distances and angles.[17] Moreover, chain ordering would be best accommodated along the length of the helical microstructure, rather than around the tubule, because of the lower curvature associated with the direction of elongation, and this could explain why diacetylene polymerization results in fusion of the seam edges in the polymerized hybrid materials.

Finally, addition of ethanol to the polymerized silica–lipid tubules/ribbons resulted in a blue-to-red solvatochromic response that corresponded to a shift in the diffuse reflectance UV/Vis band at 650 nm (blue sample) to two bands at 496 and 536 nm (red material) (Figure 5). The change in color, which is attributed to shortening of the conjugation length of the polydiactylenic backbone by solvation stresses,[18] was not reversed when the ethanol was removed by evaporation. However, the blue-to-red response was also observed when samples of the polymerized silica–lipid tubules were heated to above 40°C, exposed to an X-ray beam, or mechanically scratched or sheared, indicating that a range of external stress fields can induce the chromatic response.

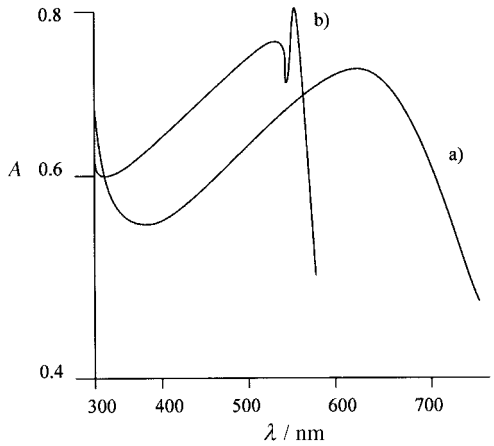


Figure 5. Diffuse reflectance UV/Vis spectra of polymerized silica–lipid tubules; a) before (blue material), and b) after addition of ethanol (red material). A = absorbance.

In conclusion, in situ synthesis of silica by acid hydrolysis and condensation of TEOS in the presence of $DC_{8,9}PC$ lipid molecules results in the synergistic coassembly of a lamellar hybrid mesostructure containing polymerizable diacetylinic groups, which is subsequently twisted into high aspect ratio tubules and ribbons with helical architecture. The resulting solvatochromic, thermochromic, and mechanochromic responses suggest that the hybrid materials could have a range of uses as colorimetric transduction agents, for example in sensors, thin films, and smart coatings.

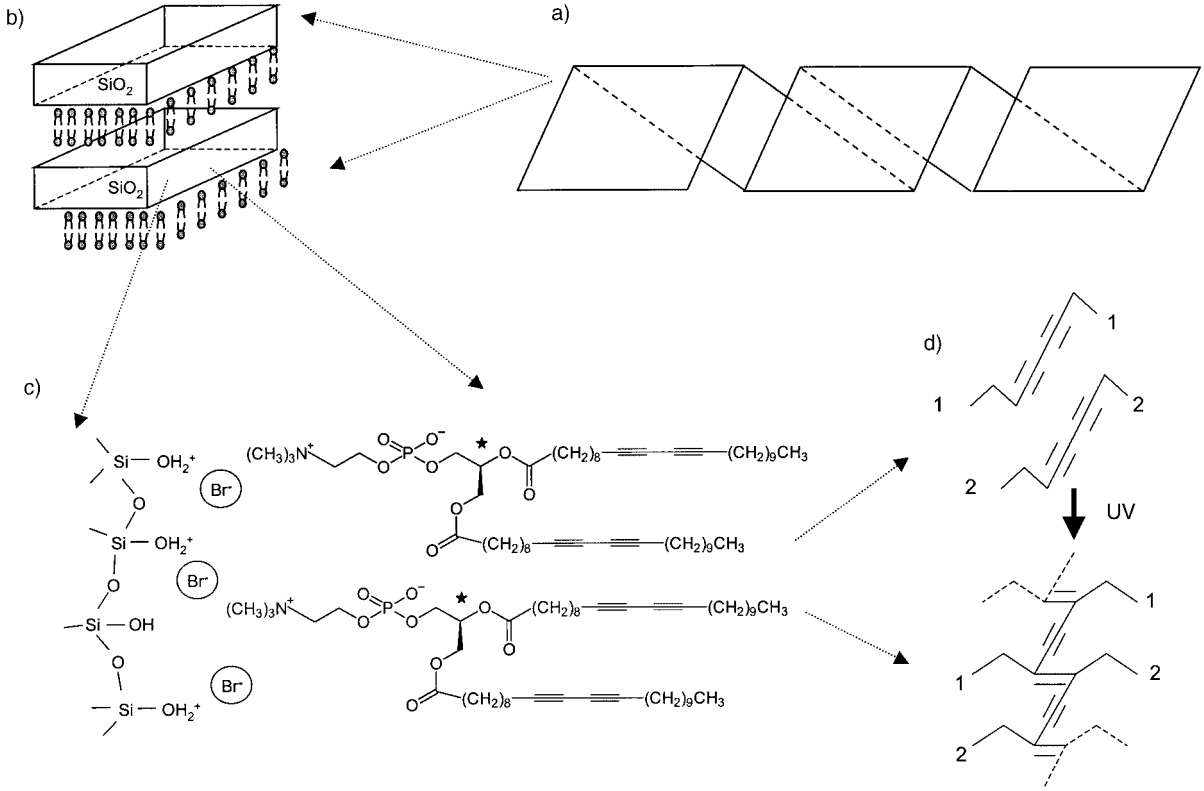


Figure 4. Schematic representation showing silica–lipid lamellar mesostructure and diacetylenic polymerization. a) Helical silica–lipid tubule with twisted multilamellar architecture; b) 3 nm-thick sheets of silica interspaced with lipid bilayers, 5.6 nm in width; c) hypothetical section across the interface showing interactions between the lipid headgroup, Br^- counterions and protonated silica surface; d) formation of ene–yne linkages.

  0044-8249/02/4116-2990 $ 20.00+.50/0

Experimental Section

$DC_{8,9}PC$ was obtained from Avanti Polar Lipids and used without further purification. TEOS was obtained from Aldrich and used as received. Mineralized lipid tubules were prepared in situ as follows. Typically, $DC_{8,9}PC$ (40 mg) was dissolved in ethanol (2 mL) by sonication (lipid concentration, 0.044 mM), and TEOS (82.4 μL) was added to give a TEOS:lipid molar ratio of 8.3:1. A solution (0.38 g) prepared from H_2O (0.8 g) and 48 wt% aqueous HBr (3.0 g) was added to the lipid/TEOS mixture (final pH 0.5) and a white precipitate formed instantly. The sample was stirred for 5 min, left sealed overnight, and then centrifuged at 5000 rpm for 10 min and the supernatant decanted. Similar preparations were undertaken at TEOS:lipid molar ratios between 4:1 and 1:4. Polydiacetylenic derivatives were prepared by leaving samples of the dried mineralized lipid tubules for two days under ambient conditions in the laboratory. Unmineralized lipid tubules were prepared by addition of H_2O (1 mL) to a solution of $DC_{8,9}PC$ (0.0044 mM) in ethanol (1 mL). Lipid microstructures were also coated externally with silica by addition of TEOS (82.4 μL) to a suspension (20 mg mL^{-1}) of preformed tubules.

Samples were characterized by TEM (JEOL 1200EX), SEM (JEOL JSM 5600 LV), EDXA (Oxford Instruments, ISIS300), and XRD (Siemens D500 diffractometer, $Cu_{K\alpha}$ radiation, $\lambda = 0.15405$ nm). Samples were prepared either as a suspension in ethanol in a quartz cuvette or evaporated from ethanol onto a quartz slide for UV/Vis (800–200 nm) and diffuse reflectance UV/Vis spectroscopy (Perkin Elmer Lambda II with Labsphere titania mirrors), respectively. FT-IR spectroscopy (Perkin Elmer Spectrum 1) was carried out using KBr discs. Raman spectra (Renishaw System 2000) were recorded using a 35 mW HeNe laser at an excitation frequency of 632.8 nm, and probe size of about 1 μm. TGA (Netzsch TG409EP) was carried out at a heating rate of 5 K min^{-1} from room temperature to 600 °C in air with a flow rate of 90 mL min^{-1}. Calcined samples were prepared at 410 °C for 2 h using a heating rate of 3 K min^{-1}.

Received: February 8, 2002
Revised: July 8, 2002 [Z18671]

[1] a) J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem.* **1999**, *111*, 58–82; *Angew. Chem. Int. Ed.* **1999**, *38*, 56–77; b) F. Schuth, *Chem. Mater.* **2001**, *10*, 3184–3195.
[2] a) C. E. Fowler, D. Khushalani, B. Lebeau, S. Mann, *Adv. Mater.* **2001**, *13*, 649–652; b) Y. Lu, H. Fan, A. Stump, T. L. Ward, T. Rieker, C. J. Brinker, *Nature* **1999**, *398*, 223–226.
[3] S. S. Kim, W. Zhang, T. J. Pinnavaia, *Science* **1998**, *282*, 1302–1303.
[4] a) H.-P. Lin, C.-Y. Mou, *Science* **1996**, *273*, 765–768; b) H.-P. Lin, Y.-R. Cheng, C.-Y. Mou, *Chem. Mater.* **1998**, *10*, 581–589.
[5] a) F. Kleitz, F. Marlow, G. D. Stucky, F. Schuth, *Chem. Mater.* **2001**, *13*, 3587–3595; b) H.-P. Lin, C.-Y. Mou, S.-B. Liu, *Adv. Mater.* **2000**, *12*, 103–106.
[6] a) C. E. Fowler, D. Khushalani, S. Mann, *Chem. Commun.* **2001**, 2028–2029; b) H.-P. Lin, Y.-R. Cheng, C.-Y. Mou, *Chem. Mater.* **1998**, *10*, 3772–3776; c) S. Schacht, Q. Huo, I. G. Voigt-Martin, G. D. Stucky, F. Schüth, *Science* **1996**, *273*, 768–771.
[7] a) S. Oliver, A. Kuperman, N. Coombs, A. Lough, G. A. Ozin, *Nature* **1995**, *378*, 47–50; b) G. A. Ozin, *Can. J. Chem.* **1999**, 77, 2001–2014.
[8] a) Y. Ono, K. Nakashima, M. Sano, J. Hojo, S. Shinkai, *Chem. Lett.* **1999**, 1119–1120; b) Y. Ono, K. Nakashima, M. Sano, J. Hojo, S. Shinkai, *J. Mater. Chem.* **2001**, *11*, 2412–2419; c) J. H. Jung, H. Kobayashi, M. Masuda, T. Shimizu, S. Shinkai, *J. Am. Chem. Soc.* **2001**, *123*, 8785–8789.
[9] a) P. Yager, P. E. Schoen, *Mol. Cryst. Liq Cryst.* **1984**, *106*, 371–381; b) J. M. Schnur, *Science* **1993**, *262*, 1669–1676.
[10] S. Baral, P. Schoen, *Chem. Mater.* **1993**, *5*, 145–147.
[11] a) J. M. Schnur, R. Price, P. Schoen, P. Yager, J. M. Calvert, J. Georger, *Thin Solid Films* **1987**, *152*, 181–206; b) J. S. Chappel, P. Yager, *J. Mater. Sci. Lett.* **1992**, *11*, 633–636.
[12] S. L. Burkett, S. Mann, *Chem. Commun.* **1996**, 321–322.
[13] M. Goren, Z. Qi, R. B. Lennox, *Chem. Mater.* **2000**, *12*, 1222–1228.
[14] M. Caffrey, J. Hogan, A. S. Rudolph, *Biochemistry* **1991**, *30*, 2134–2146.
[15] P. E. Schoen, P. Yager, *J. Polym. Sci.* **1985**, *23*, 2203–2216.
[16] H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **1988**, *100*, 117–162; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 113–158.
[17] a) D. F. O'Brien, T. H. Whitesides, R. T. Klingbiel, *J. Polym. Sci. Polym. Lett. Ed.* **1981**, *19*, 95–101; b) P. E. Schoen, P. Yager, R. G. Priest in *Polydiacetylenes: Synthesis, Structure and Electronic Properties* (Eds.: D. B. Bloor, R. R. Chance), Marinus Nijhoff, Dordrecht, **1985**, pp. 223–232.
[18] a) G. N. Patel, R. R. Chance, J. D. Witt, *J. Chem. Phys.* **1979**, *70*, 4387–4392; b) B. J. Orchard, S. K. Tripathy, *Macromolecules* **1986**, *19*, 1844–1850; c) H. Tanaka, M. A. Gomez, A. E. Tonelli, M. Thakur, *Macromolecules* **1989**, *22*, 1208–1215.
[19] A. D. Bangham, R. C. M. Dawson, *Biochem. J.* **1959**, *72*, 486–492.

Aryl C–H Activation by Cu^{II} To Form an Organometallic Aryl–Cu^{III} Species: A Novel Twist on Copper Disproportionation**

Xavi Ribas, Deanne A. Jackson, Bruno Donnadieu, José Mahía, Teodor Parella, Raül Xifra, Britt Hedman,* Keith O. Hodgson,* Antoni Llobet,* and T. Daniel P. Stack*

Selective activation of hydrocarbon C–H bonds by metals under mild conditions is an important pursuit in the functionalization of organic substrates.[1] While such oxidative trans-

[*] Prof. A. Llobet, Dr. X. Ribas, R. Xifra
Departament de Química, Universitat de Girona
Campus de Montilivi, E-17071, Girona (Spain)
Fax: (+34) 972-41-8150
E-mail: antoni.llobet@udg.es
Dr. B. Hedman, Prof. K. O. Hodgson, D. A. Jackson
Department of Chemistry and
Stanford Synchrotron Radiation Laboratory
Stanford University
Stanford, CA 94305-5080 (USA)
Fax: (+1) 650-725-0259
E-mail: hedman@slac.stanford.edu, hodgson@ssrl.slac.stanford.edu
Prof. T. D. P. Stack
Department of Chemistry, Stanford University
Stanford, CA 94305-5080 (USA)
Fax: (+1) 650-725-0259)
E-mail: stack@stanford.edu
Dr. J. Mahía
Servicios Xerais de Apoio Á Investigación
Universidade da Coruña
15071 A Coruña (Spain)
Dr. B. Donnadieu
Service de Cristallochimie
Laboratoire de Chimie de Coordination, UPR CNRS 8241
Route de Narbonne 205, 31077 Toulouse Cedex 4 (France)
Dr. T. Parella
Departament de Química, Universitat Autònoma de Barcelona
Bellaterra, 08193 Barcelona (Spain)

[**] This research was supported by MICYT of Spain through project PBQ2000-0548 and with the grant SGR-3102-UG-01 as well as the Distinction award from from CIRIT Generalitat de Catalunya (Spain). An FI doctoral grant from CIRIT to X.R. and financial support from the National Institutes of Health (USA; T.D.P.S. GM-50730; K.O.H. RR-01209) are also acknowledged. SSRL operations are funded by the Department of Energy, Basic Energy Sciences, and the SSRL Structural Molecular Biology Program is supported by the NIH NCRR BTP and the DOE OBER.

  0044-8249/02/4116-2991 $ 20.00+.50/0