surface concentrations. Second, surface-confined dendrimers undergo a dramatic conformational change upon exposure to C16SH, resulting from shear compression. Third, and most significantly, the dendrimers act as molecular gates in that they can be tailored to permit selective intradendrimer mass transfer. Finally, we have shown that the primary amines of the surface-confined dendrimers can be easily functionalized without significant desorption of dendrimer. These four key results open the door to a new generation of dendrimer-modified surfaces suitable for a range of technologically important applications.

Received: May 20, 1997 [Z10459IE]
German version: *Angew. Chem.* **1997**, *109*, 2707-2710

**Keywords:** dendrimers • electrochemistry • molecular recognition • supramolecular chemistry • thin films

---

[1] M. Wells, R. M. Crooks, *J. Am. Chem. Soc.* **1996**, *118*, 3988.
[2] B. Alonso, M. Morán, C. M. Casado, F. Lobete, J. Losada, I. Cuadrado, *Chem. Mater.* **1995**, *7*, 1440.
[3] P. M. Saville, P. A. Reynolds, J. W. White, C. J. Hawker, J. M. J. Fréchet, K. L. Wooley, J. Penfold, J. R. P. Webster, *J. Phys. Chem.* **1995**, *99*, 8283.
[4] S. Watanabe, S. L. Regen, *J. Am. Chem. Soc.* **1994**, *116*, 8855.
[5] V. V. Tsukruk, F. Rinderspacher, V. N. Bliznyuk, *Langmuir* **1997**, *13*, 2171.
[6] L. H. Dubois, R. G. Nuzzo, *Annu. Rev. Phys. Chem.* **1992**, *43*, 437, and references therein.
[7] O. Chailapakul, R. M. Crooks, *Langmuir* **1995**, *11*, 1329.
[8] R. Bilewicz, M. Majda, *J. Am. Chem. Soc.* **1991**, *113*, 5464.
[9] H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **1988**, *100*, 117, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 113.
[10] D. A. Tomalia, A. M. Naylor, W. A. Goddard III, *Angew. Chem.* **1990**, *102*, 119; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138, and references therein.
[11] L. Sun, R. M. Crooks, A. J. Ricco, *Langmuir* **1993**, *9*, 1775.
[12] Technical data supplied by Dendritech, Inc. (Midland, MI).
[13] J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Science* **1994**, *266*, 1226.
[14] J. F. G. A. Jansen, E. W. Meijer, E. M. M. de Brabander-van den Berg, *J. Am. Chem. Soc.* **1995**, *117*, 4417.
[15] M. F. Ottaviani, S. Bossmann, N. J. Turro, D. A. Tomalia, *J. Am. Chem. Soc.* **1994**, *116*, 661.
[16] D. Lin-Vien, N. B. Colthup, W. G. Fateley, J. G. Grasselli, *Infrared and Raman Characteristic Frequencies of Organic Molecules* Academic, San Diego, **1991**, Chap. 2.
[17] D. L. Dermody, R. M. Crooks, T. Kim, *J. Am. Chem. Soc.* **1996**, *118*, 11912.
[18] Ellipsometric measurements indicate that a G4-modified surface changes in thickness from 1.9 ± 0.2 to 3.7 ± 0.2 nm after exposure to an ethanolic C16SH solution. Ellipsometric modeling results derived from the Bruggemann effective-medium approximation data suggest a change in the calculated, single-dendrimer height from 2.8 to 5.5 nm. H. Tompkins, *A Users Guide to Ellipsometry*, Academic, New York, **1993**, Apendix B.) Previously reported theoretical calculations (see ref. [10]) are consistent with this result.

---

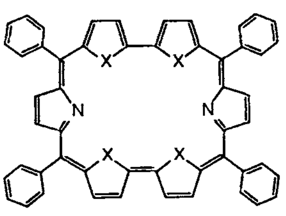
# Tetrathia- and Tetraoxarubyrins: Aromatic, Core-Modified, Expanded Porphyrins[**]

Alagar Srinivasan, VenkatRam M. Reddy,
S. Jeyaprakash Narayanan, Bashyam Sridevi,
Simi K. Pushpan, Murugaeson Ravikumar, and
Tavarekere K. Chandrashekar[*]

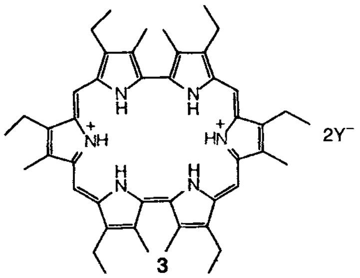
*Dedicated to Professor Varadachari Krishnan on the occasion of his 60th birthday*

The current trend towards broadening the basis of porphyrin chemistry by developing novel polypyrrolic systems has stimulated an immense research effort in the area of "expanded porphyrins".[1] Synthetic work in this direction has led to several classes of expanded porphyrins including sapphyrin,[2] pentaphyrin,[3] hexaphyrin,[4] rosarin,[5] rubyrin,[6] and octaphyrin.[7] These generally have more than four pyrrole units linked through three or four *meso* carbon bridges. Many related studies have provided valuable information on ring size, aromaticity, macrocyclic stability, and the ability of the compounds to act as chelating receptors for the complexation of anions, cations, and neutral substrates.[8]

Replacement of one or more pyrrole rings by other heterocycles such as thiophene or furan rings leads to core-modified, expanded porphyrins that might have properties that are substantially different to those of well-studied nitrogen analogues[9] due to altered electronic structures. We have been interested in such core modification of porphyrin systems, and our efforts in this direction have revealed many similarities and differences in electrochemical, photochemical, and optical properties relative to the corresponding nitrogen analogues.[10] Here we report the first examples of expanded porphyrins containing either two bithiophene or two bifuran units covalently linked to two pyrrole rings through four methine bridges.[11] We refer to them as tetrathia- and tetraoxarubyrins **1** and **2**, which are analogous to the hexapyrrolic homologue rubyrin **3** reported by Sessler et al.[6]



**1** X = S
**2** X = O



**3**

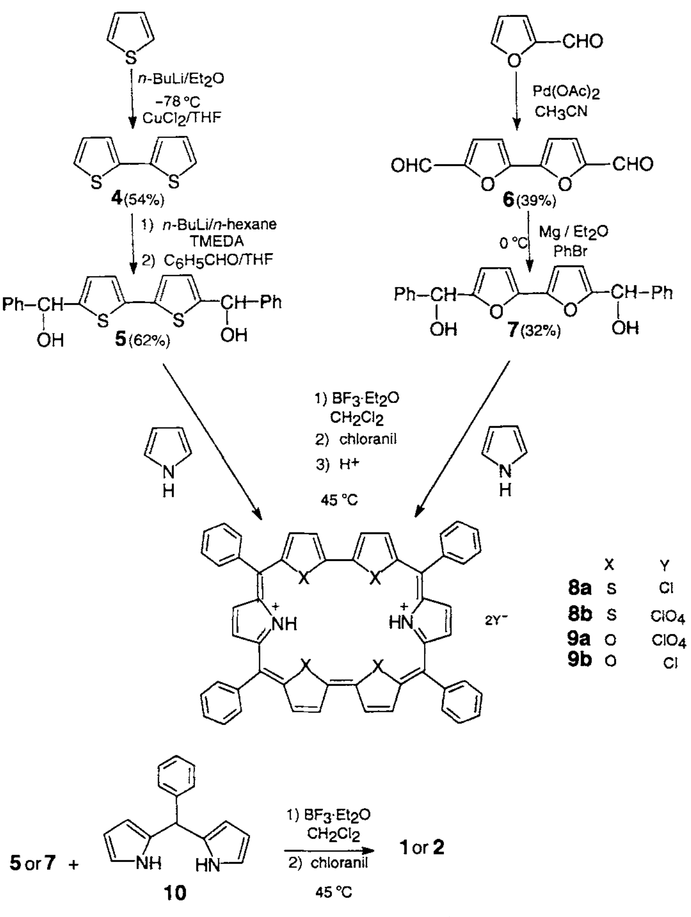
The synthetic method currently available for preparing five- or six-membered expanded porphyrins is based on an acid-catalyzed [3+2] or [4+2] MacDonald condensation between a dicarboxyl-substituted tripyrromethane or tetrapyrrolic unit with diformyl bipyrroles.[2b,c,6] The present method adopts a different approach based on the synthesis

---

[*] Prof. Dr. T. K. Chandrashekar, A. Srinivasan, Dr. V. M. Reddy, S. J. Narayanan, B. Sridevi, S. K. Pushpan, M. Ravikumar
Department of Chemistry
Indian Institute of Technology
Kanpur 208016 (India)
Fax: Int. code + (512) 590-007/597-436
e-mail: tkc@iitk.ernet.in

[**] This work was supported by the Department of Science and Technology (DST) of the government of India, New Delhi.

of core-modified mono- and dithiaporphyrins[9] (Scheme 1). Thus, the two key precursors bithiophenediol **5** and bifurandiol **7**—synthesized from thiophene via **4** or from furfual via **6**, respectively—provide **1** and **2** as shiny green metallic solids in 28 and 15 % yield, respectively, upon condensation with pyrrole under Lindsey conditions[12a] followed by oxidation with chloranil. Alternatively, reaction of **5** or **7** with dipyrromethane[12b] **10** under Lindsey conditions followed by oxidation afforded **1** or **2** in 20 % yield. Treatment of **1** and **2** with HCl and HClO$_4$ gave **8a**, **8b** and **9a**, **9b**, respectively, in 85–90 % yield.



Scheme 1. Synthesis of tetraoxa- and tetrathiarubyrins **1** and **2**.

The compositions of **1** and **2** were established from FAB mass spectra, which show peaks at 813 and 750, respectively, with 100 % fragmentation. The electronic absorption spectra[13] of **1** and **2** in CH$_2$Cl$_2$ (Figure 1 a) exhibit an intense Soret band and four Q bands. The electronic spectra generally resemble those of *meso*-tetraphenylporphyrins, but are significantly red-shifted; this is not surprising considering the larger aromatic systems (26 π electrons) in **1** and **2** relative to the 18 π electronic systems of *meso*-tetraphenylporphyrins.[14] Protonation of **1** and **2** by addition of a dilute solution of trifluoroacetic acid (TFA) in CH$_2$Cl$_2$ leads to further red shifting of both the Q and Soret bands (Figure 1 b); this effect is typical of *meso*-tetraarylporphyrins. Changing the counterions in **8a** and **9a** produces only minor changes. Therefore, the similarity of the electronic absorption spectra of **1**, **2** and their protonated derivatives with that of *meso*-arylporphyrin and its protonated derivative confirms the aromatic nature of the former.

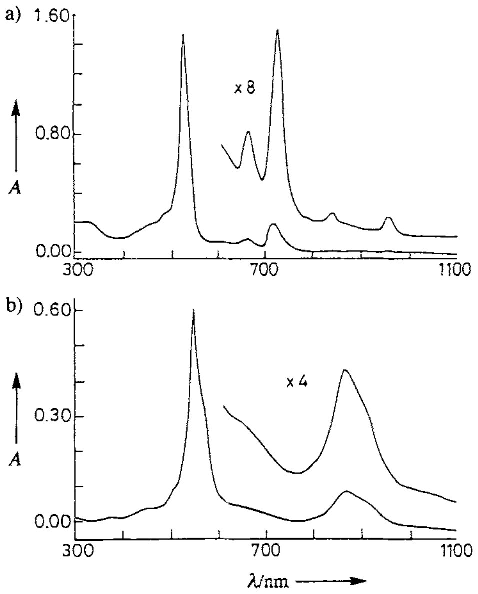


Figure 1. Electronic absorption spectra of **1** in CH$_2$Cl$_2$ ($1.85 \times 10^{-5}$ M) a) without TFA and b) with about $10^{-3}$ M TFA.

Energy-optimized structures for **1** and **2** are shown in Figure 2. It is clear from the structures of **1** and **2** that the two bithiophene/bifuran units, one containing a double bond and the other only a single bond, occupy different planes. This reflects their different magnetic environments. In fact, the observation of two doublets separated by 1.15 ppm for

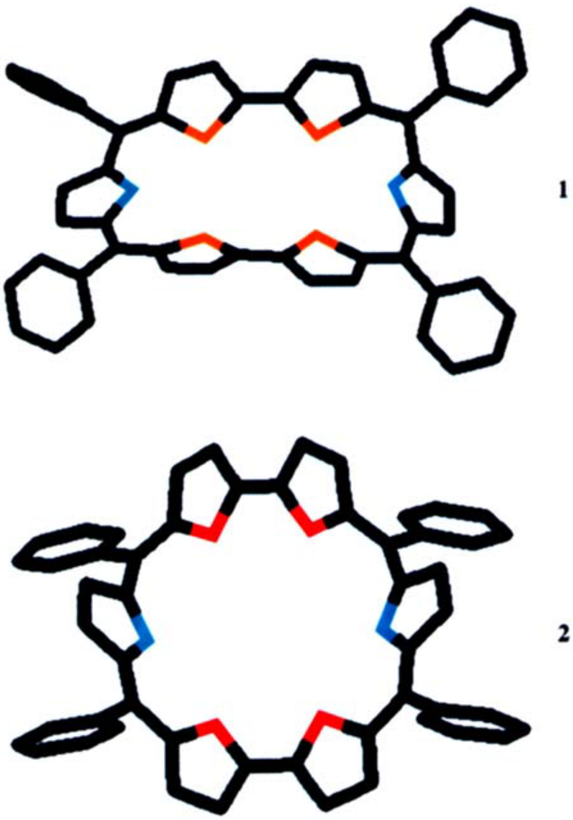
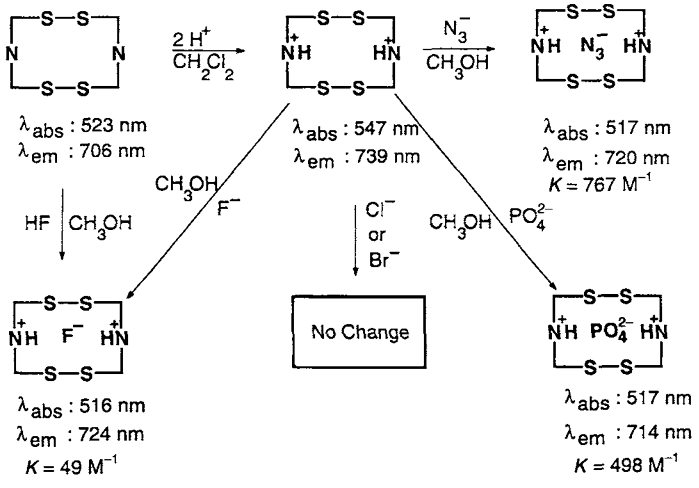


Figure 2. Geometry-optimized structures (Hyperchem 5.0 with AM1 basis set) of **1** and **2**; red: oxygen; yellow: sulfur; blue: nitrogen.

bithiophene and by 1.00 ppm for bifuran protons in the $^1$H NMR apectrum clearly reveals their magnetic inequivalence. Compound **3** also shows a difference in the chemical shift for the bipyrrole ethyl-methyl substituents of about 2 ppm .[6] The chemical shifts for the inner NH protons of $\delta = -5.15$ and $-4.82$ observed for **1** and **2**, respectively, in $CDCl_3$ containing deuterated TFA further establishes their aromatic character.

Additional evidence for the aromatic character of **1**, **8a**, and **8b** comes from preliminary cyclic voltammetric studies. The two quasi- reversible ring reductions observed for **1** in $CH_2Cl_2$ suggest stabilization of the corresponding LUMOs relative to the LUMOs of *meso*-tetraarylporphyrins by 370 mV. An estimated HOMO-LUMO gap of 1.64 V for **8b** in $CH_3CN$ indicates a significant reduction relative to sapphyrin (1.88 V)[14] and *meso*-tetraphenyl porphyrin (2.26 V),[10] thus explaining the large red shifts for **1** and its protonated derivatives.

Spectral titrations of a methanolic solution of **8a** and **8b** with anions ($F^-$, $N_3^-$, and adenosine 5′-monophosphate (AMP)) results in a decrease in absorbance, a blue shift of the Soret bands in the absorption spectra by about 30 nm, and a blue shift of the emission bands by about 15 nm together with enhanced emission intensity (AMP shows the greatest increase of about 200%, probably due to charge neutralization); this suggests anion binding that is similar to that observed for sapphyrins[8] (Scheme 2). Binding constants evaluated by an analysis of absorption data using the Nash equation[15] vary as $N_3^- > AMP > F^-$. Transport studies[16] in U tubes reveal the transport of $F^-$ and AMP at lower rates than observed for sapphyrins and **3**.



Scheme 2. Characteristics of anion binding of tetrathiarubyrin.

In summary, we have synthesized two new core-modified, expanded porphyrins with 26 $\pi$ electrons by a relatively easy method under mild conditions and demonstrated their anion-binding capabilities. This method avoids the difficult synthesis of sensitive precursors such as tripyrromethanes and tetrapyrrole units required for [3+2] and [4+2] condensations. The availability of gram quantities of these materials permits detailed spectroscopic and photochemical investigations that might in turn shed more light on the suitability of these materials for medicinal applications, including their use as sensitizers for photodynamic therapy and MRI contrasting agents.

## *Experimental Section*

**1**: 5,5′-Bis(phenylhydroxymethyl)-2,2′-bithiophene (1 g, 2.65 mmol) and pyrrole (0.184 mL, 2.65 mmol) in dry $CH_2Cl_2$ (800 mL) were stirred under a nitrogen atmosphere for 15 min at room temperature. A freshly distilled solution of $BF_3 \cdot Et_2O$ (2.5 M, 10 mol%) in dry $CH_2Cl_2$ was added, and the reaction mixture stirred for one additional hour. The resulting solution was opened to air, chloranil (1 g, 4 mmol) was added, and the mixture was heated at reflux in a preheated oil bath at 45 °C. After removal of solvent, the crude product was purified by column chromatography. After an initial brown fraction was eluted with $CH_2Cl_2$/ethyl acetate (70/30), the second dark violet fraction was identified as **1** (28% yield). Alternatively, pyrrole was replaced by dipyrromethane **10** in the above procedure to generate **1** in 20% yield. A similar procedure was followed for the synthesis of **2** using bifurandiol.

**1**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.98$ (m, 12H), 8.55 (m, 8H), 9.06 (s, 4H), 10.49–10.50 (d, $J = 3.00$ Hz, 4H), 11.64–11.66 (d, $J = 6$ Hz, 4H); $^1$H NMR (300 MHz, $CDCl_3$/TFA): $\delta = -5.15$ (s, 2H), 8.32–8.34 (m, 12H), 9.02–9.04 (m, 8H), 9.41 (s, 4H), 10.96–10.98 (d, $J = 3$ Hz), 11.74–11.76 (d, $J = 6$ Hz); UV/Vis ($CH_2Cl_2$/1% $Et_3N$): $\lambda_{max}$ ($\varepsilon \times 10^{-3}$) = 523 (79.81), 659 (4.88), 717 (10.18), 837 (0.55), 958 nm (0.60); emission ($CH_2Cl_2$): $\lambda = 706, 768$ nm; MS (FAB): *m/z* (%) = 813 (100); CV ($CH_2Cl_2$/tetrabutyl ammonium perchlorate (TBAP, $1 \times 10^{-2}$‰M)): $E_{1/2}(R1) = -0.86$ V ($\Delta E_p = 150$ mV); $E_{1/2}(R2) = -1.05$ V ($\Delta E_p = 110$ mV); $\Delta E(red) = 190$ mV; UV/Vis ($CH_2Cl_2$/TFA): $\lambda_{max}$ ($\varepsilon \times 10^{-3}$) = 449 (3.3), 543 (44.0), 867 nm (6.2).

**2:** UV/Vis ($CH_2Cl_2$/1% $Et_3N$): $\lambda_{max}$ ($\varepsilon \times 10^{-3}$) = 525 (5.97), 674 (1.04), 739 (1.86), 860 (0.70), 968 nm (0.93); MS (FAB): *m/z* (%) = 750 (100); $^1$H NMR (300 MHz, $CDCl_3$/TFA) $\delta = -4.82$ (s, 2H), 8.13–8.15 (m, 12H), 8.27–8.29 (m, 8H), 9.00 (s, 4H), 10.71–10.72 (d, $J = 3$ Hz, 4H), 11.29–11.30 (d, $J = 3$ Hz, 4H); UV/Vis ($CH_2Cl_2$/TFA): $\lambda_{max}$ ($\varepsilon \times 10^{-3}$) = 544 (15.7), 836 nm (3.96).

**8a**: UV/Vis (MeOH/1% HCl): $\lambda_{max}$ ($\varepsilon \times 10^{-3}$) = 449 (3.50), 542 (29.95), 866 nm (6.53); emission (MeOH/1% HCl): $\lambda = 739$ nm; MS (FAB): *m/z* (%) = 815 (65).

**8b**: UV/Vis (MeOH/1% $HClO_4$): $\lambda_{max}$ ($\varepsilon \times 10^{-3}$) = 448 (5.21), 542 (26.80), 863 nm (5.04); MS (FAB): *m/z* (%) = 815 (35); CV: ($CH_2Cl_2$/TBAP ($1 \times 10^{-2}$ M)): $E_{1/2}(R1) = -0.78$ V ($\Delta E_p = 130$ mV); $E_{1/2}(R2) = -1.41$ V ($\Delta E_p = 110$ mV); $\Delta E(red) = 630$ mV; ($CH_3CN$/TBAP ($1 \times 10^{-2}$ M)): $E_{1/2}(O1) = +0.86$ V (irreversible); $E_{1/2}(O2) = +1.12$ V ($\Delta E_p = 170$ mV); $E_{1/2}(O3) = +1.32$ V ($\Delta E_p = 110$ mV).

**9a**: UV/Vis (MeOH/1% HCl): $\lambda_{max}$ ($\varepsilon \times 10^{-3}$) = 533 (12.4), 830 nm (2.40).

**9b**: UV/Vis (MeOH/1% $HClO_4$): $\lambda_{max}$ ($\varepsilon \times 10^{-3}$) = 532 (10.1), 829 nm (1.98).

Received: April 1, 1997
Supplemented version: July 25, 1997 [Z10297IE]
German version: *Angew. Chem.* **1997**, *109*, 2710–2713

**Keywords:** bithiophenes · porphyrinoids · rubyrin · sensitizers

---

[1] For a comprehensive review of expanded porphyrins, see J. L. Sessler, A. K. Burrel, *Top. Curr. Chem.* **1991**, *161*, 177–273.

[2] a) V. J. Bauer, L. J. Derrick Clive, D. Dolphin, J. B. Paine III, F. L. Harris, M. M. King, J. Lodger, S.-W. Chien Wang, R. B. Woodward, *J. Am. Chem. Soc.* **1983**, *105*, 6429–6436; b) J. L. Sessler, M. Cyr, A. K. Burrel, *Tetrahedron* **1992**, *48*, 9661–9672, and references therein; c) M. J. Broadhurst, R. Grigg, A. W. Johnson, *J. Chem. Soc. Perkin Trans. 1* **1972**, 2111–2116; d) P. J. Chmielewski, L. Latos-Grazynski, K. Rachlewicz, *Chem. Eur. J.* **1995**, *1*, 68–73.

[3] a) H. Rexhausen, A. Gossauer, *J. Chem. Soc. Chem. Commun.* **1983**, 275; b) A. Gossauer, *Bull. Soc. Chim. Belg.* **1983**, *92*, 793–795.

[4] J. L. Sessler, S. J. Weghorn, Y. Hiseada, V. Lynch, *Chem. Eur. J.* **1995**, *1*, 56–67.

[5] J. L. Sessler, S. J. Weghorn, T. Morishima, M. Rosingana, V. Lynch, V. Lee, *J. Am. Chem. Soc.* **1992**, *114*, 8306–8307.

[6] J. L.Sessler, T. Morishima, V. Lynch, *Angew. Chem.* **1991**, *103*, 1018–1021; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 977–980.

[7] M. Broring, J. Jendrny, L. Zander, H. Schmickler, J. Lex, Y.-D. Wu, M. Nendel, J. Chen, D. A. Plattner, K. N. Houk, E. Vogel, *Angew. Chem.* **1995**, *107*, 2709–2711; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2515–2517.

[8] a) H. Furuta, M. J. Cyr, J. L. Sessler, *J. Am. Chem. Soc.* **1991**, *113*, 6677–6678; b) H. Furuta, K. Furuta, J. L. Sessler, *ibid.* **1991**, *113*, 4706–4707; c) H. Furuta, D. Magda, J. L. Sessler, *ibid.* **1991**, *113*, 978–985.

[9] a) L. Latos-Grazynski, J. Lisowski, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **1987**, *109*, 4428–4429; b) A. Ulman, J. Manassen, *ibid.* **1975**, *97*, 6540–6544; c) P. Chmielewski, M. Grazeszczuk, L. Latos-Grazynski, T. Lisowski, *Inorg. Chem.* **1989**, *28*, 3546–3552; d) A. Ulman, J. Manassen, F. Frolow, D. Rabinovich, *J. Am. Chem. Soc.* **1979**, *101*, 7055–7059.

[10] a) M. Ravikanth, T. K. Chandrashekar, *Struct. Bonding (Berlin)* **1995**, *82*, 105–188; b) R. P. Pandian, T. K. Chandrashekar, *Inorg. Chem.* **1994**, *33*, 3317–3324; c) R. P. Pandian, T. K. Chandrashekar, *J. Chem. Soc. Dalton*

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 1997 0570-0833/97/3623-2600 $ 17.50+.50/0

*Trans.* **1993**, 119–125; d) M. Ravikanth, A. Mishra, T. K. Chandrashekar, S. Sathaiah, H. D. Bist, *Inorg. Chem.* **1994**, *33*, 392–394; e) R. P. Pandian, T. K. Chandrashekar, H. van Willigen, *Chem. Phys. Lett.* **1993**, *202*, 127–132.

[11] Two examples of core-modified expanded porphyrins that were previously reported are ozaphyrins and bronzaphyrin: a) D. C. Miller, M. R. Johnson, J. J. Becker, J. A. Ibers, *J. Heterocycl. Chem.* **1993**, *30*, 1485–1490; b) D. C. Miller, M. R. Johnson, J. A. Ibers, *J. Org. Chem.* **1994**, *59*, 2877–2879; c) M. R. Johnson, D. C. Miller, K. Bush, J. J. Becker, J. A. Ibers, *ibid.* **1992**, *57*, 4414–4417; d) H. Zhongying, C. Scordilis-Kelley, M. P. Cava, *Tetrahedron Lett.* **1993**, *34*, 1879–1882.

[12] a) J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, A. M. Marguerettaz, *J. Org. Chem.* **1987**, *52*, 827–836; b) C.-H. Lee, J. S. Lindsey, *Tetrahedron* **1994**, *50*, 11427–11440.

[13] M. Gouterman in *The Porphyrins, Vol. III* (Ed.: D. Dolphin), Academic Press, New York, **1978**, pp. 1–165.

[14] M. Shionoya, H. Furuta, V. Lynch, A. Harriman, J. L. Sessler, *J. Am. Chem. Soc.* **1992**, *114*, 5714–5722.

[15] C. Nash, *J. Phys. Chem.* **1960**, *64*, 950–953.

[16] Transport experiments were carried out using a glass U tube with three compartments containing a solution of AMP (2 mL, 30 mM, sodium salt, Sigma, pH = 3), a solution of **8a** in $CH_2Cl_2$ ($3 \times 10^{-4}$ M), and water (2 mL, pH = 10).

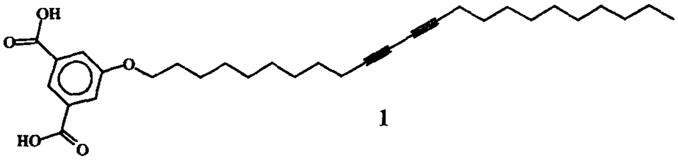
---

# Submolecularly Resolved Polymerization of Diacetylene Molecules on the Graphite Surface Observed with Scanning Tunneling Microscopy

Petrus C. M. Grim, Steven De Feyter, André Gesquière, Peter Vanoppen, Markus Rücker, Suresh Valiyaveettil, Georg Moessner, Klaus Müllen, and Frans C. De Schryver*

Polydiacetylenes (PDA) have become an important class of materials because of their interesting optical and electronic properties. Diacetylenes can in principle polymerize in the solid, liquid crystalline, or the molten state.[1] The solid-state topochemical 1,4-polymerization was first documented by Wegner in 1969.[2] The polymerization of thin films, such as Langmuir–Blodgett[3] and chemisorbed self-assembled monolayers on gold,[4] has been reported. A few studies dealt with physisorbed self-assembling monolayers on graphite. Ozaki et al. have shown evidence of polymerization in a vapor-deposited monolayer of diacetylene molecules with Penning ionization electron spectroscopy.[5] Rabe et al. have observed a physisorbed monolayer of a diacetylene compound at the liquid/graphite interface, with scanning tunneling microscopy (STM).[6] Since the first STM related publications of physisorbed monolayers on alkanes and long-chain alcohols,[7] such self-organized monomolecular adlayers have been studied with STM for a broad range of compounds.[8] Physisorbed monolayers of organic molecules at the liquid/graphite interface containing photoactive groups were recently reported,[9] and the light induced *cis–trans* isomerization could be imaged with submolecular resolution.[10,11] In this communication, we report the photopolymerization of a physisorbed monolayer containing diacetylene moieties, self-assembled from solution at the liquid/graphite interface. The monolayer structures before and after the polymerization have been imaged with submolecular resolution by means of STM. The visualization of the transformation from diacetylene to polydiacetylene in two dimensions might lead to a better understanding of the parametrization of such a polymerization.

When a drop of the solution of the isophthalic acid derivative **1** in 1-undecanol is applied to the graphite surface, a physisorbed monolayer is spontaneously formed at the liquid/graphite interface. Figure 1 (left) shows the image of the structure of such a monolayer observed with STM. A very clear image contrast is obtained due to an increased tunneling current over specific areas of the monolayer (e.g. aromatic moieties) and good stability of the monolayer. The structure consists of lamellae of the molecules of **1** interspersed by alternate lamellae of solvent molecules. Such a solvent incorporation (or solvent codeposition) has recently been reported for isophthalic acid derivatives.[11] The carboxyl functions of the isophthalic acid (ISA) head groups can form hydrogen bonds between neighboring molecules of **1** or between molecules of **1** and solvent molecules. The latter possibility leads to the incorporation of the solvent molecules into the monolayer structure. One of the solvent lamellae is indicated in Figure 1 (left, arrow labeled SOLV). The undecanol molecules of the solvent lamellae are oriented at an angle of 68° relative to the direction of the lamellae. The lamellae of the molecules of **1** are characterized by the positions of the ISA headgroups and the diacetylene (DIA) moieties of the molecules. The diacetylene moieties, clearly visible in the STM image, appear as two bright spots in the



**1**

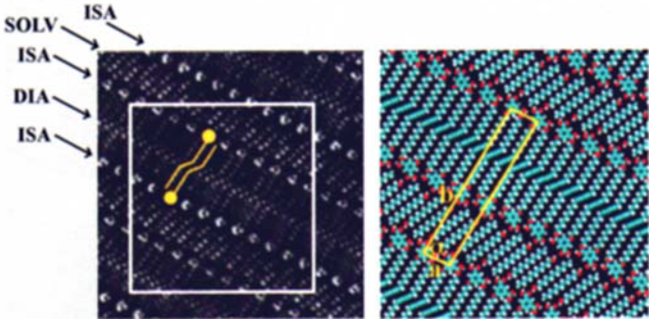


Figure 1. Left: STM image of a physisorbed monolayer of molecules of **1** from a solution in 1-undecanol (image size 12.7 × 12.7 $nm^2$). White corresponds to the highest and black to the lowest measured tunneling current in the image. Bias voltage and average tunneling current were −1.2 V and 1.0 nA, respectively. The isophthalic acid headgroups are labeled ISA, the diacetylene groups DIA and solvent molecules SOLV. Right: Model of the area indicated in the STM image, with superimposed unit cell.

---

[*] Prof. F. C. De Schryver, Dr. P. C. M. Grim, S. De Feyter, A. Gesquière, P. Vanoppen, Dr. M. Rücker
University of Leuven
Department of Chemistry
Laboratory of Molecular Dynamics and Spectroscopy
Celestijnenlaan 200-F, B-3001 Heverlee (Belgium)
Fax: Int. code + (16) 327989
e-mail: Frans.DeSchryver@chem.kuleuven.ac.be

Prof. K. Müllen, Dr. S. Valiyaveettil, G. Moessner
Max-Planck-Institut für Polymerforschung, Mainz (Germany)

[**] The authors thank FKFO and DWTC for continuing financial support through IUAP-IV-11. S. De Feyter is a predoctoral fellow of the FWO and P. Vanoppen thanks the IWT for a predoctoral scholarship.

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 1997