Synthesis of the First Fully α-Conjugated Macrocyclic Oligothiophenes: Cyclo[*n*]thiophenes with Tunable Cavities in the Nanometer Regime**

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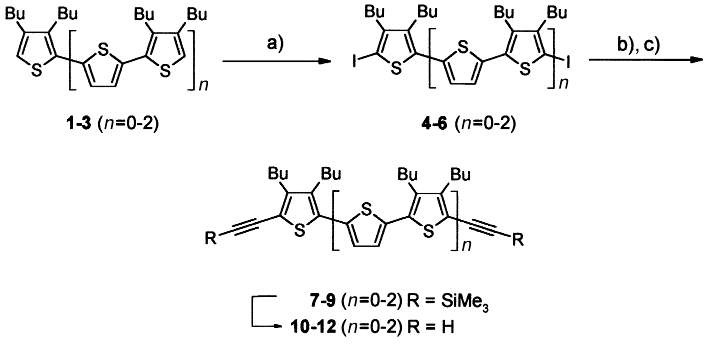
Polythiophenes and their corresponding finite model oligomers, α-conjugated oligothiophenes, belong to the most frequently investigated conjugated systems as a consequence of their chemical stability in various redox states, their outstanding electronic properties, the widespread possibilities of functionalization, and consequently their potential applicability in (molecular) electronic devices, such as organic light emitting diodes, lasers, or transistors.[1] In various series of monodisperse linear oligothiophenes with controllable and defined structure the physical properties correlate well with the (conjugated) chain length and thus valuable structure–property relationships become available.[2] In scanning probe studies on self-assembled monolayers of regioregular poly(3-alkylthiophene)s we observed that polymer folding occurs and seven or eight *syn*-arranged thiophene units form a "hairpin" or 180° semicircle,[3] hence our goal was the design and preparation of novel fully (macro)cyclic α-conjugated oligothiophenes. If these systems were sufficiently stable and large, in comparison to usual linear conjugated oligomers and polymers, completely novel perspectives and properties could arise. Cyclic derivatives could represent a model system which ideally combines an infinite π-conjugated chain of an idealized polymer with the advantages of a structurally well-defined oligomer but without any perturbing end-effects.[4] As a consequence of the resulting cavities the recognition and selective complexation of guest molecules, which may depend on the redox state of the cyclic host, additionally come into play. On the other hand, macrocyclic systems such as cyclic oligopeptides can self-assemble to form nanotubes which enables their application in biological as well as materials science.[5] Herein we now report the successful synthesis and self-organization properties of a new class of conjugated macrocycles which we designate as α-cyclo[*n*]thiophenes (α-C[*n*]T).

In the 1970s Kauffmann et al. synthesized cross-conjugated cyclo[4]- and cyclo[6]thiophene from bithiophene precursors. However, these systems are only very weakly conjugated because of α,β- or β,β-linkages of the thiophene units.[6] Thiophene-derived annulenes consisting of thiophene units and *cis* double bonds are also only partially conjugated.[7] Quantum chemical calculations on α-conjugated cyclo[12]-thiophene result in a nearly nonstrained and coplanar conformation in which all 12 thiophene rings are arranged in a *syn* fashion, which demonstrates the importance and the feasibility of such macrocycles.[8]

Typically, *m*-phenylene units or other electronically weak coupling units are used as angular building blocks to favor the formation of macrocycles.[9] The largest ring so far, a 90-membered cyclic oligophenylene synthesized by repetitive Suzuki cross-coupling reactions by Schlüter et al., contains 24 phenylene rings and an estimated cavity of 3–3.5 nm, but lacks overall conjugation because of the electronic interruption by the angular corner units.[10]

Our synthetic strategy relied on the common method to prepare macrocycles which involves oligomerization and cyclization at the same time. Since various products are generated in a single step, the yields are typically low and critically depend on the building blocks, the ring size, and the feasibility of separating the mixtures.[11] Since attempts to use transistion metal catalyzed cross-coupling reactions for the synthesis of the envisaged α-C[*n*]Ts completely failed,[12] the intramolecular oxidative coupling of novel α,α'-difunctionalized thiophenediynes was used. The subsequent reaction of the products with sulfide anions should then result in the desired macrocycles.

The butylated thiophenes **1**–**3** were chosen as the starting materials for the synthesis of the required building blocks (Scheme 1). These thiophenes were synthesized as part of a homologous series of linear oligothiophenes containing parent oligomers up to a 19-mer.[13] Symmetrical substitution of thiophene units with butyl groups proved to be ideal for



Scheme 1. Synthesis of thiophenediynes **10**–**12** as modular building blocks for the macrocyclization reactions. a) 2 I_2, $Hg(OAc)_2$, $CHCl_3$, 0–20 °C, 2 h; b) TMSA, $[Pd(PPh_3)_2Cl_2]$, CuI, NEt_3, pyridine, 60 °C, 12 h; c) KOH, MeOH, THF, RT, 1 h.

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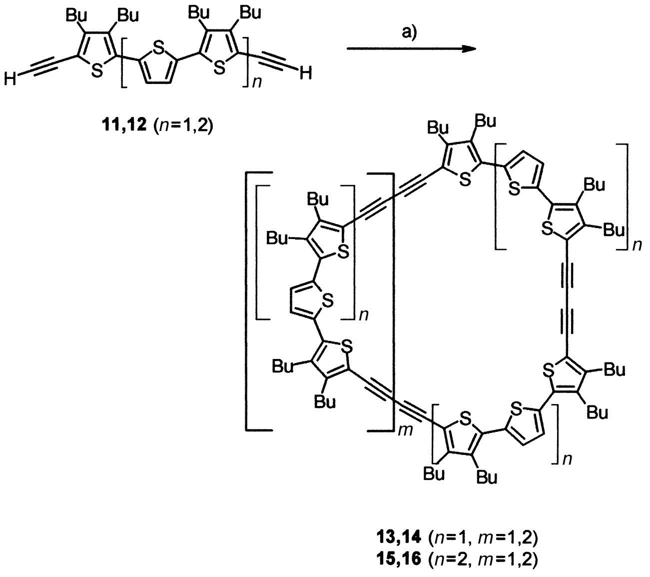
maintaining sufficient solubility and avoiding problems of regioisomer formation. In the first step, thiophenes **1**–**3** were selectively iodinated at the α-positions by elemental iodine and mercury(II) acetate in chloroform to yield diiodothiophenes **4**–**6** in 94, 85, and 87 %, respectively. The introduction of the terminal acetylenic groups was achieved by palladium-catalyzed Sonogashira–Hagihara coupling[14] of diiodothiophenes **4**–**6** and trimethylsilylacetylene (TMSA). The TMS-protected thiophenes **7**–**9** were isolated in 69, 76, and 70 %, respectively, and deprotected nearly quantitatively under mild basic conditions to yield the thiophenediynes **10**–**12**. They were immediately used for subsequent coupling reactions after chromatographic work-up because of their inherent instability and tendency to polymerize.

Oxidative coupling of the smallest building block, 3,4-dibutyl-2,5-diethynylthiophene (**10**), was performed under various high-dilution conditions (Glaser: CuCl/$CuCl_2$/pyridine;[15] Eglington: $Cu(OAc)_2$/pyridine/MeOH;[16] Hay: CuCl/O_2/TMEDA/$CHCl_3$[17] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)). An immediate reaction was observed in each case and complex, nonseparable mixtures of linear and cyclic structures with 3–12 repeating units were obtained, as indicated by the ^1H NMR, IR, and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra.[18] Much better results were obtained by a modified Eglington–Glaser coupling[9c, 19] of the higher homologues, terthiophenediyne **11** and quinquethiophenediyne **12**, under pseudo-high-dilution conditions (Scheme 2). Pyridine solutions of the oligothiophenes were added by means of a syringe-pump over 3 days to a slurry of anhydrous CuCl and $CuCl_2$ in pyridine at room temperature. Characterization of the crude product mixtures by ^1H NMR spectroscopy and MALDI-TOF mass spectrometry indicated that cyclic products had already been formed. Separation of the mixtures by preparative HPLC resulted in the isolation of analytically pure macrocyclic oligothiophenediacetylenes **13**–**16** as stable, bright yellow to red microcrystalline solids which have high solublity in most common organic solvents. In both cases the cyclotrimers **13** and **15** ($m = 1$) and the cyclotetramers **14** and **16** ($m = 2$) were isolated as the main products (yields 2–12 %).[20]

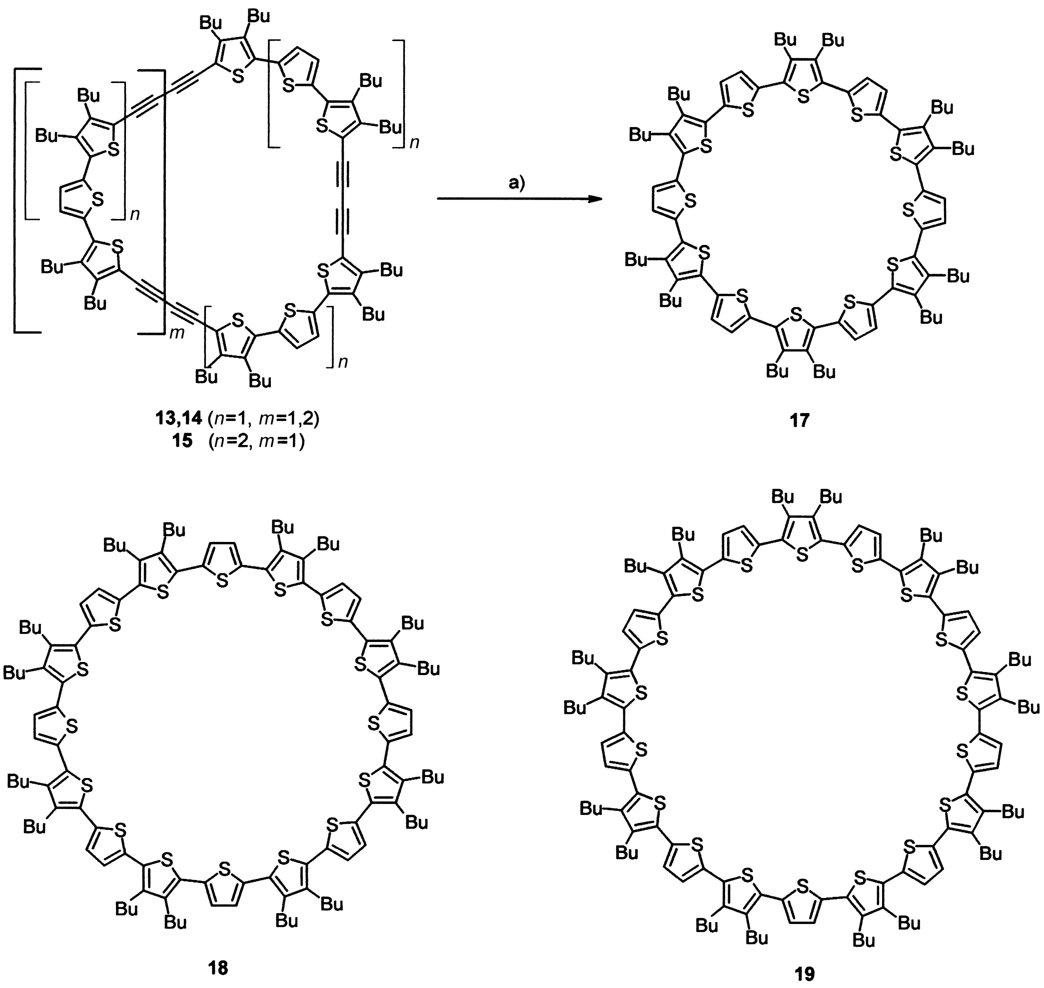


Scheme 2. Macrocyclization of thiophenediynes **11** and **12** under modified Eglington–Glaser conditions to the mixed cyclooligothiophenediacetylenes **13**–**16**. a) CuCl, $CuCl_2$, pyridine, RT, 44 + 48 h.

A cyclodimer ($n = 2$, $m = 0$) and higher homologues ($n = 1$, $m = 3$–7; $n = 2$, $m = 3$-6) could also be detected by HPLC and assigned by MALDI-TOF-MS. ^1H, ^{13}C NMR, and MALDI-TOF MS characterization of the isolated macrocycles **13**–**16** are in full accordance with the proposed structures. The high symmetry of the molecules made assignment of all the signals in the the NMR spectra possible. In each case, unambiguous structural proof came from MALDI-TOF mass spectrometry exhibiting exclusively one intense signal which corresponds to the theoretical mass of the macrocycle. Finally, we obtained macrocycles **13**–**16** with 39, 52, 57, and 76 chain members, respectively. Semiempirical calculations at the AM1 level showed the macrocycles have cavities with internal diameters of 1.37, 1.99, 2.14, and 3.07 nm, respectively (largest nonbonding $S \cdots S$ distance).[21]

Dithienylbutadiynes react with sulfur nucleophiles in methanol to give the corresponding terthiophenes in excellent yields.[22] We optimized this protocol for the synthesis of the linear parent compounds, and found that the butyl side chains exert sterical constraints on adjacent diyne units so that the reaction temperature had to be raised.[13] Analogous reactions of macrocycles **13**–**15** with sodium sulfide gave the fully α-conjugated cyclo[*n*]thiophenes **17**–**19** (Scheme 3). Transformation of three diyne units in compounds **13** and **15** resulted in analytically pure cyclo[12]thiophene **17** and cyclo[18]thiophene **19** in 23 % and 27 % yield, respectively, after purification. Cyclo[16]thiophene **18** was isolated in 7 % yield after the reaction of the four diyne moieties in macrocycle **15**. These values correspond to 52–64 % per cyclization step and are in good agreement with the reactions of linear derivatives. The three macrocycles **17**–**19** are stable, bright yellow to red microcrystalline solids which are highly soluble in most common organic solvents. Characterization of the cyclo[*n*]thiophenes from their ^1H, ^{13}C NMR, and MALDI-TOF mass spectra unequivocally proved the proposed structures.[23] Although the novel macrocycles could be considered as $(4n)\pi$ antiaromatics, no obvious ring current shifts are observed, which indicates they have a benzenoid rather than annulenoid character. Cyclo[*n*]thiophenes **17**–**19** comprise 36, 48, and 54 chain members, respectively, and according to semiempirical calculations form cavities with inner diameters of 1.28, 1.81, and 2.00 nm, respectively (largest nonbonding $S \cdots S$ distance). The calculated strain energies of the cycles is rather low (0.0–1.8 kcal mol^{-1}).

Investigations of the optical and electrochemical properties of the new macrocycles and their correlation to structural and conformational features revealed rather surprising results and will be reported in detail elsewhere. The detailed structure of the macrocycles and their intermolecular interactions in the solid state are important features with respect to their use as large molecular building blocks to assemble new materials in a controlled manner. X-ray structure analysis of ring-shaped structures, however, are inherently difficult since the large



13,14 (n=1, m=1,2)
15 (n=2, m=1)

17

18

19

Scheme 3. Reaction of the mixed cyclooligothiophenediacetylenes **13**–**15** to the fully α-conjugated cyclo[*n*]thiophenes **17**–**19**. a) $Na_2S \cdot 9H_2O$, 2-methoxyethanol, *p*-xylene, 4 h reflux.

cavities in the crystal are typically filled by solvent molecules and cause structural disorder or destruction of the crystal when the solvent is lost.[9c, 24] Both series of thiophene-containing macrocycles exhibited relatively high melting points which indicate strong π–π interactions between the molecules in the solid state. Oligothiophenediacetylene **14** crystallizes from toluene in orange prisms suitable for X-ray structure analysis.[25] Their investigation gave unambiguous proof of the macrocyclic structure of **14** although the disorder of some of the butyl side chains made the refinement very difficult (R value after anisotropic refinement 0.145). The top view of an individual molecule (including atomic labeling), views of the unit cell, and the structure along various axes are given in Figure 1. The macrocycle forms a nearly planar rounded rectangle comprising all-*syn*-oriented terthiophene units at the edges which are connected by moderately strained diacetylene units (Figure 1a). Their angles are typical for distorted dehydroannulenes[26] and cyclophanes[27] and are convexly bowed at the longer side of the rectangle (C13-C15-C17 176°; C15-C17-C19 174°) and concavely at the smaller side (C33-C35-C37 173°; C35-C37-C39 173°). The alternating carbon–carbon bond lengths of the diyne units fall within the normal range. The central rings of the terthiophene moieties are distorted by 23–40° as a result of the steric constraints of the butyl side chains. The nonbonding distances S5···S5′ (1.94 nm), S2···S5 (1.48 nm), and S2···S5′ (1.34 nm) reflect the size of the interior cavity of the 52-membered ring, which is good agreement with semiempirical calculations (S5···S5′: 1.99 nm).

The side-view projection, which corresponds to a view along the molecular plane of the unit cell, shows that the single molecules are oriented parallel to each other and clearly form dimers. The molecules are slightly laterally displaced in the dimers and show a stacking distance of 4.27 Å between the planes, the distance between dimers is 7.64 Å (Figure 1b). Although the top-view projection along the a-axis reveals some overlaps of the macrocycles, most interestingly, channels with diameters of about 1 nm are formed (Figure 1c), which compare well with those of self-assembled peptide nanotubes.[5] The closest intermolecular S···S distances of 3.5 Å (S1···S1′) are slightly smaller than the sum of the van der Waals radii (sulfur 1.8 Å[28]), which indicates intermolecular interactions occur.

Scanning tunneling microscopy (STM) offers an excellent and alternative way to directly investigate ordered structures in situ on the relevant length scales. Depending on the substitution pattern, linear oligothiophenes physisorb from solution to the basal plane of highly oriented pyrolythic

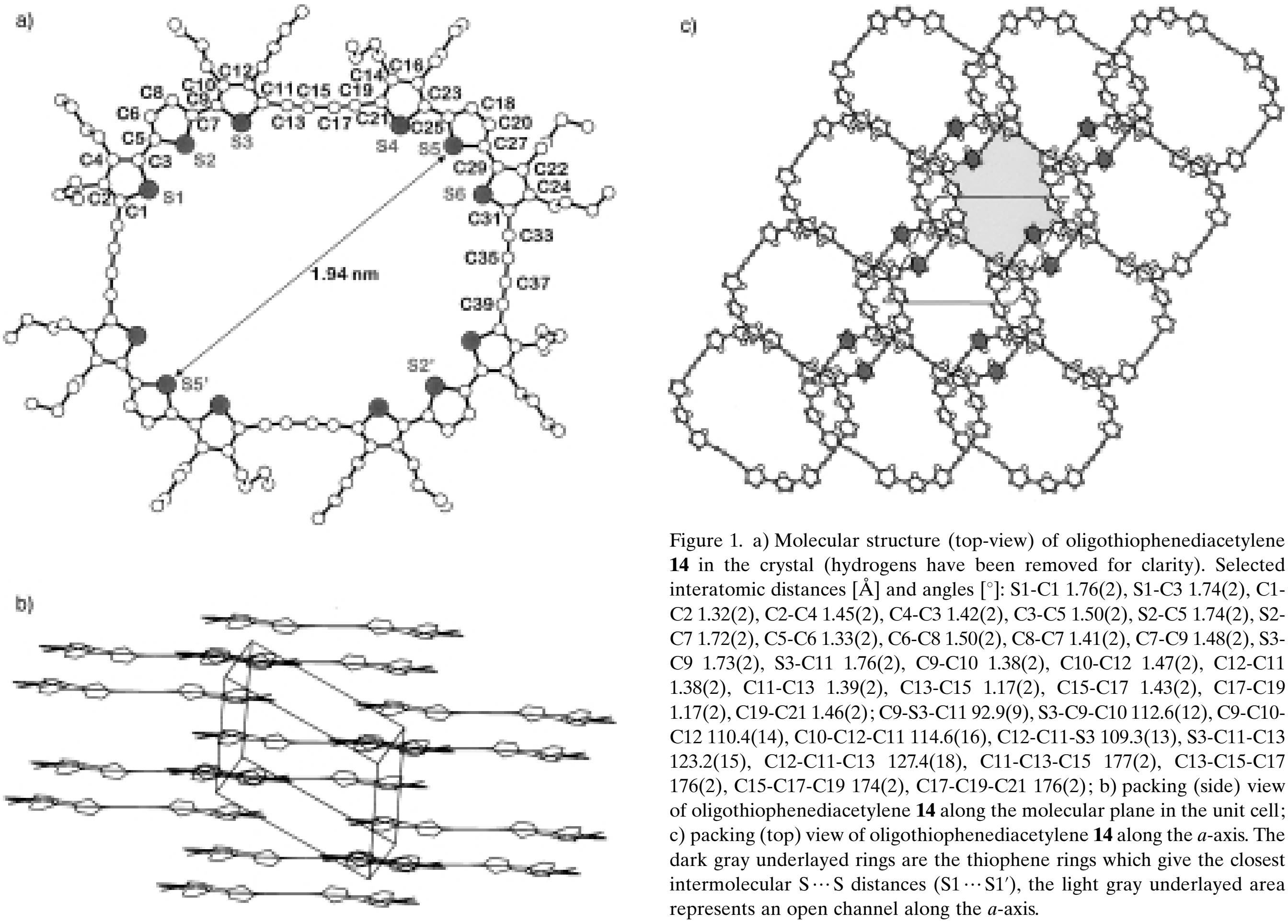


Figure 1. a) Molecular structure (top-view) of oligothiophenediacetylene **14** in the crystal (hydrogens have been removed for clarity). Selected interatomic distances [Å] and angles [°]: S1-C1 1.76(2), S1-C3 1.74(2), C1-C2 1.32(2), C2-C4 1.45(2), C4-C3 1.42(2), C3-C5 1.50(2), S2-C5 1.74(2), S2-C7 1.72(2), C5-C6 1.33(2), C6-C8 1.50(2), C8-C7 1.41(2), C7-C9 1.48(2), S3-C9 1.73(2), S3-C11 1.76(2), C9-C10 1.38(2), C10-C12 1.47(2), C12-C11 1.38(2), C11-C13 1.39(2), C13-C15 1.17(2), C15-C17 1.43(2), C17-C19 1.17(2), C19-C21 1.46(2); C9-S3-C11 92.9(9), S3-C9-C10 112.6(12), C9-C10-C12 110.4(14), C10-C12-C11 114.6(16), C12-C11-S3 109.3(13), S3-C11-C13 123.2(15), C12-C11-C13 127.4(18), C11-C13-C15 177(2), C13-C15-C17 176(2), C15-C17-C19 174(2), C17-C19-C21 176(2); b) packing (side) view of oligothiophenediacetylene **14** along the molecular plane in the unit cell; c) packing (top) view of oligothiophenediacetylene **14** along the *a*-axis. The dark gray underlayed rings are the thiophene rings which give the closest intermolecular S ⋯ S distances (S1 ⋯ S1′), the light gray underlayed area represents an open channel along the *a*-axis.

graphite (HOPG) and form highly ordered two-dimensional (2D) crystalline monolayers which can be imaged by STM.[29] Furthermore, in some cases the 2D ordering at the HOPG surface is most notably coincident with the molecular packing in the 3D crystal and gives valuable information about intermolecular and molecule – substrate interactions, which are important for the application of these materials in thin-film electronic devices.[29a] We find spontaneous ordering at the solution/HOPG interface with the novel macrocyclic systems **13** – **19**. In Figure 2a (top) representative and characteristic STM images of well-ordered and very stable 2D crystalline monolayers of cyclo[12]thiophene **17** are shown.[30] The images are typically found on larger areas ($\geq 1 \times 1\ \mu m^2$) and display a long-range ordering of molecularly resolved individual macrocycles. A perfect hexagonal "honeycomb" pattern of the cycles with an optimal packing density and consequently only one persistent domain is observed. The lattice constants are 2.39, 2.36, and 2.28 nm and the molecules are oriented in the directions of the three main crystallographic axes of the underlying substrate. A height profile along one of these directions (cross-section) clearly reveals a perfect and regular alignment of the individual molecules. We can also observe submolecular resolution in this diagram: each molecule gives two separated signals with a peak-to-peak separation of 1.13 nm, which agrees well with the inner aromatic borders of the toroidal structure (Figure 2a, bottom). This is in good agreement to calculated nonbonding S ⋯ S van der Waals distances. Semiempirical calculations and simulations confirm the arrangment and dimensions of the individual macrocycles (Figure 2b, top). The energy minimum of α-C[12]T does not correspond to a fully planar molecule (diameter 2.68 nm), but rather to a "spiderlike" conformation in which the butyl side chains are bent downwards (diameter 2.34 nm; diameter of the conjugated π system 1.83 nm) as a consequence of the uniform distorsion of each second thiophene ring. The height of the molecule (0.48 nm) is in full accordance with the STM measurements, which indicates that a monolayer has been formed at the solution/HOPG interface (Figure 2b, bottom).

Large conjugated macrocycles **13** – **19** comprising up to 76 chain members and cavities up to 3 nm have been synthesized and their self-assembling properties investigated. We are currently optimizing the synthesis and broadening the scope of both macrocyclic series and we are most interested in the possible formation of channels or nanotubes from these conjugated materials. For the first time, these circular structures combine the excellent electronic properties of corresponding conjugated oligomers with complexation sites for larger organic guest molecules, and we anticipate novel fundamental properties and applications. Recognition experiments are currently under way in our laboratory. Calculations predict, for example, that fullerene C_{60} could be recognized by

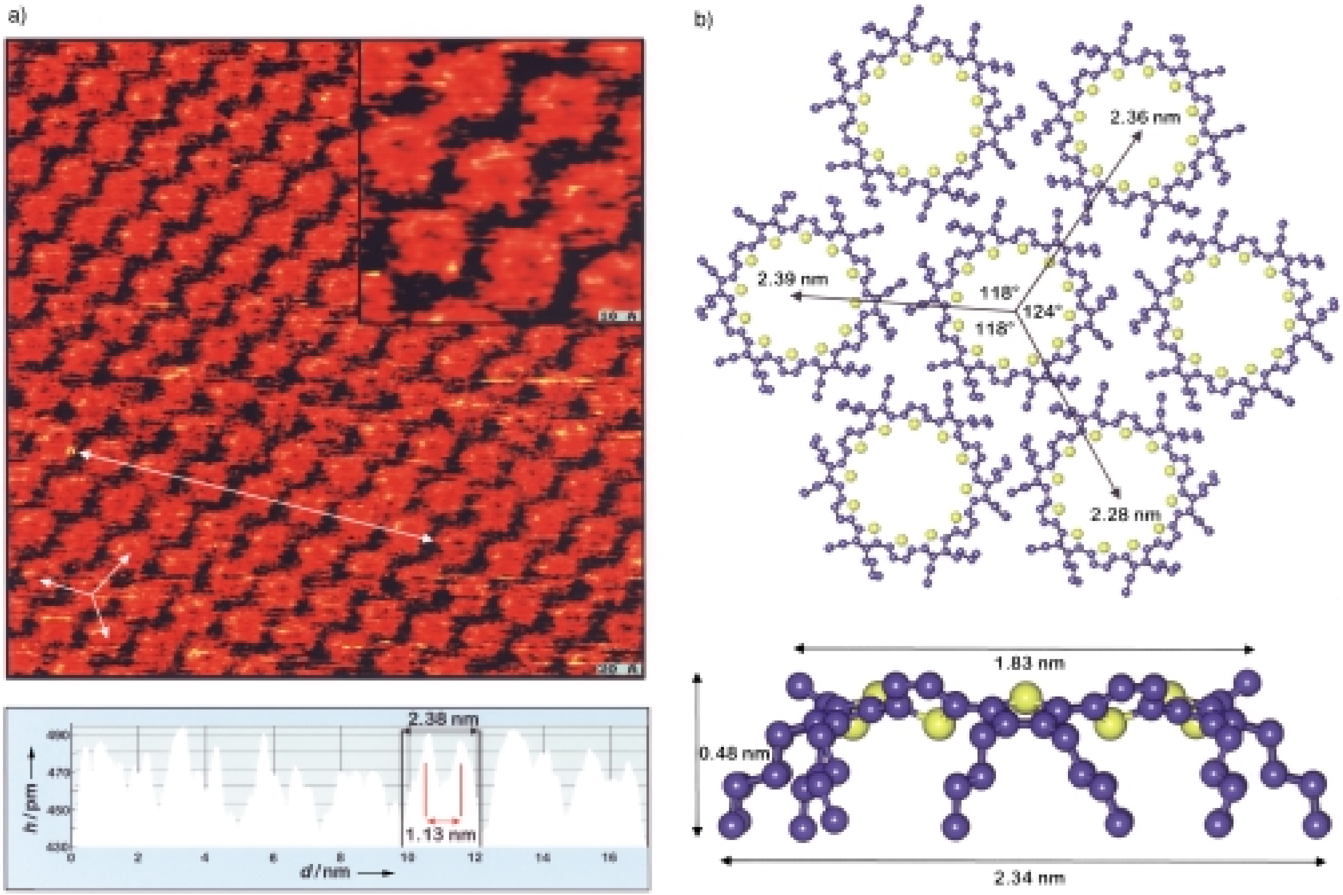


Figure 2. a) Top: STM image (280 × 280 Å^2) viewing the long-range ordering and 2D crystal of cyclo[12]thiophene **17** adsorbed on graphite. The inset shows the short-range ordering (67 × 67 Å^2). Both images were obtained with bias voltage of −430 mV (the sample is positive) and a tunnel current of 24 pA. Bottom: Height profile and cross-section along eight macrocycles (the white line is ca. 17 nm long). b) Schematic representation of the molecular arrangement of cyclo[12]thiophene **17**: hexagonal cluster consisting of seven molecules (top) and the calculated energy-minimum conformation of an individual macrocycle (bottom).

α-cyclo[12]thiophene and form a ring/sphere-shaped donor–acceptor complex.

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[23] Representative physical data of the cyclo[*n*]thiophenes **17**–**19**: **17**: ^{1}H NMR ($CDCl_3$): $\delta = 7.06$ (s, 12H, Th-H), 2.70 (t, 24H, α-CH_2), 1.42 (m, 48H, β,γ-CH_2), 0.95 (t, 36H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 140.31$ (β-Th-C), 136.55, 130.07 (α-Th-C), 125.43 (β-Th-C), 32.80 (β-CH_2), 27.80 (α-CH_2), 23.01 (γ-CH_2), 13.88 (CH_3); m.p. $> 250\,^\circ$C; MALDI-TOF-MS: m/z: 1656.80 [M^+]. **18**: ^{1}H NMR ($CDCl_3$): $\delta = 7.09$ (s, 16H, Th-H), 2.69 (t, 32H, α-CH_2), 1.45 (m, 64H, β,γ-CH_2), 0.97 (t, 48H, CH_3); m.p. $> 250\,^\circ$C; MALDI-TOF-MS: m/z: 2210.81 [M^+]. **19**: ^{1}H NMR ($CDCl_3$): $\delta = 7.10$ (s, 18H, Th-H), 2.75 (t, 36H, α-CH_2), 1.54 (m, 36H, β-CH_2), 1.47 (m, 36H, γ-CH_2), 0.99 (t, 54H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 140.11$ (β-Th-C), 136.18, 129.98 (α-Th-C), 125.72 (β-Th-C), 32.86 (β-CH_2), 27.94 (α-CH_2), 23.06 (γ-CH_2), 13.90 (CH_3); m.p. 210 °C; MALDI-TOF-MS: m/z: 2486 [M^+].

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[25] Crystal data: $C_{128}H_{82}S_{12}$, $M_r = 2004.66$, triclinic, space group $P\bar{1}$, $a = 11.914(3)$, $b = 16.444(3)$, $c = 17.749(4)$ Å, $\alpha = 113.17(2)$, $\beta = 98.40(3)$, $\gamma = 104.63(3)^\circ$, $V = 2973.0$ Å^3, $Z = 1$, $\rho_{\text{calcd}} = 1.120\,\text{g cm}^{-3}$, crystal dimensions $0.11 \times 0.22 \times 0.53$ mm, $T = 293(2)$ K, $\mu = 0.266\,\text{mm}^{-1}$. Intensity data were collected on a STOE-IPDS image-plate diffractometer ($Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator) in the φ rotation scan mode, $\theta_{\max} = 26^\circ$, 23195 reflections measured, 10776 unique reflections were measured and used in the refinement. Lorentz and polarization correction. The structure was solved by direct methods (XMY93 program system: T. Debaerdemaeker, *Z. Kristallogr.* **1993**, *206*, 173–182). The molecule is located on a crystallographic inversion centre. Refinement (SHELXL97; G. M. Sheldrick, University of Göttingen, **1993**) of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to $R1 = 0.1446$ ($wR2 = 0.3344$) for 1483 reflections with $I \geq 2\sigma(I)$. No attempt was made to locate the hydrogen atoms. The relatively poor R value is probably a result of the large disorder in some of the butyl chains. Unfortunately, no suitable crystals were available for data collection at low-temperature. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142083. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[30] The STM images were recorded at ambient temperature with the aid of low-current STM (RHK) regulated by a RHK STM-1000 control system equipped with a mechanically cut Pt/Ir tip. All of the images presented were obtained at quasi-constant height in the variable current mode without further manipulation or using a voltage pulse in order to induce the ordering, and without digital image processing. The bias voltages were typically around −400 to −450 mV and the setpoint currents around 0.3–0.5 nA. A freshly cleaved surface of HOPG was first carefully characterized under ambient conditions, then solutions of the macrocycles in 1,2,4-trichlorobenzene were deposited onto the substrate. In situ STM imaging of the self-assembled 2D monolayers was performed at the interface between HOPG and concentrated solutions of the macrocycles.

Investigating the Surface Morphology of Triacontyl Phases with Spin-Diffusion Solid-State NMR Spectroscopy**

Martin Raitza, Jürgen Wegmann, Stefan Bachmann, and Klaus Albert*

The detailed characterization of molecular recognition structures is one of the essential prerequisites for the development of new materials for specific applications in catalysis, sensor technology, and for the analysis of mixtures of compounds.

Highly selective stationary phases are needed for the efficient separation of complex mixtures of compounds in high-performance liquid chromatography (HPLC).[1] The tailored synthesis of these phases is impossible without any detailed knowledge of the surface structure of the materials and a detailed understanding of the structural and dynamic properties of the separation phase. Routine applications in HPLC can be successfully performed with reversed-phase materials,[2] which are prepared by modifying silica gel with *n*-alkylsilanes (for example, *n*-octadecylsilane). Reversed phas-

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