

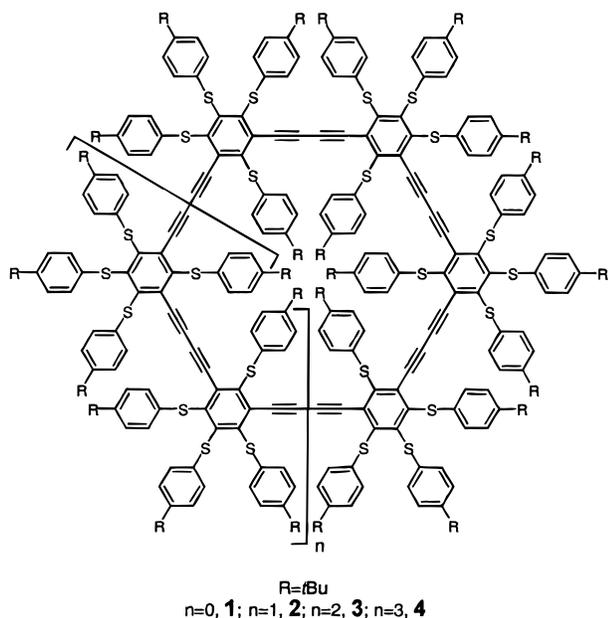
Reducible Nanosize Macrocycles

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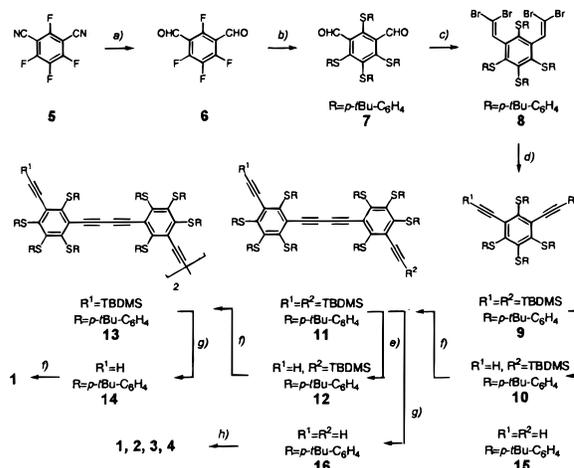
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The synthesis of well-defined redox-active nanoscale structures is of major interest for the design of electronic and/or logical functions on a nanometer scale and requires adequate functional building blocks such as wires, switches, batteries, etc.^{1–3} Herein we present the synthesis and isolation of the nanoscale polyunsaturated molecular cycles **1–4** presenting an annular arrangement of 4, 6, 8, and 10 reducible subunits linked by unsaturated bridges.



These macrocyclic structures are able to store several electrons and have therefore features of “molecular batteries”.

The bottom-up approach to nanoscale structures via chemical synthesis leads to geometrically defined, size- and shape-persistent, monodisperse systems.² With electron-accepting units as building blocks, the structures are enriched by their reducibility and are of particular interest as electron reservoirs³ or reducible molecular wires.⁴ Whereas entities built from electron-rich groups (i.e., thiophene,⁵ pyrrole⁶) lead to electronic conduction upon

Scheme 1: Synthesis of the Macrocycles **1**, **2**, **3**, and **4**^a

^a (a) PhMe, DIBAL-H, RT; (b) DMI, NaSR, RT; (c) CBr₄, PPh₃, CH₂Cl₂, RT; (d) LDA, THF, −78 °C, Cl-TBDMS; (e) THF, AcOH, TBAF, RT; (f) CuAc₂·H₂O, CHCl₃, 60 °C; (g) THF, TBAF, RT; (h) 2 × 10^{−4} M **16** in CHCl₃, 5.5 equiv CuAc₂·H₂O, CHCl₃, 60 °C.

oxidation (p-doping), reducible wires are susceptible to n-doping through reduction and may therefore show higher electron mobility.

Poly(phenylthio) aromatic systems, well-known for their host–guest chemistry in the solid state,⁷ have been shown to possess remarkably low reduction potentials.⁸ As electron-acceptor sites they have already been incorporated in a macrobicyclic ligand⁹ and in reducible rodlike molecular wires, based on *p*-diacetylene-linked poly(phenylthio)-substituted benzenes.¹⁰ In particular the promising electrochemistry of the latter prompted us to investigate other types of nanostructures based on diacetylene-linked poly(phenylthio)-benzene subunits.

Herein we present the synthesis, the structural characterization, and some physical properties of the cyclic structures **1–4**, in which 4, 6, 8, and 10 tetra(*p*-*tert*-butylthiophenyl)benzene subunits are connected in the *meta*-position by diacetylene bridges as π -conjugation connectors. *meta*-Acetylen- and/or diacetylen-linked benzene cores as building blocks for conformationally rigid and shape-persistent cyclic macromolecules have been described^{11,12} and oxidative acetylene-coupling strategies have already been used to form cyclic structures.^{12,13}

Starting from tetrafluoro isophthalonitrile, the cyclic structures were synthesized in eight steps (Scheme 1). Reduction of the isophthalonitrile **5** gave the tetrafluoro isophthalaldehyde **6** in 45% yield. Substitution of the fluorines by *p*-*tert*-butylthiophenyl anions in 1,3-dimethyl-2-imidazolidinone (DMI) yielded the phenylsulfanyl-substituted isophthalaldehyde **7** in 85% yield. Treatment with CBr₄/PPh₃ gave the dibromoethylenederivative

(7) MacNicol, D. D.; Downing, G. A. *Comprehensive Supramolecular Chemistry*; Altwood, J. L.; Davis, J. E. D.; MacNicol, D. D.; Vögtle, F.; Lehn, J.-M., Eds.; Elsevier: Oxford, 1996; Vol. 6, pp 421–464.

(8) Tucker, J. H. R.; Gingras, M.; Brand, H.; Lehn, J.-M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1303–1307.

(9) Mayor, M.; Lehn, J.-M. *Helv. Chim. Acta* **1997**, *80*, 2277–2285.

(10) Mayor, M.; Lehn, J.-M.; Fromm, K. M.; Fenske, D. *Angew. Chem.* **1997**, *109*, 2468–2471; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2370–2372.

(11) Young, J. K.; Moore, J. S. *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995, pp 415–442.

(12) Tobe, Y.; Utsumi, N.; Nagano, A.; Naemura, K. *Angew. Chem.* **1998**, *110*, 1347–1349; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1285–1287. Tobe, Y.; Utsumi, N.; Kawabata, K.; Naemura, K. *Tetrahedron Lett.* **1996**, *37*, 9325–9328.

(13) Examples are: Diederich, F. *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; pp 443–471. Haley, M. M. *Synlett* **1998**, 557–565. Höger, S.; Enkelmann, V. *Angew. Chem.* **1995**, *107*, 2917–2919; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2713–2716.

(1) Jortner, J.; Ratner, M. *Molecular Electronics*; Eds.; Blackwell: Oxford, 1997.

(2) Tour, J. M. *Chem. Rev.* **1996**, *96*, 573–553.

(3) Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377–383.

(4) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, 1995, Chapter 8.

(5) Bäuerle, P. Sulfur-Containing Oligomers. In *Electronic Materials: The Oligomer Approach*; Müllen, K., Eds.; Wegner, G. VCH: Weinheim, 1998; Chapter 2.

(6) Evans, G. P. *Advances in Electrochemical Science and Engineering*; Gerischer, H.; Tobias, C. W., Eds.; VCH: Weinheim, 1990; Vol. 1, pp 1–74. Skotheim, T. A. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Higgins, S. J. *Chem. Soc. Rev.* **1997**, *26*, 247–257.

8 in yields greater than 90%. Reduction with excess lithium diisopropylamide (LDA), followed by quenching with *tert*-butyldimethylsilyl chloride gave the doubly protected bis-silyl diacetylene **9** in 56% yield. Single deprotection with tetra *n*-butylammoniumfluoride (TBAF) with 1.5 equiv of acetic acid in wet THF yielded the monosilylated diacetylene **10** in 48% yield. Oxidative acetylene coupling gave the doubly silylated dimer **11** in 75% yield. The same procedure as for **9** allowed the single deprotection of compound **11** to form the monoprotected dimer **12** in 45% yield. The acetylene coupling procedure already used for **10** successfully transformed dimer **12** to the tetramer **13** in 88% yield. Full deprotection of **13** with TBAF in wet THF yielded the tetrameric diacetylene compound **14** in 70% yield. Subsequent oxidative acetylene coupling of **14** was performed in pseudo high dilution conditions. Finally, 14% of the cyclic tetrameric structure **1** could be isolated by column chromatography as an orange dye. The compound was identified and characterized by ¹H and ¹³C NMR and FAB-mass spectrometry.

Another synthetic strategy focused on the formation of cyclic structures starting from the deprotected diacetylene monomer **15** or dimer **16**. Attempts starting from the monomer **15** yielded complex mixtures, from which no defined compound could be isolated. However, a FAB-MS analysis of such a mixture presented peaks at 3907 for a pentamer and at 3125 for a tetramer. Whether these peaks arise from open diacetylene units or from closed cyclic structures could not be clarified.

When a 0.2 mM solution of diacetylene dimer **16** in CHCl₃ with 5.5 equiv of copper acetate monohydrate was heated to 60 °C for 16 h, clearly defined spots could be observed by TLC (silica, hexane/Et₂O 9/1) of the reaction mixture, and the resulting products could be isolated by preparative TLC. Several cyclic structures were obtained in quite acceptable yields considering the goal pursued: 10% of the tetramer **1**, 17% of the hexamer **2** as main product, 12% of the octamer **3**, and finally 2% of the decamer **4**. The diameters of the cyclic compounds are about 2 nm for **1** (distance between peripheral sulfur atoms) and 2.6 nm for **2**. The diameters of the larger macrocycles **3** and **4** is dependent on the shape of the rings and may be up to 3.2 and 3.6 nm respectively for a fully planar arrangement. All four compounds gave satisfactory ¹H NMR spectra corresponding to the highly symmetric cyclic structure, and in particular, no free acetylene-H was observed. The first three compounds were as well identified and characterized by their ¹³C NMR spectra, but not enough material was available for the decamer **4**. FAB-MS signals were observed for the tetramer **1** and the hexamer **2**, whereas the method failed for the larger rings **3** and **4**. MALDI-TOF MS analysis of **3** and **4** yielded a regular pattern, for which the peak with the highest mass corresponded to the molecule ions. The peaks with lower masses corresponded to the loss of up to four *tert*-butyl benzenes or *tert*-butyl thiophenols. All four compounds were light-orange dyes and soluble in organic solvents such as CH₂Cl₂, CHCl₃, or toluene.

The UV/vis spectra of **1**, **2**, **3**, and **4** in CH₂Cl₂ at 25 °C display an absorption maximum at about 255 nm, which may be attributed to the allowed $\pi \rightarrow \pi^*$ transition in the *tert*-butylthiophenyl groups. The relative extinction coefficients are proportional to the number of these subunits and therefore to the ring size. Additional

transitions at longer wavelength were observed at about 345, 390–400, and 445 nm for the smallest cycle **1**. With increasing size of the rings, the 390–400 nm transition dominates the longer wavelength transitions. These transitions presumably arise from electronic interactions between poly(phenylthio)benzene and diacetylene units. Excitation of **1–4** in CH₂Cl₂ at 400 nm results in a moderately intense structureless fluorescence with maxima between 520 and 580 nm. Whereas the larger rings **2–4** display each a broad maximum at about 550–570 nm, **1** shows a sharper emission at about 525 nm with a shoulder toward longer wavelengths. The difference in the UV/vis and fluorescence spectra of **1** compared to **2–4** may be due to the higher ring strain in the smallest cycle.

Of particular interest are the redox properties of this new series of macrocycles with respect to ring size. The cyclic voltammetry data, collected in a 0.1 M TBAPF₆/DMF solution with a three electrode setup, are given as formal reduction potentials with respect to SCE. The relative number of electrons was determined by measurements at limiting current with a rotating disk electrode. None of the compounds **1–3** is oxidized up to +1.3 V. The tetrameric cycle **1** has a reversible two-electron reduction at –1.07 V and two reversible one-electron reductions at –1.19 and –1.44 V, respectively. The hexameric cycle **2** has a reversible three-electron reduction at –1.09 V, a reversible one-electron reduction at –1.24 V, and a reversible two-electron reduction at –1.40 V. The octameric cycle **3** displays one broad reduction wave at about –1.09 V with a large shoulder toward more negative values; it arises probably from the unresolved overlay of several reductions. In contrast to the *p*-diacetylene linked linear rods,¹⁰ a trend toward more positive values for the first reduction potential is not observed. *m*-Diacetylene benzenes are known to be conjugation passive centers.¹⁴ The fact that in the present case these groups are themselves the redox active subunits does not overcome this passivity, so that they behave more or less as isolated units. On the other hand, the combination of several independent reducible sites in a single molecule gives to compounds **1–4** the character of electron reservoirs³ or “molecular batteries”.

In summary, the set of cycles **1–4** was synthesized in one step from the corresponding dimer **16** in useful global yield. Their solubility and stability combined with their structural, optical, and electrochemical properties make them promising candidates for the design of nanoscale molecular devices for molecular electronics and photonics.⁴

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Supporting Information Available: Detailed synthetic procedure and spectroscopic characterization of compounds **1–16**; UV/vis and normalized fluorescence spectra of **1**, **2**, **3**, and **4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) Uno, M.; Dixneuf, P. H. *Angew. Chem.* **1998**, *110*, 1822–1824; *Angew. Chem., Int. Ed.* **1998**, *37*, 1714–1717. Fink, H.; Long, N. J.; Martin, A. J.; Opromolla, G.; White, A. J. P.; Williams, D. J.; Zanello, P. *Organometallics* **1997**, *16*, 2646–2650.