Yuka Fine Chemicals Co., Ltd.; Mitsubishi Petrochemical Co., Ltd.), JP-A 6191138, **1986** [*Chem. Abstr.* **1986**, *105*, 227505d]; d) H. Nozima, N. Kawata, Y. Nakamura, K. Maruya, T. Mizoroki, A. Ozaki, *Chem. Lett.* **1973**, 1163–1164; e) M. G. Barlow, M. J. Bryant, R. N. Hazeldine, A. G. Mackie, *J. Organomet. Chem.* **1970**, *21*, 215–226; f) K. Kawamoto, T. Imanaka, S. Teranishi, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2512–2515; g) S. Hattori, H. Munakata, K. Tatsuoka, T. Shimizu (Mitsubishi Chemical Industries Co., Ltd.), US-A 3803254, **1974** [*Chem. Abstr.* **1974**, *80*, 145725]; h) G. Muller, J. I. Ordinas, *J. Mol. Catal. A* **1997**, *125*, 97–108.

[7] a) B. Bogdanovic, *Adv. Organomet. Chem.* **1979**, *17*, 105–140; b) W. Jolly, G. Wilke, *Applied homogeneous catalysis with organometallic compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1992**, p. 1024; c) G. Wilke, *Angew. Chem.* **1988**, *100*, 189–211; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 185–206; d) N. Nomura, J. Jin, H. Park, T. V. Rajanbabu, *J. Am. Chem. Soc.* **1998**, *120*, 459–460.

[8] R. Bayersdörfer, B. Ganter, U. Englert, W. Keim, D. Vogt, *J. Organomet. Chem.* **1998**, *552*, 187–194.

[9] a) G. J. P. Britovsek, W. Keim, S. Mecking, D. Sainz, T. Wagner, *J. Chem. Soc. Chem Commun.* **1993**, 1632–1634; b) G. J. P. Britovsek, K. J. Cavell, W. Keim, *J. Mol. Catal. A* **1996**, *110*, 77–87; c) W. Keim, H. Maas, S. Mecking, *Z. Naturforsch. B* **1995**, *50*, 430–438.

[10] The structure of the novel functionalized dendrimers were confirmed by elemental microanalysis, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, and FAB-MS.

[11] The compounds were fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, FAB-MS, and elemental microanalysis. Elemental microanalysis of **7a** did not give satisfying results because of its air sensitivity.

[12] There is also a significant induction period in the batch reactions, but this is much shorter than that obtained here. As the catalyst is fed into the reactor together with the styrene, complexes other than that initially present in the batch reactions could be formed. This is presently under investigation.

[13] D. A. White, *Inorg. Synth.* **1972**, *13*, 55–65.

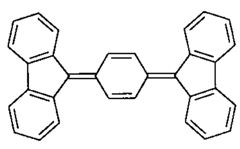
Self-Assembly of Quinodimethanes through Covalent Bonds: A Novel Principle for the Synthesis of Functional Macrocycles[**]

Junes Ipaktschi,[*] Rahman Hosseinzadeh, and
Peter Schlaf

Dedicated to Professor Fritz Vögtle
on the occasion of his 60th birthday

The development of methods for the synthesis of very large molecules such as dendrimers, supramolecules, and nanostructures with specific functions has increasingly become the center of attention in recent years.[1, 2] We have developed a synthetic strategy which is based on a directed tetramerization of basic building blocks in the final synthetic step.[3] With this method it is possible to obtain large and uniform molecular structures in one step from small molecules.

We could recently demonstrate that the quinodimethane derivative **1** assembles itself to a spherical cyclic tetramer in high yield.[3, 4] This spontaneous self-assembly process is driven by the four weak C_{sp^3}–C_{sp^3} bonds between the fluorene units that are formed during the tetramerization, and also by the *gauche* arrangement of these units to one another.[3, 5] Furthermore, these products have a remarkable property: Upon addition of energy they undergo a reversible color change to blue-violet as the reverse reaction to form the quinodimethane units occurs to a certain extent.[3]



1

We have tested this synthetic strategy towards the construction of highly branched systems as well as multifunctional metallocenes, which combine the reversible color change with the potential applications of side chains. We report herein the preparation of metallocene **3** containing 16 ferrocene units on the periphery of the molecule, as well as the synthesis of dendrimer **5**.

The key compounds for the synthesis of **3** and **5** are diol **2** and dichloride **4**, respectively.[6] These compounds can be obtained in only a few steps from the corresponding substituted fluorenone derivatives and 1,4-dilithiumbenzene.

Reduction of diol **2** with a $SnCl_2$/HCl solution at room temperature in THF as the solvent led to the macrocycle **3** in 82% yield (Scheme 1). The results of the molecular mass determination using the analytical ultracentrifuge are in agreement with the molecular formula of $C_{448}H_{400}Fe_{16}$. NMR spectroscopic data confirm the structure of **3**.[7] Owing to the S_4 symmetry of the molecular conformation, the ^{13}C NMR spectrum of **3** shows two characteristic signals at $\delta = 65.45$ and 65.24 for the C9 atoms of the fluorene units. Important information about the constitution of the macrocycle can be obtained from the ^{1}H NMR spectrum, which shows two signals for the protons of the inner phenyl rings at $\delta = 8.70$ and 8.26 (broad doublets) and two singlets each at $\delta = 5.93/5.90$ and 7.85/7.72.[8] Because of the S_4 symmetry of the molecule, the protons on the unsubstituted Cp ring of the ferrocenyl groups show up as four singlets at $\delta = 4.09$, 4.07, 3.98, and 3.97.

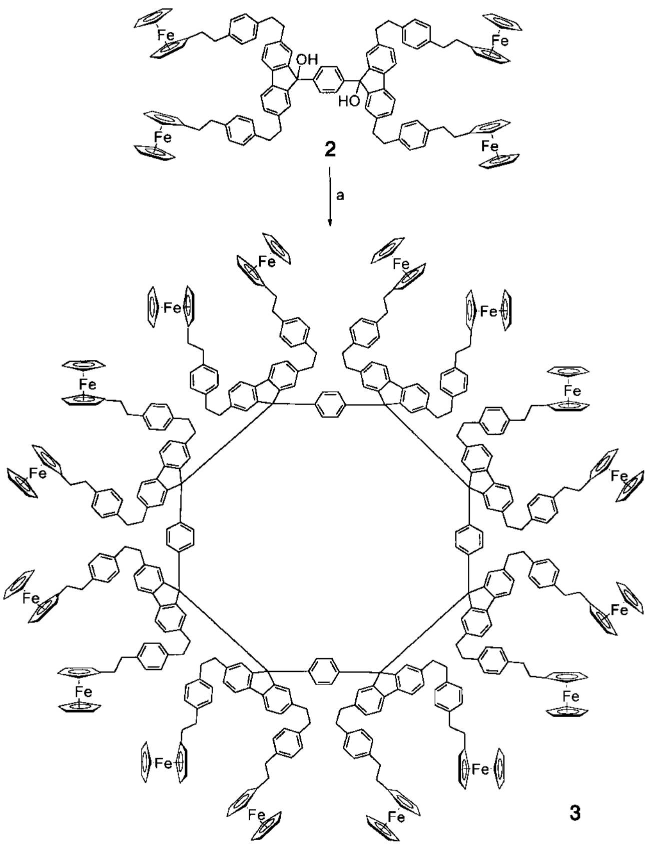
It was determined by cyclovoltammetry that all ferrocene units of **3** are reversibly oxidized at $E_{1/2} = 0.49$ V.[9] A redox splitting of consecutive electron transfer processes was not observed. The number of electrons transferred per molecule of **3** was determined by addition of $[(\eta^6\text{-}C_6H_6)_2Cr]$ in a ratio of 1:16 and comparison of the respective peak currents, which showed an approximate ratio of 1:1. The deviation in the peak currents is caused by the different diffusion coefficients of the two molecules, which result from the differences in size.

The principle of the synthesis of **3** was applied towards the preparation of **5**. In this case, the synthesis started from dichloride **4**, which afforded **5** in 63% yield upon reaction

---

[*] Prof. Dr. J. Ipaktschi, Dipl.-Chem. R. Hosseinzadeh,
Dipl.-Chem. P. Schlaf
Institut für Organische Chemie der Universität
Heinrich-Buff-Ring 58, D-35392 Giessen (Germany)
Fax: (+49) 641-99-34309
E-mail: junes.ipaktschi@org.chemie.uni-giessen.de

[**] This research was supported by the Fonds der Chemischen Industrie. We thank Mr. A. Lippek und Prof. C. Elschenbroich (Marburg) for recording the cyclovoltammogram, and Dr. R. Krüger (Bundesanstalt für Materialforschung und -prüfung, Berlin) as well as Dr. C. Urbanke (Medizinische Hochschule Hannover) for the determination of the molecular masses of **3** und **5**. R.H. thanks the Iranian Research Minister, Tehran, for a doctoral stipend.

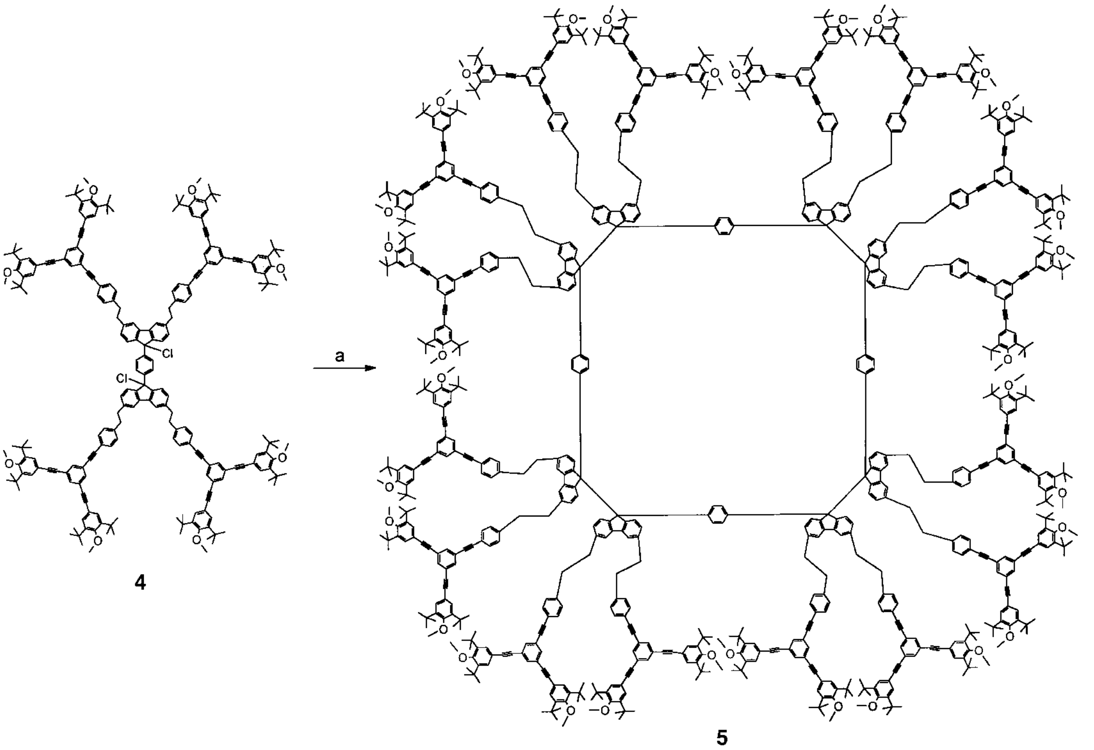


Scheme 1. a) 3.7 M $SnCl_2$/conc. HCl solution, THF, 4 h, reflux.

with $SnCl_2 \cdot 2H_2O$ (Schema 2). The molecular mass of 12642 Dalton was confirmed with matrix-supported laser desorption/ionization time of flight(MALDI-TOF) mass spectrometry. As in the previous example, the large substituents did not prevent or alter the desired tetramerization process. Owing to the substitution pattern at the fluorene ring, the intramolecular dynamics of the molecule leads to the observation of a time-averaged NMR spectrum for **5**, which, as a result, appears to have a molecular symmetry twice as high as the symmetry of **3**. Thus, two of the four protons of the inner phenyl ring appear as a broad singlet[8] at $\delta = 8.06$ in the ^1H NMR spectrum, and the signals for H2/H7 and H1/H8 of the fluorene units appear at $\delta = 6.52$ and 6.06.[10] Additional NMR spectroscopic indications for the seemingly higher symmetry of **5** in comparison to that of **3** are the number of signals for the protons of the *tert*-butyl groups ($\delta = 1.39$ and 1.37), the methoxy groups ($\delta = 3.65$ and 3.63), and the C9 atoms of the fluorene units ($\delta = 64.97$).

We assume that during the reduction of **2** or **4** with $SnCl_2$ the corresponding substituted quinodimethane derivative of type **1** is formed first. This derivative subsequently tetramerizes selectively to give **3** and **5**, respectively, in a stepwise process. We believe that these macrocycles are formed in very high yields because the newly formed, relatively weak C–C σ bonds are reversibly cleaved during the cyclization process.[11] This would mean that errors in the construction process can easily be reversed and corrected. In addition, steric factors that lead to the *gauche* arrangement of the fluorene units linked at the 9-position facilitate a ring closure to **3** and **5**.

Analogous to the parent system, **3** and **5** turn blue-violet upon heating above about 50 °C in a solvent such as cyclohexane (**3**: $\lambda_{max} = 582$ nm; **5**: $\lambda_{max} = 587$ nm). Upon cooling the solution becomes colorless. Under an inert atmosphere, this process can be repeated infinitely. The blue-violet color also appears upon grinding of these compounds.



Scheme 2. a) $SnCl_2 \cdot 2H_2O$, benzene, 30 min, RT.

The herein discussed principle of self-assembly of four basic units to form one large macrocyclic molecule can be used as a basis for the synthesis of novel macromolecules which also exhibit the characteristic to change their color reversibly upon mechanical impact.

Experimental Section

3: Diol **2** (150 mg, 88 μmol) was dissolved in degassed THF (20 mL) in a Schlenk tube. A $SnCl_2$/HCl solution (2 mL, 5.3 mmol) was added, and the resulting mixture was stirred under reflux for 4 h. After removal of the solvent, the residue was suspended in CH_2Cl_2 (5 mL) and purified by chromatography on silica gel with CH_2Cl_2/petroleum ether (1/2 – 1/1). A yellow powder (120 mg, 18 μmol, 82 %) was obtained; m.p. 150 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.70$ (br d, $J = 7.70$ Hz, 4 H), 8.26 (br d, $J = 7.70$ Hz, 4 H), 7.85 (br d and s, 8 H), 7.72 (s, 4 H), 7.48 – 6.55 (m, 84 H), 6.14 (s, 16 H), 5.93 (s, 4 H), 5.90 (s, 4 H), 4.12 – 3.80 (m, 64 H), 4.09 (s, 20 H), 4.07 (s, 20 H), 3.98 (s, 20 H), 3.97 (s, 20 H), 2.95 – 2.15 (m, 128 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.93 – 137.11$ (22 signals for C), 133.08 – 118.19 (22 signals for CH), 89.22 – 67.20 (13 signals for Cp), 65.45 (C), 65.24 (C), 38.56 – 31.21 (14 signals for CH_2); molecular mass calcd for $C_{448}H_{400}Fe_{16}$: 6677.7; found: 7200 ± 800 (analytical equilibrium – ultracentrifugation); elemental analysis calcd for $C_{448}H_{400}Fe_{16}$: C 80.58, H 6.04; found: C 80.28, H 6.00.

5: Dichloride **4** (161 mg, 50 μmol) was stirred for 30 min with $SnCl_2 \cdot 2H_2O$ (1 g)in degassed benzene (5 mL) under argon in a Schlenk tube at room temperature. After that, the mixture was allowed to stand for about 14 h. The solution was filtered through ALOX (basic) and the filtrate was evaporated. The residue was filtered through silica gel with CH_2Cl_2/*n*-pentane (1/1). A light orange solid (100 mg, 7.9 μmol, 63 %) was obtained; m.p. 180 °C (decomp.). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.06$ (br s, 8 H), 7.63 – 7.58 (m, 24 H), 7.56 (d, $J = 1.4$ Hz, 16 H), 7.51 (d, $J = 1.3$ Hz, 16 H), 7.46 – 7.30 (m, 112 H), 7.21 (br s, 8 H), 7.18 (d, $J = 8.1$ Hz, 16 H), 7.02 (d, $J = 8.2$ Hz, 16 H), 6.95 (d, $J = 7.6$ Hz, 8 H), 6.52 (d, $J = 7.5$ Hz, 8 H), 6.06 (d, $J = 7.5$ Hz, 8 H), 3.65 (s, 48 H), 3.63 (s, 48 H), 3.07 – 2.84 (m, 32 H), 2.83 – 2.64 (m, 32 H), 1.39 (s, 288 H), 1.37 (s, 288 H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 160.86 – 140.80$ (11 signals for C), 133.85 – 129.03 (6 signals for CH), 124.78 – 120.60 (5 signals for C), 119.32 (CH), 117.41 (C), 91.85 – 86.74 (8 signals for $C{\equiv}C$), 64.97 (C), 64.76 (OMe), 64.75 (OMe), 38.37 (CH_2), 37.95 (CH_2), 36.05 (C), 36.03 (C), 32.12 (Me); MS (MALDI-TOF): m/z: 12643.9; elemental analysis calcd for $C_{928}H_{976}O_{32} \cdot 3CH_2Cl_2$: C 86.71, H 7.67; found: C 86.69, H 8.10.

Received: November 27, 1998 [Z 12717]
German version: *Angew. Chem.* **1999**, *111*, 1765 – 1768

Keywords: dendrimers · ferrocene · macrocycles · quinodimethane · supramolecular chemistry

---

[1] Self-assembly and supramolecular chemistry: a) *Comprehensive Supramolecular Chemistry, Vol. 1 – 11* (Eds.: J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Pergamon, Oxford, **1996**; b) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; c) *Monographs in Supramolecular Chemistry, Vol. 1 – 6* (Eds.: J. F. Stoddart), RSC, Cambridge, **1989**, **1991**, **1994** – **1996**; d) P. Ball, *Designing the Molecular World*, Princeton University Press, **1994**; e) M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393 – 401; f) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242 – 1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154 – 1196; g) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, D. M. Gordon, *Acc. Chem. Res.* **1995**, *28*, 37 – 44; h) D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229 – 2260.

[2] Dendrimers: a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules: Concepts, Synthesis, Perspectives*, VCH, Weinheim, **1996**; b) A. Archut, F. Vögtle, *Chem. Soc. Rev.* **1998**, *27*, 233 – 240; c) F. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681 – 1712; d) H. Frey, K. Lorenz, C. Lach, *Chem. Unserer Zeit* **1996**, *30*, 75 – 85; e) J. Issberner, R. Moors, F. Vögtle, *Angew. Chem.* **1994**, *106*, 2507 – 2514; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 2413 – 2420; f) D. A. Tomalia, H. E. Durst, *Top. Curr. Chem.* **1993**, *165*, 193 – 314.

[3] J. Ipaktschi, R. Hosseinzadeh, P. Schlaf, E. Dreiseidler, R. Goddard, *Helv. Chim. Acta* **1998**, *81*, 1821 – 1834.

[4] G. Wittig, E. Dreher, W. Reuther, H. Weidinger, R. Steinmetz, *Liebigs Ann. Chem.* **1969**, *726*, 188 – 200.

[5] Macrocycles of type **3** and **5** contain 9,9′-diphenyl-9,9′-bi[9*H*-fluorene] as a partial structure. For the conformational analysis of bifluorenyls, see also a) G. A. Olah, L. D. Field, M. I. Watkins, R. Malhotra, *J. Org. Chem.* **1981**, *46*, 1761; b) S. Kajigaeshi, S. Fujisaki, I. Aizu, H. Hara, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3569; c) D. A. Dougherty, F. M. Llort, K. Mislow, J. F. Blount, *Tetrahedron* **1978**, *34*, 1301; d) W. D. Hounshell, D. A. Dougherty, J. P. Hummel, K. Mislow, *J. Am. Chem. Soc.* **1977**, *99*, 1916.

[6] P. Schlaf, unpublished results; R. Hosseinzadeh, unpublished results.

[7] The structures of two methyl- and ethyl-substituted derivatives of **3** and **5** were characterized by crystallography, and the NMR data of these compounds were analyzed.[3] Accordingly, these macrocycles have a conformation with S_4 symmetry. In the case of the unsubstituted derivatives as well as those substituted at positions 3 and 6 of the fluorene unit, a transition between two equivalent conformations with S_4 symmetrie is possible which leads to the observation of time-averaged NMR spectra. This information serves as the basis for assigning the structures of **3** and **5**.

[8] For derivatives which are substituted at positions 2 and 7 on the fluorene ring the inner phenyl protons show four broad doublets (*ortho* und *meta* coupling), whereas the fluorene protons show four groups each with one singlet and two doublets. In the ^{13}C NMR spectrum the eight C9 atoms of the fluorene unit show two signals at $\delta = 65 – 66$. For the 3,6-substituted derivatives the protons of the inner phenyl rings show two broad singlets (only *meta* coupling), whereas the protons of the fluorene unit form two groups of one singlet and two doublets each. The eight C9 atoms in the ^{13}C NMR spectrum give rise to one signal at $\delta \approx 65$. The characteristc signals of these compounds spread over the range of $\delta \approx 8.70 – 5.60$ in the ^{1}H NMR spectrum. The individual assignments of all signals is difficult as they are partially hidden by substituent absorptions or overlap which each other. Therefore, the low-field and high-field signals were used for the structure elucidation.

[9] Measured in THF/0.1 M nBu$_4$NClO$_4$ on a glassy carbon electrode against a saturated calomel electrode, 298 K, $v = 100$ mV s^{-1}.

[10] Of the six chemically different protons on each fluorene ring, two can be observed separately shifted towards high field.

[11] Dissociation energies of 9,9′-bifluorenyl derivatives: K. Rakus, S.-P. Verevkin, J. Schätzer, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1994**, *127*, 1095 – 1103; E. M. Arnett, S. Venimadhavan, *J. Am. Chem. Soc.* **1991**, *113*, 6967 – 6975.