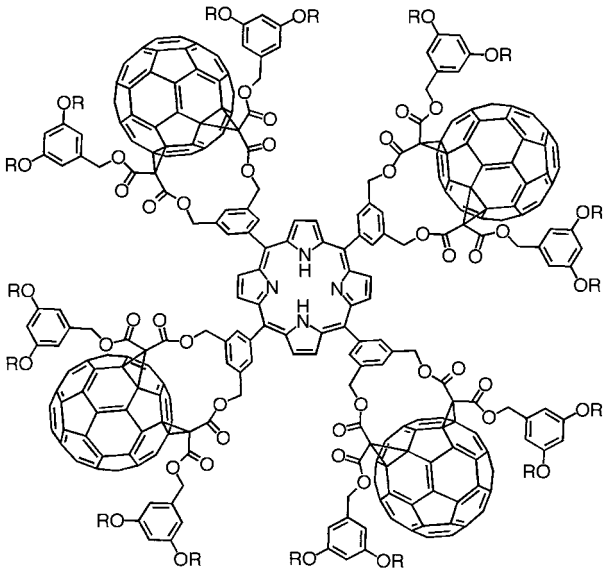
A Tetraphenylporphyrin with Four Fullerene Substituents**

Jean-François Nierengarten,* Corinne Schall, and Jean-François Nicoud

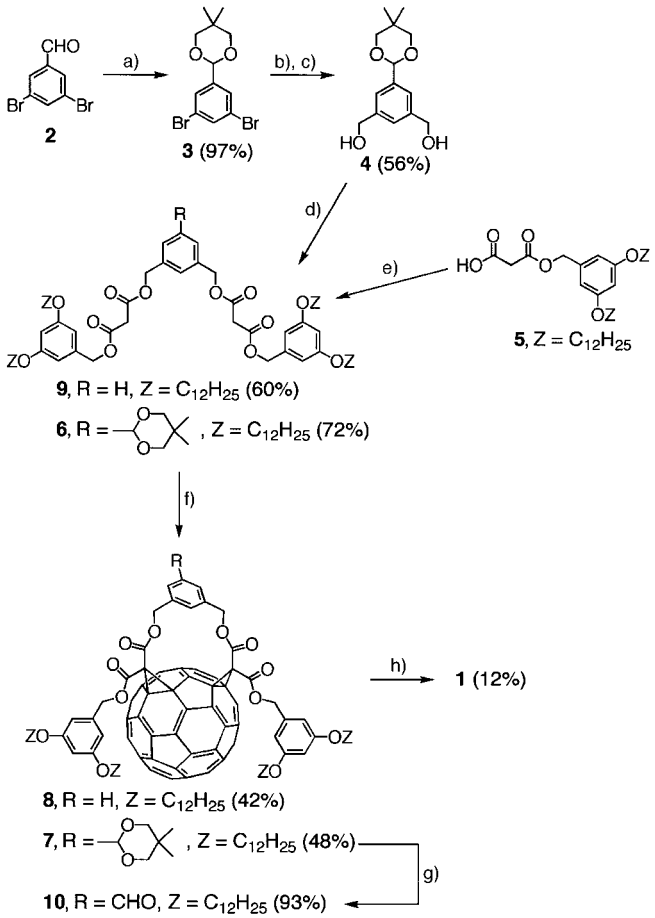
Dedicated to Dr. Arlette Solladié-Cavallo on the occasion of her 60th birthday

In light of their special electrochemical and electronic properties, C_{60} and porphyrins have proven to be interesting building blocks for the construction of new photochemical molecular devices.[1, 2] Recent progress in the chemistry of C_{60}[3] allows the preparation of many fullerene derivatives covalently bound to donor moieties.[1, 4] Gust and co-workers described the first preparation of a C_{60}-linked porphyrin,[5] and several other fullerene–porphyrin hybrids have since been reported.[6, 7] These systems provide entry into intramolecular processes such as electron transfer and energy transfer.[1, 4–7] The C_{60} group appears to be a particularly interesting electron acceptor in artificial photosynthetic models because of its symmetrical shape, its large size, and the properties of its π-electron system.[1] All the porphyrin–C_{60} dyads reported to date have been synthesized by reaction of a preconstructed porphyrin derivative with C_{60} itself[5, 6] or with a C_{60}–acid derivative,[7] and no porphyrin with more than one fullerene substituent has been described until now. We report here the preparation of the soluble tetraphenylporphyrin **1** with four fullerene substituents by reaction between a bis-adduct of C_{60} bearing an aldehyde functionality and pyrrole in the presence of an acid catalyst. Electrochemical investigations reveal a strong effect on the redox properties of the porphyrin moiety in **1** owing to the presence of the surrounding fullerene subunits.



1, R = $C_{12}H_{25}$

Porphyrin **1** was synthesized as depicted in Scheme 1. 3,5-Dibromobenzaldehyde (**2**) was prepared from 1,3,5-tribromobenzene according to the literature procedure[8] and allowed to react with 2,2-dimethyl-1,3-propanediol in refluxing benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) to give **3** (97% yield). Treatment of **3** with excess *t*BuLi[9] in THF followed by quenching with *N*,*N*-dimethylformamide (DMF) and subsequent reduction of the resulting dialdehyde with diisobutylaluminum hydride (DIBAL-H) produced diol **4** in an overall yield of 56%. Esterification of **4** with the mono-ester **5**[11] of malonic acid in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC)[10] yielded bis-malonate **6**. The functionalization of C_{60} was based on the highly regioselective Diederich reaction,[12] which led to macrocyclic bis-adducts of C_{60} through a



Scheme 1. Synthesis of porphyrin **1**. a) 2,2-Dimethyl-1,3-propanediol, C_6H_6, *p*-TsOH (cat.), △, Dean–Stark trap; b) *t*BuLi (4 equiv), THF, −78→0°C, then DMF, −78→0°C, then 2M HCl in H_2O; c) DIBAL-H, CH_2Cl_2, 0°C; d) **5**, DCC, DMAP, CH_2Cl_2, 0°C→RT; e) 3-hydroxymethylbenzyl alcohol, DCC, DMAP, CH_2Cl_2, 0°C→RT; f) C_{60}, DBU, I_2, toluene, RT; g) CF_3CO_2H, H_2O, CH_2Cl_2, RT; h) pyrrole, $BF_3 \cdot Et_2O$, $CHCl_3$ (containing 0.75% EtOH), RT, then *p*-chloranil, △.

[*] Dr. J.-F. Nierengarten, Dipl.-Ing. C. Schall, Prof. J.-F. Nicoud
Groupe des Matériaux Organiques
Institut de Physique et Chimie des Matériaux de Strasbourg
Université Louis Pasteur and CNRS
23, rue du Loess, F-67037 Strasbourg (France)
Fax: (+33) 3-8810-7246
E-mail: niereng@michelangelo.u-strasbg.fr

[**] This work was supported by the CNRS. We thank J.-D. Sauer for NMR measurements, Dr. J.-P. Collin for help with the electrochemical measurements, and Dr. N. Solladié for helpful discussions.

  1433-7851/98/3713-1934 $ 17.50+.50/0

macrocyclization reaction of the carbon sphere with bis-malonate derivatives in a double Bingel addition.[13] Treatment of C_{60} with **6**, iodine, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the C_s-symmetric *cis*-2 bis-adduct **7** in 48 % yield. Model compound **8** was prepared in a similar manner from 3-hydroxymethylbenzyl alcohol by esterification of **5** with DCC followed by treatment of the resulting bis-malonate **9** with C_{60} in toluene in the presence of DBU and iodine (25 % overall yield). Treatment of **7** with CF_3CO_2H in CH_2Cl_2/H_2O (1/1) afforded the orange-red glassy benzaldehyde **10** in 93 % yield. The preparation is thus easily carried out on a gram scale.

Preparation of porphyrin **1** was first attempted under the classical conditions reported by Lindsey and co-workers.[14] Reaction of benzaldehyde **10** with pyrrole in CH_2Cl_2 in the presence of CF_3CO_2H as catalyst followed by oxidation with *p*-chloranil (tetrachlorobenzoquinone) yielded mainly **10** and polymers; no trace of **1** could be detected in the reaction mixture. However, **1** could be obtained through use of the reaction conditions developed by Lindsey[15] for the synthesis of sterically hindered porphyrins such as tetramesitylporphyrin. A key feature of these conditions is BF_3–ethanol cocatalysis. The condensation of **10** with pyrrole was performed in commercial $CHCl_3$ (which contains 0.75 % ethanol as stabilizer) at room temperature in the presence of $BF_3 \cdot Et_2O$. After a reaction period of five hours *p*-chloranil was added to irreversibly convert the porphyrinogen into a porphyrin. The desired tetraphenylporphyrin **1** was subsequently isolated in 12 % yield after a tedious chromatographic separation. Characterization of **1** was complicated, because there proved to be a mixture of several conformers in slow equilibrium on the NMR time scale at room temperature; nevertheless, all the anticipated signals were present in the spectrum. Force-field calculations with the model compound **8** revealed that the fullerene sphere is located above the phenyl ring of the bridge. In tetraphenylporphyrin **1**, all the fullerene substituents can be situated on one side or the other of the phenyl rings of the bridge. Free rotation of the four phenyl substituents on the porphyrin is therefore necessary to produce an NMR spectrum with sharp, symmetric signals. A study of the temperature dependence of the NMR spectrum ($CDCl_2CDCl_2$, 400 MHz) demonstrated a perfectly reversible narrowing of all signals at 125 °C, but a sharp spectrum could not be obtained below the maximum measurement temperature. Nevertheless, this NMR study unambiguously documents the existence of a dynamic effect. The UV/Vis spectrum of **1** in CH_2Cl_2 (Figure 1) shows the characteristic porphyrin absorption bands. The Soret band (420 nm) and the four Q bands (513, 547, 587, and 644 nm) are clearly visible, as is the characteristic absorption profile of a fullerene *cis*-2 bis-adduct. Furthermore, the absorption coefficients are consistent with a fullerene-to-porphyrin ratio of 4:1.

The redox potential for the first oxidation of the porphyrin moiety in **1** (Table 1) is significantly more anodic ($\Delta E \approx$ 175 mV) than for *meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin[16] (H_2TBP). This observation could be related to the strong electron-withdrawing effect of the four fullerene substituents, which could substantially destabilize the first oxidized state of the porphyrin moiety. However, solvation

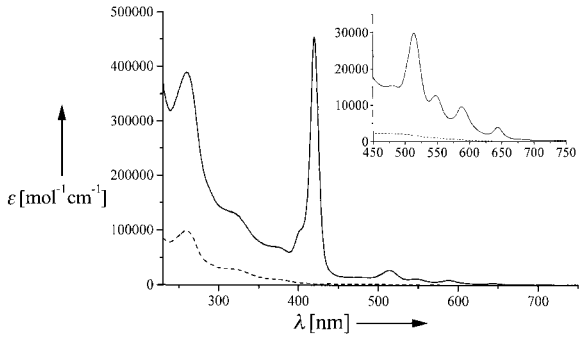


Figure 1. UV/Vis spectrum of **1** (——) and of **8** (– – –) in CH_2Cl_2.

Table 1. Electrochemical properties of **1**, **8**, and H_2TBP. Values for $(E_pa + E_pc)/2$ [V] (vs. SCE) and ΔE_pc [mV] (in parentheses) are given.[a]

Compound	Reduction E_1	E_2	E_3	E_4	Oxidation E_1
1	−0.55 (70)	−0.85 (100)[b]	−1.16 (85)[b]	−1.55 (80)[b]	+1.195 (80)
8	−0.55 (85)	−0.86 (100)[b]	−1.16 (110)[b]	−1.55 (110)[b]	
H_2TBP	−1.16 (85)	−1.50 (120)			+1.02 (90)

[a] Cyclic voltammetry measurements: platinum electrode, degassed CH_2Cl_2, 0.1 M Bu_4NBF_4, scan rate 0.1 $V s^{-1}$. [b] Irreversible process.

effects caused by the presence of the surrounding fullerene groups could also be the source of the observed shift in potential. This effect in the case of **1** can be related to recently reported results with a Cu^I-complexed rotaxane that bears two fullerene stoppers.[4c, 17] In this molecular assembly, the redox potential of the Cu^I/Cu^{II} couple is also significantly more anodic than for similar mononuclear complexes ($\Delta E =$ 200–300 mV). Although the redox properties of the porphyrin moiety in **1** are apparently influenced significantly by the C_{60} substituents, those of the fullerene subunits seem to remain unchanged by the porphyrin. Compounds **1** and **8** show effectively similar behavior, entirely consistent with previously reported data for fullerene *cis*-2 bis-adducts.[12c, 18] The third reduction, which occurs at approximately −1.16 V (relative to the standard calomel electrode, SCE), is characteristic of *cis*-2 bis-adducts. Indeed, it has been shown that the second electron transfer in the *cis*-2 derivatives is followed by a chemical reaction, which generates a species reducible at about −1.16 V.[12c, 18] The porphyrin and fullerene reduction waves for compound **1** could not be clearly distinguished because both constituents are reduced at similar potentials.

Preliminary luminescence measurements indicate that emission from the porphyrin part of **1** is completely quenched at room temperature by the surrounding fullerene subunits. The anodic shift observed by cyclic voltammetry for oxidation of the porphyrin moiety in **1** together with the absence of emission seems to indicate electronic interaction between the molecular components in the ground state as well as in the excited states.

Experimental Section

7: DBU (422 mg, 2.775 mmol) was added under Ar at room temperature to a stirred solution of C_{60} (400 mg, 0.555 mmol), I_2 (352 mg, 1.387 mmol), and **6** (745 mg, 0.555 mmol) in toluene (700 mL). The mixture was stirred for 12 h and then filtered through a short column of silica gel (toluene, then

CH_2Cl_2). Compound **7** was isolated by column chromatography (SiO_2; CH_2Cl_2/hexane, 8/3; 548 mg, 48%). Orange-red glassy product; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 259 (117170), 323 (28230), 375 (sh, 12110), 437 (sh, 4510), 467 nm (3760); IR ($CHCl_3$): $\tilde{\nu}$ = 2927 (s), 2855 (s), 1749 (s), 1598 (s), 1458 (m), 1394 (w), 1294 (m), 1281 (m), 1264 (s), 1235 (s), 1206 (m), 1170 (s), 1107 (s), 1062 cm^{-1} (w); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.84 (s, 3H), 0.89 (t, J = 6.5 Hz, 12H), 1.27 (m, 72H), 1.31 (s, 3H), 1.73 (m, 8H), 3.75 (AB, J = 11 Hz, 4H), 3.85 (t, J = 6.5 Hz, 8H), 5.09 (d, J = 13 Hz, 2H), 5.24 (d, J = 12 Hz, 2H), 5.33 (d, J = 12 Hz, 2H), 5.46 (s, 1H), 5.84 (d, J = 13 Hz, 2H), 6.36 (t, J = 2 Hz, 2H), 6.47 (d, J = 2 Hz, 4H), 7.42 (br s, 2H), 7.49 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.12, 21.82, 22.67, 23.06, 26.07, 29.22, 29.35, 29.41, 29.61, 30.21, 31.90, 49.00, 66.83, 67.17, 68.02, 68.60, 70.55, 77.62, 100.65, 101.57, 107.02, 123.45, 124.04, 134.39, 135.73, 136.08, 136.52, 136.78, 137.81, 139.07, 140.00, 141.00, 141.06, 142.27, 142.68, 143.10, 143.52, 143.68, 143.90, 144.09, 144.28, 144.51, 144.89, 144.95, 145.11, 145.28, 145.53, 145.70, 146.00, 147.25, 147.40, 148.58, 160.33, 162.52; elemental analysis calcd for $C_{142}H_{128}O_{14}$ (2059): C 82.8, H 6.3; found: C 82.9, H 6.3.

1: A 0.8 M solution of $BF_3 \cdot Et_2O$ in $CHCl_3$ (0.04 mL) was added under Ar at room temperature to a stirred solution of **10** (601 mg, 0.305 mmol) and pyrrole (20.4 mg, 0.305 mmol) in $CHCl_3$ that contained 0.75% EtOH (30.5 mL, reagents: 10^{-2} M each, BF_3: 10^{-3} M). After 5 h *p*-chloranil (100 mg, 0.407 mmol) was added, and the solution was heated under reflux for 1.5 h and then concentrated. Two successive filtrations through short silica gel columns (CH_2Cl_2/hexane, 5/3–5/2) followed by gel permeation chromatography (Biorads, Biobeads SX-*1*, toluene) yielded unchanged **10** (89 mg) and crude **1**. Two successive column chromatographic separations (Al_2O_3, hexane/CH_2Cl_2, 3/1–3/2) followed by precipitation from CH_2Cl_2/Et_2O led to pure **1** (74 mg, 12%). Red-brown glassy product; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 259 (390000), 319 (sh, 131400), 378 (sh, 67900), 403 (sh, 101150), 420 (454260), 479 (15500), 513 (29850), 547 (12750), 587 (9650), 644 nm (4030); IR ($CHCl_3$): $\tilde{\nu}$ = 2965 (s), 2854 (s), 1748 (s), 1597 (s), 1457 (s), 1376 (w), 1345 (w), 1294 (m), 1280 (m), 1235 (s), 1205 (s), 1189 (w), 1171 (s), 1112 (w), 1104 (w), 1060 cm^{-1} (m); ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = −2.78 (br s, 2H), 0.86 (t, J = 6.5 Hz, 48H), 1.26 (m, 288H), 1.66 (m, 32H), 3.82 (br t, 32H), 5.25–5.60 (m, 24H), 6.05–6.20 (m, 8H), 6.33 (br s, 8H), 6.48 (br s, 16H), 7.85–8.05 (m, 4H), 8.10–8.25 (m, 8H), 8.75–9.10 (m, 8H); elemental analysis calcd for $C_{564}H_{478}N_4O_{48}$ (8080): C 83.8, H 6.0, N 0.7; found: C 83.8, H 6.5, N 0.6.

Received: March 2, 1998 [Z11543IE]
German version: *Angew. Chem.* **1998**, *110*, 2037–2040

Keywords: electrochemistry · fullerenes · porphyrinoids

[1] Review of donor-linked fullerenes: H. Imahori, Y. Sakata, *Adv. Mat.* **1997**, *9*, 537–546.

[2] For recent examples of light-harvesting devices based on porphyrins, see a) A. Ozuka, N. Tanabe, R.-P. Zhang, K. Maruyama, *Chem. Lett.* **1993**, 1505–1508; b) S. Prathapan, T. E. Johnson, J. S. Lindsey, *J. Am. Chem. Soc.* **1993**, *115*, 7519–7520; c) R. W. Wagner, J. S. Lindsey, *ibid.* **1994**, *116*, 9759–9760; d) H. L. Anderson, S. J. Martin, D. D. C. Bradley, *Angew. Chem.* **1994**, *106*, 711–713; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 655–657; e) N. Solladié, J.-C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage, *ibid*. **1996**, *108*, 957—960 and **1996**, *35*, 906–909; f) D. B. Amabilino, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1996**, *118*, 3285–3286; g) C. A. Hunter, R. J. Shannon, *Chem. Commun.* **1996**, 1361–1362; h) A. K. Burrell, W. Campbell, D. L. Officer, *Tetrahedron Lett*. **1997**, *38*, 1249–1252; i) S. Kawabata, I. Yamazaki, Y. Nishimura, A. Osuka, *Perkin Trans. 2* **1997**, 479–484.

[3] a) A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, **1994**; b) F. Diederich, C. Thilgen, *Science* **1996**, *271*, 317–323.

[4] a) S. I. Khan, A. M. Oliver, M. N. Paddon-Row, Y. Rubin, *J. Am. Chem. Soc.* **1993**, *115*, 4919–4920; b) T. G. Linssen, K. Dürr, M. Hanack, A. Hirsch, *J. Chem. Soc. Chem. Commun.* **1995**, 103–104; c) F. Diederich, C. O. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, *ibid.* **1995**, 781–782; d) R. M. Williams, J. M. Zwier, J. W. Verhoeven, *J. Am. Chem. Soc*. **1995**, *117*, 4093–4099; e) M. Maggini, A. Donò, G. Scorrano, M. Prato, *J. Chem. Soc. Chem. Commun*. **1995**, 845–846; f) J. M. Lawson, A. M. Oliver, D. F. Rothenfluh, Y.-Z. An, G. A. Ellis, M. G. Ranasinghe, S. I. Khan, A. G. Franz, P. S. Ganapathi, M. J. Shephard, M. N. Paddon-Row, Y. Rubin, *J. Org. Chem.* **1996**, *61*, 5032–5054; g) D. Armspach, E. C. Constable, F. Diederich, C. E. Housecroft, J.-F. Nierengarten, *Chem. Commun.* **1996**, 2009–2010; h) K. Dürr, S. Fielder, T. Linssen, A. Hirsch, M. Hanack, *Chem. Ber.* **1997**, *130*, 1375–1378; i) D. M. Guldi, M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc*. **1997**, *119*, 974–980; j) P. R. Ashton, F. Diederich, M. Gómez-López, J.-F. Nierengarten, J. A. Preece, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **1997**, *109*, 1611–1614; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1448–1451.

[5] P. A. Liddell, J. P. Sumida, A. N. Macpherson, L. Noss, G. R. Seely, K. N. Clark, A. L. Moore, T. A. Moore, D. Gust, *Photochem. Photobiol*. **1994**, *60*, 537–541.

[6] a) H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada, Y. Sakata, *Chem. Lett*. **1995**, 265–266; b) T. Drovetskaya, C. A. Reed, P. Boyd, *Tetrahedron Lett*. **1995**, *36*, 7971–7974; c) H. Imahori, Y. Sakata, *Chem. Lett*. **1996**, 199–200; d) H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, Y. Sakata, *J. Am. Chem. Soc.* **1996**, *118*, 11771–11782; e) D. Kuciausskas, S. Lin, G. R. Seely, A. L. Moore, T. A. Moore, D. Gust, T. Drovetskaya, C. A. Reed, P. Boyd, *J. Phys. Chem.* **1996**, *100*, 15926–15932; f) M. G. Ranasinghe, A. M. Olivier, D. F. Rothenfluh, A. Salek, M. N. Paddon-Row, *Tetrahedron Lett.* **1996**, *37*, 4797–4800; g) H. Imahori, K. Yamada, M. Hasegawa, S. Taniguchi, T. Okada, Y. Sakata, *Angew. Chem*. **1997**, *109*, 2738–2739; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2626–2629.

[7] I. G. Safanov, P. S. Baran, D. I. Schuster, *Tetrahedron Lett.* **1997**, *38*, 8133–8136.

[8] L. S. Chen, G. J. Chen, C. Tamborski, *J. Organometal. Chem.* **1981**, *215*, 281–291.

[9] a) D. Seebach, H. Neumann, *Chem. Ber.* **1974**, *107*, 847–853; b) J.-C. Chambron, C. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, N. Solladié, A.-M. Albrecht-Gary, M. Meyer, *New J. Chem*. **1995**, *19*, 409–426; c) R. F. Carina, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc*. **1996**, *118*, 9110–9116.

[10] M. Bodansky, *Principles of Peptide Synthesis*, 2nd ed., Springer, Berlin, **1993**.

[11] J.-F. Nierengarten, J.-F. Nicoud, *Tetrahedron Lett.* **1997**, *38*, 7737–7740.

[12] a) J.-F. Nierengarten, V. Gramlich, F. Cardullo, F. Diederich, *Angew. Chem.* **1996**, *108*, 2242–2244; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2101–2103; b) J.-F. Nierengarten, A. Herrmann, R. R. Tykwinski, M. Rüttimann, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 293–316; c) J.-F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J.-P. Gisselbrecht, C. Boudon, M. Gross, *ibid.* **1997**, *80*, 2238–2276.

[13] C. Bingel, *Chem. Ber.* **1993**, *126*, 1957–1959.

[14] a) J. S. Lindsey, H. C. Hsu, I. C. Schreiman, *Tetrahedron Lett*. **1986**, *27*, 4969–4970; b) J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, A. M. Marguerettaz, *J. Org. Chem.* **1987**, *52*, 827–836.

[15] a) R. W. Wagner, D. S. Lawrence, J. S. Lindsey, *Tetrahedron Lett.* **1987**, *28*, 3069–3070; b) J. S. Lindsey, R. W. Wagner, *J. Org. Chem*. **1989**, *54*, 828–836.

[16] S. Chardon-Noblat, J.-P. Sauvage, P. Mathis, *Angew. Chem*. **1989**, *101*, 631–633; *Angew. Chem. Int. Ed. Engl*. **1989**, *28*, 593–595.

[17] N. Armaroli, F. Diederich, C. O. Dietrich-Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten, J.-P. Sauvage, *Chem. Eur. J.* **1998**, *4*, 406–416.

[18] F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343–371.

  1433-7851/98/3713-1936 $ 17.50+.50/0