Monatshefte für Chemie 130, 1365–1371 (1999)

Monatshefte für Chemie
Chemical Monthly

Synthesis of a Difullerenopyrrole[a]

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Summary. The synthesis and spectroscopic characterization of a difullerenopyrrole is described. The synthesis starts from the easily accessible 2,3,6,7-tetramethylanthracene, and its final step involves treatment of the pyrrole derivative 2,3,6,7-*tetrakis*(bromomethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene with iodide in the presence of excess [60]-fullerene. The difullerenopyrrole is directly assembled in this key step and is thought to arise from the *in situ* generation of an *o*-quinodimethane intermediate followed by a regiocontrolled cycloaddition at one of the thirty (6,6)-bonds of [60]-fullerene. This symmetric difullerenopyrrole represents a versatile building block for a variety of pyrrolic molecules, such as fullerenoporphyrins.

Keywords. [60]-Fullerene; Pyrrole; Difullerenopyrrole; *Diels-Alder* reaction; Cycloaddition reaction.

Synthese eines Difullerenopyrrols

Zusammenfassung. Die Herstellung und die spektroskopische Charakterisierung eines Difullerenopyrrols wird beschrieben. Die hier entwickelte Reaktionssequenz geht vom leicht zugänglichen 2,3,6,7-Tetramethylanthracen aus, und ihr letzter Schritt ist eine iodidinduzierte Reaktion des Pyrrolderivates 2,3,6,7-*Tetrakis*(bromomethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracen in der Gegenwart eines Überschusses an [60]-Fulleren. In dieser Schlüsselstufe wird das Difullerenopyrrol direkt aufgebaut, wobei es über eine regiokontrollierte Addition der hypothetischen *o*-Chinodimethanzwischenstufe an eine der dreißig (6,6)-Doppelbindungen von C_{60} entstehen dürfte. Das symmetrische Difullerenopyrrol stellt einen vielversprechenden Synthesebaustein für verschiedene pyrrolische Moleküle dar, wie zum Beispiel für Fullerenoporphyrine.

Introduction

Since the discovery of C_{60} ([60]-fullerene, **1**) [1] and other fullerenes [2] and the development of an efficient synthetic access to **1** [3], studies on the chemistry of this carbon molecule have attracted considerable interest [4–8]. A variety of procedures for exohedral functionalization of fullerenes with organic groups are now available, most notably by cycloaddition reactions [4–8]. The polyunsaturated carbon molecule C_{60} is characteristically electron deficient [9], and [4+2]-cycloaddition reactions of the dienophilic fullerenes with a variety of 1,3-dienes and functionally related compounds have been used with great success to prepare

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[a] Dedicated to Professor *Karl Schlögl* on the occasion of his 75th birthday

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mono- and multi-substituted fullerenes [10–15]. [4+2]-Cycloadditions have been found to occur without exception at one of the thirty symmetry equivalent fullerene-(6,6)-bonds in these reactions [4, 5].

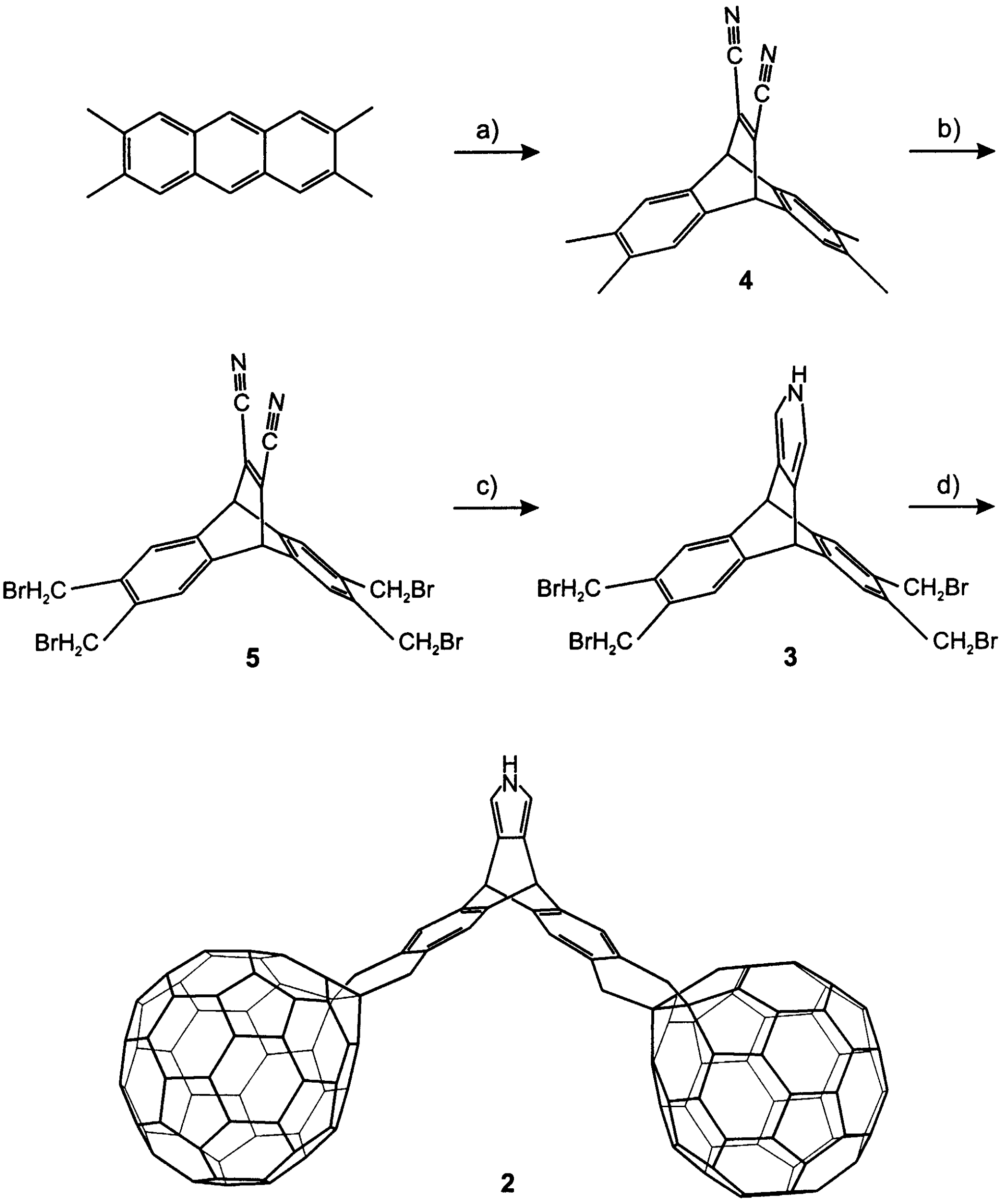
The polyunsaturated carbon molecule C_{60} is able to undergo up to six reversible one-electron reductions [16, 17], and solid alkali metal fullerides appear to provide access to unique organic conductors [9]. The covalent incorporation of fullerenes into functionalized electroactive compounds seems therefore particularly attractive. A variety of fullerene-containing compounds with interesting electronic and photochemical properties have become available, for example, by covalent attachment of **1** to porphyrins [18–27], quinones [28], transition metal centers [29], and *DNA* [30, 31] as well as by the incorporation of **1** into a covalent porphyrin-carotene-fullerene triad [32]. These diads and triads of C_{60} with covalently linked electro- and photoactive groups have been prepared mainly to serve as model compounds for the investigation of light-induced electron-transfer processes [18–27, 30–32].

We have previously described the synthesis of biconcave porphyrins with a three-dimensionally structured framework [33, 34]. The building blocks used for the preparation of these porphyrins were 9,10-dihydro-9,10-[3,4]epipyrroloanthracenes which are rigidly structured β,β'-disubstituted pyrroles [33]. These pyrroles are readily available by the cycloaddition of anthracenes and acetylenedicarbonitrile [35] and subsequent reduction of the resultant dinitrile with di-*iso*-butylaluminum hydride (*DIBAH*) [33]. In line with these studies, the synthesis of symmetric covalent fullerene adducts of pyrroles with rigid frameworks appeared attractive. Here we report the synthesis of the difullerenopyrrole **2**. The β,β'-disubstituted pyrrole **2** carries two fullerene units and is built up from a rigid core (a "triptyrrole" unit) that is structurally analogous to triptycenes.

Results and Discussion

The first reports on the preparation of stable and well characterized *Diels-Alder* adducts of C_{60} by the use of *o*-quinodimethane derivatives as the diene component were published in 1993 by *Müllen* and coworkers [36] and by others [11, 37]. *o*-Quinodimethane intermediates could be conveniently prepared *in situ* from 1,2-*bis*(bromomethyl)benzenes by iodide induced 1,4-elimination with potassium iodide and [18]crown-6 in boiling toluene [36]. By analogy, the *tetrakis*(bromomethyl)pyrrole **3** seemed to be the suitable precursor for the difullerenopyrrole **2**. By sequential [4+2]-cycloaddition reactions of *o*-quinodimethane intermediates from **3** with two [60]-fullerenes, the difullerenopyrrole **2** would be accessible.

Bromination of the dinitrile **4** [33] with N-bromosuccinimide (*NBS*) in carbon tetrachloride at 60°C under irradiation from a 100 W tungsten lamp gave the tetrabromide **5** in 40% yield (Scheme 1). Byproducts due to insufficient and further bromination were also obtained. Reduction of **5** with di-*iso*-butylaluminum hydride in dichloromethane at −20°C gave the potential diene precursor *tetrakis*(bromomethyl)pyrrole **3** in 22% yield. Initial attempts to produce the difullerenopyrrole **2** using the conditions of *Belik et al.* [36] were unsuccessful. The low solubility of C_{60} in toluene (2.9 mg/cm^3 [38]) was presumably a major problem with these conditions. Higher concentrations and an excess of C_{60} were apparently desirable



Scheme 1. a) Acetylenedicarbonitrile, C_6H_6, reflux, 15 h; b) N-bromosuccinimide, CCl_4, 60°C, 2 h; c) di-*iso*-butylaluminum hydride, CH_2Cl_2, −20°C, 2 h; d) C_{60}, $Bu_4N^+I^-$, 1,2-dichlorobenzene, 100°C, 4 h

to rapidly trap the presumed *o*-quinodimethane intermediates and to avoid the formation of higher fullerene adducts. Indeed, better results were obtained with tetrabutylammonium iodide in 1,2-dichlorobenzene (in which 24.6 mg/cm^3 of C_{60} can be dissolved at ambient temperature [38]) at 100°C. Under these conditions the difullerenopyrrole **2** was obtained as a dark brown solid in 27% yield.

The constitution of the symmetrically structured fullerenopyrrole **2** was confirmed on the basis of its spectroscopic data. The UV/Vis spectrum of a solution

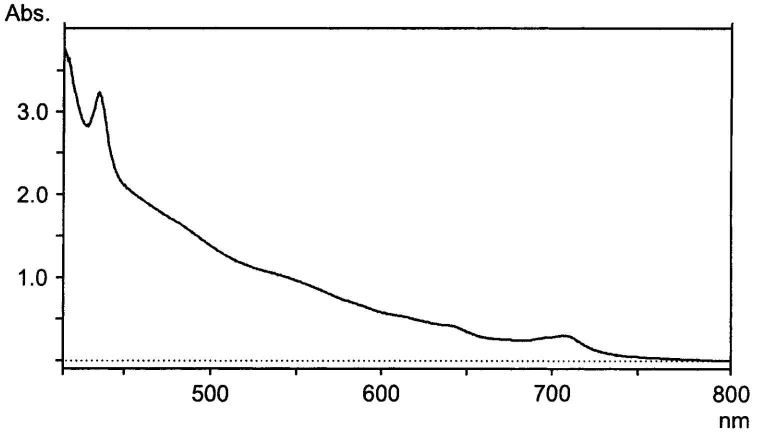


Fig. 1. UV/Vis spectrum of difullerenopyrrole **2** (0.365 m*M*) in 1,2-dichlorobenzene

of **2** in 1,2-dichlorobenzene shows the characteristics of a C_{60}-monoadduct, with maxima at 707 nm and at 435 nm [11, 12] (Fig. 1).

The three higher field resonances in the ^{13}C NMR spectrum of **2** at 45.4, 47.6, and 65.9 ppm were assigned as the benzylic carbons, the bridgehead carbons, and the tetracoordinate fullerene carbons, respectively, with the aid of a ^{1}H,^{13}C-HSQC spectrum. Of the 21 resonances observed at lower field in the ^{13}C NMR spectrum, 16 are due to 116 unsaturated carbons in the fullerene moieties. This is consistent with the fullerene moieties having C_{2v} symmetry which would be expected from a single addition to a (6,6)-bond of C_{60}. The constitution of **2** was also confirmed by a mass spectrum (FAB) which showed a weak signal for the molecular ion ($M^{+}+1$) at $m/z = 1736.1$ and a fragment at $m/z = 720$ due to the fullerene moieties.

An interesting feature of the ^{1}H NMR spectrum of **2** is the presence of two broad signals for the protons of the symmetry equivalent methylene groups. The observation of diastereotopicity of geminal methylene hydrogens in the spectrum of **2** suggests slow conformational inversion of the cyclohexane-like rings on the NMR time scale [39, 40].

The directed synthesis of several fullerene-derivatives with two, three, and more fullerene moieties per molecule has been reported [26, 36, 41–43]. Most of these apolar difullerenocompounds have been reported to have low solubility in a variety of common solvents [26, 41, 42]. The diffullerenopyrrole **2** has turned out to be sufficiently soluble for full spectroscopic characterization and has a solubility of about 2 mg/cm^3 in 1,2-dichlorobenzene.

In conclusion, we have developed a synthetic route to the pyrrole **2**, a first example for a difullerenopyrrole. This new compound appears to represent a useful and synthetically versatile building block for the preparation of further pyrrolic fullerene containing molecules.

Experimental

General remarks

Hexane, carbon tetrachloride, carbon disulfide, toluene: all Fluka *puriss p.a.*; 1,2-dichlorobenzene; Fluka *purum*; dichloromethane and petrol ether for column chromatography: Fluka *purum*;

N-bromosuccinimide (*NBS*): Fluka *purum*; di-*iso*-butylaluminiumhydride (*DIBAH*, 1 *M*, in hexane): Fluka *purum*; fullerene C_{60} (**1**): Hoechst Lab-Grade, purified according to Ref. [44]; tetrabutylammonium iodide: Aldrich; TLC: Polygram SIL G/UV254 from Macherey-Nagel; column chromatography: Silica gel 60 (0.040–0.063 mm) from Merck.

NMR spectra: Varian Unity 500 or Bruker AM 300 spectrometers, chemical shifts (δ, ppm relative to *TMS* with $\delta(\mathrm{C}\mathit{H}\mathrm{Cl}_3) = 7.24$ ppm, $\delta(\mathit{C}\mathrm{DCl}_3)$ 77.0 ppm, $\delta(\mathrm{C}_6\mathrm{D}_5\mathit{H}) = 7.15$ pm, $\delta(\mathit{C}_6\mathrm{D}_6) = 128$ ppm); in the ^{13}C spectra, s, d, t, and q specify singlet, doublet, triplet, and quadruplet multiplicity from coupling with directly bound protons. UV/Vis spectra: Hitachi U 3000, λ_{max} (nm logε). IR: Mattson FTIR 3000 instrument, ν(cm^{-1}). MS: Finnigan MAT-95; positive-ion-FAB (Cs^+ bomdardment at 20 keV, 2 μA), matrix 3-nitrobenzyl alcohol; EI pos: 70 eV; *m/z* (%).

All reactions were carried out in oven-dried glassware under a dry argon atmosphere. Reactions with C_{60} were performed with protection from light.

2,3,6,7-Tetrakis(bromomethyl)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarbonitrile (**5**; $C_{22}H_{14}Br_4N_2$)

9,10-Dihydro-2,3,6,7-tetramethyl-9,10-ethenoanthracene-11,12-dicarbonitrile (**4**) [33] (500 mg, 1.6 mmol) was dissolved in 200 cm^3 of CCl_4 at 60°C. *NBS* (1.18 g, 6.6 mmol) was added, and the resulting suspension was stirred for 2 h with irradiation (100 W tungsten lamp). The reaction mixture was diluted with 100 cm^3 CH_2Cl_2 and washed with water. After drying over $MgSO_4$ the organic solvent was distilled off and the crude product purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 1:1). Recrystallization from acetonitrile gave 400 mg of **5** as colourless crystals (40% yield).

Decomp.: >270°C ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.42$ (s, 4H), 5.37 (s, 2H), 4.55 (s, 8H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 141.3$ (s), 136.2 (s), 135.6 (s), 127.0 (d), 113.1 (CN), 52.9 (d), 28.7 (t) ppm; IR (KBr): $\nu = 2220$ (CN) cm^{-1}; MS (EI): *m/z* (%) = 629.6 (2), 628.6 (3), 627.6 (7), 626.6 (8), 625.5 (15), 624.6 (12), 623.6 (9), 622.6 (7), 621.6 (2, M^+), 620.6 (1.4), 549.8 (7), 548.8 (33), 547.8 (30), 546.8 (99), 545.8 (30), 544.8 (100), 543.8 (9), 542.8 (30, $(M\text{-}Br)^+$), 468.8 (21), 467.9 (15), 466.9 (42), 465.8 (20), 464.8 (27), 463.8 (6, $(M\text{-}2Br)^+$), 388.0 (6), 387.0 (24), 386.0 (6), 385.0 (16, $(M\text{-}3Br)^+$), 307.1 (20), 306.1 (26, $(M\text{-}4Br)^+$), 305.1 (24).

2,3,6,7-Tetrakis(bromomethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene (**3**; $C_{22}H_{17}Br_4N$)

A solution of *DIBAH* in hexane (1 *M*, 4.8 cm^3) was placed in a three-necked flask with an efficient mechanical stirrer under argon at −20°C. A solution of the dinitrile **5** (500 mg, 0.80 mmol) in 30 cm^3 of CH_2Cl_2 was added slowly such as to maintain the temperature below −15°C. The resultant yellow solution was stirred for further 2 h at −20°C. The reaction mixture was diluted with 30 cm^3 CH_2Cl_2, and 30 cm^3 of a 0.5 *M* aqueous solution of citric acid were added carefully at 0°C. The organic phase was separated, washed with brine, and dried over $MgSO_4$. Evaporation of the solvent and column chromatography (silica gel, CH_2Cl_2) gave the crude pyrrole which was crystallized from dichloromethane/hexane (yield: 108 mg of **3**, white solid, 22%).

Decomp.: >275°C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.28$ (s, 4H), 6.58 (d, 2H, $J = 2.3$ Hz), 5.26 (s, 2H), 4.55 (s, 8H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 147.7$ (s), 133.3 (s), 129.3 (s), 126.1 (d), 110.2 (d,α-pyrrole), 46.4 (d), 30.2 (t) ppm; IR (KBr): $\nu = 3439$ cm^{-1}; MS (FAB, NOBA): *m/z* (%) = 618.4 (38), 617.4 (45), 616.4 (85), 615.4 (63), 614.5 (100), 613.5 (44), 612.5 (54), 611.5 (14, $M^+ + 1$), 536.9 (91), 534.9 (87, $(M\text{-}Br)^+$).

1,2,3,4,6,8,9,10,11,13-Decahydrodi(1,2-dihydrofullereno)-[1,2-b;1′,2′-m]-6,13-[3,4]epipyrrolopentacene (**2**; $C_{142}H_{17}N$)

A mixture of the pyrrole **3** (20 mg, 0.0325 mmol), C_{60} (80 mg, 0.11 mmol), and tetrabutylammonium iodide (240 mg) in 1,2-dichlorobenzene (6 cm^3) was heated in a sealed glass tube for 4 h at 100°C (argon atmosphere). After cooling, the volume of the dark brown solution was reduced by distillation under vacuum to about 0.5 cm^3. The crude product was diluted with 10 cm^3 of CS_2, absorbed on silica gel, and chromatographed (toluene/hexane 1:1 for eluation of **1**, then toluene for eluation of **2**). The toluene solution of **2** was treated with hexane, and the precipitate filtered and dried under vacuum (15 mg of **2**, dark brown powder, 27%).

^{1}H NMR ($CS_2/C_6D_6 = 5:1$, 500 MHz): $\delta = 7.47$ (s, 4H), 6.42 (dd, 2H, $J_{1,2} = 2.5$ Hz), 5.36 (d, 2H, $J = 2.5$ Hz), 4.59 (s, broad, 4H), 4.24 (s, broad, 4H) ppm; ^{13}C NMR ($CS_2/C_6D_6 = 5:1$, 125 MHz): $\delta = 156.9$ (s), 147.9 (s), 146.7 (s), 146.5 (s), 146.1 (s), 145.8 (s), 145.7 (s), 145.5 (s), 144.9 (s), 142.8 (s), 142.4 (s), 142.3 (s), 141.9 (s), 140.4 (s), 136.9 (s), 135.6 (s), 134.4 (s), 128.7 (s), 126.9 (s), 123.5 (d), 110.4 (d, α-pyrrole), 65.9 (s, tetracoordinate fullerene carbons), 47.6(d), 45.4(t) ppm; MS (FAB, NOBA): m/z (%) = 1740.1 (0.6), 1739.2 (1.2), 1738.2 (2.5), 1737.2 (2.7), 1736.1 (2.6, $M^+ + 1$), 1735.1 (0.95), 720.0 (100, C_{60}); UV/Vis (1,2-dichlorobenzene): $\lambda_{max}(\log \varepsilon) = 707$ (2.91), 640.5 (sh, 3.04), 435 (3.94).

Acknowledgements

The authors thank Prof. *Robert Konrat* for recording the NMR spectra and Prof. *Karl-Hans Ongania* for the mass spectra. We are grateful to Dr. *Ludwig Call* and Dr. *Reinhold Schwenninger* for helpful discussions. This work was supported financially by the *Jubiläumsfonds der Oesterreichischen Nationalbank* (project number 5969).

References

[1] Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE (1985) Nature **318**: 162
[2] Diederich F, Whetten RL (1992) Acc Chem Res **25**: 119
[3] Krätschmer W, Lamb LD, Fostiropoulos K, Huffman DR (1990) Nature **347**: 354
[4] Hirsch A (1994) The Chemistry of the Fullerenes. Thieme, Stuttgart
[5] Hirsch A (1998) Fullerenes and Related Structures. In: Top Curr Chem, vol 199. Springer, Berlin, p 1
[6] Diederich F, Thilgen C (1996) Science **271**: 317
[7] Wudl F (1992) Acc Chem Res **25**: 157
[8] Prato M, Maggini M (1998) Acc Chem Res **31**: 519
[9] Haddon RC (1992) Acc Chem Res **25**: 127
[10] Isaacs L, Haldimann RF, Diederich (1994) Angew Chem **106**: 2434; Angew Chem Int Ed Engl **33**: 2339
[11] Rubin Y, Khan S, Freedberg DI, Yeretzian C (1993) J Am Chem Soc **115**: 344
[12] Tsuda M, Ishida T, Nogami T, Kurono S, Ohashi M (1993) J Chem Soc Chem Commun 1296
[13] Kräutler B, Puchberger M (1993) Helv Chim Acta **76**: 1626
[14] Kräutler B, Maynollo J (1995) Angew Chem **107**: 69; Angew Chem Int Ed Engl **34**: 87
[15] Kräutler B, Müller T, Maynollo J, Gruber K, Oshsenbein P, Schwarzenbach D, Bürgi H-B (1996) Angew Chem **108**: 1294; Angew Chem Int Ed Engl **35**: 1204
[16] Chlistunoff J, Cliffel D, Bard AJ (1998) Electrochemistry of Fullerenes. In: Handbook of Organic Conductive Molecules and Polymers, vol 1. Wiley, New York, p 334
[17] Echegoyen L, Echegoyen LE (1998) Acc Chem Res **31**: 593
[18] Liddell PA, Sumida JP, Macpherson AN, Noss L, Seely GR, Clark KN, Moore AL, Moore TA, Gust D (1994) Photochem Photobiol **60**: 537
[19] Imahori H, Hagiwara K, Akiyama T, Taniguchi S, Okada T, Sakata Y (1995) Chem Lett 265
[20] Drovetskaya T, Reed CA (1995) Tetrahedron Lett **36**: 7971
[21] Baran PS, Monaco RR, Khan AU, Schuster DI, Stephen RW (1997) J Am Chem Soc **119**: 8363
[22] Dietel E, Hirsch A, Zhou J, Rieker A (1998) J Chem Soc Perkin Trans 2, 1357

[23] Tomé AC, Enes RF, Tomé JPC, Rocha J, Neves MGPMS, Cavaleiro JAS, Elguero J (1998) Tetrahedron **54**: 11141

[24] Maruyama H, Fujiwara M, Tanaka K (1998) Chem Lett 805

[25] Bourgeois JP, Diederich F, Echgoyen L, Nierengarten JF (1998) Helv Chim Acta **81**: 1835

[26] Nierengarten JF, Schall C, Nicoud JF (1998) Angew Chem **110**: 2037; Angew Chem **37**: 1934

[27] Ranasinghe MG, Oliver AM, Rothenfluh DF, Salek A, Paddon-Row MN (1996) Tetrahedron Lett **37**: 4797

[28] Iyoda M, Sultana F, Sasaki S, Yoshida M (1994) J Chem Soc Chem Commun 1929

[29] Balch AL, Olmstead MM (1998) Chem Rev **98**: 2135

[30] Boutorine AS, Tokuyama H, Takasugi M, Isobe H, Nakamura E, Hèlène C (1994) Angew Chem **106**: 2526; Angew Chem Int Ed Engl **33**: 2462

[31] Cassell AM, Scrivens WA, Tour AM (1998) Angew Chem **110**: 1670; Angew Chem Int Ed Engl **37**: 1528

[32] Liddell PA, Kuciauskas D, Sumida JP, Nash B, Ngyen D, Moore AL, Moore T, Gust D (1997) J Am Chem Soc **119**: 1400

[33] Ramondenc Y, Schwenninger R, Phan T, Gruber K, Kratky C, Kräutler B (1994) Angew Chem **106**: 939; Angew Chem Int Ed Engl **33**: 889

[34] Schlögl J, Kräutler B (1999) Synlett **S1**: 969

[35] Hinshaw JC (1972) Org Prep and Proc Int **4**: 211 (and references therein)

[36] Belik P, Gügel A, Spickermann J, Müllen K (1993) Angew Chem **105**: 95; Angew Chem Int Ed Engl **32**: 78

[37] Tago T, Minowa T, Okada Y, Nishimura J (1993) Tetrahedron Lett **43**: 8464

[38] Scrivens WA, Tour JM (1993) J Chem Soc Chem Commun 1207

[39] An YZ, Anderson JL, Rubin Y (1993) J Org Chem **58**: 4799

[40] Kräutler B, Maynollo J (1996) Tetrahedron **52**: 5033

[41] Paquette LA, Graham RJ (1995) J Org Chem **60**: 2958

[42] Lebedkin S, Ballenweg S, Gross J, Taylor R, Krätschmer W (1995) Tetrahedron Lett **36**: 4971

[43] Diederich F (1997) Pure Appl Chem **69**: 395

[44] Isaacs L, Wehrsig A, Diederich F (1993) Helv Chim Acta **76**: 1231

Received May 3, 1999. Accepted May 12, 1999