[10] Crystal data for **1** and **2** (conventional/IAM refinement): The data were collected from shock-cooled crystals for **1** on an ENRAF-NONIUS CAD4 diffractometer and for **2** on an BRUKER APEX diffractometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) equipped with a low-temperature device at 193(2) K (**1**) and 100(2) K (**2**).[20] The structures were solved by direct methods (SHELXS-97)[20] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[22] R values defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2,0) + 2F_c^2]$. **1**: $C_{37}H_{80}Li_2N_6O_3S_2$, $M_r = 735.07$, monoclinic, space group $P2_1/c$, $a = 16.143(8)$, $b = 14.5340(18)$, $c = 19.429(8)$ Å, $\beta = 92.779(18)$, $V = 4553(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.072$ Mg m^{-3}, $\mu = 0.155$ mm^{-1}, $F(000) = 1624$, 10144 reflections measured, 5527 unique, $R(int) = 0.0660$, $wR2$ (all data) $= 0.1768$, $R1(I > 2\sigma(I)) = 0.0639$, $g_1 = 0.0695$, $g_2 = 9.0558$ for 602 parameters and 566 restraints. **2**: $C_{25}H_{58}N_6S_2$, $M_r = 506.89$, monoclinic, space group $C2/c$, $a = 29.8239(8)$, $b = 11.4206(3)$, $c = 18.0801(4)$ Å, $\beta = 91.041(1)$, $V = 6157.2(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.094$ Mg m^{-3}, $\mu = 0.196$ mm^{-1}, $F(000) = 2256$, 136761 reflections measured (low-angle batch, $\sin\theta/\lambda < 0.625$ Å^{-1}), 6629 unique, $R(int) = 0.0435$, 217620 reflections measured (high-angle batch, 0.625 Å$^{-1} < \sin\theta/\lambda < 1.111$ Å^{-1}), 29791 unique, $R(int) = 0.0646$, $wR2$(all data) $= 0.0932$, $R1(I > 2\sigma(I)) = 0.0315$, $g_1 = 0.0538$, $g_2 = 0.0$ for 475 parameters. All hydrogen atoms in **2** were located by difference Fourier synthesis and refined without any distance restraints. The isotropic thermal parameters of the hydrogen atoms H1 and H4 were refined independently. All other hydrogen atoms of the molecule were refined using a riding model ($U_{iso} = 1.2\,U_{eq}$ (C) for H71 and H72 and $U_{iso} = 1.5\,U_{eq}$ (C) for all other hydrogen atoms). CCDC-171900 (**1**) and CCDC-171901 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

[11] N. K. Hansen, P. Coppens, *Acta Crystallogr. Sect. A* **1978**, *34*, 909.

[12] T. Koritsanszky, S. Howard, T. Richter, Z. W. Su, P. R. Mallinson, N. K. Hansen, *XD—A Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data*, Freie Universität Berlin, **1995**

[13] Multipole refinement of **2**: data integration was performed with SAINT-NT,[23] empirical absorption correction based on Blessing's algorithm[24] with MULABS implemented in PLATON:[25] $R(int) = 0.0435$ (low-angle batch), $R(int) = 0.0646$ (high-angle batch), structure solution with SHELXS,[21] high-order refinement with SHELXL-97;[22] $wR1 = 0.0147$, $wR2 = 0.0280$, GoF = 1.3015, after multipole refinement. In the refinement both S(NH*t*Bu)(N*t*Bu)$_2$ moieties at the methylene bridge shared the same multipole parameters. In the pseudoatom model the deformation density was described by an expansion over spherical harmonics multiplied by Slater-type radial functions with energy-optimized exponents.[26] Atomic densities were expanded to hexadecapolar level for S, N, and C7, octapolar level for all other carbon atoms, for H atoms one bond-directed dipole as well as a quadrupole population were employed. The final difference Fourier syntheses after multipole refinement are virtually featureless.

[14] R. F. W. Bader, *Atoms in Molecules—A Quantum Theory*, Clarendon Press, Oxford **1990**.

[15] S. Pillet, M. Souhassou, Y. Pontillon, A. Caneschi, D. Gatteschi, C. Lecomte, *New J. Chem.* **2001**, *25*, 131.

[16] P. Rademacher, *Strukturen organischer Moleküle*, VCH, Weinheim **1987**.

[17] W. Scherer, M. Spiegler, B. Pedersen, M. Tafipolsky, W. Hieringer, B. Reinhard, A. J. Downs, G. S. McGrady, *Chem. Commun.* **2000**, 635.

[18] T.-H. Tang, R. F. W. Bader, P. J. MacDougall, *Inorg. Chem.* **1985**, *24*, 2047.

[19] a) W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272; b) A. E. Reed, F. Weinhold, *J. Am. Chem. Soc.* **1986**, *108*, 3586; c) D. A. Bors, A. Streitwieser, *J. Am. Chem. Soc.* **1986**, *108*, 1397; d) A. E. Reed, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434; e) U. Salzner, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1993**, *115*, 10231; f) T. Stefan, R. Janoschek, *J. Mol. Model.* **2000**, *6*, 282.

[20] D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171.

[21] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[22] G. M. Sheldrick, SHELXL-97—Program for Crystal Structure Refinement, University of Göttingen, **1997**.

[23] Bruker Nonius Inc., *SAINT-NT—*Program for Integration of Diffraction Data from Area Detectors, Madison WI **2000**.

[24] B. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33.

[25] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[26] E. Clementi, C. Roetti, *At. Data Nucl. Data Tables*, **1974**, *14*, 177

Structural Dependence of Redox-Induced Dimerization as Studied by In Situ ESR/UV/Vis-NIR Spectroelectrochemistry: The Fluoranthenopyracylene Oligomers[**]

Lothar Dunsch,[*] Peter Rapta, Niels Schulte, and
A. Dieter Schlüter

Reversible dimerization reactions of electrochemically produced organic radical ions are used as a general model for the explanation of charge injection in conducting oligomers and polymers.[1–4] Our main interest in this field is to investigate the driving force of dimerization in such structures. While detailed electrochemical and spectroscopic studies of conjugated compounds have been presented by several groups,[5–11] the number of in situ spectroelectrochemical investigations resulting in more direct information on the structural situation during dimerization is limited and the formation of σ dimers has not been demonstrated by in situ techniques. Furthermore, a variety of structures is needed to understand the dimerization as a general reaction of oligomeric systems. Thus monodisperse organic compounds with low molecular weight such as naphthalene diimides,[5] thianthrenes,[6] bipyrrols,[7] bithiophenes,[8] and extended conjugated oligomers, for example, oligothiophenes,[9] oligophenylenes,[10] and oligopyrroles[11] were used for such studies.

For structural studies of the reaction products at electrode surfaces the spectroelectrochemical techniques (including ESR/UV/Vis-NIR spectroscopy at different temperatures) were applied.[12] The existence of both π and σ dimers of oligopyrrols after a charge-transfer reaction has been dem-

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onstrated.[7] We report here the oligomer-length dependence of such dimerization reactions and the stabilization of charged states in conjugated π systems.

While single-stranded oligomer chains are used to support the general scheme of redox-induced dimerization, we have used the recently synthesized unsaturated fluoranthene-type structures with ladder topologies. Such molecules have extended 2D π conjugation so can stabilize their charged state better than single-stranded oligomers and are thus a good model with which to study for the chain-length dependence of oligomer dimerization reactions following an electron-transfer step. Furthermore, they carry solubilizing chains which enable the study of single solvated molecules without the interference of ordering phenomena.

Compounds **3a–d** ($n = 1,2,4,6$) were prepared according to the literature (**3a**)[13] or from compounds **1** and **2** (Scheme 1). In the latter case the main steps are Diels–Alder reactions of the bisdiene **1**[14] with dienophiles **2** ($n = 1,2$), cheletropic CO elimination, and dehydrogenation of the primary adducts with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

The optical, redox, and magnetic properties of the oligofluoranthenes **3** (Scheme 1) were investigated by cyclic voltammetry and in situ ESR/UV/Vis-NIR spectroelectrochemistry and the structures of the products generated by the charge transfer in solution were also determined spectroscopically.

The increase in the π-conjugation length of **3a–3d** is reflected by the bathochromic shift of the absorption bands (Figure 1a): **3a** $\lambda = 310$, 429 nm, **3b** $\lambda = 340$, 496 nm, **3c** $\lambda = 357$, 546 nm, and **3d** $\lambda = 370$, 565 nm. The optical band gap for infinite ladder-type polymer ($n \rightarrow \infty$), $E_g = 2.05$ eV, was found by extrapolation assuming the linear dependence of the evaluated optical gap (E_g) with the inverse of the degree of polymerization (n^{-1}; see Figure 1b; even though the first indications that this linearity is not generally found in conjugated systems were recently reported[15]). The electrochemical half-wave redox potentials of **3a–3d** (Figure 1b) for the first electron transfer ($E_{1/2}$) correlate well with the inverse of the oligomer length and the linear extrapolation to $n \rightarrow \infty$ results in $E_{1/2} = -0.9$ V (versus Ag/AgCl).

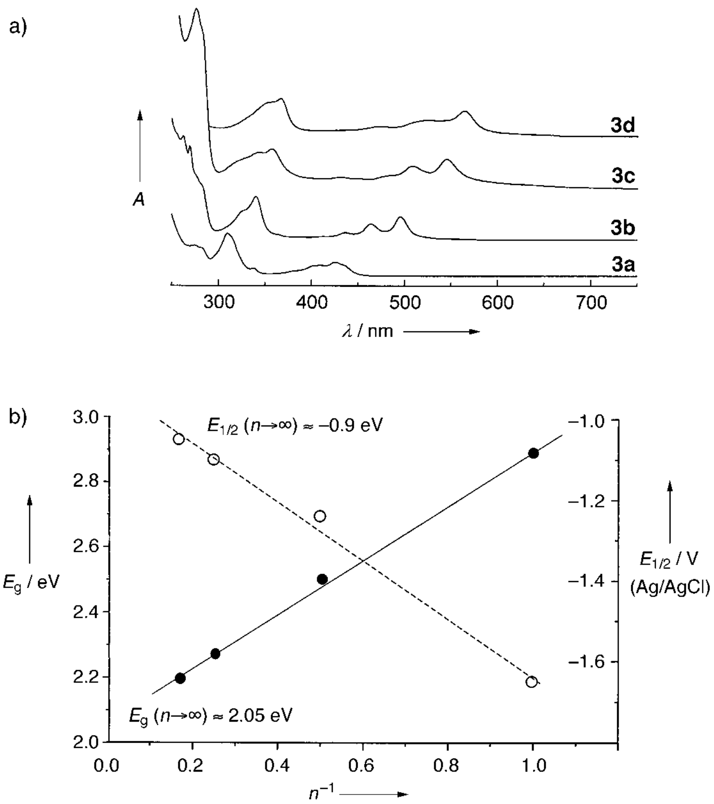
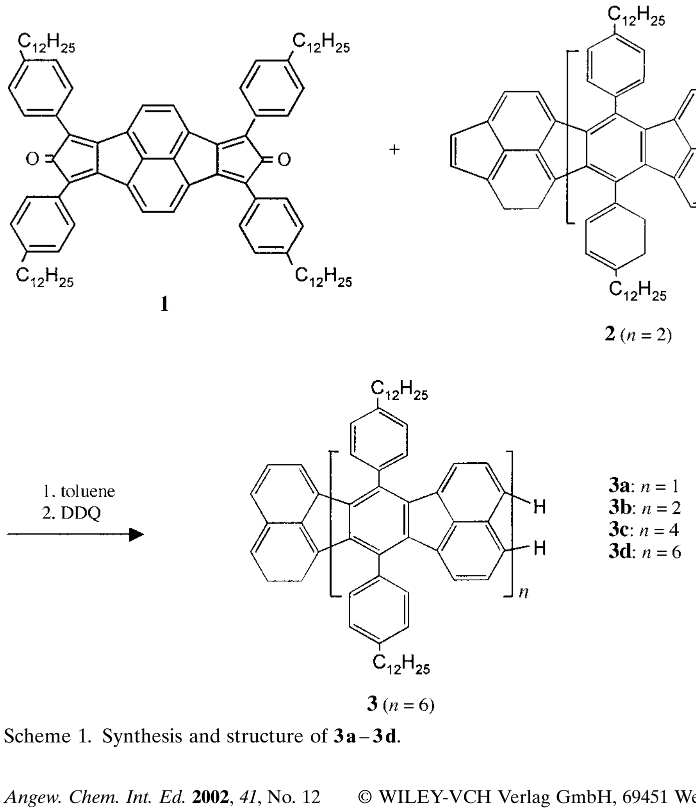


Figure 1. a) Absorption spectra of **3a–3d** in *o*-dichlorobenzene, b) dependence of optical band width E_g (●) and of redox potential $E_{1/2}$ (○) on the reciprocal chain length of the oligomer n^{-1}.



Scheme 1. Synthesis and structure of **3a–3d**.

3a ($n = 1$) is electrochemically reduced in an one-electron step at $E_{1/2} = -1.65$ V (versus Ag/AgCl; Figure 2a). In the anodic back scan the appearance of a full re-oxidation peak points to a high stability of the generated anion radical. The UV/Vis-NIR and the ESR spectra of **3a** (Figure 3a) and its reduction products, measured during cyclic voltammetry, show that the one-electron reduction generates a radical anion with optical bands in the visible (555 nm) and the NIR (1390 nm) region. The intensity of the corresponding ESR signal (inset in Figure 3a) correlate well with the above-mentioned optical bands arising from transitions between the SOMO → LUMO and HOMO → SOMO orbitals. The analysis of the ESR spectrum gives the experimental splitting constants $8a_H = 0.28$ mT and $4a_H = 0.05$ mT. Semiempirical AM1 (geometry) and ab initio 6-31G* (spin distribution) calculations indicate that the $C_6H_4C_{12}H_{25}$ substituents are twisted out of plane with a twist angle of 85° and most of the spin density is

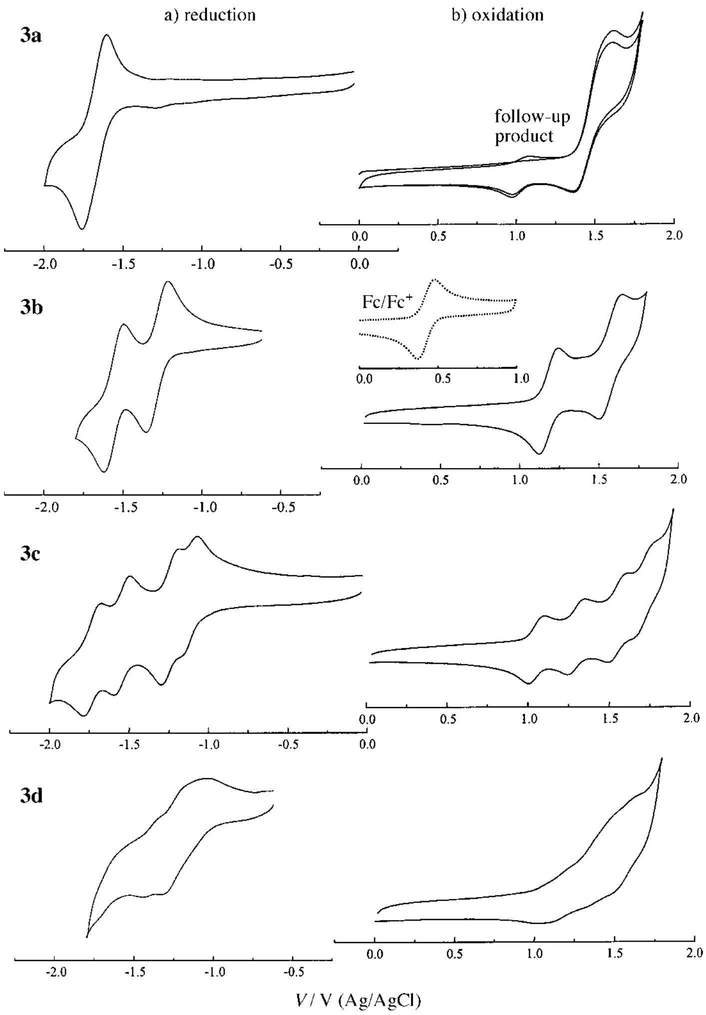


Figure 2. Cyclic voltammograms of **3a**–**3d** in 0.1 M TBABF$_4$/*o*-dichlorobenzene at a platinum electrode and a scan rate of 200 mV s^{-1}.

delocalized over the whole planar part of the molecule. Therefore, the 12 splittings assigned to hydrogen atoms can be attributed to the protons of the two naphthalene groups on the periphery. A similar spin-density distribution was observed in the case of the radical anion of 9,10-diphenylanthracene, where the assignment of the splitting constants was determined unambiguously by using ENDOR splittings and selective deuteration.[16]

In addition to the optical spectra of radical anions we observed a new absorption band at 685 nm in the region of the first electron transfer, which increased during the reduction (Figure 3 a). This can be attributed to a σ dimer ($\mathbf{3a}$–$\mathbf{3a}$)$^{2-}$ formed by a chemical follow-up reaction of the radical anion $\mathbf{3a}^{\bullet-}$ as observed for short π-conjugated molecules.[7]

The oxidation of **3a** is more complex than the reduction. The cyclic voltammogram indicates the irreversible reaction of a less-stable radical cation. The presence of the follow-up products formed can be seen in the second cyclic voltammetric scan (Figure 2 b; a detailed analysis of the oxidation products will be described elsewhere). According to recent results on photophysical and electrochemical properties of substituted 7,12-diphenylbenzo[*k*]fluoranthenes we can attribute these products to a singly or doubly σ-bound dimer, formed irreversibly during the oxidation under elimination of protons.[17]

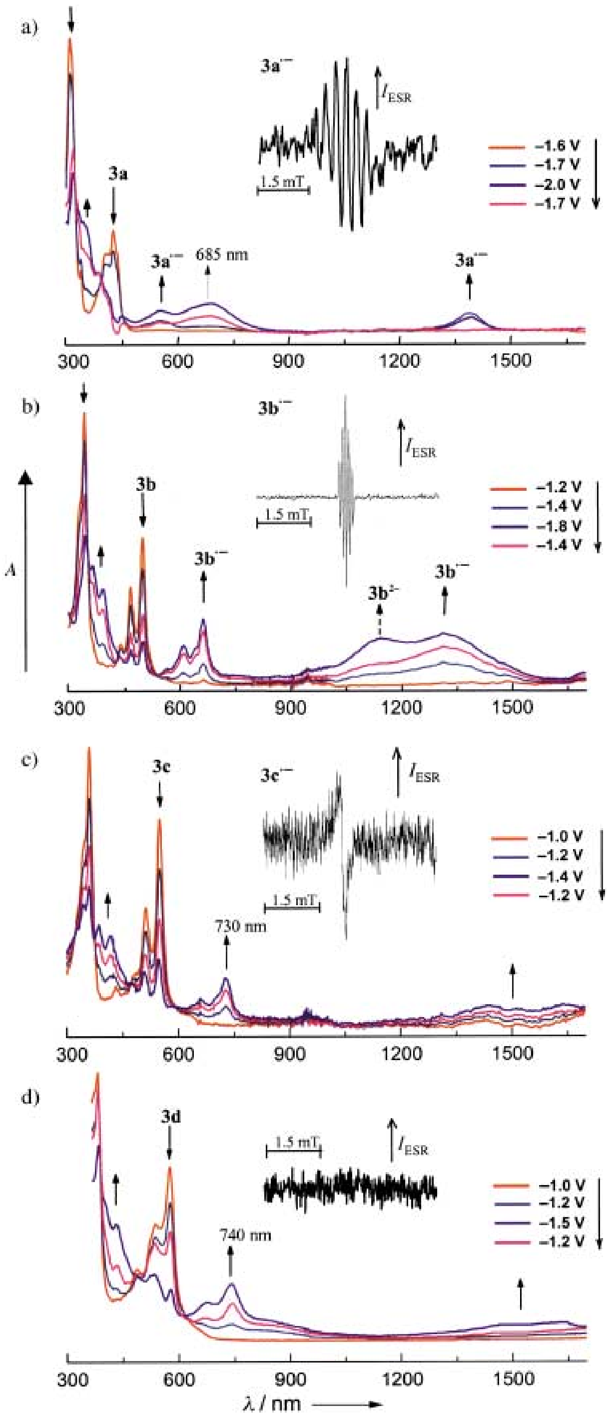


Figure 3. Vis-NIR and ESR (insets) spectroelectrochemistry of **3a**–**3d** and their reduction products, the spectra were recorded simultaneously to the voltammetric cycles (the potentials correspond to Figure 2 a). a) **3a** at the first reduction peak, b) **3b** at the first two reduction peaks, c) **3c** at the first two reduction peaks, d) **3d** scan from –0.6 to –1.5 V.

In **3b** ($n = 2$), the next higher homologue of **3a**, the radical anion is more stable and the cathodic formation of a stable dianion is observed (Figure 2 a). The cyclic voltammogram shows two reversible one-electron reduction steps at $E_{1/2} =$

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-1.24 V and -1.5 V. In the first reduction peak a stable radical anion (inset in Figure 3b) formed in high yield was detected by in situ ESR spectroscopy. The well resolved five-line ESR spectrum with a very small coupling constant $4a_H = 0.06$ mT indicates a similar spin distribution to that in **3a**$^{\bullet-}$. The spin is preferably localized on the planar part of the molecule which is larger than in **3a** while the twisted $C_6H_4C_{12}H_{25}$ substituents again do not conjugate effectively with the planar part. The electrochemical reduction of such structures containing the indeno[1,2,3-*cd*]fluoranthrene moiety which form stable radical anions has been reported.[18] In the UV/Vis-NIR spectrum a remarkable shift of the NIR absorption of the radical anion **3b**$^{\bullet-}$ to the lower values (1310 nm) and of the visible absorption to the higher values (660 nm) in comparison to **3a**$^{\bullet-}$ (1390 nm and 555 nm) was found. No reaction products of **3b**$^{\bullet-}$ were detected and no changes with time were observed both in its optical and ESR spectra even at 260 K. The absence of a follow-up reaction supports a stabilization of the charged **3b** and points to negligible dimer formation. In the second reduction step a new optical band at 1145 nm is found as expected for the ion **3b**$^{2-}$.

Further extension of the π-system in **3c** ($n = 4$) results in four reversible reduction steps (Figure 2a). The first cyclic voltammetric peak which is less cathodic than for **3a** and **3b** is a superposition of two one-electron transfers with close half-wave potentials (-1.1 V and -1.2 V) indicating that the two electrons are transferred successively to the tetramer. A very weak single-line ESR signal was recorded during the voltammetric scan in this potential region (inset in Figure 3c). The tetramer exists as a dianion and only a minor amount of an radical anion is formed by symproportionation of **3c** with **3c**$^{2-}$ in the diffusion layer at the electrode. A new absorption band at 730 nm and a very broad one in the NIR region (1200–1800 nm) appear during the cathodic scan (Figure 3c) which are attributed to the **3c**$^{2-}$ ion. The extended π system of the tetramer stabilizes the *dianionic* structure by minimizing the interactions between the two negative charges and dimerization is thus prevented.

The redox behavior of the hexamer **3d** with the largest π-system gives a broad cyclic voltammetric response. Several successive one-electron transfers (similar to first two one-electron transfers to the tetramer **3c**) are detected (Figure 2). No ESR signal was detected in this case (inset in Figure 3d). The optical absorption band at 740 nm and the broad one in the region 1200–1800 nm (Figure 3d) are also attributed to multicharged structures as for **3c**. The ESR-silent doubly charged structures are similar to the electronic state of a bipolaron or a dication in a ^1A_g singlet ground state carrying two individual polarons.[19]

Summarizing the influence of the oligomer length on the dimerization of the compounds **3a**–**3d** (Scheme 1) as studied by cyclic voltammetry and in situ ESR/UV/Vis-NIR spectroelectrochemistry, radical anions were found in the first reduction step for structures **3a**, **3b**, and to a very small extent for **3c**. While **3a**$^{\bullet-}$ is in equilibrium with its σ-dimer in solution, **3b**$^{\bullet-}$ is already strongly stabilized and its dimerization is negligible in the studied temperature range (260–290 K). The extended π-conjugation in structures **3c** and **3d** is found to be sufficient for stabilization of charges in the molecule without dimerization. Thus, extension of the π systems in the homologous series described here disfavors chemical dimerization. This finding is an indication that dimerization in organic conducting polymers may not necessarily be a general mechanism for the stabilization of radical ions.

Experimental Section

Synthesis of **3d** ($n = 6$): **1** (50 mg, 0.04 mM) and **2** ($n = 2$) (137 mg; 0.09 mM) were heated under reflux in toluene (20 mL) for 48 h under nitrogen. After cooling, neat DDQ (20 g, 0.09 mM) was added and the resulting solution stirred for 30 min. The solution was then filtered through a short silica-gel column and the solvent removed. The residue was purified by chromatography on silica gel (eluent: hexane/toluene = 5/1) to give **3d** ($n = 6$) as an intensely purple powder (114 mg, 67 %). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.9, 1.4, 1.8, 2.7, 6.1, 6.6, 7.4$ ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.1, 19.7, 22.7, 24.5, 27.1, 29.4, 30.1, 31.9, 32.8, 35.7, 37.1, 37.4, 124–142$ ppm (aromatic C); LD-MS: m/z 4250 [M^+].

The cyclic voltammograms were obtained using platinum wire as working and counter electrodes. An Ag/AgCl electrode served as reference, and the cyclic voltammetric measurements were carried out in a glove box (oxygen and water content below 1 ppm) with a Princeton Applied Research (PAR 270) universal electrochemical system. Ferrocene/ferricenium ion (Fc/Fc$^+$ ($E_{1/2}$(Fc/Fc$^+$) = 0.44 V vs. Ag/AgCl) was used as an internal potential marker. The scan rate was 200 mV s^{-1}.

Laminated platinum-mesh electrodes were used in all spectroelectrochemical experiments. Redox cycling of the solutions of the compounds under study in simultaneous ESR and UV/Vis-NIR measurements[12] was carried out in 0.1M tetrabutylammoniumtetrafluoroborate ($TBABF_4$; Fluka, dried under reduced pressure at 70 °C for 24 h and stored in a glove box) in *o*-dichlorbenzene (Aldrich, doubly distilled under argon over calcium hydride before use), the scan rate was 10 mV s^{-1}. A silver wire served as a pseudo reference electrode and a platinum wire as a counter electrode. ESR spectra were recorded by the 300D X-Band ESR spectrometer (Bruker, Germany), and UV/Vis-NIR spectra by the diode array UV/Vis-NIR spectrometer system TIDAS (J&M, Aalen, Germany). A PG 284 potentiostat/galvanostat (HEKA, Lambrecht, Germany) was used for these measurements.

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[1] H. Shirakawa, *Angew. Chem.* **2001**, *113*, 2642; *Angew. Chem. Int. Ed.* **2001**, *40*, 2574.

[2] A. MacDiarmid, *Angew. Chem.* **2001**, *113*, 2649; *Angew. Chem. Int. Ed.* **2001**, *40*, 2581.

[3] A. Heeger, *Angew. Chem.* **2001**, *113*, 2660; *Angew. Chem. Int. Ed.* **2001**, *40*, 2591.

[4] *Electronic Materials: The Oligomeric Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**.

[5] J. F. Penneau, L. L. Miller, *Angew. Chem.* **1991**, *103*, 1002; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 986.

[6] P. Hübler, J. Heinze, *Ber. Bunsen-Ges.* **1998**, *102*, 1506, and references therein.

[7] A. Merz, J. Kronberger, L. Dunsch, A. Neudeck, A. Petr, L. Parkanyi, *Angew. Chem.* **1999**, *111*, 1533; *Angew. Chem. Int. Ed.* **1999**, *38*, 1442.

[8] P. Tschuncky, J. Heinze, A. Smie, G. Engelmann, G. Koßmehl, *J. Electroanal. Chem.* **1997**, *433*, 223.

[9] a) Y. Yu, E. Gunic, B. Zinger, L. Miller, *J. Am. Chem. Soc.* **1996**, *118*, 1013; b) Y. Harima, H. Tang, L. Zhu, K. Yamashita, J. Ohsita, A. Kunai, *J. Electroanal. Chem.* **1999**, *472*, 157; c) H. Nakanishi, N. Sumi, S. Ueno, K. Takimiya, Y. Aso, T. Otsubo, K. Komaguchi, M. Shiotani, N. Ohta, *Synth. Met.* **2001**, *119*, 413.

[10] A. Smie, J. Heinze, *Angew. Chem.* **1997**, *109*, 375; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 363.

[11] J. A. E. van Haare, L. Groenendaal, E. E. Havinga, R. A. J. Janssen, E. W. Meijer, *Angew. Chem.* **1996**, *108*, 696; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 638.

[12] a) A. Neudeck, A. Petr, L. Dunsch, *Synth. Met.* **1999**, *107*, 143; b) P. Rapta and L. Dunsch, *J. Electroanal. Chem.* **2001**, *507*, 287.

[13] B. Schlicke, J. Frahn, A. D. Schlüter, *Synth. Met.* **1996**, *83*, 173.

[14] W. D. Neudroff, N. Schulte, D. Lentz, A. D. Schlüter, *Org. Lett.* **2001**, *3*, 3115.

[15] H. Meier, U. Stalmach, H. Kolshorn, *Acta Polym.* **1991**, *48*, 379; see also: P. Bäuerle, Paper presented at 10th International Symposium on Novel Aromatic Compounds 2001, San Diego **2001**.

[16] R. Biehl, K. Hinricks, H. Kurreck, W. Lubitz, U. Mennenga, K. Roth, *J. Am. Chem. Soc.* **1977**, *99*, 4278.

[17] a) E. F. Fabrizio, A. Payne, N. E. Westlund, A. J. Bard, P. P. Magnus, *J. Phys. Chem. A* **2002**, *106*, 1516; b) J. D. Debad, J. C. Morris, V. Lynch, P. Magnus, A. J. Bard, *J. Am. Chem. Soc.* **1996**, *118*, 2374; c) J. D. Debad, J. C. Morris, P. Magnus, A. J. Bard, *J. Org. Chem.* **1997**, *62*, 530.

[18] F. Gerson, J. H. Hammons in *Nonbenzenoid Aromatics* (Ed.: J. P. Synder), New York, Academic Press, **1971**, p. 81.

[19] J. A. E. H van Haare, E. E. Havinga, J. L. J. van Dongen, R. A. J. Janssen, J. Comil, J.-L. Brédas, *Chem. Eur. J.* **1998**, *4*, 1509.

Synthesis and Stereoselective Self-Assembly of Double- and Triple-Stranded Helicates**

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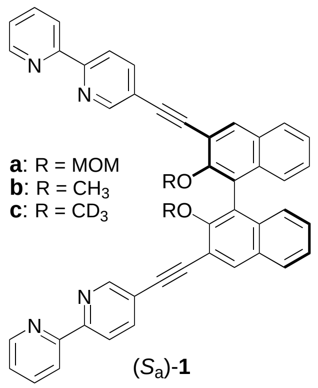
The last decade has seen a tremendous development in the design and synthesis of self-assembled supramolecular architectures through metal-ion coordination.[1–3] Although examples have been reported in which chiral ligand units[2f,g, 4–11] were used, only a few of these units bear additional inwardly directed functional groups.[10a,c, 11] Therefore, our aim was to design and synthesize a double-branched chelating ligand, held together by a chiral core fragment bearing functional groups.

As part of our approach, the feasibility of the proposed metal–ligand complexes was explored by force-field and semiempirical calculations prior to ligand synthesis.[12] By following this approach we designed ligand **1**, which should self-assemble to form dinuclear coordination complexes with suitable metal ions (Figure 1). 5-ethynyl-2,2′-bipyridine (**4**; Scheme 1) was prepared from 2-bromopyridine (**2**). A modi-



(S_a)-**1**

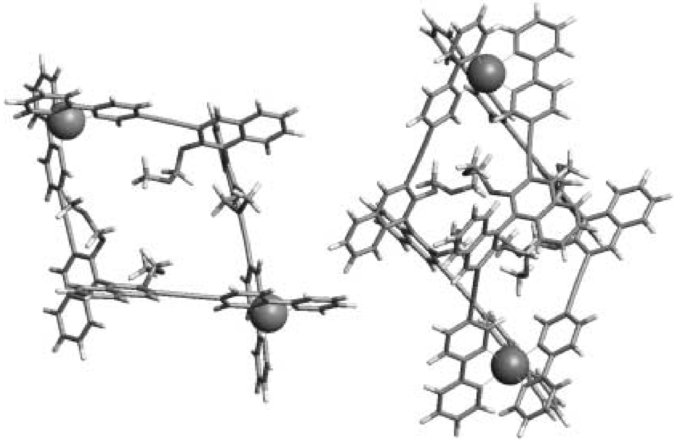
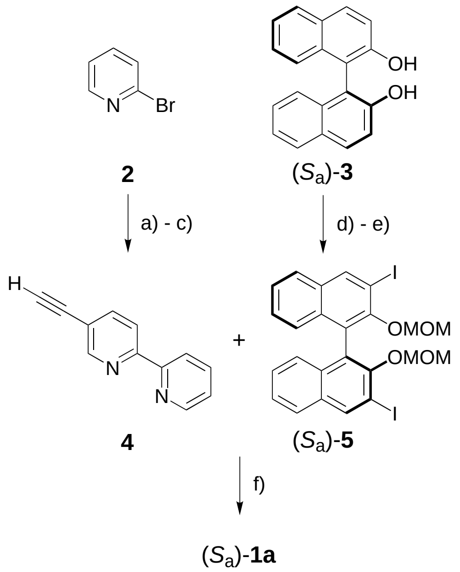


Figure 1. Energy-minimized structures (PM3-TM calculations) of the complexes $[Cu_2\{(S_a)\text{-}\mathbf{1a}\}_2]^{2+}$ (left) and $[Zn_2\{(S_a)\text{-}\mathbf{1a}\}_3]^{4+}$ (right); only one of the three possible stereoisomeric complexes is shown for each.



Scheme 1. Synthesis of (S_a)-**1a**. a) *t*BuLi, THF, −78 °C, then $ZnCl_2$, −78 °C → RT, 2 h; b) 2-chloro-5-trimethylsilylethynylpyridine, $[Pd_2(dba)_3] \cdot CHCl_3$, tBu_3P, THF, 83 %; c) KF, MeOH, 97 %; d) NaH, DMF, MOMCl, 80 %; e) *n*BuLi, TMEDA, RT, 6.5 h, I_2, −78 °C, 65 %; f) Et_3N, CuI, $[Pd_2(dba)_3] \cdot CHCl_3$, dppf, 50 °C, 78 %. dba = *trans,trans*-dibenzylideneacetone; TMEDA = *N,N,N′N′*-tetramethylethylenediamine; dppf = 1,1′-bis-(diphenylphosphanyl)ferrocene.

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