First crystallographic structure determination of an oligothiophene metal π-complex

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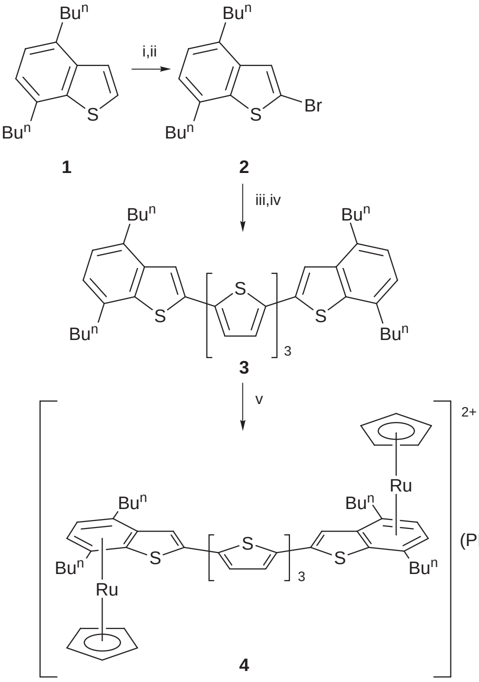
A novel oligothiophene metal π-complex containing the, as yet, longest α-conjugated oligothiophene as ligand is described; characterisation by X-ray and other physicochemical methods clearly reveals the influence of the metal units upon the electronic and the geometric structure.

Oligothiophenes represent ideal model compounds for the corresponding polydisperse conducting polymers[1] and novel materials used in organic transistors[2] or light emitting devices.[3] Therefore, the tailoring of the electronic properties by electronically active substituents,[4] the replacement of thiophene moieties by other heteroaromatic units,[5] and the coordination of transition metals to an oligothiophene core lead to pronounced alterations of the (electronic) properties.[6] The molecular arrangement of the oligothiophenes in the solid state may be crucial for the performance of the devices.[2] However, X-ray data for oligothiophenes have been sparse, since the growth of suited single crystals is very difficult, and the crystals often contain intrinsic disorder and defects.[5,7]

Herein we present the synthesis and characterisation of $[(CpRu)_2(\eta^6,\eta^6\text{-DB5T})](PF_6)_2$ **4**, a novel bis-ruthenium π-complex of ‘benzo-capped’ quinquethiophene **3**. In contrast to other examples,[6] the planar and stiff terminal benzo[*b*]thiophene units provide good stability and an optimal influence of the metal fragments onto the electronic properties.

According to Scheme 1, 4,7-di-*n*-butylbenzo[*b*]thiophene **1**[8] was reacted with Bu^nLi and bromine to yield the 2-bromo derivative **2** in 69% yield. Nickel-catalysed cross-coupling of the Grignard reagent of **2** and 5,5″-dibromoterthiophene yielded oligothiophene (DB5T) **3** (56%). The doubly ruthenated quinquethiophene $[(CpRu)_2(\eta^6,\eta^6\text{-DB5T})](PF_6)_2$ **4** was effectively formed by the reaction of **3** with two equiv. of $[CpRu(MeCN)_3]PF_6$ [9] (73% yield). The resulting metal complex **4** was purified by reprecipitation and is stable in air, is highly soluble in polar solvents such as dichloromethane, 1,2-dichloroethane, and in coordinating solvents such as acetone.†



Scheme 1 *Reagents and conditions*: i, Bu^nLi, THF, −20 °C; ii, Br_2, −20 °C; iii, Mg; iv, $Ni(dppp)Cl_2$, Et_2O, $Br–T_3–Br$; v, $[CpRu(MeCN)_3]PF_6$, $C_2H_4Cl_2$, reflux.

Various 2D NMR spectroscopic experiments enabled the assignment of all ^1H and ^{13}C resonances in comparison to the non-complexed quinquethiophene **3**. The $CpRu^+$-fragments are exclusively η^6-bound to the anellated benzene rings. Owing to the influence of the metal, the proton resonances of the terminal benzo[b]thiophene units are strongly shifted upfield ($\Delta\delta$: $H^{3''',3''''} = -0.20$, $H^{5''',5''''} = -1.02$, $H^{6''',6''''} = -1.00$ ppm). In contrast, resonances of the central terthiophene moiety are shifted downfield ($\Delta\delta$: $H^{4,4''} = +0.18$, $H^{3,3''} = +0.13$, $H^{3',4'} = +0.14$ ppm). The most pronounced changes in the ^{13}C NMR spectra are evident for the benzo carbons ($\Delta\delta$: $C^{3a'''}$, $C^{3a''''} = -32.3$, $C^{4'''}$, $C^{4''''} = -34.5$, $C^{5'''}$, $C^{5''''} = -39.8$, $C^{6'''}C^{6''''} = -42.0$, $C^{7'''}$, $C^{7''''} = -36.2$, $C^{7b''',7b''''} = -30.4$ ppm).

To enable comparison with the non-complexed oligothiophene DB5T **3**, the electronic properties of metal complex **4** were determined by optical measurements and by cyclic voltammetry. In the absorption spectrum metallation of the oligothiophene causes a displacement of the unstructured π–π* transition to lower energies and a decrease of the absorption coefficient [**3**: λ_{max} (lg ε) = 436 nm (4.76); **4**: λ_{max} (lg ε) = 454 nm (4.72)]. The emission spectrum of **3** exhibits a structured band at λ_{max} = 501 nm. Owing to a strong metal ligand interaction the fluorescence of **4** at λ_{max} = 533 nm is strongly quenched. The electrochemical characterisation of **3** reveals two fully reversible oxidation waves corresponding to two one electron transfer steps ($E°_1 = 0.39$ V, $E°_2 = 0.75$ V *vs*. Fc/Fc^+). As typical for electron-rich oligothiopenes, no reduction process can be observed in the negative potential regime ($E \geq -2$ V). Owing to the electron withdrawing character of the metal fragments, oxidation of **4** is shifted to positive potentials ($E°_1 = 0.75$ V, $E°_2 = 1.06$ V *vs*. Fc/Fc^+). Additionally, in the CV of **4** a reversible two electron reduction wave arises at $E°_3 = -1.76$ V *vs*. Fc/Fc^+ which corresponds well to the values obtained for other $[CpRu(arene)]^+PF_6^-$ salts.[10] Thus, the oxidation process is located on the oligothiophene core, whereas reduction occurs at the metal fragments.

Since no splitting of the reduction wave can be seen, electron transfer to the ruthenium centers occurs at the same energy indicating none, or at best weak, interaction *via* the conjugated π system (Fig. 1).

Small ruby red crystals of the oligothiophene metal complex **4** suitable for X-ray structure determination were grown by recrystallisation from $CH_2Cl_2–Et_2O$.‡ Views of the molecule in Fig. 2 verify the composition of the molecule. The oligothiophene core is nearly coplanar exhibiting small interplanar angles (ring 1,2: 5.0°; ring 2,3: 9.4°). Rather unique *syn*

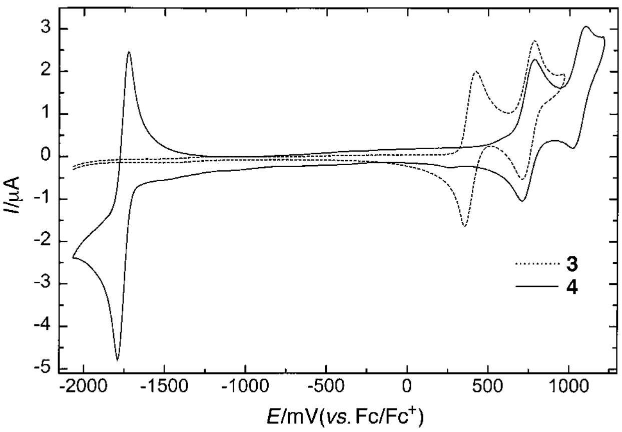


Fig. 1 Cyclic voltammograms (c = 10^{-3} mol l^{-1} substrate in CH_2Cl_2–TBAHFP (0.1 M), v = 100 mV s^{-1}; Pt disk working electrode, Pt wire counter electrode, Ag/AgCl reference electrode internally calibrated with the Fc/Fc^+-couple) of metallated oligothiophene $[(CpRu)_2(\eta^6,\eta^6\text{-}DB5T)](PF_6)_2$ **4** (solid line) in comparison to the non-metallated ligand **3** (dashed line).

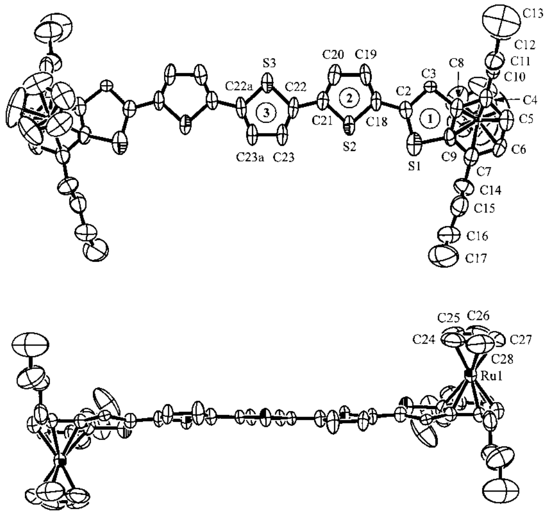


Fig. 2 ORTEP front view of oligothiophene metal complex **4** showing atomic labeling, 50% thermal ellipsoids (top). Side view of **4** (bottom). The PF_6^- counter ions have been omitted for clarity. Selected bond distances (Å): S(1)–C(2) 1.706(14), Ru(1)–C(4) 2.232(13), S(1)–C(9) 1.720(12), Ru(1)–C(5) 2.181(14), C(2)–C(3) 1.600(15), Ru(1)–C(6) 2.185(13), C(3)–C(8) 1.621(15), Ru(1)–C(7) 2.210(14), C(8)–C(9) 1.425(18), Ru(1)–C(8) 2.263(12), C(8)–C(4) 1.439(17), Ru(1)–C(9) 2.251(13), C(4)–C(5) 1.432(19), Ru(1)–C(24) 2.170(19), C(5)–C(6) 1.360(20), Ru(1)–C(25) 2.186(17), C(6)–C(7) 1.410(18), Ru(1)–C(26) 2.178(18), C(7)–C(9) 1.392(18), Ru(1)–C(27) 2.159(19), C(2)–C(18) 1.449(16), Ru(1)–C(28) 2.140 (20).

conformations of the terminal benzo[*b*]thiophene units are observed with respect to the central all *anti* terthiophene moiety which shows quite normal bond length and angles. The occurrence of *syn* conformers in coplanar arrangements has only been verified once previously in a mixed pentamer containing four thiophene and one 1,3,4-oxadiazole unit.[5] In accordance with the NMR assignments, the $CpRu^+$-fragments are η^6-coordinated to the terminal benzene rings and not η^5 to any thiophene ring. The two metal fragments are directed to opposite sides with respect to the oligothiophene plane representing one of two possible isomers.§ Simultaneously, the butyl side chains on each benzo[*b*]thiophene unit point in the opposite direction with respect to the coordinated metal. The distances Ru–C5/C6 are found to be shorter than Ru–C8/C9 indicating a transversal displacement of the metal atom by 0.07 Å from the center of the benzene ring to the ends of the molecule. This has been observed in the benzo[*b*]thiophene complex $[(CpRu)(\eta^6\text{-benzo}[b]\text{thiophene})]BF_4$ and other transition-metal complexes containing fused arene ligands.[11] As a consequence, bonds C2–C3, C3–C8, and S1–C9 are longer than expected, while the corresponding bond angles are distorted.

Current efforts in our laboratory are now directed to the variation of the length of the oligothiophene ligand and variation of the transition metal.

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Notes and references

† All new compounds had spectral (^1H NMR, ^{13}C NMR, UV–VIS) and microanalytical properties (C, H, S) consistent with the assigned structures.

‡ *Crystal data*: $[(CpRu)_2(\eta^6,\eta^6\text{-}DB5T)](PF_6)_2$ **4**: $C_{54}H_{58}F_{12}P_2Ru_2S_5$, M = 1359.38, monoclinic, space group $I2/a$, a = 14.444(2), b = 16.998(3), c = 27.623(3) Å, β = 99.94(1)°, V = 6680.3(16) Å^3, Z = 2, D_c = 1.352 g cm^{-3}, crystal dimensions 0.15 × 0.27 × 0.77 mm, T = 220(2) K, μ = 0.721 cm^{-1} (analytical absorption correction). Intensity data were collected on a STOE-IPDS image-plate diffractometer [Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator] in the φ rotation scan mode. 5186 unique reflections were measured and used in the refinement. The structure was solved by direct methods with the XMY93 program system.[12] The molecule is located on a crystallographic twofold axes passing through S3 and between C23 and C23a. Refinement (SHELXL93)[13] of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to R = 0.0937 for 1873 reflections with $F_o \geq 4\sigma(F_o)$. The relatively poor R value is probably due to a disordered PF_6^- anion which was therefore only refined isotropically and to a high anisotropy of the terminal atoms. These effects could not be eliminated by low-temperature data collection.

CCDC 182/1243. See: http://www.rsc.org/suppdata/1999/1097/ for crystallographic files in .cif format.

§ Evidently, during the crystallization process only one possible isomer of compound **4** precipitated. The other isomer would comprise the same conformation of the oligothiophene core but with the two metal centers on the same side. Both isomers, presumably present in solution, can not be distinguished in NMR experiments.

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