Second Harmonic Generation and Two-Photon Fluorescence as Nonlinear Optical Properties of Dipolar Mononuclear Sesquifulvalene Complexes

Hans Wong,[a] Timo Meyer-Friedrichsen,[a] Tony Farrell,[a] Christoph Mecker,[a] and Jürgen Heck*[a]

Dedicated to Prof. Dr. Dr. eh. Dr. h.c. H. Sinn on the occasion of his 70th birthday

Keywords: NLO materials / Second harmonic generation / Two-photon fluorescence / Solvatochromism / Electrochemistry / Sesquifulvalene / Sandwich complex

In order to investigate nonlinear optical properties, in particular second harmonic generation (SHG) of organometallic complexes, numerous dipolar monocationic sesquifulvalene complexes of the general form $[\mathrm{Mc{-}Z{-}C_7H_6}]^+$ have been synthesised (Mc = metallocenyl), wherein the metallocenyl moiety Mc acts as an electron donor, and the tropylium cation $\mathrm{C_7H_6}^+$ as an electron acceptor. The mutual electronic influence of the donor and the acceptor groups is warranted by a linking spacer Z, which is a single bond [Mc = $\mathrm{CpFeC_5H_4}$ (**4a**); Mc = $\mathrm{CpRuC_5H_4}$ (**4b**)], an unsaturated bridge containing olefins [Z = $(E\text{-CH=CH})_n$: n = 1, Mc = $\mathrm{CpFeC_5H_4}$ (**25a**); Mc = $\mathrm{CpRuC_5H_4}$ (**25b**); n = 2, Mc = $\mathrm{CpFeC_5H_4}$ (**26**); n = 3, Mc = $\mathrm{CpFeC_5H_4}$ (**27**)], or thiophene units [Z = 2,5-$\mathrm{C_4H_2S}$, Mc = $\mathrm{CpFeC_5H_4}$ (**28**); Z = 5,5′-(2,2′-$\mathrm{C_4H_2S})_2$, Mc = $\mathrm{CpFeC_5H_4}$ (**29**); Z = 2-(5-E-CH=CH)$\mathrm{C_4H_2S}$, Mc = $\mathrm{CpFeC_5H_4}$ (**30**)]. For the salts of **4a**·$\mathrm{BF_4}$, **4b**·$\mathrm{PF_6}$ and **25a**·$\mathrm{PF_6}$ X-ray structure determinations have been performed [**4a**·$\mathrm{BF_4}$: orthorhombic, $Pnma$, a = 21.75(2), b = 9.900(2), c = 6.881(3) Å, V = 1482.0(15) Å^3, Z = 4; **4b**·$\mathrm{PF_6}$: monoclinic, $P2(1)/c$, a = 8.104(3), b = 18.206(14), c = 11.228(4) Å, β = 107.59(3), V = 1579.1(15) Å^3, Z = 4; **25a**·$\mathrm{PF_6}$: triclinic, $P\bar{1}$, a = 10.067(6), b = 10.496(6), c = 11.418(6) Å, α = 94.07(4), β = 110.96(4), γ = 102.88(5)°, V = 1083.1(11) Å^3, Z = 2]; the solid state structures indicate an almost coplanar arrangement of the organic π-system. Cyclic voltammetry studies reveal an irreversible one-electron reduction and an electrochemically reversible one-electron oxidation step for the ferrocenyl derivatives, whereas the ruthenocenyl derivatives demonstrate an irreversible two-electron oxidation. The redox potentials clearly indicate that the oxidation occurs at the metallocene unit, and the reduction is localised on the tropylium entity. In the electronic absorption spectra two intense bands are observed in the region $400 < \lambda < 900$ nm which undergo strong negative solvatochromic shifts. The origin of the high-energy absorption band is assumed to be an interligand charge-transfer (LL−CT) transition, and the low-energy absorption band is assigned to a donor-acceptor charge-transfer (DA−CT) transition. Whereas the LL−CT is continuously shifted to lower energy with increasing spacer length, the energy of the DA−CT approaches a limiting value. A comparable phenomenon is also observed for the difference between the oxidation and reduction potentials obtained from electrochemical studies. Investigations concerning the nonlinear optical properties of the dipolar cationic sesquifulvalene complexes by means of hyper-Rayleigh scattering (HRS) indicate that the ferrocenyl derivatives fluoresce due to two-photon absorption whereas the ruthenocenyl congeners exhibit second harmonic generation with considerably large first hyperpolarizability which is partly resonance-enhancement based.

Introduction

Materials showing nonlinear optical (NLO) properties have potential applications in photonic devices i.e. for optical data acquisition, storage, transmission and processing. The most prominent NLO features are frequency doubling or even tripling [second and third harmonic generation (SHG and THG)] of incident light, the linear electro-optical effect (Pockels effect) which describes the change of the refractive index of matter with the strength of an applied external electric field, and photorefractivity.[1]

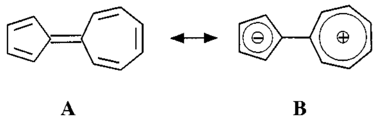
An important class of compounds capable of frequency doubling is composed of an electron donor (D), an acceptor (A) and a π-bridge providing the electronic communication between the donor and acceptor. Such D-π-A compounds are highly polarizable and experimental NLO studies on this kind of organic compounds in a molecular arrangement, incorporated in a polymer, or used as a self-assembled monolayer indeed reveal large SHG effects.[1−3] Our approach to NLO chromophores has been to synthesise organometallic sesquifulvalene-type complexes suitable for SHG, whose NLO properties are characterised by the first hyperpolarizability β. The special features of organometallic complexes have been well documented,[4−6] and include fine-tuning of the molecular polarisation, tailoring of the crystal formation, or fixing additional functional groups as docking spots in supramolecular chemistry.

Very often the change-transfer (CT) states which are very important to achieve high β values (vide infra), can be represented by polar resonance forms[1a] and this also holds for sesquifulvalene (**1**). Although it can be described in terms

---

[a] Institut für Anorganische und Angewandte Chemie, Universität Hamburg,
Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany,
Fax: (internat.) + 49-4042/838-6348,
E-mail: heck@chemie.uni-hamburg.de

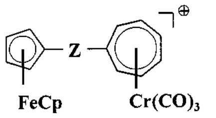
of two resonance forms of different polarities (Scheme 1), sesquifulvalene behaves like a polyene with alternating bond lengths,[7] and its ground state is thus best described by the nonpolar resonance form **A**. Upon excitation charge separation occurs and the resulting structure is likely to be related to the polar resonance form **B**.



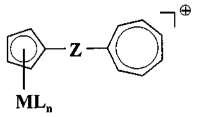
1

Scheme 1. Resonance forms of sesquifulvalene (**1**)

Calculation of the first hyperpolarizability β[8][9] of **1** confirms a change in the dipole moment on excitation, but the high reactivity of **1**[10] prevents the experimental determination of its NLO properties. In previous papers we reported the NLO properties of sesquifulvalene-type complexes wherein both aromatic termini of the resonance form **B** are coordinated to metal centres (**2a**, **2b**).[11]



Z = C≡C : **2a**
Z = *E*-CH=CH : **2b**



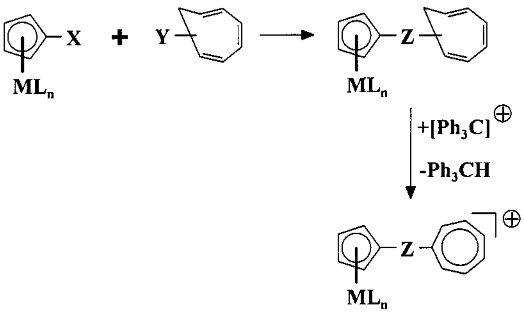
ML$_n$ = FeCp, RuCp: **3**

The objective of the present work was to stabilise only the five-membered ring of the aromatic units in **1** by coordination to (η^5-cyclopentadienyl)iron and -ruthenium. Hence, the neutral five-membered ring moiety of the sesquifulvalene complex would act as an electron donor whereas the uncoordinated tropylium cation would behave as an electron accepting group. Such a molecular arrangement creates a dipolar structure in the ground state, which could change upon excitation. Additionally, it was proposed to introduce various bridging functions Z, i.e. olefins and thiophenes, in order to modulate the interaction between the five- and seven-membered ring (**3**). Thiophenes are often used because of their superior thermal stability, and because of their lower resonance stabilisation energy relative to other aromatic spacers. The former HRS studies on the ethenediyl bridged heterodinuclear complex **2b** revealed a large first hyperpolarizability β.[11] It is well-known from dipolar organic NLO chromophores that increasing the number of π-bonds by one between the donor and acceptor increases the experimental β value by a factor of 1.5−2. Therefore the introduction of additional double bonds between the five- and seven-membered ring of the sesquifulvalene complexes appeared to be a very promising endeavour to improve the NLO properties. Just recently, NLO results of related mononuclear sesquifulvalene complexes with a cymantrenyl entity [ML$_n$ = Mn(CO)$_2$L; L = CO, PR$_3$] instead of MCp as the electron donating group have been published wherein the donor is directly coupled to the tropylium cation or separated by an ethynediyl linker.[12] Thus it would be worthwhile to compare the two families of mononuclear sesquifulvalene complexes concerning their NLO properties.

Results and Discussion

Synthesis

The general strategy to form the desired cationic mononuclear sesquifulvalene complexes was the coupling of functionalised metallocenes with the corresponding cycloheptatriene derivatives to obtain the neutral mononuclear monohydro-sesquifulvalene precursor. The monohydro-sesquifulvalene complexes were converted into the mononuclear cationic sesquifulvalene species by hydride abstraction (Scheme 2).



Scheme 2. General strategy for the synthesis of cationic mononuclear sesquifulvalene complexes

Complexes Without a π-Linker (Z = Single Bond)

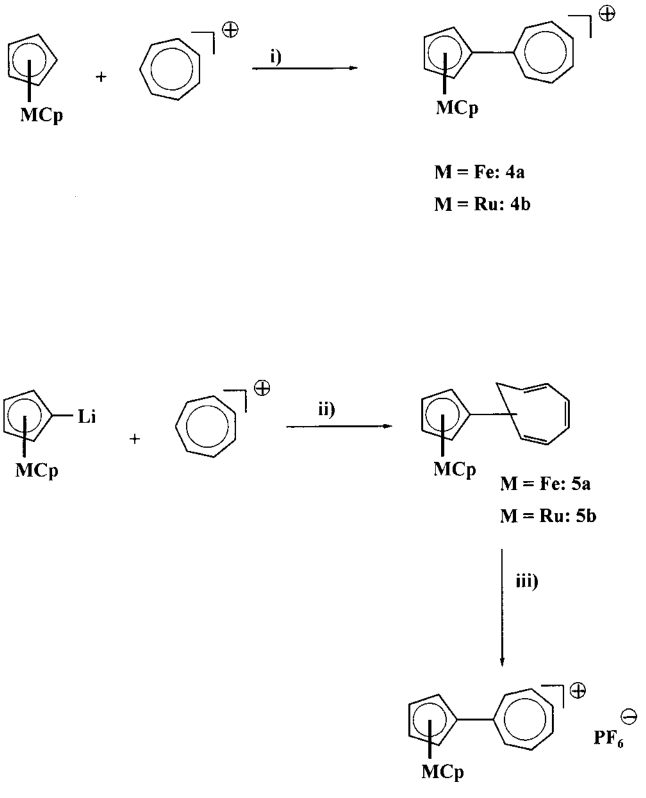
The first published route to the archetypal mononuclear sesquifulvalene complex with the metallocenyl substituent directly linked to the tropylium cation (Z = single bond: **4a**, **4b**) was the electrophilic substitution reaction of ferrocene with the tropylium cation (Scheme 3, i).[13] This method is also applicable to ruthenocene under more vigorous conditions.

However, our experience with the electrophilic substitution reaction revealed difficulties in the purification of the products **4a** and **4b** which were polluted with $[C_7H_7]^+$. Additionally, **4a** was contaminated with paramagnetic impurities which were not easy to remove. Therefore, the nucleophilic addition of monolithiated metallocene[14] to the tropylium cation was preferred yielding the neutral complexes **5a** and **5b** (Scheme 3, ii). The formation of the cationic complexes **4a** and **4b** was subsequently achieved by the reaction of **5a** and **5b** with $[Ph_3C][PF_6]$ (vide infra).

Complexes With Olefinic Linkers [Z = (*E*-CH=CH)$_n$, n = 1, 2, 3]

The introduction of one, two or three double bonds between the five- and seven-membered rings was afforded by

Wittig-type reactions of different formyl metallocenes with nucleophiles of the corresponding cycloheptatrienes. Since deprotonated phosphonates are known to react more stereoselectively than phosphoranes in the formation of *E*-olefins,[15] (cycloheptatrienylmethyl)diethylphosphonate (**6**) was prepared in a Michaelis-Arbuzov reaction from 1-chloromethyl-1,3,5-cycloheptatriene.[16] For $n = 1$ the phosphonate **6** underwent a Wittig-Horner-Wadsworth-Emmons (WHWE) reaction in the presence of NaH with the formyl metallocene (M = Fe: **7a**; M = Ru: **7b**[17]) to form the neutral compounds **8a** and **8b** (Scheme 4, i). The elongation of the olefinic bridge (Scheme 4, ii−vii) could be performed by the reaction of the formyl metallocenes **7a** and **7b** with (ethoxycarbonylmethyl)diethylphosphonate in a WHWE reaction. The reduction of the formed ester **9** by $LiAlH_4$ yielded the alcohol **10** which was oxidised with $BaMnO_4$[18] to the vinylogous metallocenyl carbaldehyde **11**. The aldehyde **11** was reacted either with **6**, yielding the cycloheptatrienyl derivative **12**, or was further subjected to the elongation sequence to form the dienyl formyl derivative **13**, which was then linked to the seven-membered ring to give the neutral complex **14**.



Scheme 3. Formation of the monometallic sesquifulvalene complexes **4a** and **4b**: (i) M = Fe, MeCN, reflux; M = Ru, 1,2-$C_2H_4Cl_2$, reflux; (ii) Et_2O, −20°C; (iii) CH_2Cl_2, $[Ph_3C][PF_6]$

Complexes With Thiophene Linkers {Z = 2,5-C_4H_2S or 5,5′-[2,2′-$(C_4H_2S)_2$]}

Another preparatively convenient method to warrant the electronic interaction in dipolar NLO chromophores upon elongation of the dipole is the use of thiophenes as π-linkers.[19−21] These types of complexes have been synthesised starting from 2,5-dibromothiophene[22] (**15**) (Scheme 5). Lithium-bromine exchange and subsequent nucleophilic addition to the tropylium cation led to the formation of 2-bromo-5-cycloheptatrienylthiophene (**16**).[23] Compound **16** was allowed to react with ferrocenyl zinc chloride[24] in a cross-coupling reaction[25] affording a mixture of isomers **A**, **B** and **C** of the monothiophene species **17** (Scheme 5). Thermolysis of the mixture only revealed the isomers **B** and **C** (40:60), which facilitated the final hydride abstraction (vide infra).

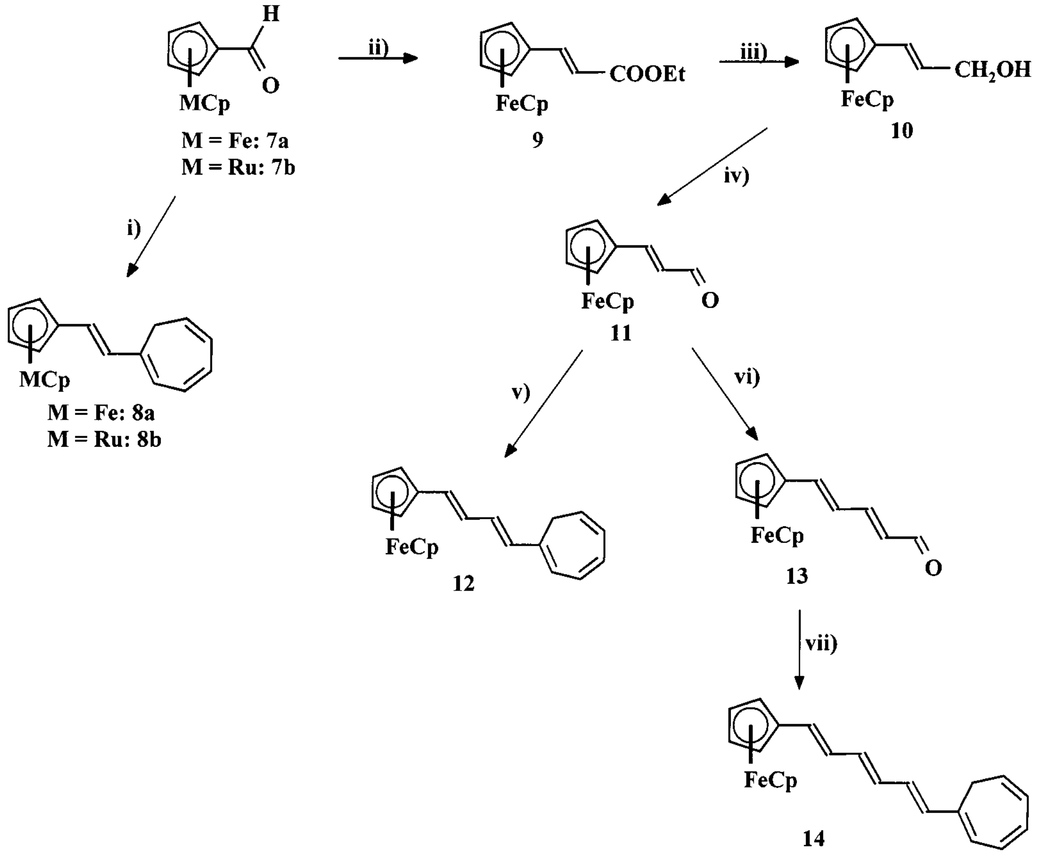
The elongation of the 2,5-thienylene bridge by an additional thiophene unit has been achieved in a Ni-catalysed cross-coupling reaction[26] of the Grignard reagent 2-thienyl magnesium bromide (**18**) with **16** resulting in the formation of the bithiophene derivative **19**[27] (Scheme 6). The bithiophene **19** was lithiated, followed by a zinc-lithium exchange and cross-coupled with iodoferrocene,[14] subsequently yielding the bithiophene bridged monohydro-sesquifulvalene complex **20** as the isomer **A**, which was thermally isomerized to **B**.

Complexes With a Vinylenethienylene Linker [Z = 2-(5-*E*-C_2H_2)C_4H_2S]

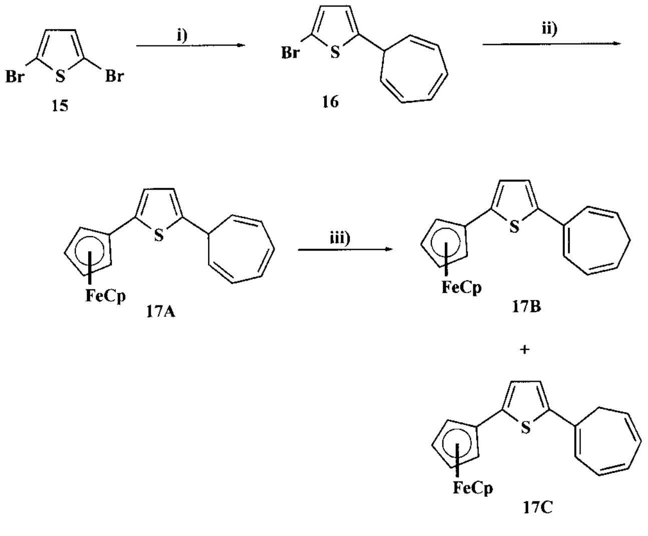
A third way to extend the π-bridge was the combination of an olefinic bond and a thiophene forming a vinylenethienylene bridge.[28] These types of bridges between the donor and an acceptor moiety are easy to synthesise by the formylation[29] of 2-cycloheptatrienylthiophene (**21**),[25] to form compound **22**. Subsequent Wittig reaction of **22** with (ferrocenylmethyl)triphenylphosphorane (**23**)[30][31] afforded the vinylenethienylene-bridged mononuclear monohydro-sesquifulvalene complex **24** (Scheme 7) as a mixture of *E* and *Z* isomers, each of which consisted of two further isomers differing in the position of the sp^3-carbon atom in the seven-membered ring. The isomers were not isolated as, after the hydride abstraction, only one isomer was formed (vide infra).

Formation of the Cationic Sesquifulvalene Complexes

All the sesquifulvalene complexes described above were subjected to hydride abstraction by adding trityl cation to a solution of the neutral complexes (Scheme 8), and was accompanied by a dramatic change in colour from orange-red to deep violet-blue indicating a strong enhancement in the electronic communication between the metallocene and the cationic tropylium entity. All the cations were fully characterised except the cationic sesquifulvalene complex **27** which suffers from a limited stability in solution and in solid state which prevented complete analysis.



Scheme 4. Formation of the olefinic bridged monohydro-sesquifulvalene complexes: (i) THF, −78 °C, $(EtO)_2(O)PCH_2C_7H_7$ (**6**), *n*BuLi; (ii) toluene, 0 °C, $(EtO)_2(O)PCH_2CO_2Et$, *n*BuLi; (iii) Et_2O, $LiAlH_4$, $AlCl_3$; (iv) CH_2Cl_2, $BaMnO_4$; (v) **6**, NaH, DME; (vi) 1. toluene, 0 °C, $(EtO)_2(O)PCH_2CO_2Et$, *n*BuLi, 2. Et_2O, $LiAlH_4$, $AlCl_3$, 3. CH_2Cl_2, $BaMnO_4$; (vii) **6**, NaH, DME



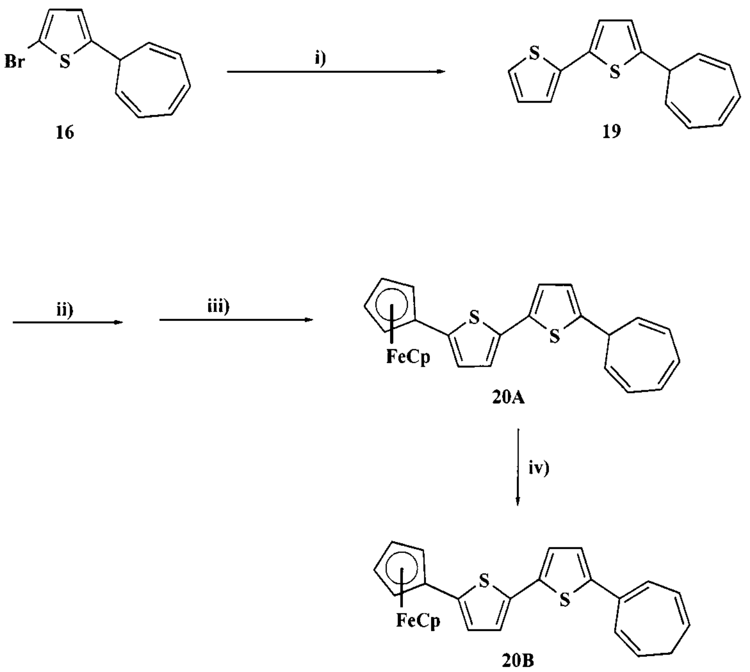
Scheme 5. Formation of the thiophene bridged monohydro-sesquifulvalene complex **17**: (i) 1. THF, −78 °C, *n*BuLi, 2. $[C_7H_7][BF_4]$; (ii) THF, FcZnCl, $Pd(PPh_3)_4$; (iii) toluene, reflux

Structural Results

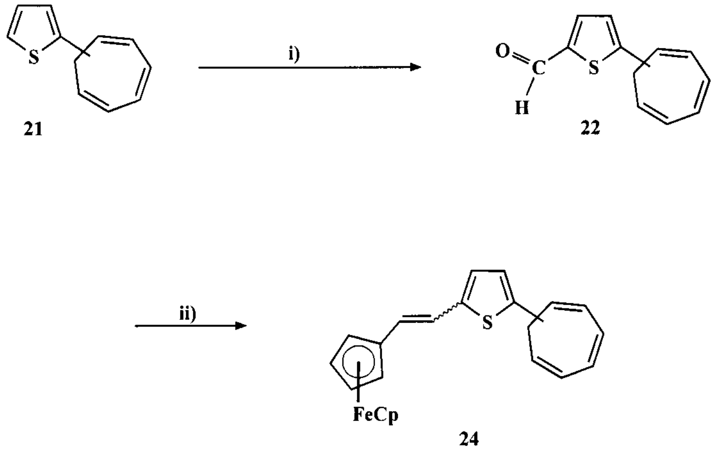
A very important conclusion of the studies on the structural parameters and molecular factors governing the NLO properties, in particular the first hyperpolarizability β, is the correlation between the bond length alternation (BLA) of olefinic bridged D-π-A systems and (i) the dipole change $\Delta\mu_{eg}$ between the ground and the excited CT state, (ii) the electronic transition moment M^2 of the CT transition, and (iii) the energy ΔE of the CT transition.[32][33]

From the sesquifulvalene complexes **4a**, **4b** and **25a** X-ray structure analyses were performed (Figure 1), although for **25a** the accuracy of the structural analysis, which is absolutely necessary for the discussion of a structure-property relationship, suffered from molecular disorder. Two different molecules in the ratio 70:30 lie in almost identical positions and the uncoordinated carbon-carbon double bonds between the five- and seven-membered rings are in a crossed position to each other (Figure 1). The result of an X-ray structure analysis of **4a** has already been published[34] but with less accuracy than obtained in the present work.

The complexes **4a**, **4b** and **25a** all crystallise in centrosymmetric space groups and hence could not be used in the crystalline state for NLO studies to evaluate the SHG. The crystal structures of **4a**, **4b** and **25a** all reveal a virtually coplanar arrangement of the π-termini of the sesquifulvalene ligand (Figure 1, Table 1) as has already been observed in the cymantrenyl congeners.[12][35] The interplanar angle between the five- and seven-membered ring is less than 5°. Within experimental error, the C−C and C−metal dis-



Scheme 6. Formation of the 5,5′-bithienylene bridged monohydro-sesquifulvalene complex **20**: (i) THF, 2-(C_4H_3S)MgBr (**18**), $NiCl_2$dppe; (ii) 1. THF, −78 °C, *n*BuLi, 2. $ZnCl_2$; (iii) THF FcI, $Pd(PPh_3)_4$; (iv) toluene, reflux

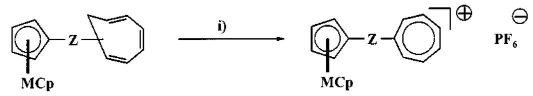


Scheme 7. Synthesis of the vinylenethienylene bridged monohydro-sesquifulvalene complex **24**: (i). 1. THF, −78 °C, *n*BuLi, 2. DMF; (ii) THF, *n*BuLi, $[FcCH_2PPh_3]I$

tances in the metallocene moieties are very similar to the corresponding structural data of other metallocene derivatives. The C−C bond lengths of the seven-membered ring in **4a** and **4b** show a small but distinct bond alternation suggesting a slight contribution of the polyene resonance structure **A** (vide supra) to the ground state. Concomitantly the C−C bond linking the five- and seven-membered rings is somewhat shorter than expected for a sp^2-sp^2 carbon-carbon bond. Additionally, it is worth mentioning that the vector of the connecting bond between the two π-termini in **4a** and **4b** is slightly tilted towards the metal centre indicating the electron-withdrawing property of the tropylium part[36] (Table 1).

Redox Properties

The ferrocenyl-containing compounds reveal an electrochemically reversible one-electron oxidation (Figure 2) which is anodically shifted with respect to ferrocene. The amount of the anodic shift depends on the length of the π-linker (Table 2). The reduction of the sesquifulvalene complexes occurs in an irreversible one-electron transfer and at very similar potentials as reported for the unsubstituted tropylium cation.[37] The peak potential E_{pc} also depends on the length of the π-connection. Comparable trends in the redox behaviour are observed for the ruthenocenyl-containing complexes, although the oxidation step is normally



M	Z	
Fe	-	**4a**
Ru	-	**4b**
Fe	*E*-CH=CH	**25a**
Ru	*E*-CH=CH	**25b**
Fe	$(E\text{-CH=CH})_2$	**26**
Fe	$(E\text{-CH=CH})_3$	**27**
Fe	2,5-C_4H_2S	**28**
Fe	5,5'-[2,2'-(C_4H_2S)]	**29**
Fe	2-(5-*E*-CH=CH)C_4H_2S	**30**

Scheme 8. Synthesis of the cationic mononuclear sesquifulvalene complexes by hydride abstraction: (i) CH_2Cl_2, $[Ph_3C][PF_6]$

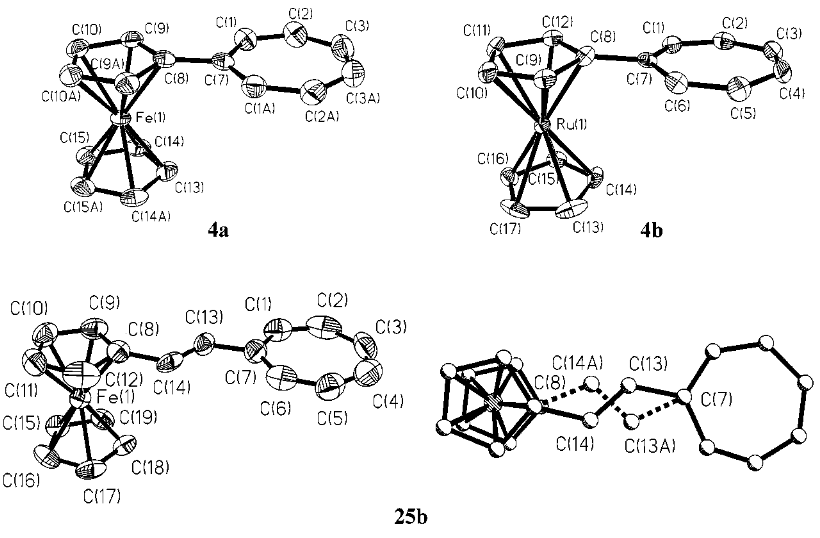


Figure 1. Molecular structures of **4a**, **4b** and **25a** (50% ellipsoids; for **25a** the disordered double bonds are additionally shown (right); the hydrogen atoms, counter ions (BF_4^- and PF_6^-, respectively) and solvent molecules are omitted for clarity)

400−700 mV more anodically shifted (Table 2), and includes an irreversible two-electron transfer.[38] As the π-bridge between the electrophores is extended, the difference of the potentials Δ*E* between the oxidation and reduction resembles more and more the Δ*E* value between the oxidation of the free metallocene and the reduction of the unsubstituted tropylium cation.

The electrochemical data make clear that in these sesquifulvalene complexes the nature of the HOMO is still dominated by the neutral donating sandwich units, whereas the character of the LUMO is determined by the cationic tropylium moiety. This combination favours a dipole change upon electronic excitation from the HOMO to the LUMO; ΔE is a relative measure of the energy gap between the HOMO and the LUMO.

Electronic Absorption Spectra

The UV/Vis spectra of the complexes under study are comparable in that the spectra consist of two strong absorption bands in the visible region (Figure 3) with the exception of the ruthenocenyl derivatives in which the high energy absorption bands are shifted towards the near-UV. As can be seen from Table 3 the electronic excitations are governed by a strong blue-shift on increasing the solvent polarity. This strong negative solvatochromism indicates that in the ground state the positive charge is more or less localised on the tropylium moiety of the complexes, whereas upon excitation the positive charge is delocalized or even localised on the opposite part of the complex.

Figure 3 demonstrates the influence of the length of the π-bridge on the electronic absorption spectra: whereas the high energy absorption band is still considerably red shifted, when the π-linker is elongated the longer wavelength absorption band moves to a certain value which may be regarded as the merocyanine limit[39][40] of these mononuclear sesquifulvalene complexes. This behaviour is in accordance with the assignment of the low energy absorption band to a donor-acceptor charge transfer (DA−CT) transition. As can be deduced from the electrochemical data the oxidation potential of the ferrocenyl donor continuously approaches the potential of free ferrocene as the π-bridge is extended; similarly, the reduction potential of the acceptor tends towards that of the unsubstituted tropylium cation. Therefore, the energy difference between the donor (HOMO) and the acceptor (LUMO) orbitals has to reach a constant value with increasing π-bridge length, and thus the excitation energy must also reach a limiting value. The close relationship between the electrochemical data and the UV/Vis spectroscopic results is demonstrated by a graphical representation of the Δ*E* values of the ferrocene-containing complexes as a function of the λ_{max} value of the DA−CT transition (Figure 4).

Table 1. Selected structural data of **4a**, **4b**, and **25a**

Interatomic distances (pm)	**4a**	**4b**	**25a**
C8−C12		145.4(7)	140.6(15)
C8−C9	144.6(3)	144.4(7)	143.9(13)
C9−C10	142.7(4)	141.5(7)	139.5(15)
C10−C11	141.2(6)[a]	143.3(7)	139.4(16)
C11−C12		142.6(7)	141.6(17)
C7−C1	141.5(3)	141.5(7)	137.9(15)
C1−C2	137.7(4)	137.0(7)	140.9(17)
C2−C3	140.0(4)	141.4(8)	145(2)
C3−C4	136.1(7)[b]	136.2(8)	138(2)
C4−C5		140.7(8)	132.9(19)
C5−C6		138.9(7)	131.2(17)
C6−C7		141.0(7)	141.7(14)
M−C8	203.5(3)	215.8(5)	204.2(9)
M−C9	204.8(3)	218.0(5)	202.7(10)
M−C10	206.8(3)	220.5(5)	205.5(11)
M−C11		221.3(5)	205.4(10)
M−C12		216.9(5)	201.3(11)
C7−C8	145.0(5)	147.2(7)	
C8−C13			146.0(19)
C13−C14			131(3)
C7−C14			145(2)
Angles/°			
C8−12[c]/[bridge][d]	175.5°	174.0°	169.8°
[bridge][d]/C1−7[e]	177.0°	177.5°	173.7°
C8−12/C1−7	0°	3.84°	1.69°

[a] Interatomic distance C10−C10a. − [b] Interatomic distance C3−C3a. − [c] C8−12: plane of the five-membered ring. − [d] [bridge]: vector of the C7−C8 bond for **4a** and **4b**, and plane defined by the carbon atoms C7, C8, C13 and C14 for complex **25a**. − [e] C1−7: plane of the seven-membered rings.

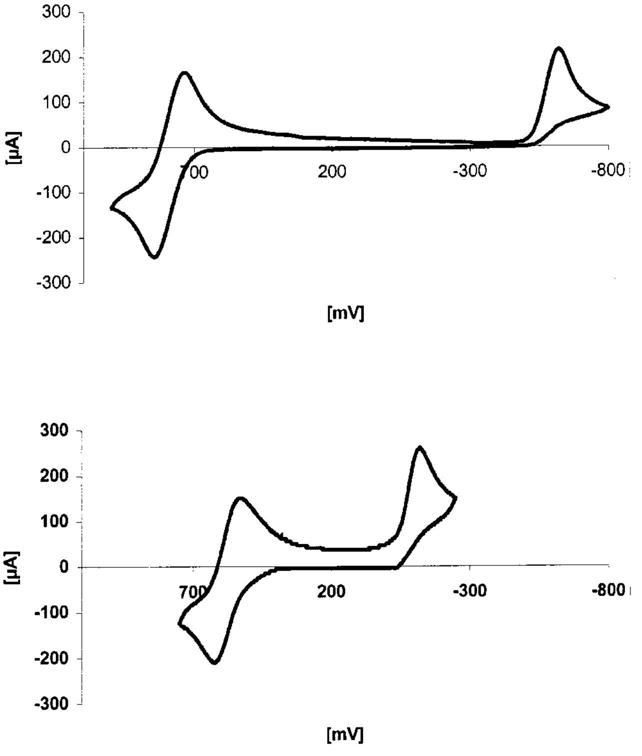


Figure 2. Representative cyclic voltammograms of mononuclear sesquifulvalene complexes: **4a** (top) and **27** (bottom) (E vs. Ag/AgI)

Table 2. Redox potentials[a] of the cationic mononuclear sesquifulvalene complexes of the general form of **3**

ML_n	Z		$E_{1/2}$[a,b]	E_{pc}[a,b,c]	ΔE[b]
FeCp[d]	−	**4a**	0.40	−0.82	1.22
FeCp[d]	*E*-CH=CH	**25a**	0.22	−0.68	0.90
FeCp[d]	(*E*-CH=CH)$_2$	**26**	0.08	−0.60	0.68
FeCp[d]	(*E*-CH=CH)$_3$	**27**	0.09	−0.58	0.67
FeCp[d]	2,5-C_4H_2S	**28**	0.20	−0.66	0.82
FeCp[d]	5,5′-(2,2′-C_4H_2S)$_2$	**29**	0.10	−0.62	0.72
FeCp[d]	2-(5-*E*-CH=CH)C_4H_2S	**30**	0.10	−0.61	0.71
RuCp[e]	−	**4b**	1.12[f]	−0.85	1.97
RuCp[e]	*E*-CH=CH	**25b**	0.61[f]	−0.68	1.29
			0.61[f,g]	−	−
$[(C_7H_7)]PF_6$[e]	−	**−**	−	−0.63[h]	

[a] vs. $[FeCp_2]/[FeCp_2]^+$. − [b] in Volts. − [c] Irreversible one-electron reduction, scan rate 100 mV. − [d] In CH_2Cl_2. − [e] In $MeNO_2$. − [f] Irreversible oxidation. − [g] This work, other data ref.[38] − [h] This work, other data ref.[37]

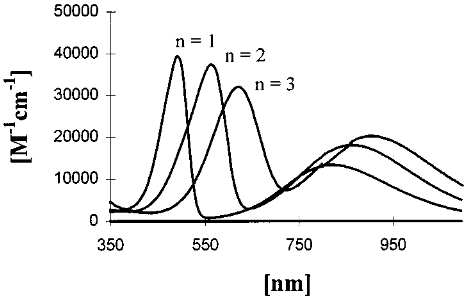


Figure 3. Representative UV/Vis spectra of mononuclear sesquifulvalene complexes $[Fc(E\text{-}CH{=}CH)_nC_7H_6]^+$ demonstrating the effect of different numbers of olefinic spacers between the five- and seven-membered rings on the absorption maxima

The assignment of the low-energy absorption to the DA−CT transition is also in agreement with the results of the organic dye studies in that unusually long-wavelength absorptions are to be expected when the HOMO and the LUMO are located in different parts of the molecule.[40] Additionally, this assignment is corroborated by the relationship of the positions of the absorption bands on the nature of the donor: the absorption band at higher energy is considerably less influenced than the low lying absorption band upon changing the donating capability as demonstrated for **4a**, **4b** and **25a**, **25b**. It is therefore supposed that the higher-lying absorption band is due to an interligand π-π* transition (LL−CT), which also agrees with the dramatic bathochromic shift of this absorption band when the number of double bonds between the five- and seven-membered ring increases. Several theoretical models[2] have been proposed in an attempt to understand and relate the electronic structure of metallocenyl chromophores to their spectroscopic properties. Our assignment of the absorption bands is in excellent agreement with the latest theoretical treatment[2c] and is based on experimental results.

Non-Linear Optical Studies

The low lying excited states, the facile polarizability and the assignment of the HOMO and LUMO to the donor

Table 3. UV/Vis data of the monometallic sesquifulvalene complexes of the general form of **3**

ML_n	Z		LL−CT λ_{max}[a] (ε)[b]		$\Delta\tilde{\nu}$[c]	DA−CT λ_{max}[a] (ε)[b]		$\Delta\tilde{\nu}$[c]
			CH_2Cl_2	$MeNO_2$		CH_2Cl_2	$MeNO_2$	
FeCp	–	**4a**	400 (14710)	395 (13360)	−316	726 (3570)	700 (3330)	−511
FeCp	*E*-CH=CH	**25a**	490 (39440)	470 (24360)	−868	816 (10460)	765 (9510)	−817
FeCp	(*E*-CH=CH)$_2$	**26**	560 (37380)	520 (24860)	−1373	865 (18090)	780 (12770)	−1260
FeCp	(*E*-CH=CH)$_3$	**27**	621 (32040)	542 (43645)	−2347	903 (20215)	782 (23900)	−1714
FeCp	2,5-C_4H_2S[d]	**28**	530 (42870)	510 (33690)	−740	845 (11210)	760 (9470)	−1324
FeCp	5,5′-[2,2′-$C_4H_2S)_2$][e]	**29**	618 (31130)	560 (27800)	−1676	844 (11210)	700 (9820)	−2437
FeCp	2-(5-*E*-CH=CH)C_4H_2S[f]	**30**	595 20550)	520 (34820)	−2424	885 (8120)	775 (2440)	−1604
RuCp	–	**4b**	410 (14020)	398 (6660)	−740	560 (7360)	536 (18657)	−800
RuCp	*E*-CH=CH	**25b**	477 (16270)	455 (12040)	−1014	642 (22560)	600 (20345)	

[a] In nm. – [b] In $M^{-1}cm^{-1}$. – [c] In cm^{-1}. – [d] 2,5-thienylene bridge. – [e] 5,5′-(2,2′-dithienylene) bridge. – [f] 2-(5-*E*-vinylene)thienylene bridge.

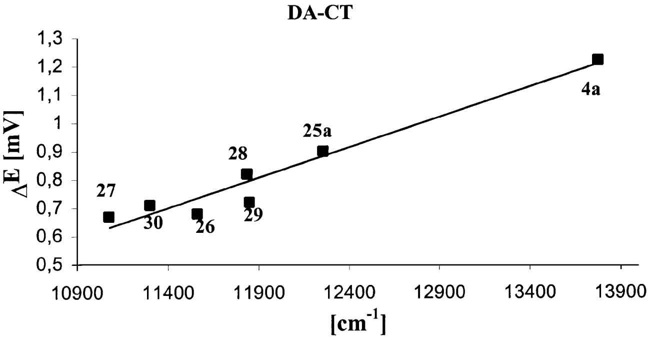


Figure 4. Correlation between the difference of the redox potentials and the λ_{max} values of the DA−CT bands of the ferrocenyl containing sesquifulvalene complexes

and acceptor orbitals, respectively, make sesquifulvalene type complexes most promising NLO candidates. Therefore these complexes were subjected to HRS studies. However, an intrinsic shortcoming of this method may be fluorescence due to two-photon absorption.[41−43]

Using the two-level approximation (Equation 1)[44] to calculate the first hyperpolarizability β indicates that β increases when the energy difference $\Delta E = \hbar\omega_{eg}$ between the ground and the excited states decreases. Nevertheless, in an HRS experiment, the excited state will not be populated although the uptake of two photons of the irradiating frequency ω, and the instantaneous emission of one photon of 2ω will be more probable as the energy $E_{2\omega}$ approaches the energy of the excited state (E_{eg}).[45] When $E_{2\omega}$ equals E_{eg}, the CT state can be populated by the absorption of two photons, whereupon relaxation can occur by means of fluorescence, which may affect considerably the intensity of the measured frequency of the HRS signal (Figure 5).

Since the realisation of the problem of multiphoton absorption-induced fluorescence concerning the determination of first hyperpolarizabilities using the HRS method, several techniques to overcome this problem have been investigated. These include long wavelength measurement,[47a,47b] time resolved HRS[47c] and the measurement of the two-photon fluorescence spectrum to abstract the fluorescence contribution to the HRS signal.[47d] Recently, Persoons et al.[47e] reported a high frequency demodulating technique to suppress the multiphoton fluorescence contribution to the HRS signal.

$$\beta\ (-2\omega,\omega,\omega)=\frac{3\Delta\mu g M_{eg}^2}{(\hbar\omega)^2}\cdot\frac{\omega_{eg}^2}{(1-4\omega/\omega_{eg}^2)\cdot(\omega_{eg}^2-\omega^2)} \qquad (1)$$

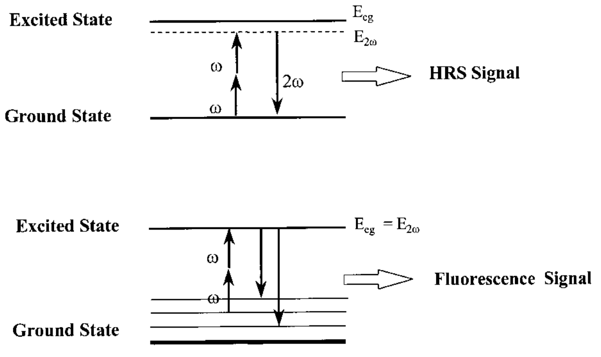


Figure 5. Schematic drawing of the origin of the HRS and the fluorescence signal

In order to check for fluorescence enhancement of the complexes under study we introduced bandpass filters with peak transmittances at different wavelengths in front of the photomultiplier of the HRS set-up.[46] A fluorescence signal should have a very broad line width and a maximum of the emission band which occurs at λ/2 only by chance.[47d] In sharp contrast to this the line width of the HRS signal is narrow and the maximum has to be fixed. In our investigations we used a Q-switched Nd:YAG laser with λ =

1064 nm, and detected the intensity of the scattered light at λ = 532 nm to determine the first hyperpolarizability as well as at λ = 400, 450, 500, 560, 600, 650 and 700 nm to obtain indications of fluorescence.

In Figure 6 the corresponding absorption and emission spectra of the reference *p*-nitroaniline (pNA) are shown corroborating the emission characteristics of the HRS signal of the second harmonic. Comparable HRS signals were recorded for the ruthenocenyl-containing sesquifulvalene complexes **4b** and **25b** as shown in Figure 7, whereas most of the ferrocene derivatives reveal broader emission spectra with a maximum not at λ = 532 nm (Figure 8), indicating that these ferrocene derivatives exhibit fluorescence. In some cases the solutions of the compounds under study were irradiated at the wavelength of the absorption bands. The failure of any subsequent fluorescence is a strong indication that the fluorescence for the ferrocene derivatives originates from a two-photon absorption.

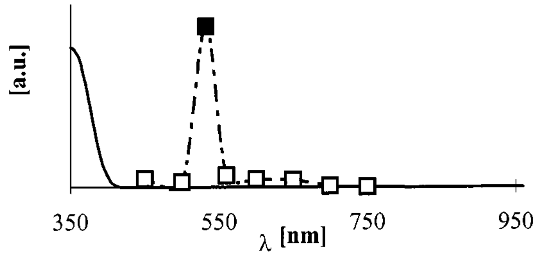


Figure 6. Absorption and emission spectra of the HRS reference *p*-nitroaniline (pNA) (irradiation wavelength λ = 1064 nm) [squares: λ of measured emission intensities; filled square: position of the HRS signal (λ = 532 nm)]

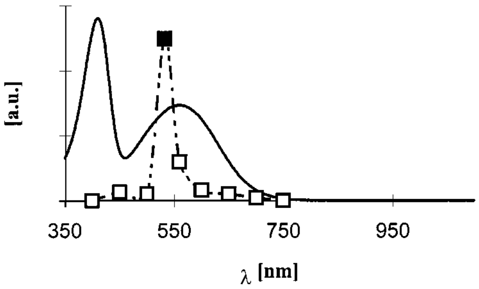


Figure 7. Absorption and emission spectra of the ruthenium sesquifulvalene complex **4b** (irradiation wavelength λ = 1064 nm; squares: λ of measured emission intensities; filled square: position of the HRS signal (λ = 532 nm))

In Table 4 the determined β values of the nonfluorescent complexes **4b** and **25b** are shown. Comparing the experimental first hyperpolarizability β and the calculated static hyperpolarizability β_0[50] of **4b** and **25b** it is obvious that the β_0 values are less reliable as the DA−CT maximum approaches the position of the HRS signal. Several features of the estimated β and β_0 values are remarkable:

- As expected from organic NLO chromophores, the first hyperpolarizability increases with increasing chain length (compare **4b** and **25b**). The β and β_0 value of **25b** determined from CH_2Cl_2 and $MeNO_2$ solutions confirm the long wavelength absorption as the DA−CT absorption band and its greater contribution to the first hyperpolarizability. Upon changing the solvent from CH_2Cl_2 to $MeNO_2$ both absorption bands undergo a distinct blue shift, which brings the low energy donor-acceptor absorption band closer to the HRS signal, whereas the LL−CT absorption band is shifted further away; thus, the resonance enhancement is greater for **25b** in $MeNO_2$ than in CH_2Cl_2 solution.
- These results illustrate that the metallocenes are stronger electron donors than cymantrenyl derivatives.
- Compared to other organometallic mononuclear NLO chromophores with extended π-linkers the results are very promising with regard to the short donor-acceptor distance in the sesquifulvalene-type complexes.

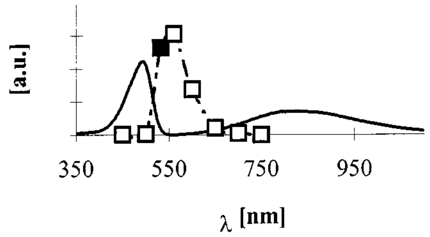


Figure 8. Absorption and emission spectra of the ferrocenyl-containing sesquifulvalene complex **25a** (irradiation wavelength λ = 1064 nm; squares: λ of measured emission intensities; filled square: position of the HRS signal (λ = 532 nm))

A comparison of the SHG effect between other ferrocenyl complexes[1d,2,36,49] and the corresponding mononuclear sesquifulvalene congeners (**4a**, **25a, 26−30**) is not possible since the latter ferrocene derivatives all show fluorescence. However, our results demonstrate the necessity to check the ferrocenyl-containing D-π-A complexes for fluorescence. Much less work has been performed on NLO chromophores with a ruthenocenyl unit as a donor.[2a, 49] The published data have been obtained from EFISH-measurements at 1.907 μm. In addition to the problem of comparing EFISH and HRS data[41][42] a very recent paper show that first hyperpolarizabilities obtained at different fundamental wavelengths can hardly be compared. However, the β and β_0 values of **25b** listed in Table 4 correspond to values obtained for other sesquifulvalene complexes with ferrocenyl donor units.[11a,51,52]

Conclusions

Various synthetic routes to different dipolar cationic, mononuclear sesquifulvalene complexes, whose application as NLO chromophores appears to be successful, have been reported. Despite the relatively short dipole lengths, strong NLO effects can be obtained which are very promising with respect to longer π-linkers between the neutral donating sandwich and the cationic acceptor group of the seven-membered ring moiety.

Modification of the electronic properties of the donors and acceptors, and of the π-bridge, by chemical means presents the possibility of modulating the NLO properties in-

Table 4. Experimental first hyperpolarizability β[a] and static first hyperpolarizability β_0 (calcd. from Equation 1) of sesquifulvalene complexes tested as nonfluorescent, and examples from the literature for comparison

ML_n		acceptor	Z	λ_{max} [nm]	$\beta \times 10^{30}$ [esu]	$\beta_0 \times 10^{30}$ [esu]	ref.
RuCp[b]	**4b**	$C_7H_6^+$	–	536	378	4	
RuCp	**25b**	$C_7H_6^+$	*E*-CH=CH	600[b]	649	120	
				640[d]	362	105	
$Mn(CO)_3$[c]		$C_7H_6^+$	–	506	38		12
$Mn(CO)_2P(OMe)_3$[c]		$C_7H_6^+$	–	581	53		12
$Mn(CO)_3$[c]		$C_7H_6^+$	C≡C	491	95		12
$Mn(CO)_2P(OMe)_3$[c]		$C_7H_6^+$	C≡C	583	151		12
$Ind(Ph_3P)_2Ru$[b]		$Ph-NO_2$	C≡C	476	746	119	48a
$Cp(Ph_3P)_2Ru$[e]		*p*-$C_6H_4NO_2$	C≡C−C_6H_4-4-*E*-CH=CH	476	1455	232	48b
FeCp		$Ind(Ph_3P)_2Ru^+$	=C=CH−CH=CH	301[d]	117	73	49a
FeCp		$(\eta^5\text{-}C_4H_3S)Mn(CO)_3^+$	–	514[b]	260	13	49b
FeCp		$(\eta^5\text{-}C_4H_3S)Mn(CO)_3^+$	*E*-CH=CH	536[b]	670	−8	49b
FeCp		$(\eta^5\text{-}C_4H_3S)Mn(CO)_3^+$	$(E\text{-}CH=CH)_2$	548[b]	771	34	49b

[a] Determined by hyper-Rayleigh scattering. – [b] Measured in $MeNO_2$, reference: pNA ($\beta = 34.6 \times 10^{-30}$ esu).[46] – [c] Measured in MeCN, reference: pNA ($\beta = 29.2 \times 10^{-30}$ esu). – [d] Measured in CH_2Cl_2, reference: pNA ($\beta = 21.6 \times 10^{-30}$ esu).[46] – [e] Measured in thf, reference: pNA ($\beta = 21.4 \times 10^{-30}$ esu).

volving the results of the first hyperpolarizability β and of the influence on the two-photon absorption. The two-photon fluorescence is observed in particular for mononuclear ferrocenyl derivatives possessing low-lying DA−CT and LL−CT transitions, and is not necessarily a disadvantage because of its potential use in devices for NIR detectors and optical data storage.[53]

Since the chemical modification of metallocenes, particularly ferrocene, is straightforward,[54] the linkage of the sesquifulvalene-type NLO chromophores to polymers or liquid crystalline phases is quite obvious. On the other hand the presented cationic complexes are amphiphilic; hence, they may also have some potential applications for Langmuir−Blodgett films.

Experimental Section

Manipulations were carried out under a N_2 atmosphere and solvents were saturated with N_2. Tetrahydrofuran (THF), diethyl ether (Et_2O), dimethoxyethane (DME), hexane and toluene were freshly distilled from the appropriate alkali metal or metal alloy. Nitromethane ($MeNO_2$), acetonitrile (MeCN) and dichloromethane (CH_2Cl_2) were dried over CaH_2 and distilled under N_2. NMR: Bruker AM 360 and Varian Gemini 200 BB; UV/Vis: Perkin−Elmer Model 554; IR nujol mull, KBr cells, FT-IR 1720X (Perkin−Elmer); EI-MS: 70 eV, Finnigan MAT 311 A; elemental analysis: Heraeus CHN-O-Rapid, Institut für Anorganische und Angewandte Chemie, Universität Hamburg. Formylferrocene, formylruthenocene,[17] chloromethylcycloheptatriene,[16] $BaMnO_4$,[18] 2-bromo-5-cyclohepta-2′,4′,6′-trien-1-ylthiophene (**16**),[22] 2-cycloheptatrienyl-2′,5-bithiophene (**19**)[26] and 2-formyl-5-cycloheptatrienylthiophene (**22**)[30] were synthesised according to literature procedures.

Ferrocenyltropylium Hexafluorophosphate (4a) and Ruthenocenyltropylium Hexafluorophosphate (4b). − Method A

4a: Ferrocene (1.22 g, 6.56 mmol) and tropylium hexafluorophosphate (0.62 g, 2.62 mmol) were stirred in MeCN (30 mL) for 65 h at room temperature. The reaction mixture was filtered and the deep blue-green filtrate was evaporated to dryness. The residue was extracted with toluene to remove the unreacted metallocene, and redissolved in CH_2Cl_2. The product 4a was precipitated by the addition of diethyl ether. Yield: 0.77 g (69.8%). Generally, the product was contaminated by paramagnetic impurities and $[C_7H_7][PF_6]$. Recrystallisation to obtain pure 4a lowers the yield considerably (for spectroscopic data: see below)

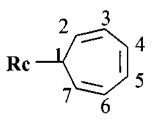
4b: Ruthenocene (0.32 g, 1.4 mmol) and tropylium hexafluorophosphate (0.20 g, 0.85 mmol) were stirred in 1,2-$C_2H_4Cl_2$ (30 mL) at 85°C for 50 h. The workup procedure as described for **4a** yielded 0.25 g (62.8%) of deep blue-violet crystals (for spectroscopic data: see below).

Method B

(Cyclohepta-2,4,6-trien-1-yl)ferrocene (5a): The synthesis of **5a** has been described elsewhere.[11a]

(Cyclohepta-2,4,6-trien-1-yl)ruthenocene (5b): Tropylium hexafluorophosphate (2.60 g, 11 mmol) was added portionwise to a suspension of ruthenocenyl lithium (2.37 g, 10 mmol) in Et_2O (50 mL) at −20 to −30°C. The reaction mixture was allowed to warm slowly to room temperature. After stirring for an additional three hours the solvent was evaporated and the colourless residue extracted with *n*-hexane. The product **5b** was obtained as slightly yellow crystals upon concentration of the hexane extracts. Yield: 2.41 g (75%).

5b: ^1H NMR ($CDCl_3$): $\delta = 2.28$ (t, $J = 5$ Hz, 1 H, H-1), 4.56 (t, 2 H, C_5H_4), 4.57 (s, 5 H, Cp), 4.67 (t, 2 H, C_5H_4), 5.27 (dd, $J = 3$ Hz, $J = 5$ Hz, 2 H, H-2,7), 6.16 (m, 2 H, H-3,6), 6.68 (t, $J = 3$ Hz, 2 H, H-4,5). − ^{13}C NMR ($CDCl_3$): $\delta = 38.2$ (C1), 70.0, 70.6 (C_5H_4, Cp), 94.7 (C_5H_4), 123.6 (C4,5), 127.4 (C2,7), 130.9 (C3,6).



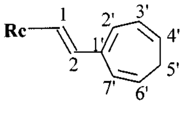
5b

− UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]) 288 (1530), 335 (sh). − EI-MS: *m/z* (%) 322 (80) [$M^+ + 1$], 321 (100) [M^+]. − $C_{17}H_{16}Ru$ (321.4): calcd. C 63.53, H 5.02; found C 63.45, H 5.13.

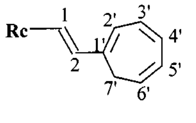
(Cyclohepta-1,3,5-trien-1-ylmethyl)diethylphosphonate (6): 1-Chloromethyl-1,3,5-cycloheptatriene[16](10.0 g, 71 mmol) was stirred in triethylphosphite (13.4 mL, 78 mmol) at 166°C for 8 h. After cooling, the reaction mixture was distilled at 2×10^{-2} mbar. Unreacted 1-chloromethylcyclohepa-1,3,5-triene was recovered at 30°C, and the product **6** obtained at 80°C as a yellow oil. Yield: 13.07 g (76%). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.36 (t, 6 H, CH_2CH_3), 2.48 (d, 2 H, C_7H_7), 2.81 (d, J_{PH} = 23 Hz, 2 H, CH_2P), 4.07 (m, 4 H, CH_2CH_3), 5.38−5.49 (m, 1 H, C_7H_7), 6.12 (m, 2 H, C_7H_7), 6.42−6.62 (m, 2 H, C_7H_7). − EI-MS: *m/z* (%) 242 (12) [M^+], 213 (19) [M^+ − Et], 185 (10) [M^+ − 2Et], 105 (40) [$C_8H_9^+$], 104 (100) [$C_8H_8^+$], 91 (23) [$C_7H_7^+$].

1-(Ferrocenyl)-2-(cycloheptatrienyl)ethene (8a): Complex **7a** was first synthesized by a Wittig reaction of formylferrocene[17] with $Ph_3PCH_2C_7H_7$ to yield a *Z*/*E* mixture of products.[11] Pure *E* isomers could be obtained from the WHWE reaction of formylferrocene with the phosphonate **6** as described for the ruthenocenyl derivative below.

1-Ruthenocenyl-2-(cycloheptatrienyl)ethene (8b): To a solution of the phosphonate **6** (0.57 g, 2.3 mmol) in 2 mL THF at −78°C was added *n*BuLi (1.6 mL of a 1.66 M hexane solution). The reaction mixture was allowed to warm to room temperature, stirred for 1 h and cooled down again to −78° C. Subsequently a solution of formylruthenocene (0.53 g, 2 mmol) in 20 mL of THF was added. The reaction mixture was allowed to warm slowly to room temperature. When the reaction, the course of which was monitored by TLC, had finished, the solvent was evaporated in vacuo, and the residue extracted with hexane. The product **8b** was purified by column chromatography (SiO_2/5% H_2O; hexane/Et_2O 1:1). Yield: 514 mg (75%) of **8b**. As can be deduced from the ^1H NMR spectra, the product is a mixture of two isomers which differ in the position of the sp^3-carbon atom in the seven-membered ring. The minor isomer (30%) is 1-ruthenocenyl-2-(cyclohepta-1′,3′,6′-trien-1′-yl)ethene (isomer A), and the main product is 1-ruthenocenyl-2-(cyclohepta-1′,3′,5′-triene-1′-yl)ethene (isomer B). Both isomers are discernible by the splitting pattern of the high field signal of the sp^3 carbon bound protons between 2 and 3 ppm.



A



B

^1H NMR (200 MHz, $CDCl_3$): δ = 2.32 (t, *J* = 6.6 Hz, 2 H, H-5, isomer A), 2.60 (d, *J* = 7.1 Hz, 2 H, H-7′, isomer B), 4.52 (s, 5 H, C_5H_5), 4.58 (m, 2 H, C_5H_4), 4.79 (m. 2 H, C_5H_4), 5.36−5.54 (m, C_7H_7), 6.12−6.56 (m, C_7H_7, H-1, H-2). − EI-MS: *m/z* (%): 260 (67) [M^+], 232 (100) [$C_{10}H_{10}Ru^+$], 167 (56) [$C_5H_5Ru^+$]. − $C_{19}H_{18}Ru$ (347.4): calcd. C 65.69, H 5.22; found C 65.52, H 5.55.

1-Ferrocenyl-2-(ethoxycarbonyl)ethene (9): To a solution of (ethoxycarbonylmethyl)diethylphosphonate (2.78 g, 12 mmol) in toluene (100 mL) at 0°C was added *n*BuLi (7.8 mL of a 1.6 M hexane solution). Stirring was continued for 1 h, and then the reaction mixture was allowed to warm to room temperature. Subsequently it was cooled to 0°C, and a solution of formylferrocene (2.88 g, 14 mmol) in toluene (20 mL) was slowly added. After stirring for 1 h at room temperature the reaction mixture was hydrolysed and extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and the solvent evaporated in vacuo. The residue was purified by column chromatography (Al_2O_3, neutral, 5% H_2O, hexane/diethyl ether 10:1). Yield: 3.15 g (90%). − ^1H NMR (200 MHz, C_6D_6): δ = 1.05 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.48 (s, 5 H, C_5H_5), 3.90−4.10 (m, 2 H, C_5H_4), 4.10−4.20 (m, 4 H, CH_2, C_5H_4), 6.24 (d, *J* = 15.8 Hz, 1 H, H-1), 7.81 (d, *J* = 15.8 Hz, 1 H, H-2).

3-Ferrocenyl-2-propenol-1 (10): To a suspension of $LiAlH_4$ (0.4 g, 11 mmol) and $AlCl_3$ (0.40 g, 3 mmol) in diethyl ether (10 mL) at −10°C was added a solution of 1-ferrocenyl-2-(ethoxycarbonyl)ethene (**9**) (2.56 g, 9 mmol) in 8 mL diethyl ether. After stirring at room temperature for 1 h the reaction mixture was hydrolyzed at 0°C and acidified with dilute sulfuric acid. The product **10** was isolated by extraction with diethyl ether. Yield: 2.01 g (99%). − ^1H NMR (200 MHz, C_6D_6): δ = 3.9 (m, 2 H, CH_2OH), 3.98 (s, 5 H, C_5H_5), 4.04 (m, 2H. C_5H_4), 4.19 (m, 2 H, C_5H_4), 5.82 (dt, 1 H, H-2), 6.21 (d, 1 H, H-1).

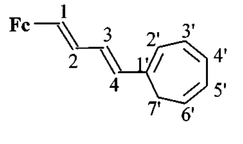
3-Ferrocenylpropenal (11): Barium manganate(VI) (13.9 g, 54 mmol) was added to a solution of 3-ferrocenylpropenol (**10**) (2.01 g, 8.3 mmol) in dichloromethane (50 mL). After 30 min stirring the suspension was filtered and the filtrate evaporated to dryness. The residue was purified by column chromatography (Al_2O_3, neutral, 5% H_2O, hexane/diethyl ether 5:1). Yield: 1.63 g (82%). − ^1H NMR (200 MHz, C_6D_6): δ = 4.17 (s, 5 H, C_5H_5), 4.53 (m, 4H. C_5H_4), 6.34 (dd, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 15.4 Hz, 1 H, H-2), 7.42 (d, $J_{2,3}$ = 15.4 Hz, 1 H, H-3), 9.56 (d, $J_{1,2}$ = 7.6 Hz, H-1).

1-Ferrocenyl-4-(ethoxycarbonyl)-1,3-butadiene: The synthesis of 1-ferrocenyl-4-(ethoxycarbonyl)butadiene-1,3 was performed under the same conditions as the synthesis of 1-ferrocenyl-2-(ethoxycarbonyl)ethene (**9**). Quantities used: 1.02 g (4.22 mmol) of (ethoxycarbonylmethyl)diethylphosphonate, 30 mL of toluene, 2.64 mL (4.22 mmol) of *n*BuLi (15% solution in hexane), 1.01 g (4.22 mmol) of 3-ferrocenylpropenal (**11**) in 10 mL of toluene. Yield: 1.10 g (84%). − ^1H NMR (200 MHz, C_6D_6): δ = 1.06 (t, *J* = 7.2 Hz, 3 H, CH_3), 3.88 (s, 5 H, C_5H_5), 4.00−4.15 (m, 6 H, CH_2, C_5H_4), 5.99 (d, *J* = 15.2 Hz, 1 H, H-1), 6.32 (m, 2 H, H-2, H-3), 7.55−7.62 (m, 1 H, H-4).

5-Ferrocenyl-2,4-pentadienal (13): To a suspension of $LiAlH_4$ (0.135 g, 3.56 mmol) and $AlCl_3$ (0.158 g, 1.18 mmol) in 5 mL of diethyl ether at 10°C was added a solution of 1-ferrocenyl-4-(ethoxycarbonyl)butadiene (1.0 g, 3.22 mmol) in 4 mL of diethyl ether over 20 minutes. After stirring at room temperature for 1 h, the reaction mixture was hydrolysed with dilute sulfuric acid. Subsequently, the reaction mixture was extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The residue of 1-ferrocenyl-1,3-pentadien-1-ol (0.78 g, 2.91 mmol) was dissolved in dichloromethane (20 mL) and oxidised by the addition of $BaMnO_4$ (6.1 g, 24 mmol). After stirring for 30 min the reaction mixture was filtered, the filtrate dried in vacuo and the product purified by column chromatography (Al_2O_3, neutral, 5% H_2O hexane/diethyl ether 5:3). Yield: 0.63 g (81%). − ^1H NMR (200 MHz, C_6D_6): δ = 3.89 (s, 5 H, C_5H_5), 4.08 (m, 2 H, C_5H_4), 4.13 (m, 2 H, C_5H_4), 6.00−6.65 (m, 4 H, H-2 − H-5), 9.54 (d, J = 7.8 Hz, 1 H, H-1).

General Procedure for the Synthesis of Mononuclear Monohydrosesquifulvalene Complexes Containing Two or Three Conjugated Double Bonds: A mixture of NaH, phosphonate **6** and the corresponding aldehyde in dimethoxyethane was slowly warmed to 85° C and stirred for 24 h. After cooling to room temperature the reaction mixture was hydrolyzed and extracted with Et_2O. The organic layer was dried with $MgSO_4$ and the product purified by column chromatography.

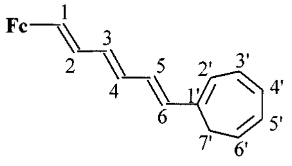
1-Ferrocenyl-4-(cyclohepta-1′,3′,5′-trien-1′-yl)-1,3-butadiene (12): 3-Ferrocenylpropenal (**11**) (1.0 g, 4.42 mmol), phosphonate **6** (1.07 g, 442 mmol), dimethoxyethane (20 mL) and NaH (0.1 g, 4.42 mmol). Column chromatography: Al_2O_3/5% H_2O, hexane/diethyl ether (5:1). Yield: 0.941 g (65%) of **12**.



12

^1H NMR (360 MHz, C_6D_6): δ = 2.70 (d, J = 7.2 Hz, 2 H, H-7′), 4.1 (s, 5 H, C_5H_5), 4.11 (m, 2 H, C_5H_4), 4.28 (m, 2 H, C_5H_4), 5.34 (m, 1 H, H-6′), 6.16 (m, 2 H, C_7H_7), 6.28 (m, 1 H, olefinic bridge) 6.43−6.65 (m, 5 H, C_7H_7 and olefinic bridge). − EI-MS: m/z (%) 328 (100) [M^+], 263 (10) [M^+ − $C_5H_5Fe^+$]. − $C_{21}H_{20}Fe$ (328.2): calcd. C 76.84, H 6.14; found C 75.45, H 6.27.

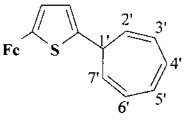
1-Ferrocenyl-6-(cyclohepta-1′,3′,5′-trien-1′-yl)-1,3,5-hexatriene (14): 5-Ferrocenyl-2,4-pentadienal (0.80 g, 3.0 mmol), THF (10 mL), phosphonate **6** (0.73 g, 3 mmol), NaH (0.073 g, 3 mmol). Column chromatography: Al_2O_3/5% H_2O, toluene. Yield: 0.45 g (63%) of **14**.



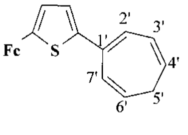
14

^1H NMR (360 MHz, C_6D_6): δ = 2.65 (d, J = 7.0 Hz, 2 H, H-7′), 4.00 (s, 5 H, C_5H_4), 4.11 (t, 2 H, C_5H_4), 4.29 (t, 2 H, C_5H_4), 5.31 (m, 1 H, H-6′), 6.13−6.18 (m, 2 H, C_7H_7), 6.29−6.66 (m, 8 H, olefinic bridge, C_7H_7). − EI-MS: m/z (%): 354 (100) [M^+], 289 (19) [M^+− C_5H_5], 263 (15) [M^+ − C_7H_7], 250 (10), 225 (25), 199 (27), 186 (67) [$C_{10}H_{10}Fe^+$], 121 (65) [$C_5H_5Fe^+$]. − $C_{23}H_{22}Fe$ (354.3): calcd. C 77.98, H 6.26; found C 77.04, H 6.34.

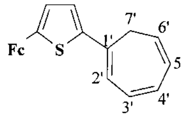
2-Ferrocenyl-5-(cycloheptatrienyl)thiophene (17): A solution of $ZnCl_2(THF)_2$ (3.37 g, 12 mmol) in THF (20 mL) was added to a solution of lithioferrocene[14] at −78 °C. After 20 min stirring at −78 °C the solution was allowed to warm slowly (40 min) to room temperature and a solution of 2-bromo-5-(cyclohepta-2′,4′,6′-trien-1′-yl)thiophene[22] (2.53 g, 10 mmol) and $Pd(PPh_3)_4$ (0.17 g, 0.1 mmol) in THF (40 mL) was added. After 15 h stirring at room temperature the reaction mixture was quenched with water (2 mL). The solvent was evaporated, the residue extracted with Et_2O (200 mL) in the presence of water (100 mL), and the ether layer was washed two times with 100 mL H_2O. The organic layer was dried over $MgSO_4$ and the product was isolated by column chromatography (Al_2O_3/5% H_2O/diethyl ether). Yield: 1.86 g (52%). The product **17** was a mixture of three isomers in the ratio 73% (**17A**), 14% (**17B**), 12% (**17C**). The composition of this mixture can be changed to 40:60 of isomers **17B** and **17C** by thermolysis in xylene (30 mL) under reflux for 33 h. The isomerisation was monitored by the disappearance of the proton signal H-1′ (2.94) of the isomer **17A**.



17A



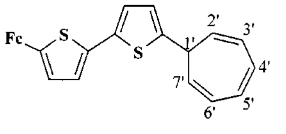
17B



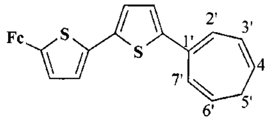
17C

^1H NMR (200 MHz, $CDCl_3$): **17A:** δ = 2.94 (t, 1 H, H-1′),), 4.10 (s, 5 H, C_5H_5) 4.26 (m, 2 H, C_5H_4), 4.54 (m, 2 H, C_5H_4), 5.53 (dd, 2 H, H-2′, H-7′), 6.27 (m, 2 H, H-3′, H-6′), 6.74 (m, 2 H, H-4′, H-5′), 6.80 (d, 1 H, C_4H_2S), 6.87 (d, 1 H, C_4H_2S). **17B**, **17C:** δ = 2.39 (t, J = 6.8 Hz, H-5′, **17B**), 2.81 (d, J = 6.8 Hz, H-7′, **17C**), 4.10 (s, C_5H_5), 4.11 (s, C_5H_5), 4.30 (m, C_5H_4), 4.58 (m, C_5H_4), 5.47−5.59 (m, 2 H, C_7H_7), 6.26 (dd, J = 9.4 Hz, J = 6.2 Hz, C_7H_7), 6.48 (d, J = 9.5 Hz, C_7H_7), 6.56−6.64 (m, C_7H_7), 6.86−7.06 (m, C_4H_2S, C_7H_7), 7.14 (d, J = 3.7 Hz, C_4H_2S), 7.20−7.42 (m, C_7H_7), 7.58−7.64 (m, C_4H_2S). − EI-MS: m/z (%) 358 (100) [M^+], 293 (3) [M^+ − C_5H_5], 202 (25) [M^+ − $C_{12}H_{12}$], 121 (21) [$C_5H_5Fe^+$]. − $C_{21}H_{18}FeS$ (358.3): calcd. C 70.40, H 5.06; found C 71.10, H 5.61.

5-Ferrocenyl-5′-(cycloheptatrienyl)-2,2′-bithiophene (20): To a cooled solution (−78 °C) of 5-(cycloheptatrienyl)-2,2′-bithiophene (**19**) (1.43 g, 5.6 mmol) in 50 mL of THF was added nBuLi (3.5 mL of a 1.6 M hexane solution). The reaction solution was allowed to warm to room temperature, stirred for 40 min and cooled again to −78 °C. A $ZnCl_2(THF)_2$ (1.56 g, 5.6 mmol) solution in THF (10 mL) was then added from a syringe. After warming to room temperature and additional stirring for 10 min this reaction mixture was added to a solution of iodoferrocene (1.73 g, 5.6 mmol) and $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol) in THF (20 mL). The red coloured reaction mixture was stirred for 15 h, hydrolyzed with water (1 mL) and dried in vacuo. The solid residue was extracted with Et_2O, the organic layer was washed with water and dried over $MgSO_4$. The pure product was isolated after column chromatography (Al_2O_3/5% H_2O, hexane/ether 8:2). Yield: 1.36 g (55%) of **20** as the isomer A.



20A



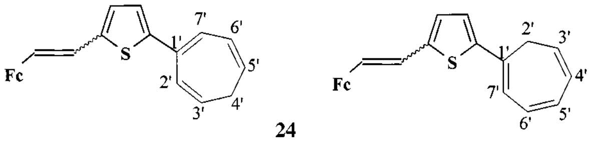
20B

20A: ^1H NMR (360 MHz, C_6D_6): δ = 3.09 (dt, J = 5.6 Hz, J = 1.0 Hz, 1 H, H-1′), 3.98 (s, 5 H, C_5H_5), 4.06 (t, 2 H, C_5H_4), 4.46 (t, 2 H, C_5H_4), 5.46 (dd, J = 8.7 Hz, J = 5.7 Hz, 2 H, H-2′, H-7′), 6.06 (m, 2 H, H-3′, H-6′), 6.52 (m, 2 H, H-4′, H-5′), 6.65 (dd, J = 1.0 Hz, J = 3.6 Hz, 1 H, C_4H_2S), 6.75 (d, J = 3.7 Hz, 1 H, C_4H_2S), 6.94 (d, J = 3.6 Hz, 1 H, C_4H_2S), 6.98 (d, J = 3.6 Hz, 1 H, C_4H_2S).

Thermal Rearrangement of the Isomer 20A: A solution of **20A** (0.77 g, 1.75 mmol) dissolved in toluene (8 mL) was refluxed for 24 h. The solution was evaporated to dryness yielding isomer **20B** quantitatively.

20B: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.16 (t, J = 6.9 Hz, 2 H, H-5′), 3.97 (s, 5 H, C_5H_5), 4.06 (t, 2 H, C_5H_4), 4.46 (t, 2 H, C_5H_4), 5.27 (m, 2 H, H-4′, H-6′), 6.10 (dd, J = 9.2 Hz, J = 6.1 Hz, 1 H, H-3′), 6.44 (d, J = 9.1 Hz, 1 H, H-7′), 6.74 (d, J = 3.7 Hz, 1 H, C_4H_2S), 6.85 (d, J = 3.7 Hz, 1 H, C_4H_2S), 6.95 (d, J = 3.7 Hz, 1 H, C_4H_2S), 6.98 (d, J = 3.7 Hz, 1 H, C_4H_2S), 7.00 (d, J = 6.1 Hz, 1 H, H-2′). − EI-MS: *m*/*z* (%) 440 (100) [M$^+$], 121 (21) [$C_5H_5Fe^+$].

1-Ferrocenyl-2-(5′-cycloheptatrienylthien-2′-yl)ethene (24): To a solution of (ferrocenylmethyl)triphenylphosphonium iodide (4.3 g, 7.4 mmol) in THF (70 mL) was added *n*BuLi (4.63 mL of 1.6 M hexane solution). After stirring for 30 min a solution of a 1:2.5 mixture of 2-(cyclohepta-1,3,5-trien-1-yl)-5-formylthiophene and 2-(cyclohepta-1,3,6-trien-1-yl)-5-formylthiophene (**22**) (1.5 g, 7.4 mmol) in THF (10 mL) was added to the Wittig reagent and subsequently stirred for 14 h. The solvent was evaporated in vacuo, and the residue extracted with hexane. The product was purified by column chromatography (Al_2O_3/5% H_2O, hexane). Yield: 1.87 g (66%) of **24**. The product is a mixture of four isomers composed of two pairs of *Z*-and *E*-isomers which differ in the position of the sp^3-carbon atom of the seven-membered ring corresponding to the isomers **22** used as starting material.



24

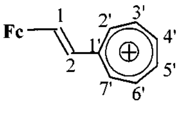
^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.36 and 2.38 (t, J = 6.8 Hz, 2 H, H-5′, *E* and *Z* isomer of **24B**), 2.77 and 2.81 (d, J = 7.2 Hz, 2 H, H-5, *E* and *Z* isomer of **24A**), 4.13 (s, Cp), 4.26 (m, C_5H_4), 4.44 (m, C_5H_4), 5.51 (m, 2 H, C_7H_7), 6.20−7.10 (C_7H_7 and olefinic bridge). − $C_{23}H_{20}FeS$ (384.3): calcd. C 71.88, H 5.25; found C 71.94, H 5.51.

General Procedure for the Formation of the Cationic Mononuclear Sesquifulvalene Complexes by Hydride Abstraction: To a solution of the corresponding neutral monohydro-sesquifulvalene complex in dichloromethane was added an equimolar amount of trityl hexafluorophosphate dissolved in CH_2Cl_2. The reaction mixture was stirred for 30 min, and the cationic sesquifulvalene complex was precipitated by diluting the dark blue (M = Fe) or dark blue-violet (M = Ru) solution with Et_2O. Recrystallisation was performed by diffusion of Et_2O into a CH_2Cl_2 solution of the sesquifulvalene complexes.

4a·PF$_6$: Starting material: 0.352 g (1.16 mmol) of **5a** in 20 mL of dichloromethane, and 0.450 g (1.16 mmol) of trityl hexafluorophosphate in 10 mL of dichloromethane. Yield: 0.324 g (63%). ^{1}H NMR (200 MHz, CD_3NO_2): δ = 4.40 (s, 5 H, C_5H_5), 5.45 (t, J = 2 Hz, 2 H, C_5H_4), 5.51 (t, J = 2 Hz, 2 H, C_5H_4), 8.49−8.78 (m, 6 H, C_7H_6). − ^{13}C NMR (50 MHz, CD_3NO_2): δ = 73.4 (C_5H_4), 75.7 (C_5H_5), 81.8 (C_5H_4), 84.5 (C_q-C_5H_4), 147.9 (C_7H_6), 148.1(C_7H_6), 148.8 (C_7H_6), 175.8 (C_q-C_7H_6). − UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 400 (14710), 725 (3570); (CH_3NO_2): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 395 (13360), 700 (3330). − EI-MS: *m*/*z* (%) 276 (100), [M$^+$ − PF$_6$], 186 (25) [M$^+$ − C_7H_6 − PF$_6$]. − $C_{17}H_{15}$ F_6FeP (420.1): calcd. C 48.60, H 3.60; found C 48.24, H 3.76.

4b·PF$_6$: Starting material: 0.643 g (2.00 mmol) of **5b** in 10 mL of dichloromethane, and 0.777 g (2.00 mmol) trityl hexafluorophosphate in 10 mL of dichloromethane. Yield: 62%. − ^{1}H NMR (200 MHz, CD_3NO_2): δ = 4.74 (s, 5 H, C_5H_5), 5.48 (t, J = 1 Hz, 2 H, C_5H_4), 5.74 (t, J = 1 Hz, 2 H, C_5H_4), 8.44−8.31 (m, 4 H, C_7H_6), 8.67−8.57 (m, 2 H, C_7H_6). − ^{13}C NMR (50 MHz, CD_3NO_2): δ = 73.9 (C_5H_4), 76.8 (C_5H_5), 80.5 (C_5H_4), 88.4 (C_q-C_5H_4), 147.1 (C_7H_6), 149.2 (C_7H_6), 149.4 (C_7H_6), 173.5 (C_q-C_7H_6). − UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 410 (14020), 560 (7360); (CH_3NO_2): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 398 (6655), 536 (3245). − EI-MS: *m*/*z* (%) 322 (10), [M$^+$ − PF$_6$], 232 (20) [M$^+$ − C_7H_6 − PF$_6$]. − $C_{17}H_{15}F_6PRu$ (465.3): calcd. C 43.88, H 3.25; found C 44.07, H 3.54.

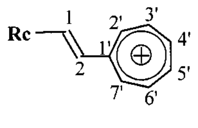
25a·PF$_6$: Starting material: 0.352 g (1.16 mmol) of **8a** in 20 mL of dichloromethane, and 0.450 g (1.16 mmol) of trityl hexafluorophosphate in 10 mL of dichloromethane. Yield: 0.324 g (63%).



25a

^{1}H NMR (200 MHz, CD_3NO_2): δ = 4.43 (s, 5 H, C_5H_5), 5.03 (t, 2 H, C_5H_4), 5.17 (t, 2 H, C_5H_4) 7.10 (d, J = 15.4 Hz, 1 H, H-2), 8.39 (d, J = 15.3 Hz, 1 H, H-1), 8.30−8.59 (m, 4 H, H-3′,6′, H-4′,5′) 8.62 (d, J = 10.4 Hz, 2 H, H-2′,7′). − ^{13}C NMR (50 MHz, CD_3NO_2): δ = 72.9 (C_5H_4), 73.6 (C_5H_5) 78.6 (C_5H_4), 83.8 (C_q-C_5H_4), 126.7 (C2), 147.9 (C_7H_6), 148.5 (C_7H_6), 148.9 (C_7H_6), 156.0 (C1), 164.7 (C_q-C_7H_6). − UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 490 (39440), 816 (10460); (CH_3NO_2): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 470 (24360), 765 (9510). − $C_{19}H_{17}F_6FeP$ (446.2): calcd: C 51.15, H 3.84; found C 51.17, H 3.93.

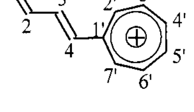
25b·PF$_6$: Starting material: 0.480 g (1.38 mmol) of **8b** in 20 mL of dichloromethane, and 0.538 g (1.38 mmol) of trityl hexafluorophosphate in 10 mL of dichloromethane. Yield: 0.52 g (77%).



25b

^{1}H NMR (200 MHz, CD_3NO_2): δ = 4.78 (s, 5 H, C_5H_5), 5.20 (t, 2 H, C_5H_4), 5.31 (t, 2 H, C_5H_4) 7.08 (d, J = 15.4 Hz, 1 H, H-2), 8.23 (d, J = 15.4 Hz, 1 H, H-1), 8.32−8.40 (m, 4 H, H-3′,6′, H-4′,5′) 8.61 (d, J = 9.7 Hz, 2 H, H-2′,7′). − ^{13}C NMR (50 MHz, CD_3NO_2): δ = 73.5 (C_5H_4), 74.8 (C_5H_5), 77.7 (C_5H_4), 125.0 (C2), 147.6 (C_7H_6), 148.6 (C_7H_6), 149.3 (C_7H_6), 152.3 (C1). − UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 477 (16270), 642 (22560); (CH_3NO_2): λ_{max} [nm] (ε [M^{-1}cm^{-1}]) = 455 (12040), 600 (20345). − $C_{19}H_{17}F_6PRu$ (491.4): calcd: C 46.44, H 3.49; found C 45.86, H 3.74.

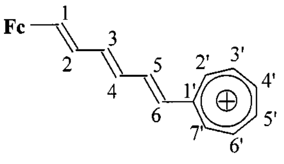
26·PF$_6$: Starting material: 0.392 g (1.2 mmol) of **12** in 20 mL of dichloromethane, and 0.466 g (1.2 mmol) trityl hexafluorophosphate in 10 mL of dichlorohexane. Yield: 0.429 g (76%).



26

^{1}H NMR (200 MHz, CD_3NO_2): δ = 4.43 (s, 5 H, C_5H_5), 4.85 (s, 2 H, C_5H_4), 4.89 (s, 2 H, C_5H_4), 6.97 (dd, $J_{1,2}$ = 14.7 Hz, $J_{2,3}$ = 3.5 Hz, 1 H, H-2), 6.95 (d, $J_{3,4}$ = 14.7 Hz, 1 H, H-4), 8.06 (dd, $J_{3,4}$ = 14.7 Hz, $J_{2,3}$ = 3.4 Hz, 1 H, H-3), 8.26−8.44 (m, 4 H, H-3′,6′, H-4′,5′), 8.53 (d, $J_{1,2}$ = 14.9 Hz, 1 H, H-1), 8.62 (d, J = 10.1 Hz, 2 H, H-2′,7′). − ^{13}C NMR (50 MHz, CD_3NO_2): δ = 71.9 (C_5H_4), 73.2 (C_5H_5), 76.5 (C_5H_4), 78.6 (C_q-C_5H_4), 128.4 (C2), 130.6 (C4), 148.1 (C_7H_6), 148.9 (C_7H_6), 149.0 (C_7H_6), 152.2 (C1), 155.5 (C3), 166.6 (C_q-C_7H_6). − UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 560 (37380), 865 (18090); (CH_3NO_2): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$]) = 520 (24860), 780 (12770). $C_{21}H_{19}F_6FeP$ (472.2): calcd. C 53.42, H 4.06; found C 52.73, H 4.31.

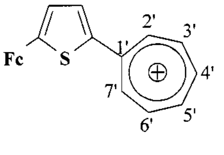
27·PF_6: Starting material: 0.668 g (1.89 mmol) of **14** in 20 mL of dichloromethane, and 0.732 g (1.89 mmol) of trityl hexafluorophosphate in 10 mL of dichloromethane. yield: 0.51 g (54%).



27

^{1}H NMR (360 MHz, CD_2Cl_2): δ = 4.62 (s, 5 H, C_5H_5), 5.18 (m, 4 H, C_5H_4), 6.34 (t, J = 12.7 Hz, 1 H, H-2), 6.47 (t, J = 12.9 Hz, 1 H, H-4), 6.68 (d, J = 14.3 Hz, 1 H, H-6), 7.01 (d, J = 14.5 Hz, 1 H, H-1), 7.27 (t, 1 H, J = 12.7 Hz, H-3), 7.98 (dd, J = 10.0, J = 3.7 Hz, 2 H, C_7H_6), 8.08 (dd, J = 14.6, 11.85 Hz, 1 H, H-5), 8.13 (m, 2 H, C_7H_6), 8.35 (d, J = 10.7 Hz, 2 H, C_7H_6).

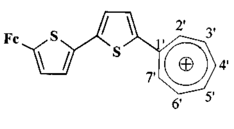
28·PF_6: Starting material: 0.260 g (0.673 mmol) of **17** in 20 mL of dichloromethane, and 0.261 g (0.673 mmol) trityl hexafluorophosphate in 5 mL of dichloromethane. Yield: 0.20 g (60%).



28

^{1}H NMR (200 MHz, CD_3NO_2): δ = 4.25 (s, 5 H, C_5H_5), 4.84 (s, 2 H, C_5H_4), 5.03 (s, 2 H, C_5H_4), 7.45 (d, J = 4.5 Hz, 1 H, C_4H_2S), 8.24 (d, J = 4.4 Hz, 1 H, C_4H_2S), 8.28−8.47 (m, 4 H, H-3′,6′, H-4′,5′), 8.79 (d, J = 10.6 Hz, 2 H, H-2′,7′). − ^{13}C NMR (50 MHz, CD_3NO_2): δ = 70.8 (C_5H_4), 73.5 (C_5H_5), 75.1 (C_5H_4), 78.4 (C_q-C_5H_4), 129.9 (C_4H_2S), 140.6 (C_4H_2S), 141.1 (C_q-C_4H_2S), 146.2 (C_7H_6), 149.4 (C_7H_6), 150.4 (C_7H_6), 160.3 (C_q-C_4H_2S), 168.4 (C_q-C_7H_6). − $C_{21}H_{17}F_6FePS$ (502.2): calcd: C 50.22, H 3.41; found C 50.27, H 3.80.

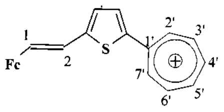
29·PF_6: Starting material: 0.305 g (0.69 mmol) of **20** in 15 mL of dichloromethane, and 0.269 g (0.69 mmol) trityl hexafluorophosphate in 10 mL of dichloromethane. Yield: 0.222 g (55%).



29

^{1}H NMR (200 MHz, CD_3NO_2) δ = 4.37 (s, 5 H, C_5H_5), 5.14 (s, 2 H, C_5H_4), 5.90 (s, 2 H, C_5H_4) 8.13−8.54 (10 H, C_4H_2S and C_7H_6). − ^{13}C NMR (50 MHz, CD_3NO_2): δ = 69.5 (C_5H_4), 72.9 (C_5H_5), 73.1 (C_5H_4), 126.4 (C_4H_2S), 129.4 (C_4H_2S), 131.1 (C_4H_2S), 140.4 (C_4H_2S), 146.4 (C_7H_6), 150.0 (C_7H_6) 150.8 (C_7H_6), (signals of quaternary ^{13}C not observed). − $C_{25}H_{19}F_6FePS$ (552.3): calcd. C 51.39, H 3.28; found C 52.34, H 3.91.

30·PF_6: Starting material: 0.238 g (0.62 mmol) of **24** in 2 mL of dichloromethane, and 0.240 g (0.62 mmol) trityl hexafluorophosphate in 2 mL of dichloromethane. Yield: 0.258 g (79%).



30

^{1}H NMR (200 MHz, CD_2Cl_2) δ = 4.28 (s, 5 H, C_5H_5), 4.70 (m, 4 H, C_5H_4), 6.91 (d, J = 15.6 Hz, 1 H, H-2), 7.34 (d, J = 4.4 Hz, 1 H, C_4H_2S), 7.39 (d, J = 15.4 Hz, 1 H, H-1), 8.17 (d, J = 4.6 Hz, 1 H, C_4H_2S), 8.05 (dd, J = 7.1 Hz, J = 4.1 Hz, 2 H, H-4′,5′), 8.20 (m, 2 H, H-3′,6′), 8.53 (d, J = 10.8 Hz, 2 H, H-2′,7′. − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 69.7 (C_5H_4), 71.2 (C_5H_5), 73.6 (C_5H_4), 81.8 (C_q-C_5H_4), 117.0 (C2), 130.8 (C_4H_2S), 140.2 (C_4H_2S), 142.1 (C1), 144.3 (C_7H_6), 147.1 (C_7H_6), 148.1 (C_7H_6), 163.4 (C_q-C_7H_6). − $C_{23}H_{19}F_6FePS$ (528.3): calcd. C 52.29, H 3.63; found C 52.28, H 3.95.

X-ray Structure Determination : Crystals suitable for an X-ray structure analysis were obtained by diffusion of Et_2O from the gas phase into CH_2Cl_2 solutions of **4a**, **4b** or **25a**. The data were collected on a four-circle diffractometer Hilger & Watts, Mo-K_α, λ = 0.71073 Å. The structures were solved by direct methods (SHELXS-86).[55] Refinement on F^2 were carried out by full-matrix least-square techniques (SHELXL-93).[56] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related by a factor of 1.2 to the value of the equivalent isotropic thermal parameter of their carrier atoms. Weights were optimised in the final refinement cycles (Table 5).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133669 (**4a**), -133670 (**4b**) and -133671 (**25a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Cyclic Voltammetry: An Amel System 5000 was used. The measurements were performed in CH_2Cl_2 and $MeNO_2$ with 0.4 M [N(n-Bu)$_4$]ClO_4 as supporting electrolyte, ca. 10^{-3} M solutions of the complexes, a Pt wire as working electrode and a Pt plate (0.6 cm^2) as auxiliary electrode. The given potentials were measured against Ag/Ag$^+$ and are referenced against $E_{1/2}$([$FeCp_2$]/[$FeCp_2$]$^+$) = 0 V.

Hyper-Rayleigh Scattering: For experimental set-up see ref.[46]; the measurements were performed at a fundamental wavelength of λ = 1064 nm with a Q-switched Nd:YAG laser; CH_2Cl_2 and $MeNO_2$ solutions were used for the measurements, with concentrations of 10^{-4} to 10^{-6} concerning the complexes under study; p-nitroaniline was used as reference [β(CH_2Cl_2) = 21.6 × 10^{-30} esu, β ($MeNO_2$) = 34.6 × 10^{-30} esu].[46]

Table 5. Crystallographic data of **4a**, **4b** and **25a**

	4a	**4b**	**25a**
Formula	$C_{17}H_{15}BF_4Fe$	$C_{17}H_{15}F_6PRu$	$C_{20}H_{19}Cl_2F_6FeP$
M_r	361.95	465.33	531.07
Crystal system	orthorhombic	monoclinic	triclinic
Space group	*Pnma*	*P*2(1)/*c*	$P\bar{1}$
a/Å	21.75(2)	8.104(3)	10.067(6)
b/Å	9.900(2)	18.206(14)	10.496(6)
c/Å	6.881(3)	11.228(4)	11.418(6)
α/°	−	−	94.07(4)
β/°	−	107.59(3)	110.96(4)
γ/°	−	−	102.88(5)
V/Å^3	1482.0(15)	1579.1(15)	1083.1(11)
Z	4	4	2
ρ_{calcd} /g cm^{-3}	1.622	1.957	1.628
abs. coeff./mm^{-1}	1.055	1.156	1.072
T /K	173(2)	173(2)	293(2)
F(000)	736	920	536
Crystal size/mm^3	0.6 × 0.4 × 0.1	0.4 × 0.3 × 0.1	0.4 × 0.5 × 0.1
θ range /°	$2.78 \le \theta \le 30.10$	$2.64 \le \theta \le 27.57$	$2.34 \le \theta \le 24.00$
Index range	$-1 \le h \le 30$	$-1 \le h \le 10$	$-2 \le h \le 11$
	$-13 \le k \le 1$	$-1 \le k \le 23$	$-12 \le k \le 11$
	$-1 \le l \le 9$	$-14 \le l \le 13$	$-13 \le l \le 12$
Total reflns	3134	4590	4715
Unique reflns	2293	3661	3388
Obs. Reflns [I>2σ(I)]	1773	2640	2147
Parameters/restraints	131/0	227/0	327/0
GooF	1.061	1.000	1.039
R_{int}	0.0175	0.0294	0.0571
R indices [$I > 2\ \sigma\ (I)$]	$R1 = 0.0496$	$R1 = 0.0455$	$R1 = 0.0981$
	$wR2 = 0.1172$	$wR2 = 0.0901$	$wR2 = 0.2490$
R indices (all data)	$R1 = 0.0690$	R1 = 0.0778	$R1 = 0.1468$
	$wR2 = 0.1280$	$wR2 = 0.1012$	$wR2 = 0.2916$
Min. max. resd/eÅ^{-3}	−0.647, 0.529	−0.838, 0.775	−0.778, 2.059

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, HE 1309/3) and by the European Community (COST D4/0003/94, TMR FMRX-CT98−0166).

---

[1] [1a] D. J. Williams, *Angew. Chem.* **1984**, *96*, 637−651; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 690−703. − [1b] R. W. Boyd, in *Nonlinear Optics*, Academic Press, Inc, **1992**; G. H. Wagnière, in *Linear and Nonlinear Optical Properties of Molecules*, VCH, Weinheim, **1993**. − [1c] P. N. Prasad, D. J. Williams, in *Nonlinear Optical Effects In Molecules & Polymers*, Wiley & Sons, New York, **1991**. − [1d] *Nonlinear Optics of Organic Molecules and Polymers* (Eds.: H. S. Nalwa, S. Miyata), CRC Press, New York, **1997**. − [1e] K. Meerholz, *Angew. Chem.* **1997**, *109*, 981−985; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 945−949.

[2] [2a] J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder, W. Tam, *J. Am. Chem. Soc.* **1991**, *113*, 7227−7232. − [2b] D. R. Canis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1990**, *112*, 8203−8204. − [2c] D. R. Canis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 10338−10357. − [2d] D. R. Canis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 195−242. − [2e] S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, I. W. Perry, S. R. Marder, *J. Am. Chem. Soc.* **1999**, *121*, 3715−3723.

[3] T. J. Marks, M. A. Ratner, *Angew. Chem.* **1995**, *107*, 167−187; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155−174.

[4] [4a] N. J. Long, *Angew. Chem.* **1995**, *107*, 37−56; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21−38. −[4b] H. S. Nalwa, *Appl. Organomet. Chem.* **1991**, *5*, 349−377. −[4c] I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **1998**, *42*, 291−362. −[4d] T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, A. Persoons, *J. Mater. Chem.* **1997**, *7* (11), 2175−2189.

[5] B. J. Coe, S. Houbrechts, I. Asselberghs, A. Persoons, *Angew. Chem.* **1999**, *111*, 377−380; *Angew. Chem. Int. Ed.* **1999**, *38*, 366−369.

[6] T. Kondo, S. Horiuchi, I. Yagi, S. Ye, K. Uosaki, *J. Am. Chem. Soc.* **1999**, *121*, 391−398.

[7] H. Prinzbach, *Pure Appl. Chem.* **1971**, *28*, 281−329.

[8] J. O. Morley, *J. Am. Chem. Soc.* **1988, 110**, 7660−7663.

[9] G. R. J. Williams, *J. Mol. Struct. (Thermochem)* **1987**, *151*, 215−222.

[10] M. Neuenschwander, W. K. Schenk, *Chimia*. **1972**, *26*, 194−197.

[11] [11a] U. Behrens, H. Bussaard, U. Hagenau, J. Heck, E. Hendrickx, J. Körnich, J. G. M. van der Linden, A. Persoons, A. L. Spek, N. Veldman, B. Voss, H. Wong, *Chem. Eur. J.* **1996**, *2*, 98−103. −[11b] J. Heck, H. C. Brussaard, S. Dabek, T. Meyer-Friedrichsen, H. Wong, *Proc. SPIE, Int. Soc. Opt. Eng.* **1997**, *3*, 53−61.

[12] M. Tamm, A. Grzegorzewski, T. Steiner, T. Jentzsch, W. Werncke, *Organometallics* **1996**, *15*, 4984−4990.

[13] M. Cais, A. Eisenstadt, *J. Am. Chem. Soc.* **1967**, *89*, 5468−5469.

[14] D. Guillaneux, H. B. Kagan, *J. Org. Chem.* **1995**, *60*, 2502−2505.

[15] J. Boutagy, R. Thomas, *Chem.* Rev. **1974**, *74*, 87−99.

[16] L. A. Paquette, H.-J. Kang, C. S. Ra, *J. Am. Chem. Soc.* **1992**, *114*, 7387−7395.

[17] R. Sanders, U. T. Mueller.-Westerhoff, *J. Organomet. Chem.* **1996**, *512*, 219−224.

[18] R. S. Nyholm, P. R. Woolliams, *Inorg. Syn.* **1968**, *11,* 56−61.

[19] F. Effenberger, F. Würthner, *Angew. Chem.* **1993**, *105*, 742−744; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 719−721; F. Effenberger, F. Wüthner, F. Steybe, *J. Org. Chem.* **1995**, *60*, 2082−2091.

[20] J. X. Zhang, P. Dubois, R. Jérôme, *J. Chem. Soc., Perkin Trans. 2* **1997**, 1209−1216; S.-S. P. Chou, C.-H. Shen, *Tetrahedron Letters*, **1997**, *36*, 6407−6410; see also ref.[1d], p. 108 ff.

[21] A. Abbotto, S. Bradamante, A. Facchetti, G. A. Pagani, *J. Org.*

Chem. **1997**, *62*, 5755−5765. D. D. Graf, K. R. Mann, *Inorg. Chem.* **1997**, *36*, 141−149.

[22] Y. Golberg, H. Alper, *J. Org. Chem.* **1993, 58**, 3072−3075.

[23] K. Takahashi, T. Sakae, K. Takase, *Chem. Lett.* **1980**, 179.

[24] W.-Y. Wong, W.-T. Wong *J. Chem. Soc., Dalton Trans.* **1996**, 3209−3214.

[25] [25a] T. Nihira, S. Tarutani, K. Takase, K. Takahashi *Heteroycles*, **1995** *41*, 2169−2172. − [25b] E. Negishi, T. Takahashi, A. O. King *Organic Synthesis* **1987**, *66*, 67−72.

[26] R. J. P. Corriu, J. P. Masse, *J. Chem. Soc., Chem. Commun.* **1972**, 141; K. Tamao, K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, 94, 4374−4376.

[27] J. M. Tour, R. Wu, *Macromolecules* **1992**, *25*, 1901−1907.

[28] [28a] I.-Y. Wu, J. T. Lin, J. Luo, C.-S. Li, C. Tsai, Y. S. Wen, C.-C. Hsu, F.-F. Yeh, S. Liou, *Organometallics* **1998**, *17*, 2188−2198. − [28b] J. X. Zhang, P. Dubois, R. Jérome, *J. Chem. Soc., Perkin. Trans.* **1997**, *2*, 1209−1216.

[29] M. R. Detty, D. S. Hays, *Heterocycles* **1995**, *40*, 925−937.

[30] P. L. Pauson, W. E. Watts, *J. Chem. Soc*. **1963**, 2990−2996.

[31] H. E. Bunting, M. L. H. Green, S. R. Marder, M. E. Thompson, D. Bloor, V. Kolinsky, R. J. Jones, *Polyhedron* **1992**, *11*, 1489−1499.

[32] C.-T. Chen, S. R. Marder, L.-T. Cheng, *J. Chem. Soc., Chem. Commun.* **1994**, 259−260; S. R. Marder D. N. Beratan, L.-T. Cheng, *Science*, **1991**, *252*, 103−106.

[33] S. R. Marder, B. Kippelen, A. K.-Y. Jen, N. Peyghambarian, *Nature*, **1997**, *388*, 845−851.

[34] S. K. Brownstein, E. J. Gabe, R. C. Hynes, *Can. J. Chem.* **1992**, *70*, 1011−1014.

[35] M. Tamm, A. Grzegorzewski, I. Brüdgam, *J. Organomet. Chem.* **1996**, *519*, 217−220.

[36] U. Hagenau, J. Heck, E. Hendrickx, A. Persoons, T. Schuld, H. Wong, *Inorg. Chem.* **1996**, *35*, 7863−7866.

[37] A. M. Romani, A. Ceccon, A. Venzo, *J. Elektroanal. Chem.* **1981**, *130*, 245−254; A. M. Romani, A. Venzo, A. Ceccon, *J. Elektroanal. Chem.* **1980**, *112*, 147−155.

[38] U. T. Müller-Westerhoff, A. L. Rheingold, G. F. Swiegers, *Angew. Chem.* **1992**, *104*, 1398−1400; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1352−1354; A. F. Diaz, U. T. Müller-Westerhoff, A. Nazzal, M. Tanner, *J. Organomet. Chem.* **1982**, C45−C48.

[39] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed. VCH, Weinheim, **1988**.

[40] M. Klessinger, *Chemie in unserer Zeit* **1978**, *12*, 1−10.

[41] K. Clays, E. Hendrickx, T. Verbiest, A. Persoons, *Adv. Mater.* **1998**, *10*, 643−655.

[42] J. J. Wolff, R. Wortmann, *J. Prakt. Chem.* **1998**, *340*, 99−111.

[43] S. Stadler, G. Bourhill, C. Bräuchle, *J. Phys. Chem.* **1996**, *100*, 6927−6941.

[44] J. L. Oudar, D. S. Chemla, *Chem. Phys.* **1977**, *66*, 2664−2668; E. Hendrickx, K. Clays, A. Persoons, C. Dehu, J. L. Brédas, *J. Am. Chem. Soc.* **1995**, *117*, 3547−3555.

[45] D. L. Andrews, *Adv. Chem. Phys.* **1993**, *85*, 545−606.

[46] K. Clays, A. Persoons, *Rev. Sci. Instrum.* **1992**, *63*, 3285−3289; T. Verbiest, K. Clays, S. Samyn, J. Wolff, B. Reinhartt, A. Persoons, *J. Am. Chem. Soc.* **1994**, *116*, 9320−9323; E. Hendrickx, K. Clays, A. Persoons, *Acc. Chem. Res.* **1988**, *31*, 675−683.

[47] [47a] S. Stadler, R. Dietrich, G. Bourhill, C. Bräuchle, *Optics Letts.* **1996**, *21*, 251−253. − [47b] M. A. Pauley, C. H. Wang, *Rev. Sci. Instrum.* **1999**, *70*, 1277−1284. − [7c] O. F. J. Noordman, N. F. van Hulst, *Chem. Phys. Letts.* **1996**, *253*, 145−150. − [47d] N. W. Song, T.-I. Kang, K. C. Jeoung, S.-J. Jeon, B. R. Cho, D. Kim, *Chem. Phys. Letts.* **1996**, *261*, 307−312; O. K. Song, J. N. Woodford, C. H. Wang, *J. Phys. Chem. A.* **1997**, *101*, 3222−3226. − [47e] G. Olbrechts, R. Strobbe, K. Clays, A. Persoons, *Rev. Sci. Inst.* **1998**, *69*, 2233−2241

[48] [48a] S. Houbrechts, K. Clays, A. Persoons, V. Cadierno, M. P. Gamasa, J. Gimeno, *Organometallics* **1996**, *15*, 5266−5268. − [48b] I. R. Whittall, M. P. Cifuentes, M. G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G. A. Heath, D. Bogsányi, *Organometallics* **1997**, *16*, 2631−2637.

[49] [49a] V. Cadiero, S. Conejero, M. P. Camasa, J. Gimeno, I. Asselberghs, S. Houbrechts, K. Clays, A. Persoons, J. Borge, S. Garcia-Granda, *Organometallics* **1999**, *18*, 582−597. − [49b] I. S. Lee, H. Seo, Y. K. Chung, *Organometallics* **1999**, *18*, 1091−1096. − [49c] O. Briel, K. Sünkel, I. Krossing, H. Nöth, E. Schmälzlin, K. Meerholz, C. Bräuchle, W. Beck, *Eur. J. Inorg. Chem.* **1999**, 483−490. − [49d] I. S. Lee, S. S. Lee, Y. K. Chung, D. Kim, N. W. Song, *Inorg. Chim. Acta* **1998**, *279*, 243−248. − [49e] J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts, A. Persoons, *J. Organomet. Chem.* **1998**, *562*, 197−202. − [49f] E. Hendrickx, A. Persoons, S. Samson, G. R. Stephenson, *J. Organomet. Chem.* **1997**, *542*, 295−297. − [49g] V. Alain, M. Blanchard-Desce, C.-T. Chen, S. R. Marder, A. Fort, M. Barzoukas, *Synthetic Metals* **1996**, *81*, 133−136. − [49h] K. R. J. Thomas, J. T. Lin, Y. S. Wen, *J. Organomet. Chem.* **1999**, *575*, 301−309. − [49i] R. Herrmann, B. Pedersen, G. Wagner, J.-H. Youn, *J. Organomet. Chem.* **1998**, *571*, 261−266. − [49j] G. G. A. Balavoine, J.-C. Daran, G. Iftime, P. G. Lacroix, E. Manoury, J. A. Delaire, I. Maltey-Fanton, K. Nakatani, S. Di Bella, *Organometallics* **1999**, *18*, 21−29.

[50] β_0 values were calculated using the TLM taking into account only the low lying DA−CT transition. However, it has to be realised that high energy LL−CT absorption may also contribute to the resonance enhancement.

[51] H. Wong, Ph.D. Thesis, University of Hamburg, **1998**.

[52] The SHG effect of the dinuclear complexes published in ref.[11a] and ref.[36] were meanwhile checked for fluorescence due to two photon absorption (TPF). No indication for TPF effects was found: T. Meyer-Friedrichsen, J. Heck, unpublished results.

[53] A. Abota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-J. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. Mc Cord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subraniam, W. W. Webb, X.-L. Wu, C. Xu, *Science* **1998**, *281*, 1653−1656.

[54] *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VCH, **1995**; *Metallocenes* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, **1998**.

[55] G. M. Sheldrick, SHELXS-86 Program for crystal structure determination, University of Göttingen, Germany, **1986**.

[56] G. M. Sheldrick, SHELXL-93 Program for crystal structure refinement, University of Göttingen, Germany, **1993**.

Received July 5, 1999
[I99243]