Organometallics **2004,** *23,* 3853−3864

Cellulose-Based Polymers with Long-Chain Pendant Ferrocene Derivatives as Organometallic Chromophores[†]

Fan Zhang,[‡] Volkmar Vill,[§] and Jürgen Heck*[,‡]

Fachbereich Chemie, Universität Hamburg, Martin-Luther-King-Platz 6,
20146 Hamburg, Germany

Received November 25, 2003

Selective transmetalation reactions via 1,1′-distannylated ferrocene enables the synthesis of the new ferrocenyl chromophore $[Fe(\eta^5\text{-}C_5H_4\text{-}CH_2OH)(\eta^5\text{-}C_5H_4\text{-}CH{=}CH\text{-}C_7H_7)]$ (**6**). Coupling reactions of complex **6** with corresponding alkyl halides reveal the sandwich compounds $[Fe(\eta^5\text{-}C_5H_4\text{-}CH_2OCH_3)(\eta^5\text{-}C_5H_4\text{-}CH{=}CH\text{-}C_7H_7)]$ (**7**), $[Fe\{\eta^5\text{-}C_5H_4\text{-}CH_2O(CH_2)_6Br\}(\eta^5\text{-}C_5H_4\text{-}CH{=}CH\text{-}C_7H_7)]$ (**8**), $[Fe\{\eta^5\text{-}C_5H_4\text{-}CH_2O(CH_2)_6OTHP\}(\eta^5\text{-}C_5H_4\text{-}CH{=}CH\text{-}C_7H_7)]$ (**9**) (THP = tetrahydropyranyl), and $[Fe\{\eta^5\text{-}C_5H_4\text{-}CH_2O(CH_2)_6I\}(\eta^5\text{-}C_5H_4\text{-}CH{=}CH\text{-}C_7H_7)]$ (**10**), which are potential precursors for dipolar donor−acceptor complexes, providing nonlinear optical properties. The synthesis of the THP derivative **9** was intended as a precursor for the hydroxy-terminated compound $[Fe\{\eta^5\text{-}C_5H_4\text{-}CH_2O(CH_2)_6OH\}(\eta^5\text{-}C_5H_4\text{-}CH{=}CH\text{-}C_7H_7)]$ (**11**), which would be a suitable starting material for a coupling reaction with modified cellulose. However, an acid-catalyzed cleavage of the THP group of **9** in ethanol solution resulted in the formation of $[Fe(\eta^5\text{-}C_5H_4\text{-}CH_2OCH_2CH_3)(\eta^5\text{-}C_5H_4\text{-}CH{=}CH{-}C_7H_7)]$ (**12**) instead of **11**. The fixation of ferrocenyl chromophores to 2,3-di-*O*-methyl cellulose was successful by using the ferrocenyl derivative **10**, which reveals 2,3-di-*O*-methyl-6-*O*-partially$[Fe\{\eta^5\text{-}C_5H_4\text{-}CH_2O\text{-}(CH_2)_6\}(\eta^5\text{-}C_5H_4\text{-}CH{=}CH\text{-}C_7H_7)]$ cellulose (**18**) with different DS [0.1 (**18a**), 0.2 (**18b**), 0.3 (**18c**), 0.5 (**18d**), 0.6(**18e**)], depending on the reaction conditions. **18a**−**e** were characterized by ^{1}H NMR, ^{1}H−^{13}C correlation spectroscopy, UV/vis spectra, and cyclic voltammetry (**18c**). Polarization microscopy observations of the cellulose derivative **18c** demonstrate its thermotropic and lyotropic liquid crystallinities. Reaction of **12** with $[Cp^*Ru(CH_3CN)_3]PF_6$ forms the dipolar monohydro sesquifulvalene complex $[Fe(\eta^5\text{-}C_5H_4\text{-}CH_2OC_2H_5)\{\eta^5\text{-}C_5H_4\text{-}CH{=}CH\text{-}(\eta^6\text{-}C_7H_7)\}RuCp^*]PF_6$ (**13**), indicating that the ferrocenyl derivatives **7**−**10** can in principle be transformed to dinuclear, dipolar, monocationic, monohydro sesquifulvalene complexes and opens the feasibility of introducing dinuclear and dipolar sesquifulvalene units as pendant units of a cellulose backbone, which have potential nonlinear optical properties.

Introduction

Polymeric materials are particularly attractive for NLO applications because of their processability and stability characteristics. Additionally, theory indicates that alignment of polymer chains containing a series of repetition units of NLO chromophores will have a significant enhancement in their nonlinear optical properties, e.g., second-order susceptibility. Therefore, switching of NLO responses could be realized by controlling macroscopic ordering rather than by modulating molecular hyperpolarizabilities.[1,2] In comparison with other NLO materials, polymeric NLO materials that are functionalized with organometallic complexes exhibit attractive properties because of their expansive photochemical features and, in particular, facile device fabrication.[3−5]

As one of the most abundant natural polymers, cellulose has attracted our attention. After being chemically altered, the functionalized cellulose derivatives display interesting applications in optical sensor systems, electronic devices, and photophysics.[6−10] In addition, many interesting liquid crystals derived from cellulose focused interest on this material. Cellulose is composed of 1,4-linked β-D-anhydro glucopyranose units (AGU) as building blocks with three hydroxy groups in each AGU. Therefore, the various modifications of a cellulose chain could be realized on the basis of modifying each glucose unit by different numbers or positions

---

[†] Dedicated to Prof. G.-V. Röschenthaler on the occasion of his 60th birthday.

* Corresponding author. E-mail: juergen.heck@chemie.uni-hamburg.de.

[‡] Institut für Anorganische und Angewandte Chemie.

[§] Institut für Organische Chemie.

(1) Coe, B. J. *Chem. Eur. J.* **1999**, *5*, 2464.

(2) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817.

(3) Williams, D. J. *Angew. Chem.* **1984**, *96*, 637; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.

(4) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.

(5) *Materials for Nonlinear Optics*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

(6) Heinze, T.; Erler, U.; Heinze, U.; Camacho, J.; Grummt, U.-W.; Klemm, D. *Macrmol. Chem. Phys.* **1995**, *196*, 1937.

(7) Müller, M.; Zentel, R.; Keller, H. *Adv. Mater.* **1997**, *9*, 159.

(8) Löscher, F.; Ruckstuhl, T.; Seeger, S. *Adv. Mater.* **1998**, *10*, 1005.

(9) Redl, F. X.; Köthe, O.; Röckl, K.; Bauer, W.; Daub, J. *Macromol. Chem. Phys.* **2000**, *201*, 2091.

(10) Redl, F. X.; Lutz, M.; Daub, J. *Chem. Eur. J.* **2001**, *7*, 5350.

10.1021/om0343216 CCC: $27.50
Publication on Web 06/30/2004

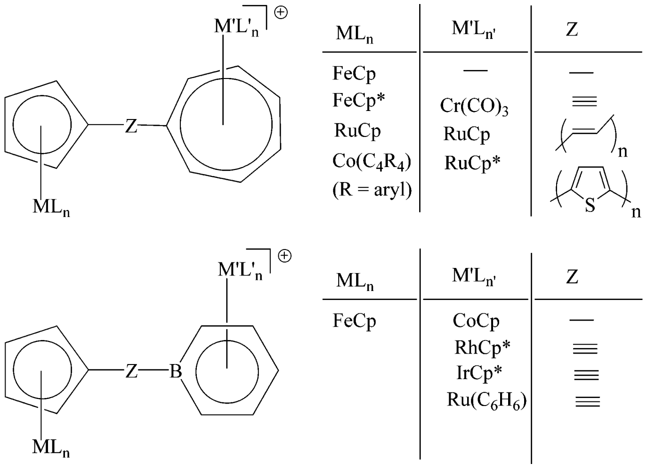


Figure 1. Dipolar cationic bis-sandwich complexes demonstrating second-harmonic generation (SHG).

of the hydroxy groups, which always results in different chemical properties.[11−13] More importantly, the side chain chemistry, such as the structure and functionality of the pendant side groups and the degree of substitution (DS) with special functionalities, plays a crucial role in the chemical and physical properties of the material based on cellulose derivatives. In particular, considering its chirality, which is expressed by the configuration of each AGU and the helical chain structure, the cellulose could be modified with suitable chromophoric groups, which give rise to a multifunctional material.[14−16] However, some minor factors, such as poor solubility in common solvents, still disfavor the development of the functionalization of cellulose.

One of our aims therefore was also to find out and optimize reaction conditions for the incorporation of organometallic NLO chromophores into cellulose material. In our group, several series of dipolar mono- and dinuclear sesquifulvalene type organometallic complexes, which make use of the excellent donor capabilities of ferrocene and ruthenocene subunits, have been successfully synthesized, and their good NLO properties have been proved concerning the second-harmonic generation (SHG) (Figure 1).[17−20] Therefore, we focused our interest on the design and synthesis of some novel materials using the cellulose polymer as a backbone with pendant dipolar mono- and dinuclear sesquifulvalene complexes as NLO chromophores.

The high chemical stability and facile modification of ferrocene has made it the springboard of organometallic chemistry,[21] for example, by using selective transmetalation reactions, which enables the linkage of different functional groups to the two different Cp rings with high selectivity.[22] Recently, polymers using ferrocene as main chain monomer or pendant side chain have been emphasized and their special properties have been illustrated.[22b,c,23−27] As far as we are aware, there is only one report about cellulose-based ferrocenyl chromophores,[28] and still no report about ferrocenes as pendant substituents in cellulose derivatives, which allow a different functionalization in the 1- and 1′-position of the ferrocene chromophore.[29] Our design starts from 1,1′-distannylated ferrocene;[22a] one stannyl substitution is used to construct the organometallic dipolar system, and the other one is used to introduce the linker to the cellulose.

Results and Discussion

Ferrocene Derivatives. Reaction of ferrocene (**1**) with 2 equiv of Li*n*Bu in the presence of TMEDA and, subsequently, with $(n\text{Bu})_3\text{SnCl}$ yielded the 1,1′-distannylated ferrocene **2** (Scheme 1, a).[22] Complex **2** was easily monolithiated by adding 1 equiv of Li*n*Bu in THF. After reaction with DMF, the formyl ferrocene **3** (Scheme 1, b) could be obtained. A Wittig−Horner−Wadsworth−Emmons (WHWE) reaction of complex **3** with (cycloheptatrienylmethyl)diethylphosphonate,[18] which was first treated with Li*n*Bu, afforded the vinylogue monohydro sesquifulvalene complex **4** (Scheme 1, c). It has to be noted that the synthesis of **4** produces two isomers in the ratio of 1:3, which differ in the position of the endocyclic methylene group of the cycloheptatriene moiety (Figure 2). Successive treatment of complex **4** with 1 equiv of Li*n*Bu and DMF yielded complex **5**, the reduction of which by $\text{Na[BH}_4]$ led to the hydroxymethyl complex **6** (Scheme 1, d, e). The coupling reaction of **6** with 6′-iodohexanyl tetrahydropyran-2-yl ether in DMF solution in the presence of sodium hydride revealed complex **9** (Scheme 1, g). Alternatively, an *ω*-bromohexyl group was introduced by reaction of complex **6** with 1,6-dibromohexane in the presence of sodium hydride, yielding the bromo derivative **8** (Scheme 1, h). For coupling of the ferrocene chromophore in **8** or **9** with the cellulose, the synthesis of the iodo derivative **10** was intended. Complex **10** was finally obtained almost

---

(11) Heinze, T.; Rahn, K.; Jaspers, M.; Berghmans, H. *Macromol. Chem. Phys.* **1996**, *197*, 4407.

(12) Arai, K.; Shitara, Y.; Ohyama, T. *J. Mater. Chem.* **1996**, *6* (1), 11.

(13) Heinze, U.; Heinze, T.; Klemm, D. *Macromol. Chem. Phys.* **1999**, *200*, 896.

(14) Harkness, B. R.; Gray, D. G. *Macromolecules* **1991**, *24*, 1800.

(15) Yue, Z.; Cowie, J. M. G. *Macromolecules* **2002**, *35*, 6572.

(16) Arrighi, V.; Cowie, J. M. G.; Vaqueiro, P.; Prior, K. A. *Macromolecules* **2002**, *35*, 7354.

(17) Heck, J.; Dabek, S.; Meyer-Friedrichsen, T.; Wong, H. *Coord. Chem. Rev.* **1999**, *109−192*, 1217.

(18) Wong, H.; Meyer-Friedrichsen, T.; Farrell, T.; Mecker, C.; Heck, J. *Eur. J. Inorg. Chem.* **2000**, 631.

(19) Farrell, T.; Meyer-Friedrichsen, T.; Malessa, M.; Haase, D.; Saak, W.; Asselberghs, I.; Wostyn, K.; Clays, K.; Persoons, A.; Heck, J.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **2001**, 29.

(20) Meyer-Friedrichsen, T.; Mecker, C.; Prosenc, M. H.; Heck, J. *Eur. J. Inorg. Chem.* **2002**, 239; Meyer-Friedrichsen, T.; Wong, H.; Prosenc, M. H.; Heck, J. *Eur. J. Inorg. Chem.* **2003**, 936.

(21) Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Schaefer, W. P. *Organometallics* **1991**, *10*, 1896.

(22) (a) Wright, M. E. *Organometallics* **1990**, *9*, 853. (b) Wright, M. E.; Sigman, M. S. *Macromolecules* **1992**, *25*, 6055. (c) Wright, M. E.; Toplikar, E. G.; Kubin, R. F.; Seltzer, M. D. *Macromolecules* **1992,** *25*, 1838.

(23) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515.

(24) Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics* **1999**, *18*, 4669.

(25) Ginzburg, M.; MacLachlan, M. J.; Yang, S. M.; Coombs, N.; Coyle, T. W.; Raju, N. P.; Greedan, J. E.; Herber, R. H.; Ozin, G. A.; Manners, I. *J. Am. Chem. Soc.* **2002**, *124*, 2625.

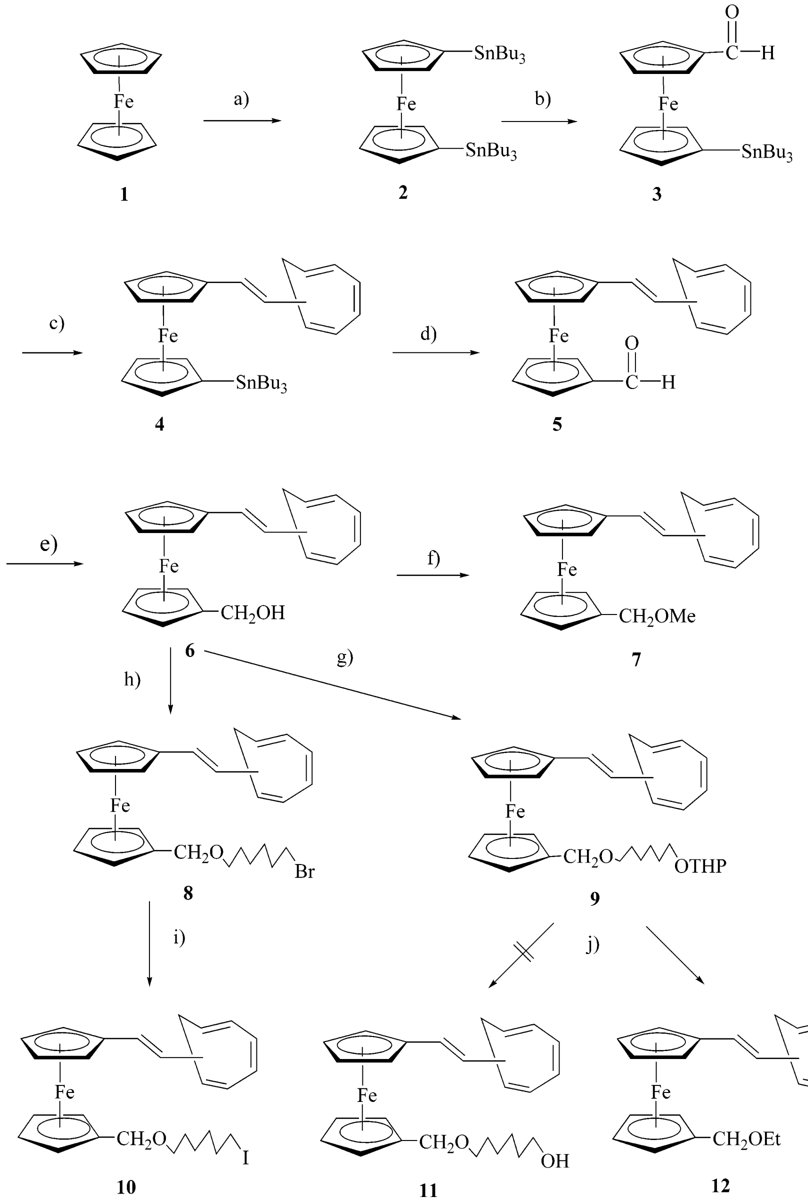
(26) Yang, Y.; Xie, Z.; Wu, C. *Macromolecules* **2002**, *35*, 3426.

(27) Bernard, J.; Schappacher, M.; Ammannati, E.; Kuhn, A.; Deffieux, A. *Macromolecules* **2002**, *35*, 8994.

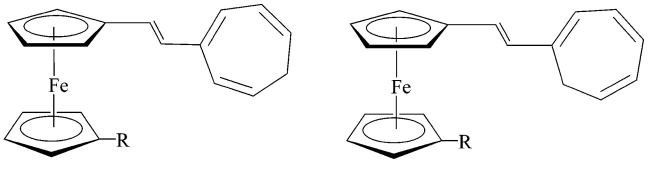
(28) Laube, B.; Radke, W.; Rehahn, M.; Wunderlich, W. *e-Polymers* **2003**, *66*, 1 (http://www.e-polymers.org).

(29) First results on cellulose-based ferrocenyl chromophores were presented at the Third International Conference on Inorganic Materials, Konstanz, Germany: Abstracts: Zhang, F.; Heck, J. 2002; p 52. An amylose-based ferrocenyl chromophore with a DS of only 0.017 was published by: Gnedenko, B. B.; Ryabov, A. D. *Anal. Chem.* **1994**, *66*, 2240.

Scheme 1. Synthesis of Differently Functionalized Cyclopentadienyl Ligands of Ferrocene[a]



[a] (a) 1. hexane, TMEDA, Li*n*Bu; 2. hexane, (nBu)$_3$SnCl; (b) 1. THF, Li*n*Bu, 2. DMF; (c) THF, (EtO)$_2$P(O)CH$_2$C$_7$H$_7$, Li*n*Bu; (d) THF, Li*n*Bu, DMF; (e) THF, MeOH, Na[BH$_4$]; (f) DMF, NaH, MeI; (g) DMF, 6′-iodohexanyl tetrahydropyran-2-yl ether, NaH; (h) DMF, 1,6-dibromohexane, NaH; (i) acetone, NaI; (j) C$_2$H$_5$OH, H$^+$.



Isomer **A** Isomer **B**

Figure 2. Different isomers of the vinylogue monohydro sesquifulvalene complexes.

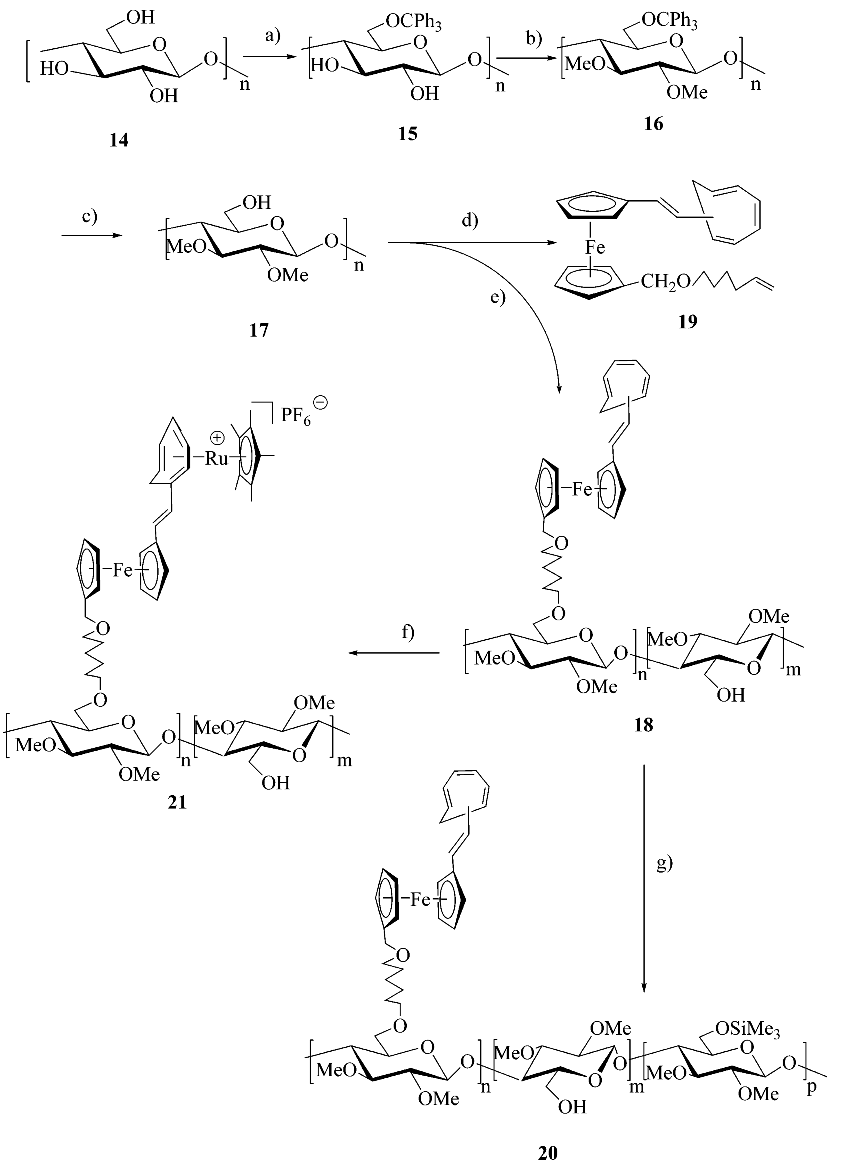
quantitatively by Finkelstein reaction from **8** (Scheme 1, i). Attempts of an acid-catalyzed THP-cleavage of complex **9** with hydrogen chloride, to form the hydroxy-terminated complex **11** (Scheme 1, j), failed, but resulted in the formation of the ethyl ether compound **12**. For comparison (vide infra), the ferrocenyl complex **7** was synthesized by the coupling reaction of complex **6** with methyl iodide under reaction conditions similar to those described for the synthesis of **8** (Scheme 1, f).

Functionalization of Cellulose. The functionalization of cellulose with pendant ferrocenyl chromophores started with the tritylation of cellulose (**14**) (Scheme 2, a), which is a well-known and useful method for selective protection of primary hydroxy groups (**15**).[30] After methylation (**16**) and subsequent detritylation (Scheme 2, b and c), 2,3-di-*O*-methyl-6-hydroxy cellulose (**17**) could be effectively converted from commercial cellulose (AVICEL PH 101).[9,30] To couple **17** with the ferrocenyl chromophores, several synthetic pathways were tested. Previously, the NaOH-DMSO route has been described,[30,31] which results in an ether function as a linker between the functional group and the cellulose backbone. For this type of reaction, a high ratio of alkyl halide and NaOH to cellulose and a considerably high reaction temperature (70−90 °C) were suggested. Using

---

(30) Kondo, T.; Gray, D. G. *Carbohydr. Res.* **1991**, *220*, 173.
(31) Isogai, A.; Ishizu, A.; Nakano, J. *J. Appl. Polym. Sci.* **1986**, *31*, 341.

Scheme 2. Functionalization of Cellulose[a]



[a] (a) DMA, LiCl, Ph_3CCl, pyridine; (b) DMSO, NaOH, MeI; (c) CH_2Cl_2, HCl gas; (d) **8**, DMF, NaH (large excess); (e) DMF, NaH, **10** (addition of NaH and **10** in portions); (f) CH_2Cl_2, $[Cp^*Ru(CH_3CN)_3]PF_6$; (g) CH_2Cl_2, pyridine, Me_3SiCl.

this protocol, only a small amount of product could be isolated, due to the decomposition of the ferrocene chromophore **8** or **10** under the above-mentioned reaction conditions.

To avoid the previous disadvantage from high reaction temperature, the NaH-DMF route was attempted.[32] According to this procedure, a high sodium hydride-to-cellulose ratio was employed in our experiments. After the reaction was worked up, the product **18** (Scheme 2, e) was still separated in a poor yield (less than 5%). Analysis of ^1H and ^{13}C NMR spectra of byproducts indicated that an elimination reaction had occurred, yielding the ferrocene complex **19** (Scheme 2, d). Apparently, the elimination reaction is in competition with the coupling reaction; a stronger base and higher base concentration favor the elimination reaction, in particular, when polar aprotic solvents (e.g., DMF) were used.[33]

Therefore, a lower ratio of NaH to cellulose (1.5:1) was used for the deprotonation of the hydroxy group in the macromolecular chain of 2,3-di-*O*-methyl-6-hydroxy cellulose; additionally, NaH was added in small portions during the different reaction stages, to keep a suitable low base concentration. Furthermore, considering the solubility of the polymer chain of cellulose with increasing deprotonation, the duration of the coupling reaction with ferrocene chromophores was prolonged to 3 days. In contrast to published results, which demonstrate that the rate of comparable coupling reaction depends on the diffusion of the halide compound into the derivatized cellulose matrix and thus a high concentration of halide was used, an increase of the concentration of the ferrocene derivative **10** leads instead to the elimination product **19**.

Consequently, the ferrocenyl complex **10** was also kept in low concentration during the reaction, which was achieved by the addition of complex **10** in several small portions. The results indeed proved that the iodo

---

[32] Weseloh, G. Ph.D. Thesis, University of Hamburg, 1996.

[33] March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985; p 895.

Table 1. Degree of Substitution (DS) of the Ferrocenyl-Containing Cellulose Derivatives Determined by Different Methods and Their Yields

compound	monomer feed[a]	determination of DS by different methods			yield (%)[b]
		^{1}H NMR	UV/vis	AAS	
18a	1.0	0.12	0.09	0.10	45
18b	1.5	0.23	0.19	0.22	53
18c	2.0	0.28	0.27	0.31	51
18d	3.0	0.52	0.53	0.49	56
18e	>3.0	0.61			~10

[a] The molar ratio of complex **10** to AGU of 2,3-di-*O*-methyl-6-hydroxy cellulose (Scheme 2, e). [b] Calculated with respect to the amount of used cellulose derivative **17**.

Table 2. Relative Solubility[a] of the Cellulose Derivatives 18a−e

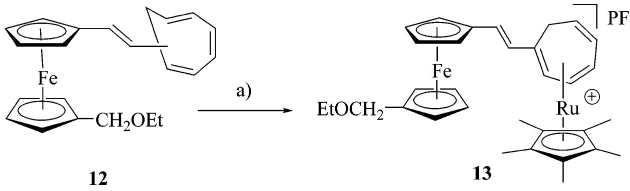
compound (DS)[b]	DMF	THF	CHCl$_3$	CH$_2$Cl$_2$	acetone	methanol
18a (0.12)	++	+	++	++	−	−
18b (0.23)	++	++	++	++	−	+
18c (0.28)	++	++	++	++	−	+
18d (0.52)	++	++	++	++	−	++
18e (0.61)	++	++	++	++	+	++

[a] ++ soluble, + partly soluble, − insoluble. [b] Determined by ^{1}H NMR.

derivative **10** is suitable to increase the yield of the described coupling product **18** (Scheme 2, e). It is well-known that the solubility of cellulose derivatives varies with the degree of substitution (DS), and a change in DS could be obtained by variation of the molar ratio of the cellulose derivative **17** to the complex **10**. When the molar ratio of the ferrocenyl complex **10** to the AGU of the cellulose derivative **17** was varied from 1.0 to 3.0, maintaining the same reaction conditions, the cellulose-based ferrocenyl compound **18** with different DS (from 0.1 to 0.6) is obtainable. The DS is calculated by analysis of ^{1}H NMR and UV/vis spectra (vide infra) and from the Fe content by means of atomic absorption spectroscopy in elemental analysis (Table 1). The samples with DS > 0.1 can be dissolved in THF, chloroform, dichloromethane, and methanol (Table 2). When DS < 0.6, the samples can be precipitated by acetone. When the DS is about 0.6, the sample could be separated by column chromatography on alumina. Furthermore, compound **18** with a higher DS (>0.6) seemed not to be obtainable by increase of the amount of complex **10** compared to cellulose. An extension of the reaction time promotes the elimination reaction to form product **19**. Apparently, the increase of the steric hindrance in the course of the reaction hampers the incorporation of more ferrocene units into the cellulose backbone. The good solubility of **18** in chloroform or dichloromethane facilitates the formation of thin films.

The average molecular mass of the cellulose-based ferrocenyl chromophore **18** was exemplarily determined for **18c** (DS = 0.3) by means of size-exclusion chromatography (SEC). A peak value was found at 30 kD with a half-width of 8.6−58 kD. The observed polydispersity is quite common for cellulose derivatives.[10,39] Taking into account an average degree of polymerization of 215−230 AGU for AVICEL PH 101, an average molecular mass of approximately 70 kD is calculated. Since the degradation of the cellulose in the course of the different chemical reactions is negligible,[10] the variation in the calculated and determined average molecular mass can be rationalized by the fact that only the chloroform-soluble fraction of the product of reaction e outlined in Scheme 2 was taken for characterization, which leads to a yield of only about 50% (see Table 1).

Scheme 3. Synthesis of the Dinuclear Dipolar Monohydro Sesquifulvalene Complex 13[a]



[a] (a) CH$_2$Cl$_2$, [Cp*Ru(CH$_3$CN)$_3$]PF$_6$.

Considering that these cellulose derivatives still contain free hydroxy groups at the primary carbon position of the cellulose backbone, other functional groups could be introduced to construct multifunctional polymers and improve polymer properties. When the cellulose derivative **18a** (DS = 0.1) was treated with trimethyl silicon chloride using pyridine as base, a new cellulose derivative (**20**) with trimethylsilyl groups can be afforded (Scheme 2, g). This derivative displays a much better solubility in organic solvents, such as acetone and dichloromethane. ^{1}H NMR and IR spectra of **20** confirm the formation of a OSiMe$_3$ derivative. The two absorption bands at 842 and 1248 cm^{-1} in the IR spectra can be assigned to O−SiCH$_3$ and Si−CH$_3$ stretching vibrations, respectively,[34,35] whereas in the ^{1}H NMR spectra the resonance signal at $\delta = 0.095$ ppm is indicative of an OSi(CH$_3$)$_3$ group.

The introduction of a dipolar structure in the monohydro sesquifulvalene moiety, which is a prerequisite for the generation of SHG effects, can be achieved by the addition of the cationic, half-sandwich complex [Cp*Ru(CH$_3$CN)$_3$]$^+$ to a mononuclear, monohydro sesquifulvalene complex.[20] As proof, the reaction outlined in Scheme 3 was conducted, resulting in an immediate color change from red to deep purple. Subsequently, a deep purple precipitate was formed, which was analyzed as the expected dinuclear dipolar monohydro sesquifulvalene complex **13**. According to our experience, the color change is due to a strong enhancement of the electronic communication between the ferrocene donor and the cationic cycloheptatriene complex moiety, which is confirmed by UV/vis spectra (vide infra, Figure 5). To obtain the cellulose polymer with pendant dipolar units for the generation of potential NLO effects (**21**, Scheme 2, f), the reaction with the cellulose derivative **18a** and [Cp*Ru(CH$_3$CN)$_3$]PF$_6$[36] was conducted in strict analogy with the reaction outlined in Scheme 3. Unfortunately, a precipitate of low solubility was formed, which prevented reliable analyses of the product. Further research work is in progress.

NMR Spectra. ^{1}H NMR spectra of compounds **10** and **18b−d** (Figure 3) confirm the attachment of the ferrocene moiety to the cellulose backbone. The position of the signals of cycloheptatriene and the ethylenic bridge are essentially identical in both **10** and **18b−d**.

---

(34) Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. *Comprehensive Cellulose Chemistry*: *Functionalization of Cellulose*; Wiley VCH: Weinheim, 1998; pp 279−301.

(35) Zollfrank, C.; Wegener, G. *Holzforschung* **2002**, *56*, 39.

(36) Steinmetz, B.; Schenk, W. A. *Organometallics* **1999**, *18*, 943.

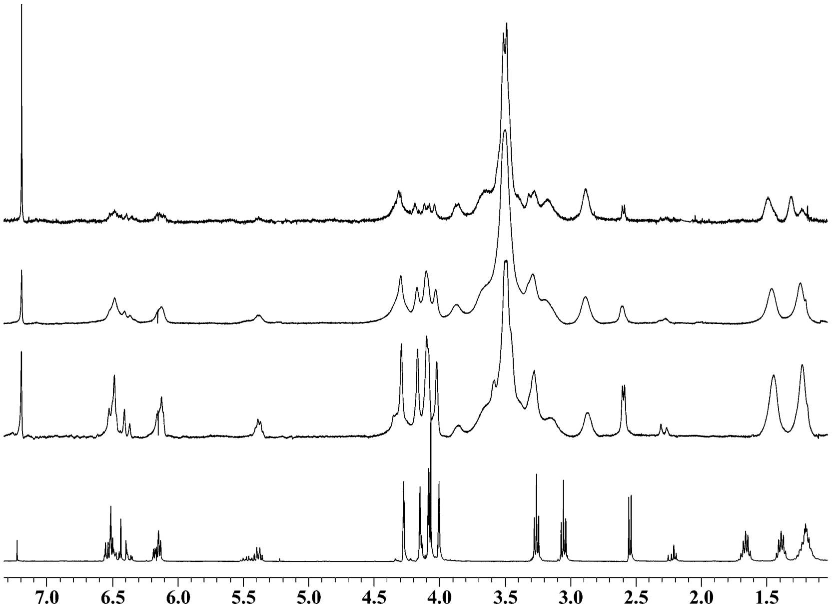


Figure 3. ^{1}H NMR spectra (from top to bottom): cellulose derivatives **18b** (DS 0.2), **18c** (DS 0.3), and **18d** (DS 0.5) and the ferrocenyl chromophore **10** (400 MHz, CDCl$_3$, room temperature).

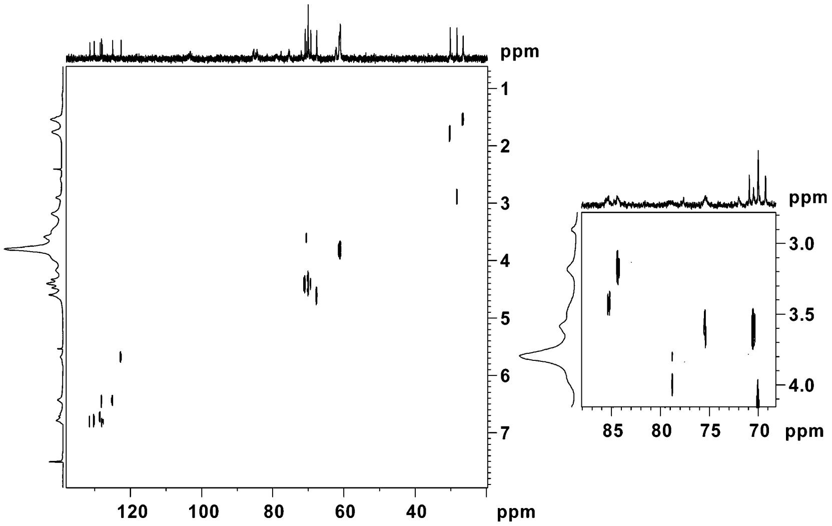


Figure 4. ^{1}H−^{13}C NMR correlation spectra of complex **18c**. The right spectrum illustrates a cutout of the left spectrum at a lower level, indicating cross-peaks of the cellulose carbon and hydrogen nuclei.

It is worthwhile to note that the triplet at 3.17 ppm and the multiplet at 1.60−1.70 ppm for complex **10**, which are assigned to the α- and the β-protons, respectively, adjacent to the iodo function in compound **10**, are not observed for **18b**−**d**, indicating the successful coupling reaction. Additionally, line broadening is observed for all of the NMR signals of the compounds **18b**−**d** due to dipolar line broadening of macromolecules. The two groups of signals at 1.42−1.60 and 1.20−1.40 ppm are separately assigned to the β- and γ-protons with respect to the oxygen atoms in the long alkyl chain. The broad signal at ~2.2 ppm and the doublet at 2.6 ppm are caused by the endocyclic methylene protons of the cycloheptatriene (compare the corresponding triplet and doublet for **10** in Figure 3) due to the different isomers with the ratio of 1:3, which are already observed in the formation of **4** (see Figure 2). A series of broad peaks at 2.96 and between 3.15 and 3.8 ppm are caused by the cellulose backbone, the α-protons adjacent to the oxygen atoms in the alkyl bridge of the side chain (~3.4 ppm), and the methoxy groups in the 2,3-position of the AGU of the cellulose hank (~3.5 ppm). The signals between 3.9 and 4.3 ppm are assigned to the Cp and α-CH$_2$ group of the ferrocene unit. The broad peaks at 5.3−5.5 and 6.2−6.6 ppm stem from the ethylene bridge and unsaturated part of the cycloheptatriene ring. The distinct separation of some resonance signals due to the ferrocene entity and the cellulose backbone allows the calculation of the different DS in **18a**−**e** (see Table 1).

The above-mentioned assignment of the ^{1}H NMR signals is confirmed by ^{1}H−^{13}C correlation NMR experiments of compound **18c** (Figure 4, left). The ^{13}C NMR signals at 122−133 ppm are attributed to the ethylenic bridge and cycloheptatriene ring of the ferrocenyl chromophore. Cross-peaks at 67.7−71.8 ppm are easily assigned to the Cp ligands of the ferrocenyl unit. A correlation spectrum at a lower level (Figure 4, right) illustrates even cross-peaks between oxygen-bearing tertiary carbon atoms and the corresponding hydrogen atoms. Despite the failure of some cross-peaks for the

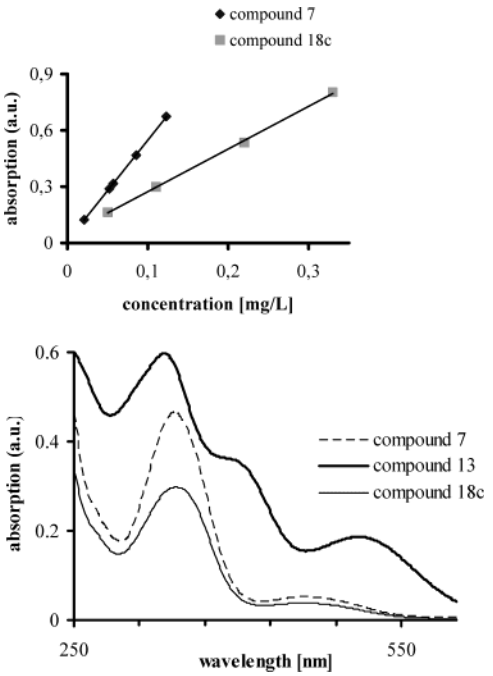


Figure 5. UV/vis spectra of the cellulose derivative **18c** (DS 0.3) (solid line), the ferrocenyl chromophore **7** (dashed line), and the monohydro sesquifulvalene complex **13** (bold line). Inset: Correlation between the absorption (au) and concentration (mg/L) of **7** and of the cellulose derivative **18c**.

glucose rings due to the line broadening of the cellulose polymer, which indicates a strong inter- or intramolecular interaction and cross-linking structure, their ^{13}C NMR signals can be confidently assigned by an additional comparison with *O*-methyl cellulose described in the literature.[9,37] Consequently, the broadened peaks at 103.8, 85.2, 84.3, 75.4, and 72.6 ppm are caused by C-1, C-3, C-2, C-4, and C-5 of the AGU, respectively, the resonance signals at 70.09 and 71.5 ppm can be assigned to the carbon atoms C-1″ and C-6″ next to the oxygen atoms within the C_6 chain, and the signals at 62.2 and 6l.1 ppm can be attributed to C-6 and the methoxy groups. The sharp signal at 28.5 ppm is originated by the endocyclic methylene group of the cycloheptatriene ring. The broad signal at 30.1 ppm includes C-2″ and C-5″, and the broad signal at 26.2 ppm is assigned to C-3″ and C-4″ of the side chain linking the ferrocenyl chromophore with the cellulose backbone.

Upon coordination of Cp*Ru to the cycloheptatriene ring, the signals of the cycloheptatriene protons in complex **13** are considerably shifted to lower frequencies (5.9−6.1 and 6.8−7.0 ppm) and are separated more clearly compared to complex **12**. Additionally, the chemical shifts of the Cp signals (4.1−4.6 and 4.9−5.1 ppm) demonstrate obvious electronic changes upon coordination.

Electronic Spectra. The cellulose derivative **18c** displays an UV/vis absorption spectrum that very much resembles the UV/vis spectrum of the ferrocene complex **7** (Figure 5) and illustrates absorption maxima with quite different extinction coefficients at 343 and 462 nm. The absorption bands were assigned to ligand-to-ligand charge-transfer transitions (LL-CT). The different intensities of the spectra are caused by the different concentrations of compounds **7** and **18c**. The graph in Figure 5 (top) indicates the linear correlation between the concentration of **18c** and **7** and the height of the absorption maximum at 343 nm. Corresponding linear correlations are also obtained for **18a**, **18b**, and **18d**. Considering the same extinction coefficient for **7** as for the ferrocene chromophore in **18a**−**d**, the DS can be calculated from the different slopes. The results of a comparative study on DS of **18a**−**d** via ^{1}H NMR spectra, UV/vis spectra, and atomic absorption spectra are summarized in Table 1 and confirm a good agreement of DS determined by different methods.

The dinuclear complex **13** revealed three absorption bands. A low-energy absorption is observed at 511 nm, which cannot be observed for compounds **7** and **18** with an uncoordinated cycloheptatriene moiety. Therefore, this lower energy absorption band may be attributed to a donor metal−acceptor charge-transfer transition (D_MA-CT). The absorption maxima at 331 and 387 nm are assigned to a donor ligand−acceptor charge-transfer transition (D_LA-CT) in accordance with other ferrocene-containing donor−acceptor complexes.[18−20] The coordination of the cationic Cp*Ru unit to the cycloheptatriene ring generates an electron-accepting terminus, giving rise to a strong donor−acceptor interaction and thus a red shift for the corresponding electronic excitation.

When a chromophore is bound to chiral polymers such as polysaccharides, the influence of chirality on the chromophore can in particular be determined by means of CD spectroscopy. However, CD spectra of **18** with different DS did not indicate any chirality of the organometallic chromophore in **18b** and **18d** (DS = 0.2 and 0.5, respectively). A strong CD signal of chromphores is normally expected when two factors are fulfilled: the conformational rigidity of the chromophores along the polymer backbone and the distance between two adjacent chromphores along the polymer backbone. The first factor concerns the length of the bridge between the chromophore and the polymer backbone. A long bridge between the polymer backbone and the ferrocenyl chromophore in **18** may cause an increase of conformational flexibility. Hence, CD signals may be too weak to be observed. The second factor concerns the exciton coupling, which depends on the DS. If the DS is too low, the interchromophore distances would be too large to generate exciton coupling. Usually, a DS of 0.5 will be sufficient to give rise to a Cotton effect due to electronic interactions between two adjacent chromophores.[10] However, the lack of any Cotton effect in **18d** (DS = 0.5) may be a consequence of the linker between the cellulose backbone and the chromophores, which is too long. Therefore, the further syntheses of cellulose-based polymers with short-chain pendant organometallic chromophores have been made in our group and will be published later.

Cyclic Voltammetry. The electrochemistry of the ferrocene chromophore **7** and the cellulose derivative **18c** (DS = 0.3) was examined by means of cyclic voltammetry (CV). In Figure 6 a typical CV of complex **7** is recorded revealing a half-wave potential of $E_{1/2}$ =

---

(37) Nehls, I.; Wagenknecht, W.; Philipp, B.; Stscherbina, D. *Prog. Polym. Sci.* **1994**, *19* (1), 29.

(38) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.

(39) Mormann, W.; Demeter, J. *Macromolecules* **1999**, *32*, 1706.

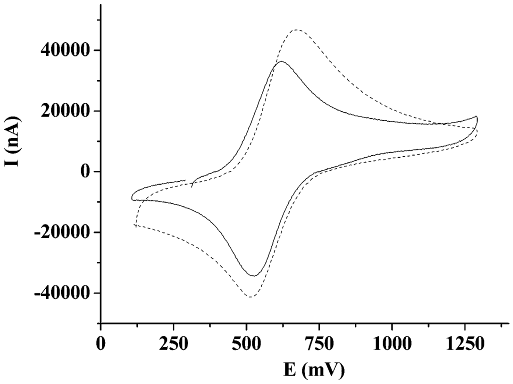


Figure 6. Representative cyclic voltammogram (sweep rate: 500 mV/s) of the cellulose derivative **18c** (DS 0.3, ca. 0.2 mM with respect to the ferrocenyl substituents in **18c**, 0.4 M [Bu_4N]PF_6/CH_2Cl_2) (dashed line) and the ferrocenyl chromophore **7** (0.2 mM in 0.4 M [Bu_4N]PF_6/CH_2Cl_2) (solid line). The potentials are measured relative to Ag/AgCl.

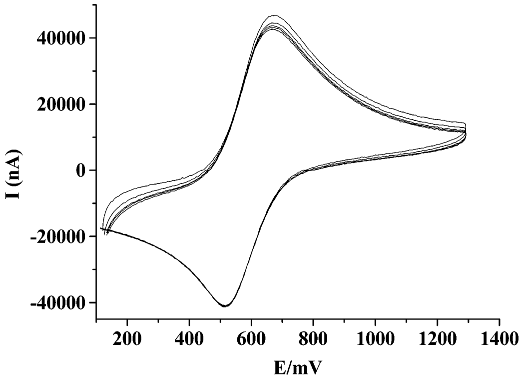


Figure 7. Cyclic voltammogram of the cellulose derivative **18c** (0.1 mM with respect to the ferrocenyl substituents **18c**, in 0.4 M Bu_4NPF_6/CH_2Cl_2, sweep rate: 500 mV/s) with 5 successive scans. The potentials are measured relative to Ag/AgCl.

−0.02 V vs FcH/FcH$^+$ (FcH = ferrocene). In accordance with the redox property of **7**, the cyclic voltammogram of the cellulose compound **18c** (DS = 0.3) also demonstrates an electrochemically reversible redox step at almost the same half-wave potential ($E_{1/2}$ = −0.01 vs FcH/FcH$^+$). In comparison to complex **7**, the redox waves of the polymer **18c** reveal a larger separation of the peak potentials (ΔE = 170 mV), which may indicate a mutual influence of neighboring ferrocene units in the polymeric chain on the electrochemical response.[25,29]

In many cases redox units with flexible, long side chain are easily wrapped in the polymer chain,[29] indicating that an electron transfer to the electrode surface becomes more complicated. Even the electrochemical behavior of the less densely functionalized cellulose (low DS) may also be easily influenced by the intramolecular Coulombic interaction of the electrophores.[9] In contrast to other electrochemical studies of electrophore-functionalized polymers,[9,29] no hints of film formation can be obtained from the cyclic voltammetric experiments of **18c**; during five different cycles only subtle changes in the peak currents of the cyclic voltammograms can be observed (Figure 7). However, in comparison to other ferrocenyl-functionalized polymers such as polystyrene chains and polystyrene combs,[29] no adsorption on the electrode can be observed for **18c** regarding the large separation of the peak potentials of almost 200 mV.

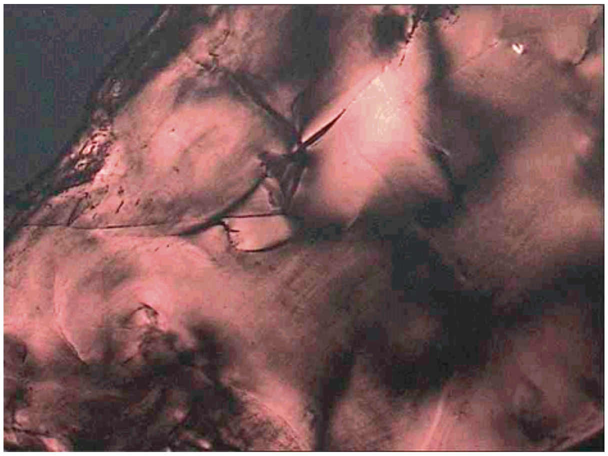


Figure 8. Image of the cellulose derivative **18c** in the thermotropic liquid crystal solid state observed in the polarizing microscope at room temperature. The texture indicates thermotropic liquid crystalline properties.

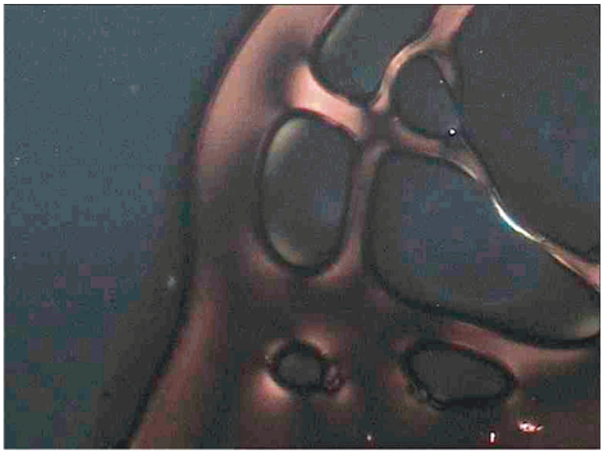


Figure 9. Image of the cellulose derivative **18c** at higher concentration in CH_2Cl_2 observed between crossed polars in a polarizing microscope at room temperature. The texture indicates a lyotropic liquid crystalline property.

Liquid Crystalline Properties. Thermotropic liquid crystalline films of cellulose derivative **18c** were prepared by placing a small quantity of the sample between glass plates. It is not crystalline, but a glassy anisotropic material at room temperature. When viewed on a polarizing microscope, this sample gave an anisotropic melt, which indicates a mesophase formation, and this sample showed the thermotropic liquid crystal until 120 °C (Figure 8). This observation is in accordance with a broad endothermic peak at T = 122.0 °C in a DSC thermogram for **18c**. A concentrated solution of **18c** in CH_2Cl_2 also shows the anisotropy expected for liquid crystal formation, when observed in a polarizing microscope (Figure 9). This lyotropic phase in CH_2Cl_2 seems to have a structure similar to that of the thermotropic phase of the pure material, because in a contact preparation no phase boundary can be observed between the lyotropic solution and the thermotropic phase of the pure compound. The observation of both thermotropic and lyotropic behavior for a ferrocene functionalized with a sugar was just recently reported.[40]

Conclusion

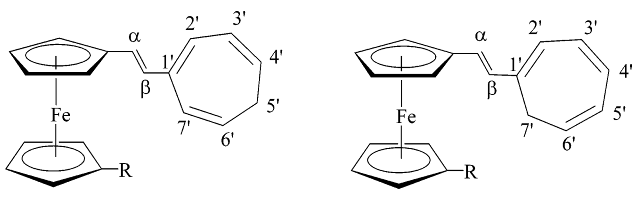
Selective transmetalation reactions of 1,1′-distannylated ferrocene revealed the new ferrocene derivative [Fe(η^5-C_5H_4-CH_2OH)(η^5-C_5H_4-CH═CH-C_7H_7)] (**6**). Subsequently, new potential NLO chromophore precursors [Fe(η^5-C_5H_4-CH_2OCH_3)(η^5-C_5H_4-CH═CH-C_7H_7)] (**7**), [Fe{η^5-C_5H_4-$CH_2O(CH_2)_6Br$}(η^5-C_5H_4-CH═CH-C_7H_7)] (**8**), and [Fe{η^5-C_5H_4-$CH_2O(CH_2)_6I$}(η^5-C_5H_4-CH═CH-C_7H_7)] (**10**) were prepared in high yields. Upon reaction of **10** with modified cellulose derivatives, the cellulose-based polymer **18** with pendant, long, ether-linked organometallic chromophores of different DS (DS = 0.1, **18a**; DS = 0.2, **18d**; DS = 0.3, **18c**; DS = 0.5, **18d**; DS = 0.6, **18e**) was synthesized in good yield. The cellulose derivatives **18a**−**d** display UV/vis spectra similar to those of the molecular ferrocenyl chromophore **7**.

The presence of liquid crystallinity of the cellulose derivative **18c**, determined by polarizing microscopy and DSC measurements, may be a consequence of the chiral superstructure of the modified cellulose. However, the chiral induction of the cellulose backbone on the electronic properties of the ferrrocenyl chromophore must be very small, since no Cotton effect could be observed in the CD spectra. In general, we have established an effective synthetic route for the incorporation of ferrocene chromophores into a cellulose backbone. A systematic investigation of the attachment of other chromophores to the cellulose backbone and corresponding NLO properties is in progress.

Experimental Section

Manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from sodium or potassium/benzophenone ketyl; dimethylformamide (DMF) and acetone were purified by distillation from 4 Å molecular sieves; dichloromethane (CH_2Cl_2) was dried over CaH_2 and distilled under N_2. UV/vis spectra were recorded on a Perkin-Elmer Model 554, and IR spectra on a Perkin-Elmer FT-IR 1720X spectrophotometer. NMR spectra were measured on a Bruker AM 400 and Varian Gemini 200 BB. EI-MS were obtained from a Finnigan MAT 311 A. Atomic absorption spectra were recorded using a Perkin-Elmer RRS 5000. Elemental analyses were performed using a Heraeus CHN-O-Rapid, Zentrale Elementanalytik, Fachbereich Chemie, Universität Hamburg. The liquid crystalline properties were studied on an Olympus BH-2 polarizing optical microscope equipped with a Mettler FP 800 hot stage. 1,1′-Bis(tri-*n*-butylstannyl)ferrocene and 1′-(tri-*n*-butylstannyl)-1-ferrocene carboxaldehyde,[22] 6′-iodohexanyl tetrahydropyran-2-yl ether,[32] pyridinium *p*-toluenesulfonate,[38] 2,3-di-*O*-methyl-6-hydroxy cellulose,[30] (cyclohepta-1,3,5-trien-1-ylmethyl)diethylphosphonate,[18] and [Cp*Ru(MeCN)$_3$](PF$_6$)][36] were prepared according to literature procedures. The cellulose used in this study was AVICEL PH 101 from Fluka.

[Fe{η^5-C_5H_4-Sn(nBu)$_3$}(η^5-C_5H_4-CH═CH-C_7H_7)] (4). Li*n*Bu (0.97 mL, 1.554 mmol, 1.6 M in hexane) was added dropwise to a solution of (cyclohepta-1,3,5-trien-1-ylmethyl)diethylphosphonate (0.342 g, 1.413 mmol) in THF (5 mL). The reaction mixture was allowed to warm to room temperature, stirred for 1 h, and cooled again to −78 °C. Subsequently, a THF solution (20 mL) containing [Fe(η^5-C_5H_4-CHO){η^5-C_5H_4-Sn(nBu)$_3$}] (0.630 g, 1.254 mmol) was added. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was evaporated in vacuo, and the residue extracted with diethyl ether. The crude product was purified by column chromatography (Al_2O_3, neutral, 10% H_2O; hexane). Yield: 0.675 g (81%) of a dark red oil. On the basis of analysis of the ^{1}H NMR spectrum, the product was composed of two isomers **A** and **B** with a ratio of 1:3, which differ in the position of the endocyclic methylene group of the seven-membered ring.



Isomer **A** R = Sn(nBu)$_3$: **4** Isomer **B**

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (m, 9H, CH_3), 0.96−1.04 (m, 6H, CH_2), 1.25−1.40 (m, 6H, CH_2), 1.43−1.67 (m, 6H, CH_2), 2.33 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.66 (d, J = 7.0 Hz, 2H, H-7′, isomer **B**); 3.93 (t, J = 2.0 Hz, 2H, Cp), 4.20 (t, J = 2.0 Hz, 2H, Cp), 4.30(t, J = 2.0 Hz, 2H, Cp), 4.34 (t, J = 2.0 Hz, 2H, Cp), 5.42−5.51 (m, C_7H_7), 6.38−6.65 (m, C_7H_7, H-α, H-β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.3 (CH_2Sn), 12.0 (CH_3), 27.4 (CH_2), 27.9 (CH_2), 29.2, 29.3 (C-5′, isomer **A**; C-7′, isomer **B**), 66.8 (Cp), 68.7 (Cp), 72.2 (Cp), 75.6 (Cp), 83.2 (ipso-Cp), 122.2 (C_7H_7), 124.4 (C_7H_7), 127.6 (C_7H_7), 127.8 (C_7H_7), 128.1 (C-β), 129.6 (C_7H_7), 31.0 (C-α), 132.4 (C-1′) ppm. Anal. Calcd for $C_{31}H_{44}FeSn$ (590.99): C, 62.98; H, 7.50. Found: C, 63.04; H, 7.52.

[Fe(η^5-C_5H_4-CHO)(η^5-C_5H_4-CH═CH-C_7H_7)] (5). A solution of [Fe{η^5-C_5H_4-Sn(nBu)$_3$}(η^5-C_5H_4-CH═CH-C_7H_7)] (**4**) (0.420 g, 0.711 mmol) in THF (20 mL) was treated with Li*n*Bu (0.49 mL, 0.78 mmol, 1.6 M in hexane) at −78 °C and allowed to react for 30 min. DMF (0.111 g, 1.42 mmol) was added to the mixture, and the cooling bath was removed. The mixture was allowed to warm to room temperature and then diluted with diethyl ether (30 mL). After washing with water, the organic layer was dried over K_2CO_3. The solvent was removed in vacuo, and the residue was purified by column chromatography (Al_2O_3, neutral, 10% H_2O; diethyl ether/hexane, 1:1), affording **5** (0.201 g, 86%) as a deep purple oil, composed of two isomers **A** and **B** in a ratio of 1:3, according to the starting material **4**. ^{1}H NMR (400 MHz, $CDCl_3$) (for assignment vide supra): δ 2.33 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.65 (d, J = 8.0 Hz, 2H, H-7′, isomer **B**), 4.34 (t, J = 2.0 Hz, 2H, Cp), 4.49 (t, J = 2.0 Hz, 2H, Cp), 4.53 (t, J = 2.0 Hz, 2H, Cp), 4.73 (t, J = 2.0 Hz, 2H, Cp), 5.47−5.51 (m, C_7H_7), 6.20−6.56 (m, C_7H_7, H-α, H-β), 9.87 (s, 1H, C*HO*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.1, 28.9 (C-5′, isomer **A**; C-7′, isomer **B**), 68.5 (Cp), 70.8 (Cp),71.0 (Cp),74.9 (Cp), 80.3 (*ipso*-Cp), 85.9 (*ipso*-Cp), 122.2 (C_7H_7), 124.4 (C_7H_7), 127.6 (C_7H_7), 127.8 (C_7H_7), 128.1 (C-β), 129.6 (C_7H_7), 131.0 (C-α), 132.4 (C-1′), 194.2 (C═O) ppm. Anal. Calcd for $C_{20}H_{18}FeO$ (330.07): C, 72.75; H, 5.49. Found: C, 72.90; H, 5.56.

[Fe(η^5-C_5H_4-CH_2OH)(η^5-C_5H_4-CH═CH-C_7H_7)] (6). Sodium tetrahydro borate (0.027 g, 1.1 mmol) was added in portions to a solution of [Fe(η^5-C_5H_4-CHO)(η^5-C_5H_4-CH═CH-C_7H_7)] (**5**) (0.182 g, 0.55 mmol) in a mixture of THF/methanol (1:1, 10 mL) below 0 °C. The reaction mixture was allowed to warm to room temperature. After stirring for 2 h, diethyl ether (30 mL) was added, and then the mixture was washed with water (3 × 10 mL). The organic layer was dried over K_2CO_3. Evaporation of the solvent and purification by column chromatography (Al_2O_3, neutral, 10% H_2O; CH_2Cl_2) afforded complex **6** as a red solid (0.122 g, 67%), composed of two isomers **A** and **B** in a ratio of 1:3, according to the starting material **5**.

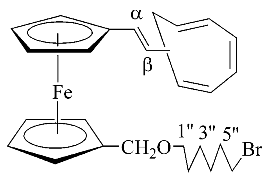
---

(40) Donnio, B.; Seddon, J. M.; Deschenaux, R. *Organometallics* **2000**, *19*, 3077.

^{1}H NMR (400 MHz, CDCl$_3$) (for assignment vide supra): δ 1.46 (s, 1H, CH$_2$O*H*), 2.27 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.59 (d, J = 8.0 Hz, 2H, H-7′, isomer **B**), 4.08 (t, J = 2.0 Hz, 2H, Cp), 4.15, (s, 2H, Cp*CH*$_2$OH), 4.22 (t, J = 2.0 Hz, 2H, Cp), 4.24 (t, J = 2.0 Hz, 2H, Cp), 4.37 (t, J = 2.0 Hz, 2H, Cp), 5.35–5.49 (m, C$_7$H$_7$), 6.17–6.58 (m, C$_7$H$_7$, H-α, H-β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 28.2 (C-7′, C$_7$H$_7$, isomer **B**), 28.4 (C-5′, C$_7$H$_7$, isomer **A)**, 61.0 (Cp*C*H$_2$O), 67.4 (Cp), 69.1 (Cp), 69.7 (Cp), 70.0 (Cp), 83.5 (*ipso*-Cp), 83.6 (*ipso*-Cp), 122.7 (C$_7$H$_7$), 124.7 (C$_7$H$_7$), 125.3 (C$_7$H$_7$), 127.5 (C$_7$H$_7$), 128.0 (C-β), 130.4 (C$_7$H$_7$), 131.3 (C-α), 132.3 (C-1′) ppm. Anal. Calcd for C$_{20}$H$_{20}$OFe (332.07): C, 72.31; H, 6.07. Found: C, 71.56; H, 6.60.

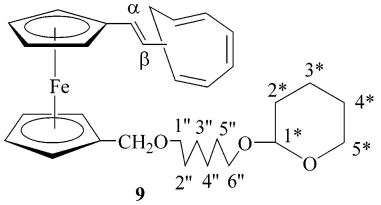
[Fe(η^5-C$_5$H$_4$-CH$_2$OCH$_3$)(η^5-C$_5$H$_4$-CH═CH-C$_7$H$_7$)] (7). Sodium hydride powder (15 mg, 0.60 mmol) was added in portions to a solution of [Fe(η^5-C$_5$H$_4$-CH$_2$OH)(η^5-C$_5$H$_4$-CH═CH-C$_7$H$_7$)] (**6**) (100 mg, 0.40 mmol) in THF (30 mL) under ice cooling. The mixture was stirred for about 15 min. To this mixture was added dropwise a solution of methyl iodide (85 mg, 0.60 mmol) in THF (10 mL). The mixture was allowed to warm to room temperature and to react for an additional 3 h. The mixture was hydrolyzed with slush water and extracted with CH$_2$Cl$_2$. The combined organic layers were dried with K$_2$CO$_3$. After removal of the solvent and separation by column chromatography (Al$_2$O$_3$, neutral, 10% H$_2$O; hexane/diethyl ether, 3:1), a pure product was afforded as a deep red oil, consisting of two isomers **A** and **B** (vide supra) in a ratio of 1:3, which solidified slowly at room temperature. Yield: 92 mg, 88%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.36 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.68 (d, J = 7.0 Hz, 2H, H-7′, isomer **B**), 3.28 (s, OCH$_3$), 4.08–4.16 (m, 4H, Cp, Cp*CH*$_2$O), 4.18 (t, J = 2.0 Hz, 2H, Cp,), 4.28 (t, J = 2.0 Hz, 2H, Cp), 4.41 (t, J = 2.0 Hz, 2H, Cp), 5.40–5.58 (m, C$_7$H$_7$), 6.15–6.68 (m, C$_7$H$_7$, H-α, H-β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 28.3 (C-7′, C$_7$H$_7$, isomer **B**), 28.4 (C-5′, C$_7$H$_7$, isomer **A**), 58.3 (OCH$_3$), 68.4 (Cp), 70.1 (Cp), 70.3 (Cp), 70.9 (Cp), 71.1, 84.5 (*ipso*-Cp), 84.6 (*ipso*-Cp), 122.4 (C$_7$H$_7$), 124.8 (C$_7$H$_7$), 127.5 (C$_7$H$_7$), 128.0 (C$_7$H$_7$), 128.7 (C-β), 130.3 (C$_7$H$_7$),131.3 (C-α); 132.6 (C-1′) ppm. Anal. Calcd for C$_{21}$H$_{22}$FeO (346.08): C, 72.85; H, 6.40. Found: C, 73.21; H, 6.19.

[Fe{η^5-C$_5$H$_4$-CH$_2$O(CH$_2$)$_6$Br}(η^5-C$_5$H$_4$-CH═CH-C$_7$H$_7$)] (8). NaH powder (0.091 g, 3.8 mmol) was added in portions to a solution of [Fe(η^5-C$_5$H$_4$-CH$_2$OH)(η^5-C$_5$H$_4$-CH═CH-C$_7$H$_7$)] (**6**) (0.125 g, 0.38 mmol) and 1,6-dibromohexane (6.14 g, 0.026 mol) in THF/DMF (50 mL, v/v 1:1) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 48 h. The mixture was hydrolyzed with ice–water (20 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with water (3 × 20 mL) and dried over K$_2$CO$_3$. After the solvent was removed in vacuo, the residue was purified by column chromatography (Al$_2$O$_3$, neutral, 10% H$_2$O; hexane/ethyl acetate, 18:1). The first orange band was collected, and the solvent was evaporated, affording **8** as a red oil (1.52 g, 81%). **8** consists of two isomers **A** and **B** (vide supra) in a ratio 1:3: ^{1}H NMR (400 MHz, CDCl$_3$) (for assignment vide supra): δ 1.24–1.46 (m, 4H, CH$_2$), 1.48–1.60 (m, 2H, CH$_2$), 1.76–1.90 (m, 2H, CH$_2$), 2.33 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.65 (d, J = 7.0 Hz, 2H, H-7′, isomer **B**), 3.33–3.47 (m, 4H, CH$_2$Br, O*CH*$_2$CH$_2$), 4.09 (t, J = 2.0 Hz, 2H, Cp), 4.15–4.19 (m, 4H, Cp, Cp*CH*$_2$OCH$_2$), 4.23 (t, J = 2.0 Hz, 2H, Cp), 4.30 (t, J = 2.0 Hz, 2H, Cp), 4.35 (t, J = 2.0 Hz, 2H, Cp), 5.38–5.53 (m, C$_7$H$_7$), 6.17–6.61 (m, C$_7$H$_7$, H-α, H-β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 25.8 (*C*H$_2$), 28.3 (*C*H$_2$), 28.4 (*C*H$_2$), 29.8 (*C*H$_2$CH$_2$Br), 29.9 (C-7′, C$_7$H$_7$, isomer **B**), 30.1 (C-5′, C$_7$H$_7$, isomer **A)**, 33.2 (*C*H$_2$Br), 67.5 (Cp), 67.6 (Cp), 69.3 (CpCH$_2$O*C*H$_2$), 70.0 (Cp), 70.3 (Cp*C*H$_2$O), 70.9 (Cp), 84.1 (*ipso*-Cp), 84.7 (Cp), 122.6 (C$_7$H$_7$), 124.8 (C$_7$H$_7$), 127.8 (C$_7$H$_7$), 128.0 (C$_7$H$_7$), 128.5 (C-β), 130.2 (C$_7$H$_7$),1 31.4 (C-α),132.7 (C-1’) ppm. EI-MS: *m/z* (%): 495 (100) [M$^+$], 315 (47) [CH$_2$FeCp C$_2$H$_2$-C$_7$H$_7$$^+$], 237 (46) [CpC$_2H_2C_7H_7Fe^+$]. Anal. Calcd for C$_{26}H_{31}$BrFeO (495.04): C, 63.05; H, 6.31. Found: C, 62.38; H, 6.38.



8

[Fe{η^5-C$_5$H$_4$-CH$_2$O(CH$_2$)$_6$OTHP}(η^5-C$_5$H$_4$-CH═CH-C$_7$H$_7$)] (9). A solution of [Fe(η^5-C$_5$H$_4$-CH$_2$OH)(η^5-C$_5$H$_4$–CH═CH-C$_7$H$_7$)] (**6**) (0.179 g, 0.51 mmol) in THF (15 mL) was slowly added to a suspension of NaH (0.036 g, 1.50 mmol) in DMF (10 mL) at 0 °C and stirred for 15 min. The reaction mixture was treated with 6′-iodohexanyl tetrahydropyran-2-yl ether (0.480 g, 1.57 mmol). The mixture was allowed to warm to room temperature and to react for another 24 h. The reaction mixture was hydrolyzed with ice–water (20 mL) and extracted three times with diethyl ether. The organic layer was dried over K$_2$CO$_3$, and the solvent was evaporated in vacuo. The residue was purified by column chromatography (Al$_2$O$_3$, neutral, 10% H$_2$O; hexane/diethyl ether, 5:1), yielding **9** as a red oil (0.176 g, 85%) composed of two isomers according to the starting material **6** (**A** and **B** in a ratio of 1:3). ^{1}H NMR (400 MHz, CDCl$_3$) (for assignment vide supra): δ 1.33–1.89 (m, 14H, CH$_2$, C-4″–C-7″ and C-2*–C-4*), 2.32 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.66 (d, J = 7.0 Hz, 2H, H-7′, isomer **B**), 3.34–3.39 (m, 2H, H-1″; 1H, H-6″), 3.46–3.50 (m, 1H, H-6″), 3.71 (dt, J = 4.0 Hz, J = 6.0 Hz, 1H, H-5*), 3.83–3.88 (m, 1H, H-5*), 4.13–4.15 (m, 4H, Cp, Cp*CH*$_2$O), 4.21 (t, J = 2.0 Hz, 2H, Cp), 4.28 (t, J = 2.0 Hz, 2H, Cp), 4.41 (t, J = 2.0 Hz, 2H, Cp), 4.56 (m, 1H, H-1*), 5.41–5.56 (m, C$_7$H$_7$), 6.14–6.61 (m, C$_7$H$_7$, H-α, H-β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.7 (C-3″), 25.5 (C-4″), 26.0 (C-3*), 26.1 (C-2″), 27.9 (C-7′, isomer **B**), 28.0 (C-5′, isomer **A)**, 29.7 (C-5″), 29.8 (C-4*), 30.8 (C-2*), 62.4 (C-1″), 67.2 (Cp), 67.3 (Cp), 67.6 (C-6″), 68.8 (C-5*), 69.8 (Cp), 70.2 (Cp*C*H$_2$O), 70.7 (Cp), 84.7 (*ipso*-Cp), 98.9 (C-1*), 122.2 (C$_7$H$_7$), 124.4 (C$_7$H$_7$), 126.6 (C$_7$H$_7$), 127.4 (C$_7$H$_7$), 128.2 (C-β), 129.8 (C$_7$H$_7$), 130.9 (C-α), 132.16 (C-1′) ppm. Anal. Calcd for C$_{31}$H$_{38}$FeO$_3$: C, 72.37; H, 7.44. Found: C, 72.78; H, 7.21.

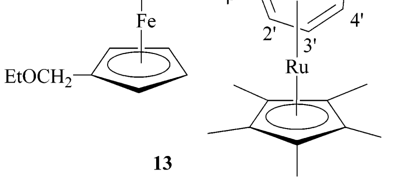


9

[Fe{η^5-C$_5$H$_4$-CH$_2$O(CH$_2$)$_6$I}(η^5-C$_5$H$_4$-CH═CH-C$_7$H$_7$)] (10). Sodium iodide (61 mg, 0.40 mmol) was added to a solution of [Fe{η^5-C$_5$H$_4$-CH$_2$O(CH$_2$)$_6$Br}(η^5-C$_5$H$_4$-CH═CH-C$_7$H$_7$)] (**8**) (0.20 g, 0.404 mmol) in anhydrous acetone (15 mL). After the solution was stirred overnight in the dark, some white precipitation of sodium bromide could be observed. The solution was washed with water (10 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were combined and dried with K$_2$CO$_3$. After removal of the solvent in vacuo, the pure product **10** was obtained as a red oil, consisting of two isomers **A** and **B** (vide supra) in a ratio of 1:3. Yield: quantitative. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.28–1.47 (m, 4H, CH$_2$), 1.48–1.61 (m, 2H, CH$_2$), 1.74–1.87 (m, 2H, CH$_2$), 2.39 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.67 (d, J = 7.0 Hz, 2H, H-7′, isomer **B**), 3.17 (m, J = 6.8 Hz, 2H, CH$_2$I), 3.37 (t, J = 6.6 Hz, 2H, CpCH$_2$OC*H*$_2$), 4.11 (t, J = 2.0 Hz, 2H, Cp), 4.15–4.19 (m, 4H, Cp, CpC*H*$_2$O), 4.25 (t, J = 2.0 Hz, 2H, Cp), 4.37 (t, J = 2.0 Hz, 2H, Cp), 5.40–5.52 (m, C$_7$H$_7$), 6.18–6.59 (m, C$_7$H$_7$, H-α, H-β) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 7.5 (CH$_2$I), 28.3 (CH$_2$), 28.4 (CH$_2$), 29.9 (C-7′, C$_7$H$_7$, isomer **B**), 30.7 (C-5′, C$_7$H$_7$, isomer **A)**, 33.9 (CH$_2$), 69.3 (CpCH$_2$O*C*H$_2$), 70.0 Cp, 70.3 (Cp*C*H$_2$O), 71.0 (Cp), 84.2 (*ipso*-Cp), 84.7 (*ipso*-Cp), 122.6 (C_7H_7), 124.8 (C_7H_7), 127.8 (C_7H_7), 128.0 (C_7H_7), 128.5 (C-β), 130.2 (C_7H_7), 131.4 (C-α), 132.7 (C-1′) ppm. Anal. Calcd for $C_{26}H_{31}FeIO$ (542.04): C, 57.59; H, 5.76. Found: C, 57.54; H, 5.87.

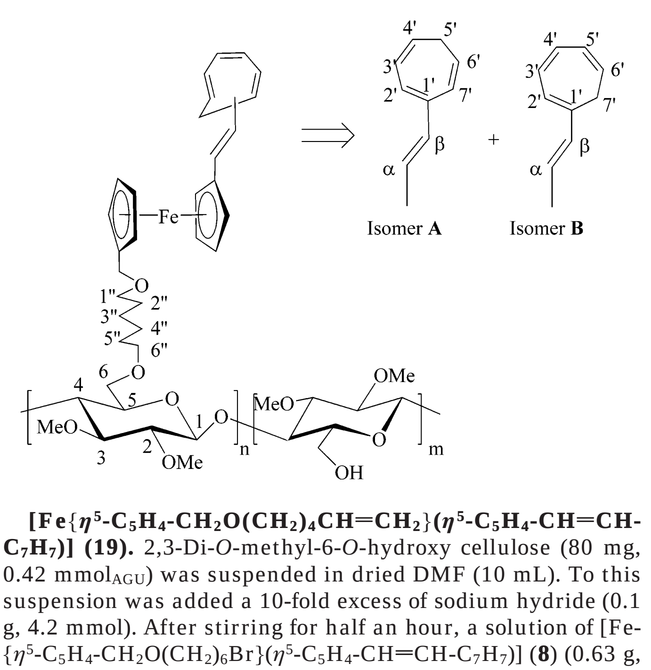
[Fe(η^5-C_5H_4-$CH_2OCH_2CH_3$)(η^5-C_5H_4-CH=CH-C_7H_7)] (12). A solution of [Fe{η^5-C_5H_4-$CH_2O(CH_2)_6$OTHP}(η^5-C_5H_4-CH=CH-C_7H_7)] (**9**) (0.113 g, 0.22 mmol) and a catalytic amount of pyridinium *p*-toluenesulfonate[38] (0.006 g, 0.022 mmol) in ethanol (4 mL) was stirred at 56 °C (bath temperature) for 2.5 h. The reaction mixture was diluted with diethyl ether (20 mL) and washed with water (10 mL). The organic layer was separated and dried over K_2CO_3. The solvent was removed in vacuo, and the residue was chromatographed on alumina (Al_2O_3, neutral, 10% H_2O; hexane/ethyl acetate, 8:1). The first red band was collected, yielding pure product **12** (0.072 g, 90%) as two isomers **A** and **B** in accordance with the starting material **9** in a ratio of 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) (for assignment vide supra): δ 1.15 (3t, J = 8.0 Hz, 3H, CH_3), 2.34 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.66 (d, J = 7.0 Hz, 2H, H-7′, isomer **B**), 3.43 (q, J = 8.0 Hz, OCH_2CH$_3$), 4.13−4.15 (t, J = 2.0 Hz, 2H, Cp), 4.22 (m, 4H, Cp, CpCH_2O), 4.29 (t, J = 2.0 Hz, 2H, Cp), 4.42 (t, J = 2.0 Hz, 2H, Cp), 5.43−5.56 (m, C_7H_7), 6.15−6.59 (m, C_7H_7, H-α, H-β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.6 (CH_3), 28.3 (C-7′, C_7H_7, isomer **B**), 28.4 (C-5′, C_7H_7, isomer **A**), 65.8 (OCH$_2$CH$_3$), 69.1 (CpCH$_2$O), 65.9 (Cp), 70.2 (Cp), 70.3 (Cp), 71.2 (Cp), 83.8 (*ipso*-Cp), 84.5 (*ipso*-Cp), 122.6 (C_7H_7), 124.8 (C_7H_7), 127.5 (C_7H_7), 128.0 (C_7H_7), 128.7 (C-β), 130.3 (C_7H_7), 131.3 (C-α); 132.6 (C-1′) ppm. EI-MS: *m*/*z* (%): 360 (100) [M$^+$], 237 (41) [CpC$_2$H$_2$C$_7$H$_7$Fe$^+$]. Anal. Calcd for $C_{22}H_{24}FeO$ (360.09): C, 73.34; H, 6.71. Found: C, 73.98; H, 6.22.

[Fe(η^5-C_5H_4-$CH_2OC_2H_5$){η^5-C_5H_4-CH=CH-[(η^6-C_7H_7)-RuCp*]}]PF_6 (13). A solution of [Fe(η^5-C_5H_4-$CH_2OC_2H_5$)(η^5-C_5H_4-CH=CH-C_7H_7)] (**12**) (0.57 g, 1.58 mmol) in CH_2Cl_2 (20 mL) was added dropwise into a solution of [Cp*Ru(MeCN)$_3$]-(PF_6) (0.84 g, 1.64 mmol) in CH_2Cl_2 (20 mL). After stirring at room temperature overnight, the mixture was filtered. The filtrate was condensed to 10 mL, and then diethyl ether (10 mL) was added. Recrystallization at T = −20 °C revealed **13** as a purple powder. Yield: 0.67 g, 57%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (3t, J = 7.0 Hz, 3H, CH_3), 1.29 (dd, J = 13.2 Hz, 2.8 Hz, 1H, H-7′$_{exo}$), 1.77 (s, 15H, C_5Me_5), 3.28 (m, 2H, H-6′, H-7′$_{endo}$), 3.45 (q, J = 7.0 Hz, 2H, CH_2CH_3), 4.17 (m, 3H, Cp and CpCH_2O), 4.24 (m, 2H, Cp), 4.37 (m, 3H, Cp), 4.56 (m, 1H, Cp), 4.90 (t, 1H, t, J = 6.0 Hz, H-5′), 5.05 (d, J = 6.2 Hz, 1H, H-2′), 6.02 (d, J = 16.0 Hz, 1H, H-α), 6.08 (m, 2H, H-3′, H-4′), 6.85 (d, J = 16.0 Hz, 1H, H-β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.4 (C_5Me_5), 15.8 (CH$_3$CH$_2$O) 23.6 (C-7′), 34.6 (C-6′), 58.1 (C-1′), 66.2 (CH$_3$$CH_2$O), 67.3 (Cp), 68.9 (Cp$CH_2$O), 70.3 (Cp), 70.8 (Cp), 71.4 (Cp), 71.6 (Cp), 72.0 (Cp), 72.3 (Cp), 80.1 (*ipso*-Cp), 93.1 (C-2), 93.9 (C-5), 94.4 (C-3′), 97.0 (C-4′), 98.5 (C_5Me$_5$), 125.1(C-α), 137.6 (C-β) ppm. Anal. Calcd for $C_{32}H_{39}$-FeRuOPF$_6$ (741.23): C, 51.85; H, 5.30. Found: C, 52.65; H, 4.89.



13

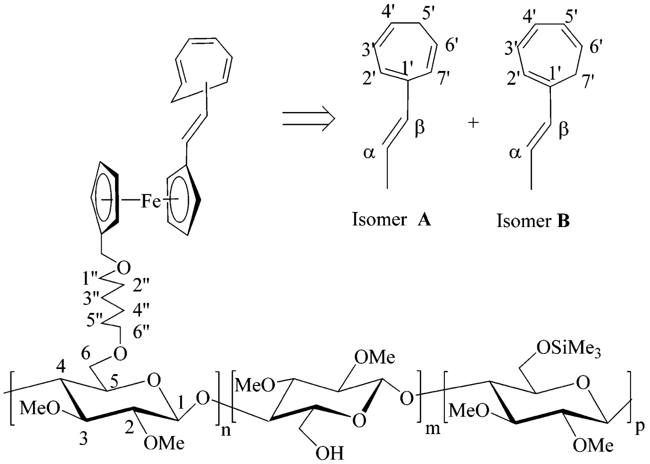
2,3-Di-*O*-methyl-6-*O*-partially[Fe{η^5-C_5H_4-$CH_2O(CH_2)_6$}-(η^5-C_5H_4-CH=CH-C_7H_7)] Cellulose (18d, DS = 0.5). 2,3-Di-*O*-methyl-6-hydroxy cellulose (80 mg, 0.42 mmol$_{AGU}$) was suspended in dry DMF (15 mL), stirred for 1 h, and then cooled to 0 °C. Sodium hydride powder (27 mg, 1.1 mmol) was added in portions. This mixture was allowed to warm to room temperature, stirred for 72 h, and then cooled to T = 0 °C again. A solution of [Fe{η^5-C_5H_4-$CH_2O(CH_2)_6$I}(η^5-C_5H_4CH=CH-C_7H_7)] (**10**) (656 mg, 0.30 mmol) in DMF (5 mL) (one-quarter of the total amount of **10**: 656 mg, 1.2 mol in 20 mL of DMF) was added dropwise. After warming to room temperature and stirring for 24 h, another quarter of the total amount of **10** was added in a similar performance. After stirring for about 24 h, the reaction mixture was cooled to 0 °C again, and additional sodium hydride powder (10 mg, 0.42 mmol) was added in portions. The mixture was allowed to warm to room temperature. Twelve and 36 h after the last addition of sodium hydride, the remainder of **10** was added in two equal portions using the same procedure. The mixture was stirred for another 48 h and then hydrolyzed with ice water (20 mL). After extraction with chloroform (30 mL), the organic layer was separated and filtered to give a red solution. After removal of solvent in vacuo, the residue was washed with acetone (3 × 15 mL) to afford a red swollen solid. This solid was redissolved in chloroform (10 mL). After filtration and removal of the solvent, the product was collected as a flaky red solid (0.120 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20−1.40 (H-3″, H-4″), 1.46−1.67 (H-2″, H-5″), 2.34 (t, J = 6.6 Hz, H-5′, isomer **A**), 2.68 (d, J = 7.0 Hz, H-7′, isomer **B**), 2.96 (H-2), 3.15−3.36 (H-3, H-6, H-1″, H-6″), 3.39−3.80 (O*Me*, H-5), 3.96 (H-4), 4.11 Cp, 4.19 (Cp, H-CpCH_2O), 4.26 (Cp), 4.36−4.41 (Cp, H-1), 5.36−5.56 (C_7H_7), 6.12−6.62 (C_7H_7, H-α, H-β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.2 (double intensity, C-3″, C-4″), 28.4 (C-7′, isomer **B**), 30.1 (double intensity, C-2″, C-5″), 61.1 (C-O*Me*), 62.2 (C-6), 67.7 (Cp), 69.4 (CpCH$_2$O), 69.9 (Cp), 70.09 (C-1″ or C-6″), 70.1 (Cp), 70.5 (C-6″ or C1″) 71.8 (Cp), 72.6 (C-5), 75.4 (C-4), 84.3 (C-2), 85.2 (C-3), 103.8 (C-1), 122.6 (C_7H_7), 124.9 (C_7H_7), 127.8 (C_7H_7), 128.0 (C_7H_7), 128.5 (C-β), 130.2 (C_7H_7),131.4 (C-α), 132.7 (C-1′) ppm. DS (calculated from ^{1}H NMR spectrum): 0.52; DS (calculated from atomic absorption spectrum) 0.53. The cellulose derivatives with DS = 0.1, 0.2, 0.3, and >0.6 (**18a**, **18b**, **18c**, **18e**) were obtained by keeping the same reaction procedure but changing the amounts of solvents and reagents according to Table 1. **18e** is soluble in acetone and was purified by column chromatography (Al_2O_3 neutral/10% H_2O, acetone/methanol, 1:3).



[Fe{η^5-C_5H_4-$CH_2O(CH_2)_4CH$=CH_2}(η^5-C_5H_4-CH=CH-C_7H_7)] (19). 2,3-Di-*O*-methyl-6-*O*-hydroxy cellulose (80 mg, 0.42 mmol$_{AGU}$) was suspended in dried DMF (10 mL). To this suspension was added a 10-fold excess of sodium hydride (0.1 g, 4.2 mmol). After stirring for half an hour, a solution of [Fe-{η^5-C_5H_4-$CH_2O(CH_2)_6$Br}(η^5-C_5H_4-CH=CH-C_7H_7)] (**8**) (0.63 g, 0.72 mmol) in DMF (15 mL) was added dropwise to this mixture under ice cooling. The mixture was allowed to warm to room temperature and stirred for 3 days. The mixture was slowly poured into slush water (30 mL). The extraction with CH_2Cl_2 (30 mL) afforded a red suspension. The solid was filtered off, and after removal of the solvent in vacuo, the residue was purified by column chromatography (Al_2O_3, neutral, 10% H_2O; hexane/ethyl acetate, 16:1) to give a deep red, oily product consisting of two isomers **A** and **B** (vide supra) in a ratio of 1:3. Yield: 0.21 g, 70%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.26−1.3 (m, 2H, CH_2), 1.40−1.56 (m, 2H, CH_2), 1.96−2.08 (m, 2H, CH_2), 2.37 (t, J = 6.6 Hz, 2H, H-5′, isomer **A**), 2.65 (d, J = 7.0 Hz, 2H, H-7′, isomer **B**), 3.32−3.39 (t, J = 6.6 Hz, 2H, OCH_2CH_2), 4.07 (t, J = 2.0 Hz, 2H, Cp), 4.14−4.17 (m, 4H, Cp, $CpCH_2O$), 4.22 (t, J = 2.0 Hz, 2H, Cp), 4.35 (t, J = 2.0 Hz, 2H, Cp), 4.88−5.51 (m, 2H, $CH{=}CH_2$), 5.39−5.55 (m, C_7H_7), 5.70−5.88 (m, 1H, $CH{=}CH_2$), 6.16−6.61 (m, C_7H_7, H-α, H-β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.9 (CH_2), 28.3 (CH_2), 29.6 (C-7′, C_7H_7, isomer **B**), 30.1 (C-5′, C_7H_7, isomer **A**), 33.9 (CH_2), 67.6 (Cp), 69.3 ($CpCH_2OCH_2$), 70.0 (double intensity, Cp), 70.4 ($CpCH_2O$), 70.9 (Cp), 84.1 (*ipso*-Cp), 84.8 (*ipso*-Cp), 114.9 ($CH{=}CH_2$),122.6 (C_7H_7), 124.9 (β), 127.9 (C_7H_7), 128.0 (C_7H_7),128.5 (C-β), 130.2 (C_7H_7), 131.4 (C-α), 132.7 (C-1′), 139.2 ($CH{=}CH_2$) ppm. Anal. Calcd for $C_{26}H_{30}FeO$ (414.13): C, 75.36; H, 7.30. Found: C, 75.80; H, 7.52.

2,3-Di-*O*-methyl-6-*O*-partially(trimethylsilyl)-6-*O*-partially[Fe{η^5-C_5H_4-$CH_2O(CH_2)_6$}(η^5-C_5H_4-CH=CH−C_7H_7)] Cellulose (20). Trimethyl chlorosilane (0.2 mL, 1.58 mmol) was added dropwise to a solution of 2,3-di-*O*-methyl-6-*O*-partially[Fe{η^5-C_5H_4-$CH_2O(CH_2)_6$}(η^5-C_5H_4-CH=CH-C_7H_7)] cellulose (DS 0.12, 0.14 g, 0.58 $mmol_{AGU}$) in THF (15 mL), and then several drops of absolute pyridine were added. After stirring at room temperature overnight, the solvent and excess trimethyl chorosilane were removed in vacuo. The residue was washed with water (20 mL) to remove pyridinium salt and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried with $MgSO_4$. After removal of the solvent and drying in vacuo for 1 h, the product was obtained as a red slurry. Yield: 0.15 g. ^1H NMR (400 MHz, $CDCl_3$): δ 0.095 ($SiMe_3$), 1.17−1.36 (H-3″, H-4″), 1.45−1.60 (H-2″, H-5″), 2.31 (t, J = 6.6 Hz, H-5′, isomer **A**), 2.63 (d, J = 7.0 Hz, H-7′, isomer **B**), 2.92 (H-2), 3.15−3.37 (H-3, H-6, H-1″, H-6″), 3.39−3.77 (O*Me*, H-5), 3.93 (H-4), 4.05−4.23(Cp, $CpCH_2O$), 4.36−4.41 (Cp, H-1), 5.36−5.52 (C_7H_7), 6.12−6.60 (C_7H_7, H-α, H-β) ppm. IR: 842 cm^{-1} (O-$SiCH_3$), 1248 cm^{-1} (Si-CH_3). DS of ferrocene derivatives (calculated from ^1H NMR spectrum): 0.10; DS of $SiMe_3$ (calculated from ^1H NMR spectrum): 0.36.

Cyclic Voltammetry. The measurements of cyclic voltammetry were carried out in CH_2Cl_2 with 0.4 M $[N(nBu)_4]PF_6$ as supporting electrolyte at room temperature with different scan rates (10−500 mV/s). An Amel 5000 system was used with a Pt wire as the working electrode and a Pt plate as the auxiliary electrode. The potentials were measured against Ag/AgCl and are referenced against $E_{1/2}(FcH/FcH^+) = 0$ V.



Size-Exclusion Chromatography (SEC). SEC was performed with a Waters 510 pump equipped with autosampler and PL Gel Mixed-B, C, and D columns (7.8 × 300 mm each), a Waters RI 410 differential refractometer, and a Waters UV/vis 486 detector. THF was used as a mobile phase (flow rate 1.0 mL/min). The concentration of the polymer solution was about 1.0 g/L, and 100 μL was injected per run. Polystyrene was used as the standard.

Differential Scanning Calorimetry (DSC). The thermal properties were determined with a differential scanning calorimeter (DSC, DuPont 2100) under argon atmosphere at a rate of 10 °C/min from 30 to 275 °C. The sample mass was about 8.8 mg.

Liquid Crystalline Properties. Lyotropic liquid crystalline films of **18c** were prepared by layering a diluted, isotropic solution of the sample in CH_2Cl_2 on the surface of the glass. The solvent was allowed to evaporate. Anisotropic textures developed at higher concentration.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (DFG) (GK611). F.Z. wishes to thank the DFG for a postdoctoral fellowship within the Graduate School GK 611.

OM0343216