

# Ferrocene derivatives containing anthracene linked by spacers<sup>1</sup>

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## Abstract

Several ferrocene derivatives linked by a non-conjugated spacer to a 9,10-diphenylanthracene unit have been prepared, among them an amphiphilic isoquinolinium salt. By X-ray structure analysis of the intermediate 9,10-bis(4-hydroxyphenyl)anthracene, an almost perpendicular arrangement of the phenyl groups with respect to the anthracene was found. The properties of the compounds were studied by NMR and cyclovoltammetry, which suggest that the isoquinolinium salt forms inverse micelles in organic solvents. No indication for intramolecular aggregation of ferrocene and isoquinolinium moieties by folding of the flexible alkyl spacers could be detected. The compound forms a monolayer when spread on water which can be transferred to a quartz surface. Repeated transfer leads to a non-centrosymmetric Z-type array of layers in the Langmuir–Blodgett film.

**Keywords:** Ferrocene; Iron; X-ray structure analysis

## 1. Introduction

Donor–acceptor compounds are of both scientific and industrial interest not only as models for the investigation of electron transfer [1,2] and solar energy storage systems like photosynthetic reaction centres [3,4], but also as basic materials for advanced technologies, such as non-linear optics [5–7], photoelectrochemical reactions [8,9], and photo-optical devices [10]. In this article, we present the synthesis and structural investigation of ferrocene derivatives, where the organometallic moiety is linked by a non-conjugated spacer to a 9,10-diphenylanthracene unit. Ferrocene is known as a good electron donor [11], and anthracene is readily excited by UV light. Attaching an acceptor such as an ammonium ion to the molecule leads to an amphiphilic material able to form Langmuir–Blodgett films. Such compounds are promising candidates for photoconducting materials. A few similar systems have been reported, but only as a mixture of structural isomers [12–14], and were not well characterized.

## 2. Synthesis of the compounds

The procedure for the preparation of the symmetrical derivatives is outlined in Fig. 1, and for the unsymmetrical compounds in Fig. 2. The synthesis is straightforward and based on the diphenol (**4**) (9,10-bis(4-hydroxyphenyl)anthracene). The best synthesis of this central building block is the palladium-catalyzed Grignard cross coupling of 9,10-dibromoanthracene [15] with the magnesium derivative of either 4-methoxy-bromobenzene or 4-benzyloxy-bromobenzene, to give the methoxy ether (**10a**) or the benzyloxy ether (**10b**), followed by cleavage of the ether group with boron tribromide (for the methoxy ether) or by hydrogenolysis (for the benzyl ether). Other procedures described in the literature for the methoxy compound start with either anthraquinone (two steps, overall yield 30%) [16] or use the diazonium salt of 4-anisidine for the alkylation of anthracene (yield 18%) [17]. The cross coupling reaction is much easier to perform and gives higher yields (79% and 63% respectively for the methoxy and benzyloxy compounds). For the synthesis of the unsymmetrical derivatives, we used a stepwise Grignard cross coupling reaction, first with one equivalent of 4-methoxyphenylmagnesium bromide, and then with 4-benzyloxyphenylmagnesium bromide, in a one-pot procedure, giving (**8**). Catalytic hydrogenation leads to the monophenol (**1**) in high yield. If two

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<sup>1</sup> Dedicated to Professor Peter L. Pauson on the occasion of his 70th birthday.

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Table 1  
Yields and properties of compounds prepared

| Compound | Yield (%)                         | $R_f^a$           | M.p. (°C)      | Formula                | Molar mass | Mass spectrum ( $M^+$ ) |
|----------|-----------------------------------|-------------------|----------------|------------------------|------------|-------------------------|
| (1)      | 59                                | 0.23              | 269 (dec.)     | $C_{28}H_{20}O_2$      | 376.43     | 376                     |
| (2)      | 54                                | 0.24              | 238–240        | $C_{33}H_{24}O_2$      | 452.52     | 452                     |
| (3)      | 68                                | 0.38              | 215 (dec.)     | $C_{50}H_{38}Fe_2O_4$  | 814.23     | 814                     |
| (4)      | 66 <sup>b</sup> ; 89 <sup>c</sup> | 0.14              | > 300 (dec.)   | $C_{26}H_{18}O_2$      | 362.41     | 362                     |
| (5)      | 88                                | 0.87              | 270 (dec.)     | $C_{54}H_{50}Fe_2O_2$  | 842.63     | 842                     |
| (6a)     | 47                                | 0.88              | 268            | $C_{39}H_{32}FeO_2$    | 588.49     | 589 <sup>d</sup>        |
| (6b)     | 54                                | 0.82              | 210            | $C_{41}H_{36}FeO_2$    | 616.55     | 616                     |
| (6c)     | 49                                | 0.90              | 187            | $C_{42}H_{38}FeO_2$    | 630.57     | 631 <sup>d</sup>        |
| (6d)     | 75                                | 0.30              | 254 (dec.)     | $C_{39}H_{30}FeO_3$    | 602.48     | 602                     |
| (7)      | 78                                | 0.35 <sup>e</sup> | 208 (dec.)     | $C_{53}H_{48}BrFeNO_2$ | 866.67     | 786.8 <sup>k</sup>      |
| (8)      | 70                                | 0.77              | 235            | $C_{34}H_{26}O_2$      | 466.55     | 466                     |
| (9a)     | 61                                | 0.23              | 205 (dec.)     | $C_{20}H_{13}BrO$      | 349.21     | 350 <sup>l</sup>        |
| (9b)     | 78                                | 0.45 <sup>f</sup> | 179            | $C_{21}H_{15}BrO$      | 363.24     | 363                     |
| (10a)    | 79                                | 0.86              | 285            | $C_{28}H_{22}O_2$      | 390.46     | 390                     |
| (10b)    | 63                                | 0.82              | 299–301 (dec.) | $C_{40}H_{30}O_2$      | 542.43     | 542                     |
| (11a)    | 82                                | 0.20 <sup>g</sup> | 75             | $C_{19}H_{20}FeO_3S$   | 384.20     | — <sup>j</sup>          |
| (11b)    | 80                                | 0.22 <sup>g</sup> | 44             | $C_{21}H_{24}FeO_3S$   | 412.31     | — <sup>j</sup>          |
| (11c)    | 86                                | 0.22 <sup>g</sup> | 74             | $C_{22}H_{26}FeO_3S$   | 426.34     | — <sup>j</sup>          |
| (13)     | 8 <sup>h</sup> ; 52 <sup>i</sup>  | 0.28              | 188 (dec.)     | $C_{40}H_{34}FeO_2$    | 602.52     | 602                     |
| (14)     | 74                                | 0.94              | 209 (dec.)     | $C_{44}H_{41}BrFeO_2$  | 737.53     | 736                     |
| (15)     | 5                                 | 0.10              | 156            | $C_{39}H_{30}FeO_3$    | 591.48     | 591                     |

<sup>a</sup> Silicagel–dichloromethane, unless otherwise stated. <sup>b</sup> From (10a). <sup>c</sup> From (10b). <sup>d</sup> FAB mass spectrum, ( $M + 1$ )<sup>+</sup> peak. <sup>e</sup> Dichloromethane–ethanol 1:1. <sup>f</sup>  $CCl_4$ . <sup>g</sup> Ether–hexane 1:5. <sup>h</sup> as by-product from diphenol (4). <sup>i</sup> from (12). <sup>j</sup> Not determined. <sup>k</sup> FAB mass spectrum,  $M^+$  of cation. <sup>l</sup> Relative to <sup>81</sup>Br.

different cleavable ethers are required, 4-trimethylsiloxyphenylmagnesium bromide is the reagent of choice for the first coupling step. The siloxy group is cleaved already during acidic workup, giving (2), which allows for selective manipulations at both phenol units. Alkyla-

tion of the phenol groups with dibromoalkanes or with tosylalkylferrocenes (11) does not provide problems. For the preparation of the donor–acceptor compound (7), the formation of the isoquinolinium salt is the final step. Yields and properties of the compounds are shown

Table 2  
NMR data <sup>a</sup> of 9-[4-(4-ferrocenylbutoxy)phenyl]-10-[4-(4-(*N*-isoquinolinio)butoxy)phenyl]anthracene bromide (7)

| <sup>1</sup> H NMR             | $\delta$                | <sup>13</sup> C NMR | $\delta$ | <sup>13</sup> C NMR            | $\delta$ |
|--------------------------------|-------------------------|---------------------|----------|--------------------------------|----------|
| H <sub>Iso</sub>               | 10.95 (s, 1H)           | C <sub>Iso</sub>    | 137.31   | CH <sub>Ar</sub>               | 114.35   |
| H <sub>Iso</sub>               | 8.75 (d, 8.3 Hz, 1H)    | C <sub>Iso</sub>    | 127.28   | CH <sub>Anth</sub>             | 126.89   |
| H <sub>Iso</sub>               | 8.55 (d, 7.0 Hz, 1H)    | C <sub>Ar</sub>     | 158.48   | CH <sub>Anth</sub>             | 124.86   |
| H <sub>Iso</sub>               | 8.35 (d, 7.0 Hz, 1H)    | C <sub>Ar</sub>     | 157.97   | CH <sub>Anth</sub>             | 124.81   |
| H <sub>Iso</sub>               | 8.12 (m, 2H)            | C <sub>Ar</sub>     | 136.81   | CH <sub>Cp</sub>               | 68.46    |
| H <sub>Iso</sub>               | 7.96 (t, 6.8 Hz, 1H)    | C <sub>Ar</sub>     | 136.45   | CH <sub>Cp-R</sub>             | 68.06    |
| H <sub>Anth</sub>              | 7.71 (m, 4H)            | C <sub>Anth</sub>   | 131.34   | CH <sub>Cp-R</sub>             | 67.09    |
| H <sub>Anth + Ar</sub>         | 7.26–7.33 (m, 8H)       | C <sub>Anth</sub>   | 130.83   | CH <sub>2</sub> N <sup>+</sup> | 61.54    |
| H <sub>Ar</sub>                | 7.10 (d, 8.6 Hz, 2H)    | C <sub>Anth</sub>   | 130.17   | CH <sub>2</sub> O              | 67.80    |
| H <sub>Ar</sub>                | 7.07 (d, 8.4 Hz, 2H)    | C <sub>Anth</sub>   | 130.12   | CH <sub>2</sub> O              | 67.17    |
| H <sub>Cp</sub>                | 4.12 (s, 5H)            | C <sub>Fc</sub>     | 88.92    | CH <sub>Anth</sub>             | 127.03   |
| H <sub>Cp-R</sub>              | 4.11 (t, 1.8 Hz, 2H)    | CH <sub>Iso</sub>   | 142.0    | CH <sub>2</sub>                | 29.22    |
| H <sub>Cp-R</sub>              | 4.07 (t, 1.7 Hz, 2H)    | CH <sub>Iso</sub>   | 137.23   | CH <sub>2</sub>                | 29.22    |
| CH <sub>2</sub> N <sup>+</sup> | 5.29 (t, 7.4 Hz, 2H)    | CH <sub>Iso</sub>   | 134.38   | CH <sub>2</sub>                | 17.56    |
| CH <sub>2</sub> O              | 4.18 (t, 5.2 Hz, 2H)    | CH <sub>Iso</sub>   | 131.49   | CH <sub>2</sub>                | 25.95    |
| CH <sub>2</sub> O              | 4.12 (t, 7.9 Hz, 2H)    | CH <sub>Iso</sub>   | 131.40   | CH <sub>2</sub>                | 29.29    |
| CH <sub>2</sub> (Fc)           | 2.46 (t, 7.6 Hz, 2H)    | CH <sub>Iso</sub>   | 127.0    |                                |          |
| CH <sub>2</sub>                | 2.48 (m, 2H)            | CH <sub>Iso</sub>   | 126.31   |                                |          |
| CH <sub>2</sub>                | 1.92 (quin. 7.2 Hz, 2H) | CH <sub>Ar</sub>    | 132.40   |                                |          |
| CH <sub>2</sub>                | 2.09 (m, 2H)            | CH <sub>Ar</sub>    | 132.26   |                                |          |
| CH <sub>2</sub>                | 1.78 (quin. 7.7 Hz, 2H) | CH <sub>Ar</sub>    | 114.35   |                                |          |

<sup>a</sup> Spectra recorded in CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ -values given. Indices: 1, isoquinolinium side; 2, ferrocenyl side; Iso, isoquinolinium moiety; Anth, anthracene moiety; Ar, phenyl groups; Fc, ferrocene moiety; Cp–R, substituted cyclopentadienyl ring.

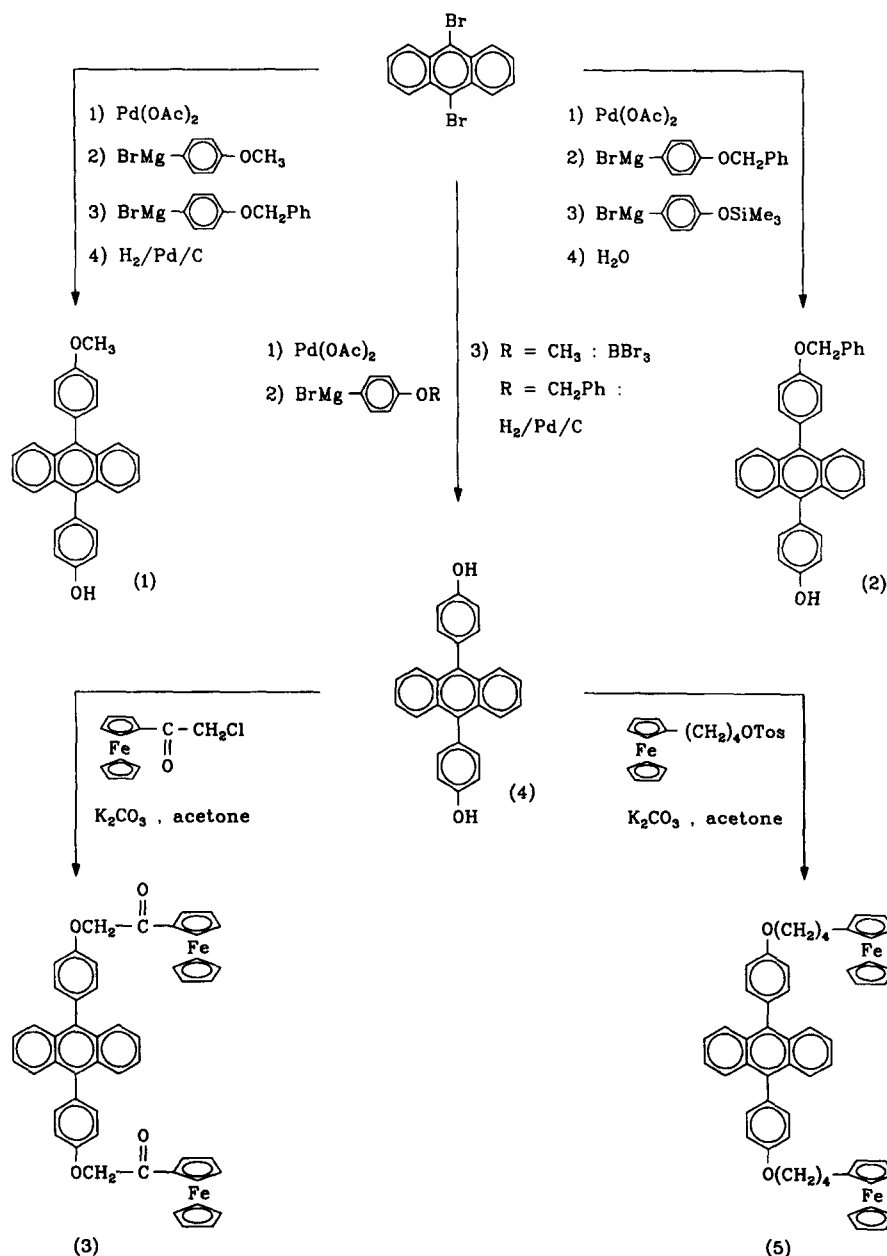


Fig. 1. Synthesis of symmetrical ferrocene derivatives containing anthracene.

in Table 1, and the NMR data of (7) are given in Table 2. NMR data for all other new compounds are available as supplementary material. Details on the intermediates are found in the experimental section.

### 3. Structure of the 9,10-bis(4-hydroxyphenyl)anthracene building block

For the optical properties of the compounds, the diphenylanthracene moiety is of central importance. Based on MO calculations, some authors have suggested that the whole unit could be either planar, allowing for extensive delocalization of the aromatic system,

or having a torsion angle of  $60^\circ$  between the anthracene and the phenyl groups. Both geometrical arrangements gave a satisfactory agreement of calculated spectra with the experimental UV spectra of the diphenylanthracene anion [18]. However, a planar arrangement seems highly improbable because of the extremely small distance between the hydrogen atoms of the anthracene and the phenyl groups in this conformation ( $0.61 \text{ \AA}$ ). Repulsion of the hydrogens should rather lead to a  $90^\circ$  torsion angle. To see how far delocalization might influence the conformation of the diphenylanthracene unit, we have conducted an X-ray structure analysis of 9,10-bis(4-hydroxyphenyl)anthracene (4). The result is shown in Fig. 3 and Table 3. The unit cell contains two independent

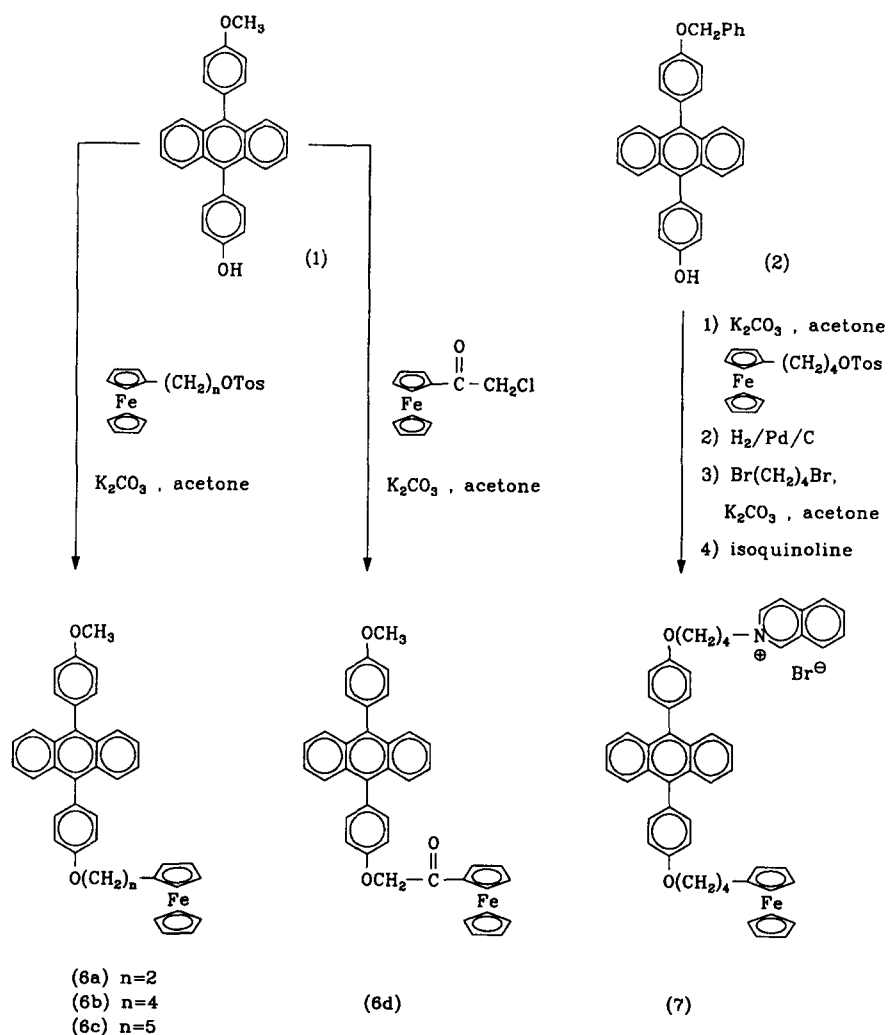


Fig. 2. Synthesis of unsymmetrical ferrocene derivatives containing anthracene.

molecules of (4) with different orientations of the phenyl groups; in molecule 1, the plane through one of the phenyl groups is almost perpendicular to the plane through the anthracene moiety (angle  $85.87^\circ$ ), while the angle for the other phenyl group is smaller ( $74.43^\circ$ ). In molecule 2, the corresponding angles are similar ( $70.48^\circ$

and  $71.19^\circ$ , respectively). These strong deviations from planarity exclude extended delocalization of the aromatic systems; this means that anthracene is the chromophore mainly responsible for UV absorption, while the phenyl groups can be considered rather as part of the spacer in the ferrocene derivatives. One molecule of

Table 3

Selected bond distances and angles in 9,10-bis(4-hydroxyphenyl)anthracene (4) with atom numbering for the first molecule as in Fig. 3; the second value is for the second independent molecule in the unit cell

| Bond length (Å) |          |          | Angle (deg) |          |          |
|-----------------|----------|----------|-------------|----------|----------|
| C1–C7           | 1.495(4) | 1.500(4) | C1–C7–C8    | 118.1(3) | 119.7(3) |
| C7–C8           | 1.420(5) | 1.411(4) | C1–C7–C20   | 121.4(3) | 120.0(3) |
| C8–C13          | 1.440(4) | 1.442(4) | C3–C4–O1    | 122.1(3) | 117.5(4) |
| C13–C14         | 1.397(5) | 1.386(5) | C5–C4–O1    | 117.8(3) | 122.4(4) |
| C14–C21         | 1.500(4) | 1.495(4) | C13–C14–C21 | 119.7(3) | 119.8(3) |
| C14–C15         | 1.416(5) | 1.412(5) | C15–C14–C21 | 120.1(3) | 120.0(3) |
| C15–C20         | 1.441(4) | 1.444(4) | C23–C24–O2  | 117.7(3) | 118.0(3) |
| C7–C20          | 1.382(5) | 1.392(5) | C25–C24–O2  | 122.1(3) | 120.9(3) |
| C4–O1           | 1.377(4) | 1.371(4) | C2–C1–C7    | 121.5(3) | 121.6(3) |
| C4–O2           | 1.375(4) | 1.387(4) | C6–C1–C7    | 120.7(3) | 121.4(3) |

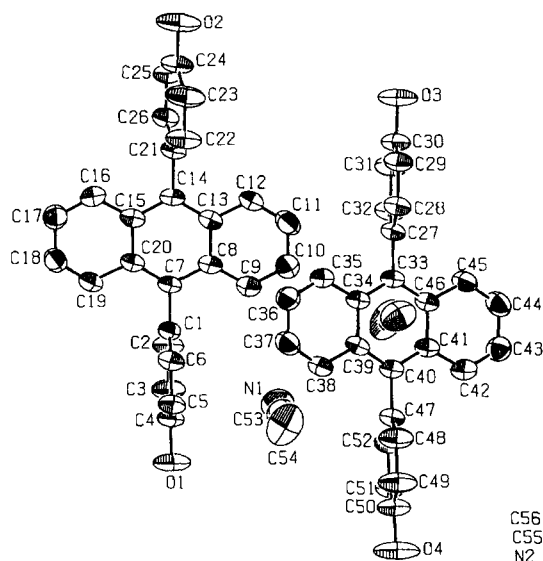


Fig. 3. ORTEP plot of the molecules of (4) in the elementary cell.

acetonitrile per molecule of (4) is included in the crystal, but this solvent of crystallization does not have close intermolecular contacts with (4). The two different orientations are therefore most likely due to crystal packing effects. Semi-empirical calculations (MNDO) suggest that, in the gas phase, the most stable conformation is of the propeller-type, with deviations of only 2 and 3° from perpendicular to the plane of anthracene.

#### 4. Redox properties, conformation and aggregation

The redox properties of the ferrocene derivatives have been determined by cyclic voltammetry in acetonitrile solution, with  $\text{NBu}_4\text{BF}_4$  as electrolyte. The results are shown in Table 4. All potentials are quoted relative to ferrocene–ferrocenium redox couple ( $E_{1/2}^{\text{ox}} = 0$  V).

The ferrocene moiety always shows a reversible oxidation at a potential comparatively close to unsubstituted ferrocene, if an alkyl chain is attached to it, or to

acetylferrocene ( $E_{1/2}^{\text{ox}} = 0.26$  V), if a carbonyl group is directly attached, as in compounds (3) and (6d). Compounds (3) and (5) contain two ferrocene units which are oxidized simultaneously. Compound (6c) does not show the oxidation of ferrocene in the first cycle, but only after reduction. This suggests that iron should initially be  $\text{Fe}^{3+}$ . In contrast, NMR measurements of (6c) in *d*-chloroform solution do not show any sign of paramagnetism. This means that the compound is oxidized to the  $\text{Fe(III)}$  state only in the strongly polar electrolyte solution, and not under any other conditions applied, by a mechanism facilitating the oxidation with increasing chain length of the spacer. A plausible explanation is the activation of the ferrocene group by light, mediated by anthracene as photosensitizer. We have estimated the free enthalpy of the light-induced oxidation of the ferrocene moiety by electron transfer using the Rehm–Weller equation [19]; for an excitation wavelength of 420 nm (which is on the low energy edge of the absorption of the diphenylanthracene moiety and present in the laboratory light), a distance of 15 Å between the charges after the electron transfer, and an effective ionic radius of 4.5 Å, one calculates a value of  $\Delta G = 0$  eV for chloroform as solvent ( $\epsilon_s = 4.8$ ), and  $\Delta G = -0.42$  eV for acetonitrile ( $\epsilon_s = 37$ ), which means that such an oxidation is thermodynamically favoured in the electrolyte solution where the dielectric constant is even higher than in pure acetonitrile, but not in chloroform used for the other experiments. That the light-induced electron transfer is thermodynamically favoured does not necessarily mean that it is kinetically possible; for the transfer to occur, donor (ferrocene) and acceptor (excited anthracene) must come in close contact. No NOE effects indicating a close spatial vicinity of ferrocene and anthracene moiety could be detected by two-dimensional ROESY techniques in any of the compounds (6), using *d*-chloroform as solvent. Thus, the molecules are either not able to adopt conformations where ferrocene comes close to the anthracene (compounds (6a) and (6b) with a short spacer), or they adopt such conformations only for periods too short to desolve a significant NOE effect (compound (6c) with a longer spacer). For short distances, electron transfer is very fast [1], and can occur in (6c) in the strongly polar electrolyte solution from the corresponding conformations with short anthracene–ferrocene distances, but not in (6a) and (6b) where no such conformations exist.

The NMR spectra of the amphiphilic compound (7) are shown in Table 2. A very characteristic feature is that the signals of the isoquinolinium unit and the  $\text{CH}_2$  groups of the  $\text{C}_4$  chain directly attached to it are strongly broadened, while all the other signals have their normal appearance. This cannot be due to the presence of paramagnetic material such as  $\text{Fe(III)}$ , as this would influence mainly the ferrocene moiety which has the lowest oxidation potential. In addition, the

Table 4  
Cyclic voltammetric study of the ferrocene derivatives, in 0.2 M  $\text{NBu}_4\text{BF}_4$  solution in acetonitrile: potentials are quoted relative to ferrocene–ferrocenium redox couple ( $E_{1/2}^{\text{ox}} = 0$  V)

| Compound | $E_{1/2}^{\text{ox}}$ (Fe) | $E^{\text{ox}}$ (others) <sup>a</sup> |
|----------|----------------------------|---------------------------------------|
| (3)      | 0.28                       | 0.77 r                                |
| (5)      | −0.04                      | 0.80 p                                |
| (6a)     | 0.01                       | 0.80 r; 1.02 i                        |
| (6b)     | −0.04                      | 0.79 p; 0.96 i                        |
| (6c)     | −0.04 <sup>b</sup>         | 0.78 r; 1.00 i                        |
| (6d)     | 0.30                       | 0.78 r                                |
| (7)      | −0.04                      | 0.70 p; 1.06 i                        |

<sup>a</sup> r, reversible,  $E_{1/2}^{\text{ox}}$  quoted; i, irreversible,  $E_p^{\text{ox}}$  quoted; p, partially reversible,  $E_p^{\text{ox}}$  quoted. <sup>b</sup> Wave only appears after reduction at  $E \leq -1.0$  V.

reversible Fe(II)–Fe(III) transition is clearly seen in the cyclovoltammograms. However, no reduction of the isoquinolinium part could be detected; an irreversible wave at about  $-1.3$  V would be expected, as for the model compound *N*-ethylisoquinolinium bromide ( $E_p^{\text{red}} = -1.34$  V under the same experimental conditions). A plausible explanation of both the NMR and the electrochemical behaviour is the formation of inverse micelles in organic solution, with the isoquinolinium and the bromide inside. This protects the ionic parts of the molecules from being oxidized at the electrode and restricts their mobility which leads to broadening of the NMR signals. In addition, no NOE effects indicating a folding of the molecule to adopt conformations where the donor ferrocene comes close to the acceptor isoquinolinium can be detected; such folding could be expected if no aggregation occurred.

### 5. Langmuir–Blodgett films

The amphiphilic compound (7) forms reasonably stable (until  $37 \text{ mN m}^{-1}$  surface tension) monolayers when spread on water. The films can be transferred to a quartz carrier at  $20 \text{ mN m}^{-1}$ . The area occupied by one molecule is determined as about  $60 \text{ \AA}^2$ . This is a bit less than the area calculated as a square from the diameters of anthracene and phenyl ( $77 \text{ \AA}^2$  when adding the hydrogen van der Waals radii to the largest distances of the nuclei obtained from the X-ray structure of (4)), indicating that the molecules do not align with either the anthracene or the phenyl groups to form perpendicular stacks, but are shifted to one side to allow for closer contacts of these most bulky groups. Repeated transfer of monolayers of (7) to the quartz carrier leads to Langmuir–Blodgett films. The transfer characteristics suggest a non-centrosymmetric Z-type array of layers, where the ferrocenes of one layer come in close contact with the isoquinolinium moieties of the following layer. Films of up to 36 monolayers have been obtained. The number of molecules in such an array corresponds to that in a  $10^{-5} \text{ M}$  solution in a conventional UV cuvette in a path of 1 cm, and the UV spectra of such solutions are therefore directly comparable in intensity with that of the film. Such a comparison is made in Fig. 4.

The UV spectra (measured in dichloromethane) of the model compounds for the building blocks from which the amphiphilic molecule is constructed, i.e. ferrocene, 9,10-bis(4-methoxyphenyl)anthracene (10a), and *N*-dodecylisoquinolinium bromide, add nicely to form the shape of the solution spectrum of (7), indicating that the units are almost independent from one another. In the Langmuir–Blodgett film, however, the part of the spectrum derived from the diphenylanthracene moiety appears broader and red-shifted for about 20 nm. This is

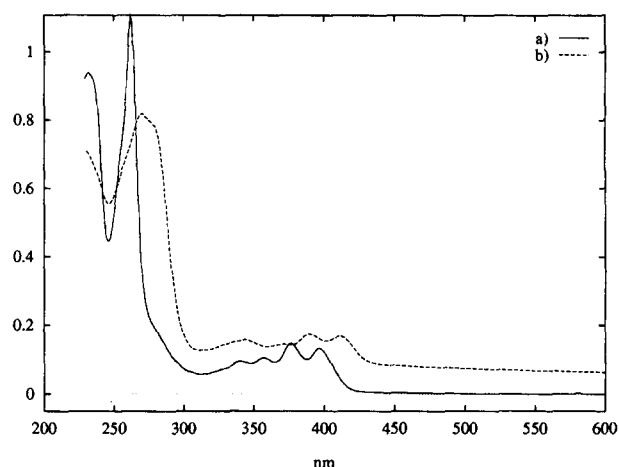


Fig. 4. UV spectrum of (7): (a) in  $10^{-5} \text{ M}$  solution in dichloromethane; (b) in a Langmuir–Blodgett film (36 layers).

clearly indicative for an intermolecular interaction of the diphenylanthracene units due to stacking in the film, and confirms the conclusions drawn from the calculated and observed areas per molecule.

The possibility to obtain non-centrosymmetric Langmuir–Blodgett films from the amphiphilic donor–acceptor compound (7) has considerable interest for the construction of materials with non-linear optical characteristics. We intend to continue the investigation of the optical properties of this and related compounds, with the aim to obtain materials for optical devices.

### 6. Experimental

#### 6.1. General

NMR spectra were measured with a Bruker AM 360 instrument (360.134 MHz for  $^1\text{H}$  and 90.556 MHz for  $^{13}\text{C}$ ). Electrochemical studies were performed with either an EG&G PAR 173 potentiostat and an EG&G PARC 175 universal programmer, or with a DT 2101 potentiostat and a PR RI waveform generator (Hi-Tek-Instruments), using a 0.2 M solution of  $\text{NBu}_4\text{BF}_4$  in acetonitrile, a platinum working electrode, and a silver reference electrode. Potentials were determined relative to the internal ferrocene–ferrocenium redox couple ( $E_{1/2}^{\text{ox}} = 0.40 \text{ V vs. SCE}$ ) for compounds (3) and (6b), or relative to the internal acetylferrocene–acetylferrocenium couple ( $E_{1/2}^{\text{ox}} = 0.66 \text{ V vs. SCE}$ ) [20] for the other compounds. They are quoted relative to ferrocene–ferrocenium ( $E_{1/2}^{\text{ox}} = 0 \text{ V}$ ).

Mass spectra were obtained with a Varian MAT CH5 spectrometer (70 eV for EI spectra). UV–VIS spectra were determined with Perkin–Elmer Lambda 17 and Lambda 2 spectrophotometers.

Langmuir–Blodgett films of (7) were obtained by spreading a  $10^{-4} \text{ M}$  solution of the compound in

dichloromethane on water (Millipore quality) as sub-phase, giving a film stable until  $37 \text{ mN m}^{-1}$ , which was transferred at a surface tension of  $20 \text{ mN m}^{-1}$  to a quartz carrier purified with  $\text{CrO}_3\text{--H}_2\text{SO}_4$ , followed by treatment with  $10^{-4} \text{ M}$  aqueous  $\text{NaOH}$ . A total of 36 layers was transferred to the carrier in a Z-type arrangement.

Semi-empirical geometry optimizations were performed with the HYPERCHEM software package, using the standard parametrization for MNDO.

## 6.2. Crystal structure determination of (4)

A colourless crystal of (4) was found to have two independent molecules and two molecules of acetonitrile in the unit cell ( $\text{C}_{28}\text{H}_{21}\text{NO}_2$ ,  $M_r = 403.48 \text{ a.m.u.}$ ). The crystal showed the centrosymmetric triclinic space group  $P\bar{1}$  (IT-number: 2). Final unit cell constants were determined by least squares refinement of 25 automatically centred reflections in the range  $78.2 < 2\theta < 88.6^\circ$ , using  $\text{Cu(K}\alpha\text{)}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ );  $a = 8.863(1)$ ,  $b = 12.681(1)$ ,  $c = 19.488(2) \text{ \AA}$ ;  $\alpha = 93.71(1)$ ,  $\beta = 94.68(1)$ ,  $\gamma = 91.14(1)^\circ$ ;  $V = 2177.8 \text{ \AA}^3$ ;  $Z = 4$ ,  $\rho_{\text{calc}} = 1.231 \text{ g cm}^{-3}$ ,  $F(000) = 848.0$ .

The data collection was performed with a CAD4 (Enraf–Nonius) diffractometer with a graphite monochromator, at  $23 \pm 1^\circ\text{C}$ , in the range  $1.0 < \theta < 65.0^\circ$  ( $h$ : 0/9;  $k$ :  $-14/14$ ;  $l$ :  $-17/17$ ). For every reflection, the maximum scan time was 90 s, using the  $\omega$ – $2\theta$  scan mode, with  $(0.7 + 0.25 \tan \theta)^\circ \pm 25\%$ . 7812 reflections were measured. From the 5849 independent reflections, 4114 had  $I > 3\sigma(I)$  and were used for the structure determination by direct methods, difference Fourier syntheses and least squares refinement. A total of 62 ‘heavy’ atoms were found in the asymmetric unit and refined with anisotropic thermal displacement parameters; 703 parameters were full matrix refined. With the exception of the acetonitrile hydrogens, all hydrogen atoms were found by difference Fourier synthesis and refined isotropically. In the last refinement step, convergence was achieved with shift/error of less than 0.0001 and  $R = (\sum \|F_o\| - \|F_c\|) / \sum \|F_o\| = 0.047$ ,  $R_w = \{[\sum (\|F_o\| - \|F_c\|)^2] / (\sum w \|F_o\|^2)\}^{1/2} = 0.044$ . The residual electron density was  $+0.15/-0.21 \text{ e \AA}^{-3}$ . Data were not corrected for absorption ( $\mu = 0.7 \text{ cm}^{-1}$ ) but for extinction (Larson’s parameter: 104.2) [21].

All calculations were performed on a DECstation 5000/25 computer with the programs SDP [22], CRYSTALS [23], and PLATON [24]. The complete material has been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenheim-Leopoldshafen, and is available upon request, by quoting the deposition number CSD-59307, the authors, and the citation.

## 6.3. Synthesis of the compounds

Yields and properties of new compounds are given in Table 1. NMR data for (7) are reported in Table 2, of all other compounds in the supplementary material.

Starting materials were prepared according to literature procedures: 4-benzoyloxy-bromobenzene [25], 4-trimethylsiloxy-bromobenzene [26], chloroacetylferrocene [27], 2-ferrocenylacetic acid, 4-ferrocenylbutanoic acid, 5-ferrocenylpentanoic acid [28]. The  $\omega$ -ferrocenylalkyltosylates (11a, b, c) were obtained from the carboxylic acid by standard  $\text{LiAlH}_4$  reduction to the alcohols, followed by conventional treatment with 4-toluene-sulfonyl chloride–pyridine–DMAP in ether.

## 6.4. Palladium-catalyzed Grignard cross coupling

### 6.4.1. For symmetric 9,10-diphenylanthracene derivatives

A Grignard solution was prepared from magnesium (0.90 g, 38 mmol) and 38 mmol of the corresponding substituted bromobenzene (4-bromoanisole, 4-benzoyloxy-bromobenzene) in 80 ml of dry ether. This solution was added dropwise within 1 h to a refluxing solution of 9,10-dibromoanthracene (5.0 g, 15 mmol) in 400 ml of dry THF containing 70 mg of palladium(II) acetate. After a further 1 h of reflux, the mixture was cooled to room temperature. 9,10-Bis(4-methoxyphenyl)anthracene (10a) was isolated by filtration with subsequent washing with dichloromethane (50 ml) to remove soluble impurities, and Soxhlett extraction of the residue with dichloromethane for about 2 days. The product was obtained by evaporation of the solvent from the extracts as slightly yellow powder. 9,10-Bis(4-benzoyloxyphenyl)anthracene (10b) was isolated by complete evaporation of the solvents, addition of hexane (150 ml), filtration and washing of the solid with dichloromethane (10 ml). The residue was purified by chromatography (silicagel, dichloromethane) to yield a pale yellow powder.

### 6.4.2. For unsymmetric anthracene derivatives

A Grignard solution was prepared from magnesium (0.45 g, 19 mmol) and 19 mmol of the corresponding substituted 4-bromobenzene (4-bromoanisole, 4-trimethylsiloxy-bromobenzene) in 40 ml of dry ether. This solution was added dropwise within 1 h to a refluxing solution of 9,10-dibromobenzene (5.0 g, 15 mmol) in 400 ml of dry THF containing 70 mg of palladium(II) acetate. After stirring for an additional 1 h at  $65^\circ\text{C}$ , the mixture was either worked up by the addition of water, to give 9-bromo-10-(4-methoxyphenyl)anthracene (9b) from 4-bromoanisole or 9-bromo-10-(4-hydroxyphenyl)anthracene (9a) from 4-trimethylsiloxy-bromobenzene, or subjected to a second cross coupling by dropwise addition of a Grignard solution, prepared from 19 mmol

(5.0 g) of 4-benzyloxy-bromobenzene in the manner described above, to the refluxing mixture, and refluxing for an additional hour. 9-(4-Benzyloxyphenyl)-10-(4-methoxyphenyl)anthracene (**8**) was isolated by complete evaporation of the solvents, addition of hexane (150 ml), and filtering. The solid was sufficiently pure for the next step. The mixture obtained from 4-trimethylsiloxy-bromobenzene was worked up in the same way, and the solid dissolved in dichloromethane (300 ml). The solution was extracted with 5% aqueous HCl (100 ml), dried ( $\text{MgSO}_4$ ), and the solvent evaporated. The residue was purified by chromatography (silicagel, dichloromethane) to give 9-(4-benzyloxyphenyl)-10-(4-hydroxyphenyl)anthracene (**2**) as slightly yellow powder. The bromo derivatives (**9a, b**) can be purified by chromatography under the same conditions.

#### 6.5. Ether cleavage of 9,10-bis(4-methoxyphenyl)anthracene

9,10-Bis(4-methoxyphenyl)anthracene (**10a**) (5.0 g, 13 mmol) was finely suspended in dichloromethane (20 ml) by means of an ultrasonic bath. After cooling to 0°C, a 1.0 M solution of  $\text{BBr}_3$  in dichloromethane (50 ml) was added dropwise with very efficient stirring. After 2 h, the mixture was allowed to come to room temperature. Water (50 ml) was added, and stirring continued for 2 h. The solid was filtered off and dissolved in 10% aqueous KOH (300 ml). After filtering, the filtrate was acidified with concentrated HCl. The precipitate was recrystallized from ethanol to give 9,10-bis(4-hydroxyphenyl)anthracene (**4**). A single crystal for X-ray structure analysis was grown from dichloromethane–ethanol–acetonitrile 50:20:1.

#### 6.6. Hydrogenolysis

Catalytic hydrogenations of the benzyloxy group to the phenol were performed with 10% Pd–C as catalyst, in a toluene–ethanol 2:1 mixture (for the ferrocene containing derivatives, a 1:1 mixture was used), at 60°C, until the calculated amount of hydrogen was consumed. 9,10-Bis(4-hydroxyphenyl)anthracene (**4**) (obtained from (**10b**)) crystallized in pure form during slow evaporation of the ethanol. 9-(4-Methoxyphenyl)-10-(4-hydroxyphenyl)anthracene (**1**) (obtained from (**8**)) and 9-[4-(4-ferrocenylbutoxy)phenyl]-10-(4-hydroxyphenyl)anthracene (**13**) (obtained from (**12**)) were purified by chromatography (silicagel, dichloromethane).

#### 6.7. Alkylation

##### 6.7.1. Alkylation of (**1**) and (**2**) with ferrocenylalkyl chlorides and tosylates

9-(4-Methoxyphenyl)-10-(4-hydroxyphenyl)anthracene (**1**) or 9-(4-benzyloxyphenyl)-10-(4-hydroxyphenyl)anthracene (**2**) (0.8 mmol),  $\text{K}_2\text{CO}_3$  (120 mg), and 0.9 mmol of alkylating reagent were finely suspended in 15 ml of dry acetone by means of an ultrasonic bath and then heated to reflux overnight. After filtering, the solvent was removed and the residue purified by chromatography (silicagel, dichloromethane). From (**1**) and the  $\omega$ -ferrocenylalkyltosylates (**11a, b, c**) were obtained 9-[4-(2-ferrocenylethoxy)phenyl]-10-(4-methoxyphenyl)anthracene (**6a**), 9-[4-(4-ferrocenylbutoxy)phenyl]-10-(4-methoxyphenyl)anthracene (**6b**), and 9-[4-(5-ferrocenylpentoxy)phenyl]-10-(4-methoxyphenyl)anthracene (**6c**), and with chloroacetylferrocene, 9-[4-(1-ferrocenylmethoxy)phenyl]-10-(4-methoxyphenyl)anthracene (**6d**). From (**2**) and 4-ferrocenylbutyltosylate (**11c**), 9-[4-(4-ferrocenylbutoxy)phenyl]-10-(4-benzyloxyphenyl)anthracene (**12**) was obtained almost quantitatively and used for further reactions without purification by chromatography.

##### 6.7.2. Alkylation of (**4**) with ferrocenylalkyl chlorides and tosylates

9,10-Bis(4-hydroxyphenyl)anthracene (**4**) (1.0 g, 2.7 mmol),  $\text{K}_2\text{CO}_3$  (0.85 g) and 6.0 mmol of alkylating reagent were finely suspended in 40 ml of dry acetone by means of an ultrasonic bath and then heated to reflux overnight. After filtering, the solvent was removed and the residue purified by chromatography (silicagel, dichloromethane). The diether was eluted first, followed by the monoether. From chloroacetylferrocene, 9,10-bis[4-(1-ferrocenylmethoxy)phenyl]anthracene (**3**) and 9-[4-(1-ferrocenylmethoxy)phenyl]-10-(4-hydroxyphenyl)anthracene (**15**) were obtained, and from (**11c**), 9,10-bis[4-(4-ferrocenylbutoxy)phenyl]anthracene (**5**) and 9-[4-(4-ferrocenylbutoxy)phenyl]-10-(4-hydroxyphenyl)anthracene (**13**).

##### 6.7.3. Alkylation of (**13**) with 1,4-dibromobutane

Using the same technique as described for 6.7.1, 9-[4-(4-ferrocenylbutoxy)phenyl]-10-[4-(4-bromobutyl)phenyl]anthracene (**14**) was prepared from (**13**) (0.1 g, 0.16 mmol) and 1,4-dibromobutane (1.0 ml).

#### 6.8. Preparation of 9-[4-(4-ferrocenylbutoxy)phenyl]-10-[4-(4-(*N*-isoquinolinio)butoxy)phenyl]anthracene bromide (**7**)

A suspension of (**14**) (50 mg, 0.07 mmol) in 5 ml of dry DMF and 2 ml of isoquinoline was kept stirring for 4 h at 60°C, whereupon a clear solution was obtained. After cooling to room temperature, 20 ml of dry ether were added, and the precipitate was filtered off and recrystallized from dichloromethane–methanol–ether (20:1:10). For NMR data, see Table 2.

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