Metal Complexes of a Biconcave Porphyrin with D_4-Structure—Versatile Chiral Shift Agents

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Dedicated to Professor Karl Rigger on the occasion of his 80th birthday

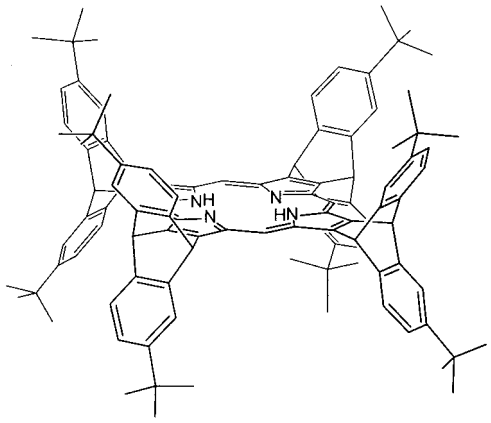
Abstract: Representative metal complexes of a biconcave D_4-symmetric porphyrin were synthesised by metal-ion insertion into the porphyrin ligand **1**. The NMR spectra suggested D_4-symmetry for the Zn^{II} and dioxo-Ru^{VI} complexes of **1** and C_4-symmetry for the unsymmetrically ligated Ru^{II} and Rh^{III} complexes. Metal complexes of **1** proved to be versatile chiral ^{1}H NMR shift agents for a broad spectrum of organic amines, alcohols, carboxylic acids, esters, nitriles and nonpolar fullerene derivatives. A practical analysis of chiral substrates with **1** covers enantiomeric excesses beyond 99%. An X-ray structure of (1:1)-cocrystals of an achiral, biconcave Co^{II} porphyrinate and C_{60} provided the first detailed insights into the structure of such a biconcave metallo–porphyrinate. It also showed remarkable packing of the carbon sphere against the main concave units of the porphyrin and gave clues about the relevant interactions between biconcave porphyrins and fullerenes.

Keywords: cage compounds · chiral shift reagent · fullerenes · porphyrinoids · structure elucidation

Introduction

In an earlier paper, we reported about the preparation of porphyrin **1**, a first representative of an effectively D_4-symmetric biconcave porphyrin. Porphyrin **1** was obtained from the tetramerizing condensation of a C_2-symmetric pyrrole building block,[1] which is available with high enantiomeric purity as the *S* isomer (99% *ee*). This work extended the scope of the recently opened synthetic route to (achiral) biconcave porphyrins with a rigid framework[2] to include chiral and effectively D_4-symmetric porphyrins.

Chiral porphyrins and their metal complexes are of considerable interest as possible hosts for stereo- and size-selective incorporation of guest molecules[3] and as enantioselective catalysts in organic transformations.[4, 5] The first examples of porphyrins, which were D_4-symmetric due to four identical chiral *meso*-substituents, were recently synthesised, and their rhodium and manganese complexes were explored as enantioselective catalysts.[6] Chiral biconcave porphyrin **1** and its cobalt(II) complex **2** were characterised[1] as well-defined, rather rigid and uniquely structured cavities.



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Upon complexation by porphyrin ligands, most transition metal ions provide a range of valuable structural and catalytic properties.[4–6] In this respect, cobalt,[1, 7] zinc,[3a, b] ruthenium[4a, 7, 8] and rhodium porphyrins,[6b, 7, 9] among others, have been studied. The unique enantiomeric purity obtained for **1**

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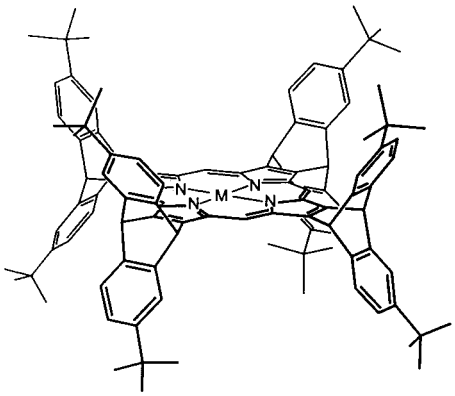
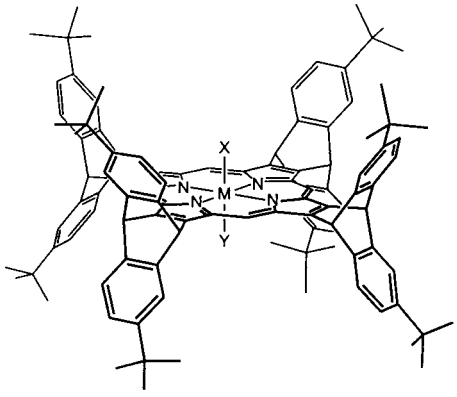
  0947-6539/01/0712-2676 $ 17.50+.50/0

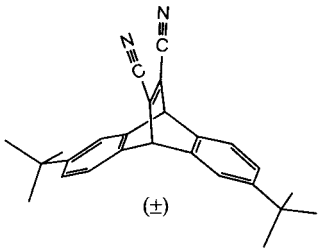
(about 10^9:1),[1] as well as its high stereochemical purity, indicates that the corresponding metal complexes of **1** are highly suitable for use in stereodifferentiation and molecular recognition reactions. Herein we describe the preparation and structural analysis in solution of diamagnetic Zn^{II}, iodo-Rh^{III}, (CO)-Ru^{II} and dioxo-Ru^{VI} complexes of chiral biconcave porphyrin **1**. Furthermore, we report the use of these stable (diamagnetic) transition metal complexes, and of paramagnetic Co^{II} complex **2**,[1] as chiral shift reagents for ^1H NMR experiments.[10] We also discuss the X-ray structure of (1:1)-cocrystals of [60]-fullerene and of an achiral biconcave Co^{II} porphyrinate.[2b]



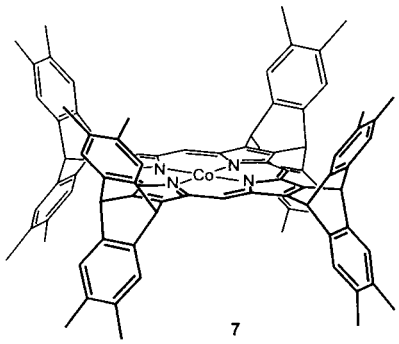
2 M = Co^{II}
3 M = Zn^{II}



4 M = Rh^{III}, X = I, Y = absent
5a M = Ru^{II}, X = CO, Y = pyridine
5b M = Ru^{VI}, X = Y = O



***rac*-6**



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Results

Preparation of transition metal complexes of biconcave porphyrin 1: Porphyrins are excellent ligands for transition metal centres and a wide range of methods for their incorporation exists.[11] Co^{II} complex **2**,[1] and the Zn^{II}, iodo-Rh^{III}, (CO)-Ru^{II} and $O=Ru^{VI}=O$ complexes of **1**, (i.e., **3**, **4**, **5a** and **5b**, respectively) were prepared in good yields from **1** under mild incorporation conditions (see Experimental Section).

Abstract in German: *Ausgewählte Metall-Komplexe eines biskonkaven D_4-symmetrischen Porphyrins wurden durch Einbau der entsprechenden Metall-Ionen in den Porphyrin Liganden **1** hergestellt. Die NMR-Spektren gaben Hinweise auf das Vorliegen D_4-symmetrischer Strukturen für die Zn^{II}- und Dioxo-Ru^{VI}-Komplexe von **1**, und auf C_4-Symmetrie für die unsymmetrisch ligandierten Ru^{II}- und Rh^{III}-Komplexe. Die Metall-Komplexe des Porphyrins **1** erwiesen sich als breit anwendbare chirale ^1H NMR Verschiebungs-Reagenzien für ein Spektrum von organischen Aminen, Alkoholen, Carbonsäuren, Estern und Nitrilen, wie auch für unpolare Fulleren Derivate. Das Porphyrin **1** eignet sich danach für eine einfache Analyse der Enantiomerenreinheit solcher Substanzen bis etwa 99 % ee.*

Eine Röntgenstrukturanalyse eines 1:1-Cokristallisates eines achiralen biskonkaven Co^{II}-Porphyrinates und C_{60} gab erstmals detaillierte Einblicke in die Struktur eines biskonkaven Metalloporphyrins. Sie zeigte auch ein bemerkenswertes Packungsverhalten des Fullerens an die konkaven Oberflächeneinheiten des Porphyrins und gab damit erste Hinweise auf form-selektive Wechselwirkungen von biskonkaven Porphyrinen und Fullerenen.

(1:1)-Cocrystals of [60]-Fullerene and Co^{II} porphyrinate **7** were prepared by mixing a solution of achiral Co^{II} porphyrinate **7**[2a] in 1,2-dichlorobenzene at room temperature with a solution of an equimolar amount of [60]-fullerene in benzene. Upon standing at room temperature, crystals appeared within two days. These crystals were used for X-ray analysis.

Spectroscopic properties and molecular structure: The constitution and effective molecular symmetries of porphyrins **3**, **4**, **5a** and **5b** were established by consistent UV/Vis, ^1H NMR, ^{13}C NMR, FAB-MS and FT-IR spectra. The UV/Vis spectra exhibited the typically intense Soret band (near 407 nm) and two weaker bands near 550 nm, which are diagnostic bands for porphyrins (see Figure 1). The ^1H NMR spectra provided the most effective structural information: the spectrum of a solution of paramagnetic Co^{II} porphyrinate **2** in benzene exhibited low-field shifts ($\Delta\delta \sim 20$ ppm for *meso* hydrogens, $\Delta\delta \sim 7$ ppm for bridgehead hydrogens, but only $\Delta\delta \sim 0.2$ ppm for those of *tert*-butyl groups), characteristic of symmetric Co^{II} porphyrins[1, 2, 15] (for a section of the spectrum, see Figure 4, below). The ^1H NMR spectrum of diamagnetic Zn^{II} and Ru^{VI}porphyrinates **3** and **5b**, respectively, in deuterochloroform likewise exhibited six signals, but within the normal chemical shift range. A CD spectrum of a solution of **3** in dichloromethane showed weak positive ellipticities, both for the Soret and for the visible bands (see Figure 1).

The ^1H NMR spectrum of diamagnetic iodo-Rh^{III} porphyrinate **4** in deuterobenzene showed splitting of five signals, but not of the low-field signal for the *meso*-hydrogens. The spectrum is indicative of an effective reduction of the

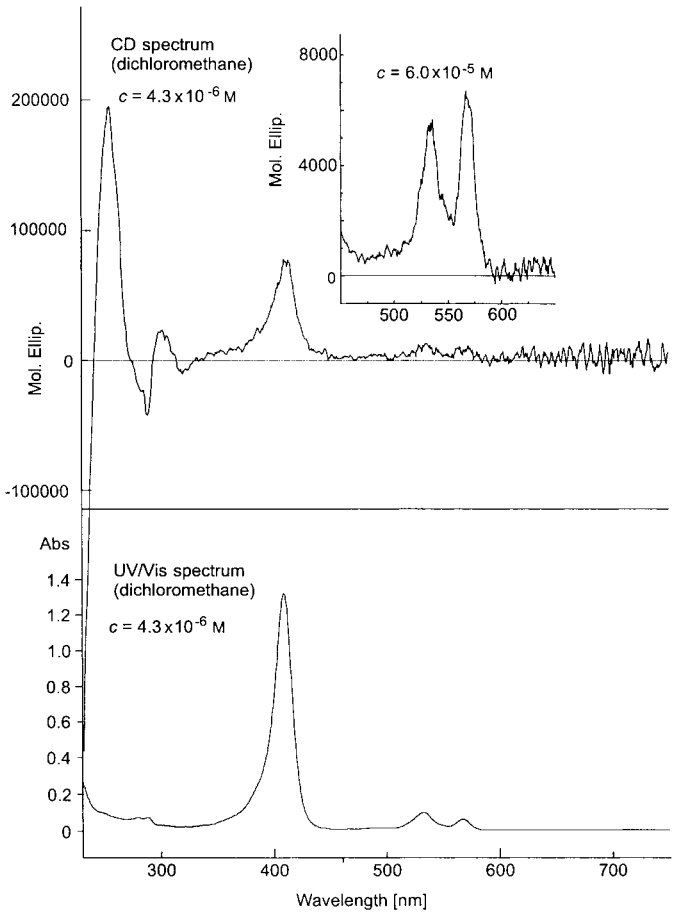

Figure 1. CD spectra (top) and UV/Vis spectrum (bottom) of Zn porphyrinate **3** in dichloromethane.

symmetry to C_4, due to the coordination of one iodide ligand. The signals are consistent with the diamagnetic nature of the Rh^{III} complex. The (diastereotopic) bridgehead hydrogens now give rise to two singlets with $\Delta\delta = 0.04$ ppm. Splitting was even more pronounced for the *tert*-butyl groups and the adjacent aromatic hydrogens ($\Delta\delta = 0.17 - 0.19$ ppm), both of which are situated at the outer rim.

Likewise, the ^{1}H NMR spectrum of diamagnetic pyridino-(CO)-Ru^{II} porphyrinate **5a** in deuterochloroform showed splitting of five signals, but not of the low-field signal for the *meso*-hydrogens. This spectrum is also indicative of an effective reduction of the symmetry to C_4, due to the coordination of two different axial ligands (see Figure 2). The signals are consistent with the diamagnetic nature of the hexacoordinate Ru^{II} complex. The bridgehead hydrogens now give rise to two singlets at $\delta = 6.94$ and $\delta = 6.95$, that is, with $\Delta\delta = 0.013$ ppm. These signals were assigned to the diastereotopic bridgehead protons of the β'-positions of a single pyrrole unit rather than to the bridgehead protons attached to two different pyrrole units. This specification was achieved by way of an ^{1}H,^{13}C HMQC spectrum, digitised to high resolution (see Figure 3). The short-range heteronuclear correlations of the two protons were shown in this way to involve the same set of two distinct pyrrole carbons, which give rise to signals at $\delta = 154.09$ and 154.13. The presence of the different axial ligands (CO and pyridine) was confirmed by inspection of the mass spectrum and of the IR spectrum of **5a**.

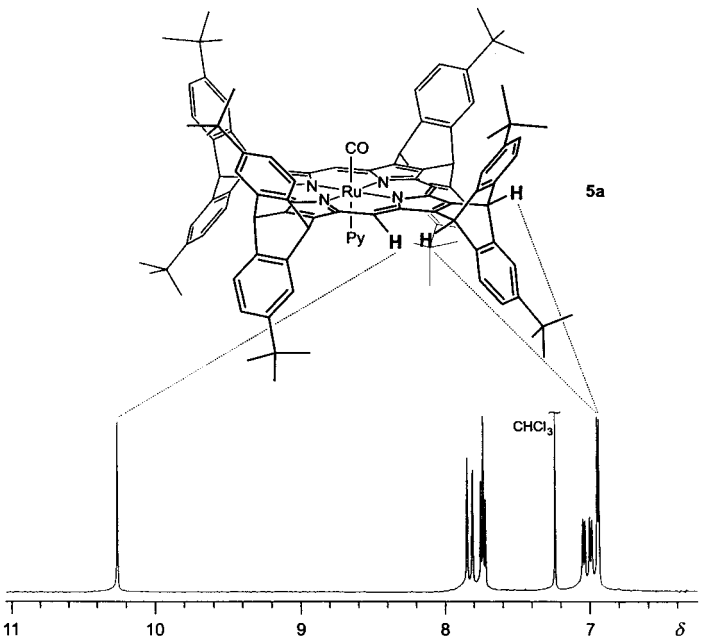

Figure 2. Low-field sections of the ^{1}H NMR spectrum of Ru^{II} porphyrinate **5a** (ca. 3 mM, in $CDCl_3$, 500 MHz).

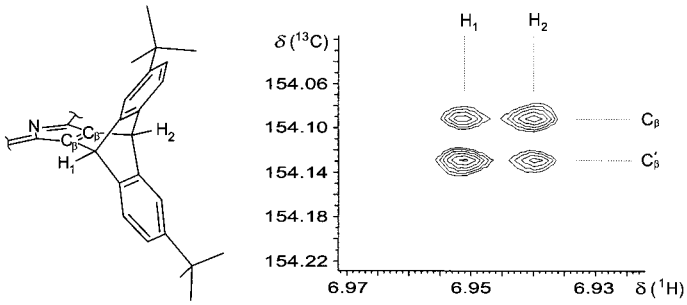

Figure 3. Section of an ^{1}H,^{13}C HMQC spectrum[28] of Ru^{II} porphyrinate **5a** (ca. 3 mM in $CDCl_3$), at high digital resolution in both frequency dimensions (^{1}H: 700 Hz spectral width, 1k data points, zero filling up to 2k; ^{13}C: 800 Hz spectral width, 400 increments zero filled to 1k data points), optimised for cabout 7 Hz long-range ^{1}H,^{13}C couplings and recorded with ^{13}C decoupling during acquisition.

X-ray analysis of (1:1)-cocrystal of [60]-fullerene and of Co^{II}-porphyrinate **7**: Early attempts to obtain single-crystal structure information about the biconcave porphyrin or metallo–porphyrinate molecules have all failed, because the obtained crystals showed very weak diffraction. In contrast, cocrystallisation of equimolar amounts of [60]-fullerene dissolved in benzene and the Co^{II} porphyrinate **7** dissolved in 1,2-dichlorobenzene yielded crystals that diffract to a resolution of 1 Å and led to the first crystal structure of a biconcave metallo–porphyrinate. The centred monoclinic unit cell contains two C_{2h}-symmetric porphyrinate molecules, four [60]-fullerene molecules, 6.60(5) molecules of dichlorobenzene and 0.89(4) molecules of benzene. The structure of the porphyrinate molecule is well defined, whereas the fullerene and solvent molecules are strongly disordered (see Experimental Section). A feature of special interest is the molecular packing, which is dominated by interactions between concave niches of the porphyrinate and the convex C_{60} molecule (see Discussion Section).

0947-6539/01/0712-2678 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 12

Use of 1 and use of transition metal complexes as chiral shift reagents in ^{1}H NMR experiments

*C_2-symmetric dinitrile rac-**6** in the presence of paramagnetic Co^{II} porphyrinate **2**:* In *rac*-**6**, both bridgehead hydrogens are symmetry equivalent, as are the *tert*-butyl groups of each molecule, thus giving rise to two singlets (relative intensities 1:9) at $\delta = 4.78$ and 1.10 in deuterobenzene. In the presence of the chiral and practically enantiopure Co^{II} complex **2**, both signals were shifted to higher fields and were split into two lines (see Figure 4).

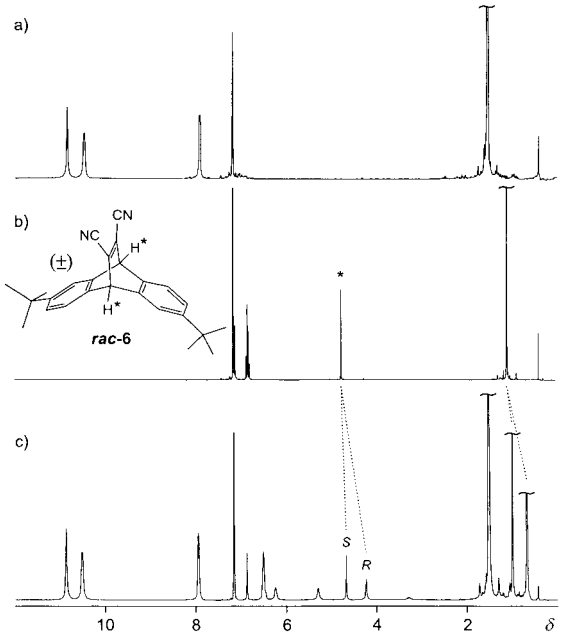

Figure 4. ^{1}H NMR spectra (at 296 K, C_6D_6, 300 MHz) a) of 25 mM Co^{II} porphyrinate **2**; b) of 50 mM racemic dinitrile *rac*-**6**; c) of 50 mM racemic dinitrile *rac*-**6** with 25 mM Co^{II} porphyrinate **2**.

In the concentration range 3.7 – 60.1 mM for **2**, the high-field shift of all signals of *rac*-**6** in benzene showed a practically linear dependence upon the concentration of **2**. With the use of nonracemic dinitrile (samples were obtained by mixing *rac*-**6** with (*S*)-**6**),[1] all of the signals of the 9*S*,10*S* isomer (*S*)-**6** were shifted less, and those of the 9*R*,10*R* isomer (*R*)-**6** were shifted accordingly more. At 60.1 mM for **2**, the high-field shifts of the signals for the bridgehead and *tert*-butyl hydrogens of (*R*)-**6** amounted to a $\Delta\delta = 1.20$ and 0.87 ppm, respectively, and thus exceeded the $\Delta\delta$s for the corresponding signals of (*S*)-**6** by $\Delta\delta = 0.86$ and 0.62 ppm, respectively.

The values of the overall high-field shifts of the signals ($\Delta\delta$) of the bridgehead hydrogens of dinitrile *rac*-**6**, induced by paramagnetic Co^{II} complex **2** (at constant $c(\mathbf{2}) = 15$ mM, in deuterobenzene, 303 K), and the shift differences for the signals ($\Delta\Delta\delta$) of bridgehead protons from different dinitrile enantiomers remained practically constant at concentrations < 20 mM for *rac*-**6**. With further increases of the concentration of dinitrile *rac*-**6** (up to 150 mM), high-field shifts decreased only slightly from $\Delta\delta = 0.34$ to 0.19 ppm, the shift differences changed from $\Delta\Delta\delta = 0.26$ to 0.21 ppm. These observations are indicative of weak complexations of both enantiomers of *rac*-**6** by complex **2**.

*C_2-symmetric dinitrile rac-**6** in the presence of metal-free porphyrin **1** and diamagnetic metalloporphyrinates*: In the presence of porphyrin **1** (25 mM), all ^{1}H NMR signals of *rac*-**6** in deuterobenzene were shifted to higher fields ($\Delta\delta = 0.06$ – 0.18 ppm); this resulted in a significant splitting of the corresponding signals of *rac*-**6**. In the presence of Zn^{II} porphyrinate **3** (25 mM), the ^{1}H NMR signals of (*R*)-**6** in deuterobenzene were also shifted to higher fields (at 300 K) by $\Delta\delta = 0.07$ and 0.08 ppm, respectively, while the signals of (*S*)-**6** were nearly unchanged; this again led to a splitting of the signals of *rac*-**6** . The upfield shifts and the splittings of the signals of *rac*-**6** in the presence of Zn^{II}-complex **3** were strongly dependent upon the solvent used. In deuteromethanol, the signals of the bridgehead protons of (*R*)-**6** were shifted by **3** (15 mM, 303 K) with a value $\Delta\delta = 0.63$ ppm, those of (*S*)-**6** with a $\Delta\delta = 0.18$ ppm, that is, with a $\Delta\Delta\delta = 0.45$ ppm. In other deuterated solvents that were investigated (benzene, chloroform, acetone and acetonitrile), smaller shifts were observed, but the position of the signals of the bridgehead protons of (*R*)-**6** was consistently more strongly affected than that of the signals of (*S*)-**6**. In deuteropyridine, however, a splitting of the signals was not observed under standard conditions.

In an analogous experiment with iodo-Rh^{III} complex **4** in deuterotoluene, the signals of the bridgehead hydrogens of both enantiomers of *rac*-**6** were shifted to higher fields and were split into two broad signals ($\Delta\delta = 0.55$ and 0.67 ppm), while the signals of the *tert*-butyl protons were shifted less ($\Delta\delta = 0.10$ and 0.15 ppm). The temperature dependence of signal splitting and of the signal position in the spectrum of *rac*-**6** in the presence of **4** indicated slowed exchange (see Figure 5).

Exploratory studies with other chiral probes

Experiments with racemic 1-(9-anthryl)-2,2,2-trifluoroethanol: In the presence of Zn^{II} porphyrinate **3**, iodo-Rh^{III} porphyrinate **4** or porphyrin **1** (25 mM), the ^{1}H NMR signals of the methine proton of both enantiomers of 1-(9-anthryl)-2,2,2-trifluoro ethanol in deuterobenzene (at 296 K) are strongly shifted to higher fields. With one enantiomer, large shifts of $\Delta\delta = 0.51$ ppm (solution with **4**) to 1.07 ppm (solution with **1**) are observed, and significant shift differences of $\Delta\Delta\delta =$ 0.17 ppm (solution with **1**) to 0.42 ppm (solution with **3**) discriminate the signals of corresponding protons of the two enantiomers in each case (see Figure 6).

Experiments with racemic menthyl acetate: In the presence of either Zn^{II} porphyrinate **3** or iodo-Rh^{III}-porphyrinate **4** (25 mM), the ^{1}H NMR signals of the methine proton at C-1 and the acetyl methyl group of both enantiomers of menthyl acetate in deuterobenzene (at 296 K) are shifted to higher fields. With rhodium complex **4**, larger shifts of $\Delta\delta = 0.39$ and 0.35 ppm were observed (for the methine and methyl protons of one enantiomer, respectively), with significant shift differences of $\Delta\Delta\delta = 0.25$ and 0.23 ppm. Both the shifts ($\Delta\delta$'s) and the shift differences ($\Delta\Delta\delta$'s) are smaller for the corresponding solutions with Zn^{II} porphyrinate **3** (see, for example, Figure 7).

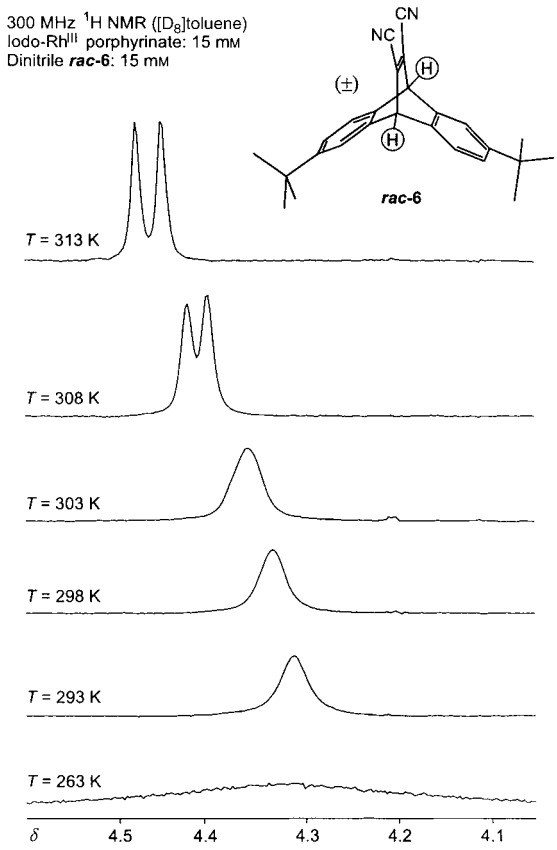

Figure 5. Temperature dependence of ^{1}H NMR spectra of racemic dinitrile *rac*-**6** (15 mM, 300 MHz) in the presence of Rh^{III} porphyrinate **4** (15 mM) in [D$_8$]toluene.

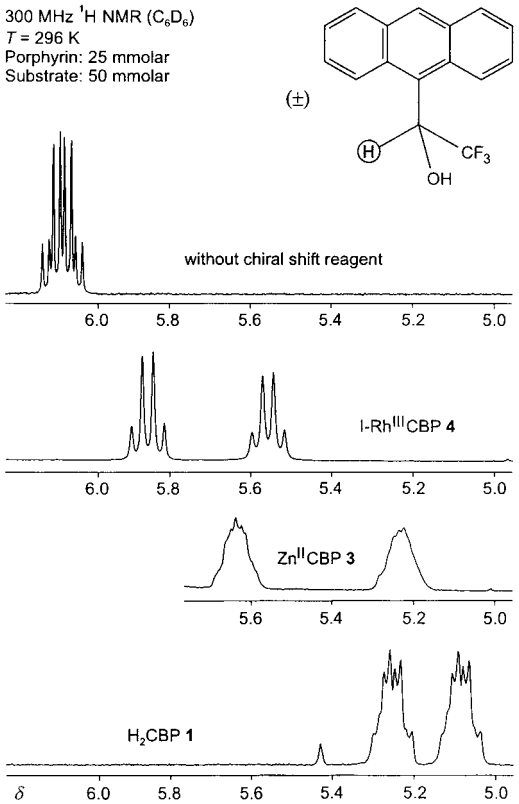

Figure 6. ^{1}H NMR shift experiments (300 MHz, 296 K, C$_6$D$_6$) of racemic 1-(9-anthryl)-2,2,2-trifluoro ethanol (50 mM) in the presence of chiral metal porphyrinates (25 mM) (CBP = chiral biconcave porphyrinate).

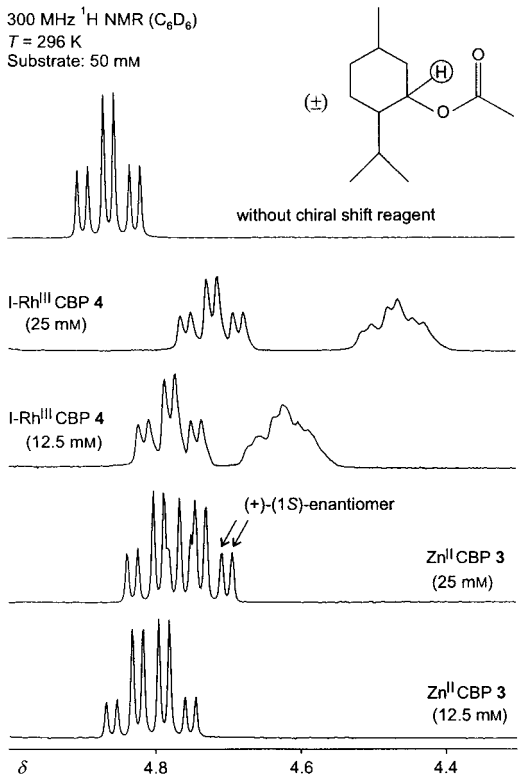

Figure 7. ^{1}H NMR shift experiments (300 MHz, 296 K, C$_6$D$_6$) of racemic menthyl acetate (50 mM) in the presence of the chiral metal porphyrinates **3** and **4** (CBP = chiral biconcave porphyrinate).

Experiments with racemic α-methoxyphenylacetic acid: In the presence of either Zn^{II} porphyrinate **3**, iodo-Rh^{III} porphyrinate **4** or porphyrin **1** (25 mM), the ^{1}H NMR signals of the methine proton of both enantiomers of α-methoxyphenylacetic acid in deuterobenzene (at 296 K) were shifted to higher fields. Significant shifts of $\Delta\delta = 0.23 - 0.30$ ppm and significant shift differences of $\Delta\Delta\delta = 0.07$ ppm were observed for solutions of α-methoxyphenylacetic acid with **3** and with **4**, respectively, while the corresponding effects of **1** were considerably smaller ($\Delta\delta = 0.03$ ppm, $\Delta\Delta\delta = 0.01$ ppm). Slightly smaller effects were seen with the signal of the methoxy methyl group of α-methoxyphenylacetic acid.

Experiments with racemic α-phenylethylamine: In the presence of Zn^{II} porphyrinate **3** (25 mM), the ^{1}H NMR signals of the methyl group of the two enantiomers of α-phenylethylamine in deuterobenzene (at 296 K) were shifted from $\delta =$ 1.15 to 0.62 and 0.69, that is, with remarkable shifts of $\Delta\delta =$ 1.77 and 1.84 ppm. From the dependence of the chemical shift values for the methyl group signals of α-phenylethylamine on the ratio between it and **3** (measured at 303 K and with concentration of **3** at 8.04 mM, see Figure 8) and with the use of an analysis adapted from ref. [16], the two enantiomers of α-phenylethylamine were estimated to be bound by **3** with complexation constants of 1020 M^{-1} and 1006 M^{-1}.

*Experiments with Co^{II} porphyrinate **2**, C$_2$-symmetric adduct rac-**8** of [60]-fullerene and 2,6-di-tert-butylanthracene*: In the presence of paramagnetic porphyrinate **2** (10.2 mM, at 300 K,

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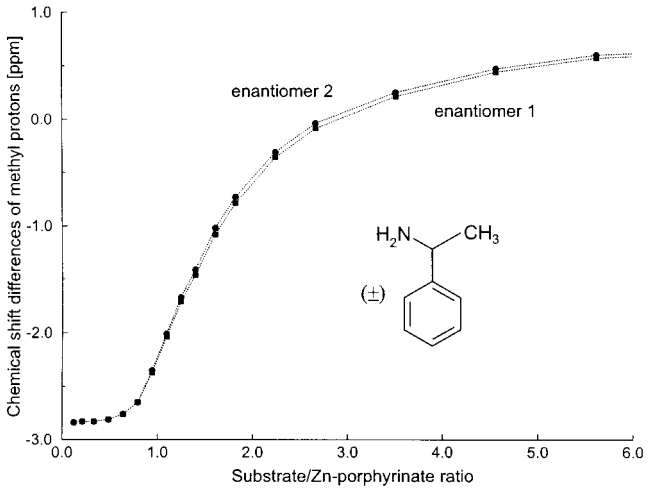


Figure 8. Chemical shift differences of methyl protons of racemic α-phenylethylamine in the presence of Zn porphyrinate **3** (8.0 mM, 200 MHz, 303 K, C_6D_6) as a function of amine concentration.

in deuterobenzene), the singlet of the bridgehead protons of racemic fullerene adduct *rac*-**8** (4.5 mM)[17a] experiences a high-field shift (from $\delta = 5.66$ to $\delta = 5.14$ and 5.13) with concomitant splitting into two barely separated signals for symmetry equivalent protons of different enantiomers (see Figure 9).

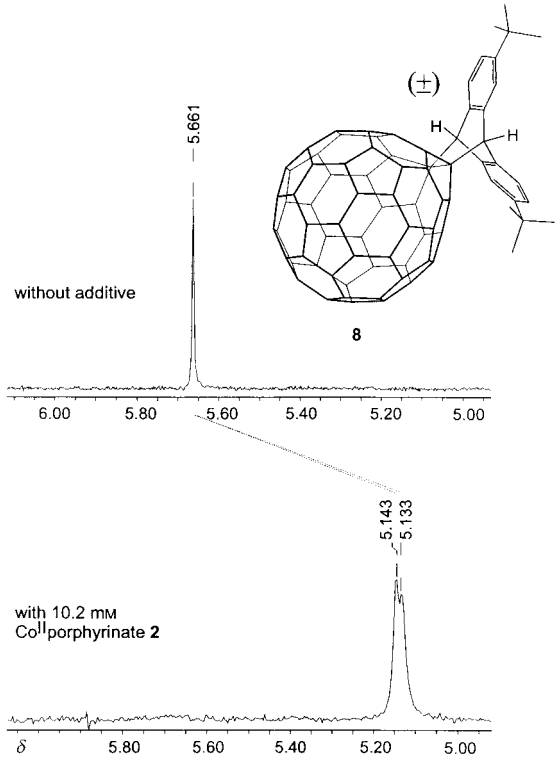


Figure 9. ^{1}H NMR spectra (296 K, C_6D_6, 300 MHz) of chiral mono-adduct **8** (4.5 mM) without additive (top) and with 10.2 mM Co^{II} porphyrinate **2** (bottom).

*Experiments with Co^{II} porphyrinate **2**, C_s-symmetric orthogonal bis-adduct **9** of [60]-fullerene and anthracene.* In the presence of paramagnetic porphyrinate **2** (1.5 mM, at 300 K, in deuterobenzene), the three individually assigned singlets of the four bridgehead protons of C_s-symmetric fullerene bis-adduct **9**[17b,c] (1.27 mM) experience high field shifts, with strongly differing shifts ($\Delta\delta$) and with a linear dependence upon the concentration of the chiral shift reagent (Figure 10).

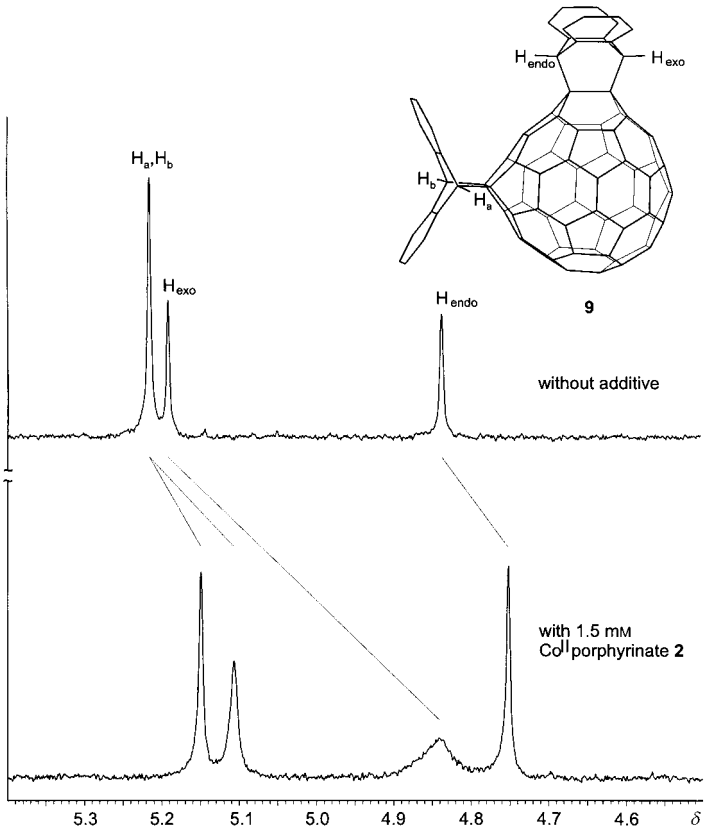


Figure 10. ^{1}H NMR spectra (296 K, C_6D_6, 300 MHz) of "orthogonal" C_S-symmetric bis-adduct **9** (1 mM) without additive (top) and with 1.5 mM Co^{II} porphyrinate **2** (bottom).

The presence of **2** influences the chemical shift of the signal of the more exposed H_{exo} of **9** strongest and splits the singlet of the enantiotopic protons H_a and H_b into two somewhat broadened singlets.

Discussion

Biconcave porphyrins **1** and **2**[1] and the four new metal complexes **3**–**5a** and **5b** are the first representatives of chiral biconcave porphyrins with fourfold symmetry. These compounds exhibit good solubility (in monomeric form) in a range of common organic solvents and show no tendency to form aggregates. Relatively simple NMR spectra indicate that highly symmetric frameworks and overall (effective) D_4-symmetry for **1** and its Co^{II} and Zn^{II} complexes (**2** and **3**) are present. The regular 2,6-disubstitution of the sterically demanding, homochiral anthracene units in **1** provides an inherently D_4-symmetric ligand in the four metal complexes **2**–**5a** and **5b**. Accordingly, metal complexes **2**, **3** and **5b** (effectively) conform to a "propeller" structure, which includes a "propeller deformation", an elusive symmetric normal-coordinate deformation of the porphyrin plane.[18]

The spectral properties of **2**, **3** and **5b** are not consistent, however, with any one of the four experimentally better known normal modes of deformation of the porphyrin plane (ruffling,[19a, b] saddling,[18] doming[19b, c] and waving[19c]).[18]

Introduction of an axial ligand or of two different axial ligands destroys the equivalence of the two faces at the metal ion and reduces the (effective) symmetry to C_4-symmetry in iodo-Rh^{III} complex **4** and pyridino-(CO)-Ru^{II} complex **5a**. Groups that are symmetry equivalent in the D_4-symmetric complexes **2**, **3** and **5b** become diastereotopic in **4** and **5a**, and a corresponding increase in complexity of the NMR spectra results. The pyridino-(CO)-Ru^{II} complex **5a** was analysed spectroscopically in great detail. While the *meso* protons showed only one sharp signal in a 500 MHz ^1H NMR spectrum of **5a**, the bridgehead protons (again) showed splitting. In a ^{13}C NMR spectrum, a corresponding splitting was also observed for the signals of the α- and β-carbons of the pyrrole rings of **5a**. A two-dimensional heteronuclear $^1H,^{13}C$ HMQC experiment indicated that the α- and β-pyrrole carbons of each pyrrole ring give rise to two sets of signals (see Figure 3). This effective equivalency of carbons (and of β'-hydrogens) of a single pyrrolic ring is consistent with their diastereotopic nature, due to the constitution of the C_4-symmetric complex **5a**. However, a conformational deformation of the porphyrin plane towards a "propeller" structure would also be consistent with the indicated symmetry, while any of the other established modes of porphyrin deformation would not be consistent.[18, 19] In the absence of more detailed crystallographic information, Rh^{III}- and Ru^{II}-porphyrins **4** and **5a** are suggested to have effective C_4-symmetry, in which the dissymmetric peripheral substitution would induce all four pyrrole units to possibly tip (propeller-like) in one direction. In analogy with the structure of the (1:1)-cocrystals of achiral Co^{II} porphyrinate **7** and of [60]-fullerene, which showed a nearly planar porphyrin chromophore, the deviation from planarity of the porphyrin moiety in **2** and **3** is likely to also be effectively small.

One major interest of this work was directed to the exploration of **1** and of metalloporphyrins **2**, **3** and **4** as enantiomerically highly pure, chiral shift reagents for ^1H NMR spectroscopy. A variety of para- and diamagnetic shift reagents are available, but most of them are either expensive, sensitive to moisture or applicable for a limited class of compounds.[10] Incorporation of different metal ions (Zn^{II}, Co^{II}, Ru^{II}, Rh^{III}) into biconcave porphyrin **1** gave a useful collection of chiral metal complexes, the proton signals of which would occupy only a small region of the ^1H NMR spectrum. Similar to other highly symmetric metallo-porphyrinates[15, 20] on one hand and to chiral concave host compounds[21] on the other, (chiral) biconcave metallo–porphyrinates would be expected to bind to a variety of organic molecules and induce significant shifts in their ^1H NMR spectra. The high enantiomeric purity (>99.99%) of biconcave porphyrin **1** would accordingly qualify **1** and its metal complexes as unique chiral shift reagents that are generally useful to conveniently detect low contents (as low as 0.5%)[1] of enantiomeric impurities.

A selection of shift experiments was carried out, as presented in the Results and Experimental Sections. Diamagnetic zinc porphyrinate **3** turned out to be a broadly useful shift reagent; for exampl, for chiral compounds with alcohol, amine, ester, nitrile and carboxylic acid functionalities as test substrates. These compounds were selected first, as it was indicated that their functional groups are able to weakly coordinate to the electrophilic metal ions in the centre of the porphyrinates. A fast ligand exchange on the NMR timescale was responsible for sharp and averaged substrate signals that allowed for the determination of the chiral purity of various tested substances up to a practical limit of about 99.0% *ee*. The metal-free porphyrin **1** likewise showed significant chiral shifts with nitrile *rac*-**6**, with alcohol (±)-1-(9-anthryl)-2,2,2-trifluoroethanol and with carboxylic acid (±)-α-methoxyphenylacetic acid. The proton signals of these substrates were also shifted strongly by the presence of diamagnetic iodo-Rh^{III} porphyrinate **4**, but with indications of slowed exchange at temperatures below ambient (see Figure 5). In the presence of α-phenylethylamine, air-saturated solutions of **4** or of paramagnetic Co^{II} porphyrinate **2** in benzene underwent slow (and still unexplored) chemical transformations.

Co^{II} porphyrinate **2** (and iodo-Rh^{III} porphyrinate **4**) were suitable chiral shift agents for dinitrile *rac*-**6** (see, for example, ref [1]). Paramagnetic complex **2** turned out to be a remarkably suitable chiral shift reagent for several nonpolar (chiral) fullerene adducts as well. These experiments should be seen in the light of the molecular structure of the achiral Co^{II} porphyrinate **7** and the unique crystal packing of **7** and [60]-fullerene (see Figures 11 and 12).

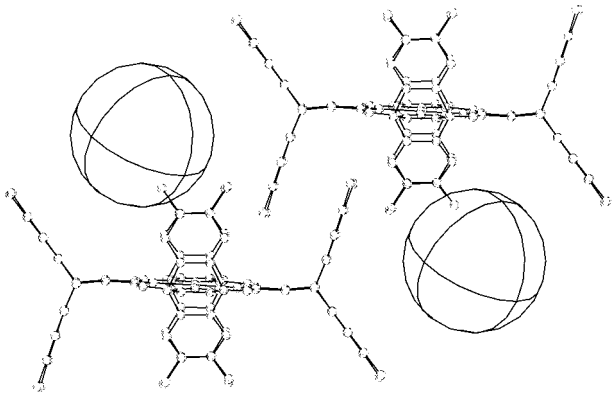


Figure 11. Packing motif from the X-ray structure of (1:1)-cocrystals, showing the interlocking of two biconcave porphyrin molecules.

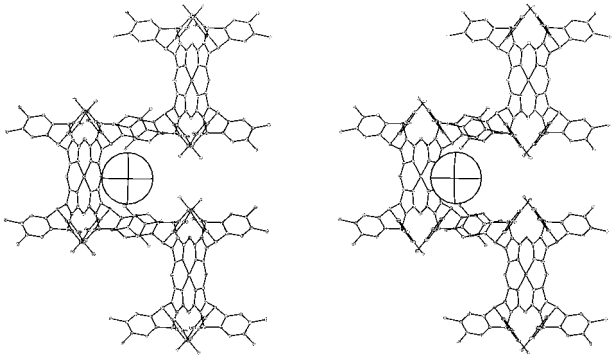


Figure 12. Stereoview that shows the filling of one of two cavities of a biconcave porphyrin by one [60]-fullerene and two dimethylbenzene fragments from neighbouring porphyrin molecules.

0947-6539/01/0712-2682 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 12

The crystal structure analysis of the Co^{II} complex of a biconcave porphyrin confirmed for the first time the existence of regularly structured cavities above and below the porphyrin plane, as well as bridged anthracene units with concave structured *exo*-faces. The Co^{II} centre has square planar coordination; the porphyrin is essentially planar (rms deviation 0.03 Å) with no unusual bonding characteristics. The porphyrin units aggregate by van der Waals' contacts with *endo*-faces of their tetramethylanthracene units (Figure 11, interplanar distance 3.46 Å).

Of particular interest was the discovery of a recurring motif for the interaction between the fullerene sphere and the two concave structure elements of porphyrin **7**; each of the fullerene molecules makes symmetric contact with the two concave *exo*-faces of one bridged anthracene moiety from two neighbouring porphyrins. At the same time, it also forms contacts to the concave surface motif of another porphyrin molecule that is spanned by the porphyrin plane and two neighbouring anthracene wings (see Figure 12). Note that the centre of the [60]-fullerene molecules lies above a *meso*-carbon atom of the porphyrin, thus implying that there is no special interaction with the cobalt atom. The closest distances from the [60]-fullerene sphere to the best planes through the anthracene wings are 3.07 and 3.12 Å; that to the best plane of the porphyrin fragment is 3.09 Å. Thus, the concave structural elements of the porphyrin complex are almost perfectly complementary to and possibly quite selective for the convex shape of [60]-fullerene. We have mentioned the crystallographic evidence for shape-selective interactions between achiral biconcave Co^{II} porphyrinate **7** and spherical [60]-fullerene in an earlier communication.[2a] In recent years, crystallographic[22] and chromatographic[23] evidence for noncovalent interactions between fullerenes and porphinoid compounds has become available from several groups, as well as evidence of interactions between fullerenes and a variety of concave receptor molecules, such as calixarenes.[24]

Considering the possibility that biconcave Co^{II} porphyrins and nonpolar fullerene derivatives would interact in a shape-selective manner in solution as well, the effect of chiral biconcave Co^{II} porphyrinate **2** on ^1H NMR spectra of solutions of fullerene anthracene adducts was examined. In a benzene solution of **2** (ca. 10 mM), the singlet for the symmetry equivalent bridgehead protons of racemic Diels–Alder adduct **8** (from 2,6-di-*tert*-butylanthracene and [60]-fullerene)[17a] experienced an upfield shift of about 0.5 ppm. Furthermore, the singlet was split by about 0.01 ppm, which indicates an induced non-equivalence of the signals of the two enantiomeric forms of **8** (fullerene adduct 4.5 mM, in C_6D_6, 300 MHz, see Figure 9). In this case, the shift differences can be rationalised by packing interactions between the shape-complementary biconcave porphyrin and the convex fullerene partners in solution, but are not likely to be a result of selective binding to the metal centre of porphyrinate **2**.

In a related experiment, the effect of **2** on the ^1H NMR spectrum of a deuterobenzene solution of C_s-symmetric orthogonal fullerene–anthracene bis-adduct **9**[17b,c] was investigated (see Figure 10). The observed high-field shifts of the protons of **9** in the presence of **2** can be rationalised by their spatial accessibility and by favourable interactions of shape-complementary surfaces of the fullerene and of the biconcave porphyrinate **2** in solution; the shift of the signals of the sterically more accessible H_{exo} is considerably larger than that of the signals of the less exposed H_{endo}.

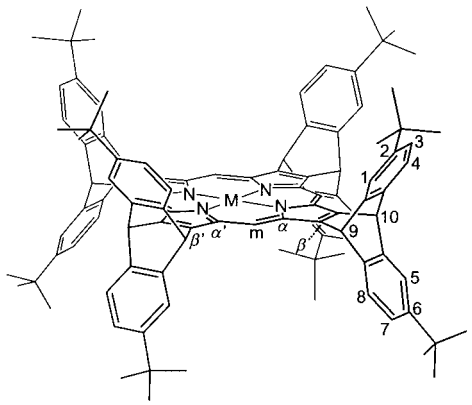
Complexation between fullerenes and the concave face of unsaturated hydrocarbon molecules in solution may be driven by solvophobic effects,[25] but may also be caused by the stabilising interactions between the convex (electrophilic) outer surface of fullerenes and the concave unsaturated hydrocarbon surfaces, which have been suggested to be sites of increased electron densities.[26] Unique interactions between shape-complementary surfaces of unsaturated hydrocarbon and fullerene molecules have been observed in a variety of crystal structures[24, 27] and may be a further contributor to the repertoire of directed noncovalent intermolecular interactions.

Conclusion

Chiral biconcave porphyrins with a rigid framework and with high enantiomeric purities are now available[1] and are shown to be very useful chiral shift reagents for a range of organic compounds with various polar functionalities. The main interactions of these compounds with metallo-porphyrinates are suggested to arise from the coordination of polar functionalities to the porphinoid metal centres. Furthermore, as shown with paramagnetic Co^{II}-porphyrinate **2**, chiral, nonpolar fullerene derivatives can also be analysed with these versatile shift reagents. The crystal packing observed between [60]-fullerene and achiral biconcave Co^{II} porphyrin **7** suggests that binding between the convex fullerene derivatives and the concave, rigidly structured porphyrins is governed by the complementary shapes. Ongoing synthetic work is directed towards the design and synthesis of other biconcave porphyrins with structural properties that are "tuned" towards improved shape-selective incorporation of spheric unsaturated molecules, such as nonpolar fullerene derivatives.

Experimental Section

General considerations: All reactions were carried out in oven-dried glassware under a dry argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on Bruker AM 300 or Varian Unity 500 spectrometers. Chemical shifts are listed in δ with $^1H/^{13}C$ signals of the solvent as reference; $\delta(CHCl_3) = 7.24$, $\delta(CDCl_3) = 77.0$, $\delta(C_6D_5H) = 7.15$, $\delta(C_6D_6) = 128$ (the atom numbering scheme is shown in Scheme 1). $^1H,^{13}C$ HMQC experiments were performed as described in ref [28]. IR spectra were recorded on a Mattson FTIR 3000 instrument. UV/Vis spectra were recorded on a Hitachi U 3000, CD spectra on a JASCO J-715. (FAB)MS experiments were performed on a Finnigan MAT-95, with 3-nitrobenzylalcohol as the FAB-matrix. Reagents and solvents: Sodium acetate (anhydrous), zinc acetate dihydrate, iodine all Fluka purum p.a.; $CoBr_2$ (anhydrous) Johnson Matthey Alfa Product; $[Rh(CO)_2Cl]_2$, ruthenium carbonyl both Strem Chemicals; 3-chloroperbenzoic acid Fluka pract.; acetone, THF, methanol, dichloromethane, 1,2-dichloroethane, pyridine all Fluka puriss. p.a.; dichloromethane and petroleum ether for column chromatography both Fluka purum; TLC: Polygram SIL G/UV254 from Macherey-Nagel; column chromatography: silica gel 60 (0.040–0.063 mm) from Merck, aluminium oxide (type 5016 A basic) from Fluka.



Scheme 1. Atom labelling used for metal complexes of chiral biconcave porphyrin **1**.

Co^{II} porphyrinate 2:[1] UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 402.5 (5.49), 514.5 (4.19), 546 nm (4.21); CD (CH_2Cl_2): λ_{max} (Mol. Ellip.) = 549 (8200), 521 (4900), 404 (82000), 299 (19000), 289 (28000), 247 nm (266000).

Zn^{II} porphyrinate 3: A sample of porphyrin **1** (65.5 mg, 44.7 μmol) was dissolved in saturated methanolic solution of zinc acetate (8 mL) and mixed with dichloromethane (8 mL). The mixture was stirred for 15 min at room temperature, 10 mL of dichloromethane were added, and the organic layer was separated and was washed with water. The solvent was evaporated, and the raw zinc porphyrin was purified by chromatography (silica gel, CH_2Cl_2/petroleum ether 1:3). Recrystallisation from acetone/water gave Zn^{II} porphyrin **3** (65.7 mg). Yield: 96%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.67 (s, 4H; H^m), 7.91 (d, J = 1.9 Hz, 8H; H^{1,5}), 7.81 (d, J = 7.8 Hz, 8H; H^{4,8}), 7.13 (s, 8H; H^{9,10}), 7.04 (dd, J = 1.9, 7.8 Hz, 8H; H^{3,7}), 1.27 (s, 72H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.00 (C$^{\alpha,\alpha'}$), 148.29, 147.80, 145.41, 142.28, 123.47, 121.57, 121.27, 99.69 (C^m), 50.34 (C^{9,10}), 34.62 (C$^{2',6'}$), 31.58 (CH_3); IR (KBr): $\tilde{\nu}$ = 2959, 2903, 2868, 1479, 1460, 1364, 1258, 1099, 1001 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 408.5 (5.49), 533.5 (4.33), 567.5 nm (4.05); CD (CH_2Cl_2): λ_{max} (Mol. Ellip.) = 568 (6500), 534 (5500), 411 (78000), 301 (22000), 287 (39000), 253 nm (195000); MS (FAB): *m/z* (%): 1531.1 (29), 1530.1 (48), 1529.2 (76), 1528.2 (87), 1527.2 (100), 1526.2 (94), 1525.2 (76) $[M+1]^+$, 1524.2 (24), 1523.1 (12).

Rh^{III} porphyrinate 4: Under an argon atmosphere, porphyrin **1** (34.3 mg, 23.4 μmol) was treated with $[Rh(CO)_2Cl]_2$ (63.8 mg, 164 μmol) and sodium acetate (25 mg, anhydr.) in absolute 1,2-dichloroethane (5 mL). After stirring for 3 h at room temperature, the reaction mixture was diluted with 1,2-dichloroethane (5 mL), and iodine (60 mg) was added at RT. Stirring was continued for an additional 2 h. After that time, a second portion of iodine (40 mg) was added and stirring was continued for 1 h. Organic solvent was removed by distillation under reduced pressure. The residue was purified by column chromatography (aluminium oxide, petroleum ether/CH_2Cl_2 2:1) and was recrystallised from acetone/water. Compound **4** was obtained as dark red crystals (32.6 mg). Yield: 82%; ^{1}H NMR (300 MHz, C_6D_6): δ = 11.06 (s, 4H; H^m), 8.07 (d, J = 1.8 Hz, 4H; H^1), 7.92 (d, J = 1.8 Hz, 4H; H^5), 7.70 (d, J = 7.8 Hz, 4H; H^4), 7.59 (d, J = 7.8 Hz, 4H; H^8), 7.26 and 7.22 (2s, 2 × 4H; H^{9,10}), 7.08 (dd, J = 1.8, 7.8 Hz, 4H; H^3), 6.89 (dd, J = 1.8, 7.8 Hz, 4H; H^7), 1.28 (s, 36H; $H_3C(C^{2'})$), 1.11 (s, 36H; $H_3C(C^{6'})$); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 155.10 (C$^{\alpha,\alpha'}$), 148.58/147.88/147.79/147.46/145.70/144.67 (C^{1a,2,4a,5a,6,8a}), 136.06 (C$^{\beta,\beta'}$), 123.91/123.33 (C^{4,8}), 121.70/121.49(× 2)/121.08 (C^{1,3,5,7}), 100.79 (C^m), 50.28 (C^{9,10}), 34.62 (C$^{2',6'}$), 31.55 (CH_3); IR (KBr): $\tilde{\nu}$ = 2957, 2903, 2866, 1479, 1460, 1362, 1259, 1109 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 405.5 (5.18), 520.5 (4.36), 550.5 nm (4.29); MS (FAB): *m/z* (%): 1692.5 (21), 1691.4 (33), 1690.5 (24) $[M+1]^+$, 1565.6 (69), 1564.5 (100), 1563.6 (88) $[M+1-127]^+$.

Ru^{II} porphyrinate 5a: Porphyrin **1** (17.0 mg, 11.6 μmol) and $[Ru_3(CO)_{12}]$ (75 mg) in *p*-xylene (5 mL) were heated under reflux for 24 h. After cooling the solution to room temperature, pyridine (0.2 mL) was added. After half an hour at RT, the solvent was distilled under vacuum and the crude product was purified by column chromatography (silica, petroleum ether/CH_2Cl_2 6:1). Porphyrinate **5a** was dissolved in pyridine and precipitated with a small amount of water. Recrystallisation from acetone/water with 5% pyridine yielded Ru porphyrin **5a** (red needles). Yield: 70%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.27 (s, 4H; H^m), 7.85 (d, J = 1.8 Hz, 4H; H^1), 7.81 (d, J = 1.8 Hz, 4H; H^5), 7.75 (d, J = 8.0 Hz, 4H; H^4), 7.73 (d, J = 8.0 Hz, 4H; H^8), 7.04 (dd, J = 1.8, 8.0 Hz, 4H; H^3), 7.00 (dd, J = 1.8, 8.0 Hz, 4H; H^7), 6.95/6.94 (2s, 2 × 4H; H^{9,10}), 5.49 (t, 1H; H$^\gamma$-py), 4.50 (t, 2H; H$^\beta$-py), 1.29/1.25 (2s, 2 × 36H; 24H_3C), 0.61 (d, 2H; H$^\alpha$-py); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.13/154.09 (C$^{\alpha,\alpha'}$), 148.44/148.14/147.52/147.49/145.62/145.32 (C^{1a,2,4a,5a,6,8a}), 143.74 (C$^\alpha$-py), 136.66/136.62 (C$^{\beta,\beta'}$), 133.3 (C$^\gamma$-py), 123.35/123.19 (C^{4,8}), 121.39/121.15 (C^{1,5}) 120.97/120.93(× 2) (C$^\beta$-py, C^{3,7}), 99.89 (C^m), 50.15 (C^{9,10}), 34.60/34.57 (C$^{2',6'}$), 31.59/31.54 (CH_3); IR (KBr): $\tilde{\nu}$ = 1954 cm^1 (CO); UV/Vis($CHCl_3$): λ_{max} (log ε) = 401.5 (5.53), 519(4.28), 548 nm (4.11); MS (FAB): *m/z* (%): 1590.6 (36) $[M-$pyridine$]^+$, 1563.6 (100), 1562.8 (75) $[M-$pyridine $-$ CO$]^+$.

Dioxo-Ru^{VI} porphyrinate 5b: Under an argon atmosphere, Ru^{II} porphyrinate **5a** (4.1 mg, 2.45 μmol) in dichloromethane (2 mL) was treated with *meta*-chloroperbenzoic acid (CH_2Cl_2 solution, 7.35 μmol) at room temperature. After 10 min, the reaction mixture was diluted with dichloromethane (10 mL) and washed with a phosphate buffer (pH 7) and water. The solvent was evaporated and the raw product was dissolved in acetonitrile and precipitated with a small amount of water. Compound **5b** was dried under high vacuum at room temperature (3.5 mg). Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.18 (s, 4H; H^m), 7.96 (d, 8H; J = 1.5 Hz, H^{1,5}), 7.86 (d, 8H; J = 8.1 Hz, H^{4,8}), 7.30 (s, 8H; H^{9,10}), 7.06 (dd, J = 1.5, 8.1 Hz, 8H; H^{3,7}), 1.28 (s, 72H; 24H_3C); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.86 (C$^{\alpha,\alpha'}$), 148.08/147.66/144.77 (C^{1a,2,4a,5a,6,8a}), 134.36 (C$^{\beta,\beta'}$), 123.71/121.72/121.50 (C^{1,3,4,5,7,8}), 101.41 (C^m), 50.07 (C^{9,10}), 34.62 (C$^{2',6'}$), 31.50 (CH_3); IR (KBr): $\tilde{\nu}$ = 820 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 407.5 (5.31), 505.5 (4.18), 535.5 nm (3.88); MS (FAB, NOBA): *m/z* (%): 1719.98 (11), 1718.98 (14), 1717.99 (21), 1717.00 (26), 1716.00 (29) $[M^+ - 2O+$NOBA$]$, 1715.01 (27), 1714.01 (24), 1713.02 (11), 1583.43 (10), 1582.43 (19), 1581.43 (25), 1580.44 (35), 1579.44 (34), 1578.44 (32) $[M-O]^+$, 1577.44 (31), 1576.44 (25), 1575.44 (15), 1574.44 (12), 1567.42 (37), 1566.43 (59), 1565.45 (79), 1564.46 (100), 1563.47 (99), 1562.48 (88) $[M-2O]^+$, 1561.41 (66), 1560.42 (43), 1559.44 (28), 1550.39 (15), 1549.39 (17), 1548.39 (23), 1547.37 (22) $[M-2O-CH_3]^+$, 1546.36 (16).

Crystal structure of (1:1)-cocrystals of [60]-fullerene and Co^{II}-porphyrinate 7

Preparation of crystals: In a small glass tube, a stock solution (0.1 mL) of Co^{II}-porphyrinate **7**[2a] (6.2 mg, 4.8 μmol) in 1,2-dichlorobenzene (4 mL) were mixed at room temperature with a solution of [60]-fullerene (0.87 mg, 0.12 μmol) in of benzene (1 mL). The tube was flushed with nitrogen and then closed. Upon standing at room temperature and protected from light, dark crystals appeared within two days. The crystals remained in contact with the mother liquor until used for X-ray analysis.

Crystal structures from X-ray analysis: Crystal data, experimental and refinement details are listed below. Some steps in the structure determination are summarised here because the disorder of the [60]-fullerene and the solvent molecules posed special problems. A partial structure solution revealed the complete porphyrin moiety, a disordered dichlorobenzene molecule and an irregular cloud of maxima on a spherical shell centred on a crystallographic mirror plane. Clearly, none of the molecular mirror planes of the disordered fullerene molecules coincided with the crystallographic one. Despite the considerable superposition of peaks, it was possible, based on distance criteria, to find two and eventually three groups of entangled fused rings. These groups were then extended to three complete [60]-fullerene molecules with the use of the FRAG-option of SHELXL.[29] Atomic coordinates were taken from ref. [30]. In summary, six [60]-fullerene molecules were located. They were related in pairs by a crystallographic mirror plane and their population coefficients were 0.267(3), 0.192(3), 0.043(3). There were two sites with solvent molecules. In one of them, two half-molecules of $C_6H_4Cl_2$ were arranged about a mirror plane. In the other, three pairs of $C_6H_4Cl_2$ molecules and a pair of C_6H_6 molecules were distributed about a centre of inversion. Their population coefficients were 0.186(3), 0.086(3), 0.052(2) and 0.111(5), respectively. For full matrix least-squares refinement, the bond lengths (but not the other parameters!) of the porphyrin molecule were restrained to show D_{4h}-symmetry (σ = 0.01 Å). The five- and six-membered rings of the [60]-fullerene molecules were restrained to be regular and flat (σ = 0.01 Å). The 6,6-distance was restrained to 1.38(1) Å. For the two major orientations, anisotropic displacement parameters were refined with the restraint that they be equidistant across the centre of the [60]-fullerene molecules

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and to neighbouring atoms within 3.6 Å. This implies a rigid body refinement. The benzene rings of all solvent molecules were restrained to C_{6h}-symmetry, the $C_6H_4Cl_2$ molecules as a whole were restrained to C_{2v}-symmetry ($\sigma = 0.01$ Å). The C–Cl distances were restrained to 1.72(1) Å. Cl atoms were refined anisotropically if their population exceeded 0.15, isotropically if otherwise. Solvent carbon atoms were refined isotropically. All hydrogen atoms with populations in excess of 0.5 were included in calculated positions. This refinement scheme lead to 1699 distance restraints, 265 planar restraints and 4560 restraints on anisotropic displacement parameters. In spite of the pronounced disorder, all results were reasonable: the 5,6-distance of [60]-fullerene refined to 1.440(4) Å is in good agreement with previous results; the C–C distance in the solvent molecules was found to be 1.365(7) Å. The principal mean square atomic displacements are between ~0.01 and ~0.1 Å^2 for the well-ordered porphyrin molecule, between ~0.01 and 0.2 Å^2 for the [60]-fullerene molecules and between 0.05 and 0.15 Å^2 for the chlorine atoms. Isotropic displacement parameters vary between ~0.06 and ~0.1 Å^2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153099. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data, experimental and refinement details for the crystal structure determination of ***7***: Crystal data: $C_{92}H_{76}N_4Co \cdot 2\,C_{60} \cdot 3.30(3)\,C_6H_4Cl_2 \cdot 0.45(2)\,C_6H_6$ M_r: 3332.2; monoclinic, *C*2/*m*; dark red platelets: $a = 19.872(3)$, $b = 17.894(3)$, $c = 20.593(5)$ Å; $\beta = 103.31(1)^\circ$; $V = 7160(3)$ Å^3; $Z = 2$; $\Delta_x = 1.511$; $Cu_{K\alpha}$ radiation; cell constants from 33 reflections; $\theta = 3.4 - 11.1^\circ$; $\mu = 2.64$ mm^{-1}; $T = 146(2)$ K. Data collection: Siemens P4 diffractometer with rotating anode generator; ω scans; 5133 measured reflections; 3641 independent reflections; 2346 reflections with $I > 2\sigma(I)$; $R_{int} = 0.102$, $R_\sigma = 0.110$; $\theta_{max} = 50^\circ$; $-16 \le h \le 16$, $-16 \le k \le 17$, $-20 \le l \le 29$; 3 standard reflections every 100 reflections; no intensity decay. Refinement: Refinement on F^2; $R[F^2 > 2\sigma(F^2)] = 0.083$, R (all data) = 0.140 $wR(F^2) = 0.216$; $S = 1.256$; 3641 reflections; 6525 restraints (see text); 1609 parameters; $w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 100P]$, where $P = (F_o^2 + 2F_c^2)/3$; $(\Delta/\sigma)_{max} = 0.004$; $\Delta\rho_{max} = 0.34$ e Å^3; $\Delta\rho_{min} = 0.33$ e Å^3; extinction correction SHELXL97; extinction coefficient 0.00011(2).

Selected ^{1}H NMR experiments with chiral shift reagents: Experiments with chiral (racemic) substrates with polar functionalities (dinitrile *rac*-**6**, *rac*-1-(9-anthryl)-2,2,2-trifluoroethanol, *rac*-menthyl-acetate, *rac*-α-methoxyphenyl-acetic acid and *rac*-α-phenylethylamine) and with chiral porphyrin **1** and metallo–porphyrinates **2**, **3** and **4**, which were used as shift reagents. The value of $\Delta\delta(1)$, the shift difference of the resonance signal of the uncomplexed substrate and enantiomer 1 in the presence of a chiral shift reagent, and $\Delta\Delta\delta$, the induced shift difference of the signals of enantiomer 1 and enantiomer 2, are reported (Bruker AM 300, at 296 K, in ppm, positive values correspond to an upfield shift). First, the racemic substrates were measured at a concentration of 50 mM. Then, the different chiral shift reagents (**2**–**4**) were added (25 mM) and the resulting shifts were compared to the signals of the free substrate.

*(±)-Dinitrile rac-**6*** (C_6D_6, shift values for bridgehead protons): with **1**: $\Delta\delta(1) = 0.11$, $\Delta\delta(2) = 0.18$, $\Delta\Delta\delta = 0.07$; with **3**: $\Delta\delta(1) = 0.01$, $\Delta\delta(2) = 0.08$, $\Delta\Delta\delta = 0.09$; with **2**: $\Delta\delta(1) = 0.10$, $\Delta\delta(2) = 0.54$, $\Delta\Delta\delta = 0.44$; with **4**: $\Delta\delta(1) = 0.55$, $\Delta\delta(2) = 0.67$, $\Delta\Delta\delta = 0.12$.

(±)-1-(9-Anthryl)-2,2,2-trifluoroethanol (C_6D_6, shift values for $F_3CC\mathit{H}$): with **1**: $\Delta\delta(1) = 0.90$, $\Delta\delta(2) = 1.07$, $\Delta\Delta\delta = 0.17$; with **3**: $\Delta\delta(1) = 0.42$, $\Delta\delta(2) = 0.84$, $\Delta\Delta\delta = 0.42$; with **4**: $\Delta\delta(1) = 0.21$, $\Delta\delta(2) = 0.51$, $\Delta\Delta\delta = 0.30$.

(±)-Menthylacetate (C_6D_6, shift values for $C\mathit{H}_3COO$): with **3**: $\Delta\delta(1) = 0.04$, $\Delta\delta(2) = 0.09$, $\Delta\Delta\delta = 0.05$; with **4**: $\Delta\delta(1) = 0.12$, $\Delta\delta(2) = 0.35$, $\Delta\Delta\delta = 0.23$.

(±)-α-Methoxyphenylacetic acid (C_6D_6, shift values for C*H*): with **1**: $\Delta\delta(1) = 0.02$, $\Delta\delta(2) = 0.03$, $\Delta\Delta\delta = 0.01$; with **3**: $\Delta\delta(1) = 0.16$, $\Delta\delta(2) = 0.23$, $\Delta\Delta\delta = 0.07$; with **4**: $\Delta\delta(1) = 0.23$, $\Delta\delta(2) = 0.30$, $\Delta\Delta\delta = 0.07$.

(±)-α-Phenylethylamine (C_6D_6, shift values for $C\mathit{H}_3$): with **3**: $\Delta\delta(1) = 1.77$, $\Delta\delta(2) = 1.84$, $\Delta\Delta\delta = 0.07$.

For experiments with nonpolar fullerene derivatives (racemic mono-adduct **8**,[17a] achiral bis-adduct **9**[17b, c]) and with chiral paramagnetic Co^{II} porphyrinate **2** as shift reagent (procedure as above), the values of $\Delta\delta(H_x)$, the shift difference of the resonance signal of H_x of the uncomplexed substrate and in the presence of **2**, and $\Delta\Delta\delta$, the induced shift difference of the signals of the indicated protons are given (Bruker AM 300, in ppm, positive values correspond to an upfield shift).

Fullerene adduct ***8***:(C_6D_6, c(**2**) = 10.2 mM, 300 K, shift values for bridgehead protons): $\Delta\delta(1) = 0.52$, $\Delta\delta(2) = 0.53$, $\Delta\Delta\delta = 0.01$.

Fullerene bis-adduct ***9***:(C_6D_6, c(**2**) = 1.5 mM, 296 K, shift values for bridgehead protons): $\Delta\delta(H_{exo}) = 0.31$, $\Delta\delta(H_{endo}) = 0.09$, enantiotopic protons $\Delta\delta(H_1) = 0.11$, $\Delta\delta(H_2) = 0.07$, $\Delta\Delta\delta = 0.04$.

Acknowledgements

The authors thank Alvaro Duarte-Ruiz for the samples of fullerene-anthracene adducts. We are grateful to Alexander Rieder and Karl-Hans Ongania for mass spectra. The work in Innsbruck was supported by the Austrian National Bank (project No. 7889).

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Received: November 27, 2000 [F2900]

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