Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Záruba, Kamil , Vašek, Petr and Král, Vladimír(2004) 'Study of Molecular Recognition of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin-β-cyclodextrin Conjugate Covalently Immobilized on a Silica Surface', Supramolecular Chemistry, 16: 7, 529 — 536
To link to this Article: DOI: 10.1080/10610270412331298776
URL: http://dx.doi.org/10.1080/10610270412331298776

Supramolecular Chemistry, October–November 2004, Vol. 16 (7), pp. 529–536

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Study of Molecular Recognition of 5,10,15,20-tetrakis-(pentafluorophenyl)porphyrin-β-cyclodextrin Conjugate Covalently Immobilized on a Silica Surface

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Received (in Austin, USA) 5 April 2004; Accepted 2 July 2004

Interactions of a new porphyrin–β-cyclodextrin conjugate (1) with a number of aromatic compounds have been studied after covalent immobilization of 1 onto a solid matrix of 3-aminopropylated silica particles. The effects of both porphyrin and β-cyclodextrin moieties on interactions with achiral aromatic compounds were studied and the influence of the achiral porphyrin spacer on chiral recognition of binaphthyl derivatives by the β-cyclodextrin moiety of 1 is discussed.

Keywords: Porphyrin; Cyclodextrin; Conjugate; Molecular recognition; Chiral

INTRODUCTION

Supramolecular chemistry deals with the design and synthesis of selective receptors for a wide variety of analytes, and the elucidation of the binding mechanism involved. Currently, synthetic protocols leading to supramolecular structures based on rational combinations of suitable building blocks (e.g. crown-ethers, calixarenes, cyclodextrins and porphyrins) are widely applied. Prepared supramolecules are expected to provide novel functionality unexplainable by a simple combination of properties of the individual building blocks. Many highly efficient receptors have been developed for selective binding of cationic, anionic and also neutral substrates [1].

Cyclodextrins (CD), cyclic oligosaccharides frequently consisting of six (α-CD), seven (β-CD) or eight (γ-CD) glucose units linked via α-1–4 glycosidic bonds, are well established in the field of molecular recognition. The origin of their popularity is in combination of two facts. First, six, seven or eight glucose units form a well-defined, hydrophobic, chiral cavity that can facilitate formation of inclusion complexes (chiral or achiral) with a variety of organic molecules present in aqueous solutions [2–5]. Second, well-determined methods are now available for the selective chemical modification of β-CD based on the acidity of the hydroxy groups present in the structure of β-CD [5–7]. Porphyrins also belong among the buildings blocks frequently used in the field of supramolecular chemistry. Several porphyrin derivatives allow important biological processes in which porphyrins and porphyrin-like species participate (e.g. electron and energy transfer in cells, dioxygen transport, etc.) to be mimicked [8–11]. Finally, much effort has also been devoted to the preparation of various cyclodextrin–porphyrin conjugates [12–14], most of which have been tested as potential catalysts of oxidation [15–17].

In the attempt to mimic live systems, efficient immobilization of synthetic receptors is essential. Another very good reason for the immobilization of receptors studied is related to the effort to avoid their self-interaction (self-aggregation, intermolecular receptor-receptor inclusion, etc.), an undesirable effect often complicating measurements in solution. Interactions taking place on the solid-liquid interface can be studied by many physico-chemical methods including spectroscopic, electrochemical and chromatographic techniques. Moreover, various solvents can be conveniently used for a fine tune-up of interactions between an immobilized receptor and analytes in solution.

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ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270412331298776

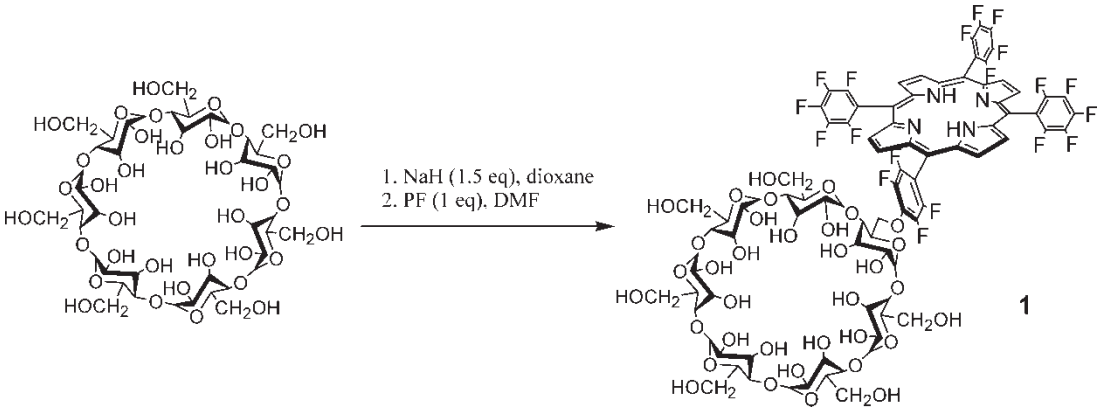

FIGURE 1 Preparation of porphyrin-β-cyclodextrin conjugate (**1**).

Beside studying receptors for anions and saccharides studied in solution [18,19], we have recently published several examples of successful covalent attachment of receptors to solid supports. We have applied macrocyclic ligands, specifically cytosine-sapphyrin and calixpyrroles, for the separation of anionic species [20,21], and self-assembled monolayers generated from porphyrin and sapphyrin compounds for the recognition of nucleotides [22]. In our previous work we have also prepared conjugate **1** (Fig. 1) by reaction of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (**PF**) with β-CD alcoholate. The conjugate was readily purified by reversed-phase chromatography [23]. Unlike Yang *et al.* [24], the thio derivative of CD was not prepared; instead direct reaction of alcoholate was used. Nucleophilic substitution of *para*-fluorine atoms of **1** and mild reaction conditions led to the formation of a monocyclodextrin–monoporphyrin conjugate (**1**) [25]. Photoactive and/or electroactive properties of the porphyrin moiety in combination with the binding capabilities of the β-CD moiety of **1** have been studied in solution by fluorescence spectroscopy [23].

We report here the immobilization of conjugate **1** on a solid surface by reaction of **1** with 3-aminopropylated silica particles. Again, nucleophilic substitution of *para*-fluorine is assumed [26]. The structure of the modified particles (chiral stationary phase **CSP-1**) is shown in Fig. 2. Interactions of covalently immobilized **1** with various optically active/inactive analytes were studied by liquid chromatography, with **CSP-1** as the stationary phase.

RESULTS AND DISCUSSION

Both the β-CD and the **PF** moieties of **1** are able to interact with aromatic compounds. Inclusion is usually considered the main interaction mode involved in interaction of β-CD with analytes [27]. On the other hand, hydrophobic π–π interaction represents the preferred mode in porphyrins [28–31]. As our primary intention was to study the influence of large porphyrin moiety on the inclusion of chiral compounds into the β-CD cavity, immobilization of **1** was necessary from the following reasons. The solubility of **1** in an aqueous

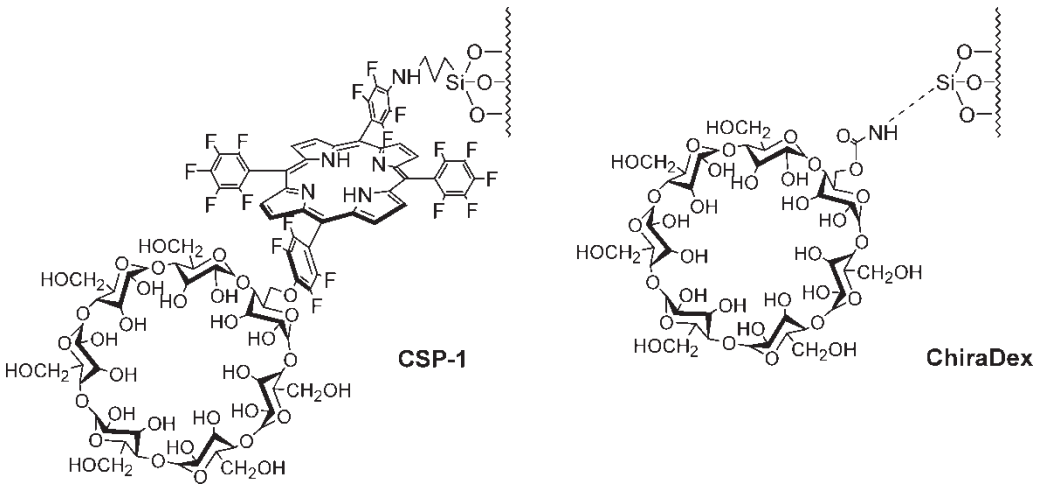

FIGURE 2 Structures of the chiral stationary phases studied.

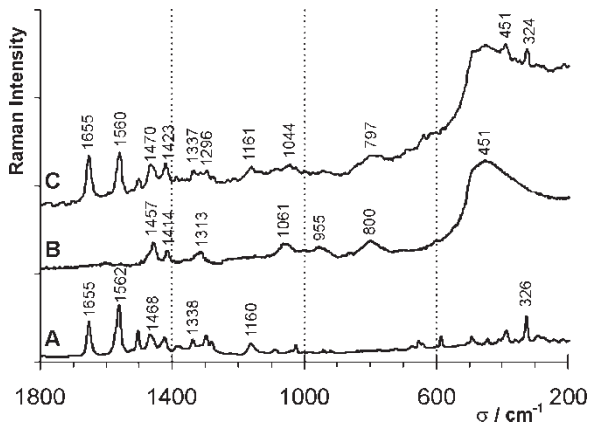

FIGURE 3 Raman spectra of pure **1** (A), starting 3-aminopropyl silica (B), and final **CSP-1** (C).

environment is poor, although it is well known that the inclusion phenomenon predominates in polar aqueous environment. Thus, **1** could not be studied directly in water-rich solution and the strategy relying on the immobilization of **1** had to be adopted.

Successful covalent immobilization of **1** was proved by Raman spectroscopy and elemental analysis. Raman spectra of the starting materials (**1** and 3-aminopropyl silica) are shown in Fig. 3A,B. A number of characteristic signals of **1** (e.g. 1655 and 1560 cm^{-1}, valence C—C vibrations of the **PF** moiety; 1470 and 1164 cm^{-1}, deformation C—O vibrations of the β-CD moiety) are clearly present in the spectrum of **CSP-1** (Fig. 3C). Prepared **CSP-1** was washed extensively with the series of solvents covering the whole polarity range from water to hexane to release physically adsorbed compounds. Thus, covalent (not physical) immobilization of **1** is assumed. Surface coverage estimated from elemental analysis [32] was 0.7 μmol m^{-2}. Residual amino groups were treated with a solution of acetyl chloride to avoid their possible interference effects (for details see Experimental).

The interaction of achiral aromatic compounds (benzene, toluene, biphenyl, perfluorobiphenyl, fluorene, chrysene and pyrene) and chiral 1,1′-binaphthyl derivatives (Fig. 4) with **CSP-1** in a methanol–water environment was studied. The results obtained were compared with data measured with a commercial β-CD-based stationary phase **ChiraDex** (Fig. 2) reportedly containing no aromatic moieties [33].

Achiral Interactions

Data demonstrating interaction of achiral aromatic compounds with **CSP-1** *versus* results achieved with **ChiraDex** sorbent are shown in Fig. 5. The intensity of interaction is expressed by the retention factor (*k*). The results obtained match our expectations. Both cyclodextrin and porphyrin are capable of interacting with aromatic compounds. However, interaction of aromatic compounds with β-CD based on inclusion of an aromatic ring into a cavity of β-CD is restricted by the size of the aromatic solute and the β-CD cavity. It is known that benzene, toluene or biphenyl fit well into the cavity of β-CD. However, chrysene, fluoranthene and pyrene are too large to enter the cavity completely; thus, the extent of their interaction with β-CD is restricted.

Steric requirements of the porphyrin unit of **1** immobilized on the silica surface are much higher in comparison to the linear spacer used in **ChiraDex**. Consequently, the surface coverage of the silica by **1** in **CSP-1** is probably lower than the coverage by β-CD in **ChiraDex** (exact value not available). This is in accordance with the higher retention factors on **ChiraDex** for benzene, toluene and biphenyl, the compounds freely entering the cavity of β-CD.

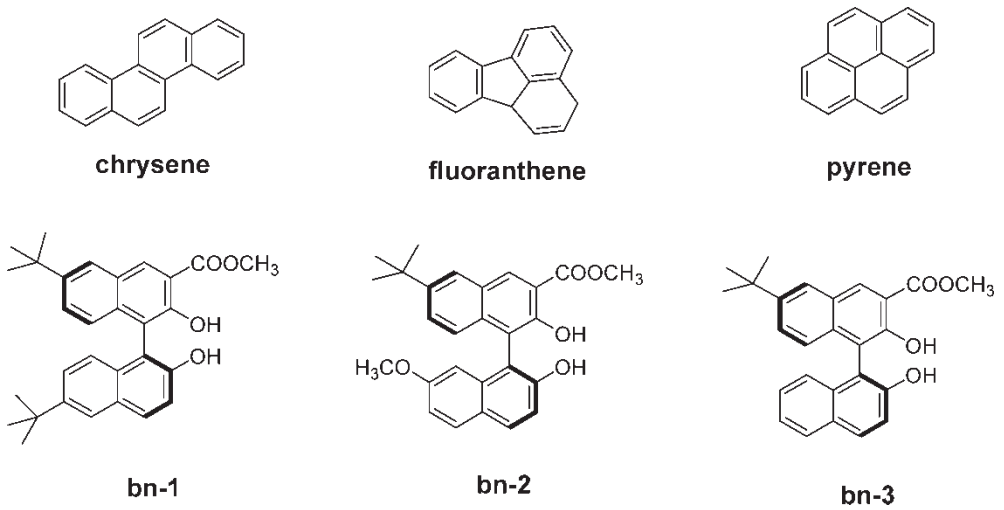

FIGURE 4 Structures of achiral polyaromatic analytes and chiral substituted 1,1′-binaphthyls.

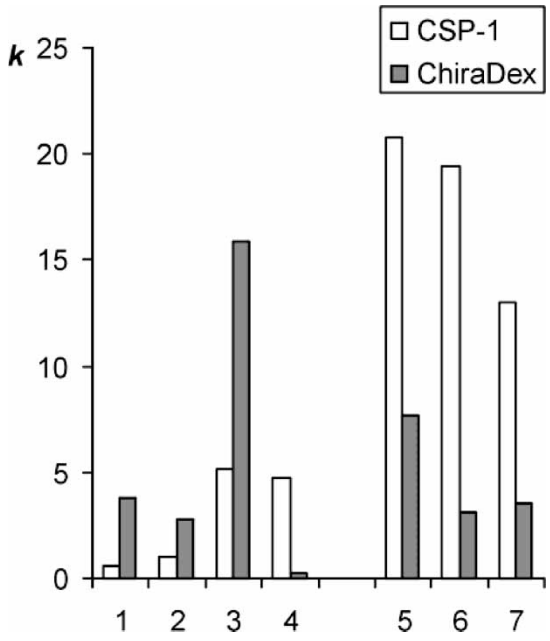

FIGURE 5 Retention factors (k) of aromatic analytes separated on **CSP-1** and **ChiraDex**. Mobile phase: methanol–water 6:4 (v/v), flow rate 0.5 mL min^{-1}. Analytes: 1, benzene; 2, toluene; 3, biphenyl; 4, perfluorobiphenyl; 5, chrysene; 6, fluoranthene; 7, pyrene.

In the case of more extended aromatic systems, where only partial inclusion of polyaromates is possible, π–π interactions of polyaromates with the porphyrin moiety of **CSP-1** can dominate, and indeed higher retention factors on **CSP-1** than on **ChiraDex** were measured (Fig. 5).

More complex and interesting behavior was observed for biphenyl and its perfluorinated derivative (Fig. 5). Biphenyl was more strongly retained on **ChiraDex** and this corresponds well with the above-mentioned substantiation. However, while perfluorobiphenyl showed significant retention on **CSP-1**, negligible interaction with immobilized β-CD was observed on **ChiraDex** and the compound was eluted close to the void time of the latter column. This behavior can be attributed to repulsion of the fluorine atoms of the perfluorobiphenyl and β-CD unit and, simultaneously, to attractive interaction of perfluorobiphenyl and fluorinated parts of **PF** (π–π interaction).

Chiral Interactions

Three model analytes, the 1,1′-binaphthyl derivatives **bn-1**, **bn-2** and **bn-3** (structures shown in Fig. 4), were used to study chiral interactions of enantiomers on **CSP-1** and **ChiraDex**. Achiral/unspecific interaction expressed by retention factors of the less retained enantiomers followed the same trend as in the case of the achiral compounds (Fig. 6). The more polar the mobile phase (the greater amount of water), the higher the retention factors are for the analytes. The highest applicable water content in mixed

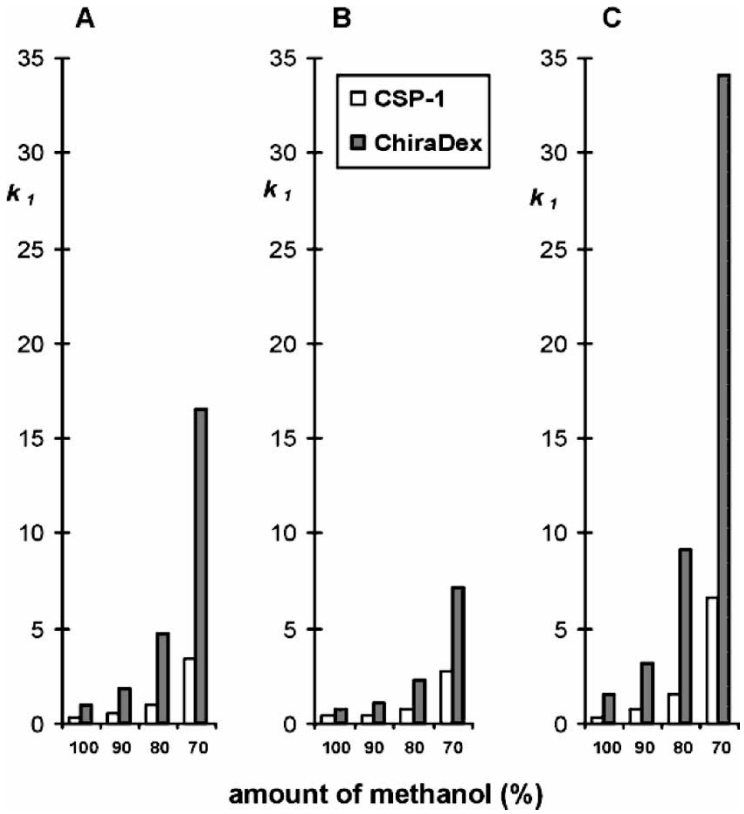

FIGURE 6 Dependence of retention factors of the first eluted enantiomer (k_1) of the derivatives **bn-1** (A), **bn-2** (B) and **bn-3** (C) on stationary phases **CSP-1** and **ChiraDex** on the amount of methanol in the mobile phase.

methanol–water mobile phases was about ~30% as the retention factors of the binaphthyl derivatives on **ChiraDex** increased unacceptably in a highly aqueous environment.

Chiral interaction of the immobilized β-CD with individual enantiomers of the selected binaphthyls can be expressed by separation factors (α), which are generally calculated as the ratio of the retention factor of the more strongly retained enantiomer to the retention factor of the less retained enantiomer of a given chiral analyte. Thus, when $\alpha = 1$, no specific chiral separation takes place on the stationary phase. On the other hand, high α-values reflect a good enantioselectivity of the immobilized selector.

Results for **CSP-1** and **ChiraDex** are summarized in Table I and Fig. 6. The data show that (a) enantiomers of **bn-1** were separated only on the **ChiraDex** stationary phase, (b) chiral separation of the two other binaphthyl derivatives, **bn-2** and **bn-3**, was obtained on both stationary phases (**CSP-1** and **ChiraDex**), and (c) enantiomers of **bn-2** were better separated on **CSP-1** whereas enantiomers of **bn-3** had higher α values on **ChiraDex**.

In an attempt to explain the measured data, several aspects are mentioned and discussed briefly. As can be seen in Fig. 2 the β-CD moiety is immobilized *via* primary hydroxyl groups located at the narrow rim of β-CD in both β-CD-based stationary phases tested. Thus, the geometry/orientation of the selector with respect to the silica surface is similar for both stationary phases – with the wider rim of β-CD oriented to the mobile phase and the narrow rim providing sterically rather restricted access for analytes, and also because of more (**CSP-1**) or less (**ChiraDex**) bulky spacers. Solely for steric reasons, interaction of the analytes with secondary hydroxyl groups present at the wider rim is assumed to have a decisive role in their retention. However, inclusion into the cavity of β-CD from its wider rim is not the only interaction mode involved in separation of chiral and achiral solutes [3]. The idea of the interaction with peripheral hydroxyls of β-CD accompanied by limited or no inclusion of analytes belongs among generally accepted hypotheses of separation mechanism in "polar-organic mode", where mobile phases consist of mixtures of organic solvents (usually acetonitrile and methanol) with acetic acid or triethylamine [27,34]. Moreover, it has been shown elsewhere that inclusion of molecules into β-CD is also feasible from the narrow side of the cavity [35]. Consequently, there is more than one interaction mechanism involved in discrimination of the separated analytes.

We expect that in the case of **1** the porphyrin moiety can play an active role in chiral recognition through π–π interaction in such a way that it influences the spatial orientation of the chiral-separated analytes towards the immobilized selector (β-CD) before and during the formation of diastereomeric complexes of the individual enantiomers with β-CD. Such a driving force is not available in **ChiraDex**, with a linear spacer. Hence, in the case of **CSP-1** we expect first non-covalent complex formation based on π–π stacking interaction between the aromatic analyte and the immobilized **PF** moiety, followed by chiral recognition of the individual enantiomers by β-CD moiety in the second step. Hence, we hypothesize that better separation of the individual enantiomers of **bn-2** in comparison to the enantiomers of **bn-3** on **CSP-1** was caused by stronger π–π non-covalent interaction between **bn-2** and the **PF** moiety of **CSP-1**. The molecule of **bn-2** contains a methoxy group on one naphthalene ring, which increases the electronic density of the ring, and consequently it can enhance the interaction with the π-electron deficient parts of the **PF** unit. Moreover, it is significant that the geometry of the non-covalent complex forming is not random but is highly controlled. Stronger and more directed interaction with the **PF** unit could also have a stronger driving effect on the simultaneous enantioselective interaction of the other part of the **bn-2** molecule with the β-CD unit. The hypothesis on the influence and cooperation of the hydrophobic interaction in chiral recognition is indirectly supported by the retention factors of the less retained enantiomers of **bn-1**, **bn-2** and **bn-3** on **ChiraDex** and **CSP-1** given in Fig. 6. A relative decrease in retention factor of **bn-2** with respect to **bn-1** is significantly more distinct on **ChiraDex** than on **CSP-1**. This proves that differences in hydrophobic interaction are taking place on the respective stationary phases. Consequently, no chiral separation of **bn-1**, a better separation of **bn-2** enantiomers

TABLE I Separation factors (α) of the individual enantiomers of **bn-1**, **bn-2** and **bn-3** on stationary phases **CSP-1** and **ChiraDex** in methanol–water mobile phases

	bn-1		**bn-2**		**bn-3**	
Amount of methanol in water (%)	*CSP-1*	*ChiraDex*	*CSP-1*	*ChiraDex*	*CSP-1*	*ChiraDex*
100	1.0	1.1	1.0	1.6	1.0	1.3
90	1.0	1.1	1.5	1.4	1.3	1.6
80	1.0	1.3	1.6	1.3	1.4	1.9
70	1.0	1.4	1.5	1.2	1.4	1.3

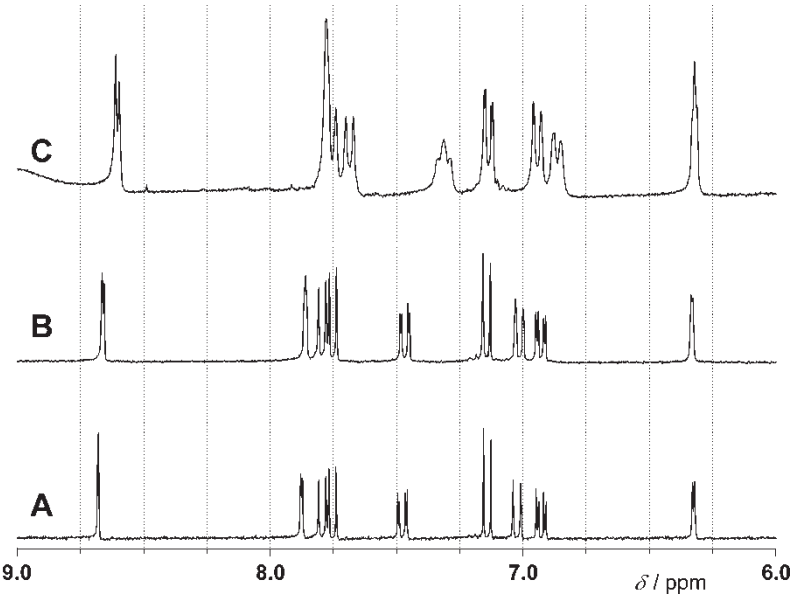

FIGURE 7 ^{1}H NMR spectra of pure **bn-2** (A), equimolar β-CD·**bn-2** (B) and equimolar **1**·**bn-2** (C). Solvent: CD_3OD – D_2O 6:1 (v/v); 25°C; all spectra referenced to DSS; concentrations of all species 4×10^{-3} mol L^{-1}.

and, at the same time, a worse separation of **bn-3** enantiomers on **CSP-1** with respect to **ChiraDex** could possibly be explained by the above-mentioned considerations. It seems that participation of hydrophobic interaction in chiral recognition can have either a positive or a negative influence in the chiral recognition depending on the particular circumstances.

In order to prove this hypothesis, we carried out fluorescence and ^{1}H NMR experiments with free (unimmobilized) **1**. The fluorescence experiments revealed a weak interaction between **1** and **bn-2** in solution. However, only a slight decrease in fluorescence (about 15%) was measured in the system where the concentration of **1** was held constant and the concentration of **bn-2** increased gradually (for a detailed description see Supplementary Material). Similar results were obtained by experiment with **bn-3**.

In the case of the NMR study in solution a mixture of deuteromethanol–deuterium oxide 6:1 (v/v) was used to track the interactions of β-CD with **bn-2** and **1** with **bn-2**, respectively. A greater amount of deuterium oxide could not be used because of solubility limitations. The ^{1}H NMR experiment (for details see Experimental) revealed a significant upfield shift of the aromatic proton signals of **bn-2** when **1** was present (Fig. 7C); this effect was not observed for the β-CD·**bn-2** system (Fig. 7B).

According to the literature, an upfield shift accompanies the inclusion of analytes into the cavity with cyclodextrins [36,37]. From the results of the ^{1}H NMR experiments it seems that the inclusion of **bn-2** into the cavity of free unmodified β-CD is limited in the given solvent for the β-CD·**bn-2** system as only a very small or no upfield shift of protons was found (Fig. 7B). The observed upfield shift in the **1**·**bn-2** system (Fig. 7C) can be explained by the interaction of **1** with **bn-2** being in mutual coplanar orientation [38]. In summary, the fluorescence and NMR experiments indicate cooperativity of the porphyrin moiety of **CSP-1** in retention and chiral recognition of the binaphthyl derivatives.

CONCLUSIONS

A porphyrin–β-cyclodextrin conjugate (**1**) was successfully immobilized on a silica support forming chiral stationary phase **CSP-1** to study the interactions on the solid–liquid interface. Interactions of achiral and chiral compounds with **CSP-1** were studied and compared with results obtained on the commercial β-cyclodextrin-based sorbent **ChiraDex**. Chromatographic experiments complemented by fluorescence and NMR studies in solution provide evidence of a cooperative effect of the porphyrin moiety in the interaction and recognition processes of achiral and chiral compounds. The immobilization strategy proved its validity and asset in studies directed toward the evaluation of non-covalent interactions of the selector-ligand type.

EXPERIMENTAL

Chemicals

All solvents and chemicals for synthesis and for further analytical measurements [methanol, water, dimethylformamide (DMF), propan-2-ol, acetone,

sodium hydride, triethylamine] were of 95% purity or higher. Deuterated chemicals [deuteromethanol (CD_3OD), deuterium oxide (D_2O) and 2,2-dimethyl-2-silapentane-5-sulfonate sodium salt (DSS)] were purchased from Merck (Germany). β-Cyclodextrin, 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (**PF**), fluoranthene, chrysene, pyrene, biphenyl and perfluorobiphenyl were purchased from Sigma (Germany). Benzene and toluene were bought from Penta (Czech Republic). Binaphthalene derivatives were prepared as described previously [39–41]. 3-Aminopropylated silica was purchased from Tessek (Czech Republic); SGX NH_2 5 μm, pore size 8 nm, specific surface area 500 m^2 g^{-1}. Elemental analysis showed 5.8% of carbon and 2.2% of nitrogen, corresponding [32] to the surface coverage of 3.5 μmol m^{-2}.

Preparation of 5,10,15,20-tetrakis (pentafluorophenyl)porphyrin–β-cyclodextrin (1)

The porphyrin–β-cyclodextrin conjugate (**1**) was prepared as described previously [23]. In brief, an equimolar mixture of β-cyclodextrin and sodium hydride in dry dioxane was added to a solution of **PF** (1 equiv.). The final product (**1**) was isolated by reversed-phase chromatography and characterized. Its structure is shown in Fig. 1.

Preparation of 5,10,15,20-tetrakis-(pentafluorophenyl)porphyrin–β-cyclodextrin Modified 3-aminopropyl silica

3-Aminopropylated silica (1 g) was washed with 1% triethylamine in dry acetonitrile and then with dry acetonitrile to remove free triethylamine. Then a solution of **1** (50 mg) was added to a suspension of 3-aminopropylated silica in dry acetonitrile (50 mL). The suspension was refluxed for 1 day. The modified silica was filtered off and washed with acetonitrile, acetonitrile–water mixture (1:1), acetonitrile, dichloromethane, hexane and dichloromethane (min. 25 mL of each). Samples intended for elemental analysis and Raman spectroscopy analysis were dried in high vacuum at 40°C. The elemental analysis showed 17.3% of carbon and 3.7% of nitrogen, corresponding [32] to a surface coverage 0.7 μmol m^{-2}. Finally, unreacted amino groups were treated with a solution of acetyl chloride in dry acetonitrile (1%) for 5 days to prevent their possible undesirable interference and the resulting product was labeled **CSP-1**. The ninhydrin test for free amino groups in the final sorbent **CSP-1** was negative [42]. However, a significant increase in C-H stretch vibrations in the Raman spectrum confirmed successful end-capping of residual amino groups (for details see Supplementary Material).

HPLC Columns

CSP-1 (1.0 g) was suspended in propan-2-ol (25 mL) and packed into a stainless steel column blank (100 × 4 mm, Tessek, Czech Republic) at 50 MPa with acetone. The β-cyclodextrin column ChiraDex® (250 × 4 mm, particle size 5 μm, pore size 10 nm, specific surface area 350 m^2 g^{-1}) was purchased from Merck, Germany.

Analytical Methods

Raman Spectroscopy

Raman spectra were collected using a Fourier-transform near-infrared (FT-NIR) spectrometer Equinox 55/S (Bruker, Germany) equipped with an FT Raman module FRA 106/S (Bruker). The focused laser beam (250 mW) of a Nd:YAG laser (1064 nm, coherent) irradiated the samples of sorbents in glass vials placed on a motorized X-Y-Z sample stage. Scattered light was collected in the backscattering geometry. Interferograms were obtained with a quartz beamsplitter and a Ge detector (liquid N_2 cooled). Typically, 128 accumulated interferograms were processed by the Fourier transformation with Blackman–Harris 4-term apodization and a zero-filling factor of 8 in order to obtain individual FT Raman spectra with a 4 cm^{-1} resolution.

HPLC

The HPLC system Series 200 (Perkin-Elmer, USA) consisted of a quaternary pump equipped with helium degassing of the mobile phase, an auto-sampler, a diode-array detector and TurboChrom™ Workstation software (version 6.1). Sample solutions (*ca* 0.5 mg mL^{-1}) were prepared by dissolving the analytes in methanol. Mobile phases were composed of a mixture of methanol with water in various volume ratios. The flow rate of the mobile phase was 0.5 mL min^{-1}. Detection was performed at 254 nm. All chromatographic experiments were carried out at laboratory temperature (24°C). Retention factors (k) were calculated as the ratio of the adjusted retention time [the retention time (t_R) minus the void time (t_M)] and the void time (t_M). Separation factors of enantiomers (α) were calculated as the ratio of retention factors of individual enantiomers; by definition, the value of the separation factor is always greater than unity (retention factor of the more retained enantiomer is in the numerator).

^{1}H NMR

^{1}H NMR experiments were performed on Varian NMR spectrometer, model Gemini 300HC. The working frequency 300.075 MHz, deuterium lock, temperature 298 K and 5 mm NMR tubes were used

for all measurements. One-dimensional ^{1}H NMR spectra were acquired using a 45° pulse (10 μs), spectral width 6000 Hz, acquisition time 1.779 s, and typically with 64 accumulations. Samples of **bn-2**, an equimolar mixture of β-CD and **bn-2** (4×10^{-3} mol L^{-1} each) and an equimolar mixture of **1** and **bn-2** (4×10^{-3} mol L^{-1} each) were prepared by dissolving appropriate amounts in CD_3OD-D_2O, 6:1 (v/v) mixture. All spectra were collected at 25°C and referenced to DSS.

Acknowledgements

The financial support of the Grant Agency of the Czech Republic (project number 203/02/0933) is gratefully acknowledged as well as the financial support of the Ministry of Education, Youth, and Health of the Czech Republic (project number MSM 223400008).

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