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# Reciprocal principle of molecular recognition in supramolecular chromatography—highly selective analytical separation of cyclodextrin congeners on a silica-bonded [60]fullerene stationary phase

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The supramolecular pair fullerene/cyclodextrin represents a new example for the concept of reciprocal molecular recognition in liquid chromatography. Through inverting their roles as selectand and selector, small-to-large-ring cyclodextrins were chromatographed on silica-bonded [60]fullerene, whereas [60]- and [70]fullerenes were previously separated on a silica-bonded β-cyclodextrin. The recognition of cyclodextrins of intermediate ring size on silica-bonded [60]fullerene is highly selective. Thus, CD8, CD9 and CD10 are separated both from lower (CD6 and CD7) and higher (CD11–CD25) congeners with a remarkable and unprecedented retention window. By using the retention-increment method, employing a reactor column (with selector) and a reference column (without selector), apparent relative complexation constants $K_{rel}$ of CD6–CD12 and [60]fullerene were determined by supramolecular liquid chromatography. The historical development of the reciprocal principle of molecular recognition in chromatography is reported in the introduction.

## Introduction

The terms selector and selectand were introduced by Mikeš into chromatography in analogy to the cybernetic terms operator-operand to avoid ambiguities that may arise from the use of the terms solvent-solute, ligand-substrate, host-guest *etc.*[1] In chromatographic partitioning systems, the selector can be present as a stationary phase or as an additive to the liquid phase.[1] Following the enantioseparation of helicenes on the optically active charge-transfer agent 2-(2,4,5,7-tetranitro-9-fluorenylideneamino-oxy)propionic acid (TAPA),[2] Mikeš speculated that the function of the selector and the selectand could be reversed, *i.e.*, helicenes used as resolving agents.[1] Thus, in a reciprocal fashion, if the selectands A1 and A2 are chromatographically separated on the selector B1 (or B2), also the selectands B1 and B2 should be separated on the selector A1 (or A2) whereby the respective pairs A1/A2 and B1/B2 refer to isomers (*e.g.*, stereoisomers) or to members of homologous series of compounds (Fig. 1). Deviations from this prediction may only arise from the environment of the selector in the stationary phase, *e.g.*, from the presence of the spacer linking the selector to a chromatographic matrix.

The *principle of reciprocity* by inverting the role of selectand and selector has first been demonstrated *via* the differentiation of enantiomers by chiral solvating agents (CSA) in NMR spectroscopy. Pirkle and Hoover stated that the roles of an enantiomeric solute and a CSA *may be interchangeable* for a given pair of compounds.[3] The reciprocal principle was later extended to enantioselective liquid chromatography.[4] Pirkle *et al.* pointed out that one can take one chiral stationary phase (CSP) to develop others: *if a CSP derived from (+)-A retains (+)-B, then a CSP comprised of immobilized (+)-B should, using the same interactions, selectively retain (+)-A*.[5] A vivid example of the *de novo* design of a CSP for a particular target analyte involved a series of CSPs developed for the separation of the enantiomers of the non-steroidal anti-inflammatory drug (NSAIDs) naproxen.[6,7] By the so-called *immobilized guest method* a single enantiomer of naproxen was immobilized to form a naproxen-derived CSP which was then used to screen potential candidate enantioselective naproxen selectors.[7] This reciprocal study identified the structural requirements for enantioselective naproxen recognition and the Whelk-O1 CSP was developed which not only showed the highest enantioseparation factor for naproxen ($\alpha = 2.25$) but also enantioseparated structurally related NSAIDs as well as a host of different racemates.[6,7] Reciprocal screening methods

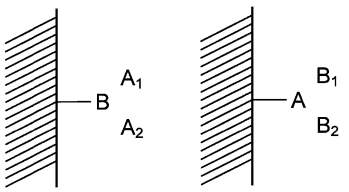


**Fig. 1** The reciprocal supramolecular recognition principle. If the selector B separates the selectands $A_1$ and $A_2$, then the selector A is expected to separate the selectands $B_1$ and $B_2$. $A_i$ and $B_i$ are homologous compounds, congeners or isomers (including enantiomers).

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have also been used in library approaches to the optimization of chiral peptide and peptidomimetic selectors in liquid chromatography.[8] Here we demonstrate that the reciprocal principle between selectands and selectors can also be used for the separation of congeners belonging to homologous series of compounds as exemplified for fullerenes and cyclodextrins CD*n* (*n* refers to the number of glucose units in the cyclic α(1 → 4)glucans) *via supramolecular chromatography*.

## Results and discussion

The molecular recognition phenomenon between fullerenes and cyclodextrins is well established. γ-Cyclodextrin (CD8)[9–13] and β-cyclodextrin (CD7)[14,15] form water-soluble bicapped 2 : 1 association complexes with [60]fullerene. This type of molecular association should be amenable for selective separations by *supramolecular chromatography*. Indeed, [60]fullerene and [70]fullerene were quantitatively resolved on a γ-cyclodextrin (CD8) selector anchored to silica in n-hexane by HPLC.[16] Through inverting the role of selector and selectand by using the reciprocal principle schematically shown in Fig. 2, it should also be possible to selectively separate CD*n* congeners on a silica-bonded [60]fullerene used as stationary phase by LC. Previously, bonded mixed [60,70]fullerene and single [60]fullerene selectors have been used for the highly selective separation of polychlorinated biphenyls (PCBs) and of polyaromatic hydrocarbons (PAHs) by LC[17–20] and of polychlorinated biphenyls (PCBs) by GC.[21] Also the self-recognition of fullerene selectands on a fullerene selector has been used for separations.[17,22,23] The semiquantitative separation of *p-tert-butyl*-calix[4]arene, *p-tert*-butyl-calix[6]arene and *p-tert*-butyl-calix[8]arene on a silica-bonded [60]fullerene stationary phase by micro-LC has been described[24] and at the same time, in a reversed mode of a calixarene, quantitative structure-retention relationships (QSRR) were studied for positional isomers of xylenes, ethyltoluenes and diethylbenzenes on *p-tert*-butyl-calix[4]arene and *p-tert*-butyl-calix[8]arene used as stationary phases in GC.[25]

With the advent of the enzymatic access to large-ring cyclodextrins (*cf.* ref. 26), the separation of the congeners CD*n* represents a considerable analytical challenge. Koizumi *et al.* separated CD6–CD85 (obtained by the action of cyclodextrin glycosyltransferase from *Bacillus macerans* on synthetic amylose) by high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection using a 250 × 4 mm I.D. Dionex CarboPac PA-100 column[27] whereas Bogdanski *et al.* separated CD6–CD21 by liquid-chromatography with electrospray ionization mass spectrometric detection (LC/ESI-MS) using a 250 × 4 mm I.D. LiChrospher $NH_2$ column.[28] With one exception (CD9 on HPAEC[27]) the congeners CD*n* were eluted from the stationary phases according to the degree of polymerization *n*.

An unusual selectivity pattern has been observed for the separation of CD6–CD15 congeners on a [60]fullerene selector anchored to silica in this work. For the evaluation of selectivity, two stationary phases, *i.e.*, one devoid of, and one containing the [60]fullerene selector, were prepared. Thus, Nucleosil (5 μm, 100 Å) was reacted in toluene with 3-glycidoxypropyltrimethoxysilane to yield 3-glycidoxypropyl-silica[29] and (i) the epoxide was reacted with bis(1-aminohexyl)malonate[30] to **1** (silica-bonded spacer without selector) and (ii) the same epoxide was reacted with bis(1-aminohexyloxycarbonyl)-malonate-dihydro[60]fullerene[30] to **2** (silica-bonded spacer with selector) (Fig. 3).

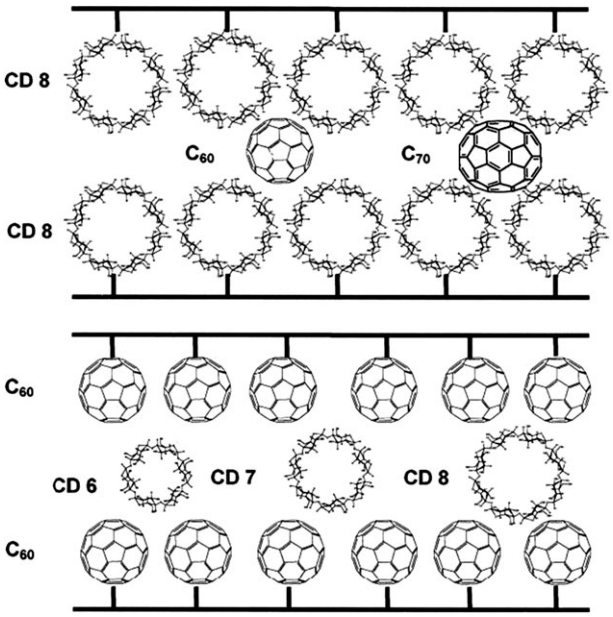


**Fig. 2** Schematic representation of the reciprocal principle between fullerenes and cyclodextrins in chromatography.

Native cyclodextrins (CD6–CD15) were analyzed by LC-ESI-MS as sodium ion adducts $[M + nNa]^{n+}$ ($n$ = 1 or 2) by gradient elution (see experimental part). The cyclodextrins were identified *via* reference compounds and/or by their mass spectra.

In Fig. 4, the overlaid LC-ESI-MS traces of sodium-adducts of the native cyclodextrins CD6–CD15 are depicted. The CD6–CD10 congeners are completely resolved. The elution order is reversed between CD9 and CD10. Striking selectivity differences are observed between CD7 and CD8 as well as between CD10 and CD11. These unprecedented selectivity changes are obviously due to strong differences in the supramolecular interaction between the CD*n* congeners and silica-bonded [60]fullerene **2** as they are not observed on the silica-bonded spacer **1** devoid of the selector. While CD6 and CD7, and CD11–CD15, respectively, are only weakly retained, CD8–CD10 are strongly retained causing a remarkable retention window of 10 min between the two sets of congeners.

In order to exclude possible artefacts or misinterpretations of the mass spectra of the sodium-adducts of CD6–CD15 congeners obtained in the LC-ESI-MS mode, the investigations were repeated with CD6–CD25 by a totally different LC detection system employing evaporative light scattering detection (ELSD). As shown in Fig. 5, the same selectivity pattern, characterized by the unusual elution order for the CD*n* congeners previously detected with LC-ESI-MS (Fig. 4), was found by this complementary LC system. Noteworthy again is the striking retention gap between CD7 and CD8 and between CD10 and CD11, respectively.

To this end, relative stability constants $K_{rel}$ between CD*n* and [60]fullerene have been measured by adopting the

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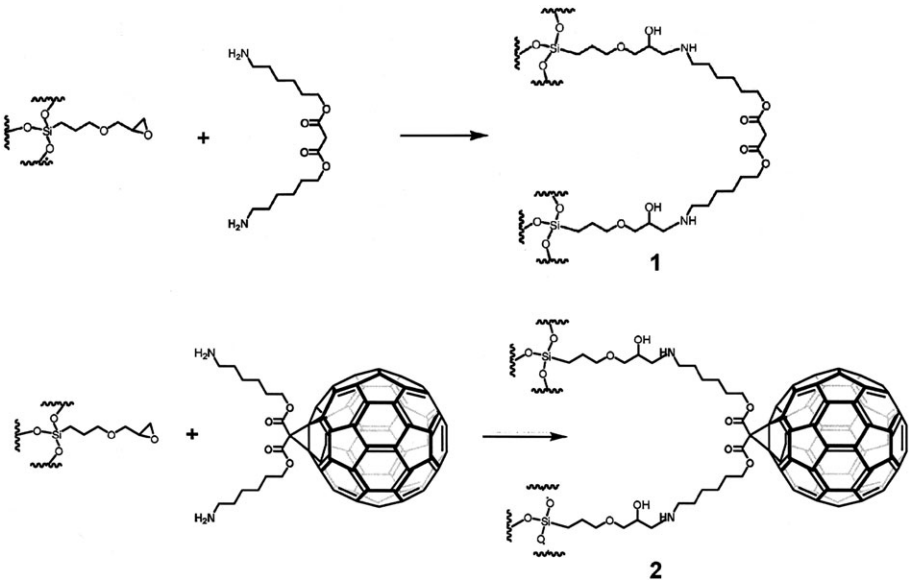


**Fig. 3** Structure of the silica-bonded spacer stationary phase **1** (top) and the silica-bonded [60]fullerene stationary phase **2** (bottom).

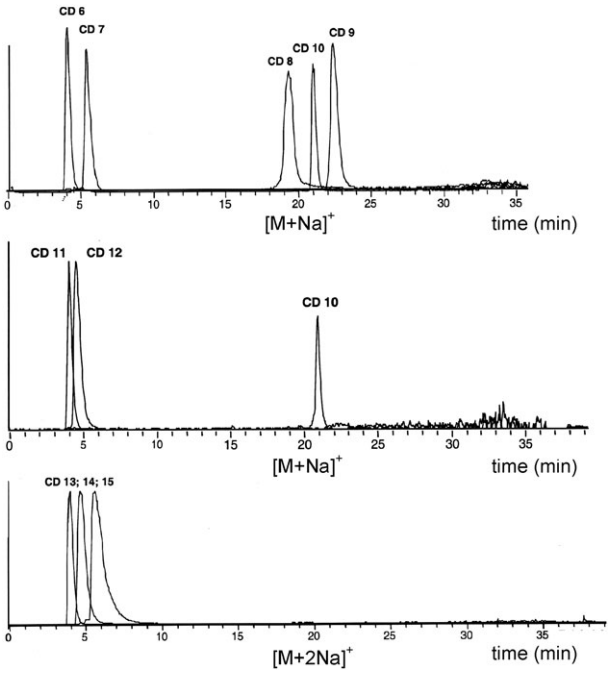


**Fig. 4** Overlaid LC-ESI-MS traces of the selective separation of CD6–CD15 congeners on the silica-bonded [60]fullerene stationary phase **2**. For chromatographic conditions see experimental part.

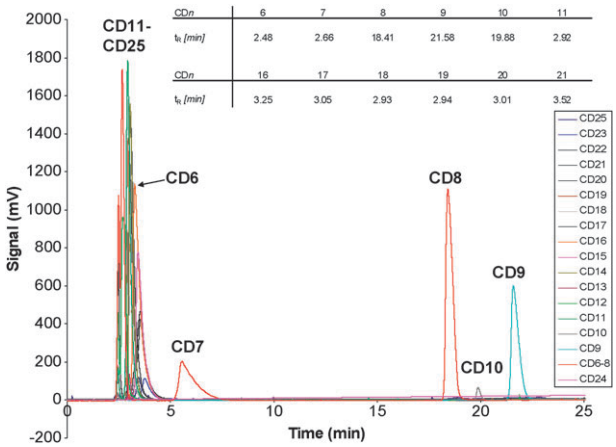


**Fig. 5** Overlaid LC-ELSD traces of the selective separation of CD6–CD25 congeners on the silica-bonded [60]fullerene stationary phase **2**. For chromatographic conditions see experimental part.

retention-increment $R'$ concept developed in complexation gas chromatography.[31,32] This approach utilizes a *reference column* devoid of the selector (the silica-bonded spacer stationary phase **1**) and a *reactor column* containing the selector (the silica-bonded [60]fullerene stationary phase **2**) (Fig. 6). A retention increment $R' = (t'_R - t'^{o}_R)/t'^{o}_R$ is caused for the analyte when a selective supramolecular interaction occurs in the reactor column between the selector F (fullerene) and the selectand CD. $R'$ is related to the thermodynamic complexation constant $K$ and the thermodynamic activity $a$ of the selector F in the stationary phase **2**, $R' = Ka$. In order to become independent of column parameters, the adjusted retention times $t'^{o}_R$ and $t'_R$ are preferentially substituted by relative retention data $r^o$ and $r$ normalized to an inert reference standard, *i.e.*, $r^o = t'^{o}_R/t'^{o}_{R(\text{standard})}$ and $r = t'_R/t'_{R(\text{standard})}$ thus affording $R' = (r - r^o)/r^o = Ka$ (Fig. 6).[31,32] Accordingly, by utilizing an inert reference standard, *i.e.*, the linear dextrin maltopentaose, which is assumed not to interact with [60]fullerene, and employing glucose as the hold-up time marker, $t_M$, quantitative selectivity data have been obtained (Table 1). Since the activity $a$ (or concentration $c$ at infinite dilution) of the [60]fullerene in the stationary phase is not known, only relative complexation constants $K_{rel}$ normalized to the smallest selectand CD6 are quoted. Furthermore, since the measurements involve an on-line gradient elution system (see experimental part) which will affect the inherent interaction equilibria for the later eluted congeners CD8–CD10, all $K_{rel}$ refer to *apparent* relative complexation constants.

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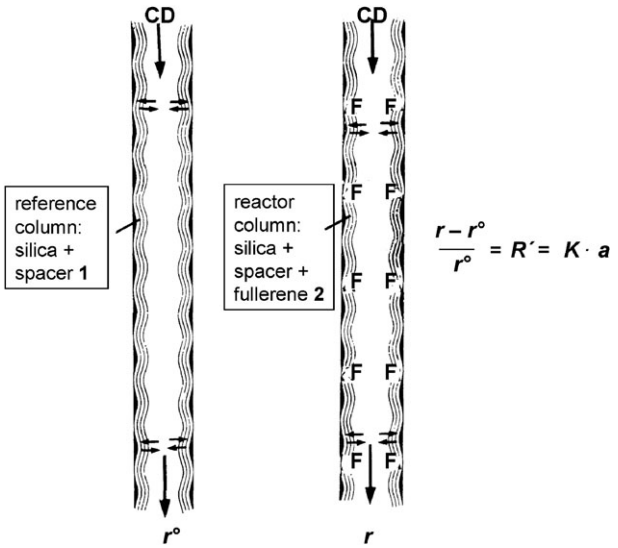


**Fig. 6** Schematic representation of the principle of calculating the apparent relative stability complexation constants between the CD*n* congeners and the fullerene selector. Refer to table for further explanations.

Inspection of Table 1 reveals the remarkable stability differences for CD*n* congeners in their supramolecular interaction with [60]fullerene.

## Conclusions

The reciprocal supramolecular recognition principle has been utilized in liquid chromatography. As fullerene selectands are distinguished by a cyclodextrin selector,[16] a fullerene selector also discriminates small-to-large-ring cyclodextrin selectands as shown herein. The unexpected selectivity pattern depicted in Fig. 4 and 5, and quantified in the Table 1, can serve as a guideline for further supramolecular chromatographic separations. Thus, it is predicted that the triplet of congeners CD8–CD10 which undergo a strong supramolecular interaction with the [60]fullerene selector (Fig. 5 and 6) will be shifted to a higher CD*n* fraction on a respective [70]fullerene selector. It is further speculated that by using a [78]fullerene as selector, the most strongly interacting CD-congener can be identified and, according to the reciprocal principle, could then be applied as a silica-bonded resolving agent for the separation of the five [78]fullerene isomers including the still elusive direct resolution of chiral $D_3$-[78]fullerene. Hitherto, only chemically modified chiral [60]fullerene- and [70]fullerene-adducts (mono-, bis-, tris-, hexakis-) have been resolved into their enantiomers by LC[33–36] both on a Whelk-O1 selector [6,7] and a (+)-TAPA-selector.[2]

Pirkle and Hoover pointed out that molecular recognition usually rests on complementary functionalities which permits their interaction.[3] The present reciprocal supramolecular system involves an abiotic aromatic cluster and a biogenic cycloamylose and their mutual molecular recognition ability is most likely governed by shape selectivity. The striking selectivity pattern (*cf.* Table 1) may be subject to molecular modelling studies. Hereby, the deviation from the ideal doughnut structure of small CD*n* ($n < 10$) due to conformational strain-induced band flips and kinks in CD*n* ($n > 10$)[37] may reveal clues of selective supramolecular recognition.

At present, the described selective separation of CD*n* congeners on the silica-bonded [60]fullerene stationary phase is restricted to an analytical scale. In the future, the observed large retention gaps between CD6–CD7/CD8–CD10, on the one hand, and CD8–CD10/CD11–CD15, on the other hand, may be employed for preparative separations of the respective fractions.

**Table 1** Retention times $t^{o}_{R}$ of CD*n* on **1** (reference column) and retention times $t_R$ of CD*n* on **2** (reactor column). The adjusted retention times are calculated according to $t'^{o}_{R} = t^{o}_{R} - t^{o}_{M}$ (reference column) and $t'_R = t_R - t_M$ (reactor column), respectively. The hold-up times $t^{o}_{M}$ and $t_M$ were measured with glucose (or dimethyl sulfoxide) which are assumed not to interact with **1** and **2**. The relative retentions (which are independent from column dimensions) $r^{o}$ and $r$ are obtained from the ratios $r^{o} = t'^{o}_{R}/t'^{o}_{R(standard)}$ and $r = t'_R/t'_{R(standard)}$, respectively, with *linear* maltopentaose used as inert reference standard which is assumed not to interact with [60]fullerene. Since the activity $a$ (concentration) of the [60]fullerene selector in the stationary phase is not known with certainty, only apparent relative complexation constants $K_{rel}$ are quoted which are normalized to CD6 (α-cyclodextrin). Measurements were performed at 25 °C[22]

| 25 °C | $t_R$/min | $t^{o}_{R}$/min | $r$ | $r^{o}$ | $R'$ | $K_{rel}$ |
|---|---|---|---|---|---|---|
| $t_M$ | 2.3 | 2.2 | — | — | — | — |
| Standard L5 | 3.0 | 3.1 | — | — | — | — |
| CD 6 | 4.1 | 4.0 | 2.57 | 2.00 | 0.29 | 1.0 |
| CD 7 | 5.5 | 4.0 | 4.57 | 2.00 | 1.29 | 4.5 |
| CD 8 | 19.5 | 4.0 | 24.57 | 2.00 | 11.29 | 39.0 |
| CD 9 | 22.3 | 4.0 | 28.57 | 2.00 | 13.29 | 46.0 |
| CD 10 | 20.9 | 4.0 | 26.57 | 2.00 | 12.29 | 42.0 |
| CD 11 | 4.1 | 4.0 | 2.57 | 2.00 | 0.29 | 1.0 |
| CD 12 | 4.0 | 4.0 | 3.14 | 2.00 | 0.57 | 2.0 |

## Experimental

### Chemicals and reagents

3-Glycidoxypropyltrimethoxysilane and trifluoroacetic acid were purchased from Sigma-Aldrich (Taufkirchen, Germany). Nucleosil (5 μm, 100 Å) was obtained from Macherey & Nagel (Düren, Germany). CD6–CD8 were gifts from the Wacker Chemie AG (Burghausen, Germany). CD9–CD25 were prepared according to Bogdanski[22] and identified by their molecular weight by MALDI-TOF mass spectrometry. The mobile phases were prepared from HPLC-grade acetonitrile, water and tetrahydrofuran (Merck, Darmstadt, Germany).

### Syntheses

**Preparation of the silica-bonded [60]fullerene stationary phase** *3-Glycidoxypropyl-silica*[29]. Dry silica (10 g, Nucleosil, 5 μm, 100 Å) was suspended in dry toluene (50 mL). After addition of 3-glycidoxypropyltrimethoxysilane (5 mL, 0.31 mmol) diluted in dry toluene (50 mL), the mixture was stirred at room temperature for 1 h and then refluxed for 5 h. The reaction mixture was filtered, washed with toluene and methanol and dried in vacuum. Elemental analysis: C = 5.12%; H = 1.06%. $^{13}$C-CP/MAS-NMR: $\delta$ [ppm] 73.32 (**3, 4**); 50.49 (**2**); 43.63 (**1**); 22.62 (**5**); 6.14 (**6**).

*Deprotection of bis(6-N-Boc-1-aminohexyl)malonate.* In a dark flask the solution of bis(6-*N*-Boc-1-aminohexyl)malonate[30] (1.13 g) in dry toluene (20 mL) was treated with trifluoroacetic

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acid (2 mL) and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC (toluene/ethyl acetate 80 : 20 v/v). The mixture was neutralized with triethylamine before further reaction.

*Stationary phase* **1**. 3-Glycidoxypropyl-silica (5 g) was added to bis(1-aminohexyl)malonate (1.13 g) in dry toluene (60 mL). The reaction mixture was stirred at 100 °C for 7 days. The mixture was filtered through a frit (Por4) and washed with toluene, acetone, diethyl ether, n-hexane, water and diethyl ether (each 150 mL) and then dried at 60 °C *in vacuo*. Elemental analysis: C = 7.34%; H = 1.08%; N = 0.01%. This corresponds to 60 μmol of selector per 1 g of silica. $^{29}$Si-CP/MAS-NMR: $\delta$ [ppm] −46.1 (**$T_1$**); −55.7 (**$T_2$**); −66.6 (**$T_3$**); −92.0 (**$Q_2$**); −101.5 (**$Q_3$**); −110.4 (**$Q_4$**). $^{13}$C-CP/MAS-NMR: $\delta$ [ppm] 155.4 (**13**); 71.88 (**3,4**); 63.73 (**12**); 52.2 (**14**); 24.2 (**11**); 23.04 (5–8); 22.3 (**2**); 8.59 (**1, 9, 10**).

*Deprotection of 1,2-bis(6-N-Boc-1-aminohexyl)malonate-1,2-dihydro-[60]fullerene*. In a dark flask the solution of 1,2-bis(6-*N*-Boc-1-aminohexyl)malonate-1,2-dihydro[60]fullerene[30] (1.20 g) in dry toluene (20 mL) was treated with trifluoroacetic acid (2 mL) and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC (toluene/ethyl acetate 80 : 20 v/v). The mixture was neutralized with triethylamine before further reaction.

*Stationary phase* **2**. 3-Glycidoxypropyl-silica (5 g) was added to bis(1-aminohexyl)malonate-1,2-dihydro[60]fullerene (1.2 g) in dry toluene (60 mL). The reaction mixture was stirred at 100 °C for 7 days. The mixture was filtered through a frit (Por4) and washed with toluene, acetone, diethyl ether, n-hexane, water and diethyl ether (each 150 mL) and then dried at 60 °C *in vacuo*. Elemental analysis: C = 10.75%; H = 1.14%; N = 0.27%. This corresponds to 62 μmol of selector per 1 g of silica. $^{29}$Si-CP/MAS-NMR: $\delta$ [ppm] −45.3 (**$T_1$**); −55.8 (**$T_2$**); −63.8 (**$T_3$**); −92.0 (**$Q_2$**); −101.5 (**$Q_3$**); −110.6 (**$Q_4$**). $^{13}$C-CP/MAS-NMR: δ [ppm] 163.38 (**13**); 144.82 (**$C_{60}$**); 73.2 (**15, 16**); 78.51 (3.4); 63.13 (**12**); 51.84 (**14**); 34.64 (**11**); 28.37 (**5, 6**); 22.12 (**2, 7, 8**); 8.12 (**1, 9, 10**).

**LC/MS- and LC/ELSD-analysis.** LC/MS-analyses were carried out using an Agilent 1100 HPLC system (Agilent Technologies, Waldbronn, Germany) coupled to Esquire-3000plus-ESI-MS (Bruker Daltonics, Bremen, Germany). LC/ELSD-analyses were carried out using a Dionex HPLC system (Dionex Corporation, Sunnyvale, CA, USA) consisting of a Dionex P680 HPLC pump, a Dionex ASI-100 autosampler and an Alltech 800 evaporative light scattering detector (Alltech Associates Inc. Deerfield, Il, USA). For data analysis the Chromeleon software (Dionex Client 6.60SP1 Build 1447, Dionex Corporation, Sunnyvale, CA, USA) was used. The HPLC column (250 × 4 mm I.D., stainless steel) was slurry-packed in-house with 3.5 g silica-bonded [60]fullerene stationary phase **2** in tetrachloroethene/1-propanol (40 mL, 2 : 1, v/v) at 500 bar and subsequently washed with methanol (1 mL min$^{-1}$) and then conditioned. The reference column containing the silica-bonded spacer stationary phase **1** was prepared accordingly. The separation of the CD*n* congeners was carried out at room temperature with a gradient elution program at a flow rate of 0.5 mL min$^{-1}$. The eluents were (i) water with 0.05% trifluoroacetic acid (A) and (ii) acetonitrile–tetrahydrofuran (54%:46%, v/v) (B). The gradient elution was programmed as follows: 0 min: 95% A, 5% B, 11 min: 94% A, 6% B and after 30 min: 100% B at a flow rate of 0.5 mL min$^{-1}$.

The linear dextrin maltopentaose has been used as an inert reference standard for the determination of relative retention data $r$ of cyclic CD*n*. Glucose has been used as hold-up time marker $t_M$. It gave the same hold-up time as the common marker dimethyl sulfoxide.

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