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Molecular recognition of *p-tert*-butylcalixarenes by surface-linked fullerenes C_{60} and C_{70}

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Abstract—The complexation processes between fullerenes (C_{60} and C_{70}) and *p-tert*-butylcalix[*n*]arenes with $n=6$ and 8 are investigated using a chromatographic method in which the fullerenes are surface-linked to HPLC silica microparticles. Thermodynamic parameters for complex formation are extracted from variable temperature chromatography in two different solvent systems. Associations are always enthalpy driven and entropy opposed, with the larger *p-tert*-butylcalix[8]arene forming the tightest complex. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

It is well known that *p-tert*-butylcalix[8]arene (hereinafter calix8) and C_{60} form an insoluble 1:1 complex from toluene solutions.[1,2] This process can be used to effectively isolate pure C_{60} from the Kratschmer–Huffman soot, with C_{60} being released from the complex by treatment with chlorinated solvents. Only small amounts of C_{70} are found in the solid material that precipitates, while higher fullerenes are completely absent. On the other hand, *p-tert*-butylcalix[6]-arene (hereinafter calix6) forms 1:2 complexes in the solid state with both C_{60} and C_{70}.[3] While a large body of knowledge is being constructed on the structural features of *p-tert*-butylcalixarene–fullerene host–guest complexes formed in the solid state,[4–6] clear-cut detection of complex formation in solution is still rather elusive. Small changes in the fullerene UV absorption spectra around 420–530 nm and at 680 nm are the only evidence so far presented for host–guest interaction in solution.[7] Recent reports on free solution complexation based on UV studies gave association equilibrium constants in the $10^2\,M^{-1}$ range for the 1:1 complex formed by *p-tert*-butylcalix[*n*]arenes ($n=6$ and 8) and fullerenes C_{60} and C_{70} in toluene.[8] A previous report pointed to free solution 1:1 complexation of C_{60} by *p-tert*-butylcalix[6]arene and no complexation by *p*-methyl-calix[8]arene.[9] Quantitative complexation data for the simplest, commercially available *p-tert*-butylcalixarenes are thus lacking at present, and this hampers a deep understanding of factors controlling size and shape selectivities of these macrocyclic hosts towards C_{60} and higher fullerenes.

Here we describe a simple chromatographic procedure for the determination of the relative stabilities of fullerene–*p-tert*-butylcalix[*n*]arene complexes and for the determination of the thermodynamic quantities (ΔH and ΔS) that characterize the association processes.

2. Results and discussion

To study host–guest complexations between fullerenes and *p-tert*-butylcalix[*n*]arenes (Scheme 1, top) we exploit a method in which immobilized C_{60} or C_{70} fullerenes function as HPLC stationary phases. On these stationary phases we collect retention data for differently sized calixarenes and extract, by variable temperature chromatography, the enthalpic and entropic contributions to the free energy change associated with the transfer of calixarenes from the mobile phase to the surface linked fullerene.

The chromatographic materials consisting of fullerenes immobilized on high-surface silica (stationary phases Si–C_{60} and Si–C_{70}, Scheme 1, bottom) were prepared by reacting spherical silica particles with C_{60}- or C_{70}-fulleropyrrolidines, whose nitrogen carries 3-triethoxysilyl-propyl groups. Si–C_{70} was synthesized in a manner similar to that used for the previously described[10] Si–C_{60}, starting from **1** (Scheme 1, middle). Fulleropyrrolidine **1** was prepared through the 1,3-dipolar cycloaddition[11,12] to C_{70}[13] of the azomethine ylide that formed upon thermal ring-opening of aziridine **2**. The reaction was carried out in refluxing

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Keywords: fullerenes; C_{60}; C_{70}; calixarenes; recognition; HPLC.

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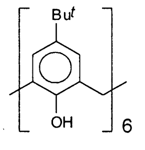

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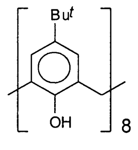

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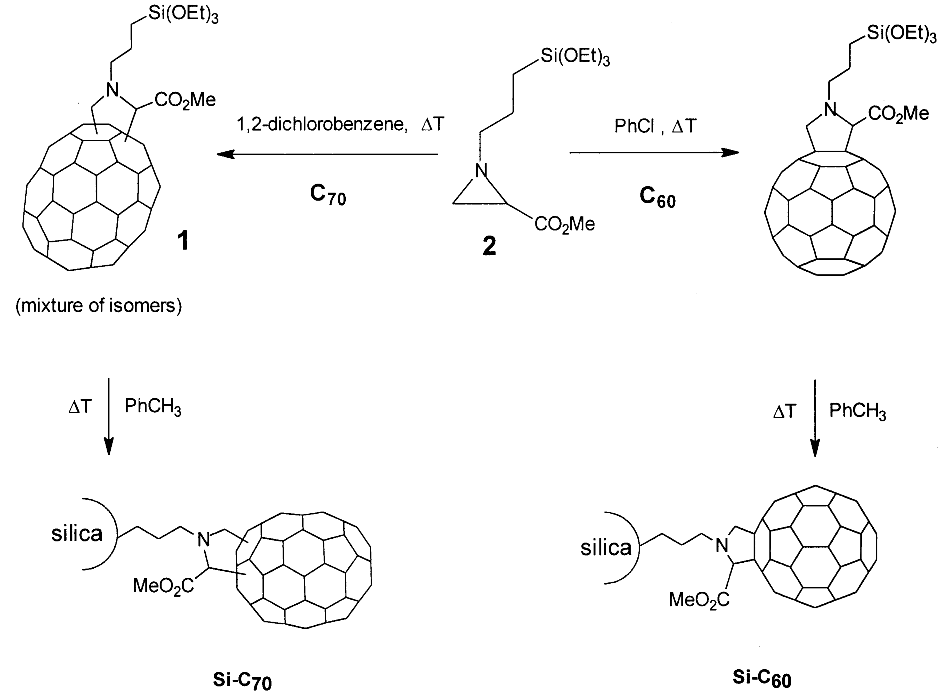

Scheme 1.

1,2-dichlorobenzene and the monoaddition product was isolated in 49% yield (along with 40% of unreacted C_{70}). Due to the known reactivity of C_{70},[14] compound **1** was an unseparable mixture of regioisomers. This could be easily seen from both the ^{1}H- and ^{13}C NMR spectra. In the proton spectrum, several singlets and AB quartets, between 4.3 and 4.7 ppm, were recognized as the characteristic resonances of the methylene and methine protons of the pyrrolidine ring. On the other hand, singlets between 3.6 and 4.1 ppm and broad multiplets at about 0.8, 1.8, 2.7 and 3.0 ppm could be assigned to the methyl and propyl groups. Intense multiplets at 1.2 and 3.8 ppm were also registered and assigned to the ethyl groups of the triethoxysilane moiety.

In the carbon spectrum, a complex host of signals, both in the aliphatic and aromatic region, was detected. Analysis of the mixture by HPLC on achiral (silica, Toluene/EtOAc 99.5/0.5) and chiral (Whelk-O1, Toluene/EtOAc 75/25+0.1% MeOH) stationary phases showed the presence of two major components along with one minor additional species. Elemental analysis showed the mixture to be pure.

The isomeric mixture **1** was considered suitable for the purposes of the present work since it was not expected that the position of the pyrrolidine ring would substantially affect the ability of a suitable guest to recognize the C_{70} spheroid host. Thus, a toluene solution of **1** was heated in the presence of spherical silica to give Si–C_{70} with a loading of 0.076 mmol of fullerene per gram of silica (based on 7.02% C), corresponding to a surface coverage of 0.42 μmol/m^2. Surface loading of the new Si–C_{70} stationary phase is thus similar to that of the parent Si–C_{60} (0.070 mmol/g, 0.40 μmol/m^2) previously prepared.

2.1. Retention

It has been demonstrated that in most host–guest systems, retention data collected on HPLC stationary phases for a set of guests (immobilized host acting as a stationary phase, guests in free solution) correlate with host–guest binding strength in free solution.[15,16] This notion is reinforced by the observation that, in model systems in which the host is alternatively in free solution or immobilized on a solid phase, solution phase selectivities correspond to solid phase selectivities for a given set of guests.[17–19] Moreover, when the same host (or guest) is immobilized on different solid phases (e.g. polystyrene and silica) it shows the same sense and magnitude of selectivity irrespective of the solid phase structure.[20,21]

However, there may be issues about the exact relationship between our chromatographic assay and binding in free solution. In particular, it is possible that the support matrix is playing a role in the binding selectivities observed in the

Table 1. Retention factors of *p-tert*-butylcalix[*n*]arenes on silica bound fullerenes Si–C_{60} and Si–C_{70} at 30°C

Compound	k'^a on Si–C_{60}	K'^a on Si–C_{70}	Eluent
Calix6	3.67	8.45	CH_2Cl_2+0.5% isopropanol
Calix6	4.35	3.65	Toluene+10% isopropanol
Calix8	49.73	24.75	CH_2Cl_2+0.5% isopropanol
Calix8	16.74	7.24	Toluene+10% isopropanol

[a] k' is the retention factor, defined as $k' = (t_i - t_0)/t_i$ where t_i is the elution time of the solute and t_0 is the elution time of a non retained solute.

HPLC assay. In addition, the grafting mode and, more specifically in our case, the *N*-alkylated pyrrolidine spacer used to graft C_{60} and C_{70} to the silica surface may interfere with binding events. In our system we excluded any effect of the underlying, unmodified silica surface on retention by performing identical HPLC experiments on a column packed with bare silica: none of the calixarenes investigated was retained using a variety of eluent systems. While potential perturbing effects of the pyrrolidine unit cannot be ruled out a priori, we note that in our stationary phases the fullerene spheroid points away from the solid phase and presents its free convex surface to the liquid phase. Additionally, access to the spacer should be hindered, at least for large molecules like calixarenes, by the spheroid itself. Thus, chromatographic retention data and thermodynamic quantities (see infra) determined by HPLC on immobilized fullerene stationary phases, can be safely used to elucidate recognition processes where affinity and selectivity are regulated solely by the specific interactions occurring between fullerenes and calix[*n*]arenes.

We used two solvent systems (methylene chloride containing 0.5% of isopropanol, eluent A and toluene containing 10% of isopropanol, eluent B) to monitor the affinities of calixarenes for the two silica bound fullerenes. The results are collected in Table 1, where the magnitude of solute retention is reported, for each mobile phase and a column temperature of 30°C, by the retention factor, $k' = (t_i - t_0)/t_i$, where t_i is the elution time of the solute and t_0 is the elution time of a non-retained solute. Typical chromatograms obtained on the two columns are shown in Fig. 1, where the 4-, 6- and 8-membered *p-tert*-butylcalixarenes are simultaneously screened for their binding preferences. While the smallest calix[4]arene shows a small (but nevertheless measurable) binding affinity for the two immobilized fullerenes, its complexation ability is not comparable with those of the larger macrocycles, at least under our experimental conditions. In the following discussion we will focus only on the relative retentions of the 6- and 8-membered calixarenes.

When eluent A is used, calix6 binds immobilized C_{60} less strongly than C_{70}. At 30°C the retention factors are in fact 3.67 on Si–C_{60} and 8.45 on Si–C_{70}, indicating a net preference of the calix6 for the C_{70} elongated spheroid. The binding preferences are reversed for the larger calix8, which forms the tightest complex with immobilized C_{60}: at 30°C the retention factors on Si–C_{60} and Si–C_{70} are 49.73 and 24.75, respectively. Note that this difference in retention factors translates, in our chromatographic system, to a difference in the residence times inside the two columns of about 1 h (see Fig. 1). Calix8 binds more strongly than calix6 to either C_{60} or C_{70} fullerene. On Si–C_{60}, however, the difference in binding affinities is much larger than on Si–C_{70}, the ratio of the retention factors between the 8- and 6-membered macrocycles being about 13 and 3, respectively.

With eluent B, calix6 binds preferentially to immobilized C_{60}, although the difference at 30°C between Si–C_{60} ($k' = 4.35$) and Si–C_{70} ($k' = 3.65$) is very small. The larger eight membered macrocycle binds preferentially to Si–C_{60}, as observed with eluent A. However, we note that the large size selectivities recorded with eluent A on either of the two immobilized fullerenes is considerably reduced here: the ratio of the retention factors between the 8- and 6-membered macrocycles now is about 4 on Si–C_{60} and 2 on Si–C_{70}.

Thus, retention data on the two solvent systems point to a preferential complexation of calix8 with C_{60}, while calix6 binds more strongly to C_{70} in CH_2Cl_2 and to C_{60} in toluene. In the two solvent systems, calix8 binds stronger than calix6 to either of the two fullerenes.

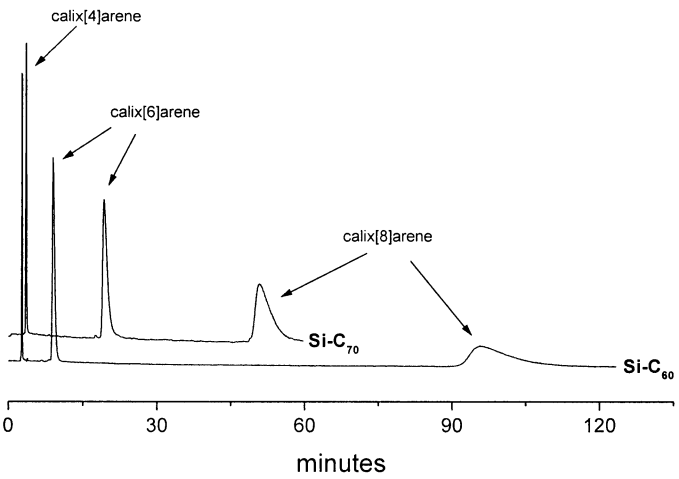

Figure 1. Chromatograms showing the relative retention of *p-tert*-butylcalix[*n*]arenes on Si–C_{60} and Si–C_{70} using CH_2Cl_2+0.5% isopropanol as mobile phase (eluent A in the text). Column dimensions: 250×1.8 mm ID; flow rate 0.25 mL/min; UV detection at 280 nm.

Table 2. Thermodynamic parameters for the association of *p-tert*-butylcalix[*n*]arenes with silica bound fullerenes Si–C_{60} and Si–C_{70}

	Si–C_{60}		Si–C_{70}	
Compound	ΔH^a (kJ/mol)	ΔS^b (J/mol K)	ΔH^a (kJ/mol)	ΔS^b (J/mol K)
Calix6[c]	−18.8	−25.5	−20.1	−23.8
Calix6[d]	−15.1	−11.7	−18.0	−23.0
Calix8[c]	−31.0	−43.1	−26.8	−36.4
Calix8[d]	−26.8	−32.2	−20.1	−24.7

[a] Three replicate runs were within ±4%.
[b] Three replicate runs were within ±10%.
[c] CH_2Cl_2+0.5% isopropanol.
[d] Toluene+10% isopropanol.

2.2. Thermodynamic data

Retention factors are related to the equilibrium constant, *K*, or to the free energy change, ΔG, associated with the solute transfer from the mobile to the stationary phase by the following equation

$$\ln k' = \ln K + \ln \phi = -\Delta G/RT + \ln \phi \quad (1)$$

where ϕ is the phase ratio of the column (i.e. the ratio of the stationary to the mobile phase volumes), *T* is the column temperature, *R* is the universal gas constant. Noting that

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

the temperature dependence of solute retention is then obtained combining Eqs. (1) and (2)

$$\ln k' = -\Delta H/RT + \Delta S/R + \ln \phi \quad (3)$$

where ΔH and ΔS are the enthalpy and entropy changes for the solute transfer from the mobile to the stationary phase. When ΔH and ΔS are temperature insensitive (no heat capacity change) and also ϕ does not change with temperature, a van't Hoff plot of $\ln k'$ vs $1/T$ will be linear (Eq. (3)). In this case the enthalpy changes associated with solute retention can be evaluated from the slopes and the entropy changes from the intercepts of van't Hoff plots. Evaluation of entropy changes, however, requires a preliminary knowledge or estimate of the column phase ratio, ϕ. Using the standard equation[22] to derive this figure we obtained for the column containing Si–C_{60} $\phi = 0.043$ and for that containing Si–C_{70} $\phi = 0.050$.

Retention of the macrocyclic solutes was monitored on the two columns across the temperature range 30–80°C at 10°C intervals. The corresponding van't Hoff plots obtained with either eluent A or B were strictly linear, with correlation coefficients larger than 0.998 in every case. The results of the variable temperature HPLC experiments are gathered in Table 2.

Association processes between the immobilized fullerenes and the two calixarenes are always enthalpy favored and entropy opposed (ΔH and ΔS have the same negative sign) and they are enthalpy driven in the temperature range explored (ΔH larger than $T\Delta S$ between 30 and 80°C).

Enthalpy changes span a range of 15.9 kJ/mol, with the smaller value observed with calix6 on Si–C_{60} (−15.1 kJ/mol, eluent B) and the larger with calix8 on Si–C_{60} (−31.0 kJ/mol, eluent A). For the same combinations of host, guest and solvent we found the extreme values of the entropy changes (−11.7 and −43.1 J/mol K).

The preferential complexation of calix6 with C_{70} over C_{60} observed with eluent A is due to both enthalpy and entropy, in that calix6 forms stronger interactions with C_{70} (by 1.3 kJ/mol) and the overall association process has a smaller entropic cost ($T\Delta S$ term at 30°C in favor of C_{70} by 0.5 kJ/mol). In the same solvent, the preference of calix8 for C_{60} is largely due to enthalpy. Adsorption on C_{60} is more exothermic than on C_{70} by 4.2 kJ/mol, while the $T\Delta S$ term favors adsorption on C_{70} by only 2.5 kJ/mol at 30°C.

For the smaller calixarene, the selectivity for the immobilized fullerenes is reversed in the toluene based eluent B: here complexation with C_{60} is slightly favored than with C_{70}. In this solvent, enthalpy favors adsorption on C_{70} by 2.9 kJ/mol but entropy favors adsorption on C_{60} by 3.3 kJ/mol at 30°C and by 3.8 kJ/mol at 80°C (i.e. the selectivity in favor of C_{60} is entropy controlled and increases with *T*).

For the 8-membered calixarene the situation, in terms of enthalpy/entropy balance, is similar to that observed with the CH_2Cl_2 solvent system. Enthalpy favors the complexation with C_{60} over C_{70} by 6.7 kJ/mol, and entropy favors C_{70} by 2.1 kJ/mol at 30°C.

While a detailed analysis of the association data in terms of specific interactions between the complexing partners is beyond the scope of this work, we believe that the greater ability of calix8 to complex with Si–C_{60} over Si–C_{70} is due to a better fit of the spherical C_{60} surface to a complementary concave surface of the calixarene (presumably populating one or more pleated-like conformations), and to the presence of a larger number of contacts between the aryl rings of the calixarene and the fullerene framework. Individual aryl:fullerene associative interactions are not expected to entail large energy changes. Nonetheless, it is the accumulation of a large number of such interactions that drives binding events and regulates selectivity.

Entropy changes upon complexation are generally due to the (partial) loss of motional freedom for host and guest and to the reorganization of the solvent structure. In our system, loss of degrees of freedom is limited to the calixarene molecules, since the immobilized fullerenes are not expected to experience any motional restriction during complexation. Solvent reorganization due to complex formation includes desolvation of both host and guest and resolvation of the complex. Complexation of calix6 and calix8 with C_{60} and C_{70} is accompanied by small, negative ΔS values. Entropy changes play a minor role in governing the complexation equilibria, which are dominated essentially by enthalpy. With a single exception (calix6, eluent B), ΔS for Si–C_{60} tends to be larger than for Si–C_{70}. We note some effects due to solvation and, to some extent, to entropy changes in the complexation of calix6 and in its switch of C_{60}/C_{70} preference on passing from eluent A to eluent B. However, the differences in the ΔS terms between the two solvent systems and between the two fullerenes are too small to draw general conclusions. Rather, it appears that both calix6 and calix8 are flexible enough to adapt their cavities to either of the immobilized fullerenes, without paying a considerable entropy cost.

HPLC thermodynamic data for the complexation of calix6 with immobilized C_{60} and C_{70} in toluene (eluent B) are of the same order of magnitude of those reported for the association of a homooxacalix[3]arene with C_{60} and C_{70} in toluene solution, where $\Delta H=-11.7$ (C_{60}) and -12.6 (C_{70}) kJ/mol and $\Delta S=-10.0$ (C_{60}) and 12.1 (C_{70}) J/mol K as determined by UV titration experiments, and $\Delta H=-10.9$ (C_{60}) and -9.2 (C_{70}) kJ/mol as determined by microcalorimetry.[23]

The complexation of C_{60} by calix[4]naphthalenes in toluene solutions, on the other hand, is accompanied by ΔH changes between -59.8 and -77.4 kJ/mol and by ΔS changes between -0.14 and -0.20 kJ/mol K, corresponding to K_{ass} in the $6–7\times10^2\ \mathrm{M}^{-1}$ range at 25°C. The larger aromatic surfaces of calix[4]naphthalenes, compared to those of simple calixarenes, are thus better suited to establish attractive interactions with the convex surface of C_{60}. Presumably, a wider opening of the calixnaphthalenes cavity is also responsible for the large increase in ΔH.[24]

Retention and thermodynamic data collected with our system using eluent A deserve a special comment. HPLC data clearly show that C_{60}, and to a lesser extent C_{70}, strongly interact with calix8. Failure to observe such interaction in free solution is certainly due to the very low solubility of C_{60} and C_{70} in methylene chloride. However, simple fullerene derivatives of either C_{60} or C_{70} are soluble in chlorinated solvents like CH_2Cl_2 and $CHCl_3$. Indeed, thermodynamic data extracted from UV titration experiments shows that a monoadduct of C_{60} forms a complex with *p*-methylcalix[5]arene[25] in $CHCl_3$ solution with $\Delta H=-24.7$ kJ/mol and $\Delta S=-28.5$ J/mol K. Our binding results in eluent A are thus relevant to the design of immobilized hosts based on calix[8]arenes, with potential applications to the analysis and purification of mono and/or polysubstituted fullerenes.

3. Conclusion

Regardless of the molecular details of the binding selectivities observed, our results indicate a strong tendency of *p-tert*-butylcalix[8]arene to complex with immobilized C_{60}, either in methylene chloride ($\Delta H=-31.0$ kJ/mol) and in toluene ($\Delta H=-26.8$ kJ/mol), with a net preference over immobilized Si–C_{70}. *p-tert*-butylcalix[6]arene shows less affinity for the two fullerenes (ΔH between -15.1 and -20.1 kJ/mol) and its C_{60}/C_{70} selectivity is solvent dependent.

Thermodynamic data from variabile temperature HPLC compare well with available data on related systems.

4. Experimental

4.1. Materials and methods

C_{70} was purchased from Bucky USA (98%). Details on instrumentation used in this work and on the preparation of Si–C_{60} are described elsewhere.[10] Variabile temperature chromatographic runs were conducted by placing the HPLC column inside a temperature-controlled module ($\Delta T\pm$ 0.5°C). Thermal equilibration of the eluent was obtained by using a 50 cm inlet capillary tube, wrapped around the column.

4.1.1. *N*-[3-(Triethoxysilyl)propyl]-2-carbomethoxy-[70]-fulleropyrrolidine (1). A solution of 100 mg (0.12 mmol) of C_{70}, 61 mg (0.2 mmol) of *N*-[3-triethoxysilyl)propyl]-2-carbomethoxy aziridine **2** in 120 ml of 1,2-dichlorobenzene was stirred at reflux temperature for 45 min. The reaction was monitored by TLC (toluene/ethyl acetate 95:5), following the formation of **1** ($R_f=0.45$). The reaction mixture was loaded on top of a silica gel flash chromatograpy column and the product eluted with toluene and then toluene/ethyl acetate 95:5. The solvent was evaporated under reduced pressure and the residue, dissolved in the minimum amount of toluene, was precipitated by addition of CH_3CN. The precipitate, isolated by centrifugation, was washed thoroughly with CH_3CN and then dried in vacuum affording **1** (68 mg, 50%) as a brownish solid along with 40 mg of unreacted C_{70}. FT-IR (KBr) 2970, 2921, 2882, 1754, 1734, 1442, 1425, 1164, 1099, 1077, 953, 572, 531 cm^{-1}. NMR (250 MHz, $CDCl_3$): NMR spectra show a complex host of resonances in the aliphatic (proton and carbon) and aromatic (carbon) regions (see text). UV–Vis (CH_2Cl_2): $\lambda_{\max}(\varepsilon)$ 236(135080), 304 (21800), 459 (17494), 522 (9937), 656 (1836). MALDI MS ($C_{83}H_{27}NO_5Si$ (MW=1145)) *m/z* 1146 ($[M+H]^+$, 100%). Anal. Calcd for $C_{83}H_{27}NO_5Si$: C, 86.97; H, 2.37; N, 1.22. Found: C, 86.0; H, 2.60; N, 1.14.

4.1.2. Si–C70. Spherical silica (900 mg, Hypersil 5 μm) was dried at 120°C at 0.1 mbar for 3 h. Dried silica was added to a solution of the fulleropyroolidine[C_{70}] mixture in toluene (20 mL). The slurry was heated at reflux under a gentle stream of argon for 6 h. After cooling to room temperature, the Si–C_{70} silica was isolated by filtration and sequentially washed with 200 mL portions of toluene, $CHCl_3$ and hexane and dried at 60°C under reduced pressure. Anal. Found: C, 7.02, H, 0.41, N, 0.15, corresponding to 0.076 mmol of C_{70} per gram of silica. Si–C_{70} (about 250 mg) was packed in 250×1.8 mm ID glass-lined stainless steel column by the slurry procedure.

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