Aromatic tripodal receptors for (C_{60}-I_h)[5,6]fullerene†

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Monotopic and ditopic tripodal benzene platforms featuring aromatic and perfluoroaromatic side-arms have been synthesized, and their binding properties toward C_{60}-fullerene have been investigated by HPLC examining retention times on a fullerene-modified silica stationary phase, using highly polar eluants (acetonitrile and acetonitrile/water). By comparison of structurally homogeneous sets of receptors, a clear trend could be found, pointing to an increased retention for ditopic derivatives, in which binding can occur on both sides of the benzene platform, over their monotopic counterparts. Among the latter, monotopic receptors containing H-substituted aromatic residues showed stronger retention than their perfluorinated analogues. This effect was ascribed to the greater availability of the π-electrons in a H-substituted aromatic ring with respect to the corresponding F-substituted counterpart in participating in a π–π interaction with the electron-poor surface of fullerene. Several NMR experiments aimed to investigate binding interactions in solution, using the much less polar solvents required by the fullerene solubility (1,1,2,2-tetrachloroethane, chloroform, toluene, and CS_2), did not provide any evidence of binding interactions. We concluded that π–π interactions between fullerene and the investigated flexible tripodal receptors cannot compete with solvation in poorly polar solvents, and that the binding interactions observed by HPLC were essentially forced by the strongly polar eluant employed for the HPLC analysis.

Introduction

The identification of effective aromatic molecular receptors such as tweezers,[1] clips,[2] and capsules[3] for aromatic guests can be considered a probing test of our capacity of understanding arene–arene interactions and successfully transferring this knowledge into practical applications. In this context, the synthesis of aromatic receptors for fullerenes extended aromatic–aromatic recognition from an essentially two-dimensional phenomenon (that is, the interaction between flat surfaces)[4] to a three-dimensional event (that is, the interaction between curved networks of conjugated carbon–carbon bonds).[5] Recent examples of curved aromatic fullerene receptors include belt-shaped cyclic oligomers of arylacetylenes (nanorings),[5,6] a tweezer[7a] and a copper surface[7b] containing corannulene subunits, several concave tetrathiafulvalene-type donors,[8] and a tris(trianthreno)-triquinacene.[9] All of these receptors exploit π–π interactions between the electron poor convex surface of the fullerene guest and the electron rich concave surface of the hosts.[5,10]

Combining our interest in aromatic–aromatic[11a–c] and aromatic–perfluoroaromatic[11d–f] interactions with that in the development of tripodal receptors for neutral molecules,[12] we decided to synthesize a series of flexible, benzene-based tripodal receptors featuring phenyl or pefluorophenyl rings, and to test them in the binding of (C_{60}-I_h)[5,6]-fullerene. Rather than the discovery of new effective receptors for fullerene, one of the goals of this work was to ascertain, through the comparison of aromatic receptors with their perfluorinated counterparts, whether "pure" π–π convex–concave interactions[7a] may be the driving force in the recognition of fullerene. We wish to report here some results of this study, showing that in media of good solvating properties toward fullerene and in the absence of pre-organization of the receptor, π–π interactions are not competing favourably for complexation. In contrast, in a polar environment a clear evidence of binding has been obtained, pointing to a stronger interaction of fullerene with H-substituted aromatic receptors than with their corresponding perfluorinated counterparts, in agreement with the higher electron availability of the former with respect to the latter.

Results and discussion

In designing simple tripodal aromatic receptors for fullerene, we took advantage of the so-called "facial segregation" experienced by 1,3,5-CH_2R-2,4,6-CH_2R′ hexasubstitued benzenes.[13] According to seminal work by Mislow and Siegel on the static and dynamic behaviour of these compounds,[14] hexasubstituted benzenes adopt a preferred conformation with an alternated *ababab* (all-*trans*) geometrical pattern, thermodynamically favoured by about 4 kcal mol^{-1} compared to the next most stable conformation. Thus, when a benzene platform carries alternated CH_2R and CH_2R′

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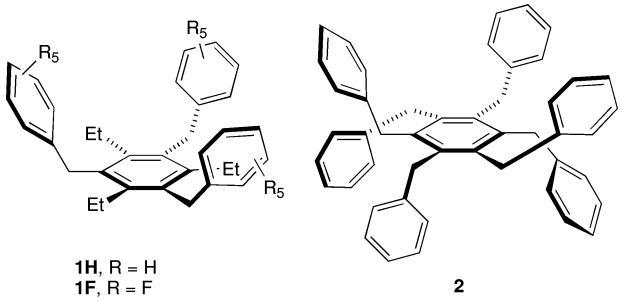
substituents, the R and R′ groups point toward opposite sides with respect to the benzene ring. The readily accessible 1,3,5-tris(halomethyl)-2,4,6-triethylbenzenes (halo = Br and Cl)[15] led to a variety of interesting structures and opened the way to an extensive exploitation of this scaffold for the development of tripodal receptors for molecular recognition studies.[13]

Following a rational design of receptor's geometry, aromatic rings and their corresponding readily available fluorinated counterparts were implemented as binding side-arms in the receptor's architecture, giving rise to a set of fullerene receptors of significantly different electronic properties. Binding domains of different size and shape were also obtained by implementing spacers of different length and conformational mobility. For this purpose, benzyloxymethyl side arms appeared to be particularly promising, since they have been shown to be involved in binding interactions with (C_{60}-I_h)[5,6]-fullerene.[16] In addition to 1,3,5-tris-CH_2R-2,4,6-triethylbenzenes, 1,2,3,4,5,6-hexa-CH_2Ar-substituted benzenes were also prepared to obtain ditopic receptors capable of binding to both sides of the platform. The structures of the receptors prepared for this study are reported in Fig. 1.



1H, R = H
1F, R = F

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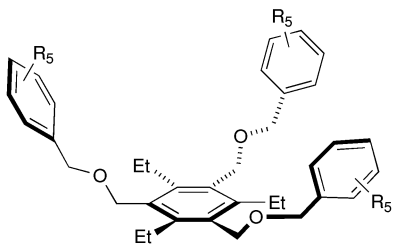

3H, R = H
3F, R = F

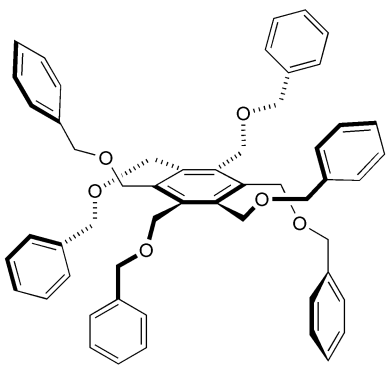

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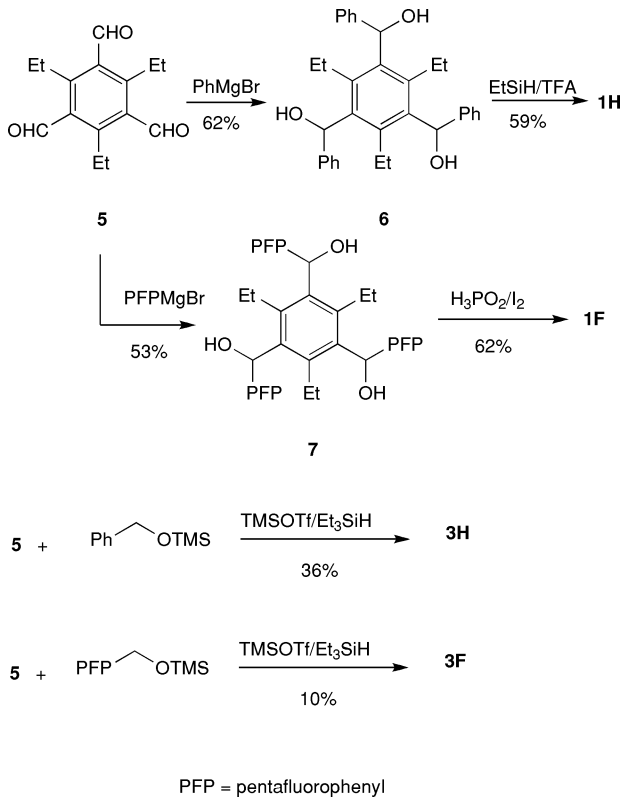
Fig. 1 Structures of hexasubstituted benzenes **1**–**4**.

Hexabenzyl benzene **2**[17] and hexabenzyloxy-methyl benzene **4**[18] were known compounds and were prepared, according to literature procedures, by the $Co_2(CO)_8$-catalyzed cyclo-trimerization of 1,4-diphenyl-2-butyne and 1,4-dibenzyloxy-2-butyne, respectively. 1,3,5-Tribenzyl-2,4,6-triethylbenzene **1H** was prepared as described in Scheme 1. The tris-aldehyde **5**,[19] obtained in 69% yield from 1,3,5-tribromomethyl-2,4,6-triethylbenzene[12a] by reaction with DMSO and $NaHCO_3$,[20] was treated with excess phenylmagnesium bromide in THF to afford the triol **6** as a mixture of diastereoisomers in 62% yield. Deoxygenation with Et_3SiH/CF_3COOH[21] gave compound **1H** in 59% yield. 1,3,5-Tris-pentafluorophenylmethyl-2,4,6-triethylbenzene **1F** was similarly obtained (Scheme 1) by reaction of the tris-aldehyde **5** with pentafluorophenylmagnesium bromide (53% yield) followed by deoxygenation of the diastereoisomeric triols **7** with H_3PO_2/I_2 in acetic acid (60% yield).[22]



Scheme 1 Synthesis of hexasubstituted benzenes **1H**, **1F**, **3H**, and **3F**.

Finally, reaction of the tris-aldehyde **5** with the trimethylsilyl ethers of benzyl and pentafluorobenzyl alcohol in the presence of trimethylsilyltriflate and triethylsilane afforded 1,3,5-tribenzyloxymethyl-2,4,6-triethylbenzene **3H** and its perfluorinated counterpart **3F**, in 36 and 10% yield, respectively.[23]

With receptors **1**–**4** available, we reasoned that elution through a HPLC column packed with fullerene-modified silica could provide a fast way of testing their binding ability toward (C_{60}-I_h)[5,6]-fullerene simply by comparing retention times. Indeed, use of the retention data obtained from HPLC analysis carried out on modified silica gel has been demonstrated to reliably correlate with the binding affinity of aromatic hosts toward aromatic guests.[24] Therefore silica **8** (Fig. 2, 0.135 mmol g^{-1} by elemental analysis) was prepared following the procedure reported

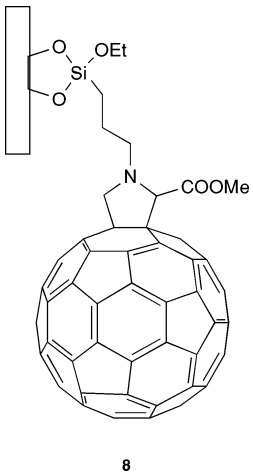


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Fig. 2 Fullerene-modified silica **8**.

by Maggini *et al.*[25] This fullerene-modified stationary phase has been used to investigate the binding affinities of some cyclic oligomeric hosts by HPLC, showing exceptional size selectivity for calixarenes and cyclodextrins. It was also demonstrated that silica **8** selectively binds to helical peptides, provided that the latter would present aromatic residues properly located for interacting with fullerene.[25]

Thus, compounds **1–4** were eluted through a HPLC column packed with **8** (column size 125 × 4.6 mm, internal diameter; efficiency: $N/m = 4000$; for efficiency determination see Experimental) using acetonitrile or acetonitrile/water 90:10 as eluant. The observed retention times were reported in Table 1, together with those observed using a commercial reversed phase RPC_{18} column having the same size (125 × 4.6 mm) but much higher efficiency ($N/m = 30000$).

The retention data obtained with acetonitrile as eluant showed that, while the RPC_{18} column was not able to discriminate compounds **1–4**, elution of the latter through the column packed with silica **8** resulted in significantly different retention times. It must be emphasized that this latter column was able to selectively retain **1–4** even though its efficiency was much lower than that of the RPC_{18} column (N/m 4000 *vs.* 30000). Comparing homogeneous sets of compounds, a clear trend could be found pointing to an increased retention for receptors in which binding can occur on both sides of the central benzene ring, whereas poorer retention was observed for perfluorinated derivatives. Thus, in the "benzyl" series (**1H**, **1F**, and **2**), the hexabenzylsubstituted compound **2** was more strongly retained than the tribenzylsubstituted **1H**, which in turn was more retained than the tripentafluorobenzyl analogue **1F**. The benzyloxymethyl series showed analogous trend of retention times (**4** > **3H** > **3F**).

Table 1 HPLC Retention times R_t (min) on modified silica **8** and on reversed phase RPC_{18} columns for compounds **1–4**, 1,3,5-triethylbenzene (TEB), naphthalene (N), 1,2,3,4-tetrafluoronaphthalene (TFN), and octafluoronaphthalene (OFN)[a]

	CH_3CN		CH_3CN/H_2O 90:10	
Compound	R_t (**8**)	$R_t(RPC_{18})$	R_t (**8**)	$R_t(RPC_{18})$
1H	4.8	1.7	7.8	1.7
1F	3.7	1.7	6.4	1.7
2	5.9	1.7	10.9	1.7
3H	5.9	1.7	9.0	1.7
3F	4.0	1.7	6.6	1.7
4	11.2	1.7	18.0	1.7
TEB	1.7	1.4	2.1	1.4
N	1.5	1.4	1.6	1.4
TFN	1.5	1.4	1.6	1.4
OFN	1.3	1.3	1.4	1.3

[a] Flow rate 1.0 mL/min; λ = 254 nm.

A comparison across the two sets showed that the benzyloxymethyl-substituted compounds were more strongly retained than their benzyl-substituted counterparts. However, the difference between each pair was larger for ditopic (**4** *vs.* **2**, 5.3 min) than for monotopic (**3H** *vs.* **1H**, $\Delta_{Rt} = 1.1$ min) receptors, whereas the difference between the fluorinated pair was negligibly small (**3F** *vs.* **1F**, $\Delta_{Rt} = 0.3$ min). While indicating a more favourable geometry/adaptability of the benzyloxy side-arms, likely due to the ability of the latter of better achieving the most appropriate geometry for binding,[26] the significantly larger retention times exhibited by the ditopic *vs.* monotopic receptors, exceeding the values expected on the basis of mere additivity, strongly suggest the occurrence of cooperative contributions from concomitant binding, which may be ascribed to multivalent interactions on the silica surface.

The observed trends were emphasized when water was added to the mobile phase, eluting with an acetonitrile/water 90:10 mixture. The higher polarity of the eluant resulted in a general and predictable increase of retention times for adducts **1–4** on fullerene-modified silica **8**. Indeed, **8** can be regarded a sort of reversed phase silica, on which apolar substances generally show larger affinities for a poorly polar stationary phase when the eluant polarity is increased. Surprisingly, a similar effect was not observed on the RPC_{18} column: the more polar eluant did not induce neither an increase in retention times, nor a discrimination among the solutes, clearly indicating binding interactions as the cause of the observed discrimination occurring on the surface of the fullerene-coated silica **8**. In addition to polarity effects, it is also tempting to suggest the occurrence of hydrophobic contributions, caused by the added water, which may boost the discrimination observed with respect to neat acetonitrile, resulting in enhanced interaction between the immobilized fullerene on silica and the receptors in the mobile phase.

Altogether, these data seem to suggest that the mechanism by which silica **8** discriminates receptors **1–4** relies on aromatic–aromatic interactions of different strength. In particular, the interaction between the convex surface of the fullerene guest[5,10] and the concave surface of the tripodal hosts is likely modulated by the electron density available on the receptor surface, which is certainly larger for the pair **1H**/**3H** than for the pair **1F**/**3F** because of the presence on the latter of the strongly electronegative fluorine atoms.[27] Apart from electronic effects and geometric/adaptability factors, the oxygen atom lone pairs of **3H** and **4** may also provide additional binding interactions with fullerene, as proposed for the formation of the adduct between (C_{60}-I_h)[5,6]-fullerene and γ-cyclodextrin.[28] However, the very small difference in retention times observed between **1F** and **3F** seems to indicate that such a contribution is negligible, being overwhelmed by the aromatic–aromatic interaction.[29]

Further support to the hypothesis that the discrimination of the tripodal receptors by the fullerene residues present on the surface

of silica **8** was mainly due to aromatic–aromatic interactions involving the receptors' side arms was obtained when 1,3,5-triethylbenzene was eluted on the column containing silica **8** and on the RPC_{18} column. Indeed, with these supports very short retention times were observed (Table 1) both in acetonitrile (1.7 and 1.4 min on silica **8** and on RPC_{18}, respectively) and in the acetonitrile/water 90:10 mixture (2.1 and 1.4 min on silica **8** and on RPC_{18}, respectively). Similarly, when a series of flat aromatic systems featuring different degrees of fluorine substituents such as naphthalene, 1,2,3,4-tetrafluoronaphthalene, and octafluoronaphthalene were eluted through the two columns, again very short and essentially identical retention times were observed with both eluants (Table 1). These results concur to indicate that the presence of properly arranged aromatic residues is essential for the receptors to be discriminated by silica **8**, and that the discrimination mainly relies on aromatic–aromatic interactions between the convex surface of fullerene and the concave surfaces of adducts **1–4**.

In order to support the results of the HPLC separations with complementary experimental techniques, we attempted to investigate the interaction of (C_{60}-I_h)[5,6]-fullerene with the monotopic receptor **3H** by NMR spectroscopy in solution.[30] Unfortunately, in the highly polar solvents where HPLC data were acquired, fullerene was completely insoluble, as was also the modified fullerene employed for the synthesis of silica **8**. Accordingly, the NMR study had to be carried out in different solvents, and a compromise between the solubility of fullerene, requiring non-polar solvents, and the polarity of the medium, necessary to emphasize aromatic–aromatic interactions, was thus mandatory.

NMR experiments carried out by adding up to a three-fold molar excess of fullerene to **3H** in deuterated 1,1,2,2-tetrachloroethane ($Cl_2CDCDCl_2$, $\varepsilon = 8.2$, $\mu = 1.3$ D) showed no shift variation in the whole concentration range (see Fig. S1 in the ESI†). The results were confirmed by following the ^{13}C NMR signal of fullerene through the addition of up to a 15-fold molar excess of **3H** in the same medium (Fig. S2). The lack of binding evidence was ascribed to the good solvating properties and the markedly lower polarity of $Cl_2CDCDCl_2$ compared to acetonitrile (CD_3CN, $\varepsilon = 37.5$, $\mu = 3.5$ D), behaving as a strongly competitive medium.

Since binding of (C_{60}-I_h)[5,6]-fullerene to a double concave receptor was measured in toluene by Sygula and co-workers,[7a] we also turned to this solvent to ascertain whether binding interactions could be observed with receptor **3H**. The results shown in Fig. S3 and S4,† confirmed that NMR spectroscopy did not provide evidence of binding in solution.

Continuing the search for a convenient medium to unravel the occurrence of binding interactions, we finally turned to $CS_2/CDCl_3$ mixtures, where fullerene binding by a concave tetrathiafulvalene-type receptor could be observed by Martin and co-workers.[8a] However, the addition of a 16-fold molar excess of fullerene to a solution of **3H** in $CS_2/CDCl_3$ 80:20, followed through the ^1H NMR signals of the receptor again showed no evidence of interaction (Fig. 3). In the hope that the use of a more polar solvent mixture could be beneficial for making binding interactions to emerge, we change the solvent to a 50:50 $CS_2/CDCl_3$ mixture. Upon addition of 1 equiv of fullerene to **3H** we found that a small but unambiguous shift could be observed on both the CH_2O signals of the receptor indicating a clear effect

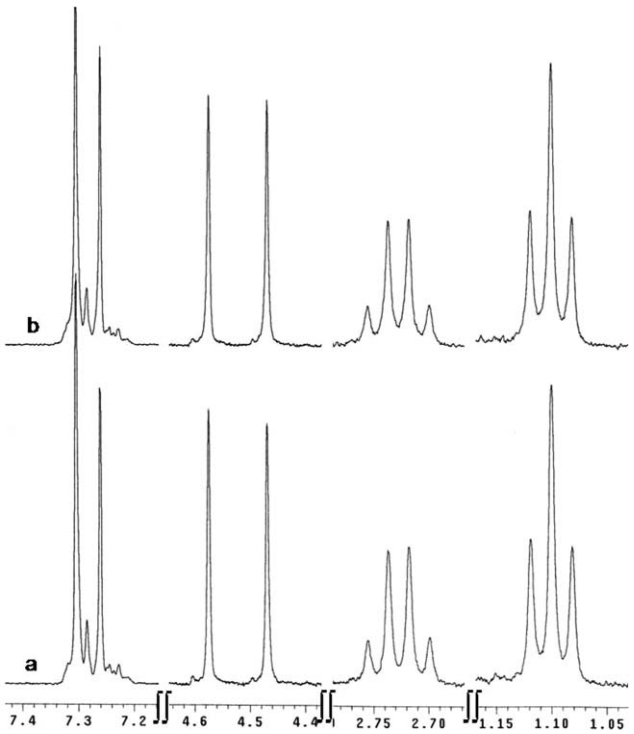

Fig. 3 ^1H-NMR spectra (400 MHz, $CS_2/CDCl_3$ 80:20) of: (a) **3H** 0.31 mM; (b) **3H** 0.31 mM, fullerene 4.86 mM.

of the increased polarity of the medium. However, when the effect of the solvent mixture was investigated by varying the solvent ratio on a pre-formed 1:1 mixture of **3H** and fullerene (Fig. 4), it appeared evident that the observed spectral changes were due to solvent-related shift variations rather than to binding interactions. These results outlined that spectral variations caused by a mere changing of the medium may bias experimental observations and should therefore be taken with caution.

Independent evidence of binding was also sought through MS spectrometry. The ESI-MS spectra of a 1:1 mixture of **3H** and fullerene in toluene/MeOH 80:20, scanned in positive and negative ion mode, are reported in Fig. S5 and S6, respectively.† While in the former only the receptor peak is detected ($M + Na^+$), in the latter only the fullerene peak can be observed (M^-). Since both species cannot be directly observed in neither one of the two spectra, the absence of the peak of the complex is not conclusive, indicating that mass spectrometry is not informative on binding of fullerene to **3H**.

Conclusions

From the results obtained in the present investigation, we concluded that the unambiguous interaction observed between fullerene and the receptors of Fig. 1, determining the marked discrimination of the receptors by the fullerene coating the surface of the stationary phase of the HPLC column, was essentially due to the "forced" interactions established between the aromatic surfaces of the host and the guest in the hostile environment of a strongly polar medium, such as acetonitrile or acetonitrile/water 90:10. The most reasonable interpretation of these data ascribes the lack of detectable interactions in solution between fullerene and receptor **3H** to the solvation of fullerene, which cannot

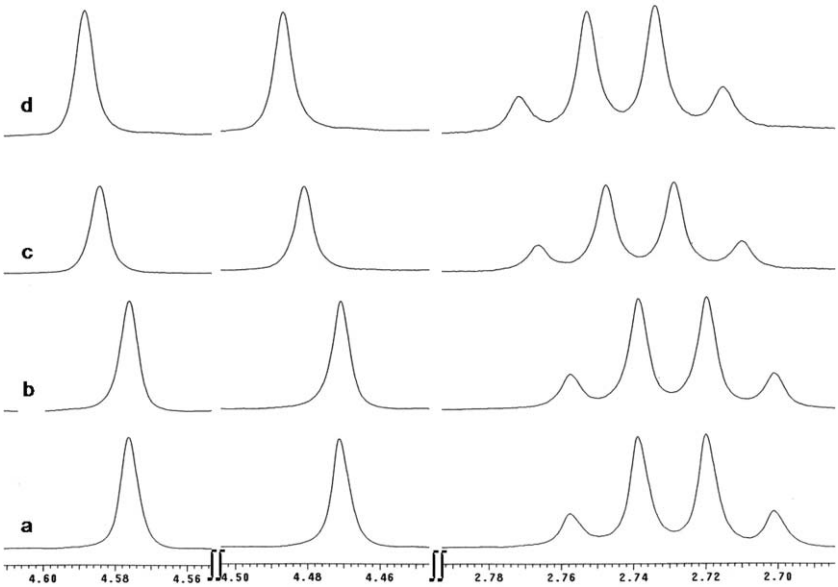

Fig. 4 ^{1}H-NMR spectra (400 MHz) of: (a) **3H** 1 mM in $CS_2/CDCl_3$ 80:20; (b) **3H** (1 mM) and fullerene (1 mM) in $CS_2/CDCl_3$ 80:20; (c) **3H** (1 mM) and fullerene (1 mM) in $CS_2/CDCl_3$ 62:38; (d) **3H** (1 mM) and fullerene (1 mM) in $CS_2/CDCl_3$ 50:50. Only the CH_2O and the CH_2(Et) signals of the receptors are shown.

be overcome by the weak π–π interactions established with the tripodal hosts in the absence of a compelling pre-organization of the structure. This interpretation of the experimental data agrees with recent results by Boyd *et al.*[31] indicating that fullerene de-solvation plays a major role in its binding by aromatic receptors and that the strength of binding increases in a medium which is a poor solvating agent for fullerene.

Experimental

Materials

All commercially available reagents including dry solvents were used as received. Organic extracts were dried over sodium sulfate, filtered, and concentrated under vacuum using a rotatory evaporator. Non-volatile materials were dried under high vacuum. Reactions were monitored by thin-layer chromatography on pre-coated Merck silica gel 60 F254 plates and visualized either by UV or by staining with a solution of cerium sulfate (1 g) and ammonium heptamolybdate tetrahydrate (27 g) in water (469 mL) and concentrated sulfuric acid (31 mL). Flash chromatography was performed on Fluka silica gel 60. The NMR spectra were obtained at 500 or 300 MHz for ^{1}H-, 125.6 or 75.3 MHz for ^{13}C-, and 470.5 or 282 MHz for ^{19}F-NMR. The NMR spectra for affinity measurements of (C_{60}-I_h)[5,6]-fullerene with **3H** were obtained at 400 and 200 MHz for ^{1}H-, 100 and 50 MHz for ^{13}C-NMR. The conditions for NMR analysis of the receptors/fullerene mixtures were reported in the text. Mass spectra were recorded on a LTQ-IT-Orbitrap equipped with a nano-spray-injector, in positive and negative mode. Adducts **2**[17] and **4**,[18] 1,3,5-triformyl-2,4,6-triethylbenzene **5**,[19] *N*-[3-(triethoxysilyl)-propyl]-2-carbomethoxy-3,4-fulleropyrrolidine[25] and 1,2,3,4-tetrafluoronaphthalene[11f] were prepared according to literature procedures and had m.p. and spectral data in agreement with those reported in the literature.

Synthesis of 1,3,5-tribenzyl-2,4,6-triethylbenzene 1H. To a stirred solution of compound **5** (626 mg, 2.54 mmol) in dry THF (25 mL) kept under nitrogen at 0 °C, a 3 M solution of PhMgBr in diethyl ether (4.2 mL, 12.7 mmol) was slowly added. The reaction mixture was allowed to slowly warm up to room temperature and was then stirred overnight. The reaction was quenched by a cautious addition of water (10 mL) and 1 N aqueous HCl (15 mL) and the resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried and concentrated to give the crude product. This was purified by flash chromatography with a 9:1 hexanes/ethyl acetate mixture as eluant. Triol **6**, a thick oil with R_f 0.2, was isolated as a mixture of diastereoisomers (756 mg, 62% yield). These were not further purified but directly subjected to de-oxygenation.[21] To a stirred solution of compound **6** (596 mg, 1.24 mmol) in dry dichloromethane (30 mL) kept under nitrogen, trifluoroacetic acid (1.11 mL, 14.5 mmol) and triethylsilane (4.66 mL, 29.2 mmol) were added in this order and the mixture was stirred for 70 h at room temperature. The reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$, and the organic phase was separated, dried and concentrated under vacuum. The residue was purified by flash chromatography with a 98:2 hexane/dichloromethane mixture as eluant to afford the product as a white solid (R_f 0.8, 319 mg, 59% yield). It had m.p. 158 °C. ^{1}H-NMR ($CDCl_3$): δ 7.26 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.2 Hz, 1H), 7.03 (d, J = 7.2 Hz, 2H), 4.17 (s, 2H), 2.48 (q, J = 7.5 Hz, 2H), 1.08 (t, J = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$): δ 141.5, 141.4, 134.0, 128.3, 127.8, 125.6, 34.6, 23.7, 15.1. Elemental analysis: $C_{33}H_{36}$ requires: C, 91.61; H, 8.39; found: C, 91.79; H, 8.21%.

Synthesis of 1,3,5-tris-pentafluorophenylmethyl-2,4,6-triethylbenzene 1F. To a stirred solution of compound **5** (713 mg, 2.89 mmol) in dry THF (30 mL) kept under nitrogen at 0 °C, a 3 M solution of C_6F_5MgBr in diethyl ether (4.8 mL, 14.5 mmol) was slowly added. The reaction mixture was allowed to slowly warm up

to room temperature and was then stirred overnight. The reaction was quenched by a cautious addition of water (10 mL) and 1 N aqueous HCl (15 mL) and the resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried and concentrated to give the crude product. This was purified by flash chromatography with a 85:15 hexanes/ethyl acetate mixture as eluant. Triol **7**, a pale yellow solid with R_f 0.44 and m.p. 78–80 °C, was isolated as a mixture of diastereoisomers (1.149 g, 53% yield). These were not further purified but directly subjected to de-oxygenation.[22] To a stirred solution of compound **7** (500 mg, 0.66 mmol) in glacial acetic acid (17 mL) kept under nitrogen, iodine (503 mg, 1.98 mmol) and a 50% w/w aqueous solution of H_3PO_2 (0.42 mL, 3.96 mmol) were added in this order and the mixture was stirred 20 h at 60 °C. Ethyl acetate (20 mL) and water (20 mL) were added and the organic phase was separated. This was washed with a saturated aqueous solution of $NaHCO_3$, and then with a saturated aqueous solution of $Na_2S_2O_3$. The organic phase was separated, dried and concentrated under vacuum. The residue was purified by flash chromatography with a 95:5 hexanes/diethyl ether mixture as eluant to afford the product as a white solid (R_f 0.7, 278 mg, 60% yield). It had m.p. 91–92 °C. ^{1}H-NMR ($CDCl_3$): δ = 4.14 (s, 2H), 2.67 (q, J = 7.5 Hz, 2H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$): δ = 145.4 (d, J = 248 Hz), 141.9, 139.6 (dt, J = 248, 15 Hz), 137.5 (dt, J = 248, 15 Hz), 131.9, 114.5, 23.8, 23.7, 14.5. ^{19}F-NMR ($CDCl_3$): δ = −142.8 (d, J = 19.4 Hz), −157.8 (t. J = 18.9 Hz), 163.1 (t, J = 21.0 Hz). Elemental analysis: $C_{33}H_{21}F_{15}$ requires: C, 56.42; H, 3.01; found: C, 56.28; H, 2.94%.

Synthesis of 1,3,5-trisphenylmethoxymethyl-2,4,6-triethylbenzene 3H. To a stirred solution of compound **5** (260 mg, 1.06 mmol) in dry dichloromethane (10 mL) kept under nitrogen at room temperature, benzyloxytrimethylsilane (582 mg, 3.23 mmol) in dichloromethane (5 mL) was added followed by triethylsilane (0.52 mL, 3.23 mmol). The mixture was then cooled at 0 °C and trimethylsilyl triflate (0.077 mL, 0.424 mmol) was added. The reaction mixture was slowly allowed to warm up to room temperature and was then stirred for 2 h. Dichloromethane (50 mL) was then added and the organic phase was washed with water (20 mL). The organic phase was dried and concentrated to give the crude product. This was purified by flash chromatography with a 8:2 hexanes/ethyl acetate mixture as eluant. Product **3H** (200 mg), a pale yellow solid with R_f 0.35, was isolated in 36% yield. It had m.p. 100–102 °C. ^{1}H-NMR ($CDCl_3$): δ = 7.30–7.43 (m, 5H), 4.64 (s, 2H), 4.55 (s, 2H), 2.81 (q, J = 7.5 Hz, 2H), 1.14 (t, J = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$): δ = 145.2, 138.4, 131.9, 128.3, 128.1, 127.6, 73.0, 66.4, 22.8, 16.4. Elemental analysis: $C_{36}H_{42}O_3$ requires: C, 82.72; H, 8.10; found: C, 82.58; H, 8.19%.

Synthesis of 1,3,5-tris-(pentafluorophenyl)-methoxymethyl-2,4,6-triethylbenzene 3F. To a stirred solution of compound **5** (200 mg, 0.8 mmol) in dry dichloromethane (10 mL) kept under nitrogen at room temperature, pentafluorophenylmethoxytrimethylsilane (654 mg, 2.42 mmol) in dichloromethane (5 mL) was added followed by triethylsilane (0.4 mL, 2.5 mmol). The mixture was then cooled at 0 °C and trimethylsilyl triflate (0.06 mL, 0.32 mmol) was added. The reaction mixture was slowly allowed to warm up to room temperature and was then stirred for 2 h. Dichloromethane (50 mL) was then added and the organic phase was washed with water (20 mL). The organic phase was dried and concentrated to give the crude product. This was purified by two flash chromatography columns, the first with a 70:30 hexanes/ethyl acetate mixture as eluant, and the second with a 95:5 pentane/diethyl ether mixture as eluant. Product **3F** (63 mg), a pale yellow solid with R_f 0.35, was isolated in 10% yield. It had m.p. 135.8–136.6 °C. ^{1}H-NMR ($CDCl_3$): δ = 4.66 (s, 2H), 4.56 (s, 2H), 2.72 (q, J = 7.5 Hz, 2H), 1.11 (t, J = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$): δ = 145.5 (d, J = 245 Hz), 145.3, 141.1 (dt, J = 247, 18 Hz), 136.8 (dt, J = 250, 21 Hz), 131.2, 111.2, 67.2, 59.4, 22.8, 16.4. ^{19}F-NMR ($CDCl_3$: δ = −143.4 (d, J = 22.8 Hz), −154.1 (t, J = 19.2 Hz), −162.5 (t, J = 15.2 Hz). Elemental analysis: $C_{36}H_{27}F_{15}O_3$ requires: C, 55.45; H, 3.43; found: C, 54.39; H, 3.36%.

Synthesis of silica 8. This was prepared as described.[25] A suspension of ApexPrepSil (particle size 8 μm, 3.0 g) in dry toluene (80 mL) was heated with stirring under a continuous stream of nitrogen until the volume of the solvent was reduced to 60 mL. To this azeotropically-dried mixture, solid *N*-[3-(triethoxysilyl)-propyl]-2-carbomethoxy-3,4-fulleropyrrolidine (727 mg, 0.7 mmol)[25] was added, and the mixture was refluxed for 20 h. After cooling to room temperature, the modified silica was collected by filtration and washed sequentially with 200 mL portions of toluene, chloroform, methanol, chloroform, and hexane, and subsequently dried under high vacuum at 60 °C to afford 3.5 g of pale brown material. Carbon elemental analysis (C = 11.13%) showed a loading of 0.135 mmol g^{-1}. Evaporation of the solvents employed to wash the silica allowed recovery of 58 mg of fulleropyrrolidine.

HPLC experiments. Silica **8** was packed in a 125 × 4.6 mm i.d. glass-lined stainless steel column by the slurry procedure (MeOH, 140 atm); efficiency test gave N/m = 4000 for 1,3-dinitrobenzene eluting with a 9:1 hexane/chloroform mixture at a flow rate of 0.2 mL/min at 25 °C. The retention times observed using a commercial RPC_{18} column (C_{18} Resolve, Waters, 125 × 4.6 mm; N/m = 30000) were obtained with a flow rate of 1.0 mL/min at 25 °C and the eluants indicated in Table 1. The retention times observed with the column packed with silica **8** were obtained under the same conditions. The results were reported in Table 1.

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