Supporting Information

Cucurbiturils as Fluorophilic Receptors

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1. Literature review on the use of cyclodextrins for PFC binding

Cyclodextrins have the ability to form host-guest complexes with different perfluorinated compounds.(1-14) In particular, β -CD forms stable inclusion complexes with variable chain-length PFCs in aqueous solution. The diameter match between the CF_2 groups and the inner diameter of the β -CD cavity plays an important role in the complex stability.(11,12) Palepu and Reinsborough studied the complexation of sodium perfluorooctanoate (SPFO) with cyclodextrins.(12) Conductance measurements were performed and the dependence of the conductance of SPFO on the concentration of α -CD, β -CD, and γ -CD was measured. The order of binding was β -CD > γ -CD > α -CD, determined by the good size-fit complementarity of the chain and the β -CD cavity. ^{19}F NMR was widely used to study the complexation of PFCs with CDs. Complexation-induced chemical shifts were generally observed.(2,8) The host-guest complexation of perfluorooctanoic acid with β -CD was investigated with different methods by Karoyo et al.(2,3) The structural characterization and dynamic properties of the inclusion complex were investigated by ^{19}F and ^{13}C solid-state and ^1H and ^{19}F solution-phase NMR spectroscopy. The

observed ^1H and ^{19}F NMR shifts in solution provided evidence for host-guest complexation. The down-field shift of the fluorine signals in solution was explained by the conformational changes of the perfluorooctanoic acid. An *all-trans* conformation (de-shielding) was suggested in the complex, which resulted in a maximization of the through-space F–F distance between neighboring CF_2 groups, while optimizing the residual van-der-Waals interactions within the cavity.(2)

2. Comment on the packing coefficients and molecular volumes

The PCs in Table 1 of the main text are based on calculated molecular volumes of the PFCs. These calculations used a commercial software,(15) which in turn employs standard van der Waals radii for the guest volume calculations. Our experience with PC calculations for host-guest complexes(16,17) and independent experimental observations from unrelated projects suggest that these calculated molecular volumes may underestimate the “real” ones for PFCs as guests. Indeed, when the molecular volumes are estimated from experimental liquid densities of PFCs (assuming 55% packing),(18) larger volumes are obtained (Table S1), especially for the spherical SF_6 . Higher PCs values would then result. For The SF_6 , the PC obtained from the liquid densities would lead to a unreasonably high PC inside CB6 (71%) which would be inconsistent with the experimentally observed strong binding (see main text). We therefore report in Table S1 the average values of both determinations as “best estimates”.

Table S1. Calculated (QSAR) and estimated (based on the liquid densities) guest molecular volumes (V) and packing coefficients (PCs) with CB7 as host.

Guest	from QSAR		from Densities		Average	
	$V / \text{\AA}^3$	PC%	$V / \text{\AA}^3$	PC%	$V / \text{\AA}^3$	PC%
2	53	22 [37] ^a	101	42 [71] ^a	77	32 [54]^a
5	107	44	127	53	117	49
6	99	41	105	44	102	43
7	133	55	163	67	148	61
8	131	54	163	67	147	61
9	153	57	179	74	166	66
14	148	61	182	75	165	68

^a Values in square brackets refer to CB6 as host.

3. Materials and Methods

Gases (CF_4 , SF_6 , and CH_2F_2) of highest commercial purity ($\geq 99\%$) were purchased from Air Liquide, Germany. $(\text{CF}_3)_3\text{COH}$, hexafluorobenzene, and perfluorohexane were purchased from Sigma-Aldrich, Germany. All other PFCs were obtained from SynQuest Laboratories and used as received without any further purification. CBs were synthesized as reported.⁽¹⁹⁾ Fluorescence measurements were done with a Varian Eclipse fluorometer at 25°C . ^1H NMR spectra were recorded with a JEOL ECX 400 MHz NMR spectrometer in D_2O (99.9% from Aldrich). Sonication of a two-phase PFC/ D_2O system was used to speed up dissolution; only the aqueous solution was used for the NMR measurements.

All binding constants (Table 1 of main text) were calculated by assuming a 1:1 complexation stoichiometry and obtained by nonlinear fitting procedures ⁽¹⁷⁾ based on the fluorescence plots ($\lambda_{\text{em}} = 469\text{ nm}$) through repetitive single-point measurements of the fluorescence intensity after addition of an excess of PFC (2 μl liquid or 0.1 mg solid) to aqueous solutions of CB7/DAPI (2.4 μM /1 μM).

4. Dye-displacement titrations for selected PFCs with CB7 as host

Fig. S1 Fluorescence displacement titrations (left) of DAPI (1 μM) from CB7 (2.4 μM) monitored by fluorescence with increasing concentrations of a) hexafluorobenzene (**6**) b) perfluoropentanoic acid (**13**), c) perfluorohexanoic acid (**15**), and d) perfluoroheptanoic acid (**16**). The nonlinear fittings (right) were based on the fluorescence titrations ($\lambda_{\text{em}} = 469 \text{ nm}$) by assuming a 1:1 binding model from which the association constants (added in graphs) were derived.

Table S2. Association constants of PFCs **1-22** with CB7 in aqueous solution, estimated and experimental solubilities, relative experimental fluorescence intensities, and calculated packing coefficients.

	$PC/\%^a$	I_{ref}^b	Solubility/mM		K_a / M^{-1}	
			Estimated ^c	Experimental	Estimated ^d	Experimental ^e
1	17	100	0.368	2.14 ^f	< 30 ^g	< 300 ^g
2	22	87		0.220 ^h	15	1.34 × 10⁴ⁱ
3	26	83	1420		4.05 × 10 ³	852
4	25	14	1700		150	10
5	44	16	0.499		3.97 × 10 ⁵	1.50 × 10⁶
6	41	50	7.36	3.33 ^j	3.57 × 10 ³	3.62 × 10^{3k}
7	55	20	3.29 × 10 ⁻⁵		3.37 × 10 ⁹	
8	54	45	1.11 × 10 ⁻⁵		2.99 × 10 ⁹	
9	63	57	1.41 × 10 ⁻⁶	6.71 × 10 ^{-4l}	1.33 × 10 ¹⁰	1.14 × 10⁸ⁱ
10	63(60) ^m	8	5.49 × 10 ⁻⁴		1.76 × 10 ⁹	
11	59	9	7.19 × 10 ⁻⁴		8.90 × 10 ⁸	1.03 × 10⁵
12	77	100	3.17 × 10 ⁻⁶			
13	52	11	6.33 × 10 ⁻²		7.25 × 10 ⁶	700
14	61	87	5.34 × 10 ⁻⁶	2.70 × 10 ^{-4l}	5.86 × 10 ⁸	1.16 × 10⁷ⁱ
15	61(49) ^m	66	2.72 × 10 ⁻³		5.15 × 10 ⁶	2.40 × 10⁴
16	70(49) ^m	46	1.16 × 10 ⁻⁴		3.00 × 10 ¹¹	8.30 × 10³
17	72(47) ^m	6	2.06 × 10 ⁻⁴		6.53 × 10 ¹⁰	
18	70(56) ^m	35	8.90 × 10 ⁻⁵		6.23 × 10 ⁸	
19	83(58) ^m	13	2.70 × 10 ⁻⁶		1.24 × 10 ¹¹	
20	76(55) ^m	72				
21	105(49)	12	1.37 × 10 ⁻⁶		2.56 × 10 ¹¹	
22	91(49) ^m	100				< 50 ^g

^a Packing coefficient, (volume of the guest) / (cavity volume of CB7, 242 Å³), where the volume of the guest was obtained by the QSAR package in the Hyperchem software from the wB97xd/6-31G*-optimized structures. ^b Relative experimental fluorescence intensity reached in displacement titrations, (Intensity after displacement)/(Intensity of CB7/DAPI). The errors refer to an experimental reproducibility of ± 3% of the final intensity. ^c Solubilities estimated by using the US Environmental Protection Agency's – EPISuiteTM according to the fragment-constant method (using the WATERNTTM program). ^d Determined by using calculated solubilities. ^e Determined experimentally by fluorescence displacement titrations with stock solutions, unless stated differently. ^f From ref. (20). ^g Lower limit, no detectable binding (< 3%) was observed. ^h From ref. (21). ⁱ Determined from single-point displacement titrations by using the experimentally determined solubilities. ^j From ref. (22). ^k Value determined from single-point displacement titrations by using the experimentally determined solubilities: 7.90 × 10³ M⁻¹. ^l From ref. (23). ^m Values in parentheses were calculated according to the volumes of the residues which were immersed in the *inner* cavity based on the DFT-optimized structures, see ref. (16)

5. NMR spectra

Fig. S2 (Top) ^{19}F NMR spectra of saturated solutions of hexafluorobenzene (**6**) in the presence and absence of CB7 (2 mM).

Fig. S3 ^1H (left) and ^{19}F NMR (right) spectra of saturated solutions of 1 mM 4-fluoroaniline in the absence (a) and presence (b) of CB7 (2 mM).

Fig. S4 ^{19}F NMR spectra of saturated solutions of perfluorosebacamide (**21**) in the absence (a) and presence (b) of CB7 (2 mM); inset: ^1H NMR of CB7 in the presence of perfluorosebacamide (**21**).

Fig. S5 ^1H NMR spectra of saturated solutions of 1-(perfluorobutyl)pentane (**20**) in the absence (top) and presence (bottom) of CB6 (2 mM) in 100 mM NaCl.

Fig. S6 ^1H (top) and ^{19}F (bottom) NMR spectra of CH_2F_2 in the presence of 8 mM CB5.

6. Quantum-chemical calculations

Dispersion-corrected DFT calculations (wb97xd/6-31G*) were performed with the Gaussian 09 software.(24)

Tetrafluoromethane (1)

Sulfurhexafluoride (2)

CF₃CH₂NH₂ (3)

Nonafluoro-*tert*-butylalcohol (5)

Hexafluorobenzene (6)

Perfluoro(methylcyclopentane) (7)

Perfluorocyclohexane (8)

Perfluoro(methylcyclohexane) (9)

perfluorocyclohexyl)methanol (**10**)

Perfluoropentanoic acid (**13**)

Perfluorohexane (**14**)

1H,1H-perfluoroheptylamine (**17**)

Perfluorooctamidine (19)

1-(perfluorbutyl)pentane (20)

Perfluorosebacamidine (21)

Fig. S7 wB97xd/6-31G*-optimized geometries of the CB7/PFC complexes.

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