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Synthesis of bambusurils with perfluoroalkylthiobenzyl groups as highly potent halide receptors†

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The preparation of anion receptors with ultrahigh binding affinities is an important, yet challenging, topic of supramolecular chemistry. The search for new structural motifs which would enhance the performance of anion receptors is therefore an important task. In this context, we report the synthesis of novel fluorinated bambus[6]urils that incorporate unique benzyl substituents with perfluoroalkylthio groups, aimed at enhancing their anion receptor capabilities. The synthetic strategy developed allows for the efficient preparation of these structural motifs. Ultrahigh stability of the complexes between halides and the prepared bambus[6]urils was observed and quantified using ^{19}F NMR competition experiments. Replacing $-CF_3$ groups on benzylated bambus[6]urils by $-SCF_3$ groups increased the affinity of the macrocycles towards anions and provided the strongest iodide receptor reported with a binding affinity of 4×10^{13} M^{-1} in acetonitrile.

Introduction

Artificial host molecules with a high binding affinity towards anions find applications in detection systems for low anion concentrations, separation, environmental scavenging, or transmembrane transport.[1–7] Macrocycles[8–13] or cages[14–17] are especially potent anion receptors as they encapsulate anions *via* multiple non-covalent interactions, often accompanied by complete anion desolvation. These host molecules are often valued not only for their high affinities but also for their high selectivity. However, their design and preparation are usually challenging. Structurally more simple acyclic host molecules are also capable of strong anion binding.[18,19] This is generally achieved by the installation of electron-withdrawing substituents for higher polarization of the anion binding groups (such as urea or triazole). Phenyl moieties bearing $-CF_3$, $-NO_2$ or –F electron-withdrawing groups are commonly used in this context.[20–22]

The strongly electron-withdrawing $-SCF_3$ group could be also attractive for this purpose, and it has a very high Hansch lipophilicity parameter as well.[23,24] Several synthetic methods have been developed to incorporate the $-SCF_3$ group into organic molecules, mostly to prepare new drug candidates.[23,25–29] Surprisingly, no anion receptors which contain the $-SCF_3$ group have been published in the literature to date other than the recently reported fluorinated bambus[6]urils (BUs).[10,30,31] BUs are a class of deep cavity anion receptors, in which the anion binding is mediated *via* C–H hydrogen bonds, originating from sp^3 hybridised carbon atoms. We have reported recently that the installation of $-SCF_3$ groups to the *para*-position of their benzyl substituents dramatically increases the binding affinity of these macrocycles to anions, up to 10^{12} M^{-1} for **BU5** and 10^{13} M^{-1} for **BU7** in acetonitrile (Fig. 1).[10,31]

This work presents the synthesis of BU derivatives bearing two electron-withdrawing $-SCF_3$ or perfluoroalkylthio groups on their benzyl substituents (Fig. 1). The synthesis of 3,5-perfluoroalkylthiobenzyl moieties is reported for the first time. Furthermore, we have determined the association constants of the newly prepared macrocycles with chloride, bromide, and iodide using ^{19}F NMR spectroscopy.

Results and discussion

Synthesis

For our study, we decided to synthesise **BU1** with two $-SCF_3$ groups per substituent as it can be directly compared with its previously studied analogue bearing two $-CF_3$ groups. We also prepared **BU2** bearing methoxy groups in addition to $-SCF_3$

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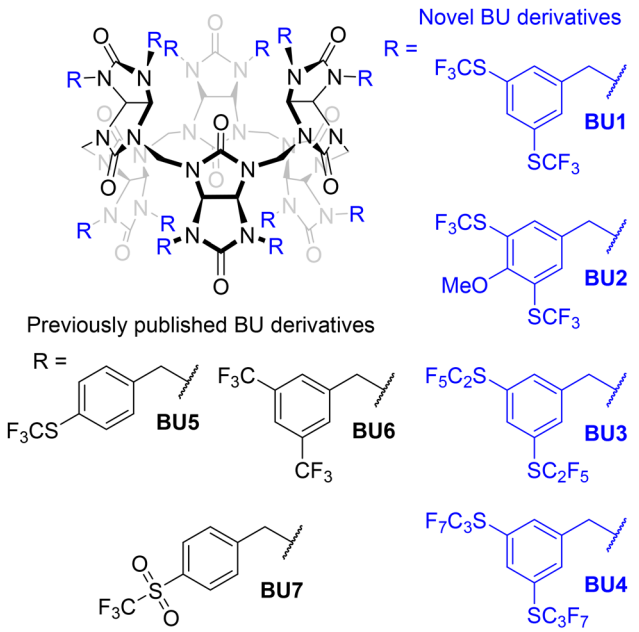


Fig. 1 Structures of bambus[6]urils studied in this work.

groups, allowing additional modifications of the macrocycle in the future. Macrocycles **BU3** and **BU4**, with perfluoroethyl or perfluoropropyl groups attached to the sulphur atoms, were prepared to evaluate the influence of the length of the fluorinated alkyl chain on the properties of the macrocycle.

The synthesis started with the inexpensive 3,5-dihydroxybenzoic acid methyl ester **1** (for **BU1**, **BU3** and **BU4**) or methoxy derivative **2** [32] (for **BU2**) (Scheme 1a). The esters **1** and **2** were converted to the corresponding *O*-aryl dimethylcarbamothioates **3** and **4** by the reaction with dimethylthiocarbamoyl chloride (DMTCC) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as a base. The intermediates **3** [33] and **4** were obtained in high yields of 88% and 72%, respectively, on a multigram scale. To obtain *S*-aryl dimethylcarbamothioates **5** and **6**, both **3** and **4** were converted by a Newman–Kwart rearrangement.[33,34] The rearrangement of **3** to **5** was performed by heating a solution of **3** in diphenyl ether to reflux until a full conversion was observed, yielding **5** in a 94% yield.[33] On the other hand, rearrangement of **4** to **6**, was proven to be more challenging, particularly on a large scale, due to the presence of an electron-donating –OMe group. In contrast to **3**, the conversion of **4** to **6** was slower and prolonging the reaction time increased the quantity of impurities resulting from the decomposition of either the product, starting material, or mono-rearranged compounds. Also, a high variation in the yield of **6** was obtained, ranging from 40 to 90%. Therefore, we tested several other reported conditions to perform the Newman–Kwart rearrangement, including heating of the reaction mixture by microwaves,[35] using different solvents,[36] or redox catalysis.[37,38] Unfortunately, none of the alternative reaction conditions gave better results than the thermal rearrangement in diphenyl ether.

The subsequent global reduction of **5** and **6** by an excess of lithium aluminium hydride provided dithiols **7** [39] and **8** in 96% and 62% yields. The presence of the –OMe group in **8** resulted in a lower stability compared to **7**. While dithiol **7** was obtained pure after the reduction, the more electron-rich dithiol **8**, had to be purified by chromatography, was prone to decomposition by oxidation with atmospheric oxygen, and could not be stored for a prolonged time.

The dithiols **7** and **8** were trifluoromethylated using Togni reagent II. Either **7** or **8** was added into a degassed solution of Togni reagent II in MeOH in the presence of *N*,*N*-diisopropylethylamine (DIPEA) as a base. Compounds **9** and **10** were obtained after chromatographic separation in yields of 88% and 83%. The alcohols **9** and **10** were converted to the corresponding chlorides **11** and **12** by reaction with thionyl chloride.

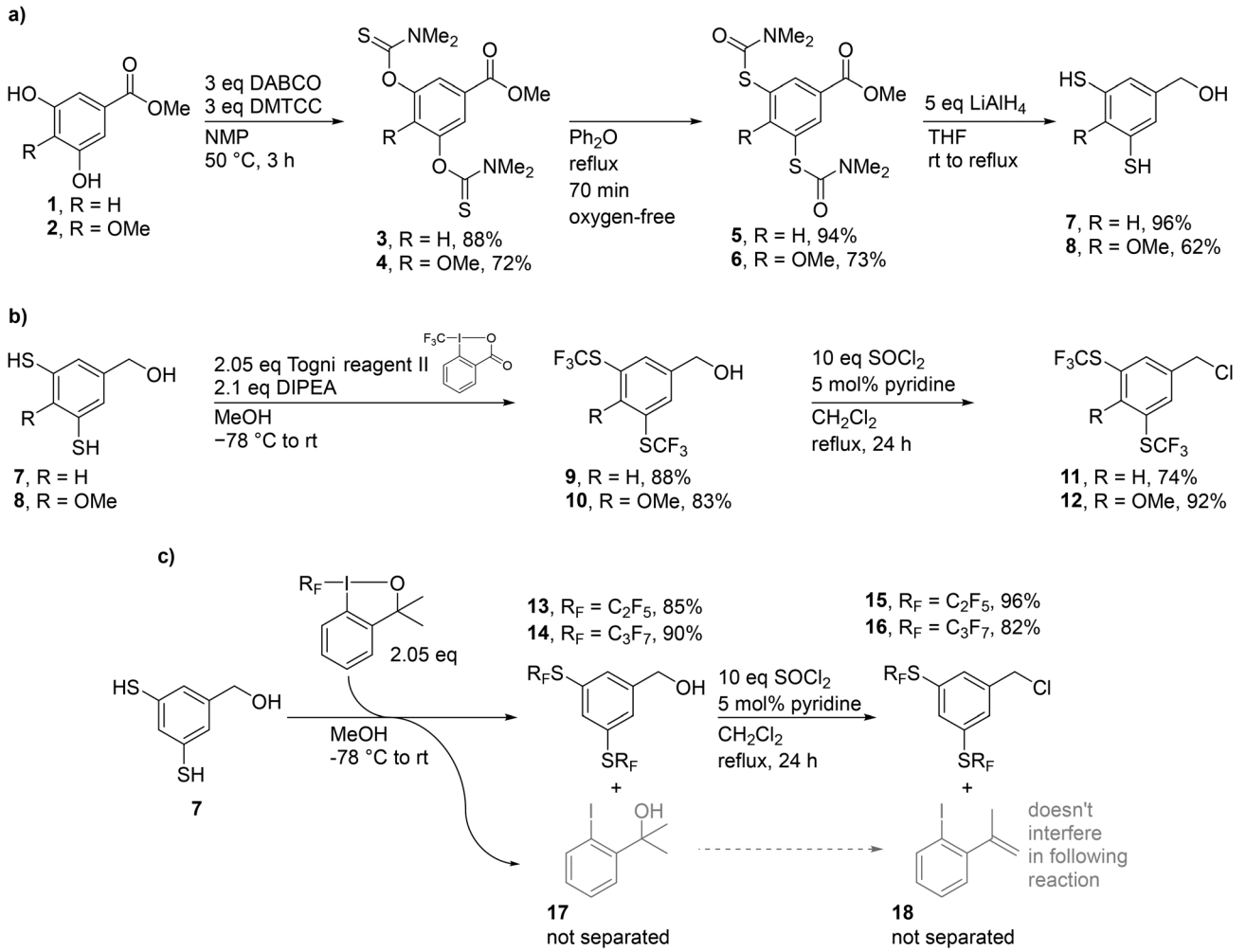
To obtain precursors **13** and **14** with perfluoroalkylthio groups, we have used the commercially available Togni reagent I analogues bearing a perfluoroalkyl instead of $-CF_3$ group (Scheme 1b). The obtained alcohols **13** and **14** with perfluoroalkylthio groups were converted to the corresponding chlorides **15** and **16**. These synthetic steps were complicated by the Togni reagent byproduct **17** which was impossible to separate from **13** and **14** due to almost identical retention factors on normal-phase silica in various mobile-phase systems. Therefore, we have decided to use the mixture of **13** or **14** with **17** in the following reactions. Tertiary alcohol **17** underwent an elimination reaction forming alkene **18** by thionyl chloride during the conversion of alcohols **13** or **14** to chlorides **15** or **16**. Compounds **15** and **16** were used in the following alkylation step as their mixtures with **18**, for which separation was again not feasible.

Alkylation of *p*-methoxybenzyl-protected glycoluril **19** with the benzyl chlorides **11**, **12**, **15**, and **16** provided tetrasubstituted glycolurils, which were used directly in the next step (Scheme 2).[30,40] The *p*-methoxybenzyl groups were cleaved by ceric ammonium nitrate (CAN) and pure glycoluril building blocks **20–23** were obtained in yields ranging from 47% to 84%. The final step was the macrocyclization reaction of the corresponding glycoluril building blocks **20–23** with formaldehyde. The reactions were performed in 1,4-dioxane in the presence of sulphuric acid acting as an acid catalyst and as a source of HSO_4^- anions templating the formation of macrocycles **BU1–BU4**, with six glycoluril units, as their complexes with HSO_4^- in 54–74% yields.

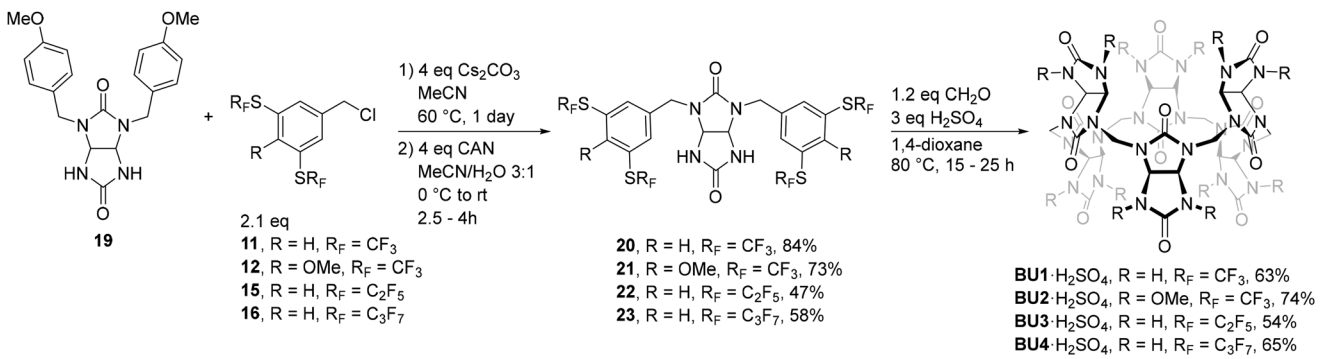
Using Togni reagents with perfluorohexyl and perfluorooctyl groups to fluoroalkylate dithiol **7**, we were able to prepare precursors with longer perfluoroalkyl chains. However, the drastic increase in the number of fluorine atoms in these molecules caused solubility issues during the preparation of corresponding glycoluril building blocks and ultimately prevented us from obtaining the other two highly fluorinated BUs (see the ESI† for the preparation of those glycolurils).

Anion binding studies

With the prepared BUs in hand, we decided to evaluate their affinity toward Cl^-, Br^-, and I^-. This choice of anions is ration-



Scheme 1 (a) Preparation of dithiol precursors **7** and **8** for all BUs; (b) preparation of fluorinated precursors **11** and **12** for **BU1** and **BU2**; (c) preparation of precursors with perfluoroalkyl groups for **BU3** and **BU4**.



Scheme 2 Preparation of BUs **BU1–BU4**.

alised by the fact that I^- is one of the strongest bound anions by BUs and the Cl^- anion is one of the most investigated anions in binding by BUs,[31,41,42] while it is also transported through lipid membranes by BUs.[10,30] Association constants of the complexes were determined by competition experiments. In this method, we utilised previously prepared **BU5** with known affinities to Cl^-, Br^-, and I^-. Moreover, further competition experiments with **BU6** or **BU7** were conducted for further verification of the obtained K_a values (see the ESI, Section 4†). We prepared complexes of **BU1–BU4** with Cl^-, Br^-,

and I^- and combined these with anion-free **BU5** (or **BU6**) in acetonitrile. These competition experiments between pairs of BUs were monitored by ^{19}F NMR spectroscopy.[31] As the host–guest exchange process is slow on the NMR chemical shift time scale, signals corresponding to free and bound BUs appeared in the spectra and association constants could be calculated based on the integral intensities (Fig. 2).

The obtained values are summarised in Table 1 together with the values for **BU5–BU7** and allow comparison between the anion affinities of new and already reported BUs. **BU1** with two $-SCF_3$ groups per benzyl substituent binds chloride with $\log K_a$ of 11.7, which is an order of magnitude stronger than **BU5** having just a single $-SCF_3$ group ($\log K_a$ of 10.6). Similar trends were found for complexes of **BU1** and **BU5** with Br^- and I^-.

This result fits with the expectation that the introduction of more electron-withdrawing groups on BU substituents decreases the electron density inside the BU cavity. Rather surprising is the comparison of anion-binding affinities of **BU6** and **BU1**. Changing $-CF_3$ groups to $-SCF_3$ increased the affinity of the BU macrocycle to Cl^- about 3 times, which was confirmed by a direct competition study between these two compounds (Fig. S86†). In theory, the $-CF_3$ and $-SCF_3$ groups should have very a similar electron-withdrawing strength.[24,43] However, there is no anion receptor series reported in which the effect of the insertion of a sulphur atom between the $-CF_3$ group and the rest of the receptor on anion binding properties was investigated. Therefore, it is yet unclear whether this trend is more general, or specific for BU macrocycles.

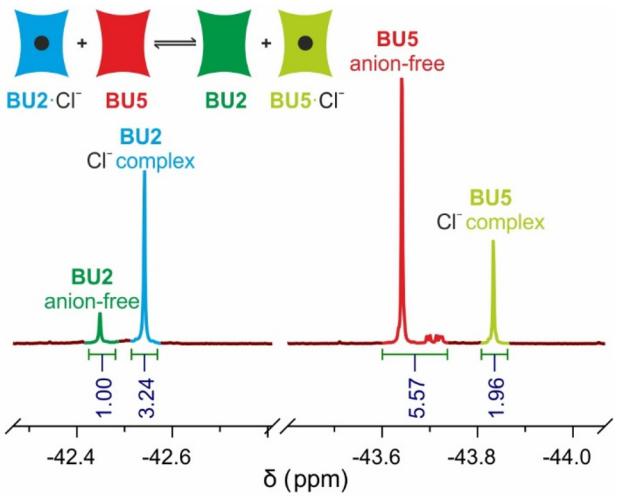


Fig. 2 ^{19}F NMR spectrum of a competition experiment between **BU2** and **BU5** for Cl^-, giving K_a(**BU2**)/K_a(**BU5**) = 9.

Table 1 Association constants (K_a) of BU – anion complexes

BU	Substituent *meta*	Substituent *para*	$\log K_a$ (Cl^-)	$\log K_a$ (Br^-)	$\log K_a$ (I^-)
BU1	SCF_3	H	11.7 ± 0.2[a]	12.7 ± 0.2[a]	13.6 ± 0.2[a]
BU2	SCF_3	OMe	11.7 ± 0.2[a]	12.8 ± 0.2[a]	13.7 ± 0.2[a]
BU5	H	SCF_3	10.6 ± 0.2[b]	11.8 ± 0.2[b]	12.2 ± 0.2[b]
BU6	CF_3	H	11.2 ± 0.3[a]	12.6 ± 0.2[a]	—[c]
BU7	H	SO_2CF_3	11.5 ± 0.2[b]	12.7 ± 0.2[b]	13.1 ± 0.2[b]

[a] Determined by competition with **BU5**. [b] Taken from ref. 31. [c] Not determined.

The methoxy group as present in **BU2** does not have any significant influence on the BU anion binding properties, as the competition experiments between **BU1** and **BU2** revealed essentially the same binding of these BUs to Cl^- and I^-. The methoxy group is a strongly electron-donating substituent by the mesomeric effect, but it weakly withdraws electrons from the aromatic ring by an inductive effect. Therefore, these two effects might cancel each other when considering the influence of the whole benzyl substituent on the electron density inside the BU cavity.

Competition between **BU1** and **BU5** for I^- revealed that **BU1** binds I^- with $\log K_a$ of 13.6, surpassing our previously reported strongest receptor **BU7** ($\log K_a$ of 13.1) for this anion,[31] as well as other potent iodide receptors.[44–46] Moreover, the direct competition experiment between **BU2** and **BU7** (Fig. S91†) confirmed that the affinity of **BU2** to iodide is approximately 3 times higher than for **BU7**.

Unfortunately, for **BU3** and **BU4**, the signals of anion-free and anion-complexed BU in ^{19}F NMR spectra overlap, which made it impossible to quantify their binding to Cl^-, Br^-, and I^-. However, we expect that these BUs would have either very similar or slightly higher binding than **BU1** and **BU2**.

Conclusions

In this work, we have developed the synthesis of 3,5-perfluoroalkylthiobenzyl derivatives and used them for the preparation of four new bambusurils **BU1–BU4**, containing different bis(perfluoroalkylthio)benzyl substituents. The host–guest complexes of these new BUs with Cl^-, Br^-, and I^- were investigated. We found that the binding affinity towards anions could be modulated by the type and number of the electron-withdrawing groups attached to the benzyl substituents of the bambusurils. These substituents made the BUs very effective anion receptors in MeCN. In particular, **BU1** and **BU2** and their complexes with iodide are characterised by a stability of $\log K_a$ of 13.6 and 13.7, exceeding the previously published **BU7** and making these novel macrocycles the strongest 1 : 1 receptors of iodide in any solvent ever reported. The methoxy-derivative **BU2** is particularly attractive due to its good solubility in various solvents and its potential for conjugation with other species through the –OMe groups. In addition, the possibility of oxidation of the $-SCF_3$ groups could increase the anion binding leading to even more potent receptors. The high anion affinities of the new BUs in combination with their lipophilic substituents suggest that these macrocycles hold promise as anion transporters. Investigations on this topic are ongoing in our laboratories. The reported synthetic

approaches provide access to aromatic compounds bearing several –SCF_3 groups and open opportunities for the preparation of other anion receptors containing these groups, which have been rarely reported in the literature.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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