 Hot Paper


An Indacenopicene-based Buckybowl Catcher for Recognition of Fullerenes

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A novel buckybowl catcher with an extended π -surface has been synthesized *via* cross-coupling of two bowl shaped bromoindacenopicene moieties with a tolyl linker. The obtained catcher has been unambiguously characterized by 2D-NMR and mass spectrometry. DFT calculations indicate that the curved shape of the receptor moieties is favourable for binding

fullerenes. Effective binding was confirmed for interactions with C_{60} and C_{70} utilizing NMR spectroscopy and isothermal titration calorimetry (ITC). The resulting binding values show a higher affinity of the catcher towards C_{70} over C_{60} . The designed catcher demonstrated the fundamental possibility of creating sensors for spherical aromaticity.

Introduction

Since the discovery of fullerenes, the development of efficient host systems for them has been of great interest.^[1] Various receptor molecules such as [n]cycloparaphenylenes,^[2] calix[n]arenes^[3] and porphyrins^[4] have been employed for the recognition based on either shape or electronic reciprocities. Such supramolecular complexes possess interesting applications, including the solubilization of pristine fullerenes^[5] and the formation of electron transfer complexes using suitable donor molecules.^[6] Given the fact that host-guest interactions strongly profit from a good shape and size complementarity,^[7] fullerene receptors employing different types of buckybowls have been demonstrated as a successful approach.^[8,9,10–12] Buckybowls are polycyclic aromatic hydrocarbons (PAHs) which are constructed

in a similar way as fullerenes, consisting of a combination of five- and six-membered rings, resulting in their curvature. However, their use in the field of supramolecular chemistry is limited by the availability of these molecules. Up to now above all corannulene – the smallest member of the buckybowl family – is synthetically available in a preparative scale,^[13] due to the elaborate procedures required for the synthesis of extended bowls.^[14] Those are mainly achieved by intramolecular aryl-aryl couplings using approaches such as Pd catalyzed intramolecular arylation^[15] and flash vacuum pyrolysis (FVP).^[16] However, these methods frequently result in low yields, limiting a possible functionalization. Especially halogenated buckybowls representing the most useful synthons for the synthesis of PAHs with complex architecture are not directly accessible by these methods. To overcome those problems, Amsharov and co-workers developed a method for the condensation of bowl-shaped PAHs based on cyclodehydrofluorination on activated γ - Al_2O_3 .^[17–19] This method tolerates the presence of other halogens including iodine^[20] and is therefore a viable alternative for the synthesis of rationally halogenated buckybowls.^[18,19,21] Indacenopicenes are curved PAHs, that were first prepared by a palladium-mediated cyclization reported by Wang and Shevlin in 2000.^[22] The molecule consists of six six-membered and two five-membered rings and shows a bowl depth of 0.925 Å which is increased compared to corannulene (0.875 Å).^[23] By applying the before mentioned cyclodehydrofluorination method, indacenopicenes are obtainable in high yields and are therefore interesting precursors for the synthesis of supramolecular host systems.

In this work, we developed a concave molecular receptor using two indacenopicene moieties as new building blocks linked by a tolyl tether. The 4-bromo-13,16-difluorobenzo[s]picene precursor was synthesized *via* cyclodehydrofluorination on activated aluminum oxide and linked to the tolyl tether in a Suzuki cross-coupling reaction. The interaction of the obtained buckycatcher with fullerenes C_{60} and C_{70} was studied by means of NMR spectroscopy and ITC.

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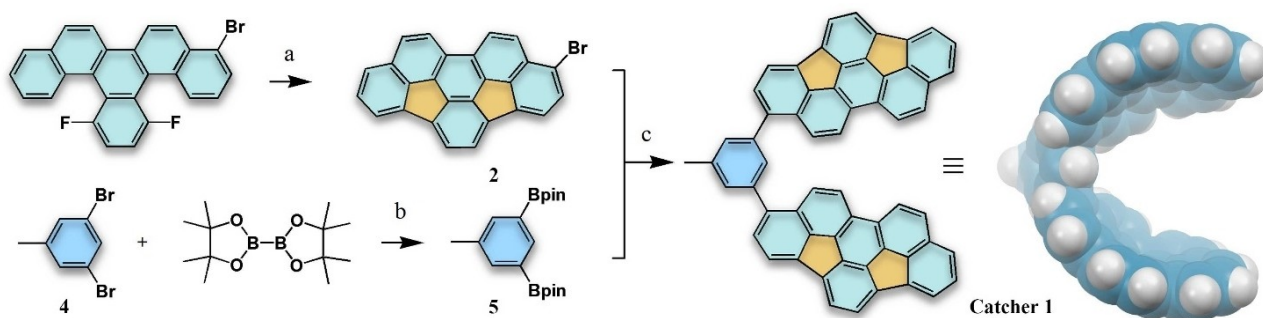
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Scheme 1. Synthetic route towards catcher 1. Reaction conditions: a) Al_2O_3 , *o*-DCB, 230 °C, 3 h, 76 %; b) $\text{Pd}(\text{dppf})\text{Cl}_2$, CH_3COOK , 1,4-dioxane, reflux, 72 h, Ar atmosphere, 48 %; c) $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , toluene:MeOH 2:1, reflux, 16 h, Ar atmosphere, 53 %.

Results and Discussion

The synthesis of molecular catcher 1 is depicted in Scheme 1. A first attempt was done starting from 4-bromo-13,16-difluorobenzo[s]picene **2**. The corresponding dioxaborolane **3** was prepared by modified Miyaura borylation following literature procedure.^[24] The next step towards obtaining catcher **1** was a Suzuki cross-coupling of **3** with 1,3-dibromo-5-methylbenzene **4** using $\text{Pd}(\text{dppf})\text{Cl}_2$ or $\text{Pd}(\text{PPh}_3)_4$ as a catalyst. In those cases, no product formation was observed. As an alternative synthetic pathway compound **4** was borylated according to a literature known procedure^[25] and subsequently used in Suzuki cross-coupling with the bromo-precursor **2** yielding the desired catcher in a moderate 53% yield. The receptor was unambiguously characterized by 2D-NMR spectroscopy and high-resolution mass spectrometry (see Supporting Information).

The electronic absorption spectrum of catcher **1** shows the typical indacenopicene band structure with two resolved bands at 370 and 390 nm, as well as several poorly resolved bands between 410 and 460 nm and a very weak absorption between 480 and 530 nm (see Figure 1, blue graph).^[26] Excitation of the compound at 388 nm results in fluorescence with a badly resolved emission band between 500 and 600 nm (see Figure 1,

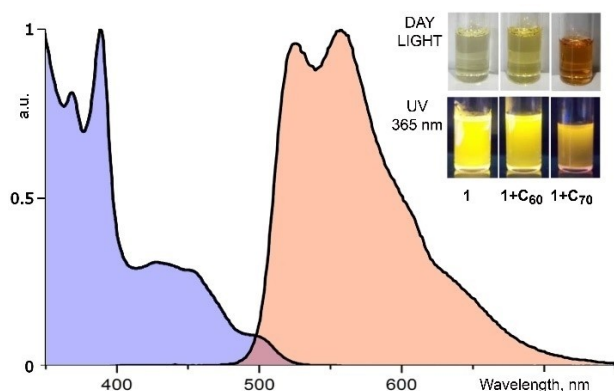


Figure 1. Electronic absorption (blue) and emission (light orange) spectra of catcher **1** in toluene. Insets: Photographs of catcher **1** (0.32×10^{-4} M) after addition of 1.0 eq. of C_{60} and C_{70} under day light and under irradiation by UV lamp at 365 nm.

light orange graph). In accordance with literature, this is the emission originating from the S_1 state located at the indacenopicene moiety.^[26]

Theoretical calculations of inclusion complexes on DFT level (r2SCAN-3c,^[27] ORCA 5.0.4,^[28] see details in the Supporting Information) of the catcher with fullerenes C_{60} and C_{70} indicated a good complementarity of the host and guest (Figure 2). As the indacenopicene bowl can invert and rotation around the indacenopicene-benzene bond is possible, there are two possible configurations of the catcher in the complex, a “symmetric” one, where indacenopicenes are mirrored, and an “asymmetric” one, where both indacenopicenes have the same chirality. DFT simulations show that with C_{60} the “asymmetric” complex is slightly favoured over the “symmetric” one (38 vs 36 kcal/mol). For C_{70} the result depends more on the orientation of the fullerene between the bowls, as both configurations of the catcher show similar maximum binding energies. Generally, C_{70} binds approx. 4 kcal/mol stronger than C_{60} (see Table S1 in the Supporting Information). Despite the high binding energy

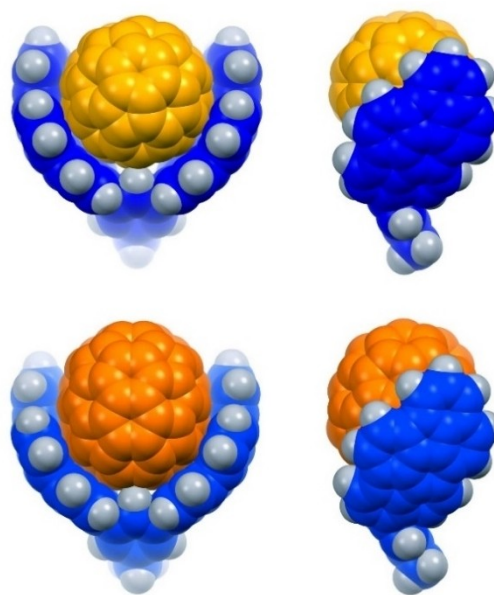


Figure 2. Calculated structures of the inclusion complexes between the catcher and C_{60} (top) and C_{70} (bottom).

of buckyball and buckycatcher, our DFT-calculations suggests that conversion between “symmetric” and “asymmetric” complexes have a limiting barrier of just 21 kcal/mol, and thus might be observed already under normal conditions, see details in SI.

The binding interactions of the buckycatcher with fullerenes C_{60} and C_{70} were investigated experimentally with different techniques. Changes in the absorption spectra of the catcher after addition of either C_{60} or C_{70} could be observed (measured in toluene at room temperature; see Figure S11 in the Supporting Information) because of the binding event. However, a significant overlap of the host and guest absorption bands precluded a binding analysis, which was then attempted *via* fluorescence spectroscopy. The titrations were done in toluene at room temperature. For both fullerenes, the catcher fluorescence is quenched upon the addition of the guest molecule which can qualitatively be observed even with naked eyes (see inset of Figure 1 and Figure S12 in the Supporting Information for the measurements). However, due to the absorption band overlap of the fullerenes with the excitation and emission wavelengths of the titration, the binding constants are overestimated because of the so called inner filter effect where a portion of the excitation light is absorbed by the fullerene, making the quenching appear more significant than it would actually be according to the interactions.^[29] Additionally we strived to evaluate the binding constant using isothermal titration calorimetry (ITC). Due to compound solubilities, those measurements were done in *o*-dichlorobenzene (*o*-DCB). However, the obtained thermograms did not result in the desired sigmoidal curve, with the so-called Wisman *c*-value only reaching a value of 3 (see Figure S21 in the Supporting Information).^[30] This value, which is determined by multiplication of the association constant K_a and the receptor concentration, determines the shape of the binding isotherm. It is obvious that for a given K_a , the isotherm can only be improved by increasing the concentration of the receptor. The limited solubility of both, the host, and the guest, prevented us from further optimizing the experiments in this regard. Measurements with low *c*-values can still be investigated regarding their bindings if the *n*-values are known before the fittings. This is because the stoichiometry is determined from the *x*-axis at the inflection point of the sigmoidal curve. As low *c*-values do not result in a sigmoidal shape, the *n*-value cannot reliably be determined from the measurement itself. For our analysis we fixed the stoichiometry to $n=1$, due to the DFT calculation of the inclusion complexes. The resulting binding value of $K_a = (2.99 \pm 0.06) \times 10^2 \text{ M}^{-1}$ for an inclusion complex between the catcher and C_{70} was achieved by a global analysis of the triplicate titration data (for all measurements and fittings see Figure S21 in the Supporting Information). Since the binding constant we obtained reaches the limit of the reliability of the instrument^[31] we decided to further evaluate the host guest interactions using NMR spectroscopy.

For comparison with the ITC evaluation, the NMR titrations were done using *o*-DCB-*d*4 as a solvent. Upon the addition of C_{70} to the catcher, several aromatic proton signals of the catcher are strongly shifted upfield (see Figure 3, influenced signals

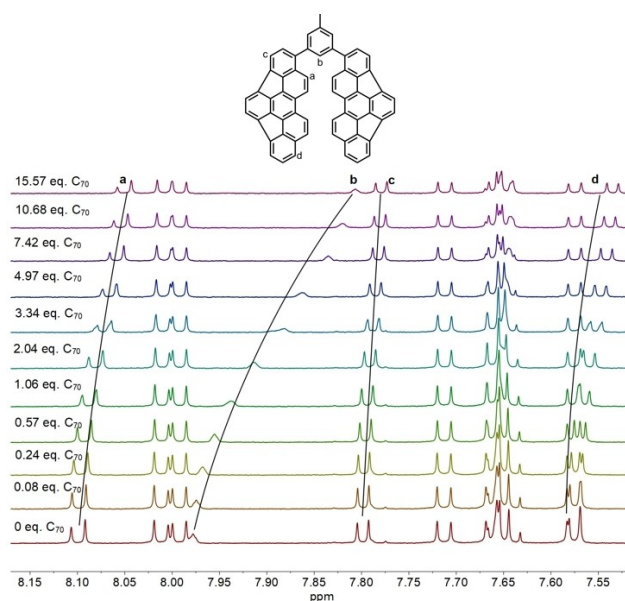


Figure 3. Top: catcher structure with the relevant protons marked a-d; bottom: ^1H NMR spectra (600 MHz, *o*-DCB-*d*4) of catcher 1 ($c = 1.6 \times 10^{-3}$ – 5.9×10^{-4} M) during the titration with C_{70} ($c = 0.0$ – 6.2×10^{-3} M).

marked a-d). The most pronounced shift can be seen for the signal at 7.98 ppm (marked b in Figure 3). This signal belongs to the proton of the tolyl linker facing into the catcher cavity. The positions of NMR-peaks of indacenopirone hydrogens can be predicted reasonably well (PBE0/cc-pVTZ, see Table S4 in the Supporting Information), and it can be shown that the tolyl hydrogen mentioned before is significantly shifted to the high field, and by complexation with fullerene getting shifted further (see Table S2 in the Supporting Information). This is independent of the configuration of the complex and in accordance with the experimental data, this proton is experiencing the highest shift in all simulated cases. In the case of a complex with C_{70} , the most stable configuration shows a shift to high field of 0.26 ppm, and for C_{60} of 0.07 ppm, which is in a very good agreement with experimental results. The proton is located perpendicular to the ring current of the π -system of a fullerene inside the catcher, indicating the binding of the fullerenes inside the host system. The same trend can be seen for the titration with C_{60} , although the observed shifts are generally smaller (see Figure S16 in the Supporting Information). This is in good agreement with the expected less pronounced spherical aromaticity of C_{60} in comparison to C_{70} .^[32] Taking into account these observations we propose that the buckybowls catcher can be used as a supramolecular sensor for the direct measurement of the spherical aromaticity of various pristine fullerenes.

Analysis of the titration data was done with a global analysis of all shifted protons using a 1:1 binding model. This resulted in binding constants of $K_a = (1.08 \pm 0.01) \times 10^3 \text{ M}^{-1}$ for C_{70} and $K_a = (1.50 \pm 0.1) \times 10^2 \text{ M}^{-1}$ for C_{60} . The obtained binding values are comparable to similar corannulene-based receptors.^[8,10–12] For ITC measurements, a corannulene receptor has been reported that reaches the same order of magnitude for the binding interactions with C_{70} as our buckybowl catcher

(literature value: $K_a = (2.0 \pm 0.1) \times 10^2 \text{ M}^{-1}$ in *o*-DCB).^[10] For NMR titrations, to the best of our knowledge no values are reported that have been measured in *o*-DCB. In the literature, it has been demonstrated, that the association constant decreased by approximately one order of magnitude when switching from toluene to chlorobenzene.^[33] Since *o*-DCB is an even better solubilizing solvent than chlorobenzene,^[34] we would assume, that this causes a further decrease in the binding strength. The literature reported association for the before mentioned corannulene receptor reaches values of $K_a = (5.2 \pm 0.2) \times 10^2 \text{ M}^{-1}$ for C_{60} and $K_a = (9.2 \pm 0.9) \times 10^2 \text{ M}^{-1}$ for C_{70} for NMR measurements in chlorobenzene.^[10] In a direct comparison, neglecting the different solvents, our buckybowl catcher shows a higher affinity and selectivity towards C_{70} by one order of magnitude. Additionally, the formation of the complex with C_{70} was corroborated in the gas phase by APPI mass spectrometry (see Figure S9 in the Supporting Information). Due to the relatively high binding constant provided by the shape complementarity and π - π -interactions, the buckybowl catcher can be employed in the future for the formation of electron transfer complexes with unsubstituted fullerenes, by the addition of donor molecules to the tether between the indacenopicene moieties.

Conclusions

In conclusion, a novel indacenopicene-based molecular fullerene catcher has been prepared and investigated. Theoretical calculations indicated the possibility of effective hosting of fullerenes inside the catcher cavity. The complex formation of the catcher with fullerenes C_{60} and C_{70} was investigated with different spectroscopic techniques. The NMR titrations were most indicative in this case were a complex formation in a 1:1 ratio with either fullerene can be observed. In addition to the expected shift of the indacenopicene proton signals upon complex formation with fullerenes, an unusual shift of the proton signal of the tolyl linker facing the fullerene was observed. Taking into account the data on spherical aromaticity of fullerenes, we can assume that this proton can serve as a sensor of aromaticity. Thus, to the best of our knowledge, the first probe catcher for spherical aromaticity was developed. Additionally, the complex between the catcher and C_{70} was detected in the gas phase. Global analysis of the NMR data showed a higher affinity of the catcher towards C_{70} compared to C_{60} . The achieved bindings could serve as the basis for future research in the application of the catcher system for more advanced supramolecular assemblies towards electron-transfer complexes with fullerenes.

Experimental Section

The synthesis of compound **2** was described by us previously.^[21] Compounds **3** and **5** were synthesized according to literature known methods.^[25,26]

Preparation of Catcher 1

4-Bromo-13,16-difluorobenzo[*s*]picene **2** (13.5 mg, 0.033 mmol, 2.2 eq.), 2,2'-(5-methyl-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **5** (5.24 mg, 0.015 mmol, 1.0 eq.), K_2CO_3 (4.21 mg, 0.030 mmol, 2.0 eq.) and 5 mol% $Pd(PPh_3)_4$ were suspended in a Tol:MeOH 2:1 mixture (30 mL), the reaction mixture was degassed, and the atmosphere was exchanged with Ar. The mixture was heated to reflux for 16 h, diluted with toluene (10 mL) and washed with water. After removal of the solvents, the resulting yellow solid was washed with toluene and the desired catcher was received in 53% yield (6.0 mg, 8.1 μ mol).

¹H NMR [600 MHz, *o*-DCB-*d*₄, 298 K]: δ (ppm) 8.09 (d, $J=8.85$ Hz, 2H), 8.02-7.98 (m, 5H), 7.80 (d, $J=7.15$ Hz, 2H), 7.71 (d, $J=8.70$ Hz, 2H), 7.67-7.63 (m, 8H), 7.58 (d, $J=7.76$ Hz, 4H), 7.36-7.32 (m, 2H), 2.60 (s, 3H).

¹³C NMR [151 MHz, *o*-DCB-*d*₄, 298 K]: δ (ppm) 140.91, 139.94, 139.35, 138.89, 138.82, 138.74, 138.56, 138.51, 138.44, 138.33, 138.05, 137.73, 137.01, 130.16, 130.10, 130.02, 129.44, 129.32, 128.97, 128.65, 127.27 (CH), 127.03 (CH), 126.84 (CH), 126.26 (CH), 125.68 (CH), 125.47, 124.40, 124.05, 123.79 (CH), 123.50, 21.69 (CH₃).

MS [LDI] m/z (rel. int.) = 736.65 [M] + (100).

HRMS [APPI, Toluene, DCM] Chemical Formula: $C_{59}H_{28}$ calc. 736.2186, found 736.2195.

Supporting Information

The authors provided additional references in the Supporting Information.^[21,25-27,35]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: host-guest systems · buckycatcher · fullerenes · indacenopicene · supramolecular chemistry

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