

Positron Annihilation Lifetimes in Cucurbiturils: Evidence of Internal Inclusion of Gold in CB[7]

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Positron annihilation lifetime (PAL) measurements are carried out to determine the cavity dimensions of hydrated and dehydrated cucurbiturils (CB[n]; $n=5,6,7,8$). In the case of hydrated samples, the dimensions of the cavity are unrelated to the number of glycoluril units of the CB, whereas for dehydrated samples the cavity dimensions measured by PAL follow the expected order, although the experimental values obtained by

PAL are significantly smaller than the dimensions of each CB determined by crystallography. For a host–guest complex in which colloidal gold nanoparticles are assumed to be included inside CB[7], a significant reduction of the cavity size is measured. This represents an experimental evidence of the inclusion of gold inside CB[7], which complements previous high-resolution transmission electron microscopy (TEM) images.

1. Introduction

Cucurbiturils (CB) are pumpkin-shaped organic capsules that have attracted considerable attention in supramolecular chemistry due to the remarkable stability of their host–guest complexes.^[1] Structurally, CBs are formed by glycoluril units linked by methylene bridges.^[1] Depending on the number of glycoluril units, the dimensions of the internal void of the organic capsule vary. The sizes of the pore opening and maximum diameter of the capsules have been determined by crystallography and match well with the expected values according to molecular models.^[1]

Typically, pore diameter and pore volume of micro- and mesoporous solids are routinely measured experimentally by isothermal gas adsorption.^[2–4] This technique for determining micro/mesoporosity is particularly important for compounds and materials whose structure is unknown or subject to the presence of structural defects. In the case of CBs there is in principle no urgent need to undertake microporosity measurements because, when chemically pure, the precise structure of these organic molecules allows the opening pore size and pore volume to be accurately known. However, when an inclusion complex is formed porosity measurements may be useful to provide experimental evidence on guest location inside the analyzed host. As will be discussed below, standard isothermal nitrogen adsorption unexpectedly cannot be used for porosity measurements in CBs. For this reason, and in order to obtain experimental data that supports the internal location of guests inside CBs, we performed positronium annihilation lifetime (PAL) measurement on CBs and the gold cucurbit[7]uril host–guest complex Au@CB[7].

Measurements of PALs have long been used to determine internal volumes in materials such as polymers and other molecular solids without pore openings that allow mass transfer from the exterior of the pore to the interior of the void space.^[5,6] The physical basis of positron annihilation resides in its capability to sense electron density in the bulk of the material. Under certain conditions, in a condensed medium a posi-

tron and an electron can form a bound state, called positronium (Ps).^[7] In condensed matter, *ortho*-positronium (*o*-Ps), in which the spins of the two particles are oriented in parallel, is commonly annihilated with an electron of the medium to give two γ quanta (pick-off).^[7] The lifetime of *o*-Ps is related to the dimensions of the void volume of a material, and there are many examples of using a well-known semi-empirical model to correlate *o*-Ps lifetime and void dimensions.^[8] For small micropores, such as those expected in CBs, the general expression correlating *o*-Ps lifetime (τ /ns) and average cavity dimension ($R/\text{Å}$) is Equation (1):

$$\tau = \frac{1}{2} \left[1 - \frac{R}{R + 1.66} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + 1.66} \right) \right]^{-1} \quad (1)$$

In related precedents to our work,^[9,10] PAL measurements were used to determine the empty volume of host–guest complexes of cyclodextrins with gases,^[11,12] organic molecules, and fullerenes.^[10,13,14] These PAL measurements support inclusion of the guest inside the cyclodextrin.^[11,14] However, as far as we know, no similar studies have yet been reported for CBs. Our interest lies specifically in providing additional evidence to support inclusion of gold nanoparticles inside CB[7] to form the supramolecular entity Au@CB[7].^[15] Prior work has shown that CB[7] exhibits the unique capability to include gold nanoparticles, while similar attempts failed for CB[6] and CB[8].^[15]

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This conclusion was based on high-resolution transmission electron microscopy (HRTEM) images as well as on other indirect evidence based on gold reactivity.^[15] In the present work, we carried out PAL measurements to determine the pore dimension of CB[n] ($n=5-8$), dry or ambient-equilibrated, and we compared the data obtained with those of an Au@CB[7] sample. The results provided by PAL measurements are also in agreement with previous data in favor of the formation of a gold-cucurbituril inclusion complex.^[15]

2. Results and Discussion

Preliminary studies on isothermal nitrogen adsorption have shown that this technique is unable to detect microporosity in CBs. This result is surprising, since nitrogen adsorption is the standard technique to determine microporosity in zeolites and related materials in which the pore opening varies from 0.4 to 0.8 nm in small to large pore zeolites.^[4] These pore sizes correspond to the range of pore sizes expected for CBs.^[2] One possible explanation for the failure of the isothermal gas adsorption technique to determine the porosity of CBs could be related to the impossibility to completely dehydrate CB samples by thermal treatment and/or that only a few residual water molecules are sufficient to block CB openings. Alternatively, the polarity of the CB portals flanked by carbonyl groups creates a high polarity in the region that could impede the access of apolar gas molecules to the interior. Whatever the reason for the failure of isothermal nitrogen adsorption measurements, we turned to PAL measurements as an alternative to obtain data on the cavity dimensions.

Two series of samples, dried by thermal treatment at 150 °C (under a reduced pressure of 0.1 Torr or ambient-equilibrated), were studied. Based on thermogravimetry it is known that ambient-equilibrated CBs contain water, which probably interacts through hydrogen bonding with the CB carbonyl groups. The percentage of water varies from 15 to 18%, depending on the number of glycoluril units. Figure 1 shows the thermogravimetric profile and its first derivative of a representative ambient-equilibrated CB[7] sample.

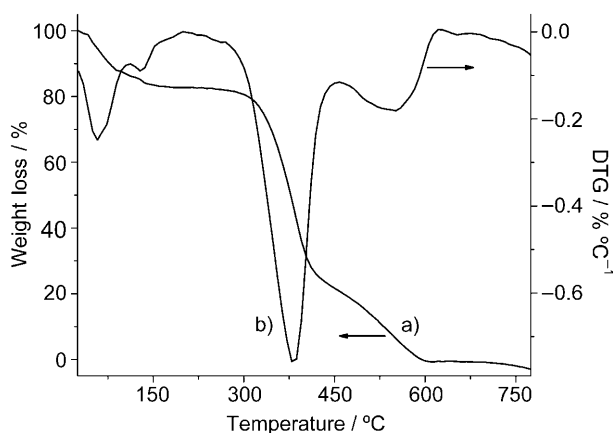


Figure 1. Thermogravimetric analysis (a) and first derivative (b) recorded for ambient-equilibrated CB[7]. The weight loss up to 300 °C (17%) is considered to be due to water desorption.

The PAL measurements were carried out on a conventional fast-fast coincidence apparatus, with an ²²Na source deposited on a kapton foil and a temporal resolution (full-width-at-half-maximum, FWHM) of 240 ps. The PAL data were fitted to three exponential decay components by using the POSITRONFIT program.^[6] The first and second lifetime components take into account positron annihilation in CB regions with different electron densities. The first lifetime τ_1 also includes *p*-Ps annihilation ($\tau_{p-Ps}=125$ ps), while τ_2 accounts for free-positron annihilation ($\tau_{\text{kapton}}=386$ ps). The long-lived component (τ_3) is the relevant one for void determination, since it corresponds to *o*-Ps annihilation in the void space, and according to the Tao-Eldrup model it correlates with the cavity dimensions through Equation (1). Figure 2a,b shows the resulting positron annihilation kinetic parameters, that is, lifetimes τ_i and their corresponding intensities I_i versus the number of glycoluril units for

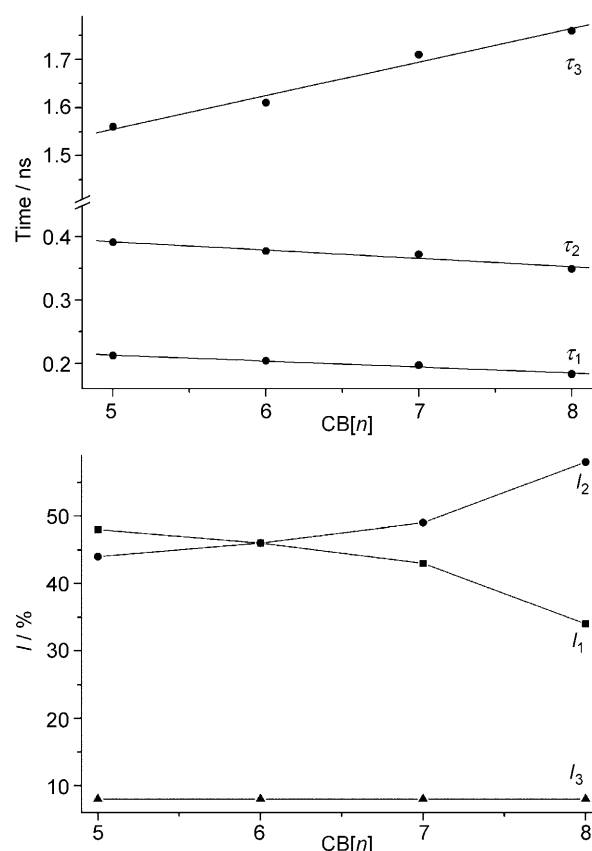


Figure 2. PAL kinetic parameters for the positron decay of dehydrated CB[n] as a function of the number of glycoluril units. a) Lifetimes τ_i . b) Intensities I_i of the relative components.

the studied CBs. The *o*-Ps lifetime τ_3 increases with the number of glycoluril units. By using Equation (1), the cavity diameter was estimated for each CB in the presence and absence of water molecules. The results are listed in Table 1, in which the crystallographic diameters of the internal spaces of CBs are also given for comparison.

As shown in Table 1, the data obtained from PAL measurements do not agree with those obtained from crystallography,

	Crystallographic diameter [nm]		PAL diameter [nm] ^[a]	
	Portal	Cavity	Dehydrated	Hydrated
CB[5]	0.24	0.44	0.48 ± 0.01	0.53 ± 0.02
CB[6]	0.39	0.58	0.49 ± 0.02	0.51 ± 0.02
CB[7]	0.54	0.73	0.51 ± 0.02	0.53 ± 0.03
CB[8]	0.69	0.88	0.52 ± 0.03	0.54 ± 0.03

[a] Errors based on the quality of temporal profile fit obtained by the POSITRONFIT software.

even for dehydrated CBs. Although the data listed in Table 1 are affected by unavoidable experimental errors, there is notable discrepancy between the crystallographic diameters and the values estimated by PAL measurements. Typically, this discrepancy is particularly relevant for the largest CB[8] (0.36 nm) and is much smaller for the smaller members of the family. One possible explanation for these differences between crystallography and PAL measurements would be that the largest CB exhibits some flexibility, and when dehydrated it could be distorted with a large deviation from the symmetric circular CB observed by crystallography on crystallized samples containing water. Alternatively, incomplete dehydration could mean that the presence of some remaining water molecules decreases the positron lifetime τ_3 ,^[16] and thus a smaller estimate for the size of the void results.

Table 1 also lists data for hydrated CBs.^[17] The PAL measurements on ambient-equilibrated CBs give larger void dimensions than those on the dehydrated samples, in spite of the fact that water should occupy some intracapsule space. It is noteworthy that the cavity dimensions of hydrated CBs do not differ much in dependence on the number of glycoluril units; the measured values are consistently around 0.53 nm. The most likely explanation for these experimental results is that, in the case of hydrated CBs, *o*-Ps experiences external cavities defined by the ensemble of water and CBs spatially arranged through hydrogen bonds rather than the internal cavity of the organic capsule. In any case, the PAL measurements on hydrated CBs seem to be uncorrelated with their internal voids. For this reason, it appears that measurements on CBs should be performed on dehydrated samples.

In Figure 2b it is noteworthy that while I_3 remains almost constant along the CB series, I_1 and I_2 depend on the CB size. Although the long-lived lifetime τ_3 is the parameter commonly correlated with the free volume, the other two lifetimes and their intensities may contain some information on the nature of the medium, because transformation of free positrons (intensity I_2) into *p*-Ps (intensity I_1) requires interaction with the medium.^[18] In the present case, the electronic density is located in the glycoluril units, while the portals and internal cavities are mainly considered to be empty spaces without matter. Then, if the transformation of free positrons into *p*-Ps requires electrons, this process should occur preferentially at the walls of the organic capsule, and consequently a relationship between intensity ratios and surface area could be experimentally

obtained. In fact, we observed an evolution of their relative intensities with CB structure. Figure 3 plots the I_2/I_1 ratio versus the ratio between the external surface area of each cavity and the corresponding entrance area defined by the carbonyl por-

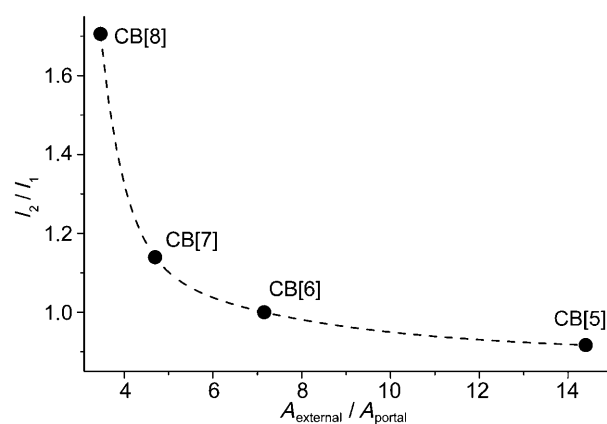


Figure 3. Influence of the external/portal area ratio of the CBs on the relative intensities of the τ_1 and τ_2 lifetimes. This relationship suggests that the τ_2 component of the positron lifetime is sensitive to the portal area of CBs.

als. It was found that the intensity ratio diminished monotonically with decreasing number of glycoluril units. This indicates that I_1 and I_2 are preferentially related to lateral and entrance CB surfaces, respectively.

Since the positron is a good probe to sense the void volume in porous materials, we applied the PAL technique to study a CB[7] sample containing gold (Au@CB[7]). This sample was prepared as previously reported by sodium borohydride reduction of HAuCl₄ in water/ethanol solutions containing CB[7] in molar proportion 1:1.^[15] High-resolution TEM images indicate that, for this Au@CB[7] sample, gold nanoparticles have a very narrow size distribution with an average diameter of less than 1 nm and that the surface is covered by a carbon layer due to the CB capsule. To illustrate gold nanoparticle size when the gold colloids are prepared in the presence of CB[7], Figure 4 shows a selected TEM image for the Au@CB[7] sample used in the present study.

This behavior of CB[7] was unique, and the same reduction procedure in the presence of other CBs give nanoparticles of average size 4–5 nm, in agreement with the particle size expected in the absence of CB capsules.^[15] Clearly, for CBs other than CB[7] particles are too large to be included inside the organic capsule, while for CB[7] the data point to the internal location of gold nanoparticles respect CB[7].

To provide evidence for the internal location of gold in CB[7] we studied by PAL three related samples, namely, dehydrated Au@CB[7], Au nanoparticles in the absence of CB[7], and dehydrated CB[7] in the absence of any gold. The PAL spectra were also fitted to three exponential decays, from which τ_3 and its corresponding intensity were obtained. Figure 5 shows the results obtained for τ_3 . From the corresponding τ_3 values, the cavity dimensions were obtained by applying the Tao–Eldrup model. The PAL measurements on the Au@CB[7] sample give a cavity dimension of 0.47 nm, with a density of pores correlated

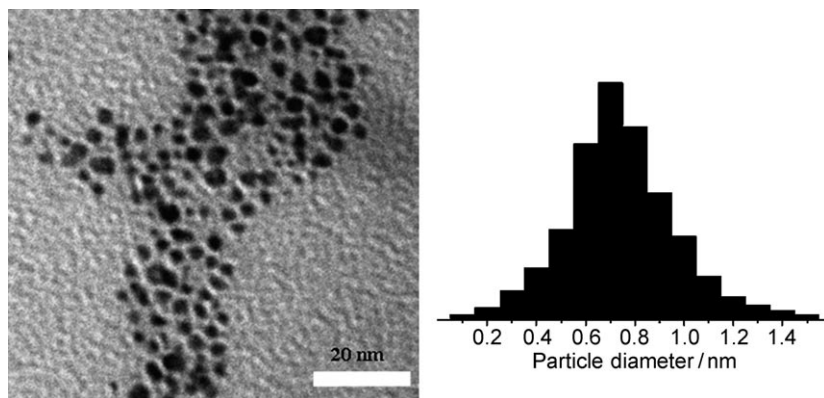


Figure 4. TEM image of Au@CB[7]. The scale bar corresponds to 20 nm. The right bar chart shows the statistical analysis of the size distribution of gold particles.

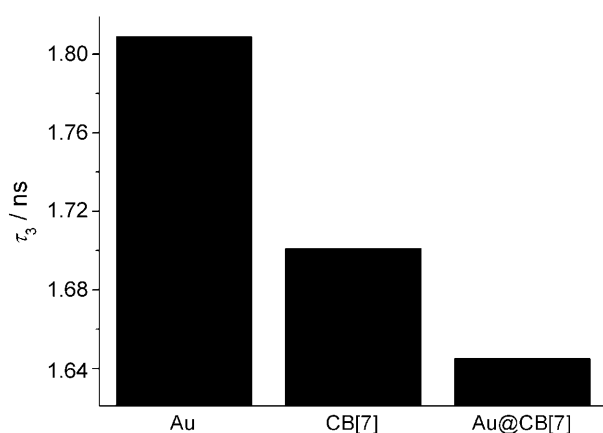


Figure 5. PAL measurements on dehydrated CB[7], the Au@CB[7] host–guest complex, and Au nanoparticles.

with an intensity factor accompanying τ_3 of $8 \pm 0.1\%$. This cavity size was smaller than that measured for dehydrated CB[7] (0.51 nm). In addition, the density of these cavities for CB[7] was $9 \pm 0.1\%$. Comparison of the experimental data for the same amount of CB[7] indicates that on going from CB[7] to Au@CB[7] the cavity dimension and its density decrease. Interestingly, the sample consisting of gold nanoparticles prepared analogously to Au@CB[7] but in the absence of CB[7] shows larger cavities (0.53 nm) but with a lower density ($5 \pm 0.1\%$). We interpret these data by considering that agglomerated gold nanoparticles tend to define some pores, but the population of these pores is low.

These results indicate that the presence of gold inside CB[7] reduces the average internal void of the capsule while still leaving some residual microporosity due to empty or incompletely filled capsules. In the case of colloidal gold, the absence of CB[7] allows the nanoparticles to agglomerate to form even larger pores, but in substantially lower intensity. Overall, the experimental data obtained by PAL measurements also support the internal location of gold in CB[7].

3. Conclusions

Measurements of PAL have been carried out to estimate the void size in polymers and semiconductors by determining the long-lived component τ_3 . Applying this technique to estimate the average cavity dimensions of CBs revealed no differences in the cavity size of hydrated CBs as a function of the number of glycoluril units. In contrast, for dehydrated CBs, the PAL measurements show that the cavity dimensions increase with the number of glycoluril units.

However, there is a remarkable discrepancy between the PAL values and those determined by crystallography. Among the possible reasons for this discrepancy, we suggest that there could be a residual population of strongly adsorbed water molecules, or large CBs may not be in the spherical conformation determined for CB crystals. In addition, we have gained information on the electronic densities of CBs on the basis of the relationship between the I_2/I_1 ratio and the external surface area of the capsule. Finally, PAL measurements on CB[7] reveal a reduction in the average cavity volume for the same amount of CB[7] on going from dry CB[7] to dehydrated Au@CB[7]. These results on CBs parallel those found previously for cyclodextrins, which were interpreted as evidence of guest inclusion inside the organic capsule.^[14] Thus, the present PAL measurements are compatible with our previous conclusion that in Au@CB[7], gold nanoparticles occupy the internal voids of CB[7].

Experimental Section

CBs, HAuCl₄, and NaBH₄ were supplied by Sigma-Aldrich and used as received to prepare gold nanoparticles Au@CB[7] by following the synthetic method previously reported.^[15] CBs were treated overnight under vacuum to remove any water molecules included in the capsules. Thermogravimetric analysis was carried out in a NETZCH SAT409 EP apparatus coupled to an ATD unit with a heating rate of 10°Cmin^{-1} , and the first derivative of the plot was obtained informatically. PAL measurements were done at room temperature in a conventional fast-fast coincidence system with two plastic detectors. The time resolution (FWHM) was 260 ps, and 3×10^6 counts were accumulated for each spectrum. The radioactive source, ²²NaCl (10 μCi), was deposited onto a kapton foil (1.42 g cm^{-3}) and sandwiched between two sample specimens. The source contribution (17% of 386 ps for annihilation in kapton foil and 1% of 1.9 ns) and the response function were evaluated from a reference sample (Ni metal) by using the RESOLUTION code.^[19,20] After subtraction of background and source contributions, positron annihilation parameters were obtained from the PATFIT program.^[19,20] TEM images and particle sizes were obtained in a 100 kV Philips microscope, whereby a drop of a suspension of the CB encapsulated gold was placed on a conductive graphitized grid.

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Keywords: cucurbiturils • gold • host–guest systems • nanoparticles • positron lifetime spectroscopy

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