

# Synthesis of *p*-tert-butylcalix[4]arene semitubes and their binding studies with C<sub>60</sub>

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**Abstract** The synthesis of *p*-tert-butylcalix[4]arene semitubes in one step reaction with fairly good yields is described. The structures of these compounds were confirmed by <sup>1</sup>H NMR, <sup>13</sup>CNMR and mass spectrometry. The complexation ability of these compounds with C<sub>60</sub> was investigated and found that they are able to form 1:1 complexes. The stability constants of these complexes were determined and found to be 15, 203 and 525 dm<sup>3</sup> mol<sup>-1</sup> for the semitubes **3a**, **3b**, **3c** respectively. The binding energies of each of C<sub>60</sub>, the semitubes and the complexes are calculated using PM6 (Semiempirical quantum chemical) and DFT (Density Functional Theory) methods and found in the order  $m > p > o$ . On the other hand, the calculated binding energies using DFT method showed that the stabilities of both centered and side complexes are in the order  $p > m > o$ .

**Keywords** *p*-tert-Butylcalix[4]arene · *p*-tert-Butylcalix[4]semitubes · Fullerene · C<sub>60</sub> · Stability constants · PM6 · DFT

## Introduction

Calix[n]arenes have been used as artificial receptors for cations, anions and neutral organic molecules. The lower or upper rims of calix[4]arene units can be modified to achieve sophisticated structures which serve as potential hosts species for specific guests [1]. Different lower-rim modifications of calix[4]arenes have been designed and

synthesized by attaching different functional groups to the phenol units [2–5].

Calixtubes are double calixarenes where two calixarene units are linked at their lower rims (tail-to-tail) using a spacer group through the four phenolic hydroxyl groups [6]. In 1997, the synthesis of the parent symmetric calix[4]tube (**1**) was reported as shown in Scheme 1 [7].

Beer et al. [8] prepared a non symmetrical calix[4]tube using xylene as a solvent in the presence of K<sub>2</sub>CO<sub>3</sub>. It was found that calix[4]tubes are highly selective for potassium ion among alkali metal ions [7].

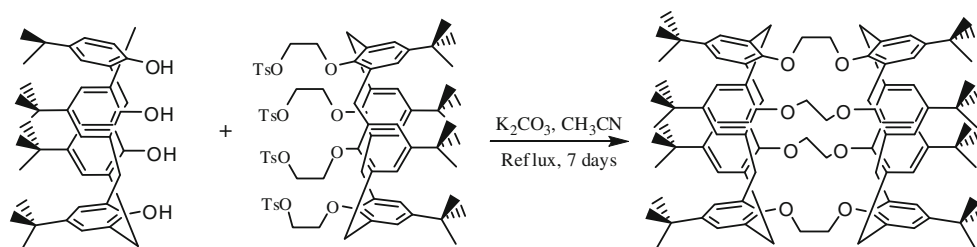
Calix[4]semitubes, such as (**2**), are also double calixarenes where the calixarene units are linked through the 1,3-phenolic hydroxyl groups [8].

In the synthesis of most calixtubes or calixsemitubes, it was found that they are highly selective for potassium ion among alkali metal ions and K<sup>+</sup> that came from K<sub>2</sub>CO<sub>3</sub> was trapped in the channel of the tube [7] (Fig. 1).

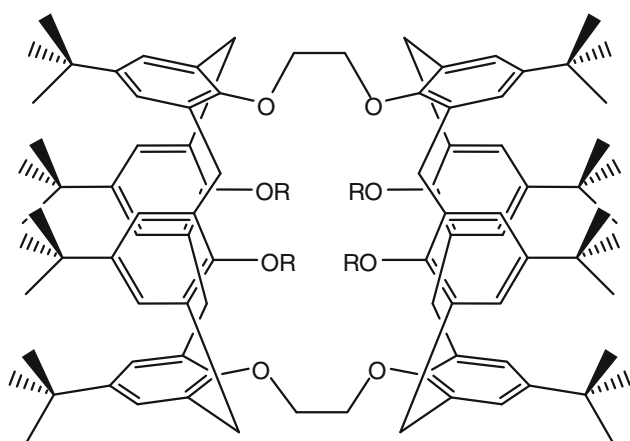
None of the reported synthesis of the tubes or semitubes were synthesized in one step, they all need more than one step.

[60]Fullerene, C<sub>60</sub>, is considered an electron acceptor due to its π-electron system and this enables it to be a potential guest in the field of host–guest chemistry, specially with calix[4]arene derivatives. This type of host–guest interaction have successfully been applied to the purification of fullerenes [9, 10], water solubilization of fullerenes [11], photocleavage of DNA [12], design of photovoltaic cells [13]. Recently, Perez [14] published a review article that includes historical notes on the noncovalent chemistry of fullerenes. Shinkai and coworkers [15–21] and Bhattacharya and coworkers [22, 23] independently reported extensive studies on the complexation of C<sub>60</sub> with different calixarene derivatives using different methods. Previously we reported complexation studies of

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**Scheme 1** Synthesis of the first symmetrical *p*-*t*-butylcalix[4]tube (**1**)



**Fig. 1** Symmetrical *p*-*t*-butylcalix[4]semitube (**2**)

naphthalene based calixarenes and corannulenes derivatives with  $C_{60}$  [24–28]. Most of the published studies on the complexation of fullerenes are with calixarene derivatives. Up to our knowledge there are no reports on the formation of complexes of calix[4]semitubes with fullerenes, this motivates us to conduct this study.

In this study we aimed to synthesize some calix[4]semitubes using (*ortho*, *meta* or *para*)  $\alpha,\beta$ -dibromoxylene (xylyl dibromide) as a spacer in single step and study their complexation with  $C_{60}$  using UV–Vis. spectroscopy and PM6 and DFT molecular modeling methods.

## Experimental

### Materials and equipment

Chemicals were purchased from Aldrich, Janssen Chimica, GCC and Fluka, and were used without further purification except  $CH_3CN$  which was distilled before using. Melting points were determined using an electrothermal–digital melting point apparatus and they were not corrected.

The  $^1H$  and  $^{13}C$  NMR spectra were recorded on 400 and 100 MHz respectively, using Bruker Avance III. Chemical shifts were recorded as  $\delta$  values in ppm. Spectra were acquired in (DMSO- $d_6$ , 1 % TMS) or  $CDCl_3$ , and the peaks due to the residual of DMSO- $d_6$  (2.50 ppm for  $^1H$

and 39.43 ppm for  $^{13}C$ ) and  $CDCl_3$  (7.26 ppm for  $^1H$  and 77.00 ppm for  $^{13}C$ ) are used as references if TMS is not available.

Mass spectra were determined by MSA/A017 or LC-MSD-Trap. The absorption spectra were measured by using double beam spectrophotometer “Shimadzu Corporation” UV-2401 (PC).

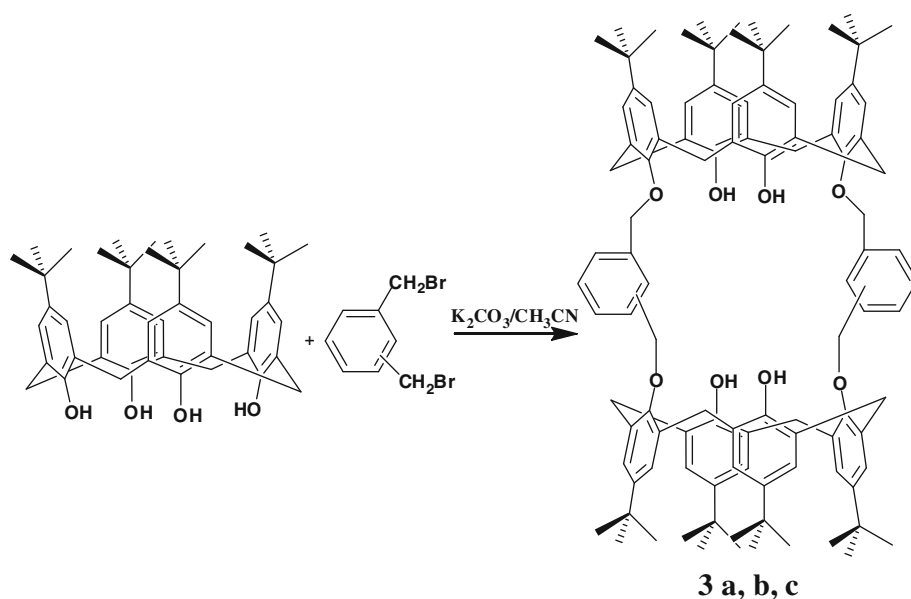
### General synthesis of compounds (**3a**, **3b**, **3c**)

In 100 ml two-necked flask equipped with a magnetic stirrer and reflux condenser, *p*-*tert*-butylcalix[4]arene and anhydrous  $M_2CO_3$  ( $M = Na, K, \text{ and } Cs$ ) were mixed with anhydrous  $CH_3CN$  and refluxed for 1 h, at the reflux temperature  $\alpha,\beta$ -dibromoxylene (*ortho*, *meta* or *para*) in  $CH_3CN$  was added dropwise, Scheme 2. Then the mixture was further refluxed for 4 days. After that the mixture was filtered and cooled, and compounds (**3a**, **3b**, **3c**) were precipitated and collected to give colorless solids that decompose at  $T > 310^\circ C$  with yield 54 %.

The spectral data of compound (**3a**):  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 1.15 (36H, s,  $C(CH_3)_3$ ), 1.22 (36H, s,  $C(CH_3)_3$ ), 3.24 (8H, d,  $J = 12.3$  Hz,  $ArCH_2$ ), 4.37 (8H, d,  $J = 12.3$  Hz,  $ArCH_2$ ), 5.75 (8H, s,  $ArCH_2O$ ), 6.73 (8H, s,  $ArH$ ), 6.93 (8H, s,  $ArH$ ), 7.54 (4H, broad s, OH), 7.86 (4H, broad s,  $ArH$ ), 8.49 (4H, broad s,  $ArH$ ). MS:  $(M+H)^+ = 1540.9, 1524.7, 1634.8$ , with  $K^+, Na^+, Cs^+$  respectively.  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$ : (31.2, 31.4, 32.0, 33.9, 34.1, 76.1, 125.1, 125.4, 126.0, 127.7, 128.6, 130.3, 135.3, 141.4, 147.0, 150.2, 150.9) dept 135: +ve (31.2, 31.4, 125.1, 125.4, 128.6, 130.3), –ve (32.0, 76.1).

Compound (**3b**) has the following spectral data:  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 0.92 (36H, s,  $C(CH_3)_3$ ), 1.19 (36H, s,  $C(CH_3)_3$ ), 3.21 (8H, d,  $J = 12.0$  Hz  $ArCH_2$ ), 4.18 (8H, d,  $J = 12.0$  Hz  $ArCH_2$ ), 4.95 (8H, s,  $ArCH_2O$ ), 6.73 (8H, s,  $ArH$ ), 6.93 (8H, s,  $ArH$ ), 7.32 (4H, broad s, OH), 7.53 (4H, s,  $ArH$ ), 7.87 (2H, s,  $ArH$ ), 7.89 (2H, s,  $ArH$ ), MS:  $(M+H)^+ = 1540.9, 1524.7, 1634.8$ , with  $K^+, Na^+, Cs^+$  respectively.

Finally the spectral data of compound (**3c**):  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 1.14 (36H, s,  $C(CH_3)_3$ ), 1.17 (36H, s,  $C(CH_3)_3$ ), 3.25 (8H, d,  $J = 12.5$  Hz,  $ArCH_2$ ), 4.20 (8H, d,

**Scheme 2** General synthesis of compounds (**3a**, **3b**, **3c**)

$J = 12.5$  Hz, ArCH<sub>2</sub>), 5.09 (8H, s, ArCH<sub>2</sub>O), 6.77 (8H, s, ArH), 6.98 (8H, s, ArH), 7.43 (4H, s, OH), 7.77 (8H, s, ArH) MS: (M+H)<sup>+</sup> = 1,540.9, 1,524.7, 1,634.8, with K<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup> respectively. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : (31.0, 31.7, 32.0, 33.8, 33.9, 77.8, 124.9, 125.5, 126.9, 127.6, 132.6, 137.2, 141.1, 146.9, 150.7, 150.9) dept 135: +ve (31.0, 31.7, 124.9, 125.5, 126.9), -ve (32.0, 77.8).

#### Computational method

For all complexes, free ligands and C<sub>60</sub> were initially optimized by the recently published semiempirical method MP6[29] using G09 [30].

Energy was calculated by implementing the B97D [31] Grimme's functional to account for dispersion forces and the  $\pi$ - $\pi$  stacking, and by using the MIDI! Basis set [32].

Considering we only need to compare the relative binding affinity for the three ligands with C<sub>60</sub> rather than computing the absolute values of binding energies, using such minimal basis set and ignoring the Basis Set Superposition Error (BSSE) was justified.

#### Results and discussion

General note: The purity of each product was checked by Thin Layer Chromatography (TLC) plate and the spots were visualized under UV light. The <sup>1</sup>H NMR spectra of *p*-*tert*-butylcalix[4]arene usually show a pair of doublets for the bridging methylenes. In our compounds where the <sup>1</sup>H NMR data was collected in DMSO-d<sub>6</sub>, this pair of doublets doesn't clearly appear as it should be, while it appears clearly in CDCl<sub>3</sub>.

Compound (**3a**) was prepared from *p*-*tert*-butylcalix[4]arene and  $\alpha,\alpha$ -dibromo-*o*-xylene in the presence of K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> or Cs<sub>2</sub>CO<sub>3</sub> with dry CH<sub>3</sub>CN as a solvent. The structure of this compound was confirmed by mass spectrometry, the positive peak shows exactly the (M+M')<sup>+</sup> with M'<sup>+</sup> (M' = Cs, K, Na) trapped inside the cavity. The structure was also confirmed by <sup>1</sup>H NMR, which displays two unresolved doublets that appear as broad singlets at  $\delta$  7.41 ppm, four H's and 7.98 ppm, four H's (suppose to be pair of doublets) for the xylene aromatic protons of the spacers. <sup>1</sup>H NMR data also displays two singlets at  $\delta$  1.15 and 1.20 ppm 36 H's each for the *tert*-butyl groups. This confirms the symmetrical structure of this semitube. This symmetrical structure is also proposed for other semitubes due to the existence of the same two singlets at nearly the same range. Using any of the K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> or Cs<sub>2</sub>CO<sub>3</sub> salts gave the proposed product with the corresponding ion trapped inside the channel of the tube.

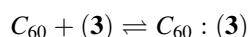
The formation of other products such as 1,2-disubstituted, monosubstituted, trisubstituted or tetrasubstituted (calixtubes) are possible. We are interested in isolating the major product in each case which is the semitube in all cases. The spectroscopic data confirms the proposed structure in each case, the rigidity of the compounds excludes the formation of 1,2-disubstituted rather than 1,3-disubstituted, since 1,2-disubstituted is more flexible and might have a 1,2-alternate conformation which is not shown by NMR. This conclusion is also applied on the isolated compounds (**3b**, **3c**).

The mass spectra of compounds (**3a**, **3b**, **3c**) show molecular ion peaks at 1,540, 1,524, and 1,634 for the corresponding semitube with alkali metal trapped inside its channel.

The synthesis of these semitubes is a novel synthesis due to its simplicity and the good yield obtained. Further investigation on the effect of base, temperature, and solvent on the yield will be conducted on due time.

#### Complexation of $C_{60}$ with compounds (**3a**, **3b**, **3c**)

When a purple toluene solution of  $C_{60}$  is mixed with a colorless solution of (**3**) a light brown solution is developed. This color change indicates the formation of a charge transfer complex which is represented by the following reaction:



as the concentration of (**3**) increases the intensity of the absorption spectrum in the range of 400–430 nm increases. However, compound (**3**) does not absorb in this range. This behavior was noted previously with the complexation of  $C_{60}$  and other host molecules [24–28].

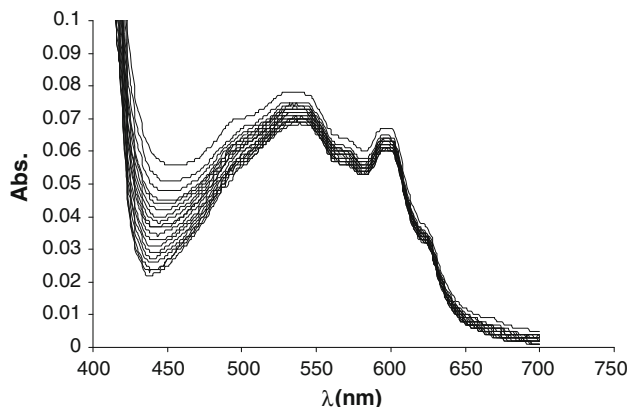
Figure 2 shows the absorption spectrum of the complex. It should be noted that the stoichiometry of this complex was determined to be 1:1, using Jobs method (continuous variation method) [33] as shown in Fig. 3.

The formation constant is determined by applying Benesi–Hildebrand equation [34]:

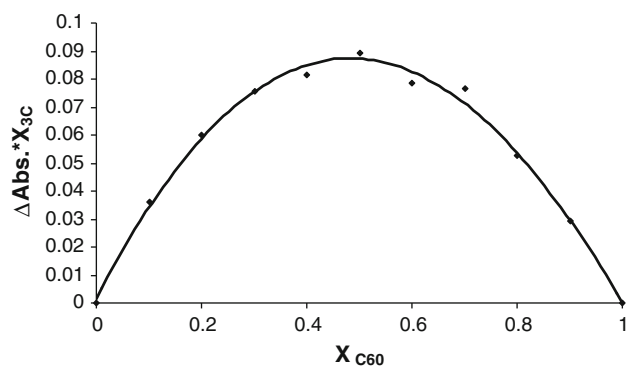
$$[A_o]/\Delta A = 1/([D_o] \cdot \epsilon \cdot K_c) + 1/(\epsilon) \quad (1)$$

where  $A_o$  is the concentration of  $C_{60}$ ,  $D_o$  is the concentration of (**3**),  $\Delta A$  is the absorbance change, at  $\lambda = 431$  nm, and  $\epsilon$  represents the molar extension of the  $C_{60} : \mathbf{3}$  complex. A plot of  $[A_o]/\Delta A$  vs  $1/[D_o]$  gives a straight line with good correlation as shown in Fig. 4,  $K_c$  value was calculated by dividing the intercept over the slope.

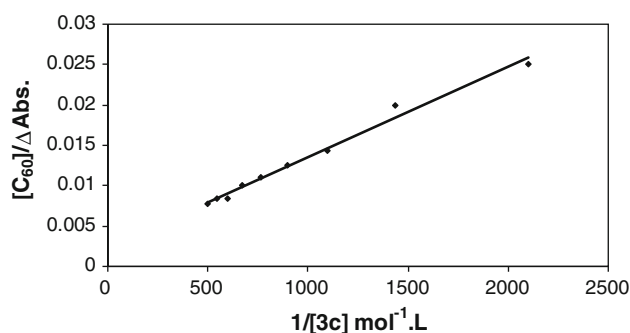
Table 1 lists the formation constant  $K_c$  values for the charge transfer complexes formed between  $C_{60}$  and compounds (**3a**, **3b** or **3c**). These values generally give an



**Fig. 2** The absorption spectra of compound **3c** with  $C_{60}$



**Fig. 3** The jobs plot of  $C_{60} : \mathbf{3c}$  complex



**Fig. 4** A typical Benesi–Hildebrand plot of  $C_{60} : \mathbf{3c}$  complex

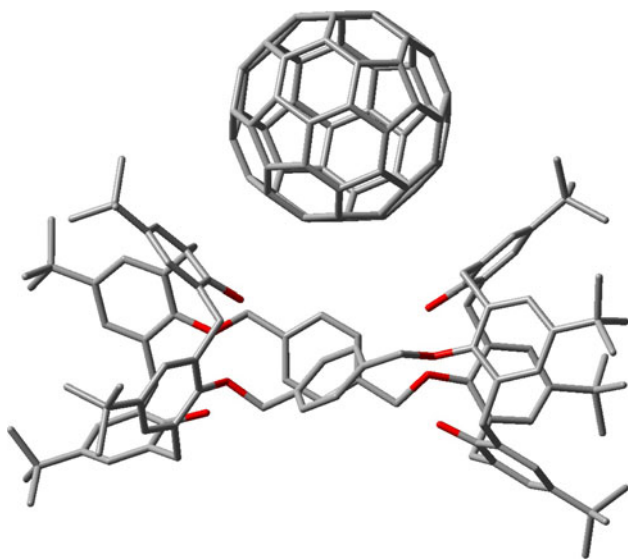
**Table 1** The formation constants ( $K_c$ ) and  $\log K_c$  values for the complexes of  $C_{60}$  with (**3a**, **3b**, **3c**)

Donor	$K_c$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$\log K_c$
( <b>3a</b> )	$15 \pm 2$	1.18
( <b>3b</b> )	$525 \pm 23$	2.72
( <b>3c</b> )	$203 \pm 18$	2.31

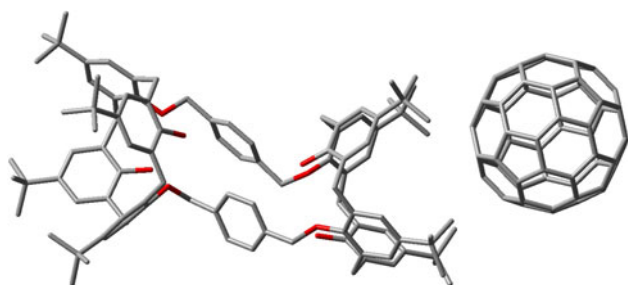
indication about the stability of the complexes between donors and acceptors.  $K_c$ -value increases as the stability of the complex increases. It also gives an indication about the strength of the interaction between the donors and the acceptors. These values may give an indication about the structure of the complex, the dependence of the stability of the complex on the size of the internal cavity of the calix[4]semitube reveals that  $C_{60}$  may be included in that cavity or included in the external groove that formed between the two calixarene units (the center complex above). The higher  $K$  value is for (**3b**) complex, this could be due to best matching between  $C_{60}$  and the cavity or the groove of *m*-calix[4]semitube, while the least matching is that of *o*-calix[4]semitube which could be too small to adopt  $C_{60}$ .

## Computational method

Since all complexes have 1:1 stoichiometry as determined by experiment, we were only concerned about 1:1 complexes in our calculations. For these complexes, there are two possible geometries; one of these possibilities is the centered complex where C<sub>60</sub> lies in the center of the ligand, Fig. 5, close to the spacer between the two calixarene units. The other possibility is the side complex where C<sub>60</sub> lies over the cavity of one of the calixarene units Fig. 6. It is more convincing to have a centered 1:1 complex rather than a side complex. The calculated energies of each of C<sub>60</sub>, the ligand and the complex using PM6 and DFT methods, revealed that with the exception of *ortho* ligand the centered complexes are more stable than the side complexes for the three ligands. It is known that the *ortho* ligand has the shortest distance between the two calixarene units, where the C<sub>60</sub> molecule will reside; this will rule out any possible wrapping around C<sub>60</sub> molecule and hence, produce the least stable complex. The results obtained from



**Fig. 5** The center structure of the C<sub>60</sub>:3c complex



**Fig. 6** The side structure of C<sub>60</sub>:3c complex

PM6 calculations showed that the stability of the centered complexes is in the order  $m > p > o$ , which is the same as that obtained by experiments. On the other hand, the calculated energies using DFT method showed that the stability of both centered and side complexes is in the order  $p > m > o$ .

In conclusion, in this study we found that *p-tert*-butylcalix[4]semitubes are able to form 1:1 complexes with C<sub>60</sub> in solution using UV–Vis. spectrophotometry, PM6 and DFT. The formation constant values are in the range found with other calixarene derivatives.

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