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Synthesis of Large Macrocyclic Azacalix[*n*]pyridines (*n* = 6 − 9) and Their Complexation with Fullerenes C_{60} and C_{70}

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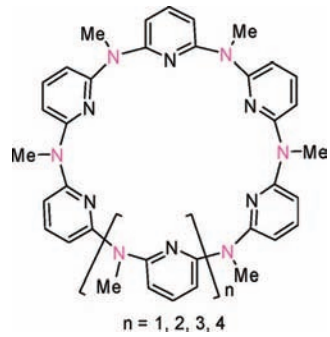
ABSTRACT



Large methylazacalix[*n*]pyridines (*n* = 6−9) were synthesized effectively from the Pd-catalyzed macrocyclic fragment coupling reactions between α,ω-dibrominated and α,ω-diaminated linear oligomers. As macrocyclic host molecules, they formed a 1:1 complex with fullerenes C_{60} and C_{70} with association constants ranging from 3 × 10^4 to 1 × 10^5 M^{-1}.

The design and the synthesis of novel and functional macrocyclic host molecules are the central theme in the study of supramolecular chemistry. Among various types of macrocyclic host molecules,[1] heteroatom-bridged calix(hetero)aromatics[2–6] have attracted a fast-growing interest in recent years. In comparison with calix[*n*]arenes[7–9] and calixheteroarenes such as calixpyrroles,[10] calixpyridines,[11] and other calixaromatics,[12] in which the (hetero)arene units are linked by methylenes, introduction of heteroatoms into the bridging positions has generated a number of novel macrocyclic molecules including thia-,[3] oxa-,[4] and azacalix[*n*]arenes.[5] On the basis of the fragment coupling strategy, for example, we have successfully synthesized azacalix[*m*]arene[*n*]pyridines (*m* = *n* = 2, 4),[5d,e] azacalix[*n*]pyridines (*n* = 4, 5, 8, 10),[5e,m] and aza- and/or oxa-calix[2]arene[2]triazines,[4a,k,l,13] while

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Katz[4b–d] and others[4e–h,j,n] reported the preparation of symmetrically substituted oxacalix[4]aromatics using a one-pot reaction method. Because of the different electronic nature of heteroatoms from carbon, the heteroatombridged calix(hetero)aromatics exhibit interesting structural and molecular recognition properties. It has been shown that, due to the intrinsic nature of nitrogen that can adopt sp^2 and/or sp^3 electronic configurations to form or not to form conjugation with its adjacent aromatic rings, azacalix[4]pyridine is able to preorganize into different conformational and cavity structures to interact with metal ions,[5f] anions,[5e] and both aromatic and aliphatic diols and monools.[5l] It has also been demonstrated that the cavity of 1,3-alternate aza- and/or oxacalix[2]arene[2]triazines can be regulated by using different combinations of heteroatoms[4a] or varied substituents[4k] on the bridging nitrogen atoms.

While the study of the preparation of smaller macrocyclic heteroatom-bridged calix[*n*]aromatics ($n = 4$) has been fruitful,[3–6] the synthesis of larger macrocycle homologues has remained largely unexplored.[14] The oligomerizations between 1,3-phenylenediamine derivatives and 1,3-dibromobenzene derivatives[5h] and oligomerization of *N*-methyl(3-bromo)aniline,[5b] for example, have been reported to give a mixture of azacalix[*n*]arene compounds in very low yields. Azacalix[*n*]pyridine ($n > 6$) derivatives were obtained in extremely low yield from condensation between 2,6-bis(*p*-tolyamino)pyridine and 2,6-dibromopyridine or oligomerization of 2-bromo-6-(*p*-tolylamino)pyridine.[5j] When we[5e,m] studied the synthesis of azacalix[4]- and -[5]pyridines using $3 + 1$ and $3 + 2$ fragment coupling approaches, azacalix[8]- and -[10]pyridines were obtained, respectively, in addition to the target molecules. Following the same stepwise $3 + 1$ strategy, Tsue reported the synthesis of azacalix[8]arene derivative in good yield.[5k] Our continuing interest in the synthesis of heteroatom-bridged calixaromatics led us to undertake the current study. We report herein the fragment coupling synthesis of azacalix[*n*]pyridines of various macrocyclic ring sizes ($n = 6-9$) and their complexation with fullerenes C_{60} and C_{70}.

Retrosynthetically, the disconnection of large macrocyclic azacalixpyridines ($n = 6-9$) can lead to two pieces of fragments either of similar sizes or of very different sizes. To achieve synthetic efficiency, a convergent fragment coupling approach using two fragments of similar sizes was pursued. Illustrated in Scheme 1 are the preparation of different types of diamine and dibromide fragments. Starting with 2,6-dibromopyridine **1** and methylamine **2**, reiterative aromatic nucleophilic substitution reactions afforded α,ω-dibrominated and α,ω-diaminated linear oligomers. It is worth noting that, except for the elevated reaction temperatures, the preparations were very practical. They were carried out in a large scale and in high yield. Besides, they required no expensive reagents or catalysts.

We started our investigation with the synthesis of methylazacalix[7]pyridine by macrocyclic cross coupling reaction between α,ω-dibrominated linear tetramer **6** and α,ω-diaminated linear trimer **10**. The reaction was systematically examined in terms of palladium catalyst, phosphine ligand, solvent, and reaction temperature. As summarized in Table 1, $Pd_2(dba)_3$ appeared as a better catalyst than $PdCl_2$ and $Pd(OAC)_2$ (entries 1−3), while dppp was superior than other ligands such as dppe, P(*c*-Hex)$_3$, and DPEphos (entries 3−6). The reaction was also sensitive toward the solvent and temperature used. This has been exemplified by a higher chemical yield of the product obtained in refluxing toluene than in other solvents including 1,4-xylene, 1,4-dioxane, and THF (entries 3 and 7−9) or in toluene but at lower temperature (entries 3, 10, and 11). It is interesting to note that while the catalyst loading did not seem critical in determining the chemical yield of the product (see the Supporting Information), the concentration of the substrate affected the formation of the product (entries 3 and 12−15).

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Scheme 1. Synthesis of α,ω-Dibrominated and α,ω-Diaminated Linear Oligomers

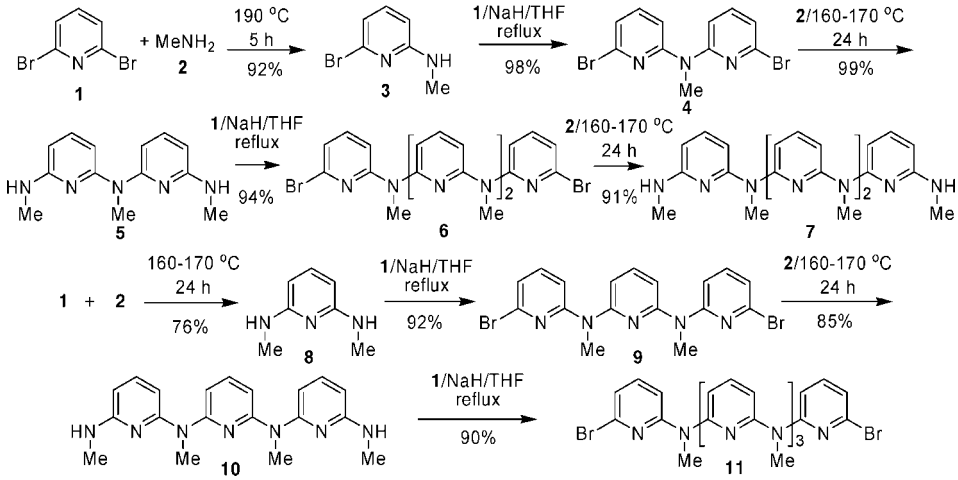
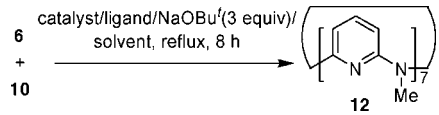


Table 1. Synthesis of Methylazacalix[7]pyridine **12**[a]



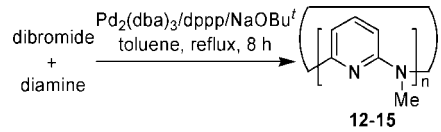
entry	catalyst (mol %)/ligand (mol %)/solvent	yield (%)[b]
1	$PdCl_2$ (20)/dppp (20)/toluene	29
2	$Pd(OAc)_2$ (20)/dppp (20)/toluene	23
3	$Pd_2(dba)_3$ (10)/dppp (20)/toluene	37
4	$Pd_2(dba)_3$ (10)/dppe (20)/toluene	26
5	$Pd_2(dba)_3$ (10)/P(*c*-Hex)$_3$ (40)/toluene	30
6	$Pd_2(dba)_3$ (10)/DPEphos (20)/toluene	30
7	$Pd_2(dba)_3$ (10)/dppp (20)/1,4-xylene	30
8	$Pd_2(dba)_3$ (10)/dppp (20)/1,4-dioxane	34
9[c]	$Pd_2(dba)_3$ (10)/dppp (20)/THF	29
10[d]	$Pd_2(dba)_3$ (10)/dppp (20)/toluene (70 °C)	26
11[e]	$Pd_2(dba)_3$ (10)/dppp (20)/toluene (90 °C)	33
12[f]	$Pd_2(dba)_3$ (10)/dppp (20)/toluene	30
13[g]	$Pd_2(dba)_3$ (10)/dppp (20)/toluene	30
14[h]	$Pd_2(dba)_3$ (10)/dppp (20)/toluene	20
15[i]	$Pd_2(dba)_3$ (10)/dppp (20)/toluene	20

[a] Concentration of substrate **10** was 2.5×10^{-3} M. [b] Isolated yield. [c] Reaction time was 10 h. [d] Reaction temperature was 70 °C. [e] Reaction temperature was 90 °C. [f] Concentration of substrate **10** was 1.25×10^{-3} M. [g] Concentration of substrate **10** was 5×10^{-3} M. [h] Concentration of substrate **10** was 7.5×10^{-3} M. [i] Concentration of substrate **10** was 10×10^{-3} M.

Thus, under the conditions using 10 mol % of $Pd_2(dba)_3$, 20 mol % of dppp, and 3 equiv of NaOBu^t, refluxing of substrates **6** (2.75×10^{-3} M) and **10** (2.5×10^{-3} M) in toluene for 8 h afforded methylazacalix[7]pyridine **12** in 37% yield (entry 3).

The macrocyclic coupling reaction was applicable to the synthesis of other large azacalix[*n*]pyridine compounds **13**−**15** (Table 2). Applying the same optimal conditions for the synthesis of methylazacalix[7]pyridine **12**, for example, methylazacalix[6]pyridine **13** was obtained in 31% yield from the reaction of a dibrominated linear trimer **9** with a diaminated linear trimer **10** (entry 1, Table 2). Reactions between larger fragments such as tetramers **6** and **7**, and **11**

Table 2. Synthesis of Methylazacalix[n]pyridines[a]



entry	dibromide	diamine	product	*n*	yield (%)[b]
1	9	10	13	6	31
2	9	7	12	7	36
3	6	10	12	7	37
4	6	7	14	8	40
5	11	7	15	9	40

[a] For reaction conditions, see entry 3, Table 1. [b] Isolated yield.

and **7** led to the formation of giant macrocyclic ring products methylazacalix[8]pyridine **14** and methylazacalix[9]pyridine **15**, respectively, in 40% yield (entries 4 and 5, Table 2). It should be noted that methylazacalix[7]pyridine **12** was also prepared from the reaction of a dibrominated trimer **9** and a diaminated tetramer **7**, albeit in a slightly lower yield (entry 2, Table 2).

The structure of all large macrocyclic azacalixpyridines synthesized was established on the basis of their spectroscopic data and microanalysis (see the Supporting Information). The single crystal of **12** grew in dichloromethane solution by slow evaporation of the solvent, and its X-ray molecular structure, which was depicted in Figure 1, allowed unambiguous determination of the macrocyclic ring structure. Being different from the solid state structure of azacalix[8]- and -[10]pyridines,[5e,m] one of the methyl groups on the bridging nitrogen atoms of **12** was directed toward the middle of the cavity (Figure 1). It is also noteworthy that azacalix[*n*]pyridine homologues showed interesting UV−vis spectral properties in solution (see the Supporting Information). The wavelength and the coefficient of absorption are listed in Table 3. For comparison, UV−vis spectroscopic data of 2,6-bis(methylamino)pyridine **8**, 2-(methylamino)pyridine **19**, 2-[*N*-methyl-*N*-(pyridin-2-yl)amino]pyridine **20**, and 2,6-

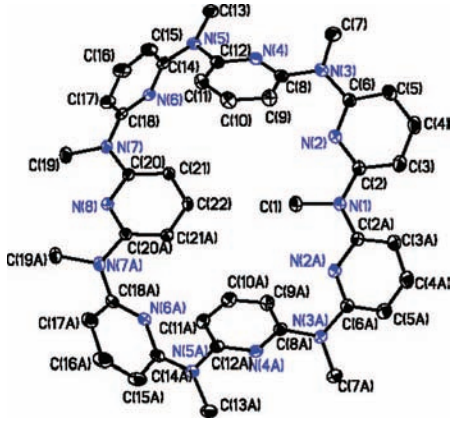


Figure 1. X-ray structure of methylazacalix[7]pyridine **12**.

bis[*N*-methyl-*N*-(pyridin-2-yl)amino]pyridine **21** are also included. While azacalix[7]- and -[9]pyridines gave two absorption bands (entries 4 and 6), all other macrocyclic compounds showed one strong absorption band ($\epsilon > 10^4$ cm^{-1} M^{-1}). Noticeably, with the increase of macrocyclic ring size, the wavelength of the maximum absorption band of azacalix[*n*]pyridines increased from 311 nm ($n = 4$) to 327−329 nm ($n = 5, 6$), 341 nm ($n = 7, 8$), and 348−349 nm ($n = 9, 10$) (Table 3). This implied the difference of the major conjugation segments in each macrocyclic ring compounds. The exhibition of other strong absorption bands at longer wavelength for azacalix[7]pyridine **12** ($\lambda_{max} = 382$ nm) and azacalix[9]pyridine **15** ($\lambda_{max} = 390$ nm) suggested the occurrence of a more extensive conjugation system in these compounds.

Table 3. UV−Vis Spectroscopic Data of azacalix[*n*]pyridines[a]

entry	compds	λ_{max} (nm)	ϵ (cm^{-1} M^{-1})
1	methylazacalix[4]pyridine **16**	311	2.28×10^4
2	methylazacalix[5]pyridine **17**	327	4.76×10^4
3	methylazacalix[6]pyridine **13**	329	4.89×10^4
4	methylazacalix[7]pyridine **12**	341	6.51×10^4
		382	1.94×10^4
5	methylazacalix[8]pyridine **14**	341	8.54×10^4
6	methylazacalix[9]pyridine **15**	349	8.64×10^4
		390	3.06×10^4
7	methylazacalix[10]pyridine **18**	348	1.20×10^5
8	2,6-bis(methylamino)pyridine **8**	314	1.03×10^4
9[b]	2-(methylamino)pyridine **19**	304	4.18×10^3
10[b]	2-[*N*-methyl-*N*-(pyridin-2-yl) amino]pyridine **20**	309	1.41×10^4
11[b]	2,6-bis[*N*-methyl-*N*-(pyridin-2-yl) amino]pyridine **21**	338	2.33×10^4

[a] UV−vis spectra were measured in toluene solution (8×10^{-6} M) at 298 K. [b] UV−vis spectra were measured in toluene solution (3×10^{-5} M) at 298 K.

Large macrocyclic methylazacalix[*n*]pyridines are powerful host molecules able to interact with fullerenes. Fluorescence titration and the Job's plot experiments (see the Supporting Information) showed that all methylazacalix[*n*-]pyridines ($n = 6-9$) synthesized formed a 1:1 complex with fullerene guests C_{60} and C_{70}, and their association constants K_a[5d,5e,15] were summarized in Table 4. The results for the

Table 4. Association constants for the 1:1 complexation of methylazacalix[n]pyridines with fullerenes C_{60} and C_{70}.[a]

n	K_a (1:1 complexation with C_{60})	K_a (1:1 complexation with C_{70})
4		
5	$(2.60 \pm 0.11) \times 10^4$	$(1.17 \pm 0.03) \times 10^5$
6	$(6.62 \pm 0.22) \times 10^4$	$(6.24 \pm 0.19) \times 10^4$
7	$(3.30 \pm 0.08) \times 10^4$	$(7.23 \pm 0.19) \times 10^4$
8	$(4.60 \pm 0.16) \times 10^4$	$(1.09 \pm 0.02) \times 10^5$
9	$(3.10 \pm 0.08) \times 10^4$	$(8.23 \pm 0.25) \times 10^4$
10	$(3.03 \pm 0.08) \times 10^4$	$(1.30 \pm 0.03) \times 10^5$

[a] Association contants were calculated on the fluoroscence titration data with the Hyperquad 2000 program.[15]

complexation of azacalix[4]-, azacalix[5]-, and azacalix[10]pyridines[5f,m] with fullerenes C_{60} and C_{70} were also included for comparison. As revealed by the results in Table 4, except for methylazacalix[4]pyridine, a small macrocycle, which did not interact at all with fullerene guests, all large macrocyclic azacalix[*n*]pyridine ($n = 5-10$) hosts exhibited a strong ability to form 1:1 complexes with C_{60} and C_{70}. In most cases, the synthetic hosts showed higher binding ability toward C_{70} than toward C_{60}. The association constants were around 10^4-10^5 M^{-1}. To the best of our knowledge, they represented the strongest monomacrocyclic hosts in complexation with C_{60} and C_{70}.[5d,e]

In summary, we have synthesized large macrocyclic methylazacalix[*n*]pyridines ($n = 6-9$) effectively using the Pd-catalyzed fragment coupling strategy. The synthetic macrocycles are powerful hosts to form 1:1 complexes with fullerenes C_{60} and C_{70}, giving the association constants ranging from 3×10^4 to 1×10^5 M^{-1}. Applications of large azacalix[*n*]pyridines are actively investigated and will be reported in due course.

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Supporting Information Available: Experimental details, ^1H and ^{13}C NMR of **12**−**15**, and X-ray molecular structure of **12** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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