doi:10.1246/cl.2011.931
Published on the web September 5, 2011

Facile Preparation of Macrocycles with Triphenylamine Backbone via C–N Coupling Reaction

Kousuke Tsuchiya,* Hiroko Miyaishi, and Kenji Ogino
Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588

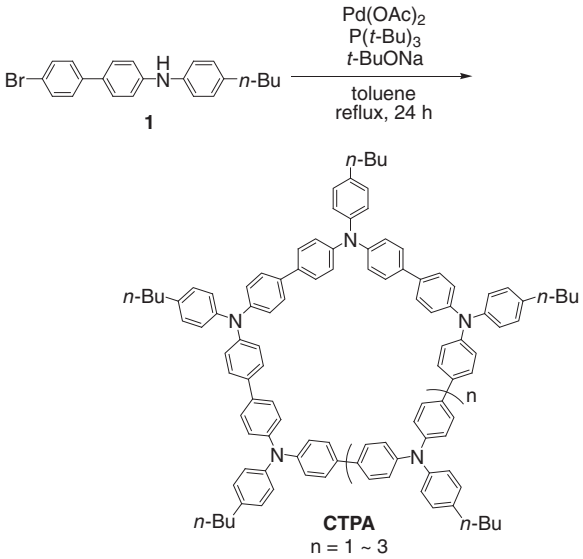
(Received April 15, 2011; CL-110321; E-mail: ktsuchiy@cc.tuat.ac.jp)

Cyclic oligomers composed of triphenylamine backbone were conveniently prepared via palladium-catalyzed one-pot synthesis. The condition for the preparation was optimized to give the cyclic oligomers with large ring sizes in good yield up to 73.7%. The type of base for the reaction dramatically influenced the yield of cyclic oligomers, and potassium *tert*-butoxide was the most effective for the cyclization. The composition of the cyclic oligomers was determined by high-performance liquid chromatography (HPLC) as a mixture of pentamer, hexamer, and heptamer. The cyclic pentamer was easily isolated by only recrystallization from *tert*-butyl methyl ether.

Arylamine derivatives have been widely applied to organic light-emitting diodes, photoconductors, and photovoltaic devices because of their excellent electrical properties.[1] Recently, we have reported that poly(4-*n*-butyltriphenylamine) (PTPA) was prepared via palladium-catalyzed C–N coupling polymerization, and that the resulting product involved a trace amount of cyclic oligomers which were proven to be a mixture of pentamer, hexamer, and heptamer by mass spectrometry.[2] High hole mobility and high photoconductivity of PTPA backbone offers the possibility of being applied to organic photovoltaic devices.[3] In addition, because of electron-donating ability of the triphenylamine moiety, charge-transfer (CT) interaction with an electron acceptor can be a driving force for the cyclic oligomers to form inclusion complex.

Macrocyclic compounds such as calixarene and cyclodextrin have lead many researchers toward designing and synthesizing new chemical backbones because of their fascinating ability to form inclusion complexes in supramolecular chemistry. Aromatic compounds containing heteroatoms such as aniline,[4] pyridine,[5] and thiophene[6] are introduced into macrocyclic structures so as to exploit strong π–π interaction with fullerenes for the complexation. Among them, azacalix[*n*]pyridines have been reported to show stronger affinity for C_{60} and C_{70} than calixarene derivatives, probably because of introduction of electron-donating heteroatoms.[5b–5d] However, the variety of the structure as well as the sizes of ring were limited in a few instances due to the difficulty of synthesis, especially for large ring size. Wang's group has prepared azacalixpyridines with up to 10 aromatic rings, which possess thermodynamically unfavorable ring size, via elaborate stepwise reactions.[5b–5d]

From a practical point of view, inclusion complexes of cyclic oligotriphenylamine (CTPA) with an electron acceptor, such as fullerene and perylenetetracarboxydiimide allow us to fabricate a new type of donor–acceptor complex which probably creates effective charge separation necessary for organic photovoltaic cells. In this communication, our interest is focused on effective methods to prepare the cyclic oligomer.



Scheme 1. Synthesis of CTPA via C–N coupling reaction.

A self-condensing monomer, 4-(4′-bromophenyl)-4″-*n*-butyldiphenylamine (**1**), was synthesized from 4,4′-dibromobiphenyl and 4-*n*-butylaniline using palladium catalyst. In a similar manner to polymerization but in diluted conditions, cyclic oligomers were prepared from **1** via C–N coupling reaction (Scheme 1).[2] The general synthetic procedure for CTPA is as follows; To a solution of **1** (0.25 g, 0.66 mmol), sodium *tert*-butoxide (0.0695 g, 0.72 mmol), and palladium(II) acetate (2.95 mg, 0.013 mmol) in dry toluene (25 mL) was added tri-*tert*-butylphosphane (12.7 µL, 0.10 mmol) under nitrogen atmosphere. The mixture was stirred under reflux for 24 h. After the reaction, the resulting solution was poured into methanol, and the mixture of polymer and oligomers was filtered as the precipitate. The collected mixture was subjected to Soxhlet extraction with acetone to separate the oligomers from the polymer. The resulting acetone solution was concentrated by rotary evaporator and the crude product was purified by silica gel column chromatography with toluene/hexane (2/3 in volume ratio) to remove linear oligomers.

Table 1 summarizes the results of the formation of cyclic oligomers under various conditions. All the products contained the linear polymer and oligomers which were easily removed by Soxhlet extraction and column chromatography, respectively. When the reaction was performed under diluted conditions without changing any parameters, the yield of cyclic oligomers is improved up to 9.4% (Runs 2 and 3) compared with that at tenfold concentration (Run 1, same condition as the polymer-

Table 1. Reaction conditions for the preparation of CTPA[a]

Run	Concentration[b] /M	Solvent	Base	Conversion[c] /%	Yield of oligomers/%[d]		CTPA5:CTPA6:CTPA7[d]
					Cyclic	Linear	
1	0.263	toluene	*t*-BuONa	99.0	1.0	0	—
2	0.0267	toluene	*t*-BuONa	71.4	4.0	2.4	73:17:10
3[e]	0.0264	toluene	*t*-BuONa	87.0	9.4	0.7	71:20:9
4[f]	0.0264	toluene	*t*-BuONa	76.3	0	45.8	—
5	0.0265	octane	*t*-BuONa	55.6	0	33.9	—
6	0.0265	toluene/octane[g]	*t*-BuONa	60.4	2.0	25.3	63:33:4
7	0.0263	cyclohexane	*t*-BuONa	96.0	4.6	12.0	76:19:5
8	0.0263	xylene	*t*-BuONa	78.3	2.1	26.0	74:26:0
9	0.0263	toluene	*t*-BuOLi	46.5	2.3	36.8	94:6:0
10	0.0263	toluene	*t*-BuOK	81.2	21.2	60.0	55:30:15
11	0.0214	toluene	*t*-BuOK	99.9	73.7	26.1	47:40:13
12	0.0175	toluene	*t*-BuOK	54.0	7.8	46.0	53:38:9

[a]Reaction was carried out using **1** (1.31 mmol), $Pd(OAc)_2$ (2 mol %), P(*t*-Bu)$_3$ (8 mol %), and base (1.44 mmol) for 24 h at reflux under nitrogen atmosphere. [b]Concentration of **1**. [c]Total yield after precipitation into methanol. [d]Determined by HPLC after Soxhlet extraction. [e]Carried out in five times scale. [f]Carried out using 6 mol % of $Pd(OAc)_2$. [g]Volume ratio was 1/1.

ization), although oligomeric products were contaminated with small amounts of linear species. Increasing the amount of palladium(II) acetate and phosphane ligand results in yielding only linear analogs (Run 4).

In the case of preparation of calixarenes, the choice of reaction media is a critical factor for the formation of cyclic oligomers with a desired size.[7] Therefore, the influence of reaction media on the formation of macrocycles was investigated as shown in Runs 5–8. Hydrocarbons such as octane or cyclohexane, in which PTPA is hardly soluble, were used as a solvent. However, the resulting mixtures showed the increase of linear instead of cyclic oligomers, indicating that the activity of the palladium catalytic system was depressed in poor solvents. Mixed solvent of toluene and octane also gives the linear-oligomer-rich product. On the other hand, when xylene, a similar reaction media to toluene with higher boiling point, was used as solvent (Run 8), the yield of cyclic oligomers was lower than using toluene.

The results of changing sodium *tert*-butoxide to various bases are listed in Runs 9–12. The sizes of cation species (Li^+, Na^+, and K^+) obviously affected the components of the resulting product. When lithium salt was used as a base, the amount of linear oligomers increased without the improvement of cyclic oligomers yield, and the total yield became low. In the meantime, interestingly, the amount of cyclic oligomers significantly increases up to 73.7% in the case of utilizing potassium *tert*-butoxide as a base. It is assumed that the size effect and/or basicity of potassium salt may be attributed to efficient cyclization, although the mechanism remains unknown. Decreasing the concentration below 0.0214 M does not improve the yield of cyclic oligomers, which results in extremely low total conversion (Run 12).

It was revealed by HPLC that the cyclic oligomers consisted of a mixture of pentamer (CTPA5), hexamer (CTPA6), and heptamer (CTPA7). The composition ratios of cyclic oligomers are listed in Table 1, and CTPA5 was the most dominantly generated. Using lithium *tert*-butoxide resulted in the selective formation of CTPA5 although the yield was low. Fascinatingly, CTPA5 was easily isolated from the mixture by recrystallization from *tert*-butyl methyl ether (yield: 11%). In the ^{1}H NMR spectra of CTPAs (see in Supporting Information; SI[8]), all assignable signals were observed without signals from the terminals which could be seen in that of linear oligomers. The maximum absorption and emission wavelengths were observed at 365 and 422 nm, respectively, in UV–vis absorption and PL spectra of CTPA5 (see in SI[8]).

In conclusion, we have synthesized a new type of cyclic compound CTPAs based on a triphenylamine backbone via palladium-catalyzed oligomerization in a facile one-pot synthesis. As a base, potassium *tert*-butoxide was quite effective for selective preparation of CTPAs. The cyclic pentamer CTPA5 was easily isolated by recrystallization from *tert*-butyl methyl ether. The further properties of CTPA for inclusion complex are under investigation.

This work was financially supported by "Research for Promoting Technological Seeds" from Japan Science and Technology Agency (JST).

This paper is in celebration of the 2010 Nobel Prize awarded to Professors Richard F. Heck, Akira Suzuki, and Ei-ichi Negishi.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

