Syntheses of Novel Carbazolylacetylene-Derived Macrocycles

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Abstract: The syntheses of novel cyclic oligomers based on the carbazolylacetylene unit are described. The desired cyclic tetramer could be synthesized in 14.3% yield by the reaction of 3,6-diethynyl-9-tetradecylcarbazole and 3,6-bis(3’-iodo-9’-tetradecylcarbazolyl)-9-tetradecylcarbazole in the presence of Pd(PPh3)4/Cul as catalysts under high dilution conditions and purified by column chromatography and isolated by preparative gel permeation chromatography. Besides the tetramer, a cyclic octamer was also isolated in 5.4% yield.

Keywords: cross-coupling, cyclizations, macrocycles, carbazolylacetylene, cyclic oligomers

Recently, syntheses and developments of cyclic oligomers have become important in several fields of research including supramolecular chemistry and organic materials science. In supramolecular chemistry, cyclic oligomers such as crown-ethers,1 calixarenes,2 and cyclodextrins3 are useful for molecular recognition. In organic materials science, cyclic oligomers are also useful for organic light-emitting diodes due to their morphological and thermal stabilities.4 Phenylacetylene-derived,5 diethylbenzene-derived,6 and thiophene-derived7 cyclic oligomers are also reported in pursuit of self-aggregation behavior, materials science, and so on. Cyclic oligomers could be a model system, which combines an infinite π-conjugated chain of an idealized polymer having the advantages of a structurally well-defined oligomer but without any perturbing end-effects.7a Moreover, cyclic oligomers have cavities which might act as the recognition site and offer selective complexation sites for guest molecules. On the other hand, polycarboxylic acids, polyarylenevinlenes, and oligoarylenes are useful for new organic materials such as light-emitting diodes, photovoltaic devices, nonlinear optics (NLO), two-photon dyes, molecular switches, and molecular wires.8,9 In our laboratory, we focus on carbazole molecules as a multifunctional material, and several types of main-chain and hyperbranched polymers with carbazole moieties have been synthesized and have shown reasonable second-order NLO and electroluminescent properties.10,11 In our on going programs, we have reported on the syntheses, emission, and electroluminescent properties of bis(cyanovinyl)carbazole-derived cyclic oligomers, which connect donor-type unit (D) and acceptor-type unit (A) alternatively, which is the D-A-D-A type.4,12 Herein we report on the syntheses of novel cyclic carbazole oligomers based on the carbazolylacetylene unit. These cyclic oligomers are only constructed from donor-type unit, D-D-D-D. These cyclic oligomers would be expected to be useful for new organic materials,13,14 host-guest chemistry, and aggregation behavior.

The molecular design was performed by Corey–Pauling–Koltun (CPK) model. Based on this molecular design, we tried to synthesize the cyclic oligomer 1a. The tetradecyl chain group was chosen to increase the solubility of 1a in organic solvents. Previously, we reported on the synthesis of 3,6-diido-9-tetradecylcarbazole by the reaction of carbazole with KI, and KIO3 followed by N-alkylation with 1-bromotetradecane6a but it was difficult to purify 3,6-diiodocarbazole and remove the by-product 3-iodocarbazole from the mixture. Moreover, this reaction was a little dangerous because of the use of KIO3 as the oxidizing reagent. So we changed the synthetic route of 3,6-diido-9-tetradecylcarbazole to be conducted under milder conditions and more conveniently. The monomer units were synthesized as shown in Scheme 1. 9-Tetradecylcarbazole (3) was obtained in quantitative yield by reacting carbazole 2 with 1-bromotetradecane in THF–DMF in the presence of NaH as a base. 9-Tetradecylcarbazole (3) was then converted to 3,6-diido-9-tetradecylcarbazole 4 by treatment with N-iodosuccinimide (NIS) in chloroform–acetic acid in 89% yield. Reaction of (4) with trimethylsilylacetylene in THF–triethylamine in the presence of bis(triphenylphosphine)palladium(II) chloride and copper(I) iodide as catalysts afforded 3,6-bis(trimethylsilyl)ethyl[6]-9-tetradecylcarbazole (5) in 99% yield as a yellow viscous oil. 3,6-Diethynyl-9-tetradecylcarbazole (6) was obtained by hydrolysis of 5 with NaOH in 95% yield.

First, we examined the synthesis of 1a by direct one-pot cross-coupling (2:2 cyclization reaction) of 4 (1.0 equiv) and 6 (1.0 equiv) in the presence of Pd(PPh3)2Cl2/Cul as...
catalysts using Sonogashira–Hagihara reaction\textsuperscript{15} as shown in Scheme 2. But it failed to give the desired molecule \textbf{1a} and only afforded polymer \textbf{1c} whose average molecular weight was more than 10^6, calibrated from polystyrene standard.

We then changed our strategy for the synthesis of \textbf{1a} by doing it step wise. A key precursor of the tetramer \textbf{1a}, the linear trimer, 3,6-bis(3'-iodo-9'-tetradecylcarbazolyl)-9'-tetradecylcarbazole (7), was synthesized by reacting 4 (1.0 equiv) and excess of 6 (4.7 equiv) in the presence of

\begin{scheme}
\textbf{Scheme 1} Reagents and conditions: i) CH$_2$(CH$_2$)$_{12}$CH$_3$, NaH, THF–DMF, r.t., quant.; ii) NIS, CHCl$_3$–AcOH, r.t., 89%; iii) trime-thylsilylacetylene, Pd(PPh$_3$)$_2$Cl$_2$/CuI, THF–Et$_3$N, r.t., 99%; iv) NaOH, H$_2$O–EtOH, r.t., 95% \\
\end{scheme}

\begin{scheme}
\textbf{Scheme 2} Reagents and conditions: i) 4:6 (1:1 mol/mol), Pd(PPh$_3$)$_2$Cl$_2$/CuI, THF–Et$_3$N, 50 °C \\
\end{scheme}

Figure 1  Molecular structures of cyclic oligomers \textbf{1a} and \textbf{1b}
Pd(PPh₃)₂Cl₂/CuI as catalysts and was obtained in 37% yield after purification by column chromatography (Scheme 3).

Finally, the desired molecule 1a was obtained by reacting equimolar amounts of 6 and 7 in the presence of Pd(PPh₃)₂/CuI as catalysts under high dilution conditions. Purification by column chromatography followed by isolation using preparative gel permeation chromatography (GPC) gave 1a in 14.3% yield (Scheme 4). From this reaction, the cyclic octamer was also isolated in 5.4% yield.

The structures of 1a and 1b were assigned by ¹H NMR, fast atom bombardment mass (FAB-MS) spectrum or Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass (MALDI-TOF-MS) spectrum, and elemental analyses. The ¹H NMR spectrum of 1a as shown in Figure 2 showed a simple and symmetrical spectrum, indicating that cyclic oligomer had been obtained.

FAB-MS of this oligomer as shown in Figure 3 exhibited the molecular-ion peak of M⁺ (required m/z 1542; found m/z 1542) which corresponds to a cyclic tetramer. From these data, the structure of 1a was assigned as a cyclic tetramer.

The structure of cyclic octamer 1b could be also assigned by the same method. As to the MS spectrum, the molecular-ion peak of 1b could not be observed in the FAB-MS spectrum, so that we used MALDI-TOF-MS spectrum and obtained the molecular-ion peak of M⁺ (required m/z 3084; found m/z 3084). Larger cyclic oligomers such as cyclic dodecamer could not be formed from this coupling reaction.

In conclusion, we could synthesize carbazolylacetylene-derived cyclic tetramer and octamer by step-wise reactions. The desired cyclic tetramer was obtained by reacting 3,6-diethynyl-9-tetradecylcarbazole (6) and 3,6-bis(3'-iodo-9'-tetradecylcarbazolyl)-9-tetradecylcarbazole (7) in the presence of Pd(PPh₃)₂/CuI as catalysts. In this reaction, we could also obtain cyclic octamer as a by-product. The yields of tetramer and octamer were 14.3% and 5.4%, respectively.

All reagents and anhyd solvents are commercially available and were used without further purification. Analytical TLCs were performed on commercial Merck plates coated with silica gel 60F₂₅₄. Silica gel used for chromatography was Merck silica gel 60. ¹H NMR spectra in CDCl₃ solution were recorded on Jeol EX-270 (270 MHz) or Jeol JNM-AL300 (300 MHz) spectrometers. Chemical shifts are reported in ppm downfield from tetramethylsilane, and coupling constants are in Hz. FAB-MS was recorded on a Jeol JMS-HX110 mass spectrometer using 3-nitrobenzyl alcohol as a matrix. MALDI-TOF-MS was recorded on a Bruker REFLEX mass spectrometer using 2,5-dihydroxybenzoic acid as a matrix. FT-IR spectra were recorded on a Shimadzu FTIR-4100 infrared spectrometer as KBr pellets. Elemental analyses were performed at the Division of Chemical Analysis of RIKEN. The preparative GPC was performed under the following conditions: columns, Shodex GPC K-
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2001 and K-2002; detector, JASCO875-UV; eluent, CHCl₃ (3.0 mL/min). The average molecular weight of polymer 1c, calibrated to a polystyrene standard, was estimated by analytical GPC under the following conditions: columns, Waters Ultrastyragel HR2, HR3, and HR4; detector, Shimadzu SPD–10 Å; eluent, CHCl₃ (1.0 mL/min).

Figure 2 1H NMR spectrum of 1a in CDCl₃ at r.t.

9-Tetradecylcarbazole (3)
To a stirred solution of carbazole (2; 20.0 g, 0.12 mol) in THF–DMF (90 mL, 30 mL) was added 1-bromotetradecane (33.187 g, 0.12 mol) at r.t. NaH (60% in oil, 7.209 g, 0.18 mol) was gradually added to the solution and stirred for 1 h. To this mixture MeOH was added to quench the remaining NaH, and the solvent was evaporated in vacuo. The residue was extracted with CH₂Cl₂ (2 ¥ 200 mL) and the CH₂Cl₂ layer was washed with 3 N aq HCl (2 ¥ 200 mL) twice. The organic layer was washed with H₂O (250 mL), dried (Na₂SO₄), and filtered. The solvent was evaporated in vacuo and the residue was reprecipitated using MeOH to give 3. This material was used for the following step without further purification.

1H NMR (CDCl₃/TMS, 270 MHz): δ = 0.88 (t, 3 H, J = 6.6 Hz, CH₃), 1.23–1.34 (m, 22 H, CH₂), 1.84–1.89 (m, 2 H, NCH₂C₆H₄), 4.29 (t, 2 H, J = 7.2 Hz, NCH₂), 7.19–7.25 (m, 2 H arom), 7.38–7.49 (m, 4 H arom), 8.10 (d, 2 H arom, J = 7.9 Hz).

3,6-Diiodo-9-tetradecylcarbazole (4)
A mixture of 3 (9.999 g, 27.501 mmol) and NIS (12.687 g, 56.39 mmol) was stirred in a mixture of CHCl₃ (250 mL) and AcOH (80 mL) at r.t. under N₂ for overnight. The CHCl₃ was evaporated in

Figure 3 FAB-MS spectrum of 1a using 3,5-dinitrobenzyl alcohol as a matrix
vacuo and the solution was poured into H$_2$O (500 mL). The resulting precipitates were collected by filtration and purified by column chromatography on silica gel using CHCl$_3$ as an eluent to give 4 (15.117 g, 89%) as a white solid.

1H NMR (CDCl$_3$/TMS, 270 MHz): δ = 0.84 (t, 3 H, J = 6.6 Hz, CH$_3$), 1.17–1.26 (m, 22 H, CH$_2$), 1.76 (m, 2 H, NCH$_2$), 4.17 (t, 2 H, J = 7.1 Hz, NCH$_2$), 7.12 (d, 2 H$_{arom}$, J = 8.6 Hz), 7.66 (dd, 2 H$_{arom}$, J = 8.6, 1.7 Hz), 8.28 (d, 2 H$_{arom}$, J = 1.7 Hz).

3.6-Bis[(trimethylsilyl)ethylenyl]-9-tetradecylcarbazole (5)

A mixture of lacetylene (14 mL, 0.1 mol), Pd(PPh$_3$)$_2$Cl$_2$ (0.14 g, 0.2 mmol), and CuI (0.032 g, 0.17 mmol) was added in THF (8.4 mL) at 50 °C under N$_2$. After vigorous stirring of this solution for 20 min under N$_2$, trimethylsilylacetylene (14 mL, 0.1 mol), Pd(PPh$_3$)$_4$Cl$_2$ (0.100 g, 0.0865 mmol), and Cu (0.010 g, 0.0525 mmol) as catalysts under N$_2$. The solution was poured into MeOH to give a viscous oil.

IR (KBr): 3288.04, 2919.70, 2848.35, 2103.96, 1626.66, 1600.63, 1597.73, 1489.74, 1381.75, 1290.14 MHz. 1H NMR (CDCl$_3$/TMS, 300 MHz): δ = 0.87 (t, 12 H, J = 6.75 Hz, CH$_3$), 1.25–1.37 (m, 88 H, CH$_2$), 1.86–1.95 (m, 8 H, CH$_2$), 4.31 (t, 8 H, J = 6.9 Hz, NCH$_2$), 7.39 (d, 8 H$_{arom}$, J = 8.4 Hz), 7.71 (d, 8 H$_{arom}$, J = 8.4, 1.5 Hz), 8.42 (d, 8 H$_{arom}$, J = 1.2 Hz).

FAB-MS: m/z = 3084 (M$^+$).

Anal. Calcd for C$_{30}$H$_{37}$N (411.6): C, 87.54; H, 9.06; N, 3.40. Found: C, 86.67; H, 9.37; N, 3.56.

MALDI-TOF-MS: m/z = 3084 (M$^+$).

Polymer 1c

A mixture of 7 (1.135 g, 0.948 mmol), Pd(PPh$_3$)$_4$Cl$_2$ (0.100 g, 0.0865 mmol), and Cu (0.038 g, 0.1955 mmol) was stirred in THF (130 mL) at r.t. under N$_2$ for 1 h. To this mixture was added dropwise a solution of 6 (0.391 g, 0.950 mmol) in THF (50 mL) during 5.5 h, and the resulting mixture was stirred at r.t. for 5 days. The solvents were evaporated in vacuo, and the resulting residue was extracted with CH$_2$Cl$_2$ (200 mL) and the CH$_2$Cl$_2$ layer was washed with 5% aq HCl (200 mL). The organic layer was washed with H$_2$O (200 mL), dried (MgSO$_4$), and filtered. The solvent was evaporated in vacuo, and the resulting residue was purified by column chromatography using CHCl$_3$–hexane, 2:3 (v/v) as an eluent to give a mixture of 1a and 1b. This mixture was purified by preparative GPC, followed by recrystallization from CH$_2$Cl$_2$–MeOH to give 1a (0.209 g, 14.3%) and 1b (0.079 g, 5.4%), as white powders.

1a

1H NMR (CDCl$_3$/TMS, 300 MHz): δ = 0.86 (t, 24 H, J = 6.6 Hz, CH$_3$), 1.24 (m, 176 H, CH$_2$), 1.74 (m, 16 H, CH$_2$), 3.94 (m, 16 H, NCH$_2$), 7.22 (d, 16 H$_{arom}$, J = 8.4 Hz), 7.70 (d, 16 H$_{arom}$, J = 8.4 Hz), 8.36 (s, 16 H$_{arom}$).

MALDI-TOF-MS: m/z = 3084 (M$^+$).

Anal. Calcd for C$_{32}$H$_{32}$N$_2$ (510.28): C, 86.71; H, 9.16; N, 3.61. Found: C, 86.67; H, 9.37; N, 3.56.

Polymer 1f

A mixture of 4 (0.340 g, 0.826 mmol), 6 (5.070 g, 0.826 mmol), and Et$_2$N (4.2 mL) was stirred in THF (8.4 mL) at 50 °C for 4 d in the presence of Pd(PPh$_3$)$_4$Cl$_2$ (0.027 g, 0.0393 mmol) and Cu (0.010 g, 0.0525 mmol) as catalysts under N$_2$. The solution was poured into MeOH (250 mL), and the resulting precipitate was collected. It was purified by precipitation from CH$_2$Cl$_2$–MeOH three times to give 1e (0.557 g). The average molecular weight determined by GPC was more than 10$^6$, calibrated to a polystyrene standard.

1H NMR (CDCl$_3$/TMS, 300 MHz): δ = 0.85 (m, 3 H, CH$_3$), 1.23 (m, 22 H, CH$_2$), 1.81 (m, 2 H, CH$_2$), 4.05 (m, 2 H, NCH$_2$), 7.31 (m, 2 H$_{arom}$), 7.68 (m, 2 H$_{arom}$), 8.31 (m, 2 H$_{arom}$).

IR (KBr): 2921.63, 2850.27, 2196.52, 1597.73, 1489.74, 1381.75, 1290.14, 1151.91, 891.92, 814.78 cm$^{-1}$.

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