JOC The Journal of Organic Chemistry

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Synthesis of Molecular Wires Strapped by π-Conjugated Side Chains: Integration of Dehydrobenzo[20]annulene Units

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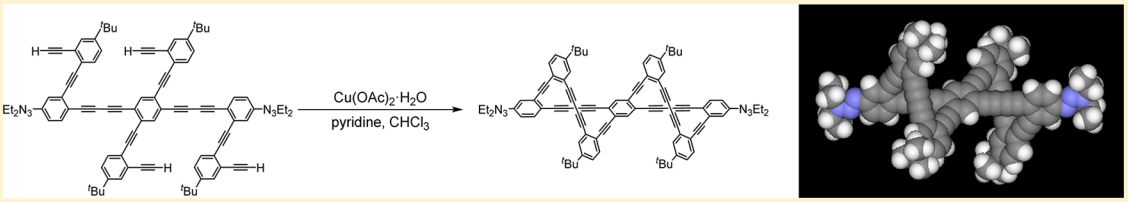
Supporting Information



ABSTRACT: In this study, π-conjugated molecular wires strapped by cyclic π-conjugated side chains were efficiently synthesized by the integration of dehydrobenzo[20]annulene units by intramolecular Glaser-type cyclization under high dilution conditions.

Electrically conductive π-conjugated molecular wires are promising wiring elements in the field of molecular electronics; however, they suffer from major drawbacks such as low solubility, caused by π−π interactions, and poor one-dimensional conductivity, caused by cross-talk between π-conjugated chains, as well as low rigidity and linearity. For these reasons, it is interesting to study insulated molecular wires, in which these π-conjugated polymers are covered with a protective sheath; this sheath limits π−π interaction as well as leads to the enhancement of organic solubility and conductivity as compared with those of the corresponding uninsulated π-conjugated polymers.[1] Previous studies have reported some methods to insulate these conductive wires by the introduction of highly bulky dendrimer side chains into π-conjugated chains and the covering of π-conjugated chains with cyclic molecules.[2]

We have successfully synthesized π-conjugated polymers by covering them with permethylated cyclodextrin, which are organic soluble and insulated cyclic molecules,[3] and have clarified that insulation by these cyclic molecules inhibits π−π interaction; the wires thus prepared exhibit excellent physical properties, such as high solubility and rigidity,[4] high intramolecular charge mobility,[5] external stimuli-responsiveness,[6] self-repair function,[7] and solid phosphorescence.[8] During the course of this study, we focused our attention on the construction of new molecular wires covered by π-conjugated moieties, which could exhibit various functions. Lupton and co-workers have prepared molecular wires bearing π-conjugated cyclic molecules around the main chain, and they reported that energy transfer occurs from the π-conjugated side chains, which are composed of light-harvesting shape-persistent phenylene−ethynylene macrocycles, to the π-conjugated polymer chain.[9] In 1997, Vollhardt et al. have reported the first synthesis of dehydrobenzo[20]annulenes ([20]DBAs) by the cyclodimerization of bis(2-ethynylphenyl)ethyne and its strain-free twisted crystal structure.[10] They have reported that the chiral configurations easily isomerize even at room temperature, and the barrier for enantiomerization via a planar structure is 9.3 kcal/mol, as determined by ^{13}C NMR (Figure 1).

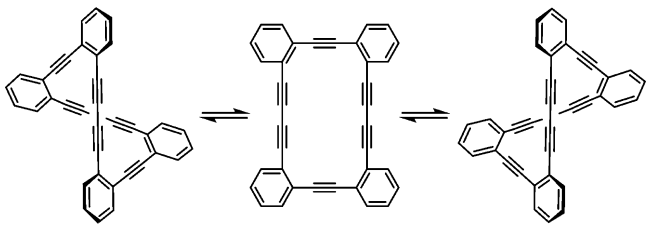


Figure 1. Enantiomerization of [20]DBA.

In this study, we focused on the structure of [20]DBAs as the cyclic π-conjugated side chain and synthesized π-conjugated-unit-strapped molecular wires[11] incorporating the [20]DBA moiety as a monomer unit and a canopy unit,[12] which can undergo conversion under thermal conditions. To synthesize [20]DBA-based π-conjugated polymer **2** by polymerization, we prepared the precursor of [20]DBA monomer **1**, containing a *tert*-butyl group for increasing the solubility of the [20]DBA unit and a diethyltriazene group for its conversion to iodide for further functionalization (Figure 2). We also synthesized

Received: June 24, 2015
Published: July 31, 2015

ACS Publications © 2015 American Chemical Society

DOI: 10.1021/acs.joc.5b01414
J. Org. Chem. 2015, 80, 8874−8880

integrated [20]DBA derivatives **3** and **4** by intramolecular Glaser-type cyclization under high dilution conditions and measured their optical properties.

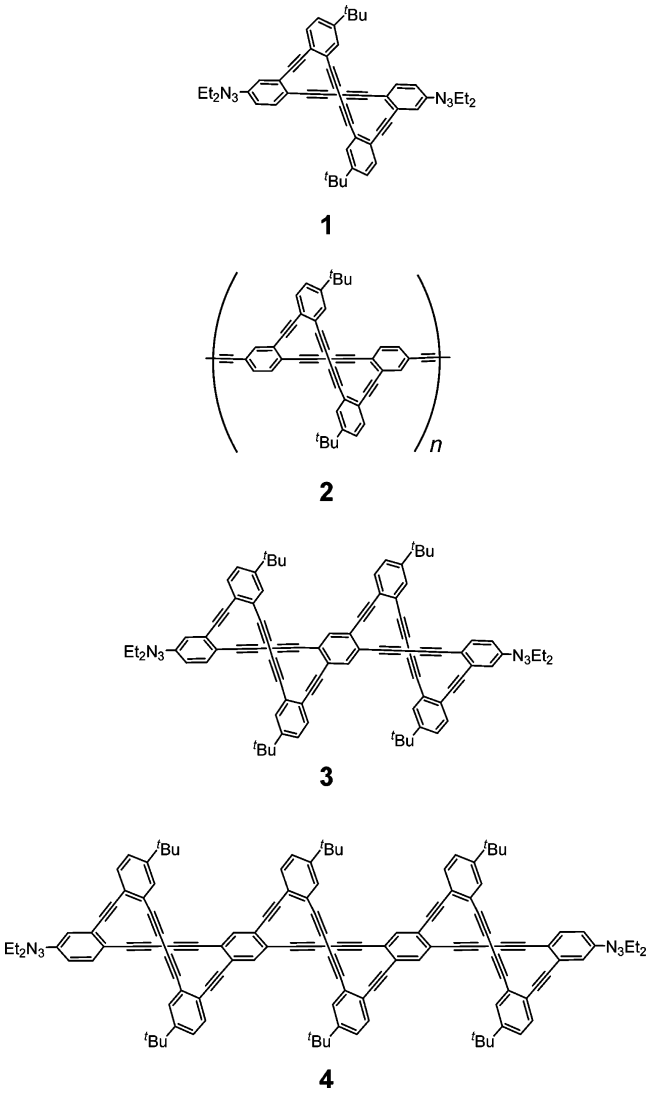
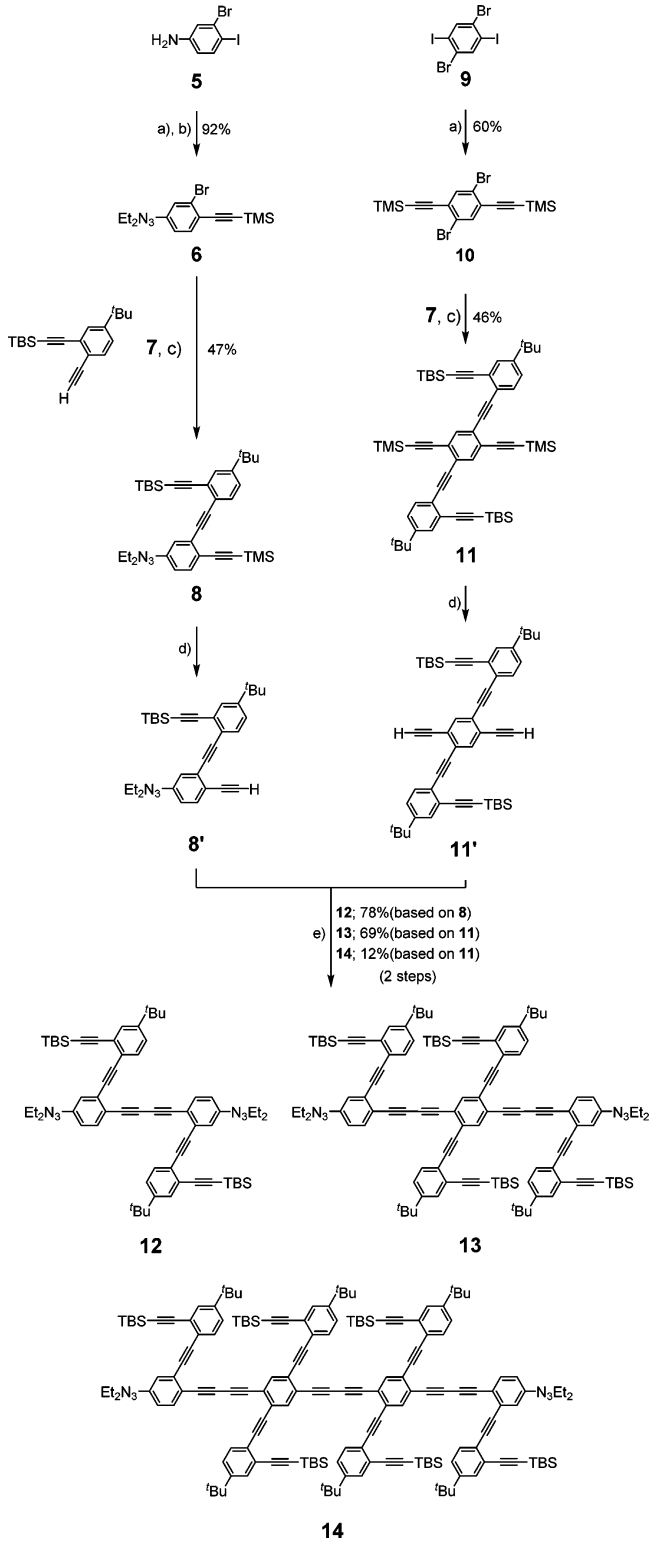


Figure 2. Structures of [20]DBA derivatives.

Scheme 1 shows the synthetic route of **12**, **13**, and **14**, which are precursors to integrated [20]DBA derivatives **1**, **3**, and **4**, respectively. The unsymmetrical unit **8** was synthesized by the Sonogashira coupling of 5-*tert*-butyl-1-*tert*-butyldimethylsilylethynyl-2-ethynylbenzene (**7**) with **6**, which was synthesized by the conversion of the amino group of **5** to the corresponding diethyltriazene group, followed by the Sonogashira cross-coupling with trimethylsilylacetylene (TMSA).[13] The Sonogashira cross-coupling was conducted using 1,4-dibromo-2,5-diiodobenzene (**9**) and TMSA to afford **10**, which underwent another Sonogashira cross-coupling with **7** to afford a symmetrical oligo(phenylene ethynylene) unit **11**, which has different silyl-protected ethynyl groups. After the selective deprotection of the TMS groups in **8** and **11** under basic condition, **8′** and **11′** were obtained, respectively. The precursors for [20]DBA derivatives **1**, **3**, and **4** were synthesized in one pot by the oxidative Glaser coupling of **11′** in the presence of an excess amount of **8′** (12 equiv), affording the corresponding precursors **12**, **13**, and **14** in 78% (based on **8**), 69% (based on **11**), and 12% yield (based on **11**), respectively, after purification by preparative size-exclusion chromatography with $CHCl_3$ as the eluent. Scheme 2 shows the

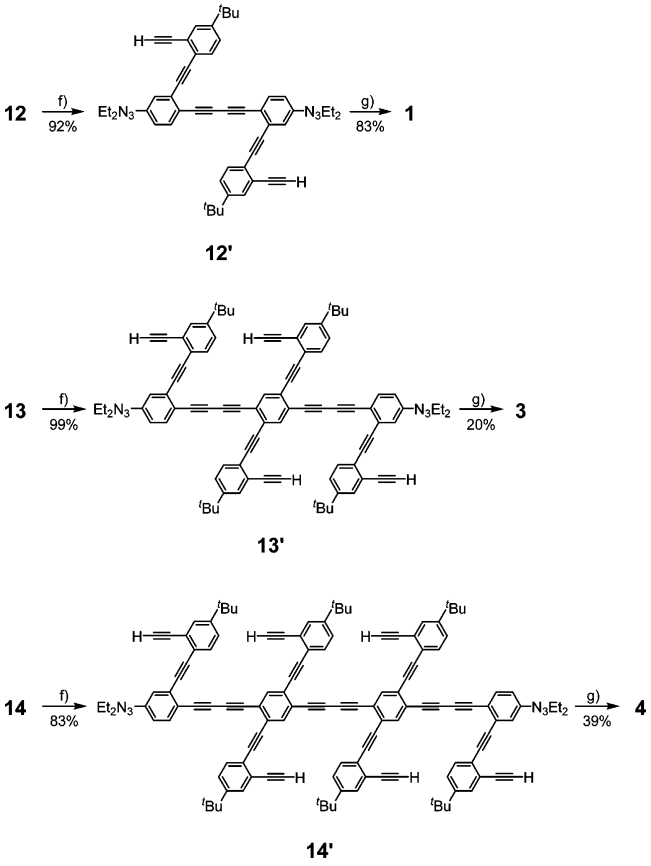
Scheme 1. Synthetic Route of Precursors to Integrated [20]DBA Derivatives[a]



[a]Reagents: (a) TMSA, $PdCl_2(PPh_3)_2$, CuI, Et_3N, toluene; (b) [i] $NaNO_2$aq, HClaq, CH_3CN, THF, [ii] Et_2NH, K_2CO_3, CH_3CN, H_2O; (c) $Pd(PPh_3)_4$, CuI, Et_3N; (d) K_2CO_3, MeOH, CH_2Cl_2; (e) $Cu(OAc)_2{\cdot}H_2O$, pyridine, CH_2Cl_2.

DOI: 10.1021/acs.joc.5b01414
J. Org. Chem. 2015, 80, 8874−8880

Scheme 2. Synthesis of [20]DBA Derivatives[a]



[a]Reagents: (f) TBAF, THF; (g) $Cu(OAc)_2 \cdot H_2O$, pyridine, $CHCl_3$.

synthetic route to integrated [20]DBA derivatives **1**, **3**, and **4** via deprotection, followed by intramolecular Glaser-type cyclization of the corresponding precursors **12**, **13**, and **14**, respectively.

With the increase of the π-conjugated units, the solubility of these precursors decreases; this is attributed to the increase in the degree of $\pi-\pi$ interaction. After the deprotection of the *tert*-butyldimethylsilyl groups of these precursors using tetrabutylammonium fluoride (TBAF), followed by intramolecular Glaser-type cyclization under high dilution conditions,[14] the desired [20]DBA derivatives **1**, **3**, and **4** were obtained in 83, 20, and 39% yield, respectively, after purification by preparative size-exclusion chromatography with $CHCl_3$ as the eluent. The solubilities of the [20]DBA derivatives thus obtained increase in comparison to those of the corresponding precursors; this can be attributed to the insulation effect by π-conjugated canopy units.

Figure 3 shows the crystals of **1** and **3** successfully grown from CH_2Cl_2/MeOH and benzene, respectively. X-ray diffraction analyses indicated that these single crystals exhibit a twisted configuration in their solid states. As can be observed in the packing structure of **1**, the enantiomers are arranged alternately, and **1** is racemic as a whole. The manner in which the rings are twisted in **3** probably indicates that **3** with two [20]DBA rings has two stable conformations.

Theoretical calculations (B3LYP/def2-TZVP-f level) suggested that the energy of the conformation in which the two [20]DBA rings face in the same direction (state A, "*syn*" conformation) and that in which they face in the opposite

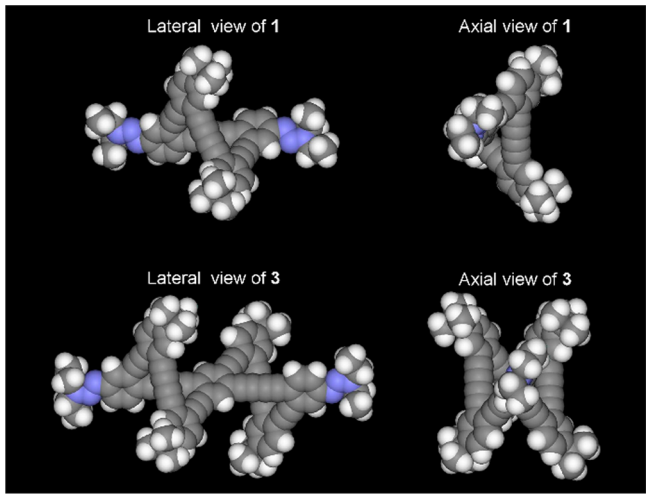


Figure 3. Space-filling model views of **1** and **3**.

direction (state C, "*anti*" conformation) are virtually the same (Figure 4). The energy difference of 0.3 kcal/mol is possibly

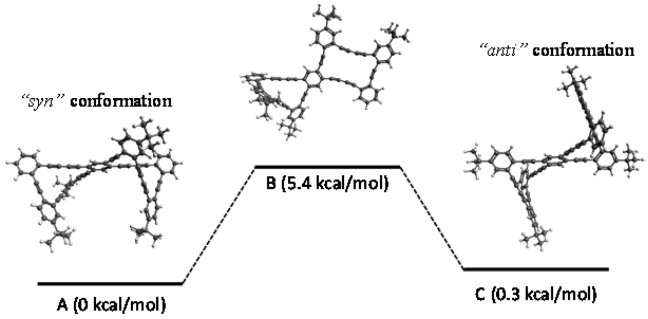
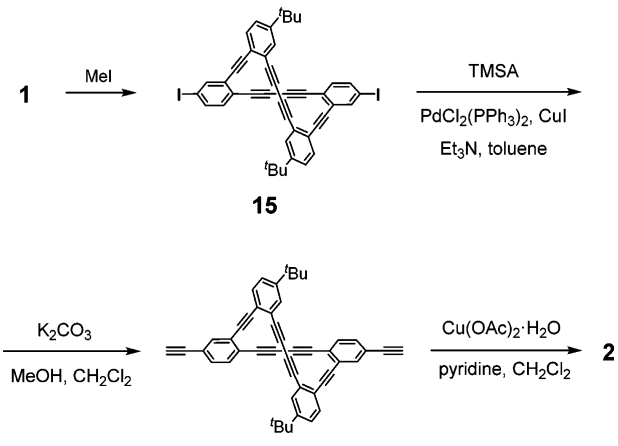


Figure 4. Calculated energy diagram for *syn* and *anti* [20]DBA conformations.

smaller than the error obtained from density functional theory. Notably, only the "*anti*" conformation is observed in the crystal structure, presumably because the molecules in the "*anti*" conformation are packed better as compared with those in the "*syn*" conformation.

Next, we synthesized [20]DBA polymer **2** from **1** (Scheme 3). This synthesis was achieved by the conversion of the N_3Et_2 group into its corresponding iodide using MeI; subsequent

Scheme 3. Synthesis of [20]DBA Polymer



DOI: 10.1021/acs.joc.5b01414
J. Org. Chem. 2015, 80, 8874−8880

Sonogashira coupling with TMSA afforded [20]DBA monomer **15**. Then, we attempted to polymerize **15** by the sequential deprotection of the TMS groups using K_2CO_3, followed by oxidative Glaser coupling. According to size-exclusion chromatograms, M_n is estimated to be 3.7×10^5 by using polystyrene as the calibration standard in the analysis. The average degree of polymerization (n) is observed to be 6.

To examine the covering effect of the oligo(phenylene diethynylene) units, we compared the UV−vis absorption spectra before and after cyclization (Figure 5). As compared

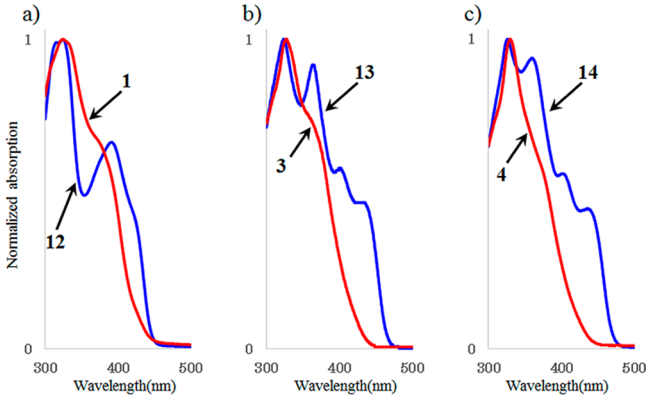


Figure 5. UV−vis absorption spectra of (a) **1** and **12**, (b) **3** and **13**, and (c) **4** and **14** in $CHCl_3$ at room temperature.

with those of the corresponding **12′**, **13′**, and **14′**, the peaks of **1**, **3**, and **4** at long wavelengths disappeared, probably caused by the decrease in the effective conjugation length because of the immobilization of the twisted structure by cyclization.

Figure 6 shows the comparison of the absorption and emission spectra of **1**, **3**, and **4**. From the results of the

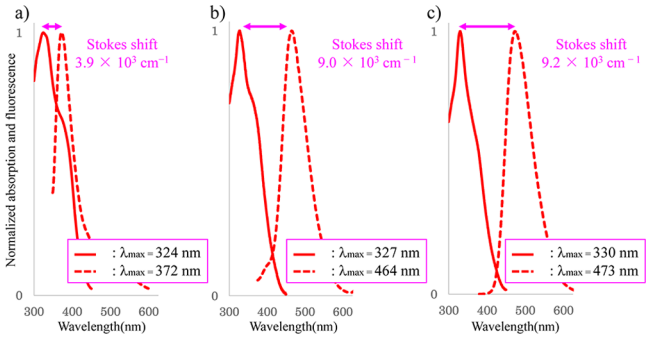


Figure 6. Absorption and emission spectra of (a) **1**, (b) **3**, and (c) **4** in $CHCl_3$ at room temperature.

absorption spectra, the spreading degree of the oligo(phenylene diethynylene) units of **1**, **3**, and **4** in the ground state is almost the same, resulting in a twisted structure, as all of the absorption maxima wavelengths are similar. The Stokes shifts of **1**, **3**, and **4** are 3.9×10^3, 9.0×10^3, and 9.2×10^3 cm^{-1}, respectively. The Stokes shifts for **3** and **4** are larger than that of **1**, implying that **3** and **4** undergo a larger change in conformation between the ground and the excited states caused by the formation of a two dimensionally expanded quinoid-type structure.

In conclusion, we succeeded in the precise synthesis of [20]DBA derivatives with the aim of using these derivatives as basic units in novel insulated molecular devices. We also successfully synthesized the integrated [20]DBA derivatives **3** and **4** as well as [20]DBA polymer **2**, which have defined structures and have not been reported previously. Moreover, our synthetic method enables the synthesis of different-sized integrated [20]DBA derivatives by simply adjusting the equivalent amount of precursors. Further derivatization of the integrated [20]DBAs thus formed is expected to result in new functions owing to the regulation of their asymmetric structures or electronic states.

EXPERIMENTAL SECTION

General Methods and Materials. Unless otherwise noted, commercially available chemicals were used as received. Solvents were purified as follows: reaction solvents were degassed by freeze−pump−thaw (three times) before use. Dry toluene, CH_2Cl_2, and THF were purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[15] 2-Bromo-4-*tert*-butyl-1-iodobenzene and 3-bromo-4-iodoaniline were prepared according to the literature.[16] ^1H NMR and ^{13}C NMR were recorded at 500 and 126 MHz, respectively. The ^1H NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protonated $CDCl_3$ (7.26 ppm). The ^{13}C NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.00 ppm) or $^{13}CDCl_3$ (77.16 ppm). Matrix-assisted laser desorption/ionization (MALDI) HRMS were obtained using 1,8-dihydroxy-9(10*H*)-anthracene as a matrix reagent on Thermo Fisher Scientific LTQ orbitrap XL. All data from the X-ray crystallographic analysis of **1** and **3** were processed using CrystalClear (Rigaku).[17] The structure was solved by SIR2008[18] and refined with the SHELXL97 program. All calculations were performed using the CrystalStructure software package.[19] Geometry optimization calculations based on density function theory (DFT) were performed using the hybrid B3LYP functional and the def2-TZVP Gaussian-type atomic orbital basis sets.[20,21] All DFT calculations were performed using the Orca software package (version 3.0.3).[22]

Crystal data for **1**: $C_{40}H_{40}ClN_4$, M = 612.24, triclinic, space group = $P\bar{1}$ (No. 2), a = 9.740(3) Å, b = 12.211(3) Å, c = 20.310(5) Å, α = 98.442(3)°, β = 100.942 (4)°, γ = 96.799 (4)°, V = 2319.2(9) Å^3, Z = 1, density (calc.) = 1.078 g/cm^3, μ(MoKα) = 0.535 cm^{-1}, unique reflections = 10 209 (R_{int} = 0.0336), GOF = 1.175. The final $R1$ factor was 0.0862 ($I > 2\sigma(I)$) ($wR2$ = 0.2523, all data).

Crystal data for **3**: $C_{80}H_{80}N_3$, M = 1083.53, triclinic, space group = $P\bar{1}$ (No. 2), a = 16.165(2) Å, b = 17.027(2) Å, c = 20.075(3) Å, α = 78.595(12)°, β = 76.463(12)°, γ = 73.597(12)°, V = 5101.8(10) Å^3, Z = 3, density (calc.) = 1.058 g/cm^3, μ(MoKα) = 0.604 cm^{-1}, unique reflections = 17 897 (R_{int} = 0.1145), GOF = 1.090. The final $R1$ factor was 0.1068 ($I > 2\sigma(I)$) ($wR2$ = 0.3031, all data).

1-[25,34-Di-*tert*-butyl-17-(diethyltriaz-1-en-1-yl)pentacyclo-[30.4.0.0^{4,9}.0^{14,19}.0^{22,27}]hexatriaconta-1(32),4-(9),5,7,14,16,18,22,24,26,33,35-dodecaen-2,10,12,20,28,30-hexayn-6-yl]-3,3-diethyltriaz-1-ene (1). Under an argon atmosphere, **12′** (165 mg, 0.217 mmol) was dissolved in degassed $CHCl_3$ (240 mL) and degassed pyridine (60 mL), and the solution was stirred at 100 °C, followed by the addition of $Cu(OAc)_2 \cdot H_2O$ (866 mg, 4.34 mmol) into the solution. The reaction mixture was stirred at 100 °C for 18 h. The solvent was removed by evaporation, and the residue was diluted with $CHCl_3$ and treated with HCl(aq). The organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane−EtOAc, 4:1) to afford the product as a yellow solid (137 mg, 83%).

^1H NMR (500 MHz, $CDCl_3$): δ = 7.59 (s, 4H), 7.48 (d, J = 4.0 Hz, 2H), 7.47 (d, J = 4.0 Hz, 2H), 7.36 (dd, J = 8.2, 1.5 Hz, 2H), 7.33 (dd, J = 8.2, 1.5 Hz, 2H), 3.78 (q, J = 7.0 Hz, 8H), 1.30−1.28 (m, 30H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.6, 151.3, 134.1, 131.5, 130.4, 127.3, 126.2, 124.9, 123.9, 123.5, 121.2, 120.6, 91.6, 91.2, 81.8, 81.6, 78.2, 77.7, 34.9, 31.1 (Two carbons are missing because of the quadrupole effect of nitrogen.). HRMS (APCI): m/z = calcd for $C_{52}H_{51}N_6$ $[M + H^+]^+$ 759.417; found: 759.415.

DOI: 10.1021/acs.joc.5b01414
J. Org. Chem. 2015, 80, 8874−8880

Poly(25,34-di-*tert*-butyl-6,17-diethynylpentacyclo-[30.4.0.0^{4,9}.0^{14,19}.0^{22,27}]hexatriaconta-1(32),4-(9),5,7,14,16,18,22,24,26,33,35-dodecaen-2,10,12,20,28,30-hexayne) (2). Under air, **15** (30.0 mg, 0.0398 mmol) was dissolved in CH_2Cl_2 (1.5 mL) and MeOH (1.5 mL), and K_2CO_3 (55.0 mg, 0.398 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 1 h, followed by the addition of pyridine (1.5 mL) and $Cu(OAc)_2{\cdot}H_2O$ (31.8 mg, 0.159 mmol). The solution was stirred at 40 °C for 18 h. The mixture was quenched with HCl(aq) and diluted with CH_2Cl_2. The organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation, and the residue was purified by preparative GPC with $CHCl_3$ as the eluent to afford the product as a brownish yellow solid (2.7 mg (n < 3), 3.5 mg (n = 3–6), and 2.9 mg (n > 6)).

3,3-Diethyl-1-[9,18,42,51-tetra-*tert*-butyl-59-(diethyltriaz-1-en-1-yl)nonacyclo[34.30.0.0^{3,34}.0^{6,11}.0^{16,21}.0^{24,29}.0^{39,44}.0^{49,54}.0^{57,62}]hexahexaconta-1(36),2,6,8,10,16(21),17,19,24(29),-25,27,34,39,41,43,49(54),50,52,57(62),58,60-henicosaen-4,12,14,22,30,32,37,45,47,55,63,65-dodecayn-26-yl]triaz-1-ene (3). Under an argon atmosphere, **13′** (25.0 mg, 0.0201 mmol) was dissolved in degassed $CHCl_3$ (40 mL) and degassed pyridine (10 mL), and the solution was stirred at 60 °C, followed by the addition of $Cu(OAc)_2{\cdot}H_2O$ (160.3 mg, 0.803 mmol) into the solution, and the reaction mixture was stirred at 60 °C for 18 h. The solvent was removed by evaporation, and the residue was diluted with $CHCl_3$ and treated with HCl(aq). The organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane–EtOAc, 17:3 to 3:1) and reprecipitation from toluene to afford the product as a yellow solid (5.1 mg, 20%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (s, 2H), 7.60 (d, J = 1.8 Hz, 2H), 7.59 (d, J = 1.8 Hz, 2H), 7.57 (d, J = 1.5 Hz, 2H), 7.48 (d, J = 3.4 Hz, 2H), 7.47 (d, J = 3.4 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.37–7.32 (m, 6H), 3.79 (q, J = 7.1 Hz, 8H), 1.31–1.28 (m, 48H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.1, 151.7, 151.5, 136.1, 134.0, 131.6, 131.5, 130.5, 127.4, 126.3, 126.2, 125.5, 125.0, 124.9, 123.9, 123.6, 123.3, 120.8, 120.6, 94.0, 91.5, 91.4, 90.2, 83.5, 81.8, 81.4, 81.0, 79.9, 77.9, 77.7, 77.6, 35.00, 34.98, 31.2, 31.1 (Two carbons are missing because of the quadrupole effect of nitrogen. Several peaks overlapped.). HRMS (APCI): m/z = calcd for $C_{90}H_{77}N_6$ [M + H$^+$]$^+$ 1241.620; found: 1241.618.

3,3-Diethyl-1-[7,16,40,49,70,79-hexa-*tert*-butyl-87-(diethyltriaz-1-en-1-yl)tridecacyclo[60.34.0.0^{4,9}.0^{14,19}.0^{22,57}.0^{24,55}.0^{29,34}.0^{37,42}.0^{47,52}.0^{64,95}.0^{67,72}.0^{77,82}.0^{85,90}]hexanonaconta-1(62),4(9),-5,7,14,16,18,22(57),23,29(34),30,32,37(42),-38,40,47,49,51,55,63,67(72),68,70,77,79,81,85,87,89,95-triacontaen-2,10,12,20,25,27,35,43,45,53,58,60,65,73,75,83,91,93-octadecayn-32-yl]triaz-1-ene (4). Under an argon atmosphere, **14′** (37.0 mg, 0.0214 mmol) was dissolved in degassed $CHCl_3$ (60 mL) and degassed pyridine (15 mL), and the solution was stirred at 100 °C, followed by the addition of $Cu(OAc)_2{\cdot}H_2O$ (256 mg, 1.28 mmol) into the solution, and the reaction mixture was stirred at 100 °C for 18 h. The solvent was removed by evaporation, and the residue was diluted with $CHCl_3$ and treated with HCl(aq). The organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane–EtOAc, 3:1) and reprecipitation from toluene to afford the product as a brownish yellow solid (14.4 mg, 39%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (s, 2H), 7.66 (s, 2H), 7.59–7.57 (m, 8H), 7.48–7.43 (m, 8H), 7.37–7.32(m, 8H), 3.79 (q, J = 6.7 Hz, 8H), 1.31–1.28 (m, 66H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.2, 152.1, 151.7, 151.6, 136.10, 136.05, 134.0, 131.6, 131.5, 130.4, 127.4, 126.4, 126.29, 126.26, 125.8, 125.03, 124.96, 124.94, 124.8, 123.9, 123.6, 123.3, 120.7, 120.6, 94.14, 94.10, 91.5, 91.4, 90.1, 90.0, 83.6, 81.8, 81.5, 81.4, 81.3, 81.2, 80.3, 79.8, 77.9, 77.8, 77.64, 77.58, 35.03, 35.00, 34.98, 31.2, 31.12, 31.10 (Two carbons are missing because of the quadrupole effect of nitrogen. Several peaks overlapped.). HRMS (MALDI): m/z = calcd for $C_{128}H_{103}N_6$ [M + H$^+$]$^+$ 1723.824; found: 1723.828.

1-[3-Bromo-4-[2-(trimethylsilyl)ethynyl]phenyl]-3,3-diethyl-1-triazene (6). Under an argon atmosphere, 1-(3-bromo-4-iodophenyl)-3,3-diethyl-1-triazene (11.9 g, 31.1 mmol), $PdCl_2(PPh_3)_2$ (437 mg, 0.622 mmol), and CuI (237 mg, 1.24 mmol) were dissolved in degassed Et_3N (100 mL), and trimethylsilylacetylene (4.51 mL, 32.4 mmol) was added into the solution. The reaction mixture was stirred at 30 °C overnight, diluted with Et_2O, and filtered through a Celite pad. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane–EtOAc, 17:3) to afford the product as a dark red oil (10.9 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, J = 2.1 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.27 (dd, J = 8.2, 2.1 Hz, 1H), 3.72 (q, J = 7.1 Hz, 4H), 1.23 (br m, 6H), 0.27 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.1, 133.9, 126.2, 123.7, 120.9, 119.6, 103.9, 98.7, 49.3, 41.4, 14.6, 11.3, 0.1. HRMS (APCI): m/z = calcd for $C_{15}H_{23}BrN_3Si$ [M + H$^+$]$^+$ 352.084; found: 352.083.

Tributyl[2-(5-*tert*-butyl-2-ethynylphenyl)ethynyl]silane (7). 4-(*tert*-Butyl)-1-(trimethylsilyl)ethynyl]-2(tributylsilyl)ethynylbenzene (18.4 g, 49.9 mmol) was dissolved in CH_2Cl_2 (100 mL) and MeOH (100 mL), and K_2CO_3 (34.5 g, 250 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched with HCl(aq) and diluted with CH_2Cl_2. The organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation to afford the product as a yellow oil (15.3 g, >99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (1H, d, J = 1.8 Hz), 7.43 (1H, d, J = 8.2 Hz), 7.30 (1H, dd, J = 8.2, 1.8 Hz), 3.23 (1H, s), 1.31 (9H, s), 1.05 (9H, s), 0.23 (6H, s). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.8, 132.4, 129.3, 126.1, 125.6, 122.4, 104.5, 96.4, 82.5, 80.5, 34.9, 31.2, 26.4, 16.9, − 4.4. HRMS (APCI): m/z = calcd for $C_{20}H_{29}Si$ [M + H$^+$]$^+$ 297.203; found: 297.203.

1-[3-(2-{4-*tert*-Butyl-2-[2-(tributylsilyl)ethynyl]phenyl}-ethynyl)-4-[2-(trimethylsilyl)ethynyl]phenyl]-3,3-diethyltriaz-1-ene (8). Under an argon atmosphere, **7** (11.8 g, 39.8 mmol), **6** (10.8 g, 30.7 mmol), $Pd(PPh_3)_4$ (1.77 g, 1.54 mmol), and CuI (146 mg, 0.768 mmol) were dissolved in degassed Et_3N (100 mL). The reaction mixture was stirred at 110 °C overnight, diluted with Et_2O, and filtered through a Celite pad. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane–EtOAc, 9:1), followed by preparative GPC using $CHCl_3$ as the eluent to afford the product as a yellow solid (8.20 g, 47%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.54–7.46 (m, 3H), 7.36–7.33 (m, 2H), 3.77 (q, J = 7.0 Hz, 4H), 1.34 (s, 9H), 1.27 (br m, 6H), 1.04 (s, 9H), 0.29 (s, 9H), 0.25 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.3, 150.8, 133.0, 132.2 129.5, 126.9, 125.6, 125.2, 124.2, 123.6, 121.7, 120.2, 104.9, 104.4, 97.7, 96.1, 91.9, 91.8, 34.8, 31.2, 26.4, 16.9, 0.3, − 4.3 (Two carbons are missing because of the quadrupole effect of nitrogen.). HRMS (APCI): m/z = calcd for $C_{35}H_{50}N_3Si_2$ [M + H$^+$]$^+$ 568.354; found: 568.353.

{2-[2,5-Bis(2-{4-*tert*-butyl-2-[2-(trimethylsilyl)ethynyl]-phenyl}ethynyl)-4-[2-(tributylsilyl)ethynyl]phenyl]ethynyl}-tributylsilane (11). Under an argon atmosphere, **7** (2.30 g, 7.76 mmol), **10** (1.11 g, 2.59 mmol), $Pd(PPh_3)_4$ (150 mg, 0.130 mmol), and CuI (12.3 mg, 0.0648 mmol) were dissolved in degassed Et_3N (50 mL). The reaction mixture was stirred at 110 °C overnight, diluted with Et_2O, and filtered through a Celite pad. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane to hexane–EtOAc, 19:1), followed by preparative GPC with $CHCl_3$ as the eluent to afford the product as a yellow solid (1.03 g, 46%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (s, 1H), 7.55 (s, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 1.34 (s, 9H), 1.06 (s, 9H), 0.29 (s, 9H), 0.27 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.9, 136.1, 132.0, 129.7, 125.7, 125.64, 125.56, 125.1, 122.9, 104.7, 102.5, 100.8, 96.5, 94.4, 90.6, 34.9, 31.2, 26.4, 16.9, 0.1, − 4.23, − 4.27. HRMS (APCI): m/z = calcd for $C_{56}H_{75}Si_4$ [M + H$^+$]$^+$ 859.494; found: 859.492.

12–14. Under air, **8** (3.17 g, 5.58 mmol) and **11** (400 mg, 0.465 mmol) were dissolved in CH_2Cl_2 (40 mL) and MeOH (40 mL), and K_2CO_3 (4.50 g, 32.6 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 1 h, followed by the addition of pyridine (40 mL) and $Cu(OAc)_2{\cdot}H_2O$ (2.60 g, 13.0 mmol). The reaction mixture was stirred at 40 °C overnight. The mixture was quenched with HCl(aq) and diluted with CH_2Cl_2. The organic layer was separated and dried over Na_2SO_4. The solvent was

DOI: 10.1021/acs.joc.5b01414
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removed by evaporation, and the residue was purified by preparative GPC with $CHCl_3$ as the eluent to afford **12** as a yellow solid (2.16 g, 78% based on **8**), **13** as a yellow solid (543 mg, 69% based on **11**), and **14** as a yellow solid (131 mg, 12% based on **11**).

1-[3-(2-{4-*tert*-Butyl-2-[2-(tributylsilyl)ethynyl]phenyl}-ethynyl)-4-{4-[2-(2-{4-*tert*-butyl-2-[2-(tributylsilyl)ethynyl]-phenyl}ethynyl)-4-(diethyltriaz-1-en-1-yl)phenyl]buta-1,3-diyn-1-yl}phenyl]-3,3-diethyltriaz-1-ene (12). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (s, 2H), 7.52 (d, J = 2.7 Hz, 2H), 7.51 (d, J = 2.7 Hz, 2H), 7.40 (s, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 3.79 (q, J = 7.0 Hz, 8H), 1.28 (br m, 12H), 1.24 (s, 18H), 1.04 (s, 18H), 0.24 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.30, 151.25, 133.5, 133.0, 129.2, 128.1, 125.9, 124.8, 123.8, 123.2, 120.9, 120.5, 105.0, 95.8, 92.9, 91.5, 82.3, 78.2, 34.8, 31.1, 26.4, 16.9, − 4.3 (Two carbons are missing because of the quadrupole effect of nitrogen.). HRMS (APCI): m/z = calcd for $C_{64}H_{81}N_6Si_2$ $[M + H^+]^+$ 989.606; found: 989.603.

1-(4-{4-[2,5-Bis(2-{4-*tert*-butyl-2-[2-(tributylsilyl)ethynyl]-phenyl}ethynyl)-4-{4-[2-(2-{4-*tert*-butyl-2-[2-(tributylsilyl)-ethynyl]phenyl}ethynyl)-4-(diethyltriaz-1-en-1-yl)phenyl]buta-1,3-diyn-1-yl}phenyl]buta-1,3-diyn-1-yl}-3-(2-{4-*tert*-butyl-2-[2-(tributylsilyl)ethynyl]phenyl}ethynyl)phenyl)-3,3-diethyltriaz-1-ene (13). ^{1}H NMR (500 MHz, $CDCl_3$): δ = ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.76 (s, 2H), 7.67 (s, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 3.1 Hz, 2H), 7.48 (d, J = 3.1 Hz, 2H), 7.41 (d, J = 7.6 Hz, 4H), 7.37 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 4H), 3.80 (q, J = 6.8 Hz, 8H), 1.29 (br m, 12H), 1.25 (s, 18H), 1.23 (s, 18H), 1.05 (s, 18H), 1.04 (s, 18H), 0.25 (s, 24H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.9, 151.6, 151.4, 136.0, 133.7, 132.9, 129.4, 129.3, 128.2, 126.7, 126.0, 125.9, 125.2, 124.94, 124.87, 124.0, 123.0, 122.5, 120.5, 120.2, 105.0, 104.7, 96.5, 95.9, 95.6, 93.0, 91.3, 90.1, 83.9, 81.0, 80.2, 77.6, 34.9, 34.8, 31.1, 26.43, 26.37, 16.9, − 4.3 (Two carbons are missing because of the quadrupole effect of nitrogen. Several peaks overlapped.). HRMS (APCI): m/z = calcd for $C_{114}H_{137}N_6Si_4$ $[M + H^+]^+$ 1701.998; found: 1701.997.

1-{4-[4-(4-{4-[2,5-Bis(2-{4-*tert*-butyl-2-[2-(tributylsilyl)-ethynyl]phenyl}ethynyl)-4-{4-[2-(2-{4-*tert*-butyl-2-[2-(tributyl-silyl)ethynyl]phenyl}ethynyl)-4-(diethyltriaz-1-en-1-yl)phenyl]-buta-1,3-diyn-1-yl}phenyl]buta-1,3-diyn-1-yl}-2,5-bis(2-{4-*tert*-butyl-2-[2-(tributylsilyl)ethynyl]phenyl}ethynyl)phenyl)buta-1,3-diyn-1-yl]-3-(2-{4-*tert*-butyl-2-[2-(tributylsilyl)ethynyl]-phenyl}ethynyl)phenyl}-3,3-diethyltriaz-1-ene (14). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77−7.76 (m, 3H), 7.66−7.65 (m, 2H), 7.54−7.35 (m, 17H), 7.19−7.18 (m, 6H), 3.80 (q, J = 6.7 Hz, 8H), 1.29 (br m, 12H), 1.25−1.23 (m, 54H), 1.04 (m, 54H), 0.25 (s, 36H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.0, 151.9, 151.6, 151.4, 136.1, 136.0, 133.7, 132.9, 132.7, 129.5, 129.4, 129.3, 128.2, 126.8, 126.7, 126.0, 125.4, 125.3, 125.2, 124.9, 124.3, 124.0, 123.0, 122.4, 122.3, 120.5, 120.2, 105.0, 104.7, 104.6, 96.6, 96.5, 95.9, 95.83, 95.80, 93.0, 91.3, 90.0, 89.9, 84.1, 81.6, 81.2, 80.1, 80.0, 77.5, 34.9, 34.8, 31.1, 26.4, 26.39, 26.37, 16.9, − 4.26, − 4.27 (Two carbons are missing because of the quadrupole effect of nitrogen. Several peaks overlapped.). HRMS (APCI): m/z = calcd for $C_{164}H_{193}N_6Si_6$ $[M + H^+]^+$ 2414.390; found: 2414.394.

1-{3-[2-(4-*tert*-Butyl-2-ethynylphenyl)ethynyl]-4-(4-{2-[2-(4-*tert*-butyl-2-ethynylphenyl)ethynyl]-4-(diethyltriaz-1-en-1-yl)-phenyl}buta-1,3-diyn-1-yl)phenyl}-3,3-diethyltriaz-1-ene (12′). Under air, **12** (235 mg, 0.237 mmol) was dissolved in THF (40 mL), and 0.475 mL of a 1.00 M solution of TBAF in THF (0.475 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 15 min. The mixture was quenched with H_2O and diluted with EtOAc. The organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane−EtOAc, 4:1) to afford the product as a yellow solid (166 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, J = 1.8 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 1.8 Hz, 2H), 7.36 (dd, J = 8.2, 1.8 Hz, 2H), 7.27 (dd, J = 8.2, 1.8 Hz, 2H), 3.80 (q, J = 7.1 Hz, 8H), 3.53 (s, 2H), 1.30 (br m, 12H), 1.26 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.5, 151.4, 133.9, 132.6, 129.6, 127.7, 126.1, 124.5, 124.2, 123.4, 120.5, 120.4, 92.2, 91.6, 82.7, 82.5, 81.4, 78.5, 34.8, 31.1 (Two carbons are missing because of the quadrupole effect of nitrogen.). HRMS (APCI): m/z = calcd for $C_{52}H_{53}N_6$ $[M + H^+]^+$ 761.433; found: 761.431.

1-[4-(4-{2,5-Bis[2-(4-*tert*-butyl-2-ethynylphenyl)ethynyl]-4-(4-{2-[2-(4-*tert*-butyl-2-ethynylphenyl)ethynyl]-4-(diethyltriaz-1-en-1-yl)phenyl}buta-1,3-diyn-1-yl)phenyl}buta-1,3-diyn-1-yl)-3-[2-(4-*tert*-butyl-2-ethynylphenyl)ethynyl]phenyl]-3,3-diethyltriaz-1-ene (13′). Under air, **13** (200 mg, 0.117 mmol) was dissolved in THF (30 mL), and 0.470 mL of a 1.00 M solution of TBAF in THF (0.470 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 10 min. The mixture was quenched with H_2O and diluted with EtOAc. The organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane−EtOAc, 17:3 to hexane−EtOAc, 3:1) to yield the product as a yellow solid (121 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (s, 2H), 7.65 (s, 2H), 7.57−7.54 (m, 6H), 7.51 (s, 4H), 7.39 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 4H), 3.80 (q, J = 6.9 Hz, 8H), 3.55 (s, 2H), 3.52 (s, 2H), 1.28−1.27 (m, 48H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.1, 151.8, 151.6, 136.6, 134.0, 132.6, 132.5, 129.61, 129.59, 127.9, 126.5, 126.1, 126.0, 124.7, 124.6, 124.5, 124.2, 123.3, 122.7, 120.4, 119.8, 95.1, 92.4, 91.4, 90.2, 84.3, 82.7, 82.5, 81.6, 81.3, 80.6, 77.8, 34.9, 34.8, 31.09, 31.07 (Two carbons are missing because of the quadrupole effect of nitrogen. Several peaks overlapped.). HRMS (APCI): m/z = calcd for $C_{90}H_{81}N_6$ $[M + H^+]^+$ 1245.652; found: 1245.650.

1-(4-{4-[4-(4-{2,5-Bis[2-(4-*tert*-butyl-2-ethynylphenyl)-ethynyl]-4-(4-{2-[2-(4-*tert*-butyl-2-ethynylphenyl)ethynyl]-4-(diethyltriaz-1-en-1-yl)phenyl}buta-1,3-diyn-1-yl)phenyl}buta-1,3-diyn-1-yl)-2,5-bis[2-(4-*tert*-butyl-2-ethynylphenyl)ethynyl]-phenyl]buta-1,3-diyn-1-yl}-3-[2-(4-*tert*-butyl-2-ethynylphenyl)-ethynyl]phenyl)-3,3-diethyltriaz-1-ene (14′). Under air, **14** (125 mg, 0.052 mmol) was dissolved in THF (20 mL), and 0.310 mL of a 1.00 M solution of TBAF in THF (0.310 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 10 min. The mixture was quenched with H_2O and diluted with EtOAc. The organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane−EtOAc, 17:3 to hexane−EtOAc, 3:1) to afford the product as a brownish yellow solid (74.5 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (s, 2H), 7.79 (s, 2H), 7.66 (s, 2H), 7.58−7.54 (m, 8H), 7.52 (s, 6H), 7.39 (d, J = 8.5 Hz, 2H), 7.31−7.29 (m, 6H), 3.80 (q, J = 7.0 Hz, 8H), 3.57 (s, 2H), 3.54 (s, 2H), 3.53 (s, 2H), 1.28 (br m, 66H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.3, 152.2, 151.8, 151.7, 136.7, 136.6, 134.0, 132.64, 132.55, 132.5, 129.7, 129.63, 129.59, 127.9, 126.6, 126.3, 126.14, 126.10, 126.0, 125.1, 124.6, 124.5, 124.2, 124.1, 123.3, 122.7, 122.6, 120.4, 119.7, 95.27, 95.26, 92.4, 91.4, 90.11, 90.05, 84.5, 82.7, 82.51, 82.49, 82.1, 81.7, 81.6, 81.3, 80.5, 80.4, 77.8, 34.9, 34.8, 31.10, 31.07 (Two carbons are missing because of the quadrupole effect of nitrogen. Several peaks overlapped.). HRMS (APCI): m/z = calcd for $C_{128}H_{109}N_6$ $[M + H^+]^+$ 1729.871; found: 1729.869.

25,34-Di-*tert*-butyl-6,17-diiodopentacyclo[30.4.0.0^{4,9}.0^{14,19}.0^{22,27}]hexatriaconta-1(32),4(9),5,7,14,16,18,22,24,26,33,35-dodecaen-2,10,12,20,28,30-hexayne (15). Under N_2, **1** (80 mg, 0.132 mmol) was dissolved in MeI (3.0 mL), and the solution was stirred at 130 °C for 12 h using a microwave reactor. The reaction mixture was diluted with $CHCl_3$ and filtered through a Celite pad. The solvent was removed by evaporation, and the residue was purified by silica-gel column chromatography (hexane−EtOAc, 9:1) to afford **15** as a brownish yellow solid (42.5 mg, 50%). ^{1}H NMR ($CDCl_3$) δ: 7.89 (d, J = 1.5 Hz, 2H), 7.59−7.57 (m, 4H), 7.45 (d, J = 8.2 Hz, 2H), 7.37 (dd, J = 8.2, 1.8 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 1.29 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.2, 140.2, 137.2, 134.2, 131.6, 130.4, 128.4, 126.4, 124.9, 124.4, 123.2, 94.4, 93.3, 89.5, 81.5, 81.0, 79.3, 77.7, 35.0, 31.1. HRMS (APCI): m/z = calcd for $C_{44}H_{31}I_2$ $[M + H^+]^+$ 813.052; found: 813.049.

DOI: 10.1021/acs.joc.5b01414
J. Org. Chem. 2015, 80, 8874−8880

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01414.

^{1}H NMR and ^{13}C NMR spectra for obtained compounds and DFT optimized structures for the model compound **3** (PDF)

X-ray data for **1** (CIF)

X-ray data for **3** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Funding Program for JSPS Research Fellow and Grant-in-Aid for Scientific Research (B) and Scientific Research on Innovative Areas ("Molecular Architectonics" and "Soft Molecular Systems") from MEXT, Japan. This research was also supported by Tokuyama Science Foundation and PRESTO, JST.

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DOI: 10.1021/acs.joc.5b01414
J. Org. Chem. 2015, 80, 8874−8880