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Gas-Phase Generation of Highly Reactive Hexatriyne-Bridged [6_n]Paracyclophynes

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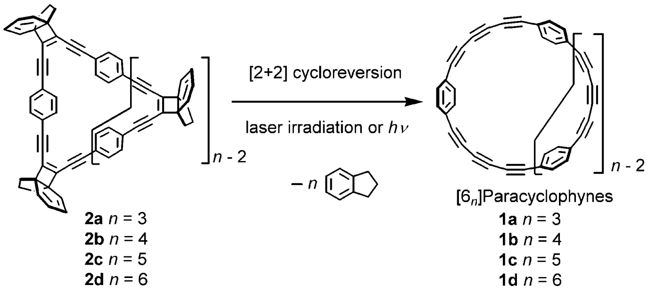
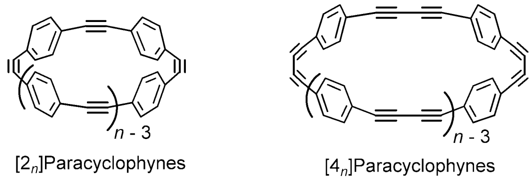
Received April 25, 2005

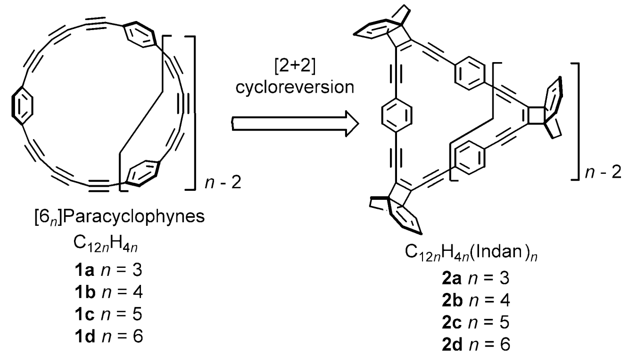


[6_n]Paracyclophenediynes **2a**−**d** ($n = 3-6$) having [4.3.2]-propellatriene units were prepared as precursors of the corresponding [6_n]paracyclophynes. Laser irradiation of **2a**−**d** produced the negative ions of [6_n]paracyclophynes **1a**−**d** ($n = 3-6$) by extrusion of the indan fragments, which were detected by time-of-flight mass spectrometry.

The [2_n]- and [4_n]paracyclophynes possessing phenylene ethynylenes or phenylene butadiynylenes as repeating units adopt rigid and belt-shaped structures with well-defined cavities.[1] Because of the deformation of the benzene rings and triple bonds, the electronic properties inside/outside the cavities are different. In this respect, considerable interest has been shown in the unique complexation behavior of these molecules. The first series of this class of compounds, [2_n]paracyclophynes (n = 6−9), were prepared by Kawase and Oda.[2] They demonstrated that [2_6]paracyclophyne having a cavity with a diameter of 1.31 nm formed 1:1 inclusion complexes with fullerenes (C_{60}, C_{70}, and a methano[60]fullerene derivatives) in solution as well as in the solid state.[2c,d] Moreover, the formation of double-inclusion complexes composed of two paracyclophyne molecules with different ring size and a C_{60} molecule was reported.[2e] The next higher homologue, a butadiyne-bridged [4_6]paracyclophyne derivative, was synthesized by Ohkita and Tsuji by using photochemical valence isomerization of the corresponding Dewar benzene valence isomer.[3] Although the individual triple bond is not much deformed, the compound is air-sensitive and decomposes gradually within several days.



In view of the known reactivity of polyynes,[4] it is expected that the elongation of the sp-carbon chains of the cyclophynes would reduce their kinetic stabilities.[5] Indeed, attempts to prepare octatetrayne-bridged [8_2]paracyclophyne by oxidative decomplexation of the corresponding cobalt complex precursor was not successful.[6] Similarly, the longer homologue, [12_2]paracyclophyne ($C_{36}H_8$), also eluded characterization, while its anion was detected in the laser-desorption time-of-flight (LD-TOF) mass spectrometry of the corresponding precursor having [4.3.2]propellatriene units.[7] It should be pointed out, however, that the corresponding chloro derivative ($C_{36}Cl_8$) lost all chlorine atoms to form a C_{36} carbon cluster, although its structure has not been clarified yet. This suggests that highly reactive [m_n]paracyclophynes with long sp-carbon chains may serve as precursors of small carbon clusters with a specific carbon number. From the above points of view, we became interested in hexatriyne-bridged [6_n]paracyclophynes (**1a**−**d**; $n = 3-6$).



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[3] Ohkita, M.; Ando, K.; Tsuji, T. *Chem. Commun.* **2001**, 2570−2571.

[4] For reviews, see: (a) Huntsman, W. D. In *The Chemistry of the Carbon−Carbon Triple Bond*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1978; Part 2, pp 553−620. (b) Tobe, Y.; Wakabayashi, T. In *Acetylene Chemistry: Chemistry, Biology and Material Science*; Diederich, F., Stang, P. J., Tykwinski, R. R., Eds.; Wiley−VCH: Weinheim, 2005; pp 387−426.

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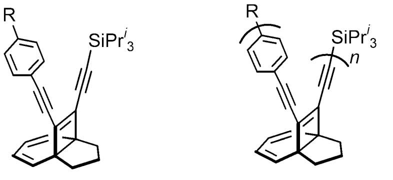
10.1021/jo050833d CCC: $30.25

Because of the expected deformations,[8] these compounds may not be accessible by the conventional coupling reactions to form a triyne unit.[9] We designed, therefore, [6_n]paracyclophynes having [4.3.2]propellatriene units **2a**–**d** (n = 3–6) as precursors of **1a**–**d** on the basis of our previous work on the generation of reactive polyynes based on [2+2] cycloreversion.[5,10] In this paper, we report the synthesis of precursors **2a**–**d**, photolysis of **2a** in solution, and the generation of the anions of **1a**–**d** from **2a**–**d** by laser irradiation.



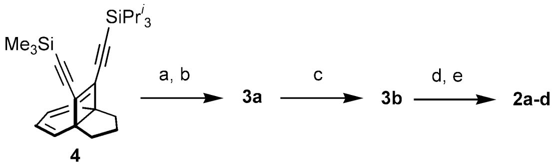
3a R = N_3Et_2
3b R = I

5a R = N_3Et_2, n = 2 **5b** R = I, n = 2
6a R = N_3Et_2, n = 3 **6b** R = I, n = 3
7 R = N_3Et_2, n = 4
8a R = N_3Et_2, n = 5 **8b** R = I, n = 5

For the preparation of cyclophenediynes **2a**–**d**, we designed **3a** as a key building block having both masked iodobenzene and protected terminal acetylene moieties. This compound **3a** was prepared from the known diethynylpropellane **4**[10] by desilylation and subsequent palladium-catalyzed coupling with 1-(4-iodophenyl)-3,3-diethyltriazene (Scheme 1). For the preparation of **2a**–**d**, we first examined the one-shot cross coupling reaction of **3b**. Triazenyl to iodo transformation[11] of **3a** gave **3b**. After removal of the protecting group of **3b** with TBAF, palladium-catalyzed coupling under high dilute conditions gave cyclic dehydrotrimer **2a**[12] as a major product (6%) together with cyclic dehydrotetramer **2b**[12] (trace), cyclic dehydropentamer **2c**,[12] and cyclic dehydrohexamer **2d**[12] (2%; combined yield of **2c** and **2d**) (Scheme 1).

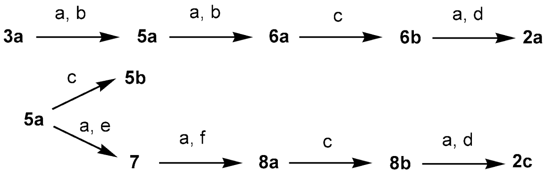
Because of the low yield of the products and the difficulty in their separation, we turned to stepwise, size-selective synthesis of **2a**–**d**. The synthesis of cyclic dehydrotrimer **2a** is shown in Scheme 2. After desilylation of **3a**, palladium-catalyzed coupling with **3b** gave dehydrodimer **5a**.[12] Linear dehydrotrimer **6a**[12] was prepared by desilylation of **5a** followed by palladium-catalyzed coupling with **3b**. The triazenyl to iodo transformation of **6a** yielded **6b**.[12] Finally, desilylation of **6b** and subsequent palladium-catalyzed coupling under high dilute conditions afforded cyclic dehydrotrimer **2a** in good yield (80%). Similarly, cyclic dehydropentamer **2c** was also prepared selectively in a stepwise manner as shown in Scheme 2. Removal of the protecting group of **5a** followed by coupling with **5b**,[12] prepared from **5a** by treatment with CH_3I, gave linear dehydrotetramer **7**.[12] Linear dehydropentamer **8a**[12] was obtained by desilylation of **7** followed by coupling with **3b**. Finally, triazenyl to iodo transformation to give **8b**,[12] desilylation, and subsequent palladium-catalyzed coupling under dilute conditions afforded cyclic dehydropentamer **2c** albeit in low yield (9%).

SCHEME 1[a]



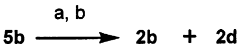
[a] Reagents and conditions: (a) K_2CO_3, rt; (b) p-$N_3Et_2C_6H_4I$, $Pd(PPh_3)_4$, CuI, Et_3N, rt, 85%; (c) CH_3I, 100 °C, 94%; (d) $Bu^n{}_4NF$, THF, rt; (e) $Pd(PPh_3)_4$, CuI, Et_3N, rt.

SCHEME 2[a]



[a] Reagents and conditions: (a) $Bu^n{}_4NF$, AcOH, THF, rt; (b) **3b**, $Pd(PPh_3)_4$, CuI, Et_3N, reflux, 87% for **5a**, 88% for **6a**; (c) CH_3I, 100 °C, 90% for **5b**, 96% for **6b**, 96% for **8b**; (d) $Pd(PPh_3)_4$, CuI, Et_3N, 50 to 70 °C, 80% for **2a**, 9% for **2c**; (e) **5b**, $Pd(PPh_3)_4$, CuI, Et_3N, 50 °C, 89%; (f) **3b**, $Pd(PPh_3)_4$, CuI, Et_3N, 50 °C, 77%.

SCHEME 3[a]



[a] Reagents and conditions: (a) $Bu^n{}_4NF$, THF, rt; (b) $Pd(PPh_3)_4$, CuI, Et_3N, rt, 54% for **2b**, 7% for **2d**.

To obtain even-numbered cyclic dehydrooligomers such as **2b** and **2d**, palladium-catalyzed coupling of the dehydrodimer unit was examined (Scheme 3). Desilylation of **5b** with TBAF followed by palladium-catalyzed coupling under dilute conditions yielded cyclic dehydrotetramer **2b** and cyclic dehydrohexamer **2d** in 54% and 7% yields, respectively.

The ^1H NMR chemical shift of the aromatic protons in cyclic dehydrotrimer **2a** (δ 7.35 ppm) exhibits slight upfield shifts as compared to those of larger cyclic dehydrooligomers **2b**–**d** (δ 7.43–7.45 ppm) because of the anisotropic shielding effect of the neighboring aromatic rings, which are located closer than in **2b**–**d**. Except for this, the spectral properties of **2a**–**d** are very similar to each other.

To generate [6_3]paracyclophyne **1a** in solution, a degassed solution of **2a** in THF-d_8 was irradiated with a low-pressure mercury lamp. However, whereas the ^1H NMR spectrum exhibited signals due to indan, we were not able to detect signals due to **1a** or intermediates such as **9** leading to **1a**, indicating that these are too reactive in solution. Photolysis was then carried out in furan to intercept reactive intermediates under similar conditions, yielding a 1:3 mixture of two different furan adducts

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[8] AM1 calculations predict that the triple bonds of **1a**–**d** are moderately deformed from linearity; the calculated bond angles of the triyne unit, $C(sp^2)-C(1)\equiv C(2)$, $C(1)\equiv C(2)-C(3)$, and $C(2)-C(3)\equiv C(4)$, are as follows: **1a**, 166.1°, 167.1°, and 167.0°; **1b**, 169.6°, 170.3°, and 170.2°; **1c**, 171.6°, 172.3°, and 172.2°; **1d**, 173.0°, 173.5°, and 173.5°.

[9] For example, see: (a) Bell, M. L.; Chiechi, R. C.; Johnson, C. A.; Kimball, D. B.; Matzger, A. J.; Wan, W. B.; Weakley, T. J. R.; Haley, M. M. *Tetrahedron* **2001**, *57*, 3507–3520. (b) Ye, F.; Orita, A.; Yaruva, J.; Hamada, T.; Otera, J. *Chem. Lett.* **2004**, *33*, 528–529.

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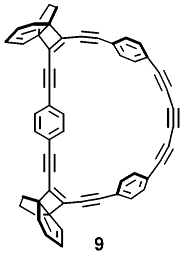
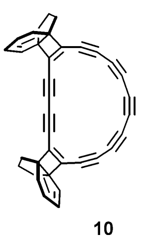
[12] Compounds **2a**–**d**, **5a**,**b**, **6a**,**b**, **7**, **8a**,**b**, and **11a**,**b** are mixtures of diastereomers. The structures of only one of them are drawn for clarity.

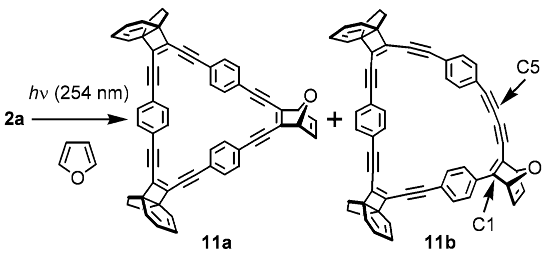
11a[12] and **11b**[12] (total yield of 26%) together with recovered **2a** (27%) (Scheme 4). Although **11a** and **11b** could not be separated, their structures were elucidated on the basis of the NMR spectra of the mixture. In particular, the ^{13}C NMR spectrum exhibited an sp carbon signal (C5) at 80 ppm, characteristic of the central carbon of a deformed butadiyne unit[3] and the quaternary sp^2 carbon signal (C1) at considerable low field (164 ppm), which we assigned to the one in the oxanorbornadiene framework adjacent to the benzene ring.[13] These signals are consistent with the unsymmetrical [4+2] adduct **11b**.


9


10

This means that the intermediate **9** reacted at the both triple bonds of the hexatriyne moiety. In contrast, we observed that related decapentayne-bridged compound **10** reacted with furan regioselectively at the central triple bond of the decapentayne moiety.[10] The difference between the regioselectivity can be explained in terms of strain of the triple bonds. The calculated bond angle of the central triple bond of the decapentayne moiety of **10** is most severely deformed (159.5° vs 162.0° (av) and 168.2° (av) for the other two triple bonds by AM1 calculations), in contrast to the similarly deformed triple bonds of the hexatriyne moiety of **9** (166.1° vs 166.5° (av) by AM1 calculations).

SCHEME 4



In view of the low efficiency of the photolysis of **2a** in solution, we examined the generation of ions of **1a**–**d** (n = 3–6) by laser irradiation in the gas phase.[14] As shown in Figure 1a–d, the negative mode LD-TOF mass spectra of **2a**–**d** exhibited the peaks due to the paracyclophynes **1a**–**d** formed by the loss of the aromatic indan fragments.[15] Although peaks of the parent anions **2a**–**d** were not observed, those due to the anions designated as **1a(indan)**$^-$, **1b(indan)**$^-$, **1c(indan)**$^-$, and **1d(indan)**$^-$, in which one of the propellane units is still intact, were also observed together with those due to the loss of C_2H_4 unit from their propellatriene moieties. However, peaks due to carbon cluster anions such as C_{36}^-, C_{48}^-, C_{60}^-, and C_{72}^-, that would be derived from cyclophynes **1a**–**d** by the loss of hydrogen atoms, were not detected, in contrast to the three-dimensional cyclophyne anion $C_{60}H_6^-$, which lost all hydrogen atoms to form C_{60}^-.[16]

In conclusion, we synthesized [6$_n$]paracyclophenediynes **2a**–**d** as precursors of [6$_n$]paracyclophynes **1a**–**d** (n = 3–6), respectively. While we were unable to spec-

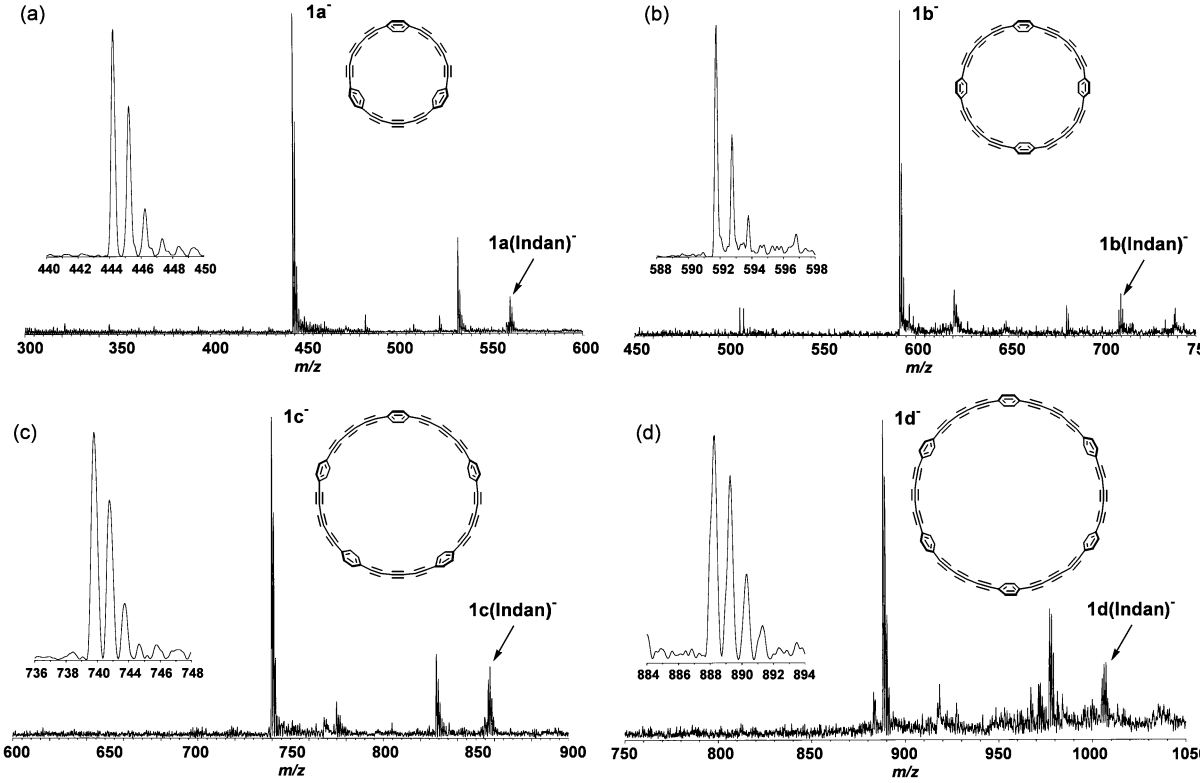


FIGURE 1. Laser-desorption time-of-flight mass spectra of cyclic dehydrooligomers: (a) **2a** [$C_{36}H_{12}$(indan)$_3$], (b) **2b** [$C_{48}H_{16}$(indan)$_4$], (c) **2c** [$C_{60}H_{20}$(indan)$_5$], and (d) **2d** [$C_{72}H_{24}$(indan)$_6$]. Inset: Expansion of the peaks of the paracyclophyne anions **1a**–**d**.

troscopically characterize [6_3]paracyclophyne **1a** by irradiation of **2a** in solution, laser irradiation of **2a**−**d** induced expulsion of the aromatic fragment, indan, giving [6_n]paracyclophyne anions **1a**−**d** ($n = 3-6$), respectively, which were detected by TOF mass spectrometry. We are planning to synthesize the chloro derivatives of **2a**−**d**, which would generate the corresponding carbon clusters in a size-selective manner by further elimination of chlorine atoms.[7]

Experimental Section

Cyclic Dehydrotrimer 2a. A solution of tetra-*n*-butylammonium fluoride (TBAF) (1 M in THF, 780 μL, 780 μmol) and acetic acid (70 μL, 74 mg, 1.2 mmol) was added dropwise into a solution of **6b** (274 mg, 253 μmol) in THF (10 mL) at room temperature. After the mixture was stirred for 2 h, water was added into the mixture. The mixture was extracted with Et_2O, and the extract was washed with saturated $NaHCO_3$ solution and brine, and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation to give deprotected product, which was used in the next step without purification. The above deprotected product was dissolved in Et_3N (180 mL), which had been degassed thoroughly by bubbling argon for 1 h, and the solution was added dropwise into a solution of $Pd(PPh_3)_4$ (292 mg, 253 μmol) and CuI (57.9 mg, 304 μmol) in degassed Et_3N (40 mL) at 50 °C over 1 h under an argon atmosphere. After being stirred for 1 h at 70 °C, the reaction mixture was cooled to room temperature and concentrated in vacuo. The residue was diluted with $CHCl_3$, and water was added. After extraction with $CHCl_3$, the organic layer was washed with water, 1 N HCl, and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to chromatography on silica gel (99:1, hexanes:AcOEt). The product was further purified by preparative HPLC to give **2a** (161 mg, 80% for two steps) as a yellow solid: dec > 188 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 12H), 6.00−5.92 (m, 12H), 2.10−1.96 (m, 6H), 1.72−1.49 (m, 6H), 1.39−1.27 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.8 (s), 131.7 (d), 128.54 (d), 128.52 (d), 123.0 (s), 121.9 (d), 96.4 (s), 85.3 (s), 56.1 (s), 33.3 (t), 19.0 (t); IR (KBr) 2161, 861, 833, 755, 704 cm^{-1}; MS (LDMS), see Figure 1a.

Cyclic Dehydropentamer 2c. Deprotection of **8b** (136 mg, 84.2 μmol) and subsequent Pd-catalyzed coupling were carried out as described above to afford **2c** (7.4 mg, 9% for two steps) as a yellow solid: dec > 210 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 20H), 5.91 (brs, 20H), 2.09−2.03 (m, 10H), 1.70−1.49 (m, 10H), 1.36−1.27 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 132.4 (s), 131.7 (d), 128.6 (d), 122.9 (s), 121.9 (d), 94.9 (s), 84.2 (s), 56.4 (s), 33.1 (t), 19.0 (t); IR (KBr) 2178, 835, 756, 709 cm^{-1}; MS (LDMS), see Figure 1c.

Cyclic Dehydrotetramer 2b and Dehydrohexamer 2d. A solution of TBAF (1 M in THF, 220 μL, 220 μmol) was added dropwise into a solution of **5b** (113 mg, 138 μmol) in THF (13 mL). After the mixture was stirred for 2 h, water was added into the reaction mixture. The mixture was extracted with Et_2O, and the extract was washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation to give deprotected product, which was used in the next step without purification. The above deprotected product was dissolved in Et_3N (30 mL), which had been degassed thoroughly by bubbling argon for 1 h, and the solution was added dropwise into a solution of $Pd(PPh_3)_4$ (150 mg, 130 μmol) and CuI (25.4 mg, 133 μmol) in degassed Et_3N (30 mL) over 90 min at room temperature under an argon atmosphere. After being stirred for 2 h, the reaction mixture was concentrated in vacuo. The residue was subjected to chromatography on silica gel (4:1:1, hexanes:$CHCl_3$:AcOEt). The products were separated by preparative HPLC to give fractions containing dehydrotetramer **2b** and dehydrohexamer **2d**, respectively. The fraction of **2b** was washed with hexanes and $CHCl_3$ to afford **2b** (40 mg, 54%) as a bright yellow solid. The fraction of **2d** was further purified by chromatography on silica gel (95:5, hexanes:AcOEt) to give **2d** (5.3 mg, 7%) as a bright yellow solid. **2b**: dec > 205 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 16H), 5.91 (brs, 16H), 2.09−2.03 (m, 8H), 1.70−1.49 (m, 8H), 1.36−1.27 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.8 (s), 131.7 (d), 128.5 (d), 122.9 (s), 121.8 (d), 95.1 (s), 84.3 (s), 56.3 (s), 33.2 (t), 19.0 (t); IR (KBr) 2175, 835, 756, 698 cm^{-1}; MS (LDMS), see Figure 1b. **2d**: mp 138−140 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 24H), 5.91 (brs, 24H), 2.09−2.02 (m, 12H), 1.70−1.49 (m, 12H), 1.36−1.26 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.4 (s), 131.7 (d), 128.6 (d), 122.9 (s), 121.8 (d), 94.9 (s), 84.1 (s), 56.4 (s), 33.1 (t), 19.0 (t); IR (KBr) 2179, 835, 756, 705 cm^{-1}; MS (LDMS), see Figure 1d.

Photolysis of 2a in Furan. A solution of cyclic dehydrotrimer **2a** (30.3 mg, 37.9 μmol) in furan (30 mL) was charged to a quartz tube, and then the reaction mixture was degassed by freeze−thaw cycles. The solution was irradiated in a water bath with a 60 W low-pressure mercury lamp for 50 h. Similarly, irradiation of a solution of **2a** (18.0 mg, 22.5 μmol) in furan (30 mL) was conducted as described above for 50 h. Both reaction mixtures were combined, the solvent and indan were removed by evaporation, and the products were subjected to chromatography on silica gel (9:1, hexanes:AcOEt). Purification by preparative HPLC afforded a 1:3 mixture of two different furan adducts **11a** and **11b** (12.6 mg, 26%) as an orange solid together with recovered **2a** (13.0 mg, 27%). **11a and 11b**: dec > 126 °C, ^1H NMR (270 MHz, $CDCl_3$) δ 7.64−7.58 (m, 2H for **11b**), 7.45−7.26 (m, 14H), 7.21−7.18 (m, 2.6H), 5.95 (brs, 11.7H), 5.61 (brs, 0.6H for **11a**), 5.57 (brs, 1H for **11b**), 2.36−2.05 (m, 5.3H), 1.66−1.50 (m, 5.3H), 1.37−1.25 (m, 5.3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 163.6 (s), 143.8 (t), 143.4 (s), 143.1 (t), 141.4 (t), 136.6 (s), 135.4 (s), 134.8 (s), 133.11 (s), 133.08 (s), 132.8 (s), 132.2 (d), 132.1 (d), 131.8 (d), 131.7 (d), 131.6 (d), 131.5 (d), 131.3 (d), 131.2 (d), 129.7 (s), 128.6 (t), 128.5 (t), 128.3 (t), 125.1 (t), 125.0 (t), 123.9 (s), 123.6 (s), 123.2 (s), 122.93 (s), 122.91 (s), 121.83 (d), 121.78 (s), 98.5 (s), 97.6 (s), 97.4 (s), 96.6 (s), 96.4 (s), 95.5 (s), 95.17 (s), 95.15 (s), 90.4 (s), 90.3 (s), 89.64 (s), 89.59 (s), 88.1 (s), 87.0 (s), 86.6 (s), 86.3 (s), 85.9 (s), 85.4 (s), 84.72 (s), 84.66 (s), 84.6 (s), 84.4 (s), 79.9 (s), 56.34 (s), 56.26 (s), 56.24 (s), 56.19 (s), 56.1 (s), 33.4 (t), 19.14 (t), 19.10 (t), 19.0 (t); IR (KBr) 2175, 1272, 1031, 882, 834, 755, 710, 696 cm^{-1}; MS (APCI) m/z 748 (M^+).

Acknowledgment. Support to R.U. from the 21st Century COE Program "Integrated Eco-Chemistry" is gratefully acknowledged.

Supporting Information Available: Experimental procedures and characterization of new compounds. Copies of ^1H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050833D

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(14) LD-TOF mass spectra were recorded by irradiation with a nitrogen laser (337 nm) of the solid samples followed by detection of the negative ions in the reflectron mode.

(15) Although we measured positive mode LD-TOF mass spectra of **2a**−**d**, their spectra did not show clearly peaks for **1a**−**d**.

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