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Published on Web 11/22/2010

Synthesis of Cyclododeciptycene Quinones

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Abstract: Cycloiptycenes are elusive and synthetically challenging molecules. We report the first synthesis of two substituted cyclododeciptycene tetraquinones via a sequence of intermolecular and intramolecular Diels−Alder reactions from *cis,cis*-heptiptycene tetraquinone **2** and substituted 7,16-dihydro-7,16-(*o*-benzeno)heptacenes **3**. Heptiptycene tetraquinone **2** was made from triptycene bisquinone **4** and 1,4-dimethoxyanthracene in three steps, and 6,8,15,17-tetramethoxy-7,16-dihydro-7,16-(*o*-benzeno)heptacene (**3a**) was synthesized from triptycene bisquinone **4** and 1,4-dihydro-2,3-benzoxathiin-3-oxide in four steps. The structure of a cyclododeciptycene, **1a**, was determined by a single-crystal X-ray analysis. The synthetic sequence is general and should allow the incorporation of various alkoxy and acetoxy substituents appended to the cycloiptycene framework.

Introduction

Since the discovery of triptycene,[1] a number of iptycenes, extended triptycenes, and iptycene-containing polymers have been synthesized.[2−6] These extended arenes contain intramolecular cavities, thermal stability,[2] self-assembly behaviors,[7] electronic properties,[8−11] chemical sensory ability,[12,13] target shape-persistent dendrimers,[14] and bioactivity.[15] Cycloiptycenes are synthetically challenging molecules[2,3] and synthesis of any members of cycloiptycenes has not been reported. In our synthetic studies of [*n*]beltenes[16−18] and their self-assemblies, we investigated the synthesis of substituted cyclododeciptycenes. Herein, we report the first and facile syntheses of two cyclododeciptycene tetraquinones **1a** and **1b** (Figure 1) possessing four methoxy and acetoxy appendages, respectively. The synthesis stems from a sequence of intermolecular and intramolecular Diels−Alder reactions. Three key intermediates, a heptiptycene tetraquinone **2** and tetramethoxy- and tetraacetoxy-heptiptycene, **3a** and **3b**, were used in the construction of cyclododeciptycenes (Figure 1). Presences of the methoxy and acetoxy moieties in the cyclododeciptycene framework indicate that other alkoxy and ester moieties can be installed for future application in the material field[2,6−14] such as the incorporation of cyclododeciptycenes into polymers.

Results and Discussion

A sequence of Diels−Alder reactions of bisdienes from 7-oxobicyclo[2.2.1]heptane or bicyclo[2.2.1]heptane with rigid dienophiles have been used in the construction of hydrocarbon macrocycles.[19,20] The bicyclo[2.2.2]octane system has not been reported in the macrocyclic synthesis. Our retrosynthesis of cyclododeciptycene hexaquinone **1** stems from a double Diels−Alder reaction of heptiptycene tetraquinone **2** and heptiptycene **3a** or **3b** (Figure 1). Heptiptycene tetraquinone **2** can readily be synthesized from triptycene bisquinone **4** (Scheme 1). The two terminal quinone moieties (D and J quinone rings) of **2** should undergo Diels−Alder cycloaddition reaction with the central ring of the two anthracene moieties (C and K rings) of **3**,[21,22] hence a cascade Diels−Alder reactions would provide cyclododeciptycene tetraquinones **1**.

The synthesis of heptiptycene tetraquinone **2** has been reported by Zhu et al.[4] using a sequence of reactions starting from a double Diels−Alder reaction of triptycene bisquinone **4**, 2 equiv of 1,4-dimethoxyanthracene (**5**), and *p*-chloranil in refluxing acetic acid. However, in their synthesis, a mixture of three inseparable 1 + 2 adducts (enolization followed by oxidation of compounds **7**, **8**, and a stereoisomer in a ratio of 1:2:1) were obtained.[4] When we treated bisquinone **4**[21] with 3 equiv of **5** in toluene at 150 °C in a sealed tube, only two

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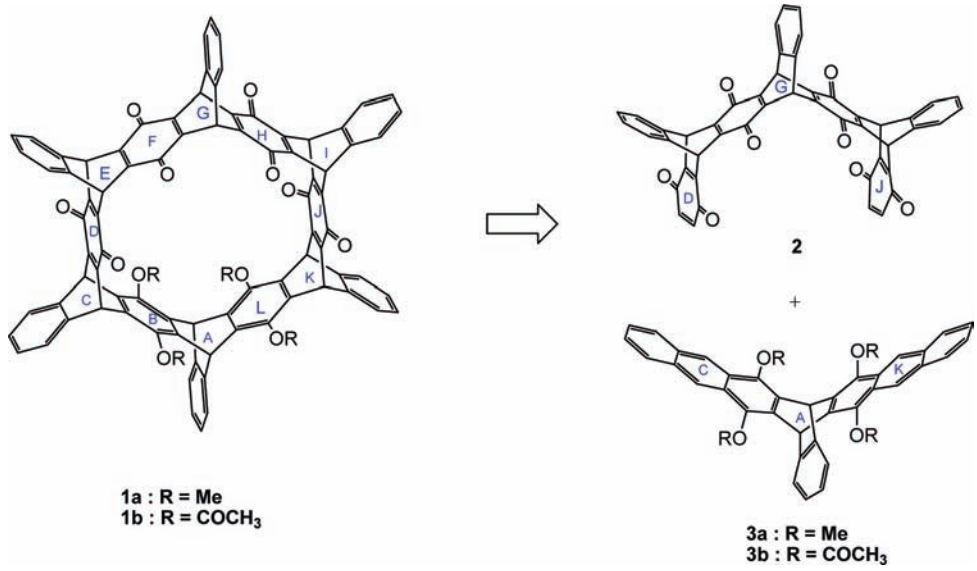
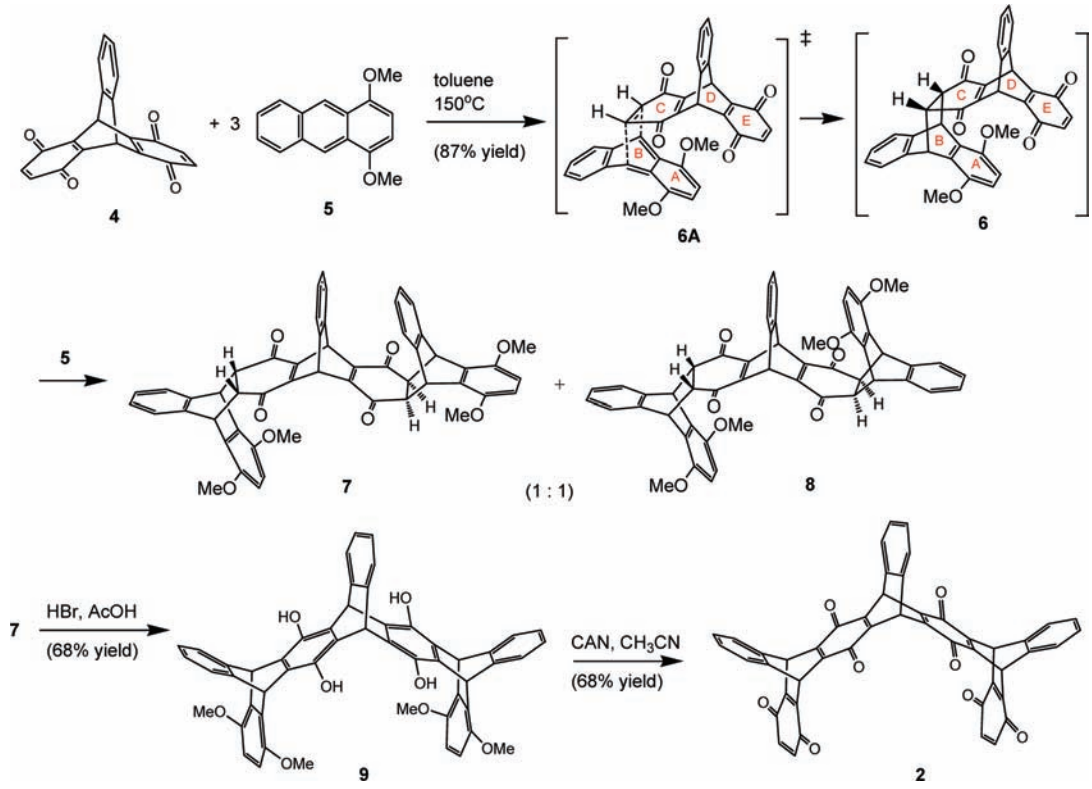


Figure 1. Retrosynthesis of cyclododeciptycene tetraquinones.

Scheme 1. Synthesis of Heptiptycene Tetraquinone **2**



isomeric 1 + 2 adducts, **7** and **8** were isolated in a ratio of 1:1 (87% yield) (Scheme 1). These two isomers were separated by silica gel column chromatography. The structure of **7** was confirmed by the transformation to tetraquinone **2**[4] (*vide infra*), whose structure was unequivocally determined by a single-crystal X-ray analysis (Figure 2).[23] The structure of **8** was verified by conversion to the corresponding tetraquinone following a similar reaction sequence as that of **7** using HBr and CAN reagents (*vide infra*) and comparison to the reported spectral data.[4] Since there were predominantly two adducts, **7** and **8**, formed in the reaction, it is suggested that in the favored transition state of the initial Diels−Alder reaction of **4** and **5**, the dimethoxyaryl ring of anthracene **5** (designated as A ring in transition state **6A** in Scheme 1) lies below the quinone ring (designated as E ring of **6A**) to form a donor (dimethoxyaryl A) and acceptor (quinone E) complex, leading to monoadduct **6**. In part, it is also possible that compounds **7** and **8** are less soluble in toluene compared with other stereoisomers and precipitate out from the reaction solution (we observed the

(23) The single-crystal X-ray structure of compound **2** has not been reported previously. The authors have deposited atomic coordinates for the structures, compound **2** and **1a** with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 175022. The coordinates can be obtained on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

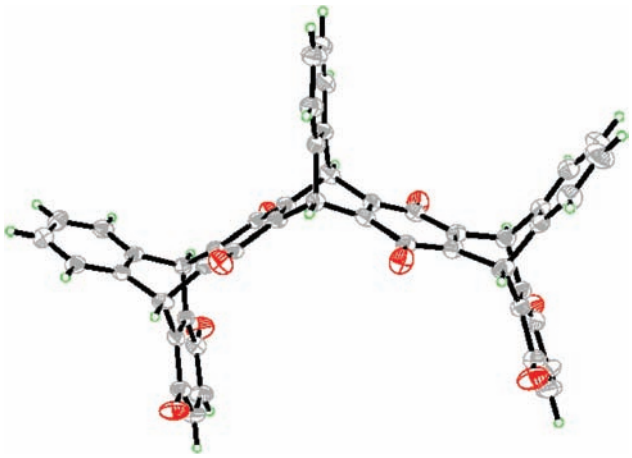


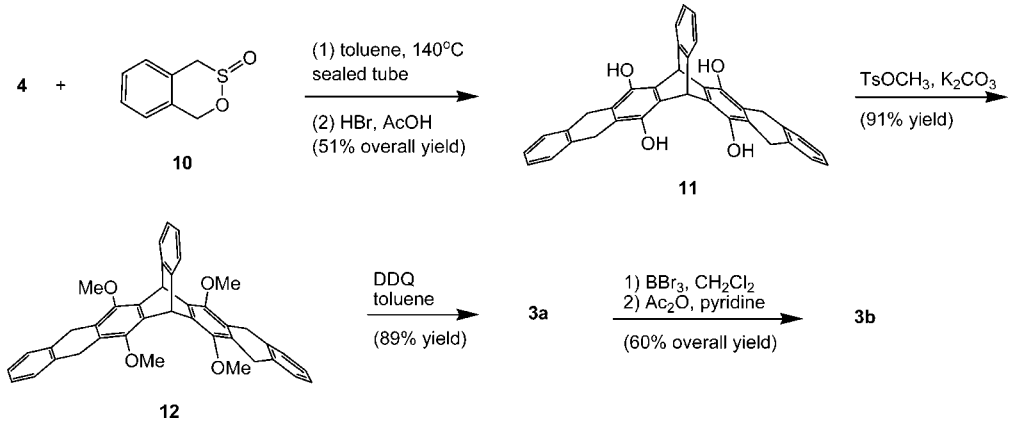
Figure 2. ORTEP drawing of X-ray crystallographically determined structure of heptiptycene tetraquinone **2**.

formation of precipitates during the course of the reaction). Since the Diels−Alder reaction of **4** and **5** is a reversible reaction, diadducts **7** and **8**, generated from monoadduct **6** and anthracene **5**, accumulated from the precipitation. Anthracene **5** approaches the quinone function of **6** (E ring) from the convex face (rings A−E; ring A blocks the concave face) to affect a second Diels−Alder reaction affording adducts **7** and **8** in a 1:1 ratio. To verify such a notion, monoadduct **6** was independently synthesized from a Diels−Alder reaction of bisquinone **4** (2 equiv were used to avoid the formations of **7** and **8**) and anthracene **5**. Treatment of quinone **6** with anthracene **5** in refluxing toluene gave a 1.6:1 ratio of **7** and **8**. The stereochemistry of quinone **6** was supported by its 2D NOESY NMR spectrum, in which the methoxy signal (δ 3.62 ppm) of **6** shows correlations with aromatic CH of ring A (δ 6.18 ppm) and quinone ═CH of ring E (δ 6.67 ppm). And ring A aromatic Hs (δ 6.18 ppm) show correlation with ring E quinone olefinic Hs (δ 6.67 ppm). Compound **7** was enolized with 40% HBr in acetic acid giving phenol **9**, which upon oxidation with ceric ammonium nitrate (CAN) afforded heptiptycene tetraquinone **2**. The stereochemistry of compounds **7** and **8** were deduced from that of quinone **6**, whose Diels−Alder reaction with anthracene **5**, and the conversions to the corresponding tetraquinones (*vide supra*). Recrystallization of tetraquinone **2** in dichloromethane afforded single crystals whose structure was shown by X-ray analysis (Figure 2) with an *R* factor value of 0.086.

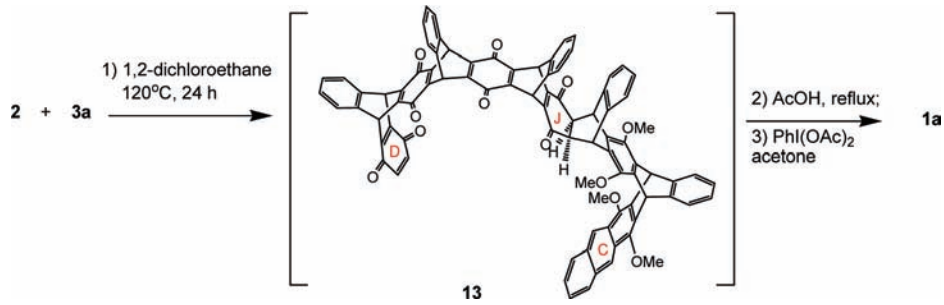
Tetramethoxyheptiptycene **3a** was synthesized via a double Diels−Alder reaction of triptycene bisquinone **4** and 2 equiv of 1,4-dihydro-2,3-benzoxathiin-3-oxide (**10**)[24] followed by functional group transformations (Scheme 2). Compound **10** is a precursor of 1,2-bis(methylene)-3,5-cyclohexadiene,[25] which readily undergoes Diels−Alder reaction and was prepared by following the reported procedure.[24] Hence, double Diels−Alder reaction of bisquinone **4** and 2 equiv of **10** in toluene followed by enolization with HBr in acetic acid provided bisdihydroquinone **11** in 51% overall yield. In the Diels−Alder reaction, a mixture of stereoisomers at the newly created stereocenters, α-C of the keto functions, formed. However, no stereocenters remain after enolization of the keto function. Methylation of **11** with methyl tosylate and potassium carbonate in 1,2-dichlorobenzene followed by oxidative aromatization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene furnished tetramethoxyheptiptycene **3a**. Tetraacetoxyheptiptycene **3b** was synthesized by the removal of the methoxy functions of **3a** with boron tribromide followed by acetylation.

The Diels−Alder reaction of tetraquinone **2** and 1 equiv of heptiptycene **3a** in refluxing 1,2-dichlorobenzene gave one-to-one adduct **13** along with other inseparable adducts (Scheme 3). Despite attempts to separate the mixture by silica gel column chromatography, preparative TLC, and HPLC, only partial separation was achieved. Hence, this mixture of adducts was directly enolized and cyclized with refluxing acetic acid followed by oxidation with diacetoxyiodobenzene in acetone afforded cyclododeciptycene **1a** in 12% overall yield (from compound **2**). The enolization of ring J of **13** changes the hybridization of the α carbons (from sp^3 to sp^2) of the carbonyl function allowing the terminal quinone moiety (ring D) to reach the anthracene function (ring C) for an intramolecular Diels−Alder reaction. Hence, under refluxing acetic acid, the enolized intermediate cyclized to give the corresponding beltene, which is not stable and was oxidatively dehydrogenated with diacetoxyiodobenzene to give **1a**. Compound **1a** was readily separated from the uncyclized stereoisomers of compound **13** by silica gel column chromatography. The stereoisomers of **13** do not undergo cyclization since the quinone moiety (ring D) and the anthracene function (ring C) are not located in close proximity. The structure of compound **1a** was confirmed by a single-crystal X-ray analysis (Figure 3).[23] Interestingly, the X-ray structure of **1a** shows an averaged structure for the cyclododeciptycene. The cycloiptycene sits on a crystallographic special position with −3 (S_6) site symmetry. The crystallographically unique symmetric unit consists of, in addition to methanol solvent, 1/6 of the cycloiptycene molecule. This is higher symmetry than the compound's chemical formula would seem to allow. The cycloiptycene contains four methoxy and eight quinone groups,

Scheme 2. Synthesis of Heptiptycenes **3a** and **3b**



Scheme 3. Synthesis of Cyclododeciptycene **1a**



which would be expected to have different geometries and packing requirements. Apparently, the loose packing of the molecules in the unit cell allows for disorder of the methyl substituent which, in turn, allows for higher site symmetry. The X-ray analytical data provided an averaged structure, with 33.3% occupancy of methoxy moieties and 66.7% of quinone moieties, which is in agreement with the assigned structure of **1a**. The inner ring diameter of **1a** is ~8.9 Å, and the distance between two hydrogens in the opposite phenyl rings is ~19.6 Å. Each unit cell in the single crystal contains sixteen cyclododeciptycene molecules, in which two molecules are parallel to each other and the other two intercalate between them. There is a very large void volume in the unit cell, which was only partially modeled by methanol solvent. Attempts to further populate the unit cell with solvent molecules were unsuccessful and did not significantly improve the fit.

Attempts to demethylate compound **1a** with various reagents including CAN, sodium iodide in DMF, and BBr_3 failed, and only starting material and unidentifiable byproduct were observed.

Tetraacetoxycyclododeciptycene **1b** was synthesized similarly to demonstrate the generality of the methodology. Hence, treatment of tetraquinone **2** with 1 equiv of tetraacetoxyheptiptycene **3b** in refluxing 1,2-dichlorobenzene and 1,4-dimethoxybenzene followed by enolization, cyclization, and oxidative dehydrogenation afforded tetraacetoxy cyclododeciptycene **1b** in 14% yield (from **3b**) (Scheme 4). Intermediate adduct **14** could not be purified from the stereoisomeric byproduct, however, cyclododeciptycene **1b** was readily separated from the uncyclized byproduct. The spectral data and physical appearance of compound **1b** are similar to that of **1a**. The acetoxy functions of **1b** were removed by the treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene[26] in methanol at 25 °C, and the resulting tetrahydroxycyclododeciptycene was oxidized with diacetoxyiodobenzene in dichloromethane. The expected product, cyclododeciptycene hexaquinone, supported by its proton NMR spectrum,[27] decomposed gradually on silica gel column chromatography and upon standing, and we are unable to obtain satisfactory analyses including ^{13}C NMR and high-resolution mass spectra of this hexaquinone. Investigation of other cycloiptycenes may shed light onto the stabilities of this class of intriguing molecules.

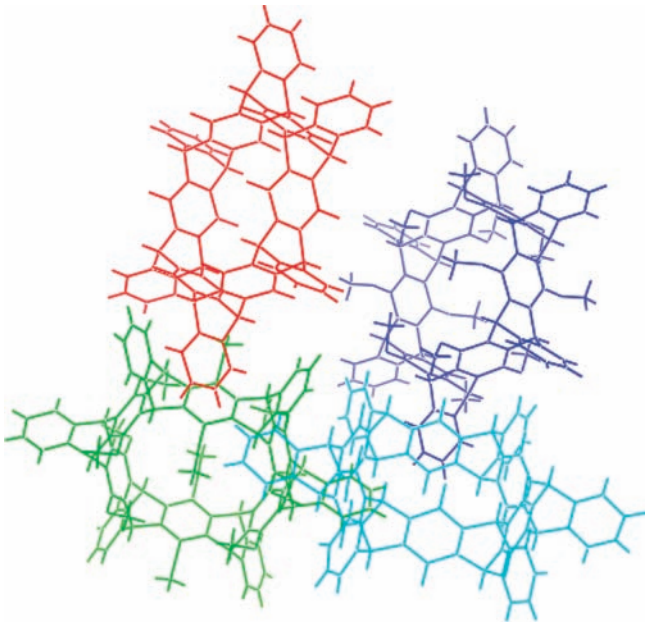


Figure 3. Unit cell of X-ray crystallographically determined structure of cyclododeciptycene tetraquinone **1a**.

Conclusion

In conclusion, two cyclododeciptycene quinones were synthesized from a sequence of intermolecular and intramolecular Diels−Alder reactions starting from heptiptycene tetraquinone **2** and heptiptycene **3**. The single-crystal X-ray structure of cyclododeciptycene **1a** shows a self-assembled tube-like structure, which may be used in electrical conducting materials and ion channels. The self-assembly of cyclododeciptycene derivatives for application in novel materials will be investigated. The presence of methoxy or acetoxy moieties of cyclododeciptycene hexaquinone **1a** or **1b**, respectively, indicates that other alkyl and acyl groups can be installed for various applications including the incorporation of the cyclododeciptycene into a polymer matrix.

Experimental Section

General Methods. NMR spectra were obtained from a 400 MHz or a 200 MHz spectrometer (Varian Inc.), in $CDCl_3$, unless otherwise indicated, and reported in ppm. Infrared spectra were taken from a Nicolet 380 FT-IR instrument (Thermo Scientific) in solid forms and are reported in wave numbers (cm^{-1}). Low-resolution mass spectra were taken from an API 2000-triple quadrupole ESI-MS/MS mass spectrometer (from Applied Biosystems). High-resolution Mass spectra were obtained from a LCT Premier (Waters Corp., Milford MA) time-of-flight mass spectrometer. The instrument was operated at 10,000 resolution (W mode) with dynamic range enhancement that attenuates large intensity signals. The cone voltage was 60 eV. Spectra were acquired at 16666 Hz pusher frequency covering the mass range 100 to 1200

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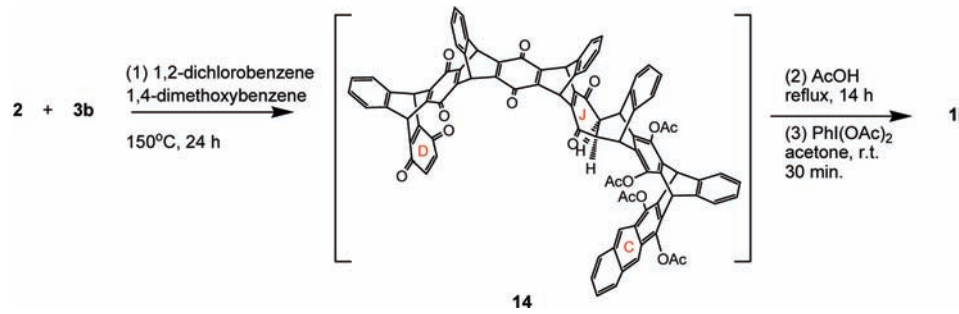
(27) The ^1H NMR spectrum ($CDCl_3$, 400 MHz) of the assumed cyclododeciptycene hexaquinone (red solid) shows three set of signals, δ 7.33 (dd, J = 7.2, 2.8 Hz, 12 H), 7.16 (dd, J = 5.6, 2.8 Hz, 12 H), and 6.04 (s, 12 H) ppm.

Scheme 4. Synthesis of Cyclododeciptycene **1b**



μ and accumulating data for 2 s per cycle. Mass correction for exact mass determinations was made automatically with the lock mass feature in the MassLynx data system. A reference compound in an auxiliary sprayer is sampled every third cycle by toggling a "shutter" between the analysis and reference needles. The reference mass is used for a linear mass correction of the analytical cycles. Chemicals were purchased from Fisher Scientific and Aldrich Chemical Co.

(5R*,5aR*,7S*,8aR*,9S*,14R*,14aS*,16S*,17aS*,18S*)-5,5a,7,8a,9,14,14a,16,17a,18-Decahydro-1,4,10,13-tetramethoxy-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-6,8,15,17-tetraone (7) and (5R*,5aS*,7R*,8aS*,9R*,14S*,14aR*,16S*,17aR*,18S*)-5,5a,7,8a,9,14,14a,16,17a,18-Decahydro-1,4,10,13-tetramethoxy-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-6,8,15,17-tetraone (8). A solution of 0.31 g (1 mmol) of triptycenebisquinone **4**[21] and 0.72 g (3 mmol) of 1,4-dimethoxyanthracene (**5**)[28] in 10 mL of toluene was heated under argon at 150 °C in a sealed tube for 48 h. After cooling the reaction mixture to 25 °C, the precipitated orange solid was filtered, washed with toluene and diethyl ether, and subjected to column chromatography on silica gel using a mixture of hexane, dichloromethane, and diethyl ether (1:2:0.12) as an eluent to give 0.35 g of compound **7** (less polar isomer) and 0.35 g of compound **8**. Compound **7** (an orange solid). Mp 220 °C dec; IR (neat) ν 3030, 2991, 2950, 1663, 1575, 1495, 1454, 1254, 1189, 1070, 968, 796, 747, 702; ^{1}H NMR δ 7.33 (dd, J = 5.4, 3.4 Hz, 2 H), 7.13 (dd, J = 5.4, 3.0 Hz, 2 H), 7.10 (dd, J = 5.4, 3.4 Hz, 2 H), 6.90 (dd, J = 5.4, 3.0 Hz, 2 H), 6.73 (dd, J = 5.2, 3.2 Hz, 2 H), 6.65 (s, 2 H), 6.24 (dd, J = 5.6, 2.8 Hz, 2 H), 6.08 (s, 2 H), 5.57 (s, 2 H), 5.10 (bs, 2 H), 5.08 (bs, 2 H), 3.83 (s, 6 H), 3.66 (s, 6 H), 3.06 (s, 2 H), 2.95 (s, 2 H); ^{13}C NMR δ 193.3, 192.9, 155.2, 155.0, 148.7, 148.6, 141.4, 141.3, 138.4, 131.1, 129.1, 126.7, 126.6, 125.6, 125.1, 124.3, 124.0, 109.3, 108.2, 56.2, 55.8, 50.9, 50.2, 43.6, 43.4, 42.6; HRMS calcd for $C_{52}H_{42}NO_8$ (M + NH_4^+) 808.2905, found 808.2888. Compound **8** (an orange solid). Mp 220 °C dec; IR (neat) ν 3025, 2990, 2850, 1667, 1593, 1495, 1454, 1254, 1185, 1074, 960, 792, 747, 706; ^{1}H NMR δ 7.40 (dd, J = 5.3, 3.3 Hz, 2 H), 7.34 (dd, J = 5.6, 3.4 Hz, 2 H), 7.16 (m, 4 H), 7.11 (dd, J = 5.5, 3.1 Hz, 2 H), 6.97 (dd, J = 5.3, 3.2 Hz, 2 H), 6.08 (s, 2 H), 5.74 (s, 2 H), 5.63 (s, 2 H), 5.14 (t, J = 1.2 Hz, 2 H), 5.09 (t, J = 1.4 Hz, 2 H), 3.66 (s, 6 H), 3.59 (s, 6 H), 3.07 (t, J = 1.2 Hz, 2 H), 2.96 (t, J = 1.4 Hz, 2 H); ^{13}C NMR δ 192.9, 192.6, 155.4, 155.0, 148.5, 148.0, 141.8, 141.50, 141.46, 128.9, 127.7, 126.8, 126.7, 125.6, 125.0, 124.3, 124.2, 109.6, 108.1, 56.0, 55.6, 50.9, 50.5, 43.4, 43.3, 42.7; HRMS calcd for $C_{52}H_{38}NaO_8$ (M + Na^+) 813.2459, found 813.2430.

(5R*,6aR*,7S*,12R*,12aS*,14S*)-8,11-Dimethoxy-5,6a,7,12,12a,14-hexahydro-5,14:7,12-di(*o*-benzeno)pentacene-1,4,6,13-tetraone (6). A solution of 1,4-dimethoxyanthracene (**5**; 0.12 g, 0.5 mmol) and triptycene bisquinone **4** (0.31 g, 1 mmol) in 10 mL toluene was heated under reflux for 8 h under argon. The reaction solution was then cooled to 25 °C, and the crude product was collected by filtration, washed with toluene (1 mL) and diethyl ether (2 mL), and dried under vacuum. The solid was column chromatographed on silica gel using a mixture of toluene, chloroform and ethyl acetate (25:25:1) as an eluent to give 85 mg (30% yield) of compound **6** as a red solid: IR (neat) ν 3031, 2933, 2905, 1655, 1577, 1491, 1454, 1262, 1070, 797 cm^{-1}; ^{1}H NMR δ 7.39 (dd, J = 5.4, 3.0 Hz, 2 H), 7.38 (dd, J = 5.3, 3.2 Hz, 2 H), 7.15 (dd, J = 5.4, 3.0 Hz, 2 H), 7.00 (dd, J = 5.4, 3.0 Hz, 2 H), 6.67 (s, 2 H), 6.18 (s, 2 H), 5,87 (s, 2 H), 5.14 (d, J = 1.2 Hz, 2 H), 3.62 (s, 6 H), 3.05 (d, J = 1.2 Hz, 2 H); ^{13}C NMR δ 192.9, 182.6, 155.6, 150.8, 149.0, 141.9, 141.4, 135.5, 129.0, 126.8, 126.0, 125.5, 124.4, 108.6, 55.9, 51.1, 43.5, 42.5; HRMS calcd for $C_{36}H_{24}NaO_6$ (M + Na^+) 575.1465, found 575.1457.

Diels–Alder Reaction of Quinone 6 with 1,4-Dimethoxyanthracene (5) Leading to a 1.6:1 Mixture of Adducts 7 and 8. A mixture of 7.0 mg (13 μmol) of quinone **6** and 6.2 mg (26 μmol) of anthracene **5** in 0.5 mL of toluene under argon was heated under reflux for 6 h. An orange colored solid precipitated out from the reaction solution. The reaction mixture was cooled to 25 °C and column chromatographed on silica gel using a mixture of toluene, chloroform, and ethyl acetate (25:25:1) as an eluent to give 5.4 mg (53% yield) of adduct **7** and 3.3 mg (32% yield) of adduct **8**. The spectral data of these products are identical to those described above.

(5R*,7S*,9S*,14R*,16S*,18S*)-5,7,9,14,16,18-Hexahydro-6,8,15,17-tetrahydroxy-1,4,10,13-tetramethoxy-5,18:7,16:9:14-tris(*o*-benzeno)-heptacene (9). A suspension of 66 mg (0.083 mmol) of **7** in 2 mL acetic acid and 2 drops of 40% aqueous hydrobromic acid was refluxed under argon for 0.5 h and then cooled to 25 °C. The gray precipitate was filtered, washed with 2 mL of toluene and 5 mL of diethyl ether, and dried under vacuum to give 45 mg (68% yield) of compound **9** as a yellow solid. Mp >300 °C; IR (neat) ν 3346 (broad s), 2917, 2844, 1610, 1450, 1250, 1189, 1066 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.38 (s, 4 H), 7.27 (dd, J = 5.4, 3.1 Hz, 4 H), 7.21 (dd, J = 5.2, 3.0 Hz, 2 H), 6.86 (dd, J = 5.2, 3.4 Hz, 4 H), 6.79 (dd, J = 5.2, 3.4 Hz, 2 H), 6.47 (s, 4 H), 6.12 (s, 4 H), 5.99 (s, 2 H), 3.69 (s, 12 H); ^{13}C NMR (DMSO-d_6) δ 148.2, 146.4, 146.2, 139.8, 136.0, 135.1, 131.4, 131.1, 124.3, 124.1, 123.4, 108.5, 55.8, 41.0, 40.5; MS (MALDI-TOF): *m/z* calcd for $C_{52}H_{39}O_8$ [(M + H)$^+$] 791.3, found 790.6; HRMS calcd for $C_{52}H_{38}NaO_8$ (M + Na^+) 813.2459, found 813.1125.

(5R*,7S*,9S*,14R*,16S*,18S*)-5,7,9,14,16,18-Hexahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-1,4,6,8,10,13,15,17-octaone (*cis,cis*-Heptiptycene Tetraquinone) (2).[4] To a suspension of 25 mg (0.032 mmol) of **9** in a mixture of 6 mL of acetonitrile and 1 mL of water was added 0.21 g (0.38 mmol) of ammonium cerium(IV) nitrate. The mixture was stirred at 25 °C for 8 h, diluted with ethyl acetate (50 mL), washed with water (50 mL) and brine (50 mL), dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a mixture of toluene, chloroform, and ethyl acetate (25:25:2) as an eluent to give 16 mg (68% yield) of compound **2** as a yellow-orange solid. Mp >300 °C (literature,[4] mp >320 °C); ^{1}H NMR δ 7.40 (dd, J = 5.4, 3.0 Hz, 4 H), 7.36 (dd, J = 5.2, 3.2 Hz, 2 H), 7.01 (dd, J = 5.2, 2.8 Hz, 4 H), 6.96 (dd, J = 5.2, 3.2 Hz, 2 H), 6.58 (s, 4 H), 6.12 (s, 2 H), 6.11 (s, 4 H); ^{13}C NMR δ 182.2, 177.7, 151.8, 151.3, 151.2, 142.1, 142.0, 135.5, 126.2 (2 peaks overlap), 125.64, 125.57, 42.5, 42.4; MS (ESI): *m/z* calcd for $C_{48}H_{23}O_8$ [(M + H)$^+$] 727.1, found 727.3; HRMS calcd for $C_{48}H_{26}NO_8$ (M + NH_4^+) 744.1653, found 744.1655.

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5,7,9,14,16,18-Hexahydro-6,8,15,17-tetrahydroxy-7,16-(*o*-benzeno)heptacene (11). A suspension of 0.47 g (1.5 mmol) of triptycene bisquinone **4** and 1.0 g (5.9 mmol) of benzosultine **10**[24] in 15 mL dry toluene under argon was heated to 140 °C in a sealed tube for 24 h. The reaction mixture was cooled to 25 °C, the yellow precipitate was filtered, washed with toluene (2 mL) and diethyl ether (5 mL), and dried under vacuum to give 0.52 g of a mixture of Diels−Alder adducts and their partially enolized derivatives. A solution of the above mixture of Diels−Alder adducts (0.40 g, 0.77 mmol) in acetic acid (10 mL) and aqueous hydrobromic acid (40%, 50 mg) was heated under reflux for 10 min. The reaction solution was cooled to 25 °C, the yellow precipitate was filtered, washed with toluene (2 mL) and diethyl ether (5 mL), and dried under vacuum to give 0.31 g (52% overall yield from **4**) of compound **11** as a brown solid. Mp > 300 °C; IR (neat) ν 3318 (bs), 3060, 3019, 2950, 1650, 1630, 1609, 1580, 1495, 1438, 1393, 1299, 1246, 1103, 1005, 902, 739; ^{1}H NMR (DMSO-d_6) δ 8.22 (s, 4 H, OH), 7.35 (dd, J = 5.2, 2.8 Hz, 2 H), 7.24 (dd, J = 5.4, 3.4 Hz, 4 H), 7.12 (dd, J = 5.6, 3.2 Hz, 4 H), 6.92 (dd, J = 5.4, 3.4 Hz, 2 H), 6.28 (s, 2 H), 3.77 (s, 8 H); ^{13}C NMR (DMSO-d_6) δ 146.5, 141.5, 135.7, 130.7, 127.4, 125.7, 124.1, 123.3, 121.5, 40.8, 30.6; MS (MALDI-TOF): *m*/*z* calcd for $C_{36}H_{27}O_4$ [(M + H)$^+$] 523.2, found 522.3; HRMS calcd for $C_{36}H_{30}O_4N$ (M + NH_4^+) 540.2169, found 540.2154.

5,7,9,14,16,18-Hexahydro-6,8,15,17-tetramethoxy-7,16-(*o*-benzeno)heptacene (12). A mixture of compound **11** (0.30 g, 0.57 mmol), potassium carbonate (0.63 g, 4.6 mmol), and methyl *p*-toluenesulfonate (1.2 g, 6.7 mmol) in 12 mL of 1,2-dichlorobenzene under argon was heated under reflux for 24 h. The reaction mixture was cooled to 25 °C and diluted with 150 mL of ethyl acetate. The organic layer was washed with water (100 mL), 1 M HCl solution (100 mL), saturated aqueous sodium bicarbonate solution (100 mL), and brine (100 mL), dried ($MgSO_4$), and concentrated on a rotary evaporator. Dichlorobenzene was removed by vacuum distillation, and the residue was applied to a flash column chromatography on silica gel using a mixture of hexane, diethyl ether, and dichloromethane (8:2:1) as an eluent to give 0.30 g (91% yield) of compound **12** as a white solid. Mp 286−288 °C; IR (neat) ν 3080, 2999, 2958, 2819, 1603, 1483, 1450, 1410, 1319, 1260, 1234, 1209, 1099, 1050, 968, 743, 706; ^{1}H NMR δ 7.44 (dd, J = 5.2, 3.4 Hz, 2 H), 7.25 (dd, J = 5.6, 3.2 Hz, 4 H), 7.13 (dd, J = 5.5, 3.3 Hz, 4 H), 7.00 (dd, J = 5.4, 3.2 Hz, 2 H), 6.15 (s, 2 H), 3.92 (s, 12 H), 3.86 (s, 8 H); ^{13}C NMR δ 148.8, 145.5, 136.8, 136.2, 128.2, 127.7, 126.3, 125.6, 123.8, 62.4, 42.8, 29.7; HRMS calcd for $C_{40}H_{38}O_4N$ (M + NH_4^+) 596.2795, found 596.2789.

7,16-Dihydro-6,8,15,17-tetramethoxy-7,16-(*o*-benzeno)heptacene (3a). To a cold (0 °C) solution of 0.12 g (0.21 mmol) of **12** in 10 mL toluene under argon was added 0.29 g (1.3 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The reaction solution was stirred at 25 °C for 24 h, diluted with 100 mL of ethyl acetate, and the organic layer was washed with water (100 mL), saturated aqueous sodium thiosulfate solution (100 mL), saturated aqueous $NaHCO_3$ solution (100 mL), and brine (100 mL), dried ($MgSO_4$), and concentrated. The residue was column chromatographed on silica gel using a mixture of hexane and diethyl ether (4:1) as an eluent to give 0.11 g (89% yield) compound **3a** as a yellow solid. Mp > 300 °C; IR (neat) ν 3044, 2933, 2823, 1675, 1642, 1614, 1573, 1450, 1319, 1274, 1060, 950, 891, 750 cm^{-1}; ^{1}H NMR δ 8.59 (s, 4 H), 7.98 (dd, J = 6.4, 3.2 Hz, 4 H), 7.62 (dd, J = 5.4, 3.4 Hz, 2 H), 7.43 (dd, J = 6.8, 3.2 Hz, 4 H), 7.17 (dd, J = 5.4, 2.8 Hz, 2 H), 6.52 (s, 2 H), 4.20 (s, 12 H); ^{13}C NMR δ 146.7, 143.5, 131.9, 130.1, 128.6, 126.9, 126.7, 125.7, 124.4, 121.3, 63.3, 41.8; MS (ESI): *m*/*z* calcd. for $C_{40}H_{31}O_4$ [(M + H)$^+$] 575.2, found 575.5; HRMS calcd for $C_{40}H_{34}NO_4$ (M + NH_4^+) 592.2488, found 592.2482.

7,16-Dihydro-6,8,15,17-tetraacetoxy-7,16-(*o*-benzeno)heptacene (3b). To a cold (−78 °C) solution of 25 mg (44 μmol) of **3a** in 2 mL of dichloromethane under argon was added 40 μL (0.42 mmol) of boron tribromide. The reaction solution was stirred at 25 °C for 12 h, cooled to −78 °C, and diluted with 5 mL of methanol. The solvents were removed from a rotary evaporator, the residue was maintained under argon, and 5 mL of pyridine and 1 mL of acetic anhydride were added. The solution was stirred at 25 °C for 24 h, concentrated under vacuum, and column chromatographed on silica gel using a mixture of toluene, chloroform, and ethyl acetate (25:25:4) as an eluent to give 19 mg (64% yield) compound **3b** as a yellow solid. Mp > 300 °C; IR (neat) ν 3044, 2929, 1748, 1610, 1500, 1425, 1368, 1315, 1176, 1025, 874, 747 cm^{-1}; ^{1}H NMR δ 8.29 (s, 4 H), 7.94 (dd, J = 6.4, 3.2 Hz, 4 H), 7.45 (m, 6 H), 7.14 (dd, J = 5.6, 3.2 Hz, 2 H), 5.69 (s, 2 H), 2.71 (s, 12 H); ^{13}C NMR δ 174.0, 141.1, 138.8, 132.1, 129.7, 128.5, 127.1, 126.4, 125.4, 125.2, 120.9, 43.0, 21.0; MS (ESI): *m*/*z* calcd for $C_{44}H_{30}NaO_8^+$ (M + Na^+) 709.2, found 709.2; HRMS calcd for $C_{44}H_{34}O_8N$ (M + NH_4^+) 704.2284, found 704.2284.

2,4,6,8,10,12,14,16,18,20,22,24-Dodecahydro-9,11,21,23-tetramethoxy-(2,14:4,16: 6,18:8,20:10,22:12,24)-hexa(*o*-benzeno)-[12]cyclacene-1,3,5,7,13,15,17,19-octaone (1a). A solution of tetraquinone **2** (0.12 g, 0.16 mmol) and tetramethoxyheptiptycene **3a** (0.11 g, 0.19 mmol) in 10 mL of 1,2-dichloroethane under argon was heated at 120 °C in a sealed tube for 24 h. The reaction solution was cooled to 25 °C, concentrated, and column chromatographed on silica gel using a mixture of toluene, chloroform, and ethyl acetate (25:25:2) as an eluent to give 0.12 g of four monoadducts in ∼2:2:1:1 based on ^{1}H NMR spectral data. A solution of the monoadducts in 50 mL of acetic acid was heated under reflux for 6 h, cooled to 25 °C, diluted with water, and extracted three times with ethyl acetate. The combined extract was washed with water twice, aqueous $NaHCO_3$ solution, and brine, dried ($MgSO_4$), and concentrated. To the residue under argon was added a solution of 87 mg (0.27 mmol) of diacetoxyiodobenzene in 6 mL of acetone. The solution was stirred for 10 min, concentrated on a rotary evaporator, and column chromatographed on silica gel using a mixture of toluene, chloroform, ethyl acetate (25:25:2) as an eluent to give 25 mg (12% overall yield from compound **2**) of compound **1a** as an orange solid. Mp > 300 °C; IR (neat) ν 3030, 2917, 2844, 1646, 1573, 1458, 1274, 1254, 1192, 1046, 890, 751 cm^{-1}; ^{1}HNMR δ 7.25−7.36 (m, 12 H), 6.85−6.98 (m, 12 H), 6.05 (s, 2 H), 6.04 (s, 4 H), 5.95 (s, 4 H), 5.89 (s, 2 H), 3.82 (s, 12 H, OMe); ^{13}C NMR δ 178.6, 177.6, 152.0, 151.4, 151.3, 151.0, 147.8, 145.0, 143.5, 141.9, 141.8, 137.4, 135.0, 126.1 (2 peaks overlap), 125.9, 125.7, 125.5 (2 peaks overlap), 124.5, 123.8, 63.4, 42.4 (3 peaks overlap), 42.2; HRMS (MALDI) calcd for $C_{88}H_{49}O_{12}$ (M + H^+) 1298.330 and $C_{88}H_{48}O_{12}Na^+$ 1319.304, found 1298.834 (parent peaks; 100%) and 1319.830, respectively.

2,4,6,8,10,12,14,16,18,20,22,24-Dodecahydro-9,11,21,23-tetraacetoxy-(2,14:4,16: 6,18:8,20:10,22:12,24)-hexa(*o*-benzeno)-[12]cyclacene-1,3,5,7,13,15,17,19-octaone (1b). A solution of tetraquinone **2** (79 mg, 0.11 mmol), tetraacetoxyheptiptycene **3b** (62 mg, 90 μmol), and 1,4-dimethoxybenzene (1.24 g, 9.0 mmol) in 15 mL of 1,2-dichlorobenzene under argon was heated at 150 °C for 24 h. The reaction mixture was directly subjected to a column chromatography on silica gel using a mixture of hexane, dichloromethane, and diethyl ether (1:2:0.3) as an eluent to give 71 mg of a mixture of four Diels−Alder monoadducts (in a ratio of 3:3:3:2 based on ^{1}H NMR spectral data) along with 20 mg of compound **3b**. A solution of the monoadducts in 10 mL of acetic acid under argon was heated under reflux for 12 h, cooled to 25 °C, concentrated to dryness, and the residue was dissolved in 5 mL of acetone. To it was added diacetoxyiodobenzene (50 mg, 0.15 mmol), and the solution was stirred at 25 °C for 30 min, concentrated on a rotary evaporator, and column chromatographed on silica gel using a mixture of hexane, dichloromethane, and diethyl ether (1:2:0.12) as an eluent to give 12 mg (14% overall yield based on reacted **3b**) of compound **1b** as a yellow solid. Mp > 300 °C; IR (neat) ν 3032, 2946, 2925, 2852, 1765, 1654, 1580, 1466, 1373, 1279, 1176, 1025, 886, 756, 702 cm^{-1}; ^{1}H NMR δ 7.26−7.34 (m, 6 H), 7.22 (dd, J = 5.2, 3.2 Hz, 4 H), 7.16 (dd, J = 5.2, 4.0 Hz, 2 H), 6.87−6.92 (m, 10 H), 6.86 (dd, J = 5.6, 3.2 Hz, 2 H), 6.07 (s, 2 H), 6.01 (s, 4 H), 5.56

(s, 4 H), 5.28 (s, 2 H), 2.61 (s, 12 H); ^{13}C NMR δ 178.1, 177.6, 168.4, 151.17, 151.12, 151.10, 151.0, 150.8, 143.4, 142.7, 142.2 (2 peaks overlap), 139.2, 136.4, 135.6, 126.0 (4 peaks overlap), 125.3, 124.7, 124.3, 43.4, 42.7, 42.3 (2 peaks overlap), 20.8; MS (ESI): *m*/*z* calcd for $C_{92}H_{48}NaO_{16}^+$ ($M + Na^+$) 1431.3, found 1431.7; HRMS calcd for $C_{92}H_{52}NO_{16}$ ($M + NH_4^+$) and $C_{92}H_{48}KO_{16}$ ($M + K^+$) 1426.3286 and 1447.2579, respectively, found 1426.3230 and 1447.2495, respectively.

Acknowledgment. We gratefully acknowledge financial support by the National Science Foundation (CHE-0555341) and the American Chemical Society, Petroleum Research Fund (40345-AC1). We are thankful to Victor Day at the University of Kansas who provided invaluable assistance for data collection of X-ray analysis for compound **1a** and Huiping Zhao for technical assistance.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **1a**, **1b**, **2**, **3a**, **3b**, **6**, **7**, **8**, **9**, **11**, and **12** and X-ray details for compounds **2** and **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA1088309