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Synthesis and Structures of Zigzag Shaped [12]Cyclo-*p*-phenylene Composed of Dinaphthofuran Units and Biphenyl Units

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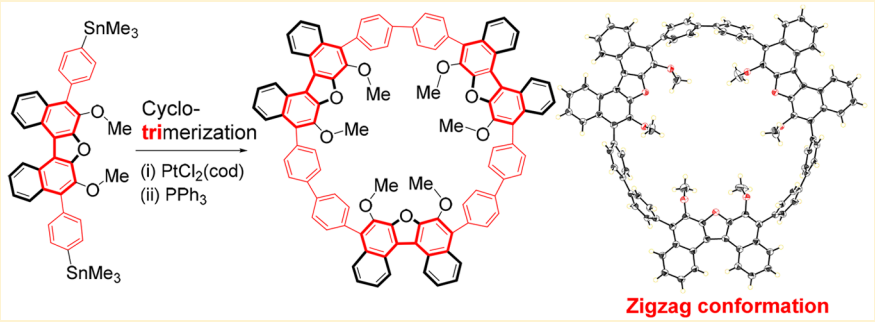
Supporting Information



ABSTRACT: A [12]Cyclo-*p*-phenylene **9** composed of dinaphthofuran units and biphenyl units was synthesized through reductive elimination of the corresponding trinuclear complex by applying Yamago's method. The X-ray crystallographic analyses of **9** revealed that it adopts a zigzag conformation in the solid state. The UV−vis and fluorescence measurements of compound **9** indicated that it also preferentially took a zigzag conformation in the solution state.

INTRODUCTION

Cyclo-*p*-phenylenes (CPPs) are three-dimensional annular π-conjugated molecules with fragmental benzene rings that are directly linked through their para positions. CPPs are also the smallest constituent segment of armchair carbon nanotubes,[1] and expected to be valuable in electronic applications and excellent functional materials. During 2008 and 2009, Jasti and Itami reported the pioneering synthetic methods for constructing CPPs with the last key step involving aromatization of a cyclohexane framework.[2] In 2010, Yamago reported a versatile synthetic method for CPPs utilizing reductive elimination of corresponding tetranuclear platinum complexes.[3] These milestone synthetic methods have been used to synthesize a variety of CPPs that have had their properties examined.[4]

Our work had focused on connecting optically active oligonaphthalenes through the 1 and 4 positions of each naphthalene to construct up to the all-(*S*)-32mer by repeated dimerization reactions.[5] More recently, we investigated spreading the π system by controlling the dihedral angles between the naphthalene rings, and achieved the synthesis of fan-shaped oligonaphthofurans, in which neighboring naphthalenes are bridged by oxygen atoms (conjugated naphthofurans with up to 8 naphthalenes and 7 furans).[6] In this paper, we describe the synthesis, structure, and properties of a CPP that combines dinaphthofuran and biphenyl units.

RESULTS AND DISCUSSION

The synthetic route for the dinaphthofuran-containing CPP is shown in Scheme 1. The starting dinaphthofuran **1**[7] was lithiated at both ortho positions, which were trapped with trimethyl borate and successively treated with hydrogen peroxide to give a corresponding diol. The diol was methylated by methyl iodide with potassium carbonate to afford compound **2** in 56% yield for two steps. Compound **2** was treated with NBS to give **3** in 84% yield. A sequence of lithiation of **3** by *n*-BuLi and boration by 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded compound **4** in 51% yield.[8] A Suzuki−Miyaura coupling between compound **4** and a large excess (10 equiv) of 1,4-dibromobenzene took place in the presence of $Pd(PPh_3)_4$ and K_3PO_4 in a DME/toluene mixed solvent to provide key intermediate **5** in 60% yield. Compound **5** was treated with *n*-BuLi (2.7 equiv) at −78 °C, followed by Me_3SnCl (3 equiv) to afford the desired bis-stannylated compound **6** in 23% yield after SiO_2 column purification.[3] The low yield of compound **6** is expected because of the low stability of aryl−stannyl bonds on SiO_2. Monostannyl and destannylated compounds **7** and **8** were also isolated in 32% and 24% yields, respectively. These compounds were used for

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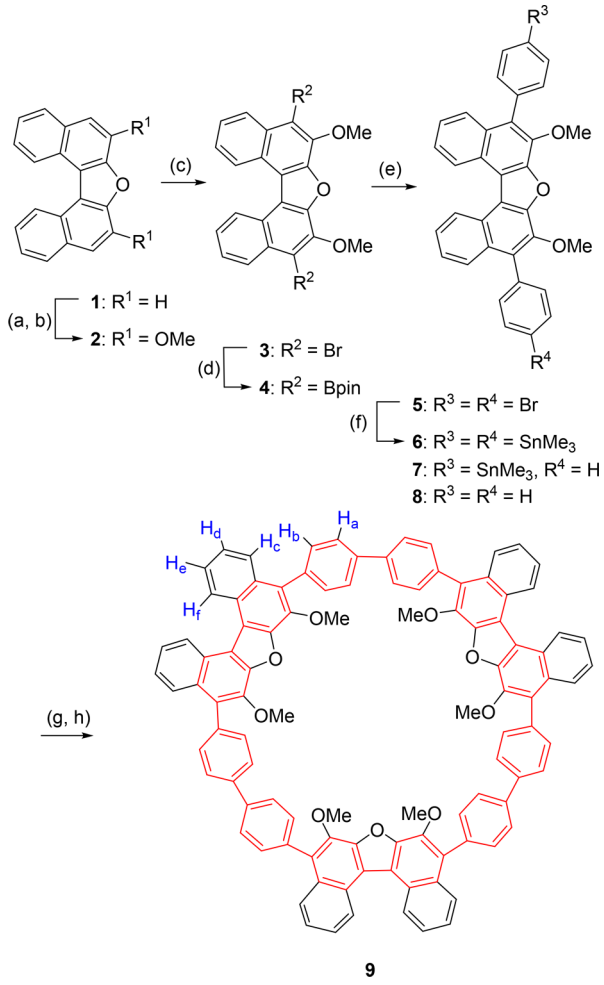
Scheme 1. Synthetic Route for Dinaphthofuran-Containing CPP 9[a]



[a]Conditions: (a) (i) *n*-BuLi, (ii) $B(OMe)_3$, (iii) H_2O_2; (b) MeI, K_2CO_3, 56% yield over two steps; (c) NBS, 84% yield; (d) (i) *n*-BuLi, (ii) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 51% yield; (e) 1,4-dibromobenzene, $Pd(PPh_3)_4$, K_3PO_4, 60% yield; (f) (i) *n*-BuLi, (ii) Me_3SnCl; **6** (23% yield), **7** (32% yield), **8** (24% yield); (g) $PtCl_2(cod)$; (h) PPh_3, 24% yield over two steps.

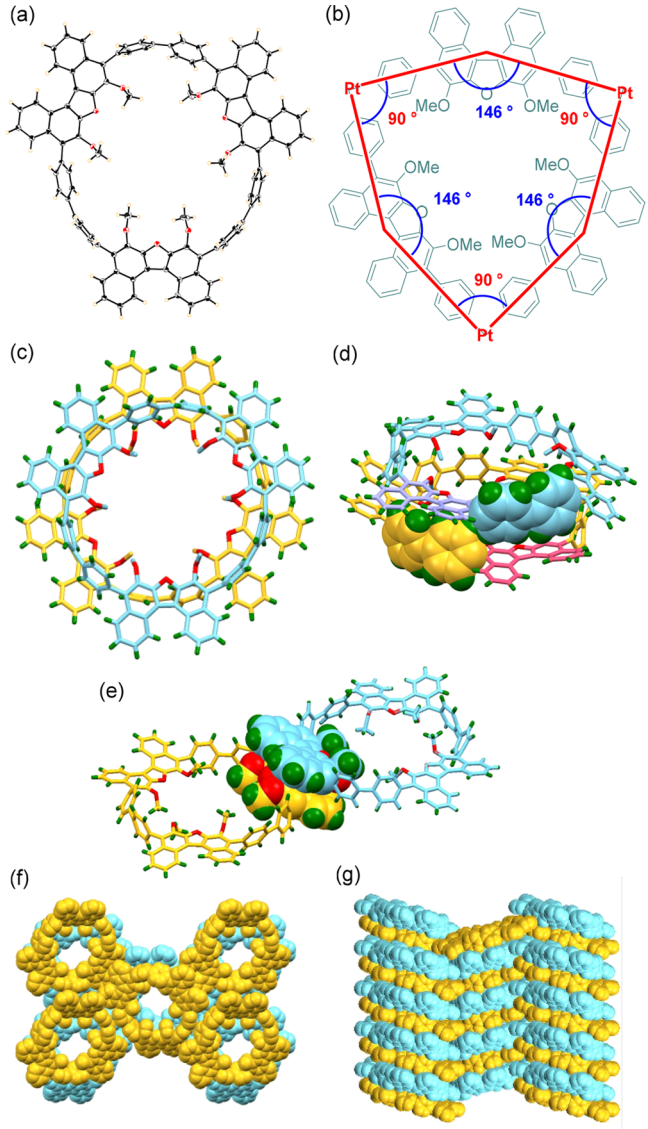


Figure 1. Single X-ray diffraction structure of compound **9**. (a) ORTEP structure of compound **9**. Thermal ellipsoids are shown at 30% probability, and disordered dichloromethane molecules are removed for clarity. (b) Proposed hexagonal trinuclear platinum complex. (c) Top view of two molecules in the vertical direction. (d) Side view of two molecules in the vertical direction. (e) Two molecules in the transverse direction. (f) Top view of the columnar structures of **9**. (g) Side view of the columnar structures of **9**.

synthesis of the linear reference compounds. The target cyclic compound was constructed according to Yamago's procedure.[3] A solution of bis-stannyl compound **6** and $PtCl_2(cod)$ (1 equiv) in dry THF was heated at reflux for 2 days under a N_2 atmosphere. A white precipitate was generated, and it was collected by filtration and subsequently treated with PPh_3 (10 equiv) in refluxing toluene for 3 h to afford desired cyclic compound **9** in 24% yield over 2 steps. At first, an informative mass spectrum of compound **9** was not obtained and structure determination was performed by X-ray crystallography.

At first, we expected that the cyclic compound should be a [16]CPP skeleton formed by the reductive elimination of the corresponding tetranuclear platinum complex, because the platinum is likely to form a complex with square planar geometry.[9] Pale yellow crystals of the CPP were obtained by allowing a dichloromethane solution to stand for a couple of days. The crystal structure of the cyclic compound was solved by X-ray analysis and is shown in Figure 1a. Contrary to our expectation, the cyclic compound has a [12]CPP framework. This result indicated that a trinuclear platinum complex was preferentially generated and created cyclic **9** through the reductive elimination.[10] This unusual selectivity can be explained by the sum of interior angles of polygons (Figure 1b).[11] From the inner product of diphenyl dinaphthofuran, this skeleton is bent inwardly at an angle of 146°. Platinum prefers a bonding angle of 90°, and the total sum of angles of the assumed hexagonal trinuclear platinum complex is 708° (=146 × 3 + 90 × 3), which is very close to the sum of the ideal interior angles of a hexagon (720°). For this reason, the most stable complex formed was trinuclear and compound **9** was preferentially generated.

The X-ray analysis revealed that compound **9** has a unique structure (Figure 1a). The constituting aryl rings face the center in most CPPs.[4] Compound **9** has a zigzag conformation with the biphenyl units facing the center and the dinaphthofuran

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units oriented almost orthogonal to the biphenyl units (described below).

The crystal packing of compound **9** forms a column-like structure, with the molecules stacked in the vertical direction (Figure 1c). The upper and lower molecules twist by about 60° and overlap with each other. The upright biphenyl moiety is in contact with the lying dinaphthofuran unit of the adjacent molecule through CH−π interactions because of the zigzag conformation of compound **9** (Figure 1d). In the transverse direction, it was found that the dinaphthofurans were in contact with each other by π−π interactions (Figure 1e). Furthermore, from a macroscopic point of view, it is also observed that the columnar structures were arrayed in a herringbone manner (Figure 1f,g).

We next compared the features of compound **9** with reported CPP derivatives regarding (1) the dihedral angles between the aromatic rings and (2) the strain energies estimated by Itami's hypothetical homodesmic reactions.[12] The correlation between the number of benzene rings of [n]CPP and the average of dihedral angles is depicted in Figure 2.[13] The average of

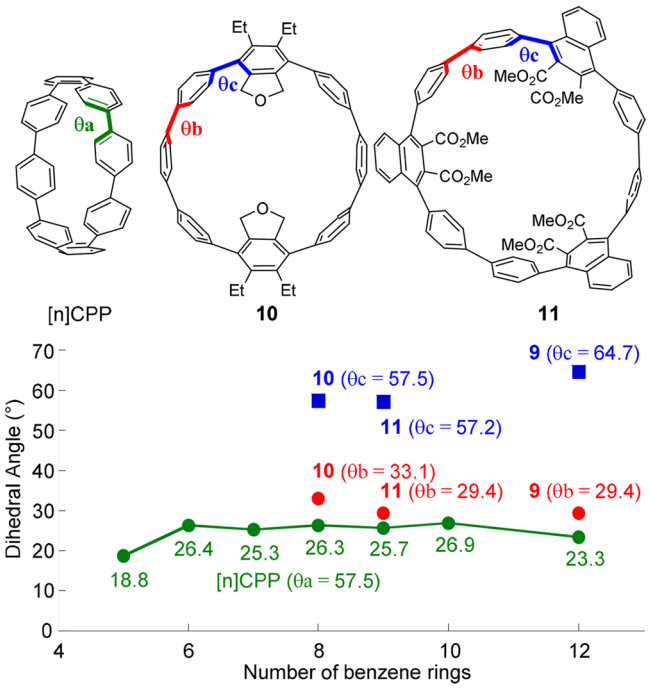
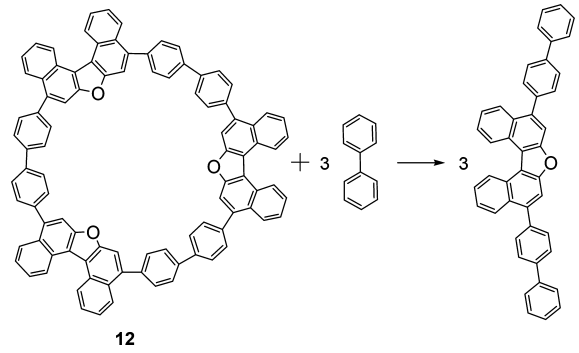


Figure 2. Correlation between the number of [n]CPP and related compounds **10** and **11**, and the average of dihedral angles.

dihedral angles of simple CPPs are shown as θa, and in the case of CPPs **10** and **11** (comprising benzene rings and other aromatic rings) the averages of dihedral angles are indicated as θb (between benzene rings) and θc (between benzene ring and other aromatic ring). The dihedral angles of simple [5−12]CPPs (θa) are around 26°; in the case of compounds **10** and **11**, θb are 33° and 29°, and θc are 58° and 57°, respectively. In contrast, compound **9** has 29° for θb and 65° for θc. These data clearly indicate that compound **9** stoutly bears a unique zigzag conformation character that is not found in other CPPs.

The strain energy (ΔH) of the model compound **12** (no side chains of compound **9**) was calculated by Itami's hypothetical homodesmic reaction under the B3LYP/6-31(d) level of theory (Scheme 2) and was compared with those reported for simple [n]CPPs.[12a,14]

Scheme 2. Isodesmic Reaction of Compound 12



The data are as follows: [12]CPP (48.1 kcal/mol), [13]CPP (45.5 kcal/mol), [14]CPP (41.0 kcal/mol), [15]CPP (39.2 kcal/mol), [16]CPP (35.6 kcal/mol), [18]CPP (31.7 kcal/mol),[12a] and compound **12** (32.0 kcal/mol). The strain energy of compound **12** is almost the same as that of [18]CPP, and is about 16 kcal/mol smaller in comparison with [12]CPP, which has the same ring size. For this reason, we consider that the dinaphthofuran unit contains a certain amount of strain energy, and to construct the cyclic framework of compound **12** the dinaphthofuran unit preferentially bends inward by 146°.

In fact, each fragment of compound **9** can quickly rotate, and the relatively small strain energy of compound **9** is consistent with the fact that no coalescence temperature was observed, even at −95 °C on variable temperature NMR measurements (Figure 3).[4c,15]

Finally, the UV−vis and fluorescence spectra of compound **9** were measured and the properties were compared with those of the noncyclic diphenyl dinaphthofuran monomer **8**, dimer **13**, and trimer **14** (Figure 4). The synthetic routes to the noncyclic diphenyl dinaphthofurans **13** and **14** are shown in Scheme 3.

In the UV−vis spectra, the maximum absorption wavelengths (λmax) of the noncyclic compounds **8**, **13**, and **14** are 358, 361, and 362 nm, respectively. A meaningfully longer wavelength shift was not observed as the number of diphenyl dinaphthofuran units increased and absorption intensity of **8**, **13**, and **14** simply increased reflecting the number of units. This shows that interaction between individual units is minimal. Compound **9**, which is a cyclic trimer of compound **8**, shows an absorption intensity that is comparable with that of the noncyclic trimer **14**, and the λmax of compound **9** (361 nm) is also very similar to those of the noncyclic compounds **8**, **13**, and **14**. These data indicate that cyclic compound **9** took a zigzag conformation—as shown by X-ray analysis—preferentially in the solution state, and the interaction between individual fragments was not substantial.

The fluorescence quantum yields of compounds **9** and **8**, **13**, and **14** in dichloromethane were as follows: cyclic **9** (Φ = 7%), noncyclic **8** (Φ = 61%), **13** (Φ = 50%), and **14** (Φ = 60%). The quantum yield of cyclic **9** was obviously smaller than those of the acyclic compounds. In addition, the maximum emission wavelength ($\lambda_{em.max}$) of compound **9** was detected at 439 nm, which is a longer wavelength than those of the noncyclic derivatives (**8**, 405 nm; **13**, 414 nm; **14**, 415 nm). The time-dependent DFT calculation at the B3LYP/6-31G(d) level of theory explained that the maximum absorption wavelength of

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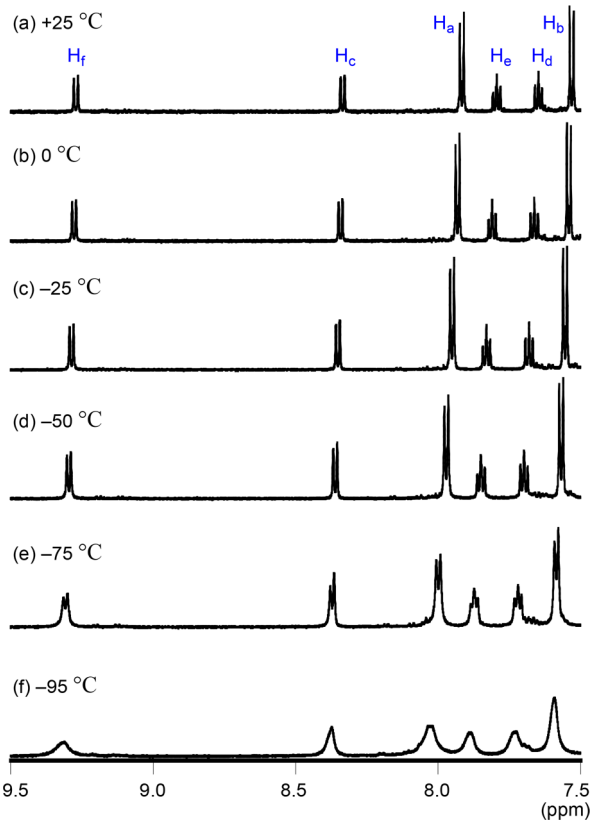


Figure 3. Variable temperature ^{1}H NMR spectra of compound **9**. Conditions: 600 MHz, CD_2Cl_2.

noncyclic **8**, **13**, and **14** should be ascribed as HOMO−LUMO transitions, whereas the HOMO−LUMO transition is forbidden for compound **9** and HOMO−LUMO+1 and HOMO−1−LUMO transitions can provide a substantial maximum absorption wavelength. This should be the reason why compound **9** has a low quantum yield, large Stokes shift, and longer emission wavelength when compared with compounds **8**, **13**, and **14**.

CONCLUSION

The construction of a zigzag shaped [12]cyclo-*p*-phenylene composed of dinaphthofuran units and biphenyl units was achieved by applying Yamago's method. The final reductive elimination step proceeded through a trinuclear platinum complex because of the bending of the diphenyl dinaphthofuran fragment. Compound **9** showed a zigzag conformation in the crystalline state, which is caused by the bending dinaphthofuran framework. Compound **9** appears to preferentially adopt a zigzag conformation in solution and has a nonconjugated UV−vis spectrum. However, a longer wavelength shift for $\lambda_{em,max}$ was observed in the fluorescence (FL) spectrum, caused by a subtle conjugated π-system. We are now attempting to complex compound **9** derivatives possessing alkyl chains on the naphthalene rings and fullerene derivatives for the purpose of conferring gate functions.

EXPERIMENTAL SECTION

Synthesis of Compound 2. *n*-BuLi (1.60 M, hexane solution, 22.4 mL, 35.8 mmol) was added dropwise to a solution of compound **1** (4.0 g, 14.9 mmol) in dry THF (40 mL) and stirred for 1.5 h at 0 °C under a N_2 atmosphere. Trimethyl borate (5.0 mL, 44.7 mmol) was added and the reaction mixture stirred at room temperature for 5 h.

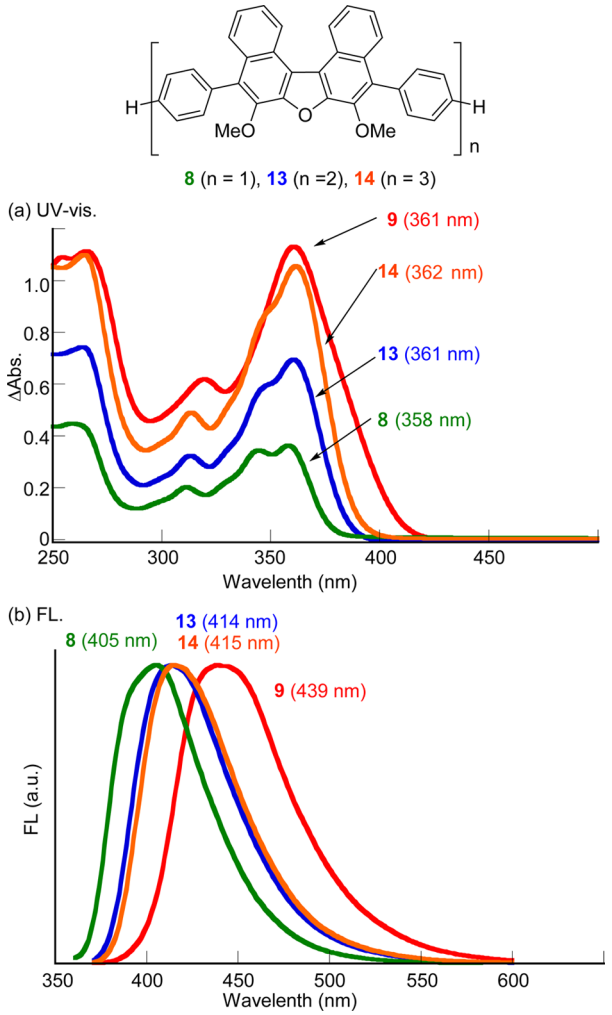
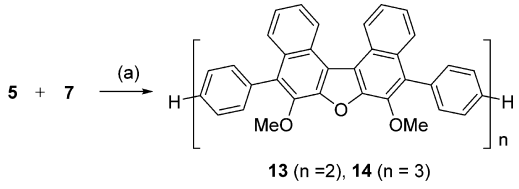


Figure 4. Structures of reference compounds **8**, **13**, and **14** and UV−vis and FL spectra of **9**, **8**, **13**, and **14**. Conditions: CH_2Cl_2, 1.0×10^{-5} M, light path length = 1.0 cm, temp = 25 °C.

Scheme 3. Synthetic Route for Linear Dimer 13 and Trimer 14[a]



[a]Conditions: (a) $Pd(PPh_3)_4$. **13** (14% yield), **14** (4% yield).

Hydrogen peroxide (30 wt % solution in water, 16 mL) was added to the solution, and the solution was refluxed for 1 h. The reaction was quenched by 1 M HCl aq and extracted with ethyl acetate. The organic layer was separated, washed with water and brine, and then dried over sodium sulfate. The solvent was evaporated in vacuo to give a residue. The residue and potassium carbonate (6.18 g, 44.7 mmol) were dissolved in DMF (50 mL), and iodomethane (2.8 mL, 44.7 mmol) was added to the solution and stirred for 5 h at room temperature. The reaction was quenched by 1 M HCl aq, and a white precipitate formed and was collected by filtration. The solid residue was washed with ethyl acetate to give **2** (2.74 g, 56%) as a white powder.

Mp 231−231.5 °C; IR (KBr) 3055, 2931, 2883, 2835, 1597, 1529, 1465, 1415, 1367, 1308, 1273, 1215, 1165, 1115, 1068, 1007, 960, 858, 823, 764, 731, 669, 617, 548 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ

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4.18 (s, 6H), 7.29 (s, 2H), 7.55 (td, J = 7.2 Hz, 1.2 Hz, 2H), 7.61 (td, J = 7.2 Hz, 1.2 Hz, 2H), 7.96 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 9.08 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 105.7, 121.2, 123.9, 124.1, 125.0, 125.5, 128.1, 132.3, 145.9, 146.1; HRMS (ESI$^+$ double-focusing magnetic sector) calcd for $C_{44}H_{32}NaO_6$ (2M + Na$^+$) 679.2097, found 679.2091.

Synthesis of Compound 3. *N*-Bromosuccinimide (2.85 g, 16.0 mmol) was added to a solution of compound **2** (2.5 g, 7.61 mmol) in CH_2Cl_2 (250 mL) and stirred at room temperature for 6 h. The reaction mixture was extracted with chloroform, and the organic layer was washed with 1 M HCl aq, water, and brine and then dried over sodium sulfate. The solvent was evaporated in vacuo to give a residue, which was washed with ethyl acetate to give **3** (3.10 g, 84%) as a pink powder.

Mp 219.5−220.5 °C; IR (KBr) 3072, 2999, 2942, 2834, 1583, 1525, 1460, 1383, 1354, 1304, 1246, 1213, 1167, 1124, 1068, 999, 964, 897, 843, 742, 646 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (s, 6H), 7.66−7.73 (m, 4H), 8.48−8.54 (m, 2H), 8.98−9.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.5, 113.8, 121.0, 125.4, 125.5, 125.6, 126.3, 128.3, 130.2, 143.0, 147.5; HRMS (ESI$^+$ double-focusing magnetic sector) calcd for $C_{44}H_{28}Br_4NaO_6$ (2M + Na$^+$) 990.8517, found 990.8512.

Synthesis of Compound 4. *n*-BuLi (1.61 M, hexane solution, 4.80 mL, 7.73 mmol) was added dropwise to a solution of compound **3** (1.5 g, 3.09 mmol) in THF (150 mL) and stirred for 30 min at −78 °C under a N_2 atmosphere. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.87 mL, 9.27 mmol) was added and stirred at room temperature for 20 min. The reaction was quenched by addition of saturated ammonium chloride solution and extracted with ethyl acetate. The organic layer was separated, washed with water and brine, and then dried over sodium sulfate. The solvent was evaporated in vacuo to give a residue, which was purified by column chromatography (SiO_2, toluene/ethyl acetate = 150/1) to give **4** (919 mg, 51%) as a pink solid.

Mp 222−223 °C; IR (KBr) 3070, 2978, 2937, 2831, 1572, 1527, 1466, 1402, 1348, 1311, 1238, 1142, 1070, 1012, 985, 914, 852, 752, 667, 604, 577 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 24H), 4.29 (s, 6H), 7.55 (t, J = 7.2 Hz, 2H), 7.61 (t, J = 7.6 Hz, 2H), 8.18 (dd, J = 8.0 Hz, 1.2 Hz, 2H), 9.06 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 61.7, 84.3, 123.4, 124.4, 125.1, 125.7, 126.0, 128.5, 134.4, 147.2, 149.1; HRMS (ESI$^+$ double-focusing magnetic sector) calcd for $C_{68}H_{76}B_4NaO_{14}$ (2M + Na$^+$) 1183.5505, found 1183.5537.

Synthesis of Compound 5. 2 M potassium phosphate solution (13.8 mL, 27.6 mmol) was added to a solution of compound **4** (1.6 g, 2.76 mmol), 1,4-dibromobenzene (6.51 g, 27.6 mmol), and tetrakis-(triphenylphosphine)palladium(0) (319 mg, 0.276 mmol) in a mixed solvent of DME and toluene (120 mL, DME/toluene = 1/1) and refluxed for 23 h under a N_2 atmosphere. The reaction mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine and then dried over sodium sulfate. The solvent was evaporated in vacuo to give a residue, which was purified by column chromatography (SiO_2, *n*-hexane/toluene = 2/1) and washed with ethyl acetate to give **5** (1.06 g, 60%) as a white powder.

Mp >300 °C; IR (KBr) 3070, 2999, 2937, 2829, 1579, 1527, 1487, 1392, 1348, 1302, 1223, 1122, 1068, 1009, 968, 908, 837, 764, 644, 517 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (s, 6H), 7.38 (dt, J = 8.4 Hz, 2.0 Hz, 4H), 7.50 (t, J = 8.0 Hz, 2H), 7.65−7.73 (m, 8H), 9.16 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.5, 121.5, 121.8, 124.9, 125.2, 125.49, 125.52, 127.1, 128.6, 131.2, 131.6, 132.7, 134.8, 142.3, 147.8; HRMS (ESI$^+$ double-focusing magnetic sector) calcd for $C_{34}H_{22}Br_2NaO_3$ (M + Na$^+$) 658.9833, found 658.9828.

Synthesis of Compound 6. *n*-BuLi (1.60 M, hexane solution, 1.5 mL, 2.35 mmol) was added dropwise to a solution of compound **5** (500 mg, 0.783 mmol) in THF (80 mL) and stirred for 20 min at −78 °C under a N_2 atmosphere. Trimethyltin chloride (623 mg, 3.13 mmol) was added and stirred for 2 h at room temperature. The reaction mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine and then dried over sodium sulfate. The solvent was evaporated in vacuo to give a residue, which was purified by column chromatography (SiO_2, *n*-hexane/toluene = 2/1) to give **6** (144.3 mg, 23%), **7** (160.9 mg, 32%) and **8** (90.0 mg, 24%).

6: white powder; mp 253.5−254.5 °C; IR (KBr) 3053, 2978, 2914, 2829, 1574, 1523, 1460, 1385, 1350, 1300, 1219, 1120, 1072, 1007, 968, 908, 831, 758, 692, 642, 528 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (s, 18H), 4.10 (s, 6H), 7.44−7.51 (m, 6H), 7.63−7.71 (m, 6H), 7.77 (dd, J = 8.4 Hz, 0.8 Hz, 2H), 9.16 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −9.4, 61.6, 121.3, 124.6, 124.8, 125.4, 125.5, 127.6, 129.9, 130.4, 131.6, 135.7, 135.8, 141.4, 142.4, 147.9; HRMS (APCI-TOF) calcd for $C_{40}H_{41}Sn_2O_3$ (M + H)$^+$ 807.1103, found 807.1081.

7: white powder; mp 195−196 °C; IR (KBr) 3055, 2978, 2933, 2829, 1576, 1525, 1462, 1389, 1348, 1300, 1219, 1120, 1065, 1007, 968, 903, 827, 702, 638, 528; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (s, 9H), 4.07 (s, 3H), 4.10 (s, 3H), 7.45−7.52 (m, 7H), 7.58 (t, J = 7.2 Hz, 2H), 7.64−7.70 (m, 4H), 7.73−7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −9.4, 61.5, 61.6, 121.2, 121.3, 124.7, 124.83, 124.85, 125.40, 125.42, 125.5, 127.4, 127.5, 128.3, 129.87, 129.88, 130.4, 130.9, 131.5, 131.6, 135.7, 135.8, 135.90, 135.95, 141.4, 142.4, 147.92, 147.95; HRMS (APCI-TOF) calcd for $C_{37}H_{33}SnO_3$ (M + H)$^+$ 645.1454, found 645.1456.

8: white powder; mp 241−242 °C; IR (KBr) 3055, 2991, 2933, 2829, 1579, 1525, 1493, 1441, 1394, 1352, 1300, 1221, 1120, 1068, 1011, 968, 901, 852, 812, 752, 702, 650, 517; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (s, 6H), 7.46−7.53 (m, 8H), 7.58 (t, J = 7.2 Hz, 2H), 7.67 (td, J = 7.8 Hz, 1.2 Hz, 2H), 7.74 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 9.17 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.5, 121.3, 124.7, 124.9, 125.4, 125.5, 127.4, 127.5, 128.3, 129.9, 130.9, 131.5, 135.9, 142.4, 147.9; HRMS (APCI-TOF) calcd for $C_{34}H_{25}O_3$ (M + H)$^+$ 481.1798 , found 481.1819.

Synthesis of Compound 9. A solution of compound **6** (91.1 mg, 0.113 mmol) and dichloro(1,5-cyclooctadiene)platinum(II) (42.3 mg, 0.113 mmol) in THF (45 mL) was refluxed for 2 days. A solution of compound **6** (91.1 mg, 0.113 mmol) in THF (45 mL) was refluxed for 2 days. A white precipitate formed and was collected by filtration. The solid residue was dissolved in toluene (50 mL). Triphenylphosphine (40.1 mg, 0.153 mmol) was added and refluxed for 3 h under a N_2 atmosphere. The solvent was evaporated in vacuo and the residue dissolved in chloroform, washed with brine, and dried over sodium sulfate. The solvent was evaporated in vacuo to give a residue, which was purified by column chromatography (SiO_2, toluene/ethyl acetate = 150/1) and washed with *n*-hexane to give **9** (12.9 mg, 24%) as a white powder.

Mp >300 °C; IR (KBr) 3467, 3059, 3026, 2989, 2933, 2829, 1903, 1819, 1726, 1660, 1593, 1570, 1527, 1495, 1462, 1394, 1346, 1298, 1217, 1122, 1057, 1005, 970, 910, 806, 754, 698, 658, 565, 532; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.63 (s, 18H), 7.51 (d, J = 8.4 Hz, 16H), 7.63 (td, J = 7.5 Hz, 1.2 Hz, 6H), 7.78 (td, J = 7.8 Hz, 1.2 Hz, 6H), 7.87 (d, J = 8.4 Hz, 12H), 8.34 (dd, J = 8.4 Hz, 1.2 Hz, 6H), 9.26 (d, J = 8.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 60.9, 122.0, 125.0, 125.3, 125.9, 126.2, 126.5, 128.3, 129.8, 130.7, 132.0, 134.1, 139.2, 143.0, 149.0; HRMS (MALDI-TOF) calcd for $C_{102}H_{66}O_9$ (M$^+$) 1435.4735, found 1435.4732.

Synthesis of Noncyclic Dimer 13 and Trimer 14. **5** (90 mg, 0.140 mmol), **7** (189.2 mg, 0.295 mmol), and tetrakis-(triphenylphosphine)palladium(0) (32.4 mg, 0.0280 mmol) were dissolved in toluene and stirred at 100 °C for 22 h. The solvent was evaporated in vacuo and the residue dissolved in chloroform, washed with brine, and dried over sodium sulfate. The solvent was evaporated in vacuo to give a residue, which was purified by column chromatography (SiO_2, toluene) and washed with toluene to give **13** (19.5 mg, 14%) and **14** (9.0 mg, 4%) as a white solid.

13: mp >300 °C; IR (KBr) 2925, 2852, 1577, 1527, 1496, 1462, 1392, 1352, 1300, 1221, 1120, 1068, 1007, 968, 829, 752, 702, 654, 515; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (s, 6H), 4.15 (s, 6H), 7.50−7.61 (m, 14H), 7.65−7.77 (m, 10H), 7.89 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.0 Hz, 4H), 9.19−9.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.5, 61.6, 121.3, 121.4, 124.7, 124.8, 125.0, 125.58, 125.64, 127.0, 127.5, 127.6, 128.3, 129.5, 130.0, 130.9, 131.5, 135.1, 135.9, 139.9,

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142.4, 142.5, 148.0; HRMS (APCI-TOF) calcd for $C_{68}H_{47}O_6$ $(M + H)^+$ 959.3367, found 959.3350.

14: mp >300 °C; IR (KBr) 2923, 2852, 1726, 1660, 1577, 1525, 1461, 1392, 1348, 1300, 1219, 1120, 1066, 1005, 968, 904, 831, 754, 702, 654, 519; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (s, 6H), 4.16 (s, 6H), 4.18 (s, 6H), 7.48−7.61 (m, 16H), 7.65−7.77 (m, 16H), 7.89−7.92 (m, 4H), 7.99 (d. J = 7.2 Hz, 8H), 9.20−9.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (no meaningful signal was observed in spite of 97776 number of 89278 scans); HRMS (APCI-TOF) calcd for $C_{102}H_{68}O_9$ (M) 1437.4892, found 1437.4854.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01053.

^{1}H and ^{13}C NMR spectra of new compounds and computational studies (PDF)

X-ray data for compound **9** (CIF)

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Notes

The authors declare no competing financial interest.

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