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Selective Syntheses of [7]–[12]Cycloparaphenylenes Using Orthogonal Suzuki–Miyaura Cross-Coupling Reactions

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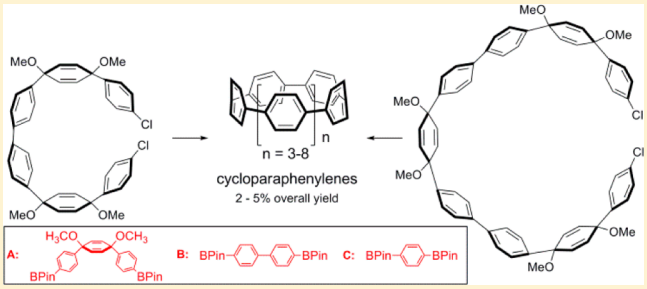
Supporting Information

ABSTRACT: The divergent, selective syntheses of [7]–[12]cycloparaphenylenes have been accomplished utilizing sequential, orthogonal Suzuki–Miyaura cross-coupling reactions from two late-stage intermediates. Quantum yields decrease dramatically as cycloparaphenylene size decreases, highlighting the unique photophysical behavior of the smaller cycloparaphenylenes.



The [*n*]cycloparaphenylenes ([*n*]CPPs) are macrocyclic molecules consisting of *n* benzene rings linked at the *para* position (Figure 1). Recently, these strained molecules have

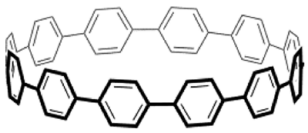


Figure 1. [*n*]Cycloparaphenylene.

received significant interest due to their potential application in carbon nanotube synthesis,[1−5] as well as for their unique optical[6−11] and supramolecular properties.[12] Several synthetic routes, both selective and unselective, to various sizes of CPPs have been reported in the past few years.[6−8,13−23] Many of these selective routes, however, use a large excess (10 equiv) of complex, multistep intermediates to impart selectivity, which in turn hampers their potential scalability and synthetic ease.[13,15,18] Utilizing a more chemoselective approach, we recently reported the selective synthesis of [7]CPP using orthogonal Suzuki–Miyaura cross-coupling reactions.[8] While investigating this highly strained molecule, we were intrigued by the possibility that this approach might be applied to a general, selective synthesis of multiple [*n*]CPPs. Herein we report the selective, divergent syntheses of [7]-[12]CPPs using orthogonal Suzuki–Miyaura cross-coupling reactions.[9]

Our synthetic strategy hinges on the gram-scale preparation of two late-stage precursors (**1** and **2**, Scheme 1). Dichlorides **1** and **2** provide a platform to divergently prepare [7]–[12]CPP in only two additional steps (Schemes 2–4). To access both dichlorides, we first prepared three different cyclohexadiene fragments (**3**–**5**) in a diastereoselective manner by methodology we have recently reported.[8,24,25] Suzuki–Miyaura cross-coupling of **3** and **4** using $Pd(PPh_3)_4$ as the catalyst yields dichloride **1** in 84% (Scheme 1) as previously reported.[8] The same reaction conditions also afford the larger terminal dichloride **2** in 72% by employing 2 equiv of cyclohexadiene **3** and 1 equiv of bisboronate **5**. Both dichlorides can be prepared easily on multigram scale. Advantageously, under these Suzuki–Miyaura cross-coupling conditions we observe no reactivity of the aryl chloride functionality.

With the dichlorides **1** and **2** in hand, we next turned our attention toward the synthesis of the macrocyclic precursors to [8]–[12]CPP. Using Buchwald's S-Phos ligand,[26] we have previously reported the Suzuki–Miyaura cross-coupling/macrocyclization of dichloride **1** with diboronic pinacol ester **6** to prepare macrocycle **8** (Scheme 2).[8] We were hopeful that these same conditions could be used to prepare the macrocyclic precursors to [8]- and [9]CPP by altering the boronate component. Gratifyingly, dichloride **1** underwent cross-coupling and macrocyclization with either boronate **7** or **5** to give macrocycles **9** and **10**, respectively (14% and 23% yield).

We then sought to address whether this same methodology would be applicable for the preparation of the larger macrocyclic precursors to [10]-, [11]-, and [12]CPP (Scheme 3). Under identical conditions as before, cross-coupling of diboronic pinacol ester **6** and dichloride **2** generated macrocycle **11** in 20% yield. Macrocyles **12** and **13** were produced in 12% and 30% yield via cross-coupling of dichloride **2** with boronates **7** and **5**.

DFT-minimized geometries of each macrocycle are also presented in Schemes 2 and 3.[27] These minimized geometries were calculated using Gaussian 03 at the B3LYP/6-31(G)[27] level of theory. Upon simple visual inspection, macrocycles **8**, **9**, and **12** suffer from significant strain resulting from the inclusion of several consecutive planar benzene rings. Accordingly, the macrocyclization reactions leading to these structures are the lowest yielding. For example, macrocycles **8** and **9** contain three

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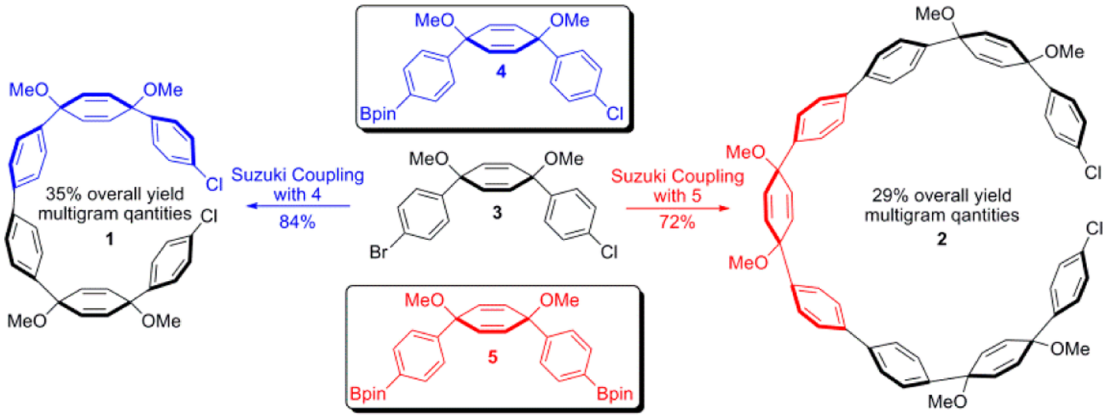
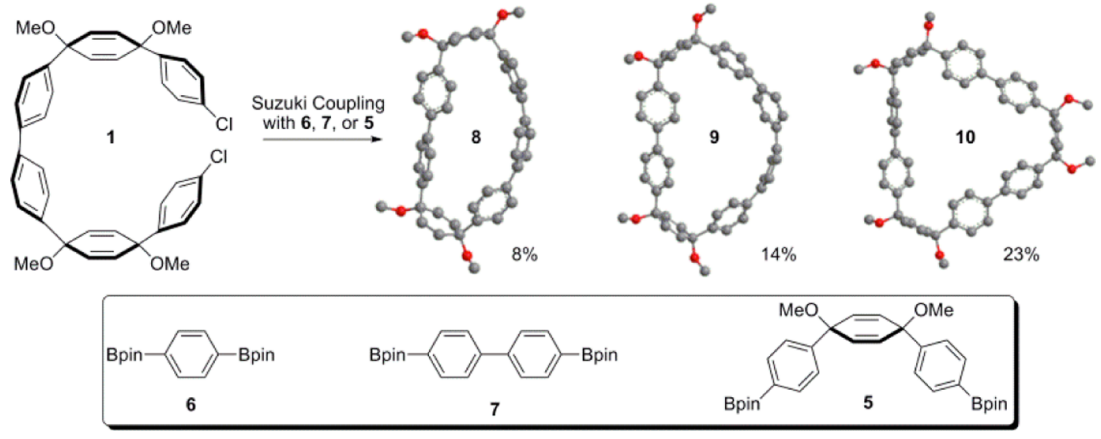
Scheme 1. Orthogonal Suzuki–Miyaura Cross-Coupling Reactions to Prepare Terminal Dichlorides 1 and 2[a]



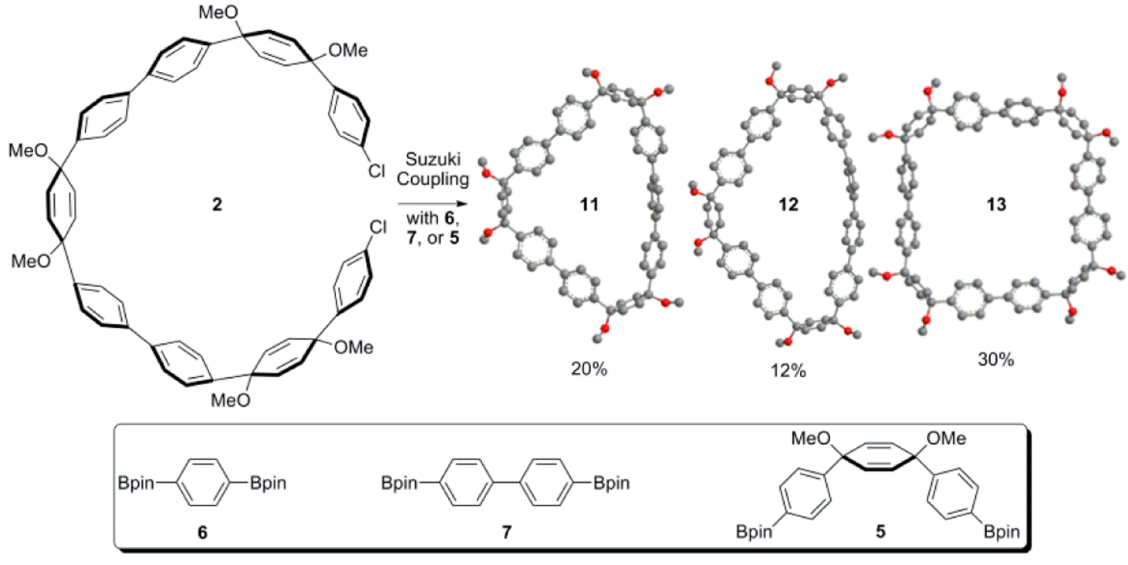
[a]Conditions to prepare **1**: fragment **3** (1 equiv), fragment **4** (1 equiv), $Pd(PPh_3)_4$ (10 mol %), $NaHCO_3$ (1 M aq), 2-propanol, 85 °C. Conditions to prepare **2**: fragment **3** (2 equiv), fragment **5** (1 equiv), $Pd(PPh_3)_4$ (10 mol %), $NaHCO_3$ (1 M aq), 2-propanol, 85 °C.

Scheme 2. Divergent Macrocyclizations for the Precursors to [7]-[9]CPP[a]



[a]Conditions: dichloride **1**, diboronate **6**, **7**, or **5**, $Pd_2(dba)_3$ (10 mol %), S-Phos, K_3PO_4, DMF, H_2O, 125 °C (155 °C for **8**). DFT optimized geometries of macrocycles **8**, **9**, and **10** are shown.

Scheme 3. Divergent Macrocyclizations for the Precursors to [10]-[12]CPP[a]



[a]Conditions: dichloride **2**, diboronate **6**, **7**, or **5**, $Pd_2(dba)_3$, S-Phos, K_3PO_4, DMF, H_2O, 125 °C. DFT-optimized geometries of macrocycles **11**, **12**, and **13** are shown.

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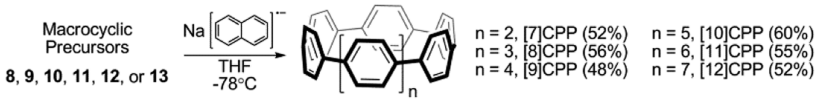
Scheme 4. General Aromatization Reaction Utilizing Sodium Naphthalide



and four consecutive benzene rings, which leads to lower yields. In contrast, macrocycle **10** has only two consecutive benzene rings and consequently forms in significantly higher yield. In the larger series (Scheme 3), the macrocycle with four consecutive benzene rings (**12**) forms in the lowest yield. Methodology to prepare less strained macrocyclic precursors by incorporating additional cyclohexadiene units is currently being investigated in our laboratory.

Our synthetic strategy to the cycloparaphenylenes relies on a key reductive aromatization of the oxidized CPP macrocyclic precursors (Scheme 4).[6,8,20,28] We have previously illustrated that single-electron reducing agents (e.g., sodium naphthalenide) can induce efficient aromatization at low temperatures to access even the most highly stained CPPs. Specifically, we have illustrated our reductive aromatization methodology is effective in preparing [6]- and [7]CPP compounds with 96 and 84 kcal/mol of strain energy.[8,20] Each of the new macrocyclic precursors (**9**−**13**) was subjected to general reductive aromatization conditions at −78 °C to afford the resultant cycloparaphenylenes in good yield. [8]-, [9]-, [10]-, [11]-, and [12]CPP were produced in 56%, 48%, 60%, 55%, and 52% yields, respectively.

Recognizing that the cycloparaphenylenes have unique size-dependent optical properties, we were pleased to have each of the [7]−[12]CPPs in hand. All known CPPs have a common absorption maxima around 340 nm regardless of size, while their fluorescence red shifts dramatically with decreasing diameter.[6,7] Moreover, we have illustrated that [6]CPP has no observable fluorescence[20] and [7]CPP has a low quantum yield of 0.007,[8] while the larger [12]CPP has a quantum efficiency of 0.81.[8] Recently, Itami and co-workers have reported the absolute quantum yields for [9], [12], [14], [15], and [16] CPP through the use of a fluorescence integrating sphere.[12] In these cases, the quantum yields are relatively uniform (Φ = 0.88−0.90) except for the smaller [9]CPP (Φ = 0.73). Our quantum yield measurements were executed using a relative quantum yield technique reported by Miller and co-workers.[29] The data from our studies are illustrated in Figure 2. We note that there is a large decrease in the quantum efficiencies from [12]- to [8]CPP, with [12]CPP having a quantum yield of 0.81, while [8]CPP displays a quantum efficiency of 0.1. [9]-, [10]-, and [11]CPP show increasing quantum yields with increasing size—0.38,[30] 0.65, and 0.73, respectively. The photophysical pathways of the smaller CPPs are clearly different from the larger CPPs.

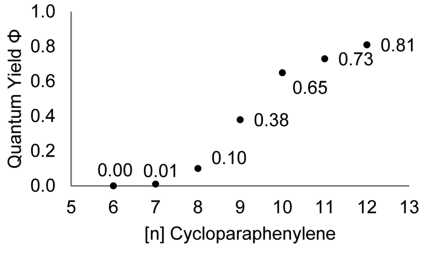


Figure 2. Quantum yields of [6]−[12]cycloparaphenylene.

In conclusion, we have developed a general strategy for the facile synthesis of [7]-[12]CPP from two late stage intermediates that can be prepared on multigram scale. The synthetic route hinges upon chemoselective Suzuki−Miyaura cross-coupling reactions that enable the selective preparation of macrocyclic precursors to the [*n*]CPPs. With the series of [*n*]CPPs (*n* = 7−12) in hand, we have illustrated the dramatic decrease in quantum yield with decreasing cycloparaphenylene size. The photophysical behavior of CPPs in this smaller size regime warrants further study.

EXPERIMENTAL SECTION

Geneal Experimental Details. ^{1}H NMR spectra were recorded at 500 MHz while ^{13}C NMR spectra were recorded at 125 MHz. All spectra were referenced to TMS. MALDI-TOF data was obtained using 7,7,8,8-tetracyanoquinodimethane (TCNQ) silver trifluoroacetate matrix. All reagents were obtained commercially. Tetrahydrofuran, dichloromethane, and dimethylformamide were dried by filtration through alumina according to the methods described by Grubbs.[31] Silica column chromatography was conducted with Zeochem Ceoprep 60 Exo 40−63 μm silica gel, while alumina chromatography utilized Sorbent Technologies 50−200 μm Basic Activity II−III alumina. Thin-layer chromatography was performed using Sorbent Technologies silica gel XHT TLC plates or Sorbent Technologies alumina TLC plates, respectively. Preparative thin-layer chromatography was performed using Watman K6 60 Å silica gel adsorption preparative plates 500 μm thick. Developed plates were visualized using UV light as wavelengths of 254 and 365 nm. All glassware was oven- or flame-dried and cooled under an inert atmosphere of nitrogen unless otherwise noted. Moisture-sensitive reactions were carried out under an inert atmosphere of nitrogen using standard syringe/septa techniques.

4,4″-Dibromo-1′,4′-dimethoxy-1′,4′-dihydro-1,1′:4′1″terphenyl (15). 4′-Bromo-1-hydroxy-[1,1′-biphenyl]-4(1*H*)-one (**14**) was synthesized as previously reported.[8] To a dry 2 L round-bottom flask was added sodium hydride (1.18 g, 29.4 mmol, 1.3 equiv). This solid was washed with dry THF (2 × 60 mL) to remove excess packing grease. THF (120 mL) was then added, and this slurry was cooled to −78 °C, at which point **14** (6 g, 22.6 mmol, 1 equiv) was added dropwise as a solution in THF (60 mL) and stirred for 2 h.

In a separate flame-dried flask equipped with a stir bar was added 1,4-dibromobenzene (12.8 g, 54.3 mmol, 2 equiv) and THF (60 mL). The reaction was then cooled to −78 °C at which point *n*-butyllithium in hexanes (22.6 mL, 54.2 mmol, 2.4 equiv) was added dropwise via cannulation to give an off-yellow solution. (It is important to note at this point that if the reaction mixture exceeds −60 °C, the reaction mixture will turn brown and must be discarded.) This yellow solution was allowed to stir at −78 °C for 30 min and was then cannulated to the reaction vessel containing deprotonated **14**. This reaction was stirred for 2 h at −78 °C before being carefully quenched with water (15 mL), at which point it was gradually warmed to room temperature.

This solution was then extracted with diethyl ether (3 × 20 mL). The pooled organic layer was then washed with saturated brine (50 mL), dried over sodium sulfate, and concentrated under reduced pressure to afford the crude diol as a yellow oil. This crude diol was immediately pushed on to the methylation step to avoid decomposition.

In a separate flame-dried 500 mL round-bottom flask equipped with a stir bar was added sodium hydride (1.4 g, 58.7 mmol, 2.6 equiv) which was washed with THF (3 × 60 mL) as before to remove excess grease. Dry THF (60 mL) was then added to the flask, and the solution was cooled to 0 °C at which point the crude diol was added

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dropwise as a solution in THF (60 mL). After the reaction had stirred for 30 min, neat methyl iodide (5.6 mL, 90.4 mmol, 4 equiv) was added dropwise via cannulation. After cannulation, the reaction was allowed to gradually warm to room temperature and stir for 15 h, at which point it was carefully quenched with water (50 mL). This solution was extracted with ethyl acetate (3 × 30 mL), washed with saturated brine (50 mL), dried over sodium sulfate, and concentrated under reduced pressure. The crude yellow oil was recrystallized in hot hexanes to afford the product **15** as a white crystalline solid (6.5 g, 64%). Mp: 134−135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.41 (s, 6H), 6.07 (s, 4H), 7.23 (d, J = 8.5, 4H), 7.43 (d, J = 9.0, 4H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 52.0, 74.4, 121.7, 127.7, 131.5, 133.3, 142.3. HRMS (Q-TOF ES+): m/z calcd for $C_{20}H_{18}Br_2O_2$ $(M)^+$ 447.9674, found (isotopic pattern) 447.1499, 449.3956. IR (neat): 2982, 2945, 2899, 2825, 1506, 1480, 1451, 1398, 1175, 1025, 1007, 948, 822, 756 cm^{-1}.

Diboronate ***5***. To a flame-dried flask charged with a stir bar were added **15** (5 g, 11.1 mmol, 1 equiv) and THF (50 mL) and the mixture was allowed to cool to −78 °C. *n*-Butyllithium (10.3 mL, 24.4 mmol, 2.2 equiv) was added dropwise to the stirring THF solution over 2 min,[6] neat 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.1 mL, 44.4 mmol, 4 equiv) was immediately added, and the solution was allowed to stir for 30 min. Water (20 mL) was used to carefully quench the reaction, at which point it was extracted with diethyl ether (3 × 100 mL), washed with saturated brine (200 mL), dried over sodium sulfate, and concentrated under reduced pressure to afford the crude product as an off white solid. This crude solid was recrystallized in hot hexanes to give the product **5** as a white crystalline solid (4.75 g, 79%). Mp: >250 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.34 (s, 24H), 3.43 (s, 6H), 6.09 (s, 4H), 7.40 (d, J = 8.5, 4H), 7.75 (d, J = 8.5, 4H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 24.9, 51.9, 74.9, 83.7, 125.3, 133.2, 134.9, 146.3, C−B not observed. HRMS (Q-TOF ES+): m/z calcd for $C_{32}H_{42}B_2O_6$ $(M - OCH_3)^+$ 514.2978, found 514.3044. IR (neat): 2988, 2974, 2938, 2822, 1609, 1398, 1358, 1324, 1272, 1141, 1090, 1080, 1066, 1016, 962, 950, 857, 835, 741 cm^{-1}.

Dichloro ***2***. A 250 mL round-bottom Schlenk flash was equipped with a stir bar and charged with **5** (2 g, 3.7 mmol, 1 equiv), **3** (3.0 g, 7.3 mmol, 2 equiv), and tetrakis(triphenylphosphine)palladium(0) (0.43 g, 0.37 mmol, 0.1 equiv). Aqueous sodium bicarbonate (1 M, 44 mL) and 2-propanol (150 mL) were sparged separately with nitrogen for 1 h. They were then introduced to the Schlenk flask, at which point the reaction mixture was heated to 85 °C and vigorously stirred for 16 h.

Once cooled, the reaction was extracted with ethyl acetate (3 × 100 mL), washed with water (10 × 100 mL) and saturated brine (100 mL), dried over sodium sulfate, and concentrated under reduced pressure to give a yellow oil. This oil was purified by flash chromatography (Al_2O_3, 5:95 ethyl acetate/hexanes) to afford **2** as a white powder (2.5 g, 72%). Mp: 148−150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.43 (s, 6H), 3.44 (s, 6H), 3.47 (s, 6H) 6.07 (d, J = 10.5, 4H), 6.16 (s, 6H), 6.16 (d, J = 10.0, 4H), 7.27 (d, J = 9, 4H), 7.34 (d, J = 8.5, 4H), 7.43 (d, J = 9, 4H), 7.48 (d, J = 8.5, 4H), 7.53 (d, J = 8.5, 4H), 7.53 (d, J = 8.5, 4H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 52.0, 74.5, 74.6, 74.7, 126.4, 126.4, 127.1, 127.1, 127.5, 128.5, 133.0, 133.4, 139.9, 140.1, 142.0, 142.3, 142.6. MALDI-TOF m/z calcd for $C_{59}H_{52}O_5$ $(M - OMe)^+$ 910.32, found 910.09. IR (neat): 3028, 2982, 2939, 2897, 2823, 1489, 1399, 1266, 1228, 1176, 1076, 1012, 949, 822, 762, 734 cm^{-1}.

Macrocycle ***9***. To a 50 mL reaction tube equipped with a rubber septa and stir bar were added dichloride **1** (50 mg, 0.076 mmol, I equiv), diboronate **7** (37 mg, 0.092 mmol, 1.2 equiv), tris-(dibenzylidenacetone)dipalladium(0) (7 mg, 0.0076 mmol, 0.1 equiv), Buchwald ligand S-Phos (11 mg, 0.024 mmol, 0.32 equiv), and tribasic potassium phosphate (32.5 mg, 0.152 mmol, 2.0 equiv). This tube was then sealed and purged with dry nitrogen for 1.5 h. Water (1.5 mL) and DMF (13.8 mL) were separately freeze−pump−thawed (5×) and introduced into the reaction vessel, which was then dropped into a 125 °C oil bath and stirred vigorously for 16 h.

After cooling, the reaction mixture was washed with water (30 mL) and DCM (30 mL) and filtered through a bed of deactivated Celite. This solution was extracted with DCM (3 × 20 mL), washed with water (10 × 20 mL), brine (100 mL) and then dried over sodium sulfate. After concentration the crude mixture was purified by preparative thin layer chromatography (SiO_2, 5:95 ethyl acetate/dichloromethane) to afford macrocycle **9** (7.8 mg, 14% yield, mp decomposition >250 °C) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.39 (s, 6H), 3.46 (s, 6H), 6.99 (d, J = 10.5, 4H), 6.26 (d, J = 10.5, 4H), 7.15 (d, J = 9.0, 4H), 7.26 (d, J = 8.5, 4H), 7.37 (d, J = 9.0, 4H), 7.44 (d, J = 8.5, 4H), 7.54 (d, J = 8.5, 4H), 7.77 (d, J = 9.0, 4H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 51.7, 52.4, 74.5, 74.7, 126.2, 126.6, 126.8, 126.9, 127.8, 128.2, 133.4, 137.9, 139.0, 139.5, 140.5, 141.4, 142.2. MALDI-TOF: m/z calcd for $C_{52}H_{44}O_4$ $(M)^+$ 732.32, found 732.35. IR (neat): 3028, 2937, 2927, 2823, 2610, 1490, 1448, 1396, 1360, 1259, 1174, 1083, 1076, 1014, 1071, 822, 755 cm^{-1}.

Macrocycle ***10***. The general procedure above was used with the exception that diboronate **5** (50 mg, 0.092 mmol, 1.2 equiv) was used in place of diboronate **7** to deliver macrocycle **10** (15.74 mg, 23%). Mp: >250 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.48 (s, 18H), 6.15 (s, 12H), 7.48 (d, J = 8.5, 12H), 7.59 (d, J = 8.5, 12H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 52.0, 74.9, 126.5, 126.8, 133.5, 139.9, 142.6. MALDI-TOF m/z: calcd for $C_{60}H_{54}O_6$ $(M)^+$ 870.39, found 870.50. IR (neat): 2922, 2852, 2824, 1728, 1490, 1464, 1261, 1081, 1022, 951, 820 cm^{-1}.

Macrocycle ***11***. The general procedure above was used with the exception that dichloride **2** (50 mg, 0.053 mmol, 1 equiv) was used in place of dichloride **1** and diboronate **6** (21 mg, 0.064 mmol, 1.2 equiv) was used in place of diboronate **7** to afford macrocycle **11** (10 mg, 20%, mp >250 °C dec) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.43 (s, 6H), 3.47 (s, 6H), 3.49 (s, 6H), 6.12 (d, J = 10.0, 4H, 6.13 (s, 6H), 6.25 (d, J = 10.5, 4H), 7.34 (d, J = 8.5, 4H), 7.47 (d, J = 8.5, 4H), 7.49 (d, J = 8.5, 4H), 7.52 (d, J = 8.5, 4H), 7.56 (d, J = 8.5, 4H), 7.57 (d, J = 8.5, 4H), 7.66 (s, 4H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 52.0, 52.0, 52.3, 74.0, 75.3, 75.3, 126.4, 126.6, 126.8, 126.8, 127.1, 127.2, 127.7, 133.0, 133.7, 139.8, 139.8, 140.0, 140.2, 142.10, 142.11, 143.0. MALDI-TOF m/z: calcd for $C_{66}H_{58}O_6$ $(M)^+$ 946.42, found 946.57. IR (neat): 3028, 2927, 2821, 1654, 1489, 1449, 1174, 1080, 1028, 1005, 949 cm^{-1}.

Macrocycle ***12***. The general procedure above was used with the exception that dichloride **2** (50 mg, 0.053 mmol, 1 equiv) was used in place of dichloride **1** and diboronate **7** (26 mg, 0.064 mmol, 1.2 equiv) was used to afford macrocycle **12** (6.5 mg, 12%, mp >250 °C dec) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.32 (s, 6H), 3.46 (s, 6H), 3.50 (s, 6H), 6.14 (d, J = 10.5, 4H), 6.18 (s, 6H), 6.25 (d, J = 10.0, 4H), 7.32 (d, J = 8.5, 4H), 7.46 (d, J = 8.5, 4H), 7.6 (d, J = 8.5, 4H), 7.49 (d, J = 8.5, 4H), 7.55 (d, J = 8.5, 4H), 7.55 (d, J = 8.5, 4H), 7.66 (d, J = 8.5, 4H), 7.72 (d, J = 8, 4H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 51.4, 51.9, 52.3, 72.9, 75.2, 75.3, 126.6, 126.6, 126.7, 126.8, 127.0, 127.1, 127.3, 127.6, 132.9, 133.4, 139.3, 139.6, 139.8, 139.9, 140.0, 141.8, 142.0, 142.8. MALDI-TOF m/z: calcd for $C_{72}H_{62}O_6$ $(M)^+$: 1022.45, found 1022.42. IR (neat): 3028, 2927, 2821, 1654, 1489, 1449, 1174, 1080, 1028, 1005, 949 cm^{-1}.

Macrocycle ***13***. The general procedure above was used with the exception that dichloride **2** (50 mg, 0.053 mmol, 1 equiv) was used in place of dichloride **1** and diboronate **5** (35 mg, 0.064 mmol, 1.2 equiv) was used in place of diboronate **7** to afford macrocycle **13** (18.5 mg, 30%, mp >250 °C dec) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.45 (s, 24H), 6.15 (s,16H), 7.44 (d, J = 8.5, 16H), 7.48 (d, J = 8.5, 4H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 52.0, 74.7, 126.4, 127.1, 133.4, 140.1, 142.5. MALDI-TOF m/z: calcd for $C_{72}H_{62}O_6$ $(M)^+$: 1160.52, found 1160.93. IR (neat): 756, 820, 984, 950, 1021, 1082, 1177, 1221, 1359, 1396, 1449, 1492, 1713, 2822, 2855, 2929 cm^{-1}.

[8]CPP. To a dry 25 mL round-bottom flask equipped with a glass stir bar was added sodium metal (274 mg, 11.9 mmol) which was subsequently washed with hexanes. Dry THF (12 mL) was added via syringe to the reaction vessel and cooled to 0 °C. Napthalene (1 g, 7.82 mmol) was added to this stirring solution and allowed to gradually warm to room temperature over the course of 18 h.

After 18 h, a separate flame-dried 25 mL flask containing **9** (5 mg, 0.007 mmol, 1 equiv), THF (5 mL), and a stir bar was cooled to −78 °C. To this stirring solution was added the deep green 1 M sodium

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naphthalide solution (0.56 mL, 0.006 mmol, 20.0 equiv per methoxy) dropwise. Upon addition, the solution went from clear to a deep purple and was allowed to stir for 1 h. Once the reaction was complete, a 1 M solution of iodine in THF (1 mL) was added dropwise.

Aqueous saturated sodium thiosulfate (10 mL) was added, and the solution was warmed to room temperature at which point it was diluted with water (20 mL) and extracted with dichloromethane (3 × 15 mL). The organic layers were pooled and then washed with saturated brine (20 mL), dried over sodium sulfate, and concentrated under reduced pressure to afford a crude yellow solid. This crude solid was purified by flash chromatography (SiO_2, 50:50 hexane/dichloromethane) to afford [**8**]**CPP** (2.4 mg, 56%, mp >250 °C dec) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.48 (s, 32H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 127.4, 135.6. MALDI-TOF *m*/*z*: calcd for $C_{48}H_{32}$ $(M)^+$ 608.25, found 608.40. IR (neat): 3958, 2925, 2947, 2934, 2837, 2893, 2852, 1716, 1588, 1484, 1397, 1277, 1254, 1080, 817, 819, 701 cm^{-1}.

[9]CPP. The general procedure above was used with macrocycle **10** (5 mg, 0.006 mmol) in place of **11** to afford [**9**]**CPP** (1.8 mg, 48%, mp >250 °C dec) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.52 (s, 36H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 127.4, 137.9. MALDI-TOF *m*/*z* calcd for $C_{54}H_{36}$ $(M)^+$ 688.28, found 688.24. IR (neat): 2984, 2955, 2928, 2855, 2823, 1481, 1461, 1253, 1089, 816 cm^{-1}.

[10]CPP. The general procedure above was used with macrocycle **11** (5 mg, 0.005 mmol) in place of **9** to afford [**10**]**CPP** (2.5 mg, 60%, mp >250 °C dec) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.56 (s, 40H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 127.4, 138.2. MALDI-TOF *m*/*z*: calcd for C_{60}H40 $(M)^+$ 760.31, found 760.53. IR (neat): 3029, 2929, 2852, 2820, 1590, 1486, 1395, 1354, 1258, 1082, 949, 816, 758, 734 cm^{-1}.

[11]CPP. The general procedure above was used with macrocycle **12** (5 mg, 0.005 mmol) in place of **9** to afford [**11**]**CPP** (2.3 mg, 55%, mp >250 °C dec) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.58 (s, 44H). ^{13}C (125 MHz, $CDCl_3$) δ (ppm): 127.3, 138.4 (Ar). MALDI-TOF *m*/*z* calcd for $C_{72}H_{62}O_6$ $(M)^+$ 1022.45, found 1022.42. IR (neat): 3044, 3030, 3021, 2959, 2950, 2912, 1732, 1593, 1486, 1090, 812, 739, 698 cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supplementary schemes, ^{1}H NMR and ^{13}C NMR spectra, B3LYP/6-31(G) computational data, and quantum yield data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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