

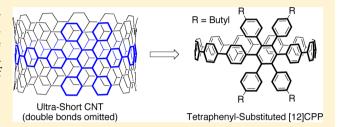
Synthesis of Tetraphenyl-Substituted [12]Cycloparaphenylene: Toward a Rationally Designed Ultrashort Carbon Nanotube

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Supporting Information

ABSTRACT: The first phenyl-substituted [n]cycloparaphenylene (1) has been synthesized. The preparation of this structure addresses several challenges toward a more elaborate phenyl-substituted [n] cycloparaphenylene (2), a molecule that may lead to the homogeneous synthesis of armchair carbon nanotubes.



he [n]cycloparaphenylene ([n]CPP) class of molecules represents the smallest possible segment of an armchair carbon nanotube (CNT), consisting of n benzene rings linked at the para position (Figure 1). Similar to other small fragments

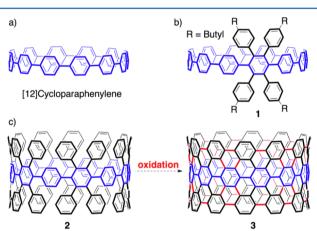


Figure 1. CNT-inspired targets: (a) [12]cycloparaphenylene, (b) tetraphenyl-substituted [12]cycloparaphenylene, (c) strategy toward an ultrashort CNT.

of CNTs, 1-3 these structures have garnered considerable interest because of their potential application in the growth of homogeneous CNTs of discrete chirality and diameter, a grand challenge in the field of nanoscience. 4-7 First synthesized by Jasti and Bertozzi in 2008, numerous synthetic routes to the CPPs have been developed.^{8–15} Despite access to various CPPs, there are currently no reports of cycloparaphenylenes being elongated into carbon nanotubes. Several studies suggest that a longer CNT fragment such as structure 3 (Figure 1) might be more amenable as a seed for CNT growth than the CPPs. 5,7,16 Ultrashort CNT (3) may be envisioned as the product of multiple cyclodehydrogenations of highly phenylsubstituted [12]CPP 2,17-22 a CPP in which every other backbone aryl ring is tetraphenyl-substituted. As an initial foray

toward this challenging synthetic target (2), we report the first synthesis of tetraphenyl-substituted [12]cycloparaphenylene 1, the first CPP with phenyl substitution.

Before embarking on the formidable syntheses of 2, and ultimately 3, we surmised that several fundamental questions must first be addressed on a more tractable model system. In our previous synthetic approaches to the CPPs, we have utilized a 3,6-syn-dimethoxycyclohexa-1,4-diene moiety as a masked aromatic ring in order to provide the curvature and rigidity necessary for macrocyclization.^{8,23} These structures are easily prepared with moderate stereoselectivity by aryllithium addition (2 equiv) to benzoquinone. We were curious as to whether this strategy could be translated to a tetraphenylsubstituted benzoquinone. To address this, we turned to the synthesis of diiodide 8 (Scheme 1). 1-Bromo-4-n-butylbenzene (4) was converted to the corresponding boronic acid (5) and carried on without purification through a 4-fold Suzuki-Miyaura coupling reaction with tetrabromoquinone.²⁴ The crude reaction mixture was then treated with DDQ to afford tetraphenyl-substituted quinone 6 in 54% yield over three steps. Addition of 2 equiv of lithiated 1,4-diiodobenzene to quinone 6 at -78 °C generated syn diol 7 in 69% yield (3.5:1 syn/anti). Standard methylation of 7 produced diiodide 8 in excellent yield. Utilizing this synthetic sequence, we were able to easily prepare over 25 g of diiodide 8.

With diiodide 8 in hand, we next investigated the preparation of macrocycle 12 (Scheme 2). We anticipated using a chemoselective Suzuki-Miyaura coupling strategy, similar to our recently reported selective synthesis of [7]CPP. 14 As expected, using $Pd(PPh_3)_4$ as catalyst allowed for the smooth coupling of 8 and boronate 9^{14} to produce dichloride 10 in 75% yield with no side reactivity of the aryl chloride functionality (Scheme 2). Of note, this reaction can be conducted on a multigram scale. With the more hindered quinone fragment included in the backbone of dichloride 10,

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Scheme 1. Synthesis of Diiodide 8

Scheme 2. Synthesis of Tetraphenyl-Substituted [12]Cycloparaphenylene 1

we were cognizant that this substitution might have a deleterious effect on the conformation necessary for cyclization. Gratifyingly, upon switching to Buchwald's S-Phos ligand,²⁵ dichloride 10 undergoes tandem Suzuki–Miyaura coupling/macrocyclization with diboronic pinacol ester 11⁸ to generate macrocycle 12 in a moderate yield of 24%.

The final step in the synthesis involved the aromatization of the 1,4-cyclohexadiene moieties to the requisite benzene rings. Treatment of macrocycle 12 at -78 °C with sodium naphthalenide, a single-electron reducing agent, induced a reductive aromatization sequence to generate tetraphenyl-substituted CPP 1 in 63% (Scheme 2). The proton and carbon NMR spectra were consistent with the target molecule, and the MALDI-TOF spectrum shows the characteristically strong CPP peak at 1441 attributed to the radical cation of 1. Although the yield for the macrocyclization step is modest, the reactions are scalable, and over 100 mg of 1 has been prepared

in a single macrocyclization/aromatization sequence from 10. Interestingly, the UV—vis absorption of 1 in dichloromethane shows a dominant absorption peak at 328 nm, similar to [12]CPP, along with a secondary peak at approximately 240 nm. This second peak may be attributed to the tetraphenyl substitution. The fluorescence spectra of 1 displays a red-shifted fluorescence with a fluorescence maximum at 423 nm (95 nm shift), similar to unsubstituted [12]CPP. The quantum yield of 1 is 0.81, identical to the parent [12]CPP.

In conclusion, we have identified highly phenyl-substituted CPP 2 as a plausible precursor to an ultrashort CNT (3), a viable seed for the preparation of homogeneous armchair carbon nanotubes. As an initial exploration of the requisite methodology to prepare 2, we have synthesized tetraphenyl-substituted [12]cycloparaphenylene 1. In order to prepare this structure, we have developed a multigram synthesis of tetraphenyl-substituted 3,6-syn-dimethoxycyclohexa-1,4-diene 8. This elaborated cyclohexadiene fragment was incorporated into the backbone of a CPP by a multigram chemoselective Suzuki-Miyaura coupling to dichloride 10 followed by macrocyclization. Our reductive aromatization strategy was proven to be equally effective upon these phenyl-substituted quinone derivatives. With this knowledge in hand, a synthesis of more elaborate phenyl-substituted 2 is underway.

■ EXPERIMENTAL SECTION

General Experimental Details. ¹H NMR spectra were recorded at 500 or 400 MHz, while 13C NMR spectra were recorded at 125 or 100 MHz. All NMR spectra were referenced to TMS. All reagents were obtained commercially. Tetrahydrofuran, dicholoromethane, and dimethylformamide were dried by filtration through alumina. Silica column chromatography was conducted with Zeochem Zeoprep 60 Eco 40-63 μm silica gel, while alumina chromatography utilized Sorbent Technologies 50–200 μm basic activity II–III alumina. Thinlayer chromatography (TLC) was performed using Sorbent Technologies silica gel XHT TLC plates or Sorbent Technologies alumina TLC plates, respectively. Developed plates were visualized using UV light at 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 technique. All solvents were degassed by sparging with N2.

Tetraphenyl-Substituted Quinone 6. 1-Bromo-4-n-butylbenzene (44.1 mL, 250 mmol) was added to a dry flask charged with a stir bar. THF (750 mL) was added, and the flask was consequently cooled to -78 °C. Once cooled, nBuLi was added dropwise (110 mL, 275 mmol), resulting in a yellow reaction mixture. The reaction mixture was stirred for 30 min. Trimethoxyborane was then added as a stream (35.3 mL, 300 mmol), resulting in a colorless reaction mixture. The reaction mixture was then warmed to room temperature and stirred for 45 min. A 6 M solution of HCl was added (600 mL), and the reaction mixture was stirred for 1 h before being transferred to a separatory funnel and diluted with diethyl ether. The aqueous layer was extracted three times with diethyl ether, which was combined and subsequently washed with a saturated solution of sodium bicarbonate followed by brine. The organic layer was then dried over sodium sulfate and concentrated to afford the corresponding (4-butylphenyl)boronic acid as a slightly wet, white solid.

A Schlenk flask was charged with tetrabromoquinone (25 g, 59 mmol), Pd(PPh₃)₄ (3.4 g, 2.95 mmol), and K₂CO₃ (40.7 g, 295 mmol) and then evacuated and backfilled with N₂. Separately, THF and H₂O were sparged with N₂. Degassed THF (180 mL) was used to transfer the freshly made boronic acid from its evacuated and backfilled (N₂) flask into the air-free Schlenk. Degassed H₂O (60 mL) was then syringed into the Schlenk, which was subsequently heated to 90 °C and stirred for 16 h.

The reaction mixture was cooled and concentrated under reduced pressure, at which point it was diluted with ether. A 6 M solution of HCl was added slowly until the mixture was pH neutral. The mixture was then transferred to a separatory funnel and extracted three times with CH₂Cl₂. The combined organic layer was dried with brine and sodium sulfate before being concentrated under reduced pressure to afford a black oil.

This crude oil was dissolved in CH₂Cl₂ (200 mL), and DDQ (15.5 g, 68.16 mmol) was added. The reaction mixture was stirred overnight open to air before being concentrated under reduced pressure. The reaction mixture was purified through a pad of silica (1:9 CH₂Cl₂/hexanes to 4:6 CH₂Cl₂/hexanes) before being recrystallized in hot hexanes to afford red needles (20.25 g, 54% over three steps): mp 157–159 °C; IR (neat) 2952, 2928, 2858, 1650, 1607, 1503, 1466, 1296, 1137 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.99 (s broad, 16H), 2.54 (t, J = 7.7 Hz, 8H), 1.54 (tt, J = 7.7, 7.2 Hz, 8H), 1.29 (qt, J = 7.2, 7.2 Hz, 8H), 0.89 (t, J = 7.2 Hz, 12H); ¹³C (125 MHz, CDCl₃) δ 187.25, 142.91, 142.78, 130.82, 130.33, 127.58, 35.38, 33.23, 22.22, 13.93; MALDI-TOF m/z calcd for C₄₆H₅₂O₂Na (M)⁺ 659.4, found 659.4.

Tetraphenyl-Substituted Diiodide Diol 7. 1,4-Diiodobenzene (43 g, 129 mmol) was placed in a flame-dried flask with a stir bar. THF (380 mL) was added, and the solution was cooled to -78 °C, at which point nBuLi (46 mL, 115 mmol) was added dropwise. The solution stirred for 30 min, at which point 6 (30.5 g, 47.9 mmol) was introduced as a solution in THF (120 mL) over 10 min. The reaction mixture was stirred for 30 min and then quenched with H₂O at -78 °C. The reaction mixture was warmed and then diluted with H2O and diethyl ether before being transferred to a separatory funnel. The aqueous layer was extracted three times with ether and then three times with CH2Cl2. The combined organic layers were washed with brine and dried over sodium sulfate before being concentrated under reduced pressure. The reaction mixture was purified by silica gel chromatography with an eluent mixture gradient of 3:7-8:2 CH₂Cl₂/ hexanes to afford a white solid (34.6 g, 69%): mp 220-221 °C; IR (neat) 2954, 2928, 2857, 1505, 1480, 1389, 1005, 906, 732 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, J = 8.3 Hz, 4H), 7.10 (d, J = 8.3Hz, 4H), 6.70 (d, J = 8.2 Hz, 8H), 6.66 (d, J = 8.2 Hz, 8H), 2.42 (s, 2H), 2.35 (t, J = 7.6 Hz, 8H), 1.38 (tt, J = 7.6, 7.2 Hz, 8H), 1.14 (qt, J= 7.2, 7.2 Hz, 8H), 0.81 (t, J = 7.2 Hz, 12H); ¹³C (125 MHz, CDCl₃) δ 142.96, 140.74, 140.34, 136.47, 134.14, 131.29, 129.60, 126.90, 92.97, 75.11, 35.00, 33.12, 22.03, 13.88; MALDI-TOF m/z calcd for C₅₈H₆₂I₂O₂Na (M)⁺ 1067.2, found 1067.3.

Tetraphenyl-Substituted Diiodide 8. Diol 7 (34.6 g, 33 mmol) was placed into a dry flask with a stir bar, at which point THF (300 mL) was added and the reaction mixture was cooled to 0 °C. A NaH powder in oil (6.6 g, 165 mmol) was added in three portions over 20 min. The reaction mixture was then stirred for 30 min, and MeI (12.3 mL, 198 mmol) was subsequently added as a stream over 5 min. The ice bath was allowed to warm to room temperature as the reaction mixture was stirred for 16 h. The reaction mixture was then quenched with H2O and diluted with diethyl ether before being transferred to a separatory funnel. The aqueous layer was extracted three times with diethyl ether, and the combined organic layers were washed with brine and dried over sodium sulfate before being concentrated under reduced pressure. The crude mixture was suspended in 150 mL of hexanes and stirred at 0 °C for 30 min. The solution was filtered and the solid was washed with cold hexanes (2 × 50 mL) to afford a white solid (26.5 g, 75%). The yield may be improved if purified through silica gel chromatography (1:9 CH2Cl2/hexanes) to afford a white solid (92%): mp 218 °C; IR (neat) 2955, 2924, 2857, 1507, 1480, 1458, 1387, 1096, 1006, 907, 758, 733 cm⁻¹; ¹H NMR (500 MHz, CD_2Cl_2) δ 7.62–7.08 (broad, 8H), 6.60 (d, J = 8.2 Hz, 8H), 6.51 (d, J = 8.2= 8.2 Hz), 3.76 (s, 6H), 2.28 (t, J = 7.6 Hz, 8H), 1.31 (tt, J = 7.6, 7.2 (tt,Hz, 8H), 1.08 (qt, J = 7.2, 7.2 Hz, 8H), 0.75 (t, J = 7.2 Hz, 12H); ¹³C (125 MHz, CDCl₃) δ 143.05, 142.36, 140.66, 136.35, 135.54, 130.96, 129.85 (broad), 126.83, 92.56, 81.14, 52.10, 34.95, 33.10, 21.95, 13.90; MALDI-TOF m/z calcd for $C_{59}H_{63}I_2O$ (M - CH_3O)⁺ 1041.3, found 1041.3.

Tetraphenyl-Substituted Terminal Dichloride 10. A Schlenk flask was charged with a stir bar, 8 (2.61 g, 2.43 mmol), 9 (2.4 g, 5.35 mmol), Pd(PPh₃)₄ (280 mg, 0.28 mmol), and CsCO₃ (3.96 g, 14 mmol). The flask was then evacuated and backfilled with N2. Toluene and methanol were sparged with N2 in separate flasks and subsequently syringed into the Schlenk flask (143 and 13 mL respectively). The reaction mixture was heated to 80 °C and stirred for 16 h. Upon cooling, the reaction mixture was diluted with H2O and transferred to a separatory funnel. The aqueous layer was extracted with CH₂Cl₂ (3x), and the combined organic layers were subsequently washed with brine and dried over sodium sulfate. Upon concentration under reduced pressure, the reaction mixture was purified by column chromatography (alumina) with an eluent of 2:8 diethyl ether/hexanes to afford a white solid (2.66 g, 75%): mp 116-128 °C; IR (neat) 2954, 2930, 1491, 1013, 951, 907, 821, 728 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.73–7.56 (broad, overlap, 4H), 7.58 (d, J = 8.6 Hz, 4H), 7.49-7.40 (broad overlap, 4H), 7.43 (d, J = 8.6)Hz, 4H), 7.36 (d, J = 8.8 Hz, 4H), 7.28 (d, J = 8.8 Hz, 4H), 6.67 (d, J= 8.3 Hz, 8H), 6.62 (d, J = 8.3 Hz, 8H), 6.16 (d, J = 10.24 Hz, 4H),6.08 (d, I = 10.24 Hz, 4H), 3.87 (s, 6H), 3.45 (s, 6H), 3.44 (s, 6H), 2.34 (t, J = 7.5 Hz, 8H), 1.37 (tt, J = 7.5, 7.4 Hz, 8H), 1.13 (qt, J = 7.4, 7.4 Hz, 8H), 0.80 (t, J = 7.4 Hz, 12H); ¹³C (125 MHz, CDCl₃) δ 142.53, 142.46, 142.06, 142.03, 140.40, 140.06, 138.34, 136.04, 133.74, 133.39, 132.95, 131.15, 128.49, 128.32 (broad), 127.48, 126.88, 126.72, 126.31, 125.72, 81.44, 74.64, 74.51, 52.14, 52.02, 52.02, 34.98, 35.14, 21.96, 13.91; MALDI-TOF m/z calcd for $C_{99}H_{99}Cl_2O_5$ (M – CH₃O)⁺ 1438.7, found 1438.7.

Macrocyclic 12. A three-necked flask was charged with a stir bar, 10 (882 mg, 0.6 mmol), 11 (424 mg, 0.78 mmol), $Pd_2(dba)_3$ (54 mg, 0.06 mmol), S-Phos (98.4 mg, 0.24 mmol), and K_3PO_4 (254.4 mg, 1.2 mmol). The flask was fitted with a condenser and septa and subsequently evacuated and backfilled with N_2 . The flask was then additionally purged with N_2 for 30 min. Separately, a flask containing DMF and a flask containing H_2O were sparged with N_2 . The DMF and H_2O were syringed into the reaction flask (540 and 60 mL, respectively), and the reaction mixture was lowered into a hot oil bath at 125 °C. The reaction mixture was stirred for 16 h.

Upon cooling, the reaction mixture was filtered through Celite, and the Celite was then washed with CH2Cl2. The filtered solution was transferred to a separatory funnel, and the organic layer was washed multiple times (\sim 15) with H₂O until the DMF was removed. Upon concentration under reduced pressure, the reaction mixture was purified by column chromatography (silica) with an eluent gradient of 10:90 to 15:85 EtOAc/hexanes to afford a white solid (244 mg, 24%): mp 185-190 °C; IR (neat) 2953, 2927, 2855, 1491, 1083, 1026, 1006, 951, 820 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.64-7.34 (m, 32H), 6.66 (d, J = 8.3 Hz, 8H), 6.62 (d, J = 8.3 Hz, 8H), 6.18-6.12 (m, 12H), 3.84 (s, 6H), 3.46 (s, 6H), 3.45 (s, 6H), 3.44 (s, 6H), 2.34 (t, J = 7.6 Hz, 8H), 1.37 (tt, J = 7.6, 7.5 Hz, 8H), 1.13 (qt, J = 7.5, 7.5 Hz,8H), 0.79 (t, J = 7.5 Hz, 12H); ¹³C (125 MHz, CDCl₃) δ 142.53, 142.52, 142.40, 142.37, 142.26, 140.41, 140.25, 140.15, 140.09, 138.76, 136.02, 133.40, 133.35, 133.34, 133.33, 131.15, 128.27, 127.14, 127.13, 126.99, 126.71, 126.39, 126.34, 125.81, 81.45, 74.70, 74.60, 74.59, 52.05, 52.00, 51.98 (2), 34.94, 33.12, 21.93, 13.89; MALDI-TOF *m/z* calcd for $C_{119}H_{118}O_7$ (M - CH₃O)⁺ 1658.8, found 1658.2.

Tetraphenyl-Substituted [12]CPP 1. A dry flask was charged with a glass stir bar, and sodium metal was washed with hexanes to remove oil (405 mg, 17.6 mmol). Dry THF (15 mL) was added, followed by naphthalene (1.92 g, 15 mmol) in portions. This reagent was allowed to stir overnight for complete formation.

Macrocycle 12 (240 mg, 0.14 mmol) was placed in a dry flask along with a glass stir bar. THF (40 mL) was added, and the reaction mixture was cooled to -78 °C. Freshly prepared sodium naphthalide (7 mL, 7 mmol) was added dropwise, and the reaction mixture immediately changed color to a dark purple solution. The reaction mixture was stirred for 40 min, at which point the excess reagent was quenched with a 1 M iodine solution in THF. A saturated solution of sodium thiosulfate was added, and the reaction mixture was allowed to warm to room temperature while stirring.

The reaction mixture was transferred to a separatory funnel and diluted with CH2Cl2 and H2O. The aqueous layer was extracted three times with CH2Cl2 and the combined organic layers were washed with brine and dried over magnesium sulfate before being concentrated under reduced pressure. The reaction mixture was then purified through column chromatography (silica) with an eluent of 25:75 CH₂Cl₂/hexanes to afford a pale yellow solid (127 mg, 63%): mp >225 °C; IR (neat) 3025, 2955, 2927, 2856, 1482, 906, 809, 729 cm⁻¹ ¹H NMR (500 MHz, CDCl₃) 7.66-7.61 (m, 28H), 7.53 (d, J = 8.5Hz, 4H), 7.19 (d, I = 8.5 Hz, 4H), 6.89 (d, I = 8.5 Hz, 4H), 6.85 (d, I= 8.5 Hz, 4H), 6.61 (d, 8.0 Hz, 4H), 6.48 (d, I = 8.0 Hz, 4H), 2.17 (t, I= 7.6 Hz, 8H), 1.24 (tt, J = 7.6, 7.3 Hz, 8H), 1.02 (qt, J = 7.3, 7.3 Hz, 8H), 0.70 (t, J = 7.3 Hz, 12H); ¹³C (125 MHz, CDCl₃) δ 140.36, 140.25, 140.12, 139.66, 139.16, 138.60, 138.59, 138.56, 138.55, 138.50 (2), 138.29, 137.91, 137.70, 137.61, 132.41, 130.71, 127.77, 127.34-127.29 (6), 127.18, 126.77, 126.32, 125.46, 34.88, 33.14, 22.02, 13.84; MALDI-TOF m/z calcd for $C_{112}H_{96}$ (M)⁺ 1441.7, found 1441.5.

ASSOCIATED CONTENT

S Supporting Information

NMR spectra of all compounds, MALDI-TOF, and optical characterization of 1. 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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