

Supporting Information

Selective Synthesis and Crystal Structure of [10]Cycloparaphenylene

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General. All reaction conditions dealing with air- and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen atmosphere. ¹H (400 MHz) and ¹³C NMR (100 or 150 MHz) spectra were measured for a CDCl₃ or CD₂Cl₂ solution of a sample and are reported in parts per million (δ) from internal tetramethylsilane or residual solvent peak. IR spectra (absorption) are reported in cm⁻¹. High resolution mass spectra (HRMS) were obtained under electron impact ionization conditions. Electro spray ionization time-of-flight mass (ESI-TOF MS) spectrum was recorded on a spectrometer in the positive mode. Sample was injected as an isopropanol solution. Matrix-assisted laser-desorption ionization time-of-flight mass (MALDI-TOF MS) spectrum was obtained on a spectrometer in the positive reflection mode and at 20 kV acceleration voltage. Samples were prepared from a tetrahydrofuran (THF) solution by mixing sample (1 mg/mL) and dithranol (1 mg/mL) in a ratio of 1:1.

Materials. Unless otherwise noted, commercially available materials were used without purification. Dichloromethane (CH₂Cl₂) was distilled successively from P₂O₅ and K₂CO₃ and stored over molecular sieves. Water content in solvents was determined by Karl-Fisher water titrator. Pt(cod)Cl₂ (cod refers to 1,5-cyclooctadiene) was synthesized according to a literature.¹

Synthesis of 4-Iodo-4'-(trimethylstanyl)-1,1'-biphenyl (3d). To a solution of 4,4'-diodobiphenyl (4.06 g, 10.0 mmol) in THF (75 mL) was slowly added BuLi (6.62 mL, 1.51 M in hexane, 10.0 mmol) by using a syringe at -78 °C. After stirring for 1 h at this temperature, a solution of trimethylstanyl chloride (1.99 g, 10.0 mmol) in THF (5 mL) was slowly added through a cannula at -78 °C, and the resulting mixture was slowly warmed to room temperature. After stirring for 6 h at this temperature, the reaction mixture was quenched with saturated aqueous NH₄Cl solution, and was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude mixture (4.35 g). The

¹ Hill, G. S.; Levy, C. J.; Rendina, L. M.; Puddephatt.; R. D. *Inorg. Synth.* **1998**, 32, 149.

residue was purified by silica gel chromatography (hexane/ethyl acetate = 6/1) to give the title compound (3.72 g, 84%) as a white solid. ^1H NMR (CDCl_3 , 400 MHz) 0.32 (s, 9H, $J_{\text{Sn-H}} = 54.4$, SnMe_3), 7.32 (d, $J = 8.4$ Hz, 2H, -ArH), 7.52 (d, $J = 7.6$ Hz, 2H, -ArH), 7.57 (d, $J = 5.2$ Hz, 2H, -ArH), 7.76 (d, $J = 8.8$ Hz, 2H, -ArH); ^{13}C NMR (CDCl_3 , 150 MHz) -9.5 (SnMe_3 , $J_{\text{Sn-C}} = 342$), 93.0 (4°), 126.4 (CH), 129.0 (CH), 136.4 (CH), 137.8 (CH), 139.9 (4°), 140.7 (4°), 141.9 (4° , $J_{\text{Sn-C}} = 440.3$); HRMS (FAB) m/z : Calcd for $\text{C}_{15}\text{H}_{17}\text{Sn}$ (M) $^+$, 443.9397; Found 443.9451; IR (KBr) 802, 999, 1379, 1474, 2911, 2980; mp 83.9-85.5 $^\circ\text{C}$.

Synthesis of Bis(4-iodo-1,1'-biphenyl)(1,5-cyclooctadiene)platinum (1a). Pt(cod)Cl₂ (0.37 mg, 1.0 mmol) and **3d** (0.89 g, 2.0 mmol) were dissolved in THF (100 mL), and the mixture was heated at 60 $^\circ\text{C}$ for 6 h under a nitrogen atmosphere. To the resulting mixture was added water, and was extracted with CH_2Cl_2 . The combined organic layer was washed with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure to give a crude mixture (4.35 g). The residue was purified by passing silica gel (hexane/ $\text{CH}_2\text{Cl}_2 = 1/1$ to 0/1) to give the title compound (0.83 g, 96%) as a yellow white solid. ^1H NMR (400 MHz, CD_2Cl_2) 2.54 (bs, 8H, cod-H), 5.10 (bs, 4H, cod-H), 7.24 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.28 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.38 (d, $J = 8.4$ Hz, 4H, Ar-H), 7.68 (d, $J = 8.4$ Hz, 4H, Ar-H); ^{13}C NMR (150 MHz, CD_2Cl_2) 30.3 (CH_2), 91.9 (4°), 105.7 (CH), 126.1 (CH), 128.8 (CH), 134.5 (4°), 135.4 (CH), 138.0 (CH), 141.6 (4°), 156.5 (4°); HRMS (ESI-TOF) m/z : Calcd for $\text{C}_{32}\text{H}_{28}\text{I}_2\text{Pt}$ ($\text{M} + \text{NH}_4$) $^+$, 879.0269; Found 879.0221; IR (KBr) 799, 997, 1070, 1470, 1580, 2359, 2884, 2999.

Synthesis of [10]CPP. 1a (86.1 mg, 0.1 mmol), Pd(dba)₂ (115.0 mg, 0.2 mmol), and 2,2'-bipyridyl (31.2 mg, 0.2 mmol) were dissolved in THF (20 mL), and the mixture was heated at 50 $^\circ\text{C}$ for 8 h under a nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue was washed with ether to give a crude mixture (109.5 mg). The crude mixture was added to a suspension of AgBF_4 (33.1 mg, 0.17 mmol) in CH_2Cl_2 /acetone (17 ml) at room temperature under a nitrogen atmosphere, and the resulting mixture was stirred at room temperature for 12 h. The mixture was filtered through a pad of celite, and the filtrate was concentrated under reduced pressure to give a crude mixture. The residue was purified by silica gel chromatography (hexane/ $\text{CH}_2\text{Cl}_2 = 4/1$) to give the [10]CPP (4.1 mg, 16%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) 7.56 (s, 40 H); ^{13}C NMR (100 MHz, CDCl_3) 127.5 (Ar-H), 138.3 (Ar-H); HRMS (MALDI-TOF) m/z calcd for $\text{C}_{60}\text{H}_{40}$ [M] $^+$: 760.3125, found 760.3136.

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for [10]CPP·Hexane are listed in Table S1. In each case, a suitable crystal was transferred to the goniometer of a Rigaku Mercury CCD area detector with graphite monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$). The structures were solved by direct methods with SIR-2002² and refined against all F² data by full-matrix least-squares techniques. The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S1. Crystal data and structure refinement for [10]CPP·Hexane.

Identification code	[10]CPP·Hexane.	
Empirical formula	C66 H54	
Formula weight	847.09	
Temperature	153(2) K	
Wavelength	0.71070 \AA	
Crystal system	monoclinic	
Space group	$P2_1/c$ (#14)	
Unit cell dimensions	$a = 15.8912(16) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 8.1477(6) \text{ \AA}$	$\beta = 108.855(2)^\circ$.
	$c = 21.033(2) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$2577.2(4) \text{ \AA}^3$	
Z	2	
Density (calculated)	1.092 Mg/m^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	900	
Crystal size	$0.30 \times 0.20 \times 0.10 \text{ mm}^3$	
Theta range for data collection	3.17 to 25.50° .	
Index ranges	$-19 \leq h \leq 19$, $-9 \leq k \leq 8$, $-25 \leq l \leq 25$	
Reflections collected	22194	
Independent reflections	4774 [R(int) = 0.0457]	
Completeness to theta = 25.50°	99.5 %	
Max. and min. transmission	0.9939 and 0.9818	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4774 / 258 / 460	
Goodness-of-fit on F ²	1.131	
Final R indices [I > 2 σ (I)]	R1 = 0.0772, wR2 = 0.2008	
R indices (all data)	R1 = 0.0973, wR2 = 0.2207	
Largest diff. peak and hole	0.441 and $-0.258 \text{ e. \AA}^{-3}$	

² Burla M, C.; Camalli, M.; Carrozzini, B.; Cascarano, GL.; Giacovazzo C.; Polidori, G.; Spagna, R. Sir2002: The program. *J. Appl. Cryst.* **2003**, *36*, 1103.

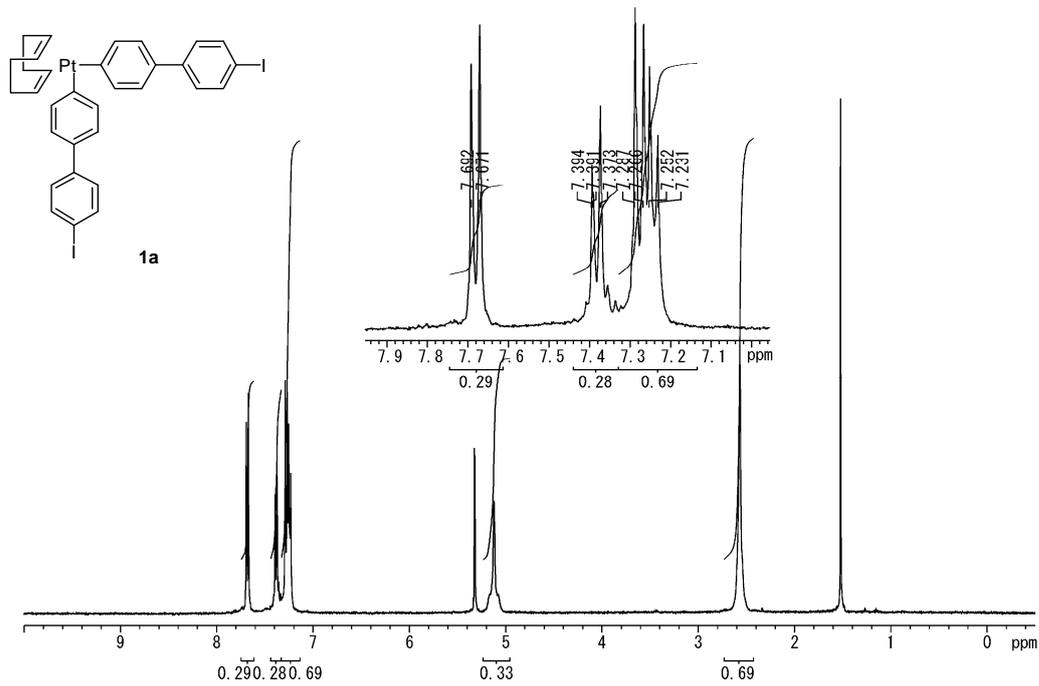


Figure S3. ¹H NMR spectra of **1a**.

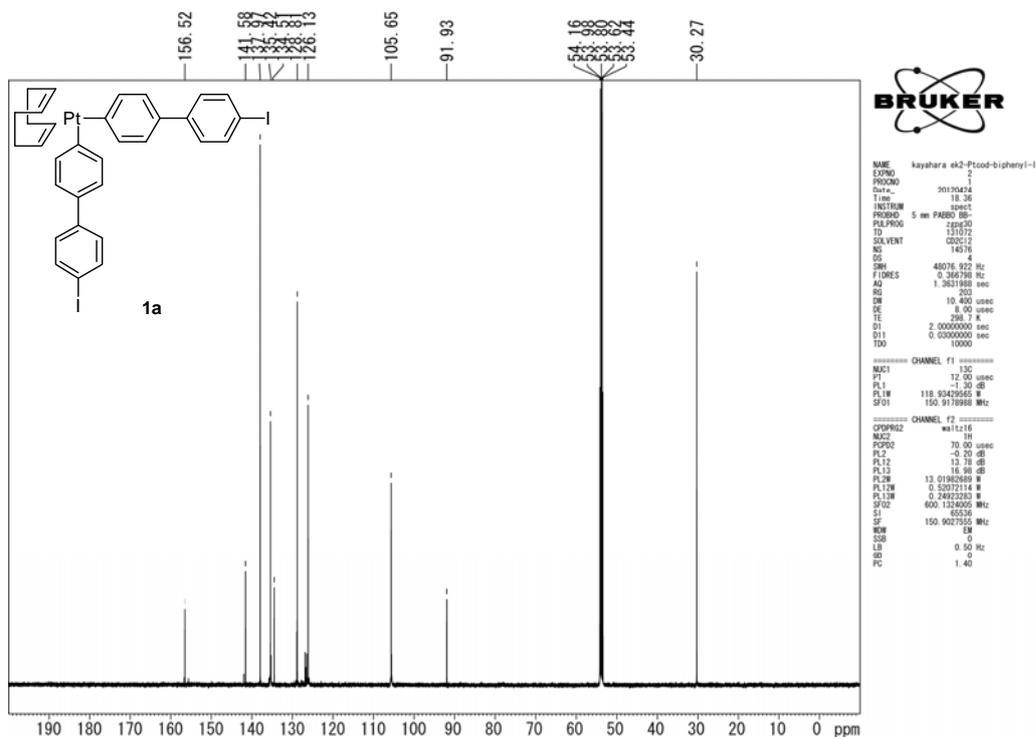


Figure S4. ¹³C NMR spectra of **1a**.

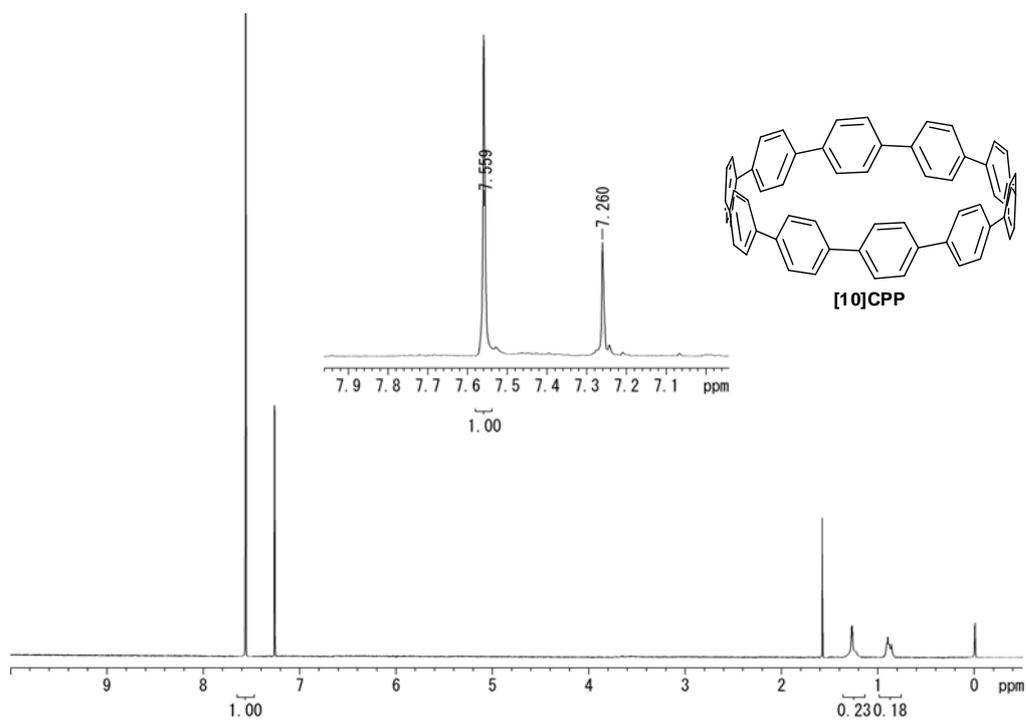


Figure S5. ^1H NMR spectra of [10]CPP.

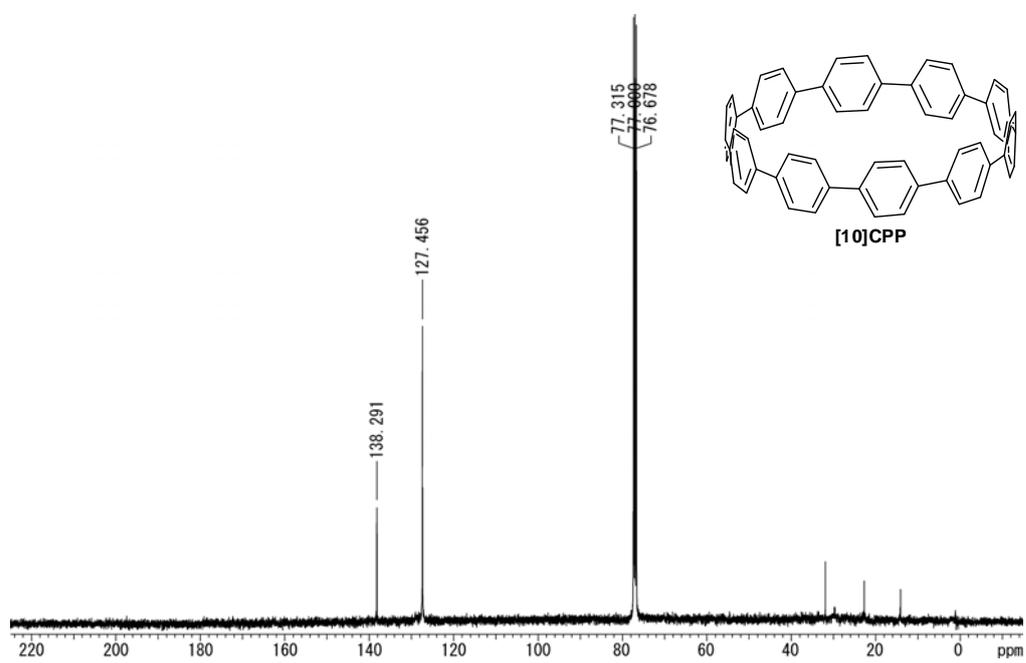


Figure S6. ^{13}C NMR spectra of [10]CPP.