Supporting Information

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“The Versatile Synthesis and Self-assembly of Star-type Hexabenzocoronenes”

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1. MALDI-MS of compound 2, 11a-c. (TCNQ as matrix)

2. MALDI-MS of compound 12a-b (TCNQ as matrix).

3. $^1$H NMR spectra (500MHz) of 11a-c (413K in d4-tetrachloroethane), 12a (d4-1,2-dichlorobenzene, 443K, only monomer exists), 12b (413K in d4-tetrachloroethane) and 15 (413K in d4-tetrachloroethane).

The synthetic route to compound 14 is outlined as shown below. Selective Hagihara coupling reaction between 1-bromo-4-iodobenzene and triisopropylsilylacetylene gave compound 16, which was followed by palladium-catalyzed Buchwald coupling reaction with di(4-octylphenyl)amine (commercially available) to provide compound 17. Compound 14 was then facilely obtained by removing the triisopropylsilyl group with tetrabutylammonium fluoride (TBAF) in THF.

**Synthesis of compound 16:**
8g 1-bromo-4-iodobenzene (28.28mmol), 991 mg Pd(PPh₃)₂Cl₂, 483.6 mg CuI and 185 mg PPh₃ were dissolved in 180 ml triethylamine and 60 ml toluene. The mixture was degassed by bubbling argon for 15 min and then 6.2 g triisopropylsilylacetylene was added. After stirring overnight at room temperature, the mixture was poured into water and extracted by dichloromethane. The organic layer was washed by water three times and dried over MgSO₄. The solvent was removed under vacuum and the residue was purified by column chromatography (Haxane, silica gel) to provide 7.8 g colorless oil (81.7%). ^1H NMR (CD₂Cl₂,250 MHz): d ppm 7.369 (d, J=8.5 Hz, 2H), 7.274 (J=8.2 Hz, 2H), 1.110 (overlapped, 21 H); FD-MS (8 kV): m/z=337.6.

**Synthesis of compound 17:**
2.38 g compound 16, 2.5 g di(4-octylphenyl)amine, 58.6 mg Pd₂(dba)₃, 20.7 mg tri-tert-butylphosphorous, 921.6 mg sodium tert-butoxide and 12 ml water-free toluene were mixed together in a 25 ml Schlenk tube in a glove box. The mixture was stirred at room temperature
for 3.5 hours and quenched by adding saturated ammonium chloride solution. After extraction with diethyl ether, washing and column chromatography (PE, Al₂O₃) work-up, 2.3g 17 was obtained (50.2%). FD-MS (8kV): m/z=650.3, ¹H NMR (CD₂Cl₂, 250 MHz): δ ppm 7.281 (d, J=8.5 Hz, 4H), 7.268 (d, J=8.8 Hz, 2H), 6.981 (d, J=8.8 Hz, 4H), 6.877 (d, J=8.8 Hz, 2H), 1.720 (m, 4H), 1.357 (m, 12H), 1.115 (m, 21H), 0.748 (m, 18H).

Synthesis of compound 14:
A solution of 1.2 g compound 17 in 10 ml THF was degassed by bubbling argon and then 873 mg tetrabutylammonium fluorid trihydrate was added. The mixture was stirred at room temperature for 30 min and was quenched by adding saturated ammonium chloride solution. The mixture was extracted by diethyl ether. The organic layer was washed by water three times and dried over MgSO₄. Removing the solvent provided compound 786 mg compound 14 (86%). No further purification is needed considering the quantitative conversion and also to avoid possible oxidation of the monosubstituted acetylene. FD-MS (8kV): m/z= 493.9; ¹H NMR (CD₂Cl₂, 250 MHz): δ ppm 7.279 (d, J=8.5 Hz, 4H), 7.260 (d, J=8.8 Hz, 2H), 6.981 (d, J=8.8 Hz, 4H), 6.867 (d, J=8.8 Hz, 2H), 3.033 (s, 1H), 1.713 (m, 4H), 1.347 (m, 12H), 0.738 (m, 18H).

5. Synthesis of compound 15---A representative Hagihara-Sonogashira coupling reaction between monoethynlenes and building block 2.
To a frame-dried 25 ml Schlenk flask was added 173.4 mg compound 2 (0.173 mmol), 17.5 mg Pd(PPh₃)₄ (2.5 mol % per I), 5.7 mg of copper iodide (5.0 mol % per I), and 10 ml piperidine. The mixture was degassed by bubbling argon for 15 min, then 592 mg 14 (2.076 mmol) was added. The solution was heated to 52°C overnight, cooled to RT, and 20 ml methanol was added. The yellow precipitate was collected, followed by column chromatography (Al₂O₃, PE/DCM=7/3) to give 253 mg pure compound 15 (64.4%). ¹H NMR (500 MHz, C₂D₂Cl₂, 413 K): δ ppm 8.831 (s, 12H), 7.828 (m, 24H), 7.484 (m, 12H), 7.267 (d, J=6.4 Hz, 24H), 7.021(d, J=6.4 Hz, 24H), 6.976(m, 12H). MALDI-MS (TCNQ as matrix): m/z=3929.80.

6. Synthesis of compound 12a ---A general procedure for six-fold Diels-Alder cycloaddition. 57 mg compound 11a and 493 mg tetraphenylcyclopentadienone were dissolved in 2 ml
diphenyl ether. The mixture was heated to 250°C for 18 h under argon and cooled down to room temperature. Then 20 ml methanol was added and the precipitate was collected and purified by column chromatography (PE/DCM=3:2, silica gel) to provide 101 mg pure product (88.6%) as yellow powder. MALDI-MS (TCNQ as matrix): m/z= 4272.22. $^1$H NMR spectrum in C$_6$Cl$_2$D$_4$ at 443K (at this temperature, only monomer exist) is shown as above.