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Synthesis of an extended hexagonal molecule as a highly symmetrical ligand

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Abstract—An extended hexagonal molecule that has high symmetry and rigidity was designed and synthesized by a cobalt-catalyzed cyclotrimerization reaction. The ligand possesses six benzoic acids at its periphery, which were connected to a central hexakis(2,5-dodesyloxyphenyl)hexaphenylbenzene core with a maximum intramolecular carboxyl group distance of approximately 3.5 nm.
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One of the growth areas of supramolecular chemistry is the construction of organic and inorganic networks. They have attracted wide interest because they provide an efficient novel route towards the synthesis of well-defined porous materials that have applications in molecular recognition, catalysis, gas storage and separation.[1] A common motif is the use of benzene and its derivatives as rigid frameworks.[2] Among these, highly symmetrical molecules with multiple interaction sites can serve to prevent the formation of interpenetrated networks to yield hexagonal networks.[2c,d] In this letter we describe the synthesis of an extended hexagonal ligand molecule **1b** by a cobalt-catalyzed cyclotrimerization reaction of ethynyl-bridged di(triphenylene)s. Ligand **1** possesses six benzoic acids at its periphery, which can serve to direct the formation of well-defined porous materials, and a diameter of 3.5 nm making it one of the largest hexagonal ligands. In addition, preliminary studies of the solution behaviour of the complex between Sn(IV) porphyrin and **1b** are reported.

As a starting point for this study, we designed an extended hexagonal ligand molecule **1** constructed from 19 benzene rings. The 6 carboxyl groups of **1** were arranged around the periphery to direct the formation of hexagonal interaction networks and 24 hexyloxy or 12 dodesyloxy groups were introduced in the middle of the triphenylene moiety to increase its solubility in common organic solvents. According to the molecular modelling calculations (MOPAC), the carboxyl groups of **1** all lie in a plane with a maximum and minimum intramolecular carboxyl group distance of approximately 3.5 and 1.6 nm, respectively (Scheme 1).

The synthesis of **1** is illustrated in Scheme 2. The route relies on the stepwise Suzuki coupling protocols[3] and transition metal catalyzed trimerization reaction[4] of ethynyl-bridged di(triphenylene) **8**.[5] First, 4,4′-diboronatetolane (**4**) was prepared by a one-step Miyaura arylboronate synthesis catalyzed by $PdCl_2$(dppf).[6] Coupling of **5** with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid methyl ester(**6**)[6] followed by coupling of the product **4** with **7** were conducted under standard Suzuki coupling conditions. Our first trial to synthesize **8a** from **7a** started with the reaction of 1,4-dibromo-2,3,5,6-tetrakis-hexyloxy-benzene (**5a**)[7a] and **6**. In the presence of an excess amount of **5a**, **7a** was obtained in 72% yield from **5a** and **6** (conditions: $Pd(PPh_3)_4$, Cs_2CO_3, DMF, 95 °C, 11 h). However, the reaction of **4** and **7a** gave **8a** in low yield (at most 20%) along with the recovery of **7a** (52%), debrominated derivative of **7a**, and a other complicated mixture of side products (conditions: $Pd(PPh_3)_4$, Cs_2CO_3, DMF, 100 °C, 24 h). In addition, in our hands, pure **8a** could not be obtained by standard purification methods such as recrystallization, silica gel column and size exclusion chromatography. Based on the hypothesis that the steric congestion around the bromo group was the main cause for the low yield using **7a**, we changed the reactant to **7b**, which

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Keywords: Cyclotrimerization; Supramolecular chemistry; Hexagonal ligand; Tin porphyrin.

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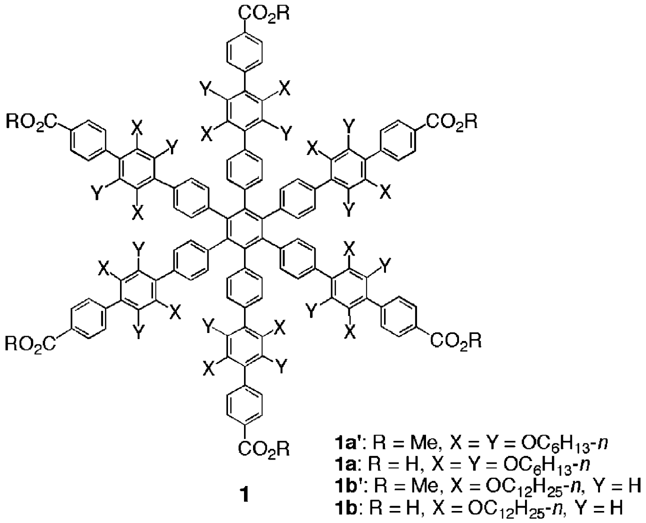
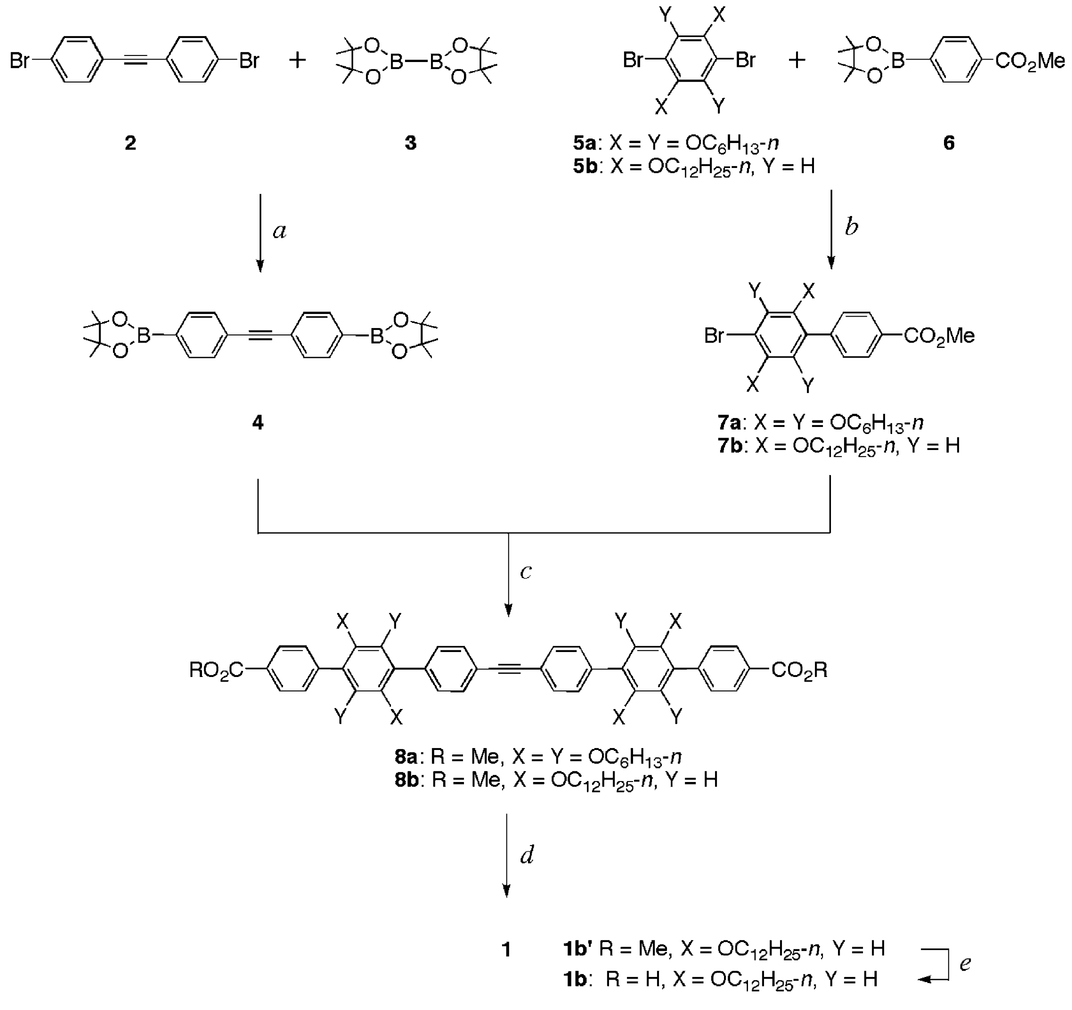


Scheme 1. Extended hexagonal molecule **1**.

was obtained from 1,4-bibromo-2,5-didodesyloxybenzene (**5b**)[7b] and **6**.[8] Under the same conditions, **7b** afforded **8b** in 67% yield as a pure form (MALDI-TOF MS (no matrix), *m*/*z* = 1337.2; calcd for $C_{90}H_{127}O_8$ = 1337.0 (MH^++1)).

In the key step, a $Co_2(CO)_8$-catalyzed cyclotrimerization reaction of **8b** gave **1b**′ in 68% yield (conditions: 10 mol % $Co_2(CO)_8$, toluene, 110 °C, 24 h). Hydrolysis of **1b**′ with KOH aq in THF afforded the target ligand **1b** in 75% yield. The molecular weight of **1b** was determined by MALDI-TOF MS (2,5-dihydroxybenzoic acid matrix) to be *m*/*z* = 3924.8 (calcd for $C_{264}H_{367}O_{24}$ = 3924.9 (MH^++3)) and its ^{1}H NMR spectrum in pyridine-d_5 was quite simple, demonstrating the hexagonal symmetry of the molecule; four doublets due to the outer and inner 1,4-phenylene aromatic protons at 8.57, 7.98, 7.76 and 7.64 ppm and two singlets due to the middle 1,4-phenylene spacer at 7.26 and 7.13 ppm.[5,9] These signals in the aromatic region of **1b**′ instead of **1b** were fully assigned by using the NOESY NMR technique because the aromatic region of **1b** was partially obscured from residual pyridine peaks.[5] Ring current effects were also apparent by comparison with ethynyl-bridged di(triphenylene) **8b**; the inner phenylene two protons of **8b** were shifted upfield by 0.41 and 0.59 ppm. As reference molecules, triphenylene

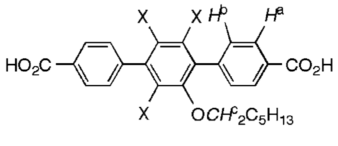


Scheme 2. Reagents: (a) $PdCl_2$(dppf), AcOK, DMF; (b) $Pd(PPh_3)_4$, Cs_2CO_3, DMF; (c) $Pd(PPh_3)_4$, Cs_2CO_3, DMF; (d) $Co_2(CO)_8$, toluene; (e) KOH aq, THF.

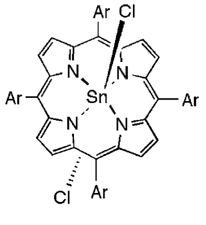
linear molecule **9** was prepared by Suzuki coupling reaction of **6** with **5a** followed by hydrolysis.[5]

We have examined the complexation behaviour between dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butyl phenyl)porphyrinato]tin(IV) (**10**) and **1b** or **9** utilizing the *trans*-bidentate coordination behaviour of the central metal of the Sn(IV) porphyrin.[10] The mixture of **9** and **10** could form linear bead-like porphyrin arrays, whereas the mixture of **1b** and **10** could be expected to lead to honeycomb-shaped arrays. The formation of a 1:1 complex between **9** and **10**, was observed by NMR from the carboxylate-ligand protons, H^a and H^b, and methylene protons, H^c, of **9** that were shifted far upfield by 2.55, 1.80 and 0.80 ppm, respectively, reflecting the porphyrin ring current, and the molar ratio of complexed **9** to **10** was determined to be approximately 1.0, as judged from the integration of the ^{1}H NMR spectrum in $CDCl_3$. These complexes were also detected using MALDI-TOF MS spectrometer (9-nitroanthracene matrix); **9·10**, **10·9·10**, **10·9·10·9**, **10·9·10·9·10**, **10·9·109·10·9** and **10·9·10·9·10·9·10**. These results suggest that efficient coordination of carboxyl group to the Sn(IV) porphyrin occurred and the desired bead-like structure was obtained. Unfortunately in the case of the complex between **1b** and **10**, however, the ^{1}H NMR spectra were very broad and no assignable peaks could be detected over a wide temperature range (−50 to 40 °C). Only small assemblies could be detected by MALDI-TOF MS spectrometer (3-hydroxypiconilic acid matrix); **1b·9**, **1b·9·9**, **1b·9·9·9**, **1b·9·9·9·9** and **1b·9·9·9·9·9**.[11] We are continuing the characterization of this complex by other methods and will report these results in the future (Scheme 3).

In summary, extended ligand molecule **1b** with hexagonal symmetry was synthesized by cobalt-catalyzed cyclotrimerization reaction and the structure was characterized by ^{1}H NMR and MALDI-TOF MS analyses. Initial studies on the Sn–porphyrin complexes may suggest the novel method to construct porphyrin arrays. Further details of characterization of the complexes as well as self-assembly of **1** will be reported elsewhere together with results on other systems.



9: X = OC_6H_{13}-*n*



10: Ar = 3,5-di-*tert*-butyl Ph

Scheme 3. Reference molecule **9** and Sn(IV) porphyrin **10**.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.01.014.

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8. Trial to synthesize arylboronate **7a** (structure was not shown), which was aimed to conduct Suzuki coupling between **2** and arylboronate **7a**, and similar reaction has done to obtain **4**, has been found to result in a debromination of **7a** quantitatively.
9. Selected spectroscopic data for **1b′**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.03 (d, $J = 8.3$ Hz, 12H), 7.59 (d, $J = 8.3$ Hz, 12H), 7.20 (d, $J = 8.2$ Hz, 12H), 7.02 (d, $J = 8.2$ Hz, 12H), 6.87 (s, 6H), 6.81 (s, 6H), 3.92 (s, 18H), 3.79 (t, $J = 6.2$ Hz, 12H), 3.61 (t, $J = 6.2$ Hz, 12H), 1.48–1.09 (m, 240H), 0.92–0.84 (m, 18H); MALDI-TOF MS (no matrix) *m/z* calcd for MH^++3 (^{13}C), $C_{270}H_{378}O_{24}$: 4008.9; found 4009.0. For **1b**: ^{1}H NMR (pyridine-d_5, 300 MHz) δ 8.57 (d, $J = 8.0$ Hz, 12H), 7.98 (d, $J = 8.0$ Hz, 12H), 7.76 (d, $J = 7.9$ Hz, 12H), 7.64 (d, $J = 7.9$ Hz, 12H), 7.26 (s, 6H), 7.13 (s, 6H), 3.91 (t, $J = 6.3$ Hz, 12H), 3.84 (t, $J = 6.3$ Hz, 12H), 1.78–1.63

(m, 24H), 1.52–1.18 (m, 216H), 0.98–0.90 (m, 18H), 0.90–0.82 (m, 18H); MALDI-TOF MS (2,5-dihydroxybenzoic acid matrix) *m/z* calcd for MH^++3 (^{13}C), $C_{264}H_{367}O_{24}$: 3924.8; found 3924.9.

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11. The molar ratio of **9/1b** was estimated from UV–vis spectrum in THF, to be approximately 1.2, as judged from the average of molar absorbance coefficients of **1b** and **9** at 285 and 335 nm.