RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2018, **8**, 20872

1,3-Phenylene-bridged naphthalene wheels synthesized by one-pot Suzuki–Miyaura coupling and the complex of the hexamer with C_{60}†

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Received 26th April 2018
Accepted 1st June 2018

DOI: 10.1039/c8ra03601b

rsc.li/rsc-advances

A large 1,3-phenylene-bridged hexameric naphthalene wheel **N6** and a heptameric wheel **N7** were synthesized simply by Suzuki–Miyaura coupling *via* one-pot reaction from monomers. We could control the distribution of **N6** and **N7** *via* the reaction conditions. The hexameric wheel structure was revealed by X-ray diffraction analysis. The wheel **N6** exhibited C_{60} encapsulation ability in the solid state, which was also confirmed by single crystal X-ray analysis.

Introduction

Bottom-up "designed organic synthesis" of benzene-based nano-carbon materials has been extensively attempted, since such synthesis will allow for tailored fine-tuning of their structures, properties, and functions.[1] These attempts are also important for cyclic aromatic molecules.[2–4] Such cyclic systems are expected to act as a host molecule and to display multiple electronic interactions with guest molecules that are not shared with normal linear compounds. Pd-catalyzed cross coupling reactions have been demonstrated to be quite powerful in the synthesis of a variety of oligomers of polycyclic aromatic hydrocarbons (PAHs). Despite this progress, 1,3-phenylene bridged cyclic PAH hexamers that can be regarded as benchmark wheels in terms of their simple hexagonal structure have been rarely synthesized.[5–8] Cyclic heptamers and higher analogues are scarcer. Schlüter *et al.* made a cyclotetraicosaphenylene by using a repetitive Suzuki–Miyaura cross coupling protocol.[5] The first [6]cyclo-*m*-phenylene was prepared by Staab *et al.*[6] and recently a series of [*n*]cyclo-*m*-phenylenes were synthesized by a one-pot Ni-mediated Yamamoto coupling.[7] The cyclic porphyrin hexamer is interesting not only as an artificial light-harvesting photosynthetic antenna but also as a shape-persistent organic molecule.[8] The conformationally rather restricted cyclic structure is amenable for studies on the structure–optical property relationship but likely poses a synthetic challenge. In this paper, we report the quick synthesis of the first 1,3-phenylene bridged hexameric and heptameric naphthalene wheels *via* one-step cross-coupling at multiple sites starting from simple monomers, and the complexization of hexamer **N6** with C_{60}. Encapsulation of C_{60} in the wheel **N6** was examined and the structure was confirmed by single-crystal X-ray analysis.

Results and discussion

For construction of cyclic frameworks, our synthetic strategy lies in using Suzuki–Miyaura cross-coupling reaction. Namely, 1,3-diborylbenzene and 1,4-dibromonaphthalene in DMF/toluene were treated with 10 mol% of Pd catalyst at 80 °C under an inert atmosphere, giving a 1,3-phenylene-bridged cyclic naphthalene hexamer **N6** in 6% yield without any detection of **N7** after repeated separations over a preparative GPC column and a silica gel column (Scheme 1).

High-resolution matrix assisted laser desorption/ionization time-of-flight (HR-MALDI-TOF) mass spectrum of **N6** displays the parent ion peaks at *m*/*z* 1212.4686 (calcd for $C_{96}H_{60}$ = 1212.4690 $[M]^+$). Although the ^1H NMR spectrum of **N6** in $CDCl_3$ at room temperature was very broad, that in $C_2D_2Cl_4$ at 60 °C became sharper and simple, exhibiting only a single set of signals that consists of two singlet peaks at 7.67 and 7.56 ppm due to the H^c and H^d, respectively, and signals due to H^a and H^b in the range of 7.66 ppm and H^e and H^f at 8.10 and 7.47 ppm, respectively. These data indicate that the wheel **N6** takes a C_6 symmetric structure in solution at 60 °C.

Definitive structural assignment of **N6** was accomplished through a single crystal X-ray diffraction analysis, which

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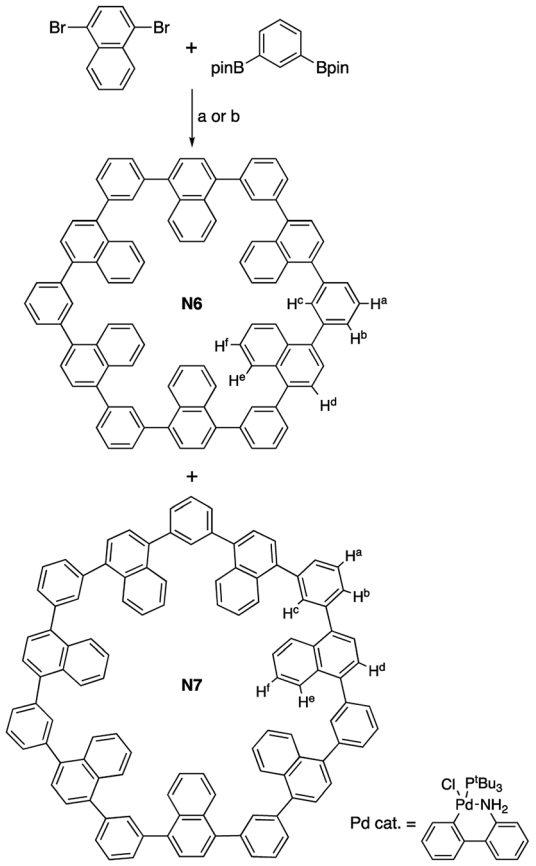
† Electronic supplementary information (ESI) available: X-ray crystal analysis and NMR and mass spectra. CCDC 1838834 (**N6**) and 1838835 (C_{60}@**N6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ra03601b



Scheme 1 Synthesis of naphthalene wheels **N6** and **N7**. Reaction conditions: (a) Pd cat., Cs_2CO_3, toluene/DMF, 80 °C, 6% (**N6**) and 0% (**N7**). (b) Pd cat., CsF, 18-crown-6, THF/H_2O, r.t. 4% (**N6**) and 13% (**N7**).

unveiled a distinct hexagonal conformation (Fig. 1a).‡ The phenylene-bridges are on the co-plane, suggesting less structural strain. The dihedral angles between the naphthalene mean-planes and phenylene groups are in the range of 58–64°. Interestingly, the hexagons are interconnected through phenylene C–H and naphthalene π-plane interactions in the crystal, forming an infinite one-dimensional tubular packing structure along the *c*-axis (Fig. 1b).

Fig. 2 shows the UV-vis absorption and fluorescence spectra of **N6** in CH_2Cl_2. Cyclic hexamer **N6** shows a single absorption band at 306 nm and a blue emission at 383 nm. This broad single band can be qualitatively understood in terms of the weak π-conjugation and the exciton coupling,[9] as similarly to previously reported 1,3-phenylene naphthalene dimer.[10] Given the rigid hexagonal conformation for the wheel, J-type exciton coupling of transition dipoles is effective. The interacting components lead to red-shifted absorption band compared with naphthalene monomer (275 nm in CH_2Cl_2). The steady-state fluorescence spectrum in toluene is also displayed in Fig. 2.

To further understand the electronic features of **N6**, the density functional theory (DFT) and the time-dependent (TD)-DFT calculations both at the B3LYP/6-31G(d) level using the Gaussian 09 software package were carried out (Fig. 3).[11] It is revealed that the frontier orbitals are degenerated. The coefficients of HOMO and LUMO of **N6** localize on the six naphthalene units. The main absorption band of **N6** at 306 nm predominantly comprises the S_2 and S_3 transitions (oscillator strength, $f = 1.03$ and $f = 1.02$), whereas the long wavelength S_1 absorption is forbidden ($f = 0.00$). The transition energies and oscillator strengths simulated by TD-DFT calculations showed a good agreement with the observed absorption spectrum of **N6**.

In the next step, the encapsulation of C_{60} into **N6** was examined, since the diameter of the interior cavity of **N6** is *ca.* 15 Å, being possibly fit to the diameter of C_{60}.[12] Unfortunately, however, the addition of C_{60} into a toluene solution of **N6** did not change the absorption spectrum probably because of weak interactions between two components. The encapsulation was also not confirmed by NMR spectroscopy. Thus we attempted to make co-crystals of **N6** with C_{60}. The host–guest binding structure was unambiguously confirmed by the single-crystal X-ray diffraction analysis (Fig. 4).‡ Higher concentration on the crystallization process could give the encapsulation complex. In the solid-state, the naphthalene units of C_{60}@**N6** take a similar structure to those of **N6** with respects to dihedral angles of phenylene toward naphthalene (51–72°), and an inside space (15 Å diameter). The positions of C_{60} are disordered at two parts (66:34). As shown in Fig. 4, a C_{60} molecule is nicely captured within the cavity. Closer inspection of the crystal structure reveals that the naphthalene planes are protruding their planar face toward the interior space, which interacts with C_{60}. Interestingly, the C_{60} molecules in the crystal are aligned with the aid of **N6** agent to form a 1D structure along the *a*-axis (Fig. 4b).

During this research, Yokozawa and co-workers reported an efficient cyclization reaction of *o*- and *m*-alternate polyphenylenes.[13] In order to check the effect of the reaction conditions, we applied Yokozawa's conditions on our cyclic naphthalene synthesis. Interestingly, the distribution of the wheel size was shifted to the larger size, and we successfully isolated **N6** and **N7** in 4% and 13% yields, respectively (Scheme 1). HR-MALDI-TOF mass spectrum of **N7** displayed the parent ion peaks at m/z 1414.5469 (calcd for $C_{112}H_{70} = 1414.5472$ $[M]^+$). To observe a relatively clear ^1H NMR spectrum in $C_2D_2Cl_4$, it was needed to measure the spectrum at higher temperature than that for **N6**. The ^1H NMR spectrum of **N7** in $C_2D_2Cl_4$ at 120 °C was simple, exhibiting only a single set of signals that consists of two singlet peaks at 7.66 and 7.59 ppm due to the H^d and H^c, respectively, at 7.75 ppm due to H^a and signals due to H^b in the range of 7.61–7.66 ppm and H^e and H^f at 8.13 and 7.40 ppm, respectively.

UV-vis absorption and fluorescence spectra of **N7** in CH_2Cl_2 are also shown in Fig. 2. Cyclic heptamer **N7** exhibits a slightly

‡ Crystallographic data for **N6**: $C_{96}H_{60}\cdot O$, $M_w = 1229.44$, monoclinic, space group $P2_1/c$ (#14), $a = 11.962(6)$, $b = 32.625(16)$, $c = 15.124(8)$ Å, $\beta = 93.619(8)°$, $V = 5890(5)$ Å^3, $T = 90(2)$ K, $Z = 2$, reflections measured 29 202, 9464 unique. The final R_1 was 0.1193 ($>2\sigma(I)$), and the final wR on F^2 was 0.3390 (all data), GOF = 1.109. Crystallographic data for C_{60}@**N6**: $C_{96}H_{60}\cdot C_{60}\cdot 4(C_6H_5Cl)$, $M_w = 2384.24$, triclinic, space group $P\bar{1}$ (#2), $a = 11.110(5)$, $b = 14.775(6)$, $c = 17.361(7)$ Å, $\alpha = 94.214(7)°$, $\beta = 94.286(7)°$, $\gamma = 101.721(7)°$, $V = 2771(2)$ Å^3, $T = 90(2)$ K, $Z = 1$, reflections measured 15 703, 10 790 unique. The final R_1 was 0.0691 ($>2\sigma(I)$), and the final wR on F^2 was 0.2025 (all data), GOF = 1.036. The contributions to the scattering arising from the presence of disordered solvents in the crystals of **N6** were removed by use of the utility SQUEEZE in the PLATON software package.[16]

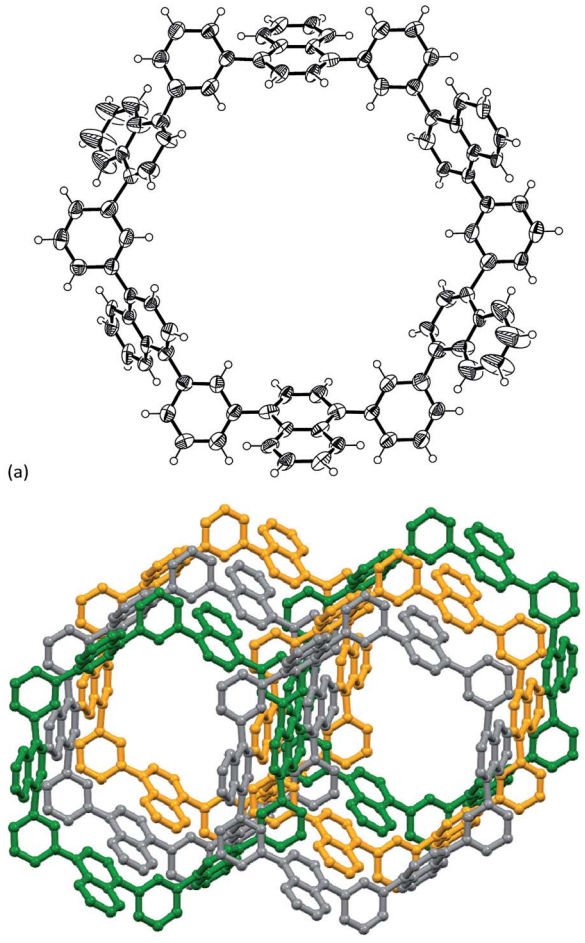


Fig. 1 (a) Single crystal X-ray structure of **N6** and (b) packing structure of **N6**. Thermal ellipsoids are scaled at 50% probability. Solvent molecules are omitted for clarity.

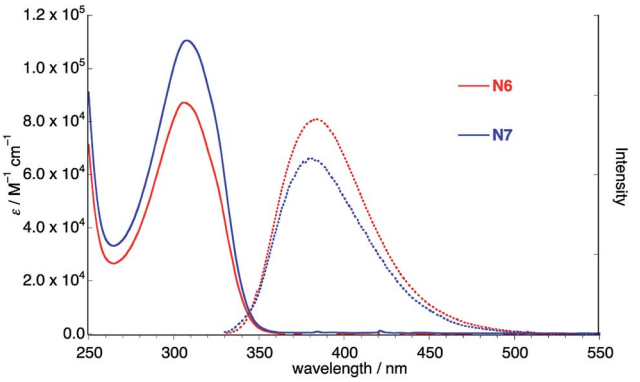


Fig. 2 UV-vis absorption (solid line) and fluorescence (dotted line) spectra of **N6** and **N7** in CH_2Cl_2. Fluorescence spectra were taken for excitation (λ_{ex} = 306 nm for **N6** and 308 nm for **N7**) with the absorbance adjusted to 0.1.

red-shifted absorption band at 308 nm and a blue-shifted emission at 382 nm. These are presumably because the conformational deformation from **N6** to **N7** makes the forbidden S_1 transition to be just a little allowed.

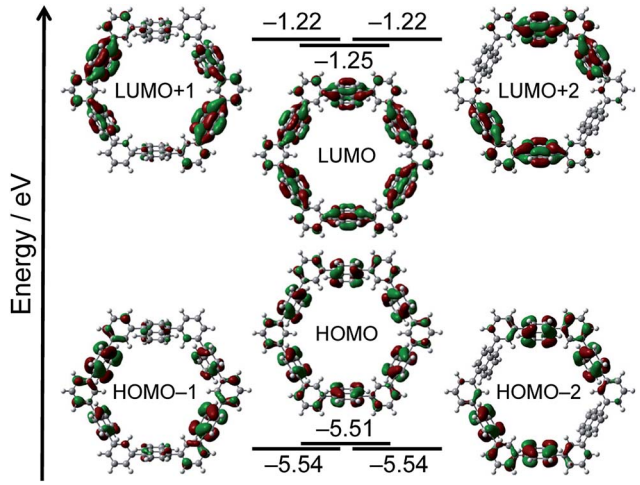


Fig. 3 MO diagrams of **N6** calculated at the B3LYP/6-31G(d) level.

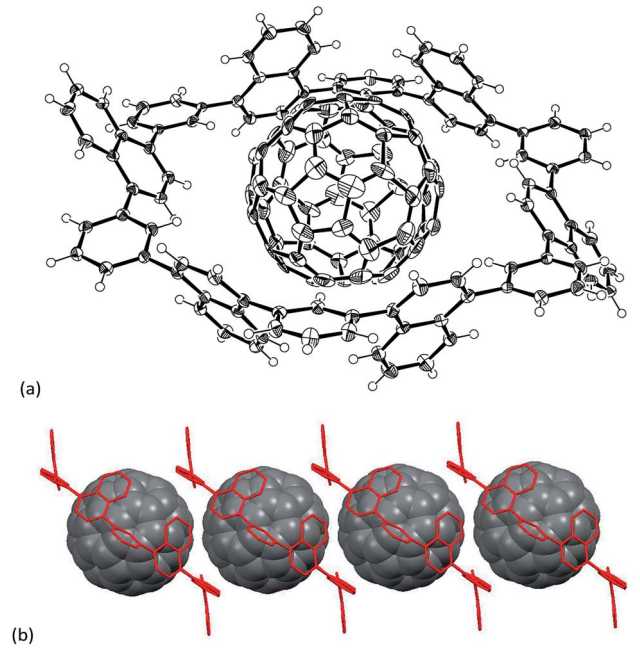


Fig. 4 (a) Single crystal X-ray structure of C_{60}@**N6** and (b) packing structure of C_{60}@**N6**. Thermal ellipsoids are scaled at 50% probability. Solvent molecules are omitted for clarity.

Conclusions

In summary, 1,3-phenylene-linked cyclic naphthalene hexamer and heptamer were simply constructed by Suzuki–Miyaura cross-coupling reaction *via* a one-pot route and the hexagonal structure of **N6** was confirmed by X-ray structural analysis. The hexameric wheel **N6** formed co-crystal with C_{60} and acted as an alignment agent in the solid state. The host–guest chemistry of **N7** with higher fullerenes, template synthesis of **N6** and **N7** and the measurement of their conductivities are currently being explored in our laboratory.

Experimental

Materials and methods

^{1}H NMR (400 MHz and 600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded with a JEOL JNM-ECX 400, a JEOL JNM-ECP 400 and a JEOL JNM-ECA 600 spectrometers by using tetramethylsilane as an internal standard. The HR-MALDI-TOF mass spectra were measured by a Bruker Autoflex II spectrometer using positive ion mode.

UV/Vis absorption spectra were measured with a JASCO UV/Vis/NIR spectrophotometer V-570.

TLC and gravity column chromatography were performed on Art. 5554 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. All other solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification. For spectral measurements, spectral-grade solvents were purchased from Nacalai Tesque.

All DFT calculations were performed with a Gaussian 09 program package. The geometries were fully optimized at the Becke's three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional abbreviated as the B3LYP level of density functional theory. The 6-31G(d) bases set implemented was used for structure optimizations and frequency analyses.

Synthetic procedures

1,3-Phenylene-bridged cyclic naphthalene hexamer N6. 1,3-Benzenediboronic acid bis(pinacol)ester (115 mg, 0.350 mmol), 1,4-dibromonaphthalene (100 mg, 0.350 mmol), Cs_2CO_3 (325 mg, 1.40 mmol), toluene (5 mL) and DMF (2 mL) were added into a 25 mL 2-neck flask. After degassing, chloro[(tri-*tert*-butylphosphine)-2-(2-aminobiphenyl)]palladium(II) (36 mg, 0.070 mmol) was quickly added under flowing argon. After degassing again, the solution was stirred at 80 °C for 24 h. The mixture was extracted with dichloromethane and washed with water and brine. Then it was purified by chromatography on silica gel (hexane : CH_2Cl_2 = 3 : 1). After being purified by a preparative GPC, 4.0 mg of **N6** was gained in 6% yield as a white solid. ^{1}H NMR ($C_2D_2Cl_4$, 600 MHz, ppm, 60 °C) δ 7.47 (q, J = 9.6 Hz, 12H), 7.56 (s, 12H), 7.66–7.67 (m, 24H) and 8.10 (q, J = 9.6 Hz, 12H). ^{13}C NMR ($C_2D_2Cl_4$, 151 MHz, ppm, 60 °C) δ 126.14, 126.60, 126.71, 128.31, 129.09, 132.05, 132.22, 139.83 and 141.01. UV-vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 306(8.7×10^4) nm. Fluorescence (CH_2Cl_2, λ_{ex} = 306 nm): λ_{max} = 383 nm.

1,3-Phenylene-bridged naphthalene heptamer N7. 1,3-Benzenediboronic acid bis(pinacol)ester (90 mg, 0.269 mmol), 1,4-dibromonaphthalene (100 mg, 0.350 mmol), CsF (184 mg, 1.21 mmol), 18-crown-6 (310 mg, 2.42 mmol), THF (10 mL) and deionized water (0.3 mL) was added to a 30 mL Schlenk flask. After degassing, chloro[(tri-*tert*-butylphosphine)-2-(2-aminobiphenyl)]palladium(II) (14 mg, 0.027 mmol) was quickly added. After degassing again, the solution was stirred at r.t. for 24 h. The mixture was extracted with dichloromethane and washed with water and brine. Then it was purified by chromatography on silica gel (hexane : CH_2Cl_2 = 3 : 1). After being purified by GPC, 7.0 mg of **N7** was gained in 13% yield and 2.0 mg of **N6** in 4% yield. ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz, ppm, 120 °C) δ 7.49 (m, 14H), 7.59 (s, 7H), 7.61 (d, 7H), 7.66 (d, 21H), 7.75 (d, 7H) and 8.13 (m, 14H). ^{13}C NMR ($C_2D_2Cl_4$, 151 MHz, ppm, 120 °C) δ 120.46, 125.92, 125.93, 126.50, 126.66, 128.24, 129.28, 131.60, 132.30, 139.85 and 141.08. UV-vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 308(1.1×10^5) nm. Fluorescence (CH_2Cl_2, λ_{ex} = 308 nm): λ_{max} = 382 nm.

Crystallography

X-ray crystallographic data were recorded at 90 K on a Bruker APEX II X-ray diffractometer equipped with a large area CCD detector by using graphite monochromated Mo-Kα radiation.

The structure was solved by using direct methods (SHELXT program).[14] Structure refinements were carried out by using SHELXL-2014/7 program.[15]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partly supported by CREST JST (No. JPMJCR15F1) and by JSPS KAKENHI Grant Numbers JP16H02286 and JP26105004 to H.·Y., JP16K17949 to M. S. and JP17H03042 to N. A. A. M. appreciates JSPS for Research Fellowships for Young Scientists. We also thank Ms Y. Nishikawa and Mr F. Asanoma, NAIST for the mass and NMR spectroscopy measurements, respectively.

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