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Synthesis of pentadecaphenylenes, their inclusion properties, and nanostructure formation with C_{60}†

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Synthesis of macrocyclic pentadecaphenylene was carried out *via* electron-transfer oxidation of the corresponding Lipshutz cuprate. Pentadecaphenylene self-aggregated in solution to form a gel. Furthermore, it incorporated C_{60} in its cavity to produce a fibrous inclusion complex which showed a high gelation ability in benzene.

The study of fully conjugated cyclic oligophenylenes with well-defined molecular diameters has become important for gaining specific information concerning structural, electronic, and optical properties especially in relation to the "inner" and "outer" domains.[1] These macrocycles with both long alkyl sidechains and shape-persistent, non-collapsible, and fully π-conjugated backbones are useful for building columnar 1D nanotubes, 2D porous surface networks, and 3D inclusion complexes *via* self-assembly.[2] Furthermore, cyclic oligoarylenes with well-defined size and inner cavities are of interest because of their ability to act as a host in host–guest chemistry and potential use in optoelectronic devices.[1f,3] Recently, Yamago and co-workers have reported that cyclo[10]paraphenylene encapsulates C_{60}.[4] In the course of our research, we have reported the synthesis of nonaphenylenes and dodecaphenylenes *via* electron-transfer oxidation of Lipshutz cuprate intermediates and the formation of nanostructures from hexadodecyloxynonaphenylene.[5,6] Herein, we report the synthesis of much larger triangular pentadecaphenylenes **1a** and **1b** (Fig. 1) and the self-aggregation and formation of a nanostructure of **1a** as well as the complexation of **1a** with C_{60}.

Pentadecaphenylenes **1a** and **1b** were synthesized by modifying our procedure for synthesizing cyclic oligophenylenes (Scheme 1).[5a] The reaction of dialkyldiiodobenzenes **2a** and **2b** with a boron reagent **3** under Suzuki coupling conditions proceeded smoothly to produce bis(trimethylsilyl)dialkylquinquephenyls **4a** and **4b** in 74% and 62% yields, respectively. The trimethylsilyl groups of **4a** and **4b** were converted into bromo and iodo groups using NBS and ICl, respectively, to afford dihalodialkylquinquephenyls **5a–c** in 85–96% yields. Although the electron-transfer oxidation of Lipshutz cuprates derived from diiodide **5c** produced **1a** in 20% yield, the yield was increased to 28% by using dibromide **5a** as the starting material. Since 2-iodo-2-methylpropane formed by the reaction of **5c** with *t*-BuLi quenches lithioaromatics in the reaction cage easier than 2-bromo-2-methylpropane does, the electron-transfer oxidation of Lipshutz cuprates prepared from dibromides **5a** and **5b** afforded linear oligophenyls as by-products in lower yields.[7] Electron-transfer oxidation of Lipshutz cuprates prepared from dibromide **5b** produced **1b** in 30% yield.

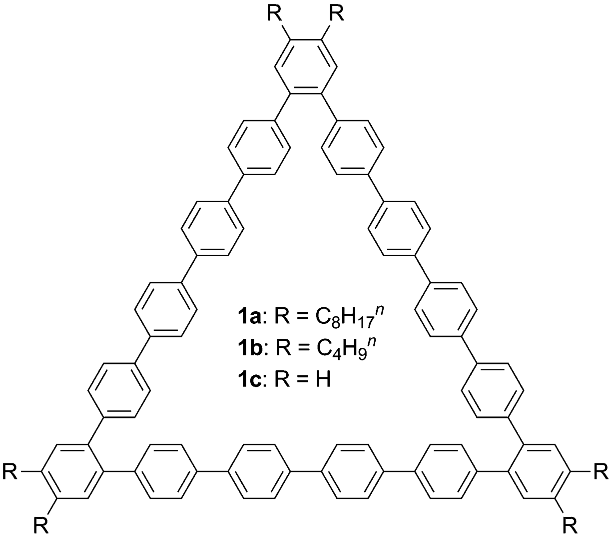

Fig. 1 Hexaoctyl- (**1a**) and hexabutylpentadecaphenylenes (**1b**) and the parent pentadecaphenylene (**1c**).

B3LYP/6-31G(d) calculations on **1c** (R = H) showed that it has a C_3 symmetric triangular structure with the torsional angle involving the *o*-terphenylene and biphenylene units being 36°–52° (ESI†). Although it is a nonplanar aromatic hydrocarbon with nonpolar

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for **1a**,**b**, **4a**,**b**, **5a**,**b**, and 2 : 1 **1a**·C_{60} fibers. Fig. S1–S24. Cartesian coordinates of the optimized structure of **1c**. See DOI: 10.1039/c3cc42922a

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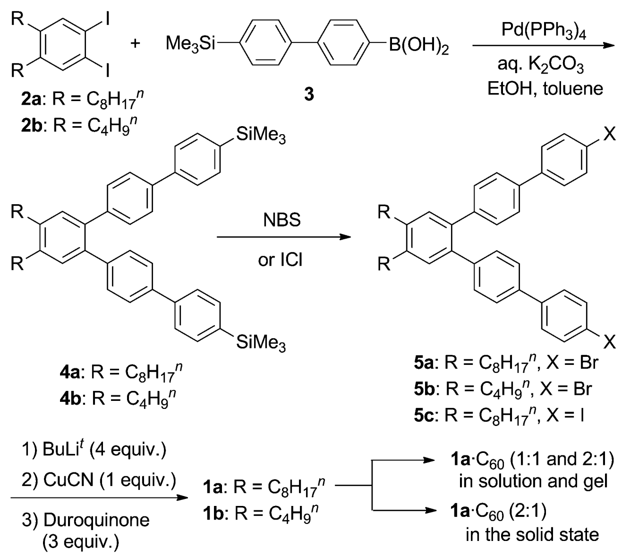

Scheme 1 Synthesis of hexaoctyl- (**1a**) and hexabutylpentadecaphenylenes (**1b**) and the formation of **1a**·C_{60} 1 : 1 and 2 : 1 complexes.

alkyl side chains, **1a** exhibited self-aggregation behavior at low temperatures in hydrocarbon solvents such as cyclohexane, benzene, and toluene. Nanophase separation of the inner cavity, outer domain, and long alkyl side chains causes the self-aggregation behavior of **1a**.

At room temperature **1a** weakly aggregated in toluene and benzene; however, much stronger aggregation was observed at lower temperatures. The aggregation ability was investigated using ^{1}H NMR spectroscopy in toluene-d_8 in the temperature range of -20 to 20 °C and with different concentrations (0.15–2.26×10^{-3} M) of **1a** (ESI†). Assuming a monomer–oligomer equilibrium, the association constant (K_a) at -20 °C was found to be 5.28×10^3 M^{-1}. The self-aggregation of **1a** is enthalpy driven and entropy opposed. The large negative enthalpy (-87.8 kJ mol^{-1}) is attributed to the van der Waals interaction in both the nonplanar pentadecaphenylene moiety and the alkyl side chains. In addition, the change in entropy was negative and very large (-276 J K^{-1} mol^{-1}) which indicates some ordering of the long alkyl side chains due to solvophobic interaction. In contrast to **1a**, **1b** is much less soluble. Therefore, further studies on the self-aggregation and nanostructure formation abilities were performed only on **1a**.

From the self-aggregation behavior of **1a** in benzene and toluene, **1a** was expected to form either one-dimensional (1D) or two-dimensional (2D) nanostructured morphologies, although **1a** neither has a planar framework nor polar side groups. When a hot solution of **1a** in benzene (15 mg ml^{-1}) was allowed to stand at room temperature, a white gel formed (Fig. 2a). As shown in SEM images (Fig. 2b), the gel of **1a** appeared to be a bundle of nanofibers with widths in the range of 200–500 nm and lengths of more than 100 μm. A ^{1}H NMR spectrum of the gel of **1a** formed in benzene-d_6 showed a small up- and downfield shift of aromatic and alkyl protons, respectively, owing to the self-aggregation of **1a**.[8]

The UV-Vis absorptions of a film (λ_{max} = 316 nm), a fiber (321 nm), and a THF solution (1.63×10^{-6} M, 318 nm, and log ε 5.27) of **1a** occurred at similar values of λ_{max} owing to a small intermolecular π–π interaction in the ground state, whereas the emission

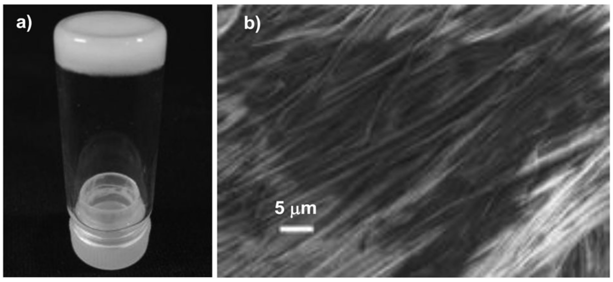

Fig. 2 (a) Photograph of a gel of **1a** and (b) SEM image of fibers of **1a**.

spectra of the film and fiber were different from that of the THF solution due to electronic interaction in the excited state (ESI†). The fluorescence spectra of the film (λ_{em} = 413 nm, Φ_F = 0.71) and fiber (414 nm, Φ_F = 0.62) were red shifted compared to that of the THF solution (388 and 404 nm, Φ_F = 0.99). From excitation spectra, it was observed that the **1a** film (λ_{ex} = 364 nm) and fiber (371 nm) had lower excitation energies than the THF solution (320 nm) (ESI†). Thus, we concluded that excimer emission occurred in the solid state.

Although the fiber and film showed similar absorption and emission behavior, their X-ray diffraction (XRD) patterns were quite different (ESI†). The XRD pattern of the fiber had reflections at 2θ = 2.94°, 4.50°, 6.20°, and 6.62° (d = 30.0, 19.6, 14.2, and 13.3 Å, respectively), with many weak reflections in the 2θ range of 8.0°–15.6°, indicating moderate crystallinity in the solid state. The XRD pattern of the film from benzene indicated an amorphous structure, whereas that of the film from THF exhibited an intense reflection at 2θ = 2.84° (d = 31.1 Å) and broad reflections in the 2θ range of 4.8°–6.0°, indicating the formation of a roughly aligned hexagonal structure.

As expected from B3LYP/6-31G(d) calculations, pentadecaphenylene **1a** formed an inclusion complex with C_{60} in benzene-d_6. The ^{1}H NMR spectrum of a 1 : 1 mixture of **1a** and C_{60} in benzene-d_6 at 25 °C (0.55×10^{-3} M) showed an upfield shift of the aromatic protons by 0.01 ppm in comparison to the chemical shifts of **1a** itself (ESI†). A Job plot prepared from UV-Vis spectra at 410 nm in toluene with a total concentration of 5.0×10^{-4} M indicated that a 1 : 1 complex formed, although the binding constant of **1a** with C_{60} could not be accurately determined from the analysis of the ^{1}H NMR spectra due to the competition between the self-aggregation of **1a** and its complexation with C_{60}.[9]

Moreover, **1a** and C_{60} combined to form a nanostructure, although the binding constant of **1a** with C_{60} is small. When a hot purple solution of a mixture of **1a** (6.9 mg) and C_{60} (1.4 mg, 0.5 molar equiv.) in benzene (1 ml) was allowed to stand at room temperature, a dark brown gel, composed of **1a** and C_{60} in a ratio of 2 : 1, formed (Fig. 3a). Similarly, a mixture of **1a** and C_{60} (1 molar equiv.) in benzene (1 ml) yielded a gel. The UV-Vis spectra of the 2 : 1 and 1 : 1 gels of **1a**·C_{60} in benzene showed an intense broad CT-absorption band at 465 nm as well as very broad tailing up to 800 nm (Fig. 3b).

When hexane was added to the 2 : 1 and 1 : 1 **1a**·C_{60} gels in benzene, a 2 : 1 **1a**·C_{60} fiber was obtained in 86 and 81%, respectively, as a brownish black solid.[10] Optical and SEM images of the xerogel showed a fibrous structure with widths in the range of 100–400 nm and lengths >100 μm (Fig. 4a and b). Much smaller amounts of **1a** and C_{60} compared to that of **1a** by

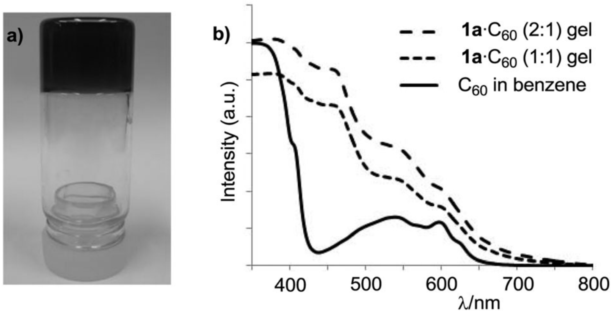

Fig. 3 (a) Photograph of a 2 : 1 **1a**·C_{60} gel. (b) UV-Vis spectra of a 2 : 1 **1a**·C_{60} gel, a 1 : 1 **1a**·C_{60} gel, and C_{60} in benzene.

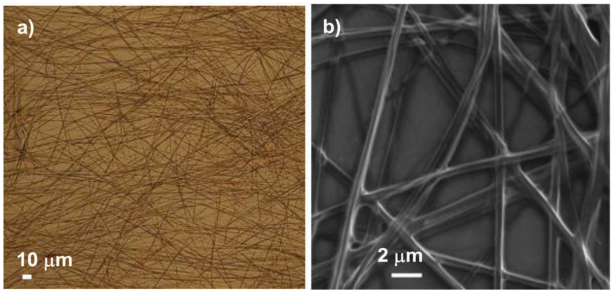

Fig. 4 (a) Optical micrograph and (b) SEM image of a 2 : 1 **1a**·C_{60} fiber.

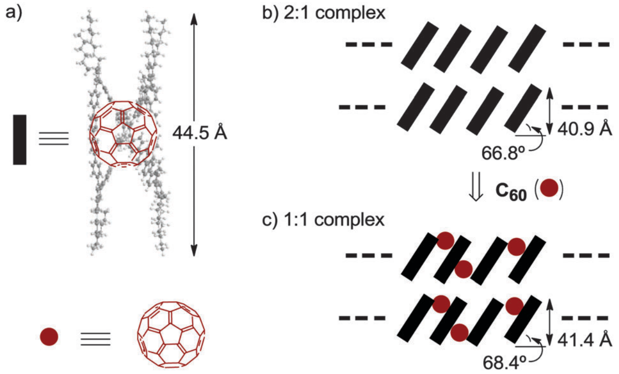

Fig. 5 (a) Structure of the 2 : 1 **1a**·C_{60} complex. (b) Possible lamellar arrangement of the 2 : 1 **1a**·C_{60} complex. (c) Possible lamellar arrangement of the 1 : 1 **1a**·C_{60} complex.

itself formed gels in benzene, also indicating the formation of a more entangled fibrous structure.

XRD profiles of the 2 : 1 **1a**·C_{60} xerogel showed a strong reflection at $2\theta = 2.16^\circ$ ($d = 40.9$ Å) with weak reflections at $2\theta = 4.32^\circ$ ($d = 20.4$ Å) and 6.48° ($d = 13.6$ Å). XRD profiles of the 1 : 1 **1a**·C_{60} xerogel exhibited a similar but more broad reflections (ESI†). Although **1a** fibers had moderate crystallinity, the 2 : 1 **1a**·C_{60} xerogel (fiber) mainly had a lamellar form, and we concluded that a giant **1a**–C_{60}–**1a** sandwich complex, aligned lamellarly and stacked in the direction of the fiber, formed (Fig. 5a and b). In the case of the 1 : 1 complex, the excess C_{60} molecules were intercalated between the **1a**–C_{60}–**1a** sandwich complex to form a gel (Fig. 5c). Interestingly, in the 2 : 1 **1a**·C_{60} fiber prepared from hexane–benzene molecules aligned hexagonally and stacked in the direction of the fiber formed (ESI†).

In summary, we synthesized large triangular pentadecaphenylenes **1a** and **1b** in moderate yields *via* electron-transfer oxidation of Lipshutz cuprate intermediates derived from dihaloquinquephenyl derivatives in a one-pot reaction. In solution **1a** and **1b** exhibited a strong UV-Vis absorption at 318 nm and intense blue emission at ~400 nm with a very high quantum efficiency ($\Phi_F \approx 100\%$). Despite the rigid non-planar framework and non-polar side arms, hexaoctylpentadecaphenylene **1a** showed self-aggregation behavior (nanophase separation) in hydrocarbon solvents such as benzene and toluene, to afford a gel composed of fibers of **1a**. Since there is a large inner cavity in **1a**, it can act as a host molecule in solution to form a 1 : 1 complex with C_{60}. Moreover, from a mixture of **1a** and C_{60} in benzene, a dark brown gel composed of entangled fibers of the 2 : 1 **1a**·C_{60} complex, which showed an intense CT-absorption band at 465 nm with tailing up to 800 nm, formed. The gelation ability of **1a**·C_{60} was much higher than that of **1a** by itself. The 2 : 1 sandwich complex aligned lamellarly and stacked parallel to the direction of the fiber. In the presence of additional C_{60} molecules, C_{60} was intercalated between the **1a**–C_{60}–**1a** sandwich complex to form 1.5 : 1 to 1 : 1.5 complexes (1.5 : 1 to 1 : 1.5 **1a**·C_{60} gels). It is noteworthy that an increase in additional C_{60} molecules enhances the gelation ability.

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8 The upfield shift (~0.06 ppm) of aromatic protons and the downfield shift (~0.01 ppm) of octyl protons except for the benzyl proton indicate the self-aggregation of **1a** (ESI†).

9 Fluorescence lifetime measurements of the **1a**·C_{60} complex from a mixture of **1a** (0.15×10^{-3} M) and C_{60} (0.15×10^{-3} M) in toluene revealed that 5–20% of the **1a**·C_{60} complex formed in solution.

10 By mixing **1a** with 0.5, 0.75, 1.0, and 1.5 molar equiv. of C_{60} in hot benzene, dark brown gels composed of 2 : 1, 1.5 : 1, 1 : 1, and 1 : 1.5 **1a**·C_{60} formed, and almost all C_{60} was incorporated in the gels.