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# Tetrabenzoperipentacene: Stable Five-Electron Donating Ability and a Discrete Triple-Layered β-Graphite Form in the Solid State**

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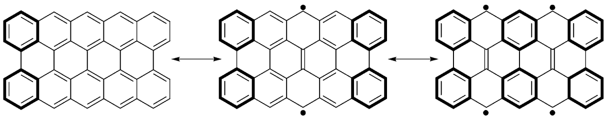
*Dedicated to Professor Atsuhiro Osuka on the occasion of his 60th birthday*

**Abstract:** *An oxidative ring-closure reaction of a tetranaphthylpyrene derivative led to the synthesis of a 56 all-carbon conjugated tetrabenzoperipentacene. In the single-crystal X-ray structure, three molecules make a triple-layered cluster by π-stacking, wherein each layer rotates by 120°, and is thus considered a petit β-graphite. As for the optical properties, the Stokes shift is extremely small (10 $cm^{-1}$), thus indicating its remarkably rigid framework. The tetrabenzoperipentacene exhibits reversible five-electron oxidation waves in cyclic voltammetry, and is regarded as a counterpart to the fullerene $C_{60}$ in terms of stable multicharge-storage nanocarbon materials.*

The synthesis of nanographenes and graphene nanoribbons is a growing field of research aimed at creating materials for use as organic semiconductors and nonlinear optical materials.[1] Graphene is a sheet in graphite and a two-dimensional honeycomb lattice of $sp^2$-hybridized carbon atoms. Modern graphene chemistry relies on its isolation by peeling off an atom-thick monolayer of graphite[2] or by reduction of the graphene oxide[3] in top-down methods. However, by such methods clear definition of the size and the edge structure is not achieved. This problem can be solved by using the bottom-up approach mentioned above.[1]

Synthesis of peri-fused acenes, which are regarded as the small zigzag-edged graphene units, is challenging because without appropriate strategies they are not stable under ambient conditions.[4] Among these acenes, peripentacene is the missing piece of the simplest polycyclic aromatic hydrocarbons (PAHs; Scheme 1).[5] Müllen and co-workers have reported a synthetic route to the peripentacene carbon framework via the tetraketo form, while the fully conjugated aromatic peripentacene has not been isolated.[6] Clar's aromatic sextet rule predicts that the intact peripentacene takes several resonance contributors, some of which exhibit radical forms (Scheme 1).[7]



**Scheme 1.** Resonance structures of a peripentacene.

In our previous study, the photophysical and electrochemical properties of the tetranaphthylpyrenes **2** and **3** were investigated (see Scheme 2).[8] We expected that the strong oxidation of **2** would give the completely planar tetrabenzoperipentacene **4**, but instead the stable radical cation $\mathbf{2}^{\cdot+}$ and dication $\mathbf{2}^{2+}$ were generated, even under powerful oxidative conditions (Scheme 2).[8,9] In contrast to **2**, the oxidation of **3** smoothly produced periphery-fused products. The tetrabenzoperipentacene is considered to be the first conjugated peripentacene, the skeleton of which is comprises 56 all-carbon atoms.[10] Herein, we report the synthesis and physical properties of the tetrabenzoperipentacene **1**, which exhibits a remarkably small Stokes shift and reversible multistep oxidation.

The synthetic route to **1** is shown in Scheme 2. The oxidation of 4,5,9,10-tetrakis(4-mesityloxynaphthyl)pyrene (**3**) with $FeCl_3$ or DDQ/Sc(OTf)$_3$ gave a mixture of the partially fused product **5** and the totally fused product **1**. Isolation of pure **1** involved a tedious separation with repeated recrystallization. Then, we tried to make **1** by a stepwise reaction. After the oxidation of **3** with $FeCl_3$, quick separation and further oxidation with DDQ/Sc(OTf)$_3$ in a microwave at 130 °C afforded **1** in 17 % yield (two steps) without any remaining **5**.

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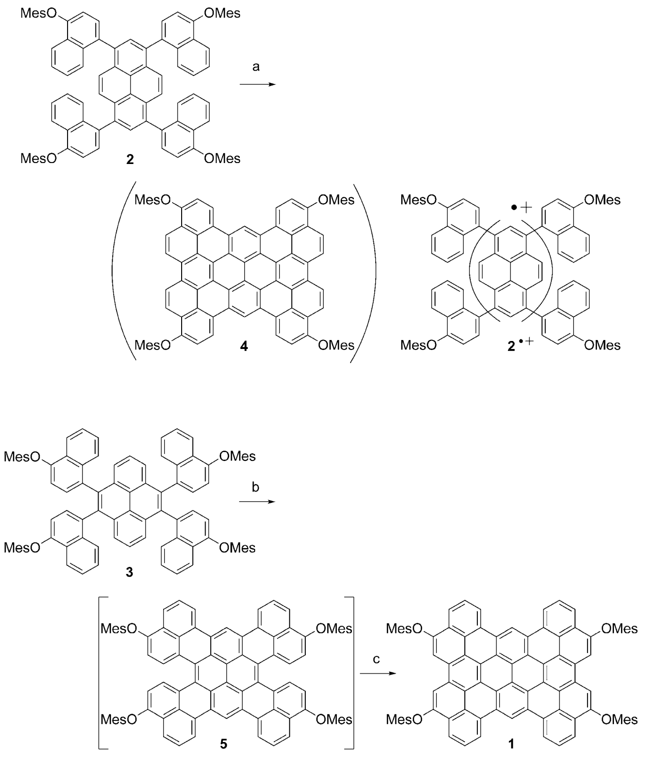

***Scheme 2.*** Synthetic approach toward the peripentecene **1**. Reaction conditions: a) i) $FeCl_3$, $CH_3NO_2$, $CH_2Cl_2$, or ii) DDQ, $Sc(OTf)_3$, toluene, or iii) DDQ, TfOH, $CH_2Cl_2$, b) $FeCl_3$, $CH_3NO_2$, $CH_2Cl_2$, room temperature, 4 h, c) DDQ, $Sc(OTf)_3$, toluene, microwave, 130 °C, 45 min. Mes = mesityl.

The high-resolution MALDI time-of-flight mass spectroscopy detected the parent ion peak of **1** at $m/z = 1230.4651$ (calcd for $C_{92}H_{62}O_4$: 1230.4643 $[M]^+$), which was smaller by 12 mass units than that of **3**. The peaks of the $^1$H NMR spectrum were very broad, possibly because **1** could be partially oxidized to form the radical cation as a result of the higher HOMO level (see below).[11] Thus the final and thoroughly unambiguous structural determination of **1** was done by single-crystal X-ray diffraction analysis (Figure 1).[12] Crystals of **1** were grown by the diffusion of 2-propanol vapors into a chlorobenzene solution of **1**. The compound **1** displays a rectangular shape (12.3 × 11.3 Å). Curiously, molecules of **1** form π-stacked trimers in the crystal, with three crystallographically independent tetrabenzoperipentacene molecules. The planes of the three molecules are almost parallel (angles between the mean planes of the 56-carbon-atom cores: 0.54 and 2.15°), and two of the tetrabenzoperipentacenes in the trimer are twisted by about 120° with respect to each other. The carbon atom cores adopt planar conformations, and the mean deviations from planarity for the 56 atoms of each core are 0.11, 0.07, and 0.09 Å. The mean distances from the central molecule to the upper and lower planes are 3.43 and 3.46 Å, which are within van der Waals contact distances. Interestingly, this ABC-layered offset stacking system of **1** is referred to as a β-type (rhombohedral) graphite, which is not naturally occurring.[13] A dipole–dipole interaction is one of the reasonable explanations for this trimerization process.[14]

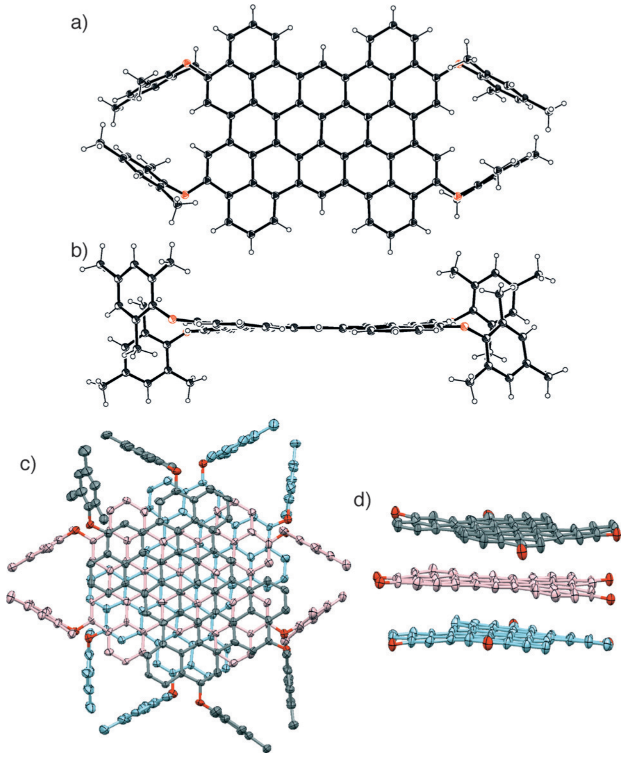

***Figure 1.*** Single-crystal X-ray structure of **1**. a,b) ORTEP representations of the central tetrabenzoperipentacene molecule in the trimeric form. c) Top view of whole structure in which each layer is colored differently. d) Side view of the structure without mesityl groups. Thermal ellipsoids are scaled at 30 % probability. Hydrogen atoms in (c) and (d), and solvent molecules are omitted for clarity.

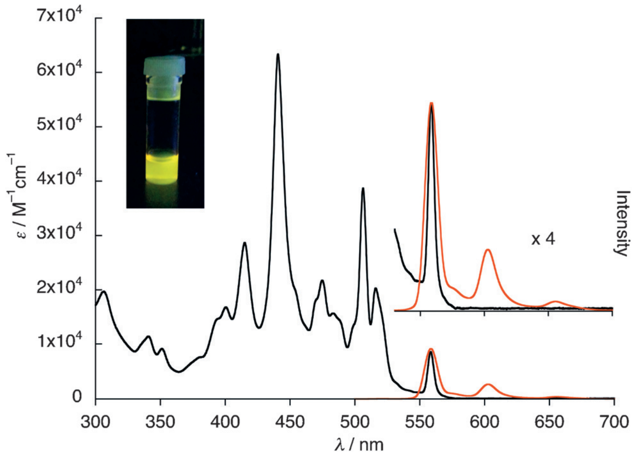

***Figure 2.*** UV/Vis absorption (black line) and fluorescence (red line) spectra of **1** in toluene at 25 °C. Inset shows a photograph of toluene solution of **1** irradiated at $\lambda = 365$ nm.

The UV/Vis absorption spectrum of **1** in toluene exhibits an extraordinary fine spikey structure (Figure 2). The longest band is at $\lambda = 558.4$ nm (optical HOMO–LUMO gap: 2.22 eV) and is extremely sharp ($\varepsilon = 8.5 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$; fwhm = 189 cm$^{-1}$), thus reflecting the rigid geometry of this carbon sheet. The intensive band indicates that the 0–0 transition is allowed, and is also supported by density functional theory (DFT) calculations (see below). Furthermore, the fluorescence peak is observed at $\lambda = 558.8$ nm, from which the Stokes shift is estimated to be only 10 $cm^{-1}$ (1.2 meV). Consequently, the absorption and fluorescence spectra overlap perfectly. Nevertheless, the fluorescence quantum yield of **1** is relatively high ($\Phi = 0.37$, $1.0 \times 10^{-6}$ M), thus suggesting no aggregation in toluene solution. The fluorescence lifetime shows a single exponential decay with 18 ns.

To further understand the electronic features, DFT and time-dependent (TD)-DFT calculations both at the B3LYP/6-31G* level using the Gaussian 09 software package were carried out (Figure 3).[15] The HOMOs and LUMOs are non-degenerative and the coefficient distribution patterns in these frontier MOs appear delocalized over the entire tetrabenzo-peripentacene framework. The longest band of **1** at around 534 nm mainly comprises the transition from $b_{2g}$ HOMO to $a_u$ LUMO (oscillator strength, $f = 0.488$), whereas the main absorption bands at around 445 nm are composed of transitions from $b_{1g}$ HOMO-1 to LUMO and from HOMO to $b_{3u}$ LUMO + 1 ($f = 1.479$). The transition energies and oscillator strengths simulated by TD-DFT calculations were in good agreement with the observed absorption spectrum of **1** (indicated by vertical bars in Figure S6 in the Supporting Information).

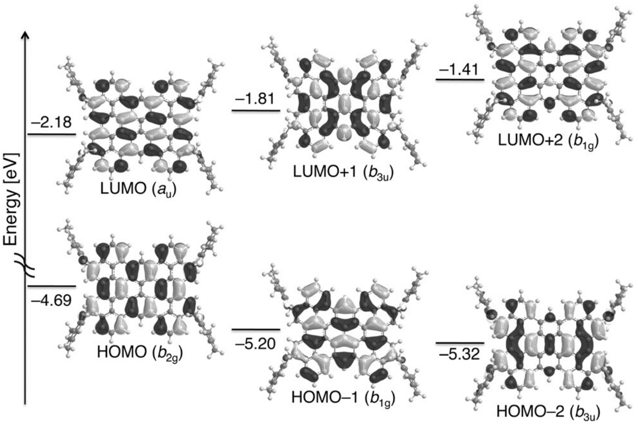

*Figure 3.* MO diagram of **1** based on calculations at the B3LYP/6-31G* level of theory.

The aromaticity of this π system was evaluated by calculating the harmonic oscillator model of aromaticity (HOMA) values,[16] which are geometry-based aromaticity indexes, as shown in Figure 4. The local aromaticity defined by the higher HOMA values absolutely depicted eight benzene rings according to the Clar's sextet rule, thus indicating that **1** should have a closed shell structure.

The π-stacking in the solid state can maximize the intermolecular orbital overlap and thus, the triple-layered structure of **1** is expected to have large intermolecular orbital couplings between the HOMOs. Intermolecular charge-transfer integrals *V*s (meV) between the HOMOs of neighboring molecules were calculated with the Amsterdam density functional (ADF) program package[17] and the calculated *V*s are 84 meV and 79 meV in the trimer and 8.8 meV between the trimers (see Figure S7 in the Supporting Information). It is noteworthy that the transfer integrals within **1** are comparable to that for pentacene (79 meV),[18] and even those for hexacene (87 meV) and rubrene (91 meV). Thus a considerably higher hole mobility of **1** should be expected upon the formation of an effective sequence of this trimeric motif and the creation of the better contact between trimers by some crystal engineering or substituent modifications.

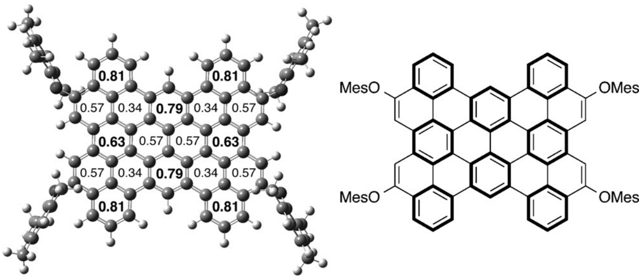

*Figure 4.* HOMA values (left; higher values are represented in bold) and Clar valence structure (right) of **1**.

Finally we investigated the electrochemical properties of **1** by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using 0.10 M $Et_4NBF_4$ as supporting electrolyte (Figure 5). The cyclic voltammogram of **1** in benzonitrile is remarkable, thus displaying four oxidation potentials for five electrons at −0.03, +0.23, +0.44, and +0.73 (for 2*e*) V (versus $Fc/Fc^+$) all as fully reversible waves, thus implying the multicharge storage ability of **1**. To the best of our knowledge, this is the largest number for electron donation from a discrete single component all-carbon structure. $C_{60}$ and $C_{70}$ are known to accept six electrons,[19] thus **1** is a nice counterpart of $C_{60}$ in terms of stable multicharge-storage nanocarbon materials. From the first oxidation potential, we could estimate the HOMO level to be −4.77 eV, which is in accord with the MO calculation.[20] The fused structure causes low oxidation potentials. Reduction potentials were not detected at these conditions.

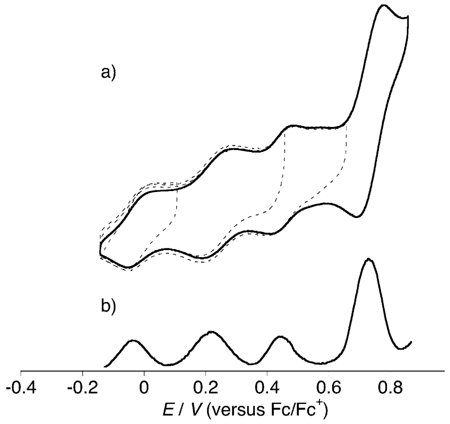

*Figure 5.* a) CV and b) DPV of **1** in PhCN (0.3 mM) at 0 °C. Scan rate: 5.0 mV $s^{-1}$, working electrode: glassy carbon, reference electrode: Ag/$AgNO_3$, electrolyte: $Et_4NBF_4$. $Fc/Fc^+$ = ferrocene/ferrocenium.

In conclusion, we succeeded in the synthesis of **1** through the strong oxidation of the pyrene derivative **3**. The crystal structure is extremely flat and the average distances between the planes in the unit are about 3.4 Å, just within van der Waals distances. The layered structure of **1** is the same as that for β-graphite. The rigidity of this carbon sheet was confirmed by the sharp 0–0 absorption band and the remarkably small Stokes shift (only 10 $cm^{-1}$). We observed reversible five-electron oxidation waves, thus revealing the superior redox behavior of the molecular multicharge-storage graphene.

**Keywords:** aromaticity · graphene · oxidation · polycycles · π interactions

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