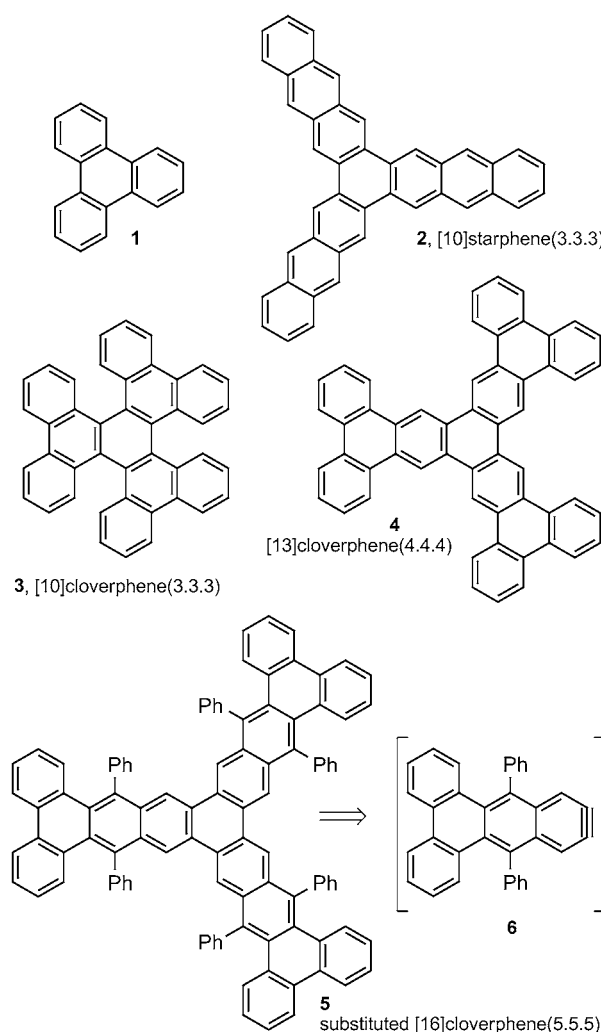


[16]Cloverphenes: a Clover-Shaped *cata*-Condensed Nanographene with Sixteen Fused Benzene Rings**

José M. Alonso, Alba E. Díaz-Álvarez, Alejandro Criado, Dolores Pérez, Diego Peña,* and Enrique Guitián

In memory of Michael M. Pollard

Since the first isolation of graphene in 2004,^[1] a huge amount of effort has been dedicated to developing efficient methodologies to prepare the two-dimensional counterpart of graphite, a material that exhibits intriguing physical properties.^[2] Structurally, graphenes are simply large polycyclic aromatic hydrocarbons (PAHs): sp^2 -bonded carbon atoms packed into a 2D structure of fused benzene rings.^[3] This molecular similarity opens up the possibility of preparing well-defined nanographenes by bottom-up approaches through organic synthesis.^[4] These chemical methods would avoid the structural inhomogeneity implicit in the current approaches to prepare graphenes and they could provide access to nanographenes with different topologies and peripheries. Müllen and co-workers have reported impressive examples of this approach, including the preparation of a graphene disk formed by 91 *peri*-fused benzene rings through cyclodehydrogenation of a suitable precursor.^[5] More recently, the same group reported the preparation of graphene nanoribbons up to 40 nm in length.^[6] It is quite remarkable, however, that examples of nanographenes exclusively formed by *cata*-fused benzene rings are scarce, although this type of condensation would definitely influence the electronic properties of the graphene-like material. In fact, the stability of large *cata*-fused PAHs strongly depends on the mode of condensation and number of benzene rings. For example, amongst acenes or linear *cata*-condensed PAHs,^[7] heptacene is an unstable molecule under ambient conditions,^[8] whereas octacene and nonacene can only be detected at 30 K in an argon matrix.^[9] Recently, Miller and Anthony independently succeeded at preparing stable substituted nonacene derivatives.^[10] By contrast, [14]helicene, a *cata*-condensed PAH with fourteen *ortho*-fused benzene rings, has been isolated under ambient conditions and is the largest *cata*-condensed PAH that had been prepared prior to this work.^[11]



Scheme 1. Starphenes and cloverphenes.

In 1998, we reported that the cyclotrimerization of benzyne to give triphenylene (**1**, Scheme 1) is efficiently catalyzed by palladium(0) complexes.^[12] The scope of this methodology was soon extended by applying it to the cyclotrimerization of polycyclic arynes.^[13] In this way, large PAHs such as hexabenzotriphenylene **3** ($C_{42}H_{24}$)^[13a] and hexabenzotriphenylene **4** ($C_{54}H_{30}$)^[13b] were obtained in reasonable yields (Scheme 1). Herein we report the successful synthesis of the hexabenzotriphenylene **5**, a threefold symmetric polyarene with sixteen *cata*-fused benzene rings

[*] Dr. J. M. Alonso, Dr. A. E. Díaz-Álvarez, A. Criado, Dr. D. Pérez, Dr. D. Peña, Prof. Dr. E. Guitián
Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Facultad de Química, Universidad de Santiago de Compostela 15782-Santiago de Compostela (Spain)
E-mail: diego.pena@usc.es

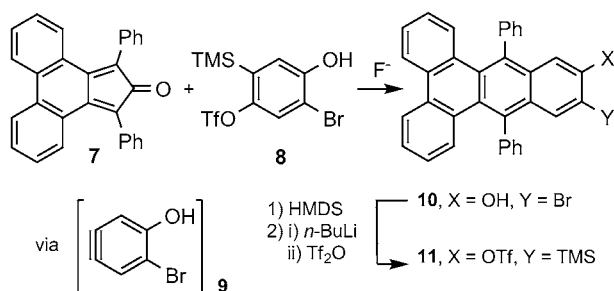
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(22 benzene rings in total), with a diameter of 2.1 nm and the molecular formula $C_{102}H_{60}$. To the best of our knowledge, this is the largest *cata*-condensed PAH that has been prepared to date.

In 1968, the term starphene was coined by Clar and Mullen for benzologues of triphenylene (**1**), in which the three branches are annellated to a central ring and radiate outwards in a linear manner.^[14] For example, compound **2** was named [10]starphene(3.3.3). Since the structure of polyarenes **3**, **4**, and **5** resembles the threefold symmetry of a three-leaf clover,^[15] we propose the trivial name cloverphene (cloverlike phene) to refer to hexabenzotriphenylene and its benzologues. Employing this system, compound **5** would have a [16]cloverphene(5.5.5) aromatic core. The figures in square brackets give the total number of *cata*-condensed benzene rings, while the figures in round brackets give the number of rings in each of the three branches annellated to the central ring.

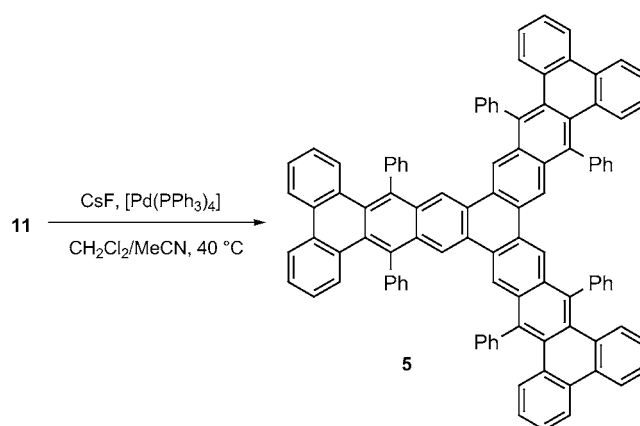
As shown in Scheme 1, hexaphenyl-substituted [16]cloverphene **5** could be obtained in a one-pot procedure by Pd-catalyzed cyclotrimerization of aryne **6**. Based on our experience in this field, we chose *ortho*-(trimethylsilyl)aryl triflate **11** as the precursor of polycyclic aryne **6**. The preparation of this triflate is shown in Scheme 2. Generation



Scheme 2. Synthesis of aryne precursor **11**.

of monocyclic aryne **9** by treatment of triflate **8** with tetrabutylammonium fluoride (TBAF) in the presence of cyclopentadienone **7**, followed by refluxing the resulting mixture in tetrachloroethane for 3 h, afforded benzotriphenylenol **10** in 44 % yield. This is a remarkable result bearing in mind the presence of an unprotected hydroxyl group that could interact with the highly electrophilic aryne. Apparently, the intermediate resulting from the Diels–Alder reaction of aryne **9** and dienone **7** evolves in situ to afford compound **10** by cheletropic extrusion of carbon monoxide. The one-pot treatment of compound **10** with hexamethyldisilazane (HMDS) in refluxing THF, followed by successive addition of *n*BuLi and Tf_2O (Tf = trifluoromethanesulfonyl) at $-100^\circ C$, afforded triflate **11** in 70 % yield. As expected, slow generation of aryne **6** by treatment of triflate **11** with CsF in the presence of 10 mol % of $[Pd(PPh_3)_4]$ in a mixture of dichloromethane/MeCN 1:6 at $40^\circ C$, led to cloverphene **5** in 22 % yield as a yellow solid after purification by column chromatography (Scheme 3).

This compound gave a molecular ion with a mass of m/z 1284.4 in its MALDI mass spectrum with the isotopic



Scheme 3. Synthesis of cloverphene **5**.

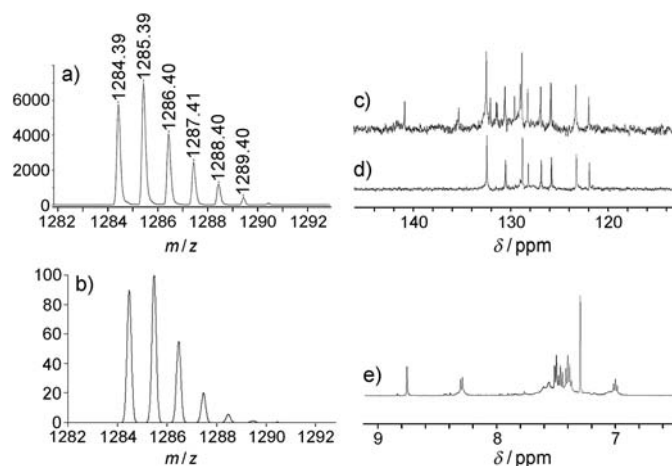


Figure 1. Spectroscopic characterization of cloverphene **5**: a) MALDI mass spectrum; b) simulated mass spectrum for $C_{102}H_{60}$; c) ^{13}C NMR spectrum; d) DEPT-135 spectrum; e) 1H NMR spectrum.

distribution expected for a hydrocarbon of the composition $C_{102}H_{60}$ (Figure 1). Despite its extremely large size, the threefold symmetry of this compound led to a simple ^{13}C NMR spectrum, with 8 CH and 7 C aromatic signals, while the 1H NMR spectrum showed a singlet and a doublet, which were particularly deshielded at $\delta = 8.71$ and 8.30 ppm, respectively.

The presence of six phenyl groups attached to the cloverphene core would induce distortion from planarity in compound **5** in order to minimize steric strain, and this, in turn, enhances the solubility of this giant PAH and allows its spectroscopic characterization. In particular, low temperature NMR experiments suggest that cloverphene **5** adopts a C_3 -symmetric molecular-like conformation (Figure 2),^[13a] which, according to computational calculations, is thermodynamically more stable than a C_2 -symmetric conformation.^[15] At the same time, the presence of these phenyl groups probably prevents the fast photooxidation of the extended aromatic core of compound **5**.^[16]

To evaluate compound **5** as a new molecular material candidate, we studied some of its electronic properties. The

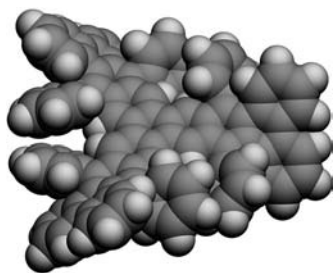


Figure 2. Optimized geometry for a C_3 -symmetric conformation of hydrocarbon **5**.

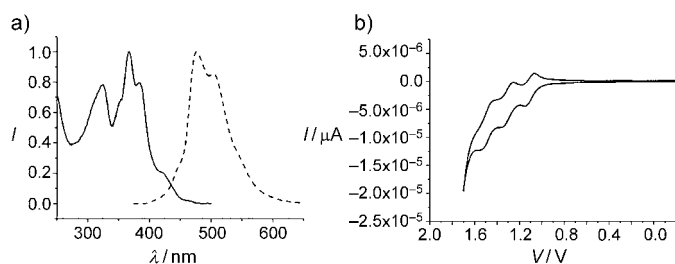


Figure 3. Electronic properties of cloverphenes **5**: a) Absorption (solid line) and emission (dashed line) spectra in dichloromethane; b) cyclic voltammogram in dichloromethane (1 mM).

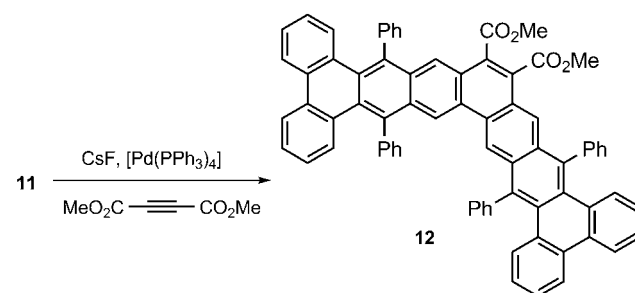
UV/Vis spectrum in dichloromethane exhibited major absorption bands at 324 nm and 366 nm with shoulders at 383 nm and 420 nm, respectively (Figure 3a). From this lowest transition we estimated a highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap of 2.74 eV, while the gap, computed by DFT at the B3LYP 6-31G(d) level, was 3.02 eV.^[15] The emission spectrum under excitation at 366 nm showed a structured fluorescence band at 476 nm with a shoulder at 504 nm, probably due to the structural restrictions of its nonplanar aromatic core. Notably, in terms of efficiency, we calculated the quantum yield of compound **5** to be 0.48 in dichloromethane solution with respect to fluorescein (0.79 in a 0.1M NaOH solution). As expected, exposure of hydrocarbon **5** in solution to ambient air and sunlight caused its degradation, probably by photooxidation. Bearing in mind the large number of fused benzene rings in its aromatic core, the photooxidation rate turns out to be relatively low, with a half-life of 24.6 min.^[15] For comparison, the half-life of 6,13-diphenylpentacene was 8.5 min under similar conditions.^[16]

Interestingly, cyclic voltammetry of cloverphenes **5** showed three reversible oxidation waves at 1108 mV, 1302 mV, and 1503 mV vs. Ag/Ag^+ , respectively (Figure 3b), in accordance with the presence of three aromatic branches in the molecule. From the first oxidation process a HOMO energy value of -5.47 eV can be estimated for cloverphenes **5**.

The synthetic route described herein to obtain cloverphenes **5** is based on two sequential aryne cycloadditions: a [4+2] cycloaddition of aryne **9**, followed by a [2+2+2] cycloaddition of aryne **6**. This route was inspired by the bisbenzyne approach to large acenes independently described by Pascal^[17] and Wudl,^[18] although their approaches are based

on two sequential [4+2] aryne cycloadditions with two molecules of the same diene.^[19] The use of a masked bisbenzyne precursor (**8**) allowed us to combine two different sequential cycloadditions: a [4+2] cycloaddition followed by a cyclotrimerization to afford large PAHs with a threefold symmetric structure. It should be highlighted that this type of topology has recently attracted considerable attention in the field of molecular electronics as single molecule logic gates.^[20]

To further explore the utility of aryne **6** to construct large PAHs, we decided to attempt its cocyclotrimerization with dimethyl acetylenedicarboxylate (DMAD).^[21] Treatment of triflate **11** with CsF in the presence of DMAD and 10 mol % of $[\text{Pd}(\text{PPh}_3)_4]$ led to the isolation of compound **12** in a remarkable 59% yield. This compound resulted from the [2+2+2] cocycloaddition of two arynes and one alkyne (Scheme 4). Remarkably, this molecule presents a tetraben-



Scheme 4. Synthesis of tetrabenzoheptaphene **12**.

zoheptaphene core, an angular nanoribbon structure with very few reported precedents.^[22] Crystals of compound **12** were obtained from a chloroform/hexane solution and these proved suitable for X-ray diffraction analysis. Curiously, tetrabenzoheptaphene **12** adopts an arch-shaped molecular structure (Figure 4), with a base 18.6 Å wide and 3.4 Å in depth.^[15] This unusual shape has recently been described by Pascal and co-workers for a structurally related tetrabenzoheptaphene derivative, which also adopts an arch-like structure in the crystalline state.^[23]

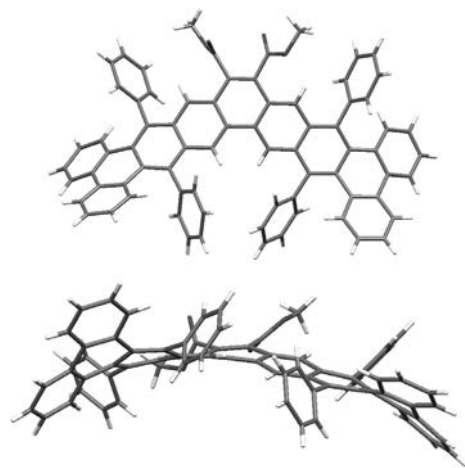


Figure 4. X-ray structure of heptaphene **12** (top and lateral views).

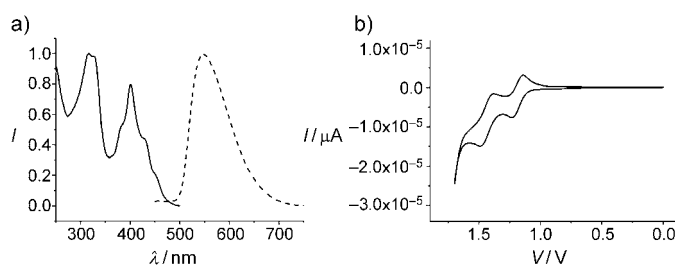


Figure 5. Electronic properties of tetrabenzoheptaphene **12**: a) absorption (solid line) and emission (dashed line) spectra in dichloromethane; b) cyclic voltammogram in dichloromethane (1 mM).

The absorption spectra of tetrabenzoheptaphene **12** in DCM solution showed a structured band with two maxima at 317 nm and 400 nm and shoulders at 328 nm, 382 nm, and 430 nm (Figure 5). Under excitation at the 400 nm maximum, this compound exhibited luminescence at 548 nm with a quantum yield of 0.18. Cyclic voltammetry of compound **12** showed two reversible oxidation waves at 1188 mV and 1435 mV, and one reduction wave at -1477 mV.^[15] From this data, a HOMO energy value of -5.53 eV and a HOMO–LUMO gap of 2.66 eV can be estimated. Bearing in mind that this compound is stable in solution to ambient air and sunlight, these electronic properties introduce tetrabenzoheptaphene **12** as a promising molecule for organic electronics.

In conclusion, we have shown that a sequence of two different aryne cycloadditions based on a masked bisaryne can be successfully used to obtain *cata*-condensed nanographenes with exotic molecular geometries such as clover- and arch-like structures. In particular, the largest *cata*-condensed PAH isolated to date with 102 sp² carbon atoms, coined as a [16]cloverphene derivative, has been introduced in this paper. Work is in progress to explore the limits of this approach and the applications of these nanosized molecules.

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