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Aryne-mediated syntheses of structurally related acene derivatives†‡

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Cycloaddition reactions of tetrakis(hexyloxy)-substituted 2,3-triphenylyne (2,3-didehydrotriphenylene) provide straightforward access to three new *cata*-condensed polyarenes characterized by the presence of 5, 8 and 11 fused benzene rings.

Large polycyclic aromatic hydrocarbons (PAHs) characterized by the fusion of various benzene rings are prominent among the most interesting materials studied in the fields of molecular electronics, supramolecular chemistry and materials science.[1] The recent entry onto the scientific scene of graphene,[2] the 2D counterpart of graphite that is structurally related to PAHs, has led to a remarkable renaissance in the synthesis of polyarenes formed by the fusion of a large number of benzene rings. Cycloaddition reactions of arynes have been widely used for the preparation of PAHs.[3] In particular, the use of polycyclic arynes has allowed the synthesis of a variety of structurally fascinating polycyclic aromatic compounds.[4]

Despite the progress in computational studies it is still challenging to predict how small changes in the structure of molecules can modify properties such as aggregation, deposition or the solid-state packing of complex molecules, and ultimately the macroscopic behaviour of molecular materials. In this context it would be useful to obtain a series of molecules with gradual structural changes in order to evaluate the influence of such modifications in structure. After several years working on the development of new strategies for the synthesis of PAHs,[5] we decided to prepare a small group of molecules with gradual changes in topology, which should in turn affect properties such as planarity and conjugation.

Recently, our group described the use of substituted triphenylyne **1** (Fig. 1) to yield polyarenes with 5, 7, 9, 10 and 13 fused benzene rings by palladium-catalyzed [2+2+2] cycloaddition reactions.[5c] We describe here the use of the same aryne to afford three new *cata*-condensed acene derivatives, namely compounds **2**, **3** and **4** with 5, 8 and 11 fused benzene rings, respectively. We envisaged that the presence of four hexyloxy groups attached to the polyaromatic cores of compounds **2–4** would provide enough solubility to manipulate and to characterize these large polyarenes.

Based on our experience in this field, we chose *o*-(trimethylsilyl)aryl triflate **5** (Scheme 1) as the precursor for 6,7,10,11-tetrakis(hexyloxy)-2,3-didehydrotriphenylene (**1**).[5c] Generation of this aryne by treatment of triflate **5** with tetrabutylammonium fluoride (TBAF) in the presence of commercially available 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (**6**) in THF afforded substituted benzo[*b*]triphenylene **2** in 72% yield. Presumably, intermediate **7**, resulting from the [4+2] cycloaddition of aryne **1** with dienone **6**, evolves *in situ* to afford polyarene **2** by cheletropic extrusion of carbon monoxide.[6] This methodology to obtain a benzo[*b*]triphenylene core has been previously used by Pascal and co-workers to isolate 9,10,11,12,13,14-hexaphenylbenzo[*b*]triphenylene in 24% yield by reaction of **6** with 1,4-diphenyl-2,3-triphenylyne, generated by thermal decomposition of the corresponding diazonium salt precursor.[4a]

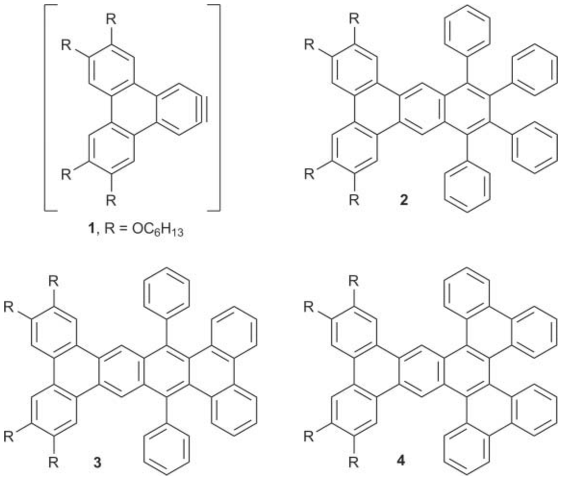
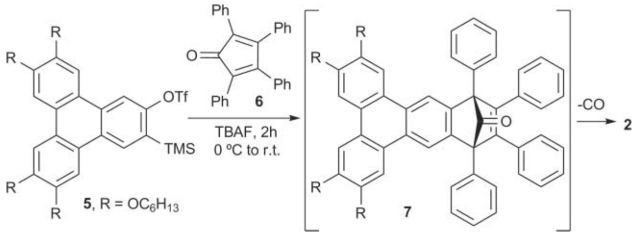


Fig. 1 Structures of triphenylyne **1** and polyarenes **2–4**.



Scheme 1 Synthesis of substituted benzo[*b*]triphenylene **2**.

Similarly, Diels–Alder cycloaddition of triphenylyne **1** with cyclopentadienone **8** (phencyclone), followed by CO extrusion[6] led to substituted tetrabenzo[*a*,*c*,*j*,*l*]tetracene **3** with 8 fused benzene rings in 55% yield (Scheme 2). Notably, Pascal and co-workers succeeded in preparing highly twisted 9,10,19,20-tetraphenyltetrabenzo[*a*,*c*,*j*,*l*]tetracene in 1–2% yield by reaction of **8** with 1,4-diphenyl-2,3-triphenylyne.[4a] Curiously, while the tetracene derivative isolated by them decomposes slowly in solution, polyarene **3** proved to be stable under ambient conditions.

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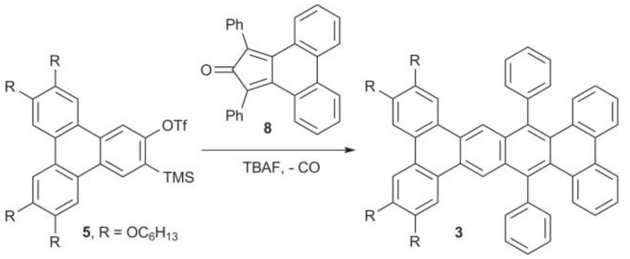
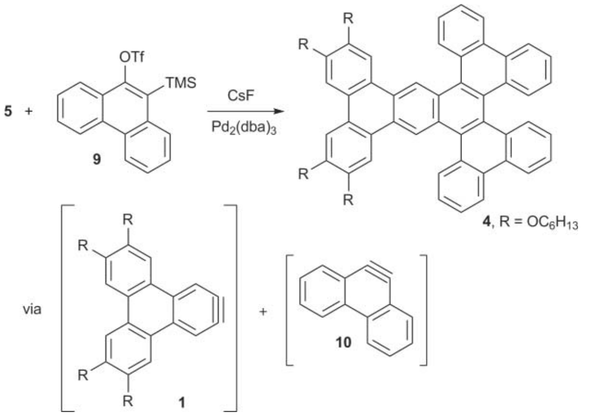


Scheme 2 Synthesis of substituted tetrabenzo[*a*,*c*,*j*,*l*]tetracene **3**.

By contrast, pentahelicene **4** (with 11 fused benzene rings) was prepared by palladium-catalyzed [2+2+2] cocycloaddition of triphenylyne **1** and two molecules of 9,10-phenanthryne (**10**, Scheme 3). In particular, treatment of triflate **5** with CsF in the presence of an excess of the 9,10-phenanthryne precursor **9** (ratio 1 : 4) and 5 mol% of $Pd_2(dba)_3$ led to the isolation of substituted dibenzo[*f*,*j*]triphenyleno[2,3-*s*]picene **4** in 30% yield together with hexabenzotriphenylene, the phenanthryne trimerization product.[5a] It should be noted that this route provides straightforward access to a hitherto unprecedented polyaromatic core by reaction of two different short-lived intermediates (arynes **1** and **10**) generated in one-pot.



Scheme 3 Synthesis of substituted pentahelicene **4**.

Compounds **3** ($C_{70}H_{76}O_4$) and **4** ($C_{70}H_{74}O_4$) can be considered as partially cyclodehydrogenated derivatives of benzo[*b*]triphenylene **2** ($C_{70}H_{78}O_4$). However, the problems in controlling the chemoselectivity in metal- or photo-promoted cyclodehydrogenation reactions would make these alternatives to obtain compounds **3** and **4** particularly arduous.[7]

Despite the fact that the differences in the molecular formulae of acene derivatives **2–4** are very small, the changes in the aromatic cores have a marked effect on their absorption spectra in solution (Fig. 2). In particular, while the major absorption band of compound **2** falls at 328 nm, polyarenes **3** and **4**, with an increased number of fused benzene rings, have red-shifted absorption maxima at 354 and 362 nm, respectively. The UV-vis spectra of substituted 10,11,12,13-hexaphenylbenzo[*b*]triphenylene **2** (DCM, λ_{max} = 380, 328, 314, 302 nm) and 9,10,11,12,13,14-hexaphenylbenzo [*b*]triphenylene (heptane, λ_{max} = 376, 328, 318 nm) isolated by Pascal and co-workers,[4a] are very similar. By contrast, the major absorption band of alkoxy-substituted 10,19-diphenyltetrabenzo[*a*,*c*,*j*,*l*]tetracene **3** (λ_{max} = 354 nm) shows a bathochromic shift when compared with that of unsubstituted tetrabenzo[*a*,*c*,*j*,*l*]tetracene (λ_{max} = 328 nm).[8]

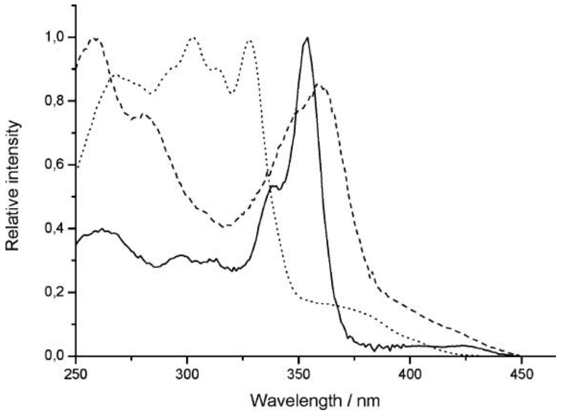


Fig. 2 Absorption spectra of polyarenes **2** (···), **3** (—) and **4** (---) in CH_2Cl_2 solution (10 μM).

The differences arising from the changes in the aromatic core were also evident in the emission spectra of these compounds in DCM solution (1 μM) under excitation at the corresponding absorption maxima (Fig. 3). While polyarenes **2** and **4** have fluorescence maxima at 460 and 474 nm, respectively, tetrabenzotetracene **3** showed a red-shift in the emission maximum to 501 nm. Notably, pentahelicene **4** shows a narrow structured band with a shoulder at 501 nm, probably due to the structural restrictions of its non-planar aromatic core. Moreover, bearing in mind that unsubstituted benzo[*b*]triphenylene exhibited luminescence at 379 nm,[9] phenyl and hexyloxy substituents attached to polyarene **2** are responsible for a large bathochromic shift (81 nm) in the emission maximum of this compound compared with its unsubstituted parent.

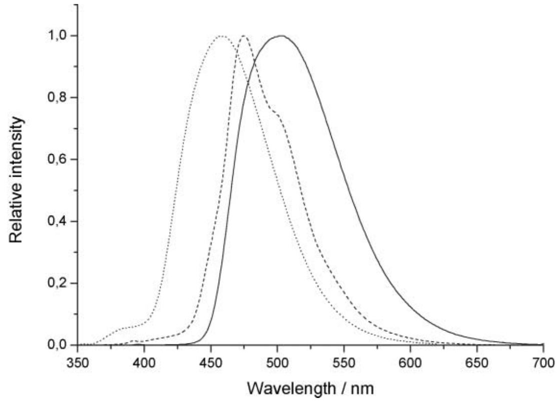


Fig. 3 Emission spectra of polyarenes **2** (···), **3** (—) and **4** (---) in CH_2Cl_2 solution (1 μM).

In conclusion, three structurally related *cata*-condensed polyarenes characterized by the presence of 5, 8 and 11 fused benzene rings have been obtained by cycloaddition reactions of the same tetrakis(hexyloxy)-substituted 2,3-triphenylyne **1**. Benzotriphenylene **2** and tetrabenzotetracene **3** were obtained from triflate **5** by a tandem one-pot fluoride-induced aryne generation/Diels–Alder reaction/CO cheletropic extrusion, while pentahelicene **4**, characterized by a hitherto unprecedented polyaromatic core, was prepared by a tandem one-pot fluoride-induced aryne generation/Pd-catalyzed cocyclotrimerization sequence. Remarkably, the differences in the structures of the aromatic cores of these closely related polyarenes became evident on comparing their absorption and emission spectra. Studies on the supramolecular behaviour of these acene derivatives with gradual increase of planarity are in progress and the results will be reported in due course.

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