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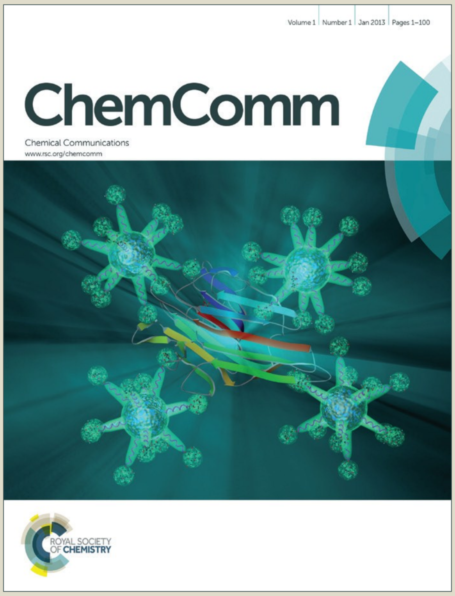

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ARTICLE TYPE

Large phenyl-substituted acenes by cycloaddition reactions of the 2,6-naphthodiyne synthon†

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Phenyl-substituted tetra-, penta-, hexa- and octacenes were easily obtained starting from a readily available naphthalene-based bisaryne precursor. This approach to large acenes involves a sequence of two Diels−Alder cycloadditions with dienones followed by two CO extrusion reactions.

Acenes are among the most widely studied molecules in organic electronics.[1] An important goal in this field is the preparation of large, stable and soluble derivatives with small band gaps. In recent years some impressive examples have been reported, including the preparation of diverse nonacenes.[2] Among the methods used to obtain oligoacenes, cycloaddition reactions of arynes have been extensively exploited as a clean and efficient approach.[3,4] In particular, the twofold cycloaddition of bisaryne synthons with dienones is notably appealing due to its simplicity. Classical examples of this approach include the preparation of tetrabenzopentacene **1**[5] and tetrabenzoheptacene **2**[6] from 1,4-benzodiyne precursors (Figure 1). The introduction by Kitamura and co-workers of bistriflate **4** as a 2,6-naphthodiyne (**3**) precursor to synthesize 1,4,7,10-tetraalkyltetracenes (**5**)[7] encouraged us to study its reaction with dienones in an attempt to prepare in one-pot tetrabenzohexacene **6** and tetrabenzooctacene **7**, which could be considered as benzologues of acenes **1** and **2**, respectively.

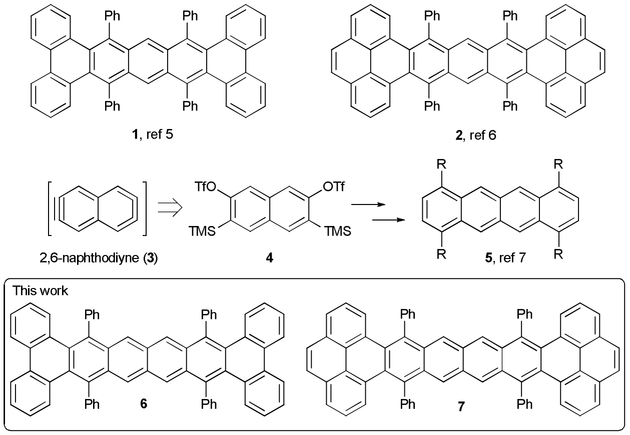
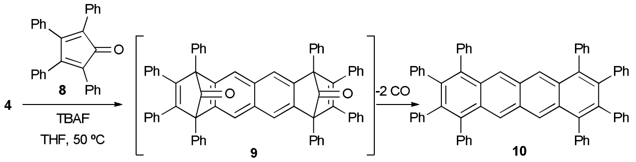


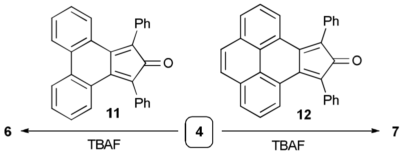
Figure 1 Acenes obtained from bisaryne synthons.

With this idea in mind, we first tested the reaction of bistriflate **4** with tetrabutylammonium fluoride (TBAF) in the presence of commercially available dienone **8** at 50 ºC for 16 h (Scheme 1). Much to our delight, 1,2,3,4,7,8,9,10-octaphenyltetracene (**10**) was isolated in 23% yield as a yellow solid. This compound is probably formed by two sequential aryne [4+2] cycloadditions with two molecules of dienone **8** to generate intermediate **9**, which could evolve *in situ* by a twofold CO extrusion reaction to afford tetracene **10**. Curiously, despite the interest in phenyl-substituted tetracenes such as rubrene,[1c] there is not a single report in the literature on compound **10**. By contrast, 1,2,3,4,5,6,7,8-octaphenylanthracene has been prepared using different 1,4-benzodiyne precursors.[8]



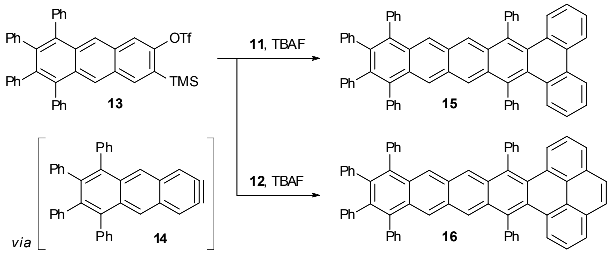
Scheme 1 Synthesis of octaphenyltetracene **10**.

In order to access benzologues of acenes **1** and **2**, we proceeded to explore the reaction of bistriflate **4** with dienones **11** and **12** (Scheme 2). Following the one-pot experimental procedure employed in the synthesis of compound **10**, we isolated tetraphenyl-substituted tetrabenzoacenes **6** and **7** as insoluble violet solids in 15% and 18% yield, respectively. As expected, exposure of hexacene **6** or octacene **7** in solution to ambient air and sunlight caused its degradation. However, careful purification of both large acenes was possible by column chromatography, which allowed a full spectroscopic characterization.



Scheme 2 Synthesis of hexacene **6** and octacene **7**.

Hydrocarbons **6** and **7** are symmetrical acenes that contain two terminal pyrene or phenanthrene units, respectively.[2e] To further explore the utility of bistriflate **4** in the preparation of non-symmetrical acenes, it was decided to attempt the synthesis of single-terminal pyrene or phenanthrene derivatives. For this purpose we explored the selecive generation of one triple bond from bisaryne precursor **4**, which could afford triflate **13** (Scheme 3) by reaction with dienone **8**. Based on our previous experience on the use of bisaryne precursors,[4d] treatment of bistriflate **4** with CsF in the presence of dienone **8** in a CH_3CN/CH_2Cl_2 mixture led to the formation of compound **13**, a precursor of tetraphenylanthracyne **14**, in 40% yield. Notably, subsequent reaction of triflate **13** with dienones **11** or **12** in the presence of TBAF in THF led to the formation of pentacene **15** and hexacene **16** in 42% and 40% yield, respectively.



Scheme 3 Synthesis of pentacene **15** and hexacene **16**.

As one would expect, the optical properties of these acenes in the solid state strongly depend on the size and shape of the aromatic core. For example, tetracene **10** is a yellow solid while symmetrical hexacene **6** and octacene **7** have a violet colour (Figure 2). By contrast, non-symmetrical hexacene **16**, which is a single-terminal pyrene derivative, is a pink solid.

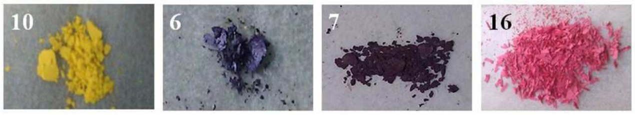


Figure 2 Solid-state colours of acenes **10**, **6**, **7** and **16**.

At this point it was decided to study the photoelectronic properties of these phenyl-substituted acenes in solution (Table 1). As expected, certain structural changes in the aromatic core had a marked effect on the absorption spectra of these acenes. For example, while the lowest-energy absorption band of tetracene **10** falls at 503 nm, pentacene **15** and hexacene **6** have red-shifted absorption bands at 558 and 603 nm, respectively. By contrast, phenanthrene or pyrene terminal units have a limited influence on the UV/Vis absorptions. In particular, there is a bathochromic shift of 3 nm in the lowest-energy band of hexacene **16** in comparison to pentacene **15**, and an 8 nm red shift on the band of octacene **7** compared with that of hexacene **6**.

Table 1 Photoelectronic data for acenes in CH_2Cl_2 solution.

	10	**15**	**16**	**6**	**7**
λ_{abs} [a]	503	558	561	603	611
λ_{em} [b]	511	572	572	618	622
E_{ox} [c]	0.41	0.28	0.27	0.19	0.20
E_{HOMO} [d]	−5.21	−5.08	−5.07	−4.99	−5.00
E_{red} [c]		−1.79	−1.77	−1.72	−1.67
E_{LUMO} [e]		−3.01	−3.03	−3.08	−3.13
$\mathrm{Gap}_{\mathrm{opt}}$ [f]	2.39	2.14	2.14	1.98	1.96
$\mathrm{Gap}_{\mathrm{elc}}$ [g]		2.07	2.04	1.91	1.87

[a] nm, lowest-energy UV/Vis absorption. [b] nm, emission maxima. [c] V, determined by cyclic voltammetry (CV, CH_2Cl_2/0.1 M Bu_4NPF_6), reference electrode: AgCl/Ag, internal standard: ferrocene. [d] eV, calculated from $E_{\mathrm{HOMO}} = -(4.8 + E_{\mathrm{ox}})$. [e] eV, calculated from $E_{\mathrm{LUMO}} = -(4.8 + E_{\mathrm{red}})$. [f] eV, calculated from the onset of λ_{abs}. [g] eV, calculated from CV data.

Notably, the same trend in the structure-property relationships was observed on comparing the emission spectra and the electrochemical data obtained by cyclic voltammetry (Table 1). These techniques showed similar values on comparing the single phenanthrene-terminated pentacene **15** and pyrene-terminated hexacene **16** pair and also the double phenanthrene-terminated hexacene **6** and double pyrene-terminated octacene **7**.

Tetraphenyl-substituted tetrabenzooctacene **7** is a particularly interesting hydrocarbon. In the UV/Vis spectrum the longest absorption band was at 611 nm (Figure 3), which represents a red-shift of 81 nm when compared to its smaller benzologue, heptacene **2**.[5] Cyclic voltammetry on octacene **7** showed two oxidation waves and one reversible reduction wave, with a HOMO-LUMO energy gap of 1.87 eV, i.e., similar to the gap reported for unsubstituted hexacene (1.84 eV).[2e]

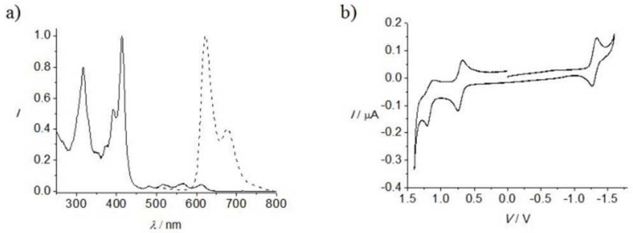


Figure 3 Electronic properties of octacene **7**: a) Absorption (solid line) and emission (dashed line) spectra in CH_2Cl_2. b) Cyclic voltammogram in CH_2Cl_2/0.1 M Bu_4NPF_6 using AgCl/Ag as reference electrode.

In conclusion, five new phenyl-substituted acenes were prepared in a straightforward manner from the same commercially available bisnaphthalyne precursor. The photoelectronic properties of these large aromatic hydrocarbons suggest their potential use as promising molecules for organic electronics.[9]

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† Electronic Supplementary Information (ESI) available: experimental details and spectroscopic cata. See DOI: 10.1039/b000000x/

‡ In memoriam of Prof. Ekkehard Winterfeldt (1932-2014).

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