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Coronenes with push-pull geometries from macrocycle-forming Perkin condensations

Luc Soliman,^a Elsa Ramassamy,^a Katia Dujarric,^a Guillaume Naulet,^a Pierre Dechambenoit,^a Harald Bock,^a Fabien Durola*^a

Although the Perkin reaction has been successful in producing ester-substituted conjugated macrocycles with four or six building blocks, macrocycles composed of only two elements remained elusive until now. Through the development of a building block derived from phenanthrene with two glyoxylic acid substituents in a pincer-like arrangement, formation of a two-block macrocycle was induced when paired with a complementary phenylenediacetic acid unit. The addition of ether functions to the phenanthrene building block not only improved the yields, but led to macrocycles with push-pull geometries. Photocyclisation of the resulting cyclophanes efficiently yield tetra- or hexasubstituted coronenes.

Introduction

Since Scholl and Meyer reported the first synthesis of coronene in 1932,¹ the synthesis of substituted and π -expanded coronenes has known a significant evolution.² Due to their circularly condensed pi electron system^{3,4} and their high symmetry, coronenes show strong tendency to form charge-transfer complexes⁵ or adducts with electron deficient molecules.⁶ Many new coronene-based structures have been developed in the last decades for various purposes such as charge-transfer supramolecular rotors,⁷ host-guest molecular nanostructures⁸ and supramolecular hydrogels.⁹ The synthetic strategies leading to coronene are not very diverse. They usually imply expansion of perylene (Figure 1a), as reported by Clar,^{10,11} or rigidification of cyclophanes (Figure 1b), as described by Reiss,^{12,13} Lo¹⁴ or Xiao.¹⁵

Using the Perkin-reaction-based synthetic strategy developed in our group for the synthesis of carboxy-substituted polycyclic aromatic compounds¹⁶ and mimicking the synthesis of coronene by expansion of perylene, we recently reported the formation of dibenzocoronenes from triphenylene- and naphthalene-based building blocks (Figure 1c).¹⁷

This synthetic approach also proved to be efficient for the formation of conjugated macrocyclic compounds. Structurally diverse macrocycles obtained with four to six building blocks were reported,^{18–20} but Perkin macrocyclisations implying only two building blocks remained challenging. The macrocyclic coronene precursor shown in Figure 1b testifies that 3,6-disubstituted phenanthrenes, with their ca. 60° angle between substituents, are suitable building blocks for such macrocyclisations.

Herein we report the rapid and easy synthesis of three short macrocycles by the Perkin approach. The resulting phenanthroparacyclophane-dienes were thereafter photocyclised to substituted coronenes (Figure 1).

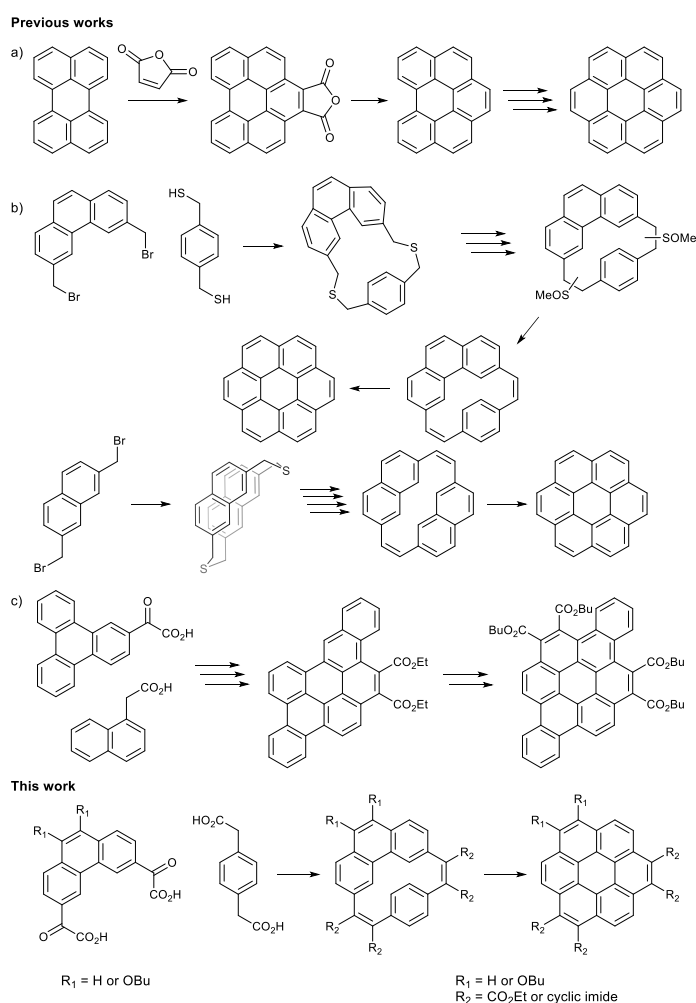


Figure 1. Some of the previous works reported in the field of coronenes and π -expanded coronenes synthesis by Clar (a), Reiss (b), and our group (c). Each arrow represents a step in the synthesis.

Results and discussion

High dilution favours the formation of conjugated macrocycles by Perkin reaction between bifunctional complementary building blocks. Following this approach, macrocycles were indeed obtained previously with relatively high yields for such non-templated reactions.²¹ Due to the opposite (para-like) positions of the reactive functions on the building blocks, the isolated products were so far always made up of at least four initial components, which corresponds to the shortest oligomer that is flexible enough to close by reacting on itself. In contrast, according to the results obtained by Reiss and coworkers,¹³ 3,6-disubstituted phenanthrene offers a suitable geometry for macrocyclisation reactions between only two units: itself and a para-disubstituted benzene.

To obtain a suitable phenanthrene for the Perkin reaction, 3,6-dibromophenanthrene **1** was first generated in two steps from *p*-bromobenzaldehyde by a known procedure.²² **1** was then submitted to halogen-lithium exchange, and the resulting doubly lithiated intermediate reacted *in situ* with diethyl oxalate to give diethyl phenanthrenylene diglyoxylate **2** in 57% yield (Figure 2). Saponification of this diester gave the diglyoxylic acid **3** in 91% yield. This building block was reacted with commercially available 1,4-phenylene diacetic acid in high dilution to yield the targeted phenanthroparacyclophane-diene tetraester **4**, which could be separated from polymeric side products by simple column chromatography on silica. Whereas ¹H and ¹³C NMR characterisation did not allow to distinguish between a 1+1 and a 2+2 macrocycle, HRMS showed that the isolated product was resulting from a macrocyclisation reaction of only two components. This strained yet still flexible macrocycle was finally rigidified by oxidative photocyclisation to give the expected coronene tetraester **5** quantitatively.

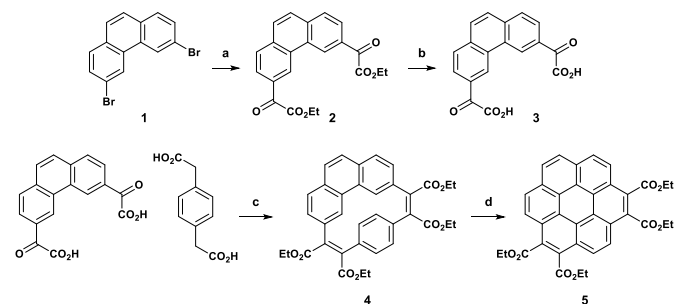


Figure 2. Synthesis of phenanthroparacyclophane-diene tetraester **4** and coronene tetraester **5**. (a) 1. *t*BuLi, THF, -100 °C, 3 h, 2. diethyl oxalate, THF, -100 °C, 30 min then rt for 90 min, 57%; (b) NaHCO₃, H₂O/EtOH (3:1), 95 °C, overnight, 91%; (c) 1. Ac₂O, NEt₃, high dilution in THF, 75 °C, 3 d, 2. EtBr, EtOH, DBU, THF, 75 °C, 2 d, 6%; (d) hv, I₂, PhMe/AcOEt (3:1), rt, 2 d, quant.

Although efficient, the production of 3,6-dibromophenanthrene is drastically limited by the scale of the reaction which can hardly exceed one gram of substrate to avoid [2π+2π] dimerisation. Other more convenient approaches were therefore considered for the synthesis of substituted 3,6-dibromophenanthrenes.

3,6-Dibromo-9,10-bisbutyloxyphenanthrene **6** appeared as a good candidate since it can be obtained in two steps by dibromination of 9,10-phenanthrenequinone,²³ followed by a reduction of the

ketones.²⁴ This easy, gram scale synthesis not only allowed a more convenient access to a 3,6-dibrominated phenanthrene, but the presence of ether chains also enhanced the solubility. Saponification of 9,10-bisbutyloxy-3,6-phenanthrenylene diglyoxylic ester **7**, prepared from **6** by the same approach as **2** from **1**, gave the corresponding diglyoxylic acid **8**. **8** and 1,4-phenylene diacetic acid were then condensed in high dilution to the macrocyclic tetraester **9** in 28% yield. Photocyclisation of the cyclophanediene **9** finally led to the expected and well soluble bisbutyloxy coronene tetraester **10** in 65% yield.

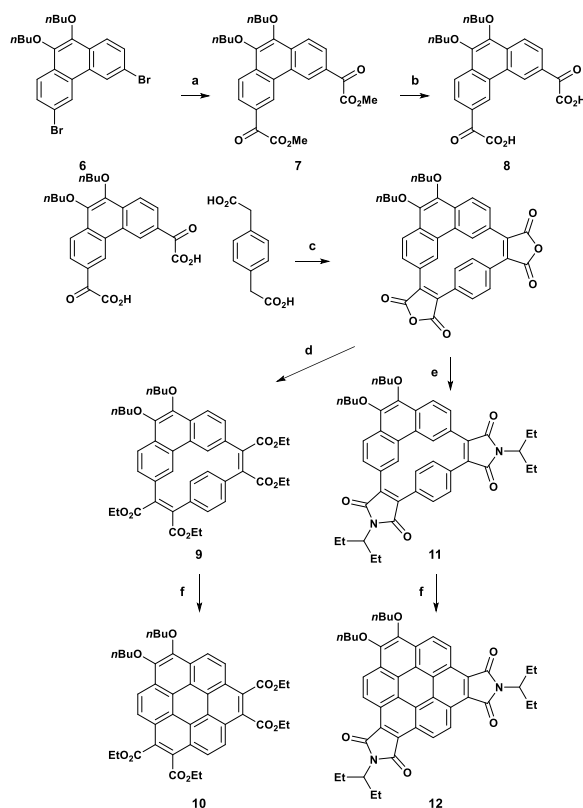


Figure 3. Synthesis of bis(butyloxy) coronenes by Perkin reaction. (a) 1. *t*BuLi, THF, -100 °C, 3 h, 2. dimethyl oxalate, THF, -100 °C, 30 min then rt for 90 min, 44%; (b) NaOH, H₂O/EtOH/THF (7:2:1), 75 °C, overnight, quantitative; (c) 1. Ac₂O, NEt₃, high dilution in THF, 75 °C, 3 d, not isolated; (d) EtBr, EtOH, DBU, THF, 75 °C, 2 d, 28%; (e) 3-aminopentane, THF, 75 °C, 2 d, 35%; (f) hv, I₂, PhMe/AcOEt (3:1), rt, overnight, 65% (**10**) and 30% (**12**).

The *in situ* esterification following the Perkin coupling reaction to avoid isolation of the initially formed anhydrides, can be replaced by the *in situ* formation of cyclic alkylimide functions by using a primary amine instead of a mixture of alcohol and bromoalkane. This variation yielded the paracyclophane-diene **11** with *N*-(1-ethylpropyl)-maleimide bridges. Mallory photocyclisation yielded bisbutyloxy coronene-tetracarboxylic diimide **12** in 30% yield. Due to its higher rigidity, **12** proved to be less soluble in organic solvent than its tetraethyl ester homologue **10**.

Single crystals of **5** suitable for XRD were obtained by slow diffusion of a dichloromethane solution of **5** into butanol. Single crystals of **10** suitable for XRD were obtained by recrystallisation of **10** in ethanol. Tetraester **5** forms columnar stacks in the crystal, with 3.398 Å between the slightly offset coronene

planes, implying π - π interactions between the aromatic cores (Figure 4).

Diether-tetraester **10** crystallises in a similar offsetted columnar arrangement, with a similarly close interaromatic distance of 3.409 Å.

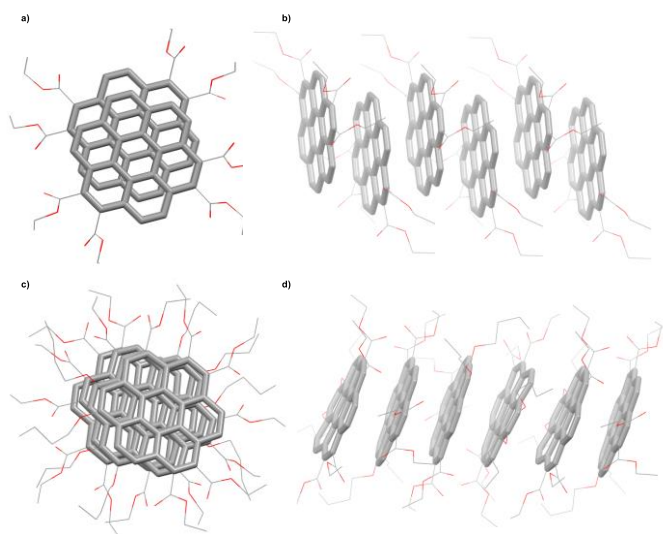


Figure 4. Coronenes **5** (a, b) and **10** (c, d). Left (a, c): one column seen along the crystallographic axis *a*. Right (b, d): one column seen along the crystallographic axis *c*. Hydrogens are omitted for clarity. Ether and ester groups = thin, aromatic cores = thick.

The absorption and emission spectra of the coronenes and their cyclophane-diene precursors were measured in dichloromethane at room temperature. (Figure 5). Using Coumarin 153 in ethanol as a standard,²⁵ the quantum yields of luminescence of **5**, **10**, **11** and **12** in dichloromethane were calculated. Ether-substituted coronenes **10** and **12** showed the highest quantum yield (18% each), while the fluorescence of **5** was somewhat weaker (11%). Whilst no fluorescence was apparent with the other macrocyclic precursors, **11** proved to be slightly emissive, with a quantum yield of ca. 1%.

Conclusions

While the Perkin reaction between aryleneglyoxylic and aryleneacetic diacids efficiently leads to the formation of conjugated macrocycles containing four or six building blocks, no macrocycle consisting of only two elements had yet been obtained by this approach. This was made possible by the development of building blocks based on phenanthrene whose two glyoxylic acid substituents are suitably oriented to allow the formation of a macrocycle using one complementary phenylenediacyclic acid unit. The resulting cyclophanes thus contain only two aromatic fragments, a phenanthrene and a benzene, orthogonal to each other, connected by two maleic bridges. The photocyclization of these compounds efficiently yields coronenes which are substituted by four carboxylic functions, with or without two further ether substituents. Highly substituted coronenes with a polar functionalization pattern are thus found to be straightforwardly accessible from

3,6-disubstituted phenanthrenes. They tend to stack with close π - π contacts in the crystal.

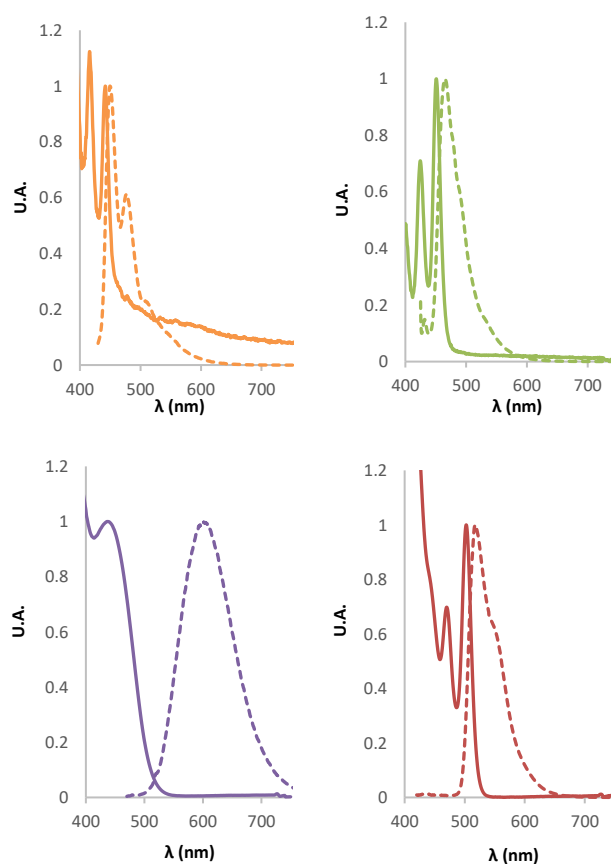


Figure 5. Normalised absorption (continuous) and fluorescence (dashed) spectra of **5** (top left), **10** (top right), **11** (bottom left) and **12** (bottom right) in dichloromethane at room temperature. Emission was measured upon excitation at 425 nm for **5**, 420 nm for **10**, 450 nm for **11** and 390 nm for **12**.

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