Graphene-like Hydrocarbons

International Edition: DOI: 10.1002/anie.201508180
German Edition: DOI: 10.1002/ange.201508180

Cyclization of Pyrene Oligomers: Cyclohexa-1,3-pyrenylene

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Abstract: *First synthesis of the macrocycle cyclohexa(1,3-pyrenylene) is achieved in six steps starting with pyrene, leading to a non-aggregating highly twisted blue-light-emitting material. The cyclodehydrogenation of the macrocycle offers a promising synthesis route to holey-nanographene.*

Shape-persistent macrocycles have become an important class of molecules owing to their unique optical and electronic properties and their role as building blocks of three-dimensional nanostructures, discotic liquid crystals, extended tubular channels, supramolecular guest-host complexes, and porous organic solids.[1] Seminal work on the synthesis of cyclohexa-*m*-phenylenes was carried out by Staab and Binnig in the 1960s[2] and recently functionalized cyclohexa-*m*-phenylenes were reported by our group.[1c] Macrocycles containing polycyclic aromatic hydrocarbons (PAHs) can be considered as monomeric and well-defined precursors to holey-nanographenes, which play an essential role in applications, such as supercapacitors, electrode materials, and energy storage.[3] Thus, the synthesis of specific graphene cutouts with holes is of importance to study the influence of the holes on the electronic structure.[4] Pyrene, the smallest *peri*-condensed aromatic hydrocarbon, has not been utilized to make a homo-macrocycle so far. Pyrene is of substantial interest in many applications owing to its optoelectronic properties. Despite this, only a few examples of oligomers and polymers containing pyrene have been studied.[5] Mainly, 1,1′-bipyrenyl, 2,2′-bipyrenyl, linear 1,6-disubstituted oligopyrenes, and [4]cyclo-2,7-pyrenylene have been investigated.[6] Recently we reported a polymer completely made up of pyrene units with highest degree of polymerization known for pyrene-containing polymers, poly-7-*tert*-butyl-1,3-pyrenylene for application in blue light-emitting diodes.[7] Herein we present the synthesis of the first pyrene-based macrocycle, namely cyclohexa-1,3-pyrenylene (**PyMC6**).

The synthesis of the pyrene macrocycle required appropriate coupling methods. The conceptual basis of this work was the 1,3- or 4,10-disubstitution on dihalo pyrene which we demonstrated recently.[7a,8] In that approach, the coupling reaction of pyrenes through 4,10-positions favors the formation of linear oligomers and polymers rather than leading to a highly strained macrocycle. This is verified through the single crystal analysis of the model compound 7′-(*tert*-butyl)-4,4′:10′,4′′-terpyrene obtained from coupling reaction of 4,10-diiodo-7-*tert*-butylpyrene with 4-pyrene boronic acid (Figure S1 in the Supporting Information).[9] The 1,3-coupling of pyrenes geometrically and electronically resembles that of *meta*-phenylenes leading to cyclohexa-*m*-phenylenes.[1c,2a,10] Therefore, we can take advantage of 1,3-substitution of pyrenes to synthesize the **PyMC6**. Pyrene (**Py**) was first mono-*tert*-butylated to afford 2-*tert*-butylpyrene (**1**), which was then treated with bromine (two equivalents) in CH_2Cl_2 at −78 °C to provide selectively the 1,3-dibromo-7-*tert*-butylpyrene (**2**) in 89 % yield (Scheme 1).[7a]

Our first attempt to obtain **PyMC6** was a direct route via Yamamoto coupling of monomer **2** under high-dilution conditions, which was not successful. Our alternative synthetic strategy was based on a chemoselective Suzuki cross-coupling reaction to get 3,3′′-dibromo-7,7′,7′′-tri-*tert*-butyl-1,1′:3′,1′′-terpyrene (**5**) followed by Yamamoto coupling (Scheme 1). To this end, dibromo pyrene derivative **2** was treated with an excess of *tert*-butyl lithium, which led to a halogen–metal exchange. The resulting carbanion was quenched with I_2 to obtain 1,3-diiodo-7-*tert*-butylpyrene (**3**) in 62 % yield.

Several attempts to selectively obtain the boronate derivative 2-[3-bromo-7-(*tert*-butyl)pyren-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**) have been made. First, lithiation using *n*BuLi and *tert*-butyl lithium were investigated but without success. The careful preparation of **4** was based on a Pd-catalyzed borylation reaction in dioxane. The borylation of compound **2** with 0.5 equivalents of bis(pinacolato)diboron was performed using a $[Pd(dppf)Cl_2]$ catalyst and KOAc as base in dioxane under reflux. However, the reaction yield of **4** was very low (< 15 %). A range of solvents, temperatures, and equivalents of bis(pinacolato)diboron were tested for optimization. The best results were achieved using one equivalent of bis(pinacolato)diboron and KOAc in anhydrous dioxane at 70 °C for 12 h. Using these conditions, dibromo pyrene **2** could be selectively converted into **4** in 62 % yield (Scheme 1).

The Suzuki cross-coupling reaction of the bis(iodo) compound **3** with two equivalents of the 1-bromo-3-boronic ester derivative **4** was performed at room temperature to provide the dibromo terpyrene analogue **5.** A chemoselective reaction was expected owing to the much higher reactivity of the iodide compared to that of the bromide. However, the reaction did not proceed at room temperature even for longer reaction times. In particular cases with such high steric hindrance or in the case of large aromatic systems, ambient conditions are not enough to promote the reaction. With the purpose of enhancing the coupling reaction between compounds **3** and **4**, the temperature was progressively increased.

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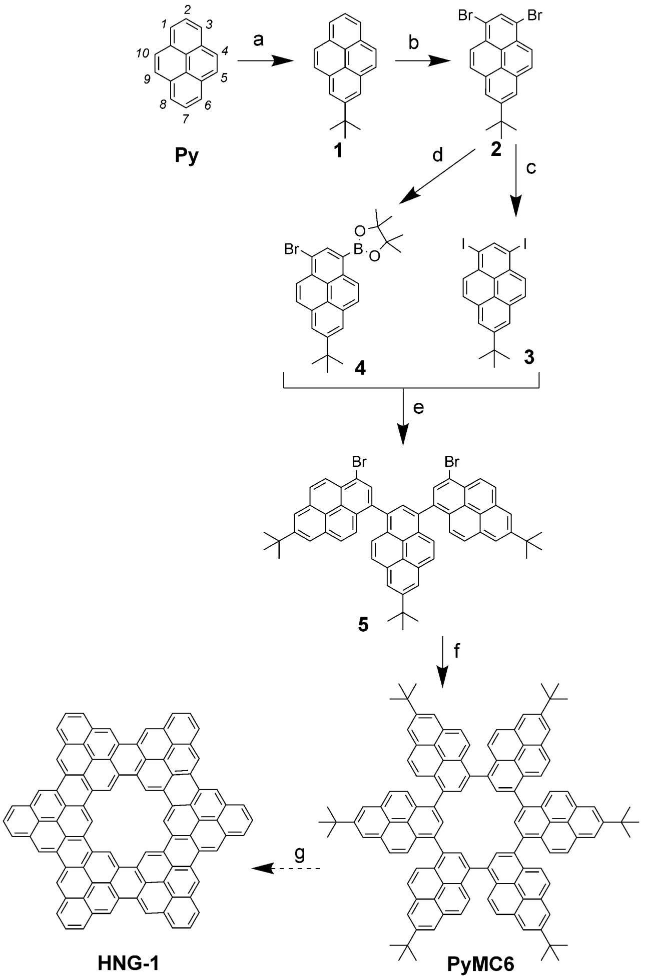
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201508180.



Scheme 1. Synthesis of pyrene macrocycle **PyMC6**. a) *tert*-butylchloride, $AlCl_3$, CH_2Cl_2, 0 °C, 65 %; b) Br_2, CH_2Cl_2, −78 °C, yield 89 %; c) *tert*-butyllithium, I_2, THF, −78 °C, yield 62 %; d) bis(pinacolato)diboron, KOAc, $[Pd(dppf)Cl_2]$, dioxane, 70 °C, yield 62 %; e) $[Pd(PPh_3)_4]$, K_2CO_3, Aliquat 336, toluene, water, 80 °C, yield 40 %; f) $[Ni(cod)_2]$, cod, 2,2′-bipyridyl, DMF, toluene, 80 °C, yield 25 %; g) $FeCl_3$, nitromethane, CH_2Cl_2, RT.

The optimal reaction temperature to promote the Suzuki reaction was found to be 80 °C without microwave radiation. Thus, the coupling between **3** and **4** using a $[Pd(PPh_3)_4]$ catalyst and K_2CO_3 as base in a 2:1 ratio of toluene/water mixture, at 80 °C afforded the functionalized terpyrenyl **5** in 40 % yield. Due to the hindered free rotation at room temperature, isomeric mixtures of a *syn*- and *trans*-atropisomer for the dibromo terpyrenyl **5** were formed, which is similar to the case of 7,7′,7′′-tri-*tert*-butyl-1,1′:3′,1′′-terpyrene[6a] and bis-3,4-benzopyrene.[11] Yamamoto coupling of **5** using $[Ni(cod)_2]$, 1,5-cyclooctadiene (cod), and 2,2′-bipyridyl in a mixture of dimethylformamide (DMF) and toluene at 80 °C led to **PyMC6** in dilute solutions ($c \approx 10^{-4}\,mol\,L^{-1}$; Scheme 1).

Only the geometry of the *syn*-atropisomer of **5** is suitable for the macrocycle formation, therefore linear oligomers such as linear sexipyrene (**Py6**), and higher oligomers were detected as byproducts. The *syn*-atropisomer **5** has two distinct possibilities to form **PyMC6** (Figure 1), wherein both central pyrenylene units can face each other in same or reverse direction (Figure 2). Careful gel permeation chromatography (GPC) analysis of **PyMC6** resulted in two different fractions, which were characterized by ^{1}H NMR spectroscopy, HPLC, MALDI TOF, and ESI mass spectrometry. These two fractions correspond to two different isomers of the pyrene macrocycle as shown by one single peak in the MALDI-TOF spectrum, two different ^{1}H NMR spectra and two peaks in HPLC. These two isomers (**PyMC6-1** and **6-2**) are stable even after several weeks at room temperature. The ^{1}H NMR spectra for the two isomers, **PyMC6-1** and **6-2** were measured in CD_2Cl_2 at 700 MHz (Figure 3). The spectrum of isomer **PyMC6-1** has two singlet and two doublet proton signals arising from six equivalent repeating pyrene units and is assigned to the macrocycle with the highest possible D_3 symmetry. The second isomer **PyMC6-2** could not be obtained in pure form as it partially contains isomer **PyMC6-1**. Its ^{1}H NMR spectra shows six doublets and six singlets, representative for an ABC system.

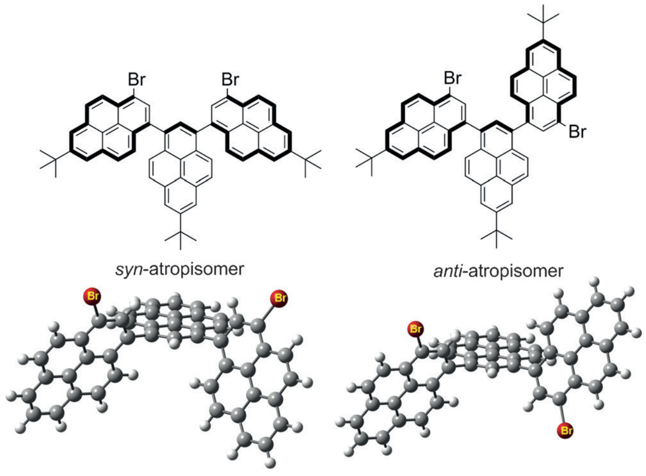


Figure 1. Possible isomers of dibromo terpyrenyl **5**, calculated with Gaussian 09, density functional B3LYP and the basis set 6-31G (d).

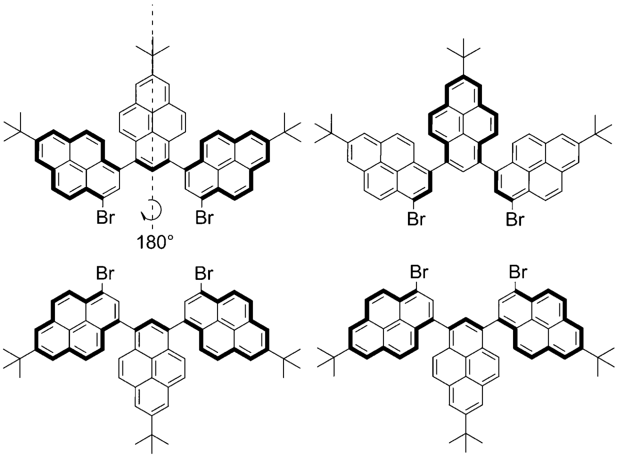


Figure 2. Possible combination of the *syn*-terpyrenyl **5** with a second reaction partner to give **PyMC6**.

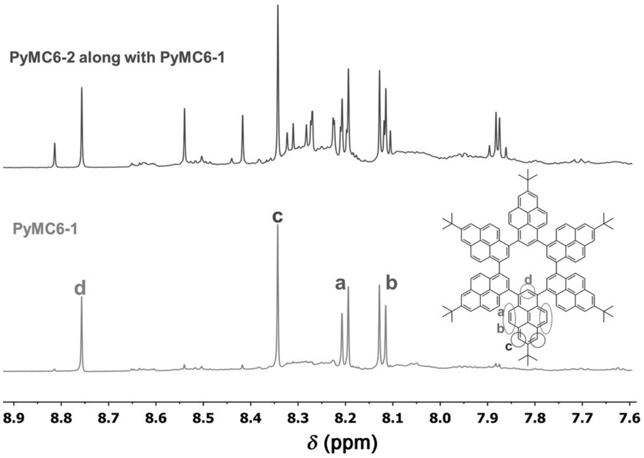


Figure 3. Aromatic region of proton NMR (700 MHz, 293 K, CD_2Cl_2) spectrum of **PyMC6** atropisomers.

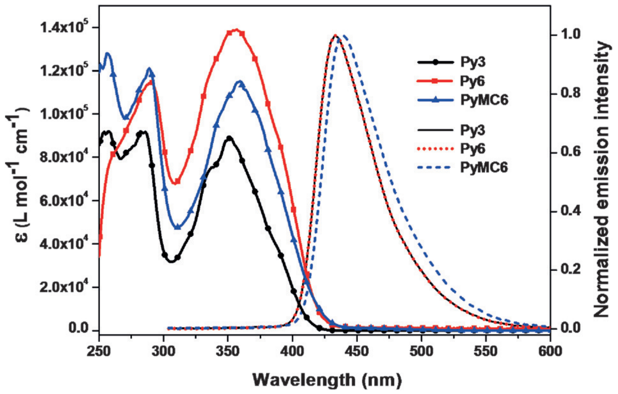


Figure 5. Extinction and normalized emission spectra of linear **Py3**, linear **Py6**, and **PyMC6** measured in CH_2Cl_2.

Calculations using Gaussian 09 with density functional B3LYP and 6-31G(d) as basis-set confirmed the existence of two isomers for the **PyMC6**, as shown experimentally. The two possible isomers **PyMC6-1** and **PyMC6-2** are depicted in Figure 4, where isomer **PyMC6-1** is energetically favored by 9.8 kcal mol^{-1}. For **PyMC6-1**, the pyrene units are aligned to each other with a dihedral angle of almost 69°, whereas for **PyMC6-2**, the dihedral angles are 57° and 108°. After heating to 200 °C in [D$_8$]sulfolane, **PyMC6-2** was entirely converted into **PyMC6-1** as evidenced by ^{1}H NMR spectroscopy (Figure S11).

Absorption and normalized fluorescence spectra of the **PyMC6**, linear sexipyrene (**Py6**), and 7,7′,7′′-tri-*tert*-butyl-1,1′:3′,1′′-terpyrene (**Py3**) solutions in dichloromethane are shown in Figure 5. The spectra exhibit an absorption peak maximum around 360 nm, corresponding to the π–π* transition of **PyMC6**. The broad absorption bands of **Py6** and **PyMC6** are slightly red shifted compared to that of **Py3** (352 nm) which can be attributed to the relatively strong twisting between the pyrene units not allowing extended conjugation upon increasing the number of repeating units. In terms of fluorescence, **PyMC6** is characterized by a broad structureless spectrum peaking at 439 nm with a small redshift compared to the emission peaks of **Py6** (433 nm) and **Py3** (432 nm). Twisted biaryls and related macromolecules typically display a strong solvatochromic effect as a consequence of the influence of solvent polarity and solvation energies on the molecular conformation and electronic transitions.[12] To investigate the solvent influence on the photoluminescence spectra of **PyMC6**, a series of solvents with increasing polarity (cyclohexane, dichloromethane, and acetonitrile) have been tested. As shown in Figure 6, an enhancement of the solvent polarity leads to a bathochromic shift of the fluorescence peak from 432 nm to 449 nm. This shift might be assigned to the formation of a charge-transfer state in solvents with higher polarity forcing the highly twisted molecules into a more planar structure.[12a,d,13] The fluorescence maximum of 432 to

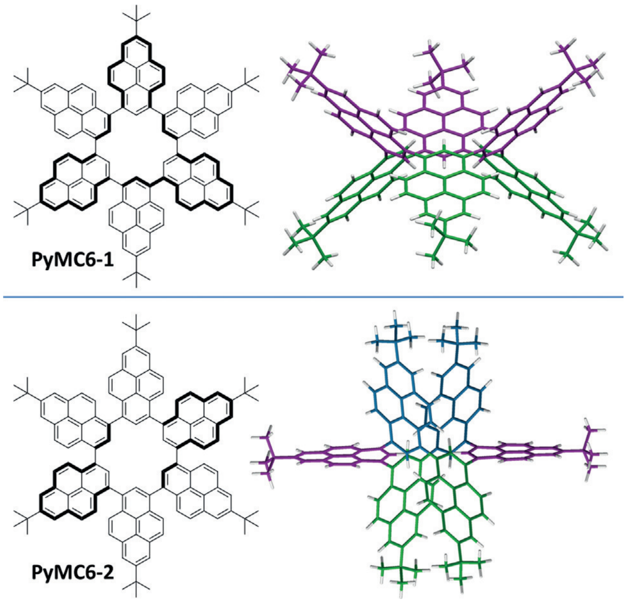


Figure 4. Isomeric structures of the two possible isomers, calculated with Gaussian 09, the density functional B3LYP and the basis set 6-31G (d).

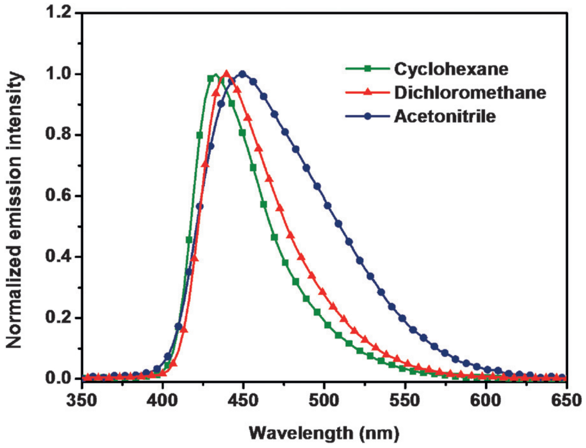


Figure 6. Solvatochromic effect. Normalized fluorescence spectra of **PyMC6** in cyclohexane (432 nm), CH_2Cl_2 (439 nm), and acetonitrile (449 nm) after excitation at 340 nm.

449 nm, depending on the solvent, emphasizes that the **PyMC6** shows blue fluorescence in solution. This provides an indication for blue emitting material with a fluorescence quantum yield (QY) of $\Phi_{\mathrm{PyMC}} = 0.91$, referenced against coumarin, which is in the range of that of poly-7-*tert*-butyl-1,3-pyrenylene (PPy; $\Phi_{\mathrm{PPy}} = 0.88$).[7,14]

The cyclodehydrogenation of **PyMC6** was carried out using $FeCl_3$ in dichloromethane at room temperature (Scheme S1). Effective fusion of adjacent pyrenes and formation of six new bonds by loss of 12 H atoms was ascertained from the solid-state MALDI-TOF measurement (Figure S3). However, under the reaction conditions employed, all the *tert*-butyl groups on pyrene units were removed and the dealkylated product was insoluble. Therefore, apart from the mass spectrum, no further structural characterization was obtained for the attained non-alkylated holey-nanographene (**HNG-1**) whose structural assignment must therefore be regarded as tentative.

In conclusion, we have successfully demonstrated a synthetic route to a six-membered pyrene macrocycle, thus extending the aromatic system of the cyclohexa-*m*-phenylene. Optical studies of the **PyMC6** showed no aggregation in solution owing to its persistent shape and large dihedral angles of 57° to 108°. With a fluorescence maximum at 439 nm in CH_2Cl_2, it shows blue-light-emitting characteristics. By heating to 200°C, the higher energetic atropisomer can be converted into the more stable one. The highly symmetric double-cone shape of the macrocycle is promising to study its supramolecular properties as a host system. From the cyclodehydrogenation results, the macrocycle **PyMC6** can be considered as a promising precursor molecule for well-defined "holey-nanographene" and detailed studies are underway using linear alkyl chains for better solubility and stability instead of *tert*-butyl groups.

Acknowledgements

We are grateful for the financial support from the European Research Council grant on NANOGRAPH and IRTG school 1404/2006-IRTG-001 (Self-Assembled Materials for Optoelectronic Applications) supported by the DFG and Korea.

Keywords: atropisomerism · cyclodehydrogenation · holey-nanographene · macrocycles · pyrene

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 418–421
Angew. Chem. **2016**, *128*, 427–431

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Received: September 1, 2015