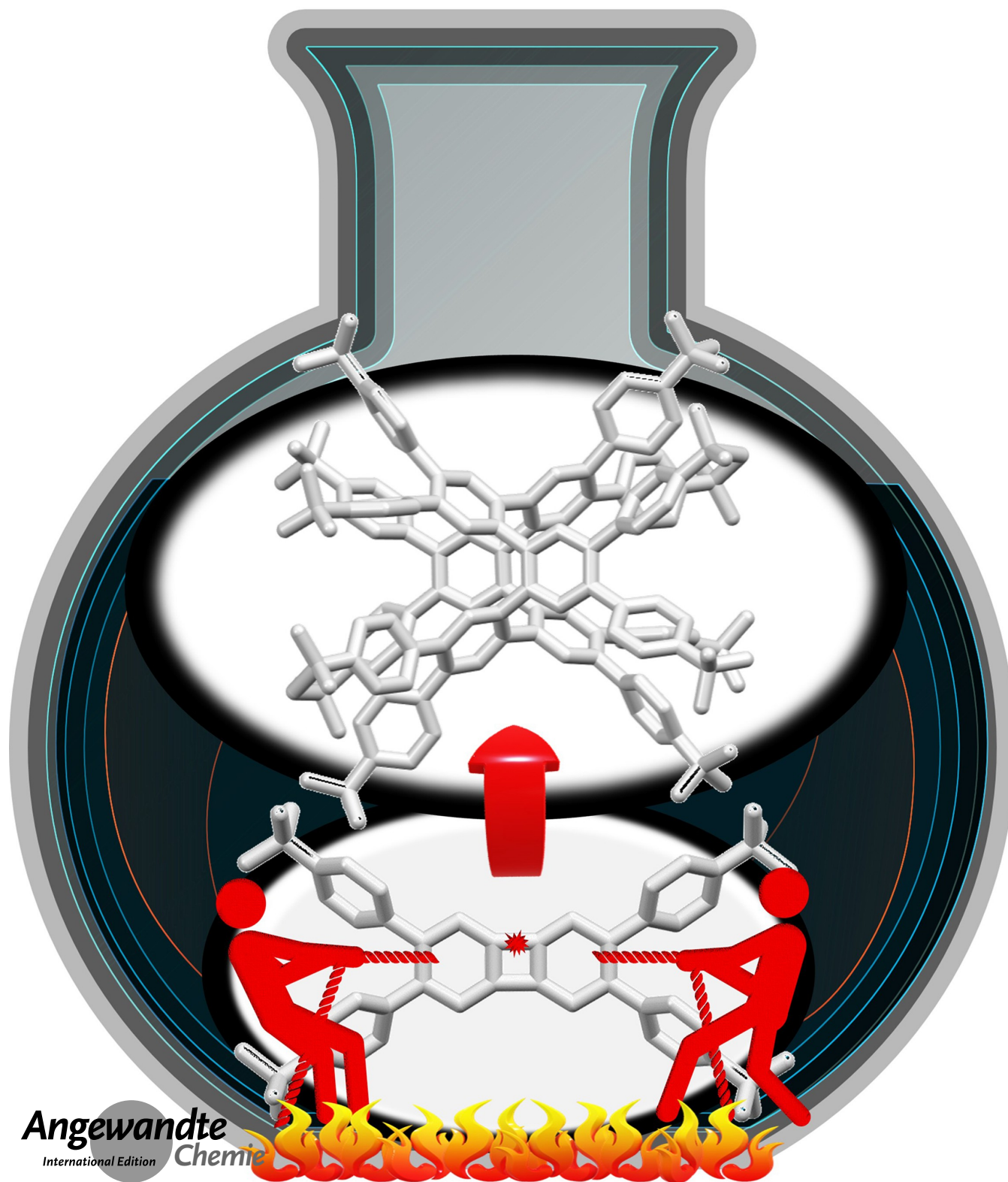


Macrocycles

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Thermolysis of Biphenylene toward Cyclo-*ortho*-phenylenes

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Abstract: The solvent and catalyst free thermolysis of biphenylenes at 350 °C furnishes [n]cyclo-*ortho*-phenylenes ([n]COPs, $n=4-10$) in one step and in high yields. At 400 °C biphenylene dimerizes into tetraphenylene, but lower reaction temperatures produce cyclooligomers. If suitably substituted, the oligomers are soluble and can be isolated and characterized. The products are exclusively cyclic. In the crystalline state, [6]COP displays an alternating crown-shaped conformation.

Aesthetically pleasing cyclophenylenes have recently attracted much attention. Cyclo-*para*-phenylenes ([n]CPPs)^[1] display size-dependent optoelectronic properties^[2] and possess cavities for host-guest chemistry.^[3] Linear polyphenylenes^[4] suffer from undefined end groups, which are absent in cyclophenylenes and beneficial for organic electronics.^[5] [n]CPPs are precursors for small molecular belts,^[6] some of which are carbon nanotube subunits.^[7]

There are no universal methods for the synthesis of cyclo-*meta*-phenylenes,^[8] cyclo-*ortho*-phenylenes^[9,10] or the combination of regioisomers.^[11] For *ortho*-phenylenes, this lack arises from 1,2-disubstituted benzene derivatives, which give arynes^[12] that cyclotrimerize^[13] or are employed in a Yamamoto reaction.^[14] To avoid triphenylenes,^[15] sterically demanding substituents at the monomers have been introduced giving higher oligomers due to steric repulsion. Acene- or pyrene-based [n]COPs **A**^[16] and **B**^[17] ($n=4-5$, yields: 1–14 %) were obtained (Figure 1) in low yields after extensive purification. Biphenyl-derived monomers avoid triphenylene formation, although transition-metal mediated tetraphenylene synthesis^[18] is accompanied by polymer formation. Wittig and Lehmann^[9] prepared cyclo-*ortho*-phenylenes such as **C** by treating 2,2'-dilithiobiphenyl with CoCl_2 . Isolation of the macrocycles formed in low yields was difficult due to the presence of linear oligophenylys. 3D models suggest that [n]COPs are suitable for charge storage,^[19] as phenylene density is high^[20] while cavities for counterions such as Li^+ are present. A tubular packing^[21] might provide channels for ion migration.

Thermolysis of biphenylene at 400 °C produces tetraphenylene in 96 % yield, but Lindow and Friedman^[22] comment

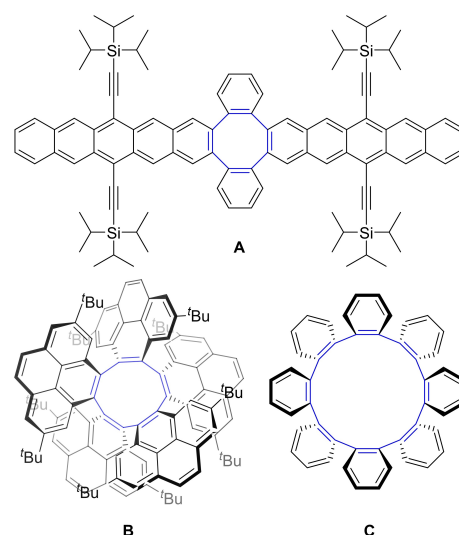


Figure 1. Examples of small [n]COPs in literature: bisacene-fused tetrabenzocyclooctatetraene **A**,^[16] [5]pyrenylene **B**^[17] and [8]cyclo-*ortho*-phenylene **C**.^[9]

in a footnote that oligomers, such as hexaphenylene (<1%), form. Here we report, that the thermolysis of arylated biphenylenes leads to cyclic oligophenylenes up to a 19-mer under optimized reaction conditions.

The temperature-dependent thermolysis of biphenylene^[23] was investigated (inert atmosphere, glass ampoule) from 300 °C to 400 °C for 60 min. The products were analyzed by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). Biphenylene, stable up to 325 °C, forms oligomers at 350 °C, evident from equidistant peaks ($\Delta m/z=152$) in the mass spectrum (biphenylene addition). At 375 °C, a mixture of cyclodimer to -decamer was detected (Figure 2 and SI, Figure S1 for full spectrum).

At 400 °C tetraphenylene is formed nearly quantitatively. We interpret the product selectivity in terms of the free biphenyl diradical concentration: at high temperature, dimerization terminates the reaction as tetraphenylene. At lower temperatures and longer reaction times oligomerization proceeds as a consequence of low biphenyl diradical concentration and, after addition, unfavorable conformations preclude immediate ring closure (see SI, Scheme S1 for a mechanistic proposal).^[24] Control experiments rule out the

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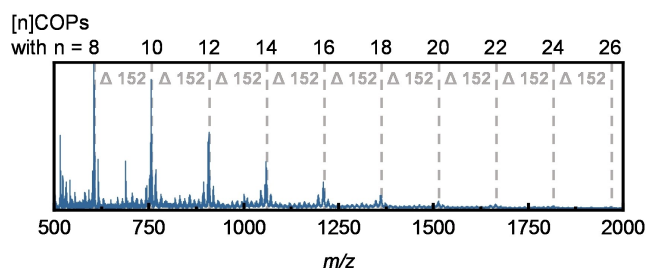
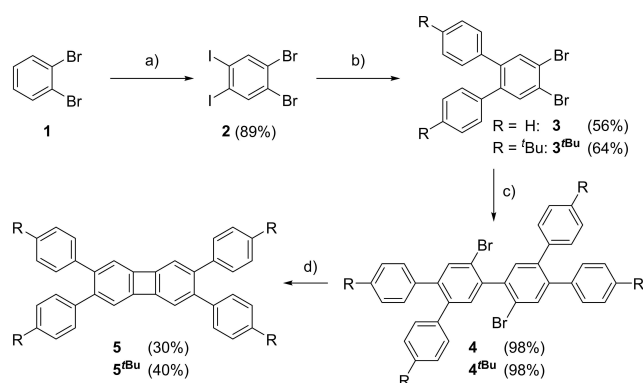


Figure 2. Mass spectrum (MALDI⁺, *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)) of oligomers after thermolysis of biphenylene at 400 °C.

homolysis of higher COPs to reparticipate again in the growth of the macrocycles (see below). Importantly, oligophenyl formation by hydrogen abstraction was not observed.

We could not isolate the thermolysis products due to poor solubility. Therefore, we prepared the symmetric tetraphenylbiphenylene **5** and tetra(4-*tert*-butylphenyl)biphenylene **5^{tBu}** in four steps (Scheme 1) starting from 1,2-dibromobenzene **1**. After its iodination to 1,2-dibromo-4,5-diiodobenzene (**2**, 89 %) and subsequent Suzuki coupling^[25] with arylboronic acids, the bisarylated dibromobenzenes **3** and **3^{tBu}** (56 % and 64 %, respectively) dimerized^[26] with *n*-butyllithium to 1,1'-dibromobiphenyls **4** and **4^{tBu}** (98 % for both). In the last step, intramolecular ring closure after lithiation and addition of ZnBr₂ and CuCl₂ furnished the target biphenylenes (30 % and 40 %, respectively).^[27] Compound **5** melts above 400 °C and exhibits an exothermic peak at 307 °C, indicative of homolytic ring-opening (differential scanning calorimetry, DSC, see SI, Figure S5). Thermolysis at 400 °C (Scheme 2) produces cyclooligomers with up to 19 biphenylene units (see SI, Figure S2).

Tert-butylphenylation increased the solubility with concomitant high yield (melting point of **5^{tBu}**: 336 °C, see SI, Figure S6) and better purification of the thermolysis products. At 335 °C no ring opening and product formation occurred in agreement to the lack of any signal indicating exothermic ring opening up to this temperature (see SI, Figure S7 for TGA/DSC analysis). In contrast, higher [n]COPs were observed at 400 °C (MALDI-MS, GPC) with a concomitant loss of *tert*-butyl groups (see SI, Figures S3, S4 and S8). Due to partial *de-tert*-butylation, separation of the individual, pure [n]COPs (flash column chromatography; gel-permeation chromatography, GPC) failed. Thermolysis is thus limited to a narrow temperature window: At 350 °C, thermal fragmentation of the *tert*-butyl groups is mainly avoided when reacting **5^{tBu}** for 1 hour and the product distribution is shifted towards larger [n]COPs (see SI, Figures S4 and S9 for the optimization of the reaction time).



Scheme 1. Synthesis of **5** and **5^{tBu}**. Reagents and conditions: a) I₂, NaIO₃, H₂SO₄, 0–40 °C, 5 h; b) phenylboronic acid or 4-*tert*-butylphenylboronic acid, Pd(PPh₃)₂Cl₂, K₂CO₃, toluene/methanol, 50 °C, 12 h; c) *n*-butyllithium, tetrahydrofuran, –78 °C–rt, 12 h; d) 1. *n*-butyllithium, 2. zinc(II) bromide, 3. copper(II) chloride, tetrahydrofuran, –78 °C–rt, 18 h.

Increasing the reaction time from 60 min to 180 min does not result in any significant change of the size distribution. This suggests that once a higher COP forms, it will not dissociate to serve as starting material for even higher COPs. Further support comes from the thermolysis of tetraphenylene at 400 °C which does not undergo any further oligomerization to higher COPs. Separation of the [n]COPs by recycling GPC (see SI, Figure S10) yielded dimer **6.2^{tBu}** (70 %), trimer **6.3^{tBu}** (10 %), tetramer **6.4^{tBu}** (7 %) and pentamer **6.5^{tBu}** (2 %) as colorless to yellow microcrystalline solids (Scheme 2) as well as remaining starting material (11 %). The products correspond to cyclooligomers from a [4]COP up to a [10]COP. The latter is the largest cyclo-*ortho*-arylene synthesized to-date. Single crystal analysis of **6.3^{tBu}** (plate-shaped single crystals grown from chloroform/methanol) provided constitutional and conformational proof of the [6]COP formation (Figure 3).^[28]

6.3^{tBu} crystallizes with 4 molecules per unit cell (see SI, Figure S11). The central 12-membered ring consists of alternating single and double bonds (1.50–1.51 Å and 1.39–1.41 Å, respectively), similar to the bond lengths of tetraphenylene (**7**).^[29] The same applies to the internal angles of the annulene ring (120.2°–126.1°). Compared to **7**, the dihedral angles are significantly increased (87.0°–119.5° vs. 64.4°–68.0°), resulting in the S-shape of the central cavity (Figure 3b), a consequence of the increased ring size. Due to steric hindrance, the outer *tert*-butylphenyl rings are twisted (49.9°–54.9°) with respect to the *ortho*-connected phenylene rings. The crystal packing of **6.3^{tBu}** displays isolated voids (as determined by Mercury 2022.3.0 © CCDC^[30] see SI, Figure S12). The solvent accessible surface area calculations predict that the radius to permeate the central 12-membered ring is 1.2 Å, significantly larger compared to tetraphenylene

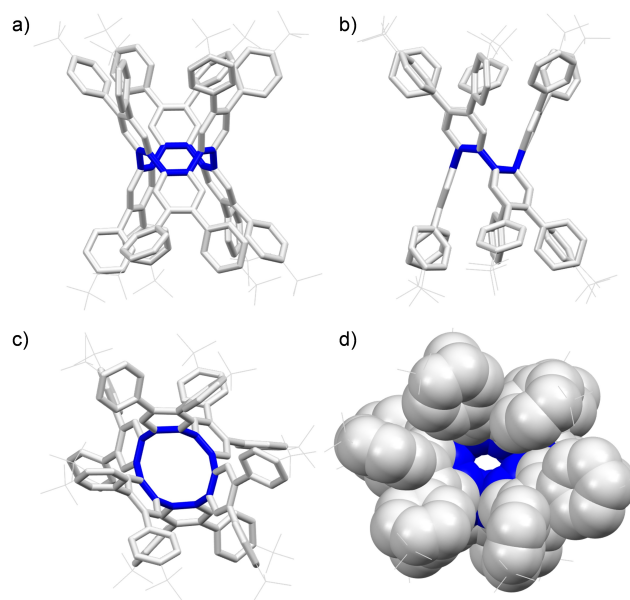
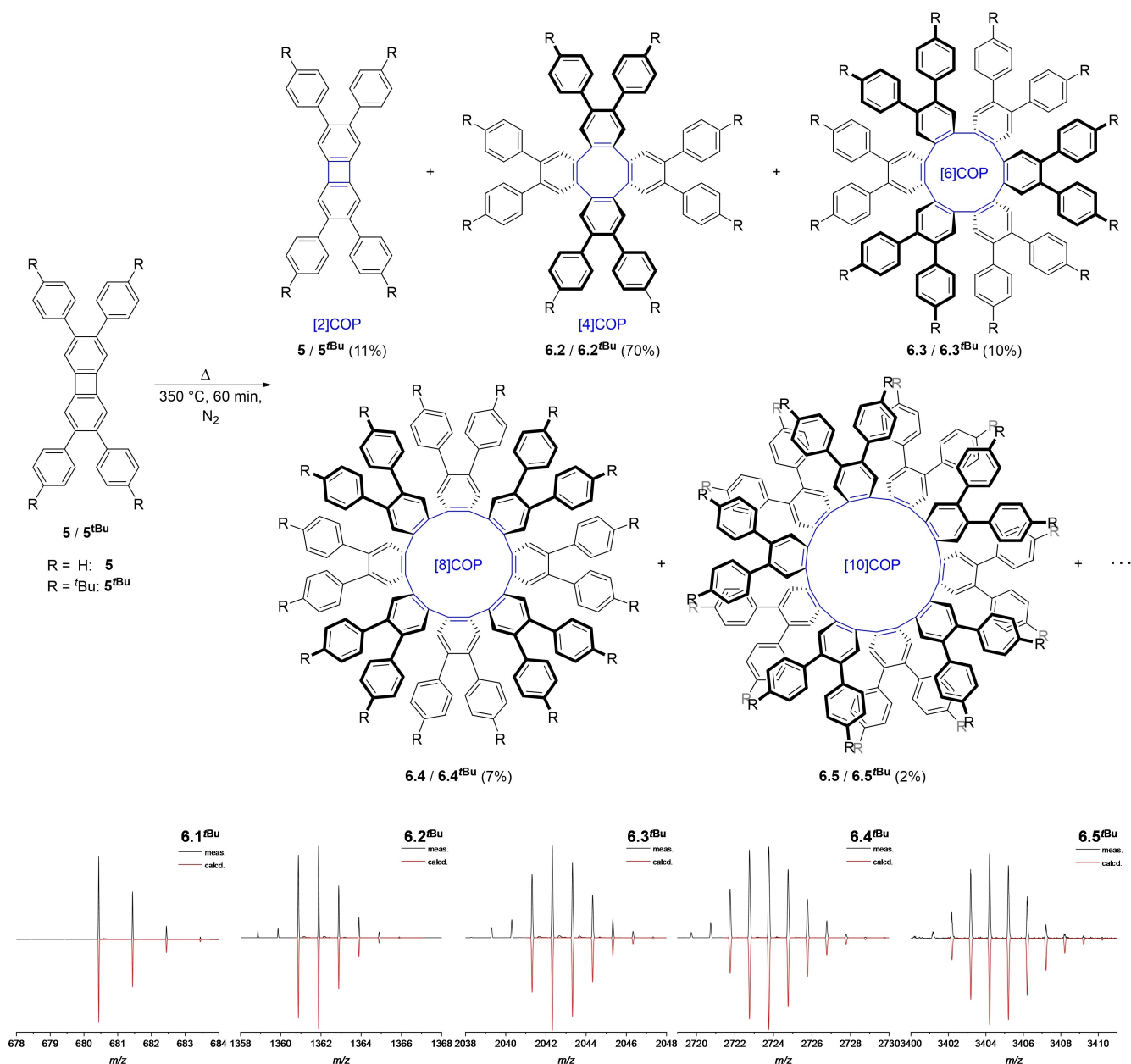


Figure 3. Single crystal structure of **6.3^{tBu}**, hydrogen atoms omitted and *tert*-butyl substituents reduced in size for clarity. a,b: Side-view. c: View along the central cavity. d: Space-filling model with view along the central cavity. The central annulene structure is highlighted in blue.



Scheme 2. Top: Homologous series of [n]COPs **6.x** and **6.x^{tBu}** obtained by thermolysis reaction of **5** and **5^{tBu}**. *x* denotes the number of monomers constituting the [n]COP. Yields refer to the isolated *tert*-butylated species. Bottom: Magnified regions of measured and calculated mass spectra (MALDI⁺, DCTB) of **6.x^{tBu}**. Thermolysis reactions were carried out in a sealed glass ampule under nitrogen atmosphere in a preheated muffle furnace at 350 °C for 60 min.

(0.3 Å, see SI, Figures S14a and b). The two cones formed by the *ortho*-phenylenes facing the same hemisphere should be able to accommodate guest species such as counterions upon reduction with radii ranging from 1.3 to 4.7 Å (see SI, Figures S13a–d). This will be investigated in the future.

The absorption and emission spectra of **5^{tBu}** and the [n]COPs **6.x^{tBu}** are presented in Figure 4 (see Supporting Information Table S1). **5^{tBu}** exhibits biphenylene bands at 365 nm/385 nm with an absorption onset at 400 nm. All [n]COPs display absorption onsets well below 400 nm. [n]COPs **6.x^{tBu}** show only a slightly broadened absorption band with little hypsochromic shift, a consequence of their

non-planar conformation. The conjugation between their *ortho*-terphenyl subunits is diminished by intramolecular *ortho*-phenylene repulsion at the perimeter of the central annulene. Absorptions are similar to those reported by Wittig.^[9] Emissions are broad and featureless with large Stokes shifts between 8.15–14.2×10³ cm⁻¹, indicating flexible structures in solution as a consequence of twisting motions between neighboring phenylenes.

To conclude, thermolysis of biphenylenes at 350 °C affords cyclo-*ortho*-phenylenes with up to 20 *ortho*-connected benzene rings. Solubilizing groups allow the isolation of the cyclic *ortho*-phenylene oligomers up to the decamer.

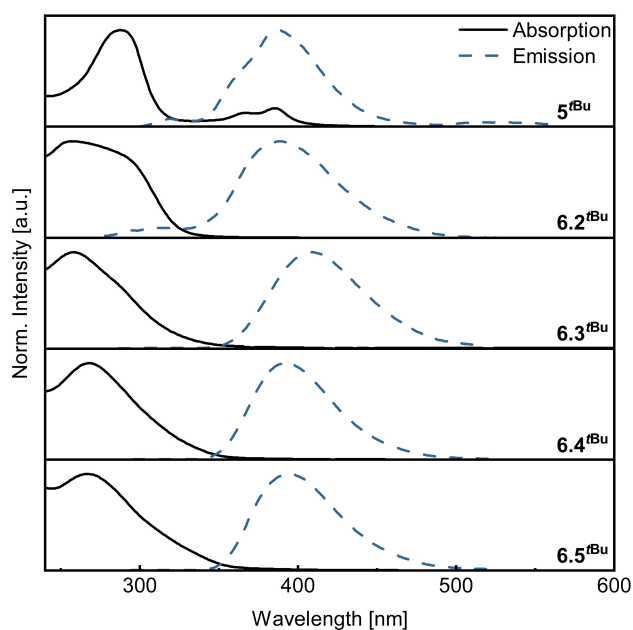


Figure 4. Normalized absorption/emission spectra of 5^{tBu} and the [n]COPs $6.x^{\text{tBu}}$ in DCM.

High-resolution mass spectra as well as the single-crystal structure of the trimer showed that the *ortho*-phenylenes are cyclic in nature, while the formation of linear congeners was not observed. This controlled thermolysis of pre-designed precursor molecules avoids the use of solvents, additives and catalysts which would complicate further work-up and separation (e.g. column chromatography and size-dependent precipitation); it appears as a valuable addition to the toolbox of synthetic chemistry. Reinvestigation of literature known biphenylenes under the conditions reported herein is expected to furnish exciting new cyclooligomers.

Supporting Information

The authors have cited additional references within the Supporting Information.^[31]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data related to this article are available via [heiDATA](https://doi.org/10.11588/data/AYVNYK) (institutional research data repository of Heidelberg University) under the following DOI: 10.11588/data/AYVNYK.

Keywords: Biphenylene · Cyclization · Cyclo-*Ortho*-Phenylene · Pyrolysis · Thermolysis

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