Chemistry–A European Journal
Research Article
doi.org/10.1002/chem.202403084
Chemistry Europe
European Chemical Societies Publishing
www.chemeurj.org

A Cycloparaphenylene Acetylene as Potential Precursor for an Armchair Carbon Nanotube

Eric Sidler,[a] Ramon Röthlisberger,[a] and Marcel Mayor*[a, b, c]

The bottom-up synthesis of carbon nanotubes (CNTs) is a long-standing goal in synthetic chemistry. Producing CNTs with defined lengths and diameters would render these materials and thus their fascinating properties accessible in a controlled way. Inspired by a recently reported synthesis of armchair graphene sheets that relied on a benzannulation and Scholl oxidation of a poly(p-phenylene ethynylene), the same strategy is applied on a cyclic substrate with a short, but well defined CNT as target structure. Herein we report the synthesis of a derivatized [12]cycloparaphenylene acetylene ([12]CPPA) that was accessible employing a *Sonogashira* macrocyclization. The obtained macrocycle is the largest [n]CPPA reported to date and displays bright turquoise fluorescence with a large quantum yield of 77%. The [12]CPPA can be transformed by a 12-fold benzannulation that converts each alkyne to a naphthalene and therefore allows formation of an armchair [12,12]CNT precursor. The final 72-fold Scholl oxidation to the [12,12]CNT turned out to be challenging and its optimization requires an improved synthetic strategy to produce large quantities of the final precursor. The developed approach poses a potential break through strategy for the production of CNTs and certainly incentivizes synthetic chemists to apply the same methodology for various conjugated macrocycles.

Introduction

The bottom-up synthesis of carbon nanotubes (CNTs) with defined lengths and diameters has been a long awaited goal of synthetic organic chemists.[1] The state-of-the-art synthetic approaches lead to a vast mixture of nanotubes with different sizes and chiralities including many impurities, which entail tedious purification processes such as complex template chemistry or size-exclusion techniques.[2,3] The fascinating properties of nanotubes with potential applications in a plethora of fields, heavily depend on its dimensions, rendering the controlled bottom-up synthesis of uniform CNTs highly sought after. While the controlled synthesis of carbon nanotubes is still to be achieved, various segments of CNTs have been synthesized and were heavily studied in recent years. The number of publications regarding different types of CNT segments has skyrocketed, and complete overviews are continuously reported in comprehensive review articles.[4–7] Not only are their molecular structure aesthetically pleasing and their syntheses an exciting challenge, they also exhibit interesting photophysical properties and were used as seeds for elongation into CNTs.[8] The first and structurally simplest segments of an armchair CNT, the so-called [n]cycloparaphenylenes ([n]CPPs), were first synthesized and isolated in 2008 by Bertozzi and coworkers (Figure 1a, left side).[9] The reported synthesis used bent 2,5-cyclohexadiene-1,4-diyl corner units as phenylene precursors which not only facilitated the macrocyclization, but also enabled the facile installation of strained phenylene units. Many different strategies have been developed since and CPPs of varying sizes are synthetically and even commercially accessible.[10–12] More recently, fully fused carbon nanobelts (Figure 1a, left side)[13] and even a *Möbius* strip[14] were reported by Itami and coworkers using *Yamamoto* homocoupling reactions on brominated ethylene-linked macrocycles. By utilizing ingenious *Diels-Alder* and retro-*Diels-Alder* reactions, even zig-zag carbon nanobelts were reported.[15,16] Apart from [n]CPP as direct subsegments of CNTs, [n]cycloparaphenylene acetylenes ([n]CPPAs), which bear alternating phenylenes and acetylenes, have also gained considerable attention due to their fullerene binding capabilities and strain-promoting reactivities.[17–19] Already in 1996, Oda and coworkers reported the synthesis of [6] and [8]CPPAs by successive *McMurry* macrocyclization, bromination and dehydrobromination reactions.[20] Alternative approaches also allow access to [n]CPPAs via alkyne metathesis[21] or Sonogashira couplings.[22]

In 2016, Dichtel and coworkers reported the synthesis of graphene nanoribbons[23] using the highly efficient benzannulation reaction they previously demonstrated on poly(*p*-phenylene ethynylene)s (PPEs).[24] The general structure and strategy is illustrated on the right-hand side of Figure 1a. Starting from a PPE of which every other phenylene has two naphthalene substituents, the alkynes were transformed to

[a] *E. Sidler, R. Röthlisberger, M. Mayor*
Department of Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel, Switzerland
E-mail: marcel.mayor@unibas.ch
[b] *M. Mayor*
Institute for Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), P. O. Box 3640, 76021 Karlsruhe, Germany
[c] *M. Mayor*
Lehn Institute of Functional Materials (LIFM), School of Chemistry, Sun Yat-Sen University (SYSU), 510275 Guangzhou, China

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202403084

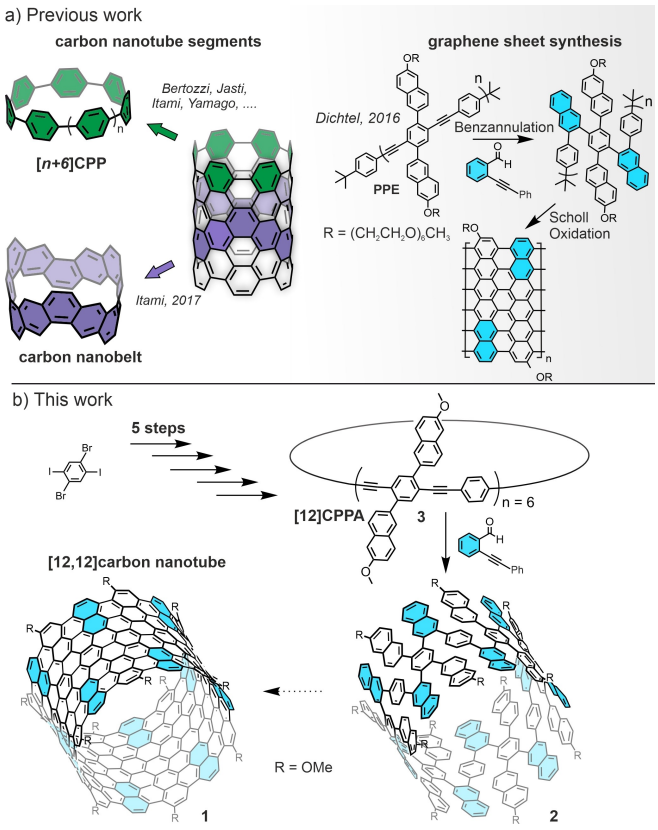


Figure 1. a) *Left:* The structure of CPPs and the carbon nanobelt, which are both segments of a CNT. *Right:* The previously reported synthesis of a graphene sheet by Dichtel and coworkers. b) Scheme displaying the general synthetic strategy towards a [12,12]CNT **1**.

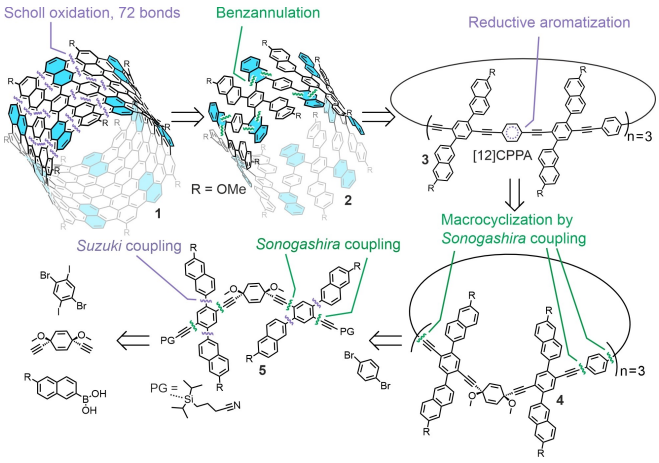
naphthalenes (in light blue) by a benzannulation,[25] followed by a *Scholl* oxidation to fully fuse the structure to a graphene sheet. Applying the same sequence of reactions on a derivatized [n]CPPA should lead to an armchair CNT with edge-decorating substituents for further derivatization or elongation (**1**, Figure 1b).

In this work we thus show our developed synthesis of a [12,12]CNT precursor **2** that is accessible in six steps by using a sequence of cross-coupling reactions and benzannulations from commercially available building blocks. The synthetic route involves the largest [n]cycloparaphenylene acetylene ([12]CPPA) reported to date, displaying a large fluorescence quantum yield. The final Scholl oxidation to the armchair CNT has proven to be extremely challenging and its careful optimization will keep us busy probably longer than appreciated.

Results and Discussion

Design & Retrosynthesis

The retrosynthetic analysis is shown in Scheme 1. In a first disconnecting step, the CNT **1** is disassembled by a 72-fold *Scholl* oxidation to the precursor **2**. *Scholl*-type oxidations are reportedly difficult to succeed in strained systems leading to

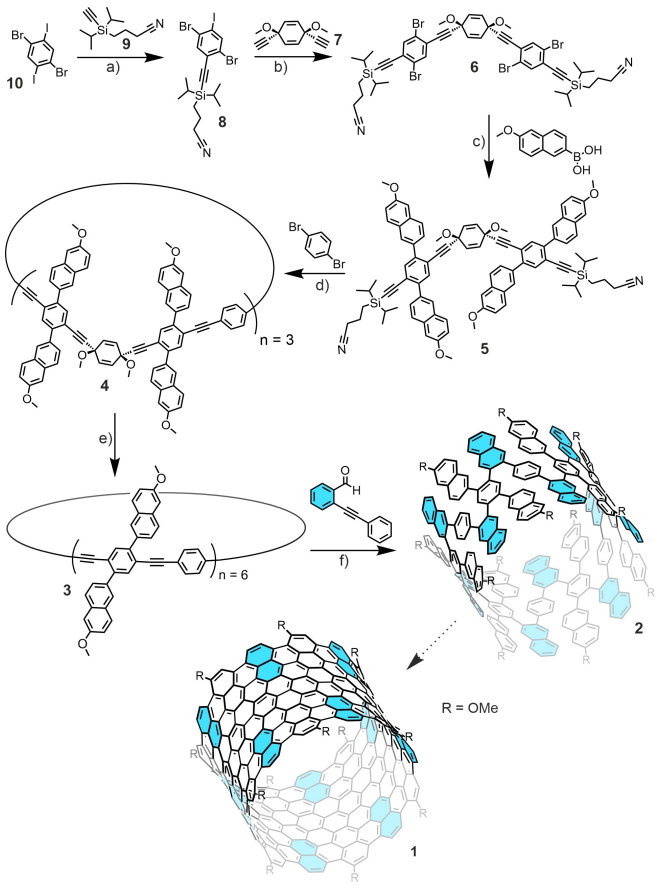


Scheme 1. Retrosynthetic analysis of the [12,12]CNT **1**.

side reactions and undesired rearrangements.[26] Thus, a [12,12]CNT was deemed to be of a reasonable dimension for a successful *Scholl* oxidation, especially since [12]cycloparaphenylene is well-characterized and shows good stability in an ambient environment.[9,27] The light-blue colored naphthalene units in **2** are formed by a 12-fold [4+2]cycloaddition benzannulation reaction from the [12]CPPA **3**.[24,25] The structure of **3** comprises 12 phenylene units within the CPPA backbone, where every other phenylene has two naphthalene substituents. The 1,4-ethynyl substituted phenylene without naphthalenes is perfectly suited to stem from a 2,5-cyclohexadiene corner unit that facilitates macrocyclization and allows build-up of strain in the reductive aromatization step from **4** to **3**. Literature reports on using cyclohexadienes as building blocks are abundant[4] and due to the angle of 1,4-substituted-2,5-cyclohexadienes, the most prevalent macrocyclization product is a trimer, although dimers and larger rings were also reported.[28] Thus, CPPA precursor **4** consists of three repeating units, each containing one cyclohexadiene moiety. Macrocycle **4** is disconnected by a *Sonogashira* coupling as macrocyclization reaction, leading back to the symmetric building block **5** and commercially available 1,4-dibromobenzene. Corner building block **5** can be built up from *Suzuki* couplings to attach the naphthalene units, and *Sonogashira* couplings to build the CPPA backbone, leading finally to commercially available 1,4-diiodo-2,5-dibromobenzene, 6-methoxynaphthalene boronic acid and literature known ethynylene substituted 2,5-cyclohexadiene.[28]

Synthesis & Characterization

The forward synthesis is displayed in Scheme 2 and starts with a statistically controlled *Sonogashira* coupling using 1,4-diiodo-2,5-dibromobenzene and [(3-cyanopropyl)diisopropylsilyl]acetylene (CPDIPSA, **9**)[29] as an acetylene substrate to yield mono-reacted product **8** in 35% yield. The use of CPDIPSA – a much more polar structural analogue of the well-known and commercially available (triisopropylsilyl)acetylene –



Scheme 2. Forward synthesis towards **1**. Conditions: a) $Pd(PPh_3)_2Cl_2$, CuI, THF/NEt_3 (3:1), rt, 16 h, 35%; b) $Pd(PPh_3)_2Cl_2$, CuI, THF/NEt_3 (3:1), rt, 24 h, 95%; c) $Pd(PPh_3)_4$, CuI, THF/H_2O (10:1), reflux, 16 h, 72%; d) 1. TBAF, THF, rt, 40 min 2. $Pd(PPh_3)_4$, CuI, THF/NEt_3 (3:1), rt, 20 h, 5%; e) $SnCl_2 \cdot 2(H_2O)$, HCl (1 N in diethyl ether), THF, −78 °C, 1 h, 37%; f) $ZnCl_2$, DCE, rt to 80 °C.

allowed simple separation of **8** from the doubly reacted side product and remaining starting material **10** by flash column chromatography (cc). The reaction can be easily scaled up to 20 g, allowing the production of several grams of **8**.

In a second twofold *Sonogashira* coupling, **8** reacted with literature known dialkyne **7**[28] at room temperature in order to benefit from the reactivity difference of aryl bromides and aryl iodides to yield **6** in 95% yield. In some cases, the reaction seemed to stall, upon which addition of additional copper iodide smoothly restarted the reaction and led to full conversion. In a subsequent fourfold *Suzuki* coupling, commercially available 6-methoxynaphthalene-2-boronic acid was coupled to the four aryl bromides on **6**, yielding corner unit **5** in 72% yield after purification by flash cc and two consecutive precipitations in a CH_2Cl_2/MeOH mixture. The CPDIPS protecting groups were then removed by treating **5** with 10 equivalents of tetrabutylammonium fluoride (TBAF) in THF. Without further purification, the deprotection mixture was directly subjected to standard *Sonogashira* coupling conditions using 1,4-dibromobenzene under high dilution (2 mM) at an elevated temperature of 80 °C. A sequence of flash cc and automated recycling gel-permeation chromatography (GPC) yielded pure trimeric macrocycle **4** in low yield of 5%. Smaller or larger ring sizes were not observed by mass spectrometry and most of the side products were open-chain oligomers and polymers, which were easily removed by GPC. The low yield can be explained by different issues. First, the designed synthetic pathway involves two substrates (**5** and 1,4-dibromobenzene) for the *Sonogashira* coupling. This design demands exact equivalents of **5** and 1,4-dibromobenzene to result in the right molecular structure of the target macrocycle. Imbalance of the equivalents directly influences the obtained yield such that human errors in weighing or presence of impurities have a large impact on the outcome. Designing an asymmetric corner unit that bears the aryl bromide and terminal alkyne in one molecule would rectify this issue and alkyne and aryl bromide would always be in a 1:1 stoichiometry. Synthetically it is, however, less appealing because it requires an asymmetric building block. Second, besides the angled corner units, there is no preorganization present in the system and thus the formation of open-chain oligomers and polymers is presumably favored.

With macrocycle **4** at hand, the aromatization of the 2,5-cyclohexadiene units was investigated. Initially, the literature-abundant conditions using in situ generated sodium naphthalenide at −78 °C in THF was employed.[9] While the molecular mass of **3** was observed in the crude mixture, purification by various techniques (flash cc, high-performance liquid chromatography (HPLC), GPC, recrystallization) proved to be impossible and intense broad peaks in the nuclear magnetic resonance (NMR) spectrum beneath the product signals remained. We then switched to the tin(II) chloride and hydrogen chloride conditions, developed by Yamago and coworkers.[30] Employing 3.3 equivalents of $SnCl_2 \cdot 2H_2O$ and 6.6 equivalents of hydrogen chloride indeed led to the formation of **3**, but we were unsuccessful in removing the impurities, which we identified by mass spectrometry to be rearrangement side products. We envisioned to reduce the amount of impurities by employing less reactive conditions and thus tried conditions that comprise a biphasic reaction mixture of CH_2Cl_2 and 1 N aqueous HCl with a large excess of $SnCl_2$.[31] While the formation of side products was indeed reduced, it was still impossible to purify [12]CPPA **3**. Guided by the observation, that lowering the reactivity seemed to improve the reaction, we decided to adapt the conditions and perform the reaction at −78 °C. For this reason, we changed the solvent to THF and used 1 N HCl in diethyl ether, which finally allowed us to isolate pure product **3** in moderate yields of 37% by a simple flash cc, which, to the best of our knowledge, is the largest reported [n]CPPA to date. The high symmetry of the large [12]CPPA **3** compared to **4** can be seen in the respective ^1H NMR spectra (Figure 2a). While for macrocycle **4** two sets of signals for the naphthalenes and their methoxy substituents were observed, only one set of signals is observed for **3**. Also, the proton of the newly formed phenylenes only shows one singlet (orange signal), which indicates free rotation of the phenylenes around the CPPA backbone axis. Figure 2a further displays the measured mass spectrum of the high-resolution matrix-assisted laser desorption/ionization (HR-MALDI) experiment of **3**, which is in well agreement with the calculated isotope pattern of the chemical formula of **3**.

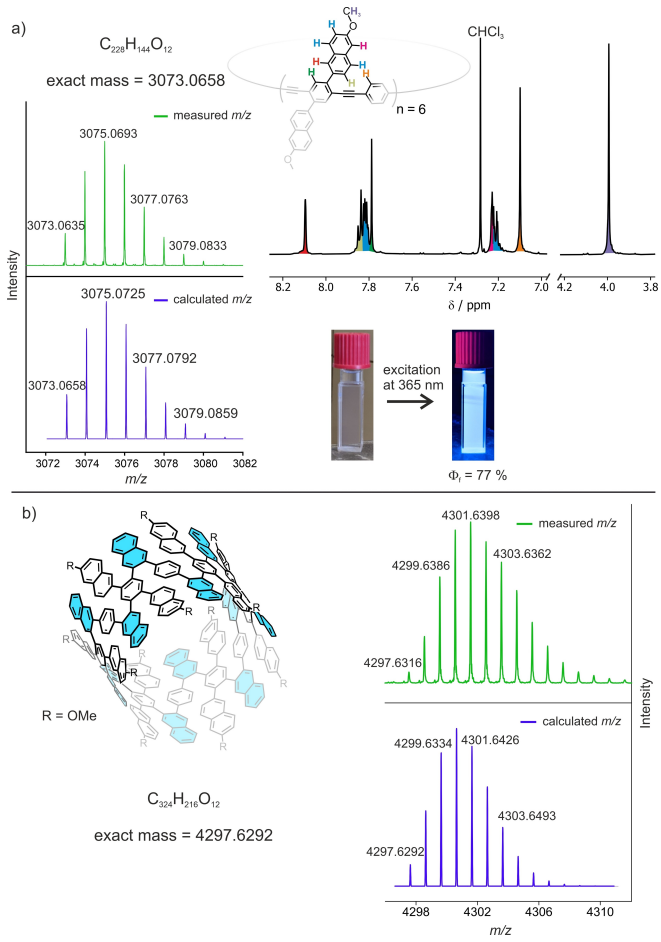


Figure 2. a) *Left:* Measured and calculated HR-MALDI-MS spectra of **3**. *Top right:* Selected regions of the ^{1}H NMR spectrum of **3**. Full assignment of the protons is represented by colored signals and colored protons in the molecular structure. *Bottom right:* Fluorescence of a solution of **3** (in CH_2Cl_2, c~10^{-6} M) upon excitation at 365 nm. b) *Left:* Structure, chemical formula and exact mass of **2**. *Right:* Measured and calculated HR-MALDI-MS spectra of **2**.

With the fully characterized [12]CPPA **3** in hand, we performed the benzannulation reaction. Commercially available 2-(phenylethynyl)benzaldehyde reacted with **3** and $ZnCl_2$ as a *Lewis* acid in 1,2-dichloroethane. Unlike in the reported conditions from Dichtel and coworkers, we initiated the reaction at room temperature and gradually increased the temperature to 80 °C.[24,32] We hypothesized that the relatively strained alkynes in **3** were much more reactive to a cycloaddition reaction than the reported PPEs, making them more prone to side reactions. The first few formed naphthalenes, however, release strain from the remaining alkynes, which thus require a higher temperature. The progress of the reaction can be easily monitored by MALDI mass spectrometry, where every intermediate is observable. After 4–5 hours, full conversion to the 12-fold benzannulated product was completed and the CNT precursor **2** was then isolated in low amounts by GPC (Figure S22). Identification of **2** was only possible by HR-MALDI mass spectrometry, where an overlap between the $[M]^+$ and $[M+H]^+$ ions was found (Figure 2b). The ^{1}H NMR spectum of **2** at room temperature is inconclusive and only very broad signals are observed, which we attributed to the high flexibility of the molecule. Since every alkyne has been transformed to a naphthalene, the strain within the backbone has been considerably reduced, enabling free rotations of the naphthalenes and thus adoptions of a wide range of different conformations, leading to broad signals in the NMR.

With CNT precursor **2** at hand, we attempted to synthesize CNT **1** by a 72-fold *Scholl* oxidation. In an initial try, we employed 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and Me_3SOH in CH_2Cl_2 at 0 °C, as reported by Dichtel and coworkers.[23] However, only decomposition was observed, deduced by the absence of masses in the region of starting material **2** or product **1**. The reaction conditions were then changed to $FeCl_3$ in CH_2Cl_2/$MeNO_2$, which resulted in the exact same observation as in the initial attempt. It should be noted that the purity of precursor **2** was difficult to assess and thus stoichiometry of the reaction was difficult to maintain, which was further hampered by the access to only very limited amounts of **2**, given the challenging prior reaction steps. Hence, optimization of the synthetic route is needed to increase accessibility of **2** and thus simplifying handling the final reaction.

Optical Properties

Absorption and emission properties of macrocyclization precursor **5**, macrocycle **4** and [12]CPPA **3** were investigated (Figure 3). Corner unit **5** shows its absorption maxima at λ = 271 nm with a high extinction coefficient of ε_{max} = 122 10^3 L mol^{-1} cm^{-1}. Its highest wavelength absorption band lies at λ_{max} = 340 nm. Upon excitation with 340 nm, an emission peak at λ_{em} = 420 nm was observed with a high quantum yield of ϕ_f = 66 %. After trimerization of **5**, macrocycle **4** displays a massively enhanced absorption with a maximum at λ = 262 nm and a very intense molar extinction coefficient of ε_{max} = 309 10^3 L mol^{-1} cm^{-1}. The strong increase in overall absorption

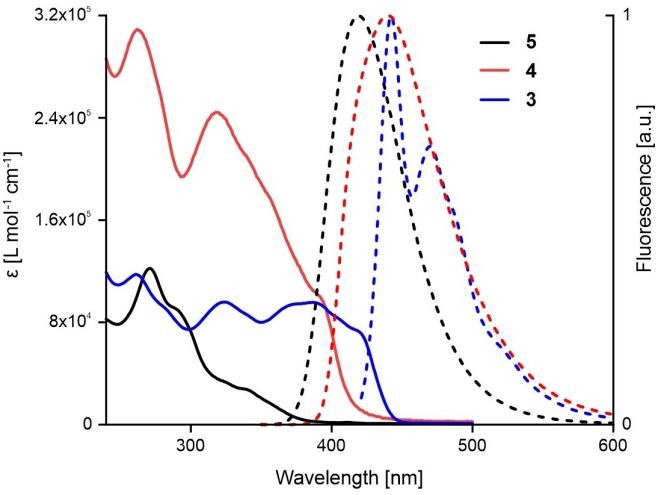


Figure 3. Absorption (solid line) and emission (dashed line) spectra of **5** (black), **4** (red) and **3** (blue) in CH_2Cl_2 (c~10^{-6} M). The molecules were excited at 340, 340 and 420 nm for **5**, **4** and **3**, respectively.

indicates moderate conjugation through the 2,5-cyclohexadiene units and rather suggests the presence of electronically separate chromophores within the macrocyclic backbone.[33] The highest wavelength absorption was redshifted by 51 nm to $\lambda_{max} = 391$ nm and excitation with 340 nm revealed an emission peak at $\lambda_{em} = 439$ nm, being redshifted by 19 nm compared to **5**. The quantum yield of **4** ($\phi_f = 65\,\%$) is comparable to **5**. In [12]CPPA **3**, the absorption maxima is at $\lambda = 262$ nm with an extinction coefficient of $\varepsilon_{max} = 117\ 10^3\,L\,mol^{-1}\,cm^{-1}$. However, the relative intensity of all transitions has levelled out and the molecule has comparable extinction coefficients throughout its whole absorption spectrum, suggesting the presence of a single chromophore species. The highest wavelength transition was redshifted even more to $\lambda_{max} = 420$ nm, indicating thorough conjugation around the macrocyclic backbone. Compound **3** displayed an emission spectrum featuring two peaks at $\lambda_{em} =$ 442 and 471 nm with a very small shoulder at 525 nm and a high quantum yield of $\phi_f = 77\,\%$. The vibronically resolved emission spectrum also indicates an increased rigidity, which is consistent with the general notion of CPPAs. Compared to other reported [n]CPPAs, **3** shows a comparable emission maximum but a redshifted absorption spectrum, presumably due to the electron-donating methoxynaphthalene substituents. Moreover, the fluorescence quantum yield of **3** is significantly enhanced in comparison to parent [n]CPPAs, for which values below 30 % were reported.[20,34,35]

The benzannulated product **2** displays a lack of fluorescence and a significantly blueshifted absorption spectrum compared to **3** and **4**, which is in line with the proposed flexibility and reduced strain of the compound (Figure S23).

Conclusions

We hereby demonstrated our synthetic investigations towards a [12,12]CNT **1** *via* a reaction sequence that was previously successfully employed for the production of graphene sheets. Inspired by the reported strategy, we developed a reliable synthesis to the final precursor **2** in six steps, employing a *Sonogashira* coupling as key macrocyclization step and benefiting from the implementation of 2,5-cyclohexadiene corner units. Analysis of the optical properties revealed very high quantum yields and small *Stokes* shifts in non-aromatized intermediate **4** and fully-conjugated intermediate [12]CPPA **3**, which, to the best of our knowledge, is the largest [n]CPPA reported to date. The final *Scholl* oxidation towards **1** has proven to be challenging and its optimization was prevented due to low available quantities of precursor **2**. We thus plan to improve the reaction sequence, in order to approach a sensible optimization strategy to obtain [12,12]CNT **1**. The reported approach, however, has the potential to become a break through strategy for the bottom-up synthesis of CNTs. In addition, the synthetic methodology is applicable for a variety of novel structures and provides inspiration for organic synthetic chemists.

Acknowledgements

The authors acknowledge generous financial support by the Swiss National Science Foundation (SNF grant number 200020-178808). M.M. acknowledges support from the 111 project (Grant No. 90002-18011002). Open Access funding provided by University of Basel is acknowledged. Open Access funding provided by Universität Basel.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Carbon nanotube · Nanohoop · Cycloparaphenylene acetylene · Macrocycle · Polyaromatic hydrocarbon

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Manuscript received: August 15, 2024
Accepted manuscript online: September 26, 2024
Version of record online: ■■, ■■

RESEARCH ARTICLE

Herein we demonstrate the synthesis and characterization of a naphthalene-decorated [12]cycloparaphenylene acetylene. Subsequent benzannulation reactions on the acetylenes allow formation of an extended macrocycle that potentially serves as a precursor for the synthesis of a defined armchair carbon nanotube. Attempts to fuse the compound to the carbon nanotube using Roland Heinrich Scholl's chemistry was so far unsuccessful.

*E. Sidler, R. Röthlisberger, M. Mayor**

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A Cycloparaphenylene Acetylene as Potential Precursor for an Armchair Carbon Nanotube