



Stepwise Lateral Extension of Phenyl-Substituted Linear Polyphenylenes

Ian Cheng-Yi Hou, Akimitsu Narita,* and Klaus Müllen*

Polyphenylenes (PPs) are unique polymers showing high mechanical strength and chemical stability, and having potential applications, for example, in proton transfer and gas-separation membranes. Moreover, phenyl-substituted linear PPs can serve as precursors for bottom-up syntheses of graphene nanoribbons (GNRs), a new class of nanoscale carbon materials that appear promising for nanoelectronics. Notably, lateral extensions of linear PPs with appropriate “branched” phenyl substituents, that is, avoiding spatial overlap of benzene rings in their projections into a plane, can lead to wider GNRs with modulated electronic and optical properties. GNRs with widths up to ≈ 2 nm are obtained, but synthetic methods to further expand PPs laterally so as to achieve even wider GNRs have not yet been developed. Here, phenyl-substituted linear PPs bearing two ethynyl groups at “outer” positions in each repeating unit, together with 3,4-diphenylcyclopentadienones bearing a trimethylsilyl-protected ethynyl group are used for stepwise lateral extension of the PPs, based on a sequence of Diels–Alder cycloadditions and deprotections. Each successive reaction step is corroborated by ^1H NMR and IR spectroscopy, as well as gel permeation chromatography, providing a new pathway toward branched polyphenylenes with linear-PP-backbones that can potentially serve as precursors of wider GNRs with tunable electronic bandgaps.

1. Introduction

Polyphenylenes (PPs) are polymers with exceptional properties,^[1,2] including outstanding mechanical strength as well as thermal and chemical stability. This qualifies them for applications under harsh conditions, such as proton transfer,^[3–7] electroanalysis,^[8]

and gas-separation^[9,10] membranes. Linear PPs with phenyl substituents can also serve as precursors for graphene nanoribbons (GNRs), nanometer-wide strips of graphene. The underlying concept is to appropriately design branched PP structures that can be fully planarized by C–C bond formation between the benzene rings, typically through oxidative cyclodehydrogenation.^[1,2,11–13] GNRs synthesized by such bottom-up methods have not only contributed to fundamental studies in condensed matter physics, but they also show potential for future applications in nanoelectronics, photonics, and quantum computing.^[14–16]

One of the most efficient methods to synthesize PPs is through the use of Diels–Alder cycloadditions between cyclopentadienone (CP) derivatives, usually 2,3,4,5-tetraarylcyclopentadienones, and alkynes leading to both linear and dendritic PPs.^[1,2] In comparison with other polymerization methods, typically involving transition metal catalyzed or

mediated reactions, Diels–Alder reactions, which proceed without metal catalysts or other reagents, also exhibit high efficiency.^[12,17] A_2B_2 -type Diels–Alder polymerizations between an A_2 monomer having two CP moieties and a bisalkyne serving as a B_2 monomer have been known for more than 70 years^[18,19] and have provided numerous linear PPs with a backbone of poly[(*p*-phenylene)-*ran*-(*m*-phenylene)].^[2] On the other hand, CP derivatives carrying an alkyne functional group can serve as bifunctional monomers that undergo AB-type Diels–Alder polymerization to yield linear PPs with surprisingly high persistence length.^[17,20] Moreover, PPs synthesized by this procedure exhibit higher degrees of polymerizations (DP) than those made by A_2B_2 -type polymerization.^[17,21,22]

In 2014, we have reported an AB-type Diels–Alder polymerization of tetraphenyl-CP **1a** leading to linear PP-**1a** with the poly[(*p*-phenylene)-*ran*-(*m*-phenylene)] backbone (Figure 1a). The weight-average molecular weight (M_w) of PP-**1a** exceeded $600\,000\text{ g mol}^{-1}$, which was much larger than values obtained with previous PPs prepared by A_2B_2 -type Diels–Alder polymerization. The structure of PP-**1a** can be projected into a plane without spatial overlap of benzene rings. “Planarization” of PP-**1a** through oxidative cyclodehydrogenation could thus provide structurally defined GNRs.^[17]

Moreover, we have demonstrated the synthesis of laterally extended linear PP-**1b** using CP-based monomer **1b** with

I. C.-Y. Hou, Prof. A. Narita, Prof. K. Müllen
Max Planck Institute for Polymer Research
Ackermannweg 10, D-55128 Mainz, Germany
E-mail: narita@mpip-mainz.mpg.de; muellen@mpip-mainz.mpg.de

Prof. A. Narita
Organic and Carbon Nanomaterials Unit
Okinawa Institute of Science and Technology Graduate University
1919-1 Tancha, Onna-son, Kunigami, Okinawa 904-0495, Japan

Prof. K. Müllen
Institute of Physical Chemistry
Johannes Gutenberg-University Mainz
Duesbergweg 10–14, D-55128 Mainz, Germany

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/macp.201900374>.

© 2019 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/macp.201900374

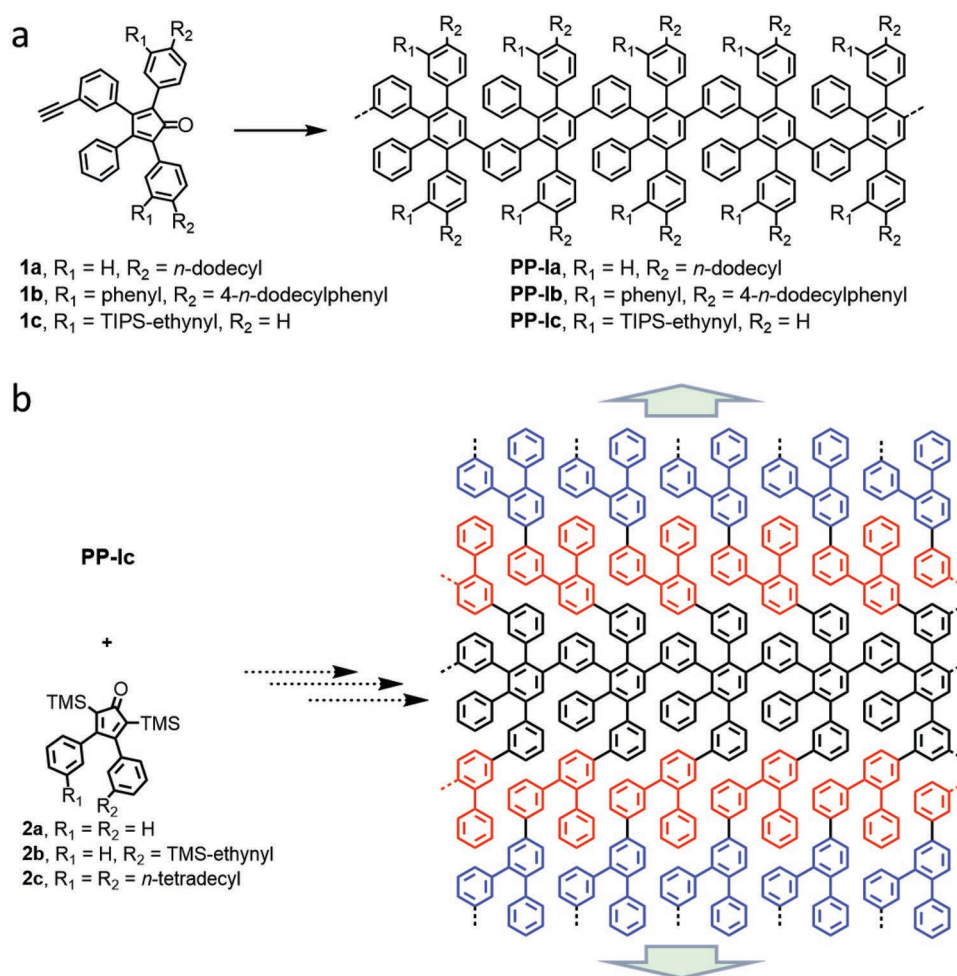


Figure 1. a) Diels–Alder polymerization of tetraphenyl-CPs **1a–c** to **PP-1a–c**, respectively. b) Proposed strategy for the lateral extension of **PP-1c** using a sequence of deprotections and Diels–Alder reactions with diphenyl-CPs **2b,c** to form PPs with architectures that are suitable for planarization into wider GNRs.

four extra phenyl rings in addition to the structure of **1a** (Figure 1a).^[21] **PP-1b** was planarized by cyclodehydrogenation furnishing an even wider GNR with a width of ≈ 2 nm. Remarkably, this quasi-1D GNR exhibited a smaller electronic bandgap than that of the narrower GNRs obtained from **PP-1a**.^[21] However, synthesis of linear PPs broader than **PP-1b** has remained elusive, although it would lead to even wider GNRs with tunable bandgaps essential for the development of GNR-based nanoelectronics.

Considering the synthetic complexity expected for further extension of monomer **1b** with more phenyl rings, as well as the importance of making PPs with different degrees of lateral extension, we have conceived a general approach to “broader” linear PPs in a stepwise manner. To this end, we employ linear PPs bearing two ethynyl groups at the “outer” positions in each repeating unit, which can be subjected to Diels–Alder reactions for “growth” in the lateral direction. We choose CPs that have trimethylsilyl (TMS)-protected ethynyl groups that allow lateral stepwise expansion of PPs through a sequence of Diels–Alder reactions and deprotections. Such a synthetic strategy, based on sequential Diels–Alder reactions, has been used for divergent

construction of dendritic PPs, but not previously considered for linear PPs (Figure 1b).^[1,23,24]

Here, we synthesized CP-based monomer **1c** bearing two triisopropylsilyl (TIPS)-protected ethynyl groups on the peripheral phenyl rings. Polymerization of **1c** provided **PP-1c**, which was subjected to deprotection to **PP-1d**, having ethynyl groups for further lateral growth (Figure 1a). As to the diene counterpart, 3,4-diphenyl-CP **2b**, with TMS-protected ethynyl groups, was utilized instead of the typical tetraphenyl-CP. It is this “trick” that avoids spatial overlap of benzene rings in the 2D projection of the resulting PPs (Figure 1b). After reaching the desired degree of lateral extension by repeating the sequence of the Diels–Alder cycloaddition with **2b** and deprotection, a reaction with 3,4-diphenyl-CP **2c** carrying solubilizing long alkyl chains can serve as an end-capping. The 2,5-positions of the CP cores of **2b,c** were substituted with TMS moieties as protecting groups, because non-substituted 3,4-diphenyl-CP can undergo irreversible Diels–Alder dimerization even at a room temperature.^[25] Diels–Alder cycloadditions of **PP-1d** with **2b**, deprotection, and subsequent Diels–Alder reaction with **2c** were corroborated by gel permeation chromatography (GPC), NMR,

and FTIR spectroscopy. Our preliminary attempts to planarize the resulting PPs through oxidative cyclodehydrogenation failed to give wider GNRs without defects, based on an analysis by UV–vis absorption spectroscopy. Nevertheless, our strategy for step-by-step lateral extension of PPs is potentially applicable to syntheses of different linear PPs with various degrees of lateral expansion, including those that potentially serve as precursors of GNRs with distinct structures.

2. Results and Discussion

2.1. Synthesis of Tetraphenyl- and Diphenyl-Substituted CP Building Blocks

2.1.1. Synthesis of Tetraphenyl-CP 1c

To synthesize 3-(*m*-ethynylphenyl)-4-phenyl-2,5-bis[*m*-(triisopropyl)silylethynyl]phenyl]cyclopenta-2,4-dien-1-one (**1c**) as the CP-based monomer for the polymerization to **PP-1c**, 1,3-bis(3-bromophenyl)acetone^[26] (**3**) was initially reacted with TIPS acetylene under Sonogashira conditions to give bis(TMS-ethynylphenyl)acetone **4**. In parallel, 3-bromobenzil^[17] (**5**) was functionalized with TMS-ethynyl groups and then deprotected with tetra-*n*-butylammonium fluoride (TBAF) to provide 3-ethynylbenzil (**7**). Subsequently, a Knoevenagel condensation between **4** and **7** afforded monomer **1c** in 59% yield (Scheme 1a).

2.1.2. Synthesis of Diphenyl-CP 2a–c

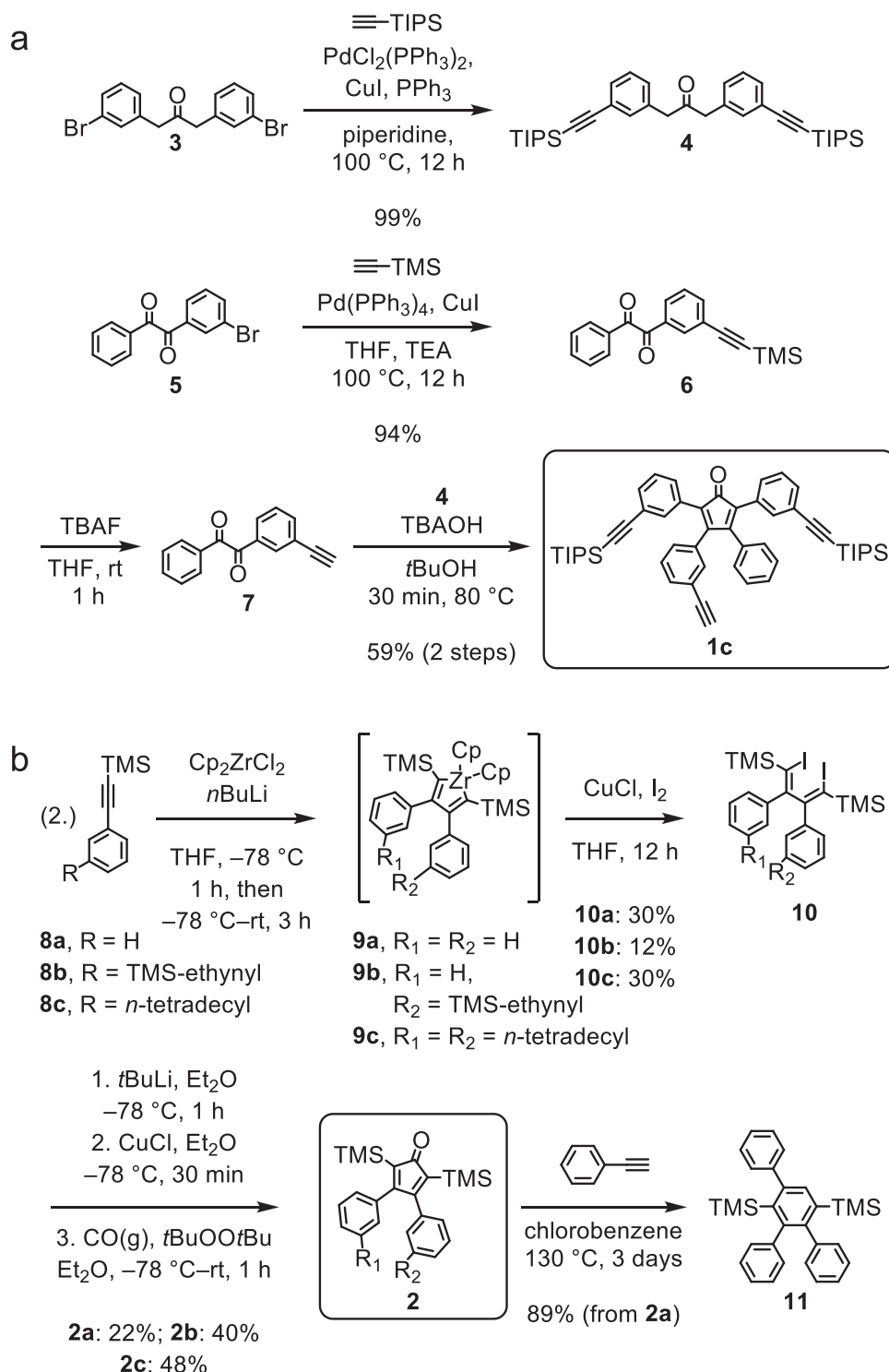
To synthesize 3,4-diphenyl-CPs **2a** and **2c**, we first carried out zirconocene-mediated dimerization of aryl TMS-acetylene derivatives **8a** and **8c**,^[27] forming Zr-metallacycle intermediates **9a** and **9c**, respectively (Scheme 1b).^[28] Attempts at direct iodination of **9a** with I₂ failed.^[28] However, after converting **9a,c** into organo-copper species in situ by reaction with CuCl, iodination of the copper species smoothly produced (1*Z*,3*Z*)-1,4-diiodo-2,3-diphenylbutadiene derivatives **10a,c** with high regio- and stereoselectivity, but moderate yields of 30% for both (Scheme 1b).^[28–30] **10b** was synthesized similarly, but starting from a mixture of **8a** and **8b**. Because large amounts of homocoupled products rendered the purification process tedious, **10b** was isolated in a much lower yield of 12%. We also tried, but failed to synthesize **10b** in a controlled manner through a tandem addition of **8a,b**, following reported conditions for coupling of other TMS alkynes.^[28,31,32] Next, iodo groups of **10a–c** were lithiated by treatment with *t*BuLi and converted again into organo-copper reagents by reacting with CuCl (Scheme 1b). We then tried to react the resulting organo-copper intermediates with different carbonyl sources for the formation of the corresponding CPs **2a–c**. After failures with carbon dioxide gas^[33] and oxalyl chloride,^[34] we found that the reaction proceeded with carbon monoxide gas, successfully furnishing 3,4-diphenyl-CPs **2a–c** after oxidation, in 22–48% yield (Scheme 1b).^[35] It was not possible to perform a one-pot synthesis of CP derivatives **2a–c** directly from **8a–c**, respectively, without isolation of the diiodo species **9a–c**.^[34]

After obtaining diphenyl-CPs **2a–c**, we first tested their stability and reactivity under conditions commonly used for Diels–Alder reactions between tetraphenyl-CPs and aromatic compounds bearing ethynyl groups. **2a** was heated at a concentration of 0.2 M at 130 °C in *o*-xylene for 3 days with no observable reaction, but could be recovered in more than 95% yield demonstrating significantly increased stability of the CP core with TMS substituents.^[33] This condition was used later in Diels–Alder reactions for lateral extensions of PPs (vide infra). Next, **2a** was heated with 1.1 eq. of phenylacetylene at 120 °C in chlorobenzene for 3 days until it was fully consumed. 1,4-Bis(trimethylsilyl)-2,3,6-triphenylbenzene (**11**) was isolated as the product in 89% yield with no byproduct, for the first time demonstrating the high reactivity of these diphenyl-CPs in Diels–Alder reactions (Scheme 1b).

2.2. Optimized Polymerization Conditions for Tetraphenyl-Substituted CP 1c

We initially attempted Diels–Alder polymerization of CP **1c** in neat phase, but only polymers with number-average molecular weights (*M_n*) lower than 7 kg mol^{−1} were obtained, although such conditions were reported to provide high molecular weight **PP-1a** from **1a**.^[21] Nevertheless, polymerization of **1c** in a highly concentrated Ph₂O solution (>2 M) at ≈140–150 °C proceeded efficiently, reaching *M_n* above 25 kg mol^{−1} in 12 h. Polymerization of **1c** at even higher temperature (>180 °C) led to **PP-1c** with a larger *M_n* of 65 kg mol^{−1}. However, such high molecular weight **PP-1c** turned out to be unsuitable for subsequent lateral extension studies (vide infra) since the products became insoluble in organic solvents after Diels–Alder reaction with **2b** or **2c**. Moreover, ¹H NMR analyses of **PP-1c** polymerized at ≈140 and 180 °C both showed a signal at 1.25 ppm (Figure 2a). This could be assigned to protons of TIPS groups that were attached to a benzene ring instead of an ethynylene unit,^[36] indicating an undesirable Diels–Alder reaction at the protected TIPS-ethynyl groups.

Therefore, we aimed at **PP-1c** with a smaller molecular weight by polymerizing **1c** at a lower concentration of 0.65 M and lower temperature of 120 °C, which was also employed to avoid the side reaction at TIPS-ethynyl groups. Under these conditions, polymerization became slower compared to rates of higher-concentration experiments. The increase of DP could be monitored by GPC (Figure 2b), and the *M_n* of **PP-1c** gradually developed to around 13 kg mol^{−1} after 78 h, together with disappearance of oligomers. The obtained **PP-1c** still gave a pale purple color in solution indicating the presence of a tetraphenyl-CP moiety at a chain end, which could interfere with the Diels–Alder reaction in the next step for the lateral extension (vide infra). **PP-1c** was thus end-capped by reaction with phenylacetylene at 160 °C overnight. After this reaction, the purple color disappeared, suggesting the absence of CP groups in the polymer chain. To our delight, **1c** exclusively reacted at the terminal alkyne moieties under these polymerization conditions at 120 °C, without showing a signal at 1.25 ppm (Figure 2a). Interestingly, the proton signals of TIPS-ethynyl groups split into two broad bands, peaking at 1.11 and 1.05 ppm. This can be attributed to *m*-(TIPS-ethynyl)phenyl



Scheme 1. Synthesis of a) tetraphenyl-CP **1c** and b) diphenyl-CP **2a–c**. THF, tetrahydrofuran; TEA, triethylamine; TBAOH, tetra-*n*-butylammonium hydroxide; Cp₂ZrCl₂, zirconocene dichloride.

groups that are present in different environments where those with two *ortho* phenyl groups (H_{a1} and H_{a2}) are more shielded (Figure 2a). Moreover, matrix-assisted laser desorption–ionization time-of-flight mass spectrometric (MALDI-TOF) analysis of treated PP-**1c** revealed peaks at an *m/z* corresponding to

the mass of tetramers to decamers. There, all TIPS-protecting groups remain intact while a phenyl group was attached through end-capping, although an ethynyl group at the other end was presumably oxidized (Figure S1, Supporting Information).

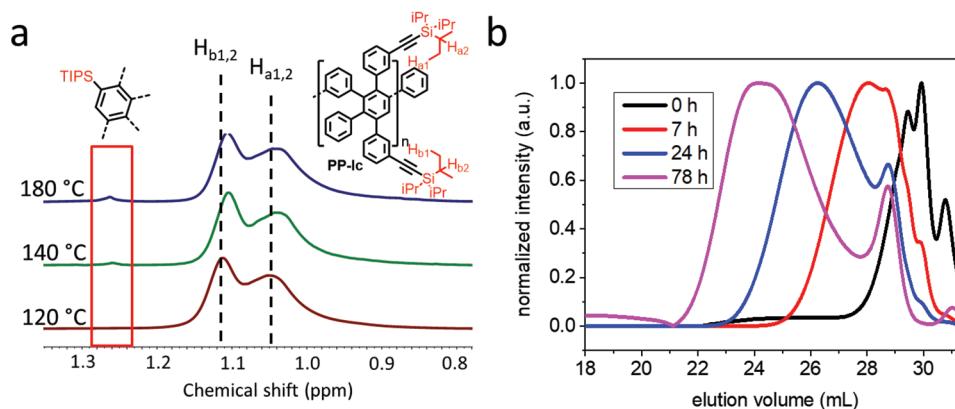


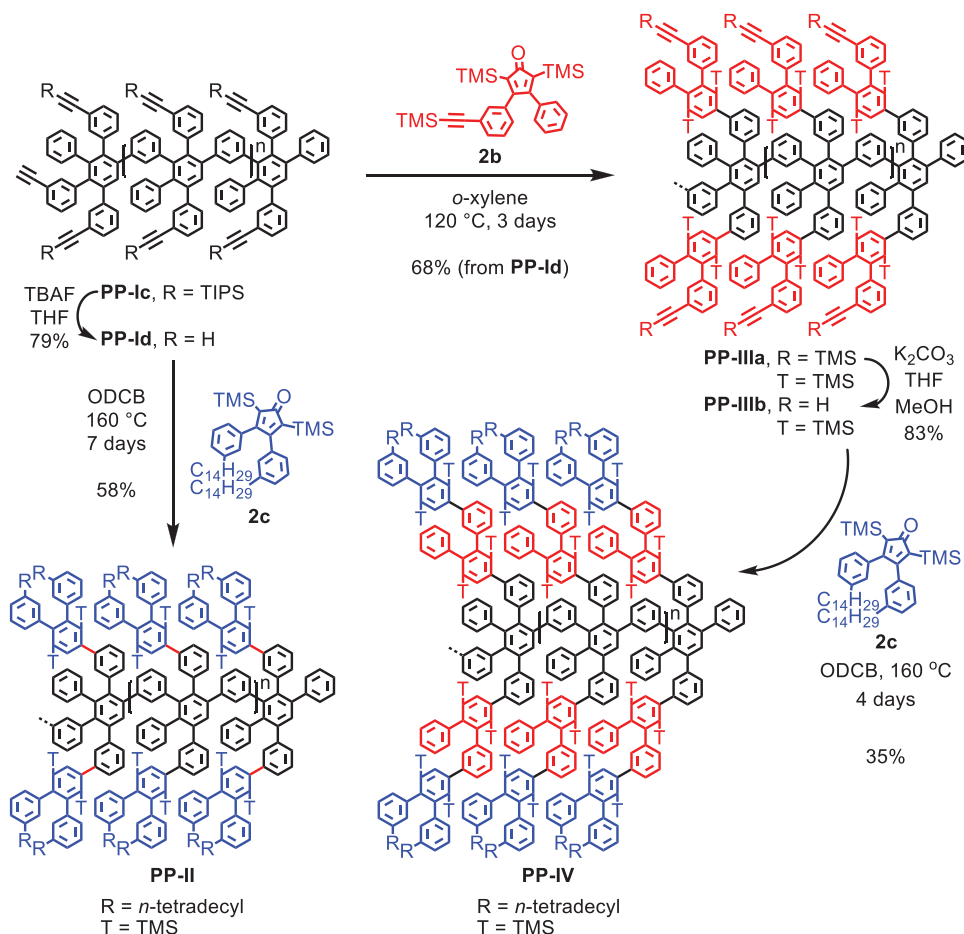
Figure 2. a) ^1H NMR signals of TIPS groups of **PP-Ic** polymerized at different temperatures, measured in CD_2Cl_2 at 290 K. b) GPC analysis at different times during polymerization of **1c** forming **PP-Ic** at 120 °C. (Solvent: THF. Flow rate: 1 mL min $^{-1}$. Temperature: 30 °C.)

2.3. Lateral Extension of **PP-Ic**

2.3.1. Extension of **PP-Ic** toward **PP-II** and **PP-IIIa**

PP-Ic with a M_n around 13 kg mol $^{-1}$ was next subjected to a sequence of deprotection and Diels–Alder cycloaddition with the diphenyl-CPs **2b** and/or **2c** for lateral growth (**Scheme 2**).

First, a dilute solution of **PP-Ic** in THF was reacted with TBAF to remove TIPS-protecting groups, furnishing **PP-Id** with multiple peripheral ethynyl functional groups as evidenced by ^1H NMR. The split signals of TIPS functional groups (vide supra) of **PP-Ic** at 0.9–1.2 ppm completely disappeared in the ^1H NMR spectrum of **PP-Id**, with simultaneous appearance of signals of ethynyl groups centered at 3.0 ppm, suggesting complete



Scheme 2. Lateral extension reactions of **PP-Ic**.

deprotection (Figure 3). The ethynyl signals of **PP-Id** were also present as two bands induced by different environments surrounding *m*-ethynylphenyl moieties (vide supra).

PP-Id retained good solubility in THF and other common organic solvents, which allowed further Diels–Alder reactions of the terminal alkynes. **PP-Id** thus reacted either with diphenyl-CP **2c** to afford **PP-II** decorated with alkyl chains, or **2b** to give **PP-IIIa**, possessing TMS-ethynyl groups ready for further expansion. The reaction of **PP-Id** with **2c** in *o*-dichlorobenzene (ODCB) at 150 °C produced **PP-II** in 48% yield. The reaction of **PP-Id** with **2b** in *o*-xylene at 120 °C, where the lower reaction temperature prevented reaction with TMS-protected internal alkynes (vide supra), produced **PP-IIIa** in 65% yield (Scheme 2). During these conversions, gel formation was commonly observed. This could explain the relatively low yields, especially for **PP-II**. The ¹H NMR spectrum of **PP-II** and **PP-IIIa** demonstrates complete conversion of all ethynyl groups since their signals at 3.0 ppm vanish (Figure S23, Supporting Information and Figure 3). On the other hand, TMS signals at −1.0 to 0.5 ppm emerge, which can be assigned to three different TMS groups introduced by the addition of diphenyl-CP **2b**. The signals of TMS groups on benzene rings at −1.0 to 0.0 ppm are also split into two bands for reasons similar to **PP-Ic** and **PP-Id**. TMS groups on ethynylene moieties are less shielded, and their signals appear at a lower field of about 0.0–0.5 ppm (Figure 3). IR spectroscopy further confirms these structural features (Figure 4). There is no signal above 3300 cm^{−1} for **PP-II** or **PP-IIIa**, suggesting a full conversion of ethynyl groups, integrated into benzene rings. Moreover, **PP-Ic** and **PP-IIIa**

possess a peak at 2154 cm^{−1} that is not observed for **PP-II**. This peak can be assigned to weak absorption of the C≡C stretching of silyl ethynyl groups^[37] that exist in the structure of **PP-Ic** and **PP-IIIa**, but not **PP-II**. Furthermore, the presence of TMS groups in **PP-II** and **PP-IIIa** is demonstrated by observation of sharp C–Si stretching peaks at 1247 cm^{−1} and strong bands at 837 cm^{−1} (Figure 4). It is worth mentioning that there are weak bands at around 1715 cm^{−1} for **PP-II** and **PP-IIIa** (Figure S4, Supporting Information), which are most likely overtones of the strong absorption band at 837 cm^{−1}. However, they could also point toward residual carbonyl groups due to incomplete carbon monoxide extrusion after Diels–Alder reaction.

2.3.2. Extension of **PP-IIIa** toward **PP-IV**

TMS-protecting groups of **PP-IIIa** can be removed, regenerating Diels–Alder reactive ethynyl groups for further reactions. To prevent possible removal of TMS groups on phenylenes, the deprotection reaction was conducted under milder conditions by reacting with K₂CO₃ in THF/MeOH (2/1) as cosolvents. To our delight, the polymer retained good solubility even in such a polar solvent combination during deprotection, resulting in fully deprotected **PP-IIIb** in high yield (Scheme 2). In the ¹H NMR spectrum of **PP-IIIb**, signals of TMS-ethynyl groups are completely gone, while those attached to benzene rings remain, confirming good selectivity and efficiency of the deprotection reaction (Figure 3). Unlike those for **PP-Id**, signals of the ethynyl groups on **PP-IIIb** exhibit a single broad band centered

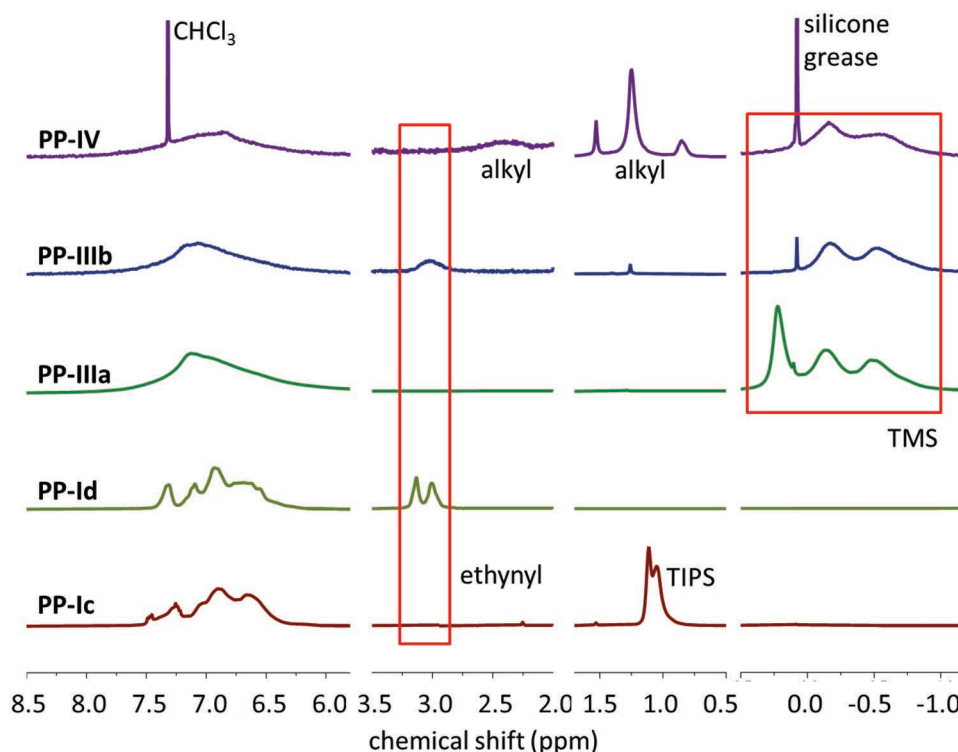


Figure 3. ¹H NMR spectra of **PP-Ic**, **PP-Id**, **PP-IIIa**, **PP-IIIb**, and **PP-IV**, measured in CD₂Cl₂ at 290 K. Regions in red boxes show characteristic signals of different functional groups.

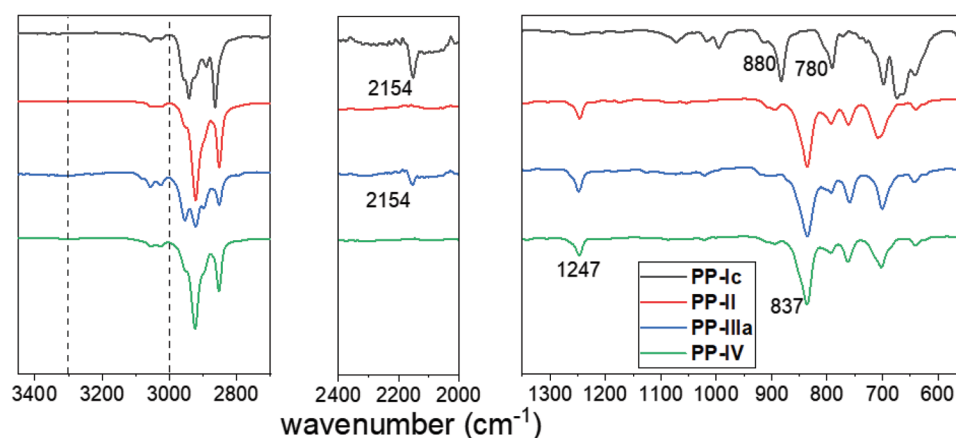


Figure 4. IR spectra of PP-Ic, PP-II, PP-IIIa, and PP-IV.

at 3.0 ppm as a result of similar local environments for every *m*-ethynylphenyl moiety.

Finally, to prove that **PP-IIIb** can still grow further, it was allowed to react with end-capping diphenyl-CP **2c** in ODCB at 150 °C to give **PP-IV** in 35% yield (Scheme 2). The low yield was again a result of the gel forming tendency of the polymer product. Signals of long alkyl chains arise at 0.75–1.5 ppm together with disappearance of the signals of ethynyl groups at 3.0 ppm in the ^1H NMR spectrum of **PP-IV**. A broad signal at 2.0–3.0 ppm is attributed to protons on α -positions of the alkyl chains. Relative signal intensities agreed with theoretical values for **PP-Ic**, **PP-Id**, **PP-II**, **PP-IIIa**, **PP-IIIb**, and **PP-IV** in their ^1H NMR spectra, corroborating their chemical structures (Figures S21–27, Supporting Information). It is important to note that since both **PP-IIIa** and **PP-IIIb** still retain good solubility in common organic solvents, **PP-IIIb** can also react repeatedly with diphenyl-CP **2b** using the same procedure to provide a series of wider and wider linear PPs.

2.3.3. Attempts to Planarize **PP-II** into GNR

Having these expanded PPs in hand, we made preliminary attempts at their planarization into GNRs. It is reported that TMS groups can be removed during oxidative cyclodehydrogenation reactions.^[38] Thus, we first attempted cyclodehydrogenation of **PP-II** under standard conditions applied for syntheses of GNRs,^[17] using FeCl_3 (15 eq. per C–C bond to be formed) in a mixture of dichloromethane and nitromethane at room temperature for 3 days. However, the resulting product exhibited broad absorption extending up to ≈ 800 nm with a shoulder at around 400–550 nm in the UV–vis spectrum measured for a suspension in 1,2,4-trichlorobenzene (Figure S2, Supporting Information). In comparison to the previously reported GNR derived from **PP-Ib**, showing a defined absorption band with a maximum at 660 nm and an onset at ≈ 1000 nm, the blue-shifted and rather featureless absorption of the product indicated incomplete planarization of **PP-II**. We then removed the TMS groups by treatment of **PP-II** with HBr under microwave conditions (see Supporting Information for details) considering that the TMS groups might have hampered efficient

planarization. The UV–vis absorption spectrum of the resulting product after cyclodehydrogenation was similar to that obtained without removal of TMS substituents. The incomplete cyclodehydrogenation of **PP-II** might be due to formation of isomers through C–C bond closure at undesired positions. This would, of course, prohibit further planarization (Figure S3, Supporting Information). In addition, although rarely reported for FeCl_3 ,^[39,40] PPs could undergo structural rearrangement, especially under strongly acidic conditions^[41,42] and for electron-rich species.^[43] Optimization of cyclodehydrogenation conditions, as well as the design of the PP for the fabrication of wider GNRs, is planned in our laboratory.

2.4. GPC Analysis of PPs

Molecular weight distributions of **PP-Ic**, **PP-II**, **PP-IIIa**, and **PP-IV** were analyzed by GPC with polystyrene as standards (Figure 5 and Table 1). Assuming an ideal conversion in each lateral extension step, a theoretical M_n of each PP can be calculated based on M_n of **PP-Ic** (Table 1). The experimental M_n ratio

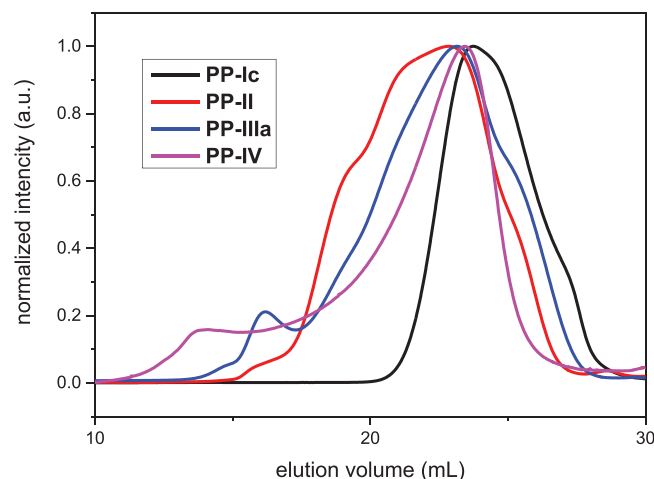


Figure 5. GPC spectra of **PP-Ic**, **PP-II**, **PP-IIIa**, and **PP-IV**. (Solvent: THF. Flow rate: 1 mL min^{−1}. Temperature: 30 °C.)

Table 1. Molecular weight data extracted from GPC analysis of polymers **PP-Ic**, **PP-II**, **PP-IIIa**, and **PP-IV**.

PPs ^{a)}	M_n [g mol ⁻¹]	M_n (calcd) ^{b)} [g mol ⁻¹]	M_p [g mol ⁻¹]	M_w [g mol ⁻¹]	PDI
PP-Ic	21 000	21 000	42 500	38 500	1.83
PP-II	66 200	52 900	74 100	211 000	3.19
PP-IIIa	46 400	36 700	60 200	154 000	3.33
PP-IV	57 500	73 200	49 000	222 000	3.87

^{a)} Polystyrene as standard; ^{b)} Calculated based on M_n of **PP-Ic**.

of **PP-Ic/PP-II/PP-IIIa** is in good agreement with theoretical values (Table 1). However, the M_n of **PP-IV** appears to be much lower than predicted. This can be explained by formation of insoluble gels during the reaction, since higher molecular weight polymers have a lower solubility and a stronger tendency toward aggregation (vide supra). Note that GPC plots of **PP-II**, **PP-IIIa**, and **PP-IV** display small shoulder peaks at retention times around 16, 16, and 13 min, respectively, corresponding to higher molecular weight species (Figure 5). In contrast, **PP-Ic** shows a simple Gaussian distribution, which suggests aggregation of **PP-II**, **PP-IIIa**, and **PP-IV** in solution. Nevertheless, after complete removal of solvent to form dry solid powders, they can be dissolved again in organic solvents as transparent solutions without any visible particles or undissolved gel. We conclude that this aggregation process is reversible.

3. Conclusion

We have developed an elegant method for lateral expansion of a linear PP by reaction with diphenyl-CP derivatives using a stepwise Diels–Alder cycloaddition/deprotection protocol. This route is commonly used in the field of dendritic PPs, but has so far not been applied to the synthesis of linear PPs. Each step of the extension procedure was monitored by recording ¹H NMR and IR spectra, showing successful functional group transformations. The resulting extended PPs were analyzed by GPC revealing stepwise evolution of the molecular weight. Preliminary attempts at cyclodehydrogenation of these PPs were not successful. However, our synthetic protocol opens further opportunities for the synthesis of wider GNRs and their bandgap engineering. Moreover, such laterally expanded PPs can also be regarded as a new class of polymers that have implications for the field of macromolecular chemistry and physics.^[20,44] For example, light scattering studies are desired to elucidate the effect of such lateral expansion on their persistence, although the issue of aggregation needs to be addressed first by devising the chemical structures. Further, substitution of their peripheral positions with different functional groups might lead to the formation of unique self-assembled nanostructures.^[44]

4. Experimental Section

General Information: Unless otherwise noted, materials were purchased from Fluka, Aldrich, Acros, abcr, Merck, and other commercial suppliers, and were used as received unless otherwise specified.

Compounds **3**, **5**, **8c**, and **10a** were synthesized according to refs [26, 17, 27, 30], respectively. All reactions working with air- or moisture-sensitive compounds were carried out under argon atmosphere using standard Schlenk line techniques. Thin layer chromatography (TLC) was performed on silica-gel-coated aluminum sheets with F254 indicator. Preparative column chromatography was performed on silica gel from Merck with a grain size of 0.063–0.200 mm (silica gel) or 0.04–0.063 mm (flash silica gel, Geduran Si 60). Melting points were determined on a Büchi hot stage apparatus without correction. Membrane filtration was performed on polyvinylidene fluoride membranes with a pore size of 0.45 µm (Merck). NMR spectra were recorded in deuterated solvents using Bruker AVANCE III 250 and Bruker AVANCE III 300 MHz NMR spectrometers. Chemical shifts (δ) were expressed in ppm relative to the residual of solvent (CD₂Cl₂ @ 5.32 ppm for ¹H NMR, 53.84 ppm for ¹³C NMR; CDCl₃ @ 7.26 ppm for ¹H NMR, 77.16 ppm for ¹³C NMR). Coupling constants (J) were recorded in Hertz (Hz) with multiplicities explained by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet; br, broad. IR was measured on a Nicolet 730 FT-IR spectrometer equipped with an attenuated total reflection (ATR) setup. Samples were deposited as pristine material on the diamond crystal and pressed on it with a stamp. Analytical GPC was performed using a PSS SECcurity Agilent 1260 Infinity Setup (Polymer Standards Service GmbH (PSS)). A column combination from PSS (SDV 10⁶, 10⁴, 500 Å, 300 × 8 mm) was connected and maintained at 30 °C. THF was used as an eluent with a flow rate of 1 mL min⁻¹. Relative molecular weights were calculated based on a universal polystyrene calibration using the signal recorded by a PSS SECcurity UV detector (254 nm). High-resolution mass spectra (HRMS) were recorded by matrix-assisted laser desorption/ionization (MALDI) using 7,7,8,8-tetracyanoquinodimethane (TCNQ) or *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix with a Bruker Reflex II-TOF spectrometer (MALDI-TOF HRMS).

Synthesis of 3-(3-Ethynylphenyl)-4-phenyl-2,5-bis[3-(triisopropylsilyl)ethynyl]-phenyl] cyclopenta-2,4-dien-1-one (1c): To a solution of 1-phenyl-2-[3-(trimethylsilyl)ethynyl]phenyl]ethane-1,2-dione (**6**) (1.00 g, 3.28 mmol) in THF (20 mL) was injected a THF solution of TBAF (4.5 mL 1 M, 4.5 mmol). The solution was stirred at room temperature for 1 h, and then passed through a short pad of silica gel with THF as eluent. Solvent was then removed in vacuo to afford 1-phenyl-2-(3-ethynylphenyl) ethane-1,2-dione (**7**) as a yellow solid (770 mg, 3.27 mmol, 99% crude yield), which was directly used in the next step without further purification. To a solution of 1,3-bis[3-(triisopropylsilyl)ethynyl]phenyl] propan-2-one (**4**) (1.62 g, 3.11 mmol) and **7** (770 mg, 3.27 mmol) in *t*BuOH (180 mL) was added at 80 °C a solution of tri-*n*-butylammonium hydroxide (0.2 g, 0.3 mmol, 40% w/w) in EtOH under vigorous stirring. The reaction was tracked by TLC until consumption of starting materials (ca. 30 min). During this time the solution gradually turned dark purple. The solution was then allowed to cool to room temperature, and diluted with ether and water. The aqueous phase was extracted three times and the combined organic phases were washed with water, and brine, and dried over MgSO₄. The solvent was then removed in vacuo and the residue was purified by triethylamine-neutralized silica gel column chromatography (eluent: dichloromethane/hexane = 1/3) to afford **1c** as a purple solid (1.40 g, 59%, over two steps from **6**): mp 130.1–131.9 °C;

¹H NMR (300 MHz, CD₂Cl₂, δ): 7.49–7.28 (m, 5H), 7.30–7.12 (m, 7H), 7.08 (s, 1H), 7.03–6.91 (m, 4H), 3.05 (s, 1H), 1.09 (s, 42H); ¹³C NMR (75 MHz, CD₂Cl₂, δ): 199.93, 155.80, 154.68, 134.23, 133.83, 133.05, 132.95, 132.88, 131.47, 131.44, 131.34, 131.16, 130.59, 130.56, 130.13, 129.63, 129.48, 128.83, 128.74, 128.66, 128.59, 125.69, 125.14, 123.92, 123.84, 122.72, 107.27, 107.21, 91.44, 91.32, 83.19, 78.22, 18.98, 11.86; MS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₅₃H₆₀OSi₂, 768.4 (100%), 769.4 (68%), 770.4 (29%), 771.4 (7.6%); found 768.4 (95%), 769.4 (100%), 770.4 (43%), 771.4 (22%).

Synthesis of 3,4-Diphenyl-2,5-bis(trimethylsilyl)cyclopenta-2,4-dien-1-one (2a): Synthesis of **2a** was carried out following a reported procedure.^[35] To a solution of [(1Z,3Z)-1,4-diiodo-2,3-diphenylbuta-1,3-diene-1,4-diyl]bis(trimethylsilane) (**10a**)^[30] (301 mg, 0.500 mmol) in diethyl ether (5 mL) was injected a hexane solution of *t*BuLi (1.18 mL, 1.7 M, 2.0 mmol) at –78 °C. After stirring at –78 °C for 1 h, CuCl (1.4 mg, 1.05 mmol) was added to the reaction mixture. The mixture was stirred at –78 °C for an additional 30 min. CO (gas) was then bubbled through the mixture under vigorous stirring for 10 min. Di-*tert*-butyl peroxide (0.19 mL, 1.1 mmol) was then injected into the mixture, which was allowed to warm up to 0 °C and stirred at this temperature for 1 h. Water was then added to quench the reaction and the organic phase was diluted with diethyl ether. The organic layer was washed with Na₂S₂O₃ (aq., 5%), water, and brine, and dried over MgSO₄. The solvent was then removed in vacuo and the residue was purified by triethylamine-neutralized silica gel column chromatography (eluent: dichloromethane/hexane = 1/8) to afford **2a** as a yellow solid (40.6 mg, 22%): ¹H NMR (300 MHz, CD₂Cl₂, δ): 7.25–7.14 (m, 6H), 7.00–6.88 (m, 4H), –0.03 (s, 18H). The NMR data agreed with those reported in the literature.^[45]

Synthesis of 3-Phenyl-2,5-bis(trimethylsilyl)-4-[3-(trimethylsilyl)ethynyl]phenyl]cyclopenta-2,4-dien-1-one (2b): Synthesis of **2b** was carried out following a reported procedure.^[35] To a solution of [(1Z,3Z)-1,4-diiodo-2-phenyl-3-[3-(trimethylsilyl)ethynyl]phenyl]buta-1,3-diene-1,4-diyl]bis(trimethylsilane) (**10b**) (4.3 g, 6.2 mmol) in diethyl ether (60 mL) was injected a hexane solution of *t*BuLi (15 mL, 1.7 M, 26 mmol) at –78 °C. After stirring at –78 °C for 1 h, CuCl (1.3 g, 13 mmol) was added to the reaction mixture. The mixture was stirred at –78 °C for another 30 min. CO (gas) was then bubbled through the mixture under vigorous stirring for 10 min. Di-*tert*-butyl peroxide (2.4 mL, 13 mmol) was then injected into the mixture, which was allowed to warm up to 0 °C and stirred at this temperature for 1 h. Water was then added to quench the reaction and the organic phase was diluted with diethyl ether. The organic layer was washed with Na₂S₂O₃ (aq., 5%), water, and brine, and dried over MgSO₄. The solvent was then removed in vacuo and the residue was purified using triethylamine-neutralized silica gel column chromatography (eluent: dichloromethane/hexane = 1/10) to afford **2b** as a yellow solid (1.2 g, 40%): mp 120.7–123.0 °C; ¹H NMR (300 MHz, CD₂Cl₂, δ): 7.30 (d, *J* = 7.7 Hz, 1H), 7.26–7.17 (m, 3H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 6.99–6.90 (m, 2H), 6.85 (d, *J* = 7.7 Hz, 1H), 0.22 (s, 9H), –0.01 (s, 9H), –0.02 (s, 9H); ¹³C NMR (75 MHz, CD₂Cl₂, δ): 210.22, 171.48, 170.54, 136.66, 136.08, 132.02, 131.89, 131.78, 131.06, 128.86, 128.78, 128.68, 128.11, 123.15, 104.84, 95.21, 0.10, 0.04; MS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₂₈H₃₆OSi₃, 472.2 (100%), 473.2 (46%), 474.2 (19%); found 472.2 (100%), 473.2 (73%), 474.2 (30%).

Synthesis of 3,4-Bis(3-tetradecylphenyl)-2,5-bis(trimethylsilyl)cyclopenta-2,4-dien-1-one (2c): Synthesis of **2c** was accomplished following a reported procedure.^[35] To a solution of [(1Z,3Z)-1,4-diiodo-2,3-bis(3-tetradecylphenyl)buta-1,3-diene-1,4-diyl]bis(trimethylsilane) (**10c**) (1.77 g, 1.78 mmol) in diethyl ether (20 mL) was injected at –78 °C a hexane solution of *t*BuLi (4.30 mL, 1.7 M, 7.30 mmol). The solution was allowed to react for 1 h, and CuCl (0.370 g, 3.74 mmol) was added to the solution. The mixture was stirred at –78 °C for an additional 30 min. CO (gas) was then bubbled through the mixture under vigorous stirring for 10 min. Di-*tert*-butyl peroxide (0.684 mL, 3.74 mmol) was then injected into the solution, which was then warmed to 0 °C and allowed to react for 1 h. Water was added to quench the reaction and the organic phase was diluted with diethyl ether. The organic layer was washed with Na₂S₂O₃ (aq., 5%), water, and brine, and dried over MgSO₄. Ether was then removed in vacuo and the residue was

purified by triethylamine-neutralized silica gel column chromatography (dichloromethane/hexane = 1/25) to afford **2c** as a yellow solid (0.659 g, 48%): mp 37.2–38.7 °C; ¹H NMR (300 MHz, CD₂Cl₂, δ): 7.08 (t, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 7.2 Hz, 2H), 6.72 (s, 2H), 2.45 (t, *J* = 7.6 Hz, 4H), 1.40 (quin, *J* = 8.2, 7.3 Hz, 4H), 1.34–1.07 (br, 44H), 0.88 (t, *J* = 6.4 Hz, 6H), –0.02 (s, 18H); ¹³C NMR (75 MHz, CD₂Cl₂, δ): 210.68, 172.32, 142.70, 136.23, 130.46, 128.93, 128.72, 127.77, 126.12, 36.26, 32.52, 31.97, 30.29, 30.25, 30.17, 30.08, 29.95, 29.69, 23.28, 14.46, 0.14; HRMS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₅₁H₈₄OSi₂, 768.6061; found 768.6130.

Synthesis of 1,3-Bis[3-(triisopropylsilyl)ethynyl]phenyl]propan-2-one (4): A mixture of 1,3-bis(3-bromophenyl)acetone (**3**)^[26] (5.0 g, 14 mmol), (triisopropylsilyl)acetylene (7.6 mL, 34 mmol), PdCl₂(PPh₃)₂ (0.48 g, 0.68 mmol), CuI (0.26 g, 1.4 mmol), PPh₃ (0.36 g, 1.4 mL), and piperidine (50 mL) was degassed by argon bubbling under vigorous stirring for 15 min. The mixture was then stirred at 100 °C overnight. After cooling to room temperature, ether and ice were added to the mixture and the organic layer was washed with HCl (aq., 2 M), water, and brine, and dried over MgSO₄. Ether was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: ethyl acetate/hexane = 1/6) to afford **4** as a pale yellow oil (7.7 g, 99%): ¹H NMR (300 MHz, CD₂Cl₂, δ): 7.39 (d, *J* = 7.5 Hz, 2H), 7.34–7.22 (s, 2H), with an embedded t, *J* = 7.4 Hz, 2H), 7.12 (d, *J* = 7.3 Hz, 2H), 3.74 (s, 4H), 1.14 (s, 42H); ¹³C NMR (75 MHz, CD₂Cl₂, δ): 205.10, 134.85, 133.57, 131.17, 130.29, 129.09, 124.38, 107.27, 91.40, 49.37, 19.02, 11.91; HRMS (MALDI-TOF) *m/z*: [M + H]⁺ calcd for C₃₇H₅₅OSi₂, 571.3791; found 571.3765.

Synthesis of 1-Phenyl-2-[3-(trimethylsilyl)ethynyl]phenyl]ethane-1,2-dione (6): A mixture of 3-bromobenzil (**5**)^[17] (2.1 g, 7.3 mmol), (trimethylsilyl)acetylene (3.0 mL, 22 mmol), Pd(PPh₃)₄ (0.26 g, 0.22 mmol), CuI (0.046 g, 0.22 mmol), THF (10 mL), and trimethylamine (10 mL) was degassed by argon bubbling under vigorous stirring for 15 min. The mixture was then stirred at 100 °C overnight. After cooling to room temperature, ether and ice were added to the mixture and the organic layer was washed with HCl (aq., 2 M), water, and brine, and dried over MgSO₄. Solvents were removed in vacuo and the residue was purified by silica gel column chromatography (eluent: ethyl acetate/hexane = 1/10) to afford **6** as a pale yellow solid (2.1 g, 94%): mp 50.2–51.3 °C; ¹H NMR (300 MHz, CD₂Cl₂, δ): 8.04 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 0.25 (s, 9H); ¹³C NMR (75 MHz, CD₂Cl₂, δ): 194.05, 193.75, 137.95, 135.15, 133.38, 133.15, 132.91, 130.08, 129.52, 129.18, 129.14, 124.53, 103.29, 96.57, –0.07; MS (MALDI-TOF) *m/z*: [M–H]⁺ calcd for C₁₉H₁₇OSi₃, 305.1 (100%), 306.1 (26%), 306.1 (5.1%); found 305.1 (100%), 306.1 (15%), 306.1 (3.6%).

Synthesis of [(1Z,3Z)-1,4-Diiodo-2-phenyl-3-[3-(trimethylsilyl)ethynyl]phenyl]buta-1,3-diene-1,4-diyl]bis(trimethylsilane) (10b): The synthetic procedure was modified from literature reports.^[28,29] To a suspension of zirconocene dichloride (18 g, 63 mmol) in THF (200 mL) was added a hexane solution of *n*BuLi (83 mL, 1.6 M, 0.13 mol) at –78 °C. The mixture was stirred at –78 °C for 1 h to generate an active zirconocene species. Trimethyl(phenylethynyl)silane (**8a**) (11 g, 63 mmol) and 1,3-bis[(trimethylsilyl)ethynyl]benzene (**8b**) (17 g, 63 mmol) were then simultaneously added to the mixture under argon flow. The mixture was stirred for 3 h while it was allowed to gradually warm to room temperature. The mixture turned dark brown during the process. The mixture was then cooled to 0 °C, and CuCl (7.5 g, 75 mmol) was added in one portion, followed by addition of I₂ (38 g, 0.15 mmol) in five portions. The mixture was allowed to gradually warm to room temperature and stirred overnight. The reaction was then quenched with water and diluted with ether. The organic layer was washed with Na₂S₂O₃ (aq., 5%), water, and brine, and dried over MgSO₄. Solvents were then removed in vacuo and the residue was purified by triethylamine-neutralized silica gel column chromatography (eluent: cyclohexane) to afford **10b** as a pale-yellow solid (5.2 g, 12%, first band): mp 136.2–137.3 °C; ¹H NMR (300 MHz, CD₂Cl₂, δ): 7.40 (d, *J* = 7.4 Hz, 1H), 7.37–7.26 (m, 3H), 7.24 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 5.5 Hz, 1H), 0.26 (s, 9H), 0.01 (s, 9H), 0.00 (s, 9H); ¹³C NMR (75 MHz, CD₂Cl₂, δ): 163.31, 162.60,

139.93, 139.66, 132.77, 132.13, 129.86, 129.70, 128.77, 128.25, 123.17, 114.06, 113.69, 104.76, 99.93, 95.01, 0.94, 0.85, −0.04; MS (MALDI-TOF) m/z : $[M-I]^+$ calcd for $C_{27}H_{36}Si_3$ 571.1 (100%), 572.1 (45%), 573.1 (19%); found 571.3 (100%), 572.3 (44%), 573.3 (20%).

Synthesis of [(1Z,3Z)-1,4-Diiodo-2,3-bis(3-tetradecylphenyl)buta-1,3-diene-1,4-diy]bis(trimethylsilane) (10c): Synthesis employed a modification of reported procedures.^[28,29] A hexane solution of *n*BuLi (8.1 mL, 1.6 M, 13 mmol) was injected into a suspension of zirconocene dichloride (1.8 g, 6.2 mmol) in THF (6 mL) at −78 °C. The solution turned pale yellow upon the injection. The mixture was allowed to react at −78 °C for 1 h to generate an active zirconocene species. Trimethyl[(3-*n*-tetradecylphenyl)ethynyl]silane (8c)^[27] (3.28 g, 12.3 mmol) was then injected into the mixture in one portion. The mixture was stirred for 3 h while it was allowed to gradually warm to room temperature. The mixture turned dark brown during the process. The mixture was then cooled to 0 °C, and CuCl (0.73 g, 7.4 mmol) was added in one portion, followed by addition of I_2 (3.76 g, 14.8 mmol) in five portions. The mixture was then gradually warmed to room temperature and allowed to react under stirring overnight. The reaction was then quenched with water and diluted with ether. The organic layer was washed with $Na_2S_2O_3$ (aq., 5%), water, and brine, and dried over $MgSO_4$. Ether was then removed in vacuo and the residue was purified by triethylamine-neutralized silica gel column chromatography (eluent: cyclohexane) to afford **10c** as a pale-yellow oil (1.85 g, 30%): 1H NMR (300 MHz, CD_2Cl_2 , δ): 7.19–7.10 (br, 4H), 7.10–7.01 (br, 2H), 7.01–6.88 (br, 2H), 2.53 (t, J = 7.5 Hz, 4H), 1.53 (quin, J = 7.5 Hz, 4H), 1.44–1.16 (br, 44H), 0.92 (t, J = 6.5 Hz, 6H), 0.00 (s, 18H); ^{13}C NMR (75 MHz, CD_2Cl_2 , δ): 164.21, 143.01, 139.98, 130.27, 128.99, 128.17, 127.08, 112.44, 36.28, 32.60, 31.98, 30.39, 30.37, 30.33, 30.27, 30.16, 30.04, 29.76, 23.36, 14.57, 1.22; MS (MALDI-TOF) m/z : $[M-C_2(TMS)_2I]^+$ calcd for $C_{42}H_{66}$ 570.5 (100%), 571.5 (45%), 572.5 (10%); found 571.1 (100%), 572.1 (42%), 573.1 (18%).

Synthesis of 1,4-Bis(trimethylsilyl)-2,3,5-triphenylbenzene (11): A solution of 3,4-diphenyl-2,5-bis(trimethylsilyl)cyclopenta-2,4-dien-1-one (**2a**) (33 mg, 0.089 mmol) and phenylacetylene (14 mg, 0.13 mmol) in ODCB (0.5 mL) was degassed using a freeze–pump–thaw technique for three cycles. The solution was then stirred at 120 °C for 3 days. Solvent was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: dichloromethane/hexane = 1/20) to afford **11** as a white solid (36 mg, 89%): mp 160.4–162.0 °C; 1H NMR (300 MHz, CD_2Cl_2 , δ): 7.56–7.33 (m, 6H), 7.18–7.01 (m, 8H), 7.01–6.93 (m, 2H), −0.08 (s, 9H), −0.47 (s, 9H); ^{13}C NMR (75 MHz, CD_2Cl_2 , δ): 149.40, 148.95, 146.60, 146.41, 143.56, 143.17, 140.07, 138.80, 135.77, 132.63, 131.87, 130.43, 128.48, 127.60, 127.34, 127.25, 126.74, 126.63, 3.08, 0.66; MS (MALDI-TOF) m/z : $[M]^+$ calcd for $C_{30}H_{34}Si_2$ 450.2 (100%), 451.2 (43%), 452.2 (15%); found 450.2 (100%), 451.2 (41%), 452.2 (12%).

Synthesis of PP-Ic: A solution of **1c** (0.50 g, 0.65 mmol of repeating unit) in Ph_2O (1 mL) was degassed using a freeze–pump–thaw technique for three cycles. The solution was then stirred at 120 °C for 78 h. During the reaction, small amounts of solution were taken from the mixture using syringes and the molecular weight was monitored by GPC analysis with PS standards (see Section 2 for details). Phenylacetylene (0.13 g, 1.3 mmol) was then added and the solution was stirred at 160 °C overnight, during which the purple color of the solution completely disappeared. After cooling to room temperature, MeOH (10 mL) was added to induce precipitation of polymeric products. A white precipitate was collected by filtration with a membrane filter and washed with methanol to afford **PP-Ic** (465 mg, 91%): 1H NMR (250 MHz, CD_2Cl_2 , δ): 7.53–6.02 (br, 18H), 1.23–1.08 (br, 21H), 1.08–0.73 (br, 21H); IR: ν = 3059 (w), 2941 (m), 2864 (w), 2154 (m), 1597 (w), 1463 (m), 1383 (w), 1244 (w), 1170 (w), 1072 (w), 995 (m), 882 (s), 791 (m), 674 (s), 553 (m), 499 (m), 462 (m).

Synthesis of PP-Id: A solution of **PP-Ic** (0.23 g, 0.31 mmol of repeating unit) in THF (10 mL) was degassed with a freeze–pump–thaw technique for three cycles. To this solution, a THF solution of TBAF (1 M, 3 mL) was injected. After the injection, the mixture was degassed using a freeze–pump–thaw technique for another three cycles. The solution was then allowed to react at room temperature for 1 day before pouring it into

methanol (100 mL). A white precipitate was collected by filtration with a membrane filter and washed with methanol to afford **PP-Id** (105 mg, 79%): 1H NMR (250 MHz, CD_2Cl_2 , δ): 7.64–5.95 (br, 18H), 3.26–3.07 (br, 1H), 3.07–2.82 (br, 1H).

Synthesis of PP-II: A solution of **PP-Id** (51 mg, 0.12 mmol of repeating unit) and **2c** (0.27 g, 0.36 mmol) in ODCB (1 mL) was degassed with a freeze–pump–thaw technique for three cycles. This solution was stirred at 160 °C for 7 days. After cooling to room temperature, the solution was poured into methanol (20 mL) to induce precipitation of polymer products. Precipitates were collected by filtration with a membrane filter and washed with methanol to afford a crude product of **PP-II** (0.15 g, 67%), which was further purified by recycling GPC to yield **PP-II** as a white powder (0.13 g, 58%): 1H NMR (250 MHz, CD_2Cl_2 , δ): 8.84–5.48 (br, 36H), 3.08–1.93 (br, 8H), 1.93–0.95 (br, 96H), 0.95–0.44 (br, 12H), 0.37 to −0.36 (br, 18H), −0.36 to −1.31 (br, 18H); IR: ν = 3054 (w), 2923 (m), 2853 (m), 1713.13065 (w), 1600.16127 (w), 1463 (w), 1400 (w), 1247 (m), 1174 (w), 1087 (w), 1054 (w), 837 (s), 762 (m), 708 (m), 641 (w), 556 (w), 446 (w).

Synthesis of PP-IIIa: A solution of **PP-Id** (54 mg, 0.13 mmol of repeating unit) and **2b** (0.17 g, 0.36 mmol) in chlorobenzene (1 mL) was degassed using a freeze–pump–thaw technique for three cycles. This solution was stirred at 125 °C for 5 days. After cooling to room temperature, the solution was poured into methanol (20 mL) to induce precipitation of polymer products. Polymer precipitates were collected by filtration with a membrane filter and washed with methanol to give a crude product, **PP-IIIa** (white powder, 0.11 g, 68%). The yellow filtrate was concentrated in vacuo and the residue was purified by silica gel column chromatography (eluent: dichloromethane/hexane = 1/6) to recover unreacted **2b** as a yellow solid (49 mg, 0.11 mmol). The crude product was further purified by recycling GPC to yield **PP-IIIa** as a white powder (0.10 g, 62%): 1H NMR (250 MHz, CD_2Cl_2 , δ): 8.02–5.72 (br, 38H), 0.44–0.04 (br, 18H), 0.44 to −0.34 (br, 18H), −0.34 to −1.00 (br, 18H); IR: ν = 3057 (w), 2923 (w), 2853 (w), 2154 (w), 1719 (w), 1597 (w), 1479 (w), 1409 (w), 1341 (w), 1248 (m), 1185 (w), 1125 (w), 1072 (w), 1021 (w), 837 (s), 759 (m), 701 (m), 642 (m), 566 (w), 450 (w).

Synthesis of PP-IIIb: A solution of **PP-IIIa** (15 mg, 0.012 mmol of repeating unit) in THF (2 mL) and methanol (1 mL) was degassed with a freeze–pump–thaw technique for three cycles. To this solution K_2CO_3 (3.3 mg, 0.024 mmol) was added under a flow of argon. The mixture was vigorously stirred overnight at room temperature and poured into methanol (20 mL) to induce precipitation of polymer products. Precipitates were collected by filtration with a membrane filter and washed with methanol to afford a white powder of **PP-IIIb** (12 mg, 83%): 1H NMR (250 MHz, CD_2Cl_2 , δ): 8.11–5.79 (br, 38H), 3.22–2.77 (br, 2H), 0.44–0.04 (br, 18H), 0.37 to −0.36 (br, 18H), −0.36 to −1.13 (br, 18H).

Synthesis of PP-IV, Procedure A: A mixture of **PP-IIIb** (14 mg, 0.012 mmol of repeating unit) and **2c** (36 mg, 0.047 mmol) in ODCB (0.2 mL) was degassed by freeze–pump–thawing for three cycles. This mixture was stirred at 160 °C for 4 days, during which a gel formed. After cooling to room temperature, THF (5 mL) was added to the mixture. The mixture was sonicated for 15 min and filtrated. The solution was poured into methanol (20 mL) to induce precipitation of polymer products. Precipitates were collected by filtration with a membrane filter and washed with methanol to afford a white powder, **PP-IV** (6.0 mg, 20%).

Procedure B: A solution of **PP-IIIa** (10 mg, 0.0077 mmol of repeating unit) in THF (2 mL) and methanol (1 mL) was degassed with freeze–pump–thawing for three cycles. To this solution K_2CO_3 (2.1 mg, 0.015 mmol) was added under a flow of argon. The mixture was vigorously stirred overnight and then dichloromethane (20 mL) was added. The organic phase was washed with water and brine, and dried over Na_2SO_4 . **2c** (24 mg, 0.031 mmol) and ODCB (0.2 mL) were added to the solution and the mixture was concentrated in vacuo to remove dichloromethane. After degassing using a freeze–pump–thaw technique for three cycles, the residual solution was stirred at 160 °C for 4 days. After cooling to room temperature, the solution was poured into methanol (20 mL) to induce precipitation of polymer products. Precipitates were collected by filtration with a membrane filter and washed with methanol to afford a white powder of **PP-IV** (6.7 mg, 34%

over two steps): ^1H NMR (250 MHz, CD_2Cl_2 , δ): 8.26–5.76 (br, 56H), 2.95–2.05 (br, 8H), 1.85–0.96 (br, 96H), 0.96–0.62 (br, 12H), 0.34 to –0.37 (br, 36H), –0.37 to –1.28 (br, 36H); IR: ν = 3054 (w), 2924 (m), 2853 (w), 1717 (w), 1600 (w), 1463 (w), 1404 (w), 1343 (w), 1247 (m), 1087 (w), 1021 (w), 837 (s), 762 (m), 702 (m), 641 (w), 429 (w).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the Max Planck Society and the EC through the Marie Skłodowska-Curie ITN project iSwitch (GA-642196).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cyclopentadienone, Diels–Alder polymers, graphene nanoribbons, lateral extension, polyphenylene

Received: September 3, 2019

Revised: October 15, 2019

Published online: November 7, 2019

- [1] B. A. G. Hammer, K. Müllen, *Chem. Rev.* **2016**, *116*, 2103.
- [2] I. C. Y. Hou, Y. Hu, A. Narita, K. Müllen, *Polym. J.* **2018**, *50*, 3.
- [3] K. Si, R. Wycisk, D. Dong, K. Cooper, M. Rodgers, P. Brooker, D. Slattery, M. Litt, *Macromolecules* **2013**, *46*, 422.
- [4] M. Adamski, T. J. G. Skalski, B. Britton, T. J. Peckham, L. Metzler, S. Holdcroft, *Angew. Chem., Int. Ed.* **2017**, *56*, 9058.
- [5] T. Holmes, T. J. G. Skalski, M. Adamski, S. Holdcroft, *Chem. Mater.* **2019**, *31*, 1441.
- [6] K. Shiino, J. Miyake, K. Miyake, *Chem. Commun.* **2019**, *55*, 7073.
- [7] B. Motealleh, F. Huang, T. D. Largier, W. Khan, C. J. Cornelius, *Polymer* **2019**, *160*, 148.
- [8] T. D. Largier, D. Wang, J. Mueller, C. J. Cornelius, *J. Membr. Sci.* **2017**, *531*, 103.
- [9] T. Largier, F. Huang, C. J. Cornelius, *Eur. Polym. J.* **2017**, *89*, 301.
- [10] T. Largier, F. Huang, W. Kahn, C. J. Cornelius, *J. Membr. Sci.* **2019**, *572*, 320.
- [11] X.-Y. Wang, X. Yao, K. Müllen, *Sci. China: Chem.* **2019**, *62*, 1099.
- [12] A. Narita, X. Y. Wang, X. Feng, K. Müllen, *Chem. Soc. Rev.* **2015**, *44*, 6616.
- [13] A. Narita, Z. Chen, Q. Chen, K. Müllen, *Chem. Sci.* **2019**, *10*, 964.
- [14] O. Gröning, S. Wang, X. Yao, C. A. Pignedoli, G. Borin Barin, C. Daniels, A. Cupo, V. Meunier, X. Feng, A. Narita, K. Müllen, P. Ruffieux, R. Fasel, *Nature* **2018**, *560*, 209. PMID:30089919.
- [15] D. J. Rizzo, G. Veber, T. Cao, C. Bronner, T. Chen, F. Zhao, H. Rodriguez, S. G. Louie, M. F. Crommie, F. R. Fischer, *Nature* **2018**, *560*, 204. PMID:30089918.
- [16] M. Slota, A. Keerthi, W. K. Myers, E. Tretyakov, M. Baumgarten, A. Ardavan, H. Sadeghi, C. J. Lambert, A. Narita, K. Müllen, L. Bogani, *Nature* **2018**, *557*, 691. PMID:29849157.
- [17] A. Narita, X. Feng, Y. Hernandez, S. A. Jensen, M. Bonn, H. Yang, I. A. Verzhbitskiy, C. Casiraghi, M. R. Hansen, A. H. R. Koch, G. Fytas, O. Ivasenko, B. Li, K. S. Mali, T. Balandina, S. Mahesh, S. De Feyter, K. Müllen, *Nat. Chem.* **2014**, *6*, 126.
- [18] W. Ried, D. Freitag, *Naturwissenschaften* **1966**, *53*, 306.
- [19] J. K. Stille, F. W. Harris, R. O. Rakutis, H. Mukamal, *J. Polym. Sci., Part B: Polym. Lett.* **1966**, *4*, 791.
- [20] N. C. Forero-Martinez, B. Baumeier, K. Kremer, *Macromolecules* **2019**, *52*, 5307. PMID:31543550.
- [21] A. Narita, I. A. Verzhbitskiy, W. Frederickx, K. S. Mali, S. A. Jensen, M. R. Hansen, M. Bonn, S. De Feyter, C. Casiraghi, X. Feng, K. Müllen, *ACS Nano* **2014**, *8*, 11622. PMID:25338208.
- [22] Y. Hu, P. Xie, M. De Corato, A. Ruini, S. Zhao, F. Meggendorfer, L. A. Straasø, L. Rondin, P. Simon, J. Li, J. J. Finley, M. R. Hansen, J. S. Lauret, E. Molinari, X. Feng, J. V. Barth, C. A. Palma, D. Prezzi, K. Müllen, A. Narita, *J. Am. Chem. Soc.* **2018**, *140*, 7803.
- [23] B. A. G. Hammer, K. Müllen, *J. Nanopart. Res.* **2018**, *20*, 262.
- [24] T. T. T. Nguyen, M. Baumgarten, A. Rouhanipour, H. J. Räder, I. Lieberwirth, K. Müllen, *J. Am. Chem. Soc.* **2013**, *135*, 4183.
- [25] B. Fuchs, M. Pasternak, B. Pazhenchevsky, *J. Org. Chem.* **1981**, *46*, 2017.
- [26] H. Sauriat-Dorizon, T. Maris, J. D. Wuest, G. D. Enright, *J. Org. Chem.* **2003**, *68*, 240.
- [27] X. C. Chen, S. Nishinaga, Y. Okuda, J. J. Zhao, J. Xu, H. Mori, Y. Nishihara, *Org. Chem. Front.* **2015**, *2*, 536.
- [28] E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson, T. Takahashi, *J. Am. Chem. Soc.* **1989**, *111*, 3336.
- [29] C. Xi, S. Hou, T. H. Afifi, R. Hara, T. Takahashi, *Tetrahedron Lett.* **1997**, *38*, 4099.
- [30] Z. Xi, Z. Song, G. Liu, X. Liu, T. Takahashi, *J. Org. Chem.* **2006**, *71*, 3154.
- [31] Z. Xi, R. Hara, T. Takahashi, *J. Org. Chem.* **1995**, *60*, 4444.
- [32] S. L. Buchwald, R. B. Nielsen, *J. Am. Chem. Soc.* **1989**, *111*, 2870.
- [33] Z. Xi, Q. Song, *J. Org. Chem.* **2000**, *65*, 9157.
- [34] C. Chen, C. Xi, Y. Jiang, X. Hong, *J. Am. Chem. Soc.* **2005**, *127*, 8024.
- [35] Q. Luo, C. Wang, W.-X. Zhang, Z. Xi, *Chem. Commun.* **2008**, 1593.
- [36] J. L. Ormsby, J. Janikowski, *Org. Lett.* **2009**, *11*, 773.
- [37] P. J. Launer, in *Silicone Compounds Register And Review* (Eds: B. Arkles, G. L. Larson), Gelest, Inc., Morrisville, NC **1987**, pp. 100–103.
- [38] A. Pradhan, P. Dechambenoit, H. Bock, F. Durola, *J. Org. Chem.* **2013**, *78*, 2266.
- [39] A. A. O. Sarhan, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 2730.
- [40] Y. Cao, X.-Y. Wang, J.-Y. Wang, J. Pei, *Synlett* **2013**, *25*, 313.
- [41] A. Ajaz, E. C. McLaughlin, S. L. Skraba, R. Thamam, R. P. Johnson, *J. Org. Chem.* **2012**, *77*, 9487.
- [42] A. Necula, A. Racoveanu-Schikentanz, M. D. Gheorghiu, L. T. Scott, *J. Org. Chem.* **1995**, *60*, 3448.
- [43] J. L. Ormsby, T. D. Black, C. L. Hilton, Bharat, B. T. King, *Tetrahedron* **2008**, *64*, 11370.
- [44] Y. Huang, Y. Mai, X. Yang, U. Beser, J. Liu, F. Zhang, D. Yan, K. Müllen, X. Feng, *J. Am. Chem. Soc.* **2015**, *137*, 11602.
- [45] L. Liu, J. Wei, Y. Chi, W. X. Zhang, Z. Xi, *Angew. Chem., Int. Ed.* **2016**, *55*, 14762.