Beyond \( p \)-Hexaphenylenes: Synthesis of Unsubstituted \( p \)-Nonaphenylene by a Precursor Protocol

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1 General Remarks

The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AVANCE 300 and Bruker AVANCE 500. For calibration the residual solvent peak was referenced.[1]

Solid-state NMR CP/MAS experiments were performed with a Bruker AVANCE III console operating at 700 MHz $^1$H Lamor frequency using a commercial double resonance MAS probe supporting zirconia rotors with 2.5 mm outer diameter. The CP/MAS experiments were performed at 25 kHz MAS spinning frequency and ambient temperature with a CP contact time of 3ms if not stated differently in the figure caption. High-power frequency –swept TPPI hetero-nuclear dipolar decoupling of 100 kHz rf nutation frequency was applied during $^{13}$C acquisition.

Thermogravimetric analysis and differential scanning calorimetry - analyses were done using a Mettler Toledo TGA/DSC1 device. Thin-films were made via spin-coating with a Spin Coater SCV-10 on quartz glass or Si-wafers. Layer-thicknesses of thin-films were determined using a profilometer (DektakXT, Bruker). Solid-state UV-Vis absorption and emission spectra were recorded at room temperature on a Jasco V660 and FP6500 spectrophotometer of thin-films on glass substrates. Microscope images were taken with a Nikon Eclipse LV100POL polarization microscope. AFM images were taken on a Bruker Nanoscope MultiMode VIII in the ScanAsyst PeakForce mode. The resulting AFM measurements were treated with the software Gwyddion for row alignment and scar correction. Melting points were determined on a Büchi B-545 hot stage apparatus.

Mass spectra (MS) were either recorded on the JEOL JMS-700 (EI+), Bruker ApexQe hybrid 9.4 T FT-ICR-MS (ESI+), MALDI-TOF-MS spectra were reordered on a Bruker Daltonics Reflex III with trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as matrix or on a Bruker ApexQe hybrid 9.4 T FT-ICR. EI-MS experiments were carried out on Varian Saturn GC/MS 2000 or a Finnigan LCQ (ESI+) mass spectrometer at the Organic Chemical Institute of the University of Heidelberg.

Precursor solutions were spun-cast at 1000 rpm for 50 s in a nitrogen glove box with both water content and oxygen concentration below 3 ppm. Film thicknesses were determined via Vis ellipsometry and a Bruker DekTak XT profilometer. Films for mass analysis of 9PP were prepared using drop coating and measured on a SynaptG2-Si using 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix. The matrix was evaporated on the films using a heat plate under air. To ensure full aromatization of the thicker films
the films were heated at 300 °C for 5 h. Sample preparation: For all IR spectroscopic measurements, silicon wafers (1.5 x 1.5 cm², intrinsic, σ > 5000 Ω⁻¹ cm⁻¹) with a native oxide layer were used as substrate. The substrates were cleaned prior to fabrication via sonication in acetone and isopropanol and dried using a dry nitrogen stream. Subsequently, the backside of the substrate was cleaned with CHCl₃. Thermal aromatization was achieved on standard thermal hotplates in nitrogen atmosphere inside the glovebox.

Infrared (IR)-Spectroscopy: All samples for IR transmission measurements were measured at room temperature using a Fourier-transform IR spectrometer (Vertex 80v) from Bruker. The spectrometer was evacuated to 3 mbar to prevent absorption from ambient air (water and CO₂). Spectra were recorded at near normal incidence (7 °) or – as specified – at 70° incident light. All spectra were recorded with an MCT detector, a resolution of 4 cm⁻¹ and averaged over 200 scans.

Time resolved photoluminescence was determined on a Horiba FluoroCube-01-NL lifetime spectrofluorometer with emission monochromator.

The heating of the thin films was done stepwise in between measurements on a hotplate. After the specified time the sample was removed from the hotplate and put on a piece of aluminum at room temperature to prevent further heating and falsifying the time scale. Heating up and cooling down to under 50 °C took below 30 s, for 300 °C below 1 min.

Density functional theory (DFT) calculations were carried out with Gaussian 09[2] under use of the B3LYP[3-4] functional and the basis set 6-311G(d,p). To speed up this process a single reduced molecule (p-pentaphenylene) was calculated in gas phase. Simulations were carried out with SCOUT.[5]

Details of the crystal data and a summary of the intensity data collection parameters are listed at the end of this chapter. Suitable crystals were measured with Bruker Smart CCD diffractometer. Graphite-monochromated Mo Kα radiation was used. The structures were solved by direct methods with SIR-97 and refined by the full-matrix least-squares techniques against F² (SHELXL-97). The intensities were corrected for Lorentz and polarization effects. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The crystals structures were visualized using Mercury.
Annealing Process in Bulk and Thin Films

2.1 Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The annealing process was studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the bulk precursor oligomers.

![Diagram of 9PPsyn,pre and 9PPanti,pre](image)

**Figure S1**: DSC and TGA-trace of 9PP\textsubscript{syn,pre} (left) and 9PP\textsubscript{anti,pre} (right) with a heating rate of 10 K/min. The TGA trace shows a loss in mass of the precursor oligomer at about 228-288 °C for the \textit{syn}-isomer and 228-271 °C for the \textit{anti}-isomer. This mass loss is attributed to demethoxylation to yield the corresponding phenylene units. Due to possible encapsulation of bulk material and the hindrance of conformational change from oligomer coils to rod-like oligomer the mass loss is slightly less than expected for both isomers (for \textit{syn}-isomer: calc: 21.3%, observed: 18.2%; for \textit{anti}-isomer: calc: 21.3%, observed: 20.0%). However, the deviation of the expected vs. the observed mass loss for its polymeric analogues is much higher (calc: 21.38%, observed: 12.55%). Nevertheless, thin spin-coated thin films of the precursor materials (oligomer and polymer) show quantitative aromatization as evidenced by IR spectroscopy.
2.2 Dewetting Process of $9PP_{\text{syn,pre}}$

![Diagram of dewetting process](image)

**Figure S2:** Illustration of the dewetting process as a result of the different shapes of the rotamers (syn- vs anti-isomer) and their impact on the packing. Heating below the aromatization temperature leads either to sole rearrangements (anti-isomer) or to dewetting (hole formation in the films as starting point for dewetting process).[6-10]

2.3 Polarization Microscopy

![Polarization micrographs](image)

**Figure S3:** Polarization micrographs of in situ-heating $9PP_{\text{anti,pre}}$. Before heating (a) and after gradually heating to 300 °C (b) the film appear identical. Only a drift of the whole sample is visible due to the hardware of the experiment.
**Figure S4:** Polarization micrographs while heating 9PP$_{syn, pre}$. Before heating (a) the film shows only small holes and a scratch used for focusing. At 150 °C (b) the dewetting has already started. At 175 °C (c) it is already quite severe and at 300 °C (d) only bubbles remain.
2.4 Absorption and Emission Spectra

Figure S5: Time-dependent absorption spectra of 9PP\textsubscript{syn,pre} annealed at 300 °C.
Figure S6: Time-dependent absorption spectra of 9PP_{anti,pre} annealed at 300 °C.
Figure S7: Emission spectra of the 9PPs (a: 9PP<sub>anti</sub>; b: 9PP<sub>syn</sub>) and PPPs (c: PPP<sub>anti</sub>; d: PPP<sub>syn</sub>).

Figure S8: Further model compounds tested in our laboratories. T<sub>m</sub> denotes respective melting temperatures.
2.5 Infrared Spectroscopy

While heating to 300 °C $9PP_{anti,pre}$ did keep a closed film whereas $9PP_{syn,pre}$ started dewetting at temperatures as low as 120 °C, see Figure S3 and Figure S4. Despite the dewetting of the films IR measurements were still possible because our IR beam is about 3 mm in diameter averaging the signal over islands and holes. This led to a wavy baseline and further artefacts in the spectra (Figure S12), which could still be used to roughly compare them to their $9PP_{anti,pre}$ counterparts and to sketch the evolution over time (Figure S13).

Table S1. Band assignment of $9PP_{anti, pre}$. δ and ν correspond to bending and stretching vibrations, respectively. The experimental wavelength $\nu_{exp}$ is compared with the predicted wavelength $\nu_{theo}$ from DFT calculations. From the latter the vibration can be assigned. Index "end" in the vibrational mode indicates that the vibration is mostly from the outermost phenyl ring, index "me" refers to vibrations only present in the methoxylated precursor and not in the converted $9PP_{anti}$. The orientation is given as in-plane (ip) or out-of-plane (oop) if assignment was possible.

| Number | Figure S9 | $\nu_{exp}$ [cm$^{-1}$] | $\nu_{theo}$ [cm$^{-1}$] | Vibrational mode | Orientation |
|--------|-----------|-------------------------|-------------------------|-----------------|-------------|
| 1      |           | 698                     | 714                     | $\delta$(C-H)$_{end}$ | ip          |
| 2      |           | 763                     | 784                     | $\delta$(C-H)$_{end}$ | ip          |
| 3      |           | 822                     | 862                     | $\delta$(C-H)    | oop         |
| 4      |           | 951                     | 967                     | $\nu$(C-O)$_{me}$ | ip          |
| 5      |           | 1017                    | 1029                    | ring deformation | ip          |
| 6      |           | 1072                    | 1103                    | $\nu$(C-O-C)$_{me}$ | ip         |
| 7      |           | 1175                    | 1188                    | $\nu$(C-C)       | ip          |
| 8      |           | 1226                    | 1238                    | $\nu$(C-C)       | ip          |
| 9      |           | 1400                    | 1432                    | $\delta$(C-H)    | ip          |
| 10     |           | 1491                    | 1520                    | $\delta$(C-H)    | ip          |
| 11     |           | 2822                    | 2999                    | $\nu$(C-H$_3$)$_{me}$ | ip         |
Figure S9: DFT calculated and simulated IR transmission spectrum (top) and experimental (bottom) spectrum of 9PP_{anti, pre}. The numbered lines indicate the assigned band vibrations in Table S1.
Figure S10: Time-resolved infrared spectroscopy of 9PP\textsubscript{anti, pre} annealed at 250 °C (top) and 300 °C (bottom). The precursor specific absorption bands (e.g. 950 cm\textsuperscript{-1} or 1076 cm\textsuperscript{-1}) gradually decrease with time, at 250 °C at a slower rate than at 300 °C.
Figure S11: FTIR spectra of 9PP<sub>syn, pre</sub>, 9PP<sub>syn</sub>, 9PP<sub>anti, pre</sub> and 9PP<sub>anti</sub> under normal (red) and flat (green) incidence. The difference of the intensity ratio of the out-of-plane (oop, dark grey) and the in-plane (ip, light grey) vibrations indicates the different preferred molecular orientation within the film. The orientations found are face-on for 9PP<sub>syn, pre</sub>, face-on for 9PP<sub>anti, pre</sub> and edge-on for 9PP<sub>anti</sub>. The dewetted 9PP<sub>syn</sub> did not exhibit a preferred molecular orientation.

Figure S12: Degree of conversion from 9PP<sub>anti, pre</sub> to 9PP<sub>anti</sub> at 300 °C (cyan), 250 °C (red), 230 °C (gold) and 200 °C (blue). Due to the long time the 200 °C series was aborted halfway through the aromatization. Each point corresponds to one measurement.
Figure S13: DFT calculated and simulated IR transmission spectrum (top) and experimental (bottom) spectrum of 9PP<sub>syn, pre</sub>. The numbered lines indicate the assigned band vibrations in Table S2.

Table S2: Band assignment of 9PP<sub>syn, pre</sub>. The nomenclature follows that of Table S1.

| Number Figure S13 | ν<sub>exp</sub> [cm<sup>-1</sup>] | ν<sub>theo</sub> [cm<sup>-1</sup>] | Vibrational mode | Orientation |
|-------------------|-----------------|-----------------|------------------|-------------|
| 1                 | 664             | 672             | ν(C-O)<sub>me</sub> | ip          |
| 2                 | 699             | 715             | δ(C-H)<sub>end</sub> | oop         |
| 3                 | 756             | 779             | δ(C-H)           | oop         |
| 4                 | 823             | 864             | δ(C-H)           | oop         |
| 5                 | 951             | 968             | ν(C-O)<sub>me</sub> | ip          |
| 6                 | 1019            | 1023            | δ(C-H)<sub>me</sub> | ip          |
| 7                 | 1082            | 1109            | ν(C-O-C)<sub>me</sub> | ip          |
| 8                 | 1174            | 1188            | ν(C-C)           | ip          |
| 9                 | 1229            | 1242            | ν(C-C)           | ip          |
| 10                | 1396            | 1433            | δ(C-H)           | ip          |
| 11                | 1491            | 1520            | δ(C-H)           | ip          |
| 12                | 2822            | 3002            | ν(C-H<sub>3</sub>)<sub>me</sub> | ip          |
Figure S14: Time-resolved infrared spectroscopy of 9PP$_{\text{syn, pre}}$ annealed at 250 °C (top) and 300 °C (bottom). As for 9PP$_{\text{anti, pre}}$ precursor specific absorption bands gradually decrease. Due to dewetting IR-measurement was stopped after 3 min.
Figure S15: Degree of conversion from 9PP<sub>syn, pre</sub> to 9PP<sub>syn</sub> at different temperatures. Dewetting leads to distortion especially at the beginning.
3 Mass analysis of thin films

Drop-coated films (2 mg/mL, chloroform) were prepared using $9PP_{\text{anti,pre}}$ as precursor. The films were thermally annealed at 300 °C and coated with a thin layer of TCNQ (7,7,8,8-tetracyanoquinodimethane) as a MALDI matrix. Due to aggregation effects of $9PP$ molecules, high laser intensities were needed for desorption during mass analysis, also resulting in partial fragmentation during the measurement, the ratio of which was highly dependent on the exact spot used for desorption. Under the same conditions, analysis of $9PP_{\text{anti,pre}}$ films was unsuccessful - measurements resulted in fragmentation, some of the observed m/z ratios being identical to peaks observed for analysis of the $9PP_{\text{anti}}$ films, but no precursor molecular peak was found. Thus, we conclude that $9PP$ is indeed formed with our thermal aromatization procedure.

Figure S16: MALDI spectra of $9PP_{\text{anti}}$ film using TCNQ as matrix.
Figure S17: Measured isotope pattern of 9PP_{anti} (black) compared to calculated isotope pattern (red).
Figure S18: MALDI-spectra of \(9\text{PP}_\text{anti}\) (black) compared to mass spectra of \(9\text{PP}_\text{anti,pre}\) (red) showing similar fragmentation patterns at around 700 m/z. Peaks observed at higher m/z ratios for \(9\text{PP}\) do not match exactly any partially aromatized \(9\text{PP}\) precursor structures (indicating incomplete conversion), as m/z ratios are by 2 m/z too low as, e.g. a fourfold demethoxylated precursor. Intensities from the spectrum cannot be regarded as a measure of purity due to the desorption problems of the fully aromatized rigid-rod-like hydrocarbon product.
4 Time-resolved photoluminescence

Table S3: Emission lifetimes of 9PP\textsubscript{anti/syn} thermally generated in thin films.

| Film   | Excitation Wavelength nm | Lifetime 1 ns/\% | Lifetime 2 ns/\% | Lifetime 3 ns/\% |
|--------|--------------------------|------------------|------------------|------------------|
| 9PP\textsubscript{anti} | 430                      | 0.2/34           | 0.4/58           | 0.7/8            |
|        | 485                      | 3.1/43           | 6.1/44           | 12.3/13          |
|        | 520                      | 3.1/44           | 6.3/51           | 12.5/5           |
|        | 560                      | 2.7/39           | 5.4/32           | 10.8/29          |
| 9PP\textsubscript{syn}   | 430                      | 0.3/41           | 0.6/48           | 1.2/11           |
|        | 485                      | 2.9/43           | 5.8/44           | 11.5/13          |
|        | 520                      | 2.6/46           | 5.2/44           | 10.4/10          |
|        | 560                      | 3.2/44           | 6.5/19           | 13.1/37          |

Lifetimes were fitted with a tris-exponential function. While the emission maxima at 485 nm, 520 nm and 560 nm show nearly the same lifetimes and fractions (both 9PP\textsubscript{anti} and 9PP\textsubscript{syn}), the lifetimes for the weak emission at 430 nm are significantly shorter. In accordance with literature,\textsuperscript{[11,12]} emission bands at 485, 520, 560 nm can be assigned to aggregates and the one at 430 nm to another species, most likely resulting from single-strand emission, as in thin-films more than one emitting species is likely to be present. The same trend was previously found for \textit{para}-hexaphenylen.\textsuperscript{[13,14]}

![Figure S19: Lifetime measurements of 9PP\textsubscript{anti/syn} in thin film.](image)
5 X-ray Crystallographic Analysis

Figure S20: Crystal structure of anti-2 (CCDC: 1981192).

Table S4: Crystal data and structure refinement.

| Description                                      | Value                      |
|--------------------------------------------------|----------------------------|
| Empirical formula                                | C\textsubscript{19}H\textsubscript{17}BrO\textsubscript{2} |
| Formula weight                                   | 357.23                     |
| Temperature                                      | 100(2) K                   |
| Wavelength                                       | 1.54178 Å                  |
| Crystal system                                   | monoclinic                 |
| Space group                                      | P2\textsubscript{1}/c      |
| Z                                                | 4                          |
| Unit cell dimensions                             | a = 19.153(6) Å, α = 90 deg. |
|                                                  | b = 7.2001(15) Å, β = 95.86(3) deg. |
|                                                  | c = 11.743(4) Å, γ = 90 deg. |
| Volume                                           | 1610.9(8) Å\textsuperscript{3} |
| Density (calculated)                             | 1.47 g/cm\textsuperscript{3} |
| Absorption coefficient                           | 3.51 mm\textsuperscript{-1} |
| Crystal shape                                    | brick                      |
| Crystal size                                     | 0.181 x 0.120 x 0.053 mm\textsuperscript{3} |
| Crystal colour                                   | colourless                 |
| Theta range for data collection                  | 4.6 to 68.5 deg.           |
| Index ranges                                     | -22 ≤ h ≤ 22, -8 ≤ k ≤ 3, -14 ≤ l ≤ 13 |
| Reflections collected                            | 7548                       |
| Independent reflections                          | 2858 (R(int) = 0.0193)     |
| Observed reflections                             | 2606 (I > 2σ(I))          |
| Absorption correction                            | Semi-empirical from equivalents |
| Max. and min. transmission                       | 1.71 and 0.46              |
| Refinement method                                | Full-matrix least-squares on F\textsuperscript{2} |
| Data/restraints/parameters                        | 2858 / 0 / 204             |
| Goodness-of-fit on F\textsuperscript{2}          | 1.04                       |
| Final R indices (I>2σ(I))                        | R1 = 0.044, wR2 = 0.105    |
| Largest diff. peak and hole                      | 1.88 and -1.39 e Å\textsuperscript{-3} |
Table S5: Atomic coordinates and equivalent isotropic displacement parameters (Å\(^2\)) . \(U_{\text{eq}}\) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

| Atom | x       | y       | z       | \(U_{\text{eq}}\) |
|------|---------|---------|---------|-------------------|
| Br1  | 0.0168(1)| 1.2851(1)| 0.6762(1)| 0.0466(2)         |
| O1   | 0.2458(1)| 0.6396(3)| 0.5141(2)| 0.0190(4)         |
| O2   | 0.3105(1)| 0.5166(3)| 0.9557(2)| 0.0226(5)         |
| H2   | 0.287(2) | 0.606(6) | 0.959(3) | 0.033(11)         |
| C11  | 0.2384(1)| 0.6695(4)| 0.6344(2)| 0.0166(6)         |
| C12  | 0.3072(1)| 0.7387(4)| 0.6930(2)| 0.0167(6)         |
| H12  | 0.3268   | 0.8478   | 0.6637   | 0.020             |
| C13  | 0.3421(2)| 0.6574(4)| 0.7825(2)| 0.0171(6)         |
| H13  | 0.3845   | 0.7134   | 0.8145   | 0.021             |
| C14  | 0.3187(1)| 0.4821(4)| 0.8368(2)| 0.0171(6)         |
| C15  | 0.2500(2)| 0.4129(4)| 0.7781(2)| 0.0182(6)         |
| H15  | 0.2306   | 0.3034   | 0.8072   | 0.022             |
| C16  | 0.2147(2)| 0.4940(4)| 0.6886(2)| 0.0191(6)         |
| H16  | 0.1721   | 0.4383   | 0.6569   | 0.023             |
| C18  | 0.2938(2)| 0.4939(4)| 0.4924(2)| 0.0238(6)         |
| H18A | 0.3011   | 0.4935   | 0.4110   | 0.036             |
| H18B | 0.2743   | 0.3740   | 0.5129   | 0.036             |
| H18C | 0.3388   | 0.5146   | 0.5384   | 0.036             |
| C21  | 0.1827(1)| 0.8195(4)| 0.6394(2)| 0.0178(6)         |
| C22  | 0.1436(2)| 0.8898(4)| 0.5425(3)| 0.0251(6)         |
| H22  | 0.1506   | 0.8425   | 0.4690   | 0.030             |
| C23  | 0.0944(2)| 1.0294(5)| 0.5531(3)| 0.0311(7)         |
| H23  | 0.0678   | 1.0777   | 0.4870   | 0.037             |
| C24  | 0.0844(2)| 1.0971(4)| 0.6598(3)| 0.0297(7)         |
| C25  | 0.1221(2)| 1.0283(4)| 0.7571(3)| 0.0277(7)         |
| H25  | 0.1147   | 1.0755   | 0.8305   | 0.033             |
| C26  | 0.1709(2)| 0.8897(4)| 0.7461(2)| 0.0222(6)         |
| H26  | 0.1968   | 0.8414   | 0.8128   | 0.027             |
| C31  | 0.3771(2)| 0.3385(4)| 0.8362(2)| 0.0167(6)         |
| C32  | 0.4315(2)| 0.3370(4)| 0.9244(2)| 0.0207(6)         |
| H32  | 0.4307   | 0.4220   | 0.9861   | 0.025             |
| C33  | 0.4868(2)| 0.2133(4)| 0.9233(3)| 0.0243(6)         |
| H33  | 0.5233   | 0.2132   | 0.9845   | 0.029             |
| C34  | 0.4891(2)| 0.0896(4)| 0.8335(3)| 0.0239(6)         |
| H34  | 0.5271   | 0.0049   | 0.8325   | 0.029             |
| C35  | 0.4353(2)| 0.0911(4)| 0.7451(2)| 0.0215(6)         |
| H35  | 0.4364   | 0.0065   | 0.6833   | 0.026             |
| C36  | 0.3798(2)| 0.2146(4)| 0.7458(2)| 0.0198(6)         |
| H36  | 0.3434   | 0.2146   | 0.6844   | 0.024             |
Table S6: Hydrogen coordinates and isotropic displacement parameters (Å²).

| Atom | x    | y    | z    | U_{eq}  |
|------|------|------|------|---------|
| H2   | 0.287(2) | 0.606(6) | 0.959(3) | 0.033(11) |
| H12  | 0.3268 | 0.8478 | 0.6637 | 0.020 |
| H13  | 0.3845 | 0.7134 | 0.8145 | 0.021 |
| H15  | 0.2306 | 0.3034 | 0.8072 | 0.022 |
| H16  | 0.1721 | 0.4383 | 0.6569 | 0.023 |
| H18A0.3011 | 0.4935 | 0.4110 | 0.036 |
| H18B0.2743 | 0.3740 | 0.5129 | 0.036 |
| H18C0.3388 | 0.5146 | 0.5384 | 0.036 |
| H22  | 0.1506 | 0.8425 | 0.4690 | 0.030 |
| H23  | 0.0678 | 1.0777 | 0.4870 | 0.037 |
| H25  | 0.1147 | 1.0755 | 0.8305 | 0.033 |
| H26  | 0.1968 | 0.8414 | 0.8128 | 0.027 |
| H32  | 0.4307 | 0.4220 | 0.9861 | 0.025 |
| H33  | 0.5233 | 0.2132 | 0.9845 | 0.029 |
| H34  | 0.5271 | 0.0049 | 0.8325 | 0.029 |
| H35  | 0.4364 | 0.0065 | 0.6833 | 0.026 |
| H36  | 0.3434 | 0.2146 | 0.6844 | 0.024 |

Table S7: Anisotropic displacement parameters (Å²) for ala24. The anisotropic displacement factor exponent takes the form: -2 pi² (h² a² U_{11} + ... + 2h k a b U_{12})

| Atom | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|------|--------|--------|--------|--------|--------|--------|
| Br1  | 0.0284(2) | 0.0331(2) | 0.0781(3) | -0.0104(2) | 0.0046(2) | 0.0110(2) |
| O1   | 0.0258(10) | 0.0190(10) | 0.0124(9) | -0.0011(8) | 0.0032(7) | 0.0031(8) |
| O2   | 0.0312(12) | 0.0238(11) | 0.0134(10) | 0.0000(8) | 0.0053(8) | 0.0077(10) |
| C11  | 0.0203(14) | 0.0193(13) | 0.0104(12) | 0.0003(10) | 0.0026(10) | -0.0013(11) |
| C12  | 0.0205(14) | 0.0161(13) | 0.0143(13) | -0.0008(10) | 0.0058(10) | -0.0025(11) |
| C13  | 0.0210(13) | 0.0151(13) | 0.0159(13) | -0.0035(10) | 0.0047(10) | -0.0011(11) |
| C14  | 0.0204(14) | 0.0187(14) | 0.0127(13) | -0.0012(10) | 0.0040(10) | 0.0001(11) |
| C15  | 0.0216(14) | 0.0164(13) | 0.0175(13) | 0.0010(11) | 0.0068(11) | -0.0007(11) |
| C16  | 0.0180(13) | 0.0171(14) | 0.0226(14) | -0.0008(11) | 0.0034(11) | -0.0026(11) |
| C18  | 0.0320(16) | 0.0215(15) | 0.0185(14) | -0.0024(11) | 0.0055(12) | 0.0058(13) |
| C21  | 0.0171(13) | 0.0153(13) | 0.0214(14) | 0.0011(11) | 0.0035(11) | -0.0028(11) |
| C22  | 0.0239(15) | 0.0284(16) | 0.0232(15) | 0.0022(12) | 0.0040(12) | 0.0028(13) |
| C23  | 0.0224(15) | 0.0313(18) | 0.0387(19) | 0.0087(15) | -0.0012(13) | 0.0039(13) |
| C24  | 0.0197(15) | 0.0208(15) | 0.049(2) | -0.0014(14) | 0.0057(14) | 0.0000(12) |
| C25  | 0.0223(15) | 0.0263(16) | 0.0356(18) | -0.0083(13) | 0.0080(13) | -0.0047(13) |
| C26  | 0.0214(14) | 0.0244(15) | 0.0212(14) | -0.0018(12) | 0.0045(11) | -0.0009(12) |
| C31  | 0.0231(14) | 0.0142(13) | 0.0136(13) | 0.0027(10) | 0.0056(10) | -0.0007(11) |
| C32  | 0.0264(15) | 0.0188(14) | 0.0168(14) | -0.0005(11) | 0.0024(11) | -0.0001(12) |
| C33  | 0.0238(15) | 0.0235(15) | 0.0252(16) | 0.0050(12) | 0.0004(12) | 0.0000(12) |
| C34  | 0.0239(15) | 0.0186(15) | 0.0301(16) | 0.0049(12) | 0.0080(12) | 0.0031(12) |
| C35  | 0.0281(15) | 0.0177(14) | 0.0201(14) | -0.0006(11) | 0.0098(12) | -0.0015(12) |
| C36  | 0.0260(15) | 0.0182(14) | 0.0153(14) | 0.0007(11) | 0.0034(11) | -0.0007(11) |
| Bond Lengths (Å) and Angles (deg) |
|----------------------------------|
| Br1-C24 1.897(3)               | O2-C14-C13 109.4(2) |
| O1-C18  1.435(3)               | O2-C14-C15 108.9(2) |
| O1-C11  1.450(3)               | C13-C14-C15 111.6(2) |
| O2-C14  1.443(3)               | O2-C14-C31 105.9(2) |
| O2-H2   0.79(4)                | C13-C14-C31 108.5(2) |
| C11-C16 1.506(4)               | C15-C14-C31 112.4(2) |
| C11-C12 1.508(4)               | C16-C15-C14 124.6(3) |
| C11-C21 1.523(4)               | C16-C15-H15 117.7 |
| C12-C13 1.323(4)               | C14-C15-H15 117.7 |
| C12-H12 0.9500                 | C15-C16-C11 123.6(3) |
| C13-C14 1.503(4)               | C15-C16-H16 118.2 |
| C13-H13 0.9500                 | C11-C16-H16 118.2 |
| C14-C15 1.507(4)               | O1-C18-H18A 109.5 |
| C14-C31 1.524(4)               | O1-C18-H18B 109.5 |
| C15-C16 1.325(4)               | H18A-C18-H18B 109.5 |
| C16-H15 0.9500                 | O1-C18-H18C 109.5 |
| C16-H16 0.9500                 | H18A-C18-H18C 109.5 |
| C18-H18A 0.9800                | H18B-C18-H18C 109.5 |
| C18-H18B 0.9800                | C22-C21-C26 118.7(3) |
| C18-H18C 0.9800                | C22-C21-C11 123.2(3) |
| C21-C22 1.392(4)               | C26-C21-C11 118.1(2) |
| C21-C26 1.392(4)               | C22-C22-C23 120.2(3) |
| C22-C23 1.393(4)               | C21-C22-H22 119.9 |
| C22-H22 0.9500                 | C23-C22-H22 119.9 |
| C23-C24 1.375(5)               | C24-C23-C22 119.7(3) |
| C23-H23 0.9500                 | C24-C23-H23 120.2 |
| C24-C25 1.381(5)               | C22-C23-H23 120.2 |
| C25-C26 1.381(4)               | C23-C24-C25 121.1(3) |
| C25-H25 0.9500                 | C23-C24-Br1 120.3(2) |
| C26-H26 0.9500                 | C25-C24-Br1 118.5(2) |
| C31-C36 1.391(4)               | C26-C25-C24 118.9(3) |
| C31-C32 1.392(4)               | C26-C25-H25 120.5 |
| C32-C33 1.386(4)               | C24-C25-H25 120.5 |
| C32-H32 0.9500                 | C25-C26-C21 121.4(3) |
| C33-C34 1.384(4)               | C25-C26-H26 119.3 |
| C33-H33 0.9500                 | C21-C26-H26 119.3 |
| C34-C35 1.387(4)               | C36-C31-C32 118.7(3) |
| C34-H34 0.9500                 | C36-C31-C14 121.5(2) |
| C35-C36 1.387(4)               | C32-C31-C14 119.7(2) |
| C35-H35 0.9500                 | C33-C32-C31 120.9(3) |
| C36-H36 0.9500                 | C33-C32-H32 119.6 |
| C18-O1-C11 114.2(2)            | C31-C32-H32 119.6 |
| C14-O2-H2 108.3(2)             | C34-C33-C32 120.3(3) |
| O1-C11-C16 110.6(2)            | C34-C33-H33 119.9 |
| O1-C11-C12 109.0(2)            | C32-C33-H33 119.9 |
| C16-C11-C12 111.8(2)           | C33-C34-C35 119.1(3) |
| O1-C11-C21 106.3(2)            | C33-C34-H34 120.5 |
| C16-C11-C21 109.6(2)           | C35-C34-H34 120.5 |
| C12-C11-C21 109.3(2)           | C36-C35-C34 120.8(3) |
| C13-C12-C11 124.2(3)           | C36-C35-H35 119.6 |
| C13-C12-H12 117.9              | C34-C35-H35 119.6 |
| C11-C12-H12 117.9              | C35-C36-C31 120.3(3) |
| C12-C13-C14 124.1(3)           | C35-C36-H36 119.9 |
| C12-C13-H13 117.9              | C31-C36-H36 119.9 |
| C14-C13-H13 117.9              | |
6 NMR Spectra

Figure S21: $^1$H NMR spectrum of *anti-2* in CD$_2$Cl$_2$ (300 MHz, 298 K).

Figure S22: $^{13}$C NMR spectrum of *anti-2* in CD$_2$Cl$_2$ (75 MHz, 298 K).
Figure S23: $^1$H NMR spectrum of anti-3 in CD$_2$Cl$_2$ (300 MHz, 298 K).

Figure S24: $^{13}$C NMR spectrum of anti-3 in CD$_2$Cl$_2$ (75 MHz, 298 K).
Figure S25: $^1$H NMR spectrum of syn-3 in CD$_2$Cl$_2$ (300 MHz, 298 K).

Figure S26: $^{13}$C NMR spectrum of syn-3 in CD$_2$Cl$_2$ (75 MHz, 298 K).
Figure S27: $^1$H NMR spectrum of 9PP$^{-}\text{anti,pre}$ in CD$_2$Cl$_2$ (300 MHz, 298 K).

Figure S28: $^1$H NMR spectrum of 9PP$^{-}\text{syn,pre}$ in CD$_2$Cl$_2$ (300 MHz, 298 K).
7 Solid-State NMR Spectra

Solid-State $^{13}$C NMR spectra of $9PP_{syn,anti,pre}$ and $9PP_{syn,anti}$, obtained from thermal aromatization in the bulk at 300 °C for 5 h. The $^{13}$C spectra of $9PP_{syn,anti}$ shows good agreement with other reported para-phenylenes.$^{[15]}$ Fitting of the $^{13}$C signals in the product spectra confirms the chain length for both, $9PP_{syn}$ and $9PP_{anti}$, of 9 phenylene units.

Figure S29: $^{13}$C($^1$H)-CP/MAS-NMR spectra of $9PP_{anti,pre}$ (25 kHz, 298 K).

Figure S30: $^{13}$C($^1$H)-CP/MAS-NMR spectra of $9PP_{anti}$ (25 kHz, 298 K).
Figure S31: $^{13}$C($^1$H)-CP/MAS-NMR spectra of 9PP<sub>syn,pre</sub> (25 kHz, 298 K).

Figure S32: $^{13}$C($^1$H)-CP/MAS-NMR spectra of 9PP<sub>syn</sub> (25 kHz, 298 K).
Figure 33. $^{13}$C-CP/MAS-NMR spectra of a) $9PP_{syn,pre}$, b) $9PP_{syn}$, c) $9PP_{anti,pre}$ and d) $9PP_{anti}$ recorded with 3ms contact time. The $^{13}$C-CP/MAS spectra clearly demonstrate the aromatization of the products.
Number of phenyl rings per chain

\[ n = \frac{10I_c}{I_e} + 2 \]

\( I_e \): intensity of aromatic CH sites at chain ends
\( I_c \): intensity of aromatic CH sites of central rings

\[ n = 8.9 \]

**Figure 34.** Fit of the \(^{13}\text{C-CH}\) signal intensity for the chain ends and central rings confirms the chain length of 9 rings for \(9\text{PP}_{\text{syn}}\).

Number of phenyl rings per chain

\[ n_1 = \frac{10I_c}{I_e} + 2 \]

\( I_c \): intensity of aromatic CH sites at chain ends
\( I_e \): intensity of aromatic CH sites of central rings

\[ n_1 = 8.5 \]

**Figure 35.** Fit of the \(^{13}\text{C-CH}\) signal intensity for the chain ends and central rings confirms the chain length of 9 rings for \(9\text{PP}_{\text{anti}}\).
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