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Curved graphene nanoribbons derived from tetrahydropyrene-based polyphenylenes *via* one-pot K-region oxidation and Scholl cyclization[†]

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Precise synthesis of graphene nanoribbons (GNRs) is of great interest to chemists and materials scientists because of their unique opto-electronic properties and potential applications in carbon-based nanoelectronics and spintronics. In addition to the tunable edge structure and width, introducing curvature in GNRs is a powerful structural feature for their chemi-physical property modification. Here, we report an efficient solution synthesis of the first pyrene-based GNR (PyGNR) with curved geometry via one-pot K-region oxidation and Scholl cyclization of its corresponding well-soluble tetrahydropyrene-based polyphenylene precursor. The efficient A2B2-type Suzuki polymerization and subsequent Scholl reaction furnishes up to \sim 35 nm long curved GNRs bearing cove- and armchairedges. The construction of model compound 1, as a cutout of PyGNR, from a tetrahydropyrene-based oligophenylene precursor proves the concept and efficiency of the one-pot K-region oxidation and Scholl cyclization, which is clearly revealed by single crystal X-ray diffraction analysis. The structure and optical properties of PyGNR are investigated by Raman, FT-IR, solid-state NMR, STM and UV-Vis analysis with the support of DFT calculations. PyGNR exhibits a narrow optical bandgap of ~1.4 eV derived from a Tauc plot, qualifying as a low-bandgap GNR. Moreover, THz spectroscopy on PyGNR estimates its macroscopic charge mobility μ as ~3.6 cm² V⁻¹ s⁻¹, outperforming several other curved GNRs reported via conventional Scholl reaction.

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Introduction

Structurally well-defined graphene nanoribbons (GNRs) are constantly developing materials, amassing more and more attention due to their unique opto-electronic properties1-3 and potential to be integrated into future nanoelectronics and spintronics.3-9 The physicochemical properties of atomically precise GNRs highly depend on their edge structures and widths.6,7,10-13 In the well-investigated armchair-edged GNRs (AGNR), three different families of ribbons can be distinguished as a function of carbon atoms along the ribbon width, exhibiting semiconducting properties.^{6,14-21} On the other hand, zigzagedged GNRs (ZGNR) possess edge states and metallic character, but could only be synthesized on surfaces to date, drastically limiting their applicability.^{2,6,22-24} In stark contrast to largely uncontrolled top-down methods, the mentioned examples were achieved by bottom-up synthesis, an approach also rendering mixed edges possible. For instance, mixing armchair edge with zigzag edge can create intriguing physical phenomena, as recently exemplified by the topological quantum phase in GNRs.7,25-27 Aside from the edge type, curvature (or non-



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planarity) is another powerful structural feature for tuning the properties of GNRs,^{28,29} such as liquid-phase dispersibility and charge transport behavior.^{30–32} A common synthetic pathway to achieve curvature in GNRs is to introduce the structural motif of small [*n*]helicene units on its periphery, such as [4]helicene or [5]helicene,^{33–35} creating the cove edge^{12,36–38} or fjord edge³⁹ respectively. For example, the regular incorporation of cove subunits by elimination of a single carbon atom along the opposite ZGNR edges can produce a series of curved GNRs with periodic cove-zigzag edge structure, providing GNRs with well-tunable band structures and effective masses (Fig. 1a).¹¹ In the context of this structural modification of ZGNRs towards cove-edge topologies, it raises the synthetic question if cove-edges can also be accessed from the parent design of AGNRs (Fig. 1b).

Pyrene (2) is one of the widely used building blocks in material science.⁴⁰ Its biphenyl-like structure with two double



Fig. 1 (a) One example of curved GNRs with periodic cove-zigzag edges; (b) curved GNRs obtained by incorporation of cove units along the 9-AGNR edges, reported in this work.



Scheme 1 Reoxidation of 4,5,9,10-tetrahydropyrene (**3**) and synthetic route to model compound **1**. Reagents and conditions: (a) (i) RANEY®-nickel, EtOAc, rt, 48 h, (ii) Pd/C (10%), EtOAc, H₂, 60 °C, 24 h; (b) FeCl₃ (10 eq.), MeNO₂, CH₂Cl₂, rt, 5 min; (c) (BPin)₂, 4,4'-di-tert-butyl-2,2'-bipyridine, [Ir(OMe)(COD)]₂, THF, 80 °C, overnight; (d) **5**, **6**, Pd(dppf) Cl₂·CH₂Cl₂, K₃PO₄, PhMe/H₂O, 115 °C, overnight; (e) (i) SnCl₂, EtOH/ EtOAc, reflux, overnight, (ii) NBS, CHCl₃, rt, 10 min; (f) **6**, Pd(dppf)Cl₂, K₃PO₄, PhMe/H₂O, 115 °C, 48 h; (g) CHBr₃, isoamylnitrite, 100 °C, overnight; (h) Pd(PPh₃)₄, K₂CO₃, PhMe/H₂O, 115 °C, 48 h; (i) DDQ, MeSO₃H, CH₂Cl₂, rt, 30 min, then DDQ, TfOH, rt, 3 min.

bond characteristics, called the K-region (Scheme 1), distinguishes pyrene from other polycyclic aromatic hydrocarbons (PAHs).^{40,41} Moreover, its full-zigzag edge structure renders it a versatile motif for constructing highly conjugated π -systems with tailored edge topologies and functions. Although it is possible to functionalize pyrene on every position by various synthetic methods,^{42–44} its incorporation into large PAHs (or nanographenes) *via* Scholl reaction of pyrene-based dendritic oligophenylene precursors is often unsuccessful due to its high reactivity and rich electron density.^{45,46} Therefore, the expansion of pyrene-based precursors toward the synthesis of GNRs remains a synthetic challenge.

Herein, we demonstrate an efficient solution synthesis of a novel curved pyrene-based GNR (PyGNR) bearing cove- and armchair-edges from the predesigned tetrahydropyrene-based polyphenylene precursor P1. It is worth mentioning that when trying to obtain PyGNR from pyrene-embedded polyphenylene directly (Fig. 1b), only short and insoluble oligomers could be obtained due to the poor solubility of the pyrene bearing polymers. To overcome this obstacle, the unsaturated polymer P1 is first obtained by A2B2-Suzuki polymerization of 2,7-bis(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-4,5,9,10-tetrahydro-pyrene (4) and alkyl-chain equipped tetraphenyl-substituted 1,4-diiodobenzene (12). Subsequently, one-pot oxidation of the tetrahydropyrene K-regions towards pyrene moieties together with the Scholl reaction, enables the desired formation of PyGNR. The resultant PyGNR reaches a length of up to \sim 35 nm according to the gel-permeation chromatography (GPC) analysis of P1. As a cutout of PyGNR, model compound 1 was successfully synthesized to evaluate the efficiency and feasibility of the one-pot cyclodehydrogenation process. The structure and optical properties of PyGNR were well investigated by solid-state NMR, FT-IR, Raman, STM imaging and UV-Vis spectroscopy. Due to the unique edge structure, a narrow optical bandgap of \sim 1.4 eV was determined by a Tauc-plot (ESI Fig. S2⁺), slightly below the value of 1.75 eV predicted by DFT. Furthermore, timeresolved terahertz spectroscopy reveals a macroscopic charge mobility of $\sim 3.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, outperforming several other examples37,39 of curved GNRs obtained by conventional Scholl reactions.

Results and discussion

Synthesis of model compound 1

The synthesis of model compound **1** is illustrated in Scheme 1. Considering the solubility issue of **1**, mesitylene side groups were installed instead of the more common *tert*-butyl groups. First, 4,5,9,10-tetrahydropyrene (3) was obtained from the commercially available pyrene (2) after desulfurization with RANEY®-nickel and hydrogenation under pressure in the presence of Pd/C among over-hydrogenated products in 31% yield (Scheme 1). Then, iridium-catalyzed borylation⁴² was used to furnish compound **4** in 73% yield. Slightly modifying the synthesis route of Lungerich *et al.*⁴⁷ allowed us to synthesize compound **10** starting from 1,2,3-tribromo-5-nitrobenzene (5, see ESI†). A Suzuki coupling reaction between **5** and **6** afforded compound **7** in 69% yield, followed by a two-step sequence of reduction and bromination to furnish compound 8 in 60% yield. Another Suzuki coupling of 8 and 6 gave compound 9 in 77% yield. In a Sandmeyer-type reaction, aniline 9 was brominated to compound 10 with a yield of 47%. Finally, building blocks 4 and 10 were cross-coupled by the Suzuki reaction, providing the oligophenylene precursor 11 in a low yield of 35% due to the steric hindrance of the inner mesitylene units in 11. For the cyclodehydrogenation of 11, we initially examined the classic Scholl conditions by use of FeCl₃ or triflic acid with DDQ in CH₂Cl₂, but failed to obtain a defined product (ESI Chapter 1.2.12†). We then turned to a milder approach using methyl-sulfonic acid, and DDQ, which furnished a time-stable MALDI-TOF signal 12 proton masses above the desired signal, indicating a partially closed intermediate (ESI Fig. S32†).

After adding the stronger triflic acid to the reaction mixture, the bright red compound **1** was obtained in 60% yield after only three minutes of additional reaction time.

The chemical identity of 1 was confirmed by high-resolution mass spectroscopy and NMR spectroscopy, whose key changes for compounds 11 and 1 are illustrated in Fig. 2, respectively. The MALDI-TOF spectra show a mass difference of 28 proton masses. This implies that in addition to the cyclodehydrogenation of 24 protons, 4 additional hydrogens were removed from the tetrahydropyrene moiety to reestablish the pyrene K-region. In addition to the reduction of NMR signals in the case of compound 1, the total amount of protons in the aliphatic region was reduced from 98 to 90 (ESI Fig. S19-S21⁺), further confirming the successful conversion of the tetrahydropyrene moieties. The anti π - π -stacking properties of the mesitylene side groups enabled NMR spectroscopy of 1 with a sufficient resolution to assign the protons using twodimensional COSY- and NOESY-NMR spectroscopy (ESI Fig. S22 and S23[†]). Furthermore, a shift in the downfield due to the aromatic ring currents was observed, especially for the protons a and b (proton labels seen in Scheme 1), resulting from their location on the cove edge.



Fig. 2 (a) MALDI-TOF-MS of compounds 11 and 1. (b) 1 H-NMR spectra of compound 11 (top) and compound 1 (bottom), recorded in CDCl₃ at 300 MHz (proton labels see Scheme 1).

Crystallographic analysis of compounds 11 and 1

Sufficiently large crystals for X-ray crystallographic analysis were obtained for 11 and 1, respectively (Fig. 3). In the case of 11, a suitable crystal for single crystal X-ray diffraction analysis (SCXRD) was grown from 11 dissolved in CH₂Cl₂ by slow evaporation of the solvent. SCXRD reveals an unconjugated phenylic structure combined with twisted sp³-bonds of the central tetrahydropyrene unit. The sp³-carbon single bonds are revealed by the bond lengths of 1.57 Å and 1.58 Å, respectively. Compound 11 crystallizes in the triclinic space group P1. In the case of 1, a single crystal was obtained by slow diffusion of methanol in its CS2-solution. The SCXRD analysis reveals 1 as a curved π -conjugated molecule featuring four [4]helicene subunits. The hexa-peri-hexabenzocoronene (HBC) units have been fully fused and share a pyrene unit in the center, revealing the successful conversion of the tetrahydropyrene moieties back to a fully sp²-hybridized pyrene core and supporting the proposed one-pot K-region oxidation and Scholl cyclization. The cove edges between the pyrene K-region and the HBC moieties possess an average torsion angle of 21°, resulting in curvature of the molecule. In contrast to compound 11, compound 1 crystallizes in the monoclinic space group $P2_1/c$. The bond lengths in the K-regions of compound 1 are significantly shorter, about 1.35 Å (1.337 Å and 1.361 Å, respectively), matching with the value for pyrene (2) reported by the literature and indicating double bond character.48 In the solid packing, the crystal layers of **1** are slightly slipped with the π -surfaces facing towards each other, forming π - π -stacks (Fig. 3c).

Synthesis of PyGNR

After confirming the model reaction formed the desired compound **1**, we further extended the synthesis towards **PyGNR** based on tetrahydropyrene monomer **4**. Early attempts of this



Fig. 3 X-ray crystallographic structure (ORTEP drawing at the 50% probability level) of (a) **11** and (b) **1** (top and side view). (c) Crystalpacking of **1**. Hydrogen atoms and solvent molecules have been omitted for clarity.

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A₂B₂ Suzuki polymerization with 2,7-diborylated pyrene gave only oligomers according to linear mode MALDI-TOF MS measurements, which remained insoluble and, therefore, unavailable for further solution processing (ESI Fig. S34[†]). When these oligomers were exposed to Scholl-reaction conditions as a suspension, partial cyclization and decomposition were observed. In consequence, the 4,5,9,10-tetrahydropyrene containing polymer P1 (Scheme 2) was designed. The monomer 12,15 substituted with 3,7-dimethyloctyl chains, was chosen as the coupling partner for the diborylated pyrene derivative 4 to increase the processibility of the GNR later. In contrast to pyrene (2), when switching to the tetrahydropyrene derivative 4, soluble polymers were obtained when refluxing the monomers, Pd(PPh₃)₄, K₂CO₃ in toluene and H₂O for 48 hours. Linear mode MALDI-TOF MS of the crude material revealed groups of signals up to $m/z \sim 10\,000$, spaced by the repetition unit of 1145 g mol⁻¹ (ESI Fig. S33[†]). After washing with HCl/MeOH, filtration and subsequent dissolution and filtration in chloroform, the crude polymer P1 was obtained after removing the chloroform in vacuo. P1 was then divided into 4 fractions by recycling GPC and further analyzed by analytical GPC against polystyrene standards. Our analysis reveals an averaged molar mass of $M_{\rm n} \sim 24\,000$ Da and a narrow polydispersity index (PDI) of 1.2 for the heaviest (10 wt%) crude polymers (ESI Fig. S36-S38†), significantly enhancing the molecular weight compared to other GNRs reported via the Suzuki polymerization method.15,39 The protons could be assigned to their positions in P1 by ¹H-NMR spectroscopy (ESI Fig. S30[†]). Due to P1's excellent solubility, even ¹³C spectra could be recorded effortlessly (ESI Fig. S31[†]). Finally, the Scholl reaction of the first fraction of P1 with FeCl₃ (7 equiv./H) as the Lewis acid and oxidant in CH₂Cl₂ for 7 days yielded the PyGNR. The resultant PyGNR possesses combined cove and armchair edges with an estimated average length of \sim 35 nm based on the $M_{\rm n}$ of the corresponding **P1**.

Structural characterizations of PyGNR

The structures of precursor P1 and PyGNR were then characterized by a combination of solid-state 1H and $^{13}C\{^1H\}$ MAS

NMR (¹H decoupled ¹³C magic angle spinning NMR) at a high spinning speed of 62.5 kHz (Fig. 4a and b), FT-IR and Raman (Fig. 4c and d). While the precursor P1 shows well-defined signals in the ¹H MAS NMR spectrum (Fig. 4a) for both the aromatic and aliphatic protons centered around 0.9 ppm and 6.6 ppm, respectively, broader lines are observed for PyGNR along with a downfield shift of the aromatic protons to 8.9 ppm. This can be attributed to a more rigid structure and extended π conjugation of PyGNR compared to P1. Deconvolution of the quantitative ¹H MAS NMR spectra shows a lower relative content of aromatic protons in PyGNR compared to P1 as a result of the graphitization and matches the expected relative intensities within the expected error margins. The graphitization process can also be confirmed by the ¹³C{¹H} MAS NMR spectra that were acquired with a short recycle delay of 3.5 s (Fig. 4b). Under the chosen experimental conditions, the ¹³C signal of the side chains only shows low intensity. In addition, the structural evolution from P1 to PyGNR is also supported by 2D solid-state NMR experiments (see ESI Chapter 9[†]).

The FT-IR spectra of P1 (Fig. 4c) exhibit typical vibrational modes for its structural elements. A more detailed discussion can be found in Chapter 10 of the ESI.[†] To assist in the identification of the corresponding vibrations, DFT calculations on the HSE/6-31G(d) level of theory were performed. The peak at 885 cm^{-1} , which was identified as the SOLO-mode (CH-wagging of an aromatic proton without adjacent protons, orange)49 of the tetrahydropyrene moiety, confirms once more the presence of unsaturated bonds in P1. The FT-IR spectrum of PyGNR was then compared to P1. The abundant aromatic CH-stretchings in the range of 3020-3060 cm⁻¹ were diminished in the graphitized ribbon due to the cyclodehydrogenation. The CHstretchings from the aliphatic side chains from 2750 to 3000 cm⁻¹ were retained. Further, characteristic vibrations were investigated in the fingerprint region and identified by comparison to the HSE/6-31G(d) prediction. First, the SOLOmodes can be found around 882 cm^{-1} (pink), a further indication of successful graphitization. Interestingly, PyGNRs CHwagging of the cove SOLO-mode and pyrene DUO moieties



Scheme 2 Synthetic route to PyGNR. Reagents and conditions: (a) 4 (stoichiometric), 12, Pd(PPh₃)₄, K₂CO₃, Aliquat 336, PhMe/H₂O, 110 °C, 48 h; (b) FeCl₃, MeNO₂, CH₂Cl₂, rt, 7 d. Inset is the optimized geometry of PyGNR, aliphatic side chains omitted for clarity.





Fig. 4 (a) Quantitative ¹H MAS NMR spectra of P1 and PyGNR with 64 s recycle delay. Signals of remaining solvent are marked with +; (b) ¹³C{1H} MAS NMR spectra with a short recycle delay of 3.5 s and 25 kHz of low-power CW decoupling. The signal of PTFE spacer material is marked with +. All spectra were acquired at a static field of 11.74 T and a spinning frequency of 62.5 kHz. (c) Measured and calculated (at the DFT HSE/6-31G(d) level) FT-IR spectra of P1 and PyGNR. In the fingerprint region (900–600 cm⁻¹), the calculated IR intensity was scaled by a factor 10; (d) Raman spectra of PyGNR, recorded at 514 nm.

(CH-wagging of two adjacent aromatic protons) can be found in a joint vibration mode around 840 cm^{-1} (red), demonstrating the successful conversion of the tetrahydro-moieties into pyrene K-regions. This claim is further supported by the ring vibrations of the pyrene K-region, which can be attributed to the newly emerged signals around 790-770 cm^{-1} (blue), absent in P1. Last, the broad signal at 640 cm^{-1} (brown) provides another strong indication of successful graphitization, as the DFTprediction assigns these modes as in plane aromatic CCscaffold vibrations. The Raman spectrum of PyGNR (Fig. 4d) shows two strong D and G bands at \sim 1340 and \sim 1590 cm⁻¹. Furthermore, double resonance peaks can be found at ~ 2605 , \sim 2880 and \sim 3170 cm⁻¹, which can be assigned as the 2D, D + G and 2G bands. The peak positions are in line with other bottomup solution-synthesized GNRs reported in the literature.13,21,37 As expected from the low twist in the cove regions observed from the crystal structure of compound 1 (21°), PyGNR shows only mediocre dispersibility and processability in polar organic solvents. However, imaging techniques such as STM vastly favor planar structures and usually fail to yield results for strongly curved geometries. Fig. 5 shows the results obtained by the STM characterization of PyGNR at the HOPG/heptanoic acid interface. Large scale (Fig. 5a) and high resolution (Fig. 5b) STM images show the presence of a clear stripe patterned structure observed in isolated areas of the HOPG surface. Line profile analysis performed in graphite calibrated STM images (Fig. 5c) confirms the presence of parallel rows comprising a periodicity

of 3.3 (± 0.2) nm which matches the expected periodicity from molecular modelling (Fig. 5d). This distance indicates that **PyGNR** is adsorbed without alkyl chain interdigitation, but instead, next to one another⁵⁰ as depicted in Fig. 5d. The stability obtained during the STM measurements suggests high on-surface adsorption energies due to strong vdW-interactions between the **PyGNR** core and the graphitic substrate. This



Fig. 5 Large scale (a) and high resolution (b) STM images of **PyGNR** self-assembled at the heptanoic acid/HOPG interface; (c) graphite-calibrated representative line-profile measured along the red arrow direction in STM image of panel (a); (d) molecular model of **PyGNR** showing packing without alkyl chain interdigitation. $U_{\text{bias}} = -0.4$ V and $I_{\text{set}} = 0.05$ nA.



Fig. 6 (a) Absorption spectra of 1, 11, P1 (CHCl₃), and PyGNR (NMP) as well as DFT-predicted 1 and PyGNR; (b) time-resolved terahertz photoconductivity of PyGNR following photoexcitation. The absorbed photon fluence is $\sim 1 \text{ mJ cm}^{-2}$. (c) The frequency-resolved THz complex conductivity measured $\sim 1.2 \text{ ps}$ after photoexcitation. The solid lines are fits to the Drude–Smith model.

allowed the acquisition of multiple STM images (see ESI Fig. S51[†]).

In contrast, the low twist of **PyGNR** seems to be sufficient to resolve the π - π -interactions observed in planar GNRs,¹⁵ as additional investigations by TEM, SEM and powder XRD revealed an amorphous structure of the material (see ESI Chapters 11–13†). Subsequent to SEM imaging, EDX confirmed the complete removal of residual iron ions (see ESI Chapter 11†).

Optical property and THz spectroscopy study of PyGNR

The UV-Vis absorption spectra were recorded in $CHCl_3$ solutions. An NMP dispersion of **PyGNR** that was allowed to settle overnight was used (Fig. 6a). Due to its lack of conjugation, polymer **P1** (dark grey) possesses only high energy absorption bands starting with a first peak at 338 nm, which agrees well with the polymer fragment **11** (light gray), exhibiting peaks at similar wavelengths (326 nm and 267 nm). Significantly redshifted to 559 nm due to its full conjugation, the first absorption of **1** (blue) can be found. Two distinct absorption peaks of **1** are visible at 437 nm and 367 nm.

Compared to its short fragment 1, the absorption spectrum of **PyGNR** (purple) is further red-shifted and displays an absorption peak with a maximum at ~680 nm as well as a shoulder at 485 nm, showing strong proof for graphitization compared to the high energy absorptions of **P1**. The optical bandgap was determined as 1.4 eV by a Tauc-plot (ESI Fig. S2†), qualifying as a low bandgap GNR. The experimental result is in good agreement with the DFT-prediction of 1.75 eV. In addition, the simulated TD-DFT curves for **1** (light blue) and **PyGNR** (light purple) match well with the experimental spectra.

To investigate the charge transport properties of **PyGNR**, we conducted optical pump-THz probe (OPTP) spectroscopy measurements (see the Experimental details in the ESI Chapter 8^{+}).^{51,52} Fig. 6b shows the time-resolved complex photoconductivity of **PyGNR** dispersed in 1,2,4-trichlorobenzene, following above-gap optical excitation (here, 1.55 eV laser pulses). The rapid sub-picosecond rise of the real photoconductivity indicates charge carrier generation, and the following rapid decay can be assigned to the carrier trapping and/or the formation of bound electron-hole states (*i.e.*, excitons) due to the strong quantum confinement and the reduced dielectric screening

effect.52,53 The exciton formation is featured by a large imaginary conductivity and a small real conductivity at the later time scale. To further study the free charge carriers' transport properties, we measured the conductivity spectrum around the peak photoconductivity (\sim 1.2 ps after photoexcitation), as shown in Fig. 6c (for Experimental details, see ESI Chapter 8†). The phenomenological Drude-Smith (DS) model was applied to describe the frequency-resolved complex conductivity (for details, see ESI[†]).^{54,55} The DS model considers the charge scattering occurring via preferential backscattering due to conjugation or structural deformation in materials. A parameter c is introduced to characterize the backscattering probability, ranging from 0 (isotropic scattering) to -1 (100% backscattering). From the results, we obtained an effective charge scattering time $\tau = 38 \pm 1$ fs and $c = -0.970 \pm 0.003$. Furthermore, by considering a reduced charge carrier effective mass $m^* =$ $0.55m_0$ from DFT (considering contributions from both electrons and holes; see the ESI† for details), we estimate the macroscopic charge mobility $\left(\mu = \frac{e\tau}{m^*}(1+c)\right)$ to be ~3.6 cm² $V^{-1} s^{-1}$, outperforming similar examples of curved GNRs in the recent literature, such as hybrid cove- and gulf-edged GNRs,37 and a 9AGNR based fjord-edged GNR.39

Conclusion

In summary, we demonstrate the efficient synthesis of the first curved pyrene-based GNR (PyGNR) by introducing cove units along 9-AGNR edges. The synthetic strategy to obtain PyGNR was carried out in a previously unreported strategy, regenerating the K-regions of the pyrene moieties in one step during the cyclodehydrogenation of a well-soluble unsaturated polyphenylene precursor P1. Proving the structural concept of the ribbon and the proposed one-pot oxidation, model compound 1 was also synthesized. The obtained PyGNR was fully characterized by solid-state NMR, FT-IR, Raman, STM and UV-Vis spectroscopy, also supported by the DFT spectra simulations. THz study of PyGNR revealed a macroscopic charge mobility of \sim 3.6 cm² V⁻¹ s⁻¹, outperforming similar GNRs reported by conventional Scholl-cyclizations.37,39 Furthermore, PyGNR is the first GNR with accessible pyrene K-regions, rendering further functionalization, e.g., by oxidation to diketones, possible.43

Strategic use of tetrahydro-derivatives demonstrates the feasibility of obtaining novel GNRs in one step from sp³-C containing polymer precursors and opens up possibilities for other GNRs suffering from polymer solubility issues or dehydrogenation problems.

Data availability

Experimental and computational data can be found in the ESI.† The cif-files of the crystal structures can be found alongside the ESI.†

Author contributions

J. Ma and X. Feng supervised the project. S. Obermann, J. Melidonie and L. A. Guerrero-León synthesized and characterized the compounds. W. Zheng, M. Bonn and H. I. Wang measured and interpreted the THz measurements. S. Böckmann and M. R. Hansen measured and interpreted the solidstate NMR. S. Osella and D. Beljonne performed the DFT calculations. N. Arisnabarreta and S. De Feyter carried out and analyzed the solid-liquid STM imaging. F. Hennersdorf and J. J. Weig and measured and refined the single crystal structures. S. Obermann, J. Ma and X. Feng co-wrote the paper with contributions from all co-authors.

Conflicts of interest

The authors declare no conflict of interest.

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References

- J. Cai, C. A. Pignedoli, L. Talirz, P. Ruffieux, H. Söde, L. Liang, V. Meunier, R. Berger, R. Li, X. Feng, K. Müllen and R. Fasel, *Nat. Nanotechnol.*, 2014, 9, 896–900.
- 2 P. Ruffieux, S. Wang, B. Yang, C. Sanchez-Sanchez, J. Liu,
 T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli,
 D. Passerone, T. Dumslaff, X. Feng, K. Müllen and R. Fasel, *Nature*, 2016, 531, 489–492.
- 3 W. Niu, J. Ma, P. Soltani, W. Zheng, F. Liu, A. A. Popov, J. J. Weigand, H. Komber, E. Poliani, C. Casiraghi, J. Droste, M. R. Hansen, S. Osella, D. Beljonne, M. Bonn, H. I. Wang, X. Feng, J. Liu and Y. Mai, *J. Am. Chem. Soc.*, 2020, **142**, 18293–18298.
- 4 X. Li, X. Wang, L. Zhang, S. Lee and H. Dai, *Science*, 2008, **319**, 1229–1231.
- 5 V. Saraswat, R. M. Jacobberger and M. S. Arnold, *ACS Nano*, 2021, **15**, 3674–3708.
- 6 O. v. Yazyev, Acc. Chem. Res., 2013, 46, 2319-2328.
- 7 D. J. Rizzo, G. Veber, T. Cao, C. Bronner, T. Chen, F. Zhao, H. Rodriguez, S. G. Louie, M. F. Crommie and F. R. Fischer, *Nature*, 2018, **560**, 204–208.
- 8 Y. Huang, W. T. Dou, F. Xu, H. B. Ru, Q. Gong, D. Wu, D. Yan, H. Tian, X. P. He, Y. Mai and X. Feng, *Angew. Chem., Int. Ed.*, 2018, 57, 3366–3371.
- 9 A. Narita, X. Y. Wang, X. Feng and K. Müllen, *Chem. Soc. Rev.*, 2015, 44, 6616–6643.
- 10 Y. F. Zhang, Y. Zhang, G. Li, J. Lu, Y. Que, H. Chen, R. Berger, X. Feng, K. Müllen, X. Lin, Y. Y. Zhang, S. Du, S. T. Pantelides and H. J. Gao, *Nano Res.*, 2017, **10**, 3377–3384.
- 11 X. Wang, J. Ma, W. Zheng, S. Osella, N. Arisnabarreta, J. Droste, G. Serra, O. Ivasenko, A. Lucotti, D. Beljonne, M. Bonn, X. Liu, M. R. Hansen, M. Tommasini, S. De Feyter, J. Liu, H. I. Wang and X. Feng, *J. Am. Chem. Soc.*, 2022, **144**, 228–235.
- 12 J. Liu, B. W. Li, Y. Z. Tan, A. Giannakopoulos, C. Sanchez-Sanchez, D. Beljonne, P. Ruffieux, R. Fasel, X. Feng and K. Müllen, J. Am. Chem. Soc., 2015, 137, 6097–6103.
- M. G. Schwab, A. Narita, Y. Hernandez, T. Balandina,
 K. S. Mali, S. de Feyter, X. Feng and K. Müllen, *J. Am. Chem. Soc.*, 2012, 134, 18169–18172.
- 14 W. Yang, A. Lucotti, M. Tommasini and W. A. Chalifoux, J. Am. Chem. Soc., 2016, 138, 9137–9144.
- 15 X. Yang, X. Dou, A. Rouhanipour, L. Zhi, H. J. Räder and K. Müllen, *J. Am. Chem. Soc.*, 2008, **130**, 4216–4217.
- 16 J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun,
 S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh,
 X. Feng, K. Müllen and R. Fasel, *Nature*, 2010, 466, 470–473.
- 17 R. S. Jordan, Y. L. Li, C. W. Lin, R. D. McCurdy, J. B. Lin, J. L. Brosmer, K. L. Marsh, S. I. Khan, K. N. Houk, R. B. Kaner and Y. Rubin, *J. Am. Chem. Soc.*, 2017, **139**, 15878–15890.
- 18 L. Talirz, H. Söde, T. Dumslaff, S. Wang, J. R. Sanchez-Valencia, J. Liu, P. Shinde, C. A. Pignedoli, L. Liang,

V. Meunier, N. C. Plumb, M. Shi, X. Feng, A. Narita, K. Müllen, R. Fasel and P. Ruffieux, *ACS Nano*, 2017, **11**, 1380–1388.

- 19 K. Sun, P. Ji, J. Zhang, J. Wang, X. Li, X. Xu, H. Zhang and L. Chi, *Small*, 2019, **15**, 1804526.
- 20 K. Y. Yoon and G. Dong, Mater. Chem. Front., 2020, 4, 29-45.
- 21 G. Li, K. Y. Yoon, X. Zhong, J. Wang, R. Zhang, J. R. Guest, J. Wen, X. Y. Zhu and G. Dong, *Nat. Commun.*, 2018, **9**, 1687.
- 22 S. Wang, L. Talirz, C. A. Pignedoli, X. Feng, K. Müllen, R. Fasel and P. Ruffieux, *Nat. Commun.*, 2016, 7, 11507.
- 23 P. P. Shinde, J. Liu, T. Dienel, O. Gröning, T. Dumslaff, M. Mühlinghaus, A. Narita, K. Müllen, C. A. Pignedoli, R. Fasel, P. Ruffieux and D. Passerone, *Carbon*, 2021, 175, 50–59.
- 24 P. P. Shinde, O. Gröning, S. Wang, P. Ruffieux, C. A. Pignedoli, R. Fasel and D. Passerone, *Carbon*, 2017, 124, 123–132.
- 25 Y. L. Lee, F. Zhao, T. Cao, J. Ihm and S. G. Louie, *Nano Lett.*, 2018, **18**, 7247–7253.
- 26 T. Cao, F. Zhao and S. G. Louie, *Phys. Rev. Lett.*, 2017, **119**, 076401.
- 27 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 and R. Fasel, *Nature*, 2018, 560, 209–213.
- 28 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 and A. Narita, *J. Am. Chem. Soc.*, 2018, **140**, 7803–7809.
- 29 W. Niu, J. Ma and X. Feng, Acc. Chem. Res., 2022, 55, 3322– 3333.
- 30 N. J. Schuster, L. A. Joyce, D. W. Paley, F. Ng, M. L. Steigerwald and C. Nuckolls, *J. Am. Chem. Soc.*, 2020, 142, 7066–7074.
- 31 M. Ball, Y. Zhong, Y. Wu, C. Schenck, F. Ng, M. Steigerwald, S. Xiao and C. Nuckolls, *Acc. Chem. Res.*, 2015, 48, 267–276.
- 32 I. Ivanov, Y. Hu, S. Osella, U. Beser, H. I. Wang, D. Beljonne, A. Narita, K. Müllen, D. Turchinovich and M. Bonn, *J. Am. Chem. Soc.*, 2017, **139**, 7982–7988.
- 33 Y. Shen and C. F. Chen, Chem. Rev., 2012, 112, 1463-1535.
- 34 M. Gingras, G. Félix and R. Peresutti, *Chem. Soc. Rev.*, 2013, 42, 1007–1050.
- 35 C. Li, Y. Yang and Q. Miao, *Chem.-Asian J.*, 2018, **13**, 884-894.
- 36 T. J. Sisto, Y. Zhong, B. Zhang, M. T. Trinh, K. Miyata, X. Zhong, X. Y. Zhu, M. L. Steigerwald, F. Ng and C. Nuckolls, *J. Am. Chem. Soc.*, 2017, **139**, 5648–5651.

- 37 L. Yang, J. Ma, W. Zheng, S. Osella, J. Droste, H. Komber,
 K. Liu, S. Böckmann, D. Beljonne, M. R. Hansen, M. Bonn,
 H. I. Wang, J. Liu and X. Feng, *Adv. Sci.*, 2022, 9, 2200708.
- 38 Y. Zhong, B. Kumar, S. Oh, M. T. Trinh, Y. Wu, K. Elbert, P. Li, X. Zhu, S. Xiao, F. Ng, M. L. Steigerwald and C. Nuckolls, *J. Am. Chem. Soc.*, 2014, **136**, 8122–8130.
- 39 X. Yao, W. Zheng, S. Osella, Z. Qiu, S. Fu, D. Schollmeyer, B. Müller, D. Beljonne, M. Bonn, H. I. Wang, K. Müllen and A. Narita, *J. Am. Chem. Soc.*, 2021, 143, 5654–5658.
- 40 T. M. Figueira-Duarte and K. Müllen, *Chem. Rev.*, 2011, **111**, 7260–7314.
- 41 S. Sasaki, S. Suzuki, K. Igawa, K. Morokuma and G. Konishi, J. Org. Chem., 2017, **82**, 6865–6873.
- 42 L. Ji, K. Fucke, S. K. Bose and T. B. Marder, *J. Org. Chem.*, 2015, **80**, 661–665.
- 43 J. Hu, D. Zhang and F. W. Harris, *J. Org. Chem.*, 2005, 70, 707–708.
- 44 X. Feng, J.-Y. Hu, C. Redshaw and T. Yamato, *Chem.–Eur. J.*, 2016, **22**, 11898–11916.
- 45 N. Ponugoti and V. Parthasarathy, *Chem.-Eur. J.*, 2022, 28, e202103530.
- 46 F. Liu, X. Shen, Y. Wu, L. Bai, H. Zhao and X. Ba, *Tetrahedron Lett.*, 2016, 57, 4157–4161.
- 47 D. Lungerich, D. Reger, H. Hölzel, R. Riedel, M. M. J. C. Martin, F. Hampel and N. Jux, *Angew. Chem.*, 2016, **128**, 5692–5696.
- 48 C. S. Frampton, K. S. Knight, N. Shankland and K. Shankland, *J. Mol. Struct.*, 2000, **520**, 29–32.
- 49 M. Tommasini, A. Lucotti, M. Alfè, A. Ciajolo and G. Zerbi, Spectrochim. Acta, Part A, 2016, 152, 134–148.
- 50 A. Narita, I. A. Verzhbitskiy, W. Frederickx, K. S. Mali, S. Alkaersig Jensen, M. R. Hansen, M. Bonn, S. De Feyter, C. Casiraghi, X. Feng and K. Müllen, *ACS Nano*, 2014, 8(11), 11622–11630.
- 51 R. Ulbricht, E. Hendry, J. Shan, T. F. Heinz and M. Bonn, *Rev. Mod. Phys.*, 2011, 83, 543–586.
- 52 A. Tries, S. Osella, P. Zhang, F. Xu, C. Ramanan, M. Kläui, Y. Mai, D. Beljonne and H. I. Wang, *Nano Lett.*, 2020, 20, 2993–3002.
- 53 G. Soavi, S. Dal Conte, C. Manzoni, D. Viola, A. Narita, Y. Hu, X. Feng, U. Hohenester, E. Molinari, D. Prezzi, K. Müllen and G. Cerullo, *Nat. Commun.*, 2016, 7, 11010.
- 54 S. A. Jensen, R. Ulbricht, A. Narita, X. Feng, K. Müllen, T. Hertel, D. Turchinovich and M. Bonn, *Nano Lett.*, 2013, 13, 5925–5930.
- 55 T. L. Cocker, D. Baillie, M. Buruma, L. V. Titova, R. D. Sydora,
 F. Marsiglio and F. A. Hegmann, *Phys. Rev. B*, 2017, 96, 205439.