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Monitoring the on-surface synthesis of graphene nanoribbons by mass spectrometry

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ABSTRACT. We present a mass spectrometric approach to monitor and characterize the intermediates of graphene nanoribbon (GNR) formation by chemical vapor deposition (CVD) on top of Au(111) surfaces. Information regarding the repeating units, lengths, and termini can be

obtained directly from the surface sample by a modified matrix assisted laser desorption/ionization (MALDI) method. The mass spectrometric results reveal ample oxidative side reactions under CVD conditions which can, however, be diminished drastically by introduction of protective H₂ gas at ambient pressure. Simultaneously, addition of hydrogen extends the lengths of the oligophenylenes and thus the final GNRs. Moreover, the prematurely formed cyclodehydrogenation products during the oligomer growth can be assigned by the mass spectrometric method. The obtained mechanistic insights provide valuable information for optimizing and upscaling the bottom-up fabrication of GNRs. Given the important role of GNRs as semiconductors, the mass spectrometric characterization provides a readily available tool to improve and characterize their structural perfection.

Graphene nanoribbons (GNRs), as quasi one-dimensional cutouts of graphene, can be prepared with atomic precision in width, length, and edge structure, and thus with a tailored band gaps^{1,2}. While “top-down” strategies suffer from limited control over the width and edge structure of the resulting GNRs³⁻⁶, one of the most promising “bottom-up” protocols is based on the surface-catalyzed dehalogenation, polymerization and cyclodehydrogenation of properly designed precursor monomers under ultrahigh vacuum (UHV) conditions with scanning probe microscopy (SPM) control⁷⁻¹⁷. Notwithstanding the conceptual value of this approach, it is labor-intensive, time-consuming and costly. Moreover, only very low amounts of material can be produced, thus limiting its further investigation and application e.g. in electronic devices. The sophisticated UHV-SPM instruments used for characterization of the GNRs are a further limitation hampering broader technological applications. Sakaguchi and Nakae *et al.*¹⁸ as well as our group¹⁹ have independently developed chemical vapor deposition (CVD) of specially designed monomers to prepare GNRs on a larger scale, with easier accessibility and under less

demanding vacuum conditions. However, the predictable fabrication of defined GNRs is still challenging due to open mechanistic issues and the lack of facile methods to characterize intermediates and side products during synthesis.^{14,20,21} Thus, a faster and less demanding characterization method was essential to avoid SPM monitoring. Whereas our method of CVD towards GNRs with essential analytical results was recently published¹⁹, we here present the mass spectrometric approach in-depth as a new and simplified method for structural analysis of GNR intermediates thereby providing unprecedented insights, not available so far. Matrix-assisted laser desorption ionization mass spectrometry (MALDI MS) enables a quick and detailed structural analysis of the key intermediate oligophenylenes directly on the metal surface during bottom-up fabrication of graphene nanoribbons. In the following we use the term “oligo-“ rather than “poly-“ because our mass spectrometric approach focuses on the low molecular weight fraction of the polymers where we can obtain the most detailed structure information. We imply that the results from the oligomers can be extrapolated to the polymers, produced under the same experimental conditions, which are also present in the samples. Our MS based method is also helpful to investigate the influence of preparative conditions on the intermediates and final GNR products during the fabrication process.

■ RESULTS AND DISCUSSION

The procedure of our recently published CVD strategy¹⁹ is illustrated in **Scheme 1**. Similar to the bottom-up fabrication of GNRs under UHV conditions⁸⁻¹⁰, the dihalo-substituted precursor monomer 6,11-dibromo-1,2,3,4-tetraphenyl triphenylene (DBTT, compound **1**) is sublimed onto the Au (111) surface. Different from the UHV approach, this is done at low vacuum conditions

(1.5 mbar) with the assistance of high temperature (250 °C) and a gas flow of argon. From experiments under UHV conditions^{9,15,22–25}, it is known that the deposited DBTT transforms into the targeted GNRs at temperatures around 400 °C. In order to check whether the fabrication mechanism follows the same principles as the already well understood UHV approach, the preparation procedure is carried out at a slightly lower temperature of 250 °C to obtain the intermediate oligomers without further annealing steps. Thereafter, the gold on mica substrate is taken out from the CVD setup, attached to a MALDI sample plate, covered with a thin layer of {(2E)-2-methyl-3-[4-(2-methyl-2-propenyl)phenyl]-2-propen-1-ylidene} malononitrile (DCTB) matrix by sublimation, and finally characterized by mass spectrometry (MS).

Scheme 1. Bottom-up fabrication of graphene nanoribbons with selected monomer precursors on gold surfaces by CVD.

Figure 1 illustrates the MALDI mass spectrum of intermediate oligophenylenes prepared from the DBTT precursor monomer. It shows signals up to a molecular weight of about 3200 Da

pointing toward oligophenylenes with six repeating units. The mass difference between neighboring signals is 530.2034 Da, which corresponds exactly to the mass of pure hydrocarbon repeating units obtained from the 1,2,3,4-tetraphenyltriphenylene biradical, similar to the chemical reaction under UHV conditions^{8,9,26}.

Figure 1. MALDI MS spectrum of intermediate oligophenylenes prepared from DBTT precursor monomer. (The intensities of the signals in black are magnified by a factor of 54.)

A closer look into the mass region near each oligomer signal, however, reveals further peaks with a regular pattern at higher m/z values. The magnified region of the trimer (inset of Figure 1), for example, shows a series of mass peaks with differences of 15.9865 Da, indicating that they correspond to oxidized species with up to six oxygen atoms. For higher homologues, oxidized byproducts with even higher numbers of oxygen atoms can be detected. We assume that this

oxidation side reaction arises from traces of oxygen in the CVD chamber due to the relatively low vacuum.

As a consequence, we introduce hydrogen gas mixed with argon at ambient pressure into the CVD tube, which should act as an oxygen scavenger and eliminate the oxidation side reactions. The effect of hydrogen introduction is obviously reflected in the mass spectra: As shown in Figure 2, the signal of oligomers up to approximately 11000 Da, representing 20 repeating units, can now be identified. The oligomers are even longer than the pentadecamer with a length of 12 nm in our previous report¹⁹. Moreover, the oxidized oligomeric byproducts are diminished to a large extent (in Figure S1). It is well known that the high molecular weight components of an oligomeric mixture are commonly underestimated in mass spectrometric analysis, thus, one can expect that in reality much longer chains could be present in these samples.

Figure 2. MALDI MS spectrum of oligomeric intermediates prepared from DBTT in ambient-pressure CVD under argon/hydrogen. (The intensities of the signals in grey and black are magnified by a factor of 630 and 5000, respectively.)

Besides the purity and chain length of an oligomer, a further important feature is the nature of end groups. Their knowledge provides a better understanding of the terminating reactions limiting a further oligomer growth. As discussed in ref. ¹⁹ and further illustrated in Figure 3, the experimental isotopic pattern of the DBTT trimer as well as the exact mass correlate with the elemental composition of C₁₂₆H₈₀, thus representing two hydrogens as end groups. Whereas it is not surprising to detect hydrogen end groups in oligomers produced under hydrogen atmosphere, it is remarkable, that also the oligomers produced without hydrogen atmosphere show the same termination by hydrogens as illustrated in Figure 3c. The H termini are also detected during the fabrication of GNRs under UHV conditions, and it was supposed²⁵ that the H atoms involved in the oligomer termination originate from a premature cyclodehydrogenation reaction during the oligomerization step since there is no other external hydrogen source present. The premature cyclodehydrogenation causes additional hydrogen loss of the desired oligophenylenes during the oligomer growth step, thus resulting in signals with lower molecular weights than those of the expected oligomers in the mass spectrum. Taking the trimer as an example, the corresponding prematurely cyclodehydrogenated products can be assigned to the signals with lower masses than the monoisotopic peak at $m/z = 1592.62$ Da (Figure 3c). These peaks are not observed in Figure 3b under identical measuring conditions, thus, one can exclude that these signals come from a laser-induced cyclization²⁷ during our MALDI MS measurements. Herein, mass spectrometry experiments for the first time unambiguously prove the existence of premature

cyclodehydrogenation. Moreover, by comparing the numbers of repeating units (Figures 1 & 2) and prematurely cyclodehydrogenated products (Figure 3) of the oligophenylenes with and without hydrogen protective atmosphere, the introduction of additional hydrogen in the CVD setup seems to be an efficient way to suppress the dehydrogenation during oligomer growth, and elongate the length of the oligomers. While the addition of external H_2 in our CVD system is a potential cause for oligomer termination and thus capable of restricting the achievable chain length, on the contrary the introduction of hydrogen gas extends the length of the resulting oligomer. One might speculate that i) the presence of oxygen inhibits the chain growth reaction on the surface and the added H_2 binds the remaining oxygen in the CVD tube and ii) the introduced H_2 suppresses the premature cyclodehydrogenation reaction, which might generate hydrogen radicals, serving as a more active termination reagent than H_2 .

Figure 3. The theoretical isotopic distribution of DBTT trimer (a); experimental MALDI MS spectra of DBTT trimeric intermediates prepared under ambient Ar/H_2 atmosphere (b) and under Ar gas (c).

The products of premature cyclodehydrogenation are even more obvious during the preparation of heteroatom “doped” GNRs, especially for the sulfur containing species. In an analogous procedure, the precursor monomer 6,11-dibromo-1,4-diphenyl-2,3-di-(thien-3-yl)-triphenylene (DBSS, compound **2**) is first sublimed onto the metal surface, then the Au(111) substrate is heated and maintained at a temperature of 200 °C for dehalogenation and oligomerization. Signals up to heptamers can be identified in the MS spectrum (Figure S2). The zoom-in spectrum (Figure 4), however, exhibits much broader signal distributions. Those peaks with m/z ratios lower than the desired monoisotopic mass ($m/z=1628.34$ Da) can be assigned to prematurely cyclodehydrogenated species. In comparison with the oligophenylene prepared from DBTT monomers (Figure 3), the prematurely cyclodehydrogenated compounds fabricated with heteroatom-containing precursor monomers are much more significant even if protective H₂ gas and lower deposition temperature is employed. 18 of 38 hydrogens, namely almost half of the hydrogens at the active sites, have already been dehydrogenated prior to the high temperature annealing. It thus appears that these heteroatom-containing oligomeric intermediates, in comparison with the non-doped analogues, are more active and easier to be dehydrogenated during the oligomer growth step. The previously described SPM^{8,9,24,25,28,29} can confirm the existence of premature cyclodehydrogenation according to the height differences of the oligophenylenes obtained on gold surfaces, however, this method cannot provide information regarding the degree of hydrogen loss during oligomer growth. The mass spectrometry results, herein, reveal the content of dehydrogenated species directly and can be further used as a feedback to tune the preparative conditions, such as pressure, heating temperature and duration, toward oligophenylenes with minimized premature cyclodehydrogenation and longer chain lengths.

Figure 4. MALDI mass spectra of DBSS trimeric intermediates prepared in ambient-pressure CVD under argon/hydrogen atmosphere.

In order to investigate GNRs with different edge structures, a new precursor monomer (2,12-dibromo-7,14-diphenylbenzo[*m*]tetraphene, DBBT, compound **3**) was designed for the tailored fabrication of zig-zag edged GNRs. However, even under optimized conditions with H₂ atmosphere, ample amounts of oxidized oligophenylenes are detected in the MALDI MS spectrum (Figure 5). Taking the trimeric signals as an example (in the inset of Figure 5), the intensities of oxidized byproducts, especially for the species with even-numbered oxygen atoms, are higher than the desired oligophenylenes. The reason might be that the zigzag edge is chemically highly active to the remaining oxygen in the CVD setup and more demanding conditions, such as UHV^{15,24}, are needed for the defect-free fabrication of GNRs containing zigzag edges.

Figure 5. MALDI MS spectrum of intermediate oligomers prepared from DBBT monomer precursor.

In case of the well-established 10,10'-dibromo-9,9'-bianthryl (DBBA, compound 4) precursor monomer, our mass spectrometry method provides the unique opportunity to compare the chemical purity of GNR precursor samples produced under UHV conditions with samples obtained from the CVD setup. For the UHV sample, the Au (111) surface was covered by 80% of a monolayer with DBBA molecules prior to the chain growth step. The results for both approaches are shown in Figure 6. Obviously very similar oligophenylene distributions are detected with regard to chain length and the trace amounts of oxidative side products, indicating that the qualities of the oligomers and thereafter the GNRs fabricated under CVD and UHV conditions are quite comparable. The tiny amounts of oxidized oligomers, also observed for the

sample from UHV, is most probably due to active intermediates reacting rapidly with air when taken out of the UHV chamber.

Figure 6. MALDI MS spectrum of oligophenylenes prepared with CVD (top) and UHV (bottom) systems, respectively.

The feasibility of co-oligomer formation by our CVD procedure was already demonstrated by mass spectrometry in Ref ¹⁹. However, the premature cyclodehydrogenations of the previously employed monomer precursors (DBTT, DBNN and DBNS) were not obvious. We are now able to differentiate the prematurely cyclodehydrogenated species from the co-oligomers. Two different heterocyclic precursor monomers, namely DBSS (compound **2**) and 4,4'-(6,11-dibromo-1,4-diphenyltriphenylene-2,3-diyl)dipyridine (DBNN, compound **5**), are sublimed onto the gold surface and heteroatom containing oligophenylene signals up to heptamers can be detected (Figure S3). As shown in the magnified region of the hydrogen-terminated dimer in Figure 7, besides the previously observed prematurely dehydrogenated species, three different

co-oligomer compositions can be detected, representing all three possible theoretical chemical constitutions formed by the two different monomers DBSS and DBNN.

Figure 7. The comparison of the experimental and theoretical isotopic distributions of intermediate dimers prepared from DBSS & DBNN precursor monomers.

The mass spectrometric results confirm the coexistence of different co-oligomer structures even in the cases where the mass peaks of prematurely cyclodehydrogenated derivatives can intermingle with the isotopic distributions of desired co-oligomers. The advantage of mass spectrometry is even more obvious for all-hexagon oligophenylenes, such as co-oligomers prepared from DBTT and DBNN. The SPM approaches usually have difficulties to distinguish N atoms from C atoms because of their similar topographic morphologies^{9,29}, especially in nonplanar oligophenylene structures. As depicted in Figure S4, mass spectrometry can directly distinguish co-oligomers with and without N-doping according to their exact mass differences.

Finally, the relative intensity of signals corresponding to different oligomers also reflects their respective amounts in the mixture.

Besides the oligomerization step toward the oligophenylenes on the metal surface, the subsequent annealing temperature is a key parameter to afford fully aromatic GNRs via the intramolecular cyclodehydrogenation reaction. A series of five DBTT oligomer samples (Compound **1**, see structures in Scheme 1) from one batch are treated at different increasing annealing temperatures for 5 minutes. The on-surface MALDI MS spectra (Figure 8) of all samples are magnified at the trimeric region and compared with the original oligomeric intermediates to monitor the process of cyclodehydrogenation. The mass spectrum of the specimen annealed at 300 °C is similar to that of the sample without annealing, showing only a minor signal intensity for slightly dehydrogenated $[M-2H]^+$ species. Accordingly, the metal-catalyzed intramolecular cyclodehydrogenation just starts at about this temperature.

Figure 8. MALDI mass spectra of DBTT trimeric intermediates prepared at different annealing temperatures.

At an annealing temperature of 350 °C, a loss of up to 10 hydrogens out of 38 for the desired fully dehydrogenated GNRs (**Scheme 1**) can be detected. If the annealing temperature is further increased, however, the signal to noise ratios of DBTT oligomers decrease rapidly without evidence of further dehydrogenation (Figure S5). The spectrum of the oligomers after annealing at 450°C mainly shows background signals without the original trimeric signals. A possible reason for this behavior could be that the “planarized”, “graphitized” GNRs have such a strong interaction with the gold surface that they are not desorbed efficiently and only the residual less dehydrogenated species are visible in the mass spectra. Therefore, the GNR thin film is transferred onto a silicon wafer¹⁹ to decrease the interaction between the fully aromatized oligophenylene with the substrate surface. The signals which could then be detected on the silicon surface represent even-numbered carbon clusters (Figure S6) and exhibit high similarity to the LDI MS spectrum of graphene reported by Kong *et al.*³⁰. Thus, no structure specific signals can be obtained from the final product by mass spectrometry. However, results from other spectroscopic characterization, such as SPM, Raman, ultraviolet-visible-near-infrared (UV-vis-NIR) and angle-resolved high-resolution electron energy loss spectroscopy (HREELS) prove the full dehydrogenation of the oligomeric intermediates into GNRs as reported in Ref. ¹⁹ We assume that mass spectrometry fails to detect the fully dehydrogenated species because of the high laser power necessary for their desorption into the gas phase which seems to be far beyond the fragmentation threshold for the GNRs. Nevertheless, one can assume that the chain length of the oligomeric intermediates detected by mass spectrometry is also representative for the GNRs produced thereof.

■ CONCLUSION

We describe a MALDI MS approach to gain important structural information on oligophenylene precursors for on-surface synthesized GNRs. These comprise the degree of oligomerization, structural purity, termination processes, and side reactions. The ratio of premature cyclodehydrogenation during oligomer growth step can be easily characterized. An important feed-back tool is thus obtained to optimize the CVD procedure: the significant oxidation of oligomeric intermediates observed under the initial growth condition with argon as inert atmosphere could be avoided almost completely by the introduction of additional hydrogen gas at ambient pressure, at the same time remarkably improving the accessible chain length. High quality materials can thus be obtained with a purity comparable to UHV samples.

The heterostructure of co-oligomers prepared from two different precursor monomers can also be successfully identified. Mass spectrometric analysis is further applicable in the case of N-doped heterojunction GNRs whereas SPM cannot differentiate N from C atoms in the GNR structures. The isotopic signals can be employed to characterize the compositions of different oligomers and possible prematurely dehydrogenated species. Further investigations may be facilitated by the mass spectrometric monitoring toward a predictable fabrication of defined heterojunction GNRs by selecting appropriate monomer pairs, substrates and preparation conditions.

The new mass spectrometric quality control of GNR formation directly at the production surface simplifies the analysis of GNR intermediates, thereby providing detailed structural information not available so far by established methods. The identification and elimination of side reactions is indispensable for improving the structural perfection and can be the headstone

for a larger scale production of well-defined GNRs, thus ensuring the availability of these attractive materials for future applications in practical devices.

Experimental parts

GNR CVD growth: The GNR synthesis procedure has been described in detail elsewhere.¹⁹ In brief, the Au/mica substrates were divided into pieces of $10 \times 10 \text{ mm}^2$ and put into a quartz tube with outer diameter of 35 mm and an inner diameter of 33 mm in a horizontal tube furnace (Nabertherm, RT 80-250/11S). Precursor monomers were loaded upstream of the Au/mica substrates and sublimed at 250-325 °C onto the Au/mica surfaces using a heated belt (Thermocoax Isopad S20). The Au/mica substrates were heated and kept at 250 °C for 30 min to induce dehalogenation and radical addition. A gas flow of Ar (500 s.c.c.m.) was used as protective gas and H₂ (100 s.c.c.m.) at ambient pressure was also employed after optimization of experimental conditions. A series of post-annealing temperatures from 300 to 450 °C have been tested and finally the temperature of 450 °C was selected. For the fabrication of doped GNRs, the preparation process was identical, except that 200 °C was used for the dehalogenation and oligomerization of the N-doped or the N, S co-doped monomers. For the growth of co-oligomer heterostructures, the two precursor species were evaporated separately by two heating belts on an Au/mica substrate held at 220 °C. After deposition, the sample was post-annealed at 450 °C.

GNR UHV growth: 7-arm-chair GNRs were synthesized from 10,10'-dibromo-9,9'-bianthryl (DBBA) precursor monomers⁸ with the following procedure: Au(111)/mica substrates $4 \times 4 \text{ mm}^2$ (200nm Au, Phasis, Switzerland) were cleaned in ultra-high-vacuum by two sputtering (1 kV Ar⁺, 10min) and annealing (470°C, 10 min) cycles. Next, the monomer was sublimed at 220°C

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2
3 onto the Au(111)/mica substrate held at 200°C. After 4 minutes deposition (which led to 0.8
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5 monolayer coverage) the substrate was annealed up to 200°C (heating rate 1K/s) to induce
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7 polymerization followed by annealing at 410°C in order to cyclodehydrogenate the polymers and
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9 form the ribbons.
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14 Mass spectrometry: All mass spectra were performed with a SYNAPT G2-Si instrument (Waters
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16 Corp., Manchester, UK) using matrix-assisted laser desorption/ionization (MALDI) mass
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18 spectrometry. The sample wafer was attached onto a sample plate by double-sided adhesive tape
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20 and put head over on top of a crucible with {(2E)-2-methyl-3-[4-(2-methyl-2-propenyl)phenyl] -
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22 2-propen-1-ylidene}malononitrile (DCTB) matrix inside. Then, a thin layer of DCTB matrix was
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24 sublimed onto the cold surface of each wafer under ambient conditions at a crucible temperature
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26 of 175°C during 30 minutes. For LDI MS tests, the analyte wafers were attached onto the sample
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28 plate without further DCTB matrix sublimation. During the MS measurements, a laser firing
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30 frequency of 100 Hz and a relative laser power of 150 were used. The spectra were processed
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32 with Masslynx V4.1 software.
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42 ASSOCIATED CONTENT

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45 **Supporting Information.** The experimental section and additional mass spectra can be found in
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47 the supporting information part. This material is available free of charge via the Internet at
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49 <http://pubs.acs.org>.
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REFERENCES

- (1) Narita, A.; Wang, X.-Y.; Feng, X.; Müllen, K. *Chem. Soc. Rev.* **2015**, *44* (18), 6616–6643.
- (2) Narita, A.; Feng, X.; Müllen, K. *Chem. Rec.* **2015**, *15* (1), 295–309.
- (3) Tour, J. M. *Chem. Mater.* **2014**, *26* (1), 163–171.
- (4) Jiao, L.; Zhang, L.; Wang, X.; Diankov, G.; Dai, H. *Nature* **2009**, *458* (7240), 877–880.
- (5) Kosynkin, D. V.; Higginbotham, A. L.; Sinitskii, A.; Lomeda, J. R.; Dimiev, A.; Price, B. K.; Tour, J. M. *Nature* **2009**, *458* (7240), 872–876.
- (6) Han, M. Y.; Özyilmaz, B.; Zhang, Y.; Kim, P. *Phys. Rev. Lett.* **2007**, *98* (20), 206805.

- (7) Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M.; Peters, M. V.; Hecht, S. *Nat. Nanotechnol.* **2007**, 2 (11), 687–691.
- (8) Cai, J.; Ruffieux, P.; Jaafar, R.; Bieri, M.; Braun, T.; Blankenburg, S.; Muoth, M.; Seitsonen, A. P.; Saleh, M.; Feng, X.; Müllen, K.; Fasel, R. *Nature* **2010**, 466 (7305), 470–473.
- (9) Cai, J.; Pignedoli, C. A.; Talirz, L.; Ruffieux, P.; Söde, H.; Liang, L.; Meunier, V.; Berger, R.; Li, R.; Feng, X.; Müllen, K.; Fasel, R. *Nat. Nanotechnol.* **2014**, 9 (11), 896–900.
- (10) Fan, Q.; Gottfried, J. M.; Zhu, J. *Acc. Chem. Res.* **2015**, 48 (8), 2484–2494.
- (11) Cloke, R. R.; Marangoni, T.; Nguyen, G. D.; Joshi, T.; Rizzo, D. J.; Bronner, C.; Cao, T.; Louie, S. G.; Crommie, M. F.; Fischer, F. R. *J. Am. Chem. Soc.* **2015**, 137 (28), 8872–8875.
- (12) Bronner, C.; Stremlau, S.; Gille, M.; Brauße, F.; Haase, A.; Hecht, S.; Tegeder, P. *Angew. Chemie Int. Ed.* **2013**, 52 (16), 4422–4425.
- (13) Saywell, A.; Schwarz, J.; Hecht, S.; Grill, L. *Angew. Chemie Int. Ed.* **2012**, 51 (21), 5096–5100.
- (14) Chen, Y. C.; De Oteyza, D. G.; Pedramrazi, Z.; Chen, C.; Fischer, F. R.; Crommie, M. F. *ACS Nano* **2013**, 7 (7), 6123–6128.
- (15) Talirz, L.; Ruffieux, P.; Fasel, R. *Adv. Mater.* **2016**, 28 (29), 6222–6231.
- (16) Massimi, L.; Ourdjini, O.; Lafferentz, L.; Koch, M.; Grill, L.; Cavaliere, E.; Gavioli, L.; Cardoso, C.; Prezzi, D.; Molinari, E.; Ferretti, A.; Mariani, C.; Betti, M. G. *J. Phys. Chem.*

- C* **2015**, *119* (5), 2427–2437.
- (17) de Oteyza, D. G.; García-Lekue, A.; Vilas-Varela, M.; Merino-Díez, N.; Carbonell-Sanromà, E.; Corso, M.; Vasseur, G.; Rogero, C.; Guitián, E.; Pascual, J. I.; Ortega, J. E.; Wakayama, Y.; Peña, D. *ACS Nano* **2016**, *10* (9), 9000–9008.
- (18) Sakaguchi, H.; Kawagoe, Y.; Hirano, Y.; Iruka, T.; Yano, M.; Nakae, T. *Adv. Mater.* **2014**, *26* (24), 4134–4138.
- (19) Chen, Z.; Zhang, W.; Palma, C.-A.; Lodi Rizzini, A.; Liu, B.; Abbas, A.; Richter, N.; Martini, L.; Wang, X.-Y.; Cavani, N.; Lu, H.; Mishra, N.; Coletti, C.; Berger, R.; Klappenberger, F.; Kläui, M.; Candini, A.; Affronte, M.; Zhou, C.; De Renzi, V.; del Pennino, U.; Barth, J. V.; Räder, H. J.; Narita, A.; Feng, X.; Müllen, K. *J. Am. Chem. Soc.* **2016**, jacs.6b10374.
- (20) Simonov, K. a.; Vinogradov, N. a.; Vinogradov, A. S.; Generalov, A. V.; Zagrebina, E. M.; Svirskiy, G. I.; Cafolla, A. a.; Carpy, T.; Cuniffe, J. P.; Taketsugu, T.; Lyalin, A.; Martensson, N.; Preobrajenski, A. B. *ACS Nano* **2015**, *9* (9), 8997–9011.
- (21) Müllen, K. *ACS Nano* **2014**, *8* (7), 6531–6541.
- (22) Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S. *Adv. Mater.* **2010**, *22* (35), 3906–3924.
- (23) Sun, Q.; Cai, L.; Wang, S.; Widmer, R.; Ju, H.; Zhu, J.; Li, L.; He, Y.; Ruffieux, P.; Fasel, R.; Xu, W. *J. Am. Chem. Soc.* **2016**, *138* (4), 1106–1109.
- (24) Ruffieux, P.; Wang, S.; Yang, B.; Sánchez-Sánchez, C.; Liu, J.; Dienel, T.; Talirz, L.;

- Shinde, P.; Pignedoli, C. A.; Passerone, D.; Dumsclaff, T.; Feng, X.; Müllen, K.; Fasel, R. *Nature* **2016**, *531* (7595), 489–492.
- (25) Talirz, L.; Söde, H.; Cai, J.; Ruffieux, P.; Blankenburg, S.; Jafaar, R.; Berger, R.; Feng, X.; Müllen, K.; Passerone, D.; Fasel, R.; Pignedoli, C. A. *J. Am. Chem. Soc.* **2013**, *135* (6), 2060–2063.
- (26) Chen, Y.-C.; Cao, T.; Chen, C.; Pedramrazi, Z.; Haberer, D.; de Oteyza, D. G.; Fischer, F. R.; Louie, S. G.; Crommie, M. F. *Nat. Nanotechnol.* **2015**, *10* (2), 156–160.
- (27) Komori-Orisaku, K.; Hirose, Y.; Iwakura, I. *Photochem. Photobiol. Sci.* **2017**, *16* (2), 146–150.
- (28) Simonov, K. A.; Vinogradov, N. A.; Vinogradov, A. S.; Generalov, A. V.; Zagrebina, E. M.; Mårtensson, N.; Cafolla, A. A.; Carpy, T.; Cuniffe, J. P.; Preobrajenski, A. B. *J. Phys. Chem. C* **2014**, *118* (23), 12532–12540.
- (29) Zhang, Y. Y.; Zhang, Y. Y.; Li, G.; Lu, J.; Lin, X.; Du, S.; Berger, R.; Feng, X.; Müllen, K.; Gao, H.-J. *Appl. Phys. Lett.* **2014**, *105* (2), 023101.
- (30) Kong, X.; Huang, Y.; Chen, Y. *J. Mass Spectrom.* **2012**, *47* (4), 523–528.