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Stabilizing edge-fluorination in graphene nanoribbons

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Abstract

The on-surface synthesis of edge-functionalized graphene nanoribbons (GNRs) is challenged by the stability of the functional groups throughout the thermal reaction

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3 steps of the synthetic pathway. Edge-fluorination is a particularly critical case, where
4 the interaction with the catalytic substrate and intermediate products can induce the
5 complete cleavage of the otherwise strong C-F bonds before the formation of the GNR.
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7 Here, we demonstrate how a rational design of the precursor can stabilize the functional
8 group, enabling for the first time the synthesis of edge-fluorinated GNRs. The survival
9 of the functionalization is demonstrated by tracking the structural and chemical trans-
10 formations occurring at each reaction step with complementary X-ray photoelectron
11 spectroscopy and scanning tunneling microscopy measurements. In contrast to pre-
12 vious attempts, we find that the C-F bond survives the cyclodehydrogenation of the
13 intermediate polymers, leaving a thermal window where GNRs withhold more than
14 80% of the fluorine atoms. We attribute this enhanced stability of the C-F bond to the
15 particular structure of our precursor, which prevents the cleavage of the C-F bond by
16 avoiding interaction with the residual hydrogen originated in the cyclodehydrogenation.
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18 This structural protection of the linking bond could be implemented in the synthesis
19 of other sp^2 -functionalized GNRs.
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34 Abbreviations

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37 CB, CDH, DFT, DOS, GNR, PDOS, RT, STM, VB, XPS
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41 Keywords

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44 Graphene nanoribbons, on-surface synthesis, edge-functionalization, fluorination, scanning
45 tunneling microscopy, density functional theory, self-assembly
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51 Introduction

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54 The functionalization of graphene nanoribbons (GNRs) is an effective method for tailoring
55 their structural, chemical and electronic properties.¹⁻⁹ Edge functionalization by replacing
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3 hydrogen with different substituents is particularly interesting since it offers a wide flexibil-
4 ity in the choice of functional groups that can, in addition to band tuning,¹ bring chemical
5 selectivity for sensing.⁸ Their peripheral position can also be employed to tune inter-ribbon
6 and substrate interactions and drive their organization, one of the most important challenges
7 in bottom-up synthetic methods.^{7,10,11} The atomic precision offered by bottom-up synthetic
8 methods in the positioning of each component makes this approach the natural candidate for
9 a controlled functionalization of the ribbons. The thermally activated sequential on-surface
10 synthesis has shown to be particularly effective for the realization of atomically precise
11 GNRs.¹²⁻¹⁴ However, such multi-step methods also face a major challenge, namely the sta-
12 bility of the functional groups that have to overcome the whole reaction pathway that leads
13 to the GNR synthesis. This is critical in the functionalization of edges, where the linking
14 groups are not as strongly bound to the aromatic backbone as hetero-atoms in substitutional
15 doping. In the absence of stabilizing intra- or inter-ribbon reactions,^{3,6,7} the thermal energy
16 supplied during the synthesis can surpass the linking bond energy, leading to a partial⁴ or a
17 total¹⁵ dissociation of the functional groups. Dissociation can occur even in carefully chosen,
18 strongly bonded groups, since the intermediate products formed during the reaction pathway
19 can destabilize the bond between the carbon backbone and the functional group, and induce
20 a premature cleavage. This was recently shown in an attempt to synthesize edge-fluorinated
21 GNRs, where it was found that the activation barrier of the otherwise strong C-F bond was
22 reduced by one order of magnitude, mainly by the formation of an additional C(*sp*³)-H bond
23 with residual H migrating from nearest neighbor C atoms during the cyclodehydrogenation
24 (CDH) step.¹⁵ The understanding of this C-F cleaving mechanism can be used for the ra-
25 tional design of fluorinated precursors that avoid the formation of undesired, destabilizing
26 transient structures, as explicitly stated by the authors. Here, we demonstrate how a suit-
27 able design of the molecular precursor can lead to the successful synthesis of edge-fluorinated
28 GNRs. These are synthesized on a Au(111) single crystal in a step-wise thermal process,
29 initially via the surface-assisted Ullmann coupling of the fluorinated monomers into poly-
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meric chains and then through the subsequent CDH leading to the formation of the graphene nanoribbons.¹⁶ The functionalized precursors have been specifically synthesized to overcome these thermally activated reaction steps. The key element in the design is the separation between the fluorinated carbon and those involved in the CDH reaction, which minimizes the defluorination rate by introducing new paths for residual H release onto the surface. Regarding the electronic properties of the functionalized GNRs, our *ab-initio* calculations reveal a significant n-type doping effect of fluorination, shifting frontier bands downwards by about 200 meV and leaving the size of the gap unchanged. The doping effect, however, can be fully screened out by the interaction with the metallic substrate, as demonstrated by both *ab-initio* and scanning tunneling spectroscopy results.

Results and discussion

First, we designed a GNR precursor core which could allow us the easy introduction of different functional groups in peripheral positions, with the goal to minimizing the possible group cleavage during the CDH step. With this idea in mind, we selected the benzo[*b*]triphenylene core which is presented in compounds **1a,b** (Figure 1a), including two Br atoms to induce the on-surface Ullmann coupling to form polymers **2a,b** and two phenyl groups to facilitate the CDH step to obtain GNRs **3a,b**. These GNRs resemble the previously reported chevron GNR,¹⁶ although **3a,b** are narrower and characterized by the combination of cove and triple-bay regions along the edges. Besides the unsubstituted GNR **3a** (R = H) we planned to obtain the fluorinated GNR **3b** (R = F). Remarkably, these GNRs were designed with the functional groups attached to remote positions with respect to the carbon atoms involved in the CDH step, in order to minimize the potential weakening and subsequent cleavage of these groups. Precursors **1a,b** were easily obtained by solution chemistry, in three steps from commercially available reagents (Figure 1b). First, bromination of 9,10-phenanthroquinone (**4**) followed by double Knoevenagel condensation with 1,3-diphenylacetone afforded dienone **5** in

good yield. Then, Diels-Alder reaction of **5** with arynes **6a,b** which were *in-situ* generated by fluoride-induced decomposition of triflates **7a,b** led to the formation of benzo[*b*]triphenylenes **1a,b** after CO extrusion of the corresponding adducts.

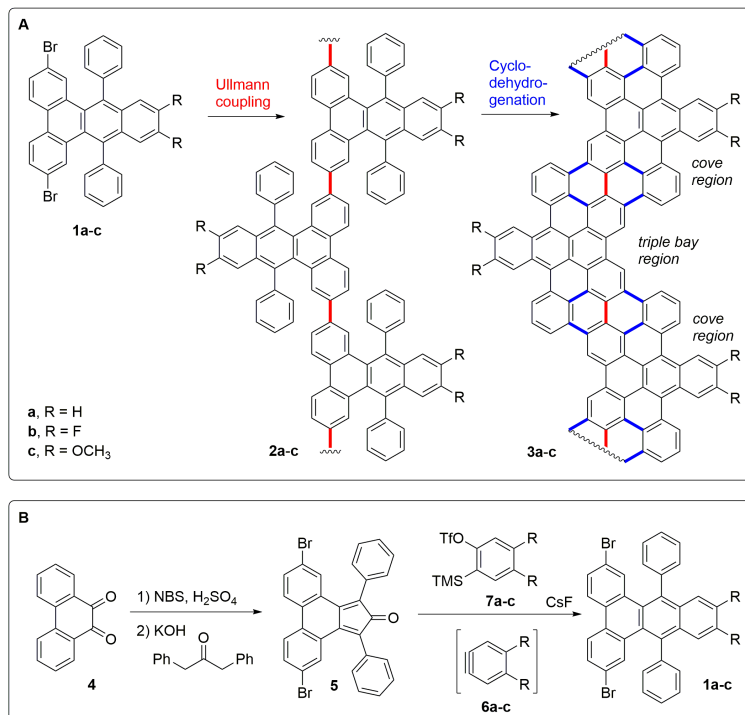


Figure 1: (a) On-surface synthesis of GNRs **3a,b** (b) In-solution synthesis of benzo[*b*]triphenylene derivatives **1a,b** used as GNR precursors.

With compounds **1a,b** in hands, we launched the on-surface studies to attempt the preparation of GNRs **3a,b** on Au(111). The formation of the expected GNRs and the stability of the functional groups throughout the on-surface synthetic protocol have been investigated by complementary scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) measurements. Exploiting the chemical sensitivity of XPS, the reactions resulting in the synthesis of the GNRs have been systematically characterized, as summarized in Figure 2. After depositing compounds **1a,b** at room temperature (RT) and annealing at 200 °C, these GNR precursors undergo a C-Br homolytic bond cleavage, leading to the formation of aryl radicals and the subsequent coupling into polymeric chains **2a,b** via the Ullmann coupling. Figure 2a shows the XPS spectra of the Br 3d core levels for precursor **1b** (R = F).

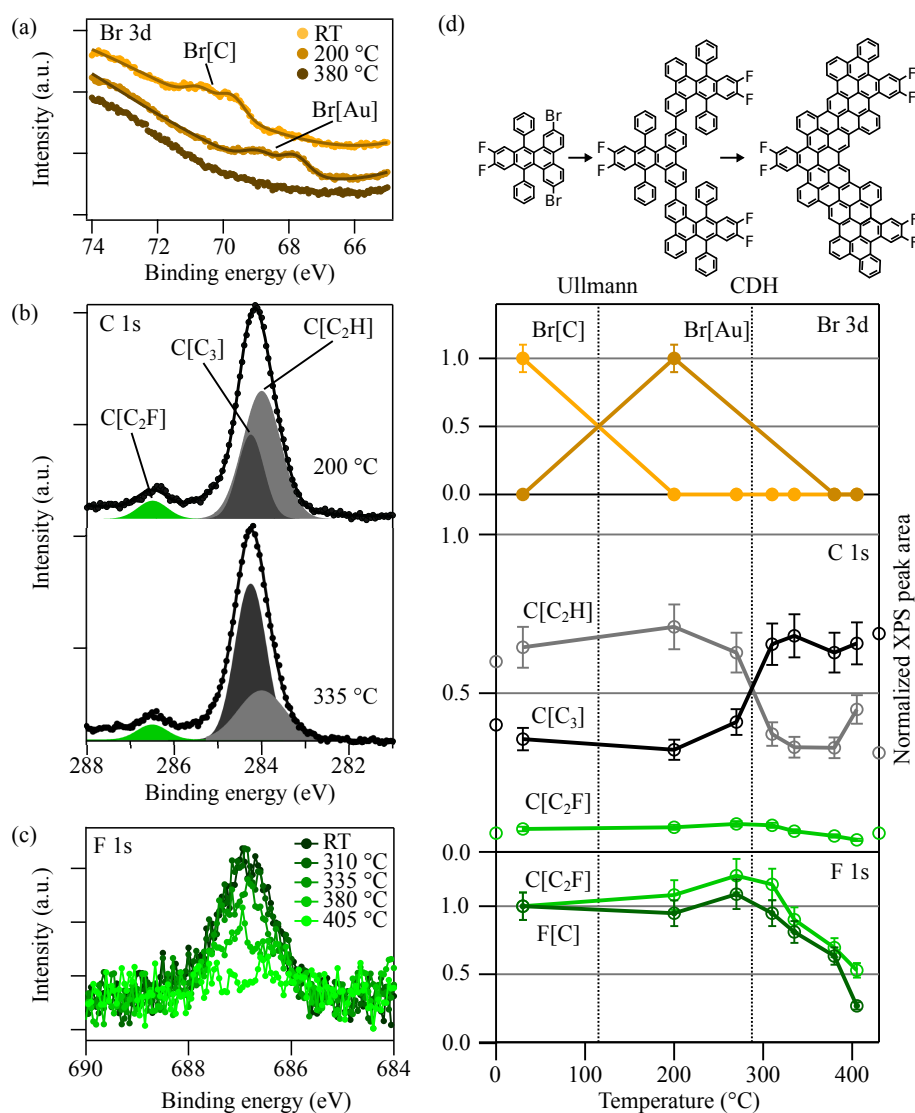


Figure 2: (a)-(c) XPS core level spectra of Br 3d (a), C 1s (b), and F 1s (c) after annealing precursor **1b** at different temperatures. The C 1s spectra fit (continuous lines) is done with multiple peaks to account C[C₃], C[C₂H] and C[C₂F] contributions. (d) Thermal evolution of the XPS atomic ratios, normalized against gold, of the different peaks in (a)-(c). The vertical lines indicate the Ullmann and CDH reaction steps of the GNR synthesis, as indicated by the respective changes in Br[C]/Br[Au] and C[C₃]/C[C₂H] ratios. In the C 1s series, the open circles at the left and right limits represent the stoichiometric relation of the different components for the precursors and the nanoribbons respectively. A normalized C[C₂F] curve has been added to the F[C] data of F 1s.

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3 The binding energy of the spin-orbit split doublet measured for precursors deposited at RT,
4 69.9/70.9 eV, corresponds to the C-bonded Br. The doublet downshifts by 2.1 eV upon
5 annealing at 200 °C, which can be assigned to C-Br cleavage and consequent formation of
6 Au-bonded Br adsorbates.¹⁷⁻¹⁹ The completion of the C-Br cleavage is in agreement with
7 the Ullmann polymerization observed by STM at the same temperature (see Figure 3). At
8 higher temperature Br adatoms desorb from the surface, as indicated by the absence of any
9 Br 3d peak in the spectrum obtained after annealing at 380 °C. This is clearly visible also
10 in Figure 2d which reports the thermal evolution of the XPS atomic ratios of the different
11 peaks normalized against gold. The CDH reaction that convert polymers **2** into GNRs **3**
12 can be tracked by following the temperature evolution of the C 1s core level components.
13 As representative examples, Figure 2b shows the C 1s core level XPS spectra after annealing
14 **1b** at 200 °C and 335 °C, which illustrate the evolution of C bond ratios that correspond to
15 the CDH step. The main C peak is best fitted with two components that can be assigned to
16 C[C₃] (284.3 eV) and C[C₂H] (284.0 eV) bonds respectively. The minor C-Br component is
17 only present at RT according to the Br 3d peak evolution, and therefore is not considered in
18 this analysis. The additional peak present at higher binding energies accounts for the C[C₂F]
19 (286.5 eV) bond component. As we increase the annealing temperature, a clear inversion of
20 the C[C₃] and C[C₂H] components is visible around 300 °C. This is evident in Figure 2d which
21 reports the thermal evolution of the XPS peak area related to the different components. By
22 comparing to the stoichiometric references of the polymeric and GNR phases indicated at the
23 two sides of the graph by open circles, this transition of the C[C₃]/C[C₂H] ratio corresponds
24 to the cyclodehydrogenation that leads to the formation of GNRs at this temperature, as
25 also confirmed by the STM measurements (see Figure 3). The relevant features regarding the
26 stability of the functional group are the C[C₂F] component of C 1s and the correlated F 1s
27 peaks. The evolution of the latter is reported in Figure 2c for the whole set of temperatures
28 investigated. Interestingly, the C[C₂F] bond survives well above the CDH threshold. As can
29 be seen in detail in Figure 2d, the intensity of the C[C₂F] components of C 1s and the F[C]

of F 1s remains unaltered during the formation of GNRs at 310 °C, and still withhold 80% of the intensity at 335 °C when the CDH is complete. Their gradual decrease down to about ~25% at the maximum studied temperature of 405 °C is accompanied by an increase of the C[C₂H] component above the stoichiometric ratio of **3b**, suggesting that cleaved C radicals are passivated by residual H.

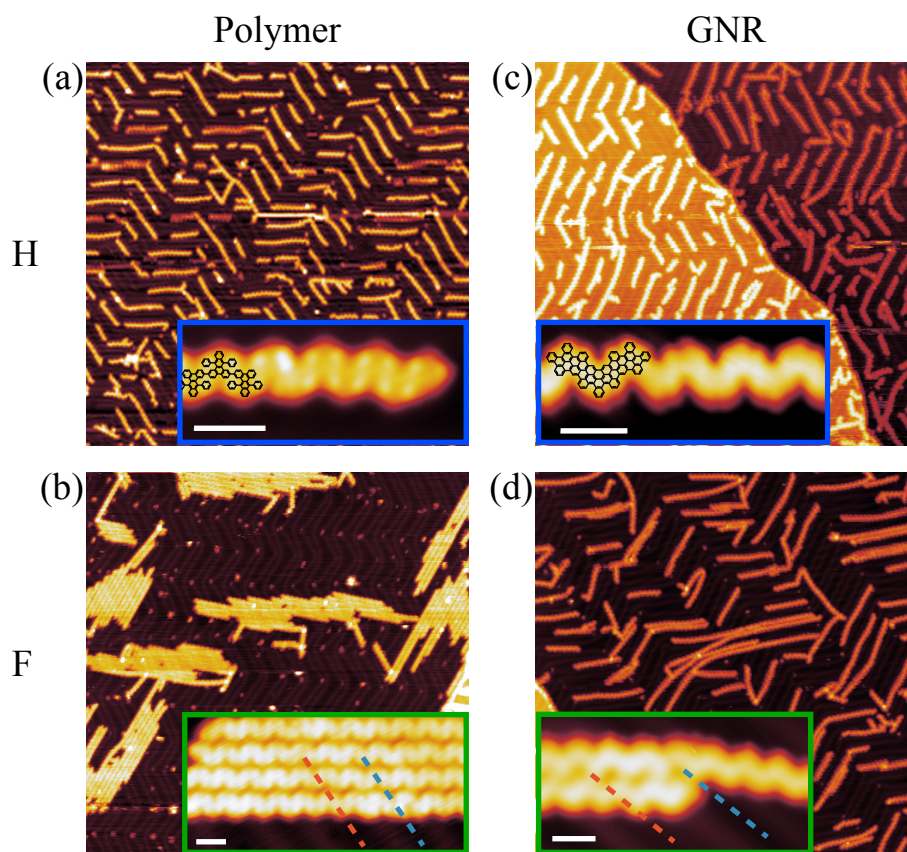


Figure 3: STM images of the polymeric chains and GNRs obtained with the hydrogenated (**1a**) and fluorinated (**1b**) precursors. (a) Polymer **2a** after annealing at 225 °C ($I_t = 85$ pA, $V_S = 1.36$ V. Inset: $I_t = 130$ pA, $V_S = 1.75$ V). (b) Polymer **2b** after annealing at 225 °C ($I_t = 46$ pA, $V_S = 2.52$ V. Inset: $I_t = 60$ pA, $V_S = 1.28$ V). (c) GNR **3a** after annealing at 400 °C ($I_t = 75$ pA, $V_S = 1.36$ V. Inset: $I_t = 250$ pA, $V_S = -0.1$ V). (d) GNR **3b** after annealing at 335 °C ($I_t = 80$ pA, $V_S = 1.30$ V. Inset: $I_t = 210$ pA, $V_S = 1.23$ V). The surface stacking domains of the Au(111) herringbone reconstruction are marked with red (face-centered cubic, fcc) and cyan (hexagonal closed packed, hcp) dashed lines. Images size is 150x150 nm². All inset scale bars correspond to 2 nm.

We next compare the XPS spectroscopic analysis with the structural information provided by STM at each reaction step. Figure 3 shows representative STM topographic images for

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3 the polymeric chains and GNRs synthesized with precursors **1a** (R = H) and **1b** (R = F).
4 In both cases, annealing at 200 °C leads to the Ullmann polymerization of precursors into
5 chains with a zig-zag backbone of an apparent height of 0.2 nm, and protrusion pairs with
6 a center-to-center distance of 0.8 nm. The comparison of the polymeric unit structure with
7 the precursor monomer confirms that the double protrusions correspond to the out-of-plane
8 phenyl rings and that functional groups stay on the protruding edge of the zig-zag backbone
9 (see insets in Figure 3a,b). Further annealing (at 335 °C for F-GNR and 400 °C for H-
10 GNR) leads to the formation of planar chevron-type structures (insets in Figure 3c,d), as
11 expected from the incorporation of the side phenyl rings into the backbone after the CDH
12 reaction. The overall apparent height of 0.15 nm of this structure is in good agreement with
13 previously reported GNRs.^{16,19} Despite their similar intra-molecular structural evolution,
14 the substituents of each precursor leads to inter-molecular interactions that dictate distinct
15 assembly patterns. This is most evident at the intermediate polymeric phase (Figure 3a). In
16 the case of **2a** the interaction with the herringbone reconstructed Au(111) surface guides the
17 polymer assembly. The single chains fill the face-centered cubic (fcc) tracks, terminating at
18 the kinks of the herringbone zigzag, and hence giving rise to a superlattice of chains with a
19 narrow length distribution that is determined by the zigzag period. In contrast, F-mediated
20 inter-chain interactions for **2b** are strong enough to bunch them in parallel arrays that
21 appear off-registry with the herringbone template, avoiding any size restriction imposed by
22 it. The differences are minimized after the aromatization of the polymers into GNRs (Figure
23 3b). In this step, GNR **3a** simply replicates the polymer superlattice, whereas the stronger
24 interaction of the planar structures with the substrate causes a debunching of **2b** arrays into
25 single **3b** GNRs that now try to follow the herringbone reconstruction. The overgrown GNRs,
26 however, do not fit in the zigzag units of the reconstruction and consequently the quality of
27 the superlattice is significantly reduced. The stability of **3b**, the chevron-type fluorinated
28 GNR synthesized in this work, is in contrast to previous attempts of synthesizing edge-
29 fluorinated armchair GNRs using different anthracene derivatives as precursors.^{15,20} In these
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3 cases polymers were fully defluorinated before turning into GNRs. With the C-F bond being
4 one of the strongest C-heteroatom single bond, the premature cleavage was unexpected and
5 attributed to a combination of surface and byproduct assisted bond weakening. According to
6 the density functional theory (DFT) calculations,¹⁵ the interaction with the underlying Au
7 atoms already reduces the activation energy of the C(*sp*²)-F bond cleavage by 100 kJ/mol.
8 A more significant weakening is induced by the *sp*³ bonding of a residual H generated in the
9 nearest neighbor C atom during the CDH, which brings the activation energy further down
10 by 400 kJ/mol. Altogether, the two effects reduce the C-F cleavage activation energy close
11 to an order of magnitude, from ~540 kJ/mol to ~40 kJ/mol.
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21 We studied the C-F bond stability of **3b** by performing gas-phase DFT calculations (see
22 Figure 4), leading to similar conclusions as for the armchair fluorinated GNRs of Ref. 15.
23 The C(*sp*³)-H bond formation leads to a similar reduction of ~400 kJ/mol of the C-F bond
24 cleavage activation energy, from 554 kJ/mol in C(*sp*²)-F to 152 kJ/mol in H-C(*sp*³)-F, in-
25 dicating that the local environment is the most important factor determining the stability
26 of these bonds. We also find that for H-C(*sp*³)-F, defluorination is favorable over dehydro-
27 genation by ~75 kJ/mol. The main conclusion of the above analysis is that the C-F bond
28 in the H-C(*sp*³)-F group is not more stable in the chevron GNRs of the present work than
29 in the armchair GNRs described in Ref. 15. The difference between the two cases lies in
30 the probability of obtaining the transient H-C(*sp*³)-F configuration. Since migration bar-
31 riers are expected to be similar for different ribbon topologies, the formation rate of the
32 H-C(*sp*³)-F group will mainly depend on the specific sites where residual H are originated
33 during the CDH reaction with respect to the fluorinated C position. For the armchair GNRs
34 described in Ref. 15, H is released from the vicinal C atom, and a low migration energy
35 barrier of ~80 kJ/mol to the fluorinated C atom results in a high formation rate of the tran-
36 sient H-C(*sp*³)-F configuration ($k \sim 10^7 \text{ s}^{-1}$ at 400 °C). In contrast, the particular design of
37 our precursor relocates the closest formation of residual H significantly further away, at the
38 5th nearest neighbor (see Figure 4b and path 1 in Figure 4c). This introduces new low acti-
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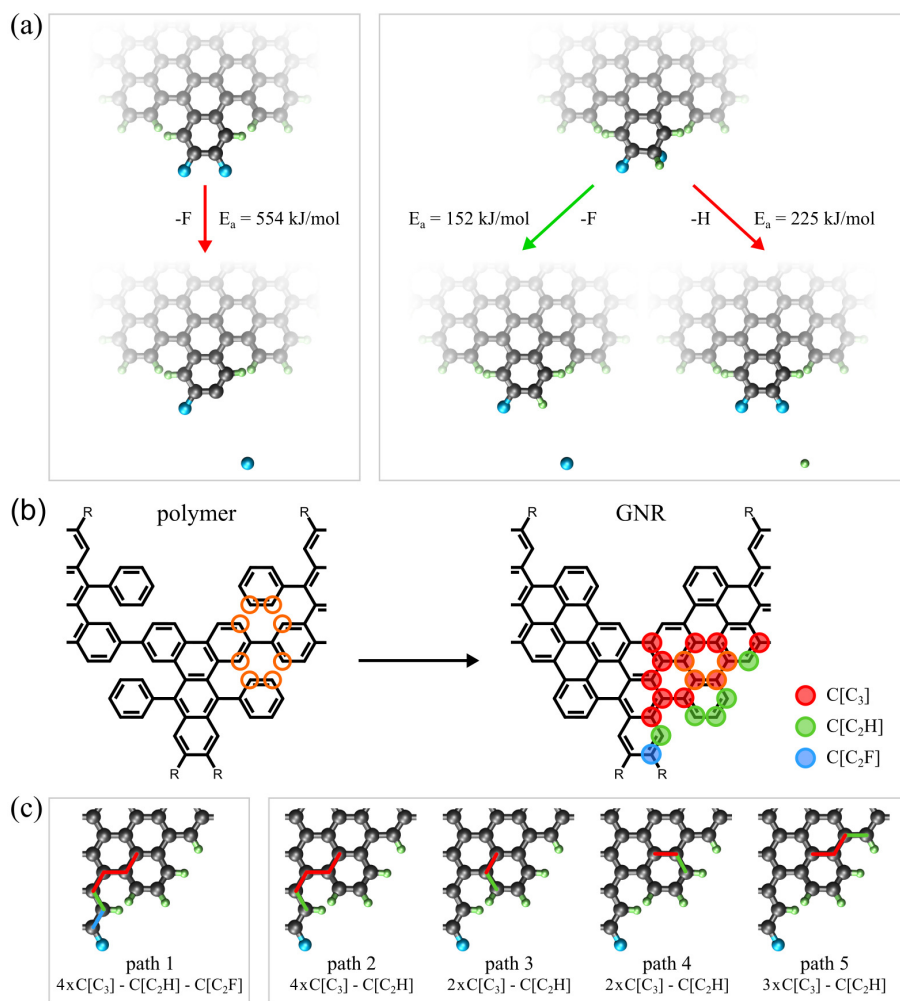


Figure 4: Stability analysis of the C-F bond. (a) Calculated dissociation energies of the $C(sp^2)$ -F bond (left) and of C-H and C-F bonds within the $H-C(sp^3)$ -F group during the formation of GNR **3b**. (b) The three different families of $C(sp^2)$ atoms depending on their local environment in the GNR sub-unit. (c) Possible migration paths of the closest H atom towards the edge C, marked with the color code of the families in b.

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3 vation barrier paths for the release of the residual H into the surface via the hydrogenated C
4 edge atoms, effectively preventing the formation of the H-C(sp^3)-F groups and therefore the
5 corresponding defluorination. In our analysis of H release paths, we only consider residual H
6 generation closest to the C-F bond, noting that the others only differ by additional migration
7 steps within the GNR backbone. This originates from the cleavage of the C-H pair marked
8 in orange circles in the polymer of Figure 4b. Each pair produces one C(sp^3)-H after the C-C
9 coupling, since the C-H pointing downwards is directly released to the surface.^{15,21} In total,
10 we find 5 possible paths from this initial position of the residual H to the nearest C edge
11 atoms, which are sketched in Figure 4c. The color of the segments in each path indicates
12 hopping to three different carbon types, C[C₃], C[C₂H] and C[C₂F], corresponding to fully
13 carbon-bonded, hydrogenated and fluorinated edge atoms respectively (see Figure 4b). Path
14 1 is the one inducing defluorination by the mechanism proposed in Ref. 15, whereas paths
15 2-5 reach hydrogenated edge C atoms that can release the residual H to the surface by an
16 equivalent dehydrogenation process.²¹ A common property shared by both fluorinated and
17 hydrogenated edges is that, in the presence of a C(sp^3)-H bond, they are both characterized
18 by an activation energy for C-F and C-H bond cleavage that is significantly smaller than the
19 migration barrier of the residual H to the vicinal C.^{15,21} The probability ratio between C-F
20 and C-H cleavage will then exclusively depend on the probability of arrival of the residual H
21 to the corresponding edge C atom. This is effectively reduced by the topology of **3b** in two
22 ways: providing multiple additional paths for H release (paths 2-5) and, more importantly,
23 interposing one of these paths (path 2) to the defluorination one (path 1). Altogether, the
24 precursor design effectively prevents defluorination during the synthesis, as demonstrated
25 directly by the temperature dependent XPS measurements.

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49 Some effects of fluorination are imprinted in the electronic properties, despite the appar-
50 ent low density of edge fluorination exhibited by GNR **3b**. DFT calculations of the gas-phase
51 structure reveal a significant downshift of valence and conduction bands of ~200 meV (see
52 Figure 5a), which can be seen as an electrostatic n-gating induced by the electron accu-
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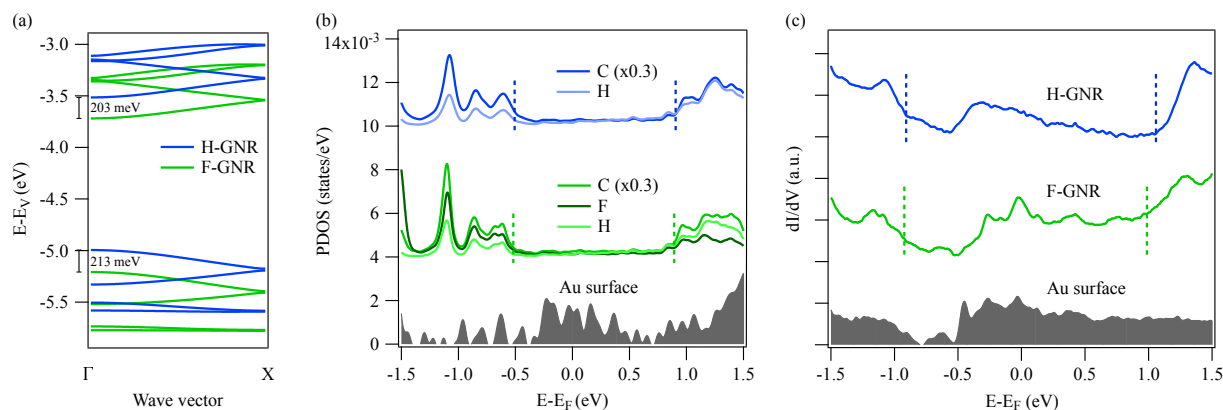


Figure 5: Electronic structure of the GNRs **3a,b**. (a) Band structures of free-standing **3a** (H-GNR, blue) and **3b** (F-GNR, green) for the structures relaxed on Au(111). Energies given with respect to the vacuum energy. (b) PDOS on the different chemical species from **3a** (blue curves, top) and from **3b** (green curves, middle), both calculated on a Au(111) substrate and with a Lorentzian broadening of 35 meV. The PDOS on the surface Au atoms far from the GNR is shown in shaded gray at the bottom (see Methods). (c) Representative constant-height dI/dV spectra taken on **3a** (after CDH at 400 °C) and **3b** (after CDH at 335 °C) in the position of the functional group. Spectrum taken on clean Au is reported in shaded gray as reference.

mulation at the fluorine atoms. As opposed to fully edge-halogenated armchair¹ and cove² GNRs, the size of the band gap is barely affected by the fluorination (1.48/1.49 eV for **3a/3b** respectively), probably due to the lower nominal density of edge-fluorination and different topology of our chevron GNRs. Indeed, a similar quasi-rigid downshift have been also observed in N-doped chevron GNRs.^{22,23} The band shift, however, is reduced to negligible values (~ 10 meV) when GNRs interact with the Au substrate, as can be noted from the projected density of states (PDOS) plotted in Figure 5b. We attribute this band realignment to interfacial charge redistribution, similar to that leading to the Fermi level pinning observed in armchair GNRs.²⁴ An additional effect of the surface is the reduction of the band gap from ~ 1.5 eV to 1.3 eV for free-standing and on-Au GNRs respectively, which is attributed to hybridization with Au states. The absence of any sizeable band gap difference and shift is reproduced in comparative spectroscopic measurements performed in **3a** and **3b** GNRs on the Au substrate (see Figure 5c). Here we find the onset of the valence band (VB) fixed at -0.91 eV for both GNRs, whereas the onset of the conduction band (CB) can be identified

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3 at 1.05 eV for **3a** and 0.95 eV for **3b**. The resulting gaps of 1.96 eV and 1.86 eV are slightly
4 larger than the 1.3 eV obtained by DFT, which is accounted by the well-known gap under-
5 estimation of this method.²⁵ According to the PDOS analysis of Figure 5b, the bands with
6 significant fluorine spectral contribution produces PDOS maxima at around 1 eV below the
7 VB, which referred to the experimental spectra would corresponds to a bias voltage of -2 eV.
8 Unfortunately, the **3b** GNRs were not stable at this large bias voltage, probably due to tip-
9 induced C-F bond cleavage, hindering the detection of any direct spectroscopic fingerprint
10 of the fluorine atoms.
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21 Conclusion

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23 We have demonstrated the on-surface synthesis of edge-fluorinated GNRs. Our combined
24 thermal evolution study of XPS and STM measurements provides chemical and structural
25 evidences of the formation of chevron type GNRs and the survival of fluorine functionaliza-
26 tion throughout the whole synthetic path. As opposed to the case of armchair type GNRs
27 based on fluorinated anthracene derivatives (DBTA), where the polymers are fully deflu-
28 orinated before the formation of GNRs, we achieve 100% of fluorination at the threshold
29 of GNR formation. In a thermal window of 40 °C above that threshold we only observe a
30 slight decrease to 80%. According to first-principle calculations, the electronegative fluorine
31 atoms tend to shift the valence and conduction bands of free-standing GNRs to lower bind-
32 ing energies by about 200 meV without affecting the size of the gap. However, this shift is
33 canceled out in the experimental dI/dV spectra due to the pinning effect of the underlying
34 metallic substrate. The stability of the fluorine substituents is attributed to the particular
35 design of the precursor, in which the F atoms are introduced in remote positions with respect
36 to the cyclodehydrogenation regions. By providing alternative H release paths, our design
37 effectively hampers the migration of residual H originated during cyclodehydrogenation to
38 the fluorinated C edge atom, and the consequent formation of the H-C(*sp*³)-F bond that
39 facilitates the C-F bond cleavage. These alternative H release pathways are independent of
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3 the functional group, and hence we expect that our approach should enable the synthesis
4 of other edge-functionalized GNRs. The structural origin of the stabilization highlights the
5 relevance of a rational design of precursors not only for achieving a particular topology of
6 the final product but also for defining reaction pathways that avoid destabilizing transient
7 structures.
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15 Methods

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18 STM and XPS measurements were performed in two separated ultra-high vacuum (UHV)
19 systems with a base pressure below 5×10^{-10} mbar. Clean Au(111) samples were prepared by
20 cycles of Ar ion sputtering at 1 keV and annealing at 470 °C for 20 minutes. Surface clean-
21 liness has been checked by low energy electron diffraction (LEED) and either STM or XPS.
22 Molecular precursors have been deposited from a resistively heated crucible on the Au(111)
23 substrate kept at RT. For the sub-monolayer coverage studied, **1a** and **1b** were sublimated
24 at 280 °C and 300 °C respectively. The sample was annealed at a rate of about 1 K/s and
25 kept 15 minutes at the indicated temperatures to promote the polymerization and cyclode-
26 hydrogenation reactions. Sample temperatures were measured with an infrared pyrometer
27 in the XPS setup and a thermocouple directly spot-welded on the sample holder in the STM
28 setup. The pyrometer was previously calibrated with the sample holder thermocouple of the
29 STM setup in order to have reliable temperature comparison between the two measuring
30 methods. STM measurements have been carried out with a Createc LT-STM operated at
31 samples temperatures of 5 K, except for the image of the inset of Figure 3c, which was ac-
32 quired at 77 K. STM topographic images have been acquired in constant-current mode and
33 analyzed and processed with Gwyddion software.²⁶ STM dI/dV spectra have been measured
34 at 5 K in constant-height mode with the lock-in technique and a bias modulation of 20 mV.
35 Due to the difficulty of determining the VB/CB maxima/minima in the broad experimental
36 features, both the theoretical and experimental band gaps have been determined by consid-
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3 ering the onset of the corresponding features. This represents a lower limit in the estimation
4 of the band gaps. XPS measurements were carried out at RT with a SPECS Phoibos 150
5 hemispherical energy analyzer using a monochromatic Al K α X-ray source at 1486.6 eV.
6 XPS spectra have been referenced to the Fermi level, fitted with a Fermi-Dirac distribution
7 at the sample temperature.
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13 First-principles calculations were performed via Density Functional Theory as imple-
14 mented in the SIESTA package.^{27,28} Here the valence electrons are described with a basis
15 set given by a linear combination of numerical atomic-orbitals, in our case a double- ζ plus
16 polarization (DZP) basis set with the orbital radii defined using a 50 meV energy shift.²⁸ We
17 adopted for the top Au atomic layer an extended DZP basis optimized for the description of
18 the Au(111) surface²⁹ as well as a Hydrogen passivation of the slab bottom layer to prevent
19 spurious effects due to the proximity of the surface states on the slab representation.³⁰ More-
20 over, for a better description of the carbon states, the basis set was extended to included 3s
21 and 3p orbitals.⁶ The core electrons were represented by norm-conserving Troullier-Martins
22 pseudopotentials.³¹ Dispersive interactions were considered via the van der Waals density
23 functional by Dion et al³² with the modified exchange by Klimeš, Bowler and Michaelides.³³
24 The fineness of the grid for integrations in real space was defined using a 300 Ry energy cut-
25 off. The self-consistency cycle was stopped when the changes of the density matrix elements
26 were less than 10^{-5} and also lower than 10^{-4} eV for the Hamiltonian matrix elements. The
27 smearing of the electronic occupations was defined by an electronic temperature of 300 K
28 with a Fermi-Dirac distribution. The structures were allowed to fully relax until the forces
29 were lower than 10 meV/Å on top of a 3-layer thick slab within a 17.65x30.57x60 Å³ sim-
30 ulation cell (with the two bottom layers kept fix with experimental lattice). We used a 15
31 k-point mesh along the GNRs periodic direction (x) and for calculations involving the Au
32 substrate 3 k-points were adopted along the other periodic direction (y) as well. The Au
33 surface density of states (DOS), shown in Figure 5b, was obtained by the difference between
34 the DOS projected on the Au atoms in the surface layer and far from the GNR and the DOS
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3 projected on the Au atoms in middle slab layer, which has been shown to provide a good
4 estimation using similar parameters.³⁴
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9 **Acknowledgement**

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Supporting Information Available

Molecular synthesis

General aspects

All reactions were carried out under argon using oven-dried glassware. THF, CH₂Cl₂, and CH₃CN were purified by a MBraun SPS-800 Solvent Purification System. Finely powdered CsF was dried under vacuum at 100 °C, cooled under argon and stored in a glove-box. TLC was performed on Merck silica gel 60 F254; chromatograms were visualized with UV light (254 nm and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ¹H and ¹³C NMR spectra were recorded at 300 and 75 MHz or 500 and 126 MHz (Varian Mercury 300, Bruker AMX-500 instruments, respectively). Low-resolution electron impact mass spectra were determined at 70 eV on a HP-5988A instrument. High-resolution mass spectra (HRMS) were obtained on a Bruker Microtof spectrometer.

Commercial reagents were purchased from ABCR GmbH or Aldrich Chemical Co. and were used without further purification. Molecules **5** and **7a-b** were prepared following published procedures (Figure S1)¹.

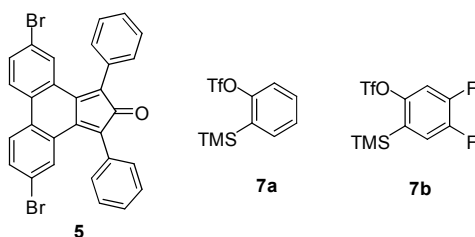
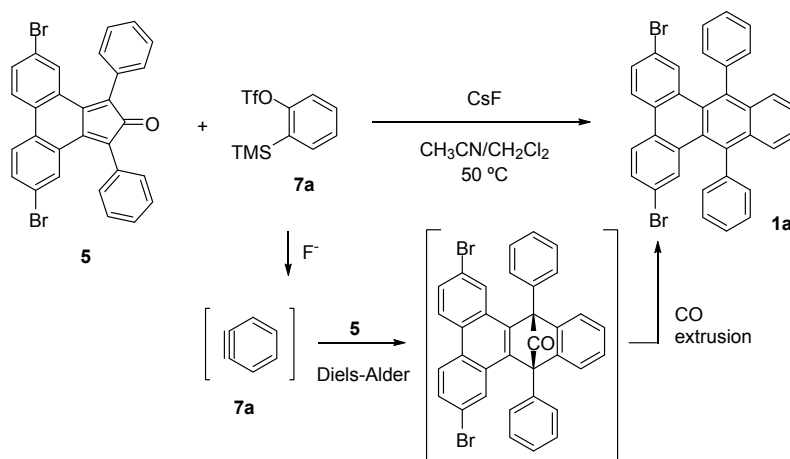


Figure 6: Structures of starting materials **5** and **7a-b**.

Figure 7: Synthesis of compound **1a**.

Synthesis of 2,7-dibromo-9,14-diphenylbenzo[*f*]tetraphene (**1a**)

Finely powdered anhydrous CsF (170 mg, 1.09 mmol) was added over a solution of dienone **5** (125 mg, 0.24 mmol) and triflate **7a** (110 mg, 0.36 mmol) in CH₃CN/CH₂Cl₂ (1:1, 6 mL). The mixture was heated at 50 °C under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO₂; hexane/CH₂Cl₂ 4:1) to isolate compound **1a** (87 mg, 61%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃) δ: 8.05 (d, *J* = 8.6 Hz, 2H), 7.95 (dd, *J* = 6.6, 3.3 Hz, 2H), 7.61 – 7.50 (m, 12H), 7.48 (d, *J* = 3.3 Hz, 2H), 7.43 (dd, *J* = 8.6, 1.9 Hz, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 141.2 (2C), 136.6 (2C), 133.6 (2CH), 133.2 (2C), 132.7 (2C), 132.5 (4CH), 130.1 (2CH), 129.5 (4CH), 129.2 (2C), 128.3 (2CH), 127.7 (2C), 127.1 (2CH), 126.5 (2CH), 124.7 (2CH), 120.6 (2C) ppm. MS (EI), *m/z* (%): 588 (M⁺, 100), 508 (14), 428 (15), 350 (20), 212 (16). HRMS (EI) for C₃₄H₂₀Br₂, calculated: 585.9932, found: 585.9949.

Synthesis of 2,7-dibromo-11,12-difluoro-9,14-diphenylbenzo[*f*]tetraphene (**1b**)

Finely powdered anhydrous CsF (198 mg, 1.31 mmol) was added over a solution of dienone **5** (150 mg, 0.29 mmol) and triflate **7b** (136 mg, 0.41 mmol) in CH₃CN/CH₂Cl₂ (1:1, 24

¹a) For synthesis of dienone **5**, see: Vo, T. H.; Shekhirev, M.; Kunkel, D. A.; Morton, M. D.; Berglund, E.; Kong, L.; Wilson, P. M.; Dowben, P. A.; Enders, A.; Sinitzkii, A. *Nat. Commun.* 2014, 5, 3189. b) For preparation triflates **7a-b**, see: Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Synthesis* 2002, 1454.

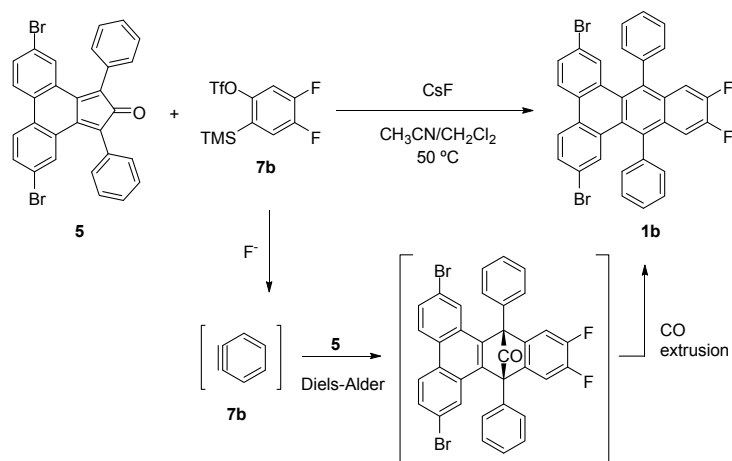


Figure 8: Synthesis of compound **1b**.

mL). The mixture was heated at 50 °C under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO₂; hexane/CH₂Cl₂ 4:1) to isolate compound **1b** (72 mg, 40%) as a pale yellow solid. ¹H NMR (353 K, 500 MHz, C₂D₂Cl₄) δ: 8.02 (d, *J* = 8.6 Hz, 2H), 7.64 – 7.52 (m, 10H), 7.49 – 7.39 (m, 6H) ppm. ¹³C NMR (353 K, 126 MHz, C₂D₂Cl₂) δ: 150.43 (dd, *J* = 253.4, 17.7 Hz, 2CF), 140.74 (2C), 136.18 (2C), 133.51 (2CH), 132.65 (2C), 132.06 (4CH), 130.49 (2CH), 130.44 (2C), 130.22 (4CH), 129.87 (2CH), 128.81 (2C), 128.38 (4CH), 124.80 (2C), 120.76 (2C), 113.19 (dd, *J* = 13.7, 6.6 Hz, 2CH) ppm. MS (EI), *m/z* (%): 623 (100), 543 (24). HRMS (APCI (M+1)) for C₃₄H₁₈Br₂F₂, calculated: 621.9738, found: 621.9730.

¹H and ¹³C NMR spectra

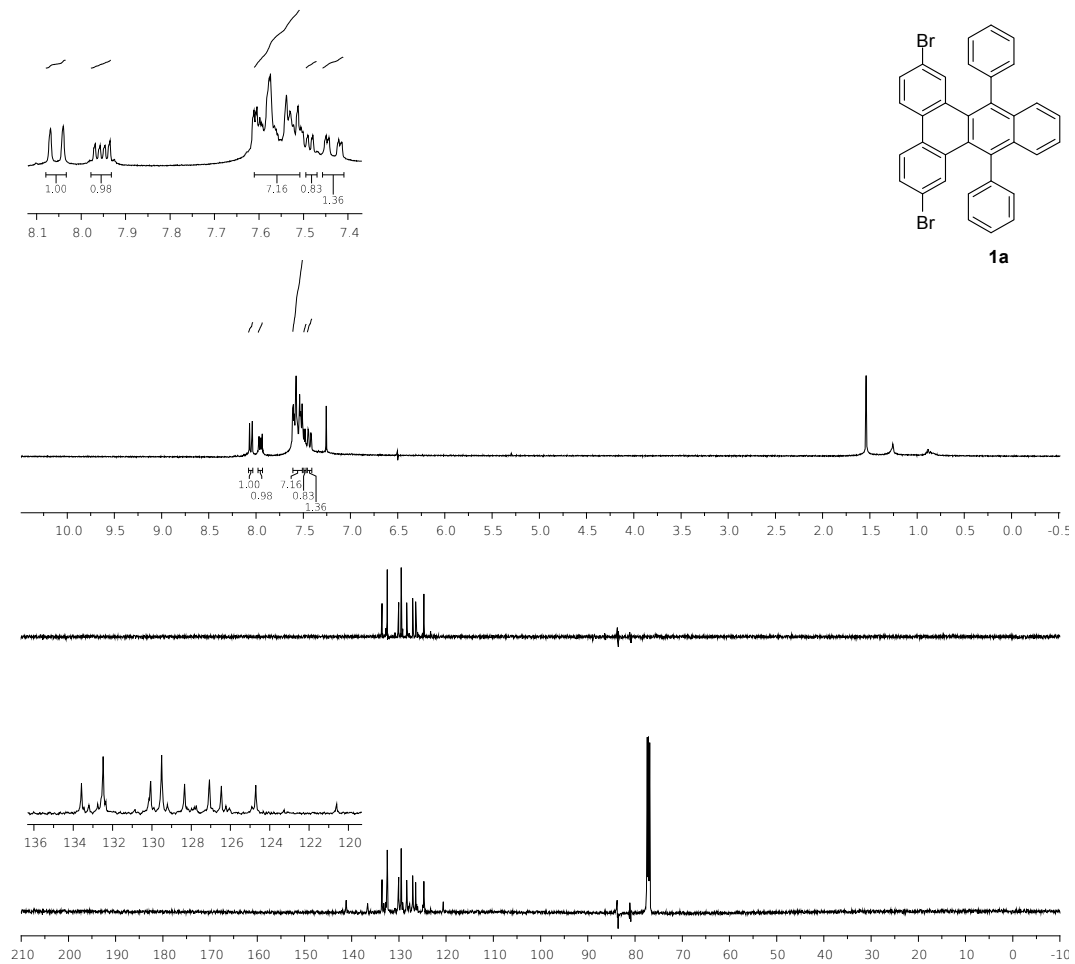
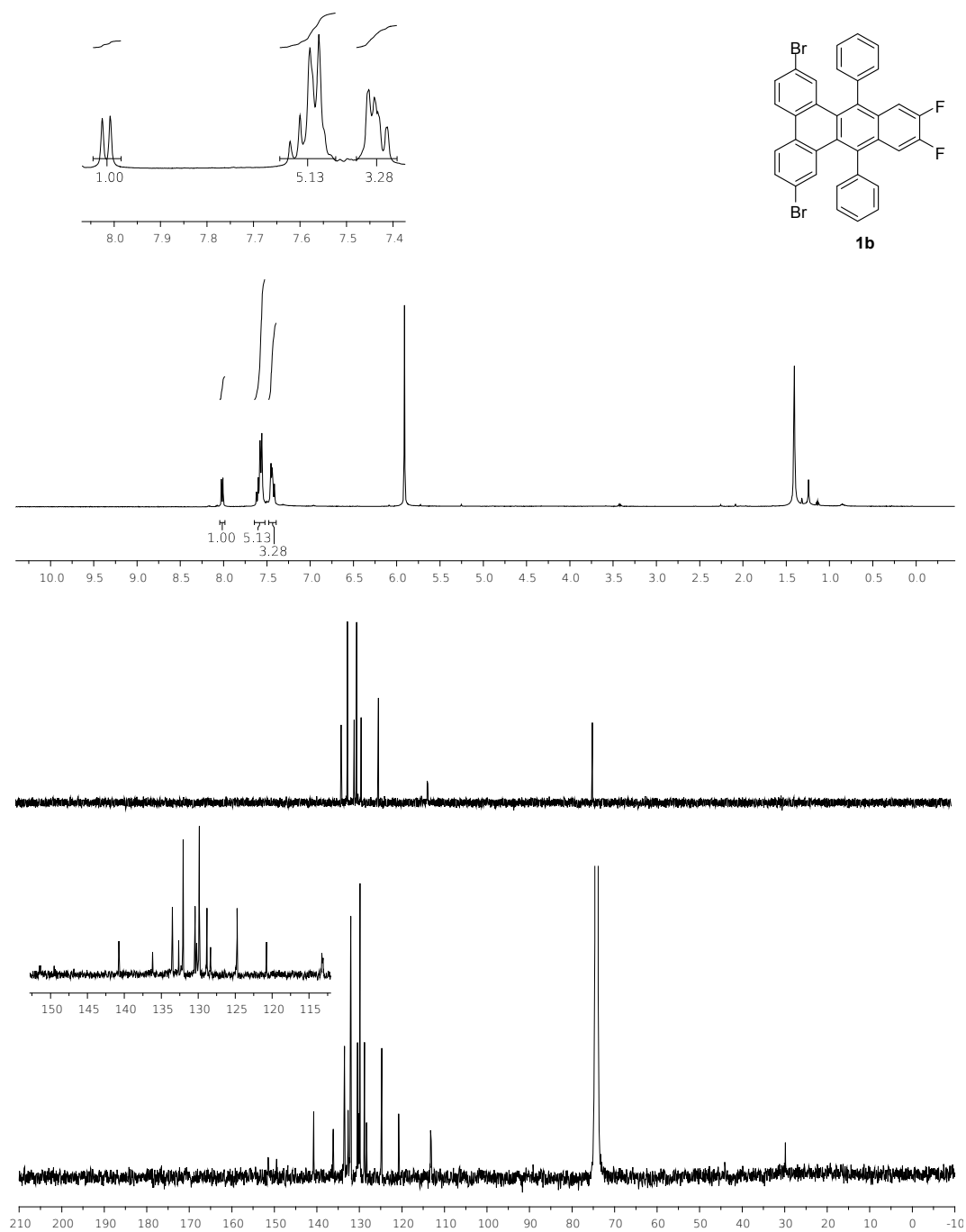


Figure 9: ^1H , DEPT 135 and ^{13}C NMR spectra of compound **1a**.



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Graphical TOC Entry

