On-surface synthesis of hydroxy-functionalized graphene nanoribbons through deprotection of methylenedioxy groups

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1. **Materials and Methods**

1.1. **Synthesis and characterization**

Reagents for synthesis were purchased from Wako, Nacalai Tesque, and Sigma Aldrich, and were reagent-grade quality, obtained commercially, and used without further purification. For spectral measurements, spectral-grade solvents were purchased from Nacalai Tesque. Unless stated otherwise, column chromatography was carried out on silica gel 60N (Kanto Chemical, 40-50 μm). Analytical thin-layer chromatography (TLC) was performed on Art. 5554 (Merck, KGaA). Melting points (m.p.) were measured with a YAMAKO MP-J3. IR spectra were recorded on a JASCO FP-6600 and are reported as wavenumbers ν in cm\(^{-1}\) with band intensities indicated as s (strong), m (medium), w (weak). \(^1\)H NMR (500 and 600 MHz) and \(^13\)C NMR (151 MHz) spectra were recorded (as indicated) either on a JEOL JNM-ECX 600 spectrometer and are reported as chemical shifts (δ) in ppm relative to TMS (δ = 0). Broad peaks are marked as br. High-resolution MS was performed on a MALDI-TOF (Bruker Autoflex II) or JEOL AccuTOF JMS-T100LC. X-ray crystallographic data were recorded at 90 K on a Bruker APEX II X-Ray diffractometer equipped with a large area CCD detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å).

1.2. **Abbreviations**

Ar: Argon; \(n\)-BuLi: \(n\)-Butyllithium; DCM: Dichloromethane; DMF: Dimethylformamide; DMSO: Dimethy sulfoxide; EtOAc: Ethylacetate; HRMS: High-resolution mass spectroscopy; MALDI-TOF: Matrix-assisted laser desorption ionization-time of flight; m.p.: Melting point; NBS: \(N\)-Bromosuccinimide; r.t.: Room temperature; MeOH: Methanol; THF: Tetrahydrofuran; TLC: Thin layer chromatography; TMS: Tetramethylsilane; TMEDA: Tetramethylenediamine.
2. Synthesis

![Synthesis Diagram]

2,3,6,7-Tetramethoxyanthraquinone was synthesized according to the previous report.¹

**Compound 1:** To a solution of 9-bromoanthracene (924 mg, 3.6 mmol) and TMEDA (0.72 ml, 4.8 mmol) in anhydrous THF (160 ml) was added n-BuLi (1.6 M in hexane, 3.2 ml, 5.1 mmol) dropwise at −78 °C under Ar atmosphere, then the solution was gradually warmed to −50 °C. The solution was stirred for 3 h at −50 °C. To a solution of 2,3,6,7-tetramethoxyanthraquinone (300 mg, 0.9 mmol) in anhydrous THF (40 ml) was added the prepared lithium reagent at −50 °C. The mixture was slowly warmed to r.t. over 3 h and kept stirring overnight, and then the reaction mixture was concentrated in vacuo. A mixture of crude product diol 1, NaI (2.98 mg, 19.9 mmol), and NaH₂PO₄•H₂O (2.55 mg, 24 mmol) in AcOH (96 ml) was heated to reflux for 2 h. After cooling to r.t., the mixture was diluted with H₂O. The resulting precipitate was filtered, and washed with H₂O and MeOH, and dried in vacuo. The residue was recrystallized from DCM/MeOH to give a pure compound 1 (370 mg, 45%, Rf = 0.15 with CHCl₃/hexane = 1:1) as a yellow needle crystal. m.p.: >300 °C; IR (KBr): 3050 (w), 2998 (w), 2950 (w), 2827 (w), 1631 (m), 1525 (m), 1490 (s), 1461 (s), 1432 (s), 1309 (w), 1238 (s), 1203 (s), 1165 (s), 1151 (s), 1046 (s), 1010 (m), 986 (w), 957 (w); ¹H NMR (600 MHz, CDCl₃): 8.72 (s, 4H), 8.20 (d, 8.4 Hz, 8H), 7.53 (t, 7.2 Hz, 8H), 7.47 (d, 8.4 Hz, 8H), 7.33 (t, 7.2 Hz 8H), 6.29 (s, 8H), 3.26 (s, 12H); ¹³C NMR (151 MHz, CDCl₃): 149.38, 133.89, 131.69, 131.27, 129.29, 128.57, 127.34, 127.21, 126.98, 125.99, 125.44, 104.11, 55.31.; HRMS (MALDI, +ve) calcd for C₄₆H₃₄O₄: 650.2452, found: 650.2454.
**Compound 2:** NBS (15 mg, 0.086 mmol) was added to the solution of compound 1 (28 mg, 0.043 mmol) in dried THF (40 ml) at 0 °C. The reaction mixture was warmed to r.t. and stirred for 15 h. Additional NBS (15 mg, 0.086 mmol) was added to the reaction mixture at r.t. and then the reaction mixture was stirred for 12 h. After quenching with Na$_2$S$_2$O$_3$ aqueous solution, the residue was extracted with CHCl$_3$, dried over Na$_2$SO$_4$, and then concentrated in vacuo. The residue was purified by silica gel column chromatography (CHCl$_3$/hexane = 2:1, $R_f = 0.25$), and further purified by reprecipitate with CHCl$_3$/Hexane to give compound 2 as a yellow powder (35 mg, quant); m.p.: >300 °C; IR (KBr): 3070 (w), 3027 (w), 2954 (w), 2826 (w), 1632 (w), 1527 (m), 1492 (s), 1462 (m), 1451 (m), 1432 (s), 1370 (w), 1302 (m), 1293 (s), 1263 (s), 1239 (m), 1173 (m), 1065 (m), 910 (s), 839 (m), 761 (s); $^1$H NMR (500 MHz, CDCl$_3$): 8.76 (d, 9Hz, 4H), 7.68–7.66 (m, 4H), 7.48 (d, 9Hz, 4H), 7.37–7.35 (m, 4H), 6.25 (s, 4H), 3.27 (s, 4H); $^{13}$C NMR (151 MHz, CDCl$_3$): 149.84, 134.77, 132.05, 130.72, 128.99, 128.17, 127.45, 127.39, 126.42, 123.61, 104.15, 55.52; HRMS (MALDI, +ve) calcd for C$_{46}$H$_{32}$O$_4$Br$_2$: 806.0667, found: 806.0662.

**THO-DBTA:** Under Ar atmosphere, BBr$_3$ (1.2 ml, 1.0 M in DCM) was added to a solution of compound 2 (200 mg, 0.31 mmol) in DCM (20 ml). The reaction mixture was stirred at r.t. for three hours. After quenching with water, the crude material was filtered and washed with water, DCM, and diethy ether to give analytically pure THO-DBTA (60 mg, 26%) as a yellow solid. The $^{13}$C NMR could not be obtained because of the instability of THO-DBTA.; $^1$H NMR (500 MHz, CDCl$_3$): 8.75 (d, 9Hz, 4H), 7.41 (d, 9Hz, 4H), 7.38–7.35 (m, 4H), 6.40 (s, 4H), 5.23 (s, 4H). HRMS (MALDI, +ve) calcd for C$_{42}$H$_{24}$O$_4$Br$_2$: 750.0036, found: 750.0038.

**Compound 3:** Under Ar atmosphere, BBr$_3$ (0.21 ml, 2.2 mmol) was added to a solution of compound 1 (350 mg, 0.54 mmol) in DCM (80 ml). The reaction mixture was stirred at r.t. for 4.5 h. After quenching with water, the crude material was filtered and washed with water, DCM, MeOH, and diethyl ether to give analytically pure compound 3 (243 mg, <76%) as a yellow solid. Compound 3 was used in the next step without further purification or $^{13}$C NMR measurement because of the instability of compound 3.; $^1$H NMR (600 MHz, DMSO-$d_6$): 9.13 (br s, 4H), 8.89 (s, 2H), 8.31 (d, 8.4Hz, 4H), 7.59 (t, 7.2Hz, 4H), 7.41–7.34 (m, 8H), 6.12 (s, 4H); HRMS (MALDI, +ve) calcd for C$_{42}$H$_{26}$O$_4$: 594.1826, found: 594.1827.

**Compound 4:** Under Ar atmosphere, chloroiodomethane (0.2 ml, 0.067 ml) and Cs$_2$CO$_3$ (546 mg, 1.7 mmol) were added to a solution of compound 3 (243 mg, 0.41 mmol) in DMF (60 ml). The reaction mixture was stirred at 110 °C for 2.5 h. After cooling to r.t., the reaction mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (DMF/hexane = 1:2, $R_f = 0.2$) to give compound 4 as a pale-yellow solid (95 mg, 28% (2 steps)); m.p.: >300 °C; IR (KBr): 3050 (w), 2998 (w), 2950 (w), 2827 (w), 1631 (m), 1525 (m), 1490 (s), 1461 (s), 1432 (s), 1309 (w), 1238 (s), 1202 (s), 1165 (s), 1151 (s), 1046 (s), 1010 (m), 986 (w), 957 (w); $^1$H NMR (600 MHz, CDCl$_3$): 8.72 (s, 4H), 8.20 (d, 8.4 Hz, 8H), 7.53 (t, 7.8 Hz, 4H), 6.12 (s, 4H).
8H), 7.42 (d, 9.0 Hz, 8H), 7.36–7.33 (m, 4H), 6.30 (s, 8H), 5.71 (s, 8H); $^1$H NMR (151 MHz, CDCl$_3$) 147.55, 133.85, 131.80, 131.37, 130.93, 128.76, 128.66, 127.37, 126.71, 126.11, 125.47, 101.70, 100.81; HRMS (MALDI, +ve) calcd for C$_{44}$H$_{26}$O$_4$: 618.1826, found: 618.1824.

**MDO-DBTA:** NBS (15 mg, 0.084 mmol) was added to the solution of compound 4 (24 mg, 0.038 mmol) in dried THF (10 ml) at 0 ºC. The reaction mixture was stirred at 0 ºC for 4 h. Then, the reaction mixture was warmed to r.t. and stirred for 13 h. Additional NBS (15 mg, 0.084 mmol) was added to the reaction mixture at 0 ºC. Then, the reaction mixture was warmed to r.t. and stirred for 7 h. After quenching with Na$_2$S$_2$O$_3$ aqueous solution, the residue was extracted with CHCl$_3$, dried over Na$_2$SO$_4$, and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (CHCl$_3$/hexane = 2:3, $R_f$ = 0.5), and further purified by recrystallization with CHCl$_3$/MeOH to give **MDO-DBTA** as a yellow needle crystal (17 mg, 59%); m.p.: >300 ºC; IR (KBr): 3066 (br w), 2893 (br m), 1600 (m), 1453 (s), 1367 (w), 1300 (m), 1226 (s), 1112 (w), 1040 (s), 950 (s), 907 (s); $^1$H NMR (600 MHz, CDCl$_3$): 8.76 (d, 9Hz, 4H), 7.68–7.66 (m, 4H), 7.43–7.37 (m, 8H), 6.27 (s, 4H), 5.73 (s, 4H); $^1$C NMR (151 MHz, CDCl$_3$) 147.80, 134.47, 131.99, 130.71, 130.54, 128.52, 128.33, 127.35, 127.11, 126.47, 123.80, 105.51, 109.99; HRMS (MALDI, +ve) calcd for C$_{44}$H$_{26}$O$_4$Br$_2$: 774.0036, found: 774.0032.
3. NMR spectra

Figure S1. $^1$H NMR spectrum of compound 1 in CDCl$_3$ at room temperature.
Figure S2. $^{13}$C NMR spectrum of compound 1 in CDCl$_3$ at room temperature.
Figure S3. $^1$H NMR spectrum of compound 2 in CDCl$_3$ at room temperature.
Figure S4. $^{13}$C NMR spectrum of compound 2 in CDCl$_3$ at 50 ºC.
Figure S5. $^1$H NMR spectrum of THO-DBTA in CDCl$_3$ at room temperature.
Figure S6. $^1$H NMR spectrum of compound 3 in DMSO-$d_6$ at room temperature.
Figure S7. $^1$H NMR spectrum of compound 4 in CDCl$_3$ at 50 ºC.

Figure S8. $^{13}$C NMR spectrum of compound 4 in CDCl$_3$ at 50 ºC.
Figure S9. $^1$H NMR spectrum of compound MDO-DBTA in CDCl$_3$ at room temperature.
Figure S10. $^{13}$C NMR spectrum of compound MDO-DBTA in CDCl$_3$ at room temperature.

4. MS

Figure S11. MS spectrum of compound 1.
Figure S12. HRMS spectrum of compound 1.

Figure S13. MS spectrum of compound 2.
Figure S14. HRMS spectrum of compound 2.

Figure S15. MS spectrum of compound 3.
Figure S16. HRMS spectrum of compound 3.
Figure S17. MS spectrum of compound 4.

Figure S18. HRMS spectrum of compound 4.
Figure S19. MS spectrum of THO-DBTA.
Figure S20. HRMS spectrum of THO-DBTA.
Figure S21. MS spectrum of MDO-DBTA.

Figure S22. HRMS spectrum of MDO-DBTA.
5. X-ray single-crystal analysis

MDO-DBTA (deposition number: 2075354)

Empirical formula \( \text{C}_{44}\text{H}_{24}\text{O}_{4}\text{Br}_{2}\cdot3(\text{CH}_{2}\text{Cl}_{2}) \)

Formula weight 1031.23

Temperature 90 K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group \( \text{C}2/c \)

Unit cell dimensions

\[ a = 23.810(3) \text{ Å} \]

\[ b = 8.3517(9) \text{ Å} \]

\[ \beta = 111.7694(18)^\circ \]

\[ c = 22.366(2) \text{ Å} \]

Volume 4130.4(8) Å\(^3\)

\( Z \) 4

Density (calculated) 1.658 g/cm\(^3\)

Absorption coefficient 2.398 mm\(^{-1}\)

\( F(000) \) 2064

Crystal size 0.150 × 0.100 × 0.100 mm\(^3\)

Theta range for data collection 1.842 to 27.150\(^\circ\)

Index ranges\(-29 \leq h \leq 30, -10 \leq k \leq 10, -28 \leq l \leq 21\)

Reflections collected 12530

Independent reflections 4556 \([R(\text{int}) = 0.0420]\)

Completeness to theta = 25.242\(^\circ\) 99.8%

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.795 and 0.679

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 4556 / 0 / 267

Goodness-of-fit on \( F^2 \) 1.007

Final \( R \) indices \([I > 2\sigma(I)]\) \( R_1 = 0.0399, wR_2 = 0.0908 \)

\( R \) indices (all data) \( R_1 = 0.0597, wR_2 = 0.0975 \)

Extinction coefficient n/a

Largest diff. peak and hole 0.659 and –0.603 e.Å\(^{-3}\)
Figure S23. X-ray single-crystal structure of MDO-DBTA. Ellipsoids are scaled at 50% probability. Solvent molecules are omitted for clarity.
6. Stability of THO-DBTA

![Figure S24](image)

**Figure S24.** $^1$H NMR spectra of THO-DBTA (a) after synthesis, and (b) after annealing at 300 ºC for 15 min under vacuum conditions.

The THO-DBTA precursor seems to be unstable and easily decomposed. In the NMR spectrum of THO-DBTA (Figure S24), additional peaks, which resulted from decomposed structure of THO-DBTA, were clearly observed after annealing at 300 ºC for 15 min under vacuum conditions (ca. $10^{-3}$ Pa), though it is difficult to characterize the decomposed structure of THO-DBTA. Considering that precursors are sublimated onto Au(111) by annealing at high temperature (>300 ºC) for on-surface synthesis, THO-DBTA was likely to be decomposed before its sublimation. The instability of THO-DBTA should be the main reason for the unsuccessful synthesis of OH-functionalized GNR using THO-DBTA.

7. The models used for the first-principles evaluation of XPS binding energies.
Figure S25. The models used for the first-principles evaluation of XPS binding energies of (a) HO-N7AGNR, (b) MDO-N7AGNR, (c) MDO-DBTA precursor, and (d) Quinone-N7AGNR, respectively. The grey, red, black, pale pink, and brown spheres are gold, oxygen, carbon, hydrogen, and bromine atoms, respectively.

8. Simulated nc-AFM images

We simulated AFM appearances of the hydroxy groups using the Probe Particle (PP) model. In the model, we used default parameters of pairwise Lennard-Jones potentials. To calculate the electrostatic force field, the local potential of the system was obtained by our DFT calculations (Figures 4b and c). We used a quadruple tip with typical parameters (a bending stiffness of 0.25 N/m and a PP effective charge of 0.05 e) to model a CO-functionalized tip. Figure S26c and d show the simulated AFM images of a 7AGNR without hydroxyl groups (Figure S26a) and a GNR with two hydroxyl group per unit cell (Figure S26b), respectively. There is a contrast difference in the brightness of the atoms in the simulation images because the calculated ribbons are not perfectly flat. Figure S26e and f show the Laplacian-filtered image which clarifies every atomic position in the GNRs. The oxygen atom of a hydroxy group is clarified as a bright spot protruding from the ribbon in the image (Figure S26d and f), which well reproduces the experimental images (Figure 1c).
Figure S26. (a,b) Calculated structures of (a) 7AGNR and (b) hydroxyl-functionalized GNR on Au(111). (c,d) Simulated nc-AFM images based on (a) and (b). The distance between the topmost Au atom of the surface and the tip was 1.14 nm. (e,f) Laplacian-filtered images of (c) and (d).
9. Inter-GNR distance

The inter-GNR distance of the closely packed aligned GNRs with edge functionalization was evaluated as follows. The total free energies of the models with two aligned GNRs in the unit cell are compared. The models are shown in Figure S27. Two geometries are considered, in which each GNR edge has (i) one hydroxy and (ii) two hydroxy groups, respectively. The models' x and y-axis coordinates were allowed to relax while those in the z-axis were fixed to the optimized geometry evaluated in the infinite distance. The total free energy was compared to that of the model in which one GNR is located 3.5 nm away from the other (quasi-infinite separation). The horizontal axis of Figure S27(b) is the inter-GNR distance, which is the distance between carbon atoms indicated by the yellow circle in Figure S27(a).

Figure S27. (a) The models used for the optimization of inter-GNR distance. We considered two types of atomistic models, (i) two hydroxy or (ii) four hydroxy at the edge of GNRs. White solid lines indicate the unit cell. (b) The relative total energy vs. inter-GNR distance for models with (i) two hydroxy and (ii) four hydroxy at the edge of GNRs.

10. The effect of hydroxy group distribution on the electronic properties of GNRs.

This section briefly summarizes hydroxy group distribution's effect on the electronic properties of GNRs. In our experimental observations, hydroxy groups are randomly distributed on the GNR edges. While the amount of hydroxy groups affects the electronic properties of GNRs, as shown in Fig. 4b, we found that the distribution of hydroxy groups does not critically affect the electronic structure of GNRs. Fig. S28 shows the density of states (DOS) of GNRs with the same amount of hydroxy groups with the various distribution. Although the DOS of GNR with a periodic distribution
of hydroxy [Fig. S28a(i)] is slightly different from those with random hydroxy distribution, the band gap is almost identical, probably because hydroxy groups merely contribute to the $\pi$ resonance.

**Figure S28** The effect of hydroxy group distribution on the electronic properties of GNRs. (a) The structure of four models considered in this study. The ordered structure with a periodic distribution of hydroxy groups is considered in (i). In (ii-iv), the amount of hydroxy groups is the same as (i), while distribution was randomly determined. (b) The density of states (DOS) of the models shown in (a).

11. **The effect of edge functionalization on the hydrogen hopping paths.**

The effect of edge-functionalization on the energetics of I3 and I3-1 in Fig. 2 is investigated using the anthracene trimer model. The model includes anthracene trimer for the sake of simplicity and computation costs. The investigated process is hydrogen hopping after making the first C-C bonding, followed by hydrogen desorption to the substrate (Scheme S1). There are two possible hopping paths of hydrogen atoms: hopping to the bottom of the functional groups or hopping to the edges of adjacent anthracene. Four functional groups are added to the edges of anthracene trimers: hydrogen, fluorine, methylenedioxy, and methoxy. Table S1 summarizes the relative total free energy ($U_{tot}^{rel}$) of final states (2a-2d and 3a-3d) with respect to the initial state (1a-1d). In the case of hydrogen-terminated anthracene trimer (1a), since all anthracenes are identical, the relative total energy of 2a is almost comparable to that of 3a. In the case of F termination, on the other hand, the relative total energy of 2b is slightly smaller than that of 3b. The activation energy ($E_a$) was defined as $U_{tot}^{rel}(\text{barrier top}) - U_{tot}^{rel}(\text{initial})$, where $U_{tot}^{rel}(X)$ is relative total free energy of the intermediate $X$. The $E_a$ required for hydrogen hopping from 1b to 2b was evaluated using NEB and determined to be 0.76 eV on the anthracene trimer model, which is almost comparable to 0.83 eV (80 kJ/mol), which was evaluated using
fluorine functionalized anthracene polymers with periodic boundary condition on Au(111). This result justifies that the anthracene trimer model is enough to discuss hydrogen hopping on anthracene polymer qualitatively. The noteworthy finding is that the relative total energy of 3c and 3d is smaller than that of 2c and 2d in the case of methylenedioxy and methoxy modification. The mechanism is associated with the donation of lone pair on oxygen to the π orbitals. Figure S29(b, c) depicts HOMO of 1c and 2c of the methylenedioxy anthracene polymer. The methylenedioxy functional groups donate lone pair on oxygen to the π orbitals when attached to aromatic molecules, manifesting themselves in Figure S29(b) as π orbital distribution on oxygen. While hydrogen hopping to 3c will remain π resonance on methylenedioxy intact, hopping to 2c will hamper π electron donation of methylenedioxy, as depicted in Figure S29(b), which will make 2c less stable.

Scheme S1. The intermediate structures of anthracene trimer models.
Table S1. The relative total energies of anthracene trimer models. See scheme 1 for the structure.

| entry   | $U_{tot}^{rel}$ (eV) |
|---------|----------------------|
| HHH     |                      |
| 2a      | -0.92                |
| 3a      | -0.97                |
| HFH     |                      |
| 2b      | -1.01                |
| 3b      | -0.91                |
| Medioxy |                      |
| 2c      | -0.71                |
| 3c      | -0.92                |
| Methoxy |                      |
| 2d      | -0.63                |
| 3d      | -0.75                |

Figure S29. (a,b) Highest occupied molecular orbital (HOMO) of (a) 1c and (b) 2c in scheme S1 estimated by the first-principles calculation. The top views are shown in the inset.
12. The band gap of free-standing GNRs

Figure S30. (a) The structural model used for evaluating band dispersion of (i) 7AGNR and (ii) 7AGNR functionalized by two hydroxy groups per unit cell. A solid white line indicates the unit cell. The red, white, and gray spheres are oxygen, hydrogen, and carbon atoms, respectively. See the experimental section of the main text for the calculation conditions. (b) The band dispersion of the models shown in (a): (i) 7AGNR and (ii) 7AGNR functionalized by two hydroxy groups per unit cell.
13. Other possible paths for cyclo-dehydrogenation.

While the representative cyclo-dehydrogenation path was considered in Fig. 2, a couple of other paths are suggested in Schemes S2-S4. The path shown in Scheme S2, for example, is characterized by the desorption of methylenedioxy biradicals. We avoided looking into these processes because our models with a closed system with limited size may overestimate the activation energy of the process like Scheme S2, in which the desorbed biradicals can be adsorbed on metallic surfaces and decomposed into more stable molecules.

Scheme S4 shows a cyclo-dehydrogenation path based on the [1,9] path suggested in the previous work. As shown in Fig. 3, I2-1 is not a kinetically-preferred intermediate. Nevertheless, we found that I2-1 also leads to deprotection of methylenedioxy, leaving hydroxy groups on the edges (I7-2).
Scheme S3. Other possible paths for cyclo-dehydrogenation.

Scheme S4. Other possible paths for cyclo-dehydrogenation.
14. HOMO and LUMO of functionalized GNRs.

**Figure S31** (a) The structural formula, (b) HOMO, and (c) LUMO of GNRs with (i) hydrogen-terminated, (ii) hydroxy-terminated, and (iii) methylenedioxy-terminated edges.

15. References

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