Electronic Supplementary Information (ESI) for

Bottom-up solution synthesis of narrow nitrogen-doped graphene nanoribbons

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Materials

Chemicals: Phenanthrene-9,10-dione 95%, potassium hydroxide 85%, diphenyl ether 99% , nitromethane 98%, iron (III) chloride anhydrous 98%, 1,3-diphenylacetone 98+%, phenylacetylene 98+%, copper (I) iodide 98%, N,N'-dimethylforamide were purchased from Alfa Aesar; N-bromosuccinimide 99%, Bis(1,5-cyclooctadiene)nickel(0), cyclooctandiene, triethylamine 99.5%; triphenylphosphine, 2,2'-bipyridyl 99%, toluene 99.5%, and methanol 99.8% were purchased from Sigma-Aldrich; 5-bromopyrimidine 98%, bis(Triphenylphosphine)palladium (II) chloride 98% were purchased from Oakwood Products, Inc.; sulfuric acid 98% was purchased from EMD.
All chemicals were used as received without any purification.

Substrates: Mica V4 grade was purchased from SPI Supplies. Gold foils (99.985%) were purchased from Alfa Aesar. Au(111) single crystal (99.999%) for STM was acquired from Princeton Scientific.

Methods

^{1}H and ^{13}C NMRs were performed with Bruker 300MHz, 400MHz and 600MHz NMR instruments. AFM was performed using a Digital Instruments Nanoscope IIIa Dimension 3100 system and Bruker RTESPA AFM probes. All STM measurements were performed using an Omicron low-temperature scanning tunneling microscope with a base pressure of 3 x 10^{-10} T and an electrochemically etched W tip. UV-vis-NIR measurements were performed using a Jasco V-670 spectrophotometer. EDX analysis was performed using a FEI Nova NanoSEM 450 scanning electron microscope equipped with an Oxford Instruments EDX system. XPS was performed using a PHI Quantera SXM scanning X-ray microprobe. Raman spectrum of GNRs was recorded using a Thermo Scientific DXR Raman Microscope with a 532 nm laser. TEM and electron energy loss spectroscopy (EELS) were performed using a JEOL JEM-2200FS high resolution TEM operated at 200 kV.

Synthesis

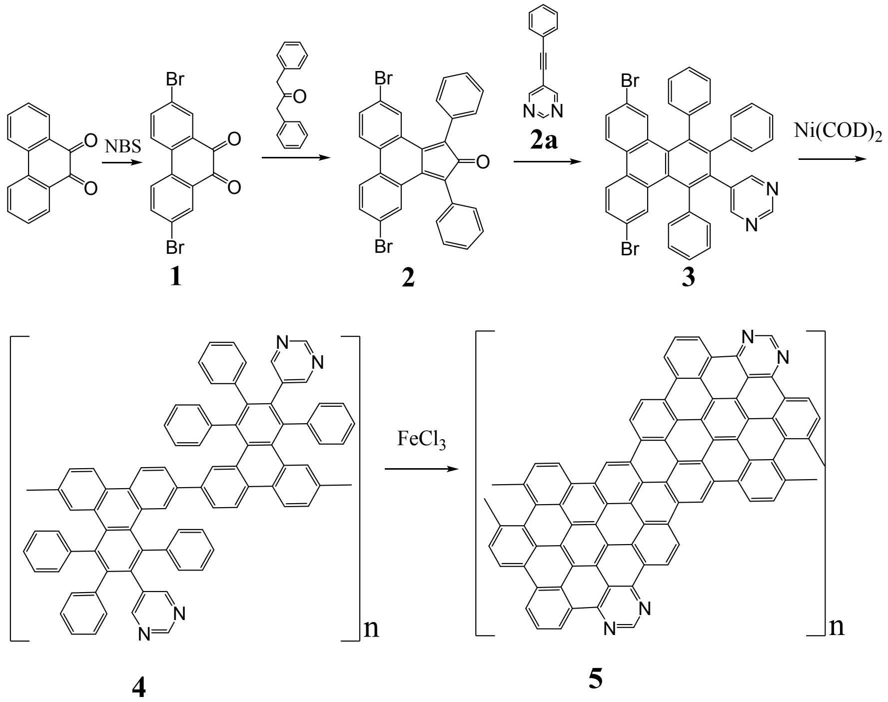

Figure S1. Scheme of the synthesis of 4N-GNRs.

2,7-dibromophenanthrene-9,10-dione (1): 7 g (33 mmol) of phenanthrene-9,10-dione was added to 190 mL of 98% sulfuric acid and followed by the addition of 12.86 g (72 mmol) of NBS. The mixture was agitated at room temperature for 8 h. After stirring, the mixture was added to ice/water bath and filtered to obtain a deep orange solid with a quantitative yield. ^{1}H NMR (300Hz, DMSO-d$_6$): δ= 8.24 (2H, d), 8.70 (2H, d), 7.95 (2H, dd).

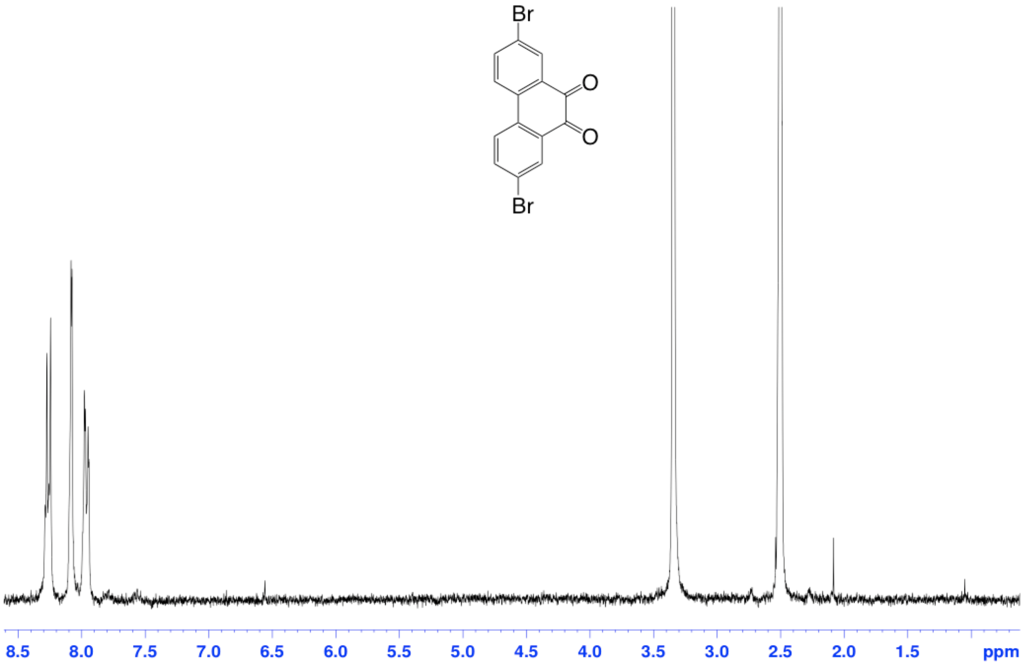

Figure S2. ^{1}H NMR spectrum of 2,7-dibromophenanthrene-9,10-dione in DMSO-d$_6$.

5,10-dibromo-1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one (**2**): 2.67 g (7.3 mmol) of **1** and 1.85 g (8.81 mmol) of 1,3-diphenylacetone were added to 15 mL of methanol under stirring. The reaction mixture was heated to reflux and 25.56 mL solution of 0.3M KOH (7.67 mmol) in methanol was added dropwise. The reaction mixture was refluxed for 2 h and then filtered. 2.5 g of green solid was obtained at 63.4% yield. ^{1}H NMR (600Hz, CD_2Cl_2): δ=7.65 (2H, d), 7.61 (2H, d), 7.49 (4H, dd), 7.45 (2H, dd,), 7.41 (2H, dd), 7.36 (2H, d).

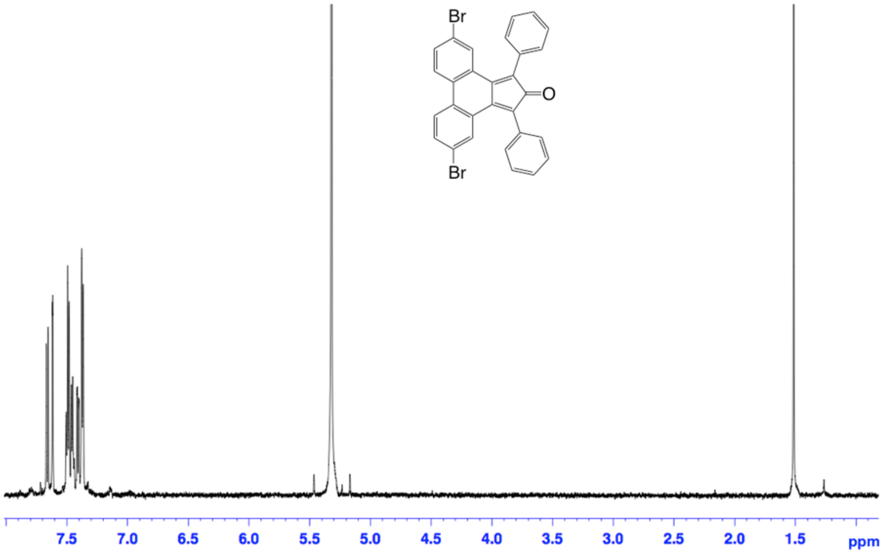

Figure S3. ^{1}H NMR spectrum of 5,10-dibromo-1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one in CD_2Cl_2.

5-(phenylethynyl)pyrimidine (2a): 25mL of triethylamine and 25mL of toluene were added to a three-neck round-bottom flask and followed by 2 g (12.57 mmol) of 5-bromopyrimidine, 65.0 mg (0.252mmol) of triphenylphosphine and 120.0 mg (0.629 mmol) of copper iodide. The suspension was degassed using nitrogen for 15 minutes. 441.5 mg (0.6294 mmol) of bis(triphenylphosphine)palladium (II) chloride was added to the reaction flask. The mixture was continued to degas for another 15 minutes and then heated to 60 °C and stirred for 30 minutes. Phenylacetylene (1.70 mL, 15.48 mmol) was added to the reaction flask. The reaction mixture was heated to 65-70 °C for 18 hours. After the stirring period was completed, the side product was filtered off, and the filtrate was concentrated to dryness. The crude product was dissolved in dichloromethane and purified by column chromatography (Ethyl acetate/Hexanes) to obtain 2.076 g of dark amber solid at 92.3% yield. ^{1}H-NMR (300Hz, CDCl$_3$): δ= 9.16 (1H, s), 8.87 (2H, s), 7.57 (2H, m), 7.41 (3H, m). ^{13}C-NMR (300Hz, CDCl$_3$): δ= 158.81, 156.89, 131.97, 129.57, 128.74, 121.97, 120.13, 96.53, 82.47.

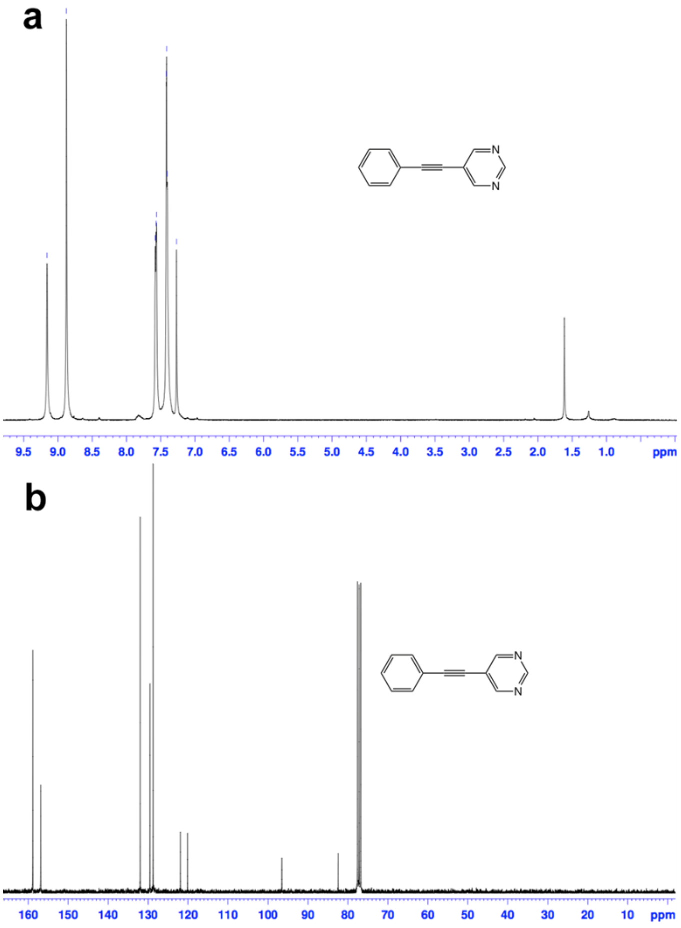

Figure S4. ^{1}H (a) and ^{13}C (b) NMR spectra of 5-(phenylethynyl) pyrimidine in CDCl$_3$.

5-(6,11-dibromo-1,3,4-triphenyltriphenylen-2-yl)pyrimidine (3): To a reaction flask, 5,10-dibromo-1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one (**2**) (1.32 g, 2.44 mmol), 5-(phenylethynyl)pyrimidine (**2a**) (0.4 g, 2.2 mmol) and 3 mL of diphenyl ether were added. The reaction mixture was heated to reflux for 24 hours. The reaction mixture was cooled to ambient temperature and purified using column chromatography with hexane and ethyl acetate (90:10) as mobile phase. 0.881 g (57.8% yield) of product was obtained. ^{1}H-NMR (300Hz, $CDCl_3$): δ= 8.78 (1H, s), 8.23 (2H, dd), 8.05 (2H, s), 7.71 (2H, d), 7.53 (2H, d), 7.25 (2H, m), 7.19 (3H, d), 7.04 (8H, m), 6.72 (2H, m); ^{13}C-NMR (300Hz, $CDCl_3$): δ= 158.01, 155.61, 141.49, 141.40, 141.03, 138.83, 138.38, 134.03, 133.18, 132.86, 132.08, 132.04, 131.89, 131.80, 131.60, 130.62, 130.35, 130.27, 129.97, 129.91, 129.34, 128.71, 127.94, 127.75, 127.38, 126.74, 124.83, 124.77, 120.56, 120.52.

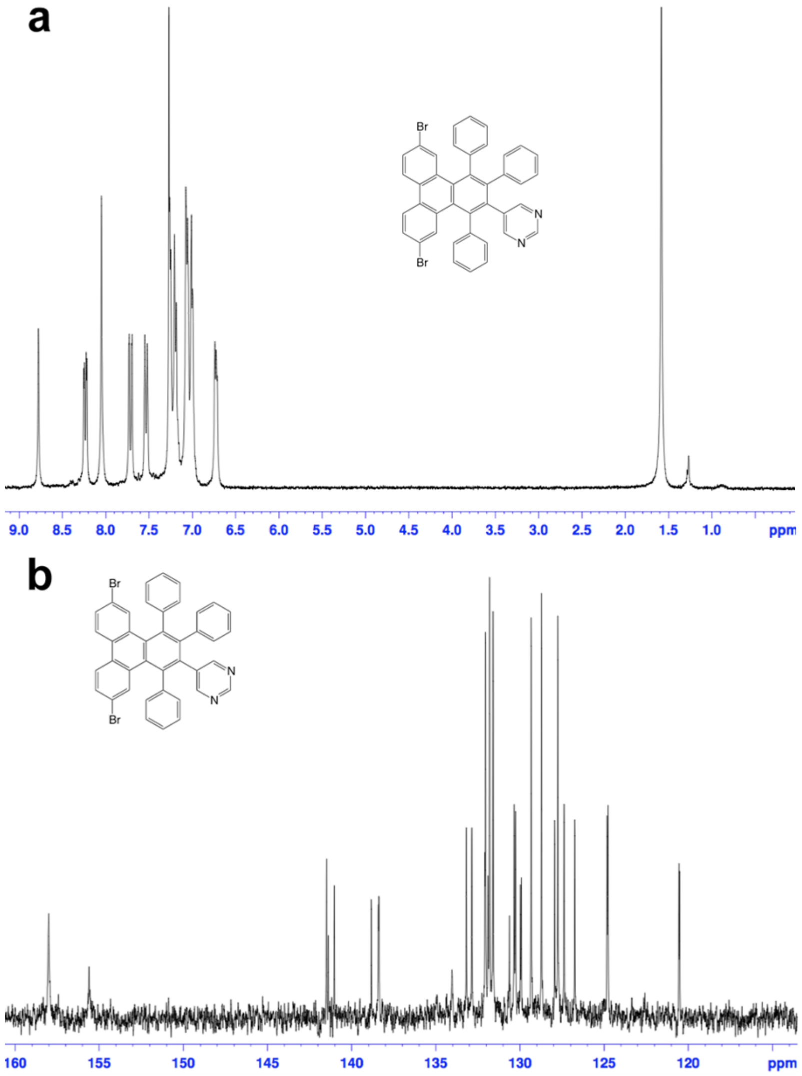

Figure S5. ^{1}H (a) and ^{13}C (b) NMR spectra of 5-(6,11-dibromo-1,3,4-triphenyltriphenylen-2-yl)pyrimidine in $CDCl_3$.

Polymer 4: To a dried and degassed reaction flask, 0.887 g (3.22 mmol) of Bis(cyclooctadiene)nickel was added and followed by a mixture of 2,2'-bipyridyl (0.54 g, 3.22 mmol) and 1,5-cyclooctandiene (0.4 mL, 3.22 mmol) in dried and degassed *N,N*-Dimethylformamide (9 mL). The reaction mixture was heated to 60 °C for 30 minutes. The degassed solution of monomer 3 (0.559 g, 0.81 mmol) in toluene (28 mL) was added to the reaction flask. The reaction mixture was heated to 80 °C for 3 days. The reaction flask was cooled to ambient temperature, and methanol/water mixture (50mL/10mL) was added. The slurry was filtered and washed with methanol, concentrated hydrochloric acid, methanol, sodium hydroxide/methanol solution, water, and hexanes. The solid was dried yielding 0.362 g (84%) of the product.

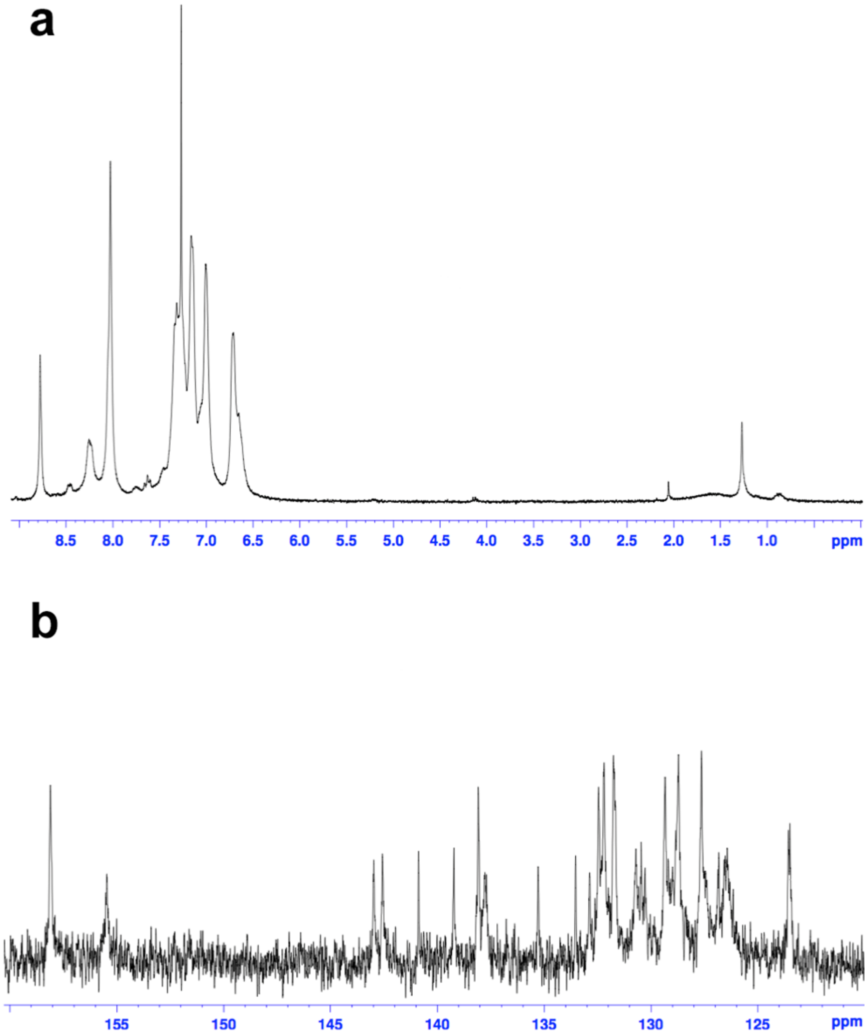

Figure S6. ^{1}H (a) and ^{13}C (b) NMR spectra of polymer **4** in $CDCl_3$

4N-GNR (5): In a reaction flask, 140 mg of polymer **4** and dichloromethane (70mL) were sonicated until all solids were dispersed well. Iron (III) chloride (7 g) was dissolved in nitromethane (8 mL) and then added to the reaction flask. Nitrogen gas was bubbled through the reaction mixture for 15-24 hours while stirring. After the stirring period was completed, ethanol was added. The reaction mixture was filtered and washed with concentrated hydrochloric acid, water, methanol/sodium hydroxide solution, water and methanol. The black solid was dried at 50 °C for 24 hrs. yielding 95.1 mg of black powder.

Sample preparation

Preparation of AFM samples: Approximately 0.3-0.5 mg of 4N-GNR powder and 7-10 mL of toluene were added to a 50 mL round bottom flask, sonicated for 1 min and then heated to reflux. Then the procedure of sonication (30 sec)/reflux was repeated twice. Using a glass pipette, two drops of 4N-GNR dispersion were deposited on the substrates while hot.

Preparation of STM sample: The substrate (Au(111) single crystal) was first cleaned by repeated cycles of Ar ion sputtering and annealing to 875 K. Cleanliness of the Au crystal was checked by STM. The 4N-GNRs dispersion was prepared as described in the 'Preparation of AFM samples' section. The clean Au substrate was removed from the ultra-high vacuum (UHV) chamber and 1-2 drops of 4N-GNR dispersion were deposited and allowed to dry in air for approximately 5 minutes. The Au(111)/4N-GNRs sample was reintroduced to the UHV system and annealed to remove adsorbates and solvent residues. Then the sample was cooled to 77 K for imaging. The annealing-cooling process was repeated with the annealing temperature gradually increasing until graphene ribbons were visible in STM images. The final annealing temperature was approximately 320 K.

Preparation of EDX/XPS samples: Several droplets of 4N-GNR dispersion in dichloromethane were deposited on a gold foil and dried in air.

Preparation of samples for UV-vis-NIR measurements: To prepare the sample for UV-vis-NIR measurements, 0.1 mg of 4N-GNRs **5** was dispersed in 6 mL of mesitylene by sonication for 1 minute at ambient temperature. The mixture was heated to reflux for 10 minutes and then sonicated for additional 30 seconds. Heating and sonication were repeated one more time. The 4N-GNR dispersion was poured to a cuvette while still hot (>100 ^{0}C).

Preparation of HRTEM samples: 4N-GNRs were first dispersed in toluene by sonication. 400 mesh copper TEM grids with an ultrathin carbon support film were dipped in the toluene dispersion of 4N-GNRs and dried in air.

Some foreign particles could be observed in Fig. 2d,e. We analyzed these particles by high resolution TEM and EELS and found that they consist of crystalline TiO_2. No titanium compounds were used at any stage of the synthesis of 4N-GNRs (Fig. S1). Furthermore, the 4N-GNR material was analyzed by EDX and XPS (Fig. 4), and no detectable amount of titanium was found in the sample. Therefore, we believe that those few particles observed in the TEM images in Fig. 2d,e are due to contamination, likely during the TEM sample preparation.