Supporting Information

Phenyl Functionalization of Atomically Precise Graphene Nanoribbons for Engineering Inter-Ribbon Interactions and Graphene Nanopores

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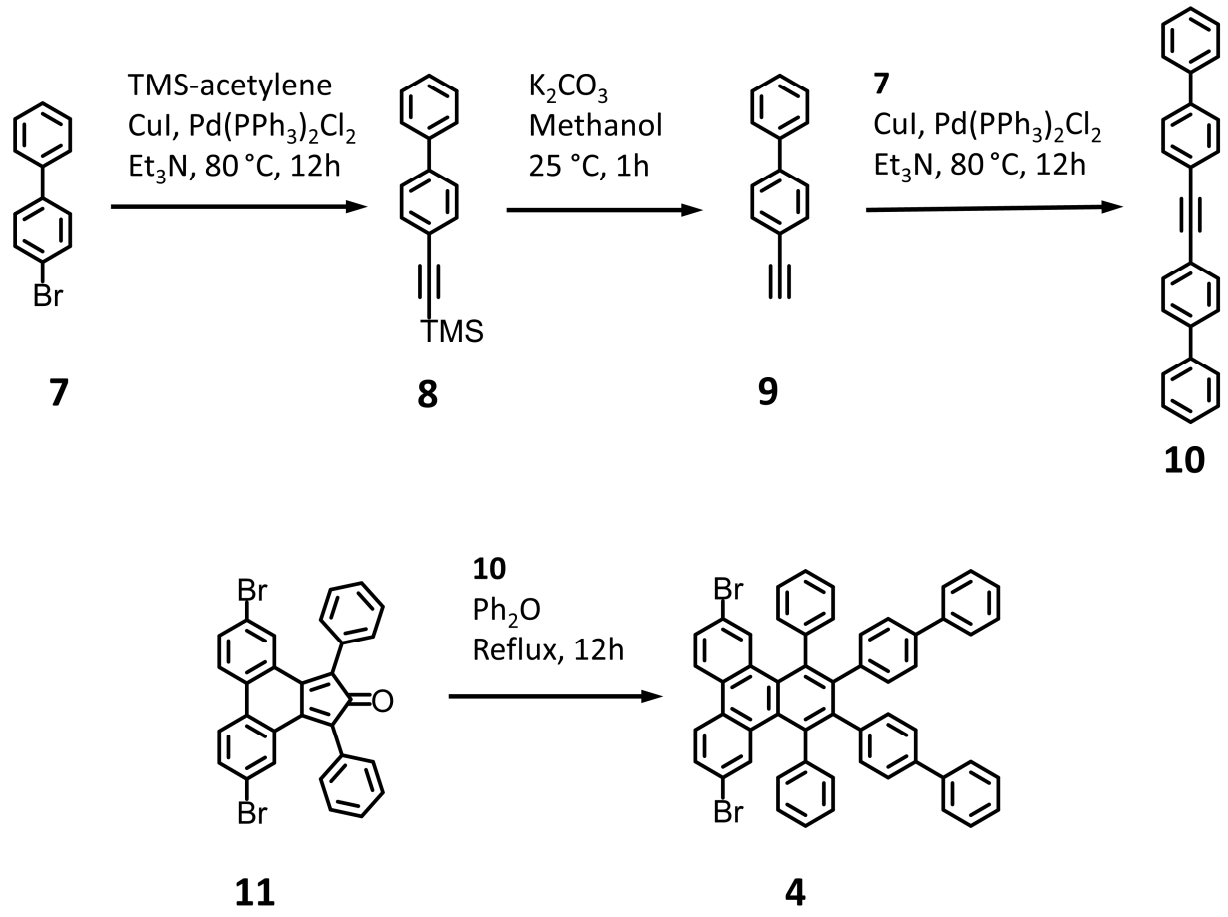
Synthesis of the mGNR precursor



Scheme S1. Synthesis of the mGNR precursor **4**.

Materials

All starting materials and solvents were purchased from Sigma-Aldrich, Alfa Aesar and other commercial suppliers and used as received without further purification. ^{1}H and ^{13}C NMR was performed using a Bruker Avance III-HD 400 MHz instrument. Compound **11** was synthesized according to the previously published procedure.[1, 2]

*Synthesis of 4-ethynyl-1,1'-biphenyl (**9**):*

500 mg of 4-bromo-1,1'-biphenyl (**7**) was dissolved in 15 mL of triethylamine and the solution was degassed by nitrogen bubbling for 15 min. 40 mg of CuI, 75 mg of $Pd(PPh_3)_2Cl_2$ and 602 µL of trimethylsilyl (TMS) acetylene were added to the reaction mixture and heated to 80 °C overnight under nitrogen atmosphere. The solvent was evaporated, the reaction mixture was filtered through a pad of silica gel using dichloromethane (DCM) and concentrated under vacuum to afford a white solid (**8**). The solid was dissolved in 25 mL of methanol, 1.5 g of K_2CO_3 was added to the flask and the reaction mixture was stirred at room temperature for 1 h. The final product was extracted with DCM/water, organic layer was dried over $MgSO_4$ and the solvent was evaporated under vacuum to afford 314 mg (82%) of white solid.

^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.63-7.57 (6H, m), 7.48 (2H, t), 7.39 (1H, t), 3.15 (1H, s).

*Synthesis of 1,2-di([1,1'-biphenyl]-4-yl)ethyne (**10**):*

200 mg of (**9**) and 262 mg of (**7**) were dissolved in 15 mL of triethylamine and degassed by nitrogen bubbling for 15 min. 21 mg of CuI, 40 mg of $Pd(PPh_3)_2Cl_2$ were added and the reaction mixture was stirred at 80 °C overnight under nitrogen atmosphere. The solvent was evaporated, and the product was purified by silica gel column chromatography using hexane/DCM (80%:20%) mixture as an eluent to afford 371 mg (68%) of white solid.

^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.66-7.58 (12H, m), 7.46 (4H, t), 7.37 (2H, t).

^{13}C NMR (400 Hz, $CDCl_3$): δ = 141.00, 140.38, 132.04, 128.87, 127.65, 127.05, 127.04, 122.22, 90.00.

*Synthesis of 2,3-di([1,1'-biphenyl]-4-yl)-6,11-dibromo-1,4-diphenyltriphenylene (**4**):*

113 mg of (**10**) and 185 mg of (**11**) were refluxed in 500 µL of diphenyl ether overnight. The reaction mixture was cooled down and purified by column chromatography using hexane/DCM (80%:20%) mixture as an eluent to yield 87 mg (30%) of white powder.

^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.24 (2H, d), 7.72 (2H, d), 7.52 (6H, m), 7.38 (4H, t), 7.30 (2H, t), 7.24-7.16 (10H, m), 7.15-7.10 (4H, m), 6.82 (4H, d).

^{13}C NMR (400 Hz, $CDCl_3$): δ = 141.93, 141.01, 140.78, 139.06, 138.04, 137.83, 133.02, 132.41, 131.99, 131.96, 130.55, 129.68, 128.73, 128.52, 127.15, 126.97, 126.91, 125.46, 124.62, 120.26.

References

1. Saleh, M.; Baumgarten, M.; Mavrinskiy, A.; Schäfer, T.; Müllen, K., Triphenylene-Based Polymers for Blue Polymeric Light Emitting Diodes. *Macromolecules* **2010,** *43*, 137-143.

2. Vo, T. H.; Shekhirev, M.; Kunkel, D. A.; Morton, M. D.; Berglund, E.; Kong, L. M.; Wilson, P. M.; Dowben, P. A.; Enders, A.; Sinitskii, A., Large-Scale Solution Synthesis of Narrow Graphene Nanoribbons. *Nat. Commun.* **2014,** *5*, 3189.