Supporting Information

Amphiphilic Pyrene Sheet for Selective Funtionalization of Graphene.

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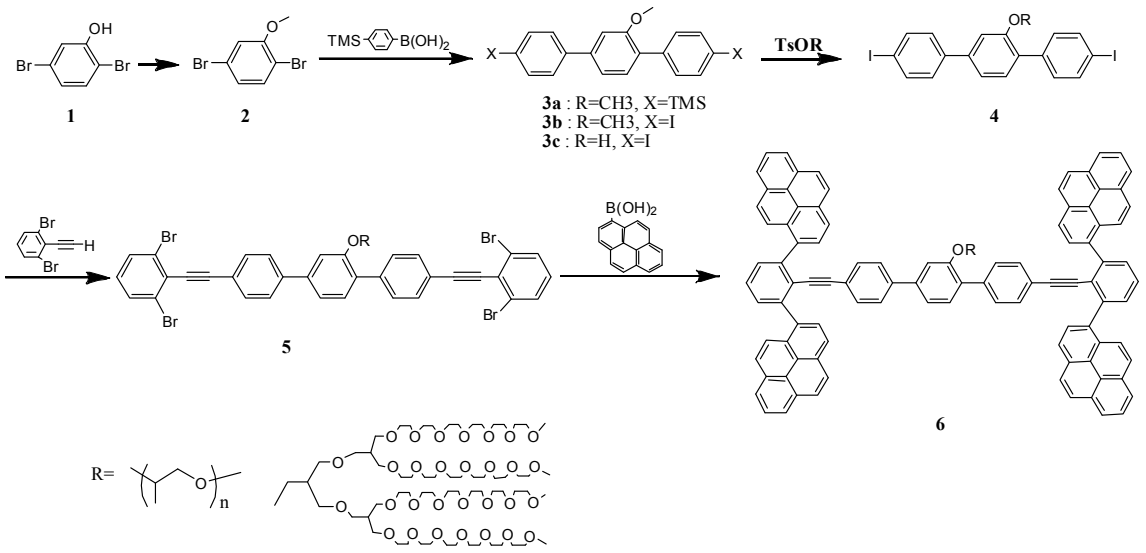
S1. Experimental Section

Materials. Tetrakis(triphenylphosphine) palladium(0) (99 %), NaH (60 %), and *p*-toluenesulfonyl chloride (98 %) from TCI and Tokyo Kasei were used as received. 2,6-dibromophenol, 4-biphenylboronic acid, Pyrene-1-boronic acid, iodine monochloride (1.0 M solution in dichloromethane), boron tribromide (1.0 M solution in dichloromethane) from Aldrich were used as received. Compound 4,4'-(trimethylsilyl) phenylboronic acid was prepared according to the similar procedures described previously. [S1] Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, and TCI, etc.) and were used without purification. Methylene chloride, hexane and Triethylamine, were distilled before use. Visualization was accomplished with UV light and iodine vapor. Flash chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science. Dry THF was obtained by vacuum transfer from sodium and benzophenone.

Techniques. ^{1}H-NMR was recorded from $CDCl_3$ solutions on a Bruker AM 300 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). The UV/vis spectrometer were obtained from Hitachi U-2900. The fluorescence spectra were obtained from a Hithachi F-7000 Fluoresence Spectrophotometer. MALDI-TOF mass spectra were performed on Perceptive Biosystems Voyager-DE STR

using a 2,5-dihydroxy benzoic acid matrix. The transmission electron microscope (TEM) was performed at 120 kV using JEOL-JEM 2010. The 0.005% aqueous solution were dropped on carbon-coated copper grid and allowing the solution evaporate under ambient conditions. Scanning electron microscopy (SEM) was performed at 500eV using Hitachi S-9380. The 0.1% aqueous solution were spin coated on Si wafer at 700rpm. Raman spectra obtained using a Renishaw Raman system model 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). Atomic force microscopy (AFM) was performed in the tapping mode under ambient condition with a Veeco Nano-Scope IIIa Atomic force microscope (Digital Instruments, Inc., Santa Barbara, CA) using Nanosensors silicon probes (dimensions: H = 3.5-4.5nm, W=30-40mm, L = 115-135 mm) The AFM scans were conducted at a scanning rate of 0.5-2 Hz. Compounds were synthesized according to the procedure described scheme 1 and then purified by silica gel column chromatography and prep. HPLC (Japan Analytical Instrument).



Scheme 1. A general outline of the synthetic procedure.

Synthesis of compound 2 : Compound **1** (1.4 g, 5.6 mmol), iodomethane (2.4 g, 16.8 mmol), and K_2CO_3 (1.16 g, 8.4 mmol) were dissolved with acetone (100 ml) in round bottom flask. The mixture was heated at reflux for 12 hrs and then cooled to room temperature. Solvent was distilled and the resulting mixture was extracted with methylene chloride and water. The crude product was dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column

chromatography (silica gel) using hexane as eluent to yield 1.2 g (80 %) of liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 7.45 (d, 2H, Ar-H), 7.02 (s, 1H, Ar-H), 6.97 (d, 2H, Ar-H), 3.92 (s, 3H, OCH_3).

Synthesis of compound 3a : Compound **2** (1.2 g, 4.5 mmol) and 4,4'-(trimethylsilyl) phenylboronic acid (1.95 g, 9.9 mmol) were dissolved in 50ml THF and added 50 ml of degassed 2.0 M Na_2CO_3 aqueous solution . Then tetrakis(triphenylphosphine) palladium(0) (0.1 g, 0.1 mmol) was added. The mixture was heated at reflux for 24 hrs with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, and the aqueous layer was then washed twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using hexane : ethyl acetate (10 : 1 v/v) as eluent to yield 1.45 g (80 %) of white powder. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 7.62-7.58 (m, 8H, Ar-H), 7.39 (d, 2H, Ar-H,), 7.19 (s, 1H, Ar-H), 3.92 (s, 3H, OCH_3), 0.32 (s, 18H, silane-CH_3).

Synthesis of compound 3b : Compound **3a** (1.4 g, 3.46 mmol) in distilled methylene chloride (200 ml) at -78 ^oC was dropped 1.0 M solution of ICl in methylene chloride (8.7 ml, 8.7 mmol) with strong stirring. The reaction mixture was stirred over 1.5 hr under nitrogen. 1.0 M aqueous $Na_2S_2O_5$ (50 ml) solution was added and stirred over 1 hr at RT. The layers were separated, and the aqueous layer was then washed twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate as eluent to yield 1.39 g (79 %) of white powder. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 7.79-7.76 (m, 4H, I-Ar-H), 7.35-7.34 (m, 4H, Ar-H), 7.27 (d, 2H, Ar-H), 7.19 (s, 1H, Ar-H), 3.93 (s, 1H, CH_3).

Synthesis of compound 3c : Compound **3b** (1.3 g, 2.53 mmol) was dissolved in 150 ml of dried methylene chloride at ice-bath condition then dropping BBr_3 (7.6 ml, 7.59 mmol) slowly. After removing ice-bath, the reaction mixture was stirred at room temperature under nitrogen for 10 hrs. The solution was quenched with MeOH at ice-bath condition for 30 min. The crude product was filtered and dried to yield 0.89 g (65.5 %) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 7.84-7.56 (m, 4H, I-Ar-H, J = 4.8 Hz), 7.36-7.33 (m, 4H, Ar-H), 7.27 (d, 2H, Ar-H), 7.19 (s, 1H, Ar-H).

Synthesis of compound 4 : Compounds **3c** (500mg, 1.0mmol), **R-OTs** (1.08g, 0.7 mmol) and excess K_2CO_3 were dissolved in 40 ml of distilled methylene chloride. The mixture was heated at reflux for 12 hrs and then cooled to room temperature. The mixture was extracted with methylene chloride and water and then dried over anhydrous magnesium sulfate, and filtered. After the solvent was removed in a rotary evaporator, the crude products were purified by column chromatography (silica gel) using hexane : ethyl acetate (7 : 1 v/v) to yield 750 mg (40 %) of a colorless liquid. Yield 44.1 %, ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 7.79-7.72 (m, 4H, I-Ar-H), 7.38-7.32 (m, 4H, Ar-H), 7.28 (s, 2H, Ar-H), 7.18 (s, 1H, Ar-H) 4.12 (s, 2H, -C*H*$_2$OAr), 3.63-3.37(m, 116H; -C*H*$_2$O), 2.13-2.05 (m, 1H;-CH$_2$C*H*CH$_2$O-), 1.67-1.64 (m, 2H; -OCH$_2$C*H*$_2$).

Synthesis of compound 5 : Compound 4 (700mg, 0.37mmol), dibromoacetylene (240mg, 0.92mmol) tetrakis(triphenylphosphine) palladium(0) (0.1 g, 0.1 mmol) and copper(I) iodide (0.1g) were dissolved in 10ml distilled triethylamine. The mixture was heated at reflux for 12 hrs and then cooled to room temperature. The mixture was filtered and the solvent was removed in a rotary evaporator, the crude products were purified by column chromatography (silica gel) using hexane : ethyl acetate (7 : 1 v/v) to yield 300 mg (38 %) of a colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 7.79-7.41(m, 15H, Ar-H), 7.07-7.04 (d, 2H, Br-Ar-H), 4.13 (s, 2H, -C*H*$_2$OAr), 3.64-3.37(m, 116H; -C*H*$_2$O), 2.13-2.05 (m, 1H;-CH$_2$C*H*CH$_2$O-), 1.67-1.64 (m, 2H; -OCH$_2$C*H*$_2$).

Synthesis of compound 6 : Compound **5** (1.3 g, 0.6 mmol) and 1-pyrenylboronic acid (1.27 g, 5.16 mmol) were dissolved in 30ml THF and added 40 ml of degassed 2.0 M Na_2CO_3 aqueous solution . Then tetrakis(triphenylphosphine) palladium(0) (0.1 g, 0.1 mmol) was added. The mixture was heated at reflux for 24 hrs with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, and the aqueous layer was then washed twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using hexane : ethyl acetate (10 : 1 v/v) as eluent to yield 1.2 g (80 %) of yellow liquid . Yield 44.1 %, ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 8.31-7.70(m, 47H, pyrene-Ar-H), 7.07-7.04 (d, 2H, Br-Ar-H), 4.13 (s, 2H, -C*H*$_2$OAr), 3.64-3.37(m, 116H; -C*H*$_2$O), 2.13-2.05 (m, 1H;-CH$_2$C*H*CH$_2$O-), 1.67-1.64 (m, 2H; -OCH$_2$C*H*$_2$). Anal. Calcd for: $C1_{62}H_{182}O_{31}$: C, 74.12; H, 6.99 Found C, 69.56 ; H, 8.07 ; MALDI-TOF-MS m/z 2649.48 ($[M+Na]^+$), Calcd 2624.27

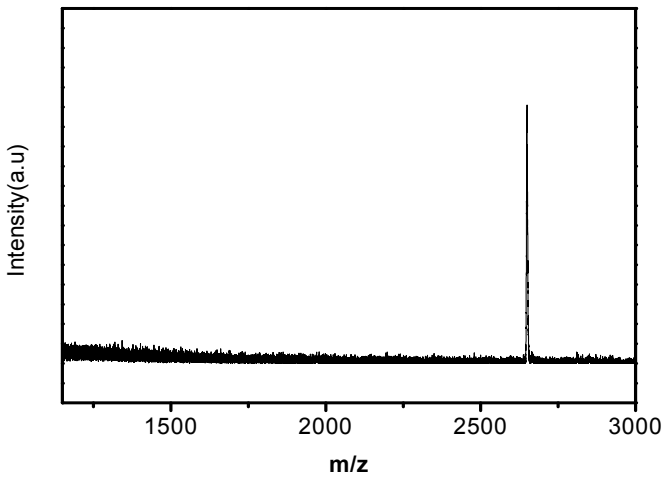


Figure S1. MALDI-TOF mass spectra Compound 6

S2. Production of graphene exfoliation solution

Figure S2 schematically shows the process of preparing graphene exfoliation solution by compound **6** (in scheme 1). Graphene exfoliation solutions were prepared by sonication a mixture of 27mg graphite powder (Aldrich, particle size <45 ㎛) and 2ml of 0.2wt% compound **6** in H_2O/MeOH mixed solvent for 24h and keep water temperature in sonicator (Branson 5510) around 10℃. In the middle of process, added more water (2 ml) to meet 0.1% solution and then sonication was continued for 12h. After finishing sonication process, the dispersion was centrifuged at 1300rpm for 30min by centrifuse (Eppendorf 5415R) and can separate black dispersion and precipitated graphite powder.

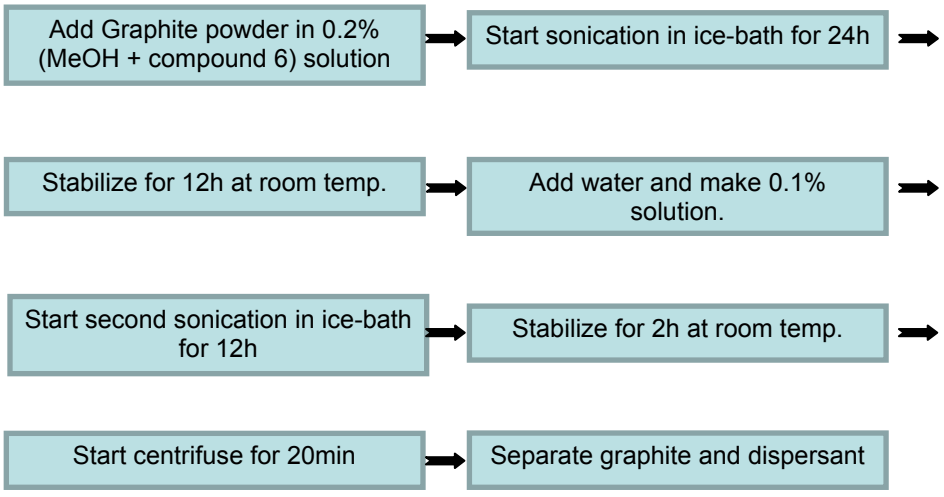


Figure S2. Graphene exfoliation procedure flowchart

S3. Preparation of grapheme film for conductivity.

Thin film of graphene were prepared by vacumm filtration of graphene suspension in water/MeOH (7 : 3) by using mixed cellulose ester membrane (Millipore) with 0.45 ㎛ pore size. The **compound 6-graphene** flakes on the filter membrane can then be transferred to glass substrate through procedure of reference paper.[S2] and was annealed at 350℃ for 30min before measuring four point probe measurement.

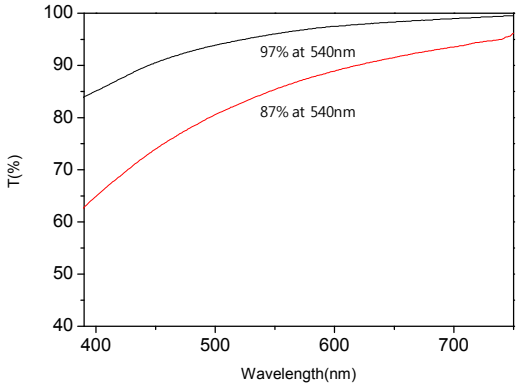


Figure S3. Optical transmittance spectra for graphene film

Figure S4. Photographs of graphene thin film on glass

Reference

S1. Ciszek, J. W.; Tour, J. M. *Tetrahedron Letters* **2004**, *45*, 2801.

S2. Eda, G.; Fanchini, G.; Chhowalla, M. *Nature Nanotech.* **2008**, *3*, 270.