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Direct Exfoliation of Carbon Allotropes using Structural Analogue of Self-Assembled Nanostructures and their Photovoltaic Applications

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Materials

Tetrakis(triphenylphosphine) palladium(0) (99%), NaH (60%), and *p*-toluenesulfonyl chloride (98%) from TCI and Tokyo Kasei were used as received. 2,6-Dibromohydroquinone, phenylboronic acid, 2-bromothiophene, tetrakis(triphenylphosphine) palladium(0) from Aldrich were used as received. 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. Solar cell materials P3HT and PCBM were purchased from Rieke Metals and Nano-C (USA), respectively. Poly(styrenesulfonate)-doped poly(ethylenedioxythiophene) (PEDOT:PSS, Clevious PH) was purchased from Bayer.

Instruments and method

^{1}H-NMR spectra was recorded from $CDCl_3$ solutions on a Bruker AM 300 spectrometer. The purity of products was checked by thin layer chromatography (TLC; Merck, silica gel 60). The UV/vis spectra were obtained from Hitachi U-2900. The fluorescence spectra were obtained from a Hitachi F-7000 Fluoresence Spectrophotometer. MALDI-TOF mass spectra were performed on Perceptive Biosystems Voyager-DE STR using a 2,5-dihydroxybenzoic acid matrix. The transmission electron microscopy (TEM) experiments were performed at 120 kV using JEOL-JEM 2010 and JEM-2100F at an accelerating electron voltage of 200 kV. The 0.05% (w/v) aqueous solutions of **1**, **2** and **3** were dropped on carbon-coated copper grid and allowing the solution to evaporate under ambient conditions. Compounds were synthesized according to the procedure described in Scheme 1 and then purified by silica gel column chromatography and prep. HPLC (Japan Analytical Instrument). MALDI TOF-MS spectrometry (MALDI-ToF-MS) was performed on a Bruker Microflex LRF20 using α-cyano-4-hydroxy cinnamic acid (CHCA) as matrix. Raman spectra were recorded with Renishaw Invia Raman spectrometer using a He-Ne laser (λ= 514 nm). The device performance was measured under AM 1.5G illumination (100 mW cm^{-2}) using a solar simulator (Peccell, Japan). The light intensity at each wavelength was calibrated using a standard Si solar cell as a reference. The current density-voltage (J-V) curves were measured with a Kethley 2400 source measurement unit. The AFM images were obtained using Nanoscope IV controller (Veeco Instruments, USA). The UPS spectra were obtained using AXIS Nova (Kratos Analytical Ltd, Japan)

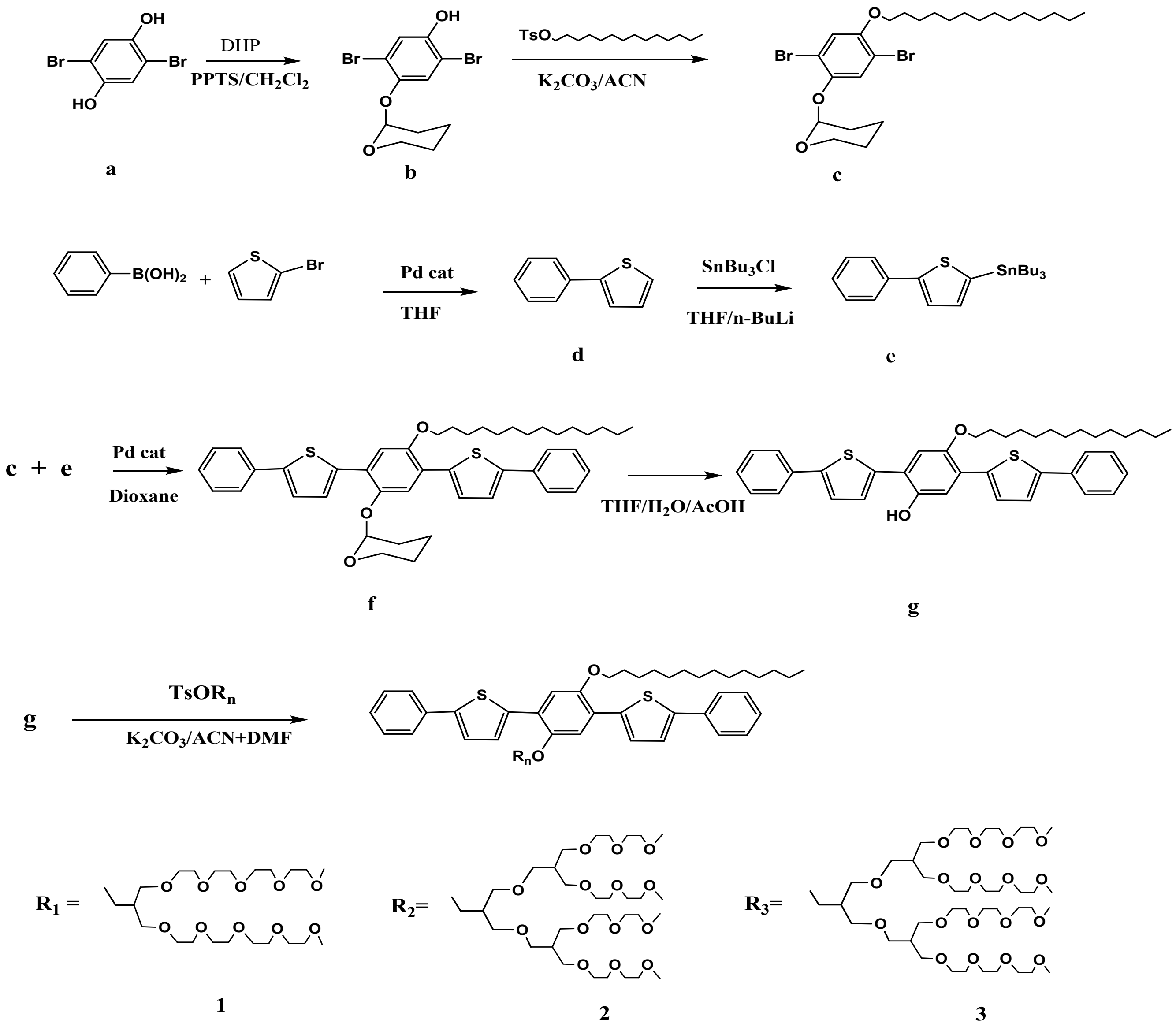
Production of carbon allotropes exfoliation solution

The process of preparing graphene/SWNT exfoliation solution by compounds **1** and **3**: graphene/SWNT exfoliation solutions were prepared by sonicating a mixture of 3 mg graphite/SWNT powder and 2 ml of 0.05 wt% compounds **1** and **3** in aqueous solution for 12 h and kept water temperature in sonicator (Branson 5510) around 10℃. After finishing sonication process, the dispersion was centrifuged at 12000 rpm for 30 min by centrifuge (Eppendorf 5415R) which separated black dispersion and precipitated graphite. Finally, a high concentration of carbon materials (> 1 mg/mL) in aqueous solution was obtained.

Photovoltaic device fabrication

Indium tin oxide (ITO) coated glass, which was cleaned by ultrasonication with detergent, followed by distilled water and 2-propanol sequentially, was used as a transparent electrode. The ITO surface was modified by spin-coating of a 50-nm-thick HTL after exposing the ITO surface to ozone for 5 min. The HTL was composed of PEDOT:PSS and **1** + G self-assembled nanostructures (0, 3, 5, and 10 wt%, w/v). The HTL was dried on a hot plate in air for 20 min at 140 °C. The P3HT:PCBM (1:0.8 w/w) blend was dissolved in chlorobenzene with stirring overnight, which was spin-coated onto the HTL at 2000 rpm.The active layer was heated on a hot plate for 10 min at 140 °C. After drying the active layer, LiF (1 nm) and Al metal (100 nm) were deposited as the cathode under vacuum below 10^{-6} torr, which yielded an active area of 4 mm^2 per pixel. Photovoltaic performance of all devices was investigated at one sun intensity (100 mW/cm^2) under simulated AM 1.5G illumination.

Preparation of R_n-OTs. The first generation chiral dendritic tetraethylene glycol monobenzyl ether coils were prepared according to the similar procedures as described previously.[1] Then, hydrogenation of the dendritic coils over 20% Pd/C for 2 h provided the desired dendrimer. The crude mixture was filtered and concentrated in vacuum to yield 73% of a colorless liquid.



Scheme 1. A general outline of the synthetic procedure.

Synthesis of compound b. PPTS (100 mg, 0.04 mol) was added to a Ar-blanked solution of 2,5-dibromohydroquinone (10 g, 37.3 mmol) in 3,4-dihydro-2H-pyran (7 mL). The suspension obtained was allowed to stir at room temperature for 12 h. The mixture was extracted with methylene chloride and water. The crude product was dried over anhydrous magnesium sulfate, and filtered. The solvent was removed by a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using CH_2Cl_2 as eluent to yield 5 g (38%) of solid. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ7.32 (d, 2H, Ar-H), 5.38-5.39 (s, 1H, OCHO), 3.90-3.61 (m, 4H,OCH_2), 2.06-1.70 (m, 4H, CH_2).

Synthesis of compound c. Compound **b** (2 g, 5.7 mmol), tetradodecyl-OTs (2.3 g, 6.3 mmol) and excess K_2CO_3 were dissolved in 40 ml of distilled acetonitrile and DMF. The mixture was heated at reflux for 12 hr and then cooled to room temperature. After solvents were removed by a rotary evaporator, the mixture was partitioned between CH_2Cl_2 and water, and the organic phase was dried over anhydrous magnesium sulfate, and filtered. After the solvent was removed, the crude product was purified by column chromatography (silica gel) using hexane to yield 2 g (75%) of a colorless liquid.^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm).δ7.32 (d, 2H, Ar-H), 5.38-5.39 (s, 1H, OCHO), 3.90-3.61 (m, 4H,OCH_2), 2.06-1.70 (m, 22H, CH_2), 0.91 (m, 3H, CH_3).

Synthesis of compound d. To a solution of 2-bromothiophene (1.2 mL, 12.25 mmol) and phenylboronic acid (1.64 g, 13.5 mmol) in THF (50 mL), 2 M aqueous solution of Na_2CO_3 (13 mL, 27 mmol) and tetrakis(triphenylphosphine) palladium(0) (700 mg) were added. The reaction mixture was heated at reflux for 10 h. After removing THF, the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed, and the crude product was purified by column chromatography (silica gel) using hexane:ethyl acetate (4:1, v/v) as eluent to yield 2 g (97%) of white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ7.56-7.60 (m, 2H), 7.21-7.43 (m, 5H), 7.01-7.05 (m, 1H).

Synthesis of compound e. In a three-necked flask equipped with a septum and stopcock, compound **d** (0.9 g, 5.61 mmol) was dissolved in anhydrous THF (30 mL) under Ar. After cooling to -78 ℃, a solution of n-BuLi (2.7 mL, 6.75 mmol, 2.5 M solution in hexane) was added by syringe. The reaction mixture was stirred at -78 ℃ under argon for 30 min, after which tributyltin chloride (1.2 eq) was added dropwise via a syringe. The mixture was stirred at room temperature overnight. Then saturated NH_4Cl solution (30 mL) was added dropwise to quench the reaction. The phase was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed to yield 1.8 g (98%) of the crude desired product as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ7.68 (dd, 2H, Ph-H), 7.47-7.42 (m, 1H for Th-H, 2H for Ph-H), 7.30 (m, 1H, Ph-H), 7.19 (d, 1H, Th-H), 1.59 (m, 6H, CH_2), 1.35-1.12 (m, 12H, CH_2), 0.91 (m, 9H, CH_3).

Synthesis of compound f. A 100 mL round bottom flask was charged with compound **c** (0.5 g, 0.91 mmol), tetrakis(triphenylphosphine) palladium(0) (2 mg, 0.7 mmol), compound **e** (0.9 g, 1.92 mmol) and anhydrous 1,4-dioxane and heated to 80 ℃ with stirring for 24 h. The reaction mixture was then cooled to room temperature. The phase was separated and the aqueous layer was extracted with ethyl acetate. 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:CH_2Cl_2 (2:1, v/v) as eluent to yield 0.5 g (80%) of a yellow waxy solid, ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 7.54 (m, 4H, Th-H), 7.30-7.26 (m, 6H, Ph-H), 6.94-6.83 (m, 6H, Ph-H), 5.38-5.39 (s, 1H, OCHO), 3.91-3.60 (m, 4H,OCH_2), 2.05-1.50 (m, 26H, CH_2), 0.93-0.91 (m, 3H, CH_3).

Synthesis of compound g. To a solution of compound **f** (150 mg, 7.7 mmol) in THF/H_2O/AcOH (10/70/30, 100 mL) was added a little amount of p-toluenesulfonic acid, and then the mixture was stirred at ~65 ℃ for 12 h. The reaction mixture was extracted with ethyl acetate and washed with H_2O to remove AcOH. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator. The product were purified by recrystallization in EtOH to yield 300 mg (38%) of a yellowish solid.^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm) δ 7.54 (m, 4H, Th-H), 7.35-7.30 (m, 6H, Ph-H), 6.94-6.83 (m, 6H, Ph-H),3.92-3.64 (m, 4H,OCH_2), 2.11-1.56 (m, 22H, CH_2), 0.93-0.90 (m, 3H, CH_3).

Synthesis of compounds 1, **2**, **and 3**: Compounds **1**, **2**, and **3** were prepared according to the procedure used for preparation of compound **c**. The crude products were purified by silica gel column chromatography (silica gel, CH_2Cl_2/MeOH = 15/1) and prep. HPLC (Japan Analytical Instrument) to yield 120 mg (60 %) of compound **1**, 100 mg (55%) of compound **2**, 115 mg (50%) of compound **3**, respectively.

Compound 1 : ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm);δ 7.54 (m, 4H, Th-H), 7.35-7.30 (m, 6H, Ph-H), 6.94-6.83 (m, 6H, Ph-H), 4.12 (s, 2H, -CH_2OAr), 3.92-3.64 (m, 4H,OCH_2), 3.65-3.48(m,34H; -CH_2O), 2.55-2.53 (m, 1H;-CH_2CHCH_2O-), 2.11-1.56 (m, 22H, CH_2), 1.67-1.64 (m, 6H; -OCH_2CH_3), 0.93-0.90 (m, 3H,CH_3), MALDI-TOF-MS m/z 1116.7 ($[M+Na]^+$), calcd 1091.5.

Compound 2 : ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm);δ 7.54 (m, 4H, Th-H), 7.35-7.30 (m, 6H, Ph-H), 6.94-6.83 (m, 6H, Ph-H), 4.12 (s, 2H, -CH_2OAr), 3.60-3.48(m,40H; -CH_2O), 3.92-3.64 (m, 8H,OCH_2), 2.55-2.53 (m,3H-CH_2CHCH_2O-), 2.11-1.56 (m, 22H, CH_2), 1.67-1.64 (m, 12H; -OCH_2CH_3), 0.93-0.90 (m, 3H, CH_3), MALDI-TOF-MS m/z 1320.91 ($[M+Na]^+$), calcd 1295.7.

Compound 3: ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm);δ 7.54 (m, 4H, Th-H), 7.35-7.30 (m, 6H, Ph-H), 6.94-6.83 (m, 6H, Ph-H), 4.12 (s, 2H, -CH_2OAr), 3.60-3.48(m,56H -CH_2O), 3.92-3.64 (m, 8H,OCH_2), 2.55-2.53 (m,3H-CH_2CHCH_2O-), 2.11-1.56 (m, 22H, CH_2), 1.67-1.64 (m, 12H; -OCH_2CH_3), 0.93-0.90 (m, 3H, CH_3), MALDI-TOF-MS m/z 1497.11 ($[M+Na]^+$), calcd 1471.9.

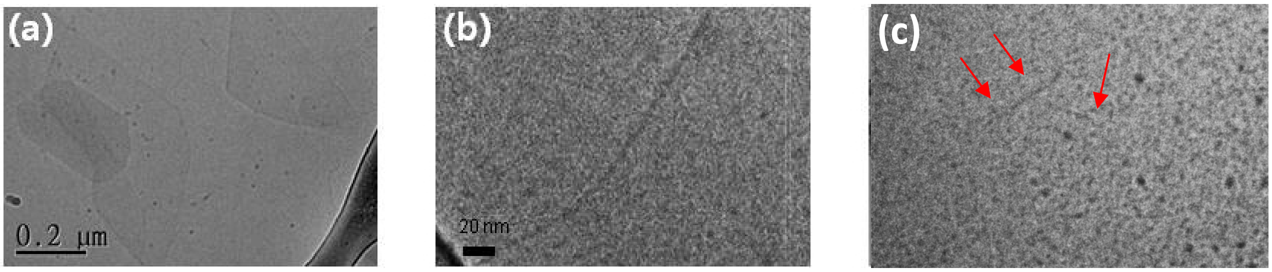


Fig. S1. Cryo-TEM images of (a) **1**, (b) **2**, and (c) **3**.

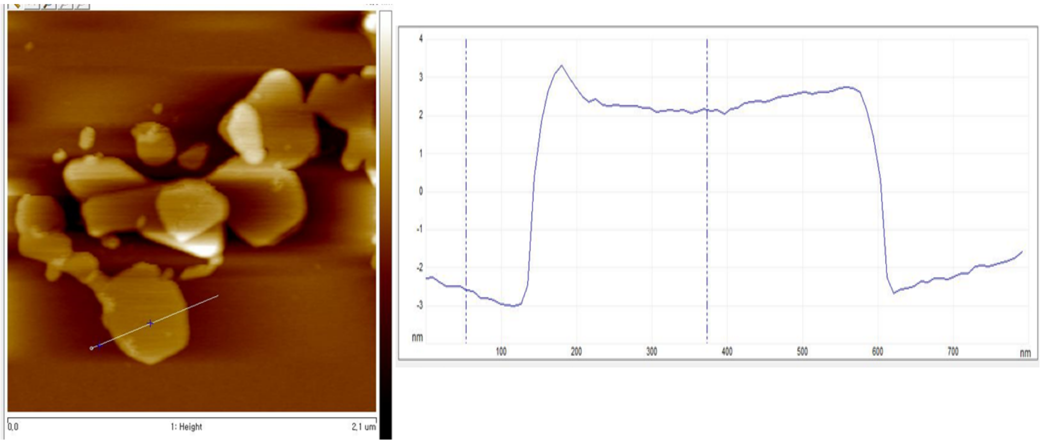


Fig. S2. AFM image of **1** on HOPG (highly ordered pyrolytic graphite).

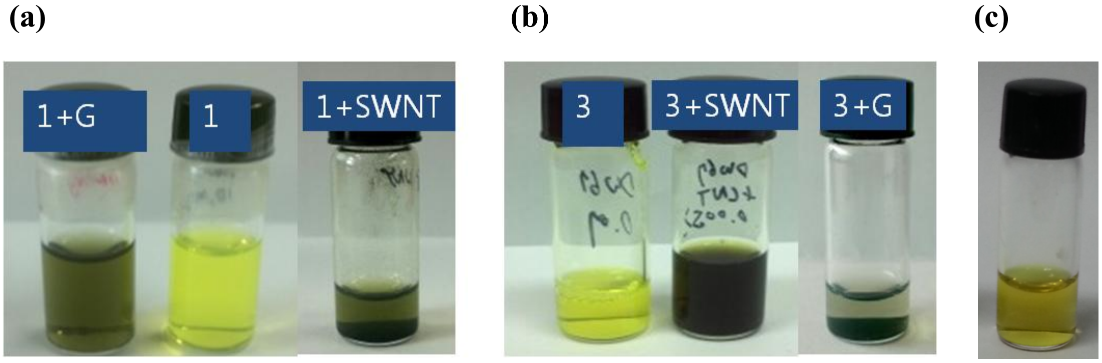


Fig. S3. Photographs of (a) **1** (0.05 wt%), **1** + G (after centrifugation) and **1** + SWNT (A clear solution was obtained after centrifugation, but SWNT was precipitated with time), (b) **3** (0.05 wt%), **3 +** SWNT (after centrifugation) and **3** + G (A clear solution was obtained after centrifugation, but graphite was precipitated with time), and (c) **1** (0.15 wt%) + G (after centrifugation) in aqueous solution. See page 2 of SI and the manuscript for details of the experimental conditions.

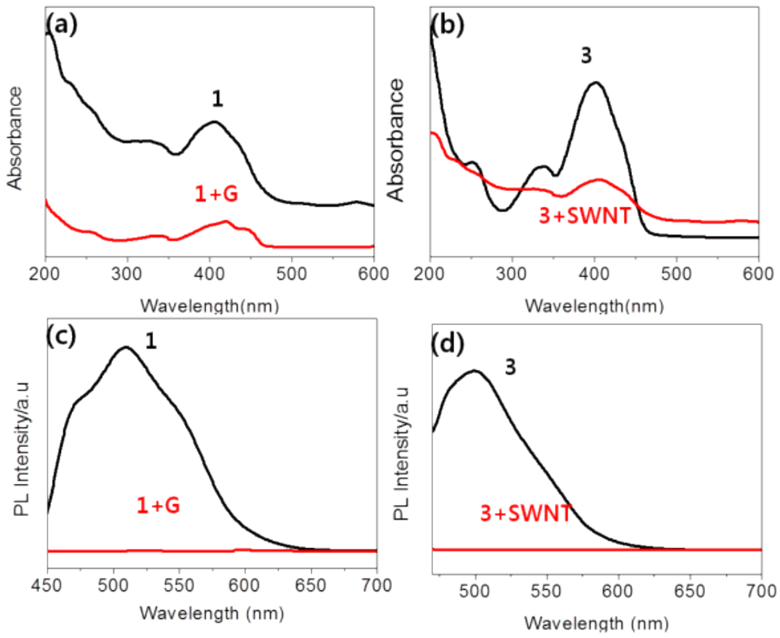


Fig. S4. Absorption spectra of (a) **1** and **1** + G, (b) **3** and **3** + SWNT, emission spectra of (c) **1** and **1** + G, (d) **3** and **3** + SWNT in 0.01 wt% (w/v) aqueous solution; $\lambda_{ex} = 400$ nm.

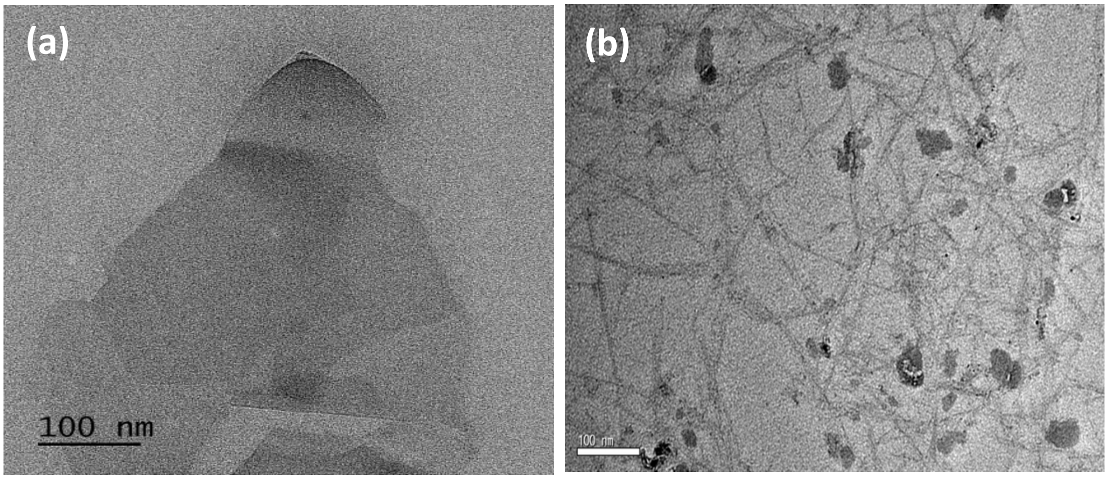


Fig. S5. TEM images (a) **1 +** G and (b) **3** + SWNT.

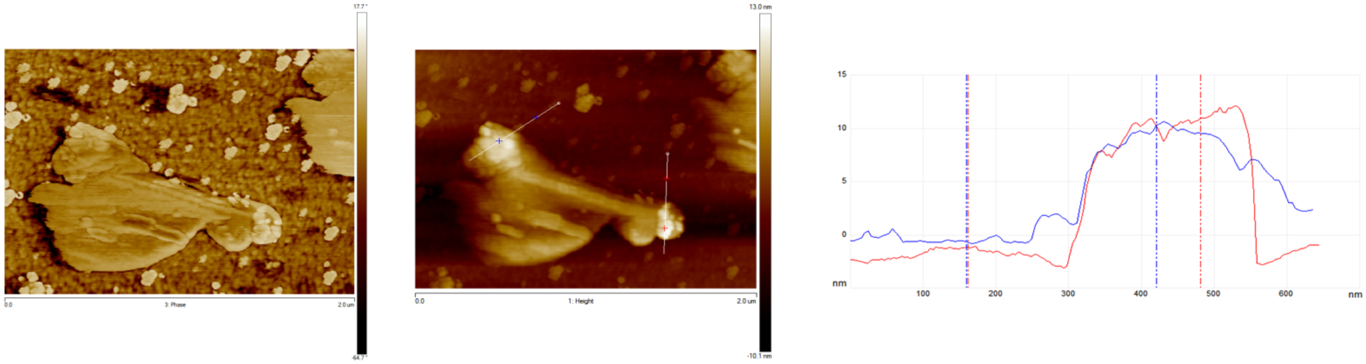


Fig. S6. AFM images and the section analysis of **1** + G.

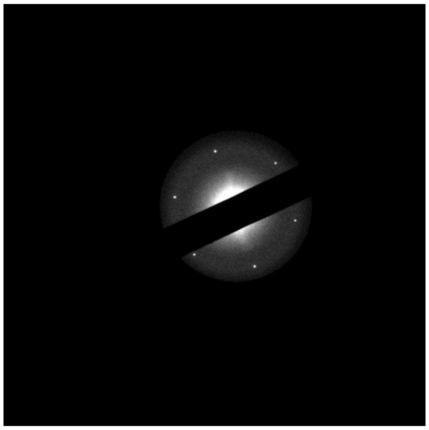


Fig. S7. Selected area electron diffraction (SAED) pattern of **1** + G.

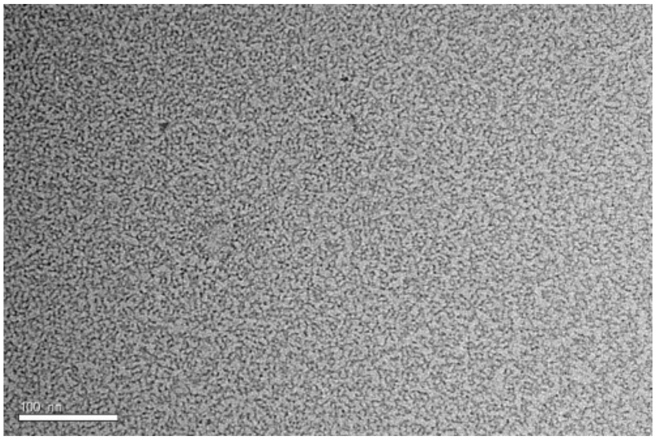


Fig. S8. TEM images of the high concentration of **1** (0.15 wt%).

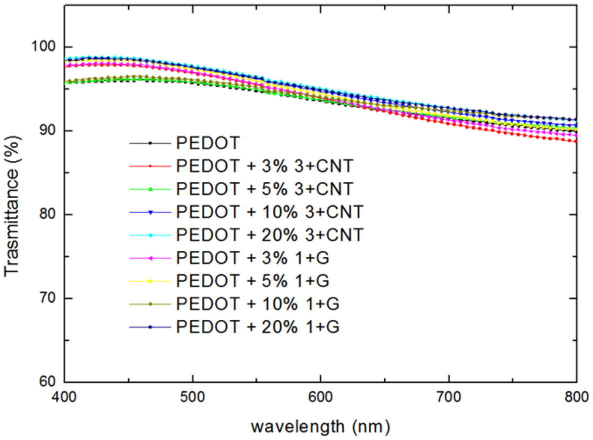


Fig. S9. Transmittance spectra of HTL

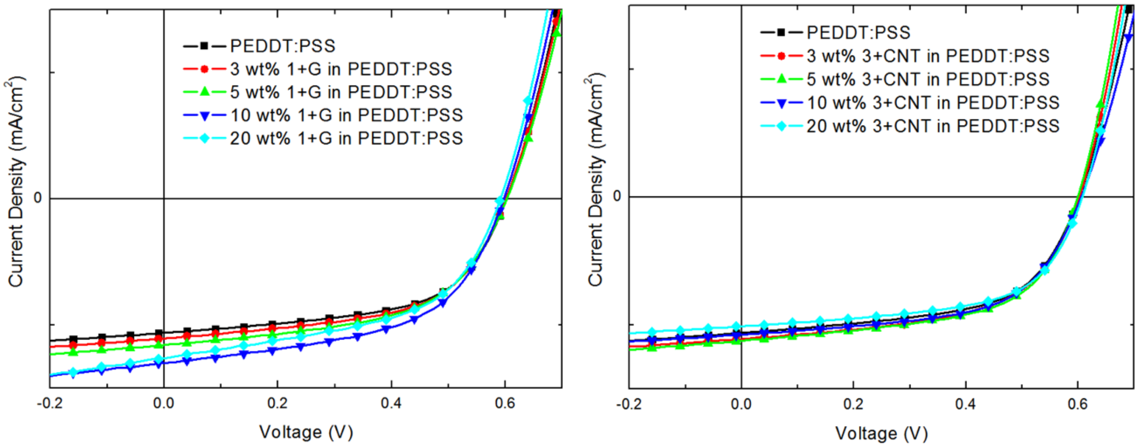


Fig. S10. I-V curve of photovoltaic cells

Table S1. Photovoltaic performance

Device	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
ref	10.49±0.47	0.60±0.01	0.58±0.01	3.63±0.17
3% 3+CNT	10.82±0.22	0.60±0.00	0.58±0.01	3.74±0.05
5% 3+CNT	11.01±0.42	0.60±0.01	0.58±0.01	3.77±0.08
10% 3+CNT	10.52±0.39	0.60±0.00	0.59±0.01	3.69±0.14
20% 3+CNT	10.07±0.66	0.60±0.00	0.59±0.01	3.55±0.20

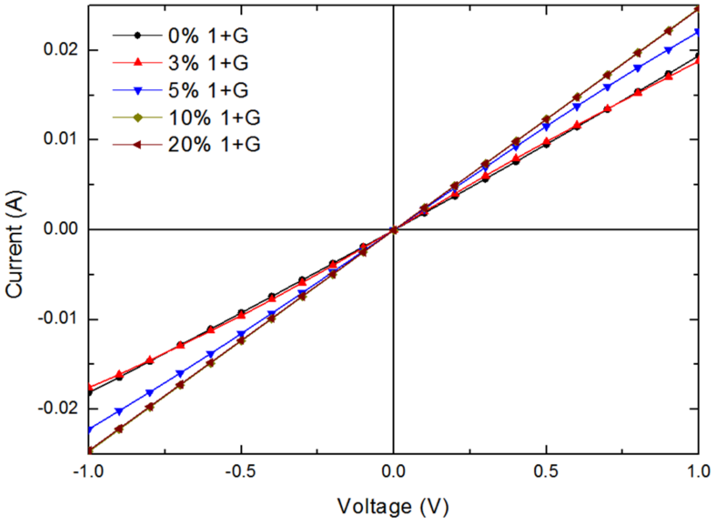


Fig. S11. I-V curve of devices (ITO/HTL/Al)

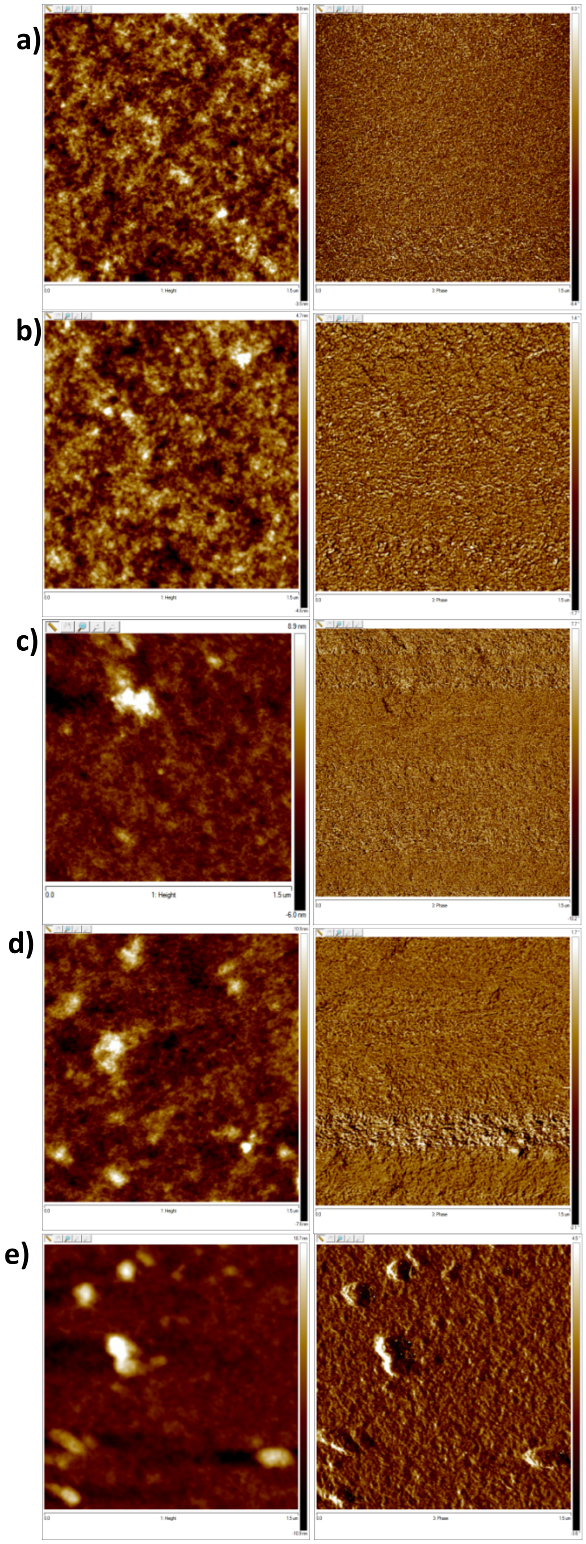


Fig. S12. AFM images of (a) 0 wt%, (b) 3 wt%, (c) 5 wt%, (d) 10 wt%, and (e) 20wt% **1** + G nanostructures with PEDOT:PSS on a glass (left; height image and right; phase image).

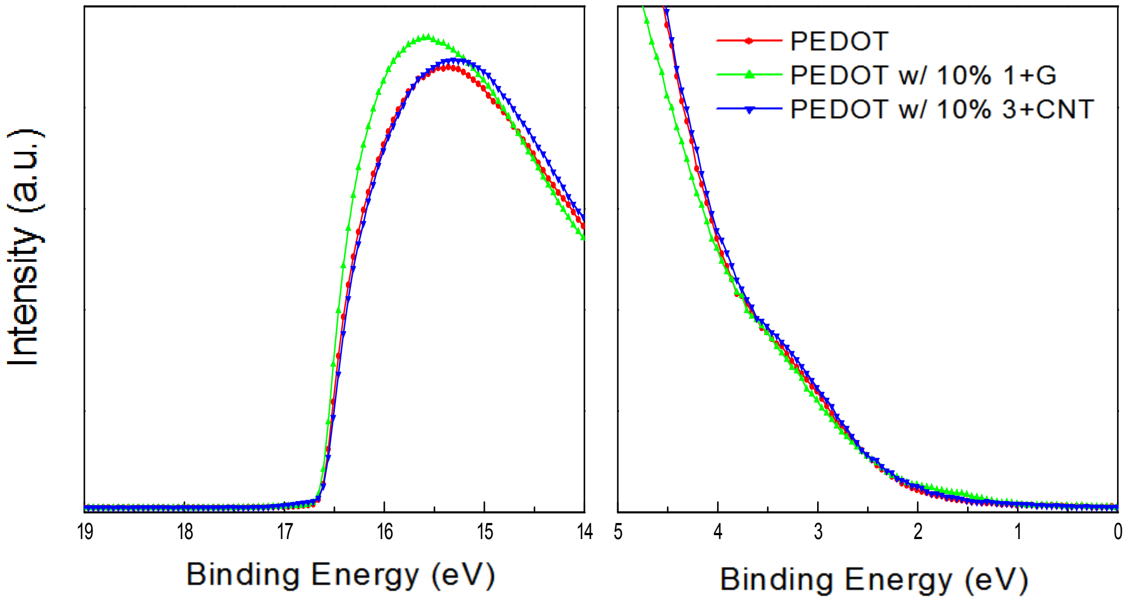


Fig. S13. UPS spectra

Reference

[1] Jayaraman, M.; Fréchet, J. M. J. *J. Am. Chem. Soc*. **1998**, *120*, 12996.