

Supporting Information

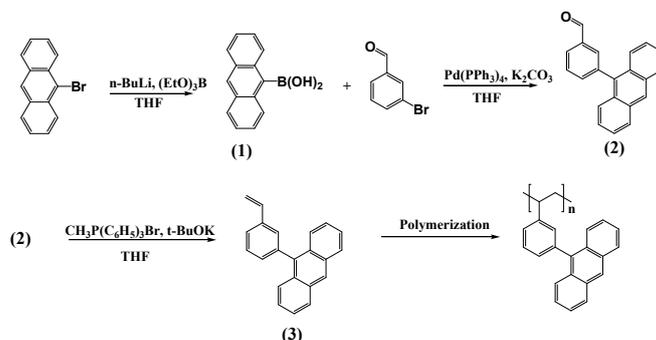
Novel Supercapacitor Materials Including OLED emitters

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Experimental section

1. Synthesis of PVPA

Scheme 1 shows the overall process of the synthesis of PVPA.



Scheme S1. Synthetic routes of PVPA.

1.1. Synthesis of anthracen-10-yl-10-boronic acid (1)

9-Bromoanthracene (10 g, 38.9 mmol) was dissolved in 500 mL of dry THF solution and stirred at $-78\text{ }^\circ\text{C}$. Then, 1.6 M $n\text{-BuLi}$ (29.3 mL, 46.7 mmol) was added and, 30 min later, triethyl borate (9.3 mL, 54.5 mmol) was added. After the reaction was finished, the solution was acidified with 2 N HCl solution and extracted with ethyl acetate and water. The organic layer was dried with anhydrous MgSO_4 and filtered. The solution was thermally evaporated under vacuum. The residue was then redissolved in hexane and added to ethyl acetate (50 mL). The resulting precipitate was filtered and washed with hexane to obtain a beige compound, **1** (7.3 g, 85%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ): 8.46 (s, 1H), 8.12 (d, 2H), 8.01 (d, 2H), 7.48 (m, 4H), 5.07 (s, 2H).

1.2. Synthesis of 3-(anthracen-10-yl)benzaldehyde (2)

In a 500 mL round-bottomed flask, 3-bromoaldehyde (3.15 mL, 27 mmol), compound **1** (7.2 g, 32 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (1.25 g, 1.1 mmol) were placed with anhydrous THF solvent. The mixture was heated to $80\text{ }^\circ\text{C}$ and

K_2CO_3 was added to the reaction flask. When the reaction was complete, the solution was extracted with toluene and water. Anhydrous $MgSO_4$ was then used to remove residual water from the mixture. The resulting mixture was subjected to column chromatography using a toluene:hexane (1:2 volume ratio) mixture as the eluant. The product was concentrated by reduced pressure and recrystallized with acetone to obtain a light yellow solid, compound **2** (3.8 g, 50%). 1H -NMR (300 MHz, THF) δ (ppm): 10.09 (s, 1H), 8.60(s, 1H), 8.11-8.07 (d, 3H), 7.96-7.95 (s, 1H), 7.83-7.78 (t, 1H), 7.73-7.69 (m, 1H), 7.57-7.54 (d, 2H), 7.48-7.43 (t, 2H), 7.37-7.34 (m, 2H)

1.3. Synthesis of 10-(3-vinylphenyl)anthracene (**3**)

Methyltriphenylphosphonium bromide (9.49 g, 27 mmol) and $KOC(CH_3)_3$ (3.18 g, 28 mmol) were dissolved in 200 mL of dry THF solution and stirred at 0 °C. Then, compound **2** (5 g, 17.7 mmol) was added. When the reaction was complete, the mixture was extracted with methylene chloride and water. Anhydrous $MgSO_4$ was then used to remove residual water from the mixture. The resulting mixture was subjected to column chromatography using a chloroform:hexane (1:10 volume ratio) mixture as the eluant. The product was concentrated under reduced pressure and reprecipitated with ethanol to obtain a yellow solid material, compound **3** (2.73 g, 55%). 1H -NMR (300 MHz, THF) δ (ppm): 8.54(s, 1H), 8.07-8.04 (d, 2H), 7.64-7.60 (m, 3H), 7.58-7.53 (t, 1H), 7.50 (s, 1H), 7.46-7.40 (t, 2H), 7.35-7.32 (m, 3H), 6.87-6.78 (d, 1H), 5.87-5.81 (dd, 1H), 5.27-5.23 (dd, 1H)

1.4. Synthesis of Poly(9-(3-vinyl-phenyl)-anthracene (PVPA)

In a 100 mL round-bottomed flask, compound **3** (monomer, 0.2 g, 0.7 mmol) and azobisisobutyronitrile (0.07 g, 0.42 mmol) were placed with 10 mL of anhydrous benzene solvent. After polymerization at 50 °C for 6 hours, PVPA polymer was precipitated from methanol solvent which is non-solvent to this polymer. The isolated polymers were dissolved in chloroform and precipitated in methanol (0.18 g, 90%). 1H -NMR (300 MHz, THF) δ (ppm): 7.61-6.81(broad peaks, aromatic rings), 1.48-1.04 (alkyl groups).

2. Characterization

1H -NMR spectra were recorded using a Bruker AM-300 spectrometer, and chemical shifts were recorded in units of ppm. UV-Vis spectra were recorded with an HP 8453 UV-VIS-NIR spectrometer. The molecular weight and polydispersity of the polymer in THF solution were determined by gel permeation chromatography (GPC) analysis following calibration using polystyrene standards. Thermal gravimetric analysis was carried out on a Perkin Elmer TGA/DSC 4000 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 10 °C/min. Photoluminescence (PL) spectra were recorded using dilute solutions (10^{-5} M) on a Perkin-Elmer LS-50 spectrometer. Solid state emission measurements were performed using films supported on a glass substrate and

mounted with front-face excitation at an angle of $<45^\circ$. The polymer film was prepared by spin casting a solution containing 1% polymer by weight in chlorobenzene. Uniform and pinhole free films with thicknesses of ~ 80 nm were easily obtained by this method. Morphological analyses were performed using a scanning electron microscope (SEM, Hitachi S-4800). The MWCNT or PVPA/MWCNT composite on an SUS substrate was used as the working electrode for electrochemical analysis. Cyclic voltammetry (CV) experiments (CHI 660D CH Instruments, USA) were conducted using three-electrode cells in a 1 M electrolyte solution. The reference electrode and the counter electrode were Ag/AgCl and platinum, respectively. CV curves were measured at various scan rates in the range of 20 mV/s to 200 mV/s. Impedance measurements were made with the above electrodes using an Autolab/FRA instrument in the frequency range of 100 kHz–0.01 Hz with an AC perturbation of 10 mV.

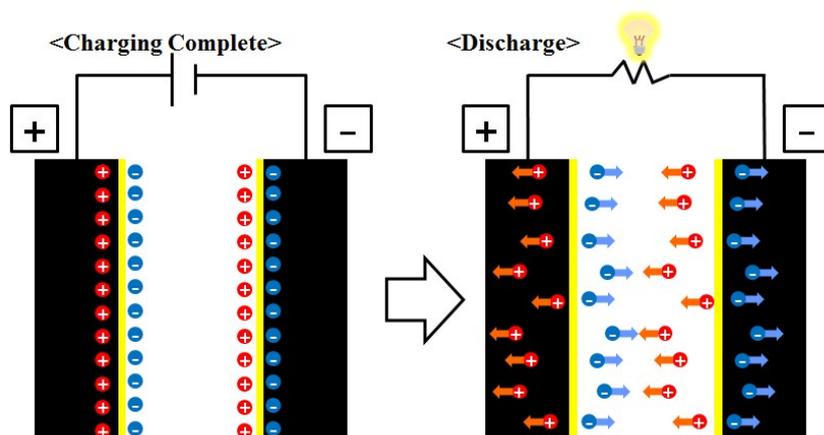


Fig. S1. Charge and discharge process of a supercapacitor cell under a voltage scan.

Table S1. Optical and electrical properties of the PVPA.

Compounds	Solution state ^a		Film state ^b		Mn ^c	Mw ^c	DP ^c	T _g ^d (°C)	T _d ^e (°C)
	UV _{max} (nm)	PL _{max} (nm)	UV _{max} (nm)	PL _{max} (nm)					
Polymer (PVPA)	351,368, 388	427	354,372,39 2	455	4000	21000	5.25	105	285

a: chloroform solution (1×10^{-5} M), b : spin coating film (1 wt%), c: determined by GPC eluted with THF, [d,e]: measured by DSC and TGA at a heating rate of 10 °C/min.

3. Preparation of MWCNT and PVPA/MWCNT films

The MWCNTs (95% purity) were purchased from Ijjin Nanotech, Korea. The diameter of these nanotubes was in the range of 15–20 nm. As shown in Fig. S2, the mixture of MWCNT and PVPA was prepared and was coated onto a clean SUS (steel use stainless) substrate by blade coating.

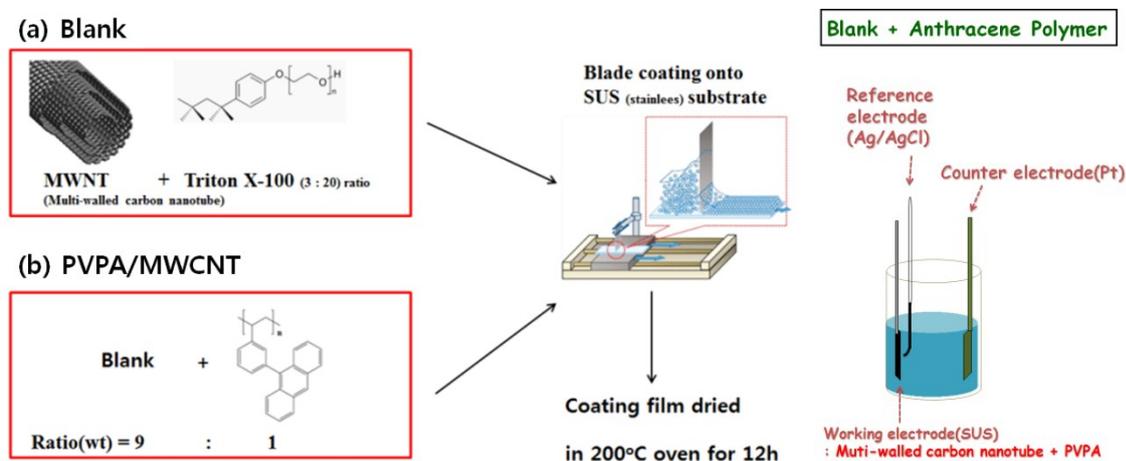


Fig. S2. Preparation of MWCNTs and the PVPA/MWCNT mixture (0.85 : 1 w/w) and coating method

3.1 Preparation of MWCNT film (blank)

MWCNTs were added to a mixed acid solution (HCl:HNO₃=3:1, v/v) and sonicated for 12 hours. The resulting mixture was washed with water, then filtered and dried for 12 hours to give activated MWCNTs. The activated MWCNTs were then stirred and mixed with Triton X-100 in a weight ratio of 3:20 to provide the electrode material. As shown in Scheme 2 (a), the activated MWCNT blank mixture was coated onto an SUS substrate by blade coating. This process was repeated 7 times to create a film of thickness ~100 μm. The blank film was dried at 200 °C for 12 hours. Triton X-100 was removed during this heating process. Sample on working electrode is 3.2 mg.

3.2. Preparation of PVPA/MWCNT film

MWCNTs were added to a mixed acid solution (HCl:HNO₃=3:1, vol%) and sonicated for 12 hours. The resulting mixture was washed with water, then filtered and dried for 12 hours to give activated MWCNTs. The activated MWCNTs were stirred and mixed with Triton X-100 in a weight ratio of 3:20. Then, as shown in Scheme 2(b), PVPA was mixed with the blank material at a weight ratio of 9:1. The PVPA/MWCNT mixture was then coated on an SUS substrate by blade coating. This process was repeated 7 times to create a film of thickness ~100 μm. The film was dried at 200 °C for 12 hours. Triton X-100 was removed during this heating process. The final weight

ratio of PVPA:MWCNT was 0.85:1. Sample on working electrode is 2.8 mg.

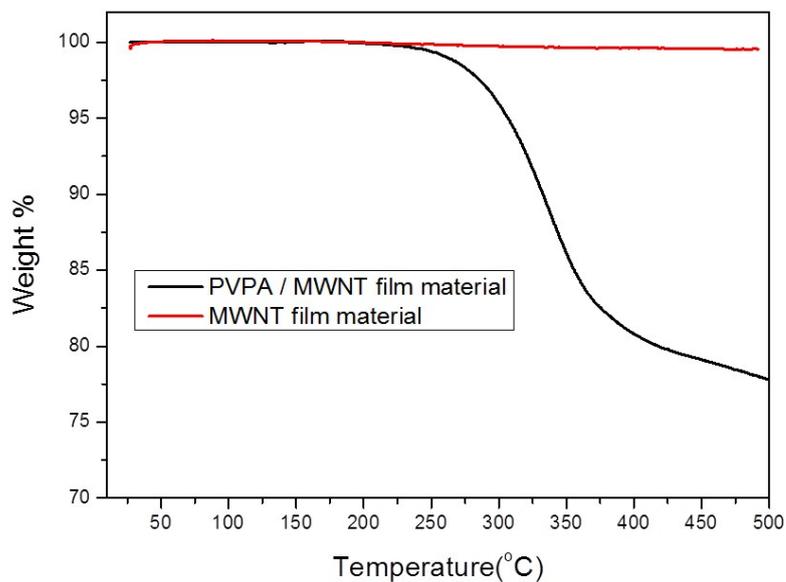


Fig. S3 Thermogravimetric analysis (TGA) data for the PVPA/MWCNT and MWNT. Conditions : N₂, 10°C/min, 30°C to 500 °C.

Table S2. Specific capacitance values of MWCNT and PVPA/MWCNT at scan rate of 20 mV/s in different electrolytes.

Sample	Electrolyte (1 M)	F/g (20 mV/s)
MWCNT	KCl	8.7
	NaCl	10.79
	KOH	7.85
	NaOH	11.07
PVPA/MWCNT	KCl	15.94
	NaCl	33.07
	KOH	10.24
	NaOH	12.51

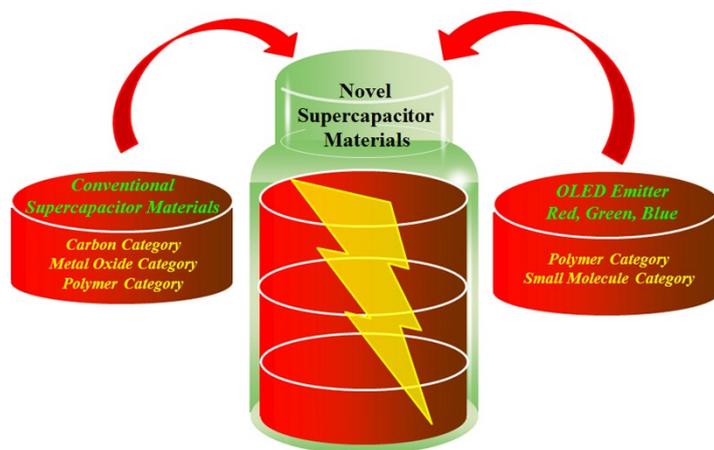


Fig. S4 Schematic diagram of the use of existing supercapacitor and OLED materials to generate novel supercapacitor materials.