Electronic Supplementary Information

1. Experimental

1.1 Chemicals and materials

All manipulations involving moisture- or air-sensitive chemicals were conducted using Schlenk techniques. The Pd-diimine catalyst, [1] 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA) [2] and 2-(methacryloyloxy)-ethyl ferrocenecarboxylate (FcEMA) [3] were synthesized according to the previously reported literature. Copper (I) bromide (CuBr, 98%), and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 98%) were purchased from J&K Scientific Ltd. Anisole (AR), diatomite (AR), petroleum ether (AR), methanol (AR), dichloromethane (CH_2Cl_2, AR), tetrahydrofuran (THF, AR) and chloroform ($CHCl_3$, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Multi-walled carbon nanotubes (MWCNTs, diameter=6-9 nm, length=5 μm, purity >95% carbon) were purchased from Sigma Aldrich. Polymerization-grade ethylene (99.99%) was further purified prior to use by passing through columns of pre-activated 4A- type molecular sieve and Ag molecular sieve. CuBr was purified according to the previously reported procedure. [4] CH_2Cl_2 was dried with activated 4A- type molecular sieve followed by distillation over calcium hydride prior to use. THF was dried with activated 4A- type molecular sieve followed by distillation over potassium prior to use. Other chemicals were used as received.

1.2 Synthesis of HBPE-Br

Hyper-branched polyethylene macro-initiator (HBPE-Br) was synthesized according to the previously reported literature. [5] The procedure was described as follow. A pre-dried 100 mL three necked flask was purged with ethylene (three times), then 40.0 mL fresh distilled CH_2Cl_2 was added by syringe. The flask was then pressurized with ethylene at 1.0 atm (25 ^{o}C). A certain amount of the freshly distilled BIEA was added into the flask. Pd-diimine (30.0 mg) catalyst was dissolved in 10 mL CH_2Cl_2, and the resultant solution was added into the flask immediately to initiate the polymerization. After 9 h, the polymerization was terminated by opening the flask to the air. The polymer was obtained after removal of the solvent by rotary evaporation at room temperature. Then the obtained polymer was redissolved in petroleum ether and passed through a diatomite column to remove the residual Pd-diimine catalyst. The eluent was collected and then precipitated in methanol after evaporating most the solvent. The obtained precipitate was further purified by three dissolution-precipitation cycles. The final precipitate was dried under vacuum at 35 °C for 48 h. Hyper-branched polyethylene (HBPE) was synthesized under the same conditions as HBPE-Br except no addition of BIEA. The polymerization conditions and GPC results of HBPE and HBPE-Br were summarized in Table S1.

1.3 Synthesis of HBPE-*g*-PFcEMA

HBPE-Br was then utilized as macro-initiator for the ATRP of FcEMA to synthesize HBPE-*g*-PFcEMA according to our previous reported procedure with minor modification [6]. The mole ratio of [monomer]:[CuBr]:[PMDETA]:[Br]=300:5:5:1, and the polymerization time was 2.0 h. The ^{1}H NMR data of HBPE-*g*-PFcMEA were summarized as follow: δ=4.83 ppm (*s*, 2H, Hd), 4.43 ppm (*s*, 4H, Hc), 4.36 ppm (*s*, 2H, He), 4. 21 ppm (*s*, 5H, Hf), δ=1.87 ppm (*br. s*, 2H, Ha), δ=1.26 ppm (methylene), δ=1.22 ppm (methine), δ=1.12, 1.00 ppm (*s*, 3H, Hb) and δ=0.88, 0.85 ppm (methyl).

1.4 Non-covalent dispersion of MWCNTs with HBPE-*g*-PFcEMA in $CHCl_3$

6.0 mg MWCNTs were dispersed employing a certain amount of HBPE-*g*-PFcEMA in 2.0 mL $CHCl_3$ by ultrasonication at 20 °C for 1.0 h. The resultant dispersion was then left undisturbed overnight. [7] The bundled MWCNTs were removed by filtration through glass wool (0.1 g) to obtain the stable MWCNTs/HBPE-*g*-PFcEMA dispersion, which was employed for further analysis. For TEM and SEM, 20.0 μL of the MWCNTs/HBPE-*g*-PFcEMA dispersion was dropped onto the copper grid and silica wafer respectively after proper dilution.

1.5 Obtaining the specific extinction coefficient of MWCNTs in $CHCl_3$ employing HBPE

In order to obtain the specific extinction coefficient of MWCNTs in $CHCl_3$, the MWCNTs (6.0 mg) were dispersed employing hyper-branched polyethylene (HBPE, 12.0 mg) according to the reported procedure [7]. Three samples for TGA measurements were prepared individually. Typically, the dispersion (0.6 mL in total) was put in TGA sample pan in batches after filtration through glass wool (0.1 g). The resultant sample was further dried under vacuum at 35 °C for 24h after evaporating the solvent at room temperature. Based on the TGA data (Figure S1a), the average weight of the MWCNTs in $CHCl_3$ was calculated according to formula 1. Then, the concentration of MWCNTs was calculated to be 320 mg/L. The MWCNTs/HBPE dispersion (320 mg/L) was then used to prepare a series of diluted solutions with different concentration of MWCNTs, and their UV-vis spectra were recorded (Figure S1b). Because HBPE have no absorbance at 600 nm, [5] thus, the absorbance of MWCNTs/HBPE dispersion at 600 nm was plotted against the concentration of MWCNTs to establish the standard curve of MWCNTs in $CHCl_3$. The specific extinction coefficient (0.09299 $L \cdot cm^{-1} \cdot mg^{-1}$) was obtained after linear fitting (Figure S1c).

$$\left\{ \begin{array}{l} m_3 = m_1 + m_2 \\ \\ m_3' = a \times m_1 + b \times m_2 \end{array} \right. \Rightarrow \quad m_1 = \frac{m_3' - b \times m_3}{a - b} \qquad m_2 = \frac{a \times m_3 - m_3'}{a - b} \qquad \cdots\cdots 1$$

m_1: the unknown initial weight of MWCNTs； m_2: the unknown initial weight of HBPE; m_3: the initial weight of WMCNTs/HBPE determined by TGA; m_3': the final weight of MWCNTs/HBPE at 600 ^oC determined by TGA; a: the weight percentage of MWCNTs at 600 ^oC determined by TGA; b: the weight percentage of HBPE at 600 ^oC determined by TGA.

1.6 Calculating the concentration of MWCNTs in the MWCNTs/HBPE-*g*-PFcEMA dispersion by UV-vis spectrum

The specific extinction coefficient obtained employing HBPE at 600 nm was applied to calculate the concentration of MWCNTs in the MWCNTs/HBPE-*g*-PFcEMA dispersion. Typically, 0.1 mL MWCNTs/HBPE-*g*-PFcEMA dispersion with different mass ratio of HBPE-*g*-PFcEMA/MWCNTs was diluted into 10.0 mL independently. Then, 2.0 mL of the diluted dispersions were taken for UV-vis spectrum test respectively. As HBPE-*g*-PFcEMA showed no absorbance at 600 nm (Fig. S1d), thus, the concentration of MWCNTs in $CHCl_3$ was calculated according to the absorbance of MWCNTs/HBPE-*g*-PFcEMA dispersion at 600 nm and the specific extinction coefficient (0.09299 $L \cdot cm^{-1} \cdot mg^{-1}$) obtained employing HBPE at 600 nm.

1.7 Study on the interactions between HBPE-*g*-PFcEMA and MWCNTs

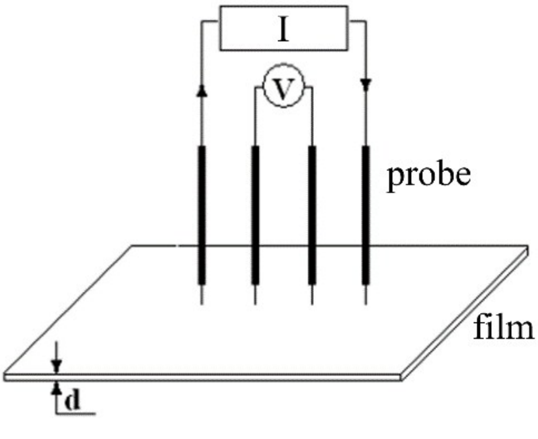
The interactions between HBPE-*g*-PFcEMA and MWCNTs were studied by UV-vis spectroscopy.[8, 9] Typically, the MWCNTs/HBPE-*g*-PFcEMA dispersion was prepared by mixing 2.5 mL of 40 μg/mL HBPE-*g*-PFcEMA/$CHCl_3$ solution with 2.5 mL of 20 μg/mL MWCNTs/ $CHCl_3$ dispersion, followed by ultra-sonication at 20 ^oC for 60 min. The resulting dispersion was diluted up to 10.0 mL for subsequent UV-vis analysis. Another HBPE-*g*-PFcEMA/$CHCl_3$ solution (10 μg/mL) and MWCNTs/ $CHCl_3$ (5 μg/mL) dispersion were prepared as a control sample. The UV-vis spectrum of HBPE-*g*-PFcEMA in the MWCNTs/HBPE-*g*-PFcEMA dispersion was corrected by subtracting the absorbance of the MWCNTs/$CHCl_3$ (5 μg/mL) dispersion [10]

1.8 Preparation of flexible conductive film

The conductive film was prepared by spin-coating of the MWCNTs/HBPE-*g*-PFcEMA dispersion (50 μL, MWCNTs/HBPE-*g*-PFcEMA=1:10 wt/wt) onto the PET substrate (length: 7 mm, width: 5 mm) at 150 r/min for 2.0 min. The resulting black film was dried at room temperature overnight, and then two piece of copper foils were pasted at the end of the conductive film for further analysis.

1.9 Characterization

^{1}H NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer using $CDCl_3$ as solvent. Gel permeation chromatography (GPC) results were obtained from Waters Wyatt GPC instrument using a light scattering (LS) detector. Thermo gravimetric analysis (TGA) was performed on TA-Q500 (Mettler-Toledo) at a heating rate of 10 ^oC/min in nitrogen atmosphere. UV-vis spectra were recorded on UNICO UV-3802. Scanning electron microscope (SEM) images were taken using Hitachi SU-8010 SEM. Transmission electron microscopy (TEM) images were taken using Hitachi HT-7700 TEM. The thickness of the blank PET film and the conductive film were measured by using TT240 eddy current thickness meter from three different places (ten times) respectively. The conductivity of the prepared film was measured in SB1002A/2 four-probe conductivity meter (Scheme S1) based on formula 2 obtained from the operation manual.



Scheme S1. Schematic model of four-probe conductivity meter.

$$\rho_F = \frac{\Pi}{\ln 2} \times \frac{V}{I} \times d \quad \cdots\cdots \quad 2$$

ρ_F: the specific resistance; *I*: the current applied in the four-probe conductivity meter; *V*: the voltage measured in the four-probe conductivity meter; *d*: the thickness of the conductive film and π: constant (3.14).

2. Tables

Table S1.Summary of the polymerization conditions and GPC results of HBPE and HBPE-Br[a].

Polymer	Pd catalyst	BIEA	T	t	Yield	BIEA[d]	Mn[b]	PDI[b]	BD[c, d]
	mg/mmol	M	°C	h	g	mol/%	kg/mol	1	%
HBPE	30.0/0.0424	--	25	9	2.2295	--	44.10	1.36	120
HBPE-Br	30.0/0.0424	0.3	25	9	0.8351	0.38	21.27	1.39	104

a) Solvent: CH_2Cl_2. Pressure of ethylene: 1.0 atm. b) Determined by GPC using a light scattering detector in THF. c) BD: Branching density and d) The contents of BIEA in HBPE-Br and the branching density of HBPE or HBPE-Br were determined using ^{1}H NMR.

3. Figures

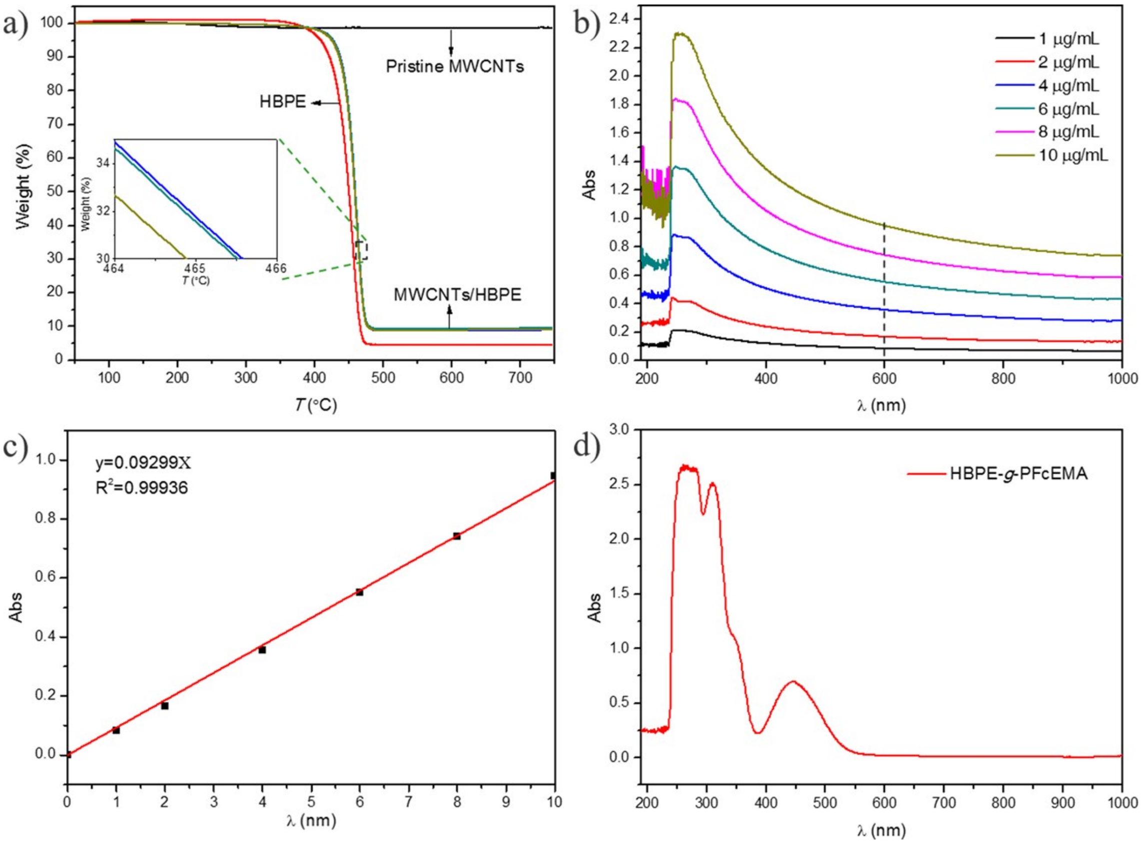


Figure S1. a) TGA curves of pristine MWCNTs, HBPE, and three MWCNTs/HBPE composites prepared from the same MWCNTs/HBPE dispersion with the mass ratio of HBPE/MWCNTs=2:1. The insert are the magnified TGA curves of the three MWCNTs/HBPE composites with temperature varied from 464 to 466 °C); b) UV-Vis spectra of MWCNTs with different concentration dispersed by HBPE (HBPE/MWCNTs=2:1 wt/wt); c) Linear fitting curve of the absorbance of MWCNTs in $CHCl_3$ at 600 nm against the concentration of MWCNTs and d) UV-Vis spectrum of HBPE-*g*-PFcEMA.

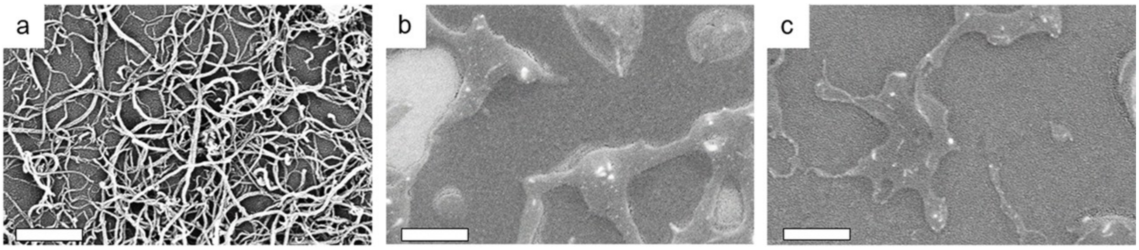


Figure S2. SEM images of pristine MWCNTs (a) and MWCNTs/HBPE-*g*-PFcEMA dispersion with different mass ratio of HBPE-*g*-PFcEMA/MWCNTs ((b) 0.5 and (c) 1.0. Scale bar: 1μm.

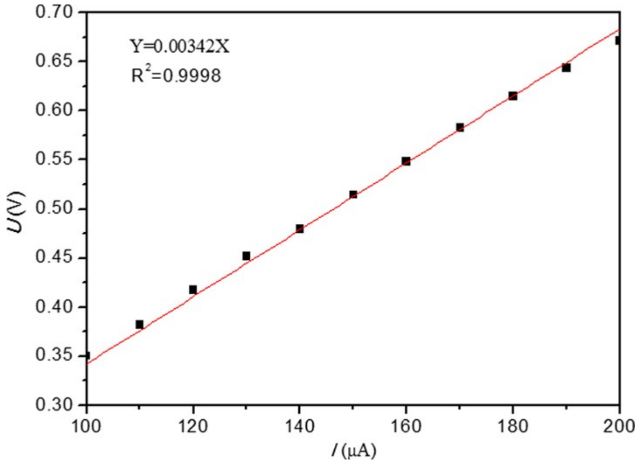


Figure S3. Linear fitting curve of the applied voltages against the current measured.

Reference:

1. L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414-6415.
2. K. Matyjaszewski, S. G. Gaynor, A. Kulfan and M. Podwika, *Macromolecules*, 1997, **30**, 5192-5194.
3. A. Xiao, *Zhejiang University Doctoral Dissertation*, 2009.
4. R. E. Rulke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. Vanleeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769-5778.
5. K. Zhang, J. Wang, R. Subramanian, Z. Ye, H. Lu and Q. Yu, *Macromol. Rapid Commun.*, 2007, **28**, 2185-2191.
6. Z. Deng, H. Yu, L. Wang, X. Zhai, Y. Chen and R. Sun, *J. Organomet. Chem.*, 2015, **799-800**, 273-280.
7. L. Xu, Z. Ye, Q. Cui and Z. Gu, *Macromol. Chem. Phys.*, 2009, **210**, 2194-2202.
8. Z. Deng, H. Yu, L. Wang and X. Zhai, *J. Organomet. Chem.*, 2015, **791**, 274-278.

9. X. Mao, G. C. Rutledge and T. A. Hatton, *Langmuir*, 2013, **29**, 9626-9634.

10. G. Diaz Costanzo, S. Ledesma, M. Mondragon and S. Goyanes, *J. Phys. Chem. C*, 2010, **114**, 14347-14352.