Supporting Information

Synthesis and Characterization of Poly(3-Hexylthiophene) –Functionalized Siloxane Nanoparticles

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Experimental Part

Materials. 2,5-dibromo-3-hexylthiophene, tert-butylmagnesiumchloride (1M in THF), 2-hydroxyethylacrylate, DMAP, DCC, chloroplatinic acid hexahydrate, n-butyllithium (1.6M in hexanes), and anhydrous tetrahydrofuran were obtained from Aldrich chemicals. Ammonium hydroxide (28%) was obtained from Fischer Scientific. Triethoxysilane, tetraethoxysilane, dichloro[bis(1,3-diphenylphosphino)propane] nickel(II) and 3-aminopropyltriethoxysilane were purchased from Alfar Aesar and used as received. Unless otherwise specified, all chemicals were used as received.

Characterization. Proton NMR spectra were recorded on a 500 MHz Jeol using $CDCl_3$, deutarated toluene and d_6-DMSO as solvents. FTIR spectra were measured using a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with a universal ATR sampling accessory. Elemental analysis was conducted at Advanced Materials Institute at Western Kentucky University. Transmission electron microscopy (TEM) observations were performed on a 100CX JEOL at 80 keV. Thermogravimetric analysis was performed at Thermal Analysis Laboratory at

Western Kentucky University. The samples were analyzed by a TA Q5000TGA. The samples were held isothermal at room temperature for 30 min and then heated from room temperature to 650 °C at 10 °C/min in nitrogen. The purge gas was heated at 10 °C/min to 800 °C. The photophysical properties in solution were performed on Fluorescence spectrometer (Perkin Elemr LS 55) and UV-visible spectrometer (Perkin Elemr, Lambda 35). Thin films were prepared by spin coating the blends onto cleaned glass coverslips. The 457 laser line from a Coherent Innova 200 Ar ion laser was used to excite the thin films with a typical excitation power of 100 μW. A Nikon TE2000U inverted microscope with a 100x 1.4 NA oil immersion objective was employed for laser excitation and also for collection of the emitted light. Spectra were dispersed using a Princeton Instruments 2150 spectrograph (150 grooves/mm grating) and detected using a Princeton Instruments ProEM EMCCD camera (1024 x 1024 pixels). To reduce filter effects on the resulting spectra, a mirror rather than a dichroic filter was employed for excitation of the sample and a long pass filter was employed in the collection of the emitted light.

General procedure for preparation of poly(3-hexyl thiophene), P3HT:

Anhydrous THF (20 mL) was injected into a 100 mL three-necked round bottom flask previously flushed with argon containing 2,5-dibromo-3-hexylthiophene (5.00g, 15.50 mmol). Slowly, t-BuMgCl (15.30 mL, 1.0M, 15.30 mmol) was added and the mixture was refluxed at 80°C for 2.0 hrs. The resulting yellow solution was then cooled to room temperature and Ni(dppp)Cl_2 (0.1085g, 0.20 mmol) was added at once. After 30 minute, one-half the portion of Ni(dppp)Cl_2 was added again. The mixture was stirred for another 30 minutes at room temperature and quenched with methanol (1 mL). The solution was poured into methanol (100 mL). The mixture was filtered and the solid was washed with hexane and dried to yield a black solid (2.54 g). ^{1}H-

NMR in $CDCl_3$ {δ, ppm}: 6.97 (s (br), 98H), 6.82 (s (br), 1H), 2.80 (s (br), 180H), 1.70-1.25 (m, 893H), 0.91 (s, 332H); Molecular weight (MW) of the polymer was determined by ^{1}H-NMR spectrum with respect to terminal hydrogen; MW = 12,500 g/mol.

Carboxylic acid terminated poly(3-hexylthiophene), 1: Anhydrous THF (30 mL) was injected into a 100 mL three-necked round bottom flask previously flushed with argon containing poly(3-methylthiophene) (0.800g, 0.11429 mmol). The solution is cooled to -78°C using a dry ice/ethanol bath. The n-BuLi solution (1.6M, 0.071 mL, 0.11429 mmol) was added drop wise and the solution was stirred for 2.0 hrs. The solution was then warmed to room temperature and compressed carbon dioxide gas was bubbled slowly over 20 min. After 30 minute stirring, an portion of carbon dioxide was bubbled in to the flask and continue stirring another 30 min. The solution was quenched with de-ionized water (1 mL) and the solution was then poured into ice water (100 mL) and acidified with hydrochloric acid (15%) until pH was about 2. The mixture was filtered and the solid was washed with hexane and dried to yield a black solid (0.470g, Yield = 59.0%). ^{1}H-NMR in $CDCl_3$ {δ, ppm}: 6.97 (s, 97H), 6.82(s (weak), 1H, terminal H), 2.80 (s (br), 180H), 1.77-1.34 (m, 900H), 0.91 (s, 323H); FT-IR stretchings (cm^{-1}): 3354-3000 (-OH from carboxylic acid), 2921- 2854 (alkyl C-H), 1694 (carbonyl, weak), 1604-1509 (aromatic C-C), 1449 and 819 (S-C).

Carboxyethylacrylate chain end-functionalized P3HT, 2:

Anhydrous THF (30 mL), carboxylic acid-terminated P3HT, **1** (1.500g, 1.130 mmol), 2-hydroxyethyl acrylate (0.176 mL, 1.533 mmol), DCC (0.345g, 1.673 mmol), and catalytic amount of DMAP (0.020g) were combined in a 100 mL single-necked round bottom flask and stirred for 16 hrs at room temperature. The resulting solution was concentrated in vacuum. The solid was washed with hexane and filtered to yield a black solid (1.400g, Yield = 87.6%). ^{1}H-NMR in $CDCl_3$ {δ, ppm}: 7.29 (s, (weak, br), 1H), 6.98 (s, 105H), 6.95 (s, br, 1H), 6.82(s (weak), 1H, terminal H), 6.44-6.41 (d, 1H), 6.16-6.12 (dd, 1H), 5.84-5.83 (d, 1H), 4.27-4.26 (t, 4H), 3.64-3.56 (m, 4H), 2.80 (s (br), 211H), 1.69-1.33 (m, 1000H), 0.94 (s, 381H); FT-IR stretchings (cm^{-1}): 2914- 2848 (alkyl C-H), 1610 (carbonyl, weak), 1507 (C=C), 1450 (aromatic C-C), 1373 and 803 (S-C).

Poly(3-hexyl thiophene) carboxy triethoxysilane, (P3HT-acrylate silane precursor), 3:

Anhydrous THF (30 mL) was injected into a flask previously flushed with argon containing compound **2** (1.200g, 0.084 mmol). Slowly, triethoxysilane (0.170 mL, 0.934 mmol) was added dropwise. A separately made dry 0.02 M solution of chloroplatinic acid (0.103g, 0.199 mmol) in anhydrous ethanol (10 mL) was slowly added to the reaction mixture. The reaction stirred for 16 hrs at room temperature under inert gas atmosphere and was concentrated in vacuum to half volume. The solution was diluted with THF (~ 5-10 mL) and added dropwise into hexane. The resulting suspension was centrifuged and the crude product was collected to yield a purple-black solid (1.020 g, Yield = 75.7%). The trace amount of unreacted P3HT-acrylate was present and hydrosilylation was performed without further purification. ^{1}H-NMR in $CDCl_3$ {δ, ppm}: 7.29 (s, (weak, br), 1H), 6.97 (s, 105H), 6.95 (s, br, 1H), 6.82(s (weak), 1H, terminal H), 4.25-4.24 (t, 4H), 3.64 (s, weak, 3H), 2.80 (s (br), 188H), 1.80-1.34 (m, 997H), 0.91 (s, 331H); FT-IR stretchings (cm^{-1}): 3368 (OH from trace amount of methanol wash), 2918- 2851 (alkyl C-H), 1700 (weak, carbonyls), 1551 (trace of C=C stretching from unreacted P3HT-acrylate), 1502-1438 (aromatic C-C), 1365 and 905 (S-C), 1295 (Si-C), 1130 (Si-O-) and 813.

General procedure for the preparation of P3HT-Acrylate-SSQ nanoparticles: Anhydrous ethanol (200 proof, 15 mL) and ammonium hydroxide (28%, 30 mL) was added at once into a one-necked round bottom flask containing chloroform (45 mL). Then tetraethoxysilane (0.0126g, 0.06 mmol) was added into the flask at once. The flask was capped and a ventilation needle was added through the septa. Two phases appeared in the reaction flask, which was vigorously stirred until the lower phase became a milky, white color. A previously mixed (by sonication) solution of P3HT-acylate silane (0.050 g, 0.0315 mmol) in chloroform (15 mL) was added at once into the reaction flask. The lower phase became purple while the upper phase remained mostly clear. As reaction time progressed, the upper phase began to become purple until there was a homogenous purple color throughout the solution. The reaction was continued for 24 hrs. The two layers (chloroform layer and ethanol layer) were separated via a separatory funnel and the chloroform layer was centrifuged to yield a purple solid. The procedure resulted in 60 nm average size particles confirmed by TEM. FT-IR stretchings (cm^{-1}): 3243 (OH from hydrolyzed silanol groups), 2912- 2842 (alkyl C-H), 1624 (ester carbonyl from acrylate), 1510-1449 (aromatic C-C), 1377 and 806 (Si-C), 1040 (Si-O-Si).

All reagent quantities and reaction times were varied from trial to trial according to the table S1.

Device preparation and characterization: Model bulk heterojunction solar cell devices were prepared on glass/ITO substrates. The substrates were subsequently cleaned in 2- propanol and acetone in ultrasonic bath for 10 minutes each and a thin layer of PEDOT:PSS (purchased from Aldrich) with a thickness of ~70-80 nm was spin coated as a hole transporting layer on top of ITO under nitrogen atmosphere. The substrates were heated at 100°C in a vacuum oven for an hour. As a first step, the active layer of P3HT-NPs: PCBM (purchase from Aldrich) with two different ratios (1:1 and 1:2) dissolved in chlorobenzene (8 mg/mL concentration of each compound for the 1:1 blend) was spin coated at a rotational speed of 1000rpm to give a film thickness of 80-100 nm. The casting of the active layer on the substrate was carried out inside a glove box under nitrogen atmosphere. The substrates were transported into e-beam evaporator and a layer of LiF (~2-5 nm) and Al (~200 nm) was evaporated on top of the active layer with a diameter of 2 x 6 mm of coating area through a mask. The final devices were annealed inside the glove box at different temperatures for ten minutes followed by transferred to a glass chamber under stream of nitrogen gas and sealed the chamber for device characterization. The testing of the devices was performed using a solar simulator with an emission spectrum close to AM 1.5G and intensity of 100 mW/cm^2. The IV curves of the devices were measured using a Keithley 2400 source meter controlled by a PC. The fill factor (FF) and power conversion efficiency (PCE) were calculated manually using following two equations.

$FF = J_m . V_m / J_{SC} . V_{OC}$; $\mathrm{PCE} = J_{SC} . V_{OC} . FF / \mathrm{P_s}$

Table S1: Reagent quantities and reaction times for the synthesis of P3HT-Acrylate-SSQ nanoparticles (in THF: EtOH).

P3HT-SSQ NPs	TEOS (mmol)	NH_4OH (mmol)	Silane:TEOS (mole ratio)	%Weight Loss from TGA	% Yield	Avg. size (nm)
1	0.0214	16	1 : 0.40	54	81	50±20
2	0.0112	16	1 : 0.21	80	50	60±10
3	0.0214	8	1 : 0.40	58	64	400±20
4	0.0101	8	1 : 0.32	70	58	100±20

*P3HT-silane mmoles used for each run is 5.35×10^{-2} mmol.

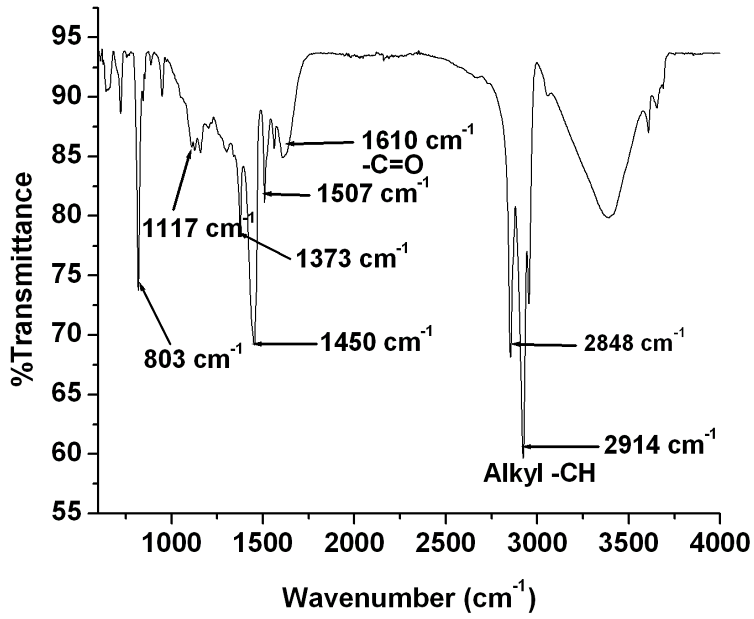

Figure S2: FT-IR spectrum of carboxyethylacrylate chain end-functionalized P3HT.

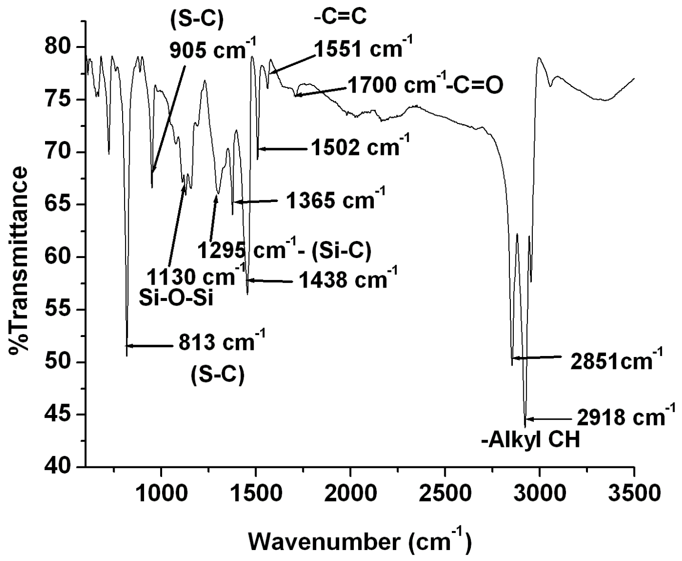

Figure S3: FT-IR spectrum of P3HT-acrylate silane.

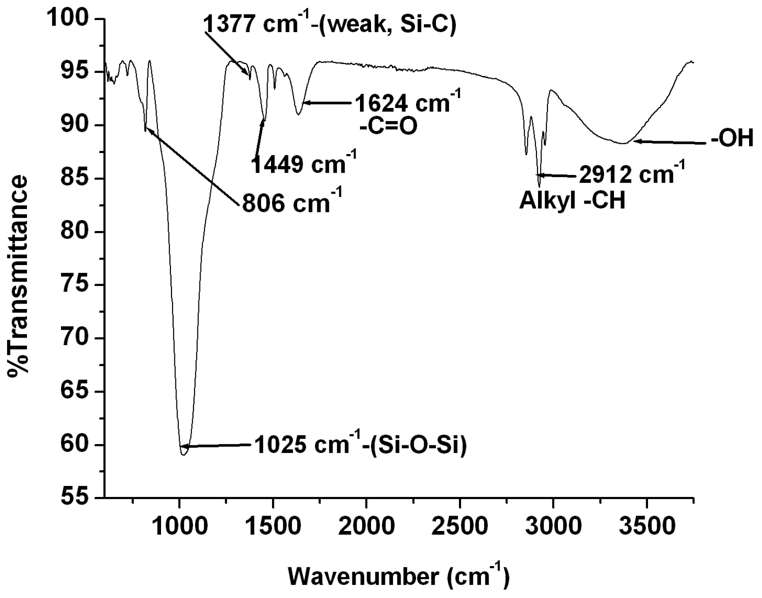

Figure S4: FT-IR spectrum of P3HT-NPs

TGA Graph

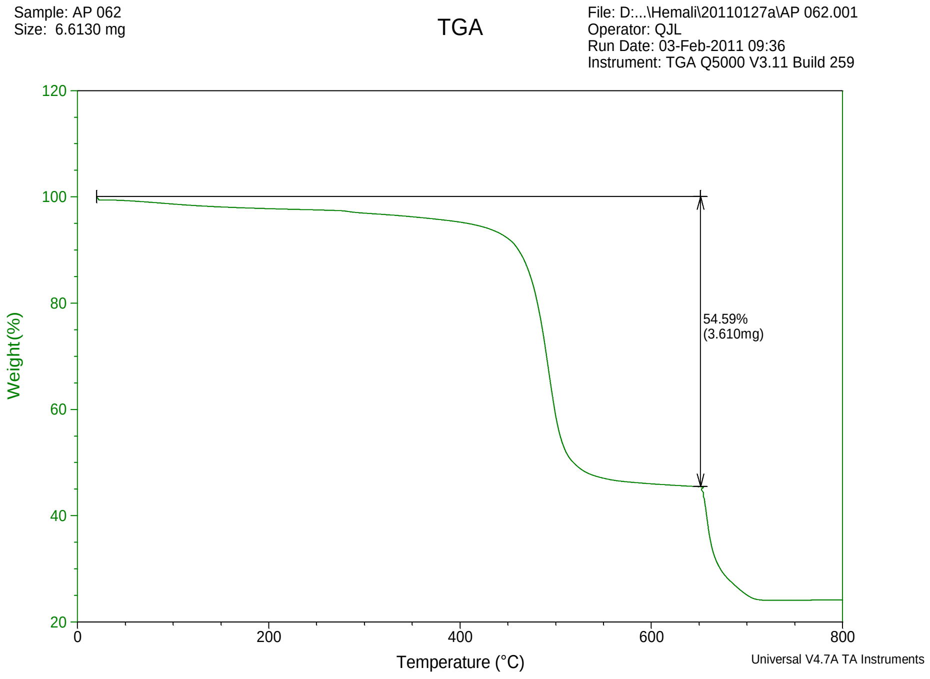

Figure S5: TGA curve of P3HT-NPs for Sample 1 in Table 1

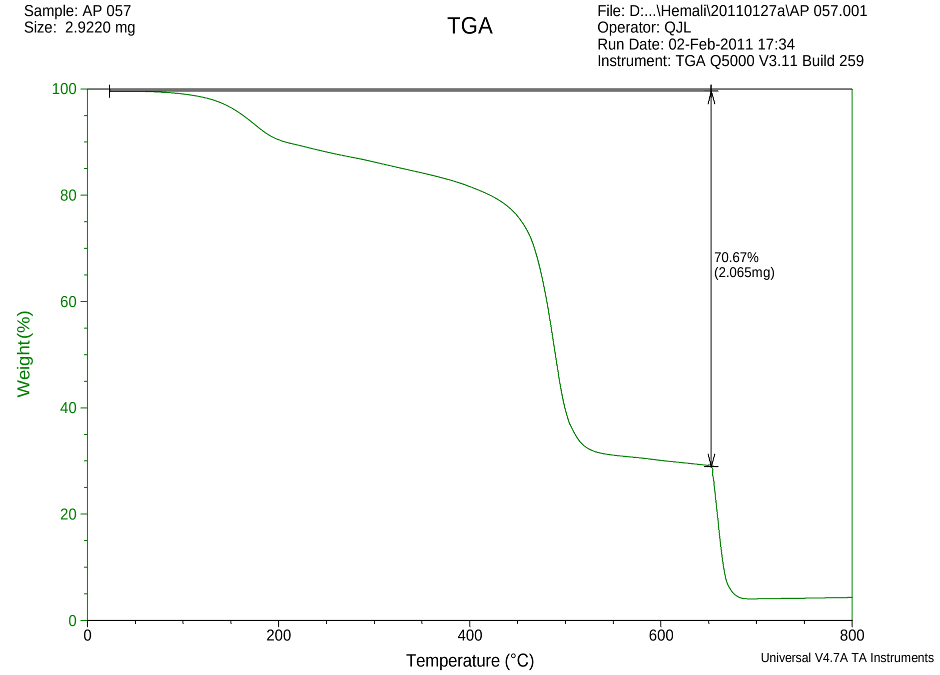

Figure S6: TGA curve of P3HT-NPs for Sample 4 in Table 1

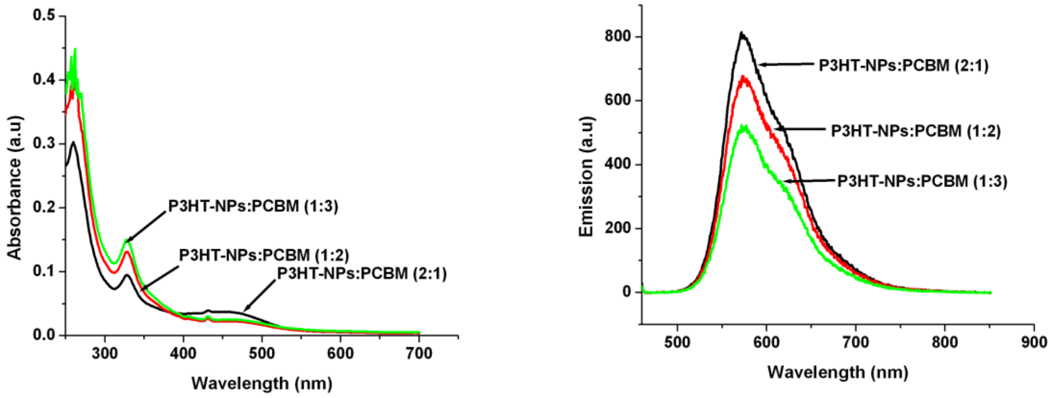

Figure S7: UV-visible absorption (left) and Fluorescence emission (right) spectra of P3HT-NPs/PCBM blends in chloroform solution.