Surface Initiated Polymerization of A-A/B-B Type Conjugated Monomers by Palladium Catalyzed Stille Polycondensation: Towards Low Band-Gap Polymer Brushes.

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EXPERIMENTAL

Materials.

All reactions were performed under pre-dried nitrogen using flame-dried glassware and conventional Schlenk techniques. Syringes used to transfer reagents or solvents were purged with nitrogen prior to use. Chemicals and reagents were used as received from Aldrich (France) and ABCR (Germany) and stored in the glove box. Solvents (Baker, France) were used as received; THF was distilled over sodium and benzophenone under nitrogen.

Instrumentations.

¹*H* Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker 400MHz instrument in $CDCl_3$ at ambient temperature.

Gel Permeation Chromatography (GPC) was performed using a bank of 4 columns (Shodex KF801, 802.5, 804 and 806) each 300 mm x 8 mm at 30 °C with THF eluent at a flow rate of 1.0 ml min⁻¹ controlled by a Malvern pump (Viskotek, VE1122) and connected to Malvern VE3580 refractive index (RI) and Malvern VE3210 UV-visible detectors. Calibration was against polystyrene standards.

Thermal gravimetric analysis (TGA) was performed on a TGA Q50, TA Instruments at a heating rate of 10 °C min⁻¹ under nitrogen. *UV-visible absorption spectra* were recorded on a Shimadzu UV-2450PC spectrophotometer.

Transmission Electronic Microscopy (TEM). Analysis of the core@shell nanoparticles shape and the thickness of the P3HT monolayer were obtained by TEM with a JEOL JEM-2100 FX transmission electron microscope, using an accelerating voltage of 200 kV at room temperature.

Synthetic procedures:

• Synthesis of ZnO nanorods. ZnO nanoparticles were prepared according to a published method.^{1,2} Zinc acetate (99.99%) potassium hydroxide (99.99%, 15% water) and methanol (anhydrous, 99.8%) were purchased from Sigma/Aldrich and used as-received without further purification. All the glassware was washed with a concentrated solution of sodium hydroxide and rinsed with deionized water prior to use. In a typical synthesis potassium hydroxide (0.047 mol in 88.75 mL of methanol) and zinc acetate (0,017 mol in 162.18 mL of methanol and 965 μ L of deionized water) solutions were prepared separately by sonication at room temperature until complete dissolution. Both solutions were transparent and colorless. Zinc acetate solution was heated in a glass flask to 60 °C under nitrogen atmosphere and potassium hydroxide solution was then added drop wise under magnetic stirring. The solution rapidly became white and turned to transparent again with further addition of potassium hydroxide. After a few hours aging at 60 °C the solution finally became white indicating formation of 4-5nm ZnO nanoparticles. The solution was condensed and

heated under magnetic stirring at 60°C for 24 h giving the nanorods. Finally as-obtained ZnO nanorods were washed for several times with methanol by decantation.

• Synthesis of [2-(4-bromo-phenyl)-ethyl)]-triethoxysilane

Scheme SI1



In a flame-dried 20 ml round bottom flask, 2.8 g (15.3 mmol, 1 eq) of 4-bromostyrene was charged with 14 mg of chloroplatinic acid (H₂PtCl₆ catalyst, 0.027 mmol, 0.003 eq) and 2 ml of absolute ethanol. Under stirring, 7 g of triethoxysilane (42.6 mmol, 4 eq) was added dropwise. The mixture was stirred at 70 °C for 5h. Finally, the product was purified by vacuum distillation. The resulting product (yield= 80%) was a mixture of Markonikov (17%) and anti-Markovnikov adducts (83%).



Figure SI1.¹H NMR of [2-(4-bromo-phenyl)-ethyl)]-triethoxysiliane (CDCl₃)

¹H NMR (400 MHz, CDCl₃) of the major adduct, δ (ppm): 7.4 (d, 2H), 7.1 (d, 2H), 3.9-3.83 (q, 6H), 2.74-2.7 (m, 2H), 1.22 (t, 9H), 0.99-0.96 (m, 2H). ¹H NMR (400 MHz, CDCl₃) of the minor adduct, 7.39 (d, 2H), 7.08 (d, 2H), 3.77-3.75 (q, 6H), 2.66-2.63 (m, 2H), 1.4 (d, 3H), 1.16 (t, 9H).¹³C NMR (CDCl₃, 100MHz) of major adduct , δ (ppm): δ 143.56, 129.8, 129.3, 119.3, 58.34, 28.7, 18.4, 12.47. ¹³C NMR (CDCl₃, 100MHz) of minor adduct, δ 143.1, 131.17, 129.6, 118.4, 59.16, 25.76, 18.25, 15.4.

• Synthesis of 4,4'-Bis (2-ethyl-hexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole





To a solution of 4,4'-Bis(2-ethyl-hexyl)- 5,5'-dibromo-dithieno[3,2- b:2',3'-d]silole (1.2 g, 2.51 mmol) in anhydrous THF (8 ml), a 2.5 M solution of n-butyllithium in hexane (4 ml, 10 mmol) was added slowly at -78°C under nitrogen. The reaction proceeded for 2h at -78°C before adding trimethyltinchloride (16 ml, 16 mmol) in one portion. After removing the cooling bath, the mixture was left at ambient temperature while stirring for overnight. Then, the mixture was poured into 50 ml of deionized (DI) water and extracted by 60 ml of diethyl ether. The organic layer was washed with DI water (5 × 20 ml), dried over anhydrous Na₂SO₄, filtered and the solvent was removed by rotary evaporation. The crude product was placed under high vacuum for 72 hours yielding a yellow-brown viscous oil (yield = 96%) which was used in the next step without any further purification.



Figure SI2. ¹H NMR of 4,4'-Bis (2-ethyl-hexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole

¹H NMR (CDCl₃, 400MHz), δ (ppm): δ 7.03(s, 2H), 1.68(m, 2H), 1.4-1.13(m, 16H), 0.90(t, 6H), 0.83(t,6H), 0.74(m, 4H).¹³C NMR (CDCl₃, 100MHz), δ (ppm): δ 154.66, 143.89, 137.91, 137.42, 35.91, 35.61, 28.97, 28.89, 23.05, 17.83, 14.20, 10.85, -8.18.

• Synthesis of 4,7-dibromo-2,1,3-benzothiadiazole monomer (M2) has been done following procedure reported in the literature (Neto BAD, Lopes AS, Wust M, Costa VEU, Ebeling G, Dupont J. Tetrahedron Lett 2005;46:6843-6.) Scheme SI3





Figure SI3. ¹H NMR of 4,7-dibromo-2,1,3-benzothiadiazole ¹H NMR (CDCl₃, 400MHz), δ (ppm): δ 7.67(s, 2H),



• UV-Visible Absorbance spectra of PSBTBT

Figure SI4: UV-visible absorption spectra of PSBTBT in chloroform solution and in thin film. λ onset was calculated to be 816 nm corresponding to an optical bandgap of 1.52 eV.

• Surface functionalization of Zinc Oxide Nanorods by [2-(4-bromo-phenyl)-ethyl)]triethoxysilane. (ZnO-PhBr)

Zinc oxide nanorods ZnO NRs with an average specific surface area of 24 m²/g were dried at 110 °C in an oven for 24 h to remove adsorbed water. Then in a 10 ml flamed-dried round flask bottom the nanoparticles were dispersed in 4 ml of anhydrous toluene using an ultrasonication bath for 1h. After complete dispersion of the nanoparticles 200 mg (0.57 mmol) of [2-(4-bromo-phenyl)-ethyl)]-triethoxysilane was added to the mixture and refluxed for 24 h at 120 °C. The modified nanoparticles were purified by several dispersions and centrifugations in toluene. The nanoparticles were stored in the glovebox after drying the solvent under reduced pressure.

• Preparation of the initiating sites on ZnO nanorods. (ZnO-C₆H₄-Pd₂(dba)₂-Br)

In glovebox, 10 mL high pressure tube equipped with a sealed septum was charged with a magnetic stirrer, 100 mg of the modified ZnO NRs, 2 ml of anhydrous THF and 10 mg (0.011 mmol) of $(Pd_2(dba)_3)$. The mixture was heated at 50 °C for 6 h. The nanoparticles were cleaned by several centrifugations in chlorobenzene and in anhydrous THF. The desired product was dried under reduced pressure and stored in the glovebox to be used directly.

• Polycondensation reaction from the Zinc oxide Nanorods: grafting Low Band Gap (PSBTBT)

In a 10 mL high pressure tube equipped with a sealed septum, 100 mg of $(ZnO-C_6H_4-Pd_2(dba)_3-Br$, 59.2 mg 4,7-dibromo-2,1,3-benzothiadiazole (BT) (0.2 mmol), 150 mg 4,4'-Bis (2-ethyl-hexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole (DTSSn) (0.2 mmol), 6.135 mg tri(o-tolyl)phosphine (0.1eq) were added and dissolved in 2 ml of anhydrous chlorobenzene solution in the glovebox. The mixture was sonicated for 1 h to disperse completely the nanoparticles. Then the tube was subjected to heating at 150 °C for 2 h. After cooling down the mixture, the particles were cleaned by several centrifugations in chloroform then dried and stored in the glovebox. The number average molar mass *Mn* of the free polymer chain was 3600 g.mol⁻¹ with D = 1.2.



Figure SI5. a) Brown solution at the beginning of the reaction b) dark-blue color solution indicates the synthesis of polymer c) clear supernatant solution after several centrifugations and precipitation of the grafted particles.

Under the same experimental conditions we repeated this experiment with an increase of the reaction time to 4 h and 6 h. The increase in molar mass was clearly seen by a colour change of the mixture to greenish and an increase in the viscosity of both samples. Cleaning the particles in these two cases became more difficult with high molar mass polymer (insoluble in THF). Thus several extra centrifugations were done in chlorobenzene solutions in both cases. For the 6 h experiment, insoluble polymer was obtained, even in chlorobenzene as shown in Figure 5.



Figure SI6. after 6h polymerization PSBTBT is insoluble in chlorobenzene

The molar mass of samples 4h and 6h could not be measured by GPC in THF because the polymers were not completely soluble in the solvent and most of the samples were blocked in the filter. According to UV-visible absorption spectra, λ_{max} was 675 nm for 4 h and 689 nm for 6 h. This shift was due to the increase in the molar mass with relatively high π - π stacking in the last case. Figure 6 shows the difference between the 6h sample before and after filtration.



Figure SI7 PSBTBT 4h free polymer before (right, green color) and after (left, blue color) filtration.

For polymerization 4 hrs, we obtained 100 mg of the grafted nanoparticles by centrifugation and 30 mg of free polymer by precipitation and soxhlet of the reaction media without the particles.

Grafting Density Calculations:

To calculate the grafting density σ of [2-(4-bromo-phenyl)-ethyl)]-triethoxysilane grafted to Zinc oxide nanoparticles from TGA the following equation was used.

$$\sigma = \frac{nbofPhBrmolecules}{ZnOnanorodsarea} = \frac{n_{PhBr}.N_a}{SSA.m_{ZnO}} = \frac{m_{PhBr}.N_a}{M_{PhBr}.SSA.m_{ZnO}} = \frac{\frac{m_{ZnO}.f_{wPhBr}}{1 - f_{wPhBr}}.N_a}{M_{PhBr}.SSA.m_{ZnO}} = \frac{\frac{f_{wPhBr}}{1 - f_{wPhBr}}.N_a}{M_{PhBr}.SSA.m_{ZnO}}$$

Where M_{PhBr} is the molecular weight of the organic part of the initiator CH₂-Ph-Br, M = 185 g.mol⁻¹. *SSA* is the specific surface area measured by BET, SSA = 24 m²/g.

 f_{wPhBr} is the mass fraction of the organic part in the hybrid materials ZnO@PhBr measured by TGA.

Calculation:

$$\sigma = \frac{\frac{0.015}{0.985} \times 6.02 \times 10^{23}}{185 \times 24} = 2.06 chains / nm^2$$



Figure SI8. Thermal gravimetric analysis of ZnO-PhBr



Figure SI9. UV-Visible absorption spectra in chloroform of ZnO@PSBTBT 2 (bold line), ZnO@PSBTBT 4 (dash), ZnO@PSBTBT 6 (plain line)



Figure SI10. UV-Visible absorption spectra of free PSBTBT 2 in chloroform (plain line), free PSBTBT 2 in thin film (dash), ZnO@PSBTBT 2 in solution (dot)



Figure SI11. UV-visible absorption spectra in chloroform of free PSBTBT obtained after 2, 4 and 6 h of reaction.



Figure SI12. XPS spectra of ZnO@PSBTBT 2, 4 and 6 and focus on the Si binding energy from 104 to 100eV. The green line shows the Si-O and the red line the Si-C.



Figure SI13. Thermal gravimetric analysis of ZnO (dash dot), ZnO@PSBTBT 2 (plain line), ZnO@PSBTBT 4 (dash), ZnO@PSBTBT 6 (dot)



Figure SI14. TEM images for bare ZnO (scale bar = 50 nm left and 20 nm right).



Figure SI15. TEM images for ZnO@PSBTBT 4 (scale bar = 50 nm).



Figure SI16. TEM images for ZnO@PSBTBT 2 (scale bar = 50 nm).



Figure SI17. TEM images for ZnO@PSBTBT 6 (scale bar = 50 nm).



Figure SI18. TEM images for ZnO@PSBTBT 6 (scale bar = 200 nm).



Figure SI19. GPC traces of free PSBTBT obtained after 2 (black plain), 4 (green dash) and 6 h (red dots) of reaction.



Figure SI20. TGA of free PSBTBT 4.

Cyclic Voltammetry (CV). A standard three-electrode electrochemical setup • (AUTOLAB PGSTAT 101) consisting of a glassy carbon or a platinium disk as working electrode (2 mm diameter), a platinum foil as counter electrode, and a Ag/AgCl as reference electrode, was used in the electrochemical experiments. At the end of each experiment performed in CH₃CN/Bu₄NPF₆ (0,1 M), the standard potential of the ferrocenium/ferrocene couple, E_{Fe}, was measured, and all potentials were referenced against SCE using a previous determination of $E_{Fe} = 0.41$ V versus SCE in CH₃CN.(ref 3) Polymers were drop casted from a 10 mg/mL polymer solution in chlorobenzene/Bu₄NPF₆ (0,1 M) on the working electrode. CV gives direct information of the oxidation and reduction potentials of materials. The oxidation process corresponds to removal of the electron from the HOMO energy level, while the reduction corresponds to electron addition to the LUMO energy level of the material. Therefore HOMO and LUMO energy levels can be estimated using the empirical equations: $E_{HOMO} = -(E_{ox} + 4,7)$ and $E_{LUMO} = -(E_{red} + 4,7)$, where E_{ox} and E_{red} are respectively the onset potentials for oxidation and reduction peaks relative to SCE and 4,7 the factor connecting SCE to vacuum. The onset potentials are determined by the tangent method (see supporting information). Only values from the first sweep on a film were used as the film is changed or destroyed during the first oxidation. The scan rate used was 0.1 V.s⁻¹.

Polymer	E _{HOMO}	E _{LUMO}	Eg (electrochemical)
Free PSBTBT 4h	-5.19 eV	-3.61 eV	1.58 eV



Figure SI21: CV reduction curve of free polymer PSBTBT 4h film performed in 0.1 M Bu_4NPF_6/CH_3CN using a sweep rate of 0.1 V.s⁻¹.



Figure SI22: CV oxydation curve of free polymer PSBTBT 4h film performed in 0.1 M Bu_4NPF_6/CH_3CN using a sweep rate of 0.1 V.s⁻¹.



Figure SI23: CV curve of ferrocene (5 mM) performed in 0.1 M Bu₄NPF₆/CH₃CN using a sweep rate of 0.1 V.s⁻¹.

"The ratio between the free and grafted chains was 90/10 (in weight)". How do we calculate it?

For polymerization 4 hrs: the TGA of ZnO@PSBTBT 4 shows a weight loss of 3.3 % due to the polymer corona. By centrifugation, we obtained 100 mg of the nanoparticles on which 3.3 mg were polymer. By precipitation and soxlet of the reaction media without the particles we obtained 30 mg of free polymer. Therefore the ratio free polymer to grafted polymer was estimated to 9/1.



Figure SI24: ¹H NMR of the free PSBTBT 4 in CDCl₃.



Figure SI25: ¹H NMR of the free PSBTBT 4 in C₂D₂Cl₄.



Figure SI26: ¹³C NMR of the free PSBTBT 4 in CDCl₃.



Figure SI27: Differential scanning calorimetry of the free PSBTBT 4 with following run: isotherm 5 min at 40°C, ramp to 250°C at 10°C/min, isotherm for 5 min at 250°C, ramp to -50°C at 10°C/min, isotherm for 5 min at 250°C, ramp to 40°C at 10°C/min. We did not detect any clear signal.

- (1) C. Pacholski, A. Kornowski, H. Weller, Angewandte Chemie International Edition 2002, 41, 1188-1191.
- (2) B. Sun, H. Sirringhaus, Nano Lett. 2005, 5, 2408-2413.
- (3) Daasbjerg, K.; Pedersen, S. U.; Lund, H. In General Aspects of the Chemistry of Radicals;

Alfassi, Z. B., Ed.; Wiley: Chichester, U. K., 1999; pp 385–427.