Supporting information

## Dispersion of multi-walled carbon nanotubes in an aqueous medium by water dispersible- conjugated polymer nanoparticles

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## Experimental

Synthesis of vertically aligned CNTs: Vertically aligned CNTs (VANTA) were synthesized through alcohol catalyzed chemical vapor deposition (ACCVD) technique on Si(100) substrates in a quartz tube furnace. First a 20nm thick oxide layer was grown on Si (100) surface by heating the substrate in air at 900°C for 30 minutes. After the preparation of the oxide layer, all of the substrates were ultrasonically cleaned in a peroxide-water mixture (50:50) for 30 minutes. All of the chemicals used for preparing solution based catalysts were purchased from Sigma-Aldrich. Two separate 5mmol  $\Gamma^{1}$ aqueous solutions of aluminium nitrate (Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, ACS reagent ≥ 98%) and iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, ACS reagent,  $\geq$  98%) were prepared. First, 20 µl of aluminium nitrate solution was applied on the oxide surface of a substrate with a micropipette and left for drying at room temperature. Following this step, 20 µl of iron nitrate solution was applied the same way and allowed for drying at room temperature. Finally, a final 20 µl of aluminium nitrate solution was applied. The dried substrates were placed on a quartz boat and loaded to the loadlock of an temperature and pressure controlled vacuum tube furnace. The loadlock and tube furnace were then pumped down to a pressure of 1 x 10<sup>-3</sup> torr using a rotary vacuum pump. The synthesis process used for the CNTs has two steps; reduction and reaction. During the reduction step, under a constant gas flow rate of 100 sccm of Argon and 20 sccm of H<sub>2</sub> metal catalysts particles were activated at 625 °C. Mass flow controllers were used to keep gas flow constant at a pressure of 3.8 torr. After 15 minutes, Ar:H<sub>2</sub> gas flow was redirected through an ethanol filled bubbler kept at room temperature to initiate the CNT growth. In figure S1, side and top view of a VANTA sample.



**Figure S1:** SEM images of (a) side (b) top viewSEM images VANTA grown on Si(100) and (c) TEM image of a CNT from VANTA samples.

Synthesis of Poly[9,9-bis-(6'-bromohexylfluoren-2,7-diyl)-co-(benzen-1,4-diyl)] (PFB): 2,7-Dibromo-9,9-bis-(6-bromo-hexyl)-9H-fluorene (500 mg, 0.78 mmol) and benzene-1,4-diboronic acid (129 mg, 0.78 mmol) were suspended in a mixture of degassed toluene (5 ml), THF (5 ml) and H<sub>2</sub>O (5 ml). [1,1 Bis(diphenyl phosphino)–ferrocene)] dichloro palladium (II) complex with dicholoromethane (32 mg, 0.039 mmol) and  $K_2CO_3$  (2.49 g, 18.0 mmol) were added sequentially. The mixture was degassed and heated at 80 °C for 3 h and then the phase transfer catalyst (TBAB) (13 mg, 0.039 mmol) was added. The mixture was further heated for 48 h under argon. After cooling the mixture to room temperature it was poured into methanol. The precipitate was collected by filtration and dissolved in chloroform. The solution was washed with water and concentrated under reduced pressure. The concentrated solution was poured into methanol; the solid residue was collected by centrifugation and dissolved in THF. The solution was added into stirred large excess of MeOH. The precipitate was collected by filtration and dried under vacuum to obtain powder. Yield: 300 mg, 60%.

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.83 (m, 6H), 7.27 (m, 4H), 3.30 (m, 4H), 2.11

(m, 4H), 1.68 (m, 4H), 1.26 (m, 24H), 0.81 (m, 14H).

Gel-permeation chromatography (GPC):  $Mn = 1.4 \times 10^4 \text{ g mol}^-$ ,  $Mw = 3.2 \times 10^4 \text{ g mol}^{-1}$ 

(Polystyrene as standard).

## Nanoparticle preparation

Conjugated polymer nanoparticles were prepared in two different sizes. 10 mg polymer was dissolved in 10 ml THF and stirred overnight. The solution was made up to volume of 100 ml by adding THF. The solution was filtered through 0.45 um syringe filter.

<u>CPNs with average sizes 70 nm</u>: 4 ml of this stock solution was injected rapidly into 40 ml of water while stirring using sonicator. The dispersion of nanoparticles was sonicated further for 20 min and stirred additionally another 30 min using magnetic stirrer. THF was removed under reduced pressure; the resulting nanoparticle dispersion was filtered through 0.45 um syringe filter. Concentration of polymer:  $0.1 \times 10^{-1}$  mg ml<sup>-1</sup>

<u>CPNs with average sizes 40 nm</u>: Procedure is the same but here 2 ml of polymer stock solution was injected into 100 ml of water to prepare CPNs.

Concentration of polymer: 0.2 x10<sup>-2</sup> mg ml<sup>-1</sup>

The size of the nanoparticles were determined by dynamic light scattering (DLS) and by scanning electron microscope (SEM) and transmission electron microscope (TEM). Figure S2 shows a images of CPNs of average size 40 nm.

<u>Interaction of CPN and CNTs</u>: Our calculations and measurements indicate that there is approximately  $\sim 6 \ge 10^{-2}$  mgs of CNT on Si substrates. These substrates with vertical CNT arrays were placed inside vials with several different sized nanoparticle solutions ranging from 0.2mg/ml to 0.002mg/ml. These VANTA samples were sonicated in these nanoparticle-water mixtures for 60 minutes at room temperature. As a control sample another CNT array was also dispersed in water. The bundled CNT clusters in dispersed in water can be easily observed in Figure S3.

In order to find out the maximum concentration of CNTs in CPNs water dispersion: VANTA sample (around 2 mg) were placed into 100 ml of CPN water dispersion (0.2 mg, 40nm-sized CPN)

containing beaker and as a control experiment the same amount of VANTA sample was placed into a 100 ml of water containing beaker. Both beakers were sonicated for an hour by keeping the temperature of the sonicator at room temperature. While most of the CNTs in CPNs dispersion were dispersed well, CNTs in water precipitated out immediately after sonication. CNTs/CPNs mixture was filtered through glass sintered funnel to separate the undispersed particles. The filtrate was clear with no sign of precipitates. The filtrate was concentrated to 5 ml in volume by removing water under reduced pressure. Concentrated dispersion also remained stable without any precipitation.

The highest CNT concentration of stable dispersions is calculated to be around 0.25 mg mL<sup>-1</sup> using 0.2:1 polymer to CNT mass ratio.



Figure S2: An TEM image showing CPNs of average size 40 nm.



Figure S3: SEM images of bundled CNT clusters dispersed in water dried on Si wafer.



Figure S4: EDX data from 40 nm (a) and 70 nm (b) CPNs attached to CNTs.

<u>Characterization</u>: A Carl-Zeiss EVO 40 XVP scanning electron microscope (SEM) was used to investigate the morphology and interaction between CNTs and nanoparticles. Nanoparticles and CNTs samples were dispersed on a Cu grid for TEM investigations. A JEOL 2100F transmission electron microscope (TEM) working at 200kV was used for TEM analysis with a JEOL EDX attachment. The Raman spectra of the samples were acquired using a HORIBA Jobin Yvon LabRam HR 800 instrument with a 532.1 nm Nd:YAG laser. UV-Vis spectra of the samples were recorded on a Thermo Scientific Evolution 300/600 UV-Visible spectrometer. Quarzt quvettes were used during the record and the base line correction was made for each of the samples at room temperature. Fluorescence spectra were recorded on The Cary Eclipse fluorescence spectrophotometer.