

# Phase Transfer Catalysts Drive Diverse Organic Solvent Solubility of Single-Walled Carbon Nanotubes Helically Wrapped by Ionic, Semi-Conducting Polymers

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**Materials.** All manipulations were carried out under nitrogen prepurified by passage through an O<sub>2</sub> scrubbing tower (Schweizerhall R3-11 catalyst) and a drying tower (Linde 3-Å molecular sieves) unless otherwise noted. Standard Schlenk techniques were employed to manipulate air sensitive solutions. All solvents utilized in this work were obtained from Fisher Scientific (HPLC grade). The catalyst, Pd(OAc)<sub>2</sub>, were obtained from Aldrich, tri(4,6-dimethyl-3-sulfonatophenyl)phosphine trisodium salt (TXPTS) were obtained from Strem. Sodium hydroxide was obtained from Fisher Scientific. 1, 5-Hydroxynaphthanol was obtained from Aldrich and used as precursor for 2,6-diiodo-1,5-hydroxynaphthanol, from which {[2,6-diiodo-1,5-bis(3-propoxy-sulfonicacid)naphthalene] sodium salt} was synthesized via reaction with 1,3-propane

sultone (Aldrich).<sup>1,2</sup> 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)ethyne (B2C2) was prepared according to literature procedure.<sup>3</sup> Chromatographic purification (Bio-Gel<sup>®</sup> P-4 Gel 90-180 mm, Bio-Rad Laboratories) of polymer compounds was performed on the bench top. HiPco (batch 81) as produced SWNTs were obtained from Rice University and used without further purification. 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6) was obtained from Aldrich and was used after re-crystallization from acetonitrile-hexanes.

**Instrumentation.** Electronic spectra were recorded on a Varian 5000 UV/vis/NIR spectrophotometry system. **PNES** emission spectra were recorded on a SPEX Fluorolog luminescence spectrophotometer that utilized a T-channel configuration with a red sensitive R2658 Hamamatsu PMT detector: these spectra were corrected for variations in photomultiplier response over wavelength using correction curves generated from the spectral output of a calibrated light source supplied by the National Bureau of Standards. All spectroscopic measurements were carried out at  $23 \pm 1$  °C. The fluorescence quantum yield of polymer PNES was determined using quinine sulfate ( $\Phi_f = 0.546$  in 1.0 N H<sub>2</sub>SO<sub>4</sub>, OD<sub>350</sub> = 0.015) as a standard.<sup>4</sup> All solutions were purged with argon prior to measurements. Solutions of OD( $\lambda_{\max}$ )  $\sim$  0.015 were used for fluorescence measurements. The molecular weights of polymers were determined by anion exchange chromatography using a Varian Prostar HPLC system equipped with an anion exchange column (NS1500; 75x7.6 mm; Biochrom Labs) and a Varian UV-Vis detector. Polymeric materials were eluted with a salt gradient (0 to 1 M NaSCN

dissolved in 20 mM MES buffer) in 10% DMF-H<sub>2</sub>O mixture at a flow rate of 2.0 mL/min over a 60 min period. Molecular weights are reported relative to the poly[4-(3-propoxysulfonicacidsodiumsalt)styrene] (PSPS) standard<sup>1,2</sup> ( $M_n = 17,596 \approx 66$  units). Microwave assisted reactions were performed with Emrys Personal Chemistry System (Biotage).

Transmission electron microscopy (TEM) images were obtained using JEOL TEM-2010 (accelerate voltage was 80 kV) equipped with a Gatan Peltier cooled CCD imaging system at the Regional Nanotechnology Facility at the University of Pennsylvania. Atomic force microscopy (AFM) images were obtained using Digital Instruments Dimension 3100.

Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopic (EDS) data were obtained at CHANL/UNC Chapel Hill. Elemental analysis was performed using a Hitachi 4700 Scanning Electron Microscope (SEM) equipped with an Oxford INCA Penta FET x3 Energy Dispersive Spectroscopy (EDS) system. Dried samples were mounted on double-stick carbon tape on an aluminum SEM sample holder.

X-ray photoelectron spectroscopic (XPS) data were obtained at CHANL/UNC Chapel Hill. All XPS data were taken with a Kratos Axis Ultra DLD system with a monochromatic Al K  $\alpha$  radiation source. Survey spectra and high resolution scans were acquired at pass energies of 80 and 20 eV, respectively. All peaks were calibrated to the C-1s peak at 284.6 eV; C1s and O1s peaks were de-convoluted after the application of Shirley background<sup>7</sup> within the Kratos Vision software.

**Transient absorption and excited state dynamics:** Experiments were performed using an experimental apparatus and conditions described previously.<sup>8</sup> Samples were interrogated in 2 mm-path-length fused-silica cells purged with argon. Steady state absorption spectra were checked before and after each laser experiment to verify sample integrity. The data presented were analyzed using Origin 7.5 software. The standard Origin tri-exponential decay formula was used for global fitting to generate figure 4B. Note that the instrument response time is approximately 180 fs.

**PNES synthesis procedure:** A 5 mL microwave vial (Biotage) was charged with 66 mg (94.3  $\mu\text{mol}$ ) of {[2,5-diiodo-1,4-bis(3-propoxy-sulfonic acid)naphthalene] sodium salt}, 33mg (120  $\mu\text{mol}$ ) of 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)ethyne,<sup>3</sup> 6.4 mg (28.6  $\mu\text{mol}$ ; 30 mol% relative to di-iodonaphthalene monomer) of Pd(OAc)<sub>2</sub>, 66 mg (101  $\mu\text{mol}$ ) of tri(4,6-dimethyl-3-sulfonatophenyl)phosphine trisodium salt (TXPTS),<sup>5</sup> and a magnetic stir bar. After sealing with a vial cap, this vessel was subjected to vacuum, followed by back-filling with argon. The vacuum-charge cycle was repeated 3 times. An aqueous 1 M NaOH solution (1.2 mL; 78.5 mM concentration with respect to the di-iodonaphthalene monomer), previously degassed with argon for 1 h, was added via syringe. The vessel was placed into the microwave cavity. The reaction mixture was stirred at room temperature for 1 min and then microwave irradiated at 30 W. The temperature was ramped from room temperature to the set point of 208 °C. Once the set temperature was reached, the reaction mixture was held at that temperature for 30 min time period. After the mixture was allowed to cool to room

temperature, the reaction vessel was opened. The resulting solution was viscous, greenish brown in color and exhibited an intense yellowish green fluorescence when illuminated with a 365 nm UV lamp. This solution was diluted with deionized water and then filtered through a glass frit and filter paper, successively. The filtrate was concentrated to *ca.* 3 mL, and loaded on the top of the size exclusion column (2 × 50 cm) packed with Bio-Gel<sup>®</sup> P-4 Gel (90-180 μm, Bio-Rad Laboratories), and eluted with deionized water without any additional buffer, providing clean separation of a yellowish green product band. Following evaporation of the solvent, a glossy film was obtained. Isolated yield = 38 mg (88 % based on 94.3 μmol {[2,5-diiodo-1,4-bis(3-propoxy-sulfonic acid)naphthalene] sodium salt}). <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): δ 8.2-7.1 p.p.m (m, 4 H), 3.24 (broad m, 8 H), 2.45 (broad m, 4 H). <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O/DMSO (~10:1 v:v)): δ 157.80 (m), 130.38 (m), 120.23 (m), 114.11 (m), 94-93 (m), 75.32 (m), 49.80 (m), 27.20 (m). Vis (H<sub>2</sub>O): 408 nm (4.14; calculated per mole of monomer unit); λ<sub>em</sub> (H<sub>2</sub>O): 461.5 nm with a fluorescence quantum yield of 0.031; λ<sub>em</sub> (3:1 MeOH:H<sub>2</sub>O): 448 nm with a fluorescence quantum yield of 0.177 (Figure S3). The number average molecular weight of **PNES** was determined to be ~18.8 kD by anion exchange chromatogram, which corresponds to a degree of polymerization (DP) of 40 and PDI of 1.11 (Figure S2).

Variation of the **PNES** molecular weight distribution was determined as a function of reaction conditions, which included decreasing the catalyst loading to 15% and running the reaction at 78.5, 39.25, and 157 μmol-level concentrations of the di-iodonaphthalene monomer; the number average molecular weights of these

preparations were found to be, respectively, 23.5 kD (DP ~50, PDI = 1.21), 23 kD (DP ~49, PDI = 1.14) and 19.3 kD (DP ~41, PDI = 1.16). Based on these results, a high catalyst loading (of 30 mole%) and short (i.e. 30 min) reaction times at high temperature (of 200 °C) were employed to synthesize PNES with a narrow molecular weight distribution ( $M_n = 18.8$  kD, DP = 40, PDI = 1.11).

**Preparation of PNES-SWNT Suspensions:** SWNTs were suspended in different solvents using the standard ultra sonication-centrifugation technique.<sup>6,7</sup> PNES of  $M_n = 18.8$  kD corresponding to degree of polymerization (DP) = 40 and HiPCO (@Rice, batch 81) were used for all suspension preparations.

**PNES-SWNTs in aqueous medium:** Ionic PNES is highly soluble in water. For Vis-NIR absorption studies, this solution was used without dilution. For microscopy experiments, this solution was diluted with water to provide an appropriate concentration.

**PNES-SWNT/H<sub>2</sub>O:** An aqueous solution of PNES (2.5 ml, 1.68 mg/ml), corresponding to a 3.5 mM concentration with respect to the naphthaleneethynylene unit, was mixed with 2 mg of HiPco tubes wet with 0.1 mL of DMF in a 5 ml vial. The mixture was sonicated using a direct contact of a tip horn sonicator (1 W/ml, 20 kHz) for 3 hours. A water bath (250 ml) was utilized to maintain a temperature of ~25 °C. During the sonication process, the mixture was vortexed at 30 min intervals. Upon completion, the suspension was centrifuged at 36000 g for 3 h using a Beckman Coulter TLX-100 centrifuge. The upper 60% of supernatant solution was carefully taken up by

syringe and transferred to a clean vial. Solutions prepared in this manner remain clear for at least 1 year.

**PNES-SWNT in Organic solvents:** PNES does not dissolve in any of the organic solvents used in this study, even after prolonged bath sonication times of hours. The phase transfer catalyst 18-crown-6 (20 mg/mL) facilitates dissolution of PNES in organic solvents. The sonication power and time used for the maximum SWNT mass uptake in the suspensions prepared in organic solvents are diminished with respect to that used for an aqueous suspension preparation. For Vis-NIR absorption studies, these solutions were used without dilution. For microscopy experiments, these solutions were diluted with the appropriate solvent.

**PNES-SWNT/DMSO:** A mixture of PNES (4.2 mg) and 18-crown-6 (50 mg) was taken in 2.5 mL DMSO (1.68 mg/ml, corresponding to a 3.5 mM concentration with respect to the naphthaleneethynylene monomer unit). PNES was dissolved following a 10 min sonication time period in a water-bath sonicator and occasional shaking. The PNES solution was then mixed with 2 mg of HiPCo nanotubes in a 5 ml vial. The mixture was sonicated at 0.4 W/ml, 20 kHz for 1 hour. A water bath (250 ml) was utilized to maintain a temperature of ~25 °C. During the sonication process, the mixture was vortexed at 20 min intervals. Upon completion, the suspension was centrifuged at 36000 g for 3 h. The upper 60% of supernatant solution was carefully taken up by syringe and transferred to a clean vial. PNES-SWNT suspensions in DMSO remain clear and stable (confirmed via electronic absorption spectroscopy and AFM; see Figures S4 and S9) for a minimum of 6 months time under an argon atmosphere.

**PNES-SWNT/MeOH:** A mixture of **PNES** (4.2 mg), and 18-crown-6 (50 mg) was taken in 2.5 mL MeOH (1.68 mg/ml, corresponding to a 3.5 mM concentration with respect to the naphthaleneethynylene monomer unit). The PNES was dissolved by sonication for 10 min with occasional shaking. The PNES solution was then mixed with 2 mg of HiPCo tube in 5 ml vial. The mixture was sonicated at 0.4 W/ml, 20 kHz for 1 hour. A water bath (250 ml) was utilized to maintain a temperature of ~25 °C. During the sonication process, the mixture was vortexed at 20 min intervals. Upon completion, the suspension was centrifuged at 36000 g for 3 h. The upper 60% of supernatant solution was carefully taken up by syringe and transferred to a clean vial. The **PNES-SWNT** suspension in MeOH remains clear and stable (confirmed via electronic absorption spectroscopy and AFM; see Figure S4) for a minimum of 5 months under an argon atmosphere.

**PNES-SWNT/DMF:** A mixture of **PNES** (4.2 mg), and 18-crown-6 (120 mg) was taken in 2.5 mL DMF (1.68 mg/ml, corresponding to a 3.5 mM concentration with respect to the naphthaleneethynylene monomer unit). PNES was dissolved by sonication for 30 min with occasional shaking. The PNES solution was then mixed with 2 mg of HiPCo nanotubes in a 5 ml vial. The mixture was sonicated at 0.4 W/ml, 20 kHz for 30 minutes. A water bath (250 ml) was placed outside of the vial to keep the temperature at ~25 °C. Upon completion, the suspension was centrifuged at 36000 g for 3 h. The upper 60% of supernatant solution was carefully taken up by syringe and transferred to a clean vial. **PNES-SWNT** suspensions in DMF remain clear and stable (confirmed via

electronic absorption spectroscopy and AFM; see Figs. **S4** and **S10**) for a minimum of 4 months under an argon atmosphere.

**Preparation of aqueous SDS-SWNT dispersions:** A SDS solution (2.5 mL of 1.91 mg/mL, 7.0 mM) was mixed with 1 mg HipCo SWNTs and sonicated for 30 min (0.4 W/mL, 20 kHz). The mixture was centrifuged at 20,000 g for 3 h.

**Transmission Electron Microscopy (TEM):** The TEM samples from the **PNES-SWNT** suspensions were prepared via drop-casting on a lacy formvar copper grid stabilized with carbon (200 mesh, Ted Pella, Inc.) followed by drying in a desiccator prior to the TEM observation.

**Atomic Force Microscopy (AFM):** The **PNES-SWNT** suspensions were deposited on mica or n-type (100) silicon wafers. The mica surface was freshly cleaved just before deposition of the **PNES-SWNTs**. Silicon wafers were used as received. On mica, the droplet was drained to assure that only limited numbers of **PNES-SWNTs** remained on the surface. On silicon wafers, droplets were dried in a desiccator for about ~30 minutes. Imaging was carried out under ambient conditions using the intermittent contact mode of a Digital Instruments Dimension 3100. The imaging conditions were: scan rate = 2 Hz, Si tips, cantilever frequency = 75 kHz. The data presented were generated via a 1<sup>st</sup> order plane fit.

**SEM/EDS:** Elemental analyses were performed with **PNES-SWNT/DMF** and **PNES-SWNT/H<sub>2</sub>O** suspensions. The suspensions were purified prior to the preparation of

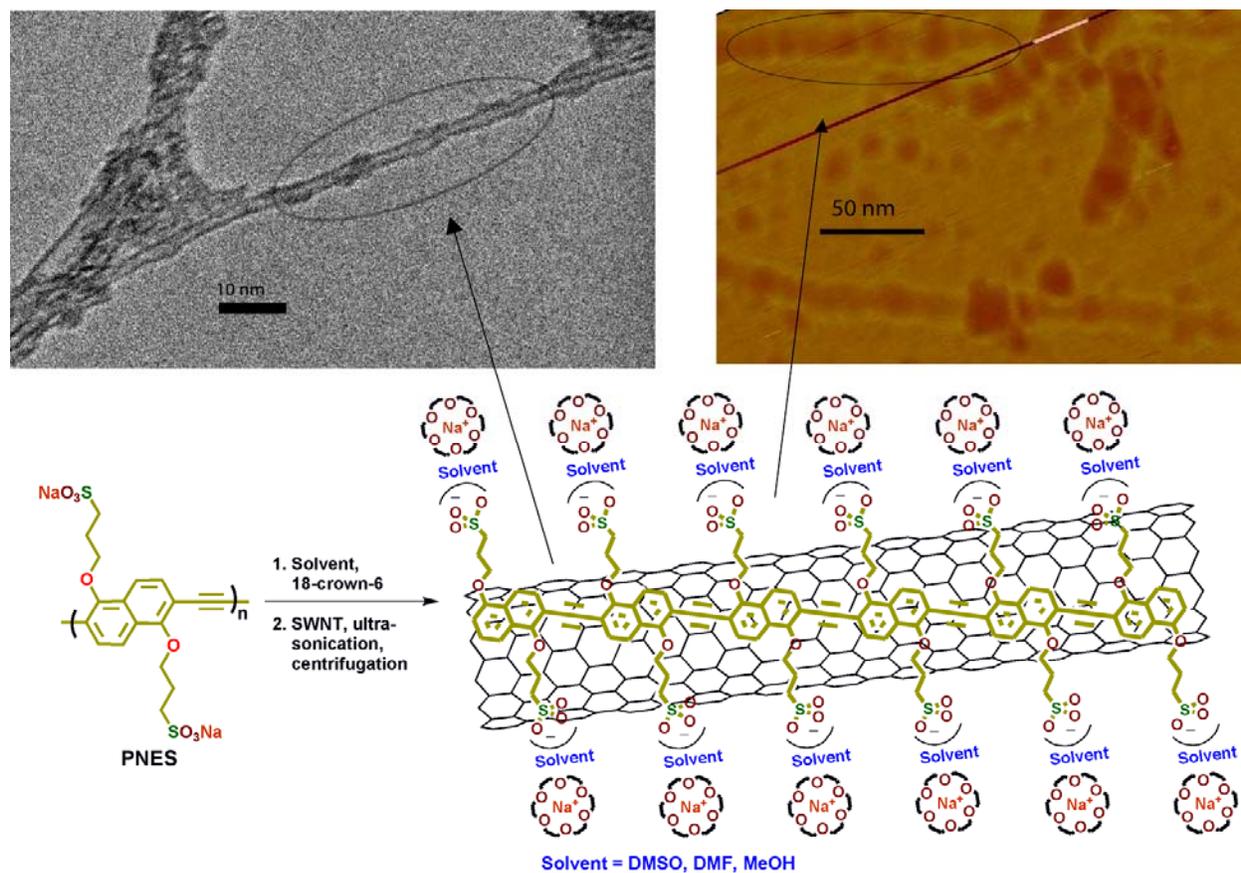
EDS sample via two methods: (1) the DMF and water suspensions were filtered through 200 nm Teflon and 100 nm pore cellulose membranes respectively; this allowed the removal of unbound polymers and low molecular weight soluble materials. The solid SWNT cakes were dissolved in either DMF or water (solvent volume kept constant with that of the initial suspension) via mild bath sonication (~1-2 min), following which the solution was filtered again through the appropriate membrane. This filtration-dissolution cycle was repeated ~7-9 times for each suspension until the filtrate was found to be free of polymer, via absorption spectroscopy. A 0.5 mL solution of each sample was then dried under reduced pressure over several days; these samples were utilized for EDS studies. (2) A PNES-SWNT/H<sub>2</sub>O suspension isolated following size exclusion chromatography [sephacryl (S-500; MW cut off 20-20000 kDa) was dried under reduced pressure; this sample was characterized via AFM (Fig. S15).

**XPS:** PNES-SWNT/H<sub>2</sub>O suspensions obtained following size exclusion chromatography [sephacryl (S-500; MW cut off 20-20000 kDa) were passed through a 100 nm cellulose membrane to give a thick, black PNES-SWNT cake which was then dried under reduced pressure. This solid, a few hundred nm thick, isolated on top of the cellulose membrane, was mounted for XPS data collection. AFM data (Fig. S15) obtained for this sample clearly evince helical wrapping of the SWNT surface by PNES.

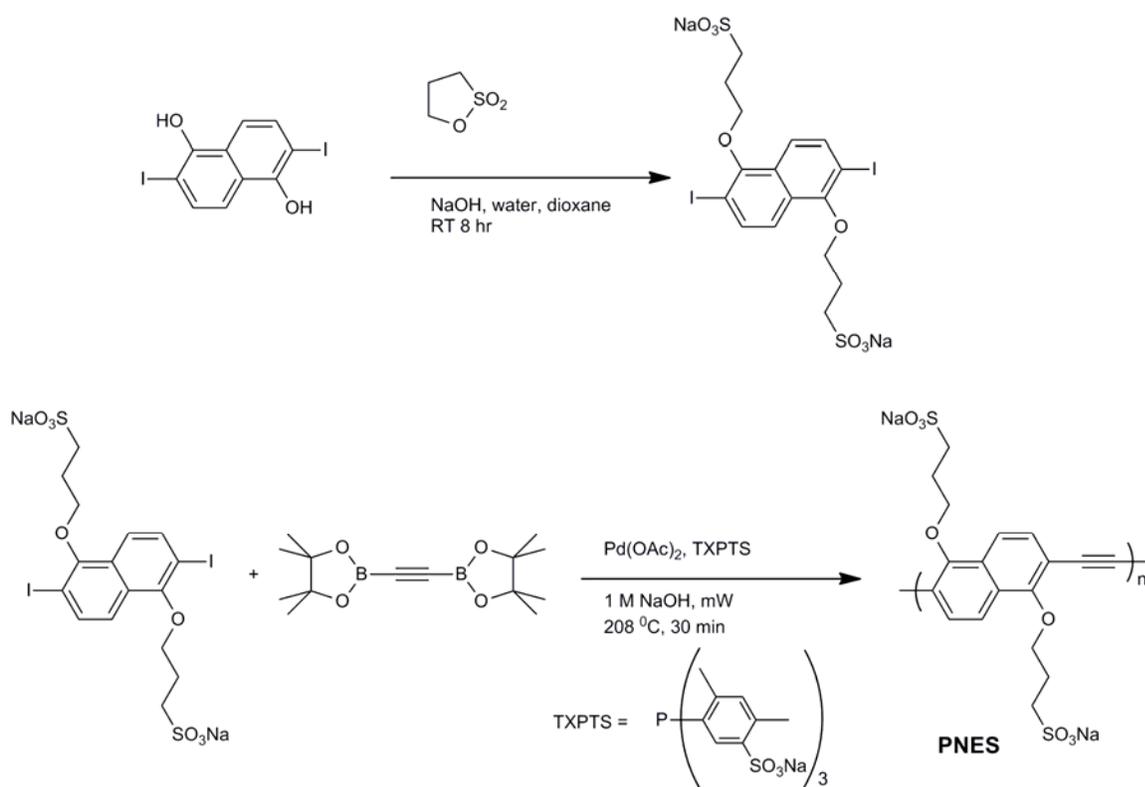
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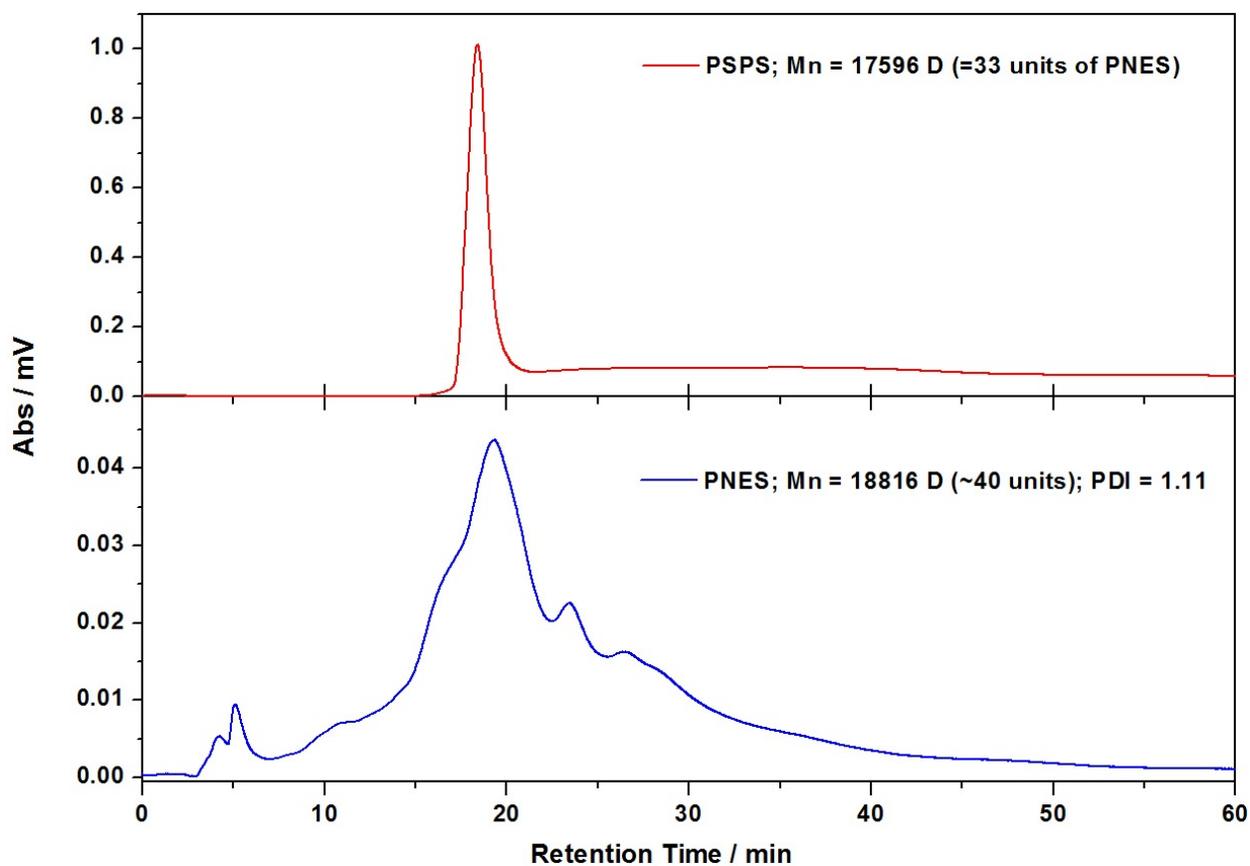
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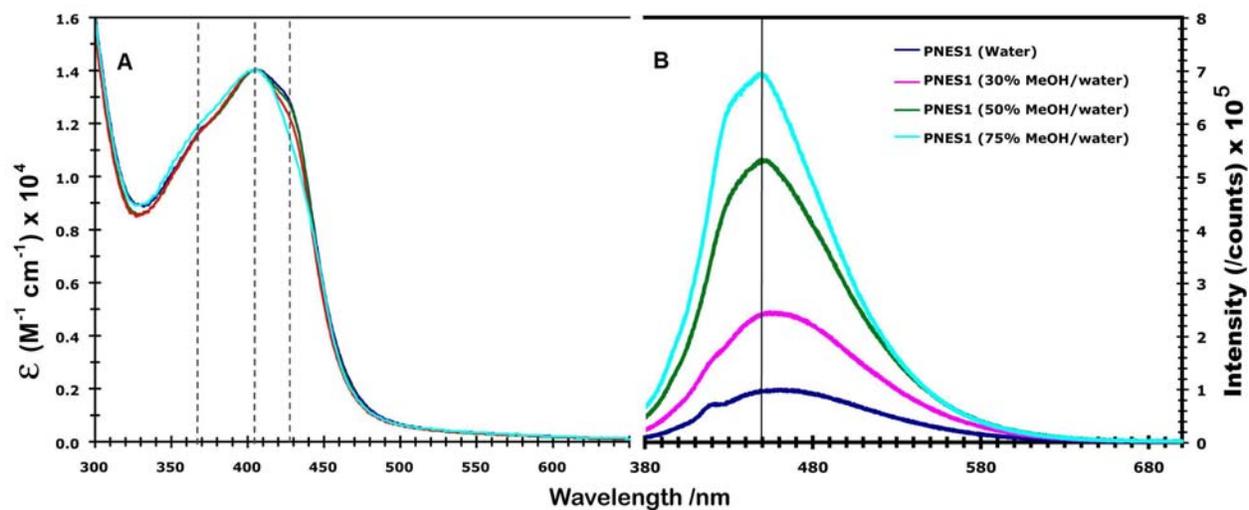
**Figure S1.** Schematic representation summarizing the key result reported in the manuscript.



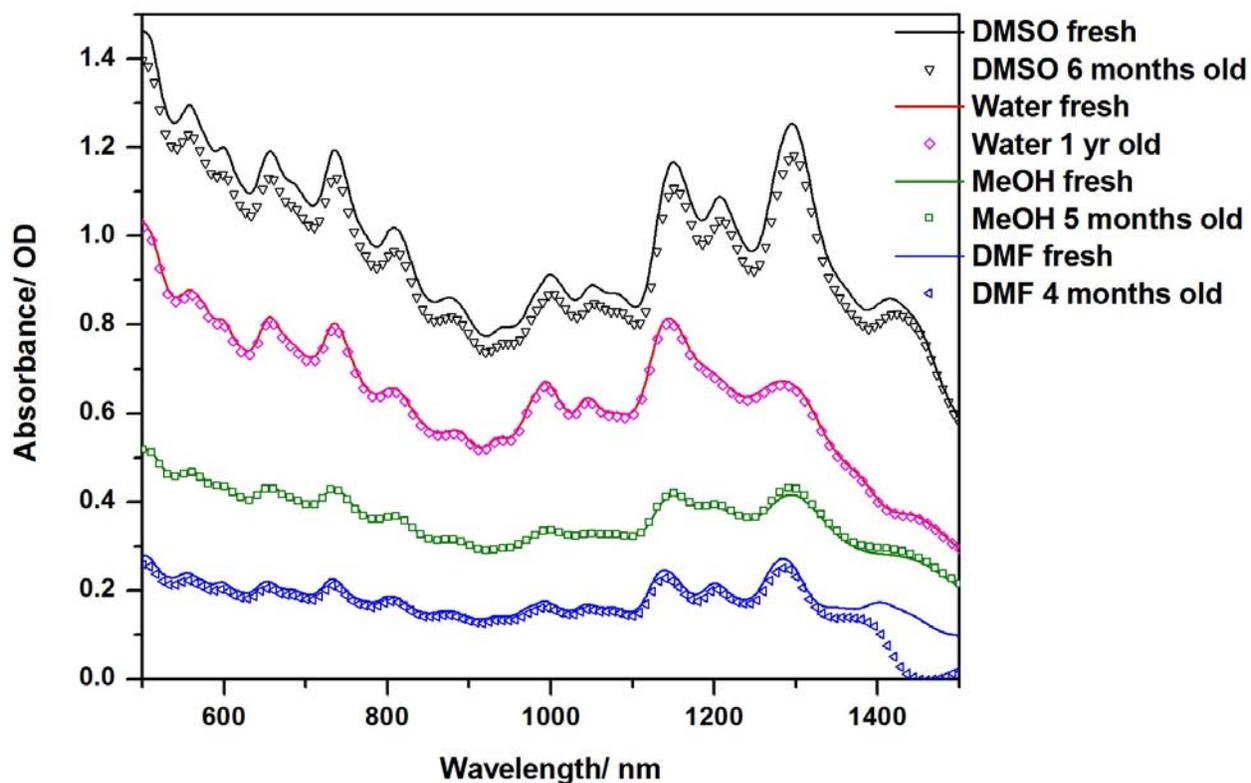
**Scheme S1:** Synthesis of PNES from 2,6-diiodo-1,5-hydroxynaphthalen-1-ol.



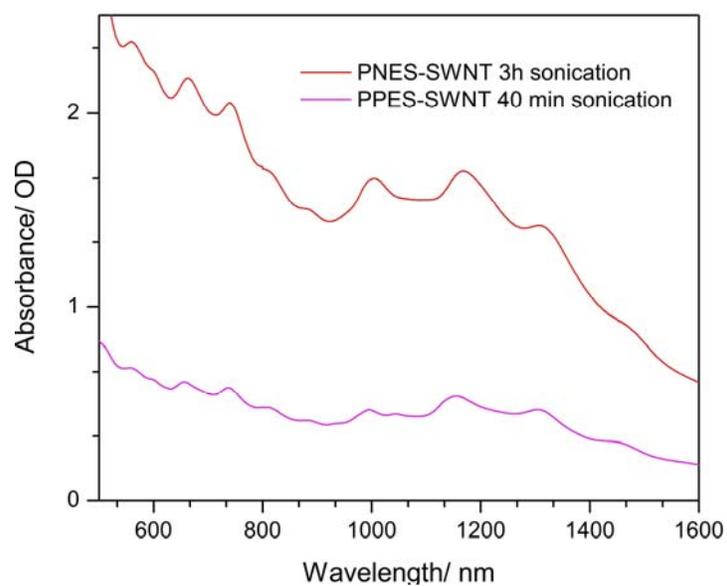
**Figure S2:** Anion exchange chromatography of PNES with respect to a PPS standard ( $M_n = 17596$  D  $\approx$  66 unit of PPS  $\approx$  33 units of PNES). These samples were eluted using a salt gradient of 0-to-1M of NaSCN in 20 mM MES buffer (in 10% DMF:H<sub>2</sub>O mixture) over a 60 minute duration at a flow rate of 2 mL/min.



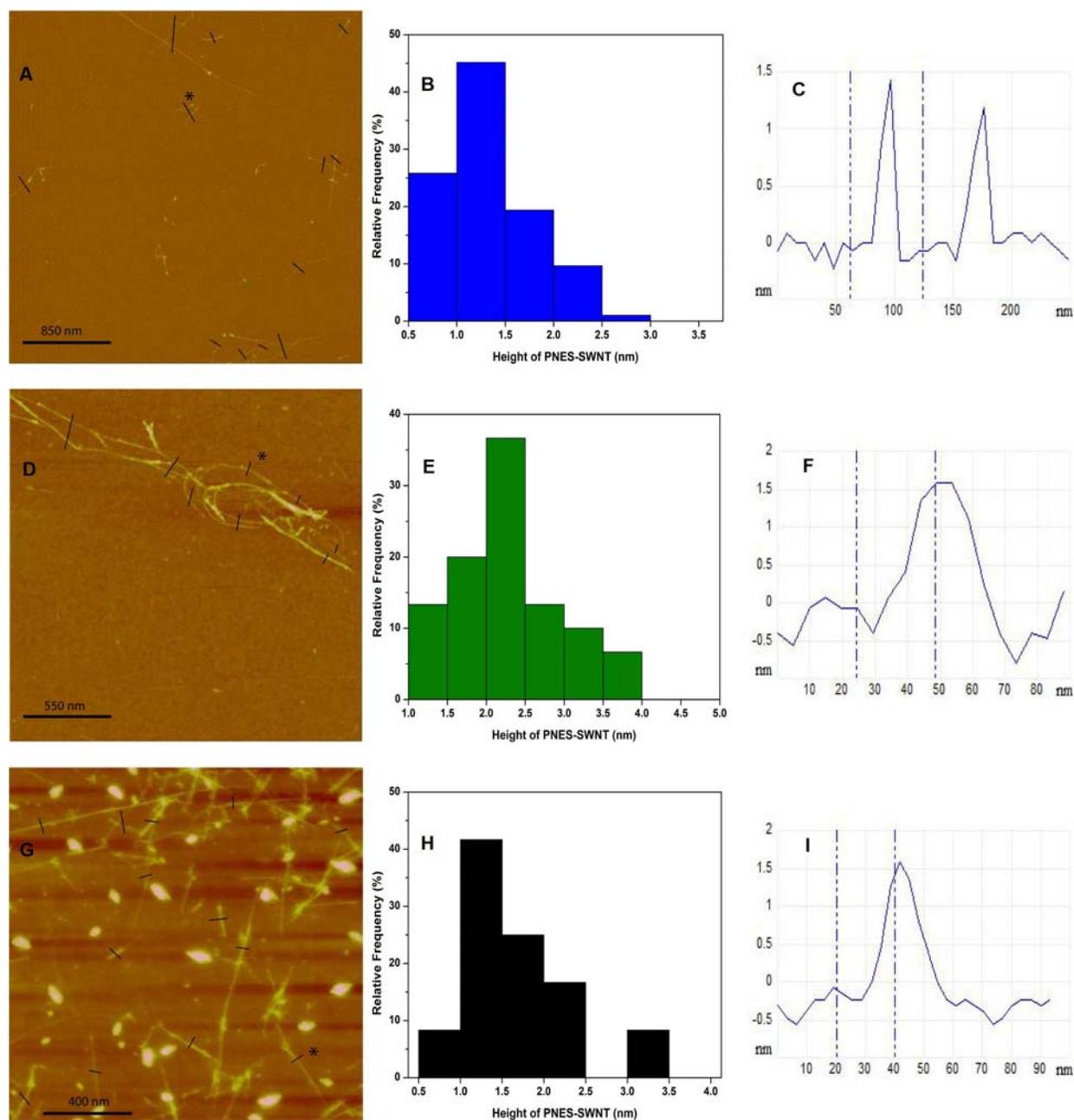
**Figure S3:** (A) Absorption spectra of PNES in H<sub>2</sub>O and in a MeOH:H<sub>2</sub>O mixed solvent system. The extinction coefficient is shown relative to the number of moles of the monomer unit. (B) Corresponding emission spectra. The emission quantum yield increases from 3.1% in neat water to 17.7% in 3:1 MeOH:H<sub>2</sub>O with respect to the quinine sulfate standard. All spectra were measured at  $296 \pm 1$  K;  $\lambda_{ex} = 350$  nm.



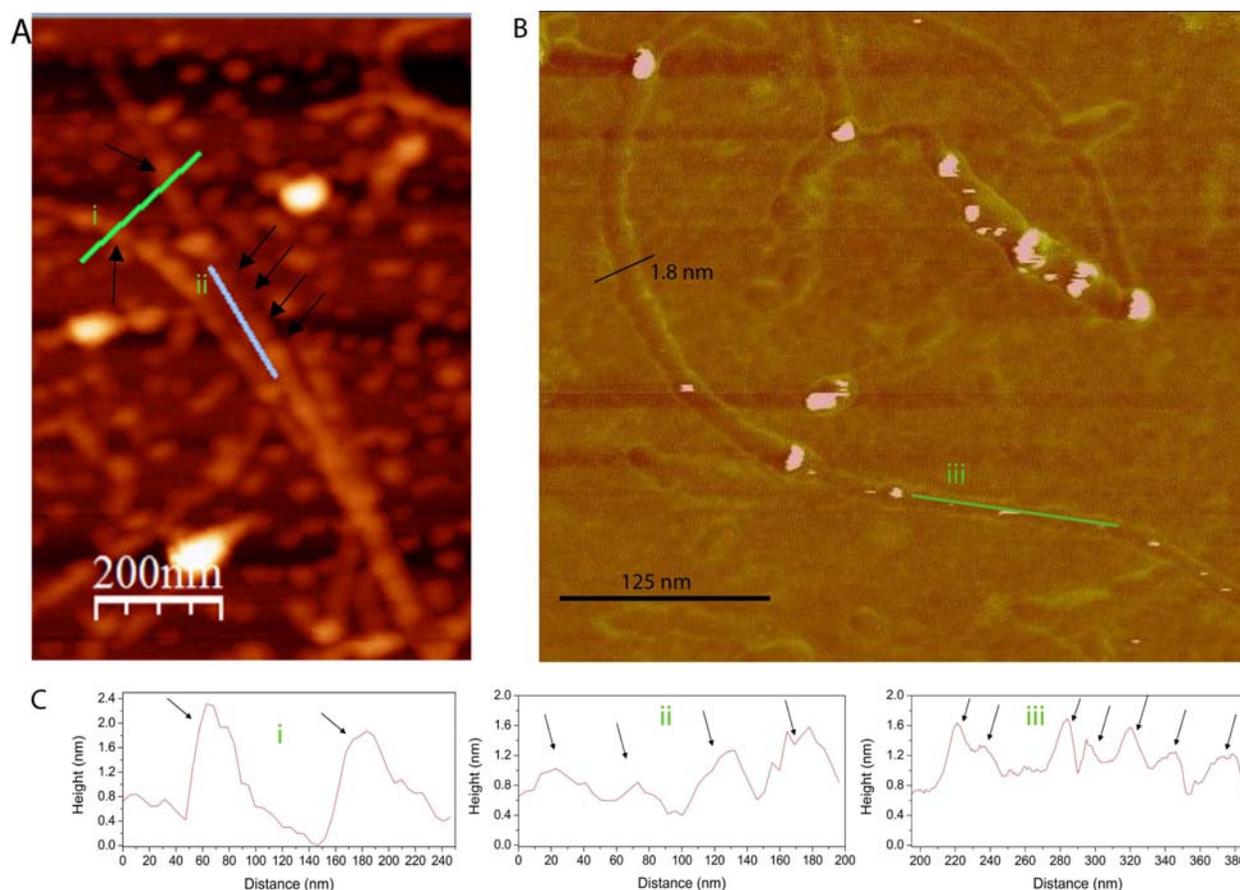
**Figure S4.** Vis-NIR absorption spectra of PNES-SWNTs in various solvents and time; the solid lines represent the spectra of a fresh sample; the scattered spectra are of the corresponding suspensions after several months of storage time under argon. (Note that the reduction of SWNT absorption intensity shown as the spectrum of old DMSO sample is due to dilution with DMSO, and the spectrum of old DMF sample has a baseline error at  $\sim 1450$  due to varying humidity conditions).



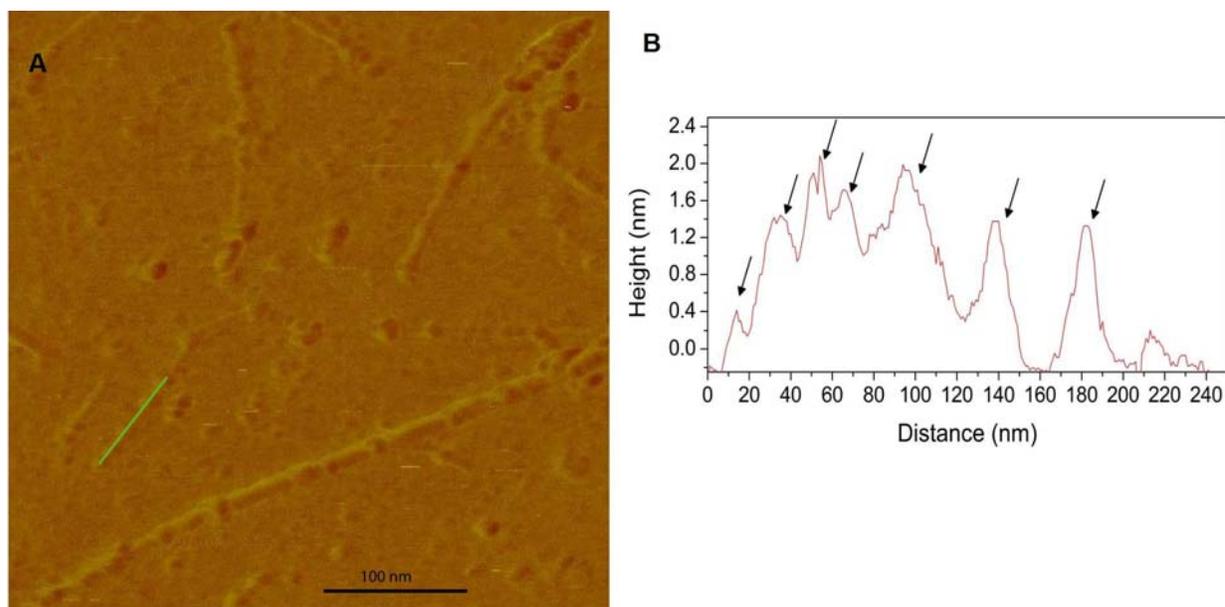
**Figure S5.** Vis-NIR absorption spectra of **PNES-SWNT** suspensions prepared in water using two different sonication times (sonication power = 1W/mL) showing the SWNT mass uptake as a function of sonication time.



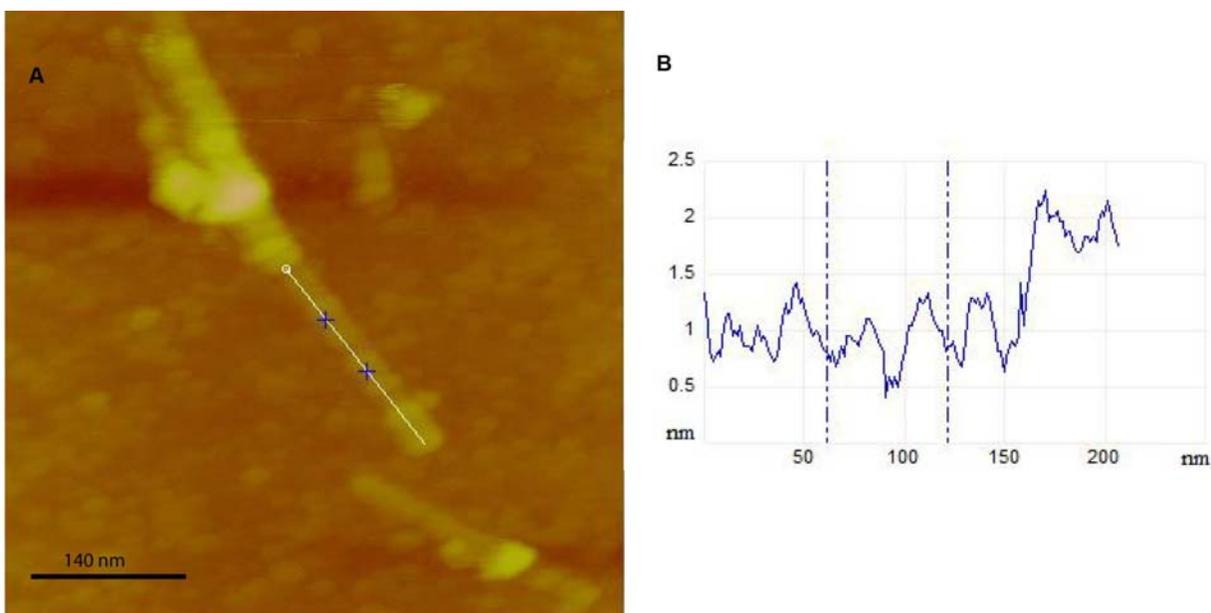
**Figure S6.** AFM analysis of PNES-SWNT suspensions in different solvents: (A), (D) and (G) topographic AFM images of PNES-SWNTs from DMF, MeOH and DMSO-solubilized suspensions respectively after they were deposited and dried on mica surfaces. (B), (E), and (H) height profile histograms of panel (A), (D), and (G) data. (C), (F) and (I) height profiles along the line marked with asterisks in panel (A), (D), and (G) data.



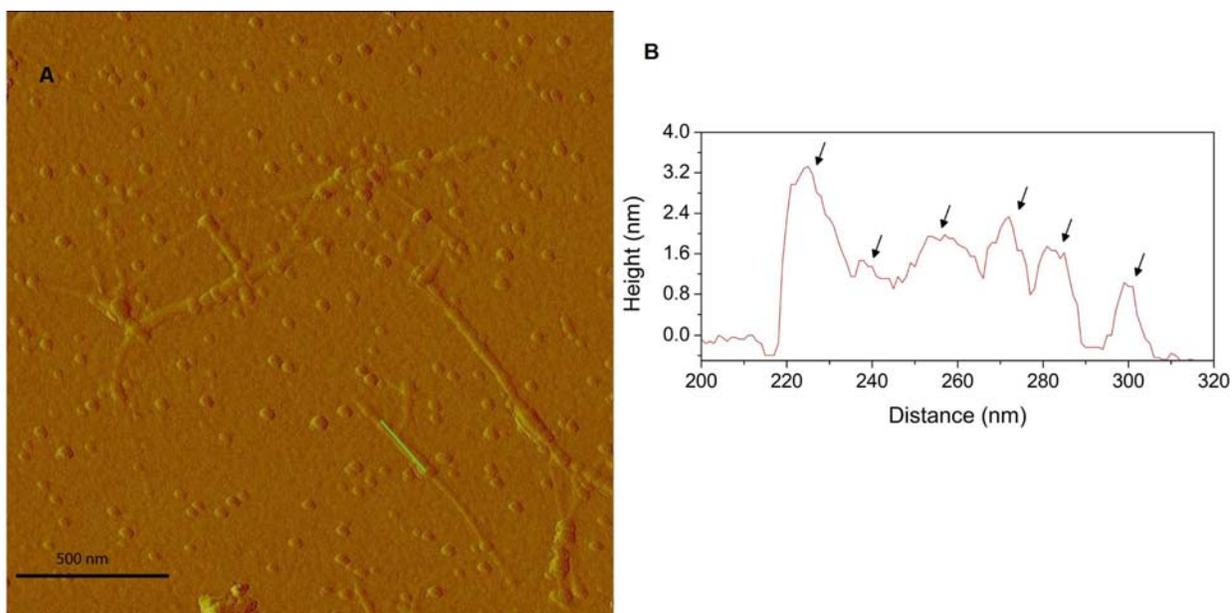
**Figure S7.** AFM images of PNES-SWNTs in protic solvents: (A) **PNES-SWNTs** from a H<sub>2</sub>O-solubilized suspension deposited and dried on a mica surface; (B) **PNES-SWNTs** from a MeOH-solubilized suspension deposited and dried on a mica surface. (C) Height profile along the green line (i), (ii) in the panel (A) and (iii) in panel (B) data; showing the height profile of two individual tubes (i) and periodic height oscillation (ii and iii) that derives from PNES helical wrapping on the SWNT.



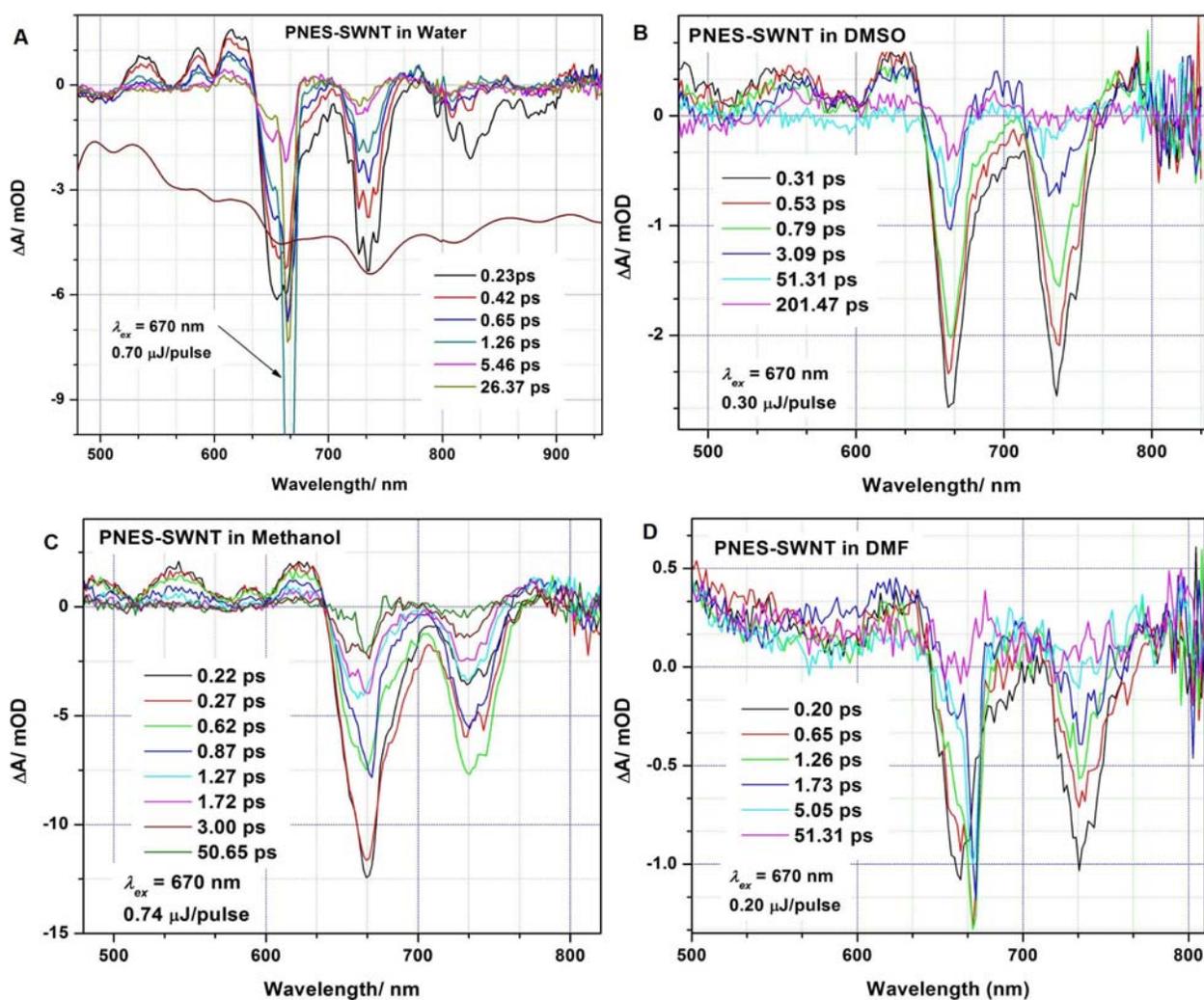
**Figure S8.** Structural stability of PNES-wrapped SWNTs in water: (A) AFM images of **PNES-SWNTs** from a 1 yr old H<sub>2</sub>O-solublized suspension deposited and dried on a mica surface; (B) height profile along the green line in the panel (A) data indicating that the helical wrapping of PNES on the SWNT surface remains stable over prolonged time periods in water.



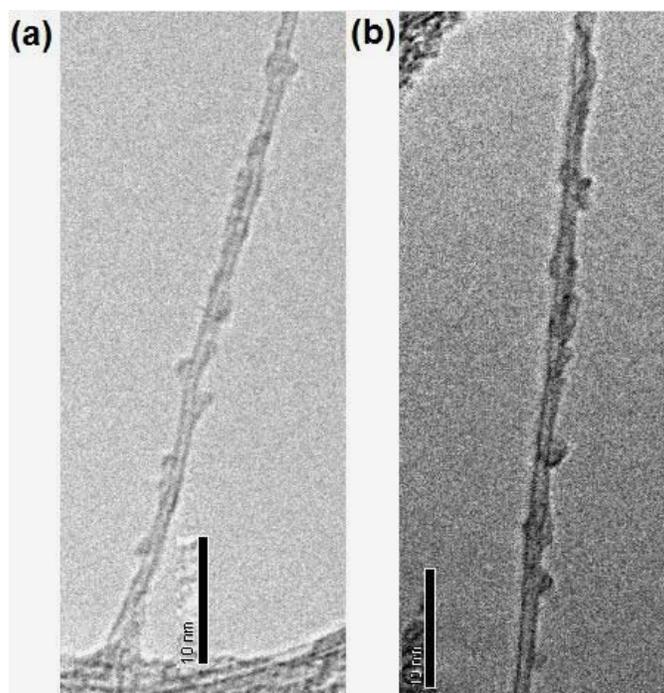
**Figure S9.** Structural stability of PNES-wrapped SWNTs in DMSO: (A) Topographic AFM images of **PNES-SWNTs** from a 3-month-old DMSO-solublized suspension deposited and dried on a mica surface; (B) height profile along the white line in the panel (A) data, indicating that the helical wrapping of PNES on the SWNT surface remains stable for prolonged time periods in DMSO solvent.



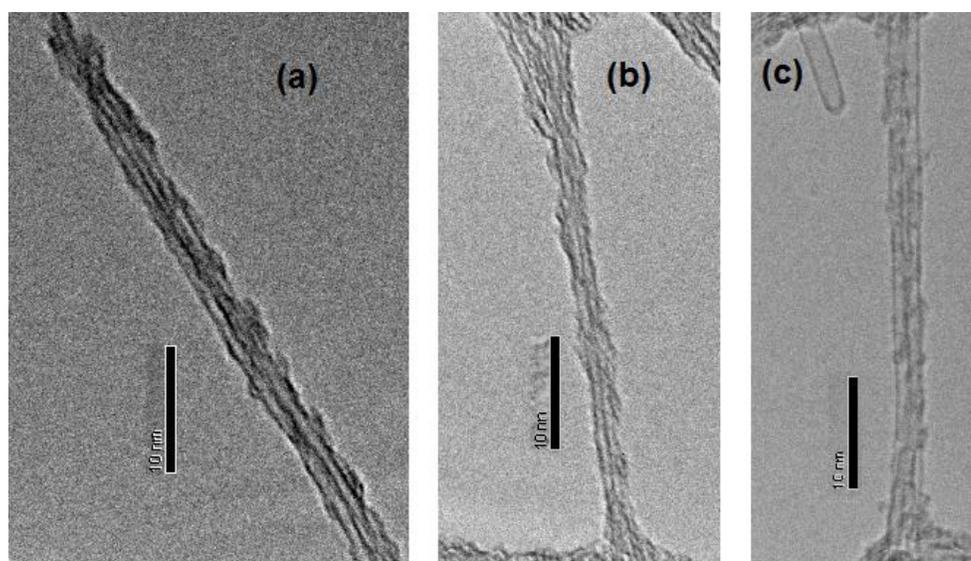
**Figure S10.** Structural stability of PNES-wrapped SWNTs in DMF: (A) AFM images of PNES-SWNTs from a 3-month-old DMF-solublized suspension deposited and dried on a mica surface; (B) height profile along the green line in the panel (A) data indicating that helical wrapping of PNES on the SWNT surface remains stable for prolonged time periods in DMF solvent.



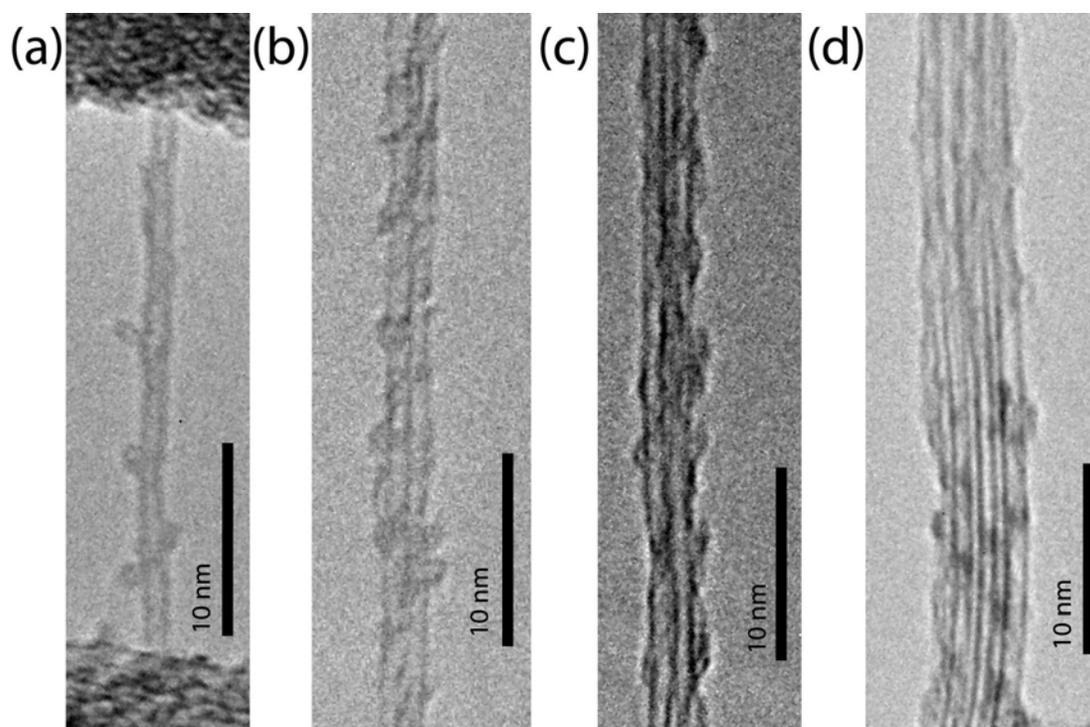
**Figure S11.** Transient absorption spectra of PNES-SWNT samples in various solvents: (A) in water; (B) DMSO; (C) MeOH; and (D) DMF, with labeled delay times and pump energies, determined at magic angle polarization ( $\lambda_{\text{ex}} = 670 \text{ nm}$ ). An inverted, scaled PNES-SWNT linear absorption spectrum in water is shown in panel A for comparison.



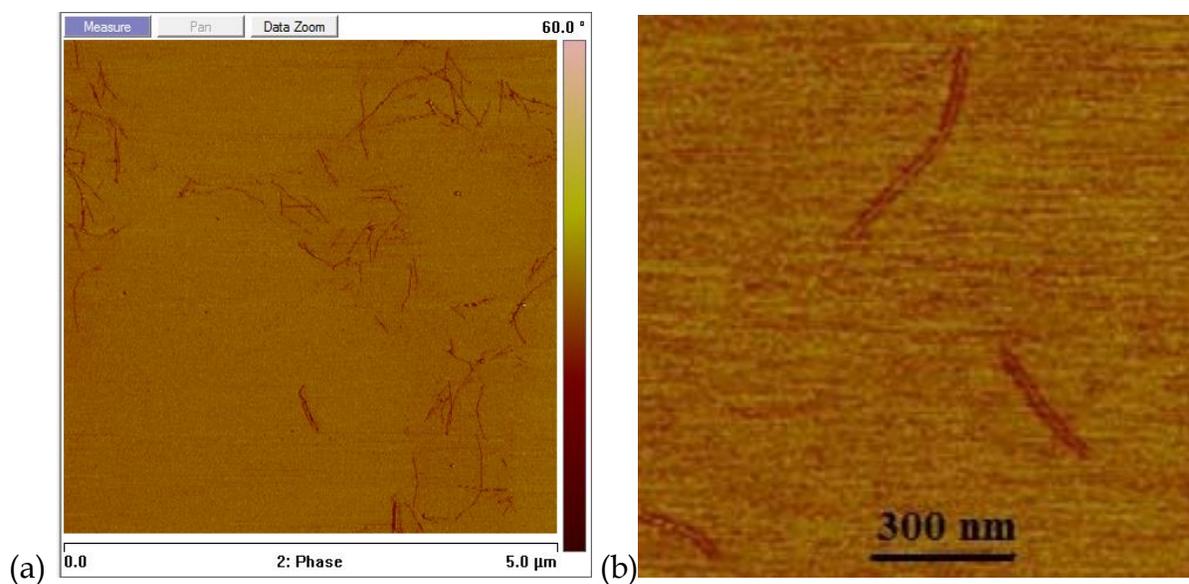
**Figure S12.** TEM images of single PNES strand-wrapped SWNTs in aqueous solvent.



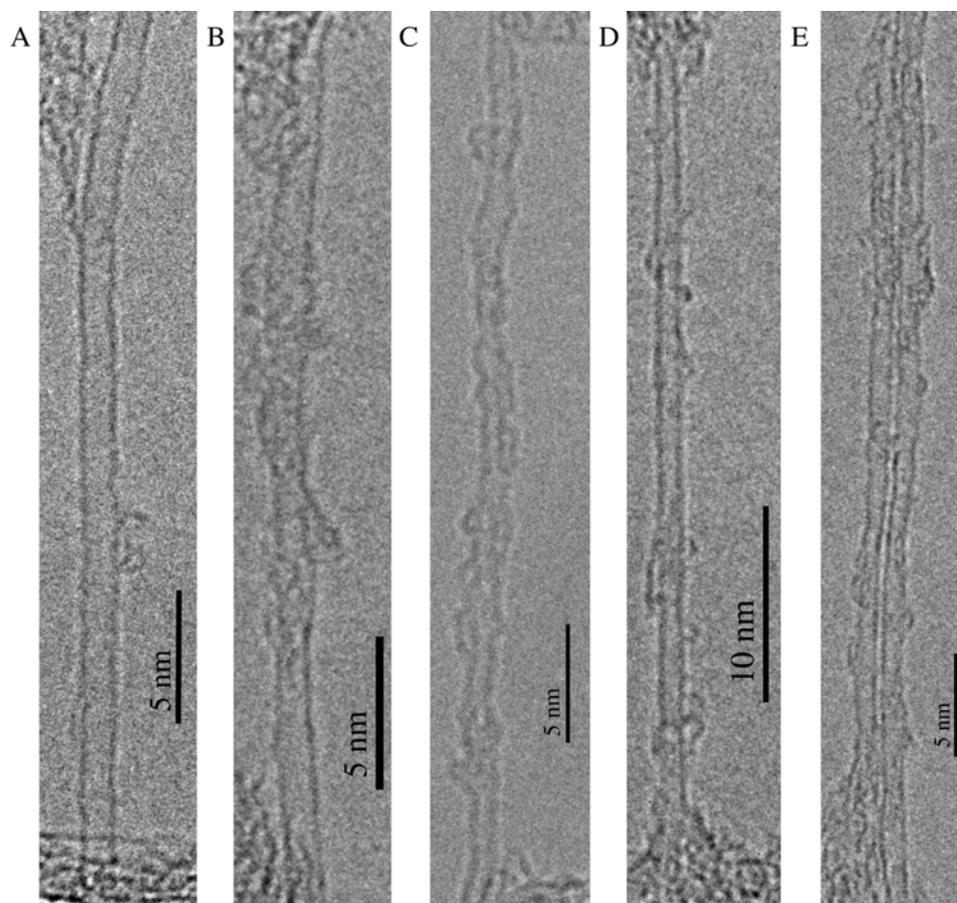
**Figure S13.** TEM images PNES-wrapped two-tube bundles in aqueous solvent.



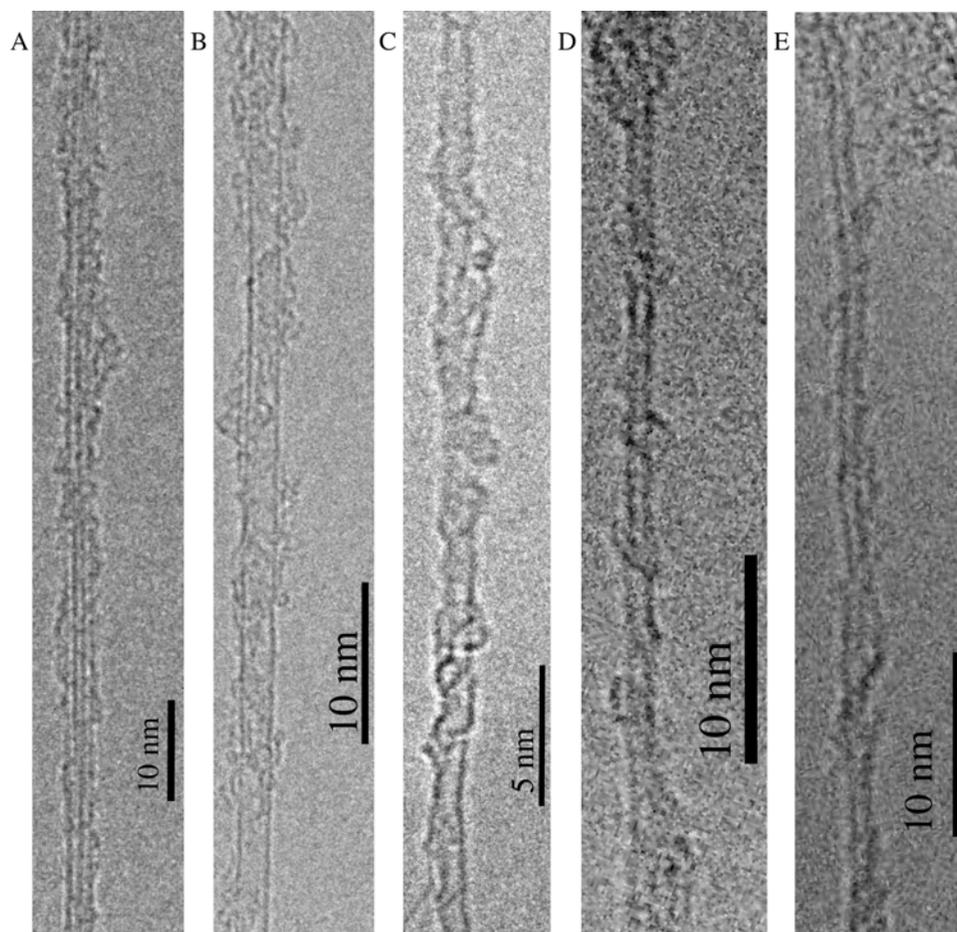
**Figure S14.** TEM images of **PNES-SWNT** samples from aqueous solvent of: (a) a single tube, (b) a two-tube bundle, and (c, d) multi-tube bundles.



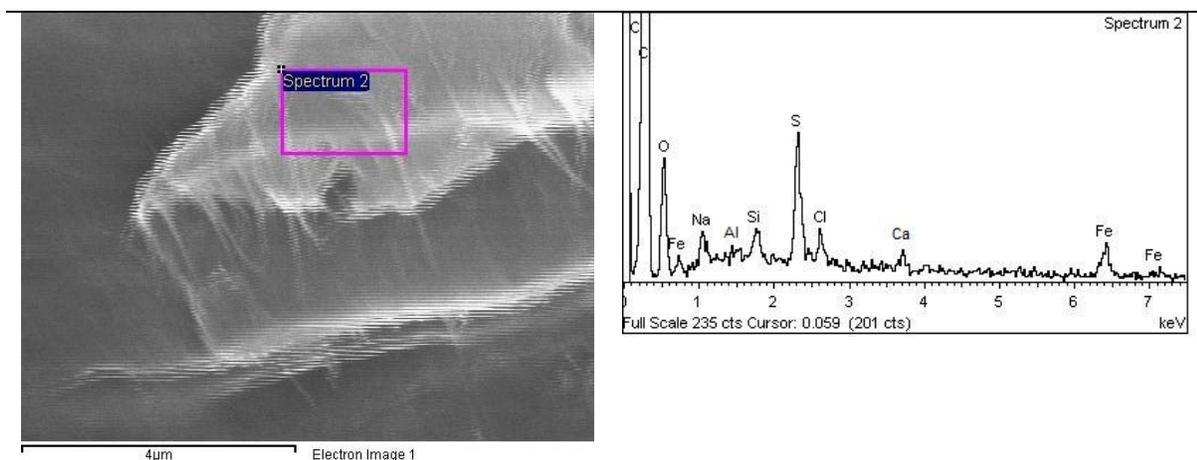
**Figure S15.** AFM images of a **PNES-SWNT** sample (Figures 3A, S7A) obtained after size exclusion chromatography [sephacryl (S-500; MW cut off 20-20000 kDa), demonstrating that **PNES-SWNT**s manifest unchanged morphology following removal of small catalyst and carbon particles.



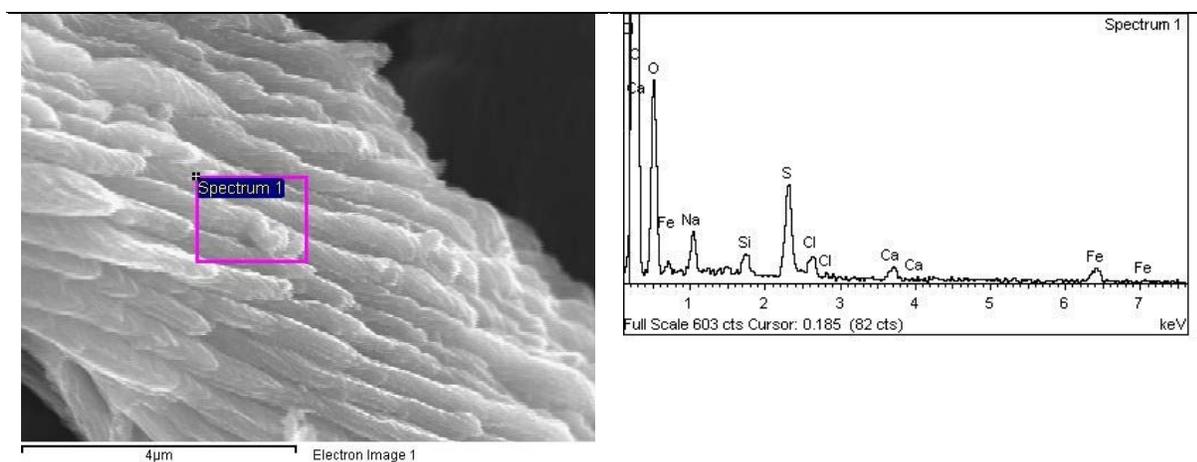
**Figure S16.** (A) TEM image of a “bare” single SWNT. (B)-(E) TEM images of **PNES-SWNT** samples from DMSO solvent showing (B)-(D) individualized tubes, and (E) a two-tube bundle.



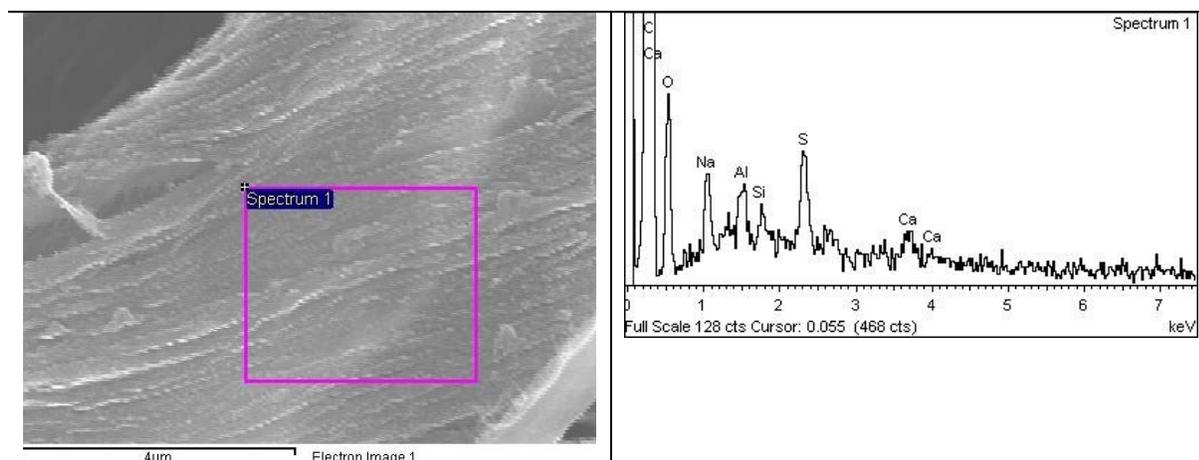
**Figure S17.** TEM images of single PNES strand-wrapped SWNTs in DMF (A)-(C) and methanol (D)-(E) solvents.



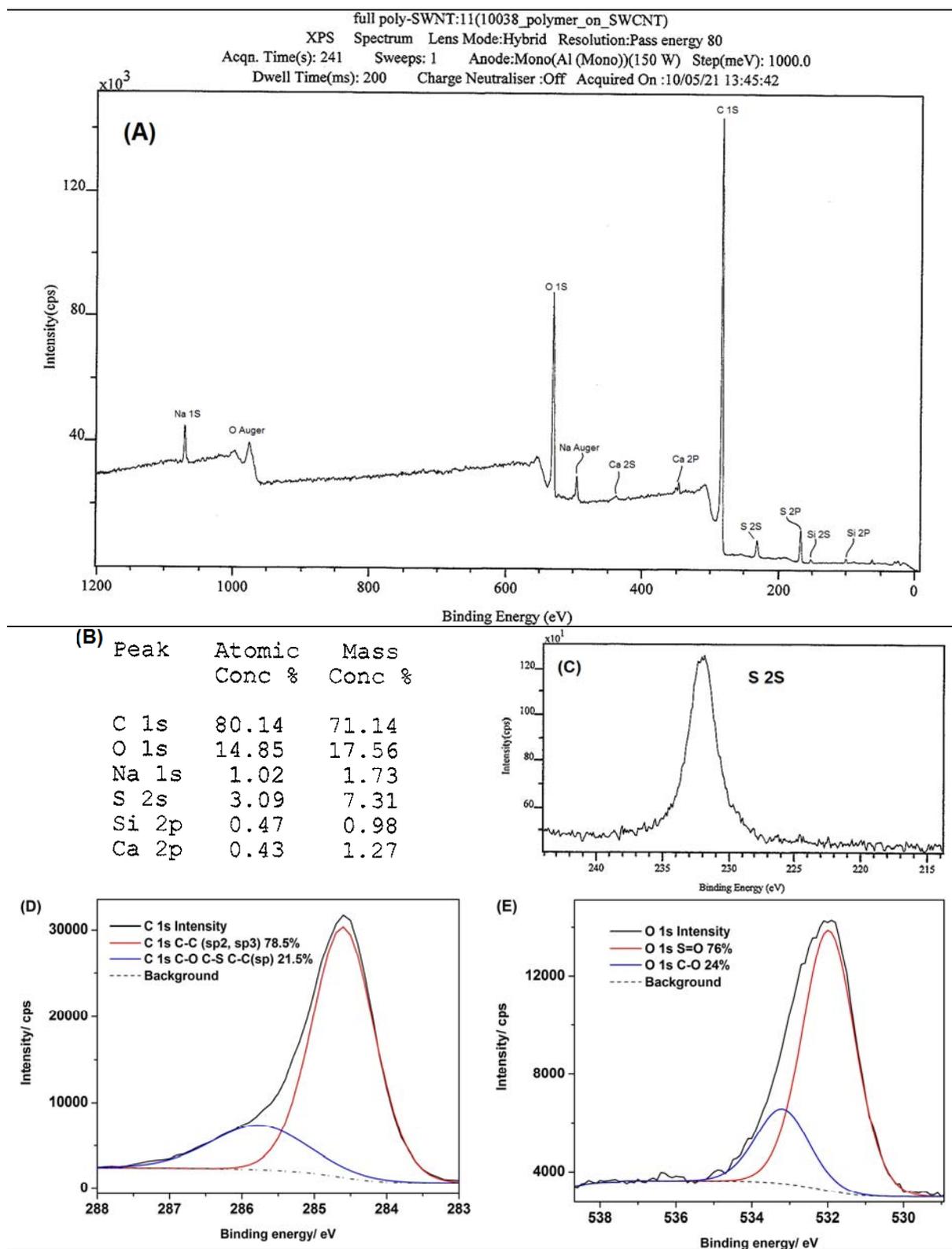
**Figure S18:** SEM image of PNES-wrapped SWNTs obtained from a DMF-solubilized sample (left); the EDS spectrum (right) was taken of the area marked with the purple rectangle. Unbound polymer was removed via several filtration-dissolution cycles as described (see SI experimental section). The source of Fe stems from the raw SWNTs used for this study, while the Ca, Si and Al were determined to derive from the glass vial used during the sonication process. These data clearly show S, O, and Na elemental signatures that derive from the SWNT-solubilizing PNES polymer.



**Figure S19:** SEM image of PNES-wrapped SWNTs obtained from a water soluble sample (left); the EDS spectrum (right) was taken of the area marked with the purple rectangle. Unbound polymer was removed via several filtration-dissolution cycles as described (see SI experimental section). The source of Fe stems from the raw SWNTs used for this study, while the Ca, Si and Al were determined to derive from the glass vial used during the sonication process. These data clearly show S, O, and Na elemental signatures that derive from the SWNT-solubilizing PNES polymer.



**Figure S20:** SEM image of PNES-wrapped SWNTs obtained from a water-soluble sample (left); the EDS spectrum (right) was taken of the area marked with the purple rectangle. Unbound polymer was removed via size exclusion chromatography [sephacryl (S-500; MW cut off 20-20000 kDa); see SI experimental section for sample preparation details and **Fig. S15** for AFM characterization data. The Fe observed in samples prepared via membrane filtration was successfully removed via SEC; Ca, Si and Al were determined to derive from the glass vial used during the sonication process. These data clearly show S, O, and Na elemental signatures that derive from the SWNT-solubilizing PNES polymer.



**Figure S21:** (A) An XPS survey spectrum and (B) elemental analysis data obtained

from a dried **PNES-SWNT** sample obtained following SEC. See **Fig. S15** for AFM characterization data. Consistent with the EDS study shown in **Fig. S20**, the elemental analysis data obtained from this XPS study show a 1:0.3:4.8:26 ratio of S:Na:O:C, where the expected values for single-chain helical polymer wrapping are 1:1:4:27 (9 polymer and ~18 SWNT carbon atoms are expected for HipCo tubes per each sulfur atom). The slightly higher oxygen ratio can be attributed to the presence of silica/silicate, as Si and Ca were determined to derive from the glass vials used for sonication and sample processing (see above). The pH (3.65) of the **PNES-SWNT/H<sub>2</sub>O** suspension used in this study confirms partial protonation of the sulfonate groups, which accounts for the reduced relative abundance of Na. Note that this purification process successfully removes the Fe-catalyst that was present in samples prepared via the filtration-dissolution method (**Fig. S16-19**). (C) High resolution XPS spectra of S-2s. (D) High resolution XPS spectra of C-1s; the deconvoluted C-1s signal shows 21% of the C atoms (BE= 285.8 eV) are bound to oxygen, sulfur and sp-carbons, which is close to the expected value (~20%). (E) High resolution XPS spectra of O-1s; the deconvoluted spectra shows ~one fourth of the total oxygen corresponds to that for a C-O bond (BE 533.2 eV), as expected.

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