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First-Order Hyperpolarizabilities of Chiral, Polymer-Wrapped Single-Walled Carbon Nanotubes

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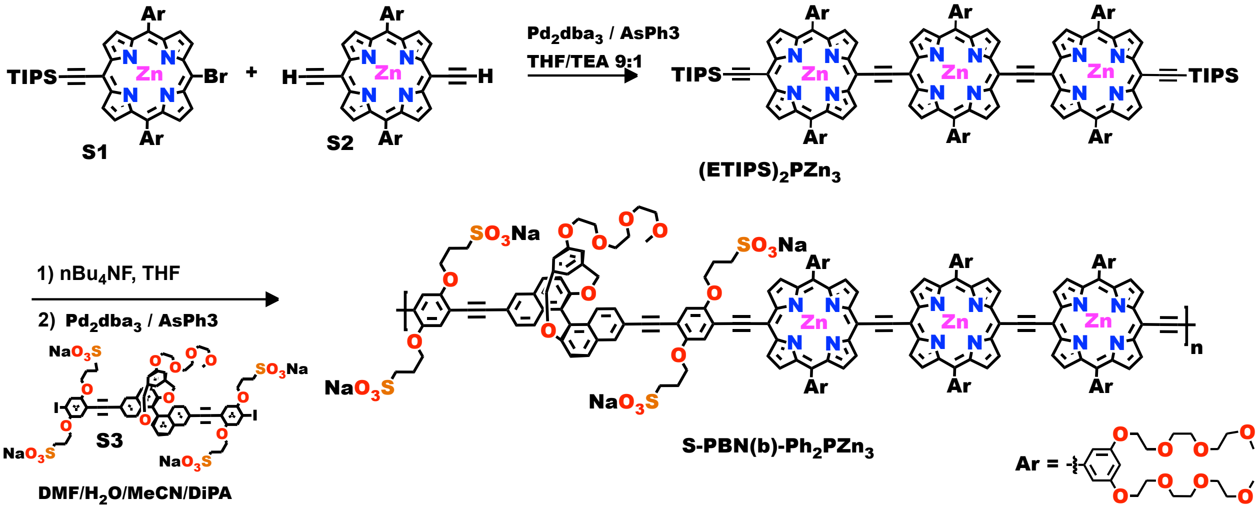
Contents:

1) Materials and Instrumentation

Materials: All manipulations were carried out under argon previously passed through an O_2 scrubbing tower (Schweitzerhall R3-11G catalyst) and a drying tower (Linde 3-Å molecular sieves) unless otherwise stated. Air-sensitive materials were handled in a Braun 150-M glove box. Standard Schlenk techniques were employed to manipulate air-sensitive solutions. Solvents utilized for chromatography in this work were obtained from Fisher Scientific (MeOH and DCM, ACS grade) and Aldrich (THF, HPLC grade). Dry, deoxygenated solvents were obtained from a solvent purification system (Puresolv™, Innovative Technologies, Inc.). Triethyleamine (TEA) was obtained from Aldrich dried over KOH pellets and distilled under argon. The NMR solvent, $CDCl_3$, was used as received. Tris(dibenzylideneacetone)-dipalladium(0) (Pd_2dba_3) and triphenylarsine ($AsPh_3$) were purchased from Strem Chemicals and stored in the glovebox. Solvents were degassed by at least three freeze-pump-thaw cycles or degassed via Ar purging. Column and preparative size exclusion chromatography were performed on the bench top, using respectively silica gel (Silicycle, 230–400 mesh) and Bio-Rad Bio-Beads SX-1 as media. (5,15-Diethynyl-10,20-bis[3,5-bis(9-methoxy-1,4,7-trioxanonyl)phenyl]porphinato)zinc(II) was synthesized according to published procedures.[1] (5-Bromo-15-triisopropylsilylethynyl-10,20-bis[3',5'-bis(9-methoxy-1,4,7-trioxanonyl)phenyl]porphinato)zinc(II) was synthesized following established procedures for the synthesis of asymmetric porphyrin derivatives.[2, 3] The bridged, ionic BINOL monomer was synthesized according to published procedures.[4]

Instrumentation: Free, unbound polymers in each polymer/SWNT sample were removed using a GE/ÄKTApurifier HPLC system (GE Healthcare Bio-Science AB, Björkgatan, Uppsala, Sweden) equipped with two preparative columns (160x16 mm each; stationary phase: sephacryl S-500 and S-200) connected in a series in the order S-500 and S-200. The HPLC system uses a three-wavelength detection unit (each ranging from 200-700 nm; *vide infra*), to determine fractions without SWNTs. Electronic spectra were recorded on a Varian 5000 UV/vis/NIR spectrophotometry system. All spectroscopic measurements were carried out at 23 ± 1 °C. Transmission electron microscopy images (JEOL TEM-2010; accelerate voltage, 200 kV) were obtained from samples prepared via drop casting on lacy Formvar copper grids stabilized with carbon followed by drying in desiccators overnight. Atomic force microscopy (AFM; Digital Instruments Dimension 3100) images were obtained via intermittent contact mode (scan rate = 0.6 Hz, ambient temperature) using super-sharp Si-tips (FORTA-SS-10 from AppNano; tip radius < 5 nm, cantilever resonant frequency ~70 kHz). AFM samples were prepared by drop-casting SWNT suspensions on Si wafer surfaces (cleaned with acetone and 2-propanol); such samples were then desiccator-dried overnight. AFM data are presented with a 1st order plane fit. 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 Kα 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. NMR spectra were recorded on a 400 and 500 MHz AC-Bruker spectrometer. Chemical shifts for ^1H NMR spectra are relative to residual protium in the deuterated solvents ($CDCl_3$ = 7.24 ppm, D_2O = 4.75 ppm). ^{13}C NMR spectra are also referenced to deuterated solvents ($CDCl_3$ = 77.23 ppm, DMSO-d_6 as 39.35 ppm). All *J* values are reported in Hertz. MALDI-TOF mass spectroscopic data were obtained with a Perspective Voyager DE instrument (Department of Chemistry, Duke University). Microwave-assisted reactions were performed using an Emrys Personal Chemistry System (Biotage).

2) Synthetic Procedures

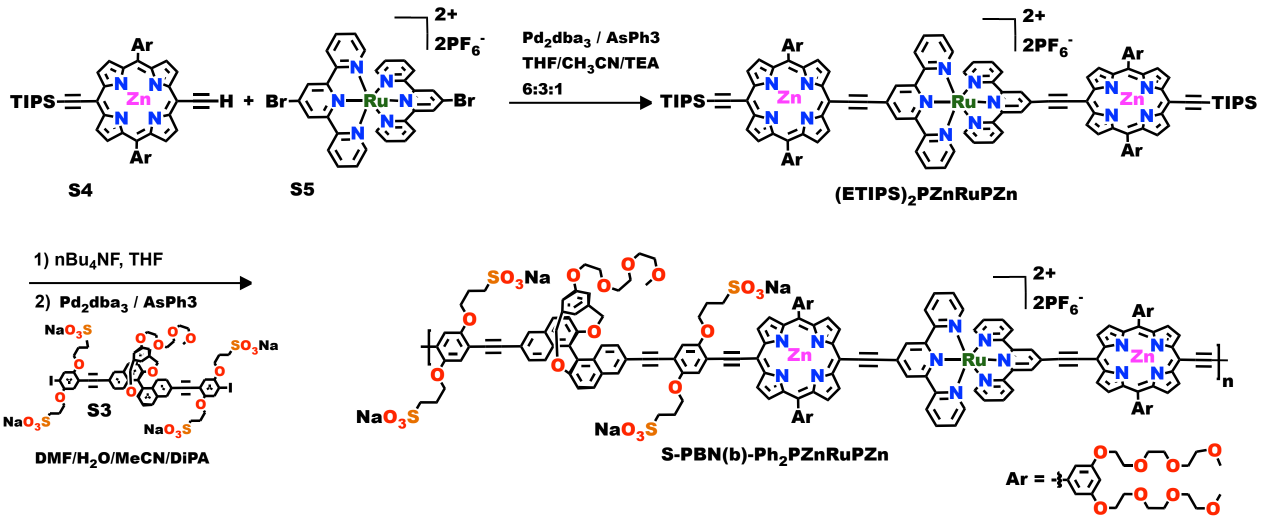


Scheme 1. Synthesis of the NLO active ***S*-PBN(b)-Ph$_2$PZn$_3$** polymer.

(5,15-Bis[(15’-triisopropylsilylethynyl-10’,20’-bis[3’’’,5’’’-bis(9’’’’-methoxy-1’’’’,4’’’’,7’’’’-trioxanonyl)phenyl]porphinato)zinc(II)ethyn-5’-yl]-10,20-bis[3’,5’-bis(9’’-methoxy-1’’,4’’,7’’-trioxanonyl)phenyl]porphinato)zinc(II) (ETIPS)$_2$PZn$_3$). A 250 mL round-bottom flask equipped with a magnetic stirbar was charged with (5-bromo-15-triisopropylsilylethynyl-10,20-bis[3’,5’-bis(9-methoxy-1,4,7-trioxanonyl)phenyl]porphinato)zinc(II) (393 mg, 0.27 mmol) and dried under vacuum. This flask was inserted into a glovebox, and $Pd_2(dba)_3$ (57 mg, 0.06 mmol) and $AsPh_3$ (165 mg, 0.54 mmol) were added, following which the flask was sealed with a septum and brought out of the glovebox. To these solids was added approximately 75 mL of a deoxygenated 9:1 mixture of THF:TEA via cannula. In a separate flask, vacuum dried (5,15-diethynyl-10,20-bis[3,5-bis(9-methoxy-1,4,7-trioxanonyl)phenyl]porphinato)zinc(II) was dissolved in approximately 75 mL of the same deoxygenated solvent mixture and this solution was cannulated into the reaction flask. The reaction was heated at 50 °C for 18 h. The reaction was then cooled, poured into H_2O, and extracted with DCM two times. The organic layers were combined, washed with brine, dried over magnesium sulfate, and filtered. The filtrate was evaporated to dryness under vacuum. The crude material was chromatographed on silica gel using

2.5-5% MeOH in DCM as the mobile phase. The desired fractions were collected and dried under vacuum, dissolved in THF, and further purified by size-exclusion chromatography using SX-1 as the stationary phase. The product band was isolated, evaporated to dryness, and chromatographed one more time on silica using 2.5-5% MeOH in DCM. The desired band was collected and dried under vacuum to yield 418 mg of desired compound **$(ETIPS)_2PZn_3$** (57% yield, based on the (5-bromo-15-triisopropylsilylethynyl-10,20-bis[3',5'-bis(9-methoxy-1,4,7-trioxanonyl)phenyl]porphinato)zinc(II) starting material). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.44 (d, 8H,J = 4.3 Hz), 9.68 (d, 4H, J = 4.5 Hz), 9.25 (d, 4H, J = 4.3 Hz), 9.21 (d, 4H, J = 4.3 Hz), 8.96 (d, 4H, J = 4.5 Hz), 7.53 (4H), 7.46 (8H), 6.72 (4H), 6.64 (2H), 4.15 (m, 16H), 4.01 (m, 8H), 3.69 (m, 16H), 3.49 (m, 24H), 3.35 (t, 16H), 3.29 (m, 8H), 3.14 (m, 8H), 3.03 (m, 16H), 2.92 (m, 8H), 2.83 (m, 16H), 2.78 (m, 8H), 2.67 (s, 24H), 2.64 (s, 12H), 1.44 (m, 42H). MALDI-TOF: m/z = 3926.5830 [$(M+H)^+$] (calcd 3925.60).

Synthesis of *S*-PBN(b)-Ph_2PZn_3. The binaphthalene-based ionic conjugated polymer was synthesized via a Sonogashira polycondensation reaction following a modified literature procedure.[4, 5] 125 mg of the **$(ETIPS)_2PZn_3$** precursor was dried under vacuum for 30 min, following which 40 mL of dry THF was added via cannula and stirred until all the starting material was fully dissolved. Tetrabutylammoniumfluoride (0.12 mL, 1M in THF) was added dropwise via syringe and the solution was stirred at r.t. under argon for 45 min. The reaction was poured into H_2O and extracted three times with DCM. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under vacuum. The crude compound was purified by silica gel chromatography using 5% MeOH in DCM as eluent. The dark brown deprotected (**E_2PZn_3**) product was isolated, confirmed by NMR, and immediately carried on to the next reaction without further purification/analysis. **E_2PZn_3** (94 mg, 0.026 mmol), the bridged, ionic BINOL monomer **S3** (46 mg, 0.028 mmol), Pd_2dba_3 (3 mg, 0.003 mmol), and $AsPh_3$ (10 mg, 0.03 mmol) were brought together in a 25 ml microwave tube and dissolved in an aqueous solvent mixture of DMF (2.5 mL), H_2O (2.5 mL), ACN (13 mL) and diisopropylamine (2.5 mL) that was previously degassed via argon purging for 4.5 h. The reaction mixture was stirred at 160 °C for 1 h under microwave irradiation. The reaction mixture was then stirred in an oil bath at 60 °C for 16.5 h under argon. A degassed DMSO solution (2 mL) of [4-iodo-1-(3-propoxy-sulfonicacid)benzene]sodium salt (2.8 mg, 0.008 mmol) was added and stirred at 60 °C for 2 h, following which phenylacetylene (4.6 mg, 0.04 mmol) was added and stirred for an additional 1 h at 60 °C. The reaction mixture was cooled to room temperature, and the crude product was precipitated by pouring the reaction mixture into 500 mL of 7:2:1 diethyl ether:acetone:ACN. The precipitate was collected and dissolved in 5.5:3.5:1 H_2O:ACN:THF and filtered through a glass frit to remove insoluble black metallic and organic impurities. The filtrate was collected, concentrated to ~20 mL, and precipitated again by pouring into 500 mL of 3.5:1:5 diethyl ether:acetone:ACN. The precipitate was collected, dissolved in 5.5:3.5:1 H_2O:ACN:THF, and filtered through a hydrophilic PTFE 0.22 μm membrane (Millipore, FGLP). The filtrate was collected, and a concentrated buffer solution was added before passing through a size exclusion column (3.8 x 32 cm) packed with a sephacryl-based separatory medium S-100 (Sigma Aldrich, MW fractionation range globular proteins 1 × 10^3 - 1× 10^5) using a buffered aqueous solvent mixture (5.5:3.5:1 H_2O:ACN:THF, 5 mM carbonate; 15 mM NaCl) as eluent. The size exclusion chromatography enabled separation of the polymeric products from the starting materials; the front running polymeric band was collected in fractions and analyzed by GPC. Fractions with an estimated M_n > 10 kDa were combined and desalted via centrifuging through a Microcon centrifugal filter YM-100 (Millipore, Bedford, MA) while washing (5 x 5 mL) with H_2O. The concentrated polymer solution was collected and dried to obtain 74 mg of the desired polymeric product as a glassy film. GPC of the resulting polymer demonstrated a M_n = 12 kDa corresponding to an average of 2.2 repeating units per polymer strand. Vis (4:6 CH_3CN:H_2O, log ε, Fig S12A): 399 nm (5.05), 460 (5.32), 490 (5.26), 808 (4.99); XPS (neat; Fig. S3-S4), obtained atomic con%: O:C:S:N:Zn = 20.60 : 74.06 : 1.06 : 2.65 : 0.50 (expected: 21.7 : 73.8 : 1.05 : 3.52 : 1.17); high resolution XPS: C1s BE of 284.5 eV (42%, expected 38%, for C bound to sp^2 and sp^3), 286.4 eV (58%, expected 62%, for C bound to O and S, and sp C); O 1s BE of 531.2 eV (14%, expected 17%, for O bound to S), O 1s BE of 532.7 eV (86%, expected 83%, for O bound to sp^2 and sp^3 C); N1s BE 398.30 eV. FTIR (solid, ATR, Fig. S11A): 3409 (hydrated sulfonate); 2918 (C_{Ph}-H, str.); 2872 (C_{alk}-H, str.; 1583; 1493, 1430 (C≡C ring str.); 1429 (CH_2 scissoring); 1343 (S-O, assym. str. + CH_2 bending); 1234 (C_{Ph}-O- C_{alk}, sym. str.); 1200 (C_{alk}-O-C_{alk}, assym. str.); 1170 (C_a-N str. C_b-H bend); 1102 (S-O, sym. str.); 1100 (C_{Ph}-O- C_{alk}, sym. str.); 1069, 1028 (C_{alk}-O- C_{alk}, sym. str.); 988; 947; 852; 825; 792; 711; 688; 608; 593; 521 cm^{-1} (various C-H bending, C-S str.).



Scheme 2. Synthesis of the NLO active ***S*-PBN(b)-Ph_2PZnRuPZn** polymer.

Ruthenium(II) bis[5-(4'-ethynyl-(2,2';6',2"-terpyridinyl))-10,20-bis(2,6-bis(3,3- dimethyl-1-butyloxy)phenyl)-15-(Trisisopropylsilylethynyl)porphinato)zinc(II)] bis(hexafluorophosphate) [(ETIPS)$_2$PZnRuPZn]. One equivalent of **Ru(brtpy)$_2$** (60 mg, 0.059 mmol) and 2.2 equivalents of **S4** (180 mg, 0.130 mmol) were placed in an appropriately sized Schlenk flask equipped with a magnetic stirbar. 0.25 equivalents of $Pd_2(dba)_3$ (14 mg, 0.0149 mmol) and 2.5 equivalents of $AsPh_3$ (46 mg, 0.149 mmol) were added under nitrogen atmosphere in a glovebox. A solvent mixture consisting of freshly-opened HPLC grade 6:3:1 MeCN:THF:triethylamine was degassed by a stream of dry argon for approximately 30 minutes. An appropriate volume (~100 mL) of this solvent mixture was added to the reaction vessel via cannula, and the resulting mixture was heated on an oil bath at 55 °C overnight (approximately 14 h), or until the starting materials were consumed as shown by thin layer chromatography (90:9:1 MeCN:water:saturated aqueous KNO_3 as eluent). The reaction mixture was then cooled to room temperature and concentrated to dryness by rotary evaporation. The crude product was purified by column chromatography using 90:9:1 MeCN:water:saturated aqueous KNO_3 as eluent; the product eluted generally second, following a small quantity of fast-moving homo-coupled butadiyne-bridged porphyrin side-product, as a dark brown band. The desired fractions were combined and concentrated, but not to dryness. Excess ammonium hexafluorophosphate was added, followed by enough water to cause the precipitation of a dark brown-green solid, which was isolated by filtration, and washed successively with water and diethyl ether to yield the desired product. Additional column chromatography was performed if the level of purity was unsatisfactory by NMR spectroscopy. (Yield = 153 mg, 72% based on the $Ru(brtpy)_2$ starting material). ^1H NMR (500 MHZ, CD_3CN): δ 10.10 (d, 4H, J = 4.6 Hz), 9.52 (s, 4H), 9.41 (d, 4H, J = 4.3 Hz), 9.18 (d, 4H, J = 4.6 Hz), 8.94 (m, 8H), 8.22 (td, 4H, J =7.7 Hz, J = 1.4 Hz), 7.92 (t, 4H, J = 8.6 Hz), 7.68 (d, 4H, J = 6.1 Hz), 7.43 (td, 4H, J = 6.4 Hz, J = 1.2 Hz), 7.32 (s, 8H), 4.15 (m, 16H), 3.69 (m, 16H), 3.48 (m, 16H), 3.35 (m, 32H), 3.29 (m, 16H), 2.87 (s, 24H), 1.44 (m, 42H). MS MALDI-TOF m/z : 3463.96 [$(M+PF_6)^+$] (calcd 3462.20).

Synthesis of *S*-PBN(b)-Ph_2PZnRuPZn. The binaphthalene-based ionic conjugated polymer was synthesized via a Sonogashira polycondensation reaction following a modified literature procedure.[4, 5] **(ETIPS)$_2$PZnRuPZn** (75 mg, 0.021 mmol) was dried under vacuum for 30 min, and approximately 40 mL of dry THF was added to dissolve the material. Tetrabutylammoniumfluoride (0.12 mL, 1M in THF) was added dropwise via syringe and the solution was stirred at rt under argon for 45 min. The reaction was poured into H_2O and extracted three times with DCM. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under vacuum. The crude compound was purified by silica gel chromatography using 90:9:1 MeCN:water:saturated aqueous KNO_3 as eluent. The dark brown product (**E_2PZnRuPZn**) band was isolated, confirmed by NMR, and immediately carried on to the next reaction without further purification/analysis. **E_2PZnRuPZn** (62 mg, 0.019 mmol), the bridged, ionic BINOL monomer **S3** (36 mg, 0.022 mmol), Pd_2dba_3 (3 mg, 0.003 mmol), and $AsPh_3$ (10 mg, 0.03 mmol) were brought together in a 25 ml microwave tube and dissolved in an aqueous solvent mixture of DMF (2.5 mL), H_2O (2.5 mL), ACN (13 mL) and diisopropylamine (2.5 mL) that was previously degassed via argon purging for 4.5 h. The reaction mixture was stirred at 160 °C for 1 h under microwave irradiation. The reaction mixture was then stirred in an oil bath at 60 °C for 16.5 h under argon. A degassed DMSO solution (2 mL) of [4-iodo-1-(3-propoxy-sulfonicacid)benzene]sodium salt (3.5 mg, 0.010 mmol) was added and stirred at 60 °C for 2 h, followed which phenylacetylene (4.6 mg, 0.04 mmol) was added, and the reaction mixture stirred for an additional 1 h at 60 °C. The solution was cooled to room temperature, and the crude product was precipitated by pouring the reaction mixture into 500 mL of 7:2:1 diethyl ether:acetone:ACN. The precipitate was collected and dissolved in 5.5:3.5:1 H_2O:ACN:THF and filtered through a glass frit to remove insoluble black metallic and organic impurities. The filtrate was collected, concentrated to ~20 mL, and precipitated again by pouring into 500 mL of 3.5:1:5 diethyl ether:acetone:ACN. The precipitate was collected, dissolved in 5.5:3.5:1 H_2O:ACN:THF, and filtered through a 200 nm membrane. The filtrate was collected and concentrated buffer solution was added before passing the material through a size exclusion column (3.8 x 32 cm) packed with a sephacryl-based separatory medium S-100 (Sigma Aldrich, MW fractionation range globular proteins 1×10^3 - 1×10^5) using a buffered aqueous solvent mixture (5.5:3.5:1 H_2O:ACN:THF, 5 mM carbonate; 15 mM NaCl) as eluent; the front running polymeric band was collected as 10 fractions of 25 ml each. The 1st 4 fractions that contain the longest polymeric strands (retention time 12.02 min. Figure S5) corresponding to a M_n = 20.1 kDa corresponding to an average of 4.6 repeating units per polymer strand; these fractions were desalted via centrifuging through a Microcon centrifugal filter YM-100 (Millipore, Bedford, MA) while washing (~7 x 5 ml) with aqueous solvent mixture (4:6 CH_3CN:H_2O) containing no salt. After evaporation, 40 mg of the desired polymeric product as a glassy film was obtained. Vis-NIR, (4:6 CH_3CN:H_2O, log ε; Fig. S12B): 314 nm (5.04), 460 (5.30), 529 (4.83), 710 (5.02). XPS (neat; Figure S1-2), obtained atomic con%: O:C:S:N:Zn:Ru = 19.35 : 76.95 : 0.95: 2.12: 0.18: 0.10 (expected: 18.40 : 73.66 : 1.30 : 4.04: 0.66: 0.33); FTIR (solid ATR, cm^{-1}; Fig. S11B): 3412 (hydrated sulfonate); 2915 (C_{Ph}-H, str.); 2866 (C_{alk}-H, str.); 1639 (C=N, str), 1586, 1498, 1430 (C≡C ring str.); 1458 (CH_2 scissoring); 1342 (S-O, assym. str. + CH_2 bending); 1299 (C_{Ph}-O- C_{alk}, sym. str.); 1201 (C_{alk}-O-C_{alk}, assym. str.); 1170 (C_a-N str. C_b-H bend); 1125 (S-O, sym. str.); 1100 (C_{Ph}-O- C_{alk}, sym. str.); 1066, 1066 (C_{alk}-O- C_{alk}, sym. str.); 946, 848, 823, 787, 709, 667, 608, 519 cm^{-1} (various C-H bending, C-S str.).

Chirality enriched [(6,5) SWNTs] suspensions. Sodium cholate (SC) dispersions of carbon nanotubes were prepared using the standard ultrasonication centrifugation technique;[4-8] a 20 ml aqueous solution of SC (2 wt%) was sonicated with 8 mg of CoMoCat SWNTs with a tip horn sonicator (20 kHz; 12 W total power; @ 0°C and centrifuged (90000 g; 0.5 h, 2x). The upper 60% of the suspension volume was collected and used as the starting material in a two-cycle, density gradient ultracentrifuge (DGU) separation technique[9] that utilizes a step-gradient, composed of 30% (3 ml) and 12% (1.5 ml) iodixanol density gradient layers, and a mixed surfactant system (0.4 and 1.6 wt% SDS and SC, respectively).

General procedure for the synthesis of polymer-wrapped [(6,5) SWNT] superstructure. A procedure identical to that previously published was employed.[5, 9, 10] An aqueous suspension of chirality enriched [(6,5) SWNTs] (10 mL) was added over a course of 3 h to a 10 mL solution of the corresponding polymer (3:7 MeOH:H_2O, 0.5 mg/ml). The mixture was stirred overnight and was exchanged into a 5 mM carbonate/15 mM NaCl buffer (pH ~9) using a Microcon centrifugal filter YM-100 (Millipore, Bedford, MA). Free, unbound polymer was removed via gel permeation chromatography: a 2 mL polymer/SWNT solution (SWNT concentration of ~0.5 mg/ml) was injected into a series of two preparative columns (160x16 mm each) loaded with sephacryl-based separatory medium connected in the order of S-500 (Sigma Aldrich; MW fractionation range 40-20000 kDa (dextran) and S-200 (Sigma Aldrich; MW fractionation range 1-80 kDa (dextran)), mounted on a GE/ÄKTApurifier HPLC System (GE Healthcare Bio-Science AB, Björkgatan, Uppsala, Sweden), and eluted with a 5 mM carbonate/15 mM NaCl buffer in 3:7 MeOH:H_2O at a flow rate of 1 ml/min; three-wavelength detection (for all samples, carbon nanotubes were detected at 580 nm; phenylene-based polymers were detected at 315 and 440 nm) was used to identify fractions that did not contain nanotubes. The fractions were collected as 1 ml aliquots; the polymer/SWNT fractions eluted at an earlier time (19-27 min range) followed by the free, unbound polymer (28-48 min range; see Figure S6). Polymer/SWNT-containing fractions (eluting over an 19-27 min range) were collected together and desalted via centrifuging through a Microcon centrifugal filter YM-100 (Millipore, Bedford, MA) while washing (~4x5 ml) with an aqueous solvent mixture (4:6 CH_3CN/D_2O) containing no salt. The volume of the *polymer-wrapped* [(6,5) SWNTs] solution was adjusted to 4 mL (4:6 CH_3CN/D_2O) and the pH was adjusted to ~8 by adding an appropriate amount of 0.1 mM NaOD in D_2O. An exemplary GPC profile of ***S*-PBN(b)-Ph$_2$PZnRuPZn-[(6,5) SWNT]** is presented Figure S6.

3) Figures

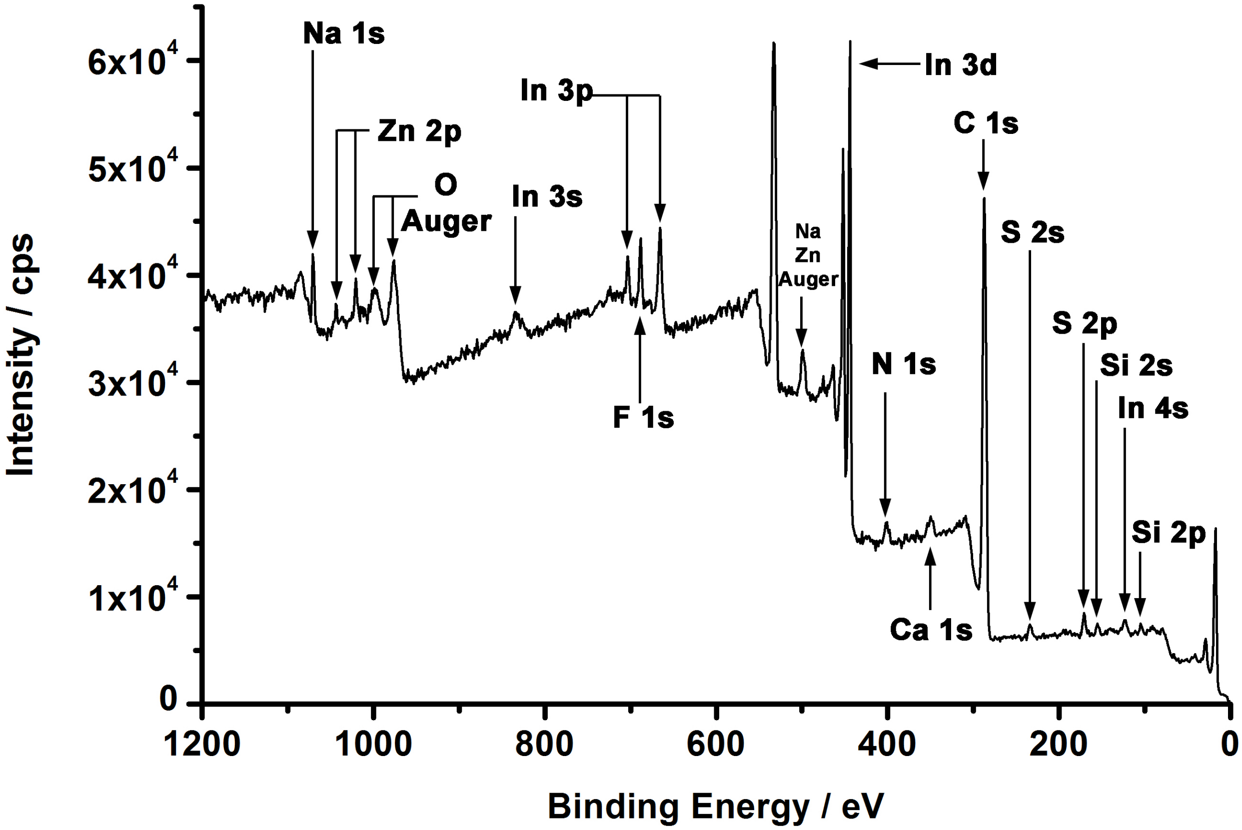


Figure S1: XPS survey spectra of a solid ***S*-PBN(b)-Ph$_2$PZnRuPZn** sample. Note that due to the limited quantity of available material, the analyzed sample has been mounted on an Indium support. Presence of Si and Ca signals trace their genesis to glass vial residue.

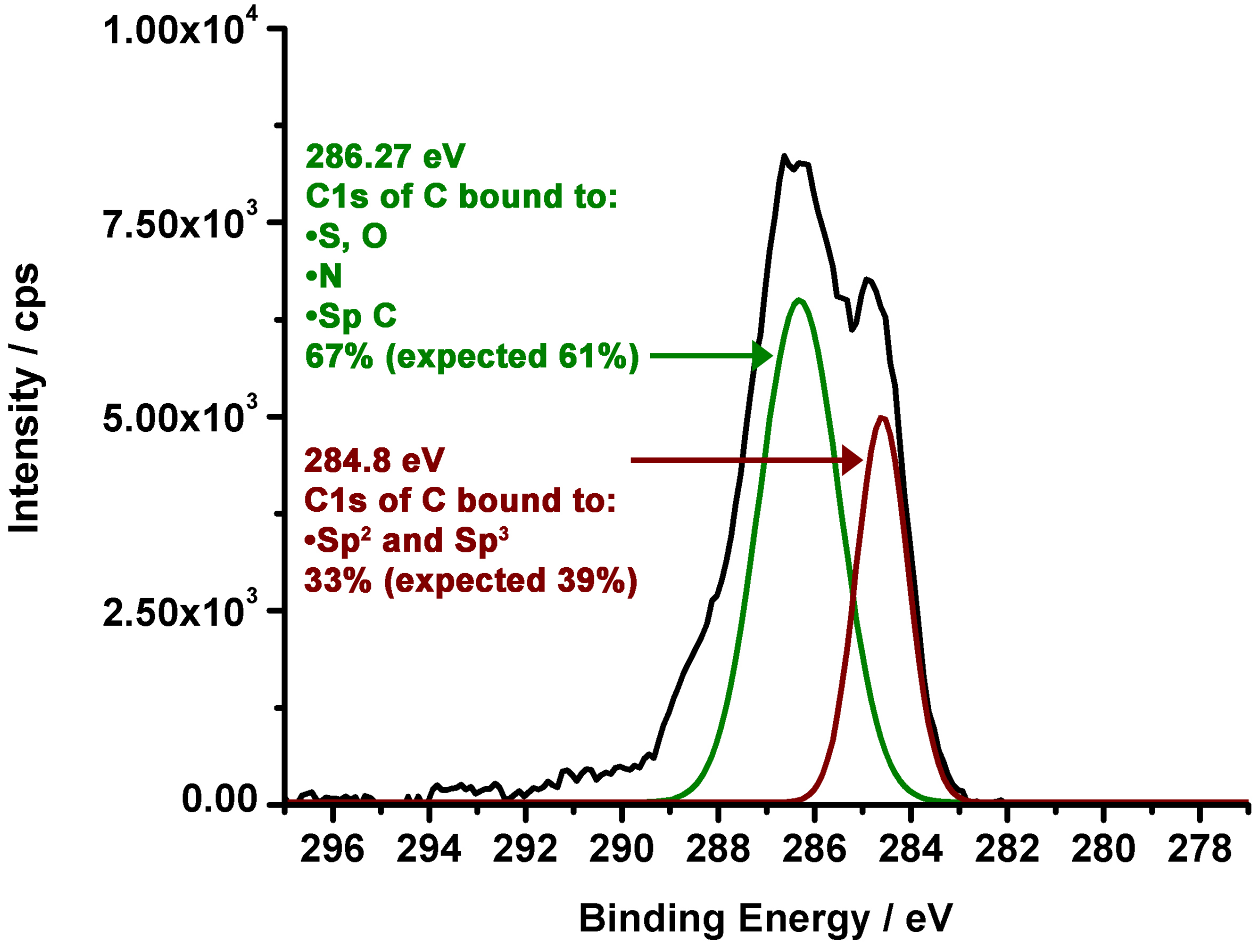


Figure S2. High resolution XPS spectra of ***S*-PBN(b)-Ph$_2$PZnRuPZn** C-1s; Gaussian deconvolution of the C-1s signal analyzes the population of electronically distinct C atoms.

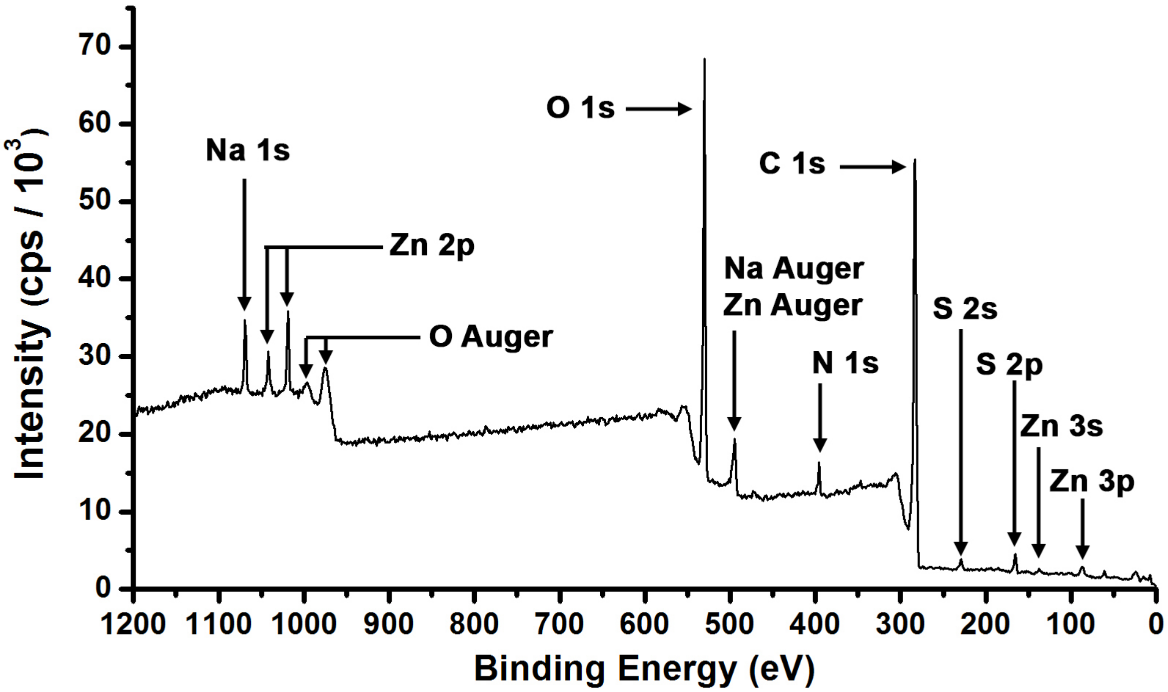


Figure S3. XPS survey spectra of a solid ***S*-PBN(b)-Ph$_2$PZn$_3$** sample.

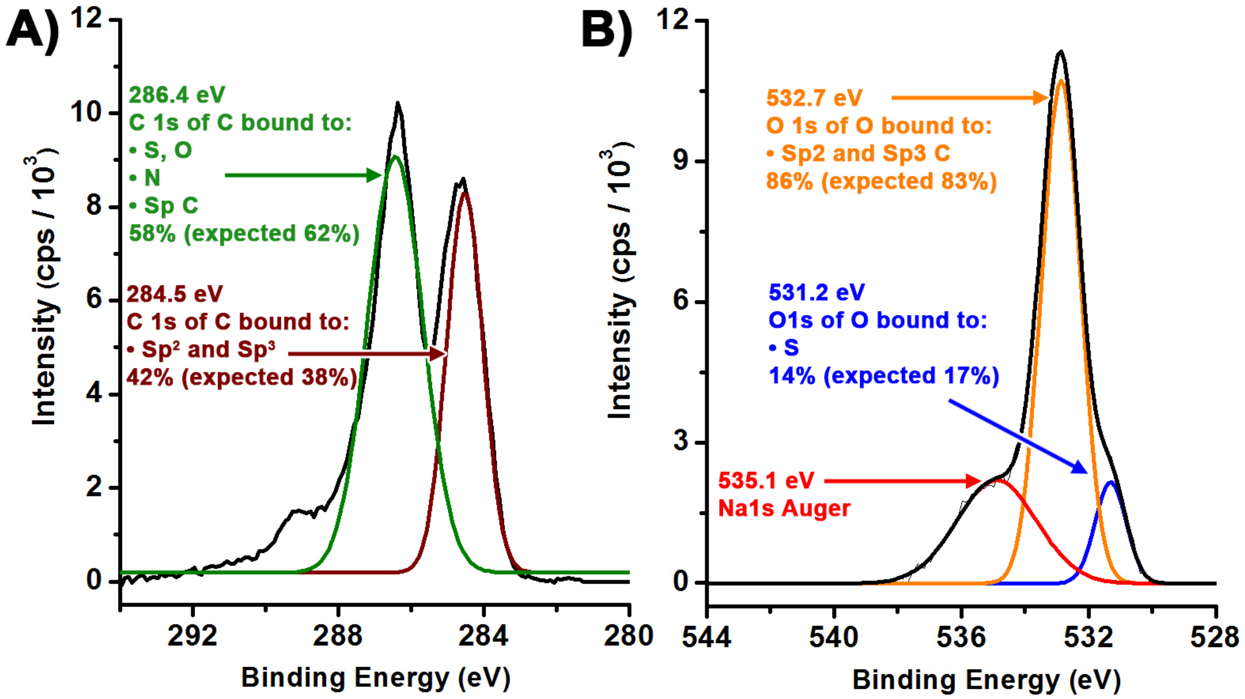


Figure S4. High resolution XPS spectra of ***S*-PBN(b)-Ph$_2$PZn$_3$.** A) C-1s; Gaussian deconvolution of the C-1s signal analyzes the population of electronically distinct C atoms; B) O-1s region; Gaussian deconvolution (Origin 8.1 software) of the N-1s signal determines the populations of electronically distinct O atoms.

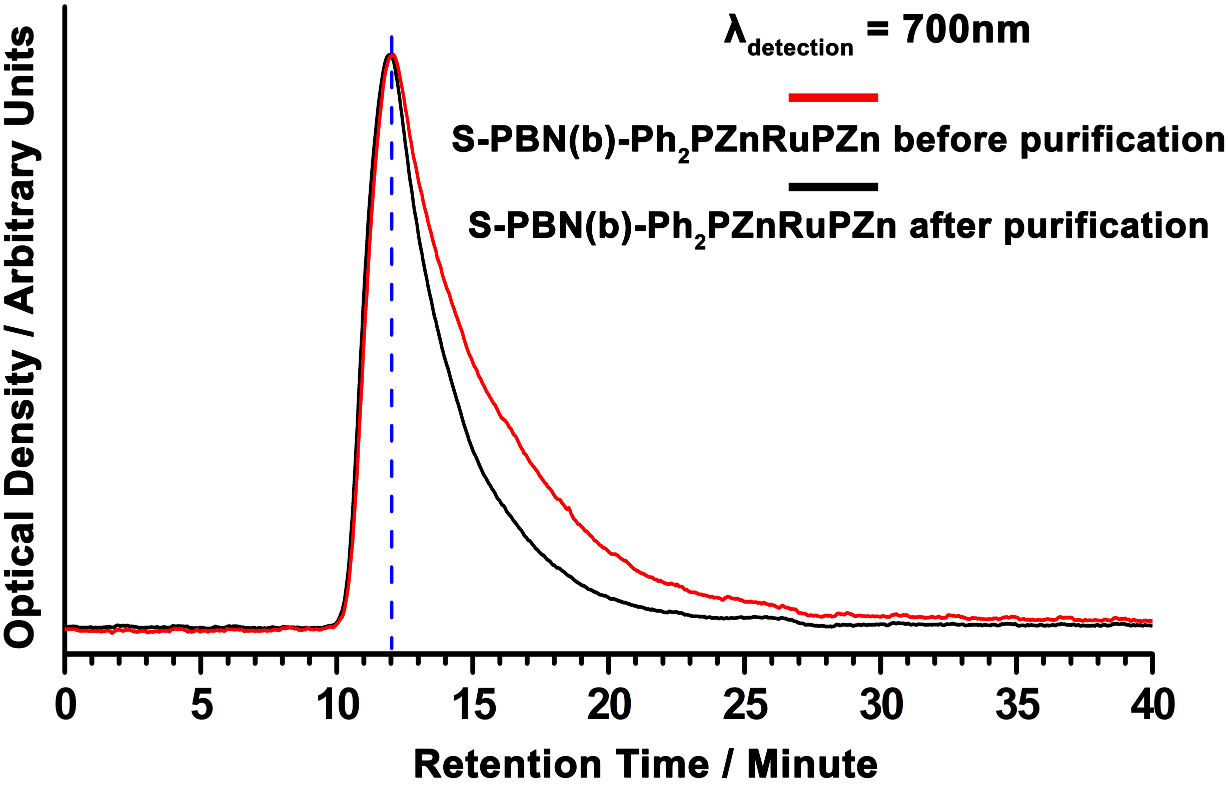


Figure S5. GPC profile of ***S*-PBN(b)-Ph$_2$PZnRuPZn** before (red) and after (black) size exclusion chromatography (Sephacryl S-200); these samples were eluted using a 5 mM carbonate/15 mM NaCl buffer (in 4:6 CH_3CN:H_2O) over a 40 min duration at a flow rate of 1 ml/min.

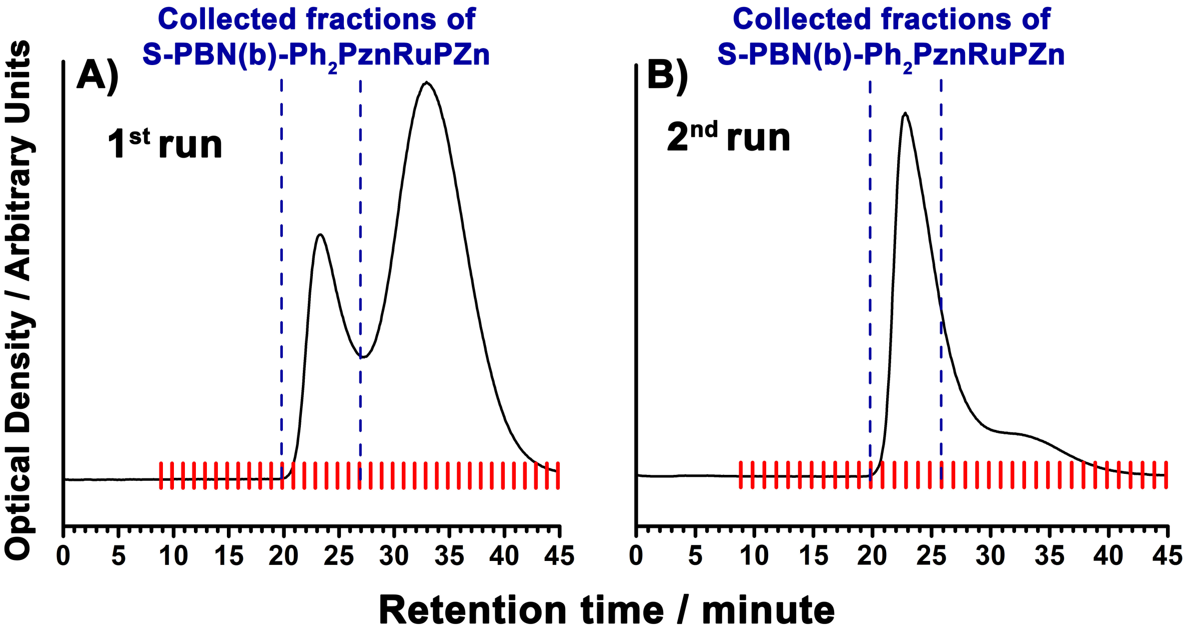


Figure S6. A) GPC profile highlighting the purification of ***S*-PBN(b)-Ph$_2$PZnRuPZn-[(6,5) SWNTs]**. The black traces show detection of polymer and the E_{22} transition of [(6,5) SWNTs] (580 nm). The collected fractions of polymer-wrapped SWNTs correspond to retention times that range from 19-27 min. (blue-dotted line). B) GPC profile after a 2nd run of the fractions collected in a) that highlights complete removal of the unbound polyelectrolyte ***S*-PBN(b)-Ph$_2$PZnRuPZn**.

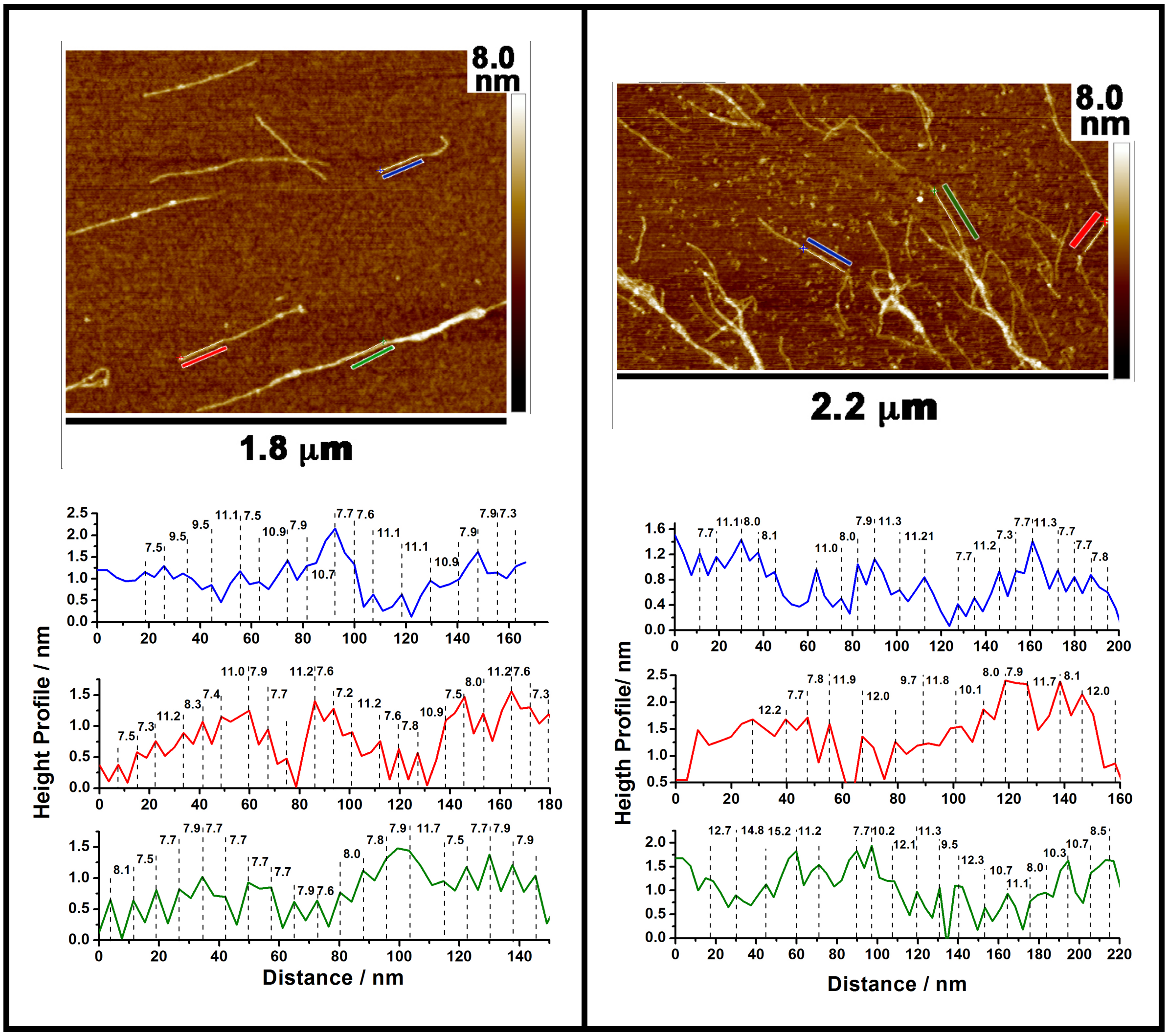


Figure S7. A) Topographic intermittent contact mode AFM images of **S-PBN(b)-Ph$_2$PZnRuPZn-[(6,5) SWNTs]** from a MeCN/D$_2$O solubilized suspension on a Si surface, and corresponding height profiles along the red, green and blue lines. The distance between peak maxima corresponds to the helical pitch length of the polymer (9 ± 2 nm).

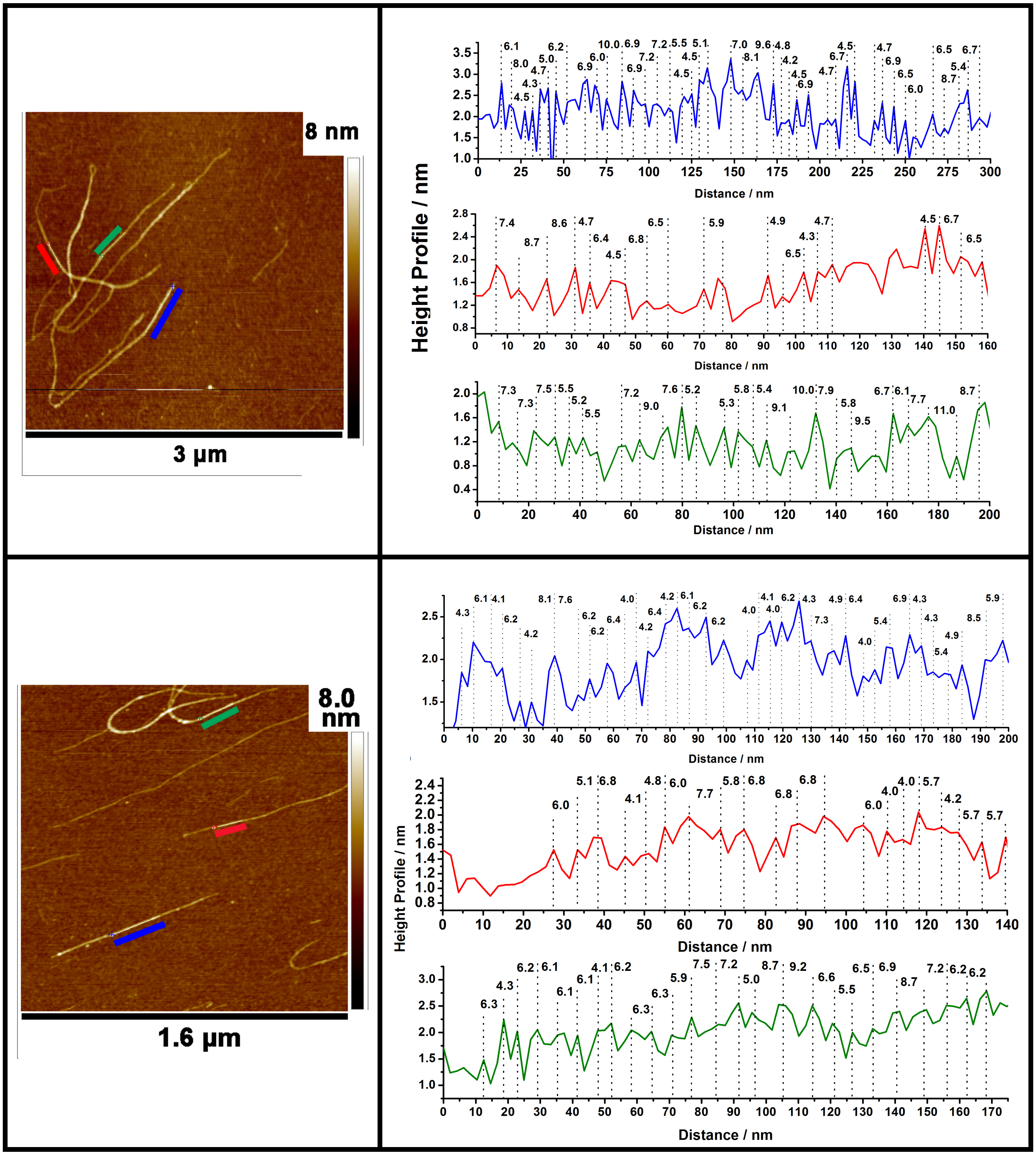


Figure S8. Topographic intermittent contact mode AFM images of ***S*-PBN(b)-Ph$_2$PZn$_3$-[(6,5) SWNTs]** from a MeCN/D$_2$O solubilized suspension on a Si surface, and corresponding height profile along the red, green and blue lines. The distance between peak maxima corresponds to the helical pitch length of the polymer (6 ± 2 nm).

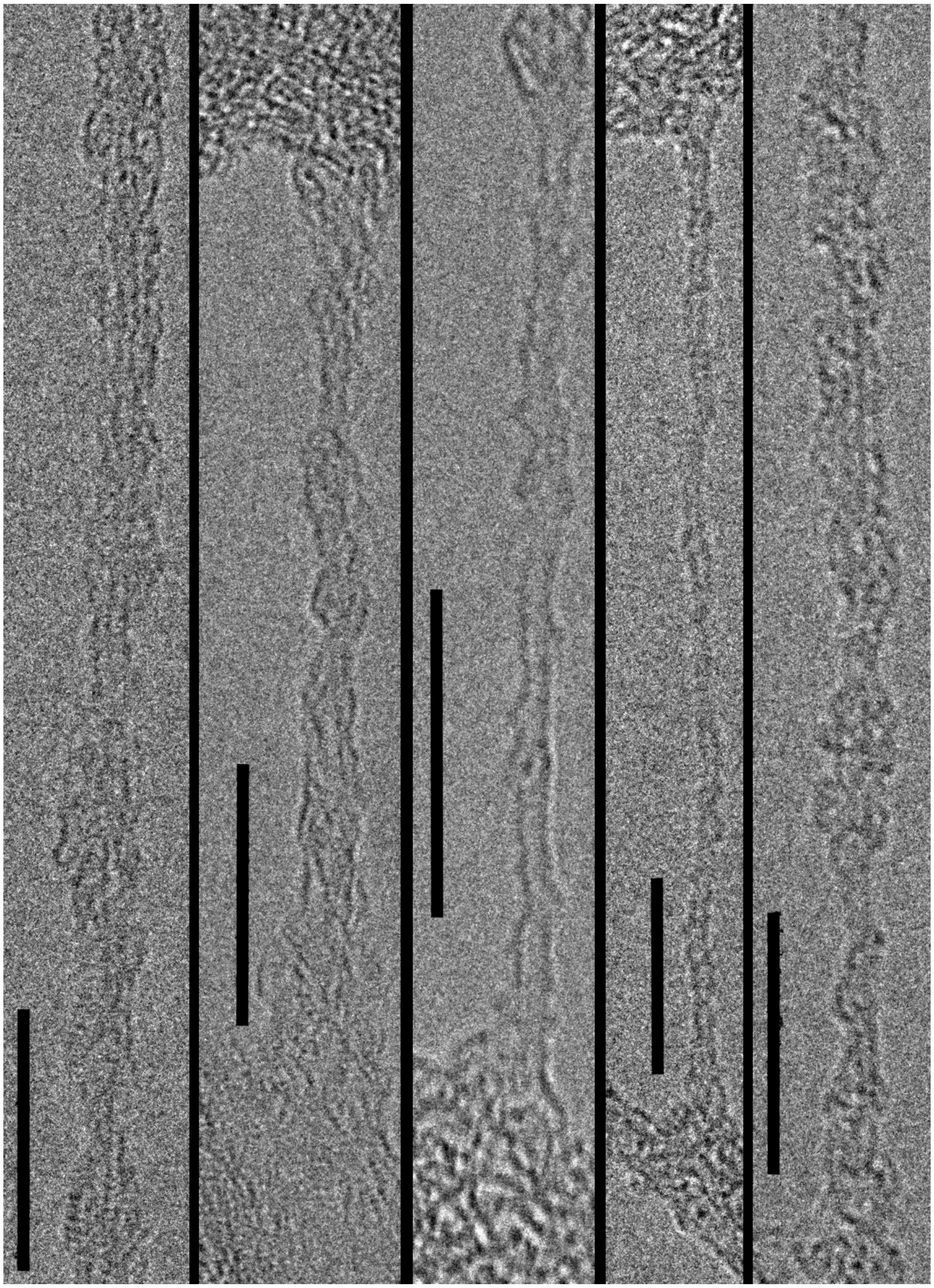


Figure S9. TEM images of ***S*-PBN(b)-Ph$_2$PZnRuPZn** assemblies obtained from aqueous suspension (scale 10 nm).

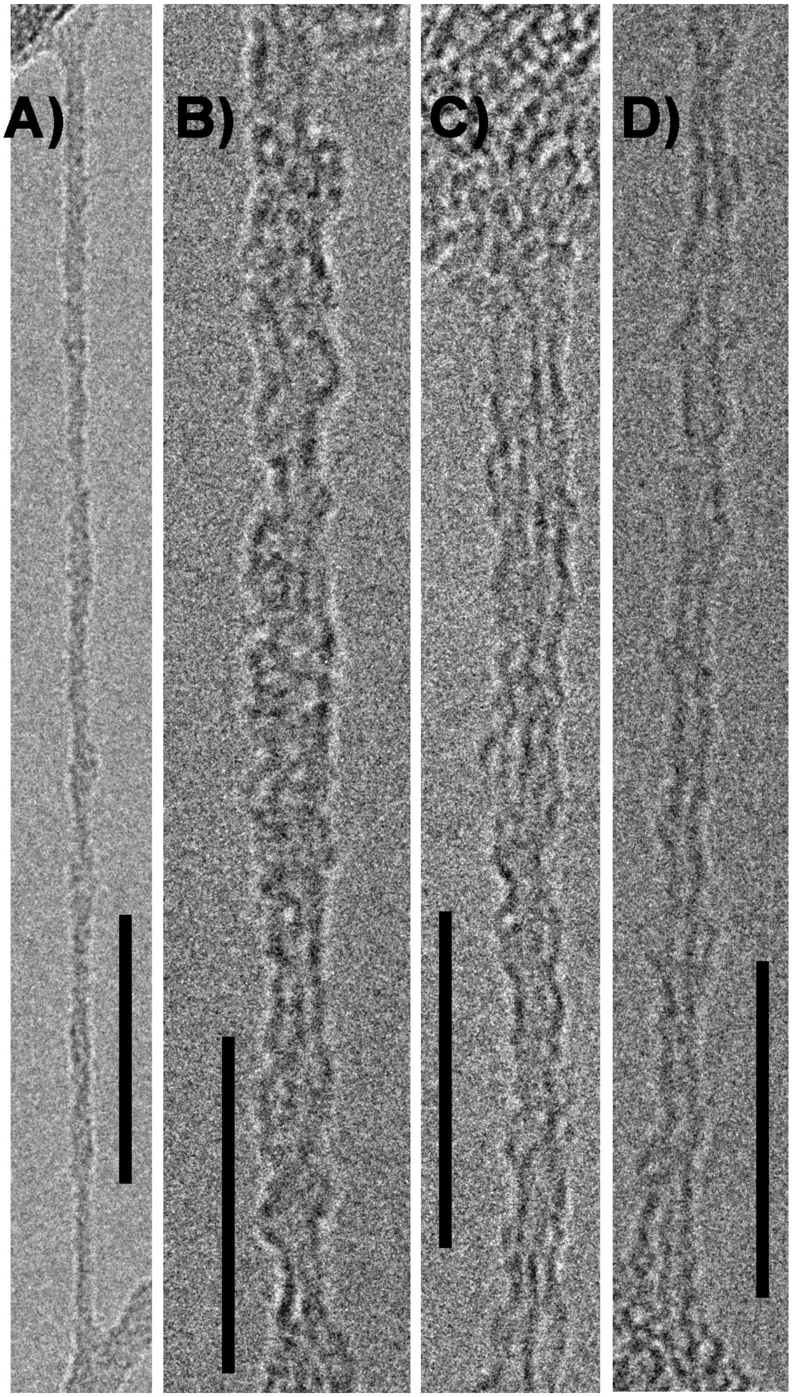


Figure S10. TEM images of ***S*****-PBN(b)-Ph$_2$PZn$_3$** assembly obtained from aqueous suspension (scale : A = 50 nm; B-D = 10 nm).

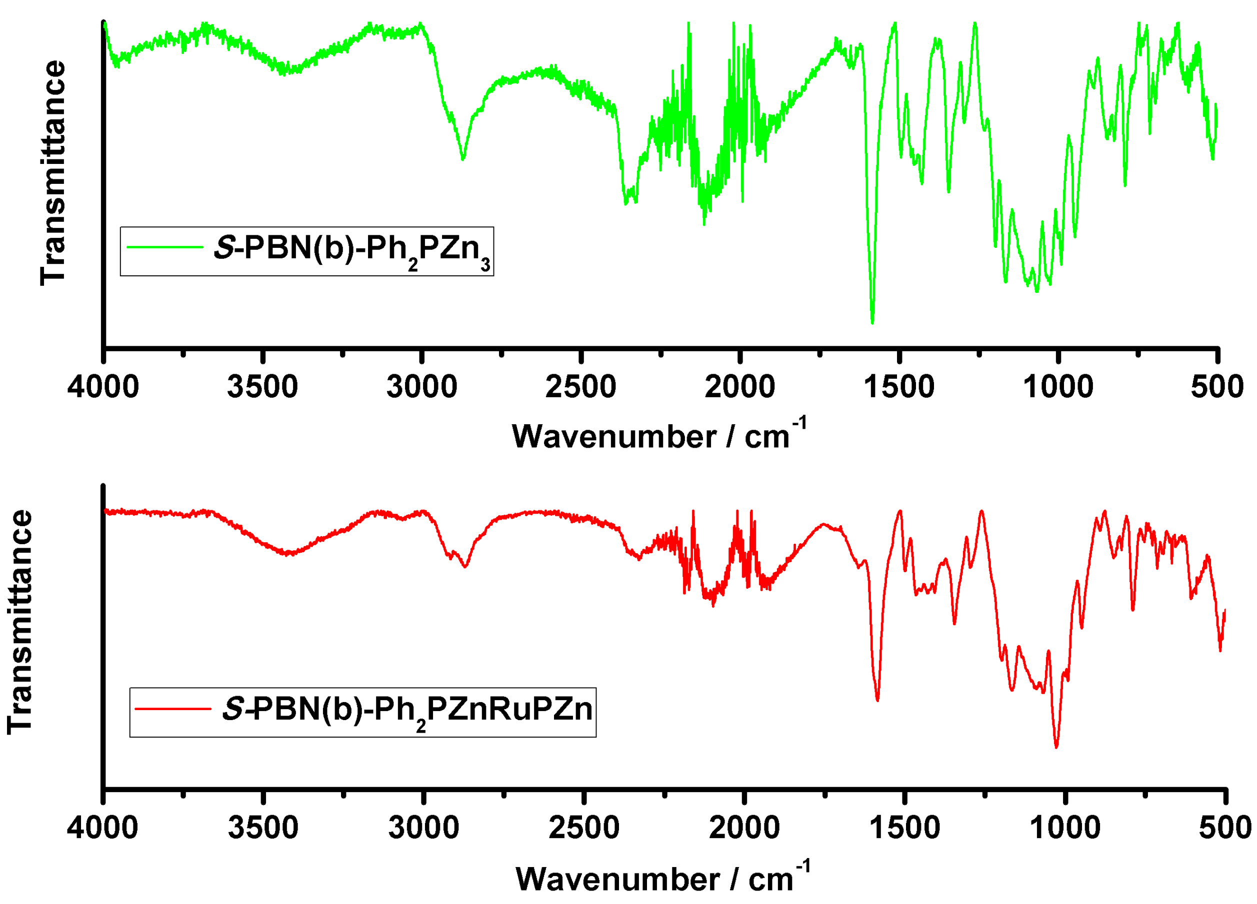


Figure S11: FTIR (ATR) spectra of solid (A) ***S*-PBN(b)-Ph$_2$PZn$_3$**, and (B) ***S*-PBN(b)-Ph$_2$PZnRuPZn**.

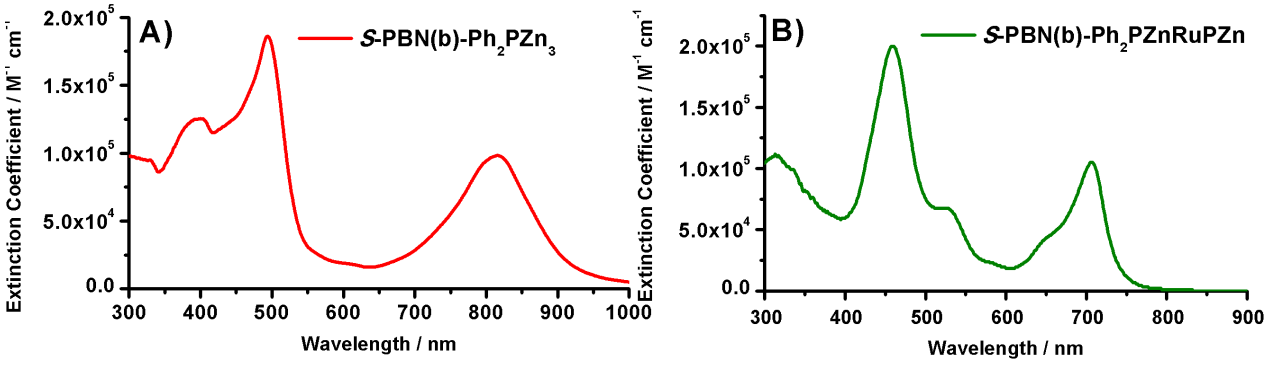


Figure S12: Electronic spectral signature of ***S*-PBN(b)-Ph$_2$PZn$_3$** (A) and ***S*-PBN(b)-Ph$_2$PznRuPZn** (B) polymers recorded in H_2O:CH_3CN 7:3 at 20 °C.

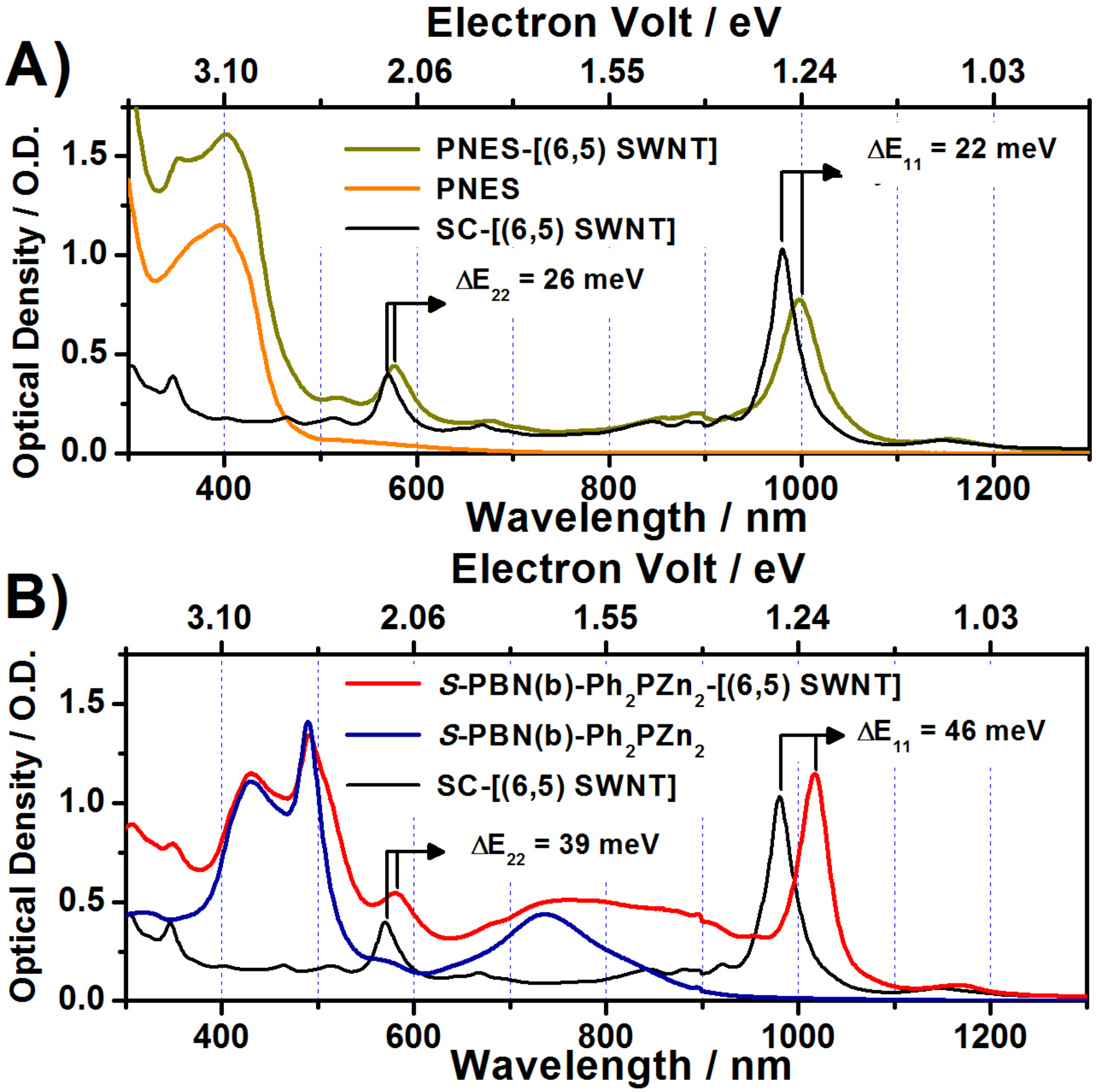


Figure S13. (A) **PNES-[(6,5) SWNTs]** (purple) and the unbound **PNES** polymer (orange) recorded in D_2O solvent; [(6,5) SWNT] = 73.9 nM. (B) ***S*-PBN(b)-Ph$_2$Zn$_2$-[(6,5) SWNTs]** (red) and the unbound ***S*-PBN(b)-Ph$_2$Zn$_2$** polymer (royal) recorded in 2:4:5 THF/MeOH/D_2O solvent; [(6,5) SWNT] = 102.9 nM. Note that in each panel, the spectrum of surfactant-dispersed **SC-[(6,5 SWNTs]** is shown at [(6,5) SWNT] = 94.0 nM. Note that these data show that relative to the **SC-[(6,5) SWNT]** composition the ***S*-PBN(b)-Ph$_2$Zn$_2$-[(6,5) SWNT]** E_{11} and E_{22} transitions are respectively red-shifted by 46 and 39 meV. These bathochromic shifts, double in magnitude to that determined for **PNES-[(6,5) SWNTs],** trace their genesis to the stronger polymer-SWNT electronic interaction in the ***S*-PBN(b)-Ph$_2$Zn$_2$-[(6,5) SWNT]** superstructure enforced by the chiral polymer scaffold.[5] Here the PZn$_2$ Q_x-derived transition manifold of the parent ***S*-PBN(B)-Ph$_2$PZn$_2$** polymer (λ_{max} ~ 735 nm; FWHM = 0.340 eV) extensively broadens (FWHM = 0.502 eV) and red shifts (0.118 eV) in the ***S*-PBN(B)-Ph$_2$PZn$_2$-[(6,5) SWNT]** superstructure.

4) Hyper Rayleigh Light Scattering (HRS) Measurements.

The second-order nonlinear optical responses of the Table S1 materials were probed by femtosecond hyper-Rayleigh scattering.[11, 12] A Spectra-Physics Insight DeepSee femtosecond pulsed laser, tunable from 690 nm to 1300 nm, was used as the light source. In order to maximize the signal to noise ratio, measurements were performed at a fundamental wavelength of 1280 nm. The fundamental light intensity was adjusted using a half-wave plate and an uncoated Glan-Taylor linear polarizer, with a maximum of 700 mW. A small portion of the beam intensity was sent to a photodiode (Hamamatsu G3476-03) using a beam splitter for fundamental beam input intensity monitoring. The laser beam then passed an FEL700 cut-on long pass filter to remove all intensity with wavelengths shorter than 700 nm. The light was focused (aspheric lens f = 8 mm) into the solution and collected at 90° (aspheric achromat f = 30 mm). Having passed the optical filters (KG5), the generated light was sent through a calibrated Bruker Surespectrum 500is spectrometer and detected using an EMCCD (Ixon 897 Andor) cooled to -85 °C.

For this particular study, the nonlinear scattering of a dilution series was compared for the free polymers and for the SWNT-based nanohybrid compositions [based on (6,5) chirality enriched, length-sorted (700 ± 50 nm long) SWNTs ([(6,5) SWNTs]) and chiral polymers that have previously been established to wrap SWNTs in an exclusive left-handed helical fashion], with the response under identical conditions for the reference chromophore disperse red one (DR1) in chloroform, with a reference dipolar hyperpolarizability value at 1280 nm of 54×10^{-30} esu. Differences in local field factor (from the different solvents) were taken into account. Any contribution of multiphoton fluorescence to the second harmonic scattering signal was corrected for by using the spectral HRS approach.[13-15] The difference in spectral width can be exploited to differentiate between the broad multiphoton fluorescence background and the narrow HRS peak. Therefore, the spectrum around the HRS peak is recorded to be able to subtract the fluorescence background. Through spectral deconvolution the response originating from the HRS process can be deduced.

The interpretation of the nonlinear scattering measurements was performed towards a first hyperpolarizability value per monomer repeat unit (β_{mono}) for the free polymers or towards a first hyperpolarizability value per nanotube for the polymer-wrapped (or SC-solubilized) carbon nanotube (β_{SWNT}). SWNT concentrations corresponded to 5.67×10^{-8} M for the *S*-PBN(b)-PZnRuPZn[(6,5) SWNT] sample, 9.98×10^{-8} M for the *S*-PBN(b)-Ph_2PZn_3-[(6,5) SWNT] sample, and 9.00×10^{-8} M for the other samples. The maximal polymer concentration of PNES was 1.4×10^{-5} M, and ranged between 2 and 5×10^{-6} M for the other polymers.

Without correlation, the nonlinear scattering intensity from two independent components is given as

$$I^{(2w)} = g[N_1<\beta_{HRS,1}>^2 + N_2<\beta_{HRS,2}>^2]$$

with N_1 the number density of component i and $\beta_{HRS,1}$ its corresponding first hyperpolarizability value, and g a proportionality constant taking into account all theoretical and instrumental factors involved. The most frequently involved two-component system is the well-known solvent-solute system, for which the above equation allows for the internal reference method if a value for $\beta_{HRS,solvent}$ is available.[16]

In the case of no correlation between the nonlinearity of the wrapped SWNT, β_{SWNT}, and the nonlinearity of the wrapping polymer, the following relation should hold:

$$<\beta_{SWNT}>^2 = <\beta_{SWNT,SC}>^2 + N_{MRP} <\beta_{mono,wrap}>^2$$

with $\beta_{SWNT,SC}$ the hyperpolarizability of the benchmark sodium cholate dispersed SWNT, N_{MRP} the number of uncorrelated monomer repeat units, and $\beta_{mono,wrap}$ their hyperpolarizability value when wrapped around the SWNT. With N_{MRP} calculated from the concentrations of polymer and the wrapped SWNT in solution, and $\beta_{SWNT,SC}$ (1050 x 10^{-30} esu) experimentally determined, it is possible to calculate $\beta_{mono,wrap}$ from β_{SWNT} for the polymers wrapped around the nanotubes under the assumption of no correlation.

5) Estimation of potential bulk susceptibility values, $\chi^{(2)}_{xyz}$ for polymer-wrapped SWNT solid-state materials.

Based on the formula noted in reference 22 of this contribution, and on the values provided in Table 1, the unit cell volume is estimated as 10^{-21} cm³. A number density of 10^{21} multiplied by the value of the molecular hyperpolarizability per nanotube of ~10^{-27} esu gives 10^{-6} esu for the bulk $\chi^{(2)}_{xyz}$, the order of magnitude estimate of the scale of the $\chi^{(2)}$ reported in reference 22. This estimate neglects the wavelength dependence and the factors that arise from conversion of the β_{HRS} to a β_{xyz} and from the specific summation of the molecular β_{xyz} towards a bulk $\chi^{(2)}_{xyz}$.

6) Table S1

Table S1: Ground-state electronic spectral data for ***S*-PBN(b)-Ph$_2$PZn$_2$-[(6,5) SWNT]**, ***S*-PBN(b)-Ph$_2$PZn$_3$-[(6,5) SWNT]**, and ***S*-PBN(b)-Ph$_2$PZnRuPZn-[(6,5) SWNT]** superstructures, the benchmark **SC-[(6,5) SWNT]** and **PNES-[(6,5) SWNT]** samples, and corresponding unbound semiconducting polymers.

Opto-Electronic Material	**Prominent Polymer Electronic Transition**	**(6,5) SWNT Electronic Transitions ($\lambda_{max;}$ FWHM)**	**Opto-Electronic Material**	**Prominent Polymer Electronic Transition**	**(6,5) SWNT Electronic Transitions ($\lambda_{max;}$ FWHM)**
SC- [(6,5) SWNT]		**E_{11}** = 980 nm (1.26 eV); (E_{11} FWHM = 42 meV) **E_{22}** = 570 nm (2.17 eV); (E_{22} FWHM = 87 meV) **E_{33}** = 346 nm (3.58 eV); (E_{22} FWHM = 138 meV)	***S*-PBN(b)-Ph$_2$PZn$_3$**	**B_y** = 399 nm (3.11 eV) **B_x** = 490 nm (2.53 eV) **Q_x** = 808 nm (1.53 eV); (^1Q_x FWHM = 245 meV)	
PNES	**π-π*** = 400 nm (3.1 eV)		***S*-PBN(b)-Ph$_2$PZn$_3$-[(6,5) SWNT]**	**B_y** = 402 nm (3.08 eV) **B_x** = 502 nm (2.47 eV) **Q_x** = 901 nm (1.38 eV); (^1Q_x FWHM = 180 meV)	**E_{11}** = 1022 nm (1.21 eV); (E_{11} FWHM = 45 meV) **E_{22}** = 580 nm (2.14 eV) **E_{33}** = 349 nm (3.55 eV)
PNES-[(6,5) SWNT]	**π-π*** = 403 nm (3.08 eV)	**E_{11}** = 998 nm (1.24 eV); (E_{11} FWHM = 66 meV) **E_{22}** = 576 nm (2.15 eV); (E_{22} FWHM = 115 meV); **E_{33}** = 352 nm (3.52 eV)			
***S*-PBN(b)-Ph$_2$PZn$_2$**	**B_y** = 432 nm (2.87 eV) **B_x** = 490 nm (2.53 eV) **Q_x** = 735 nm (1.69 eV); (^1Q_x FWHM = 340 meV)		***S*-PBN(b)-PZnRuPZn**	**B_x** = 460 nm (2.69 eV) **MLCT** = 529 nm (2.34 eV) **Q_x =** 710 nm (1.75 eV)eV; (^1Q_x FWHM	
***S*-PBN(b)-Ph$_2$PZn$_2$-[(6,5) SWNT]**	**B_y** = 431 nm (2.88 eV) **B_x** = 491 nm (2.52 eV) **Q_x** = 790 nm (1.57 eV) (^1Q_x FWHM = 502 meV)	**E_{11}** = 1017 nm (1.22 eV); (E_{11} FWHM = 50 meV) **E_{22}** = 580 nm (2.14 eV) **E_{33}** = 349 nm (3.55 eV)	***S*-PBN(b)-PZnRuPZn-[(6,5) SWNT]**	**B_x** = 469 nm (2.64 eV) **MLCT** = 530 nm (2.34 eV) **Q_x** = 718 nm (1.73 eV); (^1Q_x FWHM = 154meV)	**E_{11}** = 1011 nm (1.23 eV); (E_{11} FWHM = 45 meV) **E_{22}** = 585 nm (2.12 eV) **E_{33}** = 350 nm (3.54 eV)

7) References

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