Supplementary Information

Explicating conjugated polymer extraction used for the differentiation of single-walled carbon nanotubes

Dominik Just^{1,*}, Tomasz Wasiak¹, Andrzej Dzienia¹,

Karolina Z. Milowska^{2,3}, Anna Mielańczyk¹, Dawid Janas^{1,*}

¹ Department of Chemistry, Silesian University of Technology, B. Krzywoustego 4, 44-100,

Gliwice, Poland

² CIC nanoGUNE, Donostia-San Sebastián 20018, Spain

³ Ikerbasque, Basque Foundation for Science, Bilbao 48013, Spain

* Corresponding authors: <u>dominik.just@polsl.pl</u>, <u>dawid.janas@polsl.pl</u>

Table of Contents

1. M	aterials	. 2			
1.1.	Reagents for polymer synthesis	. 2			
1.2.	Single-walled carbon nanotubes	. 3			
2. Methods					
2.1.	Synthesis of 9,9-di-n-dodecylfluorene-2,7-diboronic acid bis(pinacol)ester (PA)	. 3			
2.2.	Polymer synthesis	. 3			
2.3.	CPE process	.4			
2.4.	Modeling details	. 5			
2.4.1. MD simulations					
2.4.2. DFT calculations					
2	4.3. DFTB calculations	.9			
3. Characterization					
3.1.	Nuclear Magnetic Resonance (¹ H NMR)	12			
3.2.	Size Exclusion Chromatography (SEC)	16			
3.3.	Absorption spectroscopy1	17			
3.4.	Deconvolution of absorption spectra	18			
3.5.	PL excitation-emission mapping	19			
4. R	esults	20			
5. Li	terature	29			

1. Materials

The materials used in the experiments were employed in the form that they were supplied. The purity of the reagents, along with the manufacturer and data allowing identification, can be found below.

1.1. Reagents for polymer synthesis

9,9-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (Angene, cat. number: AG0034EZ, CAS: 196207-58-6, purity: 98%), 2,7-dibromo-9H-fluorene (Apollo Scientific, cat. number: OR6144-25g, CAS: 16433-88-8, purity: N/A), 2,7-dibromo-9,9-dihexyl-9H-fluorene (AmBeed, cat. number: A3628950-25g, CAS: 189367-54-2, purity: 97%), 2,7-dibromo-9,9dioctyl-9H-fluorene (Sigma Aldrich, cat. number: 560073-25g, CAS: 198964-46-4, purity: 96%), 9,9-dioctyl-9H-fluorene (AmBeed, cat. number: A79303 4-1g, CAS: 123863-99-0, purity: 97%), 2,7-dibromo-9,9-didecyl-9H-fluorene (AmBeed, cat. number: A202147-25g, CAS: 175922-78-8, purity: 97%), 2,7-dibromo-9,9-didodecyl-9H-fluorene (Angene, cat. number: AG002VYB, CAS: 286438-45-7, purity: 97%), thiophene (Alfa Aesar, cat. number: A13941.18, CAS: 110-02-1, purity: 99%), 2,5-dibromothiophene (AmBeed, cat. number: A137367-10g, CAS: 3141-27-3, purity: 98%), 2,5-dibromo-3-dodecylthiophene (Ambeed, cat. number: A16618 3-25g, CAS: 148256-63-7, purity: 98%), 2,4-dibromothiophene (AmBeed, cat. number: A712271-5g, CAS: 140-92-9, purity: 95%), 3,4-dibromothiophene 3141-26-2, (AmBeed, cat. number: A404368-25g, CAS: purity: 99.85%), bis(pinacolato)diboron (Angene, cat. number: AG0034J4, CAS: 73183-34-3, purity: 98%), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Apollo Scientific, cat. number: OR8775-1g, CAS: 72287-26-4, purity: N/A), Aliquat 336 TG (Alfa Aesar, cat. number: A17247, CAS: 63393-96-4, purity: N/A), tetrakis(triphenylphosphine)palladium – Pd(PPh₃)₄ (Apollo Scientific, cat. number: OR4225, CAS: 14221-01-3, purity: >99%), toluene (Alfa Aesar, cat. number: 19376.K2, CAS: 108-88-3, spectrophotometric grade, purity: >99.7%), (POCH, number: 466400426, CAS: 92112-69-1, hexane cat. purity: 95%), dimethylformamide (Acros Organics, cat. number: 348435000, CAS: 68-12-2, purity: 99.8%, extra dry over molecular sieves AcroSeal®), methanol (CHEMPUR, cat. number: 116219904, CAS: 67-56-1, purity: pure p.a.), ethanol (STANLAB, cat. number: 603-002-00-5, CAS: 64-17-5, purity: 96%), chloroform (STANLAB, cat. number: 062-006-00-4, CAS: 67-66-3, purity: p.a.), ethyl acetate (PureLand, cat. number: CL0S0502-1000, CAS: 141-78-6, purity: 99.9%), acetone (ChemLand, cat. number: 102480111, CAS: 67-64-1, purity: pure p.a.).

1.2. Single-walled carbon nanotubes

This study was conducted using (6,5)-enriched CoMoCAT SWCNTs (Sigma Aldrich, product number: 773735, lot: MKCM5514, purity: 95%-carbon basis) and (7,6)-enriched CoMoCAT SWCNTs (Sigma Aldrich, product number: 704121-1G, lot: MKBZ1157V, purity: 90%-carbon basis), while HiPco SWCNTs (NanoIntegris, lot: HP30-006) were used as a reference.

2. Methods

2.1. Synthesis of 9,9-di-n-dodecylfluorene-2,7-diboronic acid bis(pinacol)ester (PA)

A reaction flask was charged with a magnetic stirrer and the following reactants: bis(pinacolato)diboron (0.4017 g, 0.00158 mol, 2.20 mol. eq.), 9,9-didodecyl-2,7-dibromofluorene (0.5 g, 0.00072 mol, 1.00 mol. eq.), KOAc (0.2822 g, 0.00288 mol, 4.00 mol. eq.), and DMF (20 mL). The reaction mixture was well purged with argon gas, and the catalyst, Pd(dppf)Cl₂ (0.0390 g, 0.00007 mol, 0.10 mol. eq.), was then added. The reaction mixture was stirred vigorously at 80°C for 4h, cooled, poured into water (50 mL), and extracted with chloroform three times (3x50 mL). The organic layer was collected and dried over MgSO₄. The MgSO₄ was then removed by filtration, and the organic layer was evaporated to dryness. The dry product was dissolved in a small amount of hexane and transferred to a chromatography column for separation on silica gel using an eluent mixture of hexane and ethyl acetate at concentrations up to 4%; it was then recrystallized from hot ethanol and filtered to collect the crystals.

2.2. Polymer synthesis

The syntheses of PFO-F, PFO-FH, PFO, PFO-FD, PFO-FDD, PFDD, and PFO-3HT were carried out in accordance with the Suzuki coupling procedure presented below. The structures of the obtained polymers were confirmed using ¹H NMR spectroscopy, and their macromolecular parameters were determined with size exclusion chromatography (SEC). In brief, organoboron derivative PA (9,9-di-n-alkylfluorene-2,7-diboronic acid bis(pinacol)ester, purity: 98%) (0.500 g, 0.763 mmol, 1.00mol. eq.) and a sufficient amount of dibromo derivative PB (9,9-dialkyl-2,7-dibromofluorene purity: 96%) (0.418 g, 0.763 mmol, 1.00 mol. eq. eq.) were added to the high-pressure glass reaction vessel. The reactor was then filled with 1M Na₂CO₃ solution (12 mL) and toluene (12 mL). Three drops of Aliquat 336 phase transfer catalyst (PTC) were added. The mixture was purged with argon for 30 min, and subsequently, Pd(PPh₃)₄ (0.022g, 0.019 mmol, 0.025 eq.) was added. The reaction mixture

was stirred vigorously at 80°C for 3 days. Afterward, the reaction mixture was cooled down, diluted with 250 mL of chloroform, and washed four times with 150 mL of water. The organic phase was collected and dried with anhydrous MgSO₄, which was then removed by filtration. The collected material was evaporated to dryness and dissolved in a sufficient volume of chloroform (till all the solid particles dissolved). The final product was precipitated in methanol. The fibrous polymer was collected by filtration, washed twice with 50 mL of freezing methanol, and finally twice with 50 mL of freezing acetone.

Name	Common descrp.	Polymer no.	PA	PB	PB no.	
Poly[2,7-(9,9'-dioctylfluorene)-co-alt-2,7- (fluorene)]	PFO-F	P1	9,9-di-n-octylf bi	9,9	2,7-dibromofluorene	PB1
Poly[2,7-(9,9'-dioctylfluorene)-co-alt-2,7- (-9,9'-hexylfluorene)]	PFO-FH	P2-P9		9,9-dihexyl-2,7- dibromofluorene	PB2	
Poly(9,9'-dioctylfluorenyl-2,7-diyl)	PFO	P10-12		9,9-dioctyl-2,7- dibromofluorene	PB3	
Poly[2,7-(9,9'-dioctylfluorene)-co-alt-2,7- (-9,9'-didecylfluorene)]	PFO-FD	P13-14	luoren s(pina	9,9-didecyl-2,7- dibromofluorene	PB4	
Poly[2,7-(9,9'-dioctylfluorene)-co-alt-2,7- (-9,9'-didodecylfluorene)]	PFO- FDD	P15	ıe-2,7- col)esi	9,9-didodecyl-2,7- dibromofluorene	PB5	
Poly(9,9-didodecylfluorenyl-2,7-diyl)	PFDD	P16	-dibor ter	9,9-didodecyl-2,7- dibromofluorene	PB6	
Poly[2,7-(9,9'-dioctylfluorene)-co-alt-2,5- (tiophene)]	PFO-T	P17	onic a	2,5-dibromo- thiophene	PB7	
Poly[2,7-(9,9'-dioctylfluorene)-co-alt-2,5- (3-dodecylltiophene)]	PFO- 3DDT	P18	cid	2,5-dibromo-3- dodecylthiophene	PB8	

Table S1 List of synthesized polymers with the various subunits used for the synthesis.

2.3. CPE process

1.5 mg of SWCNTs and 9 mg of polymer were introduced to a 19 mL glass vial. 5 mL of toluene was then added to the mixture and homogenized in a bath sonicator for 15 minutes (Polsonic, Sonic-2, 250 W) at 5°C. Further, more vigorous sonication with a tip sonotrode (Hielscher UP200St ultrasonic generator) was performed to disentangle SWCNTs and wrap them with the conjugated polymer for 8 minutes at a power of 30W. After sonication, the obtained suspension was transferred to 15 mL conical tubes and centrifuged at 10,000 rpm (15,314×g) for 2 minutes to precipitate the bundled and non-wrapped SWCNTs, as well as polymer aggregates. 80% of the generated supernatant containing purified SWCNTs was transferred to a fresh vial and analyzed by UV-VIS spectroscopy and PL excitation-emission mapping. If necessary, a considerable amount of the polymer may be released from the SWCNT surface by filtration using hot toluene.

2.4. Modeling details

2.4.1. MD simulations

The effect of copolymer side chain length on the interaction of the polymers with SWCNTs was investigated using a reactive force field (ReaxFF)¹, as implemented in the QuantumATK numerical package ^{2,3}. The ReaxFF accounted for bond, lone pair, over- and under-coordination stability, valence, double-bond penalty, correction for C_2 and triple body, three-body conjugation, torsion, hydrogen bond, van der Waals, and Coulomb interactions. The van der Waals interactions were described using a distance-corrected Morse potential.

To determine the interactions between the polymers and SWCNTs, we performed a series of molecular dynamics (MD) simulations of two systems containing infinite (6,5) SWCNTs interacting with 10 units of PFO-F (8:0) or 10 units of PFDD (12:12) polymers in toluene and two systems containing PFDD (12:12) polymers interacting with infinite (7,5) or (7,6) SWCNTs in toluene (see Figure 2a and Figure S1). Due to the applied 3D periodic boundary conditions, the simulation boxes contained 5 units of (6,5), (7,5) or (7,6) SWCNTs. The simulation boxes with dimensions sufficient to avoid direct interactions between SWCNT-polymer complex images (5.1 nm, 5.1 nm, and 20.3/22.3/24.0 nm along the X, Y, and Z directions for systems containing (6,5), (7,5) and (7,6) SWCNTs, respectively) were filled with toluene (3,900 molecules for the (6,5)+PFO-F (8:0), 3,800 molecules for the (6,5)+PFDD (12:12), 4,186 molecules for the (7,5)+PFDD (12:12), and 4171 molecules for the (7,6)+PFDD (12:12)) using Packmol⁴.

The MD simulations were performed as follows:

- 1. Both systems were pre-optimized (500 steps) using the FIRE algorithm ⁵.
- 2. MD simulations were first carried out in an NVT ensemble employing the Berendsen thermostat ⁶ at 300 K. Random initial velocities for all the atoms were assigned according to the Maxwell-Boltzmann distribution. The relaxation time of the thermostat was set to 100 fs, and the simulations were carried out with a time-step of 0.1 fs over 0.5 ps (50,000 steps). These simulations were followed by 5 ps (50,000 steps) NPT simulations at 300 K and 1 bar employing the Berendsen thermostat and barostat. The thermostat and barostat relaxation times were set to 100 fs, respectively. The time step was kept the same as for previous simulations. The estimated compressibility of the system relating volume changes to pressure changes

was set to 0.0001 bar⁻¹. The Martyna-Tobias-Klein ⁷barostat and thermostat were then used for 20 ps (2,000,000 steps) NPT simulations, employing the same parameters.

- 3. Next, the models were optimized (2,000 steps) using the L-BFGS algorithm ⁸ and further equilibrated in a microcanonical (NVE) ensemble with a time-step of 0.1 fs over 5 ps (50,000 steps) at 300K and again optimized using the FIRE (2,000 steps) and L-BFGS (1,000 steps) algorithms.
- 4. Simulations described in the second step were repeated twice in case of (6,5) SWCNT or only once in case of (7,5) and (7,6) SWCNTs, with the time step increased to 0.1 fs.

Radial distribution functions were calculated using the data obtained during the last 50 ps of the NPT simulations in the last step. The diffusion coefficients (D) were calculated from the slope of the mean square displacement (MSD) curve of the SWCNT atoms according to MSD(t) = 6Dt, where t is the observation time (t=17 ps for the (6,5)+FDD(12:12) system and 9 ps for the (7,5)+FDD(12:12) and (7,6)+FDD(12:12) systems).

In addition, we performed MD simulations of (6,5) SWCNTs (2 units in the box) interacting with 4 units of PFO-F (8:0) or 4 units of PFDD (12:12) polymers in toluene (1,595 molecules). Calculations followed 1-3 steps described above. In the final step, as for (7,5) and (7,6) SWCNTs, we repeated only once simulations described in the second step with the time step increased to 0.1 fs. Radial distribution functions were calculated using the data obtained during the last 50 ps of the NPT simulations in the last step.



Figure S1 Snapshots of the final configurations for the simulation boxes containing five units of (a) (7,5) SWCNTs interacting with PFDD (12:12) (ten monomers) in toluene (4186 molecules) and (7,6) SWCNTs interacting with PFDD (12:12) (ten monomers) in toluene (4171 molecules). SWCNTs, solvent, and polymer molecules are shown by stick, line, and ball-and-stick models, respectively. For clarity, solvent molecules are drawn with a higher transparency than other components. Also, all carbon atoms constituting the polymer backbone are marked in teal, whereas carbon atoms forming side chains are cyan. PFDD (12:12) interacting with (7,5) and (7,6) prefers to deposit the main polymer chain on the SWCNT surface rather than the alkyl side chains. However, the difference in diffusion coefficients of both SWCNTs (D_(7,5) = 9.77 x $10^{-7} \pm 7.04 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (R²=0.985) vs D_(7,6) = 1.29 x $10^{-5} \pm 1.84 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (R²=0.983)) suggest different preference of PFDD (12:12) for the (7,5) SWCNT compared to the (7,6) SWCNT.



Figure S2 (a) Snapshots of the final configurations for the simulation boxes containing two units of (6,5) SWCNTs interacting with (left) PFO-F (8:0) (four monomers) or (right) PFDD (12:12) (four monomers) in toluene (1,595 molecules). SWCNTs, solvent, and polymer molecules are shown by stick, line, and ball-and-stick models, respectively. For clarity, solvent molecules are drawn with a higher transparency than other components. Also, all carbon atoms constituting the polymer backbone are marked in teal, whereas carbon atoms forming side chains are cyan. (b) The radial distribution function (RDF) of nanotube-polymer carbon atoms for (6,5) SWCNT interacting with either PFO-F(8:0) or PFDD (12:12) polymers. (c) RDF between nanotube carbon and polymer backbone carbon (C_{ring}) atoms, and nanotube carbon and polymer side chain (C_{chain}) atoms for both types of polymers immersed in toluene solution. The difference in interaction between (6,5) SWCNT and PFO-F (8:0) and between (6,5) SWCNT and PFDD (12:12) is less visible for the shorter polymers (cf. RDFs presented in panel b and in Figure 2b).

2.4.2. DFT calculations

The spin-polarized Density Functional Theory (DFT) ^{9,10}calculations for (6,5) SWCNT, (7,5) SWCNT, PFO, PFO-BPy6,6', 2,5DBT, and 2,7DBF were carried out using a generalized gradient approximation (GGA) employing a hybrid non-local exchange and correlation functional (B3LYP ^{11–14}) and double- ζ plus polarization numerical basis (DZP) sets, as implemented in QuantumATK ^{2,15}. Previous studies have shown that the B3LYP functional performs reasonably well in predicting the electronic structure of various nanostructures ^{16–19}.

The DFT calculations of the 2,5DBT and 2,7DBF molecules were performed in the "molecule configuration" mode without any periodic boundary conditions being applied. The Brillouin zone was sampled only at the Γ point, while the density mesh cut-off for real-space integrals was set at 300 Ry. In the case of polymers and SWCNTs, calculations were carried out in "bulk configuration" mode with 1D periodic boundary conditions being applied, so the sampling of the Brillouin zone was increased to $(1 \times 1 \times 3)$ and $(1 \times 1 \times 7)$ k-points, respectively, using the Monkhorst-Pack scheme ²⁰. All the structures were relaxed until the maximum force acting on any atom was lower than 0.004 eV/Å, the maximum stress changed by less than 0.1 GPa, the self-consistent field (SCF) cycle was iterated until the total energy changed by less than 10^{-6} Ha, and the density matrix elements changed by less than 10^{-6} per iteration.

2.4.3. DFTB calculations

The density functional-based tight-binding (DFTB) method²¹ was used to further analyze the differences in the interaction between both polymers and the (6,5) SWCNT. From the final snapshots of MD simulations of systems containing two units of (6,5) SWCNT and only four units of conjugated polymers (shown in Figure S2a), polymer-coated SWCNTs with 8 Å thick toluene layer were extracted. Due to computational constraints, those reduced structures were used as input structures for DFTB modeling. We also performed DFTB calculations for a reference system in which no polymer molecules were present (two units of (6,5) SWCNT covered with 8 Å thick toluene layer; Figure S3a). Slater-Koster parametrization for C, N, S, and H atoms (mio-1-1) was implemented in QuantumATK^{2,3,22-24}. The DFTB calculations included a self-consistent charge correction that considered the charge fluctuations due to interatomic electron-electron interactions. Due to the size of the system, the Brillouin zone was sampled only at the Γ point. The density mesh cut-off was set to 10 Ha for real-space integrals, and the interaction maximum range was set to 10 Å. All systems were relaxed until the maximum force acting on any atom was lower than 0.2 eV/Å and the maximum stress changed by less than 0.03 GPa. The SCF cycle was iterated until the density matrix elements changed by less than 10^{-5} per iteration. During the DFTB calculations, 3D periodic boundary conditions were applied.



Figure S3 DFTB-computed electronic properties of (6,5) SWCNT coated with 8 Å thick toluene layer and (6,5) SWCNT interacting with PFO-F(8:0) or PFDD(12:12) polymers in toluene. (a) Visualizations of all fully optimized systems. SWCNTs, solvent, and polymer molecules are shown by stick, line, and ball-and-stick models, respectively. For clarity,

solvent molecules are drawn with a higher transparency than other components. Also, all carbon atoms constituting the polymer backbone are marked in teal, whereas carbon atoms forming side chains are cyan. (b) Electrostatic difference potential (ΔV_E) plotted as a 1D projection on the z-axis (along SWCNT symmetry axis). ΔV_E is the difference between the electrostatic potential of the self-consistent valence charge density and the electrostatic potential from a superposition of atomic valence densities. SWCNTs and both polymers represented by stick and ball-and-stick models are shown on all cut-planes, while toluene molecules are not shown. (c) The density of states (PDOS) projected on SWCNT, polymers, and toluene for all three systems.

3. Characterization

3.1. Nuclear Magnetic Resonance (¹H NMR)

Proton nuclear magnetic resonance (¹H NMR) spectra of the synthesized monomer and polymers (Figures S4-S10) in CDCl₃ were registered using a Varian Unity Inova spectrometer operating at 400 MHz. ¹H-chemical shifts were measured in δ (ppm), using the chloroform-d residual peak (set at δ 7.26) as a reference. Standard experimental conditions were used.



Figure S4 ¹H NMR spectrum of 2,2'-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) synthesized in-house.



Figure S5 ¹H NMR spectrum of PFO-F synthesized in-house.



Figure S6¹H NMR spectrum of PFO-FH synthesized in-house.



Figure S7¹H NMR spectrum of PFO synthesized in-house.



Figure S8 ¹H NMR spectrum of PFO-FD synthesized in-house.



Figure S9¹H NMR spectrum of PFO-FDD synthesized in-house.



Figure S10 ¹H NMR spectrum of PFDD synthesized in-house.

3.2. Size Exclusion Chromatography (SEC)

The molecular characteristics of the synthesized polymers, i.e., approximate molecular weights and dispersity (Đ) indices, were measured using a Size Exclusion Chromatograph (SEC, Agilent 1260 Infinity) (Agilent Technologies). The setup was equipped with an isocratic pump, autosampler, degasser, a thermostatic box for columns, and a differential refractometer MDS RI Detector. Addon Rev. B.01.02 data analysis software (Agilent Technologies) was employed for data acquisition and processing. Linear polystyrene standards (580–300,000 g/mol) were used for the calibration, enabling the determination of the SEC-calculated molecular weight. A pre-column guard (5 μ m 50 \times 7.5 mm) and two columns (PLGel 5 μ m MIXED-C 300 \times 7.5 mm and PLGel 5 μ m MIXED-D 300 \times 7.5 mm) were used for separation of the analytes. The measurements were conducted using CHCl₃ (HPLC grade) as the solvent (flow rate of the solvent: 0.8 mL/min, room temperature: 30°C). **Table S2.** List of molecular parameters for in-house synthesized polymers.

Name	Common descrp.	Polymer no.	M _N [g/mol]	Mw [g/mol]	Ð
Poly[2,7-(9,9'-dioctylfluorene)- co-alt-2,7-(fluorene)]	PFO-F	P1	2,900	6,330	2.18
	PFO-FH	P2	2,230	3,320	1.49
		P3	2,600	4,500	1.74
		P4	4,060	7,477	1.84
Poly[2,7-(9,9'-dioctylfluorene)-		P5	7,110	12,364	1.74
co-alt-2,7-(-9,9'-hexylfluorene)]		P6	10,470	16,347	1.56
		P7	11,910	18,707	1.57
		P8	11,570	27,811	2.40
		P9	13,920	38,245	2.75
	PFO	P10	8,080	11,310	1.40
Poly(9,9'-dioctylfluorenyl-2,7-		P11	1,880	3,060	1.63
ulyl)		P12	15,610	49,740	3.19
Poly[2,7-(9,9'-dioctylfluorene)-	PFO-FD	P13	3,570	6,010	1.68
co-alt-2,7-(-9,9'-didecylfluorene)]		P14	9,330	23,300	2.50
Poly[2,7-(9,9'-dioctylfluorene)- co-alt-2,7-(-9,9'- didodecylfluorene)]	PFO-FDD	P15	21,900	71,900	3.28
Poly(9,9-didodecylfluorenyl-2,7- diyl)	PFDD	P16	6,920	16,600	2.40
Poly(9,9'-dioctylfluorenyl-2,7- diyl-alt-2,5-tiophene)	PFO-T	P17	3,250	4,230	1.3
Poly(9,9'-dioctylfluorenyl-2,7- diyl-alt-2,5-(3-dodecyltiophene))	PFO- 3DDT	P18	17,800	42,150	2.37



Figure S11 SEM chromatograms of the synthesized polymers.

3.3. Absorption spectroscopy

Optical absorption spectra of freshly-collected supernatants were measured in the wavelength range of 280–1100 nm using a Hitachi U-2910 spectrophotometer and a wider range of 300–1600 nm using a PerkinElmer Lambda 1050 spectrophotometer. A double beam mode was used with a pure solvent cuvette placed in the reference channel. Measurements were performed using 5 mm quartz cuvettes.

3.4. Deconvolution of absorption spectra

Deconvolution was performed using the Voigt function embedded in the PTF Fit application 25 . Due to large redshifts between observed peak positions in organic solvents and the values determined by Weisman in D₂O 26 , it was necessary to tune the reference file to enable accurate peak fitting based on literature data $^{26-28}$. The generated spectral data for a broad range of SWCNT types was used for further analysis. Optical absorbance spectra deconvoluted using this approach are shown below (Figure S12).



Figure S12 Deconvolution of the optical absorbance spectra of SWCNTs dispersed with the specified conjugated polymers (EPS stands for electron-phonon sideband), including the E_{11} and E_{22} transitions as well as the electron-phonon sidebands (EPSs).

3.5. PL excitation-emission mapping

Excitation-emission photoluminescent maps (PL) were acquired using a ClaIR microplate reader (Photonetc, Canada). The data were registered in the ranges of 480–900 nm (excitation) and 900–1600 nm (emission). The results were then visualized using OriginPro 2022 software.

4. Results

4.1. Examination of affinity of polyfluorene derivatives toward specific SWCNT types

We also explored the influence of the SWCNT raw material on the isolation results when using copolymers containing polyfluorene derivatives with different alkyl chains. For this, we selected (6,5)- and (7,6)-enriched CoMoCAT SWCNTs as well as chirally heterogeneous HiPco SWCNTs. As illustrated in Figure S13, these materials contained dissimilar chiral distributions and had a gradually increasing average diameter ((6,5)-enriched < (7,6)-enriched < HiPco SWCNTs).



Figure S13 PL excitation-emission maps of (a) (6,5)-enriched CoMoCAT SWCNTs, (b) (7,6)-enriched CoMoCAT SWCNTs, and (c) HiPco SWCNTs suspended with PFO-3DDT in toluene. (d) Corresponding optical absorbance spectra normalized to the highest intensity peak and offset for clarity.

While the synthesized PFO and PFO-FH exhibited a selective character when processing (6,5)-enriched SWCNTs, the (7,5) rectification level of the generated suspensions was much less apparent in the case of (7,6)-enriched SWCNTs (Figure S14). These samples were notably contaminated with the predominant (7,6) SWCNTs and other minor species. Nonetheless, the preference for (7,5) SWCNTs was evident both in terms of the share of (7,5) SWCNTs in the obtained suspensions (Figure S15a, S15b) as well as when enrichment factors, calculated considering the concentration of individual species in the parent material,

were determined (Figure S15c, S15d). Furthermore, when an even larger raw material (HiPco SWCNTs) was sorted, no signs of chiral enrichment could be discerned (Figure S16). These results highlighted one of the most vital (although typically unmentioned) aspects of the CPE process. Namely, a given polymer may be selective, but its selectivity can only be exploited when used in conjunction with a parent SWCNT material of appropriate chiral distribution.



Figure S14 Optical absorbance spectra of (7,6)-enriched CoMoCAT SWCNTs suspended with the indicated polyfluorene derivatives. Data was normalized to the highest intensity peak and offset for clarity.

Initially, the presence of particular chiralities in the raw materials ((6,5)- and (7,6)-enriched SWCNTs) suspended with non-selective PFO-3DDT was determined by studying the recorded PL maps and optical absorbance spectra (Figure S13; with the assistance of PTF Fit software, as discussed above). Deconvolution of the absorbance data enabled us to estimate the percentage of various SWCNT species in the reference material (Figure S15ab). The compositions of suspensions created using the abovementioned two parent materials and a spectrum of analyzed polymers (PFO-F, PFO-FH, PFO, PFO-FD, PFO-FDD, and PFDD) were determined analogously. We calculated the enrichment factors (EFs, $EF_{(n,m),PFX}$) of specific SWCNTs based on the relative concentration data. For this purpose, the share of (n,m) chirality ($X_{(n,m),PFX}$) in the suspension generated using PFX polymer (where X was O-F, O-FH, O, O-FDD, or DD) was related to the content of the same chirality in the raw material suspended with the non-selective PFO-3DDT ($X_{(n,m),PFO-3DDT}$). The following equation was used to quantify EFs. The resulting data is presented in Figure S15cd.

$$EF_{(n,m),PFX} = \frac{X_{(n,m),PFX}}{X_{(n,m),PFO-3DDT}}$$



Figure S15 (a,b) Percentage values and (c,d) enrichment factors determined after purification of the (6,5)- and (7,6)-enriched CoMoCAT SWCNTs using the specified polymers.



Figure S16 Optical absorbance spectra of HiPco SWCNTs suspended with the indicated polyfluorene derivatives. Data was normalized to the highest intensity peak and offset for clarity.

4.2. Adjustment of PFO's DPI

We investigated how mixing PFO (Mw = 49,740 g/mol) with PFO batches of different molecular weights ($M_w = 3,060$ g/mol and 11,310 g/mol) affects the results of SWCNT purification. The dispersion produced using only a high molecular weight PFO was pure. It contained nearly exclusively (7,5) SWCNTs with an appreciable absorbance value. On the other hand, when this polymer was blended with PFOs of a low (3,060 g/mol) or medium (11,310 g/mol) M_w, both the yield and the purity of the generated SWCNT suspensions were unsatisfactory. This outcome can be attributed to the fact that a highly effective polymer was mixed with less favorable ones in a substantial ratio (1:1). So, the PDIs of the polymer blends substantially deviated from the optimum values.

The result of this experiment confirmed the hypothesized self-enhancing effect of the PFO-FH polymer discussed in the main text. It appears that sufficiently long polymer chains are necessary to ensure the selectivity of extraction. At the same time, the presence of a lower MW fraction may enhance the extraction system performance. Such short polymer chains have a higher diffusivity, so they more readily reach the SWCNT surface in the liquid medium because of their improved mobility. Moreover, due to their relatively small size, they can easily fit into the interstitial space between the large polymer molecules on the SWCNT surface. This is further supported by their much lower energy of adsorption on SWCNTs, which enables optimization of their conformation so that they can deposit on the SWCNTs in a low-energy configuration. A lower affinity to SWCNTs than longer polymers enables multiple adsorption/desorption cycles when the mixture is mechanically agitated by sonication or shear mixing until the macromolecules reach the most stable structure on the SWCNTs.



Figure S17 (a) As-recorded and (b) normalized and offset optical absorbance spectra of SWCNTs suspended using PFO:PFO mixtures of various molecular weights using the weight ratio of 4.5:4.5 mg/mg. Molecular parameters for each specified polymer may be found in Table S2 (PFO_low – P10, PFO_med – P11, PFO_high – P12).

4.3. Two-component systems based on PFO for highly effective isolation of (7,5) SWCNTs

Initially, we evaluated the addition of PFO-T to PFO, as, according to our published work, this polymer greatly enhanced the operation of PFO-BPy6,6' for harvesting (6,5) SWCNTs by facilitating folding of this polymer ²⁷. However, the outcome of this experiment proved to be unfavorable for (7,5)-selective PFO (Figure S18). The suspension generated using the PFO/PFO-T approach had a comparable amount of (7,5) SWCNTs to when PFO was utilized exclusively for the separation. Additionally, the collected fraction was substantially contaminated with (6,5) SWCNTs this time. We suspected that the strong bonding between PFO-T and the SWCNT surface compromised the selectivity, causing displacement of PFO from the SWCNTs. PFO binds weakly to SWCNTs compared to PFO-BPy ^{27,29–31}, so we hypothesized that it could be readily removed from the SWCNT surface by PFO-T, making the application of PFO-T futile.



Figure S18 (a) As-recorded and (b) normalized and offset optical absorbance spectra of SWCNTs suspended with PFO, PFO-T, and a combination of PFO with PFO-T (6:3 mg/mg). Molecular parameters for each specified polymer may be found in Table S2 (PFO – P12).



Figure S19 Normalized and offset optical absorbance spectra of SWCNTs suspended using PFO:PFO-FH mixtures at various weight ratios given in milligrams. The amount of PFO-FH and PFO remained the same, i.e., 9 mg per extraction. Molecular parameters for each specified polymer may be found in Table S2 (PFO-FH – P3, PFO – P12).

Interestingly, the yield of (7,5) SWCNT extraction was not enhanced in all of the examined cases. It should be noted that it was crucial to use a PFO-FH batch of low molecular weight (4,500 g/mol), which was previously found non-selective (Figure 3a) since the combination of PFO-FH of high molecular weight (38,245 g/mol) with PFO was not beneficial (Figure S20). Presumably, the latter exhibited excessive binding strength to (7,5) SWCNTs and hence competed with PFO for access to the SWCNT surface.



Figure S20 Optical absorbance spectra of SWCNTs suspended using PFO:PFO-FH with high molecular weights using the specified weight ratio expressed in milligrams. The amount of PFO and PFO-FH remained the same, i.e., 9 mg per extraction. Molecular parameters for each specified polymer may be found in Table S2 (PFO – P12, PFO-FH – P9).



Figure S21 (a) Chemical formula of structural isomers of dibromothiophene used in this experiment. (b) As-recorded and (c) normalized and offset optical absorbance spectra of PFO/SWCNT suspensions prepared in the presence of 18 mg of 2,5DBT, 2,4DBT, and 3,4DBT.

To ensure that the difference in molecular weights of these compounds did not lead to improper assignment of the best enhancer, we also evaluated these compounds on an equimolar molar basis. In each extraction, 74.4 mmol (the previously determined optimum amount corresponding to 18 mg of 2,5DBT used to promote (6,5) SWCNT extraction with PFO-BPy6,6'²⁷) of these compounds was added, guaranteeing that the same number of additive molecules was present in every experiment. Again, 2,7DBF showed the highest performance in terms of extraction yield and selectivity (Figure S22), the absorbance value of the collected (7,5) SWCNTs being as high as A = 1.60 a.u. It seemed that the lack of alkyl chains facilitated the penetration of these species between the PFO chains on the SWCNT surface to reach the uncovered parts of the SWCNTs. Consequently, the deposition of these molecules on the surface improved the stability of SWCNTs in the liquid medium. Such hybrids, better coated with fluorene moieties, not only from PFO but also from 2,7DBF, were more resistant to sedimentation during centrifugation.



Figure S22 Optical absorbance spectra of SWCNTs suspended using PFO (denoted as P12 in Table S2) along with the specified low molecular weight enhancers.

5. Literature

- 1 M. M. Rahman, M. M. Alam and K. A. Alamry, *Journal of Industrial and Engineering Chemistry*, DOI:10.1016/j.jiec.2019.04.053.
- 2 J. Schneider, J. Hamaekers, S. T. Chill, S. Smidstrup, J. Bulin, R. Thesen, A. Blom and K. Stokbro, *Model Simul Mat Sci Eng*, 2017, **25**, 085007.
- 3 Synopsis QuantumATK version 2022.03-SP1,https://www.synopsys.com/silicon/quantumatk.html (accessed 07-06-2023).
- 4 L. Martinez, R. Andrade, E. G. Birgin and J. M. Martínez, *J Comput Chem*, 2009, **30**, 2157–2164.
- 5 E. Bitzek, P. Koskinen, F. Gähler, M. Moseler and P. Gumbsch, *Phys Rev Lett*, 2006, **97**, 170201.
- 6 H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola and J. R. Haak, *J Chem Phys*, 1984, **81**, 3684–3690.
- 7 G. J. Martyna, M. L. Klein and M. Tuckerman, *J Chem Phys*, 1992, **97**, 2635–2643.
- 8 D. C. Liu and J. Nocedal, *Math Program*, 1989, **45**, 503–528.
- 9 P. Hohenberg and W. Kohn, *Physical Review*, 1964, **136**, B864–B871.
- 10 W. Kohn and L. J. Sham, *Physical Review*, 1965, **140**, A1133–A1138.
- 11 A. D. Becke, J Chem Phys, 1993, 98, 5648–5652.
- 12 C. Lee, W. Yang and R. G. Parr, *Phys Rev B*, 1988, **37**, 785–789.
- P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J Phys Chem*, 2002, 98, 11623–11627.
- 14 L. Wilk A N and D. M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis1, 1980, vol. 58.
- S. Smidstrup, T. Markussen, P. Vancraeyveld, J. Wellendorff, J. Schneider, T. Gunst,
 B. Verstichel, D. Stradi, P. A. Khomyakov, U. G. Vej-Hansen, M.-E. Lee, S. T. Chill,
 F. Rasmussen, G. Penazzi, F. Corsetti, A. Ojanperä, K. Jensen, M. L. N. Palsgaard, U.
 Martinez, A. Blom, M. Brandbyge and K. Stokbro, *Journal of Physics: Condensed Matter*, 2020, **32**, 015901.
- 16 H. Elhaes, M. Morsy, I. S. Yahia and M. Ibrahim, *Opt Quantum Electron*, 2021, **53**, 269.
- 17 E. Chełmecka, K. Pasterny, T. Kupka and L. Stobiński, *J Mol Model*, 2012, **18**, 2241–2246.
- 18 M. Wykes, B. Milián-Medina and J. Gierschner, *Front Chem*, , DOI:10.3389/fchem.2013.00035.
- 19 G. Ye, W. Talsma, K. Tran, Y. Liu, S. Dijkstra, J. Cao, J. Chen, J. Qu, J. Song, M. Antonietta Loi and R. C. Chiechi, *Macromolecules*, 2022, **55**, 1386–1397.
- 20 H. J. Monkhorst and J. D. Pack, *Phys Rev B*, 1976, **13**, 5188–5192.

- 21 M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai and G. Seifert, *Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties*, 1998.
- 22 A. Fihey, C. Hettich, J. Touzeau, F. Maurel, A. Perrier, C. Köhler, B. Aradi and T. Frauenheim, *J Comput Chem*, 2015, **36**, 2075–2087.
- 23 T. A. Niehaus, M. Elstner, T. Frauenheim and S. Suhai, *Application of an approximate density-functional method to sulfur containing compounds*, .
- 24 K. Stokbro, D. E. Petersen, S. Smidstrup, A. Blom, M. Ipsen and K. Kaasbjerg, *Phys Rev B*, 2010, **82**, 075420.
- 25 M. Pfohl, D. D. Tune, A. Graf, J. Zaumseil, R. Krupke and B. S. Flavel, *ACS Omega*, 2017, **2**, 1163–1171.
- 26 R. B. Weisman and S. M. Bachilo, *Nano Lett*, 2003, **3**, 1235–1238.
- 27 D. Just, A. Dzienia, K. Z. Milowska, A. Mielańczyk and D. Janas, *Mater Horiz*, , DOI:10.1039/d3mh01687k.
- 28 A. Dzienia, D. Just and D. Janas, *Nanoscale*, 2023, **15**, 9510–9524.
- 29 S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas and H. J. Snaith, *Journal of Physical Chemistry Letters*, 2014, **5**, 4207–4212.
- 30 S. D. Stranks, A. M. R. Baker, J. A. Alexander-Webber, B. Dirks and R. J. Nicholas, *Small*, 2013, **9**, 2245–2249.
- 31 S. D. Stranks, S. N. Habisreutinger, B. Dirks and R. J. Nicholas, *Advanced Materials*, 2013, **25**, 4365–4371.