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DEPARTMENT OF ORGANIC CHEMISTRY, BIOORGANIC CHEMISTRY, AND
BIOTECHNOLOGY

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DOCTORAL DISSERTATION

**Chemical modification of carbon nanotubes as
a tool for the enrichment of their optical
properties**

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"You can have the best ship in the world. You can have the best crew. But if the captain doesn't know where to go, the ship will drift around forever and never end up anywhere. It's exactly the same in life. If you don't have a goal or a vision, you'll just drift around and you'll never be happy."

Arnold Schwarzenegger

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Abstract

This dissertation is devoted to the chemical modification of single-walled carbon nanotubes (SWCNTs) as a tool for shaping their optical properties. The work demonstrates that appropriately selected conjugated polymers and low-molecular-weight agents enable the selective isolation of specific chiral SWCNTs species, followed by their controlled functionalization, leading to the formation of photoluminescent defects with desired emission parameters. Particular attention is paid to systems based on polyfluorenes, including copolymers containing bipyridyl units, which exhibit high selectivity for (6,5)-type SWCNTs. It has been demonstrated that the presence of heteroatoms and the appropriate macromolecular architecture determine both the extraction efficiency and the structure of the resulting polymer shell. The use of molecular additives, such as thiophene derivatives and aromatic hydrazines, significantly increased the process efficiency and modulated the reactivity of the SWCNTs surface. The conducted functionalization studies involving radicals demonstrated the possibility of precisely introducing defect states, the energy of which depends on the nature of the substituents and the reaction environment. Furthermore, it was demonstrated that the solvent and polymer conformation play a key role in determining the reaction course and product stability. The resulting materials exhibit enhanced near-infrared emission, making them promising candidates for applications in nanosensors and bioimaging. This work significantly contributes to the understanding of the relationship between the chemical structure, reaction environment, and optical properties of SWCNTs, paving the way for the rational design of functional materials with tightly controlled emission parameters.

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List of monothematic publications used for this thesis

This doctoral dissertation is based on a thematically coherent collection of five original research articles published in peer-reviewed international journals indexed in the Journal Citation Reports (JCR, Clarivate) and the Web of Science Core Collection.

P.1 Just, D., Dzienia, A., Milowska, K. Z., Mielańczyk, A., Janas, D., High-yield and chirality-selective isolation of single-walled carbon nanotubes using conjugated polymers and small molecular chaperones.

Materials Horizons, 2024, 11(3), 758-767.

<https://doi.org/10.1039/D3MH01687K>.

Impact Factor: 13.2, 200 points of MNI_{SW}

P.2 Just, D., Wasiak, T., Dzienia, A., Milowska, K. Z., Mielańczyk, A., Janas, D., Explicating conjugated polymer extraction used for the differentiation of single-walled carbon nanotubes.

Nanoscale Horizons, 2024, 9(12), 2349–2359.

<https://doi.org/10.1039/D4NH00427B>.

Impact Factor: 8.0, 200 points of MNI_{SW}

P.3 Just, D., Uzoma, C., Milowska, K. Z., Waśkiewicz, S., Janas, D., Conjugated polymer architectures with highly improved affinity to specific single-walled carbon nanotubes.

Materials Horizons, 2026, (in press)

<https://doi.org/10.1039/d6mh00979d>.

Impact Factor: 11.4, 200 points of MNI_{SW}

P.4 Just, D., Siedlecki, R., Podleśny, B., Janas, D., Synchronous sorting and functionalization of single-walled carbon nanotubes using organic derivatives of hydrazine.

Advanced Optical Materials, 2025, 13, 2402873.

<https://doi.org/10.1002/adom.202402873>.

Impact Factor: 8.0, 140 points of MNiSW

P.5 Just, D., Siedlecki R., Krzywiecki, M., Er-Riyahi, O., Pouillon, Y., Junquera, J., Milowska, K. Z., Janas, D., Rapid Functionalization of Single-Walled Carbon Nanotubes in High Dipole Moment Media.

Science Advances, 2026, (accepted)

<https://doi.org/10.1126/sciadv.aeb3240>.

Impact Factor: 13.9, 200 points of MNiSW

The total Impact Factor of the above works is 54.5.

The average Impact Factor for the above papers is 10.9

The total number of MNiSW points for these works is 940.

Scientific achievements

List of publications not included in monothematic series

- Dzienia, A., **Just, D.**, Janas, D., Solvatochromism in SWCNTs suspended by conjugated polymers in organic solvents.

Nanoscale, 2023, 15(21), 9510–9524.

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Impact Factor: 5.8, 140 points of MNiSW.

- Dzienia, A., **Just, D.**, Taborowska, P., Mielanczyk, A., Milowska, K. Z., Yorozya, S., Naka, S., Shiraki, T., Janas, D., Mixed-Solvent Engineering as a Way around the Trade-Off between Yield and Purity of (7,3) Single-Walled Carbon Nanotubes Obtained Using Conjugated Polymer Extraction.

Small, 2023, 19(46).

<https://doi.org/10.1002/sml.202304211>,

Impact Factor: 13.0, 200 points of MNiSW.

- Dzienia, A., **Just, D.**, Wasiak, T., Milowska, K. Z., Mielańczyk, A., Labedzki, N., Kruss, S., Janas, D., Size Matters in Conjugated Polymer Chirality-Selective SWCNT Extraction.

Advanced Science, 2024, 11, 2402176.

<https://doi.org/10.1002/advs.202402176>,

Impact Factor: 14.3, 200 points of MNiSW.

- Wasiak, T., **Just, D.**, Dzienia, A., Łukowiec, D., Wacławek, S., Mielańczyk, A., Kodan, S., Bansal, A., Chandra, R., Janas, D., PdNPs/NiNWs as a welding tool for the synthesis of polyfluorene derivatives by Suzuki polycondensation under microwave radiation.

Scientific Reports, 2024, 14(1), 2336.

<https://doi.org/10.1038/s41598-024-52795-w>,

Impact Factor: 3.8, 140 points of MNiSW.

- Choudhary, N., Tomar, A., Bhardwaj, S., Ćwiertnia, J., **Just, D.**, Janas, D., Chandra, R., Maji, P. K., Advancements in biomass-derived cellulose composite electrodes for supercapacitors: a review.

Journal of Materials Chemistry A, 2025, 13(6), 4012–4042.

<https://doi.org/10.1039/D4TA05470A>,

Impact Factor: 10.7, 140 points of MNI_{SW}.

- Basu, S., **Just, D.**, Hendler-Neumark, A., Janas, D., Bisker, G., Post-functionalization modification as a modular strategy for size-selective fluorescence response of single-walled carbon nanotubes to polycyclic aromatic hydrocarbons.

Materials Horizons, 2026, 13 (5), 2520-2536.

<https://doi.org/10.1039/D5MH02318A>,

Impact Factor: 10.7, 200 points of MNSi_W.

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- **Just, D.**; Dzienia, A.; Janas, D., Solvatochromism of single-walled carbon nanotubes suspended in various organic media. 13th International Conference on Nanomaterials: Applications & Properties (IEEE NAP 2023), 10–15.09.2023, Bratislava, Slovakia.
- Wasiak, T.; **Just, D.**; Dzienia, A.; Łukowiec, D.; Waclawek, S.; Mielańczyk, A.; Janas, D., Nickel nanowires decorated with palladium nanoparticles as powerful catalysts facilitating synthesis of polyfluorene derivatives by Suzuki polycondensation. 13th International Conference on Nanomaterials: Applications & Properties (IEEE NAP 2023), 10–15.09.2023, Bratislava, Slovakia.
- **Just, D.**; Janas, D., High-yield separation of single-walled carbon nanotubes using conjugated polymer extraction. 24th International Conference on Science and Application of Nanotubes and Low-Dimensional Materials (NT24), 23–28.06.2024, Cambridge, USA.
- Dzienia, A.; **Just, D.**; Janas, D., Selective and effective extraction of monochiral single-walled carbon nanotubes with conjugated polymers. 24th International Conference on Science and Application of Nanotubes and Low-Dimensional Materials (NT24), Cambridge, USA, 23–28.06.2024, Cambridge, USA.
- Dzienia, A.; **Just, D.**; Wasiak, T.; Janas, D., The underappreciated importance of polymer characteristics in extractive purification of single-walled carbon nanotubes. 24th International Conference on Science and Application of Nanotubes and Low-Dimensional Materials (NT24), Cambridge, USA, 23–28.06.2024, Cambridge, USA.
- **Just, D.**, Jednościenne nanorurki węglowe – ponad limitami. European 360RG-CHEM Challenge 2024, 02.12.2024, Gliwice, Poland.
- Siedlecki, R.; **Just, D.**; Janas, D. (2024). Luminescencyjne defekty jako kluczowa metoda modyfikacji chemicznej jednościennych nanorurek węglowych. Zjazd Zimowy Sekcji Młodych Polskiego Towarzystwa Chemicznego 2024, 14.12.2024, Lublin, Poland.
- Haba, P.; **Just, D.**; Janas, D. (2024). Chemiczna modyfikacja SWCNT do zastosowań w biosensorach i optoelektronice. Zjazd Zimowy Sekcji Młodych Polskiego Towarzystwa Chemicznego 2024, 14.12.2024, Lublin, Poland.
- Borda, J.; **Just, D.**; Janas, D. (2024). Polimery skoniugowane w mediach organicznych: klucz do zaawansowanej separacji jednościennych nanorurek

węglowych. Zjazd Zimowy Sekcji Młodych Polskiego Towarzystwa Chemicznego 2024, 14.12.2024, Lublin, Poland.

- Dzienia, A.; **Just, D.**; Janas, D. (2025). Decydująca rola charakterystyki makromolekularnej polimeru w metodzie selektywnej względem chiralności izolacji jednościennych nanorurek węglowych. Zjazd Zimowy Sekcji Młodych Polskiego Towarzystwa Chemicznego 2025, 13.12.2025, Gliwice, Poland.
- **Just, D.**; Janas, D. (2025). Highly Effective Sorting and Functionalization of Single-Walled Carbon Nanotubes. 247th ECS Meeting, 18–22.05.2025, Montréal, Canada.
- **Just, D.** (2025). Wrapped Right: Targeted Extraction of SWCNTs with Conjugated Polymers. E-MRS 2025 Fall Meeting, 15–18.09.2025, Warsaw, Poland.
- **Just, D.**; Dzienia, A.; Podleśny, B.; Janas, D. (2026). Pushing the Boundaries of Chirality-Selective Separation of Single-Walled Carbon Nanotubes. 2026 MRS Spring Meeting & Exhibit, 26.04–01.05.2026, Honolulu, USA.
- **Just, D.**; Janas, D. (2026). Dual Function of Hydrazine Derivatives Enabling Enhanced Separation and Photoluminescence of SWCNTs. 249th ECS Meeting, 24–28.05.2026, Seattle, USA.
- **Just, D.**; Janas, D. (2026). Interactions of organic hydrazine derivatives with single-walled carbon nanotubes – mechanism and process control. ChemSpot 2026, 18.06.2026, Gliwice, Poland.
- **Just, D.**; Dzienia, A.; Janas, D. (2026). Polar Express: Rapid Functionalization of Single-Walled Carbon Nanotubes in High Dipole Moment Media. 26th International Conference on Science and Application of Nanotubes and Low-Dimensional Materials (NT26), 23–28.08.2026, Berlin, Germany.

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Internal projects of Silesian University of Technology

- Initiative of Excellence – Research University (IDUB), Silesian University of Technology – Photoluminescent Properties of Carbon Nanotubes through Controlled Chemical Modification, 32/014/SDU/10-21-20 – principal investigator.
- BKM 2023 – Silesian University of Technology – Separation of single-walled carbon nanotubes using conjugated polymers in organic solutions and their subsequent functionalization, 04/020/BKM23/1079 – BKM-537/RCH-2/2023 – principal investigator.
- BKM 2024 – Silesian University of Technology – Separation and functionalization of single-walled carbon nanotubes in organic solutions, 04/020/BKM24/1100 – BKM-691/RCH2/2024 – principal investigator.
- BKM 2025 – Silesian University of Technology – Interactions of organic hydrazine derivatives with single-walled carbon nanotubes – mechanism and process control, 04/020/BKM25/1118 – BKM-608/RCH2/2025 – principal investigator.

Patents

- Method of Selective Isolation of Semiconducting SWCNTs. Polish Patent: PL248351.
- Technique of Selective Isolation of Semiconducting SWCNTs. Polish Patent: PL246683.

Other awards

- Honorable Mention – NASA & The Mars Society ‘Mars Colony Prize’ (2019)
- Best Oral Presentation – The 11th Torunian Carbon Symposium (2024)
- Rector’s Scientific Excellence Award – Silesian University of Technology (2024)
- Young Researcher Award – E-MRS Fall Meeting (2025)
- 3rd place poster Award – ECS spring meeting (2026)

List of abbreviations (alphabetical order)

Analytical techniques and research methods

ATPE – Aqueous Two-Phase Extraction

DGU – Density Gradient Ultracentrifugation

NMR – Nuclear Magnetic Resonance Spectroscopy

PL – Photoluminescence

PLE – Photoluminescence Excitation Spectroscopy/Photoluminescence Excitation Mapping

SEC – Size-Exclusion Chromatography

TCSPC – Time-Correlated Single-Photon Counting

XPS – X-ray Photoelectron Spectroscopy

Abbreviations of chemical compounds and materials

Low molecular weight compounds

BPO – benzoyl peroxide

BV – benzyl viologen

DBT – dibromothiophene

DDQ – 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

PhH-Br – 4-bromophenylhydrazine

PhH-CF₃ – 4-(trifluoromethyl)phenylhydrazine

PhH-CN – 4-hydrazinylbenzonitrile

PhH-COOH – 4-hydrazinobenzoic acid

PhH-NO₂ – 4-nitrophenylhydrazine

PhH-SO₂NH₂ – 4-sulfonamidophenylhydrazine

PhN₂H₃ or PhH – phenylhydrazine

PHN – 1,10-phenanthroline

TEMPO – 2,2,6,6-tetramethylpiperidin-1-oxyl

Polymers and materials

CP – Conjugated polymer

PFDD – Poly(9,9-didodecylfluorenyl-2,7-diyl)

PFO – Poly(9,9'-dioctylfluorenyl-2,7-diyl)

PFO-3DDT – Poly[2,7-(9,9'-dioctylfluorene)-co-alt-2,5-(3-dodecylthiophene)]

PFO-BPh3,3' – Poly(9,9'-dioctylfluorenyl-2,7-diyl)-alt-3,3'-(1,1'-biphenyl)

PFO-BPh4,4' – Poly(9,9'-dioctylfluorenyl-2,7-diyl)-alt-4,4'-(1,1'-biphenyl)

PFO-BPy4,4' – Poly[(9,9'-dioctylfluorenyl-2,7-diyl)-alt-(2,2'-bipyridine-4,4'-diyl)]

PFO-BPy5,5' – Poly[(9,9'-dioctylfluorenyl-2,7-diyl)-alt-(2,2'-bipyridine-5,5'-diyl)]

PFO-BPy6,6' – Poly[(9,9'-dioctylfluorenyl-2,7-diyl)-alt-(2,2'-bipyridine-6,6'-diyl)]

PFO-F – Poly[2,7-(9,9'-dioctylfluorene)-alt-2,7-fluorene]

PFO-FD – Poly[2,7-(9,9'-dioctylfluorene)-alt-2,7-(9,9'-didecylfluorene)]

PFO-FDD – Poly[2,7-(9,9'-dioctylfluorene)-alt-2,7-(9,9'-didodecylfluorene)]

PFO-FH – Poly[2,7-(9,9'-dioctylfluorene)-alt-2,7-(9,9'-hexylfluorene)]

PFO-N1,4 – Poly(9,9'-dioctylfluorenyl-2,7-diyl)-alt-(1,4-naphthalene)

PFO-ONCz – Poly[(9,9'-dioctylfluorenyl-2,7-diyl)-alt-2,7'-(9-(9-heptadecyl)-carbazole)]

PFO-T – Poly[2,7-(9,9'-dioctylfluorene)-alt-2,5-thiophene]

PONCz – Poly[9-(9-heptadecyl)-carbazol-2,7-diyl]

PONCz-BPh3,3' – Poly[(9-(9-heptadecyl)-carbazol-2,7-diyl)-alt-3,3'-(1,1'-biphenyl)]

PONCz-BPh4,4' – Poly[(9-(9-heptadecyl)-carbazol-2,7-diyl)-alt-4,4'-(1,1'-biphenyl)]

PONCz-BPy5,5' – Poly[(9-(9-heptadecyl)-carbazol-2,7-diyl)-alt-(2,2'-bipyridine-5,5'-diyl)]

PONCz-BPy6,6' – Poly[(9-(9-heptadecyl)-carbazol-2,7-diyl)-alt-(2,2'-bipyridine-6,6'-diyl)]

PONCz-BT – Poly[(9-(9-heptadecyl)-carbazol-2,7-diyl)-alt-benzothiadiazole]

PONCz-N1,4 – Poly[(9-(9-heptadecyl)-carbazol-2,7-diyl)-alt-(1,4-naphthalene)]

SWCNTs – Single-walled carbon nanotubes

Abbreviations and designations of physical phenomena/parameters

AL – alkyl group (alkyl)

AR – aryl group (aryl)

DFT – density functional theory

ΔE_{opt} - exciton trap depth

E_{11} – first excitonic transition of SWCNT

E_{22} – second excitonic transition of SWCNT

E_{33} – third excitonic transition of SWCNT

E_{11}^* – transition associated with a luminescent defect

E_{11}^{*-} – deeper defect state/level associated with E_{11}^{*-} emission

EVET – electron-vibrational energy transfer

MPD – multiphonon decay

MD – molecular dynamics

MC – Monte Carlo method

NIR – near-infrared

NIR-II – second near-infrared window

PLQY – photoluminescence quantum yield

RDF – radial distribution function

SWIR – short-wave infrared

1. Research objective and scope

The goal of this dissertation was to develop a modern platform enabling the synthesis of highly purified single-walled carbon nanotubes (SWCNTs) with defined chirality and their controlled chemical functionalization, leading to the design of new optical properties. Achieving this goal required solving two fundamental problems limiting the practical use of SWCNTs. The first was the low efficiency of conjugated polymer (CP) extraction (CPE), which hindered the acquisition of sufficient quantities of material for further research and applications. The second was the limited understanding of the mechanisms responsible for the formation of luminescent defects and the influence of the reaction environment on the functionalization process.

Unlike most previous studies, which focused on the optimization of single process parameters, the goal of this work was to understand the relationships between CP architecture, their interactions with the SWCNT surface, the reaction environment, and the optical properties of the resulting materials. The acquired knowledge was then used to develop new strategies for both the selective separation and controlled functionalization of SWCNTs.

The series of publications comprising this dissertation presents the successive stages of achieving this goal.

Paper P.1 was devoted to the development of CPE. The first publication developed a strategy for using low-molecular-weight enhancers (molecular chaperones), which enabled an eleven-fold increase in the extraction efficiency of near-monochiral SWCNTs while maintaining high process selectivity. The obtained results demonstrated for the first time that the limitations of CPE are not fundamental in nature but stem from the ability to control the conformation of CP macromolecules.

The next publication (P.2) focused on elucidating the mechanism of CPE action by systematically examining the influence of CP architecture and the length and arrangement of alkyl chains on process selectivity. Experiments and multiscale modeling demonstrated that the extraction outcome is determined by a delicate balance between the strength of the CP–SWCNT interaction and the stability of the resulting complexes in solution. These results provided new insights into the

mechanism of CPE action and allowed for the proposal of principles for the rational design of new extraction CP.

A natural extension of this research was paper P.3, which focused on fundamentally understanding the influence of CP chemical architecture on their affinity for SWCNT surfaces. Particular attention was paid to the role of heteroatoms and their arrangement within the CP backbone. Experimental studies supported by theoretical calculations clarified why some CP exhibit exceptionally high selectivity for specific chiralities and provided guidance for designing the next generation of CP for SWCNT separation.

After developing an efficient separation platform, further research focused on the controlled functionalization of purified SWCNTs. Paper P.4 proposed a new strategy for the simultaneous separation and chemical modification of SWCNTs using phenylhydrazine (PhN_2H_3) derivatives. It was demonstrated that appropriately selected organic compounds can simultaneously increase extraction efficiency and initiate the formation of luminescent defects responsible for enhanced photoluminescence efficiency. The developed method significantly shortened the functionalization time – from many hours to just a few minutes – and enabled the process to be conducted in both organic and aqueous environments.

The latest publication (P.5) represents the culmination of the research and focused on the influence of the reaction environment on SWCNT functionalization. It demonstrated that the solvent and dispersing molecules actively affect the reaction kinetics and the type of luminescent defects formed, enabling deliberate control of SWCNT optical properties, including their application in cholesterol detection.

Although the individual publications address different aspects of SWCNTs chemistry and physics, they all share a common goal: understanding the relationships between CP structure, interactions at the CP–SWCNT–solvent interface, and the optical properties of the SWCNTs. The knowledge gained at each stage of the research provided the foundation for subsequent work, ranging from increasing extraction efficiency, through elucidating the CPE mechanism and designing new CP architectures, to developing new chemical functionalization strategies enabling the deliberate programming of light emission from SWCNTs.

2. Introduction to research topics

2.1. Nanomaterials as a platform for modern materials engineering

The development of nanotechnology has led to a fundamental shift in the approach to designing functional materials. Unlike classical materials engineering, in which the properties of materials are determined primarily by their chemical composition, nanotechnology enables their conscious shaping through structural control at the atomic and molecular levels. At the nanometer scale, matter exhibits properties different from those observed in macroscopic materials, resulting from the growing importance of surface phenomena and quantum effects ^{1–3}. This enables the design of materials with precisely controlled optical, electrical, mechanical, and chemical properties.

Nanomaterials are considered materials with at least one characteristic dimension in the range of 1 to 100 nm. Such a significant reduction in size leads to an increased surface-to-volume ratio and a restriction of electron and phonon movement, often resulting in the emergence of properties unavailable to materials with larger dimensions ^{2,3}. The nature and intensity of these phenomena depend not only on the material's chemical composition but also on its geometry, dimensionality, and degree of structural order.

Depending on the number of dimensions limited to the nanometer scale, nanomaterials are classified as zero-dimensional (0D) ⁴, one-dimensional (1D) ⁵, two-dimensional (2D) ⁶, and three-dimensional (3D) ⁷. The first group includes, among others, quantum dots and nanoparticles, in which the movement of charge carriers is restricted in all three spatial directions. One-dimensional materials, represented by SWCNTs, are characterized by free carrier transport only along a single axis. Graphene, on the other hand, is an example of a two-dimensional material, while nanostructured porous materials and composites belong to the group of three-dimensional materials.

The ability to control the structure of materials at the atomic level means that nanotechnology is now used in almost all areas of modern science and technology. Nanomaterials are used in electronics ⁵, photonics ⁸, catalysis ⁹, energy storage ^{9,10}, medicine ¹¹, environmental technologies ¹², and biomaterials engineering ¹³, among

others. Carbon nanomaterials are of particular interest. Thanks to their diverse allotropic forms and excellent physicochemical properties, they constitute one of the most intensively developed groups of functional materials ⁵.

Among carbon nanomaterials, SWCNTs have attracted particular attention. Their specific one-dimensional structure leads to a strong restriction of charge carrier motion ^{3,5}, endowing them with exceptional electronic and optical properties. Furthermore, these properties can be programmed through the appropriate selection of the atomic structure and controlled chemical modification of the nanotube surface. Therefore, SWCNTs currently represent one of the most promising platforms for research into modern materials for nanophotonics, optoelectronics, and quantum technologies.

2.2. SWCNTs – a unique class of one-dimensional materials

Among all carbon nanomaterials, SWCNTs hold a special place, they are materials in which the motion of charge carriers is restricted in two spatial directions, retaining freedom only along the nanotube axis ¹⁴. This strong dimensionality restriction leads to the emergence of a number of quantum phenomena that do not occur in three-dimensional materials, while simultaneously endowing SWCNTs with outstanding electronic and optical properties ¹⁵.

Unlike most semiconducting materials, the properties of SWCNTs are determined not solely by their chemical composition, but primarily by their atomic structure. All SWCNTs are composed of sp^2 -hybridized carbon atoms, but the way a single graphene plane is rolled up leads to the formation of SWCNTs with distinct electronic, optical, and mechanical properties ^{15,16}. The nanotube geometry is described by the chirality vector $C = na_1 + ma_2$, whose coordinates (n,m) uniquely define the diameter, chiral angle, and the arrangement of the hexagonal rings relative to the nanotube axis ^{15,17,18}.

As shown in Figure 1a, even small changes in the chirality indices lead to significant changes in the material's band structure. This is because graphene rolling imposes boundary conditions on the electron wavefunction, causing quantization of the wave vector in the nanotube's circumferential direction. As a result, the position of allowed electronic states relative to the K points in the graphene Brillouin zone ^{19,20} changes, directly affecting the band gap width and the energies of optical transitions ^{21,22}. This

mechanism allows SWCNTs with very similar diameters to exhibit completely different physical properties.

A particularly interesting consequence of the relationship between geometry and electronic structure is the possibility of both metallic and semiconducting SWCNTs. A SWCNT is considered metallic if the difference $(n-m)$ is divisible by three, while the remaining configurations correspond to semiconducting materials with an energy gap inversely proportional to the nanotube diameter^{19,23}. In practice, this means that a single change in the chirality index can lead to a complete change in the nature of electrical conductivity.

The relationship between chirality and band structure is also directly reflected in the optical properties of SWCNTs. The one-dimensional nature of SWCNTs leads to the formation of van Hove singularities in the density of electronic states, which determine the energies of optical transitions designated E_{11} , E_{22} , and subsequent higher transitions between the valence and conduction bands^{24–26} presented in Figure 1b. As a result, each chirality is characterized by a distinctive set of absorption (Figure 1c and d) and emission energies, constituting a specific "fingerprint" used in the identification of individual nanotube species by spectroscopic methods^{17,27–29}. This unique relationship between atomic structure and optical properties forms the basis of all methods for the selective separation of SWCNTs and their subsequent use in photonics, optoelectronics, and nanosensors.

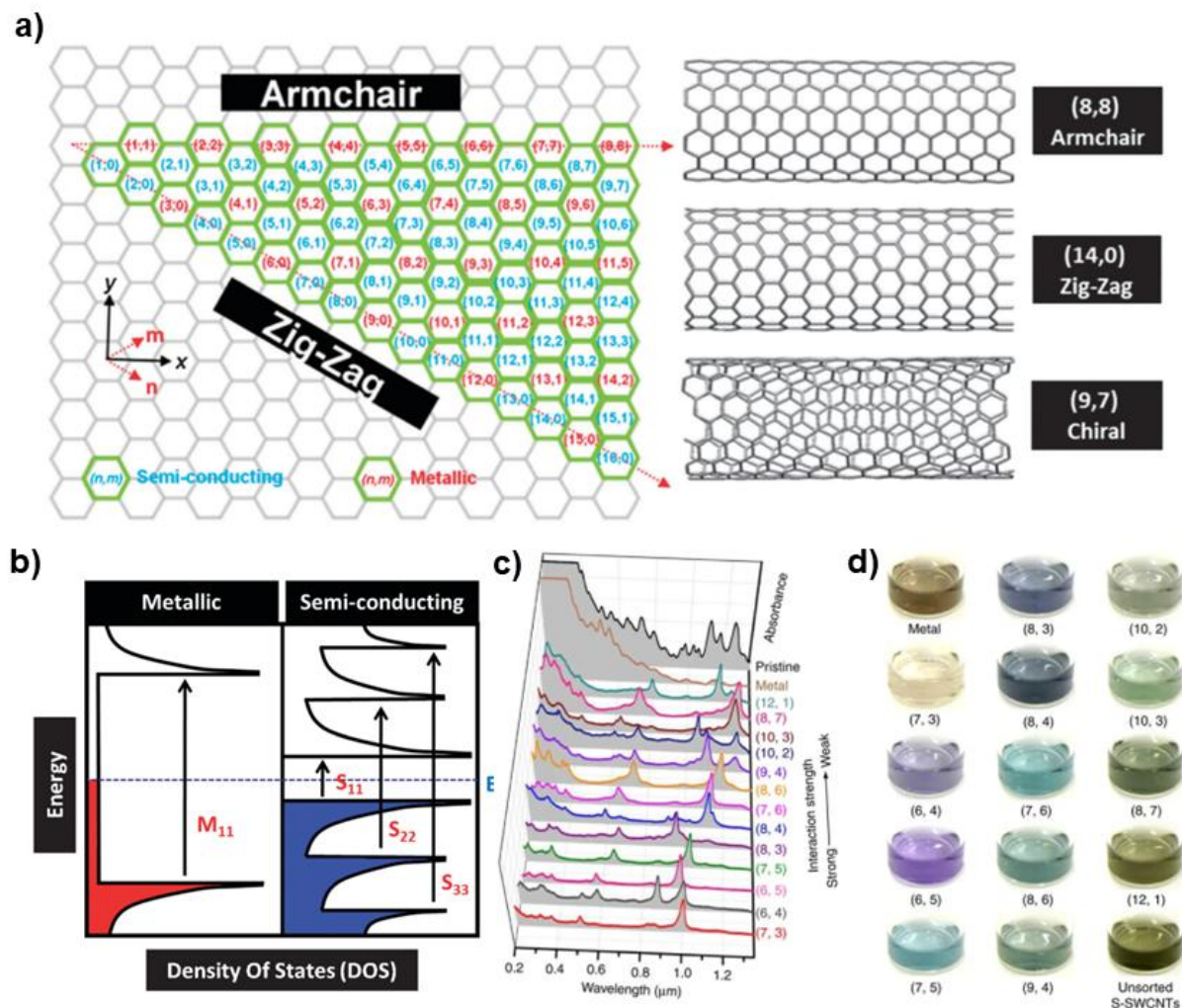


Figure 1. Structural, electronic, and optical characteristics of SWCNTs. (a) Helicity map illustrating the relationship between the chiral indices (n, m) and the resulting armchair, zigzag, and chiral nanotube structures³⁰. (b) Schematic density of states of metallic and semiconducting SWCNTs³⁰. M_{11} denotes the first allowed optical transition in metallic SWCNTs, whereas S_{11} , S_{22} , and S_{33} correspond to the first, second, and third excitonic transitions in semiconducting SWCNTs (hereafter referred to as E_{11} , E_{22} , and E_{33} , respectively). (c) Representative optical absorption spectra of chirality-enriched semiconducting SWCNTs³¹. (d) Photographs of chirality-enriched SWCNT dispersions exhibiting characteristic colors depending on nanotube chirality³¹. Adapted from Refs. 30 and 31.

This exceptional relationship between atomic structure and physical properties makes SWCNTs among the most versatile functional materials developed to date.

They find applications in optoelectronics ^{5,18}, photonics ³², quantum technologies ³³, flexible electronics ³⁴, energy storage ³⁵, and modern biosensors ^{36–40}. Of particular interest, however, are their optical properties, including strong absorption and emission of light in the near-infrared range, corresponding to the so-called biological window ^{39,41–44}. As a result, SWCNTs are currently considered one of the most promising platforms for designing light-emitting materials and next-generation optical sensors.

Despite their enormous application potential, the practical use of SWCNTs remains limited by their complex structural nature. Materials obtained by synthetic methods consist of a mixture of SWCNTs varying in diameter, length, and graphene lattice folding ^{45–49}. Each of these parameters influences electronic and optical properties, leading to complex absorption and photoluminescence spectra and hindering both fundamental research and the development of technological applications. Therefore, one of the most important challenges in modern nanotube chemistry is obtaining materials with a uniform atomic structure and the ability to consciously shape their properties through controlled chemical modification ^{39,41,50,51}.

2.3. Chirality-selective sorting of SWCNTs

One of the greatest challenges limiting the use of SWCNTs is the lack of selective synthesis ^{45–49}. Most available methods for obtaining SWCNTs lead to the formation of a mixture of SWCNTs with different diameters, chiralities, and conductivity characteristics. As a result, commercially available materials typically contain dozens of different nanotube species, whose optical and electronic properties differ significantly ^{52,53}. This heterogeneity hinders both fundamental research and the development of optoelectronic devices, sensors, and light sources using SWCNTs.

Theoretically, this problem can be solved in three ways: by selective synthesis of SWCNTs with a specific chirality ^{54,55}, selective elimination of undesirable fractions ^{54,56–58}, or separation of the post-synthetic mixture ^{18,42}. Despite significant progress in controlling the nanotube growth process ^{46,55}, the direct synthesis of single-chiral materials remains beyond the reach of methods applicable on a larger scale. Selective destruction methods, on the other hand, inevitably lead to the loss of some of the material, limiting their practical application. For this reason, separation techniques have gained the greatest importance, enabling the isolation of desired SWCNT species without permanently modifying their structure.

Over the past two decades, a number of methods have been developed (Figure 2) to separate SWCNTs based on their conductivity, diameter, chirality, or enantiomeric nature. The most commonly used include column chromatography, density gradient ultracentrifugation (DGU) ⁵⁹, aqueous two-phase extraction (ATPE) ^{60–62}, (di)electrophoresis ⁶³, and nucleic acid separation ^{64–67}. Each of these methods has a different separation mechanism and its own advantages and limitations. DGU provides very high resolution, but requires expensive equipment and long-term ultracentrifugation. ATPE enables efficient and relatively easy separation of many nanotube species, but requires precise selection of surfactant systems and multi-stage process optimization. Chromatography and electrophoresis allow for obtaining high purity of selected fractions, but their efficiency and scalability remain limited ^{42,68}.

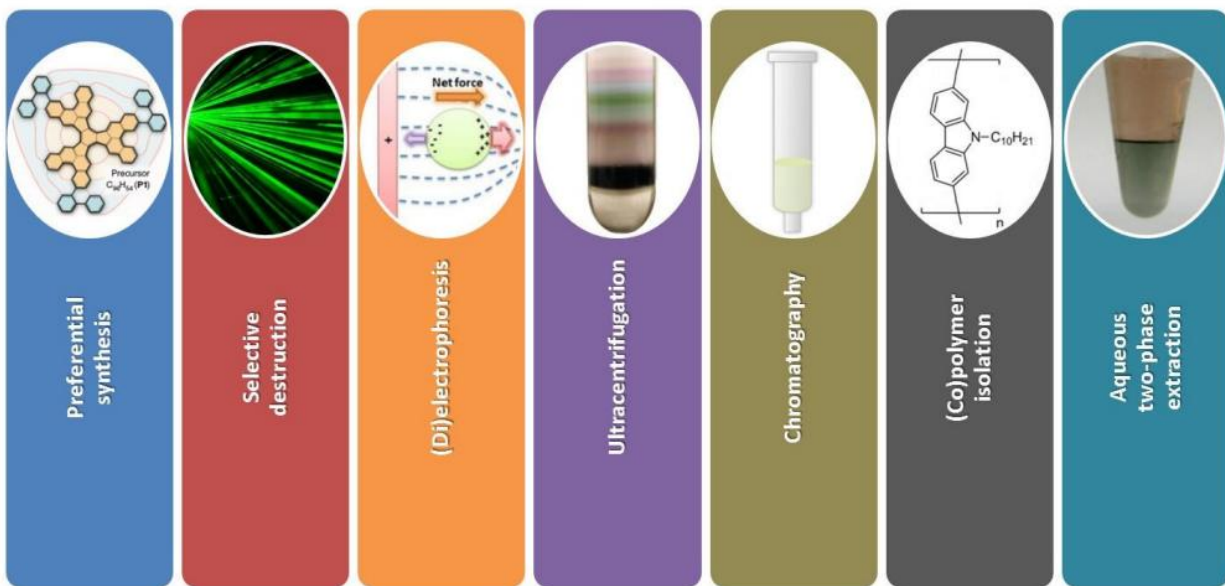


Figure 2. Overview of the principal approaches for the chirality-selective separation of SWCNTs. The illustrated methods include preferential synthesis, selective destruction, (di)electrophoresis, DGU, chromatographic separation, CPE, and ATPE ⁴². Adapted from Ref. 42.

Of all available methods, CPE has gained particular importance ^{69–72}. This technique is based on the selective interaction between CP chains and the surface SWCNTs. A suitably designed polymer wraps the surface of selected SWCNT species, stabilizing them in an organic solvent, while the remaining SWCNTs aggregate and are removed

by centrifugation as presented in Figure 3. Unlike methods using aqueous surfactants, CPE allows for the production of highly purified dispersions directly in organic solvents, which is particularly advantageous for further chemical functionalization and applications in printed electronics and photonics.

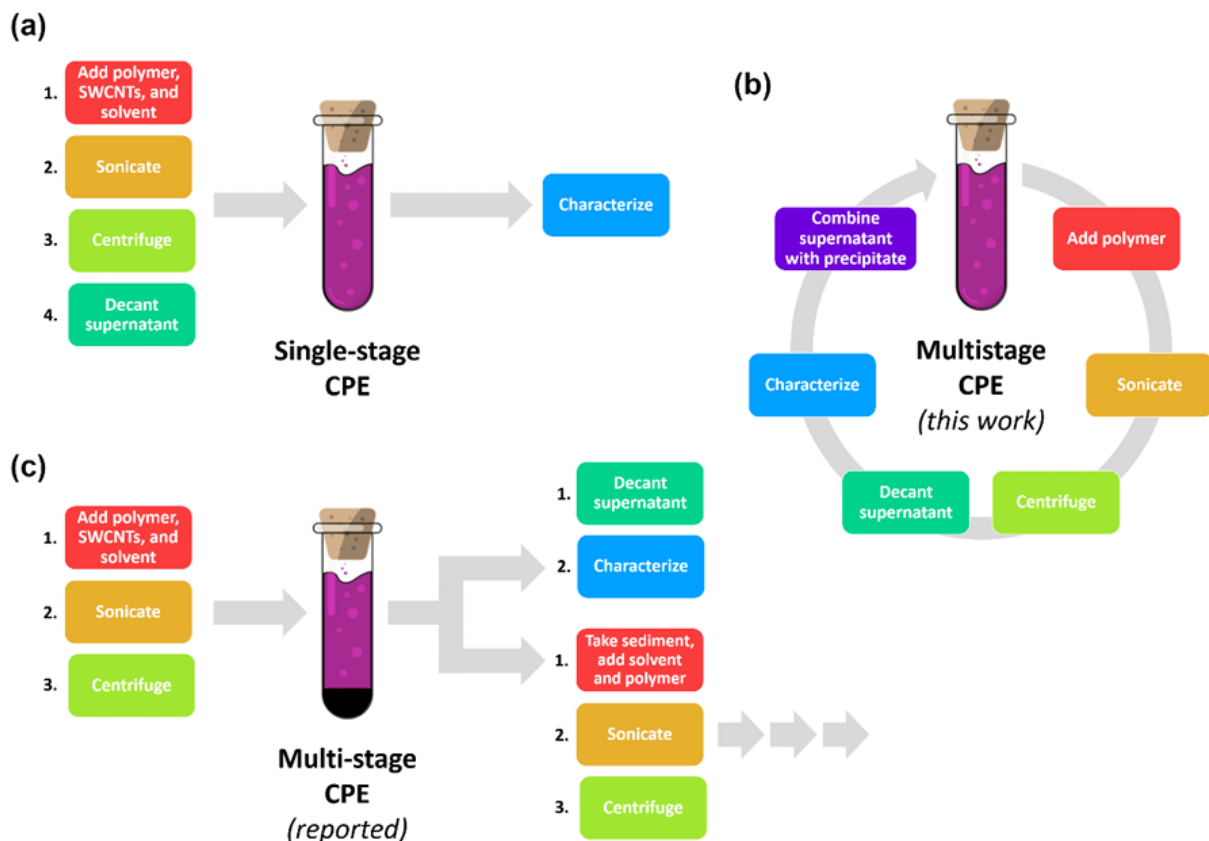


Figure 3. (a) Schematic diagram of the classical one-step CPE process, which involves dispersion of SWCNTs in the presence of a polymer, sonication, centrifugation, and separation of the supernatant containing the selected SWCNTs. (b) The multi-step CPE process is performed iteratively, in which subsequent cycles of polymer addition, sonication, and centrifugation are performed, reusing both the supernatant and the pellet⁷³. This approach allows for a gradual increase in extraction efficiency and improved selectivity through dynamic reorganization of the polymer–SWCNT system. (c) The previously reported multi-step approach, in which subsequent extraction steps are performed solely on the pellet after centrifugation, without reincorporating the supernatant into the process. In contrast to the method

presented in this work, this approach does not utilize the full potential of the material and leads to lower extraction efficiency. Adapted from Ref. 73.

The rarity of the CPE method stems from the fact that the process of recognizing the chirality of SWCNTs is not determined by a single type of interaction, but by a complex thermodynamic and kinetic equilibrium between many factors ^{70,71}. Extraction selectivity is assumed to result from the π - π interactions between the polymer backbone and the nanotube surface, the ability of the macromolecule to conformally adapt to its curvature, the stabilization of the polymer-SWCNT complex by the solvent, and the free energy accompanying the process of nanotube wrapping and dispersion ^{71,74,75}. The ultimate efficiency of the process therefore depends on the overall stability of the formed complex, not on the strength of a single type of interaction ⁷⁴⁻⁷⁶. For this reason, the design of new systems for selective SWCNT extraction has for many years been based primarily on an empirical approach, and the molecular basis for recognizing individual chiralities remains only partially understood.

The high complexity of the process is also demonstrated by the number of parameters influencing the final extraction result. Even small changes in polymer architecture, including its chemical structure ⁷⁵⁻⁷⁹, molecular weight ^{73,80-84} or the length and nature of side chains ^{74,76,77}, can lead to significant changes in process selectivity. Experimental parameters, such as the type of solvent used ^{85,86}, process temperature ^{73,87}, sonication time and energy ^{73,86-88}, polymer-to-nanotube ratio ^{77,86}, and centrifugation conditions ⁸⁸, play an equally important role. Consequently, CPE should be viewed not only as a separation method but also as a molecular engineering platform enabling informed design of selectivity through appropriate selection of polymer architecture and process parameters ^{73,77,86}. At the same time, the interrelationships between these factors remain poorly understood and constitute one of the most important challenges in contemporary research on the selective extraction of SWCNTs.

To date, the use of appropriate conjugated polymers has been shown to enable the selective isolation of both metallic and semiconducting SWCNTs, as well as single chiral SWCNTs, such as (6,5) ⁸⁹, (7,5) ⁹⁰, and (7,3) ⁸⁶. The most commonly used materials include derivatives of poly(9,9-dioctylfluorene) (PFO) ^{77,90-94}, fluorene-bipyridine copolymers (PFO-BPy) ^{72,80,89,95}, fluorene-benzothiadiazole (PFO-BT) ^{81,86,96}, and

numerous derivatives of polythiophenes^{97,98} and polycarbazoles^{74,99}. The appropriate selection of polymers enables the production of dispersions with very high chiral purity, making CPE as presented in Figure 4 one of the most versatile and frequently used methods for SWCNT separation.

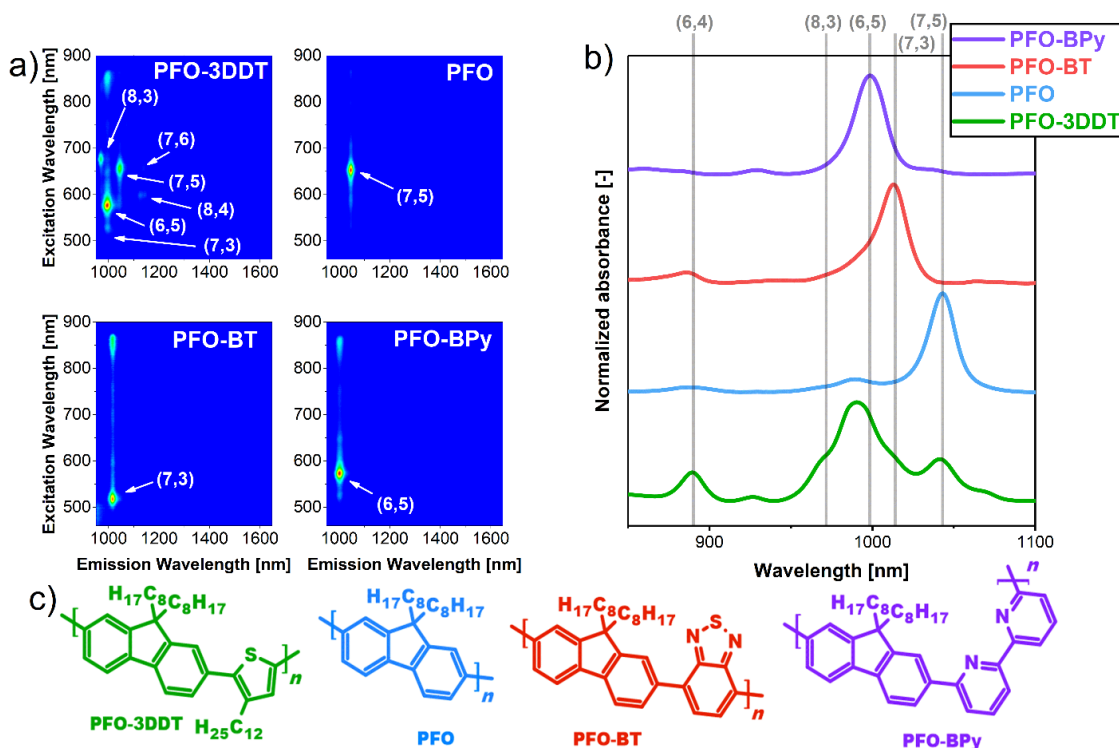


Figure 4. a) Excitation–emission photoluminescence (PLE) maps of SWCNTs dispersions prepared using selective PFO, PFO-BPy, and PFO-BT polymers, demonstrating their chirality-selective extraction behavior. A dispersion obtained using non-selective PFO-3DDT is shown in the upper right corner as a reference. b) Corresponding optical absorption spectra of the obtained SWCNT dispersions, confirming selective enrichment of semiconducting nanotube species. c) Chemical structures of the conjugated polymers used for SWCNT extraction. All results were obtained within our own research using self-synthesized conjugated polymers.

The particular importance of CPE also stems from the fact that separation and subsequent chemical functionalization can be carried out in the same organic medium. This eliminates the need to exchange surfactants or transfer SWCNTs between different solvents, reducing material losses and improving process reproducibility. For this reason, extraction with conjugated polymers is currently one

of the most promising methods for obtaining highly purified SWCNTs intended for research on controlled modification of their optical properties compared with other methods presented in Table 1. This technique was used in this thesis as a starting point for the development of new strategies for the selective separation and further chemical functionalization of SWCNTs.

Table 1. Comparison of the features of the most important SWCNT separation methods (Division based on: S/M – conductivity character, (n,m) – chirality index; E – enantiomeric character)

		CPE	Chromatography	(Di)electrophoresis	DGU	ATPE
Sorting capabilities	S/M	Yes	Yes	Yes	Yes	Yes
	(n,m)	Yes	Yes	No	Yes	Yes
	E	Yes	Yes	No	Yes	Yes
Commercial availability of reagents		High	High	High	High	High
Reagent costs		Moderate	High	Low	High (iodixanol)	Low
Additional instruments		Tip horn sonicator / Shear mixer	Chromatographic column	Electrophoreser	Ultracentrifuge	Tip horn sonicator / Shear mixer
Solvent		Organic solvent	Water	Water	Water	Water
Non-sorted fraction occurrence		Precipitate	Dispersion	Dispersion	Dispersion	Dispersion

Over the past two decades, CPE and ATPE have remained two competing methods for the selective separation of SWCNTs, each with its distinct advantages and limitations. Due to its high process efficiency and ability to separate multiple chiral species, ATPE was long considered the reference method. However, the development of CPE was limited primarily by low extraction efficiency and insufficient understanding of the mechanisms responsible for process selectivity. As a result, the true potential of CPE remained untapped for many years. The research presented in this thesis developed a new extraction strategy using conjugated polymers, which allowed for an eleven-fold increase in process efficiency while maintaining high chiral selectivity. This result significantly changes the perception of CPE's capabilities and indicates that this method may be an attractive alternative to ATPE, particularly in applications requiring direct chemical functionalization of SWCNTs in an organic environment.

2.4. Electronic and optical properties of SWCNTs and luminescent defects

SWCNTs are among the most special semiconductor materials known to date as already mentioned. Their one-dimensional structure strongly restricts the movement of charge carriers in two spatial directions, leading to the formation of a discrete band structure with characteristic Van Hove singularities^{24–26}. The position of these energy levels is directly determined by the SWCNT's chirality, so each chirality has its own set of optical transitions and a characteristic absorption and photoluminescence spectrum^{22,24}. This allows SWCNTs to be considered a family of several hundred different semiconductors, whose properties result solely from their atomic structure, not their chemical composition. Unlike classical semiconductor materials, where property changes are most often achieved through chemical doping, in the case of SWCNTs, even a small change in diameter or chiral angle leads to significant changes in the band gap width and the energy of optical transitions. This means that each chirality constitutes a distinct material with its own electronic and optical properties. This matchless relationship between atomic structure and physical properties is why SWCNTs are often referred to as "programmable" quantum materials. At the same time, this diversity poses one of the greatest technological challenges, as most synthesis methods result in a mixture of multiple chiralities with distinct properties, as mentioned in section 2.2.

Light absorption leads to the excitation of an electron to a higher energy level and the formation of an exciton, a bound electron-hole pair held together by the Coulomb interaction^{39,41,50,100}. Unlike classical semiconductors, excitons in SWCNTs are characterized by very high binding energies, reaching several hundred millielectronvolts, due to the one-dimensional nature of the material and limited dielectric screening¹⁰¹. Upon excitation to higher optical transitions (usually E_{22} or E_{33}), the exciton rapidly relaxes to the lowest bright state, E_{11} ^{39,102}, from which it can radiatively recombine, emitting a photon in the near-infrared range^{103,104}. The characteristic E_{11} emission underlies most SWCNT applications in photonics, bioimaging, and optical chemical sensors^{40,44}.

A significant distinguishing feature of SWCNTs is that the observed emission does not originate from free electrons and holes, but from excitons. Due to the strong dimensionality restriction, the Coulomb interaction between carriers is much larger

than in bulk materials, making the exciton the dominant quasi-particle responsible for the optical response of SWCNTs. In practice, this means that all processes affecting the motion, localization, or recombination of excitons directly determine the photoluminescence efficiency. Understanding exciton dynamics therefore provides a foundation for the design of new SWCNT-based materials.

Despite their exceptional optical properties, the photoluminescence efficiency of unmodified SWCNTs remains relatively low^{33,105}. This is due to the fact that only one of the sixteen possible excitonic states is optically allowed^{39,41}, while the remaining states are dark and relax without emitting light. Furthermore, excitons in SWCNTs are characterized by very high mobility and a diffusion length of several hundred nanometers. During their lifetime, they travel along the nanotube and are highly likely to encounter luminescence-quenching sites, such as nanotube ends, uncontrolled structural defects, impurities, charge carriers, or interactions with the environment¹⁰⁶. As a result, a significant portion of the excitation energy is dissipated in non-radiative processes, limiting the emission quantum yield. For this reason, the optical properties of SWCNTs are extremely sensitive to the chemical environment. Even small changes in the solvent, surfactant type, polymer surrounding the nanotube, or the presence of adsorbed molecules can affect the energy of optical transitions and the emission efficiency¹⁰⁴. This characteristic is both a disadvantage and an advantage. On the one hand, it hinders the production of materials with reproducible properties, but on the other, it enables SWCNTs to be used as extremely sensitive molecular sensors that respond to changes in the local environment.

For many years, structural defects were considered solely as undesirable recombination centers, leading to degradation of the optical properties of SWCNTs^{39,41,50,100}. However, this view has fundamentally changed with the discovery that appropriately designed covalent defects can not only impair light emission but actually enhance it¹⁰⁷. The introduction of single sp^3 centers through controlled chemical functionalization locally disrupts π -coupling and leads to the formation of new electronic states located energetically below the native E_{11} state as presented in Figure 5. These centers are referred to in the literature as luminescent defects, sp^3 defects, quantum defects, or organic color centers. This discovery has led to a shift in the way defects in nanomaterials are viewed. In classical semiconductor physics, defects are typically viewed as elements that degrade charge transport and optical properties. In SWCNTs, appropriately designed defects can act as functional quantum

centers, enabling conscious control of the fate of excitons. For this reason, modern research increasingly focuses not on eliminating defects, but on their precise design and controlled introduction ¹⁰⁸.

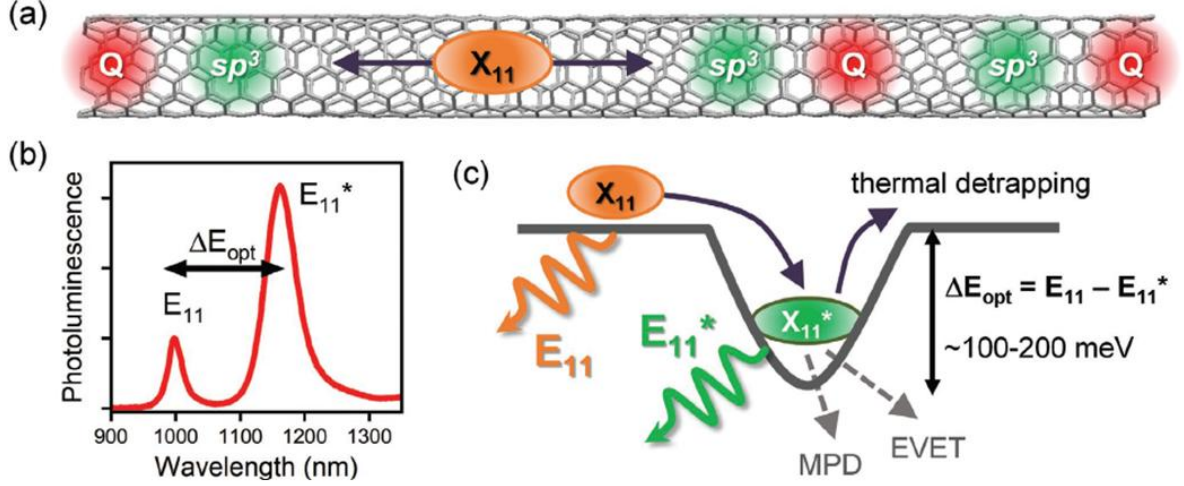


Figure 5. (a) Schematic illustration of a SWCNT containing a mobile exciton (X_{11}) quenching centers (Q), and luminescent sp_3 defects that enable exciton trapping and radiative recombination. (b) Representative photoluminescence spectrum of chemically functionalized (6,5) SWCNTs showing the native E_{11} emission and the defect-related E_{11}^* band. The energy difference between these transitions is defined as the optical trap depth exciton trap depth (ΔE_{opt}). (c) Schematic representation of exciton dynamics in the presence of sp_3 defects, including exciton trapping, radiative recombination, multiphonon decay (MPD), electron-vibrational energy transfer (EVET), and thermal detrapping. Adapted from Ref. 41.

One of the most characteristic consequences of introducing luminescent defects into the SWCNT structure is the appearance of new emission bands, termed E_{11}^* and the more red-shifted E_{11}^{*-} . These bands result from the formation of localized electronic states with lower energy than the native E_{11} transition, which act as excitonic traps and enable emission with extended wavelengths and often increased quantum yields ^{39,41,50,100}.

The energy position of these bands depends not only on the nanotube's chirality but primarily on the precise geometry of functional group attachment and their electronic properties. In particular, it has been shown that different defect bond configurations (e.g., ortho-L₉₀ and ortho-L₃₀ which influence on emission is presented

in Figure 6) lead to the formation of distinct energy levels, corresponding to E_{11}^* (~1160 nm) and E_{11}^{*-} (~1260–1300 nm) for (6,5) SWCNTs emission, respectively^{108–110}.

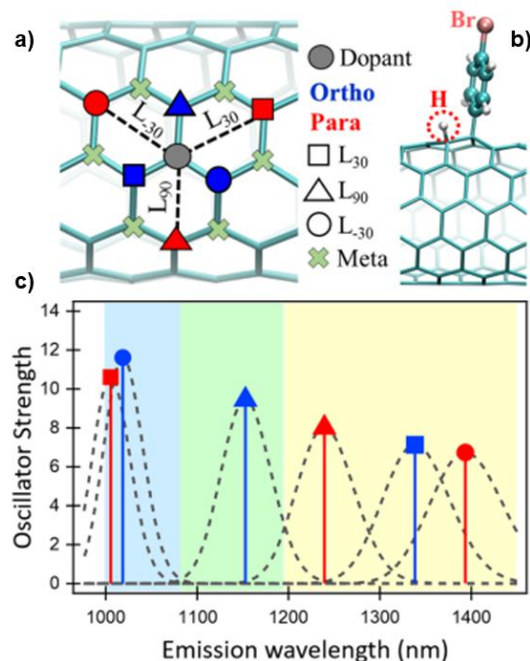


Figure 6. a) Top view of a SWCNT (6,5) nanotube, showing the aryl defect site (gray circle) and the allowed (circle, triangle, square) and forbidden (cross) positions for hydrogen atom attachment. Sites immediately adjacent to the defect (marked in blue) are referred to as ortho positions, while sites three carbon atoms away (red) are referred to as para positions. Both ortho and para positions are further divided into three types based on bond orientation: L_{30} (square), L_{90} (triangle), and L_{-30} (circle). b) Side view of a nanotube (6,5) with an attached 4-bromobenzene group and a hydrogen atom. c) Dependence of the oscillator strength and the emission wavelength of the lowest emission state for different transition configurations: Para L_{30} , Ortho L_{-30} , Ortho L_{90} , Para L_{90} , Ortho L_{30} , and Para L_{-30} in the case of (6,5) SWCNTs functionalized with 4-bromobenzene. Ortho transitions are marked in blue, while para transitions are marked in red. Different bond angles (30° , -30° , and 90°) are marked analogously to panel a). Dashed Gaussian lines represent the predicted inhomogeneity of the energy distribution for individual transitions. On this basis, the blue band (1000–1080 nm) was assigned to the Para L_{30} and Ortho L_{-30} transitions, the green band (1080–1190 nm) to the Ortho L_{90} transition, and the yellow band (>1190 nm) was assigned to the Para L_{90} , Ortho L_{30} and Para L_{-30} transitions. Adapted from Ref. 108.

Importantly, even small changes in the bond configuration or the nature of the substituents (e.g., their donor or acceptor properties) can lead to significant changes in the emission energy. It has been shown that the electronic properties of functional groups can modulate the spectral shift according to their electrostatic nature, opening the possibility of chemical programming of the emission wavelength.

The development of this concept was made possible by the development of a number of methods for the controlled covalent functionalization of SWCNTs. The most commonly used methods include radical reactions using diazonium salts ^{107,111–113}, nucleophilic reactions (e.g., with haloanilines) ¹¹⁴, photochemical cycloadditions ¹¹⁵, reductive reactions (e.g., with alkyl halides) ¹¹⁶, methods involving peroxides ^{117,118}, and oxidation processes leading to the introduction of oxygen defects (epoxides and ether) ^{119–123} where some of methods are presented in Figure 7.

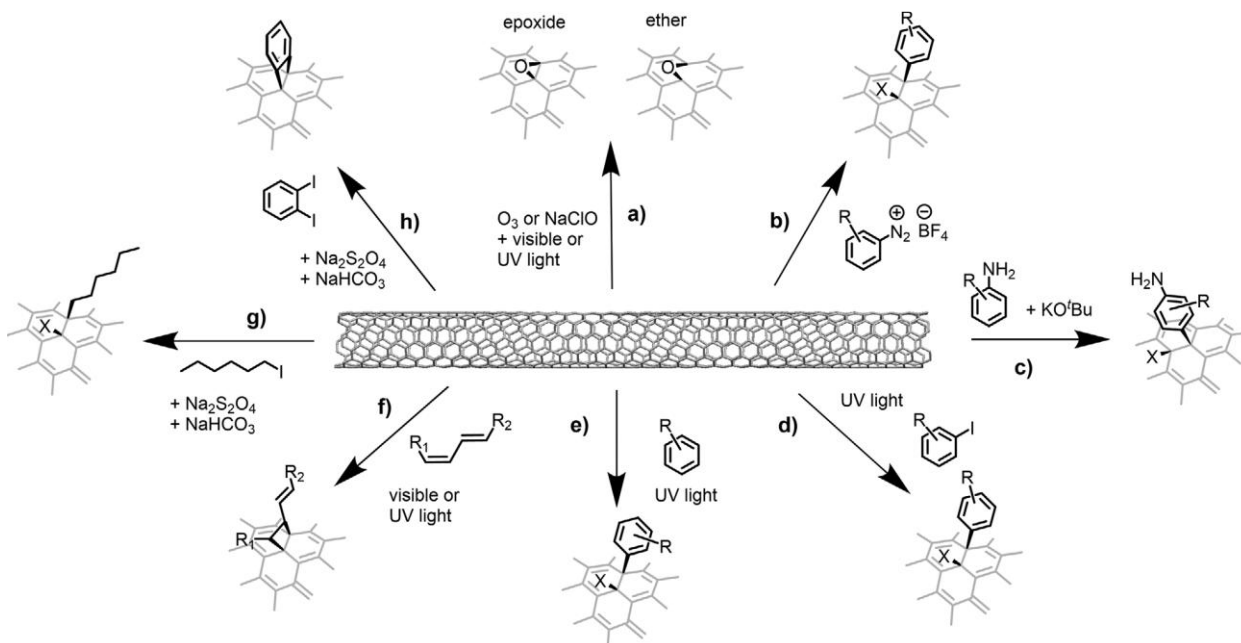


Figure 7. A review of selected chemical reactions enabling the introduction of luminescent defects into carbon SWCNTs along with proposed bonding configurations, including: (a) ozonation and oxygen doping leading to the formation of ether and epoxy groups, (b) reactions with aryl diazonium salts, (c) nucleophilic addition with 2-haloanilines in the presence of strong organic bases, (d) activation of aryl halides by UV radiation, (e) functionalization with nitroarenes and aminoarenes, (f) $[2\pi + 2\pi]$ photocycloaddition of enones, (g) reductive coupling with alkyl iodides, and (h) coupling with aryl diiodides. Adapted from Ref. 43.

Another key factor determining the luminescent properties of defects in SWCNTs is the chemical nature of the functional group attached to a given position. The introduction of substituents leads not only to the formation of an sp^3 center with a specific configuration but also to a modification of the local electrostatic potential in its vicinity, which directly affects the energy of the trap state E_{11}^* and the observed emission wavelength^{51,107,114,117,124}. In particular, it has been shown that the electronic properties of substituents – their donor or acceptor nature – modulate the exciton trap depth (Figure 8). Electron-accepting substituents lead to stabilization of the localized exciton and the formation of deeper energy states, which manifests as a redshift of emission. Donor groups, in turn, lead to shallower traps and smaller spectral shifts^{109,125}.

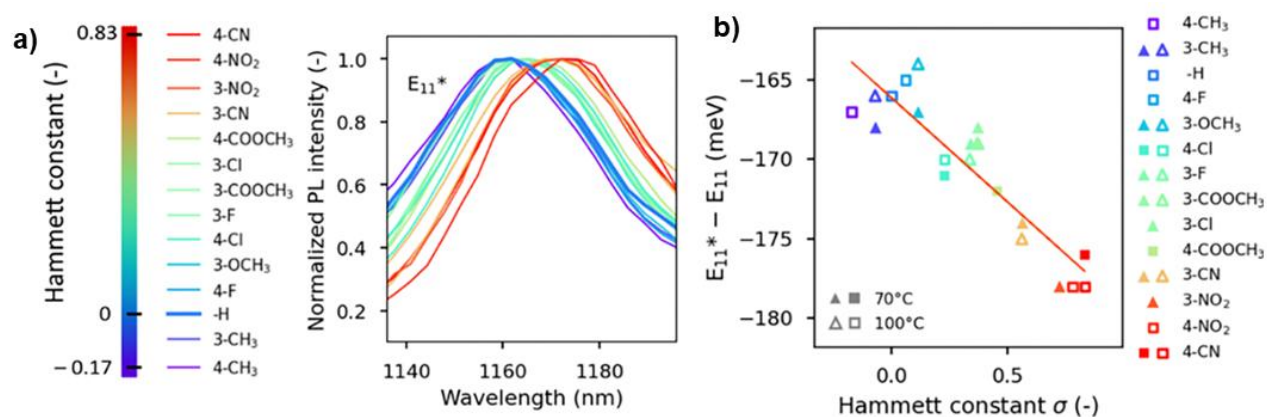


Figure 8. a) Normalized defect emission spectra (E_{11}^*) for SWCNTs (6,5) after functionalization with benzyloxy radicals containing different substituents. The colors of the curves were chosen according to the value of the Hammett constant (σ), which reflects the systematic influence of the electronic properties of the substituents on the position of the emission maximum. b) The dependence of the optical trap energy ($E_{11}^* - E_{11}$ difference) on the Hammett constant shows an approximately linear trend. For clarity, data for substituents at the meta and para positions are marked with different symbols (triangles and squares), respectively¹¹⁷. Adapted from Ref. 117.

It should also be emphasized that the effect of substituents is secondary to the defect attachment geometry. Experimental and theoretical studies have shown that for a given bond configuration (e.g., ortho- L_{90} or ortho- L_{30}), changing the functional group leads to only relatively small shifts in the emission energy (on the order of several to

several dozen meV), while changing the defect configuration itself results in much larger changes in the spectrum.

The ability to chemically tune the emission energy is one of the greatest advantages of SWCNTs over many other light-emitting materials. Selecting the appropriate functional group and its attachment method allows for control of both the emission wavelength, exciton lifetime, and photoluminescence efficiency. As a consequence, defects cease to be just a local disturbance of the crystal lattice but become a tool for designing new quantum states with predetermined properties.

2.5. Potential applicability of photoluminescent defects on SWCNTs

The introduction of sp^3 luminescent defects into SWCNTs enables a fundamental change in their optical properties by creating localized energy states below the E_{11} transition. Importantly, defect emission is more resistant to quenching processes, opening the way to applications in environments with high nanotube density and in real systems^{126,127}.

One of the most advanced applications is optical chemical and biological sensors. Experimentally, it has been demonstrated that SWCNT functionalization leading to defect formation enables direct modulation of emission in response to interactions with the chemical environment. Defects act as local interaction centers, and changes in their electrostatic or chemical environment translate into changes in the emission intensity or energy^{119,128}. Near-infrared emission enables detection in biological environments with minimal autofluorescence interference, making these systems particularly attractive for real-time biosensing. A natural extension of these properties is their use in bioimaging, especially in the NIR-II range (Figure 9)¹²⁹. Numerous experimental studies have shown that SWCNTs with oxygen or aryl defects exhibit increased emission brightness and the ability to image biological structures in-vivo at very low material doses^{40,130–132}, as demonstrated in Figure 10. Furthermore, their high photostability and resistance to photobleaching constitute a significant advantage over classical organic fluorophores. At the same time, the ability to chemically tune the emission wavelength by selecting the defect type or substituents allows for tailoring the optical properties to a specific application.

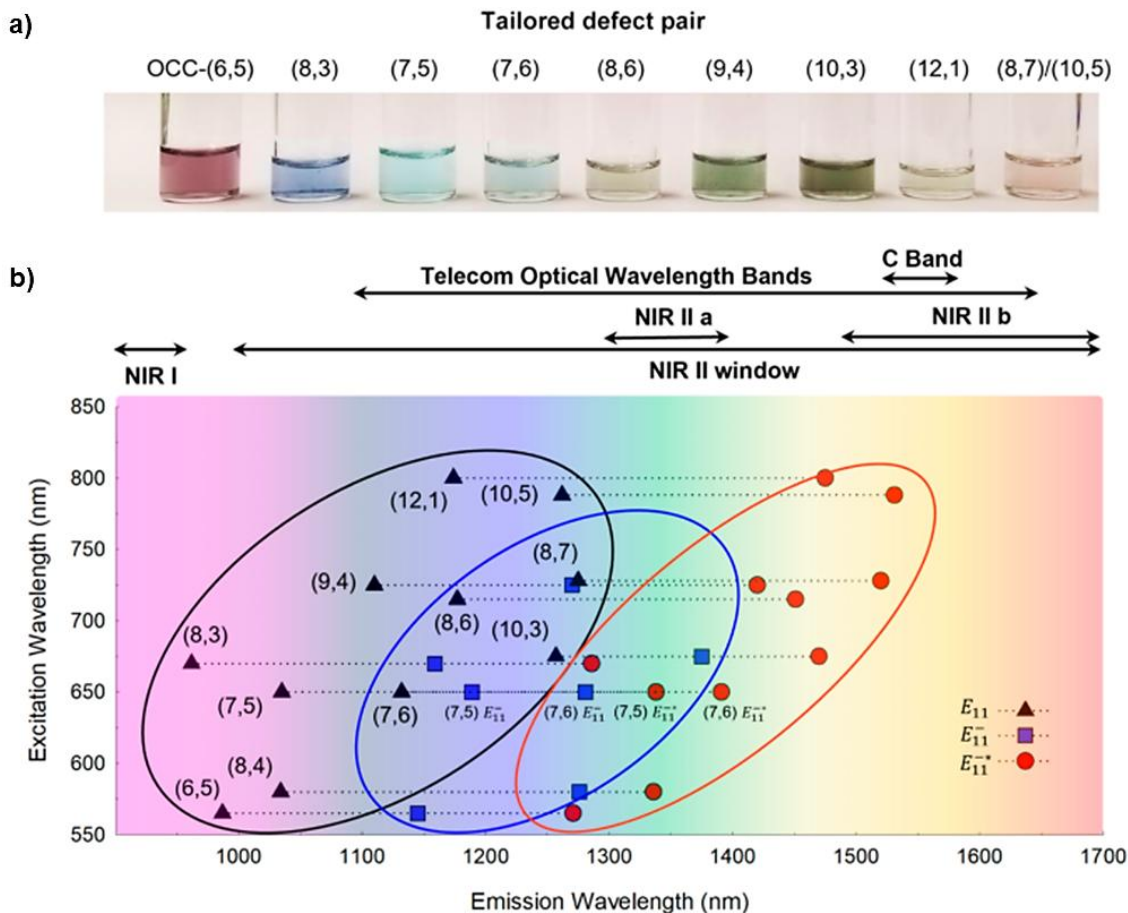


Figure 9. a) Photograph of aqueous SWCNT dispersions containing engineered photoluminescent defects for different chiralities (indicated in parentheses), illustrating the color changes resulting from their optical properties. (b) Summary of achievable emission wavelengths for the E_{11} (black triangles), E_{11}^- (blue squares), and E_{11}^{-*} (red circles) transitions. The points corresponding to SWCNTs (7,5) and (7,6) for the E_{11}^- and E_{11}^{-*} states are additionally highlighted due to their similar excitation wavelengths, facilitating their identification¹²⁹. Adapted from Ref. 129.

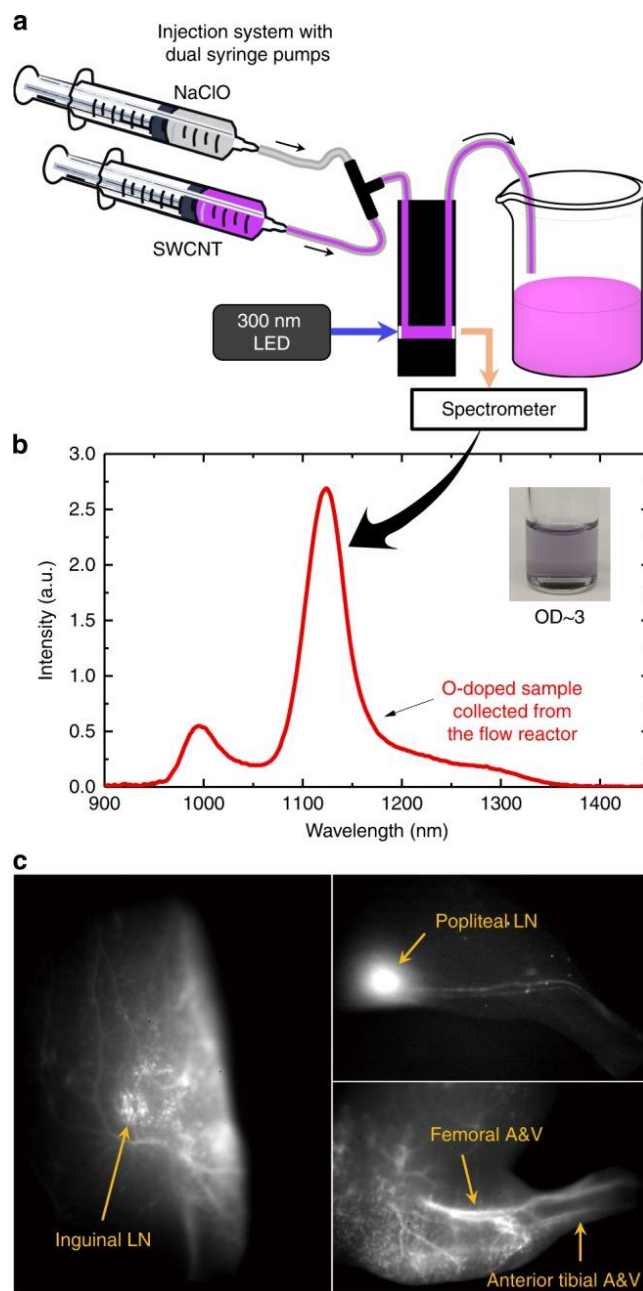


Figure 10. Efficient synthesis of O-doped SWCNTs and their application in fluorescence in vivo imaging ¹³⁰. (a) Schematic of a flow-through reactor equipped with syringe pumps and a UV source (300 nm) to initiate the reaction and excite emission, with detection in the SWIR range. (b) Emission spectrum of oxygen-doped SWCNTs prepared in the flow-through system (measured after dilution). Inset: photograph of a (6,5)-SWCNT sample immediately after synthesis. (c) In vivo SWIR fluorescence images showing visualization of lymph nodes and blood vessels after administration of small amounts of the material. Adapted from Ref. 130.

Another important area is quantum technologies, in which luminescent defects in SWCNTs act as single-photon sources. Room-temperature single-photon emission with high purity and the possibility of wavelength tuning in the telecommunications range has been experimentally demonstrated by selecting the nanotube chirality and defect type ¹³³. Localizing the exciton within a single defect center enables emission with high stability and narrow spectral distribution, which is crucial for applications in quantum communication.

Applications in optoelectronics and solid-state materials are being developed in parallel. In classical SWCNT systems, emission is strongly quenched because of different SWCNT species present in the system. The exciton energy can then be transferred to the adjacent less luminous SWCNT and eventually undergo radiationless relaxation instead of leading to photon emission, causing so-called self-quenching photoluminescence. ¹²⁷. The introduction of defects circumvents this problem by creating an alternative exciton recombination pathway. It has been experimentally demonstrated that defect emission can be more than an order of magnitude even in mixed systems and significantly more resistant to quenching than native emission ¹²⁷. Additionally, methods for locally introducing defects (e.g., photoactivated defects) are being developed, enabling spatial patterning of emission and potential integration with photonic systems ^{39,41}.

Despite its broad application potential, this technology still faces significant challenges. The most important problem remains limited control over the availability of monochiral SWCNTs, the number, type, and location of defects, which directly translates into the dispersion of optical properties. Although methods for quantitatively determining defect density have been developed, for example, based on Raman spectroscopy, universal standards enabling direct comparison of results between different samples and synthesis methods are still lacking ^{119,128,134,135}. An additional limitation is the strong dependence of optical properties on the SWCNT environment, including the surfactant or polymer corona used, which complicates the interpretation of results, particularly in sensor applications ^{38,136,137}. A critical assessment indicates that although luminescent defects in SWCNTs represent one of the most promising platforms for nanophotonics and biosensing, their full exploitation requires a transition from statistical functionalization methods to precise, deterministic engineering of single emissive centers capable of interacting with a specific analyte. The development of methods for controlling defect

configurations (e.g., ortho/para), their density, and electrostatic interactions, as well as integrating these processes with chirality separation techniques, will be crucial. Only a combination of structural and chemical control will enable the true potential of these systems to be realized in scalable optoelectronic and quantum technologies.

3. Experimental

3.1. Materials

The study utilized SWCNTs, CPs, and low-molecular-weight compounds used as additives in the CPE process and reagents for the chemical modification of SWCNTs. Surfactants, separation media, and solvents with diverse physicochemical properties were also used. Detailed information on the materials used, their origin, purity, and conditions of use are presented in the relevant publications P1-P5 that form the basis of this dissertation.

3.1.1. Reagents used for CP synthesis

Appropriately selected boron and dibromo derivatives containing fluorene, carbazole, thiophene, bipyridine, biphenyl, naphthalene, and benzothiadiazole units were used to synthesize the conjugated polymers. The set of monomers used allowed for the preparation of polymers with diverse architectures, adapted to the subsequent stages of the research.

In P.1, systems containing small-molecule extraction enhancers, referred to as molecular chaperones, were analyzed. In P.2, a series of fluorene polymers varying in length and alkyl chain combinations were used, while in P.3, the material library was expanded to include carbazole-based polymers and structures designed to replicate the characteristics of polymers exhibiting high selectivity for specific chiralities of SWCNTs.

A detailed list of substrates and other reagents used during the synthesis is presented in publications P.1–P.3.

3.1.2. Reagents used for modification of SWCNTs

Studies on the chemical modification of SWCNTs were conducted in P.4 and P.5. In P.4, phenylhydrazine and a number of its derivatives with diverse chemical structures and electronic properties were used. Other compounds used as initiators or additives

that influence the extraction and functionalization processes of SWCNTs were also analyzed.

A detailed range of tested reagents and their applications are described in publication P.4.

3.1.3. Surfactants and separation media

The studies presented in P.4 utilized selected surfactants and polymeric separation media used to prepare and stabilize SWCNT dispersions. The systems used included both classical surfactants and polymeric materials used to control dispersion properties. Detailed information on the materials used is presented in publication P.4.

3.1.4. Solvents

Organic solvents with varying physicochemical properties were used in the individual stages of the research. In the studies on CPE, they served as the medium responsible for the preparation and stabilization of SWCNT dispersions and polymer–SWCNT complexes. In P.5, media with varying physicochemical properties were used to determine the effect of the reaction environment on the SWCNT modification process and the optical properties of the resulting materials. Detailed information on the media used is presented in the relevant publications, particularly in P.5.

3.1.5. SWCNTs

Commercially available SWCNTs of various chiral compositions were used in this study, including CoMoCAT materials enriched in selected chiralities and HiPco material. Detailed information on the starting materials and their parameters is provided in the relevant publications.

3.2. Methods

3.2.1. Polymer synthesis

The syntheses of polyfluorene and polycarbazole derivatives were performed using the Suzuki coupling method. The structure of the products was confirmed by ^1H NMR spectroscopy (P1-P5) and their macromolecular parameters were determined by size-exclusion chromatography presented in series of publications P1-P5.

In a typical procedure, the appropriate boronate and dibromofluorene derivatives were introduced into a reactor in equal molar amounts (Figure 11), followed by the

addition of aqueous Na_2CO_3 solution, toluene, and a phase transfer catalyst (Aliquat 336). After degassing the mixture with argon, the $\text{Pd}(\text{PPh}_3)_4$ catalyst was added and the reaction was conducted at 80°C for 4 days. After the reaction was complete, the product was precipitated in a mixture of methanol and water, filtered, dissolved in chloroform, and dried over MgSO_4 . The solvent was then evaporated, and the polymer was reprecipitated in methanol. The resulting material was purified by washing with cold methanol and acetone and collected by filtration.

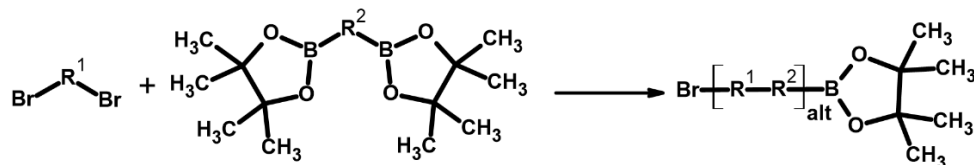


Figure 11. Representative simplified scheme of polymer synthesis via Suzuki polycondensation.

3.2.2. CPE process

Solution consisting of SWCNTs (0.33 mg/mL) and polymer (2 mg/mL) was poured inside glass vial and then mixture was homogenized via sonication for 15 min (POLSONIC, SONIC-2, 250 W) at 10°C . Subsequently, more vigorous sonication with a tip sonotrode (Hielscher UP200St ultrasonic generator) was performed to disentangle the SWCNTs and wrap them with the conjugated polymer. After sonication, the obtained suspension was transferred to conical tubes and centrifuged at 9,000 rpm ($15,314 \times g$) for 3 min, promoting the precipitation of the bundled and unwrapped SWCNTs, as well as polymer aggregates. After centrifugation around 80% of the supernatant was transferred to a fresh vial and analyzed by absorbance spectroscopy and PL excitation-emission mapping.

3.2.3. Functionalization of dispersed SWCNTs

1.5 mg of raw (6,5)-enriched SWCNTs (CoMoCAT, SG65i) was dispersed in the presence of conjugated polymer in toluene using a tip-horn sonicator to obtain near monochiral (6,5) and (7,5) SWCNT fractions. Then, toluene was evaporated, and the remaining precipitate was redispersed in a spectrum of indicated solvents using a sonication bath. Subsequently, the material was subjected to covalent modification. Once the 1-hour-long heating was complete, (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) was added to halt the progress of the reaction. The mixture was then filtered

and redispersed in 1 mg/mL toluene solutions of PFO-BPy and PFO respectively for each SWCNTs species. The process of transferring SWCNTs back to toluene was crucial for performing the measurement, because it is not possible to maintain them in a stable state in some of the liquid media also due to solvatochromic shifts. The concentration of the SWCNTs was adjusted to 0.5 a.u. (measured at the E_{11} optical transition for 5 mm quartz cuvettes) for suspensions prepared in various solvents.

3.2.4. Functionalization of undispersed SWCNTs

1.5 mg of raw (6,5)-enriched SWCNTs raw (CoMoCAT, SG65i) was dispersed in 5 mL of each of the indicated solvents (Table 2) using a tip-horn sonicator, then 2.75 mg of PhH was added to the dispersion, vortexed, and then heated for one hour at 80°C. After thermal functionalization, TEMPO was added to the material to trap radicals resulting from PhN_2H_3 decomposition, bath sonicated, vortexed, and filtered using a Teflon membrane. Consequently, the radicals were quenched, and non-SWCNT compounds were removed. For characterization purposes, purified functionalized (6,5) SWCNTs were selectively extracted PFO-BPy_{6,6'} in toluene and then analyzed by PL spectroscopy. To avoid detector saturation and to ensure the reliability of the measurements, the SWCNT concentration was set to an absorbance value of 0.5 a.u. before the measurements.

Table 2. List of solvents of choice with their physical properties used in SWCNT modification

Solvent	Dipole Moment [D]	Density [g/mL]	Dielectric Constant [F/m]	Boiling Point [°C]	Viscosity at 20°C [mPa·s]
Benzene	0.00	0.876	2.274	80.1	0.61
Toluene	0.36	0.867	2.38	110.6	0.59
<i>o</i> -xylene	0.62	0.880	2.56	144.4	0.80
<i>m</i> -xylene	0.37	0.864	2.31	139.1	0.64
<i>p</i> -xylene	0.00	0.861	2.27	138.3	0.60
<i>p</i> -cymene	0.00	0.857	2.72	177.0	0.85
Carvacrol	1.7	0.9772	9.8	237.7	6.1
Tetralin	0.61	0.970	2.32	207.0	2.35
Chlorobenzene	1.54	1.106	5.62	132.0	0.80
Anisole	1.38	0.995	4.33	154.0	1.30
Acetonitrile	3.92	0.786	35.9	81.6	0.36
Dimethylformamide	3.82	0.944	36.7	153.0	0.80
Dimethyl sulfoxide	3.96	1.100	47.2	189.0	2.00
Water	1.85	0.998	78.5	100.0	1.00

3.3. Characterization of the obtained materials

The obtained SWCNTs and polymers were characterized using spectroscopic and chromatographic methods selected according to the purpose of each study. These included absorption spectroscopy, photoluminescence and excitation-emission mapping, Raman spectroscopy, infrared spectroscopy, size exclusion chromatography, and nuclear magnetic resonance spectroscopy.

The structures of the obtained polymers were confirmed using ^1H NMR spectroscopy, while their macromolecular parameters were determined by SEC. Complete NMR data for all polymers obtained and analyzed in P.1–P.3 are presented in these publications.

4. Results and discussions

4.1. Increasing the extraction efficiency of conjugated polymers using molecular enhancers

CPE is currently one of the most selective methods for separating SWCNTs based on chirality. The process mechanism is based on the spontaneous wrapping of appropriately designed macromolecules around the SWCNT surface, leading to the formation of stable complexes soluble in organic solvents. Proper selection of the polymer architecture enables the use of molecular matching, which preferentially stabilizes only SWCNTs with specific diameters and chiral angles. Despite its very high selectivity, this method has for many years struggled with a fundamental limitation: low process efficiency. An additional problem is that the efficiency of most developed extraction systems is strongly dependent on the type of starting material. A polymer that provides near-monochiral separation for the (6,5)-enriched CoMoCAT material often exhibits significantly lower selectivity when applied to more complex mixtures, such as HiPco or (7,6)-enriched CoMoCAT SWCNTs, containing a significantly larger number of different SWCNT species. This means that most existing CPE protocols are not universal and require re-optimization after each change in the starting material, significantly limiting the practical application of this technology.

In the first stage of research, it was hypothesized that it would be possible to increase extraction efficiency without compromising selectivity by simultaneously using two polymers with different adsorption properties. Polymer PFO-BPy6,6' was selected

which exhibits very high selectivity for (6,5) SWCNTs but moderate extraction efficiency, and the PFO-T polymer, which exhibits significantly greater affinity for the SWCNT surface but leads to non-selective extraction of a wide range of chiralities (Figure 12a). It was assumed that an appropriately selected ratio of both macromolecules would allow for the stronger interaction of PFO-T with the nanotube surface while maintaining the selectivity resulting from the presence of PFO-BPy6,6'. This hypothesis was particularly interesting because previous literature reports indicated competition between the different polymers rather than the possibility of their cooperation. In practice, this meant trying to combine two seemingly contradictory features – high selectivity and high process efficiency – which had previously been considered difficult to achieve simultaneously.

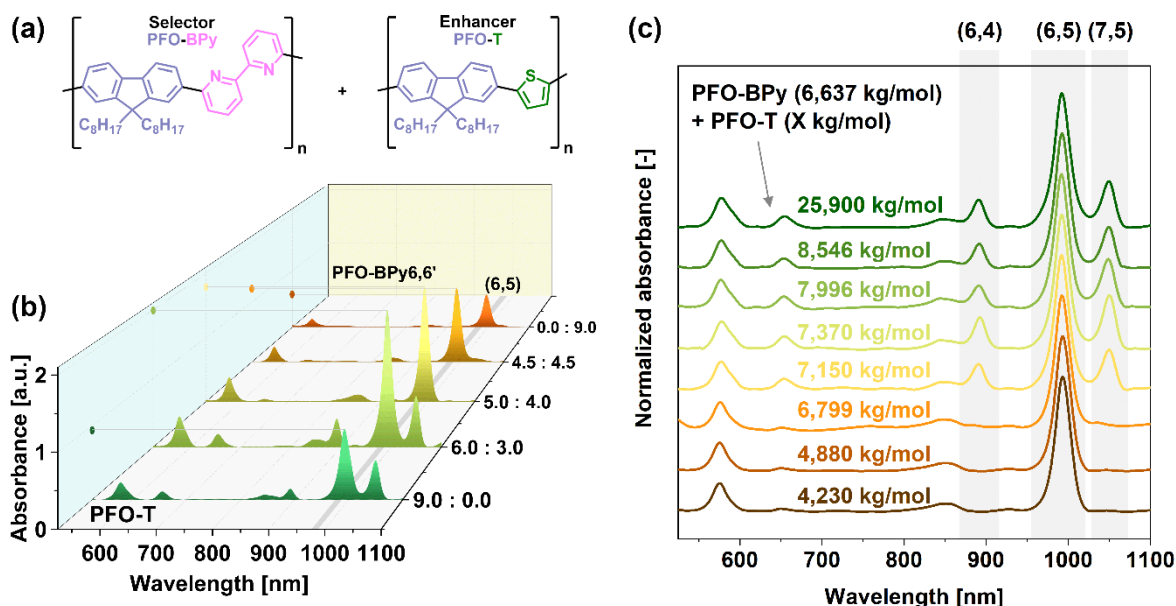


Figure 12. (a) Scheme of the application of the mixture of PFO-BPy6,6' (selector) and PFO-T (enhancer). (b) Effect of the mass ratio of PFO-T:PFO-BPy6,6' on the extraction efficiency and selectivity (for 1.5 mg of SWCNTs in 8 mL of toluene). (c) Effect of the molecular weight of PFO-T on the purity of the obtained fractions; a 5:4 ratio was used in the studies⁸⁰. Adapted from Ref. 80.

The conducted tests confirmed the hypothesis. A properly selected ratio of both polymers enabled a nearly threefold increase in the number of isolated (6,5) SWCNTs while maintaining virtually unchanged chiral purity. This meant that the addition of an appropriate amount of PFO-T did not interfere with the process of recognition of

the correct SWCNT species by the selective polymer, but merely increased the efficiency of polymer-nanotube complex formation. Simultaneously, it was demonstrated that the synergistic effect was observed only within a precisely defined range of the two polymer ratios (Figure 12b). Both too low and too high a share of the enhancer led to deterioration of the process parameters, indicating the existence of an optimal range of interaction between the two macromolecules. The findings obtained provided the first evidence that a properly designed multipolymer system can overcome the current compromise between the efficiency and selectivity of CPE extraction.

A particularly interesting finding was the demonstration of the crucial role of the molecular weight of the polymer acting as the enhancer (Figure 12c). It was shown that the efficiency increase was observed only for short PFO-T chains, while increasing molecular weight led to a gradual loss of process selectivity. This means that long macromolecules begin to compete with the selective polymer for adsorption sites on the SWCNT surface, disrupting its ordered conformation. Short oligomers, however, are unable to stabilize the suspension on their own, but they effectively complement the surface areas remaining uncovered by PFO-BPy6,6', increasing the stability of the entire complex. This result identified molecular weight as a new parameter for the design of extraction systems, which had not previously been considered in the context of mixed polymer systems.

The next stage of the research was to determine whether the use of entire macromolecules was necessary to achieve the strengthening effect, or whether only their building blocks would be sufficient (Figure 13a and Figure 13b). For this purpose, a series of low-molecular-weight compounds corresponding to the structural fragments of the polymers used were tested, including fluorene, bipyridine, and thiophene units. Experiments showed that virtually all additives improved the process efficiency, but by far the best results were obtained with compounds containing a thiophene ring. 2,5-Dibromothiophene proved particularly effective, enabling a nearly eleven-fold increase in the concentration of isolated nanotubes while maintaining virtually unchanged process selectivity (Figure 13c-13g). The obtained results demonstrated that appropriately selected low-molecular-weight additives can replace oligomers, which are much more complex to synthesize, simplifying the entire extraction procedure. From a practical perspective, this represented a significant step towards the commercialization of CPE technology.

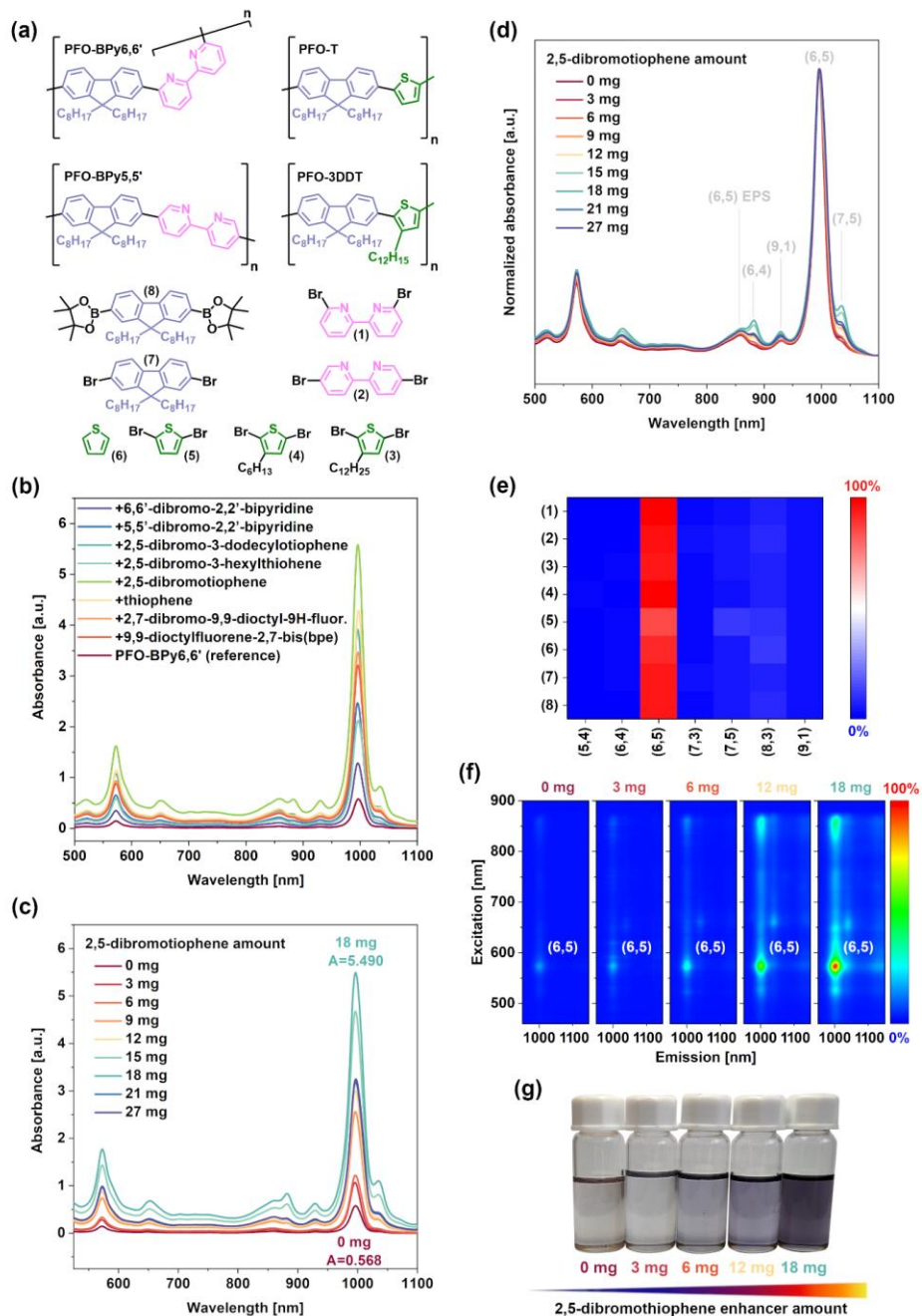


Figure 13. (a) Set of tested molecular enhancers improving the isolation efficiency of (6,5) SWCNTs. (b) Effect of their addition (18 mg) on extraction compared to PFO-BPy6,6' alone. (c-d) Changes in absorbance (including normalized absorbance) as a function of the amount of 2,5-dibromothiophene. (e) Contribution of individual chiralities in the supernatant for different enhancers. (f) PLE maps for systems with different amounts of 2,5-dibromothiophene. (g) Optical images confirming the increase in SWCNTs concentration after its addition⁸⁰. Adapted from Ref. 80.

Molecular modeling provided a better understanding of the cause of the observed phenomenon. Simulations showed that the presence of thiophene derivatives significantly accelerates the process of wrapping PFO-BPy6,6' macromolecules around the nanotube surface and leads to the formation of more ordered polymer-SWCNT complexes (Figure 14a-c). A reduction in the number of solvent molecules located directly at the nanotube surface was also observed, further promoting polymer adsorption. This effect increased the rate of formation of stable complexes responsible for suspension stabilization and limited the process of their re-unwinding, which leads to sedimentation of the material. Importantly, an identical trend was also observed during the separation of much more complex HiPco materials, where, despite the presence of dozens of different chiralities, a significant enrichment of the different species some selectivity toward (6,5) type was still achieved. These results indicate that the discovered mechanism is universal and not limited to a single type of commercial SWCNT source.

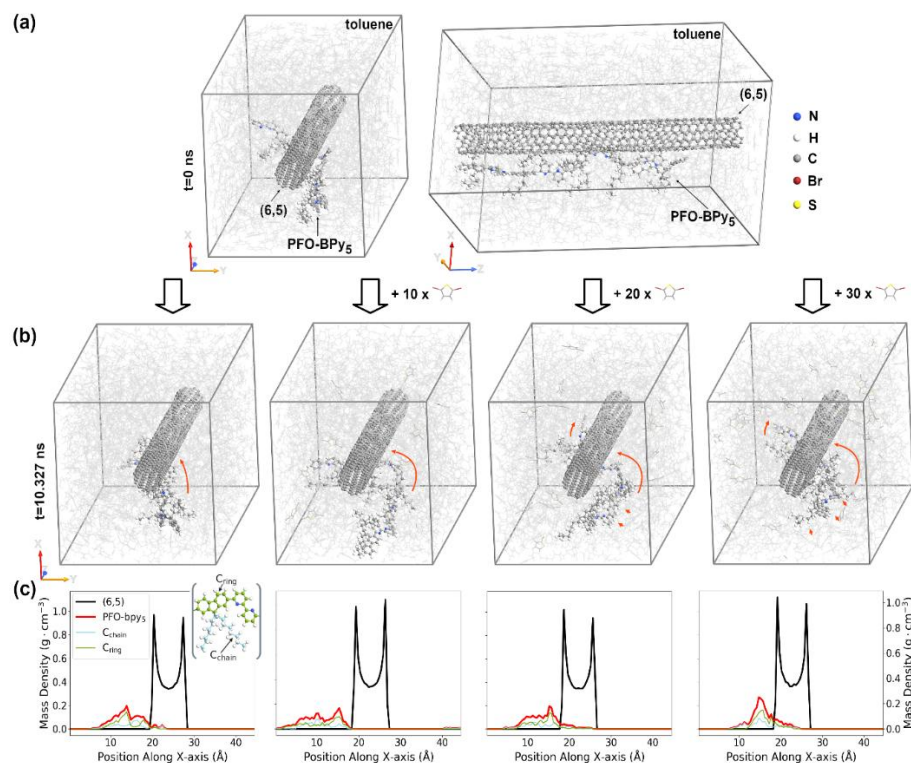


Figure 14. (a) Initial MD model of PFO-BPy6,6'-wrapped (6,5) SWCNTs in toluene. (b) Final configurations with increasing 2,5-dibromothiophene concentration, showing accelerated polymer wrapping. (c) Mass density profiles of the SWCNT, PFO-BPy6,6' backbone (C_{ring}), and alkyl chains (C_{chain})⁸⁰. Adapted from Ref. 80.

Based on all the experiments conducted, a mechanism of action for so-called molecular chaperones was proposed. The most likely explanation for the observed effect is the reorganization of the selective polymer conformation induced by the presence of small molecules containing a thiophene ring. It can be assumed that a significant role is played here by the favorable distribution of electron density in the aromatic system, the strong adsorption of the thiophene ring on the surface of SWCNTs, and additional interactions between the sulfur atoms present in the additive and the nitrogen atoms found in the bipyridine units of the PFO-BPy_{6,6'} polymer. Although the exact nature of these interactions requires further investigation, the data collected clearly indicate that these additives do not directly participate in the chirality selection process, but rather accelerate the formation of the most stable complexes responsible for the extraction of the selected SWCNT species. This discovery led to the formulation of a new concept of molecular chaperones, which allowed for an increase in process efficiency by up to elevenfold without sacrificing high selectivity and is one of the most important achievements of this doctoral dissertation.

4.2. Explanation of the mechanism of interactions between polymers and SWCNTs during CPE extraction

The considerable extension of the research presented in paper P.1 raised another question: what chemical properties must a process enhancer possess to improve extraction without completely disrupting the interactions responsible for the selective recognition of specific SWCNT chirality? The aim of this work was therefore to understand the mechanism responsible for the action of molecular chaperones and to determine the limits of their applicability⁷⁷.

The research methodology conducted in P2 was similar to that used in publication P.1. The CPE technique was performed in toluene and a set of spectroscopic methods were used to characterize the obtained SWCNT dispersions, including absorption spectroscopy, photoluminescence mapping, and analysis of the chiral composition of the material. Additionally, the research was expanded to include the synthesis of new fluorene copolymers, molecular dynamics modeling, and DFT calculations, enabling analysis of the strength of interactions between the individual components of the extraction system.

The first achievement of this work was the design and synthesis of a complete family of copolymers based on a polyfluorene backbone, differing in length and combination of alkyl chains attached to the fluorene units. In addition to the classic poly(9,9-dioctylfluorene) (PFO), which is the reference material for (7,5) SWCNT separation, new copolymers were also obtained (where the numbers in parentheses refer to the number of carbons in the alkyl chain of each fluorene subunit, respectively): PFO-F (8:0), PFO-FH (8:6), PFO-FD (8:10), PFO-FDD (8:12), and PFDD (12:12), enabling a systematic study of the effect of side chain length on the CPE process (Figure 15a). A particularly significant achievement was the discovery of a previously unreported PFO-FH copolymer, which—like classical PFO—exhibited exceptionally high selectivity for (7,5) SWCNTs, enabling the production of dispersions with purity approaching 90% (Figure 15b-e). Furthermore, it was demonstrated that virtually all fluorene polymers tested exhibited a natural affinity for SWCNTs with chiralities (6,5) and (7,5), but even small changes in side chain length led to significant changes in the balance between extraction efficiency and selectivity. PFO-FD and PFDD primarily preferred nanotubes with smaller diameters, while PFO-FDD retained partial selectivity for (7,5), but at the expense of a significantly higher proportion of the remaining chiralities. PFO-F, on the other hand, lacking alkyl chains in every other unit, proved to be a virtually nonselective polymer, capable of stabilizing a wide range of different SWCNT species. These results clearly demonstrated that the presence of appropriately selected alkyl chains is not directly responsible for the recognition of a specific chirality, but rather stabilizes the conformation of the macromolecule on the nanotube surface and regulates the interaction of the polymer backbone with the carbon atom network. This challenged the commonly accepted hypothesis that extending alkyl chains leads to the preferential separation of SWCNTs with larger diameters. The gathered data demonstrated that this relationship is much more complex and results from the balance between π - π interactions, the flexibility of the macromolecule, and its adsorption mode on the SWCNT surface. This was one of the first systematic studies demonstrating that rational design of polymer side chain architecture can be as effective a tool for controlling extraction selectivity as modifying the conjugated polymer backbone itself.

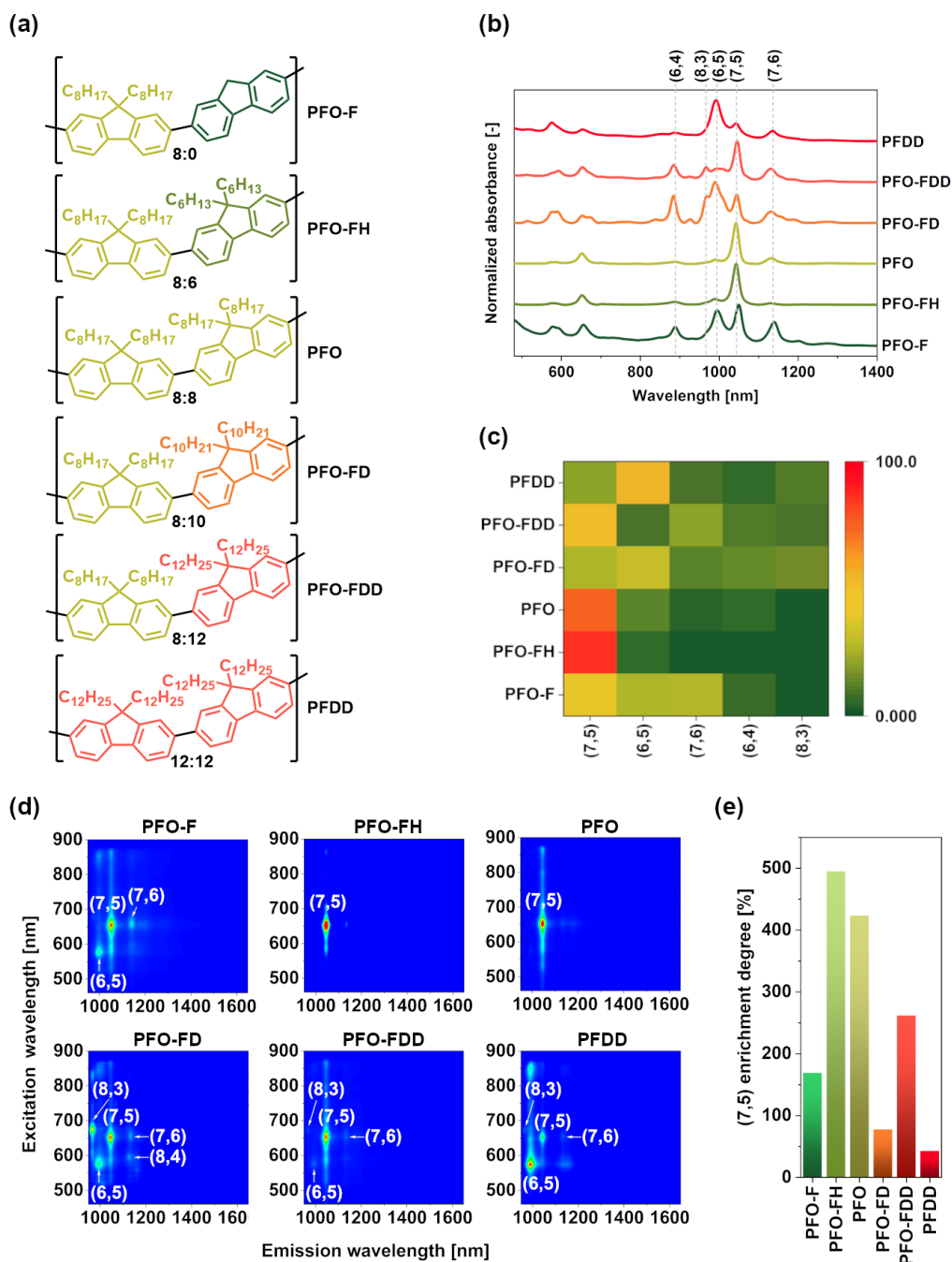


Figure 15. (a) Structures of the obtained polymers. (b) Absorption spectra of SWCNT dispersions prepared using them. (c) Analysis of chiral composition based on spectral deconvolution. (d) Corresponding PLE maps. (e) Degree of enrichment of fraction (7,5) depending on the polymer used ⁷⁷. Adapted from Ref. 77.

The next step in the study was to test whether the CPE enhancement strategy previously developed for the PFO-BPy system could be transferred to the PFO

polymer, which selectively isolates chiral nanotubes (7,5). To this end, a two-component extraction system was constructed based solely on polymers exhibiting a natural affinity for the same chirality, thus avoiding competition between macromolecules with different adsorption preferences. It was demonstrated that the use of polymers preferring different SWCNT species leads to a complete loss of process selectivity, as the more strongly interacting macromolecules displace the polymer responsible for chirality recognition from the nanotube surface (Figure 16). The obtained results indicated that the design of multicomponent CPE systems requires maintaining consistent affinity of all components for the same SWCNT chirality, and that mixing random polymers and monomers is not an effective strategy for increasing extraction efficiency.

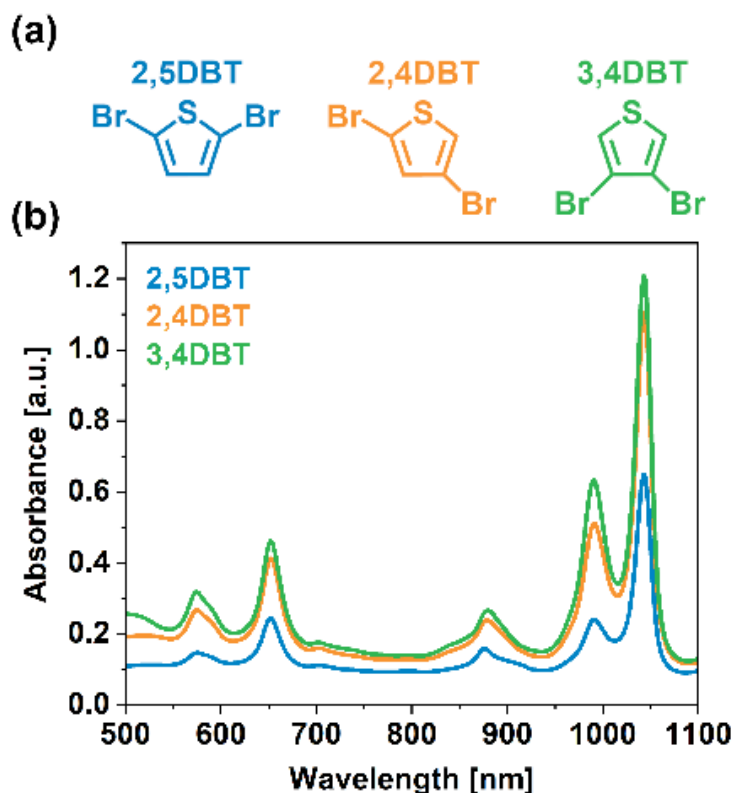


Figure 16. (a) Chemical formula of structural isomers of dibromothiophene used in this experiment. (b) As-recorded optical absorbance spectra of PFO/SWCNT suspensions prepared in the presence of 18 mg of 2,5DBT, 2,4DBT, and 3,4DBT.

Detailed analysis revealed that the addition of the PFO-FH fraction, a polymer also exhibiting selectivity for (7,5) SWCNTs, allows for a nearly two-fold increase in the

concentration of isolated SWCNTs while maintaining their very high optical purity (Figure 17). The most favorable results were obtained for a PFO:PFO-FH mass ratio of 3:6, for which the absorbance corresponding to the E_{11} transition of the (7,5) SWCNTs increased from 0.68 to 1.16 without the appearance of additional signals from other chiralities. These results led to the formulation of the concept of the self-enhancing effect of fluorene polymers, which involves the interaction of fractions with different molecular weights. Longer polymer chains are responsible for the selective recognition and wrapping of the nanotube surface, while shorter macromolecules stabilize the resulting polymer-SWCNT complexes in solution, limiting their aggregation and precipitation during centrifugation. At the same time, it was demonstrated that this effect occurs only when the appropriate balance between the two fractions is maintained. An excess of short chains leads to reduced selectivity by hindering the adsorption of long macromolecules on the SWCNT surface, while an excessive proportion of the high-molecular-weight fraction promotes the entanglement of polymer chains, reducing their ability to effectively wrap nanotubes. This discovery demonstrated for the first time that the molecular weight distribution of a polymer and its polydispersity are not merely technological parameters but are key factors determining both the efficiency and selectivity of the CPE process. In practice, this means that the extraction properties of a polymer can be regulated not only through its chemical structure but also by deliberately controlling the molecular weight characteristics during synthesis, opening up new possibilities for designing significantly more effective systems for SWCNT separation.

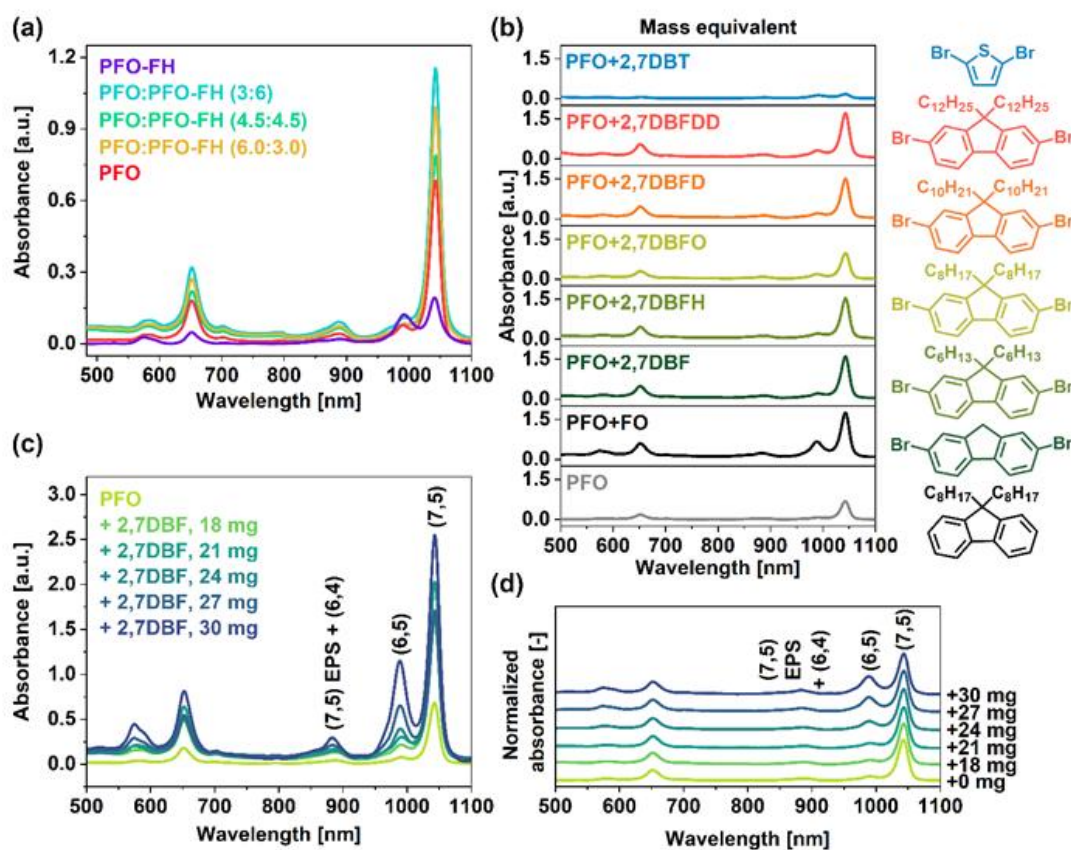


Figure 17. (a) Absorption spectra of SWCNTs dispersed in PFO, PFO-FH, and their mixtures (mass ratios given in mg/5mL). (b) Spectra for systems with the addition of selected extraction enhancers. (c–d) Absorption spectra (raw and normalized) for dispersions prepared from PFO and 2,7DBF at different mass ratios in mg/5mL.

The most important finding of this work, however, was the demonstration that the effectiveness of molecular chaperones does not depend solely on their chemical structure or their ability to interact with the SWCNT surface. The first publication from presented in this thesis monothematic series demonstrated that 2,5-dibromothiophene is an extremely effective enhancer of nanotube extraction (6,5) using the PFO-BPy copolymer. Therefore, it was initially assumed that a similar effect should be observed for other extraction systems based on fluorene polymers. This hypothesis seemed justified, as all the polymers tested had a similar conjugated aromatic skeleton, and their adsorption on the SWCNT surface was based on π - π interactions and van der Waals forces. Contrary to these expectations, the use of 2,5-dibromothiophene in the PFO-based system not only failed to improve the process

efficiency but also led to an almost complete loss of selectivity for (7,5) SWCNTs. This result clearly indicated that there is no universal molecular chaperone suitable for all CPE systems, and that the effectiveness of the additive is strictly dependent on the nature of the interactions occurring between the specific polymer and the nanotube surface.

Analysis of the obtained results allowed me to propose a new explanation for this phenomenon. In the case of the PFO-BPy copolymer, bipyridine units containing nitrogen atoms play a key role in the adsorption process, their presence leading to significantly stronger interactions with the SWCNT surface than in the case of classic polyfluorenes. It can be assumed that the presence of a sulfur atom in the 2,5-dibromothiophene molecule promotes additional stabilization of these complexes through favorable interactions between sulfur and nitrogen heteroatoms and the appropriate distribution of electron density within both aromatic systems. As a result, the additive molecule does not compete with the polymer for adsorption sites but supports its organization on the nanotube surface, accelerating the formation of a stable complex responsible for selective extraction. A different situation occurs with classical PFO, whose interaction with the SWCNT surface is determined almost exclusively by the contact of conjugated fluorene rings with the graphene surface and van der Waals interactions. In this system, 2,5-dibromothiophene exhibits an affinity for the nanotube surface comparable to or even greater than the polymer itself, thus competing with it for adsorption sites. This leads to disruption of the ordered process of wrapping the macromolecule around the SWCNT and destabilization of the complexes responsible for selective (7,5) nanotube recognition. Consequently, a loss of process selectivity was observed despite the use of an additive that demonstrated very favorable effects in another extraction system.

Data that was obtained led to the formulation of a new principle for the design of molecular chaperones used in the CPE technique. It was demonstrated that an effective enhancer cannot interact with the SWCNT surface more strongly than the polymer responsible for extraction selectivity. Its role should be limited to stabilizing the macromolecule's conformation and facilitating its adsorption process, without displacing the polymer from the nanotube surface. This means that the design of new chaperones should always be tailored to the nature of the interactions of a specific selective polymer, rather than relying on the search for universal additives applicable to all CPE systems. This was the first such unequivocal demonstration that the

effectiveness of molecular enhancers is a function of the relative adsorption strength of the additive and polymer, not solely their chemical structure or charge transfer capacity. In practice, this discovery created a new paradigm for the design of extraction systems, in which the key parameter becomes the balance of interactions at the polymer–chaperone–SWCNT interface, rather than the properties of a single component of the system.

The presented concept represents the first formulation of a universal principle for the design of molecular enhancers for the CPE technique. The proposed model not only explains the results obtained in this work but also explains numerous discrepancies previously observed in the literature when using the same additives with different families of conjugated polymers. Importantly, this principle is general in nature and can be used in the design of subsequent generations of materials for the selective separation of SWCNTs. This opens the possibility of rationally designing extraction systems not through trial and error, but through conscious control of the energy of interactions between all process components. Consequently, this publication provided the first universal guidelines enabling the selection of molecular chaperones based on physicochemical parameters rather than solely on empirical observations, which constitutes one of its most important scientific achievements.

4.3. Unravelling the structure–affinity relationship between CP and SWCNT surfaces

The next research demonstrated the potential for increasing the efficiency of the CPE process through the use of appropriately selected macromolecules and molecular chaperones. The primary goal was to understand the mechanisms responsible for molecular recognition of nanotube surfaces by conjugated polymers. Despite the long-standing use of fluorene polymers for SWCNT separation, the relationship between their chemical architecture and extraction selectivity remained virtually unknown. Most known materials were developed through trial and error, and the literature did not provide clear answers as to which polymer structural elements are responsible for recognizing specific nanotube chirality. The aim of this work was therefore to systematically analyze the influence of polymer chemical structure on their interaction with SWCNT surfaces and to develop general principles for the design of new macromolecules for CPE applications.

To this end, a library of new CP structures was designed P3, whose architecture was based on deliberately mimicking the most selective systems described in the literature to date as presented in Figure 18a. The starting point were three polymers currently used in CPE: PFO-BPy6,6', which selectively isolates (6,5) nanotubes ⁸⁹, PFO-BT, responsible for (7,3) nanotube separation ⁸⁶, and poly(9,9-dioctylfluorene) (PFO), which exhibits high selectivity for (7,5) chirality ⁹⁰. Additionally, the study included a non-selective copolymer, PFO-BPy5,5', whose extraction properties differ significantly from those of its isomer, PFO-BPy6,6'. This polymer was a particularly interesting reference point because it differs from its selective counterpart only in the position of nitrogen atoms in the bipyridine moiety, which suggested that even small structural changes can lead to a complete change in extraction properties.

The most important goal of the project was to eliminate as many structural variables as possible that could complicate the interpretation of results. Unlike previous studies, which compared polymers differing in multiple chemical features, in this study, each subsequent macromolecule was designed as a direct analogue of the reference material. This meant that the new polymers differed from their prototypes only in one or two strictly controlled elements of their chemical structure. This approach allowed for the unambiguous attribution of observed changes in selectivity or extraction efficiency to a specific structural modification, eliminating the influence of other parameters. The basic premise of the project was to create families of polymers that "mimic" each other, maintaining the greatest possible electronic and structural similarity. The alkyl chain lengths responsible for the polymers' solubility in organic solvents were identical, the length of the π -conjugated system similar, and the geometry of the entire macromolecular backbone as similar as possible. This resulted in systems differing almost exclusively in the presence or absence of specific heteroatoms, their position in the structure, or the electronic nature of the second building block. This allowed for the separation of steric and electronic effects, a feat previously impossible in CPE research.

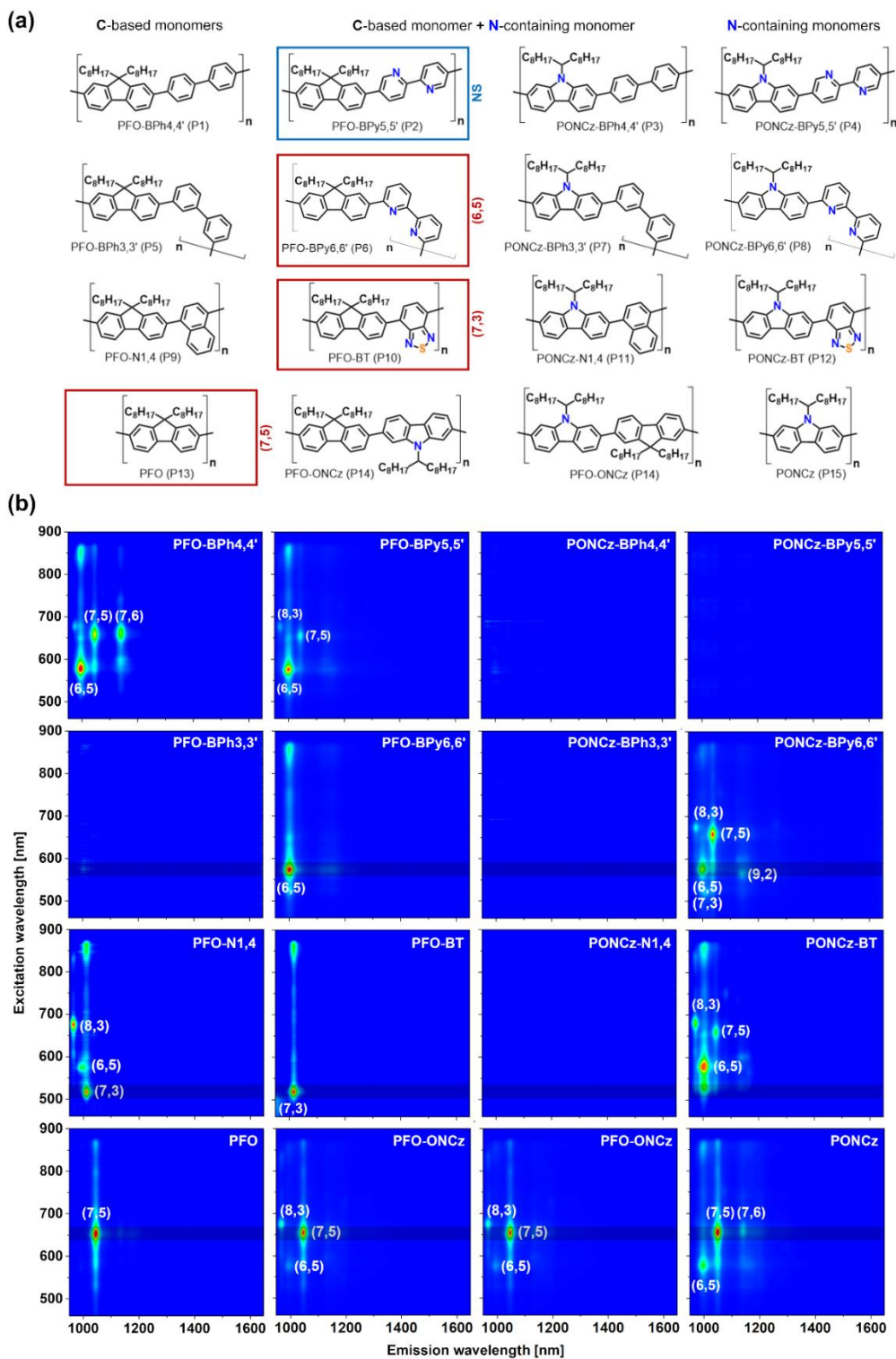


Figure 18. (a) Structures of synthesized conjugated polymers (CPs); brackets indicate chiral preference, NS – no selectivity. (b) PLE maps for SWCNTs dispersed using them. Adapted from Ref. 74.

In a family of copolymers containing bipyridine units, nitrogen atoms were replaced with corresponding biphenyl systems with analogous spatial geometry. This allowed to determine whether the high selectivity was primarily due to the presence of nitrogen atoms or solely to the stiffness and geometry of the aromatic system. A similar approach was used in the polycarbazole family, where classic fluorene units were replaced with carbazole. This modification allowed to investigate the effect of a single nitrogen atom incorporated directly into the polymer backbone while maintaining a very similar spatial architecture of the entire macromolecule. This allowed to separate the influence of geometry from the influence of the local electron density distribution.

The greatest design challenge was developing an equivalent of benzothiadiazole (BT), the second building block of the PFO-BT polymer. Removing the nitrogen and sulfur atoms from this unit would have led to a loss of aromaticity and a change in the geometry of the entire system, preventing a reliable comparison of the properties of both materials. For this reason, use of 1,4-substituted naphthalene, which, despite the absence of heteroatoms, retains a similar size and number of delocalized π electrons. Both fragments can be treated as isoelectronic systems, allowing to separate the influence of molecular geometry from the influence of heteroatoms on the CPE process. This was the first systematic comparison of isoelectronic building blocks used to design polymers for SWCNT separation.

Ultimately, a library of fifteen polymer structures, including fluorene and carbazole derivatives, and their copolymers with various aromatic units, was obtained and tested in the CPE process, and PLE map analyses are presented in Figure 18b. This designed set of materials allowed for the first time a systematic study of the relationship between the polymer's chemical structure, the electronic properties of individual building blocks, and their ability to recognize specific SWCNT chiralities. The resulting library of structures subsequently became the basis for comprehensive experimental studies and multiscale molecular modeling, the goal of which was to formulate general principles for the design of new polymers for CPE.

The experiments conducted unequivocally demonstrated that the presence of heteroatoms in the second building block of the polymer significantly increases the strength of the interaction with the SWCNT surface. Polymers containing nitrogen or sulfur atoms formed significantly more stable complexes with nanotubes, providing

both higher extraction efficiency and higher selectivity for specific chiralities. This effect was observed regardless of the polymer family analyzed, indicating that heteroatoms are a key element responsible for molecular recognition of the SWCNT surface. At the same time, it was demonstrated that the presence of heteroatoms alone does not guarantee selectivity. The final effect is determined by their appropriate arrangement within the polymer backbone and the ability to create a favorable electrostatic potential distribution along the entire macromolecule.

One of the most interesting results of this work was the demonstration that even complete removal of heteroatoms does not necessarily lead to a complete loss of chiral preference. This is particularly well illustrated by the PFO-N1,4 system, designed as an isoelectronic counterpart of PFO-BT. Despite significantly weaker interactions with the nanotube surface and a significant deterioration in process efficiency, as investigated and suggested by molecular dynamics (MD) and time-stamped force-bias Monte Carlo (MC) methods (Figure 19a-c), this polymer still showed a preference for (7,3) nanotubes even after its desorption proving its high affinity toward (7,3) species (Figure 19d-f). This indicates that the selectivity of CPE is not solely due to the geometry of the macromolecule or the presence of heteroatoms. The derived data indicate that the local distribution of electron density and electrostatic potential generated by individual polymer fragments play an equally important role. In other words, geometry is responsible for the ability of the macromolecule to fit onto the SWCNT surface, while the electronic properties determine the strength and stability of the resulting complex.

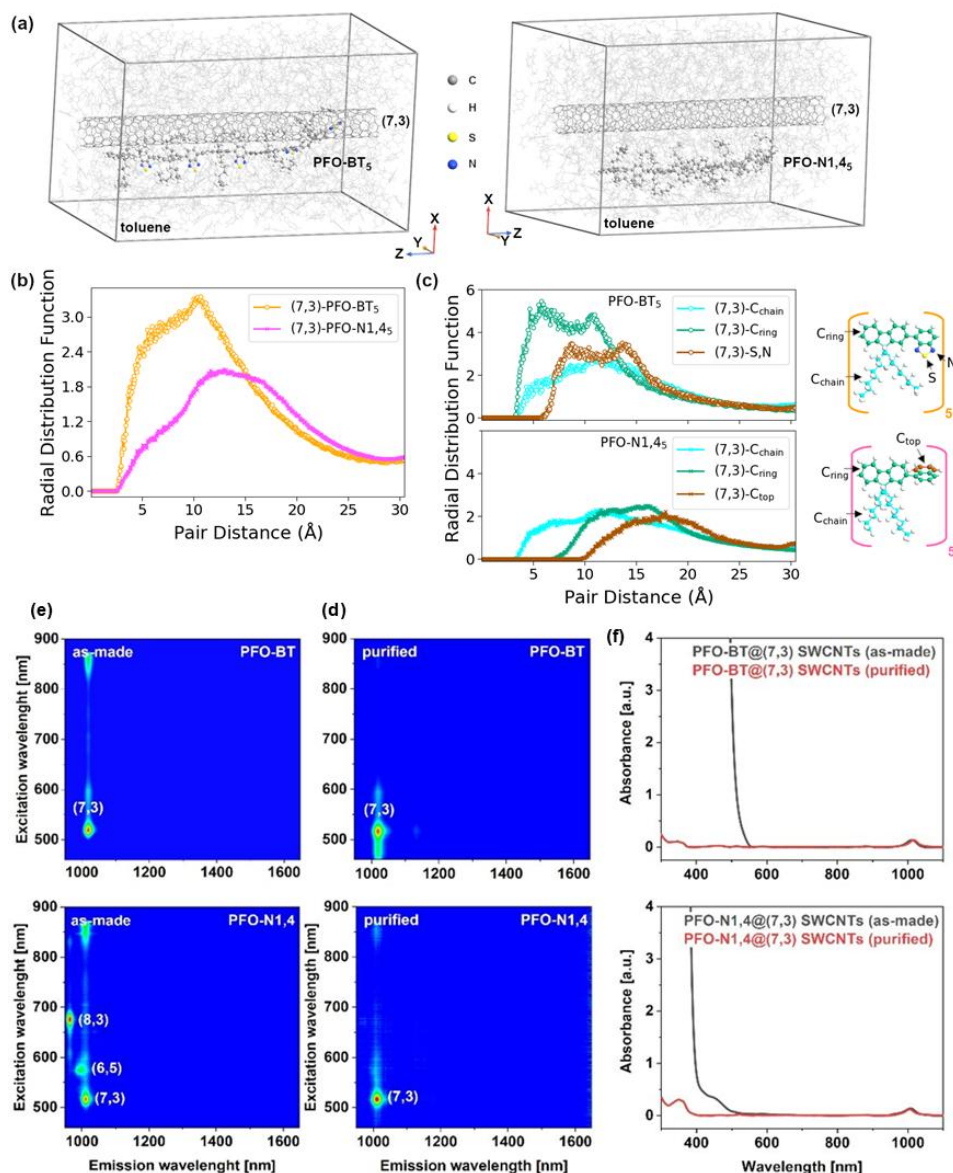


Figure 19. (a) MD/MC simulations of SWCNT–polymer interactions in toluene solution; the final configurations for (7,3) SWCNTs with PFO-BT and PFO-N1,4 are shown. (b) Radial distribution functions (RDFs) for SWCNT–polymer carbon atom interactions. (c) Detailed RDFs for different polymer fragments (core, side chains, and functional groups), indicating differences in the mode of interaction with the SWCNTs surface. (d–e) PLE maps of SWCNT dispersions before and after purification (polymer removal), confirming adsorption on the surface. (f) Corresponding absorption spectra, showing a clear decrease in polymer content after the purification process. Adapted from Ref. 74.

The conducted studies also allowed to formulate new hypotheses regarding the further development of the CPE technique. The obtained results suggest that, in addition to electronic properties, adsorption energy, and the presence of heteroatoms, the type of linkage between successive polymer building blocks can also significantly influence extraction selectivity. As demonstrated by the performed calculations (Figure 20a-b), this parameter directly influences the length of the effective π -conjugated system and, consequently, the band gap width of the entire macromolecule. In the case of polymers containing units connected via meta-bonds, such as PFO-BPy6,6', electronic coupling is locally broken, preventing polymer chain extension from leading to further electron delocalization. As a result, the band gap width remains virtually constant regardless of the macromolecule length. A different relationship is observed for classical PFO, whose units are connected via para-bonds. In this case, electronic coupling propagates along the entire polymer backbone, causing a gradual decrease in the band gap value with increasing number of building blocks. This means that even a small change in the way two aromatic fragments are connected leads to a fundamental change in the electronic properties of the entire polymer.

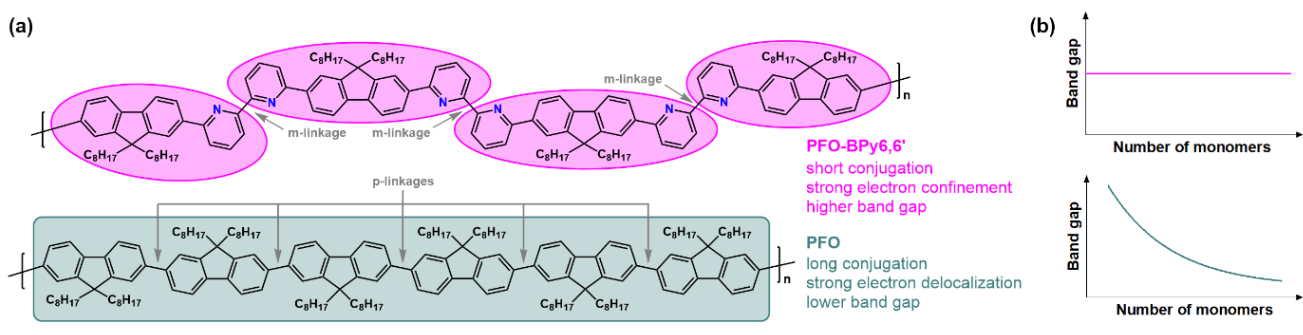


Figure 20. (a) Structures of PFO-BPy6,6' and PFO and comparison of the coupling length. (b) Bandgap decreases with the number of mers; the type of coupling (meta vs. pair) affects its value and the rate of change. Adapted from Ref. 74.

The gathered findings indicate that the band gap width of a polymer may be one of the key parameters determining its ability to selectively adsorb on the SWCNT surface. Changing the band gap influences the degree of π -electron delocalization, the electron density distribution, and the local polarizability of the macromolecule, and thus the interaction energy with the graphene nanotube surface. Therefore, it can be assumed that the selectivity of the CPE process results not only from the

geometrical matching of the polymer to the SWCNT diameter, but also from the appropriate matching of its electronic properties to the local electronic structure of the nanotube surface. Consequently, conscious control of the way building blocks are connected becomes a tool enabling the design of polymers with a predetermined band gap, and indirectly, with a predictable affinity for selected SWCNT chiralities.

In my opinion, this is one of the most important conclusions of the presented work, as it demonstrates for the first time that the band gap of a polymer is not solely an optoelectronic property but can also serve as a design parameter determining the selectivity of CPE extraction. This opens a completely new research direction in the rational design of polymers for CPE, where extraction properties can be predicted based on the electronic parameters of the macromolecule, rather than solely by empirical trial and error. Furthermore, the analyzed dataset suggest that the influence of the nanotube's chiral angle on the coupling propagation mode and polymer adsorption orientation is equally important. Different SWCNT chiralities are characterized by different hexagonal lattice arrangements on the cylindrical surface, which can influence both the local contact geometry and the efficiency of π -system overlap between the polymer and the nanotube. Investigating this relationship could constitute the next step in the development of CPE techniques and enable the development of the first model predicting extraction selectivity based on the polymer's electronic parameters and the SWCNT surface geometry.

4.4. Large scale sorting and chemical modification of SWCNTs using PhN_2H_3 derivatives

The next stage of the research was to utilize the knowledge gained from developing molecular extraction enhancers to create a completely new platform combining the selective separation process and the chemical functionalization of SWCNTs. Previously, both processes had been performed independently – first, a single chiral element was isolated using CPE, and then the purified material was subjected to multi-step functionalization. This approach was time-consuming, led to material losses, and required the use of different reaction conditions for each step. The aim of this work (P4) was to determine whether previously developed molecular extraction enhancers could simultaneously act as promoters of chemical reactions occurring on the surface of SWCNTs, enabling the production of large quantities of homogeneous and simultaneously modified nanotubes.

To verify the hypothesis, a systematic screening of compounds previously used for chemical doping and functionalization of SWCNTs was performed. Representatives of several different classes of reagents were selected for the study, including both classical radical initiators and the compounds described in ⁸⁰ namely small chaperones. Among the additional compounds analyzed were benzoyl peroxide (BPO), which is a commonly used radical initiator ^{117,118}, phenylhydrazine (PhN₂H₃, in this part of the work in graphics denoted as PhH), capable of generating aryl radicals ^{124,138,139}, benzyl viologen (BV) representing a group of strong n-dopants ¹⁴⁰, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) belonging to the most frequently used p-dopants ¹⁴⁰, 1,10-phenanthroline (PHN) used to stabilize nanoinks ⁹⁵, as well as a number of molecular enhancers developed in previous works, including 2,5-dibromothiophene, dibromofluorene and other aromatic polymer building blocks ^{77,80}.

The obtained dataset showed that the individual compounds presented in Figure 21a interact with the CPE system in different ways. BV and DDQ caused only a moderate increase in extraction efficiency, without significantly affecting either the chiral purity or the optical properties of the obtained SWCNTs. Benzoyl peroxide improved the process efficiency, but also led to less controlled functionalization and a greater scatter of results between experimental replicates. Significantly better results were obtained for systems containing 1,10-phenanthroline and PhN₂H₃, which showed a clear synergy effect with the previously developed PFO-BPy6,6'/2,5-dibromothiophene system, as shown by the maximum absorption spectral value comparison in Figure 21b.

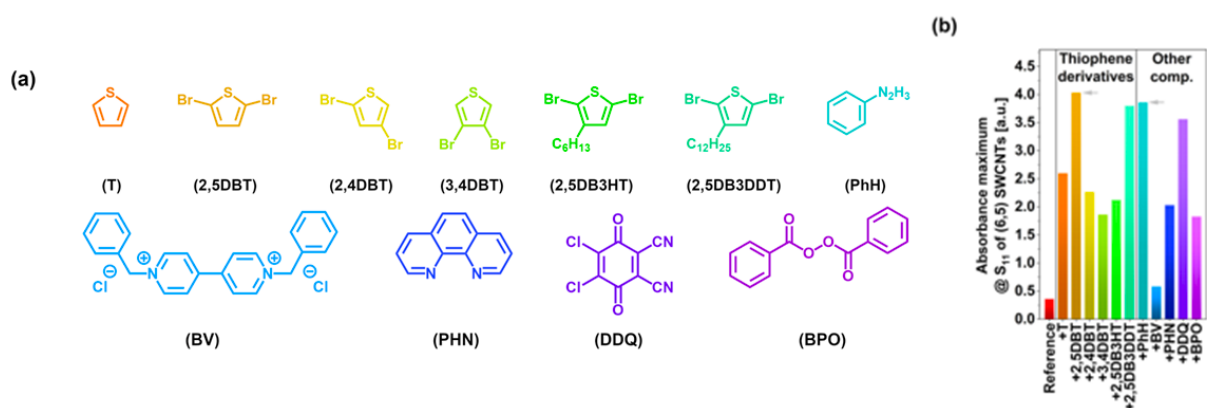


Figure 21. (a) Structures of the investigated small-molecule additives affecting the isolation efficiency of (6,5) SWCNTs ¹²⁴, including thiophene derivatives and other compounds with diverse electronic properties. (b) Comparison of the absorption

intensity of the E_{11} transition for (6,5) SWCNTs obtained using PFO-BPy6,6' and individual additives, indicating a significant effect of their structure on the extraction efficiency. Adapted from Ref. 124.

Comparing the performance of the two best additives proved particularly interesting. Despite their very similar impact on the extraction efficiency, they led to completely different final materials. The addition of 1,10-phenanthroline enabled the obtaining of the highest concentrations of highly purified (6,5) nanotubes, retaining their native electronic structure and original optical properties (shown in Figure 22a). This material provided an ideal starting point for further chemical modification steps. In turn, the use of PhN_2H_3 led to a simultaneous increase in extraction efficiency and the spontaneous formation of luminescent sp^3 defects during the sonication process (the sonication time is shown in Figure 22b). As a result, chirally homogeneous nanotubes with a controlled degree of functionalization were obtained without the need for additional chemical reactions after separation.

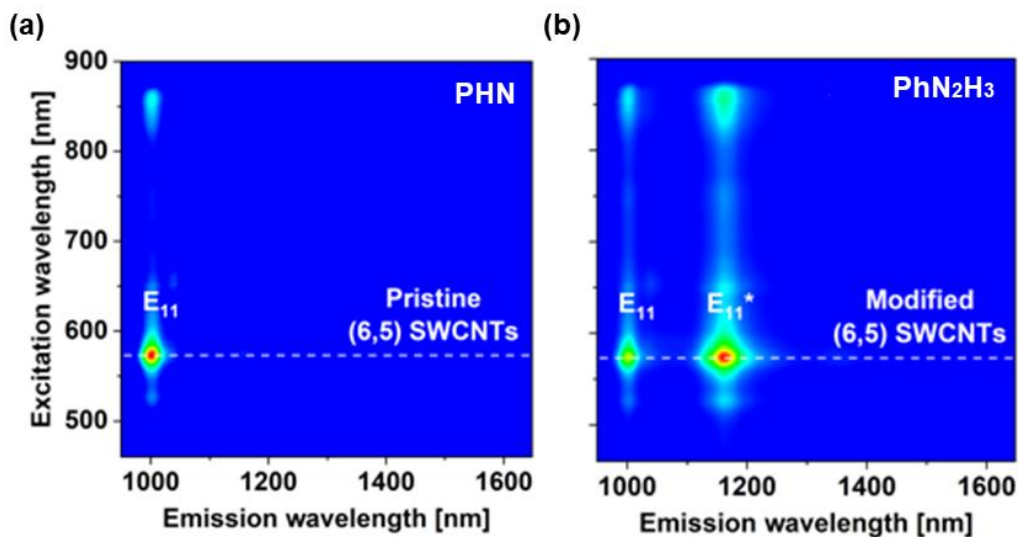


Figure 22. PLE maps of SWCNTs dispersions obtained by CPE method after sonication in the presence of (a) PHN and (b) PhN_2H_3 .

This comparison allowed to distinguish two new classes of molecular additives used in the CPE technique. The first are extraction enhancers, whose role is solely to stabilize the polymer-SWCNT complex and increase process efficiency, as exemplified by 1,10-phenanthroline. The second group consists of reactive enhancers, represented by PhN_2H_3 , which, in addition to enhancing the extraction process, also

initiate controlled functionalization of the nanotube surface. Distinguishing between these two mechanisms of action is one of the most important achievements of the presented work.

Further research focused on developing conditions that would enable precise control of the degree of functionalization and the type of luminescent defects formed. It was demonstrated that the process can be regulated by varying the sonication parameters of the CPE process, the reaction time and temperature, the amount of PhN_2H_3 used, and the amount of polymer remaining on the nanotube surface. Increasing the PhN_2H_3 content led to a gradual quenching of SWCNT photoluminescence, which may indicate the formation of non-radiative sp^3 defects. Each sample with different PhN_2H_3 ratio was left after direct sonication for several days and its dynamics were measured, as shown in Figure 23. It was also shown that increasing the sonication time from 8 to 64 minutes propagates the modification process, as does the sonication power. Furthermore, reducing the amount of PFO-BPy6,6' polymer from 6 to 3 mg during the CPE process significantly alters both the extraction efficiency and the rate of functional group attachment, with the reaction rate being faster for reduced CP content. Furthermore, it was shown that the reaction can also be effectively initiated solely thermally, conducted for 1 hour at temperatures of 80, 90, and 100 °C, without the need for sonication.

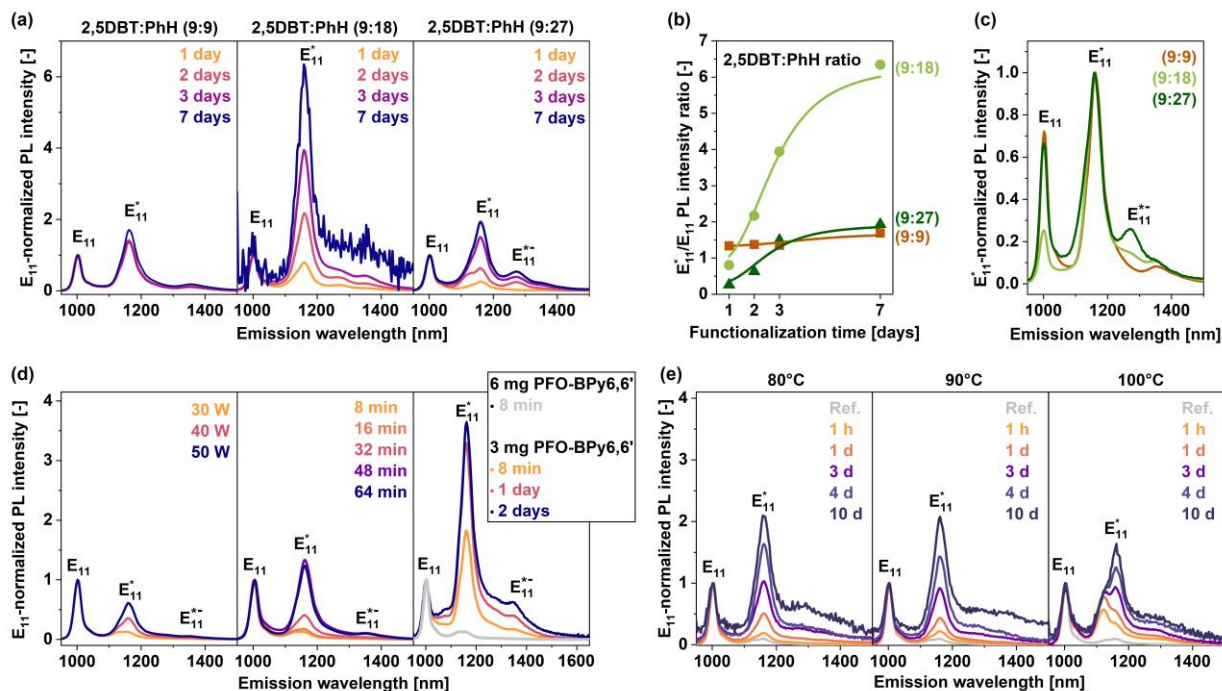


Figure 23. (a) Effect of 2,5DBT:PhH namely PhN_2H_3 ratio in mg on PL properties over time (1–7 days from preparation). (b) Maximum E_{11}/E_{11}^* intensity ratios. (c) Data normalized to E_{11} intensity after 3 days. (d) Changes in PL as a function of sonication power/time and the amount of PFO-BPy6,6' (optimal conditions 9:18 mg). (e) Effect of thermal treatment on PL for the same conditions. Adapted from Ref. 124.

A key achievement of this work was also the demonstration that the developed method provides a universal platform for programming the optical properties of SWCNTs through the selection of an appropriate PhN_2H_3 derivative shown on Figure 24. Phenylhydrazine (PhH, also referred to as PhN_2H_3), 4-bromophenylhydrazine (PhH-Br), 4-hydrazinobenzoate (PhH-COOH), 4-sulfonamidophenylhydrazine (PhH-SO₂NH₂), 4-(trifluoromethyl)phenylhydrazine (PhH-CF₃), 4-hydrazinylbenzonitrile (PhH-CN), and 4-nitrophenylhydrazine (PhH-NO₂) were used in the study. Each of these derivatives led to the formation of defects emitting at a different wavelength. For the phenyl group, the E_{11}^* emission maximum was observed at approximately 1161 nm, while the use of a strongly electron-withdrawing p-nitro group shifted the emission to approximately 1176 nm, corresponding to deeper excitonic traps. The energy of these states was shown to be directly correlated with the Hammett constant of aromatic substituents – the greater the electron-withdrawing nature of the substituent, the greater the depth of the optical trap and the greater the bathochromic shift of the emission. At the same time, the most electron-withdrawing derivatives exhibited the lowest reactivity, indicating an inverse relationship between charge acceptance and the rate of functionalization. The obtained materials were characterized by approximately twice the photoluminescence quantum yield compared to unmodified nanotubes, with only a slight increase in the degree of structural disorder assessed by Raman spectroscopy.

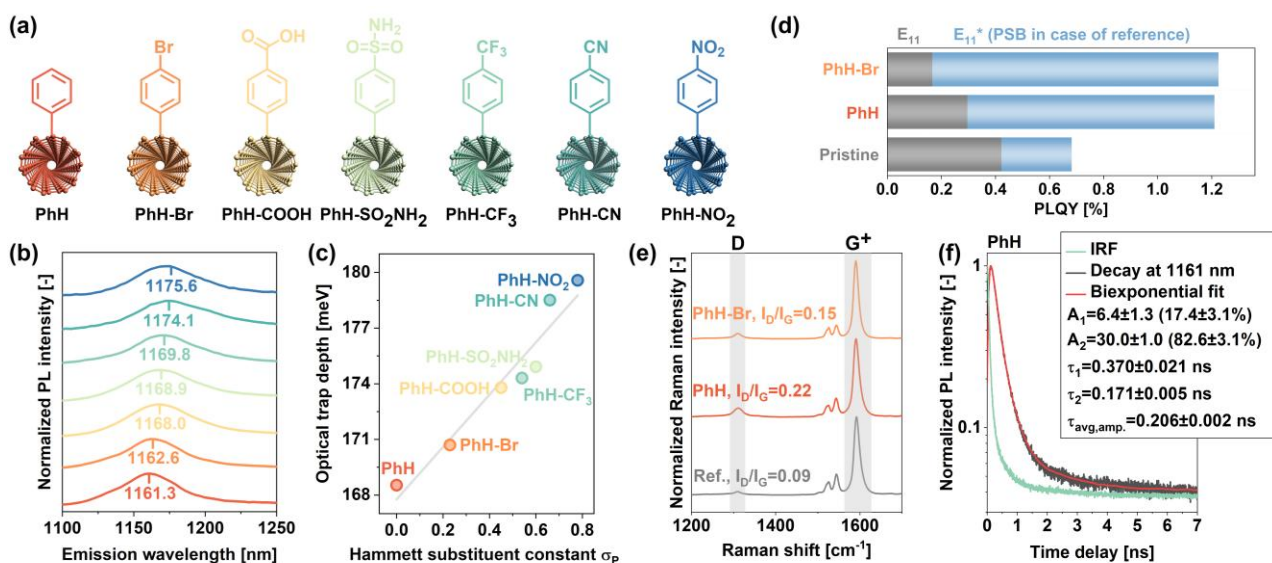


Figure 24. (a) Structures of speculated attached to SWCNT phenyls obtained from radical reactions of PhN_2H_3 derivatives used for SWCNT functionalization. (b) Shift of the E_{11}^* emission maximum depending on the substituents. (c) Correlation of trap depth with Hammett parameters. (d) PLQY for reference and modified samples. (e) Normalized Raman spectra. (f) Time-correlated single-photon counting (TCSPC) with biexponential fitting. Adapted from Ref. 124.

A particularly significant result was the demonstration that the identical functionalization concept can be applied in both organic solvents and aqueous media (Figure 25). In toluene, the reaction was carried out at a concentration of approximately $3.7 \mu\text{g/mL}$ PhN_2H_3 , while in water, concentrations nearly four orders of magnitude lower proved sufficient. Optimal results were obtained at a concentration of $0.1125 \mu\text{g/mL}$, yielding an E_{11}/E_{11}^* intensity ratio close to 10. Importantly, in an aqueous environment, the process required no additional activation in the form of heating, sonication, or radiation and occurred spontaneously within a few minutes for (6,5) nanotubes, while for less reactive (7,5) nanotubes, the process was completed after approximately two hours. Similarly to toluene, the position of the E_{11}^* band depended on the type of PhN_2H_3 derivative used and the Hammett constant value, confirming the universal nature of the developed functionalization platform.

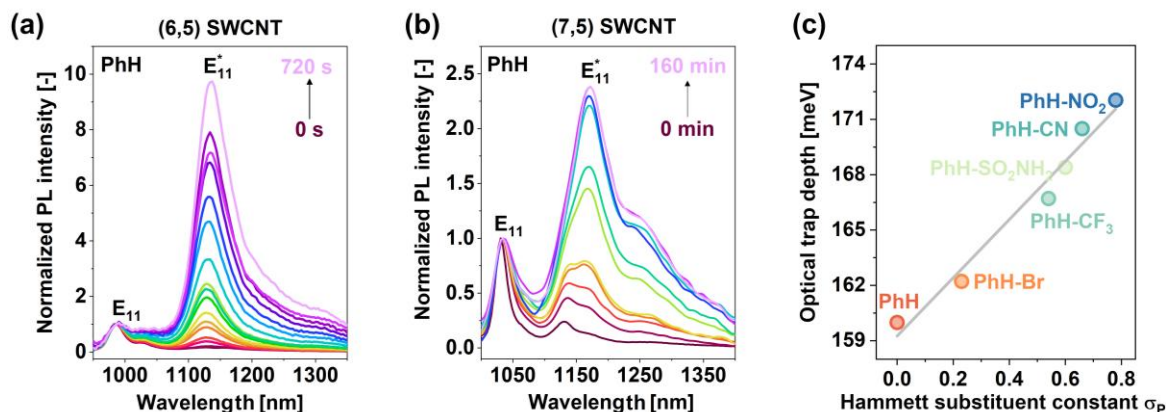


Figure 25. (a,b) Normalized PL intensity for (6,5) and (7,5) SWCNTs functionalized in aqueous medium for SWCNTs prepared by the protocol described in this work ¹⁴¹, SWCNTs modified with PhN₂H₃ over time. (c) Correlation of optical trapping depth with Hammett parameters of substituents. Adapted from Ref. 124.

Analysis of the reaction mechanism revealed that the process proceeds via a radical mechanism initiated by atmospheric oxygen. It was speculated that PhN₂H₃ undergoes gradual oxidation, leading to the formation of a phenyldiazine intermediate, which, after elimination of a nitrogen molecule, generates a phenyl radical capable of permanently attaching to the SWCNT surface where mechanism is presented in Figure 26. The presence of radicals was confirmed by the use of the TEMPO quencher, which completely inhibited the reaction. However, experiments conducted in an oxygen-free atmosphere showed no signs of functionalization, clearly indicating the key role of oxygen in the initiation of the process. Studies also demonstrated that during the reaction conducted in hot toluene, transient benzyl groups or reactive oxygen species may initially form, responsible for emission around 1125 nm, which are subsequently replaced by more stable phenyl groups emitting around 1160 nm. The possibility of coexistence of oxygen defects resulting from singlet oxygen generation was also considered, but the dominant product of functionalization turned out to be aryl defects resulting from the attachment of phenyl radicals to the nanotube wall.

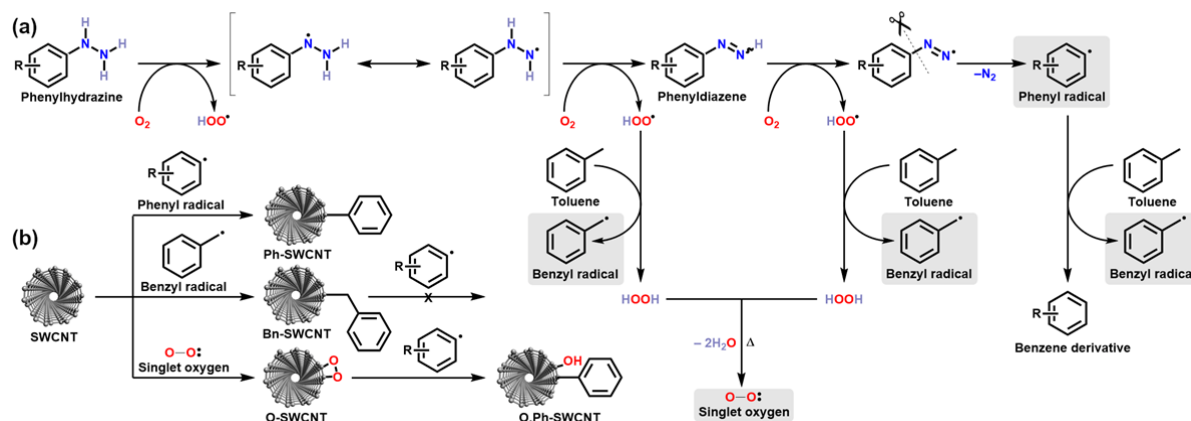


Figure 26. (a) Scheme of the formation of phenyl/benzyl radicals from PhN_2H_3 derivatives with simultaneous generation of singlet oxygen. (b) Proposed chemical groups attached to the SWCNTs surface. Adapted from Ref. 124.

In summary, the presented work not only led to the development of a new method for the simultaneous separation and functionalization of SWCNTs but also provided a fundamental understanding of the mechanism responsible for the formation of luminescent defects. The possibility of deliberately controlling the density and energy of the created emission states by selecting reaction conditions and the electronic properties of the reactants was demonstrated. This makes the developed platform a universal tool for designing the optical properties of SWCNTs, paving the way for obtaining materials with precisely programmed emission characteristics for photonics, bioimaging, and modern optical sensors in both environments.

4.5. Influence of reaction medium on chemical modification of SWCNTs

To date, research on the covalent functionalization of SWCNTs has focused almost exclusively on selecting the reagent responsible for generating reactive radicals and analyzing the final properties of the resulting materials. The vast majority of publications adopted a simplified model, assuming that the reaction is solely driven by direct interaction between the radical and the SWCNT surface. This approach has led to the development of numerous effective methods for implanting luminescent sp^3 defects, but it has also led to the belief that the remaining components of the reaction system play only a supporting role. In practice, this meant that the solvent was treated solely as a reaction medium, the polymer, or the surfactant as a factor

enabling individualization of SWCNTs, allowing for their uniform reaction, while the presence of atmospheric oxygen, moisture, or byproducts of radical reactions were considered secondary factors, not requiring detailed analysis. As a consequence, the possibility of competitive reactions of radicals with solvent, dispersant or oxygen molecules has not been practically investigated, even though from the point of view of radical chemistry they are often much more probable than direct attack on the SWCNT surface.

This situation is particularly surprising when considering the actual conditions of functionalization. The solvent concentration exceeds the concentration of the radical initiator by several orders of magnitude, the SWCNT surface is almost completely covered by a polymer or surfactant layer, and the oxygen present in the system constantly participates in oxidation reactions and the generation of secondary radical species. This means that each of the resulting reactive species can undergo numerous transformations even before contact with the SWCNTs. Furthermore, the radicals can react not only with the SWCNT surface but also with each other, with solvent molecules, the dispersion-stabilizing polymer, or with products of earlier reaction stages, creating a complex network of competing chemical processes. Despite the obvious importance of these phenomena, their influence on the type of luminescent defects and the functionalization process has remained virtually unknown.

The main goal of this work (P5) was to move away from the classical view of SWCNT functionalization as a reaction occurring solely between the nanotube and a radical initiator¹³⁷. Instead, the entire reaction system was treated as a dynamic system of interacting components, encompassing the nanotube, polymer or surfactant, solvent, atmospheric oxygen, moisture, and all intermediate products of radical reactions. The study aimed to answer the question of which of these elements actually determines the course of functionalization and whether it is possible to consciously control the type of defects generated by designing the reaction environment, rather than simply selecting the appropriate reagent. Consequently, this work has changed the perspective on the chemistry of SWCNT functionalization, demonstrating that the properties of the final material are determined not by a single radical initiator, but by the entire network of interactions occurring between all components of the reaction system.

The first stage of the research involved the functionalization of raw, undispersed SWCNTs, completely devoid of a CP or surfactant shell. This experiment represented a deliberate departure from the classical approach used in the literature, in which almost all reactions are conducted on previously dispersed SWCNTs. By eliminating all additional components of the system, it was possible to investigate the actual reactivity of the SWCNT surface and determine which products are formed solely as a result of the interaction of the radical initiator with the carbon material. This experimental design allowed to answer the fundamental question of whether the polymer merely facilitates nanotube dispersion or actively participates in the process of optical defect formation, where the results are presented in Figure 27.

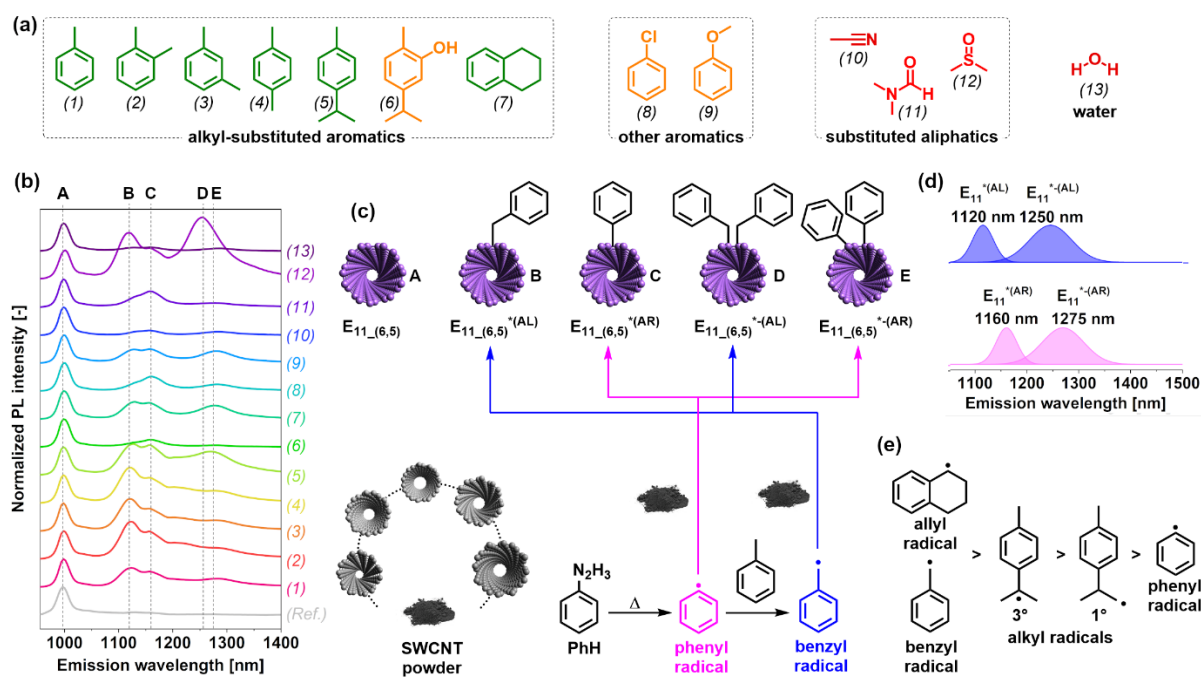


Figure 27. (a) Set of solvents used for the modification of SWCNTs with PhN_2H_3 , grouped by polarity (nonpolar, medium polar, polar). (b) PL spectra ($\lambda_{\text{ex}} = 579 \text{ nm}$) for raw SWCNTs functionalized in these environments. (c) Assignment of observed spectral features (A–E) to possible reaction pathways occurring in different solvents (for clarity, radical transfer is shown in toluene), followed by extraction of PFO-BPy6,6' to isolate the modified (6,5) SWCNTs. (d) Peak positions for (6,5) SWCNTs with alkyl (AL) and aryl (AR) substituents, depending on the degree of functionalization. (e) Dominant radicals generated in individual solvents, ordered by their stability. Adapted from Ref. 137.

The obtained results clearly demonstrated that covalent functionalization also occurs in the complete absence of a dispersant, but this process is much less selective (Figure 27b) and leads to the formation of a complex mixture of different emission centers. In contrast to the polymer-stabilized systems, where a single type of defect dominated, the photoluminescence spectra of the obtained samples contained several distinct bands corresponding to different chemical configurations of the attached functional groups. The observed emission was around 1120 nm, corresponding to alkyl defects $E_{11}^*(AL)$, a dominant band around 1160 nm (Figure 27d), attributed to classical aryl defects $E_{11}^*(AR)$, and a broad band located in the range of approximately 1250–1300 nm, corresponding to deep excitonic traps $E_{11}^{*-}(AL)$. The simultaneous presence of all these signals indicated that several competing reaction pathways were occurring on the nanotube surface, leading to distinct functionalization products. This means that in the absence of the polymer, the SWCNT surface remains virtually chemically undirected, and the resulting radicals can attach to many different sites and create several types of defects with distinct electronic structures. This result had significant mechanistic significance. It demonstrated that the radical initiator alone does not determine the type of emission states formed. If this were the case, a single dominant emission band should have been observed regardless of the presence or absence of polymer. In fact, the complete lack of control over the reaction course led to the formation of a wide variety of end products, indicating that the chemical environment of the nanotube plays a much more significant role than previously assumed. This was the first direct evidence that the selectivity of functionalization is not solely due to the properties of the radical initiator but is strongly dependent on the presence of a layer stabilizing the SWCNT surface.

The next step in the research was to determine whether the observed product diversity was solely due to the lack of polymer or to the reaction medium itself. To this end, a series of experiments were conducted using various organic solvents, including classic aromatic solvents such as toluene, o-, m-, and p-xylene, ethylbenzene, and tetralin, as well as solvents with a higher dipole moment (Figure 28a). The achieved outcomes revealed that simply changing the solvent led to noticeable changes in the position of the emission bands and the relative intensities of individual defect types. Particularly pronounced effects were observed for aromatic solvents containing stable benzylic sites, where additional signals appeared, indicating the formation of new types of chemical defects.

Analysis of the obtained spectra suggested that phenyl radicals resulting from PhN_2H_3 decomposition did not always directly attach to the SWCNT surface. In many cases, the more likely mechanism was prior transfer of the radical center to the solvent molecule (Figure 28e). This phenomenon seems consistent with classical radical chemistry, as phenyl radicals are very short-living and can create high-energy intermediates^{142,143}, additionally concentration of this phenylic radical species during the reaction was nearly three orders of magnitude lower than the number of solvent molecules. Under such conditions, hydrogen atom abstraction from the solvent becomes much more likely, forming more stable benzylic or allyl radicals, which then take over as the actual reagents responsible for functionalizing the SWCNT surface. In practice, this means that the radical initiator only serves to initiate the chain reaction, while the actual source of groups attached to the nanotubes may be the surrounding solvent molecules.

This hypothesis was further supported by the observed shifts in the photoluminescence spectra. Defects formed in the presence of different solvents exhibited different energies of the E_{11}^* states, suggesting that their chemical structures were not identical. If all products originated solely from phenyl radicals, the position of the emission maximum would remain virtually constant regardless of the reaction medium used. The produced outcomes indicate, however, that the solvent can actively participate in the formation of new functional groups attached to the nanotube surface. This was the first experimental confirmation that the solvent is not a passive reaction medium but can act as a full-fledged reagent participating in the SWCNT functionalization process. This discovery changes the current interpretation of radical reactions conducted on nanotubes and indicates that the deliberate selection of the reaction medium can be as important a tool for designing the optical properties of SWCNTs as the selection of the radical initiator itself.

The next stage of the study was to conduct analogous experiments on (6,5) nanotubes previously selectively isolated using the PFO-BPy6,6' copolymer (Figure 28a). The aim of this work was to determine whether the presence of the polymer shell affects only the dispersion stability or also actively participates in the formation of luminescent defects. In contrast to the raw nanotubes without dispersant, a radically different spectroscopic pattern was obtained (Figure 28b). The signals corresponding to defects emitting around 1120 nm practically disappeared, and the emission around 1160 nm, characteristic of classical aryl $E_{11}^*(\text{AR})$ defects, became the dominant band. At the

same time, the broad E_{11}^* -band previously observed for undispersed nanotubes was almost completely eliminated, indicating a significant reduction in the number of competing reaction paths. This meant that the presence of CP not only improved the uniformity of the functionalization process but also directed the reaction toward the formation of a single dominant defect type.

This result had significant mechanistic implications. If the polymer were solely dispersion-stabilizing, the type of defects formed should have remained the same as for SWCNTs without a shell. However, a completely different reaction course was observed, indicating that the macromolecule actively participated in the functionalization process. It can be assumed that the presence of PFO-BPy6,6' leads to spatial restriction of the SWCNT surface and local shielding of some reactive sites. Simultaneously, π - π interactions between the polymer and the nanotube surface stabilize specific reactant conformations and direct radicals to selected sites on the SWCNT surface. Consequently, the polymer acts as a molecular template, which not only enables the selective extraction of a specific chirality but also determines the course of subsequent chemical functionalization.

After demonstrating the active role of CP, the next step was to determine whether its properties remained unchanged in various reaction environments. To this end, systematic absorption spectroscopy studies of the PFO-BPy6,6' copolymer were conducted in a wide range of solvents differing in polarity (Figure 28d), dipole moment, and donor-acceptor interaction capacity. Analysis of the absorption and photoluminescence spectra demonstrated that the reaction environment exerted a significant influence on the macromolecule's conformation. Depending on the solvent used, a shift in equilibrium between the α phase and the more ordered β phase was observed, corresponding to greater straightening of the polymer chains and an extension of the effective π -conjugation system. These changes directly influenced the degree of contact between the polymer and the SWCNT surface and the availability of reactive sites for the formation of radicals.

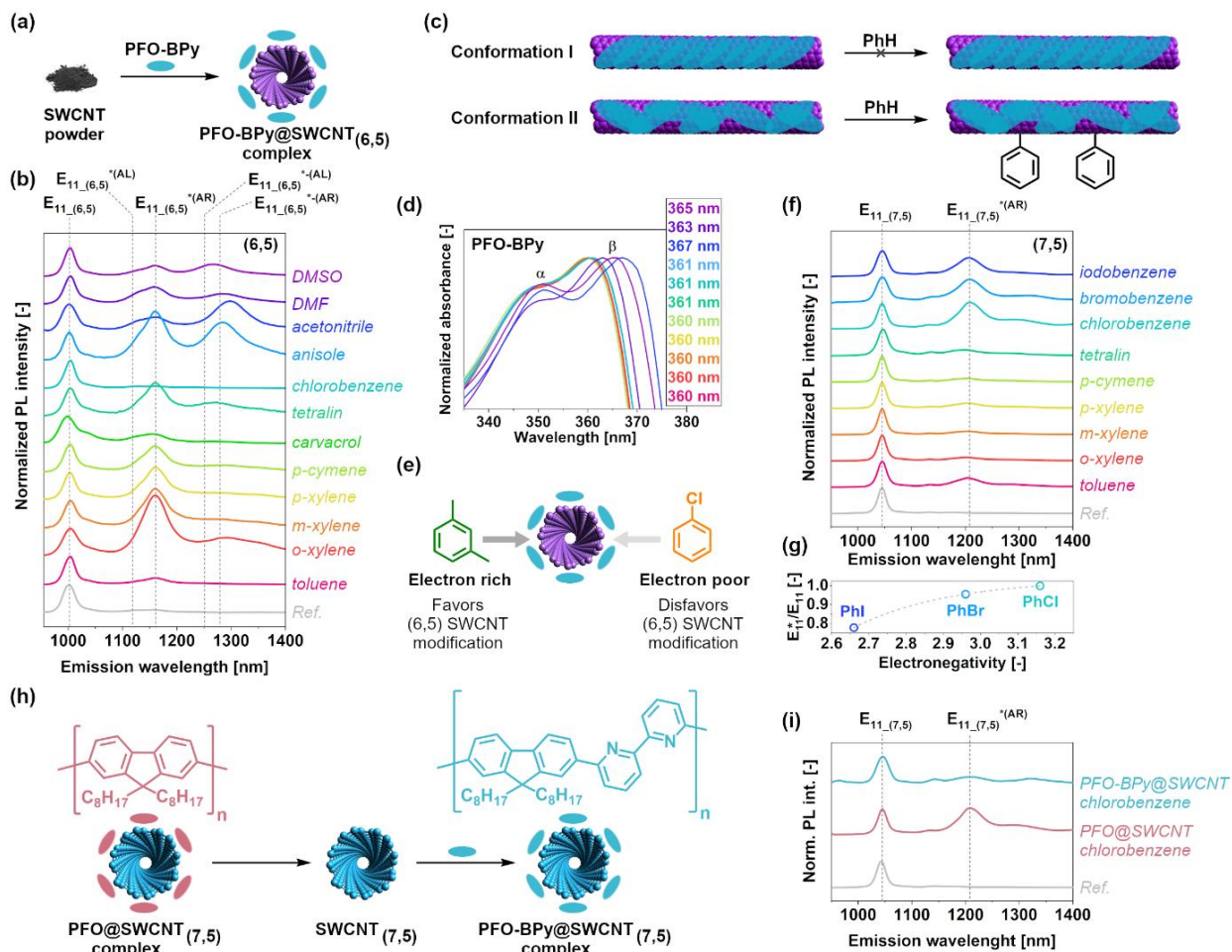


Figure 28. (a) Selective extraction of (6,5) SWCNTs by PFO-BPy. (b) PL spectra of modified (6,5) in different solvents. (c) Scheme of the polymer conformation determining reactivity. (d) Absorption spectra of PFO-BPy in different solvents. (e) Higher reactivity in electron-donating solvents. (f) PL spectra of modified (7,5) SWCNTs. (g) Dependence of E_{11}^*/E_{11} on the electronegativity of substituents. (h) PFO $\rightarrow$ PFO-BPy shell exchange. (i) Comparison of PL spectra for both polymers. Adapted from Ref. 137.

Importantly, the observed conformational changes correlated very well with the functionalization results. Solvents stabilizing specific CP conformations simultaneously led to significantly higher aryl defect formation. This indicates that the solvent does not interact solely with the reagent or the SWCNT itself, but also influences the spatial structure of the polymer shell. Therefore, the functionalization process should be considered as the result of simultaneous interactions between three components of the system: the SWCNT, the CP, and the reaction environment.

This represents a fundamentally different perspective from the previously dominant model, which treated the solvent solely as a passive reaction medium.

The universality of the presented mechanism was then verified for nanotubes of various chiralities. For this purpose, analogous experiments were performed on (7,5) nanotubes selectively isolated using the classic PFO polymer. The data collected proved to be surprising. The solvents exhibiting the highest activity towards the PFO-BPy6,6'@(6,5) system were no longer among the most effective for the (7,5) nanotubes. The highest reactivity was observed for halogenated aromatic solvents, among which chlorobenzene was particularly prominent. In its presence, an intense emission band around 1205 nm was obtained, corresponding to the type of luminescent defects characteristic for the (7,5) chirality, the same as 1160 nm for (6,5). Interestingly, the same chlorobenzene was also among the practically inactive solvents for the PFO-BPy6,6'@(6,5) system, indicating a completely different reaction mechanism of both systems (Figure 29h-i).

To clearly confirm the crucial role of the polymer shell, a control experiment was conducted, consisting of replacing the classic PFO with a PFO-BPy6,6' copolymer while maintaining the same nanotube chirality – (7,5). Changing only one element of the reaction system led to an almost complete inhibition of the functionalization process, despite the use of an identical solvent and the same reagents. This result is one of the most important outcomes of this work, as it clearly demonstrates that the effectiveness of functionalization is not a property of the radical initiator or solvent alone. The mutual matching of all system elements, including the SWCNT chirality, polymer architecture, and the properties of the reaction environment, is crucial. This means that there is no universal functionalization system suitable for all nanotubes. Each system requires the individual selection of the polymer shell and reaction environment, and only the proper matching of these parameters enables the controlled creation of the desired luminescent defects.

A significant element of this work was also examining the effect of solvent moisture on the course of SWCNT functionalization. To date, most publications have treated the presence of trace amounts of water as a secondary factor or completely ignored it, assuming that the reaction course is primarily determined by the type of radical initiator used. However, the conducted studies have shown that even a seemingly routine step of solvent preparation can completely alter the nature of the chemical

transformations occurring. For this purpose, water content was determined by Karl Fischer titration both before and after drying the solvents using molecular sieves, and then functionalization products obtained under identical reaction conditions were compared (Figure 29a). It turned out that even small changes in moisture content led to significant differences in the type of luminescent defects generated, their density, and the final optical properties of the material. The most spectacular effect was observed for acetonitrile (Figure 29b). In the case of a solvent containing natural moisture, the dominant signal was a deeply shifted E_{11}^{*-} band emitting near 1300 nm, indicating the formation of strongly perturbed excitonic centers. After drying the same solvent using molecular sieves, the reaction almost completely switched to the formation of classical E_{11}^{*} defects emitting around 1160 nm. Such a large change in the reaction course could not be explained solely by the removal of trace amounts of water. It was shown that molecular sieves not only adsorb H_2O molecules but also simultaneously alter the acid-base properties of the environment^{144–147}, affecting the equilibrium between individual radical reactions. This means that even standard laboratory procedures commonly used in solvent preparation can completely alter the functionalization mechanism and the type of defects formed.

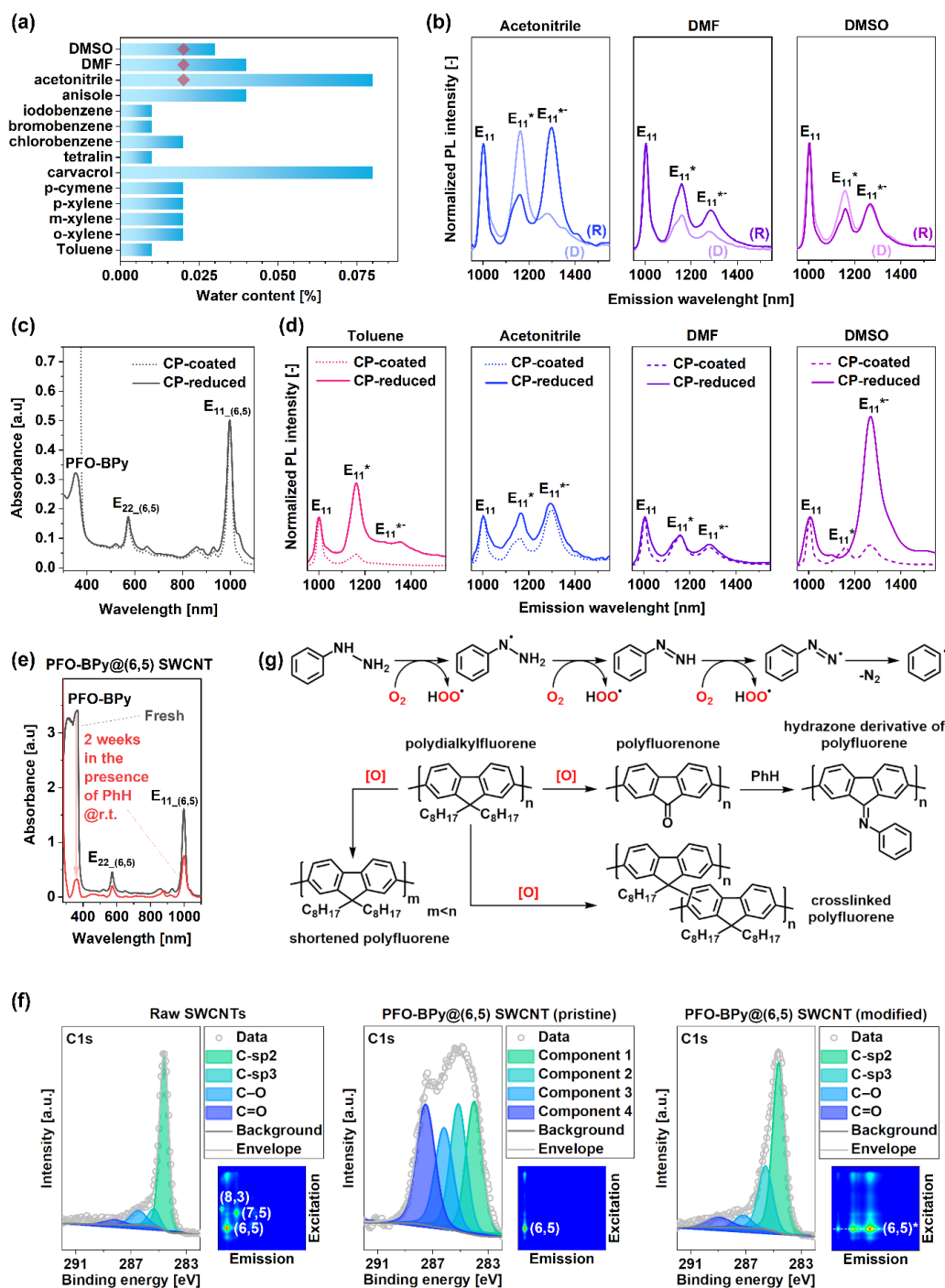


Figure 29. (a) Water content in the solvents used. (b) PL spectra of (6,5) before and after drying. (c) Absorption spectra before and after polymer removal. (d) PL spectra before and after CP washing. (e) Absorption changes after reaction with PhN₂H₃. (f) XPS spectra (C1s) and PLE maps for subsequent steps. (g) Scheme of phenyl radical generation and possible polymer transformations. Adapted from Ref. 137.

Another surprising finding was the demonstration that the presence of PhN_2H_3 leads to the gradual removal of excess CP from the SWCNT surface. Spectroscopic analyses, optical absorption studies, and XPS measurements revealed that the polymer is not chemically inert to the generated radicals but actively participates in the ongoing transformations (Figure 29f). A gradual decrease in the intensity of the signals characteristic of PFO-BPy6,6' was observed, accompanied by an increase in the proportion of signals originating from the modified SWCNTs. These results clearly indicate that the radicals present in the system do not react exclusively with the SWCNT surface but also competitively interact with the macromolecules forming the polymer corona.

Analysis of possible reaction pathways allowed to propose several mechanisms responsible for the observed phenomenon. Phenyl radicals and peroxide radicals ($\text{HOO}\bullet$) generated during PhN_2H_3 decomposition can initiate degradation of the polyfluorene skeleton by cleaving the main chain of the macromolecule, leading to a gradual reduction in its molecular weight (Figure 29g). Simultaneously, some fluorene units can be oxidized to fluorenones, which then react with PhN_2H_3 to form hydrazone derivatives. Polymer–polymer reactions, leading to cross-linking of adjacent chains due to interactions with the radicals and dissolved oxygen in the reaction medium, cannot be ruled out. Such processes can alter both the effective π -conjugation length and the conformation of the macromolecules, weakening their interaction with the SWCNT surface and facilitating their detachment from the nanotubes. The resulting product is no longer an ordered polymer corona capable of selective adsorption, but a mixture of shorter fragments and oxidation products with significantly lower affinity for the SWCNT surface.

The discovered phenomenon of self-cleaning of SWCNT surfaces is one of the most important consequences of the presented work. Previously, removing polymers after selective extraction required multi-step procedures involving filtration, rinsing, and medium exchange, which inevitably led to significant material losses and a deterioration in dispersion quality. In the developed system, part of this process occurs spontaneously during the functionalization process itself. This gradually exposes the SWCNT surface, increasing its accessibility to subsequent chemical reactions and interactions with the environment (Figure 29g). This means that the radical initiator simultaneously performs three functions: generating reactive centers responsible for the formation of sp^3 defects, restructuring the chemical environment

surrounding the SWCNT, and modifying the structure of the CP corona itself. These results demonstrate for the first time that three parallel classes of interactions compete during SWCNT functionalization: radical–SWCNT, radical–solvent, and radical–polymer (including polymer–polymer interactions). Consequently, the final structure of the resulting material is the result of a dynamic balance between all these processes, not just the direct attachment of the radical to the nanotube surface. This discovery significantly changes the way functionalization reactions are designed and demonstrates that full control over the optical properties of SWCNTs requires conscious design of the entire reaction environment, not just the selection of an appropriate radical initiator.

Understanding the relationships between each of the analyzed parameters allowed for the conscious control of both the functionalization kinetics and the emission shifts of the created luminescent defects. Instead of treating the reaction medium as a passive medium, it became a tool for programming the optical properties of the resulting SWCNTs through the appropriate selection of all system components. The knowledge gained during the research was then used to design materials for the optical detection of cholesterol, one of the most important biomarkers of cardiovascular disease. The developed SWCNTs utilized luminescent defects as active sites responsible for interacting with the analyte and generating an optical signal. It was once again confirmed that a too thick polymer shell, although necessary for effective dispersion and selective isolation of SWCNTs using CPE, simultaneously constitutes a barrier limiting contact between the nanotube surface and the surrounding environment. As a result, access of cholesterol molecules to the active sites was significantly hindered, leading to reduced sensory sensitivity. Only a partial reduction in the amount of polymer on the SWCNT surface, made possible by previously understood processes of remodeling and degradation of the polymer corona during functionalization, allowed for increased accessibility of luminescent defects and their effective interaction with the analyzed environment. This resulted in a more pronounced photoluminescent response and improved performance of the developed nanosensor.

The presented research culminated in the development of the first optical sensor reported in the literature operating in an organic environment, using SWCNTs isolated by the CPE method (Figure 30). This achievement provides direct evidence that selective extraction, controlled functionalization, and the deliberate design of

the reaction environment can be combined into a single, coherent platform leading to the production of materials with specific functional properties. These results also demonstrate that CPE-derived nanotubes are not merely materials for basic research but can form the foundation for a new generation of functional materials for applications in photonics, optoelectronics, and nanosensors.

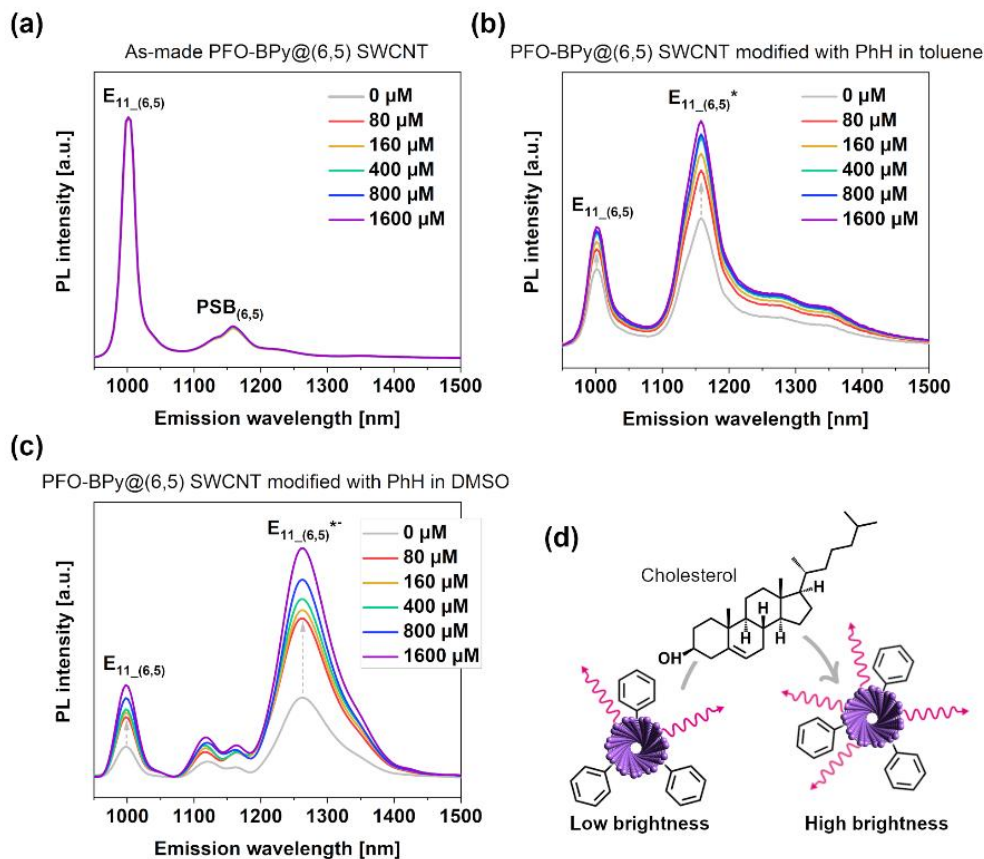


Figure 30. (a–c) PL spectra ($\lambda_{\text{ex}} = 579 \text{ nm}$) for unmodified and functionalized (6,5) SWCNTs in toluene and DMSO as a function of cholesterol concentration. (d) Simplified scheme of emission enhancement for SWCNTs with photoluminescent defects in the presence of cholesterol. Adapted from Ref. 137.

These results represent the pinnacle of the entire research cycle described in this dissertation. Subsequent publications have allowed us to advance from the development of efficient methods for selective extraction of SWCNTs, through understanding the mechanisms responsible for polymer-nanotube interactions and designing molecular amplifiers for the CPE process, to controlled chemical functionalization leading to the programming of the nanotubes' optical properties.

The latest publication consolidates all previously acquired information, demonstrating that the functionalization process is determined not by a single reactant but by the entire system architecture, including the nanotube, polymer, solvent, reaction atmosphere, and intermediate products of the radical processes. Consequently, this work changes the current perception of the chemistry of SWCNT functionalization and shows that rational design of the entire reaction environment is an effective tool for programming their optical properties and creating materials with previously unavailable application possibilities.

5. Conclusions

This doctoral dissertation was devoted to solving two key problems limiting the practical use of SWCNTs:

1. The low efficiency of their selective separation by chirality
2. The limited understanding of the mechanisms responsible for controlled chemical functionalization leading to the shaping of optical properties.

Despite over twenty years of intensive research on these issues, most available methods were still based on empirical optimization of experimental conditions, without a full understanding of the phenomena occurring at the CP–SWCNT–reaction environment interface. The main goal of this work was therefore not only to develop new methods for the separation and functionalization of SWCNTs, but above all to understand the mechanisms responsible for these processes and to use the acquired knowledge for the informed design of materials with programmed optical properties.

The first part of the research demonstrated that the current limitations of the CPE technique stem not from the fundamental properties of the method itself, but from an insufficient understanding of the interactions between the CP and the nanotube surface. The developed concept of molecular extraction enhancers (molecular chaperones) enabled an increase in the isolation efficiency of (6,5) nanotubes by up to eleven times while maintaining very high process selectivity. This result represents a significant breakthrough in the development of CPE technology, demonstrating that this method can be a viable alternative to previously dominant separation techniques

while retaining all the advantages of conducting the process in an organic environment.

Subsequent studies elucidated the mechanism responsible for the selectivity of the CPE process. It was demonstrated that extraction efficiency depends on the balance between the CP-SWCNT interaction energy, the adsorption energy of small-molecule additives, and the stability of the resulting complexes in solution. This allowed for the first time to formulate universal principles for the design of molecular extraction enhancers and demonstrate that universal additives do not exist – the effectiveness of each enhancer is determined by the nature of the interactions within a specific polymer-SWCNT system. The obtained results are changing the way in which new extraction systems are designed, moving the development process from empirical trial and error to the level of rational molecular design. A significant achievement of this dissertation was also the deepening of knowledge regarding the influence of CP architecture on their ability to selectively separate SWCNTs. A library of new CPs based on fluorene and carbazole structures was designed and synthesized, enabling a systematic analysis of the influence of individual chemical structural elements on the extraction process. It was demonstrated that the presence of heteroatoms significantly enhances interactions with the nanotube surface, but the geometry itself and the planar structure of the aromatic system can also lead to high selectivity. Molecular modeling confirmed the experimental observations and demonstrated that extraction efficiency is determined not by a single structural parameter, but by a complex interplay between the chemical structure of the CP, its electronic properties, the width of the energy gap, and the mode of adsorption on the SWCNT surface.

The second main research line was the controlled chemical functionalization of isolated SWCNTs. This dissertation developed the first method enabling simultaneous selective extraction and covalent functionalization of SWCNTs in a single technological process. It was demonstrated that appropriately selected PhN_2H_3 derivatives not only increase extraction efficiency but also lead to the formation of luminescent sp^3 defects responsible for near-infrared light emission. The collected data reduced the functionalization time from many hours to just a few minutes and demonstrated the feasibility of conducting the process in both organic and aqueous environments.

One of the most important achievements of this dissertation was the demonstration that SWCNT functionalization is not a simple reaction between the nanotube and a radical initiator. For the first time, it was reported that the entire reaction environment, including the SWCNT-stabilizing polymer, the solvent, the moisture content, the presence of oxygen, and the competing reactions occurring between all components of the system, determines the course of the process. It was demonstrated that both the CP and the solvent can actively participate in the formation of luminescent defects and direct the reaction toward different end products. The gathered outcomes completely change the current understanding of the SWCNT functionalization mechanism, demonstrating that the properties of the resulting materials can be programmed through conscious design of the entire chemical environment, rather than solely through the selection of the functionalizing reagent.

The acquired knowledge was then used to consciously design materials for optical applications has been demonstrated. The possibility of controlling the type of luminescent defects and their corresponding emission wavelengths through the appropriate selection of the reaction medium and process conditions has been demonstrated. This has allowed the development of the first optical sensor described in the literature operating in an organic environment based on covalently modified SWCNTs isolated by the CPE method, confirming the importance of selecting the appropriate polymer shell for effective interaction of the nanotubes with the analyzed environment.

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Appendix: Publications