Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Chirality enriched carbon nanotubes with tunable wrapping *via* corona phase exchange purification (CPEP)

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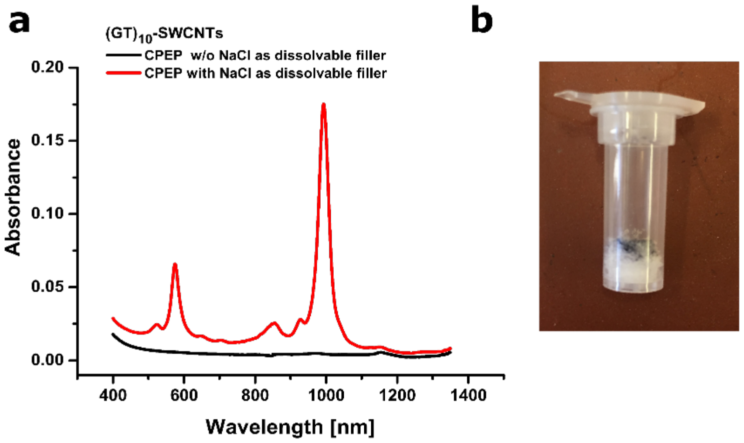

Figure S1: Effect of using NaCl as filler material during PFO-polymer removal. Remaining PFO-BPy was removed by a stepwise filtration process with hot toluene (see Figure 1). Without NaCl SWCNTs agglomerated with themselves and the filter material and the nanotube pellet could not be dispersed with ssDNA in a tip sonication step (black line in a). By using NaCl as toluene-resistant but water-soluble filler SWCNTs adsorbed/agglomerated mainly on the filler material (photograph in b). After dissolving the NaCl the SWCNT could be redispersed (red line in a).

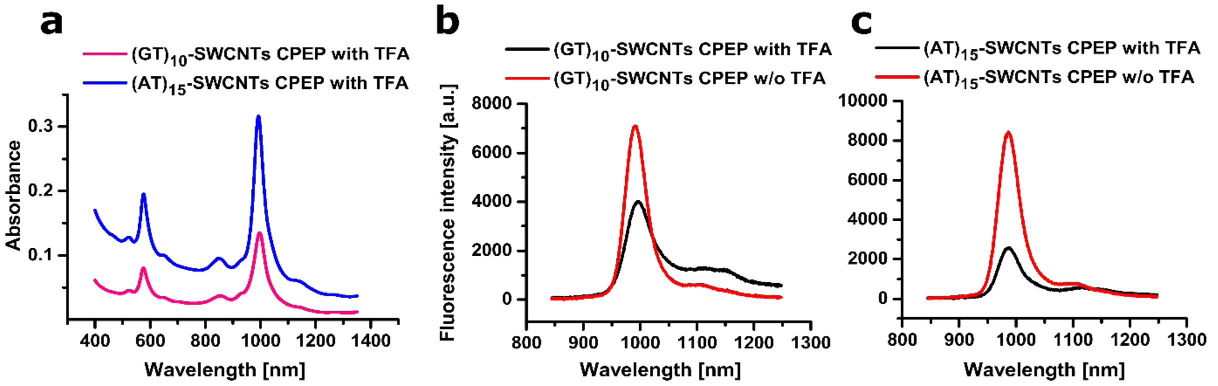

Figure S2: Effect of trifluoroacetic acid (TFA) during CPEP. To support the separation of the purified SWCNT material and the PFO-BPy, 1 µl TFA was added to the mixture of toluene and iso-propyl alcohol (10 ml). Redispersion with ssDNA was not to affected (a) but the nIR-fluorescence emission decreased compared to a protocol without TFA (b,c - compared to samples from Figure 3 and Figure 4). Therefore, we did not use TFA in the CPEP protocol and relied solely on precipitation of SWCNTs by iso-propyl alcohol addition and centrifugation.

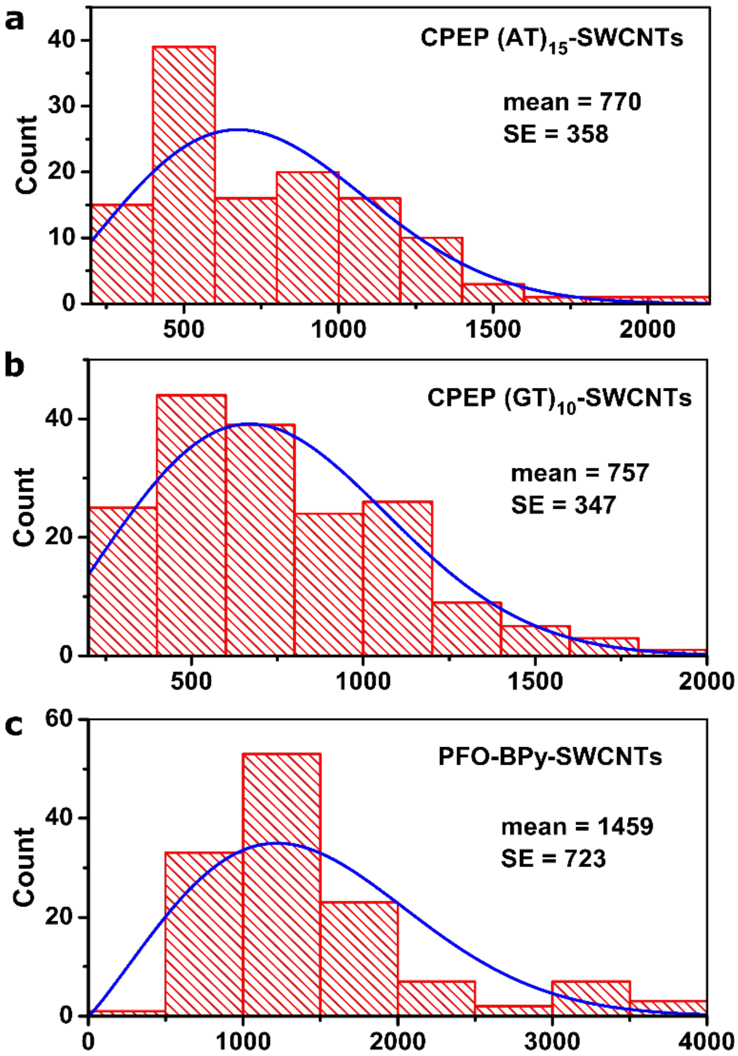

Figure S3. SWCNT length analysis *via* atomic force microscopy (AFM). The lengths of total 427 SWCNTs were evaluated in Gwyddion and fitted with an asymmetric probability density function (Weibull distribution; OriginPro 9.1). AFM measurements in intermittent contact mode were performed on an Asylum Research MFP-3D Infinity microscope with Olympus AC-160-TS cantilevers. Freshly cleaved muscovite mica substrates were incubated for 12 h at 4 °C with 20 µl ssDNA-(6,5)-SWCNTs and subsequently rinsed carefully with ddH_2O. PFO-BPy wrapped SWCNTs were spin coated on a silica wafer and washed with 20 µl toluene. n(CPEP $(AT)_{15}$-SWCNTs) = 122; n(CPEP $(GT)_{10}$-SWCNTs) = 176; n(PFOBPy-SWCNTs) = 129

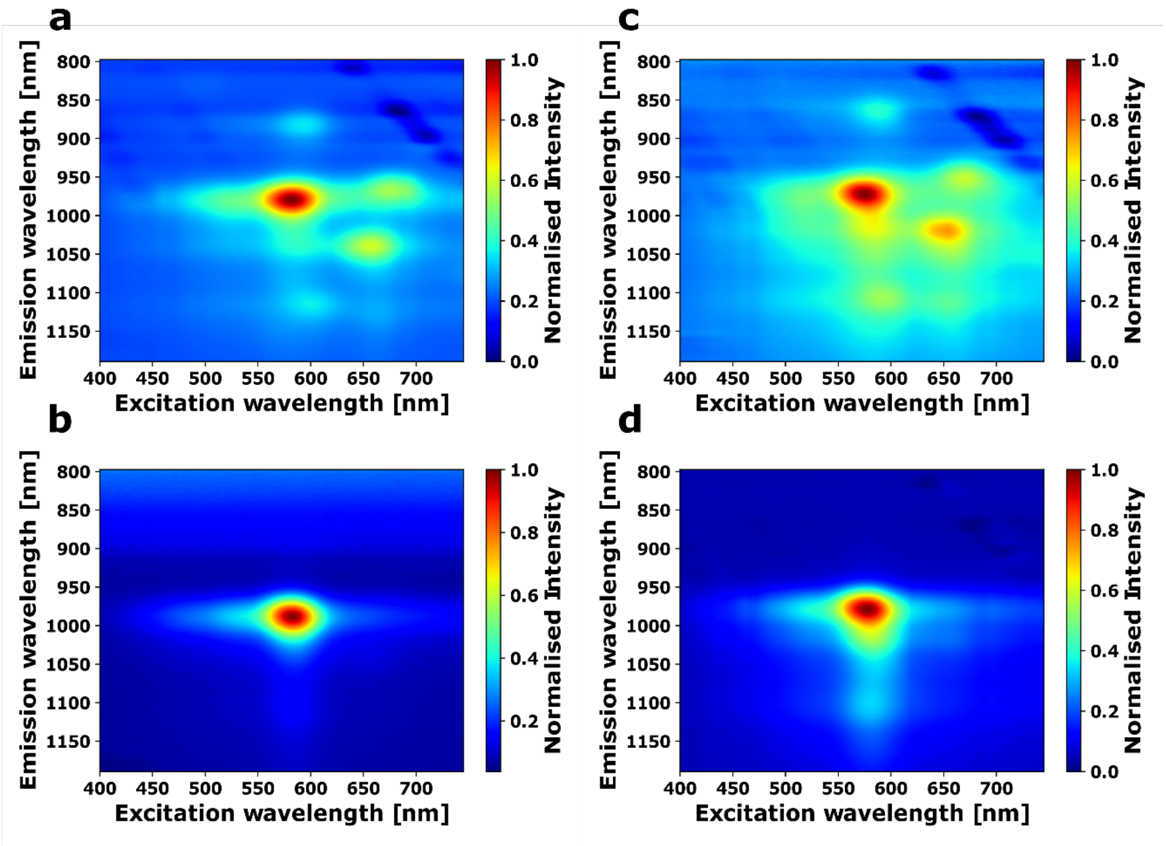

Figure S4. 2D-nIR-fluorescence spectra of CPEP enriched (6,5)-SWCNTs versus their unpurified counterparts. a) 2D spectra of $(AT)_{15}$-SWCNTs using the SWCNT starting material. b) 2D spectra of CPEP $(AT)_{15}$-(6,5)-SWCNTs (same as Figure 4) c) 2D spectra of SWCNTs starting material dispersed in SDBS. d) 2D spectra of CPEP SDBS-(6,5)-SWCNTs shows an enhanced fluorescence feature at ~1120 nm in the fluorescence spectra but no additional feature in the absorption spectra. This peak could be attributed to SWCNTs with oxygen defects.[1]

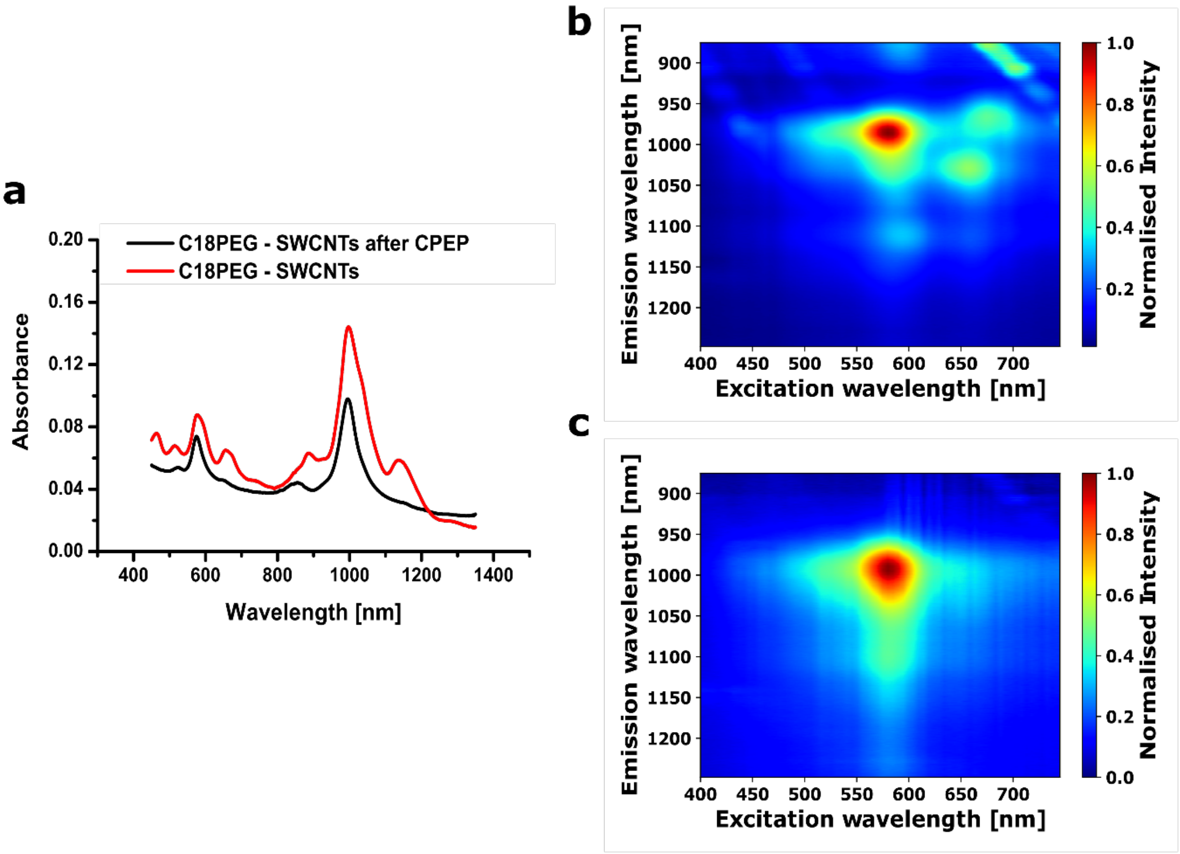

Figure S5. CPEP of (6,5)-SWCNTs with PEG-functionalization. a) Vis-nIR absorption spectra of CPEP and non-purified PMAC18PEG-SWCNTs. b) 2D-fluorescence spectrum of the crude PMAC18PEG-SWCNTs. c) 2D-fluorescence spectra of the crude PMAC18PEG-(6,5)-SWCNTs.

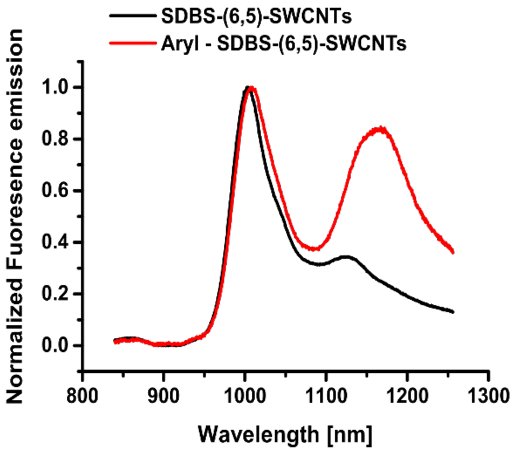

Figure S6. Fluorescence emission spectra of CPEP processed SDBS-(6,5)-SWCNTs. The black line represents the normalized fluorescence emission spectrum before defect reaction vs. the red line, which was acquired after defect reaction (excited at 570 nm). Compared to the SDBS-(6,5)-SWCNTs, the CPEP purified ssDNA functionalized SWCNTs (see Figure 4c-d) do not show an emission shoulder (black line; ~1120 nm) that could be attributed to oxygen defects[1].

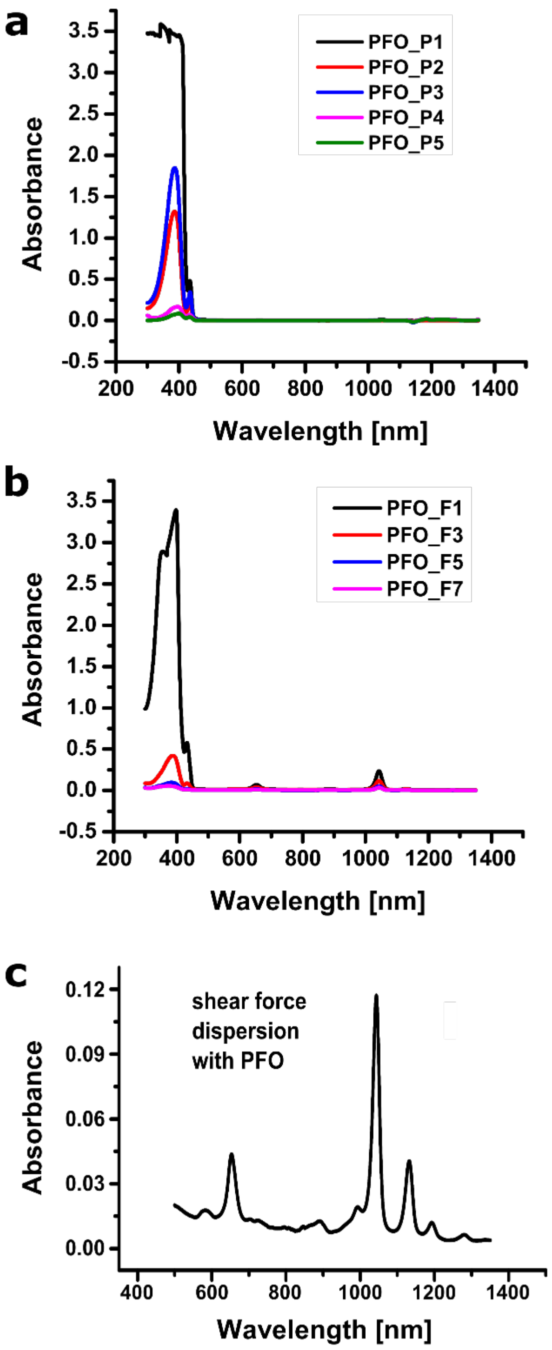

Figure S7. Removal of PFO-polymer during the CPEP process. UV-Vis-nIR absorption spectra monitor the polymer concentration in toluene to follow the stepwise removal. a) Decreasing PFO concentration due to the precipitation (P) steps with isopropyl alcohol. The majority of PFO stays in solution, while the (7,5)-SWCNTs precipitated during centrifugation. b) Stepwise filtration (F) process with 90 °C toluene removes the residue PFO from the SWCNT-pellet, which is loaded on NaCl crystals. A minor (7,5)-SWCNT fraction is solubilized and therefore removed. The general procedure of PFO-polymer removal for PFO-BPy and PFO were similar besides two additional precipitation steps during PFO-removal. c) UV-Vis-nIR absorption spectra after large scale shear force mixing. PFO mainly disperses (7,5)-SWCNTs and a minor fraction of (7,6)-SWCNTs.

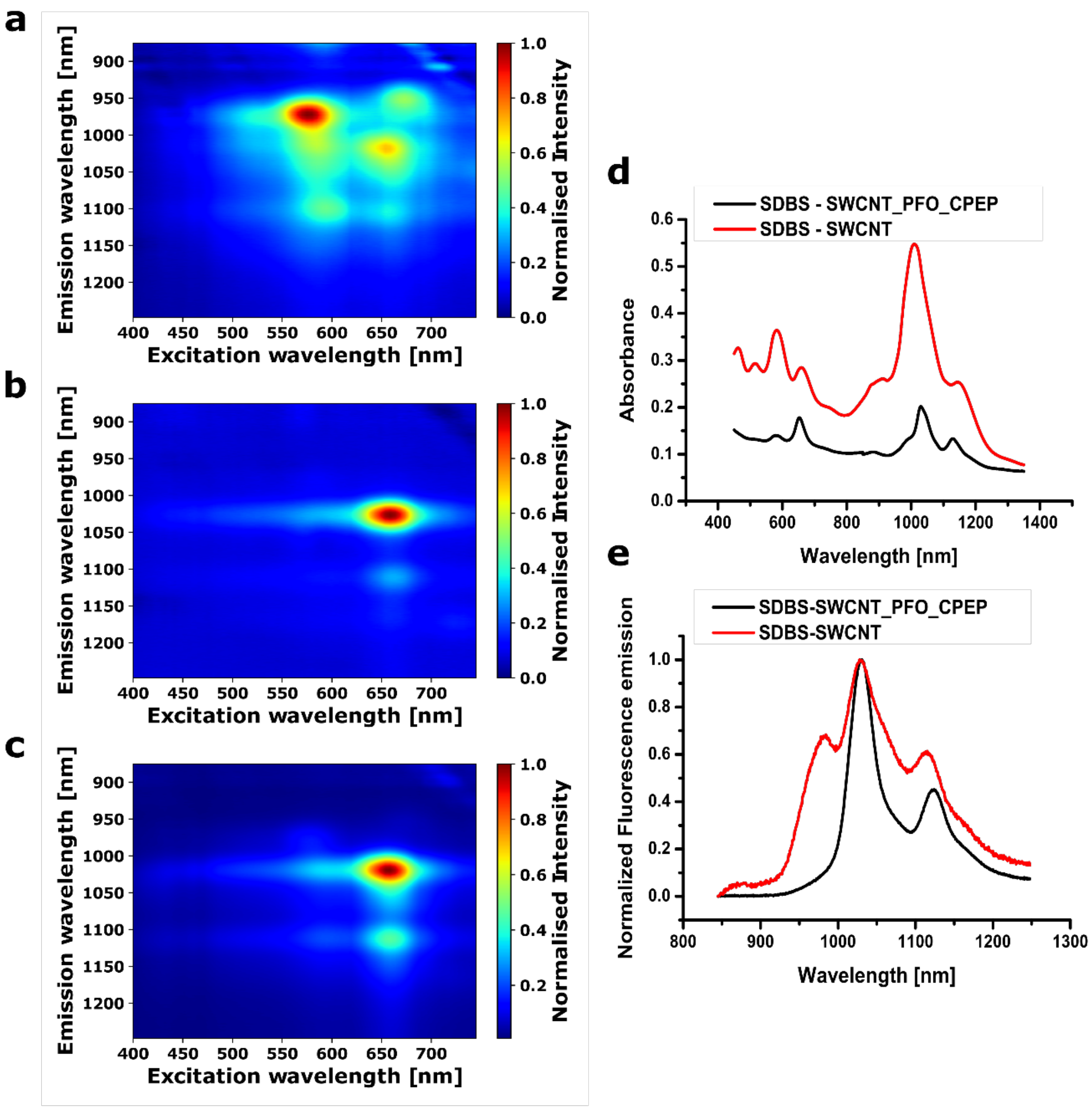

Figure S8. CPEP with PFO to enrich (7,5)-SWCNTs. a) 2D-fluorescece spectra of the raw SWCNT starting material, dispersed with SDBS. b) 2D-fluorescence spectra of the raw SWCNT starting material, dispersed with PFO in toluene. Mainly (7,5)-SWCNTs and a minor fraction of (7,6)-SWCNTs are solubilized. c) 2D-fluorescecne spectra of enriched SWCNTs after CPEP dispersed in SDBS. d) Vis-nIR absorption spectra of SDBS dispersed SWCNTs, before and after CPEP. e) Fluorescence spectrum of SDBS dispersed SWCNTs before and after CPEP reveals the drastic removal of (6,5)-SWCNTs (excited at 630 nm).

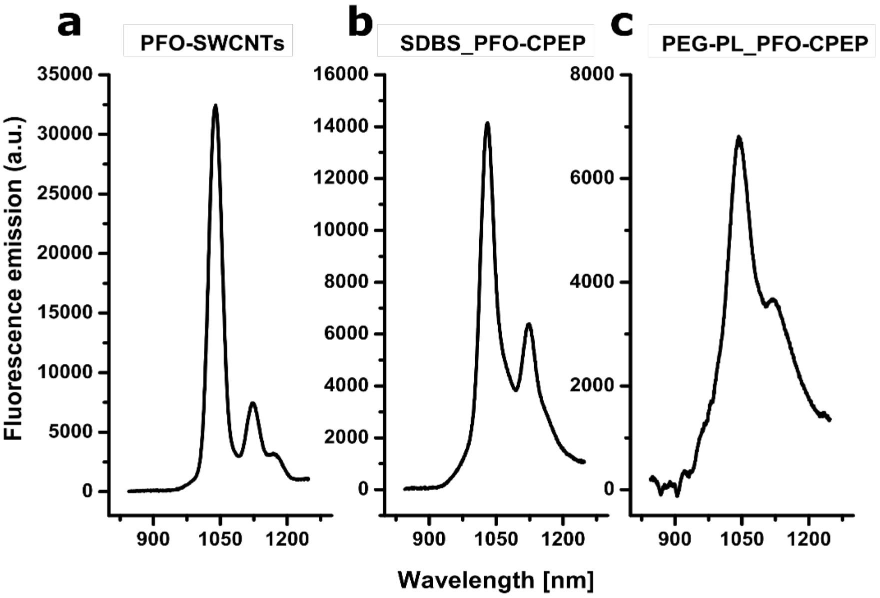

Figure S9. nIR-fluorescence spectra of CPEP enriched (7,5)-SWCNTS. a) SWCNT stock dispersed by PFO in toluene. b) SWCNTs dispersed in SDBS after CPEP process with PFO. c) SWCNTs dispersed in PEG-Phospho-lipid (MW 5 kDa) after CPEP process with PFO.

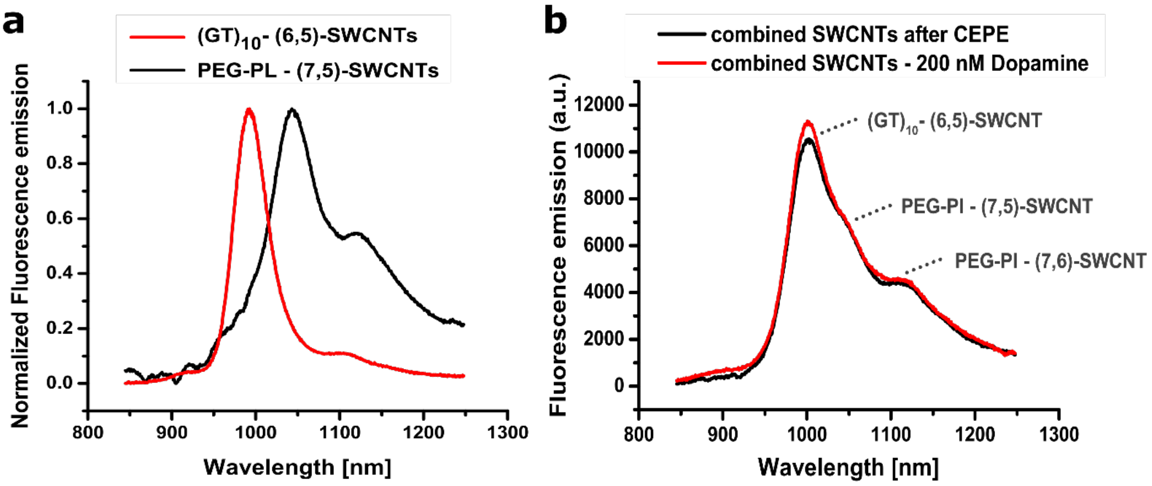

Figure S10. CPEP enriched SWCNTs for ratiometric sensing. a) Normalized nIR-fluorescence spectra of $(GT)_{10}$-(6,5)-SWCNTs and PEG-PL-(7,5)-SWCNTs. The highly enriched (6,5)-SWCNT sample does not contain (7,5) or (7,6)-SWCNTs after the CPEP process from PFO-BPy, and the same applies *vice versa* for the SWCNTs from CPEP after PFO dispersion. b) A combination of a dopamine sensitive $(GT)_{10}$-SWCNTs and a non-sensitive PEG-PL-SWCNT act as a ratiometric sensor for dopamine detection.

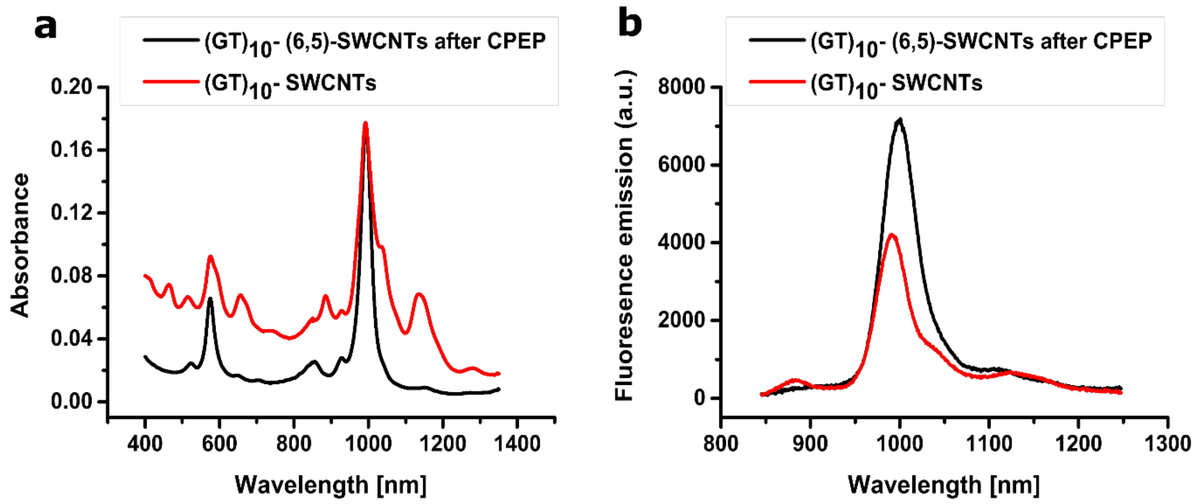

Figure S11. Comparison of absorption and fluorescence emission spectra of CPEP purified and non-purified $(GT)_{10}$-SWCNTs. a) Absorption spectra, diluted to the same absorption of the (6,5)-SWCNT peak. b) nIR-fluorescence spectra of the same samples reveal a stronger fluorescence emission by CPEP purified $(GT)_{10}$-SWCNTs.

Synthesis of 4-nitrobenzenediazonium tetrafluoroborate

A recently published protocol was used[2]**.** Chemicals were received from Sigma-Aldrich, unless declared elsewhere. NMR spectra were recorded on a Bruker Avance III HD 300 MHz device. ^{1}H and ^{13}C spectra were internally calibrated to the residual proton solvent or carbon solvent peaks, respectively.

In a snap-cap vial, 4-nitroaniline (104 mg, 0.753 mmol, 1.0 eq.) is dissolved in ethanol (500 mL) and tetrafluoroboric acid (Alfa Aesar) (50% aq., 190 mL, 1.49 mmol, 2.0 eq). The mixture is cooled to 0 °C and *tert.*-butylnitrite (200 mL, 1.68 mmol, 2.3 eq.) is added dropwise *via* syringe. The mixture is stirred for 30 min at 0 °C and for 1 h at room temperature. The product is precipitated with diethyl ether (1 mL), centrifuged (2 min at 16100 *g*) and the supernatant is discarded. The crude product is washed with diethyl ether (3x 1 mL) and dried at room temperature under reduced pressure for 30 min. The compound is isolated as a brownish solid which can be stored at -20 °C for several weeks.

^{1}H NMR (300 MHz, CD_3CN) δ 8.76 (d, J = 9.2 Hz, 2H), 8.62 (d, *J* = 9.2 Hz, 2H).

^{11}B NMR (96 MHz, CD_3CN) δ -1.15.

^{19}F NMR (282 MHz, CD_3CN) δ -151.14, -151.19. (two signals due to the two NMR-active boron isotopomers)

^{13}C NMR (75 MHz, CD_3CN) δ 155.18, 135.33, 127.51, 121.43.

The NMR data is in accordance with literature.[3]

HR-MS (negative mode): calculated: 150.0298 (C4H4N3O2); found: 150.0295

Defect introduction to (6,5)-SWCNTs

In a 96-well plate, 90 µL of a 2 nM (6,5)-SWNT dispersion in 0.2 % SDBS was mixed with 10 µL of a 20 µM aqueous solution of 4-nitrobenzenediazonium tetrafluoroborate (DzNO2). The solution is irradiated (λ= 561 nm) for 10 min using a monochromator (MSH150) connected to a LSE341 light source (LOT-Quantum Design GmbH, Darmstadt, Germany). Spectra are taken every 10 s.

Synthesis of PMAC18PEG

This synthesis was recently published[4]. Methoxypolyethylene glycol amine (5000 Da, 214 mg) and Poly(maleic anhydride-*alt*-1-octadecene) (15 mg) are dissolved in methylene chloride (3 mL). Triethylamine (300 mL) is added and the solution is stirred at room temperature for 3 h. Volatile compounds are removed in a stream of argon and the crude product is dissolved in water (7.5 mL). The mixture is purified *via* dialysis (14 kDa MWCO dialysis tube, Sartorius) against water and lyophilized to yield a colourless solid.

Dispersion of PMAC18PEG -SWCNTs.

A recently published protocol was used and adapted[5]. A mixture of (6,5)-SWCNTs and PMAC18PEG (2 mg/mL in ddH$_2$O, 300 µL) was sonicated (30 min / 30 % Amplitude Fisher, Scientific™ Model 120) and larger aggregates were removed by centrifugation (10 min /10.000 *g*).

^{1}H NMR (500 MHz, CDCl$_3$) δ 3.7-3.6 (m, CH$_2$ of mPEG), 1.13-1.12 (m, CH$_2$ of C$_{18}$ chains), 0.85 (m, CH$_3$ of PMHC$_{18}$)

The NMR data is in accordance with literature.[5]

References

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(5) Liu, X.; Tao, H.; Yang, K.; Zhang, S.; Lee, S.; Liu, Z. Biomaterials Optimization of Surface Chemistry on Single-Walled Carbon Nanotubes for in Vivo Photothermal Ablation of Tumors. *Biomaterials* **2011**, *32* (1), 144–151.