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Supplementary Information

Influence of DNA conformation on the dispersion of SWNTs: single-strand DNA vs. hairpin DNA

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Sample preparation and characterization

Typically, 0.5 mg of (6,5) enriched CoMoCAT raw material (*SWeNT SG 65, South West Nanotechnologies*) were exposed to 2.0 mL phosphate buffered saline (PBS, *Fisher Scientific*), diluted with *Chromasolv Plus* water (HPLC grade, *Sigma-Aldrich*) before. The DNA oligomers purchased by *biomers.net* had a concentration of about 0.5 mmol L^{-1}, refering to the concentration of single nucleotides. Dispersion was achieved by applying medium power CW bath sonication (*Sonifier S450A, Branson*) for a period of 2 h at ambient or enhanced temperature (25 or 60 °C).

The non-solubilized residue was removed as sediment from the as-prepared suspension by centrifugation with a tabletop centrifuge (*Rotina 35R, Hettich*). The supernatant was inserted into an ultracentrifuge vial with a density gradient.[1] The gradient consisted of layers with different portions of aqueous 60 (*w*/*V*)% iodixanol solution (*OptiPrep, Sigma-Aldrich*).

content of iodixanol	composition of density gradient
20 (*w*/*V*)%	1.33 mL *OptiPrep* & 2.67 mL PBS
30 (*w*/*V*)%	1.50 mL *OptiPrep* & 1.50 mL PBS
40 (*w*/*V*)%	2.67 mL *OptiPrep* & 1.33 mL PBS

Table S1 Characteristics of the step gradient applied. The raw dispersion was put in the middle layer.

Steps in the layered density gradient were allowed to blend diffusively by capping and carefully aligning centrifuge vials horizontally for 2 h. DGU treatment was then performed at 41 krpm with an *Optima L-90K* ultracentrifuge (*Beckman Coulter*), equipped with a *SW 41 Ti* swinging bucket rotor. After 12 hours, single fractions (200 µL) were collected using a home-built upward displacement apparatus, driven by a syringe pump and filled with a water-immiscible high-density chase medium (*Fluorinert FC-40, Sigma-Aldrich*).

The samples were characterized by measuring optical absorption spectra with an UV-Vis-NIR spectrophotometer (*Cary 5000, Varian*). Background correction was achieved using appropriate reference spectra. Here control samples were obtained from DGU runs without dispersed CNTs.

Fluorescence measurements (CW) were either carried out with a *FP-6300* spectrometer (*Jasco*) or with a *Triax 320* monochromator (*Horiba Jobin Yvon*) in conjunction with a mercury lamp (*Intensilight, Nikon*), depending on the emission wavelength to be detected.

[1] M. S. Arnold, S. I. Stupp and M. C. Hersam, *Nano Lett.*, 2005, **5**, 713-718.

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Comparison of buoyant densities

As mentioned in the main text, the buoyant density of hpDNA-SWNT conjugates is slightly larger than those of their ssDNA-SWNT equivalents. This can be demonstrated by plotting the maximum of optical density vs. fraction index. Consistently, the maximum of optical density is the S_1 excitonic transition of the (6,5) nanotubes. Since all preparation steps were accomplished under the same conditions, increasing fraction index corresponds to an increase of the specific buoyant density.

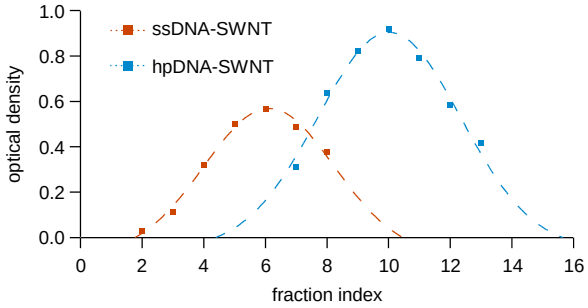

Fig. S1 Optical density after DGU vs. fraction index. The dashed lines are a guide to the eye.

Fig. S1 confirms that hpDNA-SWNT conjugates have higher buoyant densities. This quantitative analysis is in agreement with visible maxima in the vertical position of carbon nanotube-rich layers in centrifuge vials after DGU.

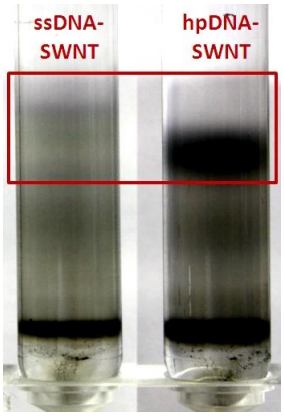

Fig. S2 Centrifugal vials of ssDNA-SWNT and hpDNA-SWNT conjugates after DGU treatment.

The layers containing dispersed carbon nanotubes are highlighted by the red frame in Fig. S2. In case of the single-strand conjugates, various differently colored layers can be identified. The hairpin motif, however, leads to a broader band lying closer to the bottom of the vial due to its higher buoyant density. Its unstructured dark shape is due to the inferior separation efficiency and higher optical density.

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Determination of hairpin melting point

The melting point of the hp motif 5'-GGCACG$(CA)_{10}$CGTGCC-3' was identified by investigating the denaturation behavior in the UV regime at 260 nm. It is marked by the maximum in the first derivative of the hyperchromic profile and shows a sigmoid character.

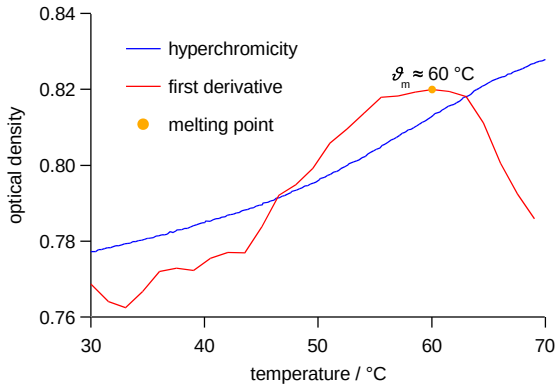

Fig. S3 Melting curve of 5'-GGCACG$(CA)_{10}$CGTGCC-3' (stem: 2 x 6 bases, loop: 20 bases).

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Filtration and resuspension scheme

Centrifugal filters *Microcon YM-100* (*Millipore*) were used, when removal of oligonucleotides remaining free in solution was required.[2]

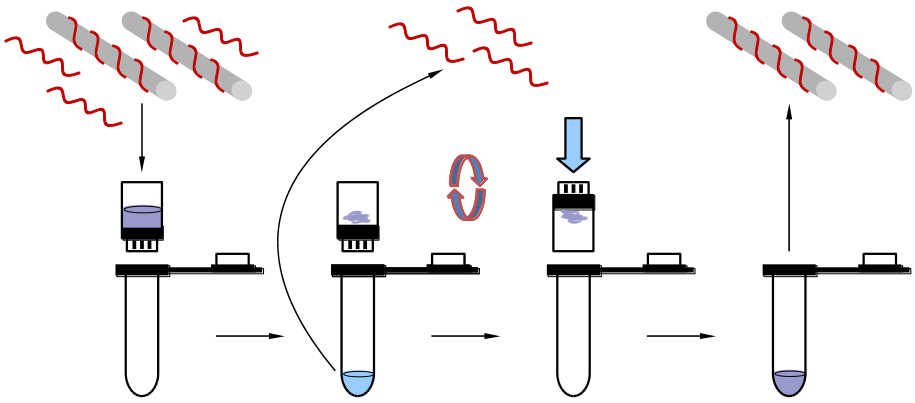

Fig. S4 Filtration and resuspension procedure, shown for SWNTs dispersed with ssDNA.

[2] S. R. Vogel, M. M. Kappes, F. Hennrich and C. Richert, *Chem. Eur. J.*, 2007, **13**, 1815-1820.

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Description of 6-FAM emitter

6-Carboxyfluorescein adopts several differently charged forms, with some of them existing in tautomeric equilibria.[3] Considering the pH value of phosphate buffered saline at 7.4, only the anionic species and the dianionic one are appreciably present in solution, and contributed to the measured fluorescence signal.[4]

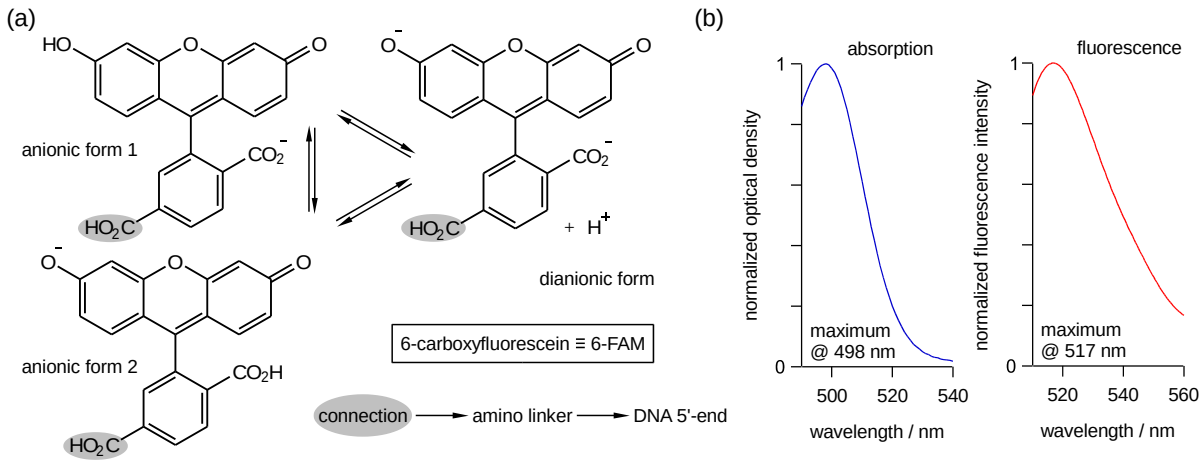

Fig. S5 Characterization of the fluorescent dye label: (a) structure and connection, (b) spectral features.

To cope with the polymorphism of the attached dye molecule, time-resolved fluorescence from the dye was analyzed using a biexponential fit function.

[3] R. Sjöback, J. Nygren and M. Kubista, *Spectrochim. Acta A*, 1995, **51**, L7-L21.
[4] J. M. Alvarez-Pez, L. Ballesteros, E. Talavera and J. Yguerabide, *J. Phys. Chem. A*, 2001, **105**, 6320-6332.

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TCSPC setup

Fluorescence decay of the DNA attached 6-FAM emitter occurs on the nanosecond timescale. Low repetition rates thus need to be used. Here we used a regenerative amplifier with 250 kHz repetition rate, corresponding to a pulse interval of 4 µs. The emitter was excited at 400 nm by the second harmonic signal of the regenerative amplifier output.

To determine the pure fluorescence decay, magic angle conditions were applied to ensure the proper weighting of parallel and perpendicular emission intensities $I_{\parallel}(t)$ and $I_{\perp}(t)$. Instead of aligning the polarizer under 54.7° with respect to the incident radiation, we measured $I_{\parallel}(t)$ and $I_{\perp}(t)$ individually and obtained $I(t)$ by simple addition. By this, no additional measurements were required to obtain the anisotropy data.