Electronic Supplementary Material (ESI) for RSC Advances

A simple pyrene "click"-type modification of DNA affects solubilisation and photoluminescence of single-walled carbon nanotubes

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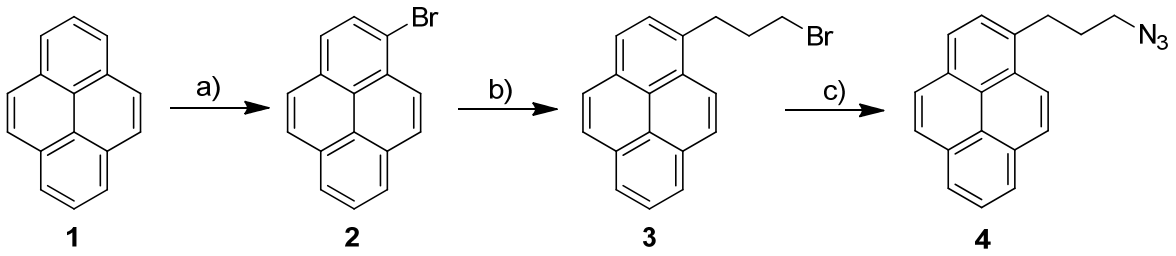
Supporting Information

Contents **Page**

Materials and Methods

Chemicals and dry solvents were purchased from commercial suppliers and were used without further purification unless otherwise mentioned. TLC was performed on Fluka silica gel F254 coated aluminium foil. Flash chromatography was carried out with Silica Gel 60 from Aldrich (43 – 60 µm). Spectroscopic measurements were recorded in Na-Pi buffer solution (10 mM, pH 7) using quartz glass cuvettes (l = 1 cm). Mass spectra were measured in the central analytical facility of the institute. NMR spectra were recorded on a Bruker Advance 300 spectrometer at 300 K in deuterated solvents. Chemical shifts are given in ppm relative to TMS. Absorption were recorded on a Perkin Elmer Lambda 750 spectrometer with a pelltier system PTP 6+6. Fluorescence was measured on a Jobin-Yvon Fluoromax 3 fluorimeter with a step width of 1 nm an integration time of 0.2 s. All spectra were recorded with an excitation and emission bypass of 5 nm and are corrected for Raman emission of the buffer solution.The pyrene azide **4** was synthesized according to scheme 1. The precursors **2** and **3** were synthesized according to literature.[1,2]

Synthesis of the pyrene azide 4



Scheme S1: Synthesis of the pyrene azide **4**: *Reagents and conditions*: a) HBr (1,1 eq.), H_2O_2 (1 eq.), MeOH:Et_2O 1:1, 15 °C – rt, 16 h, 96%; b) n-BuLi (1,2 eq.), 1,3-dibrompropane (10 eq.), abs. Et_2O, 0 °C –reflux, 2 h, 18%; c) NaN_3 (eq.), DMF, rt, 16 h, 75%.

1-(3-azidopropyl)-pyrene (4). 100 mg (0.31 mmol) 1-(3-bromopropyl)-pyrene and 30 mg (0.18 mmol, 0.6 equiv.) KI were dissolved in 5 mL DMF. To this mixture 80 mg NaN_3 (1.23 mmol, 4 eqjuiv.) were added and heated over night at 80 °C. The mixture was extracted with CH_2Cl_2 and water. The organic layer was dried over $MgSO_4$. Afterwards the solvent was removed and the crude product was purified by flash chromatographie (hexane: CH_2Cl_2 5:1) to yield 4 (68 mg, 0.24 mmol, 76%.) as a yellow oil.

^{1}H-NMR (300MHz, $CDCl_3$): δ [ppm] 8.53 – 7.84(m, 9H), 3.42 (dt, *J* = 11.3, 4.3 Hz, 4H), 2.19-2.10 (m, 2H) **^{13}C NMR** (300 MHz, $CDCl_3$) δ [ppm] 135.2, 131.6, 131.0, 130.2, 128.8, 127.7, 127.6, 127.5, 127.0, 126.1, 125.3, 125.2, 125.0, 123.2, 77.4, 75.0, 51.1, 30.9, 30.5. **EI-MS** m/z (%): 285.2 (50) $[M]^+$ **HR-ESI-MS** m/z (calcd.) = 286.1339 $[M-H]^+$; m/z (found): 286.1351 $[M-H]^+$

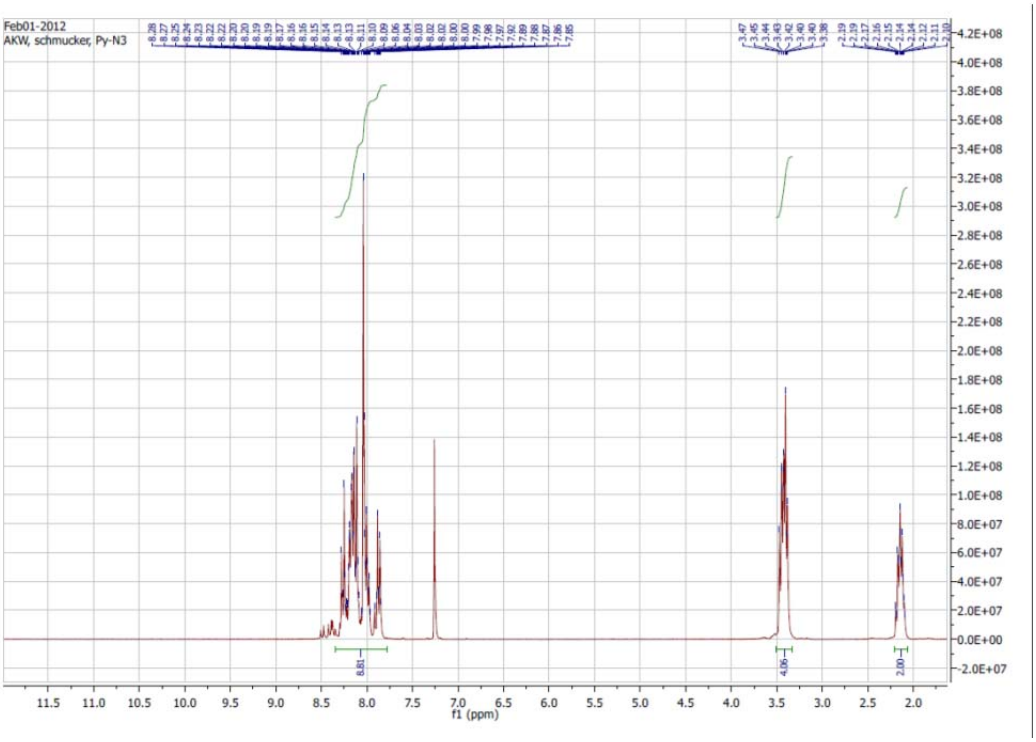


Figure S1: Image ^{1}H-NMR of **4.**

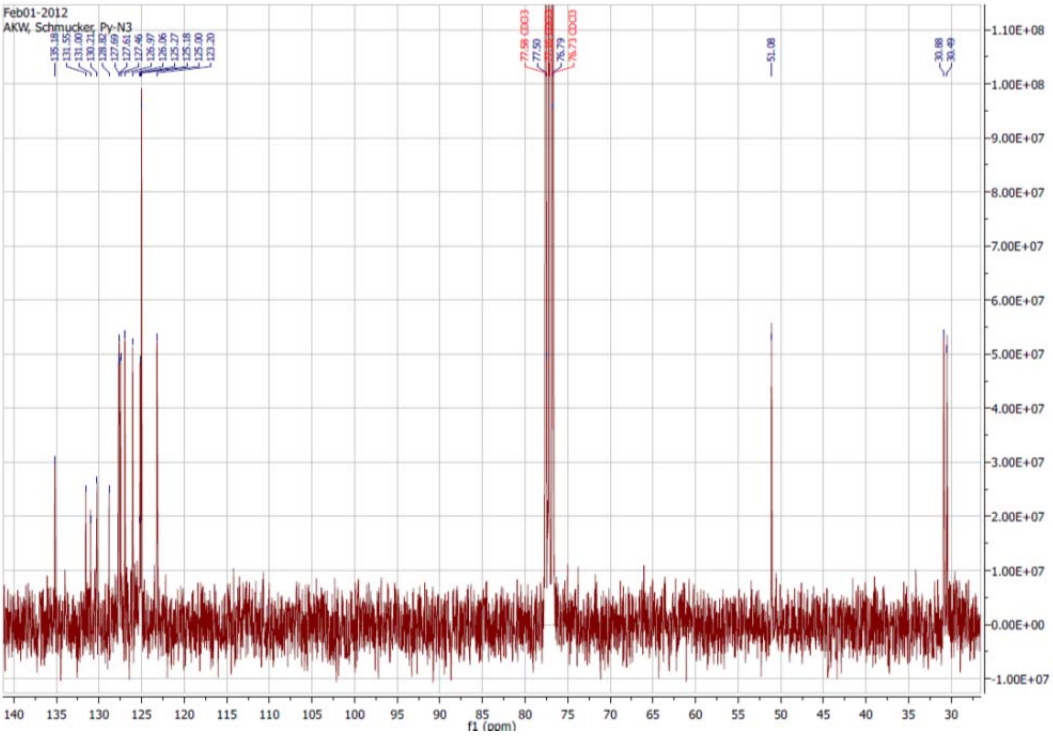
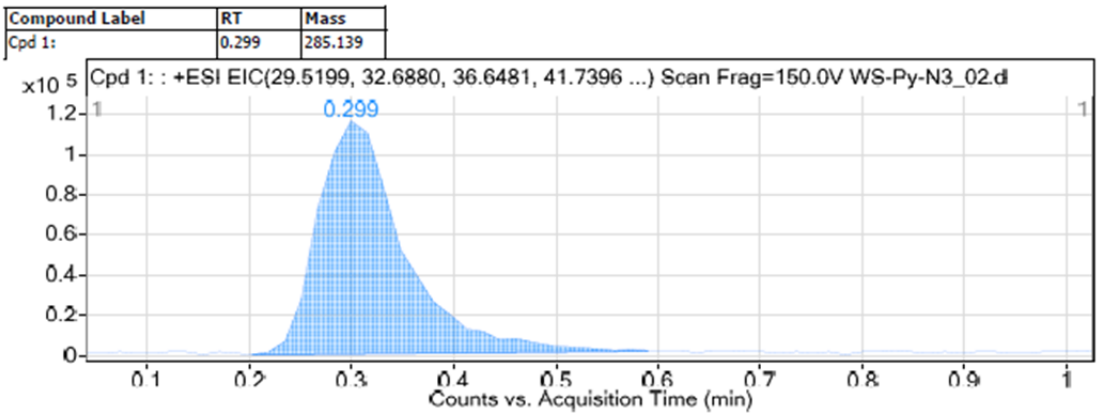
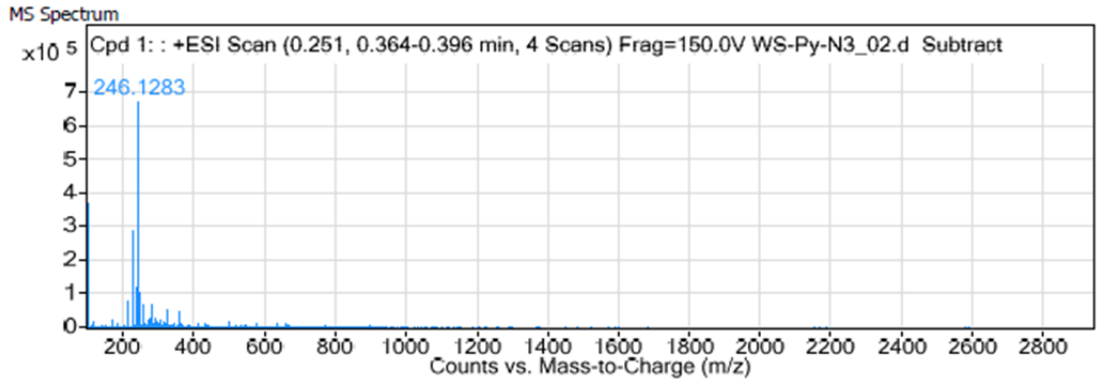


Figure S2: Image of ^{13}C-NMR of **4.**





MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Ion
246.1283				
286.1351	286.1339	4.41	1	(M+H)+
287.1328	287.1369	-14.55	1	(M+H)+
303.1395	303.1604	-68.94	1	(M+NH4)+
304.1398	304.1634	-77.67	1	(M+NH4)+
308.1283	308.1158	40.52	1	(M+Na)+
309.1304	309.1189	37.35	1	(M+Na)+

Figure S3: Image of HR-ESI-MS of **4**.

Synthesis and Characterization of DNA1–5

The oligonucleotides were prepared on an Expetide 8909 DNA synthesizer (Applied Biosystems) via standard phosphoramidite protocols using CPGs (1 µmol) with longer coupling times of 120 s. The chemicals for the DNA synthesis were purchased from ABI and Glen Reasearch. 2'-(O-propargyl)-uridine was ordered from Chem Genes.After preparation, the trityl-off oligonucleotides were cleaved of the resin and deprotected with conc. NH_4OH at 37°C for 16 h. Afterwards 25 µL of an aqueous sodium ascorbate solution (0.1 mM in water), 34 µL tris-[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (0.1 mM DMSO/ t-butanol 3:1), 17 µL of a solution of tetrakis(acetonitrile)copper(I)hexafluorophosphate (0.1 mM DMSO/ tbutanol 3/1) and finally 114 µL of the azide **4** (0.01 M, DMSO/t-butanol 3:1) were added to the 2´-propargyl-uridine modified DNA. The reaction mixture was vortexed, shaken overnight at r.t. and evaporated to dryness using a speedvac the next day. Then 100 µL of an aqueous solution of sodium acetate (0.3 M) were added and the mixture stored for 1 h at r.t.. Then ethanol (1 mL) was added to the mixture, vortexed and frozen (-20 °C) overnight. The suspension was centrifuged (13000 rpm, 15 min) and the supernatant removed. The pellet was washed twice with ethanol (500 *µ*L) and then dissolved in water (500 *µ*L). Prior to purification by HPLC, the DNA was desalted by NAP-5 column (GE Healthcare). The modified oligonucleotides were dried and purified by reversed phase HPLC using the

following conditions: A = NH_4OAc buffer (50 mM), pH = 6.5; B = MeCN; gradient = 0 - 25% B over 50 min. The oligonucleotides were lyophilized and quantified by their absorbance at 260 nm on a NanoDrop ND-1000. **DNA6-8** were ordered from Metabion and used without further putification.

Table S1 Maldi-MS analysis and extinction coefficients of **DNA1-5**

Oligonucleotide	Calculated mass [g/mol]	Observed mass [m/z]	ε_{260} [mM^{-1} cm^{-1}]
DNA1	3948	3947.9	128.9
DNA2	2741	2738.5	78.6
DNA3	4062	4062.8	120.8
DNA4	3939	3938.1	123.0
DNA5	3404	3401.4	99.7

SWCNT sample preparation

In a typical experiment 60 -70 µg of as-produced HiPco SWCNTs (Nanointegris, batch number R1-912) were mixed with an equivalent mass of DNA in 2 mL of 100 mM NaCL and 5 mM NaPi-buffer pH 7 in H_2O (for fluorescence) or only D_2O (for photoluminescence/absorption measurements). The sample was sonicated in an ultrasonic bath (Merck eurolab, USR 18 H) for 2 hours. After sonication, the sample was incubated for 1 d. Then it was centrifuged at 15600 g for 90 min. 90% of the supernatant were collected. In fluorescence quenching experiments the supernatant was centrifuged through Amicon Ultra-0.5 mL centrifugal filters from Millipore (50 kDa, 9000 g) and washed four times with 100 mM NaCl and 5 mM NaPi. After measuring the fluorescence a few µL of a 5 wt-% SDBS solution were added and incubated for 1 h at room temperature. Afterwards the fluorescence was measured again. In photoluminescence/absorption measurements 500 µL of the supernatant mixed with an equal volume of a 2.2 wt% solution of SDBS were subsequently added to a final concentration of 0.11 wt% SDBS. After incubation for several hours at room temperature absorption- and PL- measurements were carried out.

Photoluminescence map to identify suitable oligonucleotides

SWCNTs were solubilized in D_2O in a 0.1 wt-% SDBS solution by sonication in an ultrasonic bath. After incubation and centrifugation (see experimental section) a photoluminescence map of the supernatant was acquired.

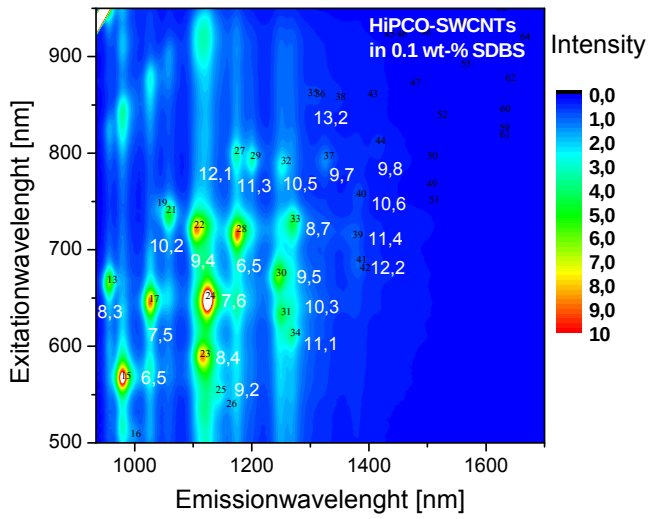


Figure S4: photoluminescence map of HiPCo-SWCNTs dissolved in a 0.1 wt-% SDBS solution. 22 (n,m) species can be clearly identified.

E_{11} range for calculating the denominator for photoluminescence/absorption-ratio

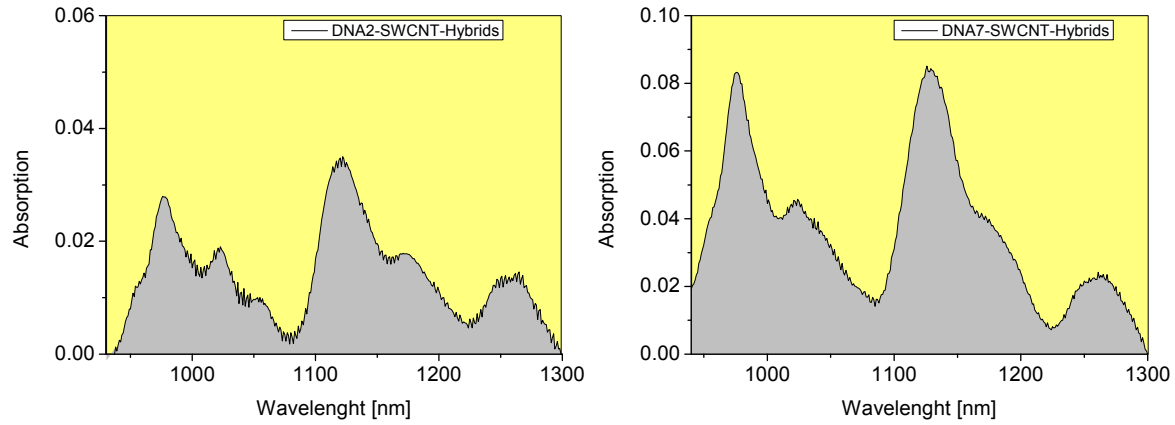


Figure S5: E_{11} range for **DNA2** and **DNA7** (The observable differences in are not reproducible and hence are the result of differences in the sample concentration that are caused by the preparation (centrifugation etc.)

Photoluminescence/absorption ratios of DNA1 vs. DNA6 and DNA5 vs. DNA8.

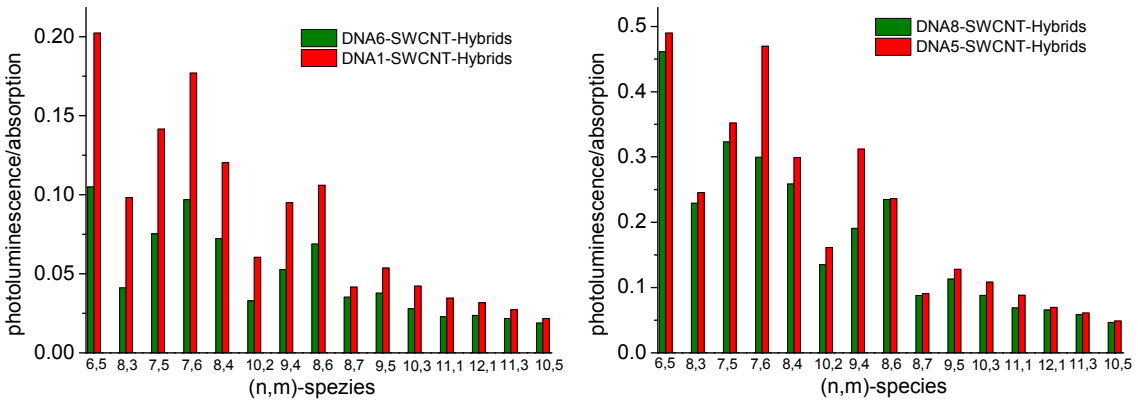


Figure S6: Photoluminescence/absorption of **DNA1** vs. **DNA6** and **DNA5** vs. **DNA8**.

Additional references

1 C. He, Q. G. He, Q. Chen, L. Shi, H. M. Cao, J. G. Cheng, C. M. Deng, T. Lin, *Tetrahedron Lett.* **2010**, *51*, 1317-1321.

2 H. W. Rhee, C. R. Lee, S. H. Cho, M. R. Song, M. Cashel, H. E. Choy, Y. J. Seok, J. I. Hong, *J. Am. Chem. Soc.* **2008**, *130*, 784-785.