Naphthalenenbisimides as photofunctional surfactants for SWCNT: Towards water soluble donor/acceptor hybrids

Supplementary Information

Synthesis of NBI 1

***N,N'*-bis(5-carboxy)-pentyl-naphthalene-1,4,5,8-tetracarboxy-bisimide (3):** 1,4,5,8-Naphthalenedianhydride (**2**) (500 mg, 1.86 mmol) and 6-aminocaproic acid (2.44 g, 18.60 mmol) were added to a solution of anhydrous toluene/ethanol (1:1). The mixture was stirred overnight at 100 °C. After reaction, the solution was cooled to room temperature and 100 mL water were added. The crude product was filtered and washed sufficiently with water. After drying on vacuum a pale yellow powder was obtained (yield: 919 mg, 1.85 mmol, 100%).

^{1}H-NMR (DMSO, 400 MHz): δ = 1.34 (m, 4H, CH_2); 1.55 (m, 4H, CH_2**)**; 1.60 (m, 4H, CH_2) 2.21 (t, ^3J = 7.2 Hz, 2H, CH_2COO); 4.00 (t, ^3J = 6.9 Hz, 2H, CH_2N); 8.56 (s, 4H, Ar-H); 11.99 (br s, 2H, COOH) ppm.

^{13}C-NMR (DMSO, 100 MHz): δ = 24.2 (1C, CH_2); 26.0 (1C, CH_2); 27.1 (1C, CH_2); 33.5 (1C, CH_2); 40.1 (1C, CH_2N); 125.9 (2C, Ar-C); 126.1 (4C, Ar-CH); 130.4 (4C, Ar-C), 162.4 (4C, C=O), 174.4 (2C, COOH) ppm.

MS (MALDI, dhb): m/z = 495 $[M + Na+]^+$;

EA Calc. for $C_{26}H_{26}N_2O_8$: C, 63.15; H, 5.30; N, 5.67: found: C, 62.95; H, 5.08; N, 5.52

***N,N'*-bis-(5-carboxy{di-*tert*-butyl-4[(2-*tert*-butoxycarbonyl)ethyl]-4-aminoheptane-dioate}pentyl)-naphthalene-1,4,5,8-tetracarboxy-bisimide (1a):** A mixture of NBI **3** (919 mg, 1.85 mmol) and NG-1 (846 mg, 2.04 mmol) in THF (30 mL) was stirred at room temperature for 10 min. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methoxy-morpholinium chloride (DMTMM) (565 mg 2.04 mmol) was added to the mixture and stirred for 5 h at room temperature. The reaction mixture was poured into water and extracted with ether. The organic phase was combined and washed successively with saturated sodium carbonate, water, 1N HCl, water, and brine and dried over $MgSO_4$. After recrystallization from hexane/methanol a pale yellow powder was isolated as product (yield: 2.37 g, 1.84 mmol, 99%).

^{1}H-NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 1.40 (s, 54H, CH_3); 1.46 (m, 4H, CH_2); 1.72 (m, 8H, CH_2); 1.94 (t, ^3J = 7.3 Hz, 12H, CH_2); 2.11 (t, ^3J = 7.9 Hz, 4H, CH_2); 2.19 (t, ^3J = 7.3 Hz, 12H, CH_2); 4.16 (t, ^3J = 7.6 Hz, 4H, CH_2); 5.92 (s, 2H, N-H); 8.72 (s, 4H, Ar-H) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 25.7, 26.8, 27.8 (6C, CH_2); 28.3 (18C, CH_3); 30.0, 30.2 (12C, CH_2); 37.4 (2C, CH_2); 40.8 (2C, CH_2); 57.5 (2C, C_{quart}); 80.9 (6C, C_{quart}); 126.8 (4C, Ar-C); 126.9 (2C, Ar-C); 131.2 (4C, Ar-C); 163.0 (4C, C=O); 172.4 (2C, C=O); 173.1 (6C, C=O) ppm.

HRMS (ESI-TOF, pos. mode): Calc. for: $C_{70}H_{105}N_4O_{18}$: 1289.742 $[M+H]^+$; found: 1289.745.

EA Calc. for: $C_{70}H_{104}N_4O_{18}$ x 1/6 $CHCl_3$: C, 64.19; H, 8.00; N, 4.27: found: C, 64.03; H, 8.04; N, 4.19.

***N,N'*-bis-(5-carboxy{di-*tert*-butyl-4[(2-carbonyl)ethyl]-4-aminoheptane}pentyl)-naphthalene-1,4,5,8-tetracarboxy-bisimide (1):** In a 100 mL flask, NBI **1a** (50 mg, 0.039 mmol) was dissolved in 20 mL of formic acid and stirred at room temperature for 12 h. Afterwards, formic acid was evaporated and toluene was added to the residue and removed in vacuum for three times in order to remove formic acid residues. After drying in vacuum, a pale yellow solid was obtained (yield: 36 mg, 0.039 mmol, 100%).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.53 (m, 4H, CH_2); 1.78 (m, 8H, CH_2); 2.20 (t, 3J = 7.3 Hz, 12H, CH_2); 2.44 (m, 4H, CH_2); 2.52 (t, ^3J = 7.3 Hz, 12H, CH_2); 4.25 (t, ^3J = 7.1 Hz, 4H, CH_2); 6.82 (s, 2H. N-H); 8.86 (d, ^3J = 2.1 Hz, 4H, Ar-H) ppm.

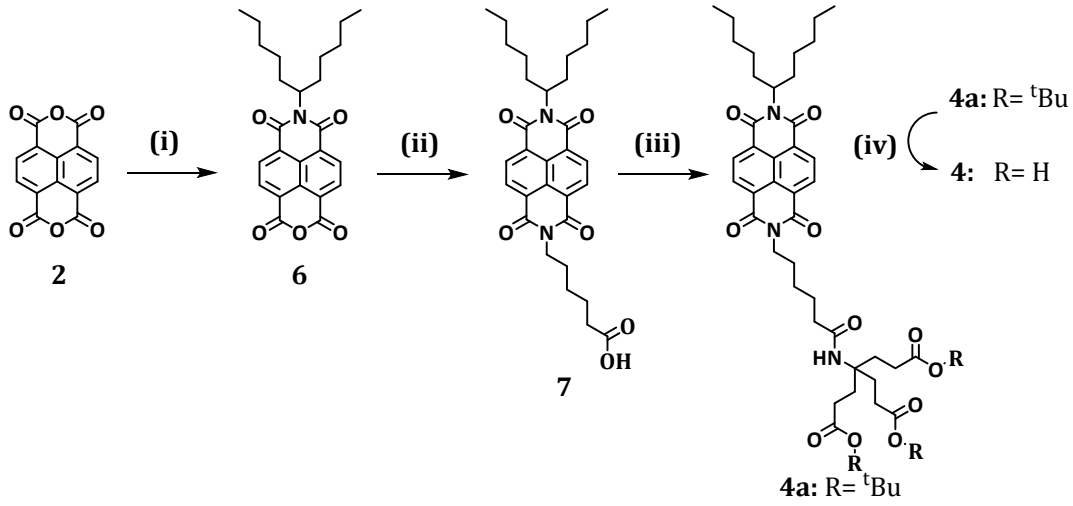
^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 25.7, 27.2 (4C, CH_2); 26.4 (2C, CH_2); 28.4 (6C, CH_2); 29.4 (6C, CH_2); 36.5 (2C, CH_2); 41.7 (2C, C_{quart}); 59.9 (2C, C_{quart}); 126.8 (4C, Ar-C); 127.1 (4C, Ar-C); 132.7 (4C, Ar-C); 164.9 (4C, C=O); 178.8 (2C, C=O); 180.8 (6C, COOH) ppm.

HRMS (ESI-TOF, pos. mode): Calc. for $C_{46}H_{57}N_4O_{18}$: 953.366 [M+H]; found: 953.366.

EA Calc. for $C_{46}H_{57}N_4O_{18}$: C, 61.20; H, 6.75; N, 4.98: found: C, 61.62; H, 6.82; N, 4.98.

UV/Vis (borate buffer pH10, 1 x 10^{-4} M): λ_{max} (ε) = 327 (6616), 346 (11907), 363 (19747), 385 (23597) nm.

Synthesis of reference compounds NBI 4 and NMI 5



Scheme 1: Synthesis of NBI 4: (i) 6-undecylamine, DMF, microwave, 140° C, 15 min (ii) 6-aminocapronicacid, DMF, microwave, 140° C, 15 min. (iii) NG-1, DMTMM, THF, 5h. (iv) HCOOH, rt, 12h.

***N*-(6-Undecyl)-1,4:5,8-naphthalene-tetracarboxylicacid-1,4-anhydride-5,8-imide (NBI 6):** 1,4,5,8-naphthalene-tetracarboxylic dianhydride **2** (500 mg, 1.86 mmol) and 6-undecylamine (156 mg, 0.93 mmol) were suspended in dry dimethylformamide (5mL) in a pressure-tight microwave tube. The suspension was sonicated until the mixture became homogenous. The reaction mixture was heated under microwave irradiation for 5 min at 75 °C and then for 15 min at 140 °C. After cooling down to room temperature, 50 mL 1 N HCl were added and the residue was filtered and washed with water. The solid was dried in vacuum and purified via column chromatography (SiO_2, $CHCl_3$). A pale yellow powder was obtained (yield: 351 mg, 0.84 mmol, 90%).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.87 (s, 4H, Ar-H), 5.13 (m, 1H, N-CH), 2.18 (m, 2H, CH_2), 1.84 (m, 2H, CH_2), 1.24 (m, 12H, CH_2), 0.80 (t, 6H, ^3J = 6.0 Hz, CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 158.9 (4C, C=O), 133.1 (4C,Ar-CH), 128.8 (1C, Ar-C), 127.0 (1C, Ar-C), 122.6 (4C, Ar-C), 55.5 (1C, CH), 32.1 (2C, CH_2), 31.6 (2C, CH_2), 26.5 (2C, CH_2), 22.5(2C, CH_2), 14.0 (2C, CH_3), ppm.

ESI-HRMS: 421.193 (calculated for $C_{25}H_{27}NO_5$: 421.188)

EA calc. for $C_{25}H_{26}NO_5$: C, 71.24; H, 6.46; N, 3.32:found: C 71.11; H, 6.57; N, 3.54.

IR spectroscopy: ν = 2928, 2859, 1784, 1736, 1710, 1665, 1624, 1579, 1446, 1360, 1328, 1279, 1240, 1178, 1147, 1011, 884, 761, 710 cm^{-1}.

***N*-(6-Undecyl)-*N'*-(5-carboxy)-pentyl-naphthalene-1,4,5,8-tetracarboxy-bisimide (NBI 7):** The naphthalenemonoimid derivative **6** (500 mg, 1.19 mmol) and 6-aminocaproic acid (313 mg, 2.39 mmol) were suspended in dry dimethylformamide (5 mL) in a pressure-tight microwave tube. To this suspension was added dry Et_3N (1 equiv). The suspension was sonicated until the mixture became homogenous. The reaction mixture was heated under microwave irradiation for 5 min at 75 °C and then for 15 min at 140 °C. After cooling down to room temperature, acetone (10 mL) acetone was added. The suspension was added slowly to vigorously stirred 1 M HCl (50 mL). The residue was filtered and washed with water. The solid was dried in vacuum. (yield: 635 mg, 1.19 mmol, 100%).

^{1}H-NMR (Aceton-d_6, 400 MHz): δ = 8.72 (s, 4H, Ar-H), 5.18 (m, 1H, N-CH), 4.14 (t, 2H, ^3J = 7.6 Hz, N-CH_2), 2.31 (m, 4H, CH_2), 1.84 (m, 2H, CH_2), 1.74 (m, 4H, CH_2), 1.49 (m, 2H, CH_2), 1.28 (m, 12H, CH_2), 0.80 (t, 6H, ^3J = 4.4 Hz, CH_3) ppm.

^{13}C-NMR (Aceton-d_6, 100 MHz): δ = 174.4, 163.6 (4C, C=O), 131.3 (4C, Ar-CH), 127.7, 127.6, 127.5 (6C, Ar-C); 55.3 (1C, N-C), 41.0(1C, N-C), 33.9 (1C, $\underline{C}H_2$-COOH), 32.9, 32.4, 25.3, 27.2, 28.4 (9C, CH_2), 23.1 (2C, $\underline{C}H_2$-CH_3), 14.2 (2C, CH_3) ppm.

HRMS (ESI-TOF, pos. mode): calculated for $C_{31}H_{39}N_2O_6$: 535.280 [M+H]; found: 535.281.

EA calculated for $C_{31}H_{38}N_2O_6$: C, 69.64; H, 7.16; N, 5.24; found: C 70.06; H, 7.49; N, 5.11.

IR spectroscopy: ν = 2955, 2926, 2859, 2360, 1702, 1656, 1579, 1454, 1327, 1246, 1183, 1099, 1069, 886, 772, 729 cm^{-1}.

***N*-(6-Undecyl)-*N'*-(5-carboxy{di-*tert*-butyl-4[(2-*tert*-butoxycarbonyl)ethyl]-4-aminoheptane-dioate}pentyl)-naphthalene-1,4,5,8-tetracarboxy-bisimide (NBI 4a):** A mixture of the asymmetrical Naphthalenediimides derivatives **7** (635 mg, 1.19 mmol), and NG-1 (544 mg, 1.31 mmol) in THF (30 mL) was stirred at room temperature for 10 min. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methoxymorpholinium Chloride (DMTMM) (1.1 equiv) was added to the mixture and stirred for 5 h at room temperature. The reaction mixture was poured into water and extracted with ether. The organic phase was combined and washed successively with saturated sodium carbonate, water, 1N HCl, water, and brine and dried over $MgSO_4$. After recrystallization from hexane/methanol a pale yellow powder was isolated as product. (yield: 1.02 g, 1.10 mmol, 92%).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.67 (s, 4H, Ar-H), 5.83 (s, 1H, N-H), 5.08 (m, 1H, N-CH), 4.12 (t, ^3J = 7.4 Hz, 2H, N-CH_2), 2.15 (t, ^3J = 7.2 Hz, 6H, CH_2), 2.11 (m, 4H, CH_2), 1.90 (t, ^3J = 7.2 Hz. 6H, CH_2), 1.80 (m, 2H, CH_2), 1.69 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 1.41 (m, 2H, CH_2), 1.36 (s, 27H, CH_3), 1.20 (m, 12H, CH_2), 0.74 (t, ^3J = 6.8 Hz, 6H, CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 172.7 (3C, C=O), 172.1 (1C, C=O) 162.7 (4C, C=O), 130.8 (4C, Ar-CH), 126.7, 126.5, 126.3 (6C, Ar-C), 80.6 (3C, C_{quart}), 57.2 (1C, N-CH), 55.0 (1C, C_{quart}), 40.4 (1C, N-CH_2), 37.0, 32.1, 31.5, 29.8, 29.7 (9C, CH_2), 27.9 (9C, CH_3), 27.5, 26.4, 25.2, 22.4 (4C, CH_2), 13.9 (2C, CH_3) ppm.

HRMS (ESI-TOF, pos. mode): calculated for $C_{53}H_{78}N_3O_{11}$: 932.563 [M+H]; found: 932.564.

EA calculated for $C_{53}H_{77}N_3O_{11}$: C, 68.29; H, 8.33; N, 4.51:found: C 68.20; H, 8.43; N, 4.50.

UV/Vis ($CHCl_3$, 1 x 10^{-4} M): λ_{max} (ε) = 324 (6402), 342 (10558), 360 (18206), 381 (22637) nm.

IR spectroscopy: ν = 2929, 2860, 1728, 1705, 1661, 1580, 1528, 1454, 1366, 1327, 1248, 1140, 110, 950, 879, 848, 770, 727 cm^{-1}.

***N*-(6-undecyl)-*N'*-(5-carboxy{di-*tert*-butyl-4[(2-carbonyl)ethyl]-4-aminoheptane}pentyl)-naphthalene-1,4,5,8-tetracarboxy-bisimide (NBI 4):** NBI **4a** (500 mg, 0.54 mmol) was dissolved in 10 mL of formic acid and stirred at room temperature for 12 h. Afterwards, formic acid was evaporated and toluene was added to the residue and removed in vacuum for three times in order to remove formic acid residues. After drying in vacuum, a pale yellow solid was obtained. (yield: 410 mg, 0.54 mmol, 100%)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.77 (s, 4H, Ar-H), 6.55 (s, 1H, N-H), 5.14 (m, 1H, N-CH), 4.19 (t, 2H, ^3J = 7.6 Hz, N-CH_2), 2.46 (t, 6H, ^3J = 8.0 Hz, CH_2), 2.33 (t, 2H, ^3J = 7.6 Hz. CH_2), 2.14 (m, 8H, CH_2), 1.86 (m, 2H, CH_2), 1.74 (m, 4H, CH_2), 1.48 (m, 2H, CH_2), 1.25 (m, 12 H, CH_2), 0.80 (t, 6H, ^3J = 6.8 Hz, CH_3) ppm.

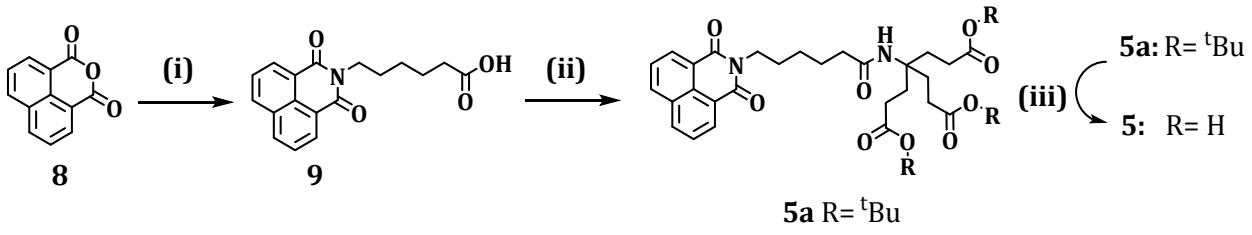
^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 179.9 (3C, COOH), 177.2 (1C, C=O), 163.9 (4C, C=O), 131.8 (4C, Ar-CH), 126.8, 126.6, 125.9 (6C, Ar-C), 58.8 (1C, NH-C_{quart}), 56.2 (1C, N-CH), 40.8 (1C, N-CH_2), 36.3 (1C, CH_2-C=O), 40.8, 36.3, 32.2, 31.5, 29.2, 27.5, 26.9, 26.5,, 25.9, 25.0, 22.4 (17C, CH_2), 13.8 (2C, CH_3) ppm.

ESI-HRMS: 764.377 (calculated for $C_{41}H_{54}N_3O_{11}$: 764.375)

EA calculated for $C_{41}H_{53}N_3O_{11}$ x 1/8 TFA: C, 63.56; H, 6.87; N, 5.39; found: C, 63.52; H, 7.05; N, 5.35.

UV/Vis (borate buffer pH10, 1 x 10^{-4} M): λ_{max} (ε) = 328 (6874), 347 (12711), 364 (20778), 385 (23911) nm.

IR spectroscopy: ν = 2928, 2860, 1702, 1656, 1579, 1543, 1455, 1328, 1248, 1161, 1100, 880, 770, 722 cm^{-1}.



Scheme 2: Synthesis of NMI 5 (i) 6-aminocaproic acid, toluene/ethanol (1:1), 90 °C, o.n.; (ii) PyBOB, NMM, NG-1, DCM/DMF (1:1) (iii) TFA, $CHCl_3$, 12 h.

***N*-(5-carboxy)-pentyl-naphthalene-1,8-tetracarboxyimide (NMI 9):** 1,8-naphthaleneanhydride **8** (500 mg, 2.52 mmol) and 6-aminocaproic acid (2.93 g, 25.20 mmol) were added to a solution of anhydrous toluene/ethanol (1:1). The mixture was stirred overnight at 100 °C. After reaction, the solution was cooled to room temperature and 100 mL water was added. The crude product was filtered and washed sufficiently with water. After drying on vacuum a pale yellow powder was obtained (yield: 785 mg, 2.25 mmol, 100%).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.47 (m, 2H, CH_2); 1.71 (m, 4H, CH_2); 2.34 (t, ^3J = 7.4 Hz, 2H, CH_2); 4.13 (t, ^3J = 7.4 Hz, 2H, CH_2); 7.68 (t, ^3J = 7.6 Hz, 2H, Ar-H); 8.14 (d, ^3J = 7.6 Hz, 2H, Ar-H); 8.52 (d, ^3J = 7.2 Hz, 2H, Ar-H); 10.62 (br s, 1H, CH) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 24.4 (1C, CH_2); 26.6 (1C, CH_2); 27.7 (1C, CH_2); 33.9 (1C, CH_2); 40.1 (1C, CH_2); 122.6, 126.9, 128.1, 131.2, 131.5 133.9 (10C, Ar-C), 164.2 (2C, C=O), 179.7 (1C, C=O) ppm.

MS (MALDI, dhb): m/z = 266 $[M\text{-}CO_2]^+$.

EA calculated for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50: found: C 69.43; H, 5.51; N, 4.46.

IR spectroscopy: ν = 2938, 2864, 1692, 1656, 1586, 1438, 1385, 1342, 1311, 1259, 1233, 1067, 846, 778, 738 cm^{-1}.

***N*-(5-carboxy{di-*tert*-butyl-4[(2-*tert*-butoxycarbonyl)ethyl])-4-aminoheptane-dioate}pentyl)-naphthalene-1,8-tetracarboxyimide (NMI 5a):** Under nitrogen NMI **9** (300mg, 0.964 mmol) was added to 100 mL DCM/DMF (1:1) mixture. After cooling down to 0°C PyBOP (502mg, 0.964 mmol) and 212 µL NMM were added and the solution was stirred for 3 hours. Due to formation of the active-ester the color of the solution turned to yellow. After adding **NG-1** (267 mg, 0.642 mmol) the yellow solution was stirred for another 4 days. The formation of the product can be followed via TLC (DCM/EtOAc 2:1). After evaporation of the solvent the crude product was dissolved in dichloromethane and extracted with 10% citric acid, saturated $NaHCO_3$ and saturated sodiumchloride. Then the product was dried over $MgSO_4$, and purified by column chromatography on silica gel (CH_2Cl_2/EtOAc 2:1; 403 mg, 0.495 mmol, 59% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.39 (s, 27H, CH_3); 1.45(m, 2H, CH_2); 1.70 (m, 4H, CH_2); 1.94 (t, t, ^3J = 7.3 Hz, 6H, CH_2); 2.11 (t, ^3J = 8.0 Hz, 2H, CH_2); 2.18 (t, ^3J = 7.3 Hz, 6H, CH_2); 4.14 (t, ^3J = 7.6 Hz, 2H, CH_2); 5.82 (s, 1H, N-H); 7.72 (t, ^3J = 7.3 Hz, 2H, Ar-H); 8.19 (dd, ^3J = 7.3 Hz, t, ^4J = 0.9 Hz, 2H, Ar-H); 8.57 (dd, ^3J = 7.3 Hz, t, ^4J = 1.0 Hz, 2H, Ar-H) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 25.7, 27.9 (2C, CH_2); 26.9 (1C, CH_2); 28.4 (9C, CH_3); 30.2, 30.3 (6C, CH_2); 37.6 (1C, CH_2); 40.4 (1C, CH_2); 57.7 (1C, C_{quart}); 81.0 (3C, C_{quart}); 123.2 (2C, Ar-C); 127.4 (2C, Ar-C); 128.6 (1C, Ar-C); 131.7 (2C, Ar-C); 132.1 (1C, Ar-C); 134.4. (2C, Ar-C); 164.7 (2C, C=O); 172.9 (1C, C=O); 173. (3C, C=O) ppm. **MS** (MALDI, dhb): m/z = 731 $[M + Na^+]^+$.

HRMS (ESI-TOF, pos. mode): calculated for $C_{40}H_{57}N_2O_9$: 709.406 $[M+H]^+$; found: 709.406.

EA calculated for $C_{40}H_{57}N_2O_9$: C, 67.77; H, 7.96; N, 3.95: found: C, 67.76; H, 8.06; N, 3.99.

UV/Vis ($CHCl_3$, 1 x 10^{-4} M): λ_{max} (ε) = 322 (10700), 335 (13968), 349 (12067) nm.

IR spectroscopy: ν = 3314, 2977, 2934, 1725, 1701, 1659, 1592, 1543, 1457, 1365, 1236, 1097, 848, 774 cm^{-1}.

***N*-(5-carboxy{di-*tert*-butyl-4[(2-carbonyl)ethyl]-4-aminoheptane}pentyl)-naphthalene-1,8-tetracarboxy-imide (NMI 5):** In 5 mL $CHCl_3$ and 5 mL trifluoroacetic acid (TFA), NMI **5a**(100mg, 0.141 mmol) was dissolved and stirred at room temperature for 24 hours. After evaporation of the solvent a light-blue fluorescent solid was obtained (76 mg, 0.141 mmol, 100% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.51 (m, 2H, CH_2); 1.77 (m, 4H, CH_2); 2.16 (t, ^3J = 7.4 Hz, 6H, CH_2); 2.40 (t, ^3J = 8.0 Hz, 2H, CH_2); 2.47 (t, ^3J = 7.3 Hz, 6H, CH_2); 4.23 (t, ^3J = 7.7 Hz, 2H, CH_2); 6.73 (s, 1H. N-H); 7.86 (t, ^3J = 7.9, 2H, Ar-CH); 8.38 (d, ^3J = 8.1 Hz, 2H, Ar-CH); 8.64 (d, ^3J = 7.3 Hz, 2H, Ar-CH) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 25.4, 26.9 (2C, CH_2); 26.2 (1C, CH_2); 28.3 (3C, CH_2); 29.1 (3C, CH_2); 36.2 (1C, CH_2); 41.2 (1C, CH_2); 59.5 (1C, C_{quart}); 121.1 (2C, Ar-C); 127.8 (2C, Ar-C); 128.2 (1C, Ar-C); 131.9 (1C, Ar-C); 133.3 (2C, Ar-C); 136.5 (2C, Ar-C); 166.9 (2C, C=O); 178.5 (1C, C=O); 180.5 (3C, C=O) ppm.

MS (MALDI, dhb): m/z = 541 $[M]^+$.

ESI-HRMS: calculated for $C_{28}H_{33}N_2O_9$: 541.218 $[M+H]^+$; found: 541.219.

EA calculated for $C_{28}H_{32}N_2O_9$ x 1/8 TFA: C 61.01; H 5.82; N 5.03; found: C 61.05; H, 5.87; N, 5.02.

UV/Vis ($CHCl_3$, 1 x 10^{-4} M): λ_{max} (ε) = 345 (9764) nm.

IR Spectroscopy: ν = 3092, 2931, 1726, 1693, 1640, 1615, 1523, 1236, 1200, 1168, 849, 783, 624 cm^{-1}.

Preparation of SWCNT hybrids

To obtain stable HipCO-SWCNT/SDBS dispersions, 0.5 mg of HipCO-SWCNT were added to 10 ml of D_2O containing 1 wt% of SDBS and the sample was stirred for four days. Afterwards the sample was sonicated for 30 min, followed by another 90 min of stirring and 30 min sonication. Finally, the dispersion was centrifuged at 21.1 kG for 10 min and the stable supernatant was collected.

For the preparation of HipCO-SWCNT/**1**, 0.5 mg of HipCO- SWCNT were added to 10 mL of D_2O containing 0.1 M HPO_4^{2-}/ $H_2PO_4^-$ and stirred for 7 days. Then, $5x10^{-7}$ mol of **1** was added to give a concentration of $5x10^{-5}$ M. The resulting samples were stirred for another 48 hours. Finally, the samples were sonicated in two steps each 15 min and centrifuged at 21.1 kG for five minutes.

Absorption and emission spectroscopy of NBI

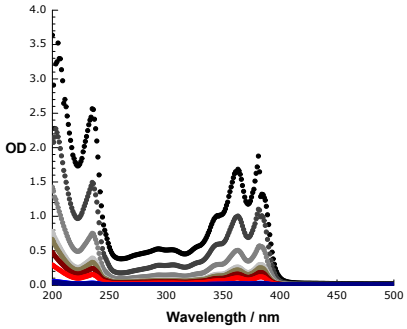


Figure S1: Concentration dependent absorption spectra of **1** in D_2O/ $H_2PO_4^-$/HPO_4^2 with concentrations from $5x10^{-7}$M (dark blue) to $1x10^{-4}$ M (black).

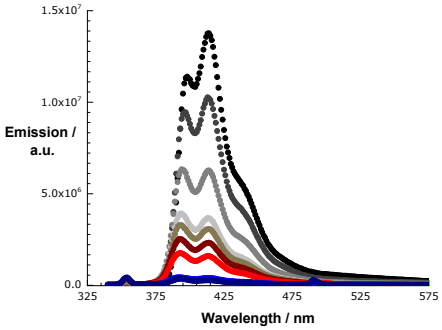


Figure S2: Concentration dependent emission spectra of **1** in D_2O/ $H_2PO_4^-$/HPO_4^{2-} with concentrations from $5x10^{-7}$M (blue) to $1x10^{-4}$ M (black). All spectra are shown as received and are not corrected for inner filter effects.

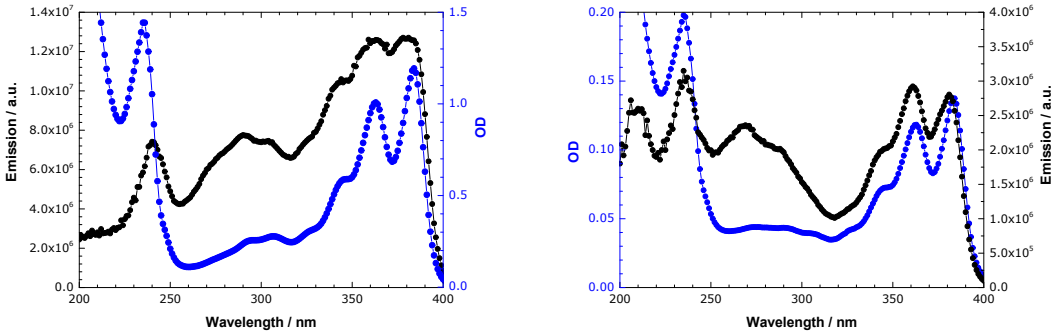


Figure S3: Left: Comparison of absorption (blue) and emission spectra (black) of **1** at 5x10^{-5} M in D_2O/ $H_2PO_4^-$/HPO_4^{2-}. Right: Comparison of absorption (blue) and emission spectra (black) of **1** at 7.25x10^{-6} M in D_2O/ $H_2PO_4^-$/HPO_4^{2-}.

Voltammetry of NBI

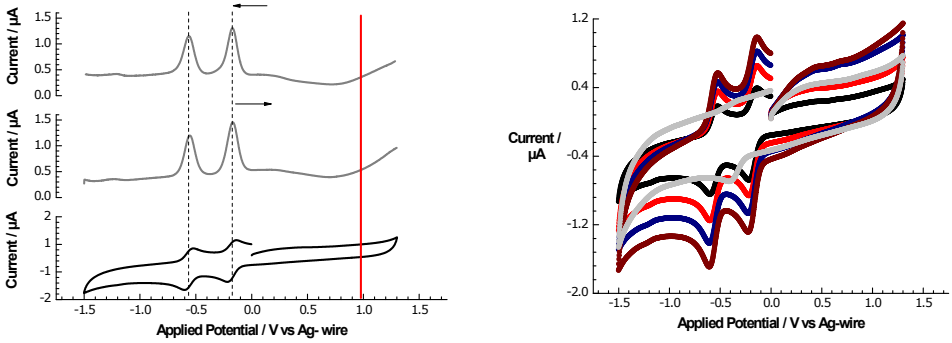


Figure S4: Left: CV and SWV of **1**. Right: CV of **1** (c = 5x10^{-4} M) taken at different scan rates (25-100 mV) in DMSO containing 0.1 mol of $TBAPF_6$. The voltammogram of DMSO is shown for comparison (grey).

Spectroelectrochemistry of NBI

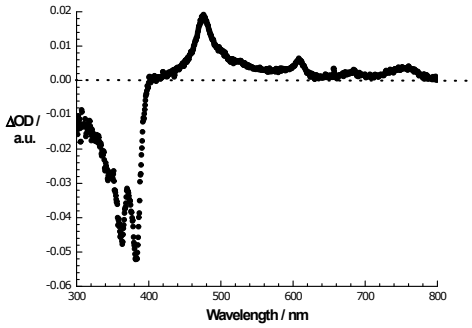


Figure S5: Differential absorption spectrum of **1** in DMSO containing 0.1M $TBAPF_6$ obtained upon electrochemical reduction with an applied potential of -300 mV *vs.* Ag-wire.

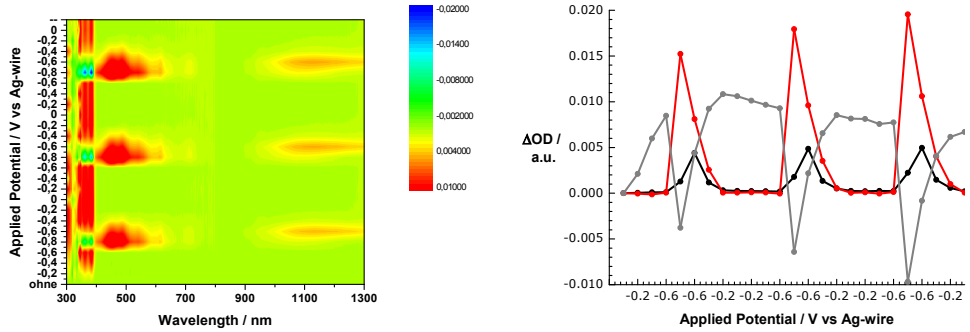


Figure S6: Left: 3D map of three electrochemical cycles (0 – 800 mV, 200 mV steps) of **1** in $D_2O/H_2PO_4^-/H_2PO_4^{2-}$. Right: Corresponding potential-absorption profiles at 370 nm (grey), 450 nm (red) and 1150 nm (black).

Femtosecond transient absorption spectroscopy of NBI

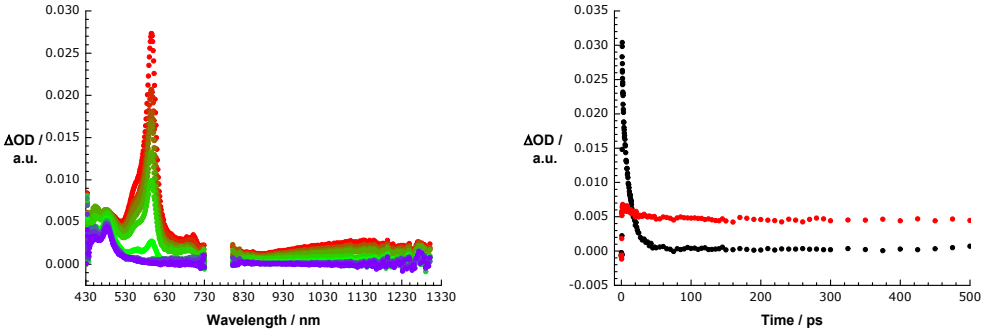


Figure S7: Left: Differential absorption spectra of **1a** in THF obtained upon femtosecond flash photolysis (387 nm) with time delays from 1.5 ps (red) to 3000 ps (dark blue). Right: Corresponding kinetics at 597 nm (black) and 480 nm (red) monitoring inter system crossing.

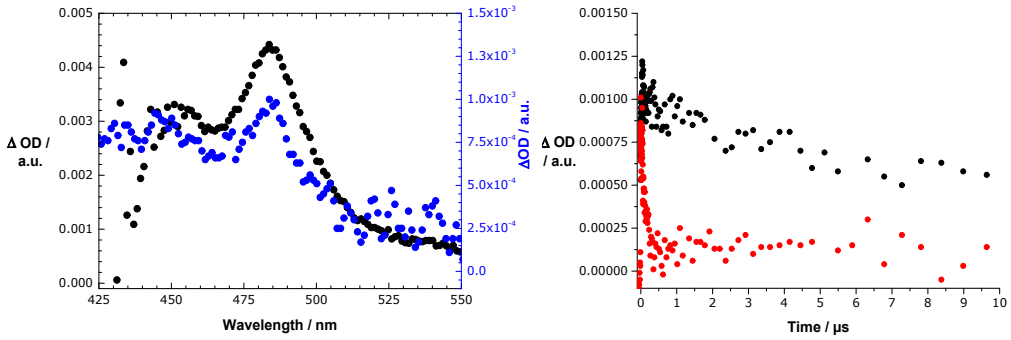


Figure S8: Left: Comparison of different transient absorption spectra of **1a** in THF after 3ns (black) and 300 ns (blue) upon femtosecond flash photolysis (387 nm). Right: Time absorption profiles of **1a** in THF at 482 nm in the absence (black) and the presence of molecular oxygen (red).

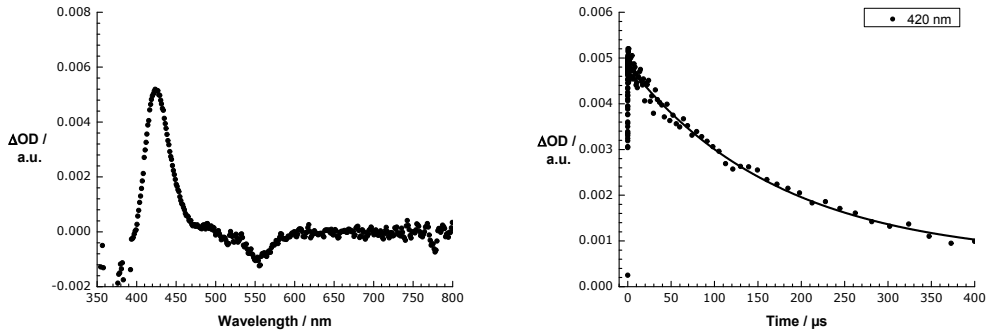


Figure S9: Left: Differential absorption spectrum of **1** in latent $D_2O/H_2PO_4^-/HPO_4^{2-}$ obtained upon femtosecond flash photolysis (387 nm) with a time delay of 1 µs. Right: Time-absorption profile at 420 nm monitoring the decay of the formed photoproduct.

Peak assignment

E_{11}	E_{22}	(n,m)
1376	**763 (sh)**	(10,6)
1061	**735**	(10,2)
1107	**722 (sh)**	(9,4)
1177	**719 (sh)**	(8,6)
1262	**724 (sh)**	(8,7)
-	**693 (sh)**	(12,2)
-	**-**	(9,5)
1025	**650**	(7,5)
1123	**-**	(7,6)
1257	**611 (sh)**	(11,1)
-	**598**	**(8,4)**

Table S1: Assignment of the E_{11} and E_{22} absorptions to the corresponding (n,m) chiralities.

System	RBM	G-mode	2D-mode	FWHM/G-mode	FWHM 2D - mode	FWHM RBM
Pristine SWCNT	**267**	**1592**	**2549**	**30 / 16[a]**	**41**	**9**
SDBS/SWCNT	**268**	**1592**	**2550**	**12**	**37**	**7**
1/SWCNT	**268**	**1594**	**2553**	**15/11[a]**	**18**	**8**

Table S2: Raman data obtained upon 1064 nm excitation of pristine HipCO-SWCNT, HipCO-SWCNT/SDBS, and HipCO-SWCNT/**1**. All values are given in cm^{-1}. The experimental error was determined as +/- 2 cm^{-1}. FWHM values were determined by application of Lorentzians. a) denotes the application of two Lorentzians.

NIR-fluorescence spectroscopy of SWCNTs

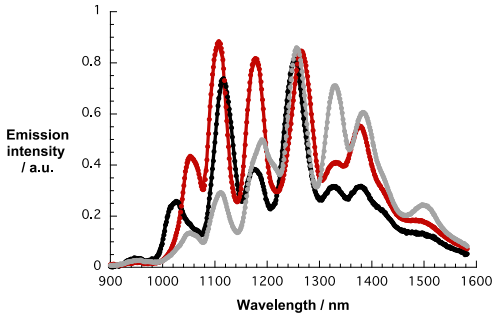


Figure S10: Fluorescence spectra of HipCO-SWCNT/SDBS in D_2O upon 631 nm (black), 724 nm (red), and 770 nm (grey) excitation.

Raman spectroscopy of SWCNTs

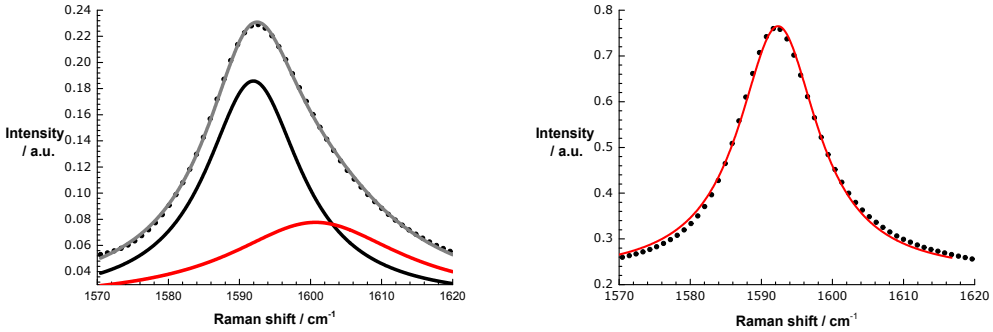


Figure S11: Left: Raman spectra of the G-mode of pristine HipCO-SWCNTs fitted by two Lorentzians. Right: Raman spectra of the G-mode of HipCO-SWCNT/SDBS fitted by one single Lorentzian. λ_{ex} = 1064 nm

Spectroelectrochemistry of SWCNTs

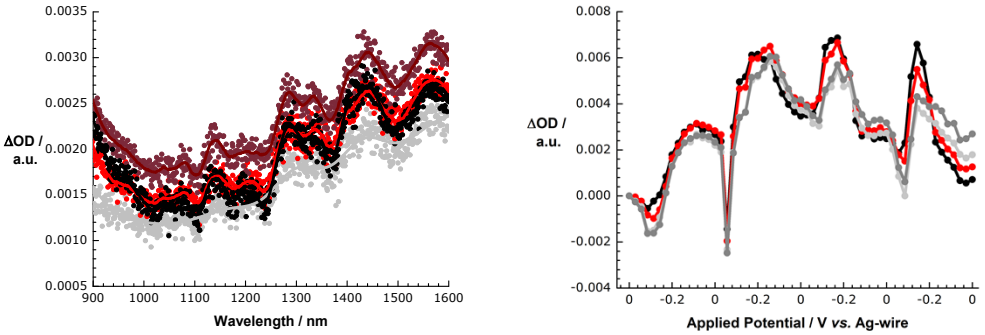


Figure S12: Left: Differential absorption spectra of HipCO-SWCNT/SBDS/0.05 M NaCl upon 0 mV (grey), 200 mV (red), 600 mV (brown) vs. Ag-wire. The black data is recorded upon reductive conditions (0 mV). Right: ΔOD *vs.* potential profiles of HipCO-SWCNT/SDBS in D_2O/0.05 M NaCl obtained during four electrochemical cycles, that is, from 0 to -800 to +600 and back to 0 mV in 200 mV intervals at 1290 nm (grey), 1335 nm (light grey), 1440 nm (red), and 1560 nm (black), monitoring the *quasi* reversibility of the electrochemical process.

NMR spectroscopy of NBI

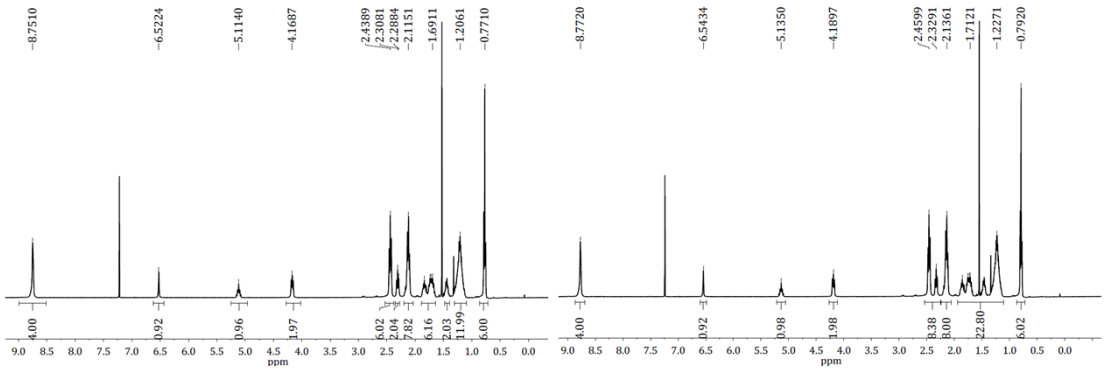


Figure S13: Left: ^{1}H-NMR spectrum of **1** before sonication Right: ^{1}H-NMR spectrum of **1** after sonication.

Absorption spectroscopy of the hybrids

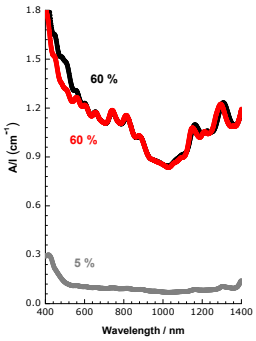


Figure S14: Vis/nIR absorption spectra of HipCO-SWCNT/**1** (black), HipCO-SWCNT/**4** (red) and HipCO-SWCNT/**5** (grey) in pH10/H_2O.

TEM images of the hybrids

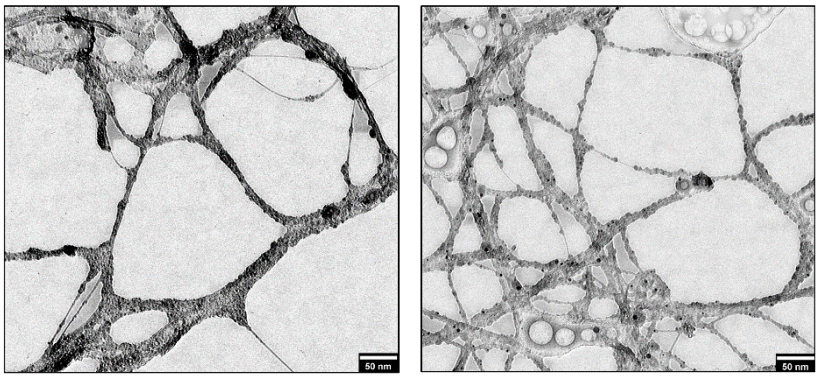


Figure S15: Representative TEM (80 kV) images of freestanding HipCO-SWCNT/**1** on a Lacey carbon support film.

Raman spectroscopy of the hybrids

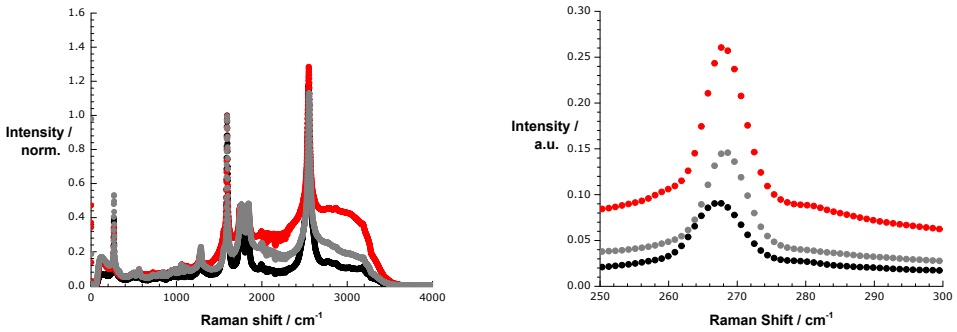


Figure S16: Left: Raman spectra (λ_{ex}= 1064 nm) of pristine HipCO-SWCNT (black), HipCO-SWCNT/SDBS (red) and HipCO-SWCNT/**1** (grey). Right: RBM region of pristine HipCO-SWCNT (black), HipCO-SWCNT/SDBS (red) and HipCO-SWCNT/**1** (grey).

Replacement experiments of HipCO-SWCNT/1 and HipCO-SWCNT/4 with SDBS

In the case of HipCO-SWCNT/**1**, the addition of SDBS gives rise to a recovery of the HipCO-SWCNT centered band gap emission in both pH ranges – Figures 9 and S18. The latter goes along with a partial fluorescence recovery of **1 -** Figure S17. Reactivation of the fluorescence of **1** and HipCO-SWCNT points to a decreasing charge transfer efficiency. The latter is due to the successful replacement of **1** by SDBS. This results served, however, as starting point to study the diameter selective desorption in alkaline solutions of HipCO-SWCNT/**1** and HipCO-SWCNT/**4**. A closer look reveals that the fluorescence spectra of HipCO-SWCNT/**1** infer that all SWCNTs, which are resonant at higher energies are depleted and those resonant at lower energies are enriched when compared to HipCO-SWCNT/SDBS – Figures 9 and S18. From the aforementioned we conclude a lower affinity of **1** towards smaller diameter SWCNTs. Interestingly, no diameter specific events were monitored for HipCO-SWCNT/**4** – Figure S18.

To rationalize the affinity differences we turned to determine the packing densities.[SI1] Packing densities are compared in replacement titrations with SDBS.[SI1,SI2,SI3] In the corresponding SWCNT near-infrared fluorescence the spectra are intensified and blue-shifted when SDBS is present. The titration curves were fit to sigmoidal curves to yield the inflection points, which, in turn, provide relative measures of the packing density. In general, the replacement occurs for **1** at lower SDBS to SWCNT concentration ratios than for **4**. As such, the packing density of **4** is higher than for **1**. We believe that this is the reason why no selective interactions with given SWCNT diameters or chiralities is observed for **4**. No evident difference in packing density is seen for different SWCNTs with the same NBI.

Additional support for the replacement came from steady state and time resolved absorption measurements. Firstly, the S_{11} and S_{22} transitions shift to the blue as a consequence of SDBS addition – Figure S19. Secondly, the transient differential absorption spectra of HipCO-SWCNT/**1** in the presence of SDBS mirror image the processes occurring in the ground state. In particular, transient bleaching after a time delay of 3 ps shift for HipCO-SWCNT/**1** from 470, 503, 533, 582, 628, 681, 1318, and 1445 nm in the absence of SDBS to 467, 498, 530, 576, 623, 676, 1286, and 1419 nm in the presence of SDBS – Figure S20. Kinetic comparison of HipCO-SWCNT/**1** and HipCO-SWCNT/**1** plus SDBS at 470/466 nm unravels notable changes, that is, elongated excited state lifetimes – Figure S21.

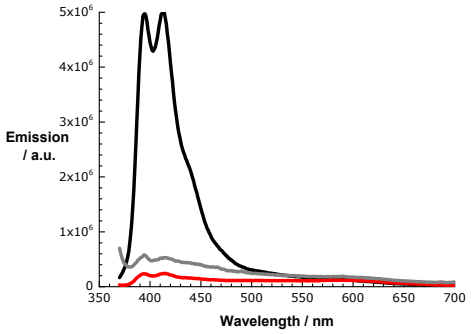


Figure S17: Emission spectra obtained upon 325 nm excitation of **1** (black), which was treated in the same way than HipCO-SWCNT/**1** (red) and HipCO-SWCNT/**1**/SDBS (grey). All spectra were recorded in D_2O/ $H_2PO_4^-$/HPO_4^{2-}. All spectra are not corrected for inner filter effects.

NIR-fluorescence spectroscopy of the hybrids

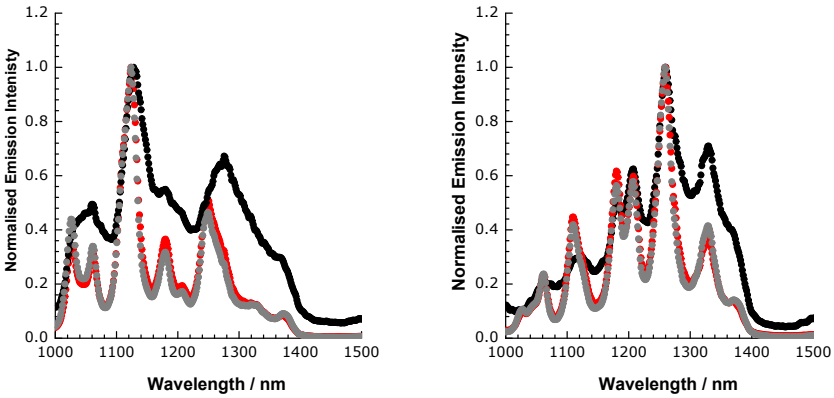


Figure S18: Left: nIR Emission spectra of HipCO-SWCNT/**1**/SDBS (black), HipCO-SWCNT/**4**/SDBS (red), and HipCO-SWCNT/SDBS (grey) obtained upon 660 nm excitation in pH10/H_2O. Right: : nIR Emission spectra of HipCO-SWCNT/**1**/SDBS (black), HipCO-SWCNT/**4**/SDBS (red), and HipCO-SWCNT/SDBS (grey) obtained upon 785 nm (right) excitation in pH10/H_2O.

Absorption spectroscopy of the hybrids

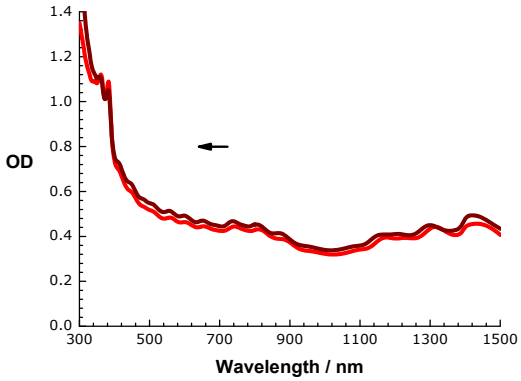


Figure S19: UV/Vis/nIR absorption spectra of HipCO-SWCNT/**1** (red) and HipCO-SWCNT/**1**/SDBS (wine) recorded in D_2O/ $H_2PO_4^-$/HPO_4^{2-}.

Femtosecond transient absorption spectroscopy of the hybrids

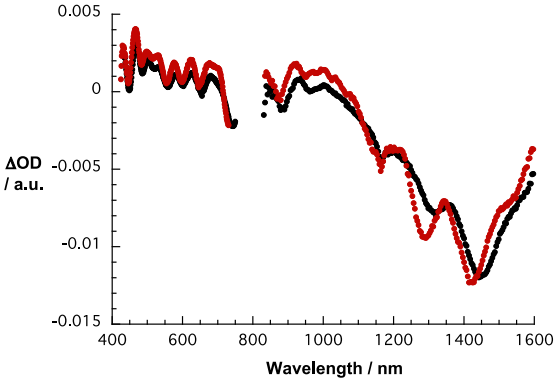


Figure S20: Differential absorption spectrum of HipCO-SWCNT/**1** (black) and HipCO-SWCNT/**1**/SDBS (red) in D_2O/ $H_2PO_4^-$/HPO_4^{2-} obtained upon femtosecond flash photolysis (387 nm) with time delays of 3 ps.

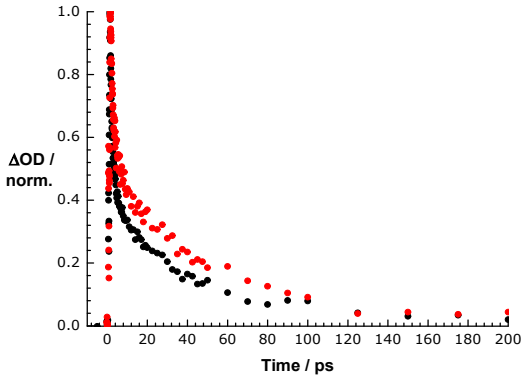


Figure S21: Normalized time absorption profiles of HipCO-SWCNT/1 recorded at 470nm (black) and HipCO-SWCNT/1/SDBS recorded at 466 nm (red) upon 387 nm excitation in $D_2O/H_2PO_4^-/HPO_4^{2-}$.

References

SI1 Backes, C.; Hauke, F.; Hirsch, A. *physica status solidi (b)*, 2013, **250**, 2592.

SI2 a) Backes, C.; Mundloch, U.; Schmidt, C. D.; Coleman, J. N.; Wohlleben, W.; Hauke, F.; Hirsch, A. *Chem. Eur. J.* 2010, **16**, 13185. b) Backes, C.; Schmidt, C.D.; Hauke, F.; Hirsch, A. *Chem. Asian. J.* 2011, **6,** 438.

SI3 a) Backes, C.; Schmidt, C.D.; Hauke, F.; Hirsch, A. *Chem. Commun.* 2009, **19**, 2643. b) Backes, C.; Karabudak, E.; Schmidt, C.D.; Hauke, F.; Hirsch, A. *Chem. Eur. J.* 2010, **16**, 13176.