SUPPLEMENTARY INFORMATION

Tunable Functionalization of Nano-emulsions Using Amphiphilic Polymers

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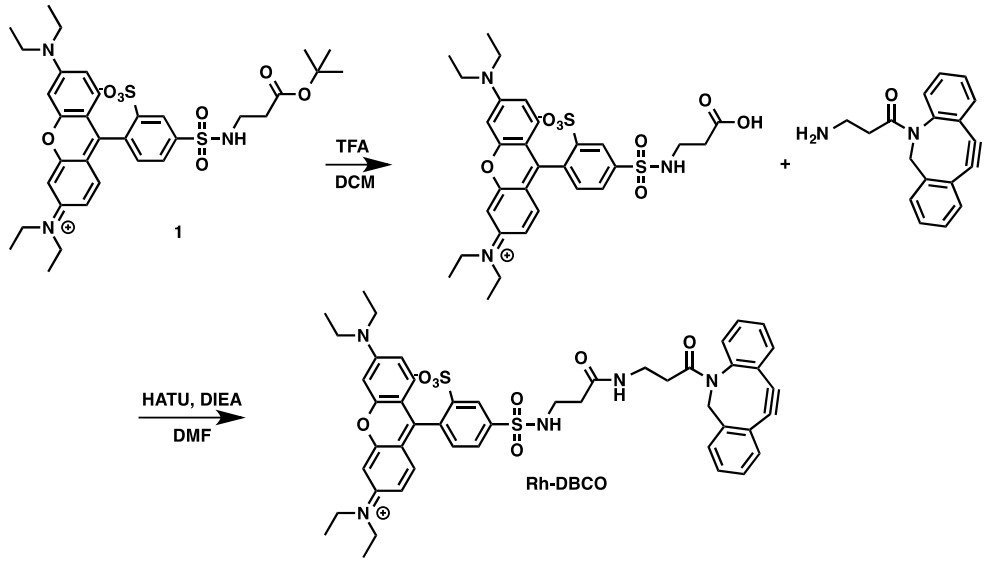
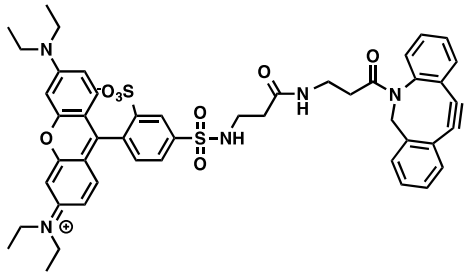
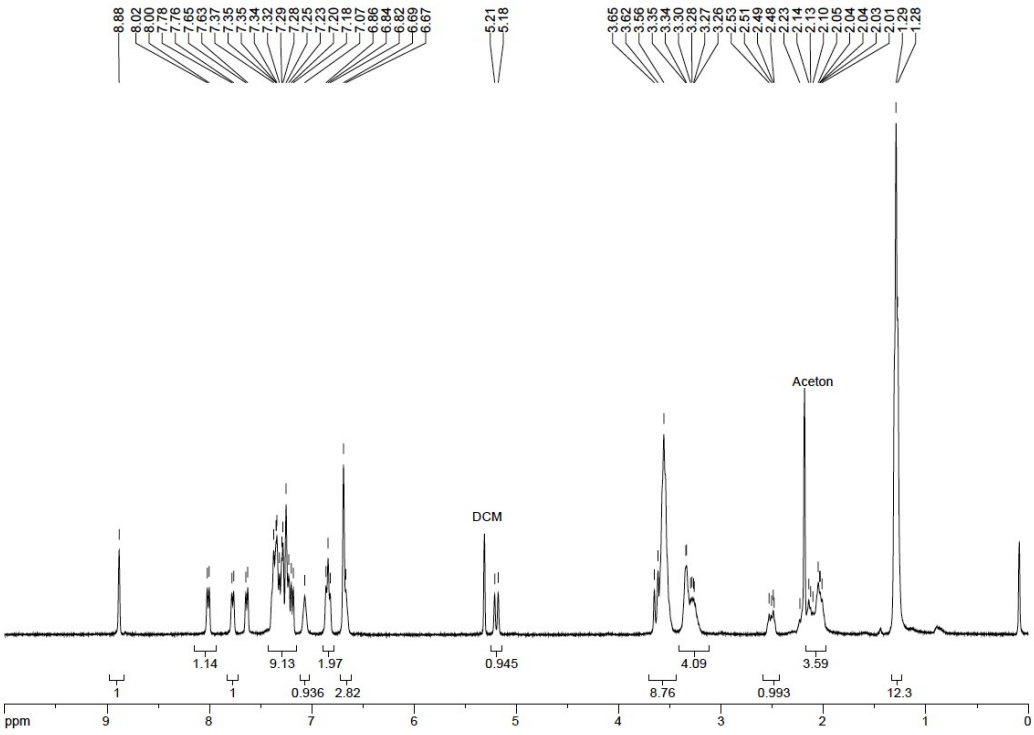
Synthesis of Rh-DBCO

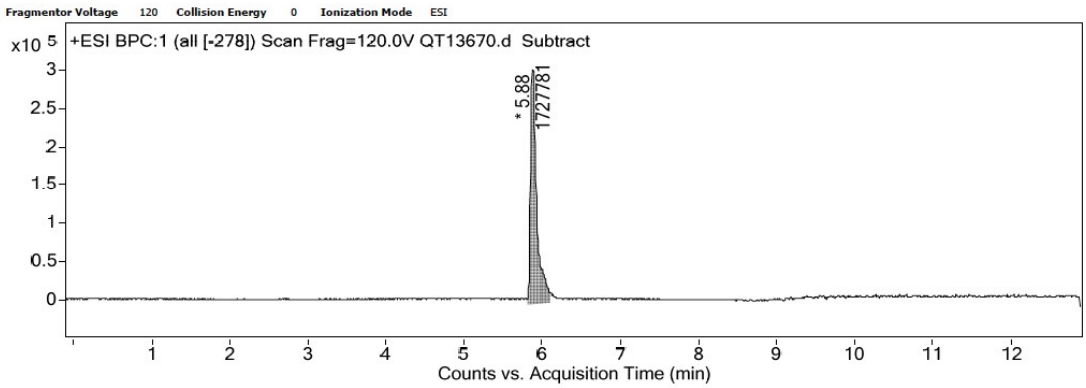




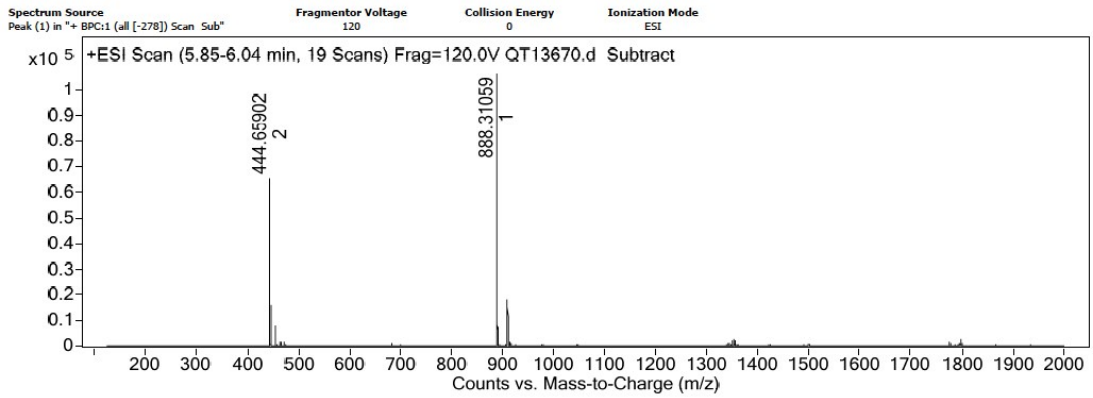
Rh-DBCO. To a solution of sulforhodamine 1 (50 mg, 0.073 mmol) in DCM (2 mL) were added 2 mL of TFA. After 2h, the solvents were evaporated and the deprotected carboxylic acid was involved in the next step without any further purification. To a solution of deprotected 1 (46 mg, 0.073 mmol) and DBCO-NH_2 (20 mg, 0.073 mmol, 1 eq) in DMF (5 mL) was added HATU (33 mg, 0.087 mmol, 1.2 eq) followed by DIEA (28 □L, 0.219 mmol, 3 eq). After 1 h00 the solvents were evaporated and the crude was first purified by column chromatography on silica gel (DCM/MeOH: 95/5 to 9/1) to obtain 59 mg g of **Rh-DBCO** (92% yield) as a dark violet syrup. Rf= 0.62 (DCM/MeOH: 9/1). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H, H-Ar Rhod), 8.02-8.00 (m, 1H, H-Ar Rhod), 7.77 (br s, 1H, NH), 7.64 (d, *J* = 7.6 Hz, 1H, H-Ar Rhod), 7.37-7.18 (m, 8H, H-Ar DBCO + $CDCl_3$), 7.07 (s, 1H, H-Ar Rhod), 6.84 (t, *J* = 8.3 Hz, 2H, H-Ar Rhod), 6.69-6.66 (m, 3H, H-Ar Rhod), 5.20 (d, *J* = 13.4 Hz, 1H, PhN-CH DBCO), 3.65-3.53 (m, 9H, PhN-CH DBCO + NCH_2 Rhod), 3.34-3.24 (m, 4H, CH_2 and CH_2 DBCO), 2.54-2.48 (m, 1H, CH DBCO), 2.16-2.02 (m, 4H, CH_2), 1.29 (s, 12H, CH_3 Rhod). HRMS (ESI+), calcd for $C_{48}H_{50}N_5O_8S_2$ $[M+H]^+$ 888.0670, found 888.3106.



^{1}H NMR spectrum of **Rh-DBCO**.



HPLC trace of **Rh-DBCO**. Conditions: column Zorbax SB-C18 50 mm x 2.1 mm, particles size = 1.8 µm. Temperature = 40°C. 0.5 mL/min, ACN (0.05% formic acid)/Water (0.05% formic acid): 2/98 to 100/0 in 8 min.



HRMS spectrum of **Rh-DBCO**.

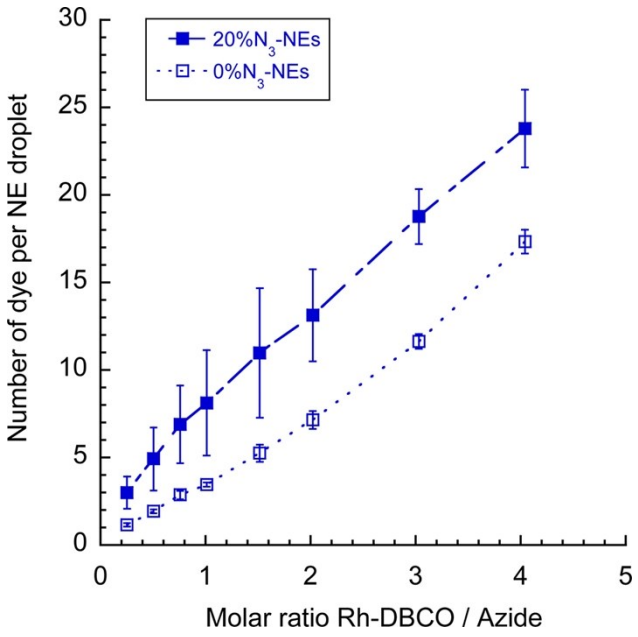


Figure S1: Quantification of the total number of dye molecules (Rh-DBCO) which are attached to the NEs droplets. Comparison of the 20%N_3-NEs and the control without azides, 0%N_3-NEs.

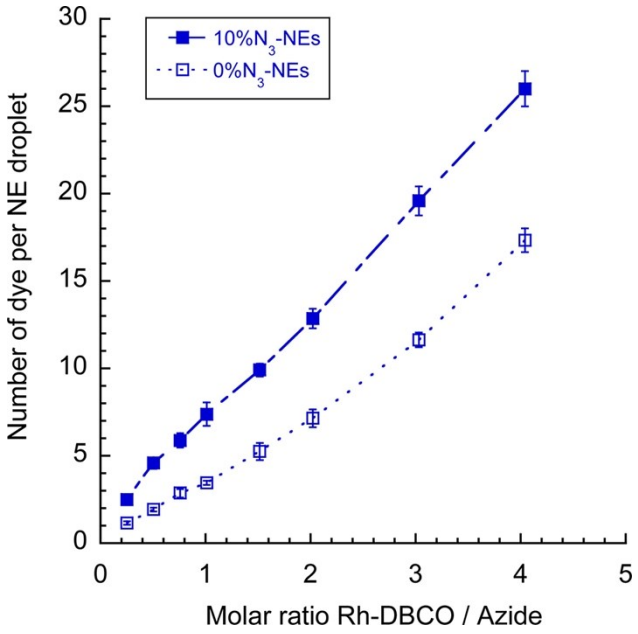


Figure S2: Quantification of the total number of dye molecules (Rh-DBCO) which are attached to the NEs droplets. Comparison of the 10%N_3-NEs and the control without azides, 0%N_3-NEs.