Supporting Information

Functional Nanoparticles from Dendritic Precursors: Hierarchical Assembly in Miniemulsion

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Preparation of dendritic macromonomers (1, 7 and 8).

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 (250 MHz; 125 MHz) or on a AMX 500 (500 MHz) instrument. As deuterated solvents, $(CD_3)_2CO$, $CDCl_3$ were used. Chemical shifts δ are given in ppm according to the literature (^{1}H-NMR: acetone: δ = 2.05 ppm, chloroform: δ = 7.26 ppm; ^{13}C NMR: acetone: δ = 29.84 and 206.26 ppm, chloroform: δ = 77.00 ppm. FT-IR spectra were recorded on a Nicolet Avator 320 FT-IR spectrometer operating from 4000-400 cm^{-1} as film on potassium bromide plates from Aldrich. Dialysis was performed in benzoylated cellulose dialyse tubes (SIGMA-ALDRICH, (MWCO = 1000 g mol^{-1}).

Hydrophobic alkynyl polyglycerol (1)

$PG_{5000}(-OCH_2C{\equiv}CH)_{0.8}$: PG_{5000} (8.26 g, 109 mmol OH groups) was dissolved in dry DMF (80 ml) and NaH (6.05 g, 240 mmol, 2.2 eq.) was added. After stirring for 3 h at 0 °C to room temperature the mixture was cooled down again to 0 °C and propargylbromide (27.55 g, 185 mmol, 1.7 eq.) was added slowly *via* syringe. The colour of the solution changed to brown and a precipitation was observed. The ice bath was removed and after stirring for 20 hours at room temperature the reaction was quenched with water. Following, extraction with ethyl acetate (3 x 60 ml), the combined organic layers were concentrated *in vacuo* and the crude product was purified by dialysis in chloroform (48 h) to obtain product (**1**) as a dark brown viscous oil in 80 % yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.29 - 4.14 ($OC\underline{H}_2C{\equiv}CH$), 3.84 – 3.52 (PG backbone), 2.45 ($C{\equiv}C\underline{H}$), 1.69 ($C\underline{H}_2$-PG starter unit), 0.80 ppm ($C\underline{H}_3$-PG starter unit). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 80.5 – 55.6 (PG backbone and alkyne groups), 30.3 ppm ($C{\equiv}\underline{C}H$). IR (KBr): ν = 3441 (ν-H_2O, ν-$C{\equiv}\underline{C}H$), 2922 (ν-CH_3, ν-CH_2), 2114 (ν-C≡CH)cm^{-1}.

Azidopolyglycerol (7)

The synthesis of azido-terminated polyglycerol (PG) was carried out in a two step protocol. In the first step, hyperbranched polyglycerol was activated to polyglycerol mesylate, in the second step was reacted with sodium azide to give the desired azido-polyglycerol.

$PG_{5000}(OMs)_{0.80}$: To achieve a loading of 80%, 1.7 eq. (per OH group) of MsCl (25.7 g, 224 mmol) was added dropwise to a cooled solution (0°C) of PG_{5000} (10.0 g, 132 mmol OH groups) in abs.

pyridine (80 ml). The reaction mixture was stirred for 22h in the thawing ice bath. After reaction ice was added to obtain a brown honey-like precipitate. The mixture was decanted and the crude product was washed with water (3 x 25 ml). Dialysis in acetone (30 h) yielded a light-brown viscous product. Conversion: quant.; yield: 95%.

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ = 5.18 – 4.83 (functionalised sec. OH groups), 4.62 – 4.27 (functionalised prim. OH groups), 4.01 – 3.52 (PG backbone), 3.17 (Ms-C$\underline{H}_3$), 1.28 (C$\underline{H}_2$-PG starter unit), 0.86 ppm (C$\underline{H}_3$-PG starter unit). ^{13}C NMR (500 MHz, $(CD_3)_2CO$): δ = 77.7 – 68.0 (PG backbone), 37.9 – 36.5 ppm (Ms-C).

IR (KBr): ν = 3030, 2941, 2361, 1709, 1457, 1362, 1184, 971, 813, 753 cm^{-1}.

$PG_{5000}(N_3)_{0.8}$: $PG_{5000}(OMs)_{0.8}$ (5.0 g, 33 mmol OMs groups) and NaN_3 (9.7 g, 149 mmol, 4.6 eq.) were mixed in 50 ml dry DMF and heated at 120°C overnight. After cooling to room temperature the residual NaN_3 was removed via filtration through Celite. The orange filtrate was concentrated *in vacuo* and the crude product was purified by dialysis in chloroform or methanol (48 h) to give a light-brown viscous oil product (**7**). Conversion quant.; yield: 90%, brown viscous oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 3.84 – 3.19 (PG backbone, functionalised PG groups), 1.41 (C$\underline{H}_2$-PG starter unit), 0.86 ppm (C$\underline{H}_3$-PG starter unit). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 78.6 – 69.7 (PG backbone), 60.5 (functionalised secondary OH groups), 51.5 ppm (functionalised primary OH groups). IR (KBr): ν = 3444 (ν-H_2O), 2922 (ν-CH_3, ν-CH_2), 2102 (ν-N_3), 1457, 1273, 1122 cm^{-1}.

Hydrophilic alkynyl polyglycerol (8)

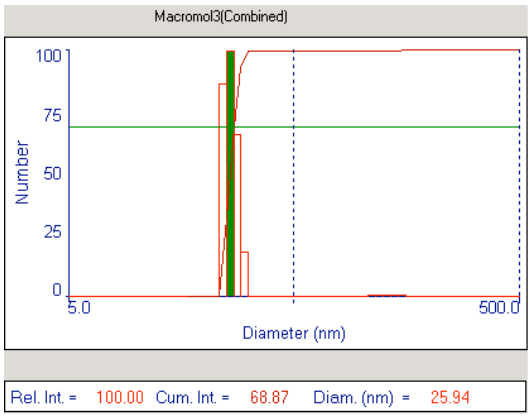
$PG_{5000}(-OCH_2C{\equiv}CH)_{0.3}$: PG_{5000} (5.0 g, 66 mmol OH groups) was dissolved in dry DMF (80 ml) and NaH (1.27 g, 53 mmol, 0.8 eq.) was added. After stirring for 3 h at 0 °C to room temperature the mixture was cooled down again to 0 °C and propargylbromide (3.14 g, 26.4 mmol, 0.4 eq.) was added slowly *via* syringe. The colour of the solution changed to amber. The ice bath was removed and after stirring for 20 hours at room temperature the reaction was quenched with water. Following, solvent was removed azeotropically with toluene addition and the crude product was purified by dialysis in methanol (48 h) to obtain a dark brown viscous oil in 85% yield.

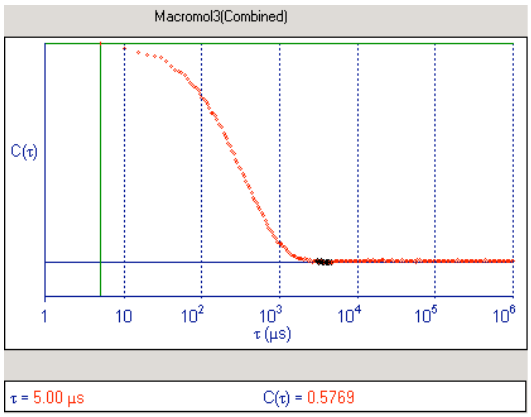
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ = 5.20 – 4.83 (functionalised sec. OH groups), 4.64 – 4.29 (functionalised prim. OH groups), 4.01 – 3.53 (PG backbone), 3.11 (Ms-C$\underline{H}_3$), 1.28 (C$\underline{H}_2$-PG starter unit), 0.86 ppm (C$\underline{H}_3$-PG starter unit). ^{13}C NMR (500 MHz, $(CD_3)_2CO$): δ = 77.0 – 68.2 (PG

backbone), 37.9 – 36.7 ppm (Ms-C).

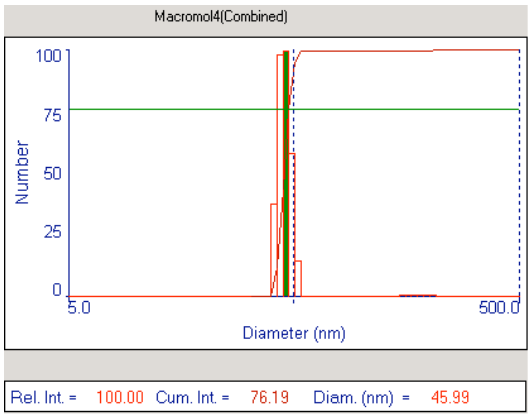
IR (KBr): ν = 3033, 2940, 2364, 1711, 1462, 1362, 1181, 970, 813, 758 cm^{-1}.

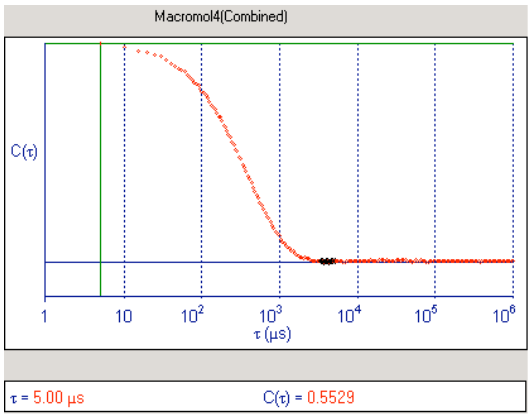
DLS data for nanoparticles (3 - 6, 10 - 12)



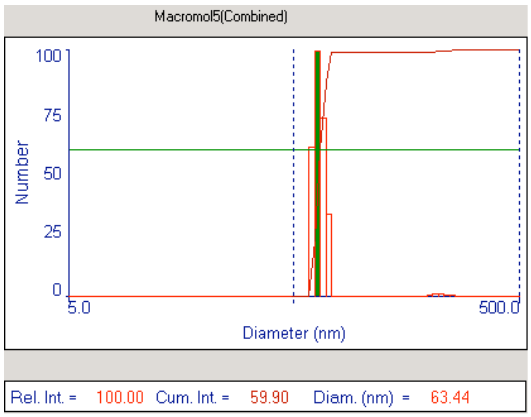


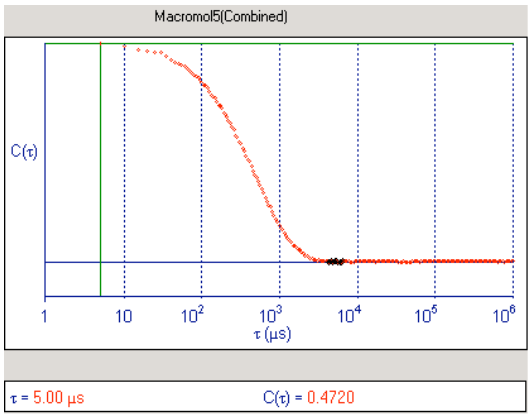
Product 3 in water



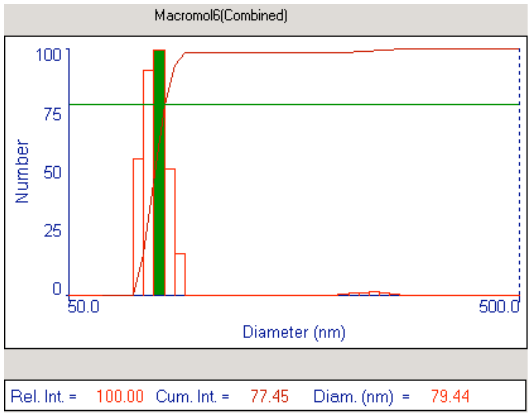


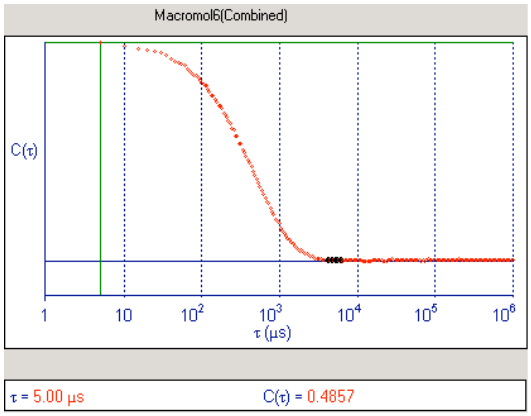
Product 4 in water



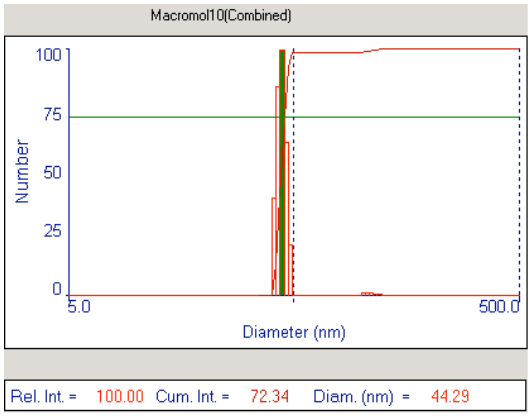


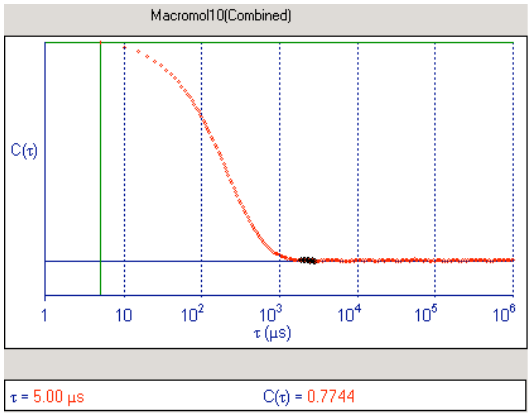
Product 5 in water



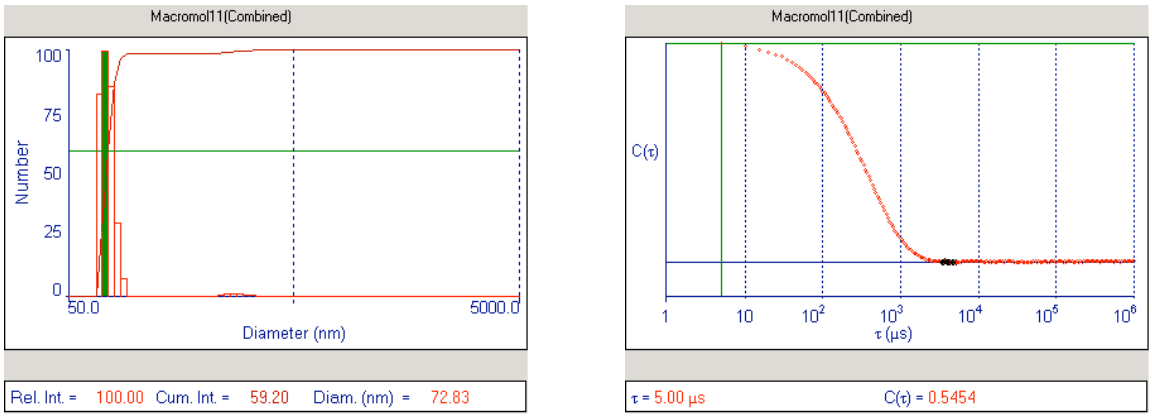


Product 6 in water

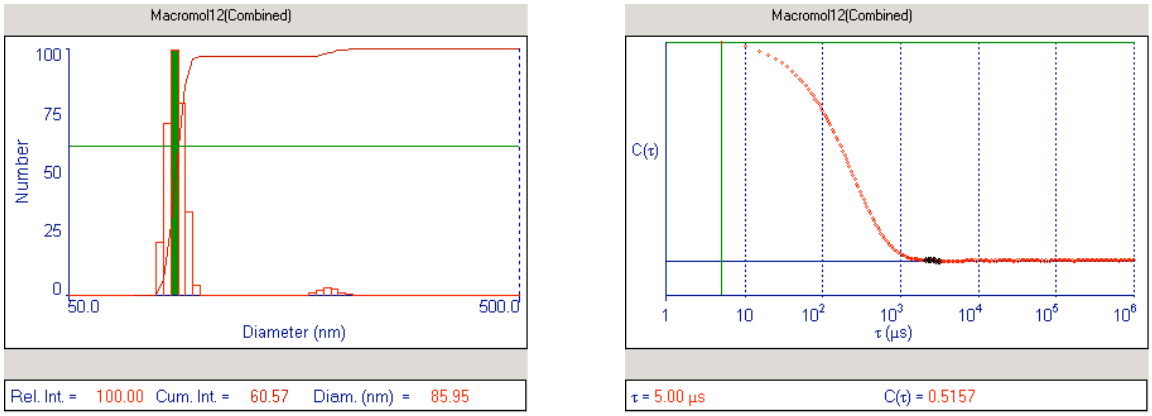




Product 10 in MeOH

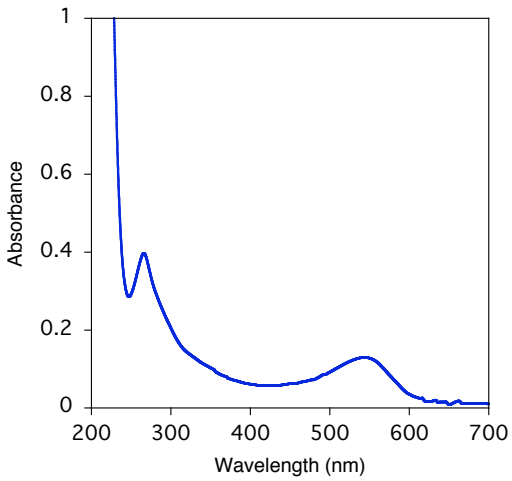


Product 11 in MeOH



Product 12 in MeOH

UV-Vis spectrum of hemicyanine dye labelled nanoparticles (10)



UV-vis spectrum of purified nanoparticles (**10**) in methanol shows a characteristic absorbance of the conjugated hemicyanine dye (**9**) in the wavelength region 500 - 600 nm.