Supporting Information

Use of RAFT Macro-Surfmers for the Synthesis of Transparent Aqueous Colloids with Tunable Interactions

Synthesis of RAFT Macro-Surfmers

The molecular weight obtained by GPC is not accurate since PS calibration was used but confirms the trend of the control of the polymerization.

The produced RAFT Macro-Surfmers were also analyzed by ^{1}H-NMR and the results are shown in Figure 2, confirming the purity of the products. Due to the high reactivity of the charged monomers – MADQUAT and SPMAK – in water, the presence of the peaks relative to the double bond is almost imperceptible and the conversion obtained by comparing the monomer and polymer peaks is very high, 96% and 98% respectively. For the PEG based RAFT Macro-Surfmers the conversion is lower (89%). In order to verify the efficacy of the purification step the ^{1}H-NMR of the positively charged RAFT Macro-Surfmer (2b) was analyzed before the dialysis step, whereas the negatively charged one (2c) was analyzed after and as expected the peak of the sodium acetate (NaOAc) relative to the acetic buffer was respectively present and not present.

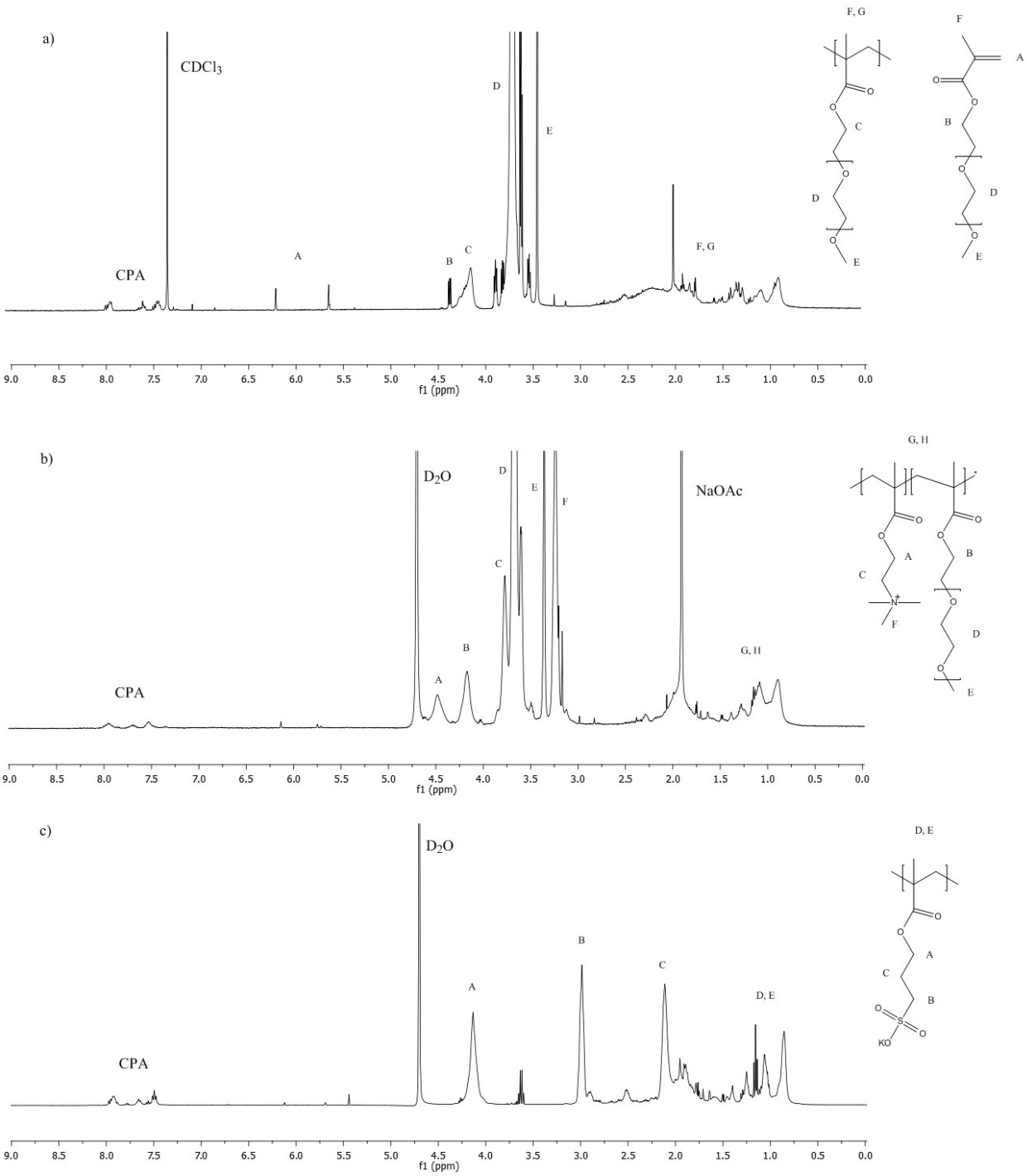

Figure S1. ^{1}H-NMR spectra of the RAFT Macro-Surfmers: a) $(PEGMA950)_{10}$; b) $(MADQUAT)_{10}(PEGMA950)_{10}$; c) $(SPMAK)_{10}$

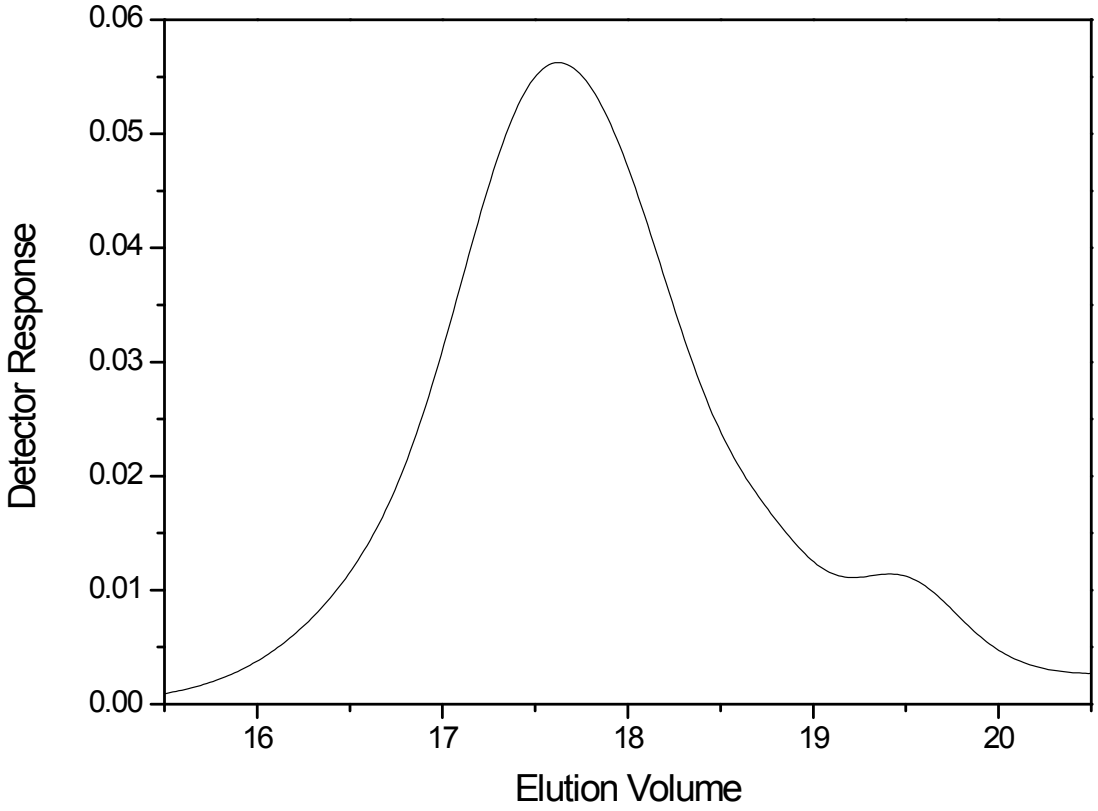

Figure S2: GPC trace of the PEGylated block-copolymer that forms the neutral fluorinated NPs reported as sample C in Table 2.

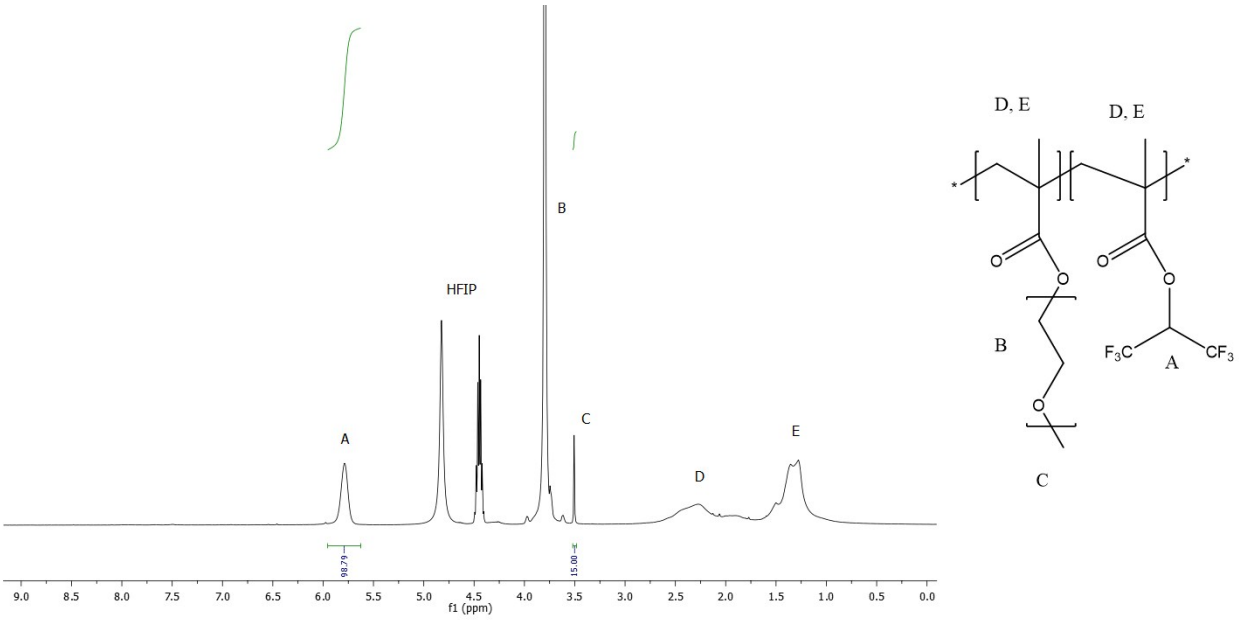

Figure S3: ^{1}H-NMR spectrum of the PEGylated block-copolymer that forms the neutral fluorinated NPs reported as sample C in Table 2. The relative content of the two monomers is evaluated as HFIPM/PEGMA2000 = A/3C

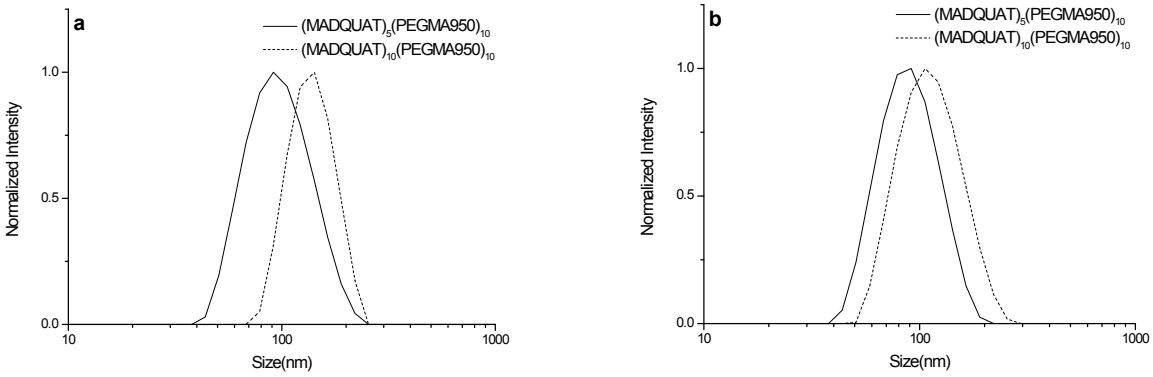

Figure S4: (a) NP size distribution of fluorinated NPs made with $(MADQUAT)_5(PEGMA950)_{10}$ and $(MADQUAT)_{10}(PEGMA950)_{10}$ at S/M = 2.5; (a) NP size distribution of fluorinated NPs made with $(MADQUAT)_5(PEGMA950)_{10}$ and $(MADQUAT)_{10}(PEGMA950)_{10}$ at S/M = 3.

Synthesis of Fluorinated NPs

Table S1. NPs made by RAFT emulsion polymerization of HFIPM with different RAFT Macro-Surfmers

Sample [#]	Clatex [a] [%]	S/M [b] [g/g]	Dn [nm]	PDI [-]	ζ-pot [mV]	Dev. ζ-pot [mV]	RAFT Macro-Surfmers
NEU1	2.9	0.51	234	0.034	-	-	$(PEGMA2000)_5$
NEU2	3.9	0.96	145	0.014	-	-	$(PEGMA2000)_5$
NEU3	4.8	1.48	91	0.083	-	-	$(PEGMA2000)_5$
NEU4	5.7	1.95	76	0.067	-	-	$(PEGMA2000)_5$
NEU5	6.5	2.55	74	0.05	-	-	$(PEGMA2000)_5$
NEU6	7.4	2.96	70	0.097	-	-	$(PEGMA2000)_5$
NEU7	2-3	0.16	320	0.248	-	-	$(PEGMA950)_{10}$
NEU8	2.9	0,51	267	0.447	-	-	$(PEGMA950)_{10}$
NEU9	3.9	0.97	142	0.383	-	-	$(PEGMA950)_{10}$
NEU10	4.8	1.51	72	0.085	-	-	$(PEGMA950)_{10}$
NEU10	5.7	1.96	83	0.042	-	-	$(PEGMA950)_{10}$
NEU10	6.6	2.45	71	0.061	-	-	$(PEGMA950)_{10}$
NEU10	7.4	3	63	0.094	-	-	$(PEGMA950)_{10}$
NEG1	2.2	0.1	386	0.156	-55	9	$(SPMAK)_{10}$
NEG2	2.4	0.2	296	0.011	-60	11	$(SPMAK)_{10}$
NEG3	2.9	0.5	180	0.022	-43	15	$(SPMAK)_{10}$
NEG4	2	1	116	0.058	-47	5	$(SPMAK)_{10}$
POS1	5.66	2	285.2	0.108	12.4	7.73	$(MADQUAT)_{10}(PEGMA950)_{10}$
POS2	6.54	2.5	130.1	0.018	25.1	8.14	$(MADQUAT)_{10}(PEGMA950)_{10}$
POS3	7.41	3	99.46	0.041	22.2	5.7	$(MADQUAT)_{10}(PEGMA950)_{10}$

a) monomer to acetic buffer weight ratio; b) RAFT Macro-Surfmers to monomer weight ratio.

Optical setup for Fluorescence Imaging and DDM

Our setup consists of a standard Olympus IX70 microscope equipped with long working distance objectives (50X, N.A. 0.55) and a Mercury Lamp (U-RLF-T) for fluorescence imaging. Fluorescent images are acquired with an industrial camera (Prosilica GX1050, Allied Vision, 12 bit, 1024 x 1024). The bleaching of the sample was compensated by software using the "*Bleach Correction*" plugin of ImageJ, using the "*Simple Ratio*" correction method. The "*Integral Image Filters-> Normalize Local Contrast*" was used to enhance the contrast and compensate for not uniform illumination.

In the case of DDM, we used the same optical setup, but in this case the microscope was used in Bright Field configuration. The typical exposure time is of few milliseconds and the condenser numerical aperture is set between 0.10<N.A.<0.15. The microscope capillary is mounted on a custom made cell holder which temperature is fixed by a Peltier module controlled through a PID temperature controller (LFI 3751 Wavelength Electronics).