Supporting Information For

Controlling Size and Fluorescence of Dye-Loaded Polymer Nanoparticles through Polymer Design

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Table S1. Overview of synthesized polymers with polymerization time and conversion, AND amounts of monomers in the polymerization mixture before polymerization and in the final purified polymer as determined by NMR.

	Hydrophilic monomer	Amount (mol%)	Hydrophobic monomer	Amount (mol%)	Charged monomer	Amount (mol%)	Polymerization time (min)	Conversion (%)	Amount of hydrophilic monomer in final polymer (%)	Amount of hydrophobic monomer in final polymer (%)
1	HEMA	0	MMA	100	MAA	1	60	33	0	100
2	HEMA	27	MMA	73	MAA	1	30	20	26	74
3	HEMA	52	MMA	48	MAA	1	30	25	53	47
4	HEMA	76	MMA	24	MAA	1	30	29	75	25
5	HEMA	0	MMA	100	MAA	5	60	36	0	100
6	HEMA	24	MMA	76	MAA	5	30	23	25	75
7	HEMA	50	MMA	50	MAA	5	30	24	48	52
8	HEMA	76	MMA	24	MAA	5	30	27	75	25
9	HEMA	0	EMA	100	MAA	1	60	36	0	100
10	HEMA	26	EMA	74	MAA	1	28	28	30	70
11	HEMA	51	EMA	49	MAA	1	28	29	50	50
12	HEMA	75	EMA	25	MAA	1	28	30	77	23
13	HEMA	0	EMA	100	MAA	5	28	<10	0	100
14	HEMA	25	EMA	75	MAA	5	28	24	25	75
15	HEMA	50	EMA	50	MAA	5	28	29	51	49
16	HEMA	74	EMA	26	MAA	5	28	32	76	24
17	HEMA	0	PMA	100	MAA	1	60	39	0	100
18	HEMA	26	PMA	74	MAA	1	30	20	22	78
19	HEMA	50	PMA	50	MAA	1	30	31	50	50
20	HEMA	74	PMA	26	MAA	1	30	35	76	24
21	HEMA	0	PMA	100	MAA	5	60	38	0	100
22	HEMA	26	PMA	74	MAA	5	30	22	22	78
23	HEMA	49	PMA	51	MAA	5	30	24	49	51
24	HEMA	74	PMA	26	MAA	5	30	29	76	24
25	HEMA	0	BMA	100	MAA	1	60	17	0	100
26	HEMA	24	BMA	76	MAA	1	30	19	20	80
27	HEMA	48	BMA	52	MAA	1	30	30	43	57
28	HEMA	72	BMA	28	MAA	1	30	33	74	26
29	HEMA	0	BMA	100	MAA	5	60	11	0	100
30	HEMA	24	BMA	76	MAA	5	30	10	20	80
31	HEMA	48	BMA	52	MAA	5	30	29	43	57
32	HEMA	72	BMA	28	MAA	5	30	31	75	25

Table S1. continued

	Hydrophilic monomer	Amount (mol%)	Hydrophobic monomer	Amount (mol%)	Charged monomer	Amount (mol%)	Polymerization time (min)	Conversion (%)	Amount of hydrophilic monomer in final polymer (%)	Amount of hydrophobic monomer in final polymer (%)
33	HEMA	0	BzMA	100	MAA	1	45	43	0	100
34	HEMA	27	BzMA	73	MAA	1	30	34	30	70
35	HEMA	51	BzMA	49	MAA	1	30	36	52	48
36	HEMA	75	BzMA	25	MAA	1	30	37	75	25
37	HEMA	0	BzMA	100	MAA	5	45	40	0	100
38	HEMA	26	BzMA	74	MAA	5	30	30	31	69
39	HEMA	51	BzMA	49	MAA	5	30	33	52	48
40	HEMA	74	BzMA	26	MAA	5	30	35	74	26
41	AMA	22	EMA	78	MAA	1	30	21	21	79
42	AMA	45	EMA	55	MAA	1	30	27	45	55
43	AMA	72	EMA	28	MAA	1	30	23	72	28
44	AMA	21	EMA	79	MAA	5	30	20	21	79
45	AMA	47	EMA	53	MAA	5	30	18	47	53
46	AMA	73	EMA	27	MAA	5	30	24	70	30
47	MAMA	23	EMA	77	MAA	1	30	22	22	78
48	MAMA	46	EMA	54	MAA	1	30	25	46	54
49	MAMA	72	EMA	28	MAA	1	30	30	72	28
50	MAMA	45	EMA	55	MAA	5	30	25	45	55
51	MEMA	26	PMA	74	MAA	1	20	<10	26	74
52	MEMA	54	PMA	46	MAA	1	20	<10	54	46
53	MEMA	71	PMA	29	MAA	1	20	10	74	26
54	MEMA	100	PMA	0	MAA	1	20	21	100	0
55	MEMA	31	PMA	69	MAA	5	20	10	31	69
56	MEMA	49	PMA	51	MAA	5	20	<10	49	51
57	MEMA	72	PMA	28	MAA	5	20	10	72	28
58	MEMA	100	PMA	0	MAA	5	20	17	100	0
59	HEMA	0	PMA	100	SMA	1	50	40	0	100
60	HEMA	25	PMA	75	SMA	1	40	38	25	75

Estimation of octanol-water partition coefficients (log P values):

Log P values were estimated using the ChemDraw 15 Professional software. For this the structure of four linked repeat units was drawn representing the relative percentages of the hydrophilic and hydrophobic monomers. Log P values are then obtained from the built-in function ClogP, which is based on Molecular Networks' cheminformatics platform MOSES.

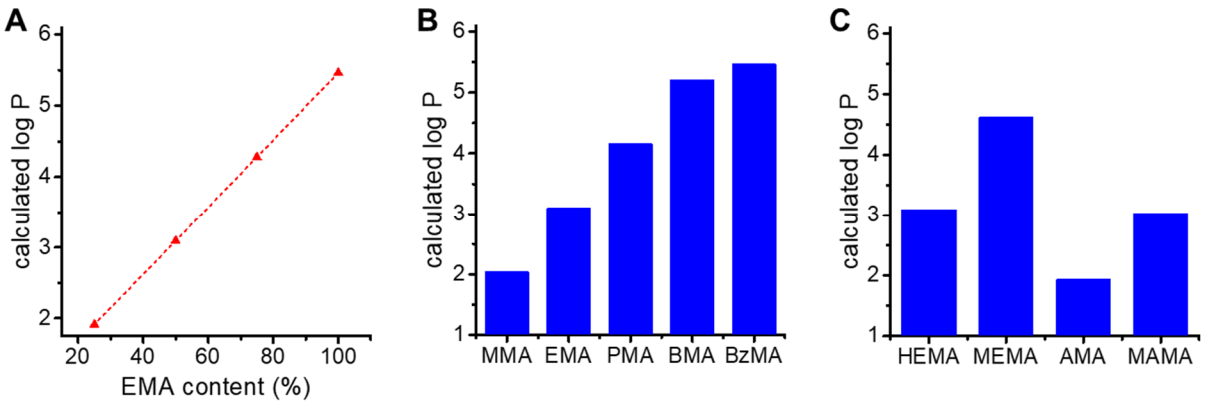

Figure S1. Calculated log P values for different copolymer compositions: (A) EMA/HEMA copolymers with varying EMA (and HEMA) content. (B) Copolymers with 50% HEMA and different hydrophobic monomers. (C) Copolymers with 50% EMA and different hydrophilic monomers.

Table S2. Sizes of prepared particles as analyzed by DLS. Volume average and standard error of the mean for at least 3 measurements are given.

Hydrophilic monomer	Amount (mol%)	Hydrophobic monomer	Amount (mol%)	Charged monomer	Amount (mol%)	Size (nm) for precipitation in	
						MilliQ	Buffer[1)]
HEMA	0	MMA	100	MAA	1	116 ± 4	508 ± 51
HEMA	26	MMA	74	MAA	1	53 ± 2	123 ± 7
HEMA	53	MMA	47	MAA	1	35 ± 1	59 ± 3
HEMA	76	MMA	24	MAA	1	28 ± 2	82 ± 3
HEMA	0	MMA	100	MAA	5	60 ± 2	15 ± 3
HEMA	25	MMA	75	MAA	5	39 ± 1	17 ± 2
HEMA	48	MMA	52	MAA	5	26 ± 1	13 ± 2
HEMA	75	MMA	25	MAA	5	20 ± 2	10 ± 3
HEMA	0	EMA	100	MAA	1	133 ± 7	142 ± 4
HEMA	30	EMA	70	MAA	1	78 ± 2	119 ± 7
HEMA	50	EMA	50	MAA	1	49 ± 2	73 ± 3
HEMA	77	EMA	23	MAA	1	32 ± 2	71 ± 3
HEMA	0	EMA	100	MAA	5	97 ± 3	22 ± 2
HEMA	25	EMA	75	MAA	5	51 ± 1	14 ± 2
HEMA	51	EMA	49	MAA	5	29 ± 2	10 ± 2
HEMA	76	EMA	24	MAA	5	26 ± 2	14 ± 2
HEMA	0	PMA	100	MAA	1	185 ± 6	270 ± 40
HEMA	22	PMA	78	MAA	1	51 ±4	74 ± 3
HEMA	50	PMA	50	MAA	1	87 ± 2	133 ± 41
HEMA	76	PMA	24	MAA	1	35 ± 2	77 ± 3
HEMA	0	PMA	100	MAA	5	106 ± 5	32 ± 1
HEMA	22	PMA	78	MAA	5	53 ± 2	24 ± 2
HEMA	49	PMA	51	MAA	5	41 ± 2	13 ± 2
HEMA	76	PMA	24	MAA	5	27 ± 2	13 ± 2
HEMA	0	BMA	100	MAA	1	133 ± 7	187 ± 13
HEMA	20	BMA	80	MAA	1	78 ± 2	176 ± 8
HEMA	43	BMA	57	MAA	1	49 ± 2	103 ± 4
HEMA	74	BMA	26	MAA	1	32 ± 2	88 ± 3
HEMA	0	BMA	100	MAA	5	97 ± 3	30 ± 2
HEMA	20	BMA	80	MAA	5	51 ± 2	25 ± 2
HEMA	43	BMA	57	MAA	5	29 ± 1	17 ± 1
HEMA	75	BMA	25	MAA	5	26 ± 2	14 ± 2

Table S2. continued

Hydrophilic monomer	Amount (mol%)	Hydrophobic monomer	Amount (mol%)	Charged monomer	Amount (mol%)	Size (nm) for precipitation in	
						MilliQ	buffer
HEMA	0	BzMA	100	MAA	1	113 ± 5	163 ± 12
HEMA	30	BzMA	70	MAA	1	96 ± 5	600 ± 99
HEMA	52	BzMA	48	MAA	1	64 ± 4	480 ± 82
HEMA	75	BzMA	25	MAA	1	43 ± 2	77 ± 4
HEMA	0	BzMA	100	MAA	5	110 ± 9	243 ± 36
HEMA	31	BzMA	69	MAA	5	86 ± 4	102 ± 41
HEMA	52	BzMA	48	MAA	5	42 ± 1	22 ± 5
HEMA	74	BzMA	26	MAA	5	33 ± 3	14 ± 2
AMA	21	EMA	79	MAA	1	27± 2	261± 90
AMA	45	EMA	55	MAA	1	37 ± 2	1100 ± 54
AMA	72	EMA	28	MAA	1	50 ± 1	1100 ± 60
AMA	21	EMA	79	MAA	5	24 ± 2	14 ± 2
AMA	47	EMA	53	MAA	5	32 ± 2	(<10)
AMA	70	EMA	30	MAA	5	33 ± 2	(<10)
MAMA	22	EMA	78	MAA	1	67 ± 3	840 ± 150
MAMA	46	EMA	54	MAA	1	45 ± 2	118 ± 3
MAMA	72	EMA	28	MAA	1	35 ± 3	700 ± 146
MAMA	45	EMA	55	MAA	5	31 ± 2	15 ± 2
MEMA	26	PMA	74	MAA	1	153 ± 8	107 ± 4
MEMA	54	PMA	46	MAA	1	120 ± 5	79 ± 3
MEMA	74	PMA	26	MAA	1	110 ± 3	93 ± 3
MEMA	100	PMA	0	MAA	1	96 ± 3	80 ± 3
MEMA	31	PMA	69	MAA	5	114 ± 3	121 ± 3
MEMA	49	PMA	51	MAA	5	87 ± 2	22 ± 2
MEMA	72	PMA	28	MAA	5	79 ± 2	21 ± 2
MEMA	100	PMA	0	MAA	5	66 ± 2	16 ± 2
HEMA	0	PMA	100	SMA	1	23 ± 2	
HEMA	22	PMA	78	SMA	1	13 ±2	

[1)] In the case of samples giving sizes < 15 nm the measurement quality was limited due to the low scattering signal at the used concentrations.

Table S3. ζ–potentials of nanoparticles prepared in MilliQ water from copolymers of EMA and HEMA with 1 mol% MAA. Measurements were performed in triplicate, errors give the standard error of the mean.

Copolymer composition		ζ–potential (mV)
HEMA	EMA	
25	75	-22 ± 4
50	50	-18 ± 6
75	25	-25 ± 6
100	0	-31 ± 2

Table S4. ζ–potentials of nanoparticles prepared in MilliQ water from copolymers of HEMA with different hydrophobic monomers in a 1:1 ratio. Measurements were performed in triplicate, errors give the standard error of the mean.

Copolymer composition			ζ–potential (mV)
hydrophobic	hydrophilic	MAA	
MMA	HEMA	1%	-17 ± 5
EMA	HEMA	1%	-18 ± 6
PMA	HEMA	1%	-28 ± 2
BMA	HEMA	1%	-39 ± 4
BzMA	HEMA	1%	-39 ± 3
EMA	HEMA	5%	-27 ± 3

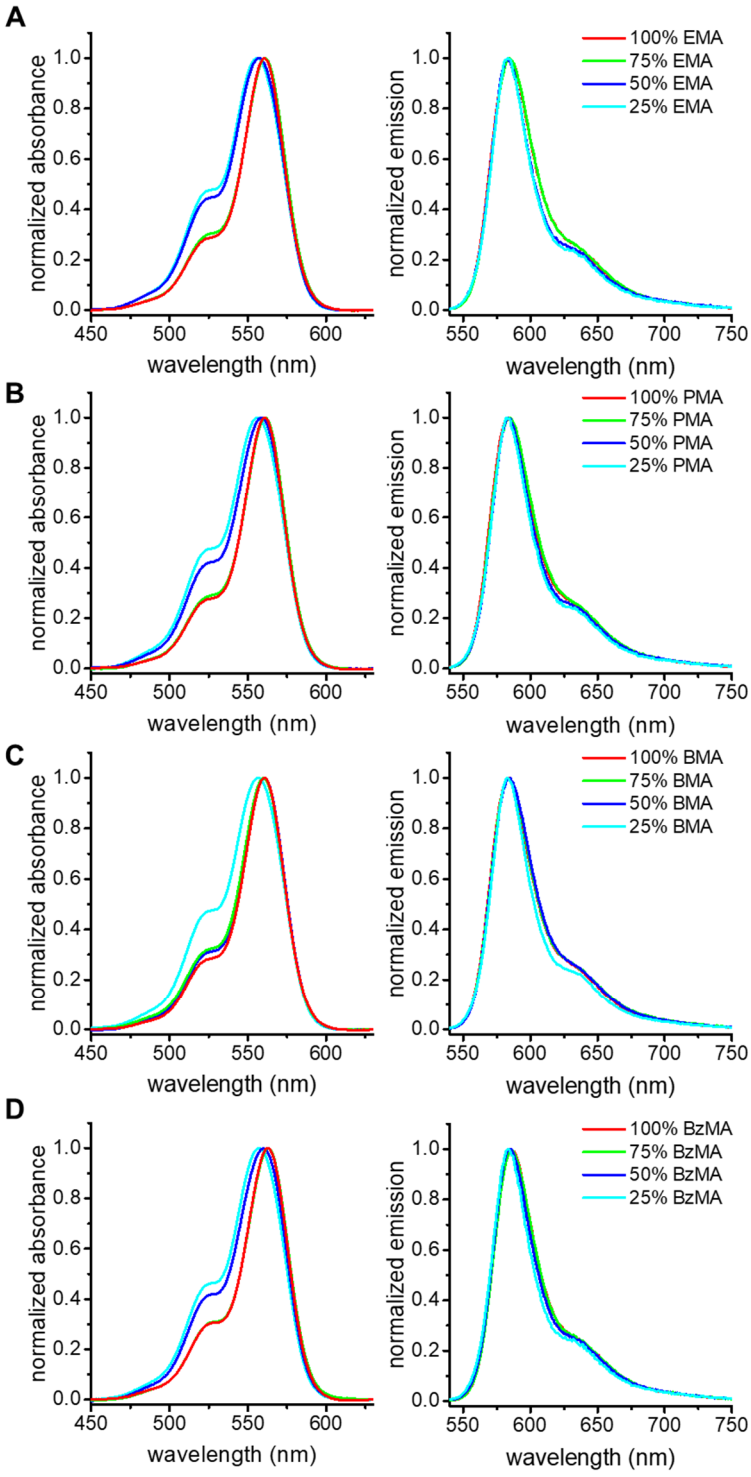

Figure S2. Normalized absorption (left) and emission (right) spectra of NPs made from copolymers with 50% HEMA and different hydrophobic monomers (1 mol% MAA) and loaded with 10 wt% of R18/F5-TPB: (A) EMA, (B) PMA, (C) BMA, (D) BzMA. Excitation was performed at 530 nm.

Table S5. Quantum yields of nanoparticles prepared from different polymers with 10 wt% R18/F5-TPB. The average of at least three measurements with the corresponding standard error of the mean is given.

Hydrophilic monomer	Amount (mol%)	Hydrophobic monomer	Amount (mol%)	Charged monomer	Amount (mol%)	Quantum yield
HEMA	0	MMA	100	MAA	1	0.66 ± 0.05
HEMA	26	MMA	74	MAA	1	0.57 ± 0.01
HEMA	53	MMA	47	MAA	1	0.26 ± 0.12
HEMA	76	MMA	24	MAA	1	0.14 ± 0.02
HEMA	0	EMA	100	MAA	1	0.60 ± 0.02
HEMA	30	EMA	70	MAA	1	0.62 ± 0.08
HEMA	50	EMA	50	MAA	1	0.37 ± 0.04
HEMA	77	EMA	23	MAA	1	0.20 ± 0.02
HEMA	0	PMA	100	MAA	1	0.69 ± 0.03
HEMA	50	PMA	50	MAA	1	0.78 ± 0.04
HEMA	22	PMA	78	MAA	1	0.43 ± 0.14
HEMA	76	PMA	24	MAA	1	0.29 ± 0.13
HEMA	0	BMA	100	MAA	1	0.61 ± 0.06
HEMA	20	BMA	80	MAA	1	0.43 ± 0.18
HEMA	43	BMA	57	MAA	1	0.57 ± 0.07
HEMA	74	BMA	26	MAA	1	0.58 ± 0.11
HEMA	0	BzMA	100	MAA	1	0.71 ± 0.10
HEMA	30	BzMA	70	MAA	1	0.55 ± 0.19
HEMA	52	BzMA	48	MAA	1	0.48 ± 0.17
HEMA	75	BzMA	25	MAA	1	0.23 ± 0.07
AMA	21	EMA	79	MAA	1	0.59 ± 0.09
AMA	45	EMA	55	MAA	1	0.32 ± 0.12
AMA	72	EMA	28	MAA	1	0.22 ± 0.13
MAMA	22	EMA	78	MAA	1	0.59 ± 0.09
MAMA	46	EMA	54	MAA	1	0.30 ± 0.17
MAMA	72	EMA	28	MAA	1	0.23 ± 0.10
MEMA	26	PMA	74	MAA	1	0.65 ± 0.07
MEMA	54	PMA	46	MAA	1	0.85 ± 0.16
MEMA	74	PMA	26	MAA	1	0.78 ± 0.08
MEMA	100	PMA	0	MAA	1	0.75 ± 0.1

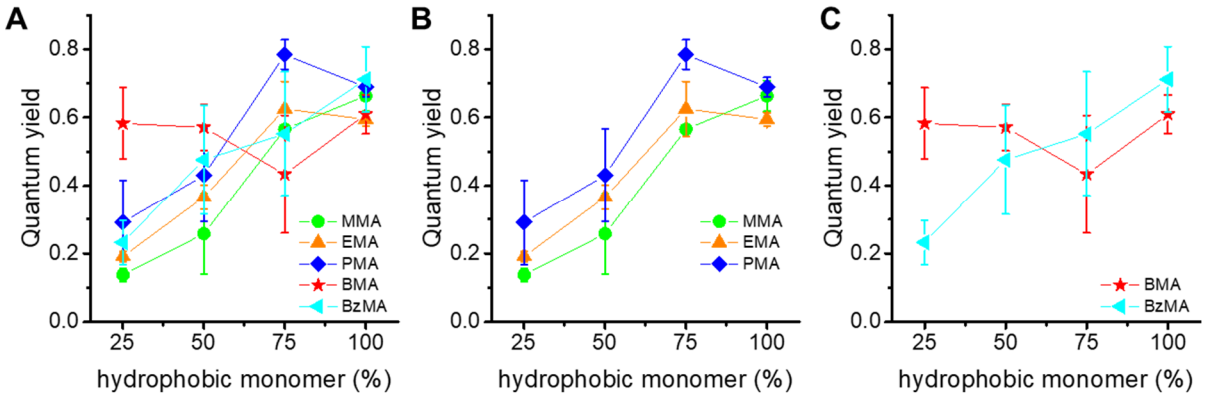

Figure S3. Fluorescence quantum yields of NPs made from different copolymers and loaded with 10 wt% of R18/F5-TPB (A: all polymers, B and C: selected series for better visibility). Quantum yields are plotted *vs* content of the hydrophobic monomer for copolymers with HEMA and 1 mol% of MAA. NPs were prepared in MilliQ water. Error bars give standard error of the mean over at least three independent experiments.

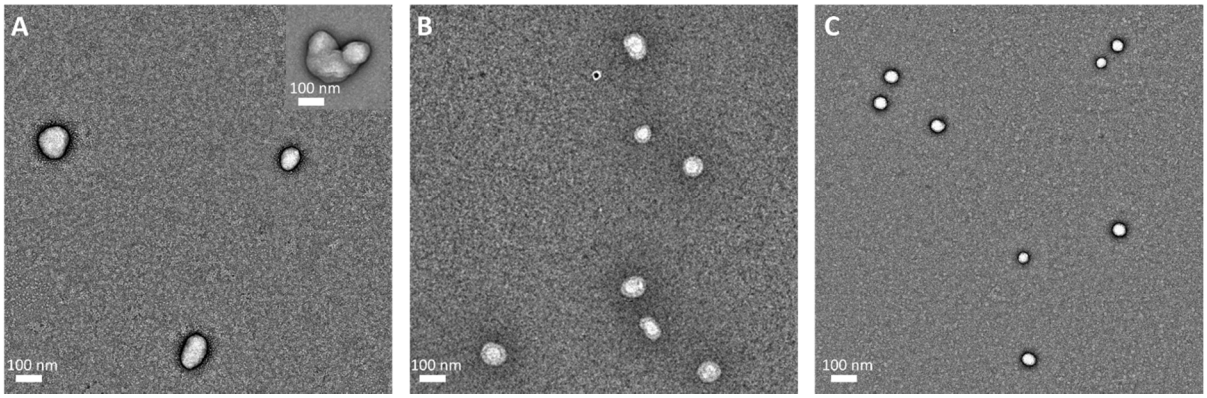

Figure S4. Transmission electron microscopy (TEM) images of NPs made from EMA/HEMA copolymers with 1 mol% MAA (A) 100% EMA (inset: example of aggregates), (B) 75% EMA, (C) 50% EMA in MilliQ water. NPs were deposited onto carbon-coated copper rhodium electron microscopy grids and treated for 1 min with a 2% uranyl acetate solution for staining.