Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Solvent evaporation from emulsion droplets (SEED)

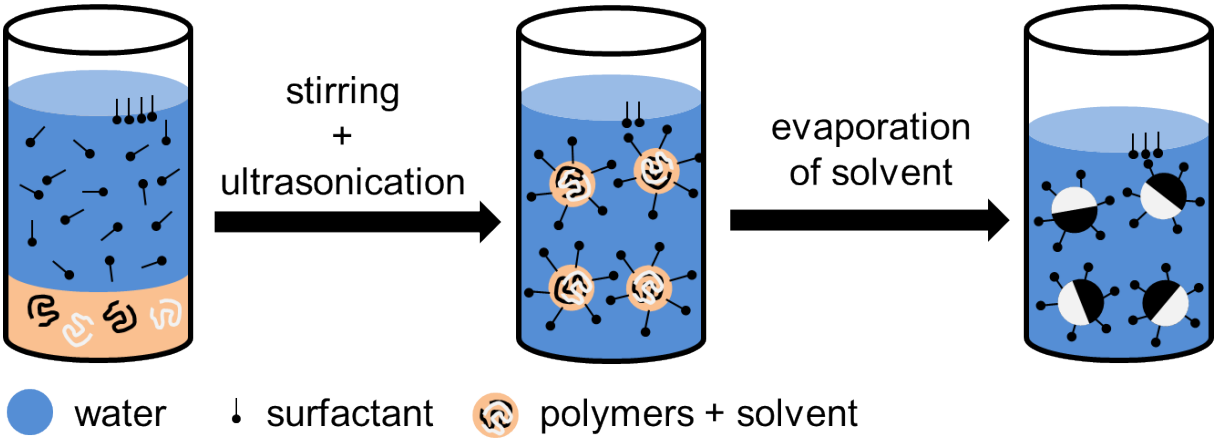

Fig. S1 In the SEED process, two polymers are dissolved in a good solvent and mixed with an aqueous solution of surfactant. Upon stirring and ultrasonication, a miniemulsion is formed. The solvent is then evaporated from the miniemulsion and a dispersion is obtained. Janus particles can be formed when a phase separation between the two polymers occurs in the dispersed phase.

Tab. S1 Amounts of monomers used for the preparation of the PS-*co*-PVBC and PMMA-*co*-PVBC copolymers.

Copolymer	$m_{monomer}$ / g			**Yield / %**
	styrene	**VBC**	**MMA**	
Co-1	18.747	3.132	-	42.8
Co-2	-	3.132	18.022	44.5
Co-3	19.789	1.565	-	42.1
Co-4	-	1.566	19.023	44.0
Co-5	20.310	0.783	-	37.2
Co-6	-	0.783	19.523	46.3

Tab. S2 Prepared post-functionalized copolymers.

Functional copolymer	Prepared from	$m_{copolymer}$ / g	Functionalization	Yield / %
Co-1-f	Co-1	8.000	alkyne	57.2
Co-2-f	Co-2	9.000	azide	57.4
Co-3-f	Co-3	8.490	alkyne	51.1
Co-4-f	Co-4	8.601	azide	69.8
Co-5-f	Co-5	7.350	alkyne	81.3
Co-6-f	Co-6	8.905	azide	64.0

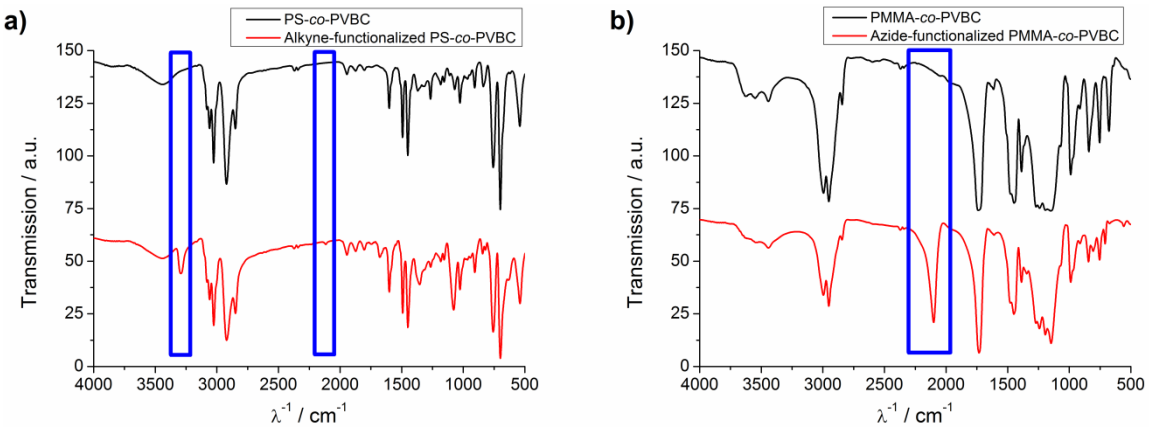

Fig. S2 IR spectra of PS-*co*-PVBC (a) and PMMA-*co*-PVBC (b) before and after post-functionalization with alkyne (a) and azide groups (b). The vibrations related to the introduced groups are marked in boxes.

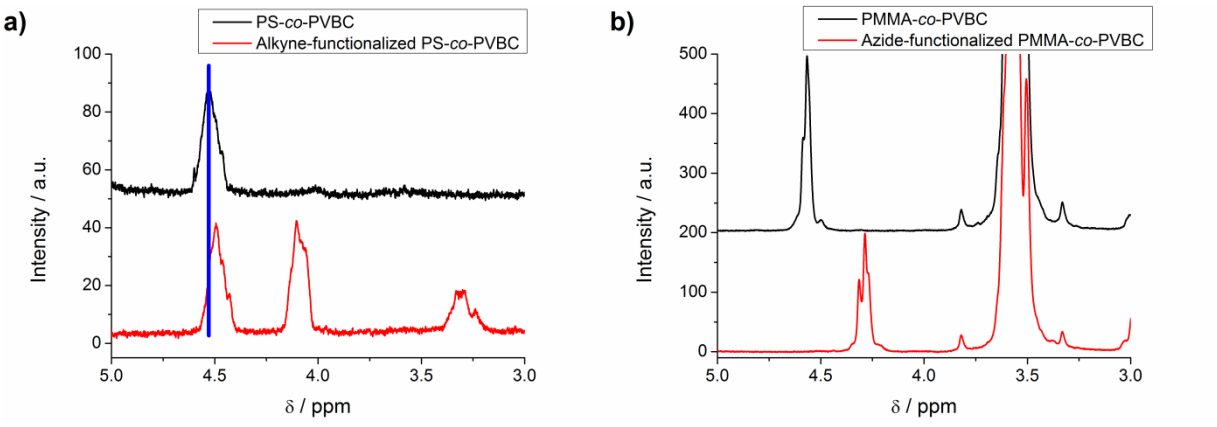

Fig. S3 NMR spectra of PS-*co*-PVBC (a) and PMMA-*co*-PVBC (b) before and after post-functionalization with alkyne (a) and azide groups (b). In the case of alkyne groups, new signals from the introduced propargylic group (at 4.1 and 3.3 ppm) and a very small chemical shift of the protons belonging to the benzyl group (at 4.5 ppm) can be observed (a). In the case of the post-functionalization with azide groups, there is a stronger up-field shift (b) of the protons belonging to the benzyl group (from 4.5 ppm to 4.25 ppm).

Synthesis of the functionalized ATRP initiators

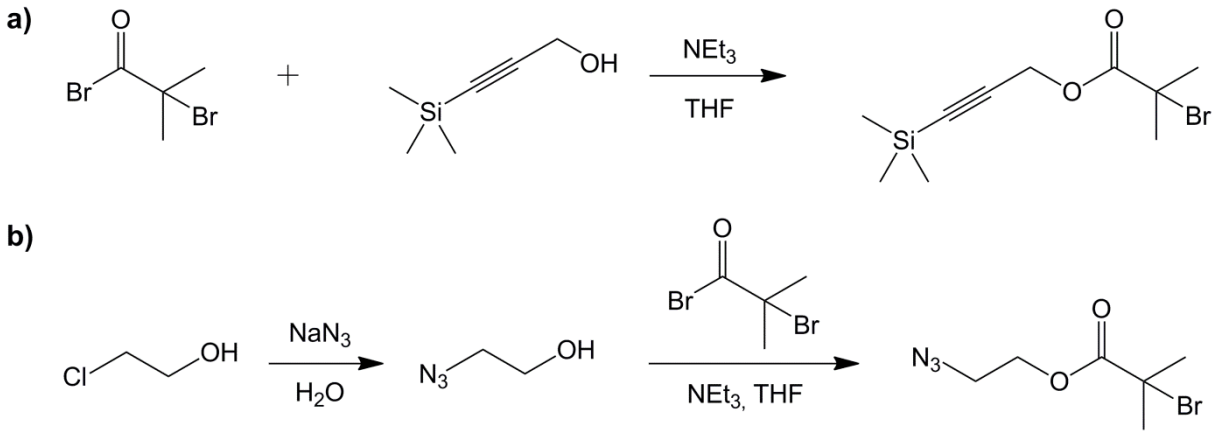

Fig. S4 Synthesis of the alkyne (a) and azide (b) functionalized ATRP initiator.

Preparation of the Janus particles

Tab. S3 Amounts of polymers used for the preparation of the Janus particles, hydrodynamic diameter D of the prepared particles, number of functional groups, area-normalized number of functional groups and number of functional groups normalized to the polymer functionality Ψ, each on one face of the Janus particles.

Sample	m_{PS} / mg	m_{PMMA} / mg	$m_{Co\text{-}1\text{-}f}$ / mg	$m_{Co\text{-}2\text{-}f}$ / mg	$m_{Co\text{-}3\text{-}f}$ / mg	$m_{Co\text{-}4\text{-}f}$ / mg	$m_{Co\text{-}5\text{-}f}$ / mg	$m_{Co\text{-}6\text{-}f}$ / mg	$m_{ATRP\text{-}1}$ / mg	$m_{ATRP\text{-}2}$ / mg	m_{SDS} / mg	group	D / nm	Groups per particle	Groups / nm^{-2}	Ψ / nm^{-2}
Quant-1	46.9	53.1	-	-	-	-	-	-	-	-	20	alkyne	96	9	$6.5\cdot10^{-4}$	-
Quant-2	46.9	53.1	-	-	-	-	-	-	-	-	20	azide	96	14	$9.8\cdot10^{-4}$	-
Quant-3	46.9	53.1	-	-	-	-	-	-	-	-	2	alkyne	220	28	$3.7\cdot10^{-4}$	-
Quant-4	46.9	53.1	-	-	-	-	-	-	-	-	2	azide	220	68	$9.0\cdot10^{-4}$	-
Quant-5	-	53.1	46.9	-	-	-	-	-	-	-	20	alkyne	100	1305	$8.3\cdot10^{-2}$	0.75
Quant-6	46.9	-	-	53.1	-	-	-	-	-	-	20	azide	105	1919	$1.1\cdot10^{-1}$	0.83
Quant-7	-	53.1	-	-	46.9	-	-	-	-	-	20	alkyne	103	709	$4.3\cdot10^{-2}$	0.77
Quant-8	46.9	-	-	-	-	53.1	-	-	-	-	20	azide	93	807	$5.9\cdot10^{-2}$	0.83
Quant-9	-	53.1	-	-	-	-	46.9	-	-	-	20	alkyne	103	373	$2.36\cdot10^{-2}$	0.75
Quant-10	46.9	-	-	-	-	-	-	53.1	-	-	20	azide	99	479	$3.2\cdot10^{-2}$	0.79
Quant-11	46.9	-	-	-	-	-	-	-	53.1	-	20	alkyne	93	66	$4.9\cdot10^{-3}$	1.42
Quant-12	-	53.1	-	-	-	-	-	-	-	46.9	20	azide	93	76	$5.6\cdot10^{-3}$	1.79
Quant-13	-	53.1	46.9	-	-	-	-	-	-	-	2	alkyne	221	6445	$8.4\cdot10^{-2}$	0.76
Quant-14	46.9	-	-	53.1	-	-	-	-	-	-	2	azide	211	7497	$1.1\cdot10^{-1}$	0.80
Quant-15	-	53.1	-	-	46.9	-	-	-	-	-	2	alkyne	200	2598	$4.1\cdot10^{-2}$	0.75
Quant-16	46.9	-	-	-	-	53.1	-	-	-	-	2	azide	197	3506	$5.8\cdot10^{-2}$	0.82
Quant-17	-	53.1	-	-	-	-	46.9	-	-	-	2	alkyne	204	1500	$2.3\cdot10^{-2}$	0.76
Quant-18	46.9	-	-	-	-	-	-	53.1	-	-	2	azide	222	2546	$3.3\cdot10^{-2}$	0.83
Quant-19	46.9	-	-	-	-	-	-	-	53.1	-	2	alkyne	221	315	$4.1\cdot10^{-3}$	1.18
Quant-20	-	53.1	-	-	-	-	-	-	-	46.9	2	azide	216	366	$5.0\cdot10^{-3}$	1.59

Synthesis of the clickable dyes

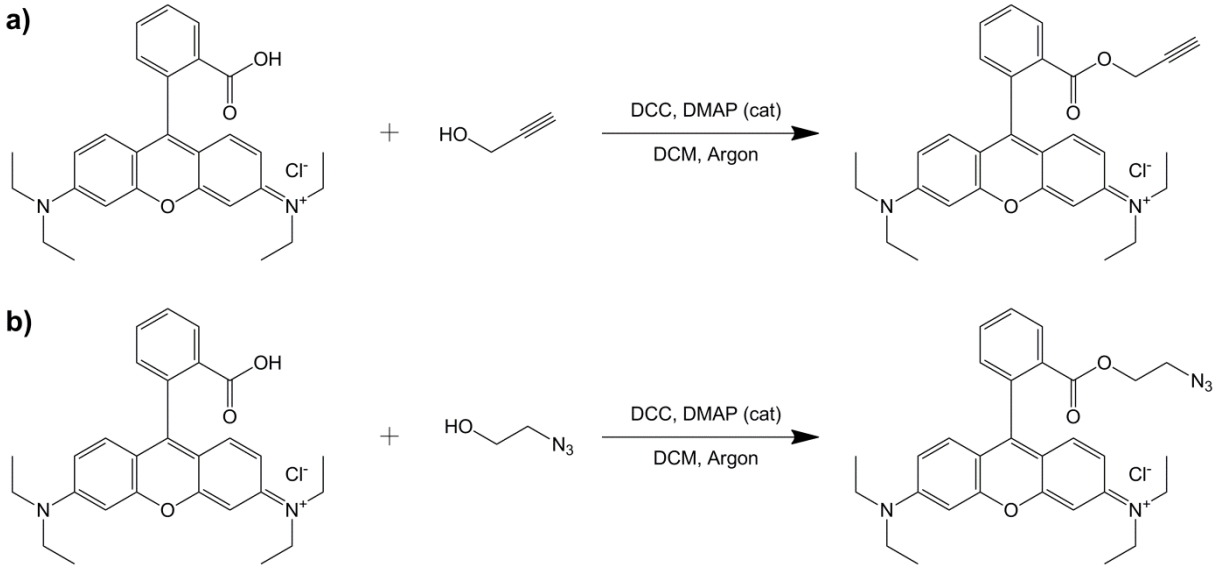

Fig. S5 Synthesis of the alkyne- (a) and azide- (b) functionalized rhodamine dye.

Composition of the copolymers

Tab. S4 Molar composition and molecular weight of the prepared copolymers before post-functionalization.

Copolymer	theoretical molar ratio			measured molar ratio			M_n / g·mol^{-1}	PDI
	PS	PMMA	PVBC	PS	PMMA	PVBC		
Co-1	90	0	10	89	0	11	30,000	1.92
Co-2	0	90	10	0	87	13	37,500	2.00
Co-3	95	0	5	94	0	6	30,600	1.73
Co-4	0	95	5	0	93	7	35,700	1.94
Co-5	97	0	3	97	0	3	32,800	1.79
Co-6	0	97	3	0	96	4	34,800	1.97

Morphology of the particles

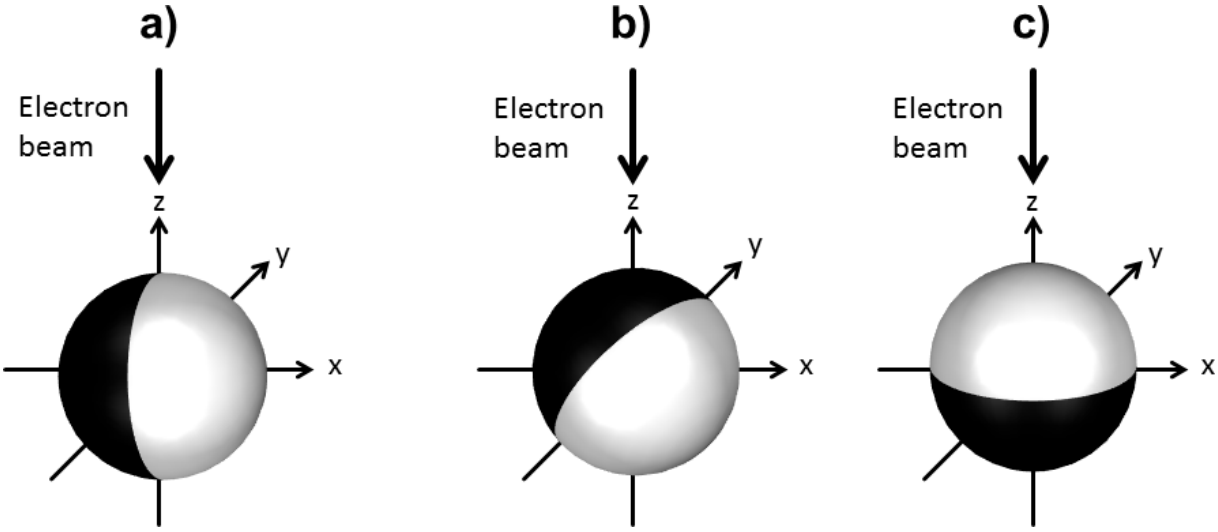

Fig. S6 Janus morphology with equal volumes for both sides can be observed if the particle is located on the TEM grid as shown in (a). Once it is tilted (b), one face of the particle appears larger than the other one. If the interface between both faces is parallel to the substrate where the particles are deposited (c), the Janus morphology cannot be observed.

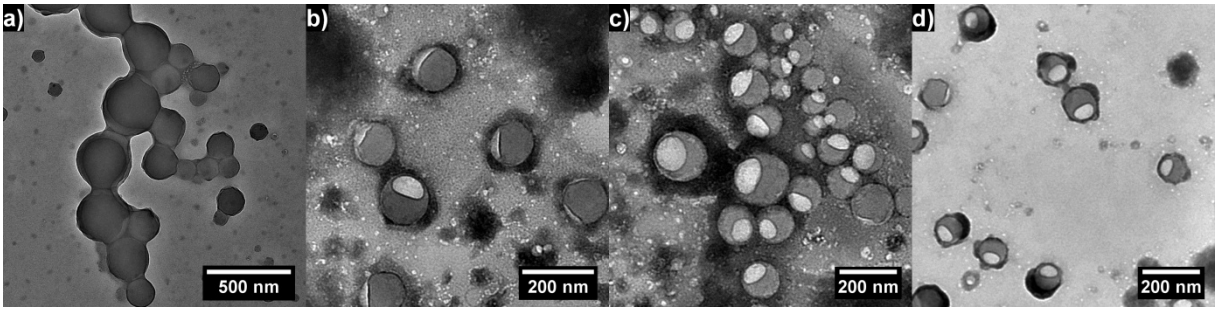

Fig. S7 TEM micrographs of particles prepared from post-functionalized copolymers Co-f-1 and Co-f-2 (a), Co-f-3 and Co-f-4 (b), Co-f-5 and Co-f-6 (c) and from the polymers ATRP-1 and ATRP-2 (d) synthesized by ATRP. In all cases, a 0.01 wt.-% solution of the surfactant was used. Only particles prepared from Co-f-1 and Co-f-2 were not Janus particles.

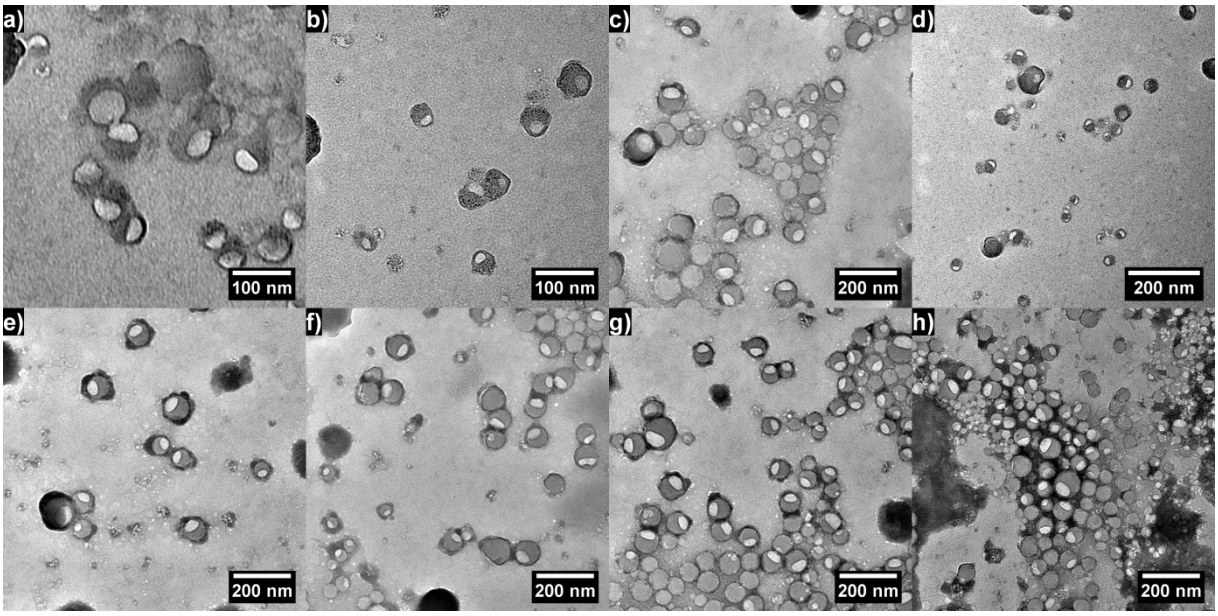

Fig. S8 TEM micrographs of Janus particles functionalized on one face prepared from the post-functionalized copolymers Co-f-1 to Co-f-6 (a to f) or from the polymers ATRP-1 and ATRP-2 (g and h) prepared by ATRP and pure PS or PMMA. In all cases, a 0.1 wt.-% solution of the surfactant was used. All particles showed a Janus morphology.

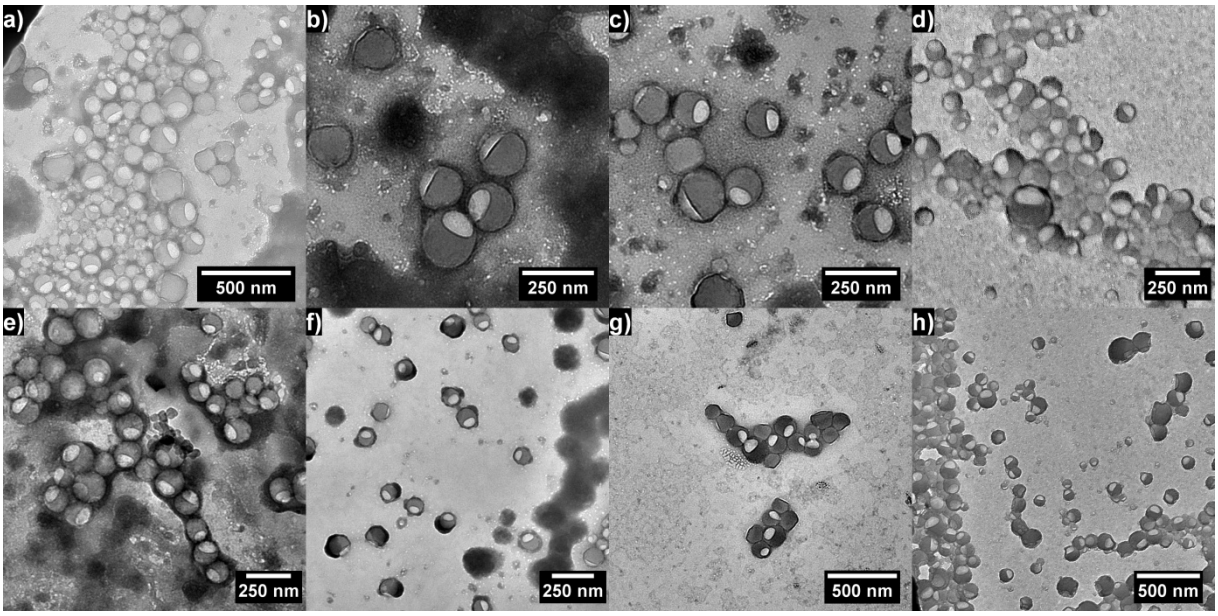

Fig. S9 TEM micrographs of Janus particles with one functionalized face prepared from the post-functionalized copolymers Co-f-1 to Co-f-6 (a to f) and from the polymers ATRP-1 and ATRP-2 (g and h) prepared by ATRP and pure PS or PMMA. In all cases, a 0.01 wt.-% solution of the surfactant was used.

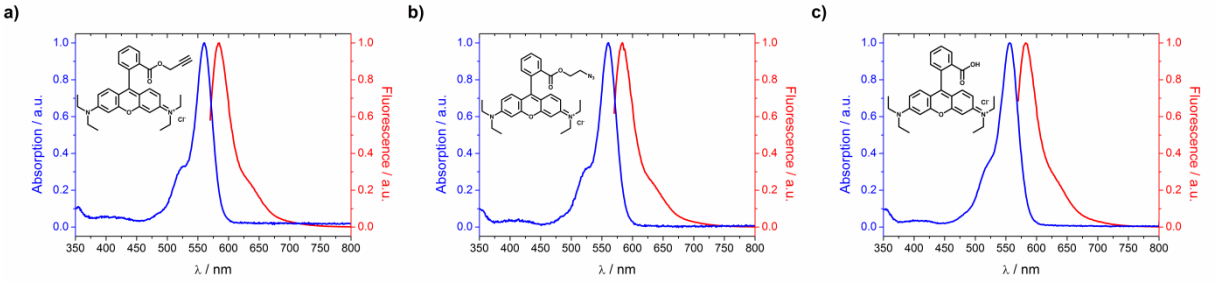

Fig. S10 Absorption- and fluorescence spectra of alkyne- (a), azide- (b), and non-functionalized rhodamine B (c).

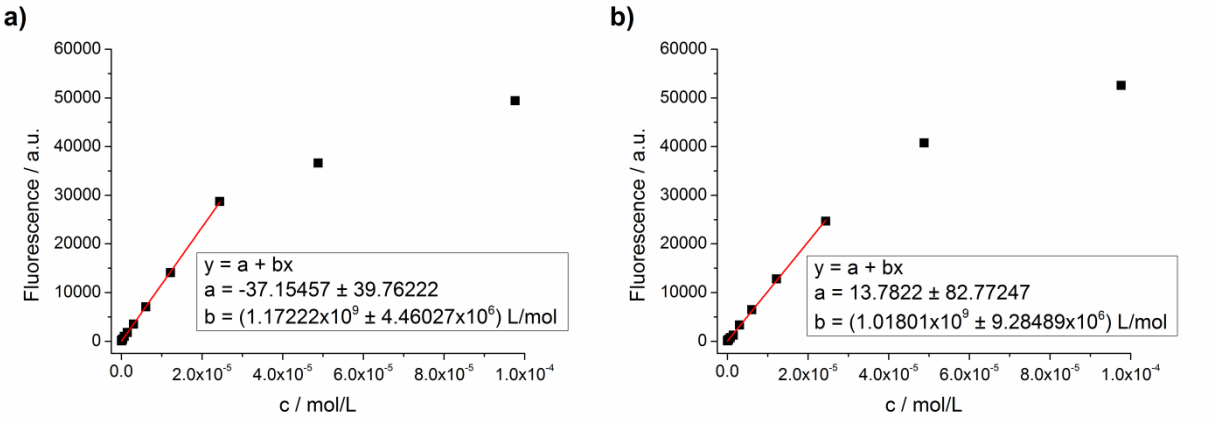

Fig. S11 Calibration curves for the quantification of the functional groups on the surface of the Janus particles. The fluorescence intensity in dependence of the concentration of a) alkyne-functionalized rhodamine B; b) azide-functionalized rhodamine B.

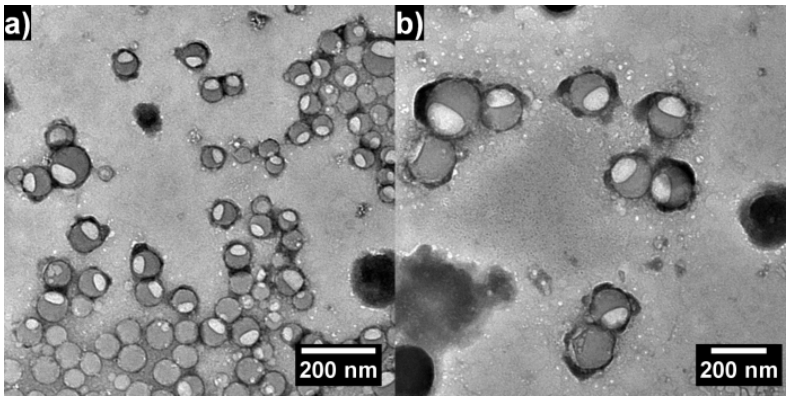

Fig. S12 TEM micrographs of Janus particles prepared from pure PS and pure PMMA with a 0.1 wt.-% (a) and a 0.01 wt.-% (b) solution of the surfactant.