Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Improved Alkali Metal Ion Capturing utilizing Crown ether-based Diblock Copolymers in a Sandwich-type complexation

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Experimental Section

Materials

2′,4′,5′,7′-tetrabromoeosin ethyl ester sodium salt (>99%, NaEE, Waldeck, Münster, Germany), 2′,4′,5′,7′-tetrabromoeosin ethyl ester potassium salt (>99%, KEE, Carl Roth, Karslruhe, Germany), lithium 3,5-diidosalicylate (>99%, LIS, Sigma-Aldrich, Schnelldorf, Germany), catechol (99%, Sigma-Aldrich, Schnelldorf, Germany), Bis-2-chloroethylether (99%, TCI Chemicals, Eschborn, Germany), benzo-15-crown-5 (98%, B15C5, TCI Chemicals, Eschborn, Germany), benzo-12-crown-4 (98%, B12C4, TCI Chemicals, Eschborn, Germany), 12-crown-4-hydroxyl (12C4-OH, Sigma-Aldrich, Schnelldorf, Germany), 15-crown-5-hydroxyl (15C5-OH, Sigma-Aldrich, Schnelldorf, Germany), hexamethylenetetramine (98%, Sigma-Aldrich, Schnelldorf, Germany), sodium borohydride (98%, B15C5, Sigma-Aldrich, Schnelldorf, Germany), dicyclohexylcarbodiimid (98%, DCC, Sigma-Aldrich, Schnelldorf, Germany), 4-(dimethylamino)-pyridin (98%, DMAP, Sigma-Aldrich, Schnelldorf, Germany), 1-propanethiol (99%, Sigma-Aldrich, Schnelldorf, Germany), MAA (>99%, Merck, Darmstadt, Germany), potassium hydroxide (KOH) (85%, Merck, Darmstadt, Germany), carbon disulfide (CS2) (99%, Merck, Darmstadt, Germany), *p*-tosyl chloride (98%, Merck, Darmstadt, Germany), 4,4-azobis(4-cyanovaleric acid) (ACVA) (>98%, Sigma-Aldrich, Schnelldorf, Germany), *N*,*N*-dimethylformamide (DMF) (99%, VWR Chemicals, Darmstadt, Germany), tetrahydrofuran (THF) (>99%, VWR Chemicals, Darmstadt, Germany), styrene (99%, Grüssing, Filsum, Germany), dichloromethane (DCM) (>99%, Acros, Schwerte, Germany), acetone (>99%, Merck, Darmstadt, Germany), *n*-hexane (95%, VWR Chemicals, Darmstadt, Germany), chloroform-d_1 (>99%, EurisoTop, Saarbrücken, Germany), THF-d_8 (>99%, Euriso-Top), dimethylsulfoxide-d_6 (>99%, Germany), deuterium oxide (D_2O) (>99%, Euriso-Top, Saarbrücken, Germany), trifluoroacetic acid (TFA) (99%, TCI Chemicals, Eschborn, Germany), $NaHCO_3$ (>99%, Grüssing, Filsum, Germany), Mg_2SO_4 (>99%, Grüssing, Filsum, Germany), and activated basic aluminum oxide (>99%, grain size between 0.063–0.200 mm, Merck, Darmstadt, Germany) were used as received without further purification unless noted otherwise. Styrene was purified by filtration through basic activated aluminum oxide to remove the inhibitor. Deionized water was purified with a Milli-Q® integral water purification system. The subscripts in the designation of the polymers represent the fraction of the respective block in wt% and the superscript represents the overall molecular weight in kDa.

General Methods

NMR spectroscopy

^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using a 300 or 400 MHz Bruker AVANCE II spectrometer in either $CDCl_3$-d_1, D_2O or THF-d_8. The residual signals at δ = 7.26 for $CDCl_3$-d_1, δ = 4.80 ppm for D_2O and δ = 3.58 ppm for THF-d_8 were used as an internal standard for the chemical shifts.

UV-vis spectroscopy

The UV-Vis spectra were recorded with a spectrophotometer UV5 from METTLER TOLEDO at room temperature. The sample was measured from 190 to 1100 nm. The scan time was 10 s.

The synthetic procedures, the two-phase extraction, as well as a more detailed calculation of the complex constant K were published elsewhere.[1]

Reaction Overviews

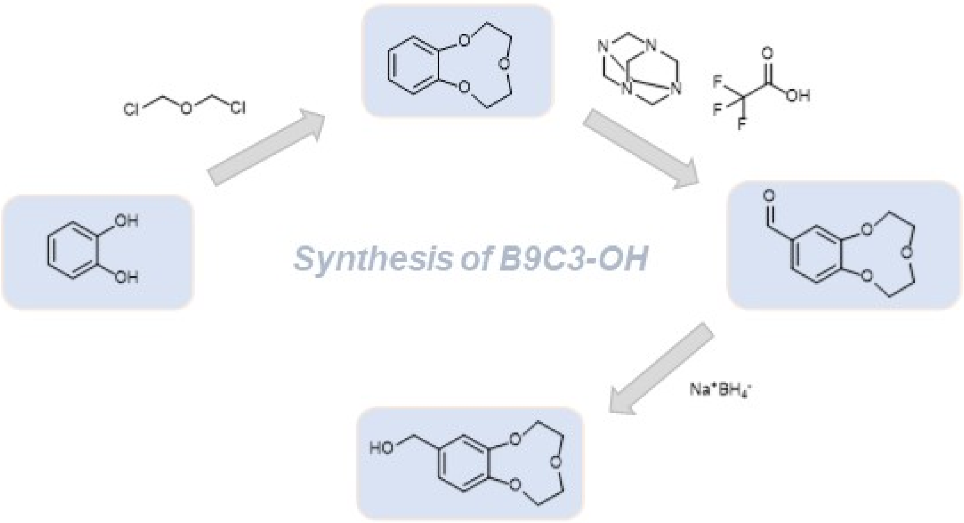

Fig. S1: Reaction overview of the B9C3-OH functionalization starting from catechol.

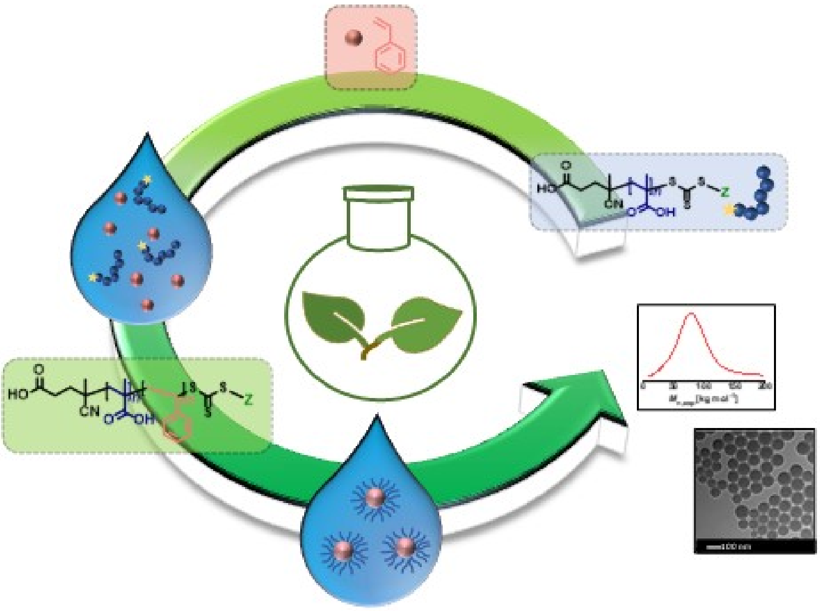

Fig. S2: Reaction overview of the one-pot PMAA-*b*-PS RAFT emulsion polymerization using water and achieving well-controlled reactions conditions.

Calibration Curves of the Salt Dyes

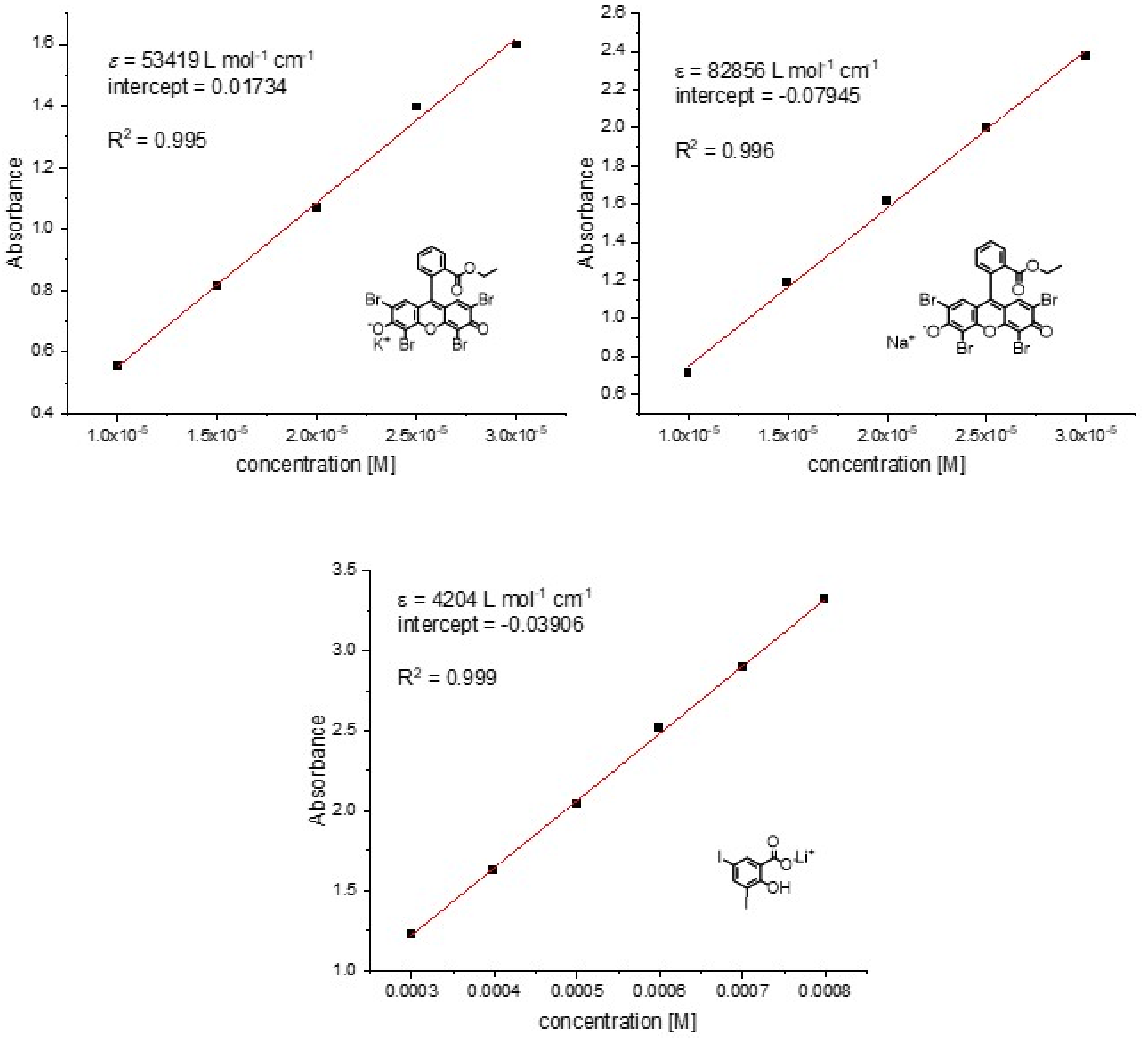

Fig. S3: Example calibration curves of the used salt dyes 2′,4′,5′,7′-tetrabromoeosin ethyl ester potassium, 2′,4′,5′,7′-tetrabromoeosin ethyl ester sodium and lithium 3,5-diidosalicylate salt.

NMR spectra of the crown ethers and the polymer-based crown ethers

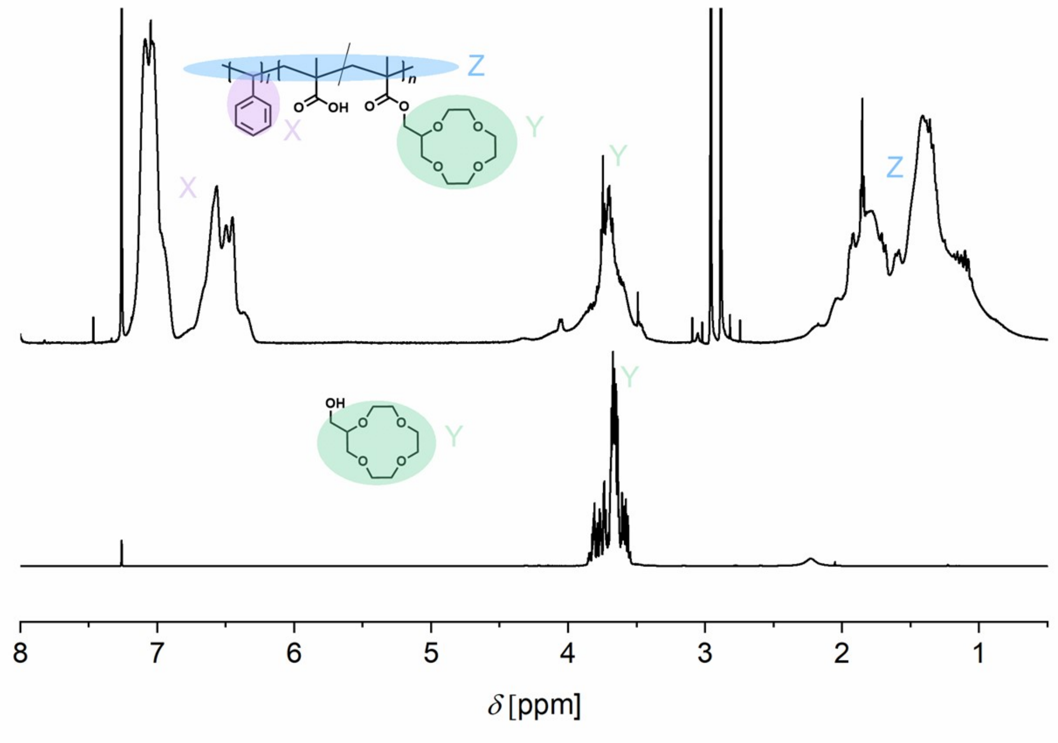

Fig. S4: ^{1}H NMR spectrum of 12C4-OH (bottom) and P(MAA$_{21}$-*r*-12C4MA$_{19}$)-*b*-PS$_{60}$$^{48.6}$ diblock copolymer containing randomly distributed CE units (top) in CDCl$_3$.

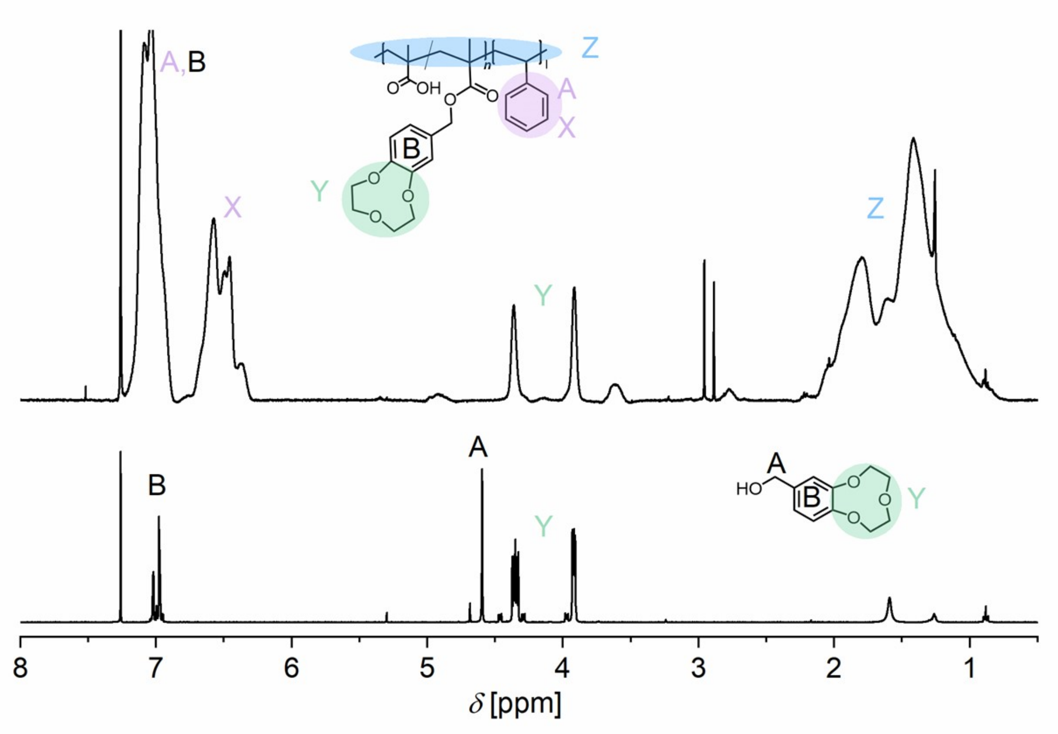

Fig. S5: ^{1}H NMR spectrum of B9C3 (bottom) and P(MAA$_{20}$-*r*-B9C3MA$_{20}$)-*b*-PS$_{60}$$^{49.1}$ diblock copolymer containing randomly distributed CE units (top) in CDCl$_3$.

Determination of the Degree of Functionalization

The theoretical molecular weights of all polymers are calculated from the following Eq. 1:[2]

$$M_{n,th} = \frac{[M]_0 \cdot p \cdot M_M}{[CTA]_0} + M_{CTA} \tag{1}$$

where $[M]_0$ and $[CTA]_0$ are the initial concentrations of monomer and chain transfer agent, p the monomer conversion and M_M and M_{CTA} are the molar masses of monomer and chain transfer agent. For calculating the degree of polymerization (DP) for PMAA or PS the molecular weight of the polymer block is divided by the formula weight of the repeating unit.

The average number of CE-esterified repeating units per chain will be called n_{CE} – not "degree of polymerization" which would, by definition, be incorrect in a statistical copolymer block. n_{CE} is calculated from ^{1}H NMR spectroscopy and given by Eq. 2.

$$n_{CE} = \frac{\int Y / H_Y}{\int X / H_X} \cdot DP_{PS} \tag{2}$$

The integral X corresponds to the phenyl protons of PS, integral Y corresponds to characteristic protons of the CE (see Fig. S4) and H_x and H_y to the corresponding protons of one respective repeating unit. DP_{PS} labels the DP of PS.

With the known DP of the PMAA (from Eq. 1, before esterification reaction) the degree of functionalization (DF) can be determined by Eq. 3.

$$\frac{n_{CE}}{DP_{PMAA}} = DF \tag{3}$$

References

1 I. Oral and V. Abetz, *Macromol. Rapid Commun.*, 2021, **42**, 2000746.

2 S. Perrier, *Macromolecules*, 2017, **50**, 7433–7447.