

Electronic Supplementary Information

**Synthesis of tailor-made bile acid sequestrants
by supplemental activator and reducing agent
atom transfer radical polymerization**

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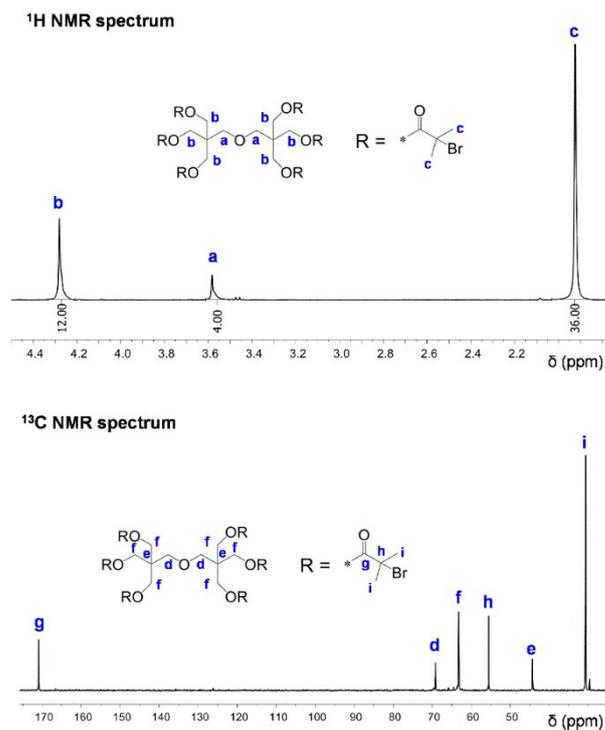


Figure S1. ¹H (top) and ¹³C (bottom) NMR spectra, in CDCl₃, of the synthesized 6f-BiB initiator.

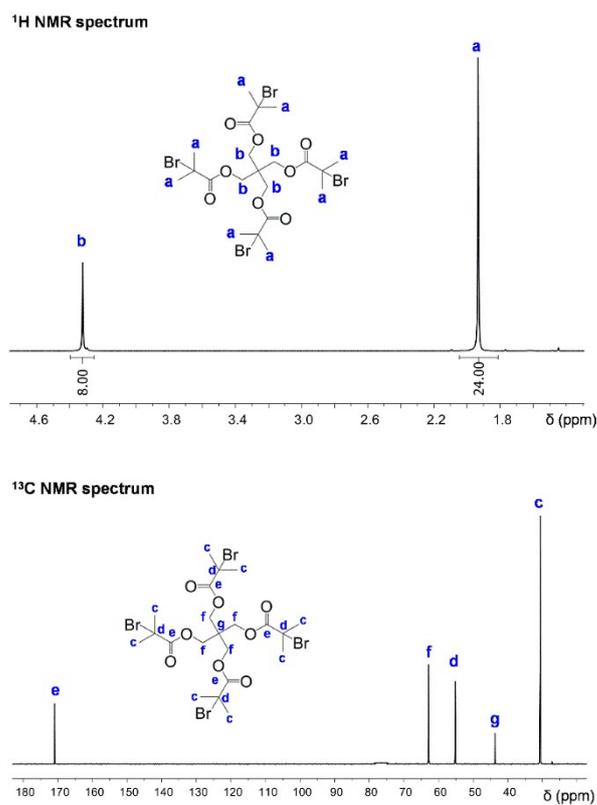


Figure S2. ¹H (top) and ¹³C (bottom) NMR spectra, in CDCl₃, of the synthesized 4f-BiB initiator.

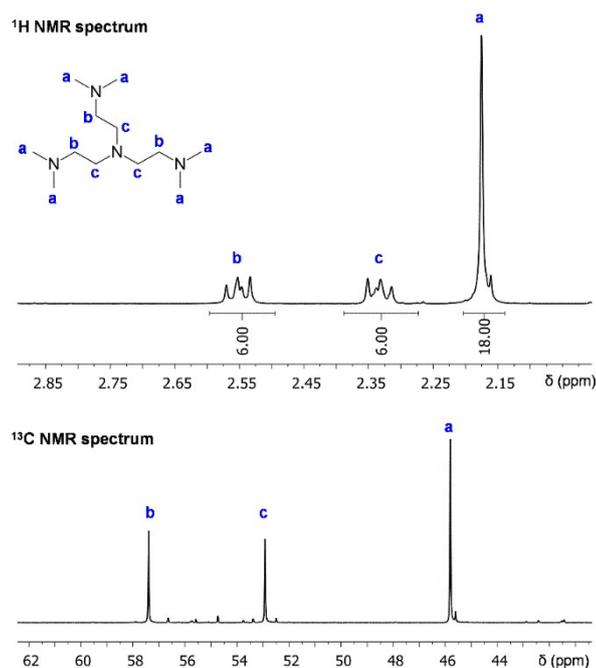


Figure S3. ^1H (top) and ^{13}C (bottom) NMR spectra, in CDCl_3 , of the synthesized Me_6TREN ligand.

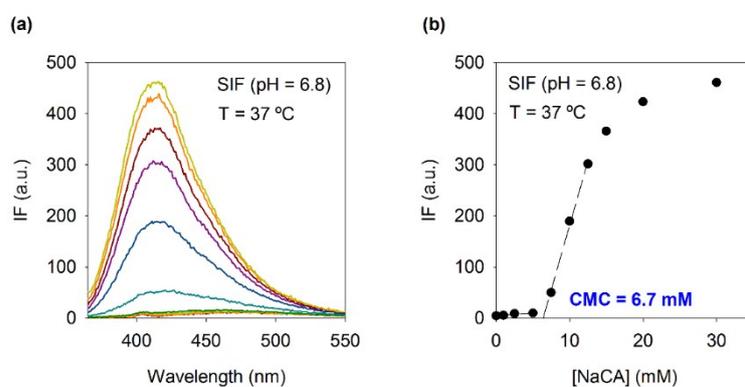


Figure S4. (a) Fluorescent emission spectra of $1\ \mu\text{M}$ NPN at increasing concentrations of NaCA (ranging from 0 to 30 mM) in SIF at $\text{pH} = 6.8$ at $37\ ^\circ\text{C}$ (excitation wavelength of 356 nm) and (b) fluorescence intensity at 411.06 nm for the different concentrations of NaCA investigated. The CMC was determined from the intersection of the extrapolated fit of the two different regimes (dashed lines in plot (b)).

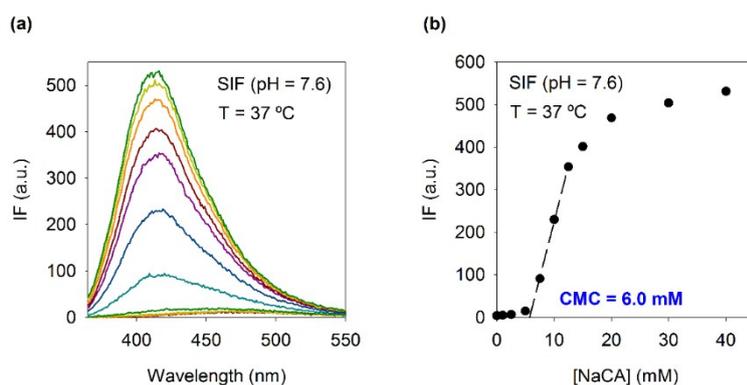


Figure S5. (a) Fluorescent emission spectra of 1 μM NPN at increasing concentrations of NaCA (ranging from 0 to 30 mM) in SIF at pH = 7.6 at 37 $^{\circ}\text{C}$ (excitation wavelength of 356 nm) and (b) fluorescence intensity at 411.06 nm for the different concentrations of NaCA investigated. The CMC was determined from the intersection of the extrapolated fit of the two different regimes (dashed lines in plot (b)).

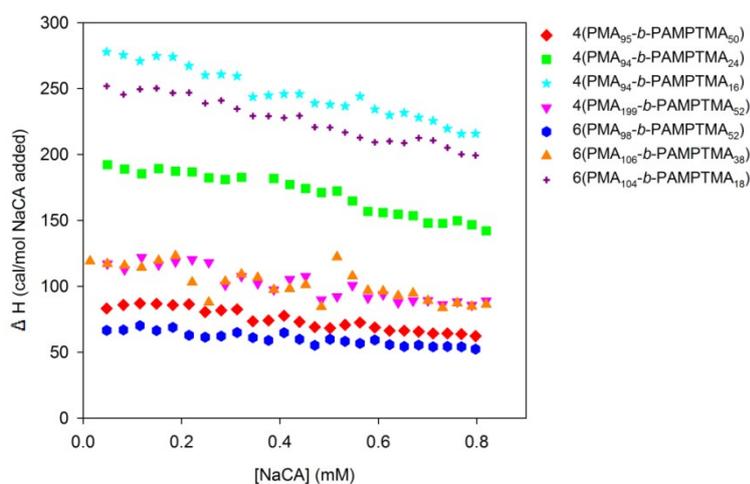


Figure S6. ITC titration curves obtained for the binding of NaCA by amphiphilic star block copolymers in Tris buffer (with 150 mM of NaCl). Conditions: T = 37 $^{\circ}\text{C}$; 459 rpm; $[\text{NaCA}]_{\text{syringe}} = 5 \text{ mM}$; $[4(\text{PMA}_{95}\text{-}b\text{-PAMPTMA}_{50})]_{\text{cell}} = 0.05 \text{ mM}$; $[4(\text{PMA}_{94}\text{-}b\text{-PAMPTMA}_{24})]_{\text{cell}} = 0.10 \text{ mM}$; $[4(\text{PMA}_{94}\text{-}b\text{-PAMPTMA}_{16})]_{\text{cell}} = 0.16 \text{ mM}$; $[4(\text{PMA}_{199}\text{-}b\text{-PAMPTMA}_{52})]_{\text{cell}} = 0.05 \text{ mM}$; $[6(\text{PMA}_{98}\text{-}b\text{-PAMPTMA}_{52})]_{\text{cell}} = 0.03 \text{ mM}$; $[6(\text{PMA}_{106}\text{-}b\text{-PAMPTMA}_{38})]_{\text{cell}} = 0.04 \text{ mM}$; $[6(\text{PMA}_{104}\text{-}b\text{-PAMPTMA}_{18})]_{\text{cell}} = 0.09 \text{ mM}$.

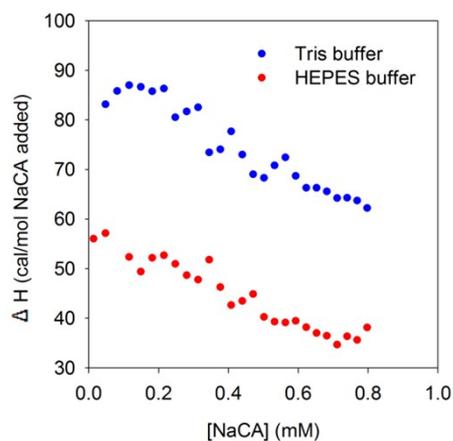


Figure S7. ITC titration curves obtained at 37 °C (459 rpm) for the binding of NaCA (5 mM) by an amphiphilic star block copolymer sample (4(PMA₉₅-*b*-PAMPTMA₅₀) (0.05 mM) in Tris buffer (blue symbols) or HEPES buffer (red symbols). The buffers contained 150 mM of NaCl.

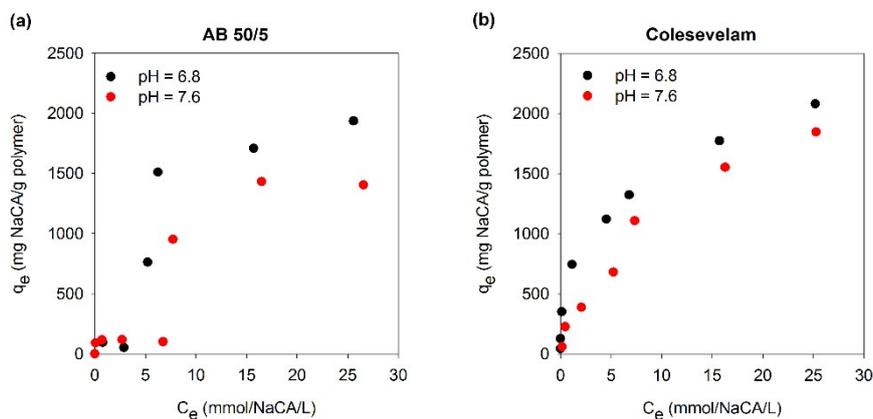


Figure S8. Isotherms for the binding of NaCA by the (a) AB 50/5 hydrogel prepared by SARA ATRP and (b) Colesevelam at pH = 7.6 (red symbols) and pH = 6.8 (black symbols). Binding conditions: 50 mM phosphate buffer at 37 °C.

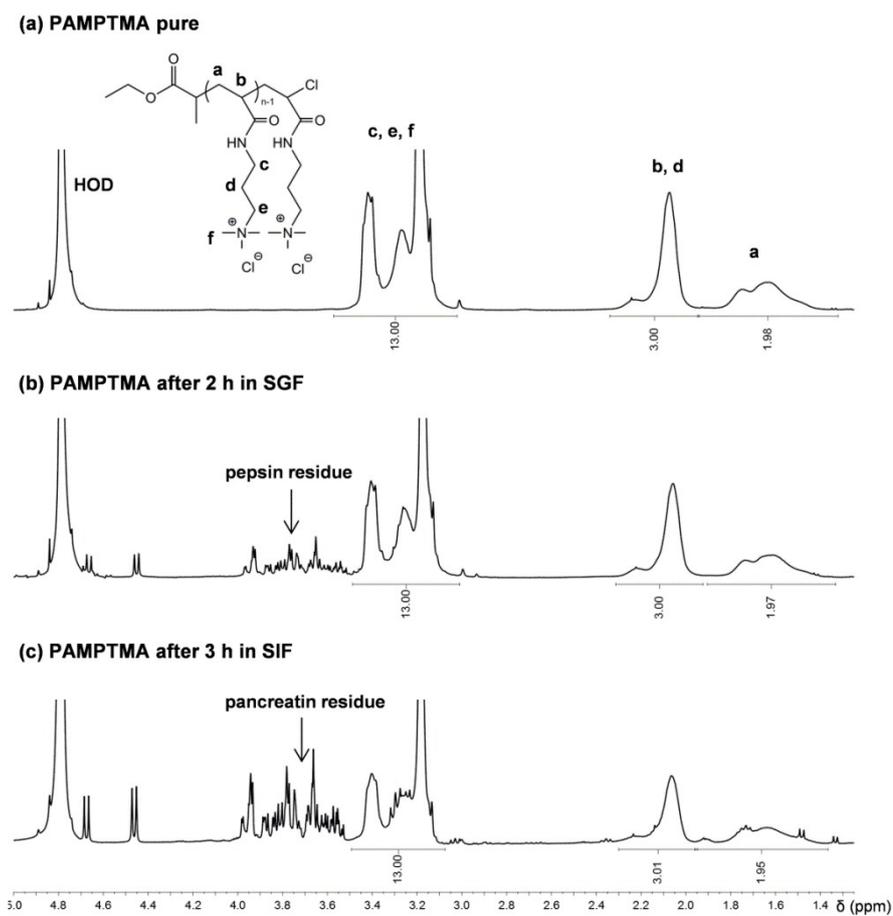
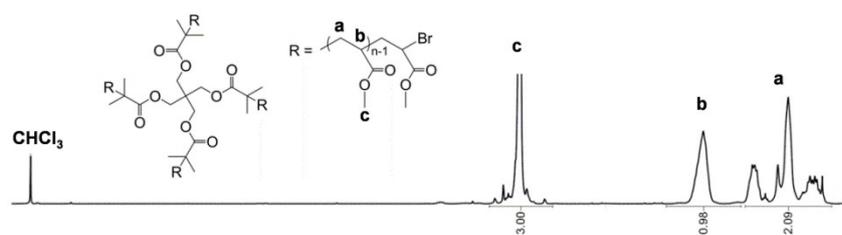


Figure S9. ^1H NMR spectra, in D_2O , of the linear PAMPTMA before and after degradation in SIF or SGF at 37°C .

(a) star-shaped PMA pure



(b) star-shaped PMA after 2 h in SGF



(c) star-shaped PMA after 3 h in SIF

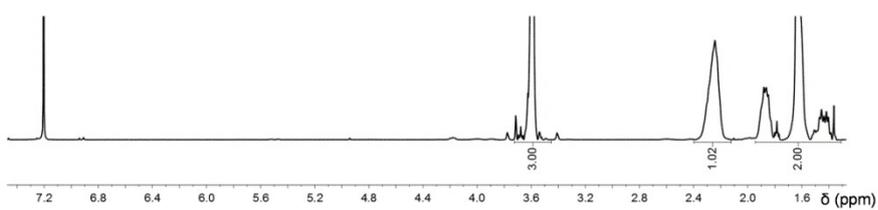


Figure S10. ^1H NMR spectra, in CDCl_3 , of the star-shaped PMA before and after degradation in SIF or SGF at 37 °C.