

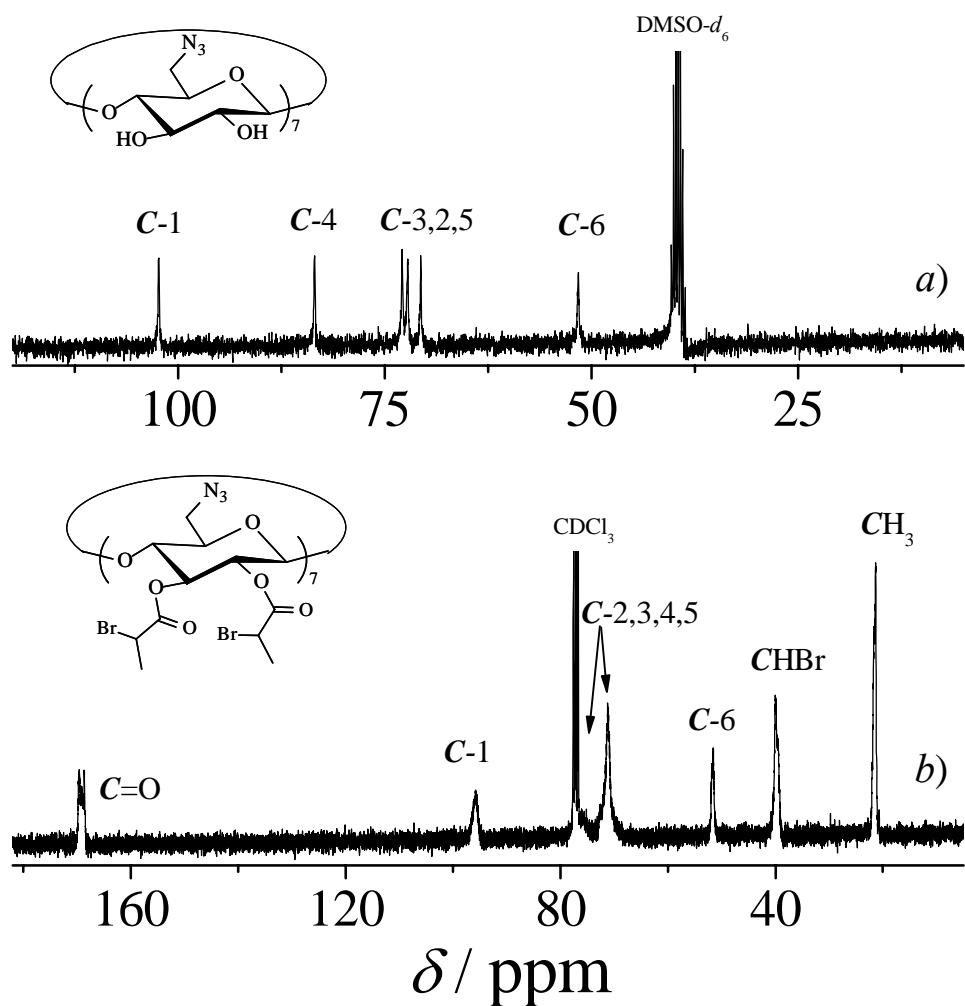
## Supporting Information

# Synthesis and Supramolecular Self-Assembly of Stimuli-Responsive Water-Soluble Janus-Type Heteroarm Star Copolymers

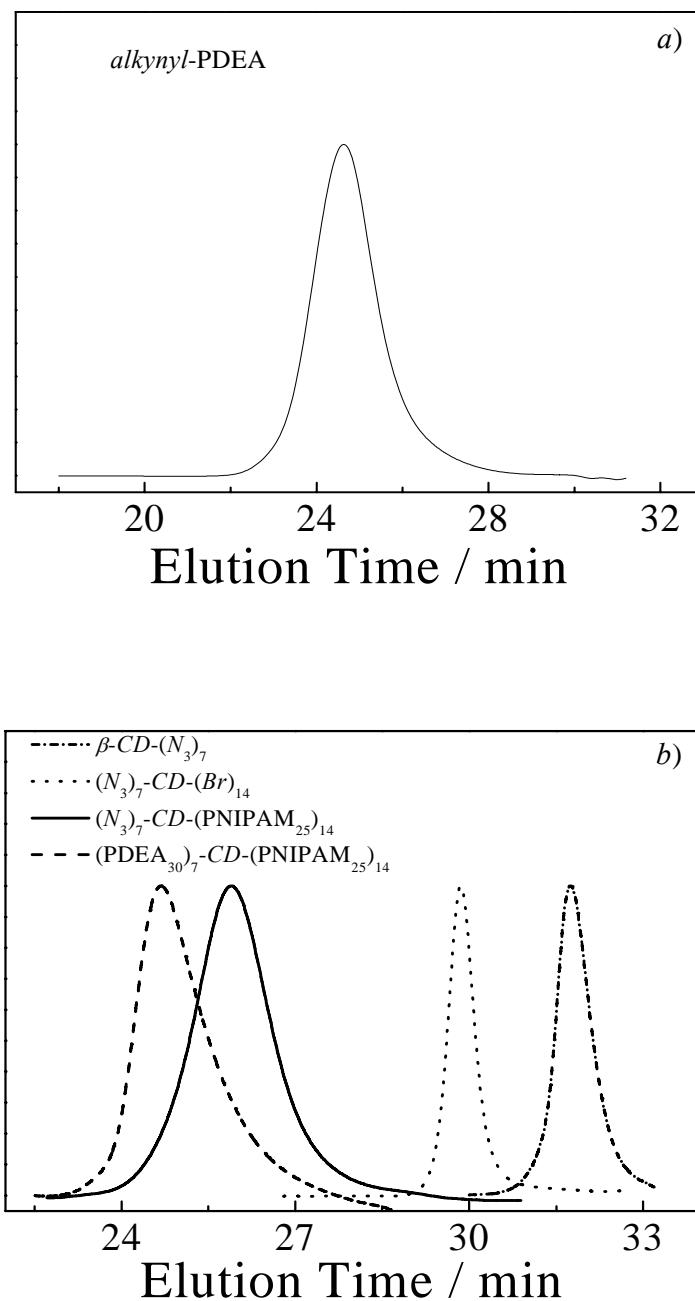
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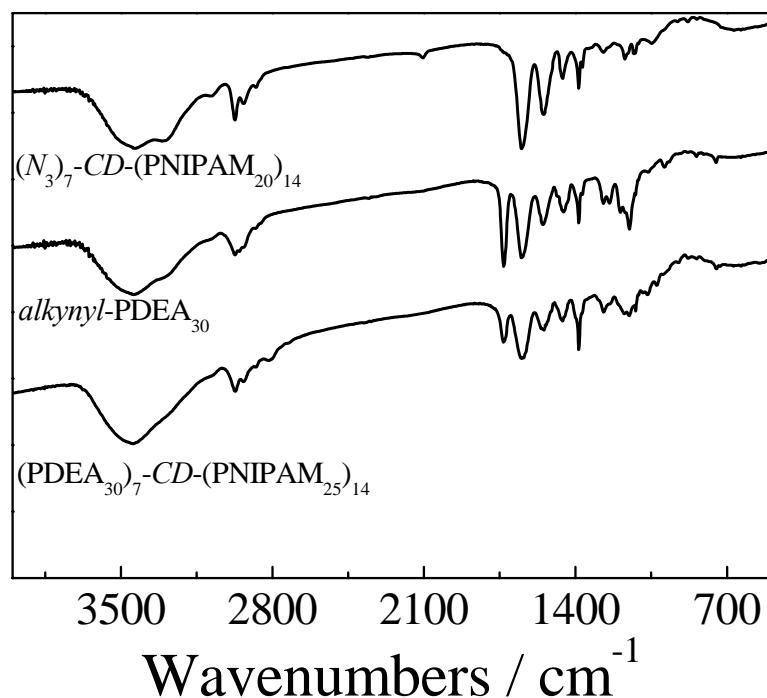
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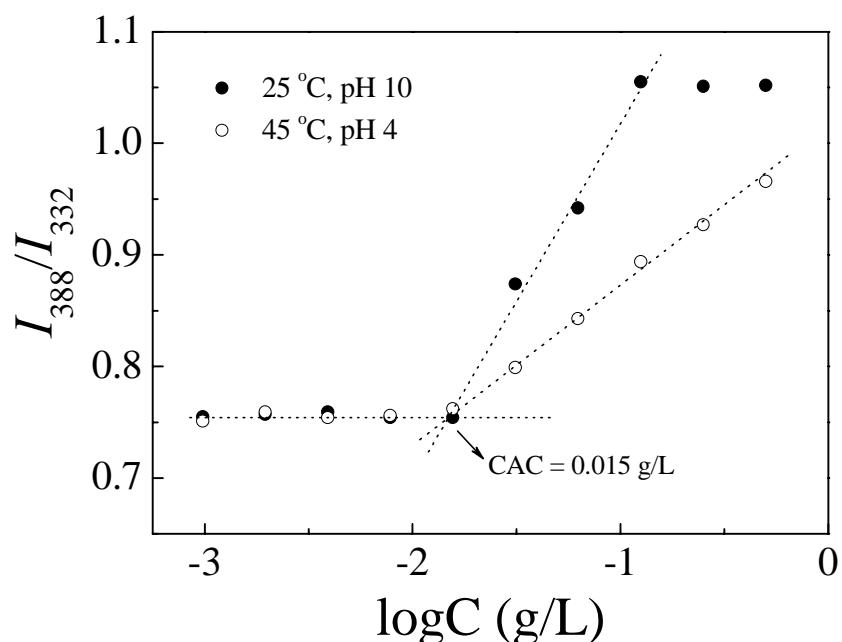
**Figure S1.**  $^{13}\text{C}$  NMR spectra recorded for (a)  $\beta$ -CD- $(\text{N}_3)_7$  precursor in DMSO- $d_6$  and (b)  $(\text{N}_3)_7$ -CD- $(\text{Br})_{14}$  precursor in CDCl<sub>3</sub>.



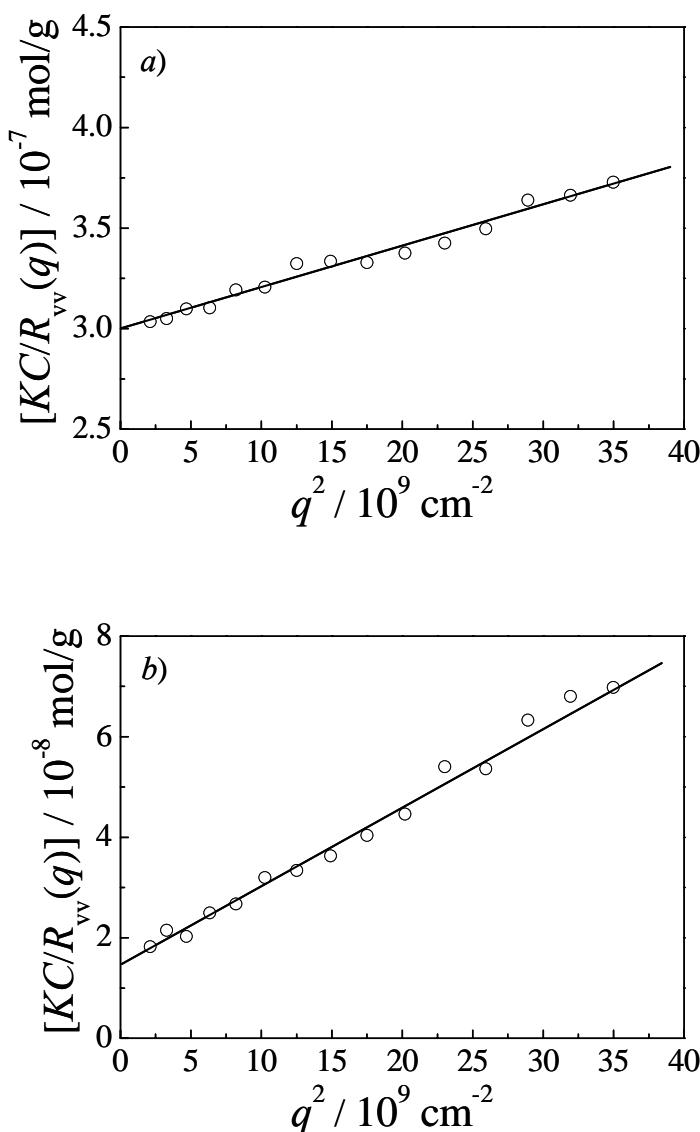
**Figure S2.** (a) THF GPC trace of *alkynyl*-PDEA<sub>30</sub> precursor and (b) DMF GPC traces of  $\beta\text{-}CD\text{-(}N_3\text{)}_7$ ,  $(N_3)_7\text{-}CD\text{-(}Br\text{)}_{14}$  precursor,  $(N_3)_7\text{-}CD\text{-(PNIPAM}_{25}\text{)}_{14}$ , and double hydrophilic Janus-type A<sub>7</sub>B<sub>14</sub> star polymer,  $(PDEA_{30})_7\text{-}CD\text{-(PNIPAM}_{25}\text{)}_{14}$ .



**Figure S3.** FT-IR spectra obtained for  $(N_3)_7\text{-}CD\text{-}(PNIPAM}_{25}\text{)}_{14}$ , *alkynyl-PDEA*<sub>30</sub>, and  $(PDEA}_{30}\text{)}_7\text{-}CD\text{-}(PNIPAM}_{25}\text{)}_{14}$ .



**Figure S4.** Plot of the intensity ratios,  $I_{388}/I_{332}$ , from pyrene excitation spectra as a function of the concentrations of  $(\text{PDEA}_{30})_7\text{-CD-(PNIPAM}_{25}\text{)}_{14}$  in aqueous solution at different conditions:  $25^\circ\text{C}$  and pH 10;  $45^\circ\text{C}$  and pH 4. Pyrene concentration was fixed at  $5 \times 10^{-7}$  M.



**Figure S5.** Angular dependence (over a scattering angle range of  $20\text{-}90\text{ }^\circ$ ) of the Rayleigh ratio,  $R_{vv}(q)$ , obtained for the aqueous dispersion of  $(\text{PDEA}_{30})_7\text{-CD-(PNIPAM}_{25}\text{)}_{14}$  at different conditions: (a)  $25\text{ }^\circ\text{C}$  and  $\text{pH } 10$ ; (b)  $\text{pH } 4$  and  $45\text{ }^\circ\text{C}$ .