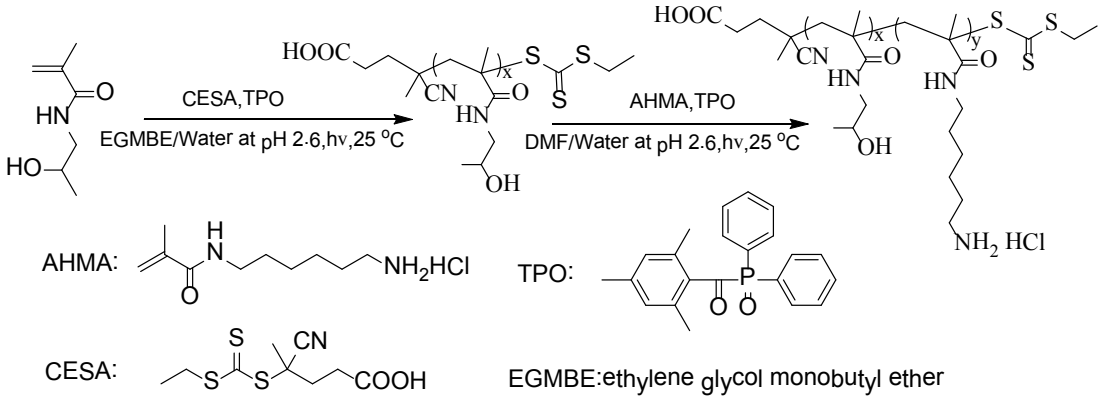
Subcomponent self-assembly of polymer chains based on dynamic and geometrical coordination diversity of the first row transition metal ions

Xuewen Wu,[a] Na Xu,[b] Zhengguang Zhu,[b] Yuanli Cai,*[,a,b] Ying Zhao*[,c] and Dujin Wang[c]

Electronic Supplementary Information

Synthesis of the targeted PHPMA-*b*-PAHMA copolymers

As shown in **Scheme S1**, poly(*N*-2-hydroxypropyl methacrylamide)-*block*-poly(*N*-6-aminohexyl methacrylamide hydrochloride) ($PHPMA_{69}$-*b*-$PAHMA_{70}$) was synthesized *via* aqueous RAFT polymerisation of HPMA monomer, and then the chain extension of AHMA monomer using an above-synthesized PHPMA macromolecular chain transfer agent (macro-CTA) under visible light irradiation at 25 °C.



Scheme S1. Synthesis of PHPMA-*b*-PAHMA copolymers *via* aqueous RAFT polymerization under visible light irradiation at 25 °C.

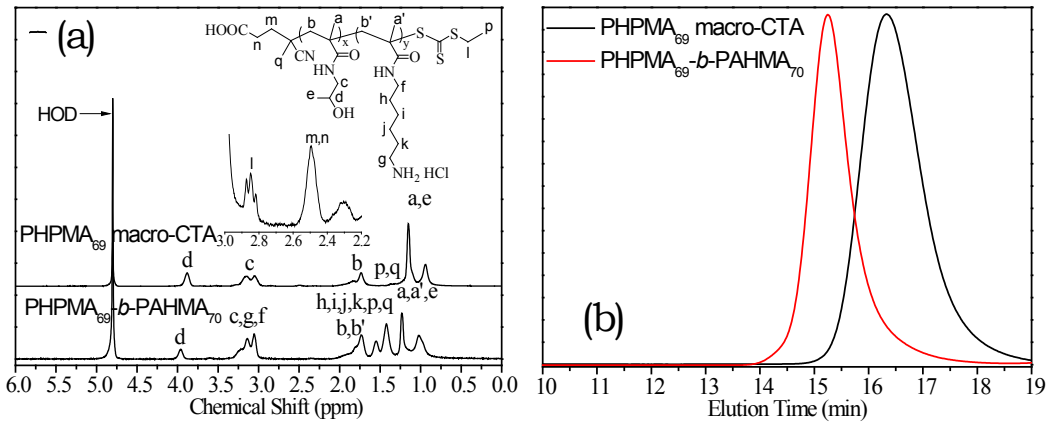


Fig. S1 ^{1}H NMR spectra (**a**) and GPC traces (**b**) of poly(*N*-2-hydroxypropylmethacrylamide) ($PHPMA_{69}$) and the corresponding block copolymer with poly(6-aminohexylmethacrylamide hydrochloride) ($PHPMA_{69}$-*b*-$PAHMA_{70}$).

As shown in **Fig. S1a**, except for **H**OD signal at δ = 4.79 ppm, no signal of other impurities could be detected. The integral ratio of $I_d : I_c : I_b : I_{a+e}$ of upper spectrum was equal to 1 : 2 : 2 : 6,

which was consistent with the proton ratio of the targeted PHPMA. Thus, the degree of polymerisation (DP_{PHPMA}) was assessed according to **Equation S1**, where I_d is the integral of the signal of $CH_3C\mathbf{H}OH$ in HPMA units and I_{m+n} is the signal $C\mathbf{H}_2C\mathbf{H}_2COOH$ at CESA chain-ends.

$$DP_{PHPMA} = \frac{4 \times I_d}{I_{m+n}} \qquad \text{(S1)}$$

$$DP_{AHMA} = \frac{I_{c+g+f} - 2I_d}{4I_d} \times DP_{HPMA} \qquad \text{(S2)}$$

The block copolymer composition was assessed according to **Equation S2**, where I_d is the integral of signal $CH_3C\mathbf{H}OH$ in HPMA units, I_{c+g+f} is the total integral of signals $CONHC\mathbf{H}_2$ in HPMA units and $CONHC\mathbf{H}_2$ $(CH_2)_4C\mathbf{H}_2NH_2$ in AHMA units.

As shown in **Fig. S1b**, these GPC traces were excellently unimodal and symmetrical, and clearly shifted to higher molecular weight side after the chain extension, suggesting the well-controlled and living character of this polymerisation. Accordingly, the molecular structure parameters are assessed as follows. PHPMA: DP_{HPMA} = 69 (^{1}H NMR); M_n = 9.20 kg mol^{-1}, M_w/M_n = 1.21 (GPC); Block copolymer: DP_{AHMA} = 70, $PHPMA_{69}$-*b*-$PAHMA_{70}$ (^{1}H NMR); M_n = 12.2 kg mol^{-1}, M_w/M_n = 1.12 (GPC).

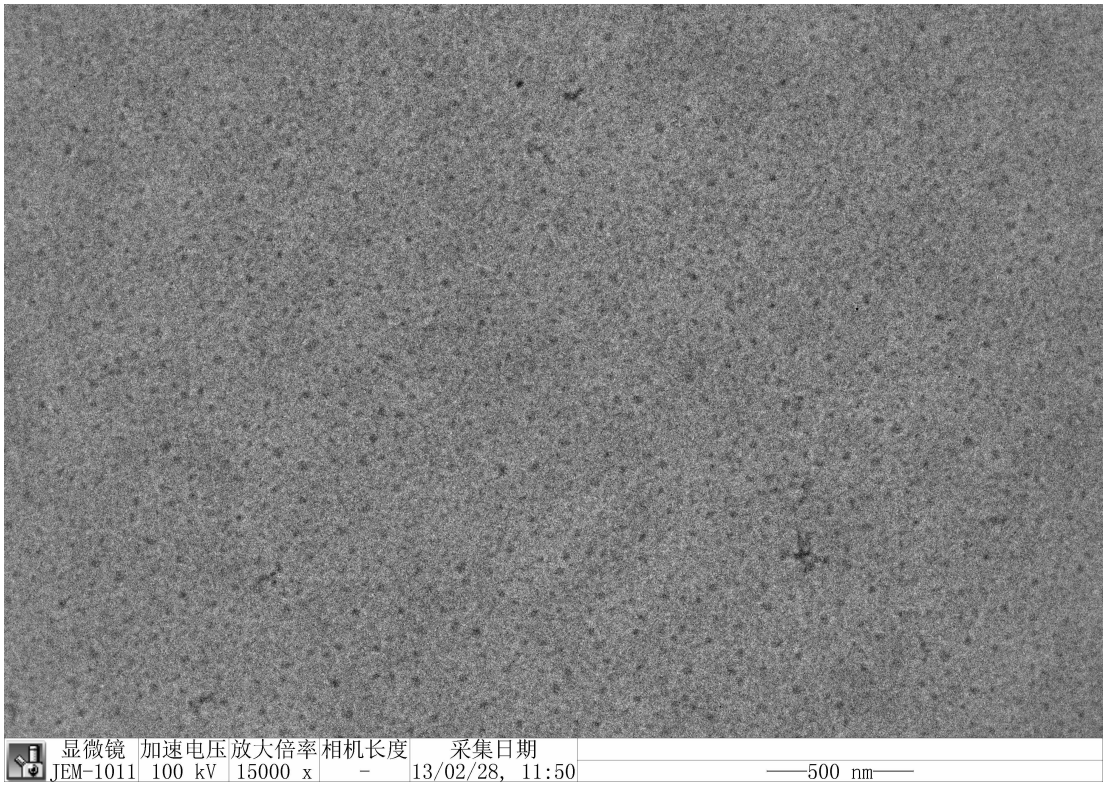


Fig. S2 TEM image of Zn(II)-bound particles formed after subcomponent self-assembly of $PHPMA_{69}$-*b*-$PAHMA_{70}$ solution (1.0 mg mL^{-1} in methanol) at a $[AHMA]_0$:$[HMBA]_0$:$[Zn(II)]_0$ = 1:1:0.5 at 25 ºC for 24 h.