

## *Supporting Information*

# Stimuli-responsive hyperbranched poly(amidoamine)s integrated with thermal and pH sensitivity, reducible degradability and intrinsic photoluminescence

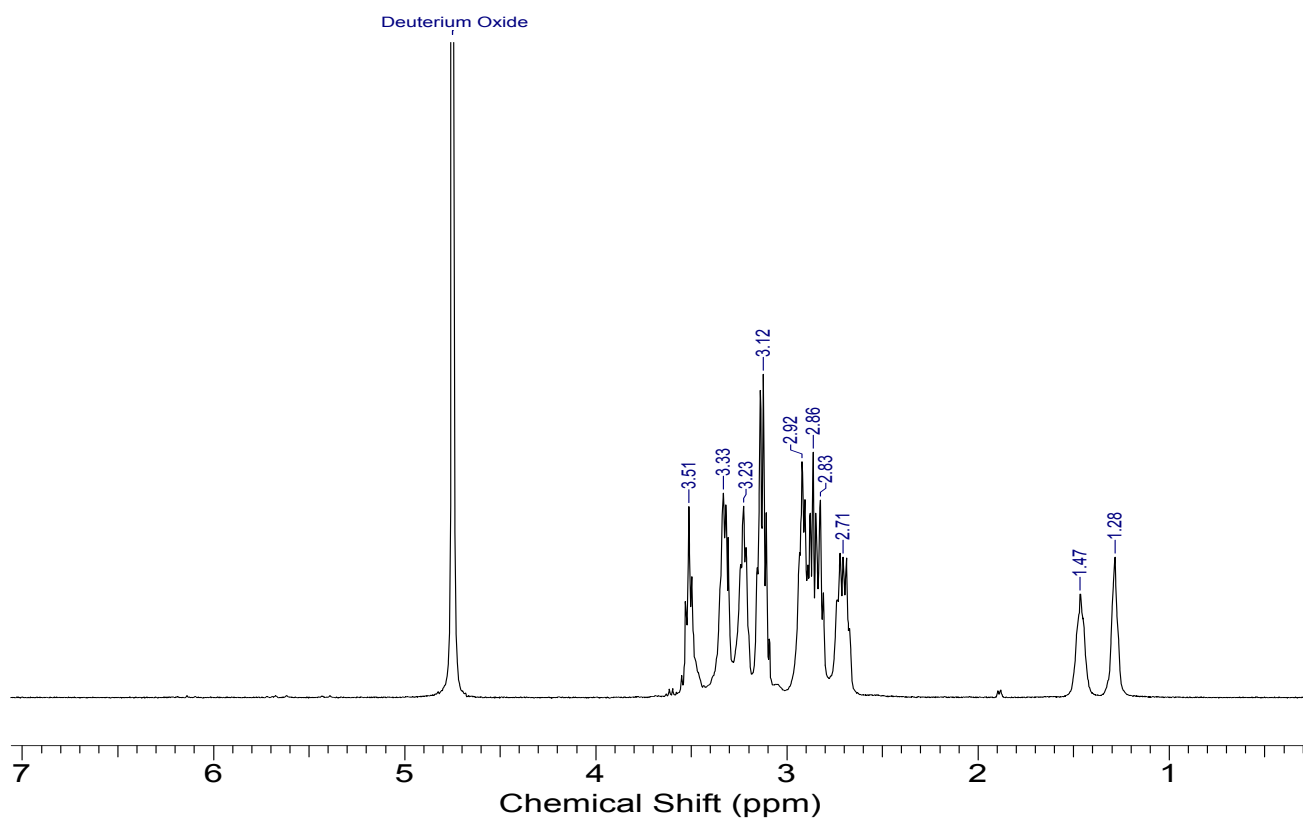
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**Fig. S1** Typical  $^1\text{H}$  NMR full spectrum of  $\text{HPA}\cdot\text{HCl}$  (HPA-S50 as the sample)

(X) in A-50 HCl

Chemical structure of the polymer repeat unit is shown above the spectrum:

$$\text{-(CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHOCCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH-)}_n$$

The structure is divided into two regions: HMBA (left) and TAEA (right).

**HMBA Region (3.5 to 2.5 ppm):**

- Peak **e** at 3.33 ppm (integral 3.99)
- Peak **d** at 3.15 ppm (integral 17.44)
- Peak **c** at 2.70 ppm (integral 3.91)

**TAEA Region (1.5 to 1.2 ppm):**

- Peak **b** at 1.47 ppm (integral 3.98)
- Peak **a** at 1.29 ppm (integral 4.00)

Chemical Shift (ppm)

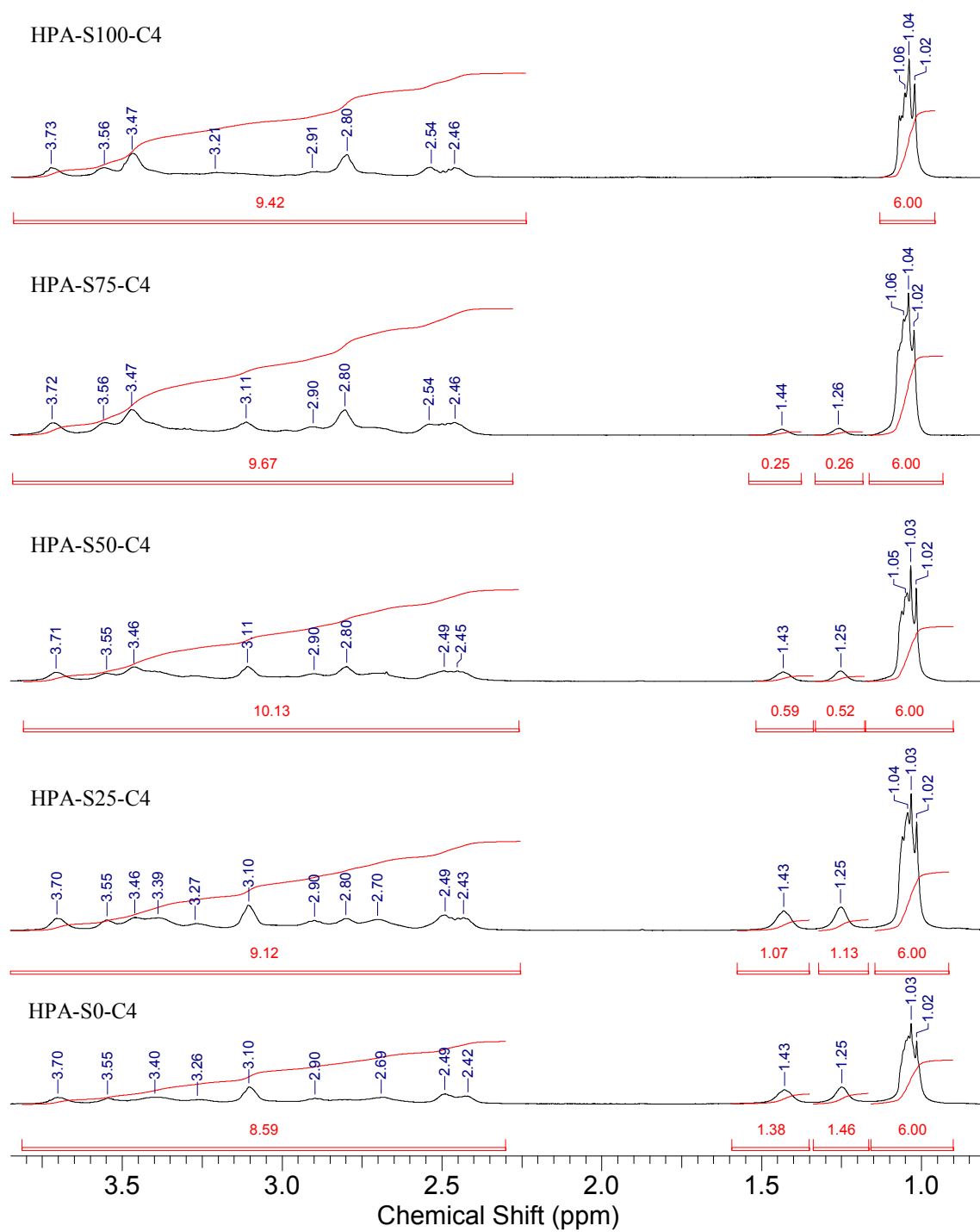
Chemical structure of the copolymer is shown above the spectrum:

$$\text{-CH}_2^{\text{b}}\text{CH}_2^{\text{a}}\text{CONHCH}_2^{\text{d}}\text{CH}_2^{\text{c}}\text{SSCH}_2^{\text{c}}\text{CH}_2^{\text{d}}\text{NHOCCCH}_2^{\text{a}}\text{CH}_2^{\text{b}}\text{NHCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH-}$$

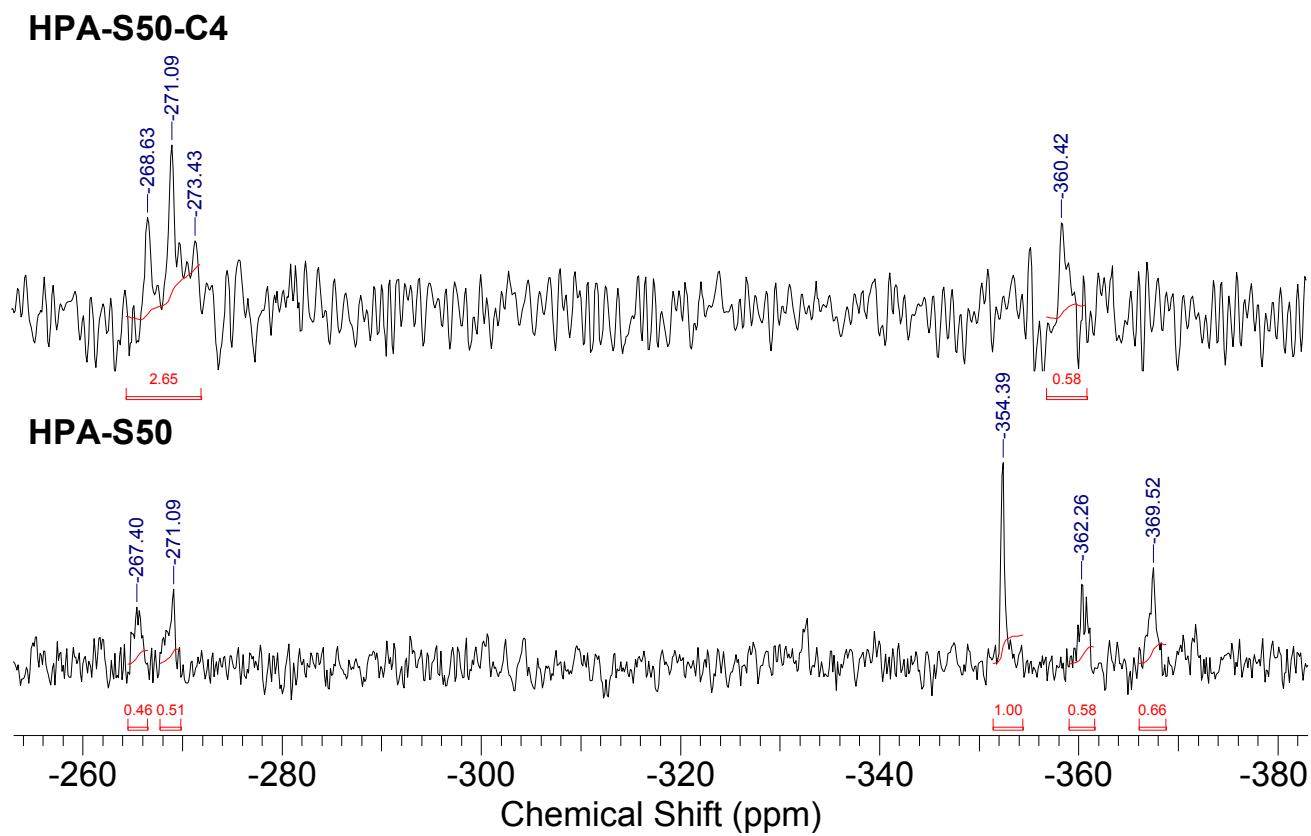
The spectrum shows peaks assigned to the protons in the structure:

- Peak d:** ~3.53 ppm (integral 4.00)
- Peak c:** ~3.36 ppm (integral 3.97)
- Peak b:** ~3.25 ppm (integral 4.01)
- Peak a:** ~3.14 ppm (integral 3.02)
- Peak c, TAEA unit:** ~3.14 ppm (integral 3.02)
- Peak b, c, TAEA unit:** ~3.14 ppm (integral 3.02)
- Peak a:** ~2.94 ppm (integral 4.00)
- Peak b:** ~2.88 ppm (integral 3.98)
- Peak c:** ~2.85 ppm (integral 4.10)
- Peak a:** ~2.75 ppm (integral 4.08)

**Fig. S2** Assignments of  $^1\text{H}$  NMR signals of  $\text{HPA} \cdot \text{HCl}$  ( $\text{HPA-S0}$  and  $\text{HPA-S100}$  as the representatives)



**Fig. S3**  $^1\text{H}$  NMR spectra of HPA-C4s



**Fig. S4** Comparison of the  $^{15}\text{N}$  NMR spectra of HPAs and HPA-C4s

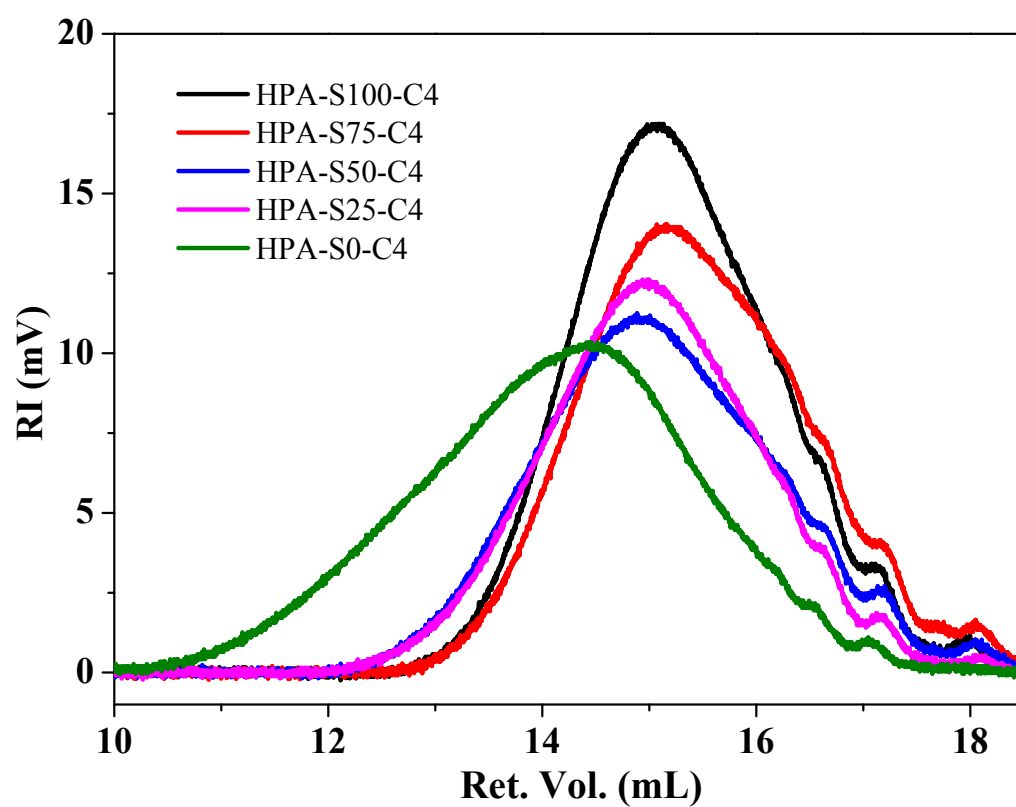
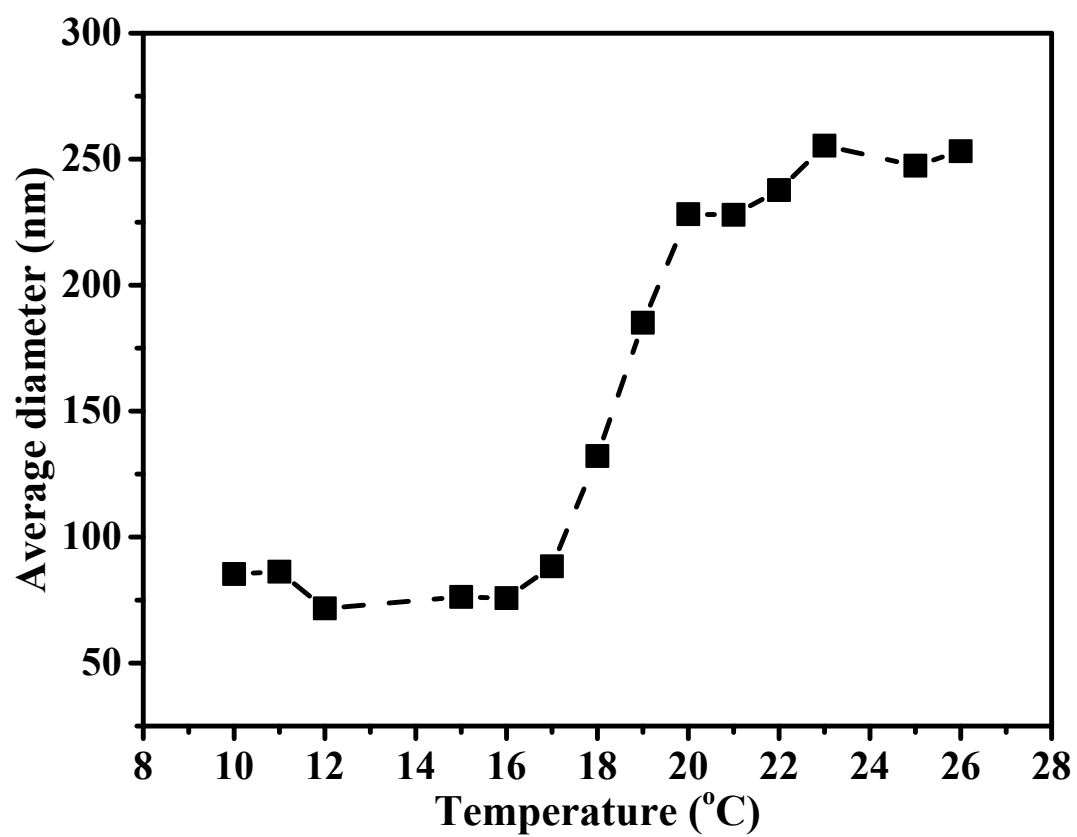
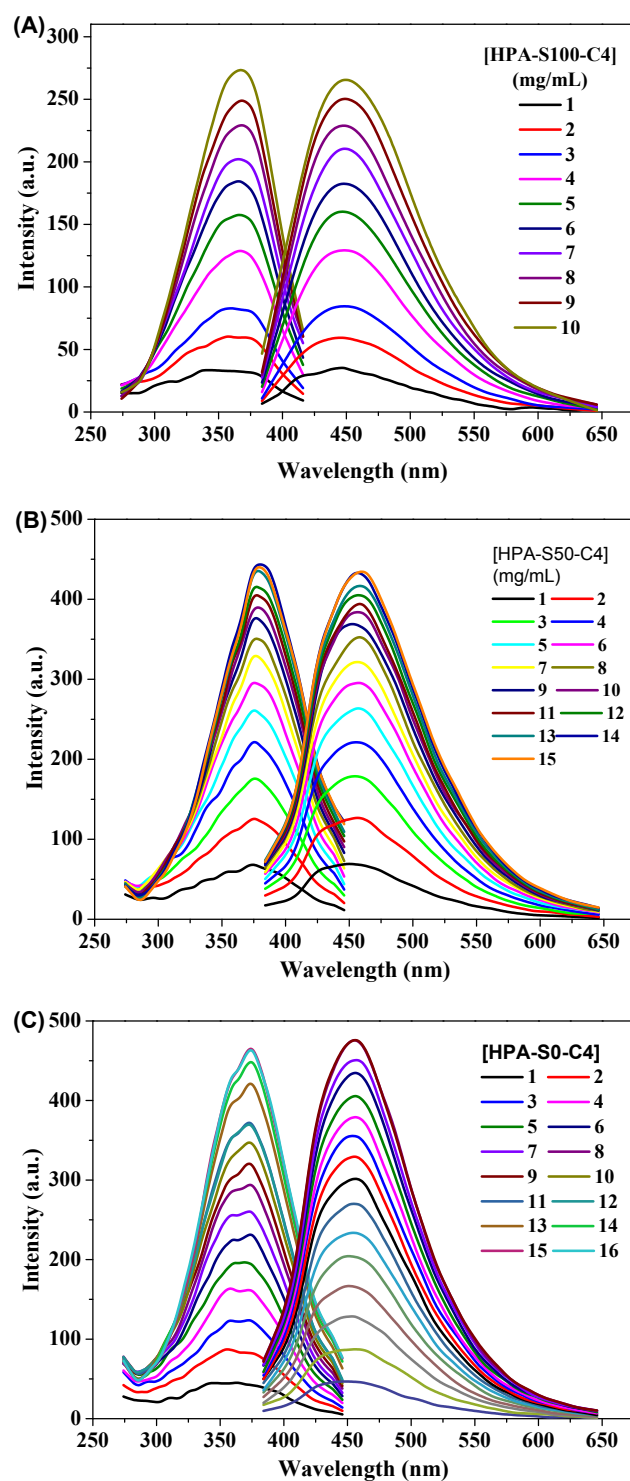


Fig. S5 GPC diagrams of HPA-C4s

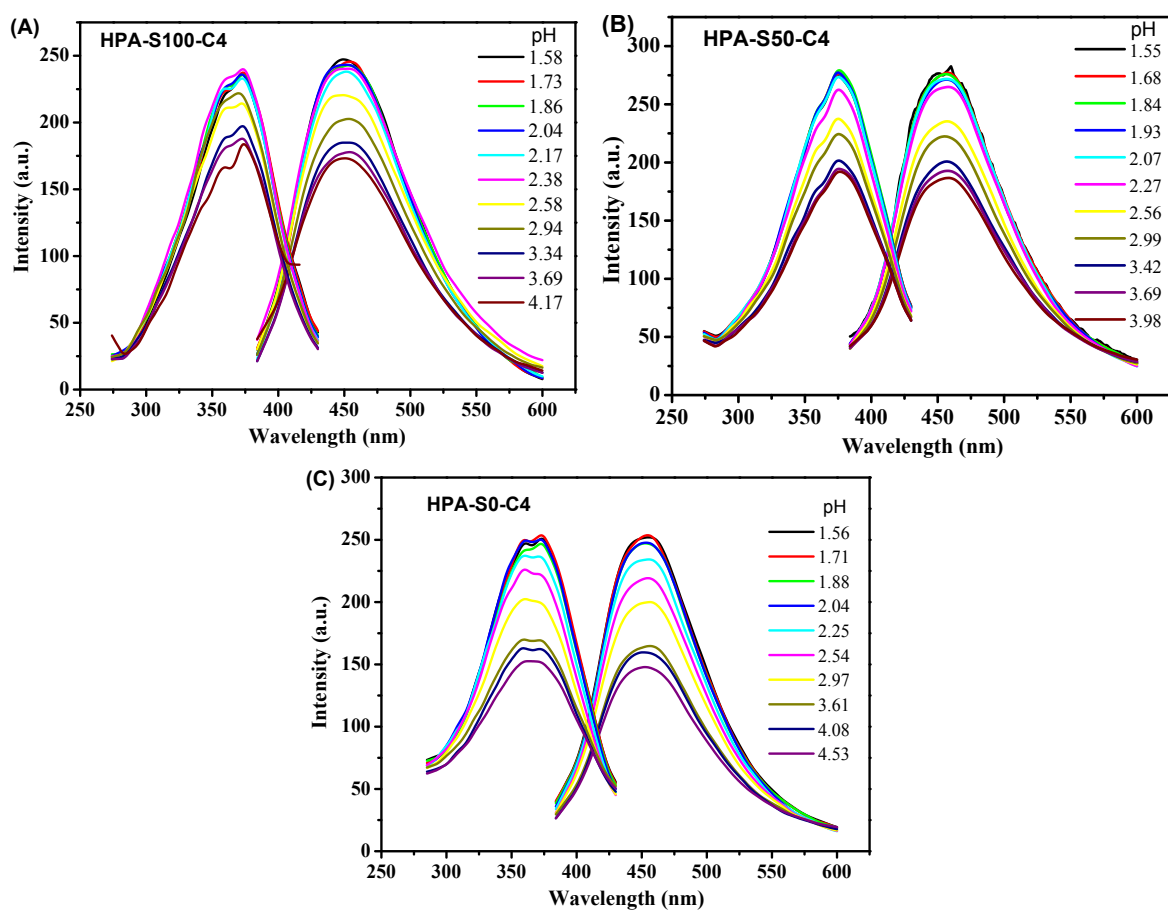


**Fig. S6** Temperature-dependent DLS curve of HPA-C4 aqueous solution (polymer concentration is 5 mg/mL).

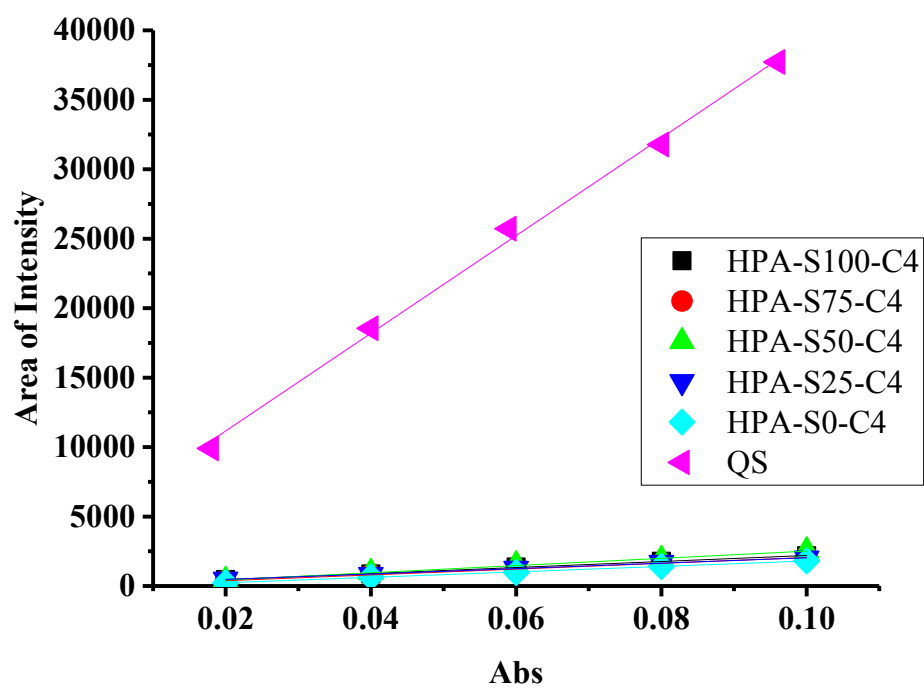


**Fig. S7** Typical fluorescence excitation and emission spectra of (A) HPA-S100-C4, (B) HPA-S50-C4 and (C) HPA-S0-C4 in water with different concentration (slit widths of excitation and emission are set to be 10 nm and 10 nm, respectively)



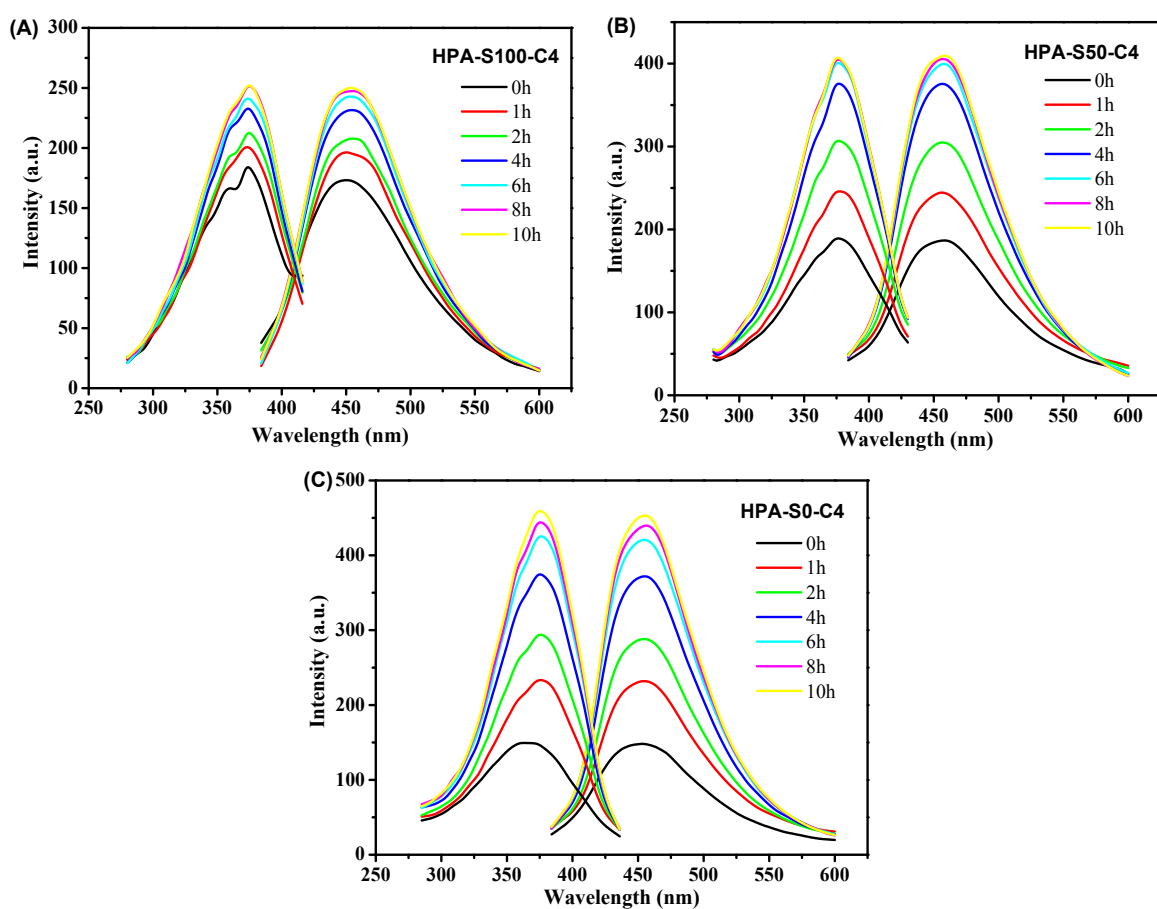


**Fig. S8** Typical fluorescence excitation and emission spectra of (A) HPA-S100-C4, (B) HPA-S50-C4 and (C) HPA-S0-C4 in water with different pH (polymer concentration is 5 mg/mL; slit widths of excitation and emission are set to be 10 nm and 10 nm, respectively)



**Fig. S9** Quantum yield measurements

	S100	S75	S50	S25	S0
QY (%)	11.4	11.0	13.7	10.3	10.3



**Fig. S10** Typical fluorescence excitation and emission spectra of (A) HPA-S100-C4, (B) HPA-S50-C4 and (C) HPA-S0-C4 in water oxidized by air for different time (polymer concentration is 5 mg/mL; slit widths of excitation and emission are set to be 10 nm and 10 nm, respectively)