Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Hyperbranched polyglycerol derivatives exhibiting normal or abnormal thermoresponsive behaviours in water: facile preparation and investigation by turbidimetry and fluorescence techniques

Yao Zhang,[a, §] Rui-Cong Wang,[a, §] Hua-Ji Liu [a,*] and Yu Chen [a,b,c,*]

[a] Tianjin Key Laboratory of Molecular Optoelectronic Science, Department of Chemistry, School of Sciences, Tianjin University, Tianjin 300354, PR China

[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300354, PR China

[c] School of Science, Tianjin Chengjian University, Tianjin 300384, PR China

Table 1. Structural information of G-CX and their properties in water

No.	Saturated fatty acid	Degree of Substitution/%	M_n /10^3	General formula	T_{cp} at 30mg/mL /℃
1	—	0	2.32	HPG	—
2	C2	34.0	2.79	G-C2$_{34.0}$	45.8
3	C2	37.1	2.83	G-C2$_{37.1}$	28.0
4	C2	53.9	3.06	G-C2$_{53.9}$	9.88
5	C3	21.6	2.72	G-C3$_{21.6}$	63.4
6	C3	26.3	2.80	G-C3$_{26.3}$	23.5
7	C3	27.4	2.82	G-C3$_{27.4}$	10.2
8	C4	14.3	2.65	G-C4$_{14.3}$	66.6
9	C4	15.2	2.67	G-C4$_{15.2}$	46.3
10	C4	15.4	2.67	G-C4$_{15.4}$	42.9
11	C4	16.8	2.71	G-C4$_{16.8}$	20.1
12	*i*-C4	14.9	2.66	G-*i*-C4$_{14.9}$	58.5
13	*i*-C4	16.3	2.69	G-*i*-C4$_{16.3}$	29.7
14	*i*-C4	19.4	2.77	G-*i*-C4$_{19.4}$	17.1
15	C5	11.9	2.65	G-C5$_{11.9}$	58.2
16	C5	12.4	2.66	G-C5$_{12.4}$	40.0
17	C5	14.7	2.73	G-C5$_{14.7}$	22.5
18	C5	15.1	2.74	G-C5$_{15.1}$	20.8
19	*i*-C5	12.4	2.66	G-*i*-C5$_{12.4}$	46.0
20	*i*-C5	13.4	2.69	G-*i*-C5$_{13.4}$	35.0
21	*i*-C5	14.7	2.73	G-*i*-C5$_{14.7}$	24.3
22	*i*-C5	15.3	2.74	G-*i*-C5$_{15.3}$	16.0
23	*t*-C5	13.3	2.69	G-*t*-C5$_{13.3}$	55.6
24	*t*-C5	14.2	2.71	G-*t*-C5$_{14.2}$	28.5
25	*t*-C5	16.1	2.76	G-*t*-C5$_{16.1}$	19.5
26	*t*-C5	16.8	2.78	G-*t*-C5$_{16.8}$	15.6
27	C6	11.4	2.69	G-C6$_{11.4}$	53.7
28	C6	12.0	2.71	G-C6$_{12.0}$	44.1
29	C6	12.4	2.72	G-C6$_{12.4}$	27.7
30	C6	13.1	2.74	G-C6$_{13.1}$	17.1
31	C8	11.3	2.79	G-C8$_{11.3}$	52.9
32	C8	11.7	2.80	G-C8$_{11.7}$	42.2
33	C8	12.2	2.83	G-C8$_{12.2}$	33.0
34	C8	13.1	2.86	G-C8$_{13.1}$	18.0
35	C10	9.40	2.80	G-C10$_{9.40}$	—
36	C12	10.6	2.95	G-C12$_{10.6}$	—

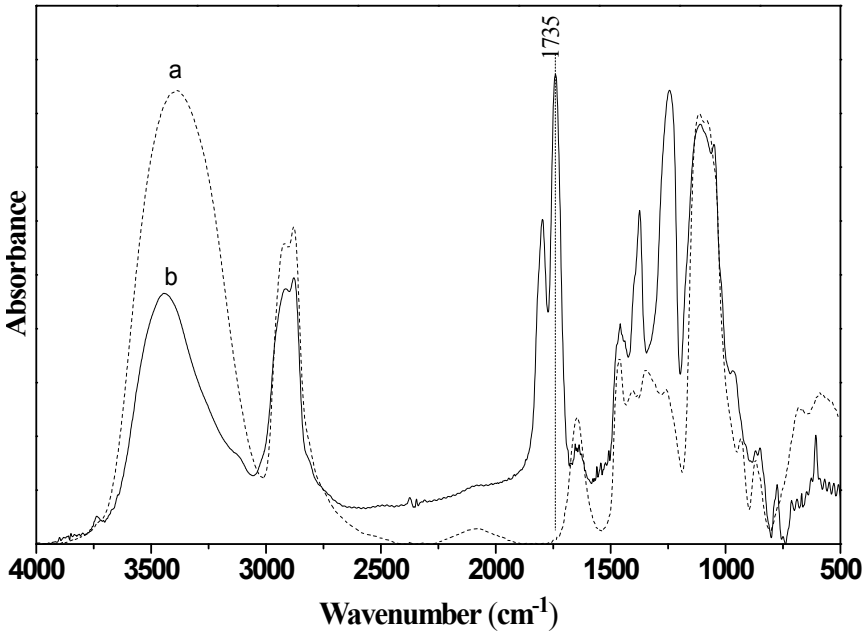

Fig. S1 FTIR absorbance spectra of (a) HPG; (b) G-C12.

The ^{1}H NMR spectra of HPG and the resulting G-C12 are given in Fig. S2a and Fig. S2b, respectively, and both the HPG and dodecanoic acid moiety can be seen clearly in the spectra. The proton peak at δ= 3.4–4.0 is assigned to the characteristic resonance of HPG scaffold protons. After the terminal modification, new proton peaks at δ = 0.8-2.5, assigned to the dodecanoic acid groups (peak a, b, c, d), appeared in the ^{1}H NMR spectrum of G-C12. Moreover, the appearance of the resonances at δ>4.0 for the protons of –$COOCH_2$– groups of G-C12 is another evidence of the successful reaction between HPG and dodecanoic acid here. From the ^{1}H NMR spectra, the degree of substitution of HPG can be also calculated through $DS_{(HPG\text{-}C12)}\%=I_{(d)}/2/(I_{(HPG)}/5)$.

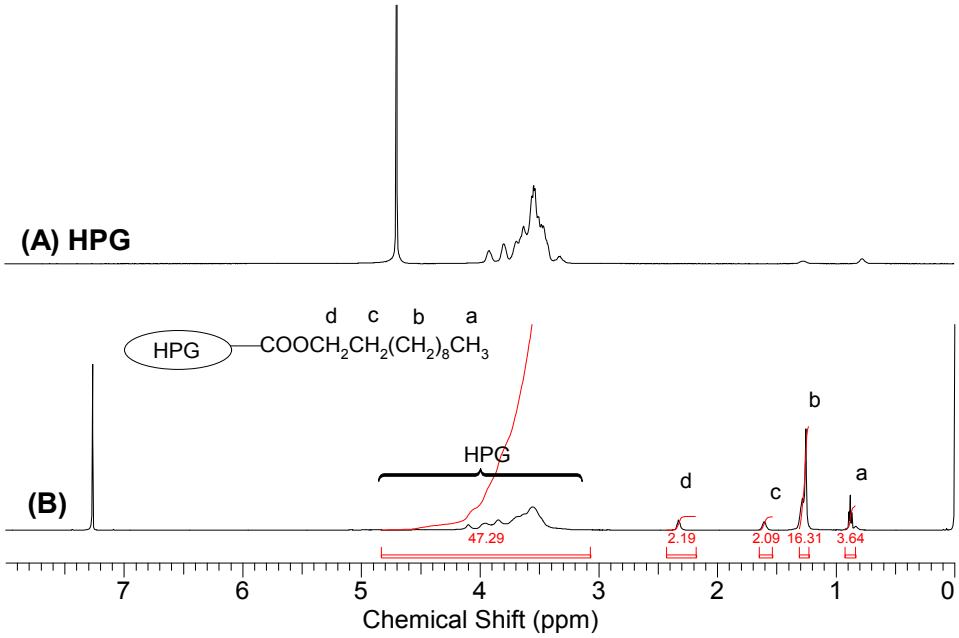

Fig. S2 ^{1}H NMR spectra of (A) HPG and (B) G-C12

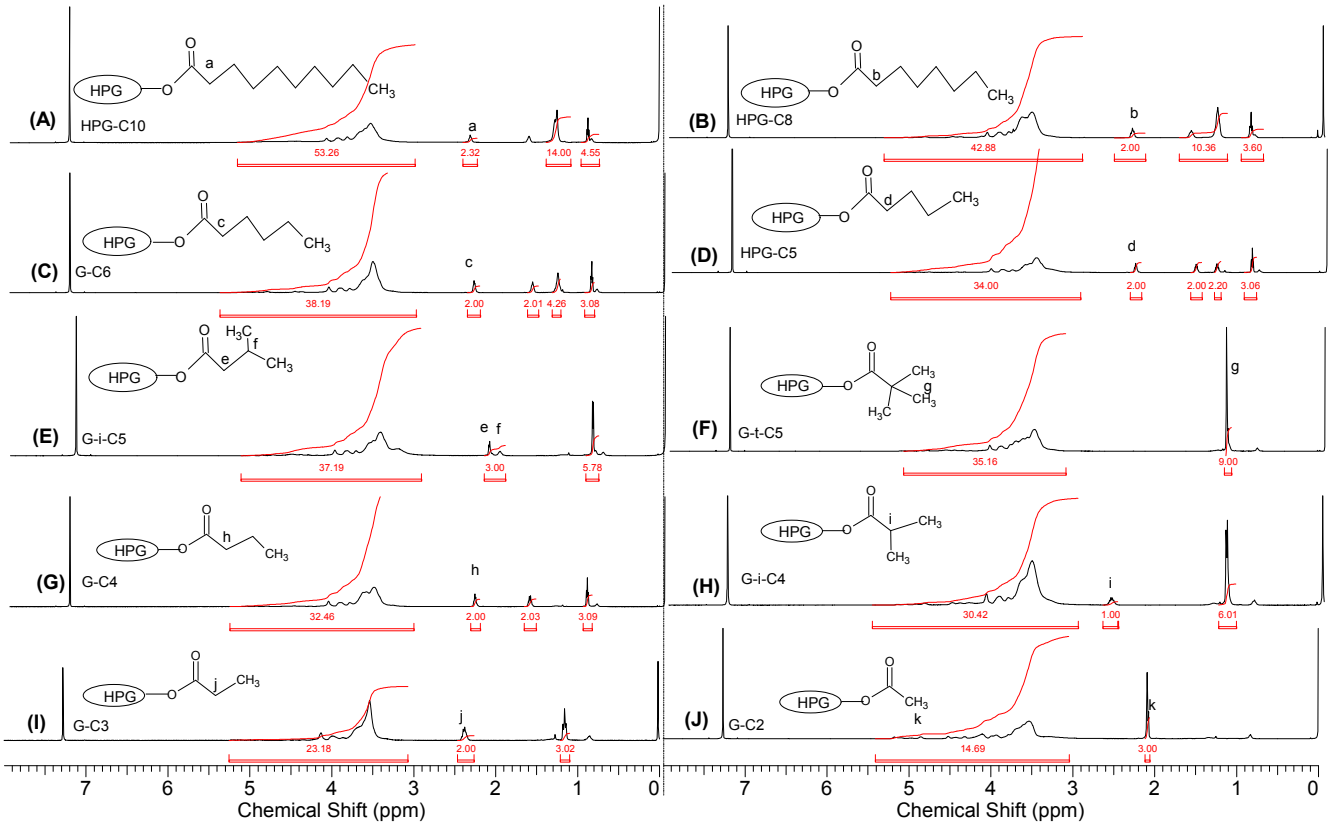

Fig. S3 ^{1}H NMR spectra of (A) G-C10; (B) G-C8; (C) G-C6; (D) G-C5; (E) G-*i*-C5; (F) G-*t*-C5; (G) G-C4; (H) G-*i*-C4; (I) G-C3; (J) G-C2

From the ^{1}H NMR spectra, the degree of substitution of HPG can be also calculated through the following formula:

$$DS_{(G\text{-}C10)}\%=I_{(a)}/2/(I_{(HPG)}/5);\ DS_{(HPG\text{-}C8)}\%=I_{(b)}/2/(I_{(HPG)}/5);\ DS_{(G\text{-}C6)}\%=I_{I}/2/(I_{(HPG)}/5);\ DS_{(G\text{-}C5)}\%=I_{(d)}/2/(I_{(HPG)}/5);\ DS_{(G\text{-}i\text{-}C5)}\%=I_{(e+f)}/3/(I_{(HPG)}/5);\ DS_{(G\text{-}t\text{-}C5)}\%=I_{(g)}/9/(I_{(HPG)}/5);\ DS_{(G\text{-}C4)}\%=I_{(h)}/2/(I_{(HPG)}/5);\ DS_{(G\text{-}i\text{-}C4)}\%=I_{(i)}/(I_{(HPG)}/5);\ DS_{(G\text{-}C3)}\%=I_{(j)}/2/(I_{(HPG)}/5);\ DS_{(G\text{-}C2)}\%=I_{(k)}/3/(I_{(HPG)}/5)$$

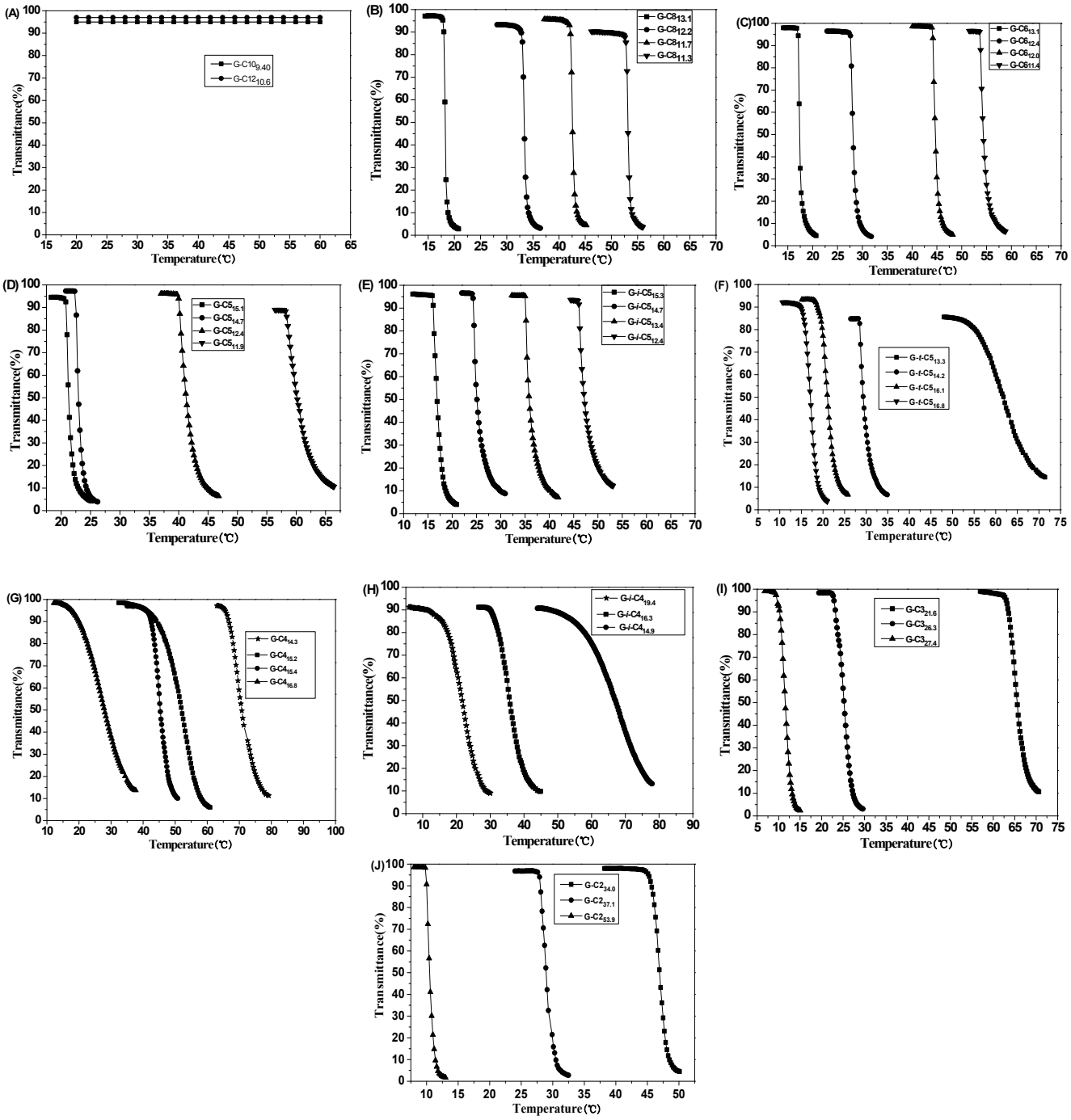

Fig. S4 Typical influence of temperature on the light transmittance of (A) G-C10$_{9.40}$ and G-C12$_{10.6}$; (B) G-C8; (C) G-C6; (D) G-C5; (E) G-*i*-C5; (F) G-*t*-C5; (G) G-C4; (H) G-*i*-C4; (I) G-C3; (J) G-C2 (concentration of polymer is 30 mg/mL)

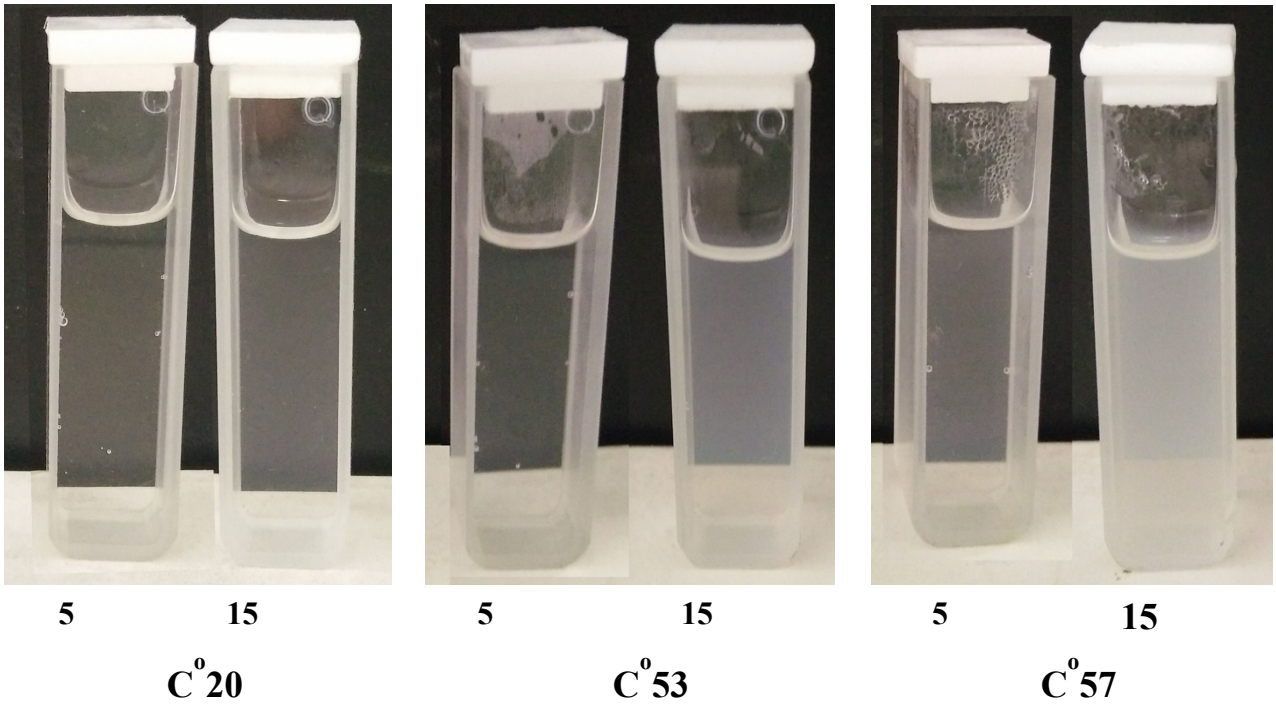

Fig. S5 Typical photographs of 5 and 13 mg/mL of G-C4 in water at different temperature

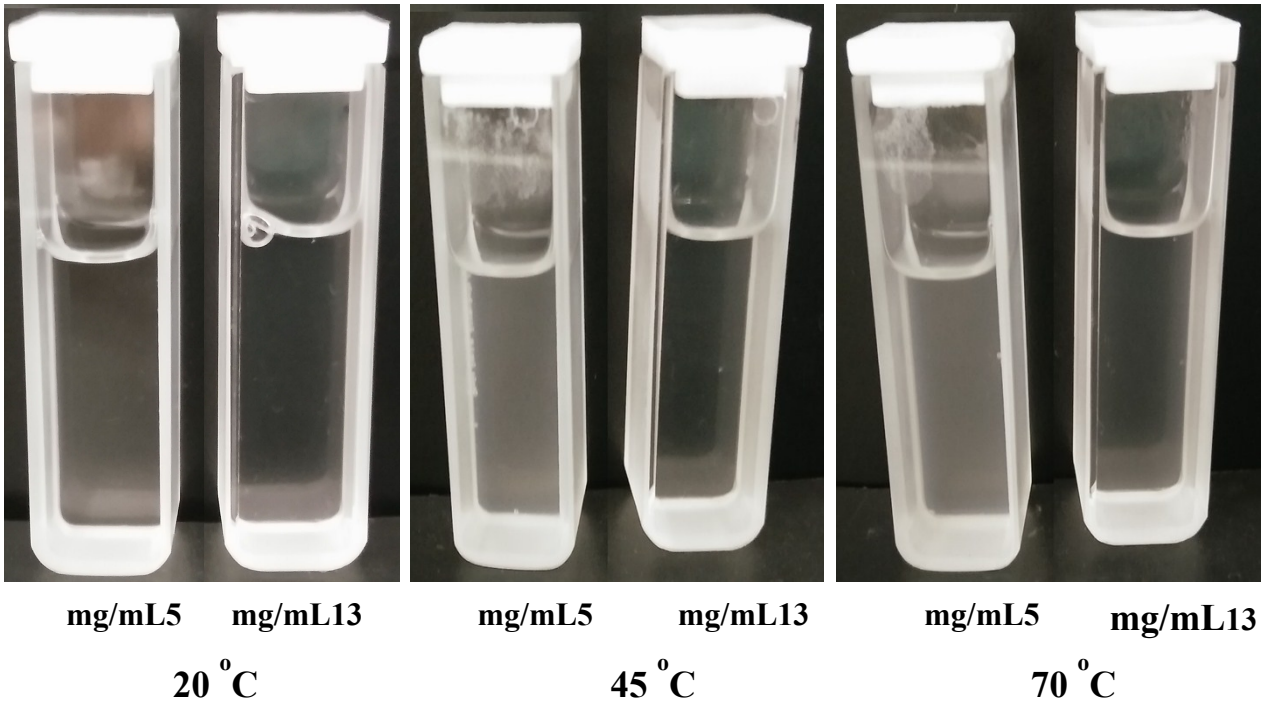

Fig. S6 Typical photographs of 5 and 15 mg/mL of G-C6 in water at different temperature

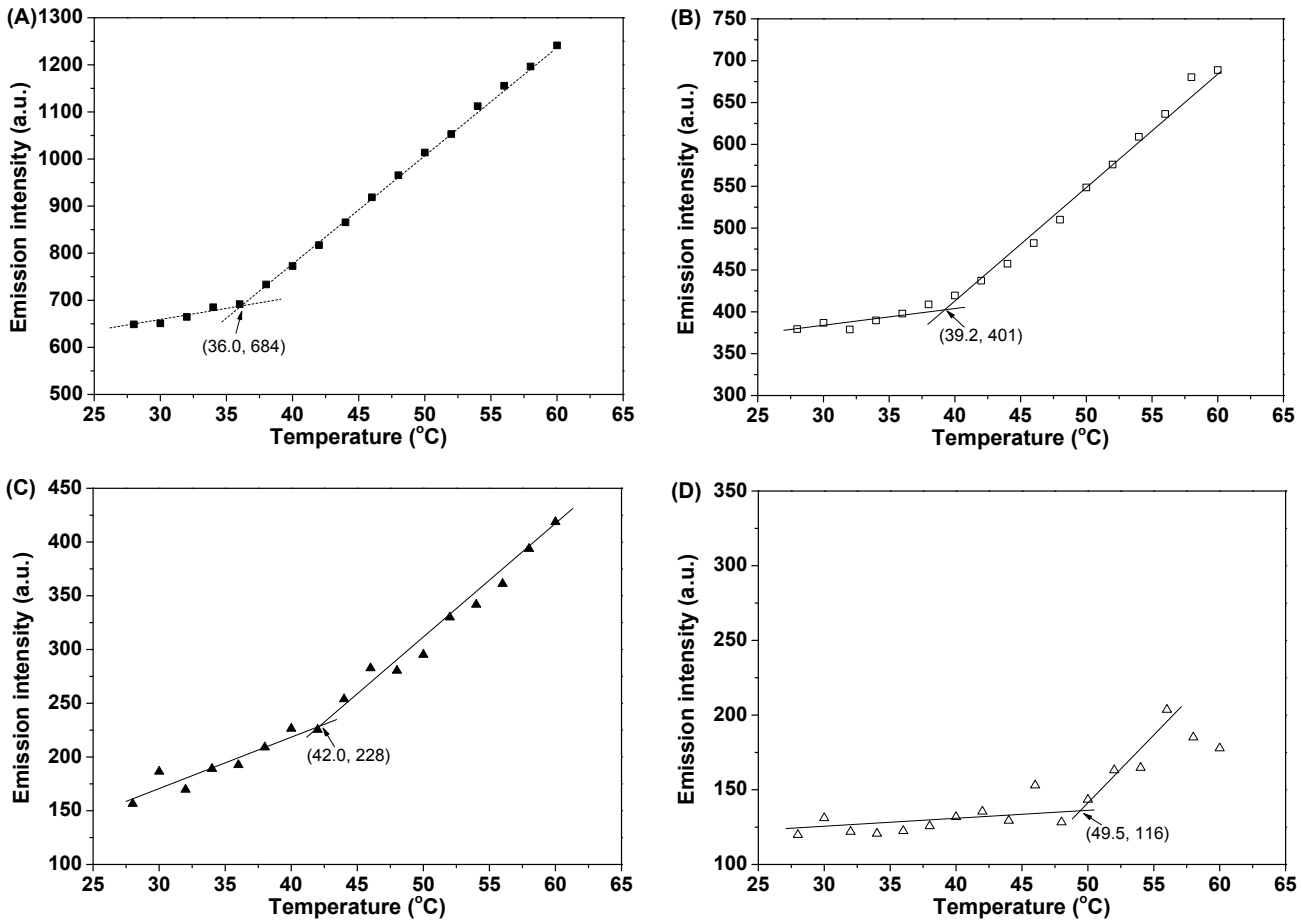

Fig. S7 Typical temperature influence on emission intensity of nile red in the presence of HPG-C4 with a different concentration (A) 4.0 mg/mL, (B) 2.0 mg/mL, (C) 1.0 mg/mL and (D) 0.5 mg/mL (concentration of nile red is 2×10^{-6} M, HPG-$C4_{16.8}$ was used as the representatives)

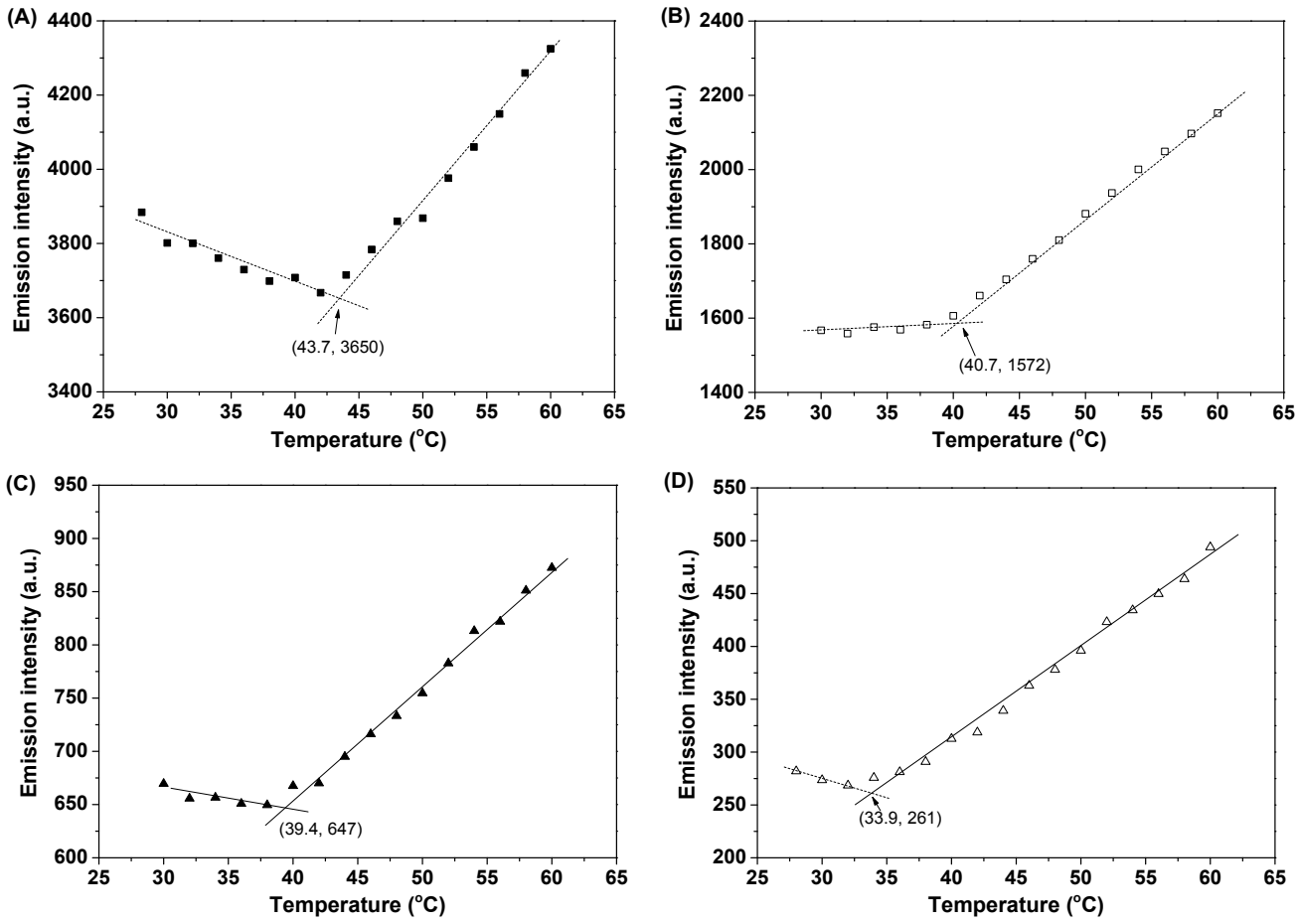

Fig. S8 Typical temperature influence on emission intensity of nile red in the presence of G-C6 with a different concentration (A) 2.0 mg/mL, (B) 1.0 mg/mL, (C) 0.5 mg/mL and (D) 0.25 mg/mL (concentration of nile red is 2×10^{-6} M, G-$C6_{11.4}$ was used as the representatives)

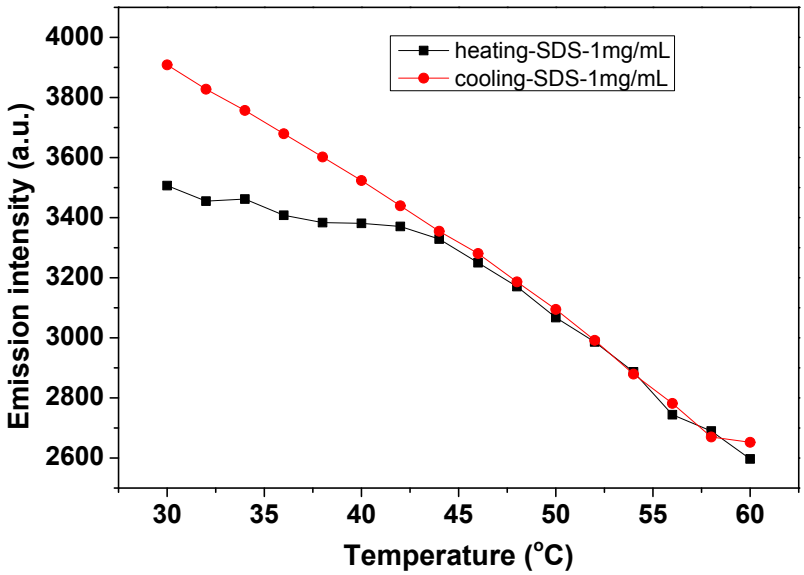

Fig. S9 Typical influence of heating and cooling on the emission intensity of nile red at 630 nm in the presence of 1 mg/mL of SDS (concentration of nile red is 2×10^{-6} M)

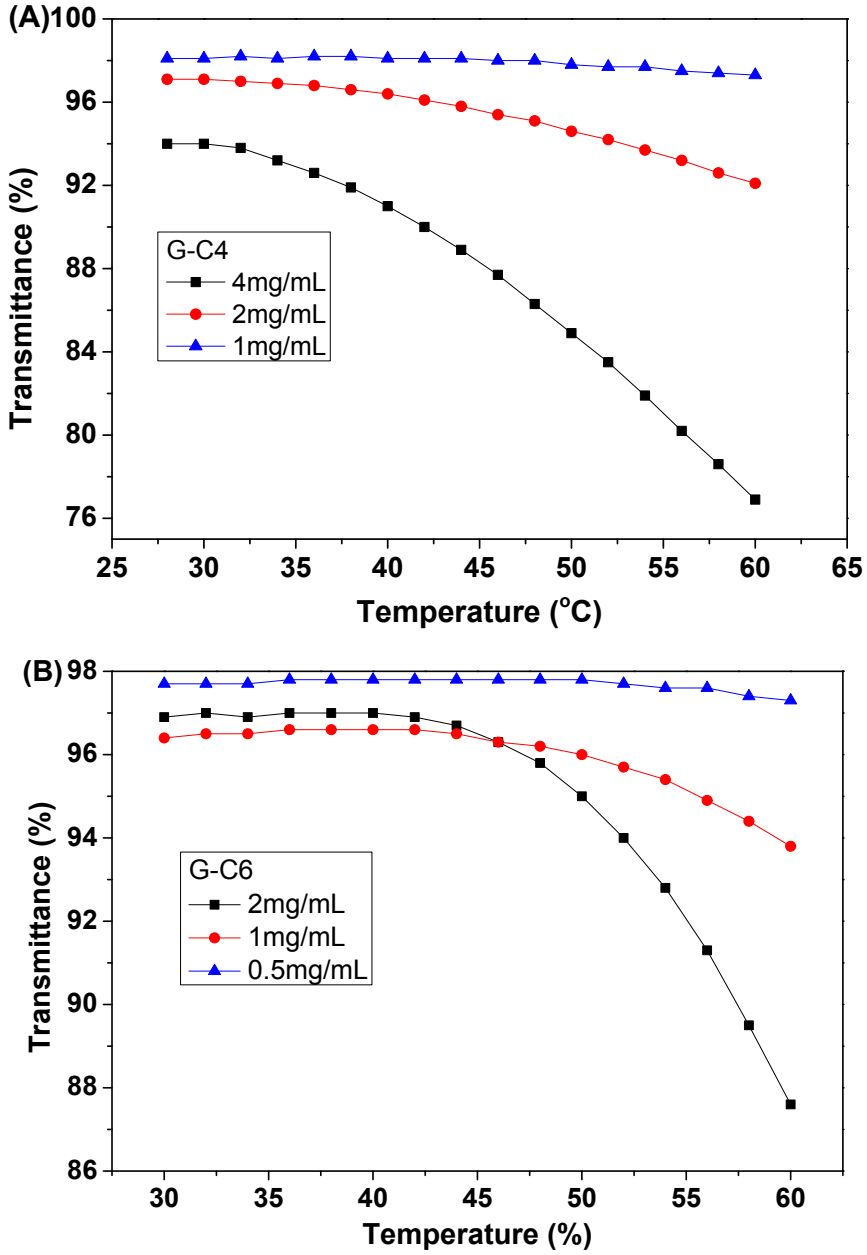

Fig. S10 Typical influence of temperature on the light transmittance of low concentration of (A) G-C4 and (B) G-C6 (G-C4$_{16.8}$ and G-C6$_{11.4}$ were used as the representatives)