Supporting Information for

Smart Molecular Butterfly: Ultra-sensitive and Range-tunable Ratiometric Thermometer Based on Dihydrophenazines

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1. Materials and instruments

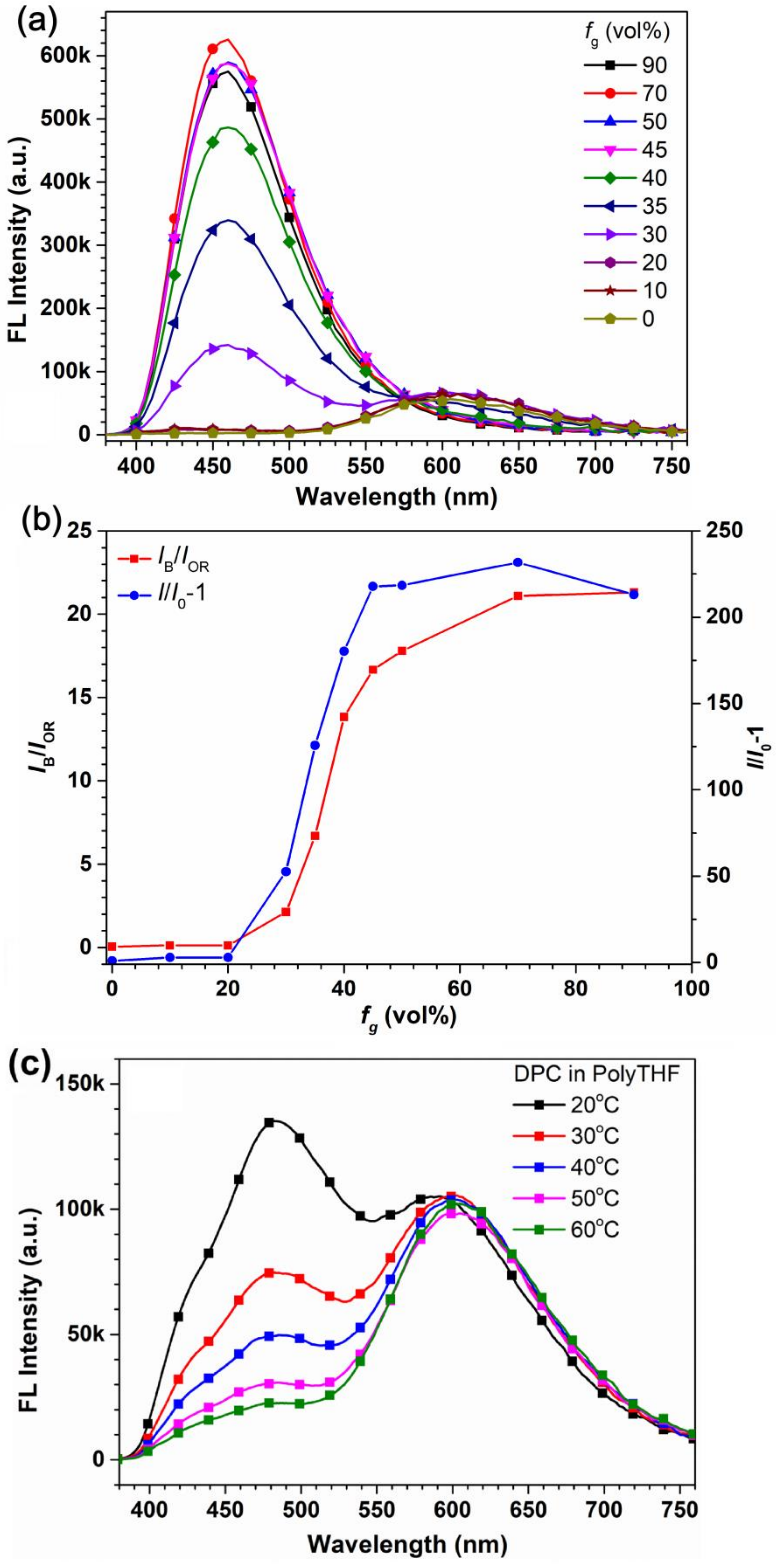
All reagents and chemicals were purchased from commercial sources and used without further purification. The fluorescence spectra were recorded on Horiba Fluoromax 4. Dynamic light scattering tests were carried out by Zetasizer Nano ZS. The viscosity was measured by TA Instruments ARES-G2. The refractive index was tested by Abbe refractometer. Two photon-excited fluorescence microscopy images were obtained by Zeiss LSM 710 (Zeiss, Germany) equipped with 80 MHz fs mode-locked Ti:sapphire laser (Mai-Tai DeepSee, Spectra-Physics).

2. Measurement methods

Solution preparation: DPC was firstly dissolved in ethanol to afford the concentrated stock solution (10^{-4} M). Solutions for temperature sensing (10^{-5} M) were prepared by mixing the stock solution (1 mL) and the corresponding ethanol/glycerol mixtures (9 mL), and stirring the resulted mixture for 5 min.

The method for temperature controlling: Temperature rising and decreasing was controlled by thermostat DC-0530. Inevitably, there is a temperature difference between the thermostat DC-0530 and the cuvette. In order to get the real temperature of the test solutions, a thermocouple wire was inserted into the cuvette, and the temperature was determined by the thermocouple thermometer. The fluorescence spectra were recorded after the thermocouple thermometer indication was stable.

3. The original/additional figures and tables



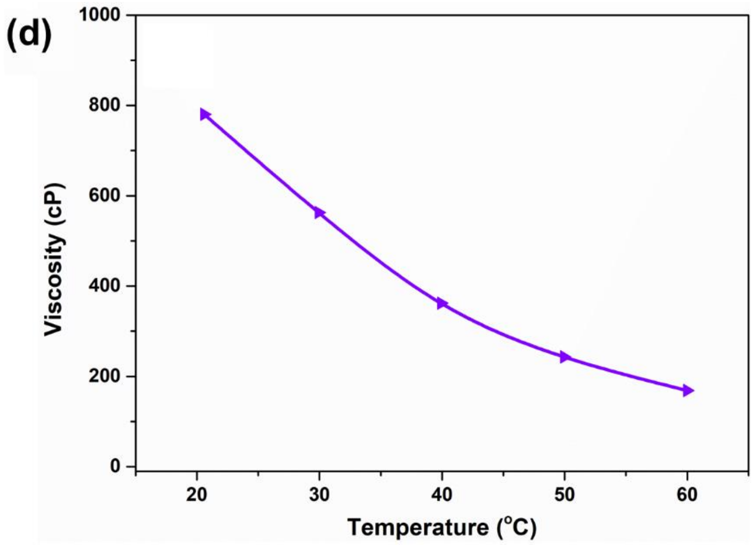


Fig. S1. (a) The fluorescence spectra of DPC in the ethanol/glycerol mixtures with different glycerol fractions (f_gs) at 25 °C. (b) The corresponding plots of I/I_0–1 *versus* f_g and I_B/I_{OR} *versus* f_g, where I and I_0 is the maximum fluorescence intensity of DPC in the mixture of ethanol/glycerol mixtures with different f_gs and in pure ethanol (f_g = 0%), respectively. (c) The fluorescence spectra of DPC in polytetrahydrofuran (PTMEG) (M_w = 1000, viscosity > 100 cP at 40 °C) at different temperatures, λ_{ex} = 360 nm, [DPC] = 10^{-5} M. (d) The viscosity values of polytetrahydrofuran at different temperatures.

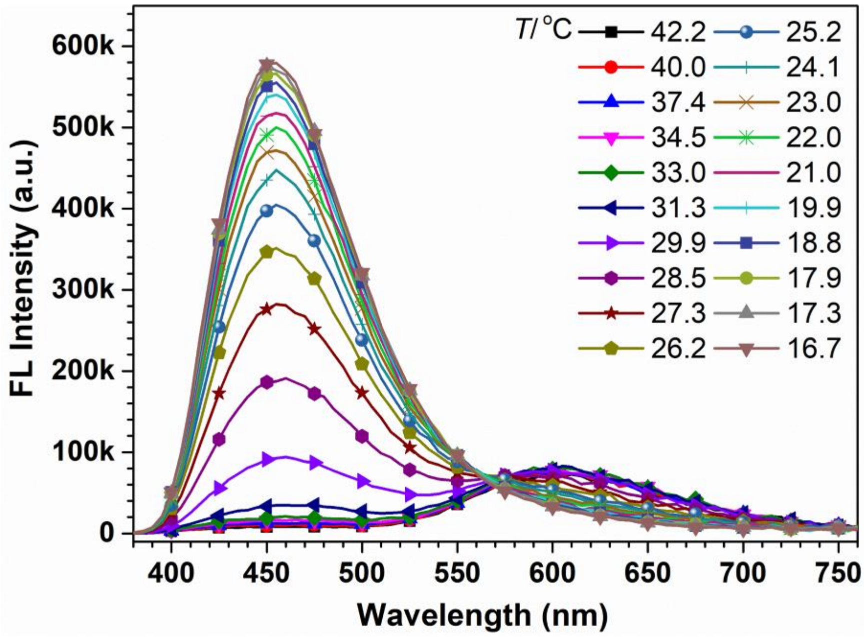


Fig. S2. Emission spectra of DPC in ethanol/glycerol mixtures with the f_g = 40% under different temperatures during the cooling process.

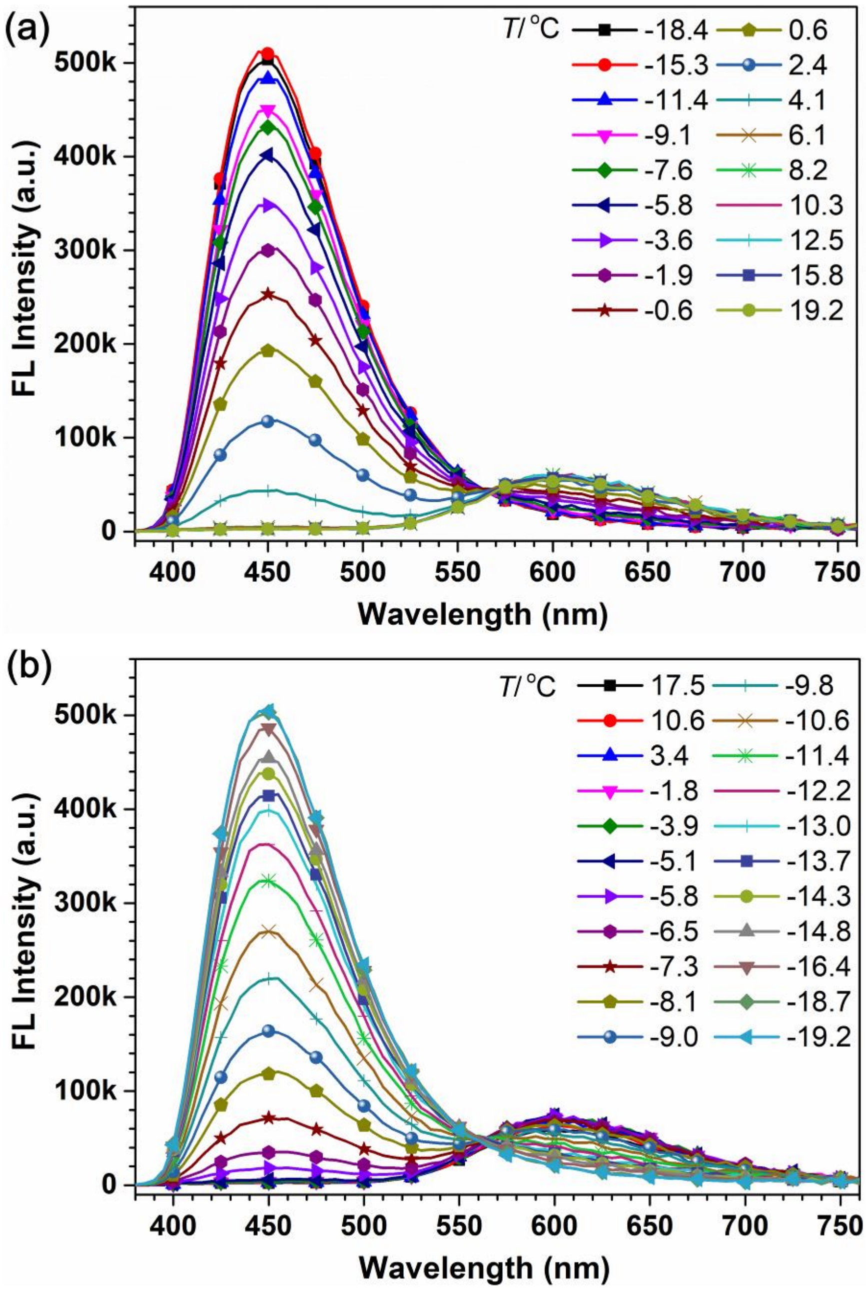


Fig. S3. Emission spectra of DPC in the ethanol/glycerol mixtures with the f_g = 0% under different temperatures during the (a) heating process and (b) cooling process.

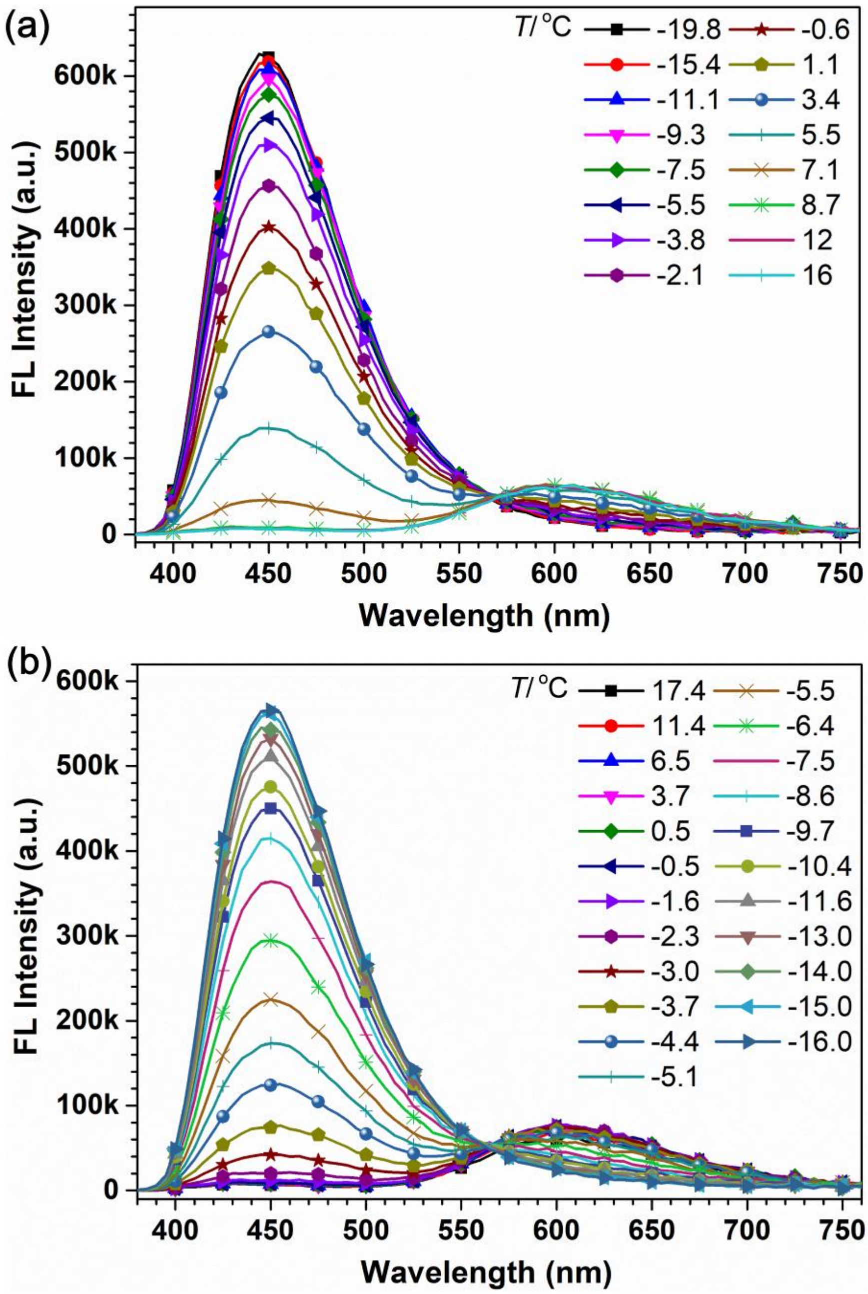


Fig. S4. Emission spectra of DPC in ethanol/glycerol mixtures with the f_g = 5% under different temperatures during the (a) heating process and (b) cooling process.

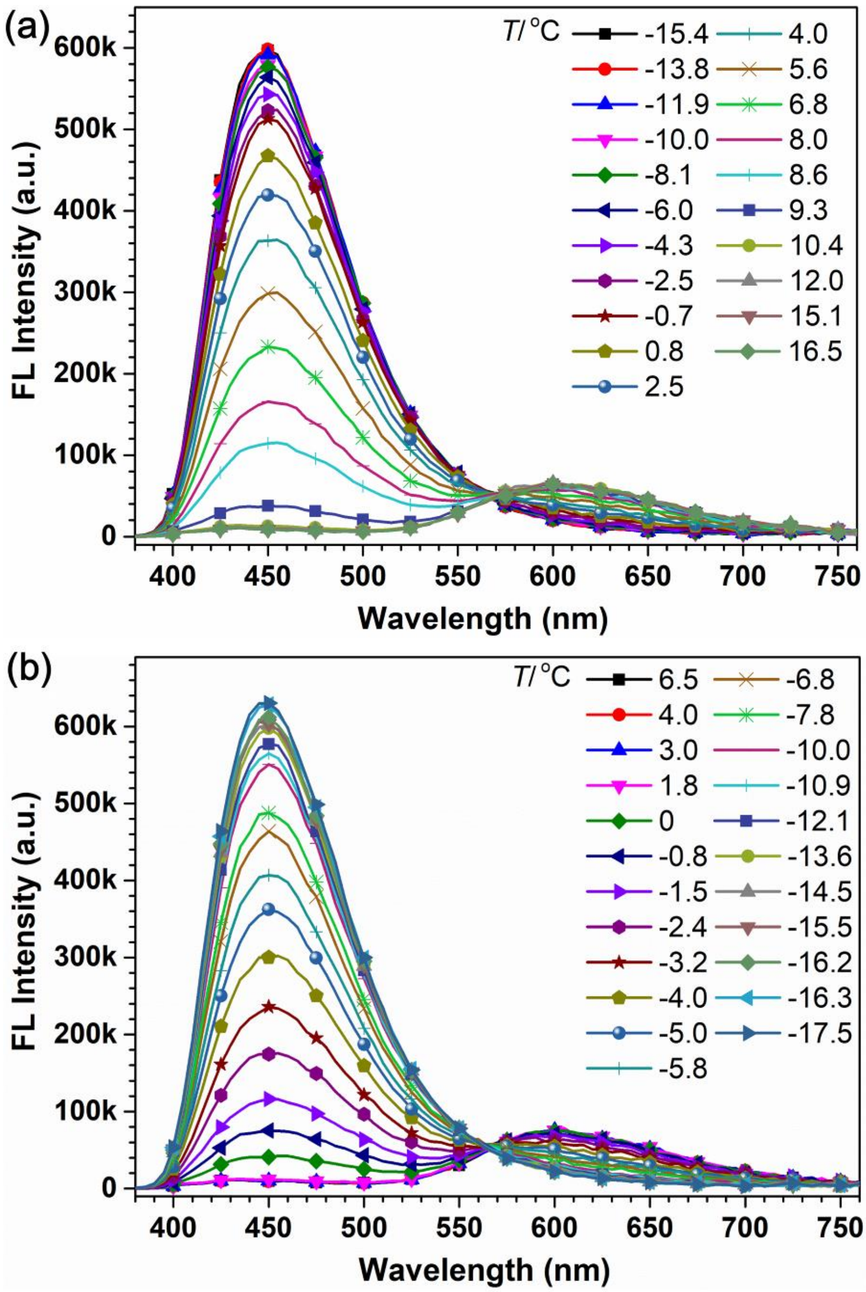


Fig. S5. Emission spectra of DPC in ethanol/glycerol mixtures with the f_g = 10% under different temperatures during the (a) heating process and (b) cooling process.

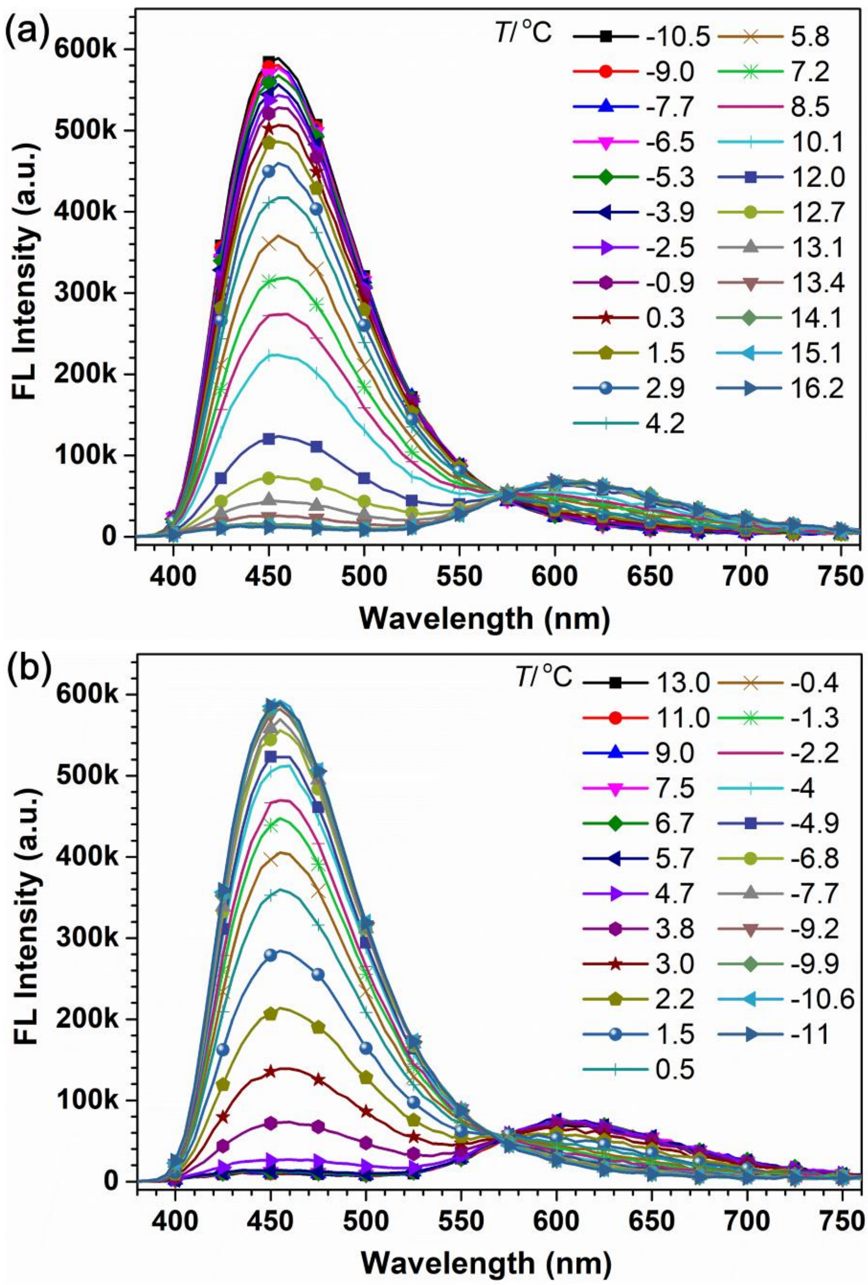


Fig. S6. Emission spectra of DPC in ethanol/glycerol mixtures with the f_g = 15% under different temperature during the (a) heating process and (b) cooling process.

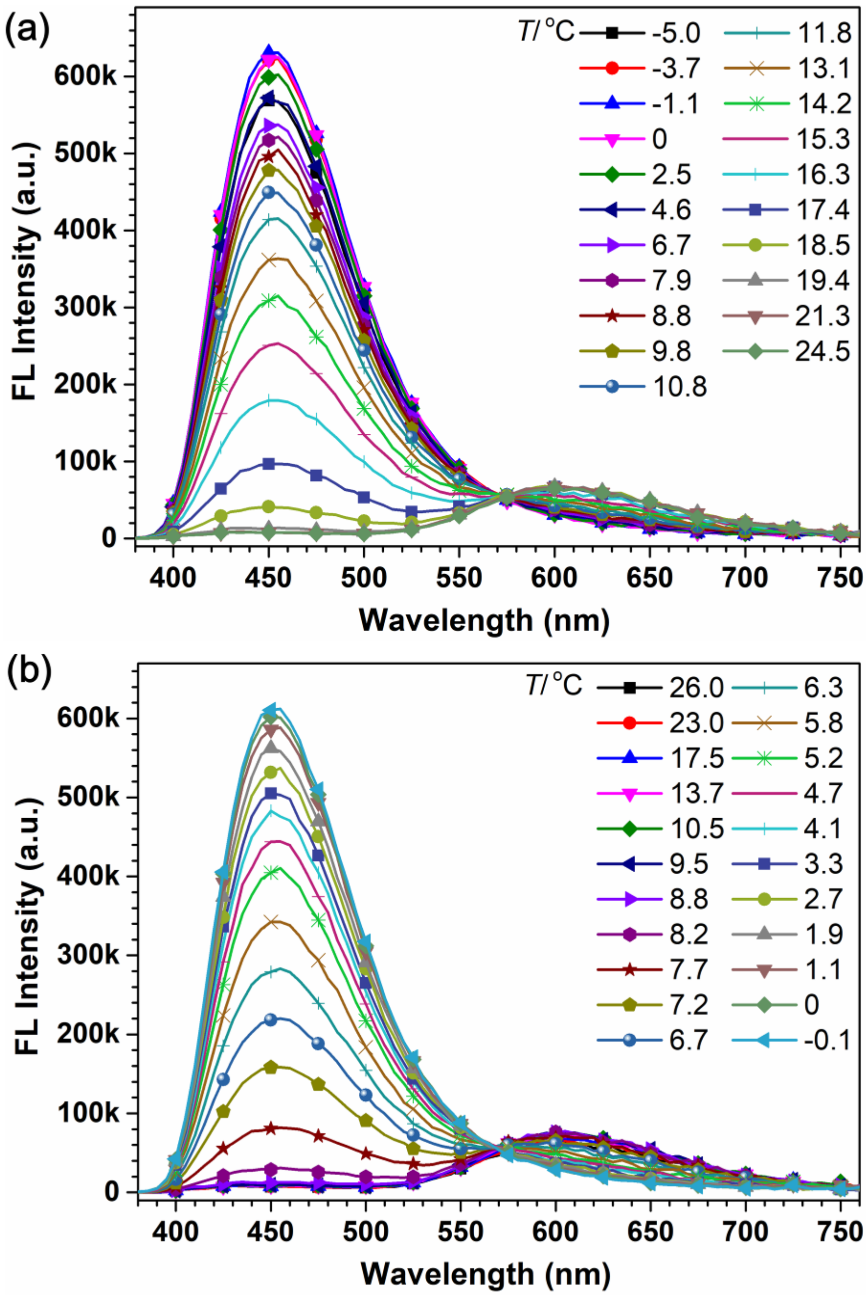


Fig. S7. Emission spectra of DPC in ethanol/glycerol mixtures with the f_g = 20% under different temperatures during the (a) heating process and (b) cooling process.

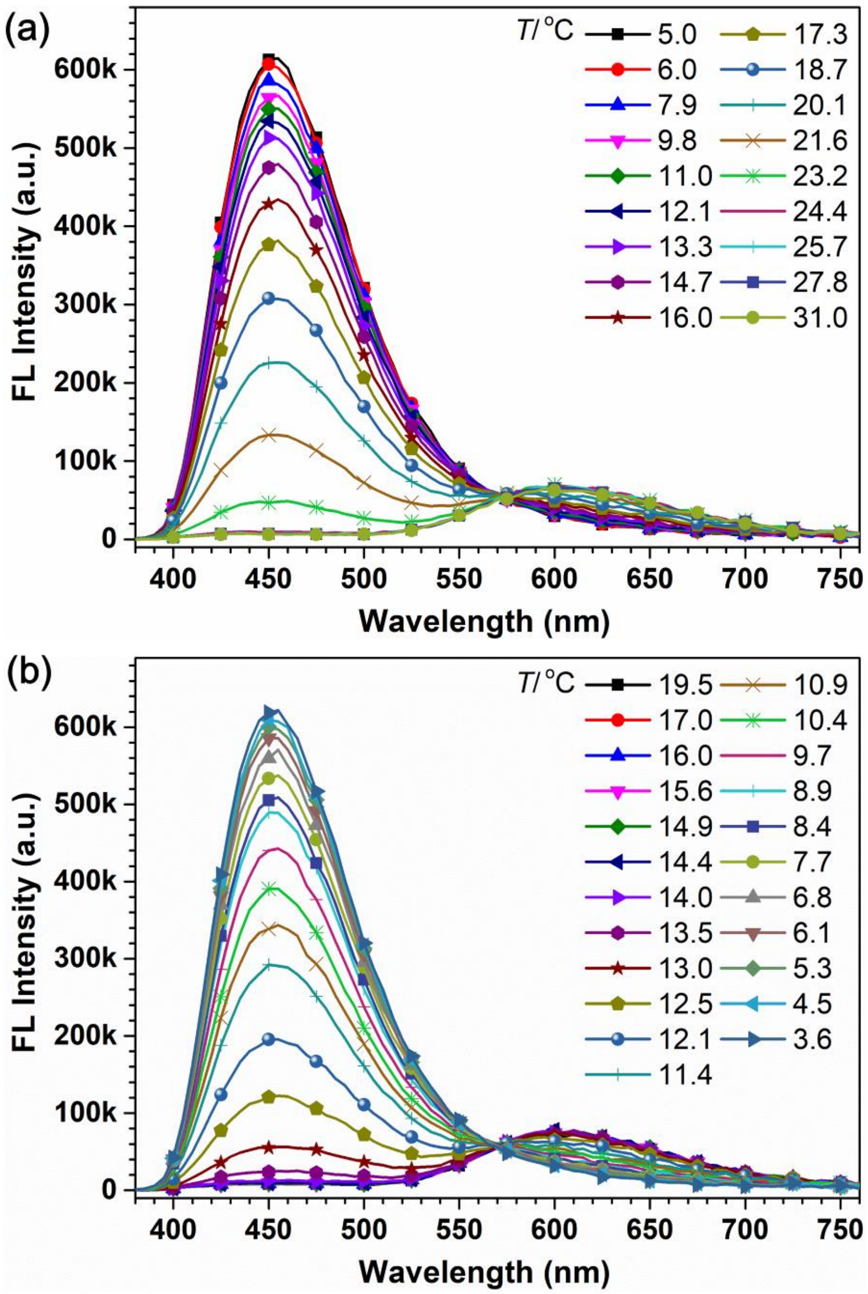


Fig. S8. Emission spectra of DPC in ethanol/glycerol mixtures with the f_g = 25% under different temperatures during the (a) heating process and (b) cooling process.

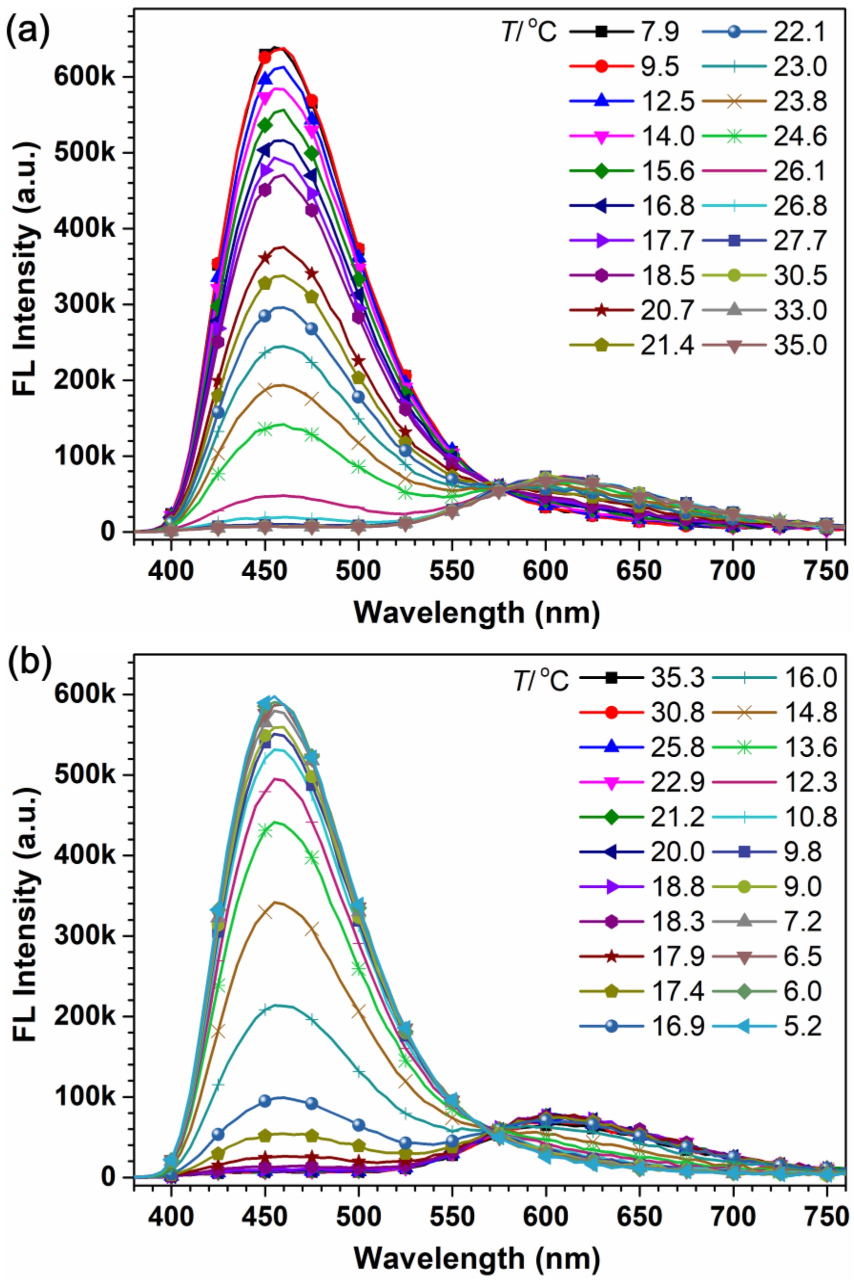


Fig. S9. Emission spectra of DPC in ethanol/glycerol mixtures with the f_g = 30% under different temperatures during the (a) heating process and (b) cooling process.

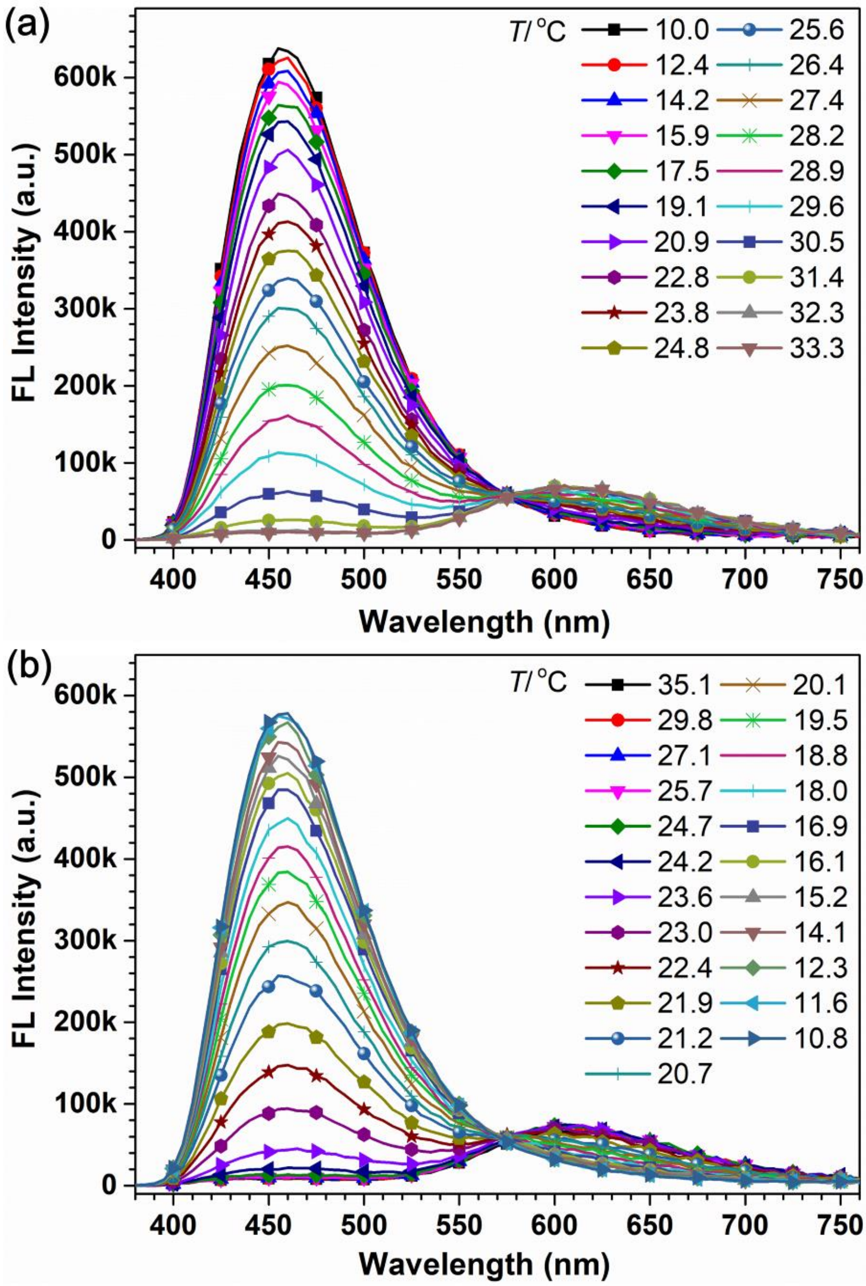


Fig. S10. Emission spectra of DPC in ethanol/glycerol mixtures with the f_g = 35% under different temperatures during the (a) heating process and (b) cooling process.

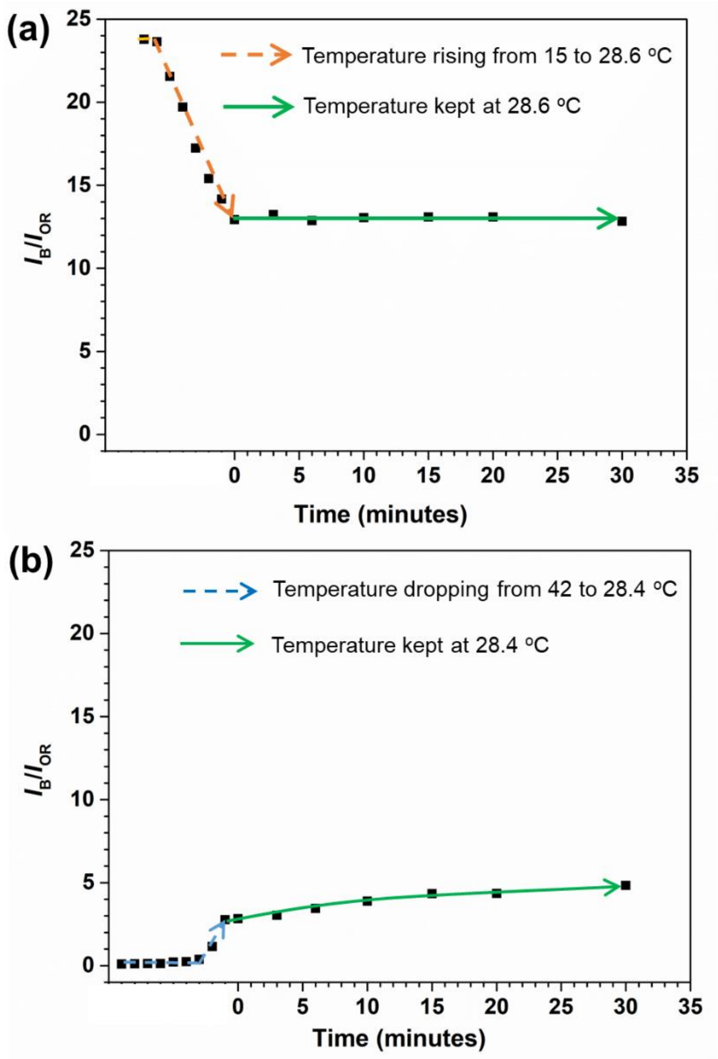


Fig. S11. Time stability evaluation of the fluorescence during the (a) heating process and (b) cooling process.

For the heating process, the DPC system was heated from 15 °C, then the temperature was kept constant at 28.5 °C and the change in fluorescence was recorded over time. The value of I_B/I_{OR} kept falling when the temperature raised from 15 °C to 28.5 °C, and then the value of I_B/I_{OR} does not change over time after the temperature stabilizes at 28.5 °C. Cooling process was slightly different from the heating process, during the constant temperature process, the I_B/I_{OR} value slightly rises in the first 15 minutes, and then remained roughly stable. After a 30-minute constant temperature, although the I_B/I_{OR} has increased, it still cannot reach the value of the heating process.

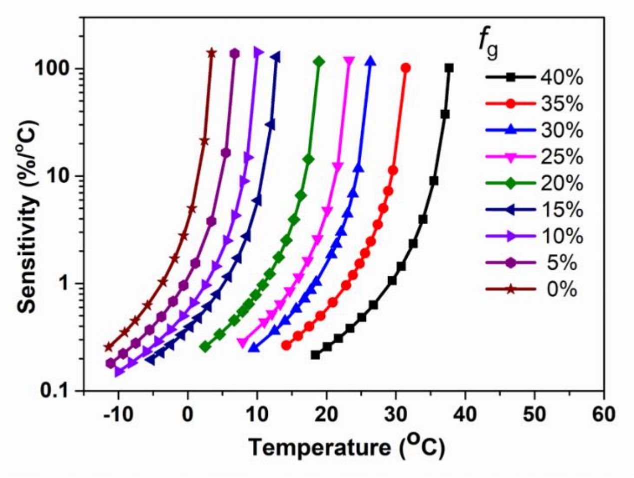
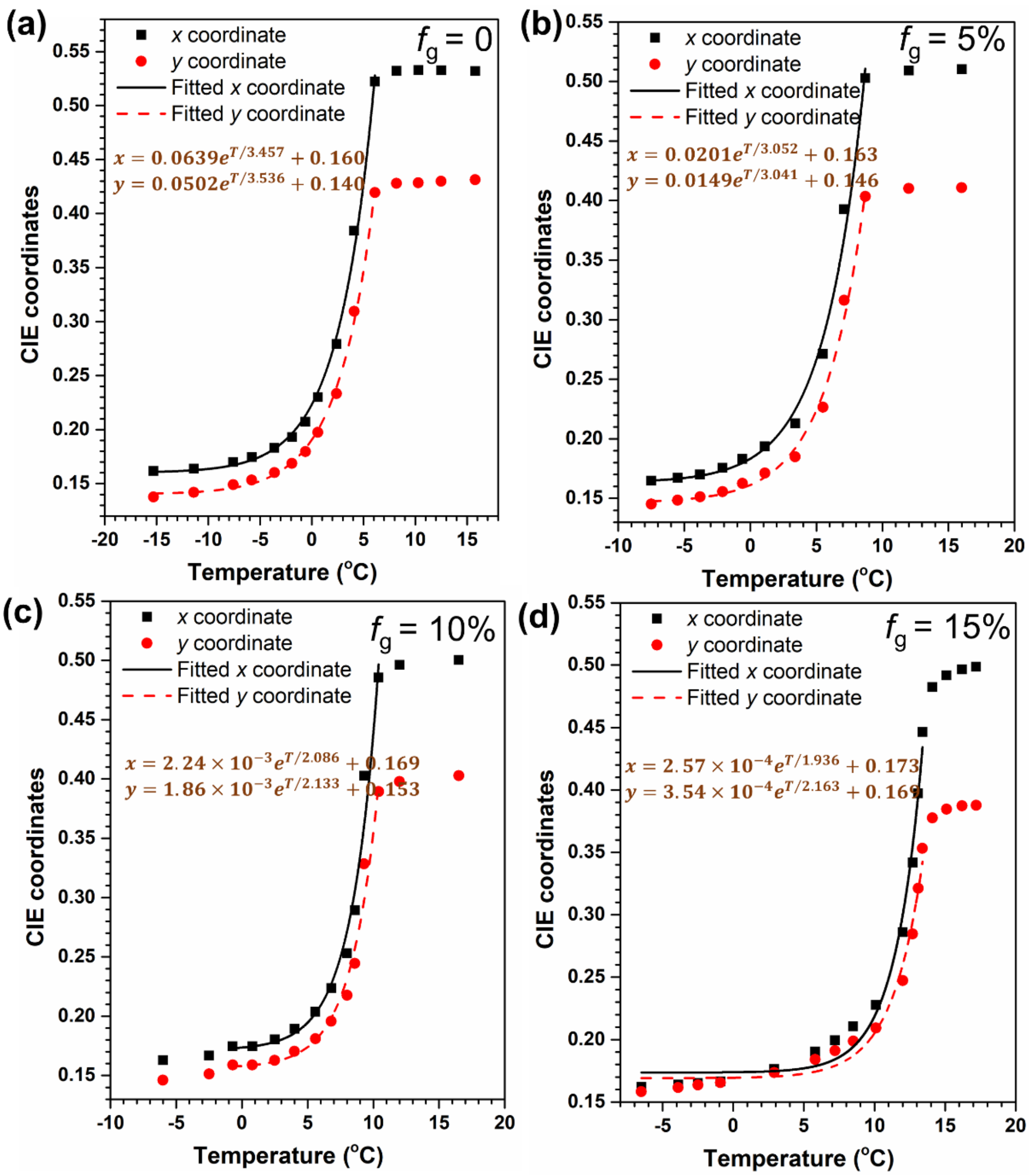


Fig. S12. The internal sensitivity versus temperature (heating process) of DPC in the ethanol/glycerol mixtures with the f_g = 0, 5, 10, 15, 20, 25, 30, 35 and 40%.



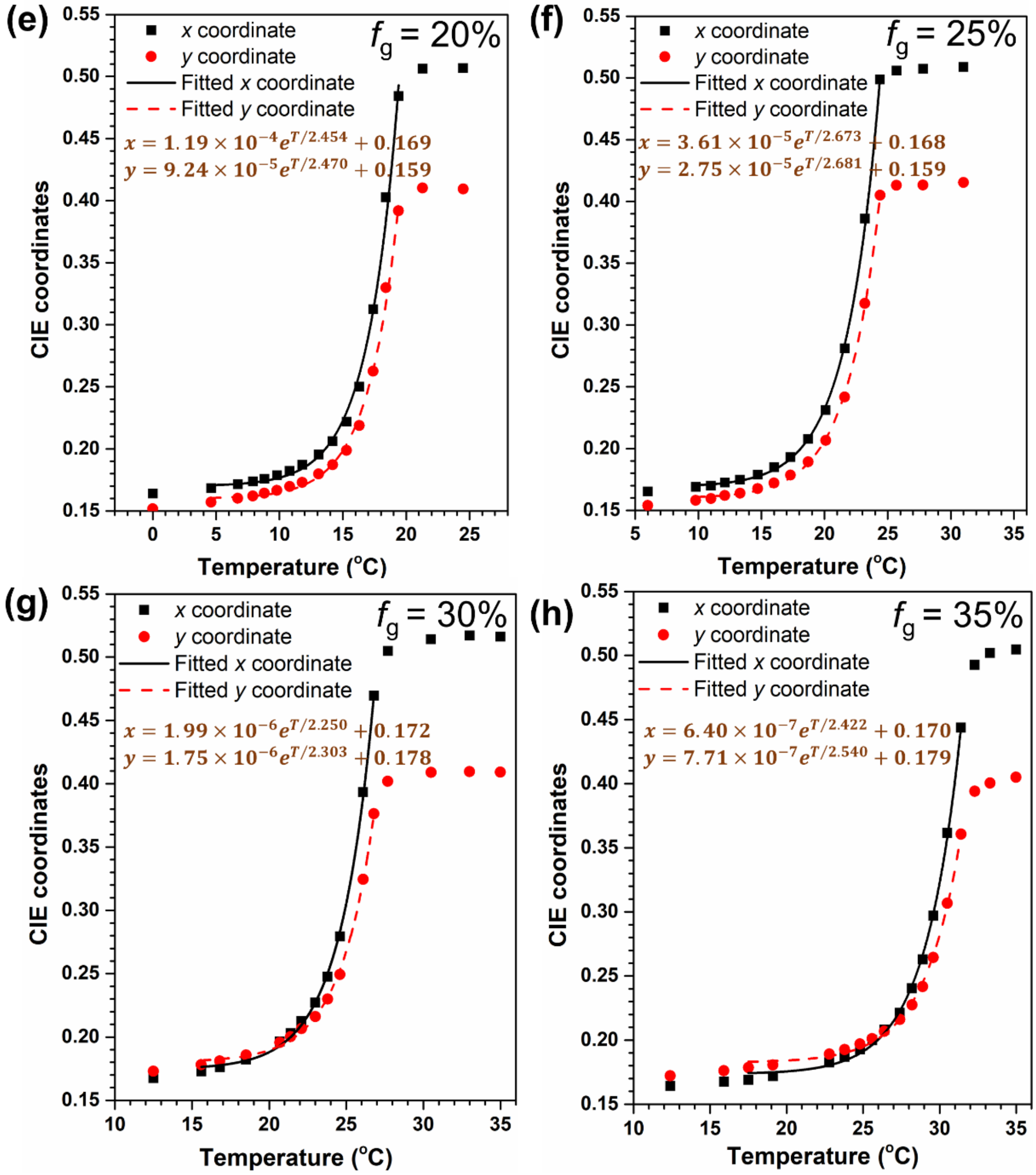


Fig. S13. The measured CIE coordinates (dots and squares) and fitted CIE coordinates curves (black and red lines) corresponding to the fluorescence spectra of DPC in ethanol/glycerol mixtures with the (a) f_g = 0%, (b) f_g = 5%, (c) f_g = 10%, (d) f_g = 15%, (e) f_g = 20%, (f) f_g = 25%, (g) f_g = 30% and (h) f_g = 35%, under different temperatures.

Table S1. The fitted functions, R-squares, and sensitivities of these thermometers with different f_gs.

f_g	Fitting function	R-Square	Relative sensitivity (%/^{o}C)	Internal sensitivity (%/^{o}C)
0%	$I_B/I_{OR} = –1.637T + 5.696$	0.989	$S_r = 1.637/(–1.637T + 5.696)$	$S_{int} = 1.637/(–1.637T + 6.696)^2$
5%	$I_B/I_{OR} = –1.609T + 10.973$	0.991	$S_r = 1.609/(–1.609T + 10.973)$	$S_{int} = 1.609/(–1.609T + 11.973)^2$
10%	$I_B/I_{OR} = –1.548T + 15.573$	0.996	$S_r = 1.548/(–1.548T + 15.573)$	$S_{int} = 1.548/(–1.548T + 16.573)^2$
15%	$I_B/I_{OR} = –1.449T + 18.581$	0.990	$S_r = 1.449/(–1.449T + 18.581)$	$S_{int} = 1.449/(–1.449T + 19.581)^2$
20%	$I_B/I_{OR} = –1.301T + 24.649$	0.995	$S_r = 1.301/(–1.301T + 24.649)$	$S_{int} = 1.301/(–1.301T + 25.649)^2$
25%	$I_B/I_{OR} = –1.341T + 31.252$	0.995	$S_r = 1.341/(-1.341T + 31.252)$	$S_{int} = 1.341/(-1.341T + 32.252)^2$
30%	$I_B/I_{OR} = –1.288T + 33.997$	0.996	$S_r = 1.288/(–1.288T + 33.997)$	$S_{int} = 1.288/(–1.288T + 34.997)^2$
35%	$I_B/I_{OR} = –1.135T + 35.764$	0.994	$S_r = 1.135/(–1.135T + 35.764)$	$S_{int} = 1.135/(–1.135T + 36.764)^2$
40%	$I_B/I_{OR} = –1.130T + 42.657$	0.997	$S_r = 1.130/(–1.130T + 42.657)$	$S_{int} = 1.130/(–1.130T + 43.657)^2$

Table S2. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 40%

Measured			Fitted		
T (^{o}C)	x coordinates	y coordinates	T (^{o}C)	x coordinates	y coordinates
13.0	0.163	0.158	29.0	0.183	0.178
14.7	0.164	0.159	31.0	0.195	0.187
16.7	0.164	0.160	32.0	0.204	0.194
18.4	0.166	0.162	33.0	0.216	0.203
20.1	0.167	0.163	34.0	0.233	0.216
21.7	0.169	0.166	35.0	0.255	0.233
23.4	0.171	0.168	35.5	0.269	0.244
25.1	0.174	0.171	36.0	0.286	0.256
26.8	0.178	0.175	36.5	0.304	0.270
29.5	0.187	0.183	37.0	0.326	0.287
30.8	0.194	0.189	37.25	0.339	0.296
32.5	0.208	0.198	37.5	0.352	0.306
33.9	0.229	0.213	37.75	0.366	0.316
35.5	0.267	0.242	38.0	0.381	0.328
37.1	0.335	0.290	38.2	0.394	0.337
39.1	0.463	0.389	38.4	0.408	0.348
40.1	0.496	0.414	38.6	0.423	0.359
41.1	0.503	0.418	38.8	0.439	0.370
42.0	0.504	0.418	39.0	0.455	0.383
42.7	0.503	0.419	39.1	0.464	0.389

Table S3. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 0%

Measured			Fitted		
T (°C)	*x* coordinates	*y* coordinates	*T* (°C)	*x* coordinates	*y* coordinates
19.2	0.532	0.431	6.1	0.528	0.422
15.8	0.532	0.431	6.0	0.517	0.414
12.5	0.533	0.430	5.8	0.497	0.399
10.3	0.533	0.429	5.6	0.478	0.385
8.2	0.532	0.428	5.4	0.460	0.371
6.1	0.522	0.419	5.2	0.444	0.359
4.1	0.384	0.310	5.0	0.428	0.347
2.4	0.279	0.233	4.75	0.409	0.333
0.6	0.230	0.197	4.5	0.392	0.319
–0.6	0.207	0.180	4.25	0.375	0.307
–1.9	0.193	0.169	4.0	0.360	0.296
–3.6	0.183	0.160	3.5	0.333	0.275
–5.8	0.175	0.153	3.0	0.310	0.257
–7.6	0.170	0.149	2.5	0.290	0.242
–11.4	0.164	0.142	2.0	0.272	0.229
–15.3	0.162	0.138	1.0	0.244	0.207
			0.0	0.223	0.190
			–2.0	0.195	0.169
			–5.0	0.175	0.152

Table S4. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 5%

Measured			Fitted		
T (°C)	*x* coordinates	*y* coordinates	*T* (°C)	*x* coordinates	*y* coordinates
16.0	0.510	0.411	8.6	0.499	0.399
12.0	0.509	0.410	8.4	0.478	0.383
8.7	0.503	0.403	8.2	0.458	0.368
7.1	0.393	0.316	8.0	0.439	0.354
5.5	0.271	0.227	7.75	0.418	0.338
3.4	0.213	0.185	7.5	0.398	0.323
1.1	0.194	0.171	7.25	0.379	0.309
–0.6	0.183	0.163	7.0	0.362	0.296
–2.1	0.176	0.156	6.5	0.332	0.273
–3.8	0.170	0.151	6.0	0.307	0.254
–5.5	0.167	0.148	5.5	0.285	0.238
–7.5	0.165	0.145	5.0	0.267	0.224
			4.0	0.238	0.202
			3.0	0.217	0.186
			1.0	0.191	0.167

Table S5. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 10%

Measured			Fitted		
T (°C)	*x* coordinates	*y* coordinates	*T* (°C)	*x* coordinates	*y* coordinates
–6.0	0.163	0.146	4.0	0.184	0.165
–2.5	0.167	0.151	6.0	0.209	0.184
–0.7	0.175	0.159	7.0	0.233	0.203
0.8	0.175	0.159	7.5	0.251	0.216
2.5	0.181	0.163	8.0	0.273	0.232
4.0	0.189	0.170	8.5	0.301	0.253
5.6	0.204	0.181	9.0	0.336	0.280
6.8	0.224	0.196	9.25	0.358	0.296
8.0	0.253	0.218	9.5	0.382	0.313
8.6	0.289	0.245	9.75	0.409	0.333
9.3	0.403	0.328	10.0	0.439	0.356
10.4	0.485	0.389	10.2	0.467	0.375
12.0	0.496	0.398	10.4	0.497	0.397
16.5	0.500	0.403			

Table S6. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 15%

Measured			Fitted		
T (°C)	*x* coordinates	*y* coordinates	*T* (°C)	*x* coordinates	*y* coordinates
–6.5	0.162	0.158	7.0	0.183	0.178
–3.9	0.164	0.162	9.0	0.200	0.192
–2.5	0.165	0.164	10.0	0.218	0.205
–0.9	0.167	0.166	11.0	0.248	0.226
2.9	0.176	0.174	11.5	0.271	0.241
5.8	0.190	0.184	12.0	0.299	0.260
7.2	0.200	0.191	12.25	0.317	0.271
8.5	0.211	0.199	12.5	0.337	0.284
10.1	0.228	0.209	12.75	0.359	0.298
12.0	0.286	0.247	13.0	0.385	0.313
12.7	0.342	0.285	13.2	0.408	0.327
13.1	0.397	0.321	13.4	0.434	0.343
13.4	0.447	0.353			
14.1	0.482	0.378			
15.1	0.492	0.385			
16.2	0.497	0.387			
17.2	0.499	0.388			

Table S7. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 20%

Measured			Fitted		
T (°C)	*x* coordinates	*y* coordinates	*T* (°C)	*x* coordinates	*y* coordinates
0.0	0.164	0.152	13.0	0.193	0.176
4.6	0.168	0.157	15.0	0.223	0.199
6.7	0.171	0.160	16.0	0.250	0.219
7.9	0.174	0.162	17.0	0.290	0.249
8.8	0.176	0.164	17.5	0.318	0.269
9.8	0.179	0.167	18.0	0.351	0.294
10.8	0.182	0.170	18.25	0.371	0.308
11.8	0.187	0.173	18.5	0.393	0.324
13.1	0.195	0.180	18.75	0.417	0.342
14.2	0.206	0.187	19.0	0.443	0.361
15.3	0.222	0.199	19.2	0.466	0.378
16.3	0.250	0.219	19.4	0.492	0.397
17.4	0.313	0.263			
18.4	0.403	0.330			
19.4	0.484	0.392			
21.3	0.506	0.410			
24.5	0.507	0.409			

Table S8. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 25%

Measured			Fitted		
T (°C)	*x* coordinates	*y* coordinates	*T* (°C)	*x* coordinates	*y* coordinates
6.0	0.165	0.154	16.0	0.183	0.169
9.8	0.169	0.158	18.0	0.199	0.181
11.0	0.170	0.160	20.0	0.232	0.206
12.1	0.172	0.162	21.0	0.261	0.228
13.3	0.175	0.164	22.0	0.304	0.259
14.7	0.179	0.168	22.5	0.332	0.280
16.0	0.185	0.172	23.0	0.365	0.305
17.3	0.193	0.179	23.25	0.384	0.319
18.7	0.208	0.189	23.5	0.406	0.335
20.1	0.231	0.207	23.75	0.429	0.352
21.6	0.281	0.242	24.0	0.455	0.371
23.2	0.386	0.318	24.2	0.477	0.387
24.4	0.499	0.405	24.4	0.501	0.405
25.7	0.506	0.413			
27.8	0.507	0.413			
31.0	0.509	0.415			

Table S9. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 30%

Measured			Fitted		
T (°C)	*x* coordinates	y coordinates	*T* (°C)	*x* coordinates	*y* coordinates
12.5	0.167	0.173	20.0	0.187	0.188
15.6	0.173	0.178	22.0	0.208	0.203
16.8	0.176	0.181	23.0	0.227	0.216
18.5	0.182	0.186	24.0	0.258	0.237
20.7	0.196	0.196	24.5	0.279	0.251
21.4	0.203	0.200	25.0	0.306	0.269
22.1	0.213	0.207	25.25	0.321	0.279
23.0	0.227	0.216	25.5	0.339	0.291
23.8	0.248	0.230	25.75	0.358	0.304
24.6	0.279	0.249	26.0	0.380	0.318
26.1	0.393	0.325	26.2	0.399	0.331
26.8	0.470	0.376	26.4	0.421	0.345
27.7	0.505	0.402	26.6	0.444	0.360
30.5	0.514	0.409	26.8	0.469	0.376
33.0	0.517	0.410			
35.0	0.516	0.409			

Table S10. The measured CIE coordinates and the CIE coordinates derived by the function of DPC in the ethanol/glycerol mixtures with the f_g = 35%

Measured			Fitted		
T (°C)	x coordinates	y coordinates	T (°C)	x coordinates	y coordinates
12.4	0.164	0.172	25.0	0.189	0.194
15.9	0.167	0.176	27.0	0.214	0.211
17.5	0.169	0.179	28.0	0.237	0.226
19.1	0.172	0.181	29.0	0.271	0.249
22.8	0.183	0.189	29.5	0.295	0.264
23.8	0.187	0.193	30.0	0.323	0.283
24.8	0.193	0.197	30.25	0.340	0.294
25.6	0.200	0.201	30.5	0.358	0.305
26.4	0.208	0.207	30.75	0.379	0.319
27.4	0.221	0.216	31.0	0.402	0.333
28.2	0.240	0.227	31.2	0.422	0.346
28.9	0.263	0.242	31.4	0.443	0.359
29.6	0.297	0.264			
30.5	0.362	0.307			
31.4	0.444	0.361			
32.3	0.493	0.394			
33.3	0.502	0.401			
35.0	0.505	0.405			