New focus of the cloud point/Krafft point of nonionic/cationic surfactants as thermochromic materials for smart windows

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1. Materials and Methods

1.1 Materials

Poly(oxyethylene) monoalkyl ether ($C_{12}(EO)_6$) were purchased from Sigma-Aldrich. Hexadecylpyridinium bromide (HPB) was supplied by Aladdin (Shanghai, China). NaBr, KBr, $NaNO_3$, NaCl and $MgCl_2$ were obtained from Sinopharm (Shanghai, China). Agarose was purchased from Macklin (Shanghai, China). The deionized water with a resistivity of 18.2 MΩ·cm (25 °C) was obtained from UPH-IV ultrapure water apparatus (China). All reagents were used directly without further purification.

1.2 Methods

1.2.1 Fabrication of liquid SW

The liquid SW was prepared from a mixture of $C_{12}(EO)_6$ and HPB solutions with inorganic salts. The appropriate amounts of $C_{12}(EO)_6$, HPB and inorganic salt were added according to Tables S1, S2 and S3. The whole components were put into a certain quantity of water and dissolved under stirring at 30 °C for 30 min and then the samples were stored at 25 °C to ready for pouring the containers.

1.2.2 Fabrication of gel SW

The gel SW was fabricated on the basis of liquid SW. The agarose (5 wt%) was added to the liquid SW undergoing a heating-cooling process. Firstly, the sample was heated at 90 °C under stirring at 600 rpm until the agarose dissolved completely. Secondly, the precursor solution was placed at 30 °C for 5 min to avoid bubbling. Thirdly, the precursor solution was poured to the container. In the end, the container containing the precursor solution was placed at room temperature to get the gel SW.

1.2.3 Measurements of Krafft point and cloud point

The T_k was determined using the differential scanning calorimetry (DSC). Because the heat flow of phase separation was too small to be detected, we ascertained T_c through visual observation. The samples were placed in water bath with the increasing temperature of 1 °C and standing time of 30 min each time. Each measurement was repeated three times.

1.2.4 Outdoor performance test of model houses

Two model houses with indoor lamps were severally equipped with SW and bare ordinary glass. The model houses with the indoor lamp off were placed under the infrared lamp at a distance of 20 cm firstly. The indoor temperatures of the model houses were monitored by thermocouple thermometer while the temperatures of window surface were measured by infrared thermometer. Then, the model houses with the indoor lamp on were transferred to constant temperature incubator (T = 10 °C). The environmental temperatures of the model houses were monitored by thermocouple thermometer.

1.2.5 Solar modulation calculation

The transmittance spectra in the wavelength range of 300 - 2500 nm were collected on a UV-visible-NIR spectrophotometer (Agilent Cary 5000, American) at normal incidence. The spectrophotometer was equipped with a heating and cooling stage. The integral solar, luminous, and infrared transmittance, T_{solar} (300-2500 nm), T_{lum} (380-780 nm) and T_{IR} (780-2500 nm) were calculated by Eq. 1:

$$T_{\text{solar, lum, IR}} = \frac{\int \phi_{\text{solar, lum, IR}}(\lambda) T(\lambda)\, \mathrm{d}\lambda}{\int \phi_{\text{solar, lum, IR}}(\lambda)\, \mathrm{d}\lambda} \quad (1)$$

$T(\lambda)$ denotes the spectral transmittance, $\varphi_{\text{solar, lum, IR}}$ (λ) is the standard luminous efficiency function of photopic vision in the wavelength range of 300-2500 nm, 380-780 nm, 780-2500 nm for an air mass 1.5. The $\varphi_{\text{solar, lum, IR}}$ (λ) is obtained at the sun standing 37° above the horizon with 1.5 atmosphere thickness, which corresponds to a solar zenith angle of 48.2°. $\Delta T_{\text{solar, lum, IR}}$ is obtained by Eq. 2:

$$\Delta T_{\text{solar, lum, IR, 25-4 °C/25-50 °C}} = T_{\text{solar, lum, IR, 25 °C}} - T_{\text{solar, lum, IR, 4 °C/50 °C}} \quad (2)$$

1.2.6 UV blocking calculation

The percentage blocking for UV (280-380 nm) was calculated by Eq. 3:

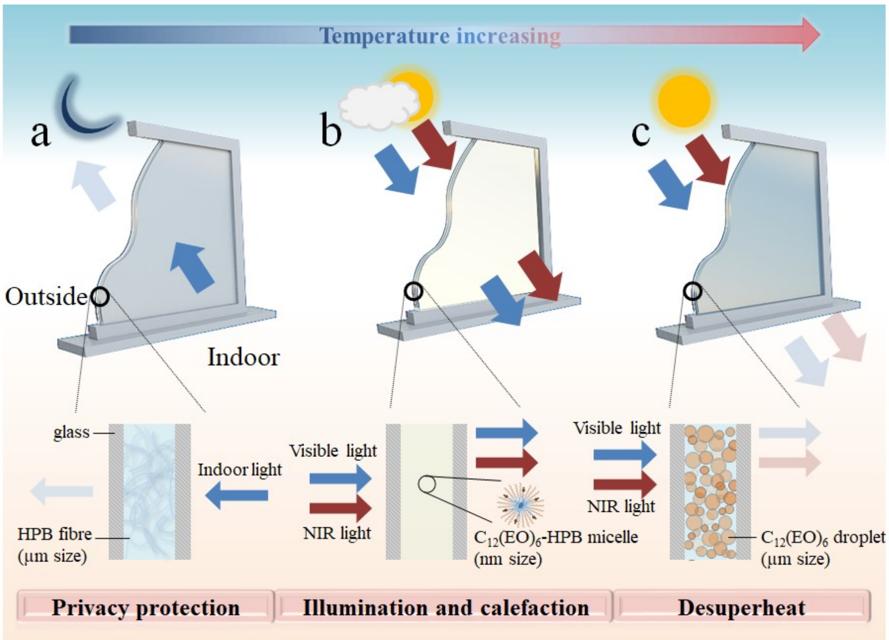
$$\text{UV blocking (\%)} = 100 - \frac{\int_{280}^{380} T(\lambda)\, \mathrm{d}\lambda}{\int_{280}^{380} \mathrm{d}\lambda} (\%) \quad (3)$$

T (λ) is average spectral transmittance, d (λ) is bandwidth, and λ is wavelength.

1.2.7 Apparatus and characterization

The gel was freeze-dried at -60 °C for 24 h to obtain xerogel powders. Scanning electron microscopy (SEM) characterizations were observed on a Zeiss G300 SEM operating at 3 kV. Differential scanning calorimetry (DSC) measurements were performed on a Tzero 250 within the temperature range of 20-70 °C with a heating rate of 5 °C·min^{-1}.

2. Supplementary Figures, Tables and Movies



Scheme S1 Schematic illustration of the SW system based on united surfactants for an opacity-transparence-opacity transition with the increase of temperature.

Table S1 Recipes of the $C_{12}(EO)_6$-HPB-n system.

Sample	$C_{12}(EO)_6$ (M)	HPB (mM)	$C_{12}(EO)_6$/HPB (wt/wt)	T_k (°C)	T_c (°C)
$C_{12}(EO)_6$-HPB-1	0.44	6.7	40：1	5	55
$C_{12}(EO)_6$-HPB-2	0.44	13.2	40：2	5	64
$C_{12}(EO)_6$-HPB-3	0.44	20	40：3	6	75
$C_{12}(EO)_6$-HPB-4	0.44	26.7	40：4	8	80
$C_{12}(EO)_6$-HPB-5	0.44	33.2	40：5	10	91
$C_{12}(EO)_6$-HPB-6	0.44	40	40：6	12	-

Table S2 Recipes of the HPB-$C_{12}(EO)_6$-n system.

Sample	$C_{12}(EO)_6$ (M)	HPB (mM)	T_k (°C)	T_c (°C)
HPB-$C_{12}(EO)_6$-1	0.28	20	7	-
HPB-$C_{12}(EO)_6$-2	0.39	20	7	73
HPB-$C_{12}(EO)_6$-3	0.48	20	6	66
HPB-$C_{12}(EO)_6$-4	0.59	20	6	61
HPB-$C_{12}(EO)_6$-5	0.69	20	5	59
HPB-$C_{12}(EO)_6$-6	0.82	20	4	57

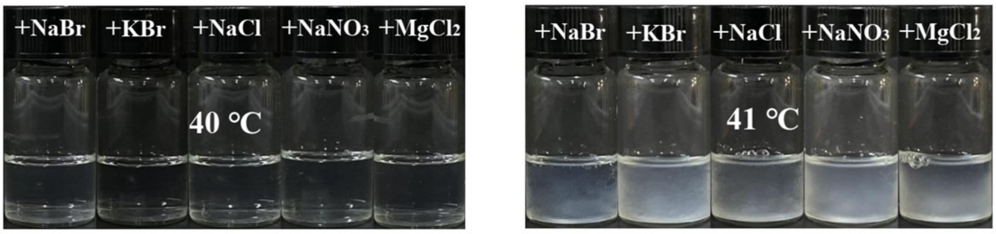


Fig. S1 Sample photos of $C_{12}(EO)_6$-HPB-3 (10 % $C_{12}(EO)_6$/20 mM HPB) at 40 and 41 °C in the presence of different inorganic salts ($MgCl_2$, $NaNO_3$, NaCl, KBr and NaBr) at c_{salt} = 1.0 M.

Table S3 The change of T_k and T_c of $C_{12}(EO)_6$-HPB-3 in the presence of different salts at 1.0 M.

Salts	T_k (°C)	T_c (°C)
NaBr	11.93	41
KBr	11.18	41
NaCl	9.12	41
$NaNO_3$	10.70	41
$MgCl_2$	9.92	41

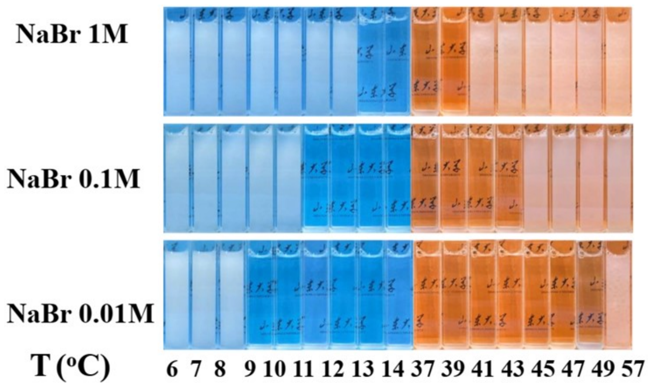


Fig. S2 Sample photos of $C_{12}(EO)_6$-HPB-3 at different temperatures in the presence of NaBr.

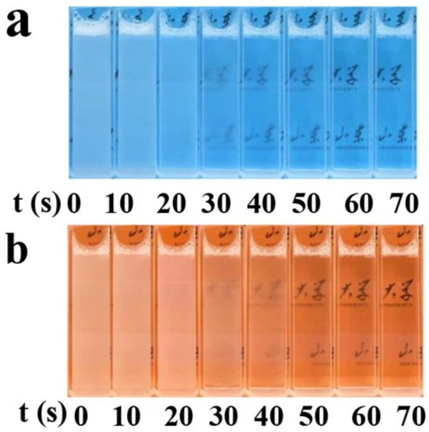


Fig. S3 Appearance change of $C_{12}(EO)_6$-HPB-3 with 1.0 M NaBr in a heating (top row, from 4 °C to room temperature) and cooling (bottom row, from 45 °C to room temperature) process.

Table S4 The change of T_k and T_c of $C_{12}(EO)_6$-HPB-3 in the presence of different contents of NaBr.

NaBr (mM)	T_k (°C)	T_c (°C)
200	8	47
400	9	46
600	10.08	44
800	10.98	43
1000	11.8	41

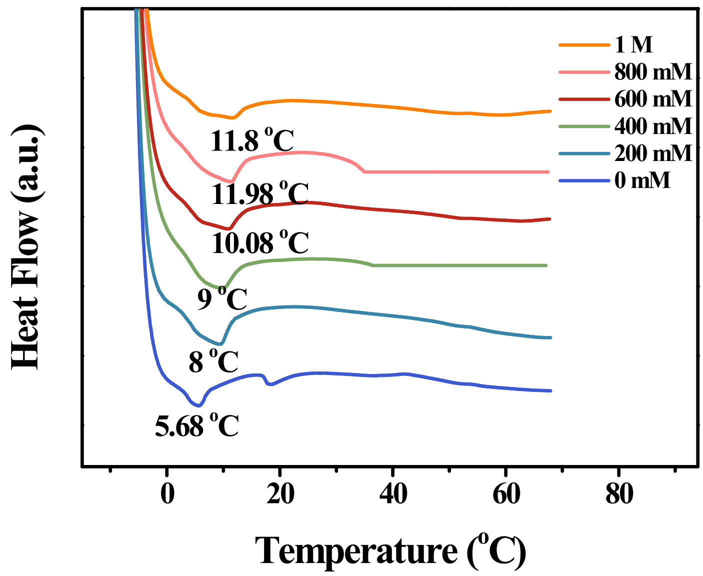


Fig. S4 DSC curves of $C_{12}(EO)_6$-HPB-3 with different concentrations of NaBr.

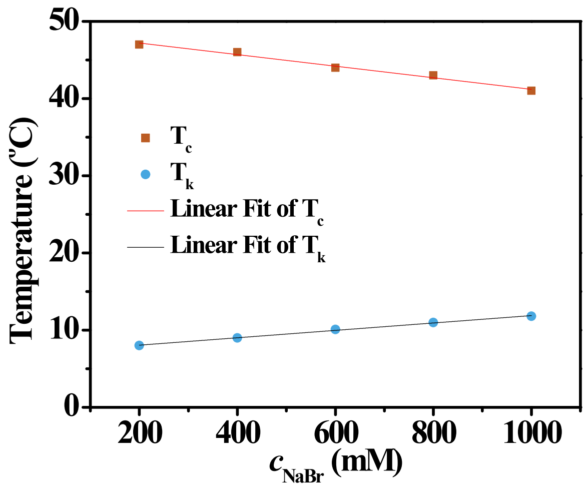


Fig. S5 Variation of T_c and T_k of $C_{12}(EO)_6$-HPB-3 with NaBr concentration.

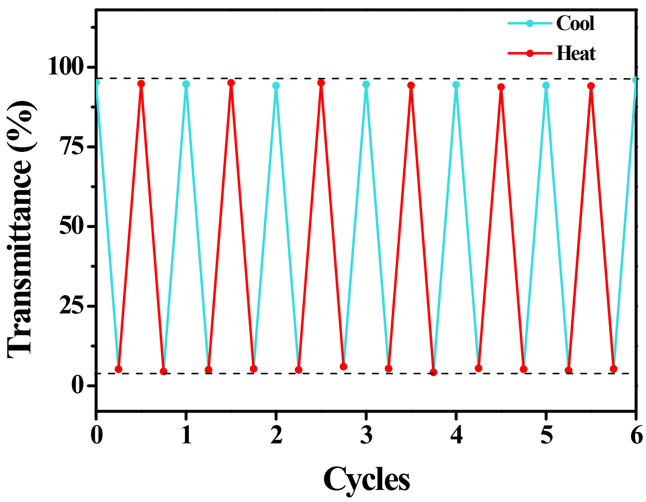


Fig. S6 The change in transmittance of the $C_{12}(EO)_6$-HPB-3 gel at the cooling-heating process for over 6 cycles.

Table S5 The transmittance and transmittance modulation of $C_{12}(EO)_6$-HPB-3/1.0 M NaBr in solution.

	T (4 °C) (%)	T (25 °C) (%)	T (50 °C) (%)	ΔT (25-4 °C) (%)	ΔT (25-50 °C) (%)
solar	0.4	40.1	0.9	39.7	39.2
lum	0.9	99.6	2.4	98.7	97.2
IR	0.2	22.1	0.5	21.9	21.6

Table S6 The transmittance and transmittance modulation of $C_{12}(EO)_6$-HPB-3/1.0 M NaBr gel.

	T (4 °C) (%)	T (25 °C) (%)	T (50 °C) (%)	ΔT (25-4 °C) (%)	ΔT (25-50 °C) (%)
solar	0.3	37.8	0.8	37.5	37.0
lum	0.8	97.9	2.0	97.1	95.9
IR	0.2	21.2	0.4	21.0	20.8