Supporting Information

Title: All-organic Room Temperature Thermally Switchable Dielectric System

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Table S1. The initial parameters of each layer in the system.

Layer	ε'_i	σ_i / S cm^{-1}	d_i / mm
I	2.5	$3.8X10^{-14}$	0.056
II	4.5	$8.5X10^{-13}$	0
III	4.8	$3.1X10^{-9}$	4.838

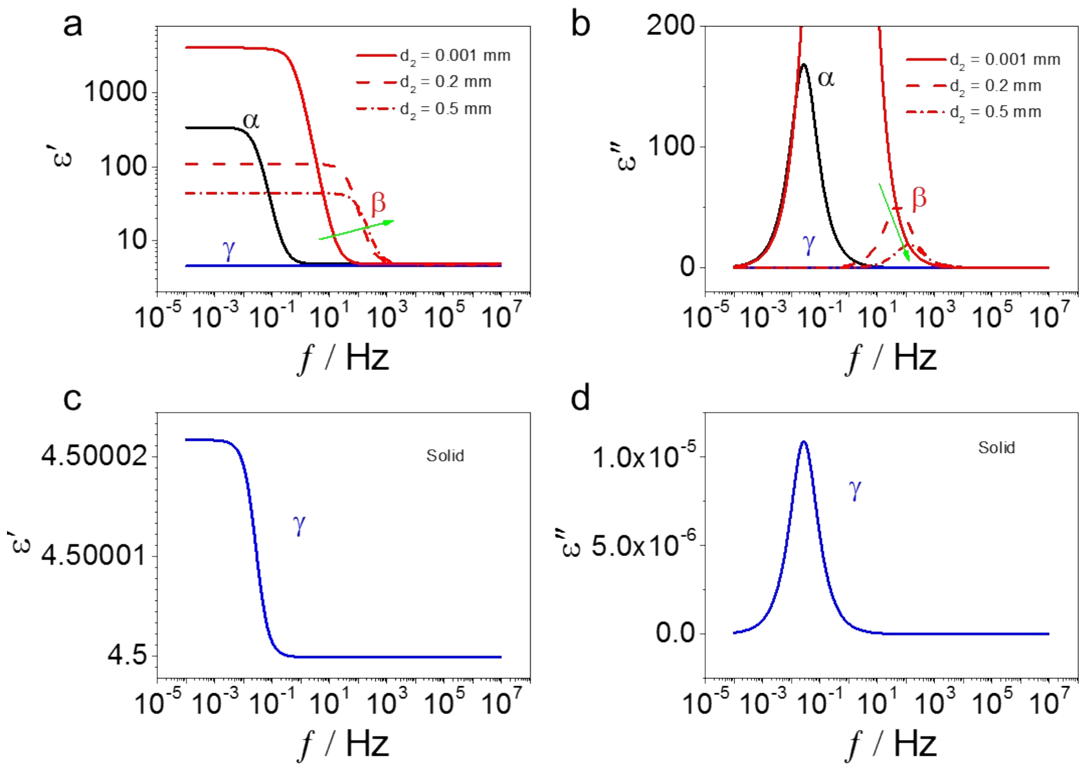

Figure S1. The (a) real and (b) imaginary dielectric spectrum of the system at different stages. The dark line, red line and blue line represent the liquid state, phase transition and solid state, respectively. (c) and (d) are the magnified plot of the relaxation γ in Figure S1 (a) and Figure S1 (b).

Here, the thickness of the insulating film (d_1) is 10^{-7} mm.

The strong relaxation α comes from the interface between the insulating film and the liquid mixture (Figure S1(a)). During the phase transition, the relaxation α is replaced by the relaxation β that stems from the interface between the solid mixture and the liquid mixture (Figure S1(b)). Whereas the relaxation γ caused by the interface between the insulating film and the solid mixture is too small that it is overlapped by the relaxation β. At the solid mixture thickness (d_2) of 0.001 mm, the strength of the relaxation β boosts the dielectric constant of the system, which is responsible to the peak trend in Figure 1(b). As the solid mixture becomes thicker, the strength of the relaxation β declines. After complete solidification, the relaxation β vanishes and the tiny strength of the relaxation γ is shown in Figure S1(c) and (d).

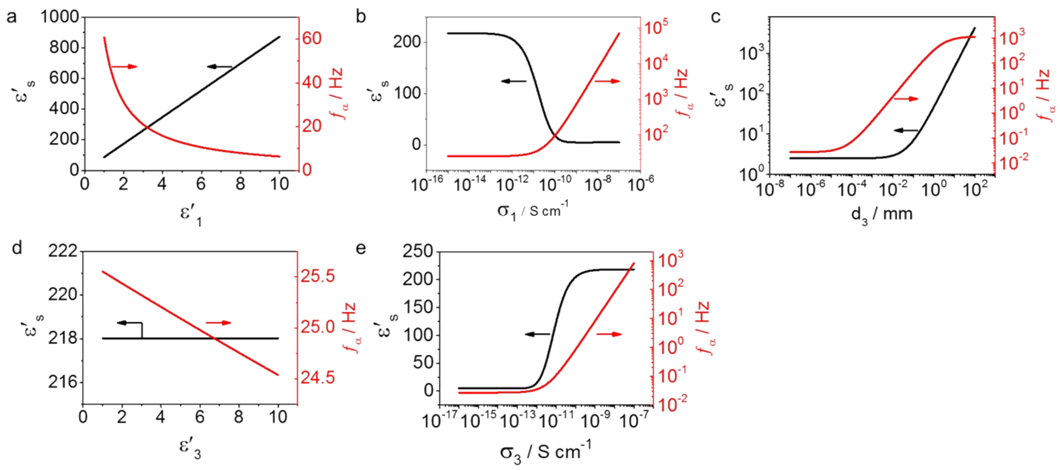

Figure S2. Influence of the parameters of (a)-(b) the insulating layer and (c)-(e) the liquid layer on the dielectric constant of the system (ε'_s) and the frequency of the relaxation α (f_α). Here, the simulation focuses on the first stage of the system.

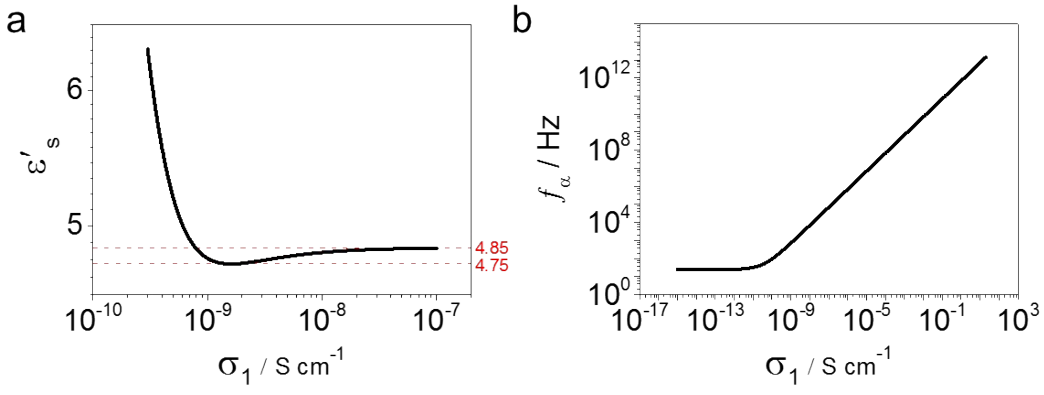

Figure S3. The influence of the conductivity of the insulating film (σ_1) on (a) the dielectric constant of the system (ε'_s) and (b) the frequency of the relaxation α (f_α) at the first stage.

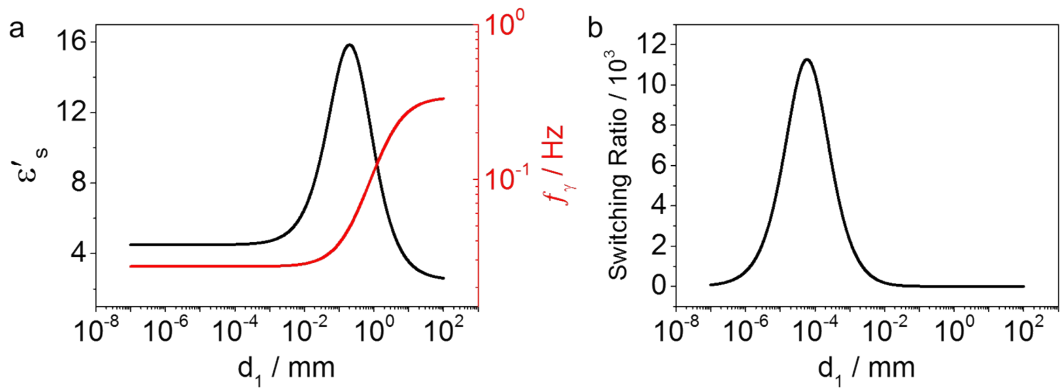

Figure S4. (a) Dependence of the dielectric constant of the system (ε'_s), the frequency of the relaxation γ (f_γ) and on the thickness of layer I (d_1) after the whole mixture becomes solid. (b) Dependence of the switching ratio on the thickness of layer I (d_1)

In the first stage, the "three-layer" model degenerates into the "two-layer" model[1] composed by layer I and layer III. The dielectric constant (ε'_s) and relaxation frequency (f) of the system is determined by the following equations,[2]

$$\varepsilon'_s = d\left(\frac{d_1\varepsilon'_1}{\sigma_1^2} + \frac{d_3\varepsilon'_3}{\sigma_3^2}\right) \Big/ \left(\frac{d_1}{\sigma_1} + \frac{d_3}{\sigma_3}\right)^2 \qquad \text{(S1)}$$

$$f = \frac{1}{2\pi\varepsilon_0}\left(\frac{\sigma_1}{d_1} + \frac{\sigma_3}{d_3}\right) \Big/ \left(\frac{\varepsilon'_1}{d_1} + \frac{\varepsilon'_3}{d_3}\right) \qquad \text{(S2)}$$

where ε_0 is the dielectric constant of vacuum. According to Equation S1 and S2, the dielectric constant of the system (ε'_s) and the frequency of the relaxation α (f_α) are profoundly affected by the dielectric constant (ε'_1) and conductivity (σ_1) of the insulating film (Figure S2(a) and (b)). Specifically, as ε_1 increases from 1 to 10, ε'_s increases from 44.9 to 449.3 in an approximately linear manner, and f_α decreases concavely from 60.8 to 6.4 as shown in Figure S2 (a). Figure S2 (b) shows the dependence of ε'_s and f on σ_1. With the increasing of σ_1, ε'_s begins at a plateau value of 218.5 (σ_1 is 1.0X10^{-15} S cm^{-1}) and quickly goes down to its low plateau of 4.9 (σ_1 is 1.0X10^{-7} S cm^{-1}). During the descending, it is interesting to find that ε'_s attains a minimum of 4.75 when σ_1 equals to 1.6X10^{-9} S cm^{-1}, as indicated in Figure S3(a)). Whereas f_α changes with the increasing of σ_1 in a different way. Initially, f is as low as 25.1 Hz (σ_1 is 1.s0X10^{-15} S cm^{-1}), and then it holds a straight increasing when σ_1 is above 1.0X10^{-11} S cm^{-1} , as Figure S2(b) and Figure S3(b) show. The liquid mixture (layer III) also plays an important role in determining the dielectric property of the system. As shown in Figure S2(c), ε'_s and f_α is positively correlated with the thickness of the liquid mixture (d_3). Specifically, as d_3 increases, ε'_s maintains a low plateau of 2.5 at first, and then keep a continuous growth after d_3 is larger than 1X10^{-2} mm). While f_α goes up from the low plateau of 0.027 Hz (d_3 is 1X10^{-7} mm) and reaches the plateau value of 1125.6 Hz at the thickness of 100 mm. Contrarily, ε'_s shows strong immunity and f_α suffers a slight falloff to the variation of the dielectric constant of the liquid mixture (ε'_3) (Figure S2(d)). Besides, by changing the conductivity of the liquid mixture (σ_3), there is a dramatic rise in both ε'_s and f_α (Figure S2(e)). Concretely, as σ_3 increases, ε'_s is enhanced from 4.9 (σ_3 is 1.0X10^{-16} S cm^{-1}) to 218.5 (σ_3 is 1.0X10^{-7} S cm^{-1}), and f_α keeps rising up when σ_3 is beyond 1.0X10^{-12} S cm^{-1}.

In the third stage where the mixture totally turns into solid, the dielectric constant of the system goes into the low state as shown in Figure 1(b). The system is composed by the insulating film (layer I) and the solid mixture (layer II). The dielectric constant of the system (ε'_s) and the frequency of the relaxation γ (f_γ) can be simulated by the following equations:

$$\varepsilon_s = d\left(\frac{d_1\varepsilon_1^{'}}{\sigma_1^2} + \frac{d_2\varepsilon_2^{'}}{\sigma_2^2}\right)\Big/\left(\frac{d_1}{\sigma_1} + \frac{d_2}{\sigma_2}\right)^2 \qquad \text{(S3)}$$

$$f = \frac{1}{2\pi\varepsilon_0}\left(\frac{\sigma_1}{d_1} + \frac{\sigma_2}{d_2}\right)\Big/\left(\frac{\varepsilon_1^{'}}{d_1} + \frac{\varepsilon_2^{'}}{d_2}\right) \qquad \text{(S4)}$$

According to Equation S3 and S4, by altering the thickness of the insulating film (d_1), ε'_s increases from 4.5 (d_1 is 1X10^{-7} mm) and peaks at 15.8 (d_1 is 0.2 mm), then it decreases rapidly to

2.6 when d_1 equals to 100 mm as shown in Figure S4. While f_γ monotonically increases from 0.027 Hz (d_1 is 1X10^{-7} mm) to 0.332Hz (d_1 is 100 mm).

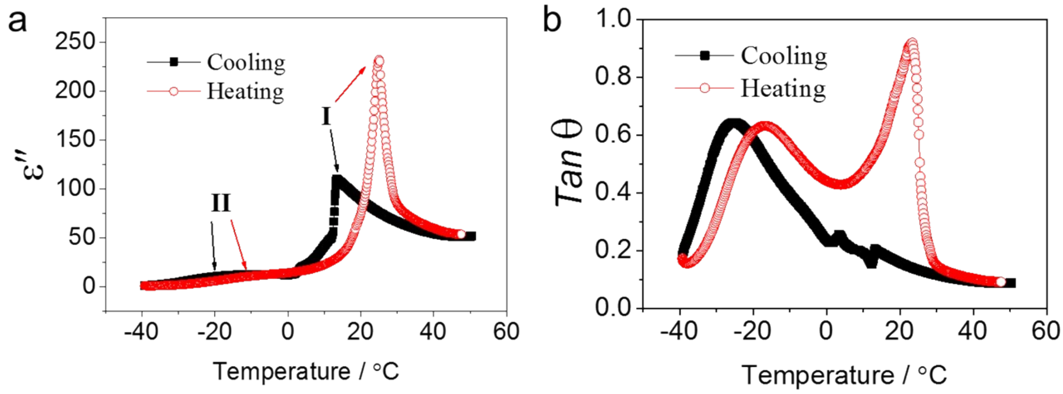

Figure S5. Dependence of (a) the imaginary part of the dielectric constant and (b) the dielectric loss of the system between 50 ˚C and -30 ˚C in the isochronous measurement (1Hz, 2 K min^{-1}).

References:

1. P. Meng, Y. L. Wu, Q. Zhang, G. Cheng, X. L. Wu and R. T. Zheng, *Adv. Funct. Mater.*, 2018, **28**, 1801421.
2. L. K. H. Van Beek, *Progress in dielectrics*, Heywood, London, 1967.