Electronic Supplementary Material (ESI) for Materials Advances.

Electronic supplementary information for

Huge Dielectric Constants of the Ferroelectric Smectic-A Phase in Bent-Shaped Dimeric Molecules

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Fig. S1 Schematic representations of (a) 16OAM5AMO16 and 4OAM5AMO4 structures, (b) the $SmCA^s$ phase, (c) the SmC_AP_A phase, and (d) the $SmAP_F$ phase.

Fig. S2 The switching current curves obtained for the $SmAP_F$ phase by applying a triangle-wave field (20 V_{pp}, 30 Hz) in a 3 μm-thick cell.

Fig. S3 Typical DSC thermogram for (a) 4OAM5AMO4, (b) 16OAM5AMO16, and (c) 4OAM5AMO4 (65 mol%) + 16OAM5AMO16 (35 mol%).

Table S1 List of Cole-Cole parameters, $\Delta\varepsilon$, ε_s, ε_∞, α and f_r determined from the data of Fig. 2 and Fig. 4.

Fig. S4 The imaginary part of the dielectric constants (ε'' in log scale) in the $SmAP_F$ phase measured under the DC bias fields in (a) a 10 μm-thick cell and (b) a 25 μm-thick cell.

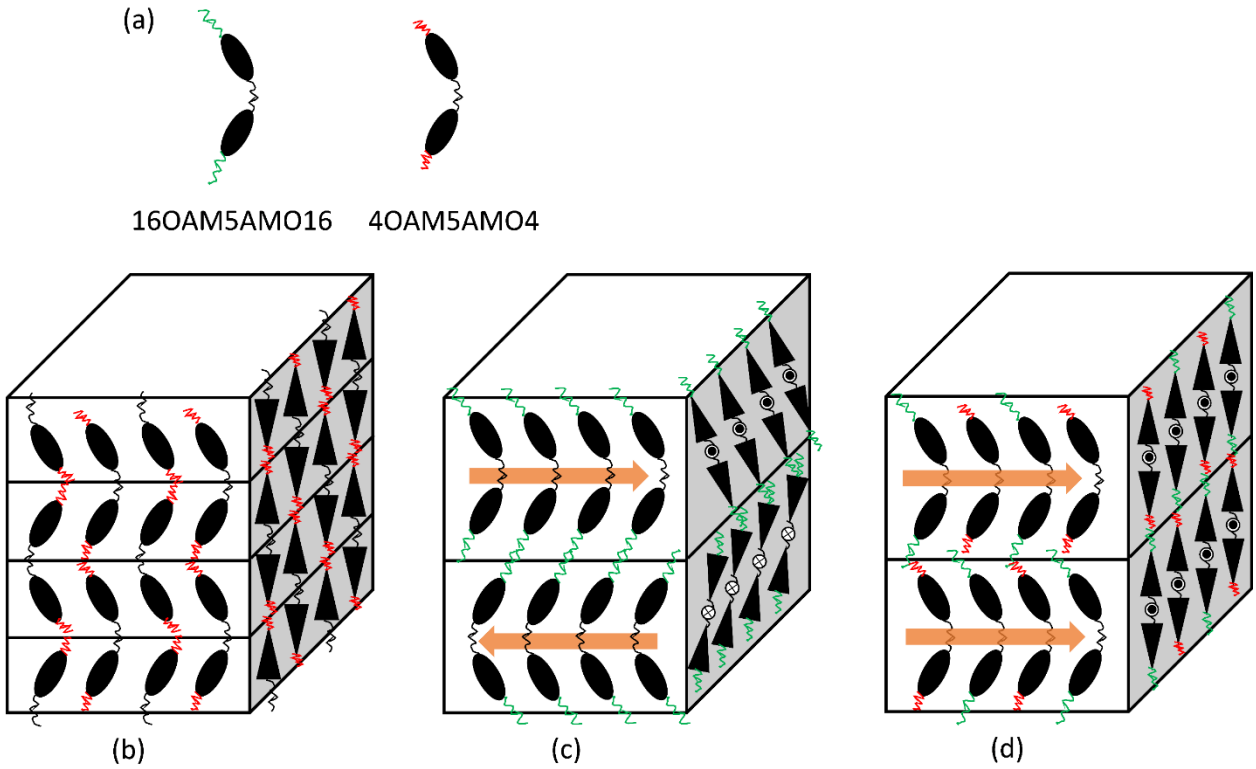

Fig. S1 Schematic representations of (a) 16OAM5AMO16 and 4OAM5AMO4 structures, (b) the $SmCA^{s}$ phase, (c) the SmC_AP_A phase, and (d) the $SmAP_F$ phase. In the $SmCA^{s}$ phase of (b), each layer is constructed by each mesogen but not each dimeric molecule, resulting from the random mixing of the alkyl spacer and the alkoxy tail groups. In (c) and (d), each layer is constructed by each molecule with the same bent (polar) direction (orange arrow). In the SmC_AP_A phase of (c), the molecules are tilted to the layer, and the polar directions are opposite between the neighboring layers. In the $SmAP_F$ phase of (d), the molecules lie perpendicular to the layer, with ferroelectric alignment of the polar directions.

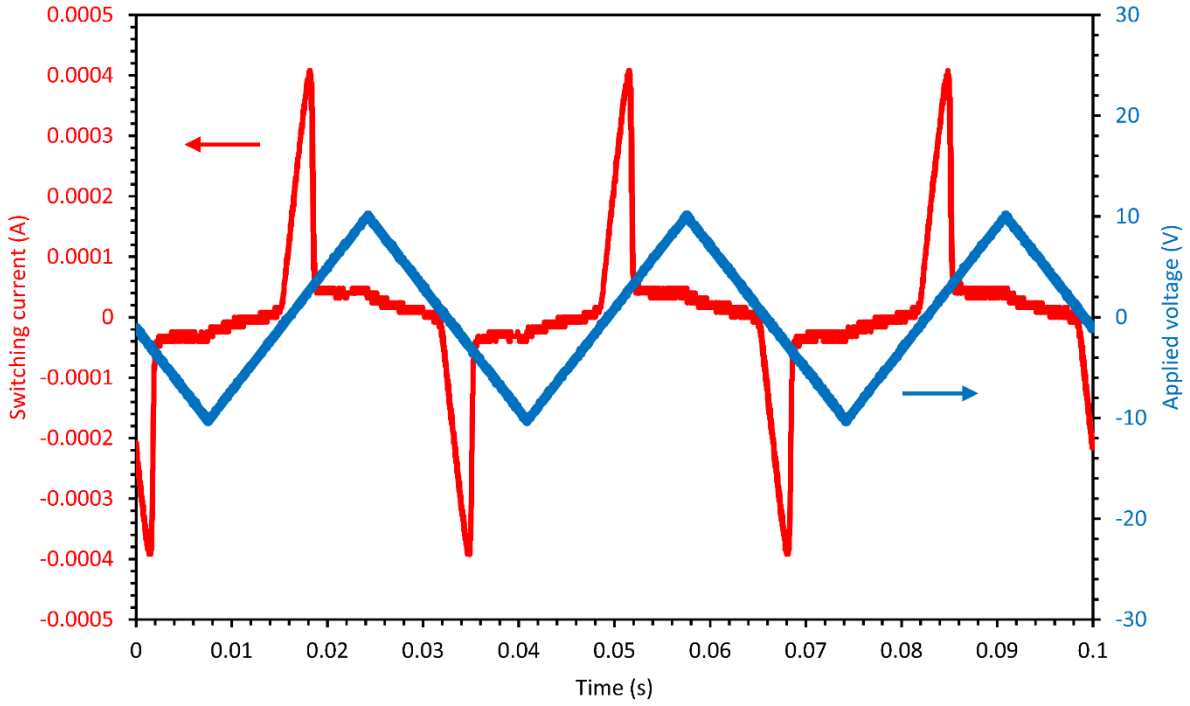

Fig. S2 The switching current curves obtained for the $SmAP_F$ phase by applying a triangle-wave field (20 V_{pp}, 30 Hz) in a 3 µm-thick cell. The spontaneous polarization is 700 $nCcm^{-2}$.

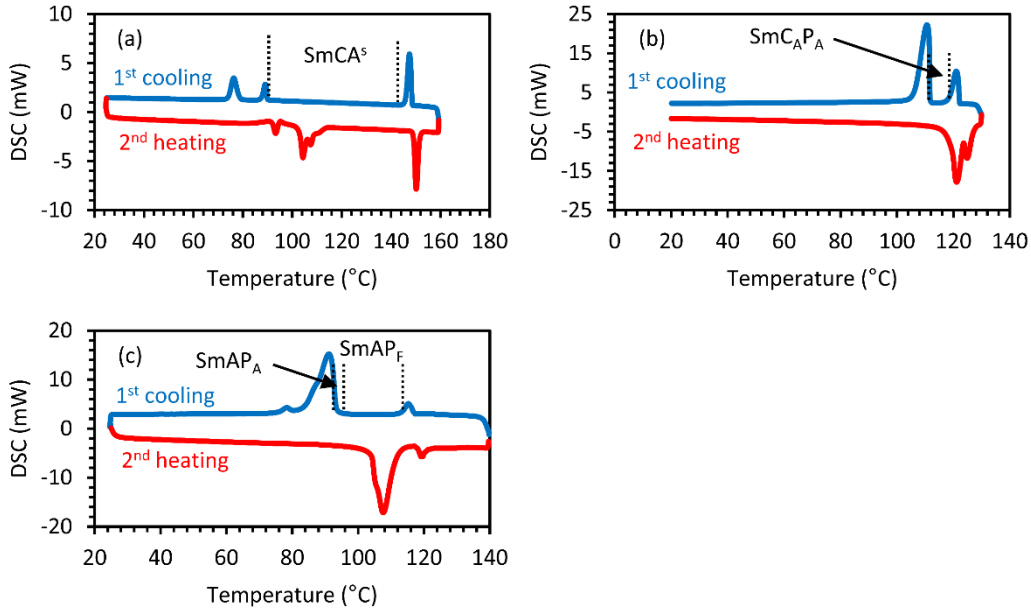

Fig. S3 Typical DSC thermogram for (a) 4OAM5AMO4, (b) 16OAM5AMO16, and (c) 4OAM5AMO4 (65 mol%) + 16OAM5AMO16 (35 mol%). Scanning rate is 5°$Cmin^{-1}$.

Table S1 List of Cole-Cole parameters, $\Delta\varepsilon$, ε_s, ε_∞, α and f_r determined from the data of Fig. 2 and Fig. 4.

	$SmAP_F$ in a 3 μm-thick cell	$SmCA^s$ in a 3 μm-thick cell	SmC_AP_A in a 3 μm-thick cell	$SmAP_F$ in a 10 μm-thick cell	$SmAP_F$ in a 25 μm-thick cell	$SmAP_F$ in a 50 μm-thick cell
$\Delta\varepsilon$	$(1.82 \pm 0.02)\times10^3$	6.8 ± 0.01	7.2 ± 0.01	$(3.20 \pm 0.05)\times10^3$	$(4.52 \pm 0.07)\times10^3$	$(7.40 \pm 0.08)\times10^3$
ε_s	$(1.82 \pm 0.02)\times10^3$	6.9 ± 0.01	7.3 ± 0.01	$(3.20 \pm 0.05)\times10^3$	$(4.52 \pm 0.07)\times10^3$	$(7.40 \pm 0.08)\times10^3$
ε_∞[a]	1 ± 0.1	0.1 ± 0.01	0.1 ± 0.01	1 ± 0.1	2 ± 0.2	2 ± 0.2
α	0.06 ± 0.01	$(1.0 \pm 0.1)\times10^{-3}$	$(1.0 \pm 0.1)\times10^{-3}$	0.05 ± 0.01	0.07 ± 0.01	0.12 ± 0.02
f_r (Hz)	$(4.9 \pm 0.2)\times10^2$	$(1.3 \pm 0.06)\times10^5$	$(8.2 \pm 0.4)\times10^4$	$(5.4 \pm 0.2)\times10^2$	$(3.5 \pm 0.1)\times10^2$	$(3.3 \pm 0.1)\times10^2$
R^2[b]	0.98	0.96	0.98	0.95	0.93	0.96

[a] The small value of ε_∞ is due to the effect of the resistance of ITO layers, which causes a decrease in dielectric constants at high frequency range above about 10^5 Hz. The precise value of the $\Delta\varepsilon$, especially for high frequency modes of the $SmCA^s$ and the SmC_AP_A phases, will be done after the correction for the resistance contribution[1] or by using the low resistance gold as an electrode.[2]

[b] R^2 (coefficient of determination) is provided based on the ε' and the ε'' from 100 Hz or higher with less ion diffusion.

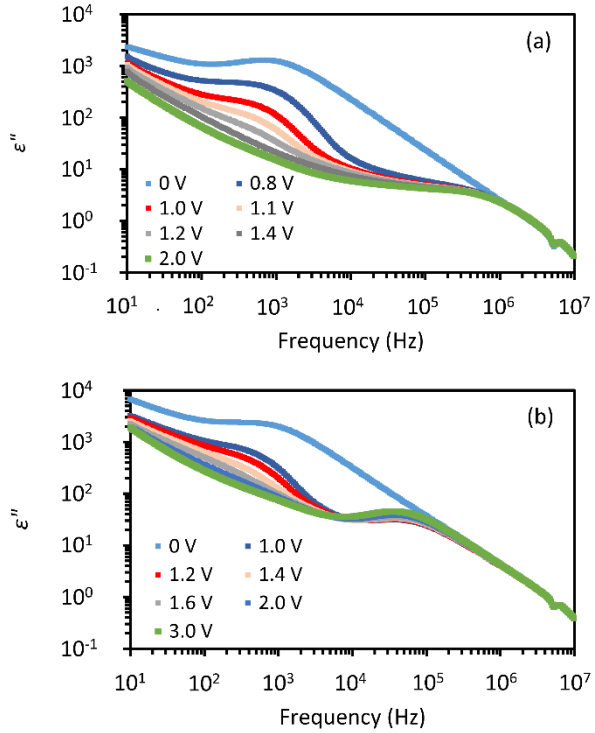

Fig. S4 The imaginary part of the dielectric constants (ε'' in log scale) in the $SmAP_F$ phase measured under the DC bias fields in (a) a 10 µm-thick cell and (b) a 25 µm-thick cell. The critical voltage is 1.4 V (0.14 $V\mu m^{-1}$) and 1.6 V (0.06 $V\mu m^{-1}$) at 10 and 25 µm, respectively. The small depression observed at 6.0×10^6 Hz is the resonance effect due to the DC bias fields.[3]

Reference

1. P. Perkowski, Dielectric spectroscopy of liquid crystals. Electrodes resistivity and connecting wires inductance influence on dielectric measurements, *Opto-Electronics Review*, 2012, **20**, 79–86.

2. P. Perkowski, D. Łada, K. Ogrodnik, J. Rutkowska, W. Piecek, and Z. Raszewski, Technical aspects of dielectric spectroscopy measurements of liquid crystals, Opto-Electronics Review, 2008, **16**, 271–276.

3. P. Perkowski, The parasitic effects in high-frequency dielectric spectroscopy of liquid crystals – the review, Liquid Crystals, 2021, **48**, 767-793.