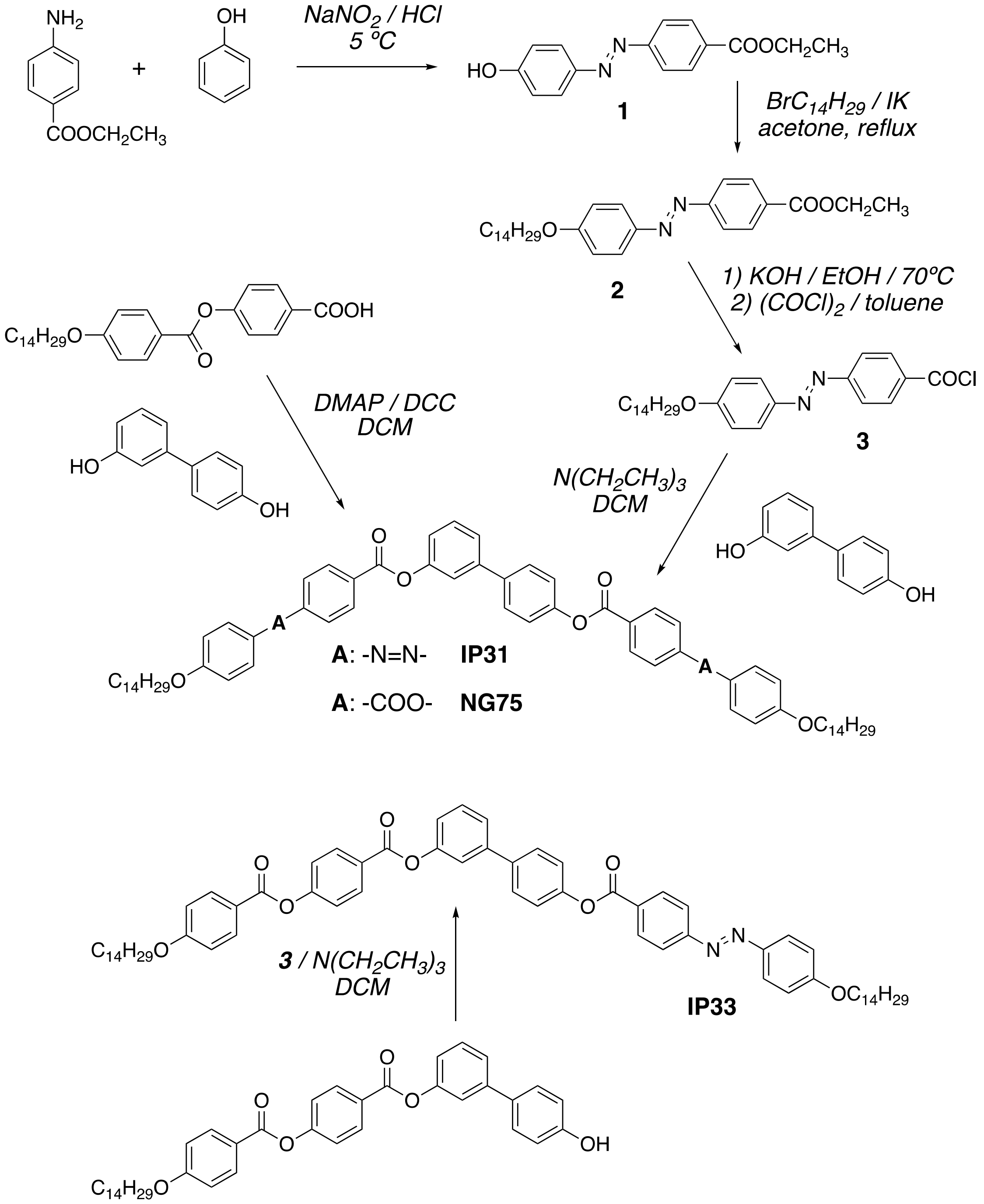
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Light-responsive bent-core liquid crystals as candidates for energy conversion and storage

Electronic Supplementary Information

1. Synthesis

The synthetic procedures for the bent-core compounds herein labeled as NG75, IP31 and IP33 are shown in Scheme 1, and are according to the experimental procedures previously reported by us in *Chem. Mater*. 18, 4617 (2006) (compound C1 = IP31 and compound C3 = IP33) and *Chem. Mater*. 21, 4620 (2009) (compound IIb = NG75).



Scheme 1. Synthesis of compounds IP31, IP33 and NG75

Organic starting materials were purchased from Sigma-Aldrich, Fluka and Lancaster and used as delivered. Solvents were purified and dried by standard techniques. Some of the intermediate products used in the synthesis were prepared according to procedures already reported in the literature: p-n-tetradecyloxybenzoic acid [1], p-(4-n-tetradecyloxybenzoyl)benzoic acid [1, 2], 3,4´-dihydroxy-biphenyl [2, 3], and 3-[4’’-(4’’’-n-tetradecyloxybenzoyloxy)benzoyloxy]biphenyl-4’-ol [1].

Ethyl 4-(4’-hydroxyphenylazo)benzoate (1). A solution of 2.27 g of sodium nitrite (32.04 mmol) in water (15.72 mL) was added dropwise over a suspension of ethyl p-aminobenzoate (4.5 g, 26.70 mmol) in a mixture of hydrochloric acid-water (10 and 30 mL respectively) at ≤5 ºC. The reaction mixture was stirred for 30 minutes and then 3.05 g of phenol (32.04 mmol) were added. After one hour of stirring at ≤5 ºC the cold reaction mixture was poured into a $NaHCO_3$ saturated solution to reach pH of 6-7. An orange coloured solid appeared that it was filtered off, washed with water and recrystallized from ethanol. Yield: 65%. Mp 162.0 ºC. ^{1}H-NMR (400 MHz, CDCl3) δ 8.18 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 5.25 (sbroad, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). IR (Nujol, NaCl) 3395, 1693, 1599, 1280 cm^{-1}.

Ethyl 4-(4’-n-tetradecyloxyphenylazo)benzoate (2). 1-bromo-n-tetradecane (6.35 g, 22.2 mmol) was added via syringe over a mixture of compound **1** (5 g, 18.5 mmol), K2CO3 anhydrous (5.11 g, 37.0 mmol) and KI (0.1 g) in dry acetone (95 mL). The reaction mixture was stirred under reflux and under argon atmosphere for16 hours. The reaction mixture was allowed to cool to room temperature and poured into cold water (180 mL). The solid was extracted with dichloromethane (4x50 mL) and the combined organic layers were dried over Na_2SO_4. The solid was collected by evaporation of the solvent and it was recrystallized from ethanol. Yield: 84 %. Crystal 79.6 ºC SmA 99.5 ºC Isotropic liquid. ^{1}H-NMR (400 MHz, CDCl3) δ 8.17 (d, J = 8.7 Hz, 2H), 7.94 (d, J = 8.7 Hz, 2H), 7.90 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 1.88-1.78 (m, 2H), 1.54-1.20 (m, 22H), 1.42 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H). IR (Nujol, NaCl) 1715, 1603, 1584, 1297 cm^{-1}.

4-(4’-n-tetradecyloxyphenylazo)benzoyl chloride (3).

1) A mixture of 6.0 g of compound **2** (12.9 mmol), KOH (5.8 g, 90 mmol) in ethanol (160 mL) was heated at 78 ºC for 21 h. The reaction mixture was allowed to cool at room temperature and poured into 480 mL of cold water. Concentrated hydrochloric acid was added to reach an acid pH. The collected solid was filtered off, washed with water and recrystallized from pure acetic acid. An orange product was obtained in 91% yield. Cr 160.3 ºC SmX 212.9 ºC

SmC 246.6 ºC Isotropic liquid. ^{1}H-NMR (300 MHz, CDCl3) δ 8.21 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 9.2 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 9.2 Hz, 2H), 4.07 (t, J = 6.5 Hz, 2H), 1.91-1.78 (m, 2H), 1.57-1.20 (m, 22H), 0.90 (t, J = 6.6 Hz, 3H). IR (KBr) 3200-2500, 2920, 2850, 1679, 1602, 1582, 1290 cm^{-1}.

2) A mixture of 4-(4'-n-tetradecyloxyphenylazo)benzoic acid (1.06 g, 2.42 mmol), oxalyl chloride (0.24 g, 1.82 mmol) and few drops of DMF in dry toluene (60 mL) was stirred under argon atmosphere and room temperature for 16 hours. When the reaction mixture became a red coloured solution, the solvent was removed and an orange solid appeared that it was dried under vacuum for 1-2 hours. The absence of the typical IR bands of carboxylic acids was checked and the product was used without further purification.

3,4'-Bis[4-(4-n-tetradecyloxyphenylazo)benzoyloxy]biphenyl (C1 = IP31). A solution of the benzoyl chloride **3** (2.42 mmol) in freshly distilled dichloromethane (10 mL) was added dropwise via syringe to a stirred solution of 3,4'-dihydroxybiphenyl (0.18 g, 0.97 mmol) and triethylamine (0.35 g, 3.43 mmol) in dry dichloromethane (50 mL) under argon atmosphere. The reaction mixture was stirred for 21 hours at room temperature, the white precipitate filtered off and the solvent removed. The orange solid was purified by flash chromatography on silica gel eluting with dichloromethane-hexane (4:1). The pure solid was recrystallized from toluene and from ethyl acetate (yield 70 %). ^{1}H-NMR (300 MHz, CDCl3): δ 8.37 (d, J = 8.5 Hz, 2H), 8.36 (d, J = 8.4 Hz, 2H), 8.04-7.43 (m, 8H), 7.69 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 5.5 Hz, 2H), 7.52-7.48 (m, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.28-7.21 (m, 1H), 7.03 (d, J = 8.9 Hz, 4H), 4.06 (t, J = 6.7 Hz, 4H), 1.90-1.80 (m, 4H), 1.55-1.20 (m, 44H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C-NMR (300 MHz, CDCl3): δ 164.6, 162.6, 156.1, 151.6, 150.9, 147.2, 142.2, 138.1, 131.2, 130.6, 130.5, 129.8, 128.3, 125.3, 124.7, 122.6, 122.1, 120.6, 120.5, 115.0, 68.6, 31.9, 29.6, 29.5, 29.3, 29.2, 26.0, 22.6, 14.0. IR (KBr) 2918, 2850, 1731, 1601, 1584, 1270, 1250 cm-1. Anal. for C66H82N4O6 (calculated 77.16% C, 8.04% H, 5.45% N) found 76.93% C, 7.96% H, 5.34% N. UV-vis (CHCl3, $9.6 \cdot 10^{-6}$ M) λ_{max}: 260 nm (ε: $45.625 \cdot 10^{3}$ M^{-1}cm^{-1}), λ_{max}: 365 nm (ε: 72.604·103 M^{-1}cm^{-1}). MS (FAB+): m/z: 307, 421, 795, 1027.

3-[4''-(4'''-n-tetradecyloxybenzoyloxy)benzoyloxy]-4'-[(4^{iv}-(4^{v}- n-tetradecyloxyfenylazo)benzoyloxy]biphenyl (C3 = IP33). This compound was synthesized following an experimental procedure similar to the one used for compound C1. For this purpose compound **3** (0.40 g, 0.91 mmol), 3-[4''-(4'''-n-tetradecyloxybenzoyloxy)benzoyloxy]biphenyl-4'-ol (0.470 g, 0.76 mmol) and triethylamine (0.17 mL, 1.2 mmol) in dry dichloromethane (60 mL) was used. Purification was carried out by flash chromatography on silica gel eluting with dichloromethane-hexane (4:1) as solvent and recrystallized from toluene and ethyl acetate (yield 80%). ^{1}H-NMR (300 MHz, CDCl3) δ 8.35 (d, J = 8.6 Hz, 2H), 8.31 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 9.0 Hz, 2H), 7.98 (d, J = 8.6 Hz, 2H), 7.97 (d, J = 9.1 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 5.2 Hz, 2H), 7.48-7.46 (m, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.25-7.22 (m, 1H), 7.03 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 9.1 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 1.89-1.78 (m, 4H), 1.55-1.20 (m, 44H), 0.89 (t, J = 6.8 Hz, 6H). ^{13}C-NMR (300 MHz, CDCl3) δ 164.7, 164.5, 164.3, 163.8, 162.5, 155.9, 155.4, 151.3, 150.7, 146.9, 142.1, 138.0, 132.4, 131.8, 131.2, 130.3, 129.9, 128.3, 126.8, 125.3, 124.7, 122.5, 122.1, 122.0, 121.0, 120.6, 120.4, 114.8, 114.4, 68.5, 68.4, 31.9, 30.5, 29.6, 29.5, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1. IR (KBr) 2918, 2850, 1732, 1604, 1581, 1286, 1252 cm^{-1}. Anal. for C66H82N2O8 (calculated 77.13% C, 7.92% H, 2.68% N) found 77.39% C, 7.80% H, 2.63% N. UV-vis (CHCl3, $2.0\cdot10^{-5}$ M): λmax: 265 nm (ε: $64.310\cdot10^{3}$ M^{-1}cm^{-1}), λmax: 365 nm (ε: $35.656\cdot10^{3}$ M^{-1}cm-^{1}). MS (FAB+): m/z: 317, 421, 1044.

3,4´- Bis[4-(4-n-tetradecyloxybenzoyloxy)benzoyloxy]biphenyl (IIb = NG75). To a solution of 3,4´-dihydroxy-biphenyl in 30 mL of distilled dichloromethane, 2.6 mmol of p-(4-n-tetradecyloxybenzoyl)benzoic acid and 0.5 mmol of N,N-dimethylaminopyridine (DMAP) were added under argon atmosphere. The mixture was cooled in a water-ice bath and after 30 minutes, 2.8 mmol of dycyclohexylcarbodiimide (DCC) were added. The reaction mixture was stirred for 24 h at room temperature. After this time, the white solid was filtered off and the solvent evaporated. The solid was purified by flash chromatography in silicagel using dichloromethane as eluent followed by crystallizations from toluene and ethyl acetate. Yield: 0.282 g of white solid (70%). Rf (hexanes: ethyl acetate 8:2): 0.76. 1H-NMR (300 MHz, CDCl3): δ 0.86 (t, J=6.6 Hz, 6H); 1.24-1.53 (m, 44H); 1.83-1.88 (m, 4H); 4.10 (t, J=6.3 Hz, 4H); 6.96 (d, J=9.0 Hz, 4H); 7.20-7.24 (m, 1H); 7.29 (d, J=8.7 Hz, 2H); 7.36 (d, J=8.4 Hz, 4H); 7.44 (s, 1H); 7.50 (d, J=5.1 Hz, 2H); 7.65 (d, J=8.7 Hz, 2H), 8.14 (d, J=8.4 Hz, 4H); 8.28 (dd, J=2.4 Hz, J=9.0 Hz, 4H). 13C-NMR (300 MHz, CDCl3) δ : 10.5, 14.1, 22.6, 26.0, 29.1, 29.3, 29.5, 29.6, 29.7, 29.8, 31.9, 38.1, 57.0, 62.8, 67.3, 68.4, 114.4, 120.5, 120.6, 121.0, 122.0, 122.1, 122.4, 124.7, 126.8, 128.3, 129.9, 131.7, 131.8, 132.4, 132.6, 138.0, 142.1, 150.7, 151.4, 155.5, 163.8, 164.3 164.5. IR (Nujol, NaCl): 1729, 1602, 1509, 1463, 1253, 1161, 758 cm^{-1}. Anal. Calc. for C68H82O10: C, 77.13; H, 7.75. Found: C, 77.23; H, 7.72. MS (FAB+) m/z: 317, 437.

Techniques. UV-Vis measurements were taken using an ATI Unicam UV4 spectrophotometer. Infrared spectra for all the compounds were obtained using ATI Mattson (FT-IR) and Nicolet Avatar 360 (FT-IR) spectrophotometers in the 400–4000 cm^{-1} spectral range. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity 300 MHz, Bruker ARX-300

MHz and Bruker AV-400 MHz spectrometers and samples were in solution. Microanalysis was performed with a Perkin-Elmer 2400 microanalyzer. Mass spectrometry studies (FAB+) were performed with a VG AutoSpec EBE.

2. Calculation of the activation energies

The Arrhenius plots corresponding to the maximum frequency of the ε'' peaks in both the α and β relaxations, f_{max}, deviate to some extent from linearity and follow Vogel-Fulcher-Tamman (VFT) behaviour, see **Fig. 5**. We have calculated apparent activation energies, E_a, from the linear regions in the Arrhenius plots of these relaxations, according to,

$$\ln(f_{max}) = \ln(f_0) - \frac{E_a}{R} \cdot \frac{1}{T}$$

where $\ln(f_0)$ is a preexponential factor, T is the absolute temperature, and R is the gas constant.

3. Figures

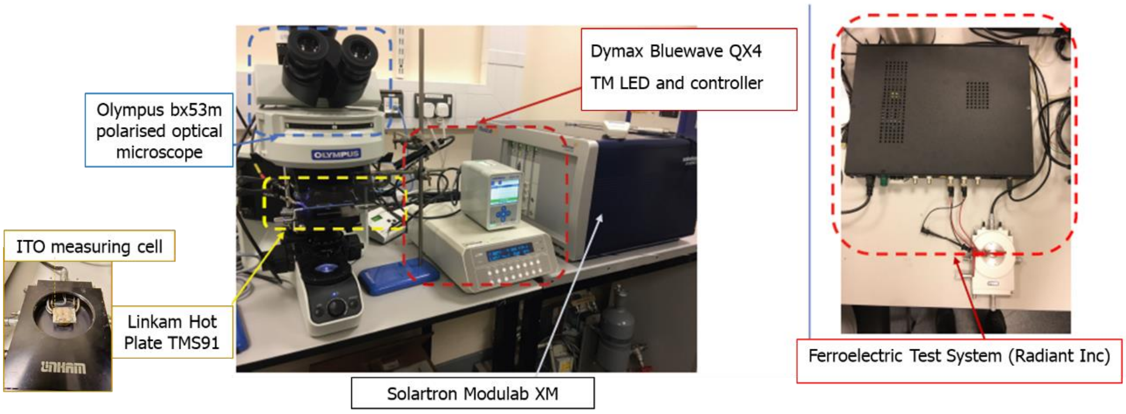


Fig. S1. Picture of the experimental setting including the polarised optical microscope, the Linkam heating stages holding the ITO measuring cells, the Dymax Bluewave QX4 TM LED probe, and connexions to the dielectric and ferroelectric analysers.

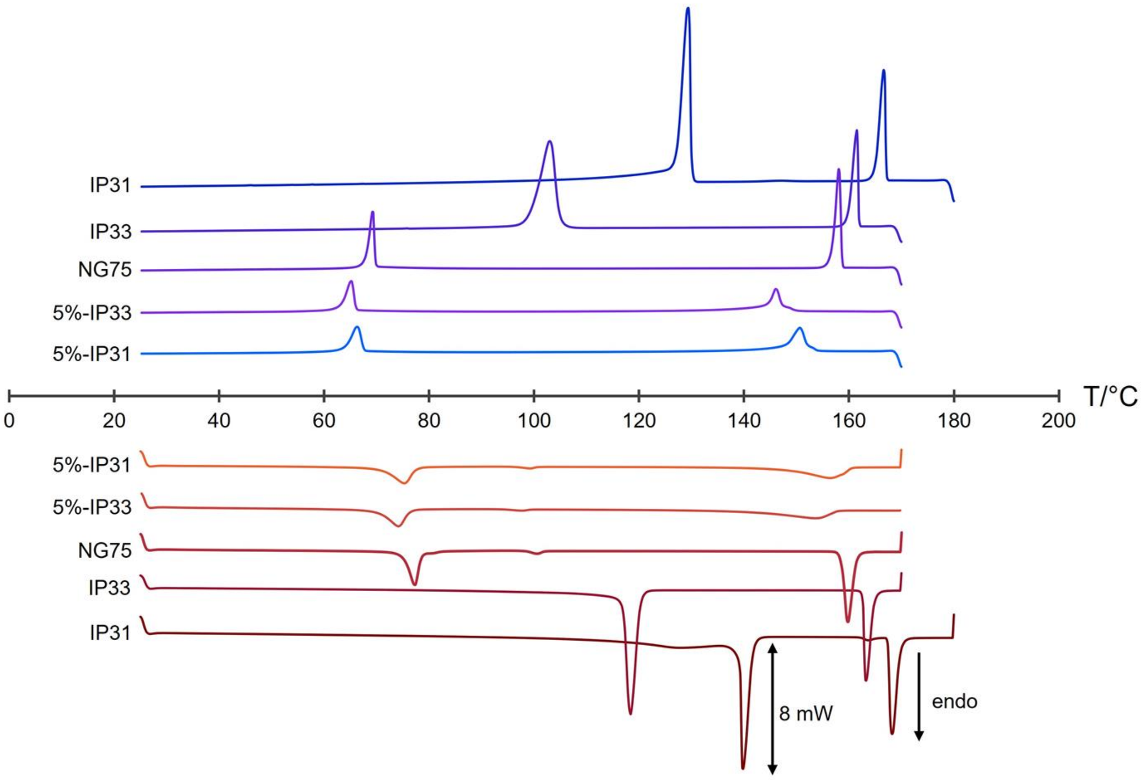


Fig. S2. Differential scanning calorimetry (DSC) thermograms obtained for the five samples under study, in their cooling (above), and second heating (below) scans at ±10^{o}C·min^{-1}. The small peak appearing at around 100^{o}C on the reheating curves of NG75-containing compounds did not correspond to any phase transition reported earlier (see **Table S1** below), nor was visible under our current microscope experiments.

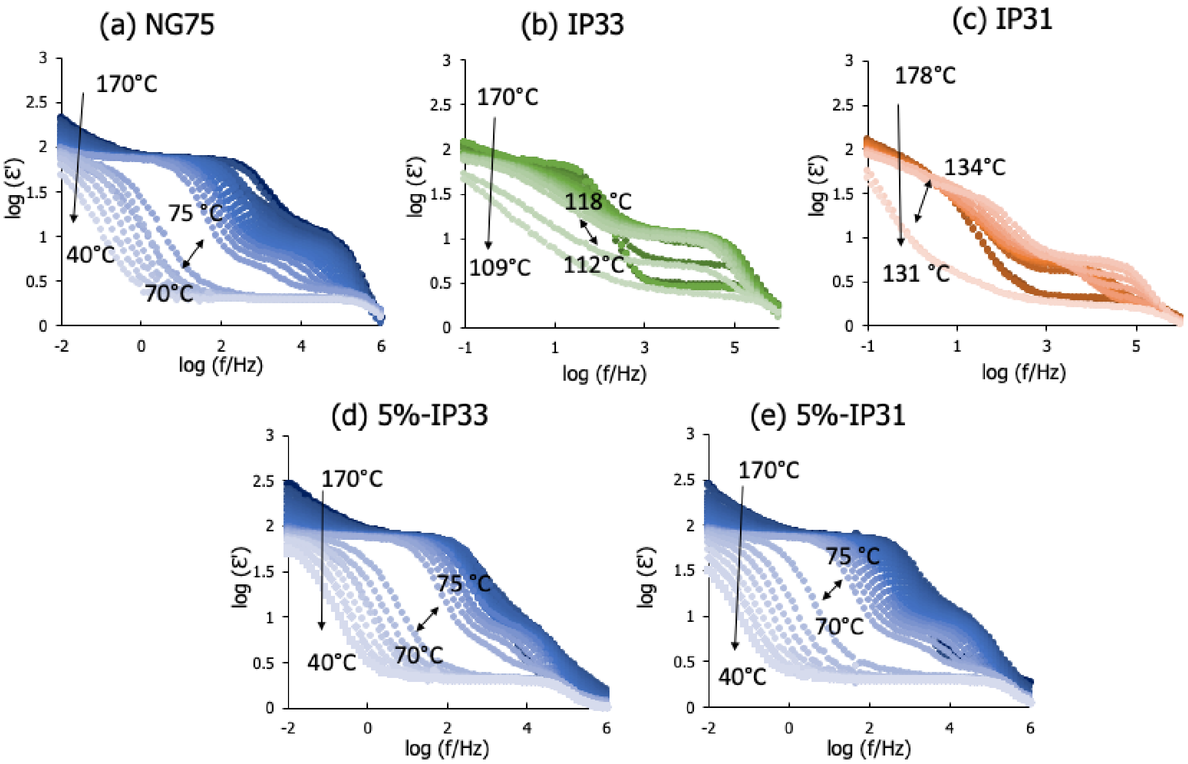


Fig. S3. Double logarithmic plots of the dielectric elastic constant, ε', as a function of frequency and temperature, corresponding to the five bent-core based materials, obtained in isothermal steps on cooling from their isotropic phases.

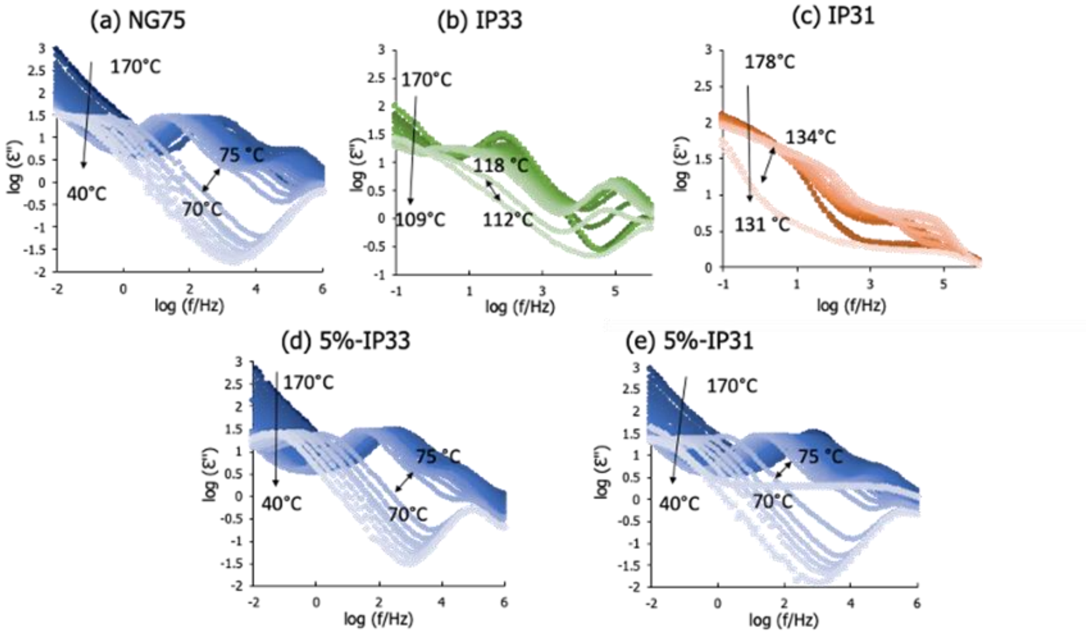


Fig. S4. Double logarithmic plots of the dielectric loss factor, ε'', as a function of frequency and temperature, corresponding to the five bent-core based materials, obtained in isothermal steps on cooling from their isotropic phases.

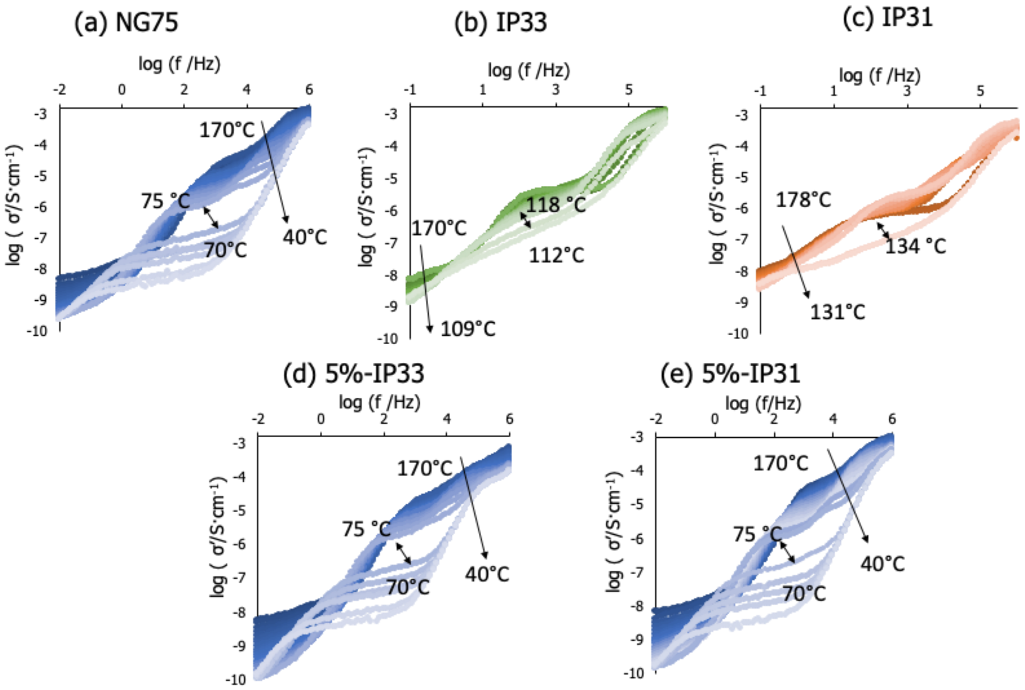


Fig. S5. Double logarithmic plots of the real component of the complex conductivity, σ', as a function of frequency and temperature, corresponding to the five bent-core based materials, obtained in isothermal steps on cooling from their isotropic phases.

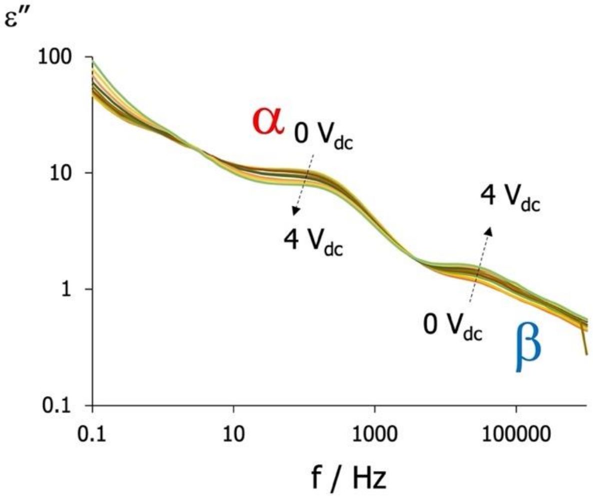


Fig. S6. Effect of direct current electrical fields of various amplitudes on the dielectric loss factor, ε'', measured in the columnar phase of IP31 (T=145°C), and assignation of the α and β relaxations.

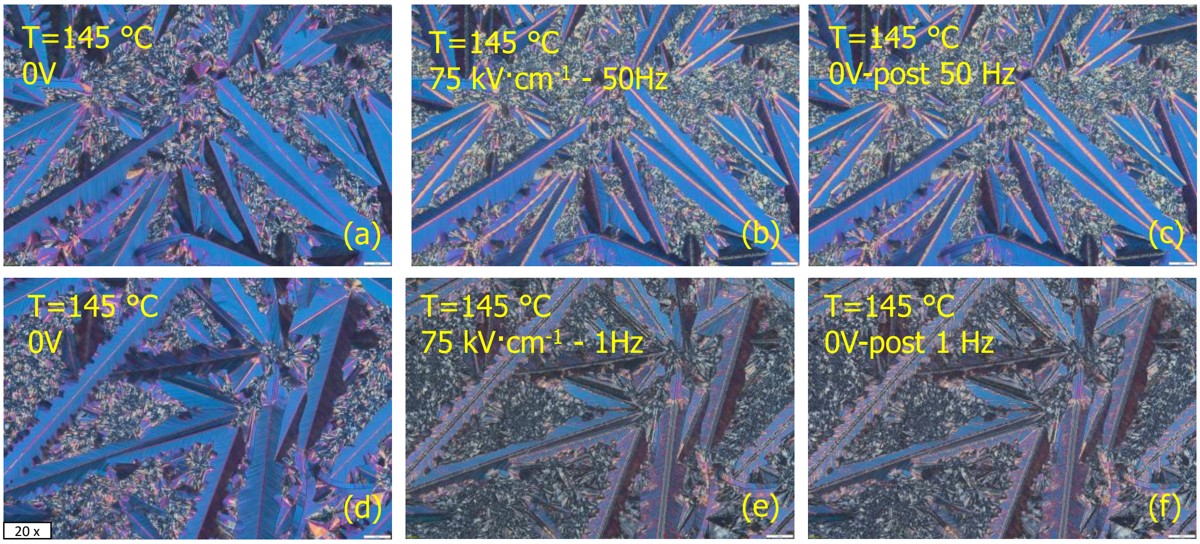


Fig. S7. Polarised optical micrographs obtained for IP31 at 145°C, showing the banana leaves textures typical of columnar phases, before (left), during (middle) and after (right) application of electrical fields at 50 Hz (up) and 1 Hz (down).

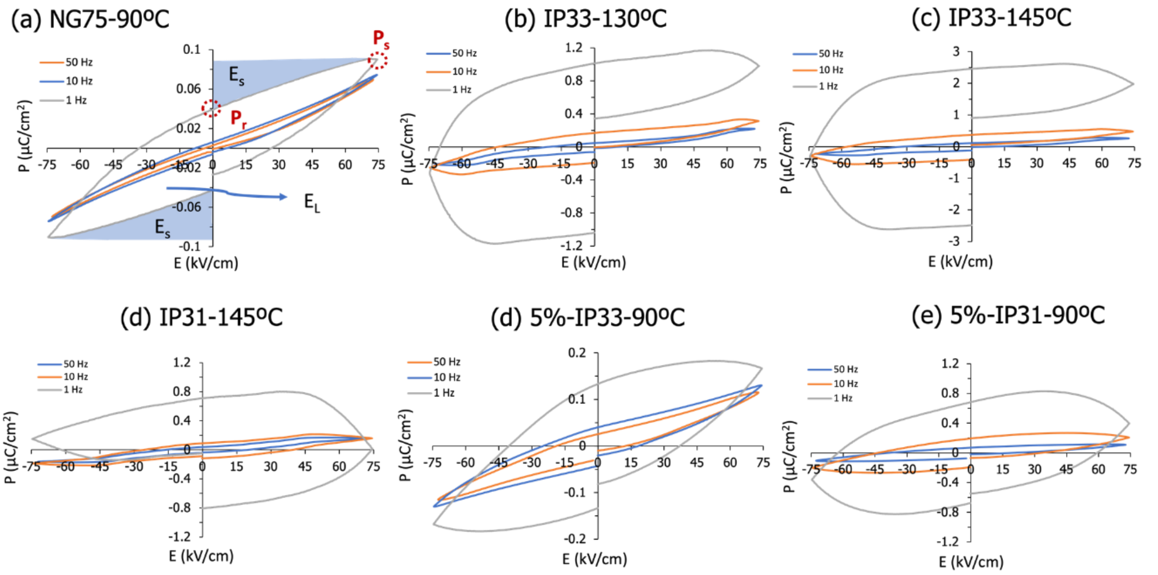


Fig. S8. Hysteresis loops showing the ferroelectric response of the five samples; frequency dependence.

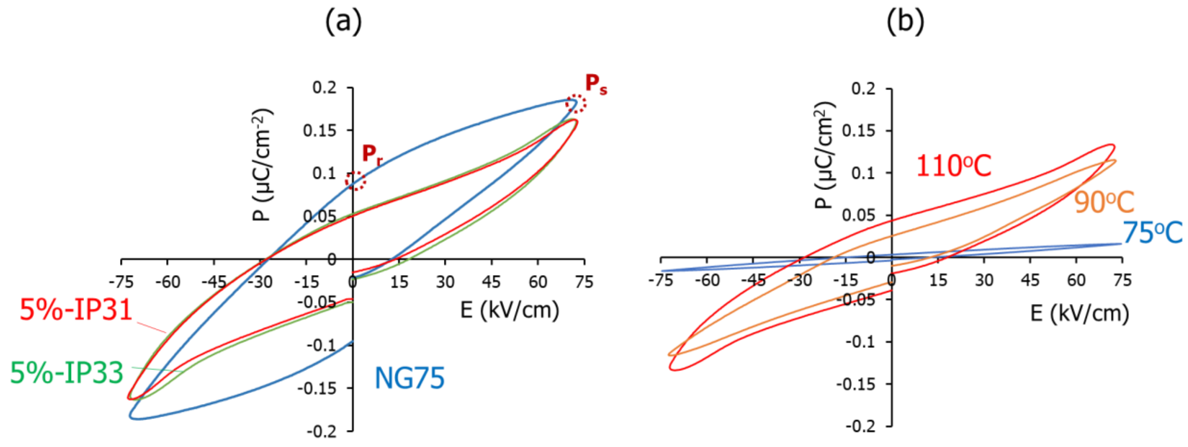


Fig. S9. Hysteresis loops showing the ferroelectric response of: (a) NG75 and its mixtures with IP33 and IP31 (130ºC, 50 Hz); (b) temperature effect on 5%-IP33 in its smectic phase (50 Hz)

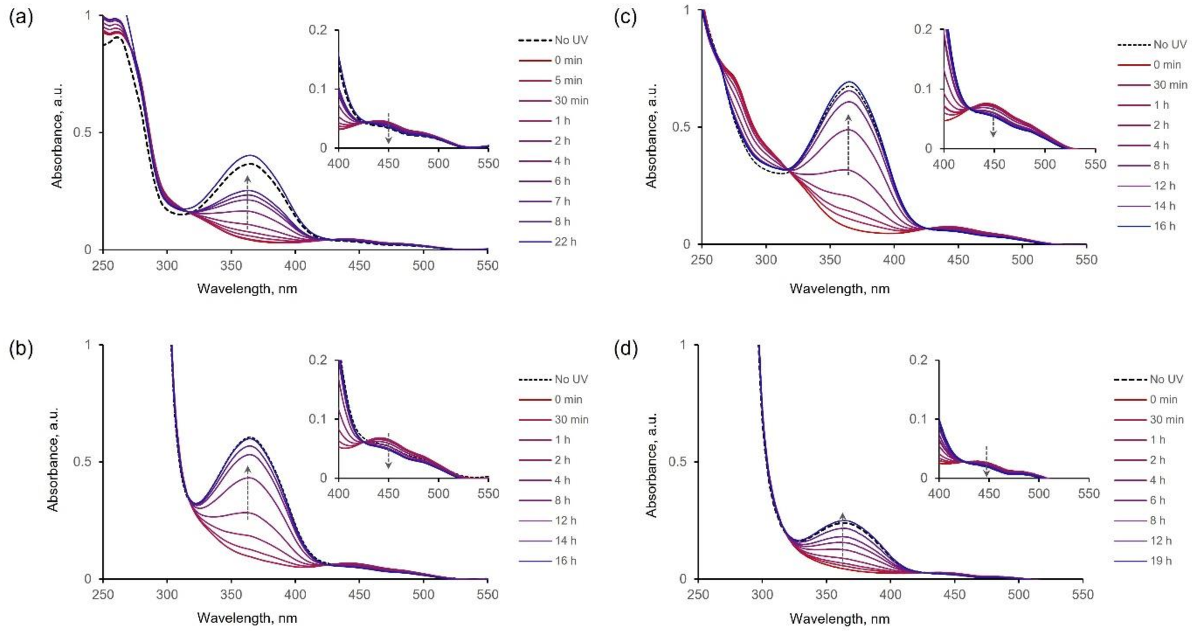


Fig. S10. UV-visible spectra of the light-responsive bent-core based materials measured before and at different times after light irradiation (260 mW·cm^{-2}; 365 nm): (a) IP33; (b) 5%-IP33; (c) IP31; (d) 5%-IP31. Insets show the π* ← n transition in the *cis*-azobenzene at peak ~440 nm. Measurements were taken for THF solutions at room temperature (IP31 and IP33: 1.2 x 10^{-5} M; 5%-IP31: 11.3 x 10^{-5} M; 5%-IP33: 37.8 x 10^{-5} M)

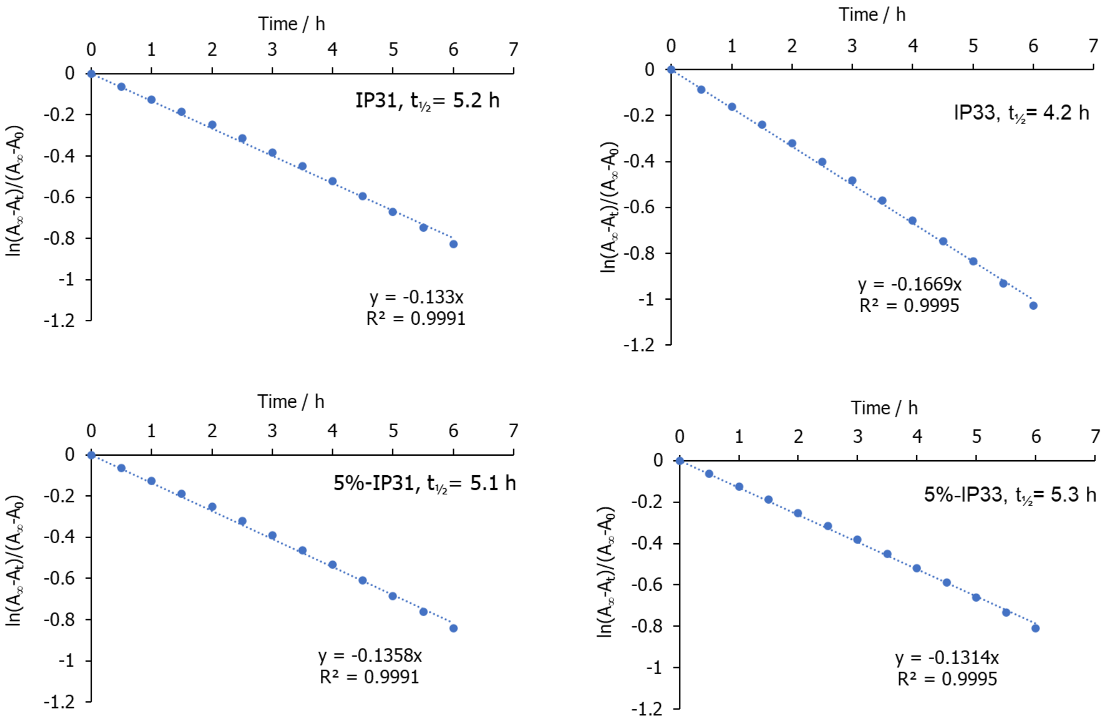


Fig. S11. Graphs showing the kinetics of *cis*-to-*trans* (thermal) back-isomerisation for the pristine samples in solution, using the maximum absorbance values (~440 nm) of their UV-visible spectra at different times while kept in the dark (A_t) after light irradiation (A_0) (260 mW·cm^{-2}; 365 nm), until the curves recover their initial values prior to irradiation (A_∞). Estimation of the half-life times, $t_{1/2}$.

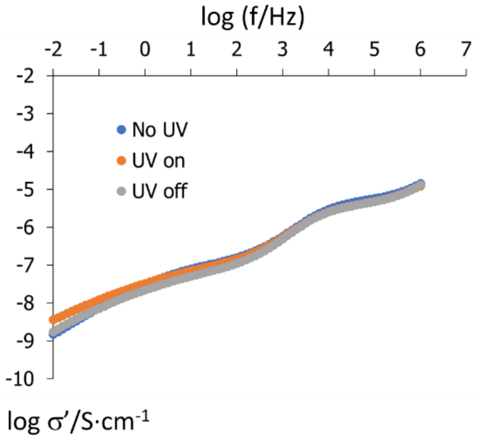


Figure S12. Frequency dependence of the real component, σ', of the complex conductivity, σ*, measured at the mesophase of NG75 before (blue), during (orange) and after (grey) UV illumination (200 mW·cm^{-2}; 365 nm)

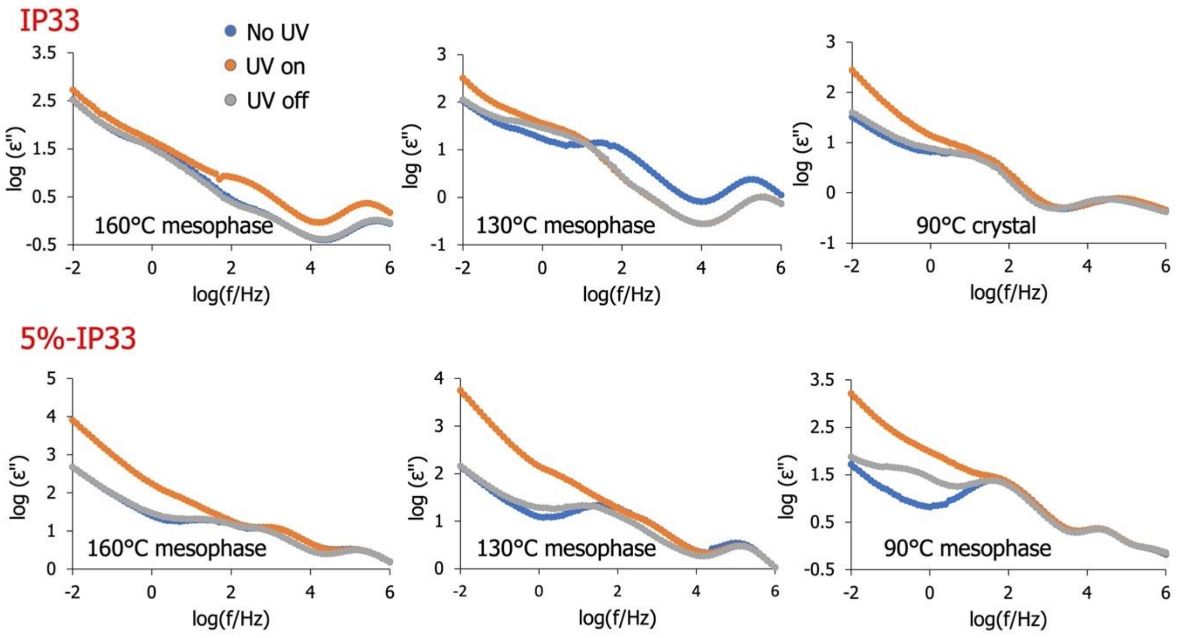


Fig. S13. Selected double logarithmic plots of the dielectric loss factor, ε'', as a function of frequency and temperature, for IP33 and 5%-IP33, measured before (No UV), during (UV on), and after (UV off), light irradiation (200 mW·cm^{-2}; 365 nm).

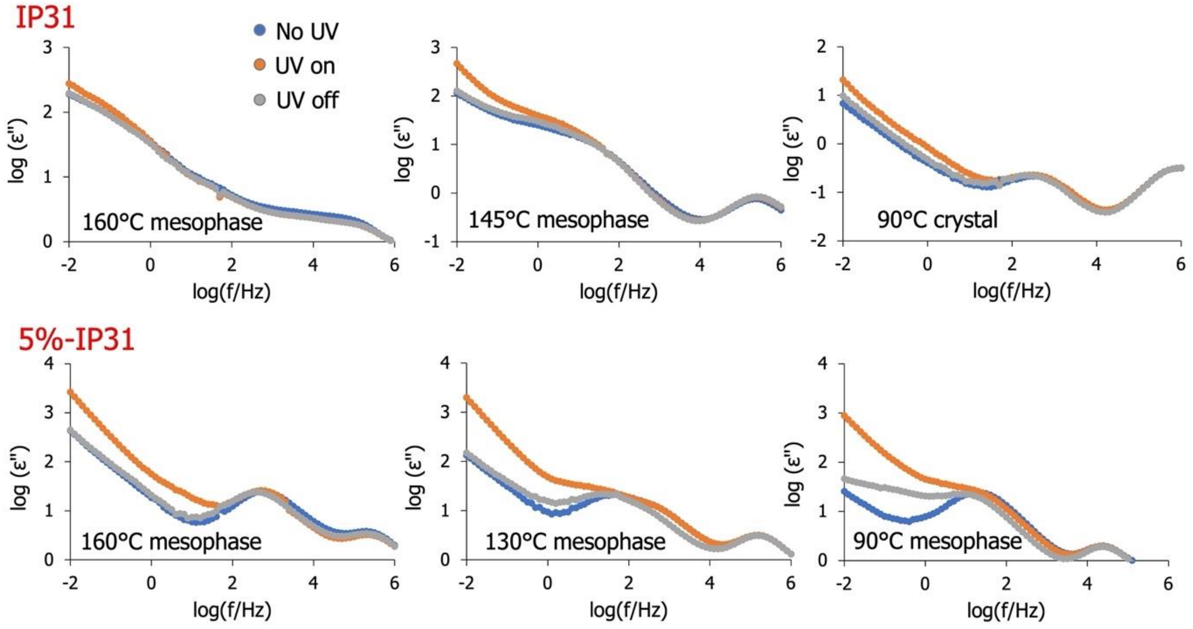


Fig. S14. Selected double logarithmic plots of the dielectric loss factor, ε'', as a function of frequency and temperature, for IP31 and 5%-IP31, measured before (No UV), during (UV on), and after (UV off), light irradiation (200 mW·cm^{-2}; 365 nm).

4. Tables

Table S1. Phase transition temperatures (obtained by polarised optical microscopy, POM, on heating and cooling ranges, 10 °C·min^{-1}); and phase structure parameters obtained by Small Angle X-ray diffraction, SAXS, for the three pristine samples.

Sample	**Mesophase range / °C (*)**	**Parameters / Å** **Measured spacings/Å *(Miller index)***
NG75	Cr 74.2 **SmC$_A$P$_A$** 156.9 I I 156.5 **SmC$_A$P$_A$** 67.7 Cr	*c*: 42.5 42.8 *(001)*, 21.2 *(002)*, 14.1 *(003)*
IP33	Cr 116.4 **SmC$_A$P$_A$** 163.1 I I 159.6 **SmC$_A$P$_A$** 101.4 Cr	*c*: 44.3 44.3 *(001)*, 22.2 *(002)*, 14.8 *(003)*
IP31	Cr 139.1 **Col$_{ob}$** 165.3 I I 160.9 **Col$_{ob}$** 127.8 Cr	*a*: 92.0 *c*: 48.0 β: 87.5° 47.8 *(001)*, 46.1 *(200)*, 43.2 *(101)* 41.7 *(-101)*, 33.9 *(201)*, 26.6 *(301)*

(*) Cr: crystal, SmC$_A$P$_A$, smectic C antiferroelectric polar (anticlinic) mesophase, Col$_{ob}$: columnar oblique mesophase, I: isotropic liquid.

Table S2. Values for saturated polarisation values, P$_s$, remanent polarisation, P$_r$, and energy storage, estimated for NG75 and its mixtures with IP33 and IP31, at 130°C, and 50 Hz.

Sample	**P$_S$ (μC·cm^{-1})**	**P$_R$ (μC·cm^{-2})**	**Energy stored (mJ·cm^{-3})**
NG75	0.182	0.0878	5.164
5%-IP33	0.159	0.0530	8.791
5%-IP31	0.159	0.0500	9.278

Table S3. Half-live ($t_{1/2}$) values estimated for the *cis*-isomers, obtained from the maxima of the UV-vis curves as a function of time, **Fig. S10**.

Sample	**$t_{1/2}$ / h**
IP33	4.2
IP31	5.2
5%-IP33	5.3
5%-IP31	5.1

Table S4. Times required to yield 95% of the steady state ε' during isothermal experiments upon irradiation (correlate to **Fig. 9**)

Sample	**UV on**	**UV off**
	Time / s	
IP33	3	32
IP31	3	32
5%-IP33	12	39
5%-IP31	28	40

5. References

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