Giant flexoelectricity of bent-core nematic liquid crystals

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Flexoelectricity is a linear coupling between orientational deformation and electric polarization; it is a unique property of orientationally ordered materials of which nematic liquid crystals (NLCs) are the best known example. We present a direct method for measuring the flexoelectric coefficients of liquid crystals via the electric current produced by periodic mechanical flexing of the NLC's bounding surfaces. This method is particularly suitable for measuring the response of bent-core liquid crystals, which are expected to demonstrate a much larger flexoelectric effect than traditional, calamitic (rod-shaped) liquid crystals. Our results reveal that not only is the bend flexoelectric coefficient of bent-core NLC's gigantic (more than three orders of magnitude larger than in calamitics) but also it is much larger than would be expected from microscopic models based on molecular geometry. Thus, bent-core nematic (BCN) materials can form the basis of a technological breakthrough for conversion between mechanical and electrical energy.

The flexoelectric effect – or coupling between electric polarization and elastic flexure – in NLCs was first predicted almost 40 years ago;[1] this effect has the potential to serve as the basis for a wide variety of technologies relying on electromechanical coupling, including strain gauges, actuators, and micropower generators. Unfortunately, the size of the effect in

traditional rod-shaped (or *calamitic*) NLCs has invariably been too small to make such applications viable. In this Letter we present both a new technique for measuring flexoelectric coefficients and results which reveal that NLC's composed of bent-core molecules exhibit a flexoelectric response more than 1000 times larger than that of typical calamitic NLCs.

A flexoelectric polarization, $\vec{P}_f$, can arise in a normally apolar NLC when the average direction for orientational order or director, $\vec{n}$, is subjected to splay or bend deformations. The effect is enhanced for molecules which possess a permanent dipole moment and shape anisotropies, specifically pear-shaped or banana-shaped molecules. In these cases orientationally deformed structures having nonzero $\vec{P}_f$ have both closer molecular packing and lower free energy than non-polar arrangements. In the continuum limit, $\vec{P}_f$ is proportional to the first order spatial derivatives of $\vec{n}$. Higher order derivatives are negligible when the deformation length scale is small compared to the molecular size. The flexoelectric polarization of a standard uniaxial nematic can then be expressed in terms of two flexoelectric coefficients, e_1 and e_3, corresponding to splay and bend deformations, respectively:

$$\vec{P}_f = e_1 \vec{n} \left(div\,\vec{n} \right) + e_3 \left(curl\,\vec{n} \right) \times \vec{n} . \tag{1}$$

A molecular statistical approach[2,3] to estimate the flexoelectric coefficients predicts that the bend flexoelectric constant e_3 of a banana shaped molecule can be related to the kink angle θ_o in the molecular core (*Figure 1/a*):

$$e_3 = \frac{\mu_\perp K_{33}}{2 k_B T} \theta_o \left(\frac{b}{a} \right)^{2/3} N^{1/3} \tag{2}$$

In this expression $\mu_\perp$ is the molecular dipole perpendicular to the molecular long axis; a and b are the length and width of a molecule (*Figure 1*/a), T is the absolute temperature, N is the number density of the molecules, and K_{33} is the bend elastic constant. This approach assumes that the molecules fluctuate independently. For rod-shaped molecules $\theta_o < 1^o$ and the flexoelectric coefficients of such NLCs are estimated to be 1-10 pC/m, in reasonable

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agreement with measured values.[4,5] For typical banana-shaped molecules, however, $\theta_o \sim 60^o$ thus one expects BCNs to have e_3 about 100 times larger.

To date, flexoelectric coefficients have mainly been measured using indirect methods, *i.e.* analyzing optical effects produced by electric field induced director distortions. Usually hybrid aligned cells are used, where either the sum or difference (depending on the cell geometry) of the coefficients can be obtained.[5] These methods require knowledge of various material parameters, (e.g. birefringence, dielectric and elastic constants, anchoring energies), which ideally should be independently measured. Published data on flexoelectric coefficients must be handled, however, with some care as various authors have obtained different values from the same experimental data sets using different evaluation techniques. This is perhaps unsurprising given how small the coefficients are for calamitic NLCs.

Our new method for measuring the flexoelectric coefficient is directly based on the definition, Eq.(1). We induce an oscillatory bend deformation by periodically flexing a thin layer of NLC contained between non-rigid conducting surfaces, and then measure the induced electric current. The method is validated by obtaining literature values on a standard calamitic material. Our experimental setup is sketched in *Figure 1*/b. The sample was placed in a temperature regulated box, which has a fixed bottom plate with two vertical, cylindrical posts, and movable side walls having vertical slots. The LC is confined between flexible electrodes and this assembly is inserted between the slots and the cylindrical posts as shown. Flexing is achieved by periodically translating the side walls using an audio speaker cone driven by a Regent Home Theater System model HT-391 amplifier with an input signal from a Perkin Elmer 7265 lock-in amplifier. In order to achieve smooth and uniform motion, the speaker's position was critical and hence was adjusted using two perpendicular micropositioners. With this arrangement, the walls of the box oscillate and the NLC sample flexes at the same frequency and amplitude as the speaker.
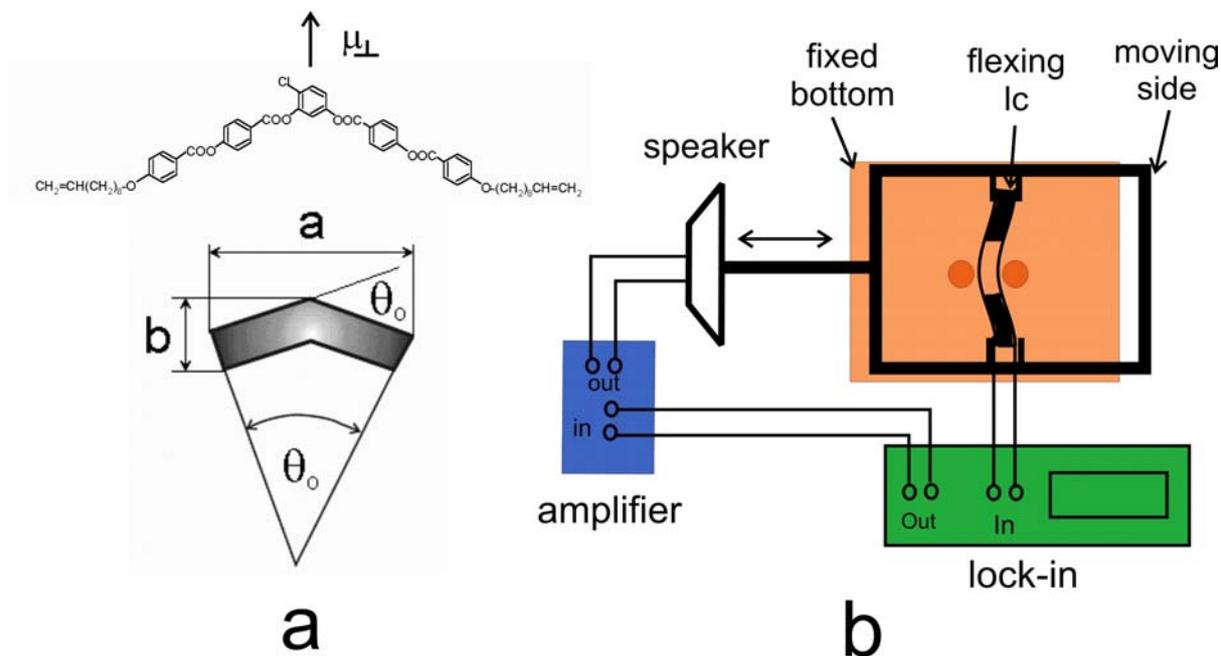
Figure 1: (a) Molecular structure of the bent-core material and its simplified geometrical model; (b) Schematics of the experimental setup.

The electrodes of the liquid crystal cell are connected to the current input of the lock-in amplifier. The precision with which the electric polarization current could be measured using this technique was a few pA. The amplitude of the applied oscillatory deformation was measured with 0.2mm precision either by mechanical detection, or by measuring the intensity of a laser diode through a neutral optical gradient filter fixed to the moving rod connecting the box to the speaker. The temperature of the box was regulated with $\Delta T < 1^o C$ precision between room temperature and $160^o C$. The present setup is limited to oscillation frequencies f = 1-10 Hz and amplitudes S = 0.2-2 mm. This apparatus allows simultaneous measurement of the temperature, amplitude and frequency dependence of the current, from which we directly determine the flexoelectric coefficient. Assuming strong planar anchoring boundary conditions of the director at the cell substrates, the periodic flexing of the cell results in a periodic bend distortion of the director, which allows us to measure e_3.

Our cell geometry is shown in *Figure 2*. The cell of total length $L_x + 2D$ and width L_y is initially located in the *x-y* plane, the mechanical displacement occurs along *z*. The cell is symmetric with respect to its center, so the deformation profile of the substrates is thus given by an even function *Z(x)*. The current induced by the flexoelectric polarization is

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$I = \dfrac{d}{dt}\iint P_f dA$, where dA is the surface area element and the integration should extend over the whole active area $(X \times Y)$ of the cell. In the planar geometry only the bend term contributes, so after integration one obtains $I = e_3 Y \dfrac{d}{dt}\left[n_z(x = X/2) - n_z(x = -X/2)\right]$. In case of the small deformations considered here n_z corresponds to the tangent of the substrates, i.e. $n_z(x) = \dfrac{\partial Z(x)}{\partial x}$, where $Z(x)$ describes the displacement of the substrates and the sample. The mechanical deformation depicted in *Figure 2* corresponds to the classical problem of 'bending an elastic sheet' found in standard texts. These reveal $Z(x) = S\beta(x)$, where

$$\beta(x) = \frac{1}{4}\left\{3\left(\frac{2x}{L_x}\right)^2 - \left(\frac{2x}{L_x}\right)^3\right\}. \tag{3}$$

So, taking into account that the direction is fixed at the edges by the slots, the flexoelectric current becomes $I = e_3 Y \dfrac{dS}{dt}\dfrac{d\beta}{dx}\bigg|_{-X/2}^{X/2} = e_3 Y \dfrac{dS}{dt}\dfrac{6X}{L_x^2}$. With periodic flexing ($S = S_0 \sin \omega t$), the flexoelectric coefficient can then be determined in terms of the rms induced current I_{rms} as

$$|e_3| = \frac{\sqrt{2}I_{rms}}{6X\omega S_0}\frac{L_x^2}{Y} \tag{4}$$
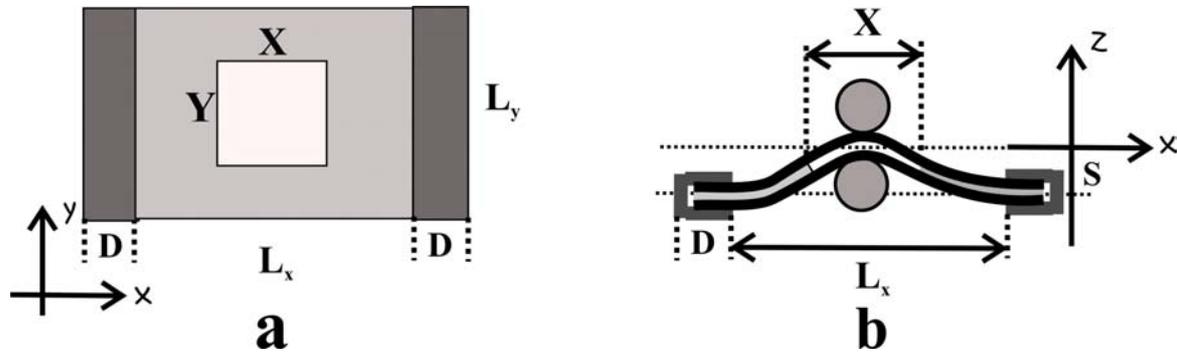
Figure 2: Model of the sample geometry and deformation of the flexible cell during the periodic vibration driven by the speaker. (a) The geometry of the cell in the xy plane (b) The cell structure during the deformation.

As flexible substrates we first used transparent, 150μm thick polycarbonate sheets with indium tin oxide (ITO) conductive coating sputtered onto their inner surfaces; these were then spin-coated with a polyimide layer and rubbed unidirectionally to achieve uniform

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planar alignment of the LC director. 20 μm thick samples of the recently characterized[6,7] bent-core NLC 4-chloro-1,3-phenylene bis 4-[4'-(9-decenyloxy) benzoyloxy] benzoate (ClPbis10BB)[8], whose molecular structure is shown in *Figure 1*/a, were loaded into cells constructed from these substrates. This material has a monotropic nematic phase during cooling between 78°C and 70°C, but it may be supercooled below 60°C before crystallization occurs. A typical example of the displacement dependence (parameters: L_x = 32mm, L_y = 15mm) of the induced current for f = 5 Hz in a sample at 74°C, which initially exhibited poor alignment, is shown in *Figure 3*/a. One observes that for S < 1.5mm the slope (which determines the flexoelectric constant) is much smaller than for S > 1.5 mm. This may indicate a possible improvement of the alignment as a result of flow occurring during periodic flexing (in analogy to flow induced orientation[9]). In this figure we have also added a point (⊗), which shows the induced current in a well aligned sample. As the dashed line indicates, the data from zero through this point extrapolates into agreement with the initially poorly aligned sample at sufficiently large S (~ 3mm). The temperature dependence of the flexoelectric constant $|e_3|$, as calculated from Eqs. (3) and (4) with S_0 = 0.7mm and f = 5Hz on the well-aligned sample, is shown in *Figure 3*/b.

a

b
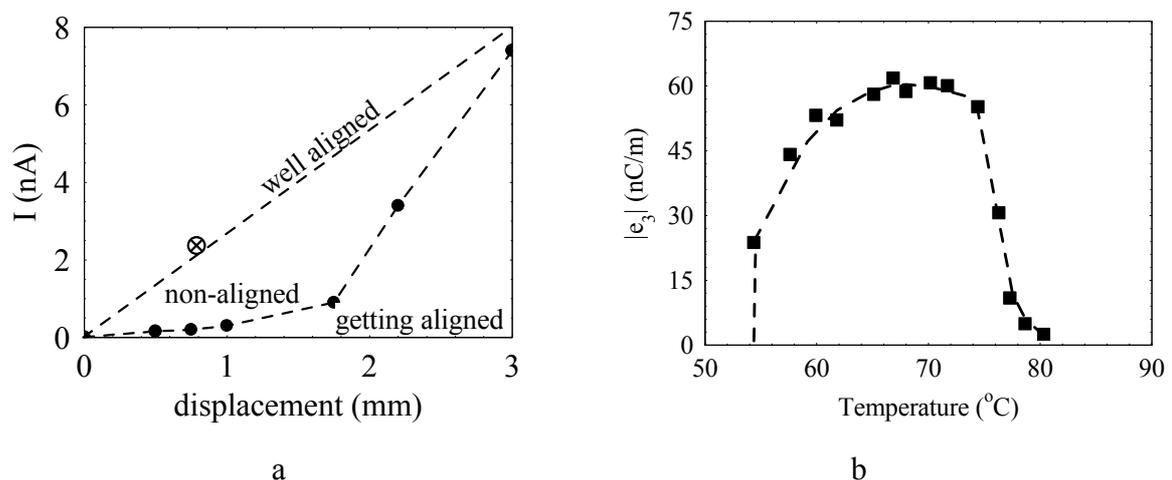
Figure 3: (a): Displacement dependence of flexoelectric current (in rms values) of ClPbis10BB at 74°C; (b) the temperature dependence of $|e_3|$ of a well aligned cell measured at 5Hz in 15mm x 15 mm active area plastic cells.

The temperature dependence of the flexoelectric response shows a sharp increase at the transition to the nematic phase, having a maximum of 62nC/m at 70°C, before the crystallization starts. This value is over *1000 times larger* than usual for calamitic NLC's, and more than 10 times larger than is predicted from calculations based upon molecular shape.[2]

Although the polycarbonate cells yielded unambiguous measurements of the flexoelectric current in the bent-core NLC material, and also permitted optical inspection of the alignment before and after making measurements, the weak flexoelectric signal from a standard calamitic NLC (4-cyano-4'-*n*-pentyl-biphenyl or 5CB) [10] was not measurable due to a 100 pA background current, which we believe to be caused by electrostatic charging of the plastic. Thus, a verification of the method's accuracy using a standard calamitic liquid crystal was not possible in the polycarbonate cell. Moreover, at the elevated temperatures necessary for the bent-core NLC, the samples degraded after a large number of flexing cycles. For this reason we also encased the bent-core compound and 5CB between 0.1mm thick brass plates with 25µm Teflon spacers interposed between them; the LC remained in a 1cm x 1cm area in the center of the plates. The inner surfaces of this cell were rubbed uni-directionally to promote uniform alignment along the rubbing direction. With this construction no NLC leaked out of the brass cell over repeated measurements, and the sensitivity of the experiment in this case was great enough so that the flexoelectric current in 5CB could be clearly measured
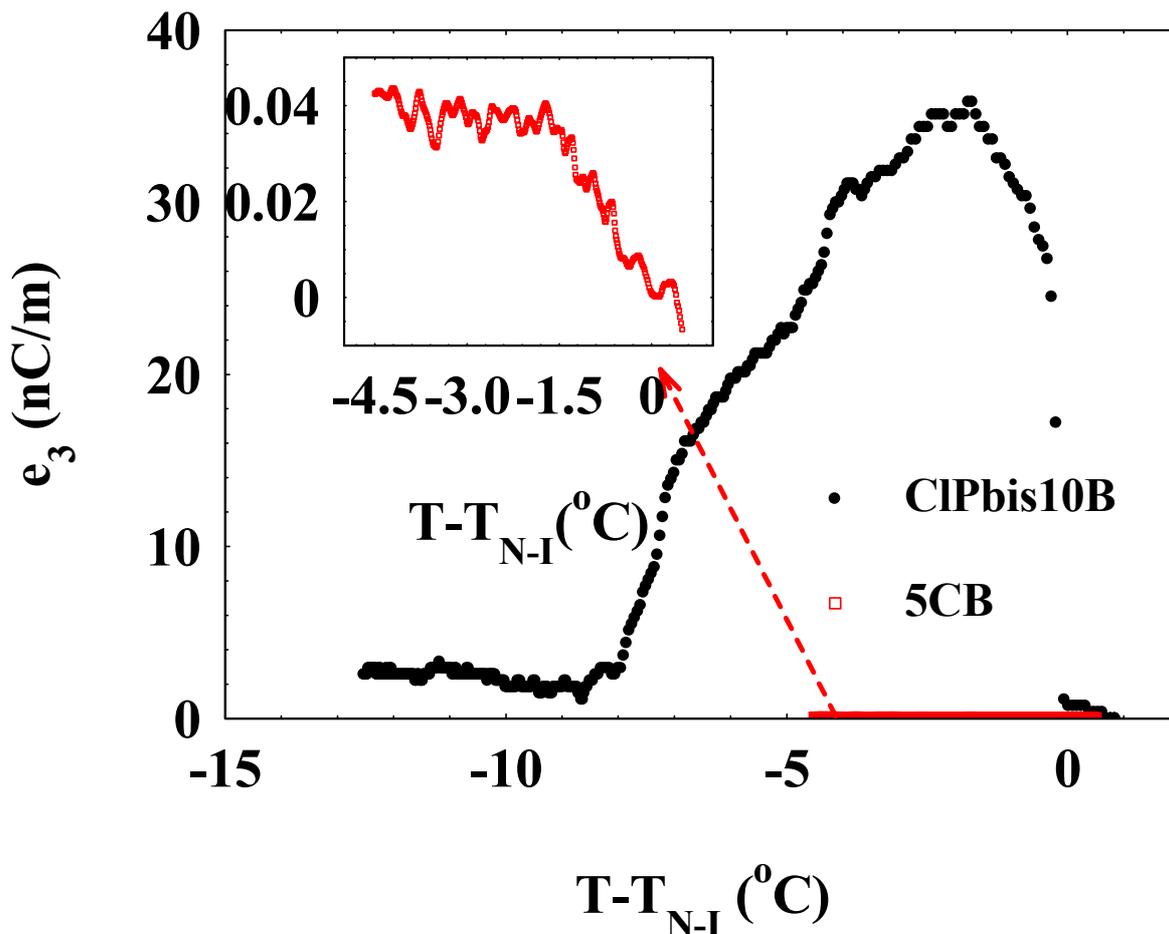
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Figure 4: Flexolectric constant in relative temperature scale for the calamitic liquid crystal 5CB and the bent-core liquid crystal ClPbis10BB measured in $A=1cm^2$ areas.

The relative temperature dependences of the bend flexoelectric constants of both ClPbis10BB and 5CB (measured with $S_0 = 2mm$ and $f = 3.2Hz$ for ClPbis10BB, and $S_0 = 1.5mm$ and $f = 5Hz$ for 5CB) are plotted in *Figure 4*. On the same overall scale, we see that the flexoelectric constant of 5CB is practically zero compared to that of the BCN material ClPbis10BB, which on cooling attains a peak value of roughly 35 nC/m about 2.5°C below the isotropic-nematic transition. In the inset it is seen that the flexoelectric coefficient e_3 of 5CB is clearly larger than the measurement error, and increases from zero to about 40pC/m on cooling into the nematic phase. Available literature data for the flexoelectric coefficients of 5CB, obtained by electro-optical techniques using hybrid aligned cells[11,12], give $e_1+e_3 = 30$ pC/m at 25°C.[10] The reasonable agreement between the magnitudes of the flexoelectric

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coefficient of 5CB measured electro-optically in previous work and directly in the present work validates our new technique for flexoelectric measurements.

The peak value of $|e_3|$ for the bent-core material measured in the brass cell is about half of that we have measured in the well-aligned plastic cell, but, as seen in Figs 3 and 4, it exhibits the same temperature dependence. Thus, since the quality of the alignment in the brass cell is not directly known, the measurements in Fig. 4 represent a *lower bound* on e_3. This is best demonstrated by Fig. 3, in which the poorly aligned plastic cell showed a flexoelectric response roughly half that of the well aligned case. In short, this set of measurements unequivocally demonstrates that the bend flexoelectric coefficient of ClPbis10BB is more than 1000 times larger than of typical calamitic materials. This flexoelectric response is truly gigantic – not only compared to calamitics, but it is also far beyond the maximum (~100-fold) enhancement expected from the microscopic model (i.e. from Eq.(2)). Furthermore, it should be noted that because ClPbis10BB is the first bent-core nematic whose flexoelectric coefficient has been carefully measured, its structure has not been designed in any way to optimize the flexoelectric response. Rational molecular design aimed at such an optimization could well deliver substantially larger responses.

All of our attempts to measure the flexoelectric response of ClPbis10BB with the classical method in hybrid aligned cells failed as the resulting alignment was almost planar even near the homeotropically aligned surface. Given the results shown above, this is perfectly understandable since in hybrid cells flexoelectric polarization results in an internal DC electric voltage[5] $U_e = \dfrac{-(e_1 + e_3)}{2\varepsilon_0 \varepsilon_a} \ln\left(\dfrac{\varepsilon_\parallel}{\varepsilon_\perp}\right)$. While in calamitics $|U_e|$ is in the order of a few V, for BCN it becomes a few kV, which due to the negative dielectric anisotropy of the material induces planar alignment in the vast majority of the volume.

Since molecular statistical considerations alone cannot account for the enormous flexoelectric effect in the bent-core nematic, we propose that the arrangement of molecules with respect to each other on the nanoscopic scale must play a decisive role. We estimate that an arrangement in which molecules are grouped together in polar "clusters" containing a few tens of molecules would be sufficient to explain the results. In fact, the results of a recent

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dynamic light scattering study[7] of the nematic phase of ClPbis10BB are consistent with local clustering or association of the molecules.

In summary, we have demonstrated a new, electromechanical method to detect flexoelectric current in NLC's. In principle, this technique is capable of measuring the individual flexoelectric coefficients by selecting planar alignment for e_3 and homeotropic alignment for e_1. We have applied the method to measure, for the first time, the flexoelectricity of bent-core liquid crystals, which was found to be three orders of magnitudes larger than in a standard calamitics. Based on this giant flexoelectric effect, bent-core nematic materials must be viewed as a highly promising platform for a new breakthrough in technology for conversion of mechanical to electrical energy at the molecular scale. Now that it is established that the bent-core molecular shape can produce such a dramatic effect, rational molecular architecture aimed at maximizing the flexoelectric coefficient (e.g. strategic placement of moieties having large dipole moments), could conservatively yield a further tenfold increase in response. Lastly, producing a bent-core NLC elastomer by either functionalizing the NLC molecules or swelling an elastomer with existing bent-core NLC's may also substantially improve the flexoelectric performance by restricting molecular motion so that much more flexing energy is converted into storable electric energy.

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