Vibrational Infrared Photothermal Spectrometer. In our setup, the pump and probe beams are collinearly combined using a dichroic mirror (DM) and focused coaxially onto the sample by a zinc-selenide (ZnSe) focusing objective (NA=0.25). The mid-IR Quantum Cascade Laser (Daylight Solutions) is focused onto the sample with a Gaussian beam waist diameter of 22 µm ± 3 µm. Losses at the beamsplitters and in the ZnSe objective lens resulted in an estimated QCL pump beam incident intensity on the sample of up to a maximum of ~ 1.2 ×10^4 W/cm². The probe beam is separated by a beamsplitter into a reference beam and a sample beam and the photothermal signal is measured as their ratio. At the sample, the probe beam has a beam waist diameter of 16 µm ± 3 µm. The incident probe beam power was set at 100 mW. Losses in the ZnSe objective and the coupling optics, due primarily to reflection losses, resulted in an estimated probe beam intensity at the sample of ~ 2×10^4 W/cm². The transmitted pump and probe beams are then collected by a ZnSe lens. The pump and probe beams are separated using a second dichroic beamsplitter. The pump beam is focused onto an InSb liquid nitrogen-cooled detector for in situ monitoring of the IR absorption. The intensity of the probe beam is measured using a Si photodetector. This set-up allows for comparison between direct mid-infrared detection and heterodyne photothermal detection in the same sample under identical conditions (Figure 1). The QCL was operated in pulse mode, with 500 ns pulses with a repetition rate of up to 100 kHz, corresponding to a maximum duty cycle of 5%. To enhance sensitivity, the probe signal is detected using a conventional Si photodetector using a lock-in amplifier, phase locked to the modulation frequency of the pump beam.

QCL Infrared spectroscopy. For mid-IR photothermal studies, the 4-Octyl-4’-Cyanobiphenyl (8CB) liquid crystal sample was sandwiched between cleaned CaF₂ windows with 50 µm Mylar spacer. In the absence of rubbing or surface coating the molecular alignment of the bulk is homogeneous, with no preferred direction at either CaF₂ window substrate. Observation with visible light under crossed
polarizers did not show homeotropic alignment of the sample as a whole. QCL mid IR laser beam was tuned across the absorption peak of the sample, centered at 1912 cm\(^{-1}\). As the QCL current was increased from the threshold of 500 mA to a maximum of 750 mA, the average output power varied over a range from ~ 5 mW to above 30 mW. The base temperature of the sample was controlled by using a circulating water bath and measured with a thermocouple integrated into the brass sample holder.

**Phothermal heterodyne scattering.** In linear photothermal spectroscopy, the signal depends on both the pump power \(P_{\text{pump}}\) and the probe power \(P_{\text{probe}}\), the absorption spectrum of the sample as a function of the pump frequency, as well as on geometric factors. In the theoretical models developed by Berciaud et al, for a sample with a characteristic absorption spectrum described by \(f(\nu)\), the linear scattering signal power \(S_{\text{linear}}\) depends on the probe wavelength \(\lambda_{\text{probe}}\) and is linearly proportional to both the probe laser power, and the pump power.

In our nonlinear experiments, the observed signals are still linear in the probe power, but nonlinear as a function of the pump power. All the data presented in the paper used a lock-in amplifier to detect the scattered probe signal modulated at the pump frequency of 100 kHz. The transmitted pump power provides an *in situ* measurement of the infrared absorption spectrum. The transmitted IR power is consistent with the FTIR linear spectrum, and does not show a bifurcation transition.

**Line-widths of Nonlinear peaks.** The narrow line-width of each branch above the bifurcation can be estimated using elementary arguments, by calculating the second moment in the neighborhood of each peak. The FWHM \(\Gamma_+\) the blue-shifted branch with a peak at \(x_+\) decreases with increasing power as \((P-P_c)^{1/2}\). The FWHM \(\Gamma_-\) of the red-shifted branch is equal to that of the blue-shifted branch in the simplest model.

Given \(x_+ = +\sqrt{1-y}\) the width \(\Gamma_+ = \left<(x - x_+)^2\right> = \frac{x_+^2 \Delta S_0 \exp\left[-\xi^2(y-e^{x_+})^2\right]}{\int_{x_-^\Delta}^{x_+^\Delta} S_0 \exp\left[-\xi^2(y-e^{x_+})^2\right]dx}

For \(\Delta < |x_+ - x_-|\) and for \(y > 1\) we have \(\left<(x - x_+)^2\right> = \frac{1}{4\xi^2(y-1)^2} + O(\Delta^2) \Rightarrow \)

Full-width-Half-Maximum \(\Gamma_+ \propto (P - P_c)^{1/2}\) and similarly for \(\Gamma_- = \Gamma_+\).
FTIR measurements on the liquid crystal sample. Linear absorbance spectra were taken using a Thermo Nicolet Nexus 670 FTIR. The pathlength was by a 50µm spacer between two CaF₂ windows. The infrared absorption spectrum of 4-octyl-4’-cyanobiphenyl (8CB) liquid crystal sample shows a narrow C≡N stretch band at 2227 cm⁻¹ and a combination band centered at 1912 cm⁻¹. The CH stretch bands in 2800-3100 cm⁻¹ range are saturated for this sample thickness.
Figure S2. a) A characteristic linear photothermal response of the 50µm 8CB liquid crystal sample. The mid-IR QCL pump beam was tuned from 1830cm\(^{-1}\) to 1990cm\(^{-1}\) and operated in pulsed mode. The Si-photodiode response of the Ti:Sapph probe beam is plotted as a function of the QCL wavenumber. Fitting of the photothermal spectrum to a single Gaussian with the peak at 1912cm\(^{-1}\). b) Nonlinear photothermal signal showing the bifurcating response. Gaussian fit indicates the central linear peak at 1912cm\(^{-1}\) and the nonlinear response shows the red and blue spectral shifting at 1899cm\(^{-1}\) and 1921cm\(^{-1}\).
Figure S3. Phase transition temperature dependent nonlinear photothermal response of 8CB liquid crystal. The 8CB liquid crystal undergoes a phase transition from smectic-A phase to nematic phase at 33.5°C. a)-f) Medium temperature in the smectic-A phase where the molecular long axis is perpendicular to the plane of layers. g)-i) Nematic phase where the molecules align along an average direction. The critical power for nonlinear bifurcation moves toward lower QCL power as the medium temperature increases towards the nematic phase. A chaotic behavior is observed right at the phase transition e) and f). Multiple bifurcations are observed at higher temperatures where clusters of nano-bubbles are being formed.
Figure S4. a) Measured QCL power as a function of wavenumber for some of the user input QCL currents. The dashed line at 1900 cm\(^{-1}\) is plotted on b). It shows the linear relation between the QCL input current and the QCL output power for the QCL frequency of 1910 cm\(^{-1}\).
Figure S5. a) Infrared response measured with the InSb detector. QCL was set at maximum input current of 750mA and there is no peak-splitting phenomenon observed. b) Photothermal response measured with the photodetector showing the characteristic peak-splitting.