

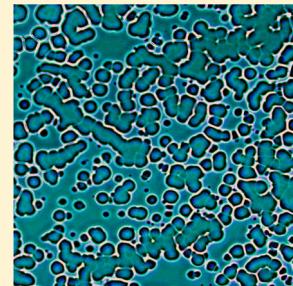
Order Parameter of the Liquid–Liquid Transition in a Molecular Liquid

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 Supporting Information

ABSTRACT: Liquid–liquid transitions (LLTs) between amorphous phases of a single (chemically unchanged) liquid were predicted to occur in most molecular liquids but have only been observed in triphenyl phosphite (TPP) and *n*-butanol, and even these examples have been dismissed as “aborted crystallization”. One of the foremost reasons that LLTs remain so controversial is the lack of an obvious order parameter, that is, a physical parameter characterizing the phase transition. Here, using the technique of fluorescence lifetime imaging, we show for the first time that the LLT in TPP is characterized by a change in polarity linked to changes in molecular ordering associated with crystal polymorphs. We conclude that the LLT in TPP is a phase transition associated with frustrated molecular clusters, explaining the paucity of examples of LLTs seen in nature.



The concept of the liquid–liquid transition (LLT) was employed¹ to explain the thermodynamic anomalies in liquid and supercooled water.² Amorphous to amorphous LLTs in strongly interacting atomic liquids are well established and have been observed in liquid Ge, Si, P, and so forth^{3–5} as well as melts of Al₂O₃–Y₂O₃.⁶ It has been predicted⁷ that LLTs should be common in all molecular liquids. However, a LLT has only been demonstrated in triphenyl phosphite (TPP) and *n*-butanol.^{8–10}

In the commonly observed phase transitions (solid–liquid and liquid–gas), density is the order parameter characterizing the transition. In liquid-crystalline transitions, it is the degree of orientational ordering that is used as the order parameter. In LLTs, it has remained unclear which parameter is most suitable to describe the phase transition. It has been suggested, mostly on theoretical grounds, that the degree of local bond order is the most suitable order parameter for the LLT.⁷ However, no experimental evidence is available to support this idea nor is it clear how to define, let alone measure, local bond order.

Most known LLTs take place in the supercooled state where the liquid is extremely viscous and metastable with respect to the crystalline state. This highly complicates the establishment of the existence of a “true” LLT as it might be confused with a metastable mixture of microcrystallites mixed with highly viscous liquid.¹¹ The change in characteristic patterns from nucleation and growth (NG) at higher temperature to spinodal decomposition (SD) at lower temperature as observed in phase-contrast microscopy has been used as proof of a phase transition.¹⁰ However, phase-contrast microscopy only reports on (very small) density changes associated with the LLT but cannot identify the order parameter. Furthermore, phase-contrast microscopy can only measure density changes away from the average in the sample. It therefore does not provide an absolute density value, thereby complicating the evaluation of the growth patterns.

Here, fluorescence lifetime imaging (FLIM) is used to show for the first time that local molecular packing, associated with those seen in the two known crystal polymorphs, is the order parameter of the LLT in TPP, giving rise to a change in the polarity of the liquid.

Experiments were carried out on TPP (melting point $T_m = 296$ K) using differential interference contrast (DIC), phase-contrast, and fluorescence microscopy using the dyes perylene and coumarin 153 (C153).¹² The phase behavior of TPP has been studied extensively.^{9–11,13,14} Upon cooling liquid TPP (liquid 1), a transformation occurs into another amorphous state (liquid 2) that may be an extremely viscous liquid, a glass, or possibly a mixture of small crystallites with very viscous liquid. The transformation exhibits two types of kinetics. When TPP is quenched (by cooling at a rate of 10 K/min) and subsequently held at a constant temperature in the range between 226 and 215.5 K, NG-type kinetics are observed. Below 215.5 K (but above the glass transition temperature of liquid 1 at ~ 205 K), liquid 1 transforms into liquid 2 by SD-type kinetics.¹⁰ The lower the quenching temperature, the longer the transformation takes, about 220 min at 220 K and almost twice as long at 213 K.

Figure 1 shows representative FLIM lifetime maps.¹² These images are consistent with previous phase-contrast microscopy studies and show the typical patterns of NG at higher temperature and SD at lower temperature. In the case of C153, the lifetimes range widely from 4.0 to 4.6 ns, while in perylene, they are confined to 3.6 to 4.0 ns, reflecting the different degrees of interaction of the electronic transitions of the two dyes with their surroundings. Also shown in Figure 1 are corresponding phase-contrast microscopy images showing

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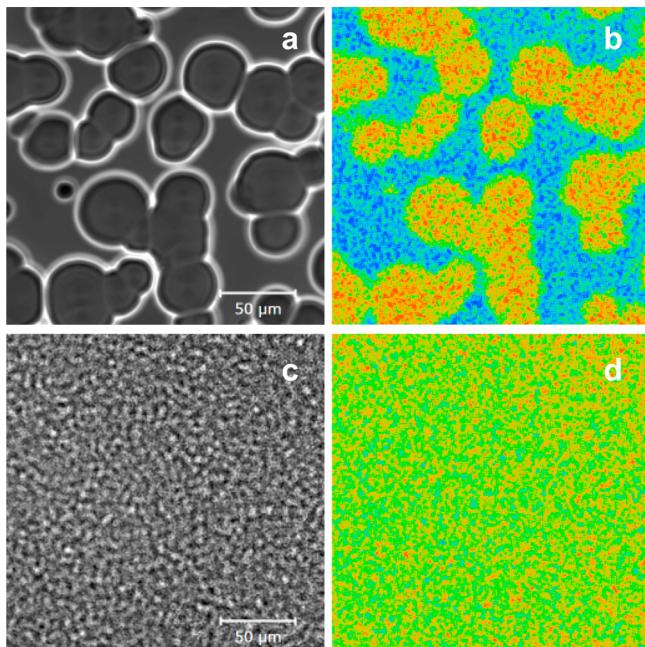


Figure 1. Representative patterns associated with the LLT in TPP. The images in the left-hand side panels were obtained using phase-contrast microscopy, while the images on the right were obtained concurrently using FLIM using the dye C153. The images in the top panels were obtained by quenching to 220 K for 170 min (NG), while those at the bottom were obtained by quenching to 213 K for 325 min (SD). FLIM scaling is 4.21 (red) to 4.46 ns (blue).

that the long excited-state lifetimes are associated with liquid 1 and the short lifetimes with liquid 2 in both NG- and SD-type transformations.

The FLIM lifetime maps are converted into lifetime distributions that can be plotted as a function of target temperature and time since initiation of the quench. FLIM is uniquely able to distinguish small differences in lifetimes in an inhomogeneous sample that would be indistinguishable in a bulk measurement.¹² Figure 2 shows the lifetime distributions of C153 and perylene in TPP undergoing NG- and SD-type transformations. The change in the average lifetime in C153 between liquid 1 and 2 is as much as 6.4%, while that for perylene was only 1–2%.

In the case of NG-type transformations, it can be seen in Figure 2 that an initial distribution of lifetimes is transformed into a new distribution with a lower average value. This two-state behavior is most obvious in the case of the dye C153 where the lifetime distributions are clearly distinct. In the case of perylene, the lifetime distributions overlap, but analysis shows the same two-state behavior.¹²

In the case of SD-type transformations, the initial distribution of lifetimes shifts gradually from a high to a lower average value, unlike the two-state behavior seen in NG-type transformation. The correlation length of the fluctuations in the SD-type transformation is¹⁰ $\sim 1 \mu\text{m}$, and the fluctuations seen in the phase-contrast image in Figure 1 are easily resolvable by FLIM. Therefore, this change in behavior confirms and proves that this is a LLT. Note that this is consistent with previously reported phase-contrast imaging results;¹⁰ however, unlike the relative measurements in phase-contrast imaging, FLIM measures absolute lifetime values.

Data such as those in Figure 2 were fitted to a Gaussian distribution to model the molecular scale fluctuations. NG-type transformation data could only be satisfactorily fitted using two Gaussian distributions with distinct average lifetimes; SD-type transformation data could be fitted with a single Gaussian

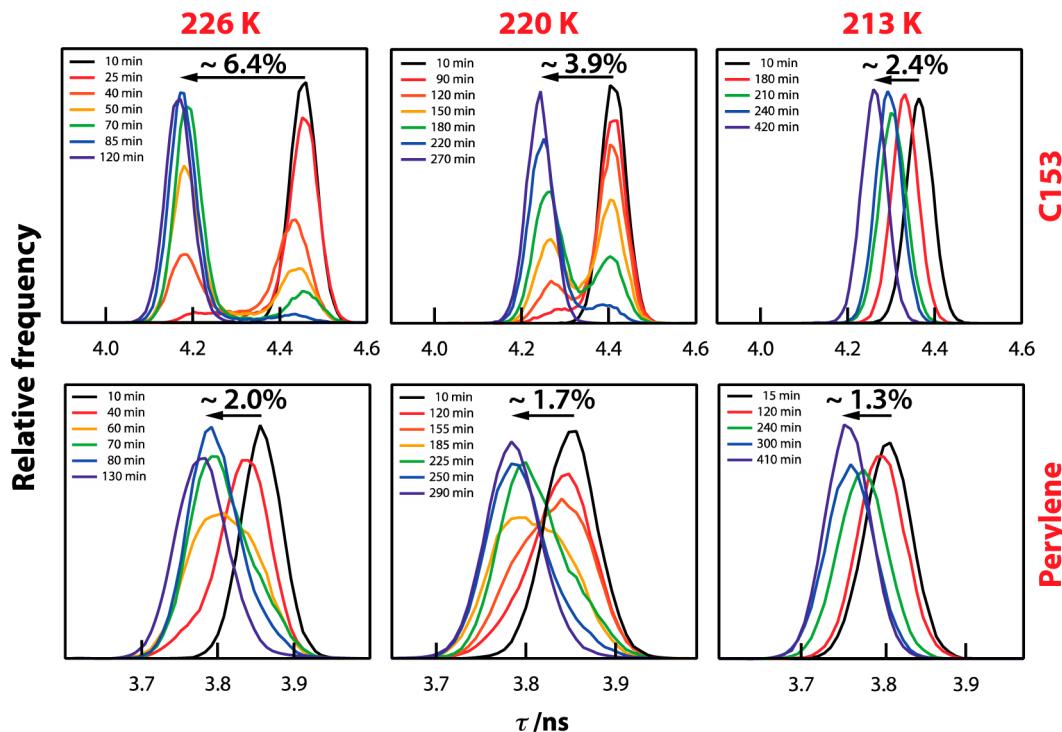


Figure 2. Normalized fluorescence lifetime distributions of the probe C153 (top row) and perylene (bottom row) in TPP quenched to 220 and 226 K (left and center, NG-type transformation) and quenched to 213 K (right, SD-type transformation). The arrows and color coding indicate the progression of time since the quench.

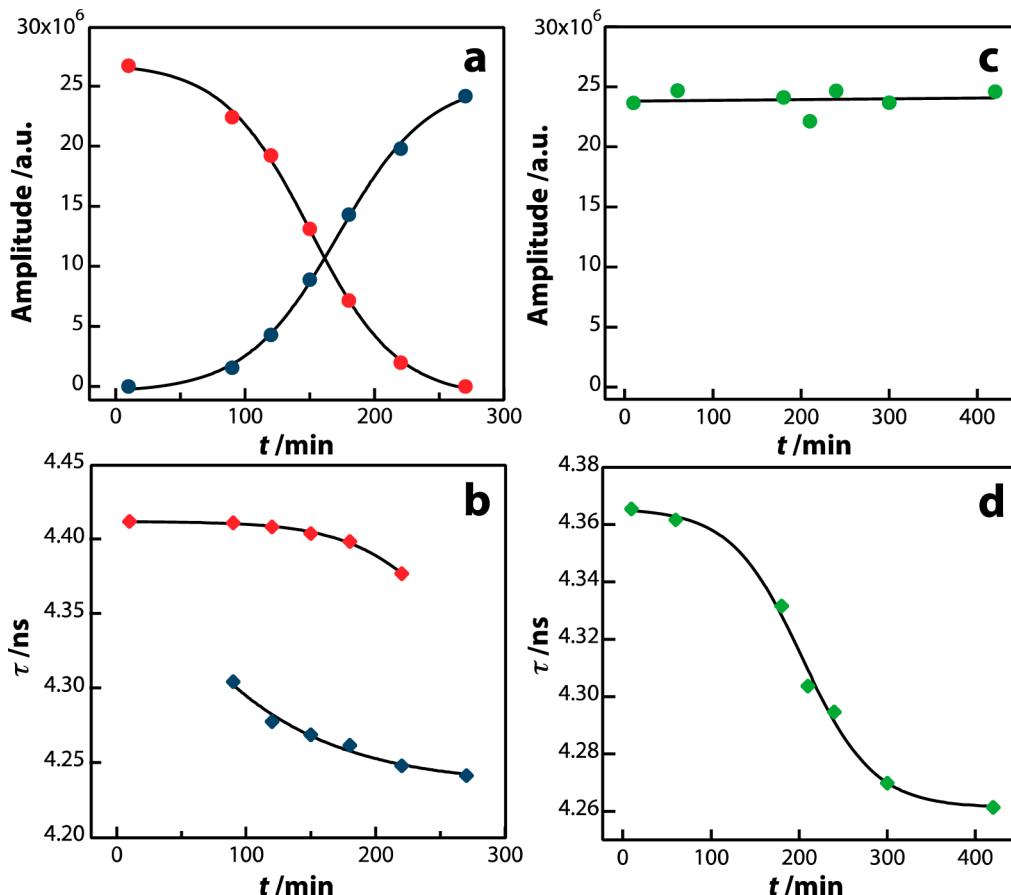


Figure 3. Temporal change of the amplitude and the average fluorescence lifetime of C153 in TPP obtained by fitting Gaussians to the lifetime distributions in Figure 2. (a) At 220 K (NG-type LLT), the gradual decrease of the amplitude of the initial distribution (liquid 1) is accompanied by a gradual increase of the amplitude of a new distribution corresponding to liquid 2. (b) The average fluorescence lifetimes of two distributions, observed during the NG-type LLT, corresponding to liquid 1 (red markers) and liquid 2 (blue markers). (c) During SD-type LLT at 213 K, the amplitude remains practically constant. (d) The temporal change of the average fluorescence lifetime at 213 K follows the sigmoidal trend characteristic for a SD-type transformation.

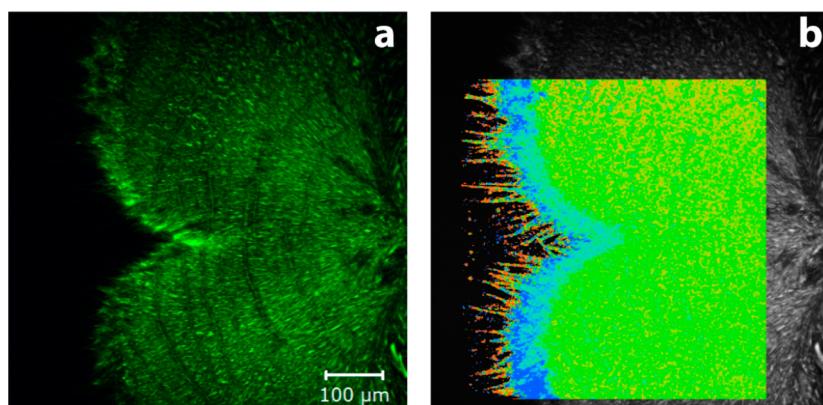


Figure 4. Fluorescence from C153 incorporated into crystal 1 of TPP at 220 K. The leftmost quarter is air, while the rightmost three-quarters contain crystalline TPP. (a) Fluorescence intensity. (b) FLIM map overlaid onto an intensity image. The lifetime varies from 4.0 (red) to 5.5 ns (blue).

distribution (see Figure 3). In the NG case, one can see that the two separate distributions exchange amplitude while their average lifetimes are nearly time-independent. In the SD case, there is only a single distribution, but its average lifetime swings from high to low during the experiment. The changeover from a double-peaked distribution in the NG-type transformation at high temperature and a single-peaked but shifting distribution

in the SD-type transformation at low temperature is characteristic of phase transitions near a critical point.^{8,10} Figure 5 shows the average lifetimes of the lifetime distributions as measured using C153 at the start of the quench (liquid 1) and at the end of the experiment (liquid 2) as a function of quenching temperature.

It has been suggested that liquid 2 might in fact be a metastable mixture of crystallites and highly viscous supercooled liquid.^{11,15} FLIM experiments were carried out on a sample that was made to crystallize into the thermodynamically stable polymorph just below the melting point. It is found that C153 is incorporated in the TPP crystal lattice as fluorescence is observed from throughout the crystal (see Figure 4). The lifetime is constant throughout the crystalline region at a value higher (4.7–4.8 ns) than that in the liquid. Only on the crystal–air interface is the lifetime much higher (5.5 ns, blue region in Figure 4b), consistent with exposure of the C153 dye molecules to (nonpolar) air.

In experiments carried out at a quenching temperature of 226 K,¹² NG-type transformation was observed followed by the immediate formation of crystallites embedded in the liquid 2 droplets. The lifetime of C153 in these crystalline regions is not as high as that in crystal 1 but is instead the same as the lifetime observed in liquid 2 at a slightly lower temperature. It is therefore concluded that these crystallites are not the thermodynamically stable crystalline phase, crystal 1, but a different crystal polymorph, crystal 2.

The fluorescence lifetimes are related to physically meaningful parameters of the dissolving liquid or crystal. Perylene is a nonpolar weakly interacting inflexible dye molecule, and therefore, changes in its excited-state lifetime are not expected to be caused by changes in the dye–solvent interaction. The viscosity of TPP at the temperatures used here is extremely high (10^6 – 10^7 cP¹⁶), and therefore, no changes in the rates of radiationless decay are to be expected. Furthermore, the extremely high viscosity makes molecular diffusion exceedingly slow, ruling out preferential partitioning¹⁷ of the dye molecules over phases on the time scale of the experiments. In this case, the relationship between the fluorescence lifetime τ_0 and the physical parameters is then simply given by the Strickler–Berg formula $\tau_0 \propto n^{-2}$, where n is the refractive index. Thus, using the observed 1.7% excited-state lifetime change in perylene at 220 K, it can be estimated that the refractive index changes by 0.9% upon going from liquid 1 to 2. This is consistent with reported estimated refractive indices of liquid 1 as 1.634 and liquid 2 as 1.655 at 220 K based on density measurements.¹⁸

C153 is widely used as a dye sensitive to polarity and microviscosity of the surrounding medium.¹⁹ Again, due to the extremely high viscosity of TPP, viscosity and diffusion do not play a role. For the same reason, dynamic solvation also does not play a role during the ~4.5 ns lifetime of the excited state.

However, the $S_0 \rightarrow S_1$ energy gap in the Franck–Condon region is sensitive to the static dielectric constant of the medium.¹² As the C153/TPP samples are prepared at room temperature—where the solvent relaxation times are subpicosecond—quenching the samples to the LLT temperatures will ensure that C153 will remain solvated in the ground state throughout the experiment. Nonradiative decay, which is known to be dominated by internal conversion from S_1 to S_0 ,²⁰ is then governed by the free-energy gap in the Franck–Condon region, resulting in a fluorescence lifetime that is very nearly linearly dependent on the dielectric constant of the medium within the range of $\epsilon_S = 3$ – 5 .¹²

Temperature-dependent changes in the C153 lifetime are a reflection of changes in the static dielectric constant or “polarity” of TPP. Thus, it is found that the LLT in TPP is associated with a change in polarity, with liquid 2 being more polar than liquid 1, which is more polar than crystal 1. Liquid 1 and crystal 1 are found to become more polar upon cooling,

which is the expected behavior. Liquid 2, however, becomes less polar upon cooling, which is anomalous.

Liquid-crystalline transitions are well-known and represent a state of matter with a degree of ordering in between that of the solid and the liquid state. Due to the orientational ordering, nematic and smectic phases are easily detected using polarized light. However, some types of local ordering are not necessarily in between the solid and the liquid state but represent a type of packing that frustrates the formation of the thermodynamically stable crystalline state.²¹ Such frustration to crystallization is thought to lead to metastable supercooled states.^{7,22} These frustrated states may also give rise to (weak) phase transitions that are, by their very nature, most likely to be found in the supercooled state. If these frustrated states are indeed characterized by local ordering (local bond order^{7,23}), the order parameter is by necessity a locally defined parameter.

Here, we have shown that, at least in the case of the LLT in TPP, the liquids are characterized by a different degree of polarity. It has been suggested previously that liquid 2 is a mixture of untransformed liquid 1 and a certain amount of crystalline fraction (crystal 1).¹¹ However, this interpretation is inconsistent with the data presented here; if liquid 2 were a mixture of liquid 1 and crystal 1, the fluorescence lifetime of C153 should be in between that of liquid 1 and the crystalline state. This is not observed.

At a temperature of 226 K, we observe the formation of droplets filled with a crystalline phase. The fluorescence lifetime of C153 in this crystalline phase is not that of crystal 1 but is instead that what would have been expected in liquid 2 at this temperature by extrapolating the lower-temperature data in Figure 5. On this basis, we have identified this phase as crystal

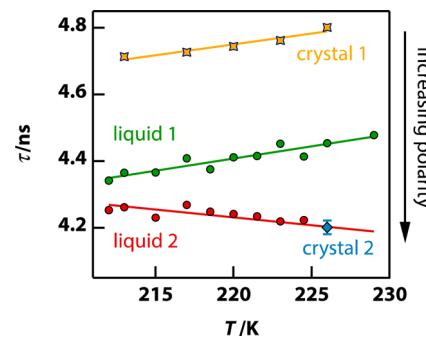


Figure 5. Temperature dependence of the average lifetime for C153 in crystal 1, liquid 1, liquid 2, and crystal 2 with corresponding linear regression lines. The data point at $T = 226$ K on the liquid 2 line (indicated with a blue diamond) is the average lifetime for crystal 2, which forms in the droplets of liquid 2. The 1σ error bar shown is based on multiple measurements at multiple temperatures and is representative for all of the data points.

2. The data demonstrate that the molecular ordering in crystal 2 is similar to that in liquid 2 and suggest that this molecular ordering frustrates the nucleation of crystal 1. This is consistent with X-ray data suggesting a “crystallite” size of about 30–50 Å¹¹ if this is interpreted as the size of a frustrated molecular cluster.²⁴ Because of the limitations of the types of microscopy used here, we cannot distinguish between the direct nucleation of crystal 2 from liquid 1 versus a LLT to liquid 2 followed by rapid nucleation of crystal 2. However, the latter is more logical and consistent with the LLT behavior of liquid Si and Ge.^{2,3,25}

The thermodynamically stable crystal 1 has a hexagonal crystal lattice in which each molecule assumes an approximately pyramidal shape.²⁶ However, a conformational polymorph was found to crystallize in a monoclinic lattice when the process was carried out by fast cooling in an ionic liquid.²⁶ In this conformational polymorph, the molecules have one phenoxy group twisted away from the base of the pyramid. The fact that the monoclinic polymorph only nucleates in an ionic liquid strongly suggests that its critical nucleus is more polar than that of the hexagonal polymorph. X-ray diffraction studies show orientational correlations between phenyl rings on adjacent TPP molecules in the supercooled liquid²⁷ consistent with local clusters similar but not identical to the monoclinic crystal. Similarly, NMR spectroscopy on TPP has suggested that liquid 2 is associated with parallel alignment of the molecules in clusters involving only a few molecules.²⁸ This is consistent with a reduction seen by X-ray diffraction studies of the P–P distance on neighboring molecules upon going from liquid 1 to 2 at 215 K.²⁴

Liquid 2 becomes more polar upon heating, which can only be explained by a temperature-dependent change in molecular structure. We surmise that the two liquid phases of TPP have distinct and temperature-dependent fractions of the hexagonal-like and monoclinic-like local structures as described by the two-state model.²⁹ This is analogous to the proposed temperature-dependent fractions of a four-coordinated low-density liquid and less structured high-density liquid in liquid water.^{1,2,30–34}

Thus, we conclude that the LLT in TPP is not simply an “aborted crystallization” process but a phase transition between two liquid phases that differ in the degree of twisting of one of the phenoxy groups²⁶ associated with local ordering that is more like either the hexagonal or the monoclinic lattice. Thus, the two liquid phases are polyamorphic “echoes” of the crystal polymorphs.

It can now easily be understood why LLTs appear to be so rare. If LLTs are transitions to frustrated configurations inhibiting the formation of thermodynamically more stable crystals, then, by definition, they are characterized by locally different configurations. In TPP, the molecular configuration characterizing liquid 2 happens to be more polar than liquid 1, which allows for visible macroscopic phase separation between polar and nonpolar domains. This separation into physically distinct phases may be rare even if the phenomenon of the LLT is not in itself rare.

ASSOCIATED CONTENT

Supporting Information

Supporting Information on methods and additional data, including details of the materials, microscopy, data acquisition and analysis, solvation, the structures of C153, perylene, and TPP, fluorescence lifetime distributions and corresponding gaussian fits of perylene, relaxation of the dye molecule C153 after excitation in the first electronically excited state, the effect of solvent polarity on the energy gap and excited-state lifetime, FLIM versus TCSPC details, representative images of typical patterns associated with the LLT in TPP, and formation of a second crystalline phase in TPP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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