Asymmetric Cyclophanes Permit Access to Supercooled Nematic Liquid Crystals with Stimuli-responsive Luminescence

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ABSTRACT: A novel material with stimuli-responsive luminescence was created by integrating a chromophore with assembly-dependent emission properties into a liquid crystalline compound that can be kinetically trapped in a supercooled liquid-crystalline state. This was achieved by synthesizing an asymmetric cyclophane containing one 1,6-bis(phenylethynyl)pyrene group. The new compound displays a broad nematic phase above ca. 110 °C on heating. Quenching to room temperature allows one to avoid crystallization, and the supercooled nematic phase is stable for at least 1 h. Upon heating, a phase transition from the kinetically trapped state to a crystalline state occurs, concomitant with a pronounced change of the photoluminescence. The crystalline phase thus accessed shows mechanoresponsive luminescence behavior.

INTRODUCTION

Molecular and polymeric materials whose photoluminescence properties depend on the temperature and/or are altered by mechanical stimulation are attracting much attention, in part due to their usefulness in sensors, memories, security and bio-imaging applications.[1-15] The origin of such effects in most low-molecular weight photoluminescent dyes is a rearrangement of the molecular assemblies, which in turn influences the interactions among luminophores and thereby their photophysical properties.[1-3,6,9,11,12,16-53] Many known molecular materials with stimuli-responsive luminescence display polymorphism, and the external stimulus promotes the transformation from one crystal structure into another.[17-22] In many cases it is also possible to induce the transformation from a crystalline to an amorphous phase (or *vice versa*) by way of an external stimulus.[21-36] Another possibility is to kinetically trap disordered or poorly ordered molecular structures by rapidly cooling an isotropic melt or a low-order mobile state, such as a nematic liquid-crystalline (LC) phase, to a temperature where the system is immobilized.[1,45-48] Heating or the application of mechanical force can then induce a phase transition to a thermodynamically more stable crystalline state, concomitant with significant changes of the photoluminescent properties. Interestingly, this concept, which is also applicable to blends of polymers and luminescent compounds,[54-58] has been relatively little explored.[45-48] In particular, related LC compounds with mechano- or thermoresponsive luminescence properties are rare.[46-48] However, LC compounds can easily be processed into thin films and phase transitions are often accompanied by significant changes of the molecular assembled structures,[59] which bodes well for the development of stimuli-responsive luminescent materials.[1-2,41,46-53] Moreover, the low crystallinity of LC compounds makes it often comparably easy to access kinetically trapped structures that display a low degree of order.[60-64]

Here, we demonstrate that exploiting the tendency of cyclic LC compounds to form kinetically trapped states in combination with the assembly-dependent optical characteristics of photoluminescent motifs is a powerful approach to create materials that display thermo- or mechanoresponsive luminescence. After Percec *et al.* demonstrated that cyclic oligomers containing multiple mesogen units in the main-chain can display nematic phases, several cyclic compounds have been reported to exhibit LC behavior.[65-68] Notably the groups of Tschierske and Hegmann reported several cyclic compounds showing nematic or smectic phases.[69-72] While previous efforts have focused on the investigation of thermodynamically stable LC states and the relationship between molecular structures and LC phase transition, little attention has been paid to either the kinetically trapped states and the photophysical properties of cyclic LC compounds. We previously investigated the stimuli-responsive characteristics of symmetric cyclophanes containing two 9,10-bis(phenylethynyl)anthracene groups that were bridged by tetra- or hexaethylene glycol linkers.[29-30] While the latter cyclophane displays a nematic phase above 168.6 °C, supercooling the latter was not possible. We show here that desymmetrization of the cyclophane and usage of long linkers affords a product whose nematic phase extends to a much lower temperature. More importantly, a low-order mobile phase can be kinetically trapped by rapidly cooling the LC phase. The latter is stable under

ambient conditions for at least 1 h and displays thermo- and mechanoresponsive luminescent behavior.

RESULTS AND DISCUSSION

Based on the assumption that breaking symmetry would lead to a reduction of the phase transition temperatures and hamper crystallization, cyclophane **1** was designed to feature one 1,6-bis(phenylethynyl)pyrene group as the luminophore and one idle naphthalene moiety (Figure 1). These π-conjugated motifs were bridged by hexaethylene glycol chains. Cyclophane **1** was synthesized from 1,6-bis(4-hydroxyphenylethynyl)pyrene and a 1,5-disubstituted naphthalene featuring bromo-terminated hexaethylene glycol groups through Williamson ether synthesis. The linear reference compounds **2** and **3** were synthesized in a similar manner (See Supporting Information).

A first inspection reveals that cyclophane **1** indeed exhibits a broad nematic phase that displays green photoluminescence under excitation with ultraviolet light (Figure 2). Rapid cooling of the nematic phase affords a waxy solid (G-form) in which the green photoluminescence is retained for ca. 1 h. By contrast, slow cooling leads to a crystalline solid (B$_{sc}$-form) that emits blue light. The G-form is metastable and exhibits thermoresponsive luminescence; upon annealing at 80 °C a phase transition to a blue-light emitting crystalline state (B-form) is observed. As will be discussed later, cyclophane **1** forms several blue-emitting polymorphs, depending on the crystallization, which exhibit similar photophysical properties and mechanoresponsive luminescence.
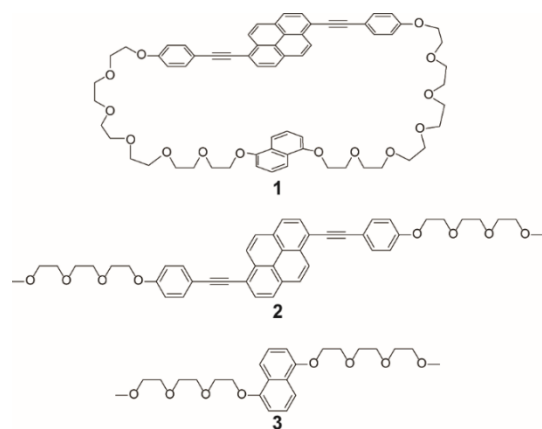

Figure 1. Molecular structures of cyclophane **1** and the monomer analogues **2** and **3**.
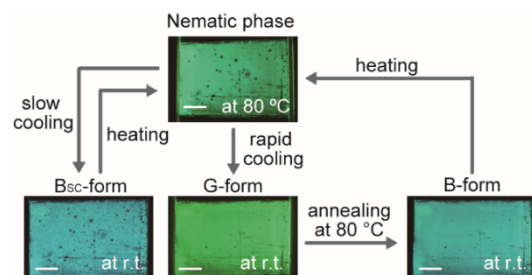

Figure 2. Images summarizing the phase behavior of **1**. All images were taken on glass substrates without a cover slide under irradiation with UV light (λ_{ex} = 365 nm). Scale bar = 5 mm.

The phase behavior of **1** was studied in more detail using polarized optical microscopy (POM, Figure 3). Upon heating the sample in the absence of a cover slip, the characteristic schlieren texture of a nematic phase (Figure 3a) was observed above ca. 110 °C. This texture was retained after the sample had been quenched into the state referred to as G-form (*vide supra*) by placing it on a metal-based heat sink maintained at 15 °C (Figure 3c). While thermally induced fluctuations were observed for the texture of the nematic phase at 120 °C, these were absent in the quenched sample, suggesting that in the G-form the molecular motions are significantly reduced. Interestingly, when the POM experiment was repeated with a cover slip, a birefringence-free texture was observed upon heating above ca. 110 °C, indicative of homeotropic alignment (Figure 3b). This structure was also retained after rapid cooling (Figure 3d). A phase transition was observed for the G-form on heating to 80 °C. As shown in Figure 3e, crystal nucleation was immediate when a quenched sample (G-form) was placed on a hot stage maintained at 80 °C and the sample crystallized quickly into the B-form (Figure 3f). Thus, the POM experiments show that the G-form is a kinetically trapped, metastable state of low order, which readily crystallizes upon heating into the thermodynamically more stable B-form.
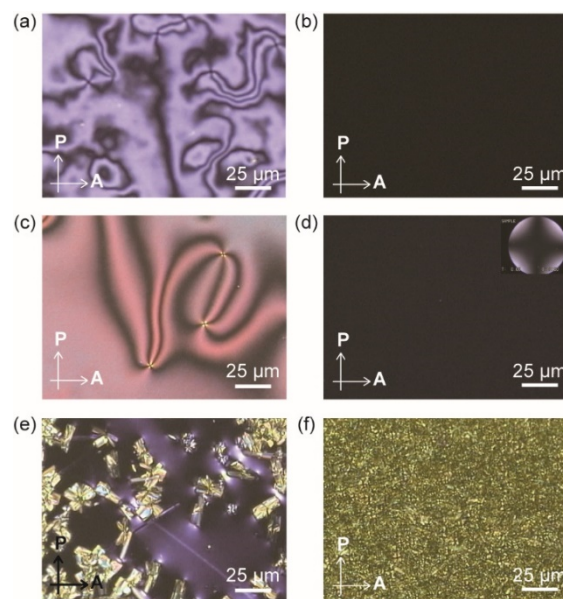

Figure 3. POM images of cyclophane **1** (a,b) in the nematic phase at 120 °C, (c,d) in the G-form at room temperature, (e) just after heating the G-form to 80 °C, and (f) in the B-form after annealing at 80 °C. The POM image shown in (f) was taken with the same sample as in (e) after further thermal treatment at 80 °C. Images were taken in the (a,c) absence or (b,d,e,f) presence of a cover slip. The inset of panel (d) represents the conoscopic image of the sample. The G-forms

shown in (c,d) were prepared by placing the nematic samples on a metal-based heat sink maintained at 15 °C.

The phase behavior of cyclophane **1** was further investigated by differential scanning calorimetry (DSC) measurements. The heating trace of the slowly crystallized B_{sc}-form (Figure 4a) displays only a sharp endothermic peak at 106.9 °C, which marks the transition from a crystalline solid (B_{sc}-form) to the nematic phase. The latter extends to ca. 280 °C, as determined by POM observations, which however also suggest some decomposition at this temperature. The DSC cooling trace acquired at a slow cooling rate (10 °C min^{-1}) shows exclusively an exothermic peak at 67.4 °C, which is associated with a phase transition from the nematic phase to the crystalline B_{sc}-form. The heating trace of the B-form is very similar to that of the B_{sc}-form, displaying only one endothermic peak at 110.3 °C upon heating (Figure S1). By contrast, the DSC heating trace of a sample that had been rapidly quenched from the nematic phase reveals a very different behavior (Figure 4b). A weak endothermic transition can be observed around 8 °C, which is associated with the glass transition and indicates that the G-form is indeed a super-cooled nematic phase, rather than a glass. Two exothermic peaks appear at 44.6 and 61.6 °C (ΔH = −21.2 and −2.6 kJ mol^{-1}, respectively). Because the B-form was obtained by annealing at a temperature above these transitions, the B-form is a thermodynamically stable state, while the G-form is a thermodynamically metastable one. Like in all other samples, the DSC trace shows an endothermic peak at 108.5 °C (ΔH = 41.9 kJ mol^{-1}), corresponding to the transition from the B-form to the nematic phase.
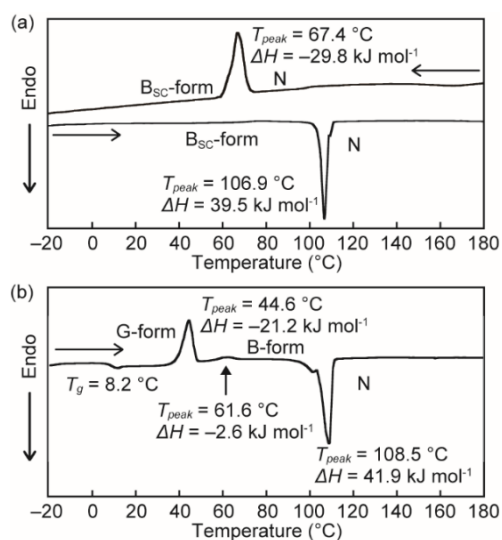

Figure 4. (a) DSC traces of cyclophane **1** in the B_{sc}-form. (b) DSC trace of **1** after kinetically trapping by rapidly cooling the DSC pan containing the sample from the nematic phase to 15 °C and placing it in a DSC sample holder that had been precooled to 0 °C. Scanning rates: 10 °C min^{-1}.
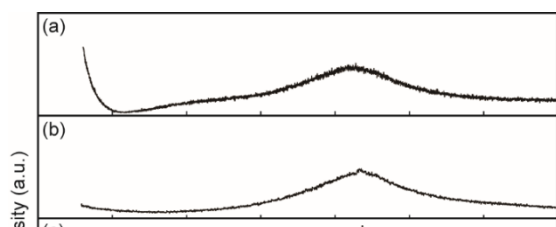

Figure 5. XRD diffractograms of cyclophane **1** (a) in the nematic phase at 120 °C, (b) in the G-form, (c) in the B-form, and (d) in the B_{sc}-form. The diffractograms shown in (b-d) were acquired at room temperature.

X-ray diffraction (XRD) measurements were performed to confirm that the G-form is indeed a kinetically trapped state and that the thermoresponsive luminescence behavior (i.e., the transformation of the G-form into the B-form upon annealing) is due to a phase transition, which in turn induces a change of the molecular assembled structures. As shown in Figure 5, the XRD patterns of **1** in the nematic phase at 120 °C and of the G-form at room temperature only feature a broad, structureless peaks, indicative of a low degree of order in both cases. Conversely, the diffractogram of the B-form features many sharp peaks (Figure 5c), which reveal that annealing at 80 °C results in a phase transition to a crystalline form. Figure 5d shows the XRD pattern of the B_{sc}-form. While the most intense peak appears at the same position as in the XRD pattern of the B-form (2θ = 21.9 °), closer inspection reveals clear differences (Figure S2), suggesting that the crystalline state accessed through slow cooling from the nematic phase is different from the B-form, obtained by annealing the quenched G-form. We hypothesize that in the B- and Bsc-forms the luminophore of **1** is surrounded by the naphthalene or linker groups, because both these crystalline forms show monomer-like emission (*vide infra*). Unfortunately, we were not able to frow any crystals suitable for single crystal X-ray analysis, which could support this hypothesis.

For reference purposes, the phase transition behavior of model compounds **2** and **3** was also explored. Compound **2** is crystalline at temperatures of up to 167.1 °C, where a phase transition to a nematic phase occurs (Figure S3a). The POM image of **2** reveals a typical schlieren texture at 180 °C (Figure S4a). Upon cooling from the nematic phase, **2** always transformed into a crystalline solid, even at the highest cooling rates attainable. Moreover, no unambiguous color changes could be discerned when compound **2** was annealed in the crystalline state or exposed to mechanical force at room temperature. Thus, compound **2** has a strong tendency to form the thermodynamically most stable crystalline structure, likely on account of its linear and highly symmetric molecular structure. As for compound **3**, the DSC trace shows only

one peak corresponding to the phase transition from a crystalline solid to an isotropic melt (Figure S3b). We also prepared an equimolar mixture of compounds **2** and **3**, but as expected, POM observation reveals phase separation (Figure S4b). Thus, the asymmetric cyclic structure appears to be a key for the kinetically-trapped metastable state of **1** and the related thermo- and mechanoresponsive luminescence behavior.
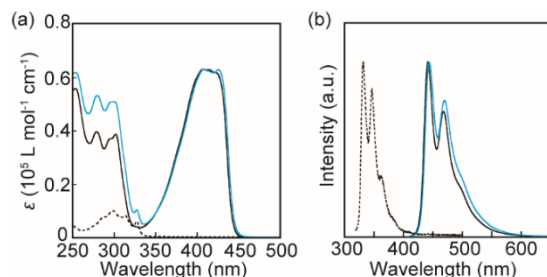

Figure 6. (a) Absorption and (b) normalized photoluminescence spectra of CHCl$_3$ solutions (c = 1.0 × 10^{-5} M) of cyclophane **1** (blue solid line) and reference compounds **2** (black solid line) and **3** (black dotted line). The emission spectra were recorded at room temperature with λ_{ex} = 400 nm (**1** and **2**) and 300 nm (**3**).

Before investigating the thermally and mechanically induced changes of the photoluminescence characteristics of cyclophane **1** in the condensed state, we examined the photophysical properties of cyclophane **1** and model compounds **2** and **3** in solution. Figure 6 shows the UV-vis absorption and photoluminescence spectra of all compounds in dilute CHCl$_3$ solution (c = 1.0 × 10^{-5} M). The absorption spectrum of the linear 1,6-bis(phenylethynyl)pyrene reference **2** shows a band between 350 and 450 nm, with a molar extinction coefficient ε of 6.3 × 10^4 L mol^{-1} cm^{-1} at 407 nm. The spectrum of the linear naphthalene **3** features an absorption band between 270 and 330 nm, with a much smaller ε (9.8 × 10^3 L mol^{-1} cm^{-1} at 298 nm) than **2**. The absorption spectrum of cyclophane **1** is largely a superposition of the absorption spectra of **2** and **3**, although closer inspection reveals a difference in the shape of the peaks between 410 and 430 nm, which is indicative of feeble ground state electronic interactions between the pyrene and naphthalene moieties in the asymmetric cyclic structure.
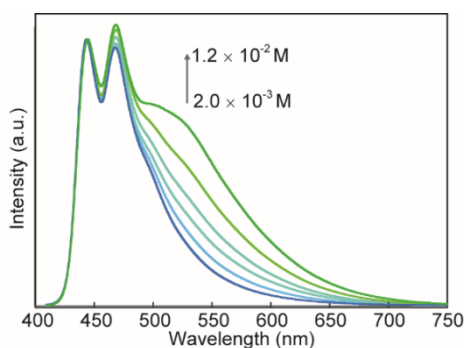

Figure 7. Photoluminescence spectra of cyclophane **1** in 2:3 v/v CHCl$_3$:methanol solutions of different concentrations (c = 2.0 × 10^{-3} - 1.2 × 10^{-2} M). The spectra were recorded at room temperature with λ_{ex} = 400 nm and are normalized at 444 nm.

The emission spectrum of the CHCl$_3$ solution of the linear 1,6-bis(phenylethynyl)pyrene reference **2** displays a vibronic structure with peaks at 444 and 470 nm and a shoulder around 495 nm (Figure 6b), indicative of well-individualized molecules.[73] Similar features can be observed in the emission spectrum of **3**, although the maxima appear at much lower wavelengths (331, 345, and 362 nm). The emission spectrum of cyclophane **1** in CHCl$_3$ is virtually identical to that of **2**, indicating that the electronic characteristics of well-individualized 1,6-bis(phenylethynyl)pyrene moieties are largely retained. The small difference between the emission spectra of **1** and **2** may be related to the aforementioned ground state interactions with the naphthalene group in the cyclophane. It is noteworthy that the emission characteristics of the asymmetric cyclophane **1** are very different from those observed for symmetric cyclophanes comprised of two 9,10-bis(phenylethynyl)anthracene moieties,[29-30] in which intramolecular excimer formation was observed. We also measured the emission spectra of **1** at higher concentration (c = 2.0 × 10^{-3} - 1.2 × 10^{-2} M) in a more polar solvent mixture (2:3 v/v CHCl$_3$:methanol) in order to probe if aggregation would lead to the formation of intermolecular excimers. Indeed, as shown in Figure 7, a broad, featureless band with a maximum around 530 nm developed when the concentration was increased above 2.0 × 10^{-3} M, which is ascribed to excimer emission; when the concentration was increased beyond 1.2 × 10^{-2} M, precipitation occurred.

The photoluminescence spectra of **1** in the condensed states (recorded at room temperature) unequivocally reveal that the emission characteristics strongly depend on the thermal history (Figure 8). The metastable G-form, obtained by rapid cooling from the nematic phase, displays a broad and structureless emission band with a maximum at 521 nm. The similarity to the excimer-band observed in high-concentration solutions (Figure 7) suggests that in the G-form the luminophores form intermolecular excimers. By contrast, the emission spectrum of the B-form, obtained by annealing the G-form at 80 °C, shows a sharp peak at 486 nm and two shoulders around at 455 and 515 nm, i.e., features that are characteristic of monomer emission (Figures 6b, 7). The emission spectrum of the B$_{sc}$-form is similar to the one of the B-form. The observed small difference is likely related to subtle changes in the molecular assembled structures, as supported by the fact that the XRD patterns are different from each other (Figure 5c,d, Figure S2).
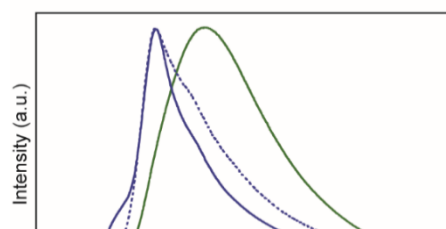
Table 1. Emission lifetimes and quantum yields.[a]

	τ_i (amplitude a_i) (ns)	X^2	Φ_{PL}
1 in chloroform[b]	0.5 (56%), 2.3 (44%)	1.00	0.95
G-form[c]	1.4 (38%), 5.7 (45%), 19 (17%)	1.08	0.54
B-form[d]	0.3 (94%), 1.2 (5%), 6.1 (1%)	1.05	0.15
2 in chloroform[b]	1.4 (100%)	1.09	0.96

[a] All measurements were carried out at room temperature. [b] Monitored at 450 nm. [c] Monitored at 520 nm. [d] Monitored at 485 nm.

Figure 8. Photoluminescence spectra of cyclophane **1** in the G-form (green solid line), B-form (blue solid line), and the B$_{sc}$-form (blue dotted line). All spectra were recorded at room temperature with λ_{ex} = 400 nm.
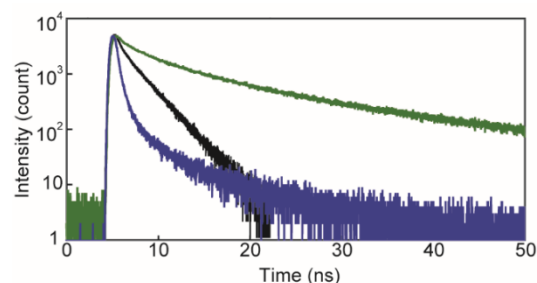

Figure 9. Emission decay profiles of cyclophane **1** in CHCl$_3$ solution (black line), the G-form (green line), and the B-form (blue line). All data were collected at room temperature with λ_{ex} = 405 nm.

Emission lifetime and quantum yield measurements confirm the conclusions drawn from the steady-state photoluminescence experiments. The analysis of the emission decay of a dilute CHCl$_3$ solution of the linear 1,6-bis(phenylethynyl)pyrene reference **2** (c = 1.0 × 10^{-6} M, Figure S5) points to a single emission process with a lifetime of 1.4 ns, which is ascribed to monomer emission. The photoluminescence quantum yield was 0.96 and the photophysical data match previously reported values.[73] A similar decay profile, albeit with different lifetimes (0.5, 2.3 ns), and an equally high quantum efficiency were measured for **1** (c = 1.0 × 10^{-6} M, Figure 9). The difference in emission lifetimes is consistent with the cyclic structure of **1**. The small intramolecular ground state interactions between the two aromatic parts should affect the lifetimes and the cyclic structure reduces the molecular rotation and vibration of the luminophores and thereby restricts radiation-less relaxation pathways. The emission decay traces of the G-form and B-form strikingly differ from the CHCl$_3$ solution of **1** (Figure 9). Both profiles are well-fitted by tri-exponential decay functions, which afford emission lifetimes and population fractions as summarized in Table 1. A long emission lifetime of 19 ns was observed for the G-form, which is associated with intermolecular excimers. However, the decay is dominated by short-lived species with lifetimes of 1.4 and 5.7 ns. Together with the appreciable quantum efficiency (54%) the data suggest the presence of a poorly ordered structure. In the case of the B-form, the long-lived species are absent, and the decay is dominated by short-lived species with lifetimes of 0.3, 1.2 ns; at the same time, the quantum efficiency is reduced to 0.15. The pronounced differences confirm unequivocally that the annealing-induced phase

Finally, the mechanoresponsive luminescence behavior of cyclophane **1** was examined. As shown in Figure 10, mechanical stimulation of the B-form at 25 °C causes the photoluminescence to change from blue to green. Interestingly, the emission color of the mechanically treated sample reverted to blue within 10 minutes if the sample was kept at 25 °C. This process was found to be strongly temperature dependent; recovery of the blue emission was immediate at 35°C (Figure S6a), whereas the mechanically induced green emission was retained for over 1 h at 15 °C (Figure S6b). The hypothesis that the mechanically induced emission is related to excimers is supported by the steady-state emission spectrum (Figure 11), which displays a characteristic, broad, structure-less band centered around 516 nm. Further, the emission decay profile (Figure S7) features a long-lived component with a lifetime of 15 ns, and is similar to the one of the G-form. While the transient nature of the mechanically induced green-emissive state makes a characterization difficult, the data support the conclusion that mechanical force transforms the well-ordered B-form, at least partially, into a disordered mobile state in which intermolecular excimer formation can occur.
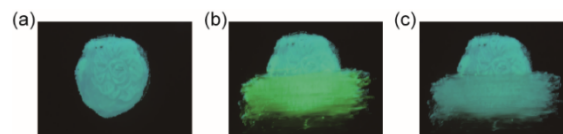

Figure 10. Photographs documenting the mechanoresponsive luminescence of cyclophane **1** at 25 °C. (a) B-form on a quartz substrate. (b) The sample immediately after grinding the lower part. (c) The same sample 10 minutes after grinding. All images were recorded under illumination with 365 nm UV light.

The photophysical properties after recovery are almost the same as those of the B-form. After the ground sample was kept at 25 °C for 10 minutes, the emission spectrum (Figure 11) and the emission decay profile (Figure S7) of the blue-emitting sample are similar to those of the B-form, although the X-ray diffraction pattern of the blue-emitting solid is different from that of the B-form (Figure

S8), reflecting the fact that cyclophanes **1** can form several polymorphs in the crystalline state. Similar mechanoresponsive luminescence behavior is also observed for the B_{sc}-form and even as-prepared powder of cyclophane **1** (Figure S9).
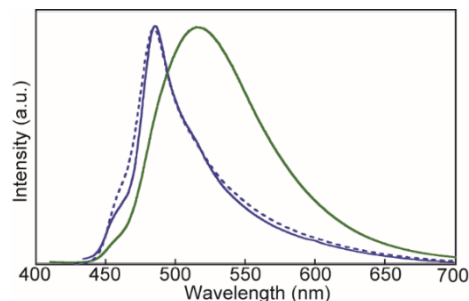

Figure 11. Photoluminescence spectra of cyclophane **1** in the B-form (blue solid line), immediately after grinding the B-form (green solid line), and the same sample 10 minutes at 25 °C after grinding (blue dotted line). All spectra were recorded at room temperature with λ_{ex} = 400 nm.

CONCLUSIONS

In conclusion, the photophysical properties of the asymmetric, "hetero-type" pyrene-based cyclophane **1** depend strongly on the molecular assembly. The material displays a broad nematic range and a low-order mobile phase can be kinetically trapped by rapidly cooling the LC phase. This metastable supercooled nematic phase is stable under ambient conditions and displays thermo- and mechanoresponsive luminescent behavior. To the best of our knowledge, this is the first example of a stimuli-responsive luminescent material based on a supercooled nematic LC phase. The design approach utilized appears to be general, should be useful to create other materials with stimuli-responsive luminescence, and can be expected to also be exploitable in connection with electric or magnetic fields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI: 10.1021/acs.chemmater.XXXXXX.

> Synthesis and characterization data of compounds **1**, **2**, and **3**. Additional POM images, emission decay profiles, DSC curves, additional XRD patterns, additional emission spectra, additional images documenting mechanoresponsive luminescent behavior (PDF).

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REFERENCES

(1) Sagara, Y.; Yamane, S.; Mitani, M.; Weder, C.; Kato, T. Mechanoresponsive Luminescent Molecular Assemblies: An Emerging Class of Materials. *Adv. Mater.* **2016**, *28*, 1073–1095.

(2) Sagara, Y.; Kato, T. Mechanically Induced Luminescence Changes in Molecular Assemblies. *Nature Chem.* **2009**, *1*, 605–610.

(3) Araki, K.; Mutai, T. Packing-directed Tuning and Switching of Organic Solid-state Luminescence. *Photochemistry* **2016**, *43*, 191–225.

(4) Würthner, F.; Saha-Möller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D. Perylene Bisimide Dye Assemblies as Archetype Functional Supramolecular Materials. *Chem. Rev.* **2016**, *116*, 962–1052.

(5) Würthner, F.; Kaiser, T. E.; Saha-Möller, C. R. J-Aggregates: From Serendipitous Discovery to Supramolecular Engineering of Functional Dye Materials. *Angew. Chem. Int. Ed.* **2011**, *50*, 3376–3410.

(6) Dong, Y. Q. ; Lam, J. W.; Tang, B. Z. Mechanochromic Luminescence of Aggregation-Induced Emission Luminogens. *J. Phys. Chem. Lett.* **2015**, *6*, 3429-3436.

(7) Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015**, *115*, 11718–11940.

(8) Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. Functional π- Gelators and Their Applications. *Chem. Rev.* **2014**, *114*, 1973-2129.

(9) Ma, Z.; Wang, Z.; Teng, M.; Xu, Z.; Jia, X. Mechanically Induced Multicolor Change of Luminescent Materials. *ChemPhysChem* **2015**, *16*, 1811–1828.

(10) Yan, D.; Evans, D. G. Molecular Crystalline Materials with Tunableluminescent Properties: From Polymorphs to Multi-component Solids. *Mater. Horiz.* **2014**, *1*, 46–57.

(11) Zhang, X. Q.; Chi, Z. G.; Zhang, Y.; Liu, S. W.; Xu, J. R. Recent Advances in Mechanochromic Luminescent Metal Complexes. *J. Mater. Chem. C* **2013**, *1*, 3376–3390.

(12) Chi, Z.; Zhang, X.; Xu, B.; Zhou, X.; Ma, C.; Zhang, Y.; Liu, S.; Xu, J. Recent Advances in Organic Mechanofluorochromic Materials. *Chem. Soc. Rev.* **2012**, *41*, 3878–3896.

(13) Ariga, K.; Mori, T.; Hill, J. P. Mechanical Control of Nanomaterials and Nanosystems. *Adv. Mater.* **2012**, *24*, 158–176.

(14) Haehnel, A. P.; Sagara, Y.; Simon, Y. C.; Weder, C. Mechanochemistry in Polymers with Supramolecular Mechanophores. *Top. Curr. Chem.* **2015**, *369*, 345–375.

(15) Calvino, C.; Neumann, L.; Weder, C.; Schrettl, S. Approaches to Polymeric Mechanochromic Materials. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 640–652.

(16) Botta, C.; Benedini, S.; Carlucci, L.; Forni, A.; Marinotto, D.; Nitti, A.; Pasini, D.; Righetto, S.; Cariati, E. Polymorphism-dependent Aggregation Induced Emission of a Push–pull Dye and Its Multi-stimuli Responsive Behavior. *J. Mater. Chem. C* **2016**, *4*, 2979–2989.

(17) Seki, T.; Takamatsu, Y.; Ito, H. A Screening Approach for the Discovery of Mechanochromic Gold(I) Isocyanide Complexes with Crystal-to-Crystal Phase Transitions. *J. Am. Chem. Soc.* **2016**, *138*, 6252–6260.

(18) Du, X.; Xu, F.; Yuan, M.-S.; Xue, P.; Zhao, L.; Wang, D.-E.; Wang, W.; Tu, Q.; Chen, S.-W.; Wang, J. Reversible Luminescence Color Switching in the Crystal Polymorphs of 2,7-Bis(2'-methyl-[1,1'-biphenyl]-4-yl)-fluorenone by Thermal and Mechanical Stimuli. *J. Mater. Chem. C* **2016**, *4*, 8724–8730.

(19) Seki, T.; Sakurada, K.; Ito, H. Controlling Mechano- and Seeding-Triggered Single-Crystal-to-Single-Crystal Phase Transition: Molecular Domino with a Disconnection of Aurophilic Bonds. *Angew. Chem. Int. Ed.* **2013**, *52*, 12828–12832.

(20) Ito, H.; Muromoto, M.; Kurenuma, S.; Ishizaka, S.; Kitamura, N.; Sato, H.; Seki, T. Mechanical Stimulation and Solid Seeding Trigger Single-crystal-to-single-crystal Molecular Domino Transformations. *Nat. Commun.* **2013**, *4*, 2009.

(21) Sagara, Y.; Kubo, K.; Nakamura, T.; Tamaoki, N.; Weder, C. Temperature-Dependent Mechanochromic Behavior of Mechanoresponsive Luminescent Compounds. *Chem. Mater.* **2017**, *29*, 1273–1278.

(22) Seki, T.; Ozaki, T.; Okura, T.; Asakura, K.; Sakon, A.; Uekusa, H.; Ito, H. Interconvertible Multiple Photoluminescence Color of a Gold(I) Isocyanide Complex in the Solid State: Solvent-induced Blue-shifted and Mechano-responsive Red-shifted Photoluminescence. *Chem. Sci.* **2015**, *6*, 2187–2195.

(23) Zhang, J. N.; Kang, H.; Li, N.; Zhou, S. M.; Sun, H. M.; Yin, S. W.; Zhao, N.; Tang, B. Z. Organic Solid Fluorophores Regulated by Subtle Structure Modification: Color-tunable and Aggregation-induced Emission. *Chem. Sci.* **2017**, *8*, 577–582.

(24) Okazaki, M.; Takeda, Y.; Data, P.; Pander, P.; Higginbotham, H.; Monkman, A. P.; Minakata, S. Thermally Activated Delayed Fluorescent Phenothiazine–dibenzo[a,j]phenazine–phenothiazine Triads Exhibiting Tricolor-changing Mechanochromic Luminescence. *Chem. Sci.* **2017**, *8*, 2677–2686.

(25) Genovese, D.; Aliprandi, A.; Prasetyanto, E. A.; Mauro, M.; Hirtz, M.; Fuchs, H.; Fujita, Y.; Uji-I, H.; Lebedkin, S.; Kappes, M.; De Cola, L. Mechano- and Photochromism from Bulk to Nanoscale: Data Storage on Individual Self-Assembled Ribbons. *Adv. Funct. Mater.* **2016**, *26*, 5271–5278.

(26) Yagai, S.; Seki, T.; Aonuma, H.; Kawaguchi, K.; Karatsu, T.; Okura, T.; Sakon, A.; Uekusa, H.; Ito, H. Mechanochromic Luminescence Based on Crystal-to-Crystal Transformation Mediated by a Transient Amorphous State. *Chem. Mater.* **2016**, *28*, 234–241.

(27) Sagara, Y.; Mutai, T.; Yoshikawa, I.; Araki, K. Material Design for Piezochromic Luminescence: Hydrogen-bond-directed Assemblies of a Pyrene Derivative. *J. Am. Chem. Soc.* **2007**, *129*, 1520–1521.

(28) Kunzelman, J.; Kinami, M.; Crenshaw, B. R.; Protasiewicz, J. D.; Weder, C. Oligo(*p*-Phenylene Vinylene)s as a "New" Class of Piezochromic Fluorophores. *Adv. Mater.* **2008**, *20*, 119–122.

(29) Sagara, Y.; Weder, C.; Tamaoki, N. Tuning the Thermo- and Mechanoresponsive Behavior of Luminescent Cyclophanes. *RSC Adv.* **2016**, *6*, 80408–80414.

(30) Sagara, Y.; Simon, Y. C.; Tamaoki, N.; Weder, C. A Mechano- and Thermoresponsive Luminescent Cyclophane. *Chem. Commun.* **2016**, *52*, 5694–5697.

(31) Sagara, Y.; Lavrenova, A.; Crochet, A.; Simon, Y. C.; Fromm, K. M.; Weder, C. A Thermo- and Mechanoresponsive Cyano-Substituted Oligo(*p*-phenylene vinylene) Derivative with Five Emissive States. *Chem. Eur. J.* **2016**, *22*, 4374–4378.

(32) Butler, T.; Morris, W. A.; Samonina-Kosicka, J.; Fraser, C. L. Mechanochromic Luminescence and Aggregation Induced Emission of Dinaphthoylmethane β-Diketones and Their Boronated Counterparts. *ACS Appl. Mater. and Interfaces* **2016**, *8*, 1242–1251.

(33) Ma, Z.; Wang, Z.; Meng, X.; Ma, Z.; Xu, Z.; Ma, Y.; Jia, X. A Mechanochromic Single Crystal: Turning Two Color Changes into a Tricolored Switch. *Angew. Chem. Int. Ed.* **2016**, *55*, 519–522.

(34) Ma, Z.; Ji, Y.; Wang, Z.; Kuang, G.; Jia, X. Mechanically Controlled FRET to Achieve an Independent Three Color Switch. *J. Mater. Chem. C* **2016**, *4*, 10914–10918.

(35) Ma, Z.; Wang, Z.; Xu, Z.; Jia, X.; Wei, Y. Controllable Multicolor Switching of Oligopeptide-based Mechanochromic Molecules: From Gel Phase to Solid Powder. *J. Mater. Chem. C* **2015**, *3*, 3399–3405.

(36) Zhao, Z.; Chen, T.; Jiang, S.; Liu, Z.; Fang, D.; Dong, Y. Q. The Construction of a Multicolored Mechanochromic Luminogen with High Contrast through the Combination of a Large Conjugation Core and Peripheral Phenyl Rings. *J. Mater. Chem. C* **2016**, *4*, 4800–4804.

(37) Balkenende, D. W. R.; Coulibaly, S.; Balog, S.; Simon, Y. C.; Fiore, G. L.; Weder, C. Mechanochemistry with Metallosupramolecular Polymers. *J. Am. Chem. Soc.* **2014**, *136*, 10493–10498.

(38) Yagai, S.; Okamura, S.; Nakano, Y.; Yamauchi, M.; Kishikawa, K.; Karatsu, T.; Kitamura, A.; Ueno, A.; Kuzuhara, D.; Yamada, H.; Seki, T.; Ito, H. Design Amphiphilic Dipolar π-systems for Stimuli-responsive Luminescent Materials Using Metastable States. *Nat. Commun.* **2014**, *5*, 4013.

(39) Sagara, Y.; Komatsu, T.; Ueno, T.; Hanaoka, K.; Kato, T.; Nagano, T. Covalent Attachment of Mechanoresponsive Luminescent Micelles to Glasses and Polymers in Aqueous Conditions. *J. Am. Chem. Soc.* **2014**, *136*, 4273–4280.

(40) Sagara, Y.; Komatsu, T.; Terai, T.; Ueno, T.; Hanaoka, K.; Kato, T.; Nagano, T. Thermal or Mechanical Stimuli-Induced Photoluminescence Color Change of a Molecular Assembly Composed of an Amphiphilic Anthracene Derivative in Water. *Chem. Eur. J.* **2014**, *20*, 10397–10403.

(41) Yamane, S.; Sagara, Y.; Mutai, T.; Araki, K.; Kato, T. Mechanochromic Luminescent Liquid Crystals Based on a Bianthryl Moiety. *J. Mater. Chem. C* **2013**, *1*, 2648–2656.

(42) Sagara, Y.; Komatsu, T.; Ueno, T.; Hanaoka, K.; Kato, T.; Nagano, T. A Water-Soluble Mechanochromic Luminescent Pyrene Derivative Exhibiting Recovery of the Initial Photoluminescence Color in a High-Humidity Environment. *Adv. Funct. Mater.* **2013**, *23*, 5277–5284.

(43) Park, S. K.; Cho, I.; Gierschner, J.; Kim, J. H.; Kim, J. H.; Kwon, J. E.; Kwon, O. K.; Whang, D. R.; Park, J.-H.; An, B.-K.; Park, S. Y. Stimuli-ResponsiveReversible Fluorescence Switching in aCrystalline Donor–Acceptor Mixture Film:Mixed Stack Charge-Transfer EmissionversusSegre-

gated Stack MonomerEmission. *Angew. Chem. Int. Ed.* **2016**, *55*, 203–207.

(44) Kim, H.-J.; Whang, D. R.; Gierschner, J.; Lee, C. H.; Park, S. Y. High-Contrast Red–Green–Blue Tricolor Fluorescence Switching in Bicomponent Molecular Film. *Angew. Chem. Int. Ed.* **2015**, *54*, 4330–4333.

(45) Chung, K.; Kwon, M. S.; Leung, B. M.; Wong-Foy, A. G.; Kim, M. S.; Kim, J.; Takayama, S.; Gierschner, J.; Matzger, A. J.; Kim, J. Shear-Triggered Crystallization and Light Emission of a Thermally Stable Organic Supercooled Liquid. *ACS Cent. Sci.* **2015**, *1*, 94–102.

(46) Mitani, M.; Ogata, S.; Yamane, S.; Yoshio, M.; Hasegawa, M.; Kato, T. Mechanoresponsive Liquid Crystals Exhibiting Reversible Luminescent Color Changes at Ambient Temperature. *J. Mater. Chem. C* **2016**, *4*, 2752–2760.

(47) Sagara, Y.; Kato, T. A Mechanical and Thermal Responsive Luminescent Liquid Crystal Forming a Colourless Film under Room Llight. *Supramol. Chem.* **2011**, *23*, 310–314.

(48) Sagara, Y.; Yamane, S.; Mutai, T.; Araki, K.; Kato, T. A Stimuli-Responsive, Photoluminescent, Anthracene-Based Liquid Crystal: Emission Color Determined by Thermal and Mechanical Processes. *Adv. Funct. Mater.* **2009**, *19*, 1869–1875.

(49) Sagara, Y.; Kato, T. Stimuli-responsive Luminescent Liquid Crystals: Change of Photoluminescent Colors Triggered by a Shear-induced Phase Transition. *Angew. Chem. Int. Ed.* **2008**, *47*, 5175–5178.

(50) Sagara, Y.; Kato, T. Brightly Tricolored Mechanochromic Luminescence from a Single-Luminophore Liquid Crystal: Reversible Writing and Erasing of Images. *Angew. Chem. Int. Ed.* **2011**, *50*, 9128–9132.

(51) Yamane, S.; Sagara, Y.; Kato, T. A Thermoresponsive Photoluminescent Smectic Liquid Crystal: Change of Photoluminescent Color on the Smectic–smectic Phase Transition. *Chem. Commun.* **2009**, 3597–3599.

(52) Yamane, S.; Tanabe, K.; Sagara, Y.; Kato, T. Stimuli-Responsive Photoluminescent Liquid Crystals. *Top. Curr. Chem.* **2012**, *318*, 395–405.

(53) Kozhevnikov, V. N.; Donnio, B.; Bruce, D. W. Phosphorescent, Terdentate, Liquid-Crystalline Complexes of Platinum(II): Stimulus-Dependent Emission. *Angew. Chem. Int. Ed.* **2008**, *47*, 6286–6289.

(54) Crenshaw, B. R.; Weder, C. Phase Separation of Excimer-Forming Fluorescent Dyes and Amorphous Polymers: A Versatile Mechanism for Sensor Application. *Adv. Mater.* **2005**, *17*, 1471-1476.

(55) Kinami, M.; Crenshaw, B. R.; Weder, C. Polyesters with Built-in Threshold Temperature and Deformation Sensors. *Chem. Mater.* **2006**, *18*, 946–955.

(56) Kunzelman, J.; Crenshaw, B. R.; Kinami, M.; Weder, C. Self-Assembly and Dispersion of Chromogenic Molecules: AVersatile and General Approach for Self-Assessing Polymers. *Macromol. Rapid Commun.* **2006**, *27*, 1981–1987.

(57) Crenshaw, B. R.; Kunzelman, J.; Sing, C. E.; Ander, C.; Weder, C. Threshold Temperature Sensors with Tunable Properties. *Macromol. Chem. Phys.* **2007**, *208*, 572–580.

(58) Kunzelman, J.; Crenshaw, B. R.; Weder, C. Self-assembly of Chromogenic Dyes—a New Mechanism for Humidity Sensors. *J. Mater. Chem.* **2007**, *17*, 2989–2991.

(59) Kato, T.; Mizoshita, N.; Kishimoto, K. Functional Liquid-Crystalline Assemblies: Self-Organized Soft Materials. *Angew. Chem. Int. Ed.* **2005**, *45*, 38–68.

(60) Tamaoki, N.; Aoki, Y.; Moriyama, M.; Kidowaki, M. Photochemical Phase Transition and Molecular Realignment of Glass-Forming Liquid Crystals Containing Cholesterol/Azobenzene Dimesogenic Compounds. *Chem. Mater.* **2003**, *15*, 719–726.

(61) Mallia, V. A.; Tamaoki, N. Design of Chiral Dimesogens Containing Cholesteryl Groups; Formation of New Molecular Organizations and Their Application to Molecular Photonics. *Chem. Soc. Rev.* **2004**, *33*, 76–84.

(62) Abraham, S.; Mallia, V. A.; Ratheesh, K. V.; Tamaoki, N.; Das, S. Reversible Thermal and Photochemical Switching of Liquid Crystalline Phases and Luminescence in Diphenylbutadiene-Based Mesogenic Dimers. *J. Am. Chem. Soc.* **2006**, *128*, 7692–7698.

(63) Vijayaraghavan, R. K.; Abraham, S.; Akiyama, H.; Furumi, S.; Tamaoki, N.; Das, S. Photoresponsive Glass-Forming Butadiene-Based Chiral Liquid Crystals with Circularly Polarized Photoluminescence. *Adv. Funct. Mater.* **2008**, *18*, 2510–2517.

(64) Akiyama, H.; Tanaka, A.; Hiramatsu, H.; Nagasawa, J.; Tamaoki, N. Reflection Colour Changes in Cholesteric Liquid Crystals after the Addition and Photochemical Isomerization of Mesogenic Azobenzenes Tethered to Sugar Alcohols. *J. Mater. Chem.* **2009**, *19*, 5956–5963.

(65) Percec, V.; Asandei, A. D.; Ungar, G. From Regioirregular Linear Main-Chain Liquid-Crystal Polyethers Exhibiting Two Uniaxial Nematic Phases to Macrocyclic Main-Chain Oligoethers Displaying Nematic and Smectic Phases. *Chem. Mater.* **1996**, *8*, 1550–1557.

(66) Percec, V.; Asandei, A. D.; Chu, P. Design of Side Chain and Main Chain Liquid Crystalline Polymers Containing Supramolecular Quasi-Rigid-Rodlike Mesogens Obtained from Collapsed Main Chain Macrocyclics. *Macromolecules* **1996**, *29*, 3736–3750.

(67) Percec, V.; Kawasumi, M.; Rinaldi, P. L.; Litman, V. E. Synthesis and Characterization of Cyclic Liquid Crystalline Oligomers Based on 1-(4-Hydroxy-4'-biphenylyl)-2-(4-hydroxyphenyl)butane and 1,10-Dibromodecane. *Macromolecules* **1992**, *25*, 3851–3861.

(68) Percec, V.; Turkaly, P. J.; Asandei, A. D. Macrocyclization Overrides the Polymer Effect in the Stabilization of Liquid Crystalline (LC) Phases with a Novel Odd-Even Alternation. A Demonstration with LC Crown Ethers. *Macromolecules* **1997**, *30*, 943–952.

(69) Neumann, B.; Joachimi, D.; Tschierske, C. Liquid Crystalline Macrocycles: Novel Glass-Forming Nematic Materials That Can Undergo Charge Transfer Induced Phase Transition. *Adv. Mater.* **1997**, *9*, 241–244.

(70) Neumann, B.; Hegmann, T.; Wolf, R.; Tschierske, C. Binuclear Cyclopalladated Cyclophanes: towards a New Family of Metallomesogens. *Chem. Commun.* **1998**, 105–106.

(71) Hegmann, T.; Neumann, B.; Wolf, R.; Tschierske, C. Liquid Crystalline Paracyclophanes and *ansa* Compounds—Series of Polyether Macrocycles Incorporating Diacetylene, Phenyl, Biphenyl, *p*-Terphenyl and 2,5-Diphenyl-1,3,4-thiadiazole Rigid Cores. *J. Mater. Chem.* **2005**, *15*, 1025–1034.

(72) Neumann, B.; Hegmann, T.; Wagner, C.; Ashton, P. R.; Wolf, R.; Tschierske, C. Liquid Crystalline Macrocycles Containing Phenylpyrimidine Units. *J. Mater. Chem.* **2003**, *13*, 778–784.

(73) Suneesh, C. V.; Gopidas, K. R. Long-Lived Photoinduced Charge Separation Due to the Inverted Region Effect in 1,6-Bis(phenylethynyl)pyrene-Phenothiazine Dyad. *J. Phys. Chem. C* **2010**, *114*, 18725–18734.

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