

Temperature-dependent Mechanochromic Behavior of Mechanoresponsive Luminescent Compounds

Yoshimitsu Sagara,^{*,†} Kazuya Kubo,[†] Takayoshi Nakamura,[†] Nobuyuki Tamaoki,[†] Christoph Weder^{*,‡}

[†]Research Institute for Electronic Science, Hokkaido University, N20, W10, Kita-Ku, Sapporo 001-0020, Japan

[‡]Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland

E-mail: sagara@es.hokudai.ac.jp; christoph.weder@unifr.ch

ABSTRACT: Mechanoresponsive luminescent (MRL) compounds change their emission color upon mechanical treatment. Hundreds of MRL compounds have been studied, but their mechanically triggered response at elevated temperature has remained virtually unexplored. Here, we demonstrate that the temperature can have a significant influence on the mechanically induced response of MRL compounds. The photoluminescence of a new cyano-substituted oligo(*p*-phenylene vinylene) derivative was shown to exhibit a significant red-shift when ground at ambient temperature, whereas the same treatment at 100 °C leads to a hypsochromic shift. The behavior at ambient is caused by a mechanically induced phase transition from a crystalline to an amorphous solid in which the dye molecules form excimers, whereas at elevated temperature the hypsochromic shift is ascribed to a crystalline-crystalline phase transition. Such temperature-dependent MRL behavior was not previously observed, but it appears to be a general effect that is useful for sophisticated mechano-sensing materials and devices.

INTRODUCTION

The ability to control the photophysical properties of molecular materials by external stimulation is broadly useful for applications in sensors, memories, security features, and other technologies.¹⁻²⁷ This has motivated the investigation of organic and organometallic mechano-responsive luminescent (MRL) materials, in which mechanical treatment causes a modification of the molecular packing, which in turn can trigger quite dramatic changes of the material's emission characteristics.^{1-10,28-62} Many of the over 300 reports on MRL compounds describe not only the effect of mechanical treatment, but also changes that occur upon heating.^{1,6,8,9} In numerous studies, the *sequential* application of mechanical force and heat was also investigated.^{29,30,32,34,36,39,43-51} In a typical sequence, the solid state structure and photoluminescence color are first changed by mechanical grinding, pressing or shearing the MRL material at room temperature (r.t.); in many cases this mechanically induced state is metastable and subsequent heating causes the recovery of the initial assembly and photoluminescence color.^{29,30,32,34,36,39,43-51} Interestingly, the effects resulting from exposing MRL materials to mechanical stimulation or thermal treatment were so far exclusively studied separately or sequentially, whereas the simultaneous exposure of MRL materials to mechanical and thermal stimulation has remained unexplored. Indeed, to our best knowledge, the only precedence in the literature is a liquid-crystalline mixture

whose phase behavior and properties are very different from those of solid MRL materials.⁵⁵ We here report our surprising discovery that the simultaneous multi-stimuli exposure of solid MRL compounds permits access to morphologies and emission colors that are not accessible by applying the stimuli either individually or consecutively. This effect was first observed during our investigation of the cyano-substituted oligo(*p*-phenylene vinylene) (cyano-OPV)⁶³ derivative **1** (Figure 1), for which a significant red-shift of the photoluminescence can be observed when the material is ground at r.t., whereas grinding at 100 °C leads to a pronounced hypsochromic shift. To our best knowledge, compound **1** is the first MRL molecule that exhibits such temperature-dependent MRL behavior, which appears to be useful for sophisticated sensing schemes, materials and devices. We show that the effect is also observed for another cyano-OPV derivative, which suggests that the phenomenon may be general. Indeed, our study suggests that hitherto unobserved morphologies and emission colors may be discoverable for many known MRL compounds, if mechanical stimulation is combined with exposure to heat. The data also reveal that temperature is a non-negligible parameter for the mechanically induced morphology changes associated with MRL behavior.

RESULTS AND DISCUSSION

The new compound **1** features the widely-investigated 1,4-bis-(α -cyano-4-alkoxystyryl)-2,5-dimethoxybenzene moiety as the emissive core and two phenoxyhexyl moieties at the termini. The strong tendency of cyano-OPVs to form excimers⁶⁴ makes this core attractive for the design of mechanochromic materials.⁶⁵⁻⁷⁰ We recently reported on the MRL behavior of cyano-OPV derivative **2**, which features two tolyloxyhexyloxy substituents.²⁹ This compound forms five different emissive states, some of which can be converted into each other through mechanical or thermal stimulation. Compound **1** was originally synthesized because a MRL behavior similar to that of **2** was expected; however, we surprisingly found that the mere exchange of the peripheral methyl groups to protons significantly changes the molecular assembled structures and external stimuli-responsive luminescent behavior. Our in-depth characterization eventually led to the discovery of temperature-dependent MRL behavior, i.e., a temperature-dependent direction of mechanically induced spectral shift.

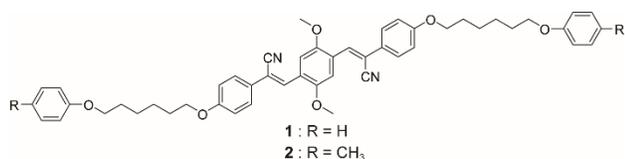


Figure 1. Molecular structures of the cyano-substituted oligo(*p*-phenylene vinylene) derivatives **1** and **2**.

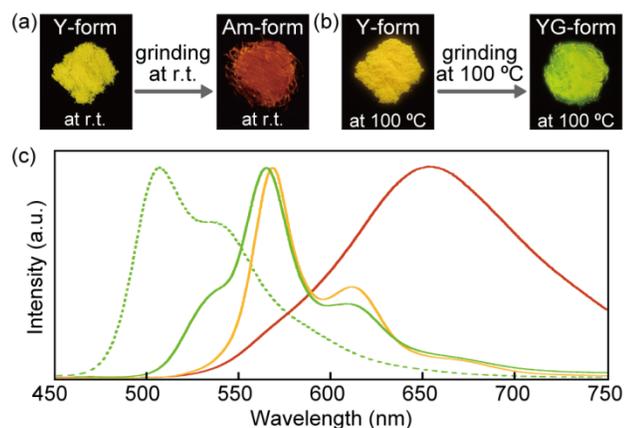


Figure 2. (a,b) Images documenting the mechanically induced photoluminescence changes of **1** at r.t. and 100 °C. The images were taken on quartz substrates under excitation light at 365 nm. (c) Photoluminescence spectra of **1** in CHCl₃ (1.0·10⁻⁶ M, green dotted line), the Y-form (yellow solid line), the Am-form (red solid line), and the YG-form (green solid line). All spectra were measured at room temperature ($\lambda_{\text{ex}} = 400$ nm).

The crystallization of **1** from dichloromethane affords a yellow-emitting crystalline form (referred to as Y-form), whereas rapid precipitation from chloroform into methanol results a form displaying reddish-orange photoluminescence (RO-form). The Y-form can be converted to an amorphous form (Am-form) that shows reddish-orange photoluminescence through mechanical grinding at am-

bient temperature (Figure 2a). The Y-form does not show any clear changes of its photoluminescence color upon heating to the melting point at 179 °C. However, the photoluminescence color changed from yellow to yellowish-green when **1** was ground at higher temperature. Figure 2b shows images illustrating the fluorescence color change when **1** was ground at 100 °C. The yellowish-green emissive form (YG-form) thus accessed is another crystalline form, but it is less ordered than the Y-form (*vide infra*). No weight decrease was observed when the pristine material (Y-form) was heated from ambient to ca. 400 °C in a thermogravimetric analysis experiment (Figure S1). This indicates the absence of trapped solvent molecules and underlines that the observed thermal effect is not related to the release of trapped solvent. Figure S2 shows that the yellowish-green photoluminescence of the YG-form persists after cooling from 100 °C to ambient. However, once the YG-form is melted, cooling always restores the Y-form, irrespective of the cooling rate. Interestingly, grinding the YG-form at r.t. afforded the Am-form and annealing of the Am-form (accessed by grinding the Y- or YG-form at r.t.) at 100 °C for 5 min caused the transition to the YG-form (Figure S2). Annealing of the RO-form at 100 °C for 30 min affords the YG-form, although a small amount of the Y-form appears to be formed as well, and energy transfer from the YG-form to the Y-form leads to an emission spectrum that is reminiscent of the Y-form (Figure S3-5).

The steady-state photoluminescence spectra of the different solid forms and a CHCl₃ solution of **1** (1.0·10⁻⁶ M) are compiled in Figure 2c and the absorption spectrum in CHCl₃ (1.0·10⁻⁵ M) is shown in Figure S6. The photoluminescence spectrum of the CHCl₃ solution displays peaks at 506 and 535 nm and a shoulder around 570 nm; these spectral features are characteristic of the emissive cyano-OPV core present in **1**.^{63,65-70} The emission spectrum of the Y-form is clearly red-shifted, but it displays a similar vibronic structure as the solution spectrum, with peaks at 568 and 612 nm and a shoulder around 670 nm (Figure 2c). The emission spectrum of the Am-form, which was obtained by grinding the Y-form at r.t., is broad and without structure and exhibits a significant red shift ($\lambda_{\text{em,max}} = 652$ nm) compared to all other forms of **1** (Figure 2c, red solid line). These spectral features are similar to those observed for compound **2** ground at r.t.,²⁹ and characteristic of excimer emission.⁶⁴ Conversely, when the Y-form was ground at 100 °C, the emission peak was blue-shifted from 568 to 565 nm and a new shoulder around 530 nm appears, leading to the yellowish-green photoluminescence appearance (Figure 2b).

Emission lifetime measurements were conducted to obtain additional information about the electronic processes associated with the various emissive species (Figure S7). The emission decay profiles of the CHCl₃ solution and the Y-form are well fitted by single exponential decay functions with emission lifetimes of 1.4 and 9.7 ns, respectively (Figure S7a,b and Table S1). In the case of the Am-form, monitoring at 570 and 650 nm resulted in different

emission decay profiles (Figure S7c). A species with a lifetime of 25.7 ns is dominant at 650 nm (Table S1), which supports the conclusion of excimer formation in the Am-form. By contrast, the photoluminescence at 570 nm was found to result mainly from species with relatively short lifetimes of 0.3, 1.1, and 5.0 ns. These results suggest that in the disordered Am-form a wide variety of molecular arrangements and electronic states exist; at the same time, efficient energy transfer appears to funnel most excitons to states of lower energy, as the emissive relaxation occurs largely from excimer sites. Three emission decay profiles were recorded for the YG-form at 530, 570, and 620 nm, in order to clarify whether the emissive species responsible for the newly observed shoulder around 530 nm are the same as those responsible for the higher-energy portion of the emission spectrum. No significant difference was observed between three emission decay profiles, which were fitted with double exponential decay functions, giving similar emission lifetimes (Table S1). These results indicate that the new shoulder is a part of vibronic structure of the emission spectrum of the YG-form instead of due to other mechanisms such as H-type exciton coupling.⁷

Wide-angle X-ray diffraction (XRD) measurements were carried out to clarify the relationship between the MRL behavior and changes in the molecular arrangements induced by external stimuli (Figure 3). The diffractogram acquired for the Y-form displays many sharp peaks reflecting its well-ordered crystalline nature. Given that only the Y-form was obtained through crystallization, it appears to be the thermodynamically most stable state of compound **1**. In the case of **2**, which was described in a previous study, green, yellow, and orange emissive crystalline solids could be obtained by variation of the solvents used for crystallization.²⁹ The diffraction pattern of the Y-form of **1** is completely different from that of yellow emissive crystals of **2**. Moreover, the clear vibronic structures seen for **1** in the Y-form were not observed for any crystalline state of **2**.²⁹ These differences indicate that the molecular arrangements of **1** in the Y-form and **2** in the yellow-light emitting crystalline state are different from each other, despite the minor molecular differences (Figure 1). XRD measurements further confirm that compound **1** exhibits both crystalline-amorphous and crystalline-crystalline phase transitions, depending on temperature. The XRD peaks disappear after grinding the Y-form at r.t. (Figure 3), confirming the amorphous nature of the Am-form. By contrast, mechanical grinding at 100 °C causes the appearance of new diffraction peaks and the disappearance of peaks corresponding to the Y-form (Figure 3), suggesting a crystalline-crystalline phase transition, although the weak intensity and broad nature of the peaks reflect a reduction of the degree of order. Thus, this change in molecular assembled structure is the basis for the blue shift of the emission spectrum as shown in Figure 2b and the significant decrease of the emission lifetime (Figure S7, Table S1). Reports of mechanically induced crystalline-crystalline transitions in MRL compounds are quite rare;^{3,28,32,37,40,42} the present findings,

however, suggest that revisiting their MRL response at elevated temperature, where different crystal structures may be accessible, may be worthwhile.

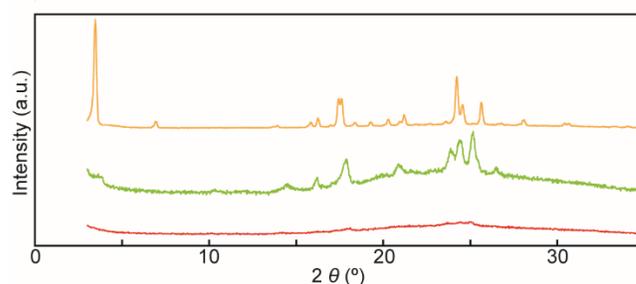


Figure 3. X-ray diffraction patterns of the Y-form (yellow line), the Am-form (red line), and the YG-form (green line) of **1**. All measurements were carried out at room temperature.

Single crystal X-ray structure analysis was conducted for the Y-form, whereas no single crystals suitable for such measurements could be obtained for the YG-form. In the few cases of cyano-OPV derivatives for which structural information from X-ray analysis is available, π -stacked architectures were reported, where the electron-rich central phenyl rings overlap with the electron-deficient cyano-ethylene moieties.^{29,50} This structure has been associated with the formation of excimers and in some cases also ground-state aggregates.^{29,50} Interestingly, the molecular assembly in the Y-form of **1** is completely different. Figure 4a shows that the dye molecules here adopt an absolutely planar conformation. The peripheral phenoxyhexyl chains of **1** do not interdigitate (Figure 4b) and the molecules are laterally and vertically shifted, so that the charge-transfer interactions seen in other cyano-OPVs are suppressed. Thus, the red-shift of the emission spectrum can be mainly ascribed to a more planar conformation, while pronounced electronic interaction between molecules that would affect the photophysical properties are absent. This behavior is completely different from that of the very similar cyano-OPV **2**, in which the peripheral tolyloxyhexyl groups interdigitate so that the tolyl groups “sandwich” the outer ring of the cyano-OPV core and pronounced electronic interactions between the molecules promote orange, excimer-dominated emission.²⁹ The striking difference in molecular packing is also reflected in the large difference of the enthalpy (ΔH) associated with the isotropic melt phase transition behavior of the two compounds (75.5 kJ mol⁻¹ for **1** vs. 172.4 kJ mol⁻¹ for **2**,²⁹ Figure S5).

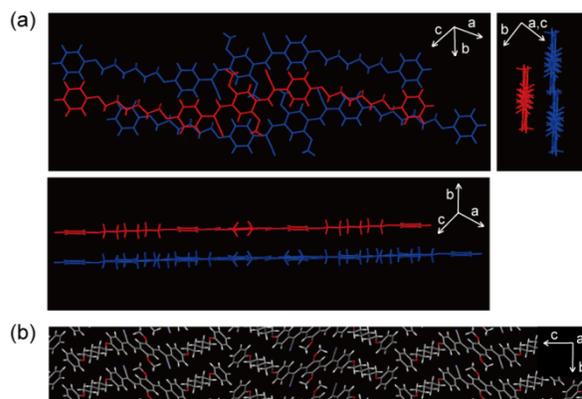


Figure 4. Crystal structure of **1** in the Y-form. (a) Three adjacent molecules. (b) Crystal structure viewed along *a* axis.

X-ray analysis was employed to explore the thermally induced conversion of the Am-form (made by grinding the Y-form at r.t., *vide supra*) to the YG-form. Indeed, several diffraction peaks corresponding to the YG-form can be observed after annealing for 5 min at 100 °C (Figure S8a). Simultaneously, the emission spectrum exhibits a significant blue shift and the spectral shape becomes similar to that of the YG-form (Figure S9). However, no clear peaks corresponding to the phase transition from the Am-form to the YG-form were observed in the differential scanning calorimetry (DSC) curves (Figure S5), which we explain with a very broad crystallization peak.²⁹ Subsequent grinding of the YG-form at r.t. restored the Am-form, as evidenced by the red-shifted emission spectrum (Figure S9).

Further, the Y-form of **1** was grinded at 50 °C to explore if the transition from the Y-form to the YG-form observed upon grinding at 100°C (Figure 2b) could perhaps proceed via the Am-form. As shown in Figure S10, the Y-form was converted to the Am-form when the sample was ground at 50 °C on a glass substrate using a spatula and applying the largest force that was manually possible. While subsequent annealing for several minutes at 50 °C did not cause any pronounced changes of the photoluminescence color, conversion to the YG-form completely occurred after 12 hours at this temperature. It is noteworthy that the Am-form did not convert back into the YG-form when kept at room temperature for 24 h, suggesting that at r.t. the Am-form is a metastable state. When the Y-form was ground on a glass substrate using a spatula and applying only very light strokes an immediate conversion to the YG-form occurred, as indicated by the photoluminescence color (Figure S10) and XRD measurements (Figure S11). These results indicate that the direct transition from the Y-form to the YG-form is possible and that a transient Am-form is not required. Moreover, the data show that at 50 °C both the YG-form and the Am-form can be selectively accessed from the Y-form by changing the mechanical force.

We also investigated the quantum yields of all solid forms of **1** and a chloroform solution of this chromophore (Table S1). In the Y-form the luminophore is fixed in a planar conformation that does not permit significant intermolecular interactions, and radiation-less decay processes are restricted; this leads to a relatively high quantum yield ($\Phi = 0.65$), which exceeds that of a dilute chloroform solution ($\Phi = 0.42$). The quantum yields of the other solid forms (YG-, Am- and RO-forms, $\Phi = 0.38, 0.39$

and 0.25) are slightly lower than that of the Y-form, which is consistent with less planar conformations and the formation of multi-chromophore excited states.

Based on the above results, we revisited the MRL behavior of compound **2**, which was recently reported to display four different interconvertible solid emissive states,²⁹ and discovered that **2** also shows temperature-dependent MRL behavior when mechanically treated at elevated temperature. In the case of **2**, grinding of an orange-emissive form at room temperature results in a red shift of the emission, whereas grinding at 140 °C causes conversion to a green-emissive state (Figure S12), which had previously not been accessed through thermal or mechanical treatment.²⁹ These data suggest that temperature-dependent MRL behavior appears to be a general phenomenon that may be exploitable in many other compounds.

CONCLUSIONS

In summary, we demonstrated that the temperature can have a significant influence on the mechanically induced morphology and fluorescence color changes displayed by MRL compounds. Our findings appear to be very significant, as they suggest that for the plethora of reported MRL compounds, hitherto not accessed luminescent forms could be discovered, if mechanical stimulation is applied at temperatures other than ambient. We also demonstrate the first examples of compounds with temperature-dependent MRL behavior, i.e., a temperature-dependent direction of the mechanically induced shift of the emission spectrum. We speculate that this observation is not merely an academic curiosity, but that the effect can be useful for sophisticated mechanosensing devices, wear monitors, data storage elements, and other applications.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization data of compound **1**, TGA data, additional images, absorption spectrum, emission decay profiles, quantum yields, DSC curves, additional XRD patterns, additional emission spectra, explanation on RO-form, the X-ray crystallographic file (CIF). This material is available free of charge via the internet at <http://pubs.acs.org>.

The X-ray crystallographic file for **1** in the Y-form was deposited in the Cambridge Crystallographic Data Centre (CCDC) (deposition code: CCDC 1476838). The CIF file can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

AUTHOR INFORMATION

Corresponding Author

*sagara@es.hokudai.ac.jp

*christoph.weder@unifr.ch

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