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Organic Mechanochromic Luminescent Materials with Self-Recovering Characters

Shotaro Nakamura,^[a] Koji Hirano,^{*,[a, b]} and Norimitsu Tohnai^{*,[a]}

Recently, applied research on stimuli-responsive materials with luminescence-switching characteristics has been conducted in various fields. A representative phenomenon of stimuli-responsive luminescent materials is mechanochromic luminescence (MCL), which exhibits luminescent color change induced by mechanical stimuli such as grinding. These materials are among the most prominent candidates for security and sensing applications. Interestingly, some mechanochromic luminescent materials have shown self-recovery character, in which their original luminescent color can be recovered by just standing

under ambient conditions after grinding. Although there have been more and more reports of such materials in recent years, the fundamental principles of molecular design still remain elusive. In this concept, we summarize distinctive advances in mechanochromic luminescent materials with self-recovery according to the core structures of luminescent molecules. Controlling amorphous state by introducing substituents such as alkyl or polar groups is effective method to provide self-recovering properties.

1. Introduction

Organic luminescent materials have attracted great attention for their impressive applications such as organic field-effect transistors (OFETs),^[1] organic light emitting diodes (OLEDs)^[2] and security printing.^[3] In the solution state, the luminescence properties mainly reflect the characteristics of single molecule depending on the molecular structure: framework and substituent. On the other hand, in the crystalline state, the characteristics of the aggregate state, such as intermolecular distance and angle, are also reflected in addition to the molecular structure. Therefore, luminescence behaviors that are not observed in the solution state (single molecule) can be observed in the crystalline state (multiple molecules).

One of the notable features of luminescent crystals is stimuli-responsive luminescence, in which the luminescent color changes in response to external stimuli.^[4] A representative example of such external stimuli is shear stress, which very often induces a phase transition of the original crystalline phase to the amorphous phase. Such luminescent materials are known as mechanochromic luminescent materials.^[5]

Self-recovery is a unique phenomenon related to mechanochromic luminescence (MCL).^[6] Typically, after the emission

color of mechanochromic luminescent materials changes upon grinding, external stimuli such as exposure to solvent vapor or heating are required to restore the original color. However, some compounds display self-recovery properties, in which the emission color returns to its initial state by simply leaving the material at room temperature without any external stimuli (Figure 1a).

From the viewpoint of energy, two approaches are considered to achieve self-recovering MCL (Figure 1b). One is the destabilization of the amorphous phase. This approach could increase the energy difference between crystalline and amorphous phases. The other is the reduction of the activation barrier for crystalline-amorphous phase transition. These two approaches enable facile transition from amorphous to crystalline phase. Despite the extensive development of mechano-

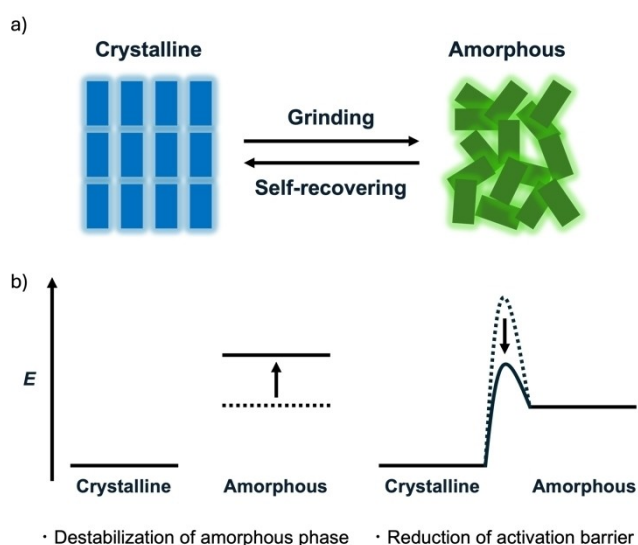


Figure 1. a) Stylized illustration for self-recovering mechanochromic luminescent behavior. b) Approaches for achieving self-recovering MCL.

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chromic luminescent materials, the fundamental principle of designing self-recovering materials is yet to be fully elucidated.^[7] To realize the practical application of self-recovering mechanochromic luminescent materials in various fields, systematic guidelines for their design should be established. In this concept, we present recent advances of self-recovering mechanochromic luminescent organic materials. The reported materials are categorized according to their central core structures, and their features, structure-property relationship, and effects of side chain substituents to control self-recovering characters are discussed.

2. Boron Difluoride

An early example of the self-recovering MCL involving difluoroboron diketonate was reported by Fraser and coworkers in 2010.^[8] The fluorescence-spectroscopic study of solid-state **1** revealed that smearing the material drastically broadened the emission spectrum and red-shifted the emission maximum (Figure 2a). The initial spectrum just after smearing showed only a small shoulder at the original emission wavelength. Over time, the original emission of the smeared film recovered with an increase in the blue shoulder, a blue shift of the main peak, and a narrowing of the spectrum. After about a day, the emission stabilized to its original color. The recovery dynamics were dependent on the film thickness, regardless of the initial state. The detailed effect of alkyl chains on the self-recovery rate of difluoroboron β -diketonates (**2a–2i**) was reported in 2011 (Figure 2b).^[9] Derivatives with relatively short alkyl chains (**2b–2d**) exhibited rapid self-recovery MCL. On the other hand, longer recovery time was required with long alkyl chains (**2e**,

2f), and the spectrum change eventually stopped before full recovery to the original emission. Additionally, **2i** did not exhibit any self-recovering properties after grinding. It is considered that intermolecular interactions affect the self-recovery rates. Other examples of alkyl-chain dependent self-recovery MCL of β -iminoenolate boron complexes (**3a**, **3b**, **4a**, **4b**) were reported in 2015,^[10] where only **3b** exhibited self-recovering MCL (Figure 2c). The as-synthesized crystals of **3b** showed yellow emission and changed to ground powder with orange emission. Moreover, the emitting color recovered to yellow after 5 min. The authors proposed that the long alkyl chain in **3b** would inhibit the π - π interactions to make amorphous state unstable.

The effect of alkoxy chains on self-recovery MCL was reported by Fraser and coworkers in 2016.^[11] Although **5a–5f** all exhibited MCL, **5b** and **5c** showed fast self-recovery, and **5e** and **5f** did not recover fully (Figure 2d). Longer alkoxy chains may create a more elastic environment and promote the formation of a much less rigid ordered emissive state compared to shorter chains. Ramamurty, Reddy, and coworkers reported that the stiffer crystal recovered quickly from the metastable state to the original state.^[12] This could explain the reason why recovery to the ordered emissive states is much slower in dyes with longer chains.

3. Tetraphenylethylene

In 2015, Zhang, Tang, and coworkers reported that tetraphenylethylenes with diethylamino groups exhibited self-recovering MCL.^[13] They prepared three tetraphenylethylene derivatives (**6a–6c**; Figure 3a). As-prepared crystalline powders of **6a** and



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Koji Hirano studied chemistry at Kyoto University where he obtained his B. Eng. (2003), M. Eng. (2005), and Dr. Eng. (2008) degrees under the supervision of Professor Koichiro Oshima. He subsequently worked as a postdoctoral fellow with Professor Tamio Hayashi at Kyoto University from April to September 2008. He then joined the research group of Professor Masahiro Miura at Osaka University as an assistant professor in October 2008, and was promoted to an associate professor in April 2015 and a full professor in May 2022. His current research interests involve organic synthesis, organometallic chemistry, and highly reactive cationic (heteroatom) species.



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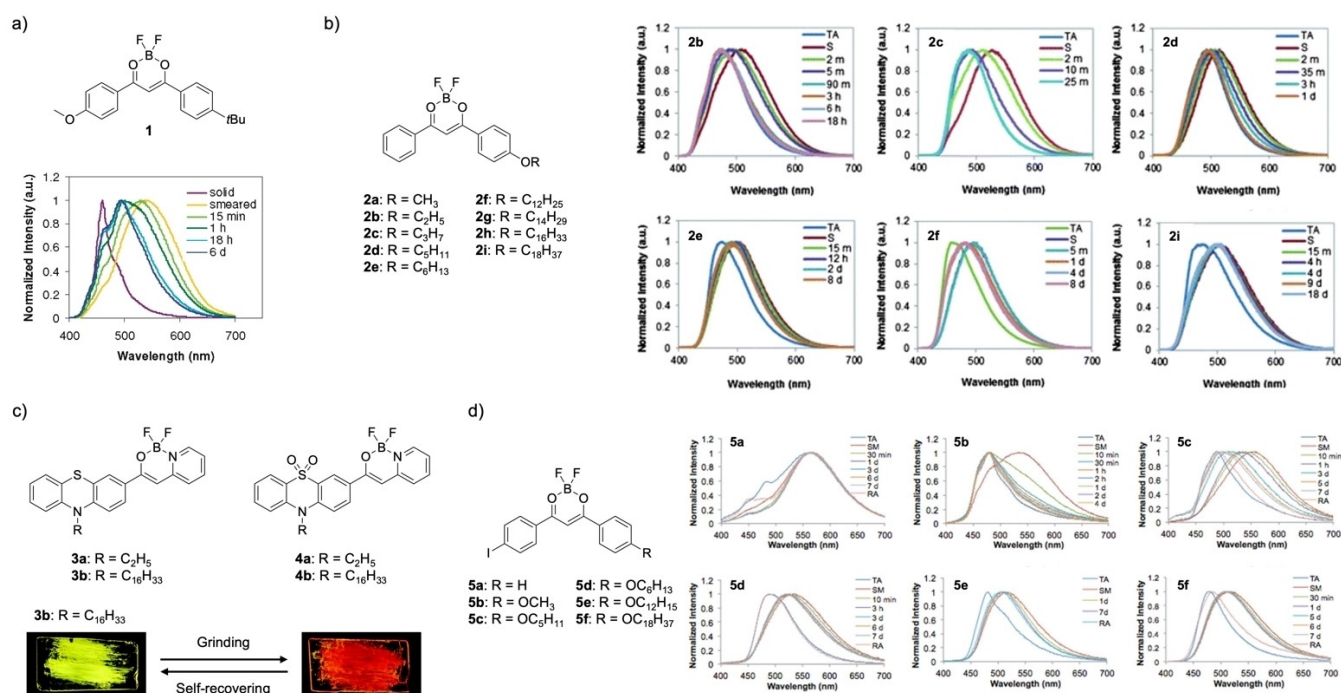


Figure 2. a) Self-recovering MCL of compound **1** (Reproduced from ref. [8]. Copyright 2010 American Chemical Society). b) Emission spectra for **2b**, **2c**, **2d**, **2e**, **2f**, and **2i** after smearing (TA = thermally annealed, S = immediately after grinding) (Reproduced from ref [9]. Copyright 2011 The Royal Society of Chemistry). c) Photographs of self-recovering MCL of **3b** (Reproduced from ref [10]. Copyright 2015 The Royal Society of Chemistry). d) Emission spectra for **5a–5f** (TA = thermally annealed, SM = smeared, RA = reannealed) (Reproduced from ref [11]. Copyright 2016 American Chemical Society).

6b emitted cyan-colored luminescence, but they emitted yellow-colored luminescence after grinding. Moreover, ground **6a** rapidly restored to the original emission within several seconds, while **6b** showed a similar self-recovering property but in a much slower manner: The ground **6b** with yellow light emission mostly returned to the original cyan color in 2–3 min, and fully restored in 5 min. The slower self-recovery rate of **6b** compared to **6a** was attributed to its stronger dipole–dipole interactions at amorphous phase, which slowed down the molecular motions. In contrast, **6c** did not show any self-recovering properties. The authors speculated that introducing strong electron-accepting groups strengthened the intermolecular interactions of amorphous phase, making the transition between the amorphous and crystalline phases unlikely to occur within a short time.

Another approach to control the self-recovering properties of tetraphenylethylene derivatives was reported by Chen, Pu, and coworkers in 2018.^[14] They synthesized three tetraphenylethylene derivatives (**7a–7c**), but only **7a** exhibited self-recovering MCL (Figure 3b). Grinding **7a** altered its emission color from blue to blue-green, and the ground powder could recover to the initial state within 3 h. The self-recovering mechanochromic luminescent process between the blue and blue-green emissions could be repeated numerous times. PXRD measurement suggested that the MCL of luminogen **7a** was attributed to the phase transition between crystalline and amorphous states, and its self-recovering mechanism was based on the spontaneous recrystallization of the amorphous state. Although compound **7b** also showed MCL, it could not robustly

self-recover back to the pale blue emission. MCL property of compound **7c** was similar to that of **7b**. Although the author did not mention the reason for the aforementioned rapid recrystallization unique to **7a**, trifluoromethyl groups could affect the energy level of the amorphous phase, resulting in exhibiting self-recovering properties.

4. Indolylbenzothiadiazole

In 2016, Ito, Asami, and coworkers reported a substitution effect of indolylbenzothiadiazole on MCL.^[15] They synthesized ten *N*-Boc-indolylbenzothiadiazoles (**8a–8j**; Figure 4a). Although derivatives **8a–8f** did not exhibit MCL, **8g–8j** exhibited self-recovering MCL. The solid-state blue emission of **8g** changed to yellow upon grinding, and the emission color immediately reverted to the original blue at room temperature. The authors speculated that the specificity of the MCL properties of **8g** was attributed to its crystal structure. The crystal structure of **8g** was antiparallel stacking of the benzothiadiazole rings, which is similar to that in **8a** with no MCL properties. However, unlike **8a**, the stacked rings in crystal structure of **8g** were slipped, probably due to the steric hindrance arising from the 3-methyl group. This slipped stacking should contribute to the relative instability of the structural integrity in crystals of **8g**, leading to the degradation of the crystal structure in response to mechanical stimulus. Similarly, **8h–8j** exhibited the same slipped antiparallel stacking in the crystalline state. Upon grinding, the emission colors of these samples were red-shifted,

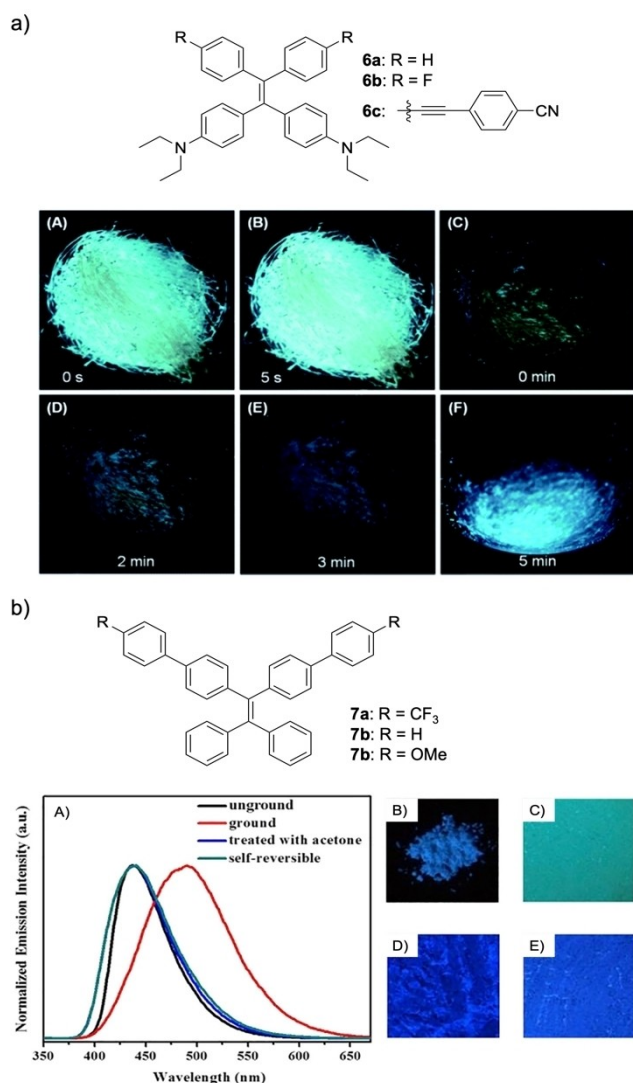


Figure 3. a) Photographs of self-recovering MCL of **6a** (A, B) and **6b** (C–F) (Reproduced from ref [13]. Copyright 2015 The Royal Society of Chemistry). b) Photoluminescence spectra of luminogen **7a** under different conditions, and photographic images of **7a** under UV light irradiation: (B) the unground sample; (C) the ground sample; (D) the sample after treatment with acetone; (E) the self-recovering sample (Reproduced from ref [14]. Copyright 2018 Elsevier).

but longer recovery periods were required in comparison to **8g**. The longer recovery time of **8i** and **8j** was likely due to the stronger intermolecular interactions in the amorphous states caused by the presence of the polar formyl and cyano groups. PXRD measurement indicated that the mechanism of the self-recovering MCL of these samples was probably based on a partial amorphization of the crystals upon exposure to the mechanical stimulus, followed by autonomous recovery through recrystallization.

In 2017, Ito and coworkers also conducted systematic study on self-recovering MCL of eight *N*-substituted-4-(3-alkyl-1H-indol-2-yl)-2,1,3-benzothiadiazole derivatives (**9a–9h**; Figure 4b).^[16] Although all derivatives exhibited self-recovering MCL, the self-recovering rates differed. Among *N*-Boc substituted derivatives, **9a** showed the fastest recovery rate (20 s),

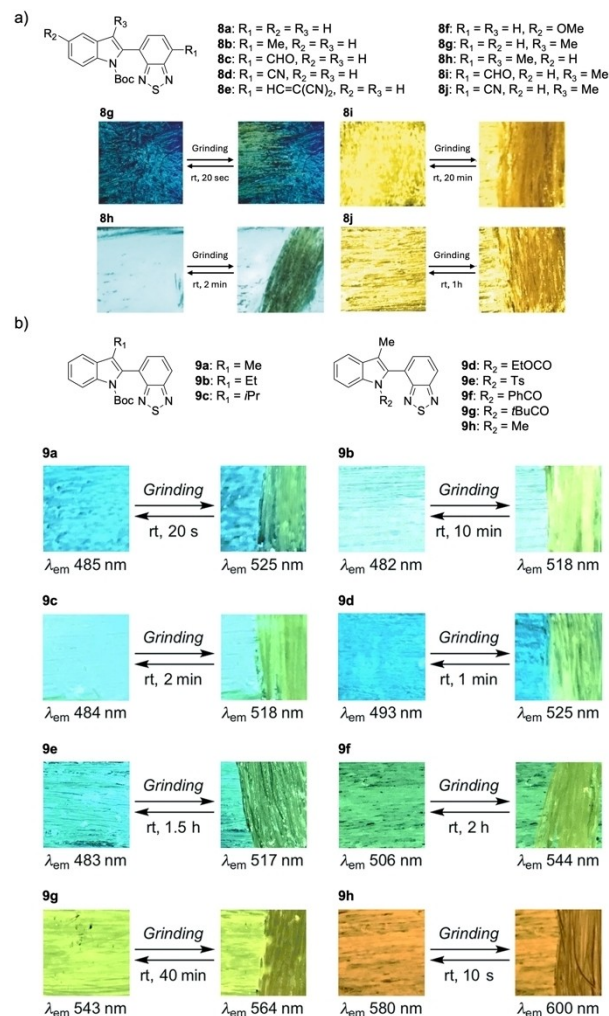


Figure 4. a) Photographs of the self-recovering MCL of compounds **8g–8j** (Reproduced from ref [15]. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). b) Photographs of the self-recovering MCL of compounds **9a–9h** (Reproduced from ref [16]. Copyright 2017 The Royal Society of Chemistry).

while **9b** had the slowest rate of 10 min. Among 3-methylated derivatives, **9h** had the fastest rate of 10 s, and **9f** had the slowest rate of 2 h. While the details were not discussed, the authors suggested that the difference in recovery time was associated with the degree of crystallinity of the crystal structure or the stabilization of the amorphous phase by polarized substituents.

5. Vinyl Aromatic Compounds

In 2013, Yang and coworkers reported self-recovering MCL of 9,10-bis[(9,9-dialkylfluorene-2-yl)vinyl]anthracenes.^[17] They prepared three derivatives **10a–10c** (Figure 5a). When the pristine sample of **10c** was ground, the emission color changed from green to yellow. When left standing at room temperature, the fluorescence color changed with increasing standing time and gradually recovered to the original green emission. Eventually,

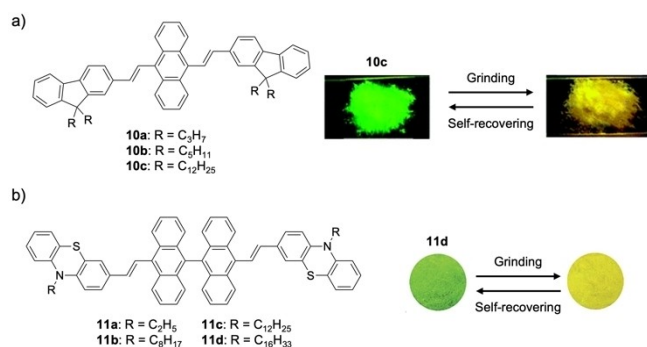


Figure 5. a) Photographs of the self-recovering MCL of compounds **10c** (Reproduced from ref [17]. Copyright 2013 The Royal Society of Chemistry) b) Photographs of the self-recovering MCL of compounds **11d** (Reproduced from ref [18]. Copyright 2015 The Royal Society of Chemistry).

both the fluorescence color and emission were almost identical to those of the pristine solid. In contrast, the fluorescence colors of ground **10a** and **10b** kept orange and yellow colors, respectively, over 24 h at room temperature. DSC measurements of these compounds revealed that amorphous phase of **10a** and **10b** had high exothermic peak values ($> 170^{\circ}\text{C}$), and isotropic melting point of ground **10c** was only about 65°C . The authors stated that grinding induced a thermodynamically and dynamically unstable morphology in the amorphized **10c** solid, thus leading to its spontaneous fluorescence recovery even at room temperature. They also suggested that amorphized **10a** and **10b** had the high value of cold-crystallization temperature, resulting in their stable amorphous states at room temperature.

Another example of alkyl-chain-length dependent MCL was reported by Xue, Lu, and coworkers in 2015.^[18] They synthesized four phenothiazine-based 10,10'-bianthracene derivatives (**11a**–**11d**; Figure 5b). Upon grinding, the emission color of **11a**

changed from yellow to orange, while the emission color of **11b**, **11c**, and **11d** changed from green to yellow. After standing at room temperature for five days, only the fluorescence color of **11d** gradually changed back to the original green emission. The ground **11a**, **11b** and **11c** did not have self-recovering properties for over two weeks at the same temperature. DSC measurements revealed that the exothermic peak of the amorphized **11a**, **11b** and **11c** solids located at a higher temperature, resulting in their stable amorphous phase at room temperature. The ground **11d** solid could cold-crystallize at room temperature because its exothermic peak was located at lower temperature. This is attributed to the longer alkyl chains providing higher molecular mobility, as the packing between alkyl chains becomes disordered more easily.

6. Polycyclic Aromatic Compounds

Self-recovering MCL of pyrene-based derivatives was reported by Bai, Bai, and coworkers in 2016.^[19] They prepared two derivatives (**12a** and **12b**) and revealed that only **12a** exhibited self-recovering MCL (Figure 6a). Upon grinding, the emission color of **12a** changed from blue to green, and the fluorescence of the ground samples returned to blue at room temperature within 5 min. In contrast, **12b** had no such properties. The authors suggested that the difference in the overlapping manner of the pyrene moieties and the rigidity of the crystals were related to the difference in the MCL properties of **12a** and **12b**. The fast self-recovery of **12a** occurred due to the ease of molecular rearrangement in the soft crystal, whereas **12b** exhibited minimal change in emission color due to its rigid crystal structure.

In 2019, Tohnai, Miura, and coworkers reported self-recovered mechanochromic luminescent properties of bisbenzofuro[2,3-*b*:2',3'-*e*]pyrazine (BBFPz: **13c**) derivatives (Fig-

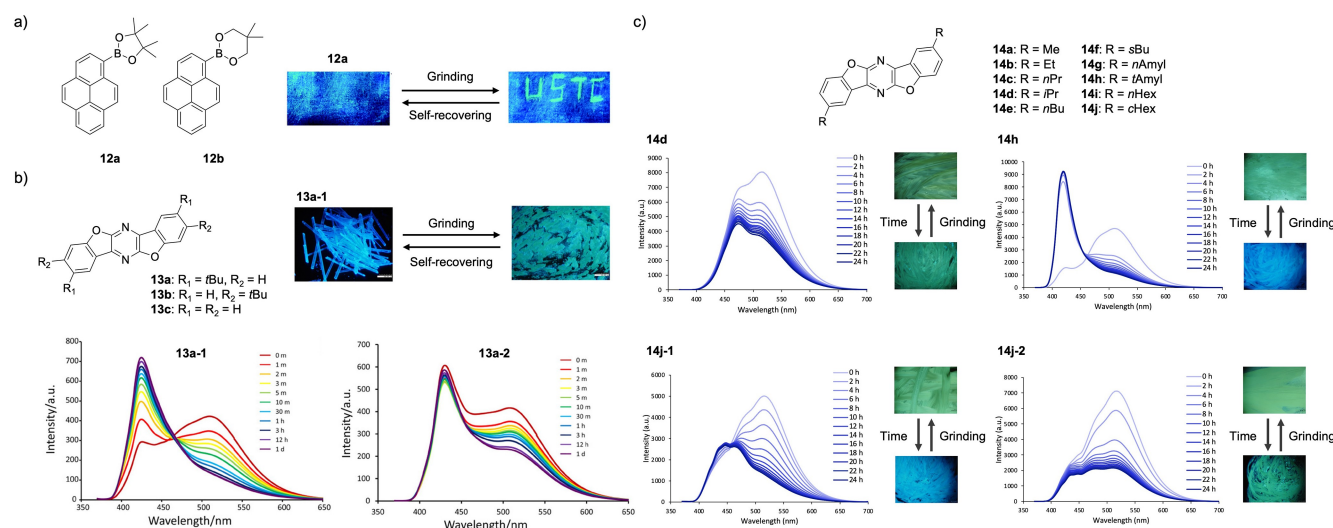


Figure 6. a) Photographs of the self-recovering MCL of compounds **12a** (Reproduced from ref [19]. Copyright 2016 The Royal Society of Chemistry). b) Photographs of the self-recovering MCL of compounds **13a-1** and change over time of luminescence after mechanical stimuli of **13a-1** and **13a-2** (Reproduced from ref [20]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). c) Photographs and emission spectra of the self-recovering MCL of compounds **14d**, **14h**, **14j-1**, and **14j-2** (Reproduced from ref [21]. Copyright 2024 The Royal Society of Chemistry).

ure 6b).^[20] Related compounds bearing *t*Bu groups at different positions on the core skeleton were also synthesized (**13a** and **13b**). Under various recrystallization conditions, **13b** and **13c** gave a single polymorph, while **13a** gave two polymorphs. These crystals provided different MCL depending on the substitution position of the alkyl groups. The crystal of **13c** did not show luminescence change when ground, and **13b** exhibited a slight blue shift after grinding. In contrast, the two polymorph crystals of **13a-1** and **13a-2** yielded significant MCL. Additionally, luminescence of these ground powders changed when left at room temperature, and their recovery rates differed. This difference in recovery rates was attributed to the size of the free volume around the skeleton. Indeed, the ground powder of the **13a-2** crystal with a smaller free volume required more time to recover.

Recently, Hirano, Tohnai, and coworkers reported tunable self-recovering behavior of bisbenzofuro[2,3-*b*:2',3'-*e*]pyrazine derivatives with various alkyl chains (**14a–14j**; Figure 6c).^[21] **14b** and **14j** crystallized as two polymorphs (**14b-1**, **14b-2**, **14j-1**, and **14j-2**) depending on the recrystallization conditions, while the eight other compounds did not give polymorphs. Crystals of BBFPz with relatively long and linear alkyl chains (**14b-2**, **14c**, **14e**, **14g**, and **14i**) did not show MCL. On the other hand, crystals of BBFPz with short or branched alkyl chains exhibited luminescent color change when they were ground. Moreover, some derivatives had self-recovering properties. The mechanically changed emission spectra of **14b-1** and **14f** recovered to the original state immediately. Upon grinding **14h**, the emission color changed from blue to green and returned to the original color after 24 h. Additionally, **14d**, **14j-1**, and **14j-2** also exhibited self-recovery character at room temperature but much slower than **14h**. This is probably due to the smaller size of free volume around the aromatic scaffold within their packing structures, requiring prolonged periods for the completion of recovery. These results suggest that the presence of relatively bulky and branched alkyl chains plays a crucial role in exhibiting self-recovering characters.

7. Other Miscellaneous Compounds

Self-recovering MCL of triphenylamine derivative was reported in 2011 by Nakano and coworkers (Figure 7a).^[22] They prepared **15** and found its mechanochromic luminescent behavior. The crystalline **15** emitted in light blue color, and the emission color was changed to greenish yellow upon grinding. Furthermore, the color was found to gradually recover to the original light blue. The authors suggested that changes in dipole–dipole and π – π intermolecular interactions played an important role for mechanochromic luminescence. Similar phenomena were observed in the related triphenylamine derivatives.^[23]

In 2016, Zhao and coworkers reported self-recovering MCL of carborane-based materials (Figure 7b).^[24] They synthesized seven derivatives (**16a–16h**) and found that only **16e** exhibited self-recovering MCL. Upon grinding, emission color of **16e** changed from blue to red. After standing at room temperature, the fluorescence color of **16e** went back to the original blue

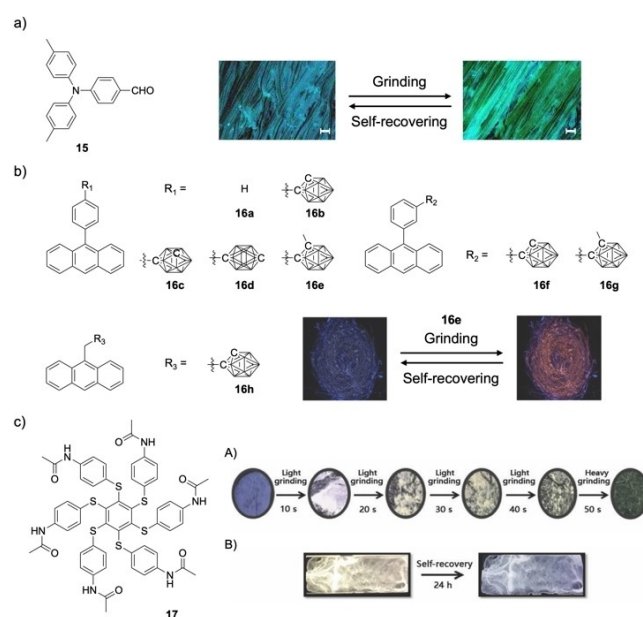


Figure 7. a) Photographs of the self-recovering MCL of compounds **15** (Reproduced from ref [22]. Copyright 2011 Elsevier B.V.) b) Mechanochromic photographs of **16e** (Reproduced from ref [24]. Copyright 2016 The Royal Society of Chemistry). c) Photographs of **17** with blue luminescence during the grinding process under UV light (A), and showing a self-recovery effect of the luminescence color from **17** (B) (Reproduced from ref [26]. Copyright 2016 The Royal Society of Chemistry).

emission. The authors suggested that the lack of intermolecular interaction facilitated conformational changes due to mechanical stimuli, resulting in mechanochromic luminescence. There is also a report of similar carborane derivatives showing not only red-shift but also blue-shift upon grinding.^[25]

In 2017, Zhang, Zhu, and coworkers reported multicolor MCL with self-recovering property on hexathiobenzene-based derivative **17** (Figure 7c).^[26] A wide-range luminescence color changes of **17** occurred from blue to white, yellow and green during UV irradiation or heavy grinding for different times. Additionally, a yellow-to-blue luminescence color change can be observed after one day in ambient atmosphere. The authors speculated that such MCL originated from the different molecular stackings upon grinding.

8. Summary and Outlook

In this concept, we focus on self-recovering mechanochromic luminescent materials, which have witnessed certain progress over the past decade. To enhance and control these properties, various strategies have been explored. One promising approach for the rational design of self-recovering mechanochromic luminescent materials is the introduction of substituents. Substituents can influence the self-recovering properties by altering the molecular packing modes and imparting flexibility to the crystal structure, thereby enhancing molecular mobility. For instance, the introduction of polar groups can modulate the interactions in both crystalline and amorphous states and lead to changes in the stability of the aggregated state, which can

either suppress or promote the recovery process. Furthermore, the incorporation of alkyl groups with varying lengths and branching can enable the fine-tuning of the aggregated state stability and crystal structure, allowing for the adjustment of recovery characteristics. These methods can destabilize the amorphous phase or decrease the barrier for phase transition between crystalline and amorphous phases (Figure 1), thereby imparting self-recovering properties. We believe that this concept article will provide material scientists with valuable insight for design and synthesis of organic materials with related self-recovery character.

However, it is important to note that the influence of substituents on self-recovery is not universal and still highly dependent on the molecular skeletons. For the certain design and prediction, advanced analytical techniques are needed. Specifically, the development of methodologies capable of measuring the structure in the amorphous state would complement common X-ray structural analyses of the crystalline state. The elucidation of the structure-property relationships governing the self-recovery phenomenon, particularly in the amorphous state, will provide more valuable insight for the rational design of advanced MCL materials with tailored recovery behavior. Additionally, computational methods for predicting MCL molecular properties and their self-recovering characteristics remain underexplored. Theoretical calculations of mechanochromic luminescent molecules in their crystalline, amorphous, and transitional states could offer valuable insights into the recovery behavior. These advancements will contribute to more comprehensive understanding of the self-recovering mechanisms for discovery of new functional organic luminescent materials.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Stimuli-responsive material • Mechanochromic luminescence • Self-recovery

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