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Tunable mechanochromic luminescence of 2-alkyl-4-(pyren-1-yl)thiophenes: Controlling the self-recovering properties and the range of chromism

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Controlling the behavior of mechanochromic luminescence (MCL) based on rational design principles is an outstanding challenge. Herein, an unprecedented self-recovering MCL that manifests in a large shift of the emission maximum (~200 nm) has been achieved for 2-alkyl-4-(pyren-1-yl)thiophenes upon introducing long alkyl chains and mixing with *N*,*N*′-dimethylquinacridone.

Mechanochromic luminescence (MCL) describes the reversible color change of solid-state emission upon exposure to mechanical stimuli, and MCL materials have recently attracted considerable interest owing to their promising potential as next-generation smart materials such as mechanosensors, wearable devices, and anti-counterfeiting paintings.[1] This interest is reflected in the publication of more than 500 articles on MCL systems in the past decade. Nevertheless, the rational design guidelines for MCL dyes with specific characteristics remain scarce.

Control over the recovery process of MCL is one great challenge in order to advance the development of MCL dyes. Usually, the mechanically switched emission color of MCL dyes reverts to the original color upon applying a second external stimulus such as heating or exposure to solvents. For several luminophores, the rare occurrence of self-recovering MCL has been reported, i.e., the mechanically changed state autonomously reverts to the original state at room temperature in the absence of a second external stimulus.[2] Such self-recovering MCL is typically attributed to the mechanical-stimuli-induced amorphization of crystalline luminophores followed by spontaneous recrystallization. Although it has been suggested in some reports that the self-recovering property is due to an increased molecular mobility after introducing suitable substituents into the luminophores,[2g,i,j,r,s,t,u] further systematic studies are still required in order to develop a comprehensive understanding and rational design guidelines for self-recovering MCL dyes.

Another critical challenge is the ability to tune the range of the mechanical-stimuli-induced shift of the maximum emission wavelength ($\Delta\lambda_{em}$). The $\Delta\lambda_{em}$ values of almost all hitherto reported MCL dyes are < 150 nm.[1] Only very few luminophores exhibit a shift of the maximum emission wavelength of more than 150 nm upon manual grinding.[3] For organic luminophores, Enomoto *et al*. reported an exceptionally large $\Delta\lambda_{em}$ (~300 nm) value of aminobenzopyrenoxanthene.[3d] A large $\Delta\lambda_{em}$ (197 nm) of a Bodipy derivative was reported by Ajayaghosh *et al*.[3c] However, reasonable predictions of as well as control over $\Delta\lambda_{em}$ of an MCL dye remain so far impossible. Considering the practical applications of MCL dyes, the development of a general method to achieve large $\Delta\lambda_{em}$ values is particularly desirable, especially because such MCL materials facilitate the detection of mechanical stimuli by distinct spectral changes. We have recently demonstrated a significant improvement of poor MCL properties of an organic dye simply by mixing with another dye that does not exhibit MCL properties.[4] In the

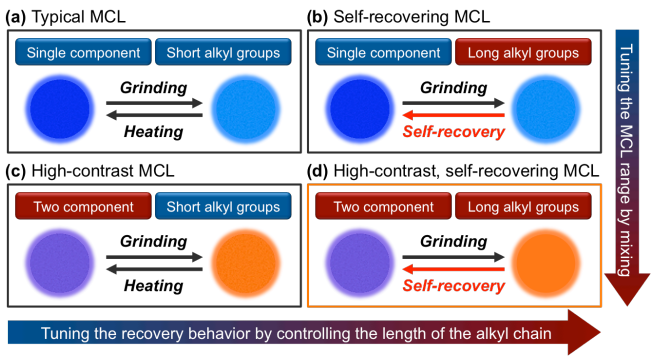

Fig. 1 Schematic illustration of the tuning of the MCL behavior. (a) Typical MCL of a single-component dye with short alkyl groups; (b) self-recovering MCL of a single-component dye with long alkyl groups (partial self-recovery was observed in this study); (c) high-contrast MCL of a two-component dye with short alkyl groups; (d) high-contrast self-recovering MCL of a two-component dye with long alkyl groups.

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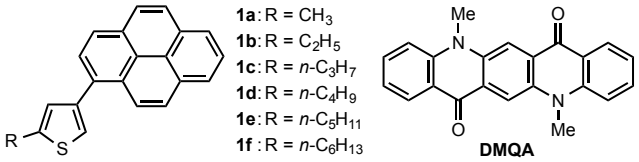

Fig. 2 Chemical structure of 2-alkyl-4-(pyren-1-yl)thiophenes **1a–f** and *N*,*N*′-dimethylquinacridone (**DMQA**).

previous study, the $\Delta\lambda_{em}$ value (13 nm) of a 3,3′-dipyrenyl-2,2′-bithiophene derivative increased to 135 nm for a two-component mixed dye that also contained *N*,*N*′-dimethylquinacridone (**DMQA**). The extension of the MCL range is due to the OFF/ON switching of the energy transfer from dipyrenylbithiophene to **DMQA**, which is triggered by the mechano-induced amorphization of the crystalline mixture.

Herein, we report the rational tuning of the MCL properties of 2-alkyl-4-(pyren-1-yl)thiophenes **1** (Fig. 1 and 2). The recovery behavior of these dyes can be controlled by the length of alkyl group (Fig. 1a and 1b), whereas the MCL range can be expanded by mixing with **DMQA** (Fig. 1a and 1c). By combining these two concepts, we accomplished an unprecedented self-recovering MCL that exhibits a high-contrast emission color change between violet and orange ($\Delta\lambda_{em} \approx 200$ nm) for two-component dyes that consist of **1** with long alkyl chains and **DMQA** (Fig. 1d).

2-Alkyl-4-(pyren-1-yl)thiophenes **1a–f**, which contain a linear alkyl substituent that varies in length from methyl (**1a**: R = CH_3) to hexyl (**1f**: R = n-C_6H_{13}), were synthesized via the Suzuki-Miyaura coupling of pyrene-1-boronic acid and the corresponding 2-alkyl-4-bromothiophenes (Scheme S1). The MCL properties and melting points of crystalline samples of **1a–f** are summarized in Table 1. Crystalline samples of **1a** (R = CH_3) exhibit blue emission (λ_{em} = 418 nm) under UV light (λ_{ex} = 365 nm). Density functional theory (DFT) calculations on **1a** at the B3LYP/6-31G(d) level of theory showed that the HOMO and LUMO of **1a** are located mainly on the pyrene ring (Fig. S6 and Table S1). In addition, a single-crystal X-ray diffraction analysis of **1a** revealed the absence of intermolecularly stacked pyrene rings (Fig. S1). The blue emission of the crystalline samples should accordingly be attributed to the monomer emission of the pyrenyl group.

Upon grinding crystalline **1a** with a spatula, the emission color changed to light blue (λ_{em} = 480 nm; $\Delta\lambda_{em}$ = +62 nm; Fig. 3a and 3c). Since the maximum excitation wavelength of ground **1a** shifted bathochromically compared to that of crystalline **1a** (Fig. S7a), the light blue emission can be reasonably assigned to the emission from a static excimer of intermolecularly stacked pyrenyl groups.[5] The mechanically changed state is stable at room temperature, and the original blue emission can be recovered by heating to 80 °C or by treatment with organic solvents (e.g., hexane or CH_3CN) followed by natural evaporation. Powder X-ray diffraction (PXRD) analyses showed that the diffraction peaks of a crystalline powder of **1a** decreased after grinding and increased after heating (Fig. 3e). Moreover, the emission band of molten amorphous **1a** (λ_{em} = 480 nm; Fig. S9a), prepared by heating **1a** above its melting point followed by cooling to room

Table 1 Maximum emission wavelengths and melting point of 2-alkyl-4-(pyren-1-yl)thiophenes **1a–f**.

Compd.	1a	1b	1c	1d	1e	1f
Crystalline powder λ_{em} (nm)[a]	418	414	413	417	416	414
Just after grinding λ_{em} (nm)[b]	480	482	478	486	481	485
5 s after grinding λ_{em} (nm)[c]	480	482	410, 475	422, 477	422, 473	410, 473
Melting point (°C)[d]	92	92	73	33	59	59

[a] Maximum emission band of crystalline powdered sample. [b] Maximum emission band of ground sample measured immediately after grinding. [c] Maximum emission band and of ground sample measured 5 s after grinding. Shoulder emission band (shorter wavelength) is also shown for **1c–f**. [d] Melting point of crystalline powdered sample.

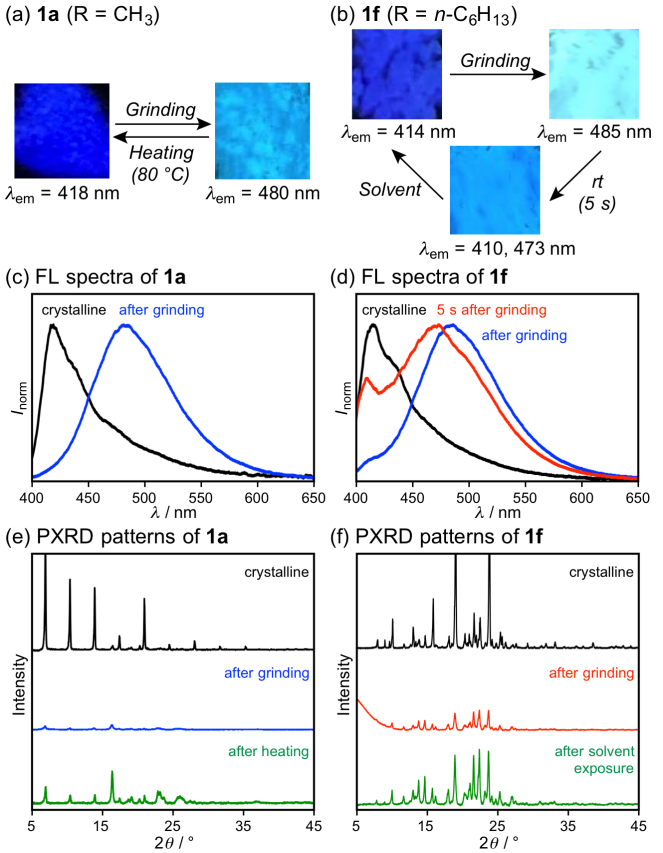

Fig. 3 Photographs (a and b), fluorescence spectra (c and d), and PXRD patterns (e and f) for the MCL of **1a** and **1f**. Excitation wavelength is 365 nm.

temperature, was observed in the same region as that of ground **1a**. Accordingly, the MCL of **1a** should proceed via a typical crystalline-to-amorphous phase-transition mechanism.[1]

Although crystalline samples of the derivatives **1b–f** also exhibit blue emission (λ_{em} = 413–417 nm), their MCL properties strongly depend on the length of the alkyl substituent (Table 1, Fig. S8). The MCL behavior of **1b** (R = C_2H_5) was almost identical to that of **1a**. The emission color of crystalline **1b** (λ_{em} = 414 nm) shifted bathochromically to light blue (λ_{em} = 482 nm, $\Delta\lambda_{em}$ = +68 nm) upon grinding, and

reversed to the original blue after heating or exposure to solvents. On the other hand, **1c–f**, which contain longer alkyl groups, exhibited partial self-recovery of the emission bands after grinding. Photographs, fluorescence spectra, and PXRD patterns for the MCL of **1f** (R = n-C_6H_{13}) as a representative example are shown in Fig. 3. Upon grinding crystalline **1f**, the emission color changed to light blue (λ_{em} = 485 nm; $\Delta\lambda_{em}$ = +71 nm; Fig. 3b and 3d), which is almost identical to that of molten amorphous **1f** (Fig. S9f). Interestingly, a slight hypsochromic shift ($\Delta\lambda_{em}$ = –12 nm) and an increase of a shoulder peak (λ_{em} = 410 nm), which is in the same region as the emission of crystalline **1f**, were observed in the fluorescence spectrum measured after keeping the ground sample at room temperature (~ 25 °C) for 5 s (Fig. 3d). A PXRD analysis indicated that this state contains portions of crystalline **1f**, indicating a partial recovery of the initial crystalline state from the ground amorphous state (Fig. 3f). In contrast to the ground state of **1a** and **1b**, the partially recovered state of **1f** was stable even when heated below the melting point of **1f**, and treatment with organic solvents (e.g., hexane or CH_3CN) was required to recover the original blue-emissive state (Fig. 3b and 3f). Similarly, **1c** (R = n-C_3H_7), **1d** (R = n-C_4H_9), and **1e** (R = n-C_5H_{11}) exhibited partially self-recovering MCL (Fig. S8b–d), i.e., the introduction of propyl or longer alkyl groups is effective to induce self-recovering properties.

Differential scanning calorimetry (DSC) measurements of molten **1a** and **1b** showed their cold-crystallization transition temperatures (T_c) at 59 °C and 48 °C, respectively (Fig. S11). In contrast, a T_c was not observed in the DSC measurements of molten **1c–f**, and their glass-transition temperatures (T_g) were observed below room temperature (**1c**: –19 °C; **1d**: –23 °C; **1e**: –26 °C; **1f**: –28 °C; Fig. S12). These results suggest high molecular mobility of ground amorphous **1c–f** at room temperature, which would at least in part explain the self-recovering properties of **1c–f**. Although the partially recovered states of **1c**, **1e**, and **1f** reverse to the initial crystalline states upon exposure to solvents (Fig. S10), **1d** required recrystallization from methanol to recover the original crystalline state, which is probably due to the low crystallinity of **1d** as evident from its low melting point (33°C).

We then attempted to expand the MCL range of **1a–f** by mixing with **DMQA**. We used slight modifications for a previously reported procedure,[4] and prepared two-component mixtures of **1a–f/DMQA** by evaporating a CH_2Cl_2 suspension of 1:1 molar mixtures of **1a–f** and **DMQA** followed by melting on a glass plate at 120 °C and cooling to room temperature. The as-prepared mixtures exhibited green emission (λ_{em} ≈ 540 nm) in all cases, and the emission color changed to orange (λ_{em} ≈ 610 nm) upon grinding (Fig. S13). Remarkably, the behavior of the orange-emissive states of **1a–f/DMQA** depends on the length of the alkyl chain in **1a–f**.

The orange-emissive states of **1a/DMQA** (λ_{em} = 616 nm) and **1b/DMQA** (λ_{em} = 604 nm) changed to violet-emissive states (**1a**: 413 nm; **1b**: 408 nm) upon heating to 80 °C. These violet-emissive states respond to mechanical stimuli and afford orange-emissive states, and therefore **1a/DMQA** and **1b/DMQA** exhibit MCL between violet and orange (Fig. 4a, S14, and S15). PXRD patterns of as-prepared **1a/DMQA** were almost identical to those of crystalline **DMQA**, indicating that the as-prepared state contains amorphous **1a** and crystalline **DMQA** (Fig. S20a). Weak PXRD peaks other than those of **DMQA** were observed for **1a/DMQA** after grinding, and their intensities increased after heating. These peaks are in good agreement with those of crystalline **1a** obtained by heating a ground sample after melting.[6] Since **1a** and **DMQA** should exist as independent crystals in the violet-emissive state, the violet emission of **1a/DMQA** should most likely be attributed to the blue emission of crystalline **1a** and a weak red emission of crystalline **DMQA**. Moreover, the as-prepared and ground states of **1a/DMQA** should contain perfectly amorphous and partially crystalline **1a**, respectively. Therefore, the green and orange emission of **1a/DMQA** should be assigned to the emission of monomeric **DMQA** and intermolecularly interacting **DMQA**, respectively, similar to the previously reported two-component system.[4]

In the case of **1c/DMQA**, the orange-emissive state (λ_{em} = 608 nm) spontaneously changed to another state at room temperature within 30 s (Fig. S16). This state showed two emission maxima at 407 and 608 nm, and further changed to a violet-emissive state (λ_{em} = 407 nm) upon heating to 60 °C. PXRD analyses revealed that the intermediate state with two emission maxima contains partially recrystallized **1c** (Fig. S20c). This behavior is similar to the partial self-recovery of single-component **1c**. Although the exposure to organic solvent is

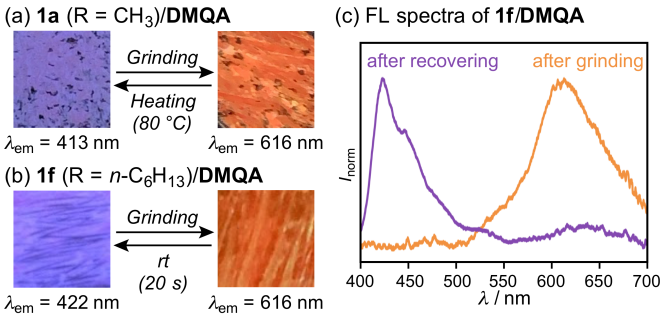

Fig. 4 (a) Photographs for the MCL of **1a/DMQA**. Photographs (b) and fluorescence spectra (c) for the MCL of **1f/DMQA**. Excitation wavelength is 365 nm.

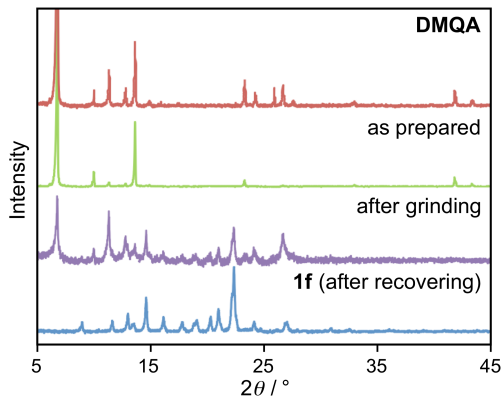

Fig. 5 PXRD patterns for **DMQA** (red), as-prepared **1f/DMQA** (green), **1f/DMQA** after grinding (violet), and **1f** after recovering (blue).

required for the single-component system, **1c** in **1c**/**DMQA** recrystallized only by heating, probably because the presence of crystalline **DMQA** facilitates the recrystallization of **1c**. On the other hand, the orange-emissive state of **1d**/**DMQA** could not be changed to the violet-emissive state by heating or exposure to organic solvents, which is probably due to the low crystallinity of **1d** (Fig. S17 and S20d).

Most notably, the self-recovering MCL between violet and orange was achieved for **1e**/**DMQA** and **1f**/**DMQA** with longer alkyl groups (Fig. 4b, 4c, and S18). The orange-emissive states of these two-component dyes (**1e**: 611 nm; **1f**: 616 nm) spontaneously changed to violet-emissive states at room temperature (**1e**: 412 nm; **1f**: 422 nm). Upon grinding these violet-emissive states, the emission maxima were shifted by ~200 nm to orange and self-recovered to violet within 30 min (**1e**/**DMQA**; Fig. S18 and S20e) or 20 s (**1f**/**DMQA**; Fig. 4b, 4c and Movie S1). Subsequently, we examined the reproducibility of this self-recovering MCL for **1f**/**DMQA**, which turned out to be fully reversible and repeatable (Fig. S19). Interestingly, the recovery time can be controlled by the temperature. When a glass plate with **1f**/**DMQA** was placed on an ice plate (0 °C), the ground orange-emissive sample required 1.5 h to recover the original violet emission. This temperature dependence suggests that the fast self-recovering behavior of **1f**/**DMQA** under room temperature should be attributed to the relatively low activation energy of crystallization compared to other derivatives. As shown in the PXRD patterns of **1f**/**DMQA** (Fig. 5), **1f** in the two-component dye recrystallized immediately after grinding the as-prepared sample. It should also be noted here that the recrystallization of **1e** and **1f** is probably facilitated significantly by the presence of crystalline **DMQA** compared to the single-component systems, where only partial self-recovery was observed.

In summary, we have systematically established control over the MCL properties of 2-alkyl-4-(pyren-1-yl)thiophenes **1**. The introduction of longer alkyl groups imparts self-recovering properties, while the MCL range and the ease of the self-recovery can be improved by mixing with **DMQA**. Consequently, fast self-recovering MCL with a high-contrast emission color change has been accomplished for **1f**/**DMQA** ($\Delta\lambda_{em}$ = 194 nm), which is, to the best of our knowledge, the first example of a self-recovering MCL that can switch its maximum emission wavelength by more than 150 nm.[2,3] The present design principles can be expected to be applicable to other luminophores, which should accelerate the development of self-recovering MCL dyes and their practical applications in e.g. rewritable papers and temporal pressure sensors.

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Conflicts of interest

There are no conflicts to declare.

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