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Mechanochromic Luminescence

A Dipeptide-Based Multicolored-Switching Luminescent Solid Material: When Molecular Assemblies Meet Mechanochemical Reaction**

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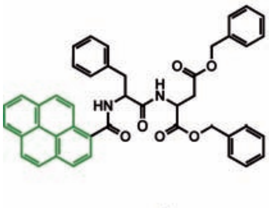
Tuning the fluorescence properties of solid-state materials reversibly and dynamically has attracted much attention for their potential applications in displays, sensors, fluorescent probes, and photoelectronic devices.[1] The newly emerged mechanochromic luminescent (ML) materials showing reversible luminescent color switching upon mechanical stimulus, termed piezochromism, are particularly suited to this purpose. As has been reported, one promising approach to afford the materials with reversible luminescent color transition in situ is to control the microstructures of the molecular assemblies by force.[2] Another is changing the chemical structures by mechanical stimuli, which has the advantages of good color stability and significant color transformation.[3] Up to now, ML materials displaying two-colored switching have been achieved due to their specific mechanistic models, but very few examples show mechanically induced multicolored transition. Recently, an excellent example of a tricolored mechanochromic liquid crystal was reported by Kato et al., in which reversible color switching was accompanied by different molecular packing architectures.[4] However, the development of a simple and effective strategy to prepare multicolored-emission ML materials, especially in the solid state, remains a huge challenge but facilitates advances because it not only possesses significance in fundamental research but also can create new applications of luminescent materials.

We initiated research to address the versatile stimuli-responsive properties of polypeptide molecules and discovered their polymorphic self-assembly properties.[5] Motivated by our previous findings that polychromic emission colors could be achieved by introducing functional moieties to polypeptide, we further co-assembled dipeptide **1** with a pyrene group and **2** with lactam rhodamine B (Rh-B) moieties to obtain their co-assemblies (hereinafter referred to as **MC-1/2**). We expected that **MC-1/2** would be endowed with the characteristics of the moieties and would show multi-luminescent colors switching from blue to green and a reddish color by applying a mechanical stimulus. Compared to one-component materials with only two-color transitions,[5b] the co-assemblies displayed unique multicolored switching from blue to green and reddish.



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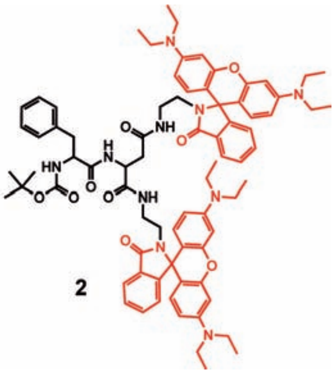

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Dipeptide **1**, bearing a pyrene moiety, displayed reversible mechanochromic behavior between blue ($\lambda_{em} = 410$ nm) and green ($\lambda_{em} = 480$ nm) due to the formation of different pyrene excimers in the crystalline and amorphous states.[5b] Surprisingly, we unexpectedly discovered that the dipeptide **2** can act as a mechanical light switch in the solid state. The as-prepared powder **2** showed low emission intensity. After shearing heavily with a spatula, a bright red luminescence at around 580 nm developed (Figure S1a in the Supporting Information), which was assigned to the emission of Rh-B opening isomer with a more conjugated structure.[6] The fluorescence intensity contrast between sheared and as-prepared samples was larger than 10. A combination of optical measurements was conducted to confirm that the generation of reddish luminescence originated from the ring-opening reaction rather than the change of Rh-B stacking. Firstly, comparison between the ground samples in diluted solution and in the solid state reveals a similar red luminescence (Figure S2a in the Supporting Information). Secondly, the UV/Vis spectrum exhibits the characteristic absorption peak of Rh-B ring-opening isomer at around 550 nm (Figure S2b in the Supporting Information). It is worth mentioning that the sample can

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recover to the original state by heating. The ring opening–closing transition upon grinding and heating could be repeated for multiple cycles (Figure S1b in the Supporting Information). Although the Rh-B moiety is well known for its sensitivity to pH and cations,[6,7] it is rarely reported to be mechanoresponsive.

Taking advantage of the complementary optical properties and different mechanochromic behaviors of **1** and **2**, we developed a new ML material by incorporating dipeptide **2** into the microstructure of **1** through a self-assembly process. In a representative procedure, **1** was dissolved in chloroform followed by addition of **2** powder. The **MC-1/2** co-assemblies, which displayed multicolored ML properties, were obtained by dilution of the stock solution in excess cyclohexane. The aggregates initially displayed a blue color. After force perturbation, such as slight shearing with a spatula, the color transition from blue to distinct green occurred. Interestingly, the green emission switched to a new reddish color with further mechanical action (Figure 1 a). To show this switching more clearly, we distributed the sample smoothly on a piece of filter paper, and it showed color transitions from blue to green then to reddish upon shearing (Figure 1 b–d). In this way, we can readily develop three different colors in one paper.

In the fluorescence spectra (Figure 1 e), the original blue emission band centered at 410 nm indicates a typical feature of the partially overlapped excimer of pyrene groups. Upon shearing, the emission band red-shifts to 480 nm for the green aggregates, which is ascribed to another pyrene excimer with sandwich packing.[5b] Notably, besides the emission band at 480 nm, a new peak at around 580 nm was detected for the reddish powder. This new band rationally results from the ring-opening form of Rh-B moieties. As shown in Figure 1 f, the intensity of the emission band at around 580 nm (I_{580}) and the ratio I_{580}/I_{480} increased with further force perturbation, which accounted for the continuous luminescence transition from green to the reddish color. The tunable emission property of **MC-1/2** in the visible-light range is expected to expand the utility of the materials in various applications (see below).

The microstructure of co-aggregates was investigated in detail by scanning electron microscopy (SEM), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). Compared to the smooth surface of microwires from free **1** prepared by similar procedures from cyclohexane (Figure 2 b), the compound deposited on the rough surface of **MC-1/2** microwires (ca. several hundred nanometers in width, tens of micrometers in length) might be from **2**, as shown by

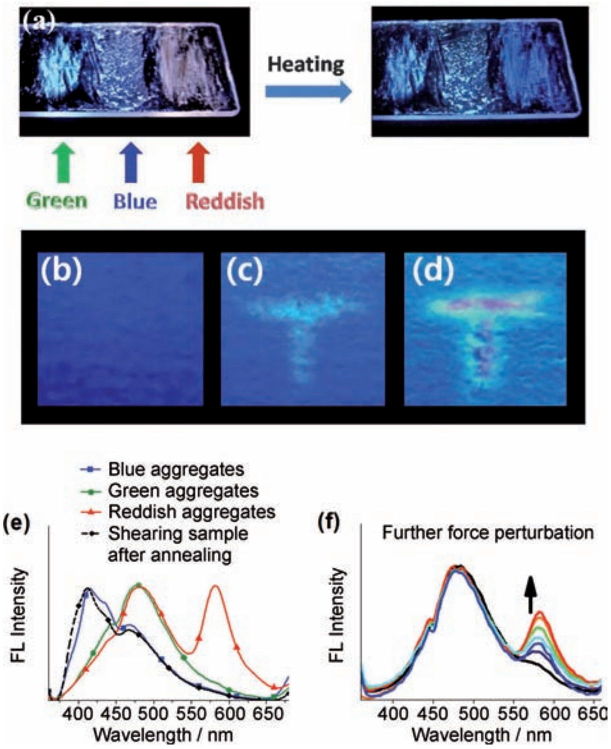

Figure 1. a) **MC-1/2** aggregates showing different emission colors under force perturbation (irradiated by 365 nm UV light) and their color restoration by heating. Blue: as-prepared aggregates without force perturbation; green: slight shearing of the aggregates with a spatula; reddish: further shearing of the green aggregates. b–d) Fluorescence images of b) **MC-1/2** on a filter paper with blue luminescence; c) force-induced green luminescence pattern; d) force-induced reddish luminescence pattern and three different emission colors in one paper. e, f) Fluorescence (FL) spectra of e) the samples with blue, green, and reddish emission colors and the sheared sample after annealing, and f) the tunable fluorescence property under force perturbation.

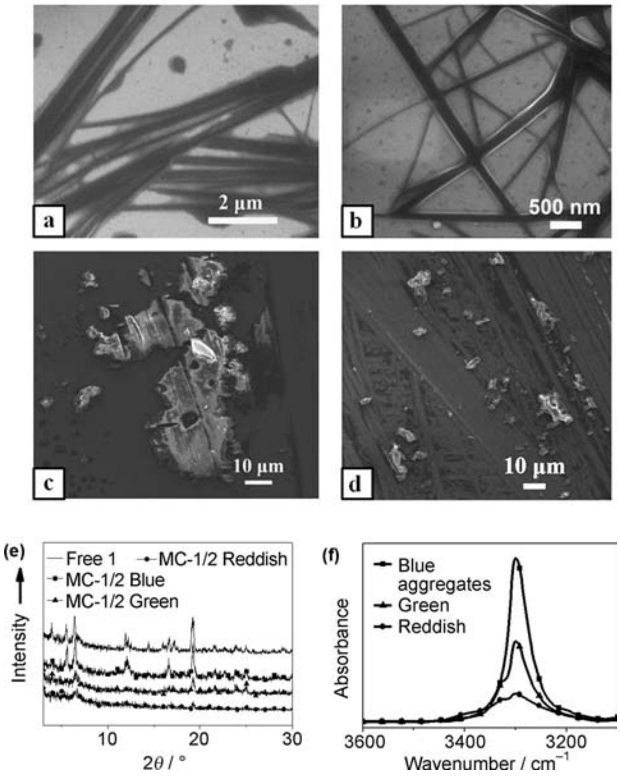

Figure 2. SEM images of a) **MC-1/2** blue aggregates obtained from cyclohexane; b) free **1** aggregates; c) **MC-1/2** green aggregates, and d) **MC-1/2** reddish aggregates. e) XRD patterns of the free **1** and **MC-1/2** aggregates with different colors. f) IR spectra of the **MC-1/2** aggregates with different colors (the absorption is normalized to the C–H stretching band at 2927 cm^{-1}).

the SEM images (see Figure 2a). This assumption is firstly evidenced by the smooth surface being restored after washing the **MC-1/2** microwires with methanol (Figure S3b in the Supporting Information). Further evidence is provided by the following three facts. 1) No reddish luminescence is observed under an external force for the microwires after washing. 2) Similar XRD patterns of free **1** and **MC-1/2** were detected. Free **2** powder shows broad diffraction peaks relative to those of free **1** aggregates, thus indicating that **2** is in an amorphous state (Figure S5 in the Supporting Information). The comparable XRD patterns of the co-assembled sample **MC-1/2** and free **1** aggregates (Figure 2e) reveal that the internal packing style of **1** is not significantly affected after introducing **2.** 3) Similar phase transition temperatures between **1** and **MC-1/2** imply microphase separation between **1** and **2** in the co-assemblies of **MC-1/2** (Figure S4 in the Supporting Information). The procedure for the preparation of **MC-1/2** guarantees that the ML behavior of each component can be retained and works without interference. The superiority of this preparation method is clearly revealed by the fact that the emission switching is facile and effective, whereas simply mixing **1** and **2** powders shows poor emission manipulation (Figure S6 in the Supporting Information). Noncovalent interactions, such as hydrogen bonding between the dipeptide backbones, may be responsible for the co-aggregation.[8]

Based on the above results and analysis, the multicolored transition may derive from the change of self-assembled microstructures of **1** and the spiro-ring-opening reaction of **2** upon application of an external force. The initial force perturbation may lead to disruption of the **1** crystalline microstructure, which accounts for the color switching from blue to green. The triggering of the ring-opening reaction of **2**, which induces the reddish color, does not occur until deeper damage of the co-assemblies is observed.

SEM, XRD, and IR measurements were applied to gain insight into the mechanical effect on the materials. SEM images provide directly visualized evidence for the morphology transformation from the wirelike ordered microstructure (blue emission) to the blurred solid (green emission), and further amorphous powder with random distribution (reddish emission; Figure 2a,c,d). The stepwise morphology transformation of **MC-1/2** was echoed by XRD measurements (Figure 2e). For the blue aggregates, the well-resolved diffraction peaks indicated a good crystalline lattice. After slight grinding, the disappearance of several diffraction peaks at the low-angle region represented damage of the self-assembled architecture. Further grinding resulted in the decreasing of the corresponding diffraction peaks, thus demonstrating more significant damage of the materials. More detailed information is provided by IR spectroscopy (Figure 2f). The strong absorption signal at 3300 cm^{-1}, ascribed to the N–H vibration band, gradually decreased its intensity and widened its band sequentially from the blue sample to the green and reddish ones, which indicated the different destruction extent of hydrogen-bonding interaction in the co-assemblies of **MC-1/2**. The crucial point here is that the different force effects on the materials at the microscopic scale can be readily monitored as the easily resolved emission color.

The multicolored luminescence switching is reversible. After annealing the sheared sample at 120 °C for 15 min, the sample restores its original blue luminescence from different grinding states (Figure 1a). Recovery of the blue color was reconfirmed by fluorescence measurement. After thermal treatment, the emission band at 410 nm became dominant, accompanied by the disappearance of the emission bands at 480 and 580 nm (Figure 1e). Two factors may be responsible for the color recovery: 1) the crystallinity of **1** is improved by annealing, which facilitates the recovery of the blue emission at 410 nm;[5b] and 2) spirocyclic Rh-B will be re-formed from the opening isomer after heating,[9] thus leading to the disappearance of the reddish luminescence.

As a result of the wide coverage of the emission spectra and facile tuning of each emission component, such as the emission intensity at 580 nm, it is possible to control the fluorescence of **MC-1/2** to offer different intermediate colors between green and reddish through carefully tuning the ratio I_{580}/I_{480} by shearing. The related study is ongoing. In addition, the direction to quantitatively elucidate the mechanochromic behavior is important yet challenging, and is in progress in our laboratory.

In summary, we have prepared a multicolored mechanochromic material by taking advantage of two distinct modulation approaches to bridge the supramolecular structures and mechanochemical reaction. Correspondingly, the multicolored transitions involve two different kinds of luminescence change: 1) the emission wavelength shift from blue to green, and 2) the unusual switching of emission intensity at long wavelength (nonluminescence to reddish luminescence). To the best of our knowledge, this is the first report to correlate the luminescence property with molecular assembly and mechanochemical reaction to afford novel multicolored ML switching. Such a binary system not only displays unique advantages in the multiple outputs, but also in the facile preparation method by exploiting already available dyes, which avoids tedious molecular synthesis and is of great importance in practical applications.

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