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ARTICLE

The Effect of Mechano-stimuli on the Amorphous-to-Crystalline Transition of Mechanochromic Luminescence Materials

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Mechanochromic luminescence via grinding-caused crystalline-to-amorphous transition in some organic materials has been well illustrated in these years. Here we focus on the luminescence reversion process induced by thermal annealing crystallization of a series of tetraphenylethene analogues. Through paired comparisons, we disclosed that the mechano-stimuli can not only destroy the crystallinity of crystalline materials, but also bring significant effect on the amorphous-to-crystalline transition of amorphous materials. That is, only when an amorphous material underwent mechano-stimuli can it crystallize by thermal annealing to recover its emission. This grinding-facilitated annealing crystallization is rationalized to originate from the twisted and rotatable intramolecular conformation that can be altered by mechano-stimuli. Besides some special usage of the material as security paper or latent memory medium, the study indicates new strategies to control the crystallization of organic semiconductors.

Introduction

Mechanochromic luminescence (ML) materials, which switch fluorescence in response to external mechano-stimuli such as grinding, pressing, or shearing,¹⁻³ have attracted increasing interest because of their potential applications in sensors, security materials, and information display/storage.⁴⁻⁶ Normally, ML materials produce obvious fluorescence intensity and/or color changes caused by the transformation of chemical or physical structures.⁷⁻¹⁰ e.g., that some organic materials tune their emissions under mechanical force through changing the chemical structures involving opened/closed cyclic form⁷ or double-bond E/Z isomerization.⁸ On the other hand, some reports focused on controlling the mode of molecular packing via crystalline-to-amorphous transition⁹ or phase shift of liquid crystalline state.¹⁰ Modifying the respective chemical structures by mechanical stress has been widely adopted in piezochromism for a long time.¹¹ Recently, people have pay more and more attentions to the scope of changing the intermolecular interactions of dyes and pigments by mechano-stimuli, which is believed to be more facile to achieve highly efficient and reversible ML.¹² Till now many researches have proved that the emission property of some organic solids has close relationship with the regularity of molecular packing.¹³ People have encountered many cases that the mechano-stimuli can induce certain crystalline materials into amorphous state accompanied by luminescence change. Moreover hand this transition can be reversed through thermal annealing, which is actually a recrystallization process and a commonly used

method to elevate crystallinity of organic semiconductors. Strategies to optimize the annealing crystallization have always been key techniques in many optoelectronic applications.¹³ However, rare few have noticed the influence of the applied mechano-stimuli on the crystallization. Diemer PJ *et al.* have reported a method of vibration assisted crystallization on organic semiconductor thin-films.¹³ In this work we investigated a series of fluorenyl-containing tetraphenylethene (TPE) analogues, discussed the relationship between the molecular conformations and the ML behavior, especially the role of mechano-stimuli on the thermal annealing crystallization process. The result disclosed that after mechanical treatment, an amorphous sample is much more prone to a phase transition to recover their crystallinity.

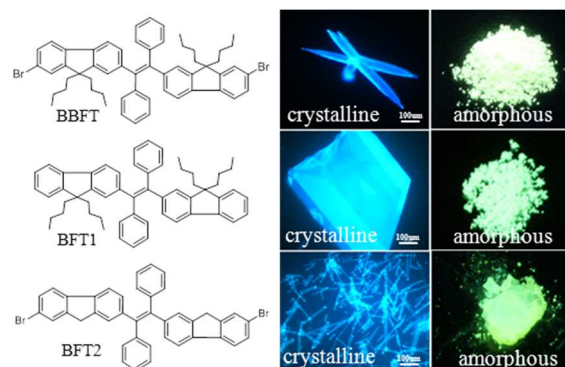


Figure 1. Chemical structures of BBFT, BFT1, and BFT2 and the corresponding fluorescent images of crystalline and amorphous samples.

Results and discussion

The chemical structures of TPE analogue 1,2-bis(7-bromo-9,9-dibutyl-fluorenyl)-1,2-diphenylethene (BBFT), 1,2-bis (9,9-dibutyl-fluorenyl)-1,2-diphenylethene (BFT1) and 1,2-bis(2-fluorenyl-7-bromo)-1,2-diphenylethene (BFT2) are shown in Figure 1. The three compounds are synthesized through the typical reactions of Zn/TiCl₄-mediated McMurry coupling.¹⁷ The greenish yellow as-prepared powders are precipitated from pouring their dichloromethane (DCM) solutions into ethanol. At the same time, the crystals of them were got by slow evaporation of ethanol/DCM solution at room temperature. The identity and purity of the new compounds were verified by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis. The crystallographic datum of BBFT (CCDC 909142), BFT1 (CCDC 974227), and BFT2 (CCDC 974229) have been deposited in the Cambridge Crystallographic Data centre. Details of the synthetic procedures and characterization data are presented in the Supporting Information.

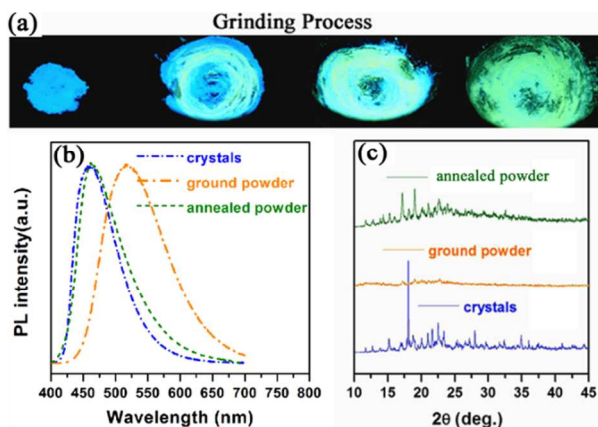


Figure 2. (a) Fluorescence images in the grinding process. (b) PL spectra of the BBFT powder in different forms. (c) XRD spectra of the BBFT powder in different forms.

As shown in Figure 1, the luminogens in different solid state display distinct fluorescence color: deep-blue in crystals and greenish-yellow in the as-prepared powders, indicating a morphology dependent luminescence. According to the previous studies, external stimuli that able to alter the molecular packing mode of such luminogens will induce fluorescence changing.¹³⁻¹⁶ When ground the crystalline sample of BBFT with a pestle or sheared it with a spatula, as shown in Figure 2 (a), its fluorescence switched simultaneously during the process of grinding, finally with the entire blue emissive sample turning into a green one. This fluorescence transition was found to be reversed by thermal annealing. Figure 2 (b) and (c) presents the photoluminescence (PL) spectra and their XRD patterns of the samples in different state, respectively. We can see both crystals and the annealed powder have sharp diffraction peaks; while the diffraction pattern of the ground powder is nearly a flat line, revealing that through grinding the crystallinity was significantly reduced to being amorphous. The crystalline-to-amorphous transition is confirmed to be responsible for the fluorescence changing from blue to green during the grinding

process. The other two compounds BFT1 and BFT2 show similar ML behavior as depicted in Figure S4.

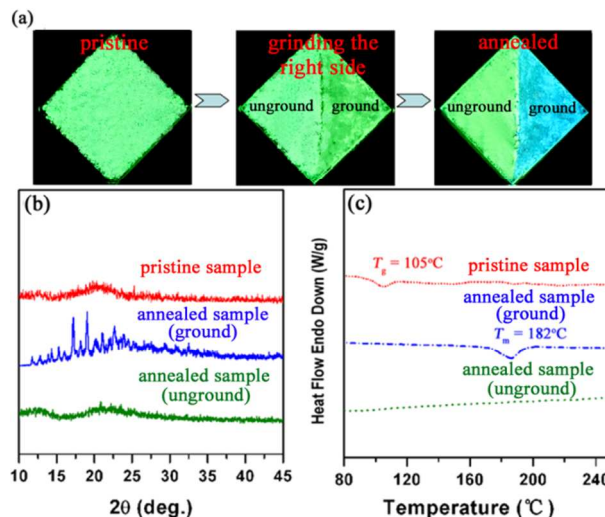


Figure 3. (a) Comparison of the grinding effect on the thermal annealing crystallization by grinding a half side of a pristine amorphous BBFT film and then annealing the whole piece of film. (b) XRD patterns of BBFT under different conditions. (c) DSC thermograms of BBFT under different conditions. Photos were taken under UV irradiation at 365 nm.

The ML behaviour demonstrates that mechano-stimuli is able to make the structured molecular packing being crushed into disorder. In this study we pay more attention to the effect of mechano-stimuli on the thermal annealing process of the amorphous materials. In order to exclude any encapsulated crystalline phase, we prepared pristine amorphous samples by directly quenching the melted compounds. Their thermal properties were firstly investigated as the referees to determine the annealing temperature. For BBFT the crystalline material possesses a melting point (T_m) of 182 °C while the amorphous powder has a glass transition temperature (T_g) of 105 °C as shown in Figure S5. When the ground powders were annealed at 130 °C for in less than 30 minutes, they have totally crystallized with the emission color changing into blue from green as mentioned above. While for the pristine amorphous sample an interesting phenomenon was noticed that they cannot crystallize even after annealing for more than one week. We have attempted to conduct the thermal annealing at different temperatures below T_m and in extension of time, but still we cannot make the transition occur. This means even in amorphous state, the mechano-stimuli has significant effect on the arrangement process of BBFT molecules. Figure 3 depicts this effect via a contrast test. On a substrate coated with the pristine amorphous BBFT, we ground a half side of the sample; then the whole sample was put into an oven set at 130 °C. After one hour's annealing the ground part have totally changed into blue-emissive crystallites; while the unground part still emits green light, even after extension of time to one week. The obvious contrast between the two halves demonstrates that without mechanical treatment the thermal annealing induced crystallization cannot be realized. The comparison tests on the other two samples BFT1 and BFT2 reveal similar results. As shown in Figure S8 and S9, after thermal annealing of BFT1 pristine amorphous sample at 110 °C for 30 minutes, only the ground part converted into blue-emissive crystallites; for BFT2 because the 9-position of the fluorenyl units is not protected by

alkyl substituents, the thermal annealing was conducted under vacuum at 180 °C for 48 hours to avoid oxidation.

To unearth the influence of grinding on the pristine amorphous sample, we examined the XRD spectra and the thermal behaviors of the sample before and after grinding, and before and after annealing, respectively. Because the sample is already in amorphous state, grinding doesn't change the XRD patterns and the thermograms. From Figure 3(b), we can see that after annealing sharp diffraction peaks appear on the XRD of the ground sample; while that of the annealed unground sample remained being a flat line. The thermal properties of BBFT in different states also reveal different morphology information: only the annealed ground powder displayed a melting point at 182 °C; the pristine powder showed a T_g transition at 105 °C; on the annealed unground powder no heat flow change has been detected. In theory, we should observe a crystallization transition on the DSC curve of the ground powder; but maybe because the speed of the crystallization process was low, no exothermic peak appeared in the measuring course.

Actually from the above results we can get little information about what has happened under the mechanical treatment on amorphous materials. Firstly we regarded that through grinding the stable glassy state of the amorphous samples will be compressed into much thinner pieces, making the nucleation of the crystallization take place more smoothly. However, in the latter experiments we found that even the sublimated films thin to several nanometres and the small pieces cut from the thin films cannot be annealed to crystallize without grinding. We believe that besides the variation of the general shape of the samples, there must be some more intrinsic influencing factors introduced by the mechano-stimuli that can facilitate crystallization. What comes to us is the novel conformational feature of the luminogens, namely, the twisted and rotatable molecular structure. Because of the dynamic intramolecular rotations of the aryl rotors in the luminogens, this kind of molecules have many different conformations which are easy to vary from each other. We consider that mechano-stimuli may possess this power. As indicated from the crystal structures of the three materials (Figure S10), in order to fit into the crystalline lattice, the molecules in crystals adopt a highly twisted conformation, with the dihedral angles between each two of the four aryl substituents ranging from 58 to 88 °. This feature induces an incompact molecular packing which is easy to be disturbed by mechano-stimuli; during a crystalline-to-amorphous transition the planarization of the twisted molecules results in the pronounced luminescence color change—that is the origin of the ML.^{8,9} That is to say, the emission red-shift in ML is attributed to the extension of the conjugation because grinding makes the highly twisted molecular conformation change to a relative planar one along with the collapse of the crystal unit cells.⁹ To learn the molecular conformation in amorphous state experimentally is difficult; thus we conducted theoretical optimization on BBFT by using density functional theory (DFT) calculations at a B3LYP/6-31G (d) level. The optimized molecular geometry in the free isolated state reveals a different form with that of obtained from the X-ray crystallography data, which is indeed more planar. (Details see Table S4 and S5 and Table S6 and S7) Subsequently, the deduced band gap from the HOMO and LUMO energy level based on the optimized geometry is 3.69 eV, which is smaller than the value of 4.02 eV obtained from the crystal structure. Besides the red-shifted emission in amorphous state, the conformational change can be also evidenced by the absorption. As shown in Figure 4a, in crystalline state the absorption spectrum of BBFT shows a peak at 410 nm with

the absorption edge at 453 nm; after being ground into amorphous, its absorption peak and absorption edge shift bathochromically to 421 and 475 nm, respectively. The blue-shift of absorption in crystals suggests H-aggregates maybe formed; wherever the enhanced and blue-shifted emission excludes the possibility. A closer check into the crystal structures also reveals no such parallel packing of H-aggregates. We are aware of the fact that change of the molecular packing also causes shift of the optical properties. Nevertheless this kind of compounds feature weak intermolecular interactions and loose packing in the aggregate, thus we believe that it is a result of the conformational planarization from crystalline to amorphous state, which prove that grinding the crystalline materials can alter the molecular conformation from a highly twisted one to a relative planar one. While speaking of the pristine amorphous samples obtained by quenching the melted compounds, we regard that in the fast process of solidification, the molecules will retain their conformation as that in the isolated free state, which is more planar than that in crystals known from the theoretical optimization. To validate the probability that mechanical grinding is able to alter the molecular conformations even in the amorphous state, we compared the two kinds of amorphous samples that before and after mechanical grinding. As shown in Figure 4, the absorption edge of the pristine amorphous sample was found at 490 nm; while after grinding it hypochromatically shifted to 475 nm. Furthermore, the emission peak of the pristine amorphous BBFT also hypochromatically shifted from 530 nm to 517 nm after grinding. The results suggest that the effective conjugation of the molecules in pristine sample is even larger than that of the ground samples. Just like the blue-shift of absorption and emission in crystals, we believe that the grinding-induced blue-shift here is also resulted from the shortened effective conjugation length. In the process of applying mechano-stimuli on the pristine samples, the more planar molecules alter their conformations to become more twisted, meaning that the molecular conformation gets similar to that in crystals after grinding although they are still in amorphous state. This reduction in conformational difference will facilitate the molecules to rearrange into a crystalline form. As shown in Figure S11 and S12, the blue-shift of absorption and emission induced by grinding was also observed in the amorphous samples of BFT1 and BFT2. The absorption peak and absorption edge of pristine BFT2 hypochromatically shifted ~35 nm after grinding.

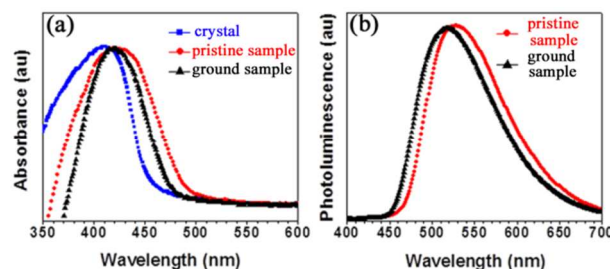


Figure 4. (a) Normalized absorption of BBFT solids under different conditions. (b) PL spectra of BBFT solids under different conditions.

Based on the above discussions we propose a mechanism for this mechano-facilitated crystallization, as the schematic illustration shown in Figure 5. Every single molecules in the pristine amorphous sample adopt a most planar conformation inherited from the melt, while a most twisted one in crystals because of the restriction of crystalline motif. We regard that

keeping a planar conformation in aggregate state makes the collective energy higher and the material a metastable state. Upon mechano-stimuli, the material will release some energy from the isolated-lowest level to an aggregate-lower level by changing the planar conformation into a relative twisted one. Specifically, we assume in the pristine molecules the dihedral angles between the central ethenyl plane and each aryl substituents are near the DFT optimization result ranging from 51.84 to 53.99 °; after grinding some of the corresponding dihedral angles become bigger and more close to those in crystals. The difference of the molecular conformations between before and after grinding is manifested in the different band gaps and the optical spectral shift. Thus the ground sample can be regarded as an intermediate state between the pristine amorphous sample and crystal, making the subsequent annealing crystallization more prone to proceed.

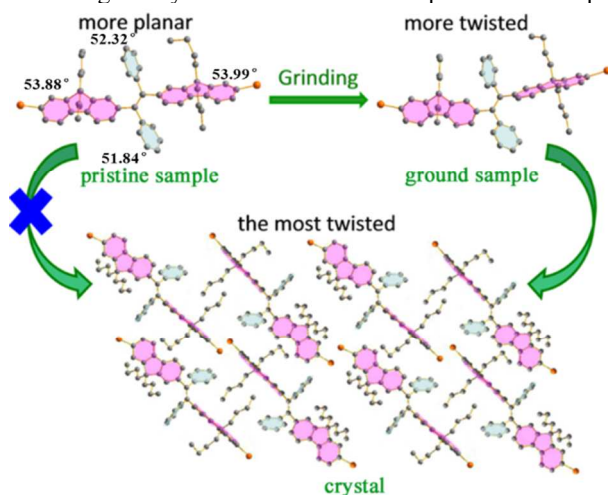


Figure 5. Schematic illustration of conformation transition of BBFT molecule in different state (pristine amorphous sample, ground sample and crystal). The degrees are dihedral angles between the central ethenyl plane and each aryl substituents.

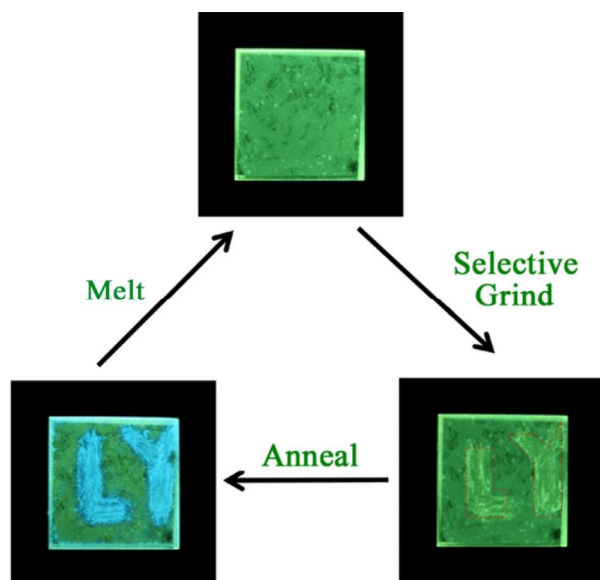


Figure 6. Procedures of writing and erasing letters on a quenched amorphous BBFT film. Photos were taken under UV irradiation at 365 nm.

The grinding-facilitated crystallization enables us control crystallization locations on a whole substrate with amorphous materials. As shown in Figure 6, when pressed letters on a pristine BBFT film, only un conspicuous trace was left on the sample. After annealing at 130 °C for one hour, the pressed parts crystallized and the letters become blue emissive; while the other parts remained unchanged, exhibiting high contrast. Promisingly this method can be used to prepare crystalline patterns of other organic semiconductors. The letters can be erased by heating the sample to 200 °C (beyond the melting point) and cooling. Via such a grind, anneal, and melt cycle, another kind of recording repeats information recording can be realized.

Conclusions

In conclusion, we reported an unprecedented phenomenon in the annealing crystallization process of a series of tetraphenylethene analogues with mechanochromic luminescence. Mechano-stimuli was found to improve the crystallization capacity essentially of their pristine amorphous samples. Through experimental and theoretical investigation we revealed that because of the rotatable intramolecular structure, the molecular conformation can be adjusted by mechano-grinding: grinding of the crystalline sample produces a relative planar conformation from a highly twisted one, while grinding of a pristine sample produces a relative twisted conformation from a planar one. The reduction in conformational difference facilitates the molecules to rearrange into a crystalline form. This mechano-facilitated annealing crystallization may introduce new strategies to tune the crystallization in organic semiconductor devices such as photovoltaics and field-effect transistors, especially for the precise control of crystalline patterns.

Acknowledgements

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Notes and references

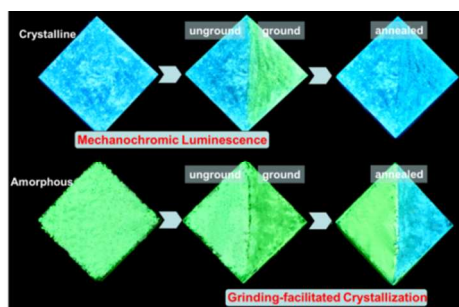
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Table of contents entry

Mechano-stimuli, on crystalline materials causes mechanochromic luminescence via crystallinity decreasing, facilitates the annealing crystallization of their amorphous state.