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Piezochromic fluorescence in liquid crystalline conjugated polymers†

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Liquid crystalline diphenylacetylene polymer derivatives showed piezochromic fluorescence *via* order-to-disorder phase transition.

Fluorescent organic chromophores are very useful materials for display and sensor applications. Recently, many challenging works have been done in order to tune and switch fluorescence emissions *in situ* in solids without chemical modification.[1] Among the many efforts, the revelation of piezochromic fluorescence (PCFL) may be one of the most interesting research issues.[2] The molecular design concepts for PCFL have preferred low molecular weight organic compounds with (liquid) crystallinity. Their molecular packing structures are based on weak intermolecular interactions such as π–π inter-action, hydrogen bonding, van der Waals force, and London dispersion force. Thus, the order-to-disorder phase transition in the solids often occurs as a result of such weak driving forces as shear or grinding stresses. To date, a few research groups have successfully developed the target solid materials of piezochromic fluorophores based on the idea that the dynamic fluorescence (FL) behavior can be modulated by controlling the molecular packing structure.[3] However, the piezochromic fluorophores are still quite rare because they require a fine molecular design to realize a highly efficient PCFL in the desired direction. Also, their stress-response performances have been conducted exclusively in powdery states due to the low molecular weight and (liquid) crystallinity.

In a practical use, film-/fiber-forming materials such as polymers have many advantages such as better processability and wider applications. Among the many types of conjugated polymers, diphenylacetylene polymer derivatives have highly twisted chain conformations due to the steric repulsion between the two bulky phenyl groups, and their backbones are essentially non-coplanar with the side phenyl ring.[4] Thus, unlike conventional conjugated polymers which show inter-molecular excimer emission in solid states due to highly cofacial chain packing structures with planar geometries and intermolecular π–π interaction,[5] diphenylacetylene polymers should be worm-like chain molecules with nonplanar geometry, leading to unstacked structures in a solid state. Moreover, very unusually, their FL emission originates from an intra-molecular excimer due to the face-to-face stack structure of the side phenyl rings.[6] To date, a large family of mesomorphic and luminescent polyacetylenes with multiple functionalities have been developed.[7] Especially, the extremely high molecular weights and main chain rigidity of poly(diphenylacetylene) derivatives with alkyl side chains (polymers **1–3** in Chart 1) drive the lyotropic liquid crystallinity well with an aid of adequate solvent, according to the Flory theory, resulting in highly ordered structures.[8] The lamellar layer distances of **1–3** are as large as 22.0, 14.9, and 13.0 Å, respectively, and are much greater than the interplanar distances (3.0–4.0 Å) needed for an effective intermolecular π–π interaction. Thus, their ordered structures should be constructed on the basis of a much weaker interchain hydrophobic interaction due to the presence of alkyl side chains rather than the interchain π–π interaction. Based on these facts, we thought that the ordered structures could be easily collapsed by external mechanical stress and their FL emission properties could also be changed as a result of the phase transition. In this study, we discovered that the polymers underwent remarkable FL emission colour changes during the grinding process. The FL emission colour was completely recovered by chain reorganization *via* solvent annealing. We will herein describe the details and suggest some molecular design rules for highly mechanical stress-responsive polymers with PCFL functions.

Polymer **1** provides a quite flexible and somewhat sticky film due to the relatively low glass transition temperature of about 5 °C.[8c] On the other hand, **3** is a glassy polymer and provides a much harder and more brittle film because the secondary thermal transition does not occur until 200 °C.[9] Thus, the bulk solid of **1** produced a nicely featured film through a

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† Electronic supplementary information (ESI) available: Details for the experiment, fluorescence spectra, fluorescence lifetimes, fluorescence decay profiles, WAXD and POM data. See DOI: 10.1039/c0cc04811a
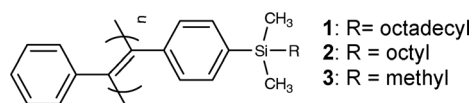
Chart 1 Chemical structures of polymers **1–3**.

consecutive mechanical process while the glassy polymer of **3** did not. In fact, the manual grinding and subsequent roll-pressing of the original bulk solid of **1** produced thick films with relatively smooth surfaces, while polymers **2** and **3** did not form such films after the same processing, but solely left powdery materials.

Fig. 1 shows the emission spectra of **1** in solution, the solvent cast film (SC-film), and the mechanically processed film (MP-film). Surprisingly, the MP-film shows a new shoulder band at 580 nm while the monomer emission at 475 nm significantly decreases. Accordingly, as shown in the inset, **1** shows an orange emission in the MP-film, while the polymer in solution and SC-film shows sky blue emissions. The largest fractional emission band around 520 nm originates from the intramolecular excimer due to the face-to-face stack structure of the side phenyl rings.[8a] If the extremely long wavelength emission at 580 nm still comes from the intra-molecular excimer, it can be observed after the mechanical process, even when the polymer is extremely diluted with an optically inactive carrier such as KBr. As shown in Fig. 2, however, the grinding of **1** mixed with KBr, when the polymer is extremely diluted in the inorganic carrier down to 0.05 wt%, induces no changes in emission colour and spectrum. On the other hand, when the polymer is concentrated in the KBr pellets as more than approximately 9.0 wt%, the **1** in the KBr pellets shows a gradual increase in FL intensity at 580 nm as the concentration increases, and the emission colour changes
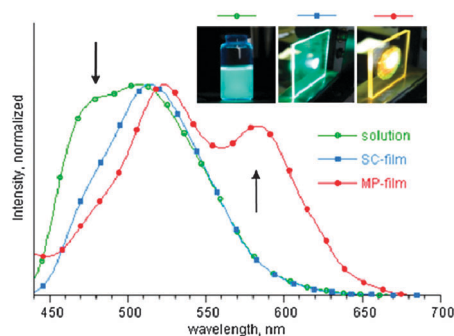
from sky blue to orange. This concentration dependency of FL emission indicates that the 580 nm emission is not due to the intramolecular excimer but due to an intermolecular one. Presumably, therefore, the new excimer emission results from a certain phase transition induced by the mechanical stress. Although polymers **2** and **3** did not produce films from the same mechanical process, these polymers in KBr pellets with high concentrations of several wt% showed the same FL changes as **1** (Fig. S1 in ESI†).

The MP-film of **1** retained its solubility in organic solvents such as chloroform and toluene. Re-precipitating of its solution to non-solvents regenerated the original bulk solid and fully restored the original sky blue emission. Moreover, the original emission colour was also able to be restored simply by annealing the MP-film with hexane liquid and/or its saturated vapour, indicating the typical PCFL. Fig. 3 shows the reversible change in the FL emission spectra of **1**. The 580 nm shoulder band disappears and the 475 nm monomer emission band regenerates after the solvent annealing. Thus, the original sky blue emission was completely restored after the solvent annealing, as shown in the inset. This chromism may be due to the fact that the polymer chains reorganize during the solvent annealing process in order to reconstruct the ordered structure. Although we also attempted to restore the original emission by thermal annealing at around 100 °C for several hours, a reversible change was not shown. This efficient restoration in solvent annealing rather than in thermal annealing is because of the intrinsic lyotropic liquid crystallinity of the present polymer.

To comprehensively understand the PCFL of the present polymers, we performed a dynamic fluorescence spectroscopy of **1** in both the SC- and MP-films. Table 1 summarizes the fluorescence lifetimes of **1**. The photoemission decay of **1** obeys biexponential decay in both the SC- and MP-films. The fractional intensities of the shorter- and longer-lived excited species between the SC- and MP-films are significantly different from each other. The emission of **1** in the SC-film

Fig. 1 FL emission spectra of **1** in the solution (concentration ≈ 1 × 10^{-6} mol L^{-1} in toluene), the SC-film (film thickness ≈ 30 μm), and the MP-film (film thickness ≈ 100 μm). Inset: digital photographs (excited at 420 nm).

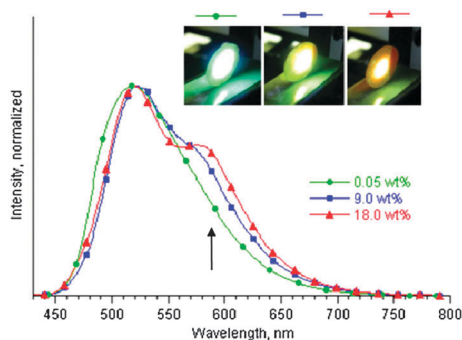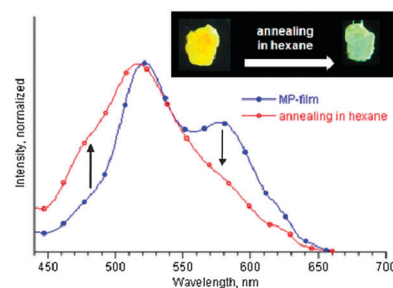**Fig. 2** FL emission spectra of **1** with different concentrations of 0.05 wt% (●), 9 wt% (■) and 18 wt% (▲) in KBr pellets (excited at 420 nm).

Fig. 3 Variation in FL emission spectra of **1** in the MP-film (film thickness ≈ 100 μm). Inset: digital photographs (excited at > 365 nm).

Table 1 Fluorescence lifetimes of **1** in the SC-and MP-films[a]

Polymer film	τ_1 (f_1)/ns	τ_2 (f_2)/ns	χ^2	τ_{avr}/ns
SC-film	0.571(0.18)	1.426(0.82)	1.026	1.272
MP-film	0.389(0.46)	1.323(0.54)	1.051	0.893

[a] Monitor wavelength is 520 nm. The τ_1 and τ_2 are lifetimes (ns), f_1 and f_2 are fractional intensities, and χ^2 is the reduced chi-square, and τ_{avr} is the average lifetime obtained from $f_1\tau_1 + f_2\tau_2$.

comes largely from longer-lived excited species (τ_2), whereas the emission of the MP-film is characterized by a shorter lifetime (τ_1) as well as the longer lifetime. This indicates that the shorter-lived excited species in the MP-film was newly formed because of a rapid energy migration into certain energy trapping sites. As a result, the τ_{avr} is much shorter in the MP-film than in the SC-film. The FL decay profiles also well exhibited the difference in dynamic fluorescence behaviour of **1** between the SC- and MP-films (Fig. S2 in ESI†). The FL decayed faster in the MP-film than in the SC-film, indicating a more significant exciton deconfinement in the MP-film. Accordingly, it should be concluded that the newly formed 580 nm emission excited species act as energy trapping sites in order to diminish the longer-lived excited species at 520 nm. This suggests that emission quantum yield of the MP-film should be lower than that of the SC-film.

To gain further insight into the PCFL of the present polymers, we conducted wide-angle X-ray diffraction (WAXD) and polarizing optical microscopy (POM) experiments. The WAXD patterns and POM images of **1** in the SC- and MP-films are shown in Fig. S3 in ESI†. The SC-film showed a very sharp diffraction signal at a small angle of 4.0° with a corresponding lamellar layer distance of 22.0 Å,[8] whereas the sharp signal almost disappeared in the MP-film, indicating the disruption of the ordered structure. Naturally, the collapse of the ordered phase also resulted in a significant change in the anisotropic phase morphology as shown in the inset. The SC-film certainly exhibited chevron texture from POM observation. Such a birefringent texture is characteristic of the liquid crystal phase due to a smectic layer, indicating that a certain, highly ordered layer structure is spontaneously formed *via* the critical concentration point during the slow solvent evaporation in the process of the SC-film preparation.[8c] However, this texture completely disappeared in the MP-film and a more complicated texture appeared. This was probably because of a smectic-to-nematic phase transition. The polymers of **2** and **3** showed the same tendency as **1** in the WAXD and POM observations (Fig. S4 in ESI†).

Here are two questions of concern: first, how can the ordered structure in the present polymers be easily disrupted by mechanical stress? As mentioned above, the anisotropic texture was clearly observed in the concentrated solutions of aromatic solvents, such as toluene, benzene, and xylene, while the texture was hardly observed in alkane solvents such as *n*-hexane and *n*-decane. Namely, the lyotropic liquid crystalline property of **1** significantly depended on the solvent. This is because the bulky alkylsilyl groups in the side chain should increase the interchain hydrophobic interaction while preventing, as much as possible, the intermolecular π–π interaction. This strongly supports the idea that the ordered structure of **1** is constructed on the basis of the interchain hydrophobic interaction rather than the interchain π–π interaction. Accordingly, the ordered structure seems to be easily disrupted because the molecular construction is based on the very weak van der Waals force interaction between the alkyl side chains. The next question is why the mechanically induced order-to-disorder phase transition leads to a significant change in the emission property of **1**. Polymer **1** originally has an

unstacked chain structure in the ordered fashion in a bulk solid. However, once the order-to-disorder phase transition occurred during the mechanical processing, the polymer chains should have been further randomly entangled and then physically crosslinked, in order to partially provide a certain intermolecular π–π stack structure in the meta-stable state of the disordered amorphous phases. The partially formed intermolecular π–π stack structure can act as an energy trapping site. Thus, intermolecular energy transfer should occur from the excited species with the higher energy (shorter wavelength emission) to the excited species with the lower energy (longer wavelength emission).

In summary, we found that the liquid crystalline diphenylacetylene polymer derivatives showed PCFL. The FL emission colour was significantly changed by mechanical stress and then recovered by solvent annealing. The mechanical stress-induced FL change was a result of the order-to-disorder phase transition. We demonstrated that liquid crystalline conjugated polymers with a very weak interchain interaction in an ordered structure can easily transform into a meta-stable phase by a mechanical stress. In this respect, the present polymers are expected to be the ideal models for the molecular design of fluorescent organic materials with PCFL function.

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