

An Aggregation-Induced Emission Luminogen with Efficient Luminescent Mechanochromism and Optical Waveguiding Properties

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Abstract: In this study, a yellow luminogen (TPE-DCV) was synthesized by treating tetraphenylethene with two dicyanovinyl units. TPE-DCV is non-emissive in solution but becomes a strong emitter when aggregated in poor solvents or in the solid state, thereby displaying a phenomenon of aggregation-induced emission. The solid-state emission of TPE-DCV can be reversibly switched between green and yellow with a moderate contrast ratio by grinding and fuming or heating processes owing to the morphological change between thermodynamically stable crystalline phase and the metastable amorphous state and vice versa. Negligible reabsorption and well-ordered molecular arrangement of the microcrystals of TPE-DCV make them promising as optical waveguide materials with low optical loss.

Recently, the development of new luminescent materials based on π -conjugated organic molecules has attracted much interest because of their wide applications in the fields of electronics,^[1] optics,^[2] storage media,^[3] and biological sciences.^[4] They are usually used in the aggregate state (e.g. solid film or aqueous solution) for practical applica-

tions. However, a common problem associated with the emission of most luminescent materials is aggregation-caused quenching (ACQ). Such compounds are highly emissive in the solution state, but become weakly emissive or non-emissive in aggregated state because of the detrimental formation of excimers.^[5] Some technologic and scientific attempts have been exploited to alleviate the ACQ effect, but these efforts have met with limited success because they are working against an intrinsic process.^[6] In 2001, we and other groups observed that some propeller-shaped molecules exhibit the aggregation-induced emission (AIE) phenomenon, which is the exact opposite of the ACQ effect.^[7] Instead of quenching, aggregate formation results in emission, although these compounds are almost non-emissive in the solution state. Based on many theoretical and experimental studies, the restriction of intramolecular rotation (RIR) has been proposed as the main cause for the AIE phenomenon.^[8] Intense emission in the aggregated state of AIE luminogens makes them promising materials for high-technological applications, particularly in the solid state. To date, various AIE luminogens have been prepared and used for many fields, such as organic light-emitting diodes,^[9] chemosensors,^[10] bioprobes,^[11] and cell imaging.^[12]

Luminescent mechanochromic materials are a class of “smart” materials and their luminescent property is very sensitive in response to external mechanical stimuli.^[13] They have received considerable attention on account of their potential applications in sensors, memory chips, security inks, and so on.^[13,14] Many excellent mechanochromic AIE materials have been developed based on their alterable molecular conformation and high emission in the solid state. Moreover, the contrast ratio can be tuned by altering the substituent groups in AIE molecules, which is instructive for molecular design.^[14,15] On the other hand, waveguides are an important topic because of their ability to transmit subwavelength information, which is promising for use in optoelectronic communications and sensors.^[16] Micro/nano-crystals of AIE luminogens have great exploitation potential in optical waveguide materials because of their strong emission and high stability.^[17] Indeed, there are few proper AIE luminogens that have both efficient luminescent mechanochromism and optical waveguiding behavior.


For widening the application of AIE materials in the photoelectronics field, in this paper, we report an AIE luminogen (TPE-DCV) by decorating the tetraphenylethene

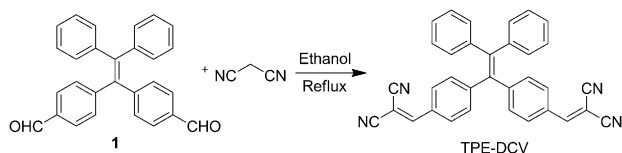
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Scheme 1. Synthetic route to TPE-DCV.

(TPE) group with dicyanovinyl units. This luminogen shows reversible luminescent mechanochromism. Moreover, two shapes of microcrystal are obtained, which exhibit excellent optical waveguiding behavior with very low optical loss.

Luminogen TPE-DCV was synthesized as a yellow solid in a yield of 56 % according to the synthetic route shown in Scheme 1. Detailed procedures for its synthesis and characterization can be found in the Supporting Information.

TPE-DCV absorbs at 384 nm in diluted THF solution, which is attributed to intramolecular charge transfer from the electron-donating TPE group to the electron-accepting cyano group (Figure S1 in the Supporting Information).^[18] The emission spectrum of TPE-DCV is a flat line parallel to the abscissa when its THF solution is photoexcited, manifesting that TPE-DCV is non-emissive when it is molecularly dissolved in a good solvent (Figure 1). However, in the THF/water mixtures with high fractions of water ($f_w >$

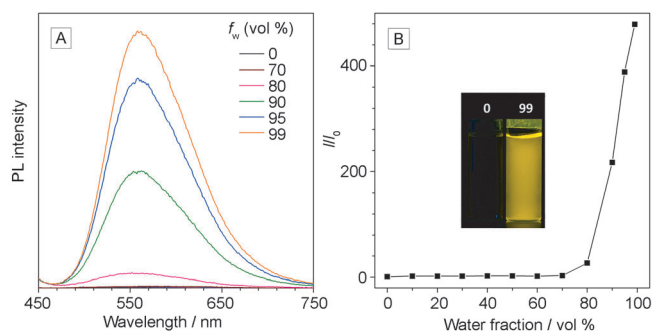


Figure 1. A) Emission spectra of TPE-DCV in THF/water mixtures with different water fraction (f_w). Solution concentration = 10 μ M. Excitation wavelength: 400 nm. B) Plot of the relative emission intensity (I/I_0) versus the composition of the aqueous mixture of TPE-DCV. I_0 = emission intensity in pure THF solution. Inset in B): Photographs of TPE-DCV THF-water mixtures with f_w values of 0 and 99% taken under 365 nm UV irradiation.

70 %), TPE-DCV gives emission spectra with a clear peak at 560 nm. At 99 % water content, bright yellow light is observed under 365 nm UV irradiation (Figure 1 B). Clearly, the introduction of dicyanovinyl red-shifts the emission spectrum of TPE.^[7b] THF is a good solvent for TPE-DCV and this gives rise to free rotation of the TPE group. However, water is a poor solvent, and TPE-DCV molecules must aggregate in aqueous solution with high water fractions, which blocks the nonradiative relaxation channel and populates radiative excitons, which thus converts TPE-DCV into a strong emitter.

After recrystallizing from ethanol, as-prepared TPE-DCV gives strong green emission with peak at 526 nm (Fig-

ure S2A in the Supporting Information). The appearance of blue-shifted emission spectrum compared with that in 99 % aqueous solution implies that TPE-DCV possesses luminescent mechanochromism.^[15c] As expected, after grinding using a metal spatula, the green powder turned into yellow powder with an emission peak at 560 nm. After fuming with acetone vapor for 10 min or heating at 150 °C for 15 min, the initial green color is reinstated. The conversion between yellow and green can be repeated several times without fatigue because these stimuli are nondestructive in nature. It is clear that TPE-DCV possesses reversible luminescent mechanochromism with a moderate contrast ratio of ca. 40 nm (Figure S2B in the Supporting Information).

Crystalline powders of TPE-DCV were smeared on a piece of filter paper as a thin film to test further potential applications (Figure 2). The film exhibits green emission

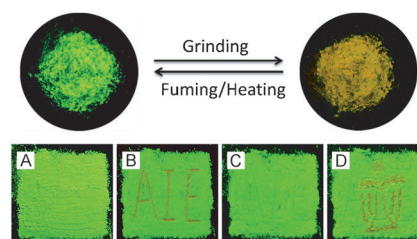


Figure 2. (Top) Switching the solid-state emission of TPE-DCV by the grinding-fuming/heating process. (Below) Fluorescent images of A) TPE-DCV adsorbed onto filter paper; B) after writing “AIE” with a metal spatula; C) the background emission restored by fuming the film with acetone vapor for 10 min; D) the rewritable mechanochromic fluorescence demonstrated by the logo of HKUST generated with a metal spatula. The photographs were taken under 365 nm UV irradiation.

under 365 nm UV irradiation. The letters “AIE” written with a metal spatula on the TPE-DCV film appear yellow and thus are readily discernible from the green background. Fuming the film with acetone vapor for ten minutes erases the letters. When the logo of HKUST was drawn again on same film, the distinct yellow color for the pattern was detected as before. The results demonstrate that TPE-DCV can serve as a recyclable optical storage medium.

To investigate the mechanism of mechanochromism of TPE-DCV, the powder X-ray diffraction (XRD) for different aggregated states was analyzed. Before grinding, the crystalline sample has many sharp diffraction peaks, which is indicative of its well-ordered crystalline nature (Figure 3 A). After grinding, the diffraction intensity becomes very weak, which suggests the ground sample is amorphous. When the ground powders are treated by heating or fuming with solvent vapor, the profiles of the diffractogram with sharp peaks appear again, although they are little different from that of the unground sample, which means that the thermal and fuming treatment can return the amorphous state of TPE-DCV to the crystalline state. Analysis by dif-

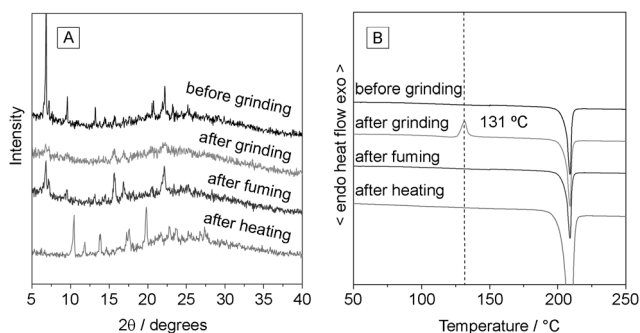


Figure 3. A) XRD diffractograms and B) DSC thermograms of TPE-DCV in different aggregated states recorded at a heating rate of $10^{\circ}\text{C min}^{-1}$.

ferential scanning calorimetry (DSC) of different states supports the above claim (Figure 4B). During the heating scan, an exothermic peak appears at 131°C for the ground sample which is aroused by the recrystallization process. No signals are detected for the unground, heated, and fume-treated samples because they are in the crystalline state. Therefore, the luminescent mechanochromism of TPE-DCV is associated with the morphology change between crystalline and amorphous state, which is consistent with that of previous reports.^[15]

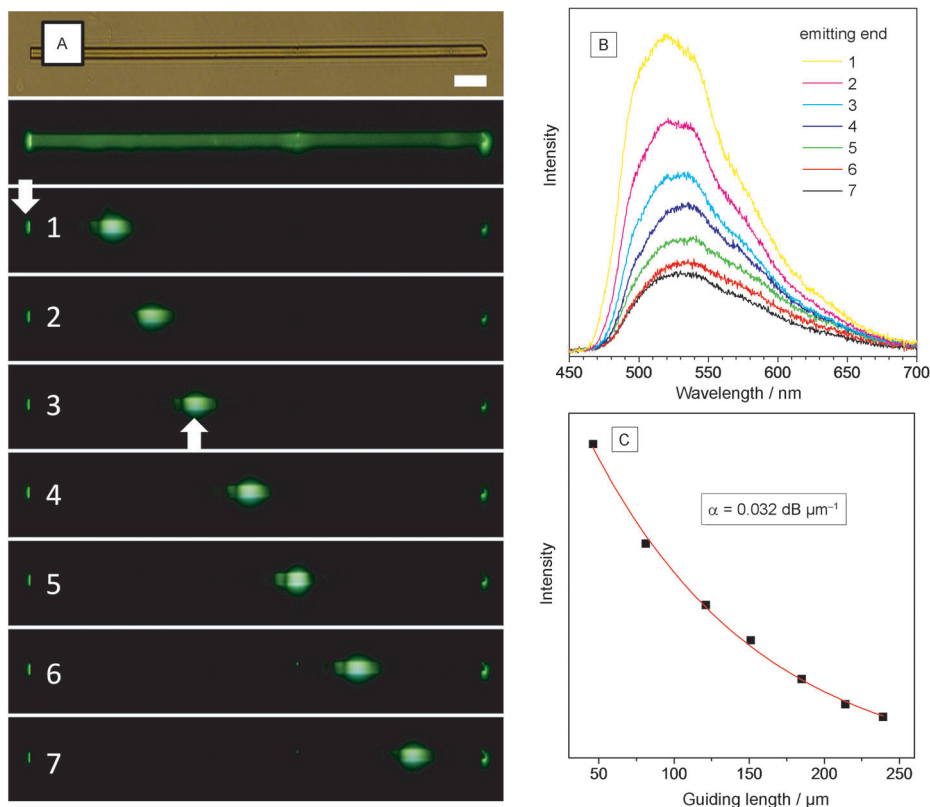


Figure 4. A) Microarea fluorescent images obtained by exciting an identical microrod at different positions, up arrow (excited site) and down arrow (emission tip). Scale bar is $20 \mu\text{m}$. B) Corresponding emission spectra in B. C) Plot of emission intensity value versus length of the waveguide.

Microcrystals can be easily obtained through slow evaporation of TPE-DCV in a dichloromethane/ethanol mixture. Unfortunately, the size of crystal is too small to be analyzed by crystal X-ray diffraction. Under the fluorescent microscope, two shapes (rod and slice) of microcrystal were observed. The fluorescent image is shown in bright green (Figure S4 in the Supporting Information). Furthermore, the distance-dependent fluorescent image of crystalline TPE-DCV was measured by near-field scanning optical microscopy. As shown in Figure 4A, a chosen microrod is excited with a uniform focused laser at seven different positions along the length of the rod, the green light appears at one end of the microrod near to the excited position. This phenomenon is the typical characteristic of a strong waveguide.^[17] With increasing of the distance of the exciting position, the emission intensity at the end is decreased without any shift of emission spectrum (Figure 4B). In this study, the emission intensity at the fixed end (I_{end}) and excited site of microrod (I_{body}) were recorded, and the optical loss coefficient (α) was calculated by a single exponential fitting.^[19] The α value of microrod TPE-DCV is calculated to be $0.032 \text{ dB } \mu\text{m}^{-1}$, which is very low compared with previous reported values.^[17] It is notable that the length of as-prepared microrods is very long, which enables them to be practical optical waveguide materials. The optical waveguiding behavior of a microslice was measured by same method (Figure S5 in the Supporting Information).

The result indicates that the microslice of TPE-DCV also exhibits excellent waveguiding behavior with an α value of $0.079 \text{ dB } \mu\text{m}^{-1}$. As far as we know, this is the first example of two different shapes for one molecule with outstanding optical waveguiding behavior. Negligible reabsorption, well-ordered arrangement, and a smooth surface contribute to their excellent optical waveguiding behavior.

In summary, a yellow AIE luminogen TPE-DCV was synthesized by incorporation of two dicyanovinyl units into a TPE group. The emission of TPE-DCV can be reversibly switched between green and yellow with a moderate contrast ratio by grinding and fuming or heating processes owing to the morphological change between thermodynamically stable crystalline phase and the

metastable amorphous state. Crystalline microrods and microslates of TPE-DCV possess excellent optical waveguiding behavior with very low optical loss. The facile synthesis of TPE-DCV with dual properties may trigger new research enthusiasm for application of AIE luminogens in the photo-electrics field.

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Keywords: aggregation-induced emission • mechanochromism • microcrystals • optical waveguides • tetraphenylethenes

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