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Two different emission enhancement of trans-stilbene crystal under high pressure: Different evolution of structure

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Mechanoresponsive luminescent (MRL) materials have drawn extensive concern due to their potential applications in mechanical sensors, memory chips, and security inks; especially these possessing high emission efficiency. In this work, we found trans-stilbene crystal exhibited two different pressure-induced emission enhancement (PIEE) behaviors at different pressure areas. The structural characterizations combined with density functional theory calculation indicate that the first emission enhancement was due to the decrease of nonradiation transition by the weaken of energy exchange process between atoms and lattice. And the second emission enhancement was attributed to the strengthen of C–H…C interactions from the non-planarization comformation. The results regarding the mechanoresponsive behavior of trans-stilbene offered a deep insight into PIEE from the structural point of view, which will facilitate the design of and search for high-performance MRL materials.

Keywords: pressure-induced emission enhancement, density functional theory, high pressure

PACS: 79.60.–i, 42.70.–a, 91.60.Gf, 82.33.Pt **DOI:** 10.1088/1674-1056/ac20c4

1. Introduction

Mechanoresponsive luminescent (MRL) materials have attracted considerable attention and show potential applications in mechanical sensors, memory chips, and security inks, because of their pressure-induced change of emission color or intensity.[1–5] However, traditional MRL materials always behave weak emission upon exposed to external pressure. That mainly due to pressure-caused sharply increasing of π–π stacking which leads to increase of nonradiative decay.[6–8] Therefore, how to weaken pressure-caused quenching (PCQ) is the key to obtaining high efficiency MRL materials. In the past several years, the pressure-induced emission enhancement (PIEE) behavior has been investigated to solve the low photoluminescence (PL) emission.[9–18] These PIEE phenomena were resulted from the restriction of intramolecular motion, self-trapped exciton, or rehybridization of nitrogen atom, etc. Nevertheless, MRL materials behaved PIEE has been rarely reported so far. The main reason was that there were few feasible design principles. Hence, it is urgently desirable to search and design MRL materials behaved PIEE.

Trans-stilbene is a typical luminogen, in which two phenyl rings are connected by ethylenic bond (Fig. 1(a)).[19] Under ambient conditions, trans-stilbene crystals form a monoclinic structure in the $P21/a$ space group. In one unit cell, there are fourteen molecules which are located at the vertices and face centers of the parallelepiped, respectively. Furthermore, molecules were connected with each other by C–H…H–C and C–H…C interactions (Fig. 1(b)). In the *ab*-plane, the molecules were stacked by 'herringbone' pattern (Fig. 1(c)). The similar packing can be found in carbazole crystal. The molecule arrangement is expected to be modified easily by external stress, thus tuning the optical properties.[20,21]

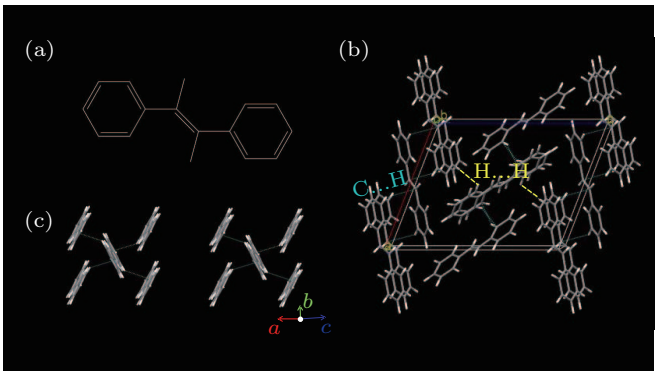


Fig. 1. (a) Chemical structure of trans-stilbene. (b) The packing of trans-stilbene molecules in unit cell. (c) The herringbone packing of trans-stilbene molecules in *ab*-plane.

In this work, the high pressure optical properties of trans-stilbene crystal were explored by *in situ* high pressure PL spectra. And then the dispersive x-ray diffraction (ADXRD), Raman spectroscopy, and theory calculation were performed to explore the mechanisms of pressure-tune optical behavior for trans-stilbene crystal from the structural point of view. PL results showed that trans-stilbene exhibited two different PIEE behaviors at different pressure areas. The experimental structural characterizations demonstrated that the first emission enhancement was due to the decrease of nonradiation transition. And the second emission enhancement was attributed to the

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strengthening C–H…C interactions resulting from the reverse direction change of the aromatic ring. Moreover, the results also were verified by theory calculation. This work investigated the relationship of abnormal optical behavior and the structure for transstilbene under high pressure using experimental and theoretical methods.

2. Experimental processing

2.1. Sample preparation and high-pressure generation

Trans-stilbene was purchased from Alfa Aesar and used as it is. High pressure was generated by a symmetric diamond anvil cell (DAC) with a culet size of 400 μm. The sample was loaded into a 150 μm size hole of the gasket which was preindented to a thickness of 40 μm. In the high-pressure PL, Raman spectra and XRD experiments, the pressure-transition medium (PTM) was the thick CCl_4 (Aldrich).

2.2. Optical measurements

The PL spectra was measured using 355 nm laser and the *in situ* PL photographs of the samples were obtained by the camera (Canon Eos 5D mark II) installed on a microscope (Ecilipse TI-U, Nikon). An Ocean Optics QE65000 spectrometer was used as the optical fiber spectrometer. The filter is 355 nm EdgeBasic^{TM} best-value long-pass edge filter. The light transmittance is zero when the wavelength is below 360.5 nm. However, the light transmittance is above 95%, when the wavelength is beyond 360.5 nm. The high-pressure Raman spectra were measured using an Acton SpectraPro 2500i spectrometer equipped with a liquid nitrogen cooled CCD camera with the excitation light of 532 nm. Photoluminescence quantum yield was measured using an integrating sphere apparatus on an Edinburgh FLS980 fluorescence spectrometer.

2.3. ADXRD measurements

The *in-situ* high-pressure ADXRD experiments of transstilbene were carried out at beamline BL15U1, Shanghai Synchrotron Radiation Facility (SSRF), China. The wavelength is 0.6199 Å. And the standard sample is CeO_2. The ADXRD patterns were collected for 300 s at each pressure.

2.4. Computation details

Geometry optimization for the trans-stilbene at different pressures was performed using the CASTEP package in Materials Studio. In the optimization process, GGA functional of Perdew, Burke, and Ernzerhof was chosen. The nonempirical scheme of the TS was used to correct for the van der Waals interactions common in molecular crystals. The convergence levels for total energy, max force, max stress, max displacement, and SCF iterations were fine. The Hirshfeld surface was calculated to exhibit the intermolecular interactions for transstilbene structure at different pressures, using the Crystal Explorer 3.1 program.

2.5. Results and discussion

Figure 2(a) shown PL spectra of trans-stilbene crystals ranging from 0 GPa to 16.9 GPa. We chose a 355 nm laser as the excitation source in high-pressure PL experiments. Under ambient conditions, solid-state trans-stilbene crystals exhibited a blue emission with several vibronic bands, which were assigned as the π^*–π transition. And the absolute quantum yield of trans-stilbene crystal was 57.37%. Upon compression up to 0.9 GPa, we found that the overall intensity of bands located in the range of 362–455 nm was enhanced. The emission enhancement would be due to the decrease of nonradiative transition.[10,16,17,22–24] The overall intensity gradually decreased when the external pressure was between 0.9 GPa to 4.0 GPa. The intensity decrease would be resulted from the increase of nonradiative transition.[16,17] Surprisingly, when continuously pressurized, the intensity showed a second increase between 4.0 GPa to 7.0 GPa. When the pressure was beyond 7.0 GPa, the intensity gradually decreased. The PL intensity of different bands and wavelength as a function of pressure were exhibited in Fig. 2(b). As can be seen, the PL intensity of different bands behaved complex changes, which demonstrated the complex evolution of the vibrational modes related to S_1 and S_0 vibronic states.[25–27] The change of whole intensity also could be observed by naked eyes, as shown in Fig. 2(c). With the change of intensity, the bands also showed a remarkable red shift (Fig. 2(b)). The red shift phenomenon would be ascribed to the strong coupling between an excited molecule and unexcited adjacent molecules. The strong coupling in the herringbone pattern was resulted from that, with increasing pressure, the intermolecular distances decreased and the molecular planes revolved.[28–30]

Structural characterizations under high pressure would provide information about the change of crystal structure and intermolecular interactions, which would give deep insight into the relationship of structure and optical properties.[31,32] Firstly, *in-situ* high pressure ADXRD patterns were measured to exhibited the change of crystal structure (Fig. 3(a)). As can be seen, the ADXRD patterns over pressures were altered little, except for a normal shift to higher diffraction angles. There was no new peak appearance, which meant that transstilbene crystal did not experience a phase transition during the whole compression up to 16.0 GPa.[33,34] Moreover, upon pressure released, the position of diffraction peaks unchanged. But the diffraction peaks were broadening and the intensity showed a slight reduction, which was attributed to the decrease of crystallinity after compression. Secondly, the *in-situ* high-pressure Raman spectra was measured to explore the imper-

ceptible changes of intramolecular geometry (Fig. 3(b)).[35,36] The modes in the frequency range before 500 cm^{-1} could be easily assigned to the deformation of molecular skeleton.[37] When the pressure was beyond 4.0 GPa, the peak at 118 cm^{-1} disappeared completely and the peak at 247 cm^{-1} (marked by red star) strengthened. Moreover, the band between 3000–3100 cm^{-1} (assigned to C–H stretching) also exhibited two styles.[37] That indicated the intramolecular geometry may be changed. The change of intramolecular geometry would be responsible for the second emission enhancement.

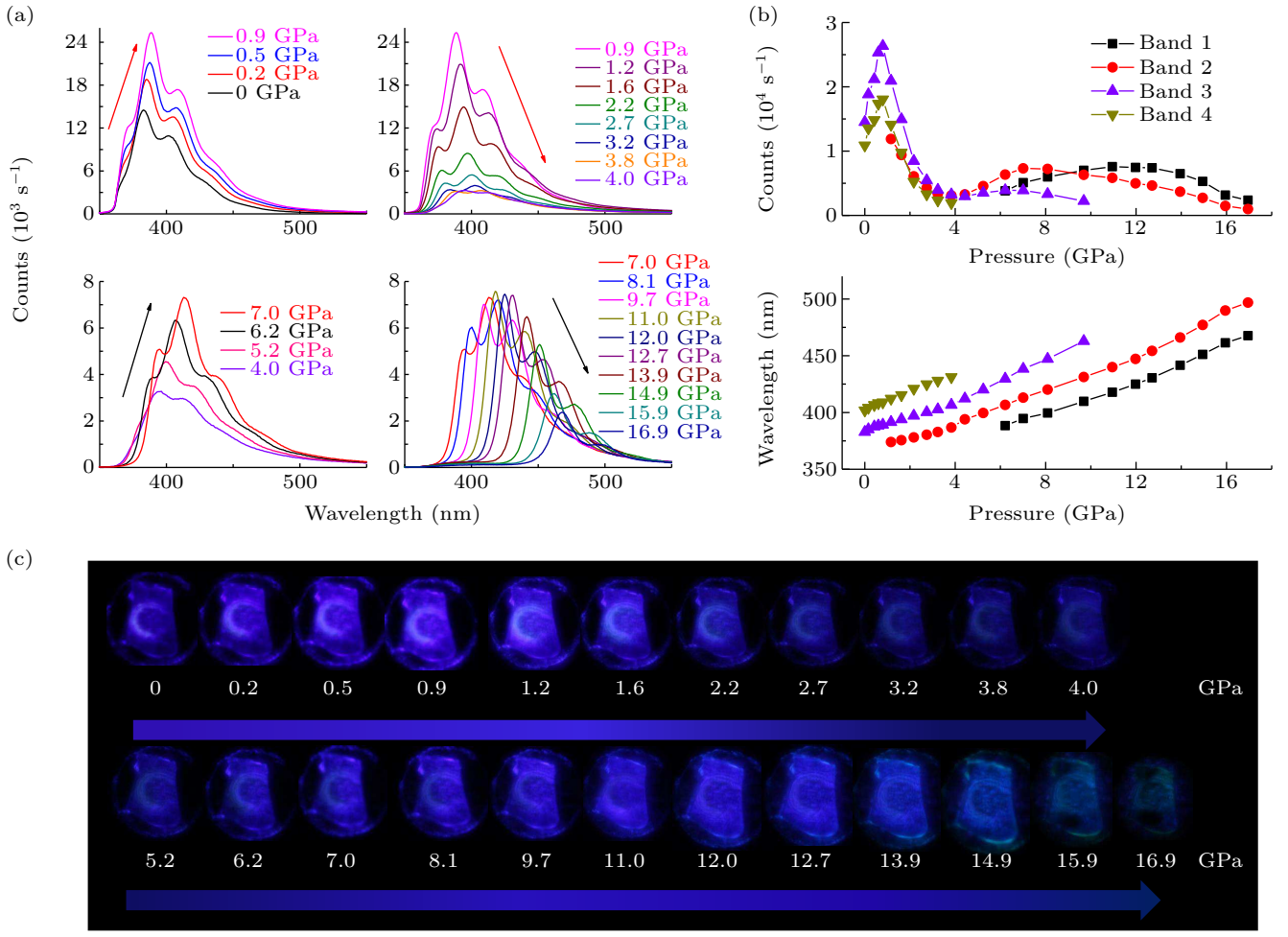


Fig. 2. (a) PL spectra of a trans-stilbene crystal in range of pressures from 0 GPa to 16.9 GPa excited by a 355 nm laser. The arrows represent the changes of the PL intensity. (b) The PL intensity of different bands and wavelength as a function of pressure. (c) Corresponding PL photographs under high pressure.

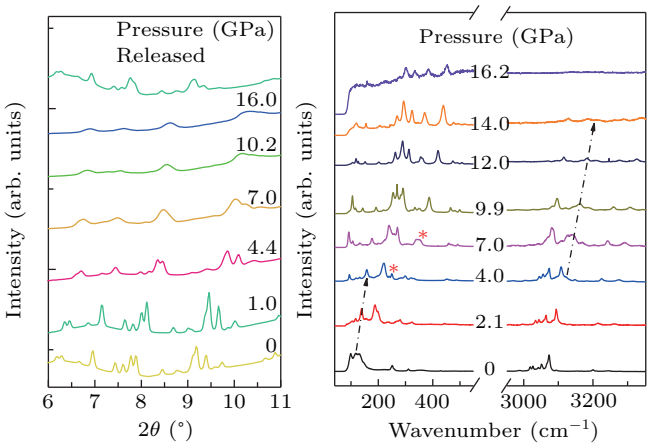


Fig. 3. (a) Selected ADXRD patterns of trans-stilbene at different pressures. (b) Selected high-pressure Raman spectra of trans-stilbene in the range 0–550 cm^{-1} and 3000–3200 cm^{-1}.

Density functional theory (DFT) calculations were performed to give the structure evolution under different pressure and then further verify the change of intramolecular geometry.[38,39] Figure 4 showed the results of change for torsion angle with pressure. As can be seen that the torsion angle kept 3.1° and unchanged until the pressure is up to 0.9 GPa. Therefore, the structure was stable during the process. The stable conformation would result in the weaken of energy exchange process between atoms and lattice, that is, the non-radiative transition decreased. Finally, the radiative transition increased and thus the emission was enhanced. When the pressure is between 0.9 GPa and 4.0 GPa, the angle decreased gradually from 3.1° to 0.8°. That meant the intermolecular distance was shortened so that the compression effect had influence on the molecules. The molecular planarization was responsible for the decrease of PL emission. When the pressure was beyond 4.0 GPa, the phenyl ring tended to the reverse direction and the torsion angle was more and more large

with pressure. The different molecular conformation and decreased degree of planarization would lead to the second emission enhancement.[23,24]

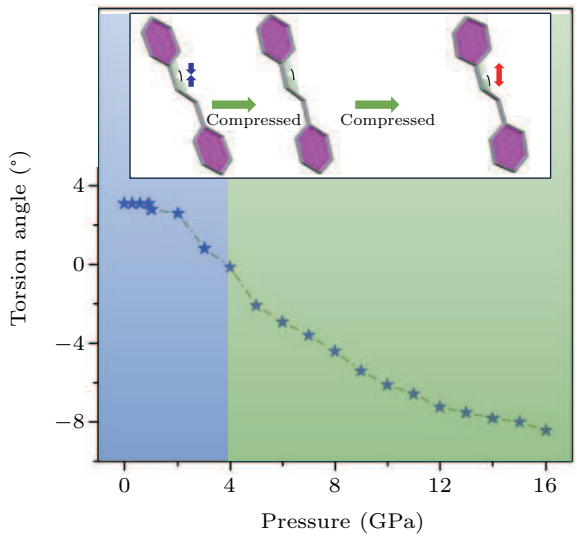


Fig. 4. The change of torsion angle with pressure. Inset is the evolution of structure under high pressure.

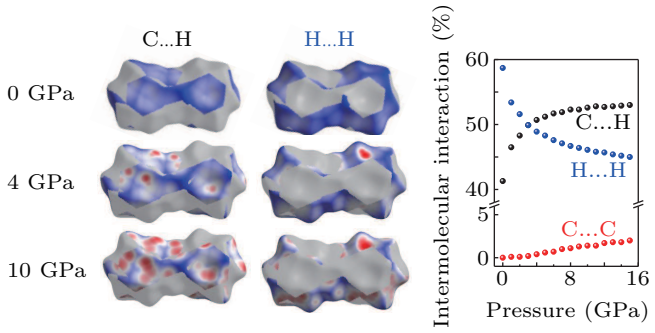


Fig. 5. (a) The position of C…H and H…H interactions on Hirshfeld surface at selected pressure, mapped with a d_{norm} distance. (b) The change of intermolecular interactions percentage under different pressure.

To further verify the change of intermolecular interactions for different structure, the Hirshfeld surface was calculated.[40] Figure 5(a) showed the position of C…H and H…H interactions on Hirshfeld surface at selected pressure, mapped with a d_{norm} distance. As can be seen, the color area representing C…H interactions increased with pressure, however, it representing H…H interactions decreased. That means the percent of C…H interactions increased and it of H…H interactions decreased with pressure. Moreover, the red area become larger when pressure increased, which means the interactions strengthen. This would be responsible for the compressed intermolecular distance upon pressure increasing. Figure 5(b) showed the percent for the main interactions on Hirshfeld surface of different structure. When the pressure was below 4.0 GPa, the percent of H…H interactions were larger than it for the C…H interactions. However, when the pressure was beyond 4.0 GPa, the percent of C…H interactions were larger than it for the H…H interactions. That is, the different molecular conformation led to the larger percent of C…H interactions, which would be the main cause of the second emission enhancement.[14,41] At the same time, the C…C interactions increased rapidly with increasing pressure. When the pressure was beyond 7 GPa, the C…C interactions played the main role, which would responsible for the second decrease of PL emission.[17,20,41]

3. Conclusion and perspectives

In summary, we found that trans-stilbene crystal presented complex emission behaviors under high pressure. The structural characterizations combined with DFT theory calculation have been performed to explore the mechanism. When the pressure was below 0.9 GPa, the emission enhancement was due to the decrease of nonradiation transition by the weaken of energy exchange process between atoms and lattice. When the pressure is between 0.9 GPa and 4.0 GPa, the PL emission decreased. The molecular planarization was responsible for the decrease of emission. When the pressure was between 4.0 GPa and 7.0 GPa, the phenyl ring tended to the reverse direction and the torsion angle was more and more large with pressure. The non-planarization comformation strengthened C–H…C interactions, which led to the second emission enhancement. When the pressure was beyond 7.0 GPa, the C…C interactions increased rapidly, which was responsible for the second decrease of PL emission. The revolving of molecules and the decreased distance between molecules explained the red shift phenomenon of PL spectra. This work has given detailed mechanisms for the distinct pizeoresponsive behavior of trans-stilbene, which would provide an idea of designing and looking for high efficiency MRL materials.

Acknowledgments

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