

Pressure-Induced Emission Enhancement and Multicolor Emission for 1,2,3,4-Tetraphenyl-1,3-cyclopentadiene: Controlled Structure Evolution

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S Supporting Information

ABSTRACT: Mechanoresponsive luminescent (MRL) materials have attracted considerable attention because of their potential applications in mechanical sensors, memory chips, and security inks; MRL materials possessing high efficiency and multicolor emission qualities are especially interesting. In this Letter, we found 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (TPC) crystal exhibited both pressure-induced emission enhancement (PIEE) and multicolor behavior. In addition, infrared spectroscopy analysis indicated that the ring-opening reaction of the phenyl ring occurred when pressure was beyond 24.7 GPa. The reaction was promoted from 24.7 to 35.9 GPa, which resulted in the redder irreversible color change for the sample released from 35.9 GPa than from 24.7 GPa. The results regarding the mechanoresponsive behavior of TPC offered a deep insight into PIEE and multicolor properties from the structural point of view and inspired the idea of capturing different colors by hydrostatic pressure, which will facilitate the design of and search for high-performance MRL materials.



Mechanoresponsive luminescent (MRL) materials, as a kind of smart functional material that can change their luminescence color or intensity upon exposure to external mechanical force like shearing, grinding, or hydrostatic pressure, have attracted considerable attention because of their potential applications in mechanical sensors, memory chips, and security inks.^{1–7} However, traditional MRL materials are usually weakly luminescent when under external pressure, which is attributed to a pressure-caused increase of π - π stacking interactions that results in nonradiative decay.^{8–10} Averting this thorny pressure-caused quenching (PCQ) process is the key to obtaining MRL materials with superior optical properties. Previous studies reported a novel phenomenon of pressure-induced emission enhancement (PIEE): some MRL materials emitted stronger luminescence under high pressure than at ambient conditions.^{11–19} These emission enhancement phenomena can be ascribed to the restriction of intramolecular motion, the change of molecular

populations, or rehybridization of nitrogen atom. In addition, photoluminescence (PL) emission in PIEE systems usually exhibits a small red shift by dozens of nanometers or less under high pressure. This is mainly because most MRL materials easily experience structural or chemical transformation when exposed to higher pressure, which greatly limits its practical application.^{13,20–22} Therefore, designing and discovering more PIEE systems with large red-shift emission under high pressure are urgent needs.

1,2,3,4-Tetraphenyl-1,3-cyclopentadiene (TPC) is a typical luminogen with highly twisted packing.^{23,24} A TPC molecule consists of one cyclopentadiene core and four phenyl rings on the core (Figure 1a). Under ambient conditions, TPC crystals form a monoclinic structure in the $C2/c$ space group. In the ac-

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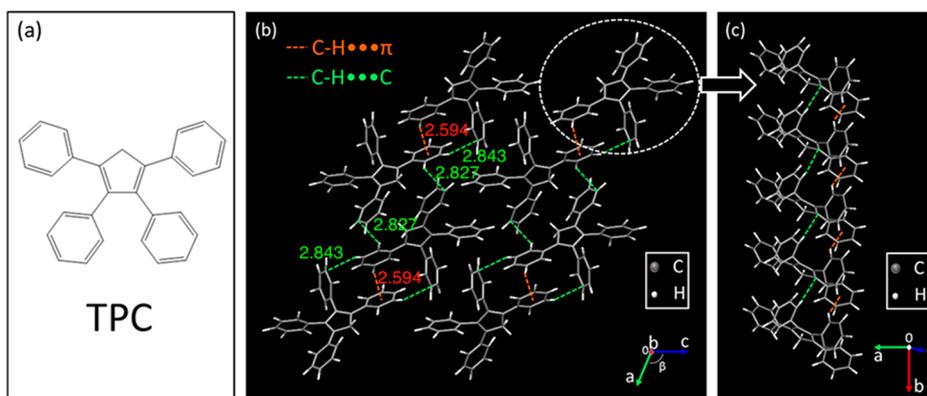


Figure 1. (a) Chemical formula of TPC. (b) Crystal structure of TPC, viewing along the *b*-axis. (c) Packing style along the *b*-axis for the selected TPC molecule in the white circle in panel b. To clarify the packing style along the *b*-axis, only one molecule in the *ac*-plane was selected.

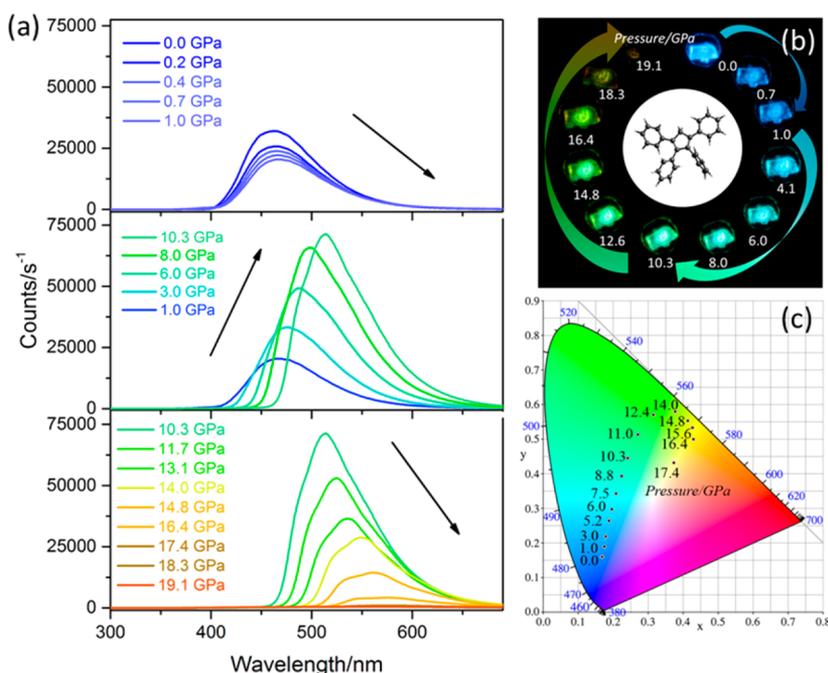


Figure 2. (a) PL spectra of a TPC crystal in pressure ranges from 0.0 to 19.1 GPa excited by a 355 nm laser. The black arrows represent the changes of the PL intensity. (b) Corresponding PL photographs under high pressure. (c) Corresponding 1931 CIE chromaticity diagram of TPC under different pressure.

plane, dispersed molecules were orderly arranged (Figure 1b). Along the *b*-axis, the molecules were stacked in parallel (Figure 1c). Furthermore, molecules were connected with each other by C–H... π and C–H...C hydrogen bonds. The molecule arrangement is expected to be modified easily by external stress, thus tuning the optical properties. Herein, we explored the high-pressure response of TPC with in situ photoluminescence (PL), UV–visible absorption, angle dispersive X-ray diffraction (ADXRD), infrared (IR) spectroscopy, transmission electron microscopy (TEM), and theory calculation. In situ PL data showed that TPC exhibited both PIEE and multicolor emission under high pressure. To further analyze the relationship between properties and structure, the powerful ADXRD, and theory calculation were utilized. The IR data demonstrated that the ring-opening reaction of the phenyl ring occurred when the pressure was beyond 24.7 GPa. Moreover, the different colors of released samples were ascribed to the different degree ring-opening reaction. ADXRD data combined with TEM image verified that the

black sample was an amorphous product. The ¹H-NMR result indicated the amorphous product consisted of amorphous TPC, unsaturated alkenes, and saturated linear alkanes. This Letter provides deep insight into the distinct mechanoresponsive behavior of TPC crystal from the structural point of view and introduces the idea of capturing different color materials by hydrostatic pressure, which could be used for designing high-performance MRL materials with PIEE and multicolor changes.

Under ambient conditions, solid-state TPC exhibited a blue emission with the maximum wavelength (λ_{em}) of 456 nm. The best excitation wavelength (λ_{ex}) was above 414 nm from the excitation spectrum (Figure S1). During the compression process, the PL maximum exhibited a continuous and significant red shift of about 120 nm up to 19.1 GPa (Figure 2a). The pressure-dependent mechano-chromic process of TPC crystal could be observed from the fluorescence photographs. Figure 2b shows the multicolor process, in which the emission color gradually changed from blue to

yellow. The step-by-step migration of emission color through cyan and green to yellow under high pressure is exhibited in the 1931 CIE chromaticity diagram in Figure 2c.²⁵ When the pressure was gradually released to ambient conditions, the PL spectra turned back to the original emission band (Figure S2). Accompanied by the continuous red shift, the intensity also changed markedly. A drastic emission enhancement was observed in the pressure range of 1.0–10.3 GPa, in contrast with the emission decrease in the other two pressure ranges, 0.0–1.0 GPa and 10.3–19.1 GPa. The maximum PL intensity at 10.3 GPa was approximately 3.5-fold higher than that at 1.0 GPa. The abnormal change could also be visualized in fluorescence photographs.

Figure 3 displayed the UV–visible absorption spectra of TPC crystal under high pressure. With increasing pressure, a

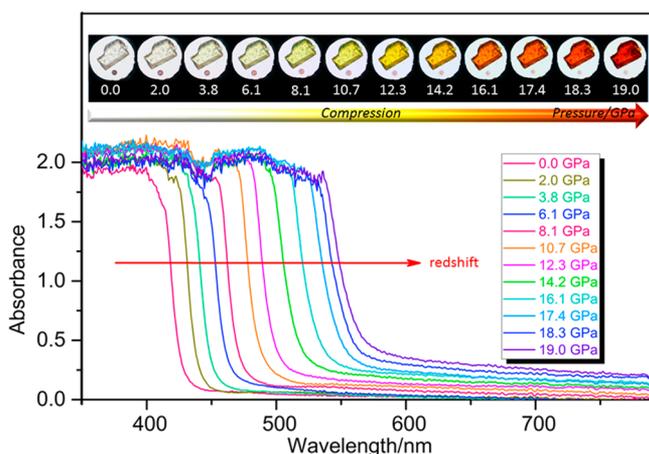


Figure 3. UV–visible absorption spectra and optical images of TPC crystal under high pressure.

distinct red shift was observed, which was in accordance with the large red shift of the PL spectra. The distinct red shift phenomenon could be directly reflected by the change of optical color through colorless, yellow, and orange. The pressure-induced conformational planarization was responsible for the red shift phenomena of propeller-shaped luminogens.^{1,26–28}

To gain insight into the distinct mechanoresponsive luminescence, an in situ high-pressure ADXRD experiment was performed. The ADXRD measurements were able to provide information on the crystal structure under high pressure, which had a significant relationship with its intrinsic properties, such as optical and mechanical properties.^{29,30} Although the changes of PL were obvious, the ADXRD patterns over pressures were altered little, except for a normal shift to higher diffraction angles (Figure S3). The overall observation of the ADXRD experiments indicated that TPC crystal did not experience a phase transition during the whole compression up to 19.4 GPa. Moreover, upon release of pressure, the ADXRD pattern returned back to its original state, which indicated that the compression process was reversible. To further analyze the structural evolution with increasing pressure, we performed Pawley refinements for these ADXRD patterns. The relative change rates of lattice parameters for TPC crystal as a function of pressure up to 19.4 GPa are elucidated in Figure 4a. A large volume collapse of approximately 32% was observed up to 19.4 GPa, which indicated that the original structure was relatively loose. At the

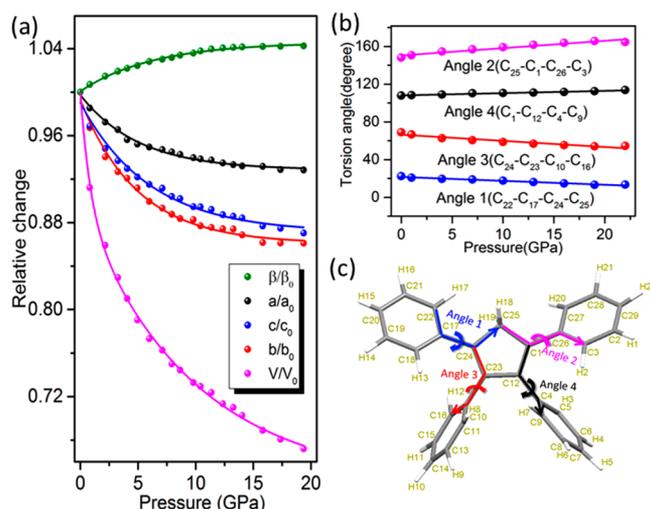


Figure 4. (a) Relative change rate of lattice constants vs. pressure. (b) Torsion angles between the core cyclopentadiene ring and the four different phenyl rings of optimized structure under different pressures. (c) Schematic diagram of structural evolution for TPC molecule under high pressure.

initial stage of compression, the intermolecular distance was too large to form new hydrogen bonds. Therefore, the structure at the initial stage of compression was relatively looser than at any other stage. As a result, the loose molecular arrangement would allow phenyl rings of every TPC molecule to rotate easily at the initial stage of compression. Because the rotation of phenyl rings increased the nonradiative vibrational process, the PL emission decreased at the beginning of compression. With increasing pressure, the molecules packed more and more closely, which meant that intermolecular interactions became stronger. It was also found that the crystal displayed anisotropic compression behavior, with the *b*-axis being the most compressible. According to the molecule arrangement, crystal structure was compressed mostly along the *b*-axis, which meant that the twisted TPC molecules possibly tended to be flattened (this result also can be verified by the following theory calculation). This tendency would be a benefit for the red shift of emission.²⁶

To further explore the relationship between structure and its optical properties, density functional theory (DFT) calculations were carried out to obtain the optimized geometries. The four optimized dihedral angles between the core cyclopentadiene ring and the four different phenyl rings are reported in Figure 4b. Angle 2 and angle 4 increased from 148.22° to 164.79° and from 107.93° to 113.70°, respectively. Angle 1 and angle 3 decreased from 22.44° to 13.42° and from 68.89° to 54.41°, respectively. The changes of these four dihedral angles demonstrated that TPC molecules tended to planarization with increasing pressure (Figure 4c). This evolution of conformation was responsible for the red shift of PL spectra under pressure.^{26,27} Accompanied with the rotation of phenyl rings and compression of volume, the distances between carbon atoms and hydrogen atoms would change. The nearest-neighbor distances between carbon atoms and hydrogen atoms of neighbor TPC molecule has been displayed in Table S1. It is clear that beyond 1 GPa, these H...C distances became shorter than the sum of van der Waals radii of C and H (1.7 and 1.2 Å, respectively, according to Bondi, 1964),³¹ and the angle of C–H...C approached 180°.

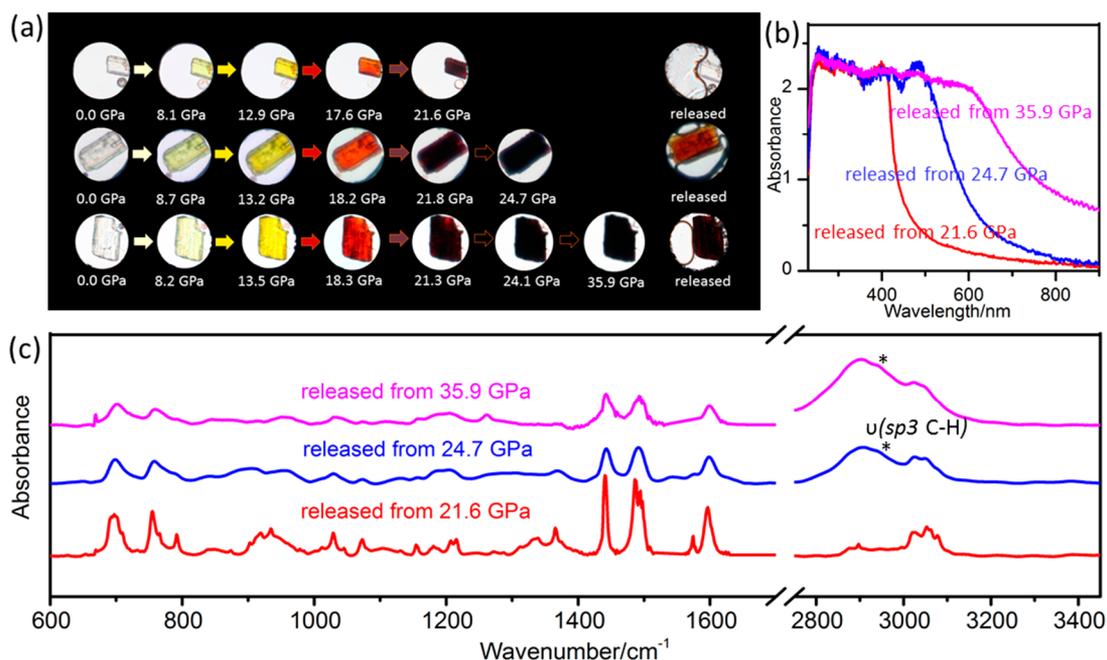


Figure 5. (a) Selected photographs of TPC crystals for three contrast experiments up to 21.6, 24.7, and 35.9 GPa, respectively. The bubbles in released photographs indicate that the pressure was released completely. (b) UV–visible absorption spectra of TPC crystals under ambient conditions and released from 21.6, 24.7, and 35.9 GPa. (c) IR spectra of TPC samples released from 21.6, 24.7, and 35.9 GPa.

The fact demonstrated that the C20–H15...C14, C22–H17...C29, and C6–H4...C2 hydrogen bonds formed.^{32–34} The formation of new hydrogen bonds restricted the rotation of aromatic parts. The energy for nonradiative vibrational transition decreased, resulting in the emission enhancement in the pressure range of 1–10 GPa.³⁵ With increasing pressure, the $\pi\cdots\pi$ interactions increased markedly (Figure S4). That would be responsible for the quenched emission.^{8,36}

Hirshfeld surface theory calculations were carried out to verify the effect of intermolecular interactions on PL emission. As shown in Table S2, the evolution of H...C intermolecular interactions were clearly exhibited on the Hirshfeld surface under elevated pressure. At ambient conditions, the red areas which represented strong interactions were produced by C–H...C hydrogen bonds. When compression began, the red regions were enlarged, which meant that initial interactions became strong. However, upon further compression, more new red regions appeared. This indicated that more hydrogen bonds were formed between adjacent molecules, which was in accordance with the results above. Therefore, new hydrogen bonds restricted the rotation of phenyl rings, which was responsible for the emission enhancement.

Upon further compression, the intermolecular distance became much smaller. In order to explore the effect of molecular arrangement on optical properties, tUV–vis absorption experiments were performed. Figure 5a presents three sets of selected photographs resulting from three different experiments, the pressure maximum of which was 21.6, 24.7, or 35.9 GPa. The detailed color evolutions of the three experiments are displayed in Figures S5–S7. When compressed, the color of TPC crystals changed from colorless to yellow, orange-red, and black, and the process of color change could be well-reproduced in different experiments. Upon releasing the pressure completely, only the sample released from 21.6 GPa turned back to the original color. However, an irreversible change occurred when pressure was

beyond 24.7 GPa, and it was intriguing that the color of the sample released from 35.9 GPa was deeper than from 24.7 GPa. The UV–visible absorption spectra are exhibited in Figure 5b. The IR spectra of the TPC samples released from 21.6, 24.7, and 35.9 GPa were displayed to investigate the local structural information (Figure 5c). A shoulder peak at ~ 2920 cm^{-1} (marked by asterisk) appeared in the sample released from 24.7 GPa, and the peak became stronger in the sample released from 35.9 GPa. According to previous studies, the appearance of this peak would be direct evidence to support the ring-opening reaction of phenyl ring, and the strengthening of the peak for sample released from 35.9 GPa indicated that the ring-opening reaction was promoted. Moreover, we can easily evaluate the percentage of samples that experienced reaction when the pressure was beyond 24.7 GPa ($\sim 36.4\%$) and 35.7 GPa ($\sim 56.5\%$).^{37–39} Therefore, the pressure-induced reaction promotion well explained the obvious red-shift behavior of UV–visible absorption spectra for TPC crystals released from 24.7 and 35.9 GPa.

The theory calculation results also verified the relationship between ring-opening reaction and the optical properties. Figure S8 showed that one TPC molecule (yellow) was surrounded by five nearest-neighbor molecules. Table S3 lists the changes of distances between carbon atoms on the center molecule and carbon atoms on nearest neighbor molecules with increasing pressure. All these distances gradually decreased when compressed. Previous experimental and theoretical studies have confirmed that the pressure-induced ring-opening reaction in benzene could be triggered only when the nearest intermolecular C...C distance approaches ~ 2.6 Å.^{37,38} In the TPC system, it could be found that the C27(1)...C27(2) distance first dropped to 2.6 Å at 25.0 GPa. Then the C7(1)...C29(6) and C29(1)...C7(6) dropped close to 2.6 Å at 36.0 GPa (Table S3). This indicated that the ring-opening reaction may occur on the site C27(1) and C27(2), C7(1)...C29(6), and C29(1)...C7(6).

To further investigate the recovered samples, we performed synchrotron ADXRD, high-resolution TEM, and ¹H-NMR spectroscopy. The ADXRD data in Figure S9 exhibited that the orange-red sample released from 25 GPa was a mixture of TPC crystals and an amorphous sample, and the black sample was in a completely amorphous state. The high-resolution TEM image selected area electron diffraction pattern in Figure S10 indeed verified that the black sample was an amorphous product. The similar amorphous state could also be found in previous studies about the benzene ring-opening reaction product.^{37–40} In Figure S11, the ¹H-NMR result indicated the amorphous product consisted of amorphous TPC, unsaturated olefin, and saturated linear alkanes. The possible structures are listed in Tables S4 and S5.

In summary, the pressure-tuned structure and optical properties of TPC crystals were systematically investigated by in situ high-pressure PL experiments, UV–visible absorption, ADXRD, IR spectroscopy, high-resolution TEM, and DFT calculations. The TPC crystals exhibited both PIEE and multicolor behavior under high pressure. Structural analysis demonstrated that PIEE in the range of 1–10 GPa was due to the restriction of intramolecular rotation by new C–H···C hydrogen bonds. Beyond 10 GPa, the $\pi\cdots\pi$ interactions dramatically quenched the emission. With increasing pressure, the four different phenyl rings in the TPC molecule rotated to the plane of core cyclopentadiene ring, which was responsible for the multicolor emission. According to the IR data combined with DFT theory calculation, when pressure was beyond 24.7 GPa, the ring-opening reaction of the phenyl ring occurred and resulted in the irreversible optical changes. Further analysis indicated that the orange-red sample released from 25 GPa was a mixture of TPC and an amorphous sample, and the black sample released from 36 GPa was a completely amorphous product. Moreover, the amorphous product was a mixture of amorphous TPC, unsaturated alkenes, and saturated linear alkanes. This work shed light on the optical response of TPC crystals to pressure from the view of structure, which will facilitate the design of and search for high-performance MRL materials. Moreover, the linear alkanes may be the major constituents of petroleum, which revealed a possibility that aromatic compounds may convert to petroleum after high-pressure treatment and provided a possible mechanism for the formation of petroleum.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcl.9b02206.

Experimental and calculation details; excitation spectrum; PL spectra; ADXRD patterns at different pressure; calculated nearest-neighbor distances between carbon atoms and hydrogen atoms of neighbor molecule; Hirshfeld surface of calculated structure; 2D fingerprint plots of calculated structures under different pressure; optical color evolution under high pressure; packing of a center TPC molecule surrounded by five nearest-neighbor molecules; distances between carbon atoms on the center molecule and carbon atoms on nearest-neighbor molecules with increasing pressure; ADXRD patterns; high-resolution TEM image; ¹H-NMR spectra; possible structure of recovered sample (PDF)

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Notes

The authors declare no competing financial interest.

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