

## Drastic Photoluminescence Shift of an Organic Molecular Crystal Modulated with High Pressure

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Complete List of Authors:	<p>Guan, Junjie; Tianjin University, School of Chemical Engineering and Technology  Zhang, Chunfang; Hebei University  Gao, Dexiang; a. Center for High Pressure Science and Technology Advanced Research  Tang, Xingyu; a. Center for High Pressure Science and Technology Advanced Research  Dong, Xiao; Nankai University, Key Laboratory of Weak-Light Nonlinear Photonics, School of Physics  Lin, Xiaohuan; a. Center for High Pressure Science and Technology Advanced Research  Wang, Yajie; Center for High Pressure Science and Technology Advanced Research  Wang, Xinxin; Center for High Pressure Science and Technology Advanced Research  Wang, Lin; Center for High Pressure Science &amp; Technology Advanced Research ,  Lee, Hyun Hwi; Pohang Accelerator Laboratory,  Xu, Jialiang; Nankai University, School of Material Science and Engineering; Collaborative Innovation Center of Chemical Science and Engineering,  Zheng, Haiyan; Center for High Pressure Science and Technology Advanced Research,  Li, Kuo; Center for High Pressure Science and Technology Advanced Research,  Mao, Ho-Kwang; Center for High Pressure Science and Technology Advanced Research,</p>

## ARTICLE

## Drastic Photoluminescence Modulation of an Organic Molecular Crystal with High Pressure

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Junjie Guan,<sup>a,b</sup> Chunfang Zhang,<sup>c</sup> Dexiang Gao,<sup>b</sup> Xingyu Tang,<sup>b</sup> Xiao Dong,<sup>d</sup> Xiaohuan Lin,<sup>b</sup> Yajie Wang,<sup>b</sup> Xinxin Wang,<sup>b</sup> Lin Wang,<sup>b</sup> Hyun Hwi Lee,<sup>e</sup> Jialiang Xu,<sup>\*a,f</sup> Haiyan Zheng,<sup>\*b</sup> Kuo Li,<sup>b</sup> and Hokuang Mao<sup>b</sup>

Pressure is an effective method to modulate the optical properties of organic solid-state light-emitting materials through enhancing intermolecular interactions and/or generating new polymorphs. Herein, we find that the organic molecular crystal of diphenylfluorenone (DPFO) undergoes large-scale and continuous red-shift of UV-vis absorption and photoluminescence (PL) spectra under high pressure, across the entire visible light region. Remarkably, a red-shift of about 300 nm was observed for its PL peak at 13.32 GPa, from greenish-yellow to the near-infrared (NIR) region. The *in situ* high-pressure IR spectra and synchrotron X-ray diffraction (XRD) analyses suggest a phase transition from the  $\alpha$ - to the  $\gamma$ -phase (newly identified) at around 3 GPa, accompanied by the phenyl unit in DPFO converting from perpendicular to parallel packing. Theoretical calculations show that the enhanced  $\pi\cdots\pi$  interactions and the overlap of the molecular orbitals in the  $\gamma$ -phase are responsible for such a tremendous red-shift in the PL spectra. Our work highlights the large red-shift phenomenon in the DPFO system under high pressure, which may have potential photonic device applications. Furthermore, the work reveals the clear structure-property relation, providing deep insight into the tailor of the optical characteristics of molecular materials.

### Introduction

Organic solid-state light-emitting materials, whose luminescence can be tuned by external stimuli, have attracted considerable research interest for their potential applications in optical storage, sensors, multi-colour displays and security papers.<sup>1-5</sup> The optical properties of these materials are not only related to the photoactivity of the molecular building blocks, but also the packing modes of these luminescent molecules.<sup>6-8</sup> By using traditional methods such as solution-processed self-assembly<sup>9,10</sup> or co-crystal strategy,<sup>11</sup> different crystal structures can be obtained from the same molecules, i.e., polymorphs, which is an effective method to tailor their luminescent properties.<sup>12-13</sup> Recently, the fast-developed high-pressure technologies provide an effective method to generate

new polymorphs, and thus, to modulate the luminescent properties by changing the molecular arrangements.<sup>14-16</sup> Due to enhanced intermolecular interactions or restricted molecular vibrations under high pressure, red-shift and/or increased emission intensity have been observed under such extreme conditions.<sup>17,18</sup> For example, by compressing the anthracene derivative, a red-shift of 100 nm was observed due to the enhanced intermolecular  $\pi\cdots\pi$  interactions.<sup>19</sup> Zou et al. reported that pressure could induce the tautomerization of spiroopyran, resulting in a red-shift over 190 nm of the luminescence.<sup>20,21</sup> The increased N-H $\cdots\pi$  interaction and the restriction of the N-H stretching vibration were responsible for the pressure-induced emission enhancement (PIEE) phenomenon detected in the carbazole system.<sup>22</sup> In this context, discovering and designing new pressure responsive systems and understanding the relationship between their photophysical properties and packing modes is extremely important for advancing their applications in diverse fields, such as optical pressure-sensing devices.

Diphenylfluorenone (DPFO), featuring a typical supramolecular structure with molecular chains held together by hydrogen bonds and C-H $\cdots\pi$  interactions, exhibits brilliant nonlinear optical properties.<sup>23</sup> It can readily be grown into large crystals for THz generators and detectors through simple solution processes at ambient conditions.<sup>24</sup> The limited rotation of DPFO upon aggregation results in a dramatic

<sup>a</sup> School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China. Email: jialiang.xu@tju.edu.cn

<sup>b</sup> Center for High Pressure Science and Technology Advanced Research (HPSTAR), Beijing 100094, China. E-mail: zhenghy@hpstar.ac.cn

<sup>c</sup> College of Chemistry and Environmental Science, Hebei University, No.180 Wusidong Road. Baoding 071002, Hebei, P. R. China.

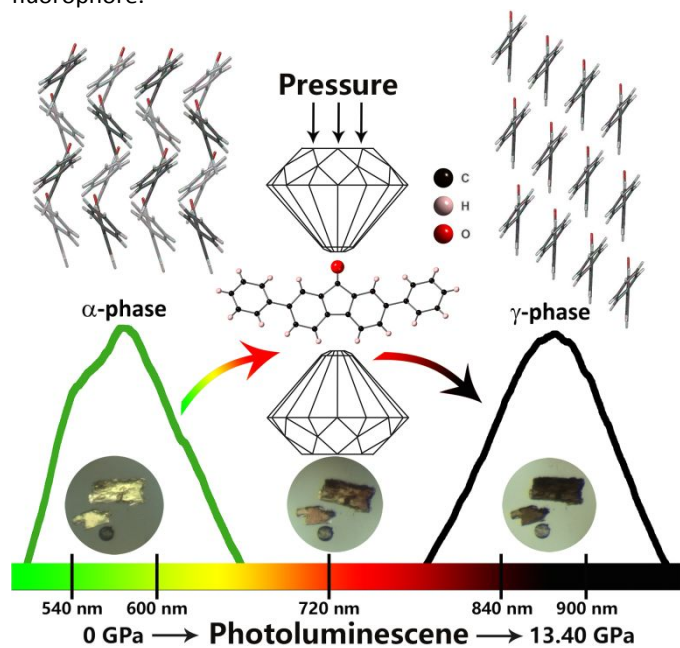
<sup>d</sup> Key Laboratory of Weak-Light Nonlinear Photonics, School of Physics, Nankai University, Tianjin 300071, China.

<sup>e</sup> Pohang Accelerator Laboratory, POSTECH, Pohang 790-784, Republic of Korea.

<sup>f</sup> School of Materials Science and Engineering, Nankai University, Tianjin 300350, China. Email: jialiang.xu@nankai.edu.cn

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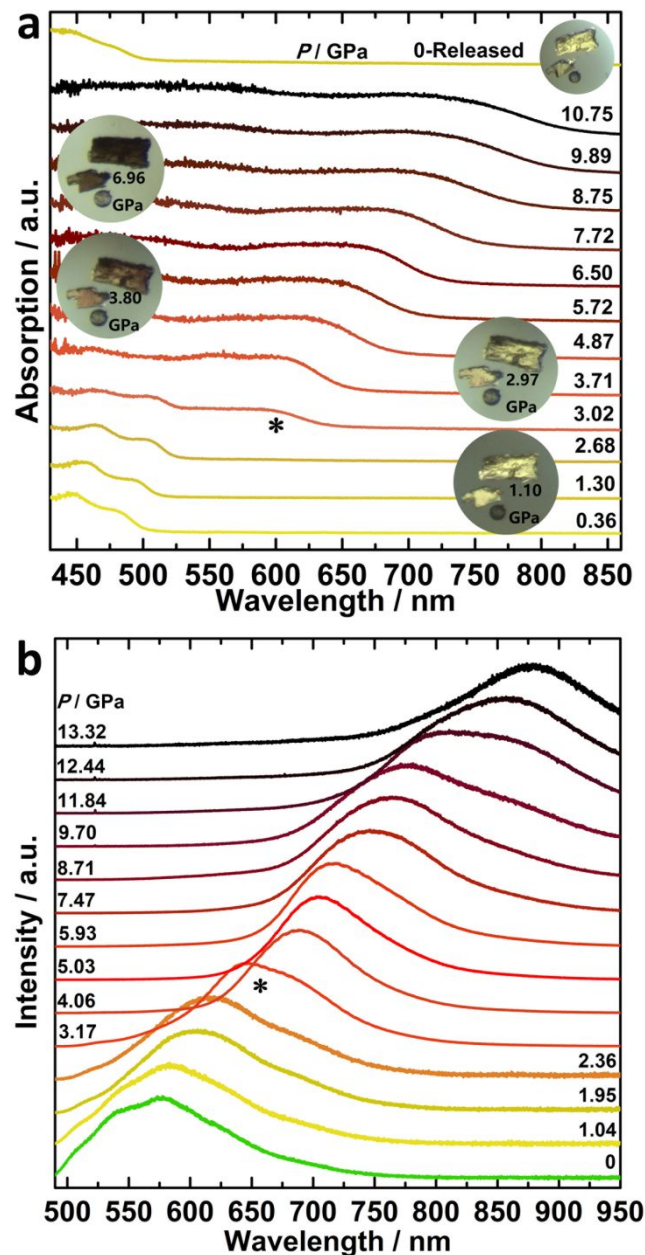
enhancement of the linear optical emission when forming self-assemblies.<sup>23,25</sup> By controlling operation conditions such as temperatures and solvents, DPFO can form two different polymorphs, namely the  $\alpha$ -phase (orthorhombic, space group  $Ccm2_1$ ) and the  $\beta$ -phase (orthorhombic, space group  $Pbca$ ), which show very different linear and nonlinear optical responses.<sup>9</sup> In this work, we applied high pressure to tailor the molecular configuration and packing modes, and therefore, modulate the optical properties of DPFO-based molecular crystals. By compressing the DPFO crystals, a colour change from yellow to dark red and a drastic and consecutive luminescence shift ( $\sim 300$  nm) was observed upon the application of high pressure ( $> 10$  GPa) (Scheme 1). The maximum emission wavelength reached 875 nm, which was in the NIR region. *In situ* IR and synchrotron X-ray diffraction (XRD) measurements suggest the generation of a new phase (referred to as the  $\gamma$ -phase) at the high pressure above 3 GPa. In this new phase, the phenyl rings turned from perpendicular packing to parallel packing, which enhanced the  $\pi\cdots\pi$  interactions. Theoretical calculations reveal that the formation of the strong face-to-face stacking of the DPFO molecules results in the orbital overlap between neighboring molecules, which can be responsible for the massive red-shift of the UV-vis absorption and the corresponding photoluminescence spectra. Our studies highlight pressure as an effective technique to fine-tune the optical properties of molecular crystalline materials by generating new polymorphs. The closed packing structure under high pressure will lead to a large-scale red-shift which is very difficult to achieve by other stimuli. The clear relationship between the high pressure crystal structure and corresponding optical properties indicated here will contribute to understanding the conformation, structure and luminescence characteristics of fluorophore.



**Scheme 1** The relationship between the optical properties and the crystal structures of DPFO crystals under high pressure.

## Results and discussion

### *In situ* high-pressure UV-vis absorption and photoluminescence spectra

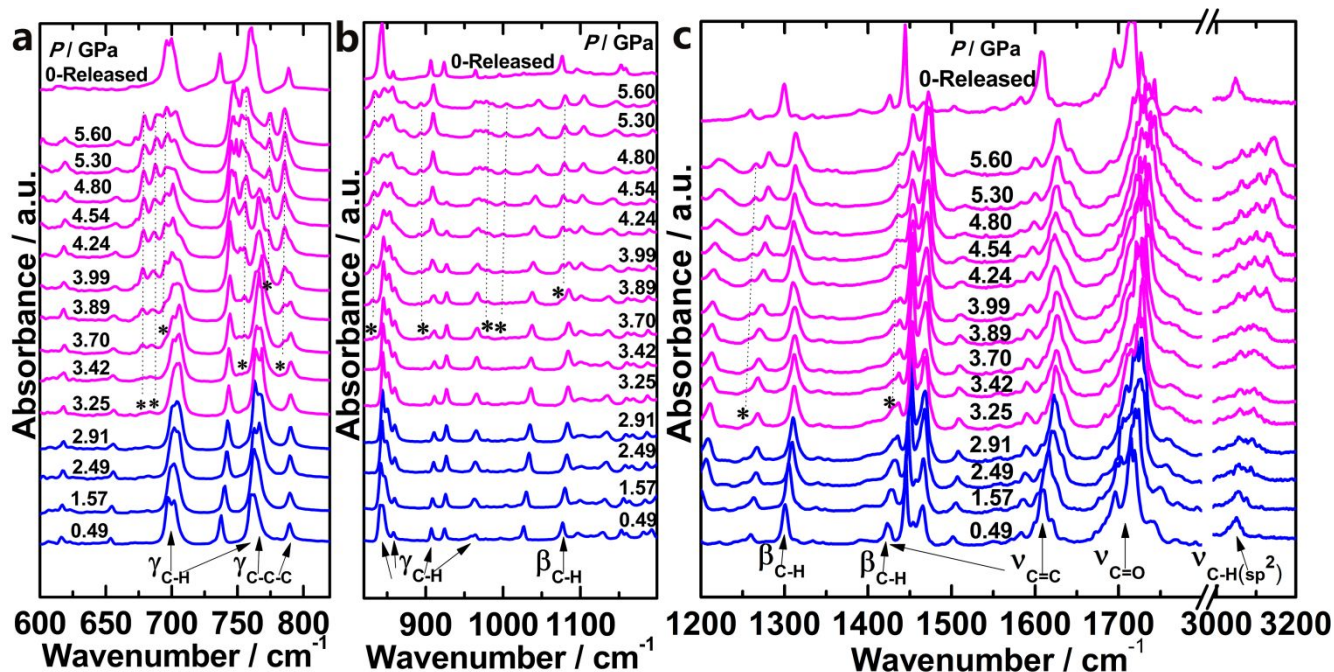


**Fig. 1** *In situ* UV-vis absorption and photoluminescence (PL) spectra of DPFO under high pressure (asterisk in the UV-vis spectra represents the observed new peak and that in the PL spectra represents the jump of red-shift). The "0-released" in UV-vis absorption spectra corresponds to the spectrum of DPFO released from 10.75 GPa. The insets in (a) are the optical images obtained from the microscope under compression (the black ball is a ruby ball for pressure measurement).

Pressure is a straightforward and effective way to regulate the optical properties of materials. As shown in the insets of Fig. 1a, the colour of the DPFO crystal is yellow with good transparency at 1.10 GPa. When compressed, it turned pale red at 2.97 GPa and finally to dark red at 6.96 GPa. Correspondingly, the UV-vis absorption spectra showed obviously red-shift upon increasing pressure. At 0.36 GPa,



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**Fig. 2** IR spectra of DPFO crystal with increasing pressure from 0.49 GPa to 5.60 GPa and decompressed from 5.60 GPa (0-released). The new peaks are indicated by the asterisks. (a) 600–820  $\text{cm}^{-1}$ , (b) 820–1200  $\text{cm}^{-1}$  and (c) 1200–3200  $\text{cm}^{-1}$ .

the main absorption peak was around 475 nm, which red-shifted upon compression. At 3.02 GPa, a new broad peak centered at 575 nm was observed, which resulted in the colour change from yellow to red (Fig. 1a). Upon further compression, this peak became broader and shifted to the longer wavelength region continuously, and finally crossed the entire visible light region at 10.75 GPa. Upon decompression to ambient pressure, the absorption spectra recovered to their original state, which provided the evidence for the reversible variation. Selected photoluminescence (PL) spectra under high pressure are shown in Fig. 1b. At ambient pressure, the emission band was centered at 575 nm. This maximum luminescence peak ( $\lambda_{\text{max}}$ ) gradually red-shifted during compression. At 3.17 GPa, a sudden red-shift jump was observed, corresponding to the new absorption peak, as shown in the UV-vis absorption spectra. Eventually, the luminescence peak  $\lambda_{\text{max}}$  reached 875 nm at 13.31 GPa, in the near-infrared region. Such a large wavelength variation of 300 nm in the luminescence spectra is rarely achievable with other stimuli. Additionally, the intensity of the photoluminescence gradually decreased during compression up to 13.31 GPa (Fig. S1). The enhancement of intermolecular interaction with increasing pressure is likely to be the reason for the red-shifted of the emission band and decrease of the PL intensity.<sup>22</sup> The new peak presented in the UV-vis absorption spectra and the sudden change of PL spectra indicate a phase transition at

around 3 GPa. Variations of the molecular conformation and aggregation under high pressure need to be investigated to understand this drastic change of optical properties in DPFO and its phase transition mechanism.

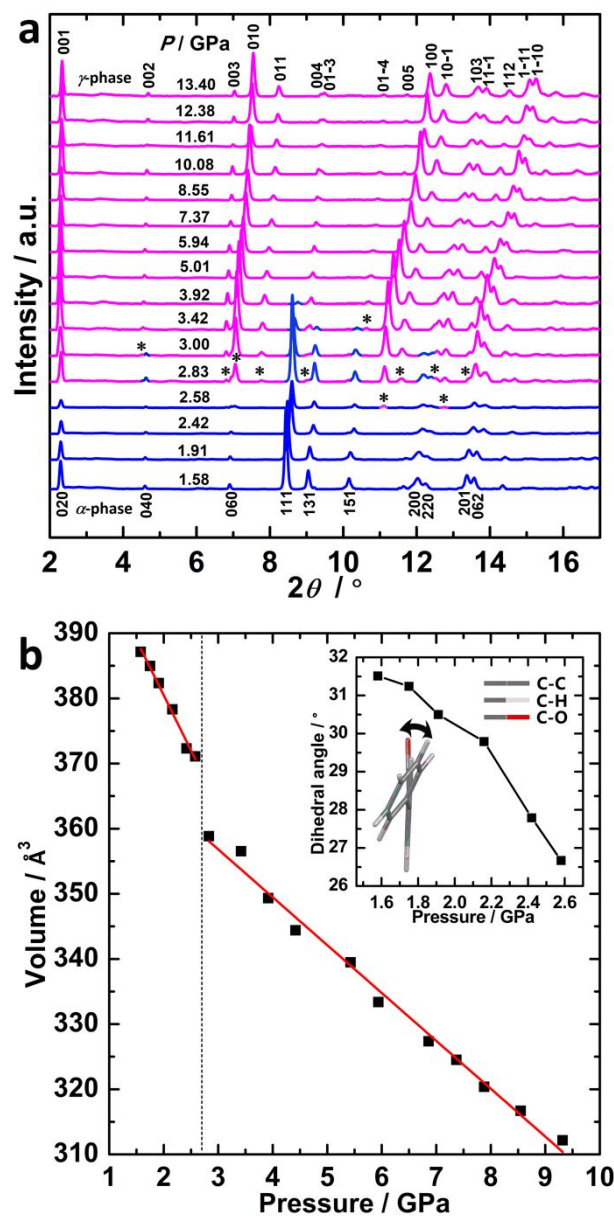
#### *In situ* high-pressure IR spectra

*In situ* IR spectra were used to clarify this phase transition. The evolution of IR spectra at various pressures is shown in Fig. 2. At ambient pressure, DPFO crystallized into an orthorhombic phase ( $C_{2m}2_1$ , the  $\alpha$ -phase) and the assignments of the DPFO IR modes are summarized in Table S1. By compressing the DPFO crystals from 0.49 to 2.91 GPa, most of the IR peaks revealed blue-shift without the appearance of new peaks (Fig. 2a, 2b and 2c). Specifically, the C-H stretching vibration ( $\nu_{\text{C-H}}$ ) band at 3048  $\text{cm}^{-1}$  blue-shifted and split upon compression, which indicated the compression of the C-H bond and a change of the complex  $\text{CH}\cdots\pi$  interaction under high pressure. At 3.25 GPa, three new IR peaks (675  $\text{cm}^{-1}$ , 680  $\text{cm}^{-1}$  and 1255  $\text{cm}^{-1}$ ) appeared in the low-frequency regions of the C-H out-of-plane bending vibration ( $\gamma_{\text{C-H}}$ ) and C-H in-plane bending vibration ( $\beta_{\text{C-H}}$ ), respectively. Meanwhile, the vibration at 1430  $\text{cm}^{-1}$  corresponding to the C-H in-plane bending vibration ( $\beta_{\text{C-H}}$ ) and C=C stretching ( $\nu_{\text{C=C}}$ ) split. At 3.42 GPa, two new peaks appeared at 754 and 784  $\text{cm}^{-1}$ , and their intensities were enhanced with increasing pressure. At 3.70 GPa and 3.89 GPa, a batch of new peaks was observed at 694, 832, 901, 981, 998

and  $1076\text{ cm}^{-1}$ . In addition, the peaks of the  $\alpha$ -phase at  $697$ ,  $760$ ,  $788$ ,  $924$ ,  $1075$ , and  $1422\text{ cm}^{-1}$  gradually degraded and were barely detectable above  $3.99\text{ GPa}$ . The non-monotonic changes of the IR modes in the pressure range of  $3.42$ – $3.99\text{ GPa}$  were also observed (Fig. S2). All of these changes indicate a phase transition starting at  $3.25\text{ GPa}$  and finishing at  $3.99\text{ GPa}$ , which is consistent with the evolution of the optical properties observed in the UV-vis and PL spectra. This new phase is quite different from the  $\beta$ -phase obtained using the solvent method, as indicated by the X-ray diffraction described below.<sup>9</sup> Thus, this new phase hereafter is referred to as the  $\gamma$ -phase. The IR spectrum of DPFO recovered from  $5.60\text{ GPa}$  is similar to the original state, which means that the phase transition from the  $\alpha$ - to the  $\gamma$ -phase is fully reversible.

### Synchrotron X-ray diffraction results and structural evolution

To obtain detailed information on the structural evolution and symmetry change of DPFO crystals under high pressure, we performed synchrotron X-ray diffraction (XRD) experiments. The blue and pink peaks in Fig. 3a correspond to the  $\alpha$ -phase and  $\gamma$ -phase, respectively. The patterns detected at  $1.58\text{ GPa}$  fitted well to the  $\alpha$ -phase by Rietveld Refinement starting from the model reported in the literature (Fig. S3).<sup>23</sup> The peaks of the  $\alpha$ -phase with  $Ccm2_1$  group was clarified by Miller indices. The XRD profile changed significantly above  $2.58\text{ GPa}$ . Two new diffraction peaks ( $100$  and  $11-1$ , marked by asterisks) emerged at around  $11.1^\circ$  and  $12.8^\circ$ , which indicated the onset of the phase transition. At  $2.83\text{ GPa}$ , a batch of new diffraction peaks were observed and later indexed as  $003$ ,  $010$ ,  $011$ ,  $004$ ,  $01-3$ ,  $10-1$ ,  $103$  and  $112$ . At  $3.00$  and  $3.42\text{ GPa}$ , two new peaks ( $002$  and  $01-4$ ) appeared at around  $4.5^\circ$  and  $10.6^\circ$ , respectively. Meanwhile, peaks of the  $\alpha$ -phase were hardly detectable above  $3.92\text{ GPa}$ . All these indicate the  $\alpha$ - to  $\gamma$ -phase transition of DPFO began at  $2.58\text{ GPa}$  and finished above  $3.92\text{ GPa}$ . During the  $\alpha$ - $\gamma$  phase transition, the averaged single molecular volume collapsed from  $371\text{ \AA}^3$  (at  $2.58\text{ GPa}$ ) to  $358\text{ \AA}^3$  (at  $2.83\text{ GPa}$ ) (Fig. 3b), and the space group turned from  $Ccm2_1$  to  $P1$ . The XRD pattern of the  $\gamma$ -phase was indexed ab initio (by software PowderX)<sup>26</sup> with a triclinic lattice of  $a = 3.4062(7)\text{ \AA}$ ,  $b = 5.5126(15)\text{ \AA}$ ,  $c = 17.434(6)\text{ \AA}$ ,  $\alpha = 98.34(3)^\circ$ ,  $\beta = 85.84(2)^\circ$ , and  $\gamma = 84.218(14)^\circ$ . The crystal structure was then solved using a simulated annealing method and Rietveld refinement (Fig. S4). The solved structural model as shown in Fig. 4a suggests the molecules were highly restrained and densely packed in the  $\gamma$ -phase (Fig. 4b). The planar fluorenone groups were aligned in the same direction, and all of the phenyl groups were also aligned parallelly. Hence, the  $\gamma$ -phase of the DPFO crystal contains strong face-to-face  $\pi\cdots\pi$  aromatic interactions,<sup>27</sup> which promotes the formation of long-wavelength absorption and emission.<sup>28,29</sup> This is in significant contrast to the structure of the  $\alpha$ -phase. In the  $\alpha$ -phase, both the phenyl and fluorenone groups are perpendicular or formed a certain angle to their neighbors owing to the  $\text{CH}\cdots\pi$  interaction. Before the phase transition, the dihedral angle (inset in Fig. 3b) between the phenyl group and the fluorenone group decreased and resulted in a better molecular co-planarity, which was responsible for the red-shift of

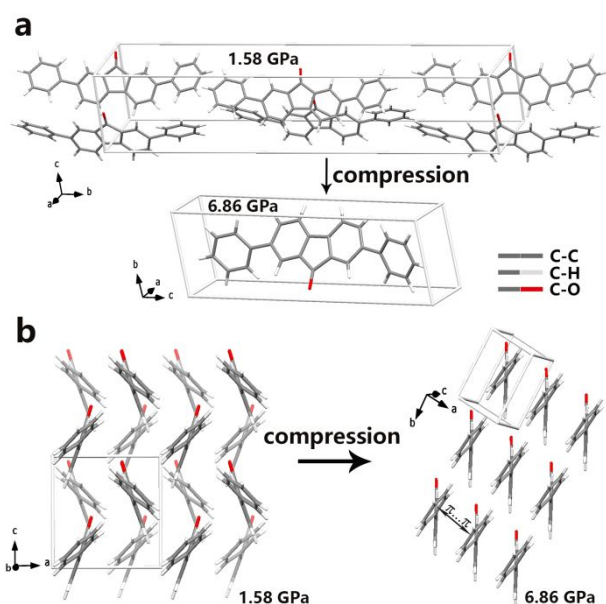


**Fig. 3** (a) Synchrotron X-ray diffraction pattern of DPFO with increasing pressure (asterisks indicate the new diffraction peaks). (b) The variation of the averaged single molecular volume of DPFO at different pressures (the dotted line indicates the cell volume collapse) (inset: the variation of the dihedral angle before phase transition).

emission and absorption spectra with a slow rate. After the phase transition, all DPFO molecules adopted face-to-face stacking, which was more energy favorable under high pressure due to the decrease in the volume. This stacking mode led to significant  $\pi\cdots\pi$  overlapping and made the DPFO reveal large-scale red-shift in their UV-vis absorption and PL spectra. With increasing pressure, the averaged single molecular volume of  $\gamma$ -phase decreased (Fig. 3b), which indicated that the  $\pi\cdots\pi$  distance between neighbored phenyl unit (indicated in Fig. 4b) was reduced. The distance at  $13.40\text{ GPa}$  was about  $3.2\text{ \AA}$ , which is much smaller than that of the  $\pi\cdots\pi$  interaction under ambient pressure in the range of  $3.3$ – $3.7\text{ \AA}$ .<sup>30</sup> The decrease of the  $\pi\cdots\pi$  distance was responsible for the continuous red-shift after the phase transition. The increasing  $\pi\cdots\pi$  interaction during compression was also



evidenced by the resistance variation of DPFO (Fig. S5), which gradually decreased with increasing pressure.<sup>31</sup>

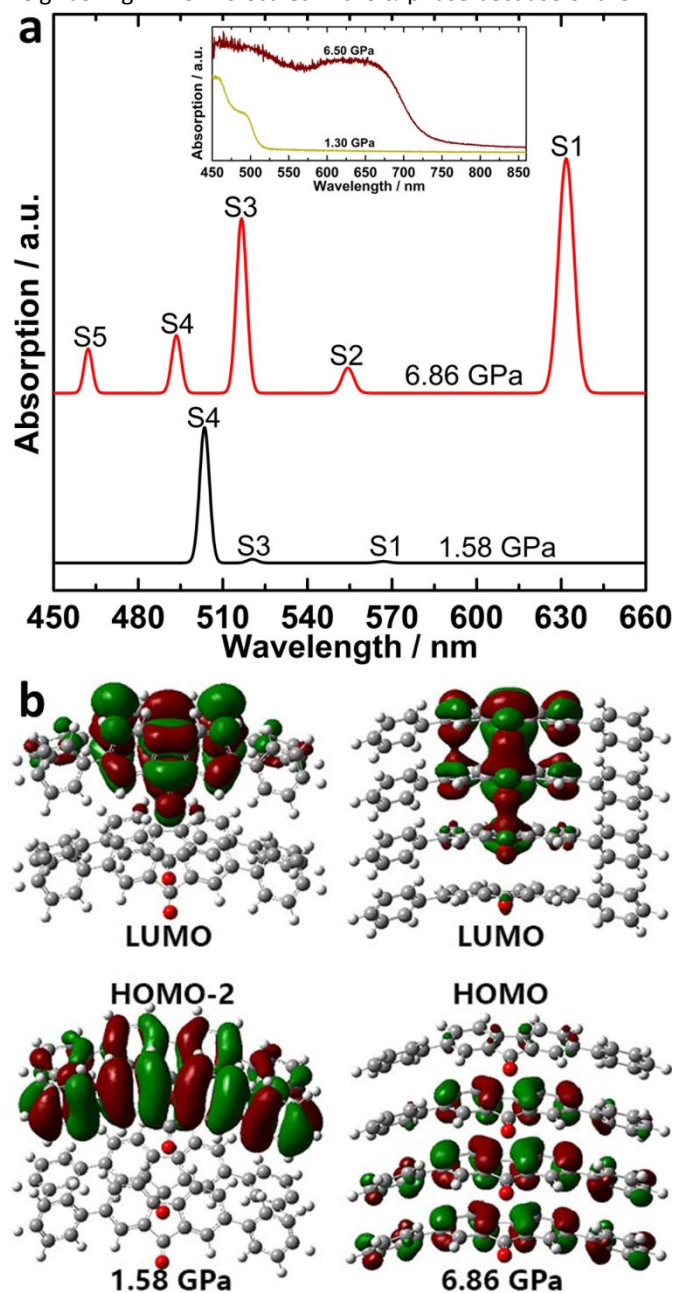


**Fig. 4** (a) The evolution of unit cell under compression. (b) The evolution of molecular packing under compression (the molecules in dark colour are closer to viewer).

### Theoretical studies

To understand the large-scale red-shift of the optical spectra under high pressure, UV-vis absorption spectra for the selected aggregates of the  $\alpha$ -phase and  $\gamma$ -phase was simulated by the Time-Dependent Density Functional Theory (TD-DFT) method.<sup>32,33</sup> The selected aggregates of the  $\alpha$ -phase and  $\gamma$ -phase included four DPFO molecules, which represent the interactions between the neighboring molecules at 1.58 GPa and 6.86 GPa (see Fig. S6 for the stacking patterns), respectively. As shown in Fig. 5a, the simulated UV-vis absorption spectra for 1.58 and 6.86 GPa exhibited strong-intensity peaks at 503 and 631 nm for the  $\alpha$ - and  $\gamma$ -phase, respectively. This simulation is in good agreement with the longest wavelength absorption peaks of the experimental values (at around 495 and 660 nm under 1.30 and 6.50 GPa in the inset of Fig. 5a). The small discrepancies between the simulated and measured results might arise from the neglect of further molecular interactions due to the computational method and limited simulation models.<sup>34-36</sup> More specifically, the strong peak of 503 nm at 1.58 GPa, which is attributed to the electronic state S4 of the  $\alpha$ -phase, corresponds to the transition from the second molecular orbital below the highest occupied molecular orbital (HOMO-2) to the lowest unoccupied molecular orbital (LUMO). The two other weak peaks at 520 and 567 nm at 1.58 GPa correspond to the S3 and S1 state, respectively. On the other hand, the strong peak of 631 nm at 6.86 GPa is from the S1 state in the  $\gamma$ -phase, which is attributed to the transition from HOMO to LUMO. The additional peaks at 554, 516, 493 and 462 nm at 6.86 GPa correspond to S2, S3, S4 and S5, respectively (see Table 1 for

the transition details of each electronic state). As shown in Fig. 5b and Fig. S7, there is less overlap of wave-function between neighboring DPFO molecules in the  $\alpha$ -phase because of the



**Fig. 5** (a) TDDFT-calculated absorption spectra for the aggregates containing four molecules (inset: the corresponding experimental results of absorption) and (b) molecular orbitals contributing to the  $S_0 \rightarrow S_3$  transition of DPFO at 1.58 GPa and to the  $S_0 \rightarrow S_1$  transition of DPFO at 6.86 GPa.

$\text{CH}\cdots\pi$  repulsion. While in the  $\gamma$ -phase, the significant overlap of wave-function between neighboring molecules imply strong  $\pi\cdots\pi$  intermolecular interactions, which leads to the decrease of the energy gap between the HOMO and LUMO for the  $\gamma$ -phase compared with the gap between the HOMO-2 and LUMO for the  $\alpha$ -phase. Consequently, the high-density packing of the  $\gamma$ -phase enhances the intermolecular interactions between the excited molecules and unexcited adjacent molecules. The smaller excitation energy of electron promotion for the  $\gamma$ -phase makes the great contribution to the

longer-wavelength absorption and emission in DPFO after the phase transition.

**Table 1** Time-Dependent Density Functional Theory (TDDFT) results for the five lowest-lying excited singlet states for diphenylfluorenone (DPFO) in  $\alpha$ -phase and  $\gamma$ -phase.

State	Excitation energy (EE) (eV)	Oscillator strengths (OS)	Dominant orbital transitions contributions (DOTC)
$\alpha$ -phase (1.58 GPa)			
S1	2.1870	0.0002	H-1 $\rightarrow$ L (51.4%), H $\rightarrow$ L (44.6%) <sup>a</sup>
S2	2.2964	0.0000	H $\rightarrow$ L (49.44%), H-1 $\rightarrow$ L (44.1%)
S3	2.3821	0.0005	H-1 $\rightarrow$ L+1 (50.5%), H $\rightarrow$ L+1 (45.0%)
S4	2.4624	0.0183	H-2 $\rightarrow$ L (66.4%)
S5	2.4815	0.0001	H $\rightarrow$ L+1 (48.4%), H-1 $\rightarrow$ L+1 (44.4%)
$\gamma$ -phase (6.86 GPa)			
S1	1.9624	0.0317	H $\rightarrow$ L (67.4%)
S2	2.2366	0.0034	H $\rightarrow$ L+1 (58.9%), H-1 $\rightarrow$ L (36.2%)
S3	2.3998	0.0236	H-1 $\rightarrow$ L (56.6%), H $\rightarrow$ L+1 (34.8%)
S4	2.5121	0.0078	H $\rightarrow$ L+2 (58.8%), H-1 $\rightarrow$ L+1 (33.9%)
S5	2.6822	0.0060	H-1 $\rightarrow$ L+1 (45.0%), H-2 $\rightarrow$ L (36.8%), H $\rightarrow$ L+2 (35.0%)

<sup>a</sup>H and L represent the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively.

## Conclusion

A reversible, tremendous, and continuous modulation of the absorption and luminescence spectra was realized by compressing DPFO crystals up to 13 GPa. Particularly, the photoluminescence spectra shifted from greenish-yellow (575 nm) to the near-IR region (875 nm), across the whole visible light region. By monitoring the evolutions of the IR spectra and synchrotron XRD patterns under high pressure, we found that the  $\alpha$ - to  $\gamma$ -phase transition was responsible for these drastic red-shift. Compared with the C-H $\cdots\pi$  interaction in the  $\alpha$ -phase, the much denser stacking mode with the face-to-face conformations of DPFO molecules in the  $\gamma$ -phase was energy-favored under high pressure. The TD-DFT calculation results further showed that the enhanced intermolecular  $\pi\cdots\pi$  interaction in the  $\gamma$ -phase led to a decrease of the energy gap between the HOMO and LUMO and thus, resulted in the jump of the absorption and luminescence spectra. Our results indicate DPFO may have a potential application in the molecular switch of modulating photoluminescence under high pressure. By measuring the crystal structure evolutions under different pressures, we found strong evidence that the  $\pi\cdots\pi$  overlapping degree and  $\pi\cdots\pi$  distance have a close relationship to the optical properties. This provides valuable insight into the construction and development of multi-colour luminescent materials.

## Experimental

### Sample Preparation and High-Pressure Generation

DPFO was synthesized by a Suzuki coupling reaction and purified by chromatography method following the literature procedures.<sup>23</sup> The sample was recrystallized in *n*-heptane three times and dried under vacuum before being used for high-pressure experiments. The purity was confirmed by <sup>1</sup>H nuclear magnetic resonance (NMR), <sup>13</sup>C NMR and mass spectroscopy (MS) results. The crystal structure of DPFO at ambient pressure was confirmed by single-crystal XRD, which shows it is in an orthorhombic phase with *Ccm2*<sub>1</sub> space group.<sup>23</sup> Single crystals were selected and ground to a powder sample with a grain size of a few micrometres in an agate mortar for high-pressure experiments. For the optical images, the single-crystal sample was used. A symmetric diamond anvil cell (DAC) with an anvil culet size of 300  $\mu$ m in diameter was adopted for *in situ* high-pressure IR and photoluminescence spectra, as well as synchrotron XRD experiments. The type-IIa diamond anvils were used for the IR experiments to avoid absorption band at 1000–1300  $\text{cm}^{-1}$ . T301 stainless steel gaskets were pre-compressed to 40  $\mu$ m in thickness and the center holes with *d* = 110  $\mu$ m were drilled to serve as the sample chamber. The ruby fluorescence was used for pressure calibration in all the *in situ* high-pressure experiments.<sup>37</sup> All experiments were carried out at room temperature.

### Optical Measurements

The optical images of the evolution of the single-crystal DPFO under high pressure were gathered using a LEICA M205C microscope with silicone oil as the pressure-transmitting medium. *In situ* high-pressure UV–vis absorption spectra were detected with a deuterium-halogen light source of 78 VA. Silicone oil was used as the pressure-transition medium. The background was calibrated by measuring the absorption without the sample at every pressure point. *In situ* high-pressure photoluminescence spectra were measured by a Renishaw Raman microscope (RM1000) with a 488 nm excitation laser. High-pressure *in situ* IR experiments were carried out on a Bruker VERTEX 70v with a HYPERION 2000 microscope. A Globar was used as a conventional source. A 20  $\times$  20  $\mu\text{m}^2$  aperture was used to collect the spectra in transmission mode in the range of 600–4000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ . The background of the IR measurements was collected from the diamond anvil absorption in the same aperture area.

### XRD Measurements

*In situ* high-pressure synchrotron XRD data was measured at the 5A-MS-XRS beamline facility of the Pohang Accelerator Laboratory. Neon was loaded as the pressure-transmitting medium by a gas loading system. The XRD data were collected by a Mar345 detector, which was calibrated by the CeO<sub>2</sub> standard sample. The focused monochromatic X-ray beam wavelength was 0.69265 Å. The Dioptas program was used for preliminary data reduction of the XRD patterns.<sup>38</sup> The Rietveld refinement of XRD data was conducted with the Jana 2006 program.<sup>39</sup>

### Electrical Resistance Measurements

The resistance measurements were performed on an electrochemical impedance system with a combination of a Solartron 1260 impedance analyser and Solartron 1296 dielectric interface. A symmetric DAC fitted with diamonds with a  $d_{\text{culet}} = 500 \text{ }\mu\text{m}$  was applied in a two-probe setting.<sup>40</sup> Steel supported cubic boron nitride gaskets and a Pt foil electrode were used for the measurements. The gaskets were pre-compressed to a thickness of 75  $\mu\text{m}$  and a hole with  $d = 350 \text{ }\mu\text{m}$  was drilled in the center to serve as the sample chamber. No pressure-transmitting medium was used for this measurement. AC voltage (100 mV) was applied in the frequency range between 0.01 Hz and 32 MHz. The experimental data were fitted and analyzed using Z-view software.

### Computation Details

For the calculation of IR spectrum of DPFO, our DFT calculations were performed within the local density approximation<sup>41</sup> (LDA) implemented in the CASTEP<sup>42</sup> module of Material Studio. The IR parameters were calculated using norm-conserving pseudopotentials with an energy cut-off for the plane wave basis set at 750 eV and k-points sampling less than  $0.03 \times 2\pi \text{ \AA}^{-1}$ .<sup>43</sup> To analyze the UV-vis spectra of the DPFO system, the TD-DFT as implemented in Gaussian 09 D01<sup>44</sup> was performed with the B3LYP functional<sup>45,46</sup> and the 6-311G\* basis set.<sup>47</sup> To obtain the simulated UV-vis absorption spectra, the excitations to the first five excited states were taken into consideration. The molecular aggregates containing four DPFO molecules were selected for the  $\alpha$ -phase and  $\gamma$ -phase. To compare with the experimental UV-vis absorption spectra, the corresponding stacking styles of the two different phases were kept fixed, where the four molecules were arranged in a herringbone stacking pattern facilitating the C-H $\cdots\pi$  interactions of the  $\alpha$ -phase and in a linear accumulation pattern emphasizing the  $\pi\cdots\pi$  stacking interactions of the  $\gamma$ -phase.

### Conflicts of interest

There are no conflicts to declare.

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