

Unraveling multichannel charge transfer via piezochromic behavior in copper-phenylacetylide

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ABSTRACT: The intrinsic competition among multiple charge transfer (CT) pathways in copper-phenylacetylide (PhC₂Cu) has hindered the desirable development of its photoactive properties, whereas substantial spectral and temporal overlap among these pathways has obscured direct mechanistic understanding. Herein, hydrostatic pressure was employed as a clean and reversible external stimulus to continuously compress the one-dimensional Cu(I)–Cu(I) ladder in pristine PhC₂Cu without modifying its chemical composition. *In situ* high-pressure photoluminescence and transient absorption (TA) spectroscopy reveal a pressure-induced evolution of CT from copper to the acetylide carbon. High-pressure crystallographic analysis and X-ray absorption near-edge structure measurements (XANES) demonstrate that anisotropic contraction of the Cu(I) ladder reconstructs the copper coordination environment and consequently modulates the relative contributions of metal-to-ligand CT pathways. These structure-dependent electronic dynamics provide direct insight into the CT mechanism of PhC₂Cu and establish hydrostatic pressure as a general and non-destructive strategy for investigating CT processes in one-dimensional (1D) coordination compounds.

KEYWORDS: copper-phenylacetylide, luminescence, piezochromic materials, pressure

1 Introduction

Copper-phenylacetylide (PhC₂Cu) constitutes a distinctive class of one-dimensional (1D) metal-organic coordination compounds in which infinite Cu(I) ladders are stabilized by phenylacetylene ligands [1–4]. This structural motif gives rise to multiple interconnected charge transfer (CT) pathways upon photoexcitation, including metal-to-ligand (MLCT), ligand-to-

metal (LMCT), ligand-to-ligand (LLCT), and metal-to-metal charge transfer (MMCT) [2, 5, 6]. The interplay among these excited-state processes underpins the considerable potential of PhC₂Cu in photocatalysis and luminescent applications [1–6]. Despite extensive investigation, the intrinsically multichannel and ultrafast characteristics of these CT processes remain poorly understood [2, 6, 7]. Conventionally all spectroscopic methods under ambient conditions are unable to resolve the substantial temporal and energetic overlap among the individual pathways, thereby obscuring their mechanistic relationships and limiting the development of ideal and high-performance PhC₂Cu-based materials. As PhC₂Cu has emerged as an important template for the design of 1D metal organic complexes, elucidating its charge transfer pathways is therefore essential [2, 8].

Previous studies have attempted to address this challenge through chemical modification strategies [2, 6, 7]. For example, extension of the π conjugation within alkynyl ligands or regulation

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of the spacing between copper ladders modulates the orbital overlap between metal centers and organic ligands, thereby promoting LMCT or MMCT processes [2, 7]. In addition, heteroatom incorporation has been used to selectively enhance MMCT while suppressing LMCT, resulting in altered excited-state relaxation dynamics [6]. Although these strategies have yielded empirical improvements in photocatalytic or luminescent performance, they do not directly clarify how individual CT pathways compete and evolve in pristine PhC_2Cu . Instead, such modifications introduce structural and compositional heterogeneity that frequently obscures the intrinsic CT mechanism. Consequently, a fundamentally different approach capable of directly probing the relationship between structure and excited-state dynamics without changing the chemical composition is highly desirable.

Hydrostatic pressure has emerged as a powerful and reversible approach for continuously tuning interatomic distances, orbital overlap, and electronic structures without changing chemical composition [9–11]. This method has successfully revealed previously inaccessible CT mechanisms in structurally complex systems, including metal-organic frameworks (MOFs) and noble metal nanoclusters, by uncovering pressure-induced evolution of emission behavior and carrier dynamics that cannot be resolved under ambient conditions [12–14]. In this context, PhC_2Cu represents an ideal model system for pressure-dependent investigation. In contrast to three-dimensional (3D) MOFs with intricate pore architectures and noble metal nanoclusters containing multiple surface ligands, both of which exhibit complicated structural responses under compression [12], PhC_2Cu possesses a well-defined 1D chain structure, weak interchain van der Waals (vdW) interactions, and ordered $\pi\cdots\pi$ stacking. This structural simplicity suppresses undesired deformation processes, including pore collapse and ligand reorientation, thereby enabling direct correlation between pressure-induced structural evolution and CT dynamics.

In this work, we investigated the evolution of luminescence behavior and CT dynamics in pristine PhC_2Cu under hydrostatic pressure without structural or compositional modification. The results clearly reveal the competitive changes between MMCT and MLCT, as well as the multi-component CT processes in MLCT, as evidenced by systematic changes in emission intensity, spectral profile, photoluminescence (PL) lifetime, and transient absorption (TA) response. Moreover, the Cu(I) ladder structure undergoes pronounced anisotropic contraction under compression, leading to substantial reconstruction of the copper coordination environment and consequent modulation of the relative contributions from distinct CT pathways. These findings provide direct insight into the photoexcitation mechanism of PhC_2Cu and establish hydrostatic pressure as a general and non-destructive approach for investigating ultrafast CT processes in 1D coordination compounds.

2 Experimental

2.1 Sample preparation

All starting materials and solvents were obtained from Aladdin Industrial Company, and used without further purification. The synthesis of the PhC_2Cu sample followed the procedure outlined in Ref. [15]. In brief, a methanolic solution of copper(II) chloride (0.05 mol/L) was prepared by dissolving 356 mg of copper(II)

chloride dihydrate ($\text{CuCl}_2\cdot 2\text{H}_2\text{O}$) in 40 mL of methanol. Under vigorous stirring, 1.12 mL of 0.2 mol/L triethylamine (Et_3N) was added to the above solution, leading to the formation of a blue precipitate. Thereafter, 0.44 mL of 0.1 mol/L phenylacetylene was introduced, and the initially formed blue flocculent precipitate gradually turned green. The resulting mixture was then heated to 65 °C and magnetically stirred continuously for 10 min until the flocculent solid transformed into pale yellow. The yellow product, designated as PhC_2Cu , was collected by centrifugation, washed repeatedly with deionized water and ethanol, and finally dried at 60 °C for 12 h.

2.2 High-pressure measurements

The resulting fine powdered samples were characterized by X-ray diffraction (XRD) using a Bruker D8 (Rigaku, Japan) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). High-pressure studies were conducted using a 400 μm diamond anvil cell (DAC). A T301 stainless steel gasket was pre-indented to a thickness of 100–120 μm , with a 100 μm diameter hole used as the sample chamber. Pressure calibration was performed using the R1-line emission from a tiny ruby ball. PL measurements were carried out using an ultraviolet diode-pumped solid-state (DPSS) laser at 365 nm, and silicone oil was used as the pressure-transmitting medium (PTM). High-pressure ultraviolet–visible (UV–Vis) absorption spectra were collected using a custom-built fluorescence microscope, equipped with a deuterium-halogen light source and Ocean Optics Pro spectrometer, and KBr was used as the PTM. High-pressure powder XRD (PXRD) patterns were conducted at the BL17UM beamline of the Shanghai Synchrotron Radiation Facility (SSRF) with the monochromatic X-ray beam of 0.5042 $\text{\AA}$. High-pressure Raman spectra were measured on a micro-Raman spectrometer (Renishaw) with a 830 nm excitation wavelength. For high-pressure time-resolved photoluminescence (TRPL) measurements, a pulsed laser (375 nm, Horiba DeltaDiode) with a maximum frequency of 100 MHz was employed as the excitation source, in conjunction with a Horiba Jobin-Yvon iHR320 spectrometer. High-pressure X-ray absorption structure (XAS) of the Cu K-edge was measured at the BL05U beamline of the SSRF, and without PTM. All XAS data were analyzed using the Athena-Artemis software package. A femtosecond laser system (Light Conversion) delivered pulses at a central wavelength of 1030 nm and a repetition rate of 1 MHz, a pulse duration of $\sim 100 \text{ fs}$ was used to measure the femtosecond transient absorption (TA) spectra, and KBr was used as the PTM. *In situ* high-pressure photoelectric measurements were recorded using a two-probe resistance measurement system in a symmetrical diamond anvil cell. Two Pt electrodes were arranged to contact the sample in the chamber without the use of any PTM. Light-emitting diode (LED) light sources were used as irradiation sources with wavelengths from 515 to 525 nm, and the photocurrent was recorded using an electrochemical workstation CHI750E.

2.3 Computational method

The synthesized PhC_2Cu had the same structure as in Ref. [16]. Structural geometry optimization was performed by using the CP2K program [17, 18]. The Perdew–Burke–Ernzerhof/double zeta valence polarized-molecular optimized-short range-Goedecker–Teter–Hutter (PBE/DZVP-MOLOPT-SR-GTH) level with the dispersion-corrected density functional theory (DFT-D3(BJ)), with a grid cutoff of 500 Ry, was used to obtain a stable structural model at ambient and high pressures. In addition, the

calculated pressure values were corrected based on experimental results. The vibrational analysis was also performed using the CP2K package. The electronic structure properties of excited states were performed by using linear response time-dependent density functional theory (TDDFT). To calculate the excited-state information more accurately, the hybrid functional Perdew–Burke–Ernzerhof hybrid (PBE0) with DZVP-MOLOPT-SR-GTH level was used. The CP2K input files, interaction region indicator (IRI), hole–electron analysis, and calculated absorbed/emitted oscillator strength were performed by the Multiwfn program. The IRI analysis was plotted via visual molecular dynamics (VMD) software.

3 Results and discussion

As illustrated in Fig. S1 in the Electronic Supplementary Material (ESM), PhC₂Cu adopts a molecular configuration analogous to that of tetraphenylethylene (TPE), in which the molecular chain exhibits a butterfly-like conformation. PhC₂Cu crystallizes in the monoclinic crystal system with the *P*21 space group, and the detailed crystallographic parameters are summarized in Table S1 in the ESM. The structure consists of phenylacetylene coordinated to a d¹⁰ Cu(I) center through a Cu–C≡C bond, thereby generating multiple photoexcitation pathways, as shown in Fig. 1(a). PL spectroscopy is widely recognized as an effective method for probing photoexcited states [19–21]. To investigate the charge transfer states of PhC₂Cu in detail, PL spectra were collected, as presented in Fig. S2 in the ESM. The PL emission spectrum of PhC₂Cu can be deconvoluted into two Gaussian components centered at approximately 509 nm, corresponding to the high energy (HE) band, and 557 nm,

corresponding to the low energy (LE) band. To further elucidate the emission behavior of PhC₂Cu, high pressure PL measurements were performed, as shown in Fig. 1(b). With increasing pressure, the HE emission gradually redshifted and simultaneously exhibited a decrease in PL intensity. In contrast, the LE emission progressively intensified up to 3.4 GPa and displayed an obvious red shift in emission position, whereas its PL intensity remained nearly unchanged between 3.4 and 6.9 GPa. Above 6.9 GPa, the PL emission continued to redshift, accompanied by a gradual decrease in PL intensity, as shown in Fig. S3 in the ESM. Previous studies proposed that the HE and LE emissions of PhC₂Cu originate from LMCT and MMCT, respectively; however, the detailed charge transfer mechanisms were not discussed [5, 6, 8]. The ordered 1D Cu(I)–Cu(I) ladder structure serves as an efficient charge transfer channel. Consequently, shortening the Cu–Cu distance is expected to enhance charge transfer efficiency and thereby reduce the fluorescence intensity of the LE emission. However, Jiang et al. reported that partial substitution of Cu atoms with Fe atoms leads to the formation of even shorter Cu–Fe bonds, yet unexpectedly enhances the LE emission intensity [6]. These observations indicate that the fluorescence origin of PhC₂Cu remains under debate. Based on a series of refined high-pressure studies, we assign the LE emission to the PhC₂-to-Cu charge transfer state, whereas the HE emission is attributed to Cu(I)–Cu(I) interactions. Detailed discussions are provided below. It should be clarified here that the photoluminescence process associated with the LE state in PhC₂Cu involves two distinct processes: absorption and emission, which correspond to MLCT and LMCT, respectively. This distinction will not be reiterated in the following discussion.

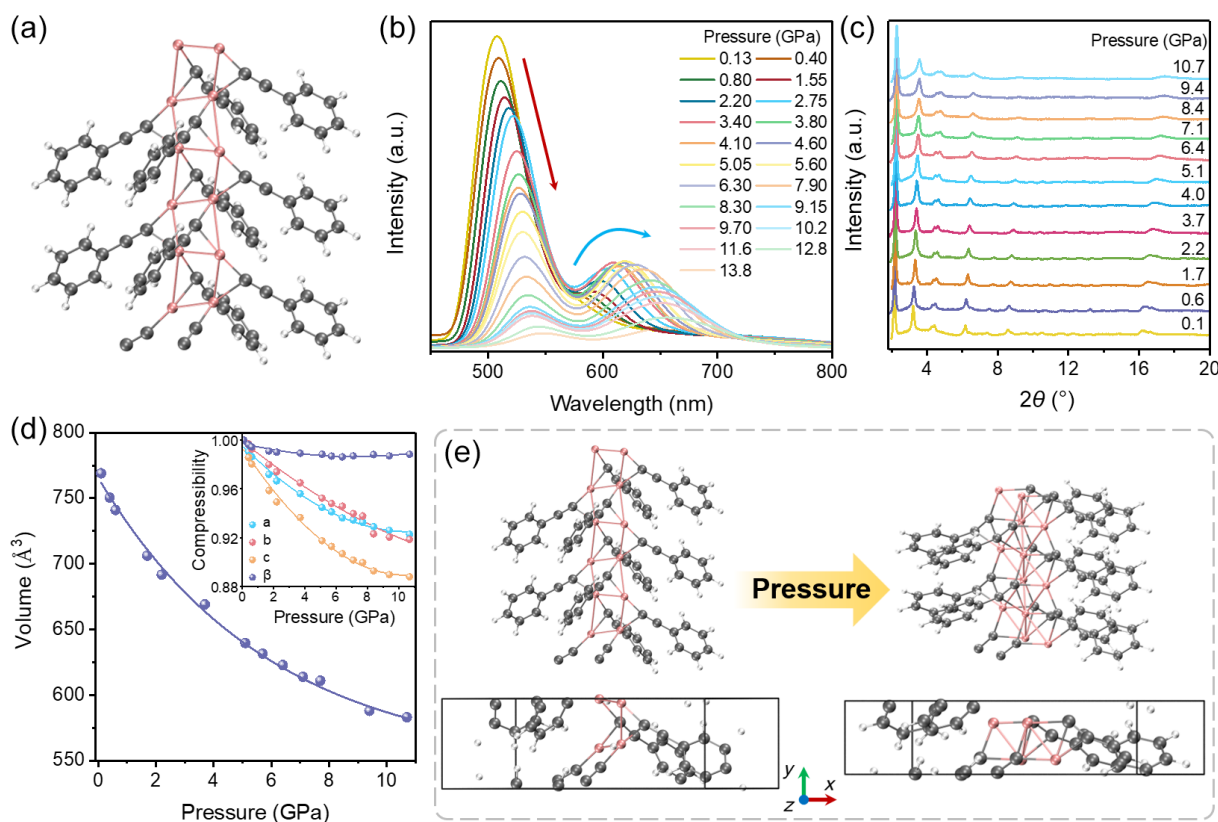


Figure 1 (a) Structural illustration of PhC₂Cu under ambient pressure. Carbon atoms are shown in black, copper in brassy, and hydrogen in grayish-white. (b) *In situ* PL spectra and (c) XRD patterns of PhC₂Cu upon compression. (d) Plotted curves for the unit cell volume of PhC₂Cu as a function of pressure. Inset shows the compression rate of lattice constants as pressure increases. (e) Schematic illustration of molecular arrangement variations upon compression.

To further investigate these optical changes, *in situ* high-pressure powder XRD experiments were conducted up to 10.7 GPa, as shown in Fig. 1(c). With increasing pressure, all Bragg diffraction peaks gradually shifted toward higher 2θ values, indicating continuous lattice compression. No additional diffraction peaks were observed throughout the compression process, confirming the structural stability of PhC_2Cu under pressure. Figure 1(d) presents the pressure-dependent evolution of the unit cell volume derived from the high pressure XRD analysis. Notably, the a -, b -, and c -axes exhibit distinct compression behaviors upon compression, as shown in the inset of Fig. 1(d). Among them, the c -axis displays significantly higher compressibility than the a - and b -axes. Considering the molecular packing arrangement shown in Fig. 1(e), such pronounced anisotropic lattice compression may facilitate a more ordered stacking of benzene rings, thereby promoting coplanar alignment of the Cu centers, alkynyl carbon atoms, and benzene rings to enhance charge transfer efficiency. Therefore, the enhanced LE emission can reasonably be assigned to the PhC_2 -to-Cu charge transfer state. Furthermore, combined experimental XRD analysis and theoretical optimization of the corresponding crystal structures (Fig. 1(e)) reveal that additional Cu-C coordination interactions are formed at higher pressures. These results suggest that, although the overall crystal symmetry remains unchanged, substantial local structural rearrangements occur within the crystal building units, leading to an isostructural phase transition. To the best of our knowledge, such behavior has not been reported previously in related systems such as silver phenylselenolate (AgSePh) [22]. The newly established Cu-C coordination environments also suppress Cu(I)-Cu(I) electronic interactions, thereby accounting for the gradual weakening of the HE emission with increasing pressure [3].

Based on the structural evolution inferred from the high-pressure XRD analysis, detailed vibrational spectroscopy studies were conducted to further clarify the pressure induced transformation of PhC_2Cu . Accordingly, *in situ* Raman spectroscopy measurements were performed under compression. As shown in Fig. 2(a), comparison with previous reports and theoretical calculations allows assignment of the intense vibrational peak at 527 cm^{-1} to the coordination interaction between Cu and phenylacetylene. The peak located at 424 cm^{-1} is attributed to C-C bond vibrations. In addition, the peaks at 144, 200, 308, and 1928 cm^{-1} are assigned to $\text{C}\equiv\text{C}$ and C-C vibrational modes. The peaks at 742 and 786 cm^{-1} correspond to C-H and C-C bond vibrations, respectively. Furthermore, the characteristic vibrational modes of the benzene ring are observed at 999, 1174, 1194, and 1596 cm^{-1} [15, 23, 24]. Upon compression, most of all Raman peaks gradually shift toward higher frequencies as a result of lattice contraction. Notably, the stretching vibrational modes associated with $\text{C}\equiv\text{C}$ and Cu-C exhibit distinct peak splitting within the pressure range from 1.8 to 5.7 GPa, as shown in Figs. 2(b) and 2(c). This behavior indicates a change in the coordination environment of Cu, and such a change may be more favorable for charge transfer between Cu and carbon atoms. Importantly, this pressure range coincides with the pronounced enhancement and red shift of the PL emission, further supporting the proposed pressure-induced electronic structural evolution of PhC_2Cu .

To directly elucidate the influence of pressure on the electronic structure and coordination environment of Cu in PhC_2Cu , high energy resolution Cu K edge XAS measurements were performed up to 10.78 GPa, as shown in Fig. 3(a). The Cu K-edge X-ray

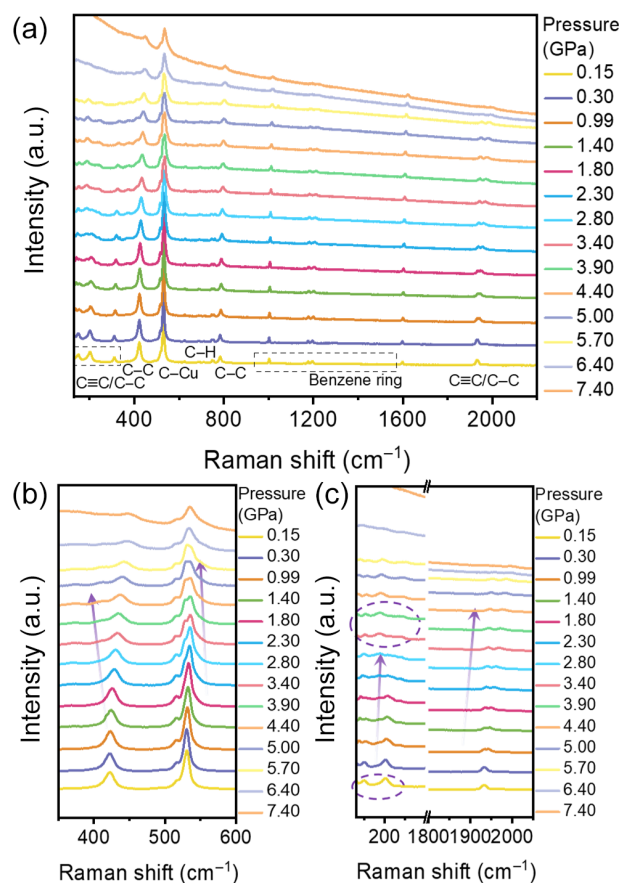


Figure 2 (a) *In situ* Raman spectra of the PhC_2Cu upon compression. ((b) and (c) The enlarged spectra for (b) the Cu-C and (c) $\text{C}\equiv\text{C}/\text{C}-\text{C}$ Raman mode upon compression.

absorption near edge structure (XANES) spectra exhibit a gradual shift of the absorption edge toward higher energies below 4.17 GPa, indicating an increase in the oxidation state of Cu, as shown in the inset of Fig. 3(a) [25–28]. To further clarify this evolution, the second derivative of the XANES spectra was calculated, since the maximum position of the second derivative directly reflects variations in the Cu oxidation state, as shown in Fig. 3(b). The first maximum shifts from 8981.6 eV at 0.05 GPa to 8989.7 eV at 4.17 GPa, as presented in Fig. S4 in the ESM, providing clear evidence for the increase in the oxidation state of Cu. At ambient pressure, the oxidation state reflects the extent of charge transfer between Cu and the surrounding ligands. Accordingly, the pressure induced increase in oxidation state suggests enhanced coordination interactions involving Cu under compression. To quantitatively evaluate the evolution of the Cu coordination environment, Fourier-transformed k^3 -weighted extended X-ray absorption fine structure (EXAFS) analysis was further performed. As shown in Fig. 3(c) and summarized in Table S2 in the ESM, rigorous fitting analysis of the EXAFS spectra reveals a dominant peak at approximately 1.46 Å, which is assigned to the Cu-C bond [29]. At ambient pressure, the fitted coordination number of the nearest neighboring carbon atoms around the central Cu atom is 2. Upon compression, the coordination number gradually increases and reaches a maximum at 4.17 GPa. In contrast, the Cu-C bond length remains nearly unchanged throughout the investigated pressure range. These results indicate that the pressure induced evolution of the Cu coordination environment mainly originates from geometric

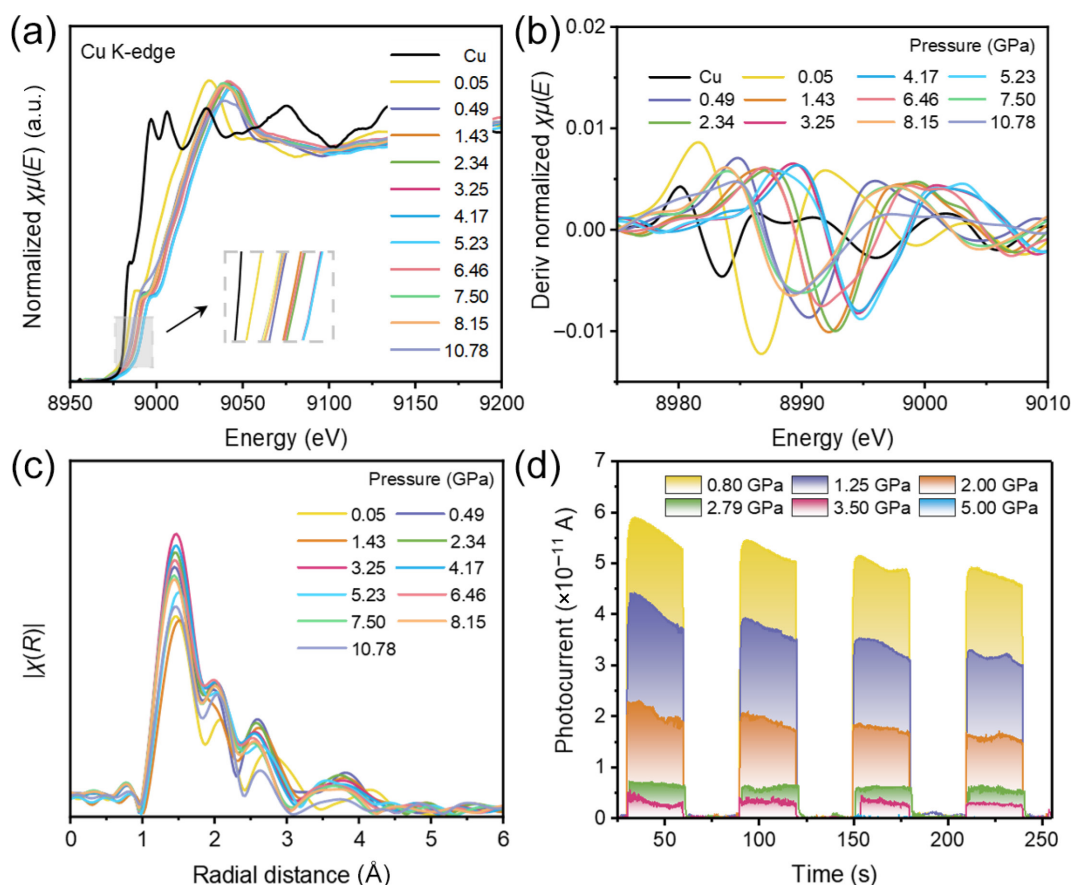


Figure 3 (a) Normalized Cu K-edge XANES spectra. (b) 2nd derivatives of XANES spectra and (c) EXAFS spectra in the *R*-space of PhC₂Cu under various pressures. (d) PhC₂Cu photocurrent during compression under illumination wavelengths of 515–525 nm at 1 V.

reorientation within the PhC₂Cu framework, leading to enhanced Cu coordination rather than substantial variation in Cu–C bond length. This interpretation is fully consistent with the high pressure XRD analysis. Furthermore, the progressive shielded Cu–Cu electronic interactions under compression suggests that the subsequent electronic regulation is dominated primarily by Cu-to-C CT. These observations strongly support the assignment of the LE emission peak to CT between Cu and PhC₂ ligands, rather than MMCT.

To further elucidate the influence of the increased Cu coordination number on Cu–Cu electronic interactions, the optoelectronic properties of PhC₂Cu were investigated under pressures up to 5 GPa [30]. The photocurrent response reflects the efficiency of photogenerated carrier separation and long-range transport, which can be directly related to the different charge transfer pathways. The MMCT excitation involves charge redistribution along the infinite one-dimensional Cu(I)–Cu(I) ladder chain. In this process, both electrons and holes are delocalized along the continuous Cu metal chain, which provides a natural pathway for charge transport. Therefore, the carriers generated through MMCT can efficiently migrate along the Cu ladder over long distances, making MMCT the dominant contributor to the photocurrent of PhC₂Cu. In contrast, the charge carriers associated with the organic ligands have much lower hopping mobility than those on the Cu metal chain, resulting in poor long-range transport for the LMCT state. The spatially separated electron–hole pairs in the LMCT state therefore tend to undergo radiative recombination, leading to luminescence but

contributing little to the photocurrent. This relationship has also been established in previous studies of metal organic coordination compounds [31–33]. The measured current of PhC₂Cu consists of both dark and photocurrent contributions. As shown in Fig. 3(d), the photocurrent of PhC₂Cu gradually decreases with increasing pressure relative to the initial ambient pressure value, indicating that compression does not promote charge transport through the Cu–Cu metal chain in PhC₂Cu. These results suggest that the increase in Cu coordination effectively suppresses MMCT, thereby reducing photocurrent generation. Consequently, the pressure-dependent optoelectronic response further supports the assignment of the HE emission to Cu(I)–Cu(I) charge transfer under high pressure.

To further clarify the mechanism underlying the pressure-induced evolution of CT behavior, *in situ* high-pressure UV–Vis absorption analyses were systematically performed. As shown in Fig. S5(a) in the ESM, PhC₂Cu exhibits an absorption edge at approximately 520 nm, corresponding to an optical band gap of 2.47 eV. This absorption feature is primarily associated with MLCT [6]. Upon compression, the absorption edge of PhC₂Cu gradually redshifts, accompanied by a reduction in the gap energy, as shown in Fig. 4(a). After complete pressure release, both the PL and UV–Vis absorption spectra of PhC₂Cu recover to the initial ambient pressure state, indicating that the pressure induced structural and electronic evolution is reversible, as shown in Figs. S5(b) and S5(c) in the ESM. To further investigate the excited state dynamics of PhC₂Cu, TA spectroscopy measurements were subsequently carried out [19, 22]. Under ambient conditions,

distinct pump induced absorption (PIA) signals originating from the benzene rings and Cu–C related CT processes are clearly observed, as shown in Fig. 4(b). Specifically, the PIA signal associated with the benzene rings near 383.8 nm is mainly detected within 140 ps, whereas the Cu–C related PIA signal in the range of 445–483 nm persists over a substantially longer timescale of approximately 350 ps. These observations indicate that the benzene ring related absorption process is dominated by localized excited states, whereas the Cu-to-C CT process exhibits characteristic MLCT behavior with a prolonged decay lifetime. Notably, the Cu–C related PIA feature exhibits an asymmetric spectral profile, suggesting the coexistence of two distinct CT pathways. Combined with the XRD and Raman analyses, these results indicate that different Cu coordination environments give rise to distinct CT processes involving neighboring carbon sites. To further evaluate the pressure-dependent TA behavior, the TA spectra recorded at 1.8 ps under different pressures were analyzed, as shown in Fig. 4(c). With increasing pressure, the PIA signals associated with both the benzene rings and Cu–C interactions exhibit obvious red shifts, consistent with the steady state UV–Vis absorption results. More importantly, a significantly broadened PIA feature gradually emerges near 550 nm upon compression and remains stable up to 7.36 GPa, as shown in Fig. 4(d). The corresponding 3D and two-dimensional (2D) TA spectra at 1.02 GPa are presented in Figs. 4(e) and 4(f), respectively. This broadened PIA signal exhibits an exceptionally long decay lifetime, with detectable spectral intensity persisting up to 6000 ps. Similar broadened PIA features have previously been reported in polycyclic conjugated systems and are generally associated with complex charge transfer states arising from intermolecular interactions between adjacent benzene rings. Combined with the high-pressure XRD analysis, these results suggest that compression effectively restricts the structural degrees of freedom of the benzene rings, thereby promoting more ordered intermolecular stacking along the polymer chain. Such ordered stacking substantially enhances CT from Cu centers to the benzene rings, thereby accounting for the emergence of the broadened PIA feature near 550 nm. Furthermore, high-pressure time-resolved photoluminescence (tr-PL) measurements were performed to investigate the decay dynamics of the HE and LE states [34, 35], as shown in Figs. 4(g) and 4(h). Upon compression, the decay lifetime of the HE emission progressively shortens, with the average lifetime decreasing from 5.55 ns at 0.2 GPa to 2.10 ns at 8.01 GPa, based on multiexponential fitting analysis, as summarized in Table S3 in the ESM. In contrast, the LE emission exhibits substantially slower decay dynamics, and the corresponding lifetime gradually increases with pressure, reaching a maximum average lifetime of 40.56 ns at 3.01 GPa, as shown in Table S3 in the ESM. These lifetime variations are consistent with the pressure-dependent evolution of PL intensity. The tr-PL results further support the TA analysis, demonstrating that the LE excited state possesses an extended decay lifetime due to coupling with long range CT states involving Cu-to-benzene ring interactions.

To further quantify the bonding characteristics and intermolecular interactions in PhC_2Cu , IRI [36–40] and atoms in molecules (AIM) [41, 42] topological analyses were performed to evaluate the electronic interactions within the crystal under different pressures. As shown in Figs. 5(a) and 5(b), representative partial IRI maps obtained under ambient pressure and 3.7 GPa are presented to clearly visualize the interaction regions, whereas the complete intermolecular interaction maps are provided in Fig. S6 in

the ESM. Under ambient pressure, a distinct attractive interaction between Cu and C atoms is observed. Unlike the typical cylindrical density distribution associated with conventional covalent bonding, the Cu–C interaction exhibits a localized disc-like density feature, as highlighted by the purple circles in Fig. 5(a). The calculated $\text{sign}(\lambda_2)\rho$ value for the Cu–C interaction is approximately -0.085 a.u., which is considerably larger in magnitude than that generally associated with typical hydrogen bonding interactions, where $\text{sign}(\lambda_2)\rho$ is usually smaller than -0.04 a.u. At 3.7 GPa, Cu atoms exhibit coordination interactions with a greater number of neighboring carbon atoms, as indicated by the purple circles in Fig. 5(b). This observation is fully consistent with the pressure-induced increase in Cu coordination identified in the previous experimental analyses. In addition, the organic ligands already display evident π – π intermolecular interactions under ambient pressure, as shown by the orange regions in Fig. 5(a). Upon compression, these intermolecular interactions become significantly enhanced, leading to a more ordered arrangement of the benzene rings and the emergence of additional intermolecular interactions, including C–H... π interactions, as indicated by the yellow regions in Fig. 5(b). These strengthened intermolecular interactions effectively restrict the structural degrees of freedom of the benzene rings, thereby facilitating more efficient CT between Cu centers and the ligands. This interpretation is in excellent agreement with the conclusions derived from the TA spectroscopy analysis.

To further investigate the charge distribution characteristics during pressure-dependent optical excitation, absorption spectra under different pressures were theoretically calculated to provide detailed insight into the excited state electronic distributions [17, 18, 21, 43]. In the excited state calculations, the excitation process was described using an electron–hole formalism to identify the spatial distribution of electron depletion and accumulation during photoexcitation. Based on the electron–hole analysis, the absorption states were classified according to their distinct excitation characteristics, as shown in Fig. 5(c). Under ambient pressure, the absorption of PhC_2Cu is mainly concentrated below 500 nm and primarily originates from π – π^* transitions of the benzene rings together with Cu-to-C CT processes. A representative electron–hole distribution corresponding to the 9th excited state at ambient pressure is presented in Fig. S7 in the ESM. Upon compression, however, a distinct low energy absorption feature gradually emerges near 600 nm. Electron–hole analysis of this absorption state, as shown in Fig. 5(d), reveals that the increasingly ordered stacking of the benzene rings significantly enhances CT from Cu centers to $\pi^*(\text{C}\equiv\text{C}-\text{Ph})$ orbitals. These calculated results are fully consistent with the experimentally observed absorption behavior. To further clarify the influence of intermolecular interactions on the excited state properties, the first excited state configurations at ambient pressure and 3.7 GPa were also calculated. As shown in Fig. 5(e), the first excited state geometry at ambient pressure differs substantially from the ground state configuration during photoexcitation, particularly with respect to the pronounced rotational distortion of the benzene rings. Combined with the IRI analysis, this behavior can be attributed to the relatively weak intermolecular constraints under ambient conditions, which allow substantial rotational freedom of the benzene rings. In contrast, enhanced intermolecular interactions at 3.7 GPa effectively restrict the rotational motion of the benzene rings, resulting in a first excited state configuration that remains largely similar to the ground state structure. Correspondingly, the calculated

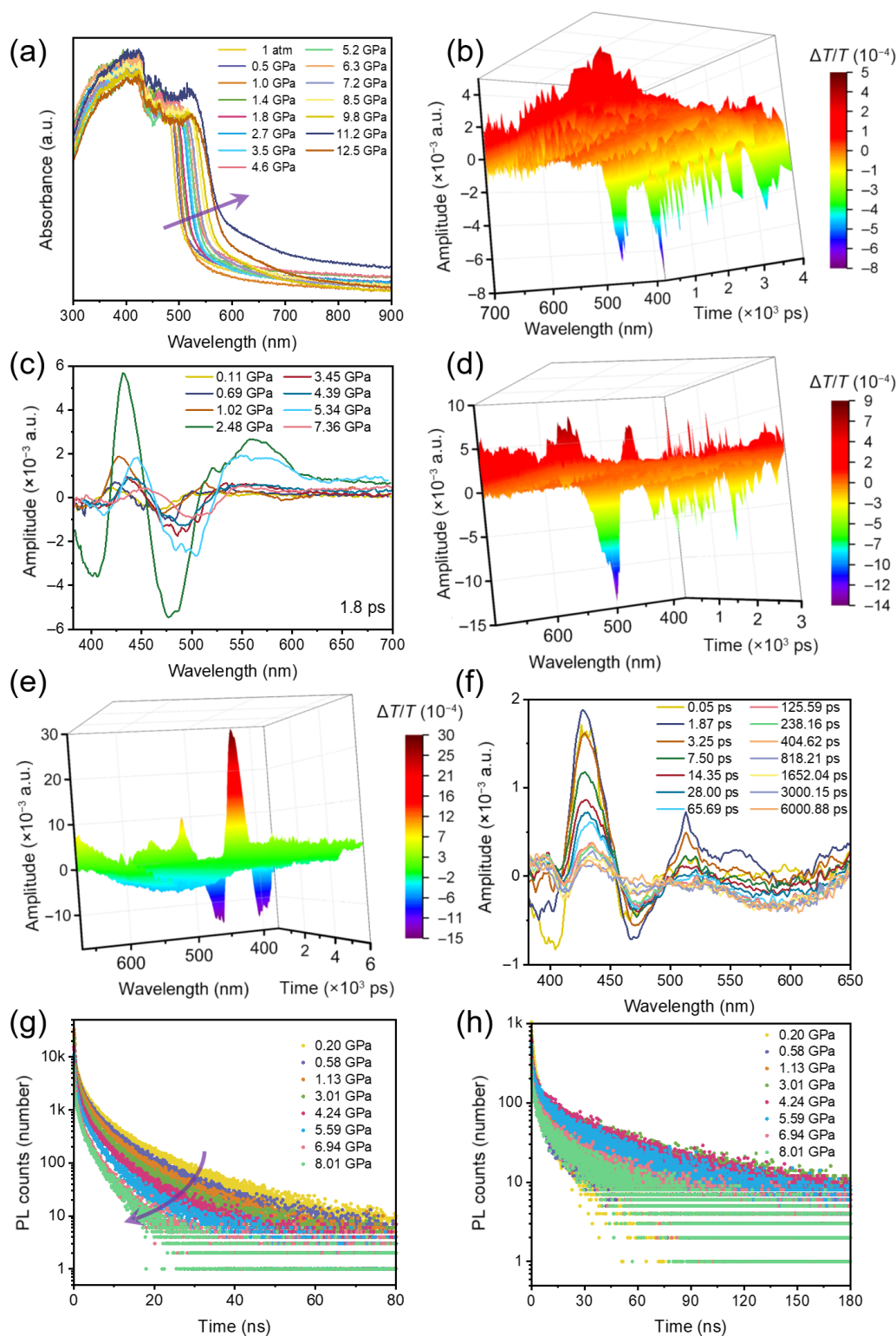


Figure 4 (a) *In situ* UV-Vis absorption spectra of PhC₂Cu. (b) 3D TA spectra of PhC₂Cu at ambient conditions. (c) 2D TA spectra of PhC₂Cu upon compression. (d) 3D TA spectra of PhC₂Cu at 7.36 GPa. (e) 3D and (f) 2D TA spectra at 1.02 GPa and the selected time delays. ((g) and (h)) TRPL spectra of (g) HE and (h) LE emission upon compression, respectively.

enhancement of the first excited state emission intensity under pressure is consistent with the experimentally observed enhancement of the LE emission, as shown in Fig. 5(f). These results indicate that pressure effectively suppresses rotational relaxation of the benzene rings and simultaneously activates lower

energy excitation states. As a consequence, both internal conversion and thermal vibrational energy dissipation are significantly reduced under compression, thereby enhancing radiative transition efficiency and leading to stronger fluorescence emission. However, it is important to emphasize that, although the ordered stacking of

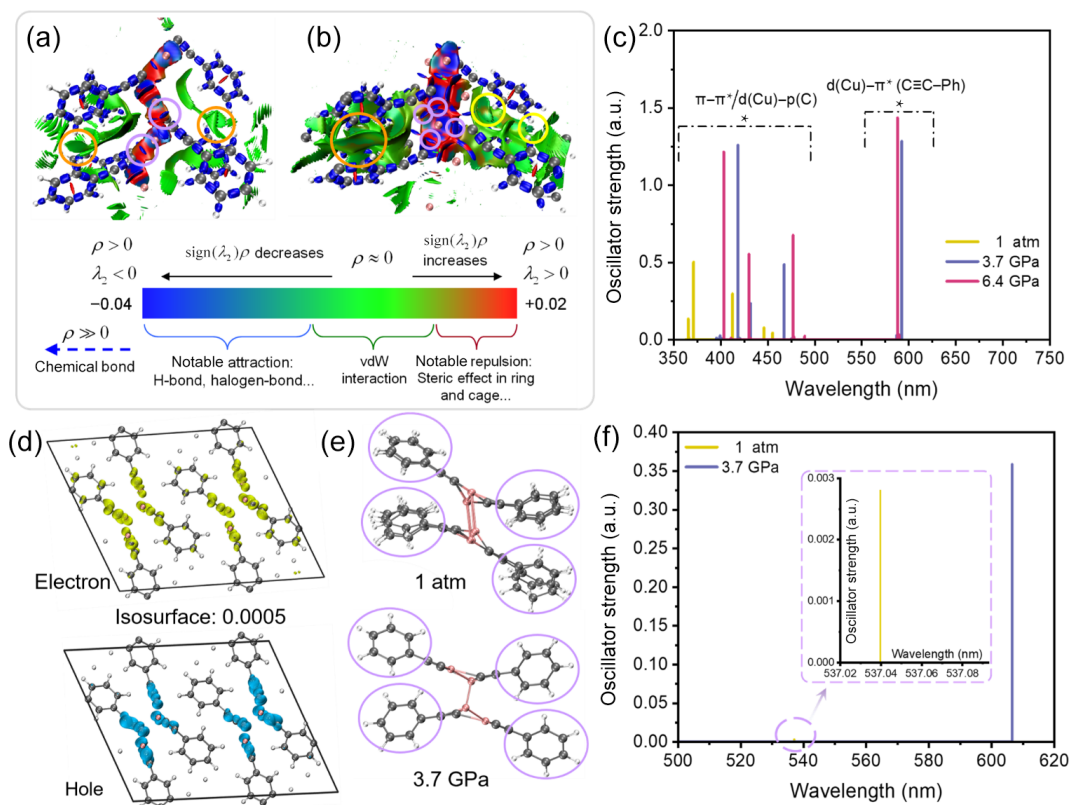


Figure 5 ((a) and (b)) The $\text{sign}(\lambda_2)\rho$ colored isosurfaces (isovalue = 1 a.u.) of PhC_2Cu at (a) ambient pressure and (b) 3.7 GPa, respectively. (c) Calculated the absorption spectra at different pressures. (d) Electron-hole distribution of PhC_2Cu at 3.7 GPa. (e) First excited-state configurations of PhC_2Cu at 1 atm and 3.7 GPa. (f) The calculated emission spectra at different pressures.

benzene rings facilitates the CT process from Cu to C, the fluorescence emission process is not only related to the CT process but is also affected by non-radiative dissipation resulting from $\pi-\pi$ stacking. Therefore, the balance between radiative and non-radiative dissipation leads to the nearly unchanged PL intensity of LE emission between 3.4 and 6.9 GPa, which also explains why the Cu coordination in the Cu K-edge XANES results reaches a maximum at 4.17 GPa, while the fluorescence enhancement range is only observed from 1 atm to 3.4 GPa.

Combined experimental and theoretical analyses demonstrate that PhC_2Cu undergoes an isostructural phase transition under pressure. In the high-pressure phase, the Cu coordination number increases together with the development of more ordered benzene ring stacking. This structural evolution substantially modifies the CT behavior of PhC_2Cu and promotes longer range CT processes. Further electron-hole analysis of the PL emission associated with the first excited state reveals that the emission process is primarily dominated by PhC_2 -to-Cu CT (Fig. S8 in the ESM). Under ambient conditions, the substantial rotational freedom of the PhC_2 units results in relatively localized emission characteristics. Upon compression, strengthened intermolecular interactions suppress rotational disorder of the benzene rings and produce a more spatially delocalized excited state distribution. Combined with the experimental and calculated absorption spectra, these results indicate that pressure activates lower energy excitation channels while simultaneously suppressing internal conversion losses. This mechanism may provide valuable insight for the future design of pressure-regulated photoactive materials and related photocatalytic systems.

4 Conclusions

In summary, we performed a comprehensive investigation on the CT behavior in PhC_2Cu , a representative metal-organic coordination compound, using a high-pressure strategy. Our systematic high-pressure investigations reveal that compression progressively increases the coordination number of Cu centers and simultaneously induces anomalous pressure enhanced luminescence behavior. By combining experimental analyses with theoretical calculations, we quantitatively characterized the pressure-induced evolution of the Cu coordination environment and clarified its influence on the excited state CT process. As Cu-ligand interactions become strengthened and the vibrational and rotational freedom of the PhC_2 units becomes increasingly restricted, the photogenerated CT pathway in PhC_2Cu undergoes a substantial transition. Specifically, MMCT is progressively suppressed, whereas the MLCT process evolves from the initial localized Cu-to-C CT pathway to a longer-range Cu-to- PhC_2 CT process. The enhanced intermolecular interactions under pressure promote ordered benzene ring stacking and suppress nonradiative relaxation pathways, thereby significantly enhancing radiative recombination efficiency and fluorescence emission. These findings provide important insight into the CT mechanism of 1D Cu(I)-Cu(I) ladder systems and establish an effective strategy for regulating excited state dynamics through pressure-induced coordination engineering. More broadly, this work offers valuable guidance for the rational design of metal-organic coordination materials with advanced photophysical and photocatalytic functionalities.

Electronic Supplementary Material: Supplementary material (Figs. S1–S8 and Tables S1–S3) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909129>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

C. G. Z. proposed the research direction and designed the research. L. Y. D. and Z. X. Y. performed the syntheses and measurements. S. L. M. performed the high pressure XAS and XRD measurements. C. G. Z. performed the DFT calculations. G. X. L. and P. W. performed the TA spectroscopy measurements. C. Y. Z., Y. J. L., Y. C. S., S. F. N., and T. C. participated in data discussions. L. Y. D., Z. X. Y., C. G. Z., and M. G. Y. wrote the manuscript. All the authors have approved the final manuscript.

Use of AI statement.

None.

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