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Luminescence lifetime thermometers based on hybrid cuprous halides with exceptional water resistance and giant thermal expansion

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Abstract

Optical probes hold great promise for temperature sensing owing to their attractive properties including rapid response, high spatial resolution, and remote non-invasive detection. However, the exploration of thermometric probes is hindered by their low relative sensitivity (S_r) or poor structural stability in water. Herein, we propose the first example of organic-inorganic metal halides based on $\text{TPP}_3\text{Cu}_2\text{Br}_2$ (TPP = triphenylphosphine) that simultaneously present excellent water resistance and sensitive temperature-dependent photoluminescence lifetime in water. Benefiting from the soft lattice induced by the organic molecule of TPP, giant thermal expansion and great lattice distortion were achieved with increasing temperature. As such, the self-trapped exciton luminescence lifetime of $\text{TPP}_3\text{Cu}_2\text{Br}_2$ can be shortened to 1.9% of the initial value from 280 to 380 K, resulting in the highest S_r of $12.82\% \text{ K}^{-1}$ among the undoped metal halides based luminescent thermometers. Significantly, $\text{TPP}_3\text{Cu}_2\text{Br}_2$ displayed extraordinary water stability with emission intensity remaining nearly unchanged after immersing in water for 15 days. Moreover, high-precision luminescence lifetime based thermal sensing in water environment was successfully conducted, which proved to be inert to the detection depth in water with a small read-out error. This work offers new routes in the exploration of novel metal halides for highly sensitive thermometric probes toward versatile application scenarios.

Introduction

Optical thermometer is widely employed for temperature sensing by monitoring optical parameters like temperature-dependent changes in photoluminescence (PL) intensity^{1–7} or PL lifetime^{8–10}. Nevertheless, intensity-based optical thermometers like infrared thermal imager are susceptible to various factors including light source, sample concentration, photobleaching, scattering, and absorption at different wavelengths^{11–14}. PL lifetime proves advantageous for precise temperature sensing as it remains unaffected by the aforementioned factors. As

such, PL lifetime-based thermometry fundamentally circumvents the limitations inherent to the conventional infrared thermal imager¹⁵. Currently, temperature sensing based on PL lifetime mainly employs Ln^{3+} ions and ns^2 ions doped phosphors. For Ln^{3+} -doped phosphors, the $4f$ - $4f$ transitions of Ln^{3+} ions are not sensitive to surroundings due to the shielding of $5s5p$ shell, therefore exhibiting a small PL lifetime variation with temperature and a low temperature sensing sensitivity¹⁶. Although ns^2 ions doped phosphors tend to display higher temperature sensing sensitivity, their lifetimes are generally located in the ns range^{17–20}. Such a small PL lifetime requires sophisticated instrumentation and short-pulsed lasers, which is not feasible for most practical scenarios. Therefore, there is an urgent need to develop novel materials with large PL lifetime variation ability for sensitive temperature sensing.

In the past decade, metal halides (MHs) have received increasing attention for PL lifetime-based temperature

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sensing^{21–26}. Particularly, some organic-inorganic metal halides (OIMHs) have significant temperature-dependent structural properties. At high temperatures, the thermal movement of organic molecules causes dramatic expansion of the crystal cells. Such crystal expansion induces the formation of defects, leading to a temperature-dependent nature of the PL lifetime. These OIMHs can provide sensitive temperature sensing based on self-trapped exciton (STE) luminescence with microseconds or longer PL lifetime, making them very suitable for applications in PL lifetime-based thermometry^{27–30}. However, their instability in water severely limits their application in humid environments^{31–33}. Despite substantial advancements being made in OIMHs, it remains challenging to explore OIMHs that are water-stable and highly temperature-sensitive in PL lifetime.

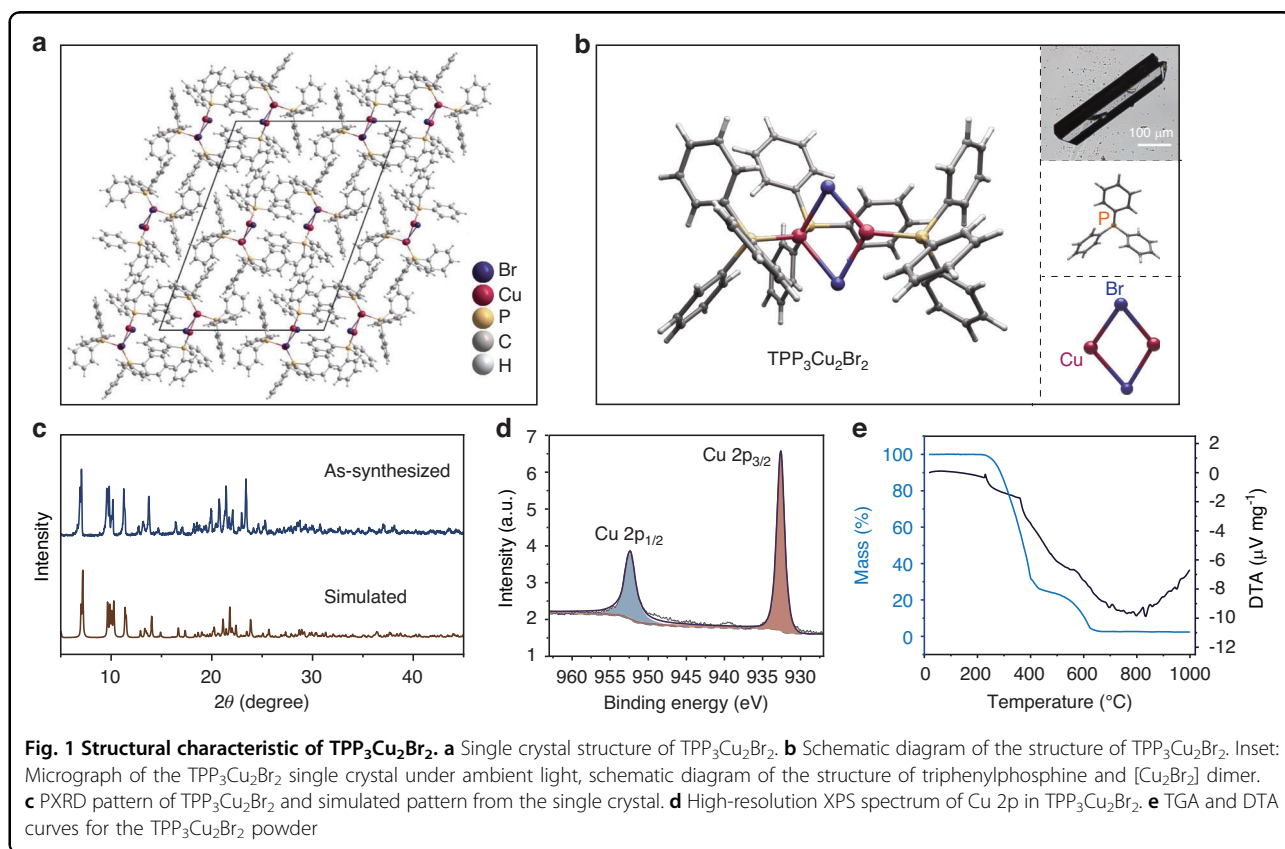
One possible strategy to address this challenge is introducing hydrophobic organic molecules into the OIMHs. Herein, we propose a novel kind of OIMH based on $\text{TPP}_3\text{Cu}_2\text{Br}_2$ (TPP = Triphenylphosphonium), presenting exceptional water stability as sensitive luminescence lifetime thermometers in water environment. Upon excitation with ultraviolet (UV) light, $\text{TPP}_3\text{Cu}_2\text{Br}_2$ emitted bright green STE luminescence with a PL quantum yield (PLQY) of 41.5%. Benefitting from its excellent temperature-dependent PL lifetime, a maximal relative sensitivity (S_r) of $12.82\% \text{ K}^{-1}$ at

380 K for temperature sensing was achieved. Moreover, $\text{TPP}_3\text{Cu}_2\text{Br}_2$ exhibited excellent water stability, whose PL intensity remained 97.3% of the initial value after 15 days of soaking in the water. We revealed that such excellent luminescent stability was owing to the protective effect of the hydrophobic organic molecules. Furthermore, we demonstrated the application of $\text{TPP}_3\text{Cu}_2\text{Br}_2$ for high-precision thermal sensing in the water environment.

Results

Crystal Structure

$\text{TPP}_3\text{Cu}_2\text{Br}_2$ was synthesized by a simple solvothermal method from the precursors of TPP-HBr and CuBr in a mixed solvent of N,N-Dimethylformamide and H_3PO_2 , resulting in subcentimeter transparent acicular crystals with green emission upon 365 nm excitation (Fig. S1, Supporting Information). The crystal structure of $\text{TPP}_3\text{Cu}_2\text{Br}_2$ was obtained by resolving single-crystal X-ray diffraction (SCXRD) data (Fig. S2 and Tables S1–S4, Supporting Information). It was determined that $\text{TPP}_3\text{Cu}_2\text{Br}_2$ crystallized in a monoclinic phase with $P2_1/n$ space group, where $a = 19.0348(2) \text{ \AA}$, $b = 9.87200(10) \text{ \AA}$ and $c = 26.1822(3) \text{ \AA}$. The $[\text{Cu}_2\text{Br}_2]$ dimer is covalently bonded to the P atom in the TPP molecule via the Cu atom, which isolates the $[\text{Cu}_2\text{Br}_2]$ dimer and constitutes the 0D structure (Fig. 1a, b). The bond lengths of Cu-P



and Cu-Br are distributed in the range of 2.193–2.563 Å, whereas the Cu-Cu distance in the nearest dimer is 8.370 Å. Such a large distance also elucidated the isolated 0D structure of $\text{TPP}_3\text{Cu}_2\text{Br}_2$. Powder X-ray diffraction (PXRD) pattern of the as-synthesized crystals agreed well with the simulated structure from single crystal data (Fig. 1c). Meanwhile, X-ray photoelectron spectroscopy (XPS) was used to probe the chemical nature of $\text{TPP}_3\text{Cu}_2\text{Br}_2$. The characteristic peaks of C, P, Cu, and Br were identified, and the peaks of Cu $2p_{1/2}$ (952.4 eV) and $2p_{3/2}$ (932.6 eV) confirmed the monovalent state of Cu (Fig. 1d and Fig. S3, Supporting Information). Scanning electron microscopy (SEM) showed that the crystals displayed an acicular shape. Energy dispersive X-ray (EDX) spectrum mapping confirmed a uniform distribution of the elements Cu, P, and Br (Fig. S4, Supporting Information). In addition, the characteristic peaks located at 3053 and 1434 cm^{-1} in the Fourier transform infrared (FTIR) spectrum were attributed to C-H stretching vibrations and C=C vibrations of benzene, indicating that the organic groups were distributed in $\text{TPP}_3\text{Cu}_2\text{Br}_2$ (Fig. S5, Supporting Information). Through thermogravimetric analysis (TGA) and differential thermal analysis (DTA), it was observed that the decomposition of $\text{TPP}_3\text{Cu}_2\text{Br}_2$ started at a temperature up to 230 °C. Such good thermal stability favors their applications in high-temperature environments (Fig. 1e).

Photoluminescence properties and mechanisms

According to the absorption spectroscopy (Fig. 2a), $\text{TPP}_3\text{Cu}_2\text{Br}_2$ displayed broad absorption across the UV region (200–400 nm) with a peak of 310 nm. The bandgap was calculated to be 3.26 eV using the Tauc plot method (Fig. S6, Supporting Information). Upon excitation at 355 nm, $\text{TPP}_3\text{Cu}_2\text{Br}_2$ exhibited broad green emission peaking at 524 nm, with a full width at half maximum (FWHM) of 120 nm and a PLQY of 41.5% (Fig. 2b and Fig. S7, Supporting Information). The PL lifetime of $\text{TPP}_3\text{Cu}_2\text{Br}_2$ was determined to be 32.95 μs based on mono-exponential fitting (Fig. 2c). We measured the excitation wavelength-dependent (280–360 nm) emission spectra and the emission wavelength-dependent (450–620 nm) excitation spectra, which indicated that both the normalized PL emission and excitation spectra were essentially unchanged with different wavelengths, demonstrating a single source of emission (Fig. 2d and Fig. S8, Supporting Information). Note that $\text{TPP}_3\text{Cu}_2\text{Br}_2$ emitted strong broadband green PL while TPPBr exhibited negligible emission (Fig. S9, Supporting Information), revealing that the TPP group in $\text{TPP}_3\text{Cu}_2\text{Br}_2$ may not act as a luminescent center.

In order to gain a deep understanding of the photo-physical mechanism of $\text{TPP}_3\text{Cu}_2\text{Br}_2$, we acquired temperature-dependent steady-state PL spectra from 80

to 300 K (Fig. 2e, f). It was discovered that the PL intensity anomalously increased with elevating the temperature from 80 to 280 K. The FWHM of the emission became progressively wider with the rising of temperature. The FWHM variation with the temperature can be fitted to derive the Huang-Ryhs factor (S) and the phonon frequency ($\hbar\omega$) by using the following equation^{34,35}:

$$\text{FWHM}(T) = 2.36\sqrt{S}\hbar\omega\sqrt{\coth\frac{\hbar\omega}{2k_B T}} \quad (1)$$

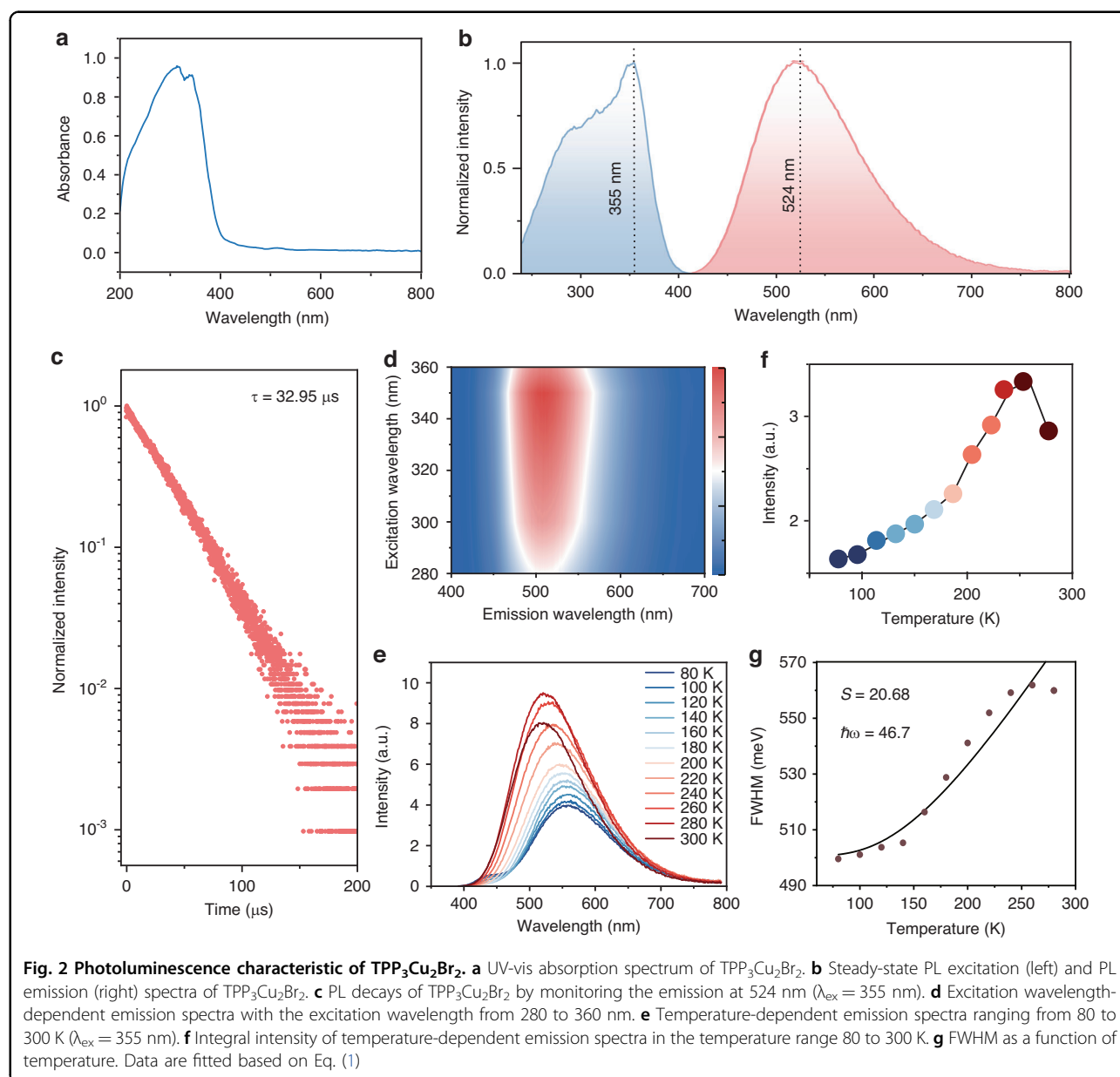
Correspondingly, S and $\hbar\omega$ were determined to be 20.68 and 46.7 meV, respectively (Fig. 2g). Such a large S revealed the strong electron-phonon coupling in $\text{TPP}_3\text{Cu}_2\text{Br}_2$ ³⁶.

Furthermore, we performed density functional theory (DFT) calculations to shed more light on the PL mechanism. As indicated by the projected density of states (DOS), $\text{TPP}_3\text{Cu}_2\text{Br}_2$ has a direct bandgap (Fig. 3a). From the charge density plots of the valence band maximum (VBM) and the conduction band minimum (CBM), it can be observed that the VBM was mainly composed of the Cu 3d and Br 4p orbitals, and the CBM was composed of TPP (Fig. 3b). The majority of the electron cloud was distributed around the TPP, with a small portion distributed on $[\text{Cu}_2\text{Br}_2]$ dimer (Fig. S10, Supporting Information). In addition, the charge density plots of the excited state were also modeled. Compared to the ground state, the electron cloud in the excited state was drastically concentrated towards $[\text{Cu}_2\text{Br}_2]$, leading to the distortion of $[\text{Cu}_2\text{Br}_2]$ dimer (Fig. 3c)³⁷. Through the excited state simulation of $\text{TPP}_3\text{Cu}_2\text{Br}_2$, theoretical lattice parameters were calculated (Table S4, Supporting Information), confirming no significant change in the lattice parameters of a and c compared to the ground state. Nevertheless, the lattice parameter b was significantly prolonged from 9.87 Å in the ground state to 9.95 Å in the excited state. As such, the lattice was distorted in the excited state, thus resulting in the emission of STE (Fig. 3d)^{38–40}.

Temperature sensing performance

Organic molecular TPP endows $\text{TPP}_3\text{Cu}_2\text{Br}_2$ with a soft lattice structure, which is sensitive to temperature change. At low temperature, the rigidity of organic molecules was strengthened, which would inhibit the deformation of $[\text{Cu}_2\text{Br}_2]$ dimer and suppress the creation of the self-trapped state^{41,42}. Consequently, the PL intensity of $\text{TPP}_3\text{Cu}_2\text{Br}_2$ was substantially boosted with the temperature increased from 80 to 280 K (Fig. 2e). Meanwhile, it was found that the lattice greatly expanded with lattice volume increased by 3.6% (from 4818.3 to 4994.0 Å³) from 300 to 380 K (Fig. S11 and Table S5, Supporting Information), which is much higher than that (< 0.5%) of





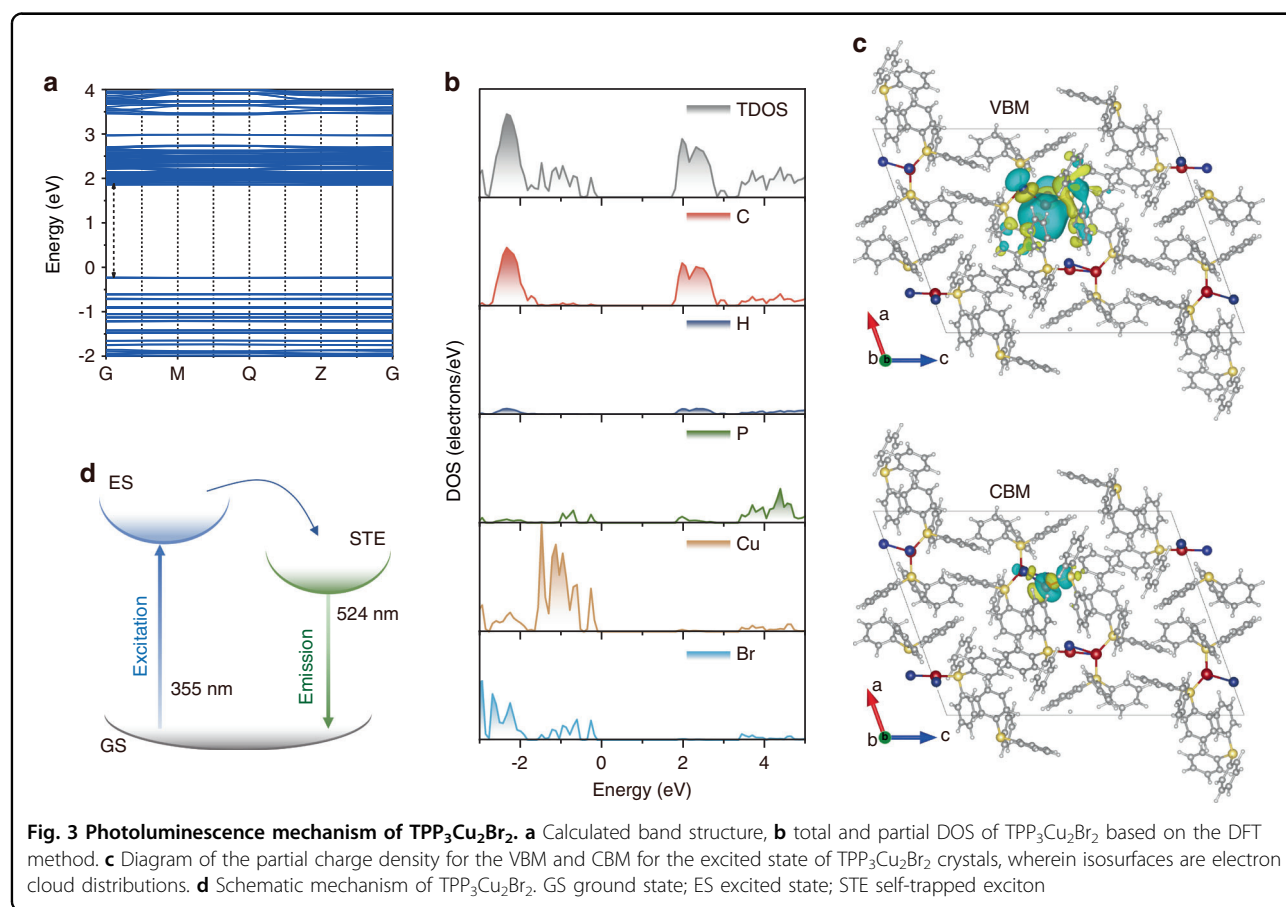
typically MHs^{19,20}. The giant thermal expansion of lattice was also confirmed by the temperature-dependent PXRD of TPP₃Cu₂Br₂, as evidenced by the shifting of diffraction peaks towards smaller angles with the rising of temperature (Fig. 4a). The dramatic lattice expansion with elevating temperature would introduce more defects within the crystal and thus quenching the luminescence. We compared the temperature dependence of PL intensity and lifetime from 280 to 380 K. It was discovered that the PL intensity decreased steadily as temperature increased, eventually dropping to 10.8% of its original value at 380 K (Fig. 4b). Intriguingly, the PL lifetime of TPP₃Cu₂Br₂ displayed a much wider range of variation from 51.2 μ s (280 K) to

0.97 μ s (380 K), which was only 1.9% of the initial value (Fig. 4c, d). The PL lifetime (τ) and temperature (T) can be fitted with the following empirical exponential equation¹⁹:

$$\tau(T) = A \cdot \exp\left(\frac{T}{t}\right) + \tau_0 \quad (2)$$

where A , t , τ_0 are constants. Furthermore, the temperature sensing performance can be evaluated with absolute sensitivity (S_a) and S_r based on the following equations:

$$S_a = \left| \frac{d\tau}{dT} \right| \quad (3)$$



$$S_r = \left| \frac{1}{\tau} \frac{d\tau}{dT} \right| \quad (4)$$

Accordingly, the maximum S_a value was determined to be $1.33 \mu\text{s K}^{-1}$ (280 K) (Fig. S12, Supporting Information), and the maximum S_r value was calculated to be $12.82\% \text{ K}^{-1}$ (380 K) (Fig. 4e). Note that the S_r value is the highest for temperature sensing among the undoped MHs. For comparison, the maximum values of S_a and S_r based on PL intensity were only $1.39\% \text{ K}^{-1}$ and $6.46\% \text{ K}^{-1}$, respectively (Figs. S13, S14, Supporting Information). Besides, the repeatability of the thermometer is a decisive parameter for its application in temperature sensing. After 11 test cycles, the PL lifetime of the TPP₃Cu₂Br₂ remained essentially unchanged, confirming its good repeatability in temperature sensing (Fig. 4f). The temperature uncertainty δT can be calculated by using the following equation¹⁹:

$$\delta T = \frac{1}{S_r} \frac{\delta\tau}{\tau} \quad (5)$$

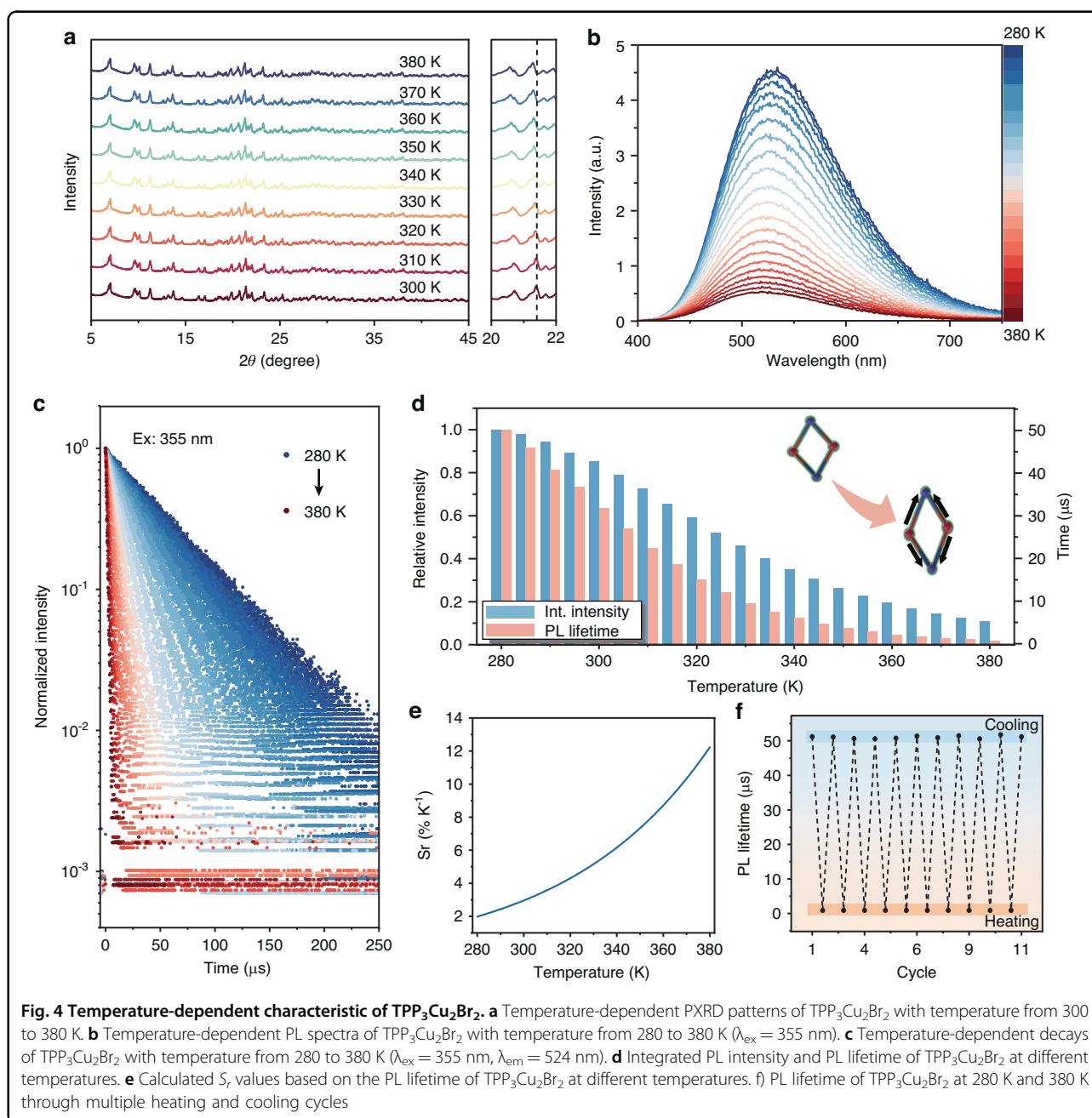
where $\delta\tau/\tau$ is the uncertainty of lifetime measurements. Accordingly, it was determined that TPP₃Cu₂Br₂ exhibited small δT values ($\leq 0.47 \text{ K}$) in the range of 280–380 K,

which is beneficial for high-precision temperature sensing (Fig. S15, Supporting Information).

Water Stability Performance

The PXRD pattern of TPP₃Cu₂Br₂ remained in the pure phase even after immersing it in water for 15 days (Fig. 5a), indicating its excellent structural stability in water. Correspondingly, TPP₃Cu₂Br₂ exhibited almost no alteration in both PL photographs and PL spectra (Fig. 5b, c). Specifically, the PL intensity was 97.3% of the initial value after 15 days, indicative of the extraordinary photostability of TPP₃Cu₂Br₂ in water (Fig. 5d). To investigate the impact of TPP, we compared the surface hydrophobicity of hybrid TPP₃Cu₂Br₂ and all-inorganic Cs₃Cu₂Br₅. Through characterization of static-contact angle, the degree of water infiltration on TPP₃Cu₂Br₂ and Cs₃Cu₂Br₅ was investigated (Fig. 5e). A larger contact angle of 66° was detected for TPP₃Cu₂Br₂ crystals, which greatly surpassed that of 23° for the Cs₃Cu₂Br₅ counterpart. Such a high contact angle indicated that the crystal surface of TPP₃Cu₂Br₂ was highly hydrophobic, thus protecting the matrix from permeability and diffusion of water molecules. Through DFT calculations, the binding energy of TPP₃Cu₂Br₂ and water molecules was



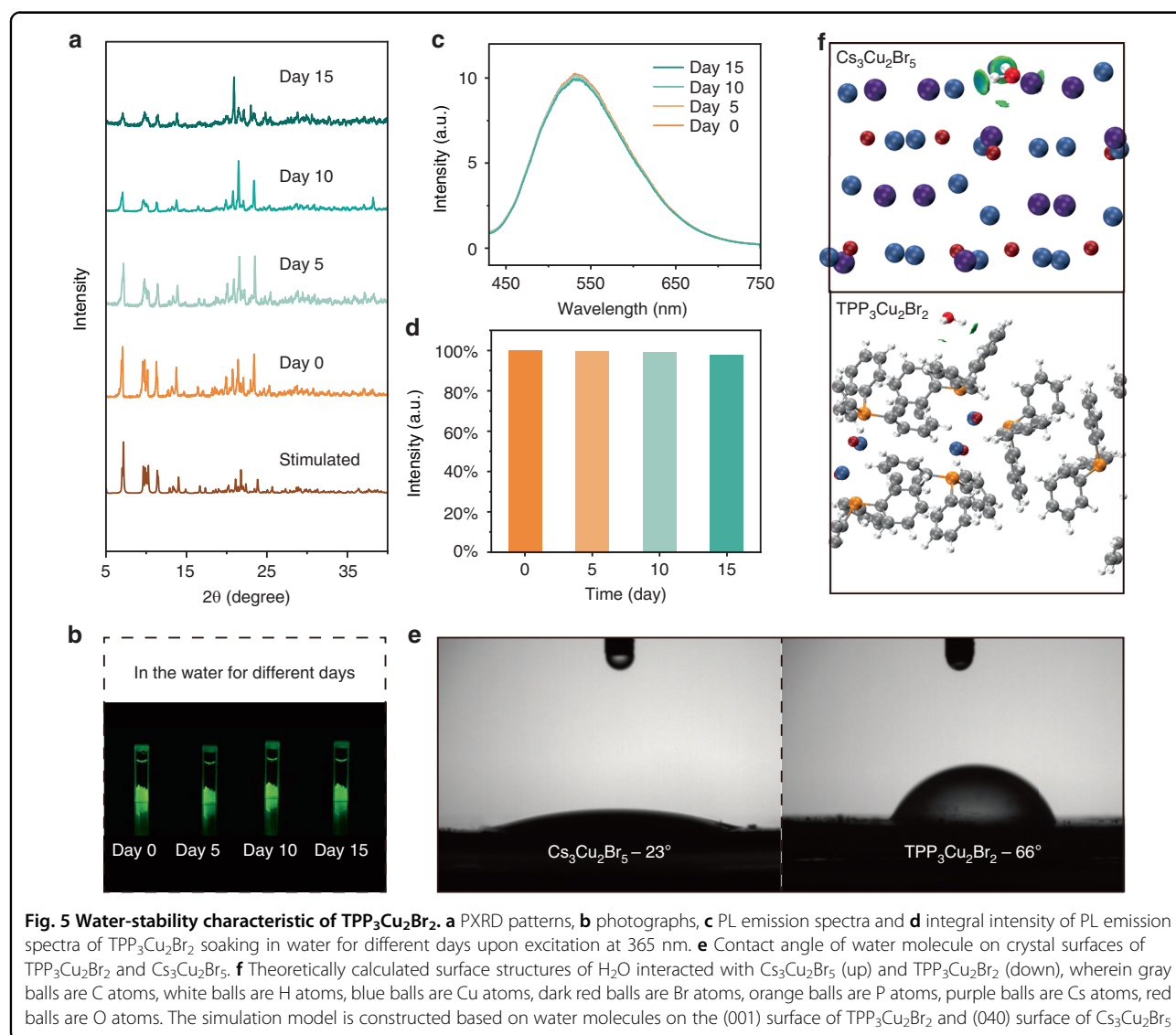


determined to be 0.223 eV (Fig. 5f), which is much lower than that of $\text{Cs}_3\text{Cu}_2\text{Br}_5$ and water molecules (0.882 eV), revealing weaker hydrophilicity of $\text{TPP}_3\text{Cu}_2\text{Br}_2$ than $\text{Cs}_3\text{Cu}_2\text{Br}_5$.

Moreover, the interaction force between atoms was reported to be proportional to their distance⁴³. The rigid molecular conformation of the TPP molecule and the large steric hindrance limit the movement of water molecules, inhibiting water molecules from directly contacting with the hydrophilic $[\text{Cu}_2\text{Br}_2]$ dimer in $\text{TPP}_3\text{Cu}_2\text{Br}_2$. The closest contact distance between water

molecule and $\text{TPP}_3\text{Cu}_2\text{Br}_2$ was calculated to be 6.583 Å for the H-Br bond length, which is much longer than the H-Br distance of 2.335 Å between water molecule and $\text{Cs}_3\text{Cu}_2\text{Br}_5$ (Fig. S16, Supporting Information). The longer contact distance between water molecule and hydrophilic $[\text{Cu}_2\text{Br}_2]$ dimer endowed superior water-resistance stability. In addition, the bond type in the matrix also significantly affects the stability of the crystal⁴⁴. The strong Cu-P covalent bond in $\text{TPP}_3\text{Cu}_2\text{Br}_2$ results in a higher energy barrier for ionization in water, facilitating the structural stability of $\text{TPP}_3\text{Cu}_2\text{Br}_2$. By contrast, the ionic





bonds in Cs₃Cu₂Br₅ are more susceptible to ionization in water, which might lead to structural disruption. Hence, the impressive resistance to water of TPP₃Cu₂Br₂ renders it an ideal material as the luminescence thermometer in water environment. To the best of our knowledge, such water-resistance MHs based luminescence lifetime thermometers have never been reported before. Note that the micron-scale dimensions of TPP₃Cu₂Br₂ crystals enable spatial resolution in microdomain thermal mapping, favoring diverse sensing scenarios like mapping microzone-temperature variations in water.

Temperature sensing in water environment

As a proof-of-concept experiment, we applied TPP₃Cu₂Br₂ for temperature sensing in aqueous solution. The PL lifetime was independently monitored three times at 37 °C (Fig. 6a). The average PL lifetime was determined

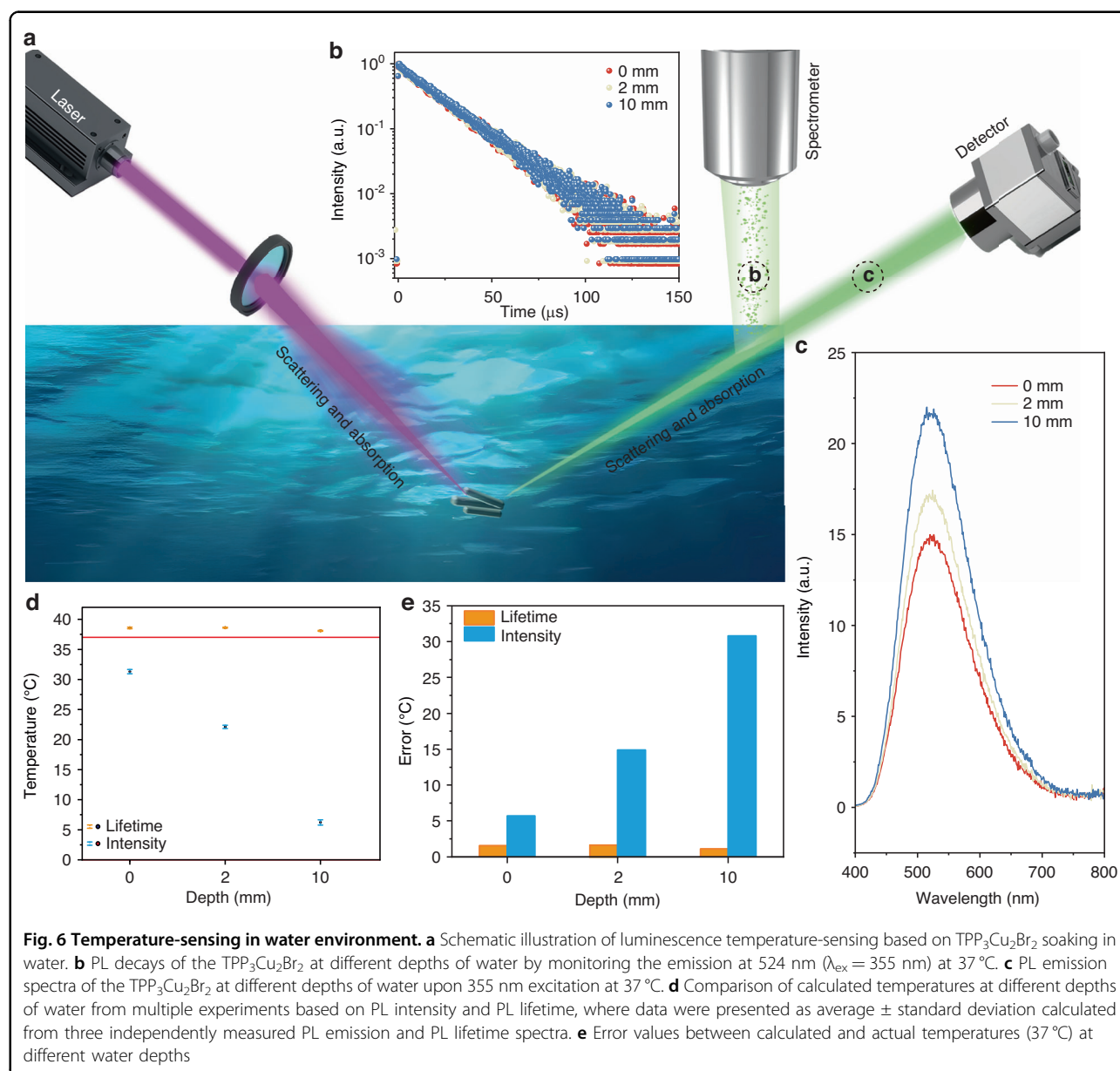
to be 19.83 μs (Fig. S17, Supporting Information). Meanwhile, the PL emission spectra were monitored under the same conditions (Fig. S18, Supporting Information). The temperature can be calculated by using Eqs. 2 and 6 as standard curves, respectively.

$$I(T) = A \cdot \exp\left(\frac{T}{t}\right) + I_0 \quad (6)$$

where A, t, and I₀ are constants. Specifically, temperatures of 38.57 ± 0.13 and 31.31 ± 0.36 °C were determined on the basis of PL lifetime and PL intensity with errors of 1.57 and 5.69 °C, respectively. Therefore, PL lifetime-based temperature sensing provides higher accuracy than PL intensity-based temperature sensing.

Moreover, the absorption and scattering of light may significantly reduce the accuracy of intensity measurements





at varying depths, which is unavoidable in practical applications. To this regard, we placed $\text{TPP}_3\text{Cu}_2\text{Br}_2$ in cuvettes filled with water at varying depths to illustrate the impact of water on light interference. We monitored the PL lifetime and PL intensity of $\text{TPP}_3\text{Cu}_2\text{Br}_2$ in different depths at 37 °C (Fig. 6b, c). The accuracy of the temperature measurements was then calculated (Fig. 6d, e). As the depth of the water increased, the PL intensity quenched significantly, while the PL lifetime remained essentially unchanged. When the water depth reached 2 mm, the error value based on PL intensity reached 14.88 °C while the value based on PL lifetime remained essentially small (1.61 °C). When the sample was immersed in 10 mm water, the detection error based on PL intensity was elevated to 30.78 °C, significantly

larger than the read-out error based on PL lifetime (1.09 °C). These results highlighted that $\text{TPP}_3\text{Cu}_2\text{Br}_2$ has great potential for accurate temperature sensing applications in water environment, offering promising opportunities for monitoring microzone-temperature variations beneath the water surface.

Discussion

In summary, we have developed a new class of zero-dimensional hybrid cuprous halide of $\text{TPP}_3\text{Cu}_2\text{Br}_2$, which presents excellent water resistance for sensitive temperature sensing. Specifically, TPP induced the soft lattice of $\text{TPP}_3\text{Cu}_2\text{Br}_2$, enabling substantial lattice distortion and significant reduction of STE luminescence lifetime to 1.9%



of the initial value from 280 to 380 K. Such remarkable temperature-dependent PL lifetime favored highly sensitive optical temperature sensing, exhibiting a S_r of 12.82% K^{-1} , representing the highest value based on the undoped MHs. Furthermore, we successfully applied $TPP_3Cu_2Br_2$ for thermal sensing with a small read-out error of 1.09 °C at a water depth of 10 mm, demonstrating the superiority of PL lifetime strategy relative to the conventional PL intensity approach. Our work reveals the great promise of $TPP_3Cu_2Br_2$ for temperature detection in water environment, which may accelerate the exploitation of novel MHs for thermometry applications in versatile scenarios.

Materials and methods

Chemicals and materials

Triphenylphosphine hydrobromide ($C_{18}H_{16}BrP$, 97%) and phosphinic acid (H_3PO_2 , 50 wt.%) were purchased from Adamas-beta Ltd. Copper(I) bromide ($CuBr$, 99.9%) was purchased from Aladdin (Shanghai, China). N,N-Dimethylformamide (DMF, 99.5%), and isopropanol (C_3H_8O , 99.7%) were purchased from Sinopharm Chemical Reagent Co (Shanghai, China). All chemicals were used without any further purification.

Synthesis of $TPP_3Cu_2Br_2$ single crystal

$TPP_3Cu_2Br_2$ single crystals were prepared by a saturated crystallization method. In a typical synthesis, 1 mmol $C_{18}H_{16}BrP$ and 1 mmol $CuBr$ were dissolved in 4 mL DMF and 1 mL H_3PO_2 at 95 °C to form a colorless transparent solution. Then the solution was cooled to room temperature slowly. After that, the transparent crystals of $TPP_3Cu_2Br_2$ were filtered off, washed with isopropanol to remove the solvent from the crystal surface, and dried in an oven at 60 °C. Finally, the crystals were ground into powder for further utilization.

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Author contributions

C.L. Li, L.P. Wang and D.T. Tu conceived the initial concept. C.L. Li and L.P. Wang prepared the sample. C.L. Li, L.P. Wang and X.Y. Shang processed the data. C.L. Li wrote the paper. L.P. Wang, D.T. Tu and X.Y. Chen supervised the work and revised the paper. All authors discussed and edited the paper.

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Conflict of interest

The authors declare no competing interests.

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