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Exciplex-induced TADF, persistent RTP and ML in a host–guest doping system†

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The development of multifunctional luminescent materials is of great importance but really difficult, since different luminescent properties have different requirements for molecular structure. Herein, a universal exciplex platform was reported to construct multifunctional luminescent materials, including thermally-activated delayed fluorescence (TADF), persistent room temperature phosphorescence (RTP) and mechanoluminescence (ML). With compound **PTZ-CN** as an electron donor and its derivative of **OPTZ-CN** as an electron acceptor, the resultant exciplex system demonstrated efficient TADF with the quantum yield up to 61%, persistent RTP lasting for more than 3 minutes and bright blue ML emission. Thus, this work opens a new way to construct multifunctional luminescent materials, which will largely promote the further development of this research area.

Introduction

The research of organic luminescent materials has drawn great attention, because of their wide applications in bio-imaging, sensors, anti-counterfeiting and displays, *etc.*^{1–7} With different luminescence properties, luminogens generally present different photophysical processes and applicable scenarios. For instance, thermally-activated delayed fluorescence (TADF) indicates a radiative transition of singlet excitons after undergoing inter-system crossing (ISC) and reverse intersystem crossing (RISC) between excited singlet and triplet states.^{8,9} On account of this unique excited process, both singlet and triplet excitons can be utilized in TADF materials. Also, the corresponding emission lifetime could be much prolonged from nanoseconds in normal fluorescence to microseconds in TADF. When the excitons decay from the excited triplet state, phosphorescence occurs. To achieve persistent organic room temperature phosphorescence (RTP), the triplet excitons should be stabilized by specific external environments, such as crystallization, polymerization,

supramolecular assembly, and host–guest doping.^{10–16} Accordingly, the lifetime of persistent RTP could even reach seconds. The advantages of long emission lifetime and full utilization of excitons in TADF and RTP materials offer them great potential in the applications of time-resolved bio-imaging, anti-counterfeiting and organic light-emitting diodes (OLEDs).^{17–19} Besides, some organic systems were found to present mechanoluminescence (ML), another important type of luminescence induced by mechanical stimulation such as grinding, rubbing, or shaking.^{20–24} Systematic studies indicated that ML was heavily related to the piezoelectric effect, in which the singlet and triplet excitons could be formed through the recombination of positive and negative charges at the broken interfaces. An ML material sensitive to mechanical force could be utilized in the applications of pressure sensors and heartbeat monitors *etc.*^{25–27} Thus, regardless of the different emissive properties, the behaviors of TADF and RTP, in addition to ML, are all heavily related to the singlet and triplet excitons; therefore, the inherent mechanism could be considered much more deeply if there were some luminogens having all these three different emitting properties.

To date, the designs of organic luminescent materials are mostly based on a single property, since different luminescent properties have different requirements for molecular structure. In the design of TADF materials, separated HOMO and LUMO orbitals in space are needed, thus minimizing the energy gap (ΔE_{ST}) between the S_1 and T_1 states.²⁸ To prolong the emission lifetime (τ_p) in RTP materials, specific intermolecular interaction forms should be presented to minimize both radiative ($k_{p,r}$) and non-radiative ($k_{p,nr}$) transitions of triplet excitons, according to the equation $\tau_p = 1/(k_{p,r} + k_{p,nr})$.²⁹ As for organic ML materials, a non-centrosymmetric crystal packing with large dipole moment

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is of great importance.³⁰ Therefore, it is difficult to construct multifunctional luminescent materials due to the lack of a universal platform to meet all of their different requirements. Nevertheless, if these luminescent properties could be successfully integrated into one system, multiple advances can be expected. On the one hand, the properties and applications of luminescent materials could be largely enriched. On the other hand, different luminescent properties might have a mutually promoting relationship. For example, the exciton transfer between TADF and RTP could largely prolong their corresponding lifetimes.³¹ Also, the full utilization of the excited state energy in TADF and RTP will contribute much to the realization of bright ML emission.³² Thus, it will be of great significance to develop multifunctional luminescent materials.

In previous works, we have found that phenothiazine (PTZ) and phenothiazine 5,5-dioxide (OPTZ) groups were good candidates to construct RTP materials.^{10,33} When they were mixed together to form a doping system, a stable exciplex with a new energy level could be formed in some cases.³⁴ To further adjust the energy level of the exciplex and construct multifunctional luminescence materials, the cyano group (–CN) with electron-withdrawing ability was introduced in this work (Fig. 1). Indeed, multifunctional luminescent properties were successfully achieved with the formation of the exciplex. For the exciplex, compound **PTZ-CN** acted as an electron donor (D), while its derivative of **OPTZ-CN** was the electron acceptor (A). Firstly, separated HOMO and LUMO orbitals in space could be realized in the exciplex, thus minimizing the energy gap (ΔE_{ST}) between the S_1 and T_1 states. Secondly, the exciton transfer between the exciplex and other components would prolong the exciton lifetime. Thirdly, an increased dipole moment could be expected in the D–A exciplex. Thus, although the individual **PTZ-CN** and **OPTZ-CN** crystals just showed a moderate RTP effect, multifunctional luminescent properties could be achieved for their host–guest doping system with the formation of an exciplex, including thermally-activated delayed fluorescence (TADF),

persistent room temperature phosphorescence (RTP) and mechanoluminescence (ML).

Results and discussion

As shown in Fig. 2(A) and Fig. S1–S5 (ESI[†]), the individual **OPTZ-CN** and **PTZ-CN** crystals only show a moderate RTP effect. For **OPTZ-CN**, two phosphorescence peaks exist, in which, one peak is at 425 nm with the lifetime of 110 ms and the other one is at 485 nm with a relatively longer lifetime of 133 ms. As for **PTZ-CN**, its RTP peak locates at about 500 nm with a much shorter lifetime of 43 ms. Also, their PL efficiencies are relatively low, at just 4% and 16%, respectively. Interestingly, when they are mixed together to crystallize with the mass ratio of 99:1, the resultant doping system of M-CN shows a much boosted PL efficiency of 61%. Furthermore, the steady-state and delayed PL spectra of M-CN are almost exactly overlapped with the emission peak at about 485 nm. Besides, the excitation spectrum of M-CN is different from those of **PTZ-CN** and **OPTZ-CN** crystals, indicating the formation of new energy levels (Fig. S4, ESI[†]). Careful measurements of PL decay curves, coupled with the luminescent photos after UV-off, demonstrated that two decay components exist in M-CN (Fig. 2(B)). Among them, the former component is strong but relatively short, which shows the characteristic of TADF with a delayed fluorescence lifetime of 37 ms.³⁵ As for the later component, a weak but long emission lasting for more than 3 min could be observed, which should be ascribed to the persistent RTP effect (Fig. 2(C) and Fig. S5, ESI[†]). Thus, the integration of TADF and persistent RTP was successfully realized in the host–guest doping system of M-CN.

To make the internal mechanism clear, the UV-Vis absorption spectra of **OPTZ-CN**, **PTZ-CN** and M-CN were firstly measured. As shown in Fig. 3(A), an additional absorption band (~ 370 nm) appears in the long wavelength region of M-CN, in comparison with **OPTZ-CN** and **PTZ-CN**. This indicates the occurrence of intermolecular charge transfer between **OPTZ-CN** and **PTZ-CN**.³⁶ Also, this new absorption band well corresponded to the excitation spectrum of M-CN (@485 nm), suggesting the formation of an exciplex (Fig. S6, ESI[†]).³⁷ Coupled with the HOMO/LUMO energy levels of compounds **OPTZ-CN** and **PTZ-CN**, it could be inferred that **OPTZ-CN** acts as an acceptor and **PTZ-CN** as a donor in the exciplex (Fig. S7 and S8, ESI[†]).³⁸ Further on, the temperature-dependent PL behaviors were studied for the M-CN crystal (Fig. 3 and Table S1, Fig. S9, ESI[†]). As shown in Fig. 3(B) and (C), its PL intensity and lifetime both decrease with the temperature increasing, due to the accelerated non-radiative transition. Nevertheless, the delayed portion in the PL decay curves (bright & short component) presents obvious enhancement in the process of heating up, showing the typical characteristic of TADF.³⁹ Also, the PL decay curve of the persistent phosphorescence (weak & long component) was measured at 77 K, which showed much slower decay than the one at room temperature for the restricted non-radiative transition (Fig. S10, ESI[†]). Thus, based on the temperature-dependent PL behaviors of the M-CN

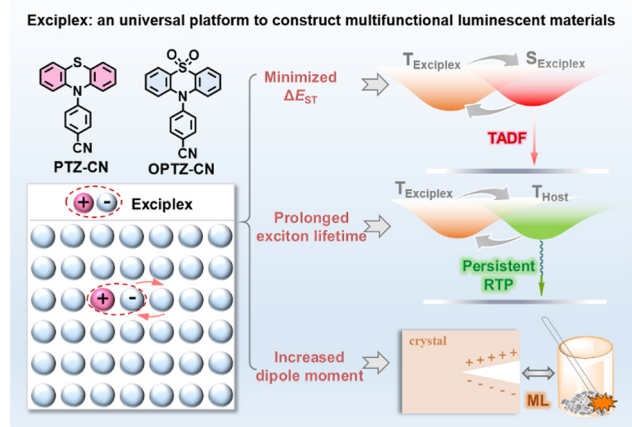


Fig. 1 Exciplex-induced thermally-activated delayed fluorescence (TADF), persistent room temperature phosphorescence (RTP) and mechanoluminescence (ML) in a doping system with **OPTZ-CN** as the host and **PTZ-CN** as the guest.

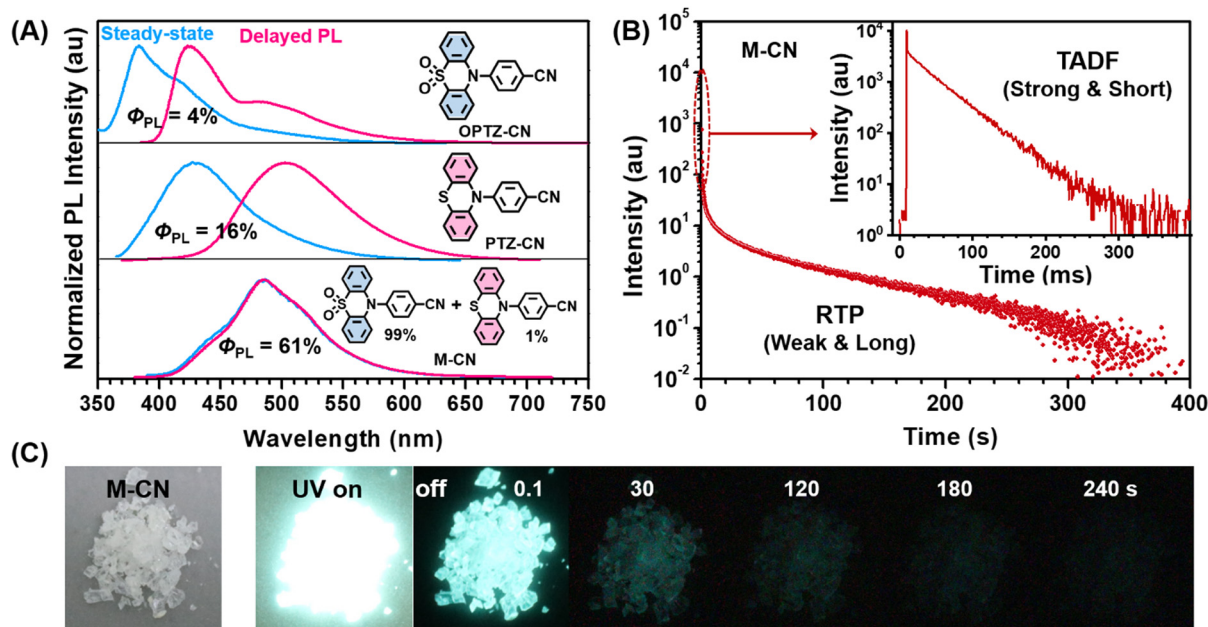


Fig. 2 (A) The steady-state and delayed photoluminescence (PL) spectra of the **OPTZ-CN** crystal, **PTZ-CN** crystal and corresponding host-guest doping system (**M-CN**); (B) the PL decay curves of **M-CN**; (C) the luminescent behavior of **M-CN** (λ_{ex} = 365 nm).

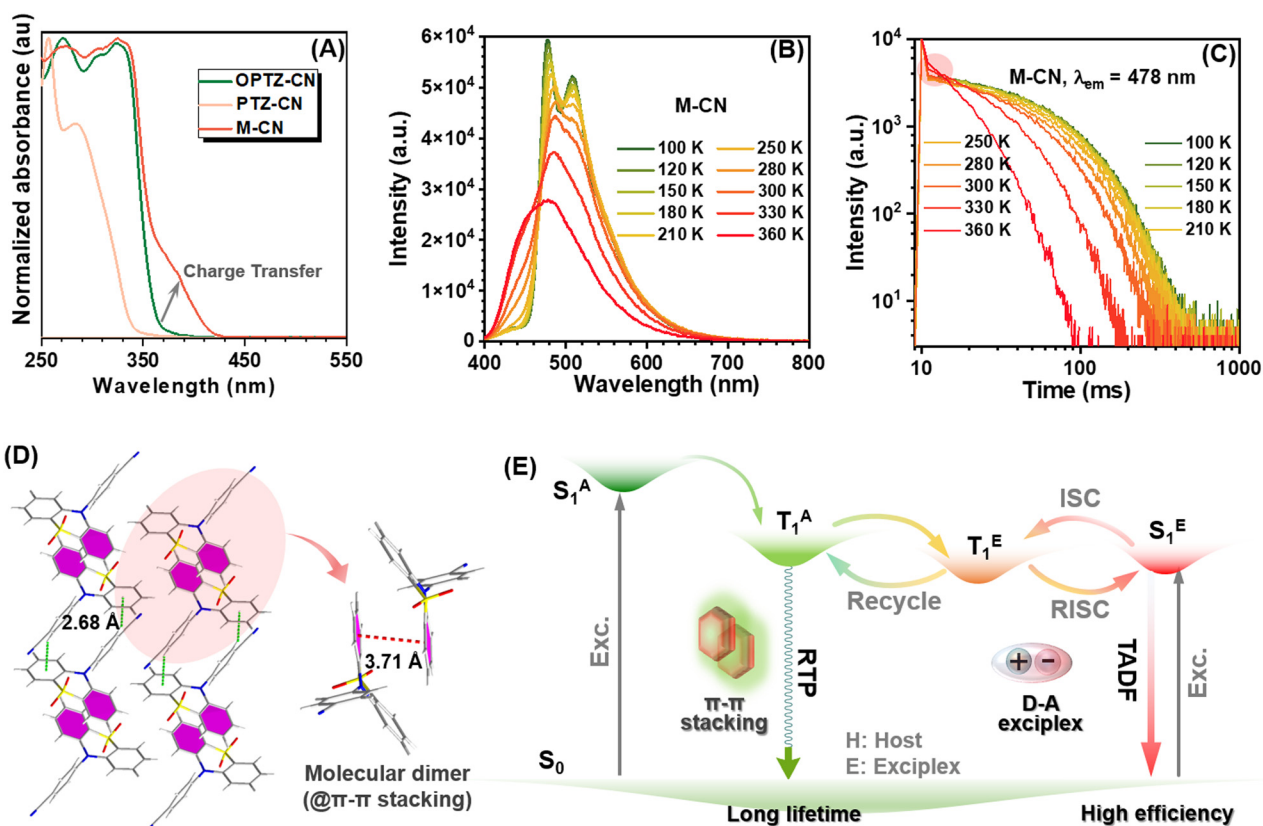


Fig. 3 (A) Normalized UV-Vis absorption spectra of the **OPTZ-CN** crystal, **PTZ-CN** solution and **M-CN** crystal; (B) temperature-dependent PL spectra of the **M-CN** crystal; (C) temperature-dependent PL decay curves of the **M-CN** crystal at 478 nm; (D) single crystal structure of the **OPTZ-CN** crystal; (E) proposed mechanism for the unique luminescent behaviors of the **M-CN** crystal.

crystal, the existence of TADF and persistent RTP effects could be further certified.

Further on, the phosphorescence behaviors of **OPTZ-CN** and **PTZ-CN** were studied at 77 K. As shown in Fig. S11 (ESI[†]), just one main phosphorescence band at about 430 nm could be observed for **OPTZ-CN** in both the solution and crystal states at 77 K, which corresponds to the RTP one of its crystal at short wavelength (425 nm). Coupled with the single crystal structure of **OPTZ-CN** (Fig. 3(D)), in which, an obvious molecular dimer with strong intermolecular π - π stacking (3.71 Å) exists, it could be inferred that the RTP peak at 425 nm should originate from the **OPTZ-CN** monomer, while the longer one at 485 nm is from the dimer-based excimer (Fig. S12, ESI[†]), just like other phenothiazine-5,5-dioxide derivatives in previous work.⁴⁰ As for **PTZ-CN**, the phosphorescence bands of its solution and crystal at 77 K both well correspond to the RTP one of the crystal (Fig. S13, ESI[†]). On the other hand, the intermolecular π - π distances in the **PTZ-CN** crystal were as long as 4.59 and 5.18 Å, suggesting the absence of π - π interaction (Fig. S14, ESI[†]). Thus, it could be concluded that the RTP emission of **PTZ-CN** is from its monomer. When **OPTZ-CN** and **PTZ-CN** are mixed together with the mass ratio of 99:1 to form M-CN, the resultant molecular packing is still dominated by the **OPTZ-CN** crystal, as indicated by their powder X-ray diffraction (PXRD) patterns in Fig. S15 (ESI[†]).

Based on these PL behaviors and crystal structures, the excited process of M-CN in PL was proposed. As shown in Fig. 3(E), upon 365 nm UV irradiation, the excimer based on the **OPTZ-CN** dimer and exciplex based on **OPTZ-CN/PTZ-CN** would be both excited and jump from the S_1 to T_1 states through ISC transition. Because of the small energy gap (ΔE_{ST}) between S_1 and T_1 in the exciplex, RISC could happen, then leading to efficient TADF emission from it. On the other hand, the T_1 states for the excimer based on the **OPTZ-CN** dimer and exciplex based on **OPTZ-CN/PTZ-CN** are both at about 2.56 eV, which allows their corresponding triplet excitons to make a cyclic

transfer between them. Thus, their exciton lifetimes are much prolonged, thus resulting in an abnormal long lifetime of TADF (37 ms) from the exciplex (**OPTZ-CN/PTZ-CN**) and persistent RTP lasting for more than 3 min from the excimer (**OPTZ-CN** dimer). Thus, the exciplex as a good platform to construct TADF and persistent RTP materials could be well certified, in which, the TADF and RTP properties have a mutually promoting relationship in emission lifetime.

It is worth emphasizing that long-lived TADF and RTP are unusual and may result from a combination of causes. Besides the cyclic transfer of different excitons to prolong their lifetimes, and rigid molecular stacking of the M-CN crystal should also be crucial.^{41–44} **OPTZ-CN** and **PTZ-CN** have similar molecular structures/conformations, so the M-CN crystal containing a small amount of **PTZ-CN** can still maintain good rigidity, which is beneficial for the suppression of non-radiative transitions. This is corroborated by the afterglow behaviours of the M-CN crystals with different mass ratios of **PTZ-CN** (Fig. S16, ESI[†]). In these doping systems, the afterglow shortens significantly with higher **PTZ-CN** ratios, indicating that the exciton lifetime decreases with lower crystal structure integrity. From another perspective, we can also assume that the excitons can be effectively blocked by the acceptor at low donor concentration, which reduces the quenching probability and prolongs the excitons' lifetime.

Further on, the M-CN crystal was found to show bright blue mechanoluminescence (ML) under the mechanical stimulation of a glass rod, such as grinding and rubbing, while both **PTZ-CN** and **OPTZ-CN** were ML in-active (Fig. 4(A)). As shown in Fig. S17 (ESI[†]), the ML intensity of M-CN decreased with the increase of the doping concentration for **PTZ-CN**, and there was almost no ML after the mass ratio of **PTZ-CN** was higher than 33%. Additionally, the ML spectrum of M-CN was well consistent with the PL one, indicating that the ML emission of M-CN is also from the excited state of the exciplex. According to the previous reports, most ML emissions came from the piezoelectric effect of the crystal, which was heavily related to the non-centrosymmetric molecular packing

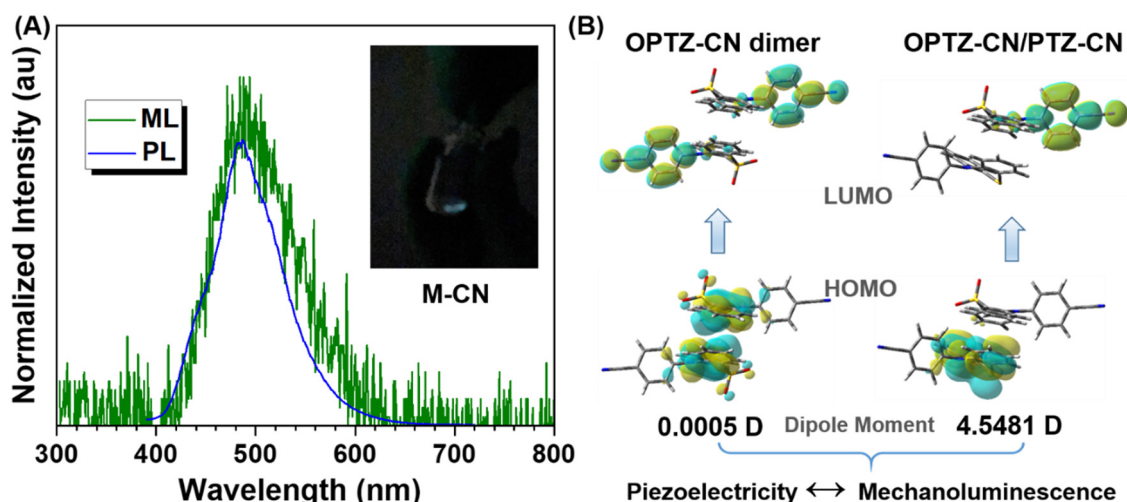


Fig. 4 (A) Normalized PL and ML spectra of the M-CN crystal; (B) theoretical calculations of the HOMO/LUMO orbitals and dipole moments for the **OPTZ-CN** dimer and **OPTZ-CN/PTZ-CN** exciplex.

with large dipole moment (Fig. S18, ESI†).⁴⁵ For the host molecule of **OPTZ-CN**, its crystal presents a centrosymmetric space group of $P\bar{1}$. Correspondingly, the dipole moment for the **OPTZ-CN** dimer with π - π stacking was calculated to be nearly zero, which is not conducive to the ML emission (Fig. 4(B)). When one **OPTZ-CN** molecule in its dimer was replaced by **PTZ-CN** to form an exciplex (**OPTZ-CN/PTZ-CN**), the dipole moment could be largely increased to 4.5418 D. Thus, after **PTZ-CN** was doped in **OPTZ-CN** to form an exciplex, the centrosymmetric molecular packing of the **OPTZ-CN** crystal was broken, which then contributed much to the piezoelectric effect and resultant ML emission. Based on this mechanism, the singlet and triplet excitons were formed through the recombination of positive and negative charges at the interface, just like electroluminescence (EL).⁴⁶ Therefore, the TADF effect induced by the exciplex would also contribute much to the promotion of bright ML emission, as it could make full use of the excited state energy from both singlet and triplet excitons. Thus, the exciplex as a good platform to construct ML materials could also be well confirmed. Also, the promotion of exciplex-induced TADF on ML effect could be realized, demonstrating the great advances in multifunctional luminescent materials.

Conclusions

In this work, a host-guest doping system was developed with compound **PTZ-CN** as the guest and its derivative of **OPTZ-CN** as the host. Although just moderate RTP effects were presented for the individual **OPTZ-CN** and **PTZ-CN** crystals, their doping system of M-CN was found to show excellent multifunctional luminescent properties, including TADF, persistent RTP and ML. Experimental results showed that the formation of an exciplex between **OPTZ-CN** and **PTZ-CN** played a significant role, as it could lead to the minimized energy gap (ΔE_{ST}) between the S_1 and T_1 states, prolonged exciton lifetime and increased dipole moment. Also, these different luminescent properties can promote each other, showing the great advances in multifunctional luminescent materials. Thus, an exciplex as a universal platform to construct multifunctional luminescent materials was well demonstrated.

Author contributions

Jie Yang and Zhen Li conceived and planned this research; Yusheng Wang, Mingxue Gao, Jia Ren, Jiayi Liang and Yao Zhao performed the experiments; Jie Yang, Yunsheng Wang and Manman Fang performed data analysis; Yunsheng Wang, Jie Yang and Zhen Li wrote the manuscript; Zhen Li and Manman Fang gave the suggestions. All authors discussed the results and approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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