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ORIGINAL ARTICLE

Reversible manipulation of organic dye aggregation through acyclic cucurbit[*n*]uril-based host-guest complexation

Wen-Chang Peng[1] · Hui Wang[1] · Dan-Wei Zhang[1] · Zhan-Ting Li[1] · Da Ma[2]

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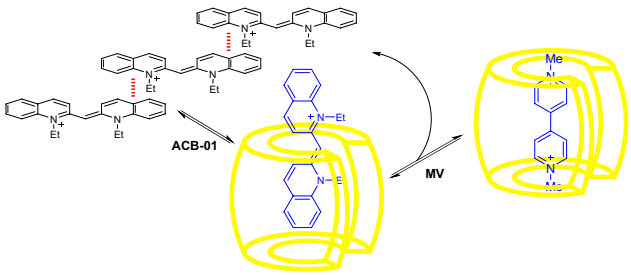
Abstract

We use a highly water-soluble acyclic cucurbit[*n*]uril **ACB-01** that bears eight carboxylate groups. **ACB-01** has excellent solubility in water and high affinity to the cyanine dyes pseudoisocyanine (**PIC**) and pinacyanol (**PIN**) to afford 1:1 complexes. The complexation has been studied by UV–vis absorption, fluorescence and nuclear magnetic resonance (NMR) spectroscopy, and the binding constants (K_a) are determined to be $(1.54 \pm 0.15) \times 10^6$ M^{-1} and $(6.09 \pm 0.82) \times 10^5$ M^{-1}, respectively. This complexation leads to the inhibition of the J-aggregation of **PIC** and H-aggregation of **PIN**. However, competitive guests methyl viologen and 1-adamantanamine hydrochloride can recover their respective J- and H-aggregation due to more stable complexation occurs between them and **ACB-01**. Thus, we have established a new method of reversibly controlling dye aggregation by regulating the concentration of **ACB-01** and competitive guests.

Graphical abstract



Keywords Acyclic cucurbit[*n*]uril · Host-guest chemistry · Cyanine dyes · J-aggregation · H-aggregation

Introduction

Cucurbit[*n*]urils (CB[*n*]s) are a family of macrocyclic host homologues [1–12]. CB[*n*]s are known for their ability to form high affinity inclusion complexes with suitable guests in water. However, further applications of CB[*n*]s are limited by their inadequate aqueous solubility, and the laborious process of isolating homologues [1, 2, 13–16]. Acyclic CB[*n*]s (ACBs), derived from glycoluril oligomers, have been developed to provide new approaches [17–22]. Acyclic CB[*n*]s are composed of glycoluril tetramers linked by methylene bridges, and two aromatic O-xylylene walls bearing substituents. Acyclic CB[*n*]s are capable of recognizing suitable ammonium salts, dyes and pharmaceuticals, and are widely used for sensing and imaging [23–26], drug delivery and controlled release [27, 28], and drug sequestration [29, 30]. The investigations well demonstrate that ACBs can create guest binding features that complement those of CB[*n*]s or other acyclic receptors [31–33].

✉ Zhan-Ting Li
ztli@fudan.edu.cn

✉ Da Ma
dama@tzc.edu.cn

[1] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200438, China

[2] School of Pharmaceutical Engineering & Institute for Advanced Studies, Taizhou University, 1139 Shifu Avenue, Taizhou 318000, Zhejiang, China

The self-aggregation of organic dyes often occurs in aqueous phase, which is mainly driven by or intermolecular noncovalent interactions like van der Waals force or π–π stacking interactions [33]. This aggregating phenomenon can be observed in UV–vis spectra, manifesting as the shifts in the absorption band compared with the monomeric species. J-aggregation and H-aggregation are two of the most common aggregation patterns. J-aggregation, which was named due to the obvious red-shifted J-bands with high absorbance coefficient, is the head-to-tail stacking of dye molecules in a staircase shape [34–36]. H-aggregation is a ladder-like face-to-face stacking of dyes, which exhibits weak blue shift H-bands [37–39].

The aggregation behavior of dyes mainly depends on dye structure, temperature and solution composition [40]. In this context, host-guest interactions have been developed as a useful strategy to control the aggregation of various organic dyes [10, 41–45]. Herein we report the use of a highly water-soluble acyclic CB[*n*] host **ACB-01** to form stable complexes with two cyanine dyes pseudoisocyanine (**PIC**) and pinacyanol (**PIN**) (Fig. 1). These host-guest complexes could disrupt the aggregation process of dyes. Moreover, dye aggregation could be recovered by adding competing guest methyl viologen (**MV**) or 1-adamantanamine hydrochloride (**AD**).

Results and discussion

Acyclic CB[*n*] host **ACB-01** was prepared by our previous work [46]. Aromatic tetraesters were synthesized by three-step nucleophilic substitution reactions. The glycoluril tetramer, synthesized from glycoluril and paraformaldehyde, underwent a double electrophilic aromatic substitution reaction with two equivalents of aromatic tetraester to form an octaester, which was hydrolyzed to obtain the final product. **ACB-01** contained a C-shape glycoluril tetramer and two terminal substituted aromatic walls with eight carboxylate groups. The glycoluril tetramer provided a hydrophobic cavity and two electron-rich carbonyl portals for the binding of cationic guests. Due to the eight carboxylate groups, ACB-01 had significantly higher solubility of 155 mM than CB [7] (~20 mM). The eight carboxylate groups not only increased the aqueous solubility of the host, but also improved the binding towards cationic guests.

In water the cyanine dye **PIC** showed maximum absorption wavelengths at 485 and 525 nm in monomeric form [47]. At a lower temperature or with higher concentrations of dye and inorganic salts, **PIC** preferred to form J-aggregates which exhibited a characteristic sharp absorption band at 575 nm [48]. In order to estimate the affinity between **ACB-01** and **PIC**, the J-aggregation has to be inhibited by controlling the condition with a low dye concentration and moderate temperature. In Fig. 2, there were two characteristic absorption bands of the monomeric form of **PIC** with a concentration of 0.01 mM and at room temperature. No absorption peak appeared at 575 nm, which indicated that no J-aggregation occurred. The absorbance of **PIC** decreased as host **ACB-01** was added, and the absorption band also had a minor red shift by 3 nm. The change of **PIC** absorption spectra revealed that **PIC** was complexed by host **ACB-01** and stabilized by the strong host-guest interaction. Fitting results from Job plots and the absorbance at 500 nm (Fig. S1) showed that **PIC** followed a 1:1 binding stoichiometry with host **ACB-01**. The binding constant (K_a) was determined to be $(1.54 \pm 0.15) \times 10^6\ M^{-1}$.

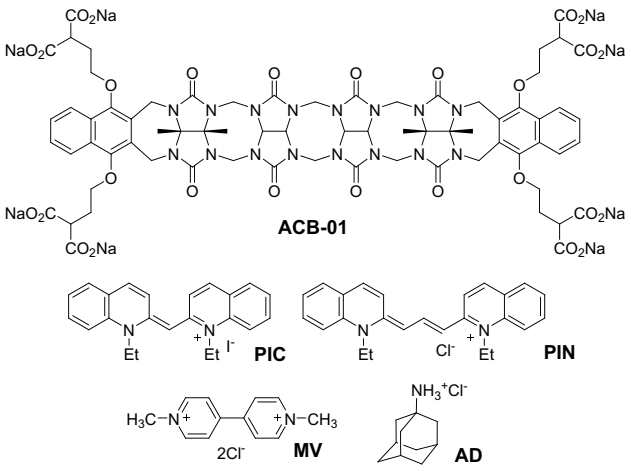


Fig. 1 Chemical structures of acyclic CB[*n*], organic dyes and cationic guests

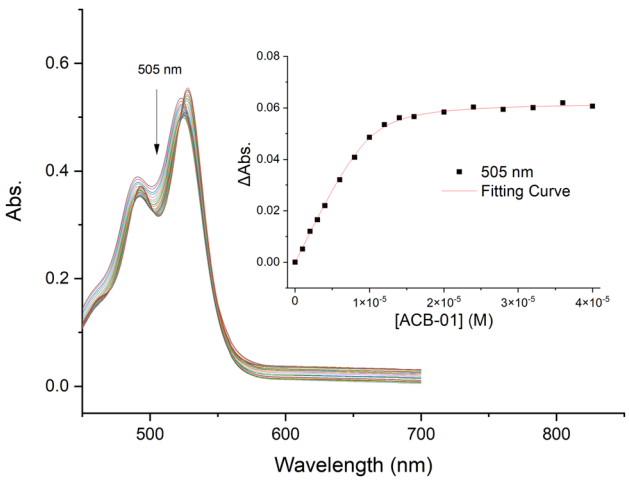


Fig. 2 UV–vis absorbance of **PIC** (0.01 mM) with **ACB-01** (0–4.0 eq.) added at 25 °C. Inset: Variation of the UV–vis absorbance of **PIC** (0.01 mM) with **ACB-01** (0–4.0 eq.) added at 505 nm

^{1}H NMR titration was used to illustrate the binding mode between **PIC** and **ACB-01**. **PIC** had a large symmetrical π-conjugated structure with only one positive charge, resulting in its poor aqueous solubility. We mixed 10% (v/v) of DMSO-d_6 with D_2O to solubilize the dye to a higher concentration of 1.0 mM, and reduced the influence of solvent effect as low as possible (Fig. S2). As **ACB-01** was added, the chemical resonances of **PIC** shifted upfield (Fig. 3a). The resonance of hydrogen near positive charge like H^a showed a relatively minor shift (~0.45 ppm), while those of terminal hydrogen like H^f underwent a larger upfield shift (~0.66 ppm). This result showed that the hydrophobic cavity of **ACB-01** was capable to encapsulate the quinolinic ring of **PIC**, and the more electropositive part was closer to the edge of the cavity where carboxylate oxygen could provide a stronger electrostatic interaction. Job's plot based on the variation of H^f chemical shift also confirmed that **PIC** and **ACB-01** formed a 1:1 complex (Fig. 3b).

The well-matched structure between **ACB-01** and **PIC** and strong host-guest interaction made it possible for **ACB-01** to depress **PIC**'s J-aggregation in aqueous phase. At low temperature such as 5 °C with 1.0 M NaCl added, the spectrum of 0.05 mM **PIC** exhibited a clear sharp absorption peak at 574 nm (Fig. 4a). As the solution was heated up

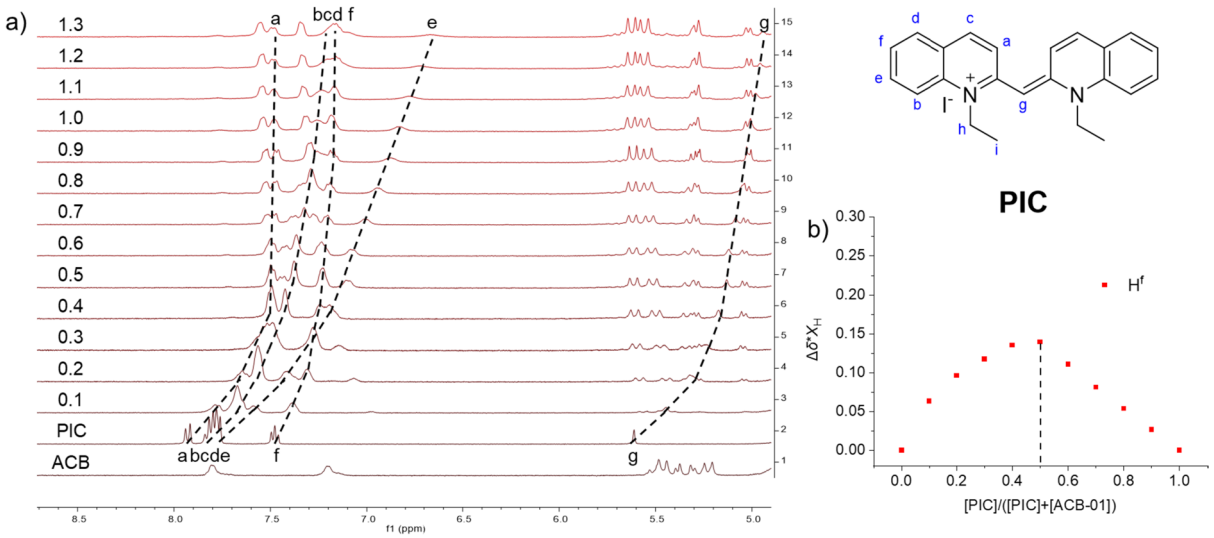


Fig. 3 **a** ^{1}H NMR spectrum (400 MHz) of **PIC** (1.0 mM) and **ACB-01** (0-1.5 mM) in D_2O (10% DMSO-d_6) at 25 °C (Aromatic moiety). **b** Job's plots of PIC and ACB-01 based on chemical shift of **PIC** proton H^f ([**ACB-01**] + [**PIC**] = 1.0 mM). The binding ratio is 1:1

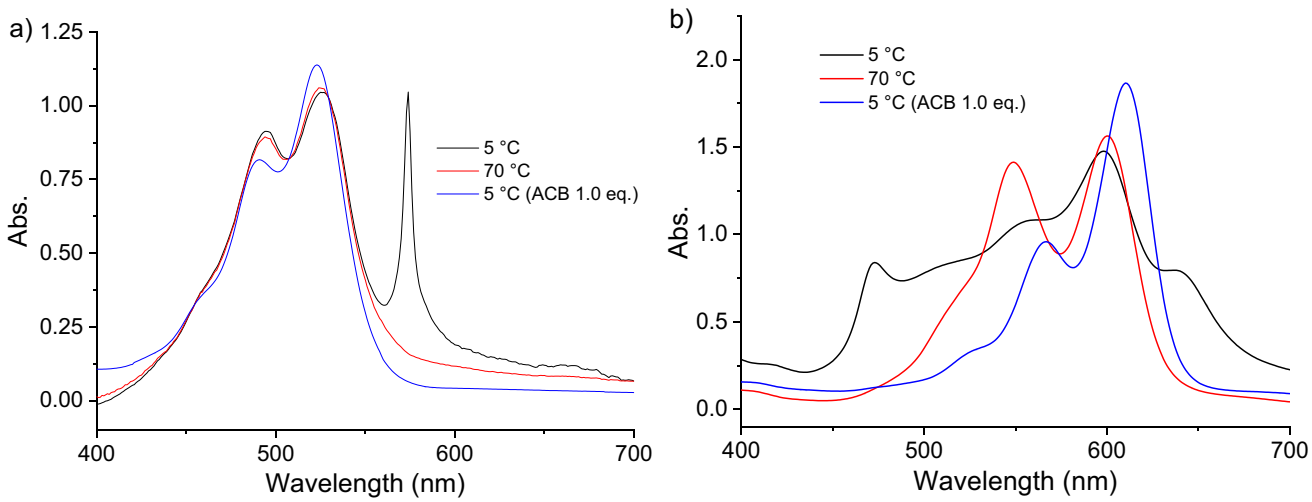


Fig. 4 UV–vis spectra of **a PIC** (0.05 mM) and **b PIN** (0.05 mM) in the presence or absence of **ACB-01** (1.0 eq.) at different temperatures. All solutions were prepared in (a) 1.0 M NaCl or (b) 0.05 M NaCl with 1% MeOH

to 70 °C, the peak disappeared completely. The aggregation of **PIC** molecules is a negative enthalpy change process. According to the van 't Hoff equation, the increase in environmental temperature led to a decrease in the equilibrium constant *K*, resulting in the deaggregation of **PIC**. After the solution was cooled down back to 5 °C, 1.0 equivalent of **ACB-01** was added and we observed the disappearance of J-band. This difference showed that the host-guest interaction between **PIC** and **ACB-01** was stronger than the π–π stacking interaction of **PIC** itself. As a result, **ACB-01** could disturb the J-aggregation of **PIC** by forming stable **PIC@ACB-01** complexes.

The disturbance from **ACB-01** could also be observed in fluorescence spectra (Fig. 5). **PIC** showed an emission band around 580 nm at 5 °C with the presence of 1.0 M NaCl on excitation at 400 nm. The J-aggregation band disappeared as the temperature rose up to 70 °C. The addition of excess **ACB-01** could also quench the fluorescence of J-aggregates, preventing **PIC** molecules from π–π stacking.

Host-guest complexation was a reversible process. The introduction of a competing guest could displace **PIC** from **PIC@ACB-01** complexes and re-establish J-aggregation. Previous researches [47] had reported that methyl viologen (**MV**) and 1-adamantanamine hydrochloride (**AD**) showed high binding affinity with acyclic CB[*n*]s. We first confirmed the binding stoichiometry between ACB-01 and two guests (Fig. S3-4). The host could form 1:1 supramolecular complex with the two guests. We also estimated the binding constants of **MV@ACB-01** and **AD@ACB-01** by UV–vis competing titration (Fig. S5-6), which was determined to be $(1.15 \pm 0.31) \times 10^8$ M^{-1} and $(2.23 \pm 0.05) \times 10^6$ M^{-1}, respectively (Table 1). The K_a value for **MV@ACB-01** was about two orders of magnitude higher than that for **PIC@ACB-01**, while the K_a value for **AD@ACB-01** was slightly higher than that of the dye. Therefore, these two competing guests were capable to displace the dye from the cavity of **ACB-01**. As expected, the J-band around 574 nm was regenerated after **MV** was added gradually into the solution of **PIC@ACB-01** complexes at 5 °C (Fig. 6a). The absorbance

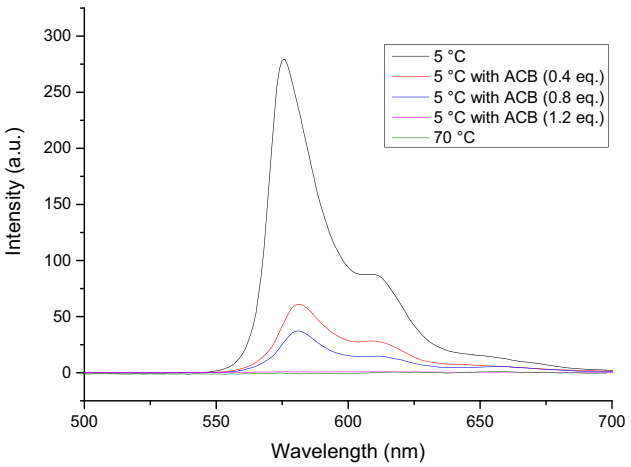


Fig. 5 Fluorescence spectra of **PIC** (0.05 mM) in the presence or absence of **ACB-01** at different temperatures. Excitation wavelength: 400 nm. All solutions were prepared in 0.2 M NaCl

Table 1 Binding constants (Ka) for ACB-01 with cationic guests

Guests	K_a (M^{-1})
PIC[a]	$(1.54 \pm 0.15) \times 10^6$
PIN[a]	$(6.09 \pm 0.82) \times 10^5$
MV[b]	$(1.15 \pm 0.31) \times 10^8$
AD[b]	$(2.23 \pm 0.05) \times 10^6$

[a]Determined by UV–vis direct titration

[b]Determined by indicator displacement assay

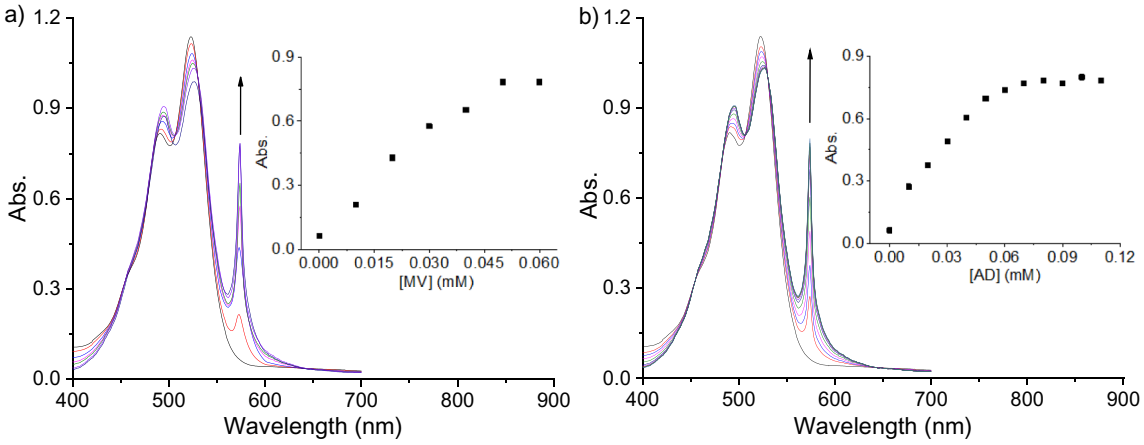


Fig. 6 UV–vis spectra of **PIC** (0.05 mM) with **ACB-01** (1.0 eq.) by adding **a MV** or **b AD** at 5 °C. Inset: absorbance at 573 nm of the dyes against [**MV**] or [**AD**]. All solutions were prepared in aqueous solution of NaCl (1.0 M)

of **PIC** J-aggregates continued to increase until the concentration of **MV** reached one equivalent. **AD** had similar affinity with **ACB-01** compared with **PIC**, which made it difficult to displace **ACB-01**. The J-band fully regenerated until 1.4 equivalents of **AD** was added (Fig. 6b). Therefore, we were certain that J-aggregation of **PIC** could be precisely controlled by the host **ACB-01** as an inhibitor and competing guests **MV** or **AD** as regenerants.

PIN was pooly soluble in water, and 1% volume ratio of methanol was added to solubilize **PIN**. UV–vis absorption measurement was first carried out to reveal the **PIN@ACB-01** complexation properties. In the concentration of 0.01 mM **PIN** showed absorption maxima at 551 and 600 nm (Fig. S7). These two absorption bands underwent obvious red shift (16 nm and 11 nm respectively) as the concentration of **ACB-01** increased, and the absorbance decreased slightly at first and then increased. The binding stoichiometry was fitted to be 1:1 and the corresponding K_a value for **PIN@ACB-01** complex was determined to be $(6.09 \pm 0.82) \times 10^5\ M^{-1}$. This value was lower than that of **PIC**. ^{1}H NMR spectroscopy was unable to be used to study the binding mode due to the poor solubility of **PIC**. We propose that the large conjugative structure of **PIN** molecule spread out the only one positive charge, which relatively weakened the electrostatic interaction between host and guest.

With 0.05 mM NaCl added, the solution of 0.05 mM **PIN** showed a new absorption band at 473 nm (Fig. 4b) at 5 °C, which should be ascribed to H-aggregation as it was blue-shifted from original [49]. Another new red-shifted peak at 642 nm was ascribed to J-aggregation [50]. The two absorption bands disappeared after the solution was heated up to 70 °C, which again suggested the decrease in equilibrium constant on H- or J- aggregation caused by enthalpy effect, similarly as **PIC**. Addition of one equivalent of **ACB-01** caused significant changes on the UV–vis spectrum. Both new absorption bands were diminished and the other two underwent a red shift like low dye concentration. The two phenomena both indicated the formation of **PIN@ACB-01** complexes and the inhibition of aggregation.

MV and **AD** were used to remove **ACB-01** from the complexes as competing guests. **PIN** was relatively weakly associated with **ACB-01** compared to **PIC**. The binding constant of the former was three and two orders of magnitude lower than that of **MV** and **AD**, respectively. As a result, one equivalent of competing guest was adequate to displace the dye from the complexes, observed in the reappearance of H-band (Fig. S8-9). The concentration of the competing guests required for complete regeneration of aggregation absorption band showed the difference of stability between two dyes.

All the optical phenomena could be summarized as three relevant equilibria:

$$\text{dye} \rightleftharpoons \text{aggregates} \quad (1)$$

$$\text{dye} + \text{ACB} - 01 \rightleftharpoons \text{dye@ACB} - 01 \quad (2)$$

$$\text{ACB} - 01 + \text{competing guest} \rightleftharpoons \text{competing guest@ACB} - 01 \quad (3)$$

Conclusions

In conclusion, we use a highly water-soluble acyclic CB[*n*] with eight carboxylate tails to bind cyanine dyes **PIC** and **PIN**. The formation of dye@**ACB-01** complexes could inhibit dyes' aggregation in aqueous solutions (J-aggregation for **PIC** and H-aggregation for **PIN**), which could be reversed by stronger competing guests **MV** and **AD** as regenerants. All these processes were under direct influence of binding ability of **ACB-01**, which could help to realize the precise control of the equilibrium between dye monomers and aggregates. These results showed us the potential application of acyclic cucurbiturils in aqueous dye stabilization.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10847-023-01209-x.

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Author contributions ZL and DM conceived the project, WP conducted the experiments and analyzed the data, WP, HW, DZ, ZL and DM wrote the paper.

Declarations

Conflict of interest The authors declare no conflict of interest.

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