Theoretical study on the noncovalent interactions involving triplet diphenylcarbene

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Abstract
The properties of some types of noncovalent interactions formed by triplet diphenylcarbene (DPC 3) have been investigated by means of density functional theory (DFT) calculations and quantum theory of atoms in molecule (QTAIM) studies. The DPC 3··· LA (LA = AlF 3, SiF 4, PF 5, SF 2, ClF) complexes have been analyzed from their equilibrium geometries, binding energies, and properties of electron density. The triel bond in the DPC 3···AlF 3 complex exhibits a partially covalent nature, with the binding energy −65.7 kJ/mol. The tetrel bond, pnicogen bond, chalcogen bond, and halogen bond in the DPC 3···LA (LA = SiF 4, PF 5, SF 2, ClF) complexes show the character of a weak closed-shell noncovalent interaction. Polarization plays an important role in the formation of the studied complexes. The strength of intermolecular interaction decreases in the order LA = AlF 3 > ClF > SF 2 > SiF 4 > PF 5. The electron spin density transfers from the radical DPC 3 to ClF and SF 2 in the formation of halogen bond and chalcogen bond, but for the DPC 3···AlF 3/SiF 4/PF 5 complexes, the transfer of electron spin density is minimal.

Keywords
Triplet diphenylcarbene · Noncovalent interaction · Electron density shift · Electron spin density

Introduction
The study of noncovalent interactions has been a hot topic in supramolecular chemistry, molecular recognition, and materials science [1]. The strength of noncovalent bonds is smaller than that of general chemical bonds about 1~2 orders of magnitude, but in the system containing large numbers of molecules, the noncovalent interactions accumulate and influence the structure, function, and physical and chemical properties of the system. Of the various noncovalent bonds, hydrogen bond and halogen bond are arguably the most important and prevalent [2–5]. Hydrogen bond is typically expressed as the positioning of two molecules such that the H atom of one molecule, R−H, acts as a bridge to another molecule R−H···D. The anisotropic charge distribution around atom of groups 12–18 allows them to act in a similar capacity. The concepts of σ-holes or π-holes that have been pointed out by Politzer and Clark et al. [6–12] reflect the fact that covalently bonded atom tends to have anisotropic electronic densities, with regions of higher and lower density. An σ-hole or π-hole is a region of lower electronic density along the extension of a covalently bonded atom, or perpendicular to a planar portion of a molecule. This region gives rise to positive electrostatic potential and can be used as a Lewis acid to interact attractively with the rich electronic center (lone pairs, π electrons, anions, etc.) of a Lewis base. One or more σ-holes or π-holes have been found for all of the main-group elements in the Periodic Table and have been classified into a wide variety of noncovalent interactions: alkaline earth bonds for group 12, triel bonds for group 13, tetrel bonds for group 14, pnicogen bonds for group 15, chalcogen bonds for group 16, halogen bonds for group 17, and aerogen bonds for group 18 [4, 5, 13–22]. Recently, noncovalent interactions involving σ-hole or σ-lump on a coinage metal have been reported [23–25].
As an organic reactive intermediate containing two unbonding valence electrons on a divalent carbon atom,
carbene can activate small molecules under mild conditions, catalyze organic reactions, and act as ligands in transition metal catalysis [26]. Depending on whether two electrons in carbon atom of carbene are located in a same or a different orbital, they give place to a singlet or a triplet configuration, respectively. Because of its lone pairs, singlet carbene can be acted as electron-pair donor in the intermolecular interaction. Del Bene and Alkorta et al. [27–30] studied a series of carbenes and silylenes as hydrogen and pnictogen bond acceptors; they also shown that nitrogen heterocyclic carbenes (NHCs) might prefer noncovalent or covalent bonding to trap CO₂ and CS₂. Some carbene lithium bonding, triel bonding, tetrel bonding, and pnictogen bonding interactions were predicted and characterized by theoretical calculations [31–35]. Sander et al. [36–38] investigated the interactions between diphenylcarbene (DPC) and H₂O, CH₃OH, or CF₃I using matrix isolation spectroscopy (IR, UV-vis, and EPR) in combination with theoretical calculations. They showed that the spin ground state of DPC switches from triplet to singlet upon formation of the strongly hydrogen-bonded and halogen-bonded complexes. Lu et al. [39] further discussed the influence of the formation of halogen bond on the spin state of DPC and the decisive factors in spin slip via density functional theory (DFT) calculations.

In view of the fact that diphenylcarbene is a prototypical transient carbene with a triplet ground state and has been subject to a large number of mechanistic studies using time-resolved or low-temperature spectroscopy, the bimolecular complexes between triplet diphenylcarbene (DPC³) and a series of Lewis acids LA (LA = AlF₃, SiF₄, PF₅, SF₂, CIF) from group 13–17 atoms were constructed in this work, in order to give insight into these kinds of noncovalent interactions. The main purposes of this paper are (1) to study the stability and strength of the complexes containing triplet DPC³, (2) to investigate the character of these σ/π-hole interactions, and (3) to analyze the influence of noncovalent interaction on the distribution of electron density and electron spin density.

**Computational methods**

All calculations were performed with Gaussian 09 program package [40]. The geometries of the monomers and complexes were fully optimized using the B3LYP functional with D3 empirical dispersion correction and 6-311++G** basis set. Harmonic frequencies were calculated to confirm the equilibrium geometries to be true minima and yielded zero-point energy. The keyword Counterpoise was used for the calculation of corrected binding energies, excluding the inherent basis set superposition error (BSSE) [41]. The binding energies of the bimolecular complexes were computed as the difference between the energy of the complex and the sum of energies of corresponding isolated monomers, in which the geometries of monomers were optimized solely. The electrostatic potentials were calculated on the 0.001 a.u. (electrons/Bohr³) contour of the electron density of the molecule with the WFA surface analysis suite [42]. To have a more detailed and in-depth understanding of the interactions, topological properties of the electron density at the bond critical points were computed by the AIMAll program [43]. Noncovalent interaction index (NCI) and electron spin density analysis were carried out using Multiwfn software [44], and the related plots were graphed using the VMD program [45].

**Results and discussion**

**Molecular electrostatic potentials**

Molecular electrostatic potential (MEP) is a fundamentally important physical characteristic that is very useful for understanding and predicting noncovalent interactions. Figure 1 shows the contour maps of MEPS for triplet biphienylocbin (DPC³) and LA (LA = AlF₃, SiF₄, PF₅, SF₂, CIF). The most positive electrostatic potentials (V₅₉₆₆) and most negative electrostatic potentials (V₅₉₆₆) on the 0.001 au contour of the molecular electron density are collected in Table 1. As shown in Fig. 1a, the contour map for DPC³ presents a few blue regions with negative MEPS. The positions of V₅₉₆₆ are located above and below the benzene ring, represented by blue dots, with the values of –13.7 and –12.2 kcal/mol, respectively. From the contour map of MEP for AlF₃ (Fig. 1b), aluminum atom acts as the Lewis acid center since it is characterized by the depletion of electron charge (π-hole) [7, 14]. This red region corresponds to the vacant ρ orbital perpendicular to the plane of AlF₃ molecular framework, with a V₅₉₆₆ value of 104.7 kcal/mol. In the case of CIF, SF₂, SiF₄, and PF₅, there are one or more ρ-holes (red regions) with positive MEPs along the extension of the corresponding Cl-F, S-F, Si-F, and P-F bond. The V₅₉₆₆ values were found to become less positive following the order AlF₃ > SiF₄ > CIF > SF₂ > PF₅.

| Molecule | V₅₉₆₆ | V₅₉₆₆ |
|----------|-------|-------|
| DPC³     | –13.7/–12.2 | -     |
| AlF₃     | -     | 104.7 |
| SiF₄     | -     | 47.4  |
| PF₅      | -     | 39.9  |
| SF₂      | -     | 41.4  |
| CIF      | -     | 44.6  |
Geometry and binding energy

Based on the analysis of MEPs, the intermolecular interaction could form between the σ-hole or π-hole regions of LA (LA = AlF₃, SiF₄, PF₅, SF₂, ClF) and the negative electrostatic potential region of DPC₃. Figure 2 shows the stable geometries of DPC₃···LA (LA = AlF₃, SiF₄, PF₅, SF₂, ClF) complexes. It can be seen that the most stable interaction between DPC₃ and LA (LA= AlF₃, SiF₄, PF₅, SF₂, ClF) occurs on the benzene ring of DPC₃. The binding energy and binding distance for the complexes are given in Table 2. The binding energy (ΔE) ranges from −15.8 kJ/mol for pnicogen-bonded complex DPC₃···PF₅ to −65.7 kJ/mol for triel-bonded complexes DPC₃···AlF₃. The strength of intermolecular interaction become stronger along the sequence LA = PF₅ < SiF₄ < SF₂ < ClF < AlF₃. Binding distance (d) in Table 2 refers to the distance between the atom of groups 13 to 17 in the LA (LA = AlF₃, SiF₄, PF₅, SF₂, ClF) and the nearest carbon atom of benzene ring in DPC₃, which can be seen that the shorter the binding distance, the stronger the interaction. By comparing the data in Tables 1 and 2, it is found that the binding energy between molecules is not well correlated with the VS,max values of Lewis acids, which may be due to the steric hindrance effect of SiF₄ and PF₅. The tetravalent/pentavalent character of Si/P atom leaves only limited room for an incoming nucleophile to approach and engage in a noncovalent bond with a tetravalent/phosphorus atom [46, 47].

Noncovalent interaction index

To verify the intermolecular interaction between DPC₃ and LA (LA = AlF₃, SiF₄, PF₅, SF₂, ClF), the complexes were analyzed by noncovalent interaction index (NCI). This method, proposed by Yang’s research group [48, 49], can not only describe the properties of the interacting molecules, but also show the characteristic information of the interaction through graphics. Based on the analysis of the electron density (ρ) and its reduced density gradient function (RDG), this approach combines with the electron density and sign (λ₂) to analyze the type and strength of interactions between molecules, where sign (λ₂) is the sign of the second eigenvalue of its Hessian. In the isosurface of the reduced density gradient function, blue represents strong attractive interaction, green represents weak interaction, and red indicates strong nonbonded overlap, such as steric effect in a ring or cage. Figure 3 shows the plots of the reduced density gradient versus the electron density multiplied by sign (λ₂) (above) and gradient isosurfaces generated for s = 0.05 au (below). In the DPC₃ complexes, several low-density isosurfaces (green regions) lie in the interacting portions between DPC₃ and LA (LA = AlF₃, SiF₄, PF₅, SF₂, ClF), where noncovalent attractions are expected. There is another area of the low-density, low-gradient nonbonded overlap (red region) located at the center of each benzene ring, where steric repulsion in the benzene ring.

### Table 2 Binding energy, binding distance, and integral charge of MFDD for the complexes DPC₃···LA (LA = AlF₃, SiF₄, PF₅, SF₂, ClF) (energy in kJ/mol, distance in Å, charge in e)

| Complex     | ΔE       | d       | Δne     |
|-------------|----------|---------|---------|
| DPC₃···AlF₃ | −65.7    | 2.368   | 0.1897  |
| DPC₃···SiF₄ | −19.7    | 3.669   | 0.0266  |
| DPC₃···PF₅  | −15.8    | 3.669   | 0.0280  |
| DPC₃···SF₂  | −20.5    | 3.183   | 0.0378  |
| DPC₃···ClF  | −30.1    | 2.651   | 0.0554  |

Fig. 1 Contour maps of MEPs on the 0.001 au contour of the molecular electron density, a DPC₃, b AlF₃, c SiF₄, d PF₅, e SF₂, f ClF (colors represent energy levels, in kcal/mol⁻¹: DPC₃, red, 8; yellow, 1; green, −6; LA, red, 30; yellow, 16; green, 2. Positions of VS,max and VS,min are indicated by black arrows)
For the triel-bonded complex, the blue isosurface lies between the $\pi$-hole of AlF$_3$ and benzene ring of DPC$_3$ and reveals stronger interaction than in the other complexes. The locations of $\rho(r)$ peaks for the complexes DPC$_3$···LA (LA = AlF$_3$, SiF$_4$, PF$_5$, SF$_2$, ClF) are consistent with the interaction strengths.

**QTAIM analysis**

Based on the quantum theory of atoms in molecules (QTAIM) [50, 51], the molecular structures, the characters of chemical bonds, and chemical reactions are closely related to the electron density distribution functions. The strength and properties of a chemical bond can be determined through the relative parameters of the electron density and the energy density at the critical points in molecules [52–54]. The common studied topological properties at the bond critical points (BCPs) are electron density ($\rho_b$), its Laplacian ($\nabla^2 \rho_b$), the local potential energy density ($V_b$), local kinetic energy density ($G_b$), and total energy density ($H_b = V_b + G_b$). According to the criteria [55, 56], a positive $\nabla^2 \rho_b$ reflects an excess of kinetic energy in bonds and a relative depletion of electronic charge along a bond path. A positive $H_b$ corresponds to a purely closed-shell interaction, whereas a negative $H_b$ value corresponds to bonds with any degree of covalent character. If $-G_b/V_b$ is greater than 1, then the interaction is noncovalent. If the ratio is between 0.5 and 1, the interaction is partly covalent in nature, and when this ratio is less than 0.5, the interaction is a shared covalent one.

The molecular graphs and the topological properties of electron density at the BCPs of the complexes are shown in Fig. 4 and Table 3. For DPC$_3$···AlF$_3$ complex, there exists a BCP between the $\pi$-hole of AlF$_3$ and C atom of DPC$_3$, and a pair of bond paths connect the BCP and the interacting Al and C atom. The values of $\rho_b$ and $\nabla^2 \rho_b$ at the C···Al BCP were calculated to be 0.0296 au and 0.0710 au. Positive $\nabla^2 \rho_b$ value, negative $H_b$ value, and $-G_b/V_b$ value of about 0.8 indicate that this triel bond is of moderate strength with a partially covalent nature. For complex DPC$_3$···SiF$_4$ and DPC$_3$···PF$_5$, there exist several C···F BCPs and one H···F BCP between DPC$_3$ and SiF$_4$/PF$_5$ molecules, the $\rho_b$ values are less than 0.0090 au.

From Fig. 4d, e, the C···S or C···Cl BCP in the DPC$_3$···SF$_2$ and DPC$_3$···ClF complexes account for the chalcogen bond or pnicogen bond between DPC$_3$ and $\sigma$-hole of SF$_2$/ClF. The $\rho_b$ and $\nabla^2 \rho_b$ values of the complexes DPC$_3$···LA (LA = SiF$_4$, PF$_5$, SF$_2$, ClF) are in the range of $0.0044$–$0.0296$ au and $0.0155$–$0.0621$ au. $\nabla^2 \rho_b > 0$, $H_b > 0$, and $-G_b/V_b > 1$ were calculated, showing the characters of a weak closed-shell noncovalent interaction.

**Density difference of molecular formation analysis**

The density difference during the formation of super molecules (A···B) can be described as $\rho_{\text{diff}}(r) = \rho_{\text{complex}}(r) - (\rho_{\text{molA}}(r) + \rho_{\text{molB}}(r))$. According to Politzer et al. [57], polarization is a real physical phenomenon, corresponding to the electron density shifts from one molecule to the electric field of another, could be observed physically from the electronic density. Density difference of molecular formation (MFDD) analysis has often been used to study the formation of

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**Fig. 2** Optimized geometries of the complexes: a DPC$^3$···AlF$_3$; b DPC$^3$···SiF$_4$; c DPC$^3$···PF$_5$; d DPC$^3$···SF$_2$; e DPC$^3$···ClF
Fig. 3  Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue (above) and gradient isosurfaces generated for $s = 0.05$ a.u (below) for complexes: a DPC$^3$--AlF$_3$, b DPC$^3$--SiF$_4$, c DPC$^3$--PF$_5$, d DPC$^3$--SF$_2$, e DPC$^3$--ClF

Table 3  Topological properties of electron density at the bond critical points for the complexes DPC$^3$--LA (LA = AlF$_3$, SiF$_4$, PF$_5$, SF$_2$, ClF) (in au)

| Complex      | BCP     | $\rho_b$ | $\nabla^2 \rho_b$ | $G_b$  | $V_b$  | $H_b$  | $- \frac{G_b}{V_b}$ |
|--------------|---------|----------|------------------|--------|-------|-------|---------------------|
| DPC$^3$--AlF$_3$ | C--Al   | 0.0296   | 0.0710           | 0.0230 | -0.0283 | -0.0053 | 0.8132 |
|              | H--H    | 0.0063   | 0.0247           | 0.0048 | -0.0035 | 0.0013 | 1.3788 |
|              | H--F    | 0.0094   | 0.0332           | 0.0072 | -0.0062 | 0.0011 | 1.1734 |
| DPC$^3$--SiF$_4$ | C--F    | 0.0052   | 0.0194           | 0.0040 | -0.0031 | 0.0009 | 1.2868 |
|              | C--F    | 0.0052   | 0.0195           | 0.0040 | -0.0030 | 0.0009 | 1.3056 |
|              | C--F    | 0.0044   | 0.0155           | 0.0031 | -0.0024 | 0.0008 | 1.3178 |
|              | H--F    | 0.0081   | 0.0306           | 0.0066 | -0.0056 | 0.0010 | 1.1853 |
| DPC$^3$--PF$_5$ | H--F    | 0.0090   | 0.0338           | 0.0073 | -0.0061 | 0.0012 | 1.1907 |
|              | C--F    | 0.0061   | 0.0251           | 0.0052 | -0.0041 | 0.0010 | 1.2623 |
|              | C--F    | 0.0066   | 0.0244           | 0.0051 | -0.0042 | 0.0010 | 1.2352 |
| DPC$^3$--SF$_2$ | C--S    | 0.0102   | 0.0292           | 0.0062 | -0.0051 | 0.0011 | 1.2219 |
|              | H--F    | 0.0080   | 0.0303           | 0.0065 | -0.0055 | 0.0010 | 1.1841 |
| DPC$^3$--ClF  | C--Cl   | 0.0258   | 0.0621           | 0.1512 | -0.0149 | 0.0003 | 1.0219 |
molecules and weak interactions [58–60]. Figure 5 present plots of computed density difference of the complexes, the shift of charge density during the forming of DPC³···LA (LA = AlF³, SiF⁴, PF⁵, SF², ClF) complexes are clearly shown. The electronic fields of the π electrons in DPC³ and σ/π-hole in LA cause charge redistributions of each segment. From Fig. 5a, e, one can see a few negative regions (blue regions) outside the carbon atoms and Al/Cl atom, which means that a decrease in electron density when DPC³ and LA interact to form the complexes. An increased region in electron density (white region) between the carbon atoms and Al/Cl atom becomes more and more slight. We chose this increased region as a cube to integrate the total charge of the density difference; the positive integral charges (Δnₑ) we obtained and shown in the last column of Table 2. Linear correlation was found between the integral charges and the binding energies, with the correlation coefficients 0.982 (Fig. 6). The stronger DPC³···LA interaction increases the electric field in the intermolecular region, resulting in a larger increase in electron density between molecules. These results indicate that polarization effect plays an important role when DPC³ interact with Lewis acids.

**Electron spin density analysis**

For open shell system, total electron density is the sum of α and β electron densities, i.e., ρ(total) = ρ(α) + ρ(β). The difference between ρ(α) and ρ(β), Δρ = ρ(α) − ρ(β), represents the electron spin density of the system. The value Δρ is equal to 0 and 2 in the LA and triplet DPC³ molecules. Figure 7 shows the maps of electron spin density of DPC³ and its complexes DPC³···ClF and DPC³···SF², the Δρ values of C atoms in DPC³ are marked out. Green regions represent positive and blue regions represent negative Δρ values. To illustrate the electron spin density transfer during bond formation, Table 4 lists the electron spin density changes of C atoms and LA in the formation of the complexes.

The calculated results show that the electron spin density is primarily concentrated on the divalent C1 atom of DPC³; the Δρ value of C1 is 1.4038e in the monomer. In the process of formation of the complexes, there is a rearrangement of electron spin density. For the complexes DPC³···LA (LA = AlF³, SiF⁴, PF⁵), the sum of spin electron densities in LA is less than 0.0009. These values are too small to be significant, indicating that spin density rearranges within the DPC³ radicals, and the transfer of spin electron density from the electron donor to acceptor can be ignored. In DPC³···AlF³ complex, the change of spin electron density occurs mainly in C15 and C18 atoms of DPC³. In DPC³···SiF⁴/PF⁵ complexes, the change of spin electron density occurs mainly in C1, C14, and C20 atoms. In the process of chalcogen bond formation, the electron spin densities of the C14 and C20 atoms decrease and those of the S and F atoms increase; the sum of spin electron densities in SF² is 0.0143. For the halogen-bonded complex DPC³···ClF, the changes of electron spin density in C1 and C14 atoms are −0.0550 and −0.0516; meanwhile, the sum of electron spin density in ClF is 0.0980. The increased values of SF²/ClF
indicate a quantity of electron spin density transfer from DPC\(^3\) to SF\(_2\)/ClF.

Therefore, in the process of the formation of DPC\(^3\)--LA (LA = AlF\(_3\), SiF\(_4\), PF\(_3\)) complexes, the transfers of the electron...
spin density from DPC$^3$ to LA is minimal, but it rearranges within the radical itself. For the chalcogen-bonded and halogen-bonded complex, certain electron spin density transfer from the radical to Lewis acid.

Conclusions

In this work, the intermolecular interactions between the triplet biphenylcarbene radical DPC$^3$ and a series of Lewis acids LA (LA = AlF$_3$, SiF$_4$, PF$_5$, SF$_2$, and ClF) have been investigated. The analyses of NCI, AIM, and MFDD generated the following conclusions:

1. The strength of intermolecular interaction between DPC$^3$ and a series of Lewis acids LA decreases gradually in the order of LA = AlF$_3$ > ClF > SF$_2$ > SiF$_4$ > PF$_5$. The triel bond in the DPC$^3$···AlF$_3$ complex is of moderate strength and partially covalent nature. Other intermolecular interactions between DPC$^3$ and LA (LA = SiF$_4$, PF$_5$, SF$_2$, and ClF) are characterized by weak closed-shell noncovalent interactions.

| Complex | DPC$^3$···AlF$_3$ | DPC$^3$···SiF$_4$ | DPC$^3$···PF$_5$ | DPC$^3$···SF$_2$ | DPC$^3$···ClF |
|---------|------------------|------------------|------------------|------------------|------------------|
| ΔΔρ (C1) | 0.0028 | 0.0087 | 0.0087 | -0.0004 | -0.0550 |
| ΔΔρ (C2) | 0.0077 | 0.0003 | 0.0016 | -0.0001 | 0.0052 |
| ΔΔρ (C3) | -0.0095 | 0.0032 | 0.0003 | -0.0008 | -0.0100 |
| ΔΔρ (C4) | -0.0130 | 0.0010 | -0.0017 | -0.0015 | -0.0097 |
| ΔΔρ (C5) | 0.0047 | -0.0007 | 0.0004 | 0.0004 | 0.0036 |
| ΔΔρ (C7) | 0.0051 | -0.0007 | 0.0004 | 0.0003 | 0.0035 |
| ΔΔρ (C9) | -0.0128 | 0.0024 | -0.0009 | -0.0019 | -0.0101 |
| ΔΔρ (C13) | 0.0160 | 0.0061 | 0.0051 | 0.0076 | 0.0089 |
| ΔΔρ (C14) | -0.0021 | -0.0138 | -0.0097 | -0.0126 | -0.0516 |
| ΔΔρ (C15) | -0.0235 | -0.0070 | -0.0052 | -0.0083 | -0.0029 |
| ΔΔρ (C16) | 0.0094 | 0.0050 | 0.0039 | 0.0068 | 0.0219 |
| ΔΔρ (C18) | 0.0203 | 0.0043 | 0.0041 | 0.0058 | 0.0087 |
| ΔΔρ (C20) | -0.0056 | -0.0103 | -0.0077 | -0.0107 | -0.0126 |
| ΔΔρ (LA) | -0.0004 | 0.0009 | 0.0002 | 0.0143 | 0.0980 |
(2) The intermolecular interaction induces a build-up of electric charge between molecules. The integral value of the positive charge of density difference is consistent with the binding energy, and polarization effect plays an important role.

(3) In the process of halogen bond and chalcogen bond formation, the electron spin density is transferred from DPC$_3$ to ClF and SF$_2$, while during the interaction of DPC$_3$ with AlF$_3$, SiF$_4$, and PF$_5$, the transfer of electron spin density between molecules is negligible, the electron spin density rearrange within the radical itself.

**Code availability** N/A.

**Author contribution** Chunhong Zhao: investigation and writing—original draft; Hui Lin: formal analysis and data curation; Aiting Shan: visualization; Shaofu Guo: writing—review and editing; Xiaoyan Li: methodology and supervision; Xueying Zhang: conceptualization and supervision.

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**Data availability** The manuscript has full control of all primary data, and the authors agree to allow the journal to review their data if requested.

**Declarations**

**Conflict of interest** The authors declare no competing interests.

**Consent for publication** Written informed consent for publication was obtained from all participants.

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