Designing Special Nonmetallic Superalkalis Based on a Cage-like Adamanzane Complexant

Ya-Ling Ye¹, Kai-Yun Pan¹, Bi-Lian Ni¹ and Wei-Ming Sun¹,²*

¹Fujian Key Laboratory of Drug Target Discovery and Structural and Functional Research, The School of Pharmacy, Fujian Medical University, Fuzhou, China, ²School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, China

In this study, to examine the possibility of using cage-like complexants to design nonmetallic superalkalis, a series of X@3⁶adz (X = H, B, C, N, O, F, and Si) complexes have been constructed and investigated by embedding nonmetallic atoms into the 3⁶adamanzane (3⁶adz) complexant. Although X atoms possess very high ionization energies, these resulting X@3⁶adz complexes possess low adiabatic ionization energies (AIEs) of 0.78–5.28 eV. In particular, the adiabatic ionization energies (AIEs) of X@3⁶adz (X = H, B, C, N, and Si) are even lower than the ionization energy (3.89 eV) of Cs atoms, and thus, can be classified as novel nonmetallic superalkalis. Moreover, due to the existence of diffuse excess electrons in B@3⁶adz, this complex not only possesses pretty low AIE of 2.16 eV but also exhibits a remarkably large first hyperpolarizability ($\beta_0$) of $1.35 \times 10^6$ au, indicating that it can also be considered as a new kind of nonlinear optical molecule. As a result, this study provides an effective approach to achieve new metal-free species with an excellent reducing capability by utilizing the cage-like organic complexants as building blocks.

Keywords: superalkali, adamanzane, superatom, nonlinear optics, reducing matters

INTRODUCTION

Reducing agents with low ionization energies (IEs) play a crucial role in chemical synthesis. As is well-known, alkali metal atoms possess the lowest ionization energies (5.39–3.89 eV) (Lide, 2003) among all the elements in the periodic table. However, it is reported that a class of extraordinary compounds possesses even lower IEs than those of alkali metal atoms. Such species were termed “superalkalis” by Gutsev and Boldyrev (1982). Initially, superalkalis were designed by decorating an electronegative central atom with alkali-metal ligands, such as FLi₂, OLi₃, and NLi₄ following the formula MLₖ₊₁ (L is an alkali-metal atom and M is an electronegative atom of valency k). In MLₖ₊₁, one more alkali metal atom will bring an extra valence electron for the electronic shell of M according to the octet rule. Consequently, such an MLₖ₊₁ complex has a great tendency to lose the extra valence electron and thus possess strong reducibility (Sun and Wu, 2019).

Owing to their excellent reducing ability, superalkalis can be used to synthesize unusual charge-transfer salts (Zintl and Morawietz, 1938; Jansen, 1976) with the counterpart possessing relatively low electron affinity and activate stable CO₂ and N₂ molecules (Park and Meloni, 2017; Zhao et al., 2017; Park and Meloni, 2018; Sun et al., 2019; Sikorska and Gaston, 2020) to produce high-value products (Zhang et al., 2021a; Zhang et al., 2021b). In particular, as a special subset of superatom (Reveles et al., 2009; Luo and Castleman, 2014), superalkalis can behave as alkali metal atoms and...
maintain their structural and electronic integrities when assembled into extended nanostructures (Reber et al., 2007). Hence, they offer an exciting prospect of serving as building blocks for nanomaterials with highly tunable properties (Jena and Sun 2018), such as supersalts (Giri et al., 2014), hydrogen storage materials (Merino et al., 2012), noble-gas-trapping agents (Pan et al., 2013), superbases (Srivastava and Misra, 2015), and nonlinear optical materials (Sun et al., 2014a; Sun et al., 2014b; Sun et al., 2016a; Sun et al., 2016b; Sun et al., 2016c; Sun et al., 2018a).

In view of the great importance of superalkalis in chemistry, various superalkalis have been theoretically (Tong et al., 2009; Tong et al., 2011, Tong et al., 2012a, Tong et al., 2012b; Hou et al., 2013; Liu et al., 2014; Sun et al., 2013; Sun et al., 2016a; Giri et al., 2016; Zhao et al., 2017; Sun et al., 2018b; Sun et al., 2019; Park and Meloni, 2018; Sun and Wu, 2019; Tkachenko et al., 2019; Sikorska and Gaston, 2020) and experimentally (Lievens et al., 1999; Yokoyama et al., 2000, 2001; Hou and Wang, 2020) characterized in the past decades. To date, conventional mononuclear MLx+ superalkalis have been expanded to dinuclear (Tong et al., 2009; Tong et al., 2011) and polynuclear (Tong et al., 2012a; Tong et al., 2012b; Liu et al., 2014) superalkalis, aromatic superalkalis (Sun et al., 2013), Zintl-ion-based superalkalis (Giri et al., 2016; Sun et al., 2018b), hyperalkalis (Sun et al., 2016a), alkali-metal complexes (Tkachenko et al., 2019), and so on. More importantly, some alkali-metal-free superalkalis (Hou et al., 2014; Liu et al., 2016), particularly nonmetallic superalkalis (Hou et al., 2013; Srivastava, 2019a; Srivastava, 2019b), have been proposed in recent years. For example, Hou et al. (2013) designed a class of MnH2x+ (M = F, O, N, C for n = 1, 2, 3, 4, respectively) superalkali cations by using hydrogen atoms as ligands. Following a similar rule, the other two series of nonmetallic superalkali cations, namely, F,Hn+ (n = 1–10) and CnH2n+ (n = 1–5), have been proposed by Srivastava (2019a, 2019b). These achievements demonstrate that the potential of designing superalkali of new type is limitless and thereby motivate us to create more diverse superalkali species by using different rules and ligands to further enrich the superalkali family.

More recently, Tkachenko et al. (2019) reported the record low ionization potentials (1.70–1.52 eV) of alkali metal complexes with crown ethers and cryptands and defined them as superalkali species. In fact, such alkali metal complexes were previously named as electrides, a special kind of ionic solids with trapped nonmetallic atoms into the cavity of this cage-like complexant in this work (see Figure 1). The 3·adz complexant is composed of tricyclic tetra-amine with aliphatic chains (Springborg, 2003), which has been used to synthesize a stable alkalide [He3·adz]Na+ (Redko et al., 2002). In this complexant, all the lone pairs of 4 N atoms direct toward the center of the cage (see Supplementary Figure S1). Under the repulsion of the lone pairs of N atoms, the outmost valence electrons of X are destabilized to different degrees, leading to the obvious rise of HOMO level of X@3·adz as compared with the isolated 3·adz complexant. As a result, these proposed complexes exhibit extraordinarily low AIE values of 0.78–5.28 eV although X atoms possess very high ionization energies (IEs) of 8.15–17.42 eV (Lide, 2003). In particular, the B@3·adz complex also has the potential to serve as a new nonlinear optical (NLO) molecule with a remarkably large first hyperpolarizability of 1.35 × 106 au because the valence electron of boron atom is pushed out of cage to form diffuse excess electrons. We hope that this work will not only provide new nonmetallic members for the superatom family, but will also open the door to design strong reducing matters by embedding nonmetallic atoms into the various cage-like complexants.

**FIGURE 1** | The schematic design strategy of X@3·adz (X = H, B, C, N, O, F, and Si) based on the cage-like 3·adz complexant.

To verify this hypothesis, the 3·adamanzane (3·adz) has been chosen as a representative to design a series of X@3·adz (X = H, B, C, N, O, F, and Si) by encapsulating nonmetallic atoms into the cavity of this cage-like complexant in this work (see Figure 1). The 3·adz complexant is composed of tricyclic tetra-amine with aliphatic chains (Springborg, 2003), which has been used to synthesize a stable alkalide [He3·adz]Na+ (Redko et al., 2002). In this complexant, all the lone pairs of 4 N atoms direct toward the center of the cage (see Supplementary Figure S1). Under the repulsion of the lone pairs of N atoms, the outmost valence electrons of X are destabilized to different degrees, leading to the obvious rise of HOMO level of X@3·adz as compared with the isolated 3·adz complexant. As a result, these proposed complexes exhibit extraordinarily low AIE values of 0.78–5.28 eV although X atoms possess very high ionization energies (IEs) of 8.15–17.42 eV (Lide, 2003). In particular, the B@3·adz complex also has the potential to serve as a new nonlinear optical (NLO) molecule with a remarkably large first hyperpolarizability of 1.35 × 106 au because the valence electron of boron atom is pushed out of cage to form diffuse excess electrons. We hope that this work will not only provide new nonmetallic members for the superatom family, but will also open the door to design strong reducing matters by embedding nonmetallic atoms into the various cage-like complexants.

**COMPUTATIONAL DETAILS**

In this work, all the calculations were carried out by using the coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP) (Tawada et al., 2004; Yanai et al., 2004), which has been reported to be capable of providing not only the molecular geometries close to the experimentally observed structures but also the (hyper)polarizabilities close to those of the coupled cluster calculations (Limacher et al., 2009). Hence, this method has been widely used to calculate the (hyper)polarizabilities of NLO molecules in the previous works (Sun et al., 2014a; Sun et al., 2014b, Sun et al., 2016c). Also, a method test has also been carried out by sampling B@3·adz (see Supplementary Table S1) to verify the reliability of this method in calculating the properties of such systems.
From Supplementary Table S1, it is found that CAM-B3LYP gives approximately equal VIE and $\beta_0$ to those obtained by several other functionals, which indicates that this method is reliable for these studied systems. Hence, all the optimized geometric structures of the studied species with real frequencies were obtained under the CAM-B3LYP/6-31+G(d) level. Based on the optimized structures, the single-point energies, nature population analysis (NPA) charges, and static electric properties were calculated at the CAM-B3LYP/6-311++G (d, p) level.

In this work, the vertical ionization energies (VIEs) of $X@3^6$adz ($X = H, B, C, N, O, F,$ and $Si$) were calculated as the energy difference between the optimized neutral complex and the cation in the geometry of the neutral complex, while their adiabatic ionization energies (AIEs) are defined as the energy difference between the neutral and cationic complex at their respective optimized structures. In addition, the TD-M06-2X calculations were performed to obtain the transition energies and oscillator strengths of the crucial excited states as well as the difference of the dipole moments between the ground state and crucial excited state of $X@3^6$adz by using the 6-311++G (d, p) basis set. Herein, the dipole moments ($\mu_0$), polarizabilities ($\alpha_0$), and first hyperpolarizabilities ($\beta_0$) are defined as follows,

$$\mu_0 = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

where $\beta_i = \frac{1}{2}\sum_j (\beta_{ij} + \beta_{ji})$, $i, j = \{x, y, z\}$.

All the above calculations were performed by using the GAUSSIAN 16 program package (Frisch et al., 2016). The dimensional plots of the molecular structures were generated with the GaussView program (Dennington et al., 2016).

RESULTS AND DISCUSSION

Initially, seven $X@3^6$adz ($X = H, B, C, N, O, F,$ and $Si$) compounds have been constructed by encapsulating one $X$ atom into a $3^6$adz cage. After optimization, the geometric structures of $X@3^6$adz are illustrated in Figure 2, while the corresponding cations are plotted in Supplementary Figure S2. Moreover, selected structural parameters of these resulting $X@3^6$adz compounds are summarized in Table 1.

As shown in Figure 1, $3^6$adz is a cage-like complexant with $S_4$ symmetry. From Figure 2, it is observed that the geometric integrity of $3^6$adz cage is well-preserved in these $X@3^6$adz compounds. However, the geometric symmetries of these compounds are lowered to $C_1$ and $C_2$, except for $H@3^6$adz, which maintains the $S_4$ symmetry of $3^6$adz. To be specific, the encapsulated hydrogen atom located at the central position of $3^6$adz in $H@3^6$adz, yields the newly formed N-H bonds of 2.11 Å and $\angle N1-X-N2$ angle (in deg) of $X@3^6$adz ($X = H, B, C, N, O, F,$ and $Si$) compounds.

$$\text{Table 1}$$

| Species     | Symmetry | $v_1$ | $d_{X-N1}$ | $d_{X-N2}$ | $\angle N1-X-N2$ |
|-------------|----------|-------|------------|------------|-----------------|
| H@3$^6$adz  | $S_4$    | 69    | 2.11       | 2.11       | 113.5           |
| B@3$^6$adz  | $C_1$    | 91    | 1.66       | 3.02       | 105.9           |
| C@3$^6$adz  | $C_2$    | 102   | 1.52       | 2.97       | 108.4           |
| N@3$^6$adz  | $C_1$    | 48    | 1.41       | 2.58       | 120.3           |
| O@3$^6$adz  | $C_1$    | 72    | 1.34       | 2.59       | 125.1           |
| F@3$^6$adz  | $C_1$    | 61    | 1.87       | 2.41       | 123.7           |
| Si@3$^6$adz | $C_1$    | 76    | 2.06       | 3.22       | 102.0           |
TABLE 2 | Adiabatic ionization energies (AIEs, in eV), vertical ionization energies (VIEs, in eV), HOMO and LUMO energy levels (in eV), and the HOMO–LUMO gaps of 3\textsuperscript{3}adz and X@3\textsuperscript{3}adz (X = H, B, C, N, O, F, and Si) compounds.

| Species      | AIE  | VIE  | HOMO | LUMO | Gap (eV) |
|--------------|------|------|------|------|----------|
| 3\textsuperscript{3}adz | 6.56 | 6.80 | −6.49 | −0.38 | 6.12     |
| H@3\textsuperscript{3}adz | 0.78 | 3.63 | −3.49 | 0.36  | 3.86     |
| B@3\textsuperscript{3}adz | 2.16 | 2.18 | −1.81 | −0.01 | 1.80     |
| C@3\textsuperscript{3}adz | 2.72 | 3.01 | −3.08 | 0.10  | 3.18     |
| N@3\textsuperscript{3}adz | 3.15 | 5.72 | −4.48 | 0.19  | 4.67     |
| O@3\textsuperscript{3}adz | 5.28 | 5.86 | −5.65 | 0.18  | 5.83     |
| F@3\textsuperscript{3}adz | 4.92 | 6.38 | −5.87 | −0.13 | 5.73     |
| Si@3\textsuperscript{3}adz | 1.79 | 2.73 | −2.61 | 0.26  | 2.87     |

carbon atom prefers to bind with 2 N atoms of 3\textsuperscript{3}adz by forming two N-C bonds of 1.52 Å. Differently, the more electronegative N, O, and F atoms are linked to only 1 N atom of the cage complexant via N-N, N-O, and N-F bonds of 1.41, 1.34, and 1.87 Å, respectively, generating the very similar structures of X@3\textsuperscript{3}adz (X = N, O, and F). Similar to B@3\textsuperscript{3}adz, the introduced silicon atom tends to bind with 3 N atoms of complexant via 3 N-Si bonds of 2.06–2.35 Å in Si@3\textsuperscript{3}adz.

By turning to the cations of X@3\textsuperscript{3}adz, it is found that only the optimized structure of [B@3\textsuperscript{3}adz]\textsuperscript{+} cation almost coincides with the geometry of the corresponding neutral one (see Supplementary Figure S2). For instance, the critical geometric parameters of d\textsubscript{B-N1}, d\textsubscript{B-N2}, and ∠N1-B-N2 are hardly changed after one electron is lost from B@3\textsuperscript{3}adz. However, for the rest of X@3\textsuperscript{3}adz (X = H, C, N, O, F, and Si), quite different geometries of cationic and neutral complexes were found. For instance, the H\textsuperscript{+} is attached to 1 N atom of the complexant in the resulting [H@3\textsuperscript{3}adz]\textsuperscript{+}, while the doped N atom turns to combine with 2 N atoms of 3\textsuperscript{3}adz in [N@3\textsuperscript{3}adz]\textsuperscript{+} and Si atom almost moves to the center of the cage in [Si@3\textsuperscript{3}adz]\textsuperscript{+}. The geometry of C@3\textsuperscript{3}adz is distorted from C\textsubscript{2} symmetry to C\textsubscript{1} with the changes of 0.29 Å for the C-N2 bond and 7.3' for ∠N1-C-N2. As for [F@3\textsuperscript{3}adz]\textsuperscript{+}, the N-F bond is shortened from 1.87 Å to 1.38 Å because the introduced F atom further loses 0.333 e (see Supplementary Table S1) and thus tends to bind more tightly with the N atom of the complexant. Also, as shown in Table 2, the difference in the geometry can also be reflected by the difference of 0.29–3.06 eV between the vertical ionization energies (VIEs) and adiabatic ionization energies (AIEs) of these X@3\textsuperscript{3}adz (X = H, C, N, O, F, and Si) species.

More interestingly, as shown in Table 2, extraordinarily low AIE values of 0.78–5.28 eV were found for all the studied X@3\textsuperscript{3}adz (X = H, B, C, N, O, F, and Si) complexes, although X atoms possess very high ionization energies (IEs) of 8.15–17.42 eV (Lide, 2003). Such low AIE values of X@3\textsuperscript{3}adz are not only lower than that of 6.56 eV for the 3\textsuperscript{3}adz complexant but also significantly lower than that of 5.39 eV (Lide, 2003) for lithium atom. In particular, the AIE values of H@3\textsuperscript{3}adz (0.78 eV), B@3\textsuperscript{3}adz (2.16 eV), C@3\textsuperscript{3}adz (2.72 eV), N@3\textsuperscript{3}adz (3.15 eV), and Si@3\textsuperscript{3}adz (1.79 eV) are even lower than the IE of 3.89 eV (Lide, 2003) for Cs atoms. Hence, these compounds should be classified as novel nonmetallic superalkalis.

How to understand the low IE values of such X@3\textsuperscript{3}adz complexes? We can find some clues from the frontier molecular orbital analysis. From Figure 3, a clear inverse correlation between the VIE values and HOMO levels of these studied compounds can be observed, that is, the higher the HOMO level is, the lower the VIE is. This is reasonable considering the fact that the valence electrons on the higher HOMOs are easier to be ionized. To be specific, all the HOMO energies (−1.81 ~ −5.87 eV) of X@3\textsuperscript{3}adz are much higher than that of −6.49 eV for 3\textsuperscript{3}adz, because of the repulsion between the lone pairs of N atoms and the outmost valence electrons of X, resulting in the lower VIEs (2.18–6.38 eV) than that (6.80 eV) of 3\textsuperscript{3}adz. In particular, B@3\textsuperscript{3}adz exhibits the highest HOMO level of −1.81 eV, and thus possesses the lowest VIE of 2.18 eV among these X@3\textsuperscript{3}adz complexes. This is because that the valence electron of embedded boron atom is pushed out of the cage by the lone pairs of N atoms of the complexant, forming a electride-like molecule [B⁺@3\textsuperscript{3}adz]⁺ with obvious diffuse electrons in the HOMO of B@3\textsuperscript{3}adz (see Supplementary Figure S3). Thus, the existence of diffuse excess electrons in its high-lying HOMO level results in the high reducibility of this B@3\textsuperscript{3}adz complex.

Differently, as shown in Supplementary Figure S3, the valence electrons are accommodated into the HOMOs mainly composed of the ls atomic orbital of embedded hydrogen atom in H@3\textsuperscript{3}adz, and the np orbitals of C and Si atoms in X@3\textsuperscript{3}adz (X = C and Si), which show obvious antibonding character with respect to the central atom-complexant interaction. Such antibonding HOMOs destabilize the neutral structures of X@3\textsuperscript{3}adz (X = H, C, and Si) and result in their low VIE values (Gutsev and Boldyrev, 1987; Tkachenko et al., 2019). Hence, these 3 species also have quite low VIE values of 2.73–3.83 eV. However, it should be mentioned that the VIEs of 5.72–6.38 eV for X@3\textsuperscript{3}adz (X = N, O, and F) are larger than that of 5.39 eV for Li atom, although their HOMOs also possess obvious

FIGURE 3 | The relationship between the VIE values and HOMO levels of X@3\textsuperscript{3}adz (X = H, B, C, N, O, F, and Si) compounds.
antibonding character. This is attributed to the larger elteronegativities of N, O, and F atoms than H, C, and Si atoms, which hinders the ionization of the valence electrons on their np orbitals in the HOMOS of X@36adz (X = N, O, and F).

On the other hand, the difference between the VIE and AIE values are also related to the different electron distribution in the HOMOs of X@36adz. To be specific, the geometric structure of B@36adz is hardly changed after its diffuse excess electron of HOMO is lost, resulting in its nearly equal VIE (2.18 eV) and AIE (2.16 eV) values. However, the destabilization of antibonding HOMOs for the neutral X@36adz (X = H, C, and Si) complexes drives the embedded X atom to lose nearly one valence electron (0.667 e~0.867 e), as shown in Supplementary Table S1), forming relatively stable [X@36adz]+ cations. After losing one electron, the formed X+ ion changes its interaction mode with the cage complexant, which leads to the large structural distortion and considerable difference between the VIE and AIE values of X@36adz (X = H, C, and Si). Note that the AIE of H@36adz is as low as 0.78 eV because the formed [H@36adz]+ is very stable and has been identified in various synthesized ionic compounds, such as [H@36adz]+X− (X = Cl, Br, I, and Na) (Kim et al., 1994; Springborg et al., 1996; Redko et al., 2002).

Finally, considering the diffuse excess electron in the HOMO of B@36adz, it is highly expected that this superalkali also exhibits considerable nonlinear optical (NLO) response. Thus, the static electric properties of these studied X@36adz compounds and 36adz complexant were calculated and listed in Table 3. It is observed that B@36adz has the largest dipole moment (3.326 au) and polarizability (1.599 au) among these X@36adz complexes because of the existence of diffuse electrons in the HOMO of this superalkali. In particular, the first hyperpolarizability (β0) of B@36adz is as large as 1.35 × 106 au, which is significantly larger than those of the reported superalkalis and superalkali-based NLO materials, such as the aromatic organometallic superalkali Au4(Py)n (3.74 × 104 au) (Parida et al., 2018), superalkali-based alkalide Li,(O)M+ (M = Li, Na, and K) (1.18 × 10−3–3.33 × 104 au) (Sun et al., 2014a), and superalkali-based electrode Li3O@Al12N12 (8.73 × 105 au) (Sun et al., 2016b), indicating that this proposed superalkali species can indeed be considered as a new kind of NLO molecule of high performance.

To understand the eminently large β0 value of B@36adz, we focus our attention on the simple two-level model (Oudar, 1977; Oudar and Chemla, 1977),

$$\beta_0 \propto \frac{\Delta \mu \cdot f_0}{\Delta \epsilon}$$  \hspace{1cm} (4)

where ΔE, f0, and Δμ are the transition energy, oscillator strength, and the difference in the dipole moment between the ground state and crucial excited state, respectively. According to this two-level expression, β0 is proportional to f0 and Δμ, while is inversely proportional to the cube of ΔE, and therefore, the transition energy is considered to be the decisive factor in the first hyperpolarizability (Sun et al., 2014a,b, 2016c, d). Hence, the ΔE, f0, and Δμ values of the crucial excited states with the largest oscillator strength of 36adz and X@36adz are summarized in Table 3. It is noted that B@36adz possesses extremely smaller ΔE and much larger f0 and Δμ values than those of other X@36adz (X = H, C, N, O, F, and Si) compounds, which rationalizes its largest β0 value among these studied X@36adz species. In addition, the proposed C@36adz and Si@36adz superalkalis also show considerable β0 values of 4.05 × 105 au and 1.95 × 105 au, respectively, because of their relatively smaller ΔE values and larger Δμ values.

### CONCLUSION

By using 36adamantane (36adz) as a complexant, a series of X@36adz (X = H, B, C, N, O, F, and Si) compounds were constructed and studied based on the density functional theory. It is interesting to find that the X@36adz (X = H, B, C, N, and Si) complexes possess lower AIE values than the IE of Cs atoms though the X atoms and 36adz possess very high IE values. Thereby, they can be regarded as a new kind of nonmetallic superalkali. In particular, different from other complexes, the low IE of B@36adz is derived from the diffuse excess electron formed by the repulsion between the valence electron of the embedded boron atom and lone pairs of N atoms of the complexant. Due to the existence of diffuse electrons, this superalkali also possesses a remarkably large β0 of 1.35 × 106 au, which can serve as a new kind of NLO molecule. Hence, it is highly hoped that the theoretical design and characterization of these nonmetallic superalkali species could provide meaningful references to further design novel reducing matters or NLO materials by using such cage-like molecules as complexants.

### DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.
AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work and approved it for publication.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.853160/full#supplementary-material

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