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# Rational design of superalkali-based novel calix[4]pyridine alkalides as high performance nonlinear optical materials†

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In the present work, novel superalkali-based calix[4]pyridine alkalides have been designed as excess electron compounds using DFT simulations. The computed interaction energies ( $-32.3$  to  $-64.5$  kcal mol<sup>-1</sup>) and vertical ionization energies (2.51 to 2.79 eV) indicate the stability of the designed alkalides. The highest charge at Li<sup>-</sup> alkalide in the K<sub>3</sub>O<sup>+</sup>CXP[4]Li<sup>-</sup> is  $-0.486$  |e| as analyzed by natural population analysis. The investigated complexes exhibit reduced HOMO–LUMO energy gaps (0.30–0.50 eV) in comparison to pure calix[4]pyridine (5.69 eV). The IRI and QTAIM analyses indicate that the CXP[4] interacts with superalkali clusters and Li metal *via* non-covalent interactions. These superalkali-based alkalides possess absorption maxima (727–1096 nm) in the visible to NIR region. The Na<sub>3</sub>O<sup>+</sup>CXP[4]Li<sup>-</sup> alkalide displays a significantly higher static first hyperpolarizability of  $2.5 \times 10^6$  au as compared to the  $\beta_o$  ( $3.4 \times 10^4$  au) for superalkali-based calix[4]pyrrole alkalides. The  $\beta_{vec}$  and  $\beta_{TL}$  values show a similar trend to the static  $\beta_o$  values. Furthermore, the highest dynamic NLO responses for second harmonic generation, hyper-Rayleigh scattering and electro-optical Pockel's effect are  $1.8 \times 10^8$  au,  $1.1 \times 10^8$  au and  $7.7 \times 10^7$  au, respectively. These findings imply that designed alkalides offer a novel perspective on the rational designing of stable high-tech NLO materials.

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## 1. Introduction

The design and synthesis of novel nanomaterials have gained substantial attention in the realm of modern science and optical communication. Nanomaterials, on interactions with high intensity ultrafast laser pulses, exhibit intriguing nonlinear optical (NLO) phenomena, including second harmonic generation (SHG),<sup>1</sup> ultrafast charge dynamics,<sup>2</sup> coherent anti-Stokes Raman scattering (CARS)<sup>3</sup> and multi-photon absorption.<sup>4</sup> Nonlinear optics has gained prominence in various fields including optical fiber communication, optical switches,<sup>5</sup> high resolution imaging,<sup>6</sup> ultrafast pulse measurement<sup>7</sup> *etc.* Several commercially available organic and inorganic nonlinear optical (NLO) crystals such as L-prolinium tartrate,<sup>8</sup> imidazolium L-tartrate (IMLT),<sup>9</sup> and lithium iodate (LiIO<sub>3</sub>) have been successfully synthesized and are employed in optoelectronic applications. However, the ongoing shift towards digitalization has spurred a significant expansion in the range of NLO materials for their on-chip integration in optoelectronics.

Organic NLO materials have surpassed inorganic ones in establishing a lead in NLO research due to their superior nonlinear optical susceptibilities, large transparency range, high laser damage thresholds, ultrafast response time, low dielectric constants, and improved processability.<sup>10</sup>

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† Electronic supplementary information (ESI) available: Additional theoretical details, including figures of optimized complexes of horizontal and vertical superalkali based M<sub>3</sub>O<sup>+</sup>CXP[4]Li<sup>-</sup> alkalides, crucial transition states of the most stable M<sub>3</sub>O<sup>+</sup>CXP[4]Li<sup>-</sup> alkalides and tables of AIM (atom in molecule) topological parameters, static first hyperpolarizabilities (au) at various functionals and dipolar ( $|\beta_{J=1}|$  (au)), octupolar ( $|\beta_{J=3}|$  (au)), depolarization ratio (DR), dipolar to octupolar contributions in the designed complexes are also provided (DOC). See DOI: <https://doi.org/10.1039/d4ra08399g>


Additionally, organic NLO materials are capable of significant chemical alterations, particularly those that enhance a desirable physical property.<sup>11</sup> In this regard, significant endeavors have been dedicated to enhancing the NLO properties of different nanomaterials. In this regard, many approaches have been put forth and these strategies encompass the designing of octupolar molecules, bond length alternation (BLA) theory, designing metal organic frameworks (MOFs), extended  $\pi$  electron systems, incorporation of diradical character, reinforcement of push–pull effects and the introduction of diffuse excess electrons.<sup>12</sup> This introduction of excess electrons has emerged as a distinctive approach for enhancing the NLO behavior of materials. The introduction of loosely bounded electrons into various nanostructures can be achieved through the doping of complexants with different metal atoms.<sup>13</sup> These excess electrons are located in diffuse molecular orbitals, often referred to as Rydberg orbitals, which are present outside the parent molecules.<sup>14</sup>

Electrides, alkalides, superalkalides, alkaline earthides, and transition metalides are typical representative of excess electron systems and exhibit remarkable optoelectronic properties.<sup>12</sup> Electrides are systems in which an electron is not attached to an atom, but localizes its density in an empty space and actively participates in the structure of the material.<sup>15</sup> Alkalides are obtained *via* placing a second metal atom far away from electrides, and the excess electrons then enwrap the second alkali metal atom to form anionic sites. These loosely bound electrons of anionic metal atoms have a dispersive character due to their low electron affinity. First of all, Dye and coworkers carried out successful synthesis of an alkalide in 1974.<sup>16</sup> They also synthesized  $\text{K}^+(\text{Me}_6\text{Aza222})\text{Na}^-$  and  $\text{K}^+(\text{Me}_6\text{Aza222})\text{K}^-$  alkalides, which are stable at room temperature. Similarly, Redko *et al.*, achieved the synthesis of the  $\text{Ba}^{2+}(\text{H}_5\text{Azacryptand}[2.2.2])\text{Na}^-$ , a barium-based sodide, thereby expanding the scope of research within the realm of alkalides.<sup>17</sup> The theoretical explorations of stable alkalides indicate that the highest NLO response ( $2.4 \times 10^4$  au) has been exhibited by  $\text{Li}^+(\text{calix}[4]\text{pyrrole})\text{M}^-$ .<sup>18</sup> Later on, Jing *et al.*, computed the optoelectronic properties of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) alkalides and hyperpolarizability values ( $7.7 \times 10^4$  au) increase as the number of  $\text{NH}_3$  ligand increases.<sup>19</sup>

However, the area of alkalides garnered significant attention after the effective development of superalkali-based alkalides. Superalkalis display better tendency to provide excess electrons to any system due to their lower ionization potential (IP) than alkali metal atoms (5.4–3.9 eV).<sup>20</sup> They retain their structural integrity like an atom and possess the ability to develop nanomaterials, hydrogen storage materials, noble gas tripping agents, as well as superbases. The intriguing implications of superalkalis have been expanded significantly, resulting in the development and assessment of pioneering superalkali-based nanosystems. In this regard, superalkali-based alkalides such as  $\text{Li}_3^+/\text{Li}_3\text{O}^+(\text{calix}[4]\text{pyrrole})\text{M}^-$  have been designed by Sun *et al.*<sup>21</sup> These superalkali-based alkalides exhibit a significant optical response of up to  $3.4 \times 10^4$  au. Similarly, a novel series of alkalides such as  $\text{Li}_3^+(\text{aza222})\text{K}^-$ ,  $\text{OLi}_3^+(\text{aza222})\text{K}^-$ ,  $\text{FLi}_2^+(\text{-aza222})\text{K}^-$ , and  $\text{NLi}_4^+(\text{aza222})\text{K}^-$  have been designed where superalkalis are encapsulated into an aza222 cage-

complexant.<sup>22</sup> These alkalides show better stability and improved NLO responses. Recently, superalkali-based crown ether  $\text{Li}_3\text{O}[12\text{-crown-4}]\text{M}$  alkalides have been designed and show significant NLO responses ( $9.30 \times 10^4$ – $5.26 \times 10^6$  au).<sup>23</sup> Besides superalkali clusters, these alkalides require a proper complexant to stabilize both the cationic and anionic states.<sup>24</sup> As a result, many ongoing efforts have been directed to designing and integrating stable electrides, alkalides, alkaline earthides and superalkalides by using specific molecules as complexants.

The calix-like, cup-shaped macromolecules, such as calix[ $n$ ]arene, calix[ $n$ ]pyrrole, and calix[ $n$ ]pyridine ( $n = 1, 2, 3 \dots$ ), have distinctive three-dimensional structures. These materials are suitable for various biological, industrial, and medicinal applications because their internal hollow region is an ideal place to locate the guest entity.<sup>25</sup> For example, these complexants were used in nanotechnology as high-resolution electron beam lithography, nonlinear optics, ion-sensitive electrodes, sensors, and selective membranes. The calix[4]pyrrole complexant has been employed widely as electride, alkalide and alkaline earthide in various NLO applications.<sup>21</sup> Recently, the nonlinear optical response of excess electron based calix[4]arenes has been computed theoretically.<sup>26</sup> The calix[4]pyridine (CXP[4]), a member of the hetero-aromatic calixarene family, is similar to calix[4]arene and contains pyridine subunits in its macrocycle, which may resemble the core ring of a porphyrin molecule. In 1998, Sessler *et al.*, have carried out the synthesis of calix[4]pyridine by the reaction of *meso*-octamethylcalix[4]pyrrole with dichlorocarbene (an insertion of the:  $\text{CCl}_2$  unit) for the first time.<sup>27</sup> For instance, scientists have theoretically employed calix[4]pyridine as an anode material for lithium and sodium atom/ion batteries.<sup>28</sup> The results depict that the adsorption and electronic properties of CXP[4] substrate were altered in the presence of Li and Na atom/ion and their cell voltage value of 2.56 V illustrated their potential as anodes of metal-ion batteries.

In spite of the numerous breakthroughs in the field of nanomaterials based on superalkalis, there remains a notable scarcity of research focused on NLO investigations, particularly in the case of calix[4]pyridine. To the best of our knowledge, superalkali-based calix[4]pyridine alkalides have not been explored yet for their geometrical, electronic and nonlinear optical responses. This gap has sparked our curiosity to investigate the alkalide properties and NLO behavior of superalkali-based calix[4]pyridine alkalides. Additionally, static and dynamic second order NLO responses have been calculated for real-world applications. It is anticipated that the ongoing research will provide valuable insights for the fabrication of superalkali-based alkalides for their high-tech applications in optoelectronics.

## 2. Computational details

The geometries of pure calix[4]pyridine and doped complexes are optimized using hybrid B3LYP functional along with 6-31G(d,p) basis set. The B3LYP functional is reliable for optimization because it provides a strong correlation between experimental and theoretical results for the geometric and



electronic properties of various nanosystems.<sup>29</sup> Frequency calculations of the optimized geometries are carried out at the same level of theory to verify the true minima at potential energy surface (PES). To check their thermodynamic stability, the binding energies of the designed alkalis are determined using the (eqn 1):

$$E_{\text{int}} = E_{\text{superalkali(CXP[4])Li}} - (E_{\text{CXP[4]}} + E_{\text{superalkali}} + E_{\text{Li}}) \quad (1)$$

here,  $E_{\text{superalkali(CXP[4])Li}}$  is the energy of superalkali-based calix [4]pyridine complexes,  $E_{\text{CXP[4]}}$  is calix[4]pyridine energy,  $E_{\text{superalkali}}$  is energy of superalkalis ( $\text{Li}_3\text{O}$ ,  $\text{Na}_3\text{O}$  &  $\text{K}_3\text{O}$ ), and  $E_{\text{Li}}$  is the energy of Li metal, respectively. In addition, the counterpoise method is used to remove the basis set superposition error (BSSE) from the interaction energies, which is brought on by the overlapping of finite basis sets. Using the following eqn (2), the counterpoise corrected interaction energies ( $E_{\text{CP}}$ ) are calculated.

$$E_{\text{CP}} = E_{\text{int}} + E_{\text{BSSE}} \quad (2)$$

Moreover, the vertical ionization energy (VIE) calculations are also done at the same level of theory. Natural population analysis (NPA), frontier molecular orbitals (FMOs), interaction region indicator (IRI), quantum theory of atoms in molecules (QTAIM) and electron localization function (ELF) analyses have been carried out at B3LYP/6-31G(d,p) level of theory. Moreover, electron densities and other parameters of designed complexes were obtained by Multiwfn<sup>30</sup> and visual molecular dynamics<sup>31</sup> softwares. The total density of states (TDOS) and partial density of states (PDOS) spectra are also generated *via* Multiwfn software.<sup>30</sup> The time dependent DFT calculations are performed at the TD-CAM-B3LYP/6-311++G(d) level of theory. The absorption spectra of the optimized structures, variations of dipole moments ( $\Delta\mu$ ), oscillator strength ( $f_o$ ), and excitation energies ( $\Delta E$ ) are obtained by these TD-DFT simulations.

The optical properties are computed using the CAM-B3LYP,  $\omega\text{B97XD}$  and M06-2X functionals along with the 6-311++G(d,p) basis set. The CAM-B3LYP is categorized as a long-range corrected functional,<sup>32</sup> which is particularly vital for precise assessments of hyperpolarizabilities. Notably, it also incorporates 0.65 fractional non-local exchange at extended distances, a parameter of significant importance in the accurate determination of hyperpolarizabilities.<sup>33</sup> This functional yields accurate results in predicting molecular structures, hyperpolarizabilities and excitation energies. Furthermore, the nonlinear optical properties computed by this functional, in contrast to results from the other functionals (such as B3LYP or M06-2X) align well with experimental data, as previously reported.<sup>34</sup> The optical parameters such as dipole moment, polarizability and hyperpolarizability are computed using the eqn (3)–(5):

$$\mu_o = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (3)$$

$$\alpha_o = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4)$$

$$\beta_o = [\beta_x^2 + \beta_y^2 + \beta_z^2]^{1/2} \quad (5)$$

The beta vector ( $\beta_{\text{vec}}$ ) can be computed by using eqn (6):

$$\beta_{\text{vec}} = \sum_i \frac{\mu_i \beta_i}{|\mu|} \quad (6)$$

To assess the practical applicability of the designed complexes, dynamic first hyperpolarizabilities ( $\beta(\omega)$ ) have been analyzed at CAM-B3LYP/6-311++G (d,p) level of theory at 532 nm, 1064 nm and 1907 nm, respectively. The  $\beta(\omega)$  can be determined as using eqn (7):

$$\beta(\omega) = (\beta_x(\omega)^2 + \beta_y(\omega)^2 + \beta_z(\omega)^2)^{1/2} \quad (7)$$

In order to predict second order NLO responses like hyper Rayleigh scattering (HRS), second harmonic generation (SHG) and electro-optical Pockel's effect (EOPE), hyperpolarizability is a crucial factor. The eqn (8a) is used to get the  $\beta_{\text{HRS}}$  values:

$$\beta_{\text{HRS}}(-2\omega; \omega, \omega) = \sqrt{\{\langle \beta_{zzz}^2 \rangle + \langle \beta_{xzz}^2 \rangle\}} \quad (8a)$$

Or the orientational average  $\langle \beta_{\text{HRS}} \rangle$  can be expressed as eqn (8b):

$$\langle \beta_{\text{HRS}} \rangle = \sqrt{\frac{2}{9}|\beta_{J=1}|^2 + \frac{2}{21}|\beta_{J=3}|^2} \quad (8b)$$

Here, the molecular  $\beta_{\text{HRS}}$  tensor is the sum of an octupolar ( $J = 3$ ) and a dipolar ( $J = 1$ ) tensorial form. The final theoretical values and the relationship between the dipolar-octupolar components of  $\beta_{\text{HRS}}$  as well as the cartesian components are obtained by using the eqn (9) and (10):

$$|\beta_{J=1}|^2 = \frac{3}{5} \sum_{\zeta}^{x,y,z} \beta_{\zeta\zeta\zeta}^2 + \frac{6}{5} \sum_{\zeta \neq \eta}^{x,y,z} \beta_{\zeta\zeta\zeta} \beta_{\zeta\eta\eta} + \frac{3}{5} \sum_{\zeta \neq \eta}^{x,y,z} \beta_{\eta\zeta\zeta}^2 + \frac{3}{5} \sum_{\zeta \neq \eta}^{x,y,z} \beta_{\zeta\eta\eta} \beta_{\zeta\zeta\zeta} \quad (9)$$

$$|\beta_{J=3}|^2 = \frac{2}{5} \sum_{\zeta}^{x,y,z} \beta_{\zeta\zeta\zeta}^2 - \frac{6}{5} \sum_{\zeta \neq \eta}^{x,y,z} \beta_{\zeta\zeta\zeta} \beta_{\zeta\eta\eta} + \frac{12}{5} \sum_{\zeta \neq \eta}^{x,y,z} \beta_{\eta\zeta\zeta}^2 - \frac{3}{5} \sum_{\zeta \neq \eta \neq \xi}^{x,y,z} \beta_{\zeta\eta\eta} \beta_{\zeta\xi\xi} + \sum_{\zeta \neq \eta \neq \xi}^{x,y,z} \beta_{\zeta\eta\xi}^2 \quad (10)$$

The depolarization ratio is computed by eqn (11):

$$\text{DR} = \frac{\langle \beta_{zzz}^2 \rangle}{\langle \beta_{xzz}^2 \rangle} \quad (11)$$

The results of hyper Rayleigh scattering measurement ( $\beta_{\text{HRS}}$ ) and DR are obtained *via* Multiwfn software.<sup>30</sup> All the above DFT simulations are executed using the Gaussian 16 software<sup>35</sup> and GaussView 6.1.1. software<sup>36</sup> is used for the visualization of geometries.



### 3. Results and discussion

#### 3.1. Geometric parameters and stabilities of designed complexes

Calix[4]pyridine (CXP[4]) is a three-dimensional macrocycle composed of four pyridyl nitrogen atoms and has been identified as a neutral ligand capable of binding to metal ions. Pure calix[4]pyridine exhibits a  $C_{2v}$  symmetry and the 1,3-alternate structure is substantially preferable in the CXP[4] host.<sup>37</sup> The reduced repulsions between lone pairs of nitrogen atoms might be responsible for the conformational stability of the pyridine moieties in CXP[4]. All of the isolated pyridine rings render a box-shape cavity due to the existence of methylene linkages in CXP[4]. The 1.33 Å, 1.39 Å and 1.51 Å bond lengths of  $N_1-C_c$ ,  $C_c-C_b$ , and  $C_c-C_d$  (methylene linked) bonds in CXP[4] are in close agreement with its previously reported bond lengths.<sup>37</sup> Additionally, the optimized  $Li_3O$  superalkali exhibits a Li–O bond length of 1.69 Å, which closely matches the experimental Li–O bond length of Li–O–Li molecule.<sup>38</sup> Based on the findings, it can be concluded that the B3LYP/6-31G(d,p) level of theory is reliable for the present study. The optimized structures of the CXP[4] as well as the isolated superalkalis subunits are shown in Fig. 1.

In the current work,  $Li_3O$ ,  $Na_3O$  &  $K_3O$  and Li metal are doped at calix[4]pyridine to examine the various interaction sites. Four orientations were considered in total, including two horizontal modes (top and bottom) and two vertical modes (top and bottom), for the each superalkali and Li metal doping on calix[4]pyridine (represented in the ESI (Fig. S1†)), as previously considered for calix[4]pyrrole complexes.<sup>21</sup> Among the various considered sites, only the horizontal top orientation was taken into account for subsequent analyses. The majority of the structures were distorted in the case of the bottom modes, and the vertical top orientations converged to the horizontal ones. Similarly, the Li metal is doped at the other side of the calix[4]pyridine. The most stable superalkali based hetero-aromatic

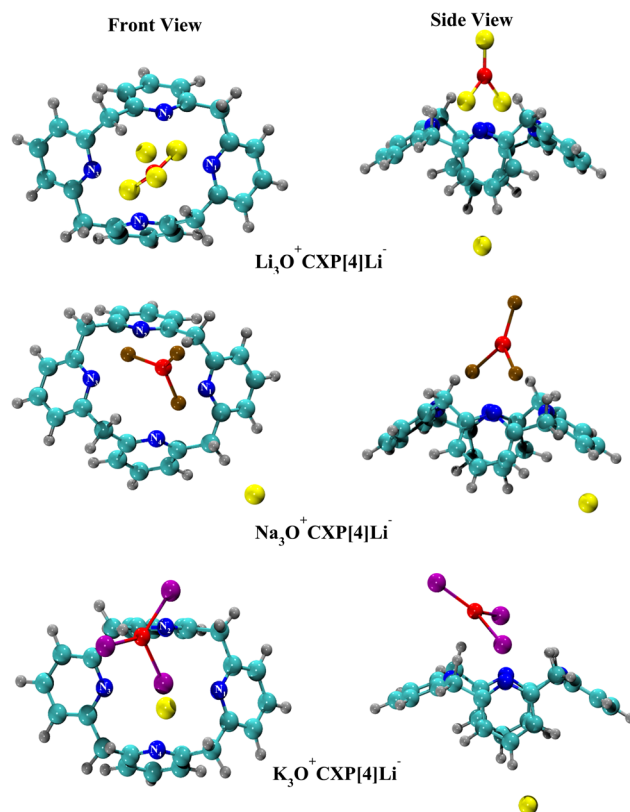


Fig. 2 Optimized complexes of superalkali based  $M_3O^+CXP[4]Li^-$  alkalides.

macrocycle complexes of  $M_3O^+CXP[4]Li^-$  (horizontal top) are depicted in Fig. 2. All other optimized complexes of superalkali based  $M_3O^+CXP[4]Li^-$  alkalides along with their energies are shown in the ESI (Fig. S2†).

The structural integrity of CXP[4] remains intact after being doped with superalkalis and metal atom as there is a small

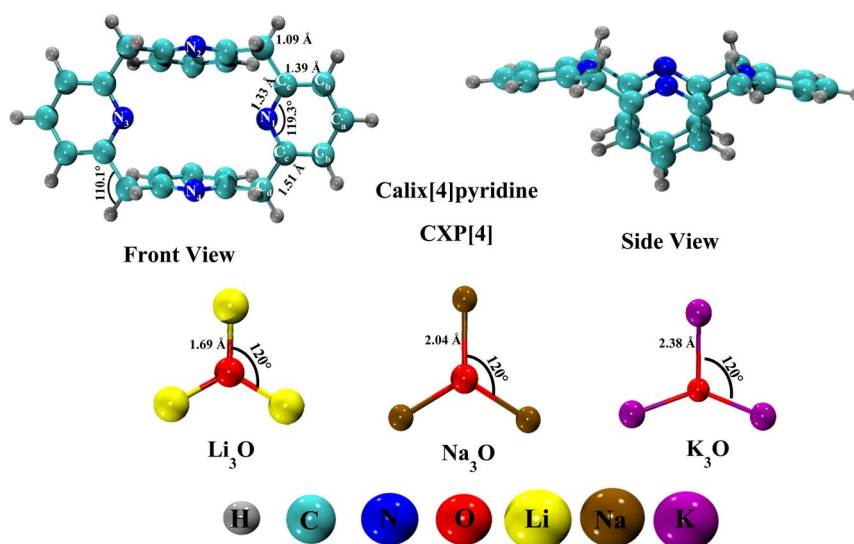


Fig. 1 Optimized structures of pure calix[4]pyridine and superalkalis ( $Li_3O$ ,  $Na_3O$  &  $K_3O$ ).





**Table 1** Optimized complexes with the first frequencies  $\nu_1$  ( $\text{cm}^{-1}$ ), symmetries, dihedral angles ( $\text{N}_1\text{--N}_2\text{--N}_3\text{--N}_4$  in degree), bond distance from CXP[4] to superalkali  $X_{\text{CXP[4]}-\text{M}_3\text{O}}$  (Å), bond distance from CXP[4] to Li metal  $X_{\text{CXP[4]}-\text{Li}}$  (Å), bond distance from superalkali to Li metal  $X_{\text{M}_3\text{O}-\text{Li}}$  (Å),  $E_{\text{int}}$  ( $\text{kcal mol}^{-1}$ ) and  $E_{\text{CP}}$  ( $\text{kcal mol}^{-1}$ )

Complex	$\nu_1$	Symmetry	$\text{N}_1\text{--N}_2\text{--N}_3\text{--N}_4$	$X_{\text{CXP[4]}-\text{M}_3\text{O}}$	$X_{\text{CXP[4]}-\text{Li}}$	$X_{\text{M}_3\text{O}-\text{Li}}$	$E_{\text{int}}$	$E_{\text{CP}}$
CXP[4]	16.29	$C_{2v}$	−2.85	—	—	—	—	—
$\text{Li}_3\text{O}^+\text{CXP[4]Li}^-$	17.19	$C_1$	−3.69	2.08	5.75	6.68	−64.5	−62.9
$\text{Na}_3\text{O}^+\text{CXP[4]Li}^-$	17.54	$C_1$	−2.67	2.40	3.41	7.72	−39.7	−36.7
$\text{K}_3\text{O}^+\text{CXP[4]Li}^-$	11.38	$C_1$	−2.67	2.89	6.20	7.53	−32.3	−32.9

variation in the dihedral angle of  $\text{N}_1\text{--N}_2\text{--N}_3\text{--N}_4$  cavity of CXP[4]. Similarly, the Li–O, Na–O, K–O bond lengths of superalkalis in the designed  $\text{M}_3\text{O}^+\text{CXP[4]Li}^-$  are 1.65 Å, 2.02 Å and 2.38 Å respectively, which are very close to those of the isolated superalkalis (Fig. 1). As a result, after being inserted into the calix[4]pyridine, the  $\text{M}_3\text{O}$  subunits maintain their structural integrity, with minimal alteration in the geometric parameters of superalkalis subunits, even in the presence of an additional Li metal atom on the opposite side. The  $\text{M}_3\text{O}^+\text{CXP[4]Li}^-$  complexes exhibit positive values for their first frequencies (Table 1), indicating the presence of true local minima on potential energy surface.

Superalkali subunits and Li metal doping have caused an alteration in the symmetry of CXP[4]. The free CXP[4] and  $\text{M}_3\text{O}$  entities exhibit  $C_{2v}$  and  $C_s$  point groups, whereas  $\text{M}_3\text{O}^+\text{CXP[4]Li}^-$  complexes have the  $C_1$  point group, providing further evidence that doping of superalkali can alter the symmetry of complexants.<sup>39</sup> The internuclear distances between  $\text{M}_3\text{O}$  and the center of the  $\text{N}_1\text{--N}_2\text{--N}_3\text{--N}_4$  cavity of CXP[4] increases in the order: 2.08 Å ( $\text{Li}_3\text{O}^+\text{CXP[4]Li}^-$ ) < 2.40 Å ( $\text{Na}_3\text{O}^+\text{CXP[4]Li}^-$ ) < 2.89 Å ( $\text{K}_3\text{O}^+\text{CXP[4]Li}^-$ ). The interaction distance between superalkalis and the center of the  $\text{N}_1\text{--N}_2\text{--N}_3\text{--N}_4$  cavity in CXP[4] elongates as the atomic number of alkali metal atoms in  $\text{M}_3\text{O}$  cluster increases from Li to K (Table 1).

A similar monotonic trend of increasing interaction distance has been observed in previous studies involving superalkalis doping on  $\text{C}_6\text{Li}_6$  and  $\text{C}_6\text{S}_6\text{Li}_6$  organometallic complexes.<sup>40,41</sup> Another factor that supports the fact is the volume of pure superalkali subunits. The increasing trend of volume of superalkali subunits is as follow;  $\text{K}_3\text{O}$  ( $84.14 \text{ cm}^3 \text{ mol}^{-1}$ ) >  $\text{Na}_3\text{O}$  ( $60.82 \text{ cm}^3 \text{ mol}^{-1}$ ) >  $\text{Li}_3\text{O}$  ( $43.85 \text{ cm}^3 \text{ mol}^{-1}$ ), respectively and is consistent with the monotonic trend of increasing interaction distances. On the other hand, the  $X_{\text{CXP[4]}-\text{Li}}$  and  $X_{\text{M}_3\text{O}-\text{Li}}$  internuclear distances follow an abnormal trend for  $\text{Na}_3\text{O}^+\text{CXP[4]Li}^-$ , but the internuclear distances increase from Li to K in the  $\text{Li}_3\text{O}^+\text{CXP[4]Li}^-$  and  $\text{K}_3\text{O}^+\text{CXP[4]Li}^-$  complexes.

The stability of complexes holds significant importance in the realm of practical uses for nonlinear optical materials. The  $E_{\text{int}}$  and VIE energies are the essential factors that determine the thermodynamic and chemical stability of any system. A higher interaction energy signifies a more stable system, indicating a closer interaction between the dopant and complexant.<sup>42</sup> The interaction energies of the  $\text{M}_3\text{O}^+\text{CXP[4]Li}^-$  alkalides reflect that these complexes have greater thermodynamic stability that can be inferred from their high exothermic nature (Table 1). The  $E_{\text{int}}$  values of  $\text{Li}_3\text{O}^+\text{CXP[4]Li}^-$ ,  $\text{Na}_3\text{O}^+\text{CXP[4]Li}^-$ , and  $\text{K}_3\text{O}^+\text{CXP[4]Li}^-$

are −64.5  $\text{kcal mol}^{-1}$ , −39.7  $\text{kcal mol}^{-1}$ , and −32.3  $\text{kcal mol}^{-1}$ , respectively. The  $\text{Li}_3\text{O}^+\text{CXP[4]Li}^-$  alkalide is recognized as the most stable one among the three superalkali based hetero-aromatic macrocycles. This stability arises from the least interaction distance between Li atom of  $\text{Li}_3\text{O/Li}^-$  (alkalide on opposite side as in  $X_{\text{CXP[4]}-\text{Li}}$ ) and the complexant, leading to a stronger interaction. Moreover, the exceptional thermal stability of  $\text{Li}_3\text{O}^+\text{CXP[4]Li}^-$  alkalide can be attributed to the low IP and small atomic size of Li metal. Consequently,  $\text{Li}_3\text{O}$  is regarded as the most favorable adsorbing species on the calix[4]pyridine macrocycle. Furthermore, the  $E_{\text{int}}$  values of  $\text{M}_3\text{O}^+\text{CXP[4]Li}^-$  alkalides are also comparable to the  $\text{Li}_3\text{O}^+(\text{calix[4]pyrrole})\text{M}^-$  alkalides,<sup>21</sup> and are greater than the  $E_{\text{int}}$  (−47.61 to −38.83  $\text{kcal mol}^{-1}$ ) of  $\text{Li}^+(\text{calix[4]pyrrole})\text{M}^-$  alkalides<sup>18</sup> reported previously. The findings suggest that the superalkali-based alkalides exhibit stronger binding compared to alkali metal-based alkalides.

In order to account for the basis set superposition error (BSSE), counterpoise correction was applied to the superalkali-based CXP[4] alkalides. The counterpoise corrected energies ( $E_{\text{CP}}$ ) of  $\text{M}_3\text{O}^+\text{CXP[4]Li}^-$  alkalides are observed to range from −32.96  $\text{kcal mol}^{-1}$  to −62.9  $\text{kcal mol}^{-1}$  (Table 1). These  $E_{\text{CP}}$  values exhibit minimal deviation from the interaction energy ( $E_{\text{int}}$ ), indicating that BSSE has a negligible impact on the doping of superalkalis and Li metal on the calix[4]pyridine. Therefore, the B3LYP/6-31G(d,p) level of theory proves to be a reliable choice for the current study. To verify the chemical stability of  $\text{M}_3\text{O}^+\text{CXP[4]Li}^-$  alkalides, the vertical ionization energy (VIE) serves as an additional parameter. The VIE values for the designed superalkali-based calix[4]pyridine alkalides falls in the range of 2.51–2.79 eV (Table 2).

The  $\text{Li}_3\text{O}^+\text{CXP[4]Li}^-$  alkalide, with  $\text{Li}_3\text{O}$  superalkali doping on the macrocycle, achieves the highest VIE value of 2.79 eV. On the other hand,  $\text{K}_3\text{O}^+\text{CXP[4]Li}^-$  alkalide, which involves  $\text{K}_3\text{O}$  doping, has the lowest VIE of 2.51 eV. Comparing all the vertical ionization energies, it can be concluded that the  $\text{M}_3\text{O}^+\text{CXP[4]Li}^-$  alkalides demonstrate chemical stability. These findings are

**Table 2** NPA charges of  $Q_{\text{Li}}$  ( $|e|$ ),  $Q_{\text{M}_1}$  ( $|e|$ ),  $Q_{\text{M}_2}$  ( $|e|$ ),  $Q_{\text{M}_3}$  ( $|e|$ ),  $Q_{\text{O}}$  ( $|e|$ ) and  $Q_{\text{M}_3\text{O}}$  ( $|e|$ ) and VIE (eV) of all complexes

Complexes	$Q_{\text{Li}}$	$Q_{\text{M}_1}$	$Q_{\text{M}_2}$	$Q_{\text{M}_3}$	$Q_{\text{O}}$	$Q_{\text{M}_3\text{O}}$	VIE
$\text{Li}_3\text{O}^+\text{CXP[4]Li}^-$	−0.397	0.811	0.812	0.828	−1.623	0.828	2.79
$\text{Na}_3\text{O}^+\text{CXP[4]Li}^-$	−0.452	0.803	0.81	0.641	−1.49	0.764	2.71
$\text{K}_3\text{O}^+\text{CXP[4]Li}^-$	−0.486	0.622	0.825	0.747	−1.439	0.755	2.51



in consistent with the previous literature,<sup>43</sup> indicating that the chemical stability of materials decreases as the size of superalkalis increases.

### 3.2. Charge transfer analysis and alkali nature

The charge transfer between superalkalis, Li metal atom, and calix[4]pyridine has been confirmed by the natural population analysis (NPA). Total charge on superalkali ( $Q_{M_3O}$ ) subunits is positive ranging from 0.755 |e| to 0.828 |e| indicating that the superalkali clusters behave as excess electron donors (Table 2). In contrast, the  $Q_{Li}$  values of Li metal doped at the other side of the CXP[4] vary in the following order:  $-0.486$  |e| ( $K_3O^+CXP[4]Li^-$ ) >  $-0.452$  |e| ( $Na_3O^+CXP[4]Li^-$ ) >  $-0.397$  |e| ( $Li_3O^+CXP[4]Li^-$ ), implying that the charge on anionic Li is affected by the superalkali subunits. The  $K_3O^+CXP[4]Li^-$  has the maximum negative charge  $Q_{Li}$  value of  $-0.486$  |e|. This can be attributed to the observed trend in VIE values among superalkali subunits, where  $2.673$  eV ( $K_3O$ ) <  $3.201$  eV ( $Na_3O$ ) <  $3.485$  eV ( $Li_3O$ ). This suggests that superalkali  $K_3O$ , with its smaller VIE value, exhibits a greater tendency to readily lose its excess electrons, leading to the maximum negative charge  $Q_{Li}$  value as observed in  $K_3O^+CXP[4]Li^-$ . In all  $M_3O^+CXP[4]Li^-$  complexes, the charge on the Li metal is negative, indicating the alkali nature of these macrocycles and these can be represented as  $M_3O^+CXP[4]Li^-$ . The alkali charge values ( $-0.397$  |e| to  $-0.486$  |e|) of  $M_3O^+CXP[4]Li^-$ , computed at the present level of theory, also follows the same trend as the net alkali charge values of previously reported  $M_3O^+(calix[4]pyrrole)M^-$  complexes (CAM-B3LYP/6-311++G(d, p)).<sup>21</sup> Moreover, alkali complexes such as  $Li_3(NH_3)_nNa^-$  alkali-ides with alkali charge values ranging from  $-0.291$  |e| to  $-0.509$  |e| (at CAM-B3LYP/6-311++G(3df,3pd)) have also been observed previously.<sup>44</sup> The findings suggest that calix[4]pyridine can serve as better complexant as compared to calix[4]pyrrole, making it a more suitable choice for designing NLO candidates.

### 3.3. Electronic properties

The optoelectronic properties of  $M_3O^+CXP[4]Li^-$  alkali-ides are examined using the frontier molecular orbital (FMO) approach. This investigation involved analyzing the energy levels of the highest occupied molecular orbitals (HOMOs), the lowest unoccupied molecular orbitals (LUMOs), corresponding energy gaps ( $E_g$ ), and their percentage reduction (%  $E_g$ ). Materials with reduced energy gaps are quite suitable for remarkable optoelectronic properties.<sup>13</sup> A wide energy gap (5.69 eV) in pure CXP[4] makes it difficult to be applied in optoelectronic devices. Its electronic properties have been improved significantly by

doping superalkali subunits ( $Li_3O$ ,  $Na_3O$  &  $K_3O$ ) and Li metal on the calix[4]pyridine (Table 3).

These findings show that the  $E_g$  values (0.30–0.50 eV) of superalkali-based  $M_3O^+CXP[4]Li^-$  alkali-ides have been reduced significantly. The formation of new HOMO orbitals is the main reason for the reduction in the energy gaps. These new HOMOs are generated when diffuse excess electron densities from superalkali subunits are transferred to the Li alkali-ide present on the opposite side of CXP[4]. Furthermore, these results are in agreement with the prior ones, demonstrating that the transfer of electronic density results in the production of new HOMOs.<sup>39</sup> The designed alkali-ides exhibit a significant percentage reduction in the energy gap, ranging from 91.1% to 94.6%. Moreover, an outstanding electronic and conducting behavior of the designed  $M_3O^+CXP[4]Li^-$  alkali-ides has been observed due to this enormous reduction in the energy gaps.<sup>10</sup> The pictorial representation of electron densities in pristine calix[4]pyridine and  $M_3O^+CXP[4]Li^-$  alkali-ides is shown in Fig. 3.

In pure calix[4]pyridine, the electron densities of HOMOs and LUMOs reside on the alternative pyridine rings with a small amount on the rest of the skeleton. The HOMOs electron densities of all the  $M_3O^+CXP[4]Li^-$  complexes are residing at the Li metal present on the opposite side of superalkalis,

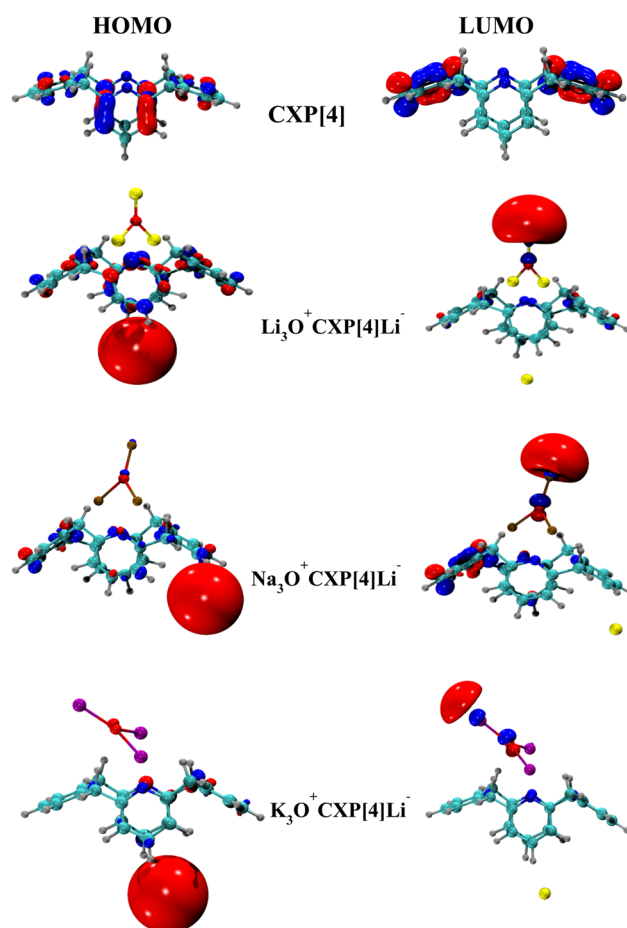


Fig. 3 Frontier molecular orbitals electron densities of  $M_3O^+CXP[4]Li^-$  alkali-ides.

Table 3 Energies of frontier molecular orbitals (eV), their energy gaps  $E_g$  (eV), and %  $E_g$  of  $M_3O^+CXP[4]Li^-$  alkali-ides

Complexes	$E_{HOMO}$	$E_{LUMO}$	$E_g$	% $E_g$
CXP[4]	−6.26	−0.58	5.69	—
$Li_3O^+CXP[4]Li^-$	−1.86	−1.36	0.50	91.1
$Na_3O^+CXP[4]Li^-$	−1.94	−1.59	0.35	93.8
$K_3O^+CXP[4]Li^-$	−1.75	−1.45	0.30	94.6



confirming their alkali nature. In the investigated alkalides, the diffuse excess electronic cloud has enwrapped the Li atom and created an anion ( $\text{Li}^-$ ) in all the three complexes. The intramolecular electron push-pull might be the major reason for the development of alkali characteristics. A similar type of alkali behavior has been observed previously by Sun *et al.*, in superalkali based alkalides of calix[4]pyrrole.<sup>21</sup>

### 3.4. Density of states analysis

The number of different states that electrons are allowed to occupy at a given energy level are commonly termed the density of states (DOS). This study examines the TDOS (total density of states) and PDOS (partial density of states) spectra to confirm the electronic properties especially the formation of new HOMOs and contribution of individual fragments in the newly designed superalkali-based alkalides. The DOS spectra of CXP[4] and superalkali-based  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides are manifested in Fig. 4.

The TDOS spectrum of bare calix[4]pyridine show that energy states are produced at lower energies in the occupied and virtual region. A substantial variation in the peak intensity of PDOS is observed after doping of CXP[4] with superalkalis and Li metal. As a result, the interaction between CXP[4], the  $\text{M}_3\text{O}$  clusters, and the Li metal leads to the creation of new high-energy HOMO orbitals. The DOS spectra of these superalkali-based alkalides show energy levels shifting, which confirms the formation of new HOMOs and a vertical dashed line indicates the presence of new HOMOs. These molecular orbitals

range from  $-1.96$  eV to  $-2$  eV (in the high energy zone), as compared to the  $-6.00$  eV of calix[4]pyridine which ultimately reduces the HOMO–LUMO energy gaps. The major contribution for the new HOMOs formation is from both superalkalis (blue line contribution) and Li alkali (pink line contribution) in all  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides as superalkali subunits have donated the excess electrons and Li metal on the opposite side of calix ring has accepted these electrons. Additionally, the rise in intensities of superalkalis and Li metal also indicates their significant contribution in the investigated complexes. The DOS spectra of  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides reveal a substantial enhancement in both electronic and conductive properties.

### 3.5. Interaction region indicator (IRI) analysis

The IRI approach<sup>45</sup> is used to identify and to better analyze the nature of intra and intermolecular interactions. The recently introduced real-space function, IRI, can simultaneously identify several interactions within chemical systems. The IRI and RDG (reduced density gradient) differ by a constant pre-factor, which is essential for ensuring a balance between non-covalent and covalent forces. The IRI expression can be written as:

$$\text{IRI}(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{[\rho(\mathbf{r})]^\alpha} \quad (12)$$

where  $\alpha$  is a variable parameter,  $\alpha = 1.1$  is an accepted value under the standard definition of IRI. It is essentially a scaled version of the gradient norm of electron density whereas the

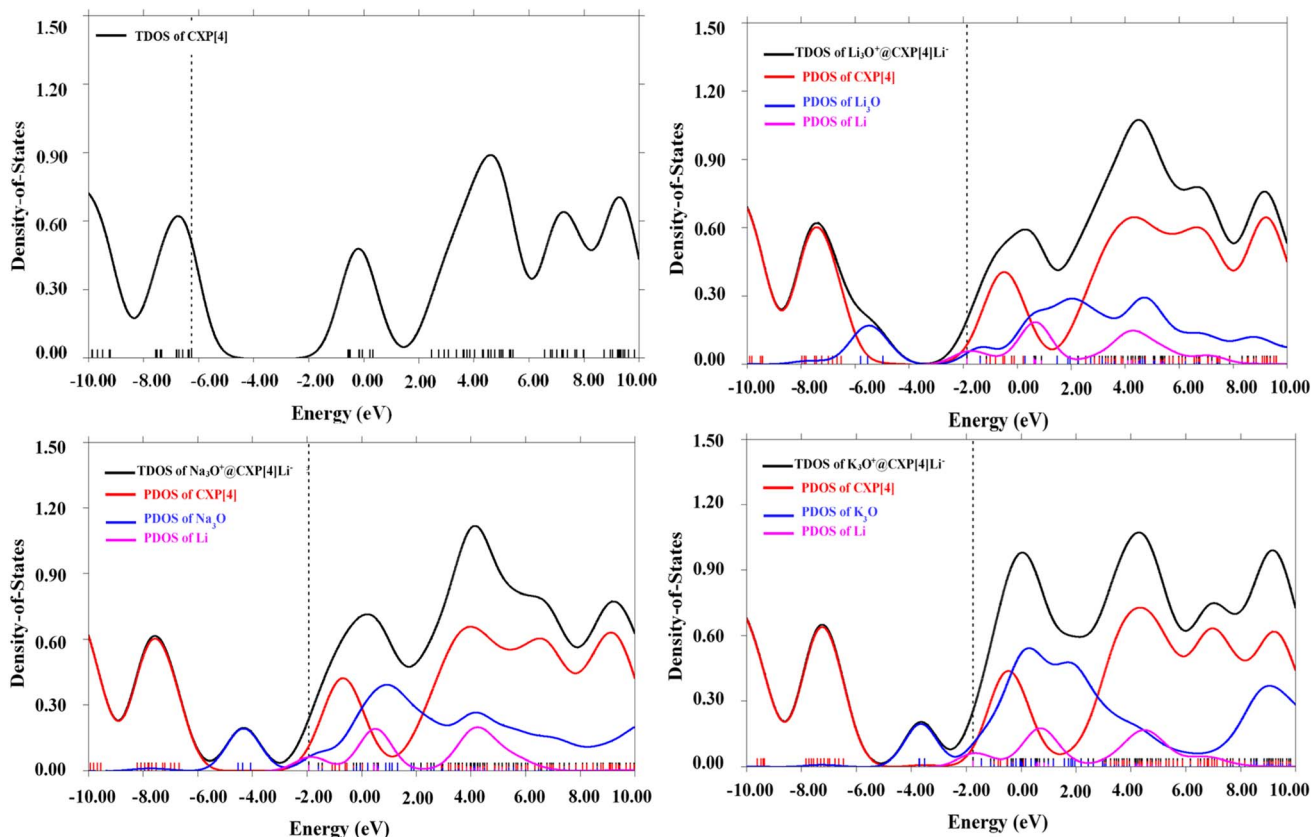


Fig. 4 Density of states spectra of CXP[4] and  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides.

RDG is a dimensionless form of electron density gradient. The RDG can be determined as:

$$\text{RDG}(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(\mathbf{r})|}{[\rho(\mathbf{r})]^{4/3}} \quad (13)$$

where  $\mathbf{r}$  is coordinate vector and  $\rho$  is the electron density. The repulsive, non-covalent, and attractive interactions are represented by the red, green, and blue patches on the 3D-IRI isosurfaces. The repulsive, non-covalent, and attractive interactions are shown by the red, green, & blue patches on the 3D-IRI isosurfaces. The nature of the interaction regions revealed by IRI can be depicted clearly by mapping sign ( $\lambda_2$ )  $\rho$  function onto the 2D-IRI plots. A region with a relatively a large magnitude of sign ( $\lambda_2$ ) $\rho$  and high electron density indicates a relatively strong interactions (hydrogen & halogen bonding *etc.*), whereas a region with a small sign ( $\lambda_2$ ) $\rho \approx 0$  and low  $\rho$  implies no apparent interaction or, at most, the van der Waals (vdW) interaction. Therefore, the interpretation of 3D-IRI isosurfaces and 2D-IRI plots of  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides has been carried out to gain an insight into the covalent and non-covalent interactions as depicted in Fig. 5.

The findings show that  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides have extensive green patches of weak dispersive vdW interactions and very small blue patches of hydrogen bonding. The  $\text{K}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalide has more noticeable green patches followed by  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  and  $\text{Li}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  complexes. Furthermore, the presence of distinct green spikes ranging from  $-0.01$  to  $0.01$  au in the 2D-IRI plots of the investigated complexes also supports the presence of weak dispersive interactions. The spikes of  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  and  $\text{Li}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  are less dense whereas the  $\text{K}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  complex has low gradient, low density, and sharp spikes and these findings also coincide with the above described interaction energies data.

### 3.6. Quantum theory of atoms in molecules (QTAIM) analysis

It is a topological tool to investigate the strength and nature of various interactions based on electron density and its various parameters at the bond critical points.<sup>46</sup> The QTAIM offers an elegant approach for determining the nature of a bond, which is dependent on its critical points, including the total electron density ( $\rho(\mathbf{r})$ ), Laplacian  $\nabla^2\rho(\mathbf{r})$ , total energy density ( $H$ ), kinetic  $V(\mathbf{r})$  and potential  $G(\mathbf{r})$  electron energy densities. The value of electron density ( $\rho(\mathbf{r})$ ) has a significant impact on the strength of interactions. The strong bondings (*i.e.* electrostatic interactions and H-bonding) are demonstrated by a  $-ive$  Laplacian  $\nabla^2\rho(\mathbf{r})$ ,  $\rho(\mathbf{r}) > 0.1$  au,  $H(\mathbf{r}) < 0$ , and  $-G(\mathbf{r})/V(\mathbf{r}) < 1$ . On the other hand, weak interactions such as van der Waals are demonstrated by the presence of a  $+ive$  Laplacian  $\nabla^2\rho(\mathbf{r})$ ,  $\rho(\mathbf{r}) < 0.1$  au,  $H(\mathbf{r}) > 0$ , and  $-G(\mathbf{r})/V(\mathbf{r}) > 1$  whereas partial covalent and partial electrostatic forces have only  $H(\mathbf{r}) < 0$  with  $+ive$  Laplacian  $\nabla^2\rho(\mathbf{r})$ . For the investigated complexes, the topological diagrams with the corresponding BCPs are shown in Fig. 6 and the interaction parameters are given in Table S1†.

The results demonstrate that the examined alkalides have three different types of bond paths. The  $\text{Li}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  has BCPs at  $\text{Li}_3\text{O}$ –carbon (Li–C),  $\text{Li}_3\text{O}$ –nitrogen (Li–N), and  $\text{Li}_3\text{O}$ –

hydrogen (O–H) bonds respectively. The  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  has bond paths at  $\text{Na}_3\text{O}$ –nitrogen (Na–N),  $\text{Na}_3\text{O}$ –hydrogen (O–H) and one lithium to hydrogen (Li–H) present on the lower side of complexant and a similar pattern of BCPs was observed for the  $\text{K}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  complex. The results of computed topological values such as  $\rho(\mathbf{r}) < 0.1$  au, positive Laplacian  $\nabla^2\rho$ ,  $H(\mathbf{r}) = 0$  or  $> 0$ , and  $-G(\mathbf{r})/V(\mathbf{r})$  value  $\geq 1$  indicate that the bondings are weak van der Waals. Thus, one may examine the noncovalent interaction behavior of  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  complexes from the bond critical points.

### 3.7. Electron localization function (ELF) analysis

An ELF map is a visualization tool that shows regions anticipated to contain electrons. It sheds light on the electronic structure and bonding of molecular systems. When an ELF map is projected onto the interval (0, 1), it can describe various types of interactions. High ELF values (around 1.0) are produced by purely ionic interactions, lone pairs of electrons or by non-bonding valence electrons, while very low values (around 0) are produced in the interstitial areas. The ELF values for the covalent bonding range from 0.6 to 0.8, depending on the bond's strength. To effectively characterize bonding, particularly in the  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  complexes, the ELF map analysis is employed and the maps are shown in Fig. 7.

The results of the color-filled shaded maps clearly depict that the regions of high electron localization are around the  $\text{Li}^-$  alkalide in all the designed  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  complexes. In contrast, the regions around C, N and H have lower values due to delocalization of electrons in the calix[4]pyridine substrate.

### 3.8. Absorption analysis

The time-dependent DFT absorption analysis has been carried out to study the absorption behavior of superalkali-based  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides. For their practical usability in optoelectronic applications, the examined alkalides should be transparent under the applied absorption region. The plotted absorption spectra of pure calix[4]pyridine and  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  complexes are displayed in Fig. 8 and their absorption maxima ( $\lambda_{\text{max}}$ ), oscillator strength ( $f_o$ ) and transition energies ( $\Delta E$ ) are given in Table 4.

According to the absorption results for pristine CXP[4], the crucial excitation (HOMO  $\rightarrow$  LUMO+3) requires 5.29 eV of energy, and the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) is observed at 235 nm. The shift of the  $\lambda_{\text{max}}$  to a longer wavelength after complexation demonstrates the strong impact of superalkalis and Li metal doping on upper and lower sides of CXP[4]. Moreover, the major electronic transitions along with their electron densities that hold electronic excitations in the maximum absorbance are also computed and are displayed in Fig. S3.† These findings demonstrate that  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides are entirely ultraviolet transparent and have maximum absorbance values of 727–1096 nm in the visible to near infrared (NIR) region. The lowering of HOMO–LUMO energy gaps of these complexes can be a reason for this bathochromic shift as observed in the previous studies.<sup>39</sup> The  $\text{K}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalide exhibits a dominant red shift in its  $\lambda_{\text{max}}$





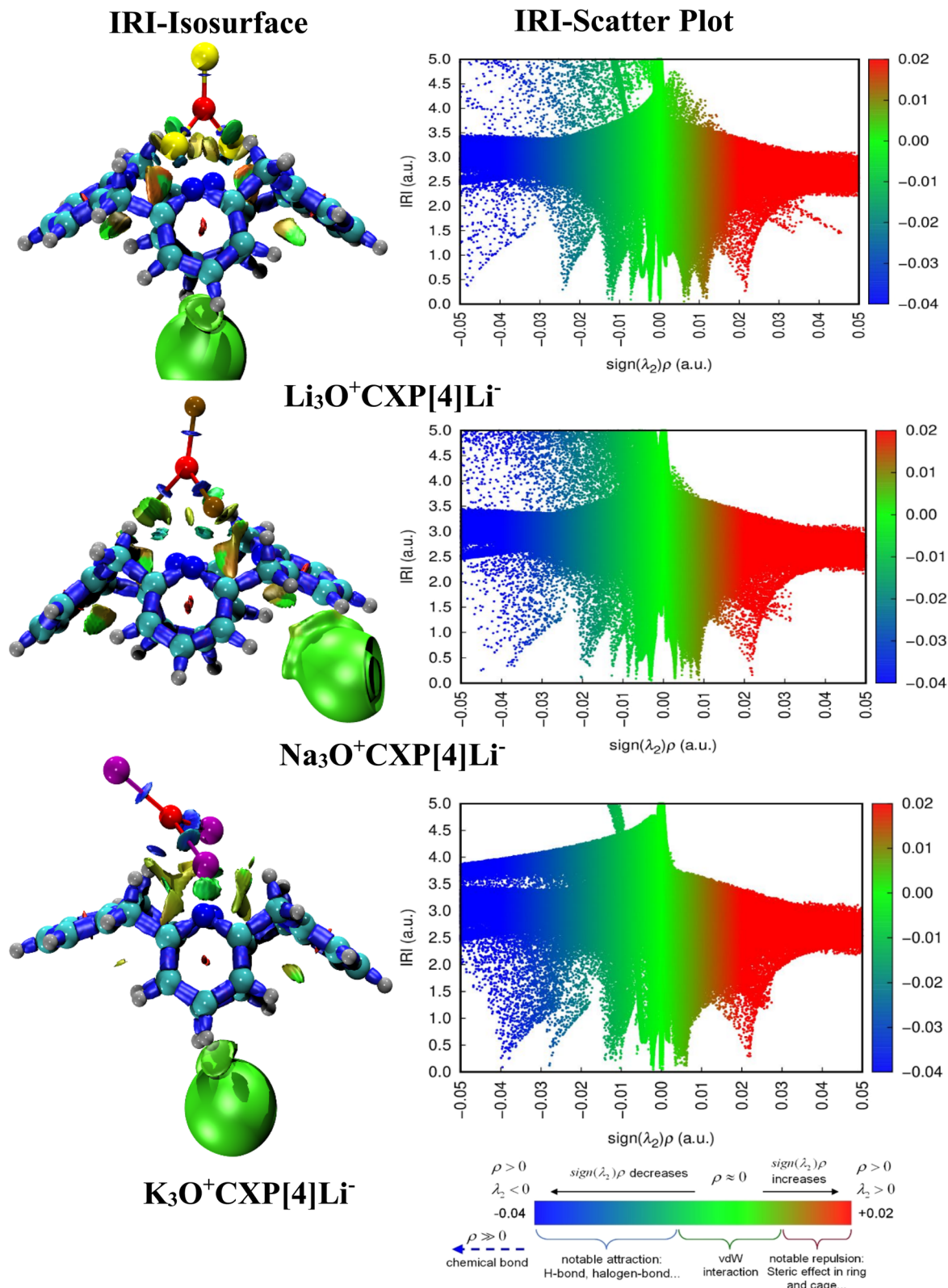


Fig. 5 2D-isosurfaces and 3D-IRI scatter plots of  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides along with the standard color bar of the IRI.<sup>45</sup>

at 1096 nm, primarily attributed to the possession of its lowest excitation energy (1.13 eV), whereas  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalide has the lowest  $\lambda_{\text{max}}$  at 727 nm with the highest excitation energy

(1.71 eV). Moreover, the oscillator strength ( $f_o$ ) values are increased for the designed complexes and falls in the range of 0.1089 to 0.1389 which indicates the strong probability of

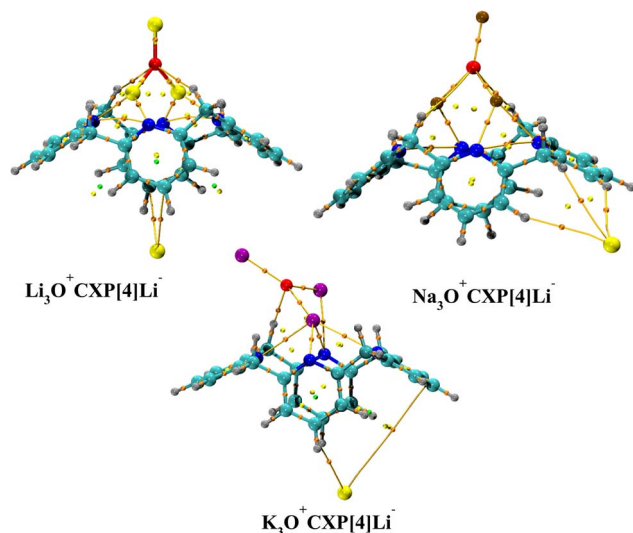


Fig. 6 Pictorial representation of QTAIM images (along BCPs) of  $M_3O^+CXP[4]Li^-$  alkalides. Orange dots represent bond critical points (BCPs), green dots indicate ring critical points (RCPs) and yellow dots denote cage or cluster critical points (CCPs).

quantum chemical transitions. These near-infrared  $M_3O^+CXP[4]Li^-$  alkalides should be the most suitable candidates for fabricating optical detectors and for improving the SHG effect of various optical materials.

### 3.9. Dipole moment and variation in dipole moments

The dipole moment is an index that describes the net polarity of molecules as the larger the dipole moment, the greater the charge separation. The mean dipole moments (15.6–26.9 au) for the investigated  $M_3O^+CXP[4]Li^-$  alkalides are significantly higher than those for the pure calix[4]pyridine complexant (Table 5).

The computed dipole moments ( $\mu_o$ ) of  $Li_3O^+CXP[4]Li^-$ ,  $Na_3O^+CXP[4]Li^-$ , and  $K_3O^+CXP[4]Li^-$  are 15.6, 25.8, and 26.9 au, respectively. The dipole moments ( $\mu_o$ ) (15.6–26.9 au) of  $M_3O^+CXP[4]Li^-$  are greater than the  $\mu_o$  values (5.96 to 15.07 au) of  $M^+(\text{hexaammine})M^-$  complexes<sup>47</sup> and the  $\mu_o$  values (0.253 to 3.698 au) of  $Li_3(NH_3)_nNa^-$  alkalides.<sup>44</sup> Furthermore, an enhancement in charge separation implied by this monotonic increase in  $\mu_o$  value from  $Li_3O$  to  $K_3O$  in the designed complexes is reflective of their distinctive optical properties, similar to the Cherepanov and his colleagues work.<sup>48</sup>

Furthermore, an increasing trend of variation in dipole moments ( $\Delta\mu$ ) from 1.61 to 5.99 au has been observed for the designed alkalides as compared to pristine calix[4]pyridine (Table 4). The  $Na_3O^+CXP[4]Li^-$  has the highest computed  $\Delta\mu$  of 5.99 au and  $K_3O^+CXP[4]Li^-$  has the lowest  $\Delta\mu$  of 1.61 au. As a result, the alteration in dipole moments (associated with the critical transition) might be responsible for improved optoelectronic features of the alkalides under consideration.

### 3.10. Optical properties of $M_3O^+CXP[4]Li^-$ alkalides

#### 3.10.1. Static linear and nonlinear optical properties.

Introduction of diffuse excess electrons *via* metal atoms (*i.e.*

alkali, superalkalis, transition, and alkaline earth) alters the optical features of nanosystems as evidenced by the prior studies.<sup>12</sup> The loosely bound excess electrons around the Li metal in the designed complexes, which are easily polarizable and exhibit typical alkalis nature, can be considered as essential candidates to trigger their nonlinear optical response. All of the variables that contribute to the potential linear and nonlinear optical response have been analyzed using DFT calculations (Table 5).

The linear optical response of newly designed  $M_3O^+CXP[4]Li^-$  complexes is investigated through their polarizabilities ( $\alpha_o$ ). In comparison to pure calix[4]pyridine, the polarizability values of superalkali-based CXP[4] alkalides are increased up to 966 au, which is much higher than 289 au of CXP[4]. All  $M_3O^+CXP[4]Li^-$  alkalides have  $\alpha_o$  values that expand monotonically in the order  $K_3O^+@CXP[4]Li^-$  (966 au) >  $Na_3O^+@CXP[4]Li^-$  (551 au) >  $Li_3O^+@CXP[4]Li^-$  (513 au). The polarization trend is mainly affected by the charge transfer and higher charge transfer is observed from superalkalis to  $Li^-$  alkalide in  $K_3O^+@CXP[4]Li^-$  (−0.486 |e|), followed by  $Na_3O^+@CXP[4]Li^-$  (−0.452 |e|) and  $Li_3O^+@CXP[4]Li^-$  (−0.397 |e|). Therefore, the charge separation greatly affects the static polarizability values of  $M_3O^+CXP[4]Li^-$  alkalides.

The static first hyperpolarizabilities ( $\beta_o$ ) of  $M_3O^+CXP[4]Li^-$  alkalides are also computed for the examination of NLO characteristics. The nonlinear optical responses of superalkali-based alkalides are greatly enhanced due to the presence of excess electrons (Table 4). It can be observed that  $\beta_o$  values ( $9.2 \times 10^4$ – $2.6 \times 10^6$  au) of  $M_3O^+CXP[4]Li^-$  alkalides are remarkably enhanced as compared to  $\beta_o$  value (289 au) of pure calix[4]pyridine. Furthermore, the designed superalkali-based alkalides show higher NLO response at CAM-B3LYP functional than at the M06-2X and  $\omega$ B97XD functionals (Table S2†) and it can be inferred that the CAM-B3LYP is a reliable functional for further investigations. The highest NLO response ( $2.6 \times 10^6$  au) is observed for the  $Na_3O^+CXP[4]Li^-$  and the lowest static first hyperpolarizability ( $9.2 \times 10^4$  au) is obtained for  $Li_3O^+CXP[4]Li^-$  alkalide. Additionally, the computed  $\beta_o$  value of the  $Na_3O^+CXP[4]Li^-$  alkalide ( $2.5 \times 10^6$  au) is substantially higher than the  $\beta_o$  value ( $3.4 \times 10^4$  au) of earlier reported  $K_3O^+(\text{calix[4]pyrrole})K^-$  alkalide at the same level of theory.<sup>21</sup> Besides this, the NLO response of designed alkalides is also compared with the some other earlier stated superalkali-based systems. The hyperpolarizabilities of investigated alkalides are also greater than  $\beta_o$  values  $3.8 \times 10^4$  au and  $9.1 \times 10^4$  au of  $Li_3(NH_3)_nNa^-$  ( $n = 1$ –4) alkalides<sup>44</sup> and ethylenediamine based superalkalides ( $M^+(\text{en})_3M_3O^-$ ).<sup>49</sup> Thus it can be concluded that the doping of superalkali and Li metal to the calix[4]pyridine complexant can be propitious for improving the NLO response of conventional alkalides.

The beta vector ( $\beta_{vec}$ ) is a useful tool for predicting the NLO properties of different nanomaterials. For the designed complexes, the  $\beta_{vec}$  outcomes are corresponding to the  $\beta_o$  values (Table 5). The  $Na_3O^+CXP[4]Li^-$  alkalide, which has the highest  $\beta_o$  of  $2.5 \times 10^6$  au, also has the greatest  $\beta_{vec}$  value of  $2.2 \times 10^6$  au. Furthermore, to provide an in depth understanding of the first order hyperpolarizability and its influencing aspects, the



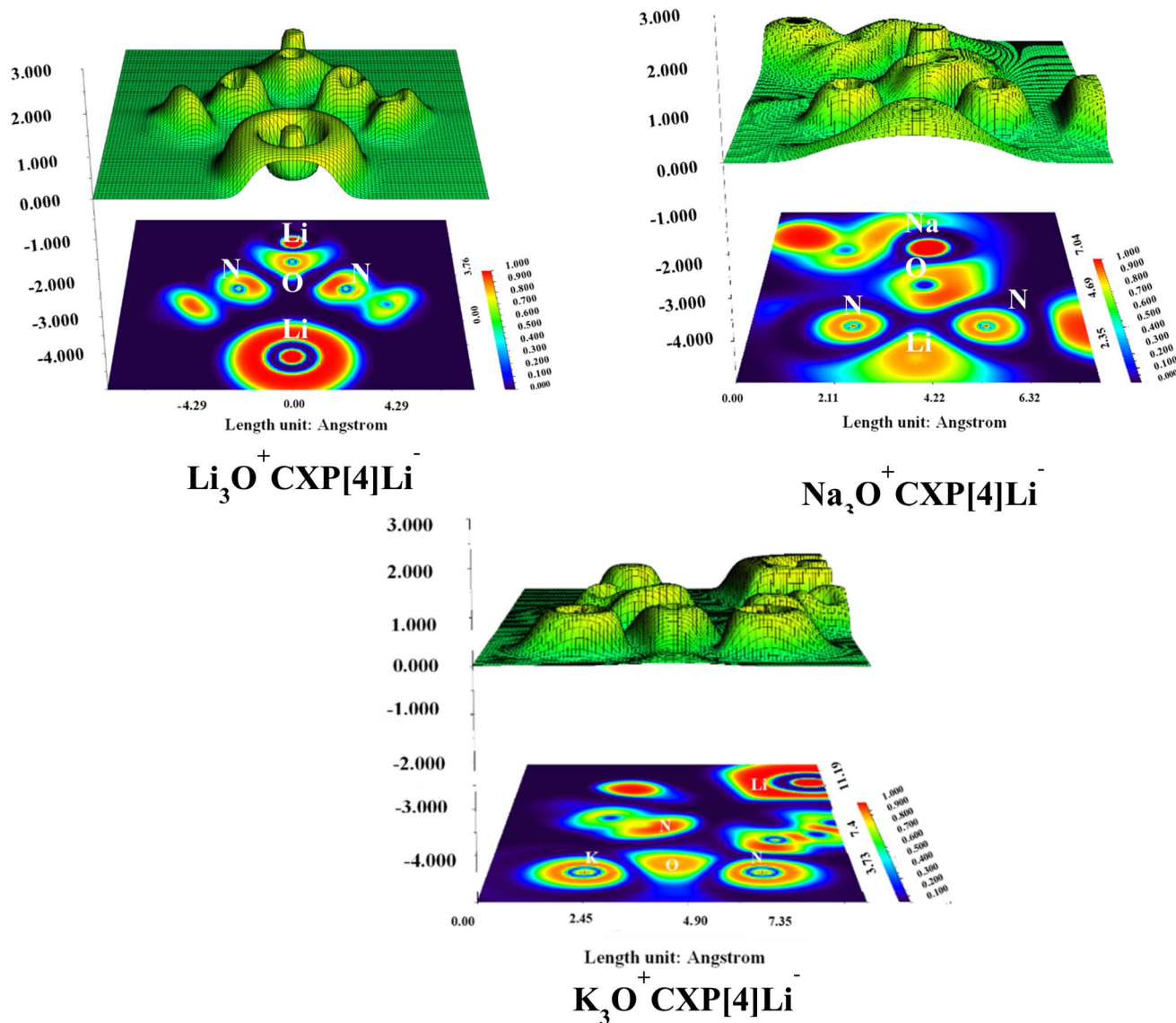


Fig. 7 Colored filled shaded electron localization function maps of  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides.

$\beta_{\text{TL}}$  values are calculated using the two-level model.<sup>50</sup> Mathematically, it can be represented as;

$$\beta_{\text{TL}} \approx \Delta\mu \frac{f_o}{\Delta E^3} \quad (14)$$

where,  $\beta_{\text{TL}}$  is obtained from the two-level expression using the sum-over-state (SOS) approach. Dipole moment variations (between ground and excited states), oscillator strength, and excitation energy are referred as  $\Delta\mu$ ,  $f_o$ , and  $\Delta E$ , respectively. There is a direct correlation between the  $\beta_{\text{TL}}$ ,  $f_o$ , and  $\Delta\mu$ , whereas the  $\beta_{\text{TL}}$  is inversely related to the 3rd power of  $\Delta E$ . The  $\beta_{\text{TL}}$  values of the  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides are significantly influenced by the crucial excitation energy and the hyperpolarizabilities of designed alkalides will increase as the critical excitation energy decreases as reported earlier.<sup>51</sup> It can be observed that  $\Delta E$  values (1.13 to 1.71 eV) of  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides are reduced as compared to  $\Delta E$  value (5.29 eV) of pure

calix[4]pyridine (Table 4). This reduction in energy difference has led to a significant enhancement in hyperpolarizabilities. The  $\beta_{\text{TL}}$  values obtained by SOS method are increasing in the following order:  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  ( $7.2 \times 10^3$  au) >  $\text{K}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  ( $3.3 \times 10^3$  au) >  $\text{Li}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  ( $1.3 \times 10^1$  au) (Table 5). Therefore, upon examining the comparison, it becomes evident that there is a strong correlation between  $\beta_o$  and  $\beta_{\text{TL}}$ . This correlation underscores the exceptional nonlinear optical (NLO) characteristics exhibited by these alkalide complexes. Strikingly, the other two factors, the highest variation in dipole moments (5.99 D) and the highest oscillator strength (0.1389) are also supporting the highest  $\beta_{\text{TL}}$  value for  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  by employing two level expression.

**3.10.2. Dynamic hyperpolarizabilities of  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides.** The assessment of the feasibility of utilizing superalkali-based  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides for NLO applications involves the computation of dynamic





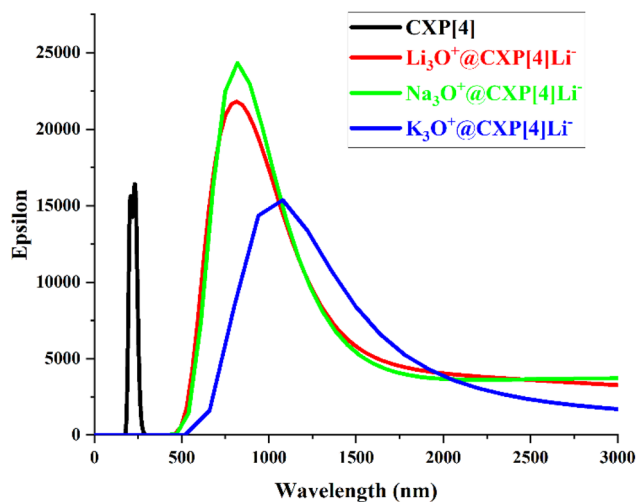


Fig. 8 UV-Visible spectra of pure and  $M_3O^+@CXP[4]Li^-$  alkalides.

hyperpolarizabilities. To mitigate the influence of damping effect and to avoid any potential overestimation of hyperpolarizabilities, three specific wavelengths (532 nm, 1064 nm & 1907 nm) are selected. The dynamic hyperpolarizability involves the computation of hyper-Rayleigh scattering (HRS), SHG and EOPE co-efficients and their results are listed in Table 6.

An encouraging method for experimentally assessing optical properties is through hyper Rayleigh scattering.<sup>52</sup> Therefore, the

$\beta_{HRS}$  values of superalkali-based  $M_3O^+CXP[4]Li^-$  alkalides are computed to offer insights that could prove valuable for the experimentalists. The results reveal distinct hyper-Rayleigh scattering based NLO responses ( $\beta_{HRS}$ ) superalkali-based alkalides at varying wavelengths. Notably, the  $Li_3O^+CXP[4]Li^-$  alkalide displays the lowest  $\beta_{HRS}$  value ( $2.3 \times 10^5$  au) at a 532 nm laser wavelength, while  $K_3O^+CXP[4]Li^-$  alkalide exhibits the highest  $\beta_{HRS}$  value ( $1.8 \times 10^8$  au) at 1064 nm. Moreover, an increasing trend of  $\beta_{HRS}$  values of the designed alkalides is observed from  $Li_3O^+CXP[4]Li^-$  to  $K_3O^+CXP[4]Li^-$  at selected wavelengths. Additionally, the dipolar to octupolar  $\beta_{HRS}$  contributions of  $M_3O^+CXP[4]Li^-$  alkalides along with their DR are also computed (Table S3†). The findings reveal that  $Li_3O^+CXP[4]Li^-$  alkalide exhibits a notable  $\beta_{J=3}$  value of  $7.5 \times 10^4$  au, accounting for 51.1% and displaying an octupolar nature with depolarization ratio of 4.06. On the other hand, the complexes  $Na_3O^+@CXP[4]Li^-$  and  $K_3O^+@CXP[4]Li^-$  are dipolar in nature, as indicated by their higher dipolar contributions with  $\beta_{J=1}$  values of  $1.9 \times 10^6$  au (59.2%) and  $9.1 \times 10^5$  au (53.9%). The corresponding depolarization ratios are 5.62 and 4.83, for these complexes, respectively. These findings strongly suggest that the investigated superalkali-based  $M_3O^+CXP[4]Li^-$  alkalides hold significant potential for nonlinear optical switches.<sup>5</sup>

Moreover, dynamic EOPE and SHG co-efficients of  $M_3O^+CXP[4]Li^-$  alkalides are also computed for optical imaging and for various other optical applications at the aforementioned laser wavelengths. Notably, the results depict that the EOPE is

Table 4 Transition energies ( $\Delta E$ ), oscillator strength ( $f_o$ ), difference in dipole moments  $\Delta\mu$  (Debye), absorption maxima ( $\lambda_{max}$ ), and major transitions

Complexes	$\Delta E$ (eV)	$f_o$	$\Delta\mu$ (Debye)	$\lambda_{max}$ (nm)	Major contribution
CXP[4]	5.29	0.0366	0.14	235	HOMO $\rightarrow$ LUMO+3
$Li_3O^+CXP[4]Li^-$	1.26	0.1267	3.38	982	HOMO $\rightarrow$ LUMO+15
$Na_3O^+CXP[4]Li^-$	1.71	0.1389	5.99	727	HOMO $\rightarrow$ LUMO+17
$K_3O^+CXP[4]Li^-$	1.13	0.1111	1.61	1096	HOMO $\rightarrow$ LUMO+10

Table 5 The dipole moment  $\mu_o$  (Debye), and linear and nonlinear optical variables:  $\alpha_o$  (au),  $\beta_o$  (au),  $\beta_{vec}$  (au), and  $\beta_{HRS}$  (au)

Complexes	$\mu_o$	$\alpha_o$	$\beta_o$	$\beta_{TL}$	$\beta_{vec}$	$\beta_{HRS}$
CXP[4]	4.02	289	74.8	—	—	—
$Li_3O^+@CXP[4]Li^-$	15.6	513	$9.2 \times 10^4$	$1.3 \times 10^1$	$9.2 \times 10^4$	$4.1 \times 10^4$
$Na_3O^+@CXP[4]Li^-$	25.8	551	$2.5 \times 10^6$	$7.2 \times 10^3$	$2.2 \times 10^6$	$1.1 \times 10^6$
$K_3O^+@CXP[4]Li^-$	26.9	966	$1.1 \times 10^6$	$3.3 \times 10^3$	$1.1 \times 10^6$	$4.9 \times 10^5$

Table 6 Frequency dependent hyperpolarizabilities of  $M_3O^+CXP[4]Li^-$  alkalides at working laser conditions

Complexes	EOPE ( $-\omega, \omega, 0$ )			SHG ( $-2\omega, \omega, \omega$ )			HRS ( $-2\omega, \omega, \omega$ )		
	$\lambda = 532$ nm	$\lambda = 1064$ nm	$\lambda = 1907$ nm	$\lambda = 532$ nm	$\lambda = 1064$ nm	$\lambda = 1907$ nm	$\lambda = 532$ nm	$\lambda = 1064$ nm	$\lambda = 1907$ nm
$Li_3O^+@CXP[4]Li^-$	$1.6 \times 10^5$	$3.7 \times 10^4$	$3.1 \times 10^4$	$2.6 \times 10^5$	$5.6 \times 10^4$	$2.3 \times 10^5$	$2.1 \times 10^5$	$2.3 \times 10^5$	$5.5 \times 10^5$
$Na_3O^+@CXP[4]Li^-$	$7.7 \times 10^7$	$1.3 \times 10^7$	$3.1 \times 10^4$	$6.4 \times 10^6$	$2.3 \times 10^6$	$2.5 \times 10^6$	$1.5 \times 10^7$	$3.2 \times 10^6$	$4.5 \times 10^6$
$K_3O^+@CXP[4]Li^-$	$2.2 \times 10^7$	$5.1 \times 10^7$	$6.7 \times 10^5$	$3.9 \times 10^6$	$1.1 \times 10^8$	$5.8 \times 10^5$	$6.2 \times 10^7$	$1.8 \times 10^8$	$6.4 \times 10^6$





particularly pronounced at 532 & 1064 nm whereas the EOPE is reduced at 1907 nm in the studied alkalides. The highest EOPE ( $7.7 \times 10^7$  au) is computed for the  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  at 532 nm, while the lowest EOPE ( $3.7 \times 10^4$  au) at 1064 nm is observed for  $\text{Li}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalide.

In the similar way, the  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides exhibit more significant second harmonic generation at 532 & 1064 nm, in comparison to 1907 nm. Specifically, the highest SHG response ( $1.1 \times 10^8$  au) is observed for  $\text{K}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalide at 1064 nm, whereas the  $\text{Li}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalide displays the least pronounced SHG effect of  $5.6 \times 10^4$  au at the same laser wavelength. These findings serve as compelling evidence supporting the utility of these superalkali-based calix[4]pyridines within the realm of nonlinear optics. Furthermore, these superalkali-based alkalides can be applied in Q-switching, cavity dumping, laser imaging and in various other fields due to the substantial impact of incident frequencies on SHG and EOPE co-efficients.

## 4. Conclusion

The concluding summary includes examination of geometric, electronic, and NLO responses of superalkali-based  $\text{M}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalides *via* DFT simulations. The designed alkalides demonstrate both thermodynamic and chemical stability, which is evidenced by their enhanced interaction energy values ( $-32.3$  to  $-64.5$  kcal mol $^{-1}$ ) and vertical ionization energies (2.51 to 2.79 eV). These alkalides, being excess electron compounds, exhibit potential electronic properties and have significantly reduced HOMO–LUMO energy gaps (0.30–0.50 eV). The highest charge transfer of  $-0.486$  |e| is obtained for the  $\text{K}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalide using natural population analysis and their the alkalide nature is confirmed by electron density distribution. The complexant interacts non-covalently with superalkali clusters and Li metal as computed by IRI and QTAIM studies. The absorption analysis reflects that the superalkali-based alkalides have absorption maximum in the visible to near infrared region 727–1096 nm and might be suitable for enhancing SHG of designed alkalides. The highest static 2nd order NLO response of  $2.5 \times 10^6$  au is computed for  $\text{Na}_3\text{O}^+\text{CXP}[4]\text{Li}^-$  alkalide which is greater than the highest  $\beta_o$  ( $3.4 \times 10^4$  au) of superalkali-based calix[4]pyrrole alkalides. The highest dynamic  $\beta_{\text{SHG}}$  and  $\beta_{\text{HRS}}$  of  $1.1 \times 10^8$  au and  $1.8 \times 10^8$  au are observed at 1064 nm whereas the highest EOPE value of  $7.7 \times 10^7$  au is computed at 532 nm. These results demonstrate that these superalkali-based calix[4]pyridine alkalides can be substantial NLO materials to be utilized in Q-switching, cavity dumping, laser imaging and as wavelength converters.

## Data availability

The data supporting this article have been included as part of the ESI.† Additional data will be available upon request from corresponding author.

## Conflicts of interest

The authors declare no competing interest.

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