

# Design of Lewis acid–base complex: enhancing the stability and first hyperpolarizability of large excess electron compound

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**Abstract** In the present paper, a new type of Lewis acid–base complex  $BX_3 \cdots Li@Calix[4]pyrrole$  ( $X = H$  and  $F$ ) was designed and assembled based on electrone molecule  $Li@calix[4]pyrrole$  (as a Lewis base) and the electron deficient molecule  $BX_3$  (as a Lewis acid) by employing quantum mechanical calculation. The new Lewis acid–base complex offers an interesting push-excess electron-pull (P-e-P) framework to enhance the stability and nonlinear optical (NLO) response. To measure the nonlinear optical response, static first hyperpolarizabilities ( $\beta_0$ ) are exhibited. Significantly, point-face assembled Lewis acid–base complex  $BF_3 \cdots Li@Calix[4]pyrrole$  (II) has considerable first hyperpolarizabilities ( $\beta_0$ ) value ( $1.4 \times 10^6$  a.u.), which is about 117 times larger than reported 11,721 a.u. of electrone  $Li@Calix[4]pyrrole$ . Further investigations show that, in  $BX_3 \cdots Li@Calix[4]pyrrole$  with P-e-P framework, a strong charge-transfer transition from the ground state to the excited state contributes to the enhancement of first hyperpolarizability. Theory calculation of enthalpies of reaction ( $\Delta_r H^0$ ) at 298 K demonstrates that it is feasible to synthesize the complexes  $BX_3 \cdots Li@Calix[4]pyrrole$ . In addition, compared with

$Li@Calix[4]pyrrole$ , the vertical ionization potential (VIP) and HOMO–LUMO gap of  $BX_3 \cdots Li@Calix[4]pyrrole$  have obviously increased, due to the introduction of the Lewis acid molecule  $BX_3$ . The novel Lewis acid–base NLO complex possesses not only a large nonlinear optical response but also higher stability.

**Keywords** Charge-transfer transition · Excess electron · Hyperpolarizability · Lewis acid–base complex · Nonlinear optical

## Introduction

Considerable works have been carried out for finding high performance nonlinear optical materials [1–13], which have been widely applied in many areas, such as optical data storage, optical communication, and optical limiting. A high second-order NLO response at the molecular level, expressed by the first hyperpolarizability  $\beta$ , is mainly achieved in organic molecules with extended  $\pi$ -electron systems, the planar D- $\pi$ -A model [14, 15], twisted  $\pi$ -electron systems [16], octupolar molecules [17–19], incorporation of ligated metal into the organic compounds [20] excess electron compound [21–26], and so forth. Especially, the push-pull frameworks are widely researched and have become successful motifs for NLO molecular design. Some people employed a large variety of donor and acceptor groups, including strong donating moieties, such as electron-rich  $\pi$ -excessive heteroaromatic rings [27], to enhance NLO response.

On the other hand, Lewis acid and base pair has been an active subject of research since Gilbert Newton Lewis developed this concept in the early 20th century. In this concept, Lewis acid is a substance that accepts and binds two electrons to form a covalent bond; A Lewis base is a substance that

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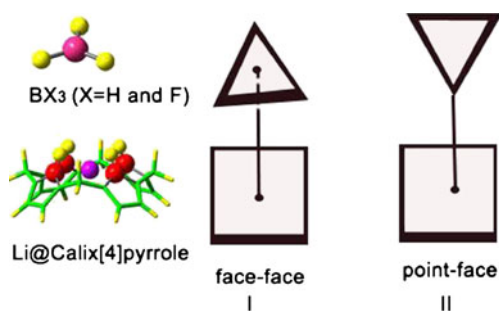
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gives two electrons in the bonding. A Lewis acid together with a Lewis base will react to make a compound called Lewis adducts.  $\text{BH}_3\text{NH}_3$  serves as a good example for Lewis acid and base adduct [28]. In addition, more Lewis acid–base adducts have also been reported, for example,  $\text{R}_3\text{PB}(\text{C}_6\text{F}_5)_3$  [29],  $\text{NHC–AlMe}_3$  Lewis adduct ( $\text{NHC} = 1,3\text{-di-tert-butylimidazol-2-ylidene}$ ) [30], and so on. Furthermore, electron charge-transfer is found in all Lewis acid–base adducts.

Here, we first report novel Lewis acid–base NLO complex  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  by assembling electrone molecule  $\text{Li@calix[4]pyrrole}$  [21] with  $\text{BH}_3$  and  $\text{BF}_3$  molecule. The possible assembly types are depicted in Fig. 1. It is well known that  $\text{BH}_3$  is an electron deficient compound. It is unstable and prefers to dimerize  $\text{B}_2\text{H}_6$ , moreover,  $\text{BH}_3$  as a Lewis acid is prone to form Lewis acid–base complexes, for example the stable complexes,  $\text{BH}_3\text{-Me}_2\text{S}$ ,  $\text{BH}_3\text{-PH}_3$ ,  $\text{BH}_3\text{-R}_3\text{N}$ ,  $\text{BH}_3\text{-THF}$ . Interestingly, the  $\text{Li@calix[4]pyrrole}$  with electrone characteristic can provide an outward pushed, loosely bound excess electron. Therefore, we expect that  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  is a novel Lewis acid–base complex, and the stability of the large electrone  $\text{Li@calix[4]pyrrole}$  can be enhanced, due to the loosely bound excess electron of the electrone being captured by the Lewis acid  $\text{BX}_3$  and the long-range charge transfer. Furthermore, in terms of molecular design of NLO, the novel Lewis acid–base complex  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  offers an interesting push-pull framework, which suggests that  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  can exhibit large first hyperpolarizability.

In the paper, novel Lewis acid–base NLO complex  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  ( $\text{X} = \text{H}$  and  $\text{F}$ ) was assembled based on Lewis acid  $\text{BX}_3$  and electrone molecule  $\text{Li@calix[4]pyrrole}$  as basic building blocks. The rational design and assembly provides a new push-excess electron-pull framework for NLO material design. The new Lewis acid–base NLO complexes possess improved nonlinear optical response and stability, due to large charge transfer between the electrone molecule  $\text{Li@calix[4]pyrrole}$  (as a Lewis base) and the electron deficient  $\text{BX}_3$  (as a Lewis acid). This work enriches the knowledge of Lewis acid–base chemistry, and these new results provide a new idea of high-performance NLO material design.



**Fig. 1** Three possible assembly types for the formation of Lewis acid–base complexes  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$

## Calculation details

The structures of the novel Lewis acid–base complex  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  ( $\text{X} = \text{H}$  and  $\text{F}$ ) with the global potential-energy minimum were obtained by the density functional theory (DFT/B3LYP, the nonlocal–correlation provided by the Lee–Yang–Parr expression) with the 6-311G(d) basis set [31]. It had been reported that B3LYP method could obtain reasonable geometry structure. Moreover, to check the result of B3LYP/6-311G(d) level of theory, a new density function, coulomb-attenuated hybrid exchange–correlation functional (CAM-B3LYP [32] and Møller–Plesset (MP2) method with 6-311G(d) basis set, and B3LYP method with larger basis set, are employed to recalculate the structure of  $\text{BH}_3\cdots\text{Li@Calix[4]pyrrole}$  (I) (see Table S1 in the Electronic supplementary material). The NBO charge and VIP values were also obtained at B3LYP/6-311G(d). With regard to the calculation of the first hyperpolarizabilities of these novel Lewis acid–base complex with strong charge transfer, choosing a proper method is important. We found that the DFT methods (B3LYP, M05-2X and CAM-B3LYP) underestimated the (hyper)polarizabilities (see Table S2 in the Electronic supplementary material). In this work, the (hyper)polarizabilities of  $\text{BX}_3\cdots\text{Li@calix[4]pyrrole}$  are calculated by finite field (FF) approach (“Polar = Eonly” keyword in the Gaussian 09 program package [33]) at the sophisticated MP2 level. In this calculation, the 6-311+G(3df) basis set is employed for the alkali Li atom and the 6-311+G(d) basis set for other atoms. The magnitude of the applied electric field is chosen as 0.001 a.u. for the calculation of the hyperpolarizability, which is proved to be the proper value for the related systems [21–26]. The spin contamination is negligible, as the expected value of the spin eigenvalue  $\langle S^2 \rangle$  for each of these species is very close to 0.75 in the calculations.

In the FF method, when a molecule is subjected to the static electric field, the energy ( $E$ ) of the molecule is expressed by [34, 35]

$$E(F) = E^0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l \cdots \quad (1)$$

where  $E^0$  is the energy of the molecule in the absence of an electronic field,  $\mu$  is the component of the dipole moment vector,  $\alpha$  is the linear polarizability tensor,  $\beta$  and  $\gamma$  are the first and second hyperpolarizability tensors, respectively.

For a molecule, the average dipole moment ( $\mu_0$ ) and polarizability ( $\alpha_0$ ) are defined as follows:

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

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

The static first hyperpolarizability is noted as

$$\beta_0 = \left( \beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{1/2}, \quad (4)$$

where

$$\beta_i = \frac{3}{5} (\beta_{iii} + \beta_{ijj} + \beta_{ikk}), i, j, k = x, y, z.$$

All of these calculations are performed with sing the Gaussian 09 program package [33].

## Results and discussion

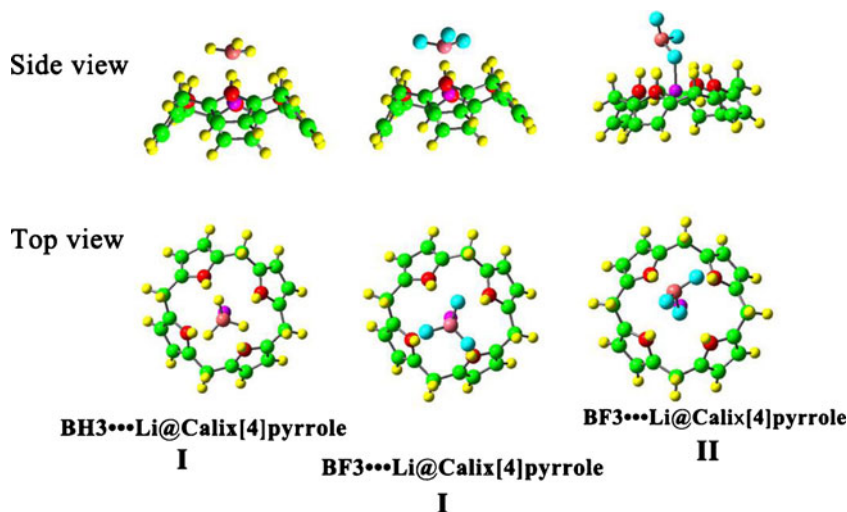
### Geometrical structures and NBO charges

Considering the possible assembly types shown in Fig. 1, we calculated the possible Lewis acid–base NLO complex based on the electron deficient molecule  $BX_3$  ( $X = H$  and  $F$ ) and electrone molecule  $Li@calix[4]pyrrole$  as basic building unit. At the B3LYP/6-311G(d) level of theory, we obtained the face-face and point-face assembled complexes  $BF_3 \cdots Li@Calix[4]pyrrole$  (I and II), but only obtained the face-face sandwich-like complex  $BH_3 \cdots Li@Calix[4]pyrrole$  (I), due to the difference of electronegativity between  $F$  and  $H$  atom. Besides, we failed to obtain the side-face assembled complexes  $BF_3 \cdots Li@Calix[4]pyrrole$ , because the side-face assembly type would transform into stable face-face or point-face assembly type. Moreover, the point-face assembled complex  $BF_3 \cdots Li@Calix[4]pyrrole$  (II) has slightly lower energy ( $1.28 \text{ kcal mol}^{-1}$ ) than the face-face assembled complex  $BF_3 \cdots Li@Calix[4]pyrrole$  (I) does. Those obtained Lewis acid–base structures are shown in Fig. 2. It shows that the structures of the two building units change slightly, and their

structural integrities are not destroyed by interactions with their counterparts. In  $BX_3 \cdots Li@Calix[4]pyrrole$  complex, the  $Li@calix[4]pyrrole$  monomer with electrone characteristic is a new lewis base, where it provides the (excess) electron formed by ionizing  $Li$  atom under the action of the lone pair of four  $N$  atoms; the electron deficient molecule  $BX_3$  is a lewis acid, which can accept electron. Thus, the unprecedented assembly provides a novel Lewis acid–base complex. Moreover, a push-excess electron-pull (P-e-P) framework is exhibited in the Lewis acid–base complex.

The important geometrical parameters were collected in Table 1. From Table 1, it is interesting to understand the change of the distance of  $N-Li$ . The face-face assembled complex  $BH_3 \cdots Li@Calix[4]pyrrole$  (I) only lead to slight change of the distance of  $N-Li$  (only  $0.008 \text{ \AA}$ ), by comparing with electrone molecule  $Li@Calix[4]pyrrole$ . However, there is an evident change of the  $N-Li$  distance in the complex  $BF_3 \cdots Li@Calix[4]pyrrole$ , the face-face assembly elongates the distance of  $N-Li$  from  $2.384\text{--}2.399 \text{ \AA}$ ; as the point-face assembled  $BF_3 \cdots Li@Calix[4]pyrrole$  (II) ( $C_1$  point group) has no high symmetry, the distance of  $N-Li$  ranges from  $2.259$  to  $2.505 \text{ \AA}$ . For the face-face assembled complexes (I), the  $B-Li$  distance in the  $BF_3 \cdots Li@Calix[4]pyrrole$  (I) is shorter than that in the  $BH_3 \cdots Li@Calix[4]pyrrole$  (I), this case maybe result from the fact that  $F$  atom is more electronegative than  $H$  atom. In addition, in the face-face assembled complexes  $BX_3 \cdots Li@Calix[4]pyrrole$  (I), the dihedral angle of  $XBXX$  becomes smaller ( $<180^\circ$  for the planar molecule  $BH_3$  and  $BF_3$ ), which indicates the attractive interaction between the excess electron ( $Li$  atom) and  $B$  atom. Comparing the point-face assembly with the face-face assembly is interesting for  $BF_3 \cdots Li@Calix[4]pyrrole$ . In the point-face assembled complex, the strong interaction between  $F$  and  $Li$  atom leads to the longer distance of  $B-Li$  and the shorter distance of  $F-Li$ .

**Fig. 2** Optimized geometries of  $BX_3 \cdots Li@Calix[4]pyrrole$  ( $X = F$  and  $H$ ). Green atoms are  $C$ , yellow atoms are  $H$ , red atoms are  $N$ , purple atom is  $Li$ , nattier blue atom is  $F$  and pink atom is  $B$



**Table 1** The main geometrical parameters (Å), XBXX is the dihedral angle (in degree)

	BH <sub>3</sub> ··· Li@Calix[4]pyrrole (I)	BF <sub>3</sub> ··· Li@Calix[4]pyrrole (I)	BF <sub>3</sub> ··· Li@Calix[4]pyrrole (II)
d <sub>N-Li</sub> <sup>a</sup>	2.376	2.399	2.259–2.505
d <sub>B-Li</sub>	2.579	2.539	2.967
d <sub>F-Li(min)</sub>		3.136	1.912
XBXX	146	129	

<sup>a</sup> The distance of d<sub>N-Li</sub> is 2.384 Å in electride molecule Li@Calix[4]pyrrole [see ref 21]

NBO charge analysis is very important to understand the geometrical characteristic of the three Lewis acid–base complexes. Due to the action on the Li atom from the electron deficient molecule BX<sub>3</sub>, we found its NBO charge q<sub>Li</sub> to be 0.740, 0.618 and 0.692, respectively (see Table 2), which shows that the Li atom was partly ionized. Whereas in the case of Li@Calix[4]pyrrole without the electron deficient molecule BX<sub>3</sub>, there is only little change in the NBO charge of the Li atom (0.089), because of lack of the Lewis acid BX<sub>3</sub> to accept excess electron coming from Li atom. What is more, an explicit charge transfer between electride molecule Li@calix[4]pyrrole and the electron deficient molecule BX<sub>3</sub> is generated in the novel Lewis acid–base complex. In well-known Lewis acid–base complexes NH<sub>3</sub>BH<sub>3</sub> and NH<sub>3</sub>BF<sub>3</sub>, the charge transfer is from Lewis acid NH<sub>3</sub> to Lewis base BX<sub>3</sub> (0.348 and 0.406 e for X = H and F, respectively). However, the charge transfer of 0.693–0.846 e is from new Lewis acid Li@Calix[4]pyrrole to Lewis base BX<sub>3</sub> in the novel Lewis acid–base complex BX<sub>3</sub>···Li@Calix[4]pyrrole at the same calculation level. We expect that the explicit charge transfer is responsible for the remarkable electronic properties of BX<sub>3</sub>···Li@Calix[4]pyrrole.

The stability of BX<sub>3</sub>···Li@Calix[4]pyrrole

Owing to the introduction of the electron deficient molecule BX<sub>3</sub> forming the novel Lewis acid–base complex, the stability

of electride BX<sub>3</sub>···Li@Calix[4]pyrrole was enhanced. To compare the stability of BX<sub>3</sub>···Li@Calix[4]pyrrole with those of previously reported works [21, 36–39], we have calculated the VIP values of BX<sub>3</sub>···Li@Calix[4]pyrrole (see Table 2). Previous investigations have shown that the VIP value is an important criterion to judge the redox ability of a molecule. The VIP values (6.217 eV for BH<sub>3</sub>···Li@Calix[4]pyrrole(I), 6.775 eV for BF<sub>3</sub>···Li@Calix[4]pyrrole(I) and 6.618 eV for BF<sub>3</sub>···Li@Calix[4]pyrrole(II)) are significantly larger than that of Li@calix[4]pyrrole (4.16 eV) [21]. They are still larger than those of other previously reported organic electride complexes, such as (Me)<sub>3</sub>NH<sup>+</sup>Na<sup>-</sup> (3.904 eV) [36], Li<sup>-</sup> [15]aneN<sub>5</sub> (2.32 eV) [37], (Li<sup>+</sup>@n<sup>6</sup>adz)Li<sup>-</sup> (2.88 eV) [26], and coordinated inorganic Li(NH<sub>3</sub>)<sub>4</sub>Na (3.27 eV) [38]. Only Li<sup>···</sup>(HCN)<sub>3</sub> (5.95 eV) [39] and Li@B<sub>10</sub>H<sub>14</sub> (6.12 eV) [40] have considerable VIPs, comparable to those of BX<sub>3</sub>···Li@Calix[4]pyrrole. Thus, the assembled Lewis acid–base complex exhibited enhanced stability.

In addition, thermochemical quantities provide an important tool for understanding of chemical reactions. A negative enthalpy change Δ<sub>r</sub>H<sup>0</sup> < 0 is often related to lower energy products than its reactants in exothermic reactions. Table 2 lists Δ<sub>r</sub>H<sup>0</sup> values of the studied complexes. Those negative Δ<sub>r</sub>H<sup>0</sup> values indicate that the synthesis of BX<sub>3</sub>···Li@Calix[4]pyrrole is feasible by combining a push group Calix[4]pyrrole with a pull group BX<sub>3</sub>.

Further, a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular

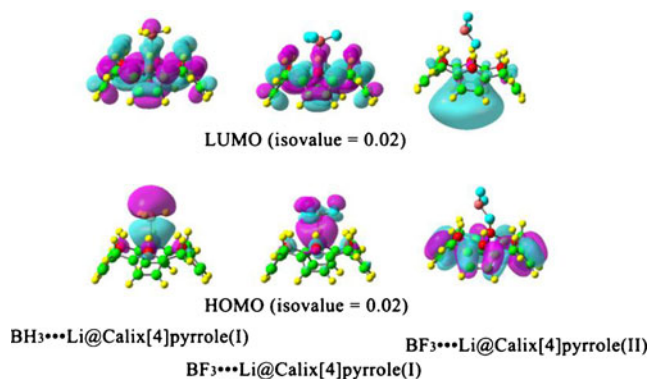
**Table 2** NBO charges, charge transfer the electron deficient molecule BX<sub>3</sub> (X = H and F) and electride molecule Li@calix[4]pyrrole CT (e), vertical ionization potential VIP (eV), HOMO-LUMO gap (eV) and the enthalpy change Δ<sub>r</sub>H<sup>0</sup> (kcal mol<sup>-1</sup>)

	BH <sub>3</sub> ··· Li@Calix[4]pyrrole (I)	BF <sub>3</sub> ··· Li@Calix[4]pyrrole (I)	BF <sub>3</sub> ··· Li@Calix[4]pyrrole (II)	Li@Calix[4]pyrrole <sup>c</sup>
q <sub>Li</sub>	0.740	0.618	0.692	0.089
q <sub>B</sub>	-0.608	0.921	0.984	
CT <sup>a</sup>	0.846	0.701	0.693	
VIP	6.217	6.775	6.618	3.710
H-L	3.584	3.910	3.815	1.221
Δ <sub>r</sub> H <sup>0</sup> <sup>b</sup>	-34.78	-22.53	-22.61	

<sup>a</sup> In well-known Lewis acid–base pair NH<sub>3</sub>BH<sub>3</sub> and NH<sub>3</sub>BF<sub>3</sub>, the charge transfer is from Lewis acid NH<sub>3</sub> to Lewis base BX<sub>3</sub> (0.348 and 0.406 e for X = H and F, respectively)

<sup>b</sup> Δ<sub>r</sub>H<sup>0</sup> = ΔH<sub>f</sub><sup>0</sup>(BX<sub>3</sub> ··· Li@Calix[4]pyrrole) - ΔH<sub>f</sub><sup>0</sup>(Li@Calix[4]pyrrole) - ΔH<sub>f</sub><sup>0</sup>(BX<sub>3</sub>)

<sup>c</sup> Ref [21]



**Fig. 3** HOMOs show the excess electron clouds are accepted by the Lewis acid BX<sub>3</sub> in BH<sub>3</sub>•••Li@Calix[4]pyrrole(I) and BF<sub>3</sub>•••Li@Calix[4]pyrrole(I). The HOMO electron cloud locates almost in the framework of the pyrrole in BF<sub>3</sub>•••Li@Calix[4]pyrrole(II)

orbital (LUMO) implies high kinetic stability and low chemical reactivity. The molecule with large HOMO–LUMO gap is unfavorable to be reduced, difficult to add electrons to a high-lying LUMO, difficult to be oxidized, and not easy to extract electrons from a low-lying HOMO. From Fig. 3, it is found that HOMOs show the excess electron clouds are accepted by the electron deficient molecule BX<sub>3</sub> in BH<sub>3</sub>•••Li@Calix[4]pyrrole(I) and BF<sub>3</sub>•••Li@Calix[4]pyrrole(I), and the HOMO electron cloud locates almost in the framework of the pyrrole in BF<sub>3</sub>•••Li@Calix[4]pyrrole(II). This finding indicates that the HOMO energy level decreases. Other frontier molecular orbitals are listed in Fig. S1 of the Electronic supplementary material). Table 2 shows that BX<sub>3</sub>•••Li@Calix[4]pyrrole have large HOMO–LUMO energy gaps of 3.584–3.910 eV, which are significantly larger as compared with the HOMO–LUMO energy gaps of 1.221 eV for Li@Calix[4]pyrrole[21] and 1.85 eV for AdzLi<sup>+</sup>Na<sup>-</sup> [36]. The HOMO–LUMO energy gaps (3.584–3.910 eV) are larger than the theoretical value of 2.735 eV for the stable C<sub>60</sub> cage [41]. These suggest that BX<sub>3</sub>•••Li@Calix[4]pyrrole have reasonable kinetic stability.

The above results show that the assembly and design enhanced the stability of large excess electron compound Li@Calix[4]pyrrole. Dye and coworkers pointed out that

electrides with inorganic cryptands [42] are resistant to thermal decomposition at room temperature due to the absence of oxygen–carbon bonds [42–44]. For small unstable excess electron compound, such as LiCN•••Li, Su proposed that a boron nitride nanotube (BNNT) as a protective shield molecule could enhance the stability of a small unstable excess electron compound [45]. However, there is no inorganic cryptands and nanotubes large enough to trap large excess electron compounds, such as Li@calix[4]pyrrole. Here, we suggested that a large excess electron compound (as a Lewis base) assembles with the electron deficient molecule (as a Lewis acid) to form a novel Lewis acid–base to enhance the stability of a large excess electron compound.

In addition, the infrared spectrum (IR) and <sup>4</sup>N, and <sup>11</sup>B NMR shielding tensors have been investigated in the [Electronic supplementary material](#). Those results may be helpful to understand the stability and charge-transfer character of novel Lewis acid–base complexes BX<sub>3</sub>•••Li@Calix[4]pyrrole with P-e-P framework.

#### Electronic properties of BX<sub>3</sub>•••Li@Calix[4]pyrrole

The electric properties of BX<sub>3</sub>•••Li@Calix[4]pyrrole are obtained at MP2 level and listed in Table 3. Comparing with the electirde Li@Calix[4]pyrrole without the electron deficient molecule BX<sub>3</sub>, it can be found that there are some great differences in the electric properties. The dipole moments of BX<sub>3</sub>•••Li@Calix[4]pyrrole computed to be 3.132, 3.506 and 4.010 D, respectively (see Table 3), are much larger than that of Li@Calix[4]pyrrole (0.759 D), but the polarizabilities of BX<sub>3</sub>•••Li@Calix[4]pyrrole (300, 248 and 293 a.u. respectively) are computed to be somewhat smaller than that of Li@Calix[4]pyrrole (363 a.u.).

Furthermore, the most significant change is in the first hyperpolarizability. Strikingly, the  $\beta_0$  values are  $5.5 \times 10^5$  (BH<sub>3</sub>•••Li@Calix[4]pyrrole (I)),  $6.3 \times 10^4$  (BF<sub>3</sub>•••Li@Calix[4]pyrrole(I)) and  $1.4 \times 10^6$  a.u. (BF<sub>3</sub>•••Li@Calix[4]pyrrole(II)). Obviously, the novel Lewis acid–base complexes BX<sub>3</sub>•••Li@Calix[4]pyrrole with P-e-P framework

**Table 3** Dipole moment  $\mu_0$  (a.u.), polarizability  $\alpha_0$  (a.u.), first hyperpolarizability  $\beta$  (a.u.)

Property	BH <sub>3</sub> ••• Li@Calix[4]pyrrole (I)	BF <sub>3</sub> ••• Li@Calix[4]pyrrole (I)	BF <sub>3</sub> ••• Li@Calix[4]pyrrole (II)	Li@Calix[4]pyrrole <sup>b</sup>
$\mu_0$	3.132	3.506	4.010	2.708
$\alpha$	300	248	293	383
$\beta_0$	$5.5 \times 10^5$	$6.3 \times 10^4$	$1.4 \times 10^6$	$1.2 \times 10^4$
$\beta_{\text{add}}$	14225	11927	14452	
$\beta_{\text{CT}}$	$5.3 \times 10^5$	$5.1 \times 10^4$	$1.4 \times 10^6$	
$\beta_{\text{CT}}/\beta_0$	96 %	81 %	100 %	
$\langle s^2 \rangle^a$	0.7584	0.7519	0.7625	

<sup>a</sup> The expected value of  $\langle s^2 \rangle$  is 0.750

<sup>b</sup> Ref [21]

**Table 4** Transition energy  $\Delta E$  (eV), oscillator strength  $f_0$ , major contribution and configuration interactions  $C_i$ , and difference of dipole moments between the ground state and the excited state  $\Delta\mu$  (D) for novel lewis acid–base complexes  $BX_3 \cdots Li@Calix[4]pyrrole$

Transition	$\Delta E$	$f_0$	Major contribution	$\Delta\mu$	$C_i$
$BH_3 \cdots Li@Calix[4]pyrrole(I)$					
$S_0 \rightarrow S_1$	4.103	0.019	H $\rightarrow$ L + 6	4.487	0.75
$S_0 \rightarrow S_2$	4.895	0.075	H-2 $\rightarrow$ L	1.594	0.76
$S_0 \rightarrow S_3$	4.904	0.066	H-3 $\rightarrow$ L	1.530	0.76
$BF_3 \cdots Li@Calix[4]pyrrole(I)$					
$S_0 \rightarrow S_1$	4.910	0.067	H-2 $\rightarrow$ L	1.871	0.75
$S_0 \rightarrow S_2$	4.927	0.071	H-3 $\rightarrow$ L	1.829	0.76
$BF_3 \cdots Li@Calix[4]pyrrole(II)$					
$S_0 \rightarrow S_1$	3.697	0.022	H $\rightarrow$ L + 4	5.967	0.94
$S_0 \rightarrow S_2$	4.262	0.016	H $\rightarrow$ L + 6	4.228	0.92
$S_0 \rightarrow S_3$	4.319	0.023	H-2 $\rightarrow$ L	5.292	0.75

increase the  $\beta_0$  values by about 46, 6 and 117 times, compared to that of  $Li@Calix[4]pyrrole$  (11,721 a.u.) at the same calculation level.

Comparing with other NLO molecules with D- $\pi$ -A framework, the  $\beta_0$  value of  $BF_3 \cdots Li@Calix[4]pyrrole(II)$  is about 8 times larger than the recorded value of  $\beta_0$  ( $1.7 \times 10^5$  a.u.) for the donor-acceptor polyene reported by Blanchard-Desce et al. [46], and near 23 times than that of the previously reported system  $H_2N-(CH=CH)-NO_2$  by Champagne et al. ( $6 \times 10^4$  a.u.) [47]. The combination of a strong donor hydrazono group and the auxiliary donor effect of p-excessive heteroaromatic rings afforded NLO chromophores with very high  $\beta_0$  values ( $2.2 \times 10^4$  a.u.) [7], which is about 64 times smaller than that of  $BF_3 \cdots Li@Calix[4]pyrrole(II)$ . Furthermore, the large  $\beta_0$  value of  $BF_3 \cdots Li@Calix[4]pyrrole(II)$  is also larger than that of the donor-CNT framework reported by Yang et al. [48], and that of D-GNR-A framework reported by Zhou [13].

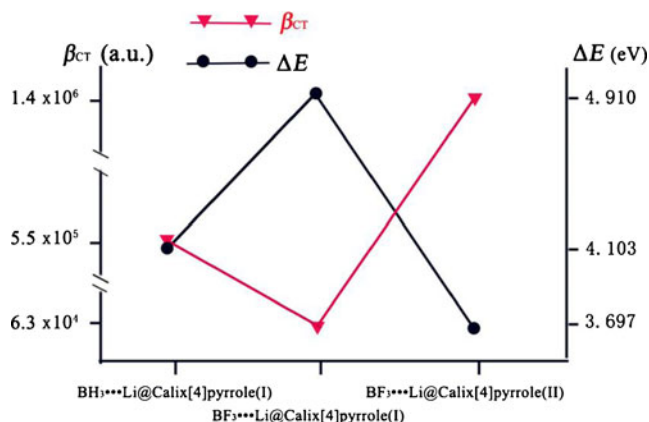
Comparing with other NLO molecules with excess electron, the  $\beta_0$  value of  $BF_3 \cdots Li@Calix[4]pyrrole(II)$  is near 25 times larger than that of the electride  $Li_n-H-(CF_2-CH_2)_3-H$  ( $n=1, 2$ ) (3,694–76,978 a.u.) [23], and is very close to that of lithium salt electride with an excess electron pair  $Li-H_3C_4N_2 \cdots Na_2$ . The alkali is another kind of compound containing excess electrons, and its  $\beta_0$  value is larger than that of corresponding electride. However, the  $\beta_0$  value of  $BF_3 \cdots Li@Calix[4]pyrrole(II)$  is still much larger than that of the previously designed cup-like alkali  $Li^+(calix[4]pyrrole)K^-$  ( $3.6 \times 10^4$  a.u.) [25] and cage-like alkalis ( $M^+@n^6adz$ ) $M^-$  ( $M=Li, Na, \text{ and } K$ ) ( $1.6 \times 10^5 \sim 3.2 \times 10^5$  a.u.) [26].

Therefore, it is clear that the unprecedented assembly affords a novel type of Lewis acid–base complex to optimize the first hyperpolarizability. Novel Lewis acid–base complex  $BX_3 \cdots Li@Calix[4]pyrrole$  with P-e-P framework not only has enhanced stability, but also exhibits large  $\beta_0$  value. However, comparing with the electride  $Li@Calix[4]pyrrole$ , what leads to so large  $\beta_0$  values of  $BX_3 \cdots Li@Calix[4]pyrrole$ ?

Oudar and Chemla proposed that the anomalously large responses in the push-pull chromophores were due to an intramolecular charge transfer interaction between acceptor and donor. The second-order response was then taken to be the sum of two contributions [49, 50]

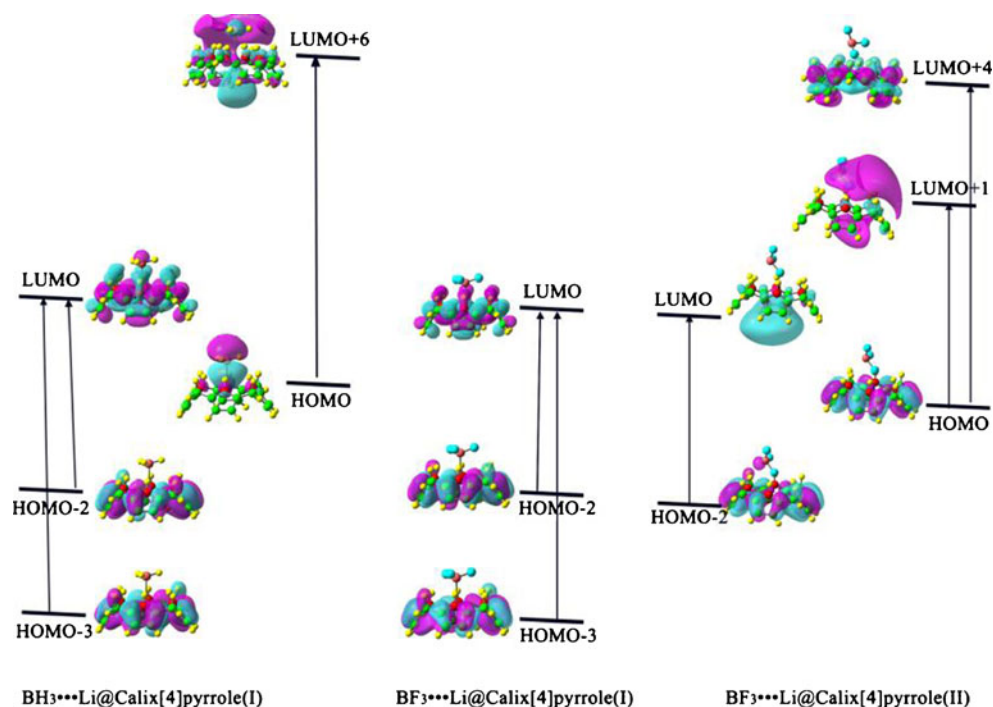
$$\beta_0 = \beta_{add} + \beta_{ct}, \quad (5)$$

where  $\beta_{add}$  is the additive portion, accounting for the interaction between the individual donor/acceptor group and the conjugated bridge, and the charge-transfer “correction” term  $\beta_{ct}$  is the contribution arising from the interaction of donor and acceptor moieties. From Table 3, we find that the  $\beta_{add}$  value is negligible for the large  $\beta_0$  value, and that is to say,  $\beta_{ct}$  is primarily responsible for a large portion of  $\beta_0$  value. This shows that large  $\beta_0$  values of the novel Lewis acid–base complexes  $BX_3 \cdots Li@Calix[4]pyrrole$  are intrinsically related to charge-transfer excited states, and indicates that the novel assembly provides a P-e-P framework with strong charge-transfer character. Thus, Lewis acid–base complex  $BX_3 \cdots Li@Calix[4]pyrrole$  with P-e-P framework exhibits unusual large  $\beta_0$  values.



**Fig. 4** A rough relationship between  $\beta_{ct}$  and  $\Delta E$  is depicted to understand the order  $\beta_{ct}$  values. Red line is  $\beta_{ct}$ , black line is  $\Delta E$

Fig. 5 Crucial transitions



The difference of  $\beta_0$  values between the complexes  $\text{BX}_3 \cdots \text{Li@Calix[4]pyrrole}$  is due to the difference of  $\beta_{\text{ct}}$  values. The charge-transfer “correction” term was described in terms of a two-level expression (as shown in eq6) [49, 50].

$$\beta_{\text{ct}} \propto \frac{\Delta\mu \cdot f_0}{\Delta E^3}, \quad (6)$$

where the  $\beta_{\text{ct}}$  value is proportional to difference of dipole moments between the ground state and excited state  $\Delta\mu$  and the oscillator strength  $f_0$ , but it is inversely proportional to the third power of the transition energy  $\Delta E$ . The transition energy is the decisive factor for  $\beta_{\text{ct}}$ . The transition energies are obtained by time-dependent (TD)-DFT approach using the B3LYP functional. Table 4 shows the crucial transitions along with their major contribution molecular orbital. From Table 4, it is found that  $\text{BF}_3 \cdots \text{Li@Calix[4]pyrrole(II)}$  has the smallest  $\Delta E$ , according to the two-level expression, it is reasonable that the  $\beta_{\text{ct}}$  value of  $\text{BF}_3 \cdots \text{Li@Calix[4]pyrrole(II)}$  is much larger than that of the other two Lewis acid–base complexes. The rough relationship between  $\beta_{\text{ct}}$  and  $\Delta E$  can be found in Fig. 4.

Besides this, we have roughly estimated the difference of dipole moments between the ground state and excited state by TD-DFT, i.e., for the first transition, the  $\Delta\mu$  values are 4.487  $\text{BH}_3 \cdots \text{Li@Calix[4]pyrrole(I)}$ , 1.871  $\text{BF}_3 \cdots \text{Li@Calix[4]pyrrole(I)}$ , and 5.967 au  $\text{BF}_3 \cdots \text{Li@Calix[4]pyrrole(II)}$ . One can see that the order of  $\Delta\mu$  is consistent with the order of  $\beta_{\text{ct}}$ . For other transitions,  $\text{BF}_3 \cdots \text{Li@Calix[4]pyrrole(II)}$  still has

largest  $\Delta\mu$  value. The largest  $\Delta\mu$  value relates to the largest  $\beta_{\text{ct}}$  value. Thus, the  $\Delta\mu$  value is another contribution factor of large  $\beta_{\text{ct}}$  value for those Lewis acid–base complexes.

To understand the relative magnitude of those  $\Delta\mu$  values, we consider those changes of electron clouds in the crucial transitions (see Fig. 5). Clearly, for the face-face assembled complexes  $\text{BX}_3 \cdots \text{Li@Calix[4]pyrrole}$  (I) ( $X = \text{H}$  and  $\text{F}$ ), they have analogous transitions ( $\text{HOMO-3} \rightarrow \text{LUMO}$  and  $\text{HOMO-2} \rightarrow \text{LUMO}$ ), moreover, the electron transitions associates with the small charge transfer in the framework of

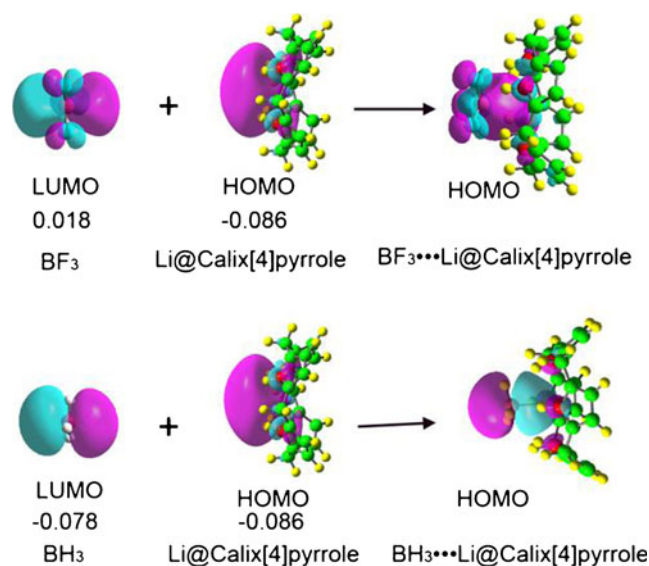


Fig. 6 Orbital interactions constructing a novel “push-excess electron-pull” framework

Calix[4]pyrrole, and their  $\Delta\mu$  values are small. Besides the two transitions,  $\text{BH}_3\cdots\text{Li@Calix[4]pyrrole}$  (I) has another important transition ( $\text{HOMO} \rightarrow \text{LUMO} + 6$ ). The transition is from HOMO formed by combination between the occupied orbital of excess electron from Li atom and the 2p orbital of B atom, to LUMO + 6, the unoccupied orbital of excess electron from Li atom. The transition associates with the large charge transfer with a long distance; therefore, its  $\Delta\mu$  value is large (4.487 D). For the point-face assembled complex  $\text{BF}_3\cdots\text{Li@Calix[4]pyrrole}$  (II), three crucial transitions are detected. As shown in Fig. 5, the three transitions associate with the large charge transfer with a long distance. For example, in the  $\text{HOMO} \rightarrow \text{LUMO} + 1$  transition, the charge transfer is large from the framework of Calix[4]pyrrole to the antibonding orbital of  $\text{BF}_3$ , and is a long-range transfer, so the  $\Delta\mu$  value is considerable large (5.967D).

On this occasion, it is interesting that we understand the formation of  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  by using the frontier molecular orbital (FMO) theory. As shown in Fig. 6, (1) the LUMO of the Lewis acid  $\text{BX}_3$  and the HOMO of the Lewis base  $\text{Li@Calix[4]pyrrole}$  complex are orbitals of similar energies; (2) the molecular orbitals have the same symmetry; (3) the molecular orbitals can overlap as much as possible. Therefore, the two MO participate in the formation of  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$ . Specially, the interesting orbital interactions construct a novel P-e-P framework.

## Conclusions

In this work, novel Lewis acid–base complexes  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  ( $X = \text{H}$  and  $\text{F}$ ) were designed and assembled based on electride molecule  $\text{Li@calix[4]pyrrole}$  (as a Lewis base) and the electron deficient molecule  $\text{BX}_3$  (as a Lewis acid). The new Lewis acid–base complex offers an interesting push-excess electron-pull (P-e-P) framework to enhance the stability and nonlinear optical response. Significantly, static first hyperpolarizabilities ( $\beta_0$ ) are exhibited. Novel Lewis acid–base complex  $\text{BF}_3\cdots\text{Li@Calix[4]pyrrole}$  (II) has a considerable first hyperpolarizabilities ( $\beta_0$ ) value ( $1.4 \times 10^6$  a.u.), which is 117 times larger than reported 11,721 a.u. of large electride  $\text{Li@Calix[4]pyrrole}$ . Further investigations show that, in  $\text{BX}_3\cdots\text{Li@Calix[4]pyrrole}$  with P-e-P framework, a strong charge transfer mainly contributes to the enhancement of first hyperpolarizability. The novel Lewis acid–base NLO complex possesses not only a large nonlinear optical property but also higher stability. They hold potential as high-performance nonlinear optical materials. This work enriches the knowledge of Lewis acid–base chemistry, and provides a valuable idea to obtain a stable electride compound with high-performance NLO response.

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