1. Introduction

During the past few decades, nonlinear optic (NLO) materials have made rapid progress in terms of both theoretical research and experimentation and have become an important component in the fields of optics and electricity. Through research, design and improvement of new nonlinear optical materials, many methods for increasing nonlinear optical responses have been proposed.

Electrides, a novel kind of ionic compound in which electrons serve as anions, have been proposed as potential second-order nonlinear optical (NLO) materials. In this work, the substituent effects on the electride characteristics and the NLO behaviour of Li@calix[4]pyrrole with an electride-like structure were studied theoretically. The results show that electron-donating and electron-withdrawing groups can effectively increase and decrease the first hyperpolarizability ($\beta_0$), respectively, without affecting the electride characteristics (electron population). More interestingly, lithiation in which four H atoms bonded to N atoms are substituted by four Li atoms within the core structure of Li@calix[4]pyrrole remarkably improves the electride characteristics, with a large electron population of 0.74 e (1.02 e) at the NNA (ELF) basins, making this structure perhaps the first formal molecular electride with almost one electron isolated from the rest of the molecules. Furthermore, a relationship between the electride characteristics and the NLO properties is found: the more delocalization the excess electron of the electride experiences, the larger the $\beta_0$ value is. The present investigation may provide useful information for exploring high-performance second-order nonlinear optical materials based on organic electrides.

Theoretical study of substituent effects on electride characteristics and the nonlinear optical properties of Li@calix[4]pyrrole

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Electrides, a novel kind of ionic compound in which electrons serve as anions, have been proposed as potential second-order nonlinear optical (NLO) materials. In this work, the substituent effects on the electride characteristics and the NLO behaviour of Li@calix[4]pyrrole with an electride-like structure were studied theoretically. The results show that electron-donating and electron-withdrawing groups can effectively increase and decrease the first hyperpolarizability ($\beta_0$), respectively, without affecting the electride characteristics (electron population). More interestingly, lithiation in which four H atoms bonded to N atoms are substituted by four Li atoms within the core structure of Li@calix[4]pyrrole remarkably improves the electride characteristics, with a large electron population of 0.74 e (1.02 e) at the NNA (ELF) basins, making this structure perhaps the first formal molecular electride with almost one electron isolated from the rest of the molecules. Furthermore, a relationship between the electride characteristics and the NLO properties is found: the more delocalization the excess electron of the electride experiences, the larger the $\beta_0$ value is. The present investigation may provide useful information for exploring high-performance second-order nonlinear optical materials based on organic electrides.
our present work. In addition to the conventional push–pull groups, lithiation by which H atoms in –NH groups are substituted by additional Li atoms is also used. In this work, we will pay attention to not only the substituent effect on the electrode characteristic but also the substituent effects on the NLO properties, as well as the relationship between the electrode characteristics and the NLO properties. The present investigation may provide useful information for exploring high-performance second-order nonlinear optical materials based on organic electrides.

2. Computational methods

The optimized geometric structures were obtained using the B3LYP method and 6-31+G(d) basis set in conjunction with the same thresholds as the article published by Luis and Matito (see ESIf). Frequency calculations were performed to confirm whether the obtained structures are real minima at the same level of theory.

For a large system, the DFT57,58 method is a good choice for calculating the first hyperpolarizability ($\beta_0$) because it considers a balance between the efficiency and the computational cost. However, different functionals may yield different results for $\beta_0$, and thus, testing different functionals is necessary. Here, different functionals were used to calculate the $\beta_0$ value of Li@calix[4]pyrrole with a medium size. In this testing, CAM-B3LYP59,60 was chosen to calculate the $\beta_0$ and polarizability ($\alpha_0$) value for all the systems in this work because the $\beta_0$ value (11 876 au) of CAM-B3LYP is closest to that of MP2 (ref. 61) (11 853 au) with the same mixed basis set where the 6-311+G(3df,3pd) basis set is employed for N, Li and the four H atoms of –NH groups and the 6-31+g(d) basis set is used for other atoms. The results are shown in the ESI (Table S1). The finite-field (FF) approach62–64 has been applied to evaluate the tensor components of the static hyperpolarizabilities. It simply requires the evaluation of the system energy for different amplitudes of the applied external electric field and can therefore be applied to a broad range of methods. When a system is in a weak and stable applied electric field, its energy can be written as:

$$E = E^0 - \mu_a F_a - \frac{1}{2} \alpha_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma$$

where $E^0$ is the molecular energy without the electric field, and $F_\alpha$ is an electric field component along $\alpha$ direction; $\mu$, $\alpha_{\alpha\beta\gamma}$ and $\beta_{\alpha\beta\gamma}$ are the dipole moment, polarizability, and first hyperpolarizability, respectively. Moreover, the vertical ionization energy (VIE) and natural bond orbital (NBO) charge65 were obtained by the CAM-B3LYP and MP2 methods. Unless otherwise specified, the above mixed basis set was used for all calculations except geometry optimization. The excited states were calculated using the TD-CAM-B3LYP method.49,66–70

Topological analysis of electron density was performed using the MP2 method since Timerghazin and Peslherbe have shown that the characterization of excess electrons is sensitive to electron correlation and large basis sets.71 The topological analysis of atoms in molecules (AIM)72,73 and the electron localization function (ELF)74–78 were conducted by using the free and open source Multiwfn program.77

We used the following equations to calculate $\beta_0$, $\alpha_0$ and VIE.

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

$$\beta_0 = (\beta_{x}^2 + \beta_{y}^2 + \beta_{z}^2)^{1/2}$$

$$\beta_i = \beta_{xx} + \beta_{yy} + \beta_{zz}$$

$$\text{VIE} = E[\text{M}^+] - E[\text{M}]$$

All calculations are performed using the Gaussian 09 program package.78

3. Results and discussion

3.1 Topological analysis of electron density

All optimized structures without imaginary frequencies are shown in Fig. 1. To facilitate the discussion, Li@calix[4]pyrrole is denoted as 1. All other structures are constructed based on this structure of 1. When eight H atoms at the $\beta$-positions of 1 are replaced with methoxy (–OCH3) and fluorine (–F) groups, octa-methoxy-1 and octafluorine-1 are obtained, respectively. In addition, four H atoms within NH– groups of 1 are substituted by four Li atoms to form tetra-lithium-1. Except for octamethoxy-1, which has $C_1$ symmetry, these complexes all have $C_{4v}$ symmetry.

3.1.1 The effects of electron-withdrawing and electron-donating substituents. 1 possesses a cup-like structure with a lithium atom near the centre of the N-plane. As reported in the literature, under the action of four N atoms, the s valence electron of the Li atom is pushed out and becomes an excess electron at the bottom of the cup.79 1 can be described in the form of $\text{Li}^{+}[\text{calix[4]pyrrole}]^-$, which was further verified by finding an NNA with a negative Laplacian value and an ELF basin below the –NH group, consistent with Luis’ report. However, the electron numbers of the NNA and ELF basins are 0.47 and 0.91 e, respectively, at the MP2 level of theory, which are 0.3 and 0.4 e larger than those (0.17 and 0.51 e) at the B3LYP level of theory reported by Luis. The significant difference in these electron numbers can be attributed to the effects of electron correlation and the basis set. For octafluorine-1 with electron-withdrawing substituents (–F), the electron numbers of NNA and ELF basins are 0.45 and 0.91 e, respectively, which are almost the same as those (0.47 and 0.91 e) of 1. For octamethoxy-1 with electron-donating substituents (–OCH3), the electron numbers of NNA and ELF basins are also the same as those of octafluorine-1 (see Table 1). Why does the donating or withdrawing nature of the groups not change the electron population? By comparing the charges of these three molecules, it is found that the charges of the atoms near the excess electron are almost unchanged (see Table S2†), which results in the same electron population. Although the electron numbers of these complexes are unchanged by the presence of substituents, their integral volumes of the respective ELF
basins are obviously different. The order of integral volume is octafluorine-1 (7976) < 1 (8763) < octamethoxy-1 (13 079 bohr³). Octafluorine-1, with electron-withdrawing substituents, has the smallest integral volume, while octamethoxy-1, with electron-donating substituents, has the largest integral volume, which indicates that the excess electron of octamethoxy-1 is more diffuse than that of octafluorine-1. The above analysis shows that the introduction of electron-donating or electron-withdrawing substituents does not change the electron population of electrides but significantly affects the diffusion of the excess electron, which may be an effective way to change the NLO properties while maintaining the electride characteristics. The NLO properties will be discussed in the following section.

3.1.2 The substituents of Li atoms (lithiation). As described in the above discussion, we found that the electrostatic field surrounding the excess electron plays an important role in the electron population. To break the original field, a new molecule was constructed, tetra-lithium-1, in which the four H atoms in the −NH groups of 1 were substituted by four Li atoms. Tetra-lithium-1 also has \( C_{n\sigma} \) symmetry, in which each Li atom is placed on the N−N bridge. The N−Li and N−Liₙₐₜₘₐₜ bond lengths are 2.351 Å and 2.010 Å, respectively, and the Liₙₐₜₘₐₜ−Liₙₐₜₘₐₜ bond lengths are 2.562 Å and 2.704 Å, respectively (see Fig. 1). Similar to 1, an NNA with a negative Laplacian value and an ELF basin were also found in tetra-lithium-1 (see Fig. 2). Interestingly, the electron numbers of the NNA (ELF) basins further increased from 0.47 (0.91 e) of 1 to 0.74 (1.02 e) in tetra-lithium-1. To the best of our knowledge, tetra-lithium-1 may be the first formal molecular electride with an isolated excess electron, except Li₂@TCNQ and Na₂@TCNQ, in which the electride characteristics are considered to derive from Li₂ and Na₂. The large electron population of tetra-lithium-1 can be understood by the NBO charges (see Table S3†). Lithiation leads to charge transfer from Li atoms to N atoms, giving the N atoms of tetra-lithium-1 a more negative charge (−0.904|e]) than that (−0.693|e]) in 1. This causes a higher percentage of the valence electron of the inner Li atom to be pushed out and captured by the cavity formed by the outer Li cations. The newly formed cavity of Li cations with a positive charge of 0.683|e on each Li atom has a stronger ability to bind the excess electron than the previous cavity formed by H cations with a positive charge of 0.350|e. Moreover, compared to octafluorine-1 and octamethoxy-1, tetra-lithium-1 has the smallest integral volume of 5353 bohr³. Tetra-lithium-1 has a larger electron number and a smaller integral volume, indicating that its excess electron should be more localized relative to the aforementioned three molecules.

![Fig. 1 Optimized structures of 1, octafluorine-1, octamethoxy-1, and tetra-lithium-1.](image)

| Chemical models | AIM | ELF |
|-----------------|-----|-----|
|                 | CP  | \( \rho(r_c) \) | \( \nabla^2 \rho(r_c) \) | N(pop) | CP | N(Ω) | Basin volume |
| 1               | NNA | 0.006 | −0.004 | 0.47 | C(NNA) | 0.91 | 8763 |
| Octafluorine-1  | NNA | 0.007 | −0.004 | 0.45 | C(NNA) | 0.91 | 7976 |
| Octamethoxy-1   | NNA | 0.005 | −0.002 | 0.47 | C(NNA) | 0.91 | 13 079 |
| Tetra-lithium-1 | NNA | 0.010 | −0.009 | 0.74 | C(NNA) | 1.02 | 5353 |
3.2 Nonlinear optical properties

The NLO properties of \(1\), octafluorine-\(1\) and octamethoxy-\(1\) have been calculated at the CAM-B3LYP level of theory, and the results are collected in Table 2. Unlike the electron population, the first hyperpolarizabilities \(\beta_0\) are very significantly affected by the substituents. When eight electron-withdrawing substituents \((-F)\) is used, the \(\beta_0\) value decreases from 11 876 au (1) to 8977 au (octafluorine-1). However, when eight electron-donating substituents \((-OCH_3)\) is used, the \(\beta_0\) value is considerably increased from 11 876 au (1) to 20 562 au (octamethoxy-1). For systems with electride or alkalide characteristics, a two-level expression is often used to explain the \(\beta_0\) value.\(^{79,80}\)

| Molecules         | \(\beta_0\) | \(\alpha_0\) | Transition | \(\Delta\epsilon\) | \(f_0\)  | Configuration | \(C_i\) | HOMO  | VIE   | \(q(Li^+)\) |
|-------------------|--------------|--------------|------------|-------------------|---------|---------------|---------|-------|-------|------------|
| Octafluorine-1    | 8977         | 383          | \(S_0 \rightarrow S_2\) | 1.603             | 0.157   | H \(\rightarrow\) L+1 | 0.86   | -4.01 | 4.38  | (4.26) 0.481 (0.361) |
| 1                 | 11 876       | 390          | \(S_0 \rightarrow S_2\) | 1.599             | 0.169   | H \(\rightarrow\) L+1 | -0.45  | -3.35 | 3.71  | (3.62) 0.477 (0.372) |
| Octamethoxy-1     | 20 562       | 581          | \(S_0 \rightarrow S_1\) | 1.369             | 0.152   | H \(\rightarrow\) L   | 0.70   | -3.03 | 3.32  | (3.23) 0.491 (0.356) |
| Tetra-lithium-1   | 5097         | 328          | \(S_0 \rightarrow S_1\) | 2.571             | 0.163   | H \(\rightarrow\) L   | 0.91   | -5.48 | 5.91  | (5.77) 0.915 (0.921) |

\(^a\) The values outside parentheses were calculated at the CAM-B3LYP/6-31+g(d)/6-311++G(3df,3pd) level of theory. The values within parentheses were obtained at the MP2/6-31+g(d)/6-311++g(3df,3pd) level of theory.

Fig. 2 (a) HOMO (isovalue = 0.02 au). (b) Non-nuclear attractor (NNA). (c) Two-dimensional (2D) plot of \(\nabla^2 \rho(r)\). (d) ELF isosurface image at a 0.800 value. (e) The colour-filled map of ELF for tetra-lithium-1.
\[ \beta_0 \propto \frac{\Delta \mu f_0}{\Delta E^3} \]

where \(\Delta E\), \(f_0\) and \(\Delta \mu\) are transition energy, oscillator strength and the difference in dipole moments between the ground state and crucial excited state. In the two-level expression, the third power of the transition energy (\(\Delta E\)) is inversely proportional to the \(\beta_0\) value; thus, the \(\Delta E\) value is the decisive factor in the first hyperpolarizability. For the polarizabilities, from Table 2, the order of the \(\alpha_0\) values is 383 (octafluorine-1) < 390 (1) < 581 au (octamethoxy-1). The properties of the related excited state are calculated using the time-dependent CAM-B3LYP method, and the results are listed in Table 2. From Table 2, the order of \(\Delta E\) is 1.369 (octamethoxy-1) < 1.599 (1) < 1.603 eV (octafluorine-1). The \(\Delta E\) value is the difference in energy between the ground state and the excited state with a large oscillator. After Franck-Condon excitation, octafluorine-1, 1, and octamethoxy-1 are excited into \(S_2\), \(S_2^*\), and \(S_1^*\), respectively. All the electronic configurations in these excited states involved the excitation of the highest occupied molecular orbital (HOMO), which is the orbital containing the excess electron. When electron-donating substituents (–OCH3) are used, the energy level of the HOMO is decreased from –3.35 (1) to –3.03 eV (octamethoxy-1), which will lead to a small \(\Delta E\). When electron-withdrawing substituents (–F) are used, the energy level of the HOMO is decreased from –3.35 (1) to –4.01 eV (octafluorine-1), which leads to a large \(\Delta E\). Moreover, the order of \(\text{VIE}\) is octafluorine-1 (4.38 eV) > 1 (3.71 eV) > octamethoxy-1 (3.32 eV), consistent with the order of the HOMO energy levels. From the above analysis, we can conclude that the electron-withdrawing or electron-donating substituents cannot affect the electrode characteristics but significantly affect the NLO behaviour.

Of the above three molecules, tetra-lithium-1 has the smallest \(\beta_0\) and \(\alpha_0\) value of 5097 and 328 au and the largest transition energy of 2.571 eV. The electronic configuration of tetra-lithium-1 is the HOMO → LUMO excitation. Due to lithiation, the energy level of the HOMO is considerably decreased from –3.35 eV (1) to –5.48 eV (tetra-lithium-1), leading to a large \(\Delta E\). As usual, the \(\text{VIE}\) value of the molecular electrode is smaller than that of alkali atoms, ranging from 5.4 to 3.9 eV (Li–Cs),39,40 and thus, sometimes, these molecules are called superalkalides. For example, the \(\text{VIE}\) values of octafluorine-1, 1, and octamethoxy-1 lie between 3.32 and 4.38 eV, which is less than that of Li. However, tetra-lithium-1 has a very large \(\text{VIE}\) value of 5.91 eV at the CAM-B3LYP level of theory, which is greater than that of Li. From the above analysis, the following relationship is obtained: the more obvious the electrode characteristic (the electron population), the larger the \(\text{VIE}\) value is. The large \(\text{VIE}\) value of tetra-lithium-1 may be attributed to the orbital of excess electron lowered by lithiation.

4. Conclusion

The effects of multiple substitutions on the electrode characteristics and the second-order NLO properties (\(\beta_0\)) of Li@calix[4]pyrrole (1) and its analogues (octafluorine-1, octamethoxy-1 and tetra-lithium-1) were theoretically studied at the CAM-B3LYP and MP2 levels of theory. Some conclusions are summarized as follows:

1. Electron-donating and electron-withdrawing groups can effectively increase and decrease the first hyperpolarizability (\(\beta_0\)), respectively, but do not damage the electrode characteristics (electron population). For example, when all the H atoms at the \(\beta\)-positions of 1 were substituted by –F groups, the \(\beta_0\) value was decreased from 11 876 (1) to 8977 au (octafluorine-1), but when all the H atoms at the \(\beta\)-positions of 1 were substituted by –OCH3 groups, the \(\beta_0\) value was substantially increased from 11 876 (1) to 20 562 au (octamethoxy-1). However, the electrode characteristics were not changed, resulting in a nearly identical electron population (approximately 0.47 e).

2. A different molecular electrode, tetra-lithium-1, was successfully theoretically designed by lithiation in which four H atoms on N atoms were substituted by four Li atoms. Due to the large electron numbers of 0.74 and 1.02 e at the NNA and ELF basins, respectively, tetra-lithium-1 may be the first formal molecular electrode with one isolated excess electron serving as an anion, except for Li3@TCNQ and Na3@TCNQ, in which the electrode characteristics are considered to derive from Li3 and Na3. Furthermore, the vertical ionization energy of tetra-lithium-1 was 5.91 eV, which is larger than those (5.4–3.9 eV) of alkali atoms from Li to Cs, indicating its higher stability. In addition, enhancement of the electrode characteristics was accompanied by a decrease in the NLO properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is financially supported by the China Postdoctoral Science Foundation (2015MS71355).

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