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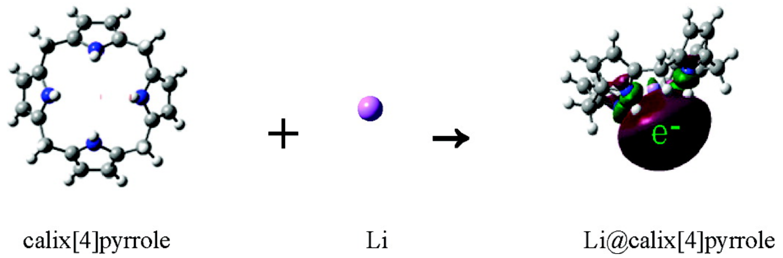

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The Structure and the Large Nonlinear Optical Properties of Li@Calix[4]pyrrole

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Abstract: A new compound with electride characteristics, Li@calix[4]pyrrole, is designed in theory. The Li atom in Li@calix[4]pyrrole is ionized to form a cation and an excess electron anion. Its structure with C_{4v} symmetry resembles a cup-like shape. It may be a stable organic electride at room temperature. The first hyperpolarizability of the cup-like electride molecule is first investigated by the DFT (B3LYP) method. The result shows that this electride molecule has a considerably large first hyperpolarizability with $\beta_0 = 7326$ au (63.3×10^{-30} esu), while the β_0 value of the related calix[4]pyrrole system is only 390 au. Obviously, the Li atom doped in calix[4]pyrrole brings a dramatic change to the electronic structure, so that the first hyperpolarizability of Li@calix[4]pyrrole is almost 20 times larger than that of calix[4]pyrrole. We find that the excess electron from the Li atom plays an important role in the large first hyperpolarizability of Li@calix[4]pyrrole. The present investigation reveals a new idea and different means for designing and synthesizing high-performance NLO materials.

Introduction

In the last two decades, a great deal of work has been carried out to study the nonlinear optical properties (NLO) of many different types of NLO materials.[1−8] Much effort has been devoted to find important influencing factors that can lead to a dramatic increase in the first hyperpolarizability and to design some new types of NLO materials. In our previous work,[9,10] it has already demonstrated that systems with solvated excess electrons, such as $(FH)_2\{e\}(HF)$ and $(H_2O)_3\{e\}$, possess a large value of the first hyperpolarizability ($\beta_0 \approx 10^7$ au). In those two models, we find that the large value of the first hyperpolarizability is mainly contributed from the loosely bound excess electron. On the basis of those findings, we focus on the compounds with loosely bound excess electrons synthesized in experiment. As a result, electrides studied by the Dye group become our focus of attention.

Electrides are a novel kind of ionic salts in which anionic sites are occupied solely by electrons.[11,12] Commonly, electrides are composed of alkali ions intercalated within cages formed from one or two organic complexants and trapped electrons. These organic complexants may be a crown ether or a cryptand.[13] $Cs^+(15\text{-crown-}5)_2e^-$ is a typical organic electride.[13] The key to the formation of organic electrides is that alkali atoms are captured and ionized by complexants to form cations and excess electrons. However, these conventional organic electrides are thermally unstable at room temperature. The instability is due to reductive cleavage of the C−O bond in the crown ether or cryptand complexant used to encapsulate the alkali cation and the counterion, *e*.[14] Therefore, in his recent paper, Dye[13] proposed a new way to search for thermally stable organic electrides. Contrary to inorganic electrides, the important strategy for organic electrides is to use organic complexants that resist reduction by the trapped electrons. Considering thermal decomposition of oxygen-based complexants by rupture of the C−O bonds, the substitution of nitrogen for oxygen imparts greater stability. It is worth mentioning that the room temperature stable alkalides, including the excess electrons, $K^+(aza222)Na^-$ and $K^+(aza222)K^-$, with the nitrogen analogue of a cryptand, have been reported.[14] On the basis of this evidence, in our present work, we theoretically design a new

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(1) Eaton, D. F. *Science* **1991**, *253*, 281−287.

(2) *Nonlinear Optical Properties of Organic Molecules and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1984.

(3) Cheng, W. D.; Xiang, K. H.; Pandey, R.; Pernisz, U. C. *J. Phys. Chem. B* **2000**, *104*, 6737−6742.

(4) Ichida, M.; Sohda, T.; Nakamura, A. *J. Phys. Chem. B* **2000**, *104*, 7082−7084.

(5) Hold, K.; Pawlowski, F.; Jørgensen, P.; Hättig, C. *J. Chem. Phys.* **2003**, *118*, 1292−1300.

(6) Hättig, C.; Larsen, H.; Olsen, J.; Jørgensen, P.; Koch, H.; Femández, B.; Rizzo, A. *J. Chem. Phys.* **1999**, *111*, 10099−10107.

(7) Horikoshi, R.; Nambu, C.; Mochida, T. *Inorg. Chem.* **2003**, *42*, 6868−6875.

(8) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586−2617.

(9) Li, Y.; Li, Z. R.; Wu, D.; Li, R. Y.; Hao, X. Y.; Sun, C. C. *J. Phys. Chem. B* **2004**, *108*, 3145−3148.

(10) Chen, W.; Li, Z. R.; Wu, D.; Gu, F. L.; Hao, X. Y.; Wang, B. Q.; Li, R. J.; Sun, C. C. *J. Chem. Phys.* **2004**, *121*, 10489−10494.

(11) Dye, J. L. *Inorg. Chem.* **1997**, *36*, 3816−3826.

(12) Ichimura, A. S.; Dye, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 1170−1171.

(13) Dye, J. L. *Science* **2003**, *301*, 607−608.

(14) Kim, J.; Ichimura, A. S.; Huang, R. H.; Redko, M.; Phillips, R. C.; Jackson, J. E.; Dye, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10666−10667.

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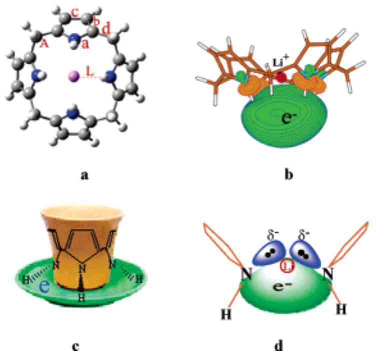

Figure 1. (a) The structure of Li@calix[4]pyrrole. (b) The HOMO of Li@calix[4]pyrrole. (c) An analogue of Li@calix[4]pyrrole; the cup resembles the framework of Li@calix[4]pyrrole, and the green saucer below resembles the excess electron. (d) The mechanism causing the excess electron; the red circle is the Li cation, the blue part represents the lone pairs of four N atoms, and the green part represents the excess electron, which is formed through the four lone pairs pushing out the 2s electron of the Li atom.

class of organic electrides, in which a calix[4]pyrrole with a C−N bond acts as a complexant to replace 15-crown-5, and the alkali Li atom is intercalated in the calix[4]pyrrole. The geometric structure of Li@calix[4]pyrrole is shown in Figure 1a.

Calix[4]pyrroles were first reported in the 1880s[15] and were treated as anion binding agents from then on.[16−19] Similar to calix[4]arenes, calix[4]pyrroles have four different conformations because of rotations around the interpyrrole bonds. The four conformations are 1,3-alternate, 1,2-alternate, partial cone, and cone conformations.[19] Among them, the cone conformation of calix[4]pyrrole is the most appropriate as a complexant in our design.

Different from a crown ether "sandwich" structure,[13] in our design, one Li atom is intercalated into one calix[4]pyrrole to form the cup-like Li@calix[4]pyrrole (see Figure 1a). The highest occupied molecular orbital (HOMO) of Li@calix[4]pyrrole is depicted in Figure 1b. Obviously, we find that, under the action of four N atoms, the s valence electron of the Li atom overflows from the bottom of the cup to become an excess electron. Consequently, Li@calix[4]pyrrole has the electride characteristics and can be expressed as $\mathrm{Li^+(calix[4]pyrrole)e^-}$. We expect that, in experiment, the strategy for the room temperature stable alkalides developed by the Dye group[14] may provide a feasible way to synthesize this Li@calix[4]pyrrole complex.

Electrides are special compounds with excess electrons. In our previous work, it has been reported that the prototype, $\mathrm{(HCN)}_n\mathrm{Li}$, with electride characteristics has quite large NLO responses.[20] In addition, another system containing the excess electron, $\mathrm{AdzH^+Na^-}$, also has been reported to have a considerably large first hyperpolarizability.[21] Therefore, it is expected that the excess electron in $\mathrm{Li^+(calix[4]pyrrole)e^-}$ can also cause large NLO responses.

Our investigation aims at predicting the structure and the large first hyperpolarizability of an organic electride Li@calix[4]pyrrole and providing possible ways to design new NLO materials in experiment. In this paper, the geometry structure, the Raman spectrum, and the electronic spectrum of Li@calix[4]pyrrole are presented. It is found that the very large first hyperpolarizability of Li@calix[4]pyrrole is mainly due to the excess electron. As we expect, this work may encourage further synthetic and chemical/physical characterization in organic electrides.

Methods

The total energy of a molecular system in the presence of a homogeneous electric field can be expressed as:[22]

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \ldots \qquad (1)$$

where E^0 is the molecular total energy without the electric field, and F_α is the electric field component along the α direction; μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the dipole, polarizability, and the first hyperpolarizability, respectively.

For a molecule with C_{4v} structure, the total dipole component is simply given by

$$\mu_0 = \mu_Z \qquad (2)$$

For the mean and the anisotropy of the dipole polarizability, we have

$$\alpha = \frac{1}{3}(2\alpha_{XX} + \alpha_{ZZ}) \qquad (3)$$

$$\Delta\alpha = \alpha_{ZZ} - \alpha_{XX} \qquad (4)$$

The first hyperpolarizability is defined as

$$\beta_0 = \beta_Z = \frac{3}{5}(2\beta_{ZXX} + \beta_{ZZZ}) \qquad (5)$$

The structure and the frequencies of the Li@calix[4]pyrrole are calculated by the density functional theory (DFT/B3LYP, the nonlocal correlation provided by the Lee−Yang−Parr expression) with the 6-31G basis set. The (hyper)polarizabilities of the Li@calix[4]pyrrole are calculated by the B3LYP method. In this calculation, the 6-311++G basis set is employed for the calix[4]pyrrole and the 6-311++G(3df,3pd) basis set for the alkali Li atom. The vertical ionization energies (VIE) are evaluated at the same level of the theory.

A widely used alternative procedure is the counterpoise (CP) method[23] to determine the contribution of the ionized Li atom to the polarizability and first hyperpolarizability in Li@calix[4]pyrrole. These contributions are defined as

$$\alpha(\mathrm{Li}^+\cdots e) = \alpha(X\mathrm{Li}) - \alpha(X) \qquad (6)$$

$$\beta(Li^+\cdots e) = \beta(X\mathrm{Li}) - \beta(X) \qquad (7)$$

where X is calix[4]pyrrole and $\alpha(X)$ is the mean dipole polarizability of the X moiety in the presence of the ghost orbitals of the Li atom. $\beta(X)$ is defined in a similar manner. Similarly, contributions of the excess electron to the polarizability and first hyperpolarizability of Li@calix[4]pyrrole are defined as:

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(15) Baeyer, A. *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 2184−2196.

(16) Anzenbacher, P., Jr.; Try, A. C.; Miyaji, H.; Jursíková, K.; Lynch, V. M.; Marquez, M.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 10268−10272.

(17) Miyaji, H.; Sato, W.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1777−1780.

(18) Blas, J. R.; Marquez, M.; Sessler, J. L.; Luque, F. J.; Orozco, M. *J. Am. Chem. Soc.* **2002**, *124*, 12796−12805.

(19) Wu, Y. D.; Wang, D. F.; Sessler, J. L. *J. Org. Chem.* **2001**, *66*, 3739−3746.

(20) Chen, W.; Li, Z. R.; Wu, D.; Li, R. Y.; Sun, C. C. *J. Phys. Chem. B* **2005**, *109*, 601−608.

(21) Chen, W.; Li, Z. R. Wu, D.; Li, Y.; Sun, C. C. *J. Phys. Chem. A* **2005**, *109*, 2920−2924.

(22) (a) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107−142. (b) Mclean, A. D.; Yoshimine, M. *J. Chem. Phys.* **1967**, *47*, 1927−1935.

(23) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553−566.

$$\alpha(e) = \alpha(X\text{Li}) - \alpha(X\text{Li}^+) \tag{8}$$

$$\beta(e) = \beta(X\text{Li}) - \beta(X\text{Li}^+) \tag{9}$$

All of the calculations in this work were carried out by using the GAUSSIAN 03 program package.[24]

Results and Discussions

A. Geometry of Stationary Points. The optimized structure with all real frequencies of the Li@calix[4]pyrrole was obtained at the B3LYP/6-31G level. In this step, four conformations of the calix[4]pyrrole (1,3-alternate, 1,2-alternate, partial cone, and cone conformations) are all considered. When a Li atom is intercalated into the calix[4]pyrrole, however, three other conformations are easily changed to the cone conformation. Finally, the stable cone conformation of Li@calix[4]pyrrole is obtained, as shown in Figure 1a.

The Li@calix[4]pyrrole with C_{4v} symmetry resembles a cup-like shape. This cup-like molecule is 3.261 Å in height. The diameters of its higher rim and lower rim are 8.577 and 4.073Å, respectively. In this structure, the four N atoms of calix[4]pyrrole are in the same plane, and the Li atom is located along the principle C_4 axis. The dihedral Li−N−N−N is only −2.9°, which indicates that the Li atom is almost located in the plane of four N atoms. Its main geometrical parameters are listed in Table 1. The Raman spectra of Li@calix[4]pyrrole and calix[4]pyrrole calculated at the B3LYP/6-31G level are presented in Figure 2. In the Raman spectrum of calix[4]pyrrole, the peaks with relatively higher intensity lie at 2988, 3285, 1552, 3107, 3267, and 3689 cm^{-1}, corresponding to the characteristic vibration modes of calix[4]pyrrole itself. The intensities of these peaks are in the region below 600 au. While in the Raman spectrum of Li@calix[4]pyrrole, the peaks with high intensity are the peaks at 3240, 746, 3228, 3294, and 3001 cm^{-1}, their intensities are in the region over 1000 au. Among these peaks, the highest peak at 3240 cm^{-1} is assigned as the alternately stretching vibration mode of four N−H bonds. Other peaks at 3228, 3294, and 3001 cm^{-1} correspond to the vibration modes of the calix[4]pyrrole framework. It is noticeable that the peak at 746 cm^{-1} is assigned as the synchronously bending vibration mode of four N−H bonds toward the Li atom, which is related to the Li atom. By inspecting the Raman spectrum of calix[4]pyrrole, we find that the vibration mode of the peak at 3689 cm^{-1} is the same as that of the peak at 3294 cm^{-1} in the Raman spectrum of Li@calix[4]pyrrole, corresponding to the simultaneously stretching vibration mode of four N−H bonds. Furthermore, for calix[4]pyrrole, there is a peak at 3682 cm^{-1}, which has the same vibration mode as the peak at 3240 cm^{-1} (the highest peak) in the Raman spectrum of Li@calix[4]pyrrole. The Raman intensity of the peak at 3682 cm^{-1} (2.5 au) is too weak to be detected in the Raman spectrum of calix[4]pyrrole.

Comparing two Raman spectra, we find that the intercalation of the Li atom causes some significant changes. First, it causes an increase in Raman intensity of the corresponding vibration mode. The Raman intensities of the peaks are in the region below 600 au in the spectrum of calix[4]pyrrole, whereas the intensities of the higher peaks are in the range of 1000−8000 au in Li@calix[4]pyrrole. Especially, the intensity of the alternately stretching vibration mode of four N−H bonds is 2.5 au for calix[4]pyrrole, while its intensity increases sharply to the value of 7012 au (3240 cm^{-1}) in the Raman spectrum of Li@calix[4]pyrrole. Second, it causes a significant red shift. For the peak corresponding to the alternately stretching vibration mode of four N−H bonds, the red shift is 442 cm^{-1} from 3682 to 3240 cm^{-1}. For the peak corresponding to the simultaneously stretching vibration mode of four N−H bonds, the red shift is 315 cm^{-1} from 3689 to 3294 cm^{-1}. Third, it causes a new peak at 746 cm^{-1} in the Raman spectrum of Li@calix[4]pyrrole. These characteristics can be used to identify the Li@calix[4]pyrrole complex. Two vibration modes are depicted clearly in Figure 3, in which mode **a** corresponds to the peaks at 3240 and mode **b** corresponds to the peak at 746 cm^{-1} in the Raman spectrum of Li@calix[4]pyrrole.

Table 1. The Main Geometrical Parameters of Li@Calix[4]pyrrole

a[a]	1.409 Å	A[a]	113.654°
b[a]	1.377 Å	<LiNNN	−2.9°
c[a]	1.437 Å		
d[a]	1.505 Å		
L[a]	2.384 Å		
height of Li@calix[4]pyrrole			3.261 Å
diameter of its higher rim			8.577 Å
diameter of its lower rim			4.073 Å

[a] Corresponds to the labels in Figure 1a.

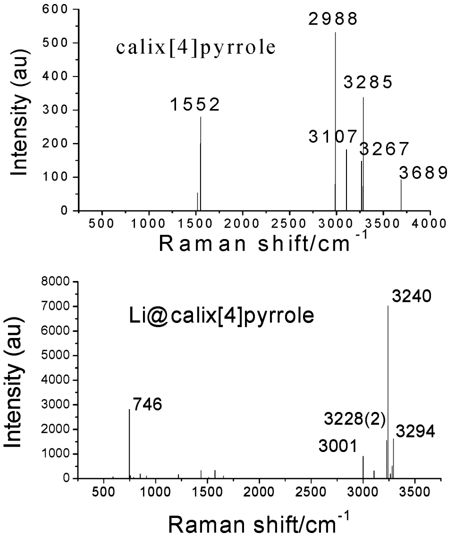
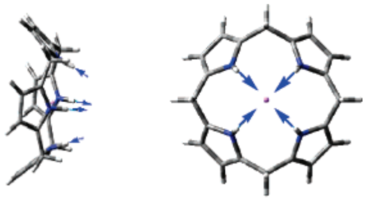


Figure 2. The Raman spectra of calix[4]pyrrole and Li@calix[4]pyrrole.



a (3240 cm^{-1}) **b** (746 cm^{-1})

Figure 3. Two vibration modes corresponding to two peaks with highest intensity in the Raman spectrum of Li@calix[4]pyrrole. (a) The alternately stretching vibration mode of four N−H bonds. (b) The synchronously bending vibration mode of four N−H bonds toward the Li atom.

B. The Electronic Properties of Li@Calix[4]pyrrole. The HOMO of Li@calix[4]pyrrole is composed of the diffuse s orbital of the Li atom, as shown in Figure 1b. It can be seen that the 2s electron of the Li atom is ejected out from the lower rim of calix[4]pyrrole, with an excess electron hanging on the

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(24) Frisch, et al. *GAUSSIAN 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

Table 2. The Dipole Moment μ (au), the Polarizability α (au), the Anisotropy $\Delta\alpha$ (au), the First Hyperpolarizability β_0 (au), the Transition Energy ΔE, and the Oscillator Strength f_0 for Li@Calix[4]pyrrole and Its Subunits

	Properties						
species	μ	α	$\Delta\alpha$	β_0	ΔE (eV)	f_0	VIE (eV)
calix[4]pyrrole	1.870	251	−75	390	6.016	0.4194	
Li@calix[4]pyrrole	−0.759	363	−116	7326	1.982	0.2054	4.16
Li^+@calix[4]pyrrole	1.830	244	−78	299			
$Li^+\cdots e$[a]		112		6936			
e[b]		119		7027			

[a] $Li^+\cdots e$ = Li@calix[4]pyrrole − calix[4]pyrrole. [b] e = Li@calix[4]pyrrole − Li^+@calix[4]pyrrole.

bottom of the cup. Vividly, the cone calix[4]pyrrole resembles a grown cup, and the excess electron is like a green saucer underneath (Figure 1c). Clearly, the excess electron results from the ionized Li atom by the action of the lone pairs of four N atoms. The vertical ionization energy (VIE) of Li@calix[4]pyrrole is 4.16 eV, which shows that the excess electron from the Li atom is comparatively stable.

In our previous work, we have shown that the excess electron can cause the large NLO responses for the systems, such as $(FH)_2\{e\}(HF)$,[9] $(H_2O)_3\{e\}$,[10] $(HCN)_nLi$,[20] and $AdzH^+Na^-$.[21] Thus, it is expected that the excess electron from the Li atom can also cause large NLO responses with Li@calix[4]pyrrole.

The (hyper)polarizabilities are calculated by numerical differentiation with an electric field magnitude of 0.001 au. The results are summarized in Table 2. For comparison purposes, the electronic properties of calix[4]pyrrole are also calculated and listed in Table 2.

From Table 2, it can be seen that, for the Li@calix[4]pyrrole, the electronic properties are significantly different from those of calix[4]pyrrole. The dipole moment of Li@calix[4]pyrrole is −0.759 au, but that of calix[4]pyrrole is 1.870 au. The α value of Li@calix[4]pyrrole (363 au) is 112 au larger than that of calix[4]pyrrole (251 au). For $\Delta\alpha$, the absolute value of Li@calix[4]pyrrole (−116 au) is 41 au larger than that of calix[4]pyrrole (−75 au).

Especially, we find that the static first hyperpolarizability of Li@calix[4]pyrrole is considerably large at 7326 au, while the first hyperpolarizability of calix[4]pyrrole is only 390 au. The former is almost 20 times larger than the latter. That is, the contribution from the Li subunit ($Li^+\cdots e$) in Li@calix[4]pyrrole accounts for 94.7%.

It is known that the β_0 value of the Li atom itself is naught. How does it cause the large first hyperpolarizability for Li@calix[4]pyrrole?

From a physics standpoint, the first hyperpolarizability β is expressed by the "sum-over-states" (SOS) expression in theory. From the complex SOS expression, Oudar and Chemla[25,26] established a simple link between β and a low-lying charge-transfer transition through the two-level model. For the static case ($\omega = 0.0$), the following two-level expression is employed to estimate β_0 in the literature:[26,27]

$$\beta_0 = (3/2)\Delta\mu \times f_0/\Delta E^3 \tag{10}$$

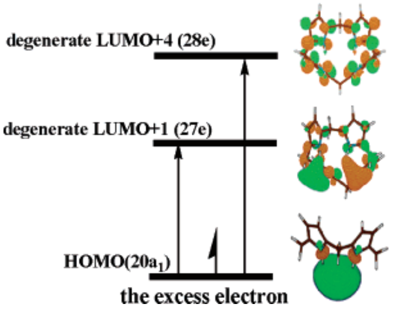

Figure 4. The crucial excited state of Li@calix[4]pyrrole.

where ΔE, f_0, and $\Delta\mu$ are the transition energy, oscillator strength, and the difference of the dipole moment between the ground state and the crucial excited state, respectively. In the two-level expression, the third power of the transition energy is inversely proportional to the β_0 value. So, for a noncentrosymmetric molecule like Li@calix[4]pyrrole, the low transition energy ($\ll$1 au) is the decisive factor in the large first hyperpolarizability.

The TD−DFT calculations were carried out to obtain the crucial excited states of Li@calix[4]pyrrole and calix[4]pyrrole. The transition energies (ΔE) and the oscillator strengths (f_0) of the crucial excited states for two structures are also listed in Table 2. The ΔE value of calix[4]pyrrole is very large (6.016 eV), whereas it is only 1.982 eV for Li@calix[4]pyrrole. The difference in the transition energies between calix[4]pyrrole and Li@calix[4]pyrrole is more than a factor of 3. From eq 10, it generates a 27-fold increase in β_0, regardless of all other factors. Clearly, such small transition energy is a decisive factor and leads to a considerably large first hyperpolarizability of Li@calix[4]pyrrole.

We find that such a small transition energy of the Li@calix[4]pyrrole is related to its structure. Due to the higher symmetry of the Li@calix[4]pyrrole, the TD−DFT results show that its crucial excited state is composed of many components, in which the main components are the HOMO → LUMO + 1 and HOMO → LUMO + 4 transitions. The HOMO and the related unoccupied molecule orbitals are shown in Figure 4. Clearly, the electron invoked in the crucial excited state is in the HOMO, which is the diffuse s electron of the Li atom. As shown in Figure 1b, the s electron from the Li atom is in the diffuse orbital. Under the action of the lone pairs of four N atoms, the 2s electron of the Li atom is ejected out as the excess electron, and accordingly, the interaction between this electron and the Li core is greatly weakened. Figure 1d depicts this mechanism clearly. Finally, the Li@calix[4]pyrrole has a much lower excited energy in the crucial transition, which naturally results in a larger first hyperpolarizability.

To further exhibit the sole contribution of the excess electron to the (hyper)polarizability of Li@calix[4]pyrrole, the electronic properties of Li^+@calix[4]pyrrole are calculated and listed in Table 2. As shown in Table 2, the β_0 value of Li^+@calix[4]pyrrole is only 299 au, even smaller than that of calix[4]pyrrole (390 au). Clearly, the difference between Li@calix[4]pyrrole and Li^+@calix[4]pyrrole is the sole contribution of the excess electron. This contribution, $\beta(e)$, is 7027 au, accounting for 96% of the total first hyperpolarizability of the Li@calix[4]pyrrole molecule. It indicates that the large first hyperpolarizability of Li@calix[4]pyrrole almost comes from the excess electron.

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(25) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664−2668.
(26) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446−457.
(27) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242.

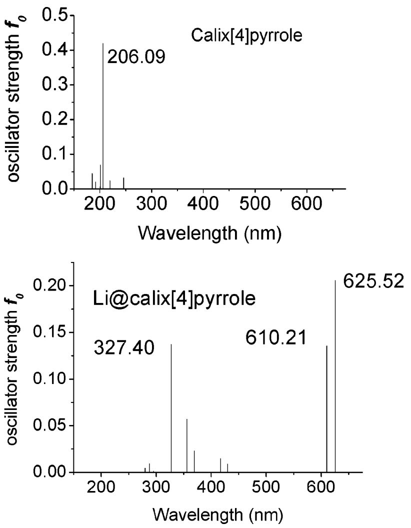

Figure 5. The UV−vis linear absorption spectra of calix[4]pyrrole and Li@calix[4]pyrrole.

Similarly, the excess electron still causes an increase in the polarizability, but to a lesser extent (33%) compared to the contribution (96%) of the first hyperpolarizability. This is because, in the two-level expression, the polarizability is inversely proportional to the transition energy, disregarding other factors.[28]

The calculated linear absorption spectra of calix[4]pyrrole and Li@calix[4]pyrrole are shown in Figure 5. There exists a dramatic difference between these two spectra. For calix[4]-pyrrole, the major absorption peak is at 206.09 nm in the UV, while in the Li@calix[4]pyrrole spectrum, the strongest peak at 625.52 nm is in the visible region, which corresponds to the transition of the excess electron (see Figure 4). This is consistent with the experimental observation in the emission spectrum of Na^+(C222)Na^-, where the low-energy emission is presumed to be from the trapped electrons.[29] In addition, for the Li@calix-[4]pyrrole, there are two additional peaks with large oscillator strengths at 610.20 and 327.40 nm, also corresponding to the transitions of the excess electron (the main HOMO → LUMO + 2 transition for 610.21 nm, the main HOMO → LUMO + 9 transition for 327.40 nm). These characteristics can be related to the color of "solvated electrons" and should be possible for experimental verification.

Conventionally, the NLO properties of traditional organic NLO materials are improved through the increase of the conjugation path and the choice of donors/acceptors. For metal−ligand NLO materials, their NLO properties are improved through the introduction of the transition metals. Those methods aim at enhancing the degree of charge transfer to decrease the excited energy and leading to an increase in the first hyperpolarizability. Different from those methods, in this paper, we present a new idea and method to decrease the excited energy and to improve the first hyperpolarizability of NLO materials. Our new idea and method are to produce the excess electron through the interaction between the alkali atom and the polar molecule in electrides. For example, the experiment shows that the macroscopic aligned film of calix[4]arenes owns the higher NLO properties (about 31×10^{-30} esu).[30] If a Li atom is inserted into these calix-type compounds to form the electride films, their NLO properties are likely to be increased significantly, as one can expect.

Conclusions

We designed a new organic electride compound in theory, Li@calix[4]pyrrole. It may be stable at room temperature. The structure with C_{4v} symmetry resembles a cup-like shape. In the cup-like Li@calix[4]pyrrole, the Li atom is ionized to form a cation and an excess electron anion. The excess electron cloud is like a saucer underneath the cup. We also find that the introduction of the Li atom has some important effects on the Raman spectrum, the electronic spectrum, and the electronic properties of Li@calix[4]pyrrole besides its structure.

The calculated results confirm our prediction that this Li@calix[4]pyrrole electride has the considerably large NLO response, $\beta_0 = 7326$ au, which is almost 20 times larger than that of calix[4]pyrrole without electride characteristics. Its large first hyperpolarizability almost comes from the excess electron saucer underneath the cup.

A new designing idea is proposed where the first hyperpolarizability can be greatly increased by the alkali atom inserting into the polar cryptand molecule to form an electride. One of its applications can be expected that the NLO responses of the calix[4]pyrrole film are enhanced through the alkali atom that is inserted in the calix[4]pyrrole molecule. It is our expectation that a new type of NLO material will appear in experiment soon.

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Supporting Information Available: Complete ref 24. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) *Handbook of Advanced Electronic and Photonic Materials and Devices: Nonlinear Optical Materials*; Nalwa, H. S., Ed.; A Harcourt Science and Technology Company: San Diego, CA, 2001; Vol. 9, p 69.

(29) Kuo C.-T.; Dye, J. L.; Pratt, W. P., Jr. *J. Phys. Chem.* **1994**, *98*, 13575−13582.

(30) Kenis, P. J. A.; Noordman, O. F. J.; Schönherr, H.; Kerver, E. G.; Snellink-Ruël, B. H. M.; Van Hummel, G. J.; Harkema, S.; Van der Vorst, C. P. J. M.; Hare, J.; Picken, S. J.; Engbersen, J. F. J.; Van Hulst, N. F. G.; Vancso, J.; Reinhoudt, D. N. *Chem.*−*Eur. J.* **1998**, *4*, 1225−1234.