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Elongation 法を用いた高分子内過剰電子移動による非線形光学特性解析

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The design of novel materials with large nonlinear optical (NLO) responses is currently of great interest due to their potential applications in optical and electro-optical devices. Chen *et al* have theoretically designed and investigated NLO properties of series of single molecule systems with excess electron [1-3], which exhibit considerably large first hyperpolarizability. For example, for the system Li^{+}[calix[4]pyrrole]M^{-} [3], as shown in the Figure 1, the lone pairs of four N atoms of calix[4]pyrrole push out the 2s electron of the inner Li atom to form the excess electron and the electron is located in the diffuse *s* orbital. Its electron cloud enwraps the outside M atom and creates anion M^{-}. The excess electron plays an important role in increasing the first hyperpolarizability.

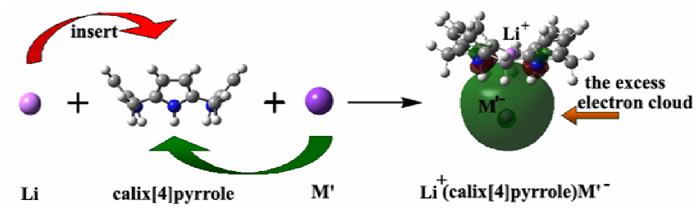

Figure 1

In the present work, a polymer $[Li^{+}$[calix[4]pyrrole]$Li^{-}]_n$ chain containing excess electrons has been theoretically devised for the first time. The NLO properties of the $[Li^{+}$[calix[4]pyrrole]$Li^{-}]_n$ chain are investigated by using elongation method. The elongation method for calculating electronic states of large systems was developed by Imamura et al [4, 5]. Recently, the elongation procedure was extended to include a perturbing static finite electric field **[**6**]** and used to determine static (hyper)polarizabilities of long-chain oligomers.

The structure of $[Li^{+}$[calix[4]pyrrole]$Li^{-}]_n$ chain is shown in Figure 2. By the elongation method, the static (hyper)polarizabilities of polymer are investigated at the HF/6-31G level under the applied electric field magnitude of 0.001 au. In the elongation calculations, the starting cluster consists of N=3 Li^{+}[calix[4]pyrrole]Li^{-}] units and elongated one by one up to N=15.

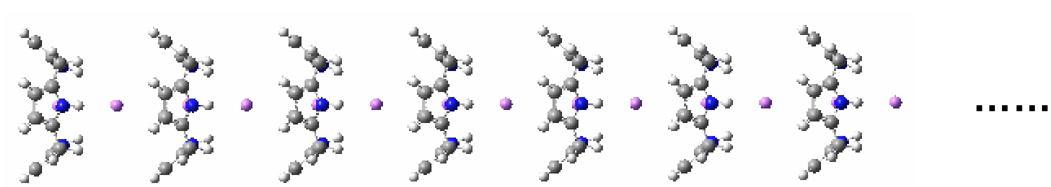

Figure 2. The structures of polymer $[Li^{+}$[calix[4]pyrrole]$Li^{-}]_n$

Plots of the α, |β|, γ and corresponding Δα, Δ|β|, Δγ ($\Delta P=P_N-P_{N-1}$, P is α, |β| or γ) versus chain length (N) are shown for $[Li^{+}$[calix[4]pyrrole]$Li^{-}]_n$ in Figure 3. It can be seen that the α, |β|, γ values are increased linearly with increasing N, and the Δα, Δ|β|, Δγ values are almost converged to constants with increasing N. By using the corresponding Δα and Δ|β| values of from N=4 to 15, the analogous curves of Δα and Δ|β| versus N are drawn, by which we can deduce that Δα and Δ|β| values are 501.23 and 19895.70 au, respectively, when N is infinite. Thus, the α and |β| of larger polymer can be estimated by a simple expression, $P_N=(N-15)\times\Delta P+P_{15}$. The $[Li^{+}$[calix[4]pyrrole]$Li^{-}]_n$ with N=15 has been shown to exist very large (hyper)polarizabilities to be α=7262.8 , $|\beta|$= 2.715 $\times 10^5$ and γ=1.523$\times 10^7$ au. Obviously, the $[Li^+[calix[4]pyrrole]Li^-]_n$ polymer owns considerable $|\beta|$ value, which indicates the possibility that the $[Li^+[calix[4]pyrrole]Li^-]_n$ polymer becomes potential high-performance NLO material.

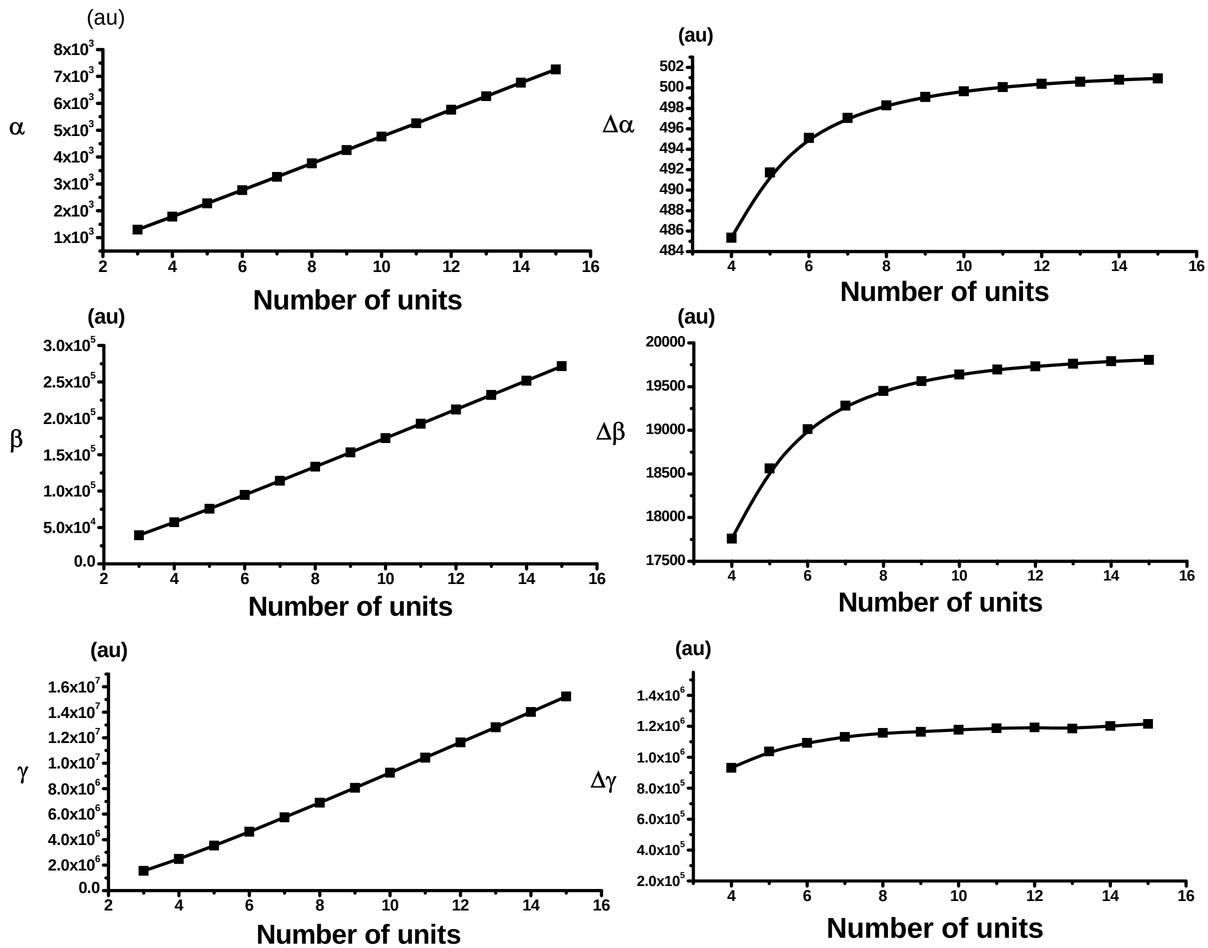

Figure 3. Dependence of (hyper)polarizabilities on the number of units, N.

References

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