

A theoretical investigation of one-dimensional lithium-bonded chain: enhanced first hyperpolarizability and little red-shift

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Abstract We present a theoretical investigation of the electric properties of two kinds of one-dimensional lithium bonded chains: $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$ ($n=1-8$). The resulting $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$ were found to exhibit enhanced first hyperpolarizabilities (β_0) with increasing n , and a slight change in the absorption maximum wavelength λ_{max} at the crucial transition. Comparing with $(\text{NC-Li})_n$, $(\text{NC-CC-Li})_n$ exhibited particularly drastically enhanced β_0 values due to clearly enhanced coupled oscillators and double-degenerated charge transitions. β_0 is known to be the microscopic origin of the second-order non-linear optical (NLO) property, and λ_{max} is an approximate measure of the transparency achievable, thus both are important indices of high-performance NLO molecules. Therefore, our investigations into one-dimensional lithium bond chains will be beneficial to understanding the relationship between β_0 and λ_{max} , thus aiding the design of one-dimensional NLO materials with excellent transparency-efficiency.

Keywords First hyperpolarizability · Lithium bond · Non-linear optical · Red-shift · Transparency-efficiency

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Introduction

One-dimensional π -conjugated systems [1–10] have been investigated extensively in second-order nonlinear optical (NLO) materials design, because large molecular hyperpolarizability, β , can be obtained by optimizing donor/acceptor moiety strengths and/or extending the π -conjugated path. However, there are some apparent drawbacks with one-dimensional structural compounds. First, the key problem is the transparency-efficiency tradeoff. According to the two-level model of Oudar and Chemla [11], the static first hyperpolarizability β_0 is proportional to oscillator strength for the single transition multiplied by the third power of the absorption maximum wavelength λ_{max}^3 , and λ_{max} is an approximate measure of the transparency achievable. Therefore, loss of transparency (the red-shift) is an unavoidable consequence of any increase in β [12]. Second, most one-dimensional D- π -A structural molecules are prone to form a centrosymmetric arrangement in the crystal due to dipole-dipole intermolecular interactions, which leads to no NLO response. Therefore, the question of how to achieve better enhancement of β_0 with little red-shift, and meanwhile avoid centrosymmetric arrangements, is important when developing high performance NLO materials.

Different strategies to limit the natural antiparallel dipolar interaction have been proposed, for example, the use of electric field poling [13]. Furthermore, significant NLO responses have also been observed in nondipolar octupolar molecules [14, 15], because the lack of a permanent dipole moment contributes to noncentrosymmetric arrangements. A third approach that can rule out of the formation of centrosymmetric arrangement is exploiting \wedge -shaped molecules [16–18] and helical/chiral compounds [19], owing to the large off-diagonal β -tensor component.

In recent years, the weak interaction of Li-bonds has attracted much attention, since Shigorin first suggested

their possible existence in 1959 [20]. Ault and Pimental [21] subsequently provided experimental proof for the existence of a lithium bond in $\text{H}_3\text{N}\cdots\text{LiX}$ ($X = \text{Cl}$ and Br) complexes. Currently, the Li-bond is being investigated in many fields [22]. Because Li-bonds are much stronger than the corresponding H-bonds [23, 24], it seems reasonable to expect a direct linking of molecules via Li-bond interactions, much like hydrogen-bond-directed linking [25]. More importantly, linking in this way can limit the formation of centrosymmetric arrangements. Thus, we expect that a Li-bond linking strategy might achieve the purpose of a large enhancement of β_0 with little red-shift.

Wu et al. [23] investigated the Li-bond dimer $(\text{NC-Li})_2$, which may be considered as the simplest one-dimensional Li-bond chain. However, they focused on the effect of Li-bond interactions on the first hyperpolarizability, and did not investigate the change rule of first hyperpolarizability with increasing n , or the absorption maximum wavelength in the crucial transition, both of which are important indices for bulk NLO materials with high transparency-efficiency. Therefore, investigating one-dimensional Li-bond chains $(\text{NC-Li})_n$ ($n=1-8$, where n is the number of the monomer NC-Li) is a meaningful project in our attempt to understand noncentrommetric arrangements and enhanced first hyperpolarizability with little red-shift.

To understand in depth the Li-bond chain effect on first hyperpolarizability, we also investigated one-dimensional Li-bond chains $(\text{NC-CC-Li})_n$, which have an excess of $-\text{C}\equiv\text{C}-$ units, compared with the structure of $(\text{NC-Li})_n$. Here, the NC-CC-Li monomer may be considered as the lithium salt of cyanoacetylene (NC-CC-H), which has been detected by spectroscopic methods [26, 27], and plays an important role in the prebiotic synthesis of amino acids, purines and pyrimidines [28].

Despite the enormous progress in research into one-dimensional π -conjugated systems, and Li-bond effect on first hyperpolarizability, few attempts have been made to utilize these systems for constructing one-dimensional Li-bond chains. Therefore, in this study, we have designed two kinds of one-dimensional Li-bond chains $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$ ($n=1-8$) theoretically. Our investigation found that the resulting $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$

exhibit enhanced β_0 with increasing n , and a slight change in the absorption maximum wavelength λ_{max} at the crucial transition. This is an important clue in the design of NLO materials, due to $\beta_0-\lambda_{\text{max}}$ relating to the transparency-efficiency of NLO materials. Compared with $(\text{NC-Li})_n$, $(\text{NC-CC-Li})_n$ exhibited particularly drastically enhanced β_0 values due to clearly enhanced coupled oscillators and double-degenerated charge transitions. Therefore, our investigation into one-dimensional Li-bond chains will be useful in the development of NLO materials.

Computational methods

Two kinds of one-dimensional Li-bond chains $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$ ($n=1-8$) with all real frequencies were obtained at the second-order Møller-Plesset (MP2) theory with 6-31+G(d) basis set. Wu et al. [29, 30] found by using the coupled-cluster CCSD(T) method with CP corrections [23] that the most favorable geometry of $\text{NC-Li}\cdots\text{NC-Li}$ was the linear structure ($C_{\infty V}$). Natural bond orbital (NBO) charges were calculated and are listed in Table S1 and S2 in the supplementary material. The intramolecular interaction energy (E_{int}) between $(\text{M})_1$ and $(\text{M})_{n-1}$ ($\text{M}=\text{NC-Li}$ or NC-CC-Li), was calculated at the MP2/6-31+G(d) level. We used the counterpoise (CP) [31] procedure to eliminate the basis set superposition error (BSSE) effect given by Eq. (1):

$$E_{\text{int}} = E_{(\text{M})_{n-1}}(X_{(\text{M})_n}) - E_{(\text{M})_n}(X_{(\text{M})_n}) - E_{\text{M}}(X_{(\text{M})_n}) \quad (1)$$

where the same basis set $X_{(\text{M})_n}$ was used for the subunit energy [$E_{(\text{M})_1}$ and $E_{(\text{M})_{n-1}}$] calculation as for the energy of $(\text{M})_n$ [$E_{(\text{M})_n}$] calculation.

The (hyper)polarizabilities of $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$ were calculated using the finite-field (FF) method at the MP2/6-31+G(d) level. Different electric fields were applied to test the hyperpolarizabilities of $(\text{NC-Li})_4$ and $(\text{NC-CC-Li})_4$. From Table S3 and S4 in the supplementary material, there is clearly a plateau for the hyperpolarizabilities when the applied electric field (AEF) ranges from 0.0005 to 0.0015 a.u. Hereby, an AEF of 0.0010 a.u. was thought most suitable in the calculation of the hyperpolarizabilities. The

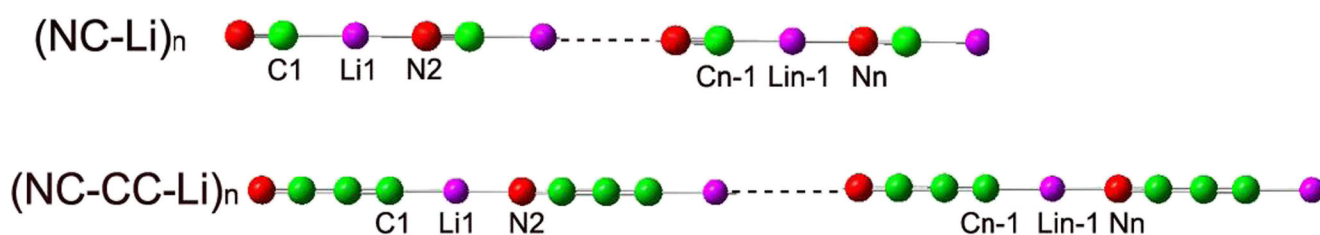


Fig 1 One-dimensional Li-bond structure

Table 1 C–Li and Li–N distances (Å) for (NC–CC–Li)_n

n	1	2	3	4	5	6	7	8
C ₁ -Li ₂	1.943	1.973	1.980	1.982	1.983	1.983	1.984	1.984
Li ₁ -N ₂		1.991	1.977	1.974	1.973	1.973	1.973	1.973
C ₂ -Li ₂		1.968	1.997	2.004	2.006	2.007	2.007	2.007
Li ₂ -N ₃			1.977	1.961	1.958	1.957	1.956	1.956
C ₃ -Li ₃			1.972	2.002	2.008	2.011	2.011	2.012
Li ₃ -N ₄				1.973	1.958	1.954	1.953	1.952
C ₄ -Li ₄				1.974	2.003	2.010	2.012	2.013
Li ₄ -N ₅					1.972	1.956	1.953	1.952
C ₅ -Li ₅					1.974	2.004	2.011	2.013
Li ₅ -N ₆						1.972	1.956	1.953
C ₆ -Li ₆						1.975	2.004	2.011
Li ₆ -N ₇							1.972	1.956
C ₇ -Li ₇							1.975	2.005
Li ₇ -N ₈								1.972
C ₈ -Li ₈								1.975

transition properties of (NC–Li)_n and (NC–CC–Li)_n, including the transition energy ΔE , oscillator strength f_0 and the difference in dipole moment $\Delta\mu$ between the ground and the excited state, were calculated from the time-dependent (TD)-DFT approach using LC-BLYP [32] functionals, which perform well for charge transfer excitations by the configuration interaction singles (CIS) method [33] (see Tables S5, S6).

In the FF method, when a molecule is subjected to a static electric field, the energy (E) of the molecule is expressed as:

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

where E^0 is the energy of the molecule in the absence of an electric field, μ is the component of the dipole moment vector, α is the linear polarizability tensor, β and γ are the first and second hyperpolarizability tensors, respectively, and i, j, and k label the x, y, and z components, respectively.

For a molecule, the average dipole moment (μ_0) and polarizability (α_0) are defined as follows:

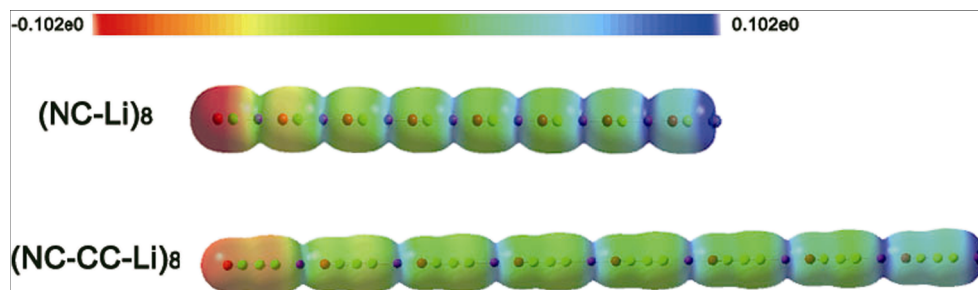
$$\mu_0 = \left(\mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{1/2} \quad (3)$$

$$\alpha_0 = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4)$$

Table 2 C–Li and Li–N distances (Å) for (NC–Li)_n

n	1	2	3	4	5	6	7	8
C ₁ -Li ₂	1.945	1.982	1.994	1.997	1.999	1.999	2.000	2.000
Li ₁ -N ₂		1.980	1.960	1.955	1.954	1.953	1.953	1.953
C ₂ -Li ₂		1.981	2.018	2.029	2.032	2.034	2.035	2.035
Li ₂ -N ₃			1.959	1.937	1.932	1.930	1.929	1.929
C ₃ -Li ₃			1.990	2.027	2.037	2.041	2.042	2.043
Li ₃ -N ₄				1.955	1.932	1.927	1.925	1.924
C ₄ -Li ₄				1.994	2.031	2.041	2.044	2.045
Li ₄ -N ₅					1.953	1.930	1.925	1.923
C ₅ -Li ₅					1.995	2.032	2.042	2.045
Li ₅ -N ₆						1.953	1.929	1.924
C ₆ -Li ₆						1.996	2.033	2.042
Li ₆ -N ₇							1.952	1.929
C ₇ -Li ₇							1.996	2.033
Li ₇ -N ₈								1.952
C ₈ -Li ₈								1.996

Fig 2 Computed electrostatic potentials as defined by the 0.004 au electronic density contour



The static first hyperpolarizability is noted as

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{1/2} \quad (5)$$

Where

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

All calculations were performed using the GAUSSIAN 09 program package [34].

Results and discussion

One dimensional Li-bond structures of (NC-CC-Li)_n and (NC-Li)_n

The unique characters of lithium bonds provide one-dimensional Li-bond chains (NC-CC-Li)_n and (NC-Li)_n, as depicted Fig. 1. For the Li-bond form of C_n-Li_n⋯N_{n+1}, striking changes in C_n-Li_n and Li_n-N_{n+1} distances are found in (NC-CC-Li)_n and (NC-Li)_n, respectively. From the C-Li and Li-N distances listed in Tables 1 and 2, respectively, we observed that: (1) the Li₁-N₂, Li₂-N₃, Li₃-N₄, Li₄-N₅, Li₅-N₆ and Li₆-N₇ distances become shortened with increasing *n*, but when *n* is large enough, distances become stable. For example, in (NC-CC-Li)_n, the Li₁-N₂ distances are 1.991 (*n*=2), 1.977 (*n*=3), 1.974 (*n*=4), 1.973 (*n*=5), 1.973 (*n*=6), 1.973 Å (*n*=7) and 1.973 Å (*n*=8). (2) The C₁-Li₁, C₂-Li₂, C₃-Li₃, C₄-Li₄, C₅-Li₅, C₆-Li₆ and C₇-Li₇ distances become longer with increasing *n*, but when *n* is large enough, their distances also reach stable values. For example, in (NC-CC-Li)_n, the C₁-Li₁ distances are 1.943 (*n*=1), 1.973 (*n*=2), 1.980 (*n*=3), 1.982 (*n*=4), 1.983 (*n*=5), 1.983 (*n*=6), 1.984 (*n*=7) and 1.984 Å (*n*=8). (3) In the same structure, C_n-Li_n with the longest bond distance and Li_n-N_{n+1} with the shortest bond distance are located in the middle of the one-dimensional structure. For example, in (NC-CC-Li)₈, C_n-Li_n with the longest bond

distance is C₄-Li₄ and Li_n-N_{n+1} with the shortest bond distance Li₄-N₅. (4) We found that changes in C-Li and Li-N distances in (NC-Li)_n are similar to those in (NC-CC-Li)_n. Furthermore, comparing (NC-Li)_n and (NC-CC-Li)_n, it was found that the distance of C₁-Li₁ in (NC-CC-Li)_n is shorter than that of C₁-Li₁ in (NC-Li)_n for the same value of *n*. However, we found that the Li₁-N₂ distance in (NC-CC-Li)_n is longer than that of corresponding Li₁-N₂ in (NC-Li)_n for the same *n*, which indicates that the Li₁-N₂ bond in (NC-Li)_n is stronger than the corresponding Li₁-N₂ bond in (NC-CC-Li)_n.

Because the interaction between NC-CC-Li and NC-Li monomers in the respective chains is electrostatic-driven [35, 36], we computed the electrostatic potentials to evaluate those chains. The isodensity plots of (NC-CC-Li)₈ and (NC-Li)₈ are shown in Fig. 2 (those of other chains are provided in Fig. S1 and S2). In addition, to demonstrate that Li-bonds are stronger than H-bonds, we also compared the electrostatic potentials on the molecular surfaces of NC-H with that of NC-Li, and of NC-CC-Li with NC-CC-H. Their isodensity plots are shown in Fig. 3. From Fig. 3, it can be found that Li-salts have a more negative electrostatic potential on the nitrogen atoms, and have a more positive electrostatic potential on the lithium atom. Furthermore, comparing the electrostatic potentials between (NC-CC-Li)₈ and

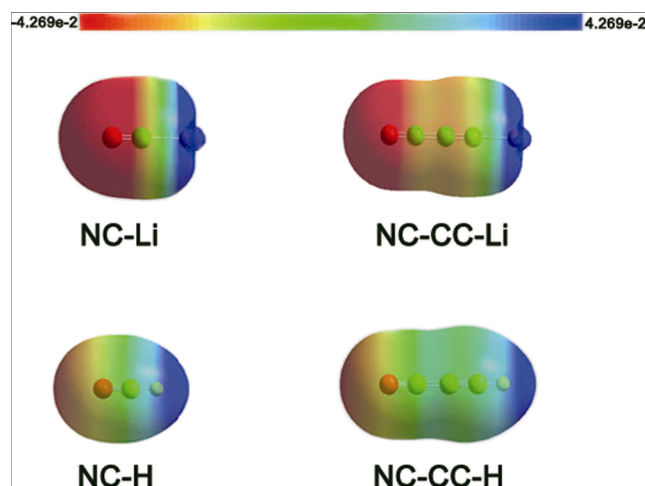


Fig 3 Comparison of the electrostatic potentials on NC-H with NC-Li, and NC-CC-Li with NC-CC-H (0.004 au electronic density contour)

Table 3 Interaction energies E_{int} (kcal mol⁻¹) and the HOMO–LUMO energy gaps (eV)

n	(NC-CC-Li) _n				(NC-Li) _n			
	E_{int}	HOMO	LUMO	H-L	E_{int}	HOMO	LUMO	H-L
1		-9.357	-0.476	8.881		-10.534	-0.624	9.909
2	26.178	-8.505	-1.256	7.249	31.493	-9.4482	-2.552	6.896
3	30.053	-8.247	-1.452	6.795	37.803	-9.0681	-1.601	7.466
4	31.091	-8.135	-1.542	6.593	39.599	-8.9052	-1.737	7.167
5	31.473	-8.075	-1.593	6.482	40.322	-8.7966	-1.819	6.977
6	31.568	-8.037	-1.626	6.411	40.672	-8.7423	-1.873	6.868
7	31.748	-8.010	-1.651	6.359	40.866	-8.71515	-1.927	6.787
8	31.803	-7.994	-1.667	6.327	40.984	-8.66085	-1.954	6.706

(NC-Li)₈, we found that the electrostatic potential on the nitrogen atom is more negative in (NC-Li)₈ than in (NC-CC-Li)₈, and that the electrostatic potential on the lithium atom is more positive in (NC-Li)₈ than in (NC-CC-Li)₈. In (NC-CC-Li)₈ and (NC-Li)₈, the positive electrostatic potentials on the lithium atoms become larger from the left to right; meanwhile, the negative electrostatic potentials on nitrogen atoms become larger from left to right. The same trend can be found in other chains (see Fig S1 and S2 in the supplementary material).

As mentioned above, the Li₁-N₂ Li-bond in (NC-Li)_n is stronger than corresponding Li₁-N₂ Li-bond in (NC-CC-Li)_n. Moreover, as shown in Tables 1 and 2, the Li₁-N₂ distances exhibit the longest Li-bonds in (NC-CC-Li)_n and (NC-Li)_n, respectively. Thus, Li₁-N₂ should be the weakest bond, with the most likely rupture zones being Li₁-N₂ bonds. Thus, we calculated the intramolecular interaction energy (E_{int}) between (M)₁ and (M)_{n-1} (M=NC-Li or NC-CC-Li) to evaluate the stabilities of those chains. As shown in Table 3, the E_{int} values of (NC-CC-Li)_n range from 26.17 to 31.8 kcal mol⁻¹, and those of (NC-Li)_n range from 31.493 to 40.984 kcal mol⁻¹, i.e., comparable to that of a moderate Li-bond. Moreover, the E_{int} of (NC-CC-Li)_n is smaller than that of the corresponding (NC-Li)_n (for the same n). From Table 1, it can be seen that E_{int} increases with increasing n , which hints that the larger the n , the more stable the Li-bond chains formed. Moreover, the

HOMO–LUMO energy gap is a useful quantity for examining chain stability. From Table 3, the HOMO–LUMO gaps of (NC-CC-Li)_n range from 6.327 to 8.881 eV, and those of (NC-Li)_n range from 6.706 to 9.909 eV, which are comparable to those of 7.58–10.58 eV for stable superalkali cations OM₃⁺ (M = Li, Na, K) [37]. Although the gaps decrease with increasing n , the difference-values become smaller and smaller. Therefore, we inferred that the gaps are still greater than 6 eV, even though n is large enough.

Large first hyperpolarizability and small red-shift

The dipole moments μ , polarizabilities α , and first hyperpolarizabilities β of (NC-CC-Li)_n and (NC-Li)_n are calculated and listed in Tables 4 and 5. From Tables 4 and 5, we found that the μ values of (NC-CC-Li)_n and (NC-Li)_n are quite large and increase with increasing n , while the increasing step of (NC-CC-Li)_n is 16 D, which is larger than that of (NC-Li)_n (12 D). Generally speaking, the magnitude of the dipole moment is determined by the charge distribution in each structure. Thus, this suggests that the charge distribution in (NC-CC-Li)_n, with a –C≡C– unit, is more favorable than that in (NC-Li)_n. We found that the change in α follows the same trend as the change in the results for μ , while the increasing step of (NC-CC-Li)_n is ~51 a.u., which is larger than that of (NC-Li)_n (~20 a.u.).

Table 4 First hyperpolarizabilities β_0 (a.u.) and their components, polarizabilities α (a.u.), dipole moments μ (Debye), absorptions maximum wavelength λ_{max} (nm), transition energy ΔE (eV) and oscillator strengths f for (NC-CC-Li)_n

n	β_{xxz}	β_{yyz}	β_{zzz}	β_z	β_0	α	μ	λ_{max}	ΔE	f
1	-136	-136	-381	-391	391	46	10.9	184.68	6.713	0.656
2	-201	-201	186	-425	425	94	27.704	174.65	7.099	1.589
3	-264	-264	291	-335	335	145	44.163	173.97	7.126	1.850
4	-325	-325	309	-204	204	196	60.828	174.85	7.090	3.220
5	-386	-386	502	-58	58	247	77.551	175.51	7.064	4.483
6	-447	-447	610	95	95	298	94.308	176.01	7.044	5.916
7	-508	-507	717	255	255	350	111.092	176.39	7.029	7.276
8	-568	-567	824	417	417	401	127.844	176.66	7.018	8.655

Table 5 First hyperpolarizabilities β_0 (a.u.) and their components, polarizabilities α (a.u.), dipole moments μ (Debye), absorptions maximum wavelength λ_{\max} (nm), transition energy ΔE (eV) and oscillator strengths f for (NC-Li) $_n$

n	β_{xxz}	β_{yyz}	β_{zzz}	β_z	β_0	α	μ	λ_{\max}	ΔE	f
1	69	69	169	184	184	21	9.8	158.50	7.079	0.159
2	83	83	205	222	222	41	22.1	175.17	7.078	0.047
3	99	99	226	254	254	61	34.7	170.32	7.230	0.051
4	113	112	240	279	279	82	47.5	169.78	7.303	0.051
5	127	127	249	302	302	103	60.4	169.56	7.312	0.052
6	89	89	261	327	327	124	73.3	169.44	7.317	0.052
7	155	155	266	345	345	144	86.2	169.38	7.320	0.052
8	169	168	274	366	366	165	99.0	169.34	7.322	0.052

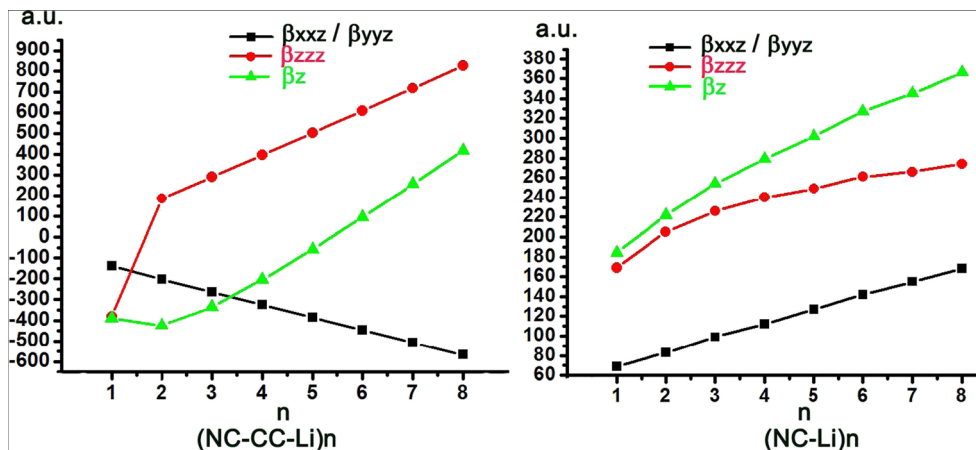
Importantly, one-dimensional Li-bond chains have an important effect on the mean first hyperpolarizability β_0 , but the effects on β_0 for (NC-CC-Li) $_n$ and (NC-Li) $_n$ are different. From Tables 4 and 5, it can be seen that the β_0 values increase with increasing n for (NC-Li) $_n$, while β_0 values for (NC-CC-Li) $_n$ at first decrease, and then increase. In this study, we were concerned with the β_{xxz} , β_{yyz} and β_{zzz} components in order to understand the change in β_0 . These latter components are listed in Tables 4 and 5, and depicted in Fig. 4; we found that the tensors of β_{xxz} (β_{yyz}) and β_{zzz} have the same signs for (NC-Li) $_n$, while the tensors of β_{xxz} (β_{yyz}) and β_{zzz} have opposite signs for (NC-CC-Li) $_n$. For (NC-CC-Li) $_n$, when $n \leq 5$, the sum of the off-diagonal β_{xxz} and β_{yyz} is larger in absolute terms than the diagonal β_{zzz} , and when $n > 5$, we found the reverse situation that the diagonal β_{zzz} component became the dominant component as compared with the off-diagonal β_{xxz} and β_{yyz} component. In this situation, the charge distribution transition appears to be along the x - and y -axis, and the Li-bond effect is along the molecular axis (z -axis). Because (NC-CC-Li) $_n$ has an extra unit $-C \equiv C-$, (NC-CC-Li) $_n$ has a charge distribution interaction with the corresponding (NC-CC-Li) $_n$. Thus, (NC-CC-Li) $_n$ has large off-diagonal β_{xxz} and

Furthermore, the maximum absorption wavelength λ_{\max} at the crucial transition is an approximated index of evaluating transparency properties in a given chromophore. But, according to the two-level model of Oudar and chemla [11, 38], the

β_0 is proportional to oscillator strength for the single transition multiplied by the third power of the absorption maximum λ_{\max}^3 , which shows that the β_0 value is a strong function of λ_{\max} . Therefore, the increase in λ_{\max} (the red-shift) is an unavoidable consequence of any increase in β . However, for (NC-CC-Li) $_n$ and (NC-Li) $_n$, we found that the β_0 values were greatly enhanced but associated with only a small red-shift (see Tables 4, 5). To further understand this finding, we defined the relationship of $\Delta\beta_{zzz}/\Delta\lambda_{\max}$ (see Fig. 5) by replacing β_0 with the tensor β_{zzz} , since both (NC-CC-Li) $_n$ and (NC-Li) $_n$ are one-dimensional Li-bond chains (the diagonal β_{zzz} tensor became the dominant tensor). From the results plotted in Fig. 5, we found that the change of $\Delta\beta_{zzz}/\Delta\lambda_{\max}$ with increasing n for (NC-CC-Li) $_n$ is very strong, that is to say, (NC-CC-Li) $_n$ can enhance first hyperpolarizability without too much red-shift. On the other hand, for (NC-Li) $_n$, the change of $\Delta\beta_{zzz}/\Delta\lambda_{\max}$ is very weak due to the small change in β_{zzz} . However, both (NC-CC-Li) $_n$ and (NC-Li) $_n$ can enhance first hyperpolarizability without too much red-shift, similar to the (dicyanomethylene)pyran derivatives with C_{2v} symmetry reported by Moylan et al. [17].

Furthermore, from Fig. 5, the interesting relationship between β_0 and λ_{\max} suggests that (NC-CC-Li) $_n$ and (NC-Li) $_n$ have a unique advantage in moderating this apparent contradiction, that is, with increasing n , they can achieve large first hyperpolarizability with only a slight red-shift. For example,

Fig 4 The relationships between β_z , β_{xxz} and β_{zzz} components



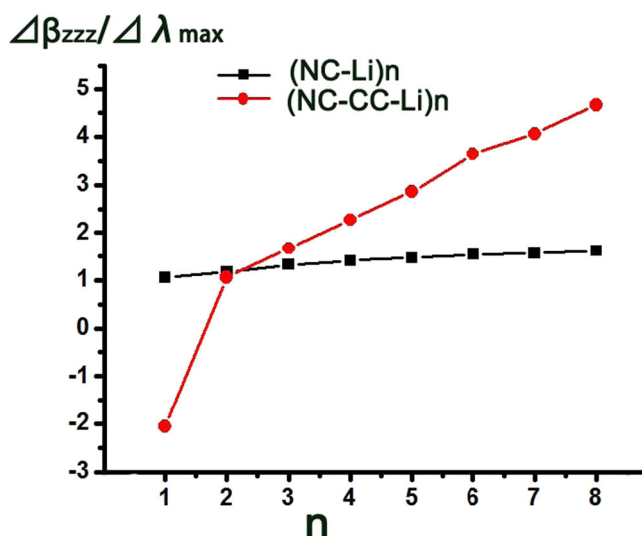


Fig 5 The relationship of $\beta_{zzz}/\lambda_{max} \sim n$

compared with other Li-bond systems, although the lithium salt of pyridazine $\text{Li-H}_3\text{C}_4\text{N}_2$ has a β_0 value of 859 a.u., which is larger than that of $(\text{NC-CC-Li})_8$ (417 a.u.), the λ_{max} of $\text{Li-H}_3\text{C}_4\text{N}_2$ (257 nm) is larger than that of $(\text{NC-CC-Li})_8$ (176 nm). From the relationship of $\Delta\beta_{zzz}/\Delta\lambda_{max} \sim n$, we can qualitatively deduce that, when $n=11$, the β_0 value of $(\text{NC-CC-Li})_8$ would be close to that of $\text{Li-H}_3\text{C}_4\text{N}_2$ (859 a.u) [39], but its λ_{max} is only ~ 170 nm. Furthermore, the one-dimensional multilithium salt $\text{Li}_5\text{-[5]cyclacene}$ has a β_0 value of 7,938 a.u. [40] and a λ_{max} of ~ 483 nm. We also infer that, when $n \sim 46$, the β_0 value of $(\text{NC-CC-Li})_8$ would be close to that of $\text{Li}_5\text{-[5]cyclacene}$ (7,938 a.u.), but its λ_{max} is only ~ 185 nm, which is much smaller than that of $(\text{NC-CC-Li})_8$ (~ 483 nm). Our deductions indicate that one-dimensional Li-bond chains can effectively moderate the contradiction of β_0 and λ_{max} .

Double degenerated charge transition and strongly coupled oscillators

One-dimensional $(\text{NC-CC-Li})_n$ and $(\text{NC-Li})_n$ both have unusually enhanced first hyperpolarizability (see Tables 4,

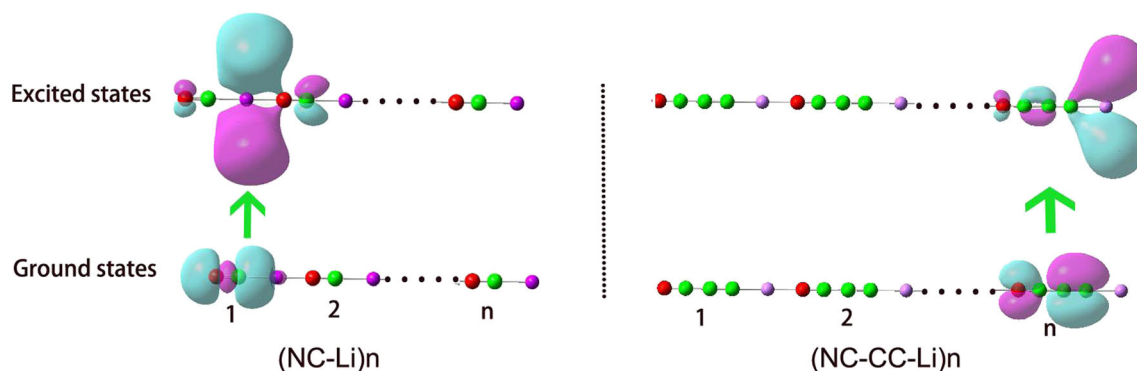


Fig 6 Sketches of crucial transitions

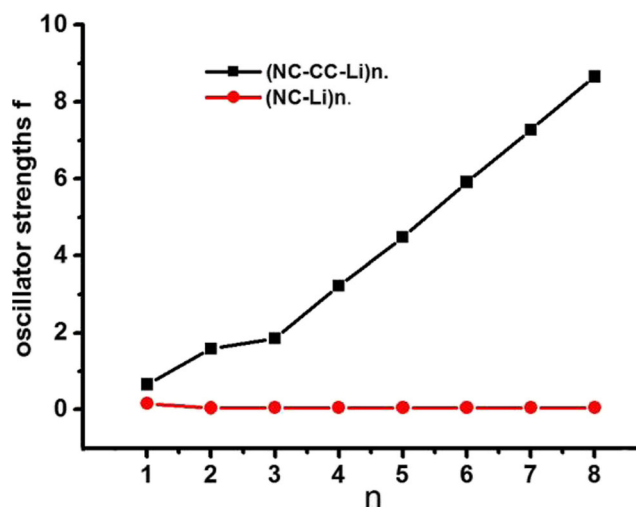


Fig 7 Comparison of oscillator strengths, f

5), which suggest that they have double degenerated charge transitions, respectively, each transition providing a contribution to β with the same sign. Accordingly, we calculated the crucial transitions between the ground state and the excited state. These are presented in sketch form in Fig. 6. Obviously, the transitions from each π_{2px} and π_{2py} orbital of the ground state to the excited state follow the same trend along the z -axis (C_∞ axis); therefore, double degenerated charge transitions contribute to the molecular hyperpolarizability β in an additive manner. However, for $(\text{NC-CC-Li})_n$, the crucial transitions locate primarily to the right end, regardless of n , while for $(\text{NC-Li})_n$, the crucial transitions locate primarily to the left end, also regardless of n . This difference arises from the difference of coupled oscillators. Figure 7 depicts the relationship between the coupled oscillators of $(\text{NC-CC-Li})_n$ and $(\text{NC-Li})_n$ and n . From Fig. 7, oscillator strengths of $(\text{NC-CC-Li})_n$ increase with increasing n , while for the oscillator strengths of $(\text{NC-Li})_n$, there is not too much change going from 0.159 down to 0.052. We conclude that $(\text{NC-CC-Li})_n$ have stronger π electron coupled interactions than the corresponding $(\text{NC-CC-Li})_n$, due to $(\text{NC-CC-Li})_n$ having more rich π

electrons. It is precisely because $(\text{NC-CC-Li})_n$ have hugely enhanced oscillator strengths that their first hyperpolarizabilities (especially for the tensor β_{zzz}) exhibit such a large increase.

Conclusions

A comparative study was carried out on two kinds of one-dimensional Li-bond chains: $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$ ($n=1-8$). We found that both $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$ exhibit enhanced first hyperpolarizabilities with increasing n , and a slight change in the absorption maximum λ_{max} at crucial transitions. Compared with $(\text{NC-Li})_n$, $(\text{NC-CC-Li})_n$ exhibits particularly drastically enhanced β_0 values, due to clearly enhanced coupled oscillators and double-degenerated charge transitions. A $\Delta\beta_{zzz}/\Delta\lambda_{\text{max}}$ relationship was proposed to evaluate those NLO molecules, i.e., $(\text{NC-Li})_n$ and $(\text{NC-CC-Li})_n$, that can enhance first hyperpolarizability without too much red-shift. Therefore, the results of this study will help the development of high performance NLO materials.

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