Electronic Supplementary Information (ESI) for

The Stability and Nonlinear Optical Properties: Encapsulation of an Excess Electron Compound LiCN…Li within Boron Nitride Nanotubes

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Computational Details for Sum-Over-States (SOS) Method

The static first hyperpolarizabilities were calculated by using the sum-over-states (SOS) formula[1]. The expression of the static first hyperpolarizabilities (β) can be obtained by the application of CIS (or TDDFT) method to the interacting electromagnetic field and microscopic system. The zeroth-order Born-Oppenheimer approximation was also employed to separate the electronic and atomic components of β. The expression for β_{ijk} is

$$\beta_{ijk} = \frac{1}{4\hbar^2} P(i, j, k; -\omega_\sigma, \omega_1, \omega_2) \times \sum_{m \neq g} \sum_{n \neq g} \left[\frac{(\mu_i)_{gm} (\overline{\mu}_j)_{mn} (\mu_k)_{gn}}{(\omega_{mg} - \omega_\sigma - i\gamma_{mg})(\omega_{ng} - \omega_I - i\gamma_{ng})} \right] \quad (1)$$

Where $(\mu_i)_{gm}$ is an electronic transition moment along the i axis of the Cartesian system, between the ground state and the excited state, $(\overline{\mu_j})_{mn}$ is the dipole difference equal to $(\mu_i)_{mn} - (\mu_i)_{gg}$, ω_{mg} is the transition energy, ω_1 and ω_2 are the frequencies of the perturbation radiation fields, and $\omega_\sigma = \omega_1 + \omega_2$ is the polarization response frequency; P (i, j, k; $-\omega_\sigma$, ω_1, ω_2) indicates all permutations of ω_1, ω_2, and ω_σ along with associated indices i, j, and k; γ_{mg} is the damping factor. Herein, a self-compiled program using the results of CIS (TDDFT) and the SOS formula to obtain the β value is adopted. Our group has used this method to investigate the NLO properties of a series of compounds[2-4]. In this work, the β_0 is defined as following

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

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

The accuracy of the SOS method mainly depends on the convergence of calculation results[2-6]. According to the convergent curves (see the following figure), employing 30 states in the present work is a reasonable approximation for the calculation of values.

Figure. The convergent curves of β_0 values as computed in the SOS formalism as a function of the number of excited states for **LiCN…Li** and **1**.

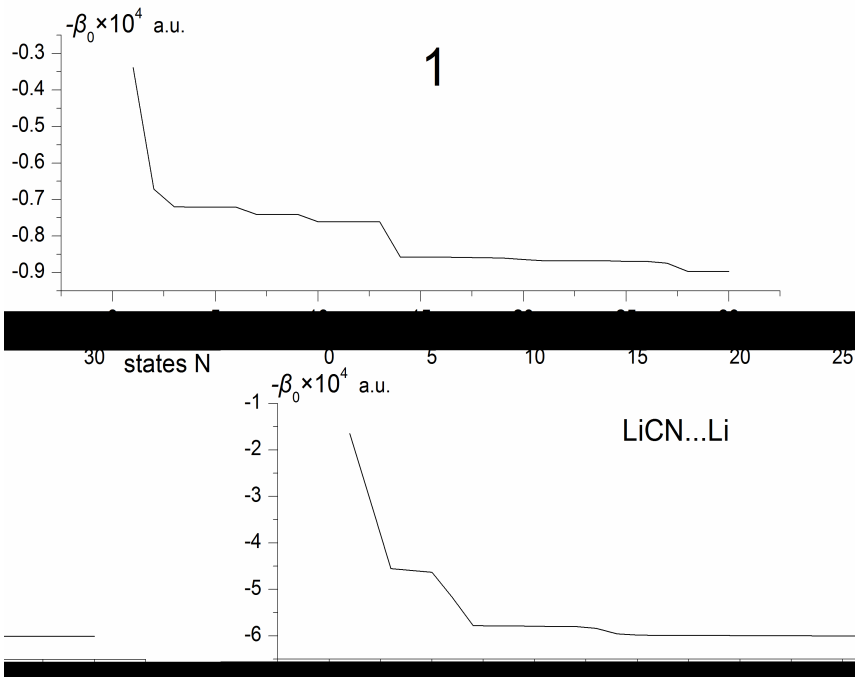

Table S1. The First Hyperpolarizability (β_0 a.u.) of **LiCN…Li** at QCISD/6-31+G(d) Level, Basis Effect on β_0 of **LiCN…Li** Calculated by the CAM-B3LYP Method and Corresponding Time Cost (s).

	CAM-B3LYP					
	6-31+G(d)	**6-31++G(d,p)**	**6-311++G(d,p)**	**6-311++G(2df,2p)**	**6-311++G(3df,3pd)**	**QCISD/6-31+G(d)**
β_X	310176	310176	272926	265043	273677	95095
β_Y	-3103	-3102	-2564	-2582	-2574	105702
β_Z	1774	1774	927	876	874	212621
β_0	310197	310197	272939	265057	273690	255781
number of basis functions	76	76	88	136	156	76
Time Cost	715.5	726.0	865.0	3329.4	4479.9	6551.9

Table S2. The Most Important Transition Energies (ΔE) and Oscillating Strengths (f_0) of **LiCN…Li, 1** and **2** Calculated at CAM-B3LYP/6-31+G(d) Level and Fragments Contributions to the Most Important Transition Molecular Orbitals of **1** and **2**.

	LiCN...Li		**1**		**2**	
f_0	0.212		0.082		0.114	
ΔE (eV)	1.442		2.139		2.327	
main contribution	SOMO-> LUMO+3	SOMO-> LUMO+11	SOMO-> LUMO+3	SOMO-> LUMO	SOMO-> LUMO+6	SOMO-> LUMO+5
contribution coefficient	0.712	0.558	0.800	0.431	0.841	0.452
fragment			**LiCN…Li**	**BNNT**	**LiCN…Li**	**BNNT**
LUMO			18.56%	81.44%	11.17%	88.83%
LUMO+3			87.24%	12.76%		
LUMO+6					9.08%	90.92%

Table S3. The Energy Values of **1** System (The Distance of **LiCN…Li** to the B-rich Edge of **1** as a Function of Energy)

	distance to the B-rich edge (**Å**)	energy (eV)
1	0	-55185.2
2	0.5	-55185.1
3	1.0	-55184.7
4	1.5	-55183.4
5	2.0	-55182.6
6	2.5	-55181.9
7	3.0	-55181.7
8	3.5	-55181.4
9	4.0	-55181.8
10	4.5	-55182.6
11	5.0	-55182.9
12	5.5	-55182.7
13	6.0	-55182.2
14	6.5	-55181.9
15	7.0	-55181.6
16	7.5	-55181.2
17	8.0	-55180.9
18	8.5	-55181.0
19	9.0	-55181.3
20	9.5	-55181.7
21	10.0	-55182.6
22	10.5	-55183.6
23	11.0	-55184.5
24	11.5	-55185.5

Table S4. The Energy Values of **1** System (The Distance of **LiCN…Li** to the wall of the BNNT as a Function of Energy)

	distance to the wall (**Å**)	energy (eV)
1	0.72	-55075.5
2	1.22	-55119.3
3	1.72	-55129.9
4	2.22	-55132.5
5	2.72	-55129.8
6	3.22	-55119.1
7	3.72	-55073.9

Figure S1. The Most Important Transition Molecular Orbitals of **LiCN…Li**, **1** and **2** Calculated at CAM-B3LYP/6-31+G(d) Level

Figure S2. The optimized structures of **LiCN…Li@BNNT[5,0]**, **LiCN…Li@BNNT[7,0]**, **LiCN…Li@BNNT[8,0]**

Figure S3. The Variation of Energy in the Process Which **LiCN…Li** Cross the BNNT from the Upper Wall to the Bottom Wall

Reference and Notes

1 B. J. Orr and J. F. Ward, *Mol. Phys.* 1971, **20**, 513–526.

2 L. K. Yan, G. C. Yang, W. Guan, Z. M. Su and R. S. Wang, *J. Phys. Chem. B*, 2005, **109**, 22332.

3 G. C. Yang, W. Guan, L. K. Yan, Z. M. Su, L. Xu and E. B. Wang, *J. Phys. Chem. B*, 2006, **110**, 23092.

4 W. Guan, G. C. Yang, L. K. Yan and Z. M. Su, *Inorg. Chem.*, 2006, **45**, 7864.

Optimized Cartesian Coordinates

LiCN…Li

N	-0.55313300	-0.00730100	0.00010500
C	0.62143500	-0.00457200	-0.00014400
Li	-2.53089200	0.01394400	-0.00003900
Li	2.57866700	0.01223500	0.00008300

BNNT

H	4.520661	0.630614	-2.340269
H	4.519964	2.348281	-0.625180
H	4.520115	1.716421	1.719596
H	4.520425	-0.630941	2.341241
H	4.520131	-2.347270	0.625051
H	4.519962	-1.717116	-1.720304
H	-4.818884	0.683209	-2.535278
H	-4.819334	2.535797	-0.676142
H	-4.820318	1.849796	1.853684
H	-4.820411	-1.849258	-1.853273
H	-4.818687	-0.683558	2.536551
H	-4.819280	-2.536206	0.676130
B	-3.645451	-0.629232	2.333169
B	-1.484556	0.615776	2.308242
B	-1.484500	-1.692813	1.687293
B	0.676330	-0.624516	2.317145
B	0.676320	-2.320820	0.618406
B	2.836912	-1.699491	1.693718
B	2.836997	-2.319945	-0.624612
B	0.676146	-1.695421	-1.699188
B	-1.484339	-2.310713	-0.622104
B	-3.645025	-2.338219	0.623240
B	-3.645552	-1.707262	-1.710499
B	-3.645552	1.707402	1.710528
B	-3.645023	2.338136	-0.623294
B	-3.645458	0.629149	-2.332928
B	-1.484537	-0.615800	-2.308368
B	-1.484446	1.692829	-1.687338
B	-1.484363	2.310751	0.622056
B	0.676293	2.320883	-0.618339
B	0.676171	1.695448	1.699105
B	2.836981	1.699549	-1.693405
B	2.836963	2.320151	0.624439

B	2.837129	-0.618487	-2.316921
B	2.837117	0.618205	2.316878
N	-2.934022	1.760543	-1.754949
N	-2.934094	-0.639532	-2.398663
N	-0.769467	0.650740	-2.415467
N	-0.769657	-1.768535	-1.772504
N	1.389144	-0.644644	-2.417707
N	1.388900	1.773177	-1.767610
N	3.512675	0.662055	-2.457012
N	3.511764	-1.801145	-1.804625
N	3.511851	2.464261	-0.656202
N	3.511916	1.800363	1.803862
N	3.512016	-2.463181	0.655980
N	3.512443	-0.662374	2.458130
N	1.389107	0.644542	2.417411
N	1.388847	-1.773431	1.767904
N	1.388716	2.418860	0.651180
N	1.388733	-2.418511	-0.651074
N	-0.769410	2.419716	-0.644560
N	-0.769410	-2.419637	0.644520
N	-0.769664	1.768492	1.772402
N	-0.769525	-0.650775	2.415523
N	-2.934136	0.639494	2.398382
N	-2.934075	-1.760487	1.754814
N	-2.934130	2.400743	0.645874
N	-2.934116	-2.400690	-0.645956
B	0.676404	0.624422	-2.317099

1

H	4.582960	-0.614411	-2.372710
H	4.581781	1.750969	-1.712670
H	4.578851	2.372439	0.660950
H	4.579241	0.616519	2.379260
H	4.581090	-1.745061	1.714400
H	4.580430	-2.375071	-0.657670
H	-4.735010	-0.683488	-2.648020
H	-4.735749	1.951122	-1.919260
H	-4.737039	2.642242	0.731480
H	-4.735480	-2.638198	-0.733870
H	-4.737039	0.684312	2.655560
H	-4.736570	-1.957088	1.918230
B	-3.577489	0.615852	2.389860

B	-1.415159	1.718941	1.749800
B	-1.414140	-0.657769	2.363750
B	0.715401	0.615960	2.384530
B	0.716650	-1.758210	1.726540
B	2.895200	-0.646960	2.333510
B	2.896150	-2.346400	0.605790
B	0.717090	-2.376730	-0.659520
B	-1.413260	-2.377939	0.612990
B	-3.576430	-1.762828	1.728060
B	-3.575070	-2.377208	-0.660960
B	-3.577319	2.378522	0.658530
B	-3.574879	1.759822	-1.730100
B	-3.573970	-0.616128	-2.388200
B	-1.412460	-1.719749	-1.752160
B	-1.411729	0.657841	-2.366060
B	-1.413789	2.377981	-0.614560
B	0.717401	1.760880	-1.725350
B	0.715731	2.375850	0.660010
B	2.898151	0.649420	-2.329210
B	2.895231	2.347960	-0.603720
B	2.897160	-1.699010	-1.726700
B	2.893631	1.697780	1.728790
N	-2.859459	0.673281	-2.424230
N	-2.860200	-1.761259	-1.794330
N	-0.706460	-0.653259	-2.532420
N	-0.707710	-2.520439	-0.700480
N	1.449160	-1.747600	-1.779010
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N	3.571841	1.823700	-1.785800
N	3.567951	2.462830	0.685430
N	3.571140	-1.818660	1.786230
N	3.568571	0.639640	2.472810
N	1.446081	1.748580	1.780330
N	1.447340	-0.667600	2.403450
N	1.447801	2.419380	-0.623220
N	1.448400	-2.415920	0.623850
N	-0.707359	1.867231	-1.832620
N	-0.708470	-1.866219	1.831050
N	-0.709859	2.519791	0.699420
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N	-2.864069	1.758661	1.790400
N	-2.862580	-0.673779	2.420330

N	-2.861949	2.435271	-0.630050
N	-2.861140	-2.436149	0.627940
N	-1.554649	-0.002069	-0.003970
C	-0.393259	-0.001309	0.001550
Li	-3.375939	0.004542	0.015890
Li	1.588561	-0.013220	-0.017510
B	0.718320	-0.615910	-2.386920

2

H	-4.52361300	-1.74856200	-1.69721700
H	-4.52241500	-2.34049300	0.66577800
H	-4.52103600	-0.59626400	2.36558800
H	-4.52109900	1.74554100	1.69897500
H	-4.52275400	2.34582900	-0.66138100
H	-4.52411400	0.59754000	-2.36012500
H	4.79435500	-1.94753100	-1.89528500
H	4.79495500	-2.61953400	0.73931000
H	4.79607300	-0.66763800	2.63984200
H	4.79232700	0.66545800	-2.63945000
H	4.79713100	1.95269000	1.89520300
H	4.79417700	2.61961200	-0.74559600
B	3.64287300	1.74515800	1.69307600
B	1.46432100	0.66724800	2.35348400
B	1.46333700	2.37417500	0.59907600
B	-0.67268700	1.76196700	1.71277100
B	-0.67424600	2.36520700	-0.66882400
B	-2.83070400	2.38200800	0.60347800
B	-2.83313400	1.71383000	-1.75978700
B	-0.67556200	0.60234000	-2.38159400
B	1.46164900	1.70648300	-1.75647200
B	3.63976400	2.34195800	-0.66608400
B	3.63781400	0.59494300	-2.35926800
B	3.64235100	-0.59653500	2.35730700
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B	3.63895300	-1.74336900	-1.69522600
B	1.46125800	-0.66772700	-2.35534300
B	1.46219600	-2.37472500	-0.60020000
B	1.46369800	-1.70666000	1.75518200
B	-0.67388400	-2.36443000	0.67168000
B	-0.67254600	-0.60161400	2.38301500
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B	-2.83389500	-0.67056000	-2.36364500

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N	0.75917700	-1.86121700	-1.80837000
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N	2.91268900	0.67657300	2.38569900
N	2.91155500	2.40790300	0.60631400
N	2.91209900	-1.73071700	1.77867200
N	2.90965900	1.73042500	-1.78243100
N	-0.46433900	-0.00045400	0.00401700
C	0.70274400	0.00034400	-0.00499600
Li	-2.31590700	-0.00875300	-0.02568800
Li	2.78101300	0.00372800	0.01729100
B	-0.67485000	-1.76277900	-1.71136300