Theoretical Study of Substituent Effects on Electride Characteristics and the Nonlinear Optical Properties of Li@calix[4]pyrrole

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Computational Details

The optimized geometric structures were obtained using the B3LYP method and 6-31+G(d) basis set. In order to obtain the high-precision geometry, the self-consistent field (SCF) convergence has also been tightened to $1 \cdot 10^{-9}$ a.u., and we used more tight optimization convergence criteria (the *verytight* option is used in Gaussian 09 package) combined with more precise integral grid (the *ultrafine* option is used in Gaussian 09 package).

Table S1 The first hyperpolarizability (β_0) of the **1** calculated by the MP2, BHandHLYP, LC-BLYP, CAM-B3LYP, wB97XD and B3LYP theory. In these calculations, the 6-311++G(3df,3pd) basis set is employed for the N atoms, alkali Li and four H atoms within NH- groups and the 6-31+g(d) basis set for other atoms.

No.	Functional	β_0
1	MP2	11853
2	BHandHLYP	12705
3	LC-BLYP	13424
4	CAM-B3LYP	11876
5	wB97XD	11300
6	B3LYP	7819

Table S2 The NBO charges (q, |e|)[a] on the N atoms and H atoms in the -NH groups of **1**, octafluorine-**1**, and octamethoxy-**1**.

Chemical Models	q^{N1}	q^{N2}	q^{N3}	q^{N4}	q^{H1}	q^{H2}	q^{H3}	q^{H4}
1	-0.693	-0.693	-0.693	-0.693	0.350	0.350	0.350	0.350
	(-0.755)	(-0.755)	(-0.755)	(-0.755)	(0.366)	(0.366)	(0.366)	(0.366)
octafluorine-**1**	-0.682	-0.683	-0.684	-0.684	0.352	0.352	0.352	0.352
	(-0.743)	(-0.743)	(-0.741)	(-0.742)	(0.368)	(0.368)	(0.368)	(0.368)
octamethoxy-**1**	-0.687	-0.690	-0.690	-0.686	0.346	0.334	0.344	0.354
	(-0.742)	(-0.745)	(-0.745)	(-0.741)	(0.361)	(0.351)	(0.360)	(0.368)

[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.

Table S3 The NBO charges (q, |e|)[a] on the N and Li_{out} of tetra-lithium-**1.**

Chemical Models	q^N	q^{Li}
tetra-lithium-**1**	-0.904(-0.978)	0.683(0.694)

[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.
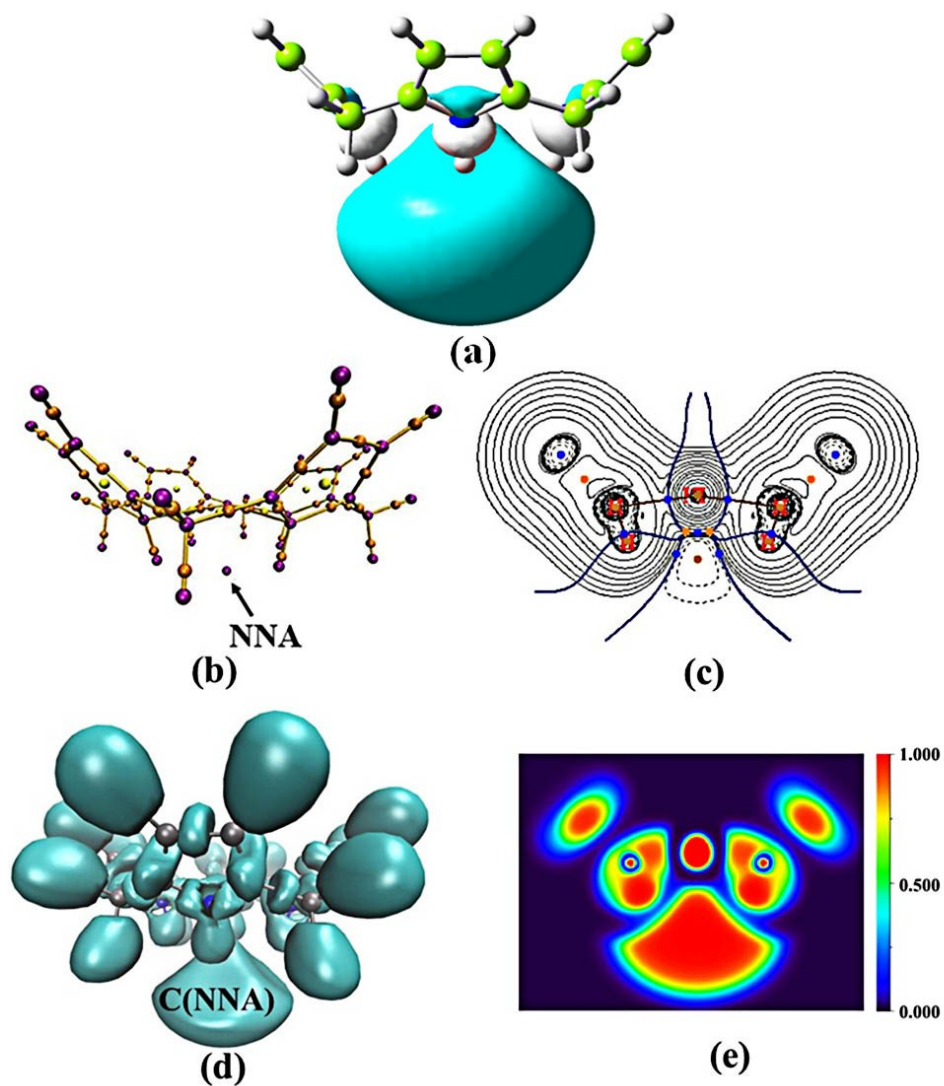
Fig. S1. (a) HOMO (isovalue = 0.02 au). (b) Non-nuclear attractor (NNA). (c) Two-dimensional (2D) plot of $\nabla^2\rho(r_c)$. (d) ELF isosurface image at a 0.800 value. (e) The colour-filled map of ELF for **1**.

Fig. S2. (a) HOMO (isovalue = 0.02 au). (b) Non-nuclear attractor (NNA). (c) Two-dimensional (2D) plot of $\nabla^2\rho(r_c)$. (d) ELF isosurface image at a 0.800 value. (e) The colour-filled map of ELF for octafluorine-**1**.
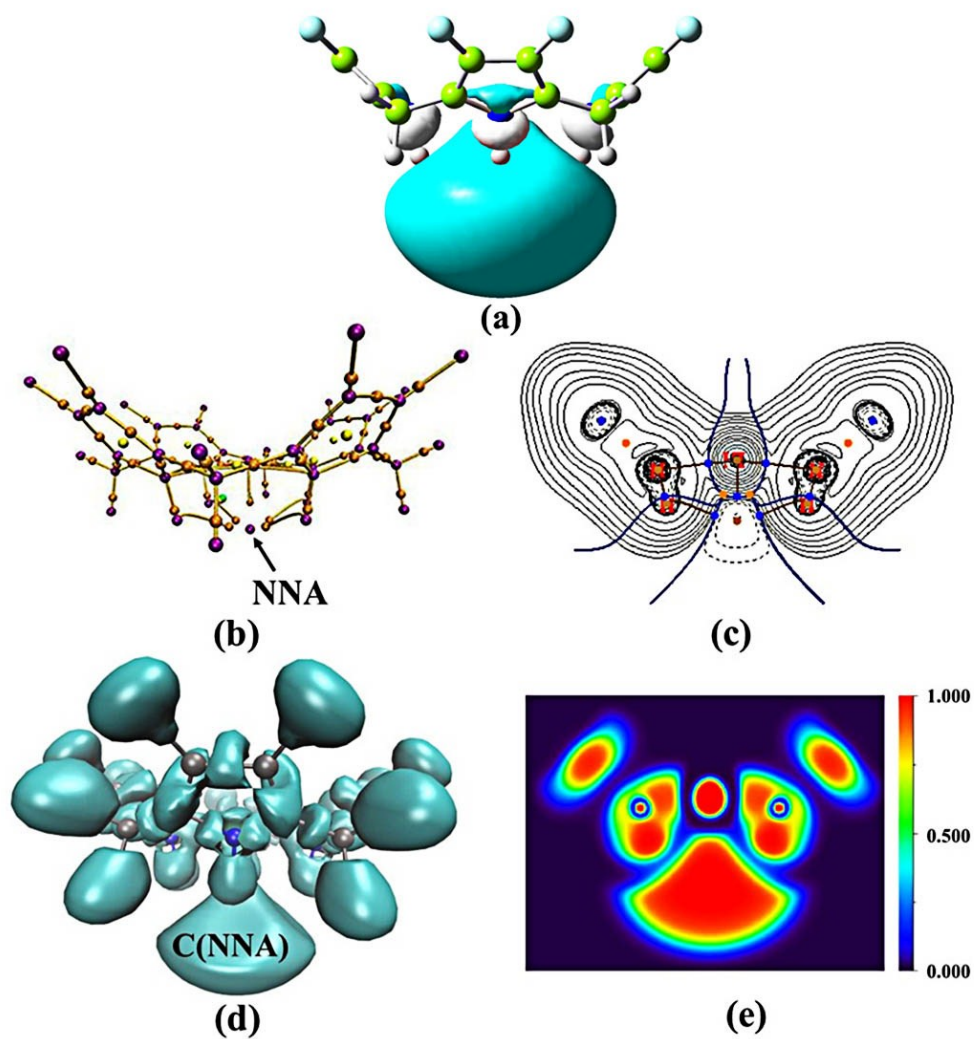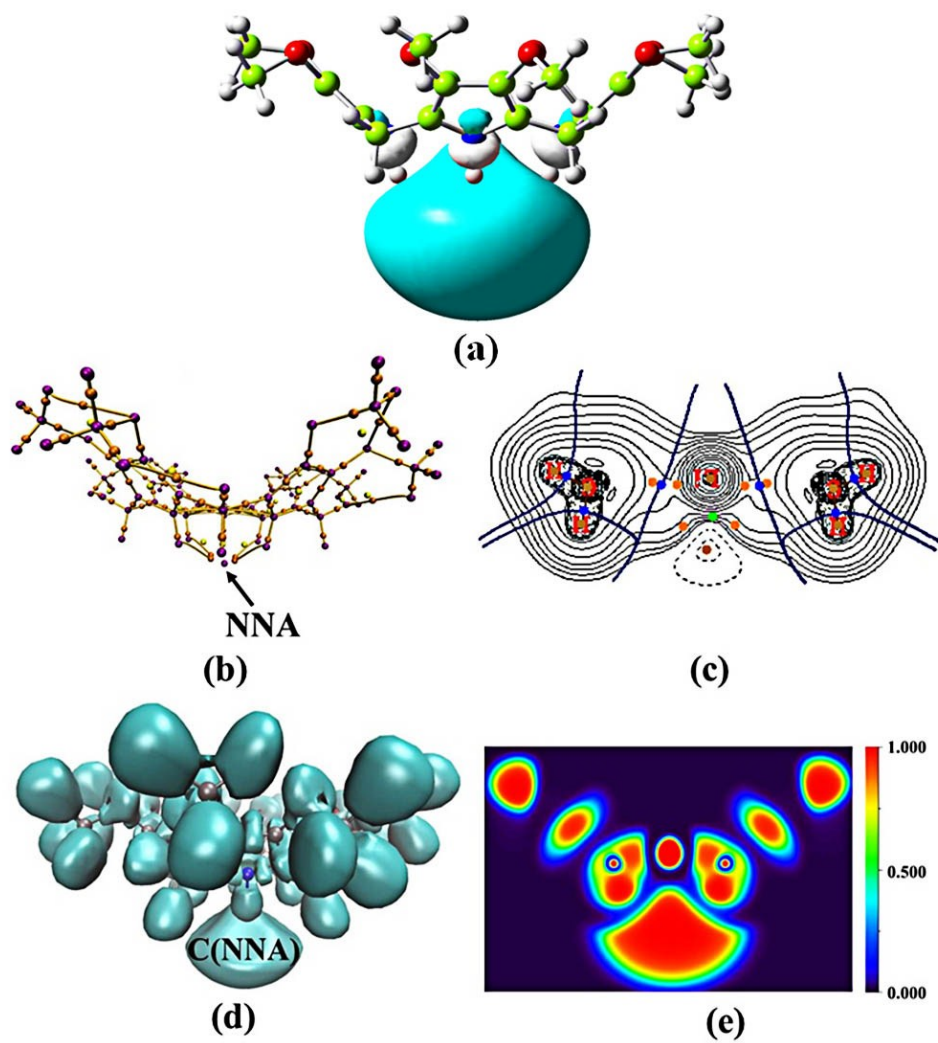
Fig. S3. (a) HOMO (isovalue = 0.02 au). (b) Non-nuclear attractor (NNA). (c) Two-dimensional (2D) plot of $\nabla^2\rho(r_c)$. (d) ELF isosurface image at a 0.800 value. (e) The colour-filled map of ELF for octamethoxy-**1**.

Cartesian Coordinates of All Optimized Structures

B3LYP/6-31+G* scf(conver=9) opt=verytight int=ultrafine

1   NImag=0

6	0.717553	3.834078	-0.822890
6	-0.717553	3.834078	-0.822890
6	1.140418	2.923375	0.111064
1	1.363139	4.436225	-1.450577
7	0.000000	2.305618	0.649700
6	-1.140418	2.923375	0.111064
6	2.521274	2.521274	0.544203
1	-1.363139	4.436225	-1.450577
1	0.000000	1.974058	1.630458
6	2.923375	1.140418	0.111064
6	-2.521274	2.521274	0.544203
1	2.608818	2.608818	1.640542
1	3.234572	3.234572	0.119141
6	3.834078	0.717553	-0.822890
7	2.305618	-0.000000	0.649700
6	-2.923375	1.140418	0.111064
1	-2.608818	-2.608818	1.640542
1	-3.234572	3.234572	0.119141
6	-3.834078	0.717553	-0.822890
6	3.834078	-0.717553	-0.822890
7	-2.305618	0.000000	0.649700
6	2.923375	-1.140418	0.111064
1	4.436225	1.363139	-1.450577
1	1.974058	-0.000000	1.630458
6	-3.834078	-0.717553	-0.822890
1	-1.974058	0.000000	1.630458
6	-2.923375	-1.140418	0.111064
6	2.521274	-2.521274	0.544203
1	-4.436225	1.363139	-1.450577
1	4.436225	-1.363139	-1.450577
6	1.140418	-2.923375	0.111064
6	-2.521274	-2.521274	0.544203
1	-4.436225	-1.363139	-1.450577
1	2.608818	-2.608818	1.640542
1	3.234572	-3.234572	0.119141
6	0.717553	-3.834078	-0.822890
7	-0.000000	-2.305618	0.649700
6	-1.140418	-2.923375	0.111064

1	-2.608818	2.608818	1.640542
1	-3.234572	-3.234572	0.119141
6	-0.717553	-3.834078	-0.822890
1	1.363139	-4.436225	-1.450577
1	-0.000000	-1.974058	1.630458
1	-1.363139	-4.436225	-1.450577
3	0.000000	0.000000	0.319735

octafluorine-**1**   **NImag=0**

6	0.713694	3.869653	-0.356086
6	-0.713694	3.869653	-0.356086
6	1.150144	2.926391	0.528746
7	0.000000	2.282192	1.032692
6	-1.150144	2.926391	0.528746
6	2.536311	2.536311	0.941488
1	0.000000	2.010609	2.035449
6	2.926391	1.150144	0.528746
6	-2.536311	2.536311	0.941488
1	2.642228	2.642228	2.034621
1	3.240909	3.240909	0.489570
6	3.869653	0.713694	-0.356086
7	2.282192	-0.000000	1.032692
6	-2.926391	1.150144	0.528746
1	-2.642228	-2.642228	2.034621
1	-3.240909	3.240909	0.489570
6	-3.869653	0.713694	-0.356086
6	3.869653	-0.713694	-0.356086
7	-2.282192	0.000000	1.032692
6	2.926391	-1.150144	0.528746
1	2.010609	-0.000000	2.035449
6	-3.869653	-0.713694	-0.356086
1	-2.010609	0.000000	2.035449
6	-2.926391	-1.150144	0.528746
6	2.536311	-2.536311	0.941488
6	1.150144	-2.926391	0.528746
6	-2.536311	-2.536311	0.941488
1	2.642228	-2.642228	2.034621
1	3.240909	-3.240909	0.489570
6	0.713694	-3.869653	-0.356086
7	-0.000000	-2.282192	1.032692
6	-1.150144	-2.926391	0.528746
1	-2.642228	2.642228	2.034621

1	-3.240909	-3.240909	0.489570
6	-0.713694	-3.869653	-0.356086
1	-0.000000	-2.010609	2.035449
9	-1.482126	-4.668233	-1.114927
9	1.482126	-4.668233	-1.114927
9	4.668233	-1.482126	-1.114927
9	4.668233	1.482126	-1.114927
9	1.482126	4.668233	-1.114927
9	-1.482126	4.668233	-1.114927
9	-4.668233	1.482126	-1.114927
9	-4.668233	-1.482126	-1.114927
3	0.000000	0.000000	0.745805

octamethoxy-**1**   **NImag=0**

6	3.221205	2.214672	-0.175688
6	2.184634	3.224610	-0.177221
6	2.854056	1.235875	0.715369
7	1.588645	1.572947	1.225899
6	1.225227	2.838508	0.723488
6	3.562375	-0.023521	1.115309
1	1.392758	1.370166	2.224457
6	2.859356	-1.288827	0.724949
6	-0.029517	3.540513	1.140429
1	3.746521	-0.018430	2.205160
1	4.540022	-0.023366	0.626571
6	3.228293	-2.271943	-0.159347
7	1.594852	-1.627760	1.239443
6	-1.298712	2.851379	0.737816
1	-3.760762	-0.024604	2.262553
1	-0.009875	4.531549	0.679377
6	-2.277526	3.218984	-0.152216
6	2.195407	-3.286917	-0.152714
7	-1.638684	1.585538	1.249463
6	1.235766	-2.900129	0.746666
1	1.405402	-1.423642	2.237542
6	-3.291403	2.185067	-0.149255
1	-1.436728	1.395155	2.247370
6	-2.907409	1.224949	0.750695
6	-0.023180	-3.591288	1.170193
6	-1.288381	-2.904237	0.759326
6	-3.609542	-0.029804	1.167944
1	-0.017059	-3.726362	2.266776

1	-0.023472	-4.589472	0.723023
6	-2.253810	-3.288334	-0.133965
7	-1.648941	-1.635658	1.262614
6	-2.921023	-1.298231	0.761014
1	-0.022762	3.692467	2.235004
1	-4.601377	-0.009319	0.708618
6	-3.291066	-2.276632	-0.127335
1	-1.456070	-1.442775	2.260554
3	-0.038589	-0.037688	0.866260
8	-2.132269	-4.382874	-0.940306
8	-4.398099	-2.273154	-0.940858
8	-4.391069	2.056665	-0.948356
8	-2.270188	4.321065	-0.972700
8	2.048750	4.321279	-0.979545
8	4.330773	2.203585	-0.987289
8	2.066172	-4.385073	-0.953149
8	4.336410	-2.263444	-0.972811
6	-5.631131	-2.626125	-0.307412
1	-6.398062	-2.576829	-1.084254
1	-5.587665	-3.643141	0.104753
1	-5.883884	-1.926147	0.498208
6	-3.284395	-5.213029	-1.094798
1	-3.668419	-5.532749	-0.116097
1	-4.071317	-4.699866	-1.656089
1	-2.947246	-6.088170	-1.654990
6	-5.196871	3.219308	-1.148626
1	-4.665869	3.973497	-1.737134
1	-6.077490	2.879256	-1.698352
1	-5.510642	3.646408	-0.186017
6	-2.622027	5.558848	-0.347677
1	-2.564417	6.321665	-1.127987
1	-3.641874	5.521724	0.058079
1	-1.926253	5.812462	0.461245
6	3.206908	5.128678	-1.195157
1	3.956897	4.596901	-1.788559
1	2.859382	6.005324	-1.746553
1	3.642449	5.449362	-0.238614
6	5.554072	2.603046	-0.362130
1	6.328133	2.528207	-1.129904
1	5.494793	3.637096	0.002219
1	5.808231	1.945469	0.478474
6	3.217094	-5.212257	-1.126086
1	2.871954	-6.090514	-1.676435
1	3.991778	-4.699721	-1.705015

1	3.620779	-5.527552	-0.153860
6	5.561343	-2.655908	-0.346677
1	5.502972	-3.685470	0.030181
1	6.333162	-2.590495	-1.117586
1	5.818362	-1.988411	0.485311

tetra-lithium-**1**   **NImag=0**

6	-0.710382	4.002281	0.763069
6	0.710382	4.002281	0.763069
6	-1.110112	2.923644	-0.000799
1	-1.367305	4.703107	1.264785
7	0.000000	2.218906	-0.485424
6	1.110112	2.923644	-0.000799
6	-2.524701	2.524701	-0.349024
1	1.367305	4.703107	1.264785
6	-2.923644	1.110112	-0.000799
6	2.524701	2.524701	-0.349024
1	-2.738750	2.738750	-1.424762
1	-3.203174	3.203174	0.174538
6	-4.002281	0.710382	0.763069
7	-2.218906	0.000000	-0.485424
6	2.923644	1.110112	-0.000799
1	2.738750	-2.738750	-1.424762
1	3.203174	3.203174	0.174538
6	4.002281	0.710382	0.763069
6	-4.002281	-0.710382	0.763069
7	2.218906	-0.000000	-0.485424
6	-2.923644	-1.110112	-0.000799
1	-4.703107	1.367305	1.264785
6	4.002281	-0.710382	0.763069
6	2.923644	-1.110112	-0.000799
6	-2.524701	-2.524701	-0.349024
1	4.703107	1.367305	1.264785
1	-4.703107	-1.367305	1.264785
6	-1.110112	-2.923644	-0.000799
6	2.524701	-2.524701	-0.349024
1	4.703107	-1.367305	1.264785
1	-2.738750	-2.738750	-1.424762
1	-3.203174	-3.203174	0.174538
6	-0.710382	-4.002281	0.763069
7	-0.000000	-2.218906	-0.485424

6	1.110112	-2.923644	-0.000799
1	2.738750	2.738750	-1.424762
1	3.203174	-3.203174	0.174538
6	0.710382	-4.002281	0.763069
1	-1.367305	-4.703107	1.264785
1	1.367305	-4.703107	1.264785
3	0.000000	0.000000	0.290054
3	-1.281242	1.281242	-1.717338
3	1.281242	1.281242	-1.717338
3	1.281242	-1.281242	-1.717338
3	-1.281242	-1.281242	-1.717338