Supplementary Information

Second-order NLO responses of two-cavity inorganic electrides $Li_n@B_{20}H_{26}$ (n = 1, 2): evolutions with increasing excess electron number and various B−B connection sites of $B_{20}H_{26}$

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General Comments

§ Fig. S1 The connection B−B bond length and angel formed by axes of **A** and **B** cavities.

§ Fig. S2 Frontier molecular orbitals involved major charge transfer transitions of **1b**−**4b**.

§ Fig. S3 The optimized geometries of $Li_2@B_{20}H_{26}$ (**1c**−**4c**).

§ Fig. S4 Spin density of **1c**−**4c** (Excess α-spin is visualized by blue regions whereas excess β-spin is green).

§ Fig. S5 Frontier molecular orbitals (HOMO and LUMO) in solution by PCM approach of **1b-4b**.

§ Table S1 Selected bond length (Å) and dihedral angle (°).

§ Table S2 B-B nature bond orbitals, occupancy, orbital coefficients and hybrids, and orbital type of systems **1a**−**4a**.

§ Table S3 NBO charge of all atoms for systems **1a**−**4a** (H11-H14 and H11'-H14' are bridging hydrogen atoms and other H atoms numbered are terminal hydrogen atoms).

§ Table S4 Selected bond lengths (Å) of the systems **1a**, **1b** and **1c**.

§ Table S5 Transition energy (ΔE), oscillating strength (f_0) and major molecular orbitals (MO) transition (>10%) obtained by CIS method for all the studied systems.

§ Table S6 Calculated α (a.u.) and β_0 values (a.u.) of all studied systems at (U)CAM-B3LYP/6−31+G(d) level

§ Table S7 Frequency-dependent first hyperpolarizabilities of the all studied systems.

§ Table S8 Calculated α (a.u.) and β_0 values (a.u.) of $B_{20}H_{26}$ (**1a**−**4a**) and $Li@B_{20}H_{26}$ (**1b**−**4b**) at (U)MP2/6−31+G(d) level in solution.

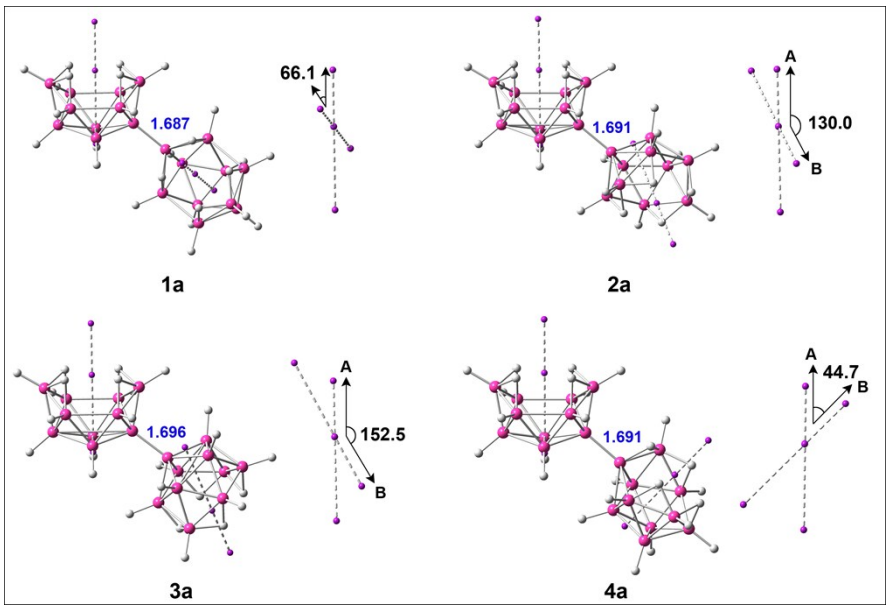

Figure S1 The connection B−B bond length and angel formed by axes of **A** and **B** cavities.

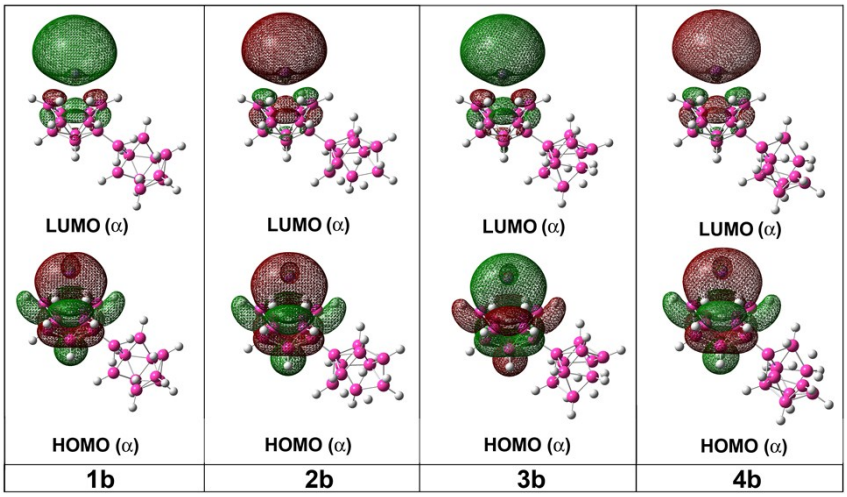

Figure S2 Frontier molecular orbitals involved major charge transfer transitions of **1b**−**4b**.

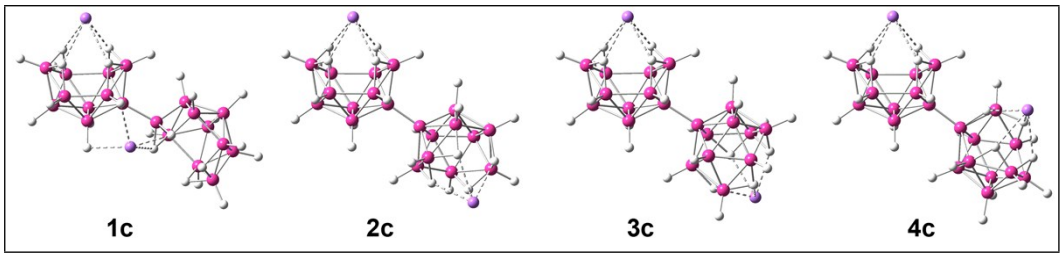

Figure S3 The optimized geometries of $Li_2@B_{20}H_{26}$ (**1c**−**4c**).

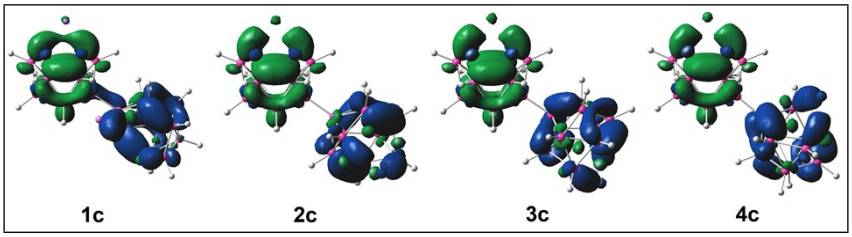

Figure S4 Spin density of **1c**−**4c** (Excess α-spin is visualized by blue regions whereas excess β-spin is green).

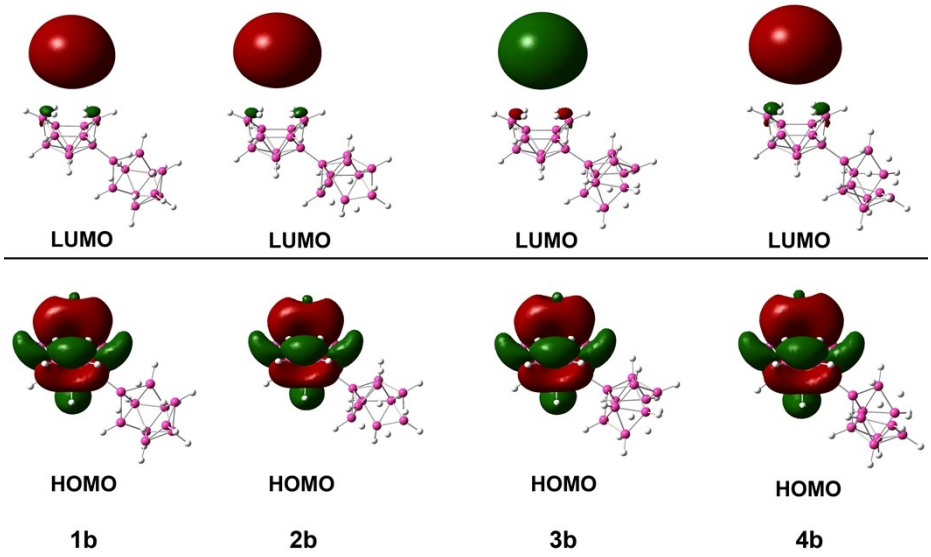

Figure S5 Frontier molecular orbitals (HOMO and LUMO) in solution by PCM approach of **1b-4b**.

Table S1 Selected bond length (Å) and dihedral angle (°)

	Exp.	MP2	B3LYP		Exp.	MP2	B3LYP
B1-B2	1.782	1.785	1.798	B1'-B2'	1.773	1.779	1.783
B1-B5	1.732	1.749	1.748	B1'-B5'	1.744	1.751	1.751
B2-B6	1.718	1.723	1.732	B2'-B6'	1.729	1.730	1.738
B5-B6	1.782	1.780	1.787	B5'-B6'	1.799	1.788	1.805
B5-H13	1.231	1.323	1.321	B5'-H13'	1.245	1.314	1.308
B6-H13	1.261	1.332	1.329	B6'-H13'	1.289	1.342	1.347
B5-B10	1.966	1.994	1.993	B5'-B10'	1.967	1.986	1.991
B2-B6'	1.679	1.687	1.698	B626'2'	-91.543	-98.845	-98.321

Table S2 B-B nature bond orbitals, occupancy, orbital coefficients and hybrids, and orbital type of systems **1a**−**4a**

system	natural bond orbital	occupancy	orbital coefficients and hybrid	orbital type
1a	B2-B6′	1.91093	$0.7171B2(sp^{2.37}) + 0.6970B6'(sp^{2.00})$	σ
2a	B2-B2′	1.89354	$0.7077B2(sp^{2.25}) + 0.7065B2'(sp^{2.17})$	σ
3a	B2-B3′	1.87868	$0.7096B2(sp^{2.31}) + 0.7046B3'(sp^{2.24})$	σ
4a	B2-B7′	1.90590	$0.7227B2(sp^{2.29}) + 0.6911B7'(sp^{1.97})$	σ

Table S3 NBO charge of all atoms for systems **1a**−**4a** (H11-H14 and H11'-H14' are bridging hydrogen atoms and other H atoms numbered are terminal hydrogen atoms)

	1a	**2a**	**3a**	**4a**		**1a**	**2a**	**3a**	**4a**
B1	-0.215	-0.219	-0.219	-0.214	H1	0.128	0.121	0.118	0.126
B2	-0.323	-0.256	-0.244	-0.318	H3	0.118	0.116	0.121	0.123
B3	-0.218	-0.220	-0.222	-0.215	H4	0.110	0.107	0.107	0.110
B4	-0.247	-0.247	-0.248	-0.247	H5	0.094	0.090	0.089	0.090
B5	-0.091	-0.104	-0.109	-0.099	H6	0.095	0.093	0.095	0.090
B6	-0.129	-0.126	-0.127	-0.140	H7	0.086	0.086	0.091	0.086
B7	-0.111	-0.108	-0.101	-0.105	H8	0.090	0.087	0.088	0.089
B8	-0.120	-0.119	-0.117	-0.119	H9	0.093	0.090	0.091	0.092
B9	-0.142	-0.147	-0.145	-0.143	H10	0.091	0.088	0.088	0.090
B10	-0.117	-0.118	-0.120	-0.119	H11	0.200	0.198	0.199	0.200
B1'	-0.231	-0.256	-0.241	-0.225	H12	0.201	0.198	0.199	0.200
B2'	-0.235	-0.219	-0.236	-0.239	H13	0.196	0.195	0.195	0.195
B3'	-0.230	-0.220	-0.223	-0.233	H14	0.195	0.195	0.195	0.195
B4'	-0.250	-0.104	-0.238	-0.247	H1'	0.119	0.121	0.108	0.122
B5'	-0.112	-0.126	-0.103	-0.077	H2'	0.106	0.116	0.118	0.107
B6'	-0.108	-0.108	-0.144	-0.130	H3'	0.118	0.107	0.104	0.120
B7'	-0.117	-0.247	-0.121	-0.123	H4'	0.106	0.090	0.091	0.107
B8'	-0.123	-0.118	-0.121	-0.124	H5'	0.089	0.093	0.091	0.086
B9'	-0.152	-0.118	-0.145	-0.147	H7'	0.084	0.086	0.087	0.086
B10'	-0.121	-0.147	-0.104	-0.104	H8'	0.085	0.087	0.087	0.090
					H9'	0.090	0.090	0.091	0.087
					H10'	0.086	0.088	0.090	0.088
					H11'	0.211	0.198	0.198	0.205
					H12'	0.210	0.198	0.195	0.195
					H13'	0.194	0.195	0.195	0.194
					H14'	0.195	0.195	0.198	0.194

Table S4 Selected optimized bond lengths (Å) of $B_{20}H_{26}$ and $Li@B_{20}H_{26}$ in gas and solution (values in parentheses).

bond length/distance	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
B7-B8 (B7'-B8')	1.989	1.861	1.992	1.867	1.993	1.869	1.989	1.864
	(1.989)	(1.851)	(1.992)	(1.854)	(1.993)	(1.855)	(1.988)	(1.853)
B5-B10(B5'-B10')	1.994	1.866	1.992	1.868	1.988	1.865	1.990	1.865
	(1.992)	(1.850)	(1.991)	(1.854)	(1.986)	(1.851)	(1.988)	(1.851)
B8-B9(B8'-B9')	1.781	1.848	1.780	1.847	1.780	1.848	1.781	1.848
	(1.780)	(1.831)	(1.780)	(1.835)	(1.779)	(1.832)	(1.780)	(1.833)
B6-B7(B6'-B7')	1.781	1.848	1.778	1.844	1.780	1.847	1.780	1.847
	(1.780)	(1.834)	(1.776)	(1.837)	(1.778)	(1.838)	(1.779)	(1.831)
B9-B10(B9'-B10')	1.781	1.853	1.781	1.851	1.781	1.848	1.781	1.851
	(1.779)	(1.838)	(1.780)	(1.839)	(1.780)	(1.832)	(1.780)	(1.838)
B5-B6(B5'-B6')	1.780	1.854	1.777	1.848	1.778	1.844	1.778	1.848
	(1.779)	(1.843)	(1.776)	(1.840)	(1.776)	(1.836)	(1.776)	(1.832)
B4-B9(B4'-B9')	1.725	1.752	1.723	1.751	1.723	1.752	1.725	1.752
	(1.725)	(1.748)	(1.723)	(1.746)	(1.723)	(1.745)	(1.725)	(1.749)
B2-B6(B2'-B6')	1.723	1.750	1.725	1.751	1.725	1.752	1.724	1.753
	(1.723)	(1.747)	(1.726)	(1.750)	(1.726)	(1.751)	(1.724)	(1.748)
B3-B4(B3'-B4')	1.777	1.779	1.779	1.780	1.779	1.780	1.778	1.779
	(1.777)	(1.777)	(1.779)	(1.778)	(1.778)	(1.778)	(1.777)	(1.777)
B2-B3(B2'-B3')	1.783	1.785	1.786	1.787	1.787	1.787	1.785	1.785
	(1.783)	(1.782)	(1.786)	(1.785)	(1.786)	(1.788)	(1.785)	(1.783)
B1-B4(B1'-B4')	1.779	1.781	1.780	1.781	1.780	1.781	1.779	1.781
	(1.779)	(1.779)	(1.779)	(1.779)	(1.779)	(1.778)	(1.778)	(1.780)
B1-B2(B1'-B2')	1.785	1.785	1.786	1.786	1.783	1.784	1.786	1.786
	(1.784)	(1.782)	(1.785)	(1.784)	(1.782)	(1.782)	(1.786)	(1.782)
B6-B9(B6'-B9')	3.587	3.468	3.587	3.478	3.587	3.477	3.583	3.471
	(3.584)	(3.444)	(3.586)	(3.452)	(3.586)	(3.456)	(3.582)	(3.448)
Li-B6(B6')	--	2.732	--	2.714	--	2.722	--	2.742
		(3.207)		(3.207)		(3.261)		(3.256)
Li-B9(B9')	--	2.725	--	2.733	--	2.746	--	2.716
		(3.096)		(3.096)		(3.011)		(3.117)
Li-μ-H11(H11')	--	2.129	--	2.118	--	2.145	--	2.144
		(2.498)		(2.480)		(2.626)		(2.503)
Li-μ-H12(H12')	--	2.123	--	2.133	--	2.168	--	2.128
		(2.555)		(2.555)		(2.624)		(2.589)
Li-μ-H13(H13')	--	2.181	--	2.171	--	2.159	--	2.156
		(2.448)		(2.448)		(2.464)		(2.712)
Li-μ-H14(H14')	--	2.177	--	2.152	--	2.140	--	2.175
		(2.409)		(2.375)		(2.454)		(2.574)

Table S5 Transition energy (ΔE), oscillating strength (f_0) and major molecular orbitals (MO) transition (>10%) obtained by CIS method for all the studied systems

system	transition	λ_{max}	ΔE	f_0	MO transition (%)
1a	$S_0 \rightarrow S_1$	216.7	5.72	0.0761	H-0→L+1 (48%) H-0→L+2 (25%) H-0→L+3 (12%)
	$S_0 \rightarrow S_2$	216.5	5.73	0.0910	H-1→L+0 (66%)
	$S_0 \rightarrow S_3$	196.8	6.30	0.0490	H-2→L+1 (29%) H-1→L+1 (16%) H-2→L+2 (14%)
2a	$S_0 \rightarrow S_1$	220.2	5.63	0.0971	H-0→L+0 (55%) H-1→L+1 (15%) H-1→L+3 (11%)
	$S_0 \rightarrow S_2$	218.3	5.68	0.0456	H-1→L+0 (42%) H-0→L+1 (22%) H-0→L+3 (16%)
	$S_0 \rightarrow S_3$	200.3	6.19	0.0380	H-2→L+0 (30%) H-1→L+0 (14%) H-3→L+0 (12%)
3a	$S_0 \rightarrow S_1$	218.3	5.68	0.0718	H-0→L+0 (32%) H-1→L+1 (27%) H-1→L+0 (13%)
	$S_0 \rightarrow S_2$	217.5	5.70	0.1032	H-1→L+0 (30%) H-0→L+1 (26%) H-0→L+0 (12%)
	$S_0 \rightarrow S_3$	195.9	6.33	0.0313	H-2→L+0(36%) H-4→L+1(13%)
4a	$S_0 \rightarrow S_1$	221.8	5.59	0.1149	H-0→L+1 (37%) H-0→L+0 (20%)
	$S_0 \rightarrow S_2$	217.9	5.69	0.1188	H-1→L+0 (38%) H-0→L+0 (21%) H-0→L+2(α) (15%)
	$S_0 \rightarrow S_3$	194.1	6.39	0.0229	H-4→L+0 (56%) H-4→L+2 (10%)

Table S6 Calculated α (a.u.) and β_0 values (a.u.) of all studied systems at (U)CAM-B3LYP/6−31+G(d) level

system	α	β_0
1a	247	97
2a	244	29
3a	244	132
4a	245	94
1b	290	11701
2b	269	3355
3b	295	16219
4b	294	14603
1c	378	29875
2c	364	17837
3c	366	11258
4c	361	55627

Table S7 Frequency-dependent first hyperpolarizabilities of the all studied systems

system	β_{MP2}^0	β_{HF}^0	β_{MP2}					
			EOPE	**SHG**	**EOPE**	**SHG**	**EOPE**	**SHG**
			1.064 μm		1.340 μm		1.910 μm	
1a	108	59	112	123	110	117	--	--
2a	53	17	56	62	56	59	--	--
3a	142	74	150	165	148	155	--	--
4a	128	58	135	148	132	139	--	--
1b	21761	21904	--	--	--	--	30139	89592
2b	7220	3976	--	--	--	--	8358	11808
3b	18878	40045	--	--	--	--	29870	526195
4b	23558	31806	--	--	--	--	35048	187959
1c	22673	17672	--	--	--	--	29827	69875
2c	5951	57105	--	--	--	--	9696	56887
3c	8434	35942	--	--	--	--	14086	103328
4c	108846	121944	--	--	--	--	207287	753745

Table S8 Calculated α (a.u.) and β_0 values (a.u.) of $B_{20}H_{26}$ (**1a**−**4a**) and $Li@B_{20}H_{26}$ (**1b**−**4b**) at (U)MP2/6−31+G(d) level in solution

	1a	**2a**	**3a**	**4a**	**1b**	**2b**	**3b**	**4b**
α	285	282	283	284	332	331	336	339
β_0	150	62	190	160	11559	11669	15059	16064