

Table S1 Longitudinal electronic first hyperpolarizability (β_L^e) of linear H-(BN) $_N$ -H chains as a function of Δr (Å) and N . These values have been obtained with the HF/6-31G method and are given in au. The extrapolated polymeric values per unit cell are given at the bottom of the table

$N/\Delta r$	0.00	0.02	0.04	0.08	0.12	0.16	0.20	0.24	0.28	0.32	0.36	0.40
1	59.6	58.5	57.4	55.2	53.0	50.8	48.7	46.5	44.4	42.3	40.3	38.2
2	323.7	299.7	277.5	237.7	203.5	174.4	149.4	128.2	110.2	94.9	81.9	70.8
3	816.4	726.8	646.7	510.9	402.2	315.6	246.8	192.4	149.8	116.5	90.6	70.4
4	1320.9	1150.8	1000.3	749.3	553.9	403.2	288.5	202.7	139.3	93.4	60.7	37.6
5	1676.9	1446.1	1239.4	891.6	620.9	415.4	264.0	156.0	81.5	32.0	0.5	-18.6
6	1895.8	1622.7	1373.2	946.0	611.7	361.6	183.4	63.0	-13.4	-58.0	-81.0	-90.2
7	2039.6	1728.4	1439.4	938.3	545.8	257.8	60.4	-64.3	-134.9	-167.9	-176.9	-172.0
8	2145.8	1793.9	1463.8	887.7	439.2	117.4	-93.4	-216.2	-275.2	-291.6	-282.5	-260.3
9	2229.6	1833.5	1459.9	806.8	303.0	-49.4	-269.3	-385.6	-428.6	-424.7	-394.6	-353.1
10	2297.0	1854.3	1435.4	703.6	145.1	-235.7	-461.3	-567.5	-591.2	-564.3	-511.2	-448.8
11	2351.6	1860.6	1395.2	583.7	-28.9	-436.1	-665.0	-758.4	-760.4	-708.6	-630.9	-546.5
12	2395.9	1855.8	1343.2	451.4	-214.8	-647.0	-877.1	-955.7	-934.3	-856.1	-752.9	-645.7
13	2432.2	1842.3	1282.0	309.5	-409.7	-865.7	-1095.6	-1157.9	-1111.7	-1006.1	-876.4	-745.9
14	2462.1	1821.9	1213.7	160.4	-611.4	-1090.3	-1318.9	-1363.7	-1291.7	-1157.8	-1001.2	-847.0
15	2486.9	1796.3	1140.0	5.7	-818.3	-1319.4	-1545.7	-1572.2	-1473.7	-1310.9	-1126.8	-948.6
16	2507.7	1766.5	1061.9	-153.3	-1029.3	-1552.0	-1775.3	-1782.8	-1657.1	-1465.0	-1253.2	-1050.6
17	2525.4	1733.3	980.4	-315.7	-1243.4	-1787.3	-2007.1	-1995.0	-1841.7	-1620.0	-1380.1	-1153.0
18	2540.5	1697.5	896.2	-480.9	-1460.1	-2024.8	-2240.6	-2208.5	-2027.2	-1775.5	-1507.4	-1255.7
19	2553.5	1659.6	809.8	-648.3	-1678.8	-2264.0	-2475.5	-2423.0	-2213.5	-1931.6	-1635.1	-1358.6
20	2564.8	1619.9	721.6	-817.4	-1899.1	-2504.6	-2711.5	-2638.3	-2400.4	-2088.1	-1763.0	-1461.7
∞	5 ± 7	-44 ± 4	-92 ± 3	-173 ± 3	-224 ± 3	-246 ± 2	-240 ± 1	-219 ± 2	-189 ± 2	-160 ± 3	-130 ± 1	-104 ± 1

Table S2 Longitudinal electronic first hyperpolarizability (β_L^e) of linear H-(BN) $_N$ -H chains as a function of Δr (Å) and N . These values have been obtained with the MP2/6-31G method and are given in au. The extrapolated polymeric values per unit cell are given at the bottom of the table

$N/\Delta r$	0.00	0.02	0.04	0.08	0.12	0.16	0.20	0.24	0.28	0.32	0.36	0.40
1	18	19	19	20	21	21	22	22	22	22	21	21
2	283	249	218	165	123	90	63	42	26	14	5	-2
3	1086	900	740	485	298	160	61	-9	-56	-87	-106	-115
4	2218	1777	1404	825	414	129	-64	-189	-263	-302	-316	-313
5	3176	2492	1910	997	357	-76	-352	-514	-594	-619	-608	-575
6	3785	2917	2160	952	103	-457	-794	-967	-1027	-1016	-959	-880
7	4159	3130	2215	732	-314	-985	-1360	-1521	-1539	-1467	-1352	-1214
8	4419	3226	2148	382	-857	-1626	-2020	-2149	-2106	-1964	-1773	-1567
9	4625	3252	2000	-62	-1494	-2350	-2752	-2833	-2714	-2486	-2213	-1933
10	4795	3230	1794	-575	-2202	-3141	-3535	-3556	-3349	-3028	-2666	-2308
11	4938	3171	1544	-1141	-2963	-3981	-4358	-4308	-4006	-3585	-3129	-2688
12	5056	3068	1259	-1747	-3764	-4851	-5210	-5083	-4679	-4122	-3598	-3074
13	5154	2949	947	-2385	-4598	-5752	-6084	-5873	-5363	-4726	-4072	-3461
14	5236	2812	613	-3046	-5454	-6673	-6972	-6675	-6055	-5306	-4551	-3852
15	5305	2690	263	-3726	-6329	-7610	-7878	-7486	-6752	-5891	-5032	-4245
16	5362	2531	-101	-4422	-7217	-8560	-8787	-8305	-7455	-6478	-5514	-4638
17	5411	2361	-476	-5129	-8119	-9519	-9706	-9129	-8162	-7068	-5999	-5033
18	5454	2185	-860	-5845	-9028	-10487	-10632	-9957	-8872	-7660	-6485	-5428
19	5489	2001	-1249	-6570	-9946	-11460	-11563	-10789	-9584	-8253	-6972	-5824
20	5520	1812	-1644	-7300	-10868	-12439	-12497	-11623	-10298	-8848	-7459	-6220
∞	-1 ± 7	-223 ± 15	-406 ± 6	-775 ± 26	-942 ± 12	-996 ± 12	-960 ± 20	-851 ± 10	-718 ± 10	-608 ± 10	-495 ± 8	-399 ± 3

Table S3 Evolution with oligomer size of the Δr at the center of H-(BN)_N-H oligomers optimized at different levels of theory. Values are given in Å

<i>N</i>	6-31G		6-311G**		<i>aug-cc-pVDZ</i>	
	RHF	MP2	RHF	MP2	RHF	MP2
3	0.1088	0.1213	0.1174	0.1171	0.1141	0.111
4	0.0903	0.1074	0.0975	0.1021	0.0946	0.0963
5	0.0744	0.0948	0.0804	0.0901	0.0780	
6	0.0632	0.0851	0.0681	0.0781		
7	0.0525	0.0748	0.0567	0.0676		
8	0.0447	0.0669	0.0482	0.0594		
9	0.0375	0.0588	0.0404	0.0514		
10	0.0320	0.0524	0.0347	0.0454		
11	0.0271	0.0462	0.0293			
12	0.0234	0.0412	0.0253			
13	0.0199	0.0368				
14	0.0174	0.0324				
15	0.0150	0.0287				
16	0.0131	0.0253				
17	0.0114	0.0228				
18	0.0101	0.0205				
19	0.0088					
20	0.0079					
21	0.0070					
22	0.0062					
23	0.0056					
24	0.0050					
25	0.0046					