Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C
This journal is © The Royal Society of Chemistry 2013

Photophysical properties of azaboradibenzo[6]helicene derivatives

Yanling Si[a] *and Guochun Yang**[b]

a. College of Resource and Environmental Science, Jilin Agricultural University, Changchun, 130118 Jilin, China

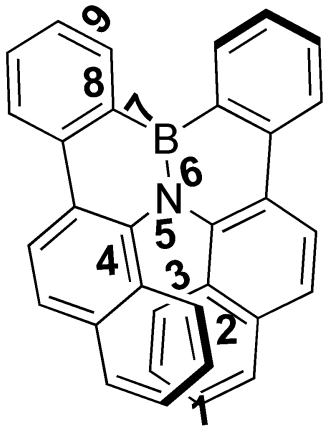
b. Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, 130024 Jilin, China.

E-mail:yanggc468@nenu.edu.cn

Contents

This journal is © The Royal Society of Chemistry 2013

Table S1. The main concerned bond length for compound **1** between experiment and calculation



Bond	B3LYP	B3LYP-D	B2PLYP-D	Experiment	Difference		
					B3LYP	B3LYP-D	B2PLYP-D
1	1.412	1.414	1.412	1.401	0.011	0.013	0.011
2	1.378	1.378	1.378	1.369	0.009	0.009	0.009
3	1.422	1.422	1.421	1.408	0.014	0.014	0.013
4	1.445	1.443	1.442	1.444	0.001	-0.001	-0.002
5	1.421	1.418	1.416	1.422	-0.001	-0.004	-0.006
6	1.451	1.448	1.447	1.431	0.020	0.017	0.016
7	1.546	1.544	1.543	1.548	-0.002	-0.004	-0.005
8	1.409	1.409	1.409	1.412	-0.003	-0.003	-0.003
9	1.390	1.391	1.390	1.386	0.004	0.005	0.004

Note: the difference is equal to calculation value minus experimental value

Table S2. Computed absorption wavelengths (nm) using the B3LYP functional at the different basis sets level for compound **1**

Basis set	Band 1	Band 2	Band 3
6-31G(d)	265.58	307.42	372.50
6-31+G(d)	265.50	313.06	376.86
6-31++G(d,p)	265.86	313.77	377.02
6-311++G(d,p)	266.74	315.37	378.82
6-311++G(2d,2p)	273.14	316.64	380.45
exp	252	310	373

This journal is © The Royal Society of Chemistry 2013

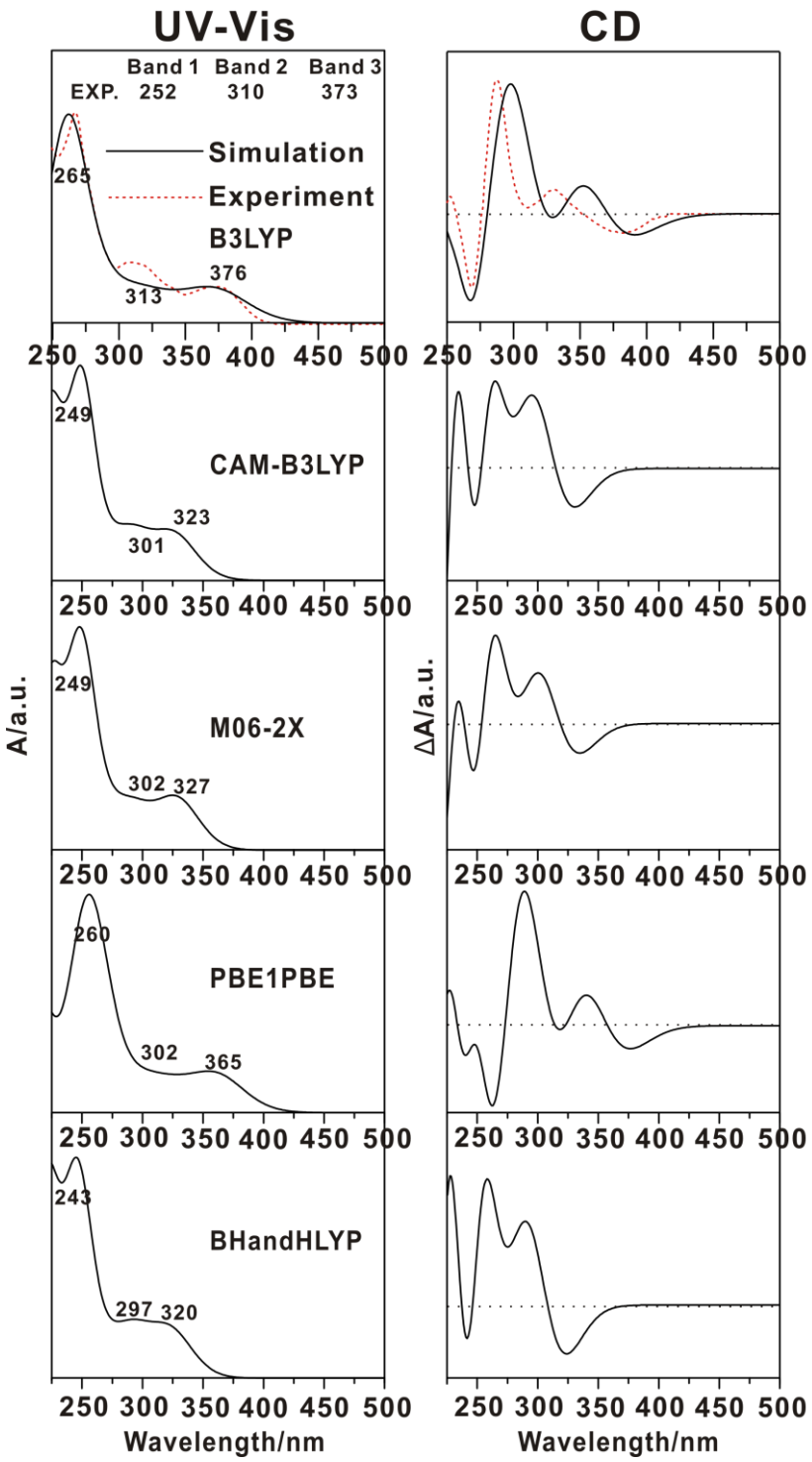


Figure S1. Calculated UV-Vis (left) and CD (right) spectra of compound **1** using five different DFT functionals.

This journal is © The Royal Society of Chemistry 2013

Table S3. Computed HOMO and LUMO energy levels and corresponding energy gaps (*E*g=LUMO-HOMO) in eV using different functionals at 6-31+G(d) basis set level for compound **1**

Functional	HOMO	LUMO	*E*g
B3LYP	-5.49	-1.66	3.83
PBE	-5.69	-1.55	4.14
M06-2X	-6.62	-0.90	5.72
CAM-B3LYP	-6.69	-0.55	6.13
BH&HLYP	-6.29	-0.62	5.67

Table S4. The calculated excitation energies, oscillator strengths and rotational strengths for compound **1** in the gas phase at the B3LYP/ 6-31+G(d) level.

states	eV	λ[a]	*f*[b]	Rlength[c]	Rvelocity[c]
1	3.2749	378.59	0.0798	-91.6153	-91.7452
2	3.2900	376.86	0.0936	-50.3600	-47.8887
3	3.5295	351.28	0.0806	228.1187	220.5851
4	3.5709	347.21	0.0152	1.3597	1.2798
5	3.7666	329.17	0.0846	-166.0210	-173.2402
6	3.7881	327.30	0.0085	-0.1802	-0.3735
7	3.9488	313.98	0.0015	-3.5842	-4.9601
8	3.9603	313.06	0.1140	17.0291	17.5108
9	4.1240	300.64	0.0500	258.6109	264.7077
10	4.1333	299.96	0.0034	-8.0858	-7.8244
11	4.1870	296.11	0.0004	-1.5663	-1.9728
12	4.2371	292.61	0.0725	203.2931	206.3888
13	4.3677	283.87	0.1427	-88.2433	-88.5035
14	4.3929	282.24	0.0343	74.7973	73.6017
15	4.4627	277.82	0.0113	-20.0280	-20.3495
16	4.5440	272.85	0.0389	146.8524	147.9948
17	4.5820	270.59	0.3381	-287.2126	-291.6210
18	4.5936	269.91	0.0035	17.5981	18.3334
19	4.6692	265.54	0.4272	-199.6715	-202.4535
20	4.7432	261.39	0.0965	-86.9053	-88.1921
21	4.8118	257.67	0.3390	271.7115	276.5727
22	4.8730	254.43	0.0015	5.8558	6.5696
23	4.8967	253.20	0.1109	23.4081	27.0172
24	4.9081	252.61	0.0006	-0.3464	-0.5764
25	4.9341	251.28	0.0486	8.0513	8.4629
26	4.9639	249.77	0.0984	-59.4499	-61.2829

This journal is © The Royal Society of Chemistry 2013

27	4.9735	249.29	0.0963	-148.8644	-152.4821
28	4.9867	248.63	0.0052	15.9670	17.4243
29	5.0607	244.99	0.0000	-0.7821	-0.3525
30	5.0923	243.48	0.0109	6.0671	8.7246
31	5.0929	243.44	0.0365	-164.2425	-172.1337
32	5.1214	242.09	0.0275	110.2489	114.0455
33	5.1517	240.67	0.0048	34.5240	38.8116
34	5.2099	237.98	0.0022	12.2194	14.8003
35	5.2290	237.11	0.0366	127.2723	130.9177
36	5.2511	236.11	0.0028	8.0441	8.2323
37	5.2683	235.34	0.0362	34.3041	35.9740
38	5.2699	235.27	0.0286	4.8582	5.0452
39	5.3002	233.92	0.0230	54.0860	55.6904
40	5.3020	233.85	0.0330	-45.4341	-47.0844
41	5.3383	232.26	0.0176	-6.7522	-7.1542
42	5.3408	232.14	0.0193	19.2419	19.0374
43	5.3546	231.54	0.0214	-20.5942	-21.3590
44	5.4102	229.17	0.0300	21.2778	22.5919
45	5.4298	228.34	0.0007	-1.4913	-1.4433
46	5.4627	226.97	0.0037	-11.6021	-11.2707
47	5.4742	226.49	0.0824	1.2008	1.2315
48	5.4836	226.10	0.0485	49.1023	49.5111
49	5.5017	225.36	0.0387	74.6276	78.2302
50	5.5094	225.04	0.0019	1.8799	1.7246
51	5.5293	224.23	0.1758	-250.6036	-259.9295
52	5.5400	223.80	0.0130	2.5683	2.5562
53	5.5413	223.74	0.0163	2.0705	3.3864
54	5.6111	220.96	0.0317	41.3472	43.0184
55	5.6145	220.83	0.0085	-14.8114	-16.3619
56	5.6614	219.00	0.0063	-41.6302	-43.2906
57	5.6827	218.18	0.0902	110.4852	113.5437
58	5.6980	217.59	0.0109	-36.4082	-36.6756
59	5.7100	217.14	0.0013	3.3983	3.9296
60	5.7212	216.71	0.0053	-10.6949	-10.2615
61	5.7253	216.56	0.0015	1.3249	1.2237
62	5.7424	215.91	0.0028	10.5607	10.0735
63	5.7631	215.13	0.0189	23.6458	24.2295
64	5.7849	214.32	0.0012	6.9698	7.0075
65	5.8139	213.26	0.0074	-7.7655	-8.9951
66	5.8224	212.94	0.0040	1.3564	1.3709
67	5.8319	212.60	0.0339	130.6848	137.7112
68	5.8331	212.55	0.0017	5.8493	7.0226
69	5.8351	212.48	0.0200	15.3023	15.3374
70	5.8545	211.78	0.0055	6.2730	4.7668

71	5.8804	210.84	0.0119	34.5659	36.1982
72	5.8838	210.72	0.1755	-353.5692	-366.3632
73	5.9109	209.76	0.0109	6.2792	6.2883
74	5.9423	208.65	0.0036	-1.7831	-1.8518
75	5.9443	208.58	0.0018	11.1553	11.3174
76	5.9594	208.05	0.0042	-24.0495	-22.2403
77	5.9686	207.73	0.0010	-5.0910	-5.0579
78	5.9803	207.32	0.0115	-29.4803	-31.7539
79	5.9939	206.85	0.0002	0.2275	1.2703
80	6.0287	205.66	0.0021	11.3892	11.9568
81	6.0305	205.59	0.0014	16.1910	16.8067
82	6.0463	205.06	0.0275	-39.0715	-39.1042
83	6.0492	204.96	0.0019	-9.3015	-9.3651
84	6.0708	204.23	0.0063	0.5767	-0.2502
85	6.0773	204.01	0.0000	-0.0028	0.1178
86	6.0848	203.76	0.0153	-17.2394	-17.5871
87	6.0882	203.65	0.0399	-9.4618	-10.5432
88	6.0915	203.54	0.0195	30.5674	33.2209
89	6.1104	202.91	0.0862	31.8055	31.7798
90	6.1423	201.85	0.1294	137.7118	141.4736
91	6.1444	201.78	0.0102	-9.9370	-10.1716
92	6.1730	200.85	0.0175	-29.8351	-29.5721
93	6.2075	199.73	0.0010	-3.6974	-3.3748
94	6.2144	199.51	0.0125	5.2249	5.5712
95	6.2222	199.26	0.0281	1.9157	1.7900
96	6.2285	199.06	0.0351	6.6910	6.8714
97	6.2592	198.08	0.0007	0.5308	0.4560
98	6.2700	197.74	0.0041	3.6471	3.4949
99	6.2854	197.26	0.0001	2.8559	3.6829
100	6.2863	197.23	0.0261	-32.6276	-33.4808
101	6.2868	197.21	0.0079	-6.5227	-6.5626
102	6.3071	196.58	0.0319	-5.4890	-5.2977
103	6.3077	196.56	0.0176	-14.6981	-15.4520
104	6.3313	195.83	0.0006	0.8834	0.7217
105	6.3465	195.36	0.0449	-24.7701	-25.2449
106	6.3627	194.86	0.0053	7.5183	7.6135
107	6.3736	194.53	0.0010	4.4952	4.0342
108	6.3923	193.96	0.0019	12.8309	14.6010
109	6.3925	193.95	0.0224	-8.2271	-8.4225
110	6.4068	193.52	0.0065	2.7858	3.6206
111	6.4210	193.09	0.0003	3.0413	3.4294
112	6.4259	192.95	0.0021	6.1682	7.0102
113	6.4340	192.70	0.0117	-17.9409	-18.4468
114	6.4446	192.39	0.0183	4.6233	3.3017

115	6.4548	192.08	0.0025	-23.6250	-23.8954
116	6.4636	191.82	0.0523	-28.5492	-30.6329
117	6.4802	191.33	0.0000	-0.3768	0.3005
118	6.4858	191.16	0.0004	-1.7297	-1.6651
119	6.5009	190.72	0.0203	5.3578	5.4267
120	6.5022	190.68	0.0412	24.5319	26.0090
121	6.5162	190.27	0.0093	-4.7037	-4.5560
122	6.5191	190.19	0.0755	1.7892	1.8256
123	6.5321	189.81	0.0000	0.2465	0.2026
124	6.5461	189.40	0.0103	-32.2695	-33.5374
125	6.5488	189.32	0.0245	51.8677	50.4166
126	6.5659	188.83	0.0099	-6.2922	-7.7872
127	6.5661	188.83	0.0101	1.8465	1.8964
128	6.5755	188.56	0.0027	4.4534	3.2429
129	6.5910	188.11	0.0093	3.6789	4.2241
130	6.6008	187.83	0.0440	32.9599	32.8860
131	6.6073	187.65	0.0012	1.4905	1.4942
132	6.6267	187.10	0.0100	-6.0440	-6.5151
133	6.6370	186.81	0.0456	95.1532	95.5948
134	6.6465	186.54	0.0519	-23.9829	-24.5051
135	6.6555	186.29	0.0093	-0.9863	-0.7300
136	6.6609	186.14	0.0002	-0.8659	-0.9187
137	6.6898	185.33	0.0342	-19.5344	-20.5403
138	6.6906	185.31	0.0080	-27.6266	-26.5278
139	6.6978	185.11	0.0297	0.8639	1.2405
140	6.7060	184.89	0.0203	-44.8926	-47.2244
141	6.7064	184.87	0.2907	-7.8371	-8.4558
142	6.7174	184.57	0.0189	15.9617	16.2264
143	6.7244	184.38	0.0013	-12.0082	-12.3936
144	6.7357	184.07	0.0019	4.4930	4.5574
145	6.7433	183.86	0.0018	4.7746	4.1061
146	6.7469	183.77	0.0000	0.0347	0.0259
147	6.7598	183.42	0.0001	1.6186	3.0656
148	6.7626	183.34	0.0245	-19.8113	-19.7327
149	6.7790	182.89	0.0924	6.7272	6.3382
150	6.7850	182.73	0.0344	4.3747	4.2810
151	6.7887	182.63	0.0135	3.6014	3.8811
152	6.7994	182.35	0.0089	1.3041	1.3546
153	6.8033	182.24	0.0006	-0.6593	-0.6070
154	6.8209	181.77	0.1064	-19.6097	-20.0434
155	6.8290	181.56	0.0007	-3.9212	-3.9308
156	6.8322	181.47	0.0362	-51.5340	-52.7377
157	6.8366	181.35	0.0065	24.5209	25.5917
158	6.8420	181.21	0.0093	1.5914	1.2487

159	6.8602	180.73	0.0030	8.1405	7.8293
160	6.8626	180.67	0.0198	2.0903	3.1269
161	6.8661	180.57	0.0021	-3.7896	-3.3867
162	6.8695	180.48	0.0078	-4.4436	-4.4698
163	6.8840	180.10	0.0223	-34.0906	-35.5441
164	6.8884	179.99	0.0000	0.7914	0.4040
165	6.8965	179.78	0.0068	-2.8554	-2.2760
166	6.9203	179.16	0.0016	-3.1915	-2.9811
167	6.9336	178.82	0.0008	-2.1207	-2.5619
168	6.9428	178.58	0.0083	0.1446	0.1462
169	6.9436	178.56	0.0054	11.7995	14.2441
170	6.9570	178.21	0.0016	-8.1981	-8.2391
171	6.9609	178.12	0.0091	-4.7140	-4.7022
172	6.9750	177.76	0.0003	-0.3729	-0.3593
173	6.9963	177.22	0.0045	-0.7897	-0.8001
174	7.0016	177.08	0.0132	16.1079	16.5575
175	7.0041	177.02	0.0030	-14.4608	-14.5767
176	7.0151	176.74	0.0015	-0.6850	-0.8429
177	7.0154	176.73	0.0186	14.3382	14.6385
178	7.0258	176.47	0.0044	9.0880	10.1530
179	7.0357	176.22	0.0056	20.6252	21.6164
180	7.0383	176.16	0.0059	1.1283	1.1893
181	7.0391	176.14	0.0050	14.5672	14.4888
182	7.0470	175.94	0.0096	1.6824	1.8553
183	7.0615	175.58	0.0168	-6.1915	-6.6387
184	7.0649	175.49	0.0000	0.4435	1.0901
185	7.0732	175.29	0.0393	70.3196	70.6962
186	7.0741	175.26	0.0140	-27.2450	-26.4415
187	7.0950	174.75	0.0395	-83.0053	-85.1133
188	7.1058	174.48	0.0266	11.0036	10.1417
189	7.1081	174.43	0.0053	-6.4901	-7.2228
190	7.1177	174.19	0.0078	-5.7856	-6.7660
191	7.1177	174.19	0.0032	16.9962	12.8217
192	7.1285	173.93	0.0093	8.3775	8.7249
193	7.1337	173.80	0.0014	-8.4367	-7.8456
194	7.1384	173.69	0.0076	3.6018	3.6597
195	7.1444	173.54	0.0023	0.2110	0.6457
196	7.1459	173.50	0.0212	-6.4407	-6.2953
197	7.1513	173.37	0.0360	21.1653	22.5504
198	7.1578	173.22	0.0197	-6.4004	-5.9324
199	7.1658	173.02	0.0000	0.9469	1.0455
200	7.1741	172.82	0.0010	1.5413	1.7219

[a]λin nm. [b] Oscillator Strengths. [c] R values (in 10^{-40} esu^2cm^2) using the velocity-gauge representation and length-gauge representation of the electric dipole operator.

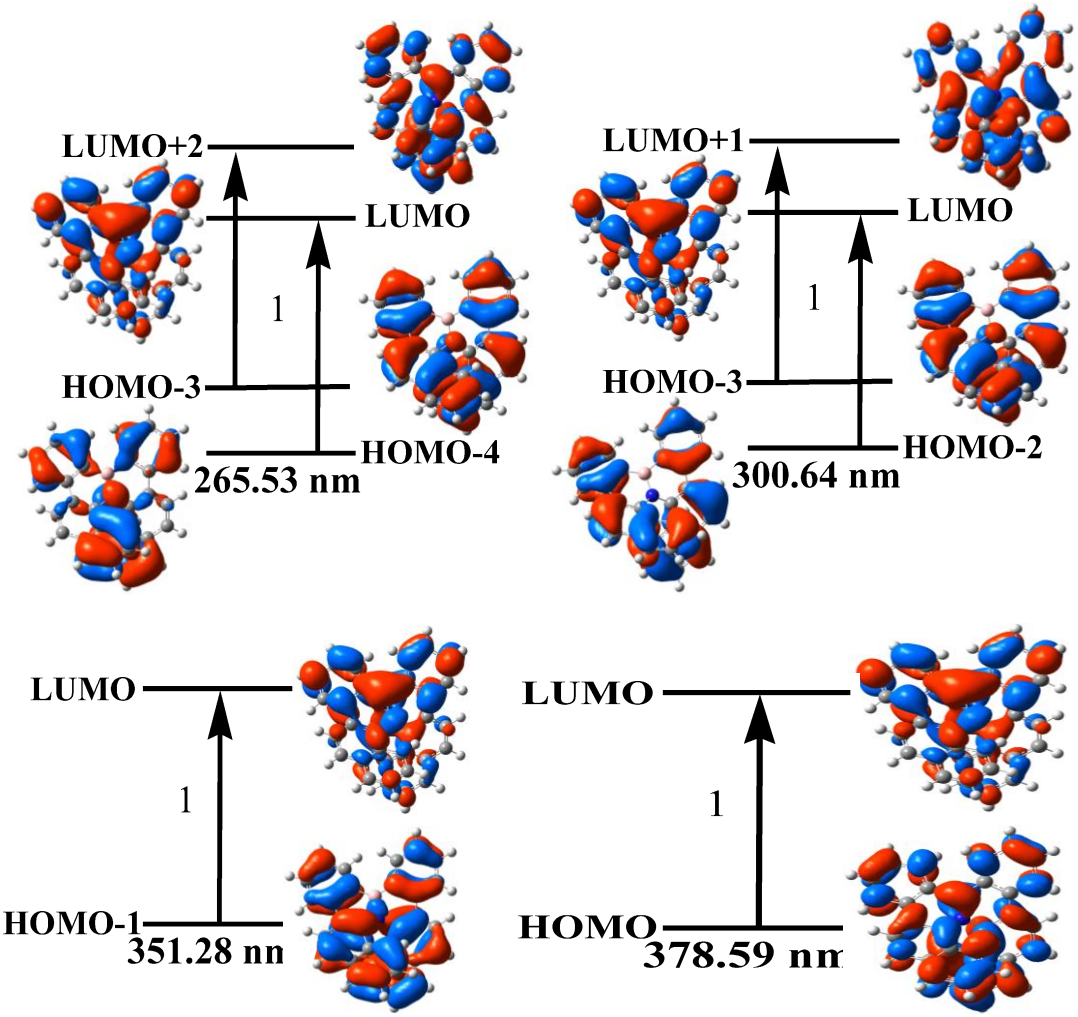
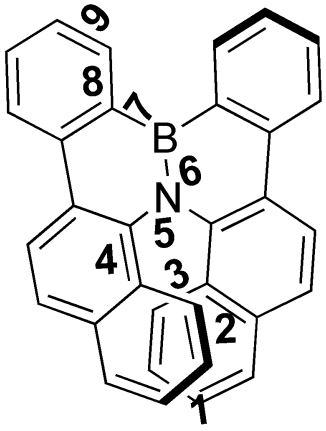


Figure S2. Molecular orbitals involved into the main CD transition of compounds **1**

TABLE S5. Selected bond lengths (Å) for compound **1**: ground states (S_0) and first exited states (S_1)

Bond	S_0	S_1	Difference
1	1.412	1.410	0.002
2	1.378	1.381	-0.003
3	1.422	1.426	-0.004
4	1.445	1.421	0.024
5	1.421	1.442	-0.021
6	1.451	1.514	**-0.063**
7	1.546	1.506	**0.040**
8	1.409	1.421	-0.012
9	1.390	1.381	0.009



This journal is © The Royal Society of Chemistry 2013

Table S6. Calculated bond-length changes (in Å) upon oxidation (CBLA, going from the neutral to the cation state) and reduction (ABLA, going from the neutral to the anion state) of the studied compounds.

Bonds	ABLA	CBLA
1	-0.003	0.006
2	0.000	-0.007
3	-0.003	0.007
4	-0.005	0.001
5	0.005	-0.006
6	**0.011**	**0.020**
7	-0.008	**-0.021**
8	**-0.053**	**-0.034**
9	**0.020**	**0.010**
10	**-0.012**	0.004
11	0.006	-0.005
12	**-0.011**	0.004
13	-0.001	-0.005
14	0.000	0.004
15	0.002	**-0.010**
16	0.000	0.010
17	0.000	-0.001
18	-0.005	-0.008
19	0.003	0.001
20	0.001	0.003
21	-0.002	-0.005

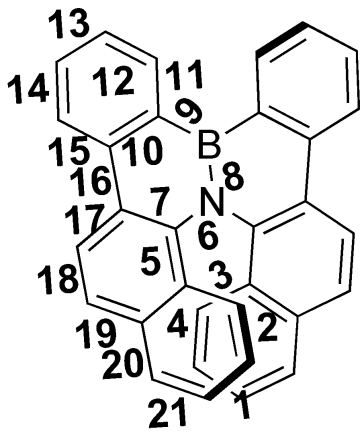


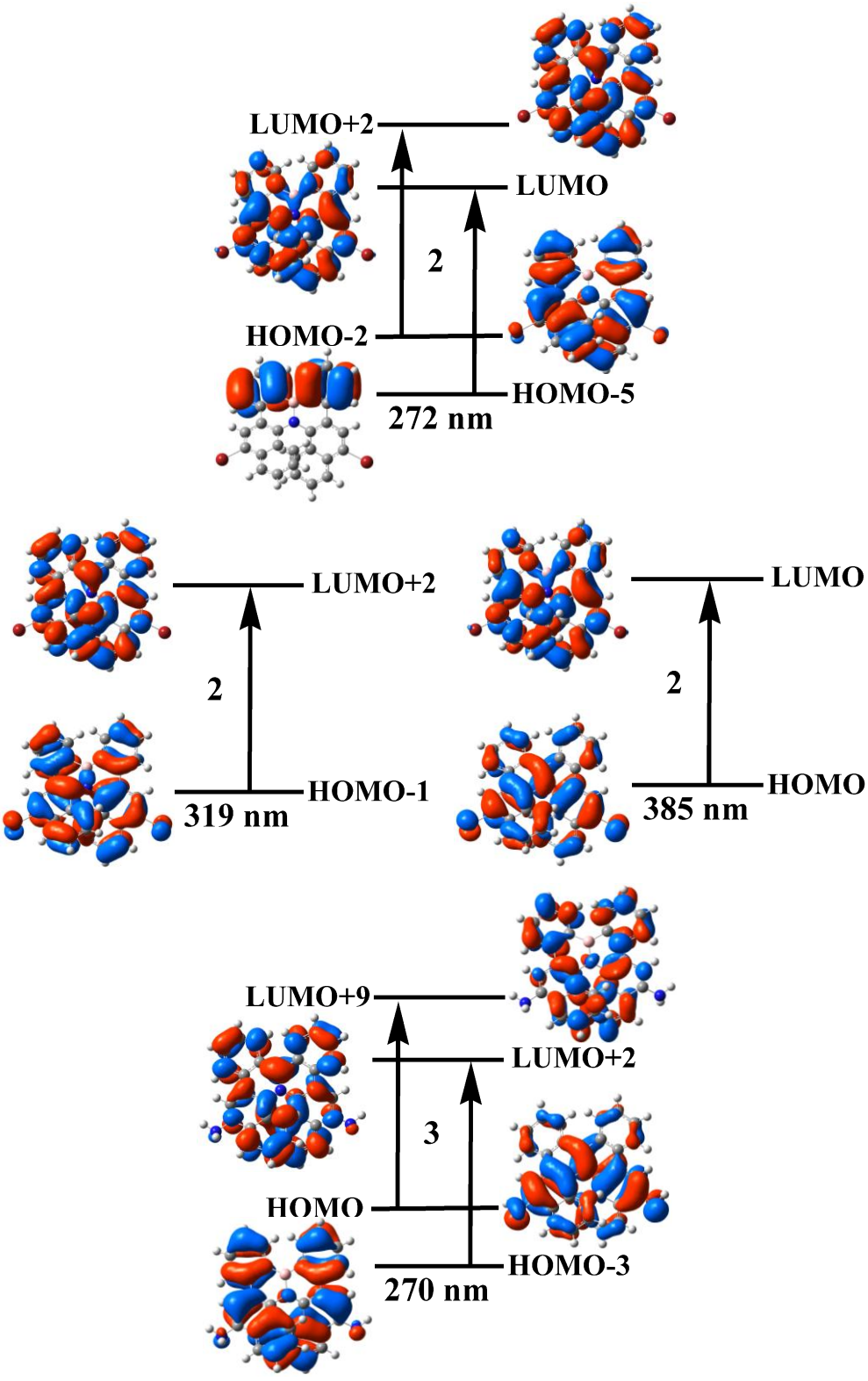
Table S7. Computed absorption wavelengths (λ in nm), oscillator strengths (*f*), and major contribution for the studied compounds **2-5**

Compound	λ	*f*	major contribution
1	265.53(252)	0.487	HOMO-4→LUMO(57%)
			HOMO-3→LUMO +2(19%)
	313.06(313)	0.114	HOMO-1→LUMO+2(88%)
			HOMO-3→LUMO+1(4%)
	376.85(373)	0.094	HOMO→LUMO+1(86%)
			HOMO-1→LUMO(9%)
2	272.02	0.376	HOMO-5→LUMO(23%)
			HOMO-2→LUMO+2(21%)

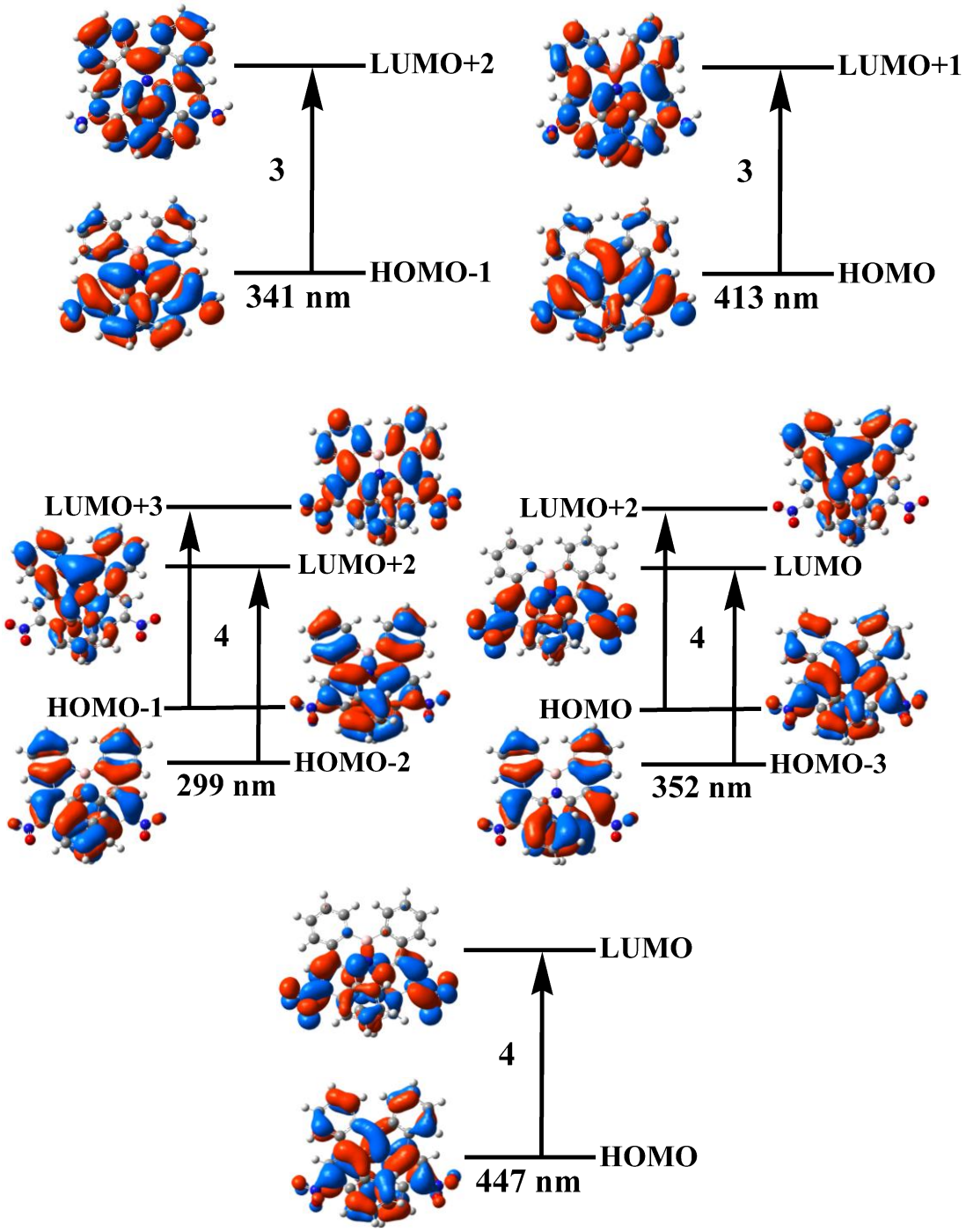
	318.82	0.153	HOMO-1→LUMO+2(89%)
	385.05	0.153	HOMO→LUMO(91%)
3	269.98	0.369	HOMO→LUMO+9(30%)
			HOMO-3→LUMO+2(21%)
	341.41	0.126	HOMO-1→LUMO+2(93%)
	413.15	0.147	HOMO→LUMO+1(92%)
4	298.67	0.129	HOMO-2→LUMO+2(32%)
			HOMO-1→LUMO+3(41%)
	352.23	0.119	HOMO→LUMO+2(74%)
			HOMO-3→LUMO(16%),
	446.99	0.2476	HOMO→LUMO(98%)
5	302.13	0.157	HOMO-2→ LUMO+1(49%)
			HOMO-1→ LUMO+3(27%)
	402.57	0.140	HOMO-1→LUMO(52%)
			HOMO→LUMO+1(42%)
	511.73	0.093	HOMO→LUMO(98%)

Table S8. Computed HOMO and LUMO energy level and corresponding energy gaps (*Eg*=LUMO-HOMO) for compounds **2-5**

Compound	HOMO	LUMO	*Eg*
1	-5.49	-1.66	3.83
2	-5.74	-1.99	3.76
3	-4.95	-1.52	3.43
4	-6.36	-3.15	3.20
5	-5.50	-2.65	2.85


LUMO+2
LUMO
2
HOMO-2
HOMO-5
272 nm
LUMO+2
LUMO
2
2
HOMO-1
HOMO
319 nm
385 nm
LUMO+9
LUMO+2
3
HOMO
HOMO-3
270 nm

This journal is © The Royal Society of Chemistry 2013



This journal is © The Royal Society of Chemistry 2013

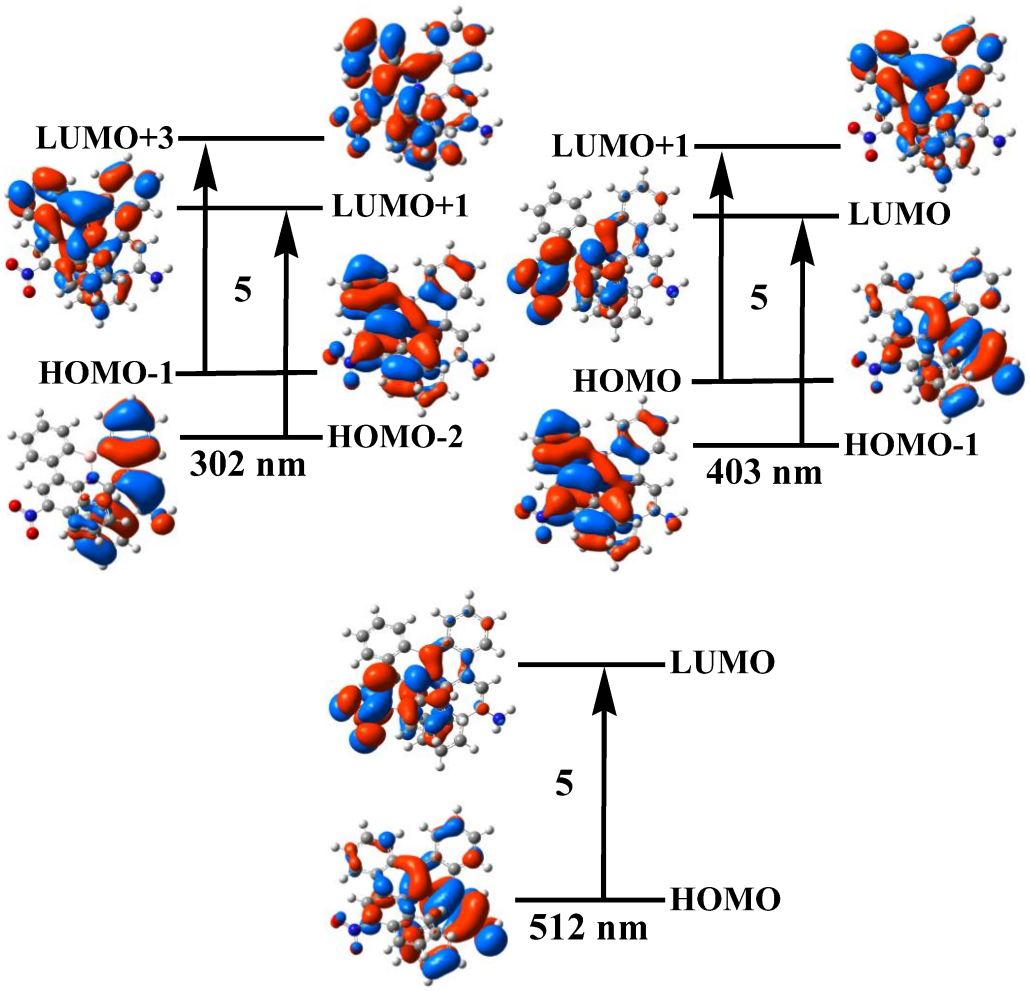


Figure S3. Molecular orbital isosurfaces involved in the main electron transitions of compounds **2-5** at the TDB3LYP/6-31+G(d) level of theory.

This journal is © The Royal Society of Chemistry 2013

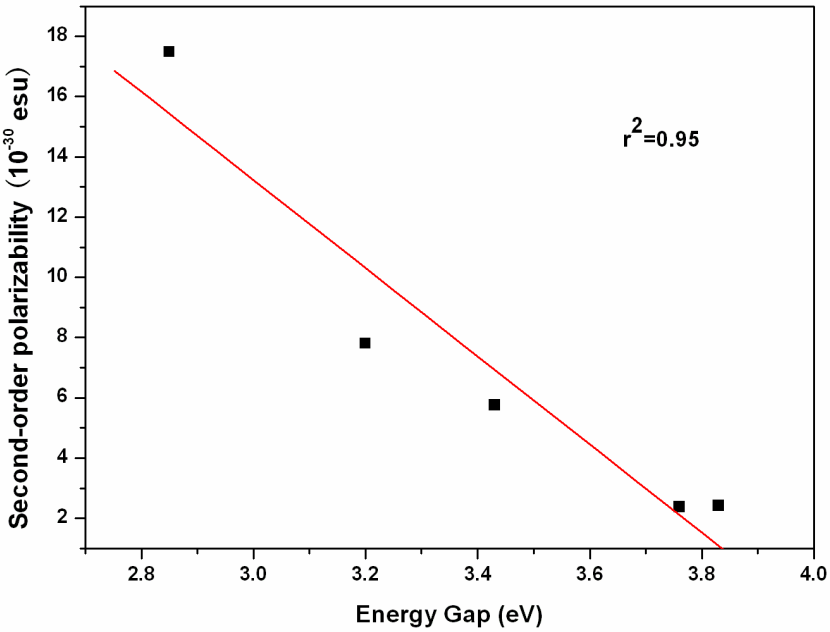


Figure S4. Dependence of the second-order NLO value and energy gap

Table S9. Cartesian Coordinates of compound **1** at B3LYP/6-31G(d,p) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			x	y	z
1	7	0	0.799752	-0.000025	5.997001
2	5	0	2.250676	-0.000023	5.997009
3	6	0	2.906900	1.362282	6.320473
4	6	0	0.131201	0.827401	6.938962
5	6	0	2.079867	2.392387	6.845199
6	6	0	0.733230	2.038473	7.318554
7	6	0	4.218124	1.690456	5.921452
8	1	0	4.843976	0.925293	5.474240
9	6	0	-1.074864	0.382081	7.599522
10	6	0	-1.594224	-0.937806	7.492955
11	1	0	-1.070516	-1.675489	6.900737
12	6	0	-2.744726	-1.312586	8.152426
13	1	0	-3.106375	-2.332063	8.057516
14	6	0	-3.450536	-0.388956	8.953416
15	1	0	-4.364566	-0.690800	9.456085
16	6	0	-2.955218	0.884439	9.113166
17	1	0	-3.463402	1.598855	9.755468
18	6	0	-1.756846	1.291300	8.471873

19	6	0	-1.186300	2.564851	8.736269
20	1	0	-1.703022	3.244423	9.407966
21	6	0	0.031943	2.897453	8.214494
22	1	0	0.492173	3.833690	8.507300
23	6	0	2.588256	3.702221	6.939568
24	1	0	1.959794	4.509941	7.298328
25	6	0	3.889536	3.991579	6.548578
26	1	0	4.259161	5.010232	6.626214
27	6	0	4.714510	2.983101	6.039094
28	1	0	5.726808	3.213069	5.720085
29	6	0	2.906911	-1.362313	5.673501
30	6	0	0.131216	-0.827433	5.055017
31	6	0	2.079890	-2.392408	5.148738
32	6	0	0.733253	-2.038488	4.675387
33	6	0	4.218141	-1.690486	6.072504
34	1	0	4.843985	-0.925331	6.519741
35	6	0	-1.074844	-0.382094	4.394467
36	6	0	-1.594217	0.937781	4.501108
37	1	0	-1.070521	1.675431	5.093379
38	6	0	-2.744716	1.312586	3.841647
39	1	0	-3.106376	2.332054	3.936612
40	6	0	-3.450509	0.388993	3.040599
41	1	0	-4.364538	0.690857	2.537939
42	6	0	-2.955181	-0.884390	2.880786
43	1	0	-3.463355	-1.598777	2.238445
44	6	0	-1.756812	-1.291276	3.522069
45	6	0	-1.186258	-2.564814	3.257626
46	1	0	-1.702970	-3.244361	2.585895
47	6	0	0.031980	-2.897435	3.779403
48	1	0	0.492217	-3.833656	3.486562
49	6	0	2.588292	-3.702233	5.054322
50	1	0	1.959840	-4.509947	4.695531
51	6	0	3.889575	-3.991591	5.445302
52	1	0	4.259211	-5.010237	5.367629
53	6	0	4.714539	-2.983122	5.954821
54	1	0	5.726839	-3.213091	6.273821