Supporting Information: A systematic analysis of excitonic properties to seek optimal singlet fission: the BN-substitution patterns in tetracene

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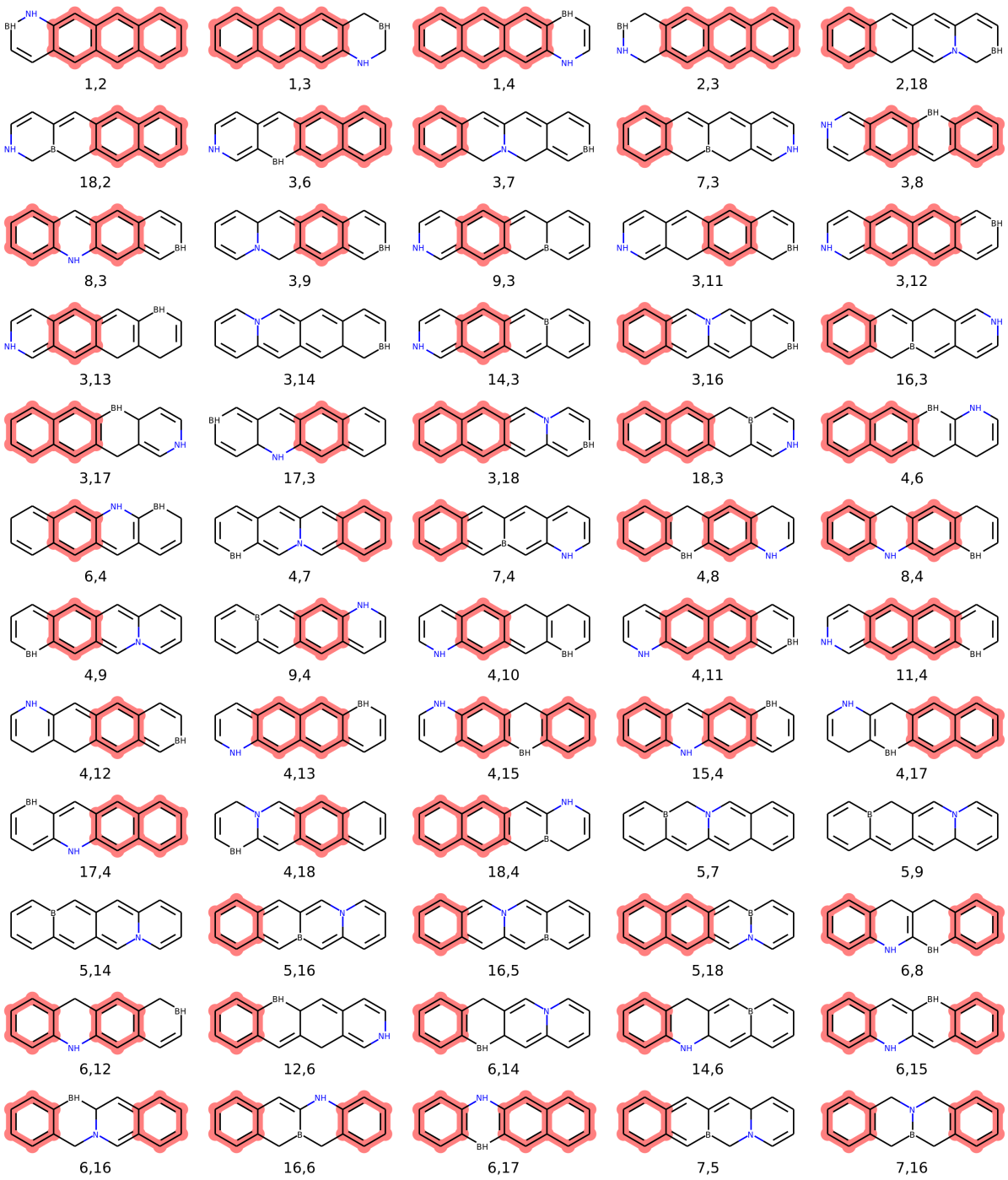

Figure S1: Chemical structures of the BN-doping configurations for tetracene. The fused hexagon rings that satisfy the Clar sextet rule of $4n + 2$ π-electrons are highlighted in red.

Table S1: B,N distances (in Å), vertical excitation energies $\Delta E(S_1, T_1, T_2)$ relative to the ground-state S_0 (in eV) and oscillator strength for S_0-S_1 transitions (f^{osc}) calculated for the series of BN-doped tetracene molecules using the CAS(12,12)/NEVPT2 approach. Rows highlighted in red (yellow) indicate the BN-tetracene molecules exhibiting exoergic (slight isoergic, SFC1 $<$ 0.25 eV) singlet fission condition (SFC).

B,N	$d_{B,N}$	$E_{tot}(S_0)$	$\Delta E(S_1)$	f^{osc}	$\Delta E(T_1)$	$\Delta E(T_2)$	SFC1	SFC2
1,2	1.4154	-18922.809	3.177	0.115	2.116	3.328	1.055	0.905
2,3	1.4572	-18921.993	2.079	0.044	0.945	2.397	-0.189	-0.507
5,18	1.4898	-18922.275	2.553	0.060	1.320	2.952	0.087	-0.312
7,16	1.4991	-18921.876	2.893	0.017	1.813	2.225	0.733	1.401
18,2	2.4564	-18921.049	2.461	0.021	1.275	2.646	0.088	-0.097
1,3	2.4882	-18921.178	2.791	0.068	1.324	2.261	-0.143	0.386
7,5	2.4948	-18921.058	2.624	0.039	1.640	2.498	0.657	0.783
5,7	2.4992	-18921.046	2.546	0.070	1.761	2.614	0.977	0.909
18,4	2.4993	-18921.169	2.045	0.040	1.142	2.487	0.238	-0.204
16,6	2.5021	-18921.466	2.365	0.032	1.655	2.112	0.945	1.198
4,6	2.5037	-18921.163	1.932	0.025	1.121	2.567	0.311	-0.324
6,8	2.5057	-18921.140	1.371	0.008	0.732	2.979	0.093	-1.516
2,18	2.5103	-18920.718	2.377	0.056	1.378	2.633	0.379	0.122
6,4	2.5118	-18921.045	1.803	0.022	1.026	2.492	0.249	-0.441
6,16	2.5475	-18921.089	2.229	0.036	1.758	2.089	1.287	1.427
4,18	2.5639	-18920.909	1.925	0.066	1.187	2.535	0.448	-0.161
18,3	2.8118	-18921.060	1.957	0.048	0.954	2.625	-0.048	-0.717
1,4	2.8523	-18921.675	3.407	0.082	1.926	3.382	0.444	0.469
6,17	2.8548	-18922.466	3.439	0.062	2.714	3.636	1.989	1.792
5,16	2.8769	-18920.797	2.747	0.036	1.552	2.800	0.357	0.303
16,5	2.8956	-18920.730	2.723	0.039	1.615	2.808	0.507	0.421
3,18	2.9136	-18920.543	1.812	0.046	0.959	2.558	0.106	-0.639
7,4	3.7643	-18920.522	1.868	0.019	1.202	2.176	0.535	0.227
3,6	3.7829	-18921.631	2.433	0.056	2.140	2.665	1.847	1.616
4,17	3.8130	-18921.285	2.037	0.075	1.843	2.705	1.648	0.980
4,7	3.8181	-18920.330	1.569	0.022	1.107	2.163	0.646	0.052
6,15	3.8303	-18921.576	1.959	0.089	1.847	3.357	1.734	0.336
17,4	3.8466	-18921.240	1.994	0.115	1.785	2.599	1.577	0.972
17,3	4.2531	-18920.834	1.650	0.067	0.984	2.561	0.318	-0.592
14,6	4.255	-18921.221	1.804	0.020	1.249	1.896	0.694	0.602
3,17	4.2870	-18920.875	1.987	0.068	1.162	2.653	0.337	-0.329
6,14	4.3470	-18920.817	1.624	0.028	1.269	1.857	0.914	0.680
7,3	4.8975	-18920.621	1.930	0.047	1.545	1.718	1.161	1.373
5,9	4.9304	-18920.587	2.036	0.024	1.663	2.169	1.290	1.157

4,8	4.9413	-18920.392	0.643	0.032	0.400	2.351	0.157	-1.551
3,7	4.9430	-18920.182	1.792	0.079	1.641	1.765	1.491	1.518
8,4	4.9685	-18920.194	0.191	0.009	0.127	2.110	0.063	-1.856
16,3	5.0892	-18920.701	2.060	0.026	1.223	2.555	0.386	-0.109
5,14	5.1365	-18920.857	2.230	0.107	1.840	2.309	1.450	1.371
3,16	5.1567	-18920.412	1.840	0.019	1.228	2.546	0.615	-0.090
4,15	5.7601	-18920.855	1.189	0.080	0.972	2.711	0.756	-0.766
15,4	5.7860	-18920.798	1.259	0.093	0.939	2.744	0.619	-0.865
3,8	6.2054	-18920.892	1.520	0.079	1.354	2.181	1.188	0.526
9,4	6.2200	-18920.417	1.370	0.067	1.168	1.714	0.967	0.623
4,9	6.2292	-18919.733	1.087	0.027	1.024	1.733	0.960	0.315
8,3	6.2374	-18920.710	1.897	0.102	1.439	2.318	0.981	0.560
6,12	6.4928	-18911.352	0.789	0.037	0.482	2.278	0.176	-1.314
12,6	6.5138	-18920.279	0.858	0.007	0.602	2.131	0.346	-0.926
9,3	7.3444	-18920.047	1.369	0.014	1.065	1.849	0.760	0.280
4,10	7.3862	-18919.785	0.405	0.022	0.104	2.181	-0.196	-1.972
3,9	7.3882	-18919.898	1.277	0.043	1.111	1.907	0.945	0.315
14,3	7.4787	-18920.279	1.482	0.080	1.534	1.956	1.585	1.111
3,14	7.5235	-18920.037	1.477	0.044	1.419	2.030	1.360	0.807
4,13	7.9999	-18919.889	1.221	0.084	0.553	2.567	-0.114	-1.460
11,4	8.6428	-18920.177	0.972	0.069	0.731	1.940	0.491	-0.477
4,11	8.6925	-18919.947	1.280	0.120	0.809	2.042	0.338	-0.424
4,12	8.8309	-18919.804	0.716	0.042	0.378	1.917	0.039	-1.161
12,4	8.8686	-18919.807	0.441	0.000	0.285	1.805	0.129	-1.234
3,11	9.8024	-18919.745	0.963	0.008	0.688	2.130	0.413	-0.754
3,12	9.9095	-18920.258	1.289	0.103	1.030	2.114	0.771	-0.054

Table S2: Vertical excitation energies ΔE(S_1, T_1, T_2) relative to the ground-state S_0 (in eV) and oscillator strength for S_0-S_1 transitions (f^{osc}) calculated for the series of BN-doped tetracene molecules using the CAS(8,8)/MR-CISD+Q approach. Rows highlighted in red (yellow) indicate the BN-tetracene molecules exhibiting exoergic (slight isoergic, SFC1 $<$ 0.25 eV) singlet fission condition (SFC).

B,N	$\Delta E(S_1^{Pople})$	$\Delta E(S_1^{CI})$	f^{osc}	$\Delta E(T_1^{Pople})$	$\Delta E(T_1^{CI})$	$\Delta E(T_2^{Pople})$	$\Delta E(T_2^{CI})$	SFC1	SFC2
1,2	3.3615	4.1830	0.030	1.9591	2.2327	3.2266	3.8419	0.557	0.692
2,3	2.5452	2.8505	0.095	0.9283	1.4024	2.4350	2.2848	-0.689	-0.578
5,18	3.0726	3.6334	0.102	1.3885	0.9413	3.1390	3.0815	-0.296	-0.362
7,16	3.1927	3.2575	0.024	1.6811	2.4936	2.1235	2.5372	0.169	1.239
18,2	2.4445	2.3982	0.038	1.2268	0.9914	2.5513	2.5220	0.009	-0.098
1,3	2.9441	3.3670	0.064	1.2117	1.6152	2.2746	2.2042	-0.521	0.149
7,5	2.6790	2.7398	0.029	1.5159	2.0944	2.4280	2.8314	0.353	0.604

5,7	2.5711	2.8513	0.073	1.6768	2.1261	2.5942	2.6951	0.782	0.759
18,4	2.1791	2.3501	0.052	1.1331	0.8554	2.4137	2.5417	0.087	-0.147
16,6	2.3130	2.4996	0.070	1.5447	1.4090	2.0020	2.3907	0.776	1.087
4,6	1.7336	1.6917	0.018	0.8549	1.1092	2.2045	2.9572	-0.024	-0.495
6,8	1.4335	1.5832	0.011	0.6757	0.3495	2.7916	2.9061	-0.082	-1.440
2,18	2.3245	2.3981	0.069	1.2926	1.0819	2.5621	2.6124	0.261	0.023
6,4	1.5290	1.7739	0.014	0.9483	0.6366	2.2875	2.6753	0.368	-0.391
6,16	2.1901	2.5121	0.087	1.6696	1.6245	1.9661	2.4127	1.149	1.373
4,18	2.0239	2.3227	0.076	1.1609	0.9252	2.4552	2.5899	0.298	-0.133
18,3	2.4249	2.5758	0.078	1.0760	0.4011	2.8348	2.6573	-0.273	-0.683
1,4	2.9074	4.5885	0.130	1.9437	1.9823	3.3470	3.7517	0.980	0.540
6,17	3.0740	4.5200	0.099	2.7217	3.1508	3.7455	4.0787	2.369	1.698
5,16	2.9828	3.4898	0.061	1.5399	1.5219	2.8746	3.1177	0.097	0.205
16,5	2.9206	3.4318	0.054	1.5972	1.7043	2.8123	3.1126	0.274	0.382
3,18	2.2955	2.3011	0.062	1.1254	0.4145	2.8135	2.6585	-0.045	-0.563
7,4	1.8255	2.2558	0.027	1.1452	0.8099	2.2545	1.9729	0.465	0.036
3,6	2.7426	3.8808	0.059	2.3241	3.0539	2.5308	3.6487	1.906	2.117
4,17	1.9262	2.6059	0.112	2.0801	2.6339	2.5595	2.5583	2.234	1.601
4,7	1.6096	2.0942	0.027	1.1260	0.9930	2.2427	1.9282	0.642	0.009
6,15	2.1331	2.4161	0.148	1.9880	1.5891	3.3135	2.9616	1.843	0.663
17,4	1.8475	2.8249	0.187	1.7346	2.1697	2.3954	3.1654	1.622	1.074
17,3	1.7202	1.7644	0.049	0.8261	0.4870	2.5080	2.8904	-0.068	-0.856
14,6	1.7323	2.2625	0.021	1.0890	0.9641	1.7611	2.6606	0.446	0.417
3,17	1.7171	2.0814	0.047	1.0385	0.2783	2.6865	2.6701	0.360	-0.609
6,14	1.6141	2.2213	0.027	1.1083	1.0758	1.8344	2.4713	0.602	0.382
7,3	1.8079	1.8077	0.067	1.2906	1.3711	1.6914	1.8007	0.773	0.890
5,9	2.0867	2.2926	0.019	1.5692	1.5059	2.0842	2.8117	1.052	1.054
4,8	0.6373	1.0544	0.057	0.3524	0.0324	2.2341	2.4334	0.067	-1.529
3,7	1.6960	1.8639	0.109	1.2749	1.6215	1.7261	1.9067	0.854	0.824
8,4	0.3914	0.4012	0.011	0.0773	-0.0379	1.9933	2.1963	-0.237	-1.839
16,3	2.1614	2.6079	0.030	1.2032	1.3836	2.4178	2.7829	0.245	-0.011
5,14	2.4684	2.6459	0.055	1.7568	2.8359	2.0895	2.7072	1.045	1.424
3,16	1.9711	2.3749	0.026	1.2071	1.3592	2.4650	2.6044	0.443	-0.051
4,15	1.4001	2.1432	0.190	1.0845	0.8837	2.7297	2.8876	0.769	-0.561
15,4	1.4700	2.1484	0.182	0.9987	1.1516	2.6689	2.9485	0.527	-0.671
3,8	1.7999	2.5857	0.195	1.3691	1.6071	2.2428	3.0960	0.938	0.495
9,4	1.3755	1.8744	0.099	1.0869	1.6849	1.5028	2.0029	0.798	0.671
4,9	1.2961	1.8028	0.094	1.0127	1.4475	1.6052	2.1352	0.729	0.420
8,3	1.7067	2.8519	0.332	1.4589	1.2139	2.2584	2.9487	1.211	0.659
6,12	0.8587	0.7135	0.034	0.2713	0.1486	2.1324	2.2335	-0.316	-1.590
12,6	0.7508	0.8390	0.007	0.3761	0.1716	2.0110	2.4817	0.001	-1.259
9,3	1.2550	1.3244	0.010	0.8482	0.6557	1.7115	1.9204	0.441	-0.015
4,10	0.6228	0.8347	0.070	0.0782	-0.0606	2.0123	2.3509	-0.466	-1.856
3,9	1.2500	1.3480	0.028	0.8460	0.7622	1.6944	1.8321	0.442	-0.002
14,3	1.8733	2.2167	0.132	1.5426	1.7243	1.9009	1.9668	1.212	1.184
3,14	1.8563	2.1266	0.111	1.4055	1.5706	1.8058	2.4095	0.955	1.005

4,13	1.1712	1.8479	0.177	0.6233	0.5219	2.3911	2.8790	0.075	-1.144
11,4	1.3528	1.9661	0.199	0.7598	1.0682	2.1369	2.4755	0.167	-0.617
4,11	1.3268	2.3529	0.236	0.7606	0.8865	1.8033	3.0435	0.194	-0.282
4,12	0.7119	1.2021	0.110	0.2122	0.1398	1.8774	2.3849	-0.288	-1.453
12,4	0.0937	0.5329	0.007	-0.0573	-0.0395	1.5414	1.8836	-0.208	-1.656
3,11	0.6038	0.4739	0.019	0.2170	-0.0388	1.6796	2.2907	-0.170	-1.245
3,12	1.5850	2.5408	0.291	0.9590	1.5038	2.2794	2.3853	0.333	-0.361

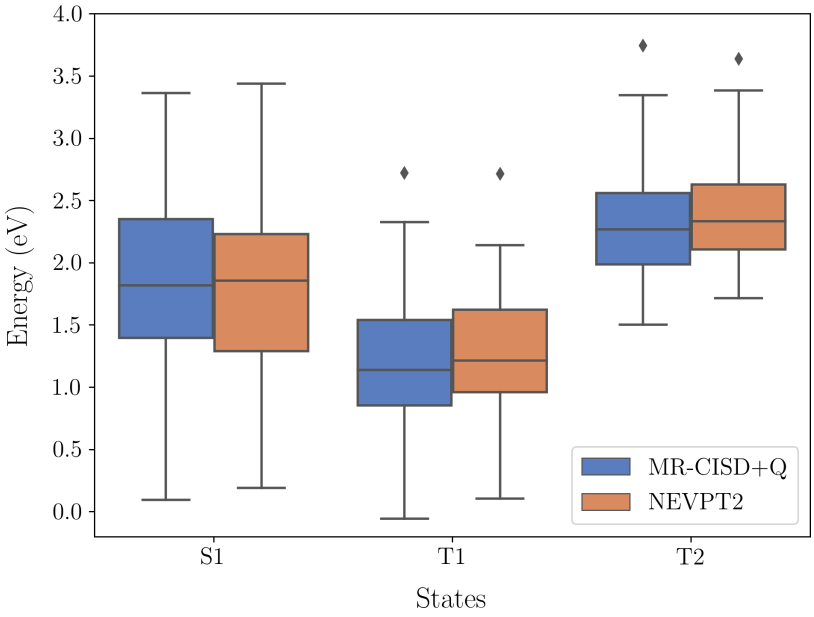

Figure S2: Box plot comparing the statistical distribution of the most relevant excited state energies $\Delta E(S_1, T_1, T_2)$ for singlet fission calculated using both NEVPT2 and MR-CISD+Q (Pople's correction) methods.

Table S3: B,N distances (in Å), vertical ionization potential and electron affinity, and binding energy of the singlet and triplet excitons (in eV) calculated for the series of BN-doped tetracene molecules using the CAS(12,12)/NEVPT2 approach.

B,N	$d_{B,N}$	IP	EA	E^s_{bin}	E^t_{bin}
1,2	1.4154	7.26940	0.73864	3.35383	4.41458
2,3	1.4572	6.29797	1.26088	2.95770	4.09177
5,18	1.4898	6.30721	1.32375	2.43051	3.66341
7,16	1.4991	7.01678	0.79948	3.32421	4.40412
18,2	2.4564	6.29716	0.94354	2.89257	4.07907
1,3	2.4882	6.54350	1.31800	2.43494	3.90164
7,5	2.4948	6.78450	0.81866	3.34198	4.32562
5,7	2.4992	6.91849	1.10139	3.27139	4.05582

18,4	2.4993	6.61639	1.08300	3.48837	4.39165
16,6	2.5021	7.00685	1.18880	3.45303	4.16327
4,6	2.5037	6.12741	0.49805	3.69711	4.50792
6,8	2.5057	6.07729	1.52284	3.18370	3.82279
2,18	2.5103	6.74986	1.30341	3.06956	4.06874
6,4	2.5118	6.57212	1.31646	3.45296	4.23001
6,16	2.5475	6.42995	0.72381	3.47734	3.94804
4,18	2.5639	6.21981	1.27784	3.01655	3.75525
18,3	2.8118	6.29970	1.03430	3.30852	4.31101
1,4	2.8523	6.79062	0.86298	2.52064	4.00200
6,17	2.8548	7.25931	0.60519	3.21552	3.94011
5,16	2.8769	6.54105	0.78032	3.01404	4.20903
16,5	2.8956	6.83840	1.06565	3.05022	4.15808
3,18	2.9136	6.43673	1.36218	3.26211	4.11524
7,4	3.7643	6.64010	1.19086	3.58096	4.24750
3,6	3.7829	5.83810	0.55663	2.84817	3.14121
4,17	3.8130	6.71819	0.66425	4.01695	4.21129
4,7	3.8181	5.54276	2.05819	1.91526	2.37709
6,15	3.8303	6.37103	1.09715	3.31447	3.42718
17,4	3.8466	6.44700	1.57522	2.87816	3.08641
17,3	4.2531	6.64628	1.65573	3.34034	4.00634
14,6	4.2546	7.17047	1.43616	3.93047	4.48563
3,17	4.2870	5.92199	0.73380	3.20078	4.02586
6,14	4.3470	6.27300	0.88816	3.76114	4.11619
7,3	4.8975	6.46082	0.61345	3.91778	4.30193
5,9	4.9304	6.79807	0.96546	3.79690	4.16986
4,8	4.9413	5.75284	1.34821	3.76209	4.00495
3,7	4.9430	6.36562	1.39447	3.17963	3.32968
8,4	4.9685	5.59500	1.81926	3.58450	3.64877
16,3	5.0892	6.36870	1.07819	3.23080	4.06747
5,14	5.1365	7.36825	0.80969	4.32894	4.71869
3,16	5.1567	6.01054	1.29983	2.87029	3.48290
4,15	5.7601	5.50482	1.75390	2.56216	2.77871
15,4	5.7860	6.04613	1.90953	2.87715	3.19737
3,8	6.2054	5.77054	0.78684	3.46375	3.62980
9,4	6.2200	6.55026	1.59265	3.58752	3.78929
4,9	6.2292	5.81941	1.57262	3.15953	3.22302
8,3	6.2374	6.60463	1.66760	3.04012	3.49812
6,12	6.4928	6.02164	1.84852	3.38456	3.69072
12,6	6.5138	5.99149	1.13531	3.99780	4.25375
9,3	7.3444	6.56975	1.50301	3.69746	4.00196

4,10	7.3862	5.50992	2.07471	3.03030	3.33099
3,9	7.3882	6.34030	1.31290	3.75002	3.91630
14,3	7.4787	6.37327	1.73373	3.15736	3.10588
3,14	7.5235	5.78582	1.49784	2.81073	2.86948
4,13	7.9999	5.58590	2.02209	2.34248	3.01036
11,4	8.6428	5.62171	1.95582	2.69414	2.93456
4,11	8.6925	5.66947	1.84090	2.54901	3.01963
4,12	8.8309	5.94434	1.90071	3.32721	3.66569
12,4	8.8686	4.84848	2.08981	2.31738	2.47355
3,11	9.8024	5.58329	1.63255	2.98781	3.26281
3,12	9.9095	6.15461	1.46698	3.39816	3.65741

Table S4: B,N distances and root-mean square electron-hole separation ($d_{B,N}$ and d_{exc} in Å), promotion number p, single-excitation character Ω and participation ratios of the natural transition orbitals PR_{NTO} calculated for the series of BN-doped tetracene molecules using the CAS(8,8)/MR-CISD method.

B,N	$d_{B,N}$	d_{exc}	p	Ω	PR_{NTO}
1,2	1.4154	3.882	1.11256	0.700	1.759
2,3	1.4572	4.523	1.64033	0.533	1.090
5,18	1.4898	3.889	1.52620	0.607	1.124
7,16	1.4991	3.733	1.61777	0.452	1.451
18,2	2.4564	4.071	1.21117	0.572	1.408
1,3	2.4882	4.038	1.52692	0.459	1.210
7,5	2.4948	3.999	1.21817	0.612	1.577
5,7	2.4992	3.750	1.22638	0.633	1.391
18,4	2.4993	3.534	1.32284	0.566	1.252
16,6	2.5021	3.576	1.34729	0.585	1.194
4,6	2.5037	4.178	1.30738	0.685	1.088
6,8	2.5057	3.686	1.18126	0.699	1.123
2,18	2.5103	3.897	1.20790	0.603	1.321
6,4	2.5118	4.433	1.32258	0.686	1.089
6,16	2.5475	3.892	1.28828	0.639	1.174
4,18	2.5639	3.816	1.27746	0.605	1.227
18,3	2.8118	3.927	1.47539	0.594	1.117
1,4	2.8523	4.109	1.15528	0.776	1.218
6,17	2.8548	3.612	1.22177	0.755	1.272

5,16	2.8769	3.689	1.35044	0.647	1.150
16,5	2.8956	3.944	1.38494	0.666	1.110
3,18	2.9136	3.741	1.46554	0.607	1.108
7,4	3.7643	4.005	1.45169	0.596	1.120
3,6	3.7829	3.883	1.15777	0.735	1.496
4,17	3.8130	3.754	1.34823	0.744	1.059
4,7	3.8181	4.142	1.42450	0.661	1.086
6,15	3.8303	4.893	1.34936	0.763	1.037
17,4	3.8466	3.603	1.33520	0.739	1.057
17,3	4.2531	5.169	1.22042	0.685	1.127
14,6	4.2546	4.433	1.19974	0.681	1.111
3,17	4.2870	4.606	1.23308	0.709	1.110
6,14	4.3470	4.019	1.17460	0.717	1.094
7,3	4.8975	4.142	1.24263	0.587	1.267
5,9	4.9304	4.056	1.09748	0.706	1.250
4,8	4.9413	4.620	1.42756	0.642	1.109
3,7	4.9430	4.189	1.24592	0.623	1.184
8,4	4.9685	4.009	1.36211	0.641	1.104
16,3	5.0892	3.709	1.48300	0.595	1.101
5,14	5.1365	3.935	1.27757	0.688	1.197
3,16	5.1567	4.192	1.45411	0.655	1.077
4,15	5.7601	4.238	1.55547	0.648	1.062
15,4	5.7860	4.073	1.55646	0.617	1.065
3,8	6.2054	4.647	1.52827	0.645	1.056
9,4	6.2200	5.365	1.47865	0.624	1.057
4,9	6.2292	4.676	1.50019	0.632	1.054
8,3	6.2374	5.508	1.48929	0.655	1.064
6,12	6.4928	5.093	1.31442	0.645	1.108
12,6	6.5138	4.258	1.29743	0.685	1.095
9,3	7.3444	4.342	1.21424	0.688	1.112
4,10	7.3862	5.878	1.46462	0.598	1.146
3,9	7.3882	4.229	1.33999	0.669	1.082
14,3	7.4787	4.400	1.44896	0.646	1.068
3,14	7.5235	4.377	1.47762	0.642	1.051
4,13	7.9999	6.155	1.58664	0.578	1.112
11,4	8.6428	4.985	1.60767	0.592	1.089

4,11	8.6925	5.676	1.58020	0.569	1.103
4,12	8.8309	5.678	1.47709	0.602	1.149
12,4	8.8686	4.604	1.29302	0.648	1.114
3,11	9.8024	5.028	1.44810	0.622	1.103
3,12	9.9095	4.866	1.51159	0.631	1.070

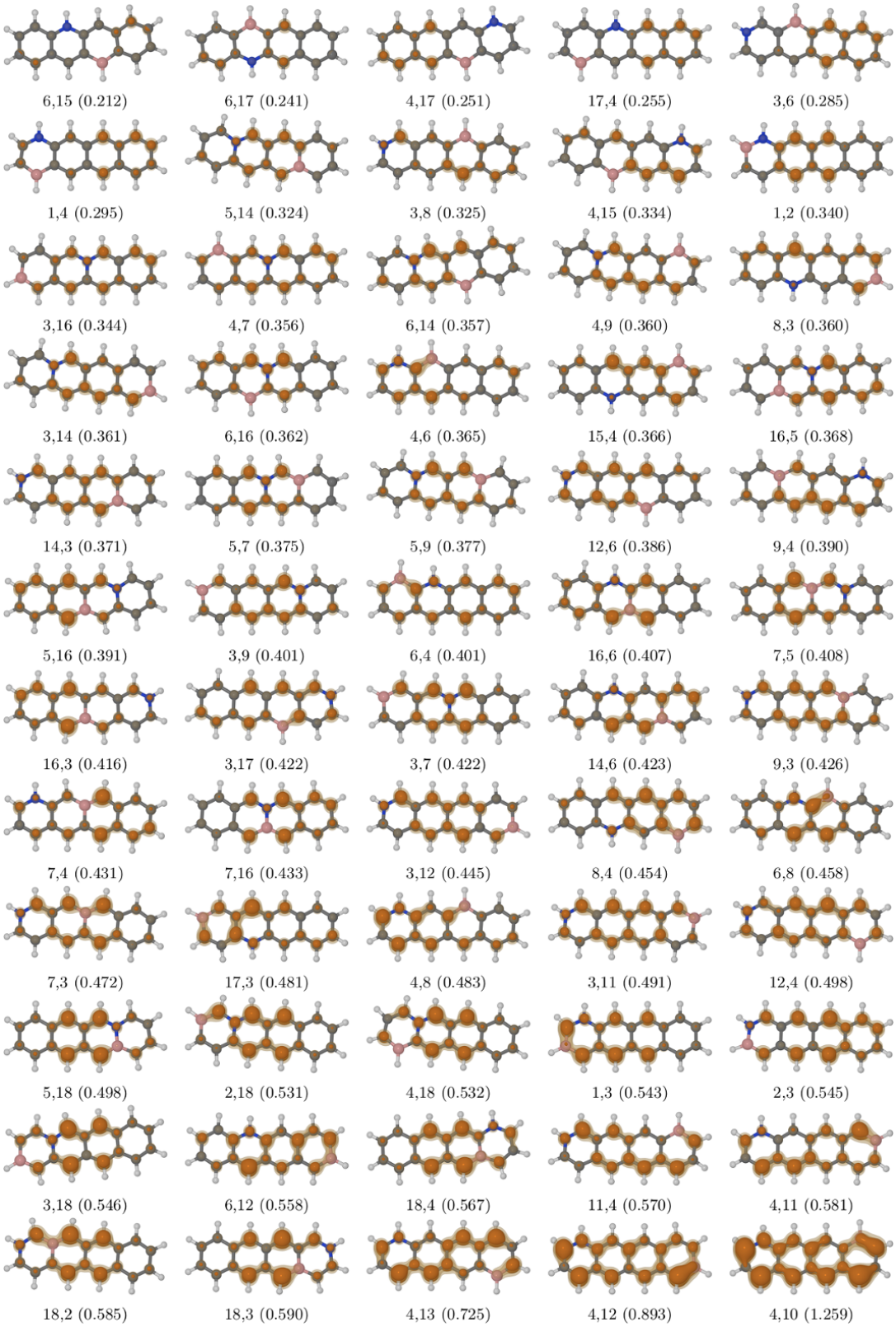

Figure S3: Density of unpaired electrons for the singlet ground-state of BN-tetracene molecules. The number of effectively unpaired electrons, N_U, is given in parentheses.