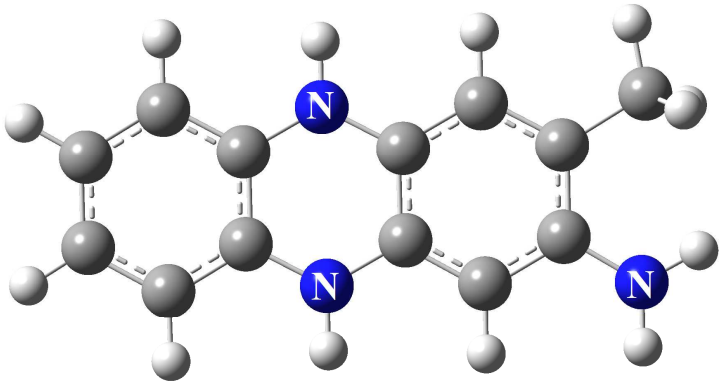
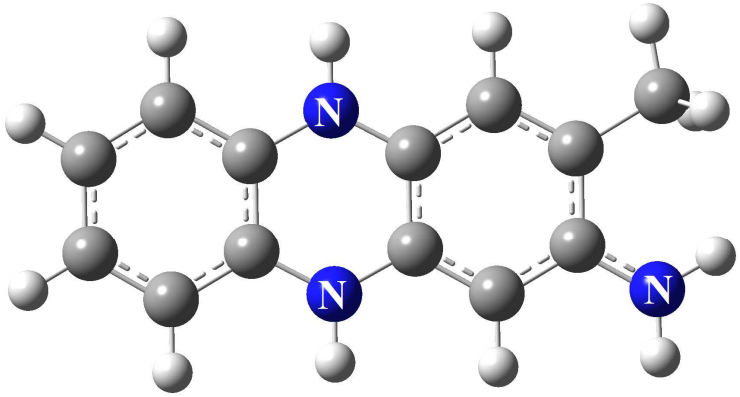
Supporting information

Structural and Spectroscopic Properties of Homo- and Co-oligomers of *o*-Phenylenediamine and *o*-Toluidine: Theoretical Insights Compared with Experimental Data

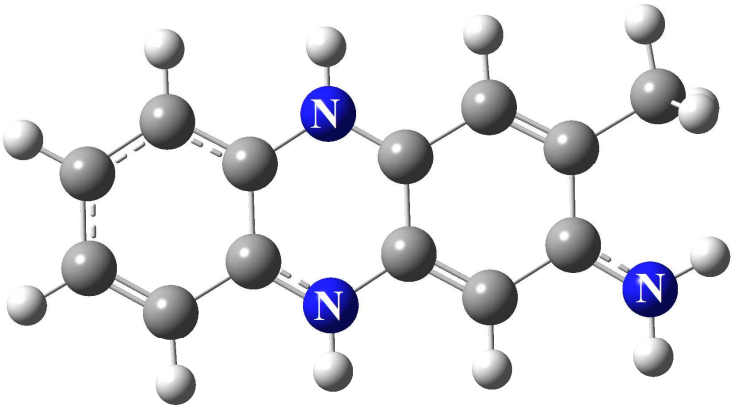
S1



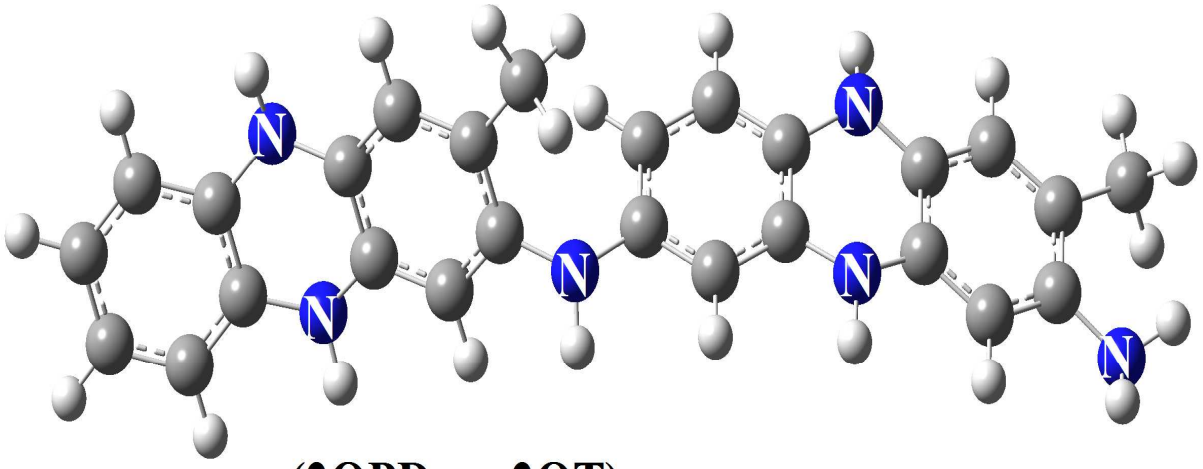
(OPD-co-OT)



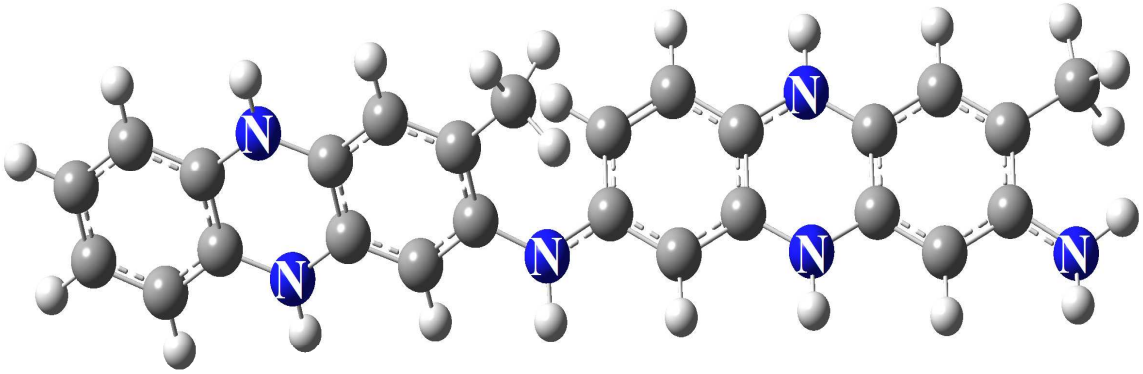
(OPD-co-OT)$^{+}$



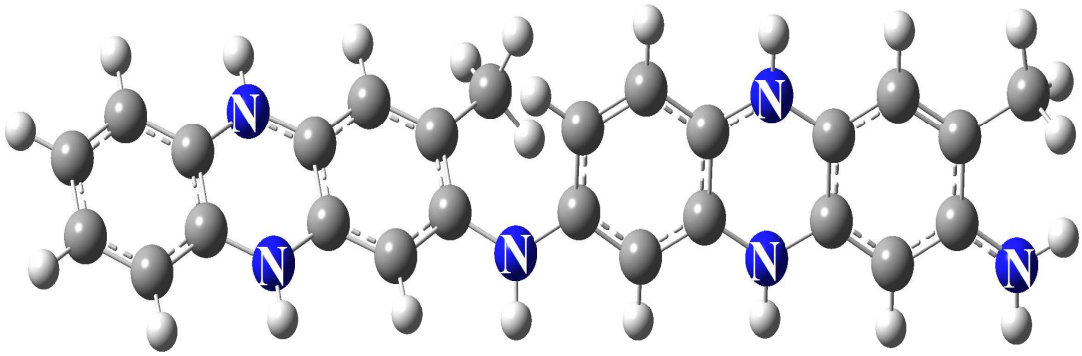
(OPD-co-OT)$^{2+}$



(2OPD-co-2OT)



$(2OPD\text{-}co\text{-}2OT)^{+}$



$(2OPD\text{-}co\text{-}2OT)^{2+}$

(OPD-co-OT)
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-0.151716	0.444423	0.081572
2	6	0	1.263863	0.390121	0.094821
3	6	0	1.997658	1.567281	-0.015984
4	6	0	1.353037	2.807207	-0.140697
5	6	0	-0.034524	2.862099	-0.154108
6	6	0	-0.782624	1.681334	-0.043031
7	1	0	3.084573	1.514697	-0.004868
8	1	0	1.945346	3.713421	-0.225945
9	1	0	-0.549627	3.813534	-0.250325
10	1	0	-1.869984	1.719770	-0.053106
11	6	0	-0.327676	-4.441141	0.556707
12	6	0	1.077934	-4.484789	0.568850
13	6	0	1.809103	-3.284635	0.456024
14	6	0	1.168222	-2.057287	0.332798
15	6	0	-0.240322	-2.003944	0.319813
16	6	0	-0.953712	-3.189687	0.431412
17	1	0	2.897334	-3.317698	0.465246
18	1	0	-2.041901	-3.150365	0.421759
19	7	0	1.878879	-0.860304	0.219959
20	7	0	-0.861065	-0.747771	0.194260
21	7	0	1.751905	-5.688584	0.689710
22	6	0	-1.139134	-5.707155	0.675149
23	1	0	-0.928076	-6.414043	-0.141432
24	1	0	-0.944130	-6.239805	1.618253
25	1	0	-2.211407	-5.490624	0.644103
26	1	0	2.756872	-5.719282	0.697534
27	1	0	1.257710	-6.559115	0.771627
28	1	0	-1.868441	-0.710090	0.184597
29	1	0	2.886588	-0.897048	0.229317

$(OPD\text{-}co\text{-}OT)^{+}$

Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-0.142893	0.434567	0.082264
2	6	0	1.275000	0.384045	0.095288
3	6	0	2.014020	1.571951	-0.016360
4	6	0	1.350730	2.789637	-0.138840
5	6	0	-0.057184	2.838881	-0.151776
6	6	0	-0.801402	1.669110	-0.041976
7	1	0	3.098398	1.533764	-0.006628
8	1	0	1.923645	3.705166	-0.224976
9	1	0	-0.564139	3.791412	-0.247826
10	1	0	-1.886101	1.701472	-0.051437
11	6	0	-0.344726	-4.424532	0.554876
12	6	0	1.098015	-4.473119	0.567835
13	6	0	1.840661	-3.282713	0.456037
14	6	0	1.196969	-2.053971	0.332457
15	6	0	-0.230692	-1.998428	0.318889
16	6	0	-0.966940	-3.192056	0.431193
17	1	0	2.924975	-3.322568	0.466019
18	1	0	-2.051382	-3.145746	0.420746
19	7	0	1.891994	-0.860266	0.219921
20	7	0	-0.842595	-0.765291	0.195279
21	7	0	1.732224	-5.674601	0.688221
22	6	0	-1.146583	-5.694631	0.673994
23	1	0	-0.927644	-6.391187	-0.146765
24	1	0	-0.941065	-6.217636	1.618000
25	1	0	-2.218421	-5.486704	0.645562
26	1	0	2.737859	-5.735549	0.699733
27	1	0	1.220953	-6.537409	0.769478
28	1	0	-1.854105	-0.729282	0.185938
29	1	0	2.902750	-0.890041	0.228541

$(OPD\text{-}co\text{-}OT)^{2+}$

Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-0.140634	0.419937	0.083392
2	6	0	1.293323	0.376796	0.095884
3	6	0	2.027654	1.572474	-0.016321
4	6	0	1.342691	2.771838	-0.136819
5	6	0	-0.081515	2.812618	-0.148925
6	6	0	-0.821956	1.649733	-0.040150
7	1	0	3.112021	1.551656	-0.008282
8	1	0	1.899130	3.697805	-0.223844
9	1	0	-0.585674	3.766689	-0.244720
10	1	0	-1.906609	1.676522	-0.048996
11	6	0	-0.362950	-4.411296	0.553417
12	6	0	1.112882	-4.463298	0.567038
13	6	0	1.869267	-3.275958	0.455527
14	6	0	1.230745	-2.052899	0.332323
15	6	0	-0.223788	-1.992013	0.317818
16	6	0	-0.978951	-3.189020	0.430356
17	1	0	2.952437	-3.326234	0.466602
18	1	0	-2.062424	-3.133817	0.418911
19	7	0	1.896704	-0.856098	0.219395
20	7	0	-0.808187	-0.782349	0.196545
21	7	0	1.716658	-5.653343	0.686288
22	6	0	-1.158338	-5.677661	0.672583
23	1	0	-0.936323	-6.372278	-0.149455
24	1	0	-0.948981	-6.198414	1.617405
25	1	0	-2.230458	-5.476646	0.645308
26	1	0	2.725590	-5.739956	0.700294
27	1	0	1.197410	-6.517202	0.767693
28	1	0	-1.827823	-0.746629	0.187159
29	1	0	2.913777	-0.878266	0.227395

(2OPD-co-2OT)
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-3.219120	-0.161008	-1.750373
2	6	0	-1.859688	0.176589	-1.777551
3	6	0	-1.433664	1.440384	-1.377059
4	6	0	-2.382478	2.384007	-0.924110
5	6	0	-3.730531	2.035570	-0.885740
6	6	0	-4.153118	0.767479	-1.305075
7	1	0	-3.532745	-1.148307	-2.076308
8	1	0	-1.122837	-0.546718	-2.120836
9	1	0	-4.455993	2.765064	-0.531597
10	1	0	-5.209803	0.518444	-1.276517
11	6	0	0.372011	2.922211	-0.676276
12	6	0	1.717706	3.128584	-0.397595
13	6	0	2.153207	4.248435	0.335251
14	6	0	1.214726	5.178360	0.813463
15	6	0	-0.139417	4.963093	0.507642
16	6	0	-0.573636	3.863832	-0.225059
17	1	0	2.454571	2.418508	-0.768688
18	1	0	-0.878987	5.672713	0.874569
19	7	0	-1.924520	3.659855	-0.558516
20	7	0	-0.085826	1.832716	-1.435640
21	7	0	3.532123	4.379334	0.646559
22	6	0	1.627323	6.354127	1.662389
23	1	0	2.381134	6.053696	2.398202
24	1	0	2.077634	7.158037	1.066238
25	1	0	0.766561	6.772026	2.194615
26	6	0	4.368940	5.368928	0.081510
27	6	0	5.718757	5.402664	0.485161
28	6	0	6.596486	6.355302	-0.018125
29	6	0	6.139632	7.315711	-0.947929
30	6	0	4.809755	7.273319	-1.348104
31	6	0	3.922140	6.311435	-0.846227
32	1	0	6.076089	4.680563	1.217540
33	1	0	4.451405	8.000457	-2.074024
34	1	0	2.896798	6.286264	-1.198062
35	1	0	4.002062	3.488895	0.758860
36	1	0	0.584111	1.095227	-1.606860
37	1	0	-2.592630	4.251756	-0.083473
38	6	0	8.888162	7.091460	-0.389817
39	6	0	10.252903	6.858116	-0.254023
40	6	0	11.193353	7.563111	-1.024377
41	6	0	10.748836	8.511383	-1.961816
42	6	0	9.368627	8.729028	-2.087414
43	6	0	8.432702	8.046279	-1.318140
44	1	0	10.596718	6.114876	0.463957
45	1	0	9.018145	9.463259	-2.811070
46	7	0	7.046085	8.299285	-1.393392
47	7	0	7.935329	6.424780	0.400028

48	1	0	8.274816	5.632515	0.928594
49	1	0	6.747861	8.818947	-2.208620
50	7	0	12.565713	7.264684	-0.904991
51	6	0	11.735375	9.265109	-2.819269
52	1	0	12.398466	9.912723	-2.224541
53	1	0	12.382671	8.583107	-3.386823
54	1	0	11.220266	9.911474	-3.536488
55	1	0	12.805428	6.824751	-0.023589
56	1	0	13.173691	8.059115	-1.069173

$(2OPD\text{-}co\text{-}2OT)^{+}$

Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-3.643587	0.112387	-1.672581
2	6	0	-2.255234	0.224358	-1.558319
3	6	0	-1.684304	1.385320	-1.039817
4	6	0	-2.517112	2.450129	-0.631395
5	6	0	-3.900934	2.331424	-0.749633
6	6	0	-4.465182	1.163626	-1.269123
7	1	0	-4.074943	-0.797670	-2.076889
8	1	0	-1.610391	-0.593081	-1.871598
9	1	0	-4.535845	3.155320	-0.433014
10	1	0	-5.543888	1.082602	-1.355190
11	6	0	0.296077	2.688284	-0.412346
12	6	0	1.672761	2.843288	-0.321558
13	6	0	2.244102	4.026421	0.186266
14	6	0	1.422848	5.081247	0.631876
15	6	0	0.035263	4.920988	0.505274
16	6	0	-0.542848	3.759725	-0.004134
17	1	0	2.325190	2.045580	-0.667996
18	1	0	-0.617834	5.720204	0.848172
19	7	0	-1.912514	3.600909	-0.116030
20	7	0	-0.301249	1.536706	-0.903407
21	7	0	3.652636	4.078198	0.307411
22	6	0	1.967480	6.327796	1.286675
23	1	0	2.876650	6.113547	1.856398
24	1	0	2.219899	7.107912	0.557797
25	1	0	1.228205	6.749820	1.974097
26	6	0	4.497977	5.015399	-0.253086
27	6	0	5.853570	5.044801	0.134842
28	6	0	6.729417	5.972723	-0.413306
29	6	0	6.258758	6.914572	-1.370924
30	6	0	4.913850	6.872950	-1.760920
31	6	0	4.044231	5.938084	-1.223078
32	1	0	6.215163	4.344528	0.884087
33	1	0	4.557054	7.571423	-2.513306
34	1	0	3.016635	5.893776	-1.563991
35	1	0	4.097068	3.246753	0.676756
36	1	0	0.291256	0.770843	-1.190503
37	1	0	-2.509854	4.359629	0.181544
38	6	0	8.970529	6.944185	-0.581849
39	6	0	10.307339	6.969971	-0.201162
40	6	0	11.196087	7.907208	-0.755754
41	6	0	10.725210	8.845553	-1.719283
42	6	0	9.384441	8.806307	-2.081975
43	6	0	8.495614	7.875636	-1.534319
44	1	0	10.670574	6.251833	0.530050
45	1	0	9.014135	9.518663	-2.815616
46	7	0	7.153774	7.827485	-1.890117
47	7	0	8.067759	6.028388	-0.053781

48	1	0	8.408254	5.360270	0.624286
49	1	0	6.817117	8.492436	-2.574695
50	7	0	12.528094	7.884915	-0.408917
51	6	0	11.669587	9.846532	-2.332872
52	1	0	12.090838	10.528848	-1.580645
53	1	0	12.512278	9.351050	-2.832488
54	1	0	11.160151	10.464005	-3.077163
55	1	0	12.796663	7.367619	0.416337
56	1	0	13.084510	8.710127	-0.577800

$(2OPD\text{-}co\text{-}2OT)^{2+}$
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-3,643587	0,112387	-1,672581
2	6	0	-2,255234	0,224358	-1,558319
3	6	0	-1,684304	1,385320	-1,039817
4	6	0	-2,517112	2,450129	-0,631395
5	6	0	-3,900934	2,331424	-0,749633
6	6	0	-4,465182	1,163626	-1,269123
7	1	0	-4,074943	-0,797670	-2,076889
8	1	0	-1,610391	-0,593081	-1,871598
9	1	0	-4,535845	3,155320	-0,433014
10	1	0	-5,543888	1,082602	-1,355190
11	6	0	0,296077	2,688284	-0,412346
12	6	0	1,672761	2,843288	-0,321558
13	6	0	2,244102	4,026421	0,186266
14	6	0	1,422848	5,081247	0,631876
15	6	0	0,035263	4,920988	0,505274
16	6	0	-0,542848	3,759725	-0,004134
17	1	0	2,325190	2,045580	-0,667996
18	1	0	-0,617834	5,720204	0,848172
19	7	0	-1,912514	3,600909	-0,116030
20	7	0	-0,301249	1,536706	-0,903407
21	7	0	3,652636	4,078198	0,307411
22	6	0	1,967480	6,327796	1,286675
23	1	0	2,876650	6,113547	1,856398
24	1	0	2,219899	7,107912	0,557797
25	1	0	1,228205	6,749820	1,974097
26	6	0	4,497977	5,015399	-0,253086
27	6	0	5,853570	5,044801	0,134842
28	6	0	6,729417	5,972723	-0,413306
29	6	0	6,258758	6,914572	-1,370924
30	6	0	4,913850	6,872950	-1,760920
31	6	0	4,044231	5,938084	-1,223078
32	1	0	6,215163	4,344528	0,884087
33	1	0	4,557054	7,571423	-2,513306
34	1	0	3,016635	5,893776	-1,563991
35	1	0	4,097068	3,246753	0,676756
36	1	0	0,291256	0,770843	-1,190503
37	1	0	-2,509854	4,359629	0,181544
38	6	0	8,970529	6,944185	-0,581849
39	6	0	10,307339	6,969971	-0,201162
40	6	0	11,196087	7,907208	-0,755754
41	6	0	10,725210	8,845553	-1,719283
42	6	0	9,384441	8,806307	-2,081975
43	6	0	8,495614	7,875636	-1,534319
44	1	0	10,670574	6,251833	0,530050
45	1	0	9,014135	9,518663	-2,815616
46	7	0	7,153774	7,827485	-1,890117
47	7	0	8,067759	6,028388	-0,053781
48	1	0	8,408254	5,360270	0,624286
49	1	0	6,817117	8,492436	-2,574695
50	7	0	12,528094	7,884915	-0,408917
51	6	0	11,669587	9,846532	-2,332872
52	1	0	12,090838	10,528848	-1,580645

53	1	0	12,512278	9,351050	-2,832488
54	1	0	11,160151	10,464005	-3,077163
55	1	0	12,796663	7,367619	0,416337
56	1	0	13,084510	8,710127	-0,577800

ST1: Optimized geometric parameters {bond length (Å), bond angle (°), dihedral angle (°)} of neutral (2OPD-co-2OT), cationic $(2OPD\text{-}co\text{-}2OT)^{+}$ and dicationic $(2OPD\text{-}co\text{-}2OT)^{2+}$ co-oligomers.

Species	$d_{C2\text{-}N3}$	$d_{C6\text{-}N7}$	$\angle C_4N_3C_2$	$\angle C_1C_2N_3C_4$
OPD-co-OT	1.40 Å	1.38 Å	123.33 °	179.99 °
$(OPD\text{-}co\text{-}OT)^{+}$	1.39 Å	1.36 Å	123.63 °	-176.99 °
$(OPD\text{-}co\text{-}OT)^{2+}$	1.37 Å	1.33Å	125.04 °	-179.97 °
2OPD-co-2OT	1.41Å	1.40 Å	123.49 °	123.68 °
$(2OPD\text{-}co\text{-}2OT)^{+}$	1.38 Å	1.37Å	126.83 °	111.15 °
$(2OPD\text{-}co\text{-}2OT)^{2+}$	1.37 Å	1.35 Å	127.66 °	-135.02 °

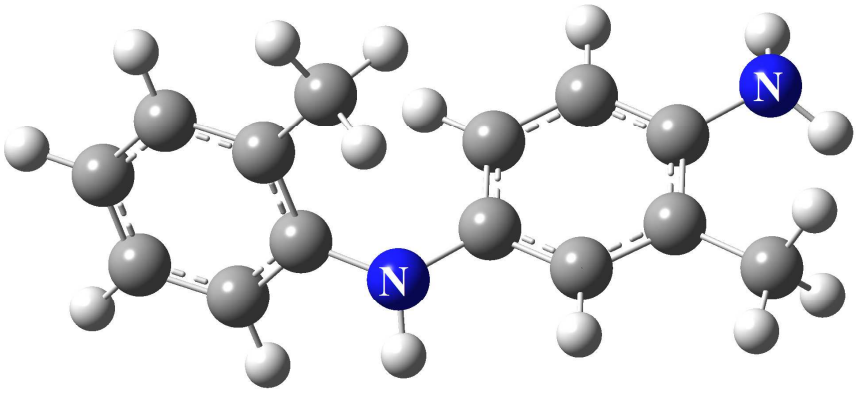
$d_{C2\text{-}N3}$: Bond distance between C_6 and N_3 of co-dimers and co-oligomers of OPD-co-OT.

$d_{C6\text{-}N7}$: Bond distance between C_6 and N_7 of co-dimers and co-oligomers of OPD-co-OT.

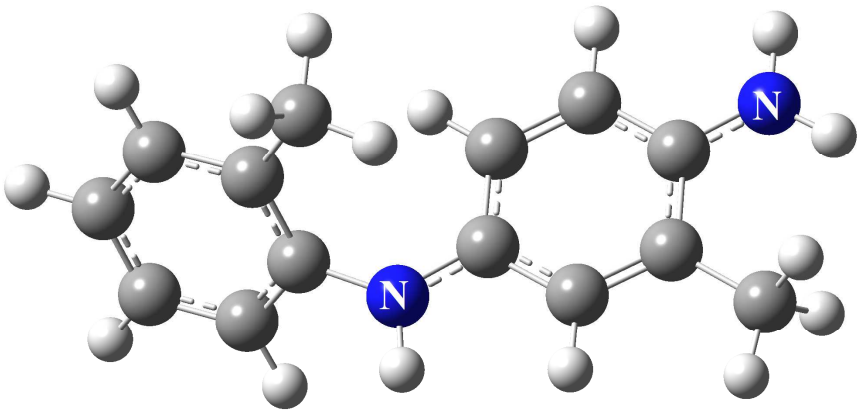
$\angle C_4C_3N_2$: Angle between C_4, C_3, N_2 of co-dimers and co-oligomers of OPD-co-OT.

$\angle C_1N_2C_3C_4$: Dihedral angle between C_1, N_2, C_3, C_4 dimers and oligomers of OPD-co-OT.

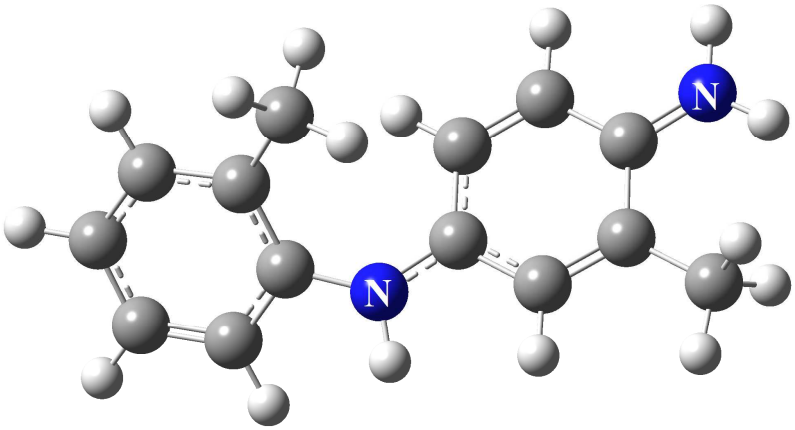
S2



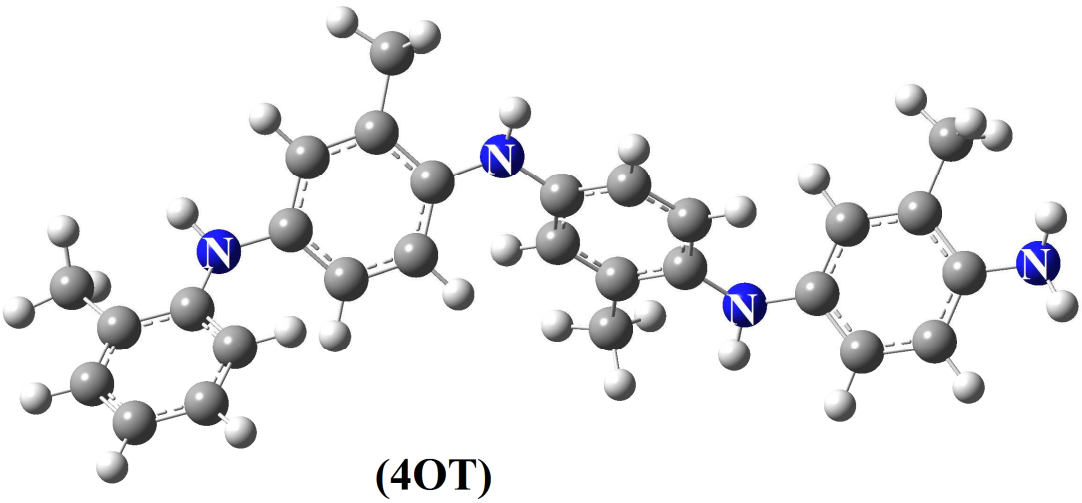
(2OT)



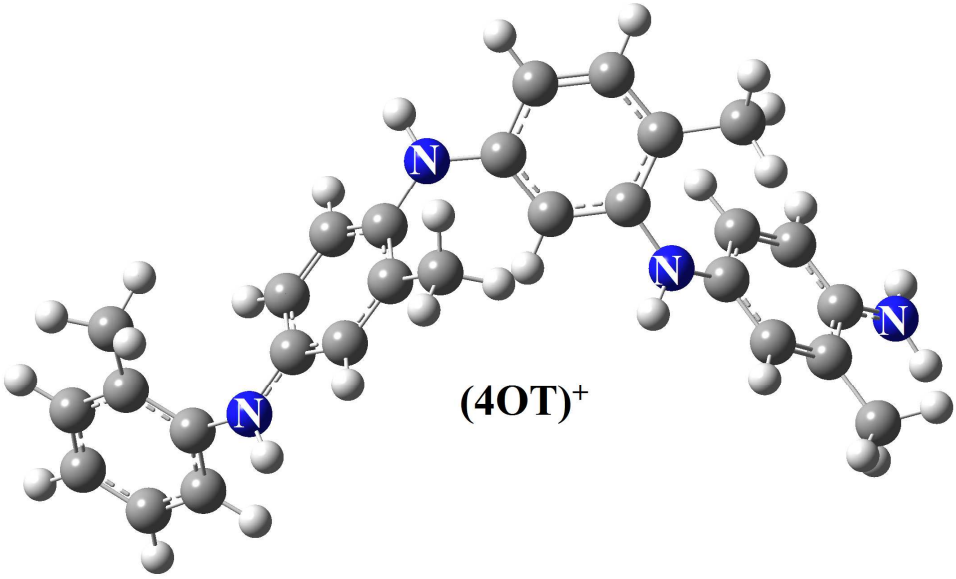
$(2OT)^{+}$



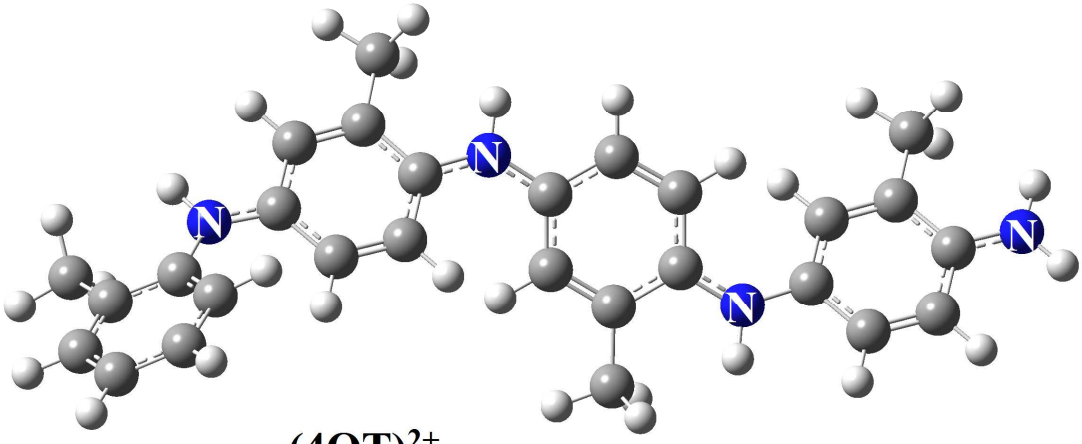
$(2OT)^{2+}$



(4OT)



$(4OT)^{+}$



$(4OT)^{2+}$

(2OT)
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-2.751674	-1.316256	-0.770390
2	6	0	-1.904393	-0.611354	0.098231
3	6	0	-2.365065	0.575536	0.715173
4	6	0	-3.651823	1.025606	0.397448
5	6	0	-4.489669	0.325741	-0.471647
6	6	0	-4.038899	-0.861455	-1.047535
7	1	0	-2.384646	-2.228575	-1.236405
8	1	0	-4.012156	1.936695	0.870529
9	1	0	-5.487762	0.698431	-0.684749
10	1	0	-4.678428	-1.426506	-1.720565
11	6	0	-1.525816	1.313400	1.727923
12	1	0	-0.722080	1.894789	1.259650
13	1	0	-2.143703	2.003187	2.311449
14	1	0	-1.041374	0.610551	2.414857
15	7	0	-0.632432	-1.145380	0.412550
16	6	0	1.786425	-1.057343	0.578512
17	6	0	3.034788	-0.506057	0.294286
18	6	0	3.102902	0.656742	-0.506067
19	6	0	1.913926	1.211336	-0.992522
20	6	0	0.673790	0.638782	-0.711803
21	6	0	0.593380	-0.507561	0.085679
22	1	0	1.733083	-1.939481	1.214146
23	1	0	1.958529	2.102879	-1.615455
24	1	0	-0.228383	1.072879	-1.131129
25	6	0	4.297604	-1.116935	0.850160
26	1	0	4.879618	-0.379819	1.418381
27	1	0	4.072130	-1.956443	1.514310
28	1	0	4.956590	-1.500060	0.055985
29	7	0	4.343600	1.279931	-0.746050
30	1	0	5.116634	0.634381	-0.863049
31	1	0	4.318867	1.933617	-1.520783
32	1	0	-0.588985	-2.150135	0.288724

$(2OT)^{+}$

Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-5.675804	-0.466761	-0.713298
2	6	0	-4.472299	-0.278444	-0.014128
3	6	0	-4.092480	0.991653	0.466038
4	6	0	-4.948096	2.063340	0.167867
5	6	0	-6.130632	1.889368	-0.545196
6	6	0	-6.503477	0.614591	-0.982995
7	1	0	-5.940296	-1.462083	-1.060084
8	1	0	-4.680744	3.053437	0.527942
9	1	0	-6.768226	2.744040	-0.749610
10	1	0	-7.427142	0.466937	-1.533358
11	6	0	-2.871222	1.243895	1.318702
12	1	0	-2.189497	1.952904	0.834391
13	1	0	-3.154523	1.680875	2.282788
14	1	0	-2.306249	0.336063	1.536705
15	7	0	-3.699241	-1.454867	0.248906
16	6	0	-1.834946	-2.960269	0.306977
17	6	0	-0.550679	-3.315789	-0.028310
18	6	0	0.212261	-2.407101	-0.842439
19	6	0	-0.375589	-1.185534	-1.281771
20	6	0	-1.656962	-0.849528	-0.933684
21	6	0	-2.423333	-1.731972	-0.118696
22	1	0	-2.423895	-3.632365	0.926532
23	1	0	0.204648	-0.520302	-1.915000
24	1	0	-2.099048	0.071731	-1.291678
25	6	0	0.056786	-4.614092	0.434495
26	1	0	0.950448	-4.445273	1.049695
27	1	0	-0.651638	-5.184755	1.039067
28	1	0	0.348286	-5.248278	-0.413130
29	7	0	1.477793	-2.707522	-1.200467
30	1	0	1.922560	-3.569160	-0.917536
31	1	0	2.023136	-2.079377	-1.775482
32	1	0	-4.207667	-2.218428	0.685061

$(2OT)^{2+}$

Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-2.850506	-1.478019	-0.468030
2	6	0	-1.907078	-0.535927	0.037391
3	6	0	-2.313158	0.764943	0.485395
4	6	0	-3.655376	1.088232	0.284216
5	6	0	-4.562260	0.196367	-0.299605
6	6	0	-4.160992	-1.104763	-0.662955
7	1	0	-2.514442	-2.470673	-0.757725
8	1	0	-4.014337	2.052171	0.633039
9	1	0	-5.596094	0.499606	-0.436183
10	1	0	-4.874038	-1.803757	-1.086850
11	6	0	-1.453635	1.707098	1.293997
12	1	0	-1.128069	2.575138	0.708619
13	1	0	-2.041413	2.097828	2.129794
14	1	0	-0.565470	1.228922	1.715981
15	7	0	-0.603596	-1.022683	0.126911
16	6	0	1.763802	-1.202285	0.352929
17	6	0	3.027570	-0.706460	0.226542
18	6	0	3.167211	0.621543	-0.371970
19	6	0	2.001591	1.351723	-0.828784
20	6	0	0.757169	0.841004	-0.663679
21	6	0	0.596297	-0.449172	-0.037457
22	1	0	1.622909	-2.184334	0.798319
23	1	0	2.144286	2.298960	-1.340935
24	1	0	-0.107962	1.358440	-1.059719
25	6	0	4.244838	-1.469664	0.667407
26	1	0	4.799409	-0.929007	1.445793
27	1	0	3.967849	-2.440591	1.082869
28	1	0	4.927366	-1.658191	-0.171953
29	7	0	4.362170	1.153218	-0.535057
30	1	0	5.211632	0.670504	-0.252908
31	1	0	4.489657	2.071272	-0.955514
32	1	0	-0.564139	-2.027757	0.312017

(4OT)
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	4.026308	2.138436	-0.144751
2	6	0	2.686408	2.516170	-0.228322
3	6	0	1.685274	1.522599	-0.119588
4	6	0	2.076363	0.191270	0.089786
5	6	0	3.417369	-0.158823	0.212564
6	6	0	4.420931	0.811723	0.082905
7	1	0	4.792274	2.904819	-0.252734
8	1	0	3.684745	-1.190977	0.413480
9	7	0	0.338447	1.912292	-0.236542
10	6	0	-1.904378	1.152806	-0.794475
11	6	0	-3.065219	0.452104	-0.478557
12	6	0	-3.157707	-0.296188	0.703128
13	6	0	-2.045395	-0.325785	1.578794
14	6	0	-0.894342	0.387899	1.246874
15	6	0	-0.796416	1.133321	0.061161
16	1	0	-1.854194	1.709731	-1.728061
17	1	0	-3.900418	0.466945	-1.169974
18	1	0	-0.059581	0.386860	1.941590
19	7	0	-4.308637	-1.025107	1.056136
20	6	0	-6.261153	-2.155484	0.140772
21	6	0	-7.537820	-2.114272	-0.413591
22	6	0	-8.155233	-0.895965	-0.721523
23	6	0	-7.468274	0.306635	-0.440854
24	6	0	-6.197386	0.247771	0.130903
25	6	0	-5.566509	-0.972538	0.421559
26	1	0	-5.796760	-3.116863	0.349890
27	1	0	-8.061182	-3.045574	-0.621420
28	1	0	-5.689431	1.176030	0.376182
29	1	0	0.169075	2.644783	-0.912154
30	1	0	-4.123235	-1.900140	1.527044
31	6	0	-2.111978	-1.104861	2.870068
32	6	0	-8.124033	1.635107	-0.729025
33	1	0	-3.006876	-0.842454	3.448280
34	1	0	-2.148986	-2.191920	2.699652
35	1	0	-1.232958	-0.910154	3.491241
36	1	0	-9.103822	1.710634	-0.239834
37	1	0	-7.504587	2.465939	-0.379045
38	1	0	-8.292206	1.788235	-1.806091
39	7	0	-9.466379	-0.860994	-1.232332
40	1	0	-9.762815	-1.739817	-1.641578
41	1	0	-9.643386	-0.099064	-1.876988
42	7	0	5.787006	0.515729	0.252238
43	1	0	6.354983	1.303997	0.527611
44	6	0	7.819717	-0.795022	0.221164
45	6	0	6.499148	-0.582213	-0.248278
46	6	0	5.957209	-1.460573	-1.201311
47	6	0	6.698266	-2.543839	-1.669113

48	6	0	7.996025	-2.764897	-1.210561
49	6	0	8.540648	-1.882306	-0.276209
50	1	0	4.959781	-1.280855	-1.586230
51	1	0	6.256387	-3.209236	-2.406634
52	1	0	1.319131	-0.581562	0.163527
53	6	0	2.309105	3.960713	-0.448869
54	1	0	1.870050	4.130383	-1.444101
55	1	0	1.566998	4.294107	0.287321
56	1	0	3.184484	4.612440	-0.372433
57	6	0	8.429092	0.133505	1.243532
58	1	0	9.409660	-0.229874	1.564767
59	1	0	8.580051	1.151052	0.850195
60	1	0	7.793605	0.226452	2.134074
61	1	0	9.553153	-2.042525	0.088682
62	1	0	8.576881	-3.608582	-1.571879
56	1	0	3.184484	4.612440	-0.372433
57	6	0	8.429092	0.133505	1.243532
58	1	0	9.409660	-0.229874	1.564767
59	1	0	8.580051	1.151052	0.850195
60	1	0	7.793605	0.226452	2.134074
61	1	0	9.553153	-2.042525	0.088682
62	1	0	8.576881	-3.608582	-1.571879

$(4OT)^{+}$

Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	-0.706499	-2.347205	-1.971138
2	6	0	-0.509731	-1.359422	-0.997257
3	6	0	-1.412812	-0.282599	-0.869832
4	6	0	-2.480011	-0.222761	-1.776037
5	6	0	-2.672211	-1.198398	-2.753337
6	6	0	-1.787219	-2.273435	-2.845706
7	1	0	0.002850	-3.167947	-2.041047
8	1	0	-3.188190	0.597695	-1.692167
9	1	0	-3.517730	-1.125561	-3.431129
10	1	0	-1.931316	-3.044439	-3.596783
11	6	0	-1.277590	0.752340	0.220568
12	1	0	-0.498017	1.491220	-0.003573
13	1	0	-2.217753	1.294997	0.353298
14	1	0	-1.010196	0.289163	1.176214
15	7	0	0.587028	-1.504917	-0.095910
16	6	0	2.674150	-0.947024	0.969852
17	6	0	3.815606	-0.165757	1.115566
18	6	0	4.007427	0.912698	0.213743
19	6	0	3.027017	1.184625	-0.756850
20	6	0	1.890663	0.405325	-0.883639
21	6	0	1.695660	-0.691048	-0.016088
22	1	0	2.504780	-1.759913	1.672884
23	1	0	3.184027	2.011946	-1.444549
24	1	0	1.168733	0.612727	-1.665245
25	6	0	4.762805	-0.428718	2.260484
26	1	0	5.071050	0.507484	2.737632
27	1	0	4.286551	-1.057602	3.017614
28	1	0	5.680850	-0.933676	1.936148
29	7	0	5.114579	1.782992	0.314462
30	1	0	4.907421	2.763948	0.171601
31	1	0	0.657933	-2.396094	0.378438
32	6	0	6.905367	0.183494	-0.172166
33	6	0	8.275615	-0.090778	-0.271785
34	6	0	9.252552	0.894306	0.024180
35	6	0	8.773204	2.168311	0.370994
36	6	0	7.421750	2.455669	0.467270
37	6	0	6.457783	1.453310	0.212551
38	1	0	6.185388	-0.578927	-0.451770
39	1	0	9.493520	2.946897	0.606679
40	1	0	7.096699	3.448108	0.768937
41	6	0	10.735285	0.617613	0.067990
42	1	0	11.217260	1.272345	0.800140
43	1	0	10.946132	-0.418360	0.348239
44	1	0	11.222763	0.795937	-0.898165
45	7	0	8.647424	-1.411081	-0.598341
46	1	0	8.080005	-2.139208	-0.180168
47	6	0	9.917116	-3.167360	-1.655105

48	6	0	10.758764	-3.648569	-2.640991
49	6	0	11.205525	-2.745608	-3.654284
50	6	0	10.762341	-1.401527	-3.629746
51	6	0	9.916186	-0.944631	-2.640467
52	6	0	9.489165	-1.819288	-1.617517
53	1	0	9.587712	-3.844240	-0.869863
54	1	0	11.077854	-0.726662	-4.420937
55	1	0	9.554582	0.077356	-2.662996
56	7	0	12.054292	-3.167620	-4.633955
57	1	0	12.289503	-4.141976	-4.741966
58	1	0	12.305766	-2.553794	-5.394667
59	6	0	11.212376	-5.085840	-2.651405
60	1	0	10.899821	-5.604512	-3.568248
61	1	0	12.305563	-5.164899	-2.584275
62	1	0	10.791531	-5.637500	-1.807227

$(4OT)^{2+}$
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	3.972948	2.145396	-0.390650
2	6	0	2.628697	2.392703	-0.554172
3	6	0	1.724072	1.279672	-0.518971
4	6	0	2.235650	-0.033204	-0.357327
5	6	0	3.584079	-0.261788	-0.218158
6	6	0	4.495780	0.830598	-0.228615
7	1	0	4.665656	2.983114	-0.403601
8	1	0	3.946354	-1.273309	-0.089463
9	7	0	0.380000	1.539393	-0.692431
10	6	0	-1.960564	1.194274	-1.033615
11	6	0	-3.130083	0.529393	-0.766073
12	6	0	-3.160974	-0.530740	0.179864
13	6	0	-1.948408	-0.913196	0.850691
14	6	0	-0.784432	-0.231448	0.561695
15	6	0	-0.751542	0.824520	-0.385180
16	1	0	-1.949515	1.972910	-1.791526
17	1	0	-4.021934	0.777275	-1.327397
18	1	0	0.108701	-0.472807	1.124987
19	7	0	-4.304030	-1.226344	0.464919
20	6	0	-6.544213	-2.040417	0.234208
21	6	0	-7.885591	-1.834754	0.030126
22	6	0	-8.399195	-0.520623	-0.151350
23	6	0	-7.505440	0.602187	-0.095394
24	6	0	-6.158043	0.366126	0.096837
25	6	0	-5.644221	-0.945390	0.243745
26	1	0	-6.168661	-3.052778	0.359282
27	1	0	-8.566762	-2.680079	0.005936
28	1	0	-5.496138	1.218406	0.198344
29	1	0	0.189046	2.434743	-1.132618
30	1	0	-4.148064	-2.123089	0.915108
31	6	0	-1.954981	-2.003801	1.893102
32	6	0	-8.046450	2.003118	-0.212051
33	1	0	-2.663798	-1.791011	2.702697
34	1	0	-2.217634	-2.980689	1.462137
35	1	0	-0.966979	-2.117289	2.344446
36	1	0	-8.784567	2.217958	0.571826
37	1	0	-7.248521	2.743482	-0.119180
38	1	0	-8.534352	2.168013	-1.182197
39	7	0	-9.720024	-0.336727	-0.349025
40	1	0	-10.361622	-1.118127	-0.366582
41	1	0	-10.120811	0.582098	-0.470786
42	7	0	5.838713	0.688132	-0.069231
43	1	0	6.341257	1.551588	0.113238
44	6	0	7.807815	-0.491302	0.697999
45	6	0	6.652163	-0.462503	-0.123005
46	6	0	6.366364	-1.512728	-1.014706
47	6	0	7.204207	-2.618845	-1.069571

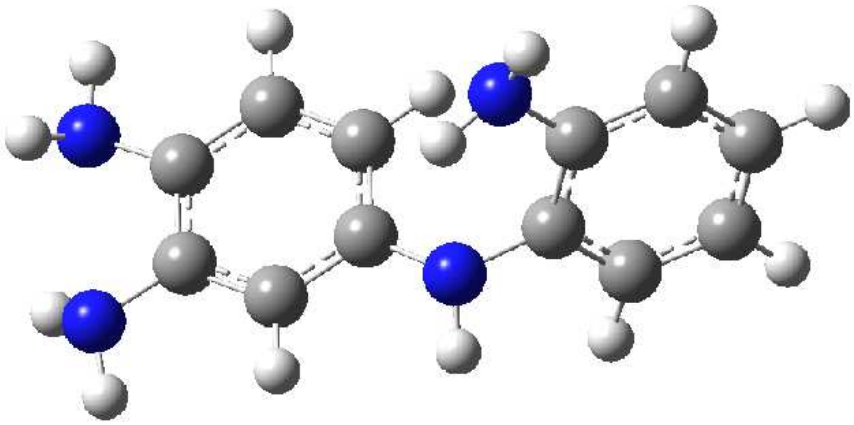
48	6	0	8.333930	-2.677052	-0.247281
49	6	0	8.627138	-1.618296	0.615350
50	1	0	5.528412	-1.431175	-1.698591
51	1	0	6.993244	-3.420644	-1.769936
52	1	0	1.564301	-0.882229	-0.387503
53	6	0	2.125216	3.803199	-0.742959
54	1	0	1.634936	3.938171	-1.717883
55	1	0	1.411912	4.091238	0.038956
56	1	0	2.951223	4.516695	-0.710649
57	6	0	8.138226	0.642667	1.637518
58	1	0	9.029527	0.408540	2.223938
59	1	0	8.355539	1.577265	1.098903
60	1	0	7.322198	0.846338	2.341341
61	1	0	9.512626	-1.667808	1.242179
62	1	0	8.994892	-3.537001	-0.289638

ST2: Optimized geometric parameters {bond length (Å), bond angle (°), dihedral angle (°)} of neutral (OT), cationic $(OT)^{+}$ and dicationic $(OT)^{2+}$ oligomers

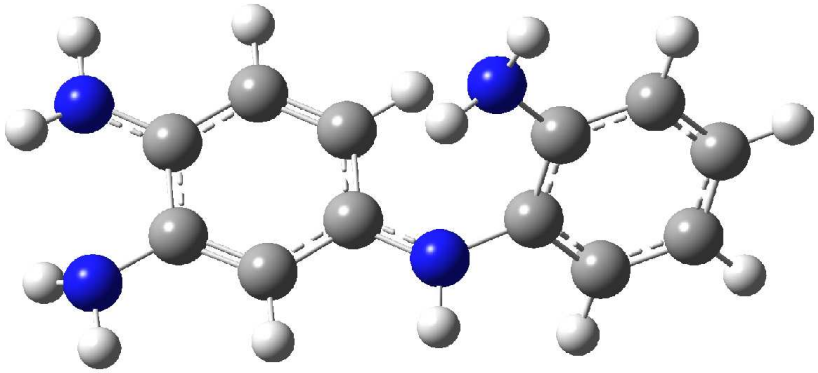
Species	d_{C2-N3}	d_{C6-N7}	$\angle C_4C_3N_2$	$\angle C_1N_2C_3C_4$
2OT	1.41Å	1.40 Å	123.73 °	172.99 °
$2OT^{+}$	1.35 Å	1.34 Å	127.87 °	177.46 °
$2OT^{2+}$	1.34 Å	1.31 Å	132.82 °	145.72 °
4OT	1.40 Å	1.40 Å	126.91 °	179.18 °
$4OT^{+}$	1.41Å	1.37Å	127.42 °	174.60 °
$4OT^{2+}$	1.37 Å	1.35 Å	132.57 °	137.64 °

d_{C2-N3}: Bond distance between C_6 and N_3 of dimers and oligomers of OT.
d_{C6-N7}: Bond distance between C_6 and N_7 of dimers and oligomers of OT.
$\angle C_4C_3N_2$: Angle between C_4, C_3, N_2 of dimers and oligomers of OT.
$\angle C_1N_2C_3C_4$: Dihedral angle between C_1, N_2, C_3, C_4 dimers and oligomers of OT.

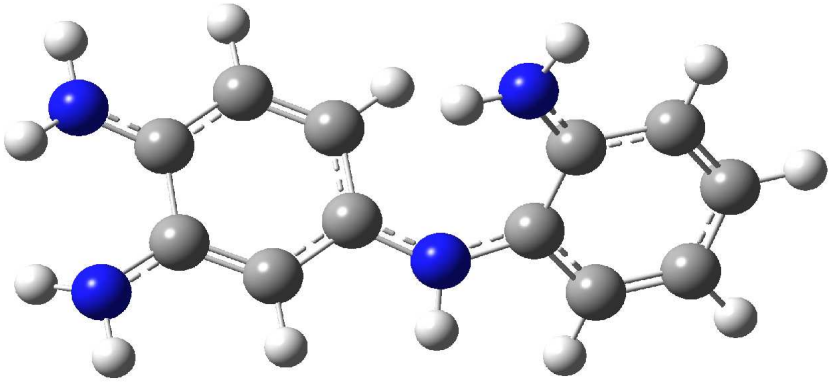
S3



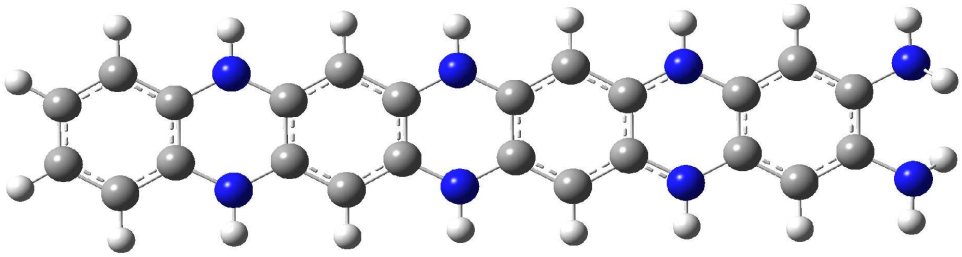
(2OPD)



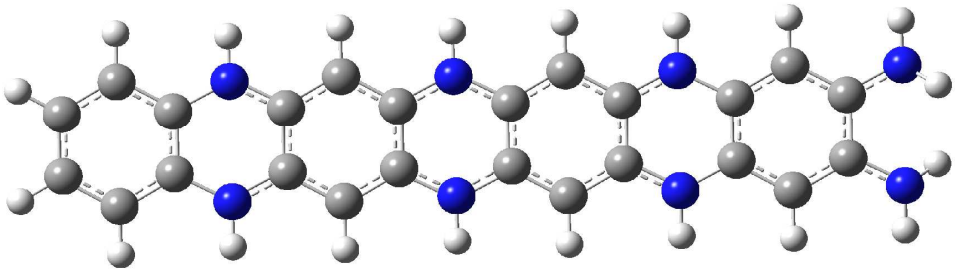
$(2OPD)^{+}$



$(2OPD)^{+2}$



$(4OPD)^{1+}$



$(4OPD)^{2+}$

(2OPD)
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	0.273597	1.015125	0.361425
2	6	0	0.519900	0.560697	1.657309
3	6	0	1.618470	-0.253278	1.945499
4	6	0	2.504214	-0.625078	0.905862
5	6	0	2.260904	-0.143064	-0.390324
6	6	0	1.157958	0.663717	-0.659933
7	6	0	3.756540	0.651751	3.773405
8	6	0	2.779344	-0.271361	4.155782
9	6	0	2.753887	-0.728025	5.484251
10	1	0	1.990994	-1.442333	5.792097
11	6	0	4.707438	1.075260	4.706896
12	1	0	0.946412	-1.019907	3.712495
13	1	0	-0.588760	1.642755	0.157033
14	1	0	-0.148883	0.836097	2.470143
15	1	0	2.942104	-0.422498	-1.191416
16	1	0	0.988359	1.013446	-1.674968
17	1	0	5.477171	1.779677	4.396269
18	1	0	2.820713	-1.157802	8.041338
19	1	0	6.311238	1.692680	6.634567
20	6	0	3.682844	-0.277890	6.421767
21	6	0	4.694069	0.626673	6.024565
22	7	0	1.819630	-0.795287	3.249207
23	7	0	5.606186	1.071887	7.020553
24	7	0	3.694729	-0.731955	7.752813
25	1	0	6.077388	0.288017	7.470266
26	1	0	3.960804	0.008303	8.397892
27	7	0	3.610766	-1.421294	1.190351
28	1	0	3.502268	-1.968549	2.037589
29	1	0	3.949353	-1.972604	0.411689
30	1	0	3.785547	1.029514	2.758392

$(2OPD)^{1+}$

Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	0.011993	-0.217154	-0.061700
2	6	0	-0.060662	-0.137335	1.320933
3	6	0	1.097214	0.058085	2.089412
4	6	0	2.371277	0.120577	1.473620
5	6	0	2.417756	0.055566	0.068386
6	6	0	1.262853	-0.106838	-0.684238
7	6	0	1.878179	2.321918	3.884214
8	6	0	1.315208	1.098986	4.363769
9	6	0	1.076109	0.938913	5.751337
10	1	0	0.597654	0.030644	6.109581
11	6	0	2.231675	3.304776	4.773156
12	1	0	0.394854	-0.641874	3.912557
13	1	0	-0.889356	-0.352815	-0.649548
14	1	0	-1.020766	-0.200212	1.826630
15	1	0	3.384728	0.113993	-0.424624
16	1	0	1.337741	-0.163967	-1.765931
17	1	0	2.672799	4.229246	4.411888
18	1	0	0.770300	0.959856	8.330544
19	1	0	3.007036	4.857446	6.742891
20	6	0	1.408432	1.931033	6.653792
21	6	0	2.062784	3.125064	6.169025
22	7	0	0.960366	0.098824	3.508965
23	7	0	2.486772	4.050643	7.063172
24	7	0	1.216803	1.816030	8.022015
25	1	0	2.646945	3.773686	8.024219
26	1	0	0.811241	2.625343	8.482202
27	7	0	3.537547	0.279824	2.213789
28	1	0	3.533251	-0.128688	3.140884
29	1	0	4.387735	0.051346	1.712421
30	1	0	2.023406	2.463393	2.821403

$(2OPD)^{2+}$
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	0.011993	-0.217154	-0.061700
2	6	0	-0.060662	-0.137335	1.320933
3	6	0	1.097214	0.058085	2.089412
4	6	0	2.371277	0.120577	1.473620
5	6	0	2.417756	0.055566	0.068386
6	6	0	1.262853	-0.106838	-0.684238
7	6	0	1.878179	2.321918	3.884214
8	6	0	1.315208	1.098986	4.363769
9	6	0	1.076109	0.938913	5.751337
10	1	0	0.597654	0.030644	6.109581
11	6	0	2.231675	3.304776	4.773156
12	1	0	0.394854	-0.641874	3.912557
13	1	0	-0.889356	-0.352815	-0.649548
14	1	0	-1.020766	-0.200212	1.826630
15	1	0	3.384728	0.113993	-0.424624
16	1	0	1.337741	-0.163967	-1.765931
17	1	0	2.672799	4.229246	4.411888
18	1	0	0.770300	0.959856	8.330544
19	1	0	3.007036	4.857446	6.742891
20	6	0	1.408432	1.931033	6.653792
21	6	0	2.062784	3.125064	6.169025
22	7	0	0.960366	0.098824	3.508965
23	7	0	2.486772	4.050643	7.063172
24	7	0	1.216803	1.816030	8.022015
25	1	0	2.646945	3.773686	8.024219
26	1	0	0.811241	2.625343	8.482202
27	7	0	3.537547	0.279824	2.213789
28	1	0	3.533251	-0.128688	3.140884
29	1	0	4.387735	0.051346	1.712421
30	1	0	2.023406	2.463393	2.821403

(4OPD)
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	0.020685	0.029481	0.086804
2	6	0	0.003042	-0.106411	1.471769
3	6	0	1.188242	-0.255111	2.217343
4	6	0	2.417209	-0.242828	1.532596
5	6	0	2.428685	-0.099972	0.138059
6	6	0	1.256668	0.021579	-0.599750
7	1	0	0.350510	-0.670559	4.072905
8	1	0	-0.951352	-0.109344	1.987945
9	1	0	3.383108	-0.081961	-0.379057
10	1	0	4.379736	-0.848063	1.827847
11	6	0	-1.162062	0.293452	-2.058806
12	6	0	-2.346823	0.426952	-2.787103
13	6	0	0.067549	0.282574	-2.742856
14	6	0	-2.345271	0.550261	-4.178937
15	1	0	-3.293552	0.435154	-2.257162
16	6	0	0.067449	0.405482	-4.136135
17	6	0	-1.117844	0.538995	-4.863754
18	1	0	1.013899	0.396790	-4.666406
19	6	0	-3.538590	0.807103	-6.317152
20	1	0	-4.416827	0.691292	-4.426033
21	6	0	-4.722216	0.938719	-7.047721
22	6	0	-2.308583	0.795913	-7.003350
23	1	0	-0.239267	0.656537	-6.756495
24	6	0	-4.717203	1.059719	-8.440144
25	6	0	-2.306172	0.917091	-8.394962
26	6	0	-3.491638	1.048637	-9.123487
27	1	0	-1.359262	0.908525	-8.924285
28	7	0	1.249210	0.149245	-2.004319
29	1	0	2.134319	0.146840	-2.495336
30	7	0	-1.157620	0.167855	-0.658661
31	1	0	-2.043224	0.172718	-0.167835
32	7	0	3.605830	-0.405749	2.325397
33	7	0	1.204367	-0.408518	3.594627
34	7	0	-1.123368	0.662994	-6.263668
35	7	0	-3.533302	0.684979	-4.919813
36	1	0	-5.669926	0.947296	-6.519857
37	7	0	-3.498768	1.170848	-10.524684
38	1	0	-2.614028	1.164107	-11.017490
39	7	0	-5.903565	1.192346	-9.183661
40	1	0	-6.787956	1.198517	-8.690202
41	6	0	-5.916833	1.312776	-10.578163
42	6	0	-4.676208	1.301723	-11.269780
43	6	0	-7.098341	1.441784	-11.303390
44	6	0	-4.670576	1.420716	-12.657070
45	6	0	-7.080364	1.560999	-12.702340
46	1	0	-8.043741	1.449572	-10.771362
47	6	0	-5.868461	1.550474	-13.377964

48	1	0	-3.721254	1.411983	-13.182056
49	1	0	-8.014019	1.660264	-13.242323
50	1	0	-5.835765	1.641357	-14.456780
51	1	0	3.912373	0.453052	2.793774
52	1	0	2.087122	-0.774123	3.949754

$(4OPD)^{1+}$
Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	0.026606	0.029240	0.050332
2	6	0	0.010205	-0.108491	1.439065
3	6	0	1.197513	-0.254202	2.159230
4	6	0	2.438460	-0.233177	1.467594
5	6	0	2.444419	-0.116600	0.076291
6	6	0	1.251650	0.006126	-0.637650
7	1	0	0.325446	-0.499343	3.986739
8	1	0	-0.941243	-0.119310	1.966245
9	1	0	3.392418	-0.105162	-0.457028
10	1	0	4.464591	-0.245713	1.701895
11	6	0	-1.169873	0.291443	-2.069853
12	6	0	-2.359030	0.432603	-2.787735
13	6	0	0.072162	0.266950	-2.767280
14	6	0	-2.345627	0.549355	-4.180119
15	1	0	-3.306984	0.451768	-2.256042
16	6	0	0.082057	0.383507	-4.158526
17	6	0	-1.109863	0.524029	-4.873973
18	1	0	1.029231	0.364322	-4.691605
19	6	0	-3.528263	0.807484	-6.305197
20	1	0	-4.389396	0.708342	-4.426220
21	6	0	-4.722790	0.947574	-7.020716
22	6	0	-2.299940	0.781838	-6.994807
23	1	0	-0.251431	0.623602	-6.748991
24	6	0	-4.713098	1.062454	-8.409473
25	6	0	-2.284906	0.896707	-8.389449
26	6	0	-3.471611	1.036166	-9.106438
27	1	0	-1.336529	0.876525	-8.920539
28	7	0	1.230587	0.127240	-2.032007
29	1	0	2.112846	0.107317	-2.524018
30	7	0	-1.149041	0.172957	-0.695797
31	1	0	-2.028286	0.191679	-0.198366
32	7	0	3.605985	-0.389636	2.220749
33	7	0	1.231389	-0.365516	3.552553
34	7	0	-1.132084	0.641575	-6.253283
35	7	0	-3.507505	0.690277	-4.919722
36	1	0	-5.669747	0.967303	-6.487082
37	7	0	-3.491775	1.151891	-10.484361
38	1	0	-2.613444	1.133743	-10.982592
39	7	0	-5.874715	1.202293	-9.146678
40	1	0	-6.757567	1.221203	-8.656535
41	6	0	-5.896709	1.318697	-10.542705
42	6	0	-4.667853	1.292454	-11.232571
43	6	0	-7.086219	1.457175	-11.254200
44	6	0	-4.651944	1.405369	-12.620880
45	6	0	-7.063589	1.570089	-12.647479
46	1	0	-8.031172	1.476831	-10.716620
47	6	0	-5.849205	1.544112	-13.329256
48	1	0	-3.701154	1.384363	-13.148020
49	1	0	-7.996986	1.677638	-13.190424
50	1	0	-5.823565	1.630964	-14.410644
51	1	0	3.607604	0.155866	3.078697
52	1	0	1.896002	-1.059852	3.883965

$(4OPD)^{2+}$

Optimized at B3LYP/6-31G

Center number	Atomic number	Atomic type	Coordinates/Ångstrom		
			X	Y	Z
1	6	0	0.014474	0.032239	0.038039
2	6	0	-0.009277	-0.107267	1.425638
3	6	0	1.177633	-0.260996	2.143470
4	6	0	2.436500	-0.218462	1.444475
5	6	0	2.443424	-0.112521	0.053002
6	6	0	1.247487	0.005274	-0.654807
7	1	0	0.316765	-0.498143	3.986515
8	1	0	-0.960165	-0.127554	1.951400
9	1	0	3.390986	-0.091652	-0.478690
10	1	0	4.468922	-0.240626	1.695085
11	6	0	-1.178997	0.291734	-2.075788
12	6	0	-2.371908	0.432904	-2.788641
13	6	0	0.071978	0.264833	-2.778491
14	6	0	-2.351166	0.548047	-4.178874
15	1	0	-3.318960	0.453554	-2.256985
16	6	0	0.088067	0.380541	-4.170389
17	6	0	-1.105783	0.521232	-4.878303
18	1	0	1.034590	0.359883	-4.702985
19	6	0	-3.532347	0.806286	-6.300098
20	1	0	-4.381859	0.708115	-4.430406
21	6	0	-4.727985	0.947197	-7.007484
22	6	0	-2.293432	0.778918	-6.995883
23	1	0	-0.259027	0.619373	-6.745301
24	6	0	-4.714834	1.061730	-8.397900
25	6	0	-2.271045	0.892693	-8.387404
26	6	0	-3.460918	1.033468	-9.102111
27	1	0	-1.323563	0.871359	-8.918384
28	7	0	1.214106	0.123535	-2.039252
29	1	0	2.099845	0.101424	-2.531571
30	7	0	-1.146082	0.176102	-0.713151
31	1	0	-2.027204	0.197066	-0.212560
32	7	0	3.588837	-0.337859	2.185960
33	7	0	1.205639	-0.402151	3.511440
34	7	0	-1.142151	0.638161	-6.247650
35	7	0	-3.497138	0.688981	-4.925202
36	1	0	-5.674239	0.968167	-6.474302
37	7	0	-3.489052	1.148139	-10.464677
38	1	0	-2.610064	1.129184	-10.967603
39	7	0	-5.859181	1.201620	-9.133662
40	1	0	-6.746196	1.222421	-8.645107
41	6	0	-5.888085	1.318516	-10.527239
42	6	0	-4.659386	1.290511	-11.217301
43	6	0	-7.083476	1.458833	-11.233446
44	6	0	-4.636098	1.403181	-12.608058
45	6	0	-7.053209	1.570833	-12.621636
46	1	0	-8.028814	1.480073	-10.697913
47	6	0	-5.832961	1.542947	-13.306990
48	1	0	-3.687038	1.381050	-13.136928
49	1	0	-7.983032	1.679967	-13.169510
50	1	0	-5.813533	1.630208	-14.388040
51	1	0	3.593677	0.114206	3.094009
52	1	0	1.921301	-1.013208	3.890160

ST3: Optimized geometric parameters {bond length (Å), bond angle (°), dihedral angle (°)} of OPD, (neutral), OPD $^{+}$ (cationic) and OPD^{2+} (dicationic) dimers and oligomers of *o*-phenylenediamine.

Species	d_{C3-N2}	d_{C5-N6}	d_{C3-C5}	$\angle C_4C_3N_2$	$\angle C_1N_2C_3C_4$
2OPD (Neutral)	1.40Å	1.37Å	1.41Å	121.38 °	177.29 °
$2OPD^{+}$ (Cationic)	1.39 Å	1.36Å	1.42Å	121.85 °	169.84 °
$2OPD^{2+}$ (Dicationic)	1.39 Å	1.35Å	1.45Å	135.46 °	-163.94 °
4OPD (Neutral)	1.40 Å	1.39 Å	1.40Å	118.20 °	143.03 °
$4OPD^{+}$ (Cationic)	1.38 Å	1.35Å	1.41Å	121.90 °	127.07 °
$4OPD^{2+}$ (Dicationic)	1.35 Å	1.32Å	1.43Å	122.05 °	-171.06 °

d_{C3-N2}: Bond distance between C_3 and N_2 of dimers and oligomers of OPD.
d_{C5-N6}: Bond distance between C_5 and N_6 of dimers and oligomers of OPD.
d_{C3-C5}: Bond distance between C_3 and C_5 of dimers and oligomers of OPD.
$\angle C_4C_3N_2$: Angle between C_4, C_3, N_2 of dimers and oligomers of OPD.
$\angle C_1N_2C_3C_4$: Dihedral angle between C_1, N_2, C_3, C_4 dimers and oligomers of OPD.

ST4: IR frequencies (in cm^{-1}) of 2OPD-co-2OT (neutral)co- oligomer of *o*-phenylenediamine and *o*-toluidine.

#	Experimental [12]	Calculated	Approximate assignments
1	3700-3000	3593	νH-N
2	1621	1596	νC=C(q)
3	1495	1456	νC=C(b)
4	1400	1364	ν ring (P)
5	1007	1018	β-CH_3
6	869	867	Head-tail coupling
7	617	621	ring def.
8	591	596	β H-C

ν: stretching, q:quinoid, b: benzoid, Def: deformation mode, β: bending, P:phenazine-type ring.

ST5: IR frequencies (in cm^{-1}) of 4OT (neutral) oligomer of *o*-toluidine.

#	Experimental [12]	Calculated	Approximate assignments
1	3243	3395	νH-N
2	2922	2893	νC-H (-CH3)
3	1635	1599	νC=C (q)
4	1500	1498	νC=C
5	1325	1324	ν C-N (q)
6	1288	1245	ν C-N (b)
7	1004	1031	β -CH3
8	883	835	Head-tail coupling
9	576	558	β C-H

ν: stretching, q:quinoid, b: benzoid, Def: deformation mode, β: bending

ST6: IR frequencies (in cm^{-1}) of 4OPD (neutral) oligomer of *o*-phenylenediamine.

#	Experimental [25]	Calculated	Approximate assignments
1	3700-3000	3412	νH-N
2	1636	1630	νC=C(q), νC-H
3	1400	1417	νC=C(b)
4	1319	1276	νC-N(q)
5	1287	1217	νC-N(b)
6	1287	1231	νC-N
7	614	608	ring (def)
8	578	557	β H-C

ν: stretching, q:quinoid, b: benzoid, Def: deformation mode, β: bending

ST7: Raman frequencies (in cm^{-1}) of 2OPD-co-2OT (neutral) co-oligomers of *o*-phenylenediamine and *o*-toluidine**.**

#	Experimental [16]	Calculated	Approximate assignments
1	1615	1625	νC=C (Sq)
2	1511	1517	νC=N+ (q)
3	138	1378	-
4	1295	1297	νC-N (Sq)
5	1101	1112	νC-C (CH3 substituted)
6	605	603	(ring) def
7	462	470	γC-H
8	370	365	δC-H

ν: stretching, q:quinoid, Sq:semiquinoid, Def: deformation mode, β: bending, γ: out of plane deformation mode, δ: in-plane deformation mode.

ST8: Raman frequencies (in cm^{-1}) of 4OT (neutral) oligomers of *o*-toluidine.

#	Experimental [16]	Calculated	Approximate assignments
1	1592	1605	νC=C
2	1488	1496	νC=N
3	1340	1338	ν C-N+(Sq)
4	1264	1255	ν C-N (Sq)
5	1173	1190	β C-H(q)
6	1122	1140	ν C-C(-CH_3 substituted)
7	584	572	δ (ring)
8	458	477	γ C-H
9	387	380	δ C-H

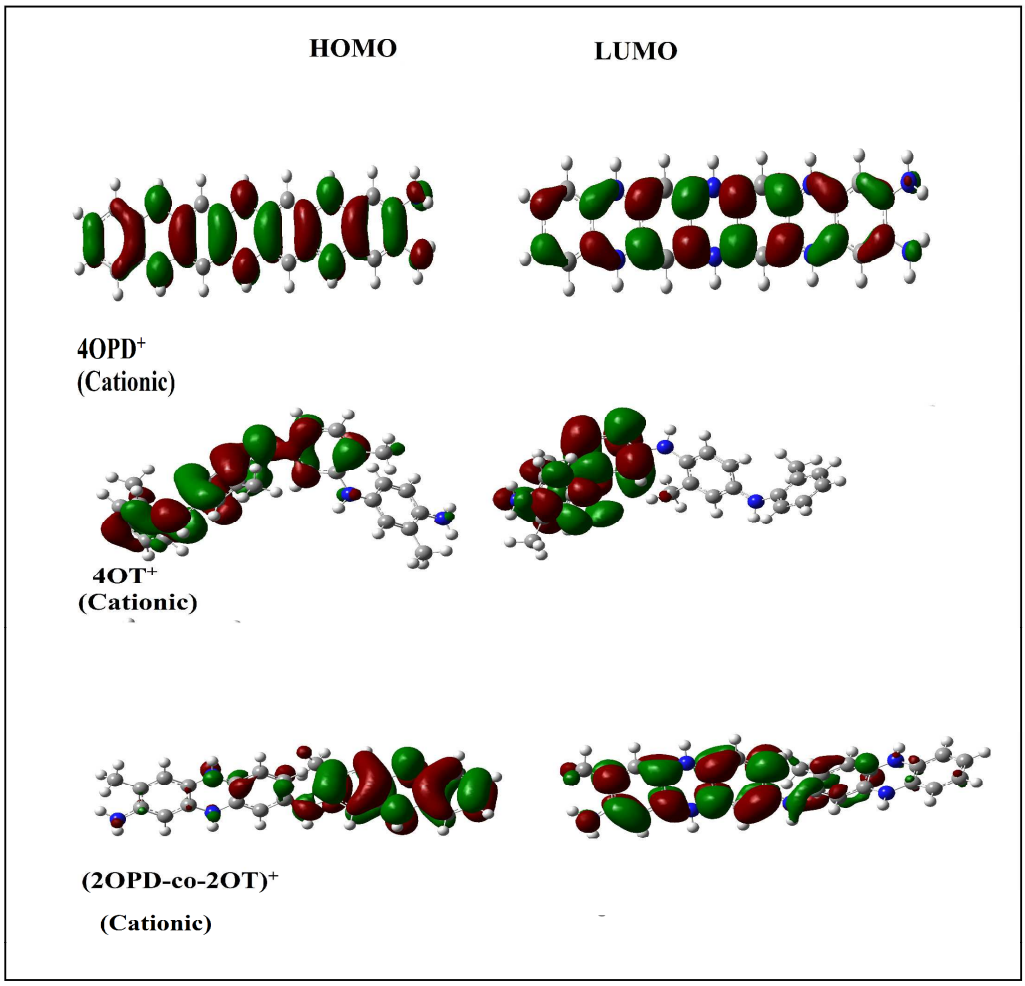
ν: stretching, q:quinoid, Sq: semiquinoid, β: bending, γ: out of plane deformation mode, δ: in-plane deformation mode.

ST9: Raman frequencies (in cm^{-1}) of 4OPD (neutral) oligomer of *o*-phenylenediamine.

#	Experimental [17]	Calculated	Approximate assignments
1	1606	1615	νC=C (q), νC-H
2	1575	1577	νC=C(q), νC-H
3	1473	1487	νC-H, N-H (wagg)
4	1269	1268	νC-N(b)
5	1248	1266	νC-N
6	1166	1147	βC-H
7	647	646	ring (def)
8	603	636	ring (def)

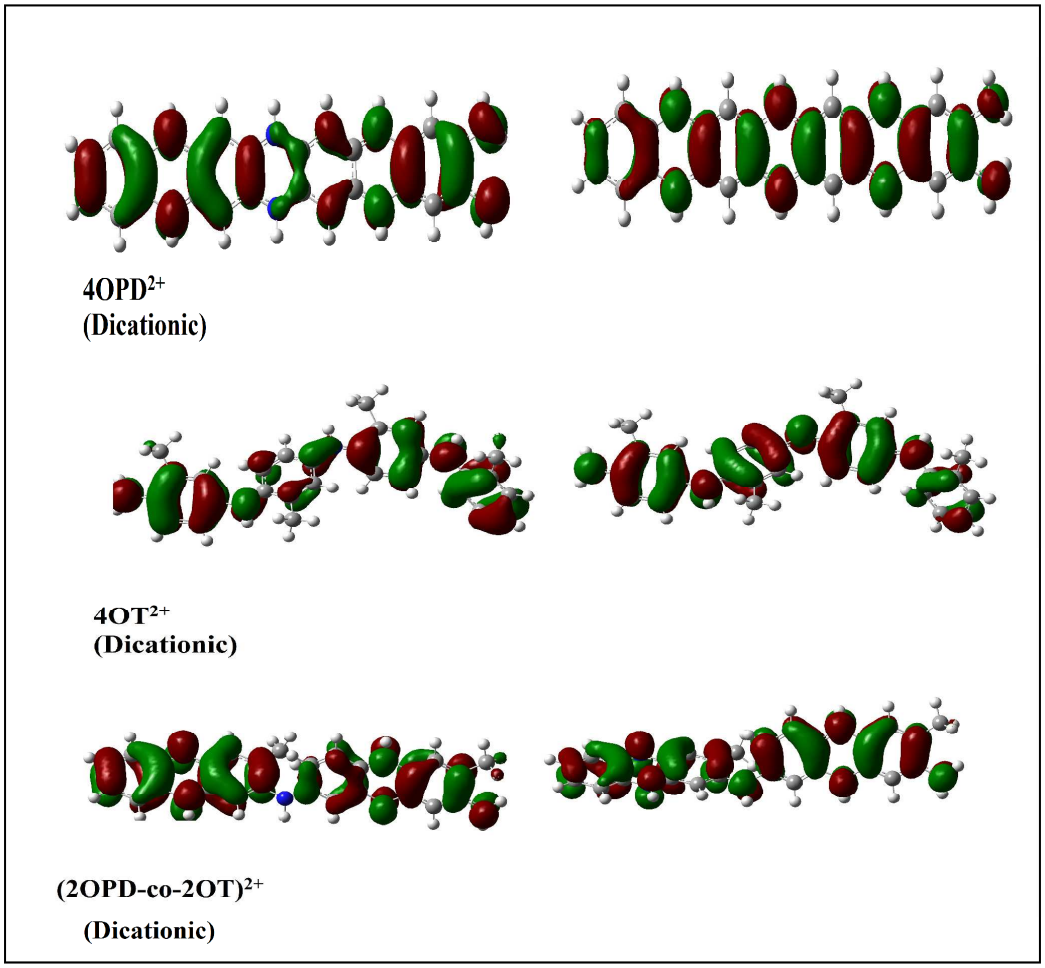
ν: stretching, q:quinoid, b: benzoid; def: deformation mode, , β: bending, wagg: wagging

S4



Calculated frontier molecular orbitals for cationic homo- and co-oligomers of OPD and OT.

S 5

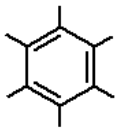
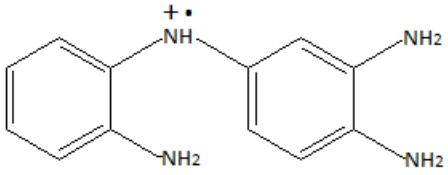
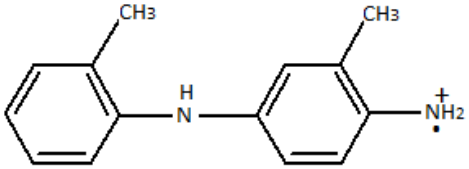
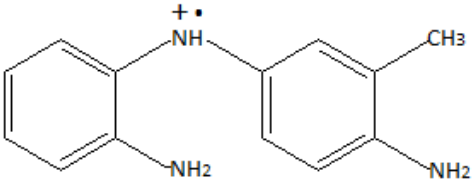


Calculated frontier molecular orbitals for dicationic homo- and co-oligomers of OPD and OT.

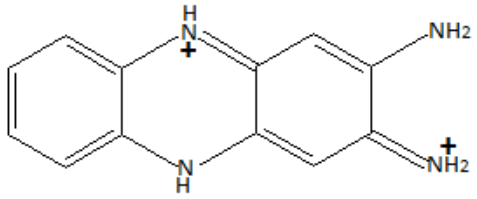
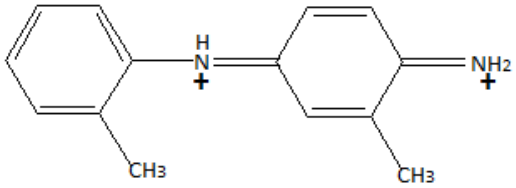
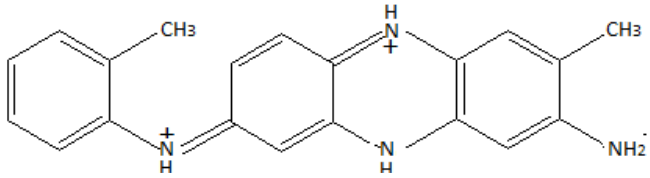
ST10: HOMOs, LUMOs, I_P, E_A and bandgap energies of neutral, cationic and dicationic homo- and co-oligomers of OPD and OT.

Species	I_P/eV	E_A/eV	HOMO/eV	LUMO/eV	Bandgap/eV
4OPD (Neutral)	4.24	0.017	-4.24	0.017	4.26
$4OPD^+$ (Cationic)	6.40	2.50	-6.40	-2.50	3.90
$4OPD^{2+}$ (Dicationic)	8.38	9.35	-8.38	-9.35	0.96
4OT (Neutral)	3.48	0.02	-3.48	-0.02	3.46
$4OT^+$ (Cationic)	7.52	3.90	-7.52	-3.90	3.62
$4OT^{2+}$ (Dicationic)	10.11	9.25	-10.11	-9.25	0.86
2OPD-co-2OT (Neutral)	3.83	0.02	-3.83	-0.02	3.81
$(2OPD\text{-}co\text{-}2OT)^+$ (Cationic)	7.07	3.30	-7.07	-3.30	3.77
$(2OPD\text{-}co\text{-}2OT)^{2+}$ (Dicationic)	10.31	9.40	-10.31	-9.40	0.91

ST11: The proposed structures and related calculated and experimental bands of cationic homo and co-dimers of OPD and OT.

#	Proposed structure	Calculated band maximum (nm)	Experimental band minimum (nm)
1.		296-363 (π-π*)	295 (π-π*)
2.		442	440
3.		414	400
4.		400	497

ST12: The proposed structures and related calculated and experimental bands of dicationic homo and co-dimers/oligomers of OPD and OT.

#	Proposed structure	Calculated band maxi-mum (nm)	Experimental band maximum (nm)
1.		789	>600
2.		701	700
3.		790	>650