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Supplementary Information for:

Investigating structure-charge transport relationships in substituted naphthyridine crystalline materials by computational model systems

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SI.1 Optimised geometries of neutral and radical species

The geometries of the parent **NTDT** monomer were optimised by means of a number of density functionals at the 6-311G(d) level as implemented in Spartan '18 (v. 1.3.0) software. In all cases, relaxed geometries were confirmed by IR analysis, which were characterised by the absence of any imaginary modes, thus consistent with real equilibrium minima. Tables SI.1.1-15 summarise the cartesian coordinates for these optimised geometries.

Table SI.1.1 Geometry of the neutral form of **NTDT**, optimised at B3LYP/6-311G(d), with absolute energy of -1672.318584 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63259	-0.01858	0.768654
C	-0.01018	-0.00637	2.558277
C	0.662299	0.006206	0.209747
C	0.968526	0.007591	1.5867
C	-0.66234	-0.00718	-0.20974
C	-1.42377	-0.01616	2.141235
H	2.014912	0.022022	1.875277
N	1.632557	0.017179	-0.76865
H	2.608304	0.023458	-0.50249
H	-2.60834	-0.02552	0.502494
C	-0.96857	-0.00881	-1.5867
H	-2.01493	-0.02407	-1.87531
C	0.010141	0.00546	-2.55826
C	1.423728	0.014145	-2.14123
O	2.381426	0.01739	-2.90569
O	-2.38147	-0.02099	2.905689
C	-0.30129	0.011068	-3.97694
C	-1.55712	0.036183	-4.55809
C	-1.53692	0.025312	-5.97006
C	-0.26187	-0.00729	-6.46944
S	0.935249	-0.02236	-5.22888
H	-2.47771	0.066604	-3.98839
H	-2.42685	0.043169	-6.58705
H	0.044398	-0.01919	-7.50593
C	0.301282	-0.01094	3.976957
S	-0.93541	0.013616	5.228961
C	0.26179	0.003088	6.46948
C	1.537	-0.02099	5.970044
C	1.557252	-0.02935	4.558057
H	-0.04453	0.011823	7.505987
H	2.427029	-0.03416	6.587002
H	2.477981	-0.05236	3.988268

Table SI.1.2 Geometry of the radical cation form of **NTDT**, optimised at B3LYP/6-311G(d), with absolute energy of -1672.073867 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.64116	0.000583	0.751011
C	-0.00899	-0.00538	2.560176
C	0.676467	-0.0014	0.218852
C	0.982394	-0.00464	1.577888
C	-0.67647	0.001324	-0.21885
C	-1.4322	-0.00263	2.127559
H	2.027308	-0.00659	1.867198
N	1.641166	-0.00066	-0.75101
H	2.61871	-0.00255	-0.48465
H	-2.61871	0.002459	0.484643
C	-0.98239	0.004585	-1.57789
H	-2.02731	0.006548	-1.8672
C	0.008987	0.005348	-2.56018
C	1.432199	0.002571	-2.12756
O	2.381359	0.002932	-2.88556
O	-2.38136	-0.003	2.885557
C	-0.28636	0.008629	-3.95203
C	-1.56413	0.011385	-4.53725
C	-1.5436	0.014226	-5.93086
C	-0.25171	0.013655	-6.42859
S	0.949716	0.009721	-5.21076
H	-2.48268	0.011323	-3.96518
H	-2.42667	0.016612	-6.55575
H	0.046707	0.015419	-7.4682
C	0.286356	-0.00862	3.952034
S	-0.94972	-0.00966	5.210755
C	0.251706	-0.01356	6.428594
C	1.543601	-0.01415	5.93086
C	1.56413	-0.01136	4.537254
H	-0.04671	-0.01528	7.468197
H	2.426673	-0.01652	6.555753
H	2.482681	-0.01132	3.965182

Table SI.1.3 Geometry of the radical anion form of **NTDT**, optimised at B3LYP/6-311G(d), with absolute energy of -1672.378221 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63637	0.000409	0.780187
C	-0.03399	-0.00529	2.572687
C	0.672621	-0.00125	0.220585
C	0.969255	-0.0044	1.572905
C	-0.67264	0.001288	-0.22058
C	-1.42046	-0.00271	2.1583
H	2.01435	-0.0062	1.869827
N	1.636352	-0.00035	-0.78018
H	2.612335	-0.00212	-0.52192
H	-2.61236	0.002193	0.521936
C	-0.96927	0.004436	-1.5729
H	-2.01437	0.006237	-1.86983
C	0.03398	0.005324	-2.57268
C	1.42045	0.002776	-2.15829
O	2.403162	0.003117	-2.91203
O	-2.40317	-0.00302	2.912043
C	-0.292	0.008663	-3.97608
C	-1.55108	0.011439	-4.56299
C	-1.53334	0.014374	-5.98005
C	-0.26826	0.013861	-6.49619
S	0.942892	0.009773	-5.24386
H	-2.4682	0.011421	-3.98655
H	-2.43166	0.016807	-6.58937
H	0.031746	0.015672	-7.535
C	0.292002	-0.00866	3.976081
S	-0.94288	-0.00967	5.243871
C	0.268288	-0.01386	6.496188
C	1.533359	-0.01448	5.980033
C	1.55108	-0.01155	4.562976
H	-0.0317	-0.01564	7.535009
H	2.431694	-0.01699	6.589348
H	2.468197	-0.01162	3.98652

Table SI.1.4 Geometry of the neutral form of **NTDT**, optimised at M08-HX/6-311G(d), with absolute energy of -1671.988223 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.6291	-0.08674	0.764984
C	-0.01195	-0.01482	2.543382
C	0.65752	0.033813	0.204078
C	0.964874	0.047537	1.588807
C	-0.65726	-0.03395	-0.20402
C	-1.42593	-0.06894	2.128781
H	2.012234	0.11829	1.884647
N	1.629258	0.087044	-0.76501
H	2.603855	0.122942	-0.49251
H	-2.60369	-0.12211	0.492374
C	-0.96468	-0.04728	-1.58871
H	-2.01215	-0.11726	-1.88426
C	0.012013	0.015121	-2.54342
C	1.425961	0.070052	-2.1288
O	2.370794	0.093829	-2.89526
O	-2.37083	-0.09122	2.89519
C	-0.29472	0.023061	-3.96963
C	-1.54799	0.108986	-4.53618
C	-1.53314	0.051192	-5.94978
C	-0.26375	-0.07738	-6.44069
S	0.920704	-0.11737	-5.2072
H	-2.46169	0.223692	-3.95737
H	-2.42141	0.108204	-6.5723
H	0.042342	-0.1365	-7.47971
C	0.294724	-0.02301	3.969567
S	-0.91984	0.128805	5.206738
C	0.264349	0.084283	6.44036
C	1.532831	-0.05484	5.949895
C	1.547351	-0.1165	4.536368
H	-0.04139	0.148046	7.479231
H	2.420637	-0.11688	6.572695
H	2.460058	-0.2401	3.957761

Table SI.1.5 Geometry of the radical cation form of **NTDT**, optimised at M08-HX/6-311G(d), with absolute energy of -1671.724862 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63768	0.000802	0.744249
C	-0.00767	-0.0059	2.549171
C	0.677159	-0.00157	0.217168
C	0.984449	-0.00523	1.577413
C	-0.67715	0.001598	-0.21718
C	-1.43052	-0.00288	2.116235
H	2.033437	-0.0075	1.868386
N	1.637682	-0.00077	-0.74425
H	2.616262	-0.00275	-0.47544
H	-2.61625	0.002794	0.475436
C	-0.98443	0.005242	-1.57741
H	-2.03342	0.00751	-1.86839
C	0.007687	0.005909	-2.54918
C	1.430524	0.00291	-2.11625
O	2.369451	0.003472	-2.87266
O	-2.36943	-0.00343	2.872652
C	-0.27942	0.009022	-3.94339
C	-1.55792	0.011418	-4.51673
C	-1.54019	0.013797	-5.9106
C	-0.24826	0.013328	-6.40288
S	0.941213	0.01009	-5.19296
H	-2.47713	0.01136	-3.93745
H	-2.42443	0.015811	-6.53896
H	0.053416	0.014862	-7.44554
C	0.279429	-0.00903	3.943393
S	-0.94122	-0.01005	5.192946
C	0.248241	-0.01332	6.402874
C	1.540171	-0.01385	5.910614
C	1.557912	-0.01148	4.516736
H	-0.05345	-0.01484	7.445535
H	2.424406	-0.01589	6.538983
H	2.477131	-0.01146	3.937465

Table SI.1.6 Geometry of the radical anion form of **NTDT**, optimised at M08-HX/6-311G(d), with absolute energy of -1672.053308 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63348	-0.00008	0.779631
C	-0.03323	-0.00548	2.559112
C	0.672964	-0.00089	0.217038
C	0.969894	-0.00418	1.56784
C	-0.67289	0.001282	-0.21706
C	-1.41853	-0.00309	2.149869
H	2.019209	-0.00559	1.866538
N	1.633536	0.000512	-0.77966
H	2.609858	-0.00099	-0.51952
H	-2.6098	0.001422	0.519491
C	-0.96982	0.004494	-1.56785
H	-2.01914	0.005864	-1.86653
C	0.033291	0.005716	-2.55913
C	1.418575	0.003418	-2.1499
O	2.391013	0.003803	-2.90488
O	-2.39095	-0.00349	2.904852
C	-0.28933	0.008842	-3.96549
C	-1.5477	0.011996	-4.5417
C	-1.52837	0.014277	-5.96032
C	-0.26179	0.01286	-6.46683
S	0.933948	0.008823	-5.22051
H	-2.46498	0.013028	-3.95878
H	-2.42495	0.016944	-6.57715
H	0.041238	0.014113	-7.50848
C	0.289333	-0.00884	3.965493
S	-0.93399	-0.00895	5.220466
C	0.261697	-0.01333	6.466822
C	1.528298	-0.01475	5.960369
C	1.547688	-0.0122	4.541754
H	-0.0414	-0.01474	7.508444
H	2.424861	-0.01759	6.577227
H	2.464971	-0.01322	3.958836

Table SI.1.7 Geometry of the neutral form of **NTDT**, optimised at M06-2X/6-311G(d), with absolute energy of -1671.920504 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63214	-0.01205	0.763935
C	-0.01416	-0.00576	2.546755
C	0.656448	0.003968	0.206274
C	0.96197	0.003888	1.590158
C	-0.65645	-0.00397	-0.20627
C	-1.42905	-0.01188	2.130485
H	2.007596	0.012691	1.880163
N	1.632143	0.01205	-0.76394
H	2.606599	0.016109	-0.49224
H	-2.6066	-0.01611	0.492236
C	-0.96197	-0.00389	-1.59016
H	-2.0076	-0.01269	-1.88016
C	0.014164	0.005756	-2.54676
C	1.429045	0.011883	-2.13049
O	2.378159	0.015915	-2.89266
O	-2.37816	-0.01592	2.892658
C	-0.29583	0.009443	-3.97259
C	-1.55143	0.025812	-4.5377
C	-1.53568	0.020571	-5.95105
C	-0.26321	0.000675	-6.44617
S	0.923698	-0.01041	-5.21483
H	-2.46771	0.042936	-3.96189
H	-2.42414	0.031523	-6.56769
H	0.043608	-0.00655	-7.48181
C	0.295825	-0.00944	3.972586
S	-0.9237	0.010413	5.214828
C	0.263209	-0.00068	6.446174
C	1.535675	-0.02057	5.95105
C	1.551431	-0.02581	4.537696
H	-0.04361	0.006553	7.481812
H	2.424136	-0.03152	6.567691
H	2.467705	-0.04294	3.961893

Table SI.1.8 Geometry of the radical cation form of **NTDT**, optimised at M06-2X/6-311G(d), with absolute energy of -1671.662396 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63936	-0.0024	0.743252
C	-0.01103	-0.00588	2.551939
C	0.675312	-0.00029	0.219181
C	0.980168	-0.00318	1.578164
C	-0.67531	0.000286	-0.21918
C	-1.43437	-0.00469	2.117658
H	2.02468	-0.00261	1.86709
N	1.639356	0.0024	-0.74325
H	2.616825	0.001925	-0.47412
H	-2.61683	-0.00193	0.47412
C	-0.98017	0.003175	-1.57816
H	-2.02468	0.002611	-1.86709
C	0.01103	0.005882	-2.55194
C	1.434374	0.004687	-2.11766
O	2.377279	0.005656	-2.87009
O	-2.37728	-0.00566	2.870093
C	-0.28025	0.009279	-3.94411
C	-1.55834	0.014438	-4.51747
C	-1.5418	0.015592	-5.91009
C	-0.25171	0.010427	-6.40357
S	0.939848	0.005673	-5.19708
H	-2.47372	0.018449	-3.94115
H	-2.42343	0.019787	-6.5349
H	0.0474	0.009606	-7.44247
C	0.280253	-0.00928	3.944105
S	-0.93985	-0.00567	5.197084
C	0.251707	-0.01043	6.403571
C	1.541802	-0.01559	5.910087
C	1.558339	-0.01444	4.517466
H	-0.0474	-0.00961	7.442472
H	2.423434	-0.01979	6.534902
H	2.47372	-0.01845	3.94115

Table SI.1.9 Geometry of the radical anion form of **NTDT**, optimised at M06-2X/6-311G(d), with absolute energy of -1671.981706 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63569	-0.00278	0.776866
C	-0.0389	-0.00533	2.561585
C	0.671146	0.000037	0.219795
C	0.96442	-0.00247	1.569929
C	-0.67115	-3.7E-05	-0.2198
C	-1.42341	-0.00469	2.150651
H	2.008674	-0.00136	1.867577
N	1.635694	0.002783	-0.77687
H	2.610853	0.002393	-0.51553
H	-2.61085	-0.00239	0.515531
C	-0.96442	0.002473	-1.56993
H	-2.00867	0.001363	-1.86758
C	0.038899	0.005333	-2.56159
C	1.423405	0.004694	-2.15065
O	2.400326	0.005676	-2.90035
O	-2.40033	-0.00568	2.900346
C	-0.28862	0.009084	-3.96744
C	-1.54638	0.014862	-4.54185
C	-1.53073	0.015666	-5.95988
C	-0.26764	0.010734	-6.46972
S	0.93194	0.004985	-5.2259
H	-2.45965	0.019489	-3.96149
H	-2.42576	0.020044	-6.57072
H	0.033163	0.010563	-7.50726
C	0.288623	-0.00908	3.967444
S	-0.93194	-0.00499	5.225896
C	0.267639	-0.01073	6.46972
C	1.530731	-0.01567	5.959876
C	1.546382	-0.01486	4.541853
H	-0.03316	-0.01056	7.507259
H	2.425761	-0.02004	6.570719
H	2.459649	-0.01949	3.961485

Table SI.1.10 Geometry of the neutral form of **NTDT**, optimised at M08-SO/6-311G(d), with absolute energy of -1671.582038 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63727	0.009503	0.770902
C	-0.00919	-0.00355	2.553631
C	0.659467	-0.0041	0.204029
C	0.969796	-0.00858	1.593703
C	-0.65955	0.004894	-0.20401
C	-1.42916	0.004935	2.138879
H	2.022677	-0.01764	1.886913
N	1.63719	-0.00873	-0.77086
H	2.616856	-0.01451	-0.50041
H	-2.61695	0.015255	0.500478
C	-0.96986	0.009135	-1.59369
H	-2.02273	0.017976	-1.88693
C	0.009148	0.003953	-2.55362
C	1.429112	-0.00443	-2.13884
O	2.374666	-0.00707	-2.91175
O	-2.37469	0.007381	2.911809
C	-0.29664	0.006733	-3.98575
C	-1.55639	0.001344	-4.55281
C	-1.53826	0.010489	-5.97237
C	-0.25933	0.022584	-6.46514
S	0.930939	0.02317	-5.22646
H	-2.47882	-0.0099	-3.97215
H	-2.43104	0.007417	-6.59544
H	0.05085	0.03059	-7.50734
C	0.296602	-0.00673	3.985773
S	-0.93088	-0.02486	5.226539
C	0.259468	-0.0243	6.465143
C	1.538353	-0.01093	5.972304
C	1.556378	-0.0008	4.552768
H	-0.05062	-0.03319	7.507361
H	2.431163	-0.0076	6.595317
H	2.478734	0.011564	3.972034

Table SI.1.11 Geometry of the radical cation form of **NTDT**, optimised at M08-SO/6-311G(d), with absolute energy of -1671.320262 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.64556	0.000656	0.750689
C	-0.00638	-0.00568	2.557651
C	0.678754	-0.00132	0.216877
C	0.988558	-0.00476	1.580194
C	-0.67872	0.001501	-0.21691
C	-1.43528	-0.00276	2.125844
H	2.040375	-0.00669	1.871784
N	1.645584	-0.00048	-0.7507
H	2.628098	-0.00237	-0.4824
H	-2.62807	0.002556	0.482384
C	-0.98851	0.004921	-1.58018
H	-2.04033	0.006838	-1.87177
C	0.006434	0.005782	-2.55768
C	1.435303	0.002875	-2.1259
O	2.373226	0.003293	-2.8907
O	-2.37316	-0.00322	2.890689
C	-0.28007	0.00904	-3.95495
C	-1.56271	0.011754	-4.53067
C	-1.54417	0.014017	-5.92917
C	-0.2472	0.013112	-6.42048
S	0.948028	0.009784	-5.20662
H	-2.48435	0.01204	-3.94989
H	-2.4302	0.01611	-6.55987
H	0.055023	0.014405	-7.46596
C	0.28008	-0.00904	3.954952
S	-0.94804	-0.01014	5.206596
C	0.247144	-0.0135	6.42048
C	1.54411	-0.01415	5.929206
C	1.562675	-0.01167	4.530696
H	-0.05512	-0.015	7.465945
H	2.43014	-0.01621	6.559919
H	2.484339	-0.01172	3.949943

Table SI.1.12 Geometry of the radical anion form of **NTDT**, optimised at M08-SO/6-311G(d), with absolute energy of -1671.648788 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.64085	0.000228	0.784842
C	-0.03283	-0.00563	2.567744
C	0.674995	-0.00135	0.21738
C	0.97286	-0.00468	1.572291
C	-0.67502	0.001264	-0.21739
C	-1.42204	-0.00298	2.159946
H	2.024992	-0.00653	1.872584
N	1.640823	-0.00034	-0.78484
H	2.621569	-0.00207	-0.52615
H	-2.6216	0.001957	0.526154
C	-0.97289	0.004626	-1.57228
H	-2.02502	0.006499	-1.87257
C	0.032811	0.005598	-2.56774
C	1.42201	0.002908	-2.15994
O	2.395733	0.003247	-2.92101
O	-2.39575	-0.00331	2.921026
C	-0.29127	0.008969	-3.98037
C	-1.5523	0.011762	-4.55726
C	-1.53249	0.014406	-5.98183
C	-0.26233	0.013643	-6.4877
S	0.938265	0.00993	-5.23601
H	-2.47221	0.011995	-3.97241
H	-2.43126	0.016662	-6.6005
H	0.04282	0.015162	-7.53187
C	0.291256	-0.00895	3.980393
S	-0.93824	-0.0099	5.236056
C	0.262377	-0.01357	6.487703
C	1.53253	-0.01432	5.981817
C	1.552297	-0.0117	4.557244
H	-0.04274	-0.01508	7.531876
H	2.431312	-0.01654	6.600458
H	2.472187	-0.01192	3.972351

Table SI.1.13 Geometry of the neutral form of **NTDT**, optimised at ωB97X-D/6-311G(d), with absolute energy of -1671.973763 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.62623	-0.16237	0.759225
C	-0.02097	-0.00265	2.542554
C	0.651046	0.073027	0.206803
C	0.951354	0.114521	1.591821
C	-0.65122	-0.06859	-0.20665
C	-1.42912	-0.11513	2.124908
H	1.986542	0.249887	1.889975
N	1.626064	0.166279	-0.75908
H	2.594114	0.245219	-0.48376
H	-2.59423	-0.24184	0.483899
C	-0.95122	-0.11219	-1.59166
H	-1.98597	-0.25128	-1.88955
C	0.020966	0.005543	-2.54253
C	1.429077	0.118046	-2.12467
O	2.379491	0.158739	-2.88625
O	-2.3792	-0.1576	2.886742
C	-0.29079	0.014903	-3.96809
C	-1.53083	0.200432	-4.53329
C	-1.53028	0.0972	-5.94313
C	-0.28508	-0.16307	-6.43557
S	0.901425	-0.26455	-5.20348
H	-2.42044	0.429025	-3.95914
H	-2.41026	0.221952	-6.56073
H	0.006518	-0.27544	-7.4701
C	0.291157	-0.01305	3.968013
S	-0.90475	0.241948	5.204725
C	0.282214	0.14418	6.436659
C	1.530749	-0.09658	5.942769
C	1.533236	-0.18756	4.53206
H	-0.01103	0.245567	7.471847
H	2.411919	-0.21551	6.559775
H	2.42574	-0.39906	3.955894

Table SI.1.14 Geometry of the radical cation form of **NTDT**, optimised at ωB97X-D /6-311G(d), with absolute energy of -1671.720689 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63869	0.00017	0.74315
C	-0.01136	-0.0051	2.550701
C	0.674361	-0.00118	0.219008
C	0.97965	-0.00415	1.575547
C	-0.67436	0.001062	-0.21901
C	-1.43284	-0.00264	2.11525
H	2.024451	-0.00572	1.863922
N	1.638693	-0.00028	-0.74315
H	2.613582	-0.00187	-0.47424
H	-2.61358	0.001749	0.474234
C	-0.97965	0.004053	-1.57555
H	-2.02445	0.00564	-1.86392
C	0.011362	0.005022	-2.5507
C	1.432842	0.002553	-2.11525
O	2.377708	0.002878	-2.86811
O	-2.37771	-0.00296	2.868104
C	-0.27999	0.008331	-3.94166
C	-1.5564	0.011598	-4.51737
C	-1.5398	0.014528	-5.9097
C	-0.25273	0.013503	-6.40399
S	0.941122	0.009016	-5.19439
H	-2.47466	0.01192	-3.94473
H	-2.4231	0.017239	-6.53315
H	0.044282	0.015194	-7.44388
C	0.279991	-0.00835	3.941658
S	-0.94112	-0.00886	5.194383
C	0.252727	-0.01328	6.40399
C	1.5398	-0.01442	5.909705
C	1.556399	-0.01162	4.517374
H	-0.04429	-0.01486	7.443876
H	2.423097	-0.01711	6.533152
H	2.474664	-0.01205	3.944736

Table SI.1.15 Geometry of the radical anion form of **NTDT**, optimised at ωB97X-D/6-311G(d), with absolute energy of -1672.031503 hartrees.

Atom	**x / Å**	**y / Å**	**z / Å**
N	-1.63465	0.000007	0.776222
C	-0.03846	-0.00509	2.560362
C	0.670517	-0.00094	0.219524
C	0.964632	-0.00392	1.56811
C	-0.67053	0.001131	-0.21952
C	-1.42073	-0.00287	2.148333
H	2.009576	-0.00531	1.865231
N	1.634639	0.000187	-0.77622
H	2.608159	-0.00131	-0.51585
H	-2.60817	0.001494	0.515856
C	-0.96464	0.004077	-1.56811
H	-2.00958	0.005436	-1.86523
C	0.038452	0.005212	-2.56036
C	1.420726	0.003013	-2.14833
O	2.399445	0.003429	-2.89842
O	-2.39945	-0.00332	2.898426
C	-0.28952	0.008579	-3.96701
C	-1.54579	0.011932	-4.54321
C	-1.52954	0.01456	-5.96044
C	-0.26732	0.013264	-6.47022
S	0.932107	0.008801	-5.2237
H	-2.46156	0.012674	-3.96518
H	-2.42584	0.017316	-6.57115
H	0.032636	0.014728	-7.50879
C	0.289517	-0.00856	3.967013
S	-0.9321	-0.00899	5.223709
C	0.267332	-0.01356	6.470223
C	1.529549	-0.01475	5.960437
C	1.54579	-0.01194	4.543199
H	-0.03262	-0.01516	7.508791
H	2.42585	-0.01754	6.571137
H	2.461557	-0.01257	3.965165

SI.2 Two-dimensional model system Δz optimisation

The relative intermonomer displacement along the z vertical axis in the **NTDT** dimer model system was optimsed at the M06-2X/6-311G(d) level. To do this, in a fully eclipsed (Δx = Δy = 0.00 Å) **NTDT** dimer, we computed the counterpoise corrected intermolecular interaction (ΔE_{CP}) by displacing one monomer with respect to the other along the z axis from 3.00 to 5.00 Å on 0.10 Å stepwise first and then from 3.65 to 3.75 Å on a 0.01 Å stepwise. Computed values are illustrated in Figure SI.2.1.

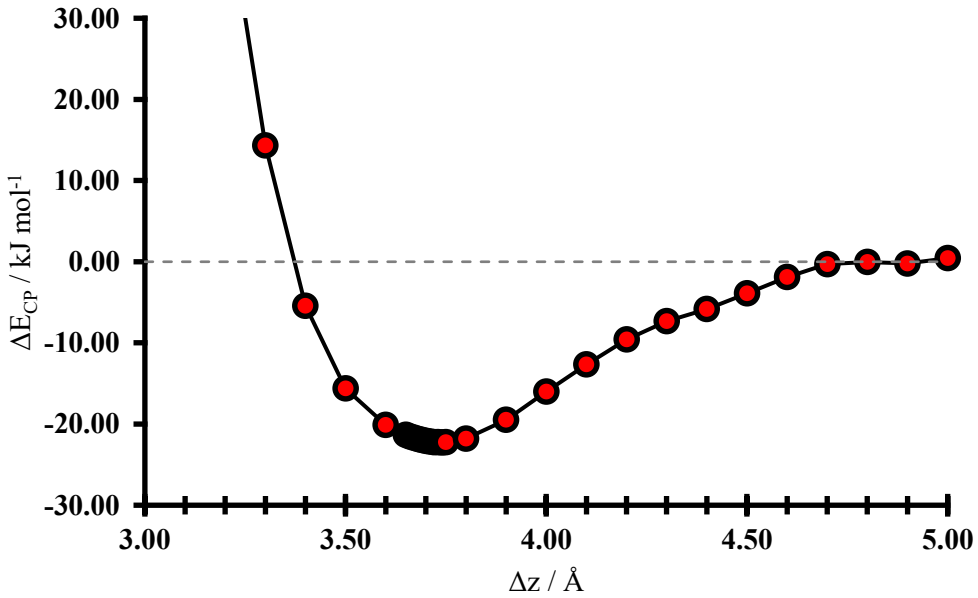

Figure SI.2.1 Illustration of the computed counterpoise-corrected intermolecular interactions (ΔE_{CP}) of a model **NTDT** dimer pair as a function of intermonomer displacements along the z axis while the monomers in a constant, fully eclipsed dimer geometry (Δx = Δy = 0.00 Å). M06-2X/6-311G(d).

SI.3 Effect of density functionals on bond length changes

Changes in bond lengths, Δ_{BL} throughout the model **NTDT** core motif as well as thiophene rings were measured for relaxed geometries and plotted againts their bond numbers (Figure 3 in the manuscript). Δ_{BL} was computed by subtracting the bond length of a given bond in the radical geometry from the bond length in the neutral specie for the same chemical bond. As such, positive (negative) changes are consistent with an elongation (shortening) of the chemical bond on going from neutral to radical relaxed geometries. These were computed using a number of density functionals at the 6-311G(d), with findings illustrated in Figure SI.3.1-5.

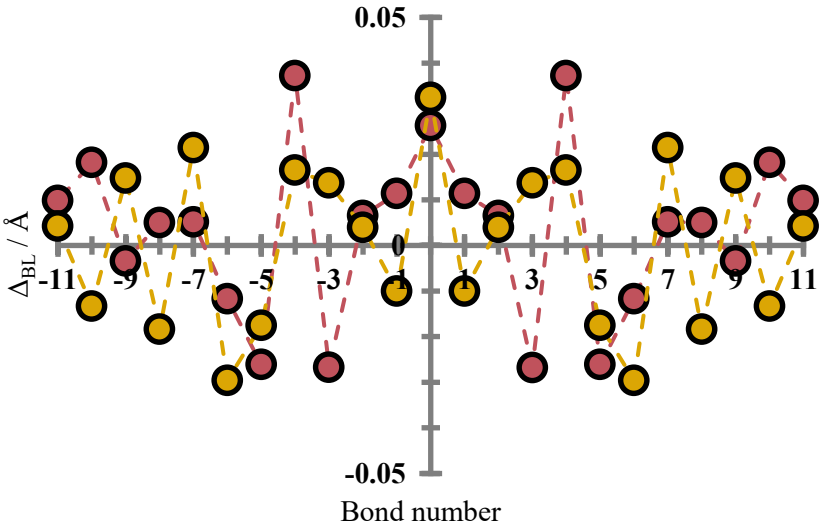

Figure SI.3.1 Computed bond length changes (Δ_{BL}) on progression from **NTDT** neutral to radical cation (yellow) and anion (red) optimised geometries employing B3LYP density functional at 6-311G(d) level.

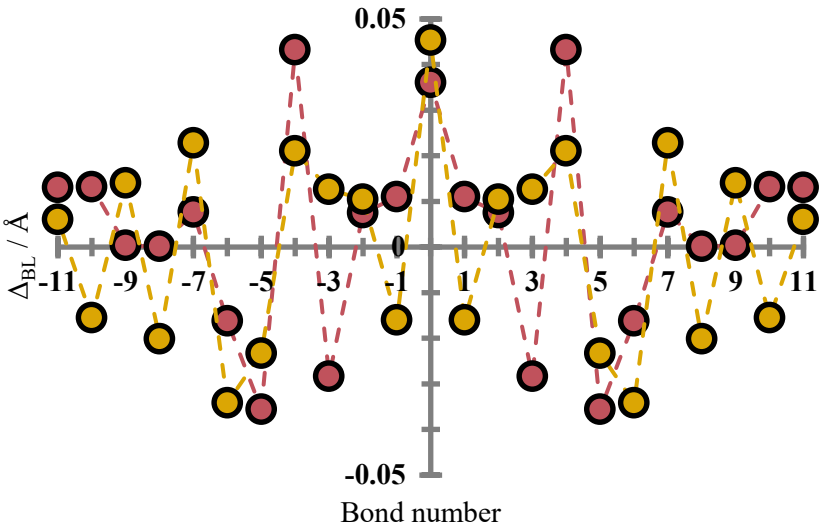

Figure SI.3.2 Computed bond length changes (Δ_{BL}) on progression from **NTDT** neutral to radical cation (yellow) and anion (red) optimised geometries employing M08-HX density functional at 6-311G(d) level.

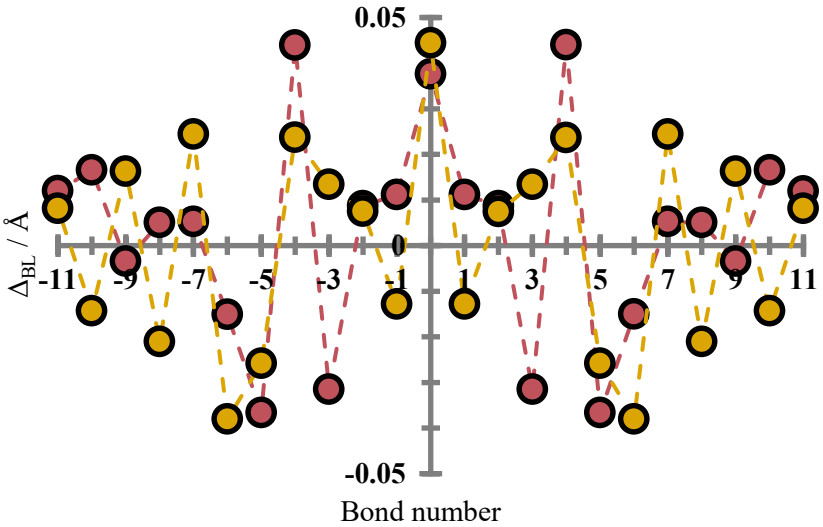

Figure SI.3.3 Computed bond length changes (Δ_{BL}) on progression from **NTDT** neutral to radical cation (yellow) and anion (red) optimised geometries employing M06-2X density functional at 6-311G(d) level.

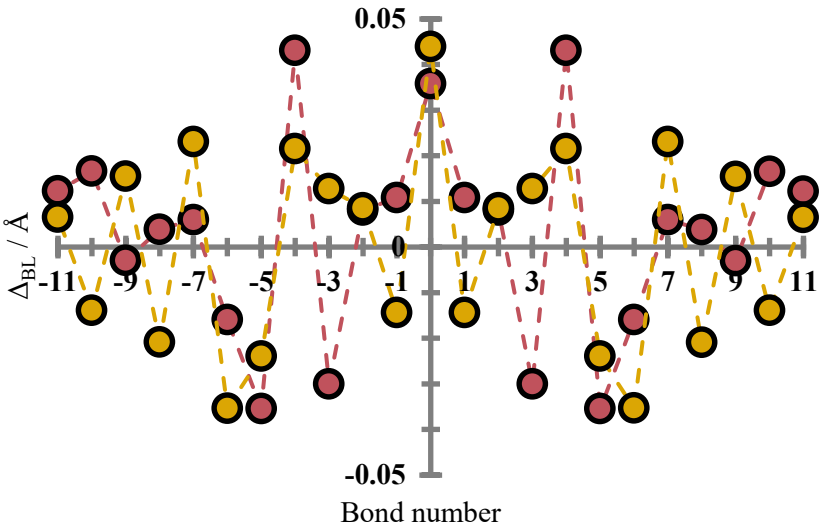

Figure SI.3.4 Computed bond length changes (Δ_{BL}) on progression from **NTDT** neutral to radical cation (yellow) and anion (red) optimised geometries employing M08-SO density functional at 6-311G(d) level.

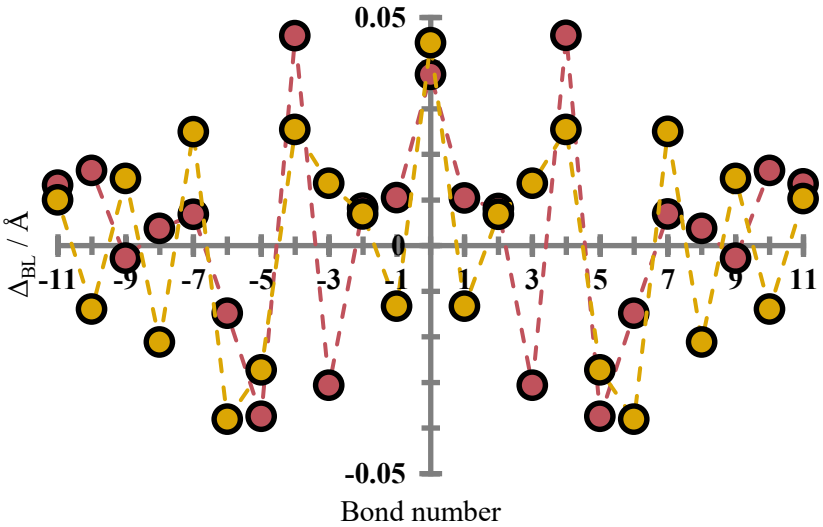

Figure SI.3.5 Computed bond length changes (Δ_{BL}) on progression from **NTDT** neutral to radical cation (yellow) and anion (red) optimised geometries employing ωB97X-D density functional at 6-311G(d) level.

SI.4 Effect of density functionals of computed $\lambda_{h/e}$

Inner-sphere reorganisation energies ($\lambda_{h/e}$) were computed for the model **NTDT** as a function of thiophene ring twist for a number of density functionals at the 6-311G(d) level as implemented in Spartan '18 (v. 1.3.0). Both, symmetric ($\theta_1 = -\theta_2$) and asymmetric ($\theta_1 = \theta_2$) torsions were explored and results are illustrated in the following in Figures SI.4.1-10.

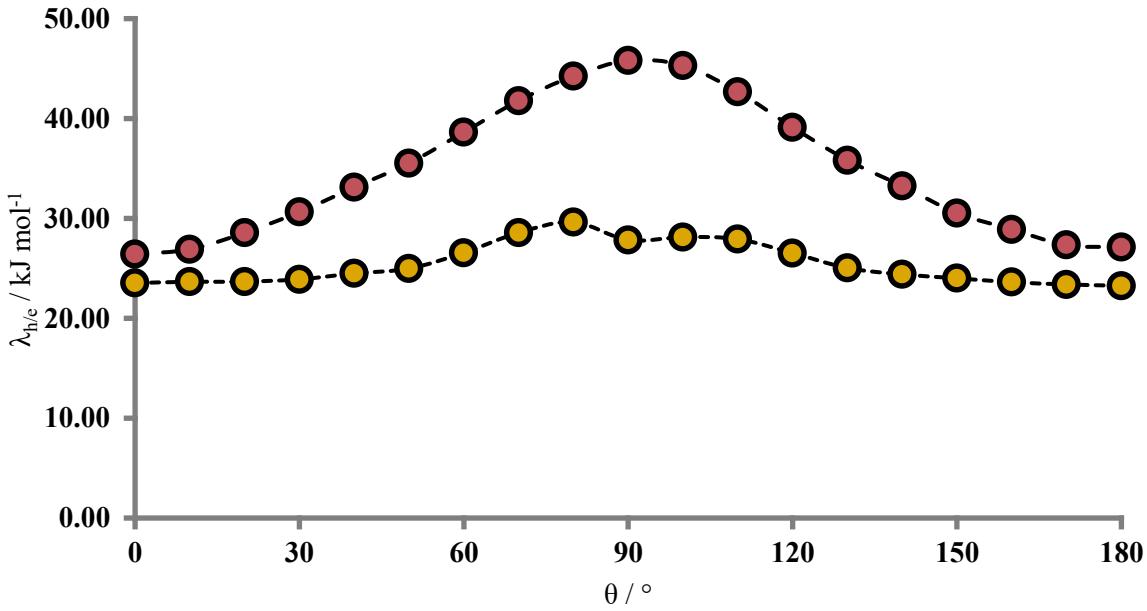

Figure SI.4.1 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous symmetrical thiophene torsion ($\theta_1 = -\theta_2$) employing B3LYP density functional at 6-311G(d) level.

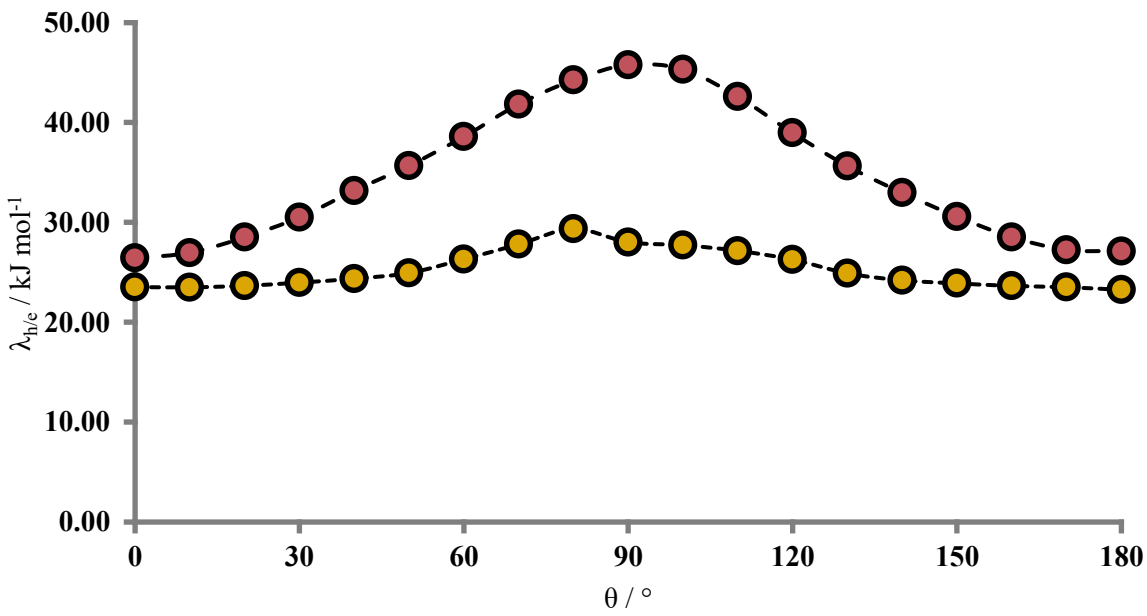

Figure SI.4.2 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous asymmetrical thiophene torsion ($\theta_1 = \theta_2$) employing B3LYP density functional at 6-311G(d) level.

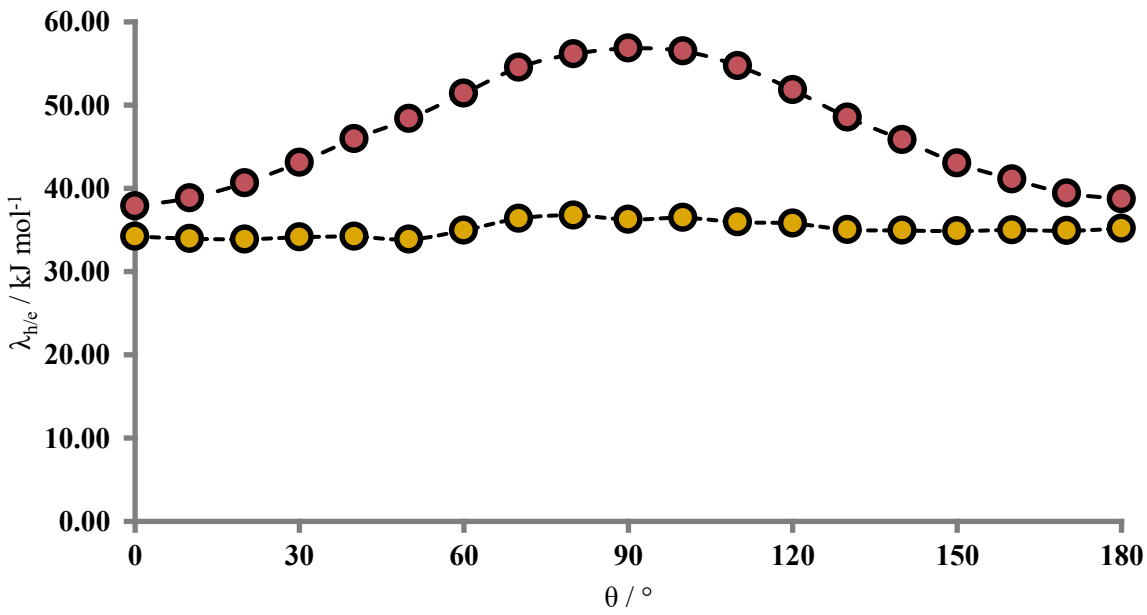

Figure SI.4.3 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous symmetrical thiophene torsion ($\theta_1 = -\theta_2$) employing M08-HX density functional at 6-311G(d) level.

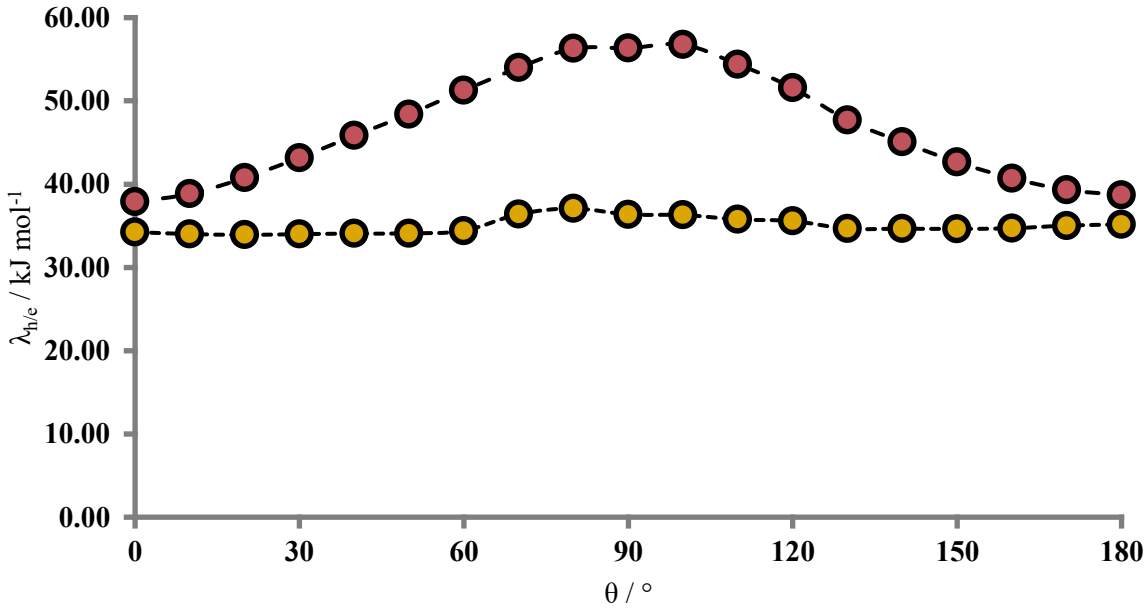

Figure SI.4.4 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous asymmetrical thiophene torsion ($\theta_1 = \theta_2$) employing M08-HX density functional at 6-311G(d) level.

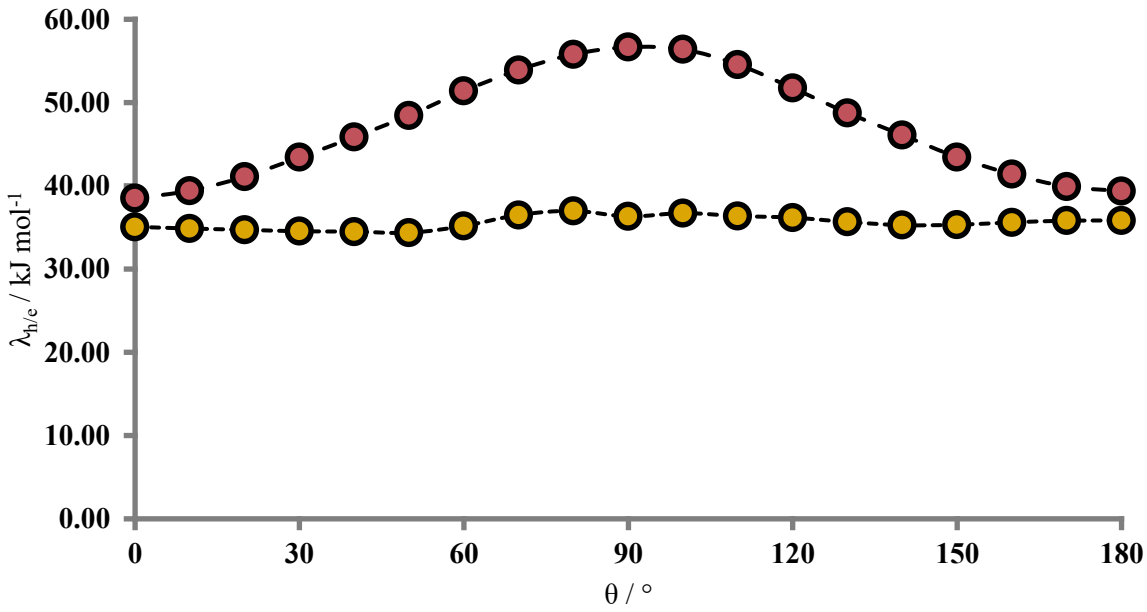

Figure SI.4.5 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous symmetrical thiophene torsion ($\theta_1 = -\theta_2$) employing M06-2X density functional at 6-311G(d) level.

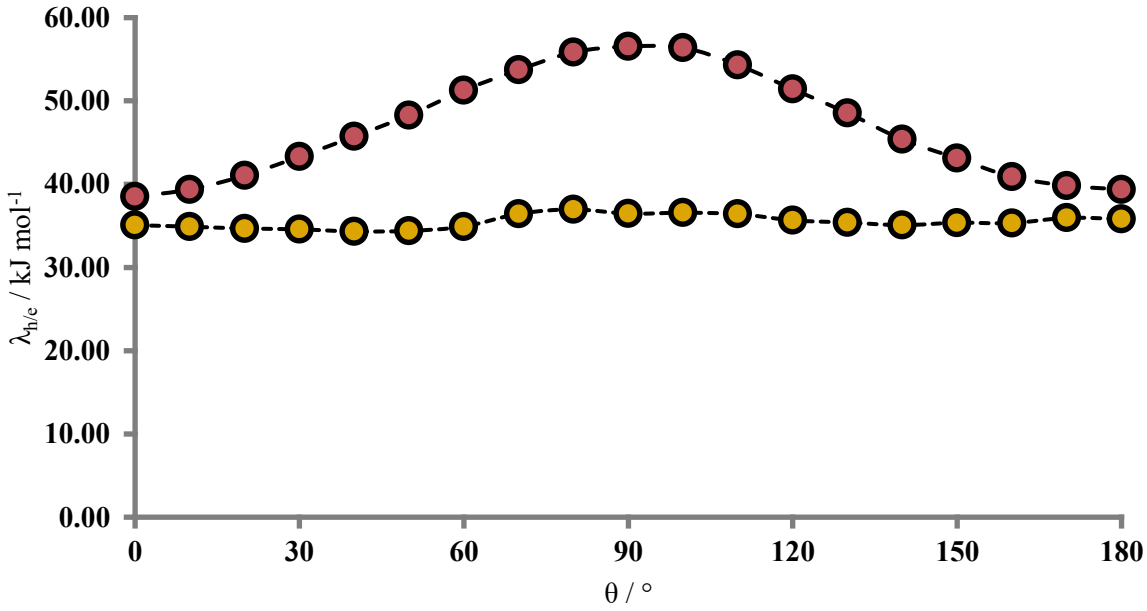

Figure SI.4.6 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous asymmetrical thiophene torsion ($\theta_1 = \theta_2$) employing M06-2X density functional at 6-311G(d) level.

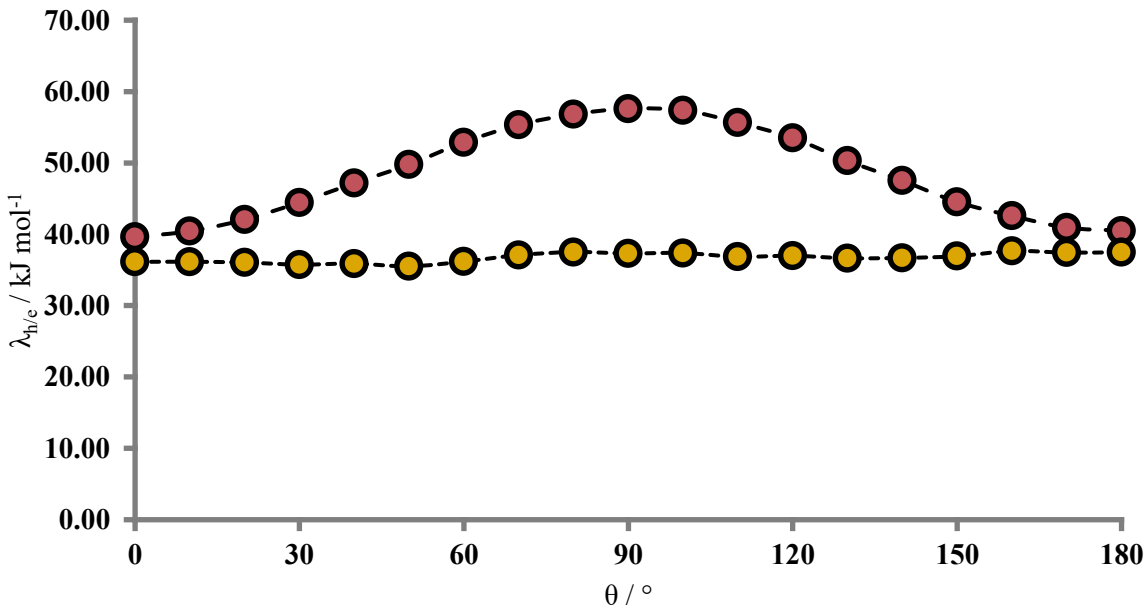

Figure SI.4.7 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous symmetrical thiophene torsion ($\theta_1 = -\theta_2$) employing M08-SO density functional at 6-311G(d) level.

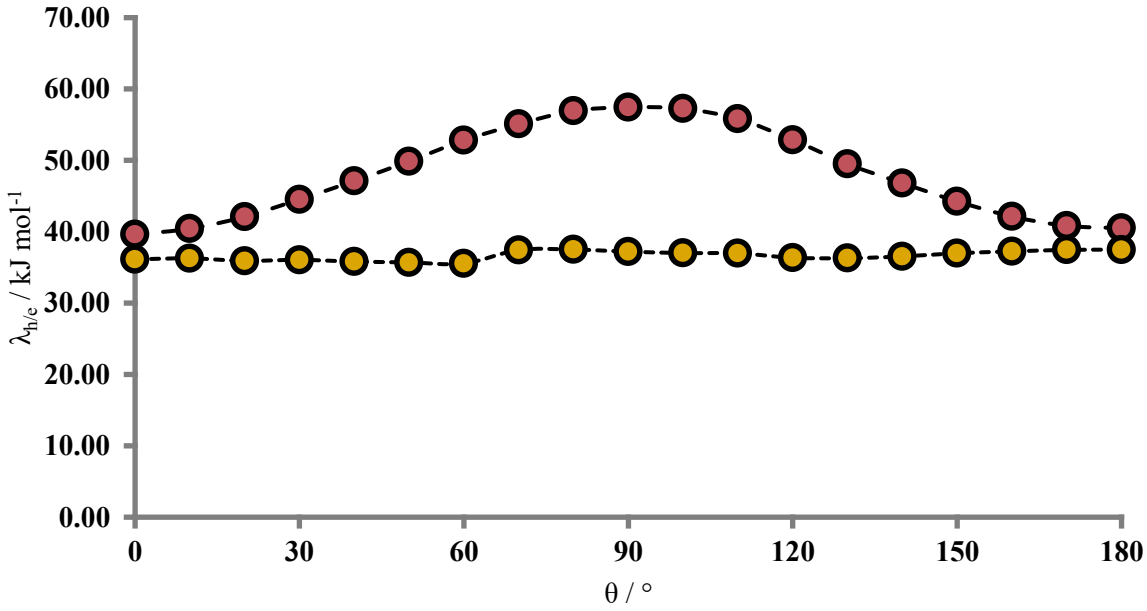

Figure SI.4.8 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous asymmetrical thiophene torsion ($\theta_1 = \theta_2$) employing M08-SO density functional at 6-311G(d) level.

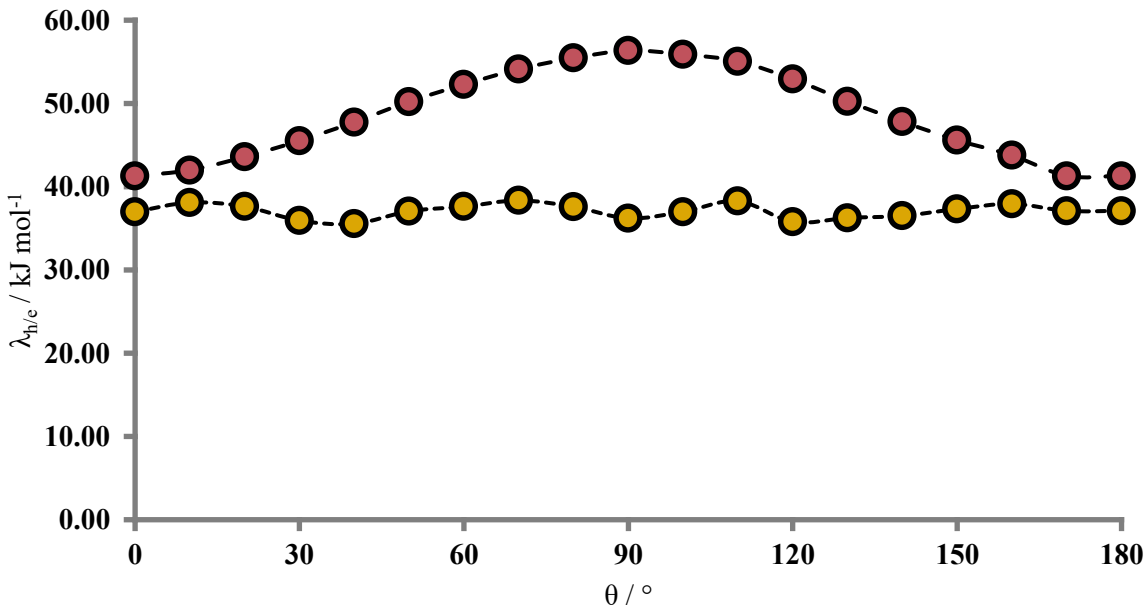

Figure SI.4.9 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous symmetrical thiophene torsion ($\theta_1 = -\theta_2$) employing ωB97X-D density functional at 6-311G(d) level.

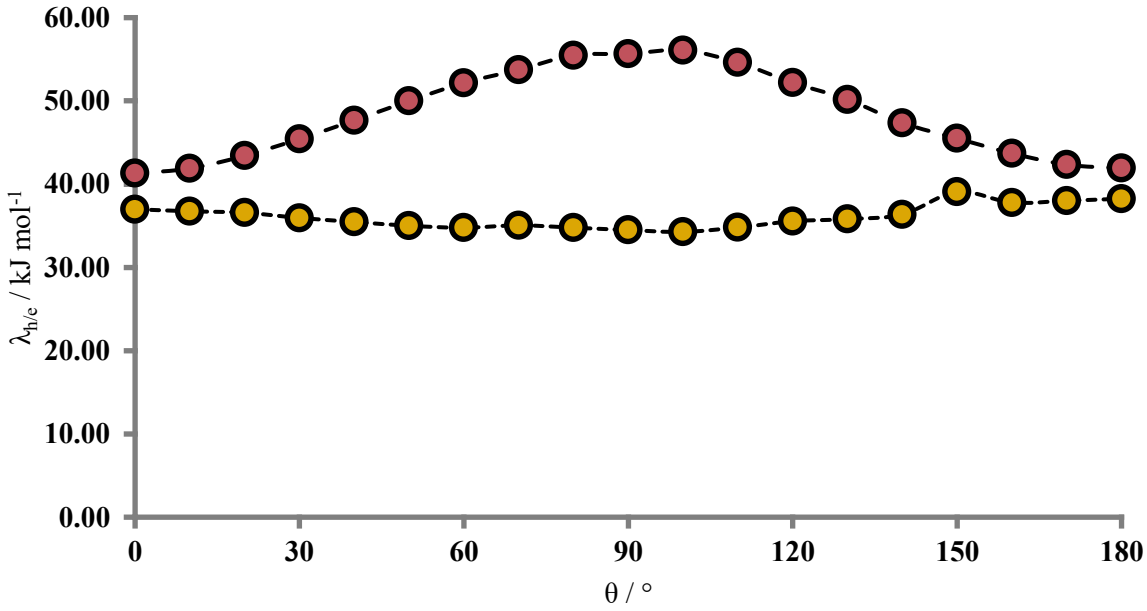

Figure SI.4.10 Computed hole (red solid cicles) and electron (yellow solid circles) inner-sphere reorganisation energies for model **NTDT** as a function of the simultaneous asymmetrical thiophene torsion ($\theta_1 = \theta_2$) employing ωB97X-D density functional at 6-311G(d) level.

SI.5 Effect of basis sets on computed $t_{h/e}$

The effect of basis sets on computed charge transfer integrals was evaluated by means of a one-dimensional **NTDT** dimer model system whereby the top monomer is displaced with respect the bottom along the long molecular axis (Δx) whilst mainitaing the alignment for the short molecular axis (Δy = 0.00 Å). This was done utilising the M06-2X density functional at the 6-31G(d), 6-311G(d), 6-311g(d)(p), 6-311+G(d), 6-311++G(d) and 6-311++G(d)(p) levels. Findings are illustrated in Figures SI.5.1-2 for t_h and t_e, respectively.

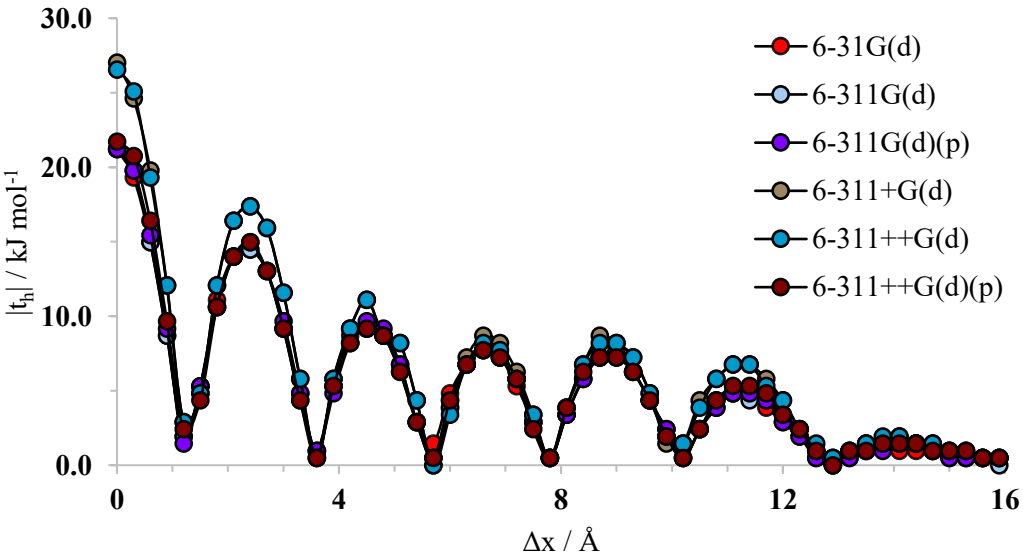

Figure SI.5.1 Computed hole transfer integrals (t_h) for the **NTDT** dimer model system as a function of Δx displacements (Δy = 0.00 Å) employing M06-2X density functional at 6-31G(d) (red filled circles), 6-311G(d) (light blue filled circles), 6-311g(d)(p) (purple filled circles), 6-311+G(d) (light brown filled circles), 6-311++G(d) (blue filled circles) and 6-311++G(d)(p) (dark brown filled circles) levels.

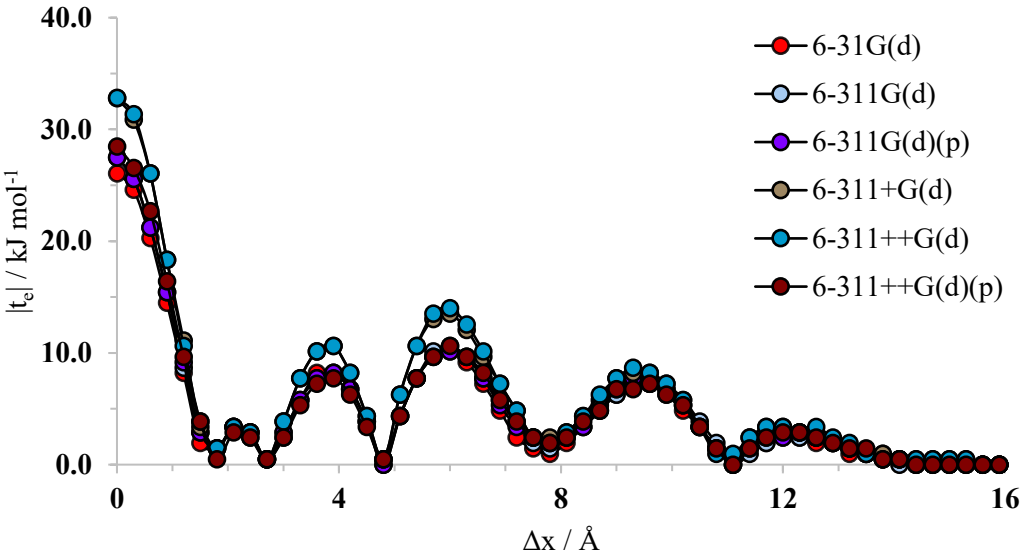

Figure SI.5.2 Computed electron transfer integrals (t_e) for the **NTDT** dimer model system as a function of Δx displacements (Δy = 0.00 Å) employing M06-2X density functional at 6-31G(d) (red filled circles), 6-311G(d) (light blue filled circles), 6-311g(d)(p) (purple filled circles), 6-311+G(d) (light brown filled circles), 6-311++G(d) (blue filled circles) and 6-311++G(d)(p) (dark brown filled circles) levels.

SI.6 Effect of density functionals on computed $t_{h/e}$

The effect of density functionals on computed charge transfer integrals was evaluated by means of a one-dimensional **NTDT** dimer model system whereby the top monomer is displaced with respect the bottom along the long molecular axis (Δx) whilst mainitaing the alignment for the short molecular axis (Δy = 0.00 Å). This was done utilising M08-HX, M06-2X, M08-SO and ωB97X-D density functional at the 6-311G(d) level. Findings are illustrated in Figures SI.6.1-2 for t_h and t_e, respectively.

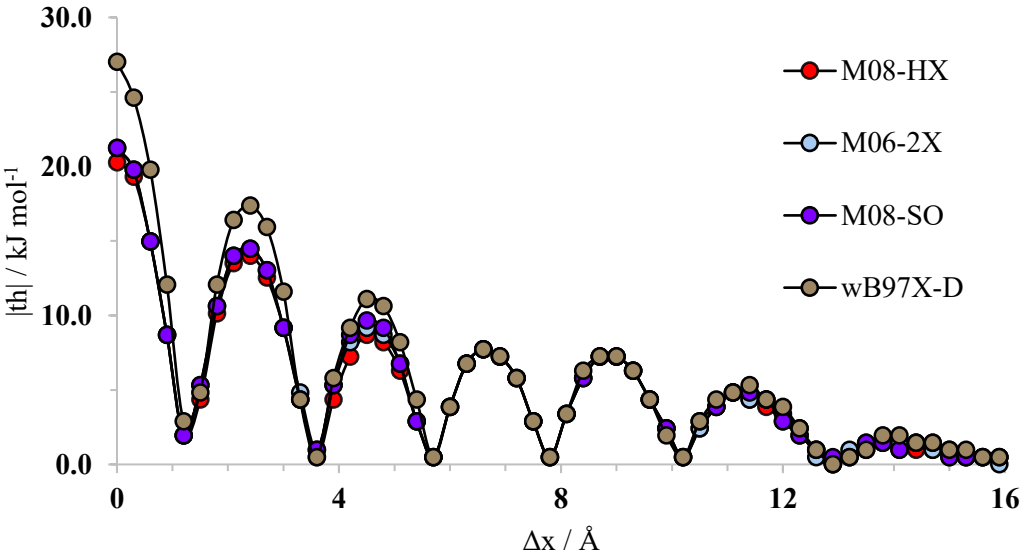

Figure SI.6.1 Computed hole transfer integrals (t_h) for the **NTDT** dimer model system as a function of Δx displacements (Δy = 0.00 Å) employing M08-HX (red filled circles), M06-2X (light blue filled circles), M08-SO (purple filled circles) and ωB97X-D (brown filled circles) at the 6-311G(d) level.

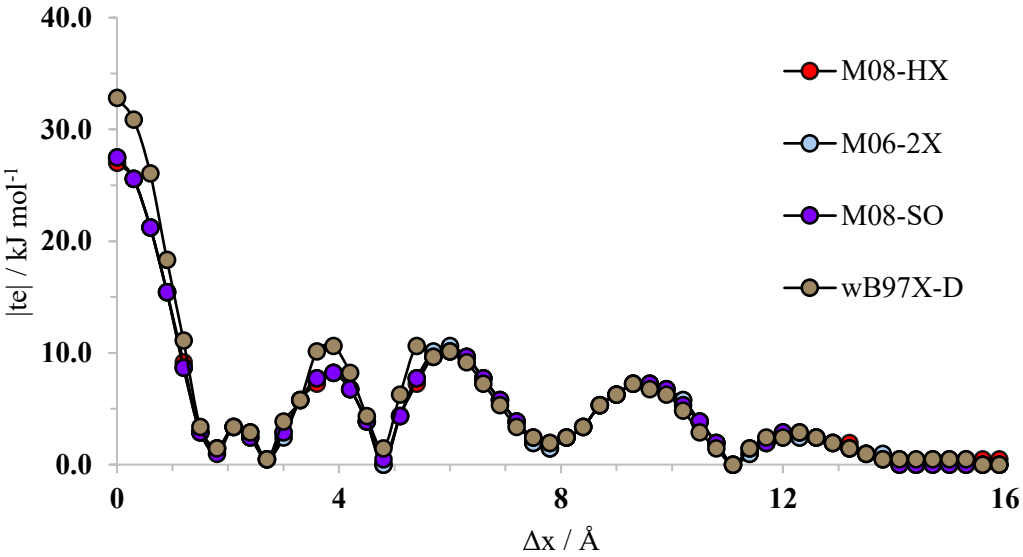

Figure SI.6.2 Computed electron transfer integrals (t_e) for the **NTDT** dimer model system as a function of Δx displacements (Δy = 0.00 Å) employing M08-HX (red filled circles), M06-2X (light blue filled circles), M08-SO (purple filled circles) and ωB97X-D (brown filled circles) at the 6-311G(d) level.

SI.7 Nearest neighbouring dimer pairs for the reported system

Nearest neighbouring dimer pairs were identified for the reported crystal structure of teh NTDT-based materials and their intermolecular interactions, ΔE_{CP} and charge transfer integrals, $t_{h/e}$ were computed in all cases by means of the density functional M06-2X at the 6-311G(d) level. Obtained results are summarised in Table SI.7.1.

Table SI.7.1 Computed intermolecular interactions, ΔE_{CP} and transfer integrals for hole, t_h and electron, t_e for all nearest neighbouring dimer pairs of the reported NTDT system.*Locations defined with respect to the monomer at (0,0,0).

Dimer pair	**Location***	**ΔE_{CP} / kJ mol^{-1}**	**t_h / kJ mol^{-1}**	**t_e / kJ mol^{-1}**
I (π-π)	(0,1,0)	-86.8	13.1	1.8
II	(0,1/2,1/2)	-18.2	3.2	1.8
III	(1,1,0)	-12.9	0.1	0.1
IV	(-1,-1/2,1)	-4.3	0.1	0.1
V	(0,3/2,1/2)	-4.1	1.0	1.0

SI.8 Effect of density functionals on computed ΔE_{CP}

The effect of density functionals on computed intermolecular interactions (ΔE_{CP}) was evaluated by means of a one-dimensional **NTDT** dimer model system whereby the top monomer is displaced with respect the bottom along the long molecular axis (Δx) whilst mainitaing the alignment for the short molecular axis (Δy = 0.00 Å). This was done utilising M08-HX, M06-2X, M08-SO and ωB97X-D density functional at the 6-311G(d) level. Findings are illustrated in Figures SI.8.1.

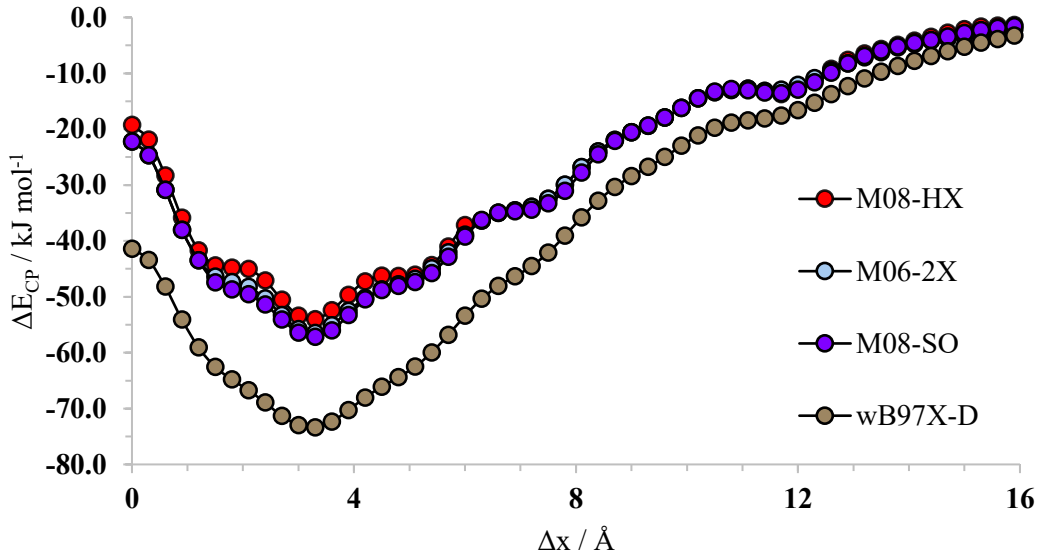

Figure SI.8.1 Computed intermolecular interactions (ΔE_{CP}) the **NTDT** dimer model system as a function of Δx displacements (Δy = 0.00 Å) employing M08-HX (red filled circles), M06-2X (light blue filled circles), M08-SO (purple filled circles) and ωB97X-D (brown filled circles) at the 6-311G(d) level.

SI.9 Effect of basis sets on computed ΔE_{CP}

The effect of basis sets on computed charge transfer integrals was evaluated by means of a one-dimensional **NTDT** dimer model system whereby the top monomer is displaced with respect the bottom along the long molecular axis (Δx) whilst mainitaing the alignment for the short molecular axis (Δy = 0.00 Å). This was done utilising the M06-2X density functional at the 6-31G(d), 6-311G(d), 6-311g(d)(p), 6-311+G(d), 6-311++G(d) and 6-311++G(d)(p) levels. Findings are illustrated in Figure SI.9.1.

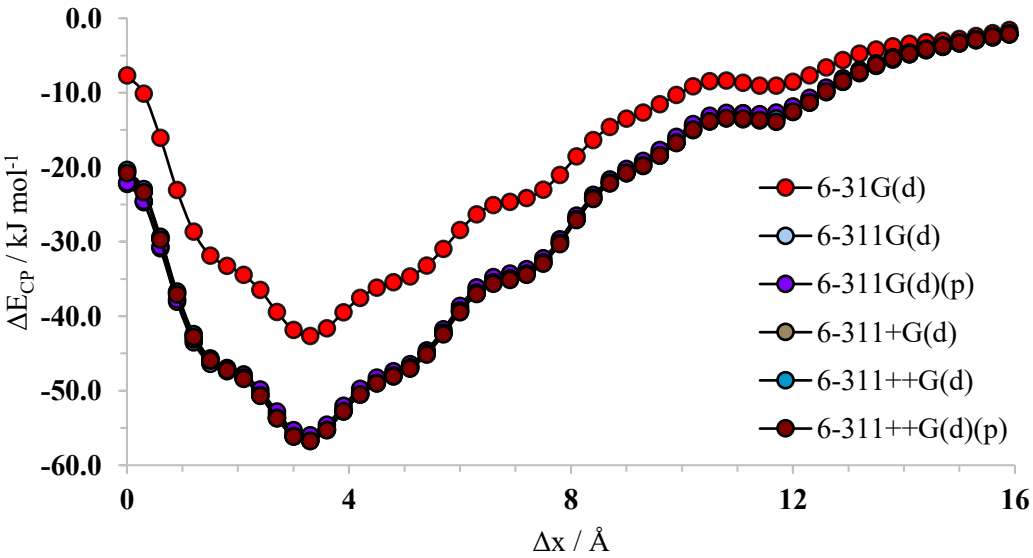

Figure SI.9.1 Computed intermolecular interaction (ΔE_{CP}) for the **NTDT** dimer model system as a function of Δx displacements (Δy = 0.00 Å) employing M06-2X density functional at 6-31G(d) (red filled circles), 6-311G(d) (light blue filled circles), 6-311g(d)(p) (purple filled circles), 6-311+G(d) (light brown filled circles), 6-311++G(d) (blue filled circles) and 6-311++G(d)(p) (dark brown filled circles) levels.