Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table S.1: The relative enthalpies (meV) of neutral DMP, DMIP, DMTP and protonated H^+DMP, H^+DMIP and H^+DMTP molecules. The ground state geometries were obtained with M06-2X/6-311G(2df,2pd), the MP2/6-311G(2df,2pd) relative enthalpies are only single point calculations for the corresponding M06-2X geometries. The proton affinities (PA in eV) were calculated as the difference of total enthalpies of two corresponding conformers, for example PA(8.77 eV) = DMP(I) - H^+DMP(I), PA(8.65 eV) = DMIP(II) – H^+DMIP(IIb).

	M06-2X	MP2		M06-2X	MP2	PA
	H_{rel} [meV]	H_{rel} [meV]		H_{rel} [meV]	H_{rel} [meV]	[eV]
DMP(I)	259	224	H^+DMP(I)	929	847	8.77
DMP(II)	268	236	H^+DMP(IIa)	664	591	9.05
			H^+DMP(IIb)	566	472	9.15
DMP(III)	315	276	H^+DMP(III)	0	0	9.76
DMIP(I)	2	15	H^+DMIP(I)	841	864	8.61
DMIP(II)	0	20	H^+DMIP(IIa)	730	717	8.72
			H^+DMIP(IIb)	800	837	8.65
DMIP(III)	14	36	H^+DMIP(III)	666	658	8.80
DMTP(I)	11	3	H^+DMTP(I)	861	839	8.60
DMTP(II)	8	0	H^+DMTP(II)	867	828	8.59

Table S.2: The calculated enthalpies (Hartree) of neutral DMP, DMIP, DMTP and protonated H^+DMP, H^+DMIP and H^+DMTP molecules. The ground state geometries were obtained with M06-2X/6-311G(2df,2pd), the MP2/6-311G(2df,2pd) enthalpies are only single point calculations for the corresponding M06-2X geometries. The proton affinities (PA in eV) were calculated as the difference of total enthalpies of two corresponding conformers, for example PA(8.77 eV) = DMP(I) - H^+DMP(I), PA(8.65 eV) = DMIP(II) – H^+DMIP(IIb).

	M06-2X	MP2		M06-2X	MP2	PA
	H [Hartree]	H [Hartree]		H [Hartree]	H [Hartree]	[eV]
DMP(I)	-687.74839	-686.69630	H^+DMP(I)	-688.07093	-687.03207	8.77
DMP(II)	-687.74806	-686.69585	H^+DMP(IIa)	-688.08066	-687.04148	9.05
			H^+DMP(IIb)	-688.08426	-687.04588	9.15
DMP(III)	-687.74631	-686.69436	H^+DMP(III)	-688.10506	-687.06321	9.76
DMIP(I)	-687.75782	-686.70399	H^+DMIP(I)	-688.07417	-687.03145	8.61
DMIP(II)	-687.75789	-686.70380	H^+DMIP(IIa)	-688.07824	-687.03685	8.72
			H^+DMIP(IIb)	-688.07566	-687.03244	8.65
DMIP(III)	-687.75738	-686.70318	H^+DMIP(III)	-688.08058	-687.03903	8.80
DMTP(I)	-687.75749	-686.70443	H^+DMTP(I)	-688.07342	-687.03238	8.60
DMTP(II)	-687.75759	-686.70452	H^+DMTP(II)	-688.07320	-687.03278	8.59

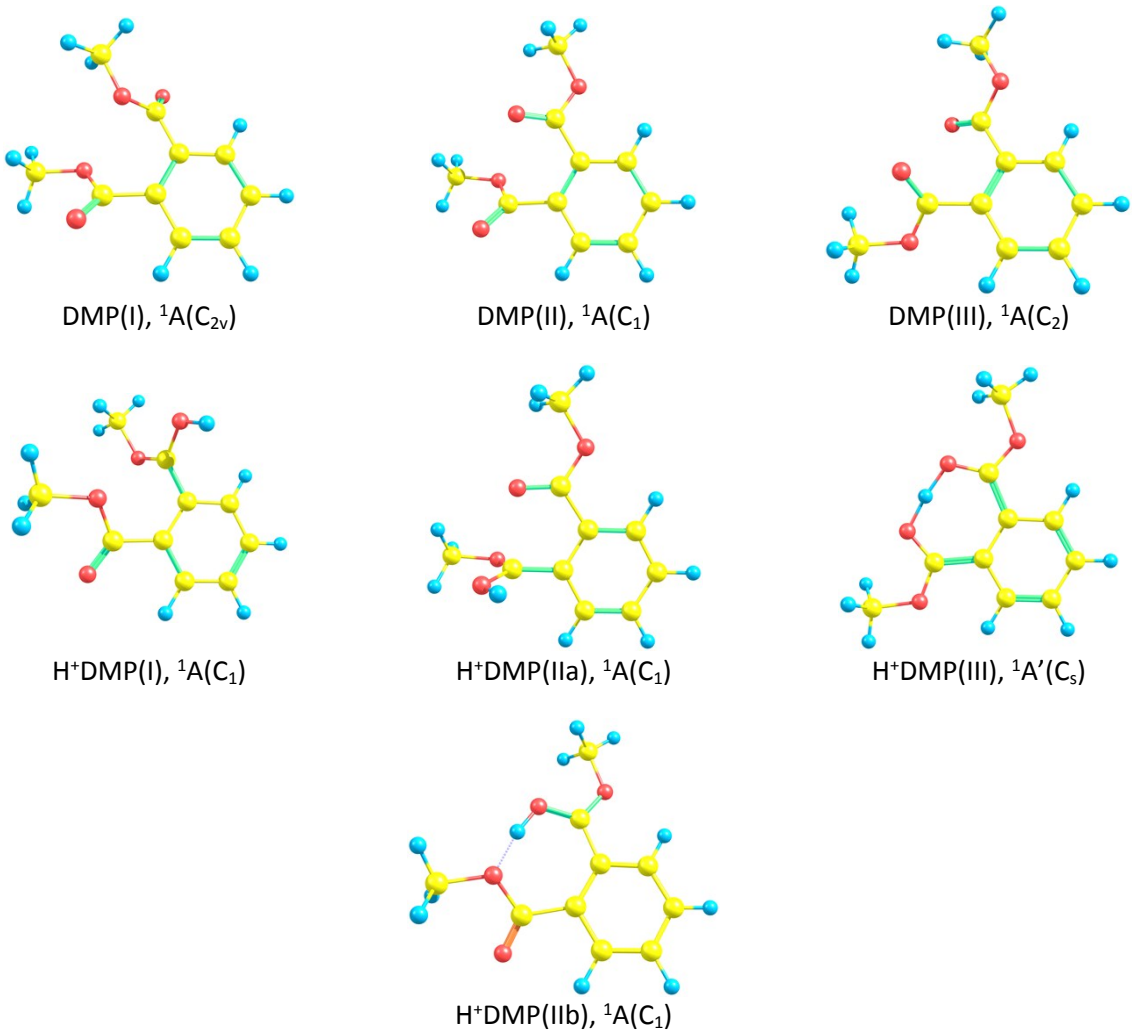


Fig. S.1: The M06-2X/6-311G(2df,2pd) ground state geometries of three different conformers of neutral DMP molecule and their corresponding protonated conformers H^+DMP. The neutral conformer DMP(II) lead to two energetically close protonated conformers H^+DMP(IIa) and H^+DMP(IIb), differing in the position of the proton attached to the out of plain carboxyl oxygen and the in plain carboxyl oxygen respectively. The final state with the symmetry of the molecule in parenthesis is listed as well.

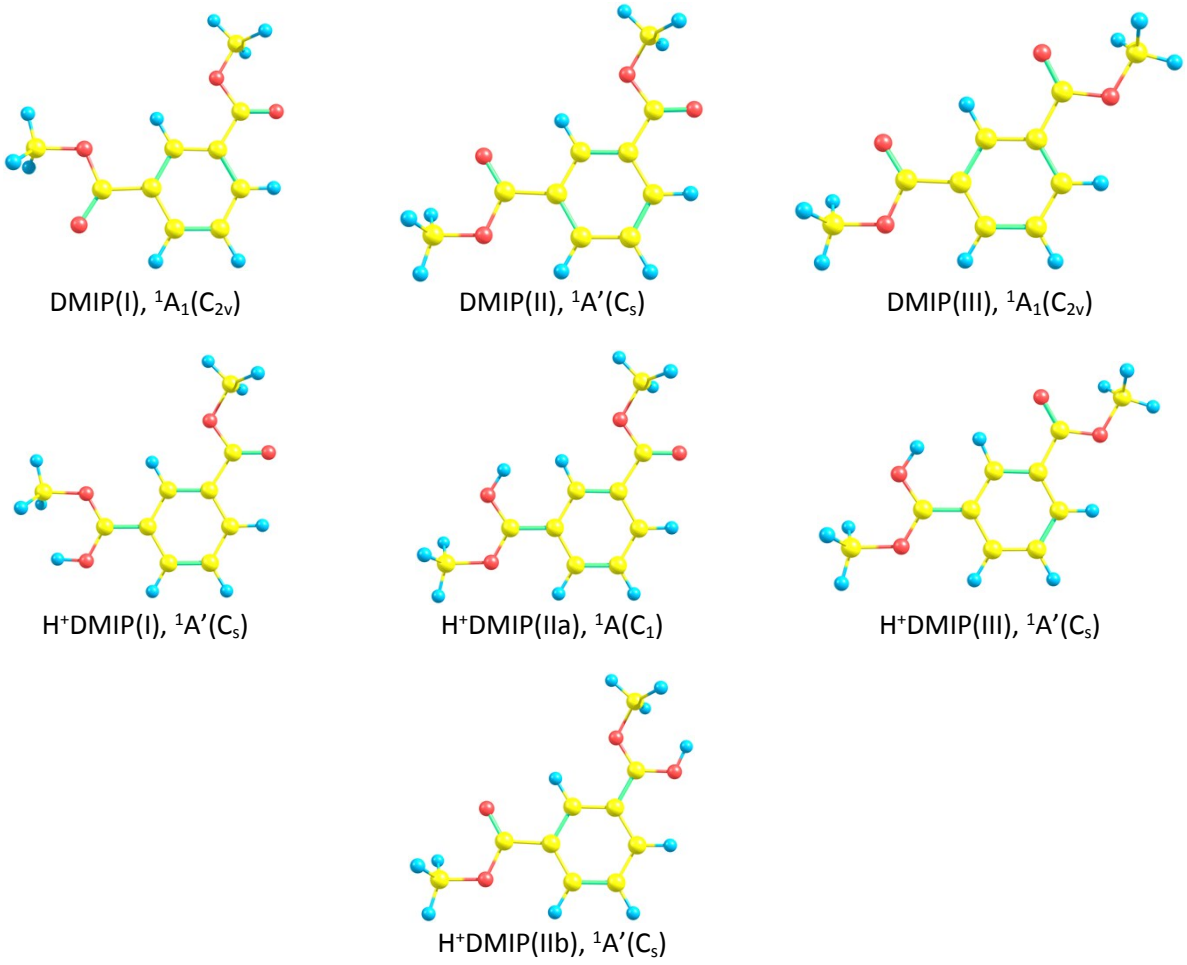


Fig. S.2: The M06-2X/6-311G(2df,2pd) ground state geometries of three different conformers of neutral DMIP molecule and their corresponding protonated conformers H^+DMIP. The neutral conformer DMIP(II) lead to two energetically close protonated conformers H^+DMIP(IIa) and H^+DMIP(IIb), differing in the position of the bound proton attached to the two possible carboxyl oxygens. The final state with the symmetry of the molecule in parenthesis is listed as well.

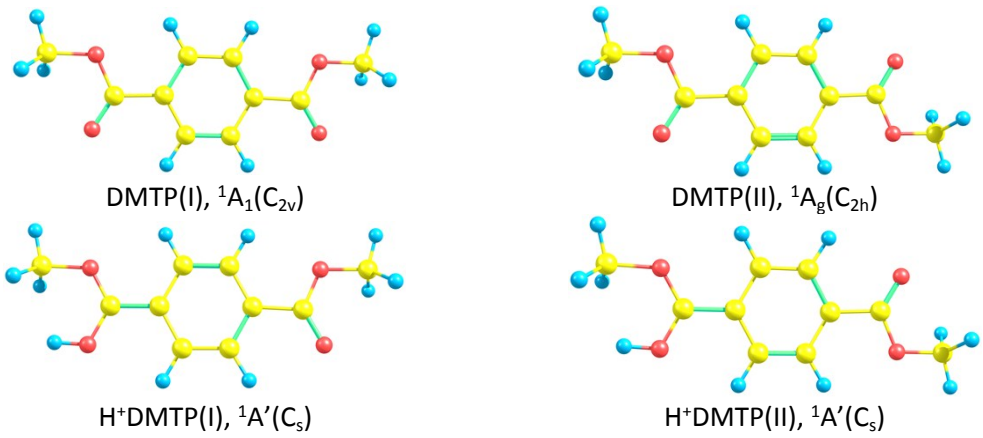


Fig. S.3: The M06-2X/6-311G(2df,2pd) ground state geometries of three different conformers of neutral DMTP molecule and their corresponding protonated conformers H^+DMTP. The final state with the symmetry of the molecule in parenthesis is listed as well.

Table S.3

Water Clusters: The proton affinities calculated from the total electronic energies of different size of protonated water clusters using M06-2X and ωB97X-D/6-311+G(2d,p) methods. The bond energies BE in protonated water clusters.

	Proton affinities (eV)			BE (eV)	
	M06-2X	ωB97X-D		M06-2X	ωB97X-D
$H_2O + H^+$	7.42	7.52			
$(H_2O)_2 + H^+$	8.77	8.82	$H_3O^+ + H_2O$	1.560	
$(H_2O)_3 + H^+$	9.27	9.36	$H_3O^+ + (H_2O)_2$ $(H_2O)H_3O^+ + H_2O$	1.069 2.371	
$(H_2O)_4 + H^+$	9.59	9.67	$H_3O^+ + (H_2O)_3$ $(H_2O)_2H_3O^+ + H_2O$	0.894 2.736	
$(H_2O)_5 + H^+$	9.81	9.87	$H_3O^+ + (H_2O)_4$ $(H_2O)_3H_3O^+ + H_2O$	0.627 2.773	
$(H_2O)_6 + H^+$	9.89	9.98	$H_3O^+ + (H_2O)_5$ $(H_2O)_4H_3O^+ + H_2O$	0.641 2.988	

Table S.4

Phthalate - Water Clusters: In the first row the ωB97X-D/6-311+G(2d,p) proton affinities (eV) are listed, calculated from the total electronic energies and reaction enthalpies H of protonated ions formed from DMP, DMIP and DMTP. The rest of the table are the reaction energies (derived for the total energies) of phthalate – water clusters of different size of protonated water cluster, the reaction enthalpies H and the Gibbs free energies G of the reactions.

	M = DMP			M = DMIP			M = DMTP		
	E(0 K) (eV)	H (eV)	G (eV)	E(0 K) (eV)	H (eV)	G (eV)	E(0 K) (eV)	H (eV)	G (eV)
$M + H^+$	9.976	9.701		9.188	8.837		9.091	8.741	
$M•H^+ + H_2O$	0.412	0.358	0.034	0.978	0.910	0.425	0.877	0.815	0.416
$M + H_3O^+$	2.869	2.900	2.479	2.645	2.589	2.103	2.446	2.397	1.988
$M•H_3O^+ + H_2O$	0.462	0.366	-0.027	0.884	0.885	0.477	0.636	0.592	0.174
$M•H^+ + (H_2O)_2$	0.617	0.543	0.100	1.604	1.614	0.996	1.255	1.225	0.685
$M + H_2O•H_3O^+$	1.771	1.688	1.256	1.968	1.896	1.385	1.521	1.411	0.967
$M•(H_2O)•H_3O^+ + H_2O$	0.553	0.478	-0.014	0.734	0.604	0.280	0.858	0.827	0.323
$M•H_3O^+ + (H_2O)_2$	0.758	0.663	0.053	1.360	1.308	0.852	1.236	1.237	0.591
$M•H^+ + (H_2O)_3$	0.641	0.853	0.100	1.809	1.780	1.291	1.584	1.614	1.022
$M + (H_2O)_2•H_3O^+$	1.256	1.211	0.613	1.633	1.545	1.036	1.310	1.282	0.661
$M•(H_2O)_2•H_3O^+ + H_2O$	0.633	0.545	0.100	0.552	0.467	0.006	0.738	0.610	0.292
$M•(H_2O)•H_3O^+ + (H_2O)_2$	0.928	0.842	0.180	1.027	0.889	0.380	1.338	1.256	0.709
$M•H_3O^+ + (H_2O)_3$	0.862	0.770	0.167	1.383	1.336	0.871	1.445	1.409	0.897
$M•H^+ + (H_2O)_4$	0.683	0.621	0.132	1.770	1.740	1.227	1.731	1.717	1.224
$M + (H_2O)_3•H_3O^+$	0.995	0.953	0.256	1.291	1.208	0.585	1.154	1.089	0.496

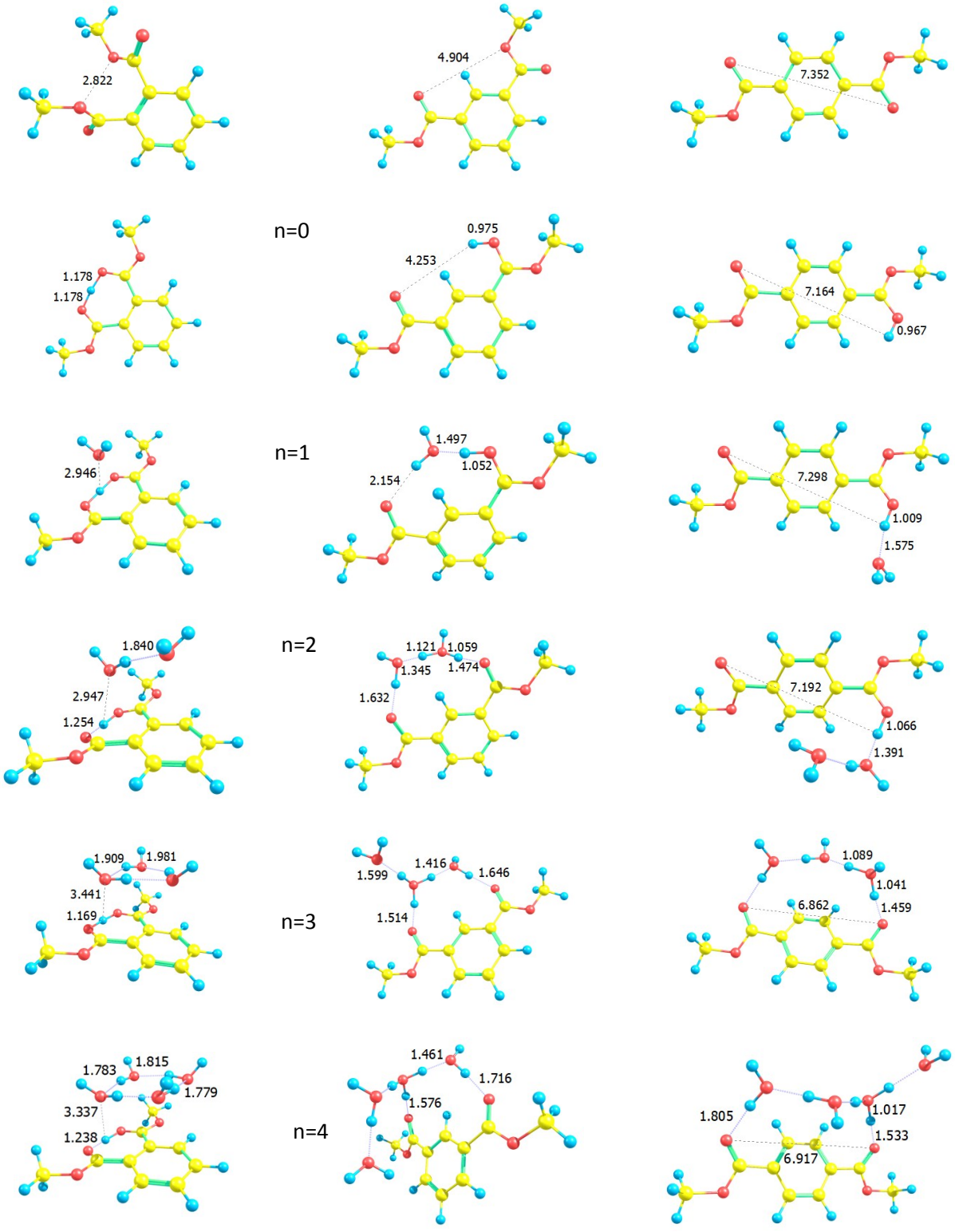


Fig. S.4: The ωB97X-D/6-311+G(2d,p) geometries of hydrated protonated ions neutral DMP (left column), DMIP (central column) and DMTP (right column). First row are neutral molecules, next rows are $M.H^{+}.(H_2O)_n$ for n=0,1,..4

Table S.5

DMP – Geometry coordinates: The M06-2X/6-311G(2df,pd) cartesian coordinates in Å of neutral and protonated DMP conformers.

DMP(I)				H^+DMP(I)			
C	-0.048	0.692	3.210	C	-3.262	0.420	-0.143
C	-0.084	1.384	2.009	C	-2.139	1.232	-0.235
C	0.048	-0.692	3.210	C	-3.130	-0.942	0.084
H	-0.145	2.463	1.986	H	-2.228	2.301	-0.378
H	0.086	-1.234	4.144	H	-4.005	-1.571	0.159
C	-0.029	0.697	0.804	C	-0.871	0.690	-0.120
C	0.084	-1.384	2.009	C	-1.868	-1.505	0.198
H	0.145	-2.463	1.986	H	-1.759	-2.575	0.326
C	0.029	-0.697	0.804	C	-0.746	-0.689	0.078
H	-0.086	1.234	4.144	H	-4.247	0.856	-0.238
C	0.029	1.514	-0.445	C	0.290	1.636	-0.084
O	-0.591	2.525	-0.621	O	0.253	2.746	-0.515
O	0.913	1.022	-1.321	O	1.349	1.102	0.547
C	-0.029	-1.514	-0.445	C	0.563	-1.342	0.078
O	0.591	-2.525	-0.621	O	0.948	-2.113	1.035
O	-0.913	-1.022	-1.321	O	1.319	-1.221	-0.924
C	-0.959	-1.704	-2.570	C	2.659	-1.794	-0.901
H	0.005	-1.623	-3.071	H	3.195	-1.377	-0.054
H	-1.191	-2.756	-2.422	H	2.581	-2.874	-0.824
H	-1.735	-1.216	-3.150	H	3.100	-1.493	-1.843
C	0.959	1.704	-2.570	C	2.477	1.985	0.675
H	1.735	1.216	-3.150	H	3.231	1.430	1.222
H	-0.005	1.623	-3.071	H	2.837	2.273	-0.310
H	1.191	2.756	-2.422	H	2.184	2.876	1.224
				H	0.333	-2.097	1.785

DMP(II)				H^+DMP(IIa)				H^+DMP(IIb)			
O	0.534	1.876	-0.807	O	2.156	0.072	-0.838	O	-1.547	1.497	0.317
C	-0.358	1.710	0.172	C	1.512	0.359	0.207	C	-1.863	0.255	-0.150
O	-0.628	2.542	0.989	O	2.104	0.221	1.341	O	-2.950	0.013	-0.558
C	-1.045	0.383	0.071	C	0.194	1.021	0.077	C	-0.764	-0.769	-0.037
C	1.351	3.034	-0.671	C	3.417	-0.651	-0.726	C	-2.608	2.485	0.258
C	-0.347	-0.824	0.018	C	-0.961	0.245	-0.019	C	0.642	-0.595	0.046
C	-2.431	0.381	0.014	C	0.134	2.406	0.042	C	-1.268	-2.063	-0.035
C	1.129	-0.840	0.244	C	-0.775	-1.229	0.067	C	1.366	0.686	-0.008
C	-1.046	-2.016	-0.130	C	-2.190	0.865	-0.159	C	1.460	-1.725	0.142
C	-3.123	-0.812	-0.131	C	-1.107	3.016	-0.096	C	-0.440	-3.171	0.077
O	1.702	-1.949	-0.237	O	-1.872	-1.919	-0.100	O	2.636	0.623	-0.149
O	1.737	0.017	0.824	O	0.321	-1.701	0.286	O	0.846	1.836	0.074
C	-2.430	-2.010	-0.211	C	-2.259	2.252	-0.198	C	0.928	-3.002	0.171
C	3.105	-2.046	-0.005	C	-1.744	-3.350	-0.014	C	3.407	1.853	-0.180

H	0.740	3.934	-0.648	H	4.128	-0.048	-0.171	H	-2.933	2.604	-0.771
H	2.010	3.040	-1.533	H	3.736	-0.805	-1.748	H	-2.177	3.399	0.651
H	1.926	2.966	0.251	H	3.214	-1.592	-0.220	H	-3.433	2.144	0.875
H	-2.956	1.324	0.081	H	1.035	3.002	0.104	H	-2.337	-2.188	-0.123
H	-0.496	-2.945	-0.164	H	-3.082	0.259	-0.232	H	2.529	-1.595	0.195
H	-4.202	-0.805	-0.182	H	-1.167	4.095	-0.129	H	-0.873	-4.161	0.087
H	-2.965	-2.942	-0.323	H	-3.218	2.737	-0.307	H	1.587	-3.854	0.257
H	3.416	-2.990	-0.439	H	-2.740	-3.743	-0.176	H	4.434	1.531	-0.286
H	3.314	-2.025	1.063	H	-1.371	-3.626	0.969	H	3.253	2.394	0.749
H	3.623	-1.216	-0.480	H	-1.056	-3.702	-0.779	H	3.090	2.451	-1.030
				H	1.523	0.439	2.084	O	-1.547	1.497	0.317

DMP(III)				H^+DMP(III)			
O	-0.3214	2.6303	-0.647	O	-0.416	0.037	2.846
C	0.2886	1.4398	-0.652	C	-0.655	-0.008	1.579
O	0.9798	1.0483	-1.548	O	-1.828	-0.052	1.176
C	0.0628	0.6949	0.625	C	0.554	-0.006	0.710
C	-0.1071	3.4115	-1.820	C	-1.548	0.035	3.749
C	-0.0628	-0.6949	0.625	C	0.554	-0.006	-0.710
C	0.1071	1.3815	1.830	C	1.774	-0.005	1.378
C	-0.2886	-1.4398	-0.652	C	-0.655	-0.008	-1.579
C	-0.1071	-1.3815	1.830	C	1.774	-0.005	-1.378
C	0.0497	0.6909	3.032	C	2.979	-0.006	0.690
O	0.3214	-2.6303	-0.647	O	-0.416	0.037	-2.846
O	-0.9798	-1.0483	-1.548	O	-1.828	-0.052	-1.176
C	-0.0497	-0.6909	3.032	C	2.979	-0.006	-0.690
C	0.1071	-3.4115	-1.820	C	-1.548	0.035	-3.749
H	0.9549	3.6061	-1.957	H	-2.186	0.885	3.528
H	-0.6509	4.3374	-1.668	H	-1.116	0.113	4.739
H	-0.4820	2.8837	-2.695	H	-2.100	-0.893	3.629
H	0.2013	2.4578	1.817	H	1.779	-0.004	2.456
H	-0.2013	-2.4578	1.817	H	1.779	-0.004	-2.456
H	0.0902	1.2333	3.967	H	3.908	-0.007	1.242
H	-0.0902	-1.2333	3.967	H	3.908	-0.007	-1.242
H	0.6509	-4.3374	-1.668	H	-1.116	0.113	-4.739
H	0.4820	-2.8837	-2.695	H	-2.186	0.885	-3.528
H	-0.9549	-3.6061	-1.957	H	-2.100	-0.893	-3.629
				H	-1.905	-0.066	0.000

Table S.6

DMIP – Geometry coordinates: The M06-2X/6-311G(2df,pd) cartesian coordinates in Å of neutral and protonated DMIP conformers.

DMIP(I)				H^+DMIP(I)			
C	0.000	1.199	2.007	C	-0.261	-2.318	0.000
C	0.000	1.199	0.616	C	-0.815	-1.029	0.000
C	0.000	0.000	2.702	C	1.111	-2.461	0.000
H	0.000	0.000	3.782	H	1.552	-3.447	0.000
C	0.000	0.000	-0.085	C	0.000	0.110	0.000
C	0.000	-1.199	2.007	C	1.922	-1.333	0.000
H	0.000	-2.149	2.521	H	3.001	-1.418	0.000
C	0.000	-1.199	0.616	C	1.370	-0.053	0.000
H	0.000	2.149	2.521	H	-0.904	-3.186	0.000
C	0.000	2.519	-0.076	C	-2.241	-0.873	0.000
O	0.000	3.577	0.491	O	-2.983	-1.931	0.000
O	0.000	2.401	-1.409	O	-2.743	0.306	0.000
C	0.000	-2.519	-0.076	C	2.313	1.114	0.000
O	0.000	-3.577	0.491	O	3.502	0.983	0.000
O	0.000	-2.401	-1.409	O	1.672	2.276	0.000
C	0.000	-3.635	-2.119	C	2.519	3.435	0.000
H	0.884	-4.217	-1.867	H	3.149	3.432	0.886
H	-0.884	-4.217	-1.867	H	3.149	3.432	-0.886
H	0.000	-3.376	-3.172	H	1.854	4.290	0.000
C	0.000	3.635	-2.119	C	-4.171	0.523	0.000
H	0.000	3.376	-3.172	H	-4.294	1.599	0.000
H	-0.884	4.217	-1.867	H	-4.607	0.101	-0.905
H	0.884	4.217	-1.867	H	-4.607	0.101	0.905
H	0.000	0.000	-1.164	H	-0.425	1.103	0.000
				H	-3.936	-1.766	0.000

DMIP(II)				H^+DMIP(IIa)				H^+DMIP(IIb)			
C	-0.334	-2.103	0.000	C	-1.275	1.723	0.000	C	-1.315	1.693	0.000
C	-0.852	-0.812	0.000	C	-1.114	0.331	0.000	C	-1.174	0.308	0.000
C	1.039	-2.297	0.000	C	-0.160	2.537	0.000	C	-0.198	2.523	0.000
H	1.443	-3.300	0.000	H	-0.276	3.610	0.000	H	-0.320	3.596	0.000
C	0.000	0.284	0.000	C	0.164	-0.237	0.000	C	0.085	-0.258	0.000
C	1.892	-1.206	0.000	C	1.108	1.971	0.000	C	1.067	1.973	0.000
H	2.966	-1.329	0.000	H	1.999	2.586	0.000	H	1.942	2.607	0.000
C	1.372	0.085	0.000	C	1.271	0.588	0.000	C	1.206	0.577	0.000
H	-1.011	-2.945	0.000	H	-2.268	2.148	0.000	H	-2.310	2.117	0.000
C	-2.319	-0.546	0.000	C	-2.289	-0.510	0.000	C	-2.345	-0.631	0.000
O	-2.806	0.550	0.000	O	-2.258	-1.801	-0.001	O	-2.215	-1.821	0.000
O	-3.045	-1.672	0.000	O	-3.439	0.029	0.001	O	-3.501	0.014	0.000
C	2.338	1.221	0.000	C	2.669	0.042	0.000	C	2.517	-0.008	0.000
O	3.532	1.089	0.000	O	3.636	0.745	0.000	O	3.545	0.775	0.000

O	1.729	2.411	0.000	O	2.686	-1.286	0.000	O	2.634	-1.282	0.000
C	2.605	3.534	0.000	C	3.996	-1.877	0.000	C	3.926	-1.928	0.000
H	3.239	3.520	0.885	H	4.542	-1.565	-0.887	H	4.471	-1.660	-0.905
H	3.239	3.520	-0.885	H	4.541	-1.564	0.887	H	4.471	-1.660	0.905
H	1.967	4.411	0.000	H	3.838	-2.949	0.001	H	3.712	-2.989	0.000
C	-4.455	-1.474	0.000	C	-4.640	-0.796	0.001	C	-4.668	-0.822	0.000
H	-4.898	-2.464	0.000	H	-5.457	-0.088	0.001	H	-5.515	-0.147	0.000
H	-4.759	-0.917	0.884	H	-4.646	-1.411	-0.894	H	-4.671	-1.451	-0.887
H	-4.759	-0.917	-0.884	H	-4.645	-1.411	0.896	H	-4.671	-1.451	0.887
H	-0.418	1.280	0.000	H	0.342	-1.306	0.000	H	0.173	-1.336	0.000
				H	-1.361	-2.162	-0.001	H	4.403	0.327	0.000

DMIP(III)				H^+DMIP(III)			
C	0.000	1.201	1.640	C	1.360	-1.562	0.000
C	0.000	1.200	0.248	C	1.248	-0.175	0.000
C	0.000	0.000	2.332	C	0.221	-2.362	0.000
H	0.000	0.000	3.412	H	0.316	-3.437	0.000
C	0.000	0.000	-0.448	C	0.000	0.416	0.000
C	0.000	-1.201	1.640	C	-1.030	-1.782	0.000
H	0.000	-2.142	2.169	H	-1.921	-2.393	0.000
C	0.000	-1.200	0.248	C	-1.143	-0.384	0.000
H	0.000	2.142	2.169	H	2.345	-2.008	0.000
C	0.000	2.464	-0.544	C	2.433	0.747	0.000
O	0.000	2.510	-1.742	O	2.312	1.940	0.000
O	0.000	3.554	0.233	O	3.578	0.090	0.000
C	0.000	-2.464	-0.544	C	-2.456	0.220	0.000
O	0.000	-2.510	-1.742	O	-2.667	1.493	0.000
O	0.000	-3.554	0.233	O	-3.483	-0.526	0.000
C	0.000	-4.792	-0.473	C	-4.818	0.058	0.000
H	-0.884	-4.867	-1.102	H	-4.939	0.660	0.895
H	0.884	-4.867	-1.102	H	-4.939	0.660	-0.895
H	0.000	-5.569	0.283	H	-5.487	-0.792	0.000
C	0.000	4.792	-0.473	C	4.758	0.910	0.000
H	0.000	5.569	0.283	H	5.595	0.222	0.000
H	0.884	4.867	-1.102	H	4.769	1.538	-0.887
H	-0.884	4.867	-1.102	H	4.769	1.538	0.887
H	0.000	0.000	-1.529	H	-0.012	1.501	0.000
				H	-1.853	2.016	0.000

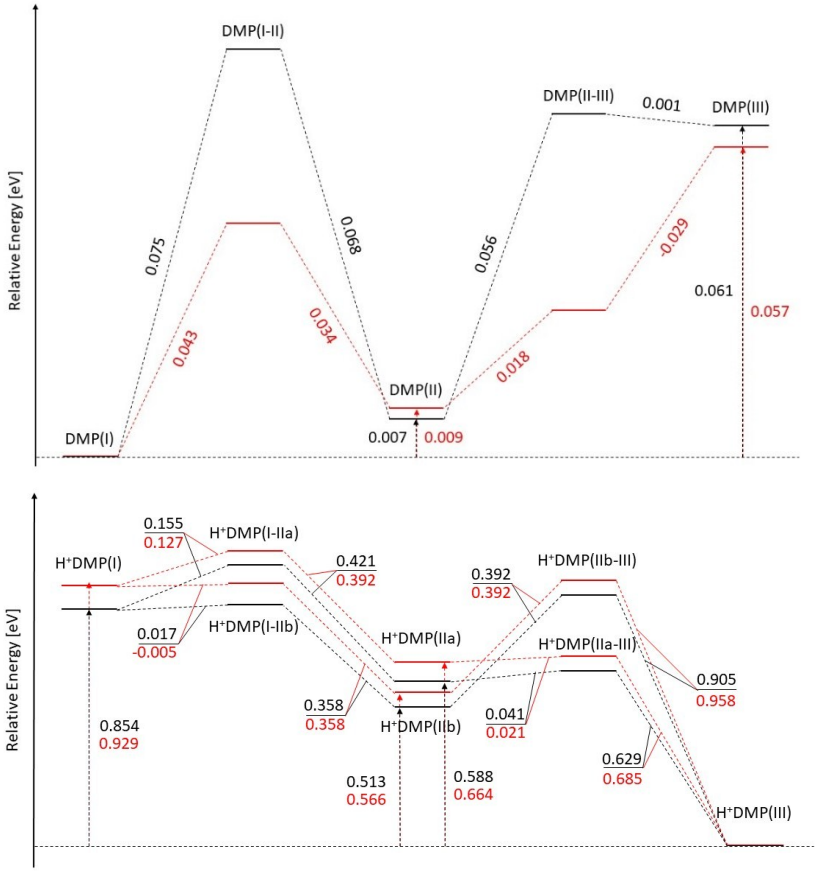
Table S.7

DMTP – Geometry coordinates: The M06-2X/6-311G(2df,pd) cartesian coordinates in Å of neutral and protonated DMTP conformers.

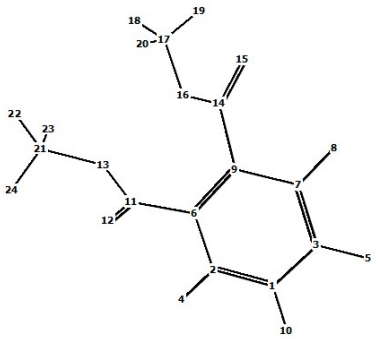
DMTP(I)				H^+DMTP(I)			
C	0.000	1.382	0.213	C	-1.090	-0.917	0.000
C	0.000	0.692	-0.994	C	-1.162	0.474	0.000
C	0.000	0.691	1.420	C	0.137	-1.576	0.000
H	0.000	1.256	2.341	H	0.144	-2.657	0.000
C	0.000	-0.692	-0.994	C	0.000	1.216	0.000
C	0.000	-0.691	1.420	C	1.306	-0.847	0.000
H	0.000	-1.256	2.341	H	2.264	-1.345	0.000
C	0.000	-1.382	0.213	C	1.234	0.553	0.000
C	0.000	2.873	0.269	C	-2.328	-1.774	0.000
O	0.000	3.509	1.287	O	-2.280	-2.970	0.000
O	0.000	3.433	-0.946	O	-3.436	-1.050	0.000
C	0.000	-2.873	0.269	C	2.448	1.320	0.000
O	0.000	-3.509	1.287	O	3.577	0.692	0.000
O	0.000	-3.433	-0.946	O	2.384	2.599	0.000
C	0.000	-4.858	-0.951	C	3.575	3.417	0.000
H	0.885	-5.238	-0.444	H	4.151	3.226	0.905
H	-0.885	-5.238	-0.444	H	4.151	3.226	-0.905
H	0.000	-5.154	-1.995	H	3.217	4.439	0.000
C	0.000	4.858	-0.951	C	-4.657	-1.804	0.000
H	0.000	5.154	-1.995	H	-5.457	-1.073	0.000
H	-0.885	5.238	-0.444	H	-4.702	-2.432	-0.887
H	0.885	5.238	-0.444	H	-4.702	-2.432	0.887
H	0.000	-1.243	-1.923	H	-0.037	2.296	0.000
H	0.000	1.243	-1.923	H	-2.127	0.958	0.000
				H	4.364	1.256	0.000

DMTP(II)				H^+DMTP(II)			
C	0.002	1.382	0.000	C	-0.016	-1.410	0.000
C	-1.207	0.695	0.000	C	1.202	-0.736	0.000
C	1.207	0.688	0.000	C	-1.225	-0.719	0.000
H	2.129	1.252	0.000	H	-2.145	-1.286	0.000
C	-1.207	-0.688	0.000	C	1.216	0.643	0.000
C	1.207	-0.695	0.000	C	-1.226	0.658	0.000
H	2.135	-1.247	0.000	H	-2.155	1.209	0.000
C	-0.002	-1.382	0.000	C	0.000	1.339	0.000
C	0.064	2.873	0.000	C	-0.089	-2.915	0.000
O	1.084	3.506	0.000	O	-1.129	-3.506	0.000
O	-1.150	3.436	0.000	O	1.111	-3.472	0.000
C	-0.064	-2.873	0.000	C	0.009	2.775	0.000
O	-1.084	-3.506	0.000	O	1.144	3.390	0.000
O	1.150	-3.436	0.000	O	-1.105	3.407	0.000

C	1.152	-4.861	0.000	C	-1.159	4.851	0.000
H	0.643	-5.240	0.885	H	-0.691	5.237	0.905
H	0.643	-5.240	-0.885	H	-0.691	5.237	-0.905
H	2.194	-5.159	0.000	H	-2.214	5.095	0.000
C	-1.152	4.861	0.000	C	1.118	-4.908	0.000
H	-2.194	5.159	0.000	H	2.161	-5.199	0.000
H	-0.643	5.240	0.885	H	0.610	-5.279	0.887
H	-0.643	5.240	-0.885	H	0.610	-5.279	-0.887
H	-2.129	-1.252	0.000	H	2.152	1.183	0.000
H	-2.135	1.247	0.000	H	2.123	-1.298	0.000
				H	1.089	4.357	0.000

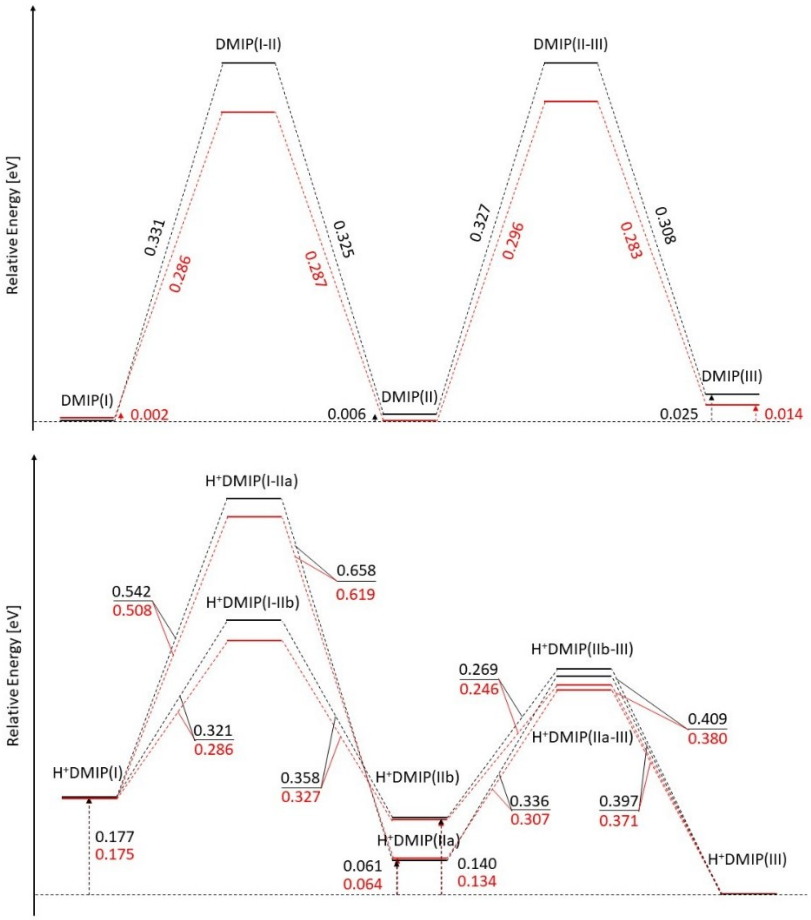


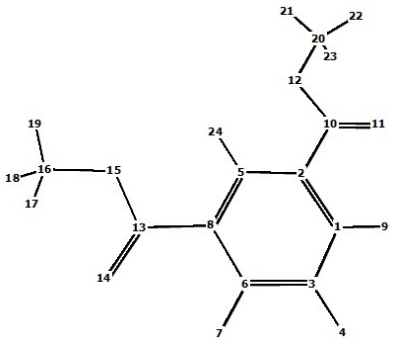
	d1	d2
DMP(I)	143.5	143.5
DMP(I-II)	169.3	-82.9
DMP(II)	21.5	-128.9
DMP(II-III)	-61.7	-22.9
DMP(III)	-38.0	-38.0



	d1	d2
H⁺DMP(I)	128.0	163.9
H⁺DMP(I-IIa)	179.8	-94.1
H⁺DMP(IIa)	99.2	4.0
H⁺DMP(I-IIb)	-92.9	-175.6
H⁺DMP(IIb)	11.2	11.8
H⁺DMP(IIa-III)	65.1	-0.5
H⁺DMP(IIb-III)	29.6	63.3
H⁺DMP(III)	-2.4	2.4

Fig. S.5: The M06-2X/6-311G(2df,2pd) relative energies in eV of neutral (left up) and protonated (left down) conformers of DMP molecule and their transition states (like DMP(I-II) being the TS between DMP(I) and DMP(II), etc.). The black lines are derived from the 0K total energies, the red lines from the enthalpies. Right columns are the values of dihedral angles defining the relative orientation of the two carboxylic oxygens, d1=C6-C9-C14-O15, d2=C9-C6-C11-O12, the proton is attached to atom O15.

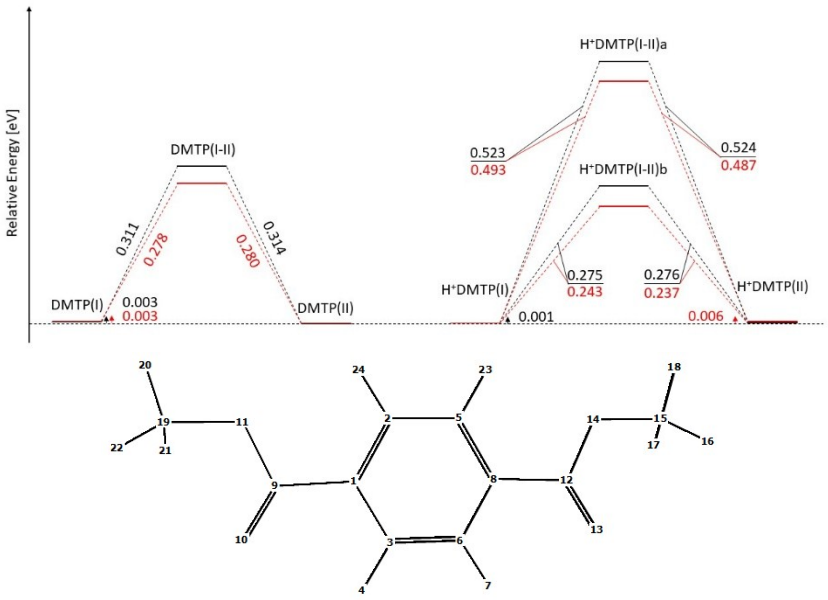




	d1	d2
DMIP(I)	180.0	180.0
DMIP(I-II)	-89.6	-179.8
DMIP(II)	0.0	180.0
DMIP(II-III)	-89.1	-0.2
DMIP(III)	0.0	0.0

	d1	d2
H^+DMIP(I)	180.0	180.0
H^+DMIP(I-IIa)	-89.8	179.5
H^+DMIP(IIa)	-0.1	-179.9
H^+DMIP(I-IIb)	-179.8	90.6
H^+DMIP(IIb)	180.0	0.0
H^+DMIP(IIa-III)	-11.3	90.2
H^+DMIP(IIb-III)	-90.1	1.6
H^+DMIP(III)	0.0	0.0

Fig. S.6: The M06-2X/6-311G(2df,2pd) relative energies in eV of neutral (left up) and protonated (left down) conformers of DMIP molecule and their transition states (like DMIP(I-IIa) being the TS between DMIP(I) and DMIP(IIa), etc.). The black lines are derived from the 0K total energies, the red lines from the enthalpies. Right columns are the values of dihedral angles defining the relative orientation of the two carboxylic oxygens, d1=C5-C2-C10-O11, d2=C2-C5-C13-O14, the proton is attached to atom O11.



	d1	d2
DMTP(I)	180.0	180.0
DMTP(I-II)	-89.4	-179.8
DMTP(II)	0.0	180.0

	d1	d2
H^+DMTP(I)	180.0	180.0
H^+DMTP(I-II)a	-90.1	-179.9
H^+DMTP(I-II)b	179.6	-88.5
H^+DMTP(II)	0.0	180.0

Fig. S.7: The M06-2X/6-311G(2df,2pd) relative energies in eV of neutral and protonated conformers of DMTP molecule and their transition states (like DMTP(I-II) being the TS between DMTP(I) and DMTP(II), etc.). The black lines are derived from the 0K total energies, the red lines from the enthalpies. Right columns are the values of dihedral angles defining the relative orientation of the two carboxylic oxygens, d1=C5-C8-C12-O13, d2=C2-C1-C9-O10, the proton is attached to atom O13.