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

Electrophilicity of Oxalic Acid Monomer Is Enhanced in the Dimer by Intermolecular Proton Transfer

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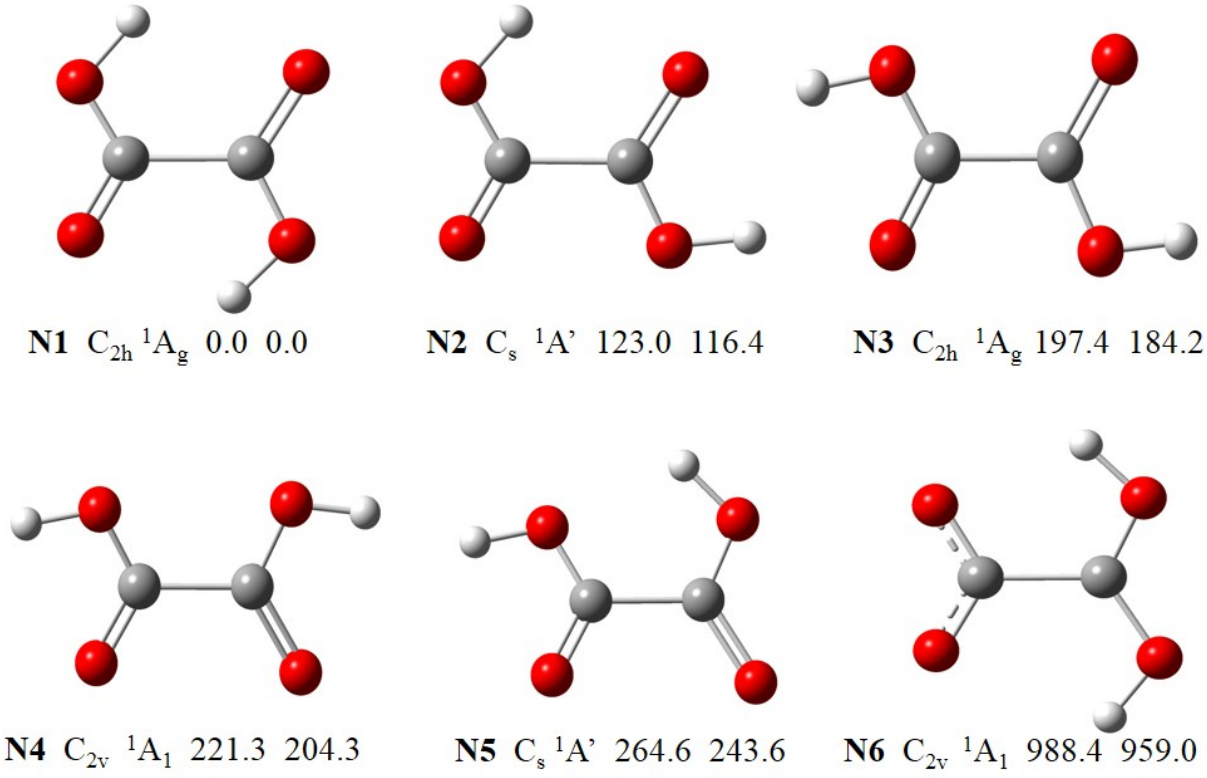


Fig. S1: Conformers and tautomers of the neutral oxalic acid monomer. The name of the species is followed by its point symmetry group, the electronic term, two relative energies (in meV) with respect to **N1:** purely electronic and electronic corrected for zero-point vibrations. All structures are planar minima. MP2/aug-cc-pVDZ geometries and frequencies. The SCF and MP2 correlation energies extrapolated to the CBS limit and supplemented with the residual CCSD(T)/aug-cc-pVDZ electron correlation energy.

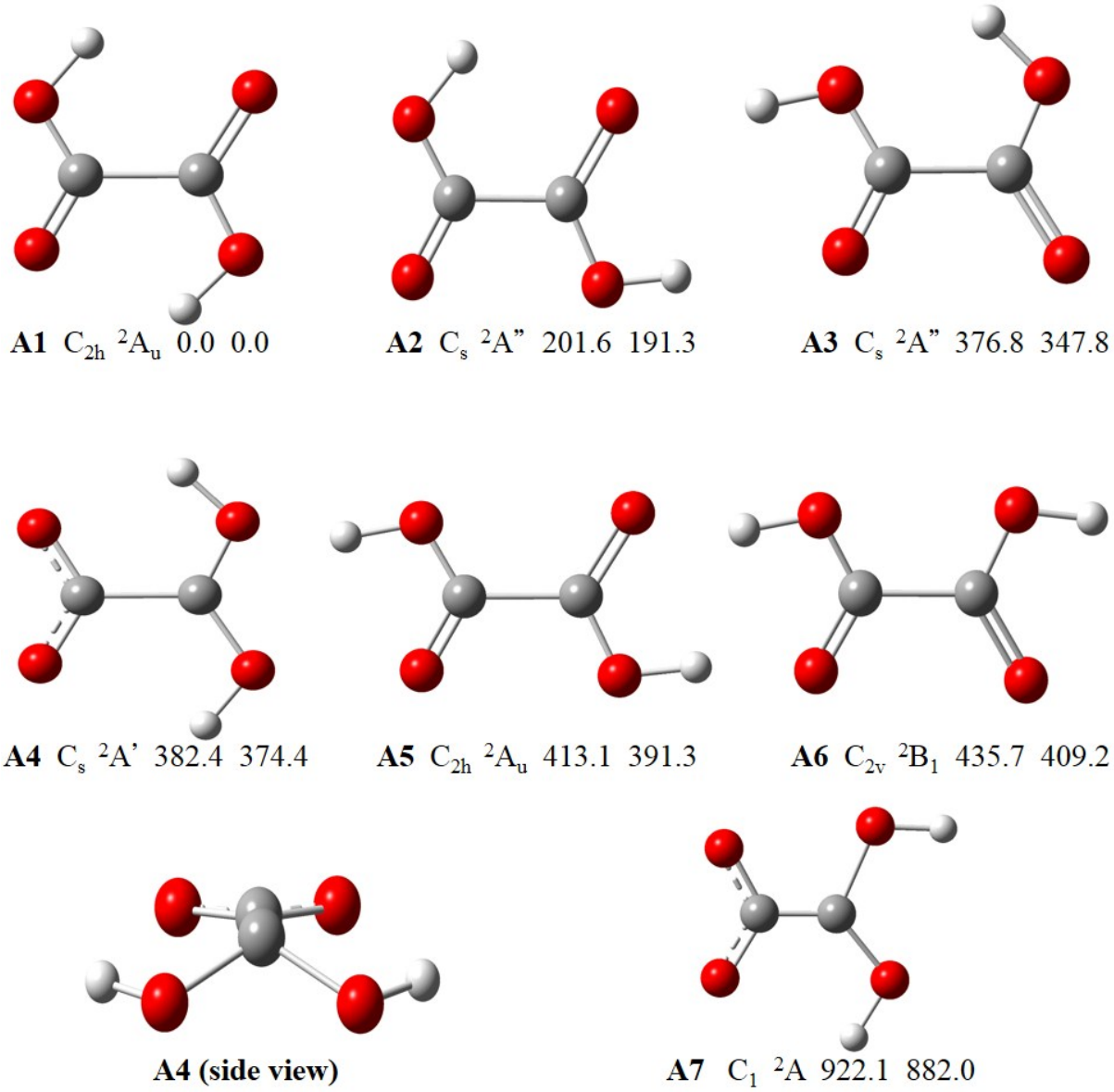
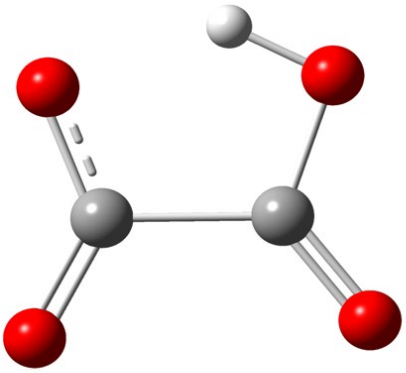
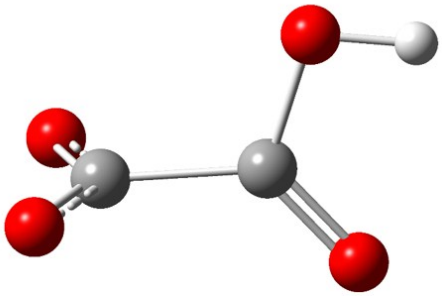


Fig. S2: Conformers and tautomers of the anionic oxalic acid monomer. All structures are minima. The name of the species is followed by its point symmetry group, the electronic term, two relative energies (in meV) with respect to **A1:** purely electronic and electronic corrected for zero-point vibrations. **A4** and **A7** are non-planar. The same computational approach as in Fig. S1.



DP1 C_s $^1A'$ 0.0 0.0



DP2 C_s $^1A'$ 433.6 419.0

Fig. S3. Two conformers of the deprotonated oxalic acid monomer. Both structures are minima. The name of the species is followed by its point symmetry group, the electronic term, two relative energies (in meV) with respect to **DP1:** purely electronic and electronic corrected for zero-point vibrations. The same computational approach as in Fig. S1.

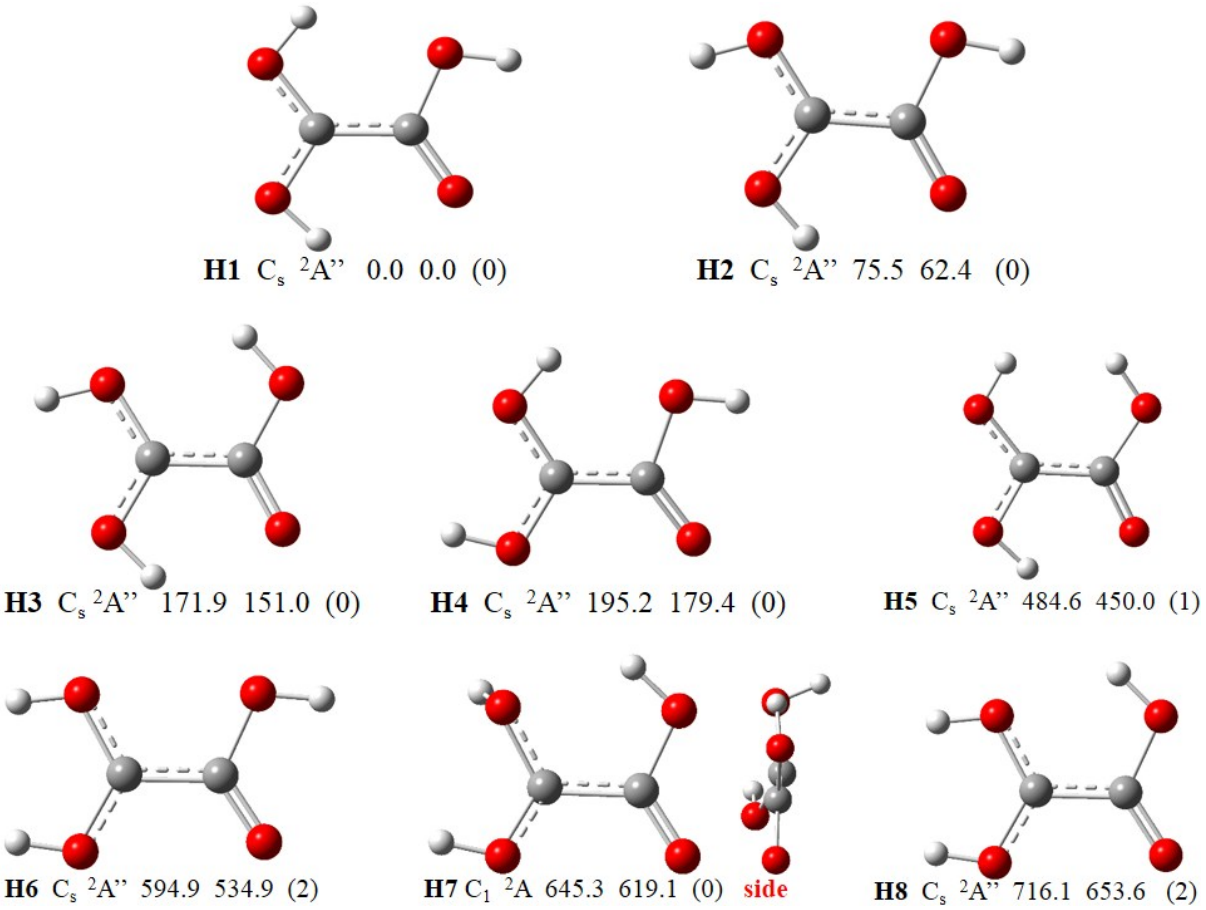


Fig. S4: Conformers of hydrogenated oxalic acid monomer. The name of the species is followed by its point symmetry group, the electronic term, two relative energies (in meV) with respect to **H1:** purely electronic and electronic corrected for zero-point vibrations, and the number of vibrational modes with negative curvatures. **H5**, **H6**, and **H8** are not minima, but there are useful for the discussion of the most stable structures of $(OA)_2^-$. The same computational approach as in Fig. S1.

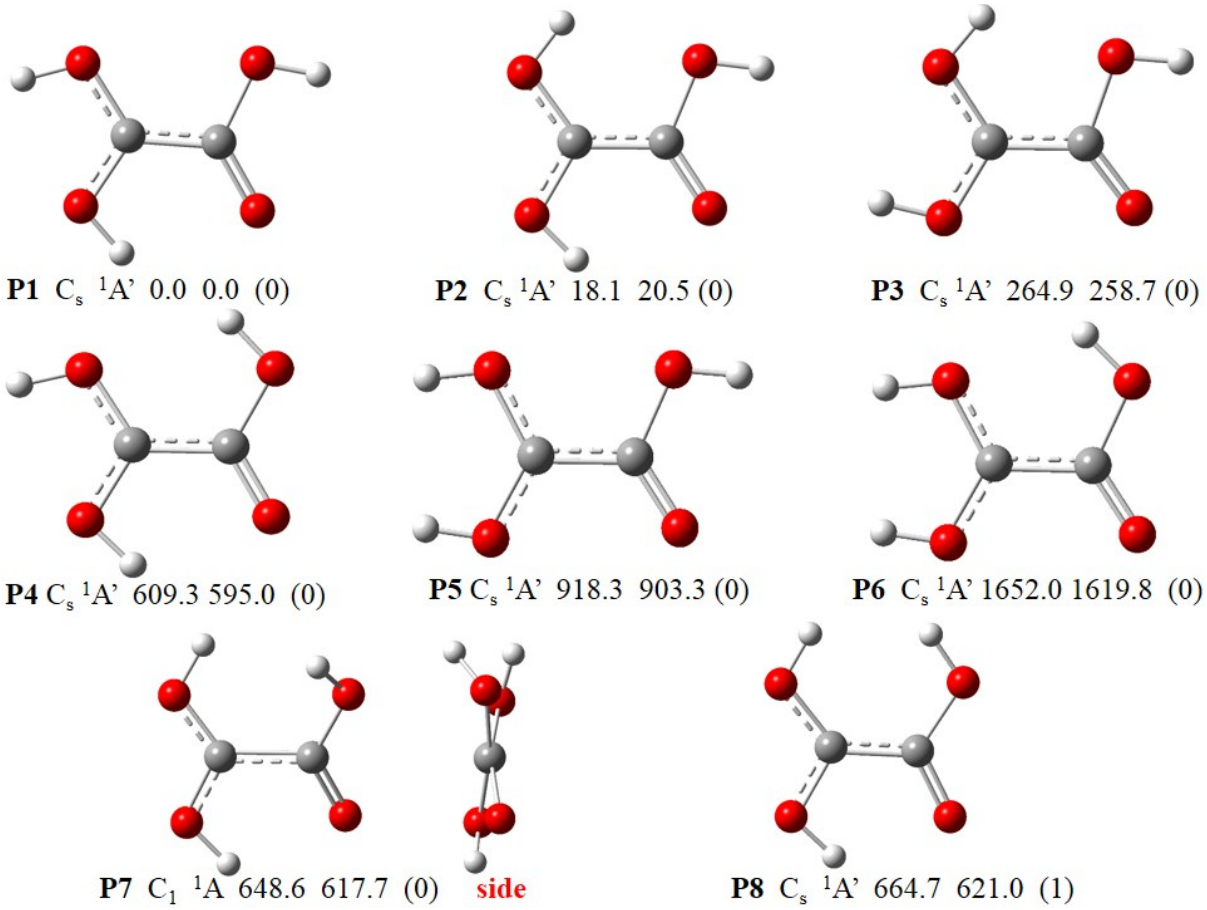


Fig. S5: Conformers of protonated oxalic acid monomer. The name of the species is followed by its point symmetry group, the electronic term, two relative energies (in meV) with respect to **P1:** purely electronic and electronic corrected for zero-point vibrations, and the number of vibrational modes with negative curvatures. **P8** is a planar transition state separating two equivalent non-planar **P7** minima. The same computational approach as in Fig. S1.

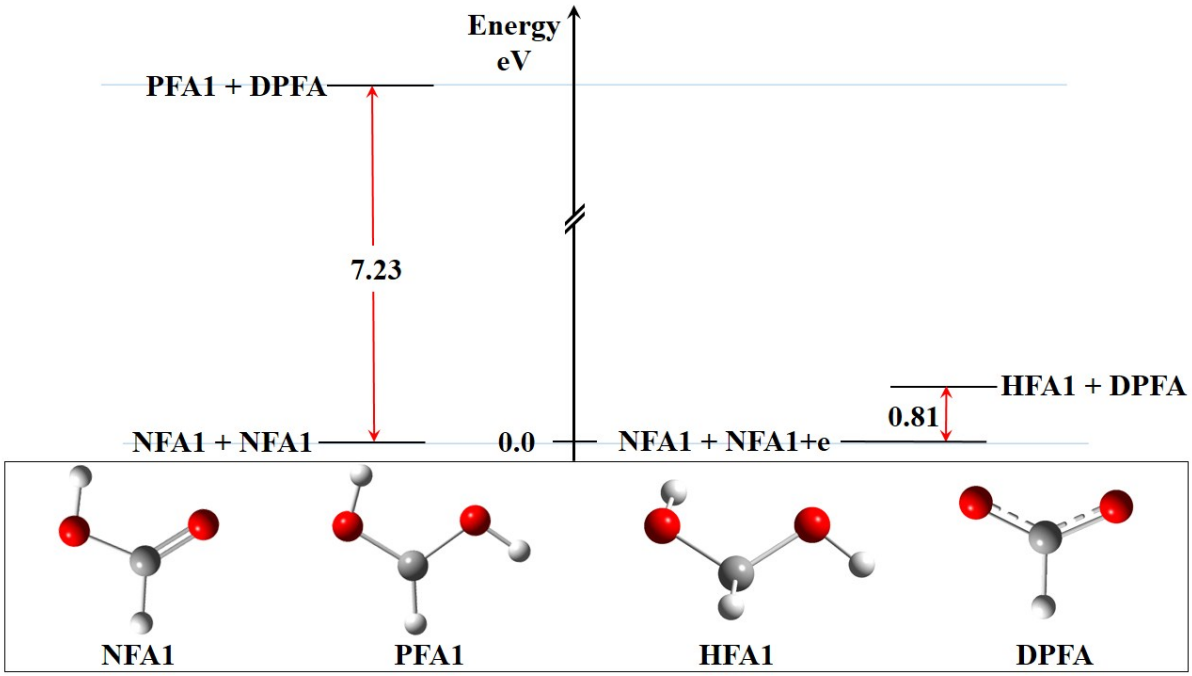


Fig. S6: Relative energies of the dissociative asymptotes for $(FA)_2$ (left) and $(FA)_2^-$ (right). The energy of the **NFA1 + NFA1** asymptote is set to zero.

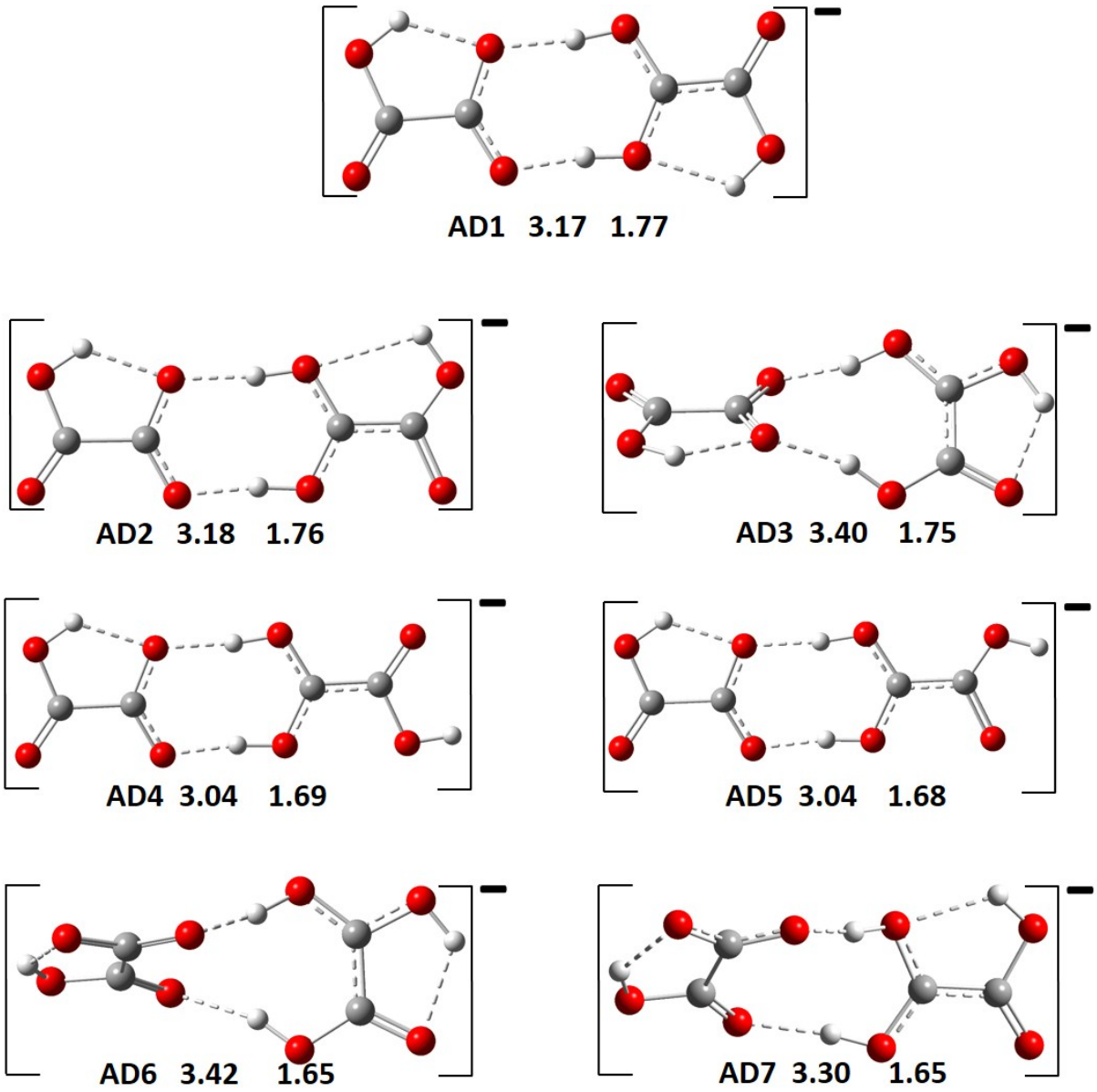


Fig. S7. The seven most stable isomers of $(OA)_2^-$. The label **ADn** is followed by the electron vertical detachment energy and the adiabatic electron affinity with respect to **ND1**. Both energies are in eV.

Table S1: Total stabilization energy, its components (Eqs. 1-7), and a correction for the zero-point vibrations for **AD1**-**AD7**. All energies are in meV.

$(OA)_2^-$	Monomers	$E_{z_n}^{1b-conf}$	$E_{z_n}^{1b-def}(G)$	$E_{z_n}^{1b}(G)$	$E_{X_mY_n}^{2b}$	$E_{X_mY_n}^{stab}$	ΔE_0^{vib}	$E_{X_mY_n}^{stab}+\Delta E_0^{vib}$
AD1	H8	716	138	854	-2267	-1387	0	-1387
	DP1	0	27	27				
AD2	H8	716	130	846	-2246	-1374	0	-1374
	DP1	0	25	25				
AD3	H5	485	160	644	-2041	-1370	2.	-1367
	DP1	0	27	27				
AD4	H6	595	148	743	-2066	-1300	-3	-1303
	DP1	0	23	23				
AD5	H6	595	147	742	-2061	-1296	-3	-1299
	DP1	0	23	23				
AD6	H5	485	99	584	-1882	-1273	4	-1269
	DP1	0	25	25				
AD7	H8	716	66	783	-2084	-1270	5	-1265
	DP1	0	32	32				

Table S2. The geometries of the most stable isomers of $(OA)_2^-$ optimized at the MP2/aug-cc-pVDZ level on the CP corrected surface. The monomers considered in the CP procedure were **Hm**'s and **DP1** specified in Table 1

AD1

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.388744
O	1.062273	0.000000	-0.621090
C	-1.328559	-0.000696	-0.565857
O	-1.485622	-0.018533	-1.890594
O	-2.376806	0.051759	0.287279
O	-4.749838	-0.489835	-0.669796
C	-4.902982	-0.232519	-1.890067
C	-6.332591	-0.345522	-2.500201
O	-6.323299	-0.037211	-3.823905
O	-4.014582	0.125269	-2.741581
O	-7.343908	-0.663391	-1.901921
H	-0.934028	-0.006635	1.663314
H	-3.265899	-0.177186	-0.143930
H	-2.449730	0.057322	-2.153213
H	-5.369317	0.167426	-3.979445

AD2

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.229846
O	1.199551	0.000000	-0.700905
C	-1.158673	0.001375	-0.862517
O	-0.947649	-0.055488	-2.199713
O	-2.382105	0.018776	-0.335371
O	-2.968847	0.577783	-3.745973
C	-4.118330	0.273665	-3.254658
O	-4.385576	-0.111792	-2.093405
C	-5.279988	0.424105	-4.283147
O	-4.815573	0.852525	-5.487488
O	-6.456691	0.196873	-4.071650
H	-3.095757	-0.054584	-1.038191
H	-1.758447	0.209090	-2.743300
H	-3.846318	0.932935	-5.315529
H	0.964855	0.006216	-1.645616

AD3

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.217654
C	1.256244	0.000000	-0.922499
O	2.395354	0.010555	-0.389873
O	-1.141173	-0.001575	-0.738823
O	0.971644	-0.011044	-2.170021
O	4.262203	-0.843086	-1.979797
C	4.735485	-0.121053	-2.984628
C	4.112097	0.868934	-3.831992
O	2.820396	1.223115	-3.688019
O	6.010305	-0.423553	-3.324518
O	4.827212	1.409877	-4.718228
H	-0.782008	0.000000	-1.660515
H	3.511790	-0.403872	-1.454814
H	6.149838	0.186844	-4.088148
H	2.290449	0.637408	-3.082244

AD4

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.393223
O	1.070310	0.000000	-0.638058
C	-1.325980	0.000162	-0.543770
O	-1.449621	-0.011658	-1.873497
O	-2.377883	0.012006	0.281170
O	-4.802112	-0.120368	-0.785369
C	-4.874859	-0.007023	-2.032406
C	-6.281997	-0.007772	-2.704130
O	-6.176891	0.123038	-4.053428
O	-3.914751	0.115227	-2.875285
O	-7.351468	-0.109478	-2.131273
H	-3.260084	-0.042694	-0.201200
H	-2.405262	0.040564	-2.173744
H	0.950850	0.000780	1.592074
H	-5.197176	0.178046	-4.174360

AD5

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.245576
O	1.197664	0.000000	-0.713129
C	-1.145082	-0.000100	-0.861973
O	-0.969197	-0.015369	-2.189011
O	-2.351667	0.014343	-0.293910
O	-3.130611	0.167180	-3.721758
C	-4.257115	0.014869	-3.124051
O	-4.469561	-0.134119	-1.897608
C	-5.472528	0.025504	-4.100870
O	-5.062286	0.196537	-5.386143
O	-6.643447	-0.099462	-3.792077
H	-3.099838	-0.047665	-0.962489
H	-1.832378	0.059007	-2.697598
H	-4.081787	0.260690	-5.276939
H	1.854364	-0.001472	0.002730

AD6

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.263867
O	0.971142	0.000000	-0.813442
C	-1.385021	0.003143	-0.719831
O	-1.233693	-0.087951	-2.053357
O	-2.482062	0.081510	-0.175695
O	-1.704719	-1.140736	2.828316
C	-2.387685	-0.353071	3.644602
O	-2.617459	-0.871731	4.873392
C	-2.993217	0.932707	3.402177
O	-2.931206	1.499815	2.176759
O	-3.574158	1.513968	4.353418
H	-1.134730	-0.621153	2.164810
H	-0.235720	-0.096493	-2.106577
H	-2.618961	0.866525	1.489674
H	-3.148953	-0.154420	5.290482

AD7

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.386096
O	1.058303	0.000000	-0.624757
C	-1.332138	0.001488	-0.560308
O	-2.387074	-0.090236	0.276625
O	-1.499914	0.040725	-1.887605
O	-4.547369	1.134969	-0.437807
C	-5.464192	0.870571	-1.264133
O	-6.670258	1.258776	-1.286881
C	-5.125244	-0.068003	-2.468823
O	-6.216658	-0.289784	-3.217580
O	-4.030390	-0.556771	-2.736754
H	-0.935389	0.013274	1.658127
H	-2.446755	-0.141644	-2.108045
H	-6.877274	0.270570	-2.714862
H	-3.216517	0.359487	-0.099449