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Supporting Materials

Correlative analysis among experimental and theoretical structural, thermochemical, and molecular spectroscopic parameters of crystals of mandelic acid

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$$i_{AB} \equiv \frac{\left(c_A^2 - c_B^2\right)}{\left(c_A^2 + c_B^2\right)}$$ Equation S1

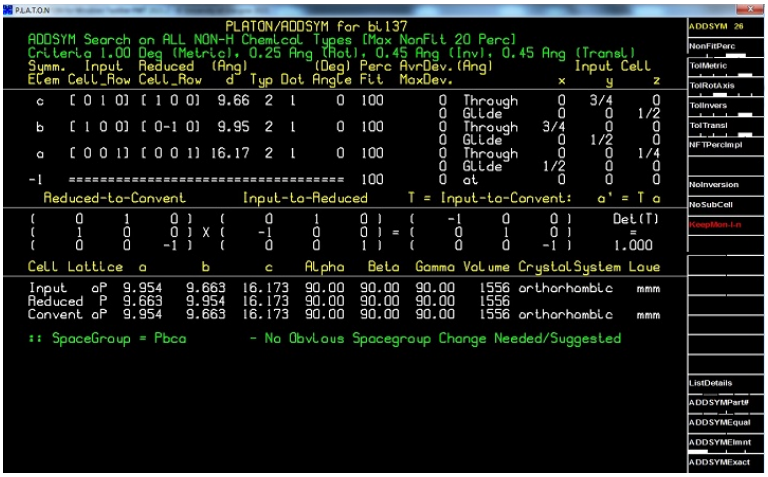


Figure S1. ADDSYM test data considering symmetry elements on (1) (CCDC 880481).

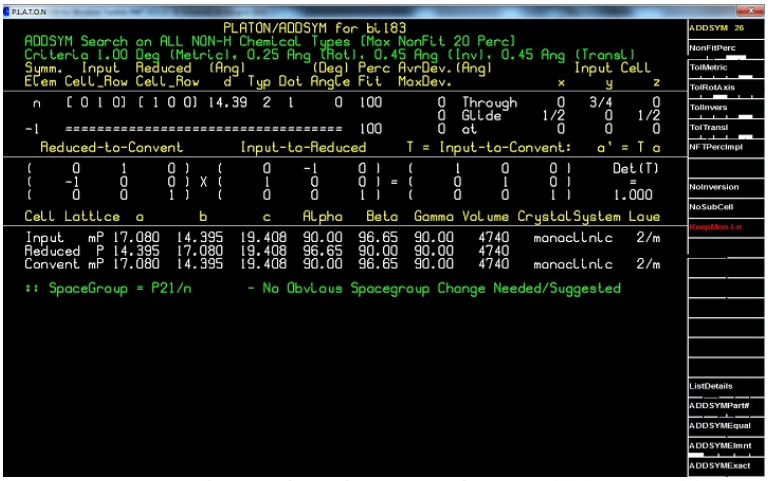


Figure S2. ADDSYM test data considering the symmetry elements in (2) (CCDC 822753).

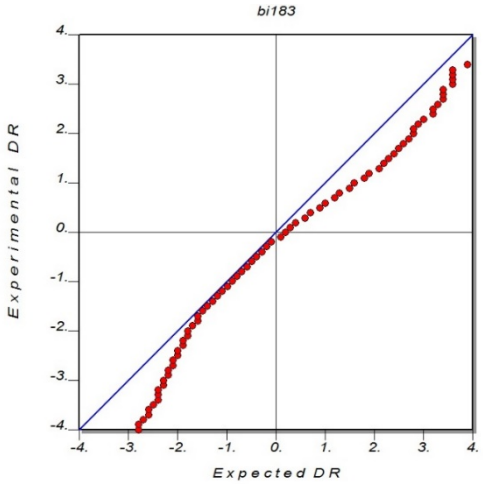


Figure S3. DRK plot of crystal (2) (CCDC 822753).

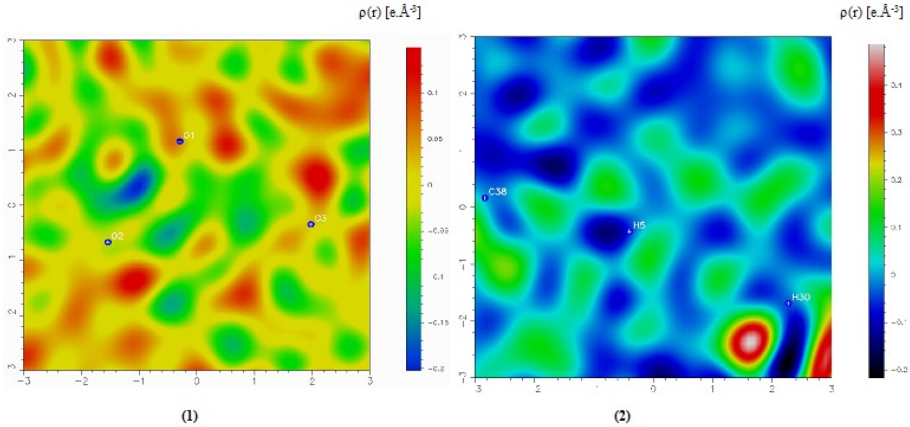


Figure S4. A: 2D Fourier electron density maps of the experimental electron density of (1) and (2).

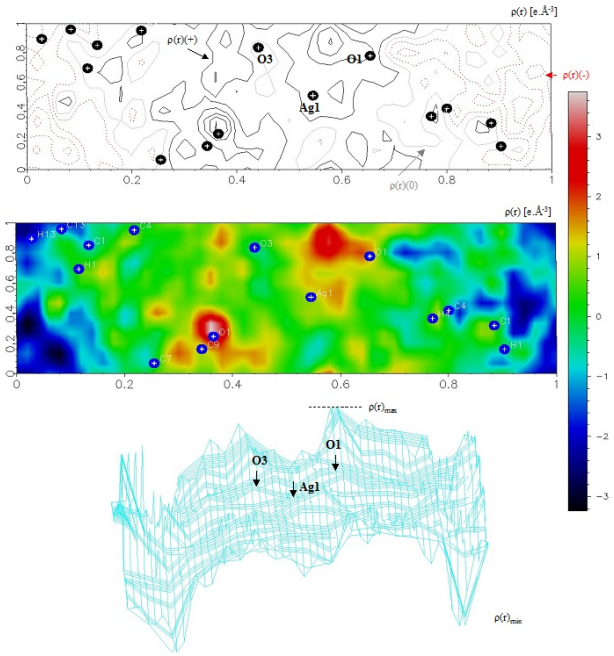


Figure S5. 2D and 3D Fourier electron density maps of the experimental electron density of (3).

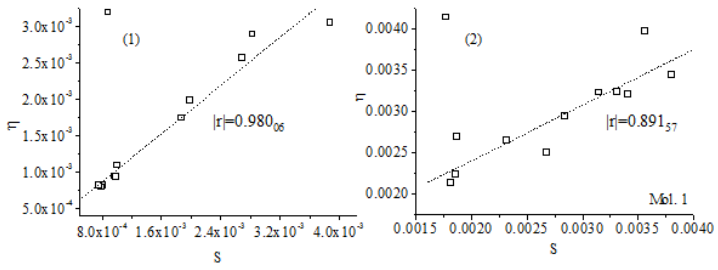


Figure S6. Correlative analysis between the experimental Hirshfeld-Shmueli S and ETA (ε) values of the crystals (1) and (2) listed in **Table S1**; chemometrics.

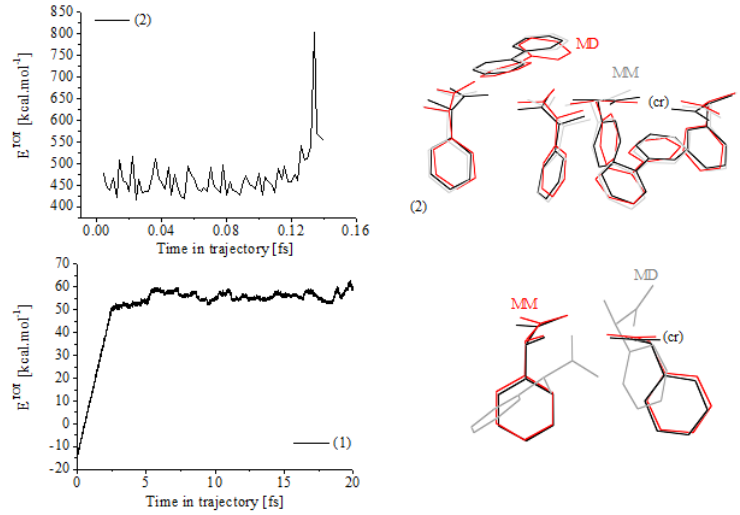


Figure S7. Molecular mechanics (MM), molecular dynamics (MD) (total energy, E^{TOT} [kcal.mol^{-1}] *versus* time in trajectory [fs]) and crystallographic 3D structures of mandelic acid species in crystals.

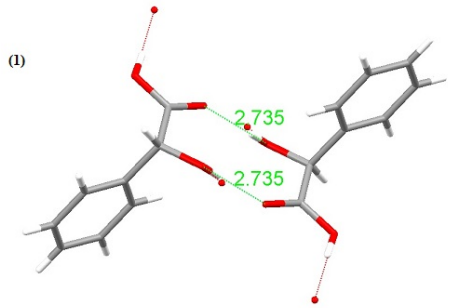


Figure S8. Hydrogen bond interaction of mandelic acid in (1) (CCDC 880481); selected bond lengths [Å].

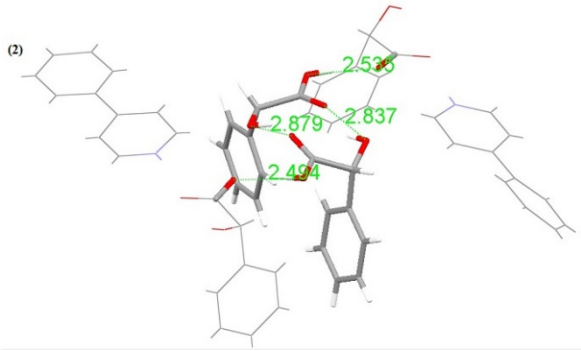


Figure S9. Hydrogen bond interaction of mandelic acid and mandelate anion in (2) (CCDC 822753); selected bond lengths [Å].

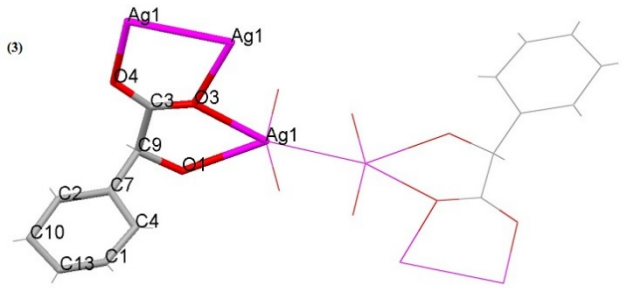
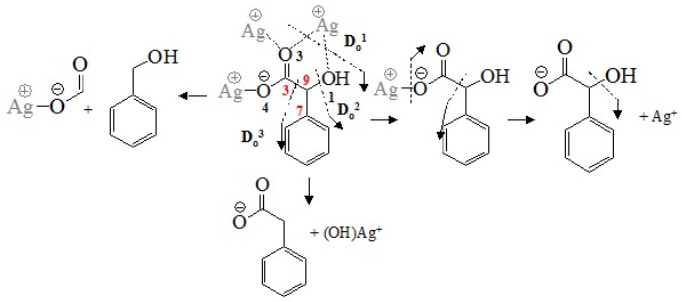


Figure S10. Coordinative bond interaction of mandelic acid and Ag^{I}-ion in (3); selected bond lengths [Å].



$$D_0^1 = E^0_{Ag^+} + E^0_{[MA]} - E^0_{\{Ag-MA\}}$$

$$D_0^2 = E^0_{[MA-OHAg^+]} + E^0_{[OHAg^+]} - E^0_{\{Ag-MA\}}$$

$$D_0^3 = E^0_{[MA-COOAg^+]} + E^0_{[COOAg^+]} - E^0_{\{Ag-MA\}}$$

Figure S11. Chemical diagrams of the dissociation species of (3).

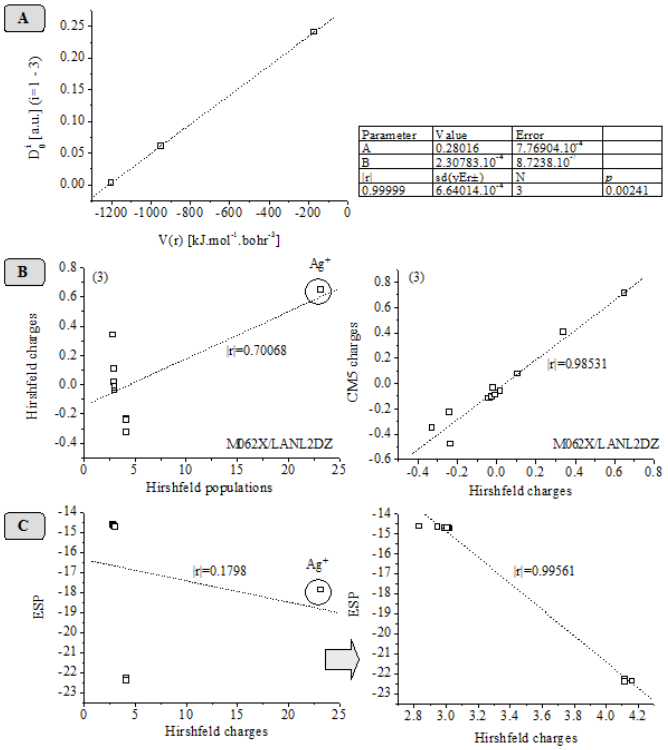
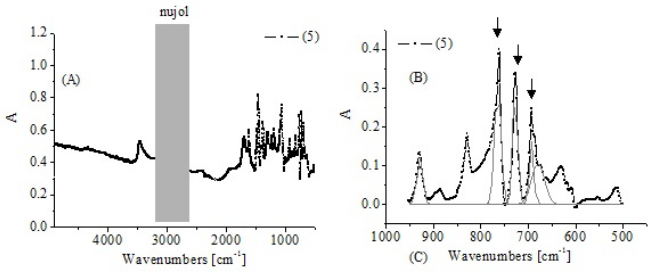


Figure S12. Correlative analysis between theoretical DFT and experimental data on crystals; chemometrics.



χ^2/DoF	0.00055	
r^2	0.9173	
xc1	929.40312	±0.72192
w1	12.75775	±1.44396
A1	1.93114	±0.1893
xc5	**764.64402**	±0.30079
w5	12.92162	±0.7859
A5	4.7909	±0.37067
xc6	**727.63601**	±0.24517
w6	9.65626	±0.52571
A6	3.86378	±0.19101
xc7	**693.06909**	±0.53416
w7	9.11399	±1.47118
A7	1.87733	±0.48963
xc8	679.64826	±3.11841
w8	27.45284	±4.39014
A8	3.56844	±0.67463

Figure S13. Solid-state IR-spectrum of crystal (5) within 5000–400 cm^{-1} (mathematically unprocessed pattern) (A); baseline corrected IR pattern of the same analyte within 1000–500 cm^{-1} (B); curve fitting data for the latter pattern using the mixed Lorentzian-Gaussian fitting function in ratio 50:50 (C).

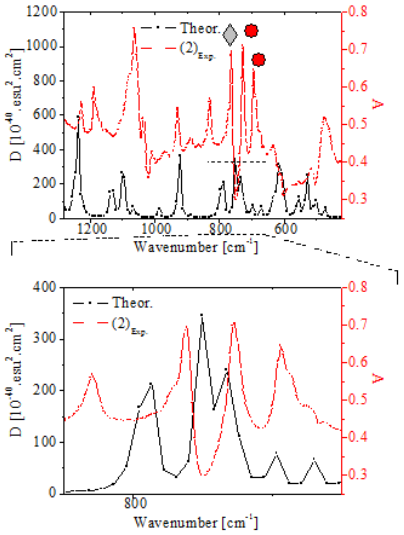
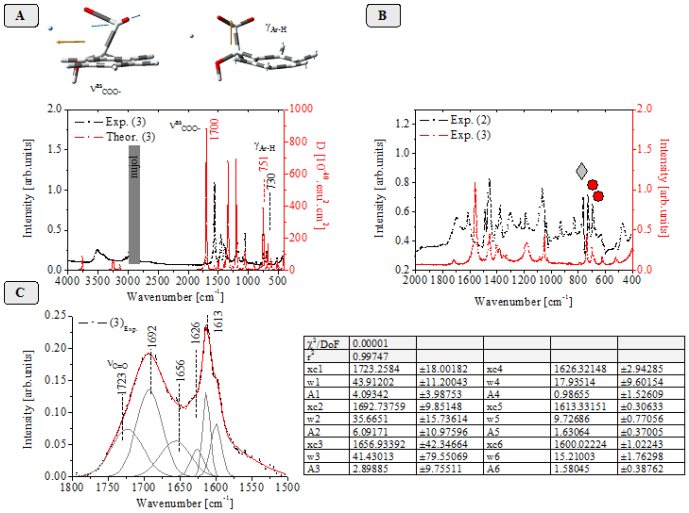


Figure S14. Experimental and theoretical IR-spectra.



χ^2/DoF	0.00001				
r^2	0.99747				
xc1	1723.2584	±18.00182	xc4	1626.32148	±2.94285
w1	43.91202	±11.20043	w4	17.93514	±9.60154
A1	4.09342	±3.98753	A4	0.98655	±1.52609
xc2	1692.73759	±9.85148	xc5	1613.33151	±0.30633
w2	35.6651	±15.73614	w5	9.72686	±0.77056
A2	6.09171	±10.97596	A5	1.63064	±0.37005
xc3	1656.93392	±42.34664	xc6	1600.02224	±1.02243
w3	41.43013	±79.55069	w6	15.21003	±1.76298
A3	2.89885	±9.75511	A6	1.58045	±0.38762

Figure S15. Theoretical (M062X/LANL2DZ) and experimental solid-state IR spectra of (2) and (3); visualization of selected theoretically obtained molecular vibrations of (3); curve-fitted experimental IR pattern of (2) using Gauss/Lorentz mixed function at ratio 1:1; chemomerics.

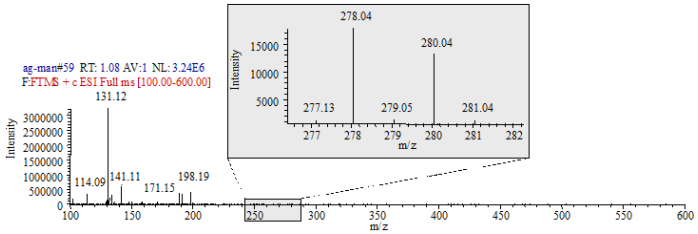


Figure S16. Mass spectrum of (3).

Table S1. The Hirshfeld-Shmueli S of isotropic variance of the mean square amplitude and the value of h reflecting the correlation coefficient between mutually perpendicular mean square amplitudes. Ideally, columns 1,2,3 and 5,6,7 should be the same. Variations; if any, indicate anisotropy of ESDS or inappropriate ETA (η). The overall average (column 9) is used as an estimate of the isotropic ESD (SQ RT of S), and the S, a standard ETA (= -0.25) of crystals (1) and (2).

ATOM	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
(1)									**$(S)^{1/2}$**
O1	0.00080	0.00081	0.00114	0.00093	0.00082	0.00095	0.00087	0.00088	0.00091
O2	0.00079	0.00079	0.00094	0.00084	0.00073	0.00081	0.00076	0.00077	0.00081
O3	0.00076	0.00081	0.00096	0.00085	0.00071	0.00082	0.00082	0.00079	0.00082
C8	0.00388	0.00305	0.00190	0.00305	0.00353	0.00290	0.00266	0.00305	0.00305
C1	0.00283	0.00289	0.00157	0.00251	0.00297	0.00221	0.00228	0.00251	0.00251
C2	0.00269	0.00257	0.00188	0.00241	0.00272	0.00216	0.00225	0.00239	0.00240
C3	0.00187	0.00174	0.00143	0.00169	0.00181	0.00159	0.00159	0.00167	0.00168
C4	0.00100	0.00109	0.00116	0.00109	0.00108	0.00101	0.00111	0.00107	0.00108
C5	0.00097	0.00094	0.00110	0.00101	0.00094	0.00096	0.00099	0.00096	0.00098
C6	0.00099	0.00093	0.00092	0.00095	0.00096	0.00094	0.00094	0.00094	0.00095
C7	0.00199	0.00198	0.00158	0.00186	0.00201	0.00183	0.00177	0.00187	0.00187
ATOM	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
(2)									**$(S)^{1/2}$**
O6	0.00173	0.00207	0.00181	0.00188	0.00205	0.00183	0.00201	0.00196	0.00192
O3	0.00188	0.00208	0.00161	0.00187	0.00210	0.00165	0.00180	0.00186	0.00186
O12	0.00186	0.00208	0.00176	0.00190	0.00191	0.00185	0.00177	0.00185	0.00188
O1	0.00186	0.00218	0.00170	0.00192	0.00199	0.00181	0.00176	0.00186	0.00189
O9	0.00181	0.00214	0.00188	0.00195	0.00204	0.00190	0.00197	0.00197	0.00196
O2	0.00193	0.00250	0.00168	0.00207	0.00213	0.00181	0.00195	0.00197	0.00202
O11	0.00187	0.00242	0.00166	0.00201	0.00204	0.00181	0.00192	0.00193	0.00197
O10	0.00209	0.00206	0.00171	0.00196	0.00221	0.00185	0.00195	0.00201	0.00199
O4	0.00183	0.00224	0.00239	0.00217	0.00207	0.00213	0.00226	0.00216	0.00216
O8	0.00186	0.00224	0.00217	0.00210	0.00195	0.00202	0.00220	0.00206	0.00208
O5	0.00209	0.00245	0.00218	0.00225	0.00218	0.00219	0.00225	0.00221	0.00223
O7	0.00187	0.00270	0.00327	0.00268	0.00215	0.00249	0.00277	0.00248	0.00258
C47	0.00247	0.00234	0.00198	0.00227	0.00272	0.00224	0.00211	0.00237	0.00232
C31	0.00217	0.00238	0.00218	0.00225	0.00223	0.00213	0.00230	0.00222	0.00223
C23	0.00254	0.00259	0.00207	0.00241	0.00280	0.00231	0.00226	0.00247	0.00244
C14	0.00236	0.00215	0.00247	0.00233	0.00237	0.00249	0.00230	0.00239	0.00236
C3	0.00234	0.00207	0.00237	0.00226	0.00218	0.00241	0.00204	0.00221	0.00224
C39	0.00232	0.00265	0.00230	0.00243	0.00247	0.00227	0.00250	0.00242	0.00242
C17	0.00257	0.00204	0.00232	0.00232	0.00231	0.00258	0.00204	0.00232	0.00232
C6	0.00260	0.00204	0.00221	0.00230	0.00230	0.00252	0.00201	0.00229	0.00229
C29	0.00242	0.00267	0.00218	0.00243	0.00254	0.00226	0.00228	0.00236	0.00240
C32	0.00270	0.00276	0.00229	0.00259	0.00268	0.00239	0.00245	0.00251	0.00255
C53	0.00243	0.00246	0.00224	0.00238	0.00247	0.00231	0.00224	0.00234	0.00236
N1	0.00609	0.00266	0.00321	0.00426	0.00452	0.00505	0.00278	0.00423	0.00425
C30	0.00317	0.00247	0.00277	0.00282	0.00277	0.00310	0.00244	0.00278	0.00280
N2	0.00526	0.00260	0.00296	0.00379	0.00387	0.00431	0.00259	0.00366	0.00373
C52	0.00266	0.00297	0.00249	0.00271	0.00283	0.00253	0.00267	0.00268	0.00270
C54	0.00296	0.00237	0.00259	0.00265	0.00266	0.00297	0.00233	0.00267	0.00266
C38	0.00291	0.00231	0.00305	0.00278	0.00249	0.00326	0.00247	0.00277	0.00277
C37	0.00258	0.00281	0.00255	0.00265	0.00271	0.00268	0.00256	0.00265	0.00265
C46	0.00268	0.00251	0.00305	0.00276	0.00254	0.00309	0.00271	0.00279	0.00277
C33	0.00313	0.00295	0.00276	0.00295	0.00297	0.00290	0.00269	0.00286	0.00290
C36	0.00276	0.00329	0.00250	0.00287	0.00299	0.00256	0.00271	0.00276	0.00281
C44	0.00341	0.00321	0.00241	0.00304	0.00320	0.00272	0.00269	0.00288	0.00296
C13	0.00274	0.00269	0.00272	0.00272	0.00274	0.00277	0.00263	0.00272	0.00272
C48	0.00299	0.00304	0.00280	0.00295	0.00304	0.00278	0.00273	0.00285	0.00290
C28	0.00271	0.00339	0.00271	0.00295	0.00292	0.00270	0.00287	0.00283	0.00289
C24	0.00294	0.00321	0.00283	0.00300	0.00315	0.00271	0.00283	0.00290	0.00295
C40	0.00315	0.00323	0.00273	0.00304	0.00312	0.00285	0.00280	0.00293	0.00299
C34	0.00277	0.00281	0.00321	0.00294	0.00272	0.00295	0.00309	0.00292	0.00293
C45	0.00284	0.00294	0.00295	0.00291	0.00283	0.00295	0.00277	0.00285	0.00288
C50	0.00426	0.00291	0.00348	0.00359	0.00414	0.00393	0.00317	0.00377	0.00368
C22	0.00317	0.00326	0.00284	0.00310	0.00305	0.00295	0.00269	0.00290	0.00300
C35	0.00301	0.00359	0.00278	0.00315	0.00324	0.00280	0.00317	0.00308	0.00311
C51	0.00357	0.00354	0.00316	0.00343	0.00379	0.00330	0.00320	0.00344	0.00344
C42	0.00331	0.00324	0.00365	0.00340	0.00324	0.00351	0.00363	0.00347	0.00344
C10	0.00549	0.00273	0.00320	0.00399	0.00431	0.00440	0.00266	0.00387	0.00393
C19	0.00589	0.00271	0.00371	0.00431	0.00467	0.00510	0.00283	0.00431	0.00431
C18	0.00384	0.00294	0.00298	0.00328	0.00320	0.00346	0.00267	0.00313	0.00321
C43	0.00380	0.00344	0.00319	0.00349	0.00360	0.00346	0.00307	0.00339	0.00344
C49	0.00361	0.00357	0.00358	0.00359	0.00355	0.00358	0.00340	0.00351	0.00355
C25	0.00374	0.00350	0.00376	0.00367	0.00363	0.00383	0.00344	0.00364	0.00365
C11	0.00368	0.00279	0.00288	0.00314	0.00319	0.00334	0.00258	0.00305	0.00310
C41	0.00356	0.00397	0.00317	0.00358	0.00371	0.00321	0.00366	0.00353	0.00356
C12	0.00475	0.00362	0.00311	0.00389	0.00416	0.00379	0.00297	0.00368	0.00378
C27	0.00321	0.00369	0.00332	0.00341	0.00360	0.00311	0.00342	0.00338	0.00340
C26	0.00418	0.00334	0.00358	0.00372	0.00424	0.00396	0.00339	0.00388	0.00380
C7	0.00315	0.00414	0.00289	0.00344	0.00340	0.00296	0.00311	0.00316	0.00330
C4	0.00287	0.00507	0.00291	0.00376	0.00368	0.00304	0.00352	0.00342	0.00359
C2	0.00305	0.00518	0.00344	0.00400	0.00364	0.00321	0.00392	0.00360	0.00381
C15	0.00356	0.00453	0.00377	0.00398	0.00404	0.00377	0.00388	0.00390	0.00394
C20	0.00639	0.00553	0.00448	0.00552	0.00591	0.00572	0.00465	0.00546	0.00549
C21	0.00539	0.00437	0.00358	0.00451	0.00468	0.00480	0.00392	0.00448	0.00450
C5	0.00403	0.00531	0.00322	0.00427	0.00447	0.00354	0.00373	0.00393	0.00411
C8	0.00452	0.00550	0.00357	0.00460	0.00486	0.00436	0.00433	0.00452	0.00456

C1	0.0033	0.00624	0.00502	0.00500	0.00424	0.00441	0.00519	0.00463	0.00482
C16	0.00472	0.00728	0.00610	0.00612	0.00565	0.00561	0.00644	0.00591	0.00602

Table S2. Experimental dihedral angle values of mandelic acid species in crystals (1)–(3) using the atom labeling scheme shown in **Figure 1**.

Compound	Species	ϕ_1	ϕ_2	ϕ_3
(1)	Neutral acid molecule	110.00	-101.77	-157.11
(2)	Neutral acid molecule	85.62	-102.55	-161.16
	Mandelate anion	-145.26	92.78	-150.60
(3)	Mandelate anion	129.34	-65.03	-22.07

Table S3. Theoretical (M062X/LANL2DZ) natural bond orbital analysis of (3).

Bond	Occupancy	Bond orbital	Coefficients	Hybrids
BD (1)Ag1–O4	1.81339	47.28%	0.6876*Ag1	s(88.81%)p0.11(10.16%)d0.01(1.03%)
		52.72%	0.7261*O4	s(0.01%)p1.00(99.99%)
BD (1) O2–C10	1.99253	71.93%	0.8481*O2	s(30.61%)p2.27(69.39%)
		28.07%	0.5298*C10	s(17.98%)p4.56(82.02%)
BD (1) O3–C7	1.98567	68.18%	0.8257*O3	s(32.25%)p2.10(67.75%)
		31.82%	0.5641*C7	s(31.13%)p2.21(68.87%)
BD (1) O4–C7	1.98625	59.27%	0.7698*O4	s(31.49%)p2.18(68.51%)
		40.73%	0.6382*C7	s(37.27%)p1.68(62.73%)

Table S4. Theoretical (M062X/LANL2DZ) thermochemistry in the ground state of Ag^{I}-mandelate species shown in **Figure S8**.

	{Ag^{I}-MA}	[Ag^{I}-MA–Ag^{I}]	[Ag^{I}-MA –$OHAg^{I}$]	[$OHAg^{I}$]	[$COOHAg^{I}$]	[Ag^{I}-MA–$COOHAg^{I}$]
E_{ZPVE}	87.06062	85.45627	74.66267	7.02921	7.17927	76.23582
E_{corr}	0.149817	0.145655	0.126960	0.014386	0.016235	0.128373
H_{corr}	0.150761	0.146599	0.127904	0.015331	0.017179	0.129318
G_{corr}	0.098558	0.099846	0.084757	-0.013603	-0.019523	0.089742
ε_0	0.138740	0.136183	0.118983	0.011202	0.011441	0.121490
E	-680.00071	-534.365238	-458.562656	-221.41684	-334.10307	-345.813313
H	-679.99976	-534.364294	-458.561712	-221.41589	-334.10212	-345.812369
G	-680.05197	-534.411047	-458.604859	-221.44483	-334.13883	-345.851945

E_{ZPVE}—zero-point vibration energy [kcal/mol]; ε_0—zero-point correction [Hartree/partice]; E_{corr}—thermal correction to energy [Hartree/partice]; H_{corr}—thermal correction to enthalpy [Hartree/partice]; G_{corr}—thermal correction to free energy [Hartree/partice]; E—sum of electronic and thermal energies [Hartree/partice]; H—sum of electronic and thermal enthalpies [Hartree/partice]; G—sum of electronic and thermal free energies [Hartree.(partice)$^{-1}$]

Table S5. Theoretical (M062X/LANL2DZ) Hirshfeld charges, dipoles and CM5 charges of (3).

Atom	Hirshfeld charges, dipoles, and CM5 charges						Hirshfeld charges with hydrogens summed into heavy atoms	
	No	Q-H	Dx	Dy	Dz	Q-CM5	Q-H	Q-CM5
Ag	1	0.648690	-0.243316	0.190465	-0.058296	0.713180	0.648690	0.713180
O	2	-0.236409	-0.112587	-0.031983	-0.039944	-0.476982	-0.021933	-0.078959
O	3	-0.327597	-0.007647	-0.031748	-0.041820	-0.349572	-0.327597	-0.349572
O	4	-0.239208	0.032972	0.022946	0.037852	-0.228391	-0.239208	-0.228391
C	5	-0.033880	0.020558	0.047591	0.091244	-0.116193	0.006307	0.007326
C	6	-0.040238	0.022877	-0.020665	-0.068183	-0.117794	-0.012827	-0.006869
C	7	0.340812	0.064868	-0.038726	0.016620	0.407001	0.340812	0.407001
C	8	-0.024945	0.010795	0.085357	0.067066	-0.101475	0.006060	0.014155
C	9	-0.019097	0.062553	0.008225	-0.053973	-0.031544	-0.019097	-0.031544
C	10	0.106212	0.022055	0.100775	-0.000988	0.076589	0.173734	0.213016
C	11	0.017968	-0.094898	-0.085942	-0.024761	-0.062573	0.069055	0.068186
C	0	-0.009285	-0.092794	-0.073358	0.027794	-0.091015	0.037674	0.037701
	Tot	1.999565	-0.066549	-0.229273	0.046593	1.999565		

Table S6. Theoretical (M062X/LANL2DZ) Hirshfeld populations at the iteration analysis of (3); electrostatic potentials (ESP); (CA, CB, DipXYZ).

Atom	Hirshfeld populations at iteration 1 (CA, CB, DipXYZ)						ESP
	No	1	2	3	4	5	
Ag	1	23.175655	23.175655	-0.243316	0.190465	-0.058296	-17.882627
O	2	4.118205	4.118205	-0.112587	-0.031983	-0.039944	-22.283282
O	3	4.163799	4.163799	-0.007647	-0.031748	-0.041820	-22.379638
O	4	4.119604	4.119604	0.032972	0.022946	0.037852	-22.400844
C	5	3.016940	3.016940	0.020558	0.047591	0.091244	-14.742870
C	6	3.020119	3.020119	0.022877	-0.020665	-0.068183	-14.749898
C	7	2.829594	2.829594	0.064868	-0.038726	0.016620	-14.646323
C	8	3.012472	3.012472	0.010795	0.085357	0.067066	-14.741044
C	9	3.009549	3.009549	0.062553	0.008225	-0.053973	-14.731828
C	10	2.946894	2.946894	0.022055	0.100775	-0.000988	-14.678925
C	11	2.991016	2.991016	-0.094898	-0.085942	-0.024761	-14.746743
C	12	3.004642	3.004642	-0.092794	-0.073358	0.027794	-14.745713

Table S7. Theoretical (M062X/LANL2DZ) EOM-CCSD data on (1) and (3) using long range transition densities.

(1)	**E [eV]**	**λ [nm]**	**f**
1	3.1342	395.59	0.0019
2	5.0551	245.27	0.0240
3	8.9596	138.38	0.0694
4	9.9140	125.06	0.0009
5	10.8049	114.75	0.0536
6	11.7394	105.61	0.0250
(3)	**E [eV]**	**λ [nm]**	**f**
1	0.7047	1759.48	0.0284
2	2.5517	485.88	0.1280
3	6.7910	182.57	0.0642
4	6.9049	179.56	0.1087
5	7.6238	162.63	0.0423
6	7.9133	156.68	0.0092