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Supporting Information

Conformational Geometry Matters: The Case of the Low-Melting-Point Systems of Tetrabutylammonium Triflate with Fumaric or Maleic Acid

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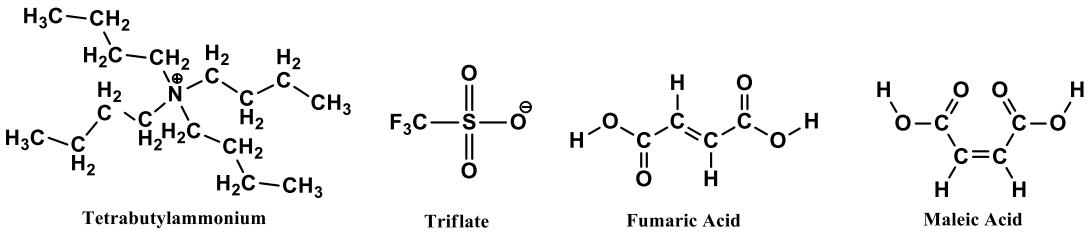


Figure S1. Chemical structure of TBA, TFO, Fumaric and Maleic acids.

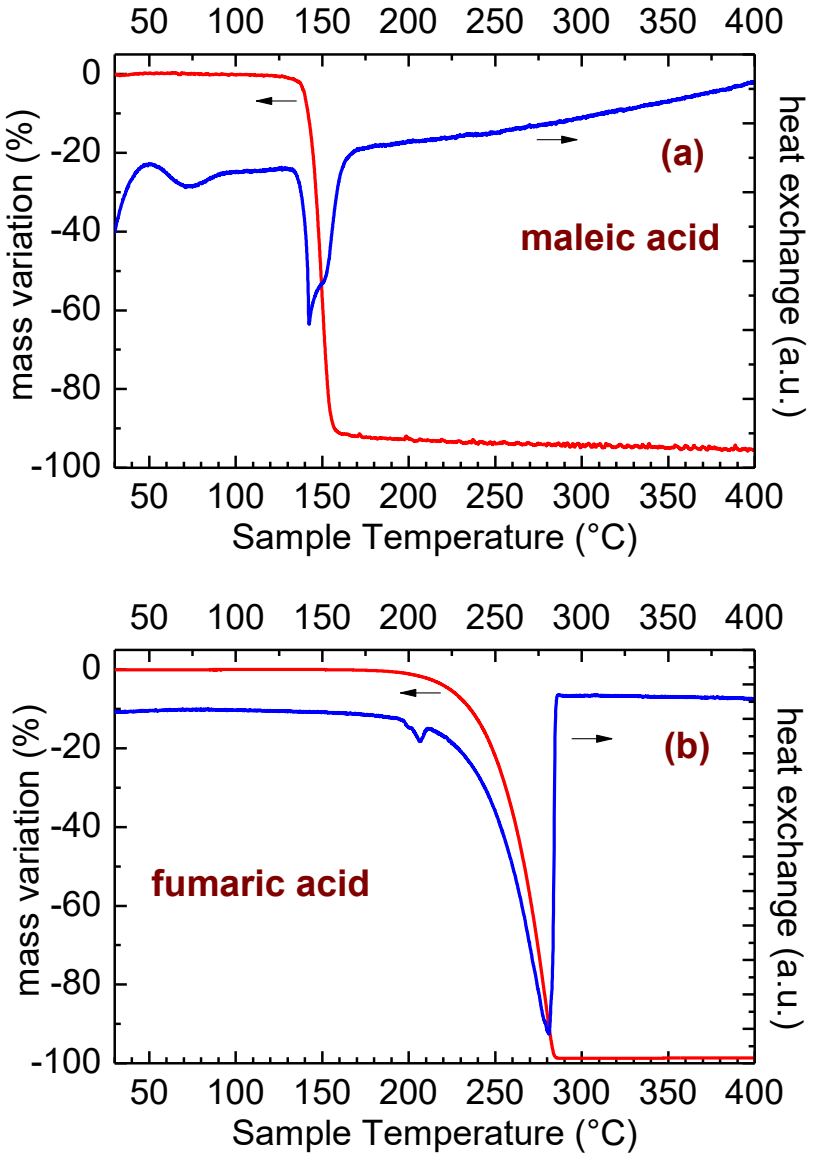


Figure S2. TGA and DTA curves of maleic (panel a) and fumaric acid (panel b).

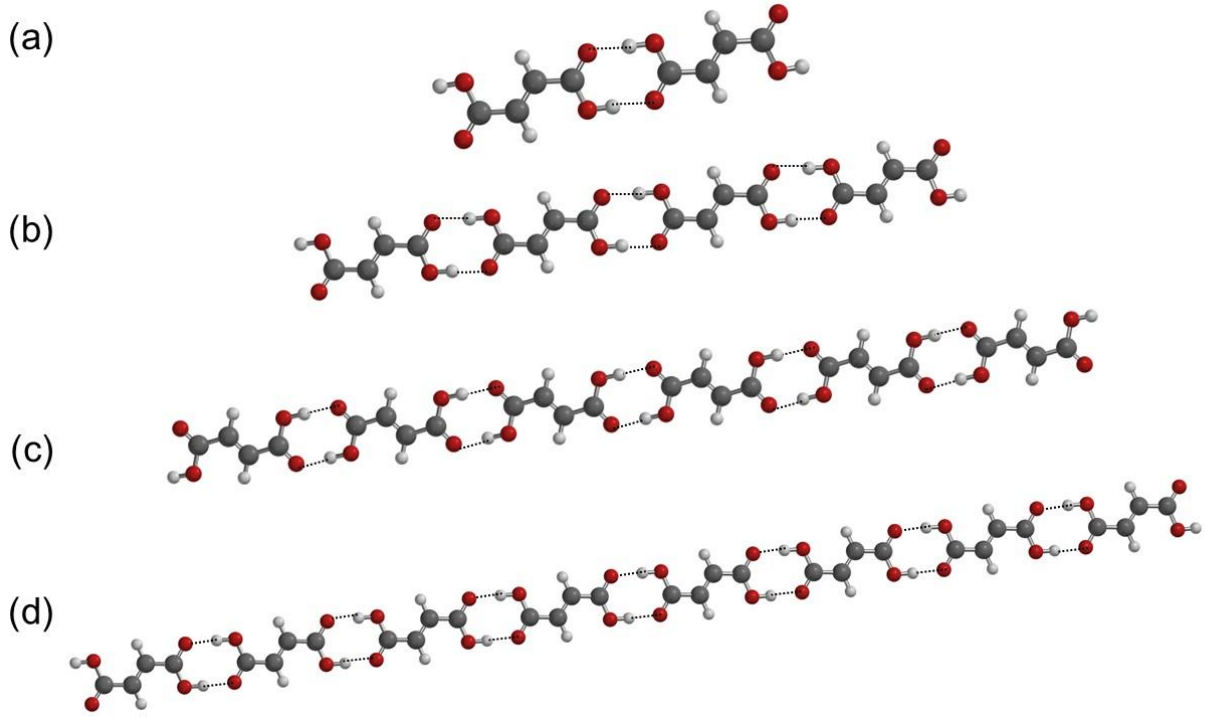


Figure S3. C_{2h} symmetry structures of dimer (a), tetramer (b), hexamer (c) and octamer (d) of fumaric acid calculated at ωB97X-D/6-311++G(d,p) level.

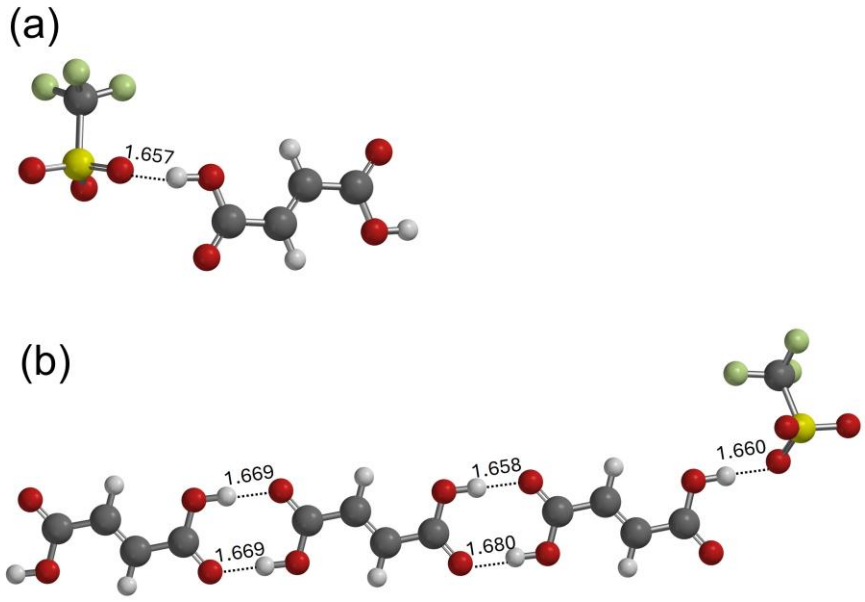


Figure S4. Complexes of TFO with fumaric acid (a) and TFO with a trimer of fumaric acid (b) calculated at ωB97X-D/6-311++G(d,p) level (Distance in Å).

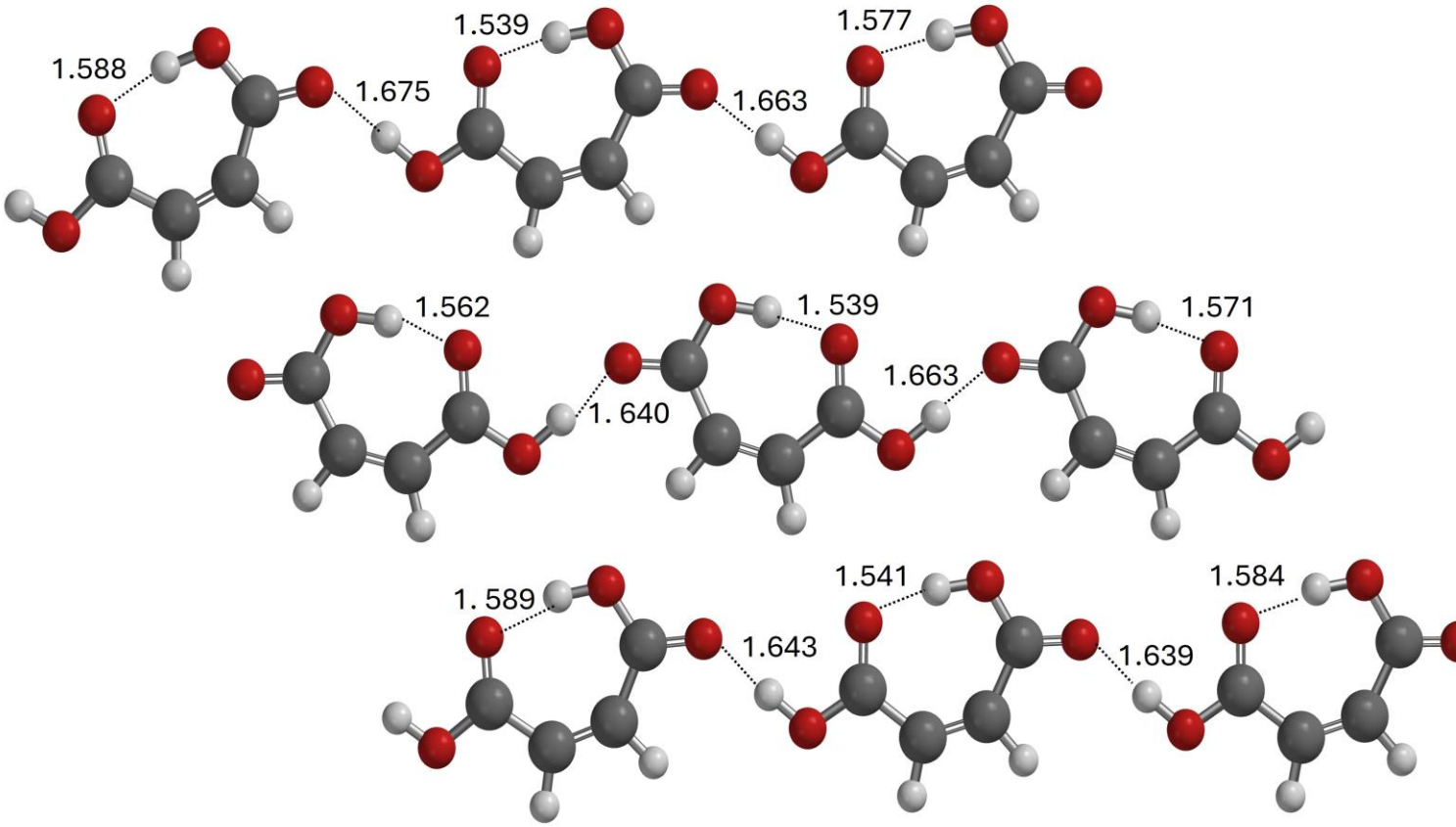


Figure S5. Nonamer of maleic acid calculated at ωB97X-D/6-311++G(d,p) level (Distance in Å)

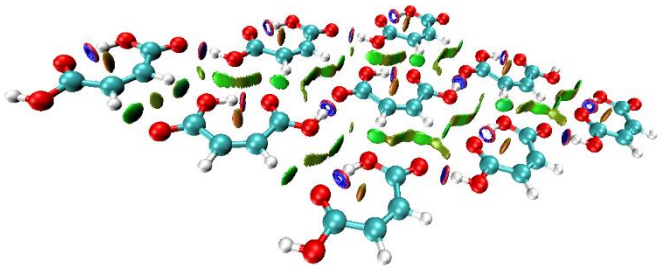


Figure S6. NIC of nonamer of maleic acid (isosurface=0.5).

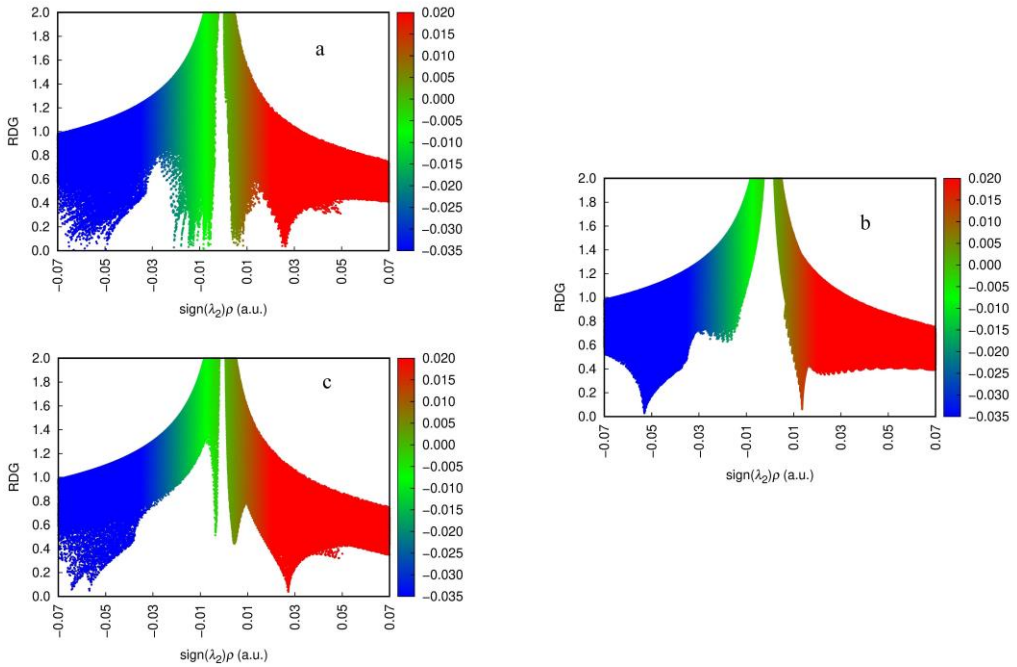


Figure S7. Scatter plot using promolecular density for MAL nonamer (a), FUM octamer (b) and TFO-MAL complexes of Fig. 4d (c).

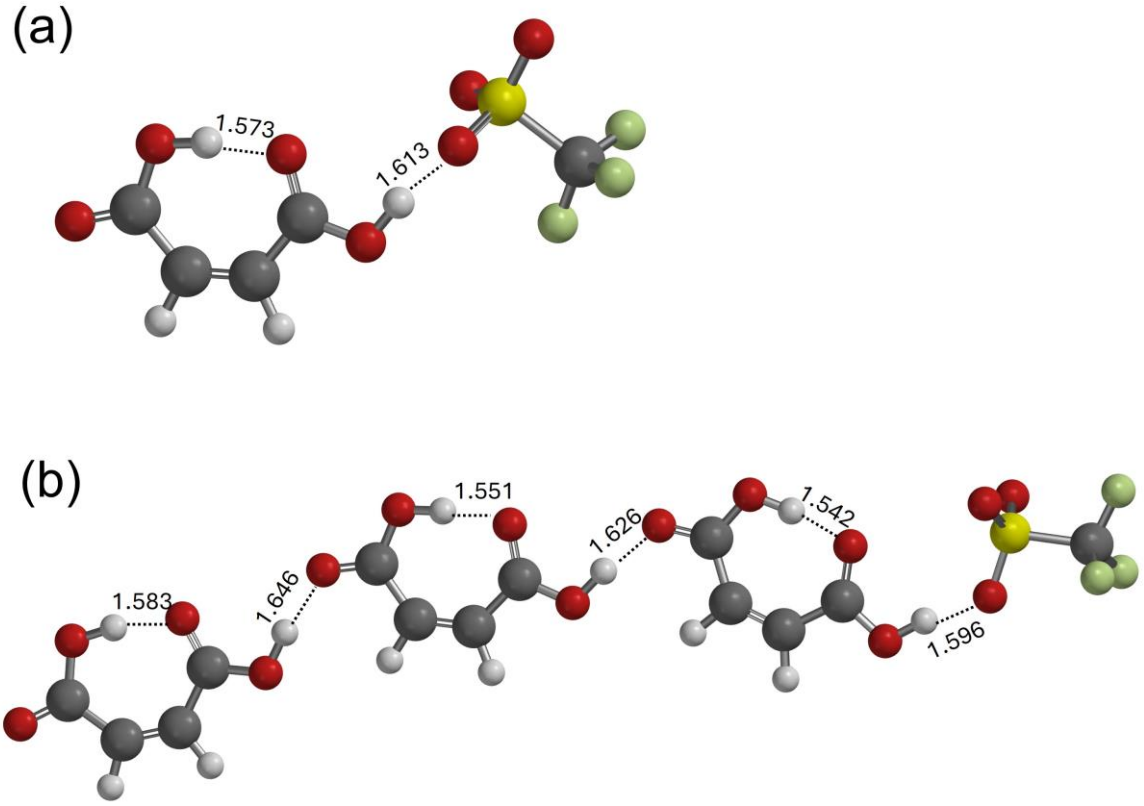


Figure S8. Complexes of TFO with maleic acid (a) and TFO with a trimer of maleic acid (b) calculated at ωB97X-D/6-311++G(d,p) level (Distances in Å).

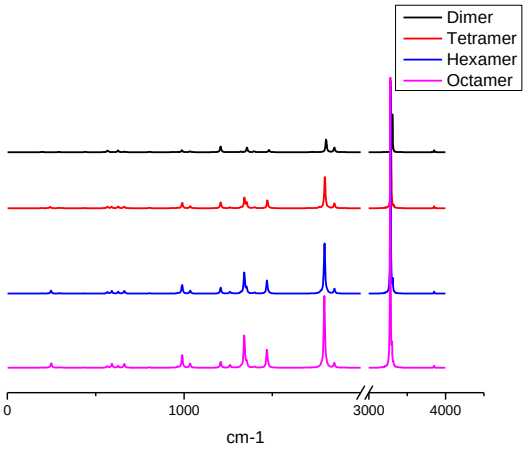


Figure S9. DFT infrared spectra of the C_{2h} symmetry oligomers of FUM.

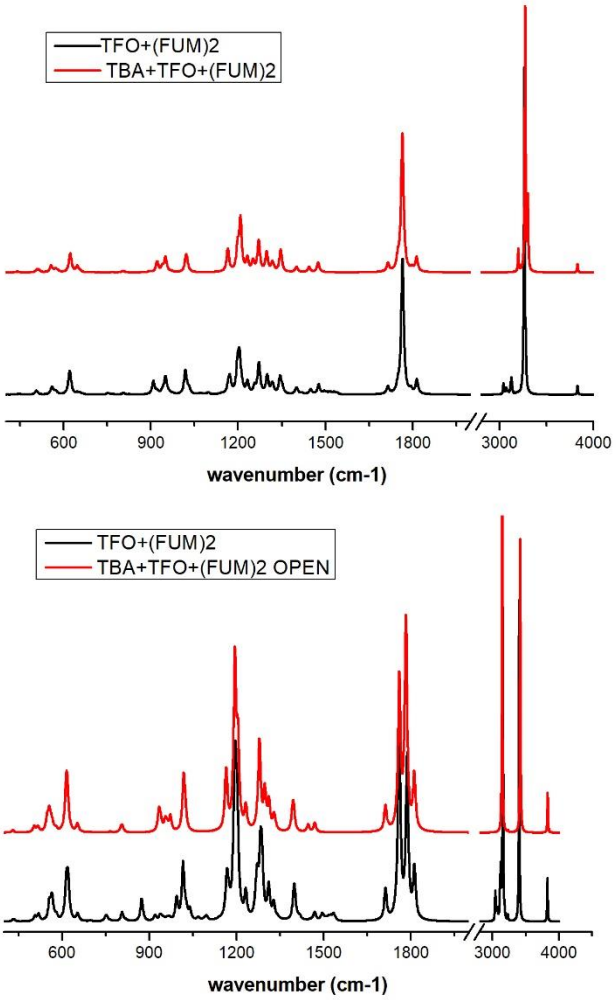


Figure S10. DFT infrared spectra for TFO+FUM dimer and the TBA+TFO+FUM dimer complexes.

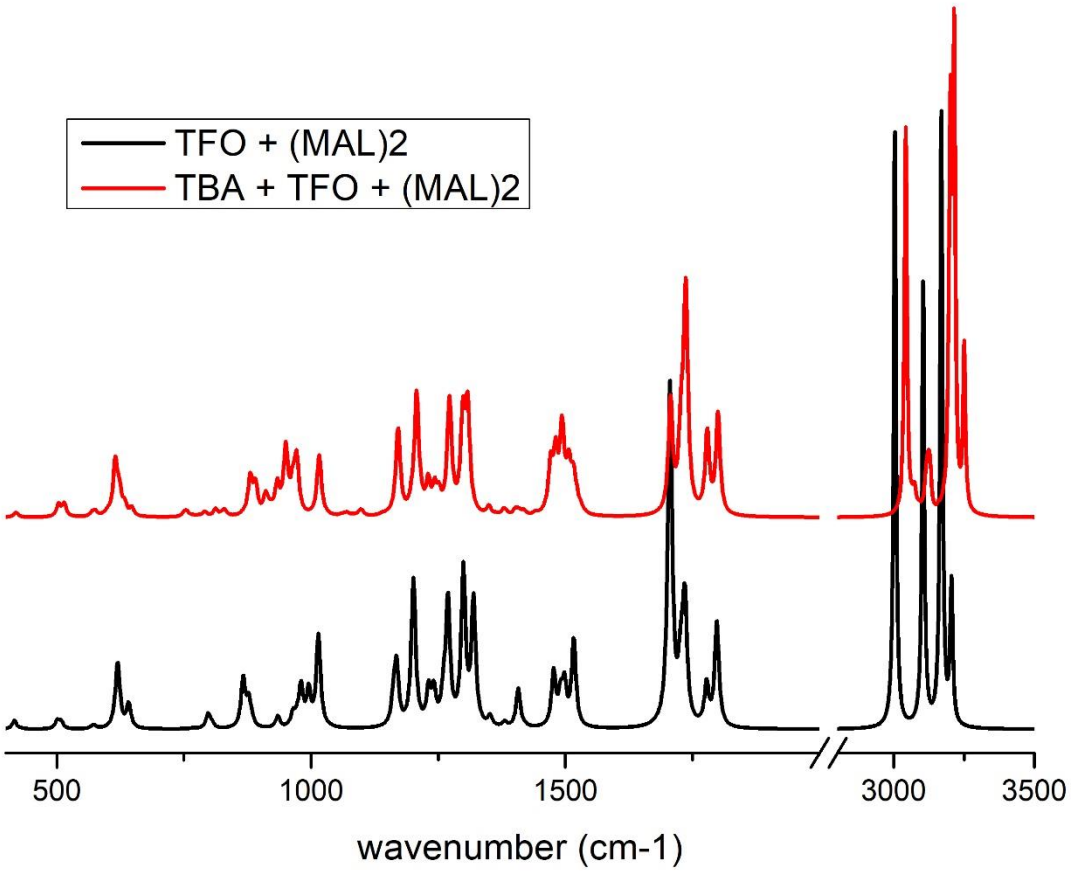


Figure S11. DFT infrared spectra for TFO+MAL dimer and the TBA+TFO+MAL dimer complexes.

Table S1. Second order perturbation theory analysis of Fock matrix of FUM complexes in NBO basis..

Donor (i)	Acceptor (j)	$E^{(2)}$ [a]	E(i) – E(j)[b]	F(i,j)[c]
FUM (Fig. 3a)				
LP(O)	σ*O-H	24,60	0,87	0,133
LP(O)	σ*O-H	24,60	0,87	0,133
FUM (Fig. 3b)				
LP(O)	σ*O-H	10,55	0,89	0,089
TFO+FUM (Fig. 3c)				
LP(O)	σ*O-H	28,31	0,87	0,142
LP(O)	σ*O-H	22,65	0,88	0,129
LP(O)TFO	σ*O-H	12,62	0,86	0,095
TFO+FUM (Fig. 3d)				
LP(O)	σ*O-H	12,59	0,89	0,097
LP(O)TFO	σ*O-H	7,67	0,84	0,075

[a] $E^{(2)}$ indicates the energy of hyperconjugate interactions (stabilization energy) (kcal/mol)

[b] Energy difference between donor and acceptor i and j NBO orbitals

[c] F(i,j) is the Fock matrix element between i and j NBO orbitals

Table S2. Second order perturbation theory analysis of Fock matrix of MAL complexes in NBO basis..

Donor (i)	Acceptor (j)	$E^{(2)}$ [a]	E(i) – E(j)[b]	F(i,j)[c]
MAL dimer				
LP(O)	σ*O-H[d]	34,47	0,90	0,161
LP(O)	σ*O-H[d]	34,45	0,90	0,161
LP(O)	σ*O-H[e]	23,61	0,87	0,131
TFO+MAL (Fig. 4d)				
LP(O)	σ*O-H[d]	44,94	0,88	0,181
LP(O)	σ*O-H[d]	36,08	0,90	0,164
LP(O)	σ*O-H[e]	28,04	0,86	0,142
LP(O)TFO	σ*O-H	17,63	1,32	0,137

[a] $E^{(2)}$ indicates the energy of hyperconjugate interactions (stabilization energy) (kcal/mol)

[b] Energy difference between donor and acceptor i and j NBO orbitals

[c] *F*(i,j) is the Fock matrix element between i and j NBO orbitals

[d] OH connected by intramolecular hydrogen bond.

[e] OH connected by intermolecular hydrogen bond.

Table S3. ωb97xd/6-311++G** energy (Hartree) within the PCM method (Solvent=2-pentanone)

TFO-TBA	-1647.631026

FUMARIC ACID

Monomer	-455.7435578
Dimer (Fig. 3a)	-911.5061604
Dimer (Fig. 3b)	-911.4943210
Tetramer (Fig. S3b)	-1823.010013
Hexamer (Fig. S3c)	-2734.529433
Octamer (Fig. S3d)	-3646.048922

TFO+FUMARIC ACID

FUM Monomer (Fig. S4a)	-1417.381723
FUM dimer (Fig. 3c)	-1873.145459
FUM dimer (Fig. 3d)	-1873.139423
FUM trimer (Fig. S4b)	-2328.909086

TBA+TFO+FUMARIC ACID

FUM dimer (Fig. 3e)	-2559.158832
FUM dimer (Fig. 3f)	-2559.157773

MALEIC ACID

Monomer	-455.7407504
Dimer	-911.4939478
Trimer (Fig. 4a)	-1367.247728
Hexamer (Fig. 4b)	-2734.512966
Nonamer (Fig. 4c)	-4101.776939

TFO+MALEIC ACID

MAL monomer (Fig. S5a)	-1417.382338
MAL dimer (Fig. 4d)	-1873.136283
MAL trimer (Fig. S5b)	-2328.890207

TBA+TFO+MALEIC ACID

MAL dimer (Fig. 4e)	-2559.154911

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