Supplementary materials:

The geometry optimization of monomer and dimer in two different configurations (with S-H---O interaction and with S---O interaction) is carried using B3LYP functional with 6-311 G(d, p). Thus, on the basis of DFT calculation (calculated energy and H-bond length), it is concluded that monomer and dimer with S---O interaction is more possible than with S-H---O interaction. Further, DFT calculation of monomer and dimer with S---O interaction is done using the basis set 6-311++G(d, p) as shown in Fig. S1 (V).

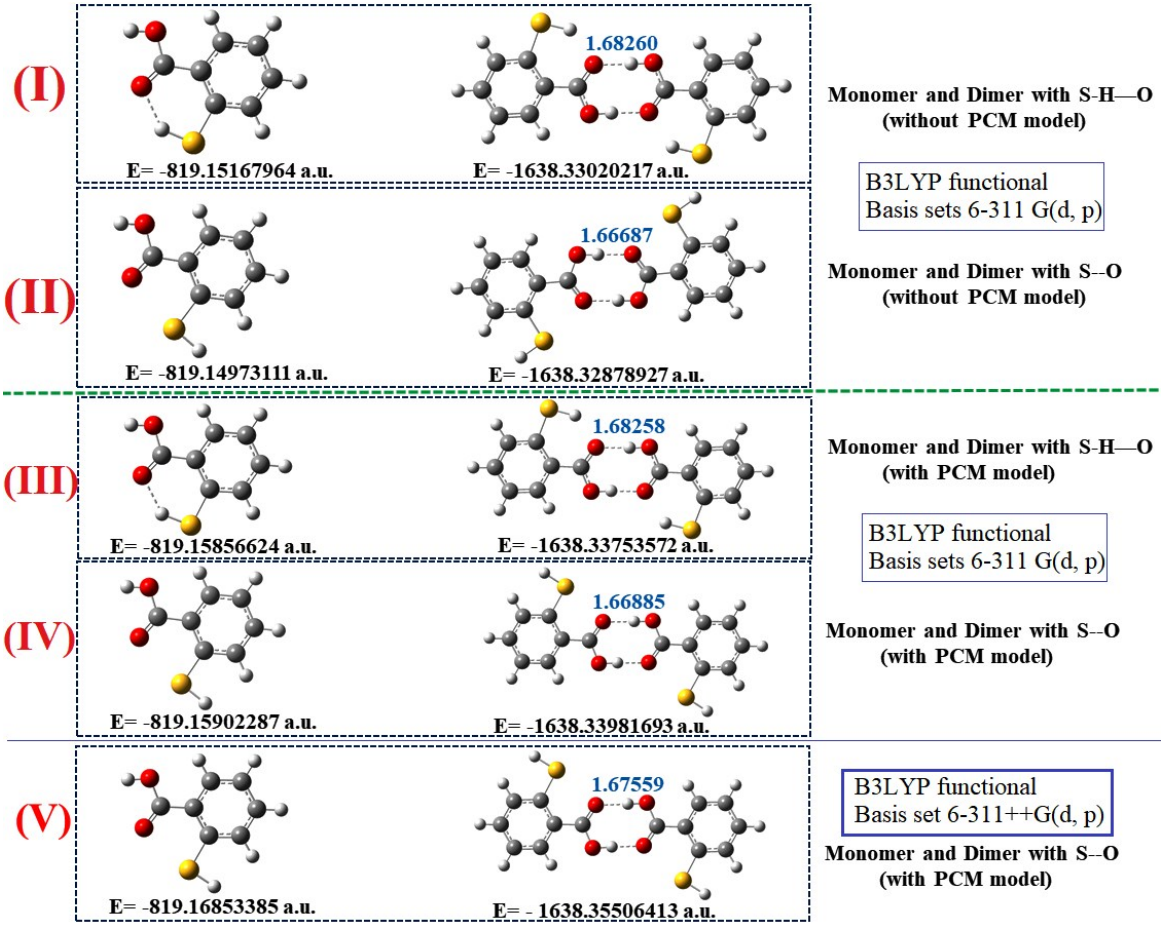

FIG. S1. Optimized geometry and corresponding energy of monomer and dimer calculated by DFT method.

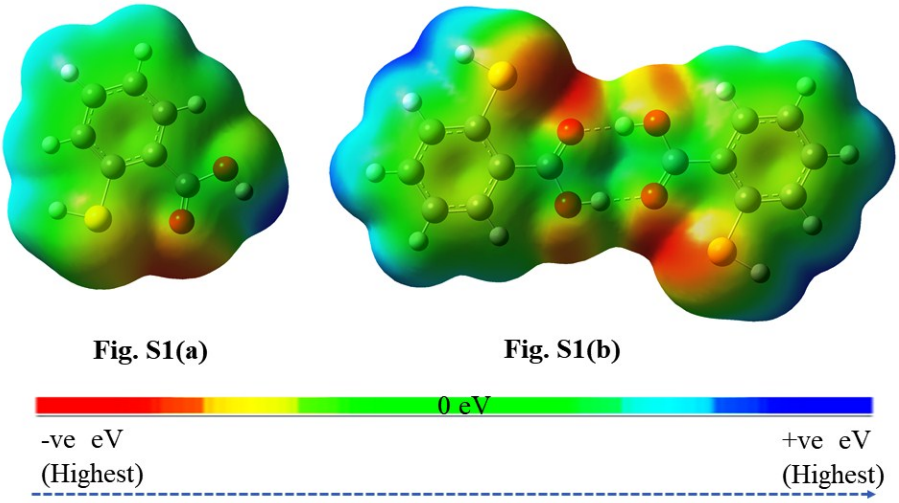

FIG. S2. DFT calculated MEP surface of (a) 2-MBA monomer, (b) self-associated 2-MBA dimer, depicting the adsorption sites.

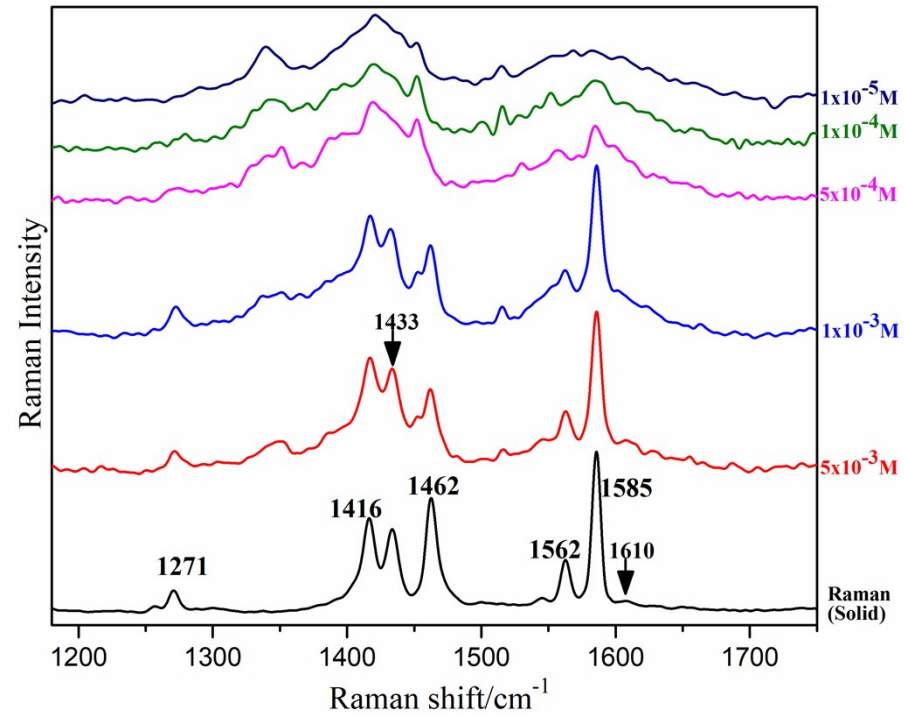

FIG. S3. Normal Raman and SERS spectra of 2-MBA in region 1180- 1750 cm^{-1}.

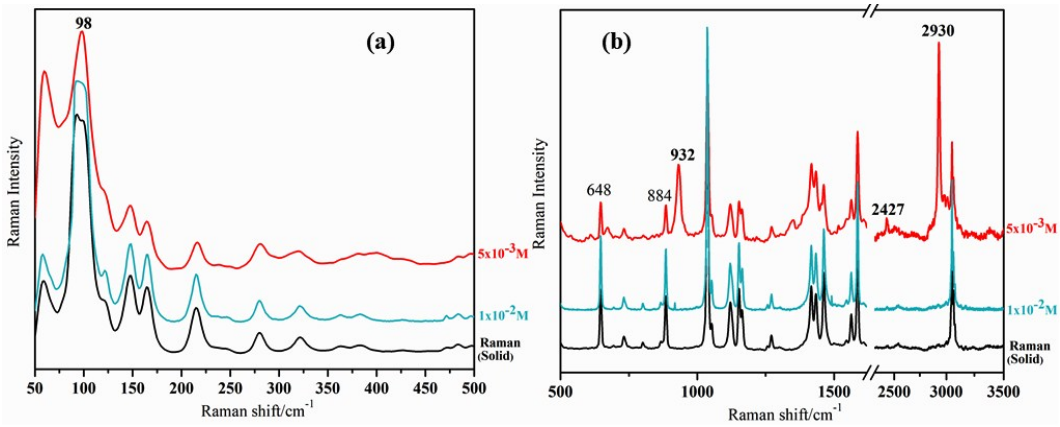

FIG. S4. Normal Raman and SERS spectra of 2-MBA at 0.01 M (a) region 50- 500 cm^{-1} and (b) region 500- 3500 cm^{-1}.

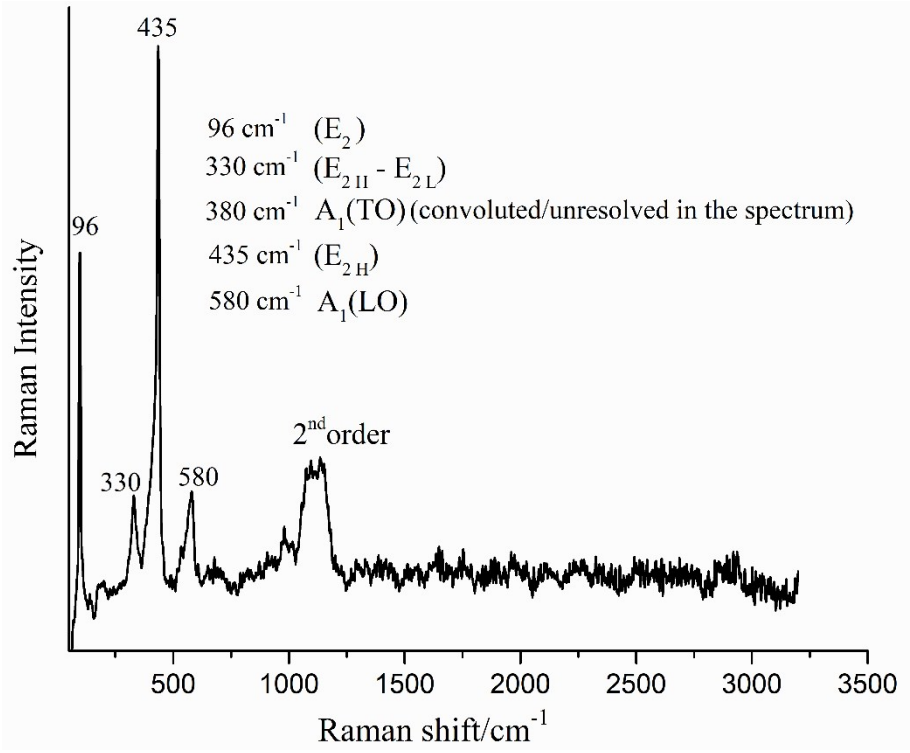

FIG. S5. Raman spectrum of bare ZnO nanoparticles

TABLE S1. (Raman/SERS bands including with bands described in TABLE 1.)

Observed normal Raman and SERS bands and their corresponding assignment for 2MBA monomer (MN) and dimer (DM) with the help of DFT calculations using B3LYP functional and 6-311++G(d, p) basis set and earlier reported literature [34-38]. The symmetry label of modes of 2-MBA monomer and dimer molecules are assigned on the basis of group theory and DFT calculation.

Raman (2-MBA: MN)	**SERS**	**Symmetry***	**Vibrational Assignments Monomer**	**Vibrational Assignments Dimer**
3064 (A')	3064	A_g	ν(C-H)	ν(C-H)
3051 (A')	3051	A_g	ν(C-H)	ν(C-H)
	2930	A_g		ν(O-H---O); symmetric mode of H-bonded carboxyl ring
	2427	A_g		ν(S-H)
1585 (A')	1585	B_u	ν(CC); asymmetric	ν(CC); asymmetric
1562 (A')	1562	A_g	ν(CC); symmetric	ν(CC); symmetric
1462 (A')	1462	A_g	ν_{asym}(CC) + δ(C-H)	ν_{asym}(CC) + δ(C-H)
1433 (A')	1433	B_u	ν_{sym}(CC) + δ(C-H)	ν_{sym}(CC) + δ(C-H)
1416 (A')	1416	A_g	ν(CC)+ δ(C-H)+ δ(O-H)	ν(CC)+ δ(C-H)+ δ(O-H)
	1347	B_u		asymmetric ring stretching +δ(O-H)$_{carboxyl\ ring}$
1271 (A')	1271	A_g	δ(O-H) + δ(C-H) + ν(CC)	δ(O-H) + δ(C-H) + ν(CC)
1164 (A')	1164	A_g	δ(C-H)	δ(C-H)
1152 (A')	1152	A_g	δ(C-H) + ν(CC)	δ(C-H) + ν(CC)
1120 (A')	1120	A_g	δ(CCC)+ ν(C-S) + ν(C-OH)	δ(CCC)+ ν(C-S) + ν(C-OH)
1053 (A')	1053	A_g	asymmetric ring breathing mode	asymmetric ring breathing mode
1037 (A')	1037	A_g	symmetric ring breathing mode	symmetric ring breathing mode
	932	A_u		γ(O-H); symmetric mode of H-bonded carboxyl ring
884 (A")	884	B_g	ω(C-H)	ω(C-H)
731 (A")	731	B_g	ω(C-H)	ω(C-H)
	672	A_g	δ_{sym}(COOH)+δ(CCC)+ ν(C-S)	δ_{sym}(COOH)+δ(CCC)+ ν(C-S)
648 (A')	648	---	γ(O-H)	
496 (A")	498	B_g	γ(CCC); asymmetric	γ(CCC); asymmetric
	398	A_u		γ(S-H); symmetric
384 (A")	380	B_g	γ(S-H)	γ(S-H); asymmetric
322 (A')	322	A_g	δ(CCC)$_{bz\ ring}$ + δ(CC=O)	δ(CCC)$_{bz\ ring}$ + δ(CC=O)
280 (A')	280	A_g	δ(HSPh-COOH) + δ(CCS)	δ(HSPh-COOH) + δ(CCS)
216 (A")	216	B_g	δ(HSPh-COOH)	
165 (A')	164	A_u	γ(HSPh-COOH); symmetric	
147 (A')	147	B_g	τ(HSPh-COOH)	τ(HSPh-COOH); symmetric
	139	A_u		τ(HSPh-COOH); asymmetric
122 (A")	125	A_u	γ(HSPh-COOH); asymmetric	γ(HSPh-COOH); asymmetric
	110	A_g		shear dimer stretching
100 (A')	98	A_g	t(-SH) + t(-COOH)	t(-SH) + t(-COOH)
92 (A')			t(-SH)	
	90	A_g		shear dimer in-plane bending
58 (A")	59 →64	B_g	t(-COOH) + t(-SH)	t(-COOH) + t(-SH)

v: stretching, δ: in-plane bending, γ: out-of-plane bending, *τ*: torsion, ω: wagging, t: twisting, HSPh: 2mercaptophenyl, sym: symmetric, asym: asymmetric, bz: benzene, {(MN)/(DM)}: representation of symmetry species of monomer (MN) and dimer (DM), Symmetry*: symmetry label of corresponding Raman modes of dimer

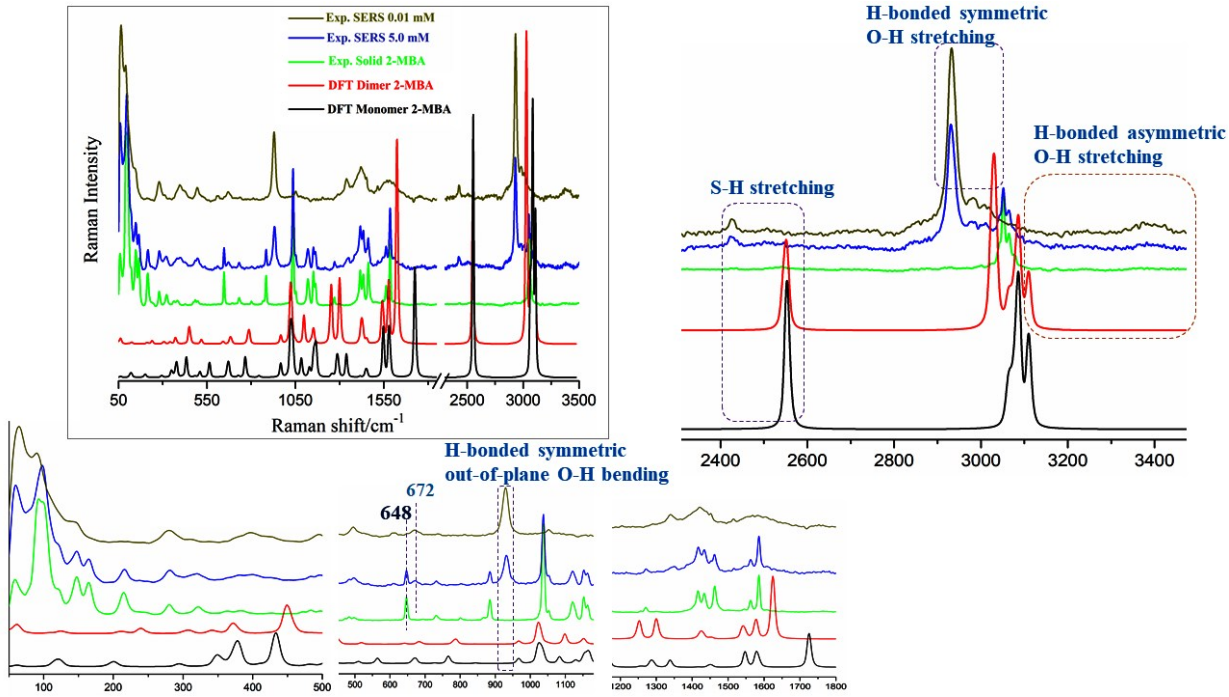

FIG. S6. Experimental Raman/SERS spectra of 2-MBA and DFT calculated Raman spectra of monomer and dimer (The spectra is further splited into four sections for precise analysis)