Supplementary material

Study on depolymerization kinetics of formic acid dimers in binary mixture

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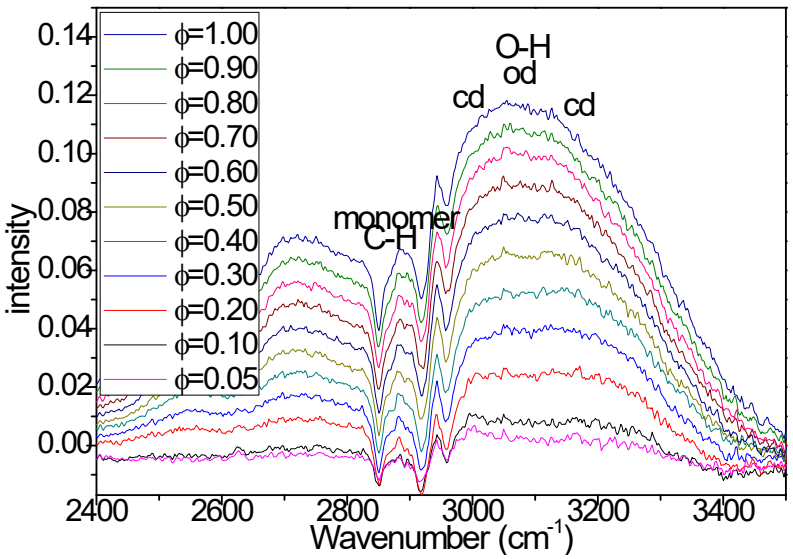

Fig S1 High resolution infrared spectroscopy of $\nu_{O\text{-}H}$ and $\nu_{O\text{-}H}$ (2400-3500cm^{-1}) in FA/CH_3CN binary system at different volume fraction

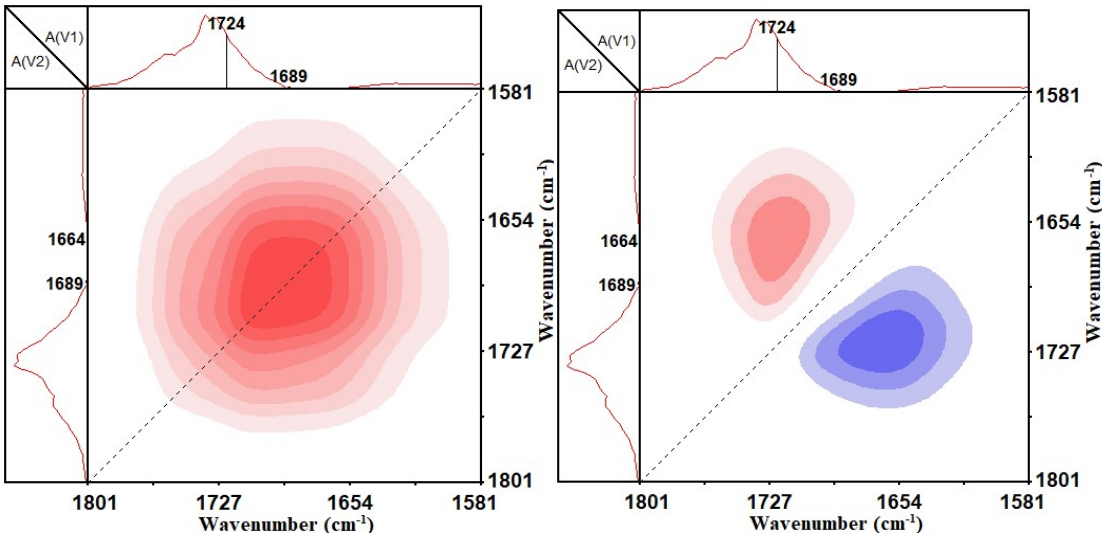

Fig S2 2-D IR of FA/CH_3CN binary system at different volume fraction

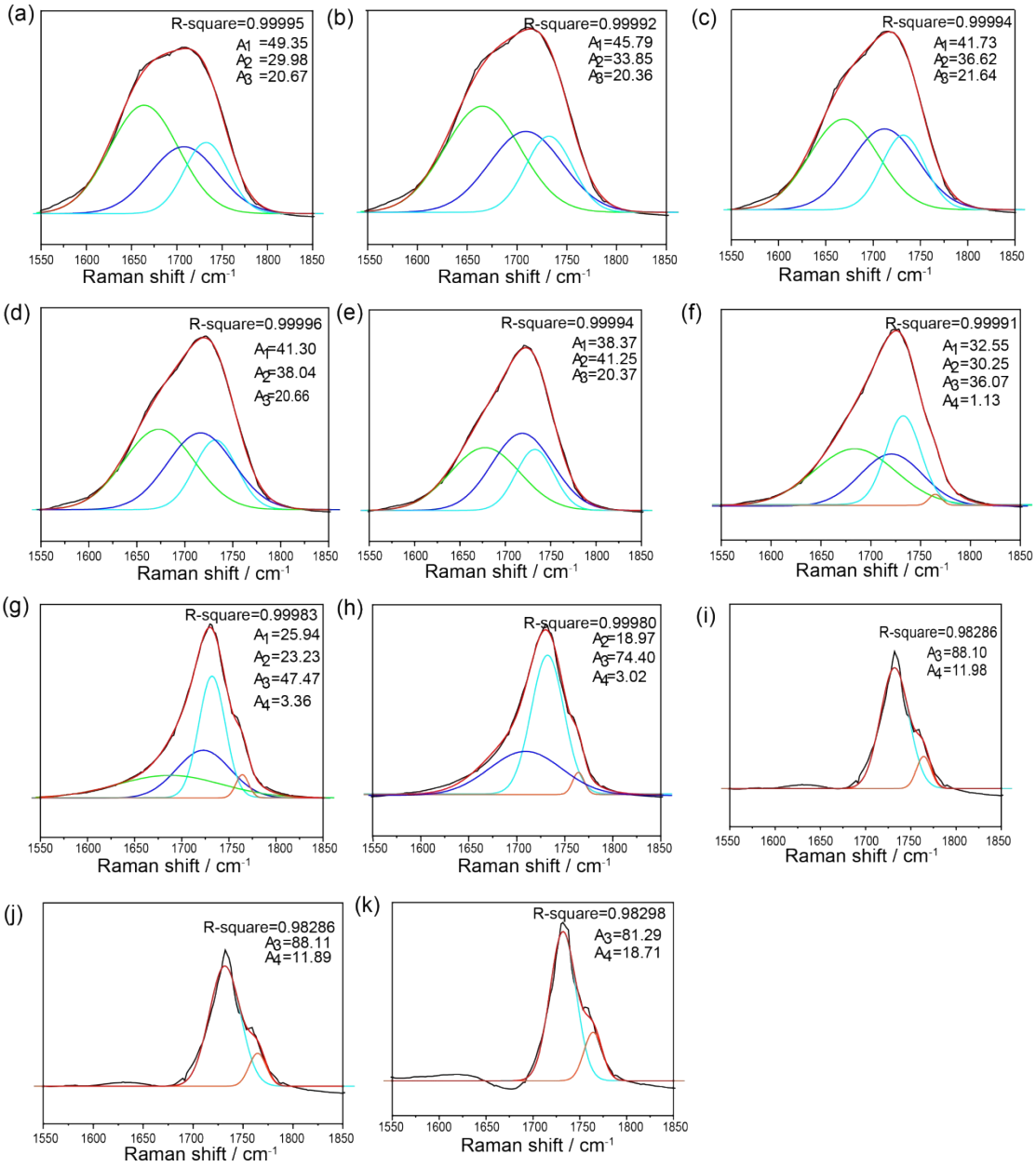

Fig S3 Band fitting for infrared spectroscopy of $\nu_{C=O}$ (1540-1830cm^{-1}) in FA/CH_3CN binary mixture at different volume fraction

Table S1 The comparison of DFT (B3LYP-D3/6-311G (d,p)) calculated vibrational frequencies, depolarization ratio of FA-CH_3CN, solvate FA monomer and FA dimer.

Computed/cm^{-1}							
modes	FA_{dimer}		$FA_{(PCM)}$		$FA\text{-}CH_3CN_{(PCM)}$		Description
	Freq.	ρ	Freq.	ρ	Freq.	ρ	
ν_1	3207/3086	0.47/0.31	3724	0.29	3388	0.32	ν_{O-H}
ν_2	3065/3058	0.29/0.49	3062	0.27	3133/3133 /3057/2984	0.75/0.75/ 0.01/0.24	ν_{C-H}
ν_3					2379	0.29	$\nu_{N\equiv C}$
ν_4	**1789/1714**	**0.73/0.11**	**1794**	**0.34**	**1809**	**0.28**	**$\nu_{C=O}$**
ν_5	1494/1457	0.39/0.58	1311	0.71	1391	0.68	β_{H-O-C}
ν_6					1454/1454/1403	0.75/0.75/0.64	β_{H-C-H}
ν_7	1407/1406	0.74/0.75	1417	0.59	1430	0.56	β_{H-C-O}
ν_8	1269/1267	0.20/0.21	1129	0.18	1184	0.39	ν_{O-C}
ν_9	1107/1082	0.26/0.75	1067	0.75			$\tau_{H-C-O-H}$
ν_{10}					1066	0.75	$\tau_{H-C-O-N}$
ν_{11}					1059	0.74	$\gamma_{C-H-C-H}$
ν_{12}					1058	0.74	$\tau_{H--C-C\equiv N}$
ν_{13}	1003/983	0.73/0.75	684	0.75			$\tau_{H-O-C-O}$
ν_{14}					939	0.14	ν_{C-C}
ν_{15}					833	0.75	$\tau_{C-O-H-N}$
ν_{16}	725/694	0.67/0.66	630	0.58	699	0.53	β_{O-C-O}
ν_{17}					404/402/ 99/43/ 29/15	0.75/0.75/ 0.75/0.75/ 0.75/0.75	$\tau_{H-N\equiv C-C}$
ν_{18}	287	0.75					β_{O-H-O}
ν_{19}	277/77	0.75/0.75					$\tau_{O-C-O-H}$
ν_{20}	216	0.12					ν_{O-H}
ν_{21}	187	0.74					$\tau_{C-O-H-O}$
ν_{22}					184	0.71	ν_{N-H}
ν_{23}	178	0.7					β_{C-O-H}
ν_{24}					134	0.75	$\tau_{O-C-O-N}$
ZPE (kJ/mol)	CH_3CN HF=-348567.44		FA_{dimer} HF=-996658.86		$FA_{(PCM)}$ HF=-498307.99	$FA\text{-}CH_3CN_{(PCM)}$ HF=-846893.58	
Remarks	ν,β,τ,γ refer the stretching vibration,bending vibration, twisting vibration and out-of-plane bending vibration respectively.ρ:depolarization ratio						

Table S2 The comparison of DFT (B3LYP-D3/6-311G (d,p)) calculated vibrational frequencies, depolarization ratio and ZPE energy of cd and od.

Computed/cm^{-1}					
modes	FA_{cd}		FA_{od}		Description
	Freq.	ρ	Freq.	ρ	
ν_1	**3207/3086**	**0.47/0.31**	**3729/3372**	**0.29/0.31**	**ν_{O-H}**
ν_2	3065/3058	0.29/0.49	3113/3030	0.21/0.29	ν_{C-H}
ν_3	**1789/1714**	**0.73/0.11**	**1807/1761**	**0.54/0.17**	**$\nu_{O=C}$**
ν_4	1494/1457	0.39/0.58	1449/1408	0.52/0.75	β_{H-O-C}
ν_5	1407/1406	0.74/0.75	1386/1336	0.76/0.49	β_{H-C-O}
ν_6	1269/1267	0.2/0.21	1218/1165	0.22/0.26	ν_{O-C}
	1107/1082	0.26/0.75	1107/1074	0.75/0.75	$\tau_{H-C-O-H}$
ν_7	1003/983	0.73/0.75	992/723	0.75/0.75	$\tau_{H-O-C=O}$
ν_8	725/694	0.67/0.66	688/653	0.62/0.61	β_{O-C-O}
ν_9	287	0.75	156	0.44	β_{O-H-O}
ν_{10}	277/77	0.75/0.75	215/67	0.75/0.75	$\tau_{O-C-O-H}$
ν_{11}	216	0.12	199	0.67	ν_{O-H}
ν_{12}	187	0.74	117	0.75	$\tau_{C-O-H-O}$
ν_{13}	178	0.7	126	0.66	β_{C-O-H}
ZPE energy (kJ/mol)	FA_{cd} HF=-996658.86		FA_{od} HF=-996628.05		
Remarks	ν,β,τ,γ refer the stretching vibration,bending vibration, twisting vibration and out-of-plane bending vibration respectively.ρ:depolarization ratio				

Table S3 The comparison of DFT (B3LYP-D3/6-311G (d,p)) calculated vibrational frequencies, depolarization ratio and ZPE of FA_{dimer}、FA_{dimer}-CH_3OH_{dimer}、FA-$CH_3OH_{(PCM)}$ and $FA_{(PCM)}$

mode	Computed/cm^{-1}								Description
	FA_{dimer}		FA_{dimer}-CH_3OH_{dimer}		FA-$CH_3OH_{(PCM)}$		$FA_{(PCM)}$		
s	Freq.	ρ	Freq.	ρ	Freq.	ρ	Freq.	ρ	
ν_1	3207/ 3086	0.47/ 0.31	3509/ 3464	0.32/ 0.25	3829/ 3127	0.26/ 0.29	3724	0.29	ν_{O-H}
ν_2	3065/ 3058	0.29/ 0.49	3117/3113/ 3088/3078/ 3043/3041/ 3022/3019/	0.65/0.67/ 0.74/0.74/ 0.68/0.20/ 0.04/0.04	3148/ 3088/ 3027/ 3019	0.59/ 0.74/ 0.12/ 0.73	3062	0.27	ν_{C-H}
ν_3			2907/2850	0.48/0.28					ν_{O-H}
ν_4	**1789 /1714**	**0.73/ 0.11**	**1771/1743**	**0.54/0.1**	**1762**	**0.16**	**1795**	**0.34**	**$\nu_{C=O}$**
ν_5	1494/ 1457	0.39/ 0.58					1311	0.71	β_{H-O-C}
ν_6			1530/1526/ 1511/1499/ 1493/1488/ 1482	0.68/0.74/ 0.60/0.66/ 0.75/0.75/ 0.72	1502/ 1493	0.72/ 0.73			β_{H-C-H}
ν_7			1477	0.74	1483	0.56			$\tau_{H-C-H-O}$
ν_8	1407/ 1406	0.74/ 0.75	1415/1409/ 1183/1178/ 1152/1124	0.70/0.68/ 0.75/0.74/ 0.73/0.63	1407	0.66	1417	0.59	β_{H-C-O}
ν_9			1464/1441	0.75/0.66	1468	0.75			β_{C-O-H}
ν_{10}	1269 /1267	0.20/ 0.21	1281/1277/ 1056/1047	0.57/0.30/ 0.34/0.22	1216/ 1017	0.48/ 0.32	1129	0.18	ν_{O-C}
ν_{11}			1219/151	0.73/0.68					$\tau_{C-O-H-O}$
ν_{12}	1107 /1082	0.26/ 0.75			1175/ 1084/ 1078	0.75/ 0.51/ 0.46	1067	0.75	$\tau_{H-C-O-H}$
ν_{13}			1106	0.56					$\tau_{O-H-O-O}$
ν_{14}			1064	0.45					$\nu_{O-C}+\tau_{H-C-O-O}$
ν_{15}	1003/ 983	0.73/ 0.75					684	0.75	$\tau_{H-O-C-O}$
ν_{16}			765/118/28	0.22/0.73/ 0.75	1365/ 390	0.73/ 0.74			β_{H-O-H}
ν_{17}			710/705	0.67/0.59	701	0.49			β_{O-C-O}
ν_{18}	725/ 694	0.67/ 0.66					630	0.58	β_{O-C-O}
ν_{19}	287	0.75	226/97	0.74/0.69					β_{O-H-O}
ν_{20}	277/77	0.75/	1032/67	0.29/0.73	958/209	0.69/			$\tau_{O-C-O-H}$

		0.75				0.74		
ν_{21}	216	0.12	369/335/178	0.69/0.65/0.75	256/168/118	0.75/0.68/0.75		ν_{O-H}
ν_{22}	187	0.74	827/475	0.74/0.75				$\tau_{C-O-H-O}$
ν_{23}			255	0.75				$\tau_{H-C-O-O}$
ν_{24}			246	0.75				$\tau_{H-C-O-H}$
ν_{25}	178	0.7	125/112/76	0.73/0.70/0.74				β_{C-O-H}
ν_{26}			137/92	0.75/0.70	107/27	0.75/0.75		$\tau_{H-C-H-O}$
ν_{27}			32	0.75				$\tau_{O-H-O-C}$
ZPE energy (KJ/mol)	CH_3OH HF=-303786.83	FA_{dimer} HF=-996658.86		FA_{dimer}-CH_3OH_{dimer} HF=-1604359.68		FA-$CH_3OH_{(PCM)}$ HF=-802158.67	$FA_{(PCM)}$ HF=-498307.91	
Remarks	ν,β,τ,γ refer the stretching vibration,bending vibration, twisting vibration and out-of-plane bending vibration respectively.ρ:depolarization ratio							

Table S4 The comparison of DFT (B3LYP-D3/6-311G (d,p)) calculated vibrational frequencies, depolarization ratio of cd and od

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	1107/1082	0.26/0.75	1107/1074	0.75/0.75	$\tau_{H-C-O-H}$
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