Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

A Theoretical Perspective of the Structure and Thermodynamics of Secondary Organic Aerosols from Toluene: Molecular Hierarchical Synergistic Effects

Table S1 Compositions of the mimicked systems.

System	N_{C7H6O2}	N_{C7H6O}	N_{C3H4O3}	N_{H2SO4}	N_{H2O}	N_{N2}	N_{O2}	$N_{H2SO4/H2O}$	T
#01	50	205	218	46	114	900	240	0.4	
#02	50	205	218	37	123	900	240	0.3	
#03	50	205	218	27	133	900	240	0.2	
#04	50	205	218	15	145	900	240	0.1	
#05	50	205	0	40	120	900	240	0.33	
#06	0	205	218	40	120	900	240	0.33	298K
#07	50	0	218	40	120	900	240	0.33	
#08	50	205	218	40	120	900	240	0.33	
#09	39	196	238	40	120	900	240	0.33	
#10	33	200	240	40	120	900	240	0.33	
#11	25	233	215	40	120	900	240	0.33	
#12	50	205	218	40	120	900	240	0.33	273K
#13	50	205	218	40	120	900	240	0.33	283K
#14	50	205	218	40	120	900	240	0.33	293K
#15	50	205	218	40	120	900	240	0.33	303K
#16	50	205	218	40	120	900	240	0.33	313K
#17	50	205	218	40	120	900	240	0.33	323K

The molar ratios of organics, including benzaldehyde, benzoic acid, and pyruvic acid, are provided from the mimicked chamber experiments reported by Qi *et al.*[S1].

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Table S2. Gibbs free energy (G) of single molecules and dimers calculated at M06-2X/6-311+G(3df,3pd) level.

Dimer	*G* (Hartree)
$C_7H_6O_2$	-420.710
C_7H_6O	-345.461
$C_3H_4O_3$	-342.353
H_2O	-700.277
H_2SO_4	-76.423
H_2SO_4-H_2O	-776.705
H_2SO_4-$C_3H_4O_3$	-1042.642
H_2SO_4-$C_7H_6O_2$	-1120.992
H_2SO_4-C_7H_6O	-1045.743
H_2O-$C_3H_4O_3$	-418.778
H_2O-$C_7H_6O_2$	-497.129
H_2O-C_7H_6O	-421.878
$C_3H_4O_3$-$C_7H_6O_2$	-763.063
$C_3H_4O_3$-C_7H_6O	-687.815
$C_7H_6O_2$-C_7H_6O	-766.168

Table S3. Molecular compositions of mimicked systems for multicomponent SOA phase diagram.

System	N C7H6O2	N C7H6O	N C3H4O3	N H2SO4	N H2O	N N2	N O2	N H2SO4/H2O	N HBs	E (KJ/mol)	Life (ps)
#01	0	0	500	40	120	900	240	0.33	734	-215.37	235.20
#02	0	50	450	40	120	900	240	0.33	684	-197.42	233.66
#03	0	100	400	40	120	900	240	0.33	636	-179.23	207.33
#04	0	150	350	40	120	900	240	0.33	595	-161.16	194.84
#05	0	200	300	40	120	900	240	0.33	550	-143.16	203.61
#06	0	250	250	40	120	900	240	0.33	504	-125.11	172.39
#07	0	300	200	40	120	900	240	0.33	452	-104.89	132.47
#08	0	350	150	40	120	900	240	0.33	413	-87.78	183.44
#09	0	400	100	40	120	900	240	0.33	376	-70.35	167.67
#10	0	450	50	40	120	900	240	0.33	331	-54.30	226.00
#11	0	500	0	40	120	900	240	0.33	281	-35.23	151.82
#12	50	0	450	40	120	900	240	0.33	723	-200.46	212.02
#13	50	50	400	40	120	900	240	0.33	686	-182.58	207.30
#14	50	100	350	40	120	900	240	0.33	636	-163.68	179.88
#15	50	150	300	40	120	900	240	0.33	579	-145.69	182.34
#16	50	200	250	40	120	900	240	0.33	554	-128.48	191.83
#17	50	250	200	40	120	900	240	0.33	501	-109.64	176.68
#18	50	300	150	40	120	900	240	0.33	461	-92.93	207.26
#19	50	350	100	40	120	900	240	0.33	402	-73.69	172.28
#20	50	400	50	40	120	900	240	0.33	366	-57.28	171.18
#21	50	450	0	40	120	900	240	0.33	314	-37.33	158.47
#22	100	0	400	40	120	900	240	0.33	721	-186.48	216.53
#23	100	50	350	40	120	900	240	0.33	670	-167.19	221.45
#24	100	100	300	40	120	900	240	0.33	628	-148.83	181.22
#25	100	150	250	40	120	900	240	0.33	582	-131.25	182.78
#26	100	200	200	40	120	900	240	0.33	536	-112.80	182.57
#27	100	250	150	40	120	900	240	0.33	497	-96.81	202.83
#28	100	300	100	40	120	900	240	0.33	445	-76.10	152.24
#29	100	350	50	40	120	900	240	0.33	400	-58.45	176.27
#30	100	400	0	40	120	900	240	0.33	350	-40.81	138.17
#31	150	0	350	40	120	900	240	0.33	706	-170.86	189.43
#32	150	50	300	40	120	900	240	0.33	657	-152.47	188.44
#33	150	100	250	40	120	900	240	0.33	632	-135.13	208.10
#34	150	150	200	40	120	900	240	0.33	587	-117.14	183.50
#35	150	200	150	40	120	900	240	0.33	548	-100.09	198.65

#36	150	250	100	40	120	900	240	0.33	482	-82.60	196.54
#37	150	300	50	40	120	900	240	0.33	435	-62.15	146.22
#38	150	350	0	40	120	900	240	0.33	395	-45.12	181.54
#39	200	0	300	40	120	900	240	0.33	701	-156.11	194.39
#40	200	50	250	40	120	900	240	0.33	648	-137.63	189.05
#41	200	100	200	40	120	900	240	0.33	631	-121.24	211.94
#42	200	150	150	40	120	900	240	0.33	566	-102.03	179.92
#43	200	200	100	40	120	900	240	0.33	514	-83.09	173.54
#44	200	250	50	40	120	900	240	0.33	472	-66.18	175.21
#45	200	300	0	40	120	900	240	0.33	433	-48.82	182.01
#46	250	0	250	40	120	900	240	0.33	682	-141.17	169.94
#47	250	50	200	40	120	900	240	0.33	648	-123.63	196.68
#48	250	100	150	40	120	900	240	0.33	600	-104.76	174.23
#49	250	150	100	40	120	900	240	0.33	569	-87.31	191.19
#50	250	200	50	40	120	900	240	0.33	513	-69.98	194.36
#51	250	250	0	40	120	900	240	0.33	468	-52.39	196.89
#52	300	0	200	40	120	900	240	0.33	685	-125.76	194.20
#53	300	50	150	40	120	900	240	0.33	648	-109.38	209.28
#54	300	100	100	40	120	900	240	0.33	589	-90.53	195.58
#55	300	150	50	40	120	900	240	0.33	559	-74.17	200.42
#56	300	200	0	40	120	900	240	0.33	495	-54.15	171.09
#57	350	0	150	40	120	900	240	0.33	677	-112.33	200.10
#58	350	50	100	40	120	900	240	0.33	624	-93.57	181.46
#59	350	100	50	40	120	900	240	0.33	568	-76.10	174.30
#60	350	150	0	40	120	900	240	0.33	526	-57.76	185.08
#61	400	0	100	40	120	900	240	0.33	670	-98.77	199.34
#62	400	50	50	40	120	900	240	0.33	610	-78.72	165.56
#63	400	100	0	40	120	900	240	0.33	573	-61.06	185.04
#64	450	0	50	40	120	900	240	0.33	646	-82.62	194.36
#65	450	50	0	40	120	900	240	0.33	596	-64.30	193.05
#66	500	0	0	40	120	900	240	0.33	621	-66.93	197.81

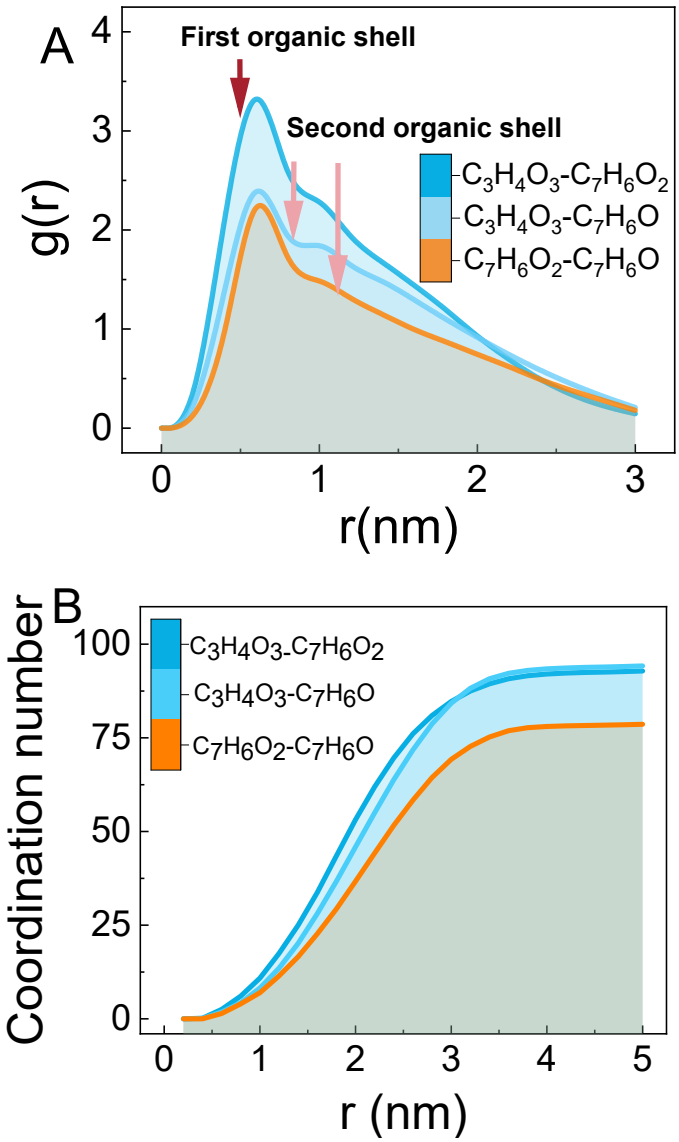


Figure S1. Hierarchical architecture characterization: (A) radial distribution function and (B) coordination number for different organics.

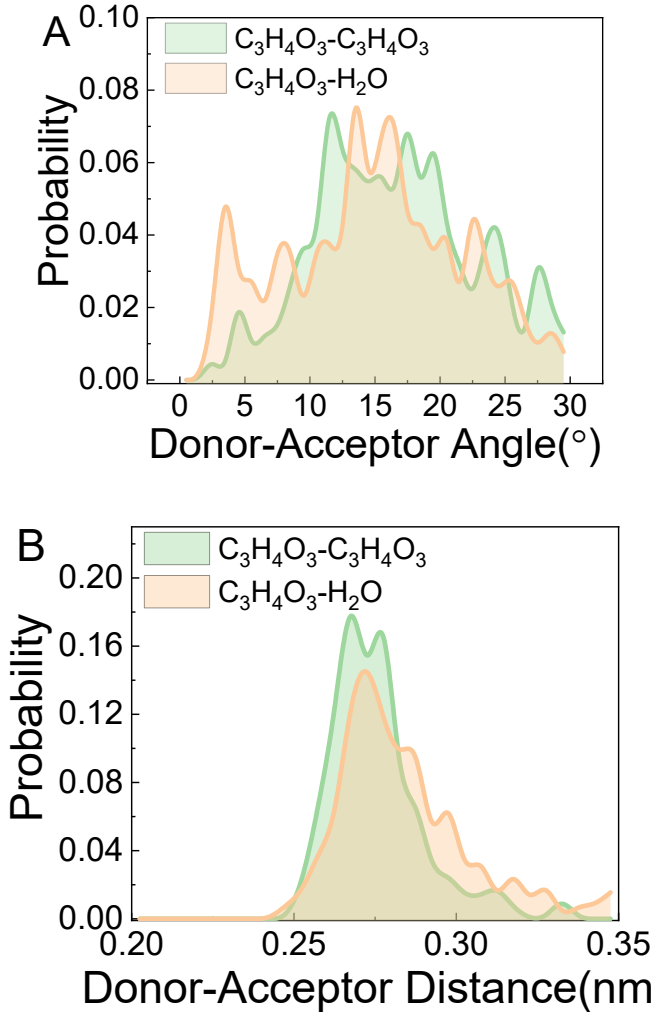


Figure S2. The probability distributions of angle and distance for donor-acceptor.

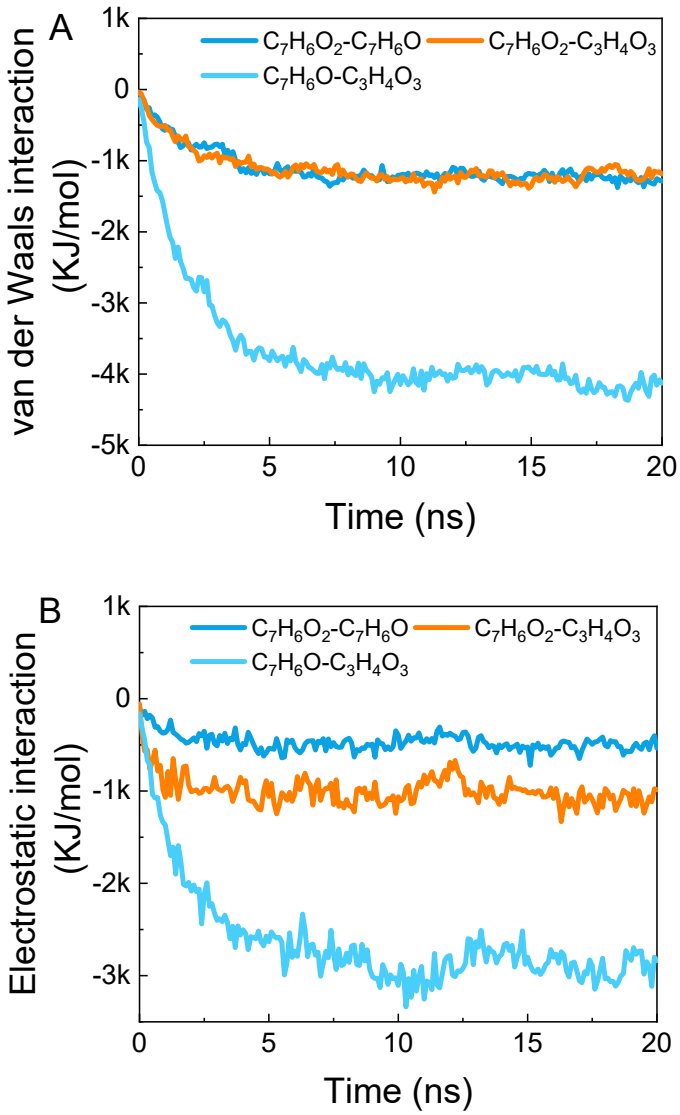


Figure S3. Intermolecular interactions: (A) van der Waals and (B) electrostatic energy profiles. The organic ratio of benzoic acid/benzaldehyde/PA is 1.0: 6.1: 7.3.

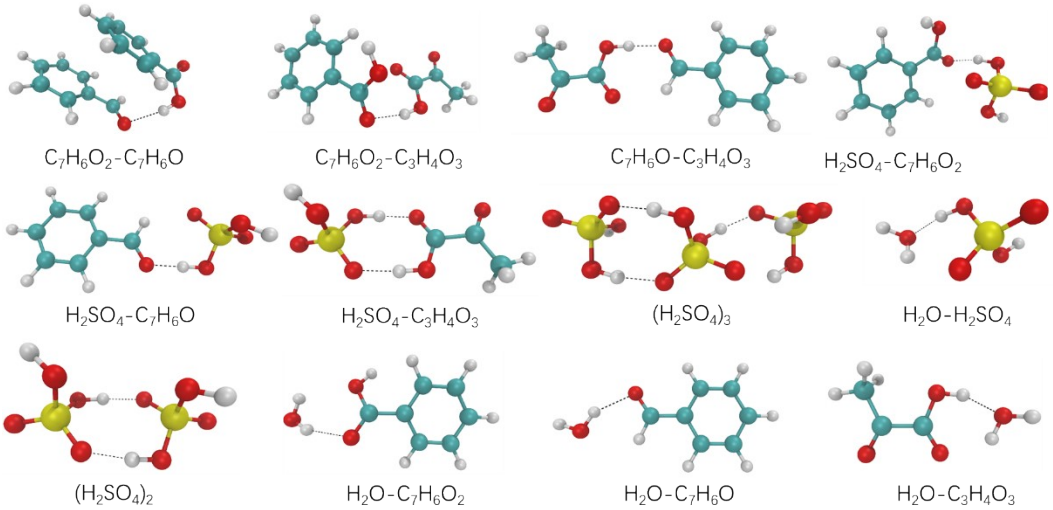


Figure S4. The binding configurations of intra-molecules, which are calculated by the DFT method at the M062X Def2qzvp level.

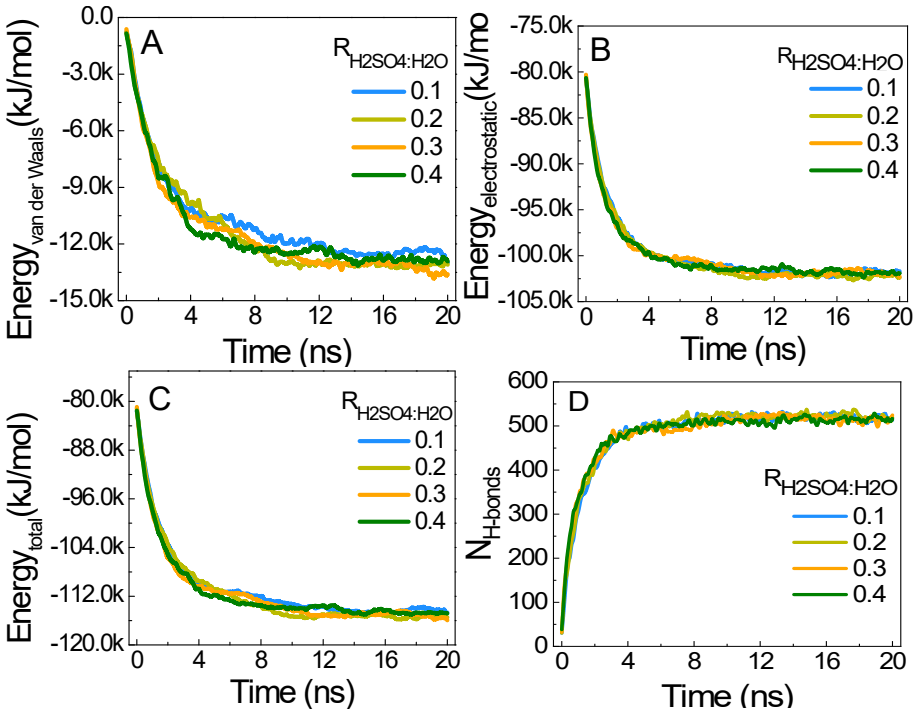
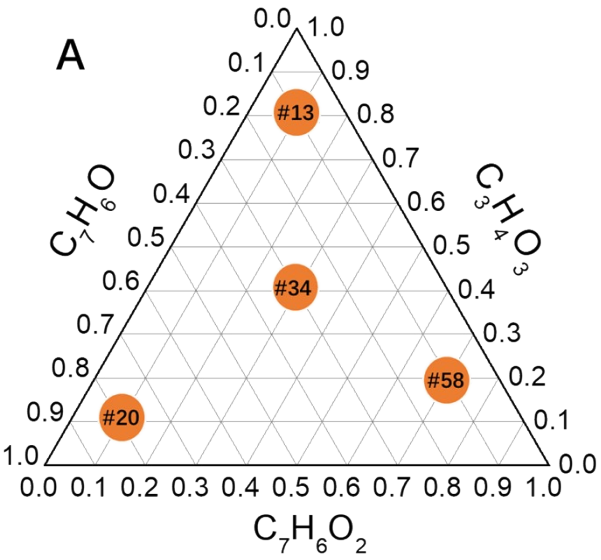
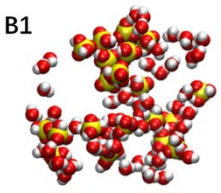
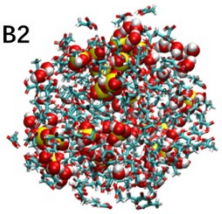


Figure S5. Thermodynamics analysis of atmospheric aerosol with different organic compositions: (A) Van der Waals interaction energy, (B) electrostatic interaction energy, (C) total energy, (D) number of hydrogen bonds.

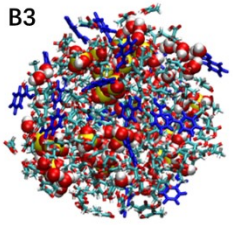




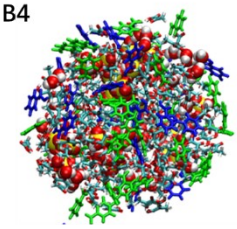
H_2SO_4-H_2O Cores



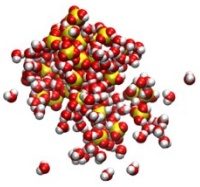
H_2SO_4-H_2O@$C_3H_4O_3$ Core-shell



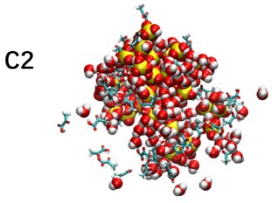
H_2SO_4-H_2O@$C_3H_4O_3$/$C_7H_6O_2$ Core-shell



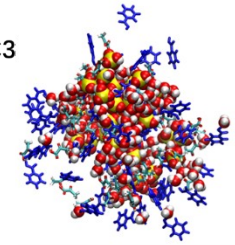
H_2SO_4-H_2O@$C_3H_4O_3$/ $C_7H_6O_2$/C_7H_6O Core-shell



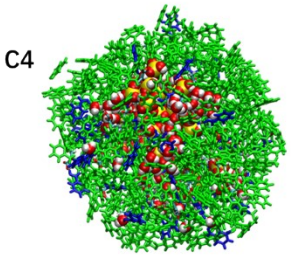
H_2SO_4-H_2O Cores



H_2SO_4-H_2O@$C_3H_4O_3$ Core-shell



H_2SO_4-H_2O@$C_3H_4O_3$/ $C_7H_6O_2$ Core-shell



H_2SO_4-H_2O@$C_3H_4O_3$/ $C_7H_6O_2$/C_7H_6O Core-shell

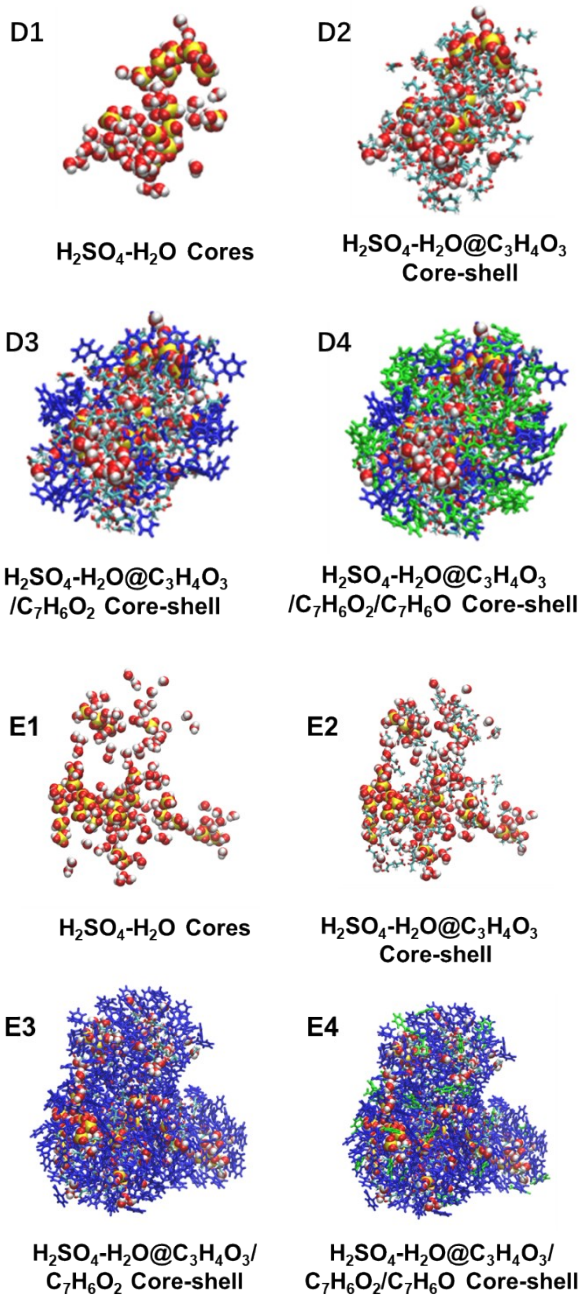
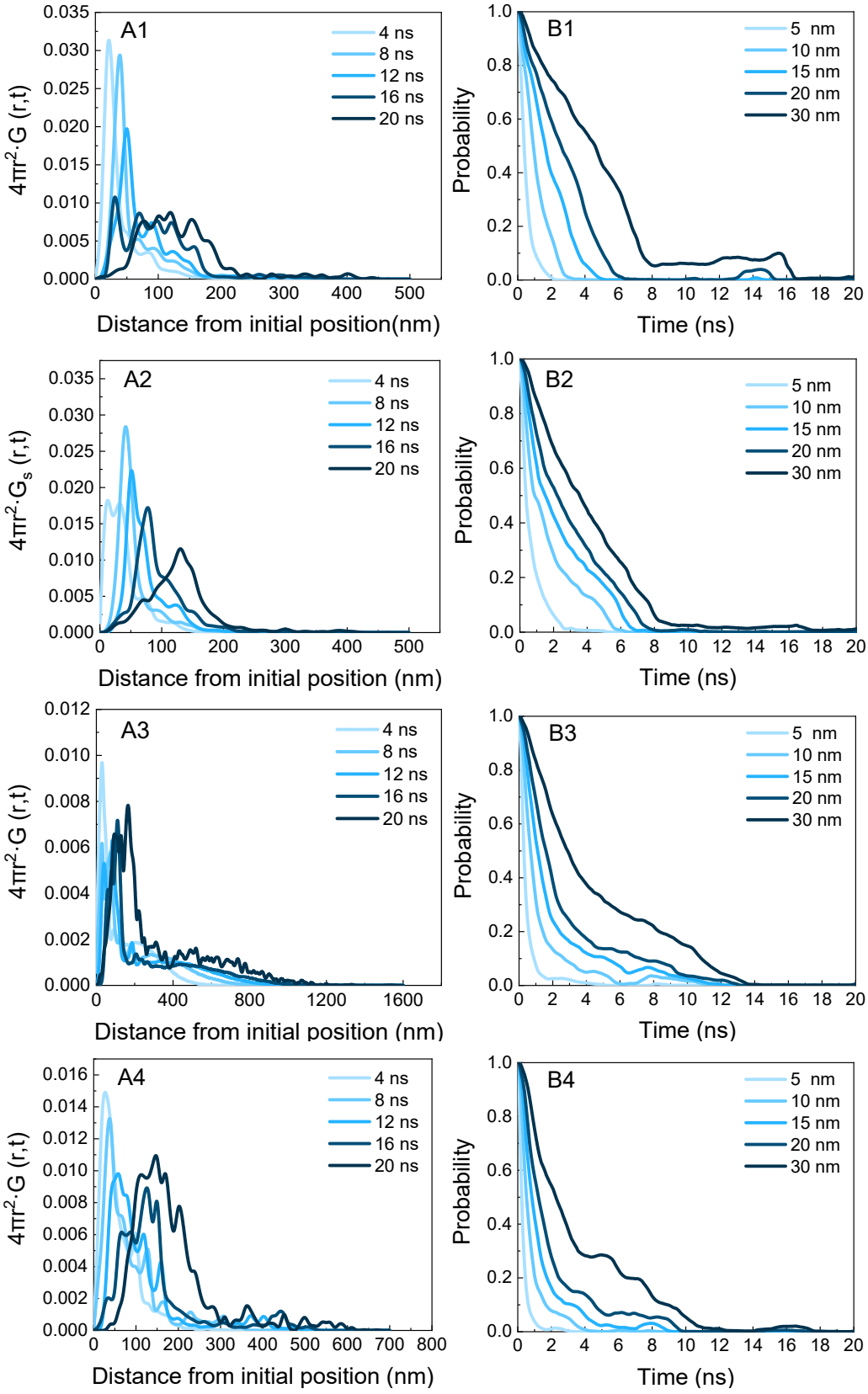


Figure S6. The Hierarchical internal structure of core-shelled nanoparticles under different organic ratios: (A) schematics of the phase diagram for a ternary organic mixture, The organic ratio of benzoic acid/benzaldehyde/PA is (B)1.0: 1.0: 8.0, (C) 1:8:2, (D) 3:3:4, (E) 7:1:2.


A1
4 ns
8 ns
12 ns
16 ns
20 ns
4πr²·G (r,t)
Distance from initial position(nm)
B1
5 nm
10 nm
15 nm
20 nm
30 nm
Probability
Time (ns)
A2
4πr²·Gs (r,t)
Distance from initial position (nm)
B2
A3
4πr²·G (r,t)
Distance from initial position (nm)
B3
A4
Distance from initial position (nm)
B4

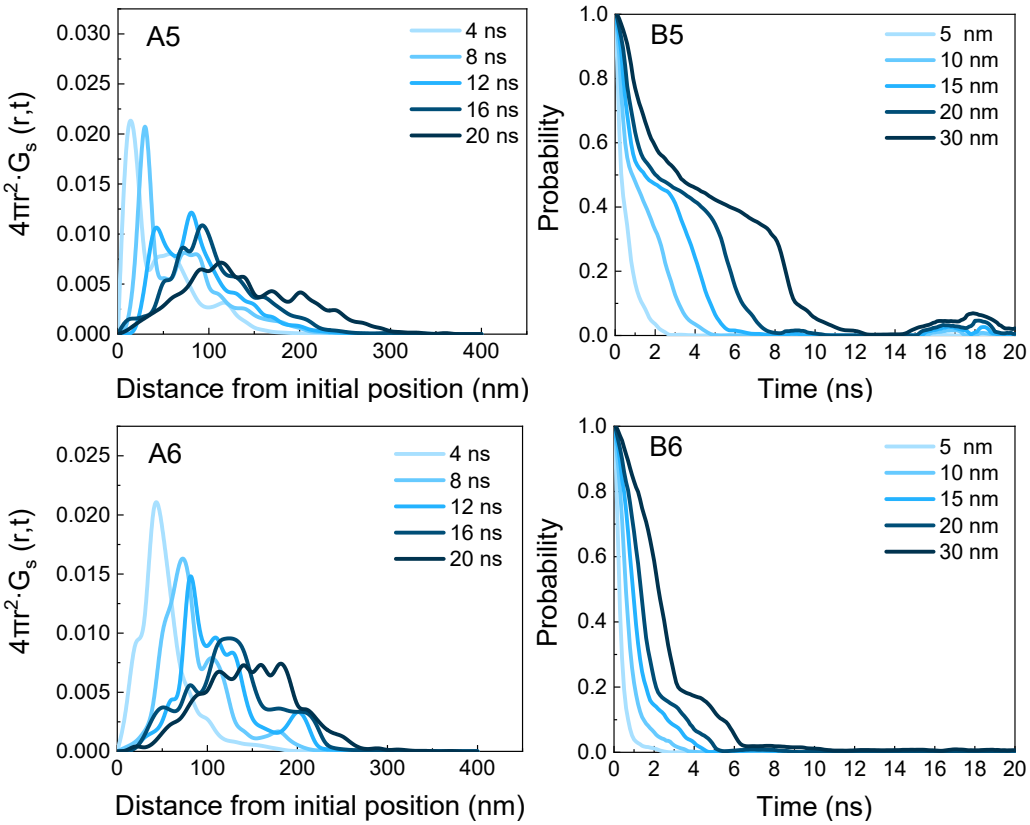


Figure S7. Migration and diffusion properties under different temperatures: (A1-A6) evolution of the probability of TSOA nanoparticles under different moving distances, and (B1-B6) van Hove function in terms of distance from the initial position under different simulation time. The simulated temperature increases from 273 to 323 K.

References

[S1] Wu, X. Cytotoxicity Studies on Main Components of Toluene Secondary Organic Aerosol. Master thesis, Harbin Institute of Technology, 2018.