Supplementary Information (SI) for Nanoscale.

Supplemental information for

Insight into the mechanism of different substituents on the zinc oxo cluster in the solubility switch

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KEYWORDS: Extreme Ultraviolet Lithography (EUVL), Zinc-oxo cluster, Reaction mechanism, Density Functional Theory (DFT)

Python code for calculation of RMSD:

```
from openbabel import openbabel
import glob

def calculate_rmsd(file1, file2):
    obConversion = openbabel.OBConversion()
    obConversion.SetInAndOutFormats("xyz", "xyz")

    mol1 = openbabel.OBMol()
    mol2 = openbabel.OBMol()

    obConversion.ReadFile(mol1, file1)
    obConversion.ReadFile(mol2, file2)

    aligner = openbabel.OBAlign(True, False)
    aligner.SetRefMol(mol1)
    aligner.SetTargetMol(mol2)
    if aligner.Align():
        rmsd = aligner.GetRMSD()
        return rmsd
    else:
        raise ValueError("Alignment failed.")

xyz_files = glob.glob("*tor.xyz")
file_list = [i.replace(".xyz","") for i in xyz_files]
print(file_list)
for i in file_list:
    file1 = i + ".xyz"
    file2 = "Zn_2-4p.xyz"

    try:
        rmsd_value = calculate_rmsd(file1, file2)
        print(f"The RMSD value between the two molecules is: {rmsd_value:.4f}")
        with open("rmsd.txt", "a") as f:
            f.write(i + "\n" + str(rmsd_value) + "\n")
    except Exception as e:
        print(f"An error occurred: {e}")
```

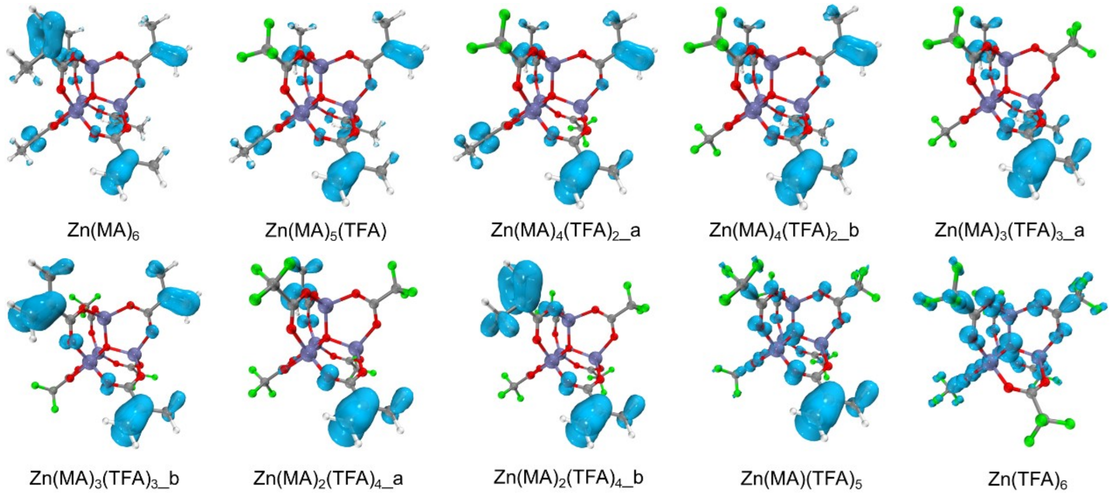
Obtaining the ionization potential (IP) using the following formula:

$$VIP = E_{N-1} - E_N$$

$$AIP = E_{N-1,\,opt} - E_N$$

where VIP and AIP represent vertical and adiabat ionization potential, respectively. E_N is the single point energy of neutral molecule. $E_{N-1,\,opt}$ and E_{N-1} are the single point energies of cations with and without optimization. The cation was obtained by removing an electron from the corresponding neutral molecule.

The spin density of all structures was calculated using Multiwfn software and shown in Fig. 1. The structures were derived from their corresponding neutral molecules with one electron removed, without further optimization. The organic ligand would lead to a significant difference in the ionization site, which is located on the carbon-carbon sigma bond in the TFA and terminal C=C bonds in MA ligands.



$Zn(MA)_6$ $Zn(MA)_5(TFA)$ $Zn(MA)_4(TFA)_2$_a $Zn(MA)_4(TFA)_2$_b $Zn(MA)_3(TFA)_3$_a

$Zn(MA)_3(TFA)_3$_b $Zn(MA)_2(TFA)_4$_a $Zn(MA)_2(TFA)_4$_b $Zn(MA)(TFA)_5$ $Zn(TFA)_6$

Fig. S1 Diagram of spin density for structure with different ligands after ionization. Isovalue = 0.002 a.u..

As depicted in Fig. 2, the geometry's deformation between after and before ionization can be evaluated using Root Mean Square Deviation (RMSD). $Zn(MA)_6$ has the lowest RMSD value of 0.03 Å, indicating that the ionization causes small deformation in this composition. However, geometry would be significantly different when a high percentage of trifluoromethyl ($-CF_3$) remains on the structure, suggesting that the structure after ionization is closely related to the type of organic ligands. The difference in structure before and after ionization would derive from the site of ionization changes.

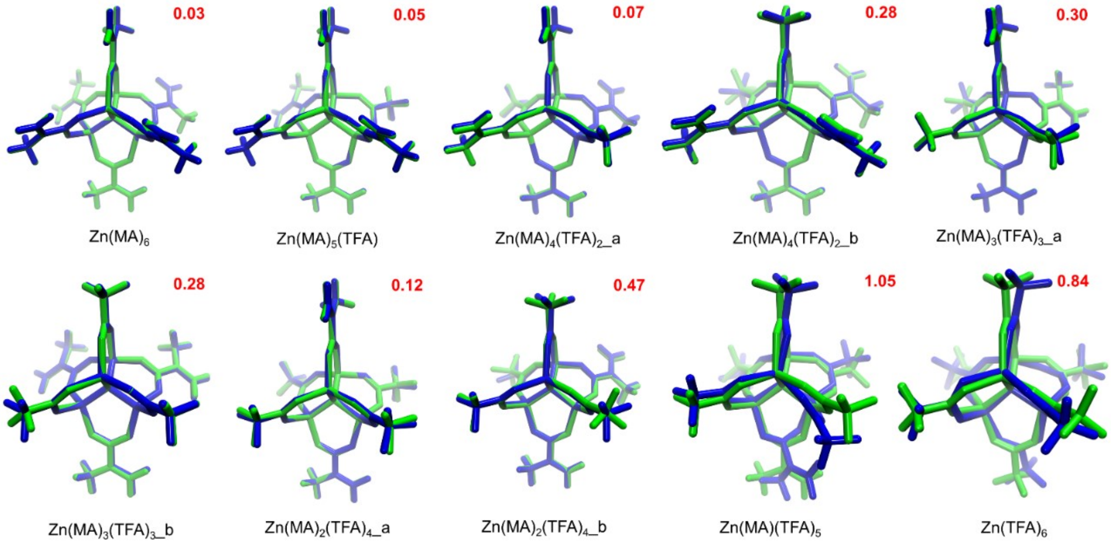


Fig. S2 The structural difference between relaxed and unrelaxed after ionization based on the structures with minimal energy. The green geometrical configuration represents unrelaxed structure. The relaxed configurations were labeled blue. The number (used red font) at the corner of each picture represents the corresponding RMSD value, and the unit is Å.

The different free radicals add to $Zn(MA)_3(TFA)_3$_a and $Zn(MA)_4(TFA)_2$_a to yield thermodynamically stable complexes.

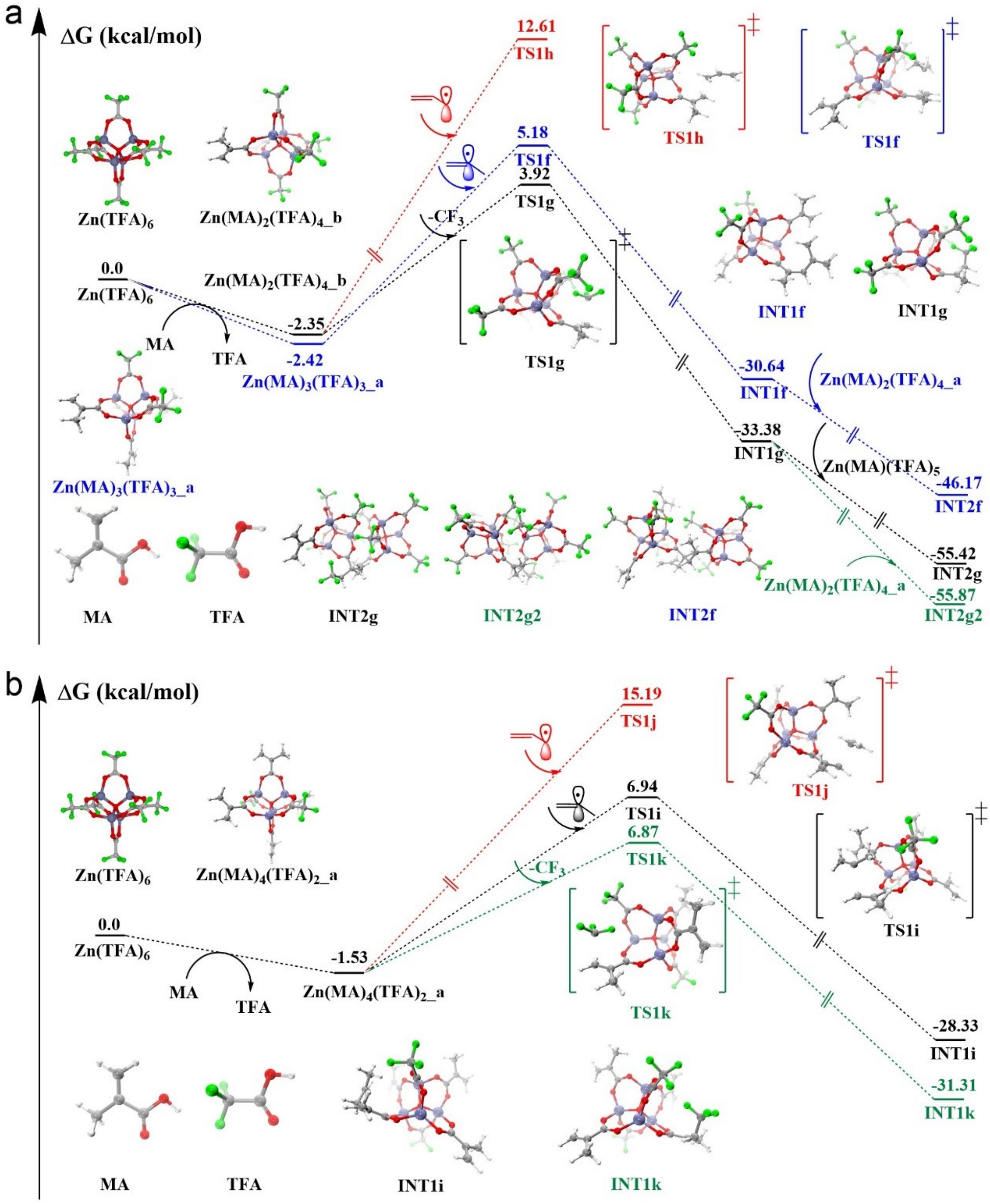


Fig. S3 The energy profile of chain propagation for (a) $Zn(MA)_3(TFA)_3$_a and (b) $Zn(MA)_4(TFA)_2$_a.

Obtaining the twisting energy (E_{TE}) using the following formula:

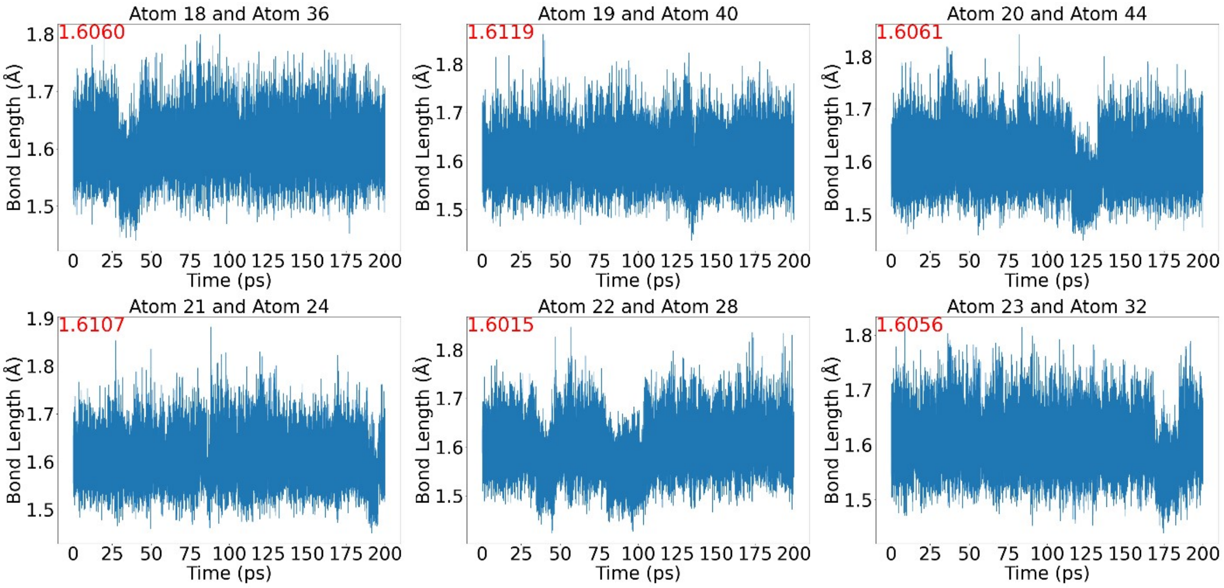
$$E_{TE} = E_{TS} - E_{original}$$

where $E_{original}$ is the single point energy of the minimal energy structure in the initial state. E_{TS} is the single point energy of the corresponding fragment in the transition state. E_{TE} could evaluate the deformation of fragments during the reaction process. The deformation usually increases the energy of the system.

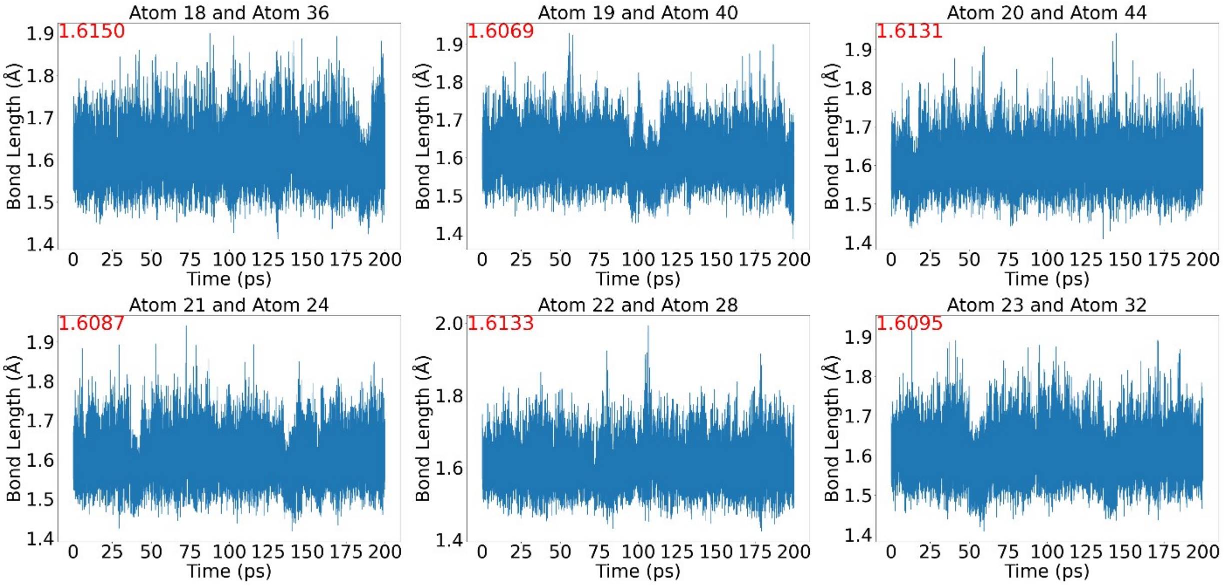
The results of molecular dynamics at different temperatures. The red font in a picture is the mean value of bond length (between two specified atoms) in run time.

$\mathrm{Zn(TFA)_6}$

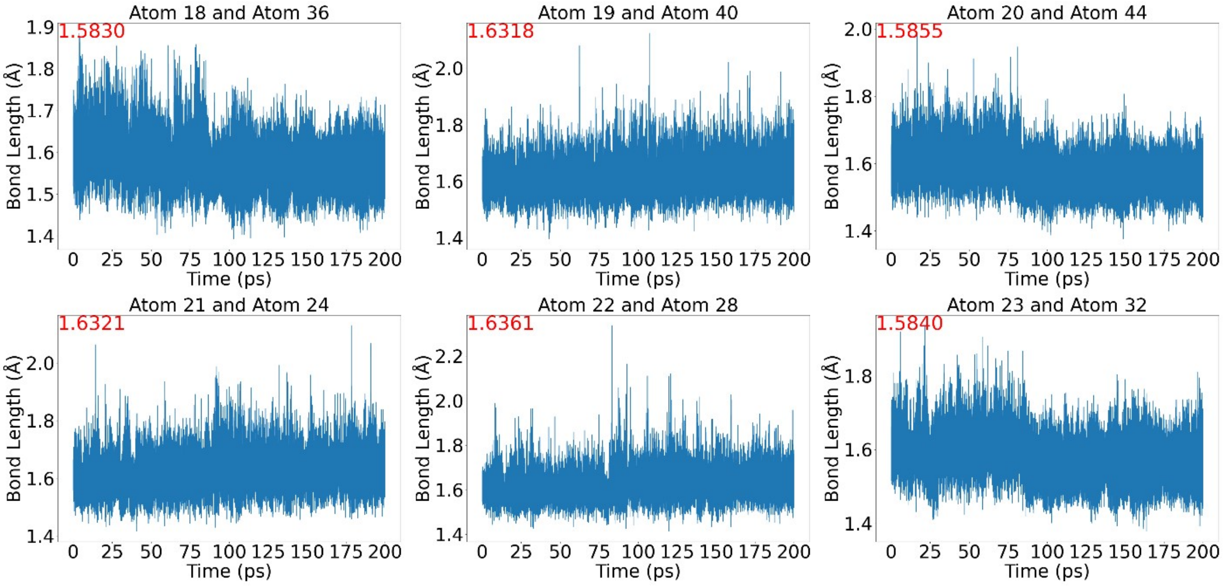
300 K



400 K



500 K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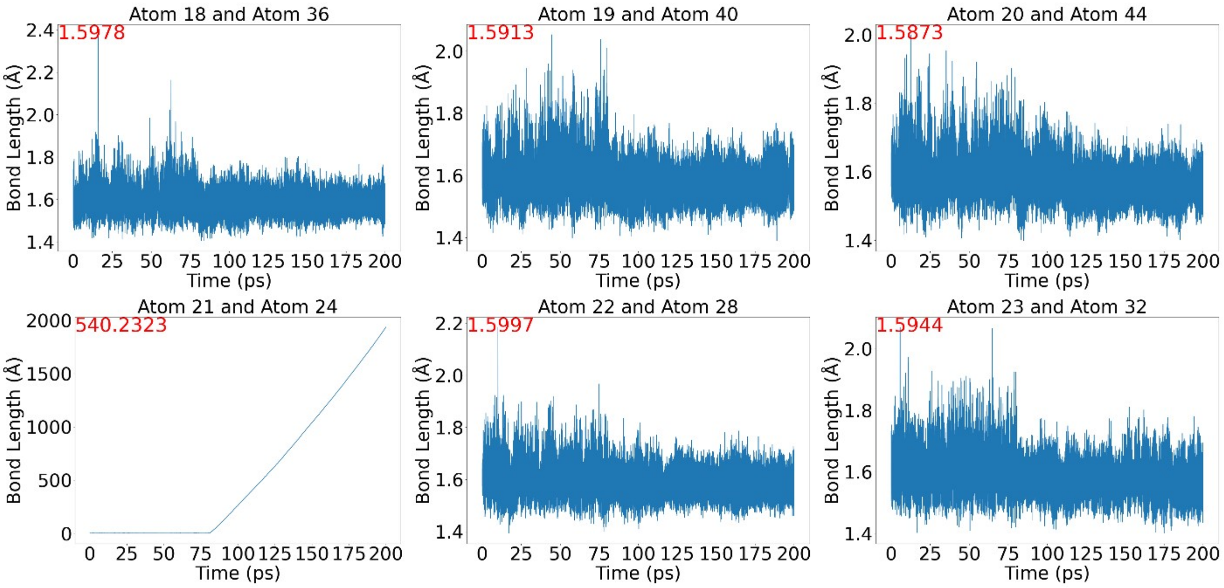
1.5830
Atom 19 and Atom 40
1.6318
Atom 20 and Atom 44
1.5855
Atom 21 and Atom 24
1.6321
Atom 22 and Atom 28
1.6361
Atom 23 and Atom 32
1.5840
Bond Length (Å)
Time (ps)
0 25 50 75 100 125 150 175 200

600 K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Atom 21 and Atom 24
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Atom 22 and Atom 28
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Atom 23 and Atom 32
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Bond Length (Å)
Time (ps)
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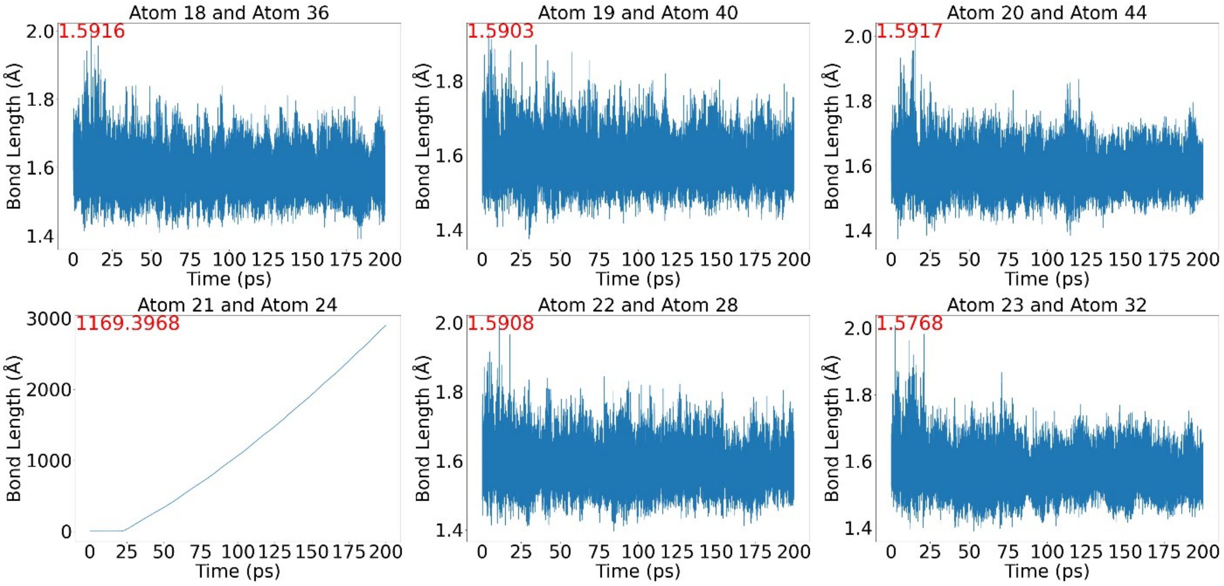
2000
1500
1000
500
0

700 K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Atom 20 and Atom 44
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Atom 21 and Atom 24
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Atom 22 and Atom 28
1.5908
Atom 23 and Atom 32
1.5768
Bond Length (Å)
Time (ps)
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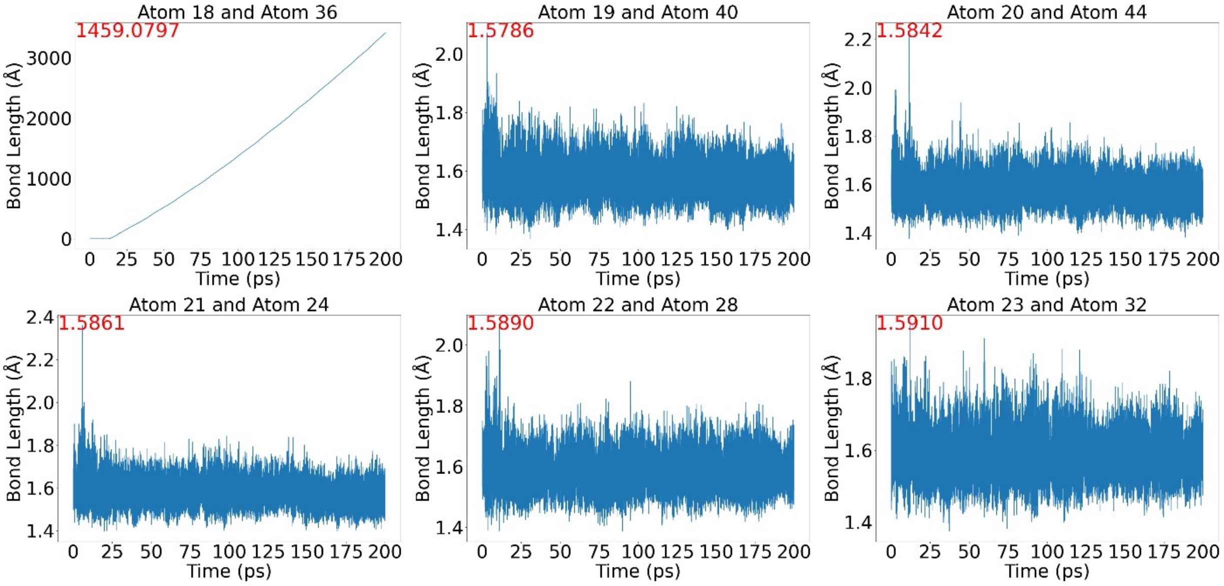
1.4 1.6 1.8 2.0
0 1000 2000 3000

800 K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Atom 22 and Atom 28
1.5890
Atom 23 and Atom 32
1.5910
Bond Length (Å)
Time (ps)
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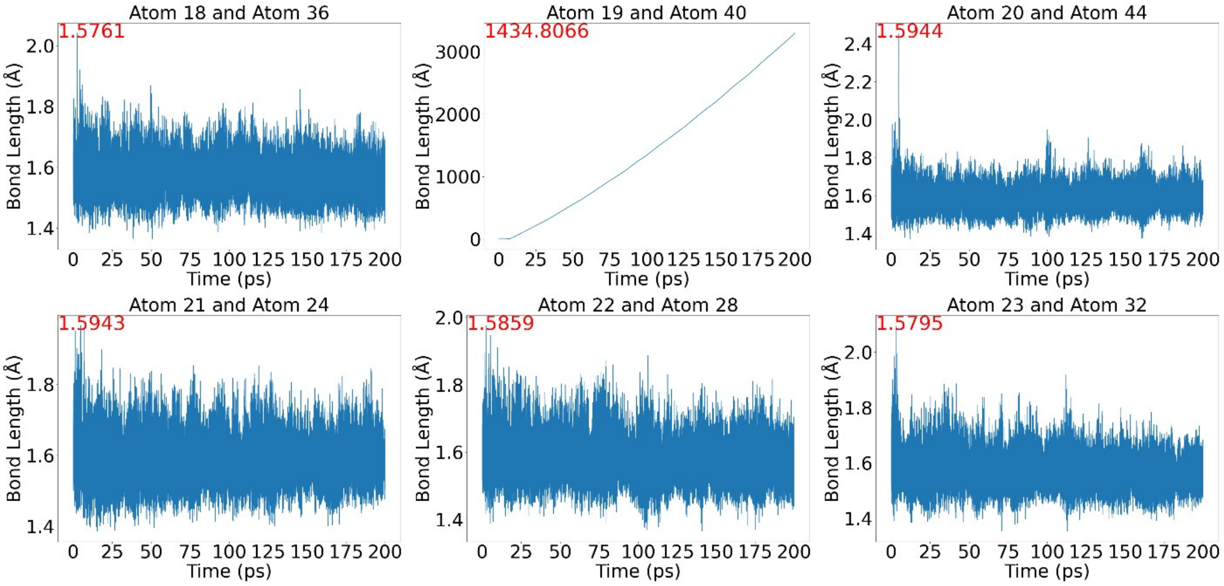
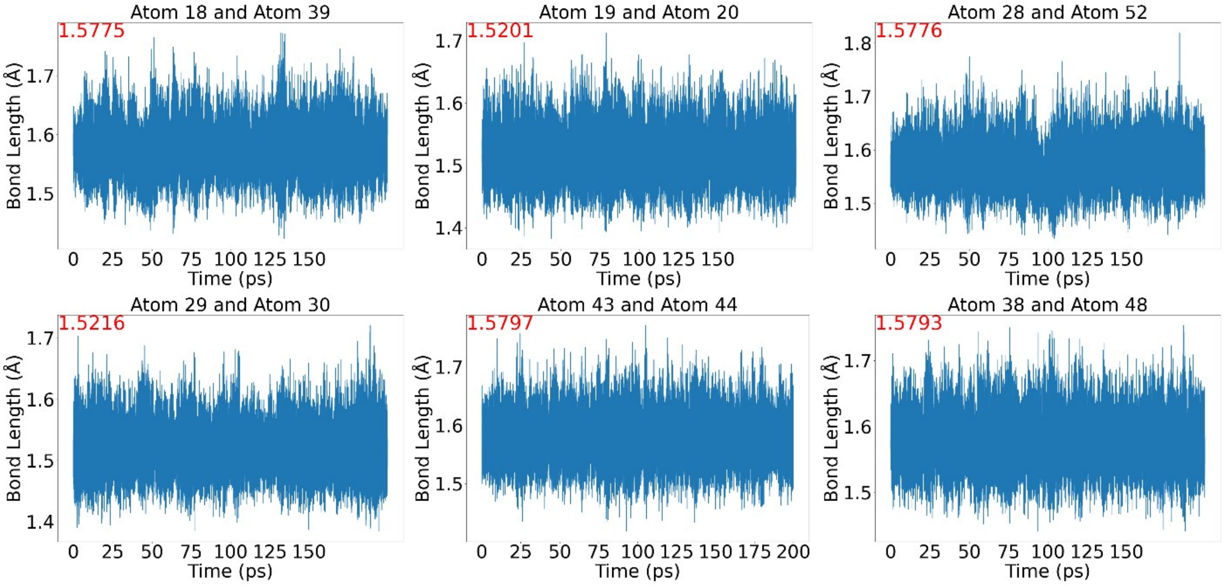
1.4 1.6 1.8 2.0 2.2 2.4
0 1000 2000 3000

900 K



Zn(MA)$_2$(TFA)$_4$_a

300 K



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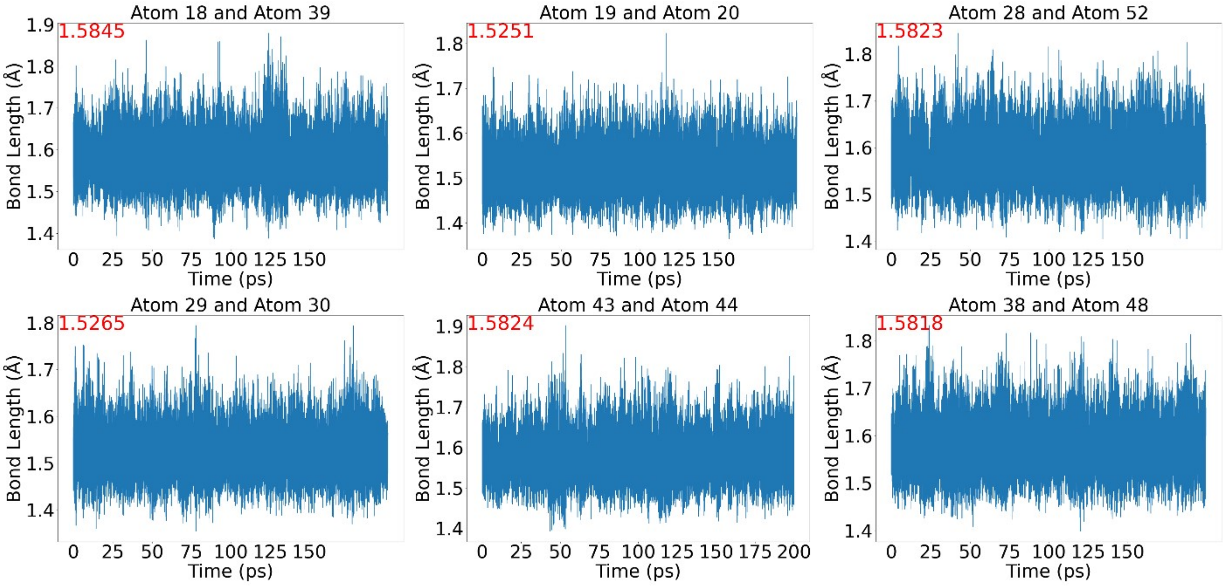
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Atom 28 and Atom 52
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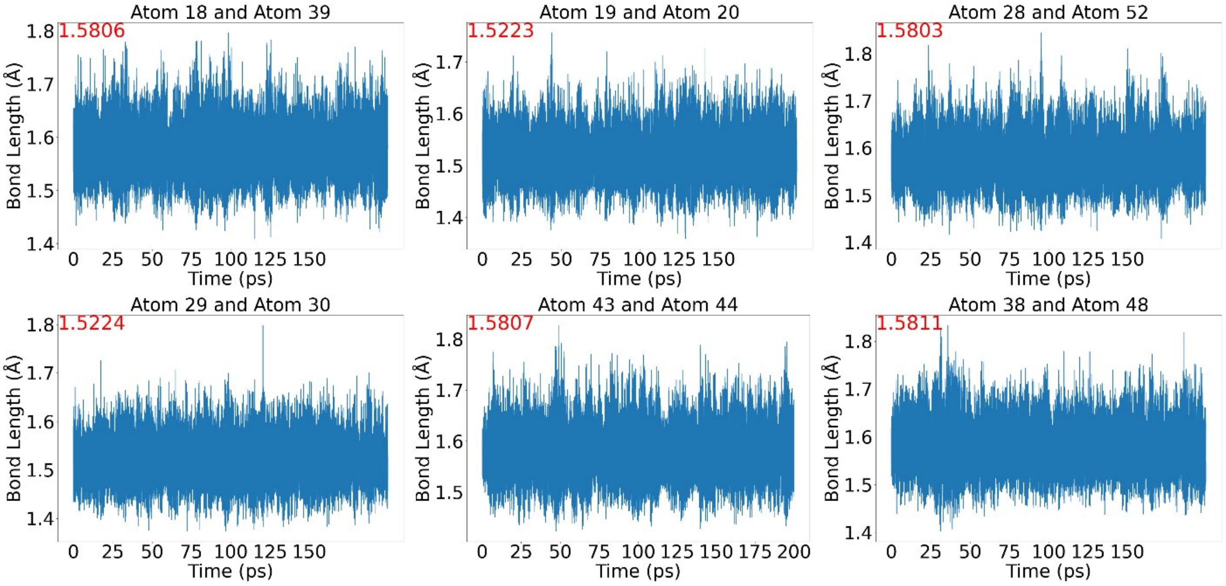
Atom 29 and Atom 30
1.5265
Atom 43 and Atom 44
1.5824
Atom 38 and Atom 48
1.5818
Bond Length (Å)
Time (ps)
1.4
1.5
1.6
1.7
1.8
1.9
0
25
50
75
100
125
150
175
200

500 K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Atom 28 and Atom 52
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Atom 29 and Atom 30
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Atom 43 and Atom 44
1.5807
Atom 38 and Atom 48
1.5811
Bond Length (Å)
Time (ps)
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1.6
1.7
1.8
0
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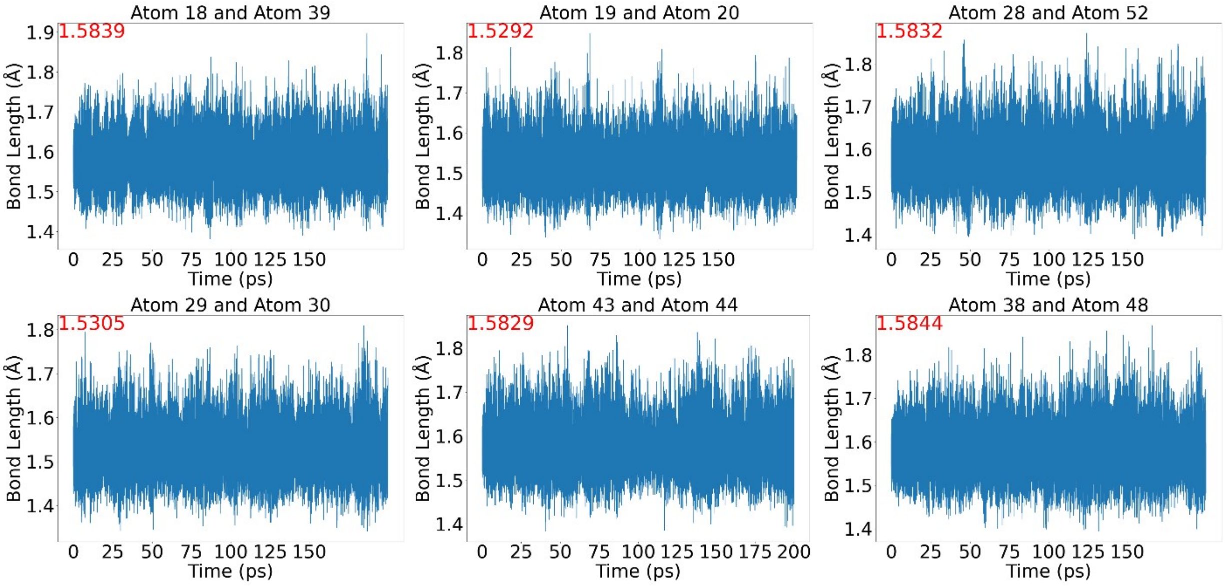
125
150
175
200

600 K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Atom 28 and Atom 52
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Atom 29 and Atom 30
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Atom 43 and Atom 44
1.5829
Atom 38 and Atom 48
1.5844
Bond Length (Å)
Time (ps)
1.4
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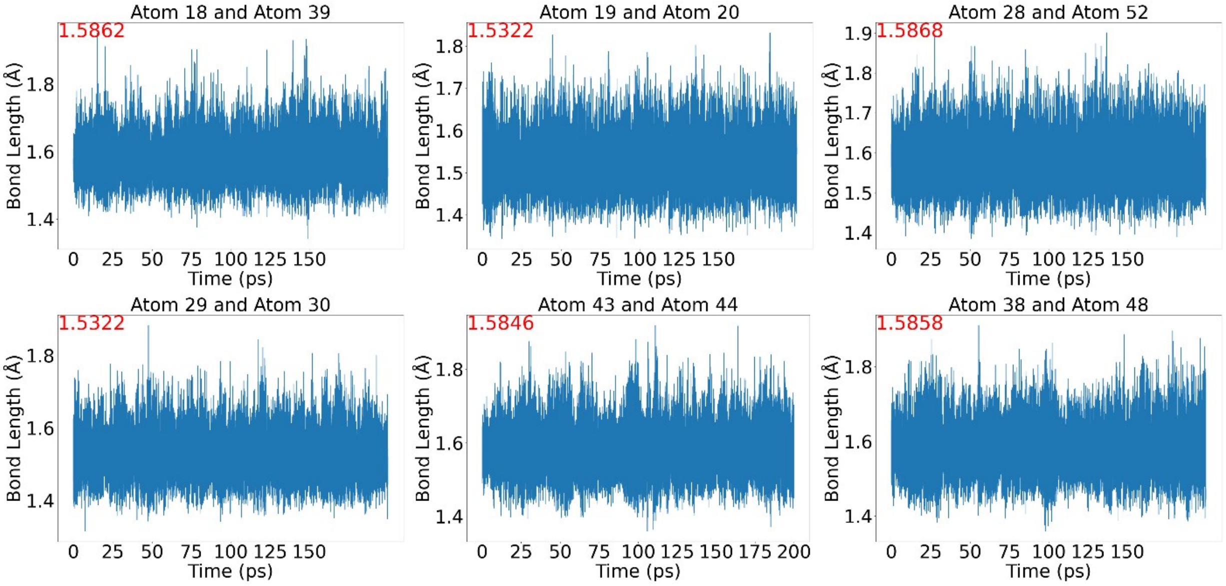
1.6
1.7
1.8
1.9
0
25
50
75
100
125
150
175
200

700 K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Atom 43 and Atom 44
1.5846
Atom 38 and Atom 48
1.5858
Bond Length (Å)
Time (ps)
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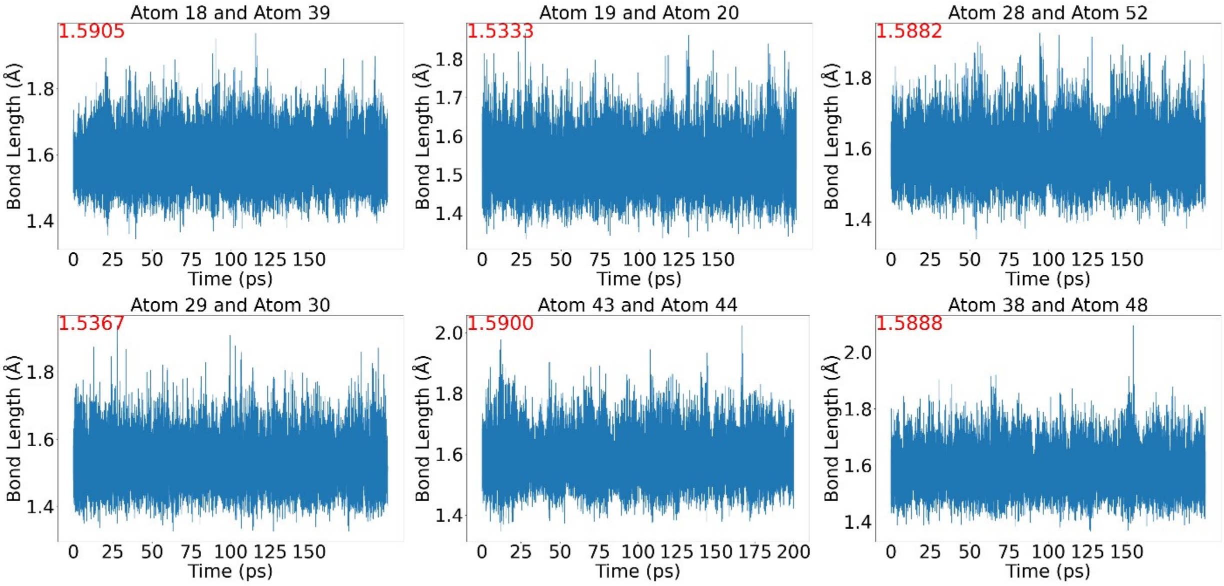
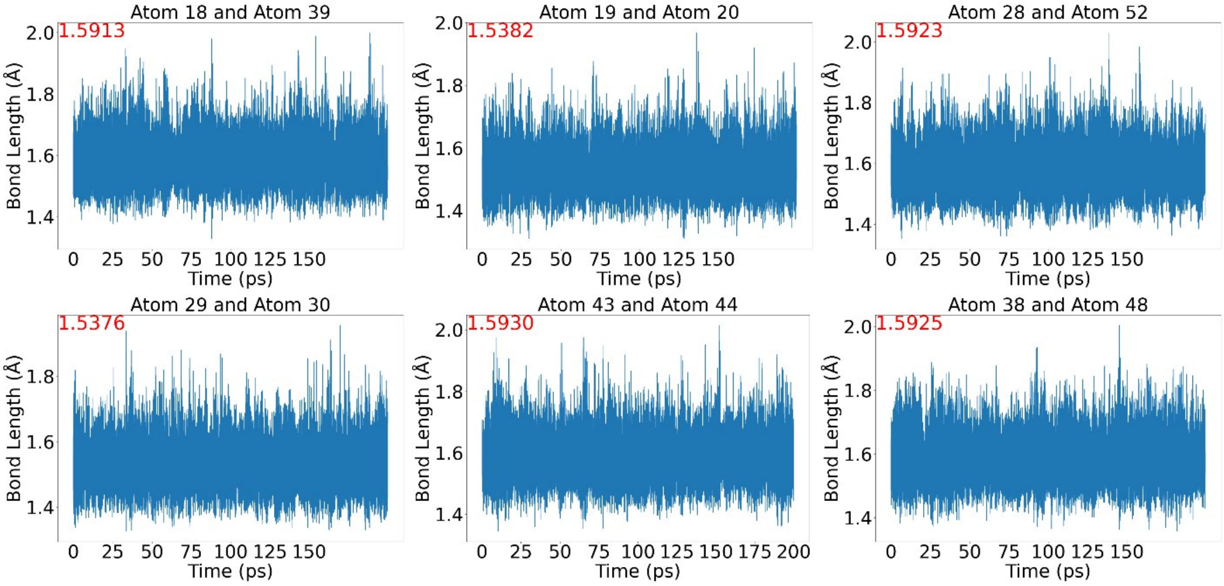
150
175
200

800 K

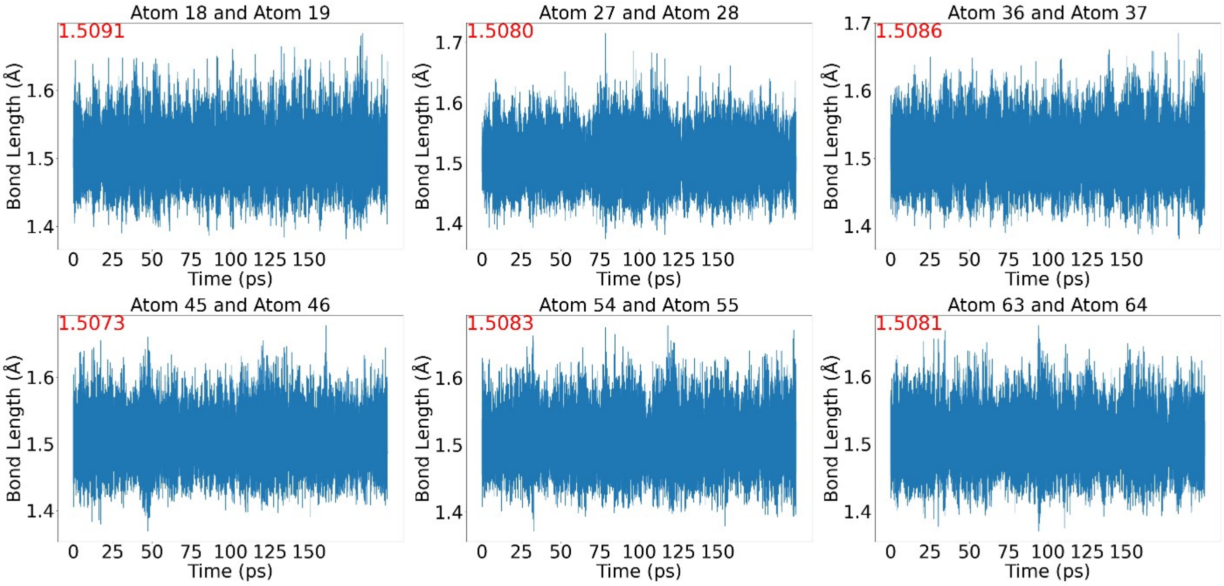


900 K



$Zn(MA)_6$

300 K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Atom 36 and Atom 37
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Atom 45 and Atom 46
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Atom 54 and Atom 55
1.5083
Atom 63 and Atom 64
1.5081
Bond Length (Å)
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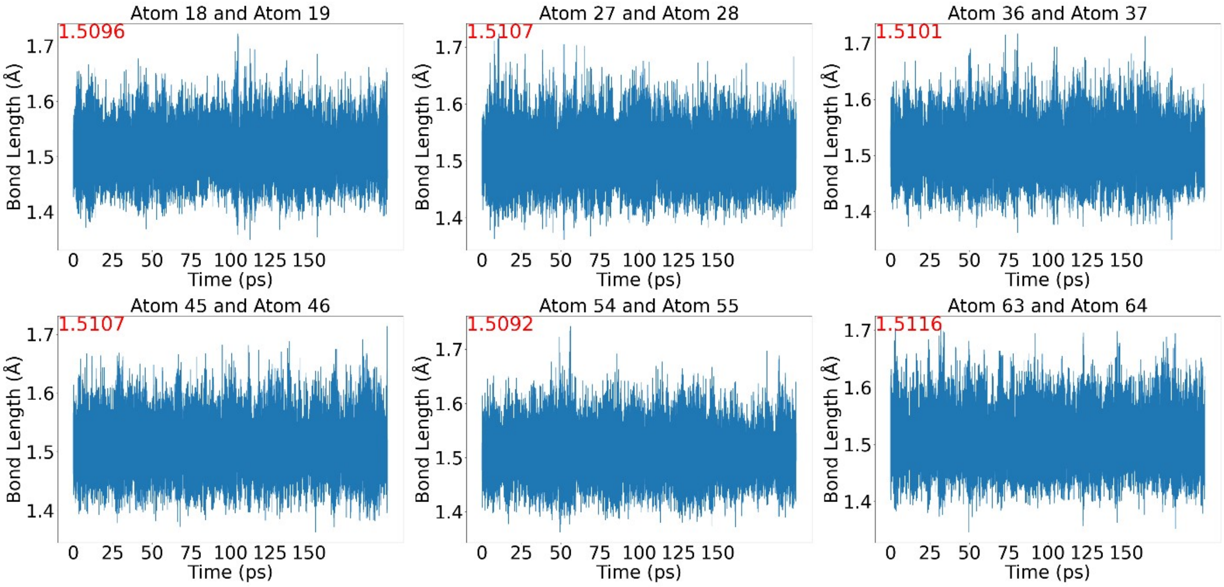
1.5
1.6
1.7
Time (ps)
0
25
50
75
100
125
150

400 K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Atom 36 and Atom 37
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Atom 45 and Atom 46
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Atom 54 and Atom 55
1.5092
Atom 63 and Atom 64
1.5116
Bond Length (Å)
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1.5
1.6
1.7
Time (ps)
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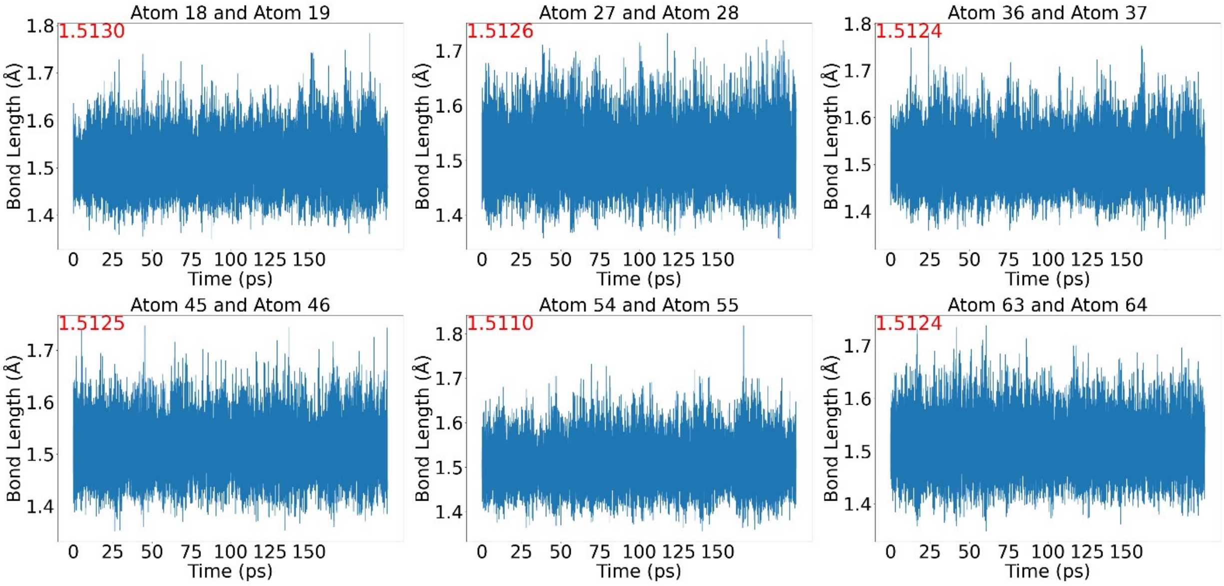
25
50
75
100
125
150

500 K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Atom 54 and Atom 55
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Bond Length (Å)
Time (ps)
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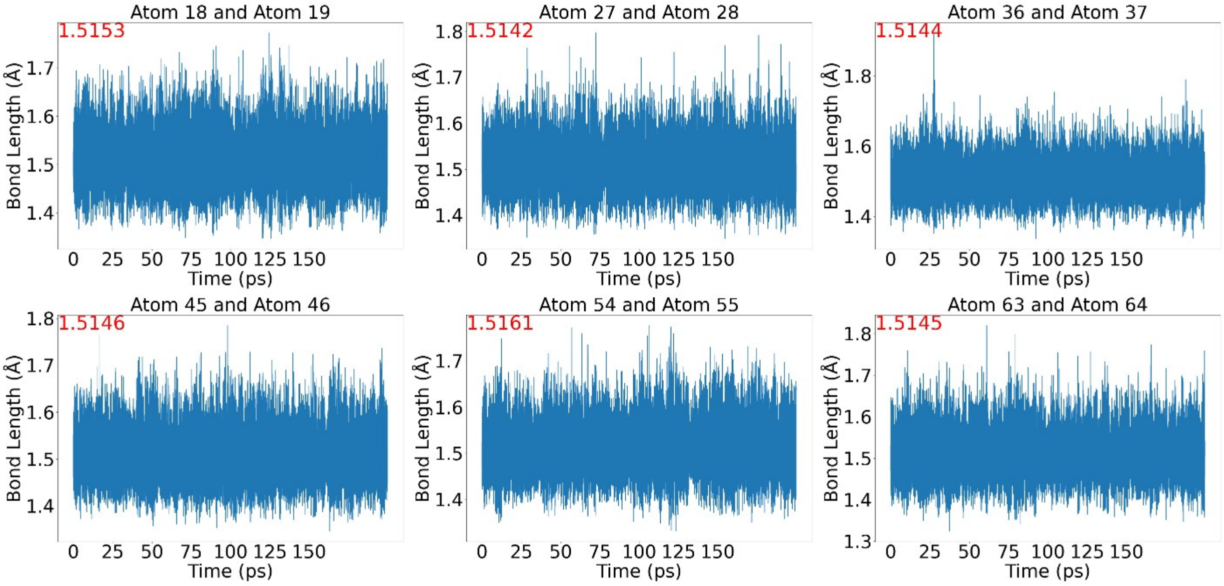
1.3 1.4 1.5 1.6 1.7 1.8

600 K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Atom 54 and Atom 55
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Time (ps)
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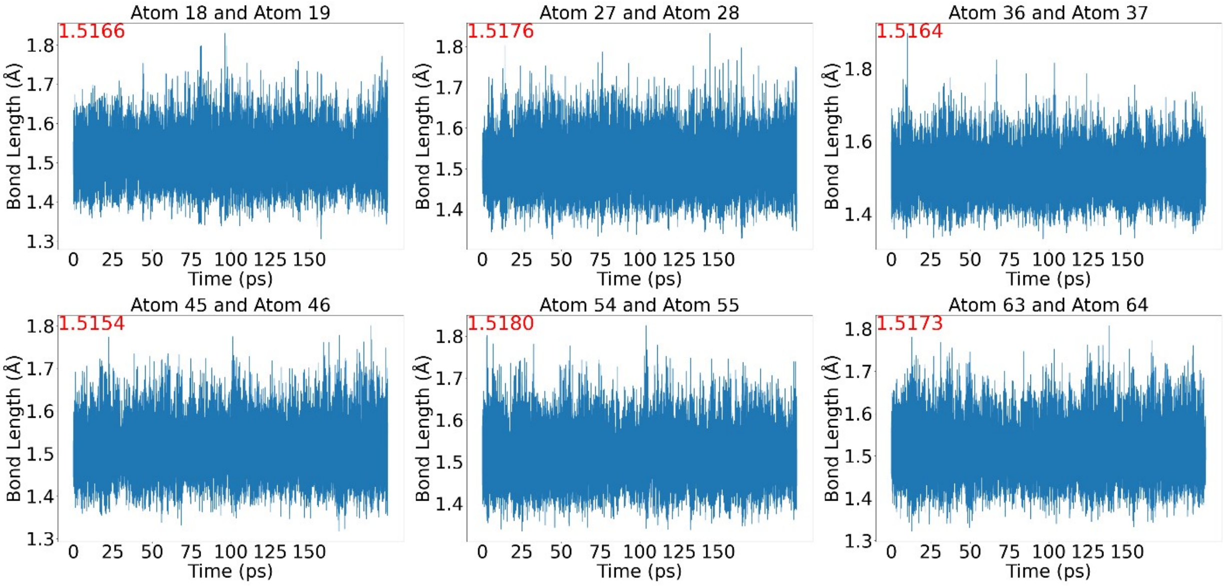
700 K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Time (ps)
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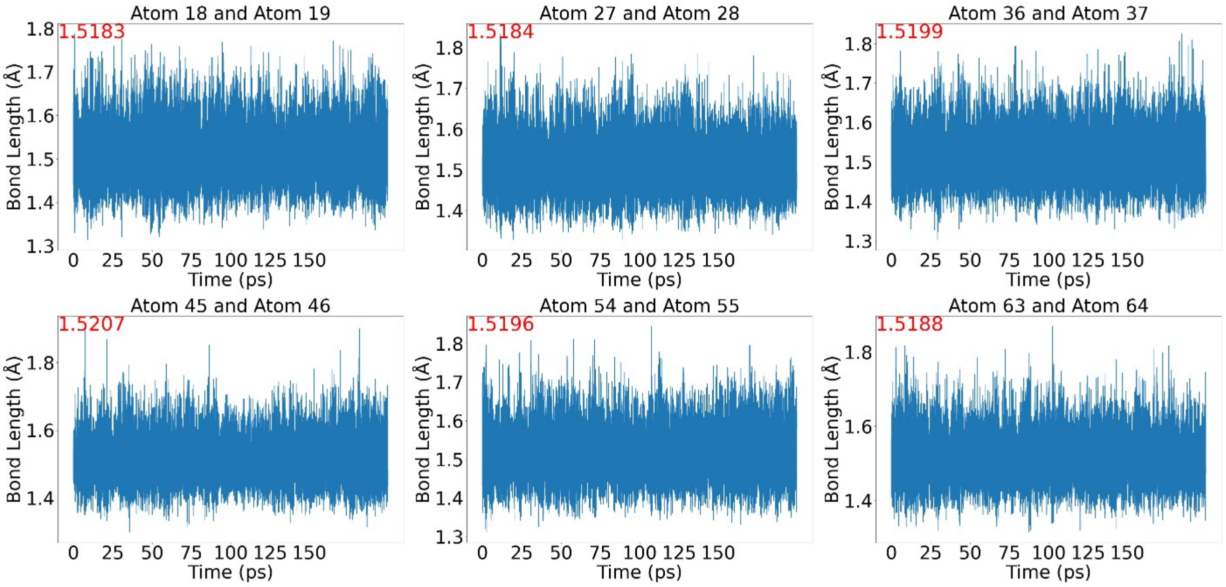
800 K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Bond Length (Å)
Time (ps)
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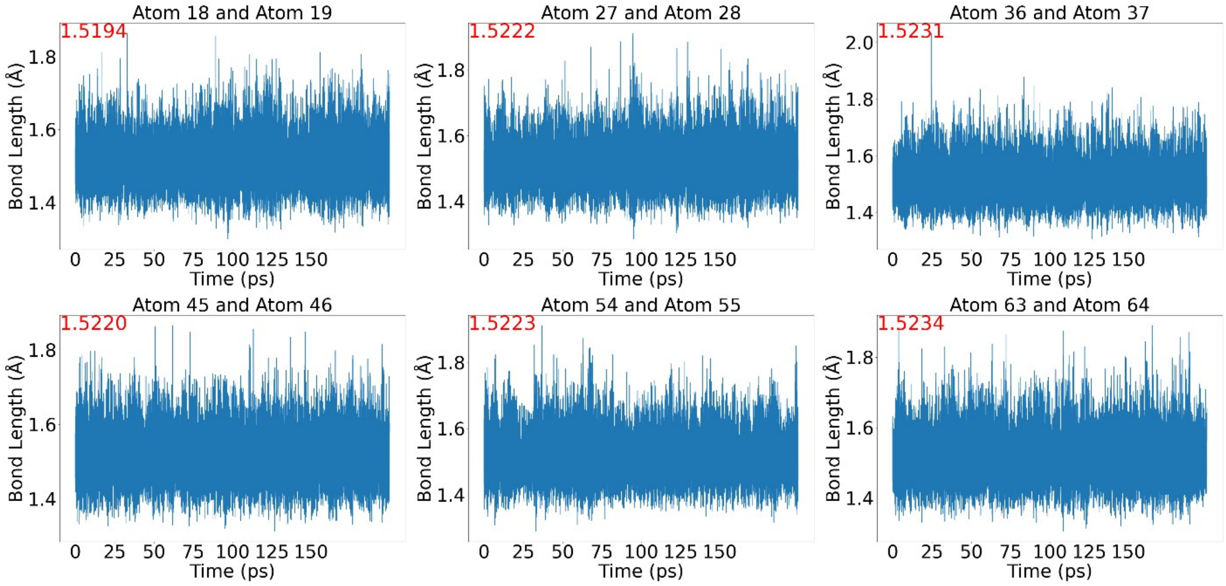
900 K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Atom 54 and Atom 55
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Bond Length (Å)
Time (ps)
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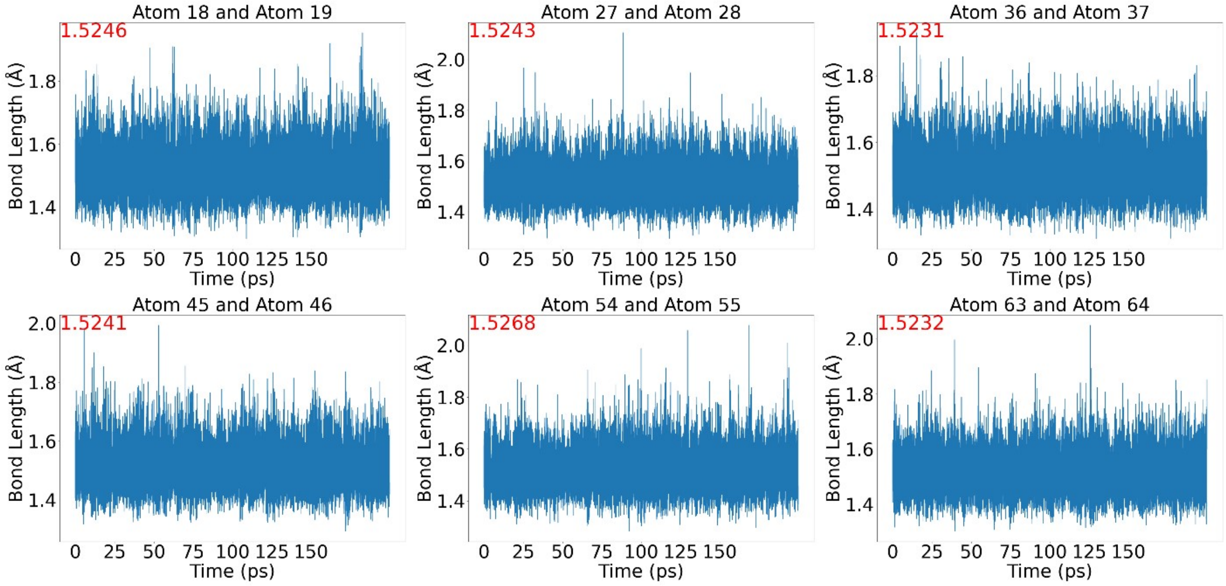
1.4 1.6 1.8 2.0

1000 K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Atom 45 and Atom 46
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Atom 54 and Atom 55
1.5268
Atom 63 and Atom 64
1.5232
Bond Length (Å)
Time (ps)
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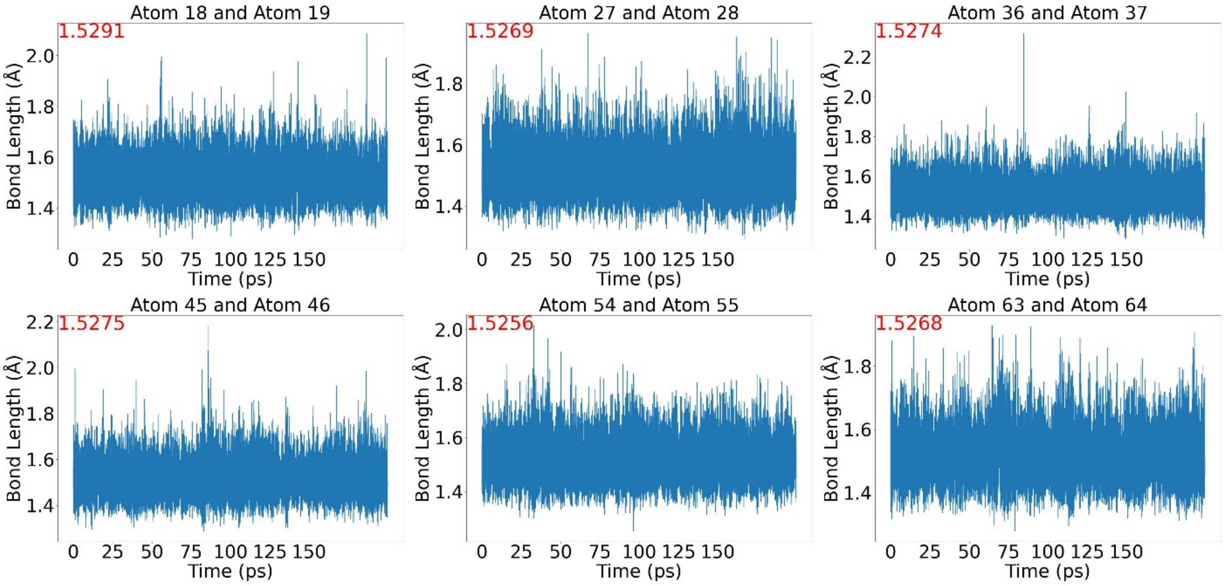
1.4 1.6 1.8 2.0

1100 K



1200 K

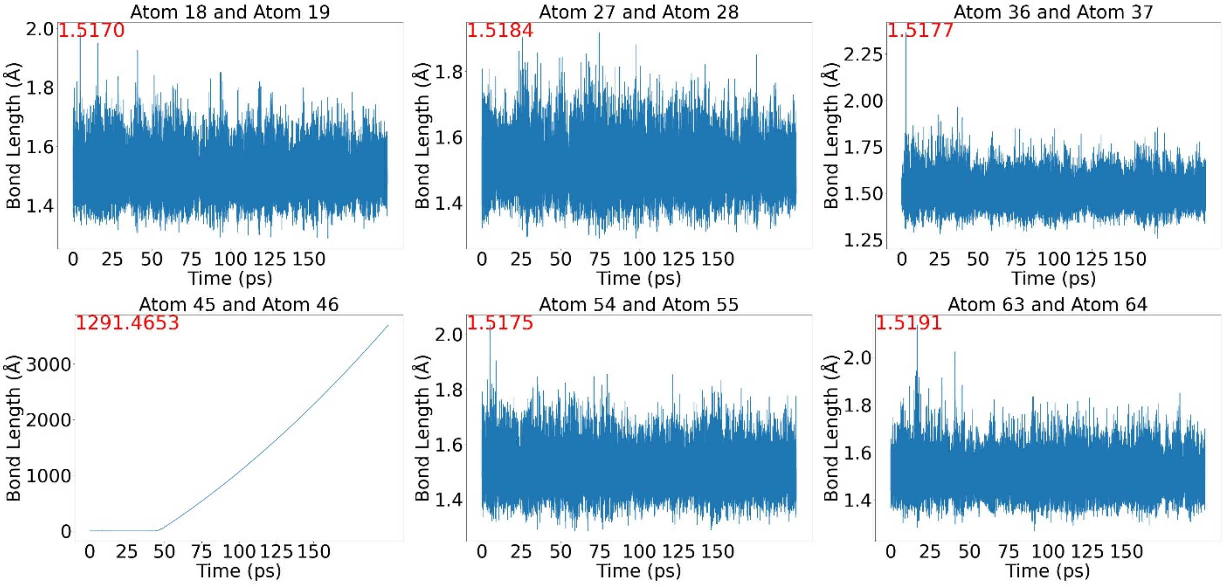


Fig. S4 The evolution of C-C bond length with time at different temperatures (from 300 to 900 K, the temperature was extended to 1200 K for Zn(MA)$_6$). The red font in the individual picture shows the mean value of C-C bond length in 200 ps.

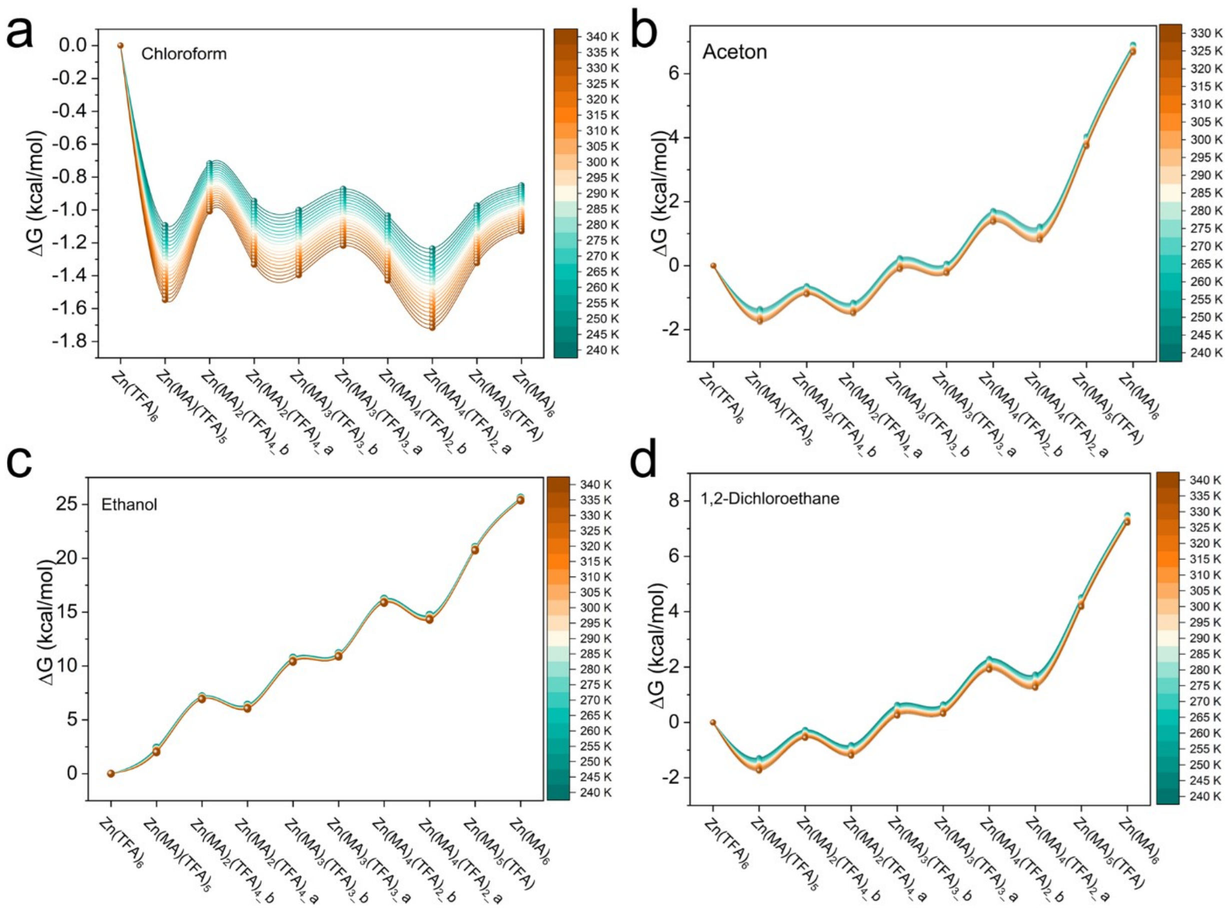


Fig. S5 The difference in Gibbs free energy for compounds (with different ratio of MA and TFA) in diverse solvents and at various temperatures.