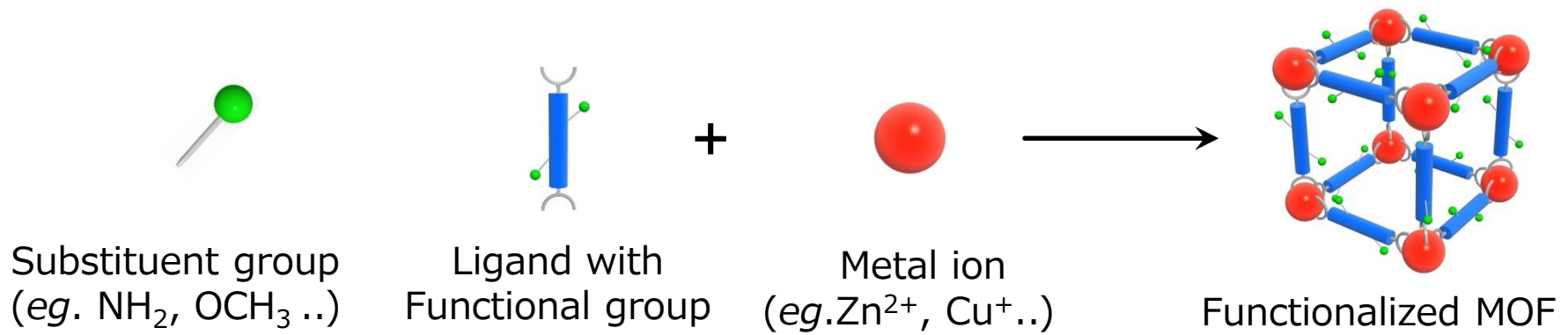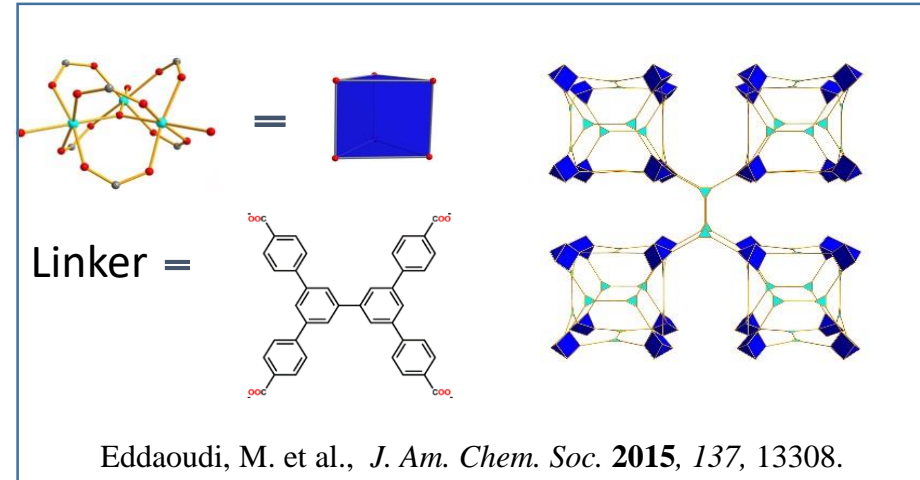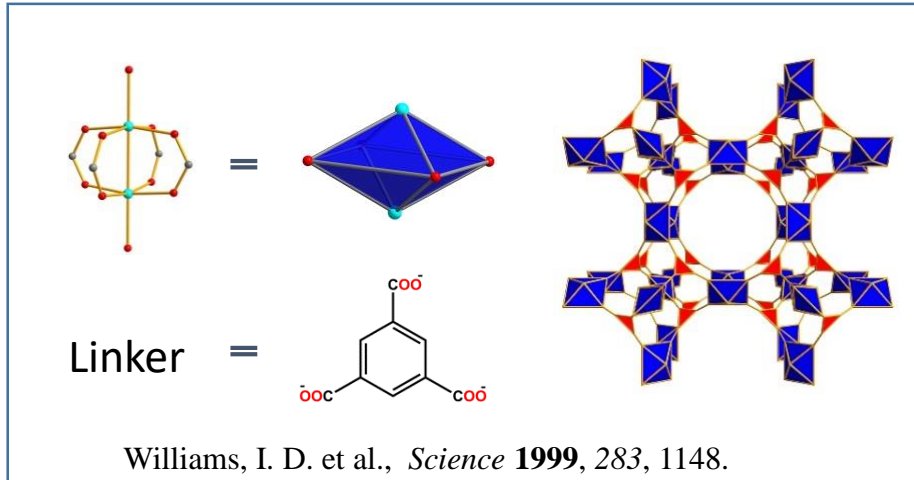# Force Field Parameters Preparation of Different Substituted Dicarboxylate Ligand in Flexible Metal-Organic Frameworks

Shanghua Xing

June 28th 2018

Metal Organic Frameworks (MOFs) as a new type of hybrid materials, consist of metal ions or metal-containing clusters connected to multidentate organic ligands via metal coordination.

Linker =

Williams, I. D. et al., *Science* **1999**, *283*, 1148.

Linker =

Eddaoudi, M. et al., *J. Am. Chem. Soc.* **2015**, *137*, 13308.

Substituent group
(*eg*. NH_2, OCH_3 ..)

Ligand with
Functional group

Metal ion
(*eg*. Zn^{2+}, Cu^+..)

+

Functionalized MOF

Rational design of functionalized MOFs by the introduction of substituents

PMMA

Radical polymerization of Poly(methyl methacrylate) (PMMA) and its tacticity

PMMA radical terminal + MMA (methyl methacrylate) monomer → Elongated PMMA
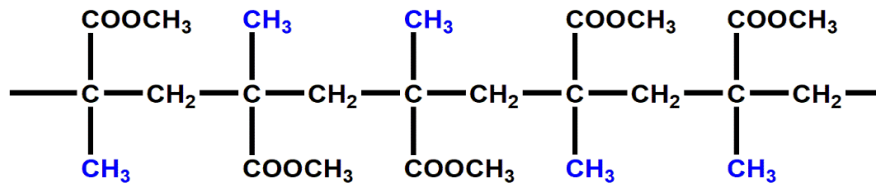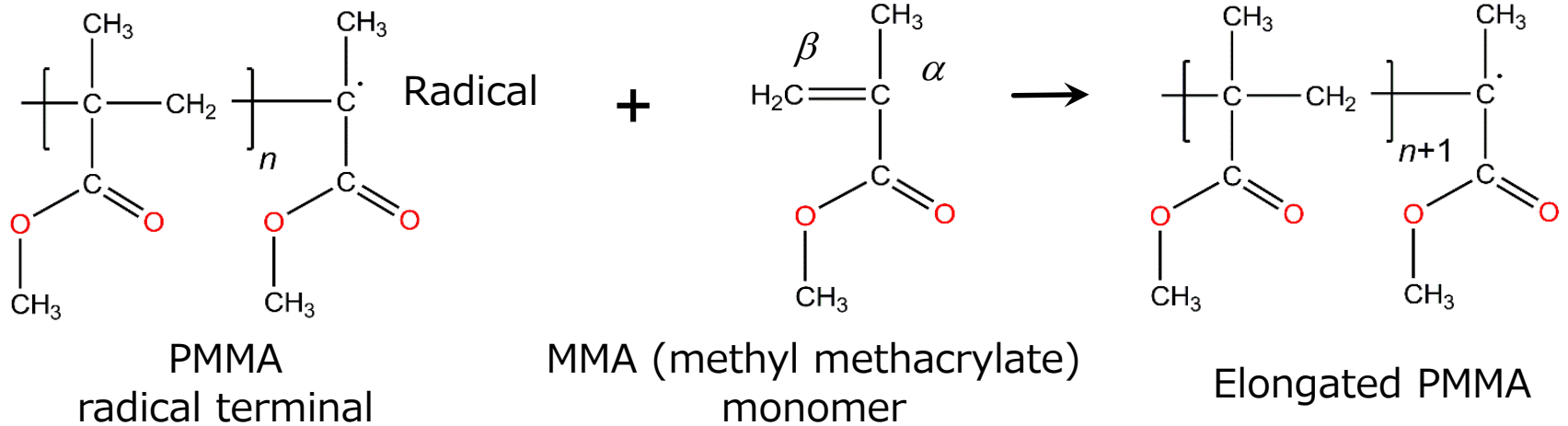
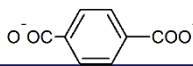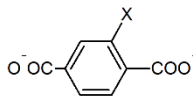meso: two adjacent structure units in the same direction

racemo: two adjacent structure units in the opposite direction

| diad	racemo (r)	meso (m)	r	m
triad		rm	mr	rm

Difficult tacticity control

Unique Tacticty Control

Radical polymerization of MMA by the different ligand in MOF channels[1-2]

BDC Linker	Substituent group	PMMA tacticity (%) mm:mr:rr (m)
Bulk polymerization		5:35:60 (22)
^-OOC-⬡-COO^-		8:40:52 (28)
^-OOC-⬡-COO^- (X)	F	9:41:50 (30)
	Cl	7:41:52 (27)
	Br	9:41:50 (29)
	NH$_2$	13:41:46 (33)
	CH$_3$	8:38:54 (27)
	OCH$_3$	13:44:43 (35)
^-OOC-⬡-COO^- (X,X)	F	10:45:45 (32)
	Cl	11:50:39 (36)
	CH$_3$	14:48:38 (38)
	Br	19:46:35 (42)
	OCH$_3$	28:53:19 (55)
^-OOC-⬡-COO^- (X,X)	F	8:40:52 (28)
	OCH$_3$	8:39:53 (28)

BDC = Terephthalic acid
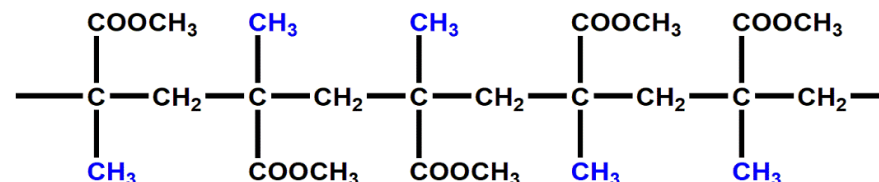
diad   racemo   meso   r   m
           (r)   (m)

triad   rm   mr   rm

However, how the ligand affect the tacticity control of PMMA by different substituent from the molecular viewpoint is still under discussion.
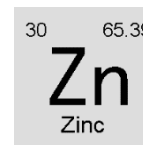
The regular and helical conformation result in significant tacticity change.

1. Uemura, T. et al., *Macromolecules* **2008**, *41*, 87.
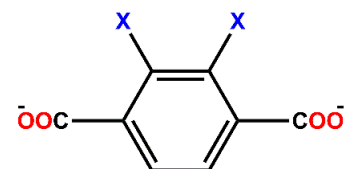2. Uemura, T. et al., *J. Am. Chem. Soc.* **2010**, *132*, 4917.

Partial DFT Optimization

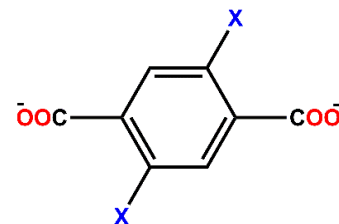The optimization model mimic the chemical environment in MOF channel

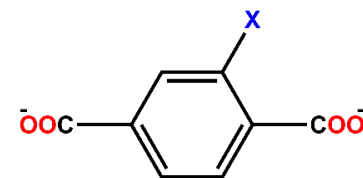TED (triethylenediamine)

BDC

Replaced by NH_3

HCOO

BDC Linker

NH_3

Metal = Zn 30 65.39 Zinc

Linker =

2,3-substituent

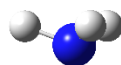2,5-substituent

Mono-substituent

X = F, Cl, Br, CH_3, NH_2, OCH_3

Partial optimizations, Method: M06-2X/LANL2DZ (for Zn), 6-31G** (for other atoms)

Equilibrium linker dihedral angle
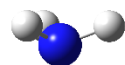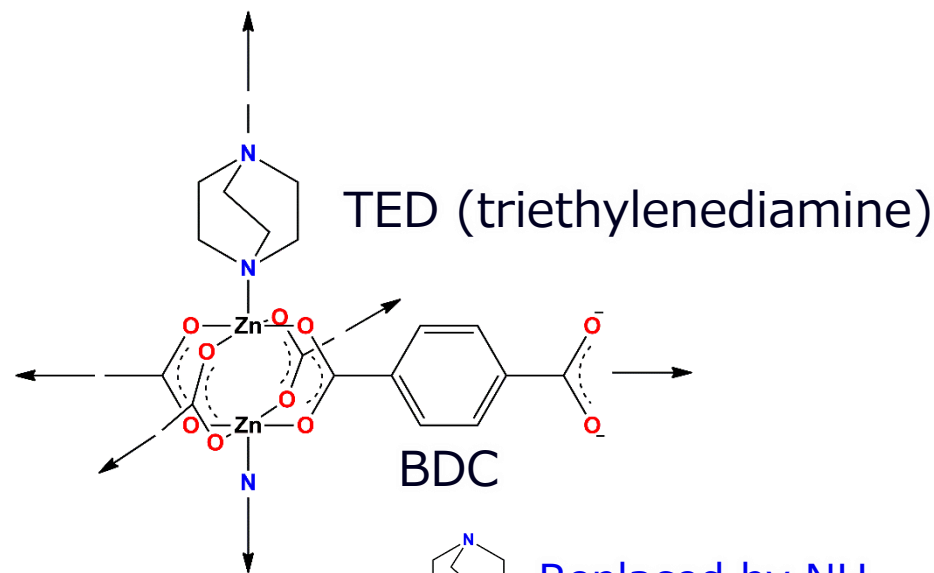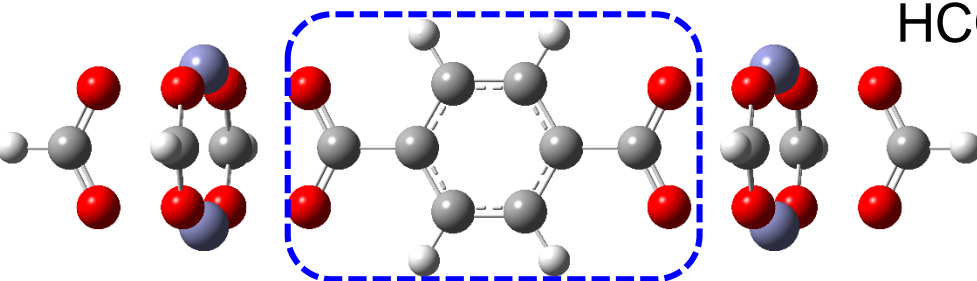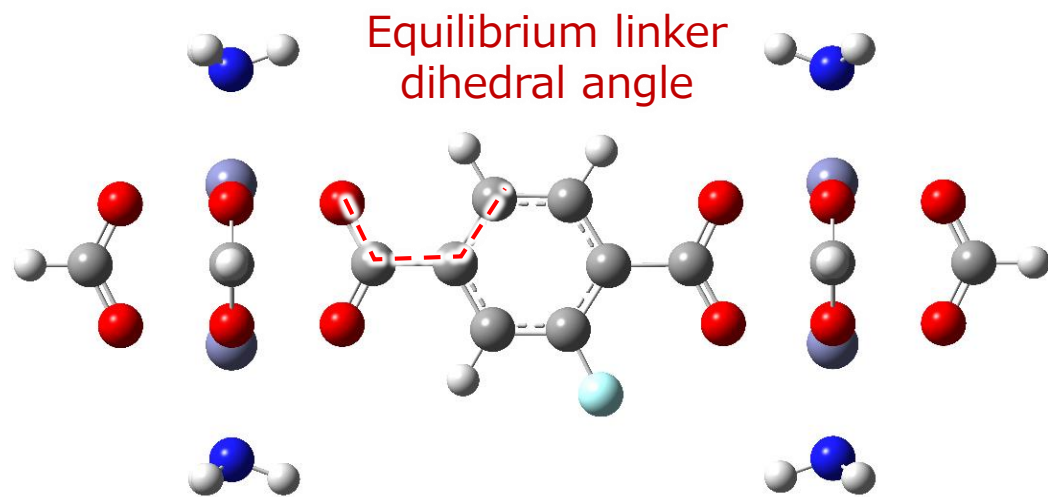
B3LYP-D3 or M06-2X/cc-pVDZ

Following this work, more preferred models are prepared.

High rotational barrier about 61 kJ/mol
The planar structure

X = F, Br

Low rotational barrier About 17 ~ 40 kJ/mol
The planar or nonplanar structure

Pakhira, S. et al., *J. Phys. Chem. C.* **2015**, *119*, 28789.

Previous model

linker
dihedral angle
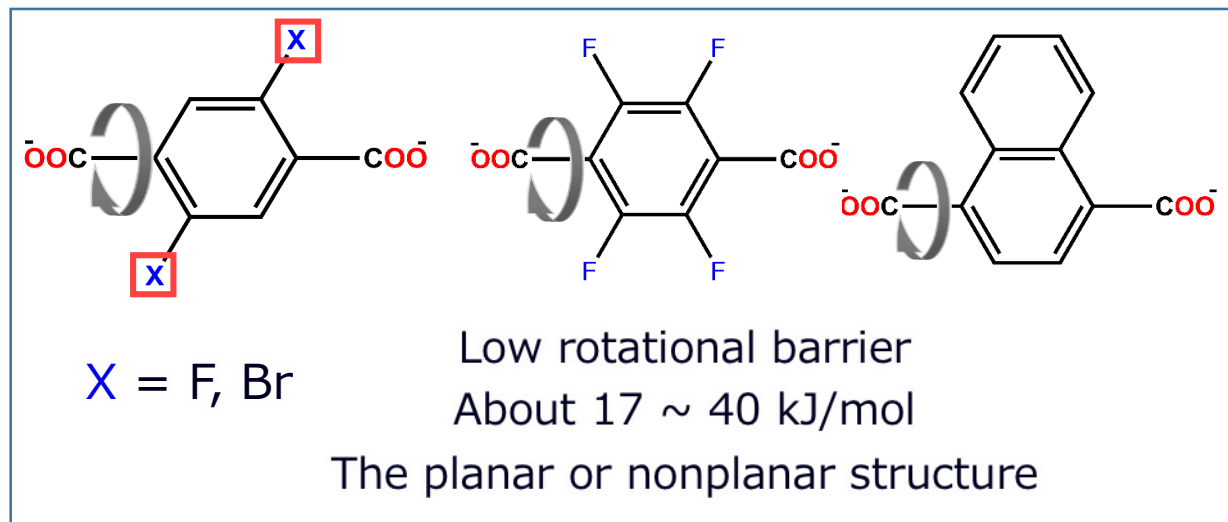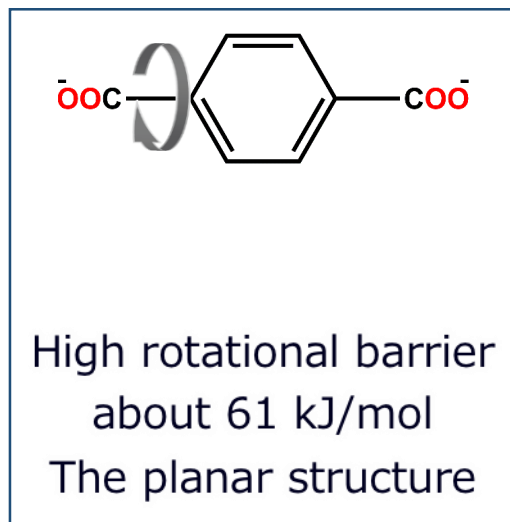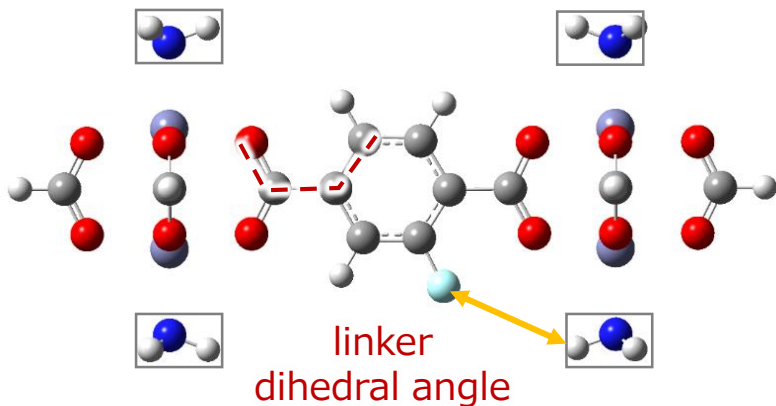
Pakhira, S. et al., *J. Phys. Chem. C.*
2015, *119*, 28789.

Proposed model

linker
dihedral angle

TMA(trimethylamine)
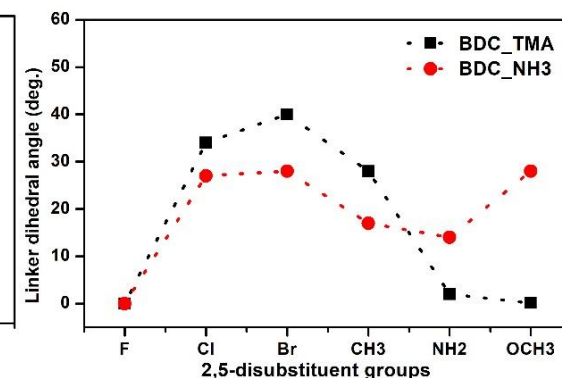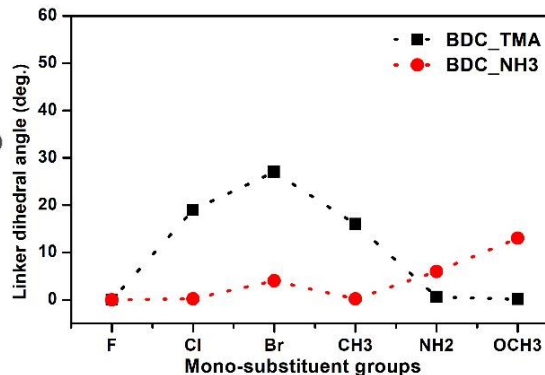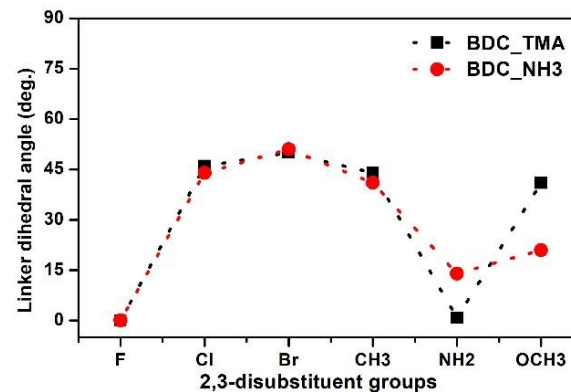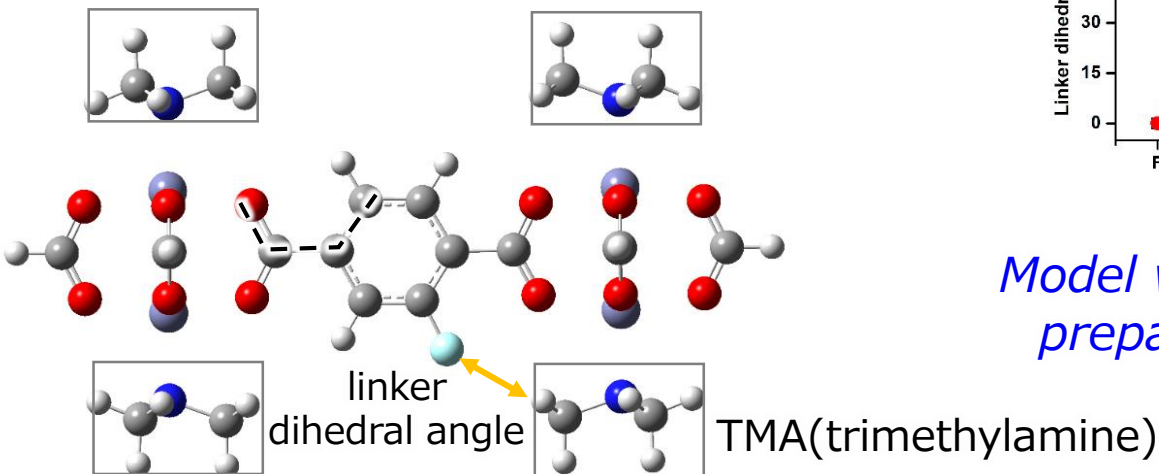
Model with TMA cap is the best to prepare force field parameters.

Partial optimizations, Method: M06-2X/LANL2DZ (for Zn), 6-31G** (for other atoms)

Substituent-dependent Planarity

❑ Halogen substituent groups (F, Cl, Br) in BDC linker

MOF_BDC with TMA cap		Linker dihedral (deg.)	Equilibrium X-H (closest on TMA) distance (Å)
F	Monosubstituent	0.0	2.82
	2,5-disubstituent	0.0	2.85
	2,3-disubstituent	0.0	2.81
Cl	Monosubstituent	19	2.69
	2,5-disubstituent	34	2.90
	2,3-disubstituent	46	3.05
Br	Monosubstituent	27	2.80
	2,5-disubstituent	40	2.98
	2,3-disubstituent	50	3.13

# VDW radius:
H=1.2Å, F=1.47Å, Cl=1.75Å, Br= 1.85Å
H-F: 2.67 Å
H-Cl: 2.95 Å
H-Br: 3.05 Å

Electrostatic attraction decrease in the order of mono > 2,5di > 2,3di. (The calculated charge of H atom in TMA molecule on each model is almost unchanged.

Planar structure because of small Van der Waals (VDW) force
Nonplanar structure because of VDW repulsion

Substituent-dependent Planarity

❑ Larger substituent groups (OCH$_3$) in BDC linker

180.0°

O
H

H bonding

70.0°

two stable minima

70.0°   180.0°
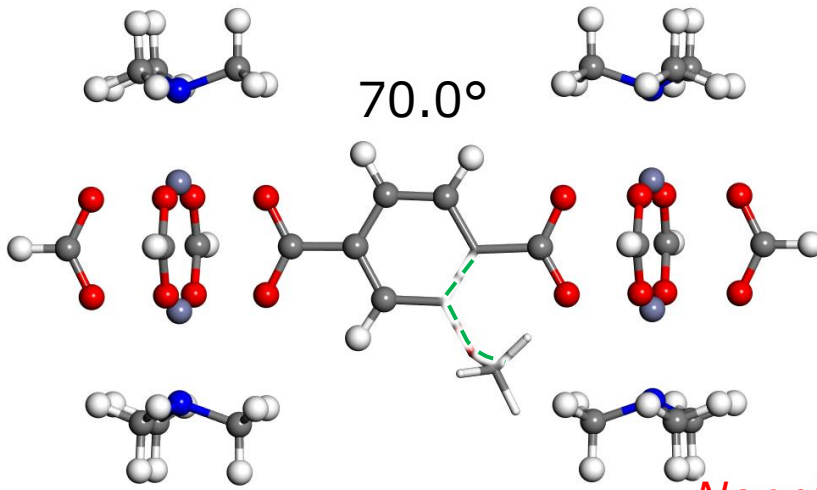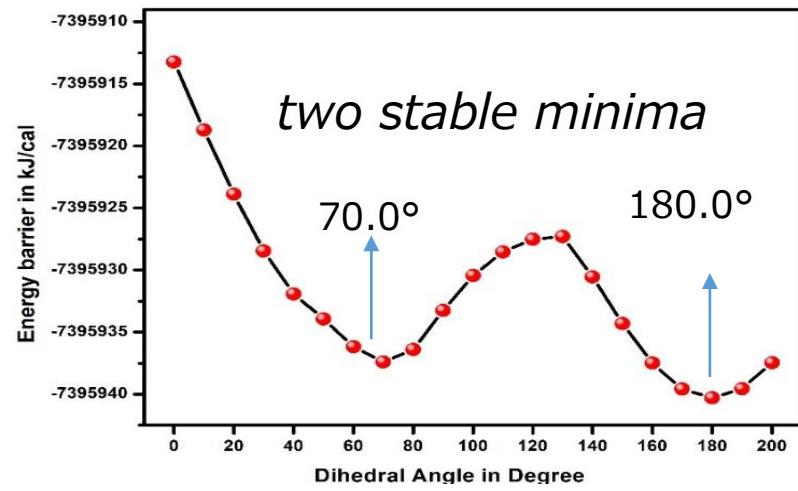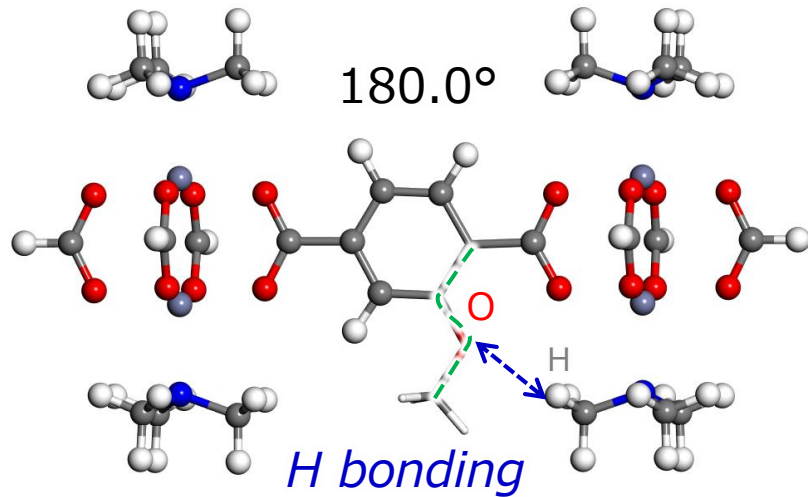
MOF_BDC with TMA cap		Linker dihedral (deg.)
OCH$_3$	Mono-substituent	0.1
	2,5-disubstituent	0.1
	2,3-disubstituent	41

Planar structure because of H bonding
Nonplanar structure because of electrostatic repulsion

Substituent-dependent Planarity

❑ Larger substituent groups (CH_3, NH_2) in BDC linker

Mono-CH_3 substituent
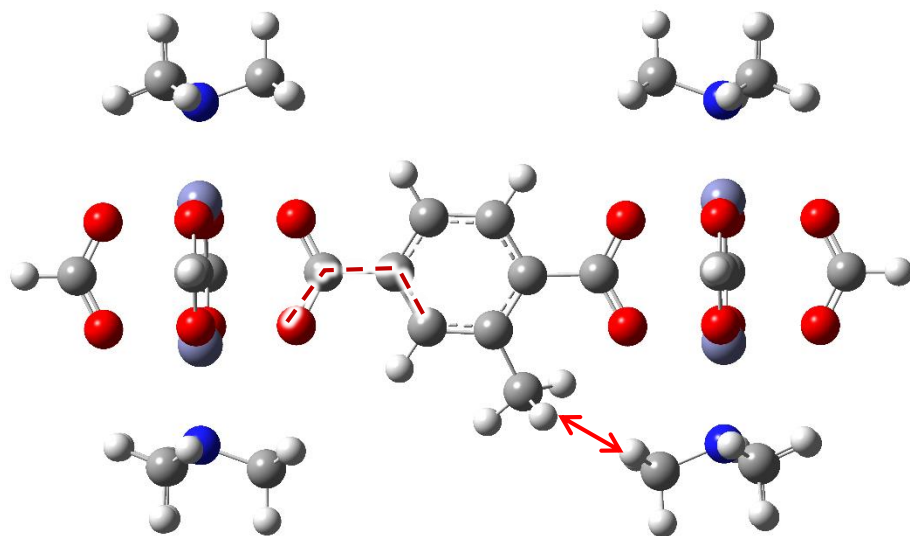
Mono-NH_2 substituent
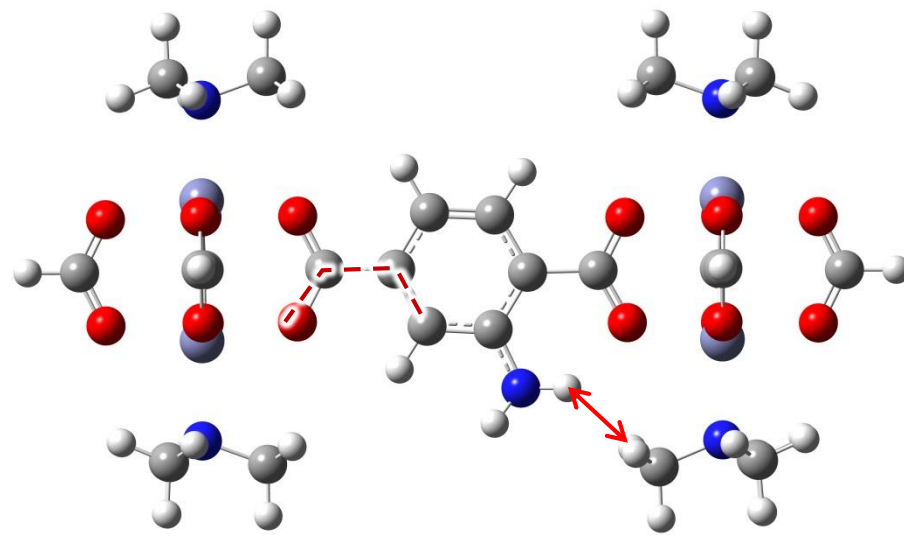
MOF_BDC with TMA cap		Linker dihedral (deg.)
CH_3	Mono-substituent	16
	2,5-disubstituent	28
	2,3-disubstituent	44
NH_2	Mono-substituent	0.6
	2,5-disubstituent	2
	2,3-disubstituent	0.8

VDW repulsion plays an important Role in CH_3 substituted models.

Electrostatic repulsion affect the NH_2 optimized models

TMA Rotation Effect

❑ BDC_MOF without substituent

❑ BDC_MOF with halogen atoms (F, Cl and Br)

Rotate 60 °

TMA _at 0 °

TMA _at 60 °

MOF_BDC with TMA cap		TMA dihedral	ΔE(at60-at0) (kJ/mol)	Linker Dihedral (deg.)	Equilibrium X-H (closest on TMA) distance (Å)
F	Monosubstituent	at 0	0.00	0.0	2.82
		at 60	1.31	0.1	2.99
	2,5-disubstituent	at 0	0.00	0.0	2.85
		at 60	0.98	0.0	3.01
	2,3-disubstituent	at 0	0.00	0.0	2.81
		at 60	0.53	0.0	2.98

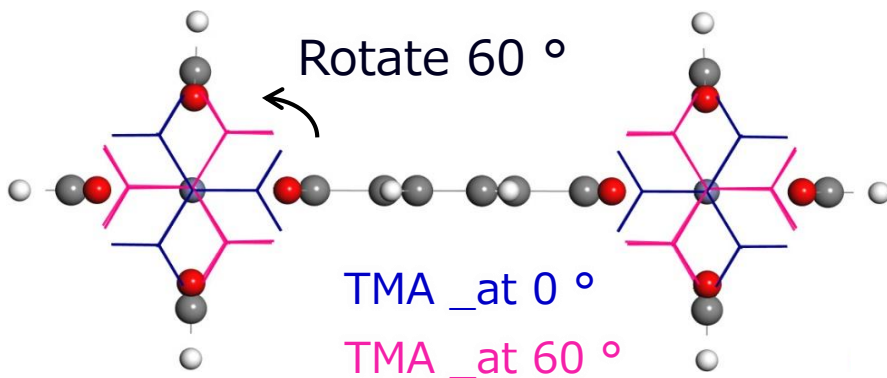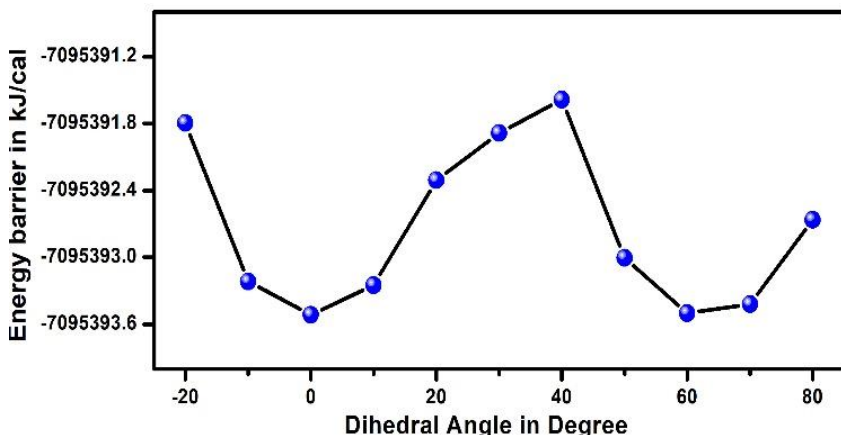| Cl	Monosubstituent	at 0	0.00	about 19	2.69
		at 60	-3.68	0.8	2.87
	2,5-disubstituent	at 0	0.00	about 34	2.90
		at 60	0.26	0.0	2.92
	2,3-disubstituent	at 0	0.00	about 46	3.05
		at 60	13.65	0.1	2.76
Br	Monosubstituent	at 0	0.00	about 27	2.80
		at 60	-4.99	0.7	2.86
	2,5-disubstituent	at 0	0.00	about 40	2.98
		at 60	0.26	0.0	2.91
	2,3-disubstituent	at 0	0.00	about 50	3.13
		at 60	27.04	0.1	2.72

The trend of the most stable conformation depends on the substituents

The sum of VDW radius:
H-F: 2.67 Å
H-Cl: 2.95 Å
H-Br: 3.05 Å

❑ BDC_MOF with CH_3, NH_2 and OCH_3 substituents

MOF_BDC with TMA cap		TMA dihedral	ΔE(at60-at0) (kJ/mol)	Linker Dihedral (deg.)	Equilibrium O-H (closest on TMA) distance (Å)
OCH_3	monosubstituent	at 0	0.00	0.1	2.73
		at 60	1.05	0.1	2.87
	2,5-disubstituent	at 0	0.00	0.1	2.76
		at 60	1.05	0.3	2.93
	2,3-disubstituent	at 0	0.00	about 41	-
		at 60	-4.99	about 23	-

NH_2	monosubstituent	at 0	0.00	0.6	2.13
		at 60	1.05	about 1	2.23
	2,5-disubstituent	at 0	0.00	about 2	2.13
		at 60	0.79	about 3	2.25
	2,3-disubstituent	at 0	0.00	0.8	2.14
		at 60	0.26	0.7	2.20
CH_3	monosubstituent	at 0	0.00	about 16	2.27
		at 60	-1.58	about 12	2.35
	2,5-disubstituent	at 0	0.00	about 28	2.22
		at 60	-2.63	about 24	2.31
	2,3-disubstituent	at 0	0.00	about 44	2.63
		at 60	-0.05	about 45	2.56

Ignorable energy difference found in BDC model with NH_3 cap

MOF_BDC with NH_3 cap		NH_3 dihedral	ΔE(at60-at0) (kJ/mol)
F	monosubstituent	at 0	0.00
		at 60	0.53
	2,5-disubstituent	at 0	0.00
		at 60	0.53
	2,3-disubstituent	at 0	0.00
		at 60	0.53
Cl	monosubstituent	at 0	0.00
		at 60	0.53
	2,5-disubstituent	at 0	0.00
		at 60	1.05
	2,3-disubstituent	at 0	0.00
		at 60	2.36
Br	monosubstituent	at 0	0.00
		at 60	0.53
	2,5-disubstituent	at 0	0.00
		at 60	1.31
	2,3-disubstituent	at 0	0.00
		at 60	0.16
OCH_3	monosubstituent	at 0	0.00
		at 60	0.79
	2,5-disubstituent	at 0	0.00
		at 60	1.05
	2,3-disubstituent	at 0	0.00
		at 60	0.79
NH_2	monosubstituent	at 0	0.00
		at 60	-0.53
	2,5-disubstituent	at 0	0.00
		at 60	0.53
	2,3-disubstituent	at 0	0.00
		at 60	-0.79
CH_3	monosubstituent	at 0	0.00
		at 60	0.26
	2,5-disubstituent	at 0	0.00
		at 60	0.26
	2,3-disubstituent	at 0	0.00
		at 60	0.26

Determine the charge of BDC linker with different substituents and TED molecule

BDC Linker

TED

The unit cell of BDC_MOF

TED
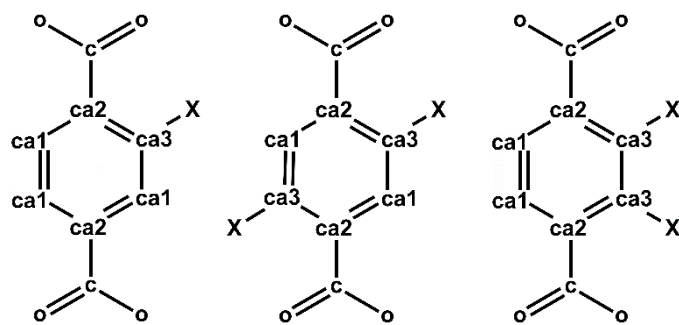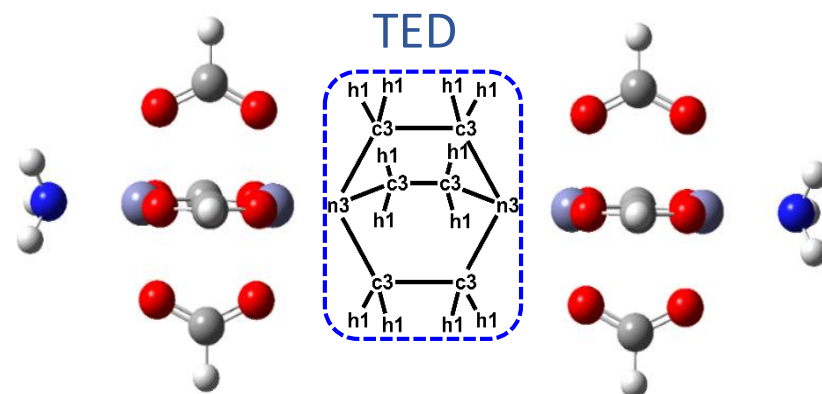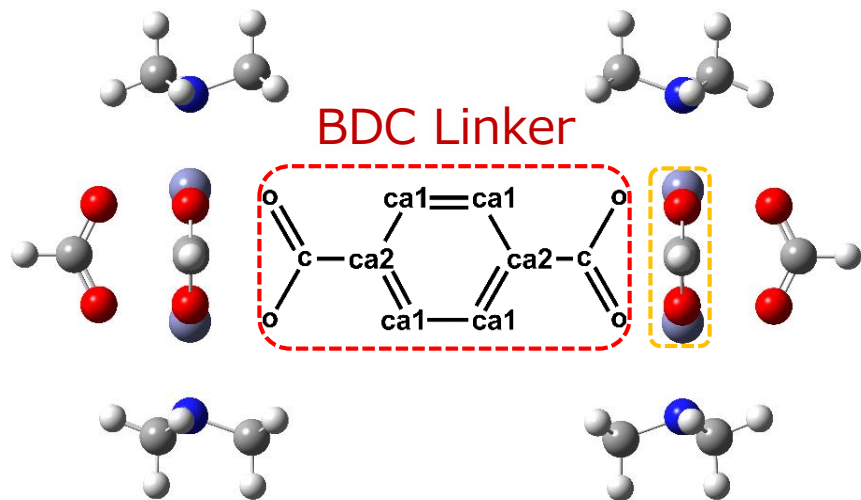
Zn   BDC linker

Mono-   2,5 di-   2,3 di-

X = F, Cl, Br, CH_3, NH_2, OCH_3
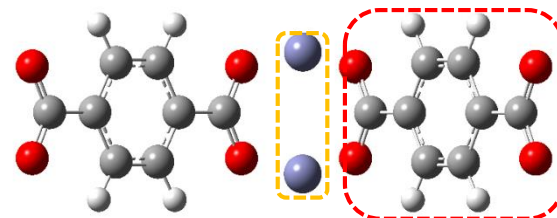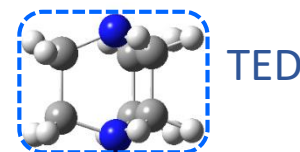
The total charge of unit cell is zero.

*The charge distribution of BDC linker is changed by different substituents*

The flexible force field parameters of BDC model without substituent have been already reported.[1]

For substituted BDC models (F, Cl, Br, CH_3, NH_2 and OCH_3), FF parameters are optimized by fitting the relative energy differences and optimized structure to DFT calculation.

4 optimized conformation (by rotating TMA cap at 0, 30, 30_1 and 60 degree, respectively).

4 partially relaxed scan with 10 degree interval for 10 times.

In total, 44 conformations used for MM optimization on each substituted model.

TMA _at 30°

TMA _at 30_1°

1. Paesani, F. et al., *J. Am. Chem. Soc.* **2012**, *134*, 4207.
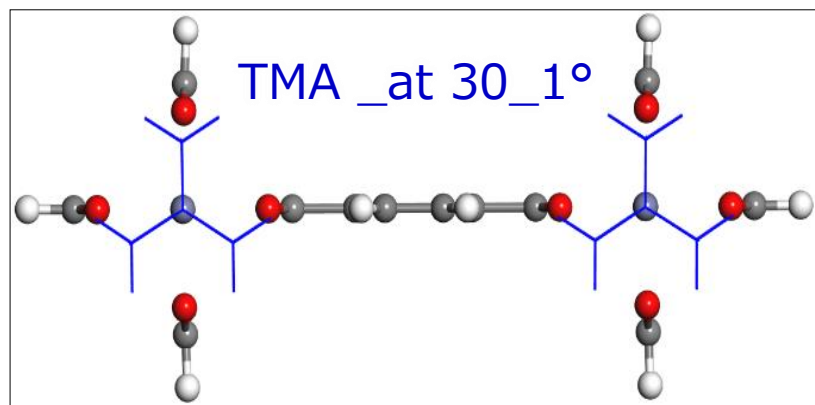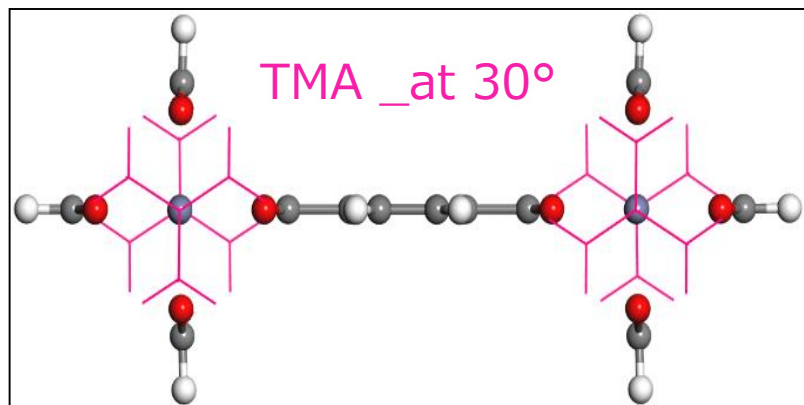
Force field Fitting

The procedure of FF fitting:

All parameters FF fitting simultaneously

```
Bond and angle
      ↓
Dihedral angle
      ↓
All parameters FF fitting
simultaneously
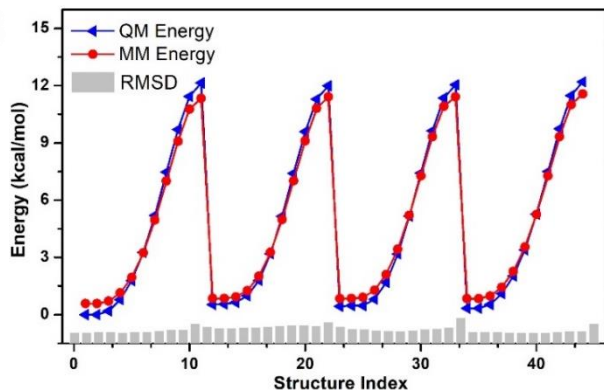```

```
Dihedral angle
      ↓
Bond and angle
      ↓
All parameters FF fitting
simultaneously
```

The order of FF fitting is determined by the initial evaluation score on each model
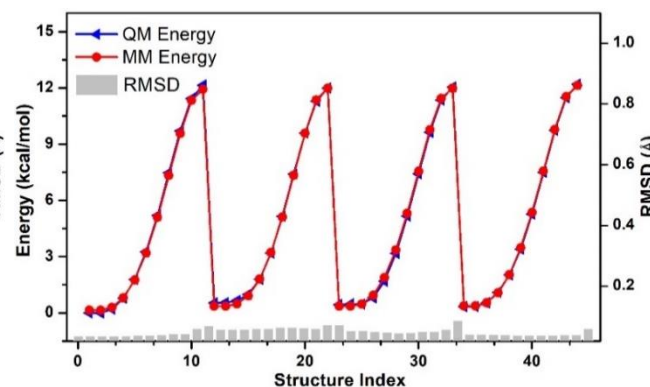
The initial FF parameters of mono-case is good enough

All parameters FF fitting simultaneously

Evaluation score = 0.097785

Mono-F before fitting

Evaluation score = 0.058977

Mono-F after fitting

Not ending………

Summary

1. The ligand-dependent equilibrium planar or nonplanar structure depends on the substituents (F, Cl, Br, NH_2, CH_3, OCH_3).

   The planar structure will have confinement effect on PMMA, in contrast, PMMA polymerization can diffuse in three dimensional direction.

2. The polarity or the charge distribution in BDC linker is changed by different substituents.

   The different electrostatic attraction or repulsion between PMMA and MOF pore surface will affect the localization of PMMA.

3. The bulky substituents (NH_2, CH_3 and OCH_3) will fill the pore space, resulting in the narrower channel than the halogen substituents.

   The steric hindrance between bulky substituents and PMMA may exist.

The above factors may play important roles in the tacticity control of PMMA polymerization in MOF channel by different substituents