Supporting Information

How External Forces Affect the Degradation Properties of Perfluorooctanoic Acid in Mechanochemical Degradation: A DFT

Study

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S1 Details of Quantum Chemical Calculations

S1.1 Hardware Configuration for Computations

The quantum chemical calculations for this study were conducted on the "Hohhot Light" high-performance computing public service platform in Inner Mongolia Autonomous Region, China. The hardware configuration is as follows: 36 computing cores and 60 GB of memory. Computational tasks were submitted using SLURM batch scripts, with a typical example of an SLURM script provided below:

#!/bin/bash

#SBATCH --job-name=Test #SBATCH -o Test%j.out #SBATCH -e Test%j.err #SBATCH --partition=cnCPU #SBATCH --partition=cnCPU #SBATCH --ntasks=1 #SBATCH --cpus-per-task=36 srun g16 PFOA_SP.gjf printf "Mission complete"

S1.2 Computational Process for Conceptual Density Functional Theory

The calculation process for Conceptual Density Functional Theory (CDFT) is as shown in Figure S1:

(1) Preparation of Wavefunction Files: Wavefunction files (in .wfn format) are required for the system's N (neutral state), N+1 (anionic state), and N-1 (cationic state) electronic states.

(2) Utilization of Multiwfn Software: The N, N+1, and N-1 wavefunction files are loaded using Multiwfn software, specifically by accessing the main function 22 to enter the CDFT calculation module.

(3) Types of CDFT Indices Calculated in This Study:

Global descriptors: Including Mulliken electronegativity, softness, electrophilicity index, nucleophilicity index, etc.

Real-space functions: Encompassing Fukui functions, dual descriptors, etc.

(4) Calculation Details in Multiwfn: The program reads energy information and wavefunction data from the loaded wavefunction files, calculates Hirshfeld charges, and computes various indices. Different grid qualities can be selected for the calculation; considering computational time and cost, this study opted for a medium-quality grid.

(5) Output of Results: The calculation results are outputted to a text file (e.g., CDFT.txt), which includes all the calculated quantities mentioned above. For real-space functions, isosurface plots can be directly generated within Multiwfn for visualization.



Figure S1 Flowchart of CDFT Calculations

S2 Python Script for Data Extraction

Quantum chemistry calculations typically yield extensive results presented in voluminous text files. In this study, the cogef model involved a large number of sampling points, which consequently generated a multitude of result files. This situation led to a significant workload in collecting and organizing the required computational data. To enhance the efficiency of gathering calculation results and minimize the manual processing effort, we have developed several Python scripts to assist in data collection and organization.

S2.1 Collect and integrate results from COGEF model

The following code is capable of integrating data from all log files generated by sampling point calculations within the "Data" folder at the root directory of the C drive. The aggregated results are then compiled into a single text file named "resultAll.txt".

import os,re,datetime,shutil
import pandas as pd
import numpy as np
def txtWrite(data,filePath,encoding='utf-8'):
 file=open(filePath,'w',encoding=encoding)

file.write(data) #data = f.read()

file.close

return data[:20],data[-20:],filePath

def log2txt(fileName):

with open(fileName,'r') as f1:

txt1=f1.read()

input1=re.search('Input=(.*?\n)',txt1).group(1)

keywords=re.search(' # ([\s\S]*?\n) ---',txt1).group(1).replace('\n ',")

```
charge=re.search( '(Charge.*?Multiplicity.*?\n)',txt1).group(1)
```

HF=re.findall('(SCF Done: E.*?)\n',txt1)

 $HF=[f'{i+1}-{HF[i]}' \text{ for } i \text{ in range}(0,len(HF))]$

HF1='\n'.join(HF)+'\n'

pattern = r"Dipole moment \(field-independent basis, Debye\):\n (.*?) Quadrupole moment"

dipole = re.search(pattern, txt1, re.DOTALL).group(1)

if 'Normal termination' in txt1:

termination='normal\n'

date=re.search('Normal termination of Gaussian 16 at(.*?\n)',txt1).group(1)

else:

termination='error\n'

date=re.search('Error termination.*?at (.*?\n)',txt1).group(1)

date

```
txtOut=".join([termination,date,input1,charge,HF1,dipole])
```

return txtOut

def log2txtCoGEF(fileName):

with open(fileName,'r') as f1:

txt1=f1.read()

input1=re.search('Input=(.*?\n)',txt1).group(1)

 $keywords=re.search(' # ([\s\S]*?\n) ---',txt1).group(1).replace('\n','')$

charge=re.search('(Charge.*?Multiplicity.*?\n)',txt1).group(1)

HF=re.findall('(SCF Done: E.*?)\n',txt1)

 $HF=[f'{i+1}-{HF[i]}' \text{ for } i \text{ in } range(0,len(HF))]$

```
HF1='\n'.join(HF)+'\n'
```

step=re.findall('(Step number.*?)\n',txt1)

if not step:

step=['step number ']

```
listData=list(zip(step,HF))
```

listData1='\n'.join([i[0]+'\n'+i[1] for i in listData])

```
if 'Normal termination' in txt1:
```

termination='normal\n'

date=re.search('Normal termination of Gaussian 16 at(.*?\n)',txt1).group(1)

else:

termination='error\n'

try:

date=re.search('Error termination.*?at (.*?\n)',txt1).group(1)

except:

date='0000-0000\n'

txtOut=".join([termination,date,input1,charge,listData1])

return txtOut

S2.2 Collect and integrate results from CDFT calculations

The following code is designed to process all CDFT calculation result files located in the "data" folder at the root directory of the C drive. It collects and consolidates all the computational results, which are then stored into an Excel file named "CDFT.XLSX". The first row of this Excel file contains the headers for each data column, such as "Vertical IP", "Vertical EA", "electronegativity", and so on.

```
import os, re
import pandas as pd
import numpy as np
os.chdir(r'C:\data')
def output(txt):
    pattern = r":(.*?)Hartree"
```

```
output1=re.search(pattern, txt,re.DOTALL).group(1).strip()
```

return output1

def getINFO(file1):

list1=[]

with open(file1, 'r', encoding='utf-8') as file:

for line in file:

list1.append(line.strip())

```
ser1=pd.Series(list1[-14:])
```

```
out1=ser1.apply(output)
```

return list(out1)

list1=[]

listN=[]

for i in os.listdir():

if '.txt' in i:

print(i)

list1.append(getINFO(i))

```
listN.append(i)
```

columns=['E(N)', 'E(N+1)', 'E(N-1)', 'E_HOMO(N)', 'E_HOMO(N+1)', 'E_HOMO(N-1)', 'Vertical IP', 'Vertical EA','electronegativity', 'Chemical potential', 'Hardness', 'Softness', 'Electrophilicity', 'Nucleophilicity']

df1=pd.DataFrame(list1,columns=columns,index=listN,dtype=float)

ratio=27.211386

df2=df1*ratio

df2['E(N)']=df2['E(N)']/ratio

df2['E(N+1)']=df2['E(N+1)']/ratio

df2['E(N-1)']=df2['E(N-1)']/ratio

df2['Softness']=df2['Softness']/ratio

df2.to_excel('cdft.xlsx')

S3 Cartesian coordinates of PFOA

The coordinates of the PFOA molecule in its initial state and under the influence of an external force are shown in Tables S1 and S2, respectively.

NO.	Atom	Х	Y	Z
0	С	4.33145974	-0.15926755	0.05993432
1	С	2.97490603	0.57400019	-0.22225580
2	С	1.71716083	-0.32335329	0.02417858
3	С	0.36056001	0.45347307	-0.06425330
4	С	-0.89834546	-0. 47699061	-0.06316932
5	С	-2.25003191	0.29159780	0.11848857
6	С	-3. 52177658	-0. 58404987	-0.13172563
7	С	-4.83627125	0.09846485	0.29904915
8	0	-4.60258399	1.42306321	0.34428459
9	Н	-5.39418258	1.96601703	0.61127267
10	0	-5.86564257	-0. 45050981	0.54704789
11	F	-3. 59669403	-0.91019872	-1.42327201
12	F	-3. 40874814	-1.75079369	0.50416882
13	F	-0.92696396	-1.17939523	-1.19618440
14	F	-0.77720368	-1.39467512	0.89667622
15	F	1.71802371	-1.33252613	-0.84713265
16	F	1.81432463	-0.91058865	1.21749128
17	F	4.44655527	-1.28541112	-0.63053422
18	F	4.47043307	-0. 48272109	1.33823649
19	F	5.38098019	0.58568992	-0.25644712
20	F	2.90437319	1.67286795	0.52880333
21	F	2.96916312	1.02221614	-1.47755642
22	F	0.28374092	1.32005383	0.94601314
23	F	0.34917470	1.21330647	-1.15974136
24	F	-2.30191732	0.80474653	1.34873990
25	F	-2.27571791	1.35068009	-0. 69035764

Table S1 Molecular coordinates of PFOA at F=0 nN

NO.	Atom	Х	Y	Z
0	С	4. 32811548	-0.16328379	0.06958969
1	С	2.97362393	0.56952727	-0.22335924
2	С	1.71362949	-0.32308460	0.02870707
3	С	0.35875363	0.45556916	-0.06955622
4	С	-0.90200688	-0. 47232789	-0.06529135
5	С	-2.25244822	0.29935592	0.11299418
6	С	-3. 52517633	-0.56976821	-0.15076906
7	С	-4.84041075	0.08501593	0.33994198
8	0	-4.60188784	1.42814841	0.30548681
9	Н	-5.37833478	1.97841323	0.59603353
10	0	-5.81199823	-0. 54103294	0.66209061
11	F	-3.62521488	-0.83515177	-1.45424309
12	F	-3.39500993	-1.76413446	0.42736944
13	F	-0.93184907	-1.17890384	-1.19569264
14	F	-0.78266819	-1.38663480	0.89802663
15	F	1.71428942	-1.34016644	-0.83334662
16	F	1.80727398	-0.89954716	1.22754028
17	F	4.44302401	-1.29642203	-0.60937578
18	F	4. 46333588	-0.47428570	1.35138375
19	F	5.37980716	0.57663603	-0.25144683
20	F	2.90319853	1.67592531	0.51657056
21	F	2.97198705	1.00528512	-1.48304937
22	F	0.28056915	1.32971327	0.93412135
23	F	0.35220556	1.20744772	-1.17056187
24	F	-2.30971469	0.80473051	1.34649020
25	F	-2.26831748	1.36467201	-0.68789892

Table S2 Molecular coordinates of PFOA at F=0.025 nN

S4 Impact of External Forces on PFOA

S4.1 Impact of External Forces on the Bond Angles and Lengths

In the initial state, the atoms on the carboxylate group are essentially coplanar. When subjected to an external force of 0.025 nN, the primary bond angles exhibit significant changes in the data (as shown in Figure S2), yet the data atoms largely remain coplanar. The changes in bond lengths and bond orders of the chemical bonds at the carboxylate end are shown in Table S3 (comparing the data in Table S3 with that in Table S1).



Figure S2 The influence of external forces on the bond angles of the carboxylate group in the PFOA molecule: (a) F = 0 nN; (b) F = 0.025 nN

	Table S3 Cl	nemical bond	properti	es of the	e PFOA	molecule	under the	e influence	of external	forces
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	Bond	length	Bond order		
	Maximum value	Minimum value	Maximum value	Minimum value	
С-О	1.36458(C8-O9)	1.19987(C8- 011)	1.91834(C8- O11)	1.06324(C8-O9)	
C-C	1.56763(C1-C2)	1.54899(C7-C8)	0.87588(C5-C6)	0.85011(C2-C3)	
C-F	1.33424(C6-F25)	1.32537(C1-F20)	1.04537(C1-F19)	0.93741(C6-F26)	

S4.2 Impact of External Forces on the Electron Localization Function

Regions with high electron localization values are typically associated with atomic nuclei, covalent bonds, lone pairs, and atomic shell structures. Electrons in these areas are highly localized and less likely to escape, while they can move freely within such regions. Through ELF analysis, a deeper understanding of the electronic behavior and reactivity of molecules can be achieved^[1-3]. In general, the areas with high electron localization values on the carboxylate group are mainly concentrated in the π -bond region of the carbonyl group, the O-H bond region of the hydroxyl group, the σ -bond regions around the carbon atom, and the lone pair regions on the oxygen atom. Comparing Figure S3a with Figure S3b, we observe that the external force has no significant effect on the electron localization function at the carboxylate end. This suggests that the electron localization function is not a good assessment indicator when studying the impact of external forces on the chemical properties of PFOA molecules. This is because for fill-color maps like those in Figure S, we can only perform qualitative analysis to fully demonstrate the impact of external forces on the chemical properties of PFOA. Consequently, in the main text, we chose the bond order of the C-C bond for a quantitative presentation.



Figure S3 The influence of external force on the electron localization function of the carboxylate group in the PFOA molecule: (a) F = 0 nN; (b) F = 0.025 nN

S4.3 Impact of External Forces on the Fukui Functions

The Fukui function is a core concept within the framework of Conceptual Density Functional Theory (CDFT), proposed by Kenichi Fukui, to describe the chemical reactivity of molecules. Primarily used to analyze the local reactivity of molecules, the Fukui function aids chemists in understanding which sites within a molecule are more prone to engage in reactions, such as undergoing attack or being attacked^[4,5]. From the perspective of Conceptual Density Functional Theory (CDFT), we have calculated the impact of external forces on the PFOA molecule. The CDFT computational results indicate that , the primary reactive sites of the PFOA molecule are located in the vicinity of the carboxylic group. Upon the application of external forces, there is no significant change in the reactive sites. This can be visualized through the three-dimensional isosurface plots of f⁺, f⁻, and f0, as depicted in Figure S4. In the main text, to more succinctly present the aforementioned results, we employed the dual descriptor function within the CDFT. This plot allows for the co-presentation of electrophilic and nucleophilic sites, among other information, on a single graph.



Figure S4 The influence of external force on the electron localization function of the carboxylate group in the PFOA molecule: (a) F = 0 nN; (b) F = 0.025 nN

References

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