Supporting information for

Theoretical Insight into the Redox-switchable Activity of Group 4 Metal Complexes for the Ring-Opening Polymerization of ε-Caprolactone

Xiaowei Xu,[a] Gen Luo,[a,*] Zhaomin Hou,[b] Paula L. Diaconescu,[c,*] Yi Luo[a,*]

Table of contents

Fig. S1 (a) SOMO of the three oxidized active species (isovalue = 0.04) and (b) Mulliken spin densities (isovalue = 0.003) of the three oxidized active species.

Fig. S2 Relaxed potential energy surface (PES) scan for the dihedral angel of Ti-O1-C-O2 (step size = 10°, number of steps = 8) of 2_a^{ox} /2_a^{red} at the DFT/BSI level.
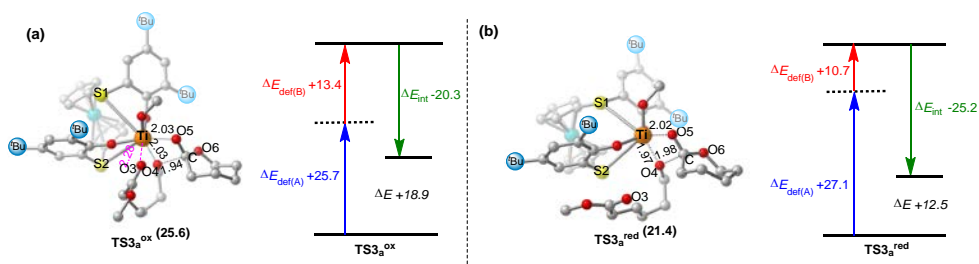
Fig. S3 Optimized structures (distances in Å) and distortion/interaction analysis of **TS3a^{ox}** and **TS3a^{red}**. Values in parentheses are the relative Gibbs free energy barriers. Energies are given in kcal mol^{-1}.

The energy distortion/interaction analyses (Fig. S3) of the transition states $\textbf{TS3}_\textbf{a}^\textbf{red}$ and $\textbf{TS3}_\textbf{a}^\textbf{ox}$ show that the interaction energy (ΔE_{int}) between the incoming CL moiety and the remaining metal complex mainly accounts for the stability difference between the two transition states (-20.3 kcal mol^{-1} for $\textbf{TS3}_\textbf{a}^\textbf{ox}$ vs -25.2 kcal mol^{-1}for $\textbf{TS3}_\textbf{a}^\textbf{red}$, Fig. 5). The more negative value of ΔE_{int} for $\textbf{TS3}_\textbf{a}^\textbf{red}$ could be ascribed to the existence of an additional chelation effect between the metal center and the carbonyl oxygen (Ti···O3 = 2.28 Å) that relatively weakens the interaction between the metal center and the incoming CL moiety (Ti···O5 = 2.03 Å and C···O4 = 1.94 Å, Fig. S3) due to steric properties.
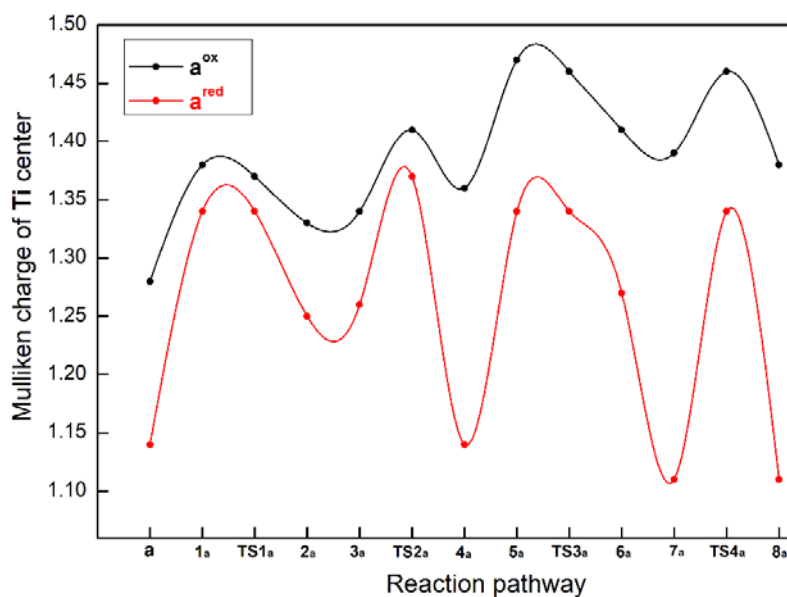
Fig. S4 Mulliken charges on the catalytic metal center in the stationary points involved in the $\textbf{a}^\textbf{ox}$ and $\textbf{a}^\textbf{red}$ mediated reaction pathways.
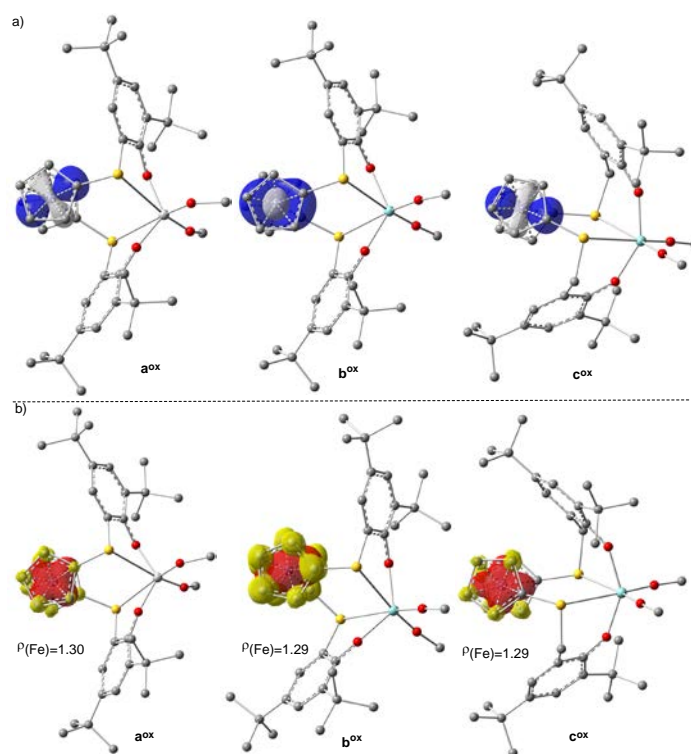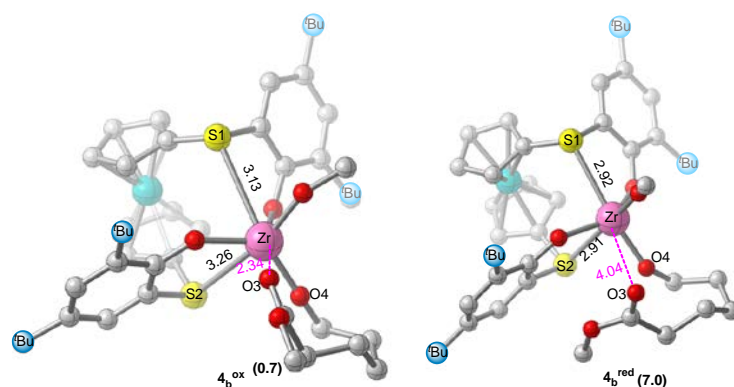

Fig. S5 Optimized structures (distances in Å) and energies (kcal mol^{-1}) of the insertion and ring-opening products $\textbf{4}_\textbf{b}^\textbf{ox}$ and $\textbf{4}_\textbf{b}^\textbf{red}$ of the first monomer. Values in parentheses are the Gibbs free energies (kcal mol^{-1}) in solution relative to the isolated reactants.
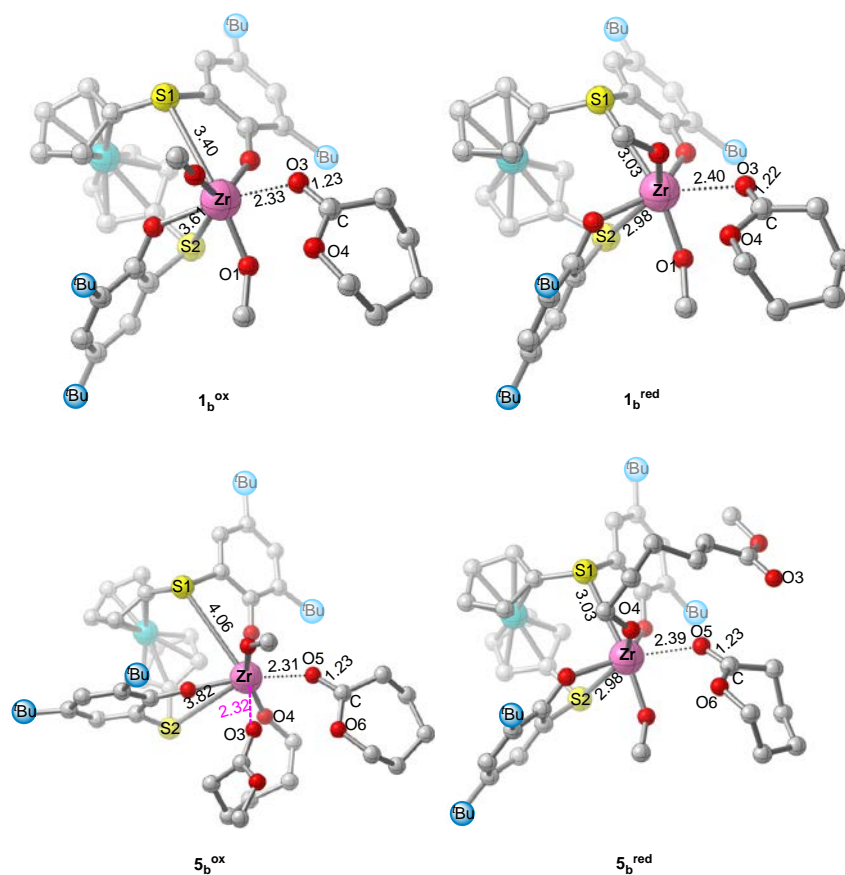
Fig. S6 Optimized structures (distances in Å) of the coordination complexes **1$_b^{ox}$** *vs* **1$_b^{red}$** and **5$_b^{ox}$** *vs* **5$_b^{red}$**.
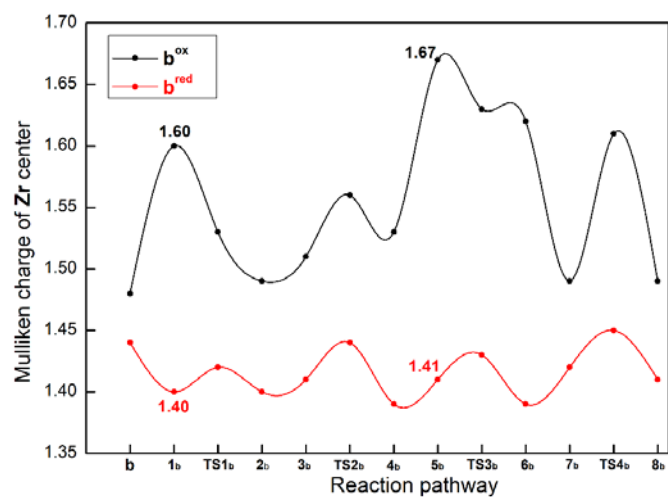
Fig. S7 Mulliken charges on the catalytic metal center of the stationary points involved in the **b^{ox}** and **b^{red}** mediated reaction pathways.
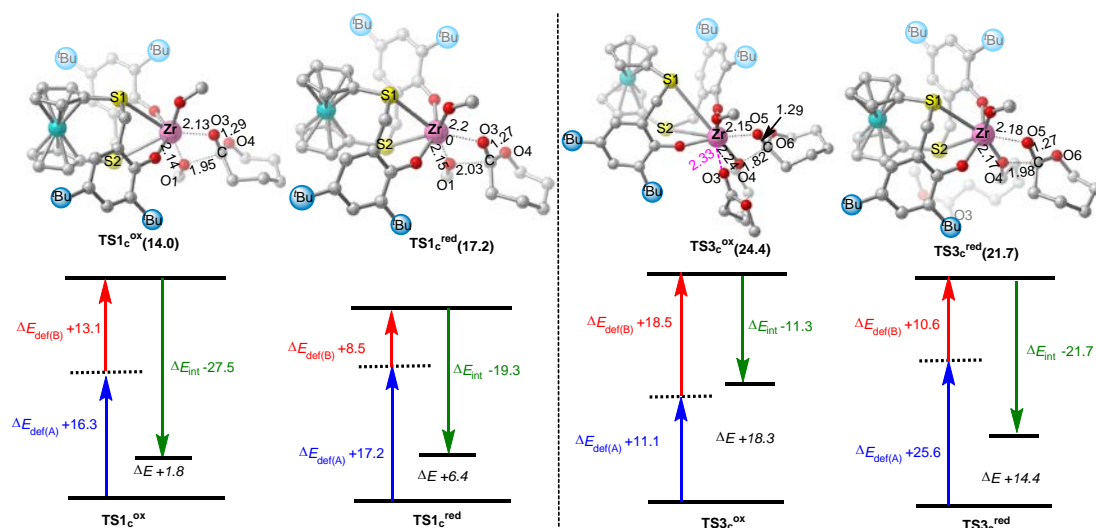
Fig. S8 Optimized structures (distances in Å) and distortion/interaction analysis (kcal mol^{-1}) of the four key transition states (**TS1$_c^{ox}$** *vs* **TS1$_c^{red}$**, **TS3$_c^{ox}$** *vs* **TS3$_c^{red}$**). Values in parentheses are the relative free energy barriers in solution (kcal mol^{-1}).
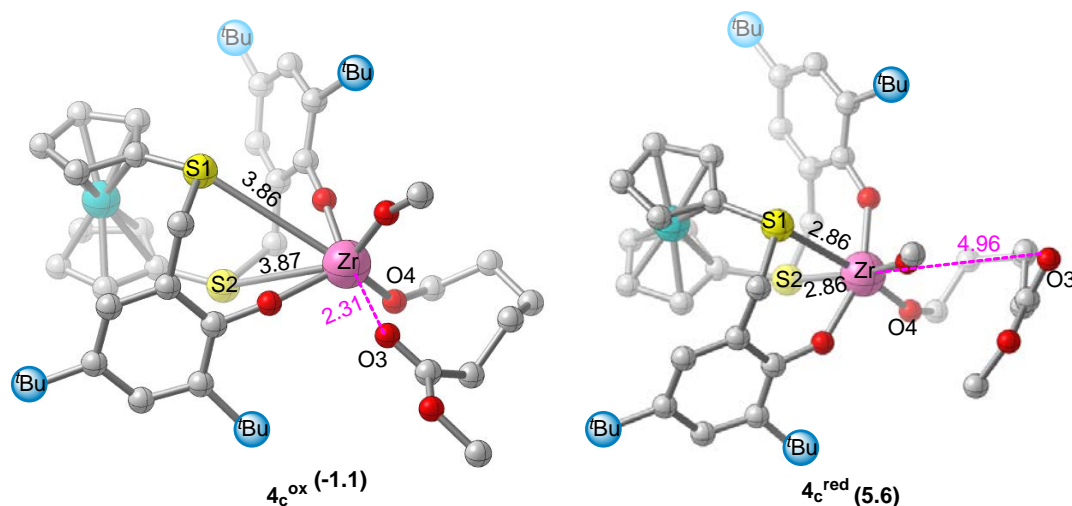
Fig. S9 Optimized structure (distances in Å) and energy (kcal mol^{-1}) of the insertion and ring-opening products **4$_c^{ox}$** and **4$_c^{red}$** of the first monomer. Values in parentheses are the relative Gibbs free energies (kcal mol^{-1}) with respect to the sum of isolated reactants.

Fig. S10 Optimized structures (distances in Å) of transition states **TS4$_c^{ox}$** and **TS4$_c^{red}$**. Values in parentheses are the relative Gibbs free energies (kcal mol^{-1}) in solution with respect to isolated reactants.
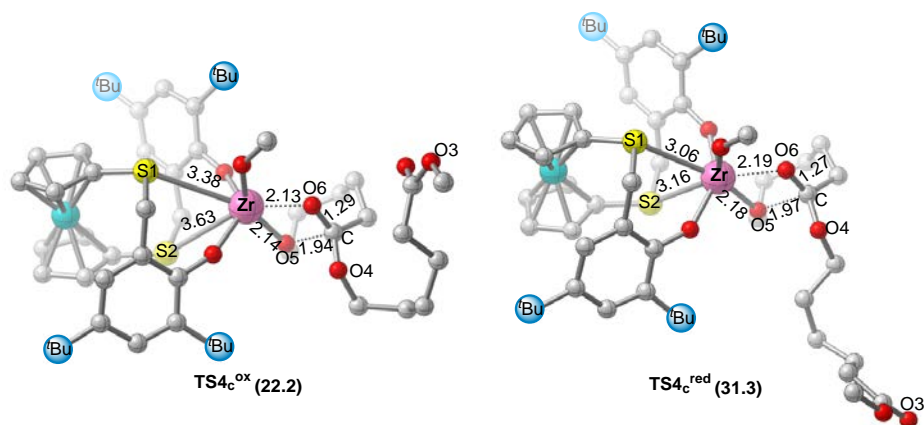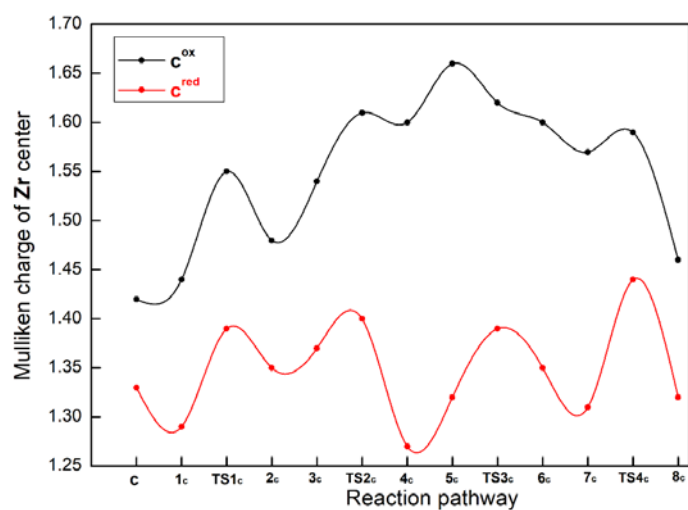

Fig. S11 Mulliken charges on the catalytic metal center in the stationary points involved in the **c^{ox}** and **c^{red}** mediated reaction pathways.
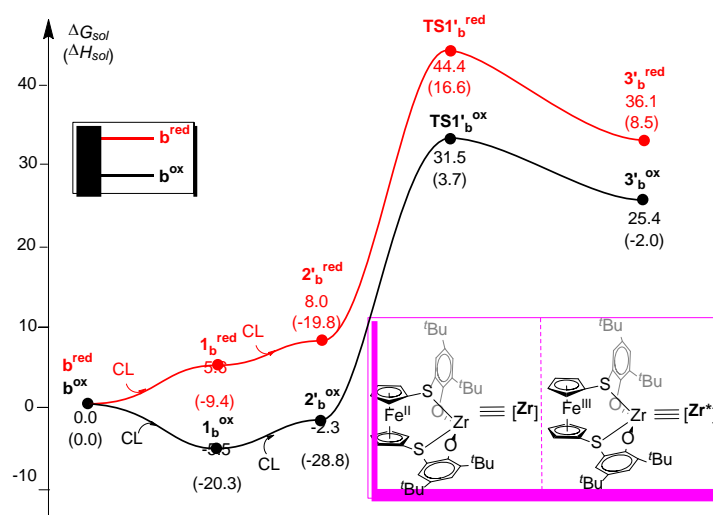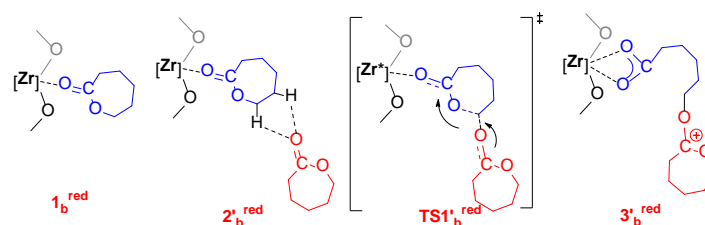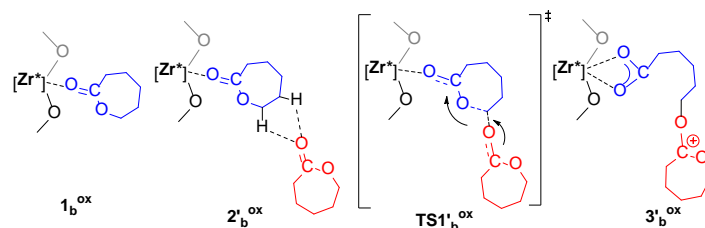
Fig. S12 Free energy profiles for the possible pathway of ROP of CL with C=O bond cleavage mediated by $\mathbf{b^{ox}}$ and $\mathbf{b^{red}}$.

Table S1 Wiberg bond orders in $\mathbf{b^{red}}$, $\mathbf{c^{red}}$, $\mathbf{b^{ox}}$, and $\mathbf{c^{ox}}$.
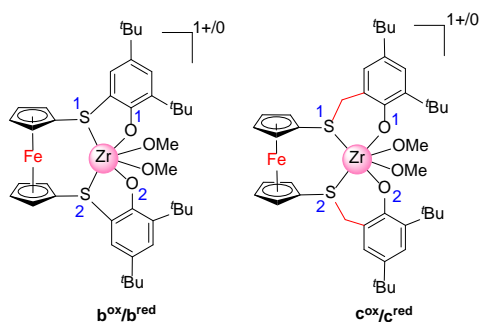
	Zr-S1	**Zr-S2**	**Zr-O1**	**Zr-O2**	**total**
$\mathbf{b^{red}}$	0.41	0.41	0.81	0.81	2.44
$\mathbf{c^{red}}$	0.45	0.45	0.61	0.61	2.12
$\mathbf{b^{ox}}$	0.08	0.08	0.22	0.22	0.60
$\mathbf{c^{ox}}$	0.09	0.09	0.15	0.15	0.48

Table S2 Relative electronic energies (ΔE, kcal/mol) of various spin states of active species.

catalyst	spin states	ΔE	catalyst	spin states	ΔE
a^{red}	singlet (closed-shell)	0.0	**a**^{ox}	doublet	0.0
	singlet (open-shell)	0.0		quartet	16.3
	triplet	20.4		sextet	26.4
	quintet	19.4			
	septet	76.2			
b^{red}	singlet (closed-shell)	0.0	**b**^{ox}	doublet	0.0
	singlet (open-shell)	0.0		quartet	8.9
	triplet	34.6		sextet	17.8
	quintet	12.7			
	septet	91.8			
c^{red}	singlet (closed-shell)	0.0	**c**^{ox}	doublet	0.0
	singlet (open-shell)	0.0		quartet	15.5
	triplet	19.0		sextet	29.6
	quintet	18.2			
	septet	85.9			

Examples of the input files

%chk=a_red.chk
%mem=8GB
%nproc=32
#p opt=(cartesian) freq=noraman ub3pw91/genecp EmpiricalDispersion=GD3

int

1 2
Ti	-0.56714100	1.85893700	0.53939700
Fe	0.88255000	-2.65768700	-1.68406800
S	-0.12170500	-1.34893200	1.38945800
S	1.58201600	0.76481300	-2.04896500
…			
O	-0.57552200	3.00756000	-0.97854700
O	-0.78631300	3.76848200	1.32457800

C H O S 0
6-31G(d)
****
Fe Ti 0
lanl2dz
****

Fe Ti 0
lanl2dz

%chk=TS1_red.chk
%mem=8GB
%nproc=24
#p opt=(calcfc,ts,cartesian,noeigentest) ub3pw91/genecp EmpiricalDispersion=GD3
freq=noraman

ts

1 2
Ti	-0.56824600	1.83473500	0.58460500
Fe	0.87774000	-2.64571500	-1.70823800
S	-0.15523400	-1.38551900	1.38228500
S	1.61760500	0.77306000	-2.03839500
…			
O	-0.52383400	3.09241600	-0.92429500
O	-0.76116700	3.70175900	1.30211000

C H O S 0
6-31G(d)
****
Fe Ti 0
lanl2dz
****

Fe Ti 0
lanl2dz

%chk= TS1_red_s.chk
%mem=8GB
%nproc=24
#p um06/genecp scrf=(cpcm, solvent=benzene)

sp

1 2
Ti   -0.92878300   1.59215800   0.43882800
Fe   1.87471800   -2.46476300   -1.19753900
S   0.28651500   -1.09873600   1.60853200
S   1.36659000   0.85776200   -2.17937100
…
O   -3.45683900   2.97849900   -0.42004300
O   -1.47870800   3.37635400   0.54665500

C H O S 0
6-311G(d,p)
****
Ti Fe 0
MDF10
****

Ti Fe 0
MDF10