

**DENSITY FUNCTIONAL THEORY STUDIES OF REACTION MECHANISMS
FOR TITANIUM ALKYLAMIDE INCORPORATION ONTO
FUNCTIONALIZED AROMATIC SELF-ASSEMBLED MONOLAYERS**

SUPPORTING INFORMATION

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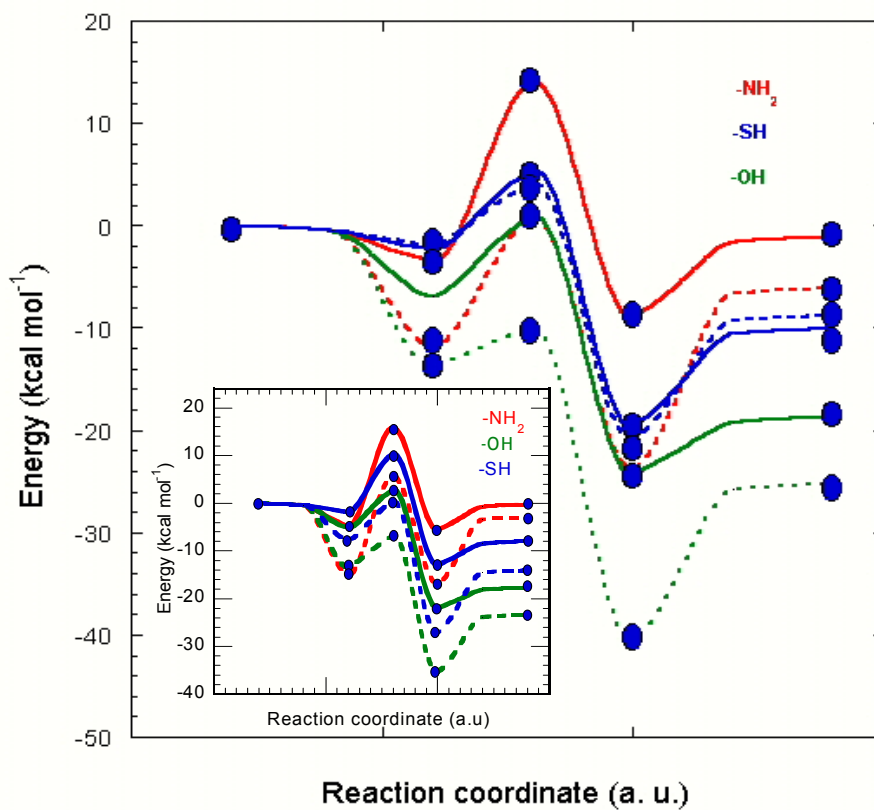


Figure S1 Potential energy diagram (PED) for reaction of Titanium tetramide on -NH₂, -OH and -SH SAMs at MP2/6-311G(D)//B3LYP/6-311G(D) (dashed lines) and B3LYP/6-311++G(D,P)//B3LYP/6-311G(D)(solid lines) model chemistries. The insert represents the corresponding PED on alkyl SAMs.

Figure 2

RXH(Terminal Group)	NH ₂		OH		SH	
	ALKYL	ARYL	ALKYL	ARYL	ALKYL	ARYL
R=CH ₃ CH ₂ /C ₆ H ₅						
Ti(NH ₂) ₄ +RXH(Vacuum)	0.00	0.00	0.00	0.00	0.00	0.00
Ti(NH ₂) ₄ ---HXR (Adduct)	-6.82	-11.83	-9.43	-13.81	-4.44	-7.07
Ti(NH ₂) ₄ ---H-- XR(Transition)	8.96	0.78	-3.40	-9.93	3.71	-1.12
Ti(NH ₂) ₃ -RX--H--NH ₂	-8.71	-23.67	-27.93	-40.47	-14.18	-26.25
Ti(NH ₂) ₃ RX+NH ₃ (Product)	-1.87	-6.03	-21.34	-25.15	-7.96	-12.91

Figure 3

XH(Terminal Group)	NH ₂		OH	
	B3LYP	MP2	B3LYP	MP2
TDMAT+RXH(Vacuum)	0.00	0.00	0.00	0.00
TDMAT---HXR (Adduct)	-2.83	-11.46	-5.02	-13.91
TDMAT---H-- XR(Transition)	18.06	3.48	0.28	-9.40
Ti(N(CH ₃) ₂) ₃ -RX--H-- N(CH ₃) ₂	-4.91	-13.78	-35.59	-54.56
Ti(N(CH ₃) ₂) ₃ RX +HN(CH ₃) ₂	-3.53	-5.16	-21.48	-22.15

Figure 5

	1Methylaniline B3LYP MP2	Aniline B3LYP MP2	Branched Fluoryl B3LYP	Isopropylaniline B3LYP	Unbranched B3LYP	Branched Alkylamine B3LYP
TDMAT+RXH(Vacuum)	0.00	0.00	0.00	0.00	0.00	0.00
TDMAT---HXR (Adduct)	-1.45	-3.12	-4.99	-0.94	0.37	-0.50
TDMAT---H-- XR(Transition)	25.02	15.62	4.80	28.45	16.96	-1.73
Ti(N(CH ₃) ₂) ₃ -RX--H-- N(CH ₃) ₂	-0.27	-6.23	-8.29	1.20	-1.14	21.24
Ti(N(CH ₃) ₂) ₃ RX +HN(CH ₃) ₂	1.52	-3.32	-5.41	4.06	-0.28	-1.58

Figure 7

Pathway	Isopropylaniline			Aniline
	2	4	3	3
Reactant	0.00	0.00	0.00	0.00
Activated complex	30.96	37.17	38.75	43.02
Adduct	16.08	21.67	21.59	22.56
Product	36.00	26.00	39.92	47.80

Figure 8

Complex Pathway	Isopropylaniline			Aniline	Isobutylaniline
	2	4	3	3	4
Reactant	0.00	0.00	0.00	0.00	0.00
Activated complex	30.96	37.17	38.75	43.02	33.74
Adduct	16.08	21.67	21.59	22.56	18.60
Product	36.00	26.00	39.92	47.80	19.19
Imine-product		49.00			27.69