

**Organic-Inorganic Hybrid Catalysts Containing New Schiff Base for Environment Friendly
Cyclohexane Oxidation**

R. Antony,[†] S. Theodore David Manickam,^{*,†} K. Karuppasamy,[†] and Pratap Kollu,[‡]
V. Chandrasekar[§]

[†]Centre for Scientific and Applied Research, PSN College of Engineering and Technology
(Autonomous), Tirunelveli-627152, Tamil Nadu, India

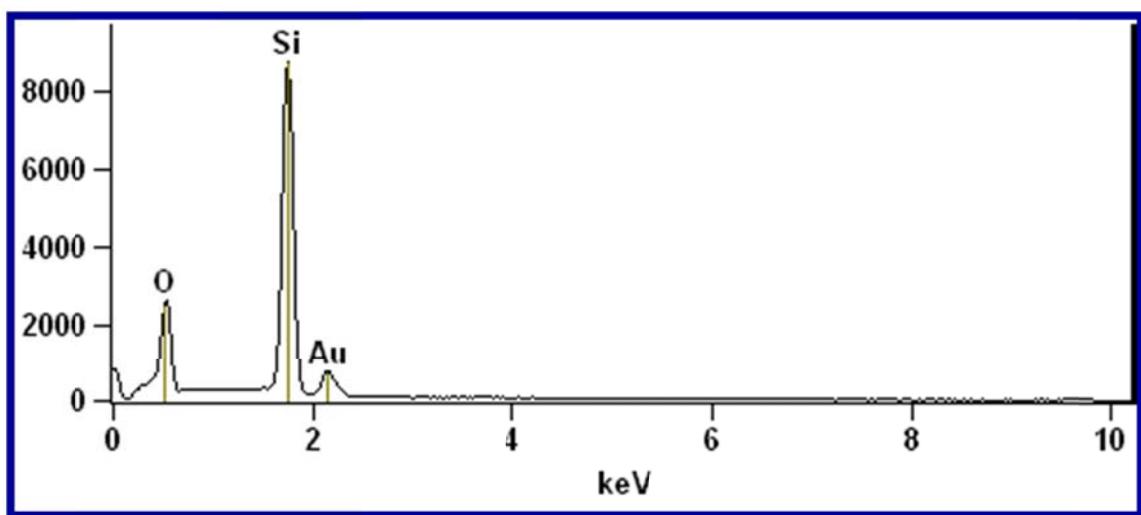
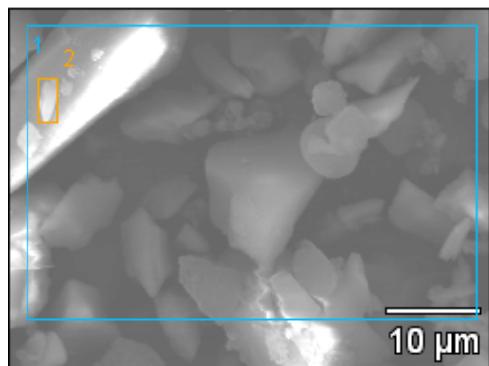
[‡]Department of Metallurgical Engineering and Material Science, Indian Institute of Technology
Bombay, Mumbai-400076, India

[§]College of Physics and Information Engineering, Institute of Optoelectronic Display, Fuzhou
University, Fuzhou-350002, PR China

Table of Contents

1. EDS analysis of SiO₂ Gel
2. EDS analysis of Si-NH₂
3. EDS analysis of Si-NH₂-DPED
4. EDS analysis of [Cu(Si-NH₂-DPED)Cl₂]
5. EDS analysis of [Co(Si-NH₂-DPED)Cl₂]
6. EDS analysis of [Ni(Si-NH₂-DPED)Cl₂]
7. UV-Vis. spectrum of SiO₂ gel (**Fig. S1**)
8. UV-Vis. Spectrum of Si-NH₂ (**Fig. S2**)
9. ²⁹Si CP MAS NMR spectrum of Si-NH₂-DPED (**Fig. S3**)
10. ²⁹Si CP MAS NMR spectrum of [Cu(Si-NH₂-DPED)Cl₂] (**Fig. S4**)
11. TG-DTG curves of SiO₂ gel (**Fig. S5**)
12. TG-DTG curves of Si-NH₂ (**Fig. S6**)
13. SEM image of SiO₂ gel (**Fig. S7**)
14. SEM image of Si-NH₂ (**Fig. S8**)
15. Synthetic Scheme of Complexes (**Fig. S9**)
16. Influence of reaction time on cyclohexane oxidation catalyzed by Cu(II), Co(II) and Ni(II) hybrid catalysts (**Table 1**)
17. Mechanism of cyclohexane oxidation
 - i. UV-Vis. spectrum of the mixture ([Cu(Si-NH₂-DPED)Cl₂], H₂O₂, HNO₃ and CH₃CN) (**Fig. S10**)
 - ii. Magnified UV-Vis. spectrum of the mixture ([Cu(Si-NH₂-DPED)Cl₂], H₂O₂, HNO₃ and CH₃CN) (**Fig. S11**)
 - iii. UV-Vis. spectrum of the mixture ([Co(Si-NH₂-DPED)Cl₂], H₂O₂, HNO₃ and CH₃CN) (**Fig. S12**)
 - iv. UV-Vis. spectrum of the mixture ([Ni(Si-NH₂-DPED)Cl₂], H₂O₂, HNO₃ and CH₃CN) (**Fig. S13**)
 - v. Peroxidative mechanism of cyclohexane oxidation (**Fig. S14**)

1. EDS Analysis of SiO₂ Gel



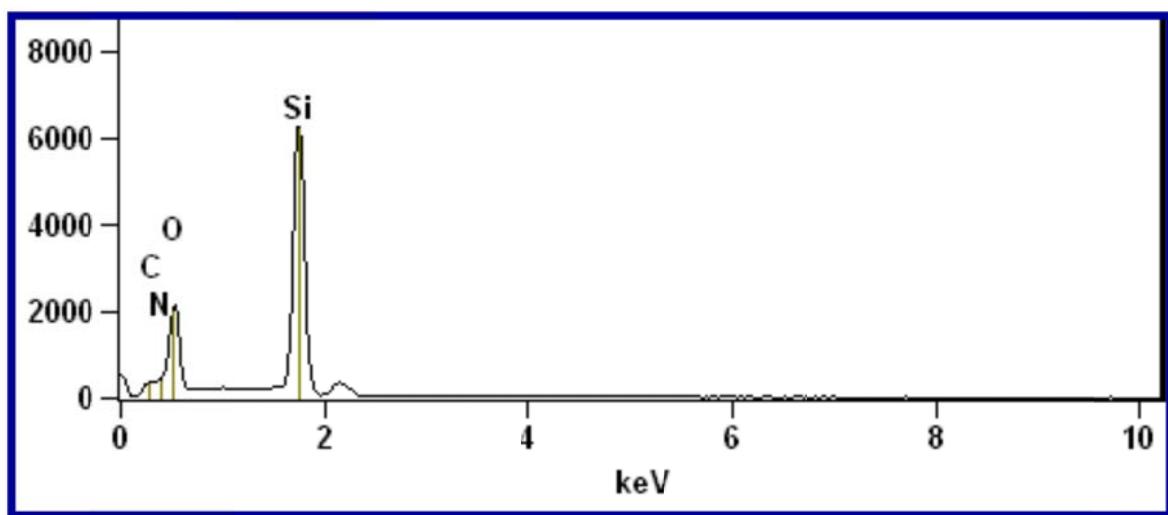
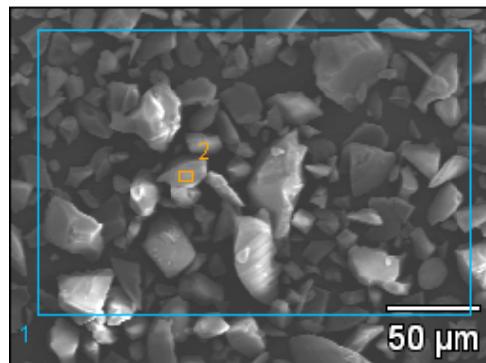
Net Counts

O	Si
19873	98836

Atom %

O	Si
55.87	44.13

2. EDS Analysis of Si-NH₂



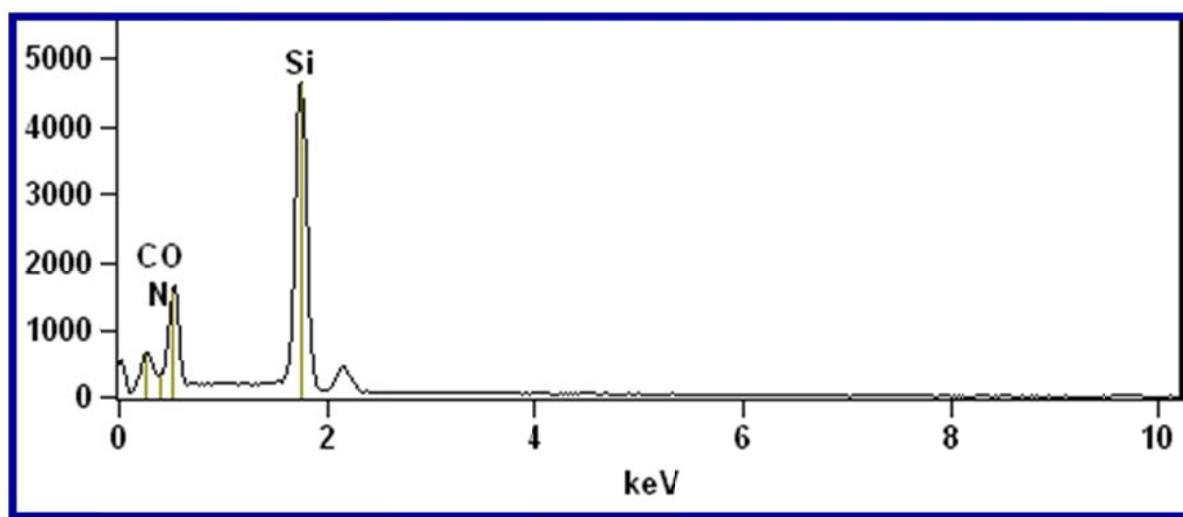
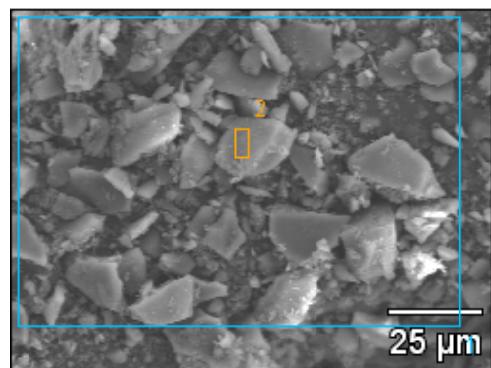
Net Counts

C	N	O	Si
3040	3005	19453	72307

Atom %

C	N	O	Si
16.35	15.23	46.49	21.93

3. EDS Analysis of Si-NH₂-DPED



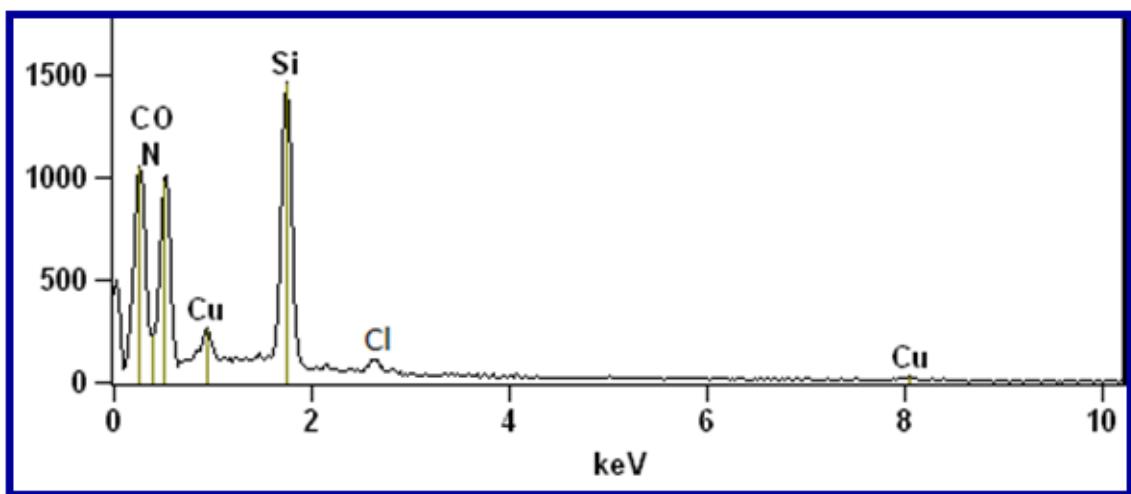
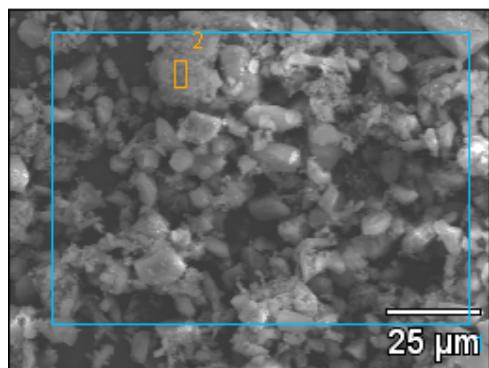
Net Counts

C	N	O	Si
5602	1504	13500	54315

Atom %

C	N	O	Si
30.86	10.84	39.72	18.57

4. EDS Analysis of [Cu(Si-NH₂-DPED)Cl₂]



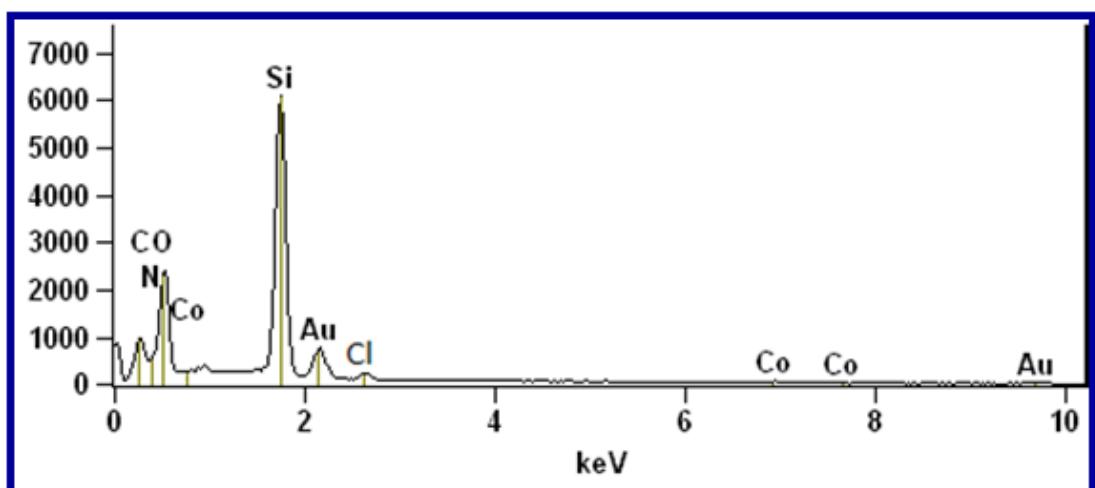
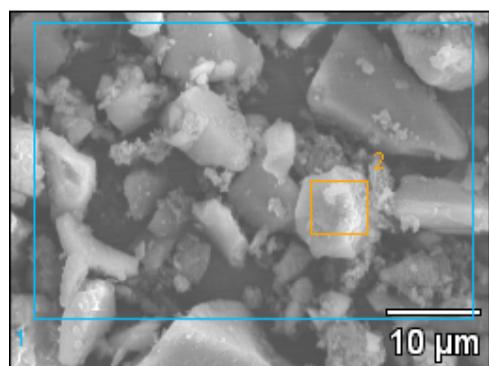
Net Counts

C	N	O	Si	Cu	Cl
9401	800	8554	15609	322	270

Atom %

C	N	O	Si	Cu	Cl
44.90	8.96	36.93	7.58	0.89	0.74

5. EDS Analysis of [Co(Si-NH₂-DPED)Cl₂]



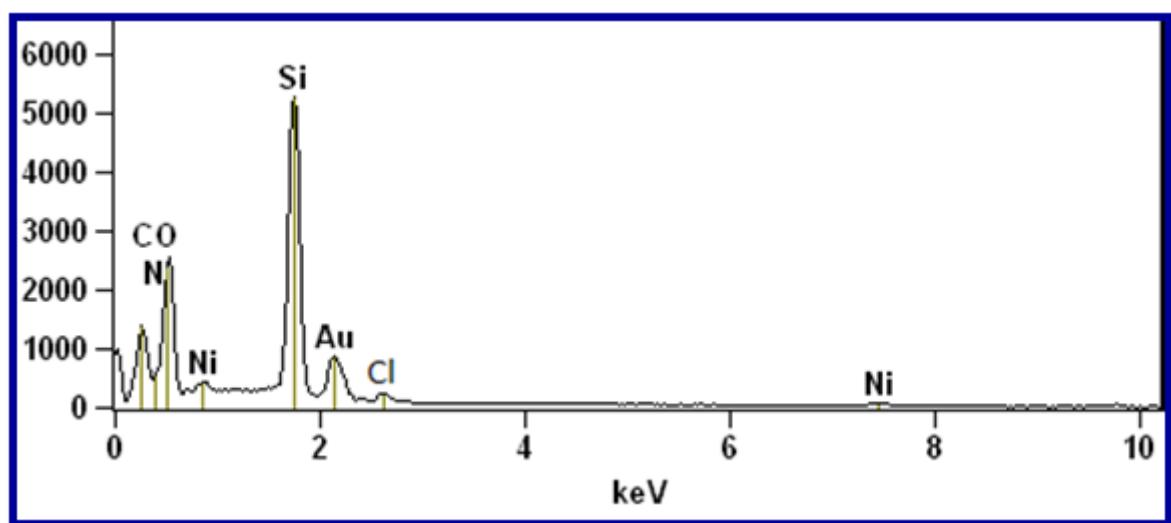
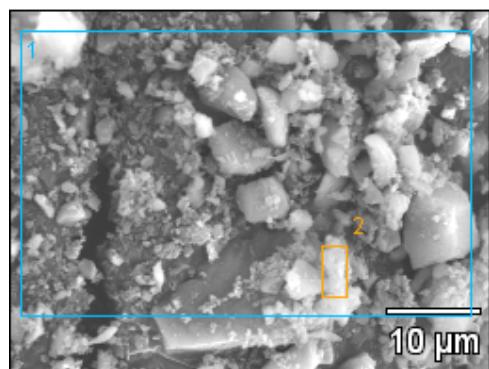
Net Counts

C	N	O	Si	Co	Cl
8006	2711	20277	66509	399	282

Atom %

C	N	O	Si	Co	Cl
28.82	12.84	41.57	16.14	0.34	0.29

6. EDS Analysis of [Ni(Si-NH₂-DPED)Cl₂]



Net Counts

C	N	O	Si	Ni	Cl
11551	2125	21304	58759	914	307

Atom %

C	N	O	Si	Ni	Cl
34.92	10.02	40.33	13.51	0.91	0.31

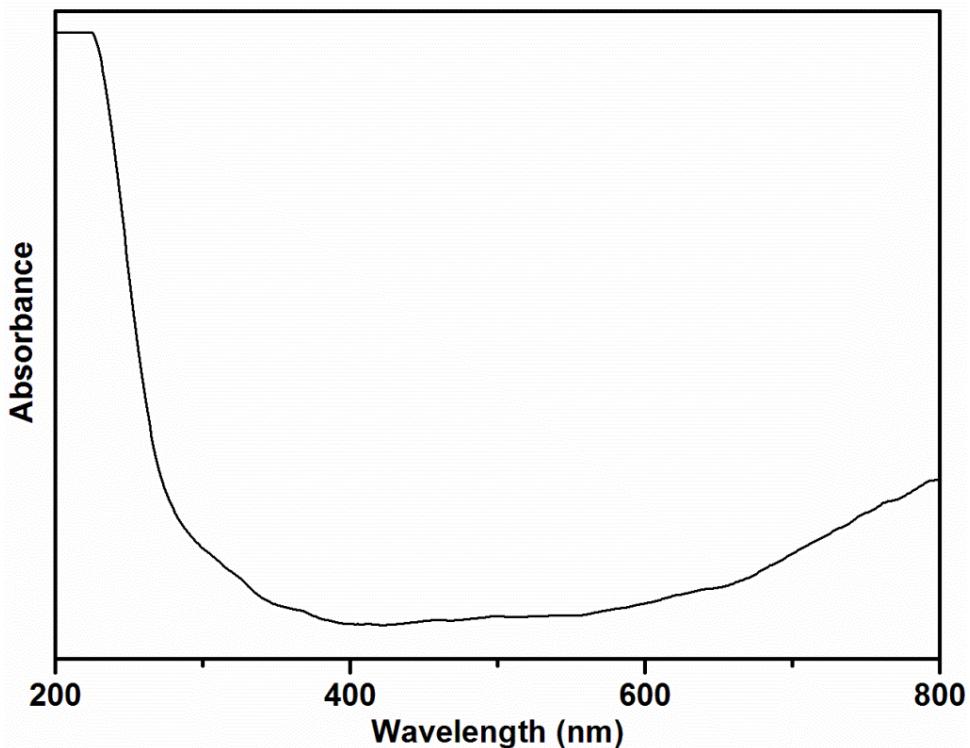


Figure S1. UV.Vis. spectrum of SiO_2 gel

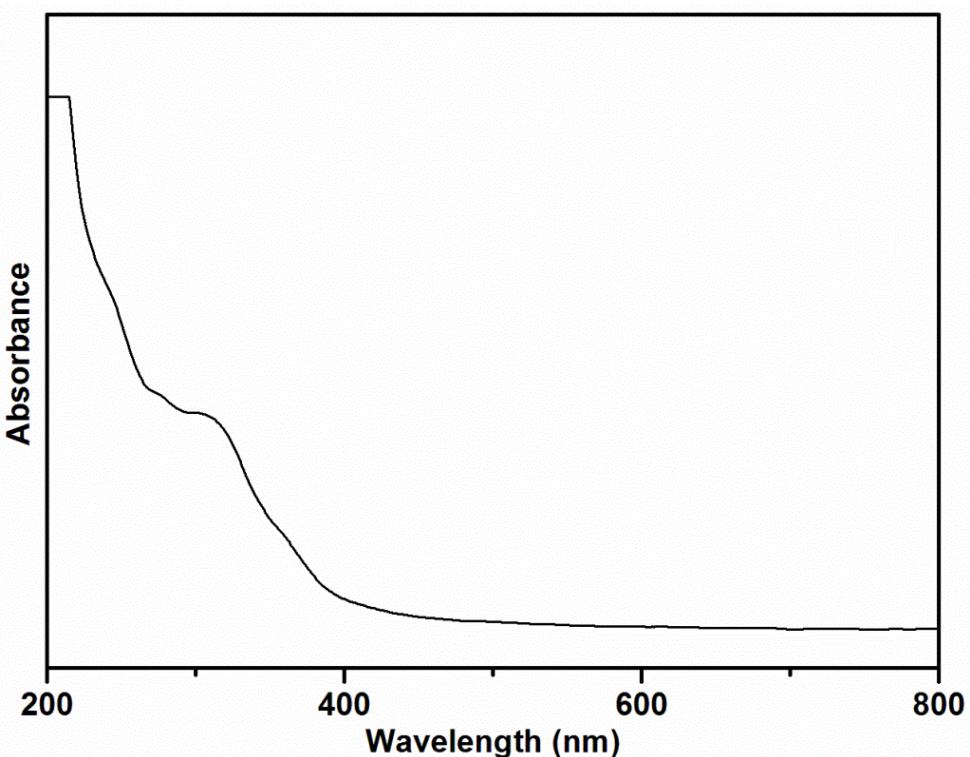


Figure S2. UV.Vis. spectrum of Si-NH_2

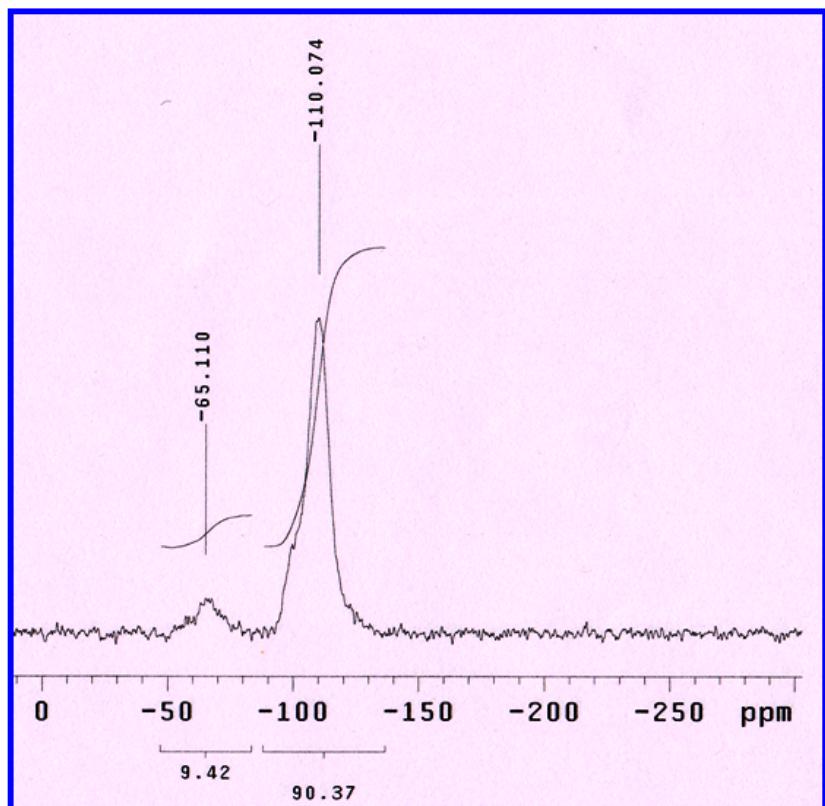


Figure S3. ^{29}Si CP MAS NMR spectrum of Si-NH₂-DPED

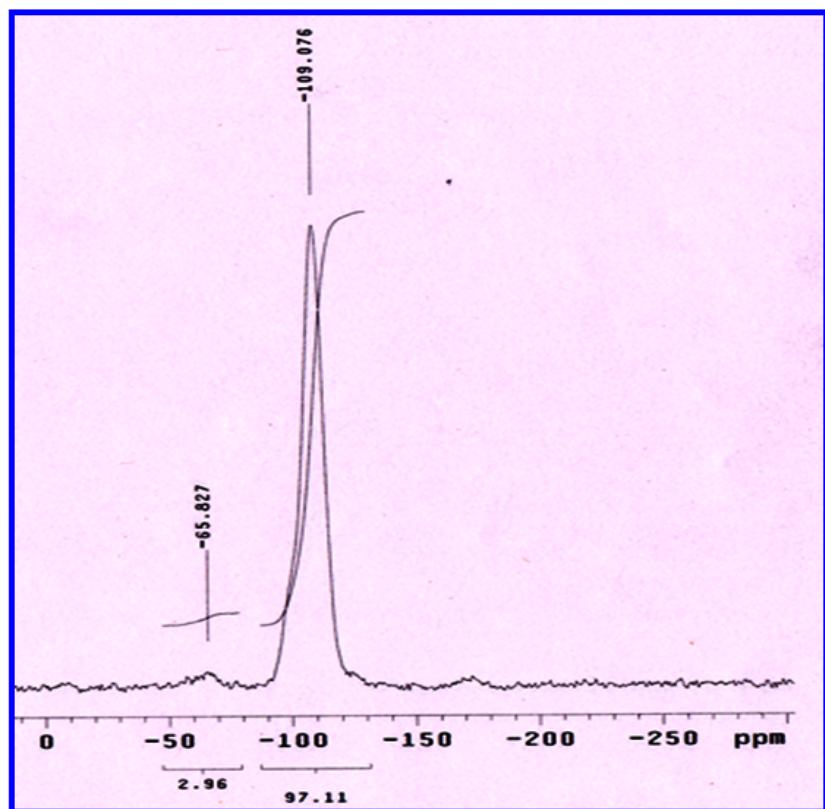


Figure S4. ^{29}Si CP MAS NMR spectrum of $[\text{Cu}(\text{Si}-\text{NH}_2\text{-DPED})\text{Cl}_2]$

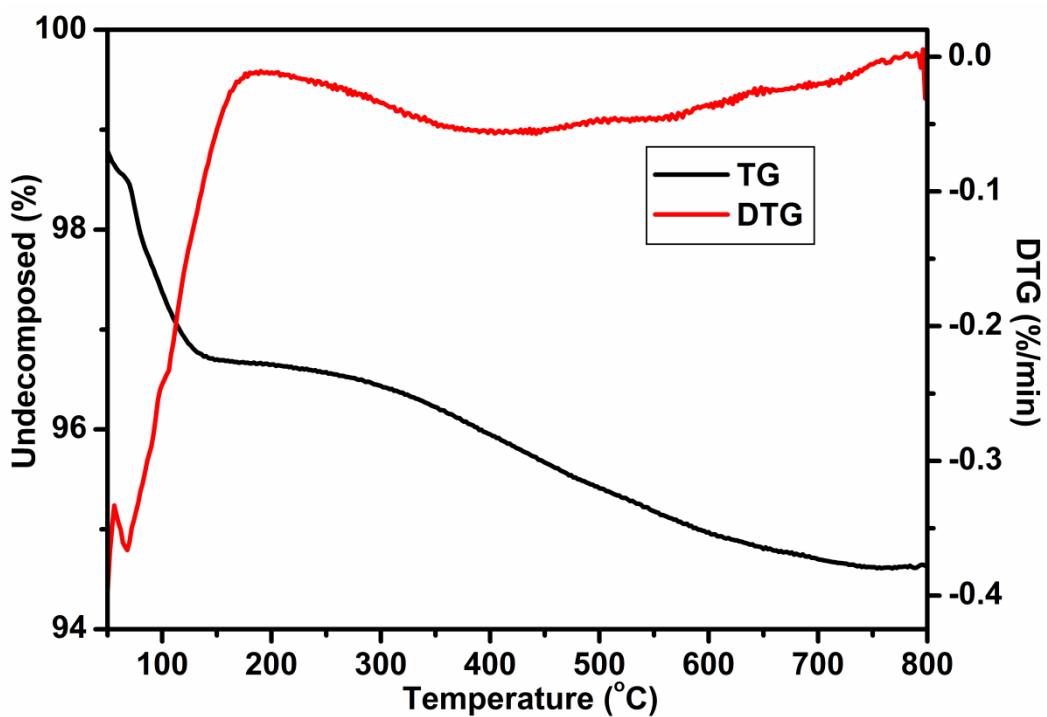


Figure S5. TG-DTG curves of SiO_2 gel

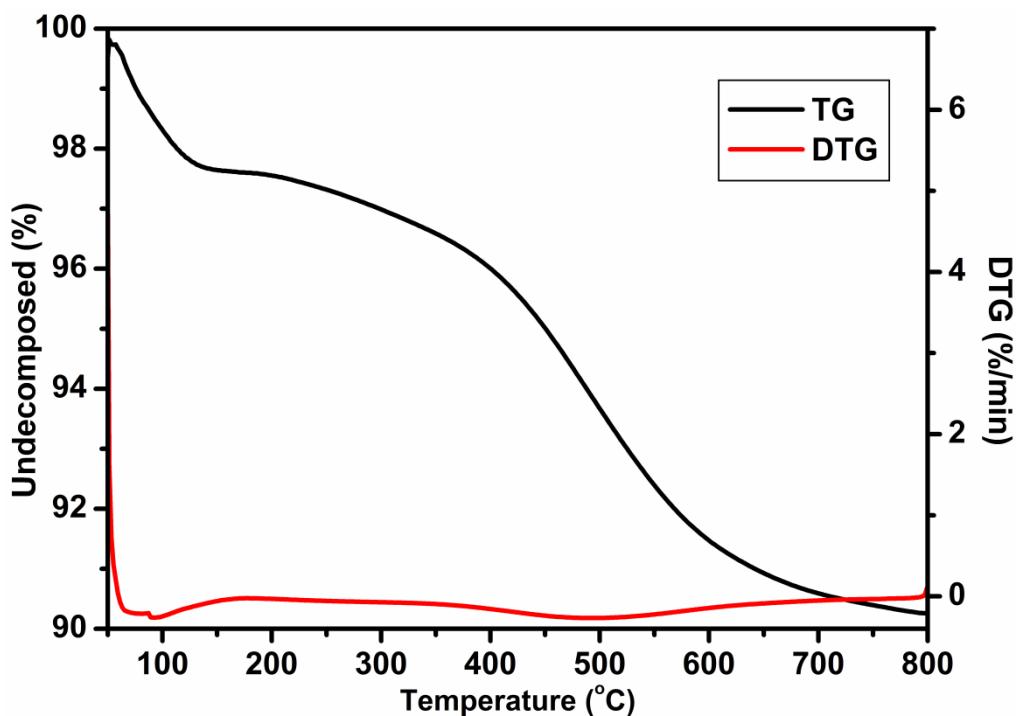
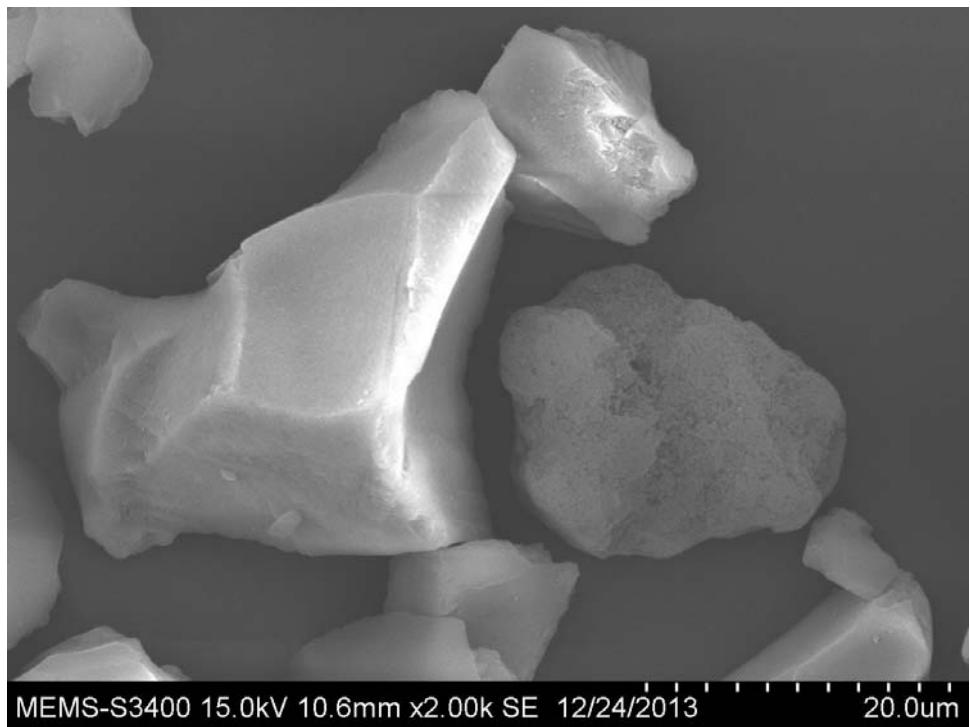
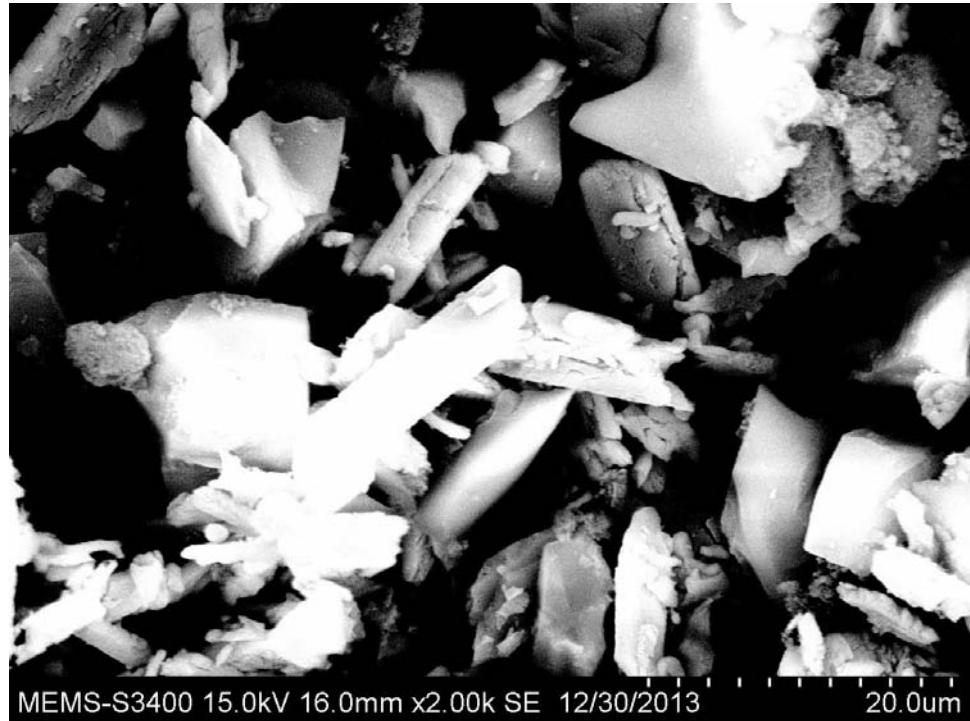


Figure S6. TG-DTG curves of Si-NH_2



MEMS-S3400 15.0kV 10.6mm x2.00k SE 12/24/2013 20.0um

Figure S7. SEM image of SiO₂ gel



MEMS-S3400 15.0kV 16.0mm x2.00k SE 12/30/2013 20.0um

Figure S8. SEM image of Si-NH₂

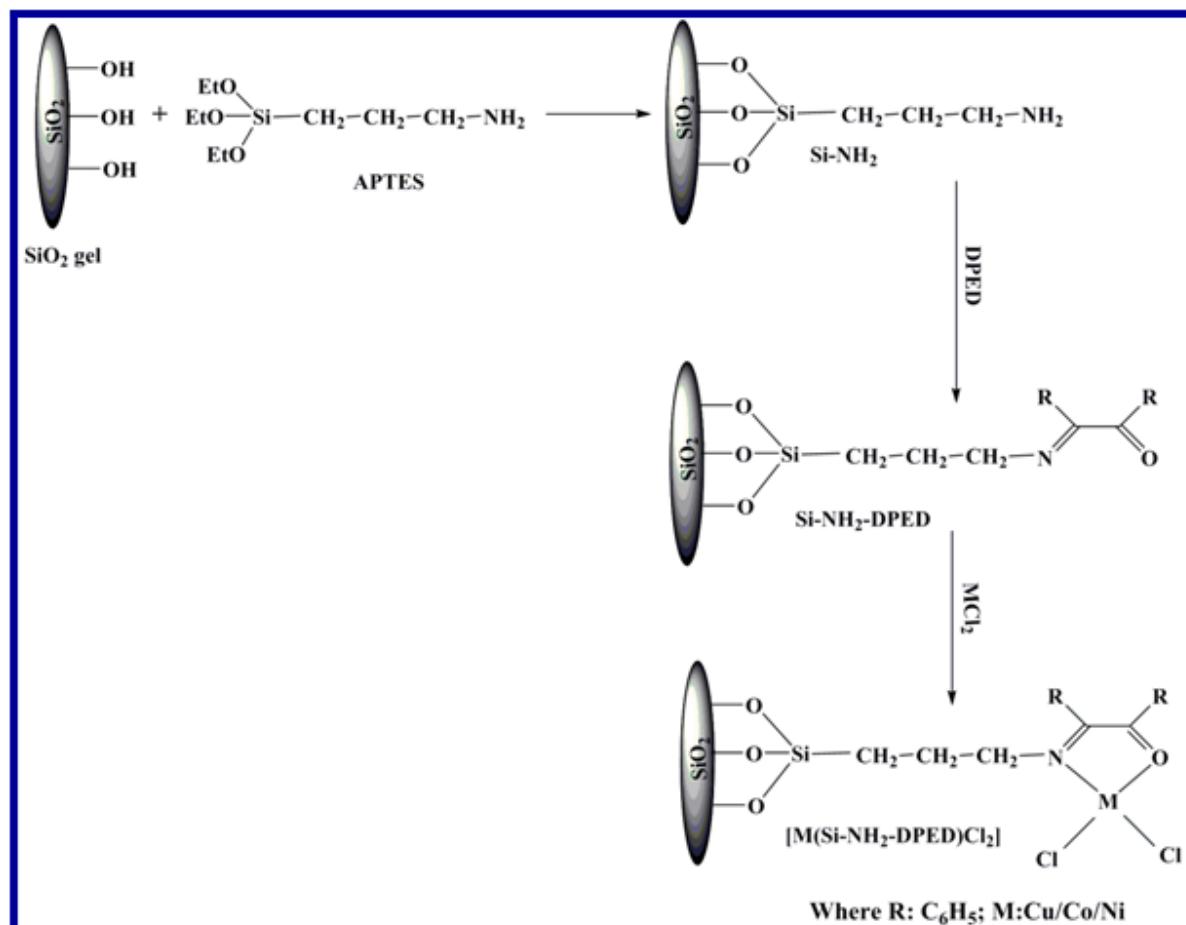


Figure S9: Schematic of the synthesis of complexes

Table 1: Influence of reaction time on cyclohexane oxidation catalyzed by Cu(II), Co(II) and Ni(II) hybrid catalysts

No.	Catalyst	Conversion (%)					
		2h	4h	6h	8 h	10h	12h
^{1a}	[Cu(Si-NH ₂ -DPED)Cl ₂]	-	-	-	-	-	-
^{2b}	[Cu(Si-NH ₂ -DPED)Cl ₂]	-	-	-	-	-	-
^{3c}	[Cu(Si-NH ₂ -DPED)Cl ₂]	-	-	-	-	-	-
^{4d}	[Cu(Si-NH ₂ -DPED)Cl ₂]	7	15	28	37	41	44
^{5c}	[Co(Si-NH ₂ -DPED)Cl ₂]	-	-	-	-	-	-
^{6d}	[Co(Si-NH ₂ -DPED)Cl ₂]	5	12	25	32	36	38
^{7c}	[Ni(Si-NH ₂ -DPED)Cl ₂]	-	-	-	-	-	-
^{8d}	[Ni(Si-NH ₂ -DPED)Cl ₂]	4	10	23	31	34	35

Mechanism of cyclohexane oxidation

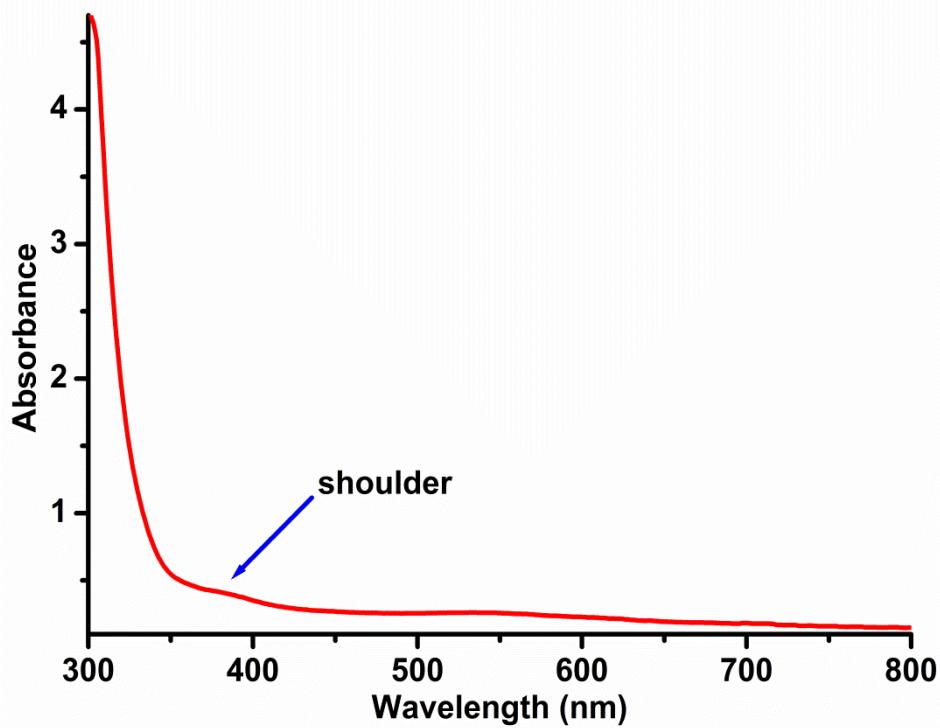


Fig. S10: UV-Vis. spectrum of the mixture ($[\text{Cu}(\text{Si}-\text{NH}_2-\text{DPED})\text{Cl}_2]$, H_2O_2 , HNO_3 and CH_3CN)

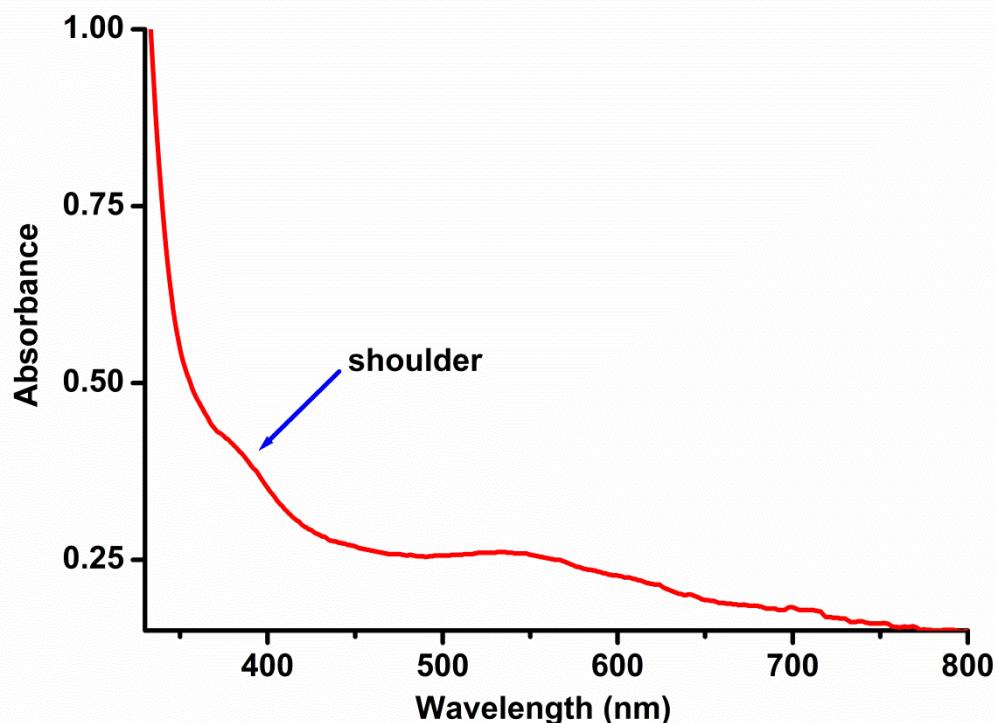


Fig. S11: Magnified UV-Vis. spectrum of the mixture ($[\text{Cu}(\text{Si}-\text{NH}_2-\text{DPED})\text{Cl}_2]$, H_2O_2 , HNO_3 and CH_3CN)

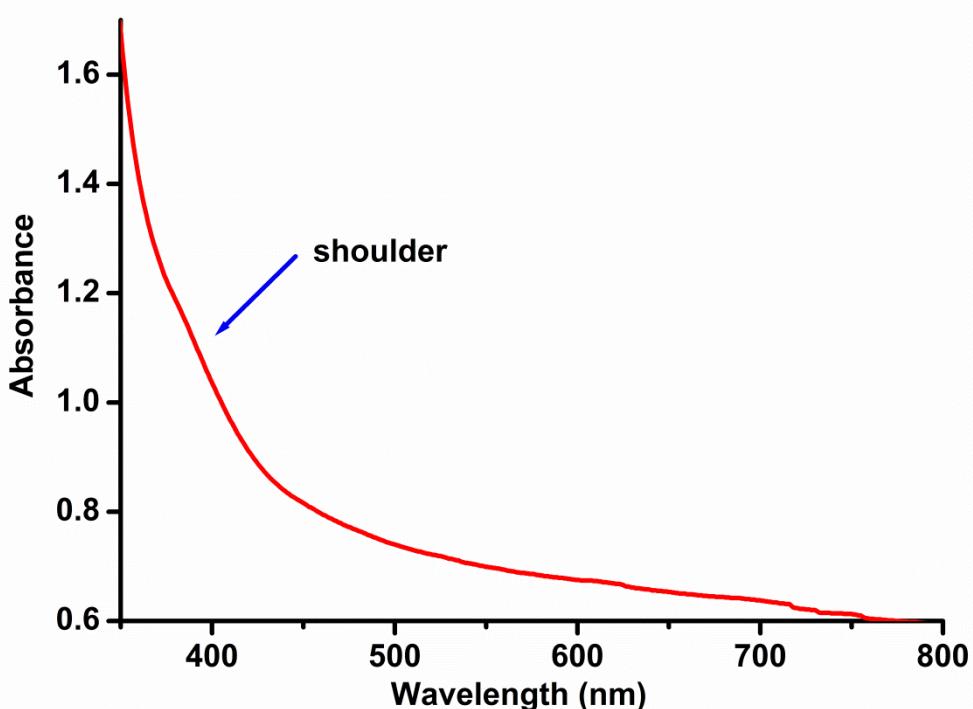


Fig. S12: UV-Vis. spectrum of the mixture ($[\text{Co}(\text{Si}-\text{NH}_2\text{-DPED})\text{Cl}_2]$, H_2O_2 , HNO_3 and CH_3CN)

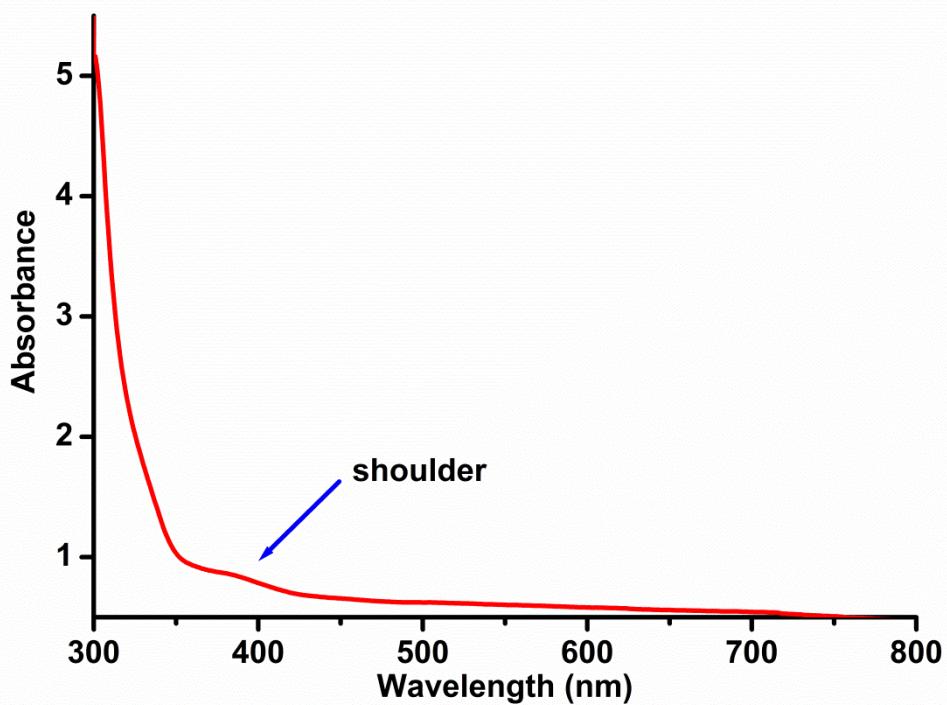


Fig. S13: UV-Vis. spectrum of the mixture ($[\text{Ni}(\text{Si}-\text{NH}_2\text{-DPED})\text{Cl}_2]$, H_2O_2 , HNO_3 and CH_3CN)

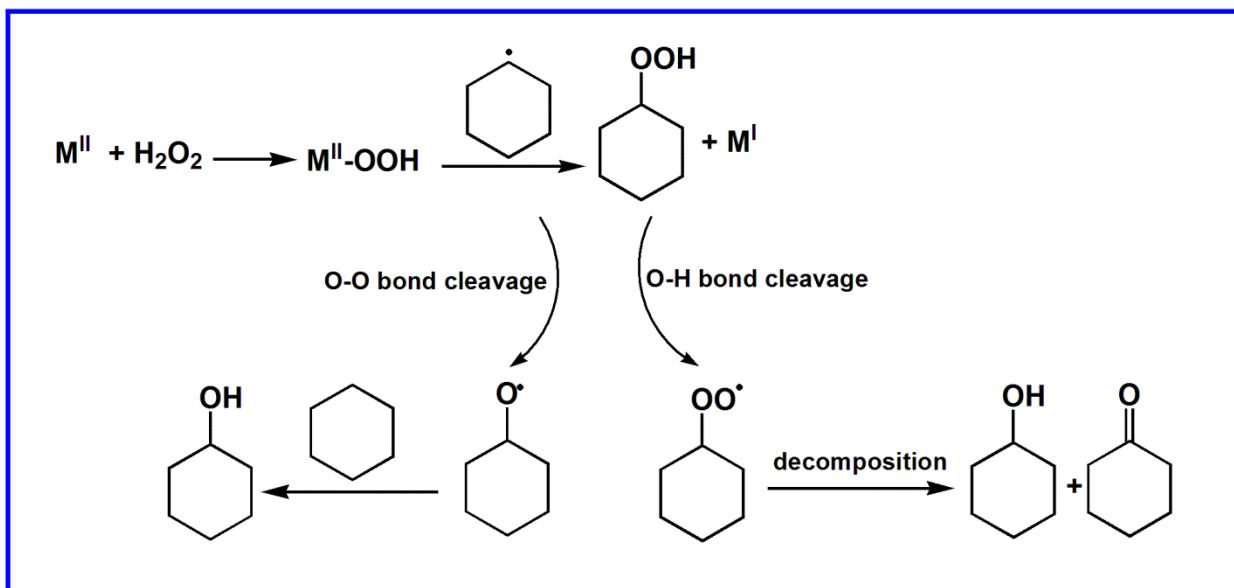


Fig. S14: Peroxidative mechanism of cyclohexane oxidation