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Supplementary Material

Optical and theoretical studies on Fe_3O_4 - imidazole nano composite and clusters

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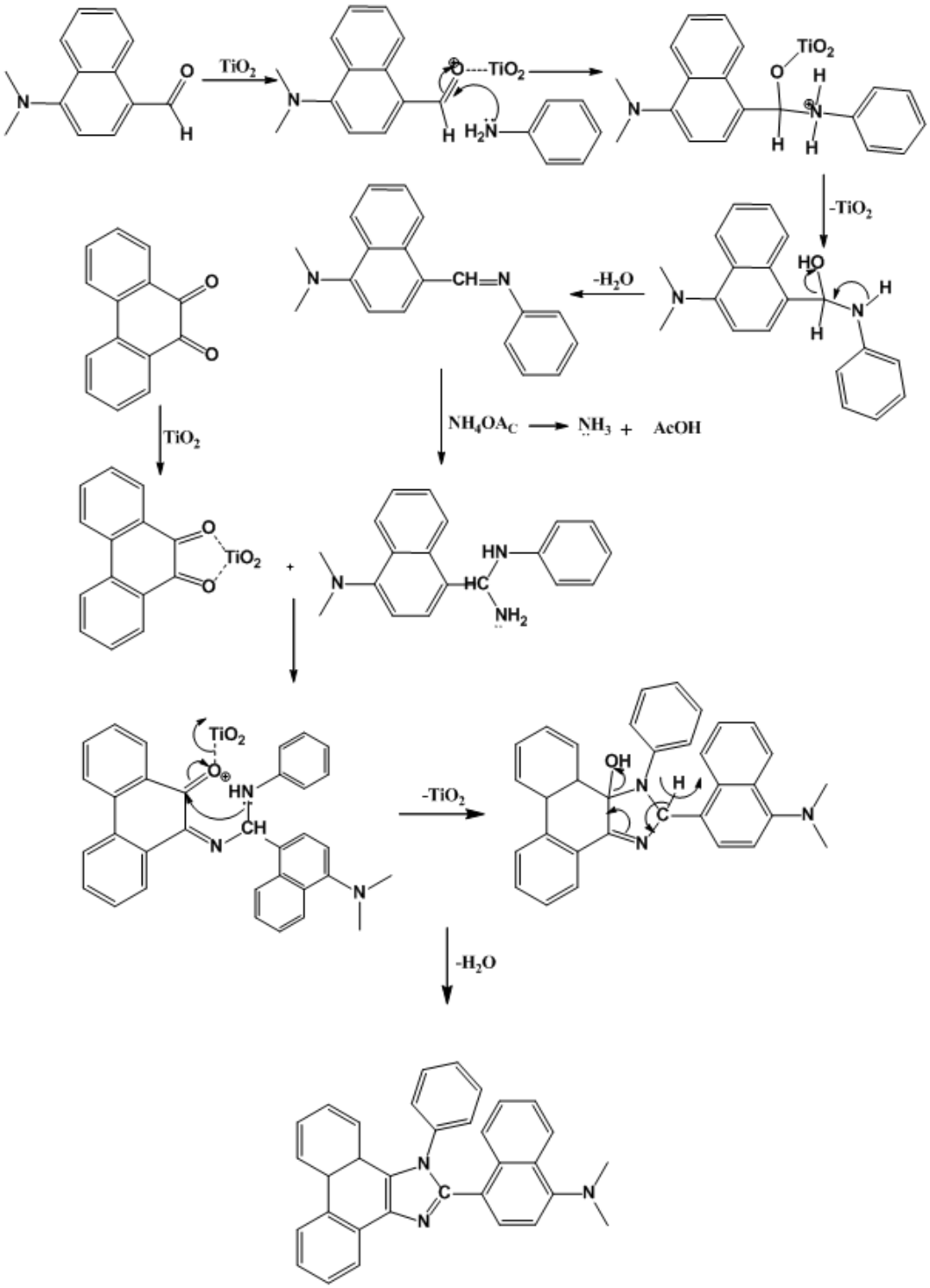
2. Experimental

2.1. Synthesis of nanocrystalline TiO_2 (R) by sol- gel method

The TiO_2 (R) nanocrystal were prepared by sol-gel hydrolysis of titanium(IV) isopropoxide, followed by calcination. About 1ml titanium isopropoxide (Merck, 97%) was dissolved in 20 ml isopropyl alcohol (Merck, 95%) under stirring. The solution was dropped slowly into 10 ml distilled water and the pH was adjusted to 2, the formed white sol-gel hydrous oxide was stirred vigorously for 4 h at room temperature and then allowed to age overnight. The solid was centrifuged and was redispersed in ethanol to minimize agglomeration. The resulting material was filtered, dried and calcinated upto 800 °C for 2 h. The sample was characterized by XRD, SEM and TEM.

2.2. Synthesis of cubic Fe_3O_4 nanoparticles

About 4g of ferric nitrate was dissolved in 25 ml of ethylene glycol with vigorous stirring for 1h at 40°C and then the temperature was raised to 80 ^{o}C. The formed brown gel was aged for 2h and dried at 150 ^{o}C for 22 h. After drying, the gel was annealed in the temperature range of 450-650°C under vacuum. The brown Fe_3O_4 nanoparticles were characterised by XRD, SEM, EDX etc.,



Scheme S1. Possible mechanism for catalytic synthesis of phenanthrimidazole

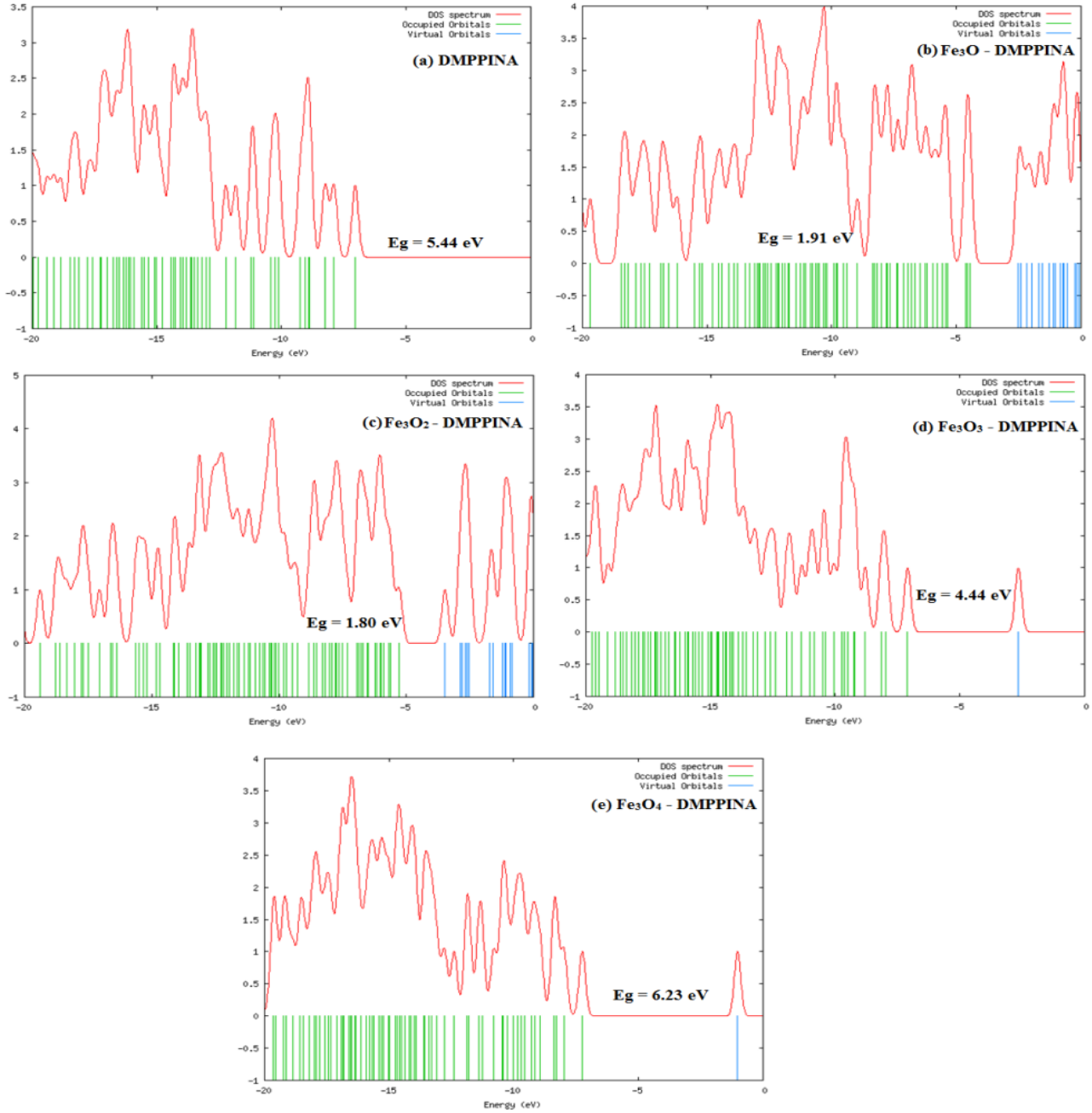


Figure S1. Density of state-plots for DMPPINA (**a**); Fe_3O–DMPPINA (**b**); Fe_3O_2–DMPPINA (**c**); Fe_3O_3–DMPPINA (**d**) and Fe_3O_4–DMPPINA (**e**)

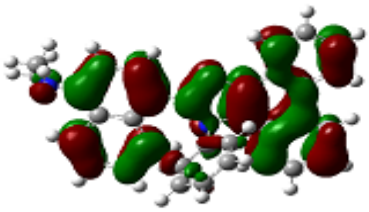
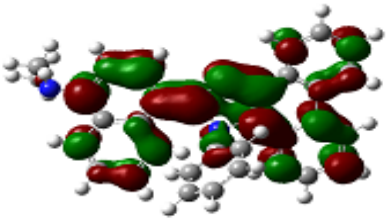
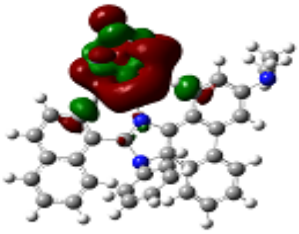
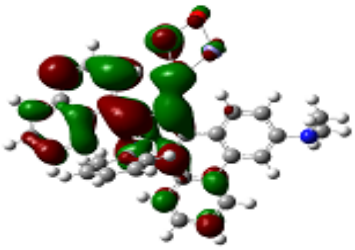
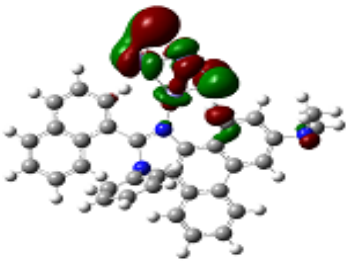
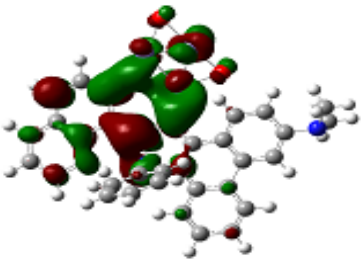
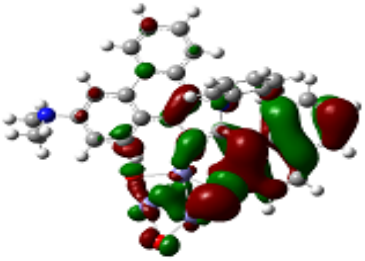
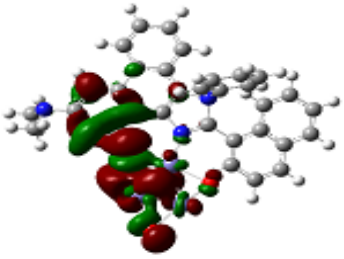
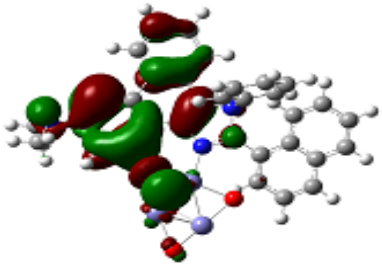
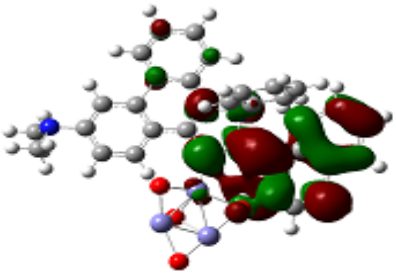
Compound	HOMO	LUMO
DMPPINA		
Fe_3O - DMPPINA		
Fe_3O_2 - DMPPINA		
Fe_3O_3 - DMPPINA		
Fe_3O_4 - DMPPINA		

Figure S2. HOMO-LUMO contour plot DMPPINA, Fe_3O–DMPPINA, Fe_3O_2–DMPPINA, Fe_3O_3–DMPPIN and Fe_3O_4–DMPPINA composites

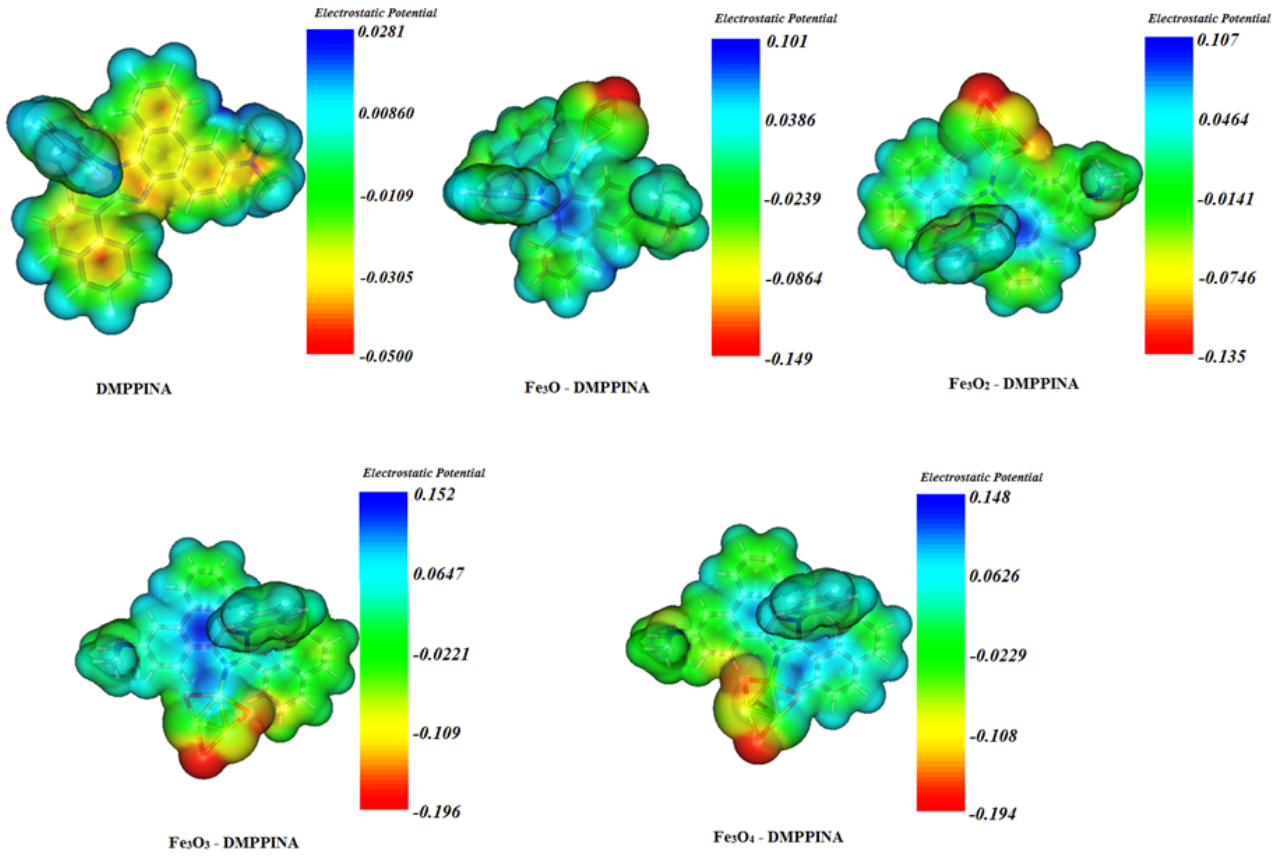


Figure S3. MEP surface diagram

Table S1. Mulliken atomic charges of **DMPPINA** and **Fe_3O_4–DMPPINA** clusters

S. No.	DMPPINA		Fe_3O–DMPPINA		Fe_3O_2–DMPPINA		Fe_3O_3–DMPPINA		Fe_3O_4–DMPPINA	
	Atoms	**Atomic charges**	**Atoms**	**Atomic charges**	**Atoms**	**Atomic charges**	**Atoms**	**Atomic charges**	**Atoms**	**Atomic charges**
1	C	-0.129527	C	-0.258120	C	-0.260666	C	-0.249022	C	-0.257789
2	C	-0.097947	C	-0.424929	C	-0.435120	C	-0.334026	C	-0.342787
3	C	-0.003879	C	0.392767	C	0.414664	C	0.289437	C	0.285614
4	C	-0.021417	C	0.153896	C	0.197295	C	0.127199	C	0.104032
5	C	-0.115864	C	-0.367201	C	-0.381572	C	-0.295584	C	-0.300040
6	C	-0.119147	C	-0.276551	C	-0.275879	C	-0.266426	C	-0.266682
7	C	-0.051867	C	-0.125608	C	-0.097032	C	0.063883	C	0.058764
8	C	-0.024296	C	0.289976	C	0.334942	C	0.200824	C	0.266385
9	C	-0.002312	C	0.214287	C	0.098442	C	0.216907	C	0.108902
10	C	-0.047079	C	0.027578	C	0.040773	C	0.237011	C	0.182602
11	C	-0.092096	C	-0.209527	C	-0.092915	C	-0.135136	C	-0.038039
12	C	-0.133202	C	-0.390642	C	-0.443174	C	-0.256102	C	-0.436190
13	C	-0.118460	C	0.418704	C	0.450763	C	0.423175	C	0.450909
14	C	-0.118153	C	-0.623489	C	-0.630412	C	-0.466543	C	-0.548057
15	N	-0.121647	N	-0.333754	N	-0.359303	N	-0.638520	N	-0.638376
16	C	0.050504	C	0.155768	C	0.191586	C	0.474436	C	0.428275
17	N	-0.135483	N	-0.310573	N	-0.428902	N	-0.780071	N	-0.605264
18	C	-0.007177	C	0.279474	C	0.266591	C	0.304579	C	0.312778
19	C	-0.130730	C	-0.245659	C	-0.241208	C	-0.203140	C	-0.196866
20	C	-0.170230	C	-0.188123	C	-0.183416	C	-0.120429	C	-0.135096
21	C	-0.118564	C	-0.264524	C	-0.262611	C	-0.253048	C	-0.246287
22	C	-0.120841	C	-0.307266	C	-0.313448	C	-0.270062	C	-0.270763

23	C	-0.126410	C	-0.225757	C	-0.219847	C	-0.219261	C	-0.220526
24	C	-0.010447	C	0.180144	C	0.184344	C	0.146235	C	0.201315
25	C	-0.012176	C	0.189836	C	0.185888	C	0.224534	C	0.221435
26	C	-0.069636	C	-0.054490	C	-0.086947	C	0.003097	C	-0.284579
27	C	-0.150552	C	-0.187741	C	-0.186068	C	-0.177097	C	-0.136917
28	C	-0.022972	C	0.454742	C	0.456250	C	0.333850	C	0.391688
29	C	-0.175059	C	-0.299057	C	-0.251300	C	-0.296386	C	-0.240601
30	C	-0.141521	C	-0.367039	C	-0.367329	C	-0.338256	C	-0.330849
31	C	-0.101232	C	-0.456483	C	-0.451562	C	-0.383211	C	-0.397610
32	C	0.021294	C	-0.478007	C	-0.466110	C	-0.384652	C	-0.404663
33	C	-0.130076	C	-0.239870	C	-0.236062	C	-0.252571	C	-0.205053
34	H	0.150188	H	0.191104	H	0.166826	H	0.203626	H	0.279560
35	H	0.131011	H	0.238263	H	0.235166	H	0.227435	H	0.218035
36	H	0.143969	H	0.270661	H	0.270061	H	0.248250	H	0.224799
37	H	0.133622	H	0.248592	H	0.253784	H	0.214912	H	0.229139
38	H	0.130110	H	0.237975	H	0.239489	H	0.227075	H	0.222577
39	H	0.131076	H	0.223262	H	0.253530	H	0.232489	H	0.203823
40	H	0.129658	H	0.269177	H	0.266026	H	0.251317	H	0.227006
41	H	0.132701	H	0.262966	H	0.272575	H	0.232714	H	0.271262
42	H	0.148225	H	0.141217	H	0.148895	H	0.118510	H	0.088523
43	H	0.202403	H	0.235891	H	0.237778	H	0.217382	H	0.232817
44	H	0.135580	H	0.236002	H	0.237058	H	0.220172	H	0.216618
45	H	0.135550	H	0.251071	H	0.259672	H	0.199170	H	0.239103
46	H	0.131521	H	0.228789	H	0.241196	H	0.217999	H	0.252822
47	H	0.201158	H	0.235902	H	0.243525	H	0.206356	H	0.235344
48	H	0.140398	H	0.245888	H	0.252223	H	0.219273	H	0.238819
49	H	0.130353	H	0.248815	H	0.255385	H	0.221598	H	0.253981

50	H	0.150238	H	0.232049	H	0.237186	H	0.210165	H	0.232997
51	H	0.129545	H	0.123430	H	0.117337	H	0.184550	H	0.647624
52	H	0.152975	N	-0.192459	N	-0.196620	N	-0.388190	N	-0.403386
53	N	-0.193640	C	-0.610193	C	-0.613986	C	-0.464215	C	-0.468711
54	C	-0.136952	H	0.200374	H	0.206763	H	0.172209	H	0.174421
55	H	0.051313	H	0.217397	H	0.214148	H	0.198772	H	0.182479
56	H	0.088860	H	0.233710	H	0.230529	H	0.203653	H	0.199260
57	H	0.094173	C	-0.616122	C	-0.616886	C	-0.474304	C	-0.471771
58	C	-0.130502	H	0.222105	H	0.218039	H	0.205885	H	0.184990
59	H	0.087660	H	0.190771	H	0.198336	H	0.156091	H	0.164536
60	H	0.054220	H	0.239965	H	0.235605	H	0.214761	H	0.214019
61	H	0.092789	H	0.232603	H	0.236290	H	0.220544	H	0.226174
62			Fe	0.248697	Fe	0.470796	Fe	1.364830	Fe	1.159606
63			Fe	-0.031431	Fe	0.065755	Fe	0.176443	Fe	0.563326
64			Fe	-0.025172	Fe	0.057038	Fe	0.204625	Fe	0.735587
65			O	-0.554059	O	-0.498650	O	-0.787705	O	-0.903451
66					O	-0.545527	O	-0.962685	O	-0.942821
67							O	-0.619329	O	-0.637867
68									O	-1.000906