Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Stable manganese carbonyl radicals as a rapid colorimetric thiol and hydrazine sensor

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Cartesian coordinates for the calculated manganese radical complexes using b3lyp/lanl2dz level of theory for structural optimization

1. Determination of Detection Limits

For phenylhydrazine, the equation of the curve obtained is $y = 1.6132x$ where y is the absorbance and x is the concentration in millimolar. A detection limit of 0.05 is chosen because this minimizes contributions from the background as well as any residual absorbance presented from the sensor itself.

Thus, the calculations for determining the limit of detection is done by setting $y = 0.05$ in the above equation. Therefore,

$0.05 = 1.6132x$

Solving for x yields $x = 0.03099$ mM.

The molar mass of phenylhydrazine is 108.14 g mol^{-1}.

Mass of phenylhydrazine in 1 $dm^3 = 0.03099 \times 10^{-3} \times 108.14 =$ **3.35×10^{-3} g**

We define the unit of ppm as 1 mg of solute in 1 liter of solution, therefore the detection limit for phenylhydrazine is thus 3.35 ppm ≈ 3.4ppm.

The same method is used to calculate the detection limit for 1-octanethiol and *p*-thiocresol.

2. Stability Data for Complex 1 and 2

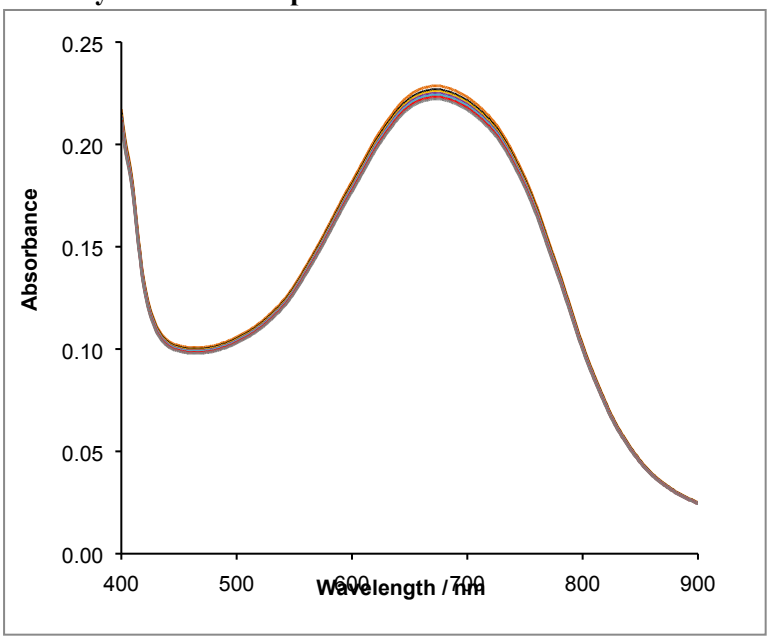

Figure S1. Changes in the UV-vis absorptions band of 0.10mM **1** over a period of 7 days. There were no changes in the colour of the complex even though small amounts of a dark brown solid was observed at the bottom of the vial.

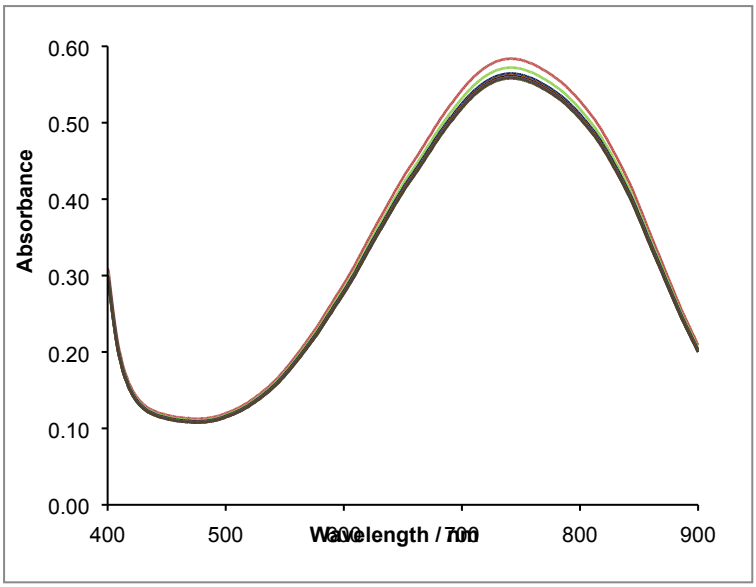

Figure S2. Changes in the UV-vis absorptions band of 0.10mM of **2** over a period of 7 days. There were no changes in the colour of the complex even though small amounts of a light brown solid was observed at the bottom of the vial.

$CpMn(CO)_2(NHPh)$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	25	0	1.161078	-0.133707	0.034589
2	6	0	1.708236	1.261370	-1.625771
3	6	0	0.564757	1.815555	-0.954948
4	6	0	2.799769	1.242236	-0.676642
5	1	0	1.757384	0.977466	-2.667153
6	6	0	0.925866	2.099418	0.399130
7	1	0	-0.416878	1.950190	-1.387218
8	6	0	2.312472	1.745242	0.568722
9	1	0	3.808977	0.908193	-0.875122
10	1	0	0.300715	2.559504	1.150261
11	1	0	2.893812	1.867065	1.472438
12	6	0	1.211155	-0.830075	1.718219
13	8	0	1.178544	-1.291763	2.801210
14	6	0	2.053104	-1.537374	-0.642754
15	8	0	2.704316	-2.412897	-1.100836
16	7	0	-0.522209	-0.952504	-0.250116
17	1	0	-0.488776	-1.906826	-0.610092
18	6	0	-1.844365	-0.495504	-0.153065
19	6	0	-2.188655	0.662115	0.595062
20	6	0	-2.894931	-1.212079	-0.800718
21	6	0	-3.522116	1.099031	0.667122
22	1	0	-1.413613	1.180722	1.146999
23	6	0	-4.222845	-0.770950	-0.718017
24	1	0	-2.651556	-2.108230	-1.369294
25	6	0	-4.549011	0.393462	0.010459

26	1	0	-3.759718	1.987059	1.249232
27	1	0	-5.005940	-1.335002	-1.220072
28	1	0	-5.579395	0.732644	0.072306

$CpMn(CO)_2(SCH_3)$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	25	0	0.223308	-0.101583	-0.003252
2	6	0	1.963010	0.603090	-1.201333
3	6	0	1.746136	1.516127	-0.114326
4	6	0	2.298112	-0.683722	-0.635801
5	1	0	1.912590	0.843665	-2.253800
6	6	0	1.932936	0.802481	1.118429
7	1	0	1.473704	2.557919	-0.207355
8	6	0	2.282059	-0.558345	0.790070
9	1	0	2.531069	-1.581942	-1.191045
10	1	0	1.852051	1.217967	2.112883
11	1	0	2.492126	-1.348740	1.497851
12	6	0	-0.600275	-1.062730	1.289322
13	8	0	-1.152349	-1.661665	2.143113
14	6	0	-0.616108	-1.077771	-1.272529
15	8	0	-1.183098	-1.689364	-2.107593
16	16	0	-1.385717	1.513385	0.002236
17	6	0	-3.113808	0.734548	-0.004164
18	1	0	-3.234342	0.071657	0.856692
19	1	0	-3.835184	1.553068	0.059714
20	1	0	-3.272041	0.178000	-0.931575

$CpMn(CO)_2(SPh)$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	25	0	-1.268849	0.007872	0.109256
2	6	0	-3.016086	1.159356	-0.649503
3	6	0	-2.777633	0.043696	-1.521671
4	6	0	-3.358737	0.635092	0.652590
5	1	0	-2.974585	2.203559	-0.925341
6	6	0	-2.961136	-1.165618	-0.767320
7	1	0	-2.500815	0.103131	-2.564814
8	6	0	-3.328312	-0.794413	0.576541
9	1	0	-3.608277	1.217671	1.528860
10	1	0	-2.865329	-2.172711	-1.147889
11	1	0	-3.540079	-1.477213	1.388263
12	6	0	-0.460742	-1.224654	1.169496
13	8	0	0.045802	-2.045211	1.845947
14	6	0	-0.481206	1.336909	1.060526
15	8	0	0.011683	2.219031	1.666189
16	16	0	0.349866	-0.068556	-1.509368
17	6	0	2.035780	-0.033017	-0.746298
18	6	0	2.701696	-1.240297	-0.450743
19	6	0	2.683726	1.198654	-0.519087
20	6	0	4.006392	-1.213353	0.078576
21	1	0	2.208412	-2.190560	-0.637273
22	6	0	3.988649	1.220767	0.009860
23	1	0	2.177117	2.129613	-0.759375
24	6	0	4.653052	0.016046	0.311625
25	1	0	4.512611	-2.148509	0.306742

26	1	0	4.481265	2.174628	0.183937
27	1	0	5.660522	0.034920	0.720742

$CpMn(CO)_2(NHNH_2)$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	25	0	-0.021584	0.001679	-0.000727
2	6	0	-1.829440	-0.873447	1.048149
3	6	0	-1.829779	0.551309	1.248185
4	6	0	-1.948894	-1.121206	-0.359993
5	1	0	-1.768620	-1.628827	1.819661
6	6	0	-1.946865	1.180237	-0.034710
7	1	0	-1.764122	1.063727	2.198331
8	6	0	-2.008162	0.146956	-1.037896
9	1	0	-1.987702	-2.094203	-0.830905
10	1	0	-1.987810	2.245383	-0.217989
11	1	0	-2.127065	0.296980	-2.101763
12	6	0	0.889369	1.357576	-0.743326
13	8	0	1.477403	2.265437	-1.222587
14	6	0	0.904381	-1.182179	-0.982001
15	8	0	1.509190	-1.977268	-1.615534
16	7	0	1.116093	-0.142371	1.475873
17	1	0	0.670591	-0.261845	2.388959
18	6	0	2.580508	-0.147330	1.580976
19	1	0	2.942395	0.643421	2.259204
20	1	0	2.960431	-1.110224	1.962714
21	1	0	3.029416	0.023367	0.597519