Electronic Supplementary Information for Dalton Transactions

Supporting Information

Peculiar Electronic and Vibrational Properties of Metal-Dithiolenes (Ni, Au) Based on 1,2,5-Thiadiazole-3,4-Dithiolato

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Table S1. IR[a] and Raman[b] peaks (cm^{-1}) of $[M(tdas)_2]^{z-}$ salts [M= Ni(II), z = 1 (1) or 2 (2); Au(III), z = 1 (3)].

$(Bu_4N)[Ni(tdas)_2]$ (**1**)		$(Bu_4N)_2[Ni(tdas)_2]$ (**2**)		$(Bu_4N)[Au(tdas)_2]$ (**3**)	
IR	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**
2959m, 2929m, 2872m	2989m, 2928m, 2868m	2958m, 2929m, 2870m	2989m, 2929ms, 2969m	2954ms, 2863ms	2930 broad
1470s		1490m, 1478m		1482 m	
	1443w	1462m	1445 w	1458 m	
1404w	1406mw	1408w	1406w		
1381w		1382m		1377m	
1322s	1323vs	1321vs	1322vs	1316vs	1319s
1237vs	n.o.*	1251w, 1224vs,	1243mw	1243vs	1252w
1169w		1174w, 1148w	1148w		
1020vw	*1070-1053vwbr*	1025m	*1070-1053vwbr*	1019m, 1000sh	*1070-1050vwbr*
921w, 882mw, 784 ms	909w	882m, 781m		872m, 782m	
769ms, 752ms	765m	764ms,	765mw	788sm	793m
736ms		734mw		735m	732m
503m, 490m	486m	488m	485w	503m, 495mw, 475w	
	382w, 326vs		385m, 326ms		388m, 368vs
	255mw		266mw		254mw
	157s		157ms		154 vs

[a] Spectra recorded on KBr pellets. [b] Spectra recorded on solid samples mixed with KBr. *not observed in the solid state, 1243s in CH_2Cl_2 solution.

Table S2. List of calculated wavenumbers of $[M(tdas)_2]^{0,1-,2-}$ (employed techniques: B3LYP/6-311+G(2df) for Ni and : B3LYP/SDD for Au)

$[Ni(tdas)_2]^0$

ν n°	cm^{-1}	I_{ir}	I_{Ra}	Symm.	Mode Assignment
5	162	0	140	Agδ(SMS)	
9	213	0	2.6	B1g	v(2MS) sy
11	269	0	1.7	B2g	batterfly wag
13	321	12.6	0	B2u	v(MS) asy
14	346	0	125	Agv(4MS) sy	
15	389	0	26	B3g	ring vibrations
18	485	0	29.4	B1g	ring vibrations
19	495	100	0	B3u	δ(SMS) + δ(NSN)
20	504	0	16.9	Ag δ(SMS) + δ(NSN)	
22	528	23.7	0	B3u	rings wag
27	764	0	2.2	Agδ(NSN)	
28	841	117	0	B1u	v(4NS) asy
29	844	0	701	Agv(4NS) sy	
30	846	0	51.8	B1g	v(2NS) sy
31	847	70.9	0	B2u	v(2NS) asy
32	1064	0.1	0	B2u	v(2CS) asy
33	1067	0	3.1	B1g	v(2CS) sy
34	1212	295	0	B3u	v(CC) asy
35	1238	0	2460	Ag	v(CC) sy
36	1283	40.4	0	B3u	v(4CN) asy
37	1297	0	37	Ag v(4CN) sy	
38	1390	0	162	B1g	v(2CN) sy
39	1392	9.5	0	B2u	v(2CN) asy

$[Ni(tdas)_2]^{1-}$

ν n°	cm^{-1}	I_{ir}	I_{Ra}	Symm.	Mode Assignment
5	155	0	41	Ag	δ(SMS)

9	188	0	57	B1g	v(2MS) sy
10	258	0	2.8	B2g	batterfly wag
13	313	19	0	B2u	v(MS) asy
14	339	0	66	Ag	v(4MS) sy
15	372	29	0	B3u	v(2MS) asy
18	477	0	36	B1g	ring vibrations
19	485	17	0	B3u	ring vibrations
20	490	0	450	Ag	δ(SMS) + δ(NSN)
23	511	21	0	B1u	rings wag
26	751	6.2	0	B3u	δ(NSN)
27	752	0	18	Ag	δ(NSN)
28	788	184	0	B3u	v(2NS) sy
29	790	0	159	Ag	v(4NS) sy
30	797	0	53	B1g	v(2NS) sy
31	798	43	0	B2u	v(2NS) asy
32	1039	0	134	B1g	v(2CS) sy
33	1041	1.4	0	B2u	v(2CS) asy
34	1227	0	8276	Ag	v(CC) sy
35	1230	69	0	B3u	v(CC) asy
36	1331	0	2986	Ag	v(4CN) sy
37	1332	1	0	B3u	v(4CN) asy
39	1446	1.9	0	B2u	v(2CN) asy

$[Ni(tdas)_2]^{2-}$

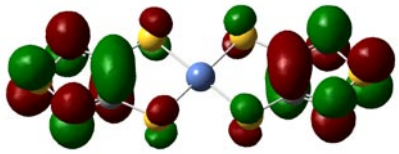
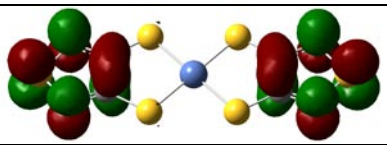
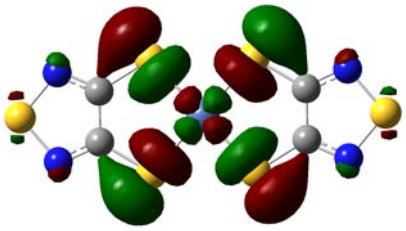
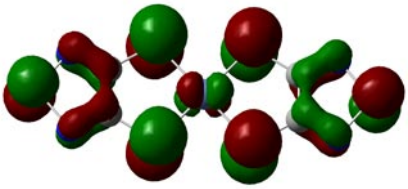
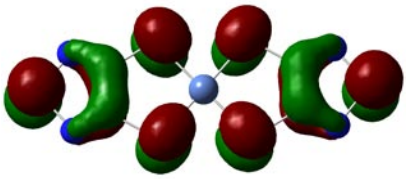
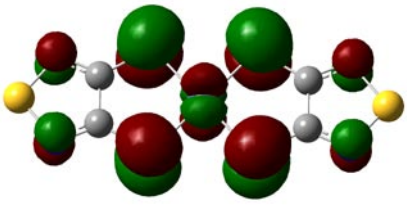
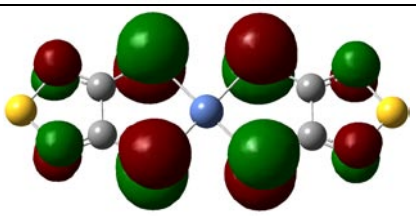
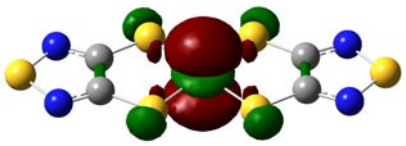
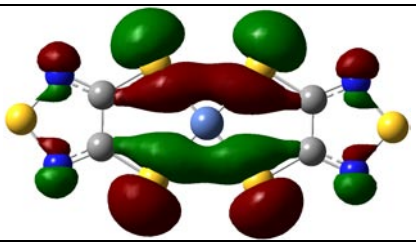
$\nu_{n°}$	cm^{-1}	I_{ir}	I_{Ra}	Symm.	Mode Assignment
5	148	0	19	Ag	δ(SMS)
10	254	0	2.6	B2g	batterfly wag
13	306	10.4	0	B2u	v(MS) asy
14	315	0	57	Ag	v(4MS) sy
15	327	35	0	B3u	(2MS) asy
16	383	0	3.4	B1g	v(2MS) sy
19	485	4.2	0	B3u	ring vibrations
20	488	0	2.4	B2g	rings wag
21	489	0	7.3	Ag	δ(SMS) + δ(NSN)
23	491	17.7	0	B1u	rings wag
26	737	18.4	0	B3u	δ(NSN)
27	738	0	4.3	Ag	δ(NSN)
28	754	202	0	B3u	v(2NS) sy
29	757	0	7.9	Ag	v(4NS) sy

30	763	0	0.5	B1g	v(2NS) sy
31	764	30.7	0	B2u	v(2NS) asy
32	1036	24.2	0	B2u	v(2CS) asy
33	1037	0	2.7	B1g	v(2CS) sy
34	1205	490	0	B3u	v(CC) asy
35	1210	0	34.5	Ag	v(CC) asy
36	1361	407	0	B3u	v(2CN) asy
37	1364	0	703	Ag	v(4CN) sy
38	1441	0	46.2	B1g	v(2CN) sy
39	1445	21.2	0	B2u	v(2CN) asy

$[Au(tdas)_2]^{1-}$

ν n°	cm^{-1}	I_{ir}	I_{Ra}	Symm.	Mode Assignment
6	138	0	70	Ag	δ(SMS)
10	231	0	6.4	B1g	v(2MS) sy
11	245	0	3.8	B2g	batterfly wag
14	345	0	52	Ag	v(4MS) sy
15	360	35	0	B2u	v(MS) asy
16	370	0	27	B1g	v(2MS) sy
17	400	1.0	0	B3u	v(2MS) asy
20	458	0	5.9	B1g	δ(SMS) + δ(NSN
22	469	24.4	0	B1u	rings wag
23	472	11.9	0	B2u	ring vibrations
24	636	0	5.2	B1g	v(2NS) sy
26	700	6.4	0	B3u	δ(NSN)
27	701	0	100.5	Ag	δ(NSN)
28	722	180	0	B3u	δ(NSN)
30	723	0	101.5	Ag	v(4NS) sy
33	1021	0	7.8	B1g	v(2CS) sy
34	1226	360	0	B3u	v(CC) asy
35	1230	0	18.9	Ag	v(CC) sy
36	1423	262	0	B3u	v(2CN) asy
37	1426	0	147	Ag	v(4CN) sy

Table S3. $[Ni(tdas)_2]^0$ (0)

MO#		Symm	E
LUMO+3		7 B2g	-0.08445
LUMO +2		8 B1u	-0.09136
LUMO +1		14 B1g	-0.12971
LUMO		6 B2g	-0.20235
HOMO		7 B1u	-0.26249
HOMO-1		4 B3g	-0.26813
HOMO-2		3 Au	-0.27447
HOMO-3		22 Ag	-0.30193
HOMO-4		15 B2u	-0.30365

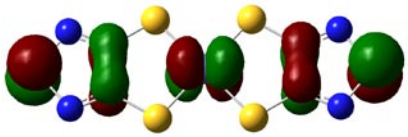
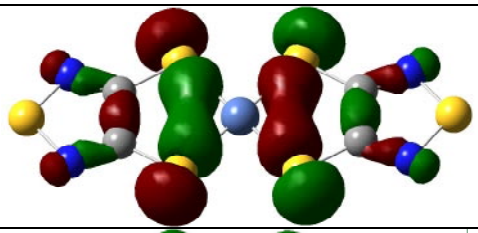
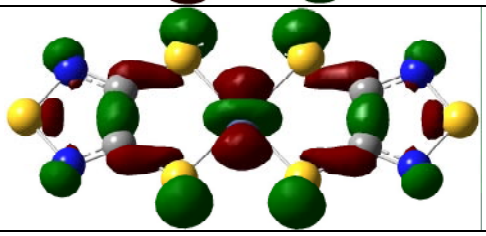
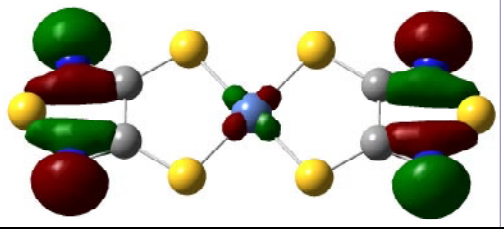
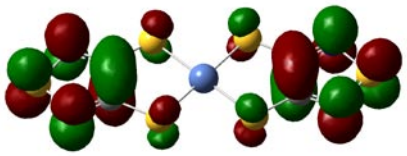
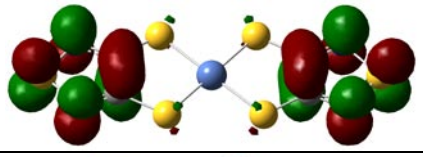
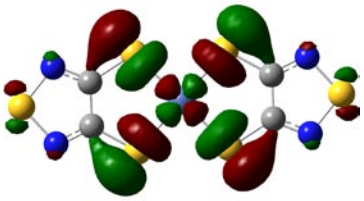
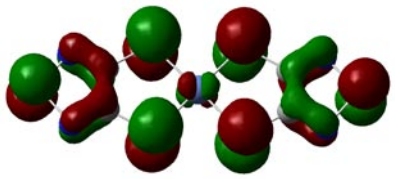
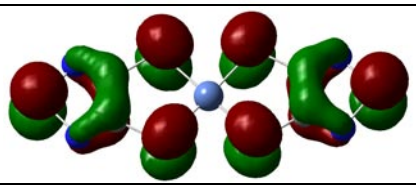
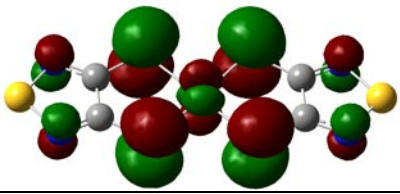
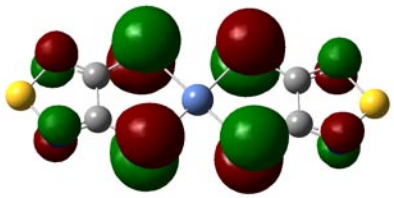
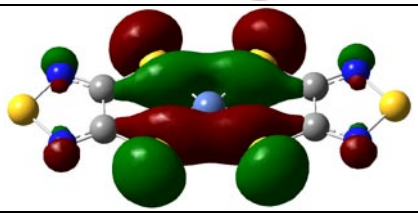
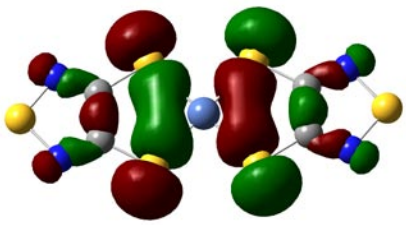
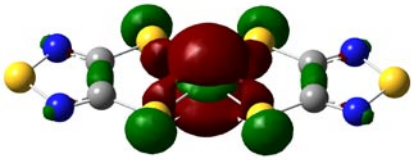
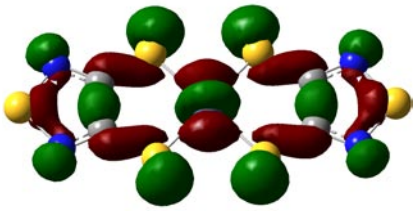
HOMO-5		5 B2g	-0.31077
HOMO-6		19 B3u	-0.31282
HOMO-7		21 Ag	-0.33045
HOMO-8		13 B1g	-0.33747

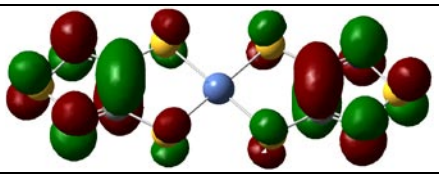
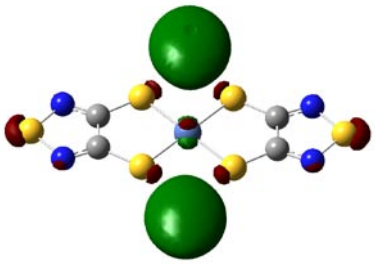
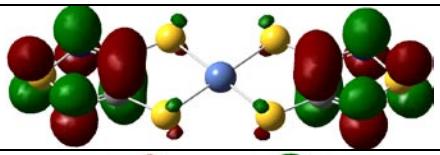
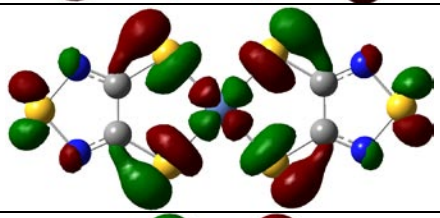
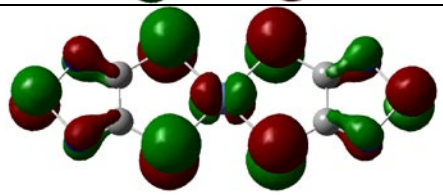
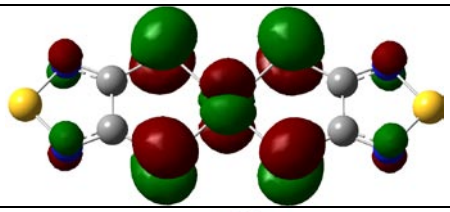
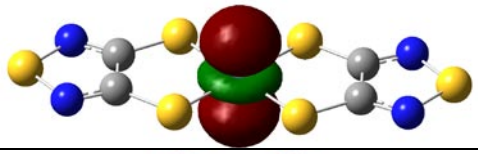
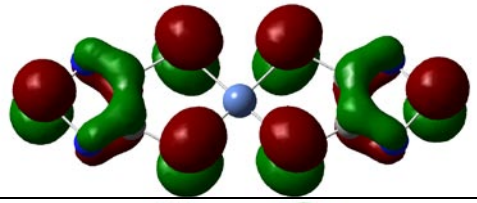
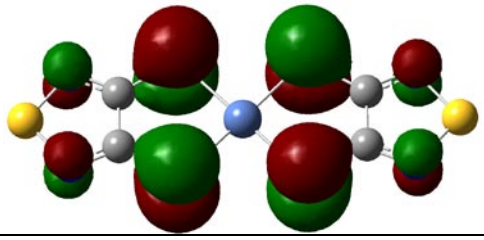
Table S4. $[Ni(tdas)_2]^{1-}$ (1)

MO#n		Symm	E alfa	E beta	Symm
LUMO +2		7 B2g	0.04637	0.05115	7 B2g
LUMO +1		8 B1u	0.03966	0.04321	8 B1u
LUMO		14 B1g	-0.00305	0.00964	13 B1g
SOMO		6 B2g	-0.10624 ↑	-0.04493 (LUMO β)	6 B2g
HOMO *		7 B1u	-0.13419 ↑	-0.12279 ↓	4 B3g
HOMO-1 *		4 B3g	-0.1348 ↑	-0.12449 ↓	7 B1u
HOMO-2		3 Au	-0.13921 ↑	-0.12733 ↓	3 Au
HOMO-3 *		15 B2u	-0.15871 ↑	-0.14112 ↓	5 B2g
HOMO-4 *		19 B3u	-0.17295	-0.15880	15 B2u

HOMO-5		22 Ag	-0.17330	-0.16496	22 Ag
HOMO-6 *		21 Ag	-0.19489	-0.1729	19 B3u
HOMO-7 *		5 B2g	-0.20344	-0.18662	21 Ag

* The drawings refer to the alfa orbitals symmetry.

Table S5. $[Ni(tdas)_2]^{2-}$ (2)

MO#		Symm	E
LUMO+3		7 B2g	0.17879
LUMO +2		23 Ag	0.17459
LUMO +1		8 B1u	0.17061
LUMO		14 B1g	0.1594
HOMO		6 B2g	0.04550
HOMO-1		4 B3g	0.02587
HOMO-2		22 Ag	0.01850
HOMO-3		7 B1u	0.00738
HOMO-4		3 Au	0.00543

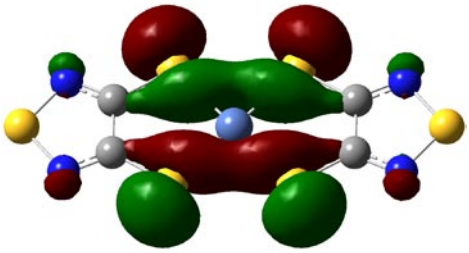
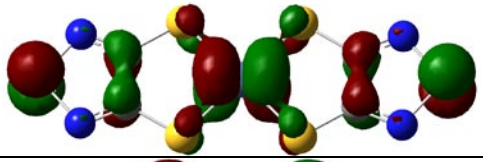
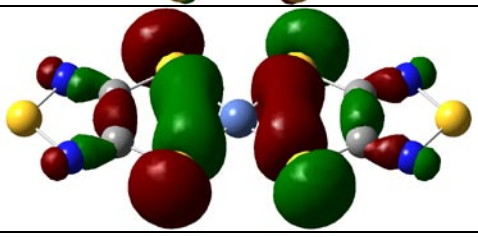
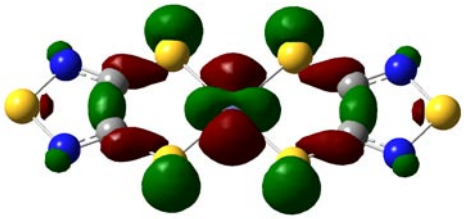
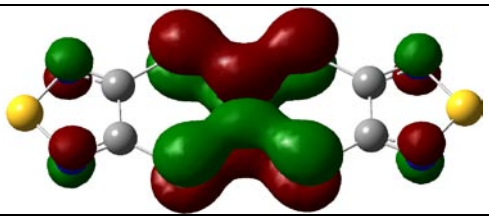
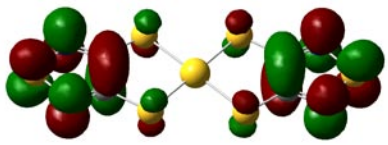
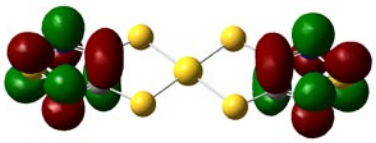
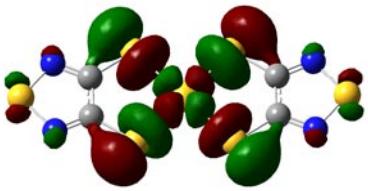
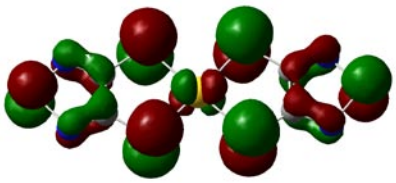
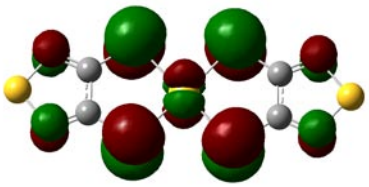
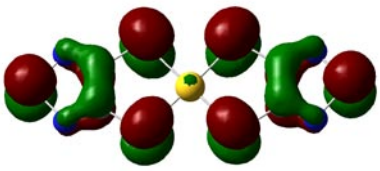
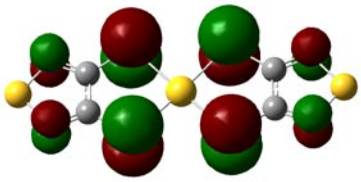
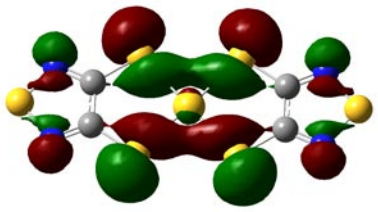
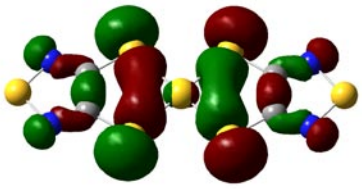
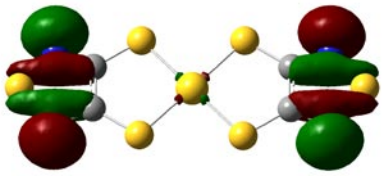
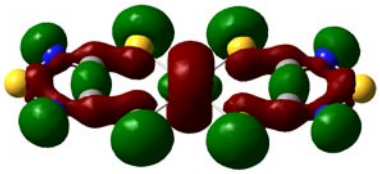
HOMO-5		15 B2u	-0.01213
HOMO-6		5 B2g	-0.01925
HOMO-7		19 B3u	-0.02715
HOMO-8		21 Ag	-0.03237
HOMO-9		3 B3g	-0.03928

Table S6. $[Au(tdas)_2]^{1-}$ (3)

DFT B3LYP/SDD

Single Point Energy calculated on the basis of X-ray average data.

MO#		Symm	E
LUMO+3		7 B2g	0.04751
LUMO +1		7 B1u	0.04206
LUMO		14 B1g	-0.00115
HOMO		6 B2g	-0.10651
HOMO-1		4 B3g	-0.13738
HOMO-2		6 B1u	-0.13993
HOMO-3		3 Au	-0.14557

HOMO-4		B2u	-0.16744
HOMO-5		B3u	-0.18348
HOMO-6		5 B2g	-0.19602
HOMO-7		5 B1u	-0.19845
HOMO-9		4 B2g	-0.21723