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Electronic Excitations in Molecular Solids:

Bridging Theory and Experiment

Electronic Supporting Information

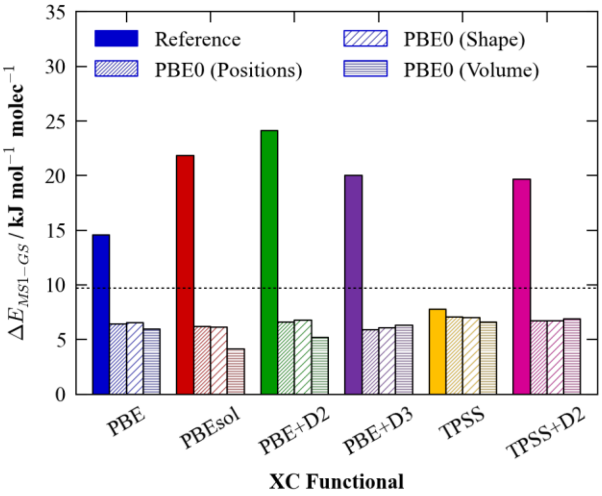

Figure S1 Recalculated GS-MS1 energy differences in the molecular crystal using the PBE0 hybrid functional[1] and structures relaxed with six different exchange-correlation (XC) functionals, at three stages during the geometry optimisation (atomic positions, cell shape, and cell volume). The differences obtained for the functionals themselves, after a full geometry relaxation, are shown alongside as references. As in Fig. 2 in the main text, the experimental enthalpy difference between the molecular crystals is overlaid as a dashed black line.

Basis Set	$\Delta E_{\mathrm{MS1\text{-}GS}}$ / kJ mol^{-1} molec^{-1}
6-31G	-2.82
6-31G(d)	-3.28
6-31G(d,p)	-3.46
6-31G(3df,3pd)	4.61
6-311G	1.48
6-311G(d)	3.02
6-311G(d,p)	3.01
6-311G(2df,2pd)	5.60
6-31++G(d,p)	2.31
6-311+G(d)	5.35
6-311++G(d,p)	4.93
6-311++G(2d,2p)	5.58
cc-pVDZ	-1.47
cc-pVTZ	7.20
aug-cc-pVDZ	7.31
aug-cc-pVTZ	6.51

Table S1 Calculated single-molecule GS-MS1 energy differences for the PBE functional[2] and various basis sets. The energies were determined from single-point energy calculations on the optimised gas-phase plane-wave geometries. This table contains additional data which is not present in Table 1 in the main text.

Basis Set	**$\Delta E_{\text{MS1-GS}}$ / kJ mol^{-1} molec^{-1}**
6-31G	-1.41
6-31G(d)	-2.20
6-31G(d,p)	-2.39
6-31G(3df,3pd)	5.18
6-311G	2.94
6-311G(d)	4.12
6-311G(d,p)	4.14
6-311G(2df,2pd)	6.40
6-31++G(d,p)	3.35
6-311+G(d)	6.39
6-311++G(d,p)	6.05
6-311++G(2d,2p)	6.30
6-311++G(3df,3pd)	7.59
cc-pVDZ	-0.40
cc-pVTZ	7.97
aug-cc-pVDZ	8.12
aug-cc-pVTZ	7.22

Table S2 Calculated single-molecule GS-MS1 energy differences for the PBE+D2 functional[3] and various basis sets. The energies were determined from single-point energy calculations on the optimised gas-phase plane-wave geometries.

	Basis Set	**$\Delta E_{\text{MS1-GS}}$ / kJ mol^{-1} molec^{-1}**	
XC Functional		**LANL2DZ PP**	**No PP**
PBE	cc-pVDZ	-1.47	4.12
	cc-pVTZ	7.20	8.74
	aug-cc-pVDZ	7.31	7.06
	aug-cc-pVTZ	6.51	-
PBE+D2	cc-pVDZ	-0.40	5.01
	cc-pVTZ	7.97	9.26
	aug-cc-pVDZ	8.12	7.92
	aug-cc-pVTZ	7.22	-
TPSS	cc-pVDZ	-4.94	-0.50
	cc-pVTZ	3.06	3.91
	aug-cc-pVDZ	3.59	2.84
	aug-cc-pVTZ	2.61	3.10

Table S3 Calculated single-molecule GS-MS1 energy differences for different functionals and with various basis sets, with and without the LANL2DZ effective-core pseudopotential[4] (PP) used to describe the Ni atom. The energies were determined from single-point energy calculations on the optimised gas-phase plane-wave geometries. As noted in the text, the use of the PP makes relatively difference with well-converged basis sets (all bar cc-pVDZ), while significantly decreasing the computational cost.

	V / Å^3	
XC Functional	**GS**	**MS1**
Experiment[5]	1687	1718
PBE	1895	1943
PBEsol	1700	1749
PBE+D2	1587	1621
PBE+D3	1667	1694
TPSS	1885	1923
TPSS+D2	1486	1509

Table S4 Predicted unit-cell volumes of the GS and MS1 crystal structures after optimisation with six different functionals, *viz.* PBE,[2] PBEsol,[6] PBE+D2,[3] PBE+D3,[7] TPSS[8] and TPSS+D2. The experimental values from Ref. [5] are included for comparison.

	GS			MS		
XC Functional	L_1 / Å	L_2 / Å	L_3 / Å	L_1 / Å	L_2 / Å	L_3 / Å
Experiment[5]	11.321	11.613	12.829	11.517	11.658	12.799
Cell Shape Relaxed						
PBE	11.350	11.586	12.827	11.540	11.633	12.802
PBEsol	11.329	11.603	12.830	11.526	11.646	12.803
PBE+D2	11.329	11.610	12.823	11.556	11.647	12.768
PBE+D3	11.344	11.597	12.821	11.522	11.654	12.797
TPSS	11.343	11.597	12.822	11.539	11.625	12.811
TPSS+D2	11.326	11.611	12.825	11.537	11.651	12.784
Cell Shape + Volume Relaxed						
PBE	11.830	11.938	13.422	12.040	12.035	13.407
PBEsol	11.383	11.608	12.863	11.601	11.689	12.900
PBE+D2	11.216	11.338	12.476	11.372	11.414	12.486
PBE+D3	11.318	11.551	12.747	11.495	11.588	12.721
TPSS	11.831	11.909	13.378	11.998	12.000	13.586
TPSS+D2	11.093	11.024	12.152	11.217	11.057	12.268

Table S5 Predicated lattice parameters of the GS and MS1 crystal structures after optimisation with six functionals, *viz.* PBE,[2] PBEsol,[6] PBE+D2,[3] PBE+D3,[7] TPSS[8] and TPSS+D2. The experimental values from Ref. [5] are included for comparison.

Bond	Bond Length / Å						
	Expt.	**PBE**	**PBEsol**	**PBE+D2**	**PBE+D3**	**TPSS**	**TPSS+D2**
Ground-State (GS)							
Ni-$\underline{\text{N}}$H (Et_4dien)	2.0142	2.03514	2.00416	2.03214	2.02969	2.04609	2.03893
Ni-N (Et_4dien)	2.2757	2.35152	2.27581	2.29031	2.32723	2.3240	2.24506
Ni-N (Et_4dien)	2.2917	2.39668	2.29647	2.29917	2.33319	2.34702	2.25610
Ni-N (η^1-NO_2)	2.0257	1.99897	1.95046	1.97718	1.98263	2.02471	1.99421
Ni-O (η^2-NO_2)	2.1025	2.10594	2.08193	2.12517	2.1489	2.10737	2.13028
Ni-O (η^2-NO_2)	2.1162	2.18482	2.12871	2.12645	2.17804	2.16334	2.10167
O--$\underline{\text{H}}$N (η^1-NO_2)	2.4480	2.21405	2.16997	2.32312	2.29722	2.18297	2.34124
Metastable State (MS1)							
Ni-$\underline{\text{N}}$H (Et_4dien)	2.0210	2.02836	2.00193	2.03522	2.02638	2.04062	2.04487
Ni-N (Et_4dien)	2.2730	2.35349	2.27808	2.29349	2.32217	2.32752	2.26383
Ni-N (Et_4dien)	2.2940	2.39047	2.28457	2.29889	2.33455	2.35843	2.25609
Ni-O (η^1-NO_2)	2.0060	2.01439	1.97649	1.99435	2.00587	2.01869	2.00273
Ni-O (η^2-NO_2)	2.1067	2.10667	2.07345	2.12965	2.13882	2.11657	2.13213
Ni-O (η^2-NO_2)	2.1250	2.16036	2.11395	2.10859	2.14025	2.14808	2.08431
O--$\underline{\text{H}}$N (η^1-NO_2)	2.2800	2.09004	2.01046	2.16512	2.13361	2.10175	2.18668

Table S6 Comparison of various bond lengths around the Ni centre in the GS and MS1 crystal structures after optimisation with six functionals, *viz.* PBE,[2] PBEsol,[6] PBE+D2,[3] PBE+D3,[7] TPSS[8] and TPSS+D2. The experimental values from Ref. [5] are included for comparison.

	GS			MS		
State	***E* / eV**	**λ / nm**	**Osc. Str.**	***E* / eV**	**λ / nm**	**Osc. Str.**
1	0.95	1308	0.0003	0.82	1511	0.0000
2	1.02	1210	0.0000	0.87	1428	0.0000
3	1.13	1093	0.0000	1.00	1239	0.0003
4	1.52	817	0.0001	1.49	835	0.0002
5	1.71	723	0.0000	1.53	808	0.0000
6	1.81	684	0.0001	1.67	741	0.0001
7	2.71	458	0.0003	2.52	493	0.0000
8	2.87	432	0.0000	2.86	434	0.0000
9	3.21	387	0.0054	3.26	380	0.0130
10	3.53	351	0.0637	3.35	370	0.0013
11	3.58	346	0.0010	3.40	364	0.0317
12	3.67	338	0.0011	3.66	339	0.0007
13	3.72	333	0.0005	3.70	335	0.0004
14	3.81	325	0.0006	3.85	322	0.0000
15	3.83	323	0.0002	3.92	317	0.0093
16	3.92	316	0.0000	4.01	309	0.0004
17	3.94	315	0.0094	4.09	303	0.1620
18	4.01	309	0.0004	4.12	301	0.0006
19	4.12	301	0.1726	4.22	294	0.0012
20	4.27	290	0.0001	4.23	293	0.0006
21	4.31	288	0.0005	4.28	289	0.0157
22	4.35	285	0.0019	4.38	283	0.0071
23	4.39	282	0.0040	4.43	280	0.0108
24	4.43	280	0.0003	4.46	278	0.0062
25	4.47	277	0.0129	4.56	272	0.0167
26	4.51	275	0.0052	4.59	270	0.0002
27	4.57	271	0.0088	4.61	269	0.0007
28	4.63	268	0.0235	4.69	264	0.0192
29	4.70	264	0.0122	4.72	263	0.0202
30	4.72	263	0.0046	4.73	262	0.0051

Table S7 Transition energies and oscillator strengths computed in the molecular TD-DFT calculation on the GS and MS1 isomers. As stated in the text, the TD-DFT calculations were performed using the Gaussian 09[9] code with the ALDA TD-DFT kernel, with M06[10] and a 6-311+G(d) basis set used to compute the ground-state reference, and using a polarisable-continuum model with a dielectric constant of 3.6.

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