Electronic Supplementary Material (ESI) for CrystEngComm.

Energetics, thermal isomerisation and photochemistry of the linkage-isomer system [Ni(Et_4dien)(η^2-O,ON)(η^1-NO_2)]

Electronic Supplementary Information

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System	M_T / BM	M_1	M_2	M_3	M_4	ΔE_{FM} / kJ mol^{-1} Per Molecule
GS	8	+	+	+	+	0.00
	0	+	-	-	+	0.00
	0	+	+	-	-	-0.07
	0	+	-	+	-	-0.08
	0	0	0	0	0	35.37
MS1	8	+	+	+	+	0.00
	0	+	-	-	+	-0.02
	0	+	+	-	-	0.02
	0	+	-	+	-	0.00
	0	0	0	0	0	38.94

Table S1 Determination of the magnetic ground states of the GS and MS1 crystals. For each isomer, the relative energies of three unique antiferromagnetic states and a closed-shell (non-magnetic) state are compared to that of the reference ferromagnetic state.

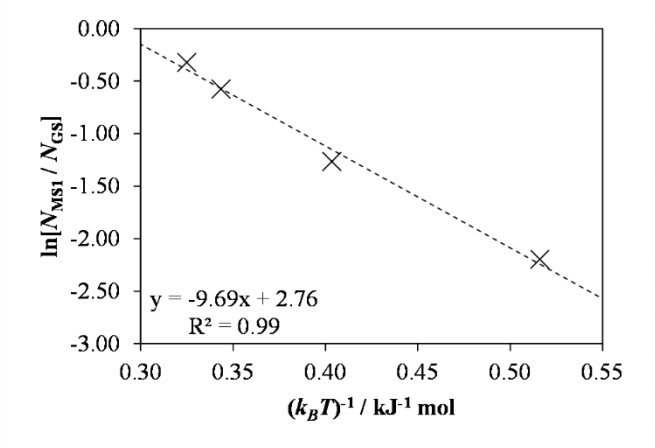

Figure S1 Fitting of the thermal population ratios of the GS and MS1 isomers published in Ref. 1 to a Boltzmann distribution, to obtain the per-molecule enthalpy difference between the two forms.

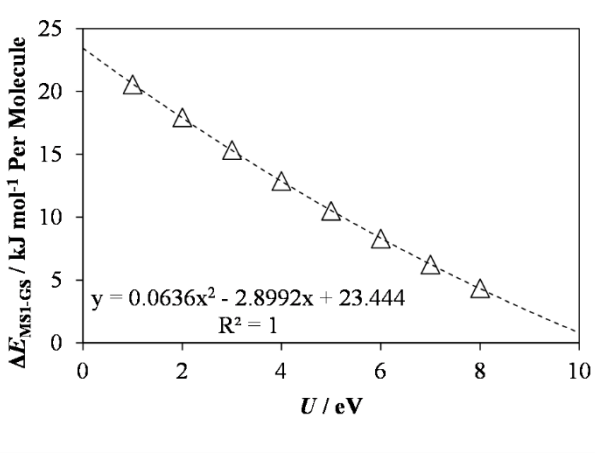

Figure S2 Effect of a Hubbard *U* correction, applied to the Ni 3*d* states, on the energy difference between the GS and MS1 isomers.

XC Functional	ΔE_{MS1-GS} / kJ mol^{-1} molec^{-1}
Exp.	9.61
PBE	16.37
PBEsol	23.91
PBE-D2	24.79
PBE-D3	21.20
vdw-DF	14.14
vdw-DF2	13.55

Table S2 Comparison of the GS-MS1 energy differences between structures optimised with six different functionals, *viz.* PBE,[2] PBEsol,[8] PBE-D2,[11] PBE-D3,[12] vdw-DF[13] and vdw-DF2,[14] with the experimental enthalpy difference obtained by fitting the temperature dependence of the isomer populations in Ref. 1 (see also Fig. S1).

Structure	Bond	*d* / Å						
		Exp.	**PBE**	**PBEsol**	**PBE-D2**	**PBE-D3**	**vdw-DF**	**vdw-DF2**
GS	Ni-O_1(η^2-NO_2)	2.10	2.11	2.08	2.12	2.14	2.15	2.17
	Ni-O_2(η^2-NO_2)	2.12	2.15	2.13	2.15	2.17	2.17	2.19
	Ni-N(η^1-NO_2)	2.03	1.98	1.95	1.98	2.01	2.01	2.03
	Ni-N(Et_4dien)	2.01	2.03	2.00	2.04	2.05	2.05	2.07
	O(η^1-NO_2)--HN	2.45	2.27	2.17	2.29	2.39	2.39	2.41
	Average $\Delta_{Exp.}$		-0.03	-0.07	-0.03	-0.02	0.01	0.03
	Std Dev $\Delta_{Exp.}$		0.09	0.12	0.08	0.09	0.05	0.05
MS1	Ni-O_1(η^2-NO_2)	2.11	2.11	2.08	2.12	2.14	2.14	2.16
	Ni-O_2(η^2-NO_2)	2.12	2.13	2.11	2.12	2.14	2.17	2.18
	Ni-O(η^1-NO_2)	2.01	2.00	1.97	2.00	2.00	2.03	2.05
	Ni-N(Et_4dien)	2.02	2.02	2.00	2.04	2.03	2.05	2.07
	O(η^1-NO_2)--HN	2.28	2.12	2.05	2.13	2.14	2.23	2.22
	Average $\Delta_{Exp.}$		-0.03	-0.07	-0.02	-0.02	0.02	0.03
	Std Dev $\Delta_{Exp.}$		0.07	0.09	0.07	0.07	0.04	0.05

Table S3 Comparison of the bond lengths in GS and MS1 crystal structures optimised with six different functionals, *viz.* PBE,[2] PBEsol,[8] PBE-D2,[11] PBE-D3,[12] vdw-DF[13] and vdw-DF2[14] with the experimental structures from Ref. 1. For each set of data, the averages and standard deviations of the differences in in the bond lengths with the experimental structures are also shown.

XC Functional	Basis Set	Continuum	$\Delta E_{GS\text{-}MS1}$/ kJ mol^{-1}
PBE[2]	LANL2DZ/6-31G(d)	None	2.45
PBE[2]	LANL2DZ/6-311G(d)	None	13.01
TPSSH[3]	LANL2DZ/6-31G(d)	None	9.71
B3LYP[4]	LANL2DZ/6-31G(d,p)	None	15.70
CAMB3LYP[5]	LANL2DZ/6-31G(d)	None	19.70
M06[6]	LANL2DZ/6-31G(d)	None	9.33
M06[6]	LANL2DZ/6-311G(d)	None	1.62
M06[6]	LANL2DZ/6-311++G(d,p)	None	1.84
M06[6]	6-311G(d)	None	2.39
M06[6]	LANL2DZ/6-31G(d)	PhMe	6.08
M06[6]	LANL2DZ/6-31G(d)	EtOH	1.62
M06[6]	LANL2DZ/6-31G(d)	H_2O	1.13
M06[6]	LANL2DZ/6-311G(d)	PhMe	0.39
M06[6]	LANL2DZ/6-311G(d)	H_2O	4.31
M06[6]	LANL2DZ/6-311++G(d,p)	PhMe	1.81
M06[6]	LANL2DZ/6-311++G(d,p)	EtOH	6.96
M06[6]	LANL2DZ/6-311++G(d,p)	H_2O	7.54
PBE0[7]	LANL2DZ/6-31G(d)	None	11.7
PBE0[7]	LANL2DZ/6-311G(d)	None	6.03
PBE0[7]	LANL2DZ/6-311G(d)	None	3.13
PBE0[7]	LANL2DZ/6-311G(d)	H_2O	5.34

Table S4 Calculated GS-MS1 energy difference for a range of functional, basis set and continuum model combinations. This table contains additional data which was omitted from Table 1 in the main text.

XC Functional	Basis Set	Continuum	$\Delta E_{MS2\text{-}MS1}$/ kJ mol^{-1}
M06[6]	LANL2DZ/6-31G(d)	None	18.72
M06[6]	LANL2DZ/6-311++G(d,p)	None	14.31
M06[6]	LANL2DZ/6-311++G(d,p)	H_2O	4.83
PBE0[7]	LANL2DZ/6-31G(d)	None	15.45
PBE0[7]	LANL2DZ/6-311++G(d)	None	8.69
PBE0[7]	LANL2DZ/6-311++G(d)	H_2O	0.86

Table S5 Calculated MS1-MS2 energy difference for a range of functional, basis set and continuum combinations. This table contains additional data which was omitted from Table 2 in the main text.

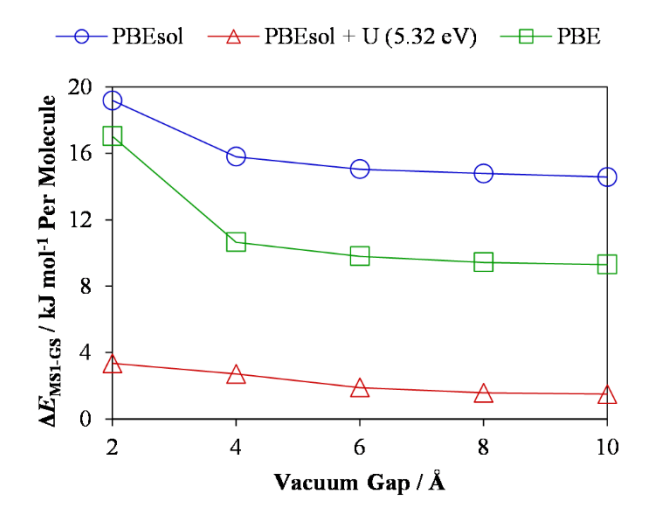

Figure S3 Calculated energy differences between isolated GS and MS1 complexes, as a function of the vacuum gap between images, using the same plane-wave pseudopotential code which was used to perform the solid-state calculations. The three lines show the energies for the PBEsol[8] (blue circles), PBEsol+*U* (5.32 eV; red triangles) and PBE[2] (green squares) functionals.

	d / Å				
	GS		MS1		MS2
Bond	**Calc.**	**Exp.**	**Calc.**	**Exp.**	**Calc.**
Ni-O_1(η^2-NO_2)	2.14	2.10	2.15	2.11	2.15
Ni-O_2(η^2-NO_2)	2.16	2.12	2.16	2.12	2.15
Ni-N(η^1-NO_2)	2.06	2.03	-	-	-
Ni-O(η^1-NO_2)	-	-	2.06	2.01	2.04
Ni-N(Et_4dien)	2.03	2.01	2.03	2.02	2.04
O(η^1-NO_2)--HN	2.21	2.45	2.05	2.28	-
N(η^1-NO_2)--HN	-	-	-	-	2.27

Table S6 Comparison of the bond lengths of the optimised GS, MS1 and MS2 complexes presented in Figure 3 in the main text with the available experimental data in Ref. 1. We note that a crystal structure containing the MS2 species was not available, and thus we were not able to compare the calculated bond lengths in this complex to experimental data.

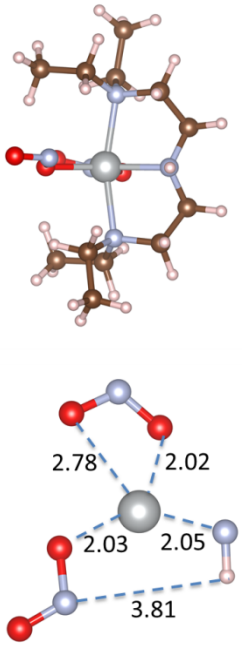

Figure S4 Optimised geometry of the transition state found by scanning in-plane rotations of the NO_2 group, which could potentially connect the GS and MS2 isomers (referred to as TS3 in the text). This transition state was found from intrinsic reaction coordinate (IRC) calculations[9] to connect two high-energy metastable states which have not yet been observed experimentally.

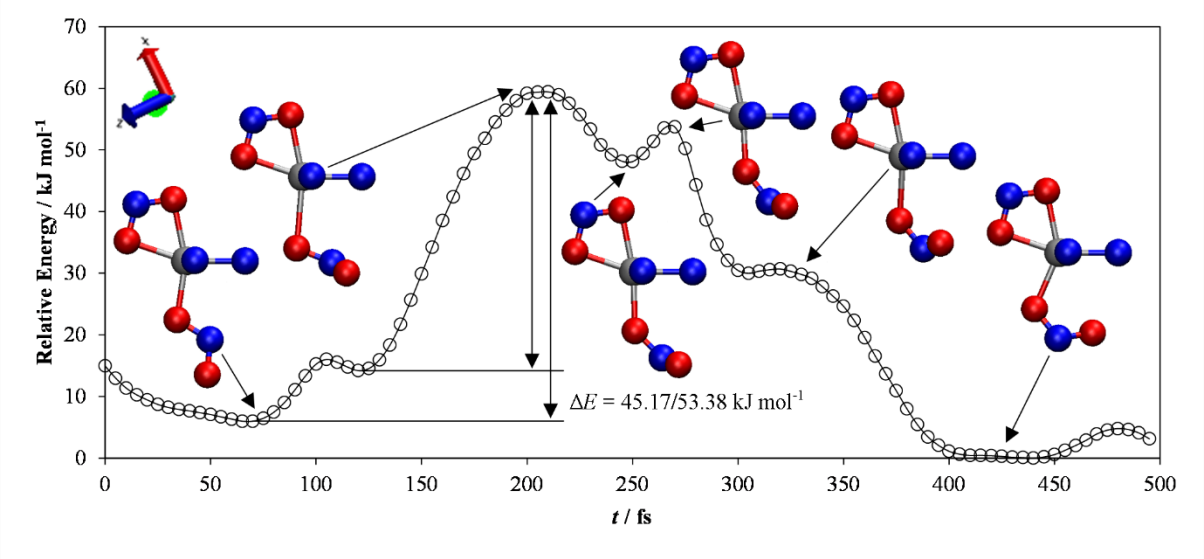

Figure S5 Energy profile for the *exo*-to-*endo* transition in [Ni(Et_4dien)(η^2-O,ON)(η^1-NO_2)], obtained from constrained *ab initio* molecular-dynamics simulations. This is essentially the reverse of the process depicted in Figure 5 in the main text. As in that figure, the atoms are colour coded as follows: N - blue, O - red, Ni - silver. The snapshots were prepared using the VMD software.[10]

	GS		MS1	
State	***E* / eV (nm)**	**Oscillator Strength**	***E* / eV (nm)**	**Oscillator Strength**
T_1	0.98 (1260)	0.0002	1.01 (1230)	0.0000
T_2	1.01 (1230)	0.0001	1.08 (1145)	0.0000
T_3	1.08 (1145)	0.0000	1.55 (799)	0.0003
T_4	1.55 (799)	0.0002	1.65 (752)	0.0000
T_5	1.65 (752)	0.0000	1.82 (682)	0.0002
T_6	1.82 (682)	0.0001	2.73 (455)	0.0001
T_7	2.73 (455)	0.0002	2.88 (431)	0.0000
T_8	2.88 (431)	0.0000	3.41 (363)	0.0000
T_9	3.41 (363)	0.0073	3.61 (343)	0.0015
T_{10}	3.61 (343)	0.0005	3.64 (340)	0.0197
T_{11}	3.64 (340)	0.0376	3.67 (338)	0.0218
T_{12}	3.67 (338)	0.0205	3.73 (332)	0.0011
T_{13}	3.73 (332)	0.0003	3.83 (324)	0.0010
T_{14}	3.83 (324)	0.0008	3.85 (322)	0.0000
T_{15}	3.85 (322)	0.0002	3.91 (317)	0.0379
T_{16}	3.91 (317)	0.0000	3.98 (312)	0.1044
T_{17}	3.98 (312)	0.0238	4.02 (309)	0.0104
T_{18}	4.02 (309)	0.1216	4.05 (306)	0.0000
T_{19}	4.05 (306)	0.0272	4.20 (295)	0.0022
T_{20}	4.20 (295)	0.0003	4.26 (291)	0.0292
T_{21}	4.26(291)	0.0001	4.27 (290)	0.0015
T_{22}	4.27 (290)	0.0064	4.36 (285)	0.0147
T_{23}	4.36 (285)	0.0268	4.38 (283)	0.0020
T_{24}	4.38 (283)	0.0016	4.45 (279)	0.0091
T_{25}	4.45 (279)	0.0024	4.56 (272)	0.0027
T_{26}	4.56 (272)	0.0017	4.64 (267)	0.0071
T_{27}	4.64 (267)	0.0343	4.81 (258)	0.0216
T_{28}	4.81 (258)	0.0020	4.82 (257)	0.0003
T_{29}	4.82 (257)	0.0021	4.83 (257)	0.0031
T_{30}	4.83 (257)	0.0056	1.01 (1230)	0.0179

Table S7 Triplet excited states calculated at the TD-DFT/M06[6] level with the LANL2DZ/6-311++G(d,p) basis set and water as a continuum.

	GS		MS1	
State	***E* / eV (nm)**	**Oscillator Strength**	***E* / eV (nm)**	**Oscillator Strength**
T_1	1.7204 (721)	0.0002	1.5612 (794)	0.0001
T_2	1.7902 (693)	0.0007	1.6068 (772)	0.0000
T_3	1.8407 (674)	0.0000	1.7733 (699)	0.0009
T_4	2.6406 (470)	0.0006	2.3816 (521)	0.0000
T_5	2.6782 (463)	0.0002	2.5595 (484)	0.0001
T_6	2.7060 (458)	0.0001	2.6119 (475)	0.0010
T_7	2.7139 (457)	0.0000	2.6904 (461)	0.0000
T_8	2.9311 (423)	0.0002	2.7943 (444)	0.0002
T_9	3.5797 (346)	0.0000	3.4756 (357)	0.0010
T_{10}	3.6150 (343)	0.0000	3.6574 (339)	0.0006
T_{11}	3.6654 (338)	0.0005	3.7275 (333)	0.0001
T_{12}	3.6881 (336)	0.0003	3.7483 (331)	0.0002
T_{13}	3.7428 (331)	0.0000	3.7653 (329)	0.0209
T_{14}	3.7975 (327)	0.0002	3.8676 (321)	0.0002
T_{15}	3.8156 (325)	0.0138	3.8979 (318)	0.0151
T_{16}	4.0219 (308)	0.0460	4.1122 (302)	0.0003
T_{17}	4.1456 (299)	0.0088	4.1333 (300)	0.0017
T_{18}	4.2124 (294)	0.0001	4.1689 (297)	0.0018
T_{19}	4.2581 (291)	0.0059	4.2594 (291)	0.0685
T_{20}	4.3073 (288)	0.1031	4.3049 (288)	0.0260
T_{21}	4.3269 (287)	0.0000	4.3248 (287)	0.0474
T_{22}	4.3375 (286)	0.0616	4.3986 (282)	0.0070
T_{23}	4.4166 (281)	0.0094	4.4702 (277)	0.0338
T_{24}	4.5446 (273)	0.0016	4.4903 (276)	0.0116
T_{25}	4.5584 (272)	0.0117	4.4952 (276)	0.0010
T_{26}	4.6341 (268)	0.0018	4.6409 (267)	0.0001
T_{27}	4.7252 (262)	0.0066	4.6747 (265)	0.0013
T_{28}	4.8036 (258)	0.0014	4.7086 (263)	0.0067
T_{29}	4.8156 (257)	0.0015	4.7883 (259)	0.0088
T_{30}	4.9268 (252)	0.0106	4.9137 (252)	0.0042

Table S8 Triplet excited states calculated at the TD-DFT/B3LYP[4] level with the LANL2DZ/6-311++G(d,p) basis set and water as a continuum.

	GS		MS1	
State	***E* / eV (nm)**	**Oscillator Strength**	***E* / eV (nm)**	**Oscillator Strength**
T_1	1.6283 (762)	0.0001	1.4706 (843)	0.0001
T_2	1.6923 (733)	0.0006	1.5253 (813)	0.0000
T_3	1.7571 (706)	0.0000	1.6777 (739)	0.0007
T_4	2.5848 (480)	0.0004	2.3175 (535)	0.0000
T_5	2.6577 (467)	0.0000	2.5100 (494)	0.0000
T_6	2.6659 (465)	0.0002	2.5547 (485)	0.0007
T_7	2.6705 (464)	0.0000	2.6526 (467)	0.0000
T_8	2.8669 (433)	0.0001	2.7306 (454)	0.0002
T_9	3.4951 (355)	0.0000	3.5116 (353)	0.0001
T_{10}	3.6868 (336)	0.0000	3.6906 (336)	0.0009
T_{11}	3.6935 (336)	0.0007	3.7996 (326)	0.0000
T_{12}	3.8004 (326)	0.0001	3.8106 (325)	0.0002
T_{13}	3.8220 (324)	0.0000	3.9140 (317)	0.0000
T_{14}	3.8352 (323)	0.0001	4.1749 (297)	0.0000
T_{15}	4.1591 (298)	0.0152	4.1845 (296)	0.0000
T_{16}	4.3304 (286)	0.0422	4.2966 (289)	0.0227
T_{17}	4.3999 (282)	0.0001	4.4353 (280)	0.0137
T_{18}	4.4125 (281)	0.0001	4.5089 (275)	0.0004
T_{19}	4.5056 (275)	0.0107	4.5234 (274)	0.0025
T_{20}	4.5818 (271)	0.0047	4.6408 (267)	0.0032
T_{21}	4.5929 (270)	0.0063	4.7027 (264)	0.1057
T_{22}	4.6799 (265)	0.1557	4.7406 (262)	0.0386
T_{23}	4.7797 (259)	0.0071	4.7689 (260)	0.0050
T_{24}	4.8871 (254)	0.0027	4.7847 (259)	0.0071
T_{25}	4.8990 (253)	0.0021	4.8684 (255)	0.0042
T_{26}	4.9557 (250)	0.0093	4.8749 (254)	0.0169
T_{27}	4.9977 (248)	0.0004	4.8997 (253)	0.0051
T_{28}	5.0427 (246)	0.0084	5.0079 (248)	0.0051
T_{29}	5.2420 (237)	0.0091	5.1485 (241)	0.0079
T_{30}	5.2995 (234)	0.0067	5.2461 (236)	0.0091

Table S9 Triplet excited states calculated at the TD-DFT/PBE0[7] level with the LANL2DZ/6-311++G(d,p) basis set and water as a continuum.

	GS		MS1	
State	***E* / eV (nm)**	**Oscillator Strength**	***E* / eV (nm)**	**Oscillator Strength**
T_1	1.0207 (1215)	0.0000	1.0602 (1170)	0.0000
T_2	1.0335 (1200)	0.0000	1.0776 (1151)	0.0000
T_3	1.0840 (1144)	0.0000	1.1259 (1101)	0.0000
T_4	1.4893 (833)	0.0001	1.4591 (850)	0.0000
T_5	1.5502 (800)	0.0001	1.4910 (832)	0.0001
T_6	1.7437 (711)	0.0000	1.6564 (749)	0.0000
T_7	2.1620 (574)	0.0000	1.7828 (696)	0.0000
T_8	2.2451 (552)	0.0001	2.1463 (578)	0.0000
T_9	2.7374 (453)	0.0000	2.4595 (504)	0.0006
T_{10}	2.8663 (433)	0.0010	2.8492 (435)	0.0005
T_{11}	2.8692 (432)	0.0002	3.3802 (367)	0.0000
T_{12}	3.3758 (367)	0.0000	3.6693 (338)	0.0000
T_{13}	3.6178 (343)	0.0000	4.0453 (307)	0.0000
T_{14}	4.0174 (309)	0.0000	4.1996 (295)	0.0000
T_{15}	4.0409 (307)	0.0000	4.4567 (278)	0.0000
T_{16}	4.4536 (278)	0.0000	4.5894 (270)	0.0000
T_{17}	6.2859 (197)	0.0639	6.3188 (196)	0.0004
T_{18}	6.3995 (194)	0.1204	6.3817 (194)	0.0557
T_{19}	6.8640 (181)	0.0039	6.6056 (188)	0.1133
T_{20}	6.9143 (179)	0.0003	6.9028 (180)	0.0002
T_{21}	7.0467 (176)	0.0035	7.0279 (176)	0.0027
T_{22}	7.1619 (173)	0.0082	7.0513 (176)	0.0027
T_{23}	7.2310 (171)	0.0143	7.1126 (174)	0.0003
T_{24}	7.2392 (171)	0.0028	7.1657 (173)	0.0009
T_{25}	7.3107 (170)	0.0156	7.2120 (172)	0.0009
T_{26}	7.3511 (169)	0.0063	7.2963 (170)	0.0220
T_{27}	7.4096 (167)	0.0017	7.3100 (170)	0.0048
T_{28}	7.4704 (166)	0.0075	7.3359 (169)	0.0014
T_{29}	7.5191 (165)	0.0059	7.4402 (167)	0.0061
T_{30}	7.5679 (164)	0.0017	7.5988 (163)	0.0059

Table S10 Triplet excited states calculated at the TD-DFT/M06HF[15, 16] level with the LANL2DZ/6-311++G(d,p) basis set and water as a continuum.

	GS		MS1	
State	***E* / eV (nm)**	**Oscillator Strength**	***E* / eV (nm)**	**Oscillator Strength**
T_1	1.6818 (737)	0.0001	1.5329 (809)	0.0001
T_2	1.7891 (693)	0.0006	1.7627 (703)	0.0006
T_3	1.9644 (631)	0.0000	1.8398 (674)	0.0000
T_4	2.7814 (446)	0.0002	2.4519 (506)	0.0000
T_5	2.8147 (441)	0.0003	2.7631 (449)	0.0000
T_6	2.8236 (439)	0.0001	2.8024 (442)	0.0004
T_7	2.9140 (426)	0.0000	2.8082 (442)	0.0003
T_8	3.1245 (397)	0.0001	3.0033 (413)	0.0001
T_9	3.5702 (347)	0.0000	3.5227 (352)	0.0011
T_{10}	3.7206 (333)	0.0007	3.7792 (328)	0.0000
T_{11}	3.7770 (328)	0.0000	3.8910 (319)	0.0005
T_{12}	3.9106 (317)	0.0005	3.9008 (318)	0.0000
T_{13}	3.9175 (317)	0.0000	4.0792 (304)	0.0000
T_{14}	4.0417 (307)	0.0000	4.2889 (289)	0.0000
T_{15}	4.4267 (280)	0.0000	4.6785 (265)	0.0000
T_{16}	4.6575 (266)	0.0004	4.7972 (258)	0.0001
T_{17}	4.7097 (263)	0.0229	4.8848 (254)	0.0345
T_{18}	4.8665 (255)	0.0353	4.9971 (248)	0.0101
T_{19}	5.0294 (247)	0.1459	5.0307 (246)	0.0088
T_{20}	5.0889 (244)	0.0068	5.0542 (245)	0.1443
T_{21}	5.2600 (236)	0.0050	5.2376 (237)	0.0033
T_{22}	5.3242 (233)	0.0368	5.3212 (233)	0.0049
T_{23}	5.3422 (232)	0.0053	5.3409 (232)	0.0067
T_{24}	5.4191 (229)	0.0047	5.3571 (231)	0.0336
T_{25}	5.4404 (228)	0.0087	5.6588 (219)	0.0234
T_{26}	5.7136 (217)	0.0480	5.7018 (217)	0.0050
T_{27}	5.7820 (214)	0.0005	5.8547 (212)	0.0041
T_{28}	5.8836 (211)	0.0036	5.9234 (209)	0.0345
T_{29}	5.9937 (207)	0.0013	6.0019 (207)	0.0001
T_{30}	6.0309 (206)	0.0011	6.0769 (204)	0.0068

Table S11 Triplet excited states calculated at the TD-DFT/wB97xd[17] level with the LANL2DZ/6-311++G(d,p) basis set and water as a continuum.

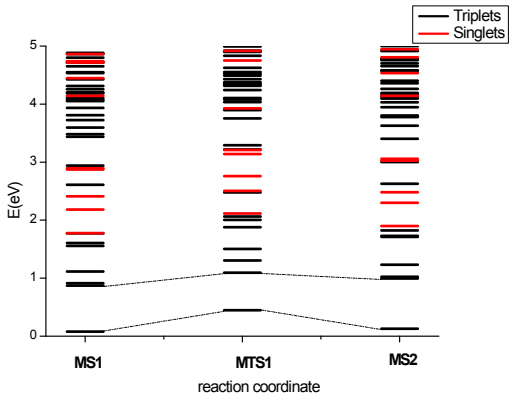

Figure S6 Energy profiles for the MTS1 MS1->MS2 transition in the ground and photoexcited states. Triplet and singlet states are indicated by black and red lines, respectively.

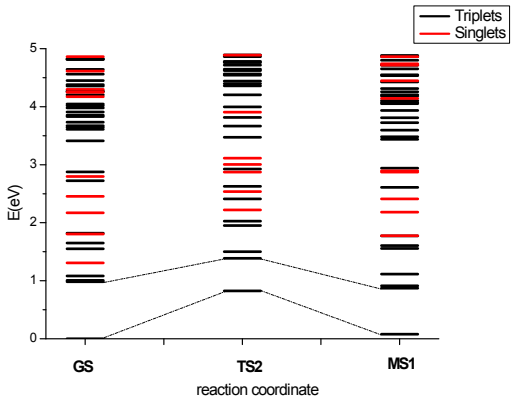

Figure S7 Energy profiles for the TS2 GS->MS1 transition in the ground and photoexcited states. Triplet and singlet states are indicated by black and red lines, respectively.

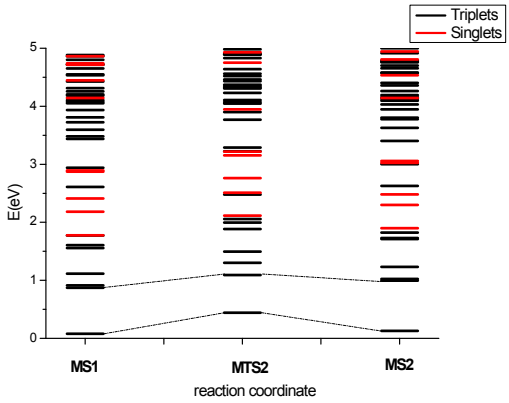

Figure S8 Energy profiles for the MTS2 MS1->MS2 transition in the ground and photoexcited states. Triplet and singlet states are indicated by black and red lines, respectively.

References

1. L. E. Hatcher, M. R. Warren, D. R. Allan, S. K. Brayshaw, A. L. Johnson, S. Fuertes, S. Schiffers, A. J. Stevenson, S. J. Teat, C. H. Woodall and P. R. Raithby, *Angewandte Chemie International Edition*, 2011, 50, 8371-8374.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, 77, 3865-3868.
3. J. M. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Physical Review Letters*, 2003, 91.
4. A. D. Becke, *J. Chem. Phys.*, 1993, 98, 1372-1377.
5. T. Yanai, D. P. Tew and N. C. Handy, *Chemical Physics Letters*, 2004, 393, 51-57.
6. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, 120, 215-241.
7. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, 110, 6158-6170.
8. L. A. Constantin, J. M. Pitarke, J. F. Dobson, A. Garcia-Lekue and J. P. Perdew, *Physical Review Letters*, 2008, 100.
9. H. P. Hratchian and H. B. Schlegel, *Journal of Chemical Physics*, 2004, 120, 9918-9924.
10. W. Humphrey, A. Dalke and K. Schulten, *J Mol Graph Model*, 1996, 14, 33-38.
11. S. Grimme, *Journal of Computational Chemistry*, 2006, 27, 1787-1799.
12. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, 132.
13. M. Dion, H. Rydberg, E. Schroder, D. C. Langreth and B. I. Lundqvist, *Physical Review Letters*, 2004, 92.
14. K. Lee, E. D. Murray, L. Z. Kong, B. I. Lundqvist and D. C. Langreth, *Physical Review B*, 2010, 82.
15. Y. Zhao and D. G. Truhlar, *J Phys Chem A*, 2006, 110, 5121-5129.
16. Y. Zhao and D. G. Truhlar, *J Phys Chem A*, 2006, 110, 13126-13130.
17. J. D. Chai and M. Head-Gordon, *Phys Chem Chem Phys*, 2008, 10, 6615-6620.