Electronic Supplementary Material (ESI) for CrystEngComm.

The Impact of Hydrogen Bonding on 100% Photo-Switching in Solid-State Nitro-Nitrito Linkage Isomers

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Supplementary Information

1. Hirshfeld surface volume analysis for the photo-active cation in [1]

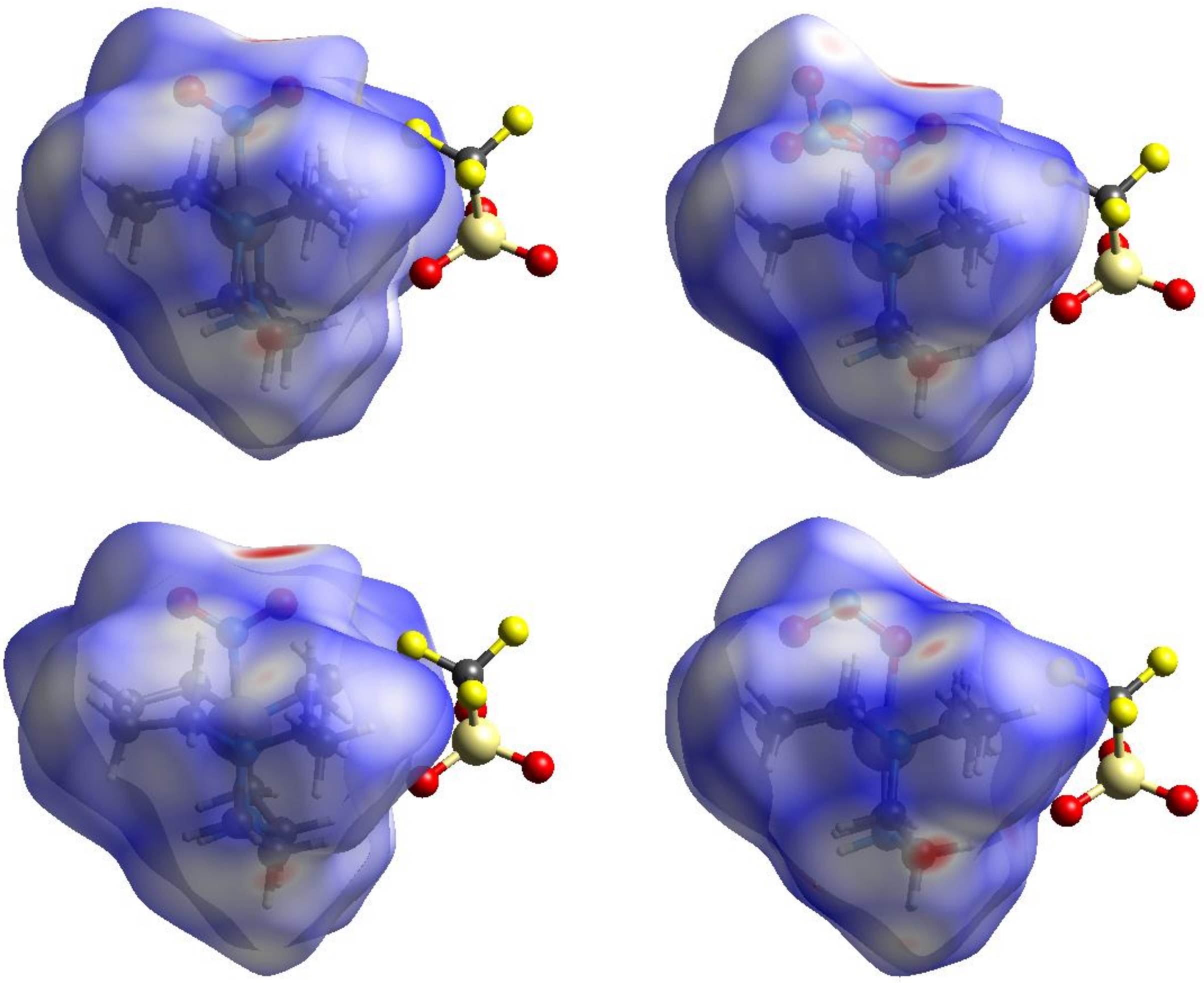

Figure S1: Hirshfeld surfaces calculated for the photo-active cation in [1] in **(a)** the GS structure at 100 K, **(b)** the MS structure at 100 K, **(c)** the GS structure at 150 K and **(d)** the MS structure at 150 K. Hirshfeld surface calculations were performed using the CrystalExplorer software.[1]

Table S1: Comparison of the Hirshfeld molecular volumes calculated for the cation in photocrystallographic experiments with [1], showing the decrease in molecular volume on photo-activation in all cases

Temp / K	Hirshfeld molecular volume of cation / Å^3		Difference Δ_{Vol} (MS – GS) / Å^3
	GS	MS	
100	394.50	389.33	- 5.17
150	397.86	384.78	-13.08

2. Ground-State Single-Crystal X-ray Structure of Complex [2]

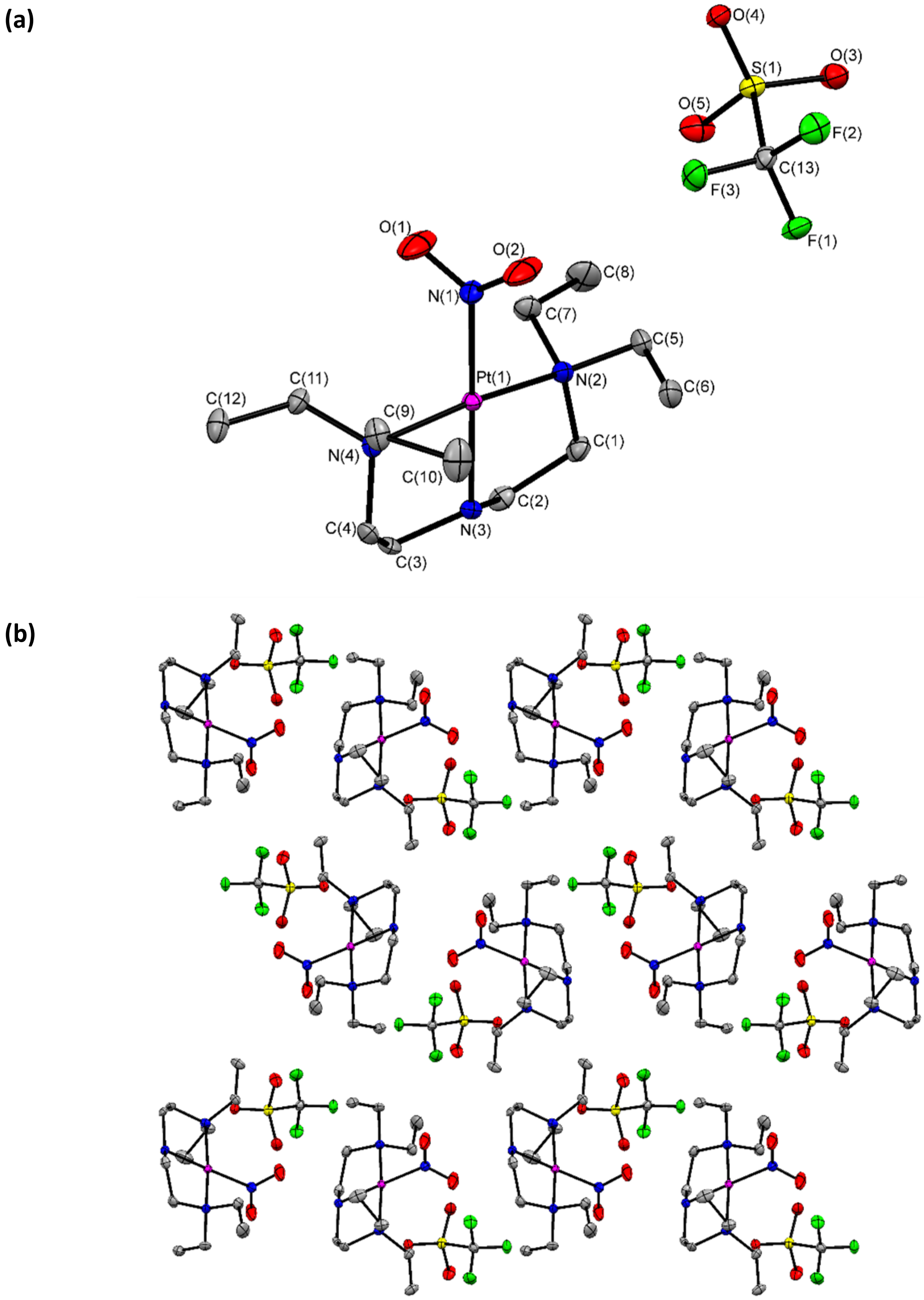

Figure S2: GS single-crystal X-ray structure of [2] at 100 K, **(a)** atomic connectivity in the asymmetric unit, ellipsoids at 50 % probability and hydrogen atoms removed for clarity, **(b)** crystal packing diagram, viewed along the *a*-axis, *b*-axis horizontal.

3. Metastable Linkage Isomers of [2] on Photo-Activation

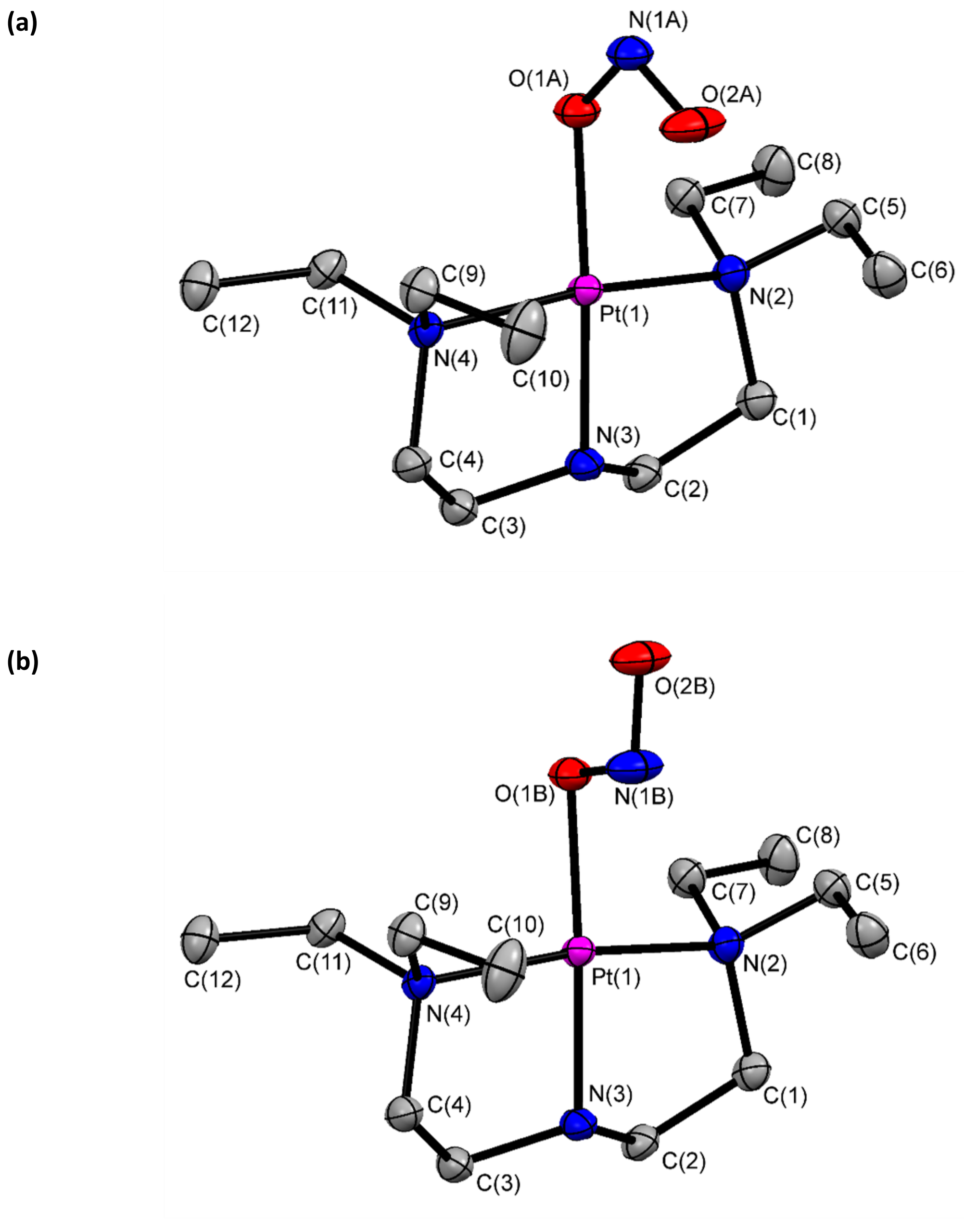

Figure S3: Single-crystal X-ray structures of photo-induced nitrite linkage isomers of [2] at 100 K, **(a)** *endo*-nitrito-(η^1-ONO), **(b)** *exo*-nitrito-(η^1-ONO). Ellipsoids at 50 % probability and hydrogen atoms removed from clarity.

4. Hirshfeld surface volume analysis for the photo-active cation in [2]

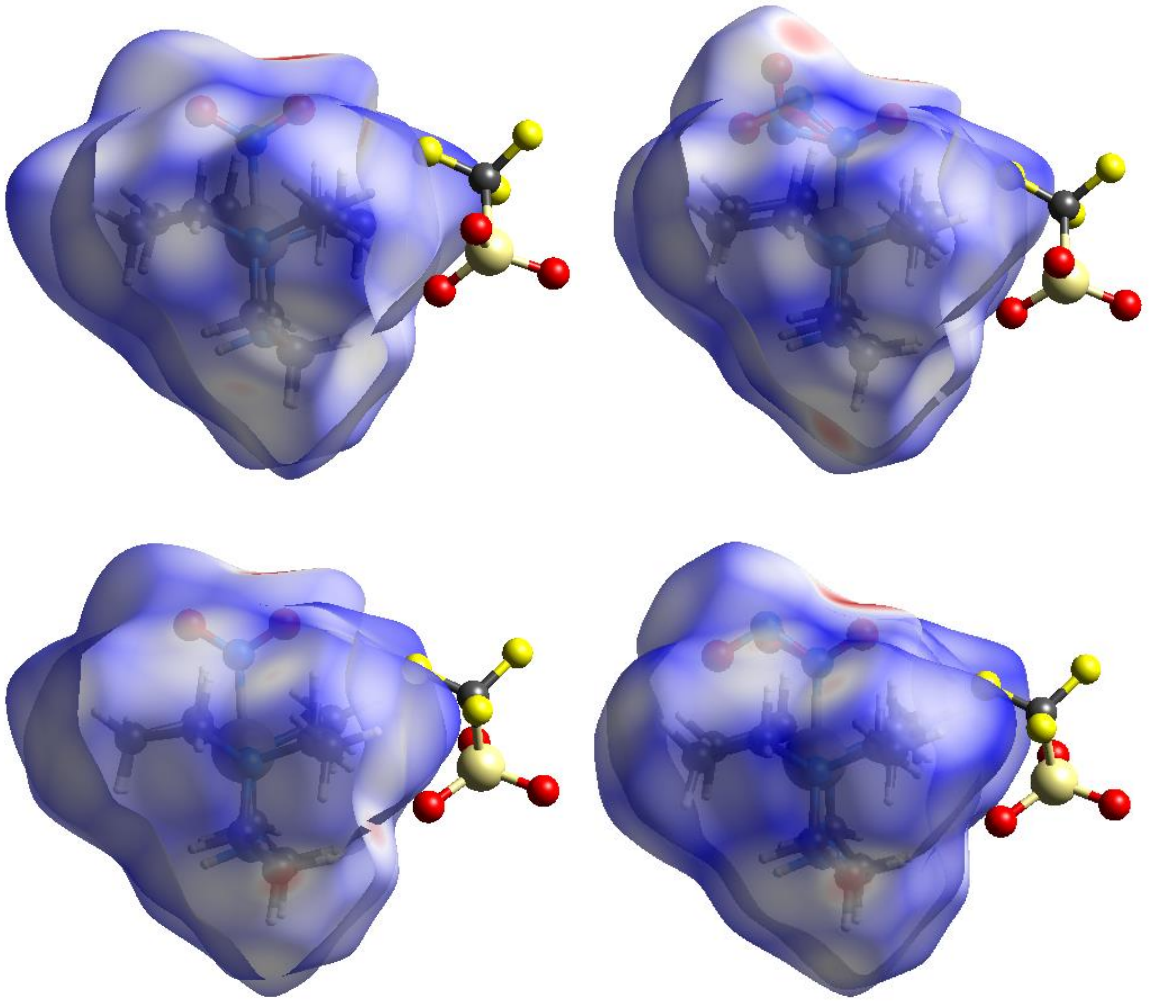

Figure S4: Hirshfeld surfaces calculated for the photo-active cation in **[2]** in **(a)** the GS structure at 100 K, **(b)** the MS structure at 100 K, **(c)** the GS structure at 200 K and **(d)** the MS structure at 200 K. Hirshfeld surface calculations were performed using the CrystalExplorer software.[1]

Table S2: Comparison of the Hirshfeld molecular volumes calculated for the cation in photocrystallographic experiments with [2], showing the decrease in molecular volume on photo-activation in all cases

Temp / K	**Hirshfeld molecular volume of cation / Å^3**		**Difference Δ$_{\text{Vol}}$ (MS – GS) / Å^3**
	GS	**MS**	
100	396.79	390.39	- 6.40
200	401.49	390.68	- 10.81

5. Reaction Cavity Analysis for Complexes [1] and [2]

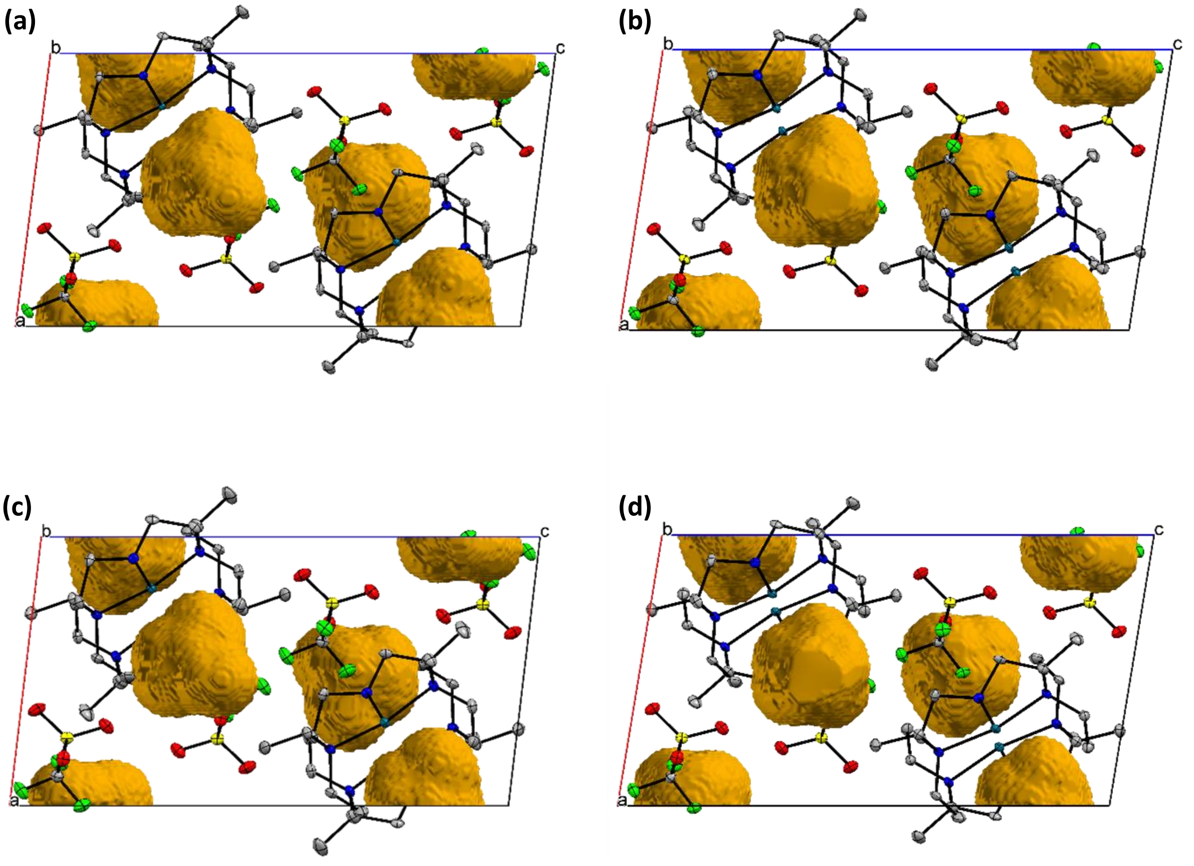

Figure S5: Reaction cavities calculated for the GS and MS structures of [1]: **(a)** 100 K GS, **(b)** 100 K MS, **(c)** 150 K GS, **(d)** 150 MS.

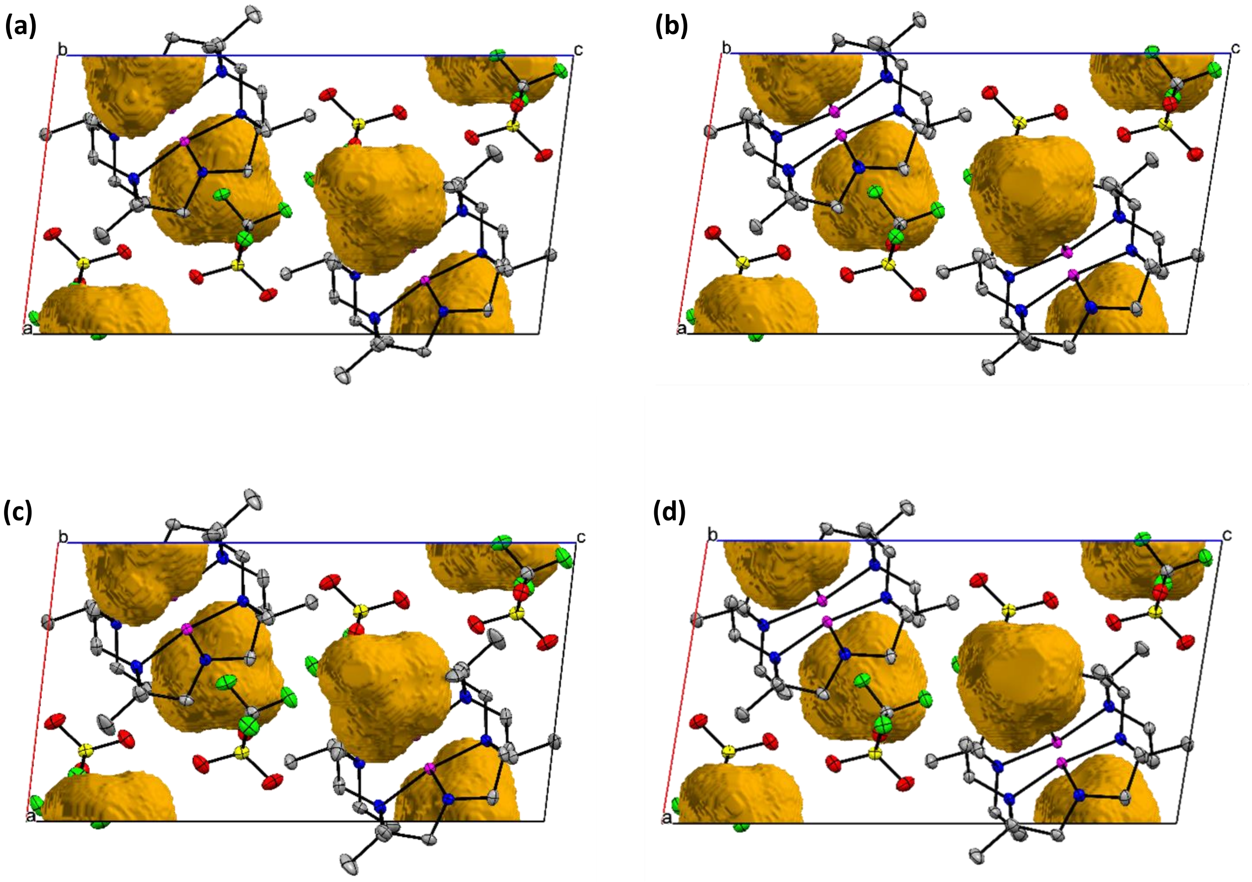

Figure S6: Reaction cavities calculated for the GS and MS structures of [2]: **(a)** 100 K GS, **(b)** 100 K MS, **(c)** 200 K GS, **(d)** 200 MS.

6. Diffuse Reflectance Spectroscopy

Solid-state diffuse reflectance spectra were collected using an Ocean Optics Maya 200 PRO High Sensitivity Spectrometer equipped with an Ocean Optics DH-2000-BCA UV-Vis-NIR light source.

Spectra were collected on evenly-ground powder samples, prepared from pure single-crystals.

Figure S5a shows the raw diffuse reflectance spectra of complexes [1] and [2]. Figure S5b shows the normalised absorption profiles for both compounds, converted from the diffuse reflectance data using the Kubelka Munk function:[2]

$$A = \frac{(1 - R_\infty)^2}{2R_\infty}$$

where A = calculated absorbance and R = diffuse reflectance.

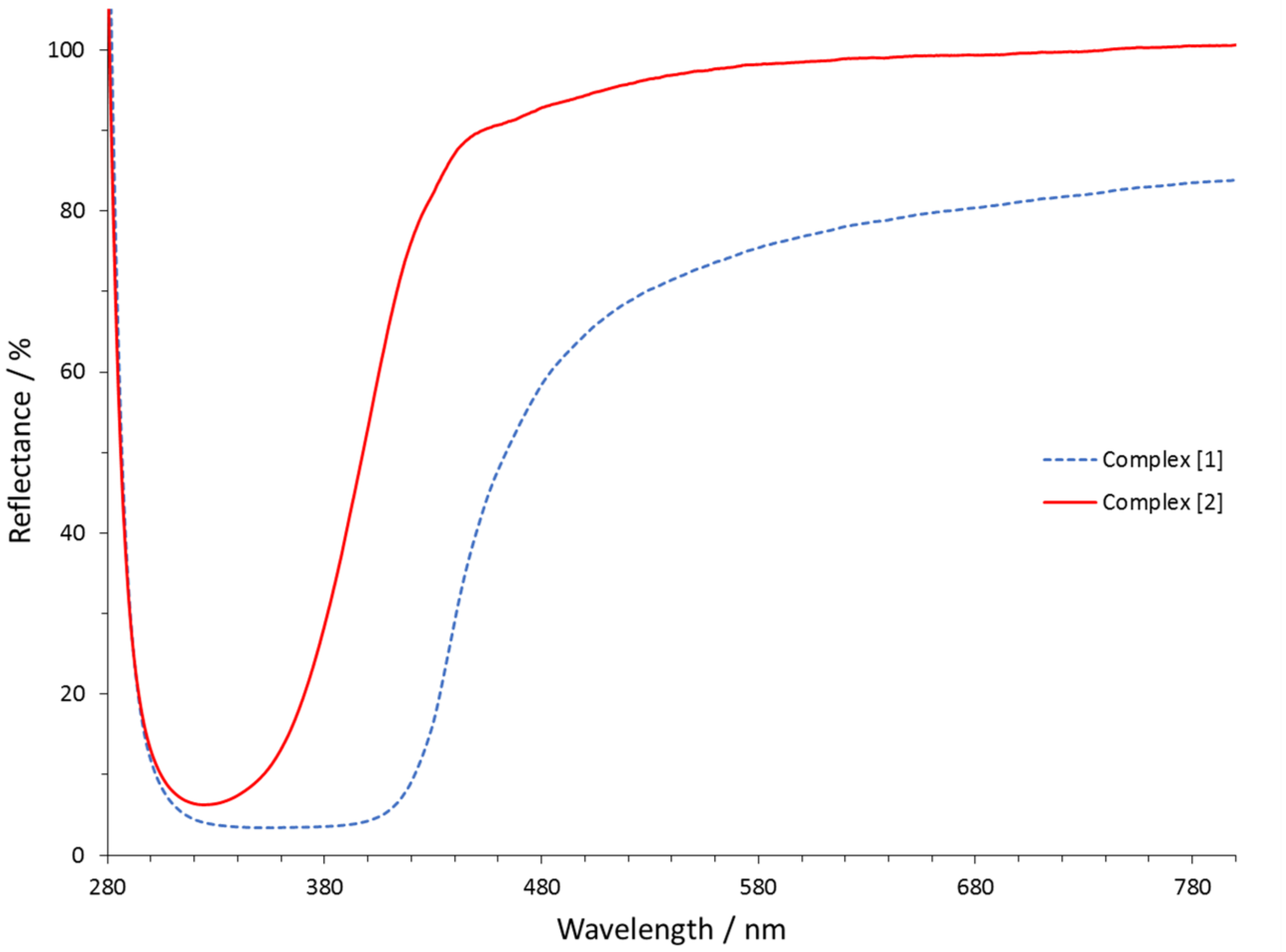

Figure S7a: Diffuse reflectance spectra for complexes [1] and [2], collected on powder samples ground from pure single crystals

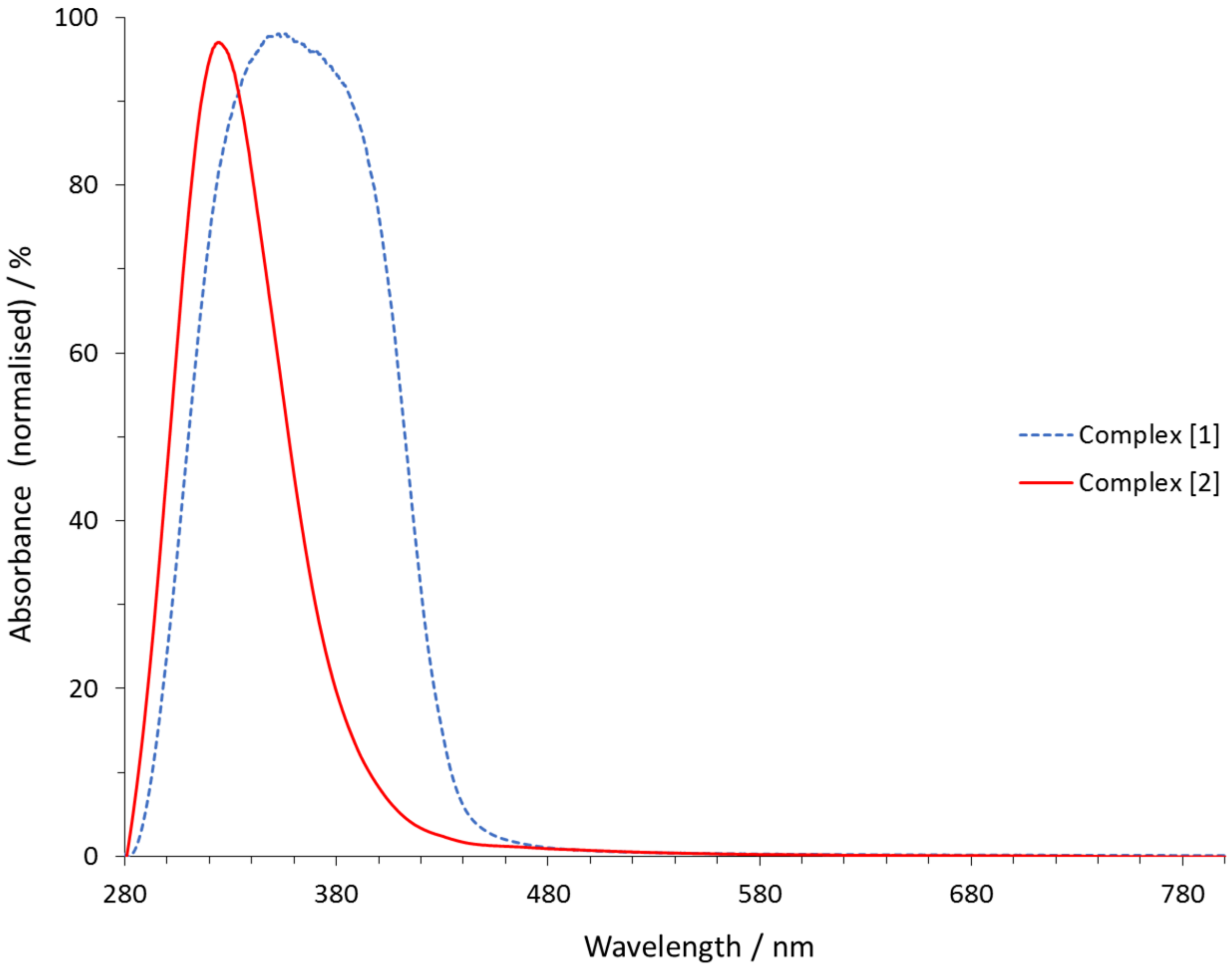

Figure S7b: Normalised absorption spectra for complexes [1] and [2], calculated using the Kubelka Munk function[2]

1. J. J. McKinnon, M. A. Spackman and A. S. Mitchell, *Acta Crystallographica Section B*, 2004, **60**, 627-668.
2. M. P. Fuller and P. R. Griffiths, *Analytical Chemistry*, 1978, **50**, 1906-1910.