Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Photoactivated Linkage Isomerism in Single Crystals of Nickel, Palladium and Platinum Di-nitro Complexes – A Photocrystallographic Investigation

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CrystalExplorer fingerprint plots

2D Fingerprint plots generated in the program CrystalExplorer[38], give a summary of the unique set of intermolecular interactions in the crystal structure and allowing comparison of the crystal packing between ground and photoactivated states.

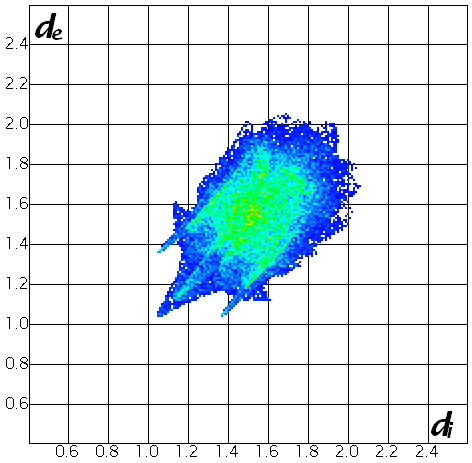
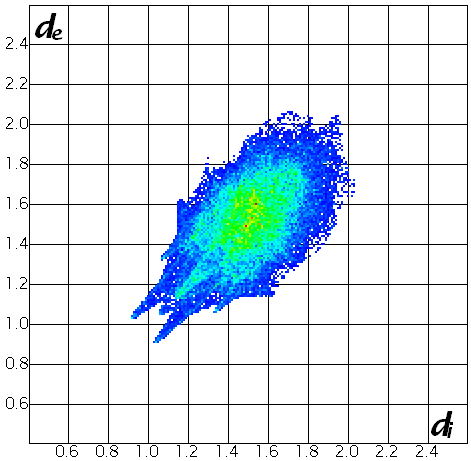
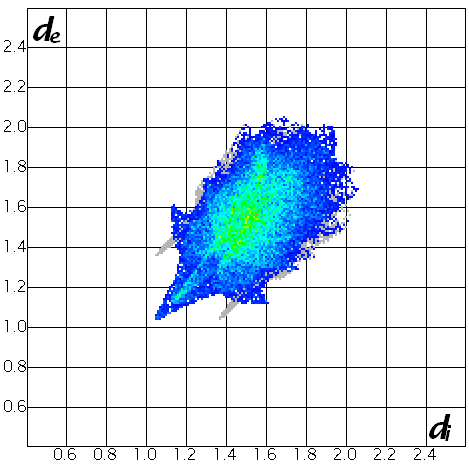
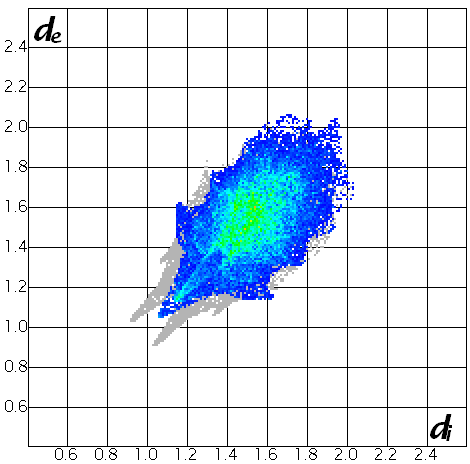
(d_e = distance from molecular surface to atom external atom, d_i = distance from molecular surface to internal atom)

Complex 1

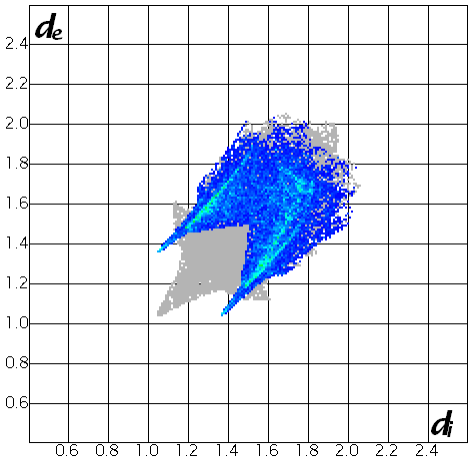
The key intermolecular interactions in **1** involve only H…H or O…H close-contacts. O…H interactions relate to changes induced by the isomerisation as oxygen is only present in nitrite group for this complex. H…H interactions represent changes in rest of structure.

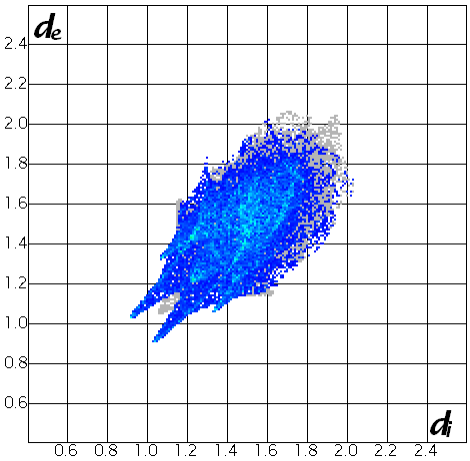
Changes in the Fingerprint plot are the result of O…H interactions; the O…H hydrogen bond "spikes" move closer to the diagonal and to a lower d_e/d_i value, showing that the hydrogen bonds shorten as a result of the isomerisation. Changes in O…H contacts are a direct result of the change in coordination mode of this ligand in 25 % of structure **1#O**.

The shape of portion of Fingerprint plot created by H…H contacts remains largely unchanged on going from GS to ES, supporting observations that the overall crystal packing is unchanged following photoactivation, excepting the isomerisation.

	1 (GS)	**1#O (ES)**
All interactions		
H…H		

O…H





Complex 2

The key intermolecular interactions in **2** consist only of C…H interactions (corresponding to changes in the whole structure) and O…H and N…H close-contacts (which can only correspond to changes involving the isomerisation, as nitrogen and oxygen atoms are only present in the nitrite ligand).

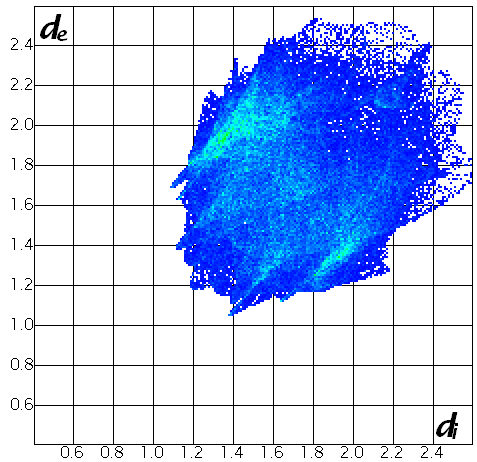
C…H and H…H plots are same shape on going from GS to ES, confirming the crystal packing is largely unchanged following photoactivation.

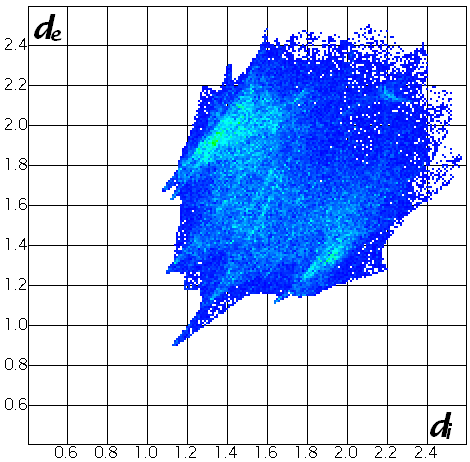
The portion of the plots corresponding to O…H contacts show O-H hydrogen bond "spikes" change position and become sharper, indicating a slight shortening of these interactions due to the isomerisation.

While no N…H close contacts are observed in **2**, a new N…H "spike" is observed in the **2#O** plot, corresponding to the formation of a new N-H interaction when N1 moves position to N1A in the metastable nitrito arrangement.

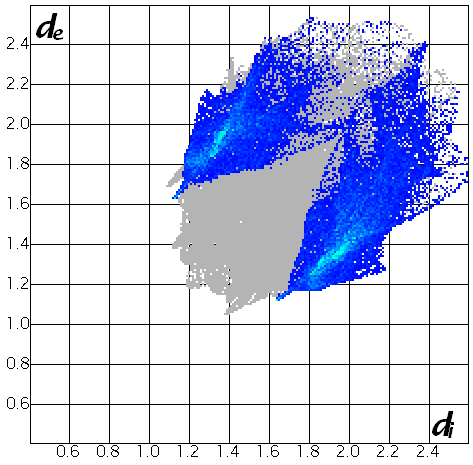
2(GS) **2#O (ES)**

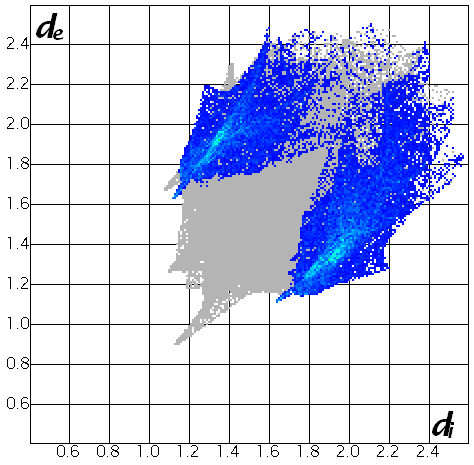
All interactions



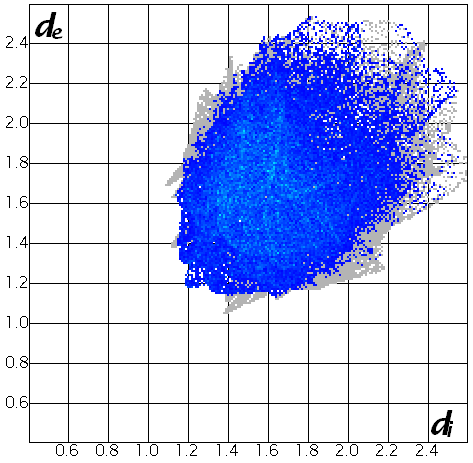


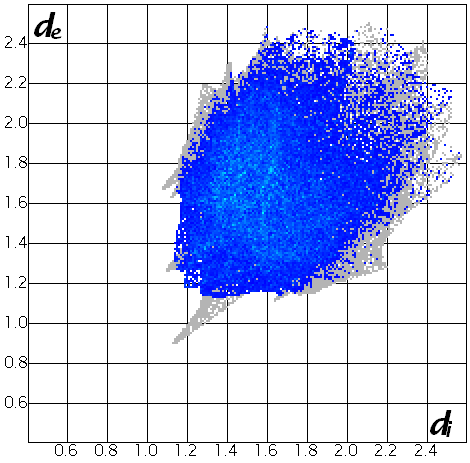
C…H


d_e
d_i
0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4

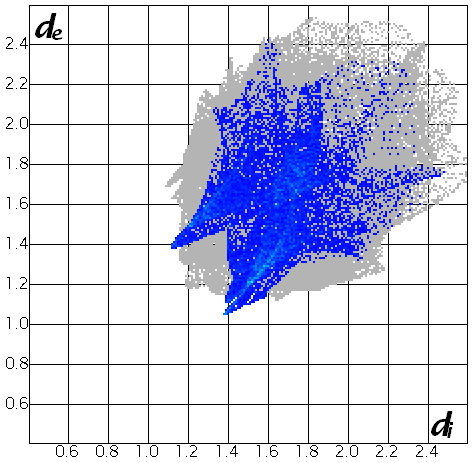

d_e
d_i
0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4

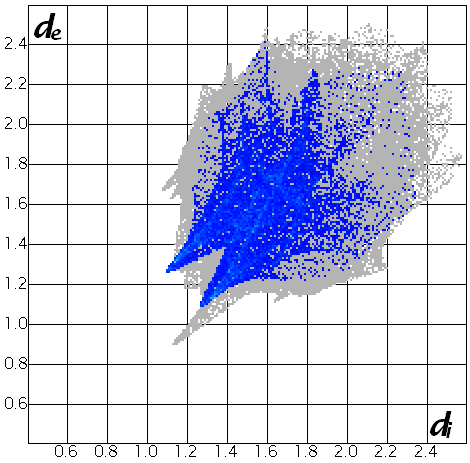
H…H


d_e
d_i
0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4

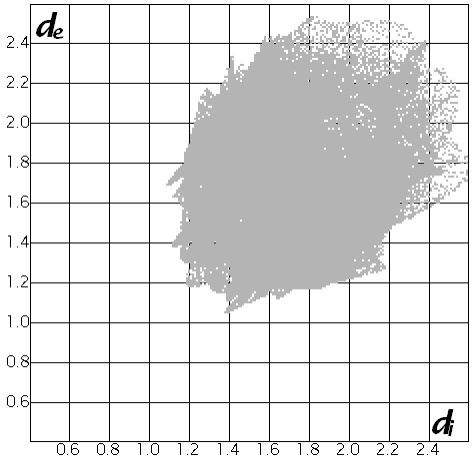

d_e
d_i
0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4

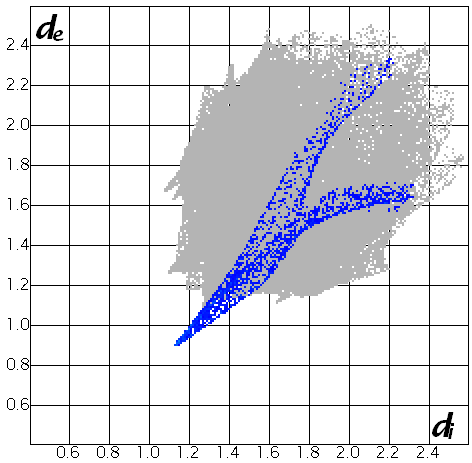
O…H


d_e
d_i
0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4


d_e
d_i
0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4

N…H





Complex 3

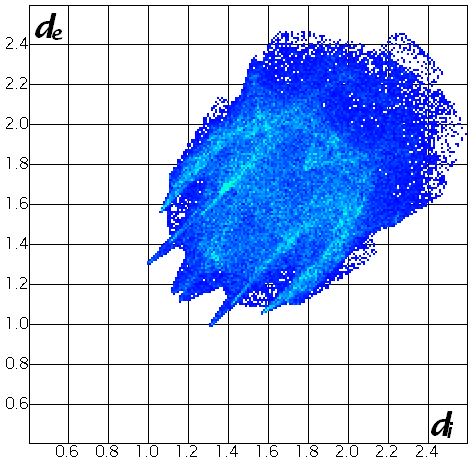
The key intermolecular interactions in **3** involve only C…H and H…H close contacts (relating to changes in the whole structure) and O…H close contacts (only related to the isomerising nitrite ligand).

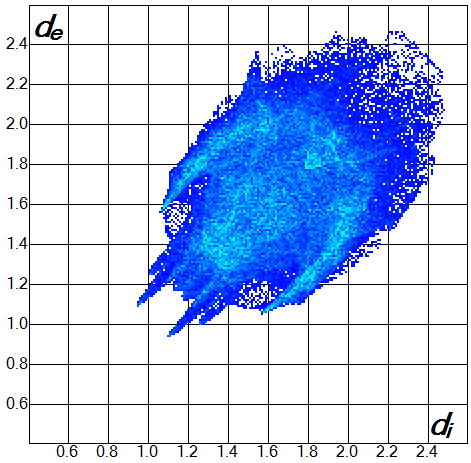
The shape of section of Fingerprint plots relating to C…H and H…H interactions are the same for **3** and **3#O**, supporting the observation that the crystal packing is unchanged excepting the isomerisation.

The only changes between the plots relate to changes in O…H interactions with hydrogen bond "spikes" moving to a lower d_e/d_i value, showing that O…H hydrogen bonds become shorter on photoexcitation.

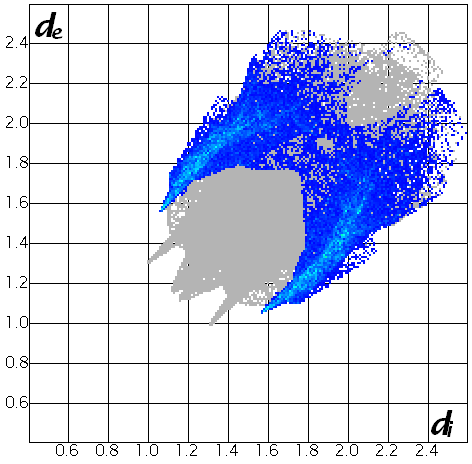
3(GS) **3#O (ES)**

All interactions





C…H


de
di
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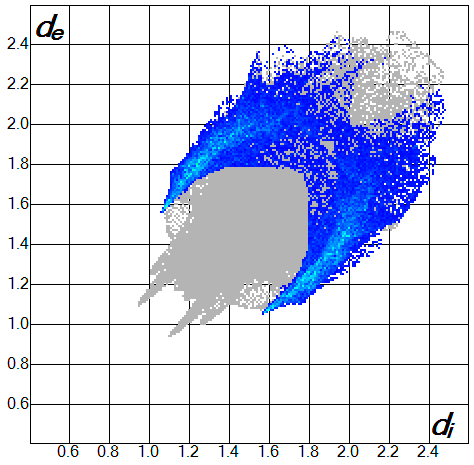
de
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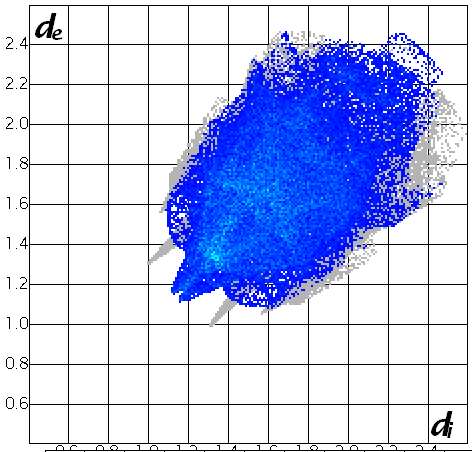
H…H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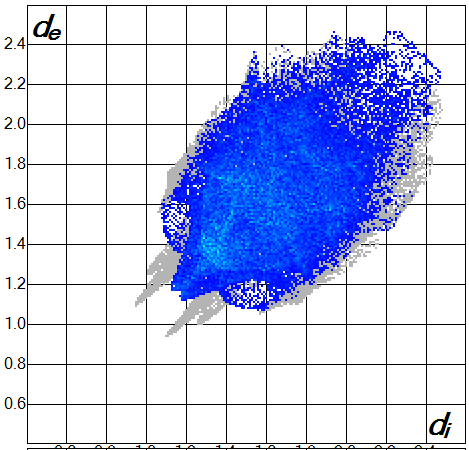
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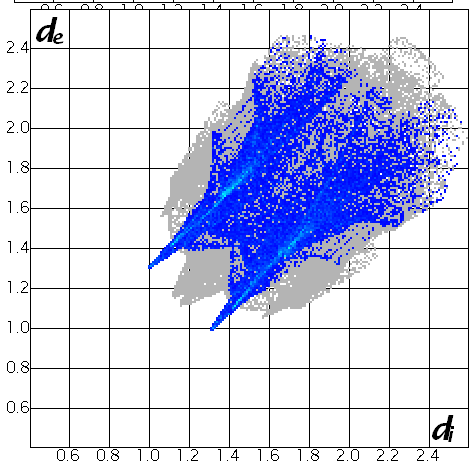
O…H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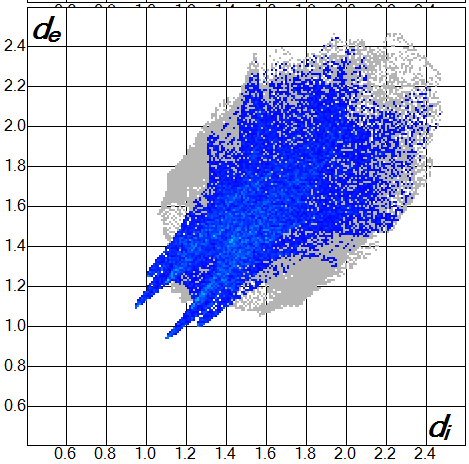
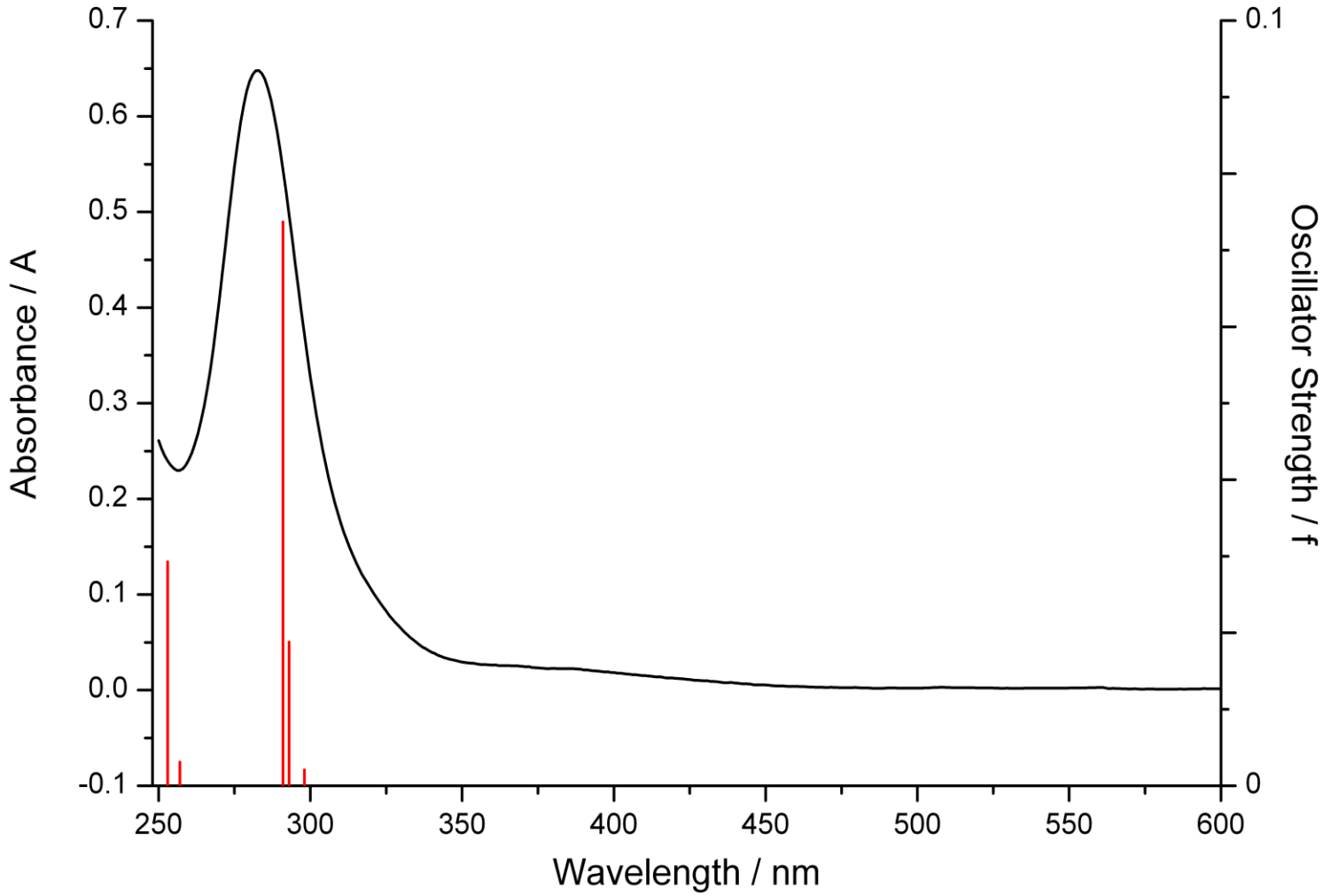
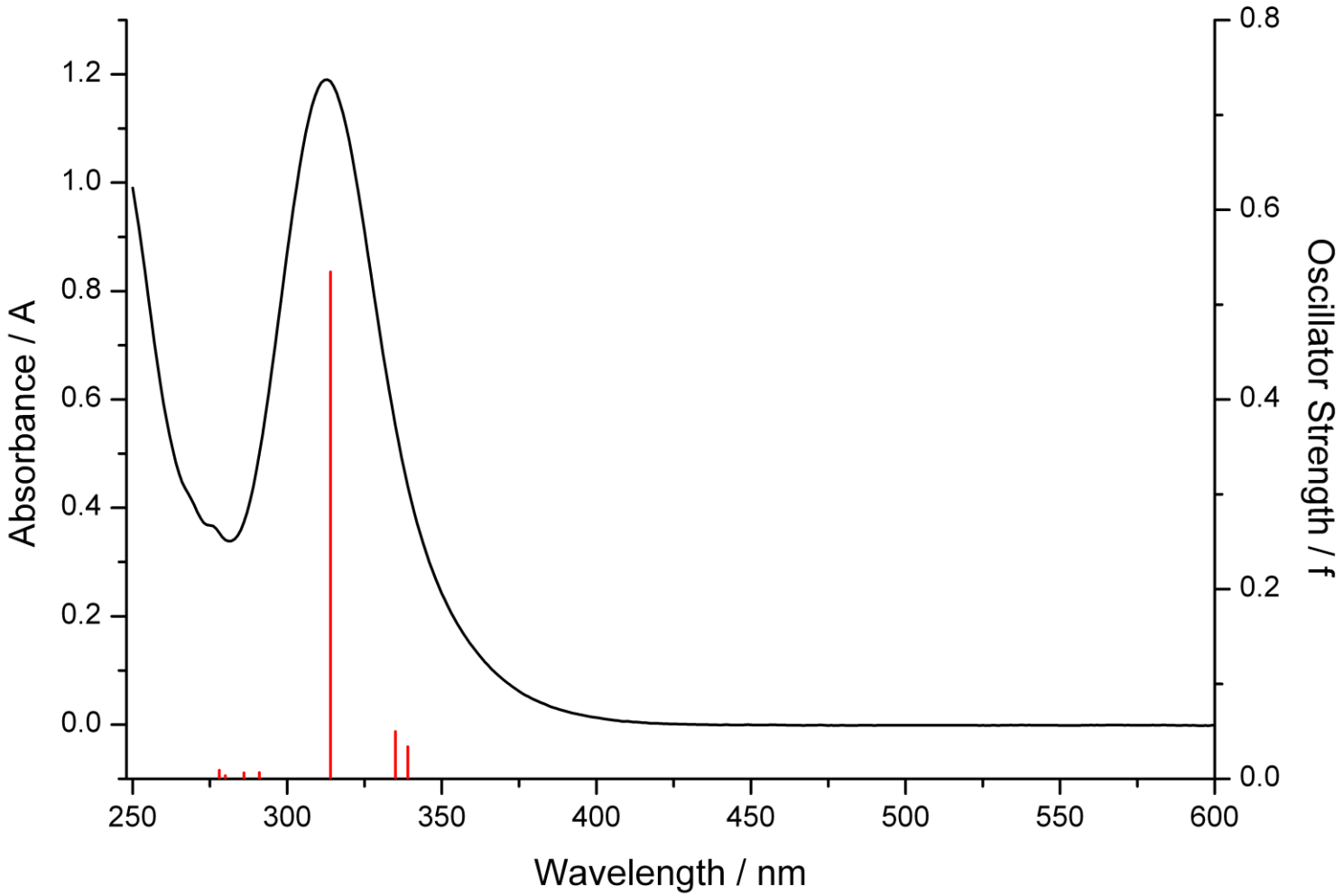

de
di
0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4

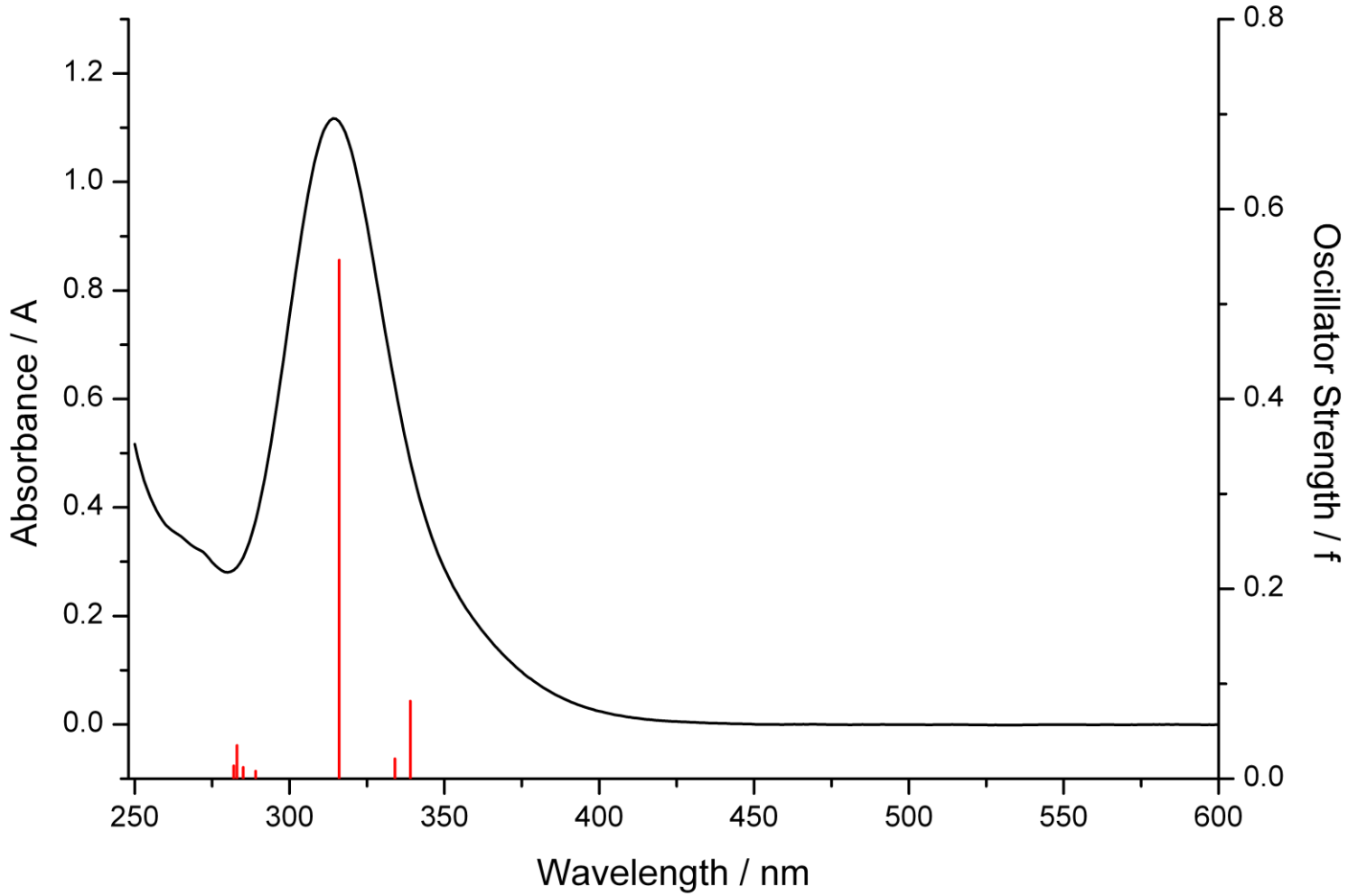
UV/vis Spectra and Calculated Electronic Transitions



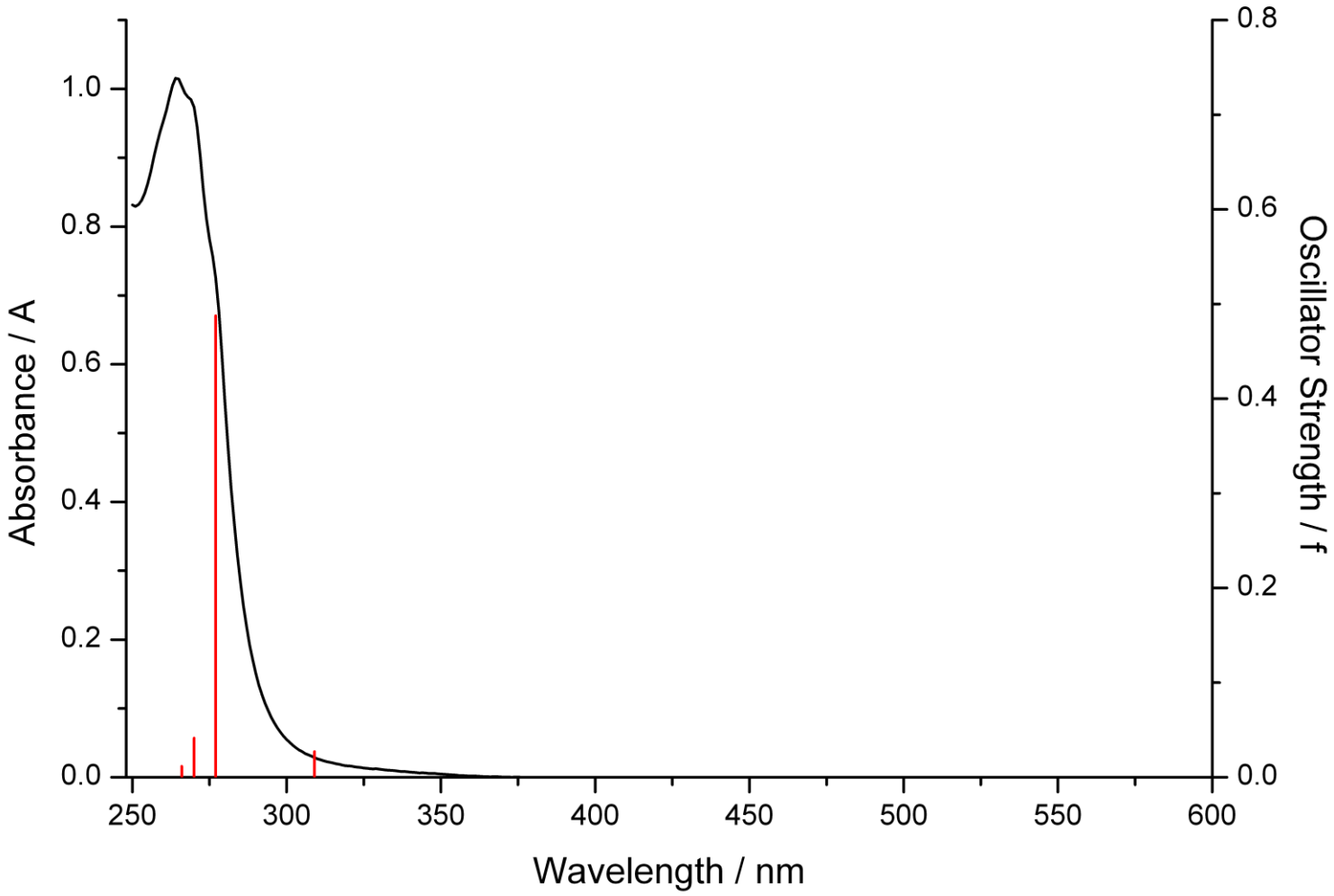
Spectrum 1: Solution UV/vis spectrum of **1** (1 x 10^{-4}M solution) and expected electronic transitions from TD-DFT calculations



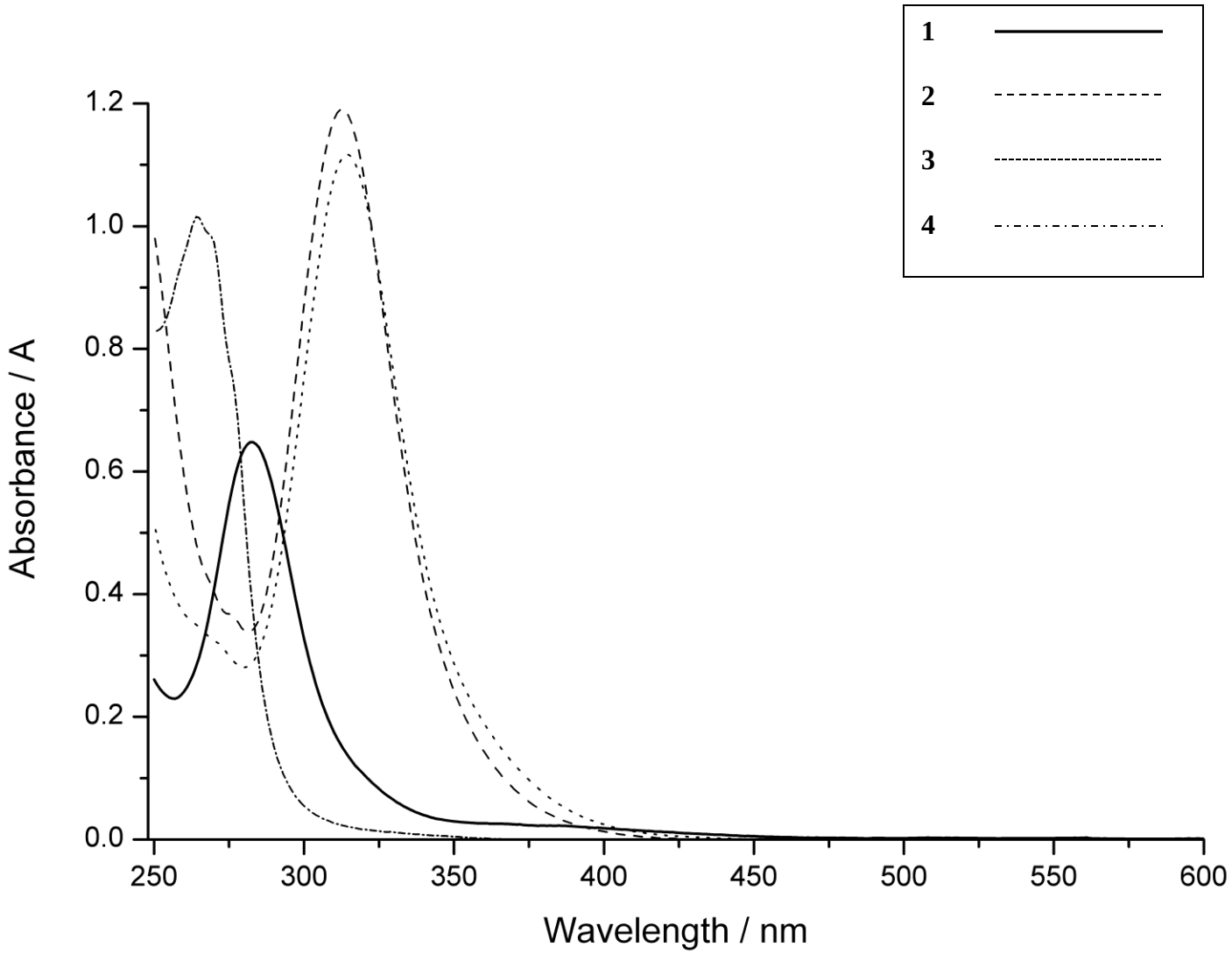
Spectrum 2: Solution UV/vis spectrum of **2** (1 x 10^{-4}M solution) and expected electronic transitions from TD-DFT calculations



Spectrum 3: Solution UV/vis spectrum of **3** (1 x 10^{-4}M solution) and expected electronic transitions from TD-DFT calculations



Spectrum 4: Solution UV/vis spectrum of **4** (1 x 10^{-4}M solution) and expected electronic transitions from TD-DFT calculations



Spectrum 5: Overlay of UV/vis spectra for complexes **1** to **4**