Electronic Supplementary Material (ESI) for CrystEngComm.

Raising the (Metastable) Bar: 100% Photo-switching in $[Pd(Bu_4dien)(\eta^1\text{-}\underline{N}O_2)]^+$ Approaches Ambient Temperature

Lauren E. Hatcher[a*]

[a] *Department of Chemistry, University of Bath, Bath, BA2 7AY, UK*

SUPPLEMENTARY INFORMATION

Contents

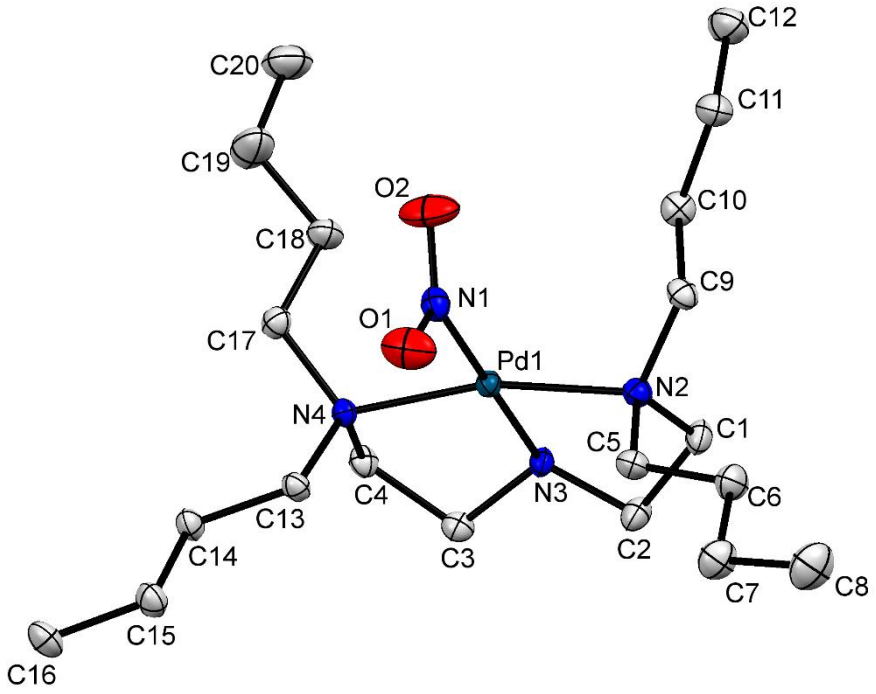

Figure S1. Single-crystal X-ray structure for the Pd(II) cation in **(1)** in the ground state. Ellipsoids shown at 50% probability and hydrogen atoms omitted for clarity

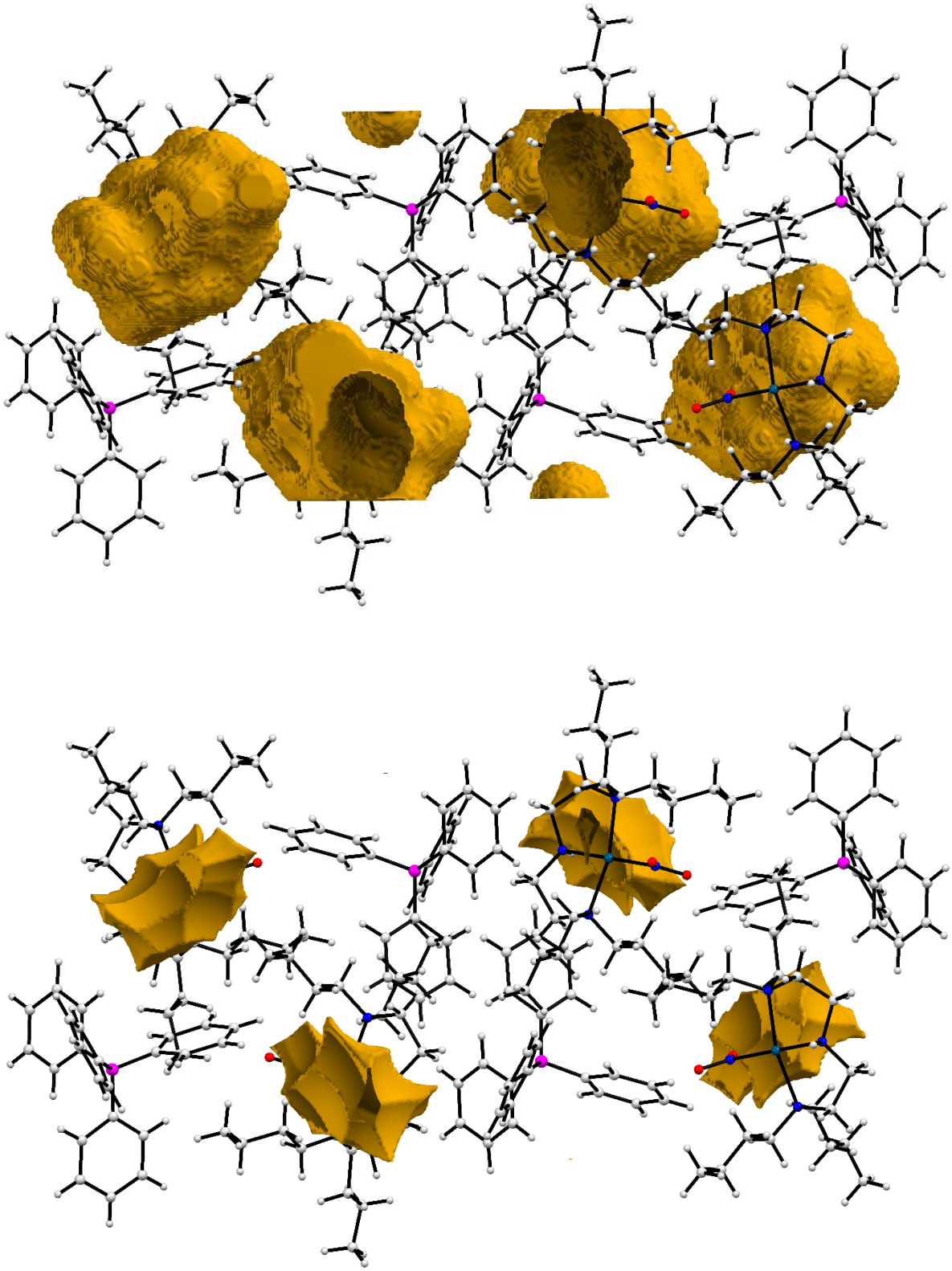

Figure S2. Void space occupied by the THF solvent molecule in one unit cell of **(1)**: *top* = contact surface void space; b*ottom:* solvent-accessible void space. Calculations conduced in Mercury[1] using a probe radius of 1.2 Å and grid spacing of 0.1 Å

Crystal Packing Coefficient Calculation

Molecular volumes by Hirshfeld Stockholder Partitioning (Crystal Explorer[2, 3]):

Fragment	Molecular volume / Å^3
Cation	580.81
Anion	432.68
THF solvent	111.41
SUM	**1124.9**

$$\textbf{Packing coefficient} = \frac{\text{Molecular volume} \times Z}{\text{Unit cell volume}} = \frac{1124.9 \times 4}{4578.4} = \mathbf{0.98}$$

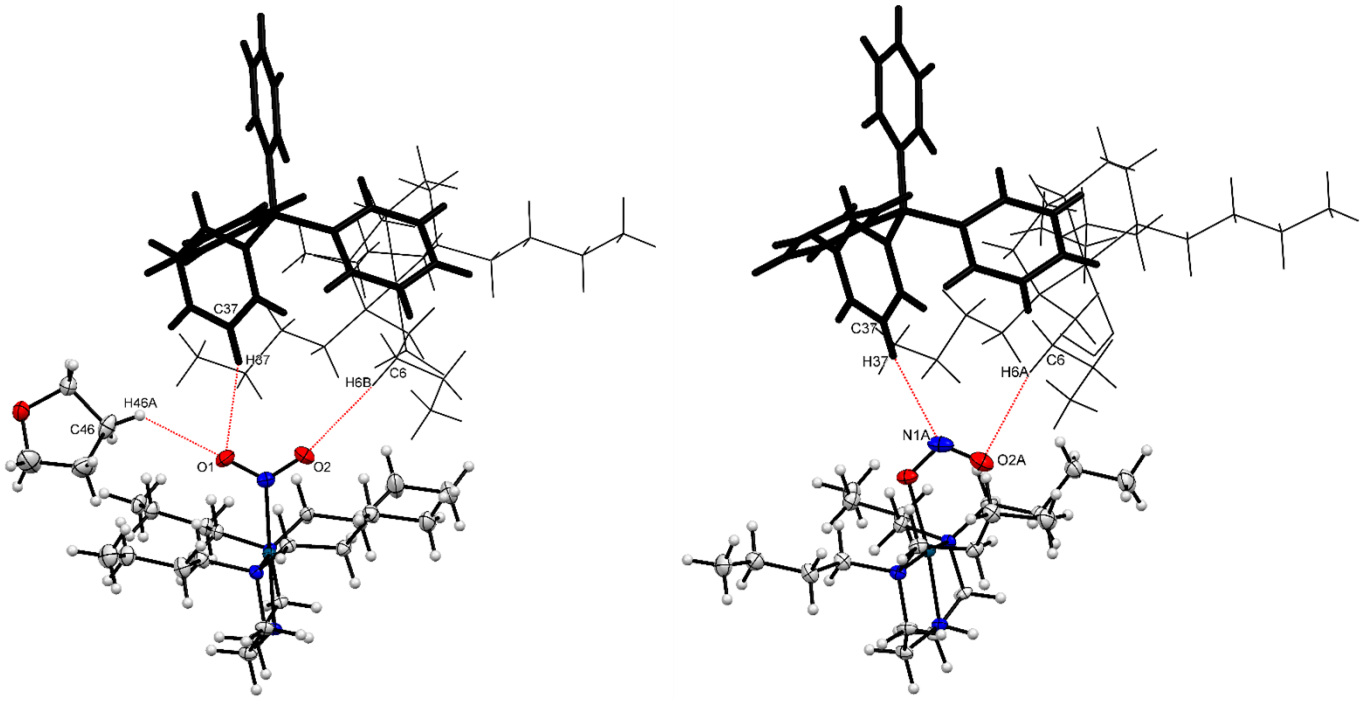

Figure S3. Close-contact intermolecular C-H…O interactions to the nitrite ligand in the GS (left) and MS (right) single-crystal X-ray structures

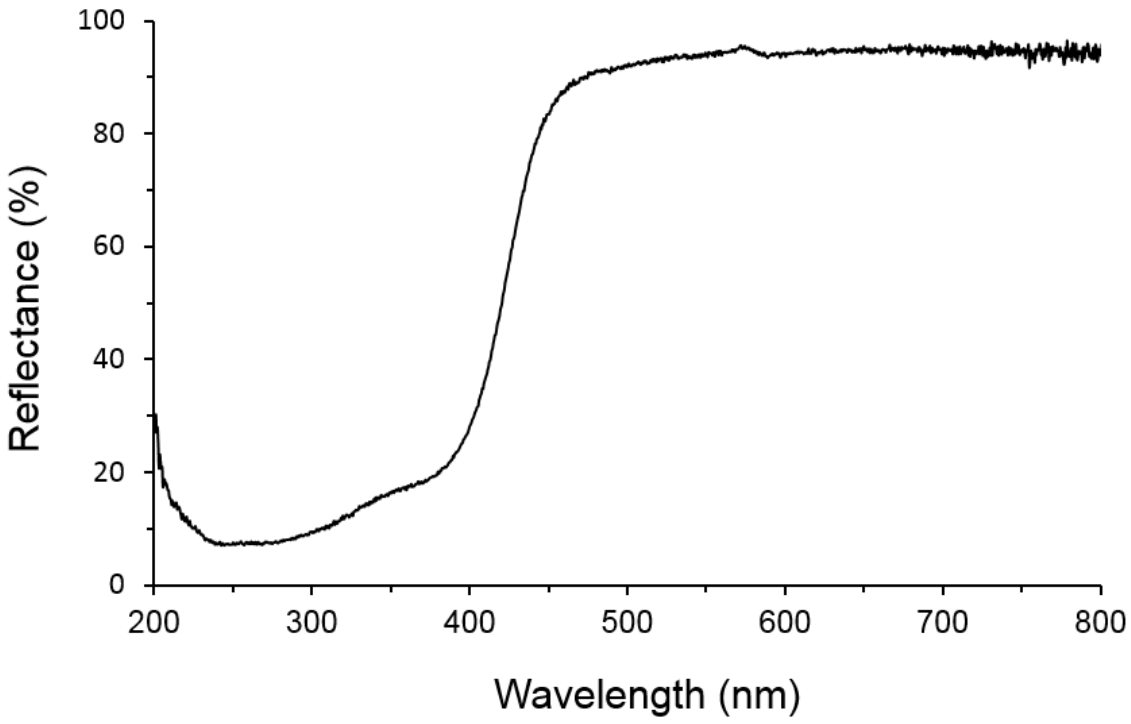

Figure S4. UV/vis diffuse reflectance spectrum of **(1)**

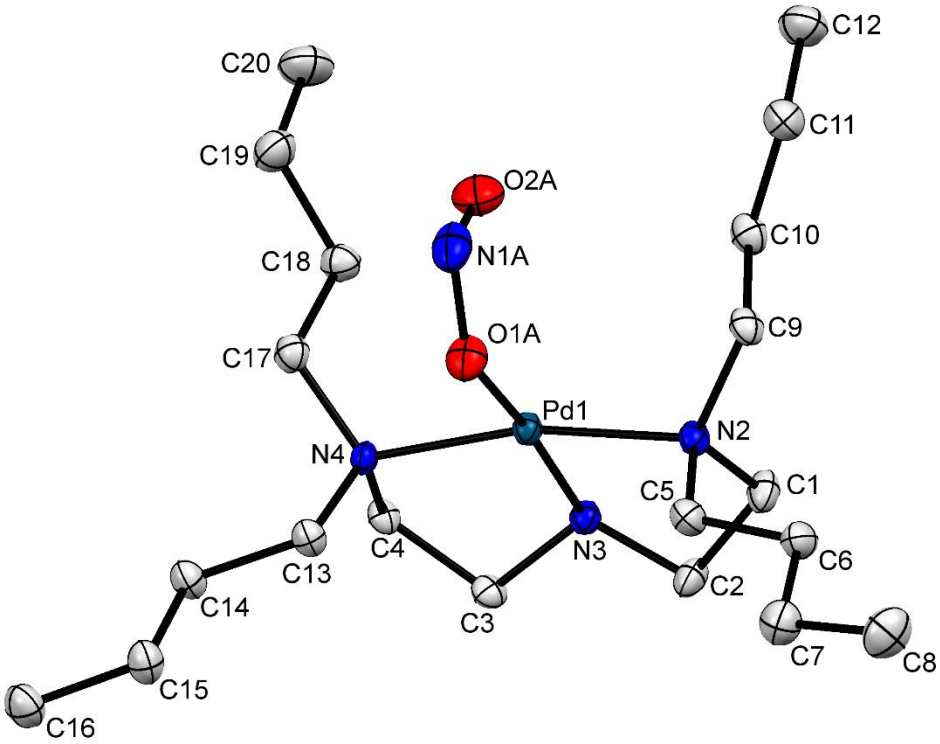

Figure S5. Single-crystal X-ray structure for the Pd(II) cation in **(1)** in the metastable state. Ellipsoids shown at 50% probability and hydrogen atoms omitted for clarity

Table S1. Nitro : nitrito occupancy ratios as a function of irradiation time at 100 K. 0 – 60 min irradiation (λ = 400 nm) and occupancies freely refined from single-crystal X-ray diffraction data

Irradiation Time (min)	Nitro-(η^1-NO_2) Occupancy	Nitrito-(η^1-ONO) Occupancy
0	1.00	0.00
1	0.75	0.25
2	0.55	0.45
5	0.20	0.80
10	0.09	0.91
15	0.00	1.00
60	0.00	1.00

Table S2. Nitro : nitrito occupancy ratios as a function of temperature after 60 min steady-state photo-excitation (MS limit search). Occupancies freely refined from single-crystal X-ray diffraction data

Temperature (K)	Nitro-(η^1-NO_2) Occupancy	Nitrito-(η^1-ONO) Occupancy
100	0.00	1.00
150	0.00	1.00
180	0.00	1.00
200	0.00	1.00
220	0.71	0.29
240	1.00	0.00
250	1.00	0.00
260	1.00	0.00

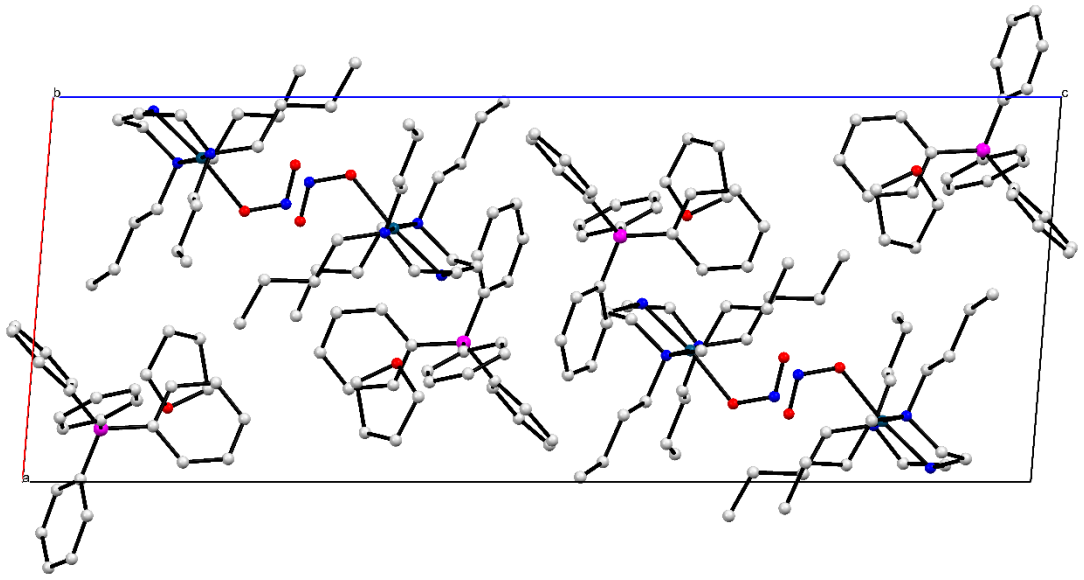

Figure S6. Single-crystal packing diagram (one unit cell) for the MS structure of **(1)**, viewed along the crystallographic *b*-axis, *c*-axis horizontal

References

1. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *Journal of Applied Crystallography*, 2008, **41**, 466-470.
2. J. J. McKinnon, A. S. Mitchell and M. A. Spackman, *Chemistry – A European Journal*, 1998, **4**, 2136-2141.
3. J. J. McKinnon, M. A. Spackman and A. S. Mitchell, *Acta Crystallographica Section B*, 2004, **60**, 627-668.