Pd(bpy4dca)(NO₂)₂: understanding the influence of polymorphism and coligand chromophores on linkage isomer photoswitching in the singlecrystal

Supplementary Information

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Section 1. Crystal structure of 2,2'-bipyridine-4,4'-dicarboxylic acid methyl ester (bpy4dca)



Figure S1: Single crystal X-ray structure of bpy4dca, with the non-hydrogen atoms of the asymmetric unit labelled. Ellipsoids at 50% probability.

The ligand 2,2'-bipyridine-4,4'-dicarboxylic acid methyl ester (bpy4dca) crystallises in the monoclinic space group $P_{2_1/c}$ with half a molecule in the asymmetric unit. The molecule is located on a special position (inversion centre) in the unit cell and the other half of the bpy4dca molecule is generated by symmetry. The molecule is highly planar, with an RMS deviation of 0.0343 from the plane for all non-hydrogen atoms in the asymmetric unit.

The planar bpy4dca pack in a flattened herringbone (or γ -type) packing arrangement, with alternating stacks of molecules extending approximately parallel to the [010] direction. The interplanar distance is 3.8010(2) Å, with evidence of π - π interactions between stacked molecules. A weak intermolecular C-H...O hydrogen bond forms a link between herringbone stacks, formed between C(7)-H(7B) of the methyl group on one molecule and O(2) of the C=O group on the neighbouring molecule.



Figure S2: Crystal packing diagrams for the crystal structure of bpy4dca, viewed along [100] (a), [010] (b) and [001] (c).

| | bpy4dca |
|---|----------------------|
| Radiation wavelength / ${ m \AA}$ | 0.71073 |
| Empirical formula | $C_{14}H_{12}N_2O_4$ |
| Formula weight | 272.26 |
| Temperature / K | 150 |
| Crystal system | monoclinic |
| Space group | P21/c |
| a / Å | 3.8010(2) |
| b / Å | 5.8557(3) |
| c / Å | 27.5948(12) |
| α/° | 90 |
| β/° | 93.720(4) |
| γ/° | 90 |
| Volume / Å ³ | 612.90(5) |
| Z | 2 |
| $ ho_{calc}$ / g cm ⁻³ | 1.475 |
| μ / mm ⁻¹ | 0.110 |
| F(000) | 284 |
| Crystal size / mm | 0.5 x 0.3 x |
| | 0.2 |
| Reflections (independent) | 3721 (1251) |
| Goodness of Fit on F ² | 1.069 |
| R _{int} | 0.0256 |
| $R_1 [l \ge 2\sigma(l)]$ | 0.0424 |
| wR ₂ [all data] | 0.1118 |
| Largest difference peak and hole / e \AA^{-3} | 0.21/-0.30 |

 Table S1: Single crystal X-ray data for the crystal structure of bpy4dca

Section 2. Photocrystallography set-up



Figure S3: Circuit diagram for LED illumination array set-up.



Figure S4: Photocrystallography set-up on a Rigaku Gemini A Ultra dual source diffractometer

Section 3. Supplementary data for complex 1



Figure S5: Microscope images of **1** crystals: polymorph I needles (left) and polymorph II powder and blocks (right).



Figure S6: Experimental powder X-ray diffraction (PXRD) pattern for as-crystallised complex **1** crystals (black), compared to the patterns for pure form I (dark grey) and form II (light grey) crystals simulated from ground state single-crystal X-ray diffraction (SCXRD) datasets. All experiments were performed at 150 K.



Figure S7: Experimental powder X-ray diffraction (PXRD) pattern for the microcrystalline powder sample of **1** formed on shattering of needle-like (black), formed on aging the as-synthesised needle crystals in acetonitrile/water solution for 2 - 3 days at room temperature, compared to the patterns for pure form I (dark grey) and form II (light grey) crystals simulated from ground state single-crystal X-ray diffraction (SCXRD) datasets. All experiments were performed at 150 K.



Table S2: CrystalExplorer^{1, 2} Fingerprint plots highlighting the key intermolecular interactions involving the crystallographically independent molecules in polymorphs I (Z' = 2) and II (Z' = 1).

| Overlaid molecules | Overlay image | RMSD | Maximum deviation / Å |
|--|---------------|--------|--------------------------|
| Polymorph I molecule a [red] and Polymorph II [blue] | | 0.1712 | 0.38 |
| Polymorph I molecule b [red] and Polymorph II [blue] | | 0.3006 | 0.77 |

Table S3: Molecular overlay data comparing the crystallographically independent molecules of **1** in polymorph I (Z' = 2) with polymorph II (Z' = 1) in their GS crystal structures

Table S4: Results of preliminary excitation wavelength testing with polymorph II crystals. In each experiment the same form II crystal was irradiated at the selected wavelength for a period of 1 h, before being subject to a steady-state photocrystallography experiment at 150 K. The crystal was confirmed to be in the GS nitro-(η^1 -NO₂) arrangement prior to each irradiation period.

| Wavelength / nm | 390 | 405 | 465 | 500 |
|---|----------------------------|--------------------------|--------------------------|----------------------------|
| Irradiation time / min | 60 | 60 | 60 | 60 |
| ES population level, [NO ₂ ligand 1 / ligand 2] / % | 0/0 | 0/0 | 55(1) / 52(1) | 0/0 |
| Radiation wavelength / Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Empirical formula | $C_{14}H_{12}N_4O_8Pd_1\\$ | $C_{14}H_{12}N_4O_8Pd_1$ | $C_{14}H_{12}N_4O_8Pd_1$ | $C_{14}H_{12}N_4O_8Pd_1\\$ |
| Formula weight | 470.68 | 470.68 | 470.68 | 470.68 |
| Temperature / K | 150 | 150 | 150 | 150 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | P21/n | P21/n | P21/n | P21/n |
| a / Å | 8.4156(4) | 8.4551(4) | 8.5072(4) | 8.4628(3) |
| b/Å | 7.7485(3) | 7.7330(3) | 7.7879(3) | 7.7311(3) |
| c / Å | 24.9321(15) | 24.8491(12) | 24.9216(8) | 24.8985(7) |
| α/° | 90 | 90 | 90 | 90 |
| 6/° | 95.374(5) | 95.093(4) | 93.899(4) | 95.132(3) |
| γ/° | 90 | 90 | 90 | 90 |
| Volume / Å ³ | 1618.63(14) | 1618.30(13) | 1647.31(11) | 1622.50(10) |
| Z | 4 | 4 | 4 | 4 |
| $ ho_{calc}$ / g cm ⁻³ | 1.931 | 1.932 | 1.898 | 1.927 |
| μ / mm ⁻¹ | 1.203 | 1.203 | 1.182 | 1.200 |
| F(000) | 936 | 936 | 936 | 936 |
| Crystal size / mm | 0.3 x 0.2 x 0.1 | 0.3 x 0.2 x 0.1 | 0.3 x 0.2 x 0.1 | 0.3 x 0.2 x 0.1 |
| Reflections (independent) | 7018 (3297) | 11902 (3310) | 6788 (3370) | 6699 (3313) |
| Goodness of Fit on F ² | 1.218 | 1.146 | 1.036 | 1.050 |
| R _{int} | 0.0276 | 0.0563 | 0.0450 | 0.0414 |
| $R_1 [l \ge 2\sigma(l)]$ | 0.0648 | 0.0685 | 0.0508 | 0.0381 |
| wR ₂ [all data] | 0.1549 | 0.1585 | 0.1112 | 0.0786 |
| Largest difference peak and hole / e Å -3 | 2.80/-2.31 | 2.18/-1.40 | 1.07/-0.74 | 0.77/-0.68 |



(b)



Figure S8: Crystal packing diagrams for the photostationary excited state of **1** polymorph II at 150 K, (a) showing the flattened herringbone pattern and (b) viewed along the [010] direction, both with the minor nitro-(η^1 -NO₂) components removed for clarity.

(a)

Table S5: Nitro : nitrito isomer ratios for photocrystallographic studies with **1** polymorph II at 150 K as a function of irradiation time and temperature, as refined from complete single-crystal X-ray diffraction datasets.

| Tomporaturo | Innodiation | Nitrite | igand #1 | Nitrite ligand #2 | | |
|-------------|-------------|---|--|---|--|--|
| (K) | time (s) | Nitro-(η ¹ -NO ₂) occupancy | Nitrito-(η ¹ -ONO) occupancy | Nitro-(η ¹ -NO ₂) occupancy | Nitrito-(η ¹ -ONO) occupancy | |
| 150 | 0 | 1.00 | 0.00 | 1.00 | 0.00 | |
| 150 | 3600 | 0.45 | 0.55 | 0.48 | 0.52 | |
| 150 | 7200 | 0.35 | 0.65 | 0.38 | 0.62 | |
| 150 | 10800 | 0.30 | 0.70 | 0.33 | 0.67 | |
| 170 | 14400 | 0.29 | 0.71 | 0.32 | 0.68 | |
| 190 | 14400 | 0.29 | 0.71 | 0.31 | 0.69 | |
| 210 | 14400 | 0.29 | 0.71 | 0.31 | 0.69 | |
| 220 | 14400 | 0.30 | 0.70 | 0.33 | 0.67 | |
| 230 | 14400 | 0.39 | 0.61 | 0.38 | 0.62 | |
| 240 | 14400 | 0.69 | 0.31 | 0.63 | 0.37 | |



Figure S9: Ground state single-crystal X-ray structure of **1** polymorph II at 200 K, ellipsoids set at 50% probability.

| T | able S6: I | Vitro | o : nitrito iso | mer ra | tios f | for photocrysta | llog | graphic st | tudies | with 1 poly | /morph II at 20 | 0 K as |
|---|------------|-------|-----------------|--------|--------|-----------------|------|------------|--------|--------------------|-----------------|--------|
| а | functior | n of | irradiation | time | and | temperature, | as | refined | from | complete | single-crystal | X-ray |
| d | iffraction | dat | asets. | | | | | | | | | |

| Temperature | Irradiation | Nitrite li | igand #1 | Nitrite ligand #2 [atoms N(2), O(3), O(4) + atoms N(2A), O(3A), O(4A)] | | |
|-------------|-------------|---|--|---|--|--|
| (К) | time (s) | Nitro-(η ¹ -NO ₂) occupancy | Nitrito-(η ¹ -ONO) occupancy | Nitro-(η ¹ -NO ₂) occupancy | Nitrito-(η ¹ -ONO) occupancy | |
| 200 | 0 | 1.00 | 0.00 | 1.00 | 0.00 | |
| 200 | 600 | 0.91 | 0.09 | 0.91 | 0.09 | |
| 200 | 1800 | 0.73 | 0.27 | 0.77 | 0.23 | |
| 200 | 3600 | 0.55 | 0.45 | 0.64 | 0.36 | |
| 200 | 7200 | 0.35 | 0.65 | 0.48 | 0.52 | |
| 200 | 10800 | 0.28 | 0.72 | 0.39 | 0.61 | |
| 200 | 18000 | 0.23 | 0.77 | 0.34 | 0.66 | |
| 200 | 36000 | 0.20 | 0.80 | 0.30 | 0.70 | |
| 210 | 36000 | 0.26 | 0.74 | 0.33 | 0.67 | |
| 220 | 36000 | 0.49 | 0.51 | 0.51 | 0.49 | |
| 230 | 36000 | 0.92 | 0.08 | 0.88 | 0.12 | |
| 240 | 36000 | 1.00 | 0.00 | 1.00 | 0.00 | |
| 250 | 36000 | 1.00 | 0.00 | 1.00 | 0.00 | |



Figure S10: Comparison of excited state nitrito-(η^1 -ONO) isomer occupancies as a function of increasing temperature in variable temperature parametric studies with **1** polymorph II, for steady-state (SS) and pseudo-steady-state (PSS) photocrystallographic experiments, both following excitation at 200 K with 465 nm LED light.



Figure S11: Crystal packing diagrams for the photostationary excited state of **1** polymorph I at 150 K, (a) viewed along the [100] direction and (b) viewed along the [010] direction, both with the minor nitro- $(\eta^{1}-NO_{2})$ components removed for clarity.

(a)

| Polymorph | Nitrite | H-bond | Symmetry | HA* / Å | DA / Å | D-HA* / ° |
|------------|----------|------------------|---------------|-------------|----------|--------------|
| (molecule) | ligand # | | | | | |
| I(a) | 1 | C(1)-H(1)O(1) | | 2.44 | 3.16(2) | 132 |
| l(a) | 1 | C(1)-H(1)O(2) | -x, -y, -z | 2.70 | 3.63(3) | 166 |
| l(a) | 1 | C(26)- | -x, -y, -z | 2.52 | 3.16(2) | 123 |
| | | H(26A)O(2) | | | | |
| l(a) | 2 | | no C-HO i | nteractions | | |
| I(b) | 3 | C(1)-H(1)O(9) | -x, -y, -z | 2.71 | 3.45(3) | 135 |
| I(b) | 3 | C(23)-H(23)O(10) | -x, -y, -z | 2.62 | 3.36(3) | 133 |
| l(b) | 4 | C(15)-H(15)O(11) | | 2.52 | 3.20(2) | 128 |
| 11 | 1 | C(2)-H(2)O(1) | -x, -y, -z | 2.586 | 3.274(6) | 129.5 |
| II | 2 | C(12)- | ½+x, ½-y, ½+z | 2.546 | 3.173(5) | 121.8 |
| | | H(12C)O(3) | | | | |
| II | 2 | C(14)- | -x, -y, -z | 2.532 | 3.426(5) | 151.6 |
| | | H(14A)O(3) | | | | |
| II | 2 | C(10)-H(10)O(4) | | 2.521 | 3.201(5) | 128.6 |

Table S7: Hydrogen bonding interactions involving the nitro- $(\eta^1 - NO_2)$ ligands in the GS structures of polymorphs I and II at 150 K.

*hydrogen atoms are treated as a riding model, therefore H...A distances and D-H..A angles have no associated esd value



Figure S12: Key C-H...O hydrogen bonding interactions in the GS structures of polymorph I, molecule **a** (a), polymorph I molecule **b** (b) and polymorph II (c)

Table S8: Comparison of the hydrogen bonding interactions involving the nitro- (η^1-NO_2) ligands in the GS structures of polymorph II at 150 and 200 K.

| Temperature | Nitrite | H-bond | Symmetry | HA* / Å | DA / Å | D-HA* |
|-------------|----------|-----------------|---------------|---------|----------|------------|
| (К) | ligand # | | | | | / ° |
| 150 | 1 | C(2)-H(2)O(1) | -x, -y, -z | 2.586 | 3.274(6) | 129.5 |
| 150 | 2 | C(12)- | ½+x, ½-y, ½+z | 2.546 | 3.173(5) | 121.8 |
| | | H(12C)O(3) | | | | |
| 150 | 2 | C(14)- | -x, -y, -z | 2.532 | 3.426(5) | 151.6 |
| | | H(14A)O(3) | | | | |
| 150 | 2 | C(10)-H(10)O(4) | | 2.521 | 3.201(5) | 128.6 |
| 200 | 1 | C(2)-H(2)O(1) | -x, -y, -z | 2.597 | 3.284(6) | 129.4 |
| 200 | 2 | C(12)- | ½+x, ½-y, ½+z | 2.561 | 3.187(6) | 121.7 |
| | | H(12C)O(3) | | | | |
| 200 | 2 | C(14)- | -x, -y, -z | 2.555 | 3.454(6) | 152.6 |
| | | H(14A)O(3) | | | | |
| 200 | 2 | C(10)-H(10)O(4) | | 2.517 | 3.192(6) | 128.0 |

*hydrogen atoms are treated as a riding model, therefore H...A distances and D-H..A angles have no associated esd value





Figure S13: Key C-H...O hydrogen bonding interactions in the ES structures of polymorph I, molecule **a** (a), polymorph I molecule **b** (b) and polymorph II (c)

Table S9: Hydrogen bonding interactions involving the nitrito-(η^1 -ONO) ligands in the ES structures of polymorphs I and II at 150 K.

| Polymorph (molecule) | Nitrite ligand # | H-bond | Symmetry | HA* / Å | DA / Å | D-HA* / ° |
|-------------------------|---------------------|-------------------|---------------|------------|----------|--------------|
| I(a) | 1 | C(26)-H(26A)O(1A) | -x, -y, -z | 2.35 | 3.08(4) | 130 |
| l(a) | 2 | | no C-HO in | teractions | | |
| l(b) | 3 | C(1)-H(1)O(9A) | -x, -y, -z | 2.68 | 3.38(4) | 131 |
| l(b) | 4 | C(15)-H(15)O(12A) | -x, -y, -z | 2.63 | 3.33(2) | 131 |
| II | 2 | C(12)-H(12C)O(4A) | ½+x, ½-y, ½+z | 2.639 | 3.418(5) | 136.6 |

*hydrogen atoms are treated as a riding model, therefore H...A distances and D-H..A angles have no associated esd value

Reaction cavity analysis using CCDC Mercury software.

Procedure:

The reaction cavity volume surrounding the isomerisable NO₂ ligand can be estimated by using the Void Space analysis tool in Mercury.

CIFs were first prepared by permanently deleting the NO₂ ligand using the Edit Structure dialogue in Mercury, before the Display \rightarrow Voids dialogue was used to conduct a void space calculation. A contact surface calculation was then performed using a probe radius of 1.2 Å and the finest attainable grid spacing of 0.1 Å.

It should be noted that, after removal of the NO₂ ligand from the structure, the software calculates all remaining atoms with their van de Waals radius. For our purposes this introduces a small systematic error into the void space calculation, as the van de Waals radius for the Pd(II) metal atom will now not take into account that there is a Pd-N bond in the real structure. In other treatments this error has been taken into account through a different approach,³ however as this analysis is being used for comparative purposes any errors introduced are systematic and so do not affect our final conclusions. As such, it seems reasonable to use the available Mercury tool as a simple means to estimate the reaction cavity in this case.



Figure S14: Reaction cavity (V_c) analysis of **1** polymorphs I and II at 150 K. V_c determined by removing the nitrite group and performing a contact surface void space calculation in Mercury (probe radius 1.2 Å, grid spacing 0.1 Å). For direct comparison between polymorphs, V_c was obtained per molecule by dividing the per unit cell value from Mercury by Z for each crystal structure.

Table S10: Reaction cavity (V_c) analysis of **1** polymorph II at 150 and 200 K. V_c determined by removing the nitrite group and performing a contact surface void space calculation in Mercury (probe radius 1.2 Å, grid spacing 0.1 Å)

| Temperature (K) | Nitrite ligand # | Nitrito-ONO occupancy | V _c per unit cell (ų) | V _c per molecule* (ų) |
|--------------------|---------------------|--------------------------|--|--|
| 150 | #1 | 0.71 | 148.31 | 37.08 |
| 150 | #2 | 0.68 | 141.44 | 35.36 |
| 200 | #1 | 0.71 | 144.70 | 36.18 |
| 200 | #2 | 0.68 | 146.55 | 36.64 |

 $^{*}V_{c}$ per molecule was obtained by dividing the value obtained per unit cell by Z for each structure, allowing direct comparison of reaction cavities for forms I and II.

Table S11: Molecular overlay data comparing the crystallographically independent molecules of **1** both within polymorph I (Z' = 2), and with polymorph II (Z' = 1) in their photostationary ES crystal structures

| Overlaid molecules | Overlay image | RMSD | Maximum deviation / Å |
|---|---------------------------------------|--------|--------------------------|
| Polymorph I molecule a [red] and Polymorph I molecule b [green] | | 0.3659 | 1.1723 |
| Polymorph I molecule a [red] and Polymorph II [blue] | i i i i i i i i i i i i i i i i i i i | 0.6669 | 2.6577 |
| Polymorph I molecule b [red] and Polymorph II [blue] | | 0.6783 | 2.7676 |



Figure S15: Molecular overlay data comparing the optimised geometries for the crystallographically independent molecules of **1** in (a) polymorph I, red = molecule **a**, green = molecule **b** (RMSD between molecules = 0.0000, zero point energy = -1489.72728807 HT for both molecules), and (b) between polymorph I = red and polymorph II = blue (RMSD between molecules = 0.3996). For all calculations: DFT(B3LYP)/6-311+G(d) for light atoms, DFT(B3LYP)/SDD for Pd.



Figure S16: Comparison of calculated and experimental absorption spectra for 1 polymorphs I and II.



Figure S17: Calculated molecular orbital diagram and key frontier molecular orbitals for the geometry-optimised GS molecule of **1** polymorph I, green = HOMO orbitals, magenta = LUMO orbitals.



Figure S18: Calculated molecular orbital diagram and key frontier molecular orbitals for the geometry-optimised GS molecule of **1** polymorph II, green = HOMO orbitals, magenta = LUMO orbitals.



Figure S19: Calculated molecular orbital diagram and key frontier molecular orbitals for the geometry-optimised GS molecule of $[Pd(Bu_4dien)(NO_2)]^{+,4}$ green = HOMO orbitals, magenta = LUMO orbitals.



Figure S20: Calculated molecular orbital diagram and key frontier molecular orbitals for the geometry-optimised molecule of [Pd(Et₄dien)(NO₂)]^{+,5} green = HOMO orbitals, magenta = LUMO orbitals.



Figure S21: Calculated molecular orbital diagram and key frontier molecular orbitals for the geometry-optimised molecule of [Pd(PPh₃)(NO₂)₂],⁶ green = HOMO orbitals, magenta = LUMO orbitals.



Figure S22: Calculated molecular orbital diagram and key frontier molecular orbitals for the geometry-optimised molecule of $[Pd(PCy_3)(NO_2)_2]$,⁶ green = HOMO orbitals, magenta = LUMO orbitals.



Figure S23: Calculated molecular orbital diagram and key frontier molecular orbitals for the geometry-optimised molecule of [Pd(AsCy₃)(NO₂)₂],⁶ green = HOMO orbitals, magenta = LUMO orbitals.

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