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Evaluating the crystalline orbital hierarchy and high-pressure structure-property response of an extended-ligand platinum(II) bis(1,2-dioximato) complex

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Supplementary Information

1: Methodology

2: Results: Crystallography

3: Results: Isolated molecule and solid state calculations

4: References

1: Methodology

1.1 Ambient-pressure Crystallography

The ambient-pressure diffraction data for [Pt(bqd-dibutyl)$_2$] were obtained from a full sphere collection on a single crystal at room temperature (283-303 K), utilising a series of ω scans, on a Bruker SMART APEX II diffractometer with monochromated Mo-Kα X-ray radiation (λ=0.71073 Å, 17.4 eV). The data were integrated using the program SAINT, with the SADABS absorption correction applied.[1]

Sir92 was utilised for the structure solutions within CRYSTALS[2], with data refined against F^2.[2-3] H-atoms were placed geometrically and not refined. H-Atoms attached to the oxygen hydroxyl group were initially found in a difference map and refined with restraints on their bond lengths to regularise their geometry (O–H = 0.84) with U[iso] set to 1.2 times U[eq] of the parent atom. On converging, all H-atoms were refined with riding constraints. All non-H atoms were refined anisotropically.

1.2 High-Pressure Crystallography

High-pressure diffraction experiments were undertaken at pressures of 0.14, 0.76 and 1.43 GPa on a single crystal of [Pt(bqd-dibutyl)$_2$] loaded in a modified Merrill-Bassett diamond anvil cell alongside a ruby crystal (acting as the in-situ pressure calibrant) and the hydrostatic pressure transmitting medium Fluorinert FC-70 (perfluorotri-N-pentylamine).[4] Above 1.43 GPa no meaningful reflection data was obtained. High-pressure data were obtained using the same diffractometer setup as for the ambient-pressure experiment; a data collection strategy based on that by Dawson et al.,[5] consisting of a series of ω scans, was utilised to minimise the shading of the detector by the cell body, with an exposure time of 30 s per frame. The data were integrated using the program SAINT, with the SADABS absorption correction applied.[1]

Structure refinements for all high-pressure data were carried out using CRYSTALS.[2] The ambient pressure-structure was used as the input model, with the structure allowed to refine against each high-pressure data set and adjust to the updated unit cell parameters. All 1,2 and 1,3 distances were restrained based on the ambient pressure structure of [Pt(bqd-dibutyl)$_2$]. All Pt-N distances were allowed to refine freely. Vibrational and thermal similarity restraints were also applied to the ligand non-H atoms. The high-pressure data was refined against F, with isotropic atomic displacement refinement utilised for all non-hydrogen atoms except for the Pt-atom, which was refined with anisotropic displacement parameters. H-Atoms attached to the oxygen hydroxyl group were initially found in a difference map and refined with restraints on their bond lengths to regularise their geometry (O–H = 0.84) with U[iso] set to 1.2 times U[eq] of the parent atom. On converging, all H-atoms were refined with riding constraints.

1.4 Isolated Molecule Calculations

The calculations to determine the ordering of molecular orbitals for [Pt(bqd)$_2$] and [Pt(bqd-dibutyl)$_2$] were undertaken using the Gaussian09 and Gaussian16 packages,[6] Minimisation of the atomic coordinates, using the ambient-pressure molecular structure as the starting model, were carried out using the hybrid B3LYP functional,[7] with the Stevens-Basch-Krauss effective core potential triple-split basis CEP-121G basis set used for all atoms,[8] with the resulting visualisations of the molecular orbitals and their energies obtained using Jmol and Avogadro.[9]

1.5 Solid state Calculations

Solid state calculations on the structures of [Pt(bqd-dibutyl)$_2$] obtained experimentally at ambient-pressure and 1.43 GPa have been performed using CRYSTAL17,[10] where DFT (PBE) and hybrid-DFT (PBE0,[11] HSE06,[12] B3LYP[7]) functionals were implemented with crystalline orbitals built from linear combinations of atomic orbitals, developed from Gaussian type functions for solid state periodic systems. Triple zeta valence with polarization quality basis sets for all ligand atoms (O, N, C and H).[13] The Pt atoms were modelled using the scalar-relativistic pseudopotential as developed by Andrae *et al* (to treat 60 core electrons),[14] with the remaining [4s4p2d] valence electrons were treated explicitly, as described in the methodology by Doll.[15] These basis sets match those used in a previous publication for Pt(bqd)$_2$, so the results obtained for the two compounds are comparable.[16]

The input geometries for the solid-state calculations were taken from the experimentally determined X-ray crystal structures. Atom minimisation of these experimentally-obtained structures, with the unit cell parameters fixed to experimentally-obtained values, were performed with Monkhorst-Pack nets[17] of 12 × 12 × 12 for [Pt(bqd-dibutyl)$_2$], corresponding to 343 k-points in the Brillouin zone (BZ) respectively. Utilising Monkhorst-Pack nets of 8 × 8 × 8 resulted in the total energy difference obtained by using larger Monkhorst-Pack nets was smaller than 10^{-7} Hartree, but to obtain higher quality electronic band structures, projected density of state (PDOS) and crystalline orbital plots, the net size of 12 × 12 × 12 was instead utilised.

The results shown in the main text refer to those obtained utilising the HSE06 functional, to allow for direct comparison to those published for [Pt(bqd)$_2$],[16] and due to multiple literature examples demonstrating its superior accuracy in replicating experimental band gaps compared to its GGA and global screen counterparts, [18] even for compounds with heavy elements which thus contain sizeable spin-orbit coupling.[19]

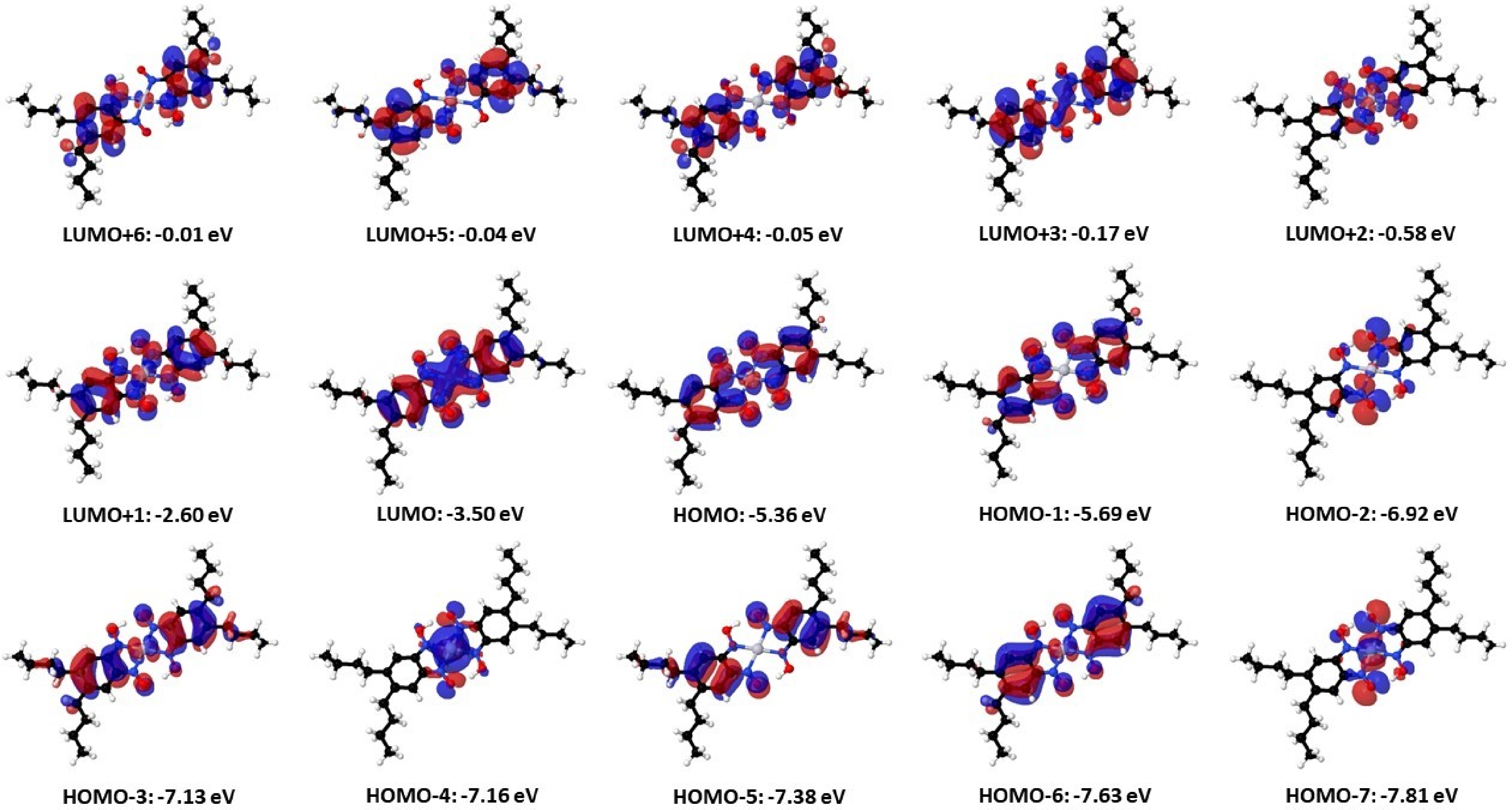
2: Experimental details (X-ray Crystallography)

For all structures: orthorhombic, *Pna*2$_1$, $Z = 4$. Experiments were carried out at 293 K with Mo *K*a radiation using a Bruker Kappa Apex2. Absorption was corrected for by multi-scan methods, *SADABS* (Siemens, 1996). H-atom parameters were constrained.

Pressure	ambient	0.14 GPa	0.76 GPa	1.43 GPa
Crystal data				
Chemical formula	$C_{28}H_{42}N_4O_4Pt$	$C_{28}H_{42}N_4O_4Pt$	$C_{28}H_{43}N_4O_4Pt$	$C_{28}H_{42}N_4O_4Pt$
M_r	693.76	693.76	694.76	693.76
a, *b*, *c* (Å)	20.7074 (11), 4.9052 (2), 28.1381 (14)	20.6020 (17), 4.8431 (1), 27.9031 (7)	20.32170 (4), 4.70070 (1), 27.45730 (3)	20.088 (3), 4.6778 (3), 27.3616 (15)
V (Å^3)	2858.1 (2)	2784.1 (2)	2622.89 (1)	2571.1 (5)
μ (mm^{-1})	4.95	5.08	5.39	5.50
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
Data collection				
$T_{\min}$, $T_{\max}$	0.49, 0.61	0.36, 0.60	0.37, 0.58	0.35, 0.58
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	30739, 6887, 5315	8690, 1963, 1309	9015, 2237, 1452	6444, 1484, 1029
R_{int}	0.042	0.068	0.083	0.108
$\theta_{\max}$ (°)	28.5	23.3	26.4	22.0
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.672	0.556	0.625	0.528
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.107, 1.17	0.060, 0.093, 1.12	0.080, 0.068, 1.08	0.083, 0.117, 1.05
No. of reflections	6873	1309	1400	1027
No. of parameters	334	145	145	145
No. of restraints	4	161	161	161
$\Delta\square_{\max}$, $\Delta\square_{\min}$ (e Å^{-3})	3.85, -1.23	1.62, -1.20	2.81, -2.97	1.29, -1.86
Absolute structure	Parsons, Flack & Wagner (2013), 2752 Friedel Pairs	Parsons, Flack & Wagner (2013), 577 Friedel Pairs	Parsons, Flack & Wagner (2013), 617 Friedel Pairs	Parsons, Flack & Wagner (2013), 453 Friedel Pairs
Absolute structure parameter	0.586 (6)	0.455 (15)	0.457 (15)	0.46 (2)

The structures obtained at each pressure point have been deposited into the Cambridge Crystallographic Data Centre (2093361-2093364). Other relevant diffraction data for each structure is contained therein.

3: Results (Isolated Molecule Calculations)



LUMO+6: -0.01 eV

LUMO+5: -0.04 eV

LUMO+4: -0.05 eV

LUMO+3: -0.17 eV

LUMO+2: -0.58 eV

LUMO+1: -2.60 eV

LUMO: -3.50 eV

HOMO: -5.36 eV

HOMO-1: -5.69 eV

HOMO-2: -6.92 eV

HOMO-3: -7.13 eV

HOMO-4: -7.16 eV

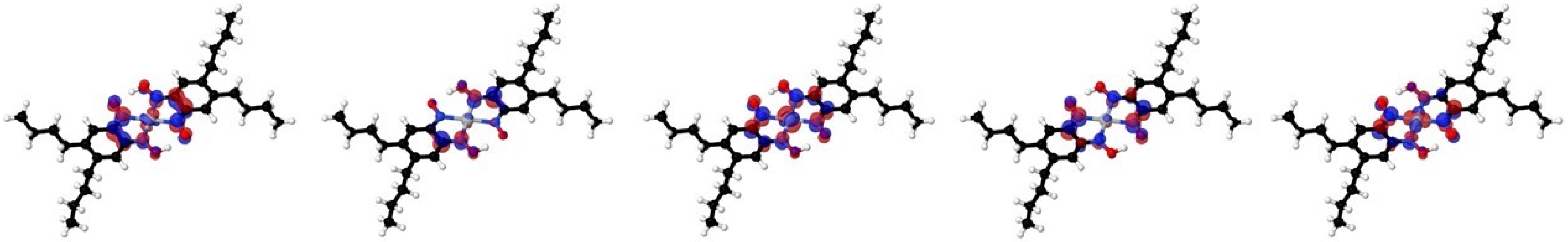
HOMO-5: -7.38 eV

HOMO-6: -7.63 eV

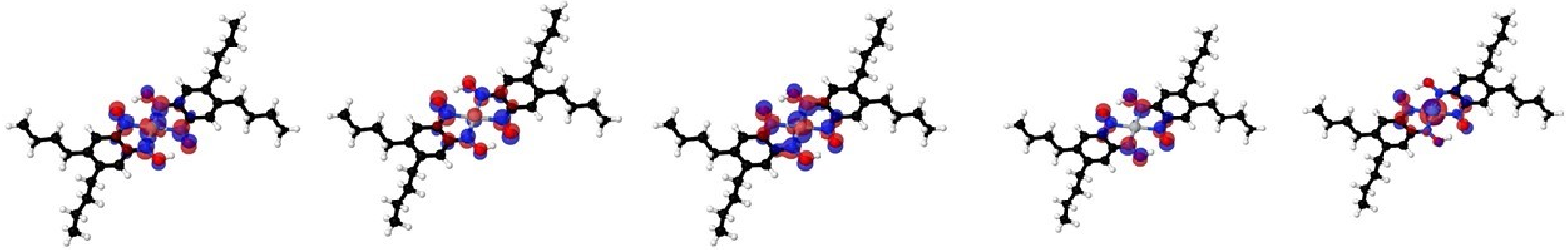
HOMO-7: -7.81 eV

Figure S1: Visualisations of the molecular orbitals in the range HOMO-7 to LUMO+6 for [Pt(bqd-dibutyl)$_2$], computed from isolated molecule calculations.

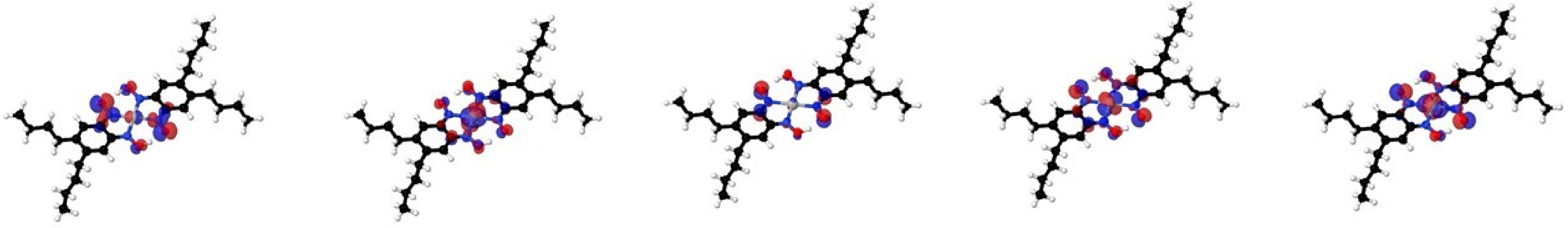
4: Results (Solid State Calculations)



LUCO+6: +5.30 eV **LUCO+5: +5.11 eV** **LUCO+4: +5.05 eV** **LUCO+3: +4.92 eV** **LUCO+2: +4.89 eV**



LUCO+1: +2.38 eV **LUCO: +1.17 eV** **HOCO: -0.04 eV** **HOCO-1: -0.45 eV** **HOCO-2: --1.63 eV**



HOCO-3: -1.78 eV **HOCO-4: -2.05 eV** **HOCO-5: -2.18 eV** **HOCO-6: -2.64 eV** **HOCO-7: -2.79 eV**

Figure S2: Visualisations of the crystalline orbitals and their respective Fermi-adjusted energies, in the range HOCO-7 to LUCO+6 for [Pt(bqd-dibutyl)$_2$], at the Γ k-point, from the solid state calculations using the HSE06 functional.

Although no experimental band gap for [Pt(bqd-dibutyl)$_2$] has yet been obtained, the successful replications of experimental band gaps of other materials in the literature by use of the HSE06 functional[12b, 16, 18b, 18c, 19a, 20] provides sufficient confidence of the calculated band gap of Pt(bqd-dibutyl)$_2$ and its much larger value compared to Pt(bqd)$_2$ (0.5 eV at ambient pressure, conductive by 1 GPa).[16]

The calculated ambient pressure electronic band structure and projected density of states (PDOS) is shown in Figure S3. The PDOS of the LUCO, one of the more delocalised bands, is still highly ligand-based orbital, with the majority contribution attributed to the C, N and O atoms.

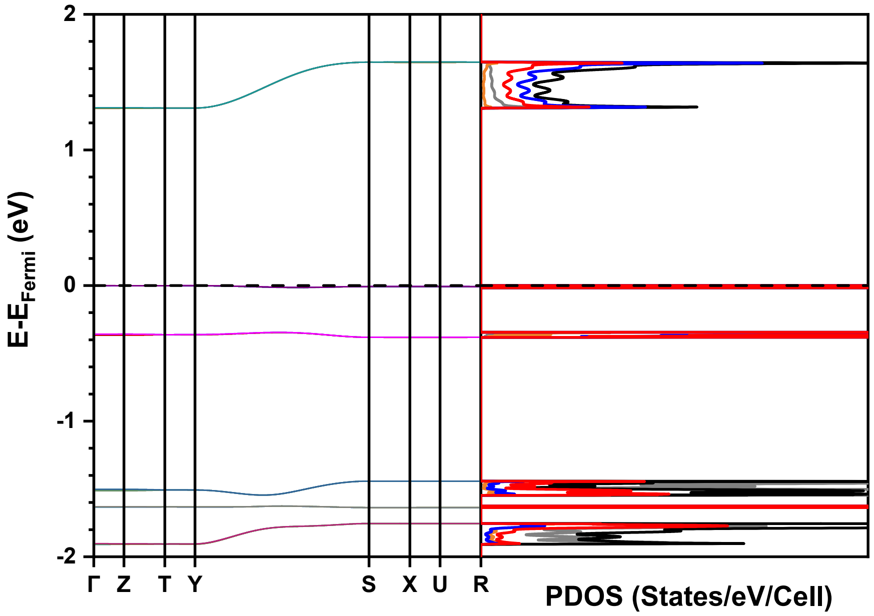


Figure S3: Electronic band structure and projected density of states (PDOS) for the ambient pressure structure of [Pt(bqd-dibutyl)$_2$]. In the PDOS, the contributions from the Pt, O, N, C and H atoms are coloured grey, red, blue, black and orange respectively.

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