Supplementary Material

Theoretical analysis of the triplet excited state of the $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4]^{4-}$ ion
and comparison with time-resolved X-ray and spectroscopic results

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Table S1. Triplet excited state geometries of $[\text{Pt}_2(\text{pop})_4]^{4-}$ calculated with various density functionals using Pauli and ZORA relativistic methods, and FC and AE_{Pt} basis sets (bond lengths in Å, angles in deg).

	B88P86			B88LYP			PW86LYP		
	Pauli FC	ZORA FC	ZORA AE_{Pt}	Pauli FC	ZORA FC	ZORA AE_{Pt}	Pauli FC	ZORA FC	ZORA AE_{Pt}
$\Delta(\text{Pt-Pt})$	-0.475	-0.164	-0.197	-0.517	-0.182	-0.204	-0.301	-0.203	-0.196
$\Delta(\text{Pt-P})$	0.008	0.01	0.027	0.007	0.019	0.039	0.011	0.031	0.060
$\Delta(\text{P-OH})$	-0.001	0.001	0.003	0.001	0.002	0.007	0.001	0.004	0.008
$\Delta(\text{P-O})$	0.006	0.001	0.001	0.007	0.001	0.002	0.002	0.001	0.002
$\Delta(\text{P-O}_b)$	-0.005	0.0	0.002	-0.005	0.001	0.004	-0.002	0.001	0.008
$\Delta(\angle \text{PO}_b\text{P})$	-9.3	-4.3	-4.8	-9.9	-4.6	-5.1	-6.1	-4.4	-5.3
$\Delta\text{SCF},^\dagger \text{ eV}$	1.89	2.42	2.97	2.22	2.81	3.23	2.71	2.81	3.12
$\Delta\text{TD-DFT, eV}$	2.58	2.45	2.97	2.79	2.65	3.20	2.67	2.82	3.18

[†] ΔSCF values correspond to energy differences between relaxed ground and excited states.