

Supporting Information:

Luminescence Rigidochromism and Redox Chemistry of Pyrazolate-Bridged Binuclear Platinum(II) Diimine Complex Intercalated into Zirconium Phosphate Layers

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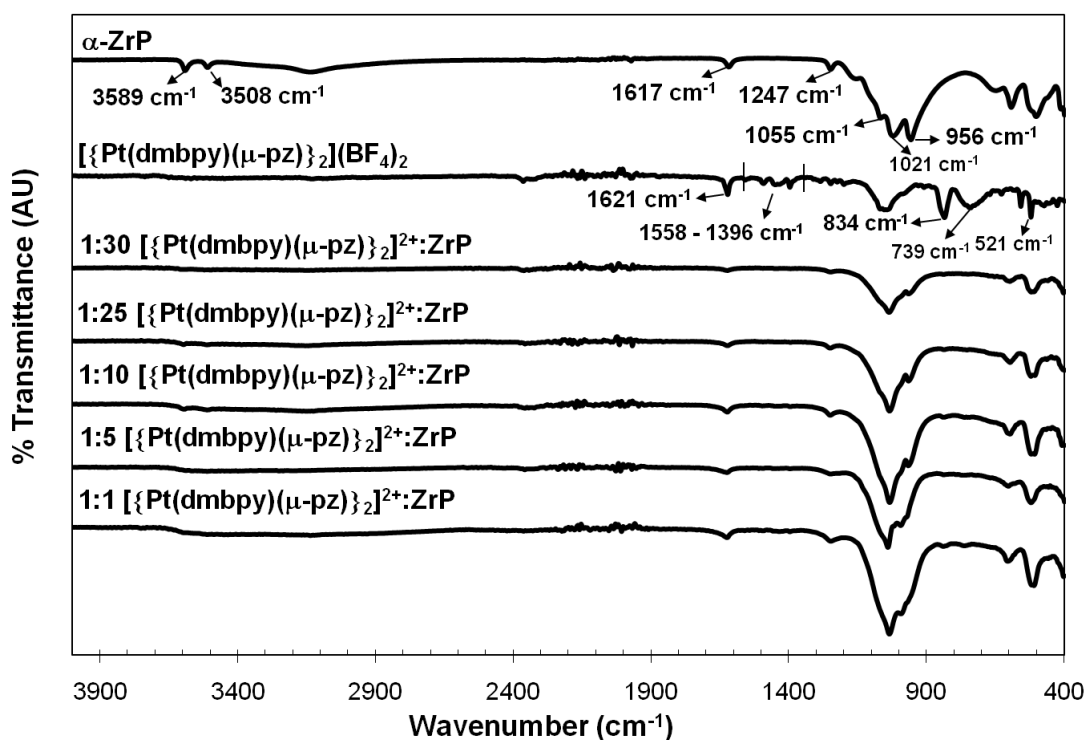


Figure S1. IR spectra of α -ZrP, $[\text{Pt}(\text{dmbpy})(\mu\text{-pz})_2](\text{BF}_4)_2$, and $[\text{Pt}(\text{dmbpy})(\mu\text{-pz})_2]^{2+}$ -exchanged ZrP at different loading levels.

FT-IR Results: The θ -ZrP material possesses an IR spectrum similar to that of α -ZrP. The α -ZrP spectrum exhibits three bands at 3589, 3508, and 1617 cm^{-1} corresponding to OH water stretching vibrations in ZrP and the “lattice” water band.^{83,84} Upon the intercalation of $[\text{Pt}(\text{dmbpy})(\mu\text{-pz})_2]^{2+}$ the water is displaced from the ZrP lattice. The phosphate groups give rise to bands near 1021 cm^{-1} due to orthophosphate vibrations, a band at 1247 cm^{-1} attributed to

the deformation of the P-O-H bond and one at 956 cm⁻¹ corresponding to the vibrations of the phosphate group with symmetry C_{3v}. The spectra of the intercalated materials show some characteristic bands of this layered material in the region from 2000 to 400 cm⁻¹. The IR spectrum of the [Pt(dmbpy)(μ-pz)₂]²⁺ complex shows bands at 1621, 834 and 739 cm⁻¹ due to ν(C=C), ν(C-H) and ν(C=N) of the bridge pyrazolate ligands.^{85,86} The vibrational bands at 1558-1396 cm⁻¹ are due to the bipyridyl ring vibrations and the 1448 and 1396 cm⁻¹ bands correspond to the CH₃ vibrations of the dmbpy ligand.^{56,87} In addition, a sharp medium intensity band located at 521 cm⁻¹ is characteristic of the Pt-N vibrational band.^{85,88,89} As the loading increases, the intercalated materials show bands at 1623, 1396, 839, 762 and 520 cm⁻¹, corresponding to vibrations of the platinum complex. There is no evidence of the presence of uncoordinated pyrazolate ligand since no ν(N-H) band is observed in the 3460-3380 cm⁻¹ region.⁹⁰ The most prominent difference occurs in the phosphate group region in which the vibrational bands are shifted to higher frequencies, from 1021 to 1035 cm⁻¹ and 956 cm⁻¹ to 993 cm⁻¹, respectively. This shift may result from more restricted phosphate group vibrational motions and a crowding of the dimer molecules as the loading level increases within the ZrP.

References:

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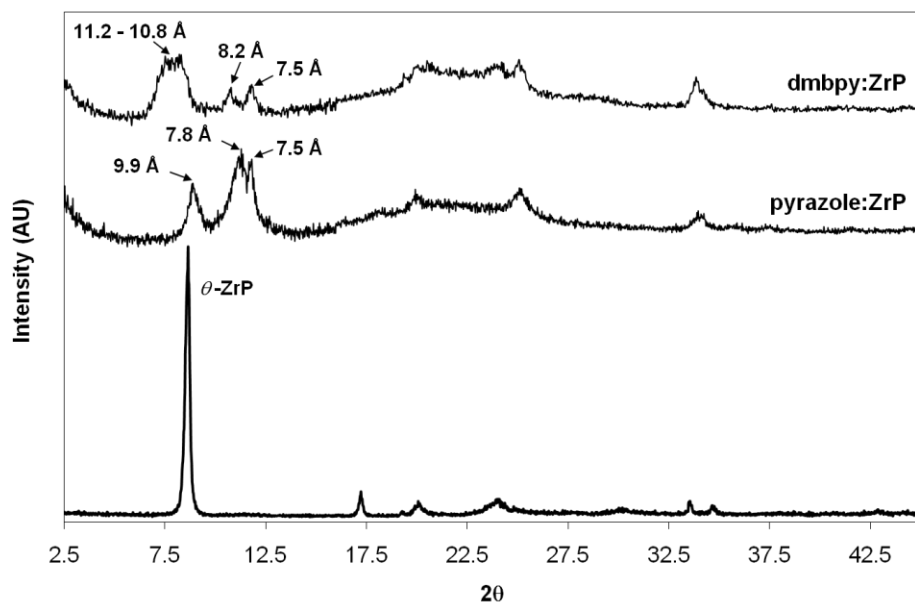


Figure S2. XRPD patterns of dmbpy- and pyrazole-intercalated ZrP materials and θ -ZrP.

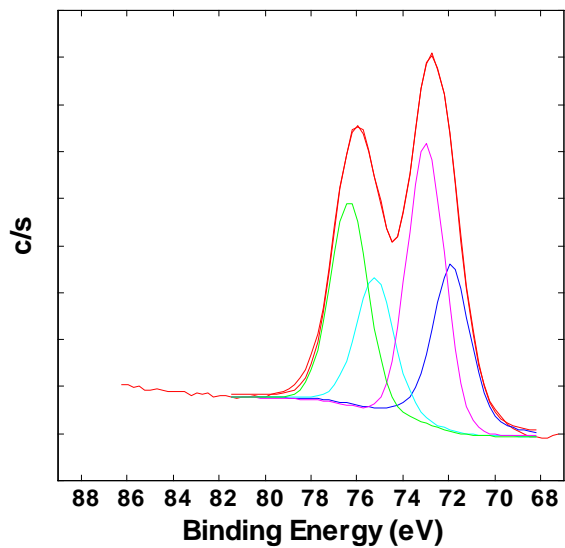


Figure S3. High resolution XPS spectra for the yellow-brown powders of 1:1 $[\{\text{Pt}(\text{dmbpy})(\mu\text{-pz})\}_2]^{2+}$ -exchanged ZrP at the Pt 4f binding energy region. The red color spectrum represents the fitted curved of the individual function doublet peaks.