

Electrochemistry, Chemical Reactivity, and Time-Resolved Infrared Spectroscopy of Donor–Acceptor Systems [(Q^x)Pt(pap^y)] (Q = Substituted *o*-Quinone or *o*-Iminoquinone; pap = Phenylazopyridine)

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The donor–acceptor complex [(^{0,N}Q²⁻)Pt(pap⁰)] (**1**; pap = phenylazopyridine, ^{0,N}Q⁰ = 4,6-di-*tert*-butyl-*N*-phenyl-*o*-iminobenzoquinone), which displays strong π -bonding interactions and shows strong absorption in the near-IR region, has been investigated with respect to its redox-induced reactivity and electrochemical and excited-state properties. The one-electron-oxidized product [(^{0,N}Q^{*-})Pt(pap⁰)](BF₄) (**[1]BF₄**) was chemically isolated. Single-crystal X-ray diffraction studies establish the iminosemiquinone form of ^{0,N}Q in **[1]**⁺. Simulation of the cyclic voltammograms of **1** recorded in the presence of PPh₃ elucidates the mechanism and delivers relevant thermodynamic and kinetic parameters for the redox-induced reaction with PPh₃. The thermodynamically stable product of this reaction, complex [(^{0,N}Q^{*-})Pt(PPh₃)₂](PF₆) (**[2]PF₆**), was isolated and characterized by X-ray crystallography, electrochemistry, and electron paramagnetic resonance spectroscopy. Picosecond time-resolved infrared spectroscopic studies on complex **1b** (one of the positional isomers of **1**) and its analogue [(^{0,O}Q²⁻)Pt(pap⁰)] (**3**; ^{0,O}Q = 3,5-di-*tert*-butyl-*o*-benzoquinone) provided insight into the excited-state dynamics and revealed that the nature of the lowest excited state in the amidophenolate complex **1b** is primarily diimine-ligand-based, while it is predominantly an interligand charge-transfer state in the case of **3**. Density functional theory calculations on **[1]**ⁿ⁺ provided further insight into the nature of the frontier orbitals of various redox forms and vibrational mode assignments. We discuss the mechanistic details of the newly established redox-induced reactivity of **1** with electron donors and propose a mechanism for this process.

Inorganic Chemistry, 2014, Volume 53 (2), pp 1021-1031

DOI: 10.1021/ic4024713