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Theoretical Studies on the Stability of Molecular Platinum Catalysts for Hydrogen Production

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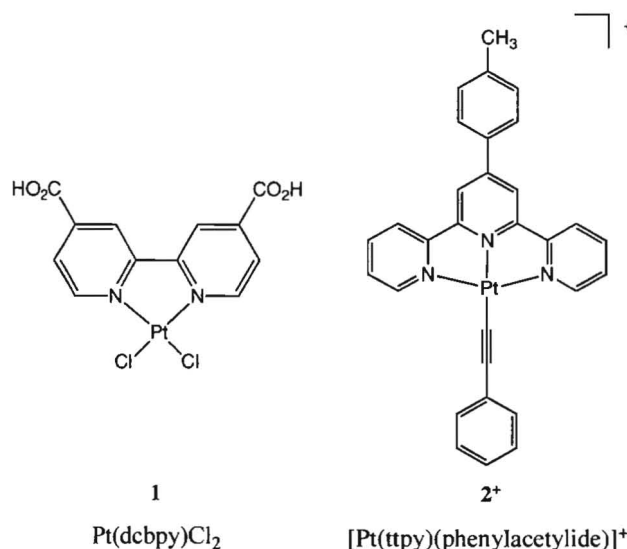
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For the past several decades, the search for processes that generate hydrogen from water under solar irradiation has received intense interest for both its fundamental aspects and potential applications.¹⁻³ Numerous studies have focused on multi-component systems that involve a photosensitizer such as Ru^{II} polypyridyl complex or TiO₂, an electron transfer relay molecule (methyl viologen, MV²⁺), a sacrificial electron donor (triethanolamine, TEOA), and colloidal Pt as a hydrogen generating catalyst.^{4,5} Recently, several groups have reported that Pd^{II} or Pt^{II} diimine complexes can act as efficient hydrogen-evolving molecular catalysts in these systems.⁶⁻¹⁰ For example, when Pt(dcbpy)Cl₂ (dcbpy = 4, 4'-dicarboxyl-2,2'-bipyridine) (**1**), or a derivative thereof is employed in place of colloidal Pt, large quantities of H₂ are observed.¹¹ However, Hammarström and Eisenberg both published separate reports outlining the photodecomposition of Pd^{II} and Pt^{II}-containing molecular catalysts to colloidal Pd or Pt, the true H₂ generating catalysts occurring in these molecular systems.^{11, 12} Eisenberg reported that after some induction period, irradiation of 1-TiO₂ system at 410 nm > λ > 455 nm leads to the presence of Pt nanoparticles on the surface of TiO₂.¹¹ In addition, when [Pt(tpy)phenylacetylide]⁺ (tpy = 4-tolyl-terpyridine) (**2**⁺) is employed as the photosensitizer with no hydrogen-generating catalyst, slow photodecomposition occurs upon irradiation with λ > 410 nm with an induction time of > 8 h with TiO₂ and at least 18 h with MV²⁺. While the evidence by Hammarstrom and Eisenberg are compelling, there are several groups that claim that Pt^{II} diimine complexes are effective molecular catalysts. To provide some insight into the stability of these Pt^{II} catalysts, we have performed DFT and TD-DFT calculations on **1** and **2**⁺ and found that while these compounds are stable upon reduction, photoexcitation of the reduced species leads to dissociation of the ligand set.

The optimized structures of **1** and **2**⁺ are in excellent agreement with reported crystallographic data for the same or related complexes.^{13, 14} The TD-DFT absorption spectra for **1** and **2**⁺ with CH₃CN are shown in Figure S1 and several of the experimental features are reproduced.^{13, 14} The high energy bands (~300 nm) in both **1** and **2**⁺ are assigned to intraligand and Cl-Pt ligand to metal (LMCT) transitions. The experimental UV/Vis spectrum of a derivative of **1** shows a shoulder at ~340 nm with weak transitions at ~355 nm;¹³ our results are consistent with these observations. In **2**⁺ the less intense band at 420 nm is a dπ(Pt)-π*(tpy) metal to ligand charge transfer (MLCT) transition (Figure S2).

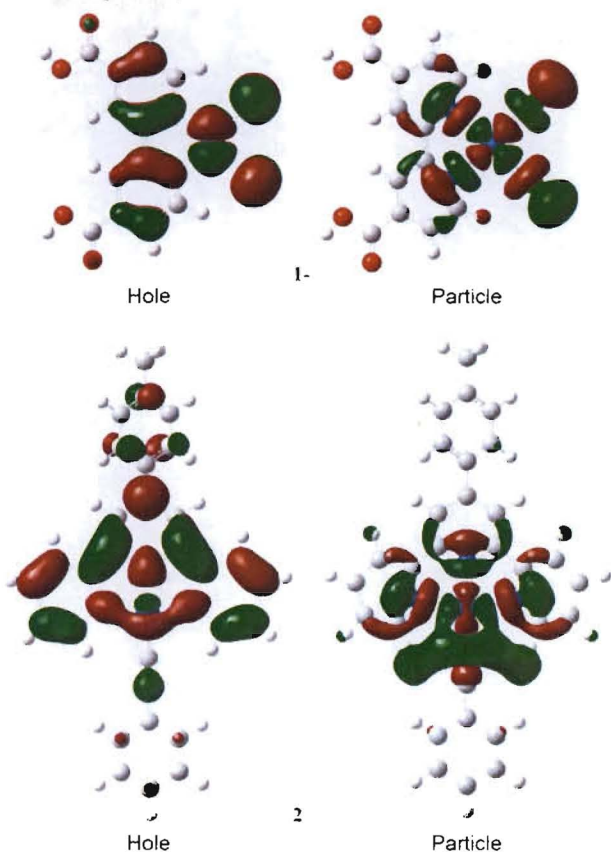
To initiate the decomposition sequence, one would expect the formation of an unstable Pt^I, or Pt⁰ species, either chemically or photochemically, by occupying a strongly σ antibonding Pt(d_{x²-y²) orbital with the surrounding ligands. This would then lengthen and weaken the metal-ligand bonds and lead to a labile Pt-Cl bond.¹⁵ In the case of **1**,}



decomposition could occur once an electron is transferred from the electron relay source or the metal complex sensitizer (e.g. TiO₂). Similarly, once complex **2**⁺ undergoes reductive quenching by TEOA, the reduced species is then unstable and decomposes. Examination of Tables S3 and S4 reveals that it is hard to justify occupation of a strongly antibonding Pt orbital upon reduction of the parent compounds. The calculated frontier orbitals of **1** confirm three dcbpy π* orbitals for the three lowest unoccupied MOs, with the highest occupied MOs having predominantly of Pt-Cl character; Similar results are also seen for **2**⁺ except the highest occupied orbitals have primarily phenylacetylide character. Geometry optimization calculations of **1**⁻ and **2** verify that upon reduction the unpaired electron resides on the pyridyl ligand and the singly occupied MO (SOMOs) compositions are very similar to the LUMO of the parent complexes. Our results are confirmed by previous electrochemical studies that show the pyridyl ligand is reduced upon one-electron reduction and not the Pt^{II} ion.^{13, 14} It is common in d⁶ catalysts that reduction of a diimine ligand can lead to expulsion of a cis-halide, for example, through a hyperconjugative interaction involving the SOMO of the π ligand and low-lying unoccupied σ*_{M-X} orbital.¹⁶ However, this mechanism is implausible for these systems since the Pt and ligands remain in the same plane.

It is also difficult to rationalize photodegradation of the parent compound in the irradiation range. The Natural Transition Orbitals (NTOs) for both the allowed and forbidden transitions of **1** and **2**⁺ show that majority of the transitions are MLCT or LLCT in character to ~300 nm. {Martin, 2003 #430} The NTOs of **1** suggest that photodegradation might occur but only at excitations ~350 nm. Another consideration is that the

Figure 1. MOs of the relevant excited state at 442 nm and 435 nm for **1**- and **2**, respectively.



pattern of the excited states may be altered to some extent after consideration of geometry-relaxation effects. The equilibrium geometries and MOs of **1** and **2**⁺ triplet state remain similar to that of the ground state.

The last scenario we considered was that the reduced species are also subjected to UV/Vis irradiation. The reduced species have doublet ground states, leading to doublet and quartet excited states. One-electron transitions from fully occupied orbitals to virtual ones result in one set of quartet excited states and two sets of doublet states. When the electron originates from the SOMO, then the resulting transition is a doublet state. Since the doublet reference is not a pure spin state in DFT, neither are the excited states and there is no simple way to assign the multiplicities. However, one can look at the reported coefficients of the MO transitions to infer the spin state of the excited state.

Using TD-DFT methods, we probed the photostability of **1**⁻ and **2**. Both **1**⁻ and **2** have a low energy transition from the pyridyl ligand to a strongly antibonding Pt-ligand orbital within the range of the experimental excitation energy for H₂ generation (~440 nm). Figure 1 depicts the MOs of major contributions from the one-electron excitations to the transitions at 442 and 435 nm for **1**⁻ and **2**, respectively. The calculated 10 lowest vertical excitation energies and oscillator strengths can be found in Table S11 and S12. In **1**⁻, the transition at 442 nm is the first doublet-quartet excitation based on the spin multiplicity and MO transition coefficients

with another doublet-quartet excitation into the antibonding Pt-Cl orbital occurring at 433 nm (Figure S7). Although we cannot predict an oscillator strength for a spin-forbidden transition, spin-orbit coupling is likely to be substantial for these Pt-based systems due to the heavy participation of Pt and will likely confer allowed character to the transition.

Description of the transition at 435 nm in **2** is less ambiguous than **1**⁻ and can be characterized as a doublet-doublet excitation from the SOMO to the antibonding Pt-ligand orbital. It is also equally important to point out that this transition is only very weakly allowed ($f=0.0001$). This might explain the long induction period prior to H₂ generation (> 8 h with TiO₂ and at least 18 h with MV²⁺). One consideration that must also be taken into account is the two competing quenching mechanisms in solution: Reductive quenching by TEOA and oxidative quenching by MV²⁺. Both rates are comparable with MV²⁺ oxidative quenching occurring twice as fast as TEOA reductive quenching.¹⁴ Perhaps the long induction period is a result of two competing mechanisms as well as a very weak doublet-doublet transition for the reduced chromophore.

In conclusion, from our calculations we can postulate that the molecular catalyst dissociates upon photoexcitation of the reduced species and that the H₂ production observed in the experiments is the result of the colloidal Pt in the vicinity of the semiconducting surface.

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Supporting Information Available: Computational details, discussion of Pt(en)Cl₂, optimized geometries, calculated absorption spectra, Natural Transition orbitals (NTOs), molecular orbitals with percent composition. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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