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

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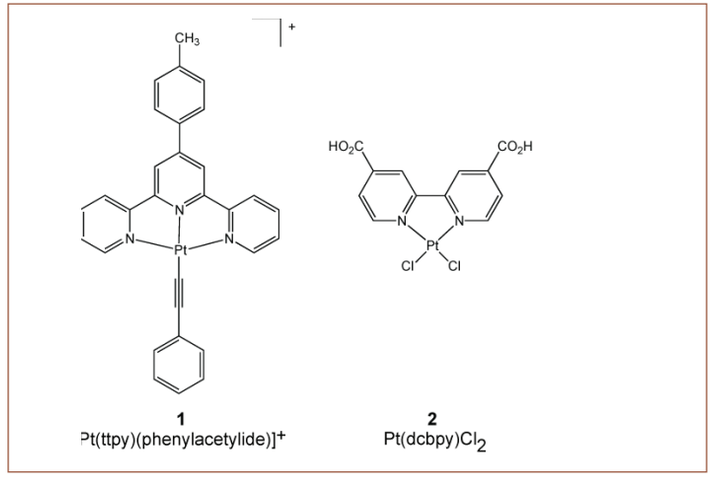
Photochemical generation of hydrogen from water has received intense interest over the past several years. Numerous studies have focused on systems that use a metal complex sensitizer such as Ru^{II} polypyridyl complex or TiO_2, an electron transfer relay molecule such as methyl viologen, a sacrifical electron donor, and colloidal Pt as a hydrogen-generating catalyst. Recently, several researchers have suggested that Pd^{II} or Pt^{II} diimine complexes can act as efficient molecular catalysts in these systems.

When either [Pt(ttpy)phenylacetylide] + (ttpy = 4-tolyl-2,2':6',2''-terpyridine) **(1)**, Pt(dcbpy)Cl_2 (dcbpy = 4, 4'-dicarboxyl-2,2'-bipyridine) **(2)** (see Scheme 1), or a derivative thereof is employed in place of colloidal Pt, large quantities of H_2 are observed. However, Hammarstrom and Eisenberg published separate reports outlining the photodecomposition of these molecular catalysts to colloidal Pd or Pt, the true H_2-generating catalysts occurring in these molecular systems [1,2]. Eisenberg reported that after some induction period, irradiation of the **1**-, and **2**-TiO_2 systems at 410 nm > λ > 455 nm leads to the presence of Pt nanoparticles on the surface of TiO_2. To provide some insight into this work, we have performed density functional (DFT) calculations on these purported Pt^{II} molecular catalysts to determine if and how these compounds decompose.

All DFT calculations have been performed with the Gaussian suite of programs, using both the commercial and development versions. Geometry optimizations were carried out using the B3LYP functional and verified by vibrational analysis. The vertical transition energies to the valence excited states were computed with time dependent density functional theory (TD-DFT) using the Coulomb-attenuating method applied to the B3LYP functional (CAM-B3LYP), and the bulk solvent effects of acetonitrile (CH_3CN) were evaluated using the polarizable continuum model (PCM). For both molecules, we neglect spin-orbit coupling.

(Scheme 1) Molecular Pt(II) Complexes Used to Generate H_2



The optimized structures of **1** and **2** are in excellent agreement with reported crystallographic data. The calculated TD-DFT absorption spectra for **1** and **2** with CH_3CN are shown in Fig. 1 and several of the experimental features are reproduced. The high-energy bands (~300 nm) in both **1** and **2** are attributable to intraligand and Cl-Pt

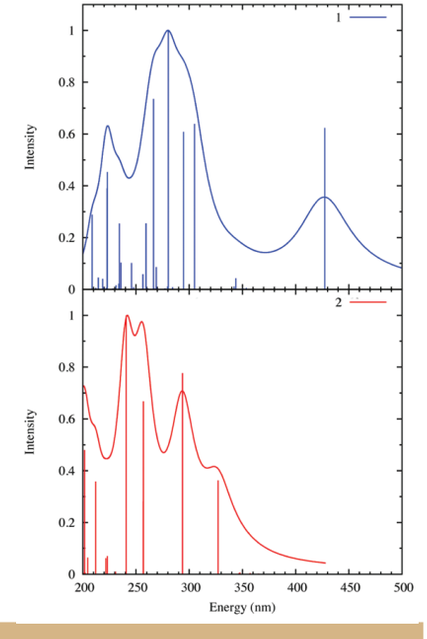


*Fig. 1. Calculated absorption spectra for **1** and **2** in CH_3CN.*

ligand to metal (LMCT) transitions. The less intense band in **1** is a dp(Pt)-p*-terpy metal to ligand charge transfer (MLCT) transition. The experimental UV/Vis spectrum of compound **2** shows a shoulder at ~340 nm with weak transitions at ~355 nm; our results are consistent with experiment.

To initiate the degradation sequence, one would expect the formation of an unstable Pt^{I} or Pt^{0} species, either photochemically or chemically, by occupying a strongly antibonding Pt orbital with the surrounding ligands. However, examination of the natural transition orbitals (NTOs) for both the allowed and forbidden transitions of **1** and **2** reveals that it is hard to justify photodegradation of the parent compound in the irradiation range. Firstly, compound **1** has not been reported to degrade upon UV/Vis excitation and all NTOs show that the transitions are MLCT or LLCT in character to ~300 nm. The NTOs of **2** suggest that photodegradation might occur, but only at excitations ~350 nm.

These results then suggest that in the Hammarstrom and Eisenberg experiments the catalysts decompose once an electron is transferred from the metal complex sensitizer (e.g., Ru^{II} polypyridyl or TiO_2) to **1** or **2**. Previous electrochemical studies have shown that the diimine ligand influences the reduction potential and the Pt^{II} ion is not reduced. Geometry optimization calculations of **1** and **2** verify that the electron resides on the diimine ligand upon reduction. Since these reduced species are also subjected to UV/Vis irradiation, we probed the photostability of **1** and **2** using TD-DFT methods. To our surprise, 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 H_2 generation (~435 nm). Figures 2 and 3 depict the MOs of major contributions from the one-electron excitations to the transitions for **1** and **2**, respectively. Also, it is equally important to point out that both of these transitions are either very weak or spin-forbidden. A very weakly allowed transition ($f = 0.0001$) might explain the long induction period for **1** prior to H_2 generation (> 8 h with TIO_2 and at least 18 h with MV^{2+}). For **2**, although we cannot predict an oscillator strength for a spin-forgidden 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.

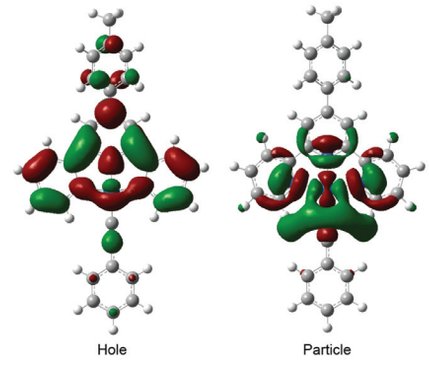


Fig. 2. MOs of the relevant excited state at 435 nm for 1.

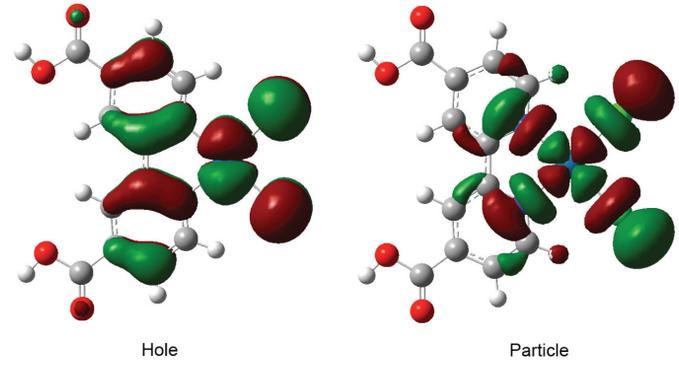


Fig. 3. MOs of the relevant excited state at 433 nm for 2.

In conclusion, from our calculations we can postulate that the molecular catalyst dissociates upon photoexcitation of the reduced species and that the H_2 production observed in the experiments is the result of the colloidal Pt in the vicinity of the semiconducting surface.

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[1] P. Lei et al., *J. Am. Chem. Soc.* **130,** 26 (2008).
[2] P. Du et al., *J. Am. Chem. Soc.* **130,** 5056 (2008).

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