

# Local Structure of Pt(II) Pyridyl Complexes Anchored onto Mesoporous Silica as Photo-induced H<sub>2</sub> Production Catalysts

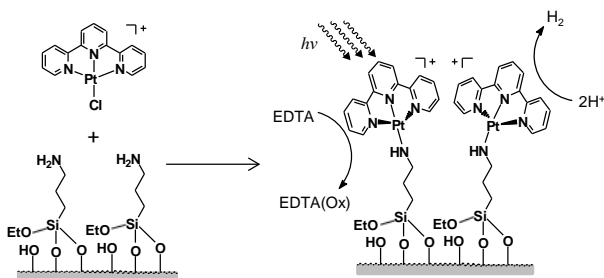
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## 1 Introduction

Recently, investigations into emissive square-planar d<sup>8</sup> Pt(II) pyridyl complexes have been numerous owing to their potential capacity for application in chemical sensing, solar energy conversion, and photocatalysis. The photoluminescence from such complexes originates from a variety of lowest triplet excited states, including ligand-centered (LC), metal-to-ligand charge-transfer (MLCT) and metal-metal-to-ligand charge-transfer (MMLCT) excited states. A low-lying <sup>3</sup>MMLCT excited state occurs in dimers and aggregates with short Pt···Pt separation, and the resulting emission is observed at longer wavelengths than those of unimolecular <sup>3</sup>LC and <sup>3</sup>MLCT emissions. These unique characteristics provide with the new photocatalyst systems allowing H<sub>2</sub> production as well as selective photooxidation using molecular oxygen.

Bearing this in mind, we developed an inorganic-organic hybrid photocatalyst by anchoring the chloro(2,2':6',2''-terpyridine)platinum(II) ([Pt(tpy)Cl]Cl) complex to mesoporous silica modified with (3-aminopropyl)trimethoxysilane (APTMS). It was proven that the anchored Pt complex creates new bifunctional heterogeneous photocatalyst enabling both visible-light photosensitization associated with the <sup>3</sup>MMLCT excited states and H<sub>2</sub>-evolution in aqueous media without an electron relay (**Scheme 1**). In this paper, the relationship between the local structure and photocatalytic activities was examined by XAFS analysis [1].



Scheme 1. Anchoring of [Pt(tpy)Cl]<sup>+</sup> complex onto the modified silica surface and schematic illustration of bifunctional heterogeneous photocatalyst for H<sub>2</sub>-evolution in aqueous media without an electron relay.

## 2 Experiment

**Anchoring of Pt complex on to MCM-48:** Mesoporous silica MCM-48 and [Pt(tpy)Cl]Cl complex were synthesized according to the literature procedures, respectively. 200 ml of chloroform solution of [Pt(tpy)Cl]Cl was stirred with 1.0 g of APTMS-modified

MCM-48 sample at room temperature for 24 h. The product was recovered by vacuum filtration, washed with chloroform, and dried under vacuum overnight to give Pt(tpy)/MCM-48 samples with different Pt loadings (Pt: 0.2, 0.4, 0.8, 1.2 and 2.4 wt%), respectively. The Pt loadings were determined by inductively coupled plasma (ICP) analysis.

**XAFS analysis:** Pt L<sub>III</sub>-edge XAFS spectra were recorded at room temperature in fluorescence mode at the BL-7C facilities of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba (2009G221). A Si(111) double crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. In a typical experiment, the sample was loaded into the *in situ* cell with plastic windows. EXAFS data were examined using the EXAFS analysis program, Rigaku EXAFS. The pre-edge peaks in the XANES regions were normalized for atomic absorption, based on the average absorption coefficient of the spectral region. Fourier transformation (FT) of *k*<sup>3</sup>-weighted normalized EXAFS data was performed over 3.5 Å < *k*/Å<sup>-1</sup> < 12 Å range to obtain the radial structure function. CN (coordination number of scatters), *R* (distance between the absorbing atom and the scatterer), and Debye-Waller factor were estimated by curve-fitting analysis with the inverse FT in the 0.8 < *R*/Å < 2.8 range assuming single scattering.

## 3 Results and Discussion

**Figure 1A** shows XANES spectra at the Pt L<sub>III</sub>-edge of the [Pt(tpy)Cl]Cl complex and anchored samples with different Pt loadings. The white line at around 11565 eV is an absorption threshold resonance, which is known to be intensified as a result of oxidation. The results show that all anchored samples afforded higher intensity peaks compared to free [Pt(tpy)Cl]Cl, suggesting that the surface anchored Pt species appear to be in a slightly electron-deficient state, because of the decrease in the σ-donor electron by replacement of the fourth coordinated ligand from chloride to a nitrogen atom.

In the FT-EXAFS spectra, all samples show a strong peak at around 1.5 Å attributable to a Pt–N bond and a small second shell at ca. 2.4 Å assignable to neighboring carbon atoms (**Figure 1B**). This corroborates a tridentate binding structure for Pt(II). In the case of the [Pt(tpy)Cl]Cl complex, an additional peak due to the Pd–Cl bond was observed at around 1.8 Å, which completely disappeared after reaction with APTMS-modified MCM-48 to generate the new Pt–N bond accompanied by elimination of the Pt–Cl bond. It is notable that the samples with high Pt loadings exhibit the additional peak

at around 3.5 Å, which may be ascribed to the short Pt··Pt interactions as discussed later. Moreover, the first peaks of Pt(tpy)/MCM-48 were slightly shifted toward shorter interatomic distances with increasing Pt content. The average Pt–N distances determined by curve-fitting analysis decreased from 2.06 to 2.02 Å as the Pt loading amount increased, which suggests that the anchored Pt complexes may undergo slight distortion within the channel, due to the steric constraints at high Pt loading.

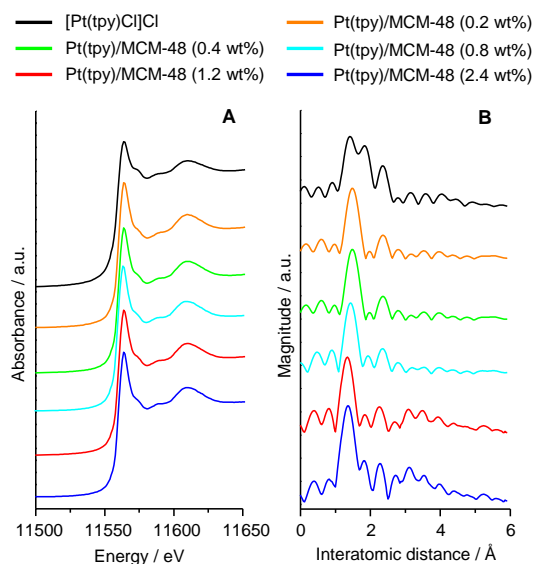


Figure 1. (A) Pt L<sub>III</sub>-edge XANES spectra and (B) FT-EXAFS spectra.

Anchoring of the [Pt(tpy)Cl]Cl complex to mesoporous silica results in photocatalysts which allows H<sub>2</sub>-evolution in aqueous media in the presence of EDTA under visible-light irradiation ( $\lambda > 420$  nm). Time course of H<sub>2</sub> production normalized based on Pt amount are shown in **Figure 2**. No significant reaction is observed under either dark condition in the presence of the photocatalyst or without EDTA under light irradiation. It should be noted that the photocatalytic activity significantly varies according to the amount of Pt loadings; no H<sub>2</sub>-evolution occur to any significant extent at less than 0.4 wt% Pt loadings, while photocatalytic activity gradually increased at more than 0.8 wt% Pt loadings. This behavior is in good accordance with the increasing intensity of the luminescence emission due to the <sup>3</sup>MMLCT states. Significantly, the maximum activity obtained by 2.4 wt% Pt loading is higher than that of the homogeneous counterparts under identical conditions.

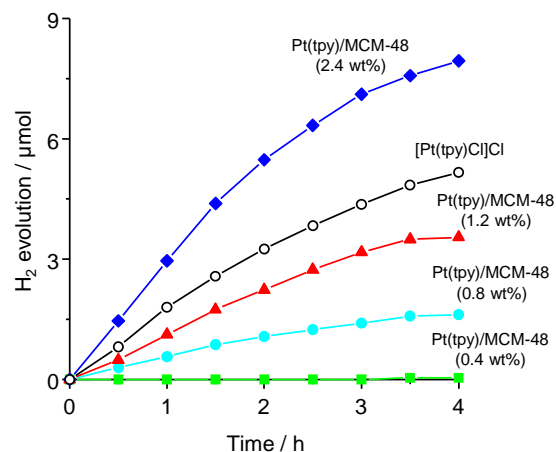


Figure 2. Photocatalytic H<sub>2</sub> production from an aqueous acetate buffer solution (pH = 5.0) and 30 mM EDTA in the presence of Pt catalyst (Pt: 4 μmol).

#### References

- [1] K. Mori, K. Watanabe, K. Fuku, H. Yamashita, *Chem. Eur. J.*, **18** (2012) 415.

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