

## Bi- and Terpyridyl Platinum(II) Chloro Complexes: Molecular Catalysts for the Photogeneration of Hydrogen from Water or Simply Precursors for Colloidal Platinum?

Pingwu Du, Jacob Schneider, Fan Li, Wei Zhao, Upali Patel, Felix N. Castellano, and Richard Eisenberg

*J. Am. Chem. Soc.*, **2008**, 130 (15), 5056-5058 • DOI: 10.1021/ja711090w • Publication Date (Web): 20 March 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

## Bi- and Terpyridyl Platinum(II) Chloro Complexes: Molecular Catalysts for the Photogeneration of Hydrogen from Water or Simply Precursors for Colloidal Platinum?

Pingwu Du,<sup>†</sup> Jacob Schneider,<sup>†</sup> Fan Li,<sup>§</sup> Wei Zhao,<sup>‡</sup> Upali Patel,<sup>‡</sup>  
Felix N. Castellano,<sup>\*,‡</sup> and Richard Eisenberg<sup>\*,†</sup>

Department of Chemistry, University of Rochester, Rochester, New York 14627, Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

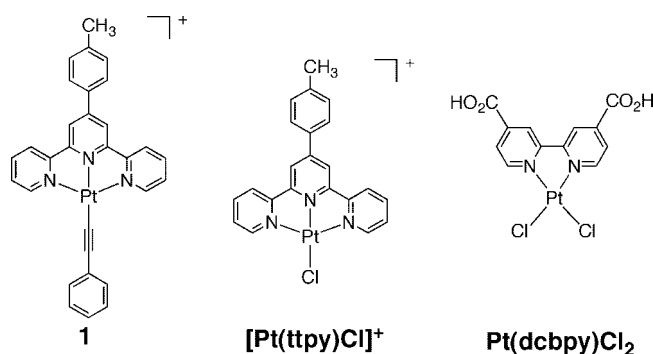
Received December 13, 2007; E-mail: castell@bgsu.edu; eisenberg@chem.rochester.edu

Because of its potential role in the conversion of light energy into stored chemical potential, the photochemical generation of hydrogen from water, which corresponds to the reductive side of water splitting, has been the subject of much recent interest.<sup>1</sup> For molecular-based systems used to carry out this reaction, the key components include a metal complex sensitizer (most often a Ru(II) bipyridine chromophore), an electron transfer relay such as viologen, a sacrificial electron donor, and a hydrogen generating catalyst that is generally colloidal Pt.<sup>1a,2</sup> Recent studies have described the use of platinum group metal complexes as *molecular* catalysts in place of colloidal platinum for greater efficiency and cost effectiveness.<sup>3</sup> In some of the systems reported, a Pt(II) molecular catalyst is covalently linked directly to the sensitizer.<sup>4</sup> In this communication, we describe studies involving Pt(II) complexes illustrating that these representative molecular catalysts actually undergo photodecomposition and are simply precursors to colloidal Pt which functions as the true H<sub>2</sub> generating catalyst.

It is known that platinumized titanium dioxide (TiO<sub>2</sub>) can produce large quantities of H<sub>2</sub> from aqueous protons in the presence of Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, or methanol under UV bandgap irradiation.<sup>5</sup> Using similar systems that contain either TiO<sub>2</sub> with colloidal Pt or platinumized TiO<sub>2</sub> in the presence of triethanolamine (TEOA, 336 μmol) as the electron source, we have obtained similar results with 41 and 73 μmol of H<sub>2</sub> generated, respectively, after only 2 h of TiO<sub>2</sub> bandgap irradiation (experimental details of all photolyses and analyses are given in Supporting Information).

When either Pt(dcbpy)Cl<sub>2</sub> (dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine) or [Pt(ttpy)Cl]<sup>+</sup> (ttpy = 4-tolyl-2,2':6',2''-terpyridine) (Scheme 1) is employed in place of colloidal Pt, similar quantities of H<sub>2</sub> are observed (53 and 117 μmol of H<sub>2</sub>, respectively) under the same UV irradiation for 2 h. In another experiment involving a system comprising Pt(dcbpy)Cl<sub>2</sub> surface-anchored to TiO<sub>2</sub> in 6:1 H<sub>2</sub>O/MeOH with MeOH as the electron source, copious amounts of H<sub>2</sub> are detected upon UV bandgap irradiation. In fact, H<sub>2</sub> evolution results show that the Pt(dcbpy)Cl<sub>2</sub>-TiO<sub>2</sub> system, which is 2% Pt complex by mass (approximately 1 wt % Pt), significantly *outperforms* platinumized TiO<sub>2</sub> systems formed from either in situ photochemical reduction of H<sub>2</sub>PtCl<sub>6</sub> or mixing of TiO<sub>2</sub> with platinum black. The results of such comparative photolyses are shown in Figure S1. For

Scheme 1. Molecular Pt(II) Complexes Used to Generate H<sub>2</sub>



the Pt(dcbpy)Cl<sub>2</sub>-TiO<sub>2</sub> system, one can clearly observe vigorous and sustained H<sub>2</sub> bubbling from the photolysis solution. For both the Pt(dcbpy)Cl<sub>2</sub>-TiO<sub>2</sub> system and the ones formed by platinumizing TiO<sub>2</sub> with Pt black or in situ photochemical reduction of H<sub>2</sub>PtCl<sub>6</sub>, the efficiency of H<sub>2</sub> production optimizes at approximately 1 wt % Pt (Figure S1). Experiments performed at low light flux (4 mW, 365 nm) indicate that the Pt(dcbpy)Cl<sub>2</sub>-TiO<sub>2</sub> system is 7.6 times more efficient at producing H<sub>2</sub> than the platinumized TiO<sub>2</sub> systems generated as mentioned at ca. 1 wt % Pt metal (Figure S1).

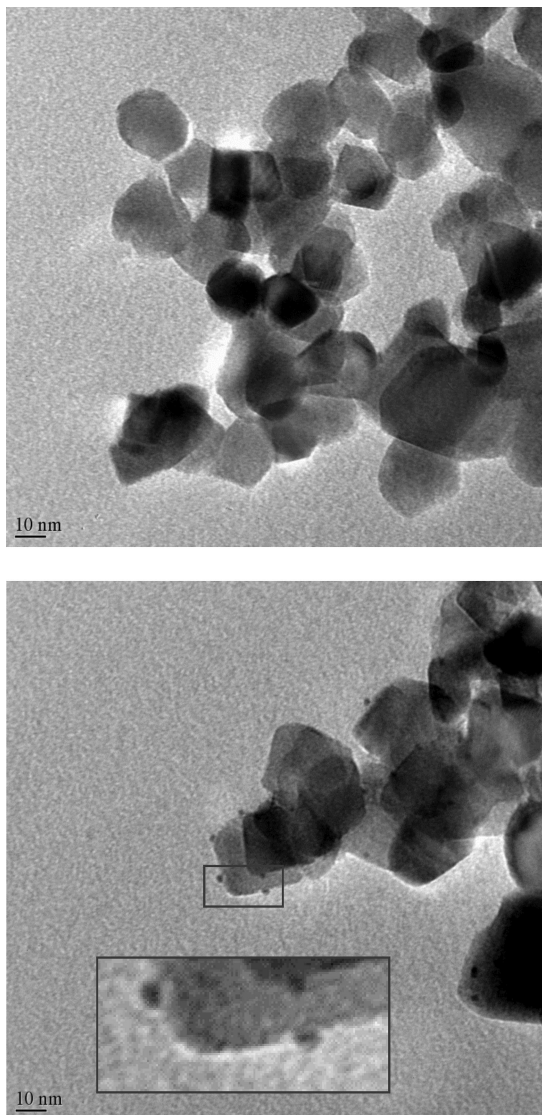
While these data suggest that the Pt(II) chloro complexes are acting as effective molecular catalysts for H<sub>2</sub> generation, TiO<sub>2</sub> samples isolated *after* the photolyses possessed a slightly gray cast, suggestive of noble metal formation. To examine this idea further, the Pt(dcbpy)Cl<sub>2</sub>-TiO<sub>2</sub> system was exposed to bandgap light for 8 h, after which the material was isolated. All surface-bound Pt(dcbpy)Cl<sub>2</sub> was then removed by stirring the sample in 1 M NaOH for 8 h followed by washing and resumption of the photolysis. The data in Figure S2 show that the catalytic activity of the NaOH-treated and washed sample from which surface-bound Pt(dcbpy)Cl<sub>2</sub> was removed is quantitatively similar to that of the original surface-anchored "molecular" material, meaning that a catalyst other than the Pt(II) complex is active in the system.

Examination of TEM images of another Pt(dcbpy)Cl<sub>2</sub>-TiO<sub>2</sub> system both before and after UV irradiation (Figure 1) clearly shows the presence of nanoscopic particles on TiO<sub>2</sub> only *after* irradiation. These particles are 2–3 nm in diameter, compared with the Degussa P25 TiO<sub>2</sub> particles of ca. 25 nm on edge. The identity of these nanoscopic particles as colloidal Pt is supported by EDAX measurements, two of which are shown in Figure 2. In the top image of Figure 2, the EDAX spectrum of a sample

<sup>†</sup> University of Rochester.

<sup>‡</sup> Bowling Green State University.

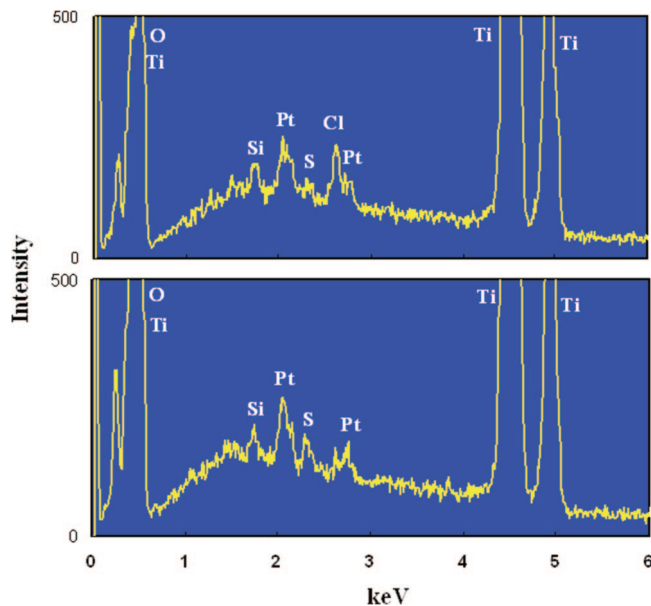
<sup>§</sup> University of Minnesota.



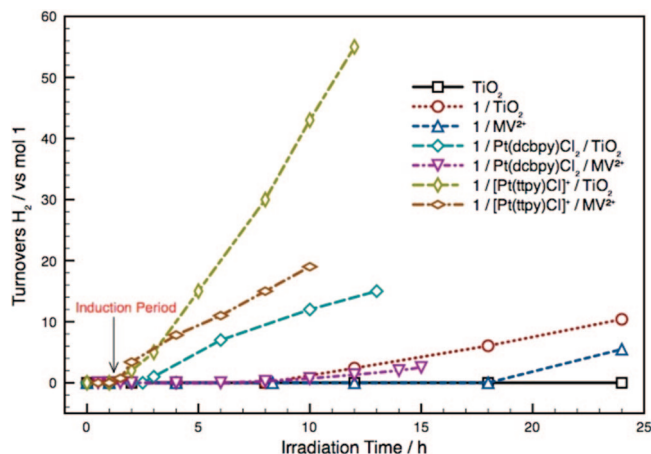
**Figure 1.** TEM images of Pt(dcbpy)Cl<sub>2</sub> mixed with TiO<sub>2</sub> before (top image) and after UV irradiation (bottom) in the presence of TEOA.

of Pt(dcbpy)Cl<sub>2</sub>–TiO<sub>2</sub> before irradiation shows both platinum and chlorine peaks, while in the bottom image of Figure 2, the EDAX spectrum of the same sample measured *after* irradiation reveals that while the Pt peak remains that arising from chlorine is no longer present. The EDAX results thus suggest that molecular Pt(dcbpy)Cl<sub>2</sub> on the surface of TiO<sub>2</sub> is no longer present. To support further the notion that the platinum peak in the EDAX of the irradiated sample is from platinum particles and not from bound Pt(dcbpy)Cl<sub>2</sub>, a Pt(dcbpy)Cl<sub>2</sub>–TiO<sub>2</sub> sample was treated with 1 M NaOH overnight to desorb the complex, followed by washing. This time the EDAX spectrum reveals no appreciable platinum present in the sample (Figure S7). On the other hand, for part of the same sample that was irradiated prior to treatment with 1 M NaOH, platinum peaks can be observed. The results thus indicate that the platinum signal does not arise from molecular Pt(dcbpy)Cl<sub>2</sub> and instead corresponds to platinum particles formed on photodecomposition of the complex on the TiO<sub>2</sub> surface (Figure S8).

The question of whether the Pt(II) complexes can indeed function as hydrogen evolution catalysts under *less energetic* irradiation was next examined using the mercury test, known for its ability to inhibit catalysis by metal colloids and particles.<sup>6</sup>



**Figure 2.** EDAX spectra of the Pt(dcbpy)Cl<sub>2</sub>–TiO<sub>2</sub> system before (top spectrum) and after (bottom spectrum) UV irradiation in the presence of TEOA. The S and Si peaks are the result of the substrate used to hold the sample.



**Figure 3.** Results from photolysis experiments ( $\lambda > 410$  nm) containing TEOA with molecular Pt(II) complexes that show varying induction times until H<sub>2</sub> is observed.

Previously, [Pt(tpy)(phenylacetylide)]<sup>+</sup> (**1**) had been used as the chromophore in a multiple-component system for the light-driven reduction of aqueous protons with  $\lambda > 410$  nm.<sup>7</sup> Specifically, a mixture of **1**, TEOA, methyl viologen (MV<sup>2+</sup>), and colloidal Pt was found to yield 82 turnovers (TNs per mol **1**) after 10 h of irradiation. When TiO<sub>2</sub> was substituted for MV<sup>2+</sup> with  $\lambda > 410$  nm irradiation, 94 TNs were obtained in 10 h, but when the same experiment was repeated with  $\sim 2$  mL of Hg added to this system (**1**–TEOA–TiO<sub>2</sub>–Pt colloid) and stirred for 10 h prior to irradiation, no H<sub>2</sub> was obtained. In these TiO<sub>2</sub>-containing photolyses with  $\lambda > 410$  nm, **1** is clearly the photosensitizer, and the results show that added mercury effectively sequesters all colloidal platinum.

Replacement of colloidal Pt by either complex [Pt(tpy)Cl]<sup>+</sup> or Pt(dcbpy)Cl<sub>2</sub> in photolyses containing **1** and MV<sup>2+</sup> with  $\lambda > 410$  nm still yielded H<sub>2</sub> generation but in reduced amounts (19 and 1 TNs, respectively, after 10 h irradiation, Figure 3). In parallel experiments using TiO<sub>2</sub> in place of MV<sup>2+</sup> as the



electron relay, 43 and 12 TNs were obtained, respectively, with  $[\text{Pt}(\text{ttpy})\text{Cl}]^+$  and  $\text{Pt}(\text{dcbpy})\text{Cl}_2$  (Figure 3). In the absence of these complexes, no appreciable  $\text{H}_2$  was generated, indicating that they are essential for photodriven  $\text{H}_2$  production. When the viologen-containing system  $\mathbf{1}$ -TEOA- $\text{MV}^{2+}$ - $[\text{Pt}(\text{ttpy})\text{Cl}]^+$  was stirred with Hg overnight followed by Hg removal prior to photolysis, no change in activity relative to the system without Hg treatment was seen, indicating that mercury does not capture, poison, or destroy the  $[\text{Pt}(\text{ttpy})\text{Cl}]^+$  complex in contrast with its behavior with colloidal Pt.

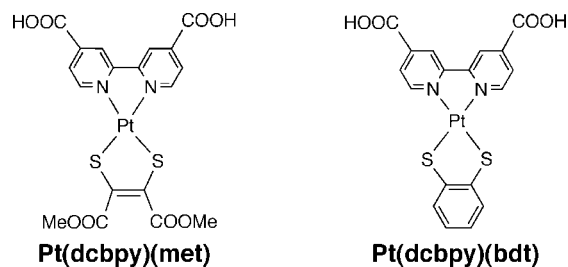
With these results suggestive of catalysis by the Pt(II) complexes, additional Hg experiments were conducted with  $\text{TiO}_2$ -containing systems in which Hg was not removed from the system before irradiation (Figure S5). For  $\mathbf{1}$ -TEOA- $\text{TiO}_2$ - $[\text{Pt}(\text{ttpy})\text{Cl}]^+$ , photolysis for 10 h with  $\lambda > 410$  nm yielded only 9 TNs of  $\text{H}_2$ , compared with 43 TNs for the same system without Hg, and for  $\mathbf{1}$ -TEOA- $\text{TiO}_2$ - $\text{Pt}(\text{dcbpy})\text{Cl}_2$ , only 2 TNs of  $\text{H}_2$  were detected after 10 h, as opposed to the same system without Hg that yielded 12 TNs. Analogous experiments with  $\text{MV}^{2+}$  in place of  $\text{TiO}_2$  gave comparable results. In light of the fact that Hg does not poison or adversely affect  $[\text{Pt}(\text{ttpy})\text{Cl}]^+$  or  $\text{Pt}(\text{dcbpy})\text{Cl}_2$  prior to irradiation, the lower efficiency of  $\text{H}_2$  production with Hg present likely results from Hg poisoning or sequestering in situ generated colloidal Pt from photodecomposition of the Pt(II) chloride complexes with  $\lambda > 410$  nm radiation.

A series of photolyses were next done to ascertain the photostability of the Pt(II) complexes used in these experiments. In fact, slow decomposition of the Pt acetylide chromophore is found on irradiation with  $>410$  nm light. For a system containing only  $\mathbf{1}$ , TEOA, and  $\text{TiO}_2$  or  $\text{MV}^{2+}$  but no hydrogen generating catalyst, irradiation with  $\lambda > 410$  nm yields very small quantities of  $\text{H}_2$  (Figure 3). In this system, the only source of Pt is  $\mathbf{1}$ , and there is no  $\text{H}_2$  observed when  $\mathbf{1}$  is omitted from the system. Furthermore, there is a substantial induction period prior to the observation of  $\text{H}_2$  that is dependent on the electron relay in the system. For  $\text{TiO}_2$ , this induction period is  $>8$  h, while for  $\text{MV}^{2+}$ , it is at least 18 h. These results indicate that  $\mathbf{1}$  undergoes slow photodecomposition with  $\lambda > 410$  nm, but it is also moderately stable for at least 8 h. When these experiments are repeated with either  $[\text{Pt}(\text{ttpy})\text{Cl}]^+$  or  $\text{Pt}(\text{dcbpy})\text{Cl}_2$  as the “ $\text{H}_2$  generating molecular catalyst”, induction periods are again observed but the induction periods are shorter (2 and 3 h, respectively) and the quantities of  $\text{H}_2$  generated substantially greater, consistent with greater rates of photodecomposition for the Pt chloro complexes. This conclusion is supported by a TEM image of the solid isolated from the system  $\mathbf{1}$ -TEOA- $\text{TiO}_2$ - $\text{Pt}(\text{dcbpy})\text{Cl}_2$  after photolysis which, like Figure 1 bottom, shows colloidal deposits on the  $\text{TiO}_2$  surface (see Figure S6).

Recently, two Pt(II) diimine dithiolate sensitizers were reported that are capable of driving  $\text{H}_2$  generation using visible light ( $\lambda > 455$  nm) with no sign of chromophore decomposition for more than 175 h.<sup>8</sup> The specific systems were composed of the sensitizer (either  $\text{Pt}(\text{dcbpy})(\text{met})$  (met = *cis*-1,2-dicarboxymethoxyethylene-1,2-dithiolate) or  $\text{Pt}(\text{dcbpy})(\text{bdt})$  (bdt = 1,2-benzendithiol) (Scheme 2), TEOA, and platinumized  $\text{TiO}_2$ .

When either of the dithiolate sensitizers is used in a system containing TEOA,  $\text{TiO}_2$ , and the purported Pt(II) molecular catalysts and irradiated with  $>455$  nm light, under which photodecomposition does not occur, no  $\text{H}_2$  is formed. These observations further support the central notion that Pt(II)

**Scheme 2.** Pt(II) Sensitizers Used To Generate  $\text{H}_2$  with  $\lambda > 455$  nm



“molecular” catalysts for light-driven hydrogen generation are essentially precursors to Pt colloids that function as the actual catalysts.

This report therefore serves as a caveat to researchers employing noble metal complexes as  $\text{H}_2$  generating catalysts that in fact photodecomposition of these complexes may be occurring and that the question of catalysis by the resultant colloids needs to be addressed rigorously. A similar message has just been reported involving a Pd complex “catalyst” less robust than the Pt systems reported here.<sup>9</sup> Our study also reveals that surface-bound molecular Pt(II) complexes can function as photochemical precursors to segregated Pt(0) nanomaterials displaying enhanced hydrogen evolving power from  $\text{TiO}_2$  surfaces.

**Acknowledgment.** The UR part of this work was supported by the Department of Energy, Division of Basic Sciences (DE-FG02-90ER14125), and the BGSU work was supported by the National Science Foundation (CHE-0719050), the ACS-PRF (44138-AC3), the Air Force Office of Scientific Research (FA9550-05-1-0276), and the BGSU Research Enhancement Initiative. P.D. gratefully acknowledges an Elon Huntington Hooker Fellowship, and J.S. gratefully acknowledges Weissberger Memorial and GAANN Fellowships from the UR. TEM images and EDAX measurements were carried out in the University of Minnesota Characterization Facility, which is partially supported by NSF through the NNIN program.

**Supporting Information Available:** Experimental details, and additional photocatalytic experiments, TEM images, and EDAX data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (a) Esswein, A. J.; Nocera, D. G. *Chem. Rev.* **2007**, *107*, 4022–4047. (b) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729–15735.
- (a) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, *28*, 141–145. (b) Keller, P.; Moradpour, A.; Amouyal, E.; Kagan, H. B. *Nouv. J. Chim.* **1980**, *4*, 377–384. (c) Kiwi, J.; Grätzel, M. *Nature* **1979**, *281*, 657–658. (d) Lehn, J.-M.; Sauvage, J.-P. *Nouv. J. Chim.* **1977**, *1*, 449–451.
- (a) Elvington, M.; Brown, J.; Arachchige, S. M.; Brewer, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 10644–10645. (b) Rau, S.; Schäfer, B.; Gleich, D.; Anders, E.; Rudolph, M.; Friedrich, M.; Görls, H.; Henry, W.; Vos, J. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 6215–6218.
- (a) Ozawa, H.; Haga, M.-A.; Sakai, K. *J. Am. Chem. Soc.* **2006**, *128*, 4926–4927. (b) Ozawa, H.; Yokoyama, Y.; Haga, M.-a.; Sakai, K. *Dalton Trans.* **2007**, 1197–1206.
- (a) Galinska, A.; Walendziewski, J. *Energy & Fuels* **2005**, *19*, 1143–1147. (b) Liu, H.; Yuan, J.; Shanguan, W. *Energy & Fuels* **2006**, *20*, 2289–2292.
- (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855–859. (b) Baba, R.; Nakabayashi, S.; Fujishima, A.; Honda, K. *J. Phys. Chem.* **1985**, *89*, 1902–1905.
- (a) Du, P.; Schneider, J.; Jarosz, P.; Eisenberg, R. *J. Am. Chem. Soc.* **2006**, *128*, 7726–7727. (b) Du, P.; Schneider, J.; Jarosz, P.; Zhang, J.; Brennessel, W. W.; Eisenberg, R. *J. Phys. Chem. B* **2007**, *111*, 6887–6894.
- Zhang, J.; Du, P.; Schneider, J.; Jarosz, P.; Eisenberg, R. *J. Am. Chem. Soc.* **2007**, *129*, 7726–7729.
- Lei, P.; Hedlund, M.; Lomoth, R.; Rensmo, H.; Johansson, O.; Hammarström, L. *J. Am. Chem. Soc.* **2008**, *130*, 26–27.

JA711090W