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Photoreduction of Water

Energy Transfer in a Hybrid Ir^{III} Carbene–Pt^{II} Acetylide Assembly for Efficient Hydrogen Production

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Abstract: A new heterometallic supramolecular complex, consisting of an iridium carbene-based unit appended to a platinum terpyridine acetylide unit, representing a new Ir^{III}–Pt^{II} structural motif, was designed and developed to act as an active species for photocatalytic hydrogen production. The results also suggested that a light-harvesting process is essential to realize the solar-to-fuel conversion in an artificial system as illustrated in the natural photosynthetic system.

Constructing artificial systems for capture and conversion of solar energy to make energy carriers such as hydrogen is imperative for creating promising opportunities for the future mitigation of energy requirements.[1] Thus far, partial mimicking of the energy- and electron-transfer processes in natural photosynthesis, along with viable photoelectrochemical and photobiological catalytic splitting of water have been developed for such a task.[2] Such catalytic reactions have utilized classical multicomponent systems, incorporating at least a light sensitizer for light harvesting and a proton reduction catalyst for receiving the electrons from the excited molecules and using them to spur hydrogen evolution, in addition to a sacrificial electron donor such as triethylamine (TEA). There have been significant advances in such complex reaction mixtures in the pursuit of outstanding hydrogen production efficiency.[3,4] However, the optimization of the active components remains a major obstacle toward improved catalytic efficiency, mainly because the key parameter is governed by a diffusion-controlled process and critically depends on the efficiency of intermolecular collisions between the species involved.[5]

Indeed, the solar-to-energy conversion in nature is realized through energy and electron transfer in a delicate supramolecular organization. In this respect, of particular interest and inspired by nature, is the use of a highly organized molecular assembly of individual functional components, that is, photosensitizer–catalyst conjugates, for the development of a single-component system capable of performing such process types.[6–15] Such architectures enable efficient collaboration in collecting the light energy and converting it efficiently into stored chemical energy. Great efforts are being directed to the design of simple integrated-photocatalyst molecular assemblies carrying two or more spatially well-defined metal-based components, which demonstrates the feasibility of creating artificial photosynthetic devices. However, these single-component systems are still hampered by relatively low efficiency for hydrogen evolution, and only a few systems have reached a turnover number (TON) on the order of hundreds versus the catalysts, a value that is still far less than that achieved with the multicomponent systems.[16] Therefore, it is highly desirable to seek new active assemblies that allow their implementation into original supramolecular light-harvesting devices with the goal of improving the efficiency of light-to-chemical energy conversion.

In the development of metallosupramolecular assemblies capable of giving rise to fuel production, we were interested in merging the properties of the cyclometalated iridium chromophore with platinum acetylide fragments. Such a platinum species, in which the carbon—platinum bond of the acetylide linkage may lead to effective electronic coupling with the adjacent fragments, was selected for its potential ability to drive photocatalytic hydrogen production.[17,18] In this work, we describe the formation of a new assembly (**1**), constructed from a iridium moiety linked to a platinum(II) acetylide terpyridine complex (Figure 1), and its use in H_2-evolving photocatalysis. A comparison with corresponding model complexes, **2** and **3**, indicates that such a molecular device enables high-efficiency photoreduction of water, via a sacrificial electron donor, into hydrogen. The strong N-heterocyclic carbene donor from the cyclometalating chelate is required to assist in contributing to the high luminescence quantum yield and high stability transition-metal complexes,[19] which may benefit solar fuel production implementation. Such a sensitizer species is expected to be a complement to the traditional phenylpyridine-based iridium complex in sensitizer design and solar-to-energy conversion applications.

Photocatalytic reactions were first conducted in deaerated acetone/water solutions (100 mL) under visible-light irradiation

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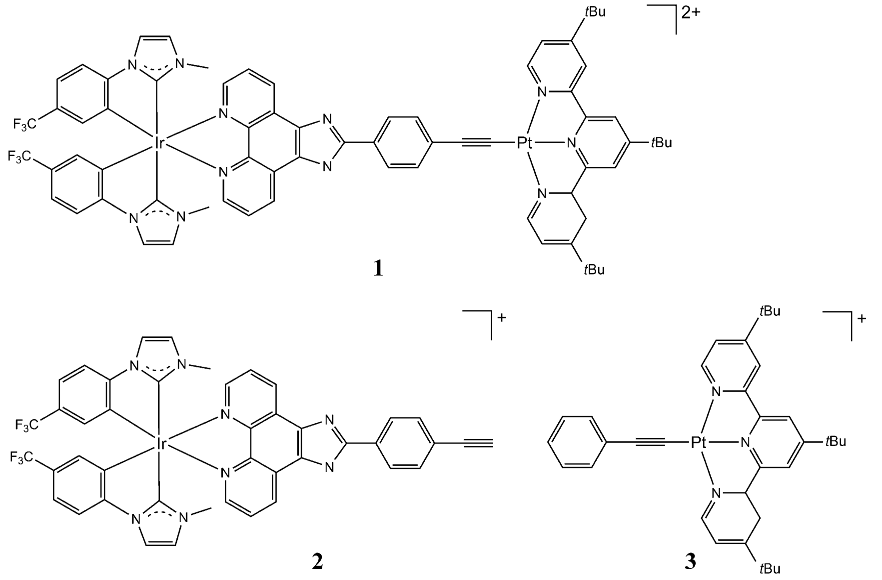

Figure 1. Structures of the complexes in this study (as their PF_6^- salts).

of the system ($\lambda > 420$ nm) with complex **1** as a catalyst at fixed concentration (10 μM) and a sacrificial reducing (SR) agent of TEA at 0.18 M. The ratio of the reaction medium of acetone/water mixture was 9:1 (v/v) based on optimizing experiments where the ratio of acetone/water was varied. Control experiments demonstrated that both the components of **1** and TEA, as well as light, are necessary for the observed hydrogen-evolution photocatalysis.

As shown in Figure S1 a (in the Supporting Information), at pH 9.0 (the natural pH value of the mixed solution containing 0.18 M TEA in the present system), hydrogen production grew continuously and approximately linearly with time for the first 30 h of photolysis (average rate, 19 μmol h^{-1}), and then the reaction rate gradually slows down. When the experiment was stopped after 60 h, the catalytic TON [TONs = n(H)/n(catalyst)] of 1672 hydrogen units versus the catalyst could be achieved on the basis of the final amount of hydrogen generated at this time (836.2 μmol; Table 1, entry 1). In the system promoted by **1**, hydrogen is produced efficiently by photocatalytic water reduction in the presence of an electron donor. As seen, the response of the photocatalytic system is highly pH-dependent between pH 6.0 and pH 9.0, with all other conditions held constant. A maximum catalytic activity was obtained at pH 9.0, which is near the pK_a of TEA, suggesting that the unprotonated TEA is the active reductant. The highest hydrogen-production activity coincides with the pH range at which the system displays its highest electron-transfer ability, as confirmed by the change in intensity of emission of complex **1** in the presence of TEA at different pH levels. Figure S1 b indicates that the quenching of the excited state of **1** by TEA decreases as the pH is decreased beyond the pK_a of TEA. The most efficient quenching takes place between **1** and TEA at pH 9.0, with 95 % quenching. Fluorescence studies revealed that the initial electron-transfer ability can be reduced by lowering the pH of the system. Thus, the protonation state of TEA is important in determining the hydrogen-production performance.

Table 1. Photoinduced hydrogen evolution under various conditions.[a]

Entry	Complex	H_2 [μmol]
1	**1**	836.2
2	**2**+**3**	327.3
3	**3**	18.8
4[b]	**3**	8.2
5[c]	**1**	1308.8
6	**2**	0

[a] Unless specified, the reactions contained 10 μM bimetallic complex (or monometallic complex) and 0.18 M TEA in an acetone/water (9:1, v/v, 100 mL) solution at an initial pH 9.0; irradiation light: $\lambda > 420$ nm; TONs = n(H)/n(catalyst). [b] In an acetonitrile/water (1:1, v/v) solution. [c] Irradiation with Xenon-arc light.

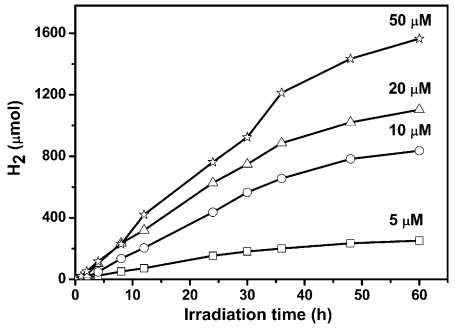

Figure 2. Hydrogen production using varying concentrations of **1** at the original pH of 9.0 ($\lambda > 420$ nm).

Moreover, the concentrations of **1** have a significant and direct impact on the amount of hydrogen produced. As can be clearly seen in Figure 2, the total amount of hydrogen production increased on increasing the concentration of **1** while keeping the TEA concentration constant at 0.18 M, an observation that is directly related to the absorbance of the reaction solution (Figure S2 in the Supporting Information). When the concentration of **1** was increased from 5 μM to 50 μM, the amount of hydrogen produced increased from 251.3 (TON = 1005) to 1565.4 μmol (TON = 626) after 60 h of irradiation, indicating a direct correlation between hydrogen formation and the catalyst concentration. The maximum TON (1672) of the catalytic system under visible-light irradiation is significantly higher than those of other artificial supramolecular catalysts such as Ru–Pd systems, Ir–Co systems and the trimetallic Ru–Rh–Ru systems.[6–14] Figure S3 (see the Supporting Information) shows the quantum efficiency of the hydrogen production by **1** as a function of the incident monochromatic light wavelength in the ranges of 400–550 nm. The maximum efficiency of 1.32% was achieved under irradiation at 450 nm after 10 h of reaction. The curve shows a similar result as the absorption spectrum, that is, clearly indicating that the hydrogen-production reaction is driven by the excited-state of **1**.

To ensure the assembly results in effective hydrogen evolution because of the linked light-harvesting and catalytic components, comparison experiments were performed by employing an equimolar mixed solution consisting of complex **2** as a sensitizer and **3** as a catalyst in place of complex **1** (Table 1, entry 2). Considerable amounts of hydrogen gas were found after 24 h of irradiation, when production plateaued, and no further increases with prolonged catalysis times could be observed. The TON value of this three-component system is 2.6 times lower than the value observed for the combined system under conditions of equivalent component concentrations. According to previous reports, in this system, which has a much larger concentration of TEA (0.18 M) than catalyst (10 μM), reductive quenching is proposed to be dominant over electron transfer. A low but significant hydrogen evolution (2%) was detected when compound **3** was used alone (Table 1, entries 3 and 4), which is in line with previous observations of Pt^{II} terpyridine complexes in photochemical hydrogen formation.[18] The photocatalytic activity of **3** decreased rapidly, and full decolorization was observed by visualizing the color change of the solution after the reaction was complete within 12 h of irradiation; however, no such color change was observed when **1** was used as a photocatalyst. The poor hydrogen-producing capability of **3** indicates that the platinum acetylide chromophore cannot to act as an effective catalytic species for generating hydrogen, as described in the previous report.[20]

The photophysical and electrochemical properties of the complexes **1**–**3** were investigated (Table S1 in the Supporting Information) to supply useful information for understanding the benefits of the introduction of a supramolecular device for solar hydrogen production application. At room temperature in dilute deoxygenated CH_2Cl_2, complex **1** exhibits a single emission band centered at 617 nm upon irradiation (Figure 3), which is assigned as an excited state of predominantly ^{3}MLCT/^{3}LLCT character. This emission maxima of complex **1** was found to be redshifted about 60 nm from that of the Ir-based model compound **2** (i.e., ~556 nm), and is rather similar in energy to the shorter-lived emission obtained from the Pt-based model complex **3** at about 603 nm, which is associated with a $d\pi(Pt)\rightarrow\pi^*(terpy)$ ^{3}MLCT state (terpy = terpyridine).[21] The excitation spectrum recorded for this heterometallic complex at 617 nm corresponds reasonably well to its absorption profile (Figure S4 in the Supporting Information), indicating the photons absorbed by the Ir group are collected by the Pt unit. In addition, by measuring the luminescence intensities of isoabsorptive solutions of **1** and **3**, under identical experimental conditions (Figure S5 in the Supporting Information), twofold enhancement of the emission intensity was seen for the binuclear complex **1** compared with that of **3**. This enhancement was accompanied by quenching of the Ir-based emission of the Ir-based unit in complex **1**, implying that the occurrence of the corresponding sensitization of the Pt–acetylide moieties by the excited Ir moiety is a possible consequence of a downhill intramolecular energy transfer from the Ir moiety to the Pt subunit at the end of the molecule, which is in line with the relative energy levels of their excited states. This is also confirmed by the fact that a rise emission lifetime and an increase in quantum efficiency of **1** relative to that of **3** can be observed.[22] The time-resolved luminescence decays for **1** were recorded as a function of the emission wavelengths. The lifetime decays are wavelength dependent when the monitoring wavelength is changed from 580 nm to 680 nm (Figure S6 in the Supporting Information), indicating of the occurrence of energy migration.

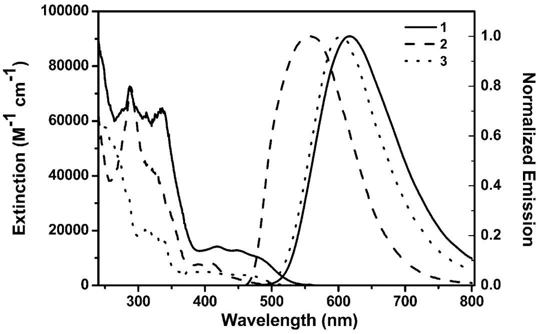

Figure 3. Absorption spectra (left axis) and normalized emission spectra (right axis) of complexes **1**–**3** in CH_2Cl_2 (10 μM) at room temperature.

DFT calculations were performed for complex **1** to ascertain the origins of its electronic properties (Table S2 in the Supporting Information). The highest-occupied molecular orbital (HOMO) involves significant contributions from both the π(tpmi) orbitals/d(Ir) of the terminal Ir units (tpmi = 1-(4-trifluorophenyl)-3-methylimidazolin-2-ylidene), which is similar to that calculated for control compound **2**. HOMO−1 is delocalized across the π system of the epip ligand (epip = 2-(4-ethynylphenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline), with only a minor extension onto the Pt center. The lowest unoccupied molecular orbital (LUMO) is located mainly on the Pt(terpy) fragment, thereby favoring efficient electron transfer to reducible substrates, such as water for photocatalytic hydrogen production, and the LUMO+1 is localized almost exclusively on the terpy moiety. The LUMO level of the bimetallic complex is mainly populated on the Pt moiety rather than that involving the Ir center, which gives it an important role in governing the emissive exited state. The time-dependent DFT calculations indicate that the lowest-lying transition for complex **1** is dominated by HOMO→LOMO excitation. This transition can be viewed as a hybrid between the two metal–ligand subunits,[23] and charge transfer may be considered as occurring partly from the Ir to the Pt moiety with a contribution from the terminal Ir units to the terpy ligand. Owing to a large admixture of tpmi π orbitals into the HOMO, this transition may be mixed with a ligand-to-ligand charge-transfer (LLCT) transition. Therefore, it must be considered that the emission may occur from the excited state partly involving the Ir center, because the emission is rather complicated and not fully understood.[24] This spatial separation of HOMO and LUMO for the complex illustrates the thermodynamic possibility of generating a charge-separated excited state between the terminal Ir and Pt metal center in the complex.[25] In addition, coupling between the metal centers can be enhanced through the HOMO of the bridge because of an efficient mixing of the dπ metal orbitals with filled π orbitals of the bridge.

The ability to photoinduce electron transfer in supramolecular devices has been exploited for solar-energy conversion.[7–15] However, if it is possible to sensitize catalytic sites by means of unidirectional energy transfer powering the intermolecular electron-transfer process, which is a key step in natural photosynthetic reactions,[26] improving features of these assembles for use in photocatalysis may become feasible.[27] Based on the above results, the importance of the supramolecular complex is clear in the formation in hydrogen. We attribute the superior activity of the molecular assembly to the intramolecular energy transfer between the light-harvesting unit and the catalytic center to form Ir–Pt* species. Energy transfer was exploited in the photocatalysis by sensitization of specific catalytic sites through which the water reduction is catalyzed, following the fast intermolecular electron transfer that is generated through the quenching of the excited state of the complex in the presence of TEA. With TEA, the decay time of complex **1** was observed to be 88 ns. The reductive quenching of the ^{3}MLCT excited state of **1** with TEA was monitored with a linear Stern–Volmer plot, which gave a rate constant (k_q) of $6.84\times 10^{10}\,\text{M}^{-1}\,\text{s}^{-1}$. Our investigation demonstrates that energy transfer in the present supramolecular systems is helpful for the light-harvesting process for hydrogen-production reactions, in which the photoharvesting unit transfers the light energy directly to the reaction center and thus increases the efficiency of the system, as in natural light-harvesting complexes.

The detailed mechanistic pathway for hydrogen production is not yet well elucidated for platinum(II) organometallic compounds.[28–30] As in previous related studies, a high yield of the Pt reduced state is required for the photoreduction of the catalyst in the presence of an electron donor, and the subsequent reduction of the protons occurs at the Pt site to achieve the observed hydrogen.[10,31] In the present system, in situ formation of colloidal Pt metal, which act as the actual active sites for the hydrogen reduction, cannot be fully excluded though no distinct metallic particles were observed as precipitates during photocatalysis with complex **1** (even at 50 μM). When the photocatalytic reaction occurred with notable deactivation after 60 h of illumination, UV/Vis spectra were recorded for samples of the reaction mixture (**1** + TEA) in acetone/water (9:1, v/v). We found a single absorption tail extending into the visible region, and the characteristic absorbance attributed to the catalyst decreased dramatically compared with that prior to photolysis (Figure S7 in the Supporting Information), suggesting the decomposition of **1** occurs as hydrogen evolution.

To shed more light on the mechanism of decomposition, the decomposition products were extracted from the mixture and characterized. ESI-MS analysis (Figure S8 in the Supporting Information) of samples of the reaction mixture of **1** that had undergone irradiation for 60 h, showed no peak for complex **1** ($m/z = 1557.50$), whereas the peak of terpy as found at $m/z = 402.58$, which revealed that complex **1** decomposes to unidentified compounds ($m/z = 751.67$, 696.42, and 651.58) and monometallic Ir compounds lacking the Pt unit such as a TEA-coordinated adduct $[\text{Ir(tpmi)}_2\text{(TEA)}]^+$ ($m/z = 744.58$) during the photocatalytic reaction. These results indicated the decomposition of the assembly occurred to release Pt species. To obtain information about the oxidation state of the decomposition species, X-ray photoelectron spectroscopy (XPS) measurements were performed on evaporated samples after photolysis as well as on the isolated powders of **1**. The binding energies (BE) were determined to be 61.49 eV (Ir $4f_{7/2}$), 72.92 eV (Pt $4f_{7/2}$), and 399.85 eV (N 1s) for the original compound (Figure S9 in the Supporting Information). After the photoreduction reaction, much broader and relative lower intensities were observed, and the resulting BE values related to decomposition products were found at 61.26, 72.24, and 398.96 eV for the selected atomic levels, respectively (Figure S10 in the Supporting Information). The energy shift is much lower than the recorded change ($\Delta E = 2.4$ eV) from Pt^{II} to Pt^0.[32] Therefore, these data provide support for the idea that colloidal species do not participate in the catalysis.[31] Quantitative poisoning experiments with carbon disulphide (CS_2) were performed to identify the true catalytically active species in the given photocatalytic reaction. These show that ten equivalents of CS_2 are required inhibit about 90 % of the activity of the catalysis system (Figure 4), indicating that the catalytic reaction seems to be homogeneous.[33] In the future, a further unravelling of the underlying mechanism involved in this complex photocatalytic process should assist in establishing the correlation between structural features and function of this type of complexes.

In this study, we have described the design and preparation of a new supramolecular structural motif for the development of a water reduction photocatalyst. It was constructed with an photosensitizer part, using an iridium(III) carbene-based sensitizer, coupled through a rigid conjugated phenanthroline derived spacer to a catalyst part based on the platinum(II) acety-

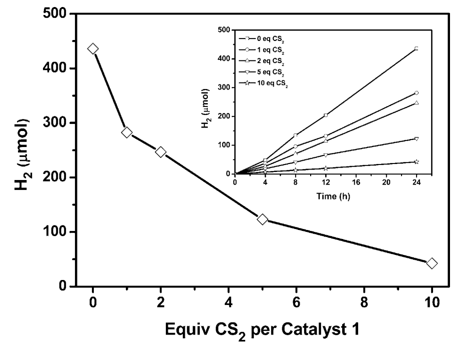

Figure 4. Effect of CS_2 poisoning on the photogeneration of hydrogen in a system of **1** + TEA. Inset: Evaluation of hydrogen production in the presence of various equivalents of CS_2 catalyst poison in a system of **1** + TEA. Reaction conditions: 0.18 M TEA and 10 μM **1** in a 100 mL 9:1 acetone/water solution ($\lambda > 420$ nm).

lide complex. In this assembly the energy-transfer process takes place from the excited iridium center to the energy acceptor, a platinum fragment. The use of supramolecular catalysts not only extends carbene chemistry to photocatalysis but also indicates that the possibility exists to employ molecular-design strategies to build attractive photochemical H_2-evolving systems.

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Keywords: hydrogen · iridium carbene complex · photochemistry · supramolecular chemistry · water reduction

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