

## Efficient photocatalytic CO<sub>2</sub> reduction using [Re(bpy)(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}]<sup>+</sup>

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### Abstract

[Re(bpy)(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}]<sup>+</sup> (**1**<sup>+</sup>) (bpy, 2,2'-bipyridine) is the most efficient homogeneous photocatalyst for the selective reduction of CO<sub>2</sub> to CO reported to date. Both the quantum yield and turnover number of the photocatalytic reaction are strongly dependent on the irradiation light intensity and wavelength because of the unusual stability of the one-electron-reduced species [Re(bpy<sup>•-</sup>)(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}] (**1**).

**Keywords:** Rhenium bipyridine complex; Triethylphosphite; CO<sub>2</sub> reduction; Photocatalyst

### 1. Introduction

It has been known for several years that XRe(bpy)(CO)<sub>3</sub> (X = Cl, Br; bpy, 2,2'-bipyridine) can act as a photocatalyst for the reduction of CO<sub>2</sub> to CO with high chemical specificity [1]. Despite the unique ability of this photocatalytic system to act as both a photosensitizer and a multi-electron redox catalyst, there have been relatively few reports of the photocatalysis of CO<sub>2</sub> reduction involving other rhenium complexes [2,3]. The first step of the photocatalytic reaction is electron transfer from an electron donor to the excited rhenium complex [1,4,5]; however, the nature of the following processes is not yet clear [6,7]. In this study, we report a new effective homogeneous CO<sub>2</sub> reduction photocatalyst [Re(bpy)(CO)<sub>3</sub>{P(OEt)<sub>3</sub>}]<sup>+</sup> (**1**<sup>+</sup>) and its unique photocatalytic behaviour.

### 2. Experimental details

#### 2.1. Preparation of **1**<sup>+</sup>SbF<sub>6</sub>

The preparation of **1**<sup>+</sup>SbF<sub>6</sub> was based on the method for Re(bpy)(CO)<sub>3</sub>PMe<sub>3</sub>]PF<sub>6</sub> [8] with some modifications as follows. [Re(bpy)(CO)<sub>3</sub>(MeCN)]SbF<sub>6</sub> (0.20 g, 0.28 nmol) and P(OEt)<sub>3</sub> (2.46 g, 14.8 mmol) were dissolved in tetrahydrofuran (THF) (40 ml). The solution was heated at

reflux under an Ar atmosphere for 8 h in dim light. After cooling to room temperature, the solution was evaporated to dryness and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O to give **1**<sup>+</sup>SbF<sub>6</sub>. Yield: 85.2%. Elemental analysis for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub>F<sub>6</sub>PREsB: calculated: C, 27.55%; H, 2.80%; N, 3.38%; found: C, 27.38%; H, 2.60%; N, 3.23%. <sup>1</sup>H-NMR (δ, 300 MHz, CDCl<sub>3</sub>): 8.91 (d, *J* = 5.5 Hz, 2H, bpy-6,6'), 8.66 (d, *J* = 8.2 Hz, 2H, bpy-3,3'), 8.31 (dd, *J* = 7.6, 8.2 Hz, 2H, bpy-4,4'), 7.64 (dd, *J* = 5.5, 7.6 Hz, 2H, bpy-5,5'), 3.82 (quintet, *J*<sub>H,P</sub> = 7.0 Hz, 6H, POCH<sub>2</sub>), 1.06 (t, *J* = 7.0 Hz, 9H, CH<sub>3</sub>). <sup>13</sup>C-NMR (δ, 75.5 MHz, CDCl<sub>3</sub>): 193.4, 193.2 (C=O), 156.2, 153.0, 141.0, 127.7, 125.3 (bpy), 62.7 (d, *J*<sub>C,P</sub> = 7.5 Hz, POCH<sub>2</sub>), 15.8 (d, *J*<sub>C,P</sub> = 5.8 Hz, CH<sub>3</sub>). IR (MeCN), ν(CO) (cm<sup>-1</sup>): 2047, 1961, 1928. UV-visible (MeCN), λ<sub>max</sub> (nm) (ε (10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>)): 307 (11.0), 317 (13.5), 351 (sh, 3.06).

#### 2.2. Photocatalysis measurements

A high pressure Hg lamp (500 W) with a monochromator was used to produce the 365 nm light. The incident light intensity was determined by a K<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> actinometer. In a typical photochemical run, a solution (4 ml, *N,N*-dimethylformamide-triethanolamine (DMF-TEOA), 5:1 v/v) containing the catalyst was placed into a quartz cell (volume, 8 ml) fitted with a rubber septum. The solution was saturated with CO<sub>2</sub> and then irradiated with stirring. In all runs, the stirring speed was kept constant. After irradiation, the gas in the cell was analysed by gas chromatography. In situ

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Table 1  
Photosensitized reduction of CO<sub>2</sub> by the Re complexes

Complex	Concentration (mM)	Wavelength (nm)	Light intensity (10 <sup>-7</sup> einstein min <sup>-1</sup> )	CO formation rate (10 <sup>-8</sup> mol min <sup>-1</sup> )	Φ <sub>CO</sub> <sup>a</sup>	TN <sup>b</sup>
1 <sup>+</sup> SbF <sub>6</sub>	2.63	365	1.06	4.00	0.38	–
1 <sup>+</sup> SbF <sub>6</sub>	2.63	365	3.99	10.18	0.26	–
1 <sup>+</sup> SbF <sub>6</sub>	2.63	365	7.63	12.56	0.17	–
1 <sup>+</sup> SbF <sub>6</sub>	2.63	365	15.19	17.34	0.11	–
ClRe(bpy)(CO) <sub>3</sub> <sup>c</sup>	2.63	365	2.04	3.33	0.16	–
1 <sup>+</sup> SbF <sub>6</sub>	0.51	365	2.04	–	–	7.5
1 <sup>+</sup> SbF <sub>6</sub>	0.51	365 + > 400 <sup>d</sup>	2.04 <sup>e</sup>	–	–	5.8
1 <sup>+</sup> SbF <sub>6</sub>	0.51	365 + > 500 <sup>d</sup>	2.04 <sup>e</sup>	–	–	7.5
1 <sup>+</sup> SbF <sub>6</sub>	0.51	> 330	–	–	–	1.7

<sup>a</sup> The quantum yield of CO formation was calculated by the following equation: (CO formation rate)/(light intensity).

<sup>b</sup> Turnover numbers of CO formation for the Re complex used were measured after 16 h irradiation.

<sup>c</sup> Et<sub>4</sub>NCl (20-fold excess) was added to the solution.

<sup>d</sup> A filtered Xe lamp was used for irradiation, in addition to 365 nm light. No difference in the intensity of 365 nm light between 365 + > 400 and 365 + > 500 nm irradiation is present.

<sup>e</sup> The intensity of the 365 nm emission band.

UV–visible spectra were measured by a Photal MCPD-1000 spectrophotometer connected to the photochemical cell through optical fibres.

### 2.3. Flash photolysis

A Continuum YG680-10 Nd<sup>3+</sup> YAG pulse laser was used as excitation light source. An MeCN solution containing 1<sup>+</sup>SbF<sub>6</sub> in a 1 cm quartz cell was irradiated by the laser light (355 nm, 10 ns FWHM, 100 mJ per pulse). The emission was monitored by an R926 photomultiplier tube (Hamamatsu Photonics) on a Jobin-Yvon HR-320 monochromator. Time profiles of the emission decays were stored with an SCD 1000 digitizer (1 GHz bandwidth).

### 2.4. Electrochemical measurements: preparation of the reduced species 1

A BAS 100B electrochemical analyser and a Ag/AgNO<sub>3</sub> (0.1 M) reference electrode were used. A flow electrolytic method [3] was used to measure the UV–visible and IR absorption spectra of the reduced species 1. The working electrode was contained in a porous glass tube (inside diameter, 1 mm; outside diameter, 2 mm; length, 30 mm) and consisted of many strands of 0.1 mm diameter Pt wire. An MeCN solution containing 1<sup>+</sup>SbF<sub>6</sub> (0.5 mM) and (*n*-Bu)<sub>4</sub>NClO<sub>4</sub> (0.1 M) as electrolyte was purged with Ar for 20 min, and then passed into a flow-through cell at a flow rate of 0.3 ml min<sup>-1</sup>. Just after electrolysis, the solution was transferred to a cell for the spectral measurements. UV–visible of 1: λ<sub>max</sub> (nm) (ε (10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>)) 390 (5.88), 475 (2.09), 506 (3.33). IR of 1: ν(CO) (cm<sup>-1</sup>) 2022, 1928, 1898.

## 3. Results and discussion

Irradiation of a TEOA–DMF solution containing 1<sup>+</sup>SbF<sub>6</sub> at 365 nm under a CO<sub>2</sub> atmosphere produces CO catalytically,

accompanied by the formation of a small amount of H<sub>2</sub>. Table 1 summarizes the results, together with those obtained using ClRe(bpy)(CO)<sub>3</sub> as the photocatalyst. Although the product distributions of 1<sup>+</sup>- and ClRe(bpy)(CO)<sub>3</sub>-photocatalysed reactions are similar, the photocatalytic behaviour of 1<sup>+</sup>, which is strongly dependent on the intensity and wavelength of the light used, is very different from that of ClRe(bpy)(CO)<sub>3</sub>. In the case of 1<sup>+</sup>, a lower intensity light favours a higher apparent quantum yield of CO formation as shown in Fig. 1; indeed, the quantum yield recorded with an intensity of 1.06 × 10<sup>-7</sup> einstein min<sup>-1</sup> is 0.38, which is the highest reported value for homogeneous photocatalytic systems. Furthermore, the absolute quantum yield at “zero” light intensity is estimated by extrapolation to be 0.44. On the other hand, the quantum yields of CO formation using ClRe(bpy)(CO)<sub>3</sub> reported by Hawecker et al. [1] and measured by us are almost the same even though the wavelength and light intensity used by the two groups are different (in Ref. [1], Φ<sub>CO</sub> = 0.14, wavelength = 385 ± 20 nm, light intensity = 5.77 × 10<sup>-5</sup> einstein s<sup>-1</sup> cm<sup>-2</sup>).

The turnover number (TN) of 1<sup>+</sup> (CO formed/1<sup>+</sup> used) is strongly dependent on the irradiation wavelength; in the case of 365 nm light, TN is about 7.5 after 16 h irradiation, but when a high pressure Hg lamp with a λ < 330 nm cut-off filter is used as the light source, CO formation levels off after only 5 h irradiation and TN is only 1.7.

In common with other rhenium(I) bipyridyl complexes, 1<sup>+</sup> shows emission (λ<sub>max</sub> = 521 nm, τ = 0.92 μs). Fig. 2(a) shows a transient UV–visible absorption spectrum of the excited state of 1<sup>+</sup>, which is very similar to the triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT) states of ClRe(bpy)(CO)<sub>3</sub> [4,5] and [Re(bpy)(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}<sub>2</sub>]<sup>+</sup> [3]. These results strongly suggest that the lowest excited state of 1<sup>+</sup> is also <sup>3</sup>MLCT. The <sup>3</sup>MLCT state of 1<sup>+</sup> is quenched by TEOA with a rate constant of 8 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> to give a new species with a different absorption spectrum as shown in Fig. 2(b). This species can be readily identified as the one-

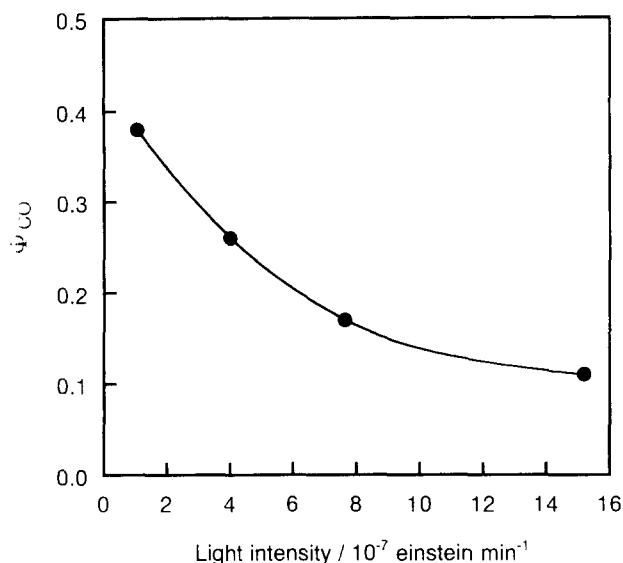


Fig. 1. Light intensity dependence of the quantum yield of CO formation ( $\Phi_{\text{CO}}$ ) using  $1^+$  (irradiated with 365 nm monochromatic light).

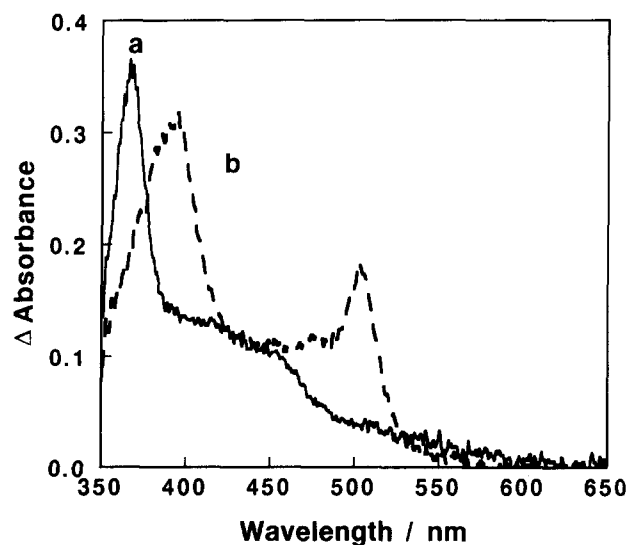
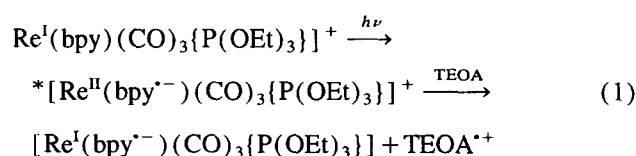


Fig. 2. Difference UV-visible transient absorption spectra of an MeCN solution of  $1^+$  (0.15 mM) under an Ar atmosphere: (a) recorded 20 ns after the laser flash (355 nm) in the absence of TEOA; (b) recorded 100 ns after the laser flash in the presence of TEOA (0.32 M).

electron-reduced complex  $[\text{Re}(\text{bpy}^{\cdot-})(\text{CO})_3\{\text{P}(\text{OEt})_3\}]$  (**1**) because of the similarity of the absorption spectrum to that of **1** produced by the flow electrolysis technique (Fig. 3). Therefore the first step in the photocatalytic reaction must be electron transfer from TEOA to the <sup>3</sup>MLCT state of  $1^+$ , as in the case of  $\text{ClRe}(\text{bpy})(\text{CO})_3$  [4,5]



However, the properties of **1** and  $[\text{ClRe}^{\text{I}}(\text{bpy}^{\cdot-})(\text{CO})_3]^-$ , produced by the photochemical reduction of

$\text{ClRe}(\text{bpy})(\text{CO})_3$  with TEOA, are very different. Compound **1** is much more stable than  $[\text{ClRe}^{\text{I}}(\text{bpy}^{\cdot-})(\text{CO})_3]^-$ , and can be accumulated in the solution by steady state irradiation using a high pressure Hg lamp even under a  $\text{CO}_2$  atmosphere (Fig. 4). The half-life ( $\tau_{1/2}$ ) for the decay of **1** after irradiation is 514 s in degassed solution and 257 s under  $\text{CO}_2$ . On the other hand,  $[\text{ClRe}^{\text{I}}(\text{bpy}^{\cdot-})(\text{CO})_3]^-$  is relatively unstable even in a degassed DMF solution, with  $\tau_{1/2} = 6$  s and 10 s in the absence and presence of excess  $\text{Cl}^-$  ions respectively. Surprisingly, the yield of **1** reaches 20%–100% after only a short irradiation time, depending on both the initial concentration of  $1^+$  used and the light intensity. One of the reasons why the apparent quantum yield of CO formation is strongly dependent on the light intensity must be the ‘‘inner filter effect’’ of **1**, i.e. the light is not absorbed only by  $1^+$  but also by **1** which is accumulated in the solution. However, the inner filter effect alone cannot explain the characteristic photocatalytic behaviour of  $1^+$  described below.

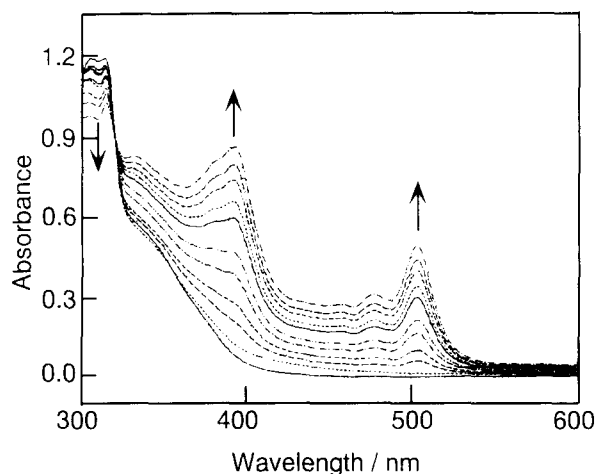


Fig. 3. UV-visible absorption spectral changes on reduction of  $1^+$  in MeCN (0.5 mM) under an Ar atmosphere by the flow electrolysis technique. The arrows indicate the changes as the solution is reduced from 0 to  $-2.7$  V vs.  $\text{Ag}/\text{AgNO}_3$ .

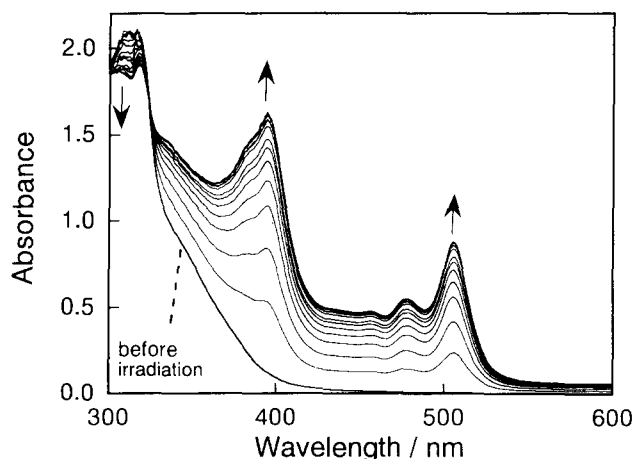


Fig. 4. UV-visible absorption spectral changes of a TEOA-DMF (1:5, v/v) solution containing  $1^+$  (0.25 mM) under a  $\text{CO}_2$  atmosphere during irradiation with a Hg lamp (365 nm), recorded at intervals of 20 s.

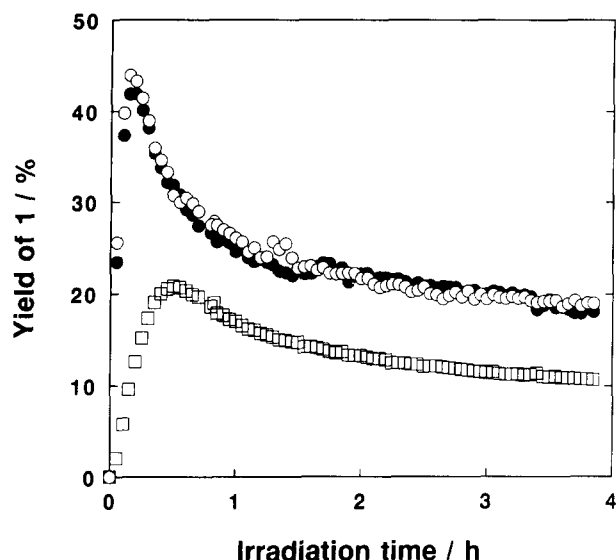


Fig. 5. Time conversion curves of **1** during the photocatalysed reduction of CO<sub>2</sub> at light intensities of  $1.06 \times 10^{-7}$  (□),  $3.99 \times 10^{-7}$  (●) and  $7.63 \times 10^{-7}$  (○) einstein min<sup>-1</sup> (irradiated with 365 nm monochromatic light). The initial concentration of **1**<sup>+</sup> was 2.63 mM. The concentration of **1** was measured using  $\epsilon(\mathbf{1}) = 950$  at 523 nm. To avoid the influence of monitoring light on CO formation, light below 500 nm was cut off during the measurements.

Compound **1** reacts slowly with CO<sub>2</sub> with a pseudo-first-order rate constant of  $1.22 \times 10^{-3} \text{ s}^{-1}$  under a CO<sub>2</sub> atmosphere; however, this dark reaction does not give any CO directly. Further irradiation causes a decrease in **1** until its concentration remains stable after 1–2 h as shown in Fig. 5. The CO formation in the photocatalytic reaction has an induction period of 1–2 h and is then produced linearly. These results strongly suggest that a thermal or photochemical reaction of **1** produces another reaction intermediate which gives CO.

The yields of **1** between irradiation times of 1 and 4 h are almost the same for light intensities of  $7.63 \times 10^{-7}$  and  $3.99 \times 10^{-7}$  einstein min<sup>-1</sup> (Fig. 5); however, the higher light intensity increases the rate of CO formation (Table 1, rows 2 and 3). Therefore CO formation may require the

absorption of another photon by either **1** or the intermediate produced from **1**, in addition to the initial excitation of **1**<sup>+</sup>.

Because **1** shows strong absorption at 400–540 nm where **1**<sup>+</sup> exhibits little or no absorption, **1** produced photochemically can be selectively excited using light wavelengths greater than 400 nm in addition to 365 nm. Experiments using two different light wavelengths showed that although light above 500 nm does not affect the photocatalytic CO<sub>2</sub> reduction (Table 1, row 8), irradiation above 400 nm (using an Xe lamp with a cut-off filter) causes TN to decrease by approximately 23% (Table 1, row 7). These results and the wavelength dependence of CO formation described above suggest that the photochemical reactivity of **1** is dependent on the light wavelength, and additional photoexcitation of **1** or the unknown intermediate at wavelengths shorter than 400 nm may be necessary for CO formation.

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