# **Inorganic Chemistry**

# Facile One-Pot Synthesis of Ruthenium(II) Quaterpyridine-Based Photosensitizers for Photocatalyzed Hydrogen Production

Elodie Rousset,<sup>†,‡</sup> Ilaria Ciofini,<sup>§</sup> Valérie Marvaud,<sup>\*,‡</sup> and Garry S. Hanan<sup>\*,†</sup>

<sup>†</sup>Département de Chimie, Université de Montréal, 2900 Edouard-Montpetit, Montréal, Québec H3T-1J4, Canada <sup>‡</sup>IPCM-CNRS-8232, UPMC-Univ Paris 6, cc 42, 4 place Jussieu, 75252 Paris Cedex 05, France <sup>§</sup>Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris, F-75005 Paris, France

S Supporting Information

**ABSTRACT:** We present here the efficient microwaveassisted synthesis and photophysical study of a family of ruthenium(II) complexes of the general formula [Ru-(bpy)<sub>x</sub>(qpy)<sub>3-x</sub>]<sup>2+</sup> (where bpy = 2,2'-bipyridine, qpy = 4,4':2',2":4",4"'-quaterpyridine, and x = 0, 1, 2 giving compounds  $\mathbf{1} = [\text{Ru}(\text{bpy})_2(\text{qpy})_1]^{2+}$ ,  $\mathbf{2} = [\text{Ru}(\text{bpy})_1(\text{qpy})_2]^{2+}$ , and  $\mathbf{3} = [\text{Ru}(\text{qpy})_3]^{2+}$ ). Compared to the standard reference,  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $\tau = 870$  ns,  $\Phi = 9.5\%$ ), the complexes display longer-lived excited state lifetimes at room temperature ( $\tau$ :  $\mathbf{1} =$ 1440 ns,  $\mathbf{2} = 1640$  ns,  $\mathbf{3} = 1780$  ns) and improved quantum yields ( $\Phi$ :  $\mathbf{1} = 14\%$ ,  $\mathbf{2} = 19\%$ ,  $\mathbf{3} = 23\%$ ). Theoretical calculations were performed to support the interpretation of these photophysical properties. These complexes are excellent



photosensitizers as they absorb light throughout the visible spectrum, have excellent excited state lifetimes at room temperature, and have high quantum yields. In combination with a cobalt dimethylglyoxime catalyst, they exhibit remarkable hydrogen evolution with blue light, and they are far more efficient than the reference in the field,  $[Ru(bpy)_3]^{2+}$ .

# INTRODUCTION

The rise in atmospheric  $CO_2$  concentrations has generated a surge in the search for non-carbon based energy sources.<sup>1</sup> In particular, research focusing on the production, storage, and efficient use of energy has attracted much interest. The scientific community has also considered many *green* approaches, which use abundant resources such as wind, water, and sunlight as a source of energy.<sup>2</sup> One approach to the energy problem that is currently in use is nuclear power; however, this energy source is nonrenewable and nuclear waste poses an environmental risk.<sup>2</sup>

Photovoltaics have risen to prominence in order to face the increasing demand for electricity while trying to abandon nuclear power and fossil fuel sources. The most extensively studied generation of devices include organic photovoltaic cells (OPV),<sup>3</sup> using organic semiconductors for conversion, and dyesensitized solar cells (DSSC),<sup>4</sup> which use metal complexes with a large absorption in the visible and near-infrared (NIR) spectral regions. The most well-known inorganic dye remains the *black dye*,<sup>5</sup> a [Ru(4,4',4''-(COOH)<sub>3</sub>-tpy)(SCN)<sub>3</sub>] complex (tpy = 2,2':6',2''-terpyridine) and the global standard that inspires the field of artificial photosynthesis.

Following this idea, sunlight and water can also be combined into solar-driven water splitting devices<sup>6</sup> to produce  $O_2$  and  $H_2$ , the latter considered as a possible new fuel.<sup>7</sup> These systems open the field of artificial photosynthesis as they mimic nature's capacity to store energy in chemical bonds. For that purpose, many metallic complexes have been studied as photosensitizers and catalysts, from heterogeneous systems, grafting active entities on a solid surfaces,<sup>8</sup> to homogeneous systems using molecular compounds in solution.<sup>9</sup>

In systems containing metallic ions, the formation of colloidal metal might be induced under irradiation<sup>10</sup> and known as an active catalyst for hydrogen evolution with, for instance, platinum.<sup>11</sup> However, as homogeneous catalysis is closest to nature's photosynthetic processes using metalloenzymes, this molecular approach is developed in the present paper.

One design of hydrogen evolution reaction (HER) catalysts harvests sunlight by coupling subunits absorbing at different wavelengths of light, which are then capable of vectorial energy transfer to the lowest energy excited state.<sup>12</sup> The best way to couple the chromophores is to build supramolecular architectures of diverse complexity<sup>13</sup> from linear arrays<sup>14</sup> to radial metallo dendrimers,<sup>15</sup> using so-called "complex-as-metal" and "complex-as-ligand" strategies. This antenna unit redirects the energy to a main chromophore, also called a primary photosensitizer (PS), which acts as a bridge with the catalytic unit of the system.

The PSs (usually Ru,<sup>16</sup> Ir,<sup>17</sup> Pt,<sup>18</sup> or Re<sup>19</sup>) are studied in the literature as the center part of a triad, coupled with an electron

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donating subunit (usually a water oxidation catalyst as Mn,<sup>20</sup>  $\operatorname{Ru}_{2}^{21}$  or  $\operatorname{Ir}^{22}$  and an electron accepting subunit (usually a water reduction catalyst as  $Pd^{23}$  or  $Co^{24}$ ). The PS should present a large extinction coefficient over a broad spectral range to absorb available sunlight, as well as stable reduced and oxidized states and photostability coupled with a high quantum yield and a sufficiently long excited state lifetime for photoinduced electron transfer to occur.<sup>25</sup> These points maximize the possibility of multielectron transfers between the subunits, generating H<sub>2</sub> and O<sub>2</sub> from water reduction and oxidation respectively, under sunlight irradiation. A powerful complete system is not reported yet as both redox processes are not equally efficient, pushing researchers to focus on the "half" reactions, in which the production of  $H_2$  or  $O_2$  are studied separately with a sacrificial donor or acceptor, for instance, triethanolamine or sodium persulfate, respectively. The efficiency of the whole system depends on the activity of the different photosensitizers and catalysts and precisely in the particular design of those subunits. Therefore, the conception of a strategy allowing researchers to rapidly synthesize a variety of PS seems to be of prime interest. Such a technique would tend to avoid multistep syntheses and ease the study of a large number of different complexes.

Therefore, we report herein a series of homogeneous Ru and Co containing systems using ruthenium photosensitizers based on the 4,4':2',2'':4'',4'''-quaterpyridine (qpy) ligand (Figure 1),



Figure 1. Generic representation of the targeted complexes 1-3.

compared to the reference in the field bearing 2,2'-bipyridine (bpy) ligands,  $[Ru(bpy)_3]^{2+}$ . To allow the fast screening of different photosensitizers, a new methodology toward the efficient synthesis of many chromophores using microwave irradiation will be presented. The design of the qpy ligand follows the perspective of grafting other chromophoric or catalytic units at the periphery since the complexes might be used as the dendritic core in supramolecular assemblies.

# EXPERIMENTAL SECTION

Instrumentation details are available in Supporting Information (Section S.I.-1).

**Synthesis.** 4,4':2',2":4",4"'-Quaterpyridine (qpy),<sup>26</sup> [Ru-(DMSO)<sub>4</sub>Cl<sub>2</sub>],<sup>27</sup> *cis*-[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>],<sup>28</sup> and [Ru(qpy)<sub>3</sub>](PF<sub>6</sub>),<sup>26</sup> were synthesized as previously reported. All other chemicals were purchased from commercial suppliers and used without further purification. [Ru(bpy)<sub>2</sub>(qpy)](PF<sub>6</sub>), was prepared in a modified literature procedure.<sup>20</sup>

 $[Ru(bpy)_2(qpy)](PF_6)_2$ .  $[Ru(bpy)_2Cl_2]$  (30 mg, 0.06 mmol) and 4,4':2',2":4",4"'-quaterpyridine (19.0 mg, 0.06 mmol) were dissolved in ethylene glycol (7 mL). The resulting suspension was heated at 240 °C for 10 min using microwave irradiation ( $P_{\text{max}}$  = 400 W). The mixture was cooled to room temperature and water was added followed by a saturated aqueous solution of potassium hexafluorophosphate. The resulting red precipitate was filtered on Celite and washed with water  $(2 \times 10 \text{ mL})$  and diethyl ether  $(2 \times 10 \text{ mL})$ . The residue was dissolved in acetonitrile and concentrated under a vacuum. Further purification was achieved by chromatography on silica gel using MeCN/H<sub>2</sub>O/KNO<sub>3(sat.)</sub> (7:2:1, v/v) as the eluent. The fractions of the second band containing the desired product were combined. After evaporation of the acetonitrile, water was added followed by a saturated aqueous solution of potassium hexafluorophosphate, resulting in a red precipitate, which was filtered over Celite and washed with water  $(2 \times 10 \text{ mL})$  and diethyl ether  $(2 \times 10 \text{ mL})$ . The resulting product was dissolved in acetonitrile, concentrated under a vacuum, and precipitated with diethyl ether to afford a red powder (45 mg, 75%). Characterizations were found as previously described.<sup>30</sup> <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  = 8.96 (d, J = 2 Hz, 2H), 8.81 (d, J = 6 Hz, 4H), 8.53 (d, J = 8 Hz, 4H), 8.08 (tdd, J = 8, 4, 1.5 Hz, 4H), 7.84 (m, 8H), 7.76 (d, J = 6 Hz, 2H), 7.72 (dd, J = 6, 2 Hz, 2H), 7.43 (m, 4H). IR (KBr pellets, cm<sup>-1</sup>): 1598, 1533, 1466, 1446, 1404, 1384, 839, 558

One-Pot Synthesis of the Complete Series [Ru- $(bpy)_{3-x}(qpy)_{x}](PF_{6})_{2}$  - General Procedure.  $[Ru(DMSO)_{4}Cl_{2}]_{2}$ 2,2'-bipyridine (bpy) and 4,4':2',2":4",4"'-quaterpyridine (qpy) were dissolved in ethylene glycol ( $C_{[Ru]} \approx 6 \mod L^{-1}$ ). The resulting suspension was heated at 240 °C for 1 h using microwave irradiation  $(P_{\text{max}} = 400 \text{ W})$ . The mixture was cooled to room temperature and water was added followed by a saturated aqueous solution of potassium hexafluorophosphate. The resulting red precipitate was filtered on Celite and washed with water  $(2 \times 10 \text{ mL})$  and diethyl ether  $(2 \times 10 \text{ mL})$ . The residue was dissolved in acetonitrile and concentrated under a vacuum. Separation of the four species was achieved by chromatography on silica gel using MeCN/H<sub>2</sub>O/KNO<sub>3</sub> (sat.) (7:2:1, v/v) as the eluent. The complexes were eluted in the following order:  $[Ru(bpy)_3]^{2+}$ ,  $[Ru(bpy)_2(qpy)]^{2+}$ ,  $[Ru(bpy)_2(qpy)_2]^{2+}$ , and finally  $[Ru(qpy)_3]^{2+}$ . Each band was treated as follows: after evaporation of the acetonitrile, water was added followed by a saturated aqueous solution of potassium hexafluorophosphate yielding a precipitate, which was isolated by filtration on Celite and washed with water  $(2 \times 10 \text{ mL})$  and diethyl ether  $(2 \times 10 \text{ mL})$ . The resulting product was dissolved in acetonitrile, concentrated under a vacuum, and precipitated with diethyl ether to afford a red powder (orange for  $[Ru(bpy)_3]^{2+}$ .<sup>31</sup>

 $[Ru(bpy)_2(qpy)](PF_6)_2$ . Yield (bpy/qpy ratio): 35% (2:1), 36% (1.5:1.5), 23% (1:2), characterizations were found as previously described.<sup>30</sup>

[*Ru(bpy)(qpy)*<sub>2</sub>](*PF*<sub>6</sub>)<sub>2</sub>. Yield (bpy/qpy ratio): 25% (2:1), 32% (1.5:1.5), 38% (1:2). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  = 8.98 (s, 4H), 8.56 (d, *J* = 8 Hz, 2H), 8.11 (td, *J* = 8, 1.5 Hz, 2H), 8.03–7.92 (m, 8H), 7.91–7.82 (m, 12H), 7.75 (td, *J* = 6, 2 Hz, 4H), 7.47 (t, *J* = 6 Hz, 2H), 7.18–7.14 (m, 2H). IR (KBr pellets, cm<sup>-1</sup>):1595, 1533, 1471, 1404, 831, 555. HRMS (ESI-TOF) *m/z*: [M – 2PF<sub>6</sub>]<sup>2+</sup> Calcd for C<sub>50</sub>H<sub>36</sub>N<sub>10</sub>Ru 439.1085; found 439.1092.

 $[Ru(qpy)_3](PF_6)_2$ . Yield (bpy/qpy ratio): 7% (2:1), 17% (1.5:1.5), 32% (1:2), Characterizations were found as previously described.<sup>26</sup>

# DISCUSSION

**Synthesis and NMR Characterization.** The efficient preparation of heteroleptic ruthenium complexes of bpy remains difficult and the classic way to obtain such ruthenium-(II) complexes is via the stepwise synthesis of a  $[Ru(L_1)_2Cl_2]$  complex followed by the addition of the ligand  $L_2$ .<sup>32</sup> Furthermore, through the use of precursor ruthenium carbonyl complexes,  $[Ru(L_1)(L_2)(L_3)]Cl_2$  complexes with three different ligands can also be obtained.<sup>33</sup>

Scheme 1. Synthetic Pathway Towards the Ruthenium(II) Complexes Reported Herein



Figure 2. Zone of interest of the <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN, 400 MHz) of the  $[Ru(bpy)_x(qpy)_y]^{2+}$  mixture:  $[Ru(bpy)_3]^{2+}$  (0) in gray,  $[Ru(bpy)_2(qpy)]^{2+}$  (1) in green,  $[Ru(bpy)(qpy)_2]^{2+}$  (2) in blue  $[Ru(qpy)_3]^{2+}$  (3) in red.

We observed from a previous study on the homoleptic  $[\text{Ru}(\text{qpy})_3]^{2+}$  complex<sup>26</sup> that the yield of the reaction, which afforded the discrete species, is decreased by the formation of oligomers through the peripheral pyridine nitrogen atoms. In fact, the formation of those oligomers can be observed following purification of the reaction mixture by size exclusion chromatography. In order to exclusively obtain the discrete species, microwave irradiation was used to allow an increased temperature and decreased reaction time compared to regular thermal methods. This process favors the formation of the bidentate bonds by a basic chelate effect versus the single bond through the peripheral pyridine nitrogen atoms. Hence, for the homoleptic complex,  $[\text{Ru}(\text{qpy})_3]^{2+}$ , the synthesis time was

reduced from hours to 15 min using microwave irradiation at 240  $^\circ\text{C}.$ 

We can follow the first mentioned procedure to rationally obtain  $[Ru(bpy)_2(qpy)]^{2+}$  from *cis*- $[Ru(bpy)_2Cl_2]$  upon the addition of the qpy ligand as reported in the literature.<sup>29</sup> In the present paper, the procedure used for the synthesis of the homoleptic complex has been applied to the heteroleptic  $[Ru(bpy)_2(qpy)]^{2+}$  complex, affording the compound after 10 min of microwave irradiation at 240 °C.

In order to simplify the entire process, a one-pot synthesis of the whole family of complexes,  $[Ru(bpy)_3]^{2+}$  (0),  $[Ru(bpy)_2(qpy)]^{2+}$  (1),  $[Ru(bpy)(qpy)_2]^{2+}$  (2), and  $[Ru(qpy)_3]^{2+}$  (3), as their racemic mixtures, has been tested under microwave

irradiation at 240  $^{\circ}$ C (Scheme 1). The classic ruthenium synthesis usually does not use this approach due to the difficulty in purification of the generated species. However, in the case of the qpy ruthenium(II) complexes, the peripheral pyridine nitrogen atoms are available to interact with a silica gel chromatographic support, giving a differential retention for each complex under chromatographic separation.

By varying the ratio of qpy to bpy, one can modulate the proportion of each ruthenium(II) complex that is formed in the reaction. One equivalent of bpy and two of qpy favor the qpy-containing species  $[Ru(bpy)(qpy)_2]^{2+}$  (38% yield) and  $[Ru-(qpy)_3]^{2+}$  (32% yield) in a statistical way (see Table S.I.-1 for details). On the contrary, two equivalents of bpy and one of qpy favor the bpy-containing species  $[Ru(bpy)_2(qpy)_2]^{2+}$  (35% yield) and  $[Ru(bpy)_3]^{2+}$  (32% yield).

A <sup>1</sup>H NMR study of the crude mixture was used to determine the proportion of each ruthenium(II) species by monitoring the integration of the signals at 9.01 ppm (attributed to six protons of [Ru(qpy)<sub>3</sub>]<sup>2+</sup>), 8.98 ppm (four protons of  $[Ru(bpy)(qpy)_2]^{2+}$ , 8.95 ppm (two protons of  $[Ru(bpy)(qpy)_2]^{2+}$ , and the multiplet between 8.57 and 8.48 ppm presenting three doublets corresponding to two protons of  $[Ru(bpy)(qpy)_2]^{2+}$ , four of  $[Ru(bpy)_2(qpy)]^{2+}$ , and six of  $[Ru(bpy)_3]^{2+}$  (Figure 2). As the peaks in the last multiplet are overlapped, the total integration was considered equal to 12 protons. The information about [Ru(bpy)<sub>3</sub>]<sup>2+</sup> can be extracted after the subtraction of the value of the two other complexes given at 8.98 and 8.95 ppm. In a 1:1:1:1 ratio, the theoretical integration of the peaks should be 6:4:2:12. Transposing that ratio to the experimental values gives access to the experimental ratio of the reaction. The overall yield in terms of ruthenium-(II) is in all cases quantitative. The pendant pyridine nitrogen atoms, once a problem for the synthesis of qpy complexes of ruthenium(II), are now the cornerstone for the rapid synthesis of families of complexes containing a bidentate ligand and qpy.

**X-ray Structure.** The X-ray crystal structure of  $[Ru(bpy)-(qpy)_2]^{2+}$  is reported herein, while the rest of the series have been reported previously by us and others.<sup>26,29,34</sup> For  $[Ru(bpy)(qpy)_2]^{2+}$  (2), suitable crystals for X-ray diffraction were grown by slow diffusion of diethyl ether into a saturated acetonitrile solution of the compound. The crystal structure is presented in Figure 3. This particular compound crystallizes in a centrosymmetric  $P\overline{1}$  triclinic space group where the asymmetric unit contains one enantiomer of the complex, two hexafluorophosphate molecules, acting as counteranions, as well as five acetonitrile solvent molecules. The other enantiomer is generated by an inversion center in order to complete the racemic mixture at the unit cell level. Intermolecular peripheral pyridines interact with each other through  $\pi$ -stacking (Section S.I.-2).

The crystallographic structure of  $[Ru(bpy)(qpy)_2]^{2+}$  can be compared to the optimized geometry at the DFT level in solution, and characteristic distances and angles across the series are compared in Table S.I.-6.

Both crystallographic structures (Figure 3) and DFT optimized geometries of the complexes show distorted octahedral coordination polyhedra with angles formed by ligands and metallic centers at  $\sim$ 79° instead of 90° in a perfect Oh geometry. The interpyridyl distances conserve the conjugation over all the bpy and qpy ligands. The 2,2′-bipyridine sites present a certain planarity (dihedral angle of 2°), while the 4-pyridyl substituent show twist angles of about 30° as classically found in bpy-based ruthenium complexes.



**Figure 3.** ORTEP representation of the  $[Ru(bpy)_2(qpy)]^{2+}$  (1),<sup>34</sup>  $[Ru(bpy)(qpy)_2]^{2+}$  (2) (this work), and  $[Ru(qpy)_3]^{2+}$  (3) complexes.<sup>26</sup> Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms, counterions, and cocrystallized solvent molecules have been omitted for clarity. Ru in red, carbon in black, and nitrogen in blue.

Consequently, the replacement of the *para* hydrogen of the 2,2'-bipyridine ligands by a 4-pyridyl substituent does not affect the global geometry of the molecule when compared to  $[\text{Ru}(\text{bpy})_3]^{2+}$ . The intrinsic properties of the complexes presented here are thus attributed to the extended  $\pi$ -system and not from a change of geometry.

**Electrochemical Analysis.** The electrochemical properties of the complexes were investigated in acetonitrile, using tetrabutylammonium hexafluorophosphate TBAPF<sub>6</sub> as electro-

Table 1. Electrochemical Data of Compounds  $0-3^a$ 

	$E_{1/2}^{Ox}$	$E_{1/2}^{\text{Red1}}$	$E_{1/2}^{\rm Red2}$	$E_{1/2}^{\rm Red3}$	band gap (V)
$[Ru(bpy)_3]^{2+}$ (0)	1.29 <sup>b</sup>	-1.33 <sup>b</sup>			2.62
$[Ru(bpy)_2(qpy)]^{2+}(1)$	1.33 (80)	-1.20 (59)	-1.52 (57)	-1.74 (56)	2.53
$[Ru(bpy)(qpy)_2]^{2+}$ (2)	1.42 (57)	-1.07 (58)	-1.25 (66)	-1.58 (56)	2.49
$[Ru(qpy)_3]^{2+}$ (3)	$1.48 (77)^c$	$-0.99 (63)^{c}$	$-1.14 (66)^{c}$	$-1.34(74)^{c}$	2.47 <sup>c</sup>
$\alpha$ otantials are given in volts $(V)$ vs	SCE Cyclic voltamm	atry was parformed in	a doggesod MoCN/T	BARE (0.1 M) solutio	n at room tomporatur

<sup>*a*</sup>Potentials are given in volts (V) vs SCE. Cyclic voltammetry was performed in a degassed MeCN/TBAPF<sub>6</sub> (0.1 M) solution at room temperature with a sweep rate of 100 mV s<sup>-1</sup>. <sup>*b*</sup>Reference 32. <sup>*c*</sup>Reference 26.

lyte. The results will be discussed in terms of increasing the proportion of qpy ligand on going from  $[Ru(bpy)_3]^{2+}$  (0) to  $[Ru(qpy)_3]^{2+}$  (3) and are presented in Table 1.

Each cyclovoltammogram of complexes 0 to 3 presents a reversible oxidation process at 1.29, 1.33, 1.42, and 1.48 V, respectively, corresponding to each Ru<sup>II</sup>/Ru<sup>III</sup> oxidation. On the reduction side, the first reduction processes for all compounds, observed at -1.33, -1.20, -1.07, or -0.99 V, respectively, correspond to a reduction of a qpy ligand, except for **0** in which a bpy is reduced. The oxidation potential, attributed to the oxidation of ruthenium(II) to ruthenium(III), increases in the series with the increasing number of qpy units, following the same trend as the reduction potentials.  $[Ru(qpy)_3]^{2+}$  is thus the easiest to reduce and the hardest to oxidize, which is in accordance with an effect of the substitution of a hydrogen atom by a more electron withdrawing pyridyl group with a Hammett parameter of 0.44.35 The band gap, defined as the difference between the energy levels of the HOMO and LUMO orbitals, decreased with an increased number of pyridyl substituents. This is in agreement with the qpy ligand exhibiting better electron delocalization than the bpy ligand.

For the heteroleptic complexes, the pattern observed in the square-wave measurements (Figure 4) allows us to localize the first reductions systematically on the qpy ligands:  $[Ru(bpy)-(qpy)_2]^{2+}$  exhibits two close peaks attributed to the qpy and a second one related to the bpy. Similarly,  $[Ru(bpy)_2(qpy)]^{2+}$  presents one peak attributed to the qpy in addition to two peaks side-by-side attributed to the bpy. These assignments were corroborated by DFT calculations. Inspection of the



**Figure 4.** Square-wave measurements of  $[\text{Ru}(\text{bpy})_2(\text{qpy})]^{2+}$  (1) (in green),  $[\text{Ru}(\text{bpy})(\text{qpy})_2]^{2+}$  (2) (in blue), and  $[\text{Ru}(\text{qpy})_3]^{2+}$  (3) (in red), performed in a degassed MeCN/TBAPF<sub>6</sub> (0.1 M) solution at room temperature.

HOMO and LUMO orbitals computed for the whole series of compounds and illustrated Figure 5 shows that all HOMOs are mainly centered on the metal site, while LUMOs are localized on the ligands. When two different ligands are present, the lower energy orbitals are found on the qpy ligand, whereas the higher energy one(s) are localized on the bpy. These calculations confirm the assignment of the reduction waves observed in the electrochemical measurements. Comparison of the simulated and experimental IR spectra

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Comparison of the simulated and experimental IR spectra validated the model used, and as seen in Figure S.I.-5, an acceptable difference is found after applying the literature scaling factor of  $0.940^{36}$  to the calculated frequencies. Peaks at 830 and 555 cm<sup>-1</sup>, attributed to the PF<sub>6</sub> counteranion, are absent from the calculated IR spectra.

**Photophysical Measurements.** The absorption spectra of the Ru complexes are presented in Figure 6.

The different bands in the absorption spectra of the qpycontaining complexes can be attributed by analogy to the  $[Ru(bpy)_3]^{2+}$  spectrum. Classically for bpy-based ruthenium-(II) complexes, the low energy bands (>350 nm) are attributed to metal-to-ligand charge transfer (MLCT) transitions, whereas the higher energy bands (<350 nm) are assigned to processes involving the ligands.<sup>32</sup>

The presence of the qpy ligand is responsible for the two new bands at ~350 nm, which are attributed to a MLCT transition involving the qpy ligand, and 307 nm, corresponding to the LC transitions centered on the qpy ligand. Moreover, the latter presents a slight bathochromic shift of about 20 nm compared to the bpy centered transitions, possibly due to an increased conjugation in the qpy ligands. This effect is also observed for the low energy MLCT band (~475 nm).

Time-dependent density functional theory (TD-DFT) was used to validate the attribution of these bands. Superimposition of experimental absorption spectra and calculated spectra can be found in Figure 7, the theoretical contribution of each being found in sections S.I.-7, S.I.-8, and S.I.-9 for **0**, **1**, and **2**, respectively. We previously reported the corresponding data for complex **3** elsewhere.<sup>26</sup> Apart from a consistent energetic shift of all spectra, the calculations qualitatively fit the experimental data quite well and confirm the original assignment.

Concerning the two homoleptic complexes, the bands at 287 and 307 nm, for **0** and **3** respectively, were attributed to LC transitions. These bands are split in two for the heteroleptic complexes, due to the before mentioned differential LC contribution of the bpy and qpy ligands. In the case of complex **2**, the TD-DFT calculation identified the band at 292 nm as the superimposition of transitions between orbitals HOMO-8 and HOMO-9, qpy-centered, to the LUMO and LUMO+1, also qpy-centered (Table S.I.-12). This band was therefore attributed as a pure LC<sub>qpy</sub>. The band at 308 nm reveals a 75% contribution of a transition between the HOMO-7 and LUMO+2, both centered on the bpy ligand. The rest of the contribution includes the HOMO-2 orbital, partially



**Figure 5.** Representation of the molecular orbitals of interest (isocontour value 0.02 a.u., HOMO, LUMO, LUMO+1, LUMO+2, from bottom to top) of the  $[Ru(bpy)_x(qpy)_{3-x}]^{2+}$  (*x* decreasing from left to right).



**Figure 6.** Absorption spectra of  $[Ru(bpy)_3]^{2+}$  (0) (in dash gray),  $[Ru(bpy)_2(qpy)]^{2+}$  (1) (in green),  $[Ru(bpy)(qpy)_2]^{2+}$  (2) (in blue), and  $[Ru(qpy)_3]^{2+}$  (3) (in red) in acetonitrile.

centered on the metal, demonstrating the mixed character of certain transitions. However, as the major contribution only is taken into consideration, that band was attributed to a  $LC_{bpy}$ . Following the same reasoning for the heteroleptic complex 1, the band at 288 nm is attributed to a transition predominantly centered on the qpy ligand ( $LC_{qpy}$ ), whereas the one at 307 nm was assigned to a pure  $LC_{bpy}$  (Table S.I.-10).

Emission data for the complexes are summarized in Table 2. The presence of the qpy ligand enhances the quantum yield in a regular fashion, from  $[Ru(bpy)_3]^{2+}$  (0) at 9.5% to  $[Ru(bpy)_2(qpy)]^{2+}$  (1) at 14%, then  $[Ru(bpy)(qpy)_2]^{2+}$  (2) at 19% and finally  $[Ru(qpy)_3]^{2+}$  (3) at 23%. The excited state

lifetimes follow the same pattern, lengthening from 870 ns for  $[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$  (0) to 1.44  $\mu$ s, 1.64  $\mu$ s, and finally 1.78  $\mu$ s for  $[\operatorname{Ru}(\operatorname{bpy})_2(\operatorname{qpy})]^{2+}$  (1),  $[\operatorname{Ru}(\operatorname{bpy})(\operatorname{qpy})_2]^{2+}$  (2), and  $[\operatorname{Ru}(\operatorname{qpy})_3]^{2+}$  (3), respectively. The efficiency of the intersystem crossing (ISC) between the first excited state singlet and the emissive triplet <sup>3</sup>MLCT being considered close to unity in these complexes, we observe a parallel increase of the quantum yield ( $\Phi$ ) and the excited state lifetimes ( $\tau$ ).

The emission spectra are presented normalized and proportional to the quantum yield in Figure 8. The emission bands are red-shifted for all qpy-containing species as compared to the classic  $[Ru(bpy)_3]^{2+}$ . The increase in the excited state lifetimes can be explained by a lower energy LUMO orbital in qpycontaining complexes, therefore increasing the difference in energy with the metal centered triplet state <sup>3</sup>MC, known to deactivate the luminescence of the <sup>3</sup>MLCT state of polypyridine ruthenium complexes.<sup>37</sup>

Photocatalytic Hydrogen Evolution. As the complexes absorb in an extended visible light range when compared to [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, with higher quantum yields and longer excited state lifetimes, the  $[Ru(bpy)_x(qpy)_{3-x}]^{2+}$  family were good candidates to be tested in a molecular homogeneous photocatalytic hydrogen evolution system. Using the ancillary pyridine groups of the quaterpyridine ligand to support the photosensitizer on TiO<sub>2</sub> surfaces, complexes similar to 1 have been previously tested in photoelectrochemical cells for water reduction.<sup>38</sup> However, the family of complexes has not been evaluated in homogeneous photocatalysis yet. In addition, the homoleptic complex  $[Ru(qpy)_3]^{2+}$  was described previously by our group in this type of photocatalysis.<sup>26</sup> In the design of bigger assemblies for hydrogen production, the system should be designed with a LUMO orbital centered on the bridging ligand in order to accelerate the electron transfer between the metallic centers acting as photosensitizer and the catalyst. As



Figure 7. Superimposition of experimental absorption spectrum (in red) and computed TD-DFT spectrum (black lines) for  $[Ru(bpy)_3]^{2+}$  (0),  $[Ru(bpy)_2(qpy)]^{2+}$  (1),  $[Ru(bpy)(qpy)_2]^{2+}$  (2), and  $[Ru(qpy)_3]^{2+}$  (3).

Table 2. Emission Data of Complexes 1, 2, and 3 in Degassed Acetonitrile ( $C = \sim 10^{-5}$  M) at Room Temperature

	$\lambda_{\max em.}$	Φ	τ
$[Ru(bpy)_3]^{2+}$ (0)	608 <sup>32</sup>	9.5 <sup>32</sup>	870 <sup>32</sup>
$[Ru(bpy)_2(qpy)]^{2+}(1)$	643	14	1440
$[Ru(bpy)(qpy)_2]^{2+}$ (2)	635	19	1640
$[Ru(qpy)_3]^{2+}$ (3)	628 <sup>26</sup>	23 <sup>26</sup>	1780 <sup>26</sup>

previously demonstrated, the mixed systems bpy/qpy are fulfilling this requirement and therefore good candidates for supramolecular hydrogen production. The primary evaluation of the building blocks **1** and **2** as photosensitizers for photocatalytic hydrogen evolution is reported here, under blue light irradiation ( $\lambda_{max} = 460 \text{ nm}, \Delta \lambda = \sim 150 \text{ nm}$ ), against the reference [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (**0**).

As many parameters are to be considered, we attempted conditions as close as possible to the literature. Thus, each experiment was carried out with the  $[Ru(bpy)_3]^{2+}$  in parallel as a direct reference, using the classic  $[Co(dmgH)_2]^{2+}$  complex as the catalyst, formed in situ as the tetrafluoroborate salt. To study only the half equation of hydrogen evolution reaction, triethanolamine (TEOA) was used as a sacrificial electron donor and aqueous tetrafluoroboric acid was the source of protons.

All the complexes present a hydrogen evolution profile, although a difference in efficiency is observed. To make sure that the observed process is photocatalyzed, the system is first measured in the dark, defining the background of the gas



**Figure 8.** Emission spectra of  $[Ru(bpy)_3]^{2+}$  (0) (in dash gray),  $[Ru(bpy)_2(qpy)]^{2+}$  (1) (in green),  $[Ru(bpy)(qpy)_2]^{2+}$  (2) (in blue), and  $[Ru(qpy)_3]^{2+}$  (3) (in red) in degassed acetonitrile. Intensities are normalized and proportional to quantum yields.

chromatographic (GC) analysis. The lamp is then turned on, defining t = 0. No induction period was noticed after turning on the lamp with maximum TOFs obtained at the start. This process is followed by a decrease, classically attributed to the decomposition of the photosensitizer.

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Under blue-light irradiation (460 nm) (Figure 9), the complex  $[Ru(bpy)_2(qpy)]^{2+}$  (1) reaches a TOF of 2350



**Figure 9.** Hydrogen evolution of  $[Ru(bpy)_2(qpy)]^{2+}$  (1) (in blue),  $[Ru(bpy)_3]^{2+}$  (0) (in red) in degassed DMF containing  $10^{-4}$  M of the photosensitizers,  $1.2 \times 10^{-3}$  M of  $[Co(dmgH)_2]^{2+}$ , 1 M of (TEOA) and 0.1 M of HBF<sub>4</sub> (48% in water). Turnover frequencies (TOF, dashed line) and turnover number (TON, plain line) are presented, measured under the same conditions using blue-light irradiation (460 nm).

 $\text{mmol}\cdot\text{mol}_{\text{PS}}^{-1}\cdot\text{min}^{-1}$ , whereas only 1240  $\text{mmol}\cdot\text{mol}_{\text{PS}}^{-1}\cdot\text{min}^{-1}$  is observed for reference **0**. After 8 h, complex **1** presents a higher activity that the reference with TON of 180 versus 70 for **1** and the reference **0**, respectively.

Finally, as depicted in Figure 10, complex 2 is revealed to be the most efficient of the series with a TOF reached at the start of 2900 mmol·mol<sub>PS</sub><sup>-1</sup>·min<sup>-1</sup> versus 2040 mmol·mol<sub>PS</sub><sup>-1</sup>·min<sup>-1</sup> for the reference. After 14 h, when the  $[Ru(bpy)_3]^{2+}$  (0) presents a TON of 75, while the heteroleptic complex 2 reaches a TON of 320.



**Figure 10.** Hydrogen evolution of  $[\text{Ru}(\text{bpy})(\text{qpy})_2]^{2^+}$  (2) (in blue),  $[\text{Ru}(\text{bpy})_3]^{2^+}$  (0) (in red) in degassed DMF containing  $10^{-4}$  M of the photosensitizers,  $1.2 \times 10^{-3}$  M of  $[\text{Co}(\text{dmgH})_2]^{2^+}$ , 1 M of (TEOA) and 0.1 M of HBF<sub>4</sub> (48% in water). Turnover frequencies (TOF, dashed line) and turnover number (TON, plain line) are presented, measured under the same conditions using blue-light irradiation (460 nm).

When the TOF of the systems reaches zero, an injection of the cobalt catalyst does not restart the hydrogen evolution. However, a new addition of the studied ruthenium complex revives the catalysis (Figure S.I.-12), confirming that the PSs are the limiting factors in such systems. These conditions allow the correct study of the PS itself, not limited by the efficiency of the catalyst. All the results presented herein demonstrate that all of the qpy-containing species are more efficient than the reference  $[Ru(bpy)_3]^{2+}$ . Concerning the relative efficiency of those PSs, the superiority of 2 compared to 1 could be attributed to the highest quantum yield and elongated lifetime of the excited state. However, further studies will be needed to quantify the importance of other parameters such as the potential interaction(s) in solution between the cobalt catalyst with the peripheral pyridine functions, the kinetic of the electron transfers or the stability, and the quenching pathway of the excited PS in such a reductive environment.

# CONCLUSION

We report here an efficient microwave assisted one-pot synthesis of a series of ruthenium(II)-based photosensitizers bearing quaterpyridine and bipyridine ligands. As the proportion of quaterpyridine increases among the series, the photophysical properties are linearly enhanced compared to the parent  $[Ru(bpy)_3]^{2+}$ , with quantum yields from 9.5% up to 23% as well as elongated excited state lifetimes from 870 to 1780 ns for **0** and **3**, respectively. The photosensitizers were tested in a hydrogen evolution reaction and proved to be more efficient and robust than the archetypal  $[Ru(bpy)_3]^{2+}$ . The facile synthesis of this series of complexes could therefore be effective in the development of larger families of efficient photosensitizers adaptable in multimetallic supramolecular arrangements for artificial photosynthesis.

### ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00771.

Experimental details, crystallographic details, as well as the full computational studies (PDF)

# Accession Codes

CCDC 1556965 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

# AUTHOR INFORMATION

# **Corresponding Authors**

\*(G.S.H.) Fax: +1 514 343 7586. Tel: +1 514 340 5156. E-mail: garry.hanan@umontreal.ca.

\*(V.M.) Fax: +33 (0)1 44 27 38 41. Tel: +33 (0)1 44 27 32 77. E-mail: valerie.marvaud@upmc.fr.

#### ORCID 0

Ilaria Ciofini: 0000-0002-5391-4522

Garry S. Hanan: 0000-0001-6671-5234

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### Notes

The authors declare no competing financial interest.

# REFERENCES

(1) Lewis, N. S.; Nocera, D. G. Powering the planet: Chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15729–15735.

(2) Muradov, N.; Veziroglu, T. Green path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies. *Int. J. Hydrogen Energy* **2008**, *33*, 6804–6839.

(3) Bessette, A.; Hanan, G. S. Design, synthesis and photophysical studies of dipyrromethene-based materials: insights into their applications in organic photovoltaic devices. *Chem. Soc. Rev.* 2014, 43, 3342–3342.

(4) (a) Grätzel, M. Dye-sensitized solar cells. J. Photochem. Photobiol., C 2003, 4, 145–153. (b) Nazeeruddin, M. K.; Baranoff, E.; Grätzel, M. Dye-sensitized solar cells: A brief overview. Sol. Energy 2011, 85, 1172–1178.

(5) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. Engineering of efficient panchromatic sensitizers for nanocrystalline  $TiO_2$ -based solar cells. J. Am. Chem. Soc. **2001**, 123, 1613–1624.

(6) McKone, J. R.; Lewis, N. S.; Gray, H. B. Will Solar-Driven Water-Splitting Devices See the Light of Day? *Chem. Mater.* **2014**, *26*, 407–414.

(7) Armaroli, N.; Balzani, V. The hydrogen issue. *ChemSusChem* 2011, 4, 21-36.

(8) (a) Ji, Z.; He, M.; Huang, Z.; Ozkan, U.; Wu, Y. Photostable p-Type Dye-Sensitized Photoelectrochemical Cells for Water Reduction. J. Am. Chem. Soc. 2013, 135, 11696–11699. (b) Sahara, G.; Kumagai, H.; Maeda, K.; Kaeffer, N.; Artero, V.; Higashi, M.; Abe, R.; Ishitani, O. Photoelectrochemical Reduction of CO<sub>2</sub> Coupled to Water Oxidation Using a Photocathode with a Ru(II)-Re(I) Complex Photocatalyst and a COO<sub>x</sub>/TaON Photoanode. J. Am. Chem. Soc. 2016, 138, 14152–14158. (c) Gentil, S.; Lalaoui, N.; Dutta, A.; Nedellec, Y.; Cosnier, S.; Shaw, W. J.; Artero, V.; Le Goff, A. Carbon-Nanotube-Supported Bio-Inspired Nickel Catalyst and Its Integration in Hybrid Hydrogen/Air Fuel Cells. Angew. Chem., Int. Ed. 2017, 56, 1845–1849. (9) Queyriaux, N.; Jane, R. T.; Massin, J.; Artero, V.; Chavarot-Kerlidou, M. Recent developments in hydrogen evolving molecular cobalt(II)-polypyridyl catalysts. Coord. Chem. Rev. 2015, 304–305, 3–19.

(10) Grzelczak, M.; Liz-Marzán, L. M. The relevance of light in the formation of colloidal metal nanoparticles. *Chem. Soc. Rev.* **2014**, *43*, 2089–2097.

(11) Lehn, J. M.; Sauvage, J. P. Nouv. J. Chim. 1977, 1, 449-451.

(12) Berardi, S.; Drouet, S.; Francàs, L.; Gimbert-Suriñach, C.; Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A. Molecular artificial photosynthesis. *Chem. Soc. Rev.* **2014**, 43, 7501–7519.

(13) Balzani, V.; Credi, A.; Venturi, M. Photochemical Conversion of Solar Energy. *ChemSusChem* **2008**, *1*, 26–58.

(14) (a) Arrigo, A.; Santoro, A.; Puntoriero, F.; Lainé, P. P.; Campagna, S. Photoinduced electron transfer in donor-bridgeacceptor assemblies: The case of Os(II)-bis(terpyridine)-(bi)pyridinium dyads. *Coord. Chem. Rev.* 2015, 304-305, 109-116.
(b) Lachmanová, Š.; Dupeyre, G.; Tarábek, J.; Ochsenbein, P.; Perruchot, C.; Ciofini, I.; Hromadová, M.; Pospíšil, L.; Lainé, P. P. Kinetics of Multielectron Transfers and Redox-Induced Structural Changes in N -Aryl-Expanded Pyridiniums: Establishing Their Unusual, Versatile Electrophoric Activity. *J. Am. Chem. Soc.* 2015, 137, 11349-11364. (15) (a) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. Designing Dendrimers Based on Transition-Metal Complexes. Light-Harvesting Properties and Predetermined Redox Patterns. *Acc. Chem. Res.* **1998**, *31*, 26–34. (b) Plevoets, M.; Vögtle, F.; De Cola, L.; Balzani, V. Supramolecular dendrimers with a  $[Ru(bpy)_3]^{2+}$  core and naphthyl peripheral units. *New J. Chem.* **1999**, *23*, 63–69.

(16) (a) Creutz, C.; Schwarz, H. A.; Sutin, N. Free radical route to formation of the metal hydride complex hydridoaquobis(2,2'-bipyridine)cobalt(III). J. Am. Chem. Soc. 1984, 106, 3036–3037. (b) Krishnan, C. V.; Brunschwig, B. S.; Creutz, C.; Sutin, N. Homogeneous catalysis of the photoreduction of water. 6. Mediation by polypyridine complexes of ruthenium(II) and cobalt(II) in alkaline media. J. Am. Chem. Soc. 1985, 107, 2005–2015. (c) Schwarz, H. A.; Creutz, C.; Sutin, N. Homogeneous catalysis of the photoreduction of water by visible light. 4. Cobalt(I) polypyridine complexes. Redox and substitutional kinetics and thermodynamics in the aqueous 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine series studied by the pulse-radiolysis technique. Inorg. Chem. 1985, 24, 433–439. (d) Fihri, A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M. Cobaloxime-Based Photocatalytic Devices for Hydrogen Production. Angew. Chem., Int. Ed. 2008, 47, 564–567.

(17) (a) Fihri, A.; Artero, V.; Pereira, A.; Fontecave, M. Efficient H<sub>2</sub>producing photocatalytic systems based on cyclometalated iridiumand tricarbonylrhenium-diimine photosensitizers and cobaloxime catalysts. Dalton Trans. 2008, 5567-5569. (b) DiSalle, B. F.; Bernhard, S. Orchestrated Photocatalytic Water Reduction Using Surface-Adsorbing Iridium Photosensitizers. J. Am. Chem. Soc. 2011, 133, 11819-11821. (c) Zhang, P.; Jacques, P.-A.; Chavarot-Kerlidou, M.; Wang, M.; Sun, L.; Fontecave, M.; Artero, V. Phosphine Coordination to a Cobalt Diimine-Dioxime Catalyst Increases Stability during Light-Driven H2 Production. Inorg. Chem. 2012, 51, 2115-2120. (d) Jacques, A.; Schott, O.; Robeyns, K.; Hanan, G. S.; Elias, B. Hydrogen Photoevolution from a Green-Absorbing Iridium-(III)-Cobalt(III) Dyad. Eur. J. Inorg. Chem. 2016, 2016, 1779-1783. (e) Lentz, C.; Schott, O.; Auvray, T.; Hanan, G. S.; Elias, B. Photocatalytic Hydrogen Production Using a Red-Absorbing Ir(III)-Co(III) Dyad Inorg. Chem. 2017, DOI: 10.1021/acs.inorgchem.7b00684.

(18) (a) Du, P.; Knowles, K.; Eisenberg, R. A Homogeneous System for the Photogeneration of Hydrogen from Water Based on a Platinum(II) Terpyridyl Acetylide Chromophore and a Molecular Cobalt Catalyst. J. Am. Chem. Soc. 2008, 130, 12576–12577. (b) Du, P.; Schneider, J.; Luo, G.; Brennessel, W. W.; Eisenberg, R. Visible Light-Driven Hydrogen Production from Aqueous Protons Catalyzed by Molecular Cobaloxime Catalysts. Inorg. Chem. 2009, 48, 4952– 4962. (c) Wang, X.-H.; Goeb, S. b.; Ji, Z.-Q.; Pogulaichenko, N. A.; Castellano, F. N. Homogeneous Photocatalytic Hydrogen Production Using  $\pi$ -Conjugated Platinum(II) Arylacetylide Sensitizers. Inorg. Chem. 2011, 50, 705–707.

(19) (a) Probst, B.; Kolano, C.; Hamm, P.; Alberto, R. An Efficient Homogeneous Intermolecular Rhenium-Based Photocatalytic System for the Production of H<sub>2</sub>. Inorg. Chem. 2009, 48, 1836-1843. (b) Probst, B.; Rodenberg, A.; Guttentag, M.; Hamm, P.; Alberto, R. A Highly Stable Rhenium-Cobalt System for Photocatalytic H<sub>2</sub> Production: Unraveling the Performance-Limiting Steps. Inorg. Chem. 2010, 49, 6453-6460. (c) Probst, B.; Guttentag, M.; Rodenberg, A.; Hamm, P.; Alberto, R. Photocatalytic H<sub>2</sub> Production from Water with Rhenium and Cobalt Complexes. Inorg. Chem. 2011, 50, 3404-3412. (d) Guttentag, M.; Rodenberg, A.; Kopelent, R.; Probst, B.; Buchwalder, C.; Brandstätter, M.; Hamm, P.; Alberto, R. Photocatalytic H<sub>2</sub> Production with a Rhenium/Cobalt System in Water under Acidic Conditions. Eur. J. Inorg. Chem. 2012, 2012, 59-64. (e) Oberholzer, M.; Probst, B.; Bernasconi, D.; Spingler, B.; Alberto, R. Photosensitizing Properties of Alkynylrhenium(I) Complexes  $[\text{Re}(-C \equiv C-R)(CO)_3(N \cap N)]$   $(N \cap N = 2,2'$ -bipy, phen) for H<sub>2</sub> Production. Eur. J. Inorg. Chem. 2014, 2014, 3002-3009.

(20) (a) Naruta, Y.; Sasayama, M.-a.; Sasaki, T. Oxygen Evolution by Oxidation of Water with Manganese Porphyrin Dimers. *Angew. Chem.*,

Int. Ed. Engl. **1994**, 33, 1839–1841. (b) Limburg, J. A Functional Model for O-O Bond Formation by the O<sub>2</sub>-Evolving Complex in Photosystem II. Science **1999**, 283, 1524–1527. (c) Limburg, J.; Vrettos, J. S.; Chen, H.; de Paula, J. C.; Crabtree, R. H.; Brudvig, G. W. Characterization of the O<sub>2</sub> -Evolving Reaction Catalyzed by [(terpy)-(H<sub>2</sub>O)Mn<sup>III</sup>(O)<sub>2</sub>Mn<sup>IV</sup>(OH<sub>2</sub>)(terpy)](NO<sub>3</sub>)<sub>3</sub> (terpy = 2,2':6,2"-Terpyridine). J. Am. Chem. Soc. **2001**, 123, 423–430. (d) Young, K. J.; Takase, M. K.; Brudvig, G. W. An anionic N-donor ligand promotes manganese-catalyzed water oxidation. Inorg. Chem. **2013**, 52, 7615– 7622. (e) Hirahara, M.; Shoji, A.; Yagi, M. Artificial Manganese Center Models for Photosynthetic Oxygen Evolution in Photosystem II. Eur. J. Inorg. Chem. **2014**, 2014, 595–606.

(21) (a) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. Catalytic oxidation of water by an oxo-bridged ruthenium dimer. J. Am. Chem. Soc. **1982**, 104, 4029–4030. (b) Sens, C.; Romero, I.; Rodríguez, M.; Llobet, A.; Parella, T.; Benet-Buchholz, J. A New Ru Complex Capable of Catalytically Oxidizing Water to Molecular Dioxygen. J. Am. Chem. Soc. **2004**, 126, 7798–7799. (c) Yang, X.; Baik, M.-H. The Mechanism of Water Oxidation Catalysis Promoted by [tpyRu(IV)=O]<sub>2</sub>L<sup>3+</sup>: A Computational Study. J. Am. Chem. Soc. **2008**, 130, 16231–16240. (d) Duan, L.; Wang, L.; Inge, A. K.; Fischer, A.; Zou, X.; Sun, L. Insights into Ru-Based Molecular Water Oxidation Catalysts: Electronic and Noncovalent-Interaction Effects on Their Catalytic Activities. Inorg. Chem. **2013**, 52, 7844–7852.

(22) (a) McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. Cyclometalated Iridium(III) Aquo Complexes: Efficient and Tunable Catalysts for the Homogeneous Oxidation of Water. J. Am. Chem. Soc. **2008**, 130, 210–217. (b) Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, G. W.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. Half-Sandwich Iridium Complexes for Homogeneous Water-Oxidation Catalysis. J. Am. Chem. Soc. **2010**, 132, 16017–16029. (c) Lewandowska-Andralojc, A.; Polyansky, D. E.; Wang, C.-H.; Wang, W.-H.; Himeda, Y.; Fujita, E. Efficient water oxidation with organometallic iridium complexes as precatalysts. Phys. Chem. Chem. Phys. **2014**, 16, 11976–11976.

(23) Ozawa, H.; Yokoyama, Y.; Haga, M.-a.; Sakai, K. Syntheses, characterization, and photo-hydrogen-evolving properties of tris(2,2'-bipyridine) ruthenium(II) derivatives tethered to a cis-Pt<sup>II</sup>Cl<sub>2</sub> unit: insights into the structure–activity relationship. *Dalton Trans.* **2007**, 1197–1206.

(24) (a) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. Splitting Water with Cobalt. *Angew. Chem., Int. Ed.* 2011, *50*, 7238–7266. (b) Khnayzer, R. S.; Thoi, V. S.; Nippe, M.; King, A. E.; Jurss, J. W.; El Roz, K. a.; Long, J. R.; Chang, C. J.; Castellano, F. N. Towards a comprehensive understanding of visible-light photogeneration of hydrogen from water using cobalt(II) polypyridyl catalysts. *Energy Environ. Sci.* 2014, *7*, 1477–1477. (c) Wakerley, D. W.; Reisner, E. Development and understanding of cobaloxime activity through electrochemical molecular catalyst screening. *Phys. Chem. Chem. Phys.* 2014, *16*, 5739–5739.

(25) Wu, L.-Z.; Chen, B.; Li, Z.-J.; Tung, C.-H. Enhancement of the Efficiency of Photocatalytic Reduction of Protons to Hydrogen via Molecular Assembly. *Acc. Chem. Res.* **2014**, *47*, 2177–2185.

(26) Rousset, E.; Chartrand, D.; Ciofini, I.; Marvaud, V.; Hanan, G. S. Red-light-driven photocatalytic hydrogen evolution using a ruthenium quaterpyridine complex. *Chem. Commun.* **2015**, *51*, 9261–9264.

(27) Dulière, E.; Devillers, M.; Marchand-Brynaert, J. Novel Phosphinite–Ruthenium(II) Complexes Covalently Bound on Silica: Synthesis, Characterization, and Catalytic Behavior versus Oxidation Reactions of Alcohols into Aldehydes. *Organometallics* **2003**, *22*, 804–811.

(28) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. Mixed phosphine 2,2'bipyridine complexes of ruthenium. *Inorg. Chem.* **1978**, *17*, 3334– 3341.

(29) Bierig, K.; Morgan, R. J.; Tysoe, S.; Gafney, H. D.; Strekas, T. C.; Baker, A. D. 2,2':4,4":4',4<sup>m</sup>-Quaterpyridyl: a building block for the preparation of novel redox reagents. 2. Bis(2,2'-bipyridine)ruthenium-(II) complexes. *Inorg. Chem.* **1991**, *30*, 4898–4903.

(30) Coe, B. J.; Harper, E. C.; Helliwell, M.; Ta, Y. T. Syntheses and properties of complexes with bis(2,2 '-bipyridyl)ruthenium(II) moieties coordinated to 4,4 ':2 ',2 ":4 ",4 "'-quaterpyridinium ligands. *Polyhedron* **2011**, 30, 1830–1841.

(31) Brimblecombe, R.; Swiegers, G. F.; Dismukes, G. C.; Spiccia, L. Sustained Water Oxidation Photocatalysis by a Bioinspired Manganese Cluster. *Angew. Chem., Int. Ed.* **2008**, *47*, 7335–7338.

(32) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. Ru(II) polypyridine complexes: photophysics, photochemistry, eletrochemistry, and chemiluminescence. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

(33) Anderson, P. a.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. a.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C. Designed Synthesis of Mononuclear Tris(heteroleptic) Ruthenium Complexes Containing Bidentate Polypyridyl Ligands. *Inorg. Chem.* **1995**, *34*, 6145–6157.

(34) Shi, P.; Coe, B. J.; Sánchez, S.; Wang, D.; Tian, Y.; Nyk, M.; Samoc, M. Uniting Ruthenium(II) and Platinum(II) Polypyridine Centers in Heteropolymetallic Complexes Giving Strong Two-Photon Absorption. *Inorg. Chem.* **2015**, *54*, 11450–11456.

(35) Hansch, C.; Leo, A.; Taft, R. W. A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev.* **1991**, *91*, 165–195.

(36) Merrick, J. P.; Moran, D.; Radom, L. An Evaluation of Harmonic Vibrational Frequency Scale Factors. *J. Phys. Chem. A* 2007, *111*, 11683–11700.

(37) Medlycott, E. A.; Hanan, G. S. Designing tridentate ligands for ruthenium(II) complexes with prolonged room temperature luminescence lifetimes. *Chem. Soc. Rev.* **2005**, *34*, 133–142.

(38) Takijiri, K.; Morita, K.; Nakazono, T.; Sakai, K.; Ozawa, H. Highly stable chemisorption of dyes with pyridyl anchors over TiO<sub>2</sub>: application in dye-sensitized photoelectrochemical water reduction in aqueous media. *Chem. Commun.* **2017**, *53*, 3042–3045.