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# Efficient light activation of a [Ru(bpy)(tpy)Cl]<sup>+</sup> catalyst by a porphyrin photosensitizer at small driving force



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# 1. Introduction

Activation of a catalyst by light is a critical process in the domain of artificial photosynthesis; besides the high performance in terms of turn-over frequency (TOF), stability (turn-over number, TON), selectivity and overpotential  $(\eta)$ , the catalyst efficient photo-activation is also required. Such process encompasses several steps: light absorption, formation of charge-separated states, as well as charge accumulation on the active site in the case of a multi-electron process such as water oxidation, an energetically and kinetically demanding 4-electrons, 4-protons reaction. An attractive way to use light to drive the catalytic process consists in integrating the chromophore and the catalyst in the same system [1], grafted onto a semiconductor surface: Upon absorption of light, the chromophore excited state injects electrons into the semiconductor conduction band and activates the catalyst in an oxidative reaction. In this configuration, the properties of the sensitizer and the catalyst need to be matched for an efficient activation of the latter. To this end, several issues need to be considered, such as energy losses occurring in exergonic reactions, competition between different processes for the deactivation of the sensitizer

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# ABSTRACT

Light activation of dyads containing porphyrins and a catalytic ruthenium complex having a high oxidation potential (~1 V vs SCE) is investigated by time-resolved spectroscopy. It is shown that activation of the ruthenium complex occurs through oxidative quenching of the chromophore in the presence of a reversible electron acceptor. Despite the lack of driving force for intramolecular electron transfer, an efficient intramolecular oxidation of the catalyst is observed, suggesting that porphyrins are attractive chromophores to activate oxidation catalysts throughout the visible spectrum.

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excited state, or unproductive pathways. Understanding the ongoing photophysical events is important in order to remediate the deleterious photophysical pathways and/or the limiting thermodynamics steps on the way towards optimization.

In a previous study, we have investigated the activation by light of the [Ru(tpy)(bpy)OH<sub>2</sub>]<sup>2+</sup> complex also known as "Meyer catalyst" [2,3] the first reported mononuclear ruthenium catalyst for water oxidation, whose mechanism of action is not completely elucidated [2,4–13]. We have shown that when the catalyst is linked to a ruthenium polypyridine chromophore, the activation mechanism proceeds either via energy transfer (antenna or photosensitizer behavior) or via electron transfer (reaction center or photoredox behavior) depending on the peripheral groups attached to the chromophore [14]. When a porphyrin was used as a photosensitizer to activate the catalyst precursor [Ru(tpy) (bpy)Cl]<sup>+</sup>, a better collection of light and bidirectional energy transfer between the chromophore and the catalyst resulted in a more efficient activation of the [Ru(tpy)(bpy)Cl]<sup>+</sup> unit [15]. In order to render the catalyst more oxidizing and possibly increase its efficiency, we have now modified the ruthenium moiety by introducing electron-withdrawing methoxycarbonyl groups on the bipyridine ligand (Chart 1). In terms of catalytic performance, it has been shown for an analogous catalyst, bearing COOH electron-withdrawing groups on the bipyridines, that such functionalization results in smaller TOF but higher TON compared to the





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Chart 1. Investigated dyads:  $H_2P\text{-}Ru_{COOMe}, ZnP\text{-}Ru_{COOMe}$  and reference dyad  $H_2P\text{-}Ru_{cat}$ 

parent molecule [5]. The smaller TOF, in the presence of electronwithdrawing groups, has been attributed [16] to the diminished accessibility of the water molecule to the Ru<sup>V</sup> = O species which constitutes the rate determining step in the water nucleophilic attack mechanism proposed by Meyer [2]. The enhanced stability has been attributed to the increased  $\pi$ -backbonding of the bipyridine which is the most labile ligand and its dissociation is responsible for the catalyst decomposition [16]. In the present study we describe the photophysical properties of two new dyads containing a porphyrin chromophore (free-base or zinc) linked through an amide bridge to a modified version of the Meyer catalyst (Chart 1), and the investigation of their photo-induced oxidation. A comparison with the dyad bearing the unmodified Meyer catalyst (H<sub>2</sub>P-**Ru<sub>cat</sub>)** [15] is also established.

# 2. Results and discussion

# 2.1. Synthesis

The synthesis of the dyads presented in this paper is outlined in Scheme 1. A two-step reaction was followed for the synthesis of the terpyridine substituted porphyrin derivative **H**<sub>2</sub>**P-tpy**. The first step included the conversion of the carboxy-terpyridine (**tpy-COOH**) [17] to the corresponding acyl chloride after refluxing in SOCl<sub>2</sub>. Subsequently, amino porphyrin (**H**<sub>2</sub>**P-NH**<sub>2</sub>) [18] was added and the reaction was left under reflux in THF overnight, in the presence of Et<sub>3</sub>N, yielding **H**<sub>2</sub>**P-tpy**. The desired free base dyad **H**<sub>2</sub>**P-Ru**<sub>COOMe</sub> was afforded by refluxing **H**<sub>2</sub>**P-tpy** and the corresponding ruthenium complex **Ru(bpy(-COOMe)**<sub>2</sub>)(**DMSO)**<sub>2</sub>**Cl**<sub>2</sub> in acetic acid. Finally, the metalated dyad **ZnP-Ru**<sub>COOMe</sub> was prepared *via* metalation of the free-base dyad with zinc acetate. The synthesis of the reference compound **Ru**<sub>COOMe</sub> is shown in Scheme S1. Initially, RuCl<sub>3</sub> reacted with **tpy-COOH** and the desired compound was obtained after the addition of **bpy-(COOMe)**<sub>2</sub>. All intermediates and final compounds were fully characterized through MALDI-TOF mass spectrometry, NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopy (see SI) and elemental analysis. The final dyads were also characterized through Infrared (IR) spectroscopy (see SI).

# 2.2. Electrochemical characterization

The electrochemical properties of the dyads and reference compounds, investigated by cyclic and square-wave voltammetry, are reported in Table 1. In the reference compound Ru<sub>COOMe</sub>, as expected, the presence of the carboxylates strongly impacts the first reduction based on bipyridines, which presents a 280 mV anodic shift as compared to the unmodified Rucat. The second reduction, based on the terpyridine, is less affected and it exhibits a 40 mV positive shift. On the anodic side, the oxidation, which is ruthenium centred, occurs at 1.08 V (+140 mV shift), close to the first oxidation process of the free-base tetra-phenyl-porphyrin (H<sub>2</sub>P) at 1.14 V. As a consequence, in the H<sub>2</sub>P-Ru<sub>COOMe</sub> dyad the first oxidation, occurring at 1.09 V, is a two-electron process (data in SI). These data suggest that the Gibbs free energy ( $\Delta G$ ) for the catalyst oxidation, driven by the oxidised porphyrin, is close to zero. The process is endergonic in the case of the ZnP-Ru<sub>coome</sub> dyad where, in the electrochemical experimental conditions, the metal oxidation appears 190 mV more positive than the first oxidation of the porphyrin.

#### 2.3. Spectroscopic characterization

Ground and excited state properties. The ground state absorption spectra of the reference  $\mathbf{Ru}_{\mathbf{COOMe}}$  and the corresponding dyads are given in Fig. 1. The Rucoome absorption spectrum is characterised by a  $\pi \rightarrow \pi^*$  transition at 373 nm, accompanied by the MLCT d  $\rightarrow \pi^*$  centred at 533 nm. These bands are respectively ~ 50 and 20 nm red-shifted as compared to  $\mathbf{Ru}_{\mathbf{cat}}.$  Such shift has been previously attributed to a low-lying  $\pi^*$  level on the bpy ligand incorporating electron withdrawing groups [19]. The H<sub>2</sub>P-Ru<sub>COOMe</sub> absorption spectrum contains the characteristic porphyrin Soret band at 415 nm, although significantly decreased compared to H<sub>2</sub>P, and four Q bands at 515, 546, 588 and 645 nm, superposed upon the bands originating from the Ru unit. It appears that the individual features of the two moieties are slightly altered in the dyads. Thus, the existence of an electronic communication between the two moieties is anticipated. In the case of the ZnP-Ru<sub>COOMe</sub> dyad the Soret band is shifted to 422 nm and the Q bands occur at 554 and 595 nm.

The steady-state emission spectrum of H<sub>2</sub>P-Ru<sub>COOMe</sub>, shown in Fig. 2a, exhibits both porphyrin fluorescence (650 and 715 nm) and Ru<sub>COOMe</sub> (780 nm) emission (SI, Fig S4). The fluorescence quantum yield  $(\Phi_F)$  of the **H<sub>2</sub>P-Ru<sub>COOMe</sub>** dyad, when excited at 515 nm, is  $1.1 \times 10^{-3}$  (for calculation see SI) with the Ru band contributing 16% of the total emission. According to the molar extinction coefficients of the two components, absorption of light at this excitation wavelength is about equally shared between the porphyrin (49%) and the Ru (51%) moieties. Thus, from the heterogeneity of singlet excited states arising from excitation at 515 nm, a  $\Phi_{\rm F}$  ~ 7.3 $imes 10^{-2}$  should be expected for the dyad emission in the absence of interactions between the two moieties. In contrast, the obtained value is more than 60 times lower, indicating that the fluorescence originating from the porphyrin is almost completely (98%) quenched by the ruthenium unit. Upon excitation at 535 nm, where porphyrin absorbs 27% of light, the  $\Phi_{\rm F}$  is 5.5  $\times$  10<sup>-4</sup>. These results indicate the presence of a supplementary deactivation channel for the singlet excited state of the porphyrin, that is either energy or electron transfer to the ruthenium moiety. In order to investigate the nature of the quenching, time-resolved measurements were performed by exciting the sample with a laser pulse



Scheme 1. Synthesis of compounds H<sub>2</sub>P-Ru<sub>COOMe</sub> and ZnP-Ru<sub>COOMe</sub>.

Table 1 Electrochemical data.

Compound	$E_{1/2} (P^{-}/P^{2-})$	$E_{1/2}(tpy^0/tpy^-)$	$E_{1/2}(P/P^{-})$	E <sub>1/2</sub> (bpy <sup>0</sup> /bpy <sup>-</sup> )	$E_{1/2} (P^+/P)$	E <sub>1/2</sub> (Ru <sup>III</sup> /Ru <sup>II</sup> )	$E_{1/2}(P^{2+}/P^{+})$
Ru <sub>COOMe</sub>	_	-1.38	-	-0.97	_	1.08	-
Ru <sup>#</sup>	-	-1.42	-	-1.25	-	0.94	-
$H_2P^{\#}$	-1.58	-	-1.08	-	1.14	-	1.42
ZnP <sup>#</sup>	-	-	-1.25	-	0.90	-	1.25
H <sub>2</sub> P-Ru <sub>COOMe</sub>	-1.53	-1.33	-1.07	-0.96	1.09	1.09	1.32
ZnP-Ru <sub>COOMe</sub>		-1.33	-1.27	-0.96	0.89	1.08	1.25

 $E_{1/2} = (E_{pa} + E_{pc})/2$  in Volts vs SCE, measured in benzonitrile, scan speed: 100 mV s<sup>-1</sup>. # From ref [8].



Fig. 1. UV–Vis absorption spectra of the dyads and the reference compound in acetone/CH\_3CN (50:50) solutions.

at 515 nm. In differential transient absorption studies, at early times (10 ns) a bleaching at 540 nm is observed. This is attributed to the presence of the triplet excited state  ${}^{3}Ru_{COOMe}{}^{*}$  (Fig. 2b), which can be formed *via* Förster energy transfer between the porphyrin singlet excited state ( ${}^{1}H_{2}P^{*}$ ) and the triplet  ${}^{3}Ru_{COOMe}{}^{*}$ . This

hypothesis is further supported by the evaluation of the overlap integral between the porphyrin emission and the **Ru**<sub>COOMe</sub> absorption (Fig. S5).

At longer times (greater than 50 ns) this depletion disappears and the remaining absorption exhibits features that are characteristic of the H<sub>2</sub>P triplet excited state which then decays within 15 µs (Fig. S6). The final quantum yield of the triplet porphyrin within the dyad, estimated using the comparative method [20] is 41% (Fig. S6). Since the singlet excited state of the porphyrin is almost completely quenched by the ruthenium moiety (steady-state measurements) and is therefore unable to evolve directly into  ${}^{3}\mathbf{H}_{2}\mathbf{P}^{*}$ , the formation of triplet porphyrin must be achieved by energy transfer from the  ${}^{3}Ru_{COOMe}{}^{*}$  to the porphyrin unit. The presence of triplet-triplet energy transfer had also been inferred for the dyad H<sub>2</sub>P-Ru<sub>cat</sub> [15] In both cases, the Dexter mechanism is operative since triplet-triplet energy transfer via a Förster mechanism, which is spin-forbidden, is unlikely [21] Dexter mechanism is possible either when the two units are in close proximity [22] or if the transfer is mediated by the bridge [23]. This is more likely to be the case here since it has been shown that the amide linkage facilitates the energy transfer via super-exchange mechanism [23,24]. To summarise, these results can be rationalised as follows (Scheme 2): excitation at 515 nm results in a heterogeneity of singlet excited states with half of molecules forming the <sup>1</sup>Ru<sub>COOMe</sub>\* state and the other half forming the  ${}^{1}H_{2}P^{*}$  state. Both singlet states evolve almost quantitatively into <sup>3</sup>Ru<sub>COOMe</sub>\*, the former via inter-system



**Fig. 2.** (a) Steady-state emission spectra obtained by excitation at 515 nm for optically diluted acetone/acetonitrile (50:50) solutions (absorption  $A_{515} = 0.1$ ); (b) gated (10 ns) transient absorption spectra (right) at different delays from laser pulse. Excitation at 515 nm with 8 mJ laser energy. A(515) = 0.32 in acetonitrile/acetone (50:50) solvent. The spectra have been cut between 400 and 450 nm because of the high absorption of the Soret band in this region.



**Scheme 2.** Simplified energetics scheme of the  $H_2P$ - $Ru_{COOMe}$  dyad describing the observed evolution of excited states upon excitation at 515 nm. Rate constants are given in  $s^{-1}$ , quantum yields in brackets. For estimation of the different parameters, see SI.

crossing, and the latter by energy transfer. The resulting triplet <sup>3</sup>-**Ru<sub>COOMe</sub>**<sup>\*</sup> (E<sub>T</sub> = 1.83 eV, cf SI) then undergoes energy transfer to form the triplet <sup>3</sup>H<sub>2</sub>P<sup>\*</sup>. The lifetime of the final <sup>3</sup>H<sub>2</sub>P-Ru<sub>COOMe</sub><sup>\*</sup> state, formed with a quantum yield of ~ 0.41 is ~ 5  $\mu$ s (kinetics in Fig. S6). Thus about 40% of the photons absorbed by the dyad are stored in a porphyrin triplet excited state having an energy of ~ 1.5 eV [15].

#### 2.4. Flash-quench experiments.

In order to investigate the possibility of activating the **Ru**<sub>COOME</sub> catalyst by the oxidised porphyrin, we performed flash-quench experiments in the presence of methyl viologen ( $MV^{2+}$ ) as a reversible electron acceptor. Upon excitation, the porphyrin triplet excited state, formed according to the energy transfer mechanism described above, is oxidatively quenched by methyl viologen creating a charge-separated state (**H**<sub>2</sub>**P-Ru**<sub>COOME</sub>)<sub>ox</sub>/MV<sup>++</sup>. This can be inferred from the absorption changes in Fig. 3; between 100 and 500 ns, a peak is formed at 395 nm concomitantly with a band at 605 nm, both characteristic of the reduced MV<sup>++</sup> species [25]. The bimolecular rate constant for quenching of the excited state by



Fig. 3. Transient spectra obtained in the presence of 10 mM  $MV^{2*}$  upon excitation at 515 nm with laser energy of 13 mJ. Absorption at 515 nm: 0.26. Solvent: acetonitrile/acetone (50:50) vol.

 $MV^{2+}$  is 2.2  $\times$   $10^8~M^{-1}~s^{-1}$ . In the presence of 10 mM of  $MV^{2+}$ , the formation of the methyl viologen radical cation, was accompanied by an absorption decrease at 540 nm corresponding to the oxidation of Ru(II) to Ru(III).

At MV<sup>2+</sup> concentrations lower than 10 mM, the rate limiting step for oxidation of the Ru catalyst appears to be the formation of the charge-separated state (H<sub>2</sub>P-Ru<sub>COOMe</sub>)<sub>ox</sub>/MV<sup>•+</sup> (Fig. S7), while at higher concentrations (20 mM), the kinetics of intramolecular Ru(III) oxidation can be isolated and the rate for intramolecular electron transfer determined to be  $3.8 \times 10^6$  s<sup>-1</sup> (Fig. S8). In terms of yield, 1.6  $\pm$  0.2  $\mu$ M of the <sup>3</sup>H<sub>2</sub>P<sup>\*</sup> formed, results in 1.3  $\pm$  0.2  $\mu$ M of MV<sup>•+</sup> and 1.2  $\pm$  0.2  $\mu$ M Ru(III), that is a yield for intramolecular oxidation close to 100% (cf SI for details). Since, as discussed above, the triplet porphyrin in the dyad is obtained with a quantum yield of  $\sim$  0.41, then a quantum yield of  $\sim$ 0.40 is obtained for Ru(III). For comparison, in the case of dyad H<sub>2</sub>P-Ru<sub>cat</sub> under the same experimental conditions, excitation at 515 nm initially produces ~ 3.0  $\mu$ M of  ${}^{3}H_{2}P^{*}$  (the porphyrin absorbs in this case 70% of light) to finally give 2.6 µM of Ru(III), corresponding to a yield for intramolecular oxidation of 87%.

Spectroscopic and flash-quench studies were also performed on the **ZnP-Ru<sub>COOMe</sub>** dyad. Upon excitation at 560 nm (A<sub>560</sub> = 0.25), deactivation of the porphyrin singlet excited state gives, as for its free base analogue, the triplet excited state of the ruthenium moiety <sup>3</sup>**Ru<sub>COOMe</sub>**<sup>\*</sup> and finally the formation of the triplet excited state of <sup>3</sup>**ZnP**<sup>\*</sup>. This was supported by the observation of bleaching of the Ru absorption at initial times in the differential transient absorption spectra, evolving toward a typical <sup>3</sup>**ZnP**<sup>\*</sup> triplet state which has a lifetime of ~ 1.7 µs (Figs. S9 and S10). In the presence of MV<sup>2+</sup> mainly the formation of the ZnP<sup>•+</sup> radical cation was observed (Fig. S11), confirming that Ru(III) oxidation by the ZnP radical cation is an energetically uphill reaction.

#### 3. Conclusions

In this paper we have collected photophysical data on a modified Meyer catalyst attached to a porphyrin chromophore which exhibits an oxidation potential higher than 1 V vs SCE. The data clearly point to the efficient light activation of the catalyst by the oxidised porphyrin in the presence of a reversible electron acceptor despite the fact that the potentials for H<sub>2</sub>P<sup>•+</sup>/H<sub>2</sub>P and Ru(III)/Ru(II), estimated from the cyclic voltammetry experiments, are very close. However, using the yield and the rate constants for intramolecular oxidation, it is possible to infer the operating  $\Delta G$ from  $k_{IET}/k_{BET} = -RT^*exp(-\Delta G)$  [26], where  $k_{IET}$  and  $k_{BET}$  are respectively the forward and back electron transfer rate constants in the equilibrium. This results in  $\Delta G \sim -25$  meV, indicating a slightly exergonic process.

The collected results shows that porphyrins are attractive chromophores to employ in the photoactivation of highly oxidising catalysts. The dyad H<sub>2</sub>P-Ru<sub>COOMe</sub> shows an increased oxidation power as compared to H<sub>2</sub>P-Ru<sub>cat</sub> previously investigated. This is beneficial for driving oxidation catalytic processes. However, in order to advance in the catalytic cycle, successive oxidations of the ruthenium moiety are necessary and they occur at higher potential. They are therefore thermodynamically more difficult to be triggered by the oxidised porphyrin. It is nevertheless worth noting that, upon exchange of the chloride ligand with a water molecule, a step occurring spontaneously in aqueous solutions [5], the successive oxidations occur in a narrow albeit higher, potential window because of proton-coupled electron transfer (PCET) processes [27,28]. Indeed, PCET facilitates the advancing in the catalytic cycle while preventing the building up of charged species, as well as stabilising the oxidised state by decreasing the driving force for the charge recombination. This is an important aspect when considering the second activation step. In fact, upon formation of the chromophore excited state, a reverse electron transfer between the oxidised catalyst and the excited state may take place. However this reaction should be less favourable if a deprotonation accompanies the oxidation reaction. The  $H_2P$ - $Ru_{cat}$  dyad was investigated in its ability to generate the doubly oxidised ruthenium species Ru (IV), a species relevant for catalysis, but no charge accumulation could be observed by pump-pump-probe experiments [29]. This was rationalised as due to the competition between intramolecular oxidation of Ru(III) to Ru(IV) by the porphyrin cation (for which  $\Delta G \sim 0$ ) and the reverse electron transfer from the porphyrin excited state to the Ru(III) to give Ru(II) and H<sub>2</sub>P<sup>•+</sup>. For the reverse electron transfer a high driving force ( $\Delta G = -1.3 \text{ V}$ ) is present. A more promising approach to minimize reverse electron transfer is by kinetic out-competition. This could be achieved by anchoring the porphyrin complex to *n*-type semiconductor particles like TiO<sub>2</sub> which results in ultrafast deactivation of the excited state by electron injection in the semiconductor conduction band to form TiO<sub>2</sub>/  $H_2P^{\bullet+}$  [30]. This can then enable the intramolecular oxidation of Ru (III) to Ru(IV).

#### 4. Experimental

Materials. Compounds **tpy-COOH** [17], **H**<sub>2</sub>**P–NH**<sub>2</sub> [18], were prepared according to published procedures. Tetrahydrofuran was freshly distilled from Na/benzophenone. All other chemicals and solvents were purchased from commercial sources and used as received.

NMR Spectra. NMR spectra were recorded on a Bruker AVANCE III-500 MHz and Bruker DPX-300 MHz spectrometers using solutions in deuterated solvents and the solvent peak was chosen as the internal standard.

Mass Spectra. High-resolution mass spectra were obtained on a Bruker UltrafleXtreme matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as matrix.

**Elemental Analysis.** Elemental analyses were carried out using Carlo-Erba EA 1110 CHNS Eager 200 analyzer.

Electrochemistry. Cyclic and square wave voltammetry experiments were carried out at room temperature using an AutoLab PGSTAT20 potentiostat and appropriate routines available in the operating software (GPES version 4.9). All measurements were carried out in freshly distilled and deoxygenated benzonitrile with a solute concentration of ca. 1.0 mM in the presence of tetrabuty-lammonium tetrafluoroborate (0.1 M) as supporting electrolyte, at a scan rate of 100 mV s<sup>-1</sup>. A three-electrode cell setup was used with a platinum working electrode, a saturated calomel (SCE) reference electrode, and a platinum wire as counter electrode. In all measurements the ferrocene/ferrocenium couple was at 0.58 V versus SCE under the above conditions.

Spectroscopy. Infrared (IR) spectra were obtained using an Agilent Cary 630 spectrometer. Ground state absorption spectra were measured either on a Shimadzu UV-1700 or an Analytic Jena Specord210 spectrophotometer. Steady-state emission spectra were obtained using a JASCO FP-6500 fluorescence spectrophotometer equipped with a red-sensitive WRE-343 photomultiplier tube (wavelength range 200–850 nm). Fluorescence quantum yields were calculated using 5,10,15,20-tetraphenylporphyrin ( $\Phi_f$  = 0.15) [31], as reference. All transient absorption experiments were performed on an Edinburgh Instruments LP920 Flash Photolysis Spectrometer system incorporating a Continuum Surelite OPO. The OPO was pumped by a Q-switched Nd:YAG laser operating at 355 nm. The LP920 system is equipped with a 450 W Xenon arc lamp as the probe for the transient absorption measurements. In the time range 10 ns to 100  $\mu$ s, the Xenon arc lamp was pulsed. Detection in the LP920 system is performed either via a Czerny-Turner blazed 500 nm monochromator (bandwidth: 1–5 nm) coupled with a Hamamatsu R928 photomultiplier tube (kinetics mode), or via a 500 nm blazed spectrograph (bandwidth: 5 nm) coupled with a water-cooled ICCD nanosecond Andor DH720 camera (spectral mode). Samples, having absorbances of ~ 0.3 at the excitation wavelength, were purged with argon prior to each experiment.

H<sub>2</sub>P-tpy: 4-([2,2':6'',2''-Terpyridin]-4'-yl)benzoic acid (tpy-COOH) (75 mg, 0.21 mmol) was dissolved in SOCl<sub>2</sub> (2.8 mL) and stirred at 80 °C for 2 h under argon atmosphere. After that, SOCl<sub>2</sub> was removed under reduced pressure and the resulting acyl chloride terpyridine was dried under high vacuum at 50 °C for 1 h. The resulting solid was dissolved in anhydrous THF (9 mL) and then H<sub>2</sub>P-NH<sub>2</sub> (44 mg, 0.07 mmol) and anhydrous triethylamine (0.1 mL) were added. The reaction mixture was heated under argon at 70 °C overnight. The solvent was removed under reduced pressure, CHCl<sub>3</sub> (80 mL) was added and the mixture was washed with water (3  $\times$  50 mL). The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH (100:6)) to obtain the desired product ( $H_2P$ -tpy) as a purple solid (60 mg, 90%). <sup>1</sup>H NMR (300 MHz,  $(CDCl_3)$ :  $\delta$  8.88 (m, 8H), 8.82 (s, 2H), 8.76 (d, J = 4.0 Hz, 2H), 8.69 (d, J = 8.0 Hz, 2H), 8.34 (s, 1H), 8.22 (m, 8H), 8.17 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.3 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H), 7.89 (dt,  $J_1 = 1.7$  Hz,  $J_2 = 7.7$  Hz, 2H), 7.76 (m, 9H), 7.37 (ddd,  $J_1 = 7.4$  Hz,  $J_2$  = 4.8 Hz,  $J_3$  = 1.0 Hz, 2H), -2.74 (s, 2H). <sup>13</sup>C NMR (75 MHz, (CDCl<sub>3</sub>):  $\delta$  165.7, 156.4, 156.1, 149.3, 149.2, 142.3, 138.6, 137.8, 137.1, 135.4, 134.7, 131.2, 128.0, 127.9, 126.8, 124.2, 121.6, 120.3, 119.6, 119.1, 118.6. HRMS (MALDI-TOF) calcd for C<sub>66</sub>H<sub>44</sub>N<sub>8</sub>O [M]<sup>+</sup> 964.3638, found 964.3645. Elemental Analysis: Calc. for C<sub>66</sub>H<sub>44</sub>N<sub>8</sub>O: C 82.14, H 4.60, N 5.16. Found: C 82.22; H 4.73; N 5.21.

**Ru(bpy(-COOMe)<sub>2</sub>)(DMSO)<sub>2</sub>Cl<sub>2</sub>**: A solution of cis-[RulI(DMSO)<sub>4</sub>-Cl<sub>2</sub>] (484 mg, 1 mmol) and dimethyl [2,2'-bipyridine]-4,4'-dicarboxylate (156 mg, 1 mmol) in mixed EtOH (9 mL) and DMSO (1 mL) was refluxed for 1.5 h. After being allowed to cool to room temperature, the resulting orange precipitate was filtered, washed with cold EtOH, and dried in vacuum (320 mg, yield = 66%). The obtained solid was a mixture of two isomers (*cis*- and *trans*-) and used without any other purification. HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>RuS<sub>2</sub>Cl<sub>2</sub> [M]<sup>+</sup> 599.9496, found 599.9483. Elemental Analysis: Calc. for C<sub>18</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>6</sub>RuS<sub>2</sub>: C 36.00, H 4.03, N 4.67. Found: C 36.19; H 4.39; N 4.49.

H<sub>2</sub>P-Ru<sub>COOMe</sub>: The ruthenium complex Ru(bpy(-COOMe)<sub>2</sub>) (DMSO)<sub>2</sub>Cl<sub>2</sub> (55 mg, 0.11 mmol) was added to a solution of H<sub>2</sub>Ptpy (65 mg, 0.07 mmol) an acetic acid (30 mL) and the mixture was stirred under nitrogen at 100 °C overnight. After removing the solvent, the residue was purified by silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH (100:7)) giving H<sub>2</sub>P-Ru<sub>COOMe</sub> as a purple solid (73 mg, 76%). <sup>1</sup>H NMR (500 MHz,  $(CD_3)_2SO$ ):  $\delta$  11.00 (s, 1H), 10.36 (d, J = 5.8 Hz, 1H), 9.44 (s, 1H), 9.40 (s, 2H), 9.14 (d, J = 1.4 Hz, 1H), 9.06 (d, J = 8.2 Hz, 2H), 8.95 (d, J = 3.9 Hz, 2H), 8.86 (m, 6H), 8.64 (d, J = 8.3 Hz, 2H), 8.52 (dd,  $J_1 = 5.8$  Hz,  $J_2 = 1.4$  Hz, 1H), 8.47 (d, J = 8.3 Hz, 2H), 8.37 (d, J = 8.4 Hz, 2H), 8.25 (m, 8H), 8.10 (t, J = 8.0 Hz, 2H), 7.84 (m, 10H) 7.67 (d, J = 5.7 Hz, 2H), 7.49 (dd,  $J_1 = 6.1$  Hz,  $J_2 = 1.5$  Hz, 1H), 7.41 (t, J = 6.3 Hz, 2H), 4.12 (s, 3H), 3.86 (s, 3H), -2.88 (s, 2H). <sup>13</sup>C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 165.4, 164.8, 164.0, 159.3, 158.2, 157.3, 156.4, 153.2, 153.0, 152.3, 145.1, 141.3, 139.2, 139.1, 137.7, 136.6, 136.2, 135.4, 134.8, 134.3, 131.7, 128.9, 128.6, 128.2, 127.7, 127.1, 126.7, 125.9, 125.2, 124.5, 123.4, 122.8, 120.5, 120.1, 120.0, 118.9, 53.3, 53.1. IR: 1727 (v(C=O) ester), 1660 (v(C=O) amide), 1257 (v(C=O) ester). HRMS (MALDI-TOF) calcd for C<sub>80</sub>H<sub>56</sub>N<sub>10</sub>O<sub>5</sub>Ru [M-Cl]<sup>+</sup> 1338.3479, found 1338.3488. Elemental Analysis: Calc. for C<sub>80</sub>H<sub>56</sub>-

 $ClN_{10}O_5Ru;$  C 69.94, H 4.11, N 10.19. Found: C 69.78; H 4.20; N 10.28.

**ZnP-Ru**<sub>COOMe</sub>: A solution of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (85 mg, 0.39 mmol) in MeOH (3 mL) was added to a CH<sub>2</sub>Cl<sub>2</sub> (20 mL) solution of H<sub>2</sub>P-Ru<sub>COOMe</sub> (27 mg, 0.02 mmol) and the mixture was stirred at room temperature overnight. After the volatiles had been distilled off under vacuum, the residue was purified by silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH (100:8)) to collect the desirable product (**ZnP-Ru<sub>COOMe</sub>**) as a purple solid (27 mg, 95%). <sup>1</sup>H NMR (500 MHz,  $(CD_3)_2SO$ ):  $\delta$  10.93 (s, 1H), 10.35 (d, J = 5.8 Hz, 1H), 9.43 (s, 1H), 9.39 (s, 2H), 9.14 (d, J = 1.3 Hz, 1H), 9.06 (d, J = 8.3 Hz, 2H), 8.89 (d, J = 4.6 Hz, 2H), 8.81 (d, J = 4.6 Hz, 2H), 8.79 (s, 4H), 8.63 (d, J = 8.1 Hz, 2H), 8.52 (dd,  $J_1 = 5.8$  Hz,  $J_2 = 1.6$  Hz, 1H), 8.47 (d, J = 8.1 Hz, 2H), 8.32 (d, J = 8.3 Hz, 2H), 8.31 (m, 8H), 8.11 (t, J = 7.7 Hz, 2H), 7.83 (m, 10H), 7.67 (d, J = 6.1 Hz, 2H), 7.49 (m, 1H), 7.41 (t, J = 6.6 Hz, 2H), 4.12 (s, 3H), 3.87 (s, 3H). <sup>13</sup>C NMR (125 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ 165.4, 164.7, 164.0, 159.3, 158.2, 157.3, 156.4, 153.2, 153.0, 152.3, 149.5, 149.3, 145.1, 142.8, 139.1, 138.6, 138.2, 137.7, 136.3, 136.2, 135.4, 134.2, 131.6, 128.8, 127.7, 127.5, 126.7, 125.9, 125.2, 124.5, 123.4, 122.8, 120.5, 120.4, 120.2, 118.6, 53.3, 53.1. IR: 1723 (v (C=O) ester), 1660 (v(C=O) amide), 1258 (v(C-O) ester). HRMS (MALDI-TOF) calcd for  $C_{80}H_{54}N_{10}O_5RuZn [M-Cl]^+$  1400.2614, found 1400.2602. Elemental Analysis: Calc. for C<sub>80</sub>H<sub>54</sub>ClN<sub>10</sub>O<sub>5</sub>-RuZn: C 66.85, H 3.79, N 9.75. Found: C 66.97; H 3.68; N 9.84.

Ru<sub>COOMe</sub>: RuCl<sub>3</sub>·3H<sub>2</sub>O (120 mg, 0.58 mmol) and tpy-COOH (180 mg, 0.58 mmol) were dissolved in EtOH and the reaction mixture was heated for 5 h at reflux. Then, the brown intermediate [Ru (tpy-COOH)Cl<sub>3</sub>] was isolated by filtration and then treated directly with the bpy(COOMe)<sub>2</sub> ligand (170 mg, 0.64 mmol) in  $H_2O$ -EtOH (1:1), heating at reflux overnight. After cooling, EtOH was evaporated and the desired complex was precipitated, filtered and washed with water. The solid was purified by flash chromatography on silica gel using as eluent a mixture CH<sub>3</sub>CN/aqueous KNO<sub>3</sub> solution at 10% of the saturating concentration. The pure product was obtained after evaporation of CH<sub>3</sub>CN in the combined fractions and addition of an excess of NH<sub>4</sub>PF<sub>6</sub>. The precipitate was filtered, washed with water and acetone and dried under vacuum to give **Ru**<sub>COOMe</sub> as red solid (320 mg, 74%). <sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>-SO + 10% (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  10.36 (d, I = 6.1 Hz, 1H), 9.41 (d, *I* = 1.1 Hz, 1H), 9.30 (s, 2H), 9.12 (d, *I* = 1.4 Hz, 1H), 8.99 (d, I = 8.1 Hz, 2H), 8.50 (dd,  $I_1 = 5.9$  Hz,  $I_2 = 1.8$  Hz, 1H), 8.47 (d, I = 7.8 Hz, 2H), 8.25 (d, I = 7.8 Hz, 2H), 8.07 (dt,  $I_1 = 1.4$  Hz,  $I_2 = 7.8$  Hz, 2H), 7.82 (d, I = 6.0 Hz, 1H), 7.67 (dd,  $I_1 = 5.5$  Hz,  $J_2 = 0.8$  Hz, 2H), 7.47 (dd,  $J_1 = 6.0$  Hz,  $J_2 = 1.8$  Hz, 1H), 7.39 (ddd,  $J_1 = 7.3$  Hz,  $J_2 = 5.8$  Hz,  $J_1 = 1.2$  Hz, 2H), 4.12 (s, 3H), 3.86 (s, 3H). <sup>13</sup>C NMR (125 MHz, (CD<sub>3</sub>)<sub>2</sub>SO + 10% (CD<sub>3</sub>)<sub>2</sub>CO): δ 166.9, 164.7, 163.9, 159.3, 158.2, 157.3, 156.5, 153.2, 153.0, 152.3, 145.1, 140.2, 137.6, 136.3, 135.4, 132.3, 130.1, 127.8, 127.6, 125.8, 125.1, 124.4, 123.3, 122.7, 120.5, 53.2, 53.0. HRMS (MALDI-TOF) calcd for C<sub>36</sub>H<sub>26</sub>N<sub>5</sub>O<sub>6</sub>RuCl [M-H]<sup>+</sup> 761.0615, found 761.0628. Elemental Analysis: Calc. for C<sub>36</sub>H<sub>27</sub>ClN<sub>5</sub>O<sub>6</sub>Ru: C 56.73, H 3.57, N 9.19. Found: C 56.84; H 3.46; N 9.31.

#### **CRediT** authorship contribution statement

Georgios Charalambidis: Writing - review & editing, Funding acquisition, Supervision, Investigation, Methodology. Asterios Charisiadis: Writing - review & editing, Investigation, Methodology. Sofia Margiola: Investigation, Methodology. Athanassios Coutsolelos: Supervision, Project administration, Resources. Ally Aukauloo: Conceptualization, Supervision, Funding acquisition, Project administration. Winfried Leibl: Validation, Visualization, Resources, Writing - review & editing, Annamaria Quaranta: Writing - original draft, Data curation, Validation, Investigation, Methodology.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

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