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# 1 Imbroglio at a Photoredox-Iron-Porphyrin Catalyst Dyad for the 2 Photocatalytic CO<sub>2</sub> Reduction

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12 **Abstract:** We have covalently connected the ruthenium trisbipyridine complex (**bpyRu**) as a photoredox module to an iron  
13 porphyrin catalyst (**porFe**) through an amido function for investigating the synergistic action to power the photocatalytic  
14 CO<sub>2</sub> reduction. The electrochemical studies of the **porFe-bpyRu** dyad did not show any marked effect on the redox  
15 properties of the constitutive units. However, the photophysical properties of the **porFe-bpyRu** dyad point to the complete  
16 extinction of the photoredox module that undergoes ultrafast quenching processes with the **porFe** acolyte, the unavoidable  
17 dilemma in this type of molecular assemblies. Nevertheless, when exogenous **bpyRu** and a sacrificial electron donor were  
18 added to this dyad, we found that it exhibits much higher turnover number and selectivity towards CO<sub>2</sub> photocatalytic  
19 reduction to CO than with the iron porphyrin analogue (**porFe**). Comprehensive analyses of the data suggest that this  
20 catalytic enhancement displayed by the dyad can be attributed to an interesting electron relay role played by the appended  
21 **bpyRu** moiety.

22 **Keywords:** Supramolecular dyad, Iron porphyrins, Carbon dioxide reduction, Photocatalysis, Flash Photolysis

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- 3

## 1 **1. Introduction**

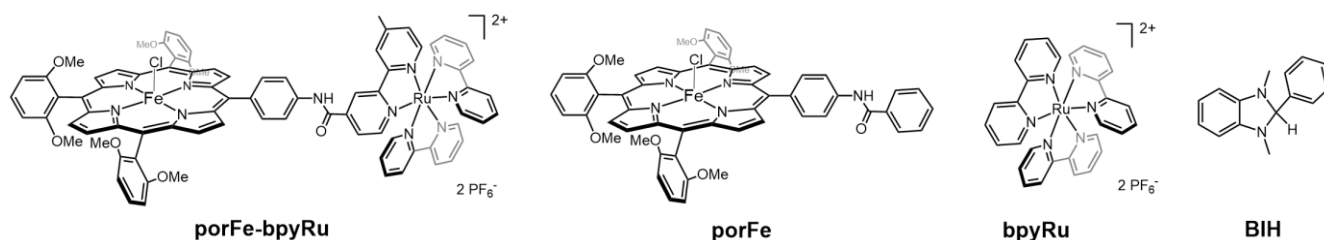
2 The photo-synthesis of reduced forms of carbon from CO<sub>2</sub> holds the promise to set us on track to mitigate the alarming  
3 anthropogenic amount of CO<sub>2</sub> we are dumping into our biosphere from the massive use of fossil fuels [1, 2]. Blueprints of  
4 this strategy are directly provided by photosynthesis and cellular respiration that have enabled the development of energy  
5 infrastructures for solar energy harnessing and its storage in chemical compounds [3]. The efficient capture of sunlight, its  
6 conversion into a chemical potential and coupled to oxidative and reductive catalytic processes are the elemental steps that  
7 must be synchronized and optimized.

8 Since the early reports in the 80s on homogeneous photocatalytic systems for CO<sub>2</sub> reduction based on transition metals  
9 [4, 5], a multitude of electron donor (ED)/photosensitizer (PS)/catalyst (Cat) combinations have been reported to reduce  
10 CO<sub>2</sub> in organic and aqueous media [6-11]. In the scheme of photocatalytic CO<sub>2</sub> reduction, the PS mediates the transfer of  
11 electrons from the ED to the Cat, but utilizes photons to drive the otherwise endergonic electron transfer steps. In a simple  
12 multicomponent approach, the three components can be simply mixed in solution and the kinetics of the electron transfer  
13 steps are expected to be diffusion-limited without kinetic advantage for a particular interaction. An alternative approach to  
14 overcome this diffusion limit and favor productive reaction steps consists of covalently attaching the PS and the Cat in a PS-  
15 Cat dyad to promote fast electron transfer from the PS to the Cat [12-15].

16 We and others have demonstrated that iron-porphyrins are one of the best performing homogeneous catalysts for the  
17 electrocatalytic reduction of CO<sub>2</sub> [16-19]. Their electrocatalytic properties such as overpotential, turnover number (TON)  
18 and turnover frequency (TOF) can be further improved by introducing substituents on the porphyrin macrocycle such as  
19 electron withdrawing or donating groups, proton relays, hydrogen bond donors or electrostatic groups [10, 11, 20-24]. When  
20 associated with a PS in a multicomponent system, iron-porphyrins were also recently shown to catalyze the photoreduction  
21 of CO<sub>2</sub> to CO [25-27], and even further to methane in some conditions [28, 29]. However, to the best of our knowledge,  
22 there are no reported supramolecular dyads consisting of an iron porphyrin catalyst and any photosensitizer [30]. This is in  
23 part due to the fact that the high absorption coefficient of the porphyrin catalyst across the visible region, overlaps and  
24 sometimes overwhelms the light-absorption role of the photosensitizer, leading to short-lived, and therefore non-productive,  
25 excited states. As such, for most multicomponent systems, there is a common trend of employing huge differences in the  
26 concentration of the iron porphyrin catalyst ( $\mu\text{M}$  range) and the photosensitizer (mM range). This piqued our curiosity to  
27 examine if a photoredox-iron-porphyrin catalyst design may lead to a new reactivity pattern.

1 In this work, we report the synthesis and characterization of a molecular assembly **porFe-bpyRu** composed of an iron  
2 porphyrin as catalyst covalently attached to a ruthenium trisbipyridine, the photosensitizer, through an amide linker (Chart  
3 1). Methoxy groups were introduced on the porphyrin as electron donating groups to enhance the nucleophilic character of  
4 the iron center and promote CO<sub>2</sub> reduction [16]. The electrochemical and photophysical properties of the **porFe-bpyRu**  
5 dyad were systematically compared with iron porphyrin (**porFe**) and ruthenium trisbipyridine (**bpyRu**) reference  
6 compounds. The electrochemical data indicate that the amide linkage does not promote strong electronic communication  
7 between the Cat and the PS, keeping the independent redox properties of the constitutive modules intact. Laser flash  
8 photolysis studies demonstrated that upon excitation of the photosensitizer in the dyad, an efficient energy transfer occurs  
9 towards the porphyrin catalyst, leading to a very fast quenching (< 20 ns) due to the presence of the Fe metal, thereby  
10 shutting off the possibility for the light activation of the catalytic unit. In the presence of an electron donor, an immediate  
11 dark electron transfer is observed in the catalyst (**porFe-bpyRu** or **porFe**) forming Fe<sup>II</sup> species from Fe<sup>III</sup>. For an  
12 independent mixture of the PS/PS-Cat and a reversible electron donor, a light induced charge shift leading to the reduced  
13 Fe(I) species was evidenced. Accordingly, upon exciting an exogenous **bpyRu** added to the **porFe-bpyRu** /electron donor  
14 mixture, a photo-induced electron transfer was observed from the exogenous Ru<sup>I</sup> photoreductant to the Fe<sup>II</sup> species,  
15 consequently forming the two-electron reduced form Fe<sup>I</sup>. More interestingly, under continuous irradiation in the presence of  
16 dimethylphenylbenzimidazole (**BIH**) as sacrificial electron donor, the **porFe-bpyRu** dyad displayed a surprisingly higher  
17 photocatalytic activity and CO<sub>2</sub>-to-CO selectivity compared to the referenced iron porphyrin (**porFe**). Comprehensive  
18 photophysical and electrochemical studies pinpoint to the fact that despite the extinction of the photophysical properties of  
19 the photosensitizer in the supramolecular dyad, its appendage to the **porFe** was beneficial inasmuch as it acts as an electron  
20 reservoir next to the catalytic unit that promotes the formation of the catalytically active species at minimal thermodynamic  
21 cost.

22



24

25 **Chart 1.** Structures and abbreviation of the **porFe-bpyRu** supramolecular complex and the corresponding model complexes **porFe** and  
26 **bpyRu** and the electron donors **BIH** and **Asc**.

26

1

2

## 3 **2. Experimental section**

### 4 **2.1. General Procedure**

5 Proton and carbon nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) spectra were recorded at room temperature on Bruker  
6 Advance spectrometers. The electrospray ionization mass spectrometry (ESI-HRMS) experiments were performed on TSQ  
7 (Thermo Scientific, 2009) with an ESI<sup>+</sup> method. Ground state absorption spectra were measured on a Specord  
8 spectrophotometer (Analytik Jena). EPR spectra were recorded at 40 K on a Bruker ELEXSYS 500 spectrometer equipped  
9 with a Bruker ER 4116DM X band resonator, an Oxford Instrument continuous flow ESR 900 cryostat, and an Oxford ITC  
10 503 temperature control system. Cyclic voltammetry measurements were performed in an electrochemical cell composed of  
11 a glassy carbon (3 mm diameter) working electrode, Ag/AgNO<sub>3</sub> (10<sup>-2</sup> M) reference electrode, and a platinum wire counter  
12 electrode with tetra-N-butylammonium hexafluorophosphate (TBAP) as supporting electrolyte. Scan rate was chosen at 100  
13 mV/s and a CH Instruments potentiostat workstation was utilized to control the applied voltages and to measure resulting  
14 current. Ferrocene was used as an internal reference and the potentials are converted to NHE. [31] Spectroelectrochemical  
15 measurements were performed in a thin-layer quartz cuvette cell using a platinum honeycomb electrode (PINE Research)  
16 and a Pt wire reference electrode. Nanosecond transient absorption measurements were performed on a home-built set-up  
17 which has been described in detail previously [32] and a commercial Edinburgh Instruments LP920 Laser Flash Photolysis  
18 Spectrometer system. Photocatalytic experiments were performed in a 41.5 mL vial containing 6.5 mL CO<sub>2</sub>-saturated  
19 DMF/H<sub>2</sub>O (9:1 v/v) + 2 μM catalyst + 50 μM photosensitizer + 50 mM electron donor. A SugarCUBE high intensity LED  
20 fiber optic illuminator was utilized with a blue light output centered at 463 nm with a full width at half maximum (FWHM)  
21 characteristic of about 50 nm, adjusted to produce 95 W m<sup>-2</sup>. The reaction vessel is connected in line with a micro gas  
22 chromatography Inficon system to analyze the products of the reaction.

23

### 24 **2.1. Synthesis and characterization**

25 **Synthesis of 1,3-dimethoxybenzene (1)**: Potassium bicarbonate, K<sub>2</sub>CO<sub>3</sub> (6.28 g, 45 mmol) and methyl iodide CH<sub>3</sub>I (2.6 mL,  
26 41.4 mmol) are added simultaneously and dropwise to a stirred solution of resorcinol (2.00 g, 18 mmol) in anhydrous  
27 acetone, at 0 °C under Ar atmosphere. The reaction mixture is stirred at room temperature for 12 h. Once reaction reached

1 completion, the volatiles are evaporated under reduced pressure and 30 mL of H<sub>2</sub>O are added to the residue. The crude  
2 product mixture is extracted with ethyl acetate (3 x 30 mL) and the combined organic layers are dried over Na<sub>2</sub>SO<sub>4</sub>. After  
3 evaporation of the solvent, the obtained residue is purified via silica column chromatography (hexane/ethyl acetate (5:1  
4 v/v)) to give 1,3-dimethoxybenzene as a light-yellow oil (1.92 g, 13.9 mmol, 77 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.19  
5 (t, J = 8.2 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 6.51 (d, J = 2.4 Hz, 1H), 6.47 (t, J = 2.4 Hz, 1H), 3.8 (s, 6H).

6  
7 **Synthesis of 2,6 dimethoxybenzaldehyde (2):** 1,3-dimethoxybenzene (1.4 mL, 1.51 g, 10.9 mmol) is dissolved in 50 mL of  
8 dry THF, under N<sub>2</sub> and the resulting solution is purged with N<sub>2</sub> for at least 20 min. Afterwards, under vigorous stirring, n-  
9 BuLi (8.2 mL, 86.8 mmol) is added dropwise at 0 °C and once the addition is completed, the reaction mixture is stirred at  
10 room temperature for 2 h under N<sub>2</sub> atmosphere. Then, dry DMF (2.1 mL, 27 mmol) is added to the solution and the mixture  
11 is stirred for an additional 2 h. After 2h, 20 mL of H<sub>2</sub>O are added and extractions with ethyl acetate (3 x 30 mL) are carried  
12 out. The collected organic layers are dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum to obtain a yellowish oily residue.  
13 The desired product was recrystallized from hexane (15 mL) and collected as a light brown solid (1.26 g, 7.6 mmol, 70%).  
14 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 10.51 (s, 1H), 7.45 (t, J = 8.5 Hz, 1H), 6.58 (d, J = 8.5 Hz, 2H) 3.90 (s, 6H).

15  
16 **Synthesis of 5-(4-nitrophenyl)-10,15,20-tris-(2,6-dimethoxyphenyl)-21H, 23H porphyrin (3):** 2,6-  
17 dimethoxybenzaldehyde (0.75 g, 4.5 mmol) and 4-nitrobenzaldehyde (0.23 g, 1.5 mmol) are dissolved in 600 mL of CHCl<sub>3</sub>  
18 and the resulting solution is subsequently purged with N<sub>2</sub> for at least 30 min under vigorous stirring. Then, pyrrole (0.42  
19 mL, 6 mmol) is added dropwise in the absence of light and the reaction mixture is purged with N<sub>2</sub> for an additional period of  
20 10 min, before BF<sub>3</sub>OEt<sub>2</sub> (233 μL, 1.88 mmol) is added. After the addition of BF<sub>3</sub>OEt<sub>2</sub>, the reaction mixture is stirred in the  
21 dark at room temperature for 3 h under N<sub>2</sub> atmosphere. Then, DDQ (1.36 g, 6 mmol) is added to the solution and it stirred  
22 for 2 h at room temperature. The resulting crude product mixture is subsequently filtered through silica pad and then is  
23 purified via silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane 4:1 (v/v)). However, only a small percentage of the desired  
24 porphyrin can be obtained clean. Given that, without any further purification, the crude mixture is used for the synthesis of  
25 5-(4-aminophenyl)-10,15,20-tris-(2,6-dimethoxyphenyl)-21H, 23H porphyrin (4). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.77 (d,  
26 J = 4.7 Hz, 2H), 8.72 (s, 4H), 8.64 (d, J = 4.7 Hz, 2H), 8.59 (d, J = 8.7 Hz, 2H), 8.39 (d, J = 8.7 Hz, 2H), 7.71 (m, 3H), 6.99  
27 (m, 6H), 3.53 (s, 6H), 3.51 (s, 12H), -2.57 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 160.7, 150.1, 147.5, 135.3, 130.3, 121.7,  
28 120.0, 119.8, 115.53, 112.2, 111.9, 104.3, 104.3, 56.2. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε, mM<sup>-1</sup> cm<sup>-1</sup>) = 419 (262.5), 514 (16.6), 550  
29 (5.5), 590 (5.3), 644 (2.5).

30

1 **Synthesis of 5-(4-aminophenyl)-10,15,20-tris-(2,6-dimethoxyphenyl)-21H, 23H porphyrin (4):** To a stirred solution of the  
2 isomeric mixture of porphyrin derivative (3) (148 mg) in DCM (15 mL), 2.5 mL of conc. HCl and SnCl<sub>2</sub>·2H<sub>2</sub>O (0.2 g, 0.89  
3 mmol) are added at 0 °C and the mixture is heated to 70 °C for at least 20 h. The progress of the reaction is monitored by  
4 thin layer chromatography (TLC, SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/ MeOH (99:1 v/v)). Upon reaction completion, 50 mL of DCM are  
5 transferred to the solution and it is left stirring for 15 min. Afterwards, the organic phase is collected, quenched with sat.  
6 aqueous solution of NaHCO<sub>3</sub> and washed thoroughly with H<sub>2</sub>O. Then, the obtained organic layer is dried over Na<sub>2</sub>SO<sub>4</sub> and  
7 evaporated until dryness. Porphyrin (4) is obtained as a purple solid after silica column chromatography (DCM/EtOH (98:2  
8 v/v)) purification (67.4 mg, 0.083 mmol, overall yield of two steps 5.5 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.77 (d, J = 4.7  
9 Hz, 2H), 8.72 (s, 4H), 8.64 (d, J = 4.7 Hz, 2H), 8.59 (d, J = 8.7 Hz, 2H), 8.39 (d, J = 8.7 Hz, 2H), 7.71 (m, 3H), 6.99 (m,  
10 6H), 3.53 (s, 6H), 3.51 (s, 12H), -2.57 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 160.7, 150.1, 147.5, 135.3, 130.3, 121.7,  
11 120.0, 119.8, 115.53, 112.2, 111.9, 104.3, 104.3, 56.2. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε, mM<sup>-1</sup> cm<sup>-1</sup>) = 419 (262.5), 514 (16.6), 550  
12 (5.5), 590 (5.3), 644 (2.5).

13

14

15 **Synthesis of 4'-methyl-4-carboxy-2,2'-bipyridine (5):** 4,4-dimethyl-2,2'-bipyridine (1.1 g, 6 mmol) is dissolved in 65 mL  
16 of 1,4-dioxane and SeO<sub>2</sub> (800 mg, 7.2 mmol) is added. The resulting solution is stirred and heated to reflux for 24 h. After  
17 24 h, the hot solution is passed through a short pad of celite to remove the elemental Se that is formed during the reaction.  
18 The filtrate once it is cooled down to room temperature, it is evaporated under reduced pressure. The obtained yellow  
19 residue is dissolved in 40 mL of EtOH and under vigorous stirring, 10 mL of aqueous solution of AgNO<sub>3</sub> (1.1 g, 6.6 mmol)  
20 is added in the absence of light. Then, over a period of 30 min, 25 mL of aqueous solution of 1M NaOH are added dropwise  
21 and the reaction mixture is stirred for 15 h at room temperature. Afterwards, the solution is concentrated under vacuum and  
22 the formed precipitate is filtered and washed first with 1.3 M NaOH (2 x 15 mL) and then with 15 mL of H<sub>2</sub>O. The filtrate is  
23 collected and extracted with DCM (4 x 30 mL). Next, the pH of the collected basic aqueous layer is adjusted to pH = 3.5 by  
24 the addition of 4.0 N HCl/CH<sub>3</sub>COOH (1:1 v/v). Upon acidification, the precipitation of a pink solid is observed and the  
25 mixture is kept at -10 °C for an additional period of 20 h for further precipitation. The precipitate is filtered and dried at 90  
26 °C for 12 h. Finally, the crude mixture is purified via a Soxhlet extractor apparatus using anhydrous acetone as the eluent for  
27 3 days. 4'-methyl-4-carboxy-2,2'-bipyridine is obtained as a light-yellow solid (255 mg, 1.19 mmol, 20 %). <sup>1</sup>H NMR (500  
28 MHz, DMSO-d<sub>6</sub>): δ = 13.89 (br s, 1H), 8.85 (br d, J = 4.9 Hz, 1H), 8.82 (br s, 1H), 8.57 (br d, J = 4.9 Hz, 1H), 8.27 (br s,  
29 1H), 7.85 (dd, J = 4.8 Hz, J = 1.4 Hz, 1H), 7.33 (br d, J = 4.8 Hz, 1H), 2.43 (s, 3H).

30



1 **Synthesis of cis-bis(2,2'-bipyridine)dichlororuthenium(II) (Ru(bpy)<sub>2</sub>Cl<sub>2</sub>) (6):** 2,2'-bipyridine (0.331 g, 2.1 mmol), 10 mL  
2 of dry DMF, RuCl<sub>3</sub> (0.200 g, 0.96 mmol) and LiCl (0.290 g, 6.75 mmol) are transferred into a two-neck round bottom flask  
3 and the resulting dark purple solution is heated to reflux overnight. After cooling down to room temperature, the formed  
4 orange precipitate is filtered and washed thoroughly first with acetone and then with H<sub>2</sub>O. Finally, it is washed with diethyl  
5 ether and hexane. Ru(bpy)<sub>2</sub>Cl<sub>2</sub> is obtained as a dark purple solid (0.160 g, 0.33 mmol, 34%). <sup>1</sup>H NMR (500 MHz, DMSO-  
6 d<sub>6</sub>): δ = 9.97 (br d, J = 4.6 Hz, 2H), 8.64 (br d, J = 7.9 Hz, 2H), 8.49 (br d, J = 7.8 Hz, 2H); 8.06 (m, 2H), 7.76 (m, 2H), 7.68  
7 (m, 2H), 7.51 (br d, J = 4.9 Hz, 2H), 7.10 (m, 2H).

8  
9 **Synthesis of compound 7:** In a schlenk tube, compound **5** (48 mg, 0.224 mmol) is dissolved in 9 mL of SOCl<sub>2</sub> and the  
10 resulting stirring solution is heated up to 78 °C under N<sub>2</sub> for 2 h. In the next step, SOCl<sub>2</sub> is evaporated under reduced  
11 pressure and to the remaining residue 15 mL of dry THF is added. Then, porphyrin (**4**) (60 mg, 0.074 mmol) and anhydrous  
12 Et<sub>3</sub>N are transferred to the solution under N<sub>2</sub>. The reaction mixture is heated up to 50 °C for 20 h. Once the reaction reaches  
13 completion, the volatiles are removed under vacuum and the crude solid is purified via column chromatography (SiO<sub>2</sub>,  
14 DCM/MeOH (99:1 v/v)) affording derivative (**7**) as a purple solid (73 mg, 0.073 mmol, 98%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  
15 δ = 8.94 (s, 1H), 8.93 (s, 1H), 8.78 (d, J = 4.7 Hz, 2H), 8.76 (s, 1H), 8.74 (d, J = 4.7 Hz, 2H), 8.71 (m, 4H), 8.61 (m, 1H),  
16 8.36 (m, 1H), 8.21 (d, J = 8.5 Hz, 2H), 8.07 (d, J = 8.3 Hz, 2H), 8.01 (dd, J<sub>1</sub> = 4.8 Hz, J<sub>2</sub> = 1.9 Hz, 1H), 7.70 (t, J = 8.5 Hz,  
17 3H), 7.23 (m, 1H), 6.99 (m, 6H), 3.52 (s, 6H), 3.50 (s, 12H), 2.53 (s, 3H), -2.59 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ =  
18 164.2, 160.7, 157.4, 155.1, 150.6, 149.2, 148.8, 143.3, 139.5, 137.1, 135.2, 131.9, 130.2, 125.6, 122.5, 122.2, 120.1, 119.9,  
19 118.6, 118.1, 117.5, 111.7, 111.0, 104.3, 56.2, 21.4. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε, mM<sup>-1</sup> cm<sup>-1</sup>) = 419 (382.9), 513 (16.5), 546  
20 (5.4), 589 (4.9), 645 (2.5).

21  
22 **Synthesis of compound 8:** To a stirring solution of porphyrin derivate (**4**) (45 mg, 0.06 mmol) in dry THF, benzoyl chloride  
23 (50 μL, 0.38 mmol) and 70 μL of dry Et<sub>3</sub>N are added. The mixture is heated up to 70 °C for 12 h under N<sub>2</sub> atm. Afterwards,  
24 THF and Et<sub>3</sub>N are evaporated under reduced pressure and the reaction product mixture is purified by column  
25 chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/ EtOH (99.7/0.3 v/v)). The desired product is afforded as a purple solid (40 mg, 0.043  
26 mmol, 73%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.76 (d, J = 4.7 Hz, 2H), 8.72 (m, 6H), 8.14 (d, J = 8.4 Hz, 2H), 8.12 (s, 1H),  
27 7.98 (m, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.69 (m, 3H), 7.58 (m, 1H), 7.52 (m, 2H), 6.98 (m, 6H), 3.51 (s, 6H), 3.49 (s, 12H), -  
28 2.53 (br s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 166.1, 160.7, 139.0, 137.4, 135.1, 132.0, 130.1, 129.0, 127.3, 126.4, 120.3,  
29 120.0, 118.2, 111.6, 110.9, 104.3, 56.2. UV/Vis (CH<sub>3</sub>CN): λ<sub>max</sub> (ε, mM<sup>-1</sup> cm<sup>-1</sup>) = 415 (401.1), 511 (17.3), 544 (6.0), 588  
30 (5.1), 644 (2.8).

1  
2 **Synthesis of compound 9:** In a two-neck round bottom flask, porphyrin (7) (60 mg, 0.06 mmol) is dissolved in 38 mL of  
3 CH<sub>3</sub>COOH and the stirring solution is purged with N<sub>2</sub> for 15 min at room temperature. After degassing, Ru(bpy)<sub>2</sub>Cl<sub>2</sub> (57.6  
4 mg, 0.12 mmol) is transferred to the flask and the reaction mixture is heated to reflux for 12 h under N<sub>2</sub>. Then CH<sub>3</sub>COOH is  
5 evaporated under reduced pressure and the obtained orange reddish residue is washed with H<sub>2</sub>O (5 x 20 mL). Then, the  
6 crude residue is purified by column chromatography (SiO<sub>2</sub>, CH<sub>3</sub>CN/H<sub>2</sub>O/KNO<sub>3(sat)</sub> (30:2:1 v/v)). Afterwards, the counter  
7 anions of Ru<sup>II</sup> are exchanged with PF<sub>6</sub><sup>-</sup> anions. More specifically, the dyad is dissolved in the minimum amount of CH<sub>3</sub>CN  
8 and to the resulting solution, a saturated solution of NH<sub>4</sub>PF<sub>6</sub> in MeOH is added. Then, H<sub>2</sub>O was added slowly. Upon  
9 addition of H<sub>2</sub>O, the precipitation of a brown-purple solid is observed. The precipitate is subsequently filtered and washed  
10 thoroughly with H<sub>2</sub>O to remove the excess of the NH<sub>4</sub>PF<sub>6</sub> salt giving porphyrin derivative (9) as an orange-purple solid (21  
11 mg, 0.012 mmol, 20%). <sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 10.50 (br s, 1H), 9.43 (s, 1H), 8.98 (s, 1H), 8.76 (s, 1H), 8.76  
12 (s, 4H), 8.73 (s, 4H), 8.64 (br s, 2H), 8.39 (br s, 2H), 8.26 (d, J = 8.2 Hz, 2H), 8.16-8.09 (m, 2H), 8.03-7.95 (m, 5H), 7.84  
13 (br d, J = 5.6 Hz, 1H), 7.79 (t, J = 8.6 Hz, 3H), 7.57-7.49 (m, 4H), 7.45 (d, J = 5.4 Hz, 1H), 7.14 (d, J = 8.6 Hz, 6H), 3.52 (s,  
14 18H), 2.61 (s, 3H), -2.50 (s, 2H). <sup>13</sup>C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 163.3, 161.3, 159.0, 157.8, 157.1, 153.2, 152.5,  
15 152.4, 151.7, 151.6, 144.2, 139.3, 138.9, 138.7, 135.5, 131.4, 129.9, 128.6, 126.7, 126.3, 125.1, 125.0, 122.9, 120.0, 199.7,  
16 119.4, 118.9, 113.0, 112.6, 104.9, 56.1, 21.2. UV/Vis (CH<sub>3</sub>CN): λ<sub>max</sub> (ε, mM<sup>-1</sup> cm<sup>-1</sup>) = 288 (87.8), 415 (413.5), 476 (22.9),  
17 510 (24.2), 544 (9.3), 587 (6.7), 642 (4.1).

18  
19 **Synthesis of porFe-bpyRu:** FeBr<sub>2</sub> (0.088 gr, 0.41 mmol) and derivate (9) (0.023 gr, 0.014 mmol) are dissolved in 5 mL of  
20 dry and degassed THF. The reaction mixture is kept under stirring and heated at 50 °C for 12h under Ar. The progress of the  
21 reaction is monitored by absorption spectroscopy. Once the reaction is completed, THF is evaporated under reduced  
22 pressure. The remaining solid is dissolved in 20 mL of DCM and treated with 4N HCl (3 x 15 mL). The organic layers are  
23 combined, washed with H<sub>2</sub>O (3 x 15 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product is purified via silica column  
24 chromatography (CH<sub>3</sub>CN/H<sub>2</sub>O/KNO<sub>3(sat)</sub> (30:2:1 v/v)). Then, the counter anions of Ru<sup>II</sup> were exchanged with PF<sub>6</sub><sup>-</sup> anions, as  
25 described previously for the synthesis of compound 9. The final compound is given as an orange-purple solid (18 mg, 0.010  
26 mmol, 71%). UV/Vis (CH<sub>3</sub>CN): λ<sub>max</sub> (ε, mM<sup>-1</sup> cm<sup>-1</sup>) = 288 (83.0), 377 (59.4), 417 (95.8), 465 (27.7), 505 (17.9), 576 (5.3),  
27 655 (4.1), 689 (4.3). **ESI-HRMS:** m/z calculated for a chemical formula C<sub>82</sub>H<sub>65</sub>ClFeN<sub>11</sub>O<sub>7</sub>Ru<sup>2+</sup> [M]<sup>2+</sup> = 754.1543, found  
28 754.1580.

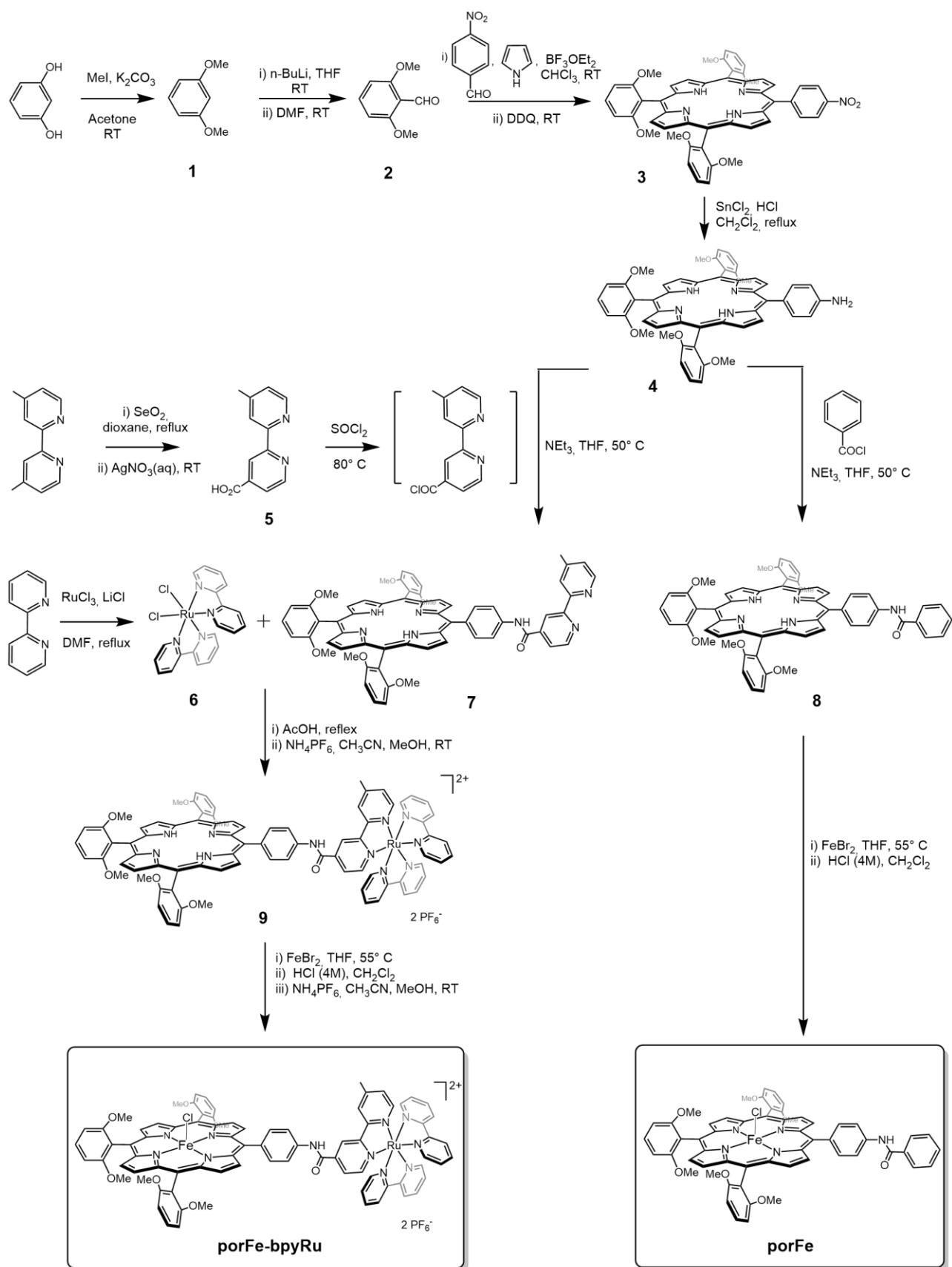
29

1 **Synthesis of porFe:** To a solution of FeBr<sub>2</sub> (0.272 gr, 1.27 mmol) in 5 mL of dry and degassed THF, porphyrin (**7**) (0.037  
2 gr, 0.041 mmol) is added and the mixture of the reaction and heated at 55 °C for 12h under Ar. After reaction reaches  
3 completion, THF is evaporated and the residue is dissolved in 20 mL of DCM. Then, 15 mL of 4N HCl is added. The  
4 organic phase is collected and extracted for additional two times with 4N HCl (2 x 15 mL). Finally, the organic layers are  
5 collected, washed with H<sub>2</sub>O (3 x 15 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. **PorFe** is afforded as an orange-purple solid after column  
6 chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (99:1 v/v)) purification (24 mg, 0.024 mmol, 58%). **UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):** λ<sub>max</sub> (ε, mM<sup>-1</sup>  
7 cm<sup>-1</sup>) = 274 (31.6), 341 (32.0), 417 (87.2), 499 (11.2), 506 (11.0), 577 (5.4), 640 (3.0). **ESI-HRMS:** m/z calculated for a  
8 chemical formula C<sub>57</sub>H<sub>45</sub>FeN<sub>5</sub>O<sub>7</sub> [M - Cl]<sup>+</sup> = 967.2619, found 967.2664.

### 9 **3. Results and discussion**

#### 10 **3.1. Synthesis**

11 As shown in Scheme 1, dyad **porFe-bpyRu** and iron-porphyrin **porFe** share the same porphyrin platform **4**. This synthetic  
12 intermediate was prepared in an acid-catalyzed condensation of four pyrroles, one *para*-nitrobenzaldehyde and three di-  
13 *ortho*-methoxybenzaldehyde (**2**) followed by an oxidation of the obtained macrocycle using dichloro-5,6-dicyano-p-  
14 benzoquinone (DDQ), then by a reduction of the nitro group into amino using tin chloride in acidic conditions. Aldehyde **2**  
15 was obtained in two steps from resorcinol by first methylating the hydroxy groups and then a lithium-mediated formylation  
16 reaction of the aromatic carbon in position 2 takes places. The coupling between porphyrin **4** and one of the bipyridines of  
17 the **bpyRu** moiety was performed using modified bipyridine **5** bearing a carboxyl group in position 4 that was prepared by a  
18 SeO<sub>2</sub> oxidation of one of the methyl groups in the 4,4'-dimethyl-2,2'-bipyridyl. After an activation of the carboxyl group  
19 using thionyl chloride, **5** reacts with the aniline group in porphyrin **4** to yield the amide-bridged porphyrin-bipyridine ligand  
20 **7**. The bipyridine in **7** can displace the two chlorides of the dichlorobis(bipyridine)ruthenium **6** to form the porphyrin-bpyRu  
21 complex (**9**) that leads, after complexation of the iron, to the aimed dyad **porFe-bpyRu**. Reference iron-porphyrin **porFe**  
22 was prepared using a similar synthetic scheme and by replacing the bipyridine **5** with benzoyl chloride.

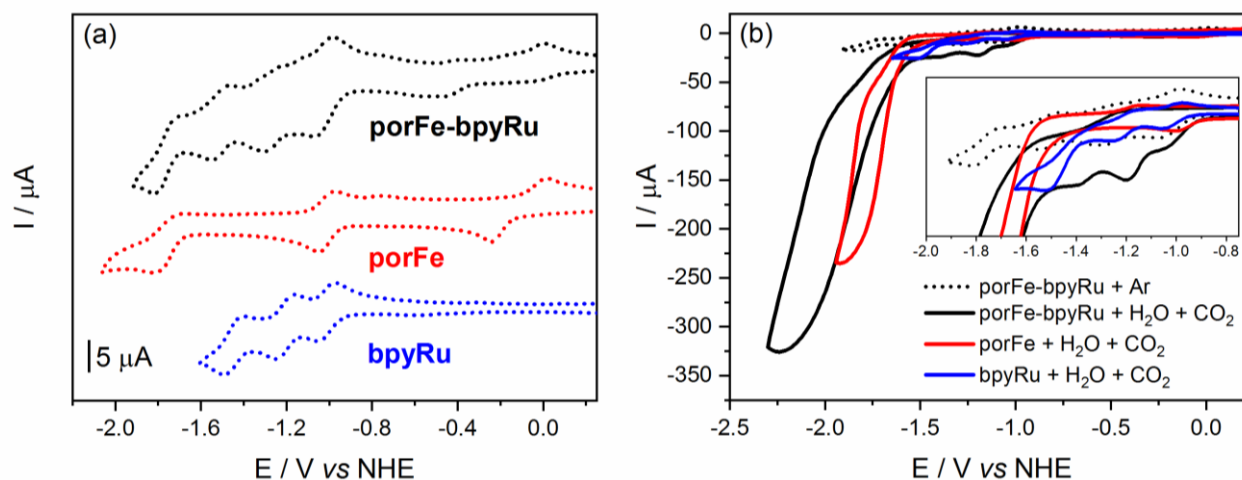


1

2 **Scheme 1.** Synthesis of the **porFe-bpyRu** supramolecular complex and the corresponding reference complex **porFe**.

### 3.2. Electrochemical characterization

Cyclic voltammetry (CV) of model compound **porFe** in argon-degassed dimethylformamide (DMF) containing 100 mM of tetra-N-butylammonium hexafluorophosphate (TBAP) shows three reversible redox waves corresponding to the formal  $\text{Fe}^{\text{III/II}}$ ,  $\text{Fe}^{\text{II/I}}$ , and  $\text{Fe}^{\text{I/0}}$  couples (Fig. 1a, Table 1). As expected, due to the presence of the methoxyl groups, these three waves are shifted to more negative potentials compared to those of the previously reported non-functionalized iron-tetraphenyl-porphyrin (**FeTPP**) [18]. Three successive reduction waves are also observed for **bpyRu** complex which were previously reported to be mainly centered on the bipyridine ligands [33]. The CV of **porFe-bpyRu** displays a combination of the **porFe** and **bpyRu** reduction waves. A noticeable anodic shift of about 100 mV is observed for the  $\text{Fe}^{\text{III/II}}$  couple in the dyad compared to the reference complex but no significant shifts are observed for the  $\text{Fe}^{\text{II/I}}$  and  $\text{Fe}^{\text{I/0}}$  redox couples. Similarly, the bpy-based reduction waves of the Ru moiety in the dyad showed minimal anodic shifts of around 5 mV. These are all indicative that the amide linker does not establish a strong electronic communication between the two moieties. The redox couples  $\text{Fe}^{\text{II/I}}$  and  $\text{Ru}^{\text{II/I}}$  overlap in the dyad as a two-electron reduction wave, which is indicative that the one-electron reduced form of the PS can reduce both the  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  states of the catalyst in the dyad with thermodynamic driving force of 0 and -800 meV, respectively. However, this same photoreductant would have an uphill penalty of +760 meV to reduce the iron-porphyrin moiety to its catalytically active  $\text{Fe}^0$  form.



**Fig. 1.** Cyclic voltammograms (CV) of the supramolecular and reference complexes at concentrations of 0.5 mM in dimethylformamide with 100 mM tetra-N-butylammonium hexafluorophosphate (a) under Ar and (b) under  $\text{CO}_2$  and 5.5 mM  $\text{H}_2\text{O}$ . Inset in (b) shows magnification of the onset of catalysis.

1 **Table 1.** Electrochemical potentials of the formal redox couples involved in the supramolecular and reference complexes, referenced vs  
 2 NHE in dimethylformamide with 100 mM tetra-N-butylammonium hexafluorophosphate.

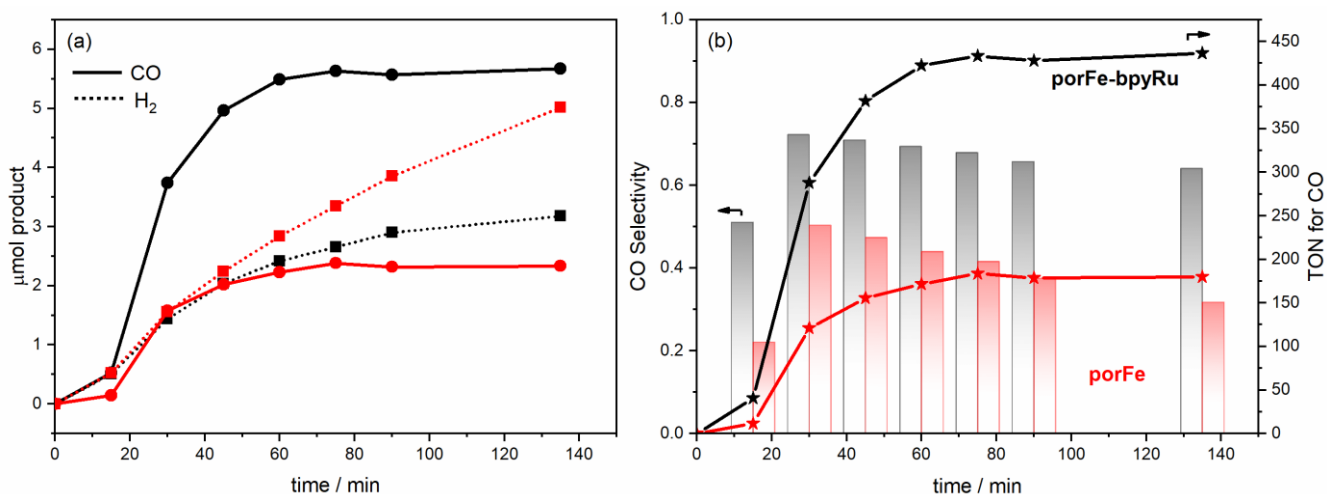
Complex	Fe <sup>III/II</sup>	Fe <sup>II/I</sup>	Fe <sup>I/0</sup>	Ru <sup>III/I</sup>	Ru <sup>I/0</sup>	Ru <sup>0/-I</sup>
<b>porFe-bpyRu</b>	-0.23	-1.03	-1.77	-1.03	-1.27	-1.51
<b>porFe</b>	-0.12	-1.02	-1.76	-	-	-
<b>bpyRu</b>	-	-	-	-1.01	-1.21	-1.45

3  
 4 When the CVs were performed under a CO<sub>2</sub> atmosphere and in presence of water as a proton source (Fig. 1b),  
 5 **porFe** and **porFe-bpyRu** displayed a typical catalytic current corresponding to CO<sub>2</sub> reduction at the last reduction wave  
 6 (Fe<sup>I/0</sup> redox couple) with a significantly higher current intensity in the case of **porFe-bpyRu**. More interestingly, the onset  
 7 potential of catalysis started at a significantly more positive potential in the dyad (Fig. 1b inset), almost at the Fe<sup>II/I</sup> and Ru<sup>III/I</sup>  
 8 waves with a smaller current intensity increase preceding a much higher current observed after -1.5 V. A control experiment  
 9 with **bpyRu** in the same conditions shows minimal current intensity increase and only at the third bpy-reduction wave,  
 10 confirming that the iron-porphyrin catalyst is responsible for the observed catalytic wave in the **porFe-bpyRu** dyad. The  
 11 early onset potential for the first catalytic regime of the dyad takes place right after the electro-generation of the Fe(I)  
 12 species that is accompanied concomitantly with addition of one electron on the bipyridine holding the PS and the Cat. This  
 13 proposal is based on the fact that the bridging bipyridine is chemically modified with a C-terminated amido group and is  
 14 under the influence of two metallic cations, rendering it the privilege locus for the addition of an electron as compare to the  
 15 other two bipyridine ligands. This species can therefore be looked at as an Fe<sup>I</sup> coupled to an anion radical species that can  
 16 trigger the catalytic activity.

### 17 3.2. Photocatalytic Evaluation

18 Motivated by the promising results from the electrochemical measurements, we undertook the evaluation of the  
 19 photocatalytic performance of the supramolecular dyad toward CO<sub>2</sub> reduction. An initial experiment was performed by  
 20 irradiating with a blue LED source a solution containing 2 μM **porFe-bpyRu** as photo-catalyst and 50 mM **BIH** as  
 21 sacrificial electron donor in DMF/H<sub>2</sub>O (9:1 v/v). Unfortunately, the gas chromatography analysis of the reaction vessel  
 22 headspace was not able to detect any gas product. In the same conditions but in a bimolecular configuration using 2 μM  
 23 **porFe** as catalyst and 50 μM **bpyRu** as PS, the reaction produces 5.0 μmol of H<sub>2</sub> as the major product and 2.3 μmol of CO.  
 24 However, in a hybrid configuration where exogenous **bpyRu** (50 μM) in combination with 2 μM **porFe-bpyRu** were used,

1 5.7  $\mu\text{mol}$  CO and 3.2  $\mu\text{mol}$  H<sub>2</sub> were produced after 135 minutes of irradiation (Fig. 2a). To ascertain that the photocatalytic  
 2 activity comes mainly from the dyad, a control experiment was performed with 50  $\mu\text{M}$  of **bpyRu** and in absence of the  
 3 dyad. Under these conditions, much smaller amounts of CO (1.4  $\mu\text{mol}$ ) and H<sub>2</sub> (0.5  $\mu\text{mol}$ ) are produced (Fig. S1), possibly  
 4 due the minor CO<sub>2</sub> reduction activity of the Ru bisbipyridyl, a degradation product of **bpyRu** that was shown to form in  
 5 absence of the electron acceptor, in this case the Cat, and exhibit some CO<sub>2</sub> reduction activity [34-36]. In the same catalytic  
 6 conditions, the **porFe-bpyRu** dyad displays a higher selectivity (~70%) for CO production (Fig. 2b) during the course of  
 7 photocatalysis, while in the case of **porFe** the selectivity was below 40%. This improved selectivity exhibited by the  
 8 supramolecular **porFe-bpyRu** dyad also translates in a significantly higher TON of 440 compared to that obtained with the  
 9 **porFe** as catalyst (TON = 180). Even though the **porFe-bpyRu** dyad didn't fulfill the initially intended photo-catalyst role,  
 10 it surprisingly improves the selectivity and TON when used as a catalyst in presence of exogenous PS.



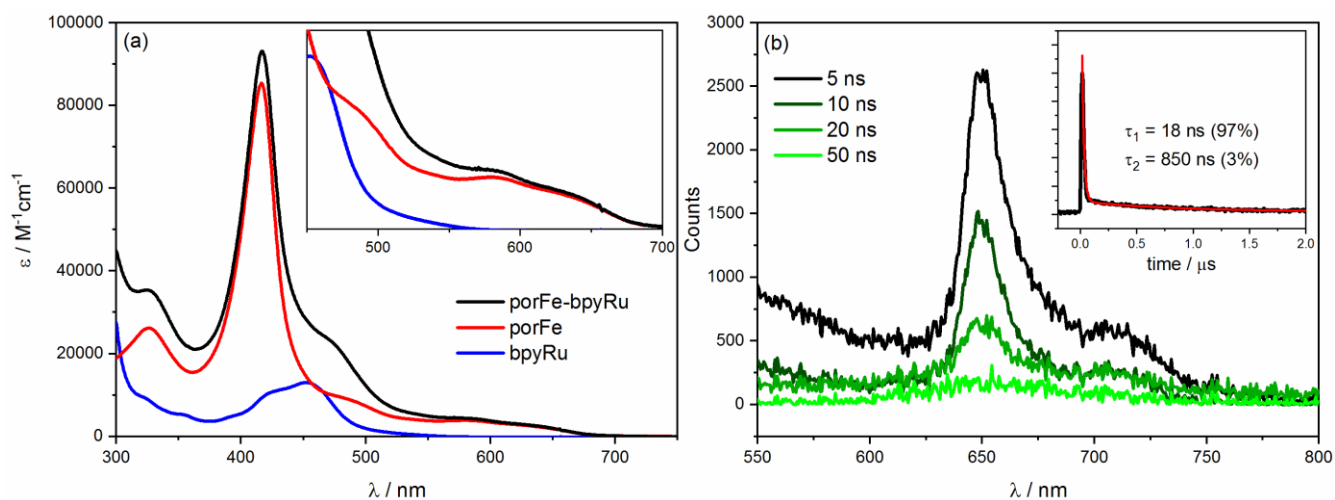
11  
 12 **Fig. 2.** (a) Photocatalytic curves for the production of CO (solid lines) and H<sub>2</sub> (dotted lines) during the irradiation of the  
 13 following in CO<sub>2</sub>-saturated DMF/H<sub>2</sub>O (9:1 v/v): 2  $\mu\text{M}$  **porFe-bpyRu** + 50  $\mu\text{M}$  **bpyRu** + 50 mM **BIH** (black); 2  $\mu\text{M}$  **porFe**  
 14 + 50  $\mu\text{M}$  **bpyRu** + 50 mM **BIH** (red). (b) Comparison of the photocatalytic performance in terms of selectivity towards CO  
 15 production (columns) and turnover numbers (TON).

16

### 17 3.3. Photophysical and mechanistic analyses

18 The intriguing and peculiar photocatalytic performance of the **porFe-bpyRu** dyad merited further photophysical  
 19 investigation. The absorption spectrum of the dyad (Fig. 3a) consists of combination of spectral features of the mononuclear  
 20 complexes **porFe** and **bpyRu**: a Soret band at 417 nm and Q bands at 490, 585, and 635 nm characteristic of the iron

1 porphyrin catalyst and the <sup>3</sup>MLCT band of Ru PS as broad shoulder at 460 nm. The absence of significant spectral changes  
 2 between the **porFe-bpyRu** dyad and the mixture of **porFe** and **bpyRu** confirm the previous observation that the amide  
 3 linkage does not alter the electronic properties of the individual components in the ground state. Upon excitation at 460 nm  
 4 to excite mainly the Ru PS (a similar excitation domain of the blue LED lamp employed in the photocatalytic experiments),  
 5 only emission from the **porFe** could be detected (Fig. 3b; narrow band at 650 nm with a shoulder at 700 nm). The absence  
 6 of emission from the Ru excited state, expected as a broad band at 610 nm, is indicative of ultrafast quenching of the Ru  
 7 excited state. As expected, the lifetime of the **porFe** fluorescence is shorter than the time resolution (20 ns) of the ns laser  
 8 flash photolysis apparatus. No transient absorption peaks were observed (even at the shortest time scale of the experiment)  
 9 indicating the absence of any long-lived excited triplet Ru species. These observations are attributed to (a) an efficient energy  
 10 transfer from the excited singlet Ru species to singlet porphyrin, which is then significantly quenched due to the presence of  
 11 the heavy Fe metal center, and (b) competing photon absorption (~ 50 %) between the PS and the Cat.  
 12



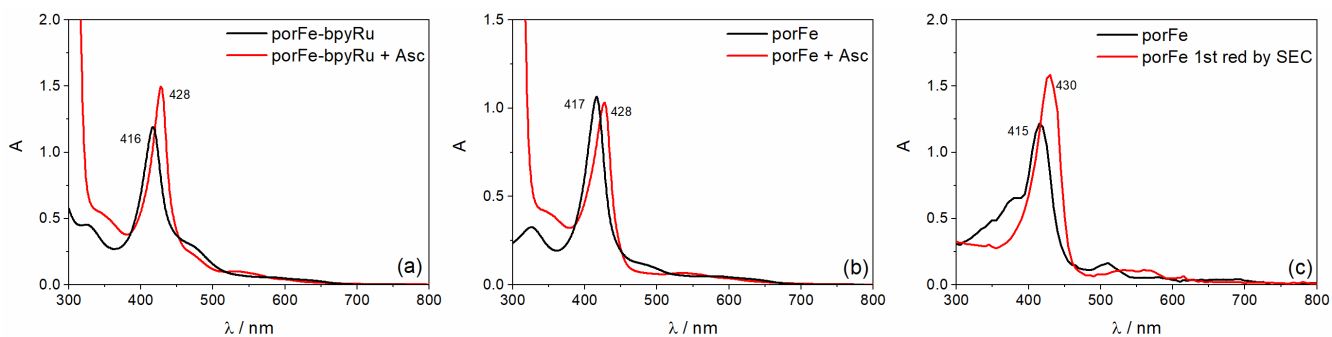
13  
 14 **Fig. 3.** (a) Absorption spectra of of the supramoleclar **porFe-bpyRu** dyad in comparison with the reference complexes in  
 15 ACN/H<sub>2</sub>O (6:4 v/v). Inset shows magnification of the Q bands region. (b) Transient emission spectra of **porFe-bpyRu** in  
 16 DMF upon laser excitation at 460 nm. Inset shows kinetics at 650 nm revealing emission lifetime of 18 ns. Similar transient  
 17 emission was recorded in ACN/H<sub>2</sub>O (Fig. S2).

18  
 19 Upon addition of sodium ascorbate (Asc) as a reversible electron donor for the photophysical measurements, a  
 20 noticeable red shift in the Soret band (416 nm  $\rightarrow$  428 nm) of the ground state spectrum of **porFe-bpyRu** was observed in  
 21 Ar-saturated ACN/H<sub>2</sub>O solutions (Fig. 4a). A similar shift was observed for the reference **porFe** catalyst (Fig. 4b),  
 22 indicating that there is a dark chemical reaction occurring between the Asc and the catalyst. Spectroelectrochemical



1 measurement on the reference complex **porFe** shows a similar characteristic red-shift of the Soret band for the Fe<sup>II</sup> species  
 2 (Fig. 4c and S3-S4) which indicates that the observed red shift of the Soret band is due to the reduction of Fe<sup>III</sup> to Fe<sup>II</sup>. A  
 3 similar reduction of Fe<sup>III</sup> is occurring when **BIH** was used as sacrificial electron donor. The electron paramagnetic  
 4 resonance (EPR) spectra of **porFe-bpyRu** (Fig. S5) shows the disappearance of the high spin Fe<sup>III</sup> signal upon addition of  
 5 the electron donor in the dark. We also investigated the photophysical properties of the singly reduced Fe<sup>II</sup> state of **porFe-**  
 6 **bpyRu** upon excitation at 460 nm. Here too, no transient absorption peaks were observed. Hence, revealing again an  
 7 efficient quenching of any excited states. Accordingly, the absence of long-lived excited species and the lack of light-  
 8 induced electron transfer processes leading to reduced species for redox reactions, explain why the **porFe-bpyRu** dyad in  
 9 the presence of **BIH** did not show any photocatalytic CO<sub>2</sub> reduction activity under continuous illumination. Therefore, these  
 10 results highlight that linking the **bpyRu** PS and **porFe** catalyst through the single amido function was disadvantageous in  
 11 the scenario of eliminating the diffusion control limits in the photo-driven electron transfer processes and catalysis. Reasons  
 12 behind this in our particular case probably originate from the competition for photon absorption between the catalyst and the  
 13 photosensitizer, a mismatch of emission and absorption properties of both constitutive chromophores and finally the short  
 14 distance between the two modules which promote an efficient energy transfer and quenching of the excited states.

15



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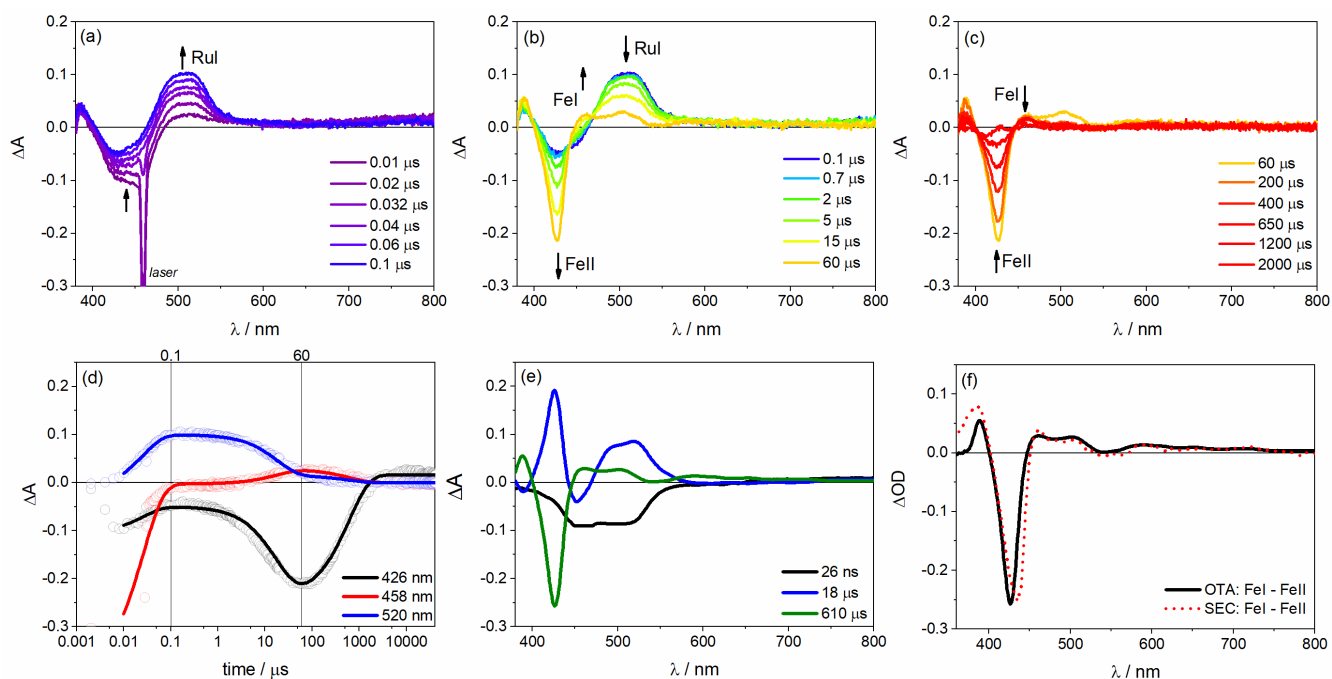
17 **Fig. 4.** UV-Vis spectral changes when **Asc** is added to a solution of (a) **porFe-bpyRu** or (b) **porFe** in Ar-saturated  
 18 ACN/H<sub>2</sub>O (6:4 v/v) and its similarity to (c) the spectral evolution during the 1<sup>st</sup> reduction Fe<sup>III</sup> → Fe<sup>II</sup> of **porFe** in ACN  
 19 using spectroelectrochemistry, SEC (more details in Fig. S3).

20

21 As it turns out, the photoredox-catalyst molecular dyad did not lead to the expected photo-induced charge  
 22 separation and charge accumulation towards the catalyst. We then pursue the photophysical investigation by the addition of  
 23 an exogenous ruthenium (II) trisbipyridine photosensitizer (**bpyRu**) together with a reversible electron donor considering  
 24 the **porFe-bpyRu** as basically a dyad with an extinct photosensitizer unit but with a functioning **porFe** catalyst unit. In this  
 25 configuration, photo-induced electron transfer steps are observed as summarized in Fig. 6a-6c. At short time domain (0 –

1 100 ns in Fig. 6a), upon laser excitation at 460 nm and formation of the excited state Ru\* (bleaching of Ru<sup>II</sup> MLCT at 450  
 2 nm), there is a simultaneous formation of the one-electron reduced form of the PS, formal Ru<sup>I</sup> species, characterized by an  
 3 absorption at 520 nm, and oxidized Asc<sup>++</sup> (absorbing at 360 nm). Global fitting of the kinetic traces with a triexponential  
 4 function  $[a_1\exp(-t/\tau_1) + a_2\exp(-t/\tau_2) + a_3\exp(-t/\tau_3) + c]$  gave satisfactory fits (Fig. 6d). This first photo-induced electron  
 5 transfer event (Ru<sup>II</sup> + Asc → Ru<sup>I</sup> + Asc<sup>++</sup>) occurs with an apparent time constant of 26 ns with 100 mM Asc. In the  
 6 proceeding time scale (100 ns to 60 μs in Fig. 6b), the Ru<sup>I</sup> species decays to give a new spectral feature at 458 nm,  
 7 corresponding to the reduction from the Fe<sup>II</sup> to Fe<sup>I</sup> oxidation state of the porphyrin catalyst moiety of the **porFe-bpyRu**  
 8 dyad. This is confirmed by two control experiments: (a) similar transient absorption changes are observed for the solution  
 9 containing the reference complexes **porFe**, **bpyRu** and **Asc** in the similar time window (Fig. S6) and (b) a similar  
 10 differential spectrum is observed during spectroelectrochemical measurement of the reference complex **porFe** when going  
 11 from the Fe<sup>II</sup> to the Fe<sup>I</sup> oxidation states (Fig. 6e, 6f and S3). This second electron transfer event (Ru<sup>I</sup> + Fe<sup>II</sup> → Ru<sup>II</sup> + Fe<sup>I</sup>)  
 12 occurs with a diffusion-limited second order rate constant of  $7.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  estimated from the apparent time constant of  
 13 18 μs and formation of 7.1 μM Fe<sup>I</sup>. Finally, at longer time scale (> 60 μs in Fig. 6c), this Fe<sup>I</sup> species decays back to the Fe<sup>II</sup>  
 14 state after charge recombination with oxidized Asc<sup>++</sup> (Fe<sup>I</sup> + Asc<sup>++</sup> → Fe<sup>II</sup> + Asc) with a time constant of 610 μs.

15



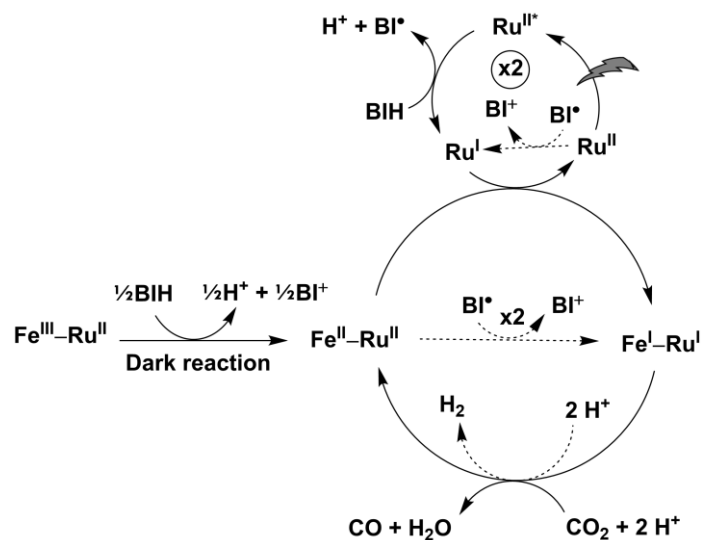
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17 **Fig. 6.** (a-c) Optical transient absorption (OTA) spectra in three time domains showing the spectral evolution of each  
 18 species during single flash photolysis of a solution containing 13 μM **porFe-bpyRu** dyad, 31 μM **bpyRu**, and 100 mM **Asc**  
 19 in ACN/H<sub>2</sub>O (6:4 v/v) [laser excitation at 460 nm, 10 mJ per pulse]. (d) Globally-fitted transient kinetics at some

1 wavelengths with fitting parameters used to plot the (e) decay-associated difference spectra. (f) Comparison of the OTA  
2 decay spectra corresponding to ( $\text{Fe}^{\text{I}} - \text{Fe}^{\text{II}}$ ) with that obtained from spectroelectrochemistry (SEC) in Fig. S3 (in the absence  
3 of  $\text{H}_2\text{O}$ ).

4  
5 These photophysical investigations have shown that when the **porFe-bpyRu** dyad is assimilated as only the  
6 catalyst in the presence of exogenous ruthenium (II) trisbipyridine photosensitizer and a sacrificial electron donor, three  
7 electrons can be accumulated on the catalyst to form the  $\text{Fe}^{\text{I}}\text{-Ru}^{\text{II}}$  species: one electron coming from a dark reaction with the  
8 electron donor and two electrons coming from the photo-induced  $\text{Ru}^{\text{I}}$  reductant. These first three electron transfer events are  
9 similarly envisioned as the initial steps in the proposed photocatalytic cycle in Fig. 7. However, from the CV of **porFe**  
10 catalyst (Fig. 1b) it is clear that the  $\text{Fe}^{\text{0}}$  oxidation state must be reached before the catalytic reduction of  $\text{CO}_2$  can proceed.  
11 With this thermodynamic constraint, the  $\text{Ru}^{\text{I}}$  photo-reductant faces an uphill thermodynamic penalty of +760 meV to  
12 proceed. An alternative route may come from the non-innocent reducing radical  $\text{BI}^{\cdot}$  resulting from the first electron donor  
13 step of BIH ( $E = -1.39 \text{ V vs NHE}$  [37] ensuing a less positive  $\Delta G \sim +370 \text{ meV}$  for this reaction), as we and others have  
14 previously reported [38-40]. However, an interesting feature of the **porFe-bpyRu** dyad is the possibility for the appended  
15 ruthenium (II) trisbipyridine to act as an electron reservoir, as suggested by the earlier onset of catalysis (Fig. 1b) occurring  
16 at a potential corresponding to the  $\text{Fe}^{\text{III}}$  and  $\text{Ru}^{\text{III}}$  couples. Since there is only a minimal driving force for the exogenous  $\text{Ru}^{\text{I}}$   
17 photo-reductant to reduce the appended Ru moiety in the dyad ( $\Delta G \sim +20 \text{ meV}$ ), we hypothesize that this occurs to form a  
18  $\text{Fe}^{\text{I}}\text{-Ru}^{\text{I}}$  state of the dyad:  $\text{Fe}^{\text{I}}\text{-Ru}^{\text{II}} + \text{Ru}^{\text{I}} \rightarrow \text{Fe}^{\text{I}}\text{-Ru}^{\text{I}} + \text{Ru}^{\text{II}}$ . The formal  $\text{Fe}^{\text{I}}\text{-Ru}^{\text{I}}$  state can then be regarded as an  $\text{Fe}^{\text{I}}$  species  
19 backed up by an additional electron with the same reducing power probably delocalized on the bipyridine extending onto  
20 the porphyrin macrocycle. Such a reduced species may then start the two-electron activation of  $\text{CO}_2$  at a lower overpotential  
21 than the classic  $\text{Fe}^{\text{0}}$  active form. The lower thermodynamic penalty along this route can account for the higher performances  
22 of the **porFe-bpyRu** dyad, in terms of TON and CO selectivity, than the **porFe** catalyst in the presence of the same amount  
23 of exogenous ruthenium (II) trisbipyridine as photosensitizer. As a consequence, even though the **bpyRu** photoredox unit in  
24 the **porFe-bpyRu** dyad is shut down due to fast deleterious energy transfer processes, it assists in lowering the overpotential  
25 for  $\text{CO}_2$  reduction by acting as a reservoir for providing an extra reducing power to ignite the catalysis at the formal  $\text{Fe}^{\text{I}}$  state  
26 of the catalyst.

27



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**Fig. 7.** Proposed photocatalytic cycle involving the supramolecular **porFe-bpyRu** dyad and exogenous **bpyRu** PS with BIH as sacrificial electron donor. Dashed arrows show competing minor pathways.

#### 5 **4. Conclusion**

6 We have synthesized a new photoredox-catalyst couple, the **porFe-bpyRu**, where a ruthenium (II) trisbipyridine  
7 photosensitizer **bpyRu** is covalently attached to an iron porphyrin catalyst **porFe** through an amide linker. We found that  
8 this molecular dyad did not lead to the expected photo-induced charge separation and charge accumulation towards the  
9 catalyst due to a non-productive quenching of the excited state of the photosensitizer by energy transfer to the catalyst. A  
10 comparative electrochemical study points to a change in the electrocatalytic pattern of the **porFe-bpyRu** dyad compared to  
11 the **porFe** catalyst. Indeed, for the **porFe**, the catalytic wave is observed at the  $\text{Fe}^0$  state while for the **porFe-bpyRu** dyad, a  
12 catalytic wave starts at the formal  $\text{Ru}^{\text{I}}\text{-Fe}^{\text{I}}$  species at some 700 mV lower overpotential than the **porFe** catalyst. This species  
13 can be best described as a formal  $\text{Fe}^{\text{I}}$  species at the catalyst in interaction with a radical anion on the bipyridine ligand  
14 holding the **porFe**. Interestingly though, in presence of exogenous **bpyRu** photosensitizer, the **porFe-bpyRu** dyad presents  
15 a significant enhancement of the turnover number and  $\text{CO}_2$ -to-CO selectivity of the catalysis compared to the **porFe** catalyst  
16 analogue under the same photocatalytic conditions. Reasons behind this probably come from the role of the **bpyRu** unit in  
17 the **porFe-bpyRu** dyad that acts an electron reservoir to power the photocatalytic activity. DFT calculations are underway  
18 to provide more insights in the functioning of such dyad.

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## 8 **Supplementary data**

9 Supporting information for this article is available on the journal's website under the article's URL [xxxxxxxxxxx](#). or  
10 from the author. It contains transient emission, transient absorption, EPR, spectroelectrochemistry, NMR and ESI-HRMS  
11 spectra.

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