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A transition-metal-assembled dyad containing a porphyrin module and an electro-deficient ruthenium complex[†]

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Summary — A porphyrin-ruthenium complex conjugate **PH_2-Ru** has been constructed, the ruthenium-based component being a strong electron and energy acceptor. The porphyrin site can be metallated by zinc(II) to afford the dyad **PZn-Ru**. The electrochemical parameters of the reference compounds (components) and the two dyads have been determined, as well as the absorption and emission characteristics. These data allow us to predict the exergonicity of the photoinduced electron and energy transfer processes likely to take place in both dyads. Low temperature emission measurements clearly show that very fast energy transfer occurs in two steps in both dyads. The singlet excited state porphyrin is first quenched by the Ru component, leading to a Ru-complex localized triplet excited state (^{3}MLCT) which, in turn, transfers its triplet energy back to the porphyrin unit attached to it so as to generate the porphyrin triplet excited state.

electro-deficient ruthenium complex / porphyrin / dyad / energy transfer

Résumé — **Synthèse d'une diade contenant un module porphyrine et un complexe de ruthénium électro-déficient.** *Un complexe* **PH_2-Ru** *a été synthétisé dans lequel l'entité ruthénium est un accepteur d'électron et d'énergie puissant. La métallation au zinc(II) du site porphyrine conduit à la diade* **PZn-Ru**. *Les données électrochimiques relatives aux composés de référence et aux deux diades ont été étudiées, ainsi que leurs spectres d'absorption et d'émission. Ces données permettent de prédire l'exergonicité des processus de transfert d'électron et d'énergie photoinduits qui sont susceptibles de se produire dans les diades. Des mesures d'émission à basse température ont mis en évidence un transfert d'énergie rapide, en deux étapes, dans ces diades. Dans un premier temps, l'état excité singulet de la porphyrine est piégé par le complexe de ruthénium, générant l'état excité triplet de ce complexe (^{3}MLCT) qui à son tour, transfère son énergie à la porphyrine adjacente conduisant à l'état excité triplet de cette porphyrine.*

complexe de ruthénium (II) électro-déficient / porphyrine / diade / transfert d'énergie

Introduction

Long-range electron transfer between an electron donor in its excited state and an electron acceptor is an essential process in photosynthesis [1]. Porphyrins have been extensively used as donors, in conjunction with several types of acceptor, extending from the most biomimetic ones like quinones [2], to transition metal complexes [3]. We recently reported multicomponent systems based on conjugates between porphyrinic modules and a ruthenium(II) bis(2,2′:6′,2″-terpyridine) [$Ru(terpy)_2^{2+}$] core complex [4]. In particular, it could be shown that photoinduced electron transfer takes place between a zinc(II) porphyrin (D) and the ruthenium(II) complex (A) attached to it, in spite of the very poor electron-acceptor character of the latter. In order (i) to increase the electron-transfer rate between (A) and (D) and (ii) to permit the use of tetraaryl porphyrins, which are less electron rich but chemically more robust than *etio*-porphyrins, the replacement of the $Ru(terpy)_2^{2+}$ unit by a more easily reducible ruthenium(II) complex seemed to be particularly promising. We would now like to describe such a dyad, consisting of a free base or zinc(II) tetraaryl porphyrin attached to a strongly electro-deficient ruthenium(II) complex containing a π-acceptor ligand such as 2,6-bis(4-phenyl-2-quinolyl) pyridine (bpqpy). We would also like to explore the performance of this new dyad in respect to its

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[†] Dedicated to Prof Raymond Weiss.

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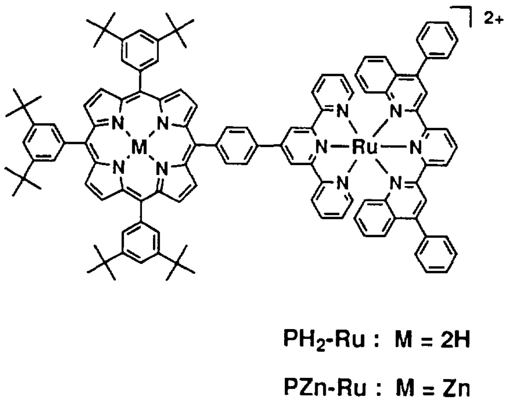
use in multicomponent systems able to undergo effective electron transfer. The compounds made and studied in the present paper are represented in scheme 1.



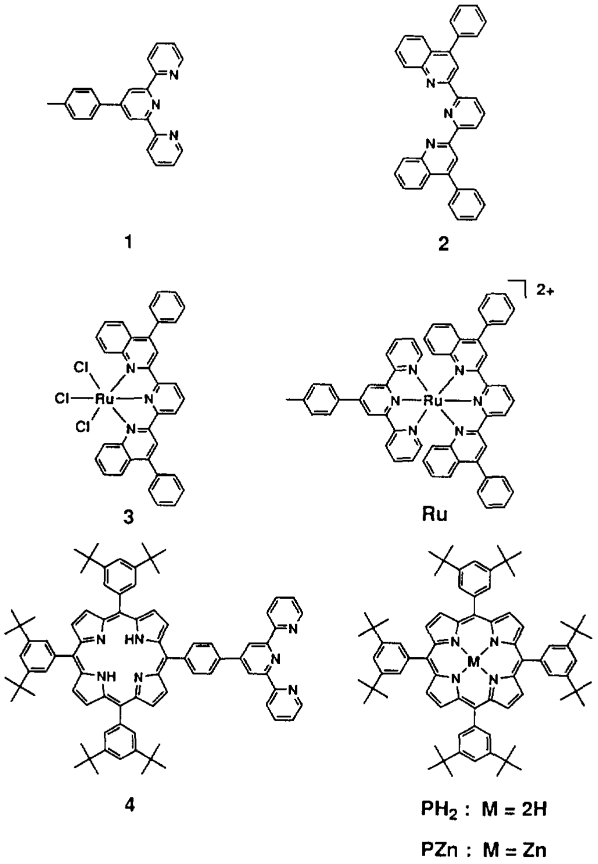
Scheme 1

Results and discussion

The synthetic strategy for making dyad **PH$_2$-Ru** and subsequently **PZn-Ru**, involves the preliminary preparation of the modules, followed by complexation on the ruthenium center. The donor porphyrin module is covalently attached to a terpy chelate. It should be noted that the metal has a dual function: (i) it is the assembling center, collecting the porphyrin module and the π-electron accepting ligand in the same multicomponent molecule; and (ii) it provides the acceptor group once the two terdentate chelates are bonded to the metal center, to generate the ruthenium(II) complex.

Synthesis of the dyads and reference compounds

The precursor compounds and the reference compounds are shown in scheme 2. Ligand **2** was prepared according to the one-pot procedure described by Mamo et al [5] in very good yield (91%). The heteroleptic complex Ru(ttpy)(bpqpy)$^{2+}$ **Ru** was obtained by a sequential method. In a first step, ttpy was reacted with $RuCl_3 \cdot 3H_2O$ and yielded nearly quantitatively Ru(ttpy)Cl$_3$. In a second step, after dechlorination with AgBF$_4$, the solvated complex Ru(ttpy)(acetone)$_3^{2+}$ was reacted with 2,6-bis(4-phenyl-2-quinolyl)pyridine (bpqpy) **2** in refluxing *n*-butanol. The porphyrin bearing a terpyridine residue **4** was prepared in 16% yield following Adler's procedure as previously described [4]. The symmetrical reference porphyrin **PH$_2$** was also obtained as a by-product of this reaction. The dyad **PH$_2$-Ru** was prepared by reaction of **4** with the solvated complex Ru(bpqpy)(acetone)$_3^{2+}$. Metallation of a free base porphyrin with zinc(II) acetate, to afford compounds **PZn-Ru** and **PZn**, was almost quantitative. The purity of each highly colored complex **PH$_2$-Ru**, **PZn-Ru**, **Ru**, **PH$_2$** and **PZn** was checked by thin-layer chromatography, UV-visible spectroscopy and high-resolution ^{1}H NMR spectrometry.



Scheme 2

Electrochemical behavior

The electrochemical results obtained in CH$_2$Cl$_2$ for the dyads **PH$_2$-Ru** and **PZn-Ru** are gathered in table I together with the data for the reference compounds **Ru**, **PH$_2$** and **PZn**.

Table I. Redox potentials measured by cyclic voltammetry for the reference compounds **Ru**, **PH$_2$**, **PZn** and the dyads **PH$_2$-Ru** and **PZn-Ru** in CH$_2$Cl$_2$.

Compound	*E 1/2 (V vs SCE)*						
Ru	1.43			−0.95		−1.37	−1.67
PH$_2$			0.98		−1.16		
PZn		1.07	0.75		−1.43		
PH$_2$-Ru	1.45	1.27	0.92	−0.95	−1.21	−1.39	−1.58
PZn-Ru	1.43	1.05	0.75	−0.95	−1.37		−1.63

Concerning the ruthenium complex **Ru** we can note the following: (i) Ru(II) is oxidized (metal-based oxidation) at much more positive potentials than the parent complex Ru(ttpy)$_2^{2+}$ [6] ($E = 1.25$ V vs SCE); and (ii) the first reduction potential (ligand-based reduction) is less negative than that of Ru(ttpy)$_2^{2+}$ ($E = -1.24$ V vs SCE). Therefore, it can be concluded that the strongly electron-withdrawing dpqpy ligand provides a more pronounced acceptor feature to the complex Ru(ttpy)(dpqpy)$^{2+}$ than the parent com-

Table II. Luminescence data in butyronitrile at 77 K.

	Ru-MLCT		*Porph-fluorescence*		*Porph-phosphorescence*	
	λ_{max}, *nm*	τ, *μs*	λ_{max}, *nm*	τ, *ns*	λ_{max}, *nm*	τ, *ms*
PZn-Ru	677	0.0057	620^a	≤0.020^a	807	12.0
PH$_2$-Ru	677	0.0046	649	0.110^a	840	5.6
Ru	677	10.8	/	/	/	/
PZn	/	/	617	2.3	804	18.9
PH$_2$	/	/	648	11.9	840^b	6.0^b

^{a} From streak camera images; ^{b} very weak signal.

pound Ru(ttpy)$_2^{2+}$. The CV curves of the reference porphyrins **PH$_2$** and **PZn** display the usual oxidation and reduction processes as previously reported [4]. In dyads **PH$_2$-Ru** and **PZn-Ru**, the different reversible waves can be straightforwardly assigned to their individual components. Since the redox potentials obtained are very close to those obtained for the individual reference compounds, the electrochemical behavior observed for **PH$_2$-Ru** and **PZn-Ru** suggests that the electronic coupling between each component is virtually non-existent. As all the redox waves display a characteristic pattern for reversible redox couples, we can use them, in association with the emission data, to predict the exergonicity of photoinduced electron- and energy-transfer reactions with a good approximation.

Absorption spectra, luminescence properties, intercomponent processes

Figures 1 and 2 show the absorption (295 K) and emission (77 K) spectra of the **PZn-Ru** dyad and the two reference compounds **Ru** and **PZn** in butyronitrile solution. A similar spectroscopic behavior is shown by the **PH$_2$-Ru** dyad. Table II collects data concerning the maximum of the emission bands and the lifetime of the luminescence excited states at 77 K for the two dyads and the three reference compounds. All decays are well described by single exponentials.

The absorption spectrum of **Ru** shows the ligand-centered (LC) and metal-to-ligand charge-transfer (MLCT) bands typical of Ru(II) polypyridine complexes. It can be noted that the charge-transfer absorption in the visible region is considerably broad, as expected because of the presence of two different charge-transfer transitions (Ru → ttpy and, at lower energy Ru → dpqpy). The strong and long-lived phosphorescence band observed at 77 K can be assigned to the lowest energy ^{3}MLCT excited state, which involves the (easier to reduce) dpqpy ligand. As occurs for most Ru(II) complexes of ttpy-type ligands, no emission can be observed at room temperature, presumably because of a fast deactivation via an upper lying ligand-centered excited state [7, 8]. Under these conditions, the lifetime of the ^{3}MLCT excited state is only 100 ps (measured by picosecond absorption spectroscopy).

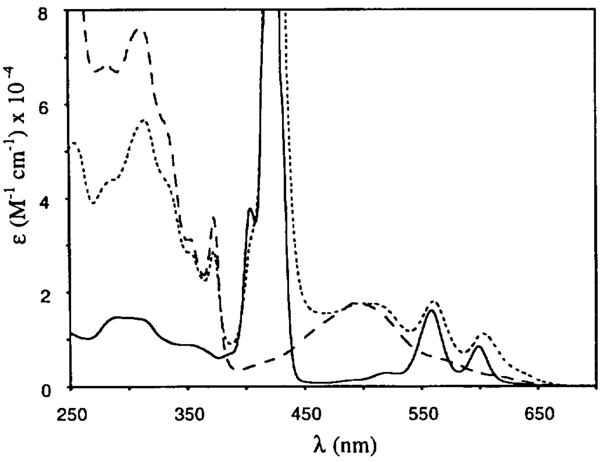


Fig 1. Absorption spectra in butyronitrile at 295 K of the **PZn-Ru** dyad (....) and of the reference compounds **PZn** (___) and Ru (---).

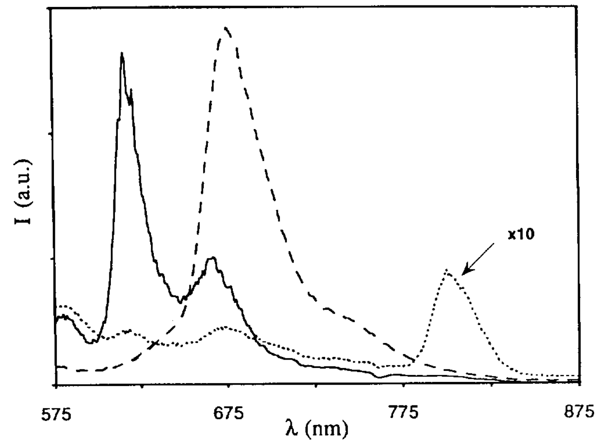


Fig 2. Emission spectra in butyronitrile at 77 K of **PZn** (___) and **PZn-Ru** (....), λ_{exc} = 450 nm, identical conditions. The spectrum of **Ru** (---), λ_{exc} = 495 nm is normalized to the maximum of **PZn** emission.

The two porphyrin reference compounds **PZn** and **PH$_2$** exhibit the well-known [9, 3f, 4b] very intense Soret bands with maxima at 425 and 418 nm, respectively, and the weaker Q bands with maxima in the 480–700 nm region. In rigid matrix at 77 K both compounds show intense and short-lived fluorescence bands and very weak and long-lived phosphorescence bands. In fluid solutions at room temperature the fluorescence band is still very intense, whereas phosphorescence cannot be seen, as usually occurs for intrinsically long-lived (and thereby very susceptible to bimolecular quenching) excited states [10].

The investigation of the photophysical behavior of the dyads at room temperature is made difficult because under such conditions there is no emission from the lowest excited state of the three reference compounds. In this paper we will confine ourselves to the discussion of the behavior in a rigid matrix at 77 K. A more complete study, including the results of picosecond absorption spectroscopy at room temperature, is underway in our laboratories.

As shown in figure 1, the absorption spectrum of the **PZn-Ru** dyad is not exactly coincident with the sum of the spectra of the two reference compounds, especially in the UV region. A similar behavior was observed for **PH_2-Ru**. Comparison with the properties of the **PZn** and **PH_2** reference compounds (table II and fig 2) indicate that the fluorescence of the porphyrin moiety is drastically quenched in both dyads. In principle, the quenching process can occur via energy or electron transfer. It should be noted that, due to the presence of the heavy metal, the spin conservation rules are not expected to be obeyed. According to the redox potentials (table I) and the energy of the S_1 excited state, in rigid matrix at 77 K neither reductive nor oxidative electron-transfer quenching are thermodynamically allowed [11]. On the other hand, the ^{3}MLCT excited state of the Ru-based moiety lies slightly below the S_1 excited state of the porphyrin moiety in both dyads, as one can see from the position of the respective emission bands (table II and fig 3). Energy transfer is therefore the most likely quenching mechanism. Excitation of **PZn-Ru** at 499 and 560 nm, where the sample shows identical absorbance but the partition of photons is respectively 5% on the zinc porphyrin and 95% on the metal complex and 70% on the zinc porphyrin and 30% on the metal complex, produces the same yield of phosphorescence. In **PH_2-Ru** the yield of porphyrin phosphorescence upon excitation at 377 nm, where 60% of the photons are absorbed by the metal complex and 40% by the porphyrin moiety, is compared to the excitation at 394 nm, where the overall absorbance is identical, but the partition of photons between the porphyrin and the metal complex is respectively of 95 and 5%. The yield of the porphyrin phosphorescence was the same within experimental error. All these facts clearly show that the energy-transfer processes are quantitative.

The rate constant of the quenching process of an excited state can be obtained from the equation

$$k_q = 1/\tau - 1/\tau^\circ \qquad (1)$$

where τ and τ° are the lifetimes of the excited state in the presence and absence of quenching. From the fluorescence lifetimes of the dyad and the reference compound (table II), the energy transfer quenching constant k_{et} for the $S_1 \rightarrow {}^3$MLCT process in **PZn-Ru** is $\geqslant 5 \times 10^{10}$ s^{-1}. The other dyad behaves very similarly ($k_{et} = 9 \times 10^9$ s^{-1}). Since these rates are much faster than the intrinsic deactivation rate of the S_1 level, the energy transfer process is almost 100% efficient.

It can be noted that the $S_1 \rightarrow {}^3$MLCT energy transfer process does not cause sensitization of the phosphorescence of the Ru-based moiety. In fact, the data shown in table II (see also fig 2) indicate that the Ru-based phosphorescence is *quenched* in the dyad. This result can be explained considering that for both dyads the lowest triplet level T_1 of the porphyrin-based moiety lies below the ^{3}MLCT excited state of the Ru-based moiety (table II, fig 3) and therefore the latter excited state, in its turn, can be quenched via energy transfer. This is indeed the case, since the phosphorescence of the porphyrin-based moiety can be observed even upon excitation of the Ru-based moiety. From the lifetime of the ^{3}MLCT excited state of the **Ru** reference compound and of the Ru-based moiety of the dyads, we used eq (1) to calculate the following values for the rate constant $k_{et'}$ of the ^{3}MLCT $\rightarrow T_1$ process: 1.7×10^8 s^{-1} for **PZn-Ru** and 2.2×10^8 s^{-1} for **PH_2-Ru**. Since these rates are much faster than the intrinsic deactivation rate of the ^{3}MLCT level, the energy transfer process is almost 100% efficient. The photoinduced processes occurring in the **PZn-Ru** dyad are shown schematically in fig 3.

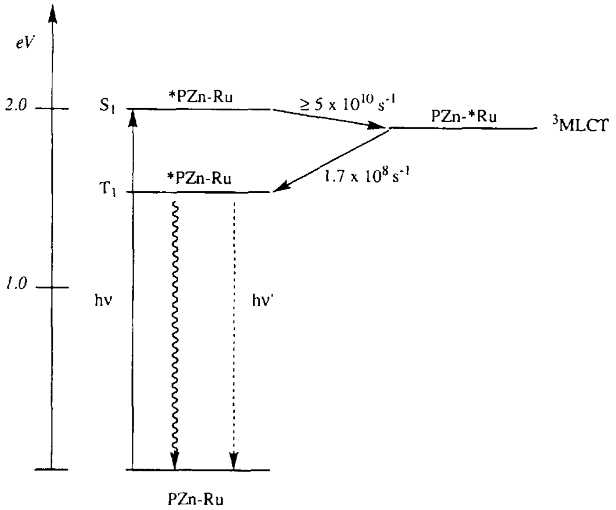


Fig 3. Energy level diagram for the **PZn-Ru** dyad in rigid matrix at 77 K. The energy level diagram for the **PH_2-Ru** dyad is qualitatively similar and can be easily constructed by using the energies of the maxima of the pertinent emission bands shown in table II.

In conclusion, as a consequence of the two very fast and highly efficient $S_1 \rightarrow {}^3$MLCT and ^{3}MLCT $\rightarrow T_1$ energy-transfer processes, for both dyads the absorbed photons lead to formation of the lowest excited state of the supramolecular structure T_1, regardless of the excitation wavelength.

Experimental section

Instrumentation

^{1}H NMR spectra were recorded with a Bruker WP 200 SY or an AM 400 spectrometer. Mass spectra were recorded on a VG ZAB-HF (FAB) spectrometer. The ground-state absorption spectra were recorded at room temperature with either a Kontron Uvikon 860 or a Perkin-Elmer Lambda 9 spectrophotometer. The instruments and procedure used to obtain cyclic voltammograms (CH_2Cl_2, n-Bu_4NBF_4 0.1 M) have been described in previous papers [4].

The solvent used for photophysical investigations was butyronitrile from Fluka. Uncorrected emission spectra were obtained at 77 K with a Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube. The delayed luminescence spectra of porphyrin triplets were measured by a Perkin-Elmer LS50 spectrofluorimeter, equipped with a red enhanced photomultiplier (Hamamatsu R3896). Luminescence lifetimes were measured with a Perkin-Elmer LS-50 spectrofluorimeter (λ_{exc} = 560 nm, millisecond timescale), an IBH single-photon counting apparatus (λ_{exc} = 337 nm, nanosecond timescale), and a system based on a Nd/YAG laser and a Hamamatsu C1587 streak camera (λ_{exc} = 532 nm, picosecond timescale) [12]. All the samples were put in special home-made 1 cm path quartz cuvette, degassed with four freeze-pump-thaw cycles, sealed under vacuum, and immersed in a quartz dewar filled with liquid nitrogen.

Materials and compounds

Solvents used for electrochemical and spectroscopic studies were of the highest available commercial grade and were used as received. Pyrrole was purified by distillation under reduced pressure from KOH and dichloromethane was distilled under argon from P_2O_5. Porphyrinic derivatives were protected from light by aluminium foil during purification on chromatography columns and during heating. 3,5-Di-*tert*-butylbenzaldehyde [13], 4′-(4-formylphenyl)-2,2′:6′,2″-terpyridine [14], 4′-*p*-tolyl-2,2′:6′,2″-terpyridine (ttpy) [6], 2,6-bis (4-phenyl-2-quinolyl) pyridine (bpqpy) [5] were prepared according to literature procedures. The precursor complex Ru(bpqpy)Cl_3 **3** was prepared as previously described for Ru(ttpy)Cl_3 [6]. Syntheses of the tetraarylporphyrins (**H_2P**, **ZnP** and H_2P-terpy **4**) were achieved following Adler's methodology [15].

Ru(ttpy)(bpqpy)(PF_6)$_2$ **Ru**

Ru(ttpy)Cl_3 (0.12 g, 0.23 mmol) and $AgBF_4$ (0.14 g, 0.7 mmol) were heated to reflux in acetone (40 mL) for 2 h. The resulting purple suspension was filtered to remove precipitated AgCl and *n*-butanol (120 mL) was added to the filtrate. After elimination of acetone, ttpy (115 mg, 0.23 mmol) was added and the solution was refluxed under argon overnight. After cooling, the solvent was evaporated and the residue dissolved in acetonitrile (50 mL). Excess KPF_6 (0.4 g) and water (200 mL) were then added. The red precipitate was collected by filtration, washed with water and redissolved in the minimum volume of CH_3CN for column chromatography over silica, using CH_3CN water, saturated aqueous KNO_3, (100:5:0.5) as the eluent. Complex **Ru** was obtained as a red powder (0.117 g, 42%).

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 9.13 (s, 2H); 8.98 (d, 2H, J = 8 Hz); 8.61 (t, 1H, J = 8.2 Hz); 8.55 (d, 2H, J = 7.6 Hz); 8.46 (s, 2H); 8.23 (d, 2H, J = 8.2 Hz); 7.82 (m, 4H); 7.66 (d, 2H, J = 8 Hz); 7.5–7.6 (m, 12H); 7.42 (t, 2H, J = 8 Hz); 7.25 (m, 4H); 6.72 (d, 2H, J = 8.6 Hz); 2.6 (s, 3H).

(H_2P-ttpy)Ru(bpqpy)(PF_6)$_2$ **PH_2-Ru**

Ru(bpqpy)Cl_3 (25 mg, 0.036 mmol) and $AgBF_4$ (22 mg, 0.113 mmol) were refluxed in a mixture of acetone (10 mL) and butanol (50 mL) for 2.5 h. After cooling to room temperature, the purple suspension was filtered and the resulting deposit of AgCl was washed with acetone. Once the acetone was removed, **4** (43 mg, 0.036 mmol) was added and the mixture was heated to reflux under argon for 6 h. The solvent was evaporated and the residue dissolved in acetonitrile before being subjected to anion exchange. Purification of the crude product was carried out by column chromatography on silica gel using CH_3CN/water/saturated aqueous KNO_3 mixture (100:10:0.1) as eluent. After anion exchange **PH_2-Ru** was isolated in yield of 43%.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 9.47 (s, 2H); 9.08 (d, 2H, J = 5.4 Hz); 9.03 (m, 4H); 8.94 (s, 4H); 8.73 (s, 4H); 8.69 (d, 2H, J = 8.8 Hz); 8.65 (t, 1H, J = 7 Hz); 8.52 (s, 2H); 8.16 (s, 4H); 8.12 (s, 2H); 7.90–7.96 (m, 4H); 7.88 (s, 3H); 7.68 (d, 2H, J = 7 Hz); 7.55–7.67 (m, 10H); 7.52 (t, 2H, J = 8 Hz); 7.45 (td, 2H, J = 8.0 and 2.0 Hz); 7.33 (t, 2H, J = 8 Hz); 6.88 (d, 2H, J = 9 Hz); 1.35 (s, 54H).

FAB-MS m/z = 1913.3 (M-PF6 requires 1913.4).

(ZnP-tpy)Ru(bpqpy) (PF_6)$_2$ **PZn-Ru**

Compound **PH_2-Ru** (20 mg, 0.010 mmol) and zinc acetate dihydrate (8.5 mg, 0.04 mmol) were dissolved in acetonitrile (5 mL), and the mixture was heated to reflux under argon for 1 h. The course of reaction was followed by UV-vis spectroscopy until metallation of the free-base porphyrin was complete. After cooling, anion exchange was made with KPF_6 and the crude product was chromatographed on silica gel using acetonitrile/water/saturated aqueous KNO_3 (100:2:0.2) as eluent. Compound **PZn-Ru** was recovered in 90% yield.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 9.59 (s, 2H); 9.17 (d, 2H, J = 8 Hz); 9.05 (d, 2H, J = 6 Hz); 8.98 (d, 2H, J = 6 Hz); 8.88 (s, 4H); 8.84 (d, 2H, J = 8.2 Hz); 8.77 (d, 2H, J = 8 Hz); 8.71 (d, 2H, J = 8.2 Hz); 8.65 (s, 2H); 8.62 (t, 1H, J = 8 Hz); 8.16 (s, 4H); 8.12 (s, 2H); 7.9–9.96 (m, 4H); 7.92 (s, 3H); 7.88 (d, 2H, J = 7 Hz); 7.55–7.7 (m, 10H); 7.52 (t, 2H, J = 8 Hz); 7.45 (td, 2H, J = 8 and 2 Hz); 7.24 (t, 2H, J = 8 Hz); 6.88 (d, 2H, J = 9 Hz); 1.35 (s, 54H).

FAB-MS m/z = 1977.6 (M-PF_6 requires 1977.6).

Acknowledgments

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