

A novel ruthenium(II) tris(bipyridine)–zinc porphyrin–rhenium carbonyl triad: synthesis and optical properties

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Abstract—A novel ruthenium(II) tris(bipyridine)–zinc porphyrin–rhenium carbonyl triad and its free base porphyrin derivative were synthesized and characterized by ¹H, ¹³C NMR, UV–vis, mass-spectrometry and elemental analysis. The redox potentials of the two compounds were measured and compared to their corresponding reference complexes. The fluorescence and transient absorption spectra of the two complexes revealed the features of two different pathways for possible photoinduced intramolecular electron transfer or energy transfer in the triads.

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1. Introduction

The preparation of multicomponent photoactive arrays by logical covalent or noncovalent connection is a rapidly growing field and an important research area in view of the following interests: (i) a better understanding of efficient electron transfer and charge separation in natural photosynthesis;¹ (ii) the construction of the nanometer-scale wires,² switches,³ logic gate,⁴ and other components for the development of molecular electronic devices.⁵ It has been known that photoexcitation results in charge transfer from Ru²⁺ ion to the bpy ligands in Ru(bpy)₃X₂ derivatives, effectively creating a Ru³⁺–(bpy)[–] metal to ligand charge transfer state.⁶ The Ru³⁺ is an extremely strong oxidant that could potentially promote facile oxidation of an adjacent porphyrin via electron transfer.⁷ In recent years, a sizable number of dyads (or larger architectures) comprised of a porphyrin and a Ru(bpy)₃ complex⁸ or Ru(tpy)₂ complex⁹ have been designed and synthesized. The photochemical properties of a number of such complexes have been reviewed.¹⁰ In addition, rhenium-containing complexes Re(CO)₃(bpy)L, in which L is a halide, have been the subject of a large number of studies. In general, the continuously

growing interest for the study of these molecules stems from their ability to act as efficient sensitizers for energy and electron transfer.¹¹ Herein, we sought to prepare a porphyrin-based triad with Ru(bpy)₃X₂ and [Re(CO)₃(bpy)L] covalently attached to porphyrin for the studies of electron transfer or energy transfer in multicomponent systems.

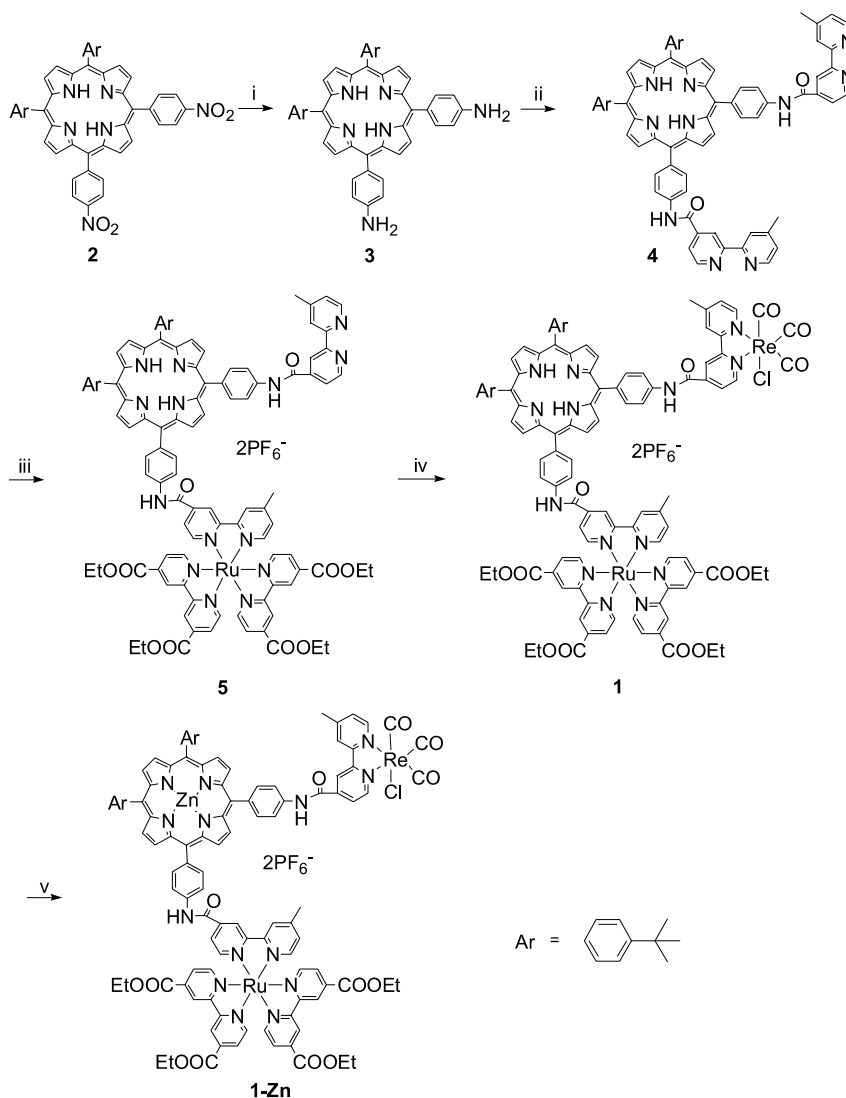
2. Results and discussion

2.1. Synthesis

The procedure for the synthesis of **1** and **1-Zn** was depicted in Scheme 1. The starting porphyrin **2** was synthesized by a mixed condensation of pyrrole, 4-nitrobenzaldehyde and 4-(*t*-butyl)benzaldehyde.¹² The 'ortho' orientated 5,10-bis-(4-nitrophenyl)porphyrin (**2**) was separated by column chromatography from other multiple porphyrin products, including mono, bis (trans), tris and tetrais nitrophenyl-substituted porphyrins. Gradient elution was used for the multicomponent separation with silica gel and a dichloromethane/hexane solvent system consisting initially of CH₂Cl₂–Hexane (1/1) and gradually ending with 100% of dichloromethane. We did not collect the trans analogue 5,15-bis-(4-nitrophenyl)porphyrin due to its extremely low yield, although TLC analysis of these mixtures indicated that the trans could be separated. The following simultaneous reduction of the two nitro groups was carried out in CHCl₃/HOAc by the usual SnCl₂/HCl procedure¹³ to give amino substituted phenylporphyrin **3** in

Keywords: Porphyrin; Ruthenium; Rhenium; Photophysics; Electron transfer; Energy transfer.

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Scheme 1. Synthesis of complex **1-Zn**. Conditions: (i) SnCl_2/HCl , CHCl_3 – HOAc reflux, 12 h, 82%; (ii) 4'-methyl-2,2'-bipyridinyl-4-carbonyl chloride, CH_2Cl_2 , reflux, 4 h, 60%; (iii) *cis*- $\text{Ru}(4,4'$ -di-COOEt-2,2'-bpy) $_2\text{Cl}_2$, HOAc , reflux, 1 h, 32%; (iv) $\text{Re}(\text{CO})_5\text{Cl}$, toluene, reflux 6 h, 98%; (v) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, CHCl_3 – EtOH , rt, 12 h, 94%.

82% yield. Porphyrin **3** was then reacted with 4'-methyl-2,2'-bipyridinyl-4-carbonyl chloride (prepared in situ from 4,4'-dimethyl-2,2'-bipyridine¹⁴) in the presence of Et_3N to form compound **4** in 60% yield, where the two amidations occurred in the same step. For the next transformation to the complex **5**, the acetic acid solution of 1 equiv of *cis*- $\text{Ru}(4,4'$ -di-COOEt-2,2'-bpy) $_2\text{Cl}_2$ ¹⁵ was carefully titrated to porphyrin **4** in order to ensure the regioselectivity. The remaining bipyridine subunit was coordinated to Re by treatment of **5** with $\text{Re}(\text{CO})_5\text{Cl}$ in toluene at reflux to give the binuclear product **1** in 98% yield. The trinuclear target complex **1-Zn** was then formed by stirring the mixture of $\text{Zn}(\text{OAc})_2$ and **1** in chloroform in the presence of a little EtOH at room temperature. All of the compounds were insoluble in hexane or alcohols but were easily dissolved in most other organic solvents.

2.2. Steady-state absorption spectra

The absorption spectra of **1** and **1-Zn** were shown in Figure 1. The spectrum of $\text{Ru}(4,4'$ -di-COOEt-2,2'-bpy) $_2(4\text{-Me-4'-COOH-2,2'-bpy})$ (PF_6) $_2$ (abbreviated as **Ru**¹⁶)

(Fig. 5) was also shown as a comparison. The absorption spectrum of **1-Zn** showed a red-shifted Soret band at 428 nm ($\text{S}_0 \rightarrow \text{S}_2$ transition) with respect to that of **1** (418 nm).

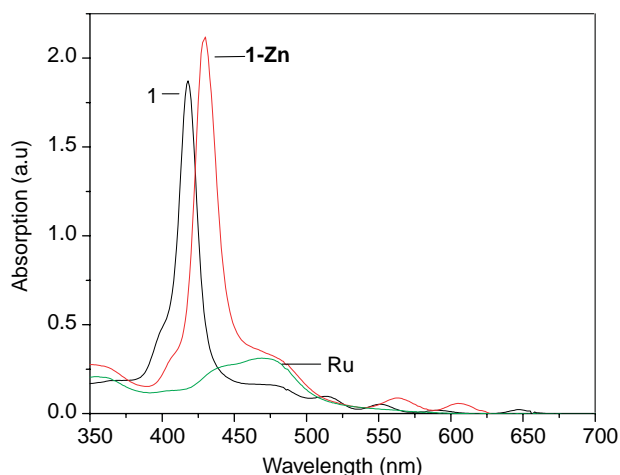


Figure 1. UV-vis absorption spectra of **1**, **1-Zn** and **Ru** in CH_2Cl_2 [5×10^{-6} M].

While the two Q bands ($S_0 \rightarrow S_1$ transition) exhibited typical pattern of regular metal porphyrins. The shoulders at 475 nm for both spectra of **1** and **1-Zn** are mainly from ruthenium moiety, since porphyrins have negligible absorption in this region. In addition, the metal to ligand charge transfer (MLCT) transition of ruthenium moieties in all cases was red shifted (25 nm) relative to the absorption of $\text{Ru}(\text{bpy})_3\text{X}_2$,¹⁷ due to the introduction of electron-withdrawing substituents in the pyridine rings.

2.3. Emission measurements

The emission spectra of **1** and **1-Zn** were shown in Figure 2a. The emission spectrum of complex **1** showed the typical porphyrin component emission at 656 and 722 nm (0–0 and 0–1 band) upon irradiation at the Q band (552 nm). While the related peaks in the emission spectrum of **1-Zn** were blue-shifted (0–0 and 0–1 band at 614 and 667 nm, respectively) upon irradiation at 558 nm, and the emission intensity was strongly quenched. The emission from Zn porphyrin component in **1-Zn** ($\Phi_f=0.0005$) and porphyrin component in **1** ($\Phi_f=0.007$) were reduced by 62-fold and 14-fold from that of zinc tetraphenylporphyrin ($\Phi_f=0.031$) and tetraphenylporphyrin ($\Phi_f=0.10$) respectively. Since energy transfer to the appended ruthenium or rhenium unit is thermodynamically infeasible, this quenching is mainly attributed to electron transfer to the ruthenium unit.⁹ Comparing with a Zn porphyrin–ruthenium complex ($\Phi_f=0.0011$),¹⁸ we deduced that rhenium carbonyl unit also played an important role in the electron transfer by quenching of the emission of zinc porphyrin component in **1-Zn**.

The emission spectra of the complex **Ru** (see Fig. 5) ($\lambda_{\text{ex}}=475$ nm) and **1-Zn** ($\lambda_{\text{ex}}=428, 475, 558$ nm) were shown in Figure 2b. We found that the emission profile of **1-Zn** was identical to that of Zn porphyrin, no matter the Soret band ($\lambda_{\text{ex}}=428$ nm) or Q band ($\lambda_{\text{ex}}=558$ nm) was excited. In addition, no contribution from ruthenium or rhenium moieties could be observed. Thus, the Soret band excitation of Zn porphyrin moiety in **1-Zn** did not generate any sensitized ruthenium or rhenium emission, and energy transfer from the S_2 state of Zn porphyrin to ruthenium or rhenium unit therefore could not be significant. When

exciting at the ruthenium band (475 nm), the emission profile of **1-Zn** was similar to that of **Ru**. However, the intensity of the emission of **1-Zn** was found to be 50% relative to that of **Ru**. The decrease of emission intensity is attributed to the quenching of ${}^3\text{MLCT}$ state of ruthenium unit by Zn porphyrin via electron or energy transfer.

2.4. Transient absorption

A preliminary time-resolved absorption and emission study of **1-Zn** was carried out in CH_3CN solution using a YAG laser with a 12 ns pulse width and excitation at 532 nm. The spectrum is characteristic of the porphyrin ${}^3(\pi,\pi^*)$ excited states with intense absorption at 480 nm (Fig. 3). The ${}^3(\pi,\pi^*)$ spectrum is also marked by a distinct near-infrared absorption peak, which is not found in the ${}^1(\pi,\pi^*)$ spectrum.¹⁹ However, there is a significant difference between the transient spectra of the **1-Zn** and regular zinc porphyrins at 780 nm, in which transient absorption of the **1-Zn** is stronger than that of regular zinc porphyrins. We attribute it to the mixture of the porphyrin ${}^3(\pi,\pi^*)$ excited states and the intraligand charge transfer transition (${}^3\text{ILCT}$) from the porphyrin (π) to bpy (π^*).^{11b} A lifetime of 783 ns was obtained for the excited triplet state of Zn porphyrin by fitting the experimental absorbance decay at 480 nm, while a lifetime of 489 ns was obtained by fitting the experimental absorbance decay at 780 nm. The different lifetime also indicated that the two absorptions at 480 and 780 nm were attributed to different excited states. A detailed investigation of photoinduced electron transfer and energy transfer processes occurring in **1-Zn** will help us to evaluate this molecular triad system as a potential light-driven molecular switch. Femtosecond transient absorption measurements on this complex are in progress.

2.5. Electrochemistry

Redox potentials of the compounds **1**, **1-Zn** and reference compounds **Ru**, **PZnRu**¹⁷ and **PZnRe**^{2c} (their formulas were shown in Fig. 5, vide infra) were compiled in Table 1. The different waves of **1** and **1-Zn** could be easily assigned to their individual components by comparison with the redox couples of the reference compounds. Compound **1-Zn** had a good reversible characteristic at all redox processes, in

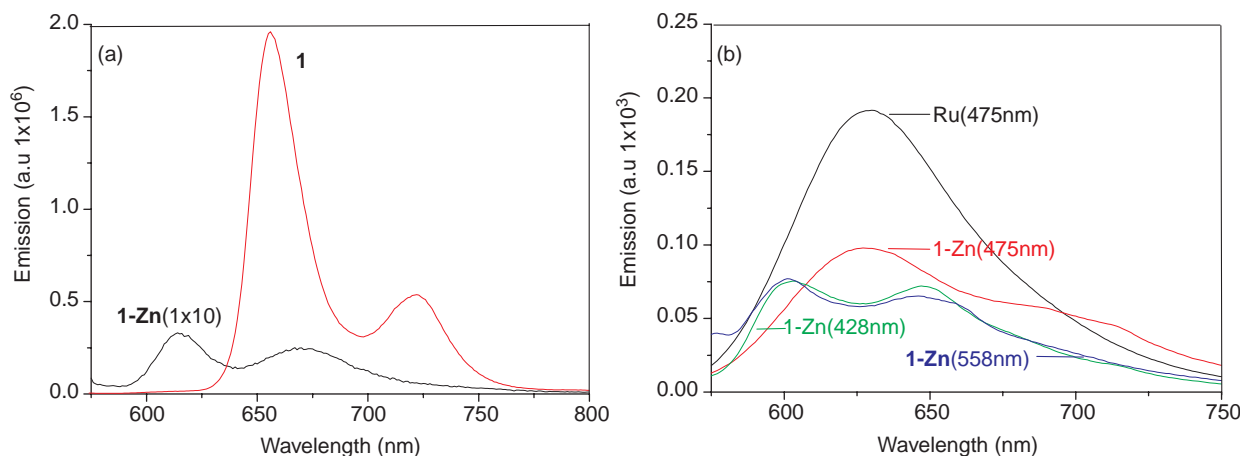


Figure 2. (a) Steady-state emission spectra of **1** ($\lambda_{\text{ex}}=552$ nm), **1-Zn** ($\lambda_{\text{ex}}=558$ nm) in CH_2Cl_2 [5×10^{-6} M]; (b) steady-state emission spectra of **1-Zn** ($\lambda_{\text{ex}}=558, 428, 475$ nm) and **Ru** ($\lambda_{\text{ex}}=475$ nm) in CH_2Cl_2 [5×10^{-6} M].

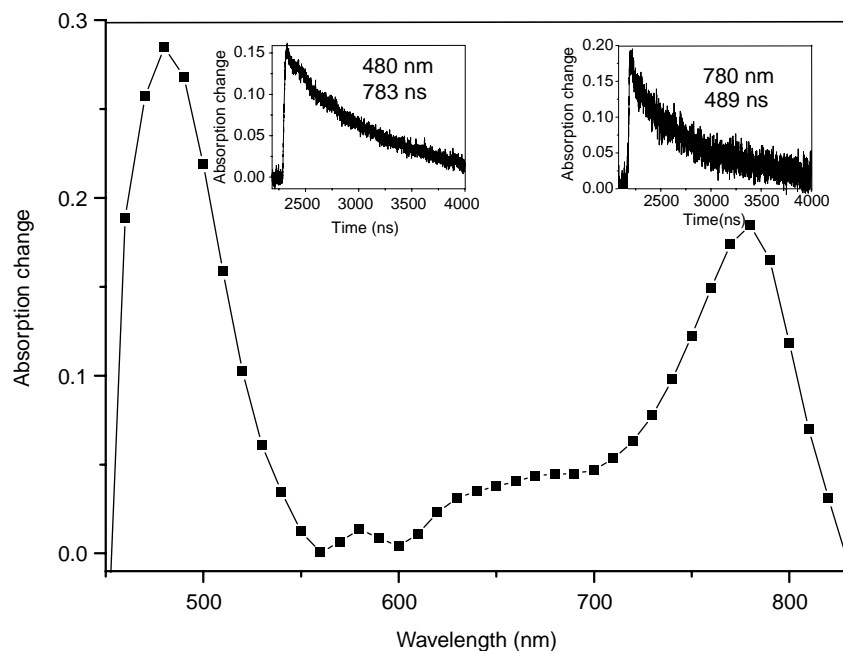


Figure 3. Differential absorption spectrum (visible and near-infrared) obtained upon nanosecond flash photolysis (532 nm) of $\sim 1 \times 10^{-5}$ M **1-Zn** in deoxygenated CH_3CN solutions.

Table 1. Redox potentials in CH_2Cl_2

	Oxidation $E_{1/2}$ (V vs SCE)				Reduction $E_{1/2}$ (V vs SCE)		
	P/P ⁺	P ⁺ /P ²⁺	Re ⁺ /Re ²⁺	Ru ²⁺ /Ru ³⁺	L/L ⁻	L'/L' ⁻	P/P ⁻
Ru				1.66	-0.76	-1.02	
PZnRe	0.81	1.22	1.53			-1.06	
PZnRu	0.78	1.17		1.68	-0.79	-1.07	-1.43
1-Zn	0.83	1.22	1.51	1.71	-0.76	-1.03	
1	—	—	1.47	1.72	-0.77	-1.14	

which there were two one-electron reductions and four one-electron oxidations (Fig. 4, e.g., **1-Zn**). We can see that potentials of the Ru²⁺/Ru³⁺ (1.71 V) and Re⁺/Re²⁺ (1.51 V) couple are more positive than that of the Zn porphyrin constituent (0.83 V). Thus, the complex has the requisite characteristics to facilitate generation of a porphyrin π -cation radical upon photoexcitation of the Ru or Re subunit, when just considering the redox properties.

This would both quench the fluorescence of the porphyrin and allow the oxidized porphyrin to quench nearby Re part

(or Ru subunit) excited states. According to the above analysis, **1-Zn** may be suitable for an all-optical switch.

3. Conclusion

To investigate intramolecular photoinduced electron or energy transfer in large light-harvesting arrays or molecular devices, two new multicomponent arrays based on porphyrin and ruthenium (or rhenium) bipyridine complexes were synthesized and characterized. Detailed

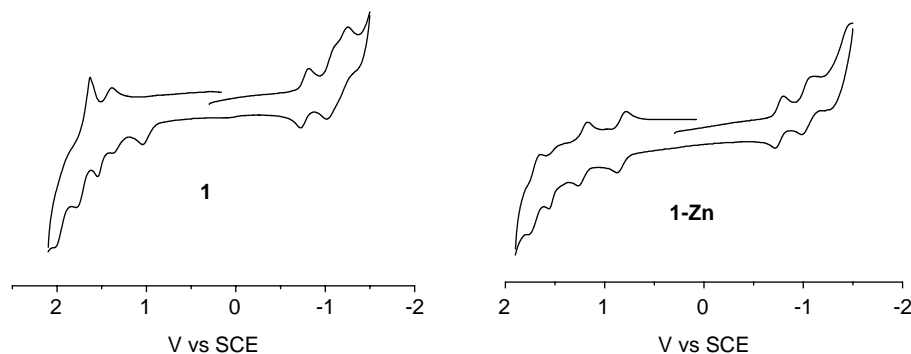


Figure 4. Cyclic voltammogram for complexes **1** and **1-Zn** in 10^{-3} M of $\text{CH}_2\text{Cl}_2/0.1$ M TBAPF₆ glassy carbon disc electrode at a scan rate of 50 mV/s and reported relative to SCE.

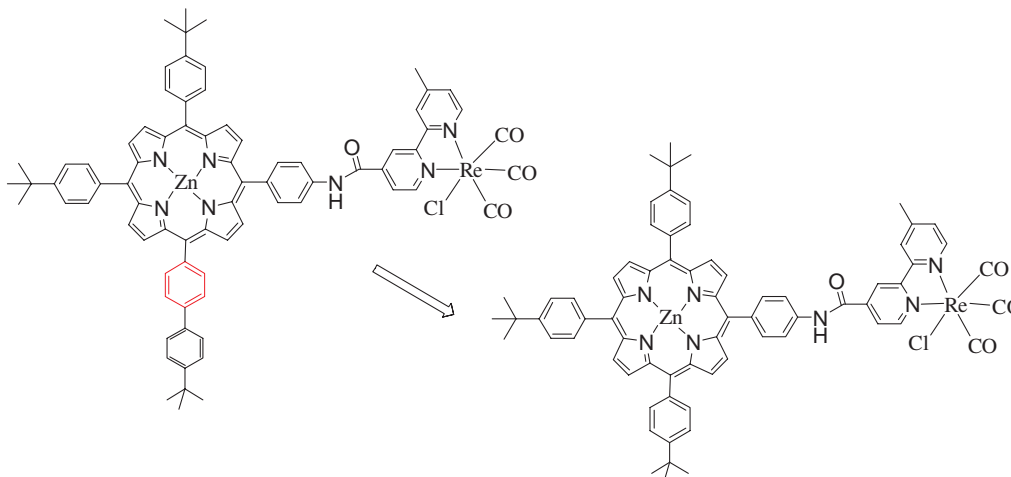


Figure 5. Schematic formulas of reference compounds studied.

photophysical and electrochemical studies of free-base and zinc-metalated multicomponents clearly showed that electronic interactions in each subunit were very weak. In fact, the absorption spectra and the electrochemical properties of the two multicomponent arrays can be described by a superposition of their monomeric subunits. Emission and transient absorption spectra recorded at room temperature showed that intramolecular photoinduced electron or energy transfer might occur.

4. Experimental

4.1. General

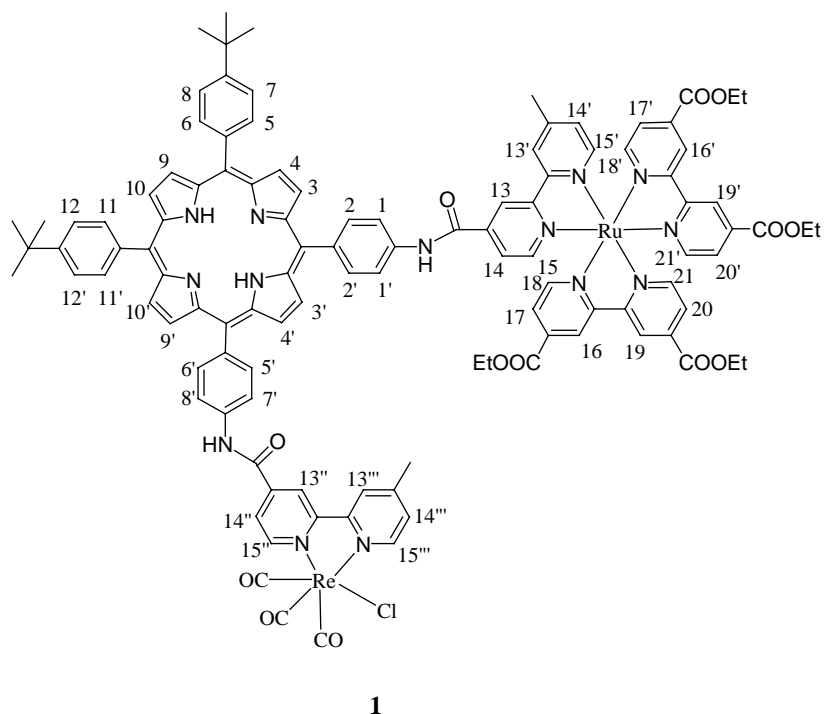
The reference compounds **Ru**, **PZnRu**¹⁷ and **PZnRe**^{2c} were prepared according to the literatures. We showed serial numbers of compound **1** so that we can easily assign the signal in ¹H NMR (see Fig. 6). All reagents were purchased from Aldrich, and all solvents were purified according to standard methods. Pyrrole was freshly distilled before use. All of the manipulations were performed under N₂. ¹H NMR spectra were recorded on a varian 400 spectrometer and reported in parts per million downfield from TMS.

4.1.1. 5,10-Bis(4-nitrophenyl)-15,20-bis(4-tert-butylphenyl)porphyrin (2). Pyrrole (0.56 mL, 8.0 mmol), 4-nitrobenzaldehyde (306 mg, 2.0 mmol) and 4-tert-butylbenzaldehyde (1.04 mL, 6.0 mmol) were added to CH₂Cl₂ (1000 mL), which was degassed with N₂ for 30 min. After the mixture was stirred under N₂ for a further 30 min, a BF₃/etherate solution (1.0 mL, 2 M in CH₂Cl₂, 2.0 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature. 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) (1.82 g, 8.0 mmol) was added to the red-brown solution, and the resulting black mixture was refluxed for 2 h. Et₃N (1.12 mL, 8.0 mmol) was added to the mixture, and the solution was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH₂Cl₂ = 50:50) to give the desired porphyrin product (196 mg, 12%). Mp > 300 °C; ¹H NMR (CDCl₃) δ 2.78 (s, br, 2H, -NH), 1.61 (s, 18H, tert-butyl-H), 7.78 (d, *J* = 8.0 Hz, 4H, H₇, H₈, H₁₂, H_{12'}), 8.14 (d, *J* = 8.0 Hz, 4H, H₅, H₆, H₁₁, H_{11'}), 8.40 (d, *J* = 8.0 Hz, 4H,

H₁, H_{1'}, H_{7'}, H_{8'}), 8.65 (d, *J* = 8.0 Hz, 4H, H₂, H_{2'}, H_{5'}, H_{6'}), 8.73 (d, *J* = 4.8 Hz, 2H, pyrrole), 8.78 (s, 2H, pyrrole), 8.91 (s, 2H, pyrrole), 8.96 (d, *J* = 4.8 Hz, 2H, pyrrole); ¹³C NMR (CDCl₃) δ 31.9, 35.1, 117.1, 122.1, 123.9, 134.7, 135.3, 138.8, 147.9, 149.2, 151.1; UV-vis in CH₂Cl₂ λ_{max} (nm) = 423.0, 518.0, 554.0, 592.0, 647.0; APCI-MS Positive: [M + H]⁺ (*m/z* = 817.4). Anal. Calcd for C₅₂H₄₄N₆O₄ · 0.1CH₂Cl₂: C, 75.81; H, 5.40; N, 10.18. Found: C, 76.00; H, 5.52; N, 10.26.

4.1.2. 5,10-Bis(4-aminophenyl)-15,20-bis(4-tert-butylphenyl)porphyrin (3). SnCl₂ · 2H₂O (915 mg, 4.0 mmol) in concentrated HCl (25 mL) was added to **2** (408 mg, 0.5 mmol) in CHCl₃-HOAc (1/2) (45 mL). The mixture was vigorously stirred in a preheated oil bath (65–70 °C) for 30 min, refluxed overnight, and then neutralized with ammonia solution (25%) to pH 8–9. Chloroform (100 mL) was added, and the mixture was stirred for 1 h. The organic phase was separated, and the water phase was extracted with CHCl₃ (2 × 100 mL). The combined organic layer was washed once with dilute ammonia solution, three times with water, and then concentrated to dryness. The residue was purified by column chromatography (silica gel, CH₂Cl₂/CH₃CH₂OH = 200:1) to give the desired porphyrin product (309 mg, 82%). Mp > 300 °C; ¹H NMR (CDCl₃) δ -2.72 (s, br, 2H, -NH), 1.60 (s, 18H, tert-butyl-H), 3.98 (s, br, 4H, -NH₂), 7.03 (d, *J* = 8.4 Hz, 4H, H₅, H₆, H₁₁, H_{11'}), 7.74 (d, *J* = 8.0 Hz, 4H, H₇, H₈, H₁₂, H_{12'}), 7.99 (d, *J* = 8.0 Hz, 4H, H₂, H_{2'}, H_{5'}, H_{6'}), 8.14 (d, *J* = 8.0 Hz, 4H, H₁, H_{1'}, H_{7'}, H_{8'}), 8.86–8.91 (m, 8H, pyrrole); ¹³C NMR (CDCl₃) δ 31.9, 35.1, 113.6, 120.0, 120.6, 123.8, 131.1, 132.8, 134.7, 135.9, 139.5, 146.1, 150.6; UV-vis in CH₂Cl₂ λ_{max} (nm) = 421.0, 517.0, 555.0, 591.0, 650.0; APCI-MS Positive: [M + H]⁺ (*m/z* = 757.5). Anal. Calcd for C₅₂H₄₈N₆ · 0.75CH₃CH₂OH: C, 81.18; H, 6.69; N, 10.62. Found: C, 81.58; H, 6.83; N, 10.21.

4.1.3. Porphyrin-(NHCO-bpy)₂(4). A mixture of 4-carboxy-4'-methyl-2,2'-bipyridine (350 mg, 1.636 mmol) and SOCl₂ (20 mL) was refluxed for 2 h. After removal of the excess SOCl₂ by distillation under reduced pressure, the acid chloride product was obtained and dried in vacuum at 70 °C for 1 h. Then dry CH₂Cl₂ (12 mL) was added and the mixture was stirred for 5 min at 50 °C. The resulting light yellow



1

Figure 6. Serial numbers of the complex 1.

solution was added dropwise to the CH_2Cl_2 solution (30 mL) of **3** (268 mg, 0.35 mmol) in which two drops of Et_3N were added. White smoke was observed in the reaction flask. The mixture was refluxed overnight, and washed with 5% of aqueous ammonia solution and then water. After removing the solvent, the residue was dissolved in CHCl_3 (20 mL) and CH_3CN (200 mL) was added dropwise. Precipitate was formed by slowly evaporating CHCl_3 under vacuum. The desired product was obtained after column chromatography on silica gel with a mixture of CH_2Cl_2 – MeOH (95/5) as eluent to give purple solid (242 mg, 60%). $\text{Mp} > 250^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3) δ –2.75 (s, br, 2H –NH), 1.58 (s, 18H, *tert*-butyl-H), 2.48 (s, 6H, bpy- CH_3), 7.21 (d, $J=4.8$ Hz, 2H, $\text{H}_{14'}$, $\text{H}_{14''}$), 7.71 (d, $J=8.0$ Hz, 4H, H_5 , H_6 , H_{11} , $\text{H}_{11'}$), 7.96 (d, $J=3.2$ Hz, 2H, H_{14} , $\text{H}_{14''}$), 8.05 (d, $J=8.4$ Hz, 4H, H_7 , H_8 , H_{12} , $\text{H}_{12'}$), 8.09 (d, $J=8.0$ Hz, 4H, H_2 , H_2' , H_5' , H_6'), 8.20 (d, $J=8.4$ Hz, 4H, H_1 , H_1' , H_7' , H_8'), 8.34 (s, 2H, $\text{H}_{13'}$, $\text{H}_{13''}$), 8.59 (d, $J=5.2$ Hz, 2H, $\text{H}_{15'}$, $\text{H}_{15''}$), 8.68 (s, 2H, amide-H), 8.85–8.86 (m, 8H, pyrrole-H), 8.88–8.91 (m, 4H, H_{13} , $\text{H}_{13''}$, H_{15} , $\text{H}_{15''}$); $^{13}\text{C NMR}$ (CDCl_3) δ 21.5, 31.9, 35.1, 117.6, 118.8, 119.2, 120.6, 121.7, 122.3, 122.6, 123.5, 125.7, 131.5, 133.3, 134.6, 135.4, 137.4, 139.2, 143.3, 149.1, 150.6, 155.1, 156.9, 163.6; UV–vis in CH_2Cl_2 λ_{max} (nm)=421.0, 518.0, 554.0, 594.0, 647.0; APCI-MS Positive: $[\text{M} + \text{H}]^+$ ($m/z=1149.5$). Anal. Calcd for $\text{C}_{76}\text{H}_{64}\text{N}_{10}\text{O}_2 \cdot 0.4\text{CH}_2\text{Cl}_2$: C, 77.54; H, 5.52; N, 11.84. Found: C, 77.82; H, 5.74; N, 12.00.

4.1.4. Porphyrin-(NHCO-bpy) $_2$ -Ru[(bpy)(COOEt) $_2$] $_2$ – PF_6] $_2$ (5**). A mixture of **4** (100 mg, 0.087 mmol) and $\text{Ru}[\text{bpy}(\text{COOEt})_2]_2\text{Cl}_2$ (134 mg, 0.174 mmol) in acetic acid (30 mL) was refluxed for 1 h under N_2 in the dark. After removing the solvent, the product was loaded on column of silica gel with a mixture of CH_2Cl_2 – MeOH (10/1) as eluent, and the anion was exchanged with NH_4PF_6 . The product was obtained as a red-brown solid, which was the desired **5** (60 mg, 32%). $\text{Mp} > 250^\circ\text{C}$; $^1\text{H NMR}$ (CD_3CN)**

δ –2.81 (s, br, 2H, –NH), 1.42–1.46 (m, 12H, – $\text{COOCH}_2\text{CH}_3$), 1.53 (s, 18H, *tert*-butyl), 2.48 (s, 3H, bpy- CH_3), 2.63 (s, 3H, Ru unit-bpy- CH_3), 4.48–4.50 (m, 8H, – $\text{COOCH}_2\text{CH}_3$), 7.29–7.31 (m, 1H, $\text{H}_{14'}$), 7.35–7.37 (m, 1H, $\text{H}_{15'}$), 7.58 (d, $J=5.2$ Hz, 1H, $\text{H}_{14''}$), 7.64–7.70 (m, 4H, H_7 , H_8 , H_{12} , $\text{H}_{12'}$), 7.84–7.88 (m, 4H, H_5 , H_6 , H_{11} , $\text{H}_{11'}$), 7.92–8.16 (m, 20H, H_1 , H_1' , H_2 , H_2' , H_5' , H_6' , H_7' , H_8' , H_{14} , $\text{H}_{14''}$, H_{15} , $\text{H}_{15''}$, H_{17} , $\text{H}_{17'}$, H_{18} , $\text{H}_{18'}$, H_{20} , $\text{H}_{20'}$, H_{21} , $\text{H}_{21'}$), 8.32 (s, 1H, $\text{H}_{15''}$), 8.59–8.61 (m, 1H, $\text{H}_{13'}$), 8.65–8.89 (m, 9H, pyrrole-H, $\text{H}_{13''}$), 8.95–8.97 (m, 1H, $\text{H}_{13''}$), 9.04–9.12 (m, 5H, H_{13} , H_{16} , $\text{H}_{16'}$, H_{19} , $\text{H}_{19'}$), 9.43 (s, 1H, amide-H), 9.51 (s, 1H, Ru unit-amide-H); UV–vis in acetonitrile λ_{max} (nm)=306.0, 418.0, 514.0, 551.0, 594.0, 646; IR (KBr, νCO): 558, 844, 1731, 3422 cm^{-1} ; API-ES-MS m/z : $[\text{M} - \text{PF}_6]^+$ 1996.3, $[\text{M} - 2\text{PF}_6]^{2+}$ 925.0. Anal. Calcd for $\text{C}_{108}\text{H}_{96}\text{F}_{12}\text{N}_{14}\text{O}_{10}\text{P}_2\text{-Ru} \cdot 1.8\text{HPF}_6$: C, 53.96; H, 4.10; N, 8.16. Found: C, 53.99; H, 3.95; N, 7.98.

4.1.5. Porphyrin-(NHCO-bpy) $_2$ -Ru[(bpy)(COOEt) $_2$] $_2$ – $\text{Re}(\text{CO})_3\text{Cl}[\text{PF}_6]_2$ (1**). A mixture of **5** (100 mg, 0.046 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ (25 mg, 0.07 mmol) in toluene (90 mL) was refluxed for 6 h under N_2 in the dark. After removing the solvent, the product was loaded on column of silica gel with a mixture of MeOH – CH_2Cl_2 (1/100) as eluent. The desired product was obtained as a yellow-brown solid (112 mg, 98%). $\text{Mp} > 250^\circ\text{C}$; $^1\text{H NMR}$ (CD_3CN) δ –2.81 (s, br, 2H, –NH), 1.40–1.44 (m, 12H, – $\text{COOCH}_2\text{CH}_3$), 1.56 (s, 9H, *tert*-butyl), 1.58 (s, 9H, *tert*-butyl), 2.61 (s, 3H, bpy- CH_3), 2.63 (s, 3H, Ru-bpy- CH_3), 4.45–4.48 (m, 8H, – $\text{COOCH}_2\text{CH}_3$), 7.34 (d, $J=5.6$ Hz, 1H, $\text{H}_{14'}$), 7.53 (d, $J=6.8$ Hz, 2H, $\text{H}_{15'}$, $\text{H}_{14''}$), 7.78–7.85 (m, 6H, H_7 , H_7' , H_8 , H_8' , H_{12} , $\text{H}_{12'}$), 7.89–8.01 (m, 10H, H_{14} , H_{15} , H_{17} , $\text{H}_{17'}$, H_{18} , $\text{H}_{18'}$, H_{20} , $\text{H}_{20'}$, H_{21} , $\text{H}_{21'}$), 8.07–8.28 (m, 12H, H_1 , H_1' , H_2 , H_2' , H_5 , H_5' , H_6 , H_6' , H_{11} , $\text{H}_{11'}$, $\text{H}_{14''}$, $\text{H}_{15''}$), 8.55 (s, 1H, $\text{H}_{15''}$), 8.71 (s, 1H, $\text{H}_{13'}$), 8.85–8.91 (m, 8H, Pyrrole-H), 8.95**

(s, 1H, H_{13^m}), 9.07–9.13 (m, 5H, H₁₃, H₁₆, H_{16'}, H₁₉, H_{19'}), 9.25 (d, 1H, *J* = 5.2 Hz, H_{13ⁿ}), 9.58 (s, br, 1H, amide-H), 9.64 (s, br, 1H, amide-H); UV–vis in acetonitrile λ_{max} (nm) = 275.0, 418.0, 515.0, 551.0, 592.0, 646; IR (KBr, νCO): 558, 844, 1729, 1917, 2022, 3398 cm⁻¹; API-ES-MS *m/z*: [M–PF₆]⁺2300.5, [M–2PF₆]²⁺1078.9. Anal. Calcd for C₁₁₁H₉₆ClF₁₂N₁₄O₁₃P₂ReRu·2CH₂Cl₂: C, 51.87; H, 3.85; N, 7.49. Found: C, 51.97; H, 3.79; N, 7.29.

4.1.6. Zn-Porphyrin-(NHCO-bpy)₂-Ru(bpy)(COOEt)₂(Re(CO)₃Cl)[PF₆]₂ (1-Zn).

Zn(OAc)₂·2H₂O (20 mg, 0.100 mmol) in ethanol (2 mL) was added to **1** (61 mg, 0.025 mmol) in chloroform (15 mL), and stirred at room temperature overnight under N₂ in the dark. This mixture was washed with water and extracted with CHCl₃. The combined organic phase was evaporated to dryness and purified by CH₂Cl₂–MeOH (10/1). The desired product was obtained as a red-brown solid (58 mg, 94%). Mp > 250 °C; ¹H NMR (CD₃CN) δ 1.41–1.45 (m, 12H, –COOCH₂CH₃), 1.57 (s, 9H, *tert*-butyl), 1.58 (s, 9H, *tert*-butyl), 2.60 (s, 3H, bpy–CH₃), 2.62 (s, 3H, Ru–bpy–CH₃), 4.46–4.50 (m, 8H, –COOCH₂CH₃), 7.36 (d, *J* = 7.6 Hz, 1H, H_{14^v}), 7.55 (d, *J* = 5.2 Hz, 2H, H_{15^v}, H_{14^m}), 7.81–7.87 (m, 6H, H₇, H_{7'}, H₈, H_{8'}, H₁₂, H_{12'}), 7.92–8.02 (m, 10H, H₁₄, H₁₅, H₁₇, H_{17'}, H₁₈, H_{18'}, H₂₀, H_{20'}, H₂₁, H_{21'}), 8.03–8.29 (m, 12H, H₁, H_{1'}, H₂, H_{2'}, H₅, H_{5'}, H₆, H_{6'}, H₁₁, H_{11ⁿ}, H_{14ⁿ}, H_{15ⁿ}), 8.56 (s, 1H, H_{15^m}), 8.73 (s, 1H, H_{13^v}), 8.87–8.95 (m, 8H, pyrrole-H), 8.98 (s, 1H, H_{13^m}), 9.06–9.13 (m, 5H, H₁₃, H₁₆, H_{16'}, H₁₉, H_{19'}), 9.27 (d, 1H, *J* = 5.2 Hz, H_{13ⁿ}), 9.60 (s, br, 1H, amide-H), 9.65 (s, br, 1H, amide-H); UV–vis in acetonitrile λ_{max} (nm) = 308.0, 428.0, 563.0, 605.0; API-ES-MS *m/z*: [M–PF₆]⁺1904.7, [M–2PF₆]²⁺, 1108.3. Anal. Calcd for C₁₁₁H₉₄ClF₁₂N₁₄O₁₃P₂ReRuZn·1.5CH₂Cl₂: C, 51.23; H, 3.71; N, 7.43. Found: C, 51.61; H, 3.65; N, 7.10.

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