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Synthesis, characterization and some properties of amide-linked porphyrin–ruthenium(II) tris(bipyridine) complexes

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Abstract—A new molecular dyad, comprised of a zinc-porphyrin and a ruthenium(II) tris(bipyridine) complex linked through an amide bond has been synthesized and characterized by ¹H, ¹³C NMR, UV–vis, mass-spectrometry and elemental analysis. The electrochemistry as well as the steady-state emission properties were investigated. The redox behavior of the dyad exhibits a favorable reversible characteristic. Substantial quenching of porphyrin emission was found when the Q band of **5** and **5-Zn** was selectively photoexcited. This observation suggests a quenching mechanism with possible intramolecular electron transfer or energy transfer between the Ru(bpy)₃ moiety and the porphyrin free-base or Zn porphyrin moieties.

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1. Introduction

In nature, many processes convert the solar energy into chemical energy, for instance, the photosynthesis. This process involves with a complicated mechanism: sunlight is captured by chlorophyll arrays, funnels the excited energy to the reaction center, and converts it to chemical potential in the form of a long-lived charge-separated state.¹ Up to now, many types of supramolecular systems have been designed and studied as model systems to mimic the natural process of sunlight conversion.² Among these, porphyrinoid arrays, dyads, triads and higher order arrays, linked by covalent bonds and non-covalent forms have been extensively studied.³ Porphyrin is the most widely used chromophore.⁴ Other elaborate systems include porphyrins–quinone assemblies,⁵ with porphyrin or metalloporphyrins as donor and quinones as acceptors.

Polypyridine,⁶ on the other hand, especially ruthenium(II) tris-(2,2'-bipyridine), is another kind of important chromophore. It has an absorption maximum in the range of 400–500 nm with increased absorptive cross sections at the wavelength of the porphyrins. Such complementary absorption spectra of porphyrin and ruthenium(II) trisbipyridine provide us with an extended absorption range favorable for the collection of light. In addition, an

intramolecular electron transfer from porphyrin to the Rucomplex occurs on the excitation of the porphyrin moiety or Ru moiety.⁷ Ruthenium(II) tris-bipyridine derivatives have favourable photophysical and redox properties, which make them ideal candidates for photosensitizer.^{6,7}

A previous work have shown intramolecular electron transfer from the higher excited state S_2 of a zinc porphyrin to a covalently linked ruthenium complex was possible.⁸ Related studies for such porphyrin–Ru systems have been reported by a few research groups.⁹ Based on these analyses, $[Ru(bpy)_3]^{2+}$ was used here for constructing some electron donor–acceptor systems based on $Ru(bpy)_3$ –porphyrin conjugates. We present here the synthesis, electrochemical and photophysical studies of porphyrin–Ru(bpy)₃ conjugates as well as related reference compounds. The deliberate introduction of electron-withdrawing substituents (carboxylate ester) on the bipyridine rings is expected to have some effects on electron transfer and energy transfer,¹⁰ because the oxidation potential is different from the unsubstitutied $Ru(bpy)_3$.

2. Results and discussion

2.1. Synthesis

This work started with the preparation of mono nitrosubstituted porphyrin $\mathbf{1}$ according to Lindsey's method¹¹ by condensation of aldehydes with pyrroles in the presence of

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BF₃/etherate, followed by oxidation with DDQ, outlined in Scheme 1. Pyrrole, 4-*tert*-butylbenzaldehyde and 4-nitrobenzaldehyde in a ratio of 4/3/1 reacted in CH₂Cl₂ at room temperature to afford 1 after usual workup and repeated column chromatography on silica gel, with bis-, tris-, and tetra-nitrophenyl analogues as the side products. The reduction of nitro group was carried out in CHCl₃/HOAc by usual SnCl₂/HCl procedure¹² to give the amino substituted phenylporphyrin **2** in good yield. It was further treated with 4'-methyl-2,2'-bipyridinyl-4-carbonyl chloride (which was prepared from 4,4'-dimethyl-2,2'-bypyridine according to literature¹³) in the presence of Et₃N to form porphyrin–bipyridine ligand **3** in 67% yield. By refluxing the mixture of **4** and **3** in acetic acid, ruthenium(II) complex **5** was obtained. ¹H NMR assignments for **5** (Fig. 1) were based on peak intensity, peak multiplicity, and were verified



Scheme 1. Synthetic route for compound 5.

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Figure 1. The aromatic region of the 1 H NMR (400 MHz) spectrum of 5 in CD₃CN.

by 2D NMR spectroscopy. Particularly diagnostic in ¹H NMR were three resonance signals at $\delta - 2.81$ (internal NHpyrrolic resonance), 1.55 (H from *t*-butyl) and 9.56 (amide H). Obviously ruthenium(II) has just coordinated to the bipyridine rather than inserting into the porphyrin ring. This can be confirmed by ¹H NMR, which shows a broad singlet at $\delta - 2.81$ corresponding to the NH proton of the free base porphyrin. The dinuclear complex **5-Zn** was then formed by stirring the mixture of Zn(OAc)₂ and **5** in chloroform with minor EtOH at room temperature (Scheme 2). This reaction is facile but has to be performed under N₂ in the dark. The target dinuclear complex **5-Zn** can be prepared by two synthetic approaches: Zn(II) was inserted into the porphyrin free base first, then ruthenium(II) was coordinated to the bpy ligand **3**; or ruthenium(II) was used to coordinate to the bpy ligand before the Zn(II) was inserted. Of the two possibilities, the former seems to be problematic for the coordination of ruthenium(II) to the bipyridine ligand, partly due to the coordination of bipyridine to the Zn-porphyrin as an axial ligand. To overcome this problem, we chose the latter approach for the preparation of **5-Zn**.

2.2. Steady-state absorption spectra

The ground-state absorption spectrum is shown in Figure 2. It exhibits the Soret band at ca. 420 nm and Q-bands ranging



Scheme 2. Synthetic route for complex 5-Zn.

from 500 to 650 nm for the porphyrin subunit, in addition to the absorption bands for the $[Ru(bpy)_3]^{2+}$ moiety at 300 nm (bipy $\pi \rightarrow \pi^*$) and 475 nm (MLCT transition). The Soret band characterizes promotion to the second-excited singlet state of porphyrin, while the Q-bands correspond to the first-excited singlet state of the porphyrin. The two Q-bands absorption of compound **5-Zn** arrised from the increasing

molecular symmetry to $D_{4 \text{ h}}$, which is a typical pattern of regular metal porphyrins. The metal to ligand charge transfer (MLCT) transition is red shifted (25 nm) corresponding to the absorption of $[\text{Ru}(\text{bpy})_3]^{2+,14}$ which is caused by esterification in the pyridine rings. The other main absorption bands of the **5-Zn** display also a slight red shift, compared to the relevant transitions for the absorption



Figure 2. UV–vis absorption spectra of 5-Zn, 5 in CH₃CN [5×10^{-6} M].

derived from the comparisons of the optical absorption and emission characteristics of such assemblies. The steady state emission spectra are shown in Figure 3. An emission profile was obtained upon excitation of the MLCT band of 5-Zn, the free base and the ruthenium(II) tris-bipyridine subunit 6. The emission spectrum of 5-Zn shows a mixture of fluorescence from porphyrin and luminescence from the $Ru(bpy)_3$ unit (Fig. 3a). However, we find that the emission from 5 is solely due to the fluorescence of porphyrin unit, and there is substantial quenching of porphyrin and $Ru(bpy)_3$ unit emission in 5-Zn compared to 5 and 6. The detailed data are listed in Table 1. This implies that there are completely different electron or energy transfer paths in the compounds 5-Zn and 5. On the other hand, when selectively exciting the Q bands in 5-Zn (558 nm) and 5 (551 nm), the fluorescent emission of 5-Zn is blue-shifted (0-0 and 0-1



Figure 3. Steady-state emission spectra of (a) 5-Zn (λ_{ex} =471 nm); (b) 6 (λ_{ex} =468 nm); (c) 5 (λ_{ex} =471 nm); (d) 5-Zn (λ_{ex} =558 nm), 5 (λ_{ex} =551 nm) with excitation of Porphyrin's Q band in deoxygenated CH₃CN [5×10⁻⁶ M].

band of **5**, suggesting some interaction between the intramolecular porphyrin and $[Ru(bpy)_3]^{2+}$ chromophores (Scheme 2).¹⁵

2.3. Emission measurements

Evidence for excited state interactions in our molecule is

band at 619 and 654 nm) with respect to **5**, but their emission profile is very similar. There is also a classic oxidizing quenching with electron transfer from porphyrin to the Ru complex. The emission from **5-Zn** was found to be 3% relative to that of **5**. Such transformation is more effective for the zinc porphyrin due to its lower oxidation potential (Table 1).

Table 1. Steady-state emission spectroscopic data of 5, 6 and 5-Zn in CH₃CN at 298 K [5×10^{-6} M]

Compd.		MLCT band	l	Soret band			
	$\lambda_{\rm ex} (\rm nm)$	$\lambda_{\rm em}$ (nm)	$I_{\rm em} \times 10^{-3}$ (a.u.)	$\lambda_{\rm ex} (\rm nm)$	$\lambda_{\rm em}$ (nm)	$I_{\rm em} \times 10^{-3}$ (a.u.)	
5-Zn	471	654	22.7	558	617	50.8	
5	471 470	656 627	2100 683	551	656	1980	



Figure 4. Cyclic voltammogram for complex **5-Zn** in 10^{-3} M CH₂Cl₂/ 0.1 M TBAPF₆ on a glassy carbon disc electrode at a scan rate of 50 mV/s. Inset A was recorded in CH₃CN/0.05 M TBAPF₆ at a glass carbon working electrode with a scan rate of 50 mV/s and reported relative to SCE.

On the reduction side, there were also three reversible peaks: $E_{1/2} = -0.79$, -1.07, and -1.43 V, corresponding to the first reduction of the Zn porphyrin unit (**2**) and the first and second reduction of the Ru(bpy)₃²⁺ unit. Inset A in Figure 4 was one part of the CV recorded in CH₃CN, which was not observed in CH₂Cl₂.^{16,17} The new reduction peak which occurs at $E_{1/2} = -1.75$ V is assigned to the third reduction of the Ru(bpy)₃²⁺ unit. To ensure a more accurate comparison between the porphyrins and ruthenium complexes, all measurements were performed in CH₂Cl₂ as a solvent.¹⁸ All six redox peaks (Fig. 4) are reversible one-electron processes.

The cyclic voltammogram for **5** was recorded in CH₂Cl₂ and 0.05 M TBAPF₆ (Fig. 5). In Figure 5, the oxidation part of the cyclic voltammogram for complex **5** exhibited two reversible one-electron process peaks: $E_{1/2}=1.18$ and 1.47 V assigned to the oxidation of its porphyrin unit and the metal-based oxidation (Ru^{II}/Ru^{III}) couple respectively,

Table 2. Electrochemical data versus SCE for complexes and model compounds

Complexes	Oxidations						Reductions					
	E _{1/2}	$\Delta E_{\rm p}$	$E_{1/2}$	$\Delta E_{ m p}$	$E_{1/2}$	$\Delta E_{ m p}$	E _{1/2}	$\Delta E_{ m p}$	E _{1/2}	$\Delta E_{\rm p}$	E _{1/2}	$\Delta E_{\rm p}$
5-Zn 5	1.68 1.47	0.09 0.11	1.17 1.18	0.1 0.12	0.78	0.08	-0.79 -1.04	0.09 0.19	-1.07 -1.56	0.07	-1.43 -1.87	0.08
$Ru(bpy)_3^{2+}$	1.35	0.07					-1.32	0.07	-1.51	0.07	-1.76	0.07

Recorded in CH₂Cl₂ 0.05 M TBAPF₆ with a scan rate of 50 mV/s.

2.4. Electrochemistry

The cyclic voltammogram for the ruthenium complex **5-Zn** recorded in CH₂Cl₂ 0.1 M TBAPF₆ (Fig. 4) exhibited a favorable reversible process. Reversible oxidation peaks of **5-Zn** were observed at $E_{1/2}=0.78$ V and $E_{1/2}=1.17$ V versus SCE assigned to the first and second oxidation of Zn porphyrin unit, and $E_{1/2}=1.68$ V assigned to metal-based oxidation (Ru^{II}/Ru^{III}) couple, being obviously shifted from the value observed for that in Ru(bpy)₃²⁺ (see Table 2). The introduction of carboxylic groups to the bipyridyl ligands affects the redox potential values. Increasing the number of electron-withdrawing groups on the ligands makes the metal oxidation more difficult and the reduction of the ligands easier.¹⁰



Figure 5. Cyclic voltammogram for complex **5** in 10^{-3} M CH₂Cl₂/0.1 M TBAPF₆ on a glassy carbon disc electrode at 50 mV/s.

which has one less oxidation peak than that in the case of **5-Zn**, and the potential value of Ru^{II}/Ru^{III} couple was obviously lower than that of **5-Zn**.

On the other hand, there are great differences between **5** and **5-Zn** in the reduction region. The diagram of **5** exhibited three consecutive reduction waves, of which the second and third ones were not reversible, corresponding to the first and second reduction of the Ru(bpy)₃²⁺ units. We also leave out here the part of the third reduction of the Ru(bpy)₃²⁺ units in acetonitrile. The presence of a reversible two-electron reduction peak at $E_{1/2} = -1.04$ V is worthy of note, corresponding to the reduction of the porphyrin subunit, and suggesting the occurrence of a chemical reaction of the two-electron-reduced species.

In summary, the free base porphyrin and the Zn-porphyrin are covalently linked to a Ru(II) tris-bipyridine complex which bears four carboxylate ester groups on the bipyridine ligands. From the electrochemical study, it has been indicated that photogenerated Ru(III), which has a higher oxidation potential than normal Ru(bpy)₃, oxidize the porphyrin moiety thermodynamically. This observation could lead to an interesting photo-induced electron transfer or energy transfer process.

3. Experimental

3.1. General

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 ppm downfield from TMS. CH₂Cl₂ (Aldrich, spectroscopy grade) used for performance of electrochemistry was dried with molecular sieves (4 Å) and then freshly distilled from CaH_2 under N_2 . Cyclic voltammograms were recorded at a scan rate of 50 mV/s in 10^{-3} M CH₂Cl₂ solutions using 0.05 M Bu₄NPF₆ as supporting electrolyte. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat. The electrolyte solution was degassed by bubbling with dry argon for 10 min before measurements. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3 and 1 µm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a nonaqueous Ag/Ag^+ electrode (0.01 M AgNO₃ in CH₃CN) and the auxiliary electrode was a platinum wire. The measured potentials in Figures 4 and 5 were corrected to the values of SCE by adding 0.30 V.

5-(4-Nitrophenyl)-10,15,20-tris(4-tert-butyl-3.1.1. phenyl)porphyrin (1). Pyrrole (0.28 mL, 4.0 mmol), 4-nitrobenzaldehyde (153 mg, 1.0 mmol) and 4-tert-butylbenzaldehyde (0.52 mL, 3.0 mmol) were added to CH_2Cl_2 (500 mL) which was degassed with N₂ for 30 min. After the mixture was stirred and purged with N₂ for a further 30 min, a BF₃/etherate solution (0.5 mL, 2 M in CH₂Cl₂, 1.0 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature. 2,3-Dichloro-5,6-dicyanobenzo-quinone (DDQ) (0.91 g, 4.0 mmol) was added to the red-brown solution, and the resulting black mixture was refluxed for 2 h. Et₃N (0.56 mL, 4.0 mmol) was added, and the solution was concentrated to dryness under reduced pressure. The residue was purified by column chromatography (silica gel, pentane $/CH_2Cl_2=60/40$) to give the desired porphyrin product in 12% yield: Mp > 300 °C; ¹H NMR (CDCl₃) δ -2.78 (s, br, 2H, -NH), 1.60 (s, 27H, tertbutyl-H), 7.74 (d, J=8.4 Hz, 6H, H₇, H₇, H₈, H₈, H₁₂, $H_{12'}$), 8.11 (dd, J=8.0 Hz, J=2.4 Hz, 6H, H_5 , $H_{5'}$ H_6 , $H_{6'}$ $H_{11}, H_{11'}$), 8.37 (d, J=8.4 Hz, 2H, $H_1, H_{1'}$), 8.60 (d, J= 8.8 Hz, 2H, H₂, H_{2'}), 8.68 (d, J = 4.0 Hz, 2H, H₃, H_{3'}), 8.86 $(s, 4H, H_4, H_{4'}, H_9, H_{9'}), 8.90 (d, J = 4.8 Hz, 2H, H_{10}, H_{10'});$ UV-vis in methylene chloride λ_{max} [nm]=422.0, 518.0, 554.0, 593.0, 650.0; APCI-MS Positive: $[M+H]^+$ (m/z =828.5); Anal. Calcd for C₅₆H₅₃N₅O₂·0.75C₆H₁₄: C, 81.40; H, 7.17; N, 7.85. Found: C, 80.91; H, 7.02; N, 7.56.

3.1.2. 5-(4-Aminophenyl)-10,15,20-tris(4-*tert***-butyl-phenyl)porphyrin (2).** To a solution of **1** (335 mg, 0.405 mmol) in 1:2 CHCl₃/HOAc (30 mL) was added a solution of SnCl₂·2H₂O (366 mg, 1.62 mmol) in concentrated HCl (10 mL). The mixture was vigorously stirred in a preheated oil bath (65–70 °C) for 30 min, refluxed overnight, 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, then concentrated to dryness. The residue was purified by column chromatography (silica gel, chloroform). Yield: 84%. Mp > 300 °C; ¹H NMR (CDCl₃): δ – 2.72 (s, br, 2H, –NH),

1.60 (s, 27H, *tert*-butyl-H), 3.91 (s, br, 2H, $-NH_2$), 6.99 (d, J=8.0 Hz, 2H, H₁, H_{1'}), 7.74 (d, J=8.0 Hz, 6H, H₇, H_{7'}, H₈, H_{8'}, H₁₂, H_{12'}), 7.98 (d, J=8.4 Hz, 2H, H₂, H₂'), 8.14 (d, J=8.0 Hz, 6H, H₅, H_{5'}, H₆, H_{6'}, H₁₁, H_{11'}), 8.86 (s, 6H, H₃, H_{3'}, H₄, H_{4'}, H₉, H_{9'}), 8.91 (d, J=4.8 Hz, 2H, H₁₀, H₁₀'); ¹³C NMR (CDCl₃) δ 31.9, 35.1, 113.6, 120.1, 120.2, 120.7, 123.8, 131.3, 132.7, 134.7, 135.9, 139.5, 146.1, 150.6; UV-vis in methylene chloride λ_{max} [nm]=421.0, 517.0, 555.0, 591.0, 650.0; APCI-MS Positive: [M+H]⁺ (*m*/*z*=798.4). Anal. Calcd for C₅₆H₅₅N₅·0.25H₂O: C, 83.81; H, 6.97; N, 8.73. Found: C, 83.83; H, 7.02; N, 8.47.

3.1.3. Porphyrin-NHCO-bpy (3). A mixture of 4-carboxy-4'-methyl-2,2'-bipyridine (146 mg, 0.680 mmol) and SOCl₂ (10 mL) was refluxed for 2 h. After removing excess SOCl₂ by distillation under reduced pressure, the acid chloride product was obtained and further dried in vacuum at 70 °C for 1 h. Then anhydrous CH₂Cl₂ (5 mL) was added and the mixture was stirred for 5 min at 50 °C. The resulting light yellow solution was added dropwise to the CH₂Cl₂ solution of 2 (0.27 g, 0.33 mmol) in which 2 drops of Et_3N had been pre-added. White smoke was observed in the reaction flask. The mixture was refluxed for 4 h, washed with 5% aqueous ammonia solution then with water. After removing the solvent, the residue was dissolved in $CHCl_3$ (10 mL) then CH₃CN (100 mL) was added dropwise. Precipitate was formed by slowly evaporating CHCl₃ under vacuum. The desired product was obtained after column chromatography on silica gel with a mixture of CH₂Cl₂/MeOH (94:6) as eluent to give purple solid (221 mg, 67%): mp >250 °C; ¹H NMR (CDCl₃): δ -2.74 (s, br, 2H -NH), 1.61 (s, 27H, *tert*butyl-H), 2.46 (s, 3H, bpy-CH₃) 7.23-7.25 (m, 1H, H_{14'}), 7.73-7.77 (m, 6H, H₇, H₇', H₈, H₈', H₁₂, H₁₂'), 8.02-8.04 (m, 1H, H₁₄), 8.12-8.16 (m, 8H, H₁, H_{1'}, H₅, H_{5'}, H₆, H_{6'}, H_{11} , $H_{11'}$), 8.26 (d, J=8.4 Hz, 2H, H_2 , $H_{2'}$), 8.36 (s, 1H, $H_{13'}$), 8.60 (d, J = 4.8 Hz, 1H, $H_{15'}$), 8.82 (s, br, 1H, amide H), 8.86–8.92 (m, 9H, H₁₃, H₃, H₃', H₄, H₄', H₉, H₉', H₁₀, H₁₀'), 8.94 (s, 1H, H₁₅); ¹³C NMR (CDCl₃) δ 21.5, 31.9, 35.1, 117.8, 118.7, 119.1, 120.4, 122.2, 122.6, 123.7, 125.5, 131.4, 134.6, 135.4, 137.4, 139.2, 143.2, 148.9, 150.5, 155.1, 157.0, 164.3; UV-vis in methylene chloride λ_{max} [nm]=420.0, 517.0, 553.0, 591.0, 649.0; APCI-MS Positive: $[M+H]^+$ (*m*/*z*=994.5); Anal. Calcd for C₆₈H₆₃N₇O·0.75 CH₂Cl₂: C, 78.05; H, 6.14; N, 9.27. Found: C, 77.82; H, 6.53; N, 8.95.

3.1.4. Porphyrin-NHCO-bpy-Ru[(bpy)(COOEt)₂]₂- $[PF_6]_2$ (5). A mixture of 3 (50 mg, 0.050 mmol) and Ru[bpy(COOEt)₂]₂Cl₂ (40 mg, 0.050 mmol) in acetic acid (10 mL) was refluxed for 1 h under N₂ in the dark. After removing the solvent, the product was loaded onto a column of silica gel with a mixture of CH₂Cl₂/MeOH (10:1) as eluent, and the anion was exchanged with NH₄PF₆. The desired product was obtained as a red-brown solid (40 mg, 40%): mp > 250 °C; ¹H NMR (CD₃CN): δ – 2.81 (s, br, 2H, -NH), 1.42-1.46 (m, 12H, -COOCH₂CH₃), 1.55 (s, 9H, tert-butyl), 1.57 (s, 18H, tert-butyl), 2.64 (s, 3H, bpy-CH₃), 4.49–4.51 (m, 8H, –COO*CH*₂CH₃), 7.36 (d, *J*=4.8 Hz, 1H, H_{14'}), 7.56–7.59 (m, 1H, H_{15'}), 7.73–7.79 (m, 6H, H₇, H_{7'}, H₈, H_{8'}, H₁₂, H_{12'}), 7.85–7.88 (m, 2H, H₁₄, H₁₅), 7.94–8.03 $(m, 8H, H_{17}, H_{17'}, H_{18}, H_{18'}, H_{20}, H_{20'}, H_{21}, H_{21'}), 8.04-8.10$ $(m, 6H, H_5, H_{5'}, H_6, H_{6'}, H_{11}, H_{11'}), 8.21 (d, J = 8.0 Hz, 2H,$ $H_1, H_{1'}$, 8.27 (d, J = 8.0 Hz, 2H, $H_2, H_{2'}$), 8.69 (s, 1H, $H_{13'}$),

8.82–8.89 (m, 8H, H₃, H₃', H₄, H₄', H₉, H₉', H₁₀, H₁₀'), 9.09–9.13 (m, 5H, H₁₃, H₁₆, H₁₆', H₁₉, H₁₉'), 9.56 (s, br, 1H, amide-H); ¹³C NMR (CD₃CN): δ 13.9, 21.3, 31.3, 34.9, 63.3, 119.3, 120.6, 121.5, 122.7, 123.8, 123.9, 124.3, 125.7, 126.5, 127.1, 129.5, 130.6, 131.3, 131.8, 131.9, 134.4, 135.3, 137.8, 138.2, 138.9, 139.0, 139.8, 139.9, 144.3, 151.1, 151.5, 152.2, 153.0, 153.2, 153.3, 153.5, 155.9, 157.7, 157.9, 162.6, 163.7.); UV–vis in methylene chloride $\lambda_{max} [nm] = 421.0, 450.0, 555.0, 650.0; API-ES-MS m/z:$ [M-PF₆]⁺ 1840.6, [M-2PF₆]²⁺ 847.4; Anal. Calcd forC₁₀₀H₉₅F₁₂N₁₁O₉P₂Ru·1.5CH₂Cl₂: C, 57.69; H, 4.67; N,7.29. Found: C, 57.56; H, 4.99; N, 6.95.

3.1.5. Zn-Porphyrin-NHCO-bpy-Ru[(bpy)(COOEt)₂]₂- $[\mathbf{PF}_6]_2$ (5-Zn). A solution of $Zn(OAc)_2 \cdot 2H_2O$ (10 mg, 0.050 mmol) in ethanol (1 mL) was added to a solution of 5 (50 mg, 0.025 mmol) in chloroform (10 mL), and stirred at rt overnight under N₂ in the dark. This mixture was washed with water and then evaporated to dryness and purified by CH₂Cl₂/MeOH (10:1). The desired product was obtained as a red-brown solid: (49 mg, 95%) mp >250 °C; ¹H NMR (CD₃CN) & 1.42–1.45 (m, 12H, –COOCH₂CH₃), 1.56 (s, 9H, tert-butyl), 1.58 (s, 18H, tert-butyl), 2.64 (s, 3H, bpy-CH₃), 4.47–4.51 (m, 8H, $-COOCH_2CH_3$), 7.37 (d, J=5.2 Hz, 1H, H_{14'}), 7.56–7.59 (m, 1H, H_{15'}), 7.73–7.78 (m, 6H, H_7 , $H_{7'}$, H_8 , $H_{8'}$, H_{12} , $H_{12'}$), 7.86–7.90 (m, 2H, H_{14} , H₁₅), 7.92–8.04 (m, 8H, H₁₇, H₁₇', H₁₈, H₁₈', H₂₀, H₂₀', H₂₁, H_{21'}), 8.06–8.15 (m, 8H, H₁, H_{1'} H₅, H_{5'}, H₆, H_{6'}, H₁₁, H_{11'}), 8.26 (d, J = 7.6 Hz, 2H, $H_2, H_{2'}$), 8.68 (s, 1H, $H_{13'}$), 8.83– 8.89 (m, 8H, H₃, H₃', H₄, H₄', H₉, H₉', H₁₀, H₁₀'), 9.06–9.13 (m, 5H, H₁₃, H₁₆, H₁₆', H₁₉, H₁₉'), 9.49 (s, br, 1H, amide-H); ¹³C NMR (CD₃CN) δ 14.4, 21.4, 31.8, 35.3, 63.8, 118.3, 119.4, 120.6, 121.7, 123.1, 124.2, 124.3, 124.9, 126.1, 126.9, 127.7, 130.1, 132.3, 132.6, 135.1, 135.8, 138.2, 140.3, 140.4, 140.9, 141.2, 144.5, 150.7, 150.9, 151.2, 152.0, 152.8, 153.5, 153.8, 153.9, 154.2, 156.5, 158.3, 158.5, 163.1, 164.4; UV-vis in methylene chloride λ_{max} [nm] = 422.0, 549.0, 468.0. API-ES-MS m/z: $[M-PF_6]$ 1904.7, $[M-2PF_6]^{2+}$, 879.0 Anal. Calcd for $C_{100}H_{93}F_{12}$ - $N_{11}O_9P_2RuZn\cdot 1.2CH_2Cl_2:\ C,\ 56.50;\ H,\ 4.47;\ N,\ 7.16.$ Found: C, 56.85; H, 4.51; N, 6.78.

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