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The synthesis of two novel hybrids containing a zinc(II) porphyrin unit and a polypyridyl ruthenium(II) complex unit and their photoinduced intramolecular electron and energy transfer

Jie Liu [a,b], Jin-Wang Huang [a,b,*], Han Shen [b], Hui Wang [b], Han-Cheng Yu [a,b], Liang-Nian Ji [a,b,c]

[a] *MOE Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China*

[b] *State Key Laboratory of Optoelectronic Material and Technologies, Sun Yat-Sen University, Guangzhou 510275, PR China*

[c] *Department of Chemistry, Tongji University, Shanghai 200092, PR China*

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Abstract

Two new hybrids, namely [C_4-ZnTPP-(ip)Ru(phen)$_2$](ClO_4)$_2$ and [C_4-ZnTPP-(ip)Ru(pip)$_2$](ClO_4)$_2$, containing a zinc(II) porphyrin unit and a polypyridyl ruthenium(II) complex unit were synthesized and characterized. Their photoinduced intramolecular electron and energy transfer properties were investigated using electronic absorption spectra, fluorescence spectra and decayed luminescence spectra. In both hybrid compounds, an electronic interaction and energy transfer between the zinc(II) porphyrin moiety and the polypyridyl ruthenium(II) moiety were observed. The efficiency of the energy transfer from ^{3}MLCT of the polypyridyl ruthenium(II) moiety to the zinc(II) porphyrin moiety and the rate of electron transfer from the singlet excited state of the porphyrin moiety to the polypyridyl ruthenium(II) may be related to the axial coordination of the N atom from pip in polypyridyl ruthenium(II) moiety to the zinc(II) ion.

Keywords: Porphyrin-polypyridyl ruthenium(II) hybrid; Energy transfer; Electron transfer

1. Introduction

In natural photosynthetic systems, the primary electron transfer step occurs from a porphyrin-based complex [1]. In order to gain a better understanding of natural photosynthetic mechanisms, artificial porphyrin derivatives have been designed and extensively investigated [2]. On the other hand, polypyridyl ruthenium(II) complexes are ideal candidates as photosensitizer owing to their rich photophysical and redox properties [3,4]. Previous reports on molecular dyads based on porphyrin and polypyridyl ruthenium(II) complex have shown that photoinduced intramolecular electron transfer and/or energy transfer can occur between the polypyridyl ruthenium(II) moiety and the porphyrin moiety [5–11]. These dyads are usually assembled through coordinative bonding [5,11], by covalent frameworks [6–9], or via supramolecular networks [10].

We have previously reported the photoinduced intramolecular electron and energy transfer phenomena in a porphyrin-polypyridyl ruthenium(II) hybrid, [C_4-TPP-(ip)Ru-(phen)$_2$](ClO_4)$_2$, in which a polypyridyl ruthenium(II) moiety is linked to a porphyrin moiety by a butyl chain [12]. On further investigation of photoinduced electron and energy transfer in this type of porphyrin-polypyridyl ruthenium(II) hybrid, we now synthesize two new hybrids [C_4-ZnTPP-(ip)Ru(phen)$_2$]-(ClO_4)$_2$ (**1**) and [C_4-ZnTPP-(ip)Ru(pip)$_2$](ClO_4)$_2$ (**2**), in which

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* Corresponding author. MOE Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China. Tel.: +86 020 84113317; fax: +86 020 84112245.

E-mail address: ceshjw@mail.sysu.edu.cn (J.-W. Huang).

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the porphyrin moiety is zinc(II) porphyrin and the ligands in polypyridyl ruthenium(II) moiety are ip and phen or pip (see Fig. 1). The effect of structure on photoinduced electron and energy transfer has been investigated.

2. Experimental

2.1. Physical measurements

Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240 Q elemental analyzer (Germany). ESI-MS data were measured on a Thermo Finnigan LCQ DECA XP spectrometer (USA). ^{1}H NMR spectra were recorded on a Varian Mercury-Plus 300 MHz spectrometer (USA) with $(CD_3)_2SO$ as solvent at room temperature and TMS as the internal standard. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 850 spectrophotometer (America). Steady-state emission measurements were carried out on a Perkin-Elmer LS55 fluorescence spectrometer (America) with both excitation and emission slit set at 5 nm. Samples were run in CH_2Cl_2 in 1 cm quartz cuvettes. A system based on an active mode-locked and frequency-doubled Nd:YAG laser (generated 130 fs pulses with a wavelength of 400 nm and the average power of 17.5 μW) and a C6860 streak camera were used to detect luminescence decay.

2.2. Materials and synthesis of hybrids

cis-Ru(pip)$_2$Cl$_2\cdot$2H$_2$O, [Ru(pip)$_2$(ip)](ClO$_4$)$_2\cdot$2H$_2$O [13], [Ru(phen)$_2$(ip)](ClO$_4$)$_2$ [14] and zinc(II) tetraphenylporphyrin (ZnTPP) [15] were synthesized and purified by published methods. CH_2Cl_2 was analytical reagent and was purified by standard methods prior to use. All other reagents were used as purchased.

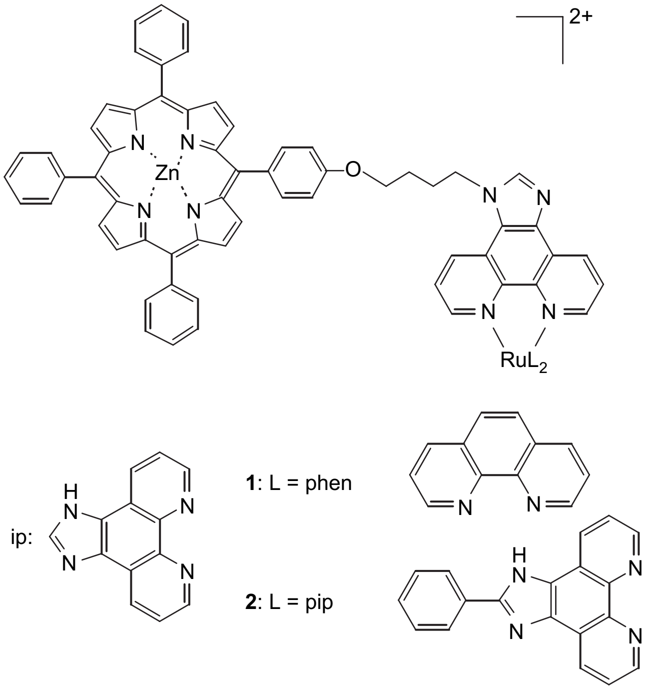

Fig. 1. Structures of the hybrids **1**and **2**.

[C$_4$-TPP-(ip)Ru(phen)$_2$](ClO$_4$)$_2$ was synthesized according to the previous method [16]. [C$_4$-TPP-(ip)Ru(pip)$_2$](ClO$_4$)$_2$ was prepared in a similar way with *cis*-Ru(pip)$_2$Cl$_2\cdot$2H$_2$O instead of *cis*-Ru(phen)$_2$Cl$_2\cdot$3H$_2$O. Yield: 73%. ESI-MS: *m*/*z* 799.3 ($[M-2ClO_4]^{2+}$). Element analysis: Found: C, 66.35; H, 3.92; N, 12.33%. [C$_4$-TPP-(ip)Ru(pip)$_2$](ClO$_4$)$_2\cdot$H$_2$O; calcd.: C, 65.49; H, 3.86; N, 12.35%. ^{1}H NMR (300 MHz; solvent $(CD_3)_2SO$): chemical shift δ 9.053 (s, 1H), 8.986–9.020 (d, 2H, $J = 9.10$ Hz), 8.847 (m, 4H), 8.776 (d, 8H, $J = 6.56$), 8.285–8.356 (m, 4H), 8.164 (dd, 6H, $J = 2.93$, 4.49 Hz), 7.988–8.089 (m, 6H), 7.795 (m, 11H), 7.751 (d, 2H, $J = 2.78$ Hz), 7.712 (d, 2H, $J = 4.90$), 7.544 (m, 4H), 7.396 (d, 2H, $J = 7.61$ Hz), 7.337 (d, 2H, $J = 7.37$ Hz), 7.240 (d, 2H, $J = 7.80$ Hz), 4.964 (t, 2H, $J = 6.77$ Hz), 4.264 (t, 2H, $J = 6.01$ Hz), 2.261 (m, 2H), 2.042 (m, 2H), −2.931 (s, 2H). IR (KBr, cm^{-1}): 3316 (ν_{N-H}), 3056 (ν_{C-H}), 2923, 2854 (ν_{C-H}), 1598, 1455 ($\nu_{C=C}$), 1242 (ν_{C-O}), 1181, 965 (δ_{C-H}), 1089 (ν_{ClO_4}), 848 (ν_{phen}), 622 (δ_{ClO_4}). (Caution! perchlorate salts of metal complexes with organic ligands are potentially explosive, and only small amounts of the material should be prepared and handled with great care.)

2.2.1. Synthesis of **1**

[C$_4$-TPP-(ip)Ru(phen)$_2$](ClO$_4$)$_2\cdot$2H$_2$O (80 mg, 0.05 mmol) and Zn(OAc)$_2\cdot$2H$_2$O (0.2 g, 1 mmol) were stirred for 2 h in glacial MeCO$_2$H (4 ml). The end of the reaction was confirmed by UV–vis absorption spectroscopy. The crude purple-red product was obtained after removing the solvent by rotary evaporation, then purified by column chromatography (Al$_2$O$_3$, CHCl$_3$/EtOH, from 20:1 to 5:1 V/V). Yield: 96%. ESI-MS: *m*/*z* 715.2 ($[M-2ClO_4]^{2+}$). Element analysis: Found: C, 61.40; H, 3.84; N, 9.97%. [C$_4$-ZnTPP-(ip)Ru(phen)$_2$](ClO$_4$)$_2\cdot$2H$_2$O; calcd.: C, 61.33; H, 3.73; N, 10.10%.

2.2.2. Synthesis of **2**

Compound **2** was synthesized in a similar way of **1**, using [C$_4$-TPP-(ip)Ru(pip)$_2$](ClO$_4$)$_2\cdot$H$_2$O (90 mg, 0.05 mmol) instead of [C$_4$-TPP-(ip)Ru(phen)$_2$](ClO$_4$)$_2\cdot$2H$_2$O.Yield: 95%. ESI-MS: *m*/*z* 1660.5 ($[M-2ClO_4]^{+}$), 831.2 ($[M-2ClO_4]^{2+}$). Element analysis: Found: C, 61.50; H, 3.76; N, 11.15%. [C$_4$-ZnTPP-(ip)Ru(pip)$_2$](ClO$_4$)$_2\cdot$4H$_2$O; calcd.: C, 61.52; H, 3.83; N, 11.60%.

3. Results and discussion

The ground-state absorption spectra of **1**, ZnTPP and [Ru(phen)$_2$(ip)]$^{2+}$ were measured in CH_2Cl_2. As shown in Fig. 2, the absorption of **1** shows not only the Soret band and Q bands of the zinc(II) porphyrin moiety but also the IL and MLCT transitions of the polypyridyl ruthenium(II) moiety. The Q band corresponds to population of the first-excited singlet state (S$_1$) of the porphyrin and the Soret band characterizes promotion to the second-excited singlet state (S$_2$) of the porphyrin. Compared with the superposition of the spectrum of ZnTPP with [Ru(phen)$_2$(ip)]$^{2+}$ (see Fig. 2), the

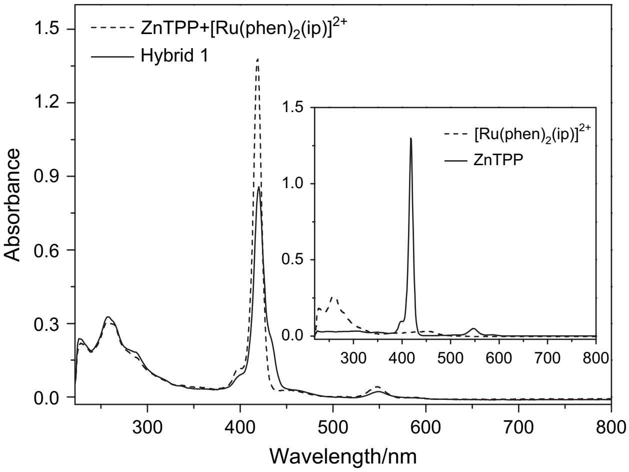

Fig. 2. The electronic absorption spectrum of **1** and the superposition of the spectra of ZnTPP and [Ru(phen)$_2$(ip)]$^{2+}$ in CH$_2$Cl$_2$ (3.0×10^{-6} mol/L). Inset: The electronic absoption spectra of [Ru(phen)$_2$(ip)]$^{2+}$ and ZnTPP.

decrease in intensity and slight red-shift of the peaks characteristic of the zinc(II) porphyrin are observed in the spectrum of **1**, indicating the electronic interaction between the zinc(II) porphyrin moiety and the polypyridyl ruthenium(II) moiety is not strong and the spectral changes result from their close coupling [9].

The electronic absorption spectrum of **2** is shown in Fig. 3. It exhibits the Soret band at 431 nm and Q bands at 564, 605 nm for the zinc(II) porphyrin moiety, in addition to the absorption band for the polypyridyl ruthenium(II) moiety. The superposition of UV–vis spectra of ZnTPP and [Ru(pip)$_2$(ip)]$^{2+}$ (Fig. 3) is also shown as a comparison. The absorption of **2** exhibits a significant red-shift (≥12 nm) as well as a decrease in intensity for absorption peaks characteristic of the porphyrin moiety with respect to that of the superposition spectrum of ZnTPP and [Ru(pip)$_2$(ip)]$^{2+}$. This observation suggests that there is a strong electronic interaction between the zinc(II) porphyrin moiety and the polypyridyl ruthenium(II) moiety.

The MLCT transition localized on ruthenium(II) complex displays a broad absorption where the porphyrin moiety exhibits little, if any, absorption. When excited by 453 nm (MLCT absorption band of [Ru(phen)$_2$(ip)]$^{2+}$), the emission profile of **1** is similar to that of zinc(II) porphyrin and the quenching of the emission of polypyridyl ruthenium(II) moiety is heavy (Fig. 4), which is due to the energy transfer from ^{3}MLCT of polypyridyl ruthenium(II) moiety to zinc(II) porphyrin moiety [7]. For comparison, the luminescence of **2** excited at 465 nm (MLCT absorption band of [Ru(pip)$_2$(ip)]$^{2+}$) is also shown in Fig. 4. It can be seen that **2** shows very weak emission and the quenching is almost 100%.

The emission spectra of **1**, **2** and the reference compound ZnTPP excited at the Soret band and Q band of zinc(II) porphyrin moiety are shown in Fig. 5. It can be seen that the emission profiles of **1** and **2** are identical to that of zinc(II) porphyrin with the emission peaks at 599 and 640 nm when excited at the Soret band (425 nm) and Q band (550 nm). However, the fluorescence of **1** or **2** is strongly quenched. The relative emission intensity reduced to about 50% and 10% for **1** and **2**, respectively, with respect to that of ZnTPP. The fluorescence quantum yields are 0.14, 0.066 and 0.020 (error limits: ±10%) for ZnTPP, **1** and **2**, respectively, which were measured in CH$_2$Cl$_2$ ($\lambda_{ex} = 420$ nm) with H$_2$TPP as the standard [17]. Since energy transfer to the appended ruthenium(II) moiety is thermodynamically infeasible, this quenching is mainly attributed to electron transfer from the singlet excited state of porphyrin moiety to ^{3}MLCT of polypyridyl ruthenium(II) moiety [18,19]. The data show that, the electron transfer occurs to a much lesser extent for **1** than that for **2**.

The difference of electron transfer from porphyrin moiety to polypyridyl ruthenium(II) moiety between **1** and **2** also can be seen from their rate constants of photoinduced electron transfer processes. The lifetimes of the hybrids and their corresponding reference compound excited at 400 nm were

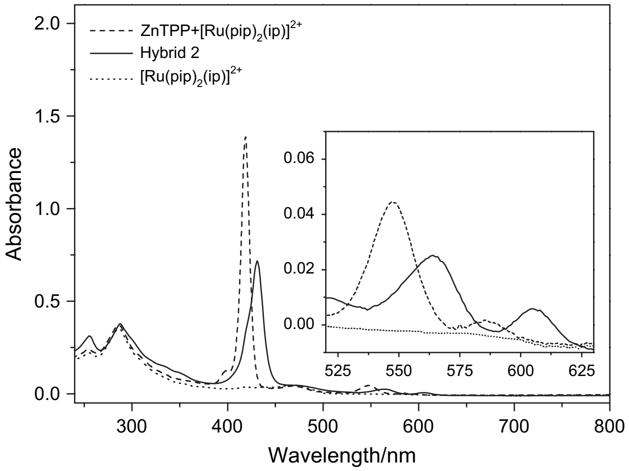

Fig. 3. The electronic absorption spectra of **2**, [Ru(pip)$_2$(ip)]$^{2+}$ and the superposition of the electronic absorption spectrum of ZnTPP and [Ru(pip)$_2$(ip)]$^{2+}$ in CH$_2$Cl$_2$ (3.0×10^{-6} mol/L).

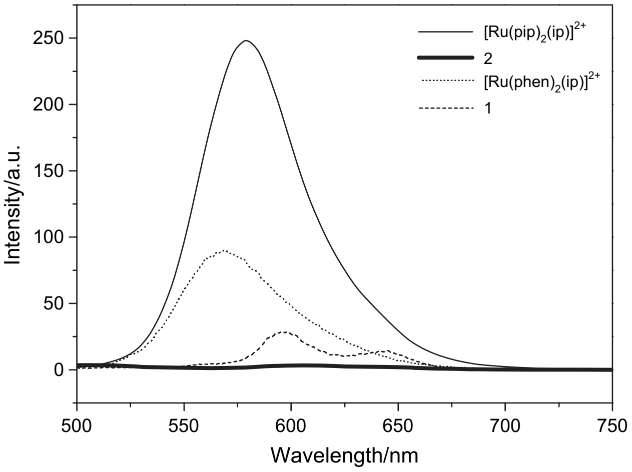

Fig. 4. The emission spectra of **1**, [Ru(phen)$_2$(ip)]$^{2+}$ excited at 453 nm and that of **2**, [Ru(pip)$_2$(ip)]$^{2+}$ excited at 467 nm in CH$_2$Cl$_2$ (5.0×10^{-6} mol/L).

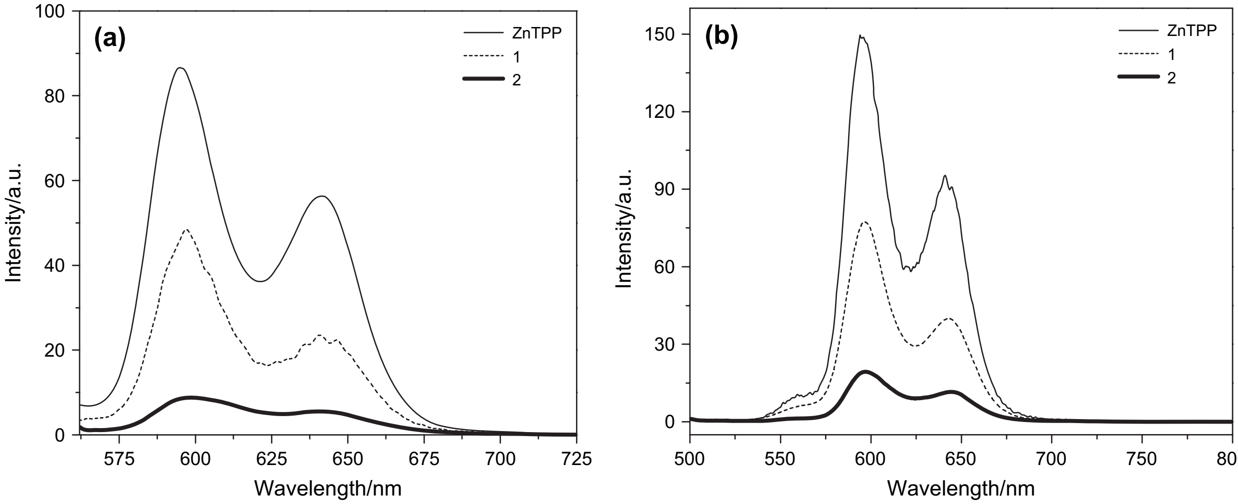

Fig. 5. The emission spectra of **1**, **2** and ZnTPP excited at 550 nm (a) and 425 nm (b) in CH_2Cl_2 (5.0×10^{-6} mol/L).

investigated in CH_2Cl_2. The decay profiles at 600 nm of **1**, **2** and ZnTPP are shown in Fig. 6. Indeed, the fluorescence-decay profile for the hybrid **2** could be explained satisfactorily in terms of a dual exponential fit. The lifetimes of the excited states are reduced on going from the reference compound ZnTPP (2.04 ns) to the hybrids (**1**: $\tau = 1.66$ ns, and **2**: $\tau_1 = 0.22$ ns (88.6%), $\tau_2 = 1.02$ ns (11.4%)). In particular, the lifetime of the excited state in **2** is strongly reduced, indicating that fast intramolecular quenching process takes place. The photoinduced electron transfer rate, k_{ET}, can be achieved by using Eq. (1) [6,20]:

$$k_{ET} = 1/\tau - 1/\tau_0 \tag{1}$$

where τ and τ_0 are the lifetimes of the excited state in the presence and absence of quencher, respectively. The k_{ET} values are 1.12×10^8 and 4.06×10^9 s^{-1}, for **1** and **2**, respectively.

As described above, the electronic interaction between zinc(II) porphyrin and polypyridyl ruthenium(II) moieties is relatively pronounced in **2**, whereas the coupling is weaker in **1**. In addition, the efficiency of energy transfer from ^{3}MLCT of polypyridyl ruthenium(II) moiety to zinc(II) porphyrin moiety and the rate of electron transfer from the singlet excited state of zinc(II) porphyrin moiety to polypyridyl ruthenium(II) moiety for **2** are much higher than that for **1**. What is the primary factor contributed to the different behaviors between **1** and **2**? Since the structural difference between **1** and **2** lies only in the polypyridyl ligands, we believe that the difference of photoinduced intramolecular electron and energy transfer properties between **1** and **2** is probably related to their coordination behaviors.

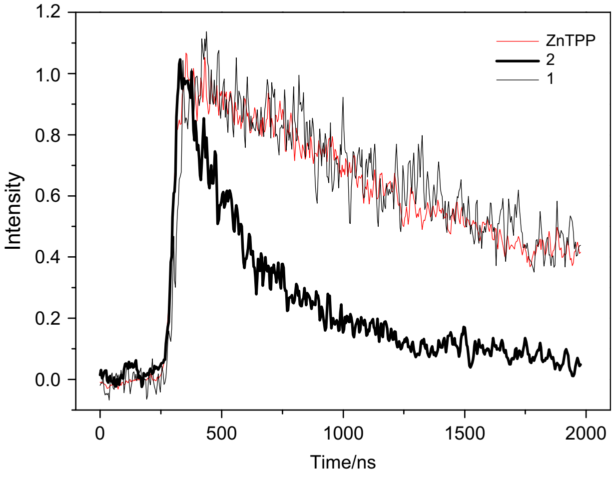

Fig. 6. The fluorescence-decay profile as measured at 600 nm for **1**, **2** and ZnTPP in CH_2Cl_2 excited at 400 nm.

As we all know, zinc(II) porphyrin has a tendency to form axial adduct in which coordination number of zinc(II) ion changes from 4 to 5 in certain conditions [21–24]. From Fig. 1, one can see that **1** has an uncoordinative N atom (N atom of ip in the polypyridyl ruthenium(II) moiety), while **2** has three (N atoms of ip and pip in the polypyridyl ruthenium(II) moiety). Because the butoxy chain linking zinc(II) porphyrin moiety and polypyridyl ruthenium(II) moiety is flexible, an uncoordinative N atom in the polypyridyl ruthenium(II) moiety may coordinate to zinc(II) ion, leading to the difference of photoinduced intramolecular electron and energy transfer properties between **1** and **2.** To identify the formation of axial adduct, the UV–vis spectra for the 1:1 molar ratio mixtures of hybrid **1**/imidazole system and hybrid **2**/imidazole system were measured. The results are shown in Fig. 7. On addition of imidazole (Im) to **1**, Soret band at 419 nm decreases in intensity and red-shifts to 431 nm, while Q bands at 548 and 586 nm shift to 567 and 608 nm, respectively. It is well known that imidazole is a strong base to coordinate to zinc(II) ion in zinc(II) porphyrin and the formation of axial adduct generally causes Soret band and Q bands shift to lower energies [25,26]. The spectral changes of **1** suggest that the formation of coordinative bond results from the coordination of imidazole to zinc(II) ion in **1**. In other words, the coordination number of zinc(II) ion in **1** is 4 and the N atom from ip does not coordinate to zinc(II) ion. In contrast to **1**, there is no observed

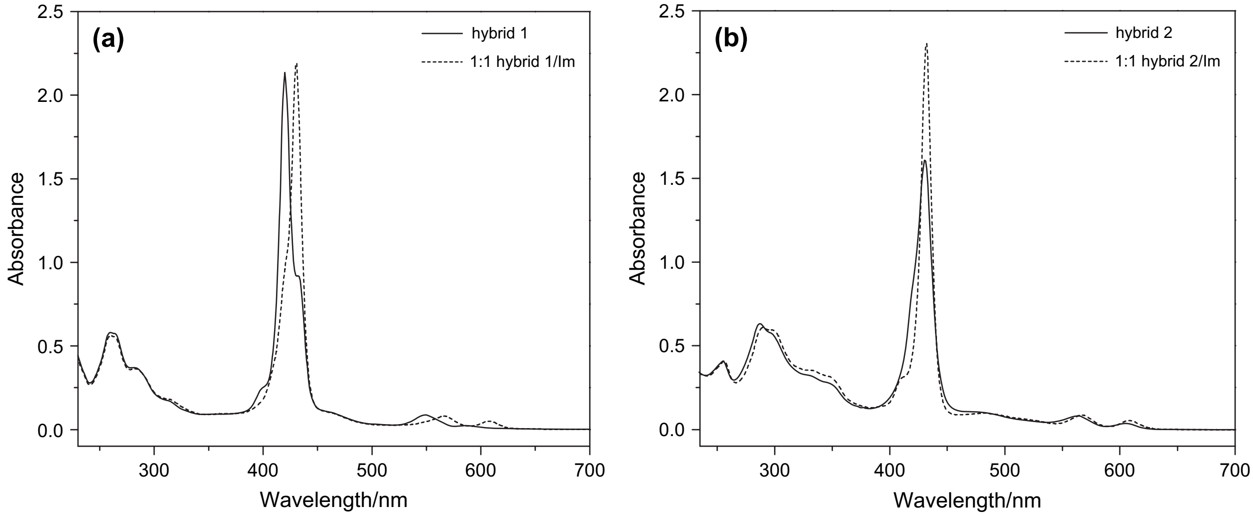

Fig. 7. The electronic absorption spectra for (a) hybrid **1** and 1:1 hybrid **1**/Im system (b) hybrid **2** and 1:1 hybrid **2**/Im system in CH_2Cl_2. The concentration of **1** or **2** was 5.0×10^{-6} mol/L.

red-shift for the absorption band position except for an increase in intensity for the absorption of Soret band of **2** upon addition of imidazole, which indicates that the coordination number of zinc(II) ion in **2** is 5 because most of zinc(II) ions in **2** have been coordinated by N atom of the ligands in the polypyridyl ruthenium(II) moiety. By comparison with **1**, we believe that the N atom coordinating to zinc(II) ions in **2** is not N atom from ip, but N atom from pip in the polypyridyl ruthenium(II) moiety. The increase of absorption intensity for Soret band may be caused by formation of coordinative bond between imidazole and foregoing uncoordinative zinc(II) ions.

Axial coordination of N atom from pip to zinc(II) ion provides a facile pathway for electron and energy transfer between zinc(II) porphyrin moiety and polypyridyl ruthenium(II) moiety [27]. We believe that formation of axial coordinative bond serves as important factor for both effective photoinduced intramolecular energy transfer and much faster electron transfer rate for **2**. The detailed mechanisms for electron and energy transfer processes in present systems need further investigation, which is currently in progress.

4. Conclusions

Two new hybrids (**1** and **2**) have been designed and synthesized in our paper. By comparison of the photoinduced energy and electron transfer efficiency and rate in the two hybrids, some conclusions can be determined. It is important that the coordination of N atom from pip to zinc(II) ion provides a facile pathway for electron and energy transfer. Thus, the electron and energy transfer is more efficient and faster in **2**. We intend to estimate the detailed mechanism of electron and energy transfer in combination with other techniques. We hope that this work will inspire further work on photoinduced process in dyads and triads based on porphyrin and metal polypyridyl complex.

Acknowledgements

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