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A series of new porphyrin dyads: The synthesis and photophysical properties

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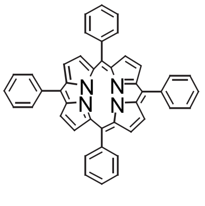
Abstract

Fluorescein and rhodamine linked porphyrin dyads were synthesized as new intramolecule electron transfer systems. The UV–vis spectra, fluorescence spectra and lifetime were measured. It is found that in the model systems fluorescence spectra of fluorescein and rhodamine are effectively quenched and the fluorescene lifetime of porphyrin section decreased. Fluorescence lifetime of rhodamine porphyrin dyads decreased more effectively showing that there are effective electronic interactions between the two subunits. We can conclude that electron and energy transfers to porphyrin section through fluorescence emission in fluorescein porphyrin dyads or through space in rhodamine porphyrin dyads.

Keywords: Porphyrin dyads; Rhodamine B; Fluorescein; Photophysical property; Fluorescent spectra

1. Introduction

Porphyrin dyads which have electron acceptor and donor have been the topic subject of research because they are very useful to understand the process of photosynthesis [1]. Many porphyrin dyads have been reported to mimic the electron transfer and energy transfer in nature, such as porphyrin–quinones, porphyrin–C_{60}, porphyrin–cyclodextrin, and in these systems the excited electrons transfer from porphyrin subunit to acceptors [2]. Furthermore there are other kinds of photoinduced electron transfer systems reported in which porphyrin acts as electron acceptors such as porphyrin–tetrathiafulvalene (TTF) [3], porphyrin–cyanines [4], porphyrin–carotenes [5], porphyrin–arene diimide [6] and so on, and these systems can be used as



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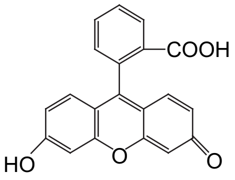

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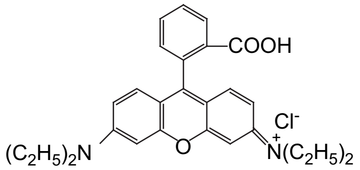

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light-harvesting materials. To our knowledge there are few reports on the xanthene chromophores [7] with appropriate redox potential linked to porphyrin to form dyads to investigate photophysical properties. The advantage of this kind of chromophores is fluorescence quenching going with energy transfer in system and offering an easy way to research the electron transfer process.

2. Experimental section

^{1}H NMR spectra were recorded on DRX500 MHz using tetramethylsilane as internal standard and $CDCl_3$ as solvent. UV–vis spectra were measured on Varian Cary 500, and steady-state fluorescence spectra were obtained on Cary Eclipse Fluorescence Phosphospectrometer, respectively. Fluorescence lifetimes were obtained at EdinBurgh FL920. IR spectra were recorded as KBr discs on Nicolet Magna IR550 Spectrophotometer. HR ESI-MS spectra were obtained from Micromass GCT CA055 Spectrometer.

Porphyrin linked with fluorescein by ester bond through four methylenes was reported by Yan et al. [7]. In the present work we synthesized three new porphyrin dyads composed of H_2TPP (tetraphenylporphyrin) (**1**) and fluorescein (**2**) or rhodamine (**3**). Rhodamine and fluorescein are dyes with strong fluorescence and different redox potential. Furthermore there are two active groups in the fluorescein molecules and we can link porphyrin and fluorescein at different active sites, so that the effect on intramolecule electron transfer of redox potential, the length of carbon chain, and energy transfer ways may be studied in these model compounds. Here we would like to give the synthesis and properties of porphyrin dyads **7–9** in Schemes 1 and 2.

In the synthesis of **7–9**, a key intermediate is **5** with a bromoalkyl group located at the *meso* position of porphyrin [8]. The 5-(*p*-hydroxy phenyl)-10,15,20-triphenyl porphyrin **4** was synthesized using the reported procedure [9] in 7% yields by condensation of benzaldehyde, *p*-hydroxy benzaldehyde and pyrrole using propionic acid as solvent. Then compound **4** reacts with 10 equiv. of 1,3-dibromopropane in dry DMF in the presence of K_2CO_3 at room temperature to give compound **5** with 90% yield (Scheme 1).

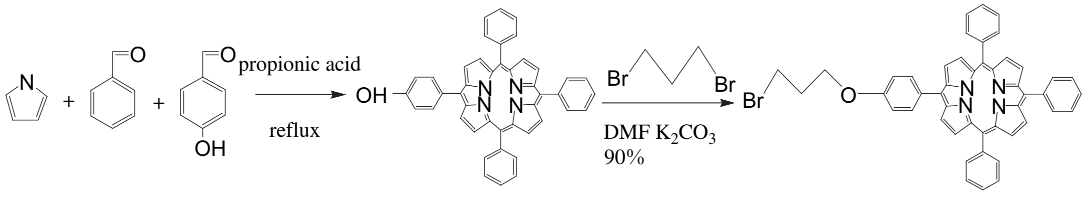
As shown in Scheme 2 there are two active groups in the fluorescein structure: hydroxyl and carboxyl, and compound **5** can react with fluorescein to form compound **7** directly because in this reaction carboxyl has high reactivity than phenolic hydroxyl group [7]. Then to obtain compound **8** fluorescein was esterificated with ethanol and then compound **6** was obtained [10]. Following that **6** was coupled with **5** in dry DMF in the presence of K_2CO_3 and KI and **8** was obtained with 50% yield.

2.1. Synthesis of 7

Fluorescein (0.33 g, 1 mmol) and K_2CO_3 (3 equiv.) were added to a solution of **5** (72 mg, 0.1 mmol) in 50 ml dried DMF. The mixture was stirred at room temperature for 24 h. Excess DMF was vacuum distilled off and the product was extracted using CH_2Cl_2 after being washed with water. The organic layer was dried using anhydrous Na_2SO_4 and solvent was evaporated to recover the product. The compound was purified over silica gel column using ethyl acetate as eluent. Brown powder. Yield: 55.5 mg, 55%. Mp: >300 °C. UV–vis λ_{max} (nm) (CH_2Cl_2) ($\varepsilon \times 10^{-5}$): 418.4 (1.982), 451.9 (0.143), 513.3 (0.099), 550.0 (0.056), 590.4 (0.035), 645.9 (0.032); ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ ppm: 8.80 (m 8H, pyrrole C–H), 8.17 (m 7H, Ph–H), 7.99 (d 2H, $J = 8.33$ Hz, Ph–H), 7.70 (m 9H, Ph–H), 7.53 (m 1H, Ph–h), 7.43 (m 1H, Ph–H), 6.93 (d 2H, $J = 8.31$, Ph–H), 6.85 (d 1H, $J = 7.38$, Ph–H), 6.76 (d 2H, $J = 9.15$, Ph–H), 6.62 (d 2H, $J = 9.14$, Ph–H), 6.57 (s 2H, Ph–H), 4.13 (m 2H, $-COOCH_2$), 3.63 (m 2H, $-O-CH_2$), 2.34 (m 2H, $-CH_2-$), −2.75 (s 2H, porphyrin N–H)Hh; HR ESI-MS ($[M + 1]^+$): calcd. for $C_{67}H_{47}N_4O_6$ 1003.3496, found 1003.3476.

2.2. Synthesis of 8

Similar to that of **7** except that KI was added and temperature was at 90 °C to enhance the validity of reaction, **8** was purified over silica column using ethyl acetate/petroleum ether (80:20 v/v) as eluent. Brown powder. Yield: 31.5 mg, 50%. Mp: >300 °C. UV–vis



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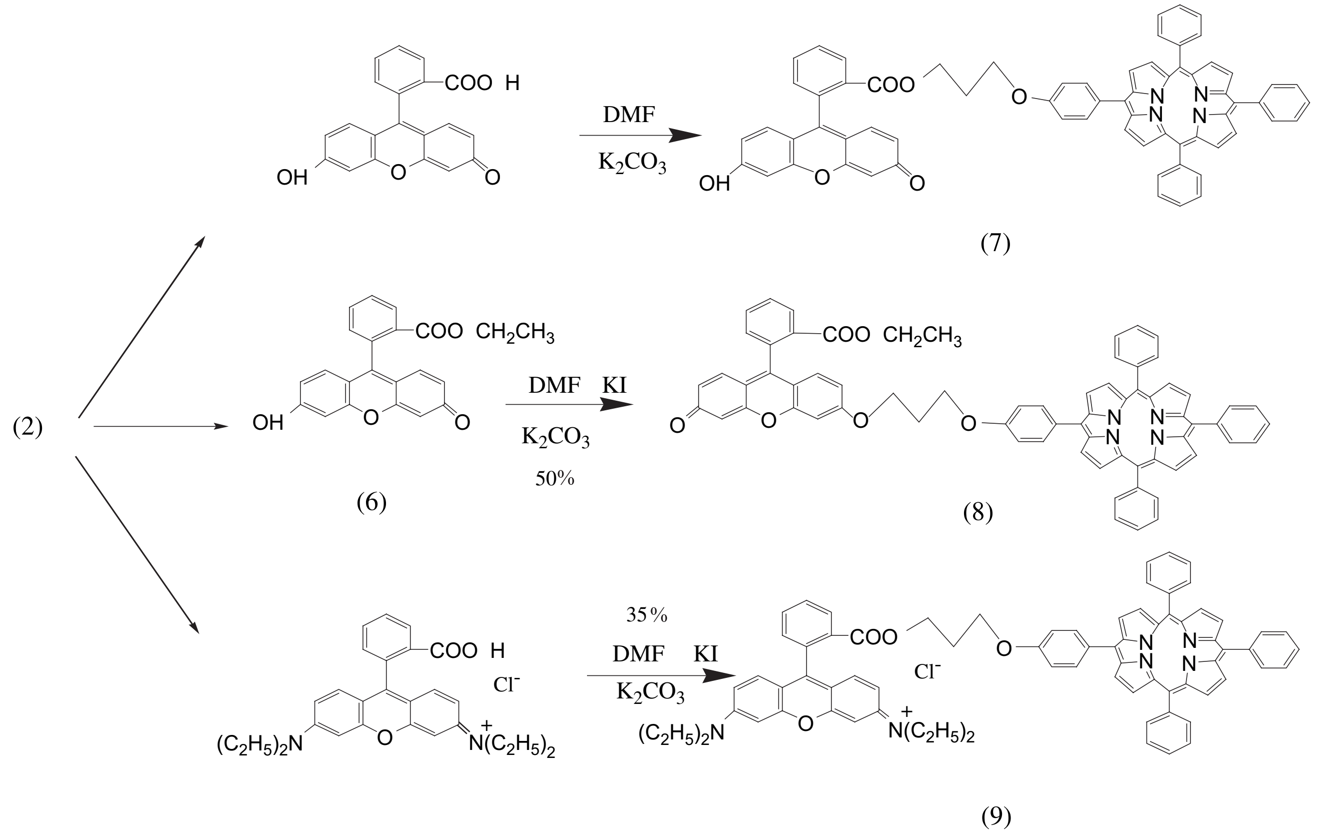
(5)

Scheme 1. Synthesis of the porphyrin intermediate **5**.



Scheme 2. Synthesis of porphyrin dyads **7**, **8**, and **9**.

λ_{max} (nm) (CH_2Cl_2) ($\varepsilon \times 10^{-5}$): 418.0 (1.672), 457.8 (0.101), 513.0 (0.077), 550.0 (0.039), 590.4 (0.023), 646.3 (0.019); ^1H NMR (500 MHz, 298 K, $CDCl_3$) δ ppm: 8.84 (m 8H, pyrrole C–H), 8.26 (m 1H, Ph–H), 8.21 (m 6H, Ph–H), 8.12 (d 2H, $J = 8.44$ Hz, Ph–H), 7.75 (m 10H, Ph–H), 7.67 (m 1H, Ph–h), 7.31 (d 1H, $J = 7.28$, Ph–H), 7.28 (d 2H, $J = 8.46$, Ph–H), 7.09 (d 1H, $J = 2.31$, Ph–H), 6.95 (d 1H, $J = 8.83$, Ph–H), 6.88 (d 1H, $J = 9.69$, Ph–H), 6.84 (m 1H, Ph–H), 6.56 (m 1H, Ph–H), 6.49 (d 1H, $J = 1.48$, Ph–H), 4.44 (m 4H, $-COOCH_2$, Ph–O–CH_2),4.05 (m 2H, –O–CH_2), 2.50 (m 2H, $-CH_2-$), 0.98 (m 3H, $-CH_3$), −2.77 (s 2H, porphyrin N–H)Hh; HR ESI-MS ($[M + 1]^+$): calcd. for $C_{69}H_{51}N_4O_6$ 1031.3809, found 1031.3809.

2.3. Synthesis of **9**

Similar to that of **8**, **9** was purified over silica column using CH_2Cl_2/CH_3CH_2OH (95:5 v/v) as eluent. Scarlet powder. Yield: 35%. Mp: >300 °C. UV–vis λ_{max} (nm) (CH_2Cl_2) ($\varepsilon \times 10^{-5}$): 418.0 (1.064), 517.7 (0.119), 557.5 (0.313), 646.2 (0.016); ^1H NMR (500 MHz, 298 K, $CDCl_3$) δ ppm: 8.84 (s 8H, pyrrole C–H), 8.42 (d 1H, $J = 7.73$ Hz, Ph–H), 8.21 (d 6H, $J = 6.39$, Ph–H), 8.08 (d 2H, $J = 8.43$, Ph–H), 7.85 (m 1H, Ph–H), 7.74 (m 10H, Ph–H), 7.38 (d 1H, $J = 7.49$, Ph–H), 7.16 (m 4H, Ph–H), 6.93 (m 2H, Ph–H), 6.87 (d 2H, $J = 2.12$, Ph–H), 4.42 (m 2H, $-COOCH_2$), 4.17 (m 2H, –O–CH_2), 2.17 (m 2H, $-CH_2-$), −2.78 (s 2H, porphyrin N–H)Hh; HR ESI-MS ($[M - Cl]^+$): calcd. for $C_{75}H_{65}N_6O_4$ 1113.5067, found 1113.5092.

3. Results and discussion

The electronic absorption and fluorescence spectra of **7**, **8**, and **9** were measured in dichloromethane and the

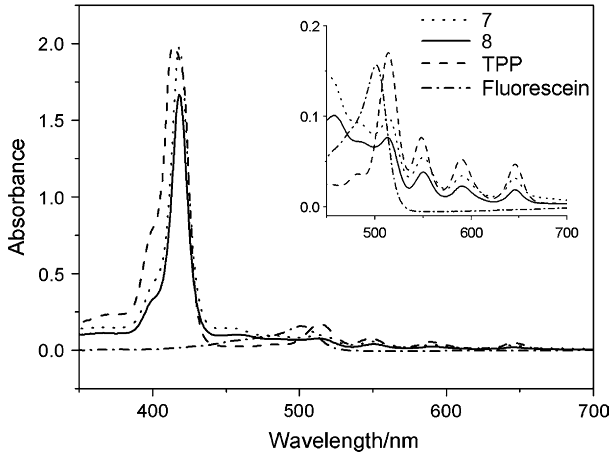


Fig. 1. The absorption spectra of **7**, **8**, H_2TPP (tetraphenylporphyrin) and fluorescein in CH_2Cl_2.

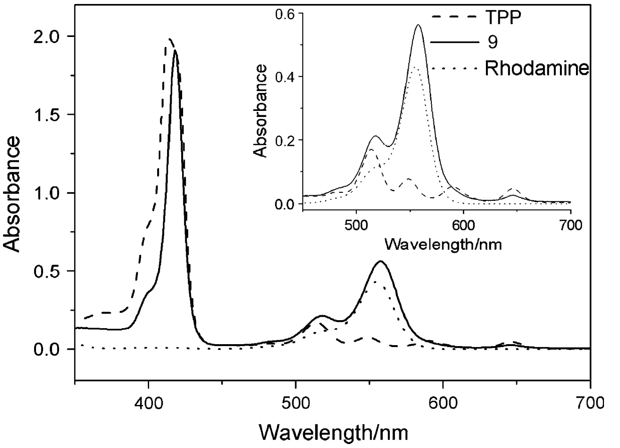


Fig. 2. The absorption spectra of **9**, H_2TPP, rhodamine B in CH_2Cl_2.

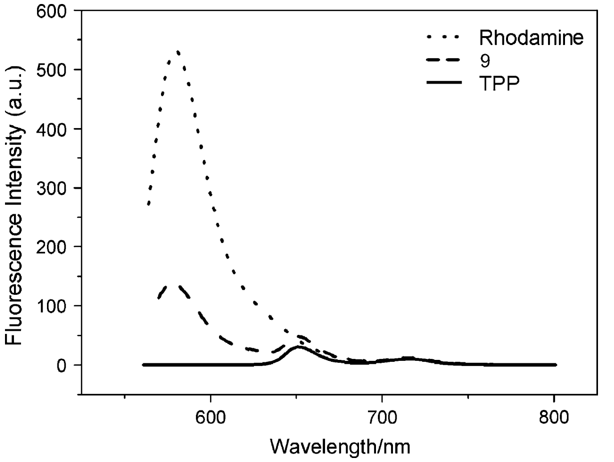


Fig. 4. Fluorescence spectra of **9**, H_2TPP and rhodamine B in CH_2Cl_2 excited at 560 nm.

results are shown in Figs. 1–4. From the absorption spectra of **7** and **8** we can find that there is electronic interaction in the ground state as shown in Fig. 1 although the linkage is saturated carbon chain. As shown in Fig. 3 the emission band belonging to fluorescein almost disappears and emission band corresponding to porphyrin is enhanced which shows that there is efficient energy transfer between the two subunits. For compound **9** there is no obvious electronic interaction in the ground state as shown in Fig. 2 and the emission band of rhodamine B is quenched not so effectively compared to **7** and **8** (Fig. 4). The maxima emission band of fluorescein is 517 nm and has large overlap with the *Q* absorption band of porphyrin and singlet excited energy can be transferred to porphyrin by fluorescence emission effectively in **7** and **8**. For compound **9** there is little overlap between the emission spectra of rhodamine B and the absorption spectra of porphyrin. So it is not the effective way that excited state energy transfer through fluorescence emission and there seems other way through which porphyrin section can receive energy from rhodamine section. From the fluorescence lifetime as shown in Fig. 5 and Table 1 we can see that in compounds **7** and **8** the fluorescence lifetime τ_f and radioactive decay rates k_f did not change obviously compared with H_2TPP. But in **9** fluorescence lifetime of porphyrin section is much less than H_2TPPs. So we can conclude that there is/maybe electronic interaction between the rhodamine and porphyrin subunits in the excited state and the excited energy can be transferred through space in compound **9**. On the other hand there is little interaction in the excited states of **7** and **8** and excited energy can be transferred by fluorescence emission in accordance with above.

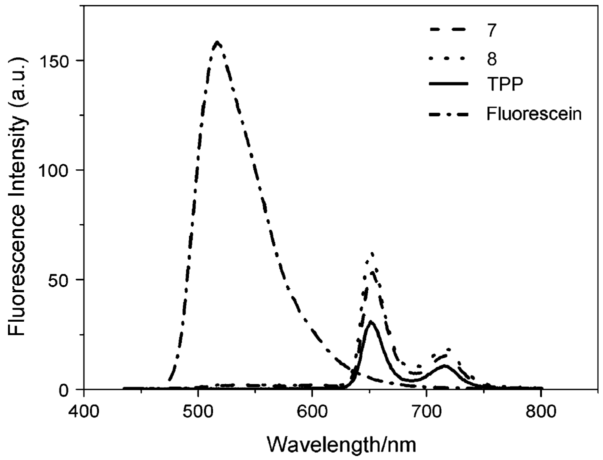


Fig. 3. Fluorescence spectra of **7**, **8**, and H_2TPP in CH_2Cl_2, excited at 450 nm.

4. Conclusions

In conclusion, we have synthesized a series of porphyrin dyads in which there are intramolecule energy

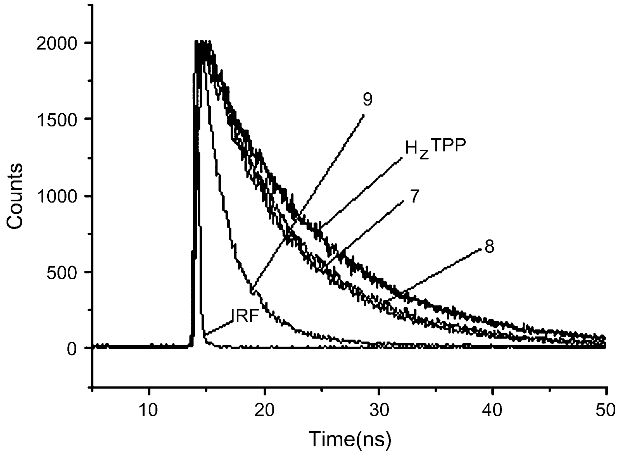


Fig. 5. Fluorescence decay signals of H_2TPP, **7**, **8**, and **9**. The detection wavelength was 650 nm and excitation wavelength was 405 nm. IRF indicates instrumental response function.

Table 1
The fluorescence lifetime of H_2TPP **7**, **8** and **9** detected at 650 nm

Compound	τ_f (ns)	k_f (1/ns)
H_2TPP	9.8	0.102
7	7.6	0.132
8	7.9	0.127
9	2.0	0.5

The excitation wavelength was 405 nm. τ_f is fluorescence lifetime and k_f $(1/\tau_f)$ is radioactive decay rates of porphyrin S_1 excited state.

transfer through space or through fluorescence emission under the light excitation. Further photophysical properties of these compounds are under investigation to show the rates of intermediate formation and the relation between the structure and their transient properties.

Acknowledgement

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References

[1] Battersby AR. Nat Prod Rep 2000;17:507.

[2] (a) Lang Kamil, Král Vladimír, Kapusta Petr, Kubát Pavel, Vašek Petr. Tetrahedron Lett 2002;43:4919;
(b) Kurreck H, Huber M. Angew Chem Int Ed Engl 1995; 34:849;
(c) Kang YK, Rubtsov IV, Iovine PM, Chen JX, Therien MJ. J Am Chem Soc 2002;124:8275;
(d) D'Souza F, Smith PM, Zandler ME, McCarty AL, Itou M, Araki Y, et al. J Am Chem Soc 2004;128:7898;
(e) Yamada H, Imahori H, Nishimura Y, Yamazaki I, Ahn TK, Kim SK, et al. J Am Chem Soc 2003;125:9129.

[3] Sadaike SI, Takimiya K, Aso Y, Otsubo T. Tetrahedron Lett 2003;44:161.

[4] Lindsey JS, Brown PA, Siesel DA. Tetrahedron 1989;45:4845.

[5] (a) Hasharoni K, Levanon H, Tang J, Bowman MK, Norris JR, Gust D, et al. J Am Chem Soc 1990;112:6477;
(b) Moore TA, Gust D, Moore AL, Bensasson RV, Seta P, Bienvenue E. Supermolecular photochemistry. In: NATO ASI Ser C, vol. 214. 1987. p. 283.

[6] Redmore NP, Rubtsov IV, Therien MJ. J Am Chem Soc 2003;125:8769.

[7] Yan XB, Weng M, Zhang MH, Shen T. Dyes Pigments 1997;35:87.

[8] Little RG. J Heterocyclic Chem 1978;15:203.

[9] Little RG, Anton JA, Loach PA, Ibers JA. J Heterocyclic Chem 1975;12:343.

[10] Miura T, Urano Y, Tanaka K, Nagano T, Ohkubo K, Fukuzum S. J Am Chem Soc 2003;28:8666.