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Synthesis and characterization of novel porphyrin Schiff bases

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Abstract: Novel porphyrin Schiff bases were synthesized by a simple Schiff base condensation in refluxing toluene between 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (ATTP) **3** and styryl aldehydes **4**–**6** or *p*-halobenzaldehydes **7**–**9**. The newly synthesized porphyrin Schiff bases were characterized on the basis of their chemical properties and spectral data. A good intramolecular energy transfer from the styryl unit to the porphyrin moiety was found.

Keywords: porphyrin Schiff base; styryl; energy transfer.

INTRODUCTION

Recently investigation of porphyrin has been of increasing interest.[1,2] In particular, focus was directed to the synthesis and study of well-designed porphyrin derivatives which could act as molecular switches,[3] as well as materials for non-linear optics[4] and solar cells.[5] In these fields, investigation of photo-induced electron and energy transfer of unsymmetrical porphyrin are essential for understanding the mechanism and evaluating the progress. Therefore, unsymmetrical porphyrin, especially tetraphenyl porphyrin derivatives substituted with an expanded π conjugated system at the meso-position, are of potential interest. There are a few reports about porphyrin Schiff bases, which are ligands produced by the reaction of porphyrin and aldehydes.[6,7] In the present study, a novel series of porphyrin Schiff bases was synthesized by a simple Schiff base condensation in refluxing toluene between 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (ATTP) **3** and styryl aldehydes **4**–**6** or *p*-halobenzaldehydes. **7**–**9**. The styryl group was firstly used to expand the π system of porphyrin macrocycle at one of the *meso*-phenyl groups.

RESULTS AND DISCUSSION

Chemistry

The synthesis of porphyrin Schiff bases was performed following the steps shown in Scheme 1. Synthesis of all the new compounds **10**–**15** was accomplished, in moderate to good yields, by a simple Schiff base condensation in re-

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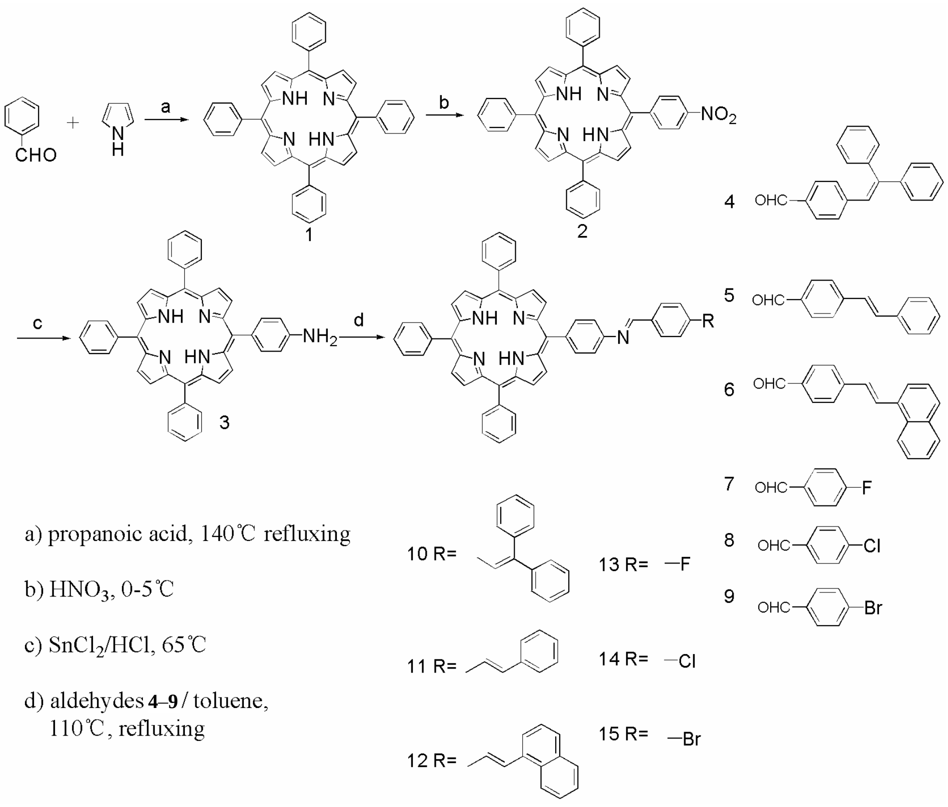
fluxing toluene between 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (ATTP) **3** and styryl aldehydes **4–6** or *p*-halobenzaldehydes **7–9**. Spectral data (IR, ^{1}H-NMR and MS) of all the newly synthesized compounds were in full agreement with the proposed structures. The reactions of ATTP with *p*-halobenzaldehydes **7–9** were easier than with those with aldehydes **4–6** due to the higher activities of the aldehyde group of the *p*-halobenzaldehydes **7–9** compared to those of aldehydes **4–6**. The styryl group is an electron donating group, hence the activities of the styryl aldehydes were lower and the Schiff base condensation reactions required a longer time. In this study, refluxing in various solvents, such as THF, $CHCl_3$, *etc.*, resulted in the formation of the required products but the reactions did not go to completion even in the presence of excess aldehyde. Besides the solvent effect, higher reaction temperatures were beneficial for the condensation. The separation and purification of porphyrin usually requires column chromatography. Thus purification of the porphyrin Schiff bases **10–15** by silica gel column chromatography, using a mixture of CH_2Cl_2 and light petroleum as the eluent, was attempted. However, the compounds eluting from the column were found to be partly degraded. Hence, the products were recrystallized to remove the excess aldehydes.



a) propanoic acid, 140℃ refluxing

b) HNO_3, 0-5℃

c) $SnCl_2$/HCl, 65℃

d) aldehydes **4–9** / toluene, 110℃, refluxing

Scheme 1.

Spectral analysis

^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra confirmed the structures of all the compounds **10**–**15**. The chemical shifts of the characteristic internal NH of the porphyrin macrocycle was found from −2.67 to −2.77 ppm. In all porphyrin Schiff bases, the eight protons of *β*-pyrrole separated into two groups, which indicated the two *β*-pyrrolic protons near C=N groups were in a different chemical environment to the other six. The unsymmetrical chemical environment of these protons showed the influence of the expanded π structure or the strong electron withdrawing effect of the halogen atom. A single peak in the range 8.62–8.63 ppm, indicated the proton of the CH=N group. The chemical shift of the proton (protons) of the C=C group (not in phenyl) at 9.90 ppm in compound **10** and 8.07 ppm in compounds **11** and **1** were also evidence of the formation of the porphyrin Schiff bases.

IR spectroscopy. The infrared absorption spectra of all the porphyrin Schiff bases presented the stretching of the C=N bond at about 1580–1590 cm^{-1}. In the spectra of the porphyrin Schiff bases **13**–**15**, the presence of the C–X (X = F, Cl, Br) bond on the phenyl ring led to the appearance of a strong absorption band at 1000–1100 cm^{-1}.

UV–Vis spectroscopy. All the porphyrin Schiff bases **10**–**15** exhibited characteristically one Soret band and four weak Q bands. Compared to ATTP (416 nm), the Soret bands of the new compounds were slightly red shifted (by about 6 nm), which indicated that the introduction of the new groups to the *meso*-phenyl of the porphyrin moiety did not greatly change the energy of S_1. The absorptions of the porphyrin Schiff bases **10**–**12**, shown in Fig. 1, indicate that each had a new weak and broad band at about 370 nm, which was slightly red shifted compared to the maximum absorption of the corresponding styryl group, due to the styryl–aryl group $\pi \rightarrow \pi^*$ region. Compound **10** had an obvious "split Soret" structure, indicating the interaction between the styryl group and the porphyrin moiety.

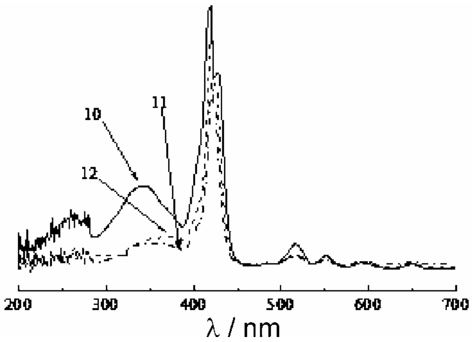


Fig. 1 The UV–Vis spectra of the porphyrin Schiff bases **10**–**12** in toluene (5×10^{-6} M).

Fluorescence spectroscopy. The fluorescence emission spectra of the porphyrin Schiff bases excited at their Soret bands are shown in Fig. 2. For compounds **13**–**15**, the fluorescence was not quenched. There are two possible reasons for this, either no substantial amount of electron transfer from porphyrin moiety to halogenated phenyl ring occurred or the rate of the back transfer of the electron was much faster than the rate of electron separation.

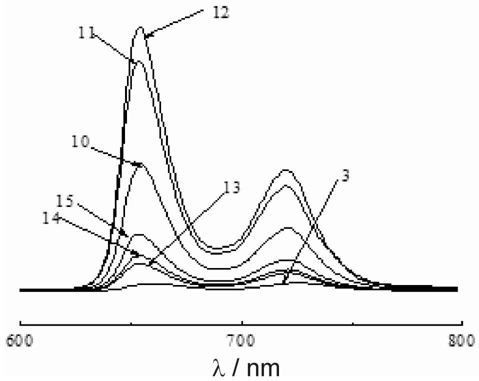


Fig. 2 The fluorescence emission spectra of the porphyrin Schiff bases **10**–**15** in toluene (5×10^{-6} M), excited at their Soret bands.

Direct excitation of compounds **10**–**15** (Soret bands) in degassed toluene gave strong fluorescence bands at about 650 and 730 nm due to the porphyrin units. Excitation of compounds **10**–**15** at the maximum absorption of the styryl aldehydes **4**–**6** (376–392 nm) resulted in the same fluorescence patterns as direct excitation (Fig. 3), while no emissions of the styryl aldehydes at 430–450 nm were observed. There is apparently good energy transfer between the styryl unit and the porphyrin moiety through the C=N bond.

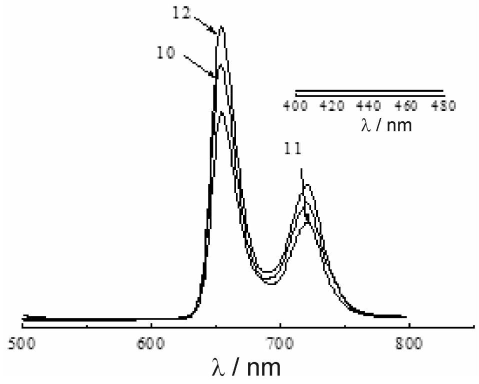


Fig. 3 The fluorescence emission spectra of porphyrin Schiff bases **10**–**12** in toluene (5×10^{-6} M), excited at the maxima of the styryl groups (at 392 nm for **10**, at 376 nm for **11** and at 380 nm for **12**).

EXPERIMENTAL

General synthesis procedure

All reagents are commercially available. The toluene was refluxed with Na. The CH_2Cl_2 was washed with a saturated solution of Na_2CO_3 and distilled. All other reagents were used without further purification.

5-(4-Nitrophenyl)-10,15,20-triphenylporphyrin (NTTP) **2** was obtained by the regioselective nitration of 5,10,15,20-tetraphenylporhyrin **1**. Then the NTTP **2** was reduced with $SnCl_2$/HCl according to a literature procedure[8] to obtain ATTP **3**. The porphyrin Schiff bases **10**–**15** were synthesized as follows: ATTP **3** (0.1 mmol, 63 mg) and the required aldehyde (0.2 mmol, 56.8 mg of **4**, 41.2 mg of **5**, 43.2 mg of **6**, 24 mg of **7**, 28 mg of **8**, 36.3 mg of **9**) were dissolved in 100 ml of dry toluene containing 4 Å molecular sieves. The resulting solution was refluxed until the disappearance of the ATTP **3,** monitored by TLC (18 h for **4**, 18 h for **5**, 15 h for **6**, 2 h for **7**, 6 h for **8**, 12 h for **9**). The solvent was removed under reduced pressure and the crude product was dissolved in CH_2Cl_2 and filtered. Evaporation of the solvent gave purple solids. All the products were recrystallized from CH_2Cl_2 and light petroleum.

Characterization

The melting points (uncorrected) were measured on a Yanagimoto MP-500 apparatus. The FT-IR spectra (KBr pellets) were measured on a Bio-Rad FTS3000 infrared spectrometer. The ^{1}H-NMR spectra were recorded on a Varian INOVA-500 Hz spectrometer at 298 K in $CDCl_3$. The mass spectra were obtained using a LCQ Advantage MAX spectrometer. The UV–Vis spectra were measured on a Therma Helios Gamma spectrometer. The fluorescence spectra were obtained using a Varian Cary Eclipse spectrometer.

Porphyrin Schiff base **10**: Yield: 70 %; purple solid; m.p. >300 °C; ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): −2.77 (*s*, 2H, internal NH), 7.01 (*s*, 1H, terminal phenyl), 7.08 (*s*, 1H, terminal phenyl), 7.15–7.21 (*m*, 8H, terminal phenyl), 7.59 (*d*, 2H, N=C–phenyl, *J* = 8.0 Hz), 7.64 (*d*, 2H, N=C–phenyl, *J* = 8.0 Hz), 7.72–7.79 (*m*, 9H, *m,p*-triphenyl), 7.84(*d*, 2H, C=N–phenyl, *J* = 8.5 Hz), 8.22–8.24 (*m*, 8H, *o*-tetraphenyl), 8.74 (*s*, 1H, –N=CH–), 8.85–8.87 (*m*, 6H, *β*-pyrrolic), 8.90 (*d*, 2H, *β*-pyrrolic, *J* = 5.0 Hz), 9.90 (*s*, 1H, –C=CH–); MS (*m/z*): 896 (M + + H)$^+$; IR (KBr, cm^{-1}): 1597 (stretching of C=N); UV–Vis λ_{max} (in toluene, nm): 342, 420 (Q band), 516, 551, 594, 645 (four Soret bands).

Porphyrin Schiff base **11**: purple solid; Yield: 68 %; m.p. >300 °C; ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): –2.74 (*s*, 2H, internal NH), 7.23 (*s*, 1H, terminal phenyl), 7.28 (*s*, 1H, terminal phenyl), 7.33 (*t*, 1H, terminal phenyl, *J* = 7.5 Hz), 7.42 (*t*, 2H, terminal phenyl, *J* = = 7.5 Hz), 7.60 (*d*, 2H, N=C–phenyl, *J* = 7.5 Hz), 7.64 (*d*, 2H, N=C–phenyl, *J* = 8.5 Hz), 7.71 (*d*, 2H, C=N–phenyl, *J* = 8.5 Hz), 7.75–7.82 (*m*, 9H, *m,p*-triphenyl), 8.07 (*d*, 2H, –CH=CH–, *J* = 8.5 Hz), 8.23–8.26 (*m*, 8H, *o*-tetraphenyl), 8.83 (*s*, 1H, –N=CH–), 8.87–8.89 (*m*, 6H, *β*-pyrrolic), 8.94 (*d*, 2H, *β*-pyrrolic, *J* = 4.5 Hz); MS (*m/z*): 820 (M + H)$^+$; IR (KBr, cm^{-1}): 1595 (stretching of C=N); UV–Vis λ_{max} (in toluene, nm): 350, 421 (Q band), 517, 552, 595, 649 (four Soret bands).

Porphyrin Schiff base **12**: purple solid; Yield: 80 %; m.p. >300 °C; ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): –2.74 (*s*, 2H, internal NH), 7.23 (*t*, 2H, naphthyl), 7.49–7.54 (*m*, 2H, N=C–phenyl), 7.57 (*t*, 1H, naphthyl, *J* = 7.0 Hz), 7.62 (*d*, 2H, N=C–phenyl, *J* = 8.0 Hz), 7.72–7.77 (*m*, 9H, *m,p*-triphenyl), 7.80 (*d*, 2H, naphthyl, *J* = 7.0 Hz), 7.82 (*d*, 2H, C=N–phenyl, *J* = 8.0 Hz), 7.88 (*d*, 1H, *J* = 8.0 Hz, naphthyl), 8.02(*s*, 1H, naphthyl), 8.06 (*d*, 2H, –CH=CH–, *J* = 8.5 Hz), 8.21–8.27 (*m*, 8H, *o*-tetraphenyl), 8.83 (*s*, 1H, –N=CH–), 8.85–8.88 (*m*, 6H, *β*-pyrrolic), 8.92 (*d*, 2H, *β*-pyrrolic, *J* = 4.5 Hz); MS (*m/z*): 870 (M + H)$^+$; IR (KBr, cm^{-1}): 1594 (stretching of C=N); UV–Vis λmax (in toluene, nm): 370, 421 (Q band), 516, 551, 593, 648 (four Soret bands).

Porphyrin Schiff base **13**: purple solid; Yield: 85 %; m.p. >300 °C; ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): –2.72 (*s*, 2H, internal NH), 7.24 (*d*, 2H, phenyl, *J* = 8.0 Hz), 7.61 (*d*, 2H, phenyl, *J* = 8.5 Hz), 7.75–7.80 (*m*, 9H, *m,p*-triphenyl), 8.04–8.07 (*m*, 2H, C=N–phenyl), 8.24–8.27 (*m*, 8H, *o*-tetraphenyl), 8.77 (*s*, 1H, –N=CH–), 8.88–8.90 (*m*, 6H, *β*-pyrrolic), 8.94 (*d*, 2H, *β*-pyrrolic, *J* = 4.5 Hz); MS (*m/z*): 736 (M + H)$^+$; IR (KBr, cm^{-1}): 1587, 1597 (stretching of C=N); UV–Vis λ_{max} (in toluene, nm): 421 (Q band), 516, 551, 593, 649 (four Soret bands).

Porphyrin Schiff base **14**: purple solid; Yield: 85 %; m.p. >300 °C; ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): –2.73 (*s*, 2H, internal NH), 7.41 (*d*, 2H, phenyl, *J* = 8.5 Hz), 7.53 (*d*, 2H, phenyl, *J* = 8.0 Hz), 7.69–7.74 (*m*, 9H, *m,p*-triphenyl), 7.85 (*d*, 2H, C=N–phenyl, *J* = 8.5 Hz), 8.19–8.22 (*m*, 8H, *o*-tetraphenyl), 8.62 (*s*, 1H, –N=CH–), 8.85–8.86 (*m*, 6H, *β*-pyrrolic), 8.89 (*d*, 2H, *β*-pyrrolic, *J* = 4.5 Hz); MS (*m/z*): 752 $(M + H)^+$; IR (KBr, cm^{-1}): 1590 (stretching of C=N); UV–Vis λ_{max} (in toluene, nm): 420 (Q band), 516, 551, 593, 649 (four Soret bands).

Porphyrin Schiff base **15**: purple solid; Yield: 75 %; m.p. >300 °C; ^1H-NMR (500 MHz, $CDCl_3$, δ, ppm): –2.67 (*s*, 2H, internal NH), 7.60 (*d*, 2H, phenyl, *J* = 8.0 Hz), 7.65 (*d*, 2H, phenyl, *J* = 8.5 Hz), 7.77–7.81 (*m*, 9H, *m,p*-triphenyl), 7.86 (*d*, 2H, C=N–phenyl, *J* = 8.5 Hz), 8.27–8.28 (*m*, 8H, *o*-tetraphenyl), 8.69 (*s*, 1H, –N=CH–), 8.91–8.92 (*m*, 6H, *β*-pyrrolic), 8.95 (*d*, 2H, *β*-pyrrolic, *J* = 5.0 Hz); MS (*m/z*): 596 $(M + H)^+$: IR (KBr, cm^{-1}): 1585, 1595 (stretching of C=N); UV–Vis λ_{max} (in toluene, nm): 421 (Q band), 516, 551, 592, 649 (four Soret bands).

CONCLUSIONS

A series of novel porphyrin Schiff bases was synthesized and structurally characterized by FAB–MS, ^1H-NMR and IR spectroscopy. As evidenced by the analysis of UV–Vis and fluorescence spectra, a good intra-molecular energy transfer from the styryl unit to the porphyrin moiety was found when the porphyrin Schiff bases **10**–**12** were excited at 370–390 nm.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НОВИХ ПОРФИРИНСКИХ ШИФОВИХ БАЗА

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Нове порфиринске Шифове базе синтетисане су једноставном кондензацијом у толуену уз рефлукс, између 5-(4-аминофенил)-10,15,20-трифенилпорфирина (ATTP) **3** и стирил-алдехида **4**–**6** или *p*-халоген-бензалдехида **7**–**9**. Новосинтетисане порфиринске Шифове базе карактерисане су на основу њихових хемијских својстава и спектралних података. Установљен је добар интрамолекулски пренос енергије са стирил јединице на порфирински део молекула.

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REFERENCES

1. G. A. Bogdanovic, V. Medakovic, M. K. Milcic, S. D. Zaric, *Int. J. Mol. Sci.* **5** (2004) 174
2. P. I. Premović, I. R. Tonsa, D. M. Đorđević, M. S. Pavlović, *J. Serb. Chem. Soc.* **65** (2000) 113
3. P. A. Liddell, G. Kodis, A. L. Moore, T. A. Moore, D. Gust, *J. Am. Chem. Soc.* **124** (2002) 7668
4. S. M. Le Cours, H. W. Guan, S. G. DiMagno, C. H. Wang, M. J. Therien, *J. Am. Chem. Soc.* **118** (1996) 1497
5. S. Antohe, L. Tugulea, *Phys. Stat. Sol.(A)* **128** (1991) 253
6. P. K. Poddutoori, B. G. Maiya, *Indian J. Chem. A* **42** (2002) 2198
7. D. M. Li, Z. X. Zhao, S. Q. Liu, G. F. Liu, T. S. Shi, X. X. Liu, *Synth. Commun.* **30** (2000) 4017
8. W. J. Kruper, J. A. Chamberlin, M. Kochanny, *J. Org. Chem.* **54** (1989) 2753.