Contents lists available at ScienceDirect





Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Schiff base bridged biporphyrin: Synthesis, characterization and spectral properties



Ya Hong Wu^a, Ling Ling Hu^a, Jing Zhang^b, Jian Yu^a, Shan Ling Tong^a, Yan Yan^{a,*}

^a College of Chemical Engineering & Light Industry, Guangdong University of Technology, Guangzhou 510006, PR China
^b College of Chemical Engineering, Zhuhai Campus, Beijing Institute of Technology, Zhuhai 519085, PR China

ARTICLE INFO

Article history: Received 20 January 2014 Accepted 19 March 2014 Available online 27 March 2014

Keywords: Schiff base Porphyrin Molecular recognition Molecular wire Halochromism Photochromism

ABSTRACT

Chromophoric molecules with mono-aminophenyl, 5-aminophenyl-10, 15, 20-triphenyl porphyrin, were chemically reduced from the precursors of 5-nitrophenyl-10, 15, 20-triphenyl porphyrin. The titled Schiff base bridged biporphyrins were furthermore prepared by condensation of 5-aminophenyl-10, 15, 20-triphenyl porphyrin with terephthalaldehyde. This novel conjugated Schiff base biporphyrin was well characterized by spectral determinations. Experimental results indicated that the titled compound possessed fluorescence enhancement in near infrared region. Compared with tetraphenyl porphyrin, both ultraviolet-visible absorption and fluorescence spectra of the titled compound appeared with slightly red shift. Photo experiments revealed that, after violet irradiation, the color of a chloroform solution with the titled compound changed sharply from pale green to dark green along with sensitively spectral variation during ultraviolet-visible absorption and electron paramagnetic resonance determinations. This sensitively photochromic mechanism was well explained by molecular recognition of the titled compound towards hydrogen chloride from the decomposition of the chloroform solvent. The titled compound was sensitive in recognizing towards hydrogen chloride.

© 2014 Elsevier B.V. All rights reserved.

Metalloporphyrins and their derivatives, including hemoglobin, vitamin B₁₂, cytochrome and chlorophyll, closely relate to vital processes occurring in living organisms, and therefore research on porphyrin chemistry has been very active in molecular design, synthesis and functional material development [1-4]. Based on their special configuration, metalloporphyrins were broadly investigated as function devices such as molecular wires, molecular switches and molecular rectifiers [5-8]. For synthesizing novel molecular devices, a condensation between 5-aminophenyl-10, 15, 20-triphenyl porphyrin (H₂APTPP) and terephthalaldehyde was designed to prepare a Schiff base bridged biporphyrin (SBBBPor) with conjugation configuration. This special conjugation system with energy transfer function is hopeful to be designed as a functional material. Using nitric acid as nitrification reagent, Kruper's nitrification-reduction was an efficient method to prepare mono-aminophenyl porphyrin with lower yield (~60%) [9]. In this work sodium nitrite was selected as nitrification reagent, and the yield of H₂NPTPP reached 80%. This nitrite method was more convenient for the following reduction and condensation, finally the titled compound with conjugation configuration was successfully prepared.

All reactions and processes were performed in air unless otherwise noted. Pyrrole was freshly distilled before using. Other reagents and solvents were commercially available and directly used as received without further purification. ¹H NMR spectra were recorded with a Varian Mercury-Plus 300 FT-NMR (300 MHz) spectrometer in chloroform-*d* with tetramethylsilane (Me₄Si) as an internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in parts per million and hertz respectively. UV-vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer, and IR determination was performed with a Nicolet Avatar 370 FT-IR infrared spectrometer (KBr pellets, $4000-400 \text{ cm}^{-1}$). Fluorescence spectra were recorded on a HORIBA Jobin Yvon Fluorescence-max4 luminescence spectrometer. EPR spectra were acquired with a Bruker A200-9.5/12 spectrometer (RF powers ranged from 200 to 400 W across the 7 MHz scanned range, and microwave power ranged from 2 to 20 mW). Element microanalysis was carried out in air on a PerkinElmer 240 C elemental analyzer. The in situ experiments of ultraviolet irradiation (UVI) and visible radiation (VR) were carried out by using a deuterium light source (30 W, Lot Oriel Company, Germany) and a halogen-tungsten light source (1000 W, Lot Oriel Company, Germany). In photochromic determinations, the distance between the light source and the sample was set at 20 cm (with 0.5 cm slit for UV-vis determinations and 0.2 mm slit for EPR determinations). X-ray data collections and structure determinations were performed on a Bruker SMART CCD. The data were collected using graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by direct methods and refined by fullmatrix least-square calculation on F^2 with SHELX-97 program package [10]. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were placed in calculated positions.

^{*} Corresponding author.

5, 10, 15, 20-Tetraphenyl porphyrin (H₂TPP) was synthesized by the reported method [11]. Using sodium nitrite as the nitrification reagent and tin dichloride as the reductant, H₂TPP was conversed into 5aminophenyl-10, 15, 20-triphenyl porphyrin (H₂TAPTPP) [12], followed by condensation with terephthalaldehyde [13], and the Schiff base bridged biporphyrin (SBBBPor) was finally prepared (Scheme 1). The product was separated and purified by the reported method: [14] The rough violet product was dissolved in dichloromethane, and purified by column chromatography (for preventing dissociation of Schiff base bond, the silica gel column was previously treated with alkaline triethylamine) using a binary eluent of dichloromethane and acetone (v:v = 300:1). The first red-violet band was collected. After vaporizing and drying under vacuum, the Schiff base bridged biporphyrin was finally obtained in yield of 20% based on the calculation of H₂APTPP. ¹H NMR for SBBBPor (300 MHz, CDCl₃) δ/ppm: 5.39-6.68 (16H, H-C in pyrrole), 7.17 (d, *J* = 8.4 Hz, 14H, phenyl), 7.33–7.40 (m, 26H, phenyl), 8.64-8.66 (s, 2H, Schiff base), -2.72 (s, 4H, N-H in pyrrole); IR (KBr)/cm⁻¹: 3314 (υ_{N-H} , pyrrole), 3024 (υ_{C-H} , phenyl), 1629 ($\upsilon_{C=N}$, Schiff base), 1594 ($\upsilon_{C=C}$, phenyl), 1167 (δ_{C-H} , pyrrole); Calc. for C96H64N10: 84.93; H, 4.75; N, 10.32%; Found: C, 85.03; H, 4.82; N, 10.21%.

In the synthetic process, the UV–vis spectra for the relative porphyrin products were recorded and their spectral data were listed in Table 1. Compared with H₂TPP, the Soret bands of its derivatives shifted differently towards red direction. The Soret band and Q bands of porphyrin derivatives are all originated from $\pi - \pi^*$ electron transition of the conjugated configuration, but the peripherally phenyl rings were not co-planar with the porphyrin ring, and therefore they were not efficiently in conjugation with the porphyrin's π -system. As a result, the slight red shift in Soret band peak (10 nm) of the product indicated the conjugation form of the peripheral substitutes that was not clearly enhanced.

Porphyrins and their derivatives have been developed as luminescent materials [15–17]. Luminescent property is closely related to the



Scheme 1. Synthetic route for Schiff base bridged biporphyrin (SBBBPor).

Table 1

UV-vis spectral data for H₂TPP and its derivatives.

Samples	_		$\lambda_{max}/nm(CHCl_3)$		
	Soret	Q(IV)	Q(III)	Q(II)	Q(1)
H ₂ TPP	410.0	514.0	549.0	589.5	645.5
H ₂ APTPP	415.5	516.5	553.0	592.0	648.0
Porphyrin-Schiff base	418.5	516.5	552.0	592.0	646.0
SBBBPor	420.0	516.0	552.5	591.5	646.5

fluorescence of materials. Therefore the fluorescence (FL) determinations for all prepared porphyrin derivatives were performed as described in Figs. 1 and 2. Compared to the spectrum of H₂TPP ($\lambda_{Ex} = 430$ nm, $\lambda_{Em} = 651$ nm), the emission peak of H₂APTPP ($\lambda_{Ex} = 434$ nm, $\lambda_{Em} =$ 655 nm) appeared with *slightly red shift*. The amino group in H₂APTPP donated electron to porphyrin ring, and it resulted in red shift in its emission spectrum. This electronic effect was similar to that in the FL determination of SBBBPor system ($\lambda_{Ex} = 439$ nm, $\lambda_{Em} = 655$ nm); while in the FL determination of porphyrin-Schiff base (Por-SB), the electron donating from -C=N- group and the electron accepting from -C=O group counteracted each other, then its emission peak position ($\lambda_{Ex} =$ 440 nm, $\lambda_{Em} = 651$ nm) was similar to that of H₂TPP. Therefore the electron donating effect from -C=N- group in SBBBPor resulted in red shift in its FL spectrum.

Violet irradiation experiments were carried out in a chloroform solution with SBBBPor $(1.0 \times 10^{-3} \text{ mol/L})$. Before and after violet irradiation, the UV-vis spectral variation was recorded (Fig. 3). At the beginning, the UV-vis spectrum of SBBBPor was just the same to those described in entries 5, Table 1; during 10 s' ultraviolet irradiation, the original Soret band at 420 nm and Q (I-IV) were weakened along with an isosbestic point at 434 nm, a new Soret band at 451 nm and a new broad and strong Q band at 669 nm emerged; and finally, the original Soret band and Q (I-IV) completely disappeared, and the new Soret and Q bands reached their maximum absorption, and accompanied color of the solution changed from pale green to dark green. This color variation seems to adopt a photochromic mechanism. If this color change was depended on the molecular structure change from trans- to cis-configurations, SBBBPor would be the potential candidate for molecular switch material [18-20], while the enhancement of Q band in absorption width and intensity would exhibit itself in spectral hole-burning materials [21].

What was the real reason for this color change? To seek an answer several experiments and investigations were carried out. Our previous molecular self-assembly indicated that H_2 TPP combined with two HCl molecules to form H_4 TPPCl₂ in solid state (Fig. 4) [22]. Therefore metal-free porphyrins possess molecular recognition towards hydrogen halides, while in aqueous solution metal-free porphyrin (H_2 Por) can



Fig. 1. Excitation spectra of the synthetic porphyrin derivatives.



Fig. 2. Emission spectra of the synthetic porphyrin derivatives.

combine two protons to form a species of H₄Por²⁺ cation with obvious color change [23]. Furthermore the reversible color change for the synthetic SBBBPor was realized by leading in dry HCl gas, and then followed by adding base solvents of pyridine, triethylamine, or strong aqua ammonia. Therefore this color change can be explained as the molecular recognition of SBBBPor towards HCl molecules, and the HCl was produced from chloroform's photodecomposition by ultraviolet irradiation [24,25]. Therefore Fig. 4 provided a model for the metal free porphyrin in molecular recognition towards hydrogen halides. This recognition towards HCl molecule is described in Scheme 2. In fact, nearly all of the metal-free porphyrins in dichloromethane and chloroform solutions exhibited the same coloring effect after ultraviolet irradiation, and their reversible color change can be simulated by halochromic experiments [26]. The detailed research and mechanism for this color change of other metal-free porphyrin derivatives would be reported elsewhere.

For the porphyrin chromophores, the delocated π -electron system in conjugated ring and the radical species O₂• from microwave irradiation of oxygen in air resulted in unpaired electron appearance [27–29], and these radical signals were easily detected by the EPR method [30,31]. But in a chloroform solution with SBBBPor, the unpaired electron was not easy to be detected before UV irradiation. Under UV irradiation, along with the molecular recognition towards decomposed HCl, the



Fig. 3. UV-vis spectral variation of SBBBPor before and after ultraviolet irradiation (λ = 360 nm) in CHCl₃ solution.



Fig. 4. Self-assembly of H₂TPP with HCl by hydrothermal method.

planar configuration of SBBBPor was partially destroyed, as a result the unpaired π -electrons were detected, and a weak EPR signal was detected around 3520 G (Fig. 5). Therefore molecular configuration change resulted in a different distribution state of π -electrons. And this change can also be monitored by EPR determinations.

Porphyrin's derivatives were favored sub-units as used in the electronic luminescent and devices. These applications are mainly based on their special molecular configurations: (1) with cyclic rigid structure of π -conjugations; (2) small energy difference between HOMO and LUMO resulted in red emission; and (3) easy to be modified in the molecular periphery, and they can conveniently ligate different

metal centers in their complexes, and furthermore to be constructed as a whole conjugated molecule to transmit electrons and photons [32–34]. Hereby a Schiff base bridged biporphyrin (SBBBPor) was prepared successfully. This novel derivative with conjugation system of porphyrin-Schiff base–Schiff base–porphyrin configuration possessed red emission property and it can easily recognize HCl molecules from the decomposition of chloroform. This supramolecular SBBBPor with conjugated structure would be a potential candidate in the design and assembly of molecular wires.

Acknowledgment

The authors acknowledge financial support from the National Scientific Foundation of China (No. 20771073), and the Key Project of Education Office from Guangdong Province, China (No. 2012CXZD0023).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2014.03.017.



Fig. 5. EPR spectra of Schiff base bridged biporphyrin (SBBBPor) before and after ultraviolet irradiation (UVI, $\lambda = 360 \text{ nm}$) in CHCl₃ solution.



Scheme 2. Molecular configurations of SBBBPor before and after UVI in CHCl₃ solution.

References

- [1] G. Mezo, L. Herenyi, J. Habdas, Syntheses and DNA binding of new cationic porphyrin-tetrapeptide conjugates, Biophys, Chem, 155 (2011) 36–44.
- F. Ricchelli, Photophysical properties of porphyrins in biological-membranes, J. Photochem. Photobiol. B Biol. 29 (1995) 109–118.
- [3] V. Gandhi, M.L. Thompson, T.D. Lash, Porphyrins with exocyclic rings. Part 24. Synthesis and spectroscopic properties of pyrenoporphyrins, potential building blocks for porphyrin molecular wires. Tetrahedron 66 (2010) 1787–1799.
- K.S. Suslick, Shape Selective Oxidation by Metalloporphyrins, in: K. Kadish, K. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 4, Academic Press, New York, 2000, pp. 41–63. (ch. 28).
- S. Ohmori, H. Kawabata, K. Tokunaga, Molecular design of high performance fused [5] porphyrin one-dimensional wire: a DFT study, Thin Solid Films 518 (2009) 901-905
- [6] H. Ozawa, M. Kawao, S. Uno, K. Nakazato, H. Tanaka, T. Ogawa, A photo-responsive molecular wire composed of a porphyrin polymer and a fullerene derivative, J. Mater Chem 19 (2009) 8307-8313
- [7] N. Bennett, G. Xu, L.J. Esdaile, H.L. Anderson, J.E. Macdonald, M. Elliott, Transition voltage spectroscopy of porphyrin molecular wires, Small 6 (2010) 2604-2611.
- Y.W. Li, Z.L. Yin, J.H. Yao, X.S. Deng, C.L. Yang, Effect of CO adsorption on the electron [8] transport behavior of single Fe-porphyrin molecular wire, Phys. E. 43 (2010) 382-386
- [9] W.J. Kruper, T.A. Chamberlin, M. Kochanny, Regiospecific arvl nitration of mesosubstituted tetraarylporphyrins; a simple route to bifunctional porphyrins, J. Org. Chem. 54 (1989) 2753-2756.
- [10] G.M. Sheldrick, SHELXL-97, program for the refinement of the crystal structures, University of Göttingen, Germany, 1997.
- [11] J.S. Lindsey, I.C. Schreiman, H.C. Hsu, P.C. Kearney, A.M. Marguerettaz, Rothemund and Adler-Longo reactions revisited: synthesis of tetraphenylporphyrins under equilibrium conditions, J. Org. Chem. 52 (1987) 827–836. [12] R. Luguya, L. Jaquinod, F.R. Fronczek, M.G.H. Vicente, K.M. Smith, Synthesis and
- reactions of meso-(p-nitrophenyl)porphyrins, Tetrahedron 60 (2004) 2757-2763.
- [13] R.H. Kratzer, K.L. Paciorek, D.W. Karle, Modified benzoin condensation of terephthalaldehyde with benzaldehyde, J. Org. Chem. 41 (1976) 2230-2230.
- [14] Y.-h Wu, L. Chen, J. Yu, S.-l. Tong, Y. Yan, Synthesis and spectroscopic characterization of meso-tetra(Schiff-base substituted phenyl) porphyrins and their zinc complexes, Dyes Pigments 97 (2013) 423-428.
- [15] O. Ohno, Y. Kaizu, H. Kobayashi, Luminescence of some metalloporphins including the complexes of the IIIb metal group, J. Chem. Phys. 82 (1985) 1779-1786.
- [16] T.J. Schaafsma, T.J. Savenije, R.B.M. Koehorst, F.J. Vergeldt, J. Wienke, Luminescent properties and photogeneration of charge carriers in porphyrin dimers and molecular photo-diodes, J. Lumin. 72-74 (1997) 81-82.
- [17] M. Sirish, B.G. Maiya, Fluorescence studies on a supramolecular porphyrin bearing anthracene donor moieties, J. Photochem. Photobiol. A Chem. 85 (1995) 127-135.
- [18] W. Auwärter, K. Seufert, F. Bischoff, D. Ecija, S. Vijayaraghavan, S. Joshi, F. Klappenberger, N. Samudrala, J.V. Barth, A surface-anchored molecular four-level conductance switch based on single proton transfer, Nat. Nanotechnol. 7 (2012) 41-66.
- [19] P. Liljeroth, Molecular electronics: flipping a single proton switch, Nat. Nanotechnol. 7 (2012) 5–6.

- [20] K. Baberschke, Magnetic switching of Fe-porphyrin molecules adsorbed on surfaces: an XAFS and XMCD study, 14th International Conference on X-Ray Absorption Fine Structure (XAFS14), J. Physics: Conference Series, 190, 2009, p. 012012.
- [21] K. Horie, Photochemical hole burning in macromolecular complexes, Macromol. Symp. 80 (1994) 353-358.
- [22] Self-assembly of H₄TPPCl₂·H₂O: H₂TPP (100 mg, 0.163 mmol), HCl (3 mL, 1 mol/L) and distilled water (5 mL) were mixed together and kept stirring at room temperature for about 2 h. The obtained solution was sealed in an autoclave and placed in an oven at 160 °C for 36 h. After cooling down to room temperature, several purple crystals in prism shape suitable for X-ray analysis were filtrated in 44% yield. Calc. for H₄TPPCl₂ · H₂O: C, 74.68; H, 4.53; N, 7.39 %. Found: C, 74.82; H, 4.28; N, 7.43%. Crystal data: Empirical formula C₄₄H₃₄Cl₂N₄O; Formula weight 705.65; Temperature $\begin{array}{l} \text{S(16)} R_{1,2} = 0.1527 \text{ Rm} + 0.527 \text{ Rm} + 0.0383 \text{ GOF on } F^{2} = 1.0147 \text{ Rm} (F^{2} + 0.0147 \text{ Rm}) \\ \text{Reted} \in 6271 \text{ reflections unique} ; \text{R}_{\text{int}} = 0.0383 \text{ GOF on } F^{2} = 1.0147 \text{ Rm} (F^{2} + 0.0147 \text{ Rm}) \\ \text{Rm} (F^{2} + 0.0592 \text{ Rm}) \\ \text{Rm}$ CCDC: 700701.
- [23] M.M. Kruk, Y.B. Ivanova, V.B. Sheinin, A.S. Starukhin, N.Z. Mamardashvili, O.I. Koifman, Highly sensitive halide ions recognition with diprotonated porphyrin, Macroheterocycles 1 (2008) 50-58.
- [24] T. Torimoto, Y. Okawa, N. Takeda, H. Yonevama, Effect of activated carbon content in TiO₂-10aded activated carbon on photodegradation behaviors of dichloromethane, J. Photochem. Photobiol. A Chem. 103 (1997) 153-157.
- [25] J. Borisch, S. Pilkenton, M.L. Miller, D. Raftery, J.S. Francisco, TiO₂ photocatalytic degradation of dichloromethane: an FTIR and solid-state NMR study, J. Phys. Chem. B 108 (2004) 5640-5646.
- [26] G.E. Khalil, P. Daddario, K.S.F. Lau, S. Imtiaz, M. King, M. Gouterman, A. Sidelev, N. Puran, M. Ghandeharic, C. Brückner, meso-Tetraarylporpholactones as high pH sensors Analyst 135 (2010) 2125-2131
- M.B. Lan, H.L. Zhao, H.H. Yuan, Absorption and EPR spectra of some porphyrins and [27] metalloporphyrins, Dyes Pig. 74 (2007) 357-362.
- [28] G.T. Luo, S.W. Zheng, Q.B. Xu, Synthesis, Optical and thermal properties of novel Schiff base complexes containing porphyrin copper (II) and zinc (II), Chem. J. Chin Univ 29 (2008) 1307-1311
- Q.S. Lin, T.L. Zhang, L.B. Yuan, Study of ESR spectra and photochemical reaction of [29] porphyrin derivatives, Chin. Appl. Chem. 5 (1988) 57-61.
- [30] W.Q. Zheng, N. Shan, L.X. Yu, UV-visible, fluorescence and EPR properties of porphyrins and metalloporphyrins, Dyes Pig. 77 (2008) 153-157.
- [31] G. Maiya, V. Krishnan, Schiff bases of nickel (II), copper (II) porphyrins and dibenzo-18-crown-6-interspersed bis-metal porphyrins, Protonation studies, I. Chem, Sci, 99 (1987) 283-296
- [32] H. Ibrahim, A. Kasselouri, B. Raynal, R. Pansu, P. Prognon, Investigating the possible use of a tetra (hydroxyphenyl) porphyrin as a fluorescence probe for the supramolecular detection of phospholipids, J. Lumin. 131 (2011) 2528-2537.
- [33] J. Larsen, J. Andersson, T. Polívka, J. Sly, M.J. Crossley, V. Sundström, E. Åkesson, Energy transfer and conformational dynamics in Zn-porphyrin dendrimers, Chem. Phys. Lett. 403 (2005) 205-210.
- [34] D. Wróbel, A. Graja, Modification of electronic structure in supramolecular fullereneporphyrin systems studied by fluorescence, photoacoustic and photothermal spectroscopy, J. Photochem, Photobiol, A Chem, 183 (2006) 79-88.