



Modulation of peripheral substituents of cobalt thioporphyrzines and their photocatalytic activity



Quan Zhou, Shuai Xu, Changjun Yang*, Bingguang Zhang, Zhe Li, Kejian Deng*

Key Laboratory of Catalysis and Material Sciences of the State Ethnic Affairs Commission & Ministry of Education, College of Chemistry and Material Sciences, South-Central University for Nationalities, Wuhan 430074, China

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ABSTRACT

A series of thioporphyrzines have been synthesized via cocondensation from 2,3-dicyano-1,4-dithiin (A) and 2,3-bis(butylthio) maleonitrile (B) and thoroughly characterized with UV–vis, ¹H NMR and MALDI-TOF MS. Through modulation of peripheral substituents of thioporphyrzines, both symmetrical and asymmetrical molecular structures in thioporphyrzines including B₄, *cis*-A₂B₂, *trans*-A₂B₂ and AB₃ were obtained, and were further used to react with cobalt acetate to form metal complexes, cobalt thioporphyrzines. Moreover, they were loaded on Al₂O₃ to form biomimetic catalysts for photocatalytic activation of dioxygen, whose efficiencies were assessed by photodegradation of Rhodamine B (RhB) in an aerated suspension under simulating sunlight irradiation. Importantly, it was found that the lower on the molecular symmetry of thioporphyrzine delivers the better on the photocatalytic activity. Electrochemical and theoretical studies demonstrated that lowering the molecular symmetry of the cobalt thioporphyrzines moderately decreased the HOMO-LUMO energy gap and increased the contribution of S atom in substituents to HOMO so as to enhance the photocatalytic activity. A possible mechanism to predict this reaction pattern was proposed through both detailed analysis of degradation products by HPLC and detection of the main reactive oxygen species (ROS) by ESR, indicating both energy transfer (major) and electron transfer (minor) to dioxygen to exist in the heterogeneous light photocatalytic system.

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1. Introduction

Metalloporphyrin and metallophthalocyanine with an extended delocalized π -electron conjugated macrocyclic system are well known for their electron-transfer and photosensitive roles in a myriad of redox systems in nature [1]. Tetraazaporphyrin or porphyrzine (Pz) which is a member of the porphyrin family has similar topology of tetrapyrrolic ring to porphyrin and phthalocyanine, but has obviously different chemical behavior. Among them, thioporphyrzine exhibits some unique electronic and optical properties that differ from their porphyrin counterparts owing to the β -position sulfur-containing groups in periphery and *meso* N atoms to replace methine groups leading to contraction of the central cavity. It suggests the importance of structure subtlety in conjugated macrocyclic system in tuning the properties. Therefore, the synthesis and application of porphyrzines and thioporphyrzines

with unique performance is still a challenge [2]. Our research group has recently found that thioporphyrzine exhibited a high thermal stability and unique photocatalytic activity for activating hydrogen peroxide and dioxygen [3–7]. Herein, we want to further investigate the molecular structure of thioporphyrzine through modulation of peripheral substituents so as to define the final photocatalytic activity.

According to the principle of crystallography, low-symmetrical structure could exhibit special physical, chemical and photoredox properties [8]. Among porphyrzines, however, the accessibility of the low-symmetrical porphyrzine is much harder than the symmetrical one [9]. To investigate the effect of molecule structure on the photocatalytic activity of metal thioporphyrzine, the symmetrical and asymmetrical metal thioporphyrzines were synthesized by introducing different type and quantity of substituent groups onto the periphery of macrocycle. Specifically, two different maleonitriles were designed to be chosen in present work: one of which is 2,3-dicyano-1,4-dithiin to be able to promote catalytic activity via periphery; the other of which is 2,3-bis(butylthio)-maleonitrile to be able to promote solubility of the porphyrzine macrocycle. And a thorough comparison of physical and chemical properties of these

* Corresponding authors.

E-mail addresses: yangchangjun@mail.scuec.edu.cn (C. Yang), dengkj@scuec.edu.cn (K. Deng).

prepared thioporphyrazines was made. In addition, neutral Al_2O_3 particles were chosen as the support for cobalt thioporphyrazines to form biomimetic heterogeneous catalysts. In the end, their photocatalytic activities were evaluated by oxidative degradation of dye Rhodamine B (RhB) under simulating sunlight irradiation in an aerated suspension.

Organic dyes are commonly present in textile, paper and printing industry effluents. However, most of the organic dyes are not readily biodegradable which present an immediate threat to aquatic life and human beings [10–12]. Hence, great attention has been paid to oxidative degradation of persistent organic dyes from wastewater because of its high mineralization efficiency [13,14]. With special attention to metalloporphyrin and metallophthalocyanine-based photocatalysts, because these technologies could use sunlight and dioxygen for the removal of persistent dye pollutants [15–17]. In our previous research, thioporphyrazines have also been proven to be excellent photocatalysts for the oxidation degradation of organic pollutants under sunlight [5–7]. In this paper, the factor of molecular structure of cobalt thioporphyrazine loaded on Al_2O_3 was examined in detail to gain fundamental insight in the application of metalloporphyrin as a biomimetic photocatalyst, opening a new door for the removal of persistent dye pollutants by using sunlight and air, and it is also a reference for photodynamic therapy of cancers.

2. Experimental

2.1. Synthesis of low-symmetrical metal-free thioporphyrazines

Porphyrazine formation is widely used the Linstead macrocyclization, and two different maleonitriles via cocondensation could form the mixed cyclization to obtain different porphyrazines including the molecules of symmetrical and asymmetrical structure. In a typical synthetic strategy, the precursors 2,3-dicyano-1,4-dithiin (0.6460 g, 4 mmol) and 2,3-bis(butylthio)maleonitrile (0.5000 g, 2 mmol) were mixed in magnesium butoxide (100 mL). Then the mixture was stirred at reflux under nitrogen for 48 h, the crude solid formed was filtered and washed with methanol until the filtrate being colorless, giving mixed products of 1a, 2a, 3a and 4a.

Subsequently, the mixed products were dissolved in 50 mL trifluoroacetic acid (TFA), and further stirred 12 h in dark so as to remove the center metal magnesium. Then the solution was poured into purified water to precipitate the target metal-free thioporphyrazine. The dark purple products were obtained by washing with ammonia solution (10%), purified water and methanol in sequence. Four thioporphyrazines, such as 1b, 2b, 3b and 4b, could be effectively obtained by separating the above products on chromatography column with silica gel using dichloromethane (CH_2Cl_2)/petroleum ether (PE) (3:1, v/v) as eluent. The target products 1b, 2b, 3b and 4b were characterized with UV–vis spectrum, ^1H NMR spectrum and MALDI-TOF MS, the characteristic structure datas for the products were shown as following:

Product 1b: tetra(2,3-bis(butylthio)maleonitrile) porphyrazine, denoted as B_4

0.2 g (yield 10%); UV–vis λ_{max} (in CH_2Cl_2): Q-band: 712 nm and 641 nm; Soret-band: 508 nm, B-band: 349 nm; ^1H NMR (400 MHz, CDCl_3): δ = 4.106 (t, 2H, $-\text{SCH}_2-$), 1.873 (m, 2H, $-\text{CH}_2-$), 1.613 (m, 2H, $-\text{CH}_2-$), 0.935 (t, 3H, $-\text{CH}_3$), -1.099 (t, 2H, $-\text{NH}-$); MALDI-TOF MS: m/z = 1019.3 [M + H] $^+$. See also Figs. S1 and S2 in supplementary materials.

Product 2b: tri(2,3-bis(butylthio)maleonitrile)-(1,4-dithiin) porphyrazine, denoted as B_3A

0.1 g (yield 6%); UV–vis λ_{max} (in CH_2Cl_2): Q-band: 712 nm and 630 nm, Soret-band: 519 nm, B-band: 360 nm; ^1H NMR (400 MHz,

CDCl_3): δ = 4.141 (t, 2H, $-\text{SCH}_2-$), 1.913 (m, 2H, $-\text{CH}_2-$), 1.665 (m, 2H, $-\text{CH}_2-$), 0.981 (t, 3H, $-\text{CH}_3-$), 3.765 (t, 2H, $-\text{SCH}_2-$), -2.37 (t, 2H, $-\text{NH}-$); MALDI-TOF MS: m/z = 934.3 [M + H] $^+$. See also Figs. S3 and S4 in supplementary materials.

Product 3b: *trans*-di(2,3-bis(butylthio)maleonitrile)-di(1,4-dithiin) porphyrazine, denoted as *trans*- B_2A_2

0.04 g (yield 2.2%); UV–vis λ_{max} (in CH_2Cl_2): Q-band: 715 nm and 614 nm, Soret-band: 522 nm, B-band: 361 nm; ^1H NMR (400 MHz, CDCl_3): δ = 4.266 (t, 2H, $-\text{SCH}_2-$), 1.922 (m, 2H, $-\text{CH}_2-$), 1.685 (m, 2H, $-\text{CH}_2-$), 0.98 (t, 3H, $-\text{CH}_3-$), 3.811 (t, 2H, $-\text{SCH}_2-$), -2.23 (t, 2H, $-\text{NH}-$); MALDI-TOF MS: m/z = 847.5 [M + H] $^+$. See also Figs. S5 and S6 in supplementary materials.

Product 4b: *cis*-di(2,3-bis(butylthio)maleonitrile)-di(1,4-dithiin) porphyrazine, denoted as *cis*- B_2A_2

0.06 g (yield 4.4%); UV–vis λ_{max} (in CH_2Cl_2): Q-band: 707 nm and 629 nm, Soret-band: 519 nm, B-band: 359 nm; ^1H NMR (400 MHz, CDCl_3): δ = 4.247 (t, 2H, $-\text{SCH}_2-$), 1.929 (m, 2H, $-\text{CH}_2-$), 1.683 (m, 2H, $-\text{CH}_2-$), 0.984 (t, 3H, $-\text{CH}_3-$), 3.759 ~ 3.817 (t, 2H, $-\text{SCH}_2-$), -3.58 (t, 2H, $-\text{NH}-$); MALDI-TOF MS: m/z = 847.2 [M + H] $^+$. See also Figs. S7 and S8 in supplementary materials.

2.2. Synthesis of low-symmetrical cobalt thioporphyrazines

Thioporphyrazine free-base (1b, 2b, 3b or 4b) (0.1000 g) and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.2400 g) were respectively added into 15 mL DMF solution, the mixture was then stirred for 10 h at 70 °C. The crude solid formed was filtered and washed with purified water and methanol until the filter liquor being colorless. The target product cobalt thioporphyrazines, such as 1c, 2c, 3c and 4c, were obtained respectively by purifying the crude solid on a silica column with CH_2Cl_2 as eluent. The target products 1c, 2c, 3c and 4c were also characterized with UV–vis spectrum and MALDI-TOF MS, the characteristic structure datas for the products were shown as following:

Complex 1c: Cobalt tetra(2,3-bis(butylthio)maleonitrile) porphyrazine, denoted as CoB_4

0.08 g (yield 75%); UV–vis λ_{max} (in CH_2Cl_2): Q-band: 645 nm, Soret-band: 440 nm, B-band: 333 nm. MALDI-TOF MS: m/z = 1076.2 [M + H] $^+$. See also Fig. S9 in supplementary materials.

Complex 2c: Cobalt tri(2,3-bis(butylthio)maleonitrile)-(1,4-dithiin) porphyrazine, denoted as CoB_3A

0.07 g (yield 70%); UV–vis λ_{max} (in CH_2Cl_2): Q-band: 643 nm, Soret-band: 436 nm, B-band: 339 nm. MALDI-TOF MS: m/z = 990.2 [M + H] $^+$. See also Fig. S10 in supplementary materials.

Complex 3c: *trans*-di(2,3-bis(butylthio)maleonitrile)-di(1,4-dithiin) porphyrazine, denoted as *trans*- CoB_2A_2

0.06 g (yield 64%); UV–vis λ_{max} (in CH_2Cl_2): Q-band: 638 nm. Soret-band: 443 nm, B-band: 338 nm; MALDI-TOF MS: m/z = 904.1 [M + H] $^+$. See also Fig. S11 in supplementary materials.

Complex 4c: *cis*-di(2,3-bis(butylthio)maleonitrile)-di(1,4-dithiin) porphyrazine, denoted as *cis*- CoB_2A_2

0.07 g (yield 70%); UV–vis λ_{max} (in CH_2Cl_2): Q-band: 644 nm. Soret-band: 433 nm, B-band: 341 nm. MALDI-TOF MS: m/z = 933.2 [M + H] $^+$. See also Fig. S12 in supplementary materials.

2.3. Cyclic voltammetric characterization of cobalt thioporphyrazines

Cyclic voltammetric datas were collected using CHI650D electrochemical workstation (Chenhua Corp., Shanghai, China) using a conventional three-electrode system. A Pt wire electrode was employed as working electrode. Ag disc electrode (2 mm) was used as reference electrode and counter electrode, respectively. 1 mmol cobalt thioporphyrazine (1c, 2c, 3c or 4c) and 341 mg tetrabutylammonium perchlorate (TBAP) were respectively dissolved in 10 mL

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