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Synthesis and spectral properties of nonclassical binuclear thienoporphyrazines

Tatiana V. Dubinina [a, b, *], Nataliya E. Borisova [a], Marina V. Sedova [c],
Larisa G. Tomilova [a, b, 1], Taniyuki Furuyama [d], Nagao Kobayashi [d, 2]

[a] Department of Chemistry, M.V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation
[b] Institute of Physiologically Active Compounds, Russian Academy of Sciences, 1 Severny proezd, 142432 Chernogolovka, Moscow Region, Russian Federation
[c] Institute for Theoretical and Applied Electromagnetics, Russian Academy of Sciences, 125412, 13 Izhorskaya St., Moscow, Russian Federation
[d] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

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ABSTRACT

The first examples of planar binuclear porphyrazines sharing a common benzene or naphthalene ring based on a 3,4-thiophene moiety have been synthesized and characterized using nuclear magnetic resonance spectroscopy, high-resolution mass spectrometry, electronic absorption spectroscopy and magnetic circular dichroism. In order to enhance the interpretation of the electronic structures, quantum chemical studies were carried out. The formation of nanoaggregates in a solid film was shown using atomic force microscopy.

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1. Introduction

Porphyrazines as being porphyrin-like systems are of great interest for use in a wide variety of applications [1–3]. The possibility of porphyrazine core modification leads to the synthesis of complexes with novel properties (Scheme 1) [4–6]. Porphyrazine fused to a heterocyclic ring possesses enhanced conductivity [7] and NLO properties [8]. Some unsubstituted [9] and alkyl-substituted [10] tetrathieno[2,3-b]porphyrazines have been investigated earlier, while recently, we described the synthesis of planar and sandwich-type tetrahydrobenzo-substituted tetrathieno[2,3-b]porphyrazines with third-order nonlinearity [11].

The main disadvantage of tetra(2,3-thieno)tetraazaporphyrines is the presence of rotational isomers [9,11]. In contrast, this problem does not occur in the case of tetra(3,4-thieno)tetraazaporphyrines. Some A$_3$B-type porphyrazines were obtained by the mixed condensation of 3,4-dicyanothiophenes and substituted phthalonitriles [6,12]. However, for many years, the efforts of self-condensation using only 2,5-dialkyl-3,4-dicyanothiophenes had always ended in failure [12], with only one successful attempt at synthesizing porphyrazines based on 3,4-dicyanothiophene being reported recently [13]. In the resulting compound, one sulfur atom was tetravalent. This unusual valence state of the sulfur atom was stabilized by introducing 2,5-diphenyl substituents into the thiophene rings.

The main aim of the present paper was to obtain novel planar binuclear 3,4-thienoporphyrazines of A$_3$BA$_3$-type stabilized by the linking B unit. Since A$_3$B-type monomeric porphyrazines are relatively easily isolated, we felt it feasible to synthesize this kind of dimer.

2. Experimental

2.1. Chemicals and instruments

Preparative TLC was performed using Merck Aluminum Oxide F$_{254}$ neutral flexible plates. Gel permeation chromatography was

* Corresponding author. Department of Chemistry, M.V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation. Tel.: +7 495 939 1243; fax: +7 495 939 0290.
E-mail addresses: dubinina.t.vid@gmail.com (T.V. Dubinina), tom@org.chem. msu.ru (L.G. Tomilova), nagaok@m.tohoku.ac.jp (N. Kobayashi).
[1] Fax: +7 496 524 9508.
[2] Tel./fax: +81 22 795 7719.
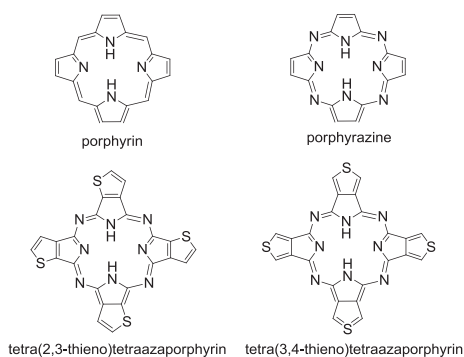
Scheme 1. Representative structures of porphyrin, porphyrazine and thienoporphyrazines.

accomplished on polymeric support Bio-Beads S-X1 (BIORAD). All reagents and solvents were obtained or distilled according to standard procedures. The salts were dried immediately before use in a vacuum desiccator for 4 h at 70 °C. All reactions were monitored by TLC and UV/Vis until complete disappearance of the starting reagents unless otherwise specified. Electronic absorption (UV–Vis) spectra were recorded on a ThermoSpectronic Helios-α spectrophotometer using quartz cells (0.5 × 1 cm). High-resolution MALDI mass spectra were registered on a Bruker ULTRAFLEX II TOF/TOF instrument with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix.

^{1}H NMR spectrum was recorded on a Bruker AVANCE 600 spectrometer (600.12 MHz) at 30 °C. The little enhancement of the temperature as against ambient lets better control it during long data accumulation. Chemical shifts are given in ppm relative to SiMe$_4$.

The calculations were performed using the resources of an MVS-50K supercomputer of the Joint Supercomputer Center (JSC) (www.jscc.ru). All calculations were carried out with the PRIRODA quantum chemistry program [14,15]. The gradient-corrected exchange-correlation Perdew, Burke and Ernzerhof (PBE) functional with no Hartree-Fock exchange [16,17] was used for calculations. The efficient resolution of identity (RI) and parallel implementation of evaluating both Coulomb and exchange-correlation integrals with optimized fitting Gaussian basis sets in the PRIRODA code permits the performance of calculations of the molecular systems with a large number of basic functions [14,15]. A large integration grid (which comprises about 800.000 points over the calculated molecules) with a 10^{-8} accuracy parameter of the adaptively generated grid was used. This parameter is responsible for the precision of the exchange-correlation energy per atom. The 10^{-7} threshold on the orbital gradients at the energy calculations tag and 10^{-6} threshold on the molecular gradient for the geometry optimization procedure were employed. In all calculations, spin-restricted formalism was chosen. For all atoms the cc-pVDZ basis set were chosen adopted for using with the program [14]. All geometries were completely optimized without any symmetry constraints. Systematic vibrational analysis was performed to confirm whether an optimized geometry corresponded to a minimum without an imaginary frequency. The starting geometries were constructed analogously to known procedures.

Atomic force microscopy (AFM) studies were carried out by means of a Solver-P47H (NT-MDT) microscope. Tapping mode and a high accuracy composite silicon/polysilicon HA_NC probe for non-contact AFM were applied to obtain images. Menzel-Gläser cover slips (18 × 18 mm) were employed as the substrate. The rounding-off radius of the probe was less than 10 nm. The films were deposited from the pyridine solution ($c = 10^{-6}$ M) on a glass substrate.

2.2. Synthesis and characterization

2.2.1. Preparation of (bis(trithieno[3,4]-5,10,15,20-tetraazaporphyrino)-[b,e]benzene) dizinc **4a**

A mixture of *bis*(diiminoisoindoline) derivative **3a** (10.0 mg, 0.05 mmol), 3,4-dicyanothiophene **1** (126.0 mg, 0.94 mmol) and Zn(OAc)$_2$·4H$_2$O (42.0 mg 0.19 mmol) in *i*-AmOH (3 mL) in the presence of DBU (0.2 mL) was heated to reflux under argon for 5 h. The reaction mixture was cooled to room temperature and a mixture of MeOH:H$_2$O (5:1 V/V) was added. The precipitate was filtered and washed with water and MeOH. The target compound was separated using gel permeation chromatography (THF:Py (5:2 V/V). Yield of **4a**: (6.0 mg, 12.0%). UV–Vis (λ_{max} (Py)/nm (lg ε)): 337 (4.60); 665(4.16); 723 (4.23); 761(4.34). ^{1}H NMR δ_H (600.13 MHz, Py-d$_5$) 8.47 (d, J = 3.3 Hz, 12H, H$_{Thio}$); 9.02 (s, 2H, H$_{Ar}$). HRMS MALDI-TOF/TOF Found: [M + H]$^+$ 1113.6232; molecular formula C$_{46}$H$_{14}$N$_{16}$S$_6$Zn$_2$ requires [M + H]$^+$ 1113.8606.

2.2.2. Preparation of (bis(trithieno[3,4]-7,12,17,22-tetraazaporphyrino)-[b,g]naphthalene) dizinc **4b**

A mixture of *bis*(diiminoisoindoline) derivative **3b** (10.0 mg, 0.04 mmol), 3,4-dicyanothiophene **1** (102.0 mg, 0.76 mmol) and Zn(OAc)$_2$·4H$_2$O (33.0 mg 0.15 mmol) in *i*-AmOH (3.5 mL) in the presence of DBU (0.2 mL) was heated to reflux under argon for 12 h. The reaction mixture was cooled to room temperature and MeOH was added. The precipitate was filtered and washed with water and MeOH. The target compound was separated using gel permeation chromatography (Py). Yield of **4b**: (2.0 mg, 5.0%). UV–Vis (λ_{max} (Py)/nm (lg ε)): 322 (4.72); 664 (3.63); 746 (4.00). ^{1}H NMR δ_H (600.13 MHz, Py-d$_5$) 8.63 (d, J = 3.2 Hz, 12H, H$_{Thio}$); 8.83 (s, 4H, H$_{Ar}$). HRMS MALDI-TOF/TOF Found: [M + 2CHCA]$^+$ 1399.3333; molecular formula C$_{68}$H$_{39}$N$_{16}$S$_6$Zn$_2$ requires [M + 2CHCA]$^+$ 1399.0451.

3. Results and discussion

3.1. Synthesis of binuclear thienoporphyrazines

A statistical condensation reaction between 3,4-dicyanothiophene **1** and the *bis*(diiminoisoindoline) derivative of pyromellitonitrile was carried out in boiling *i*-AmOH, to obtain the target binuclear complex. We used zinc as a central ion (Scheme 2). The reaction conditions optimized by us earlier [18,19] for the synthesis of planar binuclear phthalo- and naphthalocyanines were used. The possibility of self-condensation of 3,4-dicyanothiophene was first examined under the same conditions; however, no traces of porphyrazine product **2** were observed. After the addition of *bis*(diiminoisoindoline) **3a** to this reaction mixture, the color of the
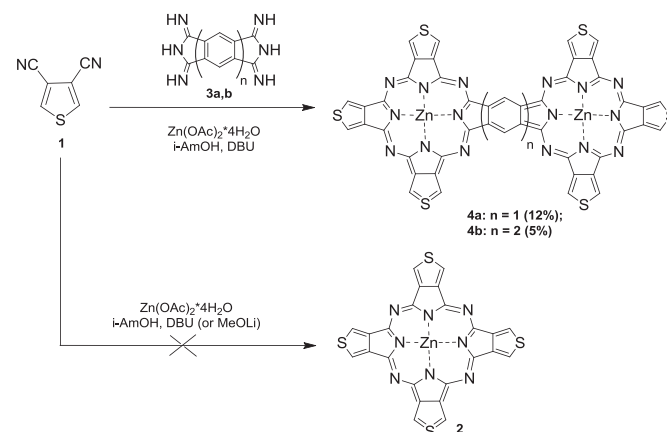
Scheme 2. Synthesis of thienoporphyrazine complexes.