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Novel planar and sandwich-type complexes of substituted tetrathieno[2,3-*b*] porphyrazine: Synthesis and investigation of properties

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ABSTRACT

An efficient synthetic approach to a novel substituted tetrathieno[2,3-*b*]porphyrazine, its Mg, Zn, Lu complexes and a Lu triple-decker complex was developed. Spectral properties and aggregation phenomena of the target compounds were investigated by UV/Vis spectroscopy and atomic force microscopy (AFM). Electrochromic behaviour of the Zn complex was studied by electrochemistry and spectroelectrochemistry.

1. Introduction

Tetrathieno[2,3-*b*]porphyrazines are the less studied analogues of phthalocyanines [1]. The presence of a sulphur-containing heterocyclic moiety in the macrocycle improves photoconductivity [2] and NLO properties [3]. Therefore such compounds are of importance for a range of functional applications including photovoltaic cells [2b], PDT [4], and optical data storage devices [5]. Previously reported unsubstituted tetrathieno[2,3-*b*]porphyrazines exhibit low solubility in organic solvents, and the synthetic strategy is inefficient (yield ≤16%) [6]. The present paper focuses on the synthesis of highly soluble tetrahydrobenzo substituted tetrathieno[2,3-*b*] porphyrazines and an investigation of their spectral and electrochemical properties.

2. Experimental

2.1. Chemicals and instruments

Column chromatography was carried out on neutral MN-Aluminiumoxid. Preparative TLC was performed using Merck Aluminium Oxide F_{254} neutral flexible plates. The electrolyte $[Bu_4N]^+[BF_4]^-$ (Sigma–Aldrich) was recrystallized twice from ethyl acetate/hexane (9:1, V/V) and dried under vacuum at 70 °C. *o*-Dichlorobenzene (DCB, 99%, Sigma–Aldrich, HPLC-grade) for voltammetric and specrtoelectrochemical studies was used as received. All other reagents and solvents were obtained or distilled according to standard procedures. The salts $Mg(OAc)_2 \cdot 4H_2O$; $Zn(OAc)_2 \cdot 4H_2O$; $Lu(OAc)_3 \cdot 4H_2O$ were dried immediately before use in a vacuum desiccator for 4 h at 70 °C. All reactions were TLC and UV/Vis controlled until complete disappearance of the starting reagents if not additionally specified.

Electronic absorption (UV/Vis) spectra were recorded on a ThermoSpectronic Helios-α spectrophotometer using quartz cells

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(0.5 × 1 cm). MALDI-TOF mass spectra were taken on a VISION-2000 mass spectrometer with 2-[(2*E*)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]-malonitrile (DCTB) as the matrix. High-resolution MALDI mass spectra were registered on a Bruker ULTRAFLEX II TOF/TOF instrument with DCTB as the matrix. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker "Avance 400" spectrometer (400.13 and 100.61 MHz, respectively) at 20 °C (if not additionally specified). ^{1}H–^{1}H COSY NMR spectra were recorded on Bruker AVANCE 600 spectrometer (600.12 MHz). Chemical shifts are given in ppm relative to $SiMe_4$.

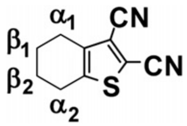
Electrochemical measurements were carried out using IPC-Pro (Econix, Moscow, Russia) and EmStat (Palm Instrument BV, Utrecht, the Netherlands) potentiostats. Cyclic voltammetry (CVA) and square-wave voltammetry (SWVA) were performed in a conventional three electrode cell using Pt-disk (2.0 mm in diameter) working and Pt-foil counter electrodes. A calomel reference electrode (SCE, 3 M NaCl) was connected to the solution through a salt-bridge and a Luggin capillary, whose tip was placed close to the working electrode. The junction potentials were corrected by ferrocenium$^+$/ferrocene (Fc^+/Fc) couple each time after a series of measurements ($E_{1/2}(FeFc_2) = 0.592$ V). Freshly distilled dichloromethane (purium, Reachim Russia) and *o*-dichlorobenzene (DCB, 99% Sigma–Aldrich, HPLC-grade) freshly passed through an Al_2O_3 layer were used as solvents, and 0.15 mol/l solution of Bu_4NBF_4 (Sigma–Aldrich, dried under vacuum at +80 °C) in *o*-dichlorobenzene containing $2–10 \times 10^{-4}$ M of sample was bubbled with argon for 20 min before measurements were taken. Blank voltammograms were recorded in the same background solution.

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 THF or C_6H_6 solution ($c = 10^{-6}$ M) on a glass substrate.

2-Iodo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile was synthesized according to the published procedures [6,7].

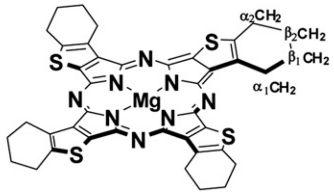
2.2. Synthesis and characterization

2.2.1. 4,5,6,7-Tetrahydrobenzo[b]thiophene-2,3-dicarbonitrile (1)



A mixture of 2-iodo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (2.400 g, 0.0083 mol) and CuCN (1.800 g, 0.020 mol) was refluxed in DMF (40 mL) for 10 h (TLC-control: Al_2O_3, C_6H_6: *n*-hexane (1:1 V/V)). The reaction mixture was cooled to room temperature and water was added. The product was collected by extraction with dichloromethane. The organic layer was dried with $CaCl_2$. The solvent was evaporated and the resulting solid was purified twice by column chromatography (Al_2O_3, $CHCl_3$). This yielded **1** as a pale yellow solid (1.020 g, 64%). mp 82.6 °C (lit. [6], 82–83 °C), $R_f = 0.4$ (Al_2O_3, C_6H_6: *n*- hexane (1:1 V/V)), ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 1.85–1.93 (m, 4H, $\beta_{1,2}$–CH_2), 2.73 (t, $J = 5.7$ Hz, 2H, α_1-CH_2), 2.81 (t, $J = 5.7$ Hz, 2H, α_2-CH_2), ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 21.38, 22.39 ($\beta_{1,2}$–CH_2); 24.36, 25.22 ($\alpha_{1,2}$-CH_2) 111.60 and 111.93 (CN), 113.70 (C2), 119.47 (C3), 138.39 (C4), 145.71 (C5).

2.2.2. 2, 3, 8, 9, 14, 15, 20, 21-Octakis [4′,5′,6′,7′-tetrahydrobenzo] tetra-2,3-thiophenophorphyrazine magnesium (2)



A mixture of **1** (0.200 g, 1.064 mmol), $Mg(OAc)_2 \cdot 4H_2O$ (0.143 g, 0.668 mmol) and lithium methoxide (0.019 g, 0.500 mmol) were refluxed in *n*-octanol (3.5 mL) for 8 h (TLC-control: Al_2O_3, C_6H_6). The reaction mixture was cooled to room temperature and a mixture MeOH:H_2O (10:1 V/V) was added. A dark green precipitate was filtered and washed with water and MeOH. This yielded **2** (0.093 g, 45%). UV–VIS (λ_{max} (THF)/nm (log ε)): 663 (4.49); 639 (3.98); 603 (3.77); 369 (4.35). ^{1}H NMR δ_H (400 MHz, $CDCl_3$:MeOH 100:1 V/V) 1.77 (m, 16H, $\beta_{1,2}$-CH_2); 2.65–2.70 (m, 16H, $\alpha_{1,2}$-CH_2). MS-MALDI-TOF *m*/*z*: 776 ($[M]^{+\cdot}$, 100%).

2.2.3. 2, 3, 8, 9, 14, 15, 20, 21-Octakis [4′,5′,6′,7′-tetrahydrobenzo] tetra-2,3-thiophenophorphyrazine zinc (3)

A mixture of **1** (0.070 g, 0.370 mmol), $Zn(OAc)_2 \cdot 4H_2O$ (0.047 g, 0.185 mmol) and lithium methoxide (0.007 g, 0.185 mmol) were refluxed in *n*-octanol (1.5 mL) for 5 h (TLC-control: Al_2O_3, C_6H_6). The reaction mixture was cooled to room temperature and a mixture MeOH:H_2O (10:1 V/V) was added. A dark green precipitate was filtered and washed with water and MeOH. This yielded **3** (0.061 g, 80%). UV–VIS (λ_{max} (THF)/nm (log ε)): 665 (4.6); 603 (3.9); 367 (4.4). ^{1}H NMR δ_H (400 MHz, Py-d_5) 2.02 (m, 8H, β_2-CH_2); 2.08 (m, 8H, β_1-CH_2); 3.11–3.16 (m, 8H, α_2-CH_2); 3.84–3.98 (m, 8H, α_1-CH_2). HRMS-MALDI-TOF/TOF *m*/*z*: $[M]^+$Calculated for $C_{40}H_{34}N_8S_4Zn$: 818.4057; found: 818.4082.

2.2.4. 2, 3, 8, 9, 14, 15, 20, 21-Octakis [4′,5′,6′,7′-tetrahydrobenzo]-25H,27H-tetra-2,3-thiophenophorphyrazine (4)

(a) Approach with concentrated sulphuric acid

The magnesium complex **2** (0.011 g, 0.014 mmol) was dissolved in concentrated sulphuric acid (3 mL). This solution was poured into the ice. At the same time the green precipitate was formed. This precipitate was filtered and washed with water and MeOH to give **4** (0.004 g, 38%). UV–VIS (λ_{max} (THF)/nm (log ε)): 699 (4.60); 655 (4.54); 352 (4.55). HRMS-MALDI-TOF/TOF: *m*/*z* $[M]^+$. Calculated for $C_{40}H_{34}N_8S_4$: 754.2912 $[M]^+$; found: 754.3190.

(b) Approach with concentrated trifluoroacetic acid

The magnesium complex **2** (0.011 g, 0.014 mmol) was dissolved in concentrated trifluoroacetic acid (3 mL). This solution was poured into the ice. At the same time the green precipitate was formed. This precipitate was filtered and washed with water and MeOH to give **4** (0.005 g, 48%). The characteristics were identical with those obtained by method (a).

(c) Approach with pyridine hydrochloride

A mixture of **3** (0.030 g, 0.0370 mmol) and pyridine hydrochloride (0.012 g, 0.10 mmol) were refluxed in pyridine (600 μL) for