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Influence of bulky pyrrolyl substitent on the physicochemical properties of porphyrazines

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ABSTRACT

The synthesis and characterization of porphyrazines possessing 2,5–diphenylpyrrol-1-yl and dimethylamino peripheral groups and their precursors are shown. Bulky pyrrolyl substituents influenced the physicochemical properties and solid-state structure of novel porphyrazines and did not hamper the formation of the porphyrazine associates in solution and solid-state. Occurrence of centrosymmetric dimers in single crystal X-ray structure of magnesium(II) porphyrazine with Mg···Mg distance of ca. 11.2 Å, impacted by interdigitation of the phenyl substituents, was noticed. In addition, an iron(II) porphyrazine derivative was investigated. The importance of Mössbauer spectroscopy in the assessment of valence and spin state of the iron ion inside the core of the iron(II) porphyrazine is shown.

1. Introduction

Porphyrazine (Pz) macrocycles, due to their special photochemical and electrochemical properties, have proved their potential for diverse medical (photosensitizers) and technological applications (catalysts, sensors). Pzs can be modified by the exchange of the metal cation inside the core or by peripheral modifications in their β positions with aliphatic, aryl, sulfur, oxygen and nitrogen residues [1–5]. Some Pzs have demonstrated a strong affinity towards metal ions, including $Fe^{2+/3+}$ [5,6]. Iron Pzs have been considered a potential catalyst in oxidation reactions [7,8]. Although, Pzs possessing β,β-substituted, fused, heterocyclic rings have been widely studied [9,10], there has been only limited data on those modified by peripheral 5-membered ring heteroaromatic group attachment. One of the examples is a two-core Pz reported by Luo et al. [11], that is substituted with trimethyl-3-thienyl groups on its periphery. The other Pzs bearing peripheral 2,5-dimethylpyrrol-1-yl, and 2,5-dithienylpyrrol-1-yl originate from our group [12–15]. Below we describe the synthesis of novel hybrid molecules that have properties beyond the sum of the Pz macrocycles and 2,5–diphenylpyrrol-1-yl fragments. These include the formation of centrosymmetric dimeric associates of magnesium(II) Pz molecules by interdigitation of their bulky substituents, as observed in the crystal. Bulky pyrrolyl substituents on the periphery of iron(II) Pz influence its physicochemical properties, which was confirmed by Mössbauer spectroscopy.

2. Experimental section

2.1. General procedures

All reactions were conducted in oven dried glassware under argon. All solvents were rotary evaporated at or below 50 °C. Reaction temperatures reported refer to external bath temperatures. Methanol, tetrahydrofurane and dichloromethane were distilled. Other solvents and all reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. Melting points were obtained on a “Stuart” Bibby apparatus

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and are uncorrected. Dry flash column chromatography was carried out on Merck silica gel 60, particle size 40–63 μm. Thin layer chromatography (TLC) was performed on silica gel Merck Kieselgel 60 F_{254} plates and visualized with UV (λ_{max} 254 or 365 nm). UV–Vis spectra were recorded on a Hitachi UV–Vis U-1900 spectrometer; λ_{max} (logε), nm. Elemental analysis and mass spectra (ES, MALDI TOF) were carried out by the Advanced Chemical Equipment and Instrumentation Facility at the Faculty of Chemistry, Adam Mickiewicz University in Poznan. HRMS (ESI) spectra were detected on a Thermo QExactive with the ESI source at the European Center of Bioinformatics and Genomics in Poznan.

2.2. Single crystal X-ray structure determination

Single, prism like yellow crystals of maleonitrile **3** and dark blue plates of magnesium porphyrazine **4a** were grown at room temperature by slow evaporation method from CH_2Cl_2/*n*-hexane (1:1) and EtOH/$CHCl_3$/*n*-PrOH (1:1:0.1) solutions, respectively. The diffraction intensity data were collected with an Oxford Diffraction Xcalibur Eos diffractometer using graphite-monochromated MoKα radiation. The structures were processed with the CrysAlis Pro software [16], solved by direct methods with SIR2004 [17], and refined by full matrix least-squares based on F^2 by SHELXL-97 [18] program. The hydrogen atoms attached to the C atoms were located at geometrically calculated positions and refined in the riding mode with isotropic temperature factors fixed at 1.2(Ueq) of the parent atoms (1.5 for methyl groups). Non-hydrogen atoms in **3** were refined anisotropically, except for the five atoms of the disordered benzene ring having minor occupancy of ca. 12% (Fig. S1, Supplementary data). Crystals of **4a** were poorly diffracting and the number of observed reflections did not allow for anisotropic refinement of non-hydrogen atoms. The highest peaks on the difference-Fourier map in the disordered part of the crystal were identified as propanol and two water solvent molecules and included in the final refinement with partial occupancy. The hydrogen atoms of the propanol O–H groups were located in electron density difference maps and their O–H distances standardized to 0.84 Å. In the final refinement cycles O–H group hydrogen atoms were treated as riding on their parent atoms with Uiso(H) = 1.2 Ueq(O). In case of water molecules, hydrogen-atom positions were not determined. A summary of the structure determination of **3** (CCDC 986312) and **4a** (CCDC 986311) is given in Supplementary data. The asymmetric unit and atom labeling scheme for **3** are shown in Figures S1, S2 (Supplementary data), and for **4a** – in Fig. S3 (Supplementary data).

2.3. NMR studies

^{1}H NMR, ^{13}C NMR spectra were recorded using a Bruker 400 and 500 spectrometers. Chemical shifts (δ) are quoted in parts per million (ppm) and are referred to a residual solvent peak. Coupling constants (*J*) are quoted in Hertz (Hz). The abbreviations s, d, h, t, and m refer to singlet, doublet, hidden, triplet, and multiplet, respectively. Chemical shifts of aggregated species of Pz **6** are signed with asterisk (*). Additional techniques (^{1}H–^{1}H COSY, HSQC, HMBC) and temperature spectra were used to assist allocation.

2.4. Mössbauer spectroscopy studies

Powder sample frozen to the temperature of liquid nitrogen was placed in a home-built cryostat at 85 K. The temperature was stabilized within 0.03 K. Mössbauer ^{57}Fe spectra were recorded using ^{57}Co(Rh)-50 mCi as a source of 14.4 keV radiation. Hyperfine parameters characterizing valence and spin states of the heme-iron in the investigated Pzs were obtained from the theoretical analysis of experimental spectra by use of Recoil software [19]. Values of isomer shifts are given relative to α-Fe at 295 K.

2.5. Synthetic procedures of 2–6

*2.5.1. 2-Amino-3-(2,5-diphenyl-1H-pyrrolyl)-(2Z)-butene-1,4-dinitrile (**2**)*

A known compound 2 was synthesized by modifying Begland's procedure [20]: The suspension of DAMN (462 mg, 4.28 mmol) (**1**), 1,2-dibenzoylethane (1.02 g, 4.82 mmol), catalytic amount of TFA (200 μL) and methanol (50 mL) was mixed under reflux for 24 h. After cooling to room temperature, the solvent was evaporated using a rotavapory vacuum evaporator to dryness and purified by column chromatography (CH_2Cl_2) to give small yellow crystals of the desired compound (1.07 g, 80% yield).

*2.5.2. 2-Dimethylamino-3-(2,5-diphenyl-1H-pyrrolyl)-(2Z)-butene-1,4-dinitrile (**3**)*

Sodium hydride (60% dispersion in mineral oil; 45 mg, 1.13 mmol) was suspended in THF (10 mL) at (−17 °C). Next 2-amino-3-(2,5-diphenyl-*1H*-pyrrolyl)-(2Z)-butene-1,4-dinitrile (**2**) (160 mg, 0.52 mmol) in THF (2 mL) was added and stirred 30 min at temperature (−15 °C). After that $(CH_3O)_2SO_2$ (99 μL, 1.04 mmol) was added dropwise to the reaction mixture for 30 min at (−10 °C) and stirred at room temperature for 20 h. The reaction was carefully quenched by adding water (2 mL) and the reaction mixture was poured into ice-water mixture (100 mL). The resulting yellow precipitate was isolated by filtration to give **3** (160 mg, 91% yield). The crude material was crystalized (CH_2Cl_2-*n*-hexane) to give light yellow crystals: mp 105–107 °C. R_f (CH_2Cl_2) 0.65. UV–Vis (CH_2Cl_2): λ_{max}, nm (logε) 300 (4.39). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H, ppm 2.49 (s, 6H, $N(CH_3)_2$), 6.41 (s, 2H, pyrrole-H), 7.38 (t, ^3J = 8 Hz, 2H, C_6H_5), 7.46 (t, ^3J = 8 Hz, 4H, C_6H_5), 7.52–7.55 (m, 4H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C, ppm 41.00 ($N(CH_3)_2$), 91.79, 111.05, 112.19, 118.61, 128.10, 128.42, 128.92, 131.91, 138.75. MS (ES neg): *m/z* 323 $[M-CH_3]^-$. MS (ES pos) 339 $[M+H]^+$, 361 $[M+Na]^+$, 378 $[M+K]^+$. Anal. Calc. for $C_{22}H_{18}N_4$: C, 78.08%; H, 5.36%; N, 16.56%. Found: C, 78.04%; H, 5.44%; N, 16.73%.

*2.5.3. [2,7,12,17-Tetrakis(dimethylamino)-3,8,13,18-tetrakis(2,5-diphenyl-1H-pyrrolyl)-porphyrazinato]magnesium(II) (**4a**) and [2,7,12,18-tetrakis(dimethylamino)-3,8,13,17-tetrakis(2,5-diphenyl-1H-pyrrolyl)porphyrazinato]magnesium(II) (**4b**)*

Mg turnings (53 mg, 2.16 mmol), a crystal of I_2, and 1-butanol (25 mL) were heated under reflux for 6 h. After the mixture was cooled to room temperature, maleonitrile derivative **3** (491 mg, 1.44 mmol) was added to the reaction mixture and heated under reflux for 20 h. After cooling to room temperature, the dark green mixture was filtered through Celite and evaporated. Chromatography (CH_2Cl_2:CH_3OH, 50:1; *n*-hexane:EtOAc, 7:3; *n*-hexane:CH_2Cl_2:CH_3OH, 7:1:1) was performed to give two products: **4a** (90 mg, 18% yield) as a dark green solid: mp > 300 °C. R_f (*n*-hexane:EtOAc 7:5) 0.83, UV–Vis (CH_2Cl_2): λ_{max}, nm (logε) 302 (3.74), 730 (3.48), 817 (2.96). ^{1}H NMR (400 MHz; pyridine-d_5): δ_H, ppm 3.26 (s, 24H, $N(CH_3)_2$), 6.73 (t, ^3J = 8 Hz, 16H, C_6H_5), 6.92 (t, ^3J = 8 Hz, 8H, C_6H_5), 7.01 (s, 8H, pyrrole-H), 7.48 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 16H, C_6H_5); ^{13}C NMR (100 MHz; pyridine-d_5): δ_C, ppm 42.67 ($N(CH_3)_2$), 110.46, 113.59, 126.68, 128.50, 128.50, 135.11, 140.03, 140.03, 150.35 h, 154.70. MS (MALDI TOF): *m/z* 1378 $[M+H]^+$. HRMS (ESI) Found: $[M+H]^+$ 1377.6078 $C_{88}H_{73}N_{16}Mg$ requires $[M+H]^+$ 1377.6054. **4b** (4 mg, 0.8% yield): mp > 300 °C. R_f (*n*-hexane:EtOAc 7:5) 0.83, (CH_2Cl_2:CH_3OH 50:1) 0.11. UV–Vis (CH_2Cl_2): λ_{max}, nm (logε) 292 (3.98), 342 (3.56), 522 (2.76), 691 (3.49). ^{1}H NMR (400 MHz; pyridine-d_5): δ_H, ppm 3.06 (s), 3.26 (s), 3.30 (s), 3.34 (s), 6.62–6.68 (m), 6.68–6.75 (m), 6.76–6.83 (m), 6.86 (s), 6.90–6.94