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Synthesis, characteristics and photochemical studies of novel porphyrazines possessing peripheral 2,5-dimethylpyrrol-1-yl and dimethylamino groups

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This Letter is dedicated to Professor Anthony G. M. Barrett on the occasion of his 60th birthday and for his contributions to porphyrazine chemistry.

Keywords: Linstead macrocyclization Porphyrazine Singlet oxygen Photochemistry X-ray

$A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

The synthesis and physicochemical properties of novel porphyrazines possessing an alternate system of two peripheral substituents, 2,5-dimethylpyrrol-1-yl and dimethylamino, are presented. All the macrocycles were subjected to HPLC purity studies. Spectroscopic studies of magnesium(II) porphyrazine encompassed steady state absorption, emission measurements, including fluorescence decays, transient absorption spectra, and thermoluminescence. Additionally, magnesium(II) porphyrazine was found to be a moderate photosensitizer with singlet oxygen generation values of 0.12 and 0.14 in DMF and DMSO, respectively. Comparison of the quantum yields of singlet oxygen generation before and after deoxygenation showed that the photodynamic effect of magnesium(II) porphyrazine is governed by the photosensitization mechanism II. Magnesium(II) and manganese(III) porphyrazines were characterized using X-ray crystallography.

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Porphyrazines (Pzs) form a distinct class of macrocycles, along with the functionalized porphyrins, phthalocyanines and corroles. Pzs can be modified by the introduction of a metal cation into the core and/or by peripheral substitutions. For the last 30 years, Pzs substituted at their β -positions with nitrogen, oxygen or sulfur residues, or rings bound to both β , β -positions have been synthesized and subjected to physicochemical as well as biological studies.¹⁻⁹ Novel porphyrazine-based macrocyclic systems have been investigated as photosensitizers for biomedical (photodynamic therapy),¹⁰ analytical applications (metal ion probes),¹¹⁻¹³ and as compounds of potential use in materials chemistry (nanotechnology, electrophotography, optical data recording systems, electronic devices, photovoltaic cells, fuel cells, and electrochromic displays).¹⁴⁻¹⁷

Donzello, Ercolani and Stuzhin first synthesized Pzs possessing peripherally annulated five-membered heteroarene rings (4,5-thiazole, 2,3-thiophene, 1,2,5-selenodiazole), and showed their broad applications.³ A synthetic approach to use 1,2,5-selenodiazole rings fused to the Pz core as synthetic precursors was later developed by Barrett and Hoffman.^{2,5,14} There are limited data on Pzs substituted directly at their β -position with five-membered heteroaromatic rings. One example, a two-core porphyrazine system, possessing 12 trimethylthienyl groups on the periphery, synthesized by Luo et al.,¹⁸ has been considered as a compound of potential use in information storage systems and molecular switches.

Begland et al. found that 2,5-hexanedione on reaction with diaminomaleonitrile undergoes the Paal–Knorr reaction to give 2,5-dimethylpyrrol-1-yl-functionalized maleonitrile.¹⁹ Our study on the reactivity of its derivative possessing methyl(3-pyridyl-methyl)amino and 2,5-dimethylpyrrol-1-yl groups, in macrocyclization reactions led to novel Pzs, which were found to contain a peripheral alternate set of 2,5-dimethylpyrrol-1-yl and methyl(3-pyridylmethyl)amino groups. These novel Pzs exhibited interesting optical, electrochemical and metal-sensor properties.²⁰ In the course of this research, we recently reported syntheses and discussed the physicochemical properties of novel Pzs possessing



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a peripheral non-alternate system of two 2,5-di(2-thienyl)pyrrol-1-yl and dimethylamino substituents.²¹

In the present Letter we report the synthesis, characterization and photochemical properties of novel Pzs possessing peripheral 2,5-dimethylpyrrol-1-yl and dimethylamino groups.

2,5-Hexanedione was subjected to the condensation reaction with diaminomaleonitrile (**1**) in benzene with oxalic acid to give maleonitrile derivative **2** following Begland's procedure.¹⁹ Next, **2** was methylated to give derivative **3** using the conditions [NaH, $(CH_3)_2SO_4$ in THF] reported by Baum et al. (Scheme 1).²²

Derivative **3** was used in the Linstead macrocyclization with $Mg(n-BuO)_2$ in *n*-butanol to give novel porphyrazine **4**, possessing an alternate system of peripheral substituents, in 25% overall yield.^{2,23} Pz **4** was carefully purified by column chromatography and further analyzed using HPLC. Interestingly, other isomers as observed in our previous studies, possessing non-alternate systems of peripheral substituents, were not detected by TLC.^{20,21} Demetallation of 4 was performed in trifluoroacetic acid (TFA) using a standard procedure^{2,21} which led to novel free base porphyrazine **5**, and other demetallated side-products. Difficulties in separating 5 from the side-products prompted us to use another macrocyclization method on 3. The macrocyclization of 3 in dimethylaminoethanol (DMAE) was found to be superior to that in *n*-pentanol with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base, mainly due to the short reaction time (2 h) and lack of side-products.^{24,25} Moreover, this free base Pz 5 was isolated in a moderate yield of 35%.

Maleonitrile **3** was also used in macrocyclization reactions in *n*-pentanol with DBU and various metal salts: $Zn(OAc)_2$, $MnCl_2 \times 4H_2O$, and $CuCl_2$ to give novel metallated porphyrazines **6–8**. Only in the macrocyclization reaction leading to copper porphyrazine **8** was an additional isomeric side-product, characterized by UV–vis, FT IR and MS, found (see Supplementary data). Porphyrazines **4–6** and **8** were found to be pure according to HPLC analyses (see Supplementary data). Unfortunately, porphyrazine **7** presented separation problems. Magnesium, free base and zinc porphyrazines **4–6** were analyzed using various NMR techniques (see Supplementary data).

Additionally, porphyrazines **4** and **7** were subjected to crystallization that fortunately resulted in single crystals suitable for X-ray analyses. In magnesium(II) Pzs **4a** and **4b** the asymmetric unit consists of the [Pz·Mg·H₂O] complex and solvent molecules, two ethanol molecules in **4a** and pyridine in **4b** (see Supplementary data). The coordination geometry of the magnesium center is square-pyramidal as expected, the Mg ion being bonded to the porphyrazine core, and one water molecule located in the apical position (Fig. 1a and b). The Mg cation is displaced from the best plane of the Pz core by 0.716(1) Å in 4a and by 0.586(2) Å in 4b. The Mg-N(Pz) distance ranges are 2.035(3)-2.049(2) and 2.025(4)–2.039(4) Å in **4a** and **4b**, respectively. The Mg–O bond is significantly shorter in **4a** [1.970(2)Å] than in **4b** [2.038(4)Å] (see Supplementary data). In manganese(III) Pz 7 the metal ion is located in the plane of the Pz core and has distorted octahedral geometry with the chloride ion and ethanol molecule placed at axial positions (Fig. 1c). The Mn–N(Pz) distances are within the range 1.936(2)-1.950(2) Å and the Mn-Cl and Mn-O bonds are 2.5147(8) and 2.409(2) Å. respectively.

In compounds **4a**, **4b** and **7** the orientation of the peripheral substituents at the β_{β} -positions is similar. The outer pyrrole rings are almost perpendicular to the porphyrazine core formed by 24 atoms, whereas the dihedral angle of the dimethylamino fragments with the macrocyclic platform is 10°-30°, except for the dimethylamino group of the unit C in 4a where this angle is 48.8(2)°. This amine N-atom acts as a hydrogen bond acceptor (see Supplementary data) from one of the ethanol molecules and is pyramidal (the sum of the bond angles around the N atom is 342.1°), in contrast to the other amine nitrogen atoms where the sum of the bond angles is closer to 360° which indicates their sp² hybridization. An average C_{Pz}-N_{amine} distance for sp²-hybridized N atoms is 1.360(5)Å (the range of 1.355(4)-1.371(4) Å, 1.339(6)–1.372(6) Å and 1.344(4)–1.365(4) Å for 4a, 4b and 7, respectively) indicating some degree of conjugation of the amine lone pair with the π system of Pz. The Pz molecules in **4a** and **7** associate to form back-to-face stacks with coordinated and solvent molecules located between adjacent Pz macrocycles. In 4b the porphyrazine platforms form edge-to-edge zig-zag chains with pyridine molecules H-bonded to the coordinated water molecules (see Supplementary data).

The absorption spectrum of 4 (Fig. 2a) has a structure typical of porphyrinoids, and consists of two bands: the Q band, between 600 and 800 nm, and the Soret band, between 300 and 400 nm.



Scheme 1. Reagents and conditions: (i) 2,5-Hexanedione, benzene, oxalic acid, reflux, 10 h; (ii) NaH, (CH₃)₂SO₄, THF, -15 °C to rt, 2.5 h; (iii) Mg(*n*-BuO)₂, *n*-BuOH, reflux, 20 h; (iv) TFA, 20 min, rt; (v) metal salt, DBU, *n*-pentanol, reflux, 24 h; (vi) DMAE, reflux, 2 h; TFA-trifluoroacetic acid, DMAE-dimethylaminoethanol, DBU-1,8-diazabicyclo[5.4.0]undec-7-ene.



Figure 1. The crystal structures of **4a**, **4b** and **7** showing the metal coordination and solvent molecules connected by $O-H\cdots O$ and $O-H\cdots N$ hydrogen bonds (dashed lines). H atoms are omitted for clarity except those involved in H-bonds. Only the major (84%) occupancy of the disordered fragment in **4b** has been shown. The atom labeling scheme is the same for the A, B, C and D units of the porphyrazine macrocycles in **4a**, **4b** and **7**.

Fluorescence is observed for wavelengths longer than 700 nm and its spectrum does not depend on the excitation wavelength in the range 290–670 nm. Therefore, it can be assumed that the observed emission originates exclusively from the first excited singlet state, S₁.

The fluorescence spectrum has mirror-image symmetry with respect to the absorption spectrum. The Stokes shift in DMF, $(480 \pm 50) \text{ cm}^{-1}$ is small, as expected for a molecule without a permanent dipole moment. The fluorescence decay (Fig. 2b) is



Figure 2. (a) Steady-state absorption (dashed) and fluorescence (solid line) spectra of **4** in DMF, (b) fluorescence decay shown together with the time-correlated single photon-counting (TCSPC) instrument response function (IRF) in DMF, (c) selected transient absorption spectra recorded with 400 nm excitation of **4** in DMF, and (d) thermoluminescence spectrum of **4** illuminated with a single flash in THF.

monoexponential with the decay time being equal to $\tau_{FI} = 3.36 \pm 0.01$ ns. Figure 2c presents selected transient absorption spectra of **4** in DMF recorded for the excitation in the Soret band, at 400 nm. Only two bands can be clearly distinguished: a broad excited state absorption (ESA) for wavelengths shorter than 600 nm and a strong negative band for longer wavelengths due to overlapped bleaching and stimulated emission.

Transient absorption decays in time at all wavelengths within the spectral window of the experiment. The data have been fitted globally using the matrix reconstruction algorithm²⁶ (see Supplementary data), and two decay times turned out to be necessary to fit the temporal evolution of the spectra. The first decay time, $\tau_1 = 8.8 \pm 1.0$ ps, corresponds to rapid initial decay, whereas the second, $\tau_2 = 3.4 \pm 1.0$ ns, is the excited state lifetime equal to the fluorescence decay time τ_{Fl} . A constant component is required to fit the data satisfactorily, which means that a fraction of molecules in the excited singlet state undergo intersystem crossing and populate the lowest triplet state. The triplet state lifetime is much longer than the temporal window of the experiment. Therefore, its decay cannot be observed.

Additional transient absorption measurements were carried out in order to identify the nature of the process behind τ_1 , in particular to test whether this process is related to the internal conversion of the molecule from higher electronic excited states into S₁. It turned out, however, that the rapid decay was still present in transient absorption data even after direct excitation to the S₁ state without excess energy, at 700 nm. Both, the amplitude and the time constant of this decay, 6.2 ± 1.0 ps, are practically the same as that after the excitation at 400 nm (see Supplementary data). It can therefore be excluded that this process is related to the internal conversion. The lack of significant differences between the spectral dynamics recorded after the excitation in the O and Soret bands means that the internal conversion for the excitation at 400 nm is completed within a time shorter or comparable to the temporal resolution of the experimental set-up (300 fs). Thus, the process corresponding to τ_1 occurs in the lowest excited singlet state and is most likely related to energy redistribution through solute-solvent interactions.

Thermoluminescence (TL) is a weak light emission stimulated by warming of irradiated samples. Photochemically separated charge pairs recombine due to increased temperature and enhanced vibrational energy which allows activation energy barriers to be overcome. TL spectra obtained for porphyrazine **4** in THF exposed to a single flash show two TL bands at about 42 °C and 106 °C (Fig. 2d). These bands can be ascribed to two different types of charge pairs as they are not observed without previous illumination. Further experiments are planned to elucidate their origin.

The singlet oxygen quantum yield determination is crucial for the potential application of novel photosensitizers in photodynamic therapy. The potential photosensitizing activity of novel magnesium(II) porphyrazine **4** was evaluated by measuring its ability for singlet oxygen production, which is the result of interaction between the activated photosensitizer and oxygen. 1,3-Diphenylisobenzofuran (DPBF) was used as a chemical quencher which undergoes a cycloaddition reaction with singlet oxygen to produce an endoperoxide.²⁷ Measurements were assessed before and after deoxygenation by comparing with a reference zinc(II) phthalocyanine (ZnPc). According to these results, **4** was found to be a moderate photosensitizer with singlet oxygen generation values of 0.12 and 0.14 in DMF and DMSO, respectively (Fig. 3). Comparison of the quantum yields of singlet oxygen generation

0.8

0.6

0.4

0.2

Absorbance



In conclusion, the synthesis of novel porphyrazines possessing a peripheral alternate system of 2,5-dimethylpyrrol-1-yl and dimethylamino substituents on the periphery has been described. Broad physicochemical, especially photochemical studies performed on magnesium(II) porphyrazine as a representative revealed its interesting optical properties. In addition, other porphyrazine analogues, such as demetallated Pz, zinc(II), copper(II) and manganese(III) Pzs were obtained. Zinc(II), magnesium(II) and demetallated porphyrazines were characterized using various NMR techniques. Moreover, the magnesium(II) and manganese(III) porphyrazines were characterized using X-ray crystallography. All the macrocycles were subjected to HPLC purity analyses. Spectroscopic studies performed on magnesium(II) porphyrazine encompassed steady state absorption and emission measurements. Its photophysical properties were typical of a molecule with a small or vanishing dipole moment. Steady-state absorption and emission spectra possess mirror-image symmetry and only emission from the lowest excited singlet state S₁ was observed, regardless of the excitation wavelength. Femtosecond transient absorption studies revealed an ultrafast process most likely related to energy redistribution in the S₁ state, but no evidence of internal conversion from higher excited states was found for pump-probe delay times longer than 300 fs. Interestingly, a single flash resulted in the appearance of two bands in the thermoluminescence spectrum. Most probably, they are related to recombination of two different charge pairs. Also, magnesium(II) porphyrazine was found to be a moderate photosensitizer with singlet oxygen generation values of 0.12 and 0.14 in DMF and DMSO, respectively. Comparison of the quantum yields of singlet oxygen generation before and after deoxygenation has provided evidence for the fact that the photodynamic effect of magnesium(II) porphyrazine was governed by photosensitization mechanism II.

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Supplementary data

The supplementary crystallographic data for **4a**, **4b** and **7** (CCDC 854143, 854144 and 854145, respectively) can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.³⁰

Supplementary data (the experimental details, synthetic, spectroscopic data and X-ray data (for **4** and **7**)) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2012.02.010. These data include MOL files and InChiKeys of the most important compounds described in this article.



λ = 417

0 s

540s

2044

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