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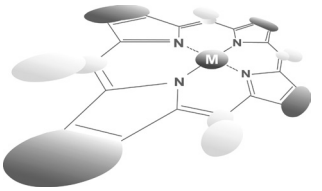

Porphyrazines with annulated diazepine rings. 4. Synthesis and properties of Mg^{II} tetradiazepinoporphyrazine carrying exocyclic styryl fragments

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Dedicated to Professor Tebello Nyokong on the occasion of her 60th birthday

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ABSTRACT: A novel tetradiazepinoporphyrazine Mg^{II} complex bearing eight peripheral styryl substituents, [St_8TDzPAMg(H_2O)] (St = -CH=CHAr, where Ar = 4-methoxyphenyl) was prepared by template cyclotetramerization of the corresponding precursor — 5,7-distyryl substituted diazepino-2,3-dicarbonitrile — in the presence of Mg^{II} butoxide in n-butanol. UV-visible and ^{1}H NMR spectral data indicate that the complex is strongly aggregated in non-coordinating solvents (dichloromethane, chloroform, benzene), it is dimeric in pyridine, whereas it is predominantly monomeric in dimethylsulfoxide and dimethylformamide. The fluorescence response is high for solutions in which the monomeric form is prevalent, but it is strongly quenched as the content of the dimer is increased. Evidence was obtained that dimerization occurs due to intermolecular hydrogen bonding between acidic CH_2 groups in the diazepine ring (6*H* form) of one molecule with *meso*- and/or diazepine N atoms of another molecule, dimerization being also contributed by the presence of chlatrated water. In the presence of fluoride anions the dimer is destroyed with formation of the monomeric species, which is changed to the 1H form upon heating, as indicated by ^{1}H NMR spectra.

KEYWORDS: porphyrinoids, stylbenoids, tetradiazepinoporphyrazines, dimerization, electronic absorption and emission spectra.

INTRODUCTION

Peripheral substituents in phthalocyanines (Pc) and related macrocyclic complexes, as well as solvation effects have a strong influence on their spectral, photochemical and photophysical properties [1]. Phthalocyanines bearing eight peripheral stylbenoid π-chromophores were synthesized [2] and are actively investigated as artificial light-harvesting systems [3] in which the excitation of eight peripheral stylbene moieties in the near UV region can be effectively transferred to the central π-chromophore followed by light emission close to the near IR region. Tetrapyrazinoporphyrazines carrying exocyclic styryl fragments were recently also prepared and their spectral and electrochemical properties investigated [4–6]. In our studies of symmetrical tetradiazepinoporphyrazines (TTDzPA) [7] and low-symmetry monodiazepinotribenzoporphyrazines [8] it was observed that the presence of non-planar quasi-aromatic 1,4-diazepine ring(s) annulated to the central pyrrole rings has remarkable effects on the physico-chemical properties of the central porphyrazine macrocycle. Very recently, evidence was obtained [9] that tetradiazepinoporphyrazines exhibit a tendency to form stable dimers with strong exciton coupling between

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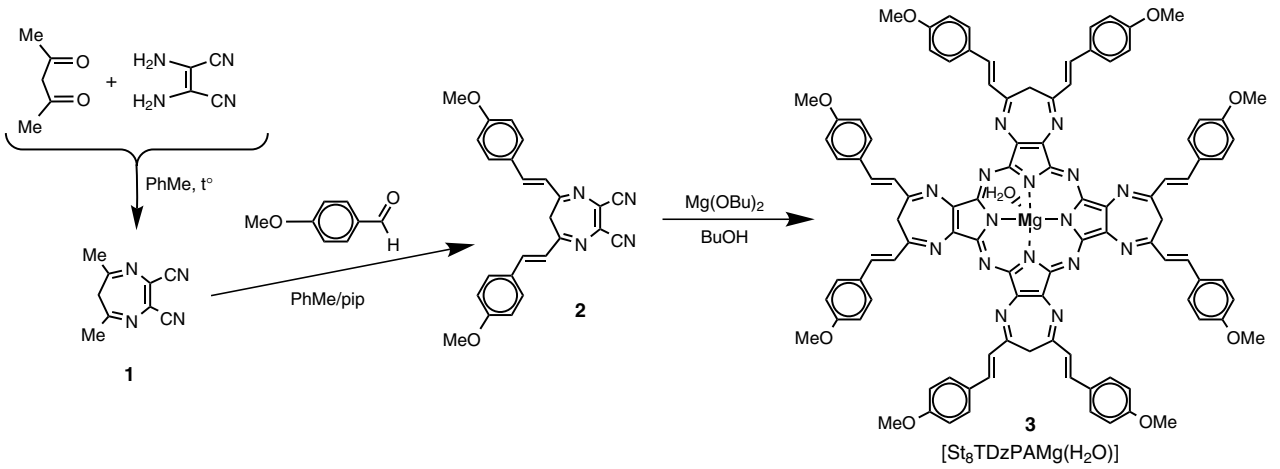

Scheme 1. Synthesis of the styryl substituted tetradiazepinoporphyrazine Mg^{II} complex [St_8TDzPAMg(H_2O)]

two porphyrazine π-chromophores, comparable with that observed in sandwich or dimeric phthalocyanine complexes [10]. Styryl substituted diazepines exhibit fluorescence with large Stokes shift and can be used as fluorescent dyes [11] or red dopants in organic electroluminescence devices [12]. It was thought that connection of the central π-chromophoric system of a porphyrazine macrocycle with peripheral styryl substituted diazepine fragments might lead to peculiar optical properties. Following a preliminary communication [13], it is reported here in detail on the synthesis and physicochemical characterization of the octastyryl substituted Mg^{II}-tetradiazepinoporphyrazine [St_8TDzPAMg(H_2O)] (St = 4-MeOPhCH=CH-, see Scheme 1). The synthesis of low-symmetry and symmetrical Mg^{II}-porphyrazines containing styryl substituted diazepine ring(s) has been also quite recently reported [14] and variations observed in the electronic absorption spectra in different solvents were connected with solvatochromic effects. Based on our electronic absorption and emission and ^{1}H NMR spectral measurements, the present work provides enough information that the spectral properties of the styryl stubstituted Mg^{II}-tetradiazepinoporphyrazines clearly depend on their tendency to dimerization, a monomer/dimer equilibrium which is very sensitive to the presence of water and other ligands in the solvents.

EXPERIMENTAL

Solvents and reagents

Solvents and chemicals were used as purchased. Pyridine was made anhydrous by distillation over KOH. 5,7-dimethyl-6*H*-1,4-diazepine-2,3-dicarbonitrile (**1**) was prepared by condensation of diaminomaleodinitrile and acetylacetone following the reported procedure [15].

Synthetic procedures

5,7-Di[(*E*)-2-(4-methoxyphenyl)ethenyl]-6*H*-1,4-diazepine-2,3-dicarbonitrile (2). A mixture of 5,7-dimethyl-6*H*-1,4-diazepine-2,3-dicarbonitrile (**1**) (1.7 g, 10 mmol), 4-methoxybenzaldehyde (2.8 g, 20 mmol), toluene (40 mL) and piperidine (5 drops) was refluxed with stirring for 6 h in a round-bottomed flask equipped with a Dean-Stark attachment. During the reaction, the color of the mixture slowly turned to orange-red. After cooling and filtration of the mixture, the bright-orange solid was washed with chloroform and combined with the residue obtained from the chloroform solution after chromatographic purification on silica (**2**; total amount: 3.5 g; yield 85%, mp = 267 °C). Anal. calcd. for $C_{25}H_{20}N_4O_2$ (408.45): C, 73.51; H, 4.94; N, 13.72%. Found: C. 73.75; H, 5.04; N, 13.66%. ^{1}H NMR (500 MHz; DMSO-d_6; Me_4Si): δ_H, ppm 8.042 (2H, d, ^3J = 16.5 Hz, -C*H*=CH-), 7.746 (4H, d, ^3J = 8.5 Hz, Ar*H*), 7.002 (4H, d, ^3J = 8.5 Hz, Ar*H*), 6.994 (2H, d, ^3J = 16.5 Hz, -C*H*=CH-), 5.34 (1H, br, *eq*-CH_2), 3.793 (6H, s, OCH_3), 2.02 (1H, br, *ax*-CH_2). IR (KBr): ν, cm^{-1} 2222w, 1599s, 1516s, 1304w, 1257s, 1173s, 978w, 827w, 771s. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 357 (4.77), 436 (4.40).

Tetrakis-2,3-{5,7-di[(*E*)-2-(4-methoxyphenyl)-ethenyl]-6*H*-1,4-diazepino}porphyrazinato(aquo)-magnesium(II), [St_8TDzPAMg(H_2O)]·4H_2O (3). Metallic magnesium (100 mg, 4 mmol) was refluxed with stirring in n-butanol (50 mL) in the presence of a few crystals of iodine until complete formation of $Mg(OBu)_2$. After addition of dicarbonitrile **2** (0.5 g, 1.2 mmol), the reaction mixture was kept boiling for further 18 h. After cooling, the solvent was evaporated and the residue was washed with water acidified with acetic acid, then with water, methanol and diethyl ether and brought to constant weight under vacuum (yield 0.44 g; 87%). Anal. calcd. for $C_{100}H_{82}MgN_{16}O_9$·4H_2O: C, 68.70; H, 5.19; N, 12.82%. Found: C, 68.55; H, 5.25; N, 12.80%. MS (MALDI-TOF): *m/z* 1659 (100%, $[M + H]^+$), 1681 (16%, $[M + Na]^+$), 1697 (8%, $[M + K]^+$), 3318 (5%, $[M_2 + 2H]^+$), 3340 (5%,

$[M_2 + H + Na]^+$). ^{1}H NMR (500 MHz, DMSO-d_6, 393 K, Me_4Si): δ_H, ppm 8.038 (8H, d, ^3J = 16.5 Hz, -C*H*=CH-), 7.671 (16H, d, ^3J = 7.9 Hz, Ar*H*), 6.993 (16H, d, ^3J = 7.9 Hz, Ar*H*), 7.545 (8H, d, ^3J = 16.5 Hz, -C*H*=CH-), 5.692 (4H, d, ^2J = 12.2 Hz, *eq*-CH_2), 4.916 (4H, d, ^2J = 12.2 Hz, *eq*-CH_2), 3.898 (24H, s, OCH_3). IR (KBr): ν, cm^{-1} 1602s, 1513s, 1462w, 1252s, 1174s, 1114w, 1031m, 967w, 824w. UV-vis (CH_2Cl_2 + 2.5% pyridine): λ_{max}, nm (log ε) 379 (4.85), 415 (4.85), 670 (4.46), 702 (4.44).

Spectral measurements

Infrared spectra were taken on the IR-spectrometer AVATAR 360 FT-IR using KBr pellets. UV-vis spectra were recorded using a Hitachi U-2000 instrument and ^{1}H NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer. Elemental analyses were performed on a CHN analyser Flash EA 1112. Mass-spectrometric measurements were carried out on a MALDI-TOF Bruker Ultraflex spectrometer. The fluorescence emission and excitation spectra were recorded on a Fluorescence Spectrophotometer (Cary Eclipse, Varian). For the emission measurements, the excitation wavelength was set at 400 nm or 630 nm, and fluorescence was recorded up to 900 nm. For the excitation spectra, the emission was observed at 740 nm. Both in emission (λ_{exc} = 400 nm) and in fluorescence excitation measurements, an internal emission filter which cut off radiations below 430 nm was used.

RESULTS AND DISCUSSION

Synthesis and characterization

The precursors for the template synthesis of styryl substituted diazepinoporphyrazines, *i.e.* 1,4-diazepine-2,3-dicarbonitriles carrying styryl groups at the 5,7-positions, can be conveniently prepared from 5,7-dimethyl-1,4-6*H*-diazepine-2,3-dicarbonitrile (**1**) [11], in which the CH-acidity of methyl groups is high enough to allow the easy condensation with aryl-aldehydes having electron-donating substituents. Previously [11b], 4-methoxystyryl substituted 1,4-6*H*-diazepine-2,3-dicarbonitrile (**2**) was prepared with 10% yield by condensation of **1** with 4-methoxybenzaldehyde in benzene in the presence of catalytic amounts of piperidine. The use of toluene instead of benzene (Scheme 1) allowed us to conduct the reaction at higher temperature and the yield of **2** was increased to 85%. The bis-styryl substituted dinitrile **2**, similarly to procedures with other diazepine-2,3-dicarbonitriles [7a, 9], can be cyclotetramerised under Linstead conditions (magnesium butoxide in refluxing n-butanol) to afford the Mg^{II} complex of the corresponding styryl substituted tetradiazepinoporphyrazine **3**. This complex shows in MALDI-TOF mass-spectrum an intense molecular ion peak $[M + H]^+$ at *m/z* = 1659 (Fig. 1). Remarkably, an additional lower intensity peak, corresponding to the molecular ion of the dimeric species, is also seen. According to elemental analyses, complex **3** was isolated as a hydrated compound, formulated as $[St_8TDzPAMg(H_2O)]\cdot 4H_2O$, in which one water molecule is assumed to be directly bound to Mg^{II}. The presence of the $Mg^{II}(H_2O)$ moiety is typical for Mg^{II} complexes of porphyrazines as was established by single-crystal X-ray work on Mg^{II} phthalocyanine [16] and observed also for other Mg^{II} porphyrazines [5,17]. The presence of additional water molecules, variable from batch to batch, is also typical for other tetradiazepinoporphyrazines [7, 9] and can be related to the hydrogen bonding abilities of diazepine and/or *meso*-nitrogen atoms.

UV-vis spectra

The UV-vis spectra in different solvents of the Mg^{II} complex **3** and the related *tert*-butylphenyl substituted complex $[(^tBuPh)_8TDzPAMg(H_2O)]$ (**4**) [9] are shown for comparison in Fig. 2. As exemplified in Fig. 2a, the spectrum of **3** in CH_2Cl_2 (dashed line), and other non-coordinating solvents ($CHCl_3$, benzene), shows the presence of a low-intensity broad featureless absorption in the *Q*-band region (600–800 nm) which is indicative of the occurrence of strong aggregation. As can be seen, the spectrum in CH_2Cl_2 containing pyridine (*ca*. 2%) or in 100% pyridine (Figs. 2a and 2b, respectively; solid lines) is better resolved and shows two peaks in the same region with maxima at *ca*. 670 and 702–705 nm. In going from pyridine to DMSO (Fig. 2c, solid line) the absorption at 670 nm is decreased and practically disappears in DMF (Fig. 2d, solid line), in which the spectrum shows the

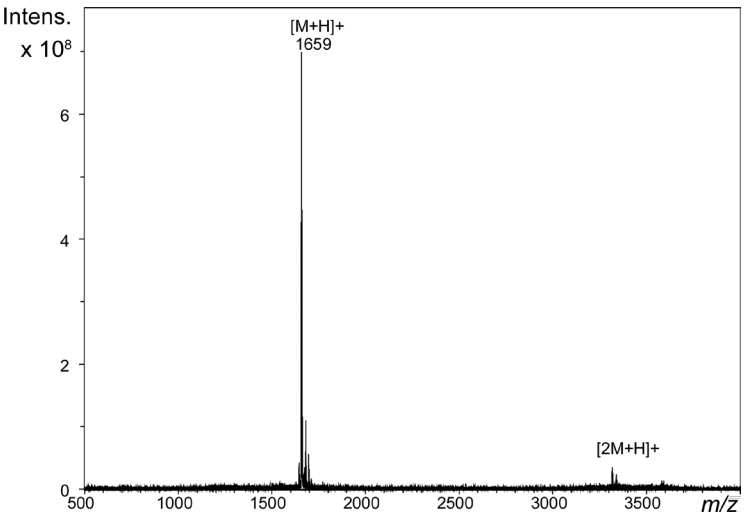

Fig. 1. MALDI-TOF mass-spectrum of styryl substituted tetradiazepinoporphyrazine **3**

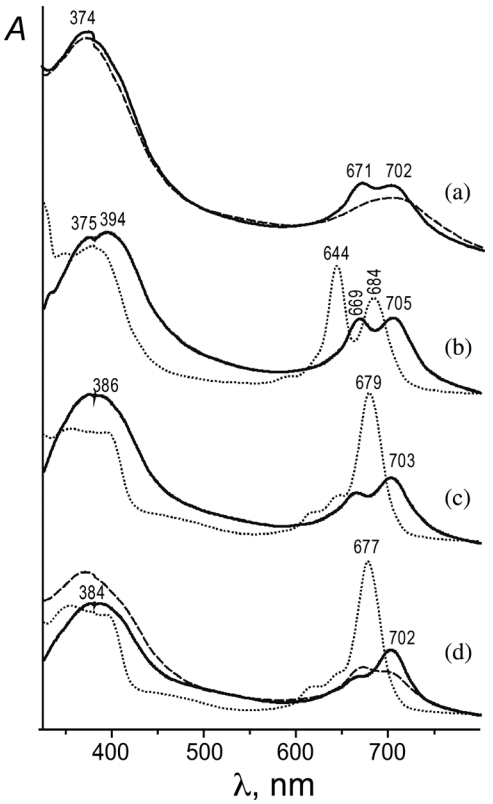

Fig. 2. UV-vis spectra of Mg^{II} complex of styryl substituted tetradiazepinoporphyrazine **3**: (a) aggregated form in CH_2Cl_2 (dashed line) and spectral change after addition of ca 2% pyridine (solid line), (b) in pyridine, (c) in DMSO, (d) in DMF (solid line), after addition of 2% water (dashed line). Spectra of *tert*-butylphenyl substituted complex [(^{t}BuPh)$_8$TDzPAMg(H_2O)] in corresponding solvents are shown by dotted lines. Adapted from Ref. [9]

single *Q*-band at 702 nm accompanied by vibrational shoulders on its higher energy side. Dotted lines in Figs. 2b, 2c, 2d indicate a parallel solvent dependence observed recently [9] for the *tert*-butylphenyl substituted complex **4** in that the spectrum goes from the presence of two well-separated absorptions with maxima at 644 and 684 nm in pyridine to a single narrow intense absorption at 677–679 nm in DMSO and DMF.

The spectra with a single *Q*-band observed in DMF are typical for monomeric metal complexes of symmetrical porphyrazines and can be definitely assigned as belonging to the usual monomeric form of complexes **3** and **4**. The spectra with a double *Q*-band were first observed for complexes of phenyl substituted tetradiazepinoporphyrazine and suggestion was made that the less-intense long-wave component might arise from n-π* transition involving lone pairs of the diazepine nitrogens [7]. However, in our recent study [9] clear evidence was obtained that the parent spectrum seen in pyridine solution for **4** (Fig. 2b, dotted line), displayed identical also in CH_2Cl_2, benzene, THF, or acetone, belongs to a stable dimeric form of the complex **4**. The splitting of the *Q*-band originates from the exciton coupling between two neighboring π-chromophores constituting the dimeric unit, similarly to sandwich and dimeric phthalocyanine and porphyrazine complexes [10]. This encourages the same assignment for the double peaked spectrum of **3**.

It should be noted that water-soluble tetrasulfonated phthalocyanines [18] and quaternized octapyridyl substituted tetrapyrazinoporphyrazines [19] show a similar double-peaked *Q*-band absorption due to essential dimerization in water solution. However, dimerization of these species is easily suppressed upon dilution of water solutions, and they exist exclusively in the monomeric form with a single *Q*-band not only in DMSO, but also in pyridine solution. In contrast to that, the dimeric form of **3** is more stable; it exhibits a double *Q*-band and obey the Lambert–Bouger–Baehr law in CH_2Cl_2 containing pyridine (> 2.5%) and in pure pyridine when explored in the 0.005–0.05 mM concentration range.

As can be seen in Fig. 2, the *Q*-band maxima for complex **3** are shifted bathochromically by 20–25 nm as compared to those of complex **4**. This is indicative that styryl substituents in **3** exhibit stronger electron-donor effect on the diazepine rings than the ^{t}BuPh groups in **4**. The minimal residual molecular aggregation can not explain the observed broadness of the *Q*-band absorptions for **3**. Such a broadening, however, might be contributed by the presence in the macrocycle **3** of conformational isomers having different orientation of the styryl fragments in respect to the diazepine rings (*e.g.* with *cisoid* and *transoid* –N=C···CH=CH- fragments). Indeed, the presence of two conformations of styryl groups was observed in the X-ray crystal structure of bis(4-diethylaminostyryl)substituted 1,4-diazepine-2,3-dicarbonitrile [11b]. We have also observed that the profile of the spectra of **3** taken in pyridine, DMSO and DMF may partly depend on the amount of water present. The component in the *Q*-band area at *ca.* 700 nm shows higher intensity in carefully dried solvents, whereas small additions of water decrease the intensity of this band with a concomitant increase of the short-wave component at *ca.* 670 nm. This is exemplified in Fig. 2d (dashed line), which shows the spectrum of **3** in DMF containing 2% of water which is characterized by the prevalent presence of the double peaked profile in the concomitant disappearance of the absorption at *ca*. 700 nm. In line with the above findings for **3**, it was observed for **4**, that a single *Q*-band spectrum of the monomeric species detected in diluted DMSO and DMF solutions with low water content (dotted lines in Figs 2c and 2d) is changed to that of the dimeric species by addition of water or pyridine [9]. It should be noted that UV-vis spectra of 3,4,5-trimethoxystyryl substituted Mg^{II}-tetradiazepinoporphyrazines in various solvents were recently reported [14b]. Similarly to our 4-methoxystyryl derivative **3**, they contain a broad *Q*-band absorption typical of strongly associated species

in CH_2Cl_2 and tetrahydrofurane and a double-peaked *Q*-band characteristic for the dimeric form in a number of other solvents. Taking into account our results on the dependence of the UV-vis spectra of **3** and **4** from residual water in DMSO and DMF, it cannot be excluded that the split *Q*-band which was observed in [14b] for the 3,4,5-trimethoxystyryl derivative in these solvents might also be correlated to the level of water content of the used solutions. We have established that the fluorescence emission spectra are even more sensitive to the factors influencing complex **3** in its monomer/dimer interchange.

Fluorescence spectra

The fluorescence measurements for the Mg^{II} complex **3** were made for aerated solutions in pyridine, DMSO and DMF. Curves 1 and 2 in Fig. 3 (left side) are the fluorescence spectra obtained under excitation with λ_{exc} = 400 and 630 nm, respectively. The fluorescence emission band at 722–727 nm observed using both types of excitation is typical of the porphyrazine core, whereas the broad emission band at *ca.* 480–490 nm is assigned to the presence of the styryl fragments. These data fit well with the fluorescence results obtained by us for the octastyryl substituted Mg^{II} complex of the tetrapyrazinoporphyrazine analog [St_8TPyzPAMg(H_2O)] which also shows two fluorescence emission bands at 480–500 and *ca.* 700 nm (λ_{exc} = 400 nm) [5]. For the corresponding styryl substituted dinitrile precursors a broad fluorescence emission band is observed in the region 400–600 nm. Noteworthy, the related pyrazinoporphyrazine Mg^{II} macrocycle bearing peripheral methyl groups instead of styryl groups, *i.e.* [Me_8TPyzPAMg(H_2O)], shows, as expected, only a single emission band in the near-IR region with maximum at 643 nm (λ_{exc} = 400 nm) due to the porphyrazine core [5].

The fluorescence excitation spectra registered in the three solvents (pyridine, DMSO and DMF) all showing the fluorescence emission at λ_{em} = 740 nm, are given in Fig. 3 (right side, curves 3). Such type of spectra is typical of symmetrical porphyrazines in their monomeric form. In the region 600–800 nm the spectra show only one narrow intense band at 702–708 nm having mirror image symmetry with the emission spectrum in the same region. Comparing the excitation spectra with the corresponding absorption spectra (Fig. 3, curves 3 and 4), it is noticed that the absorption band at *ca.* 700 nm is the one responsible for the emission band with maximum at 722–727 nm, while the absorption band at 660–670 nm seen in DMSO and pyridine does not contribute to the fluorescence response at all. These findings, in agreement with indications from the above UV-vis spectra, further support the assignment of the absorption band at *ca.* 700 nm as due to the monomeric

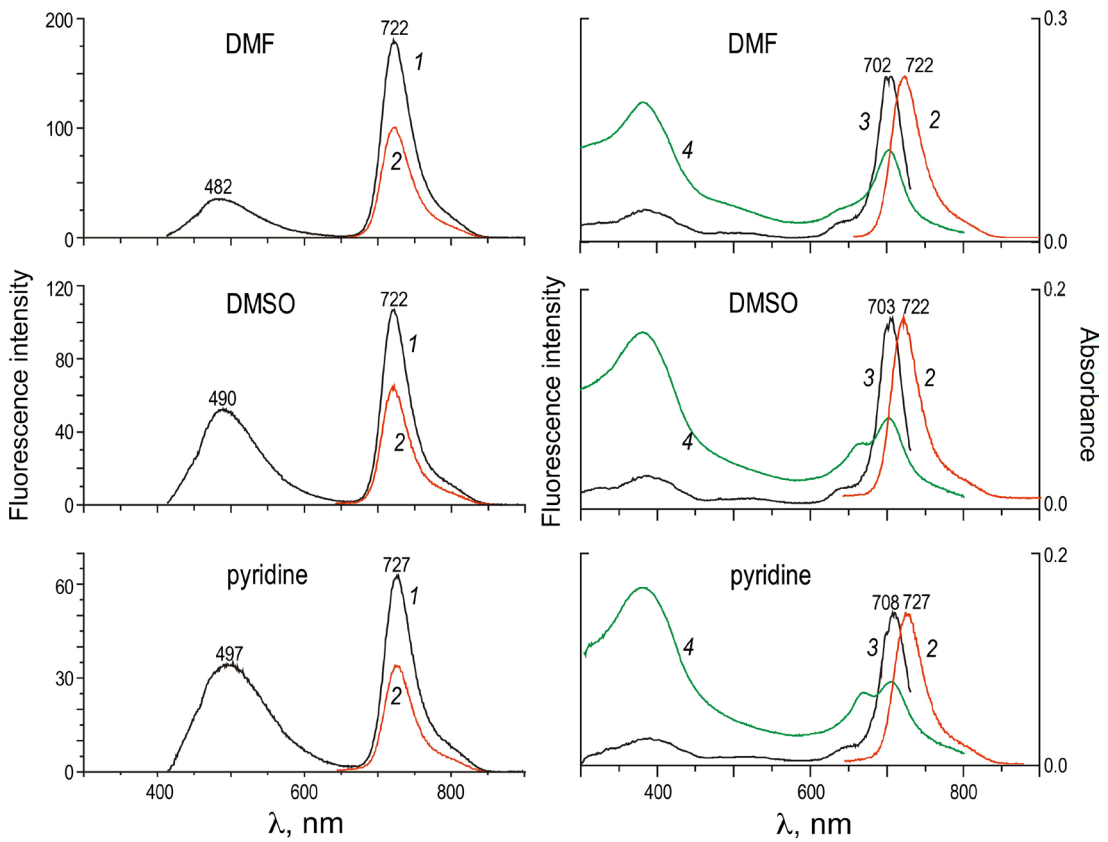

Fig. 3. Fluorescence emission (1) - λ_{exc} = 400 nm, (2) - λ_{exc} = 630 nm, fluorescence excitation (3), (λ_{reg} = 740 nm) and absorption (4) spectra of Mg^{II} complex **3** in DMF, DMSO and pyridine

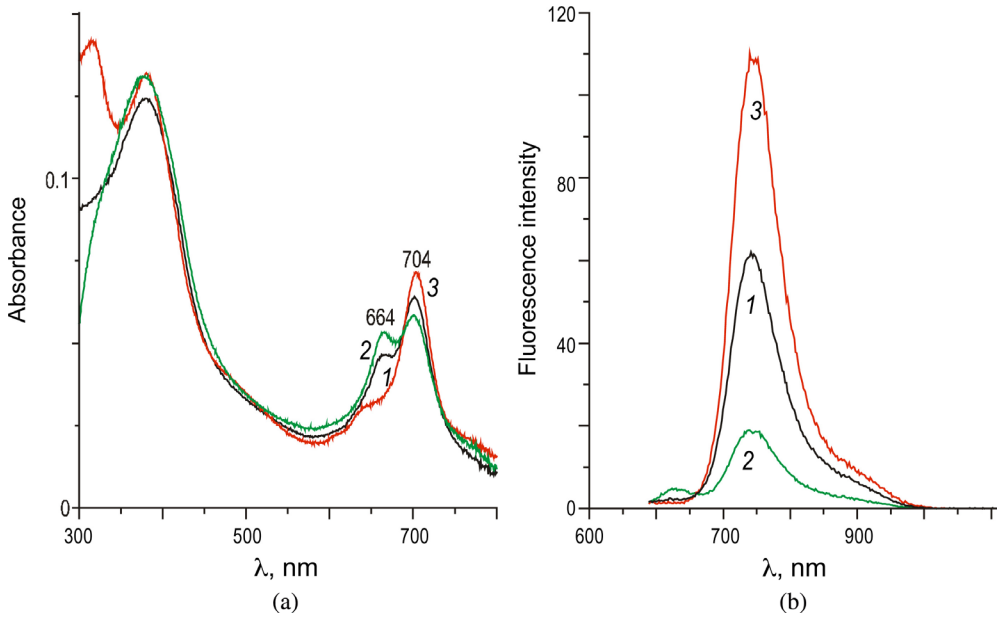

Fig. 4. Changes in absorption (a) and fluorescence emission (b) (λ_{ex} = 630 nm) spectra of the Mg^{II} complex **3** in DMSO (1) after addition of 10% water (2) and tbaF (3)

fluorescent macrocycle and of the absorption at 660–670 nm to the non-fluorescent dimeric species.

Figure 4 shows the spectral variations of both the absorption and emission spectra of **3** in DMSO caused by addition of H_2O and tetrabutylammonium fluoride (tbaF). The observed changes seen by addition of H_2O (Fig. 4a, spectra *1* and *2*, black → green) indicate a decrease of the amount of the monomeric species (maximum at 704 nm) and a concomitant increase of the dimeric species (664 nm); a reverse spectral change (black → red) favoring the monomer takes place upon addition of the fluoride ion (Fig. 4a, spectrum *3*). In keeping with these findings, the fluorescence is decreased in the presence of water and increased upon addition of fluoride (Fig. 4b) indicating coherent changes of the ratio monomer/dimer. While water stabilizes the dimeric form of the Mg^{II} complex **3**, the addition of fluoride anions destroys it with formation of the monomeric form. The effect of fluoride might be connected with its ability to substitute coordinated water and/or rearrange hydrogen bonds responsible for dimerization.

The comparison between the absorption and the excitation spectra obtained for the complex **3** leads to some additional considerations. As shown in Fig. 3 (curves *3* and *4*), absorption of the peripheral stylbenoid π-chromophores in the region 400–600 nm contributes strongly to the broad and intense Soret band in the absorption spectra. The lower intensity of this band in the excitation spectra seems to indicate that the excitation is not effectively transferred from the stylbenoid moieties to the central porphyrazine π-chromophore. Noticeably, the Stokes shift observed for complex **3** in the near-IR region is *ca.* 20 nm, which is larger than that found for the styryl substituted tetrapyrazinoporphyrazine [St_8TPyzPAMg(H_2O)] (13 nm). This suggests that the relaxed excited-state geometry is more different from the ground-state geometry for the porphyrazine macrocycle bearing diazepine rings than for the tetrapyrazino analog. In this fact may reside the reason for the low effectiveness of the excitation transfer from the periphery to the central π-chromophore. The larger conformational changes in the excited state for **3** evidently also negatively affect the fluorescence quantum yield (Φ_F). Its values measured in DMF for λ_{exc} = 630 nm (Φ_F = 0.097) and for λ_{exc} = 400 nm (Φ_F = 0.022 and 0.061 for emission of stylbenoid and porphyrazine π-chromophores, respectively) are lower than that observed for the tetrapyrazino analog (Φ_F = 0.23–0.26 in DMSO [5]). It should be also noted that the intensity of the stylbenoid fluorescence band is increased relative to that of the porphyrazine fluorescence when the content of the monomeric species is decreased in going from DMF to DMSO and pyridine solutions (compare profiles of curves *1* in Fig. 3, right side). This indicates that dimerization quenches the fluorescence of the porphyrazine chomophore, but has a lower effect on the emission of the stylbenoid fragments.

^{1}H NMR spectra

^{1}H NMR spectra of the Mg^{II} complex **3** taken at room temperature in different deuterated solvents contain broad poorly resolved lines due to strong aggregation effects at the concentrations used for measurements (0.1–1 mM). The quality of the spectra improves at elevated temperatures. The spectra of **3** recorded in DMSO-d_6 at 383 K are presented in Fig. 5 in comparison with the spectra of the corresponding dinitrile precursor **2** in DMSO-d_6. For both **3** and **2** the singlets of methoxy

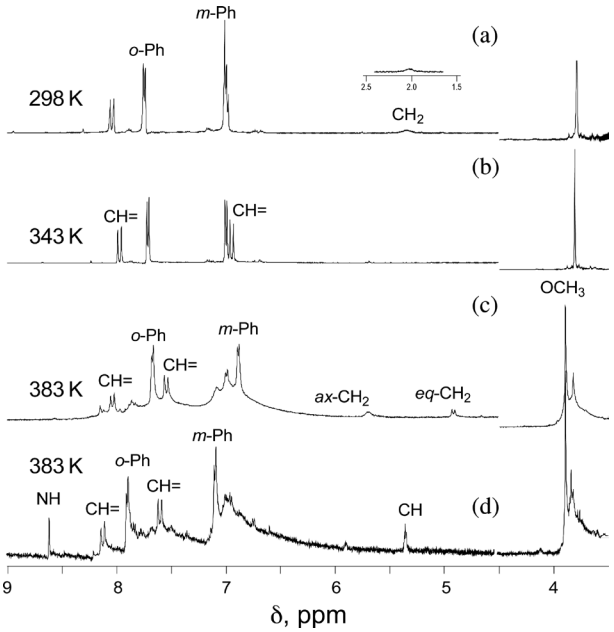

Fig. 5. ^{1}H NMR spectra of dicarbonitrile **2** ((a), (b)) and Mg^{II} complex **3** ((c), (d)) in DMSO-d_6. Spectrum D is recorded after addition of tbaF

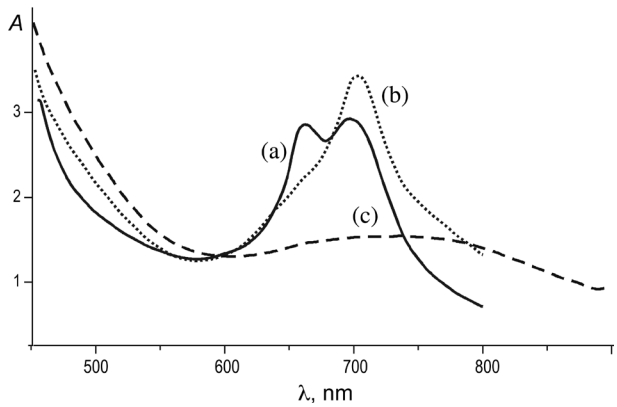

Fig. 6. UV-vis spectra of concentrated (~2 mM) solution of Mg^{II} complex **3** in DMSO-d_6 (a) and its change after addition of TBAF (b) and successive heating in the course of ^{1}H NMR measuremts (c)

groups are observed at 3.8–3.9 ppm and the characteristic doublets of aromatic *o*- and *m*-protons are at *ca*. 7.7 and 7.0 ppm. Two doublets of the CH=CH group with typical *trans*-splitting constant (^3J = 16.5 Hz) are seen at 8.04 and 7.55 ppm for complex **3** (383 K, Fig. 5c) and at *ca.* 8.0 and 7.0 ppm for the dinitrile **2** (343 K, Fig. 5b). The doublet in the higher field, which is shifted downfield by *ca.* 0.5 ppm for the Mg^{II} complex **3**, belongs to the CH protons neighboring the diazepine ring. It should be noted that in the spectrum of **3** recorded at 383 K additional broad lines of aggregates are still seen in the aromatic region along with an additional signal of the methoxy group at ca 3.8 ppm (Fig. 5c).

Two broad signals of diastereotopic CH_2 protons of the diazepine ring are detected for the dinitrile **2** at 5.3 and 2.0 ppm at room temperature (see Fig. 5a), but at elevated temperature they disappear (see Fig. 5b) due to rapid inversion of the diazepine ring. Such behaviour is typical also for other simple 1,4-diazepines existing in the 6*H* tautomeric form [7a, 9,20]. In contrast to that, for the Mg^{II} complex **3** signals of diastereotopic CH_2 protons are retained and even sharpened with the raise of temperature and in DMSO-d_6 at 383 K (Fig. 5c) they appear at 5.70 and 4.92 ppm. The resonance signal at 5.70 ppm appears little broadened, while that at 4.92 ppm is seen as a well-resolved doublet with geminal splitting constant ^2J = 12.2 Hz. For a solution of **3** in pyridine-d_5 the resonances of the olefinic CH=CH and diazepine CH_2 protons are shifted to the lower field and at 383 K they are observed at 8.49, 8.12 and 6.73, 5.98 ppm, respectively. The presence of two CH_2 resonances observed even at elevated temperatures is clearly indicative of a rigid framework and consequent inhibited inversion of the 6*H*-1,4-diazepine rings in the Mg^{II} complex **3**. This can be in connection with the existence of **3** in a stable dimeric form, in a fashion similar to the case previously discussed for the related *tert*-butylphenyl derivative [9]. These results indicate that, differently from the findings for the diluted DMSO solutions used for UV-vis and fluorescence measurements, in which the Mg^{II} complex **3** exists predominantly in its monomeric form, at the concentrations used for the ^{1}H NMR study the dimeric form is prevalent. The UV-vis spectrum of this concentrated solution taken in a thin cuvette contains a double peaked absorption (*Q*-band) expected for the dimer (Fig. 6a).

Interestingly, the addition of tbaF to this concentrated solution of **3** leads to dissociation of the dimeric species with formation of the monomer with a single *Q*-band (Fig. 6b), similarly as was observed for a diluted solution (Fig. 4). The ^{1}H NMR spectrum of this DMSO-d_6 solution containing TBAF at 383 K is shown in Fig. 5d. The signals of aromatic (7.09 and 7.90 ppm) and olefinic protons (7.60 and 8.12 ppm) are shifted downfield in comparison with the corresponding positions in the spectrum taken in the same solvent in the absence of tbaF (Fig. 5c). The most prominent feature of the spectrum in the presence of F^- ions is the disappearance of the signals of diastereotopic CH_2 protons, which are characteristic for the 1,4-diazepine ring in the 6*H* tautomeric form, and the appearance of the new signals at 8.61 and 5.37 ppm. These new signals can be assigned to the NH and CH protons of the diazepine ring in the 1*H* form. The corresponding NH and CH resonances were found at *ca.* 8.0 and 6.1–6.2 ppm for the pyrimidine fused 1*H*-1,4-diazepines (6,8-diarylpyrimido[4.5-*b*]-1.4-diazepine-4-ols) [21]. The UV-vis spectrum of the solution taken after the ^{1}H NMR measurement at elevated temperature differs from the initial spectrum obtained after addition of tbaF (Fig. 6b) and contains a broad and featurless

absorption in the 600–900 nm region (Fig. 6c). Theoretical calculations of the excited states of the Mg^{II} complex of monodiazepine annulated tribenzoporphyrazine [$DzBz_3PAMg$] [8b] predict that such broadening of the *Q*-band could be expected for the porphyrazines with fused diazepine rings in the 1*H* form. The visible spectral region for the 6*H* species [6*H*$DzBz_3PAMg$], typically for porphyrazine complexes, contains only two π–π* transitions of the macrocyclic π-chromophore (*Q*-band), while transitions involving π- and n-orbitals of the diazepine ring were found in the UV region. For the *1*H tautomer [1*H*$DzBz_3PAMg$] the π-orbital localized on the diazepine ring is located very closely to the highest occupied π-MO of porphyrazine macrocycle. This leads to a number of additional intense transitions involving charge transfer from the diazepine ring to the central porphyrazine core which are strongly mixed with the π–π* transition localised on the macrocycle.

The available UV-vis and ^{1}H NMR spectral data let us to assume that conversion of the dimeric form of the Mg^{II} complex **3** to the monomeric 1*H* form upon addition of the fluoride anions occurs in two steps. The diazepine rings in the dimer exist in the 6*H* form, as established by the presence of two characteristic signals of diastereotopic (axial and equatorial) CH_2 protons. One can suppose that dimerization occurs due to hydrogen bonding interaction involving the CH_2 group in one molecule and *meso*- or/ and diazepine N atoms of the other closely lying molecule within the dimer, locally inserted clathrated water within the two molecules presumably also contributing to dimerization. The occurrence of H-bonding leads to the observed strong downfield shift of the resonance signal belonging to the axial CH_2 proton participating in this interaction from its "normal" position (*ca.* 2 ppm in the precursor **2**) and very likely determines its broadening. Fluoride anions upon their addition substitute water molecules participating in hydrogen bonding interaction and/or coordinated to the magnesium ion. This leads to dissociation of the dimers and formation of the monomer with the diazepine rings in the 6*H* form characterised by a single *Q*-band (Fig. 6b). Upon heating the 6*H* tautomer is transformed to the 1*H* tautomer which exhibits a broad absorption in the visible region (Fig. 6c) and is evidently stabilized by the hydrogen bonding of fluoride anions with the NH groups of the enamine 1*H* form ($F^{-}\cdots$HN(diazepine)).

CONCLUSIONS

A new symmetrical tetradiazepinoporphyrazine Mg^{II} complex bearing eight peripheral 4-methoxystyryl groups has been prepared and characterized using mass-spectrometry, electronic absorption and emission spectroscopy and ^{1}H NMR measurements. UV-vis spectra indicate that the complex is strongly aggregated in non-donor solvents (CH_2Cl_2, $CHCl_3$, benzene). A stable dimer is formed in pyridine solution, characterized by a UV-vis spectrum showing a double peaked *Q*-band area with strong exciton coupling, whereas the complex appears to be largely in its monomeric form in diluted DMSO and especially in DMF solution. Results of emission spectroscopy measurements indicate that only the monomeric form is fluorescent, whereas the fluorescence of the porphyrazine π-chromophore is quenched in the dimeric form. ^{1}H NMR spectra provide evidence that dimerization occurs due to intermolecular hydrogen bonding between acidic CH_2 groups in the diazepine ring of one macrocycle with the *meso*- and/ or diazepine N atoms of the adjacent macrocycle, clathrated water also contributing to dimerization. Addition of fluoride anions to solutions of the dimer favors monomerization and the monomer is stabilized with the diazepine rings in the 1*H* form. Further studies are being conducted on the structure, dimerization processes and tautomerism of the diazepine rings in tetradiazepinoporphyrazines.

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