

Araştırma Makalesi / Research Article

Synthesis and Spectroscopic Properties of Newly Tetrapyrazinoporphyrazine Containing Gadolinium(III) Acetate

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Öz

A new tetrakis-(2-methylpyrazino)porphyrazinato gadolinium(III) acetate complex was synthesized. Elemental analysis, Fourier-Transform Infrared, Ultraviolet-visible, and fluorescence spectroscopy techniques clarified its structure. It can dissolve very well without aggregation in both Dimethyl sulfoxide and N, N-Dimethylformamide, which have high dielectric constant and high dipole moment from polar aprotic solvent type. Its aggregation property was also investigated in dimethyl sulfoxide at different concentrations, and it was determined to contain monomeric species. In addition, its fluorescence properties were investigated in Dimethyl sulfoxide, and the effect of gadolinium(III) acetate metal ion as a heavy rare earth element was determined. According to the findings in this study, it may be used as an electronic and optical material and in various technological applications such as photocatalytic applications. In addition, these findings may be useful for systems that include changes in pyrazinoporphyrazine-like forms.

Anahtar kelimeler

Tetrapyrazinoporphyrazine;
Gadolinium(III) acetate;
Synthesis; Aggregation;
Spectroscopic

Gadolinium(III) Asetat İçeren Yeni Tetrapirazinoporfirazinin Sentezi ve Spektroskopik Özellikleri

Abstract

Yeni tetrakis-(2-metilpirazino)porfirazinato gadolinium(III) asetat kompleksinin sentezlenip, saflaştırılmasının ardından yapısı element analiz, Fourier-Transform Kızılötesi, Ultraviyole görünür ve Floresan spektroskopik teknikleri ile karakterize edildi. Polar aprotik solvent olan ve yüksek dielektrik sabitine ve yüksek dipol momente sahip olan hem Dimetil sülfoksit hem de N,N-Dimetilformamid solventlerinde agregasyon yapmadan iyi bir şekilde çözünebilmektedir. Dimetil sülfoksitte hazırlanan belirli farklı konsantrasyon aralıklarındaki çözeltilerindeki agregasyon özelliği araştırılarak çoğunlukla monomerik türler içerdiği de belirlenmiştir. Ayrıca; dimetil sülfoksitte hazırlanan çözeltisinin floresan özellikleri incelenerek merkezinde ağır bir nadir toprak elementi olarak gadolinium(III) asetat metal iyonunun etkisi belirlenmiştir. Tetrakis-(2-metilpirazino)porfirazinato gadolinium(III) asetat, elektronik ve optik malzeme olarak ve fotokatalitik uygulamalar gibi çeşitli teknolojik uygulama alanlarında kullanılabilir ve pirazinoporfirazinin benzeri formlardaki değişiklikleri içeren sistemler için de faydalı olabilir.

Keywords

Tetrapirazinoporfirazinin;
Gadolinium(III) asetat;
Sentez; Agregasyon;
Spektroskopi

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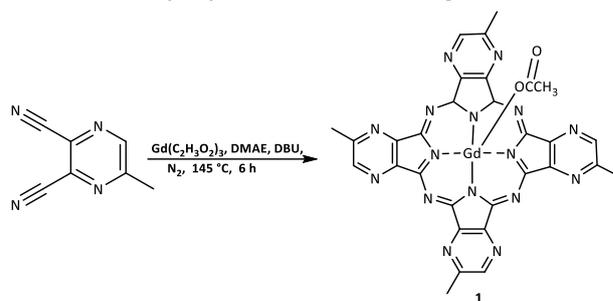
1. Introduction

Tetrapyrazinoporphyrazines (TPyzPzs), commonly known as "aza phthalocyanine or aza-phthalocyanine", are structures formed by the condensation of four pyrazine rings into the porphyrin skeleton. TPyzPzs are phthalocyanine aza

analogs with stronger acceptor properties due to the presence of four acceptor pyrazine fragments instead of phenylene groups. (Novakova *et al.* 2018, Faraonov *et al.* 2020) Azaphthalocyanines (AzaPcs) are aza analogs of phthalocyanines (Pcs), which are formed by replacing some carbons in macrocycle

systems with nitrogen (Donzello *et al.* 2016). Compared to Pcs, the additional eight nitrogen atoms in TPyzPzs cause large electronic effects in the structure. TPyzPzs form a separate class of Pc aza-analogs. Both metal-free TPyzPzs and metal complexes have shown interesting optical and electrochemical properties as well as potential applications in technology and medicine (Kolarova *et al.* 2023, Park *et al.* 2015, Donzello *et al.* 2016, Novakova *et al.* 2018, Donzello *et al.* 2008, Park *et al.* 2005, Donzello *et al.* 2010, Tomachynskiy *et al.* 2011, Lee *et al.* 2005, Kopecky *et al.* 2011). Like Pc, TPyzPzs exhibit comparable abilities to generate singlet oxygen (Kostka *et al.* 2006, Park *et al.* 2015). Unsubstituted TPyzPz's generally have extremely low solubility in organic solvents (Donzello *et al.* 2016). Substituted TPyzPz's are of great interest and importance because only the appropriate substituent groups can increase macrocyclic compound solubility in organic solvents or water and fine-tune the physicochemical properties necessary for a particular application (Donzello *et al.* 2016). Lanthanide(III) mono-AzaPcs generally show good solubility and low aggregation tendency due to the steric effect of an axial ligand and the high solubility of the central lanthanide ion (Donzello *et al.* 2022, Kosov *et al.* 2019, Tikhomirova *et al.* 2018). The incorporation of rare earth metal ions into the AzaPc cavity helps to improve the photophysical and photochemical properties, as well as to overcome their aggregation in solutions (Donzello *et al.* 2022, Kosov *et al.* 2019, Tikhomirova *et al.* 2018) Intramolecular heavy atom effect can induce relaxation through fluorescence or singlet oxygen generation. The presence of heavy atoms in the molecule can increase the intersystem crossing of the compound. Thus, it can lead to higher singlet oxygen production and a reduction in other competitive relaxation pathways, such as fluorescent emission (Svec *et al.* 2015). Despite promising properties and unique structural features, little attention has been paid to pyrazinoporphyrazine complexes of rare earth elements (Botnar, *et al.* 2022). Therefore, it is essential to develop an efficient synthesis and characterization of novel pyrazinoporphyrazine complexes containing rare earth metal ions. For this

purpose, in this study, a new tetrapyrazino porphyrazine complex (Gd(OAc)TPyzPz) 1 containing rare earth metal ion Gadolinium(III) acetate in its cavity and methyl groups as tetra from its peripheral positions was designed, synthesized, purified and isolated (Scheme 1). Its structure was characterized by widely known spectroscopic techniques and its spectroscopic, aggregation, and fluorescence properties were investigated in DMSO.



Scheme 1. Synthesis of newly Gd(OAc)TPyzPz 1

2. Experimental

Gadolinium(III) acetate and 2,3-Dicyano-5-methyl pyrazine were acquired from Fisher Scientific. The solvents were purified, dried, and retained in molecular sieves, 4Å. All reactions were carried out under a dry nitrogen atmosphere. It was purified by successive washings with various solvents using a Soxhlet apparatus. The purity of the product was tested by thin-layer chromatography after washing with each solvent and drying. FTIR Spectra and electronic spectra were recorded on a Shimadzu FTIR-8300 (ATR) and a Shimadzu UV-1601 spectrophotometer, respectively. TUBITAK Ankara Instrumental Analysis Laboratory carried out elemental analysis using LECO CHN 932. Fluorescent excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at 25 °C.

2.1 Synthesis of tetrakis-(2-methylpyrazino) porphyrazinato gadolinium(III) acetate [Gd(OAc)TPyzPz] 1

2,3-Dicyano-5-methyl pyrazine (0.10 g, 0.69 mmol), gadolinium(III) acetate (0.06 g, 0.18 mmol), and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1.50 mL of 2-Dimethylaminoethanol (DMAE) was heated with stirring at 145 °C in a leakproof glass tube for 6 hours under nitrogen

atmosphere. The resulting suspensions were cooled to room temperature and then poured into 25 ml of ethanol. The precipitates were filtered and washed sequentially with each of the solvents of water, methanol, ethyl acetate, acetonitrile, hexane, toluene, acetone, and diethyl ether and dried over phosphorus pentoxide in a vacuum desiccator. Mp: >300 °C. Yield: 45.29 mg (28.65%). The Elemental analysis result calculated for C₃₀H₂₁GdN₁₆O₂ is C, 45.33; H, 2.66; N, 28.20%. Its elemental analysis findings are C, 44.78%; H, 2.48; N 28.67%. FTIR (ATR) $\lambda_{\max}/\text{cm}^{-1}$: 1090, 950 (C–H bend.), 1201 (C–N str.), 1276 (C–O str.), 1358, 1425 (symmetrical C–H bend), 1508 (C=N- str.), 1574 (asymmetric aliphatic -CH₃), 1675 (C=C str.), 1728 (–C=O str. acetate), 2953, 2898, 2840 (>CH₂ str.), 3052(=C–H str.). UV–vis [Dimethyl sulfoxide (DMSO), 1.00 x 10⁻⁵ M]: λ_{\max} (nm), (log ϵ): 346 (4.84), 586 (4.20), 615 (4.30), 643 (5.02). UV–vis [N, N-dimethylformamide (DMF), 1.00 x 10⁻⁵ M]: 343 (4.72), 590 (4.18), 614 (4.29), 643 (4.91)

3. Results and discussion

3.1 Synthesis and characterization

The Gd(OAc)TPyzPz **1** was synthesized by the cyclotetramerization reaction of 2,3-Dicyano-5-methyl pyrazine, and gadolinium(III) acetate, in the presence of a catalytic amount of DBU as a strong non-nucleophilic base, in a dried high boiling solvent, and, under an inert atmosphere (Scheme 1). Since it adsorbed strongly to the silica and alumina stationary phases in the column, chromatographic isolation methods could not be used in this case. It was purified by washing at reflux in polar and non-polar solvents, respectively, using the soxhlet apparatus, until the colour of the solvent resulting from the interaction of these solvents with it became clear. Its structure was elucidated by elemental analysis, FTIR, UV–vis, and fluorescence spectroscopy techniques, and the data and results obtained were determined to be compatible with the proposed structure. In its FTIR spectrum, no sharp peak belonging to the nitrile group at 2220 cm⁻¹ was monitored after the conversion of 2,3-Dicyano-5-methyl pyrazine to Gd(OAc)TPyzPz **1** as

evidence of cyclotetramerization reaction. The band monitored at 3052 cm⁻¹ corresponds to the characteristic aromatic =C–H stretching vibration. Stretching vibrations of its aliphatic CH groups were monitored as sharp and intense absorption bands at 2953–2840 cm⁻¹. In the FTIR spectrum, strong and sharp vibration of the carbonyl (–C=O) group of acetate of Gadolinium(III) metal, which is the central metal ion, was observed at approximately 1728 cm⁻¹. The bands at 1358, and 1425 cm⁻¹ observed in the FTIR spectrum are attributed to symmetrical C–H bending vibrations, while the band at 1574 cm⁻¹ is attributed to asymmetric C–H bending vibrations. Bands of stretching vibrations for aromatic –C=C– and Ar–O–CH₂ were monitored at 1675 cm⁻¹ and 1276 cm⁻¹, respectively. A band of CH₃ bending vibration was monitored at 1425 cm⁻¹.

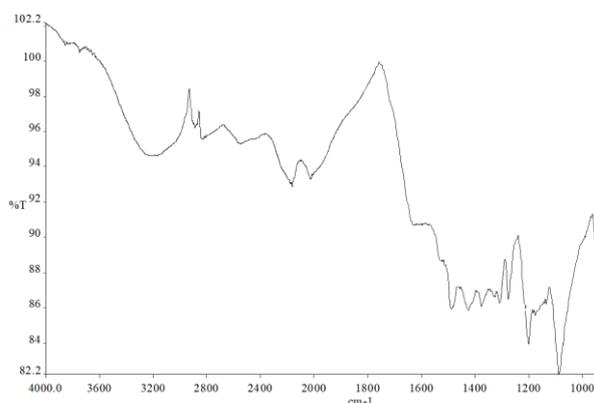


Figure 1. FTIR spectrum of Gd(OAc)TPyzPz **1**.

The Q band at 643 nm resulting from the π - π^* electronic transitions typical for metal-containing phthalocyanine and AzaPc is monitored in the UV–vis spectrum of its solution in both DMSO and DMF at 1.00 x 10⁻⁵ M, one of the two absorption bands. Its Q band is 8 nm more redshifted than unsubstituted TPyzPz in DMSO. This may be due to the inclusion of methyl groups from alkyl substituents in the π system as an electron donors. Because methyl groups activate the aromatic ring by increasing the electron density on the ring through an inductive donor effect (Kudrevich and Van Lier 2005).

The shoulder peak of its Q band was monitored at 586 nm in DMSO and at 590 nm in DMF. Its Q band at 643 nm was determined to have a high molar extinction coefficient of 85800 M⁻¹.cm⁻¹ in DMSO

and $81020 \text{ M}^{-1} \cdot \text{cm}^{-1}$ in DMF. The Soret and other B bands were monitored at 346 nm in DMSO and at 343 nm in DMF.

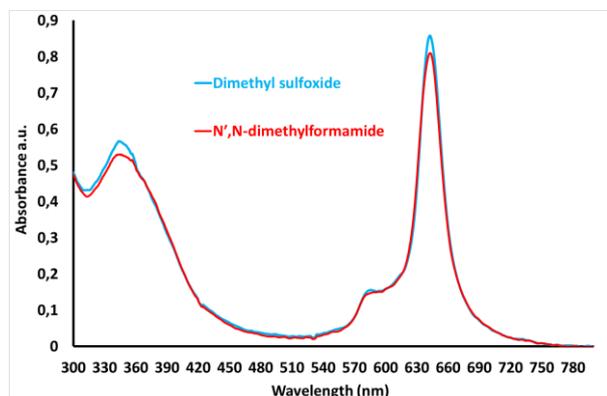


Figure 2. UV-vis absorption spectra of Gd(OAc)TPyzPz 1 in DMSO and DMF.

3.2 Aggregation studies

Aggregation is known for incorporating monomers, dimers, and rings into higher-order complexes in different types of solvents. The aggregation behavior of Gd(OAc)TPyzPz 1 in DMSO and DMF, which are polar non-protic solvents with high dielectric constant and dipole moment values, was investigated. It has been determined to easily dissolve in its solutions in these solvents without aggregation and contains monomeric species. (Fig. 2). Its aggregation behaviour was also determined by investigating whether it obeyed Lambert-Beer's law at decreasing concentration ranges from $1.20 \times 10^{-5} \text{ M}$ to $2.00 \times 10^{-6} \text{ M}$ in DMSO (Fig. 3). It was investigated by performing a linear regression analysis between the intensity and concentration of its Q-band. It has been determined to obey the Lambert-Beer law and contains monomeric species. It was also monitored that the absorbance of the Q band augmented depending on the augment in its concentration, and no novel band formation was monitored. These results confirm that it does not tend to aggregate and does not include aggregated species.

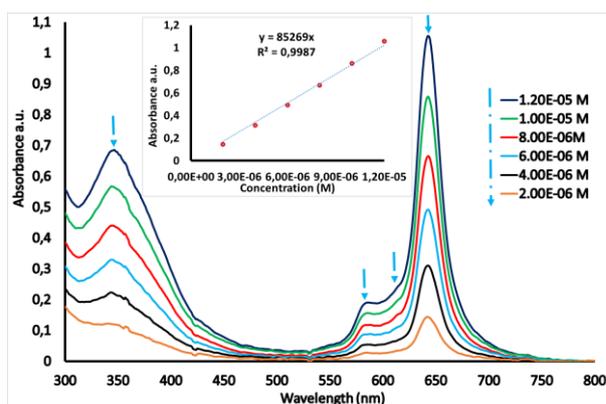


Figure 3. Aggregation demeanor of Gd(OAc)TPyzPz 1 in DMSO at particular concentrations (Inner: Concentration vs. absorbance diagrams).

3.3 Fluorescence spectra

To determine Gd(OAc)TPyzPz 1's fluorescence properties in DMSO, fluorescence emission, absorption, and excitation spectra were investigated (Figure 4). Its bands with maximum intensity in the fluorescence spectrum were monitored at 643 nm for excitation and 648 nm for emission, respectively. It has a Stokes shift of 5 nm, which is characteristic of TPyzPz (Zimcik et al. 2012). Its fluorescent emission in DMSO is low intensity and characteristic due to the presence of the heavy rare earth metal gadolinium(III) acetate. Its fluorescent emission spectrum has a typical shape for AzaPc (Zimcik et al. 2012). Its excitation spectrum is like the absorption spectrum, and both of its spectra are optical isomerism of the fluorescence spectrum. This indicates that the nuclear configurations of the ground and excited state are similar and unaffected by excitation. Furthermore, it contains only monomeric species, and the matching of absorption and fluorescence excitation spectra indicates no aggregation. The slight difference in the excitation spectrum from the absorption spectrum may be due to the presence of the heavy rare earth metal gadolinium(III) acetate in its cavity.

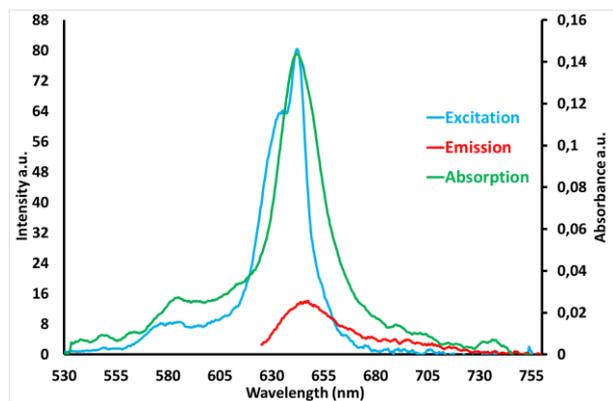


Figure 4. Excitation, emission, and absorption spectra of Gd(OAc)TPyzPz 1 in DMSO. Excitation wavelength= 615 nm.

4. Conclusions

In this research study, a novel tetrapyrazino porphyrazine containing Gadolinium as the heavy rare earth metal ion, which is tetrakis-(2-methyl pyrazino)porphyrinato gadolinium(III) acetate was synthesized. Its structure was illuminated and confirmed using elemental analysis, FTIR, UV-vis, and fluorescence spectroscopic techniques. It has been reported to dissolve very well in both dimethyl sulfoxide and *N, N*-dimethylformamide without aggregation, with a high molar extinction coefficient and absorption at long wavelengths. As a metal ion species, it has been reported to show low fluorescence emission due to the presence of gadolinium(III) acetate metal ion, which is heavy and has a high coordination number in its cavity. Due to its good solubility without aggregating in solvents and favorable fluorescent properties, it can be used in various technological applications. It may be useful for systems containing changes in forms like the tetrapyrazinoporphyrazine studied.

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