

REGULAR ARTICLE

Magnesium Trimethoxyphenylporphyrin Chain Controls Energy Dissipation in the presence of Cholesterol

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MS received 23 November 2016; revised 3 February 2017; accepted 14 February 2017

Abstract. A magnesium porphyrin compound, $[\text{Mg}(\text{TMPP})(\text{H}_2\text{O})] \cdot (\text{CH}_3\text{COCH}_3)_2\text{H}_2\text{O}$ **1** (TMPP = 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)porphyrin) has been synthesized and characterized using single crystal X-ray diffraction and other spectroscopic analysis. The luminescence properties of compound **1** were studied at different concentrations. At higher concentration (3×10^{-3} M), treatment of **1** with cholesterol enhanced the luminescence when excited at Soret band, demonstrating the role of lipid in controlling porphyrin-porphyrin interaction for tuning the bulk photophysical properties. However, at lower concentration (10^{-5} M) of porphyrin, there was no significant change in luminescence intensity in the presence of cholesterol. It suggests some role of lipids in light harvesting systems where chlorophyll is present at higher concentration.

Keywords. Porphyrin; magnesium; chlorophyll; photosynthesis; fluorescence.

1. Introduction

The green pigment chlorophyll present in green leaves initiates the photosynthesis. Chlorophyll is a porphyrin-type tetrapyrrolic macrocyclic molecule with a reduced double bond in one of the pyrrole rings. The metal present in chlorophyll is magnesium; however, some zinc containing bacteriochlorophylls are also known. Due to the presence of metal magnesium in chlorophyll there is significant interest on magnesium porphyrins.^{1–4} However, researchers usually study zinc porphyrins to understand photosynthetic systems due to the synthetic difficulties of magnesium tetrapyrroles.⁵ Supramolecular multiporphyrin arrays have been made to mimic the important reactions of electron and energy transfer of native photosynthetic system.^{6,7} Balaban and co-workers reported and designed some superstructure of tetrapyrrolic macrocycles using the self assembling properties of tailored porphyrin and chlorins in biomimetic artificial antenna system.^{8,9} We have been studying magnesium porphyrin to understand the role of magnesium metal in chlorophyll-type light-harvesting molecules. Recently, we have demonstrated the formation of chlorophyll-*a* bicarbonate¹⁰ adduct, postulated by Willstätter, by using the model complex $[\text{Bu}_4\text{N}][(\text{HCO}_3)\text{MgTPP}]$ {TPP²⁻ = *meso*-tetraphenylporphyrin dianion}.¹¹ Carbon dioxide in the form of bicarbonate by binding to

magnesium facilitates the first stage of photosynthesis. Chlorophyll molecules aggregate in chloroplast, which has a significant role in absorption and transfer of solar energy.¹² The chlorophyll-chlorophyll interaction is shown to adopt nano spherical-shaped aggregates under self organization drive.^{13,14} In a model chlorophyll aggregation reaction, we found that a six coordinated Mg(II) compound $[\text{Mg}(\text{TMPP})(\text{CH}_2\text{Cl}_2)]$, **2** exhibited a 1D polymeric structure, self-assembled in spherical shape in nano domain.¹⁵ Compound **2** formed one dimensional polymer chain due to hexa-coordination of magnesium with two axially bound methoxy-groups from the two neighbouring porphyrin molecules. The magnesium of chlorophyll is mainly present as penta-coordinated form with axial water molecule in biological environment.^{16–18} Several models of aggregation of chlorophyll molecules in the presence of water are known.¹⁹ Hydrogen bonding ability and dipole-dipole interaction in water have a key role in the chlorophyll aggregation.²⁰ In the present work, we present the crystal structure of a penta-coordinated water bound magnesium porphyrin which forms hydrogen bonding network with axial and lattice water molecules.

In the layered thylakoid membrane of chloroplasts apart from the chlorophyll-chlorophyll interactions, chlorophyll-protein and chlorophyll-lipid interactions are also present. These interactions have important implications in the light harvesting complex for collecting and funneling light energy.^{13,14} Fluorescence spectra are used to determine the photosynthetic activity of

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chlorophylls of green leaves.^{21,22} Green leaves use the light to initiate photosynthesis or dissipate the extra energy as heat energy or emit as fluorescence.²³ These processes compete among them and therefore the efficiency of photosynthesis can be measured by measuring the chlorophyll fluorescence. In chloroplast thylakoid membrane, the light harvesting complexes do work perfectly even though the chlorophyll molecules are present as solid matrix at a concentration of around 0.1 M.²⁴⁻²⁶ But in *in vitro* systems, concentration-dependent fluorescence quenching of chlorophyll is observed. To understand the interaction between native chlorophyll and lipid molecules and their role in collecting and funneling light energy, we studied the luminescence of compound **1** at different concentrations in the presence of cholesterol molecules. It is found that at a relatively higher concentration of porphyrin when chlorophyll shows concentration dependent quenching,^{27,28} the luminescence intensity increases in the presence of lipid cholesterol.

2. Experimental

2.1 Materials and method

The solvents dichloromethane, chloroform, and hexane were purchased from Merck Life Science Private Limited. Acetone was purchased from Loba Chemie. Dimethylformamide (DMF), pyrrole, propionic acid and 3,4,5-trimethoxy benzaldehyde were purchased from SRL Pvt. Ltd. Magnesium acetate was purchased from Titan Biotech Limited.

UV-Visible spectral measurements were carried out using Perkin Elmer (Lambda 35) spectrophotometer. Infrared spectra were recorded on a Shimadzu IR-affinity FT-IR spectrophotometer using pressed KBr disks. Elemental analysis for carbon, hydrogen and nitrogen were analyzed with Perkin Elmer 2400 micro-analyser. Luminescence spectral measurements were recorded in an Aligent Cary Eclipse Fluorescence Spectrophotometer.

2.2 X-ray structural analysis

The single crystal was glued to a glass fiber and mounted on BRUKER SMART APEX diffractometer. Cell constant was obtained from the least-squares refinement of three-dimensional centroids through the use of CCD recording of narrow ω rotation frames, completing almost all reciprocal space in the stated θ range. The instrument was equipped with CCD area detector and data were collected using graphite-

monochromated Mo K α radiation ($\lambda = 0.71073\text{\AA}$) at low temperature (100 K). All empirical absorption corrections were applied using the SADABS program. All data were collected with SMART 5.628 (BRUKER, 2003), and were integrated with the BRUKER SAINT program. The structure was solved using SIR97 and refined using SHELXL-97. The space group of the crystal was determined based on the lack of systematic absence and intensity statistics. Full matrix least squares/difference Fourier cycles were performed which located the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters.

2.3 Synthesis of compound **1**

The ligand 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl) porphyrin (TMPP) was synthesized following standard method of porphyrin synthesis. A sample of 250 mg (0.25 mmol) 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl) porphyrin and 250 mg (1.27 mmol) of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ was warmed in 30 mL DMF for 30 min in a round bottom flask followed by addition of 50 mg of NaHCO_3 . The mixture was refluxed for 6 h. The solvent was then slowly evaporated on water bath and the solid residue was dissolved in DCM, filtered and dried. The compound **1** was finally isolated and purified by column chromatography over neutral alumina using eluent acetone-dichloromethane (1:9). The compound was recrystallized using dichloromethane-acetone-hexane mixture. The yield of the compound **1** was 80%. Molecular Formula: $\text{C}_{59}\text{H}_{64}\text{MgN}_4\text{O}_{16}$; Molecular Weight 1105.42; UV/Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 428 (400000), 563 (13000), 603 (6100); elemental analysis calcd. (%) for $\text{C}_{59}\text{H}_{64}\text{MgN}_4\text{O}_{16}$; C 64.11, H 5.47, N 5.07; Found: C 64.22, H 5.51, N 5.11. IR analysis: characteristics peaks at 2944.1, 2839, 1704.2, 1592, 1346.4, 1234.7, 1115.5, 1003.4, 940, 807.2, 716.7 cm^{-1} .

3. Results and Discussion

Magnesium(II) was inserted to the free base TMPP by following known procedure^{29,30} in DMF using magnesium acetate. After purification by column chromatography, magnesium porphyrin was re-crystallized with CH_2Cl_2 -acetone-hexane mixture and characterized using single crystal X-ray diffraction analysis. It is important to note that upon re-crystallization using non-coordinating solvent DCM-hexane, the compound crystallized as hexa-coordinated $[\text{Mg}(\text{TMPP})](\text{CH}_2\text{Cl}_2)$ **2** which exhibited a 1D polymeric structure.¹⁵

The ligand TMPP has a strong ability to form self-assembled porphyrin chains due to interaction of methoxy oxygens with different metals.^{15,31} Saleh and Straub studied the ¹³C NMR of TMPP and ZnTMPP and predicted the possibility of porphyrin-porphyrin interaction.³¹ We observed similar ¹³C NMR spectrum for compound **2** which supports the presence of weak interaction of *m*-methoxy oxygen with the central metal in nonpolar solvent like DCM.¹⁵ This interaction is important to decide the aggregation, which is disaggregated to discrete molecules in the presence of trace amount of water or coordinating solvent like ethanol. The electronic absorption and emission spectra of compound **1** is shown in Figure 1. There is no significant change in the electronic absorption spectrum of compounds **1** and **2** (Supplementary information, Figure S1). The electronic absorption spectrum is also similar to simple MgTPP, with a slight red shift of the Soret and Q-bands.¹¹

3.1 Crystal structure of compound **1**

Good quality crystal of complex **1** for x-ray diffraction was obtained from DCM-acetone-mixture using solvent diffusion method with petroleum ether.

The perspective view of compound **1** is shown in Figure 2. The environment around the central Mg(II) is penta-coordinated with one water molecule (Figure 2). Compound **1** crystallized in the triclinic system with space group *P1*. In the complex, the Mg-N(py) bond distance varied from 2.076 Å to 2.095 Å. The axial Mg-O bond distance is 2.037 Å, which is in the range of reported for Mg-O (H₂O) distance in magnesium porphyrins.³²⁻³⁴ The magnesium(II) is 0.248 Å above the porphyrin mean plane. The crystallographic asymmetric unit comprises one water molecule bound to magnesium-porphyrin molecule along with one acetone

and two lattice water molecules. The crystallographic data of compound **1** is given in Table 1.

Compound **1** shows hydrogen bonded chain structure, due to intermolecular hydrogen bonding between two porphyrin molecules *via* one lattice water molecule. The O...O distance between lattice water and axially bound water molecule to magnesium(II) is 2.713 Å and the other O...O distance between lattice water and oxygen atom of methoxy group is 2.798 Å (Figure S3 in Supplementary Information). The O...O bond distance of around 2.713 Å between lattice water and magnesium coordinated water suggests medium strength H-bonding interaction, even though the H-atoms of the lattice water molecule could not be located. The H-atoms could not be located in the lattice water, which may be due to disorder in the water molecules. There is another hydrogen bonding interaction present in the crystal lattice between one lattice solvent molecule, acetone and water molecule of magnesium bound porphyrin through another lattice water molecule. The

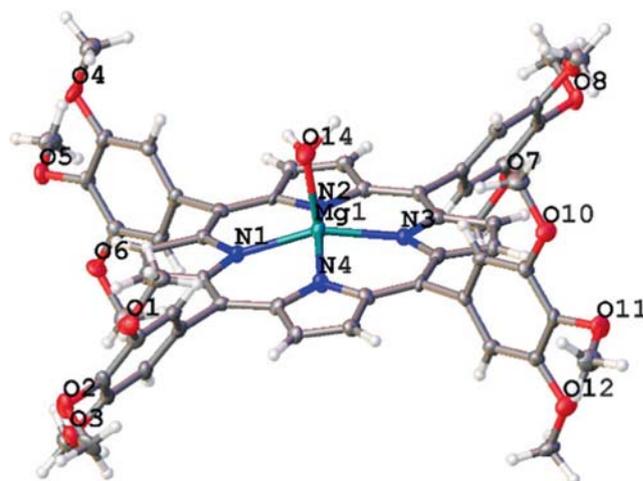


Figure 2. The perspective view of compound **1**.

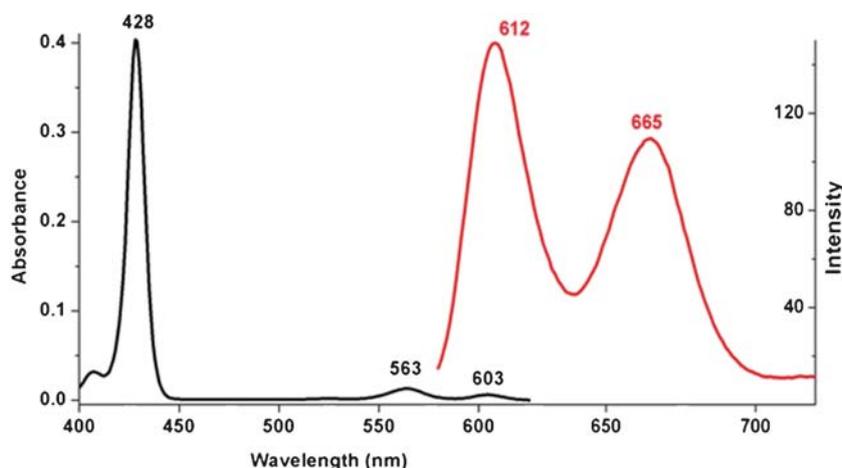


Figure 1. Electronic absorption (10^{-6} M, black trace) and emission (10^{-5} M, red trace) spectra of compound **1** in DCM.

Table 1. Crystallographic data^a for compound **1**.

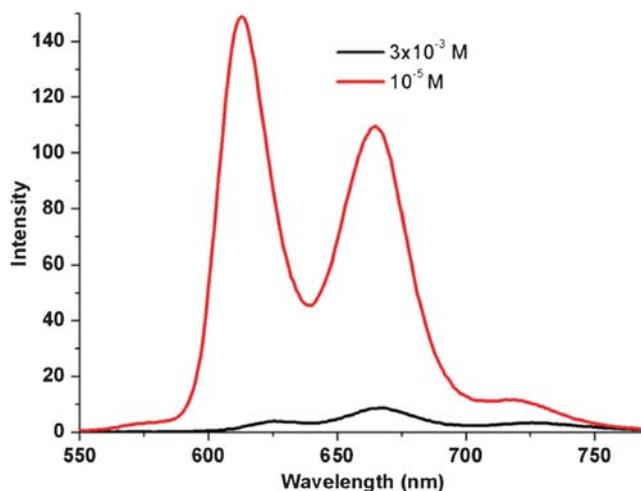
Compound	1
Formula	C ₅₉ H ₆₄ Mg N ₄ O ₁₆
Formula weight	1105.42
Crystal system	Triclinic
Space group	<i>P1</i>
T, K	100
Z	1
a, Å	7.836(5)
b, Å	12.610(5)
c, Å	14.135(5)
α, deg	85.848(5)
β, deg	78.538(5)
γ, deg	88.049(5)
V, Å ³	1365.2(11)
d _{calcd} , g/cm ³	1.345
μ, mm ⁻¹	0.108
θ range, deg	2.26 to 25.99
GOF (F ²)	1.087
R ₁ ^b (wR ₂ ^c)	0.0778(0.2213)

^aMo Kα radiation. ^bR₁ = $\sum \|F_0\| - |F_c| \sum |F_0|$. ^cwR₂ = $\{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]\}^{1/2}$.

O...O distances are 2.762 and 2.851 Å. This preferential hydrogen bonding network with water molecules is important in this case, as ethyl chlorophyllide *a* and chlorophyll molecules aggregate in a similar way as one dimensional structures through magnesium bound water molecule.³⁵ A close packed structure of compound **1** is shown in Figure S4 in Supplementary Information. In the crystal packing, neighbouring layers are stacked on each other forming a close packed polymer (Figure S4). There is a report of solvent induced reversible penta and hexa coordination system with CoTMPP which results formation of 1D and 2D coordination polymer.³⁶

3.2 Luminescence properties of compound **1**

There are reports of incorporation of monomeric or extended porphyrinoid compounds into liposomes which changes the emission bands of fluorophore.^{37,38} In thylakoid *in vivo*, chlorophyll molecules in the solid matrix do not respond to quenching of fluorescence which may be due to the separation of chlorophyll molecules by lipids.^{39,40} By maintaining the distance and orientation between chromophores of light harvesting chlorophylls, lipid or proteins help the excimer formation for efficient energy transfer displaying broad emission spectra.⁴¹ Lipids also have pronounced reducing effect on chlorophyll degradation which is not properly understood, inhibiting the enzyme chlorophyllase and it is interesting that chlorophyll degraded product

**Figure 3.** Luminescence spectra of compound **1** at 10⁻⁵ M (red trace) and 3 × 10⁻³ M (black trace) in DCM.

chlorophyllide shows high fluorescence in the presence of lipid.^{42,43}

To know the photosynthetic activity in the presence of lipid, we studied the luminescence of compound **1**. Compound **1** displays emission spectrum with peaks at (612 nm) and (665 nm) in dilute solution (10⁻⁵ M). At relatively higher concentrated solution (3 × 10⁻³ M), this emission is significantly quenched due to the known π–π stacking⁴³ as shown in Figure 3.

To get some insight of porphyrin-lipid interaction, we have performed the luminescence studies of compound **1** at different concentrations of cholesterol. To a 10⁻⁵ M solution of compound **1** in DCM, addition of cholesterol (10⁻³ M) does not show any significant change in luminescence intensity (Supplementary Information, Figure S5). But to a 3 × 10⁻³ M solution of compound **1** in DCM, addition of cholesterol (3 × 10⁻¹ M) increased the fluorescence intensity around three times (Figure 4). This increase of fluorescence intensity upon addition of cholesterol at higher concentration of porphyrin is very interesting. This suggest some role of lipid-porphyrin interaction for light harvesting process as chlorophylls perform the photosynthesis in chloroplasts where the concentration of chlorophylls is ~0.1 M. In the presence of large excess of cholesterol, the possibility of Mg(II) binding to the –OH of cholesterol cannot be ruled out. To check the possibility Mg(II) binding to the –OH of cholesterol, we carried out the UV-Visible studies of compound **1** in the presence of excess amount of cholesterol at dilute concentration (10⁻⁶ M) as well as in concentrated porphyrin solution (only for Q bands) but we did not observe any change in electronic absorption spectrum. Therefore, we believe that the enhanced intensity is not due to binding of cholesterol to Mg(II)

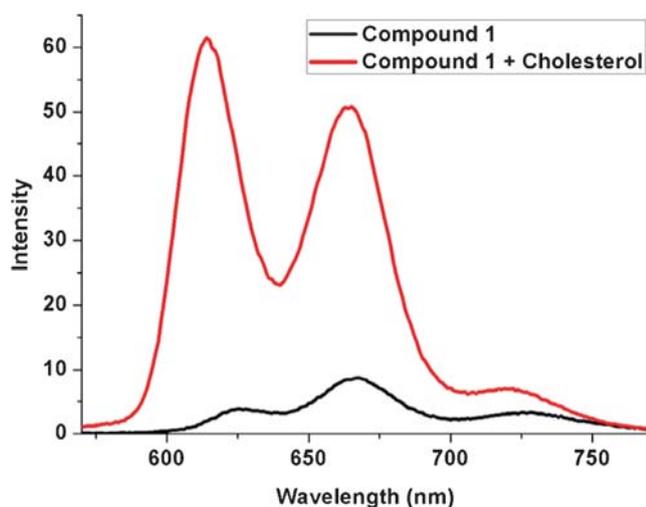


Figure 4. Emission spectra of compound **1** (3×10^{-3} M) in DCM (black line) and on addition of 100 times more cholesterol (red line).

of porphyrin. There is a report of increase in fluorescence intensity of amphiphilic porphyrin derivatives on mixing with liposomes.⁴⁴ Fluorescence spectrum of chlorophyll *a* incorporated into liposome mixture of phosphatidylcholines and phosphatidylethanolamine breaks at characteristic temperatures due to formation of solid phase of lipids.^{45,46} It is also reported that fluorescence intensity of chlorophyll *a* decreases when cholesterol lipid ratio is 1:1. Ehrenberg *et al.*, studied the fluorescence of hematoporphyrin derivatives upon binding to lipid vesicles. The fluorescence intensity of hematoporphyrin in lecithin increased six times with respect to aqueous solution, which may be due to the micro-viscosity in the lipid bilayer thereby weakening the channel for relaxation of the excited state.⁴⁷ The photophysical studies of compound **1** with isolated plant lipids and comparison with chlorophyll-lipid system is continuing in our laboratory.

4. Conclusions

In summary, the complex magnesium porphyrin **1** shows H-bonding chain structure similar to chlorophyll aggregation. The luminescence of the compound **1** in the presence of cholesterol has been studied. At higher concentration (3×10^{-3} M) treatment of **1** with cholesterol enhanced luminescence demonstrating the role of lipid in controlling porphyrin-porphyrin interaction. However, at lower concentration (10^{-5} M) of porphyrin, no significant change was observed in luminescence intensity on addition of cholesterol. It suggests some role of lipid-porphyrin interaction in light harvesting

process as chlorophylls in chloroplasts are present as solid matrix (0.1 M).

Supplementary Information (SI)

CCDC 1061635 contain the supplementary crystallographic data for complex **1**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The UV-Visible, IR, luminescence spectra are available as Supplementary Information for this article at www.ias.ac.in/chemsci.

Acknowledgements

This work was supported by start-up grant (YSS/2015/000394) from SERB, DST, New Delhi. Authors are thankful to Dr. Md. Harunar Rashid, Department of Chemistry, Rajiv Gandhi University, Itanagar for the use of fluorescence spectrophotometer.

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