

# **A combined experimental and theoretical study on the Synthesis, Spectroscopic Characterization of Magnesium(II) Porphyrin Complex with DMAP axial ligand and antifungal activity**

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## **Contents**

Section 1. Materials and Methods .....	2
Section 2. Crystallography.....	3
Section 3. <sup>1</sup> H NMR spectroscopy.....	4
Section 4. IR Spectroscopy.....	7
Section 5. Fluorescence spectroscopy .....	8
Section 6. UV/Vis.....	8
Section 7. Mass spectrometry .....	9
Section 8. DFT calculations.....	9
Section 9. References.....	10

## Section 1. Materials and methods

**UV–vis and IR spectroscopy:** The electronic absorption spectra were recorded with WinASPECT PLUS (validation for SPECORD PLUS version 4.2) scanning spectrophotometer. Solid IR spectra were obtained using a WinASPECTPLUS (validation for SPECORD PLUS version 4.2) scanning spectrophotometer.

**MS spectrometry:** Electrospray (ESI) spectra were carried out using an amaZon speed ion trap instrument and the ESI-HRMS spectra were recorded in a using LTQ Orbitrap XL apparatus (Thermo Scientific) equipped with an electrospray ionization (ESI) source. Solutions in dichloromethane were used for the analysis.

**Emission spectroscopy:** The emission spectra were recorded at room temperature with a Horiba Scientific Fluoromax-4 spectrofluorometer. The luminescence lifetime measurements were performed for excitation at  $\lambda = 450$  nm using the second harmonic of a titanium–sapphire laser (picosecond Tsunami laser spectra physics 3950-M1BB and 39868- 03 pulse picker doubler) at an 800 kHz repetition rate. Fluotime 200 from AMS technologies was used for the decay acquisition. It consists of a GaAs microchannel plate photomultiplier tube (Hamamatsu model R3809U-50) followed by a time-correlated single photon counting system from Picoquant (PicoHarp300). The ultimate time resolution of the system is close to 30 ps. The luminescence decays were analyzed with the FLUOFIT software available from Picoquant. The mission quantum yields were determined at room temperature in dichloromethane solutions by using the optically dilute method [1]. [Zn(TPP)] in air-equilibrated dichloromethane solution was used as a quantum yield standard ( $\phi_f = 0.031$ ) [2].

**Electrochemistry:** Cyclic voltammetry (CV) experiments were performed with a CH-660B potentiostat (CH Instruments). All analytical experiments were conducted at room temperature under an argon atmosphere (argon stream) in a standard one compartment, three-electrode electrochemical cell. Tetra-nbutylammonium perchlorate (TBAP) was used as a supporting electrolyte (0.2 M) in dichloromethane previously distilled over calcium hydride under argon. An automatic ohmic drop compensation procedure was systematically implemented before the CV data were recorded with electrolytic solutions containing the studied compounds at concentrations of ca.  $10^{-3}$  M. CH Instruments vitreous carbon ( $\phi = 3$  mm) working electrodes were polished with 1 mm diamond paste before each recording. The Ag/AgNO<sub>3</sub> 0.01 M (TBAP 0.2 in CH<sub>2</sub>Cl<sub>2</sub>) redox couple was used as the reference electrode. The potential of the ferrocene/ferrocenium redox couple was used as an internal reference (86 mV vs. Ag/AgNO<sub>3</sub> under our experimental conditions). For comparison with previously

published data, all potentials given in the text and in Table 7 have been converted to values relative to the saturated calomel electrode (SCE) according to the following relationship:

$$E(\text{SCE}) = E(\text{Ag}/\text{AgNO}_3) + 298 \text{ mV}.$$

## Section 2. Crystallography

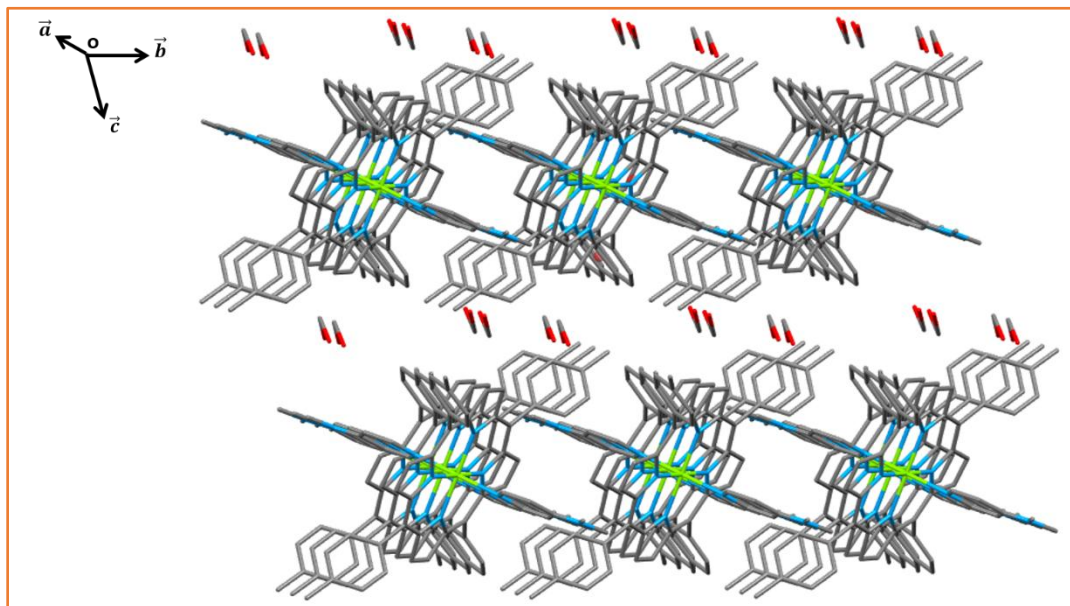


Fig.S1. Molecular packing for (I) viewed down the *a* axis.

Table-S1. Selected intermolecular interactions for complex (I).

D–H $\cdots$ A <sup>a</sup>	Symmetry of A	D $\cdots$ A (Å)	D–H $\cdots$ A (°)
C36–H36 $\cdots$ Cg2	<i>x, y, z</i>	3.296 (0)	118.75
C32–H32 $\cdots$ Cg2	$-x+1, -y+1, -z+1$	3.169 (2)	115.88
C101–H10B–Cg5	$x-1, y, z$	3.623 (3)	170

<sup>a</sup>: D = donor atom and A = acceptor atom.

Cg2 is the centroid of the N2/C6–C9 pyrrole ring.

Cg5 is the centroid of the C21/C22–C26 phenyl ring.

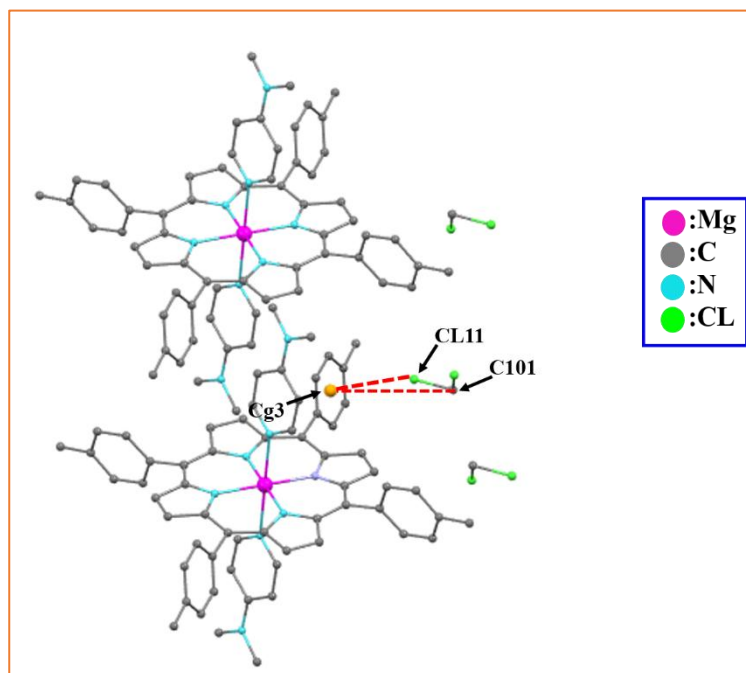


Fig. S2. Drawing showing the C—Cl $\cdots$ Cg (Cg is the centroid of a phenyl ring the TTP porphyrinate) intermolecular interactions in the structure of **I**.

### Section 3. $^1\text{H}$ NMR Spectroscopy

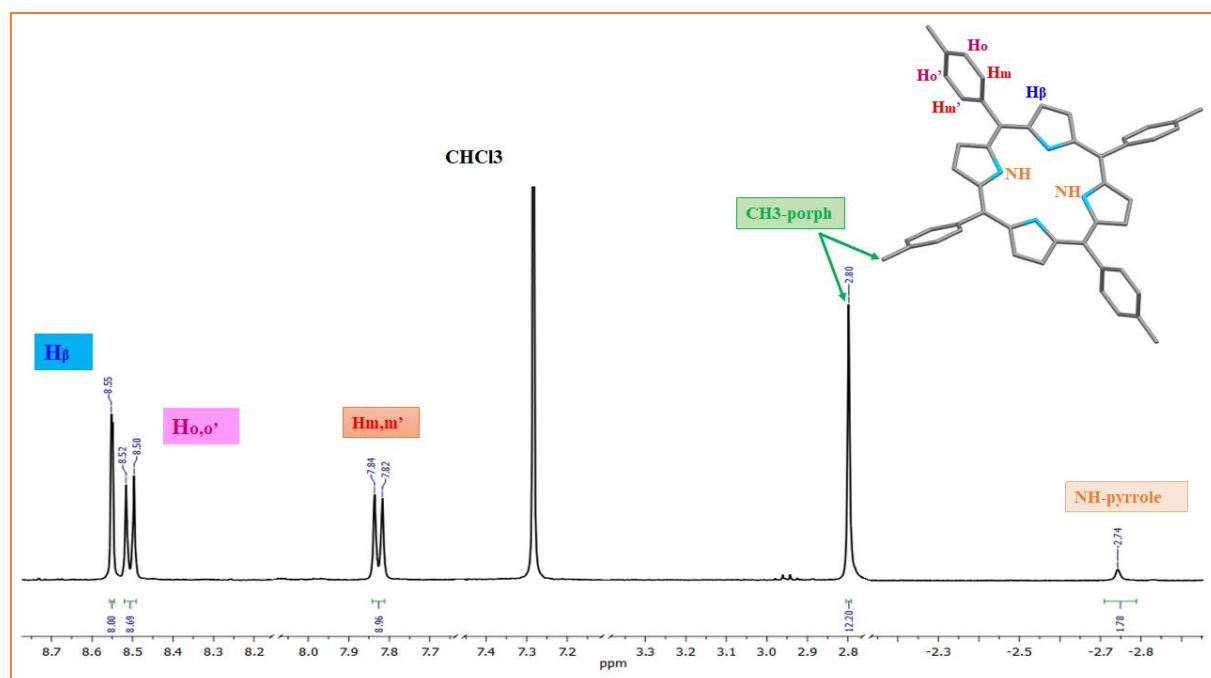


Fig. S3.  $^1\text{H}$  NMR spectrum of the  $\text{H}_2\text{TTP}$  free base porphyrin recorded in  $\text{CHCl}_3$  at room temperature with concentration  $C \sim 10^{-3}$  M.

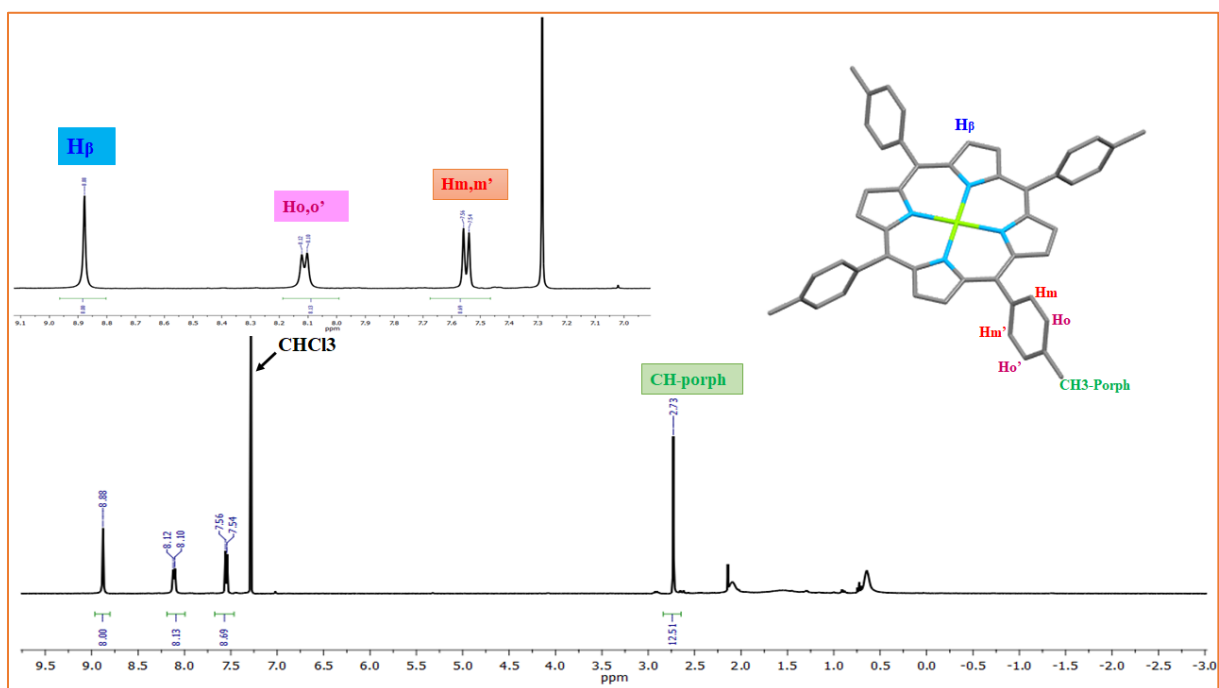


Fig. S4.  $^1\text{H}$  NMR spectrum of the [Mg(TTP)] porphyrin recorded in  $\text{CHCl}_3$  at room temperature with concentration  $C \sim 10^{-3}$  M.

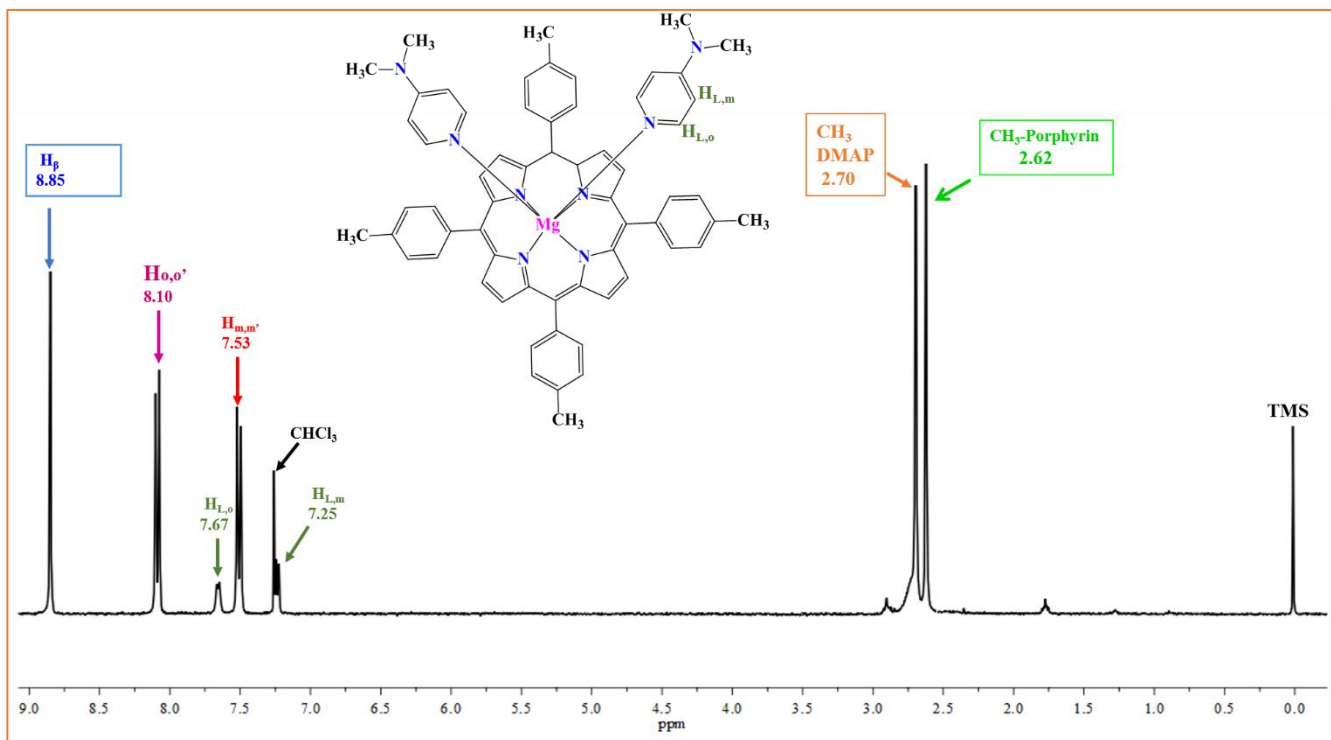


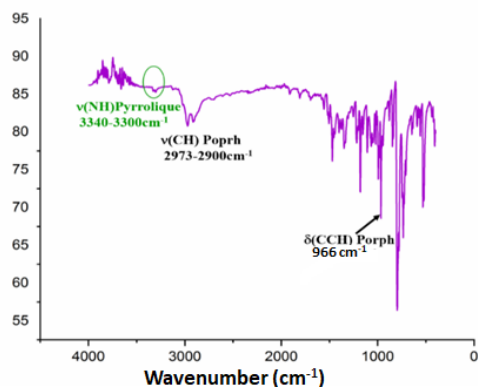
Fig. S5.  $^1\text{H}$  NMR spectrum of [Mg(TTP)(DMAP) $_2$ ] $\cdot 2\text{CH}_2\text{Cl}_2$  (I). Spectrum recorded in  $\text{CDCl}_3$  with concentration  $\sim 10^{-3}$  M.

Table S2. <sup>1</sup>H NMR experimental and theoretical data (δ in ppm) of H<sub>2</sub>TTP, [Mg(TTP)], [Mg(TTP)(DMAP)<sub>2</sub>]·2CH<sub>2</sub>Cl<sub>2</sub> (I) in CDCl<sub>3</sub> solvent.

<sup>1</sup> H NMR (ppm)												
Experimental							Theoretical					
H (ppm)	H <sub>β</sub>	H <sub>o, o'</sub>	H <sub>m, m'</sub>	P-CH <sub>3</sub>	NH	H(ligand)	H <sub>β</sub>	H <sub>o, o'</sub>	H <sub>m, m'</sub>	P-CH <sub>3</sub>	NH	H(ligand)
H <sub>2</sub> TTP	8.55	8.51	7.83	2.80	-2.74	----	8.68	8.63	7.99	3.15	-3.08	-
[Mg(TTP)]	8.88	8.11	7.55	2.73	-	-	8.91	8.52	7.74	3.05	-	-
[Mg(TTP)(DMAP) <sub>2</sub> ] •2CH <sub>2</sub> Cl <sub>2</sub> (I)	8.85	8.10	7.53	2.62	-	H <sub>L,o,o'</sub> : 7.67 H <sub>L,m,m'</sub> : 7.25 CH <sub>3</sub> -DMAP: 2.70	8.90	8.07	7.85	2.70	-	H <sub>L,o,o'</sub> : 7.79 H <sub>L,m,m'</sub> : 7.41 CH <sub>3</sub> -DMAP: 2.98

## Section 4. IR

Experimental spectra



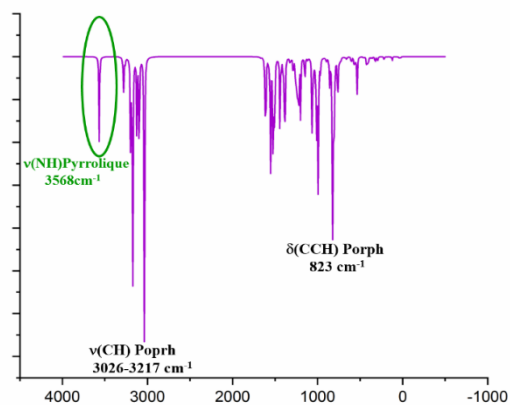
H<sub>2</sub>TTP

ctros

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Spe

Calculated spectra



[Mg(TTP)]

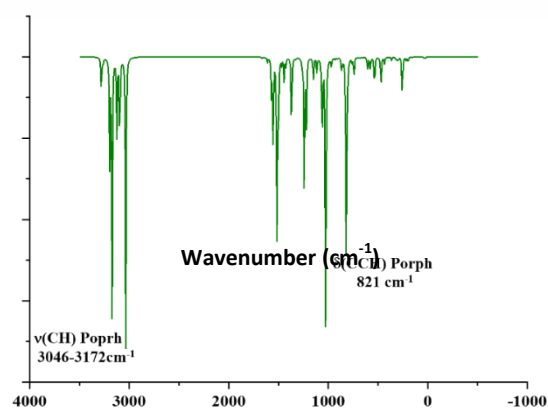
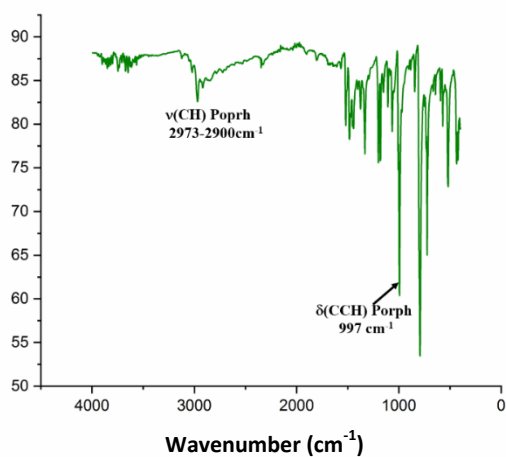
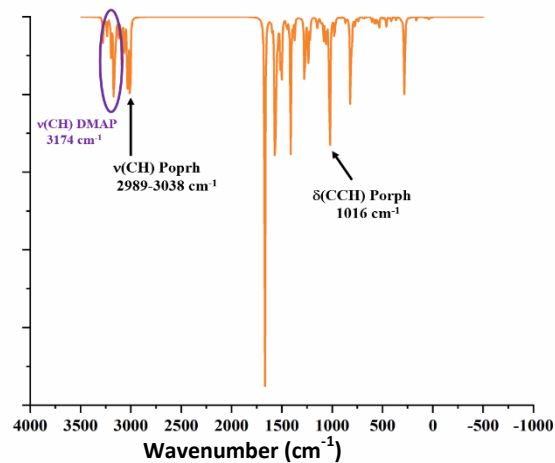
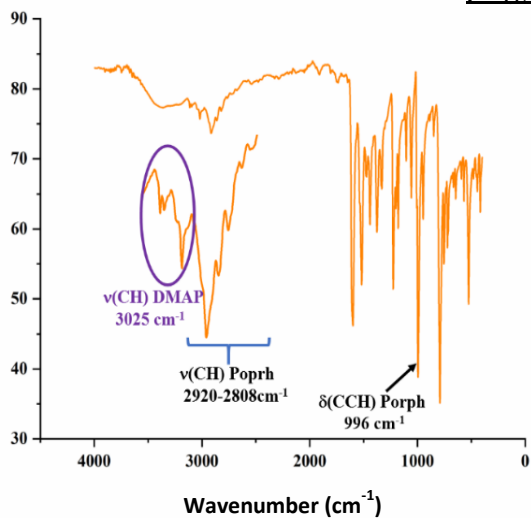


Fig. S6. Observed and calculated FT-IR spectra of H<sub>2</sub>TTP, [Mg(TTP)] complex

(I).

[Mg(TTP)(DMAP),1



## Section 5. Fluorescence spectroscopy

**Table S3.** The fluorescence data of H<sub>2</sub>TTP, [Mg(TTP)] and [Mg(TTP)(DMAP)<sub>2</sub>]•CH<sub>2</sub>Cl<sub>2</sub> (**I**) and a selected *meso*-arylporphyrins and magnesium(II) *meso*-arylporphyrins

Compound	Experimental (nm)		Theoretical (nm)		Φ <sub>f</sub>	τ <sub>f</sub> (ns)	Ref.
	Q(0,0)	Q(0,1)	Q(0,0)	Q(0,1)			
H <sub>2</sub> TTP <sup>a</sup>	653	717	-	-	0.12	9.60	[53]
H <sub>2</sub> TTP	652	721	643	753	0.098	7.9	t.w
[Mg(TPP)]	608	665	-	-	0.15	9.2	[54]
[Mg(TPBP)] <sup>b</sup>	611	665	-	-	-	-	[55]
[Mg(TTP)]	611	655	605	696	0.15	9.1	t.w
[Mg(TTP)(DMAP) <sub>2</sub> ]•2CH <sub>2</sub> Cl <sub>2</sub> ( <b>I</b> )	611	664	609	711	0.13	5.0	t.w
[Mg(TPBP)(HTMA) <sub>2</sub> ] <sup>c</sup>	611	666	-	-	0.055	-	[56]
[Mg(TPP)(THF) <sub>2</sub> ]	609	660	-	-	0.16	8.9	[57]

<sup>a</sup>:H<sub>2</sub>TTP = *meso*-tetraphenylporphyrin , <sup>b</sup>: H<sub>2</sub>TPBP = *meso*-tetrakis[4(benzoyloxy)phenyl]porphyrinato,  
<sup>c</sup>:HTMA = Hexamethylenetetramine

## Section 6. UV/Vis spectroscopy

**Table S4.** Experimental and theoretical UV/Vis data of H<sub>2</sub>TTP, [Mg(TTP)], [Mg(TTP)(4-DMAP)<sub>2</sub>]

Compound	Experimental			Theoretical	
	Band (nm)			Band (nm)	
	Soret Band	Q Bands		Soret Band	Q Bands
H <sub>2</sub> TTP	420	518	552 593	382	557
[Mg <sup>II</sup> (TTP)]	427	565	606	385	567
[Mg <sup>II</sup> (TTP)(DMAP) <sub>2</sub> ]•2Cl <sub>2</sub> Cl <sub>2</sub> ( <b>I</b> )	427	566	608	397	593



## Section 7. Mass spectrometry

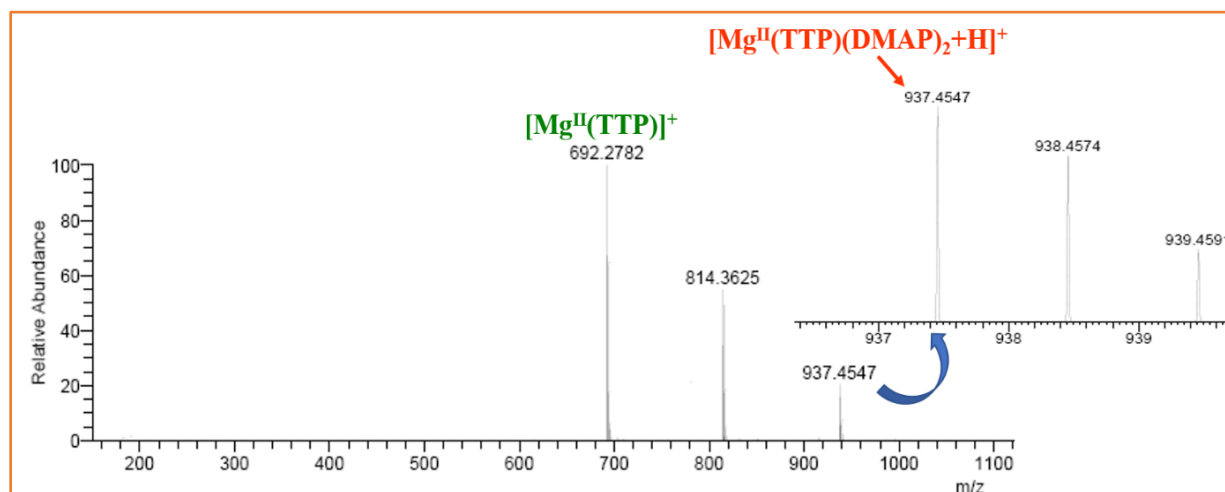


Fig. S7. ESI-HRMS spectrum of (I) showing the isotopic ratio. The solvent used is the dichloromethane with a concentration of  $5.10^{-3}$  M.

## Section 8. DFT Calculations

Table-S5. The calculated electronic properties of  $\text{H}_2\text{TTP}$ ,  $[\text{Mg}(\text{TTP})]$  and  $[\text{Mg}(\text{TTP})(\text{DMAP})_2]$  were using the TD-DFT/B3LYP-D3 method.

System	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$E_g$ (eV)	$\mu$ (eV)	$\eta$ (eV)	$\sigma$ (eV $^{-1}$ )	$\mu_D$ (D)
$\text{H}_2\text{TTP}$	-5.099	-2.415	2.684	3.757	1.342	0.745	0.045
$[\text{Mg}(\text{TTP})]$	-4.957	-2.267	2.690	3.612	1.345	0.743	0.001
$[\text{Mg}(\text{TTP})(\text{DMAP})_2]$	-4.108	-1.555	2.553	2.831	1.276	0.783	0.646

$$E_g \approx E_{\text{LUMO}} - E_{\text{HOMO}} ; \mu = -[E_{\text{HOMO}} + E_{\text{LUMO}}]/2 ; \eta = [E_{\text{LUMO}} - E_{\text{HOMO}}]/2 ; \sigma = 1/\eta$$

## Section 9. References

- [1] R. L. Hill, M. Gouterman, A. Ulman, Tetraphenylporphyrin Molecules Containing Heteroatoms Other Than Nitrogen. 7.1. Emission and Electronic Structure of Rings Containing Sulfur and Selenium, *Inorg. Chem.* 21 (1982) 1450–1455.
- [2] E. J. Shin, D. Kim, Substituent effect on the fluorescence quenching of various tetraphenylporphyrins by ruthenium tris(2,2'-bipyridine) complex, *J. Photochem. Photobiol. A* 152 (2002) 25–31.