SUPPORTING INFORMATION

Histamine-bound magnesium porphyrins: diverse coordination modes, inhibitory role in photodegradation of chlorophyll *a* and antioxidant activity

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Synthesis of ligand 5,10,15,20-tetrakis-(4-chlorophenyl)porphyrin, H_2T(4-Cl)PP. The ligand 5,10,15,20-tetrakis-(4-chlorophenyl)porphyrin, H_2T(4-Cl)PP was synthesized by refluxing 10.13 g 4-chlorobenzaldehyde (72 mmol) and 5 mL pyrrole (72 mmol) in 250 mL propionic acid following the reported procedure [1]. The yield of the compound was 20%. Molecular Formula: $C_{44}H_{26}Cl_4N_4$; Molecular Weight: 752.52; UV/Visible bands are at λ_{max}/nm (ε/$M^{-1}cm^{-1}$) (in CH_2Cl_2, 10^{-6} M): 418 (584000 $Lmol^{-1}cm^{-1}$), 514 (40000 $Lmol^{-1}cm^{-1}$), 549 (24000 $Lmol^{-1}cm^{-1}$), 589 (19200 $Lmol^{-1}$ cm^{-1}) and 647 (16800 $Lmol^{-1}cm^{-1}$), respectively. Elemental analysis calcd. (%) for $C_{44}H_{26}Cl_4$ N_4: C 70.23, H 3.48, N 7.45; Found: C 70.32, H 3.53, N 7.50.

Synthesis of ligand 5,10,15,20-tetrakis-(4-bromophenyl)porphyrin, H_2T(4-Br)PP. The ligand 5,10,15,20-tetrakis-(4-bromophenyl)porphyrin, H_2T(4-Br)PP was synthesized by refluxing 13.33 g 4-bromobenzaldehyde (72.06 mmol) and 5 mL pyrrole (72.06 mmol) in 250 mL propionic acid following the reported procedure. Yield: 30%. Molecular Formula: $C_{44}H_{26}Br_4N_4$; Molecular Weight: 930.32; UV/Vis (in CH_2Cl_2, 10^{-6} M) λ_{max}/nm (ε): 419 (560000 $Lmol^{-1}cm^{-1}$), 514 (40000 $Lmol^{-1}cm^{-1}$), 549 (24000 $Lmol^{-1}cm^{-1}$), 589 (16000 $Lmol^{-1}$ cm^{-1}) and 646 (11200 $Lmol^{-1}cm^{-1}$), respectively. Elemental analysis calcd. (%) for $C_{44}H_{26}Br_4N_4$: C 56.81, H 2.82, N 6.02; Found: C 56.90, H 2.92, N 6.11.

Synthesis of 5,10,15,20-tetrakis-(4-bromophenyl)porphyrinato magnesium(II), Mg^{II}T(4-Br)PP. Compound Mg^{II}T(4-Br)PP was synthesized following procedure reported for Mg^{II}T(4-Cl)PP). Yield: 80%. Molecular Formula: $C_{44}H_{24}Br_4MgN_4$; Molecular Weight: 952.61; UV/Vis (in CH_2Cl_2) λmax/nm (ε): 426 (624000 $Lmol^{-1}cm^{-1}$), 563 (24000 $Lmol^{-1}cm^{-1}$), 603 (16000 $Lmol^{-1}cm^{-1}$); Elemental analysis calcd. (%) for $C_{44}H_{24}Br_4MgN_4$: C 55.48, H 2.54, N 5.88; Found: C 55.59, H 2.64, N 5.97.

Synthesis of the complex [Mg^{II}T(4-Br)PP(hist)] 2. A sample of Mg^{II}T(4-Br)PP (20 mg, 0.02 mmol) was mixed with histamine (5 mg, 0.04 mmol) in 3 mL of chloroform. Crystals were obtained by slow diffusion of n-hexane through the chloroform solution over a period of one week. Molecular Formula: $C_{49}H_{32}Br_4MgN_7$; Molecular Weight: 1062.73; UV/Vis (in CH_2Cl_2) λmax/nm (ε): 429 (648000 $Lmol^{-1}cm^{-1}$), 567 (32000 $Lmol^{-1}cm^{-1}$), 607 (24000 $Lmol^{-1}cm^{-1}$); Elemental analysis calcd. (%) for $C_{49}H_{32}Br_4MgN_7$: C 65.05, H 4.25, N 14.05; Found: C 65.05, H 4.25, N 14.05. IR: Characteristics peaks at 3420, 3097, 2946, 1636, 1511, 1470, 1385, 1328, 1200, 1096, 1066, 996, 795, 746, 723 and 463 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$,298 K): δ(ppm) 8.76 (s, 8H, β-pyrrole), 7.98-8.00 (d, 8H, *o*-H, meso-phenyl), 7.77-7.79 (d, 8H, *m*-H, meso-phenyl), 7.24(s, 1H, CH-imidazole/hist), 6.55 (s, 1H, CH-imidazole/hist), 3.40 (m, 2H, NH-amine/hist), 2.82-2.85 (m, 2H, -CH_2/hist), 2.53-2.56 (m, 2H, -CH_2/hist).

Isolation of chlorophyll *a* from spinach. Chlorophyll *a* was isolated and purified from spinach leaves following the reported method [2] and the purity was checked by UV-Visible spectroscopy.

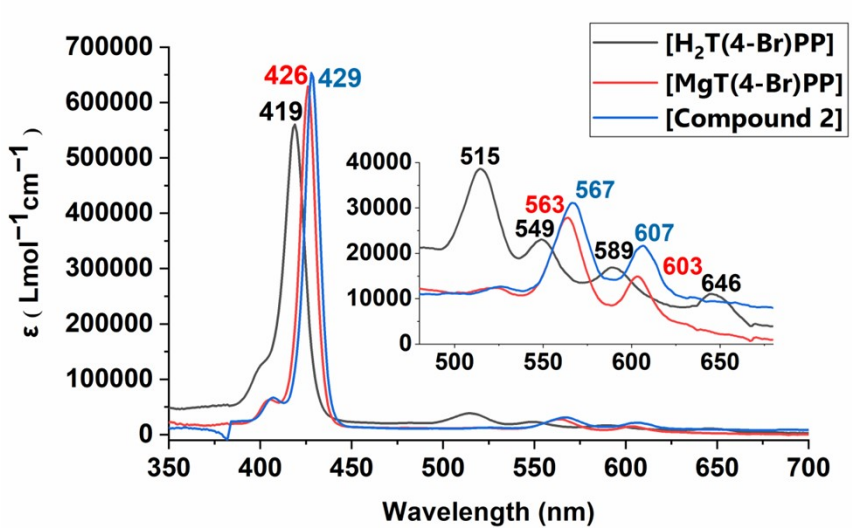
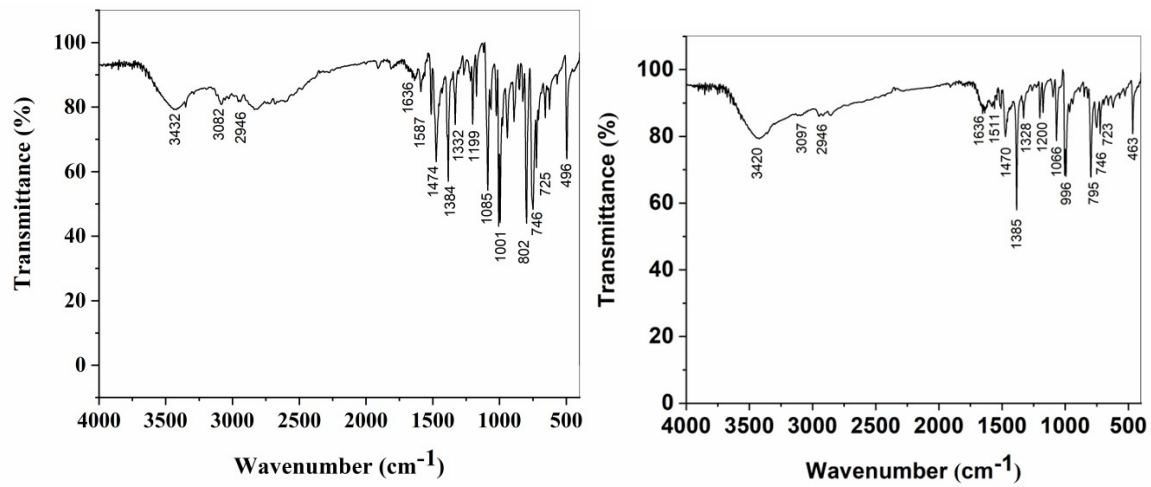


Figure S1. UV–Vis absorption spectra of H_2T(4-Br)PP, [Mg^{II}T(4-Br)PP], and **2** in DCM (1.25×10^{-6} M) at room temperature. The inset shows enlarged views of Q bands.



(A) (B)

Figure S2. IR spectra of A) **1** and B) 2.

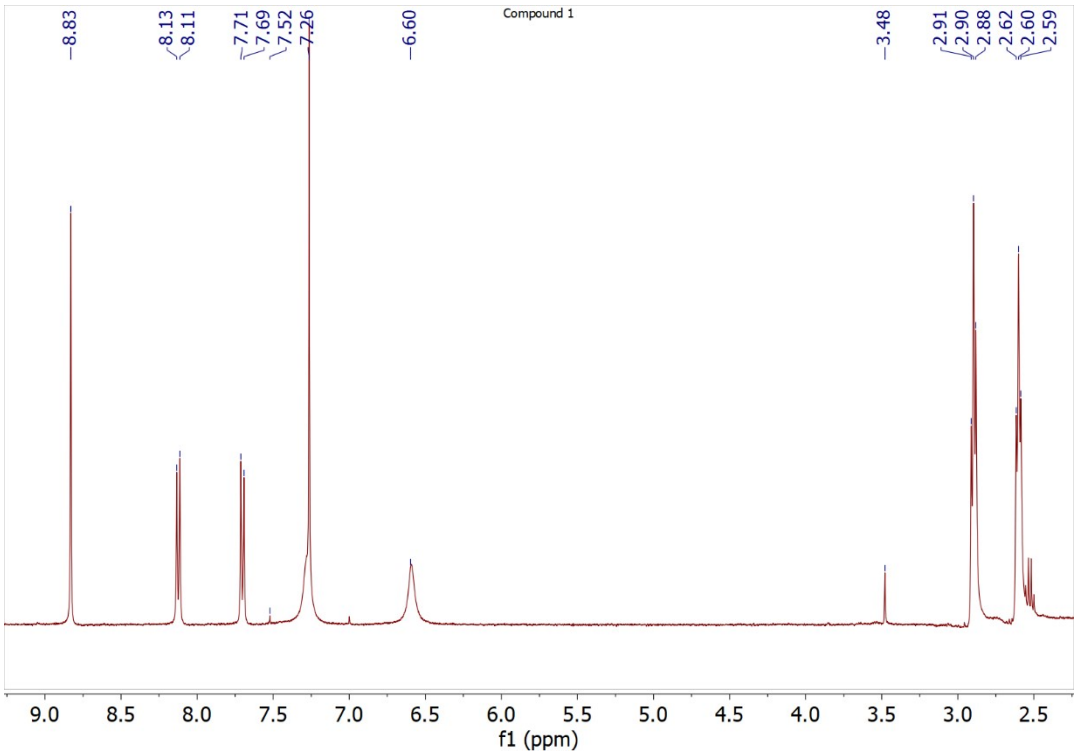


Figure S3: [1]H NMR spectrum of compound 1.

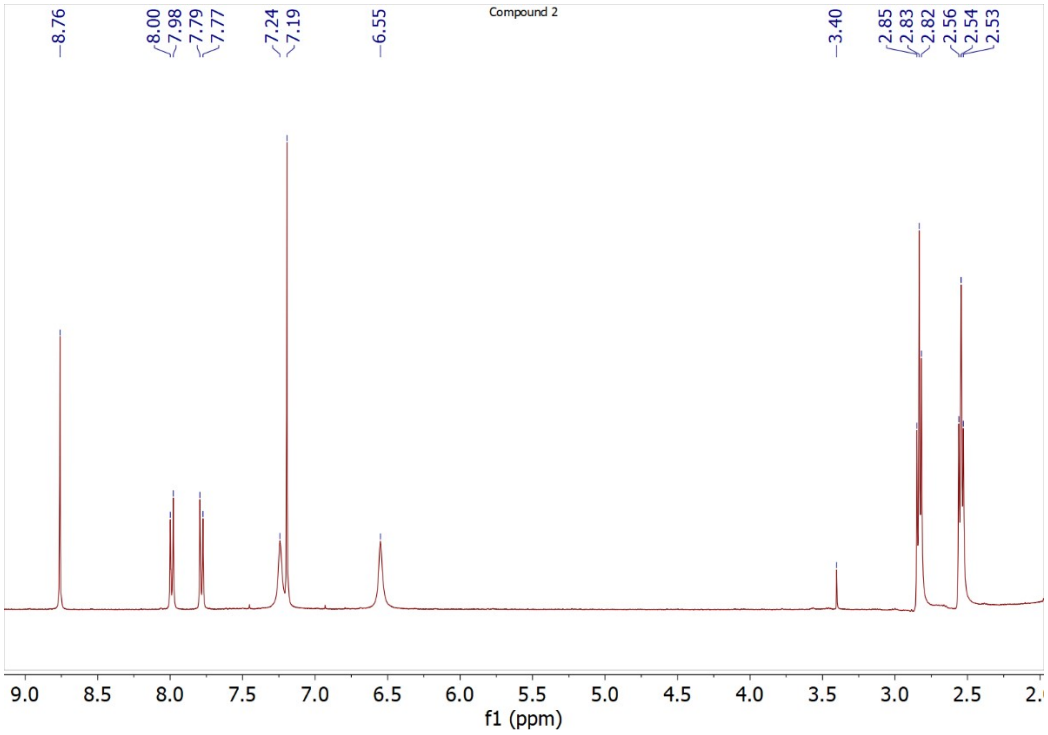


Figure S4: [1]H NMR spectrum of compound 2.

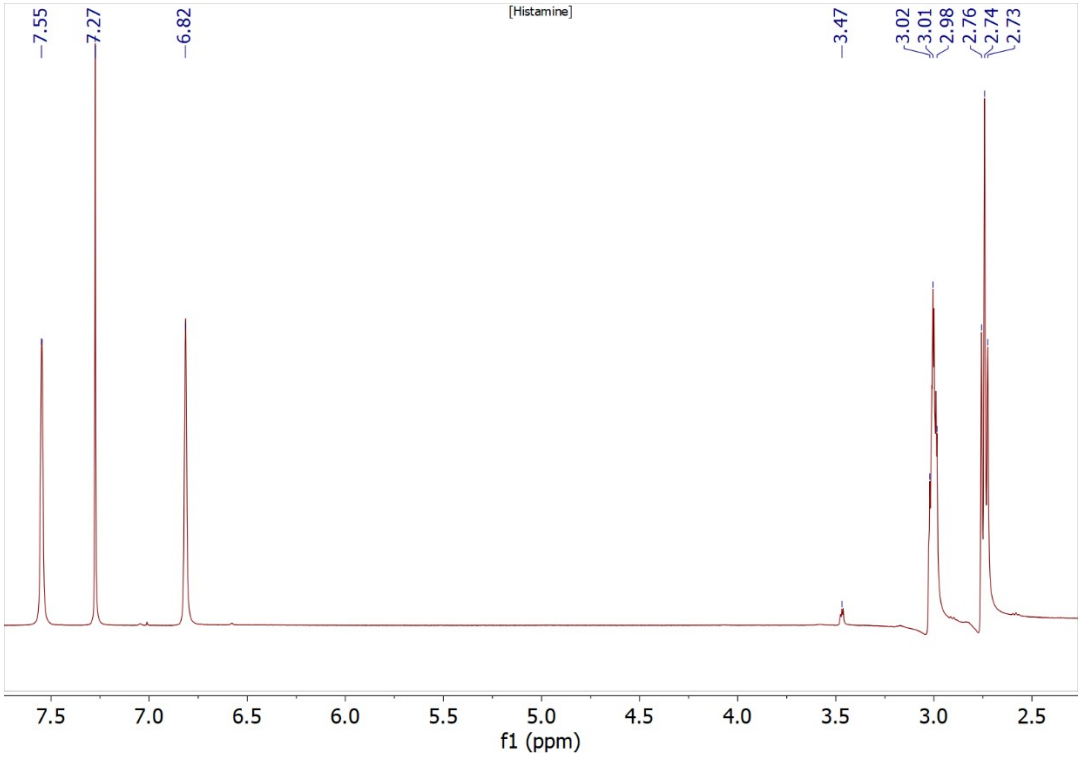


Figure S5: ^{1}H NMR spectrum of histamine.

Table S1. Selected experimental and theoretical (optimized) (i) bond lengths (Å) and (ii)angles (°) of compound **1** and **2**

	Crystal structure		Optimized structure	
(i) Bond lengths(Å)	Compound 1	Compound 2	Compound 1	Compound 2
Mg−N1	2.079(3)	2.076(5)	2.096	2.102
Mg−N1’	2.079(3)		2.096	
Mg−N2	2.080(3)	2.106(5)	2.095	2.102
Mg−N2’	2.080(3)		2.095	
Mg−N3	2.300(3)	2.088(5)	2.313	2.109
Mg−N3’	2.300(3)		2.313	
Mg−N4		2.089(5)		2.110
Mg−N5		2.145(5)		2.221

	Crystal structure		Optimized structure	
(ii)Angles (°) Compound 2	Compound 1		Compound 2	Compound 1
N3−Mg−N3’	180.00(15)		180.00	
N1−Mg−N1’	180.00(1)		180.00	
N2−Mg−N2’	180.00(1)		180.00	
N1−Mg−N3	89.06(11)	158.5(2)	89.69	159.46
N1’−Mg−N3	90.93(11)		90.30	
N1−Mg−N3’	90.94(11)		90.30	
N1’−Mg−N3’	89.06(11)		89.69	
N2−Mg−N3	89.84(11)		85.48	
N2’−Mg−N3	90.16(11)		94.52	
N2−Mg−N3’	90.16(11)		94.52	
N2’−Mg−N3’	89.84(11)		85.48	
N1−Mg−N2	89.80(11)	87.9(2)	89.69	87.95
N1−Mg−N2’	90.20(11)		90.31	
N1’−Mg−N2	90.20(11)		90.31	
N1’−Mg−N2’	89.80(11)		89.69	
N1−Mg−N4		87.8(2)		88.33
N1−Mg−N5		105.2(2)		102.95
N2−Mg−N5		105.4(2)		106.54
N3−Mg−N5		96.2(2)		97.48
N4−Mg−N5		99.4(2)		95.63

Table S2. Selected (i) bond lengths (Å) and (ii) bond angles (°) for [Mg^{II}T(4-Cl)PP(Hist)$_2$] **1**, [Mg^{II}T(4-Br)PP(hist)] **2** and several related complexes

(i) Complex	M—N_p[a]	M--X_L[b]	M--P_C[c]	Ref.
Pentacoodinated Magnesium(II) porphyrins				
[MgT(4-Br)PP(Hist)]	2.090(5)	2.145(5)	0.421	this work
[Mg(TPP)(H_2O)][d]	2.092(7)	2.012 (6)	0.460	[3]
[MgT(4-Cl)PP(DMAP)][e]	2.082 (3)	2.130 (4)	0.3709	[4]
[Mg(TPBP)(4,4'-bpy)$_2$][f,g]	2.065 (2)	2.319-2.290	0.072	[5]
Hexacoordinated Magnesium(II) porphyrins				
[MgT(4-Cl)PP(Hist)$_2$]	2.079(3)	2.300(3)	0.000	this work
[Mg(TBrPP)(H_2O)$_2$][h]	2.069	2.221	0.000	[6]
[Mg(TPP)(H_2O)$_2$][d]	2.071	2.213	0.000	[7]
[Mg(TPP)(py)$_2$][d,i]	2.072	2.376	0.000	[8]
[Mg(TPP)(HMTA)$_2$][d,j]	2.067(5)	2.473(2)	0.000	[9]

(ii) Complex	Bond angles (°)	Ref.
[MgT(4-Br)PP(Hist)]	105.2 (N1(por)-Mg-N5(axial))	This work
[Mg(TPP)(H_2O)][d]	97.6 (N(por)-Mg-O(axial))	3
[MgT(4-Cl)PP(DMAP)][e]	98.36 (N1(por)-Mg-N(axial))	4
[Mg(TPBP)(4,4'-bpy)$_2$][f,g]	88.30 (N1(por)-Mg-N3(axial))	5
	91.70 (N1(por)-Mg-N4(axial))	
[MgT(4-Cl)PP(Hist)$_2$]	89.06 (N1(por)-Mg-N3(axial))	This work
	90.94 (N1(por)-Mg-N3'(axial))	
[Mg(TPP)(py)$_2$][d,i]	94.07 (N(por)-Mg-N(axial))	8
[Mg(TPP)(HMTA)$_2$][d,j]	90.21 (N1(por)-Mg-N3(axial))	9

[a]M-N_p = average equatorial metal-nitrogen pyrrole distance

[b]M-X_L = metal-axial ligand distance

[c]M-P_C = distance between the metal atom and the mean plane made by the 24-atom core of the porphyrin (PC)

d: *meso*-tetraphenylporphyrin

e: DMAP: [4-(dimethylamino)pyridine]

f: TPBP = meso-tetrakis(4-bromophenyl)porphyrinato

g: 4,4'-bpy = 4,4-bipyridine

h: TBrPP = meso-tetrakis(4-bromophenyl)porphyrinato

i: py = pyridine

j: HTMA = hexamethylenetetramine

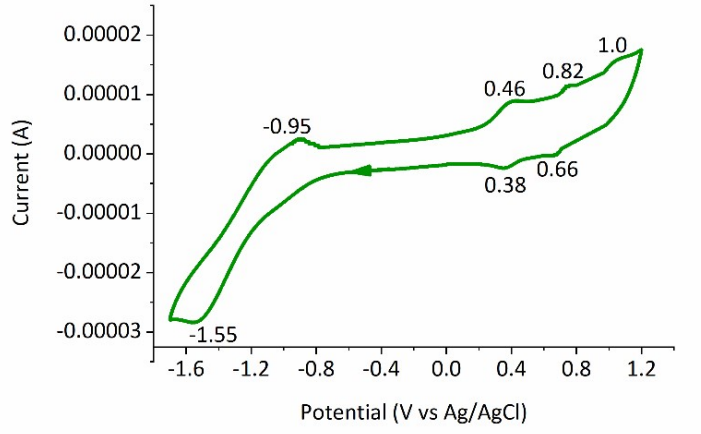


Figure S6. Cyclic voltammogram of compound 1 (10^{-3} M) in dry DCM with scan rate 0.1 V/s.

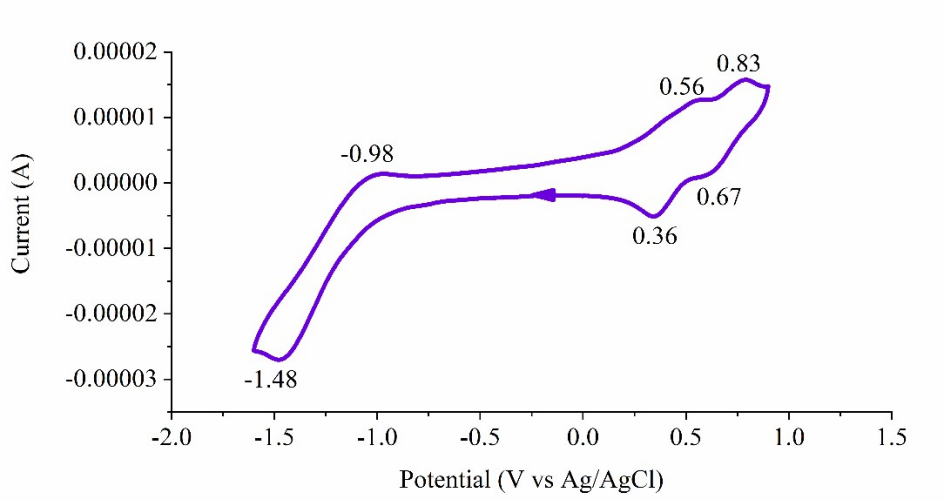


Figure S7. Cyclic voltammogram of [MgT(4-Cl)PP] (10^{-3} M) in dry DCM with scan rate 0.1 V/s.

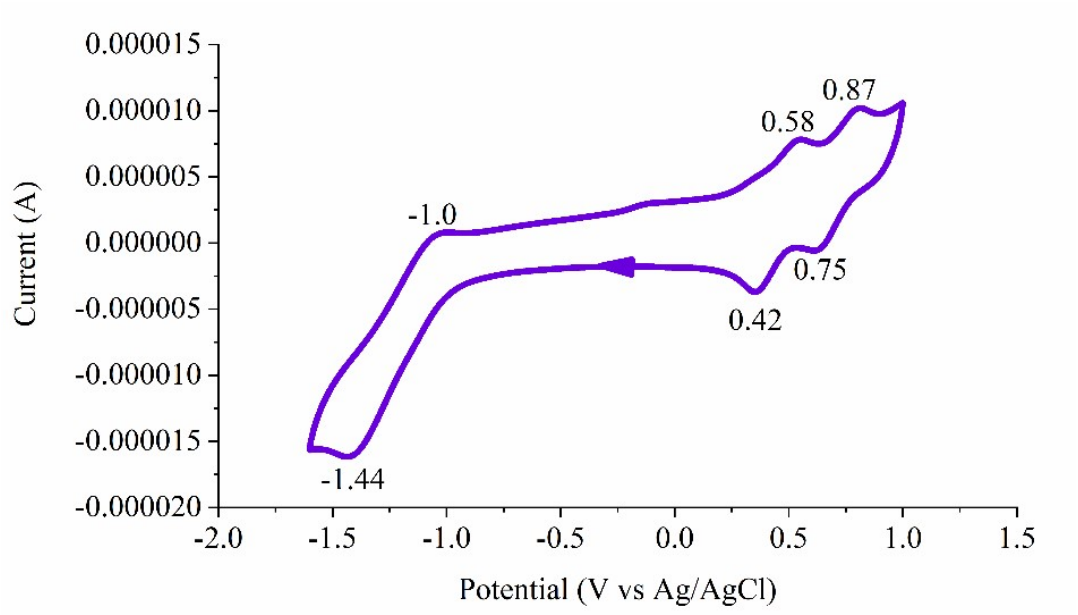


Figure S8. Cyclic voltammogram of [MgT(4-Br)PP] (10^{-3} M) in dry DCM with scan rate 0.1 V/s.

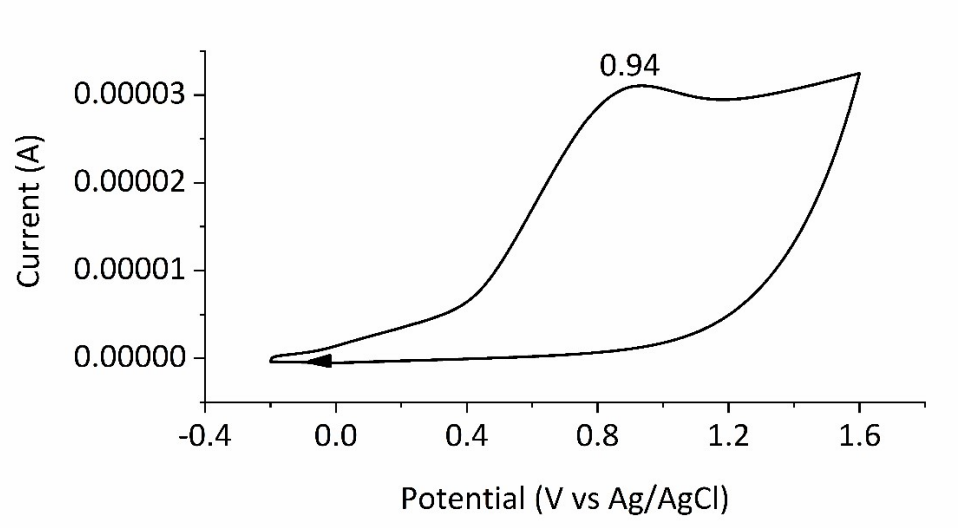


Figure S9. Cyclic voltammogram of histamine (10^{-3} M) in dry DCM with scan rate 0.1 V/s.

Table S3. Comparison of antioxidant activities of reported Mg-porphyrins

Mg-porphyrin complexes	Antioxidant activity (100 µg/mL) %	Reference
[Mg(TBrPP)(4,4′ -bpy)]	60	10
[Mg(TBrPP)$(pyz)_2$]	40	10
[Mg(TClPP)]	30	4
[Mg(TClPP)(DMAP)]	51	4
[MgTPP]	70.99	11
[MgTPP(DMF)]	75.57	11
[MgT(4-Cl)PP$(Hist)_2$]	92.45	This work
[MgT(4-Br)PP(Hist)]	86.88	This work

4,4′-bpy = 4,4′-bipyridine

pyz = pyrazine

DMAP = 4-(dimethylamino)pyridine)

DMF= Dimethylformamide

Table S4. Electronic transitions of compound **2** calculated in dichloromethane using the TD-DFT method.

Most important orbital excitations	Theoretical λ_{max}	f	Experimental λ_{max} (ϵ)
H-1→L+1, H→L	566	0.0587	607 (24000)
H-1→L, H→L+1	562	0.0421	566 (32000)
H-2→L, H-2→L+1	420	0.008	429 (648000)

λ : wavelength (nm); ϵ: molar absorption coefficient (dm^3 mol^{-1} cm^{-1}); f : oscillator strength; H : highest occupied molecular orbital(HOMO); L : lowest unoccupied molecular orbital(LUMO).

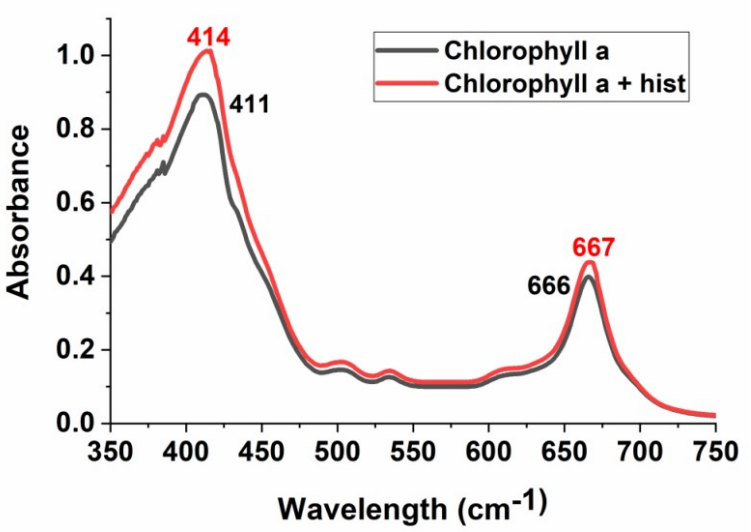


Figure S10. Electronic spectra of chlorophyll *a* (10^{-5} M in DCM) and chlorophyll *a* in the presence of histamine (10^{-4} M in DCM).

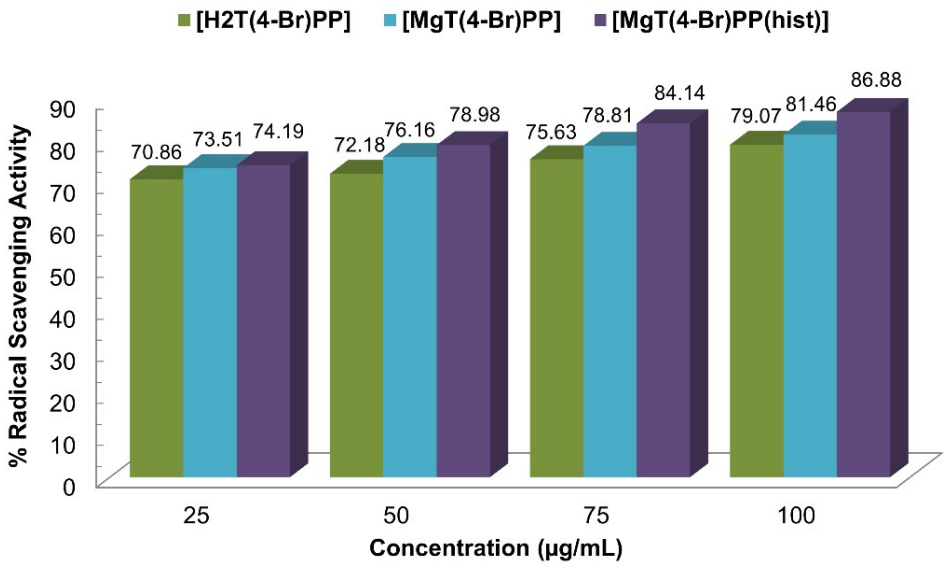


Figure S11. DPPH radical scavenging activity of H_2T(4-Br)PP, [Mg^{II}T(4-Br)PP], and **2** at different concentrations.

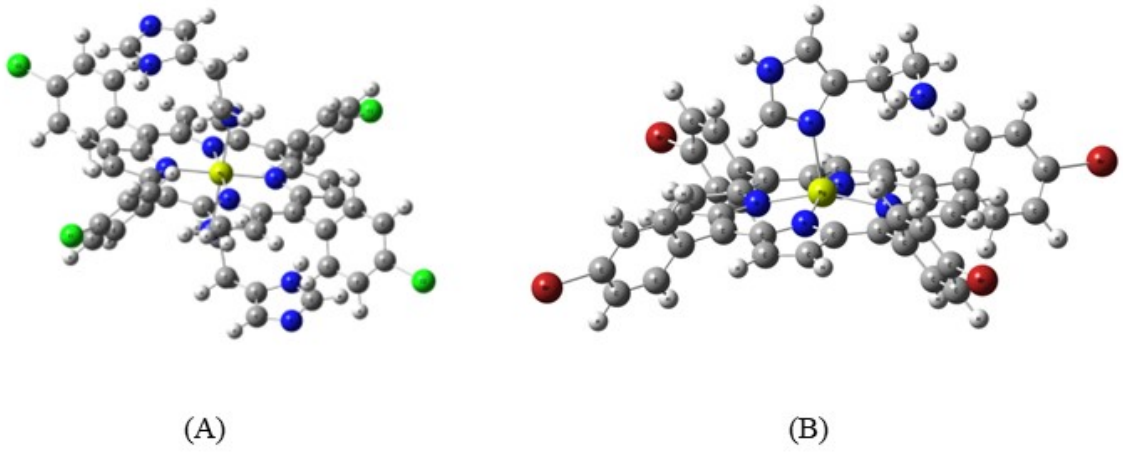


Figure S12. Optimized molecular structure of A) compound **1** and B) compound **2.**

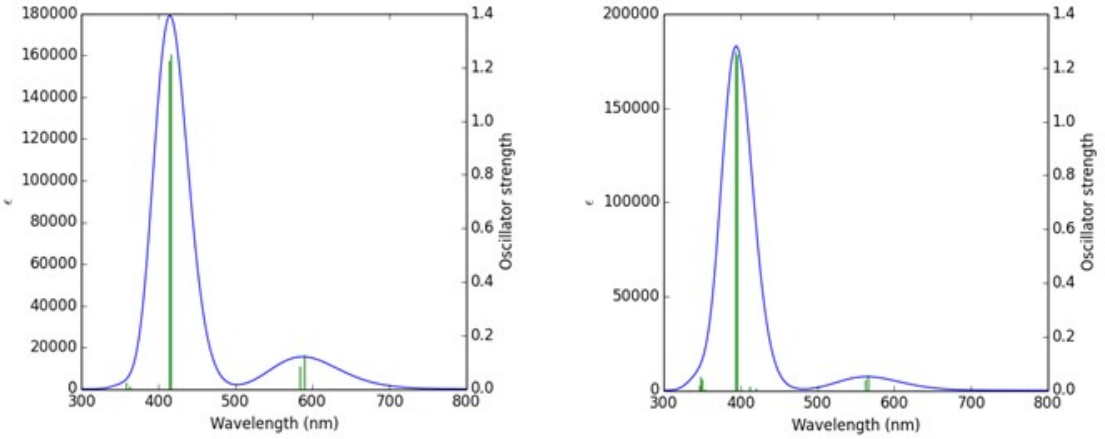


Figure S13. The simulated electronic spectrum of A) compound **1** and B) **2** obtained from theoretical calculation.

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Comments of Checkcif

Alert level of compound 1

PLAT430_ALERT_2_B Short Inter D...A Contact N4 ..N4 . 2.85 Ang.
-x,1-y,2-z = 2_567 Check

Response: The short N-N bond distance is due to the H-bonding interaction present in the structure.

PLAT430_ALERT_2_B Short Inter D...A Contact N5 ..N5 . 2.86 Ang.
1-x,1-y,2-z = 2_667 Check

Response: The short N-N bond distance is due to the H-bonding interaction present in the structure.

PLAT934_ALERT_3_B Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. 3 Check

Response: The variation is due to the reason that checkcif does the calculation in a different way than SHELXL. This is not really an issue.

PLAT990_ALERT_1_B Deprecated .res/.hkl Input Style SQUEEZE Job ... ! Note

The above B alert is due to disorders in the lattice solvent molecules. We have refined the data with the squeeze command by PLATON software. The alert level B arises due to the disorders in the crystal.

Alert level B of compound 2

PLAT353_ALERT_3_B Long N-H (N0.87,N1.01A) N7 - H7B . 1.08 Ang.

Response:

The N7 atom participates in a strong H-bonding with the imidazole/histamine ring nitrogen. This relatively long N7-H7B bond is due to H-bonding which is discussed in the paper.

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.97Ang From C49 3.03 eA-3

Response: The above B alert is due to disorders in the lattice solvent molecules.

PLAT971_ALERT_2_B Check Calcd Resid. Dens. 0.97Ang From C49 2.86 eA-3

Response: The above B alert is due to disorders in the lattice solvent molecules.

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Response: The above B alert is due to disorders in the lattice solvent molecules. We have refined the data with the squeeze command by PLATON software. The alert level B arises due to the disorders in the crystal.