Supplementary Material (ESI) for New Journal of Chemistry

Design and synthesis of water soluble (metallo)porphyrins with pendant arms: studies of binding to xanthine oxidase

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Electronic Supplementary Information

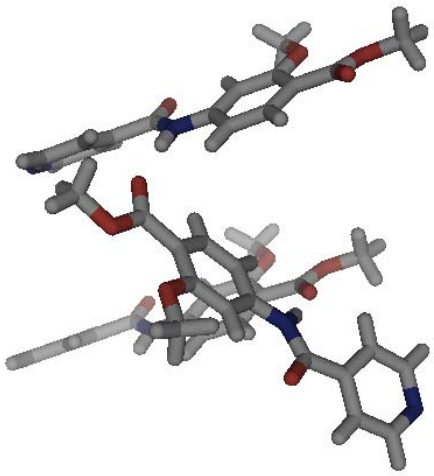


Figure S1. Capped-stick representation of the higher order solid state structure of 2, colours correspond to atom types: carbon: grey; hydrogen: white; nitrogen: blue; oxygen: red.

Table S1. Torsion angles [°] for **2**.

O(2)-C(1)-C(2)-C(7)	-12.45(15)
O(1)-C(1)-C(2)-C(7)	166.31(9)
O(2)-C(1)-C(2)-C(3)	166.15(11)
O(1)-C(1)-C(2)-C(3)	-15.09(15)
C(1)-C(2)-C(3)-O(3)	2.03(15)
O(4)-C(8)-C(9)-C(10)	24.21(15)
N(1)-C(8)-C(9)-C(10)	-155.31(10)
O(4)-C(8)-C(9)-C(13)	-153.76(11)
N(1)-C(8)-C(9)-C(13)	26.72(15)
N(2)-C(12)-C(13)-C(9)	0.36(17)
O(4)-C(8)-N(1)-C(5)	4.27(17)
C(9)-C(8)-N(1)-C(5)	-176.23(9)
C(4)-C(5)-N(1)-C(8)	2.93(17)
C(6)-C(5)-N(1)-C(8)	-178.71(10)
O(2)-C(1)-O(1)-C(14)	-3.14(15)
C(2)-C(1)-O(1)-C(14)	178.07(9)
C(4)-C(3)-O(3)-C(15)	-2.42(15)
C(2)-C(3)-O(3)-C(15)	177.92(9)

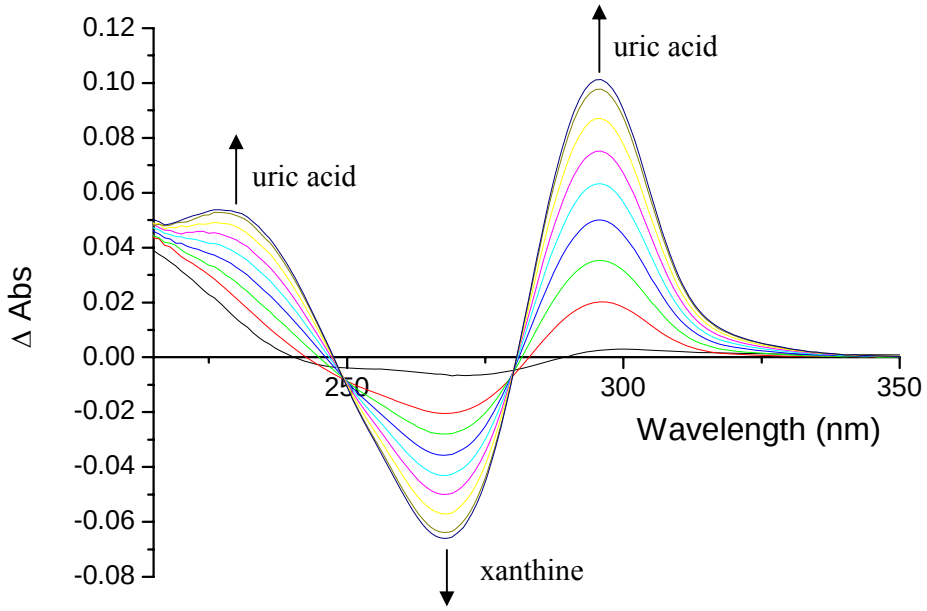


Figure S2. Difference spectra recorded at different times throughout a typical xanthine oxidase bioassay.

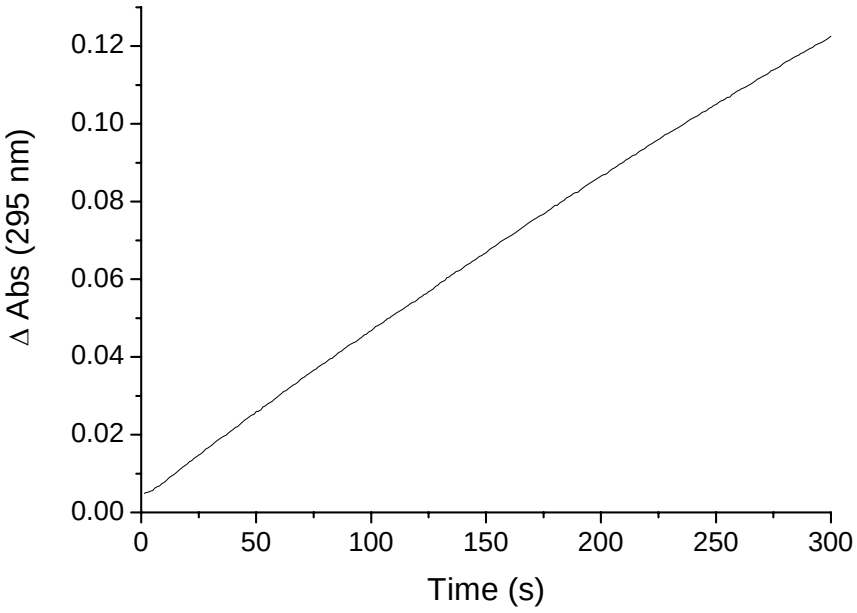


Figure S3. Plot of change in absorption at 295 nm against time.

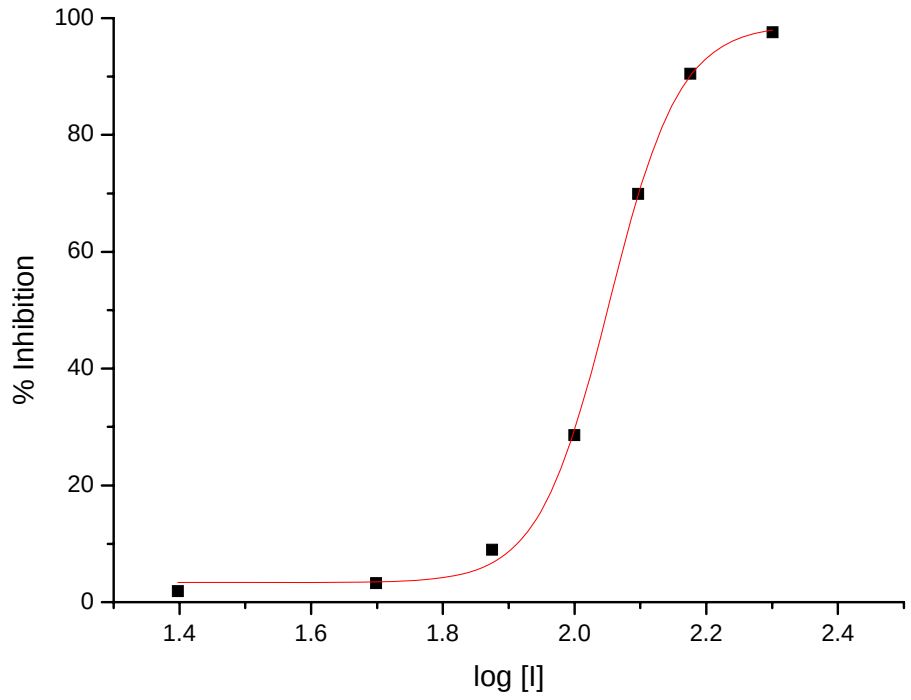


Figure S4. Plot of % inhibition vs. log [I] ([I] in μM) where I = [**8**][Cl]$_3$. IC_{50} = 113 ± 1 μM. χ^2 = 2.66, R^2 = 0.999.

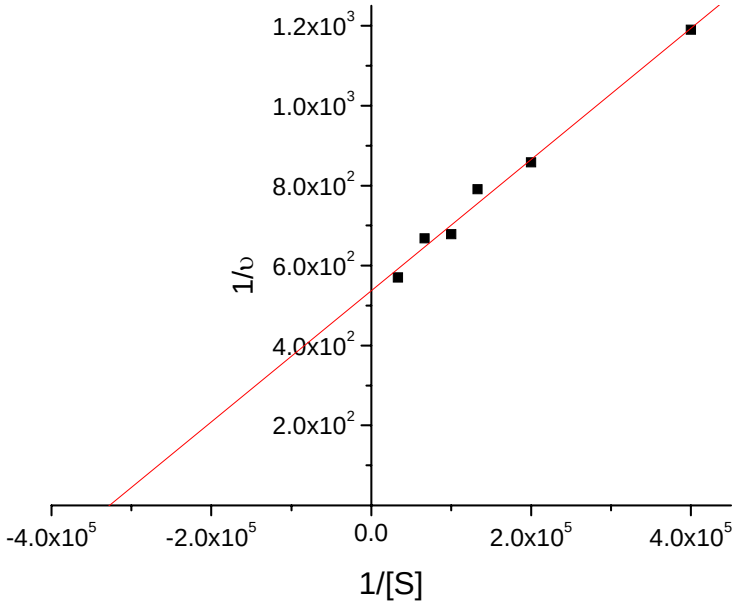
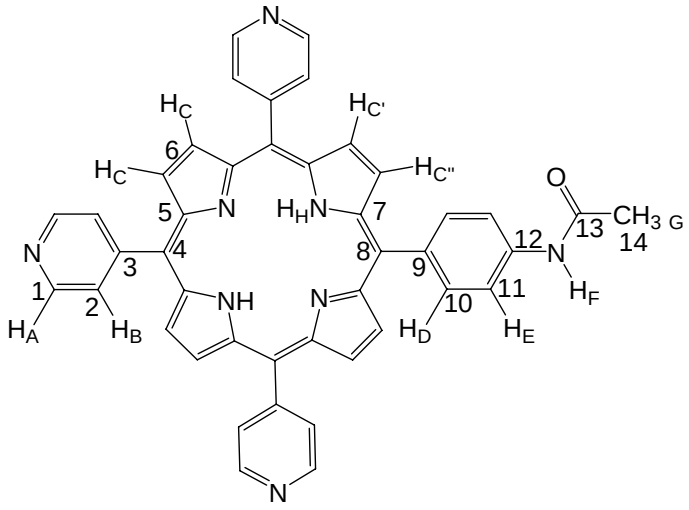


Figure S5. Example plot of 1/ υ against 1/[S] used to determine K_m. [S] in μM. $1/V_{max}$ = 537, K_m/V_{max} = 0.00164, K_m = 3.05 μM.

NMR tables

Free base m*eso*-5-10,15,-tris(4-pyridyl)-20-(4-acetamidophenyl) porphyrin.



Free base m*eso*-5-10,15,-tris(4-pyridyl)-20-(4-acetamidophenyl) porphyrin with atom labels: letters assigned to protons and numbers assigned to carbons.

Label	δ	Integration	Multiplicity	Type	COSY to ^{1}H at δ	Lit[1]
A	9.05	6	m	CH × 6	8.14	9.05
B, D	8.14	8	m	CH × 8	7.94, 9.05	8.10, 8.00
C	8.84 8.94 8.81	4 2 2	s d d	CH × 8 CH × 2 CH × 2	none 8.81 8.94	8.85 9.05
E	7.94	2	d	CH × 2	8.14	7.10
F	7.74	1	s	NH	none	none
G	2.38	3	s	CH_3	none	1.95
H	–2.89	2	s	NH × 2	none	-2.95

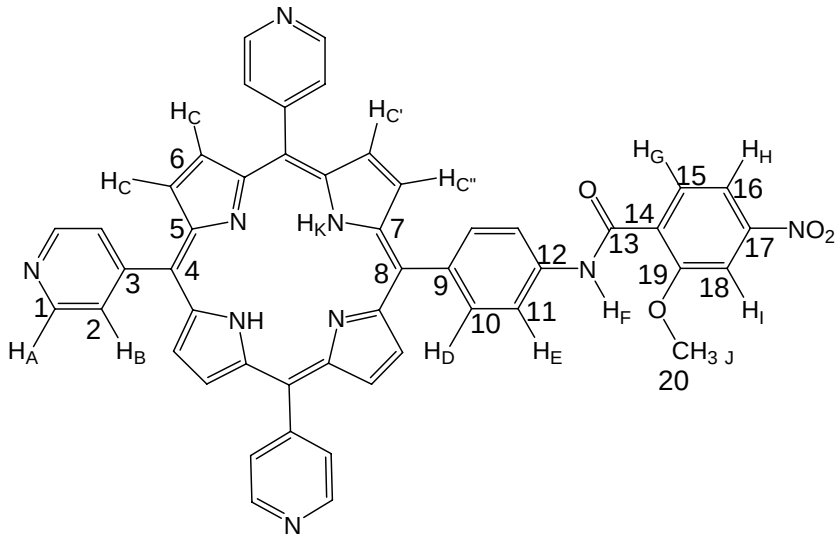
Table S2. Assignment of ^{1}H NMR chemical shifts for free base m*eso*-5-10,15,-tris(4-pyridyl)-20-(4-acetamidophenyl) porphyrin in $CDCl_3$.

[1] H. Li, O. S. Fedorova, A. N. Grachev, W. R. Trumble, G. A. Bohach and L. Czuchajowski, *Biochim. Biophys. Acta*, 1997, **1354**, 252.

Label	δ	Type	HMQC to ^{1}H at δ	HMBC to ^{1}H at δ
1	148.5	CH	9.05	8.14
2	129.4	CH	8.14	9.05
3	117.5	Q	none	8.14
4	117.1	Q	none	8.14
5	150.1	Q	none	9.05
7	150.0	Q	none	9.05
8	138.1	Q	none	8.14
9	121.2	Q	none	8.14
10	135.2	CH	8.14	8.14
11	118.2	CH	7.94	7.74
12	137.4	Q	none	7.94
13	168.8	Q	none	2.38
14	24.9	CH_3	2.38	none

Table S3 Assignment of ^{13}C NMR chemical shifts for free base m*eso*-5-10,15,-tris(4-pyridyl)-20-(4-acetamidophenyl) porphyrin in $CDCl_3$.

Free base 5,10,15-tris(4-pyridyl)-20-[4-[(2-methoxy-4-nitro-phenyl carbonyl)-amino] phenyl] porphyrin, 3.



3 with atom labels: letters assigned to protons and numbers assigned to carbons.

Label	δ	Integration	Multiplicity	Type	COSY to ^{1}H at δ	10
A	9.05	6	d	CH × 6	8.17	7.78
B	8.17	6	d	CH × 6	9.05	8.26
C	8.85 8.97	6 2	m d	CH × 6 CH × 2	8.97 8.85	8.89
D	8.23	2	d	CH × 2	8.11	8.29
E	8.11	2	d	CH × 2	8.23	8.11
F	10.02	1	s	NH	none	9.99
G	8.58	1	d	CH	8.04	8.58
H	8.04	1	dd	CH	7.98, 8.58	8.05
I	7.98	1	d	CH	8.04	7.96
J	4.29	3	s	CH_3	none	4.31
K	–2.88	2	s	NH × 2	none	-2.74

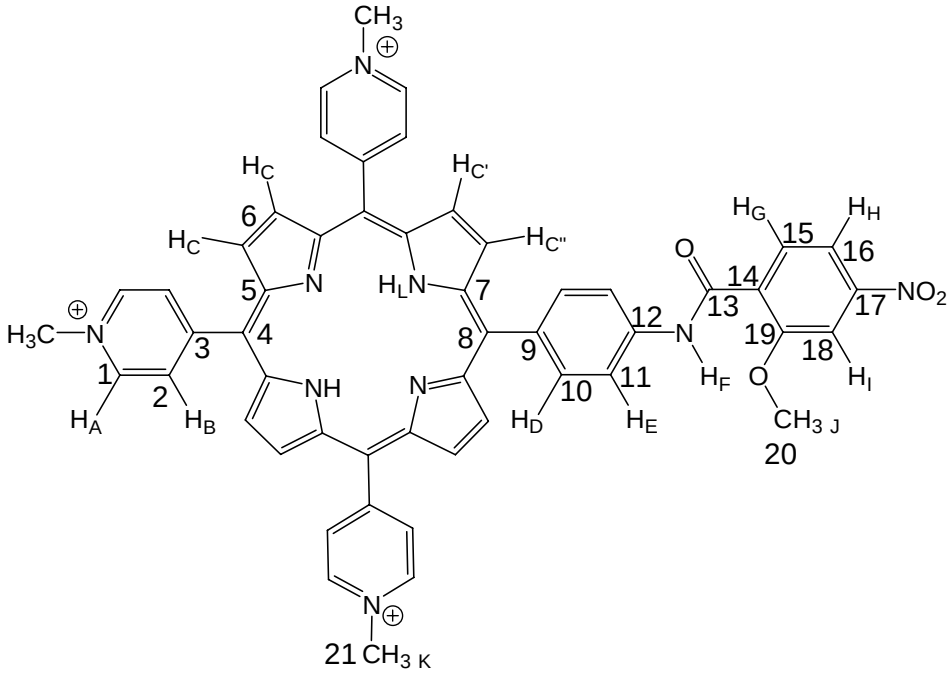
Table S4 Assignment of ^{1}H NMR chemical shifts for **3** in $CDCl_3$.

Label	δ	Type	HMQC to ^{1}H at δ	HMBC to ^{1}H at δ
1	148.3	CH	9.05	8.17
2	129.4	CH	8.17	9.05
3	117.5	Q	none	8.17
4	117.1	Q	none	none
5	150.2	Q	none	none
7	150.1	Q	none	none
8	138.0	Q	none	none
9	121.1	Q	none	8.23
10	135.3	CH	8.23	none
11	119.1	CH	8.11	4.29
12	137.9	Q	none	8.23, 8.11
13	161.6	Q	none	8.58
14	150.8	Q	none	8.58, 7.98

15	134.0	CH	8.58	none
16	116.6	CH	8.04	7.98
17	127.3	Q	none	8.04, 7.98
18	107.1	CH	7.98	none
19	157.4	Q	none	4.29, 8.58, 7.98
20	57.3	CH_3	4.29	none

Table S5 Assignment of ^{13}C NMR chemical shifts for **3** in $CDCl_3$.

Free base 5,10,15-tris(*N*-methyl-4-pyridiniumyl)-20-[4-[(2-methoxy-4-nitro-phenylcarbonyl)-amino] phenyl] porphyrin tris iodide, 4.



4 with atom labels: letters assigned to protons and numbers assigned to carbons.

Label	δ	Integration	Multiplicity	Type	COSY to ^1H at δ
A	9.49	6	d	CH × 6	4.73, 9.01
B	9.01	6	m	CH × 8	9.49
C	9.18 9.10	8	m	CH × 8	none
D, E	8.25	4	m	CH × 4	none

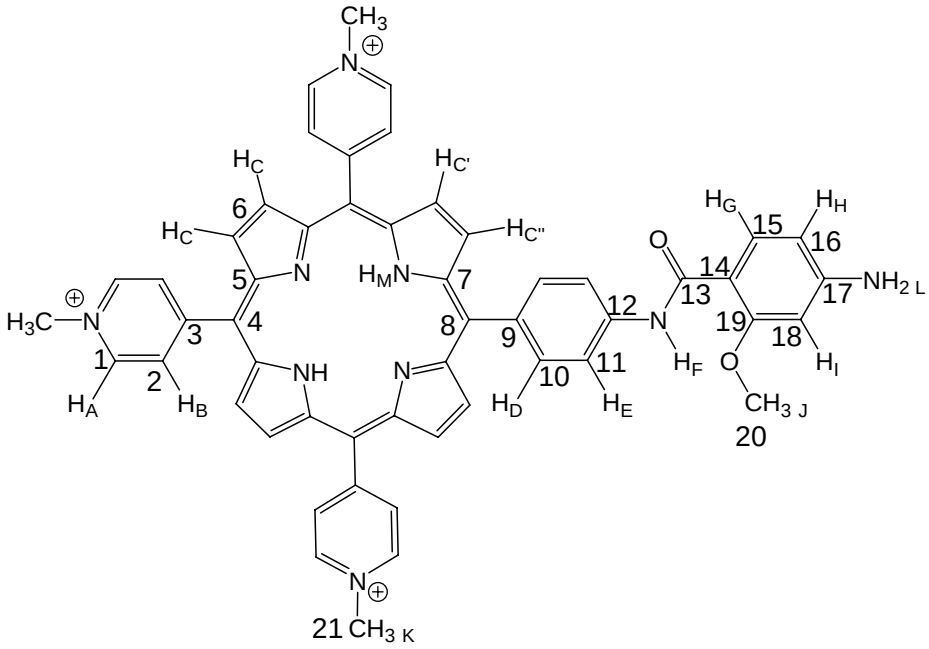
F	10.92	1	s	NH	none
G	7.94	1	m	CH	none
H	8.03	1	m	CH	7.94
I	8.03	1	s	CH	8.03
J	4.12	3	s	CH_3	none
K	4.73	9	s	CH_3 × 3	9.49
L	–2.98	2	s	NH × 2	none

Table S6 Assignment of ^{1}H NMR chemical shifts for **4** in d_6-DMSO.

Label	δ	Type	HMQC to ^{1}H at δ	HMBC to ^{1}H at δ
1	144.7	CH	9.49	4.73, 9.49, 9.01
2	132.6	CH	9.01	9.49, 9.18, 9.01
3	115.8	Q	none	9.01
4	115.0	Q	none	none
5	157.1	Q	none	none
7	157.0	Q	none	9.49
8	139.7	Q	none	8.25
9	123.2	Q	none	none
10	135.4	CH	8.25	none
11	118.7	CH	8.25	10.92
12	136.2	Q	none	8.25
13	164.5	Q	none	10.92
14	150.0	Q	none	8.03
15	130.6	CH	7.94	none
16	116.2	CH	8.03	none
17	127.6	Q	none	none
18	107.5	CH	8.03	none
19	157.4	Q	none	4.12, 8.04, 7.94
20	57.3	CH_3	4.12	none
21	48.5	CH_3	4.73	9.49

Table S7 Assignment of ^{13}C NMR chemical shifts for **4** in d_6-DMSO.

Free base 5,10,15-tris(*N*-methyl-4-pyridiniumyl)-20-[4-[(2-methoxy-4-amino-phenylcarbonyl)-amino] phenyl] porphyrin, 5.



5 with atom labels: letters assigned to protons and numbers assigned to carbons.

Label	δ	Integration	Multiplicity	Type	COSY to ^1H at δ
A	9.53	6	m	CH × 6	4.73, 9.00
B	9.00	6	m	CH × 6	9.53
C	9.13	8	m	CH × 8	none
D	8.21	2	d	CH × 2	8.19
E	8.19	2	d	CH × 2	8.21
F	10.21	1	s	NH	none
G	7.74	1	d	CH	6.33
H	6.33	1	dd	CH	7.74, 6.40
I	6.40	1	d	CH	6.33
J	4.01	3	s	CH_3	none
K	4.73	9	s	CH_3 × 3	9.53
L	5.97	2	br s	NH_2	none

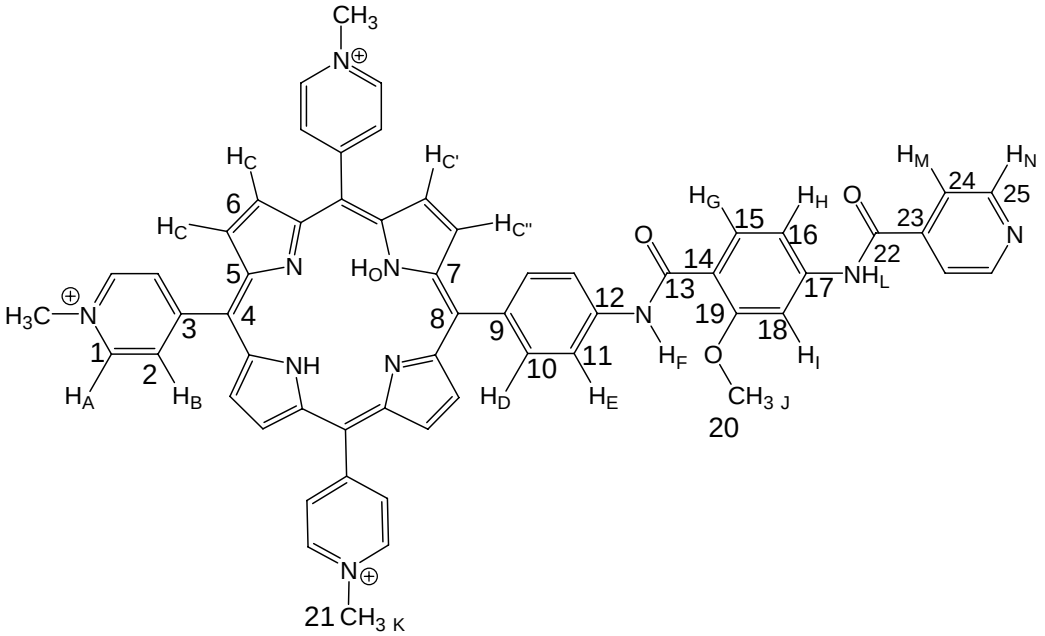
M	-2.99	2	s	NH × 2	none

Table S8 Assignment of ^{1}H NMR chemical shifts for [**5**][Cl]$_3$ in d_6-DMSO.

Label	δ	Type	HMQC to ^{1}H at δ	HMBC to ^{1}H at δ
1	144.7	CH	9.53	4.73, 9, 9.53
2	132.6	CH	9.00	9.53
3	115.8	Q	none	none
4	114.9	Q	none	none
5	157.1	Q	none	none
7	157.0	Q	none	9.53
8	140.3	Q	none	8.19
9	123.6	Q	none	none
10	135.4	CH	8.21	none
11	118.8	CH	8.24	10.21
12	135.7	Q	none	8.21
13	164.7	Q	none	none
14	154.6	Q	none	7.74
15	133.2	CH	7.74	none
16	107.0	CH	6.33	6.4
17	109.7	Q	none	6.33, 6.4
18	96.6	CH	6.40	none
19	159.6	Q	none	4.01, 7.74
20	56.3	CH_3	4.01	none
21	48.3	CH_3	4.73	9.53

Table S9 Assignment of ^{13}C NMR chemical shifts for [**5**][Cl]$_3$ in d_6-DMSO.

Free base 5,10,15-tris(*N*-methyl-4-pyridiniumyl)-20-[4-{(2-methoxy-4-[(pyridine-4-carbonyl)-amino]-phenylcarbonyl)-amino} phenyl]-porphyrin, 6.



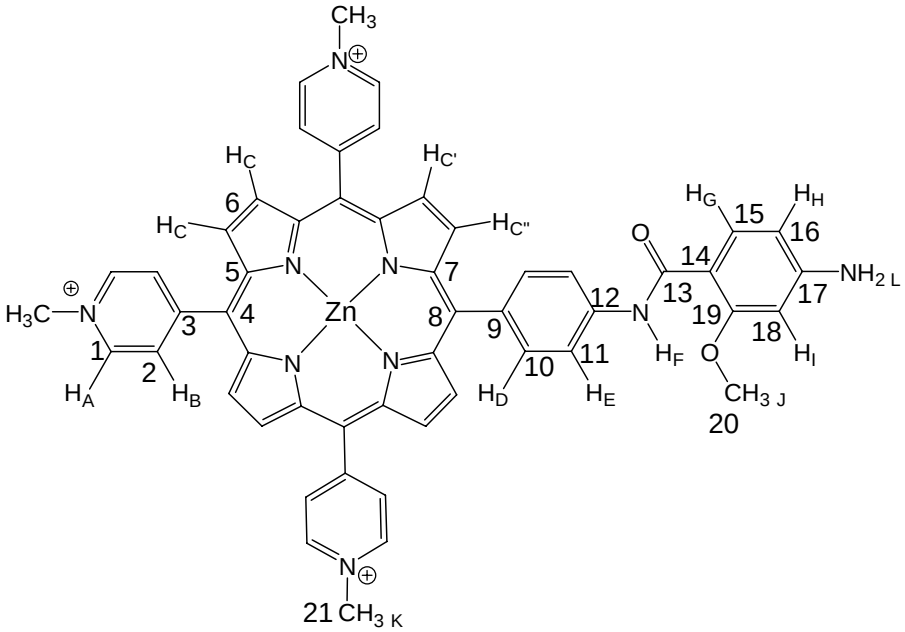
6 with atom labels: letters assigned to protons and numbers assigned to carbons.

Label	δ	Integration	Multiplicity	Type	COSY to ^{1}H at δ
A	9.55	6	m	CH × 6	4.75,9.01
B, M	9.01	8	m	CH × 8	9.55
C	9.10	8	m	CH × 8	none
D	8.29	2	d	CH × 2	8.23
E	8.23	2	d	CH × 2	8.23
F	11.35	1	s	NH	none
G	7.87	1	s	CH	7.72
H	7.72	1	d	CH	7.87
I	7.95	1	s	CH	none
J	4.06	3	s	CH_3	none
K	4.75	9	s	CH_3 × 3	9.55
L	10.58	1	s	NH	none
N	8.35	2	d	CH	9.01

O	–2.95	2	d	NH × 2	none

Table S10 Assignment of ^{1}H NMR chemical shifts for [**6**][Cl]$_3$ in d_6-DMSO.

Zinc 5,10,15-tris(*N*-methyl-4-pyridiniumyl)-20-[4-[(2-methoxy-4-amino-phenylcarbonyl)-amino] phenyl] porphyrin, 7.



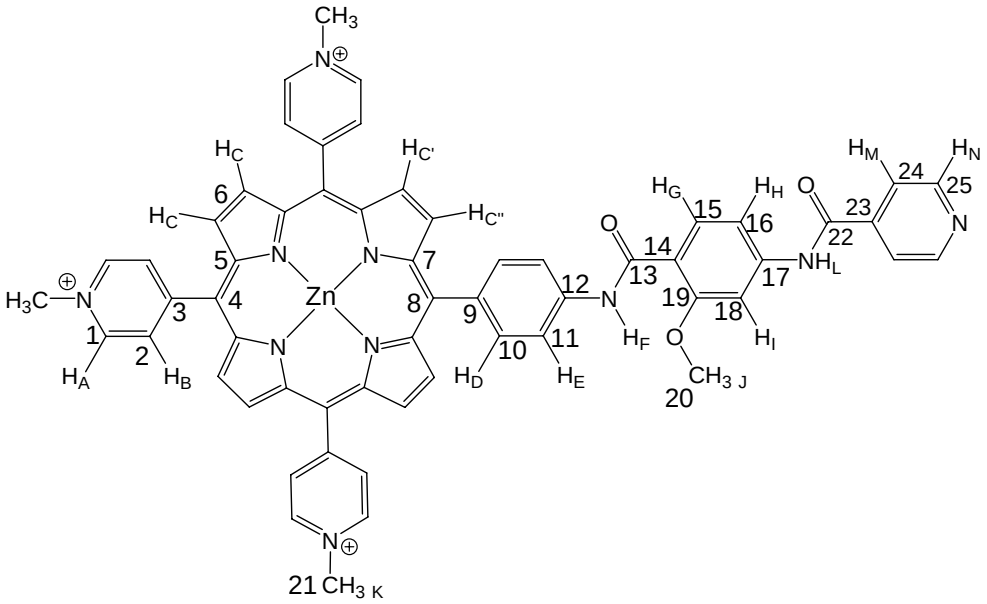
7 with atom labels: letters assigned to protons and numbers assigned to carbons.

Label	δ	Integration	Multiplicity	Type	COSY to ^{1}H at δ
A	9.41	6	m	CH × 6	4.70, 8.88
B	8.88	6	m	CH × 6	8.98
C	8.98	8	m	CH × 8	none
D	8.17	2	d	CH × 2	8.10
E	8.10	2	d	CH × 2	8.17
F	10.18	1	s	NH	none
G	7.76	1	s	CH	6.33
H	6.32	1	d	CH	7.76
I	6.39	1	s	CH	none
J	4.02	3	s	CH_3	none
K	4.70	9	s	CH_3 × 3	8.98

L	5.95	2	br s	NH_2	none

Table S11 Assignment of ^{1}H NMR chemical shifts for [**7**][Cl]$_3$ in d_6-DMSO.

Zinc 5,10,15-tris(*N*-methyl-4-pyridiniumyl)-20-[4-{(2-methoxy-4-[(pyridine-4-carbonyl)-amino]-phenylcarbonyl)-amino} phenyl]-porphyrin, 8.



8 with atom labels: letters assigned to protons and numbers assigned to carbons.

Label	δ	Integration	Multiplicity	Type	COSY to ^{1}H at δ
A	9.48	6	m	CH × 6	4.75,8.92
B	8.92	6	m	CH × 6	8.47
C	9.00	8	m	CH × 8	none
D	8.23	2	d	CH × 2	8.14
E	8.14	2	d	CH × 2	8.23
F	11.18	1	s	NH	none
G	7.82	1	s	CH	7.69
H	7.69	1	d	CH	7.82
I	7.91	1	s	CH	none
J	4.05	3	s	CH_3	none
K	4.75	9	s	CH_3 × 3	9.48
L	10.98	1	s	NH	none

M	8.81	2	d	CH	7.99
N	7.99	2	d	CH	8.81

Table S12 Assignment of ^{1}H NMR chemical shifts for [**8**][Cl]$_3$ in d_6-DMSO.