

Supporting Information for:

Supramolecular Chirogenesis in Zinc Porphyrins: Interaction with Bidentate Ligands, Formation of Tweezer Structures, and the Origin of Enhanced Optical Activity

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S2) Dependencies of the UV-vis absorbance, monitored at 410 nm (the most intense B transition, crosses) and the total CD amplitude (circles) of **1** upon the molar excess of **2_{SS}**. The solid line represents the best theoretical fit for the 1:1 host-guest complexation process.

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1 and **1•2_{R,R}** to the corresponding *meso* position, whilst the subscript (₂) indicates the furthest -CH₂CH₃ proton to the corresponding meso position.

S5) ¹H-¹H COSY spectrum of **1•2_{R,R}** in CDCl₃.

S6) ¹H-¹H ROESY spectrum of **1•2_{R,R}** in CDCl₃. Only positive NOE cross peaks are shown.

S7) A fragment of ¹H-¹H ROESY spectrum of **1•2_{R,R}** in CDCl₃ showing the ROE signals arisen from through-space interactions between the porphyrin *meso* protons and ligand protons.

S8) The observed T_1^{NS} values at 200 MHz and 500 MHz and the τ_c values.

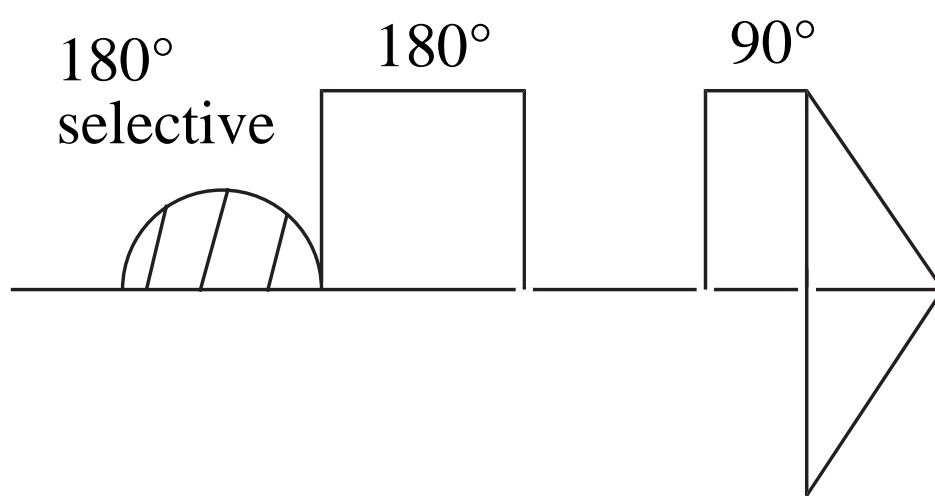
S9) Calculated plot of τ_c vs the ratio $T_1^{NS}(500)/T_1^{NS}(200)$.

S10) The observed T_1^{SNI} values (s) for selected protons at 500 MHz.

S11) The obtained σ_{ij} values.

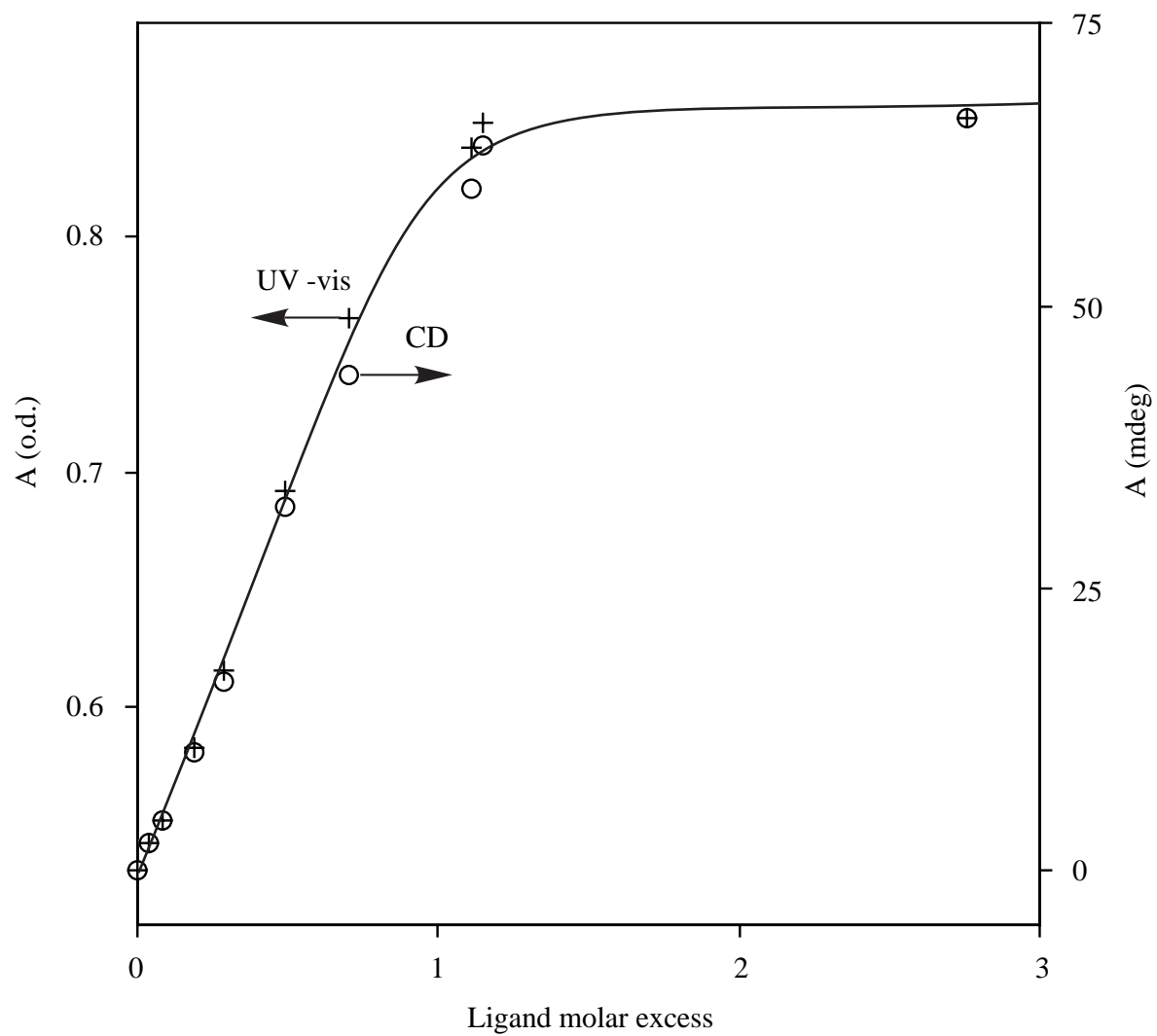
S12) The H-H distances in **1•2_{R,R}** estimated by the Selective Relaxation Method.

S1



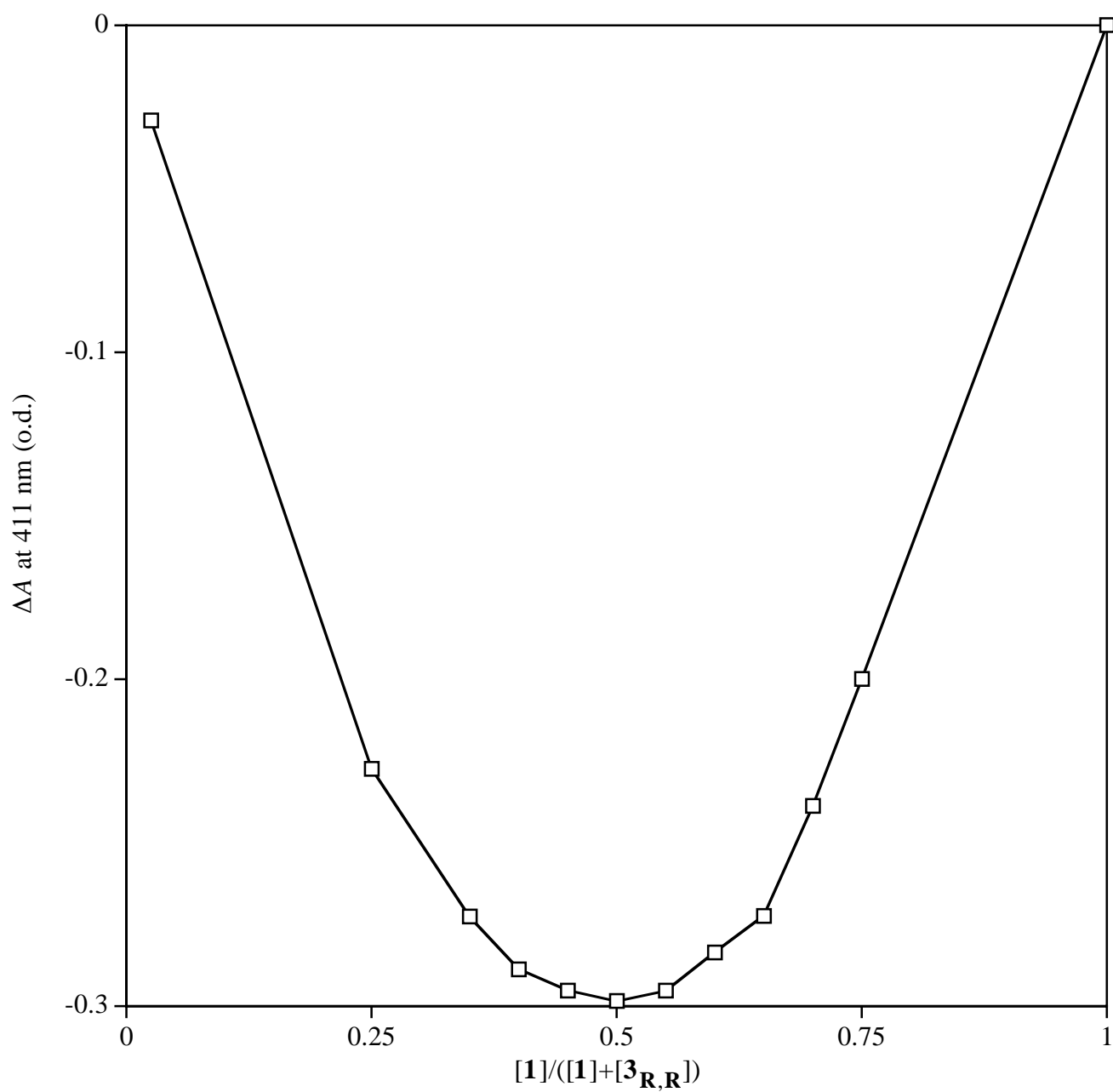
S1) Pulse sequence for measurement of T_1^{SNI} .

S2



S2) Dependencies of the UV-vis absorbance, monitored at 410 nm (the most intense B transition, crosses) and the total CD amplitude (circles) of **1** upon the molar excess of **2_{S,S}**. The solid line represents the best theoretical fit for the 1:1 host-guest complexation process.

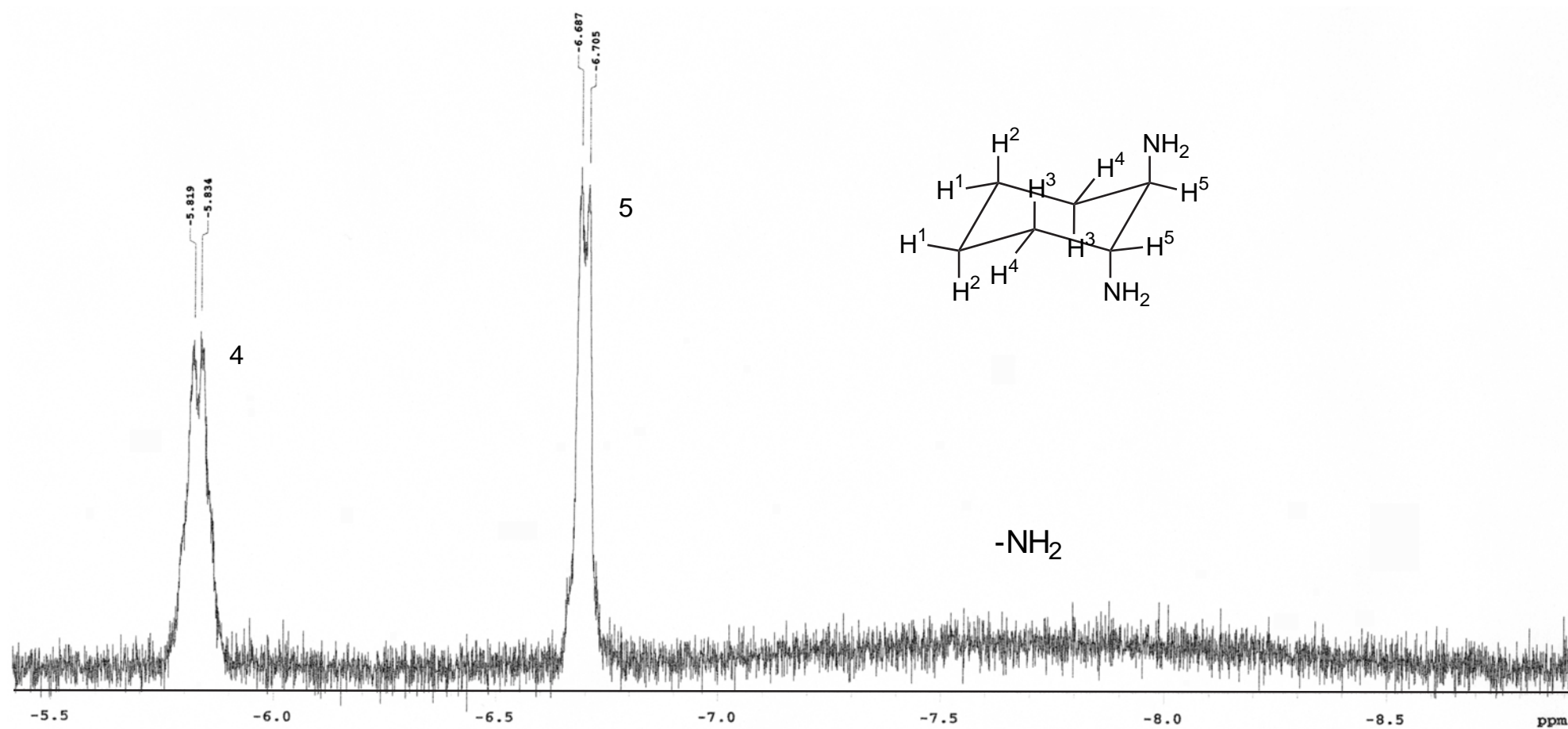
S3



S3) Job plot of the Soret band intensity changes (ΔA) at 411 nm vs. $[1]/([1]+[3_{R,R}])$ at the low ligand molar excess region.

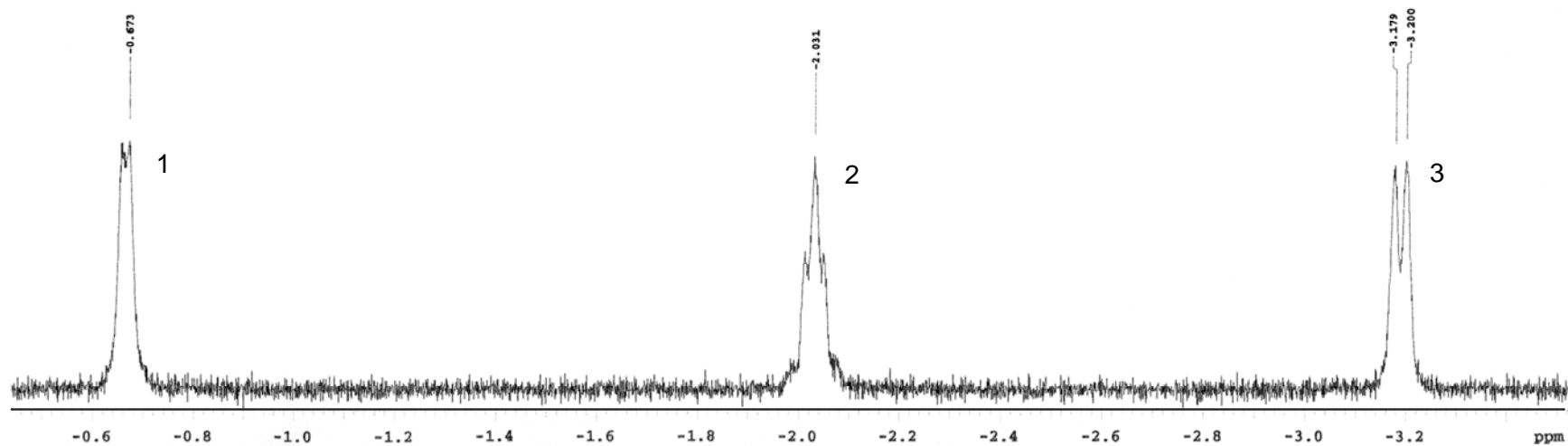
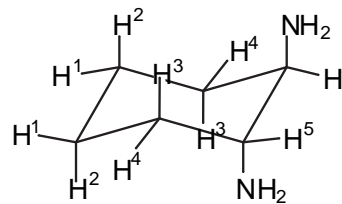
S4a

ligand's-H

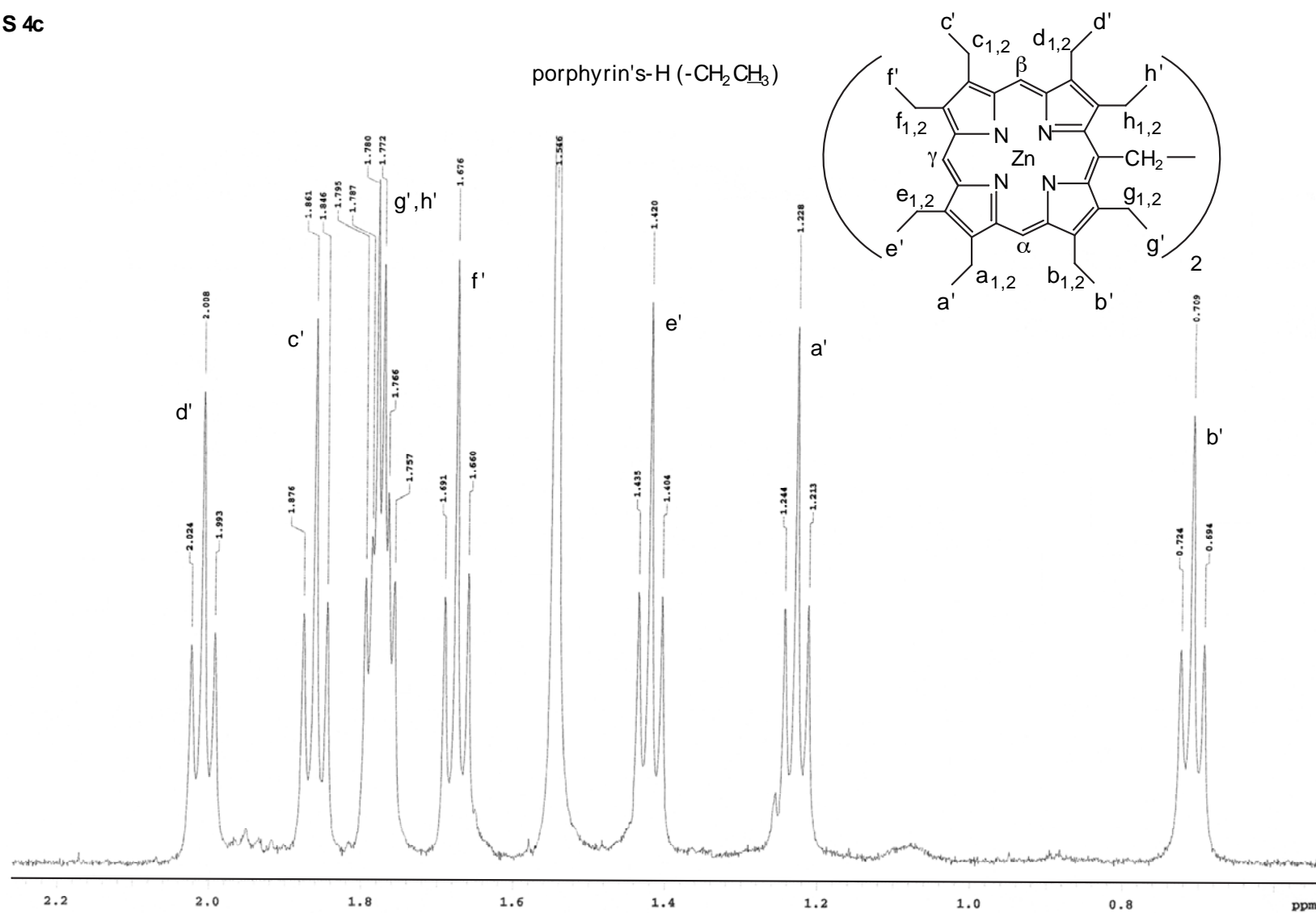


S 4b

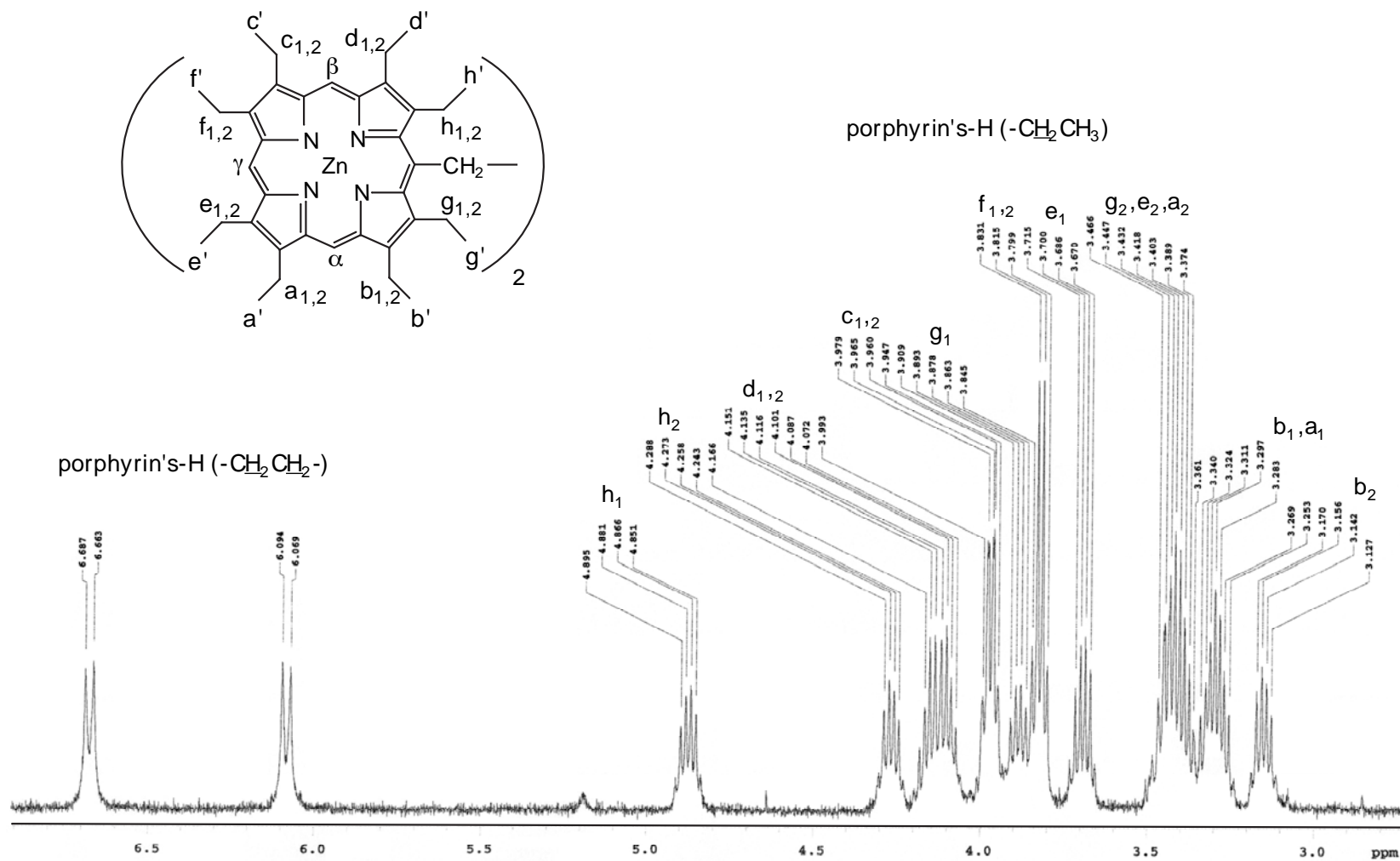
ligand's-H



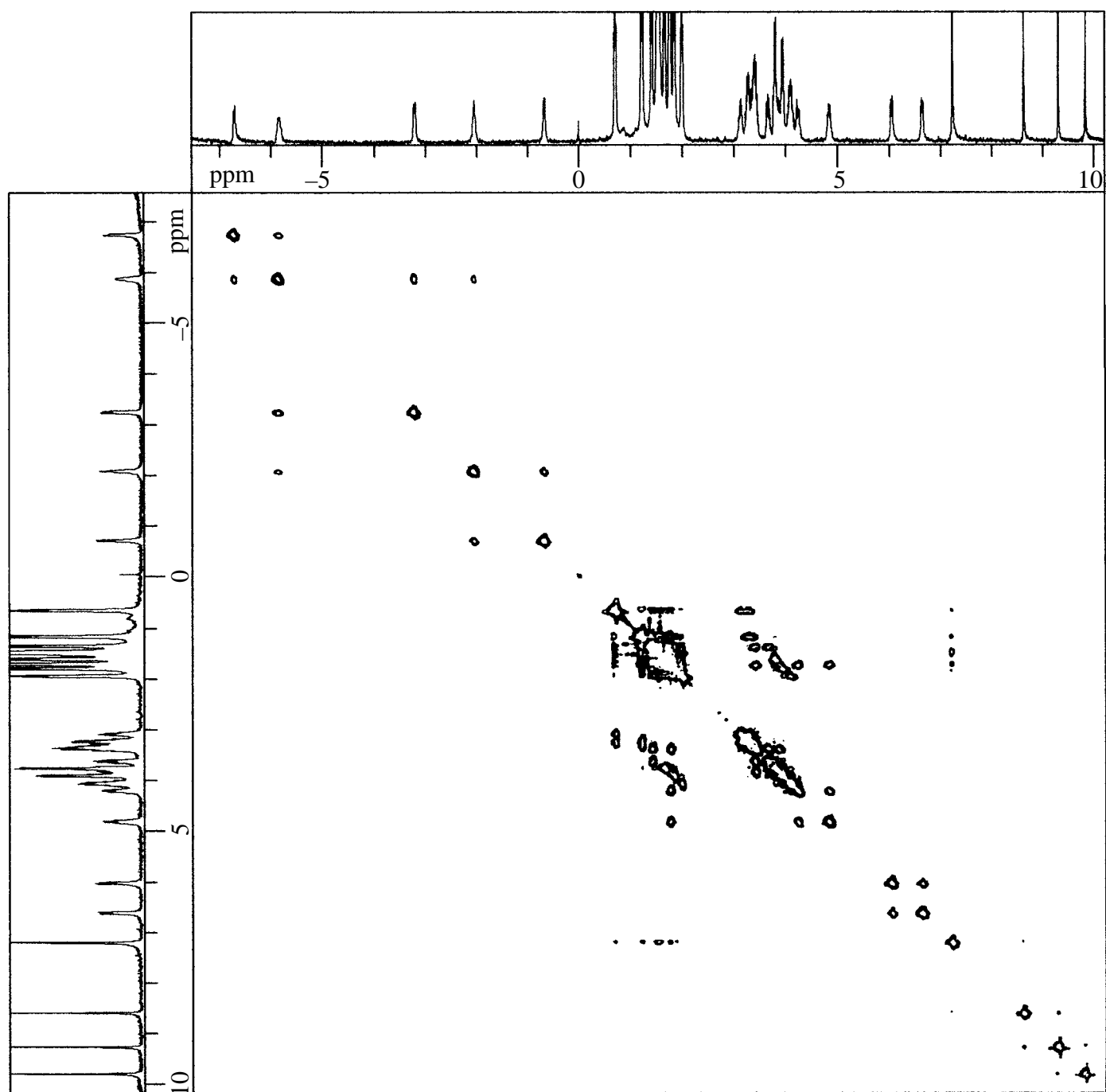
S 4c



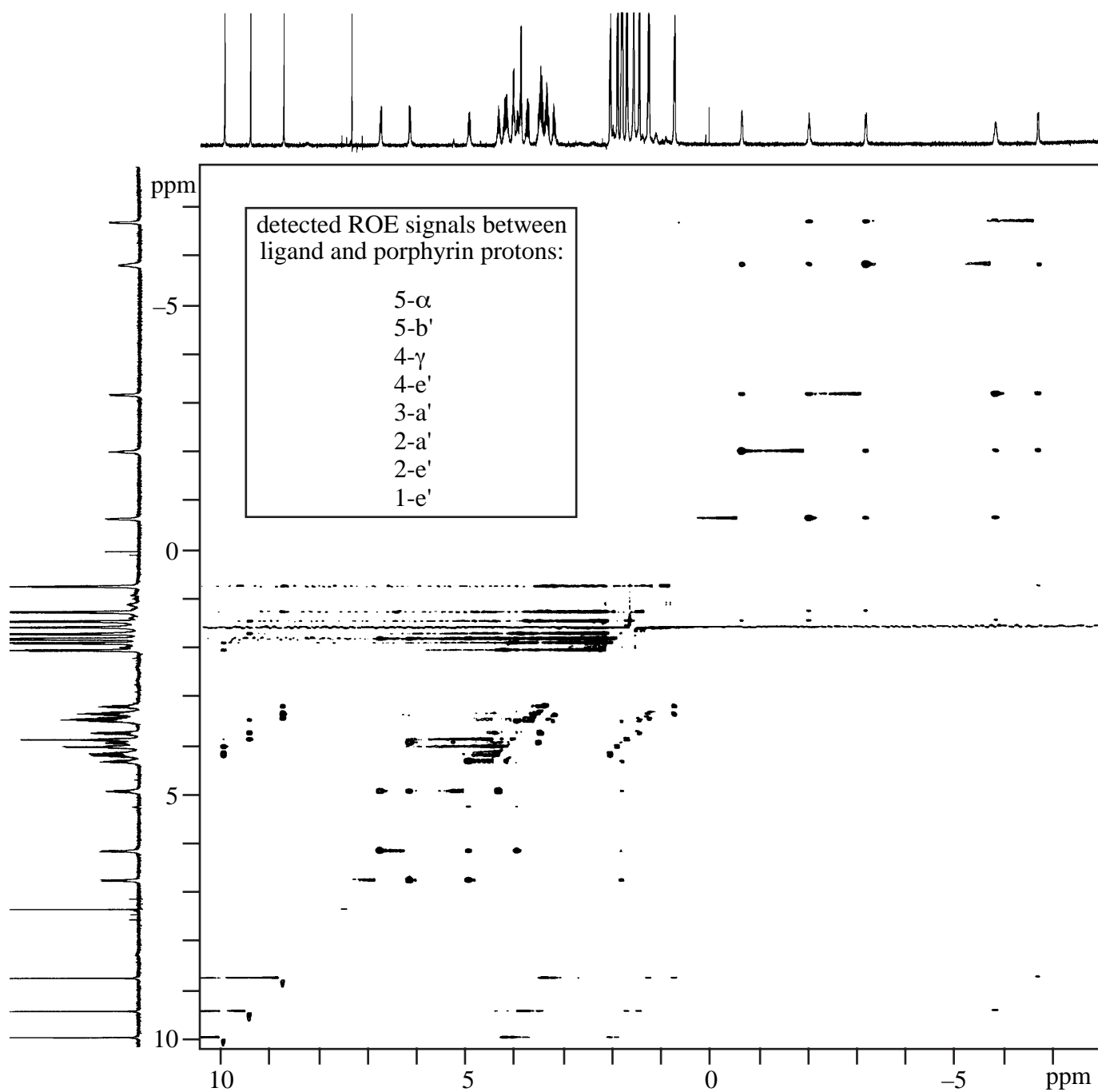
S 4d



4) Expanded areas (ligand (a and b) and porphyrin (c and d) parts) of the ^1H NMR spectrum of $\mathbf{1}\cdot\mathbf{2}_{\text{R,R}}$ in CDCl_3 . The subscript ($_1$) indicates the closest $-\text{CH}_2\text{CH}_3$ proton of $\mathbf{1}$ and $\mathbf{1}\cdot\mathbf{2}_{\text{R,R}}$ to the corresponding *meso* position, whilst the subscript ($_2$) indicates the furthest $-\text{CH}_2\text{CH}_3$ proton to the corresponding *meso* position.

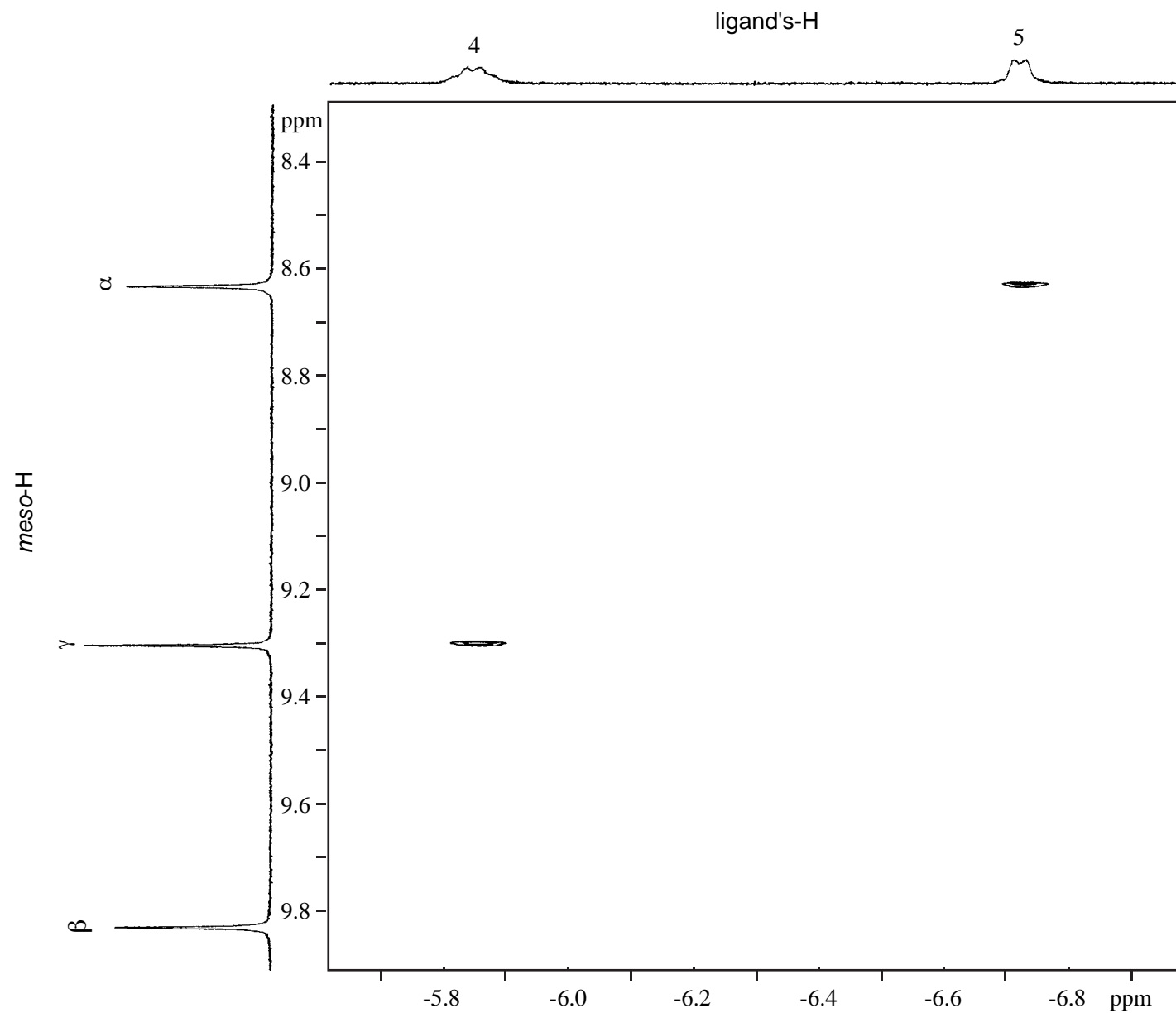


S5) ^1H - ^1H COSY spectrum of $1\cdot 2_{\text{R,R}}$ in CDCl_3 .



S6) ^1H - ^1H ROESY spectrum of **1•2_{R,R}** in CDCl_3 . Only positive NOE cross peaks are shown.

S7



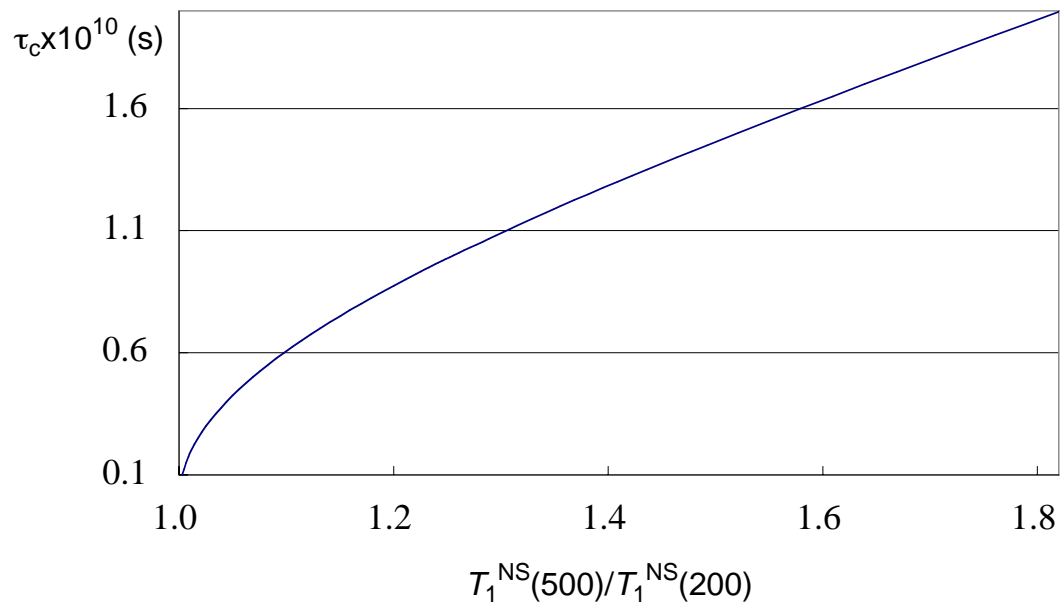
S7) A fragment of ^1H - ^1H ROESY spectrum of $\mathbf{1}\cdot\mathbf{2}_{\text{R,R}}$ in CDCl_3 showing the ROE signals arisen from through-space interactions between the porphyrin *meso* protons and ligand protons.

S8

H_i	T_1^{NS} (s)		$\tau_c/10^{-10}$
	200 MHz	500 MHz	
CH_2	0.099	0.182	2.04
CH_2	0.100	0.169	1.80
a_1/b_1	a)	0.313	
$a_2/e_2/g_2$	a)	0.315	
b_2	0.158	0.288	2.01
$c_{1,2}$	0.188	0.347	2.05
$d_{1,2}$	0.166	0.300	1.98
e_1	0.187	0.345	2.02
$f_{1,2}$	0.194	0.334	1.83
g_1	0.144	0.213	1.42
h_1	0.144	0.264	2.02
h_2	0.115	0.203	1.90
a	0.322	0.552	1.81
b	0.358	0.605	1.78
g	0.427	0.674	1.59
a'	0.432	0.622	1.36
b'	0.309	0.486	1.59
c'	0.450	0.679	1.48
d'	0.346	0.549	1.61
e'	0.401	0.604	1.47
f'	0.451	0.687	1.50
g'/h'	0.336	0.547	1.68
1	0.142	0.284	2.28
2	0.139	0.262	2.08
3	0.151	0.265	1.89
4	0.174	0.270	1.54
5	0.264	0.433	1.70

a) Undetectable due to the signal overlappings.

S8) The observed T_1^{NS} values at 200 MHz and 500 MHz and the τ_c values.



S9) Calculated plot of τ_c vs the ratio $T_1^{\text{NS}}(500)/T_1^{\text{NS}}(200)$.

S10

Selected H _i	Observed H _i							
	a	b	g	1	2	3	4	5
CH ₂	0.553	0.606	0.673	0.283	0.259	0.265	0.269	0.433
CH ₂	0.550	0.604	0.674	0.283	0.260	0.261	0.270	0.432
a ₁ /b ₁	0.581	0.608	0.675	0.282	0.261	0.263	0.269	0.430
a ₂ /e ₂ /g ₂	0.571	0.606	0.683	0.281	0.261	0.261	0.267	0.434
b ₂	0.568	0.606	0.669	0.282	0.262	0.264	0.270	0.429
c _{1,2}	0.552	0.634	0.676	0.281	0.261	0.261	0.270	0.430
d _{1,2}	0.555	0.639	0.677	0.283	0.260	0.264	0.269	0.427
e ₁	0.551	0.608	0.696	0.283	0.261	0.264	0.267	0.434
f _{1,2}	0.553	0.608	0.704	0.279	0.257	0.264	0.267	0.430
g ₁	0.553	0.608	0.676	0.282	0.261	0.264	0.267	0.434
h ₁	0.552	0.607	0.672	0.281	0.259	0.262	0.267	0.428
h ₂	0.554	0.605	0.677	0.282	0.259	0.265	0.267	0.432
a		0.603	0.676	0.283	0.257	0.264	0.267	0.434
b	0.551		0.647	0.284	0.263	0.265	0.270	0.433
g	0.553	0.596		0.279	0.261	0.266	0.265	0.431
a'	0.568	0.613	0.676	0.284	0.260	0.262	0.268	0.434
b'	0.559	0.607	0.671	0.281	0.260	0.262	0.269	0.430
c'	0.550	0.619	0.670	0.281	0.259	0.264	0.267	0.428
d'	0.551	0.616	0.674	0.283	0.258	0.263	0.270	0.431
e'	0.552	0.608	0.688	0.284	0.261	0.263	0.268	0.429
f'	0.558	0.612	0.693	0.282	0.261	0.263	0.266	0.432
g'/h'	0.553	0.606	0.671	0.280	0.257	0.261	0.267	0.432
1	0.551	0.606	0.673		0.286	0.266	0.273	0.432
2	0.554	0.610	0.673	0.313		0.264	0.267	0.437
3	0.550	0.602	0.665	0.286	0.262		0.294	0.443
4	0.552	0.608	0.677	0.287	0.256	0.292		0.436
5	0.555	0.607	0.672	0.282	0.262	0.269	0.276	

S10) The observed T_1^{SN} values(s) for selected protons at 500 MHz.

S11

H_i	H_j	$\sigma_{ij} \times 10^3$	$\sigma_{ji} \times 10^3$
α	a_1	70.2	
α	a_2	31.1	
α	$b_{1,2}$	104.2	
α	a'	18.6	
α	5	7.9	13.4
β	$c_{1,2}$	57.4	
β	$d_{1,2}$	80.6	
β	c'	14.3	
β	d'	15.1	
β	2	19.6	13.5
γ	e_1	54.9	
γ	e_2	16.7	
γ	$f_{1,2}$	60.9	
γ	f'	19.9	
1	2	330.0	327.6
1	3	18.4	27.5
1	4	41.7	42.7
2	3		8.0
2	5	21.9	28.5
3	4	297.8	351.5
3	5	53.0	56.8
4	5	19.3	94.5

S11) The obtained σ_{ij} values.

Proton pair	Distance $r_{ij}(\text{\AA})$
$\alpha\text{-a}_1$	2.4
$\alpha\text{-a}_2$	2.8
$\alpha\text{-b}_{1,2}$	2.3
$\alpha\text{-a}'$	3.2
$\alpha\text{-5}$	3.5 - 3.6
$\beta\text{-d}_{1,2}$	2.4
$\beta\text{-c}_{1,2}$	2.5
$\beta\text{-d}'$	3.5
$\beta\text{-c}'$	3.3
$\beta\text{-2}$	3.0 - 3.3
$\gamma\text{-f}_{1,2}$	2.5
$\gamma\text{-e}_1$	2.5
$\gamma\text{-e}_2$	3.1
$\gamma\text{-f}'$	3.3
1-2	1.8 - 1.9
1-3	2.8 - 3.1
1-4	2.7 – 2.8
2-3	> 3.5
2-5	2.9 – 3.0
3-4	1.9 – 2.0
3-5	2.6
4-5	3.1

^a Distances larger than 3.5 Å are not detectable.

S12) The H-H distances in **1•2_{RR}** estimated by the Selective Relaxation Method.