Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

(ESI)

Table of Contents

An unusual highly emissive water-soluble Iridium Lissamine-Alanine complex with a molecular logic gate approach.

E. Oliveira[a,b,c*], S.M. Santos[d], C. Núñez[a,e] , J. L. Capelo[a,b] and C. Lodeiro[a,b*]

[a]UCIBIO, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[b]ProteoMass Scientific Society. Madan Parque. Rua dos Inventores. 2825-182. Caparica. Portugal
[c]Veterinary Science Department and CECAV, University of Trás-os-Montes and Alto Douro, 5001-801, Vila Real, Portugal.
[d]Department of Chemistry and CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
[e]Inorganic Chemistry Department, Faculty of Chemistry, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain

[*] Corresponding authors e-mail: ej.oliveira@fct.unl.pt (E.O) and cle@fct.unl.pt (C.L.)

I - Experimental Section

Synthesis and physical characterization of compound 1. Compound HCl.H-Ala-OMe was obtained according with the procedure in (1). HCl. H-Ala-OMe (23.9 mg, 1.73×10-4 mol) was neutralized by the addition of 23 µl of triethylamine in acetonitrile for 30 minutes. Thereafter, lissamine rhodamine B sulfonyl chloride (Compound **A**) (50 mg, 8.66×10^{-5} mol) and cesium carbonate (1.73×10^{-4} mol) were added to the previous mixture and then stirred under N_2 for 30 minutes and cooled at 0ºC in an ice-water bath. The final mixture was kept under stirring for 32 hours at room temperature. The product **1** formation was confirmed by TLC (thin layer chromatography). The mixture was filtered, and the filtrate dried under N_2 atmosphere at room temperature. The residue obtained was purified by column chromatography with silica gel (eluent: CH_2Cl_2/MeOH 10:1). The fractions were combined, and the product **1** was obtained as a solid.

Red powder (40 mg, 72%), $C_{31}H_{37}N_3O_8S_2$, FW = 643.77 Elementar Analysis: (Found: C, 57.65; H, 5.79; N, 6.67; S, 9.72 % CHNS requires: C, 57.84; H, 5.79; N, 6.53; S, 9.96).

^{1}H NMR ($CDCl_3$, 400 MHz): δ_H (ppm) = 1.32 (m, 12H, H1), 1.53 (d, *J*= 4Hz 3H, βCH_3 alanine, H23), 3.59 (m, 4H, H2), 3.76 (s, 3H, OCH_3 alanine, H25), 4.23 (m, 1H, αH alanine, H22), 5.45 (m, 1H, NH alanine), 6.69 (s, 2H, H4, H14), 6.81 (m, 1H, H7, H15), 6.74 (m, 2H, H9,H10), 8.01 (m, 2H, H20, H21), 8.86 (s, 1H, H18). δ_C (ppm) = 12.62 (C1, C1'), 19.74 (CH_3 alanine, C25), 28.82 (OCH_3 alanine, C24), 45.94 (C24), 52.92-51.98 (C2, C2'), 95.51 (C4), 113.64 (C18), 114.18 (C7), 127.35-126.94 (C9, C11, C15), 129.91 (C21), 133.26 (C13), 134.20 (C10), 141.72 (C20), 148.44 (C12, C14), 155.56 (C16, C17, C19), 157.71 (C6, C8), 158.78 (C5), 172.62 (C23).

UV-Vis in miliQ water (λ, nm): Band at 570 nm (ε = 27858 $cm^{-1}.M^{-1}$). Emission spectrum in miliQ water (λ_{exc} =560 nm, λ_{emis} = 590 nm). Lifetime: τ = 2.47 ns, MALDI-TOF-MS, calc (found): [**1**H]$^+$ 644.20 (644.16) m/z.

II – MALDI-TOF-MS Spectra and Photophysical Characterization

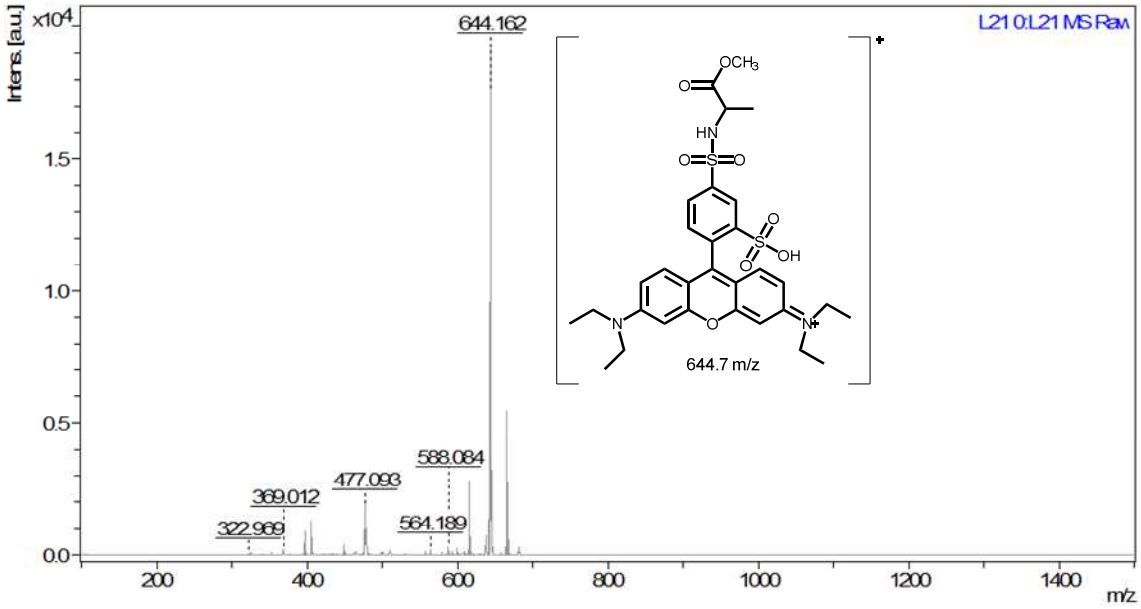


Figure S1. MALDI-TOF-MS spectra of compound **1** using as matrix the sinapic acid.

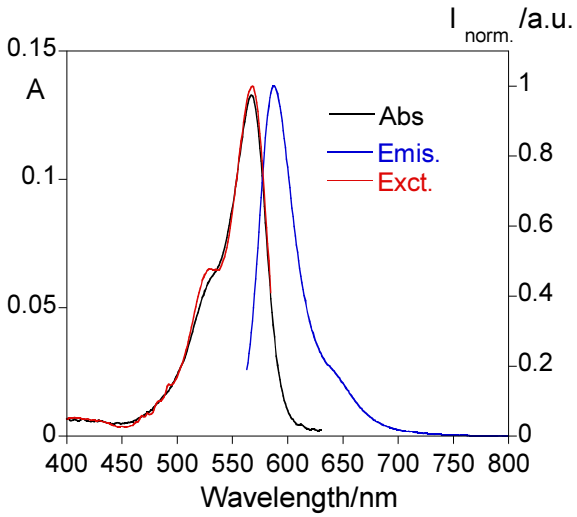
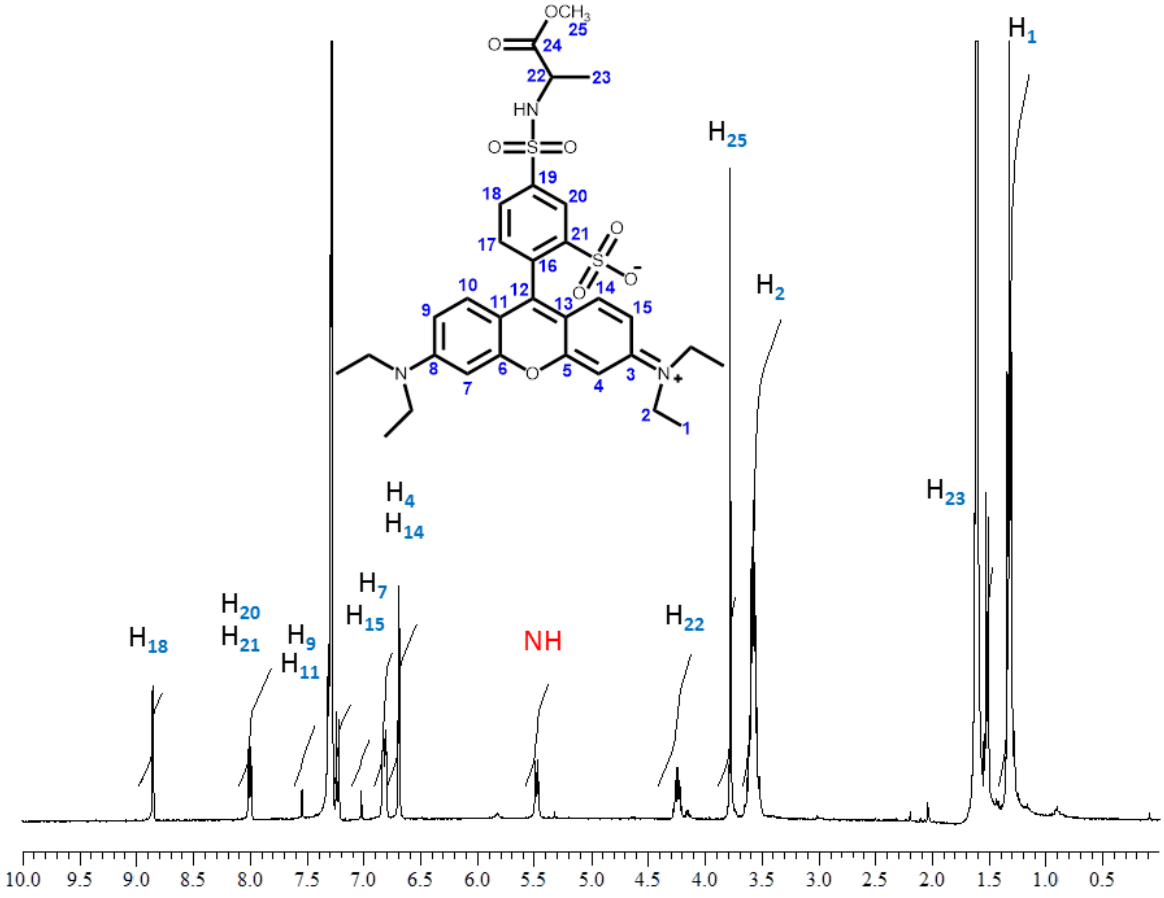


Figure S2. Absorption, emission and excitation spectra of compound **1** in aqueous solution at room temperature. ([**1**] = 4.66×10^{-6} M, $\lambda_{exc.}$= 560 nm, T = 298 K).

III – NMR data


OCH3
25
24
O
22
23
HN
O=S=O
19
18
20
17
21
16
10
12
11
13
15
9
8
7
6
5
4
3
2
1
14
N
O
N+
H1
H25
H2
H23
H4
H14
H7
H15
H20
H21
H9
H11
H18
NH
H22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

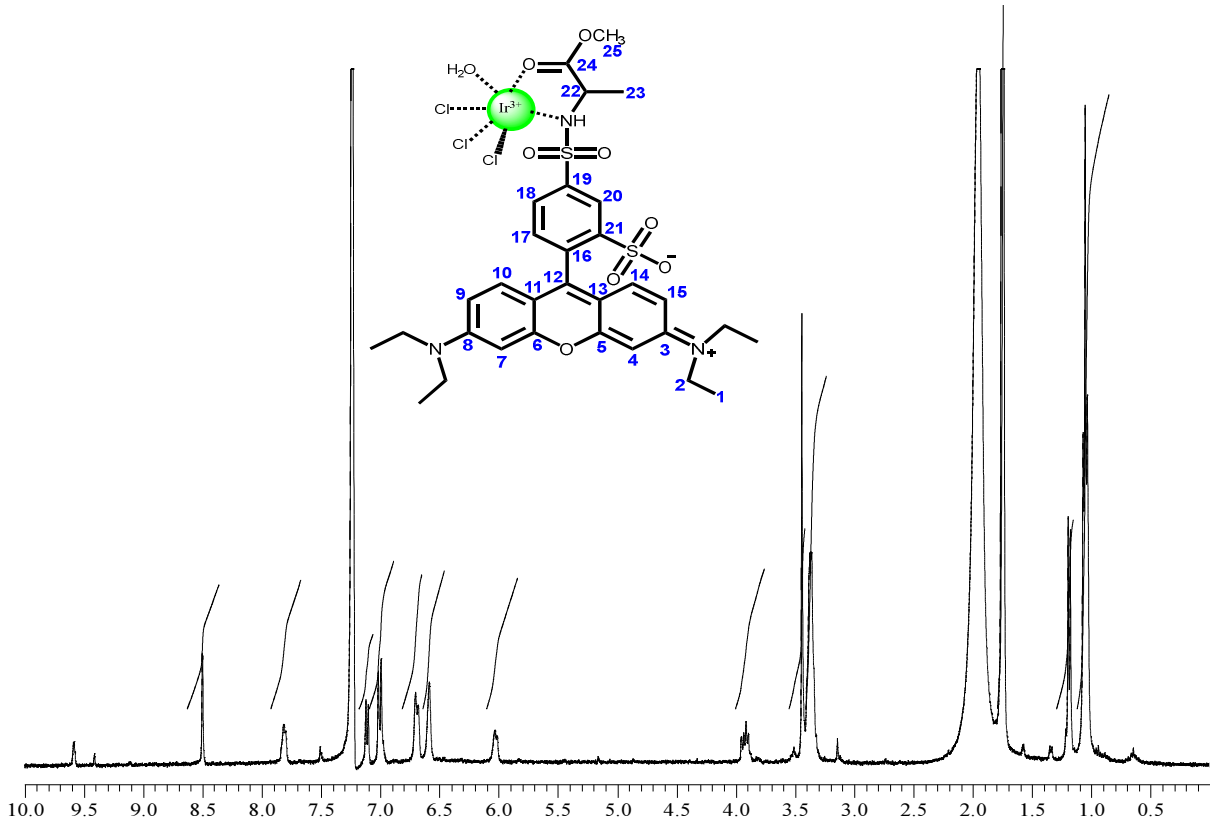


Figure S3. ^{1}H NMR spectra of compound **1** before (top) and after (down) the addition of 1 equiv. of Ir^{3+} to form the species Ir@**1** complex in $CDCl_3$.

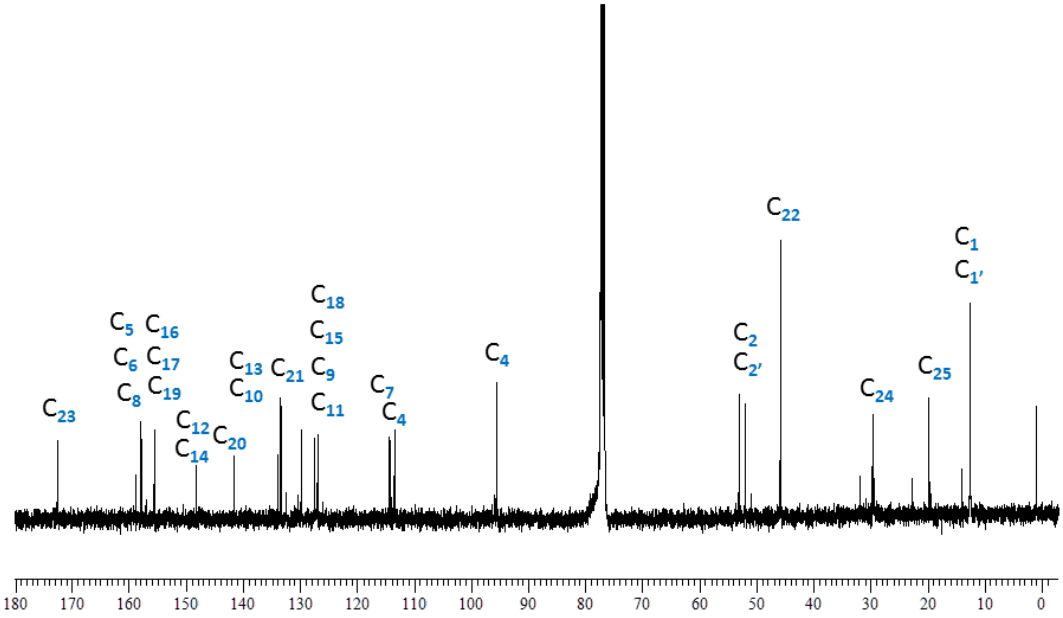


Figure S4. ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

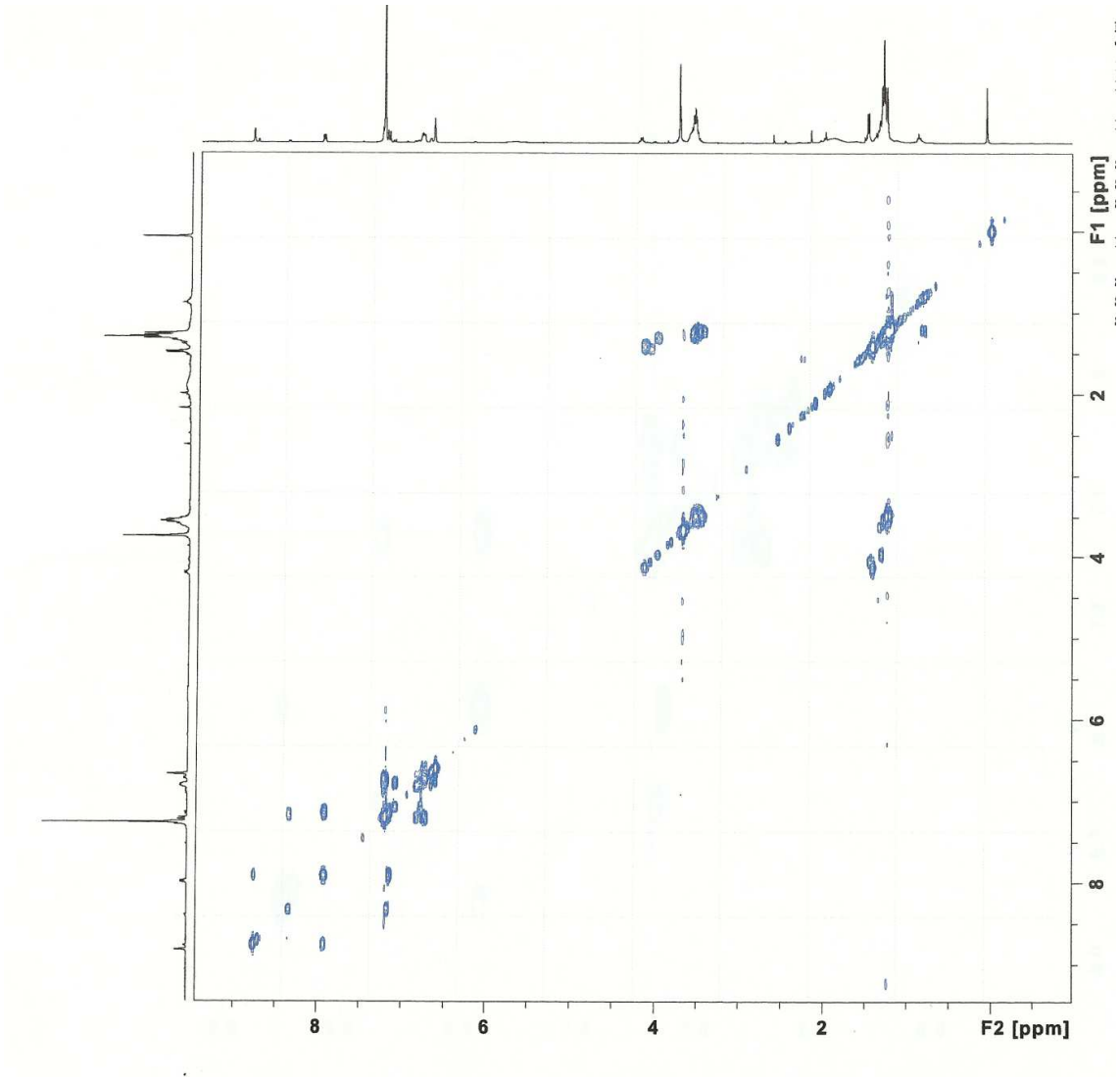


Figure S5. COSY ($^1H/^1H$) NMR spectrum of compound **1** in $CDCl_3$.

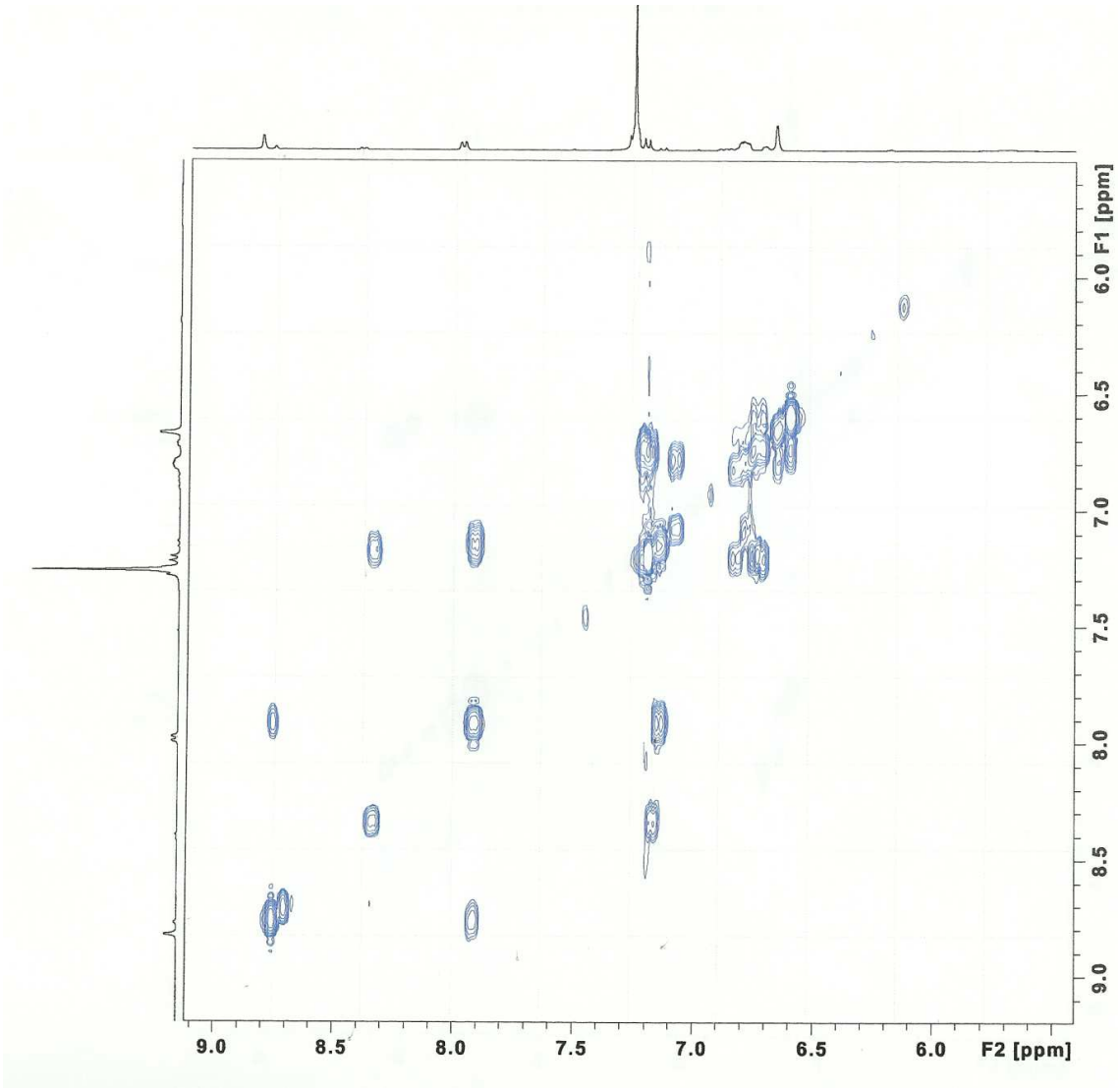


Figure S6. COSY (^{1}H/^{1}H) NMR spectrum of compound **1** in $CDCl_3$ (amplification 9.0-5.0 ppm).

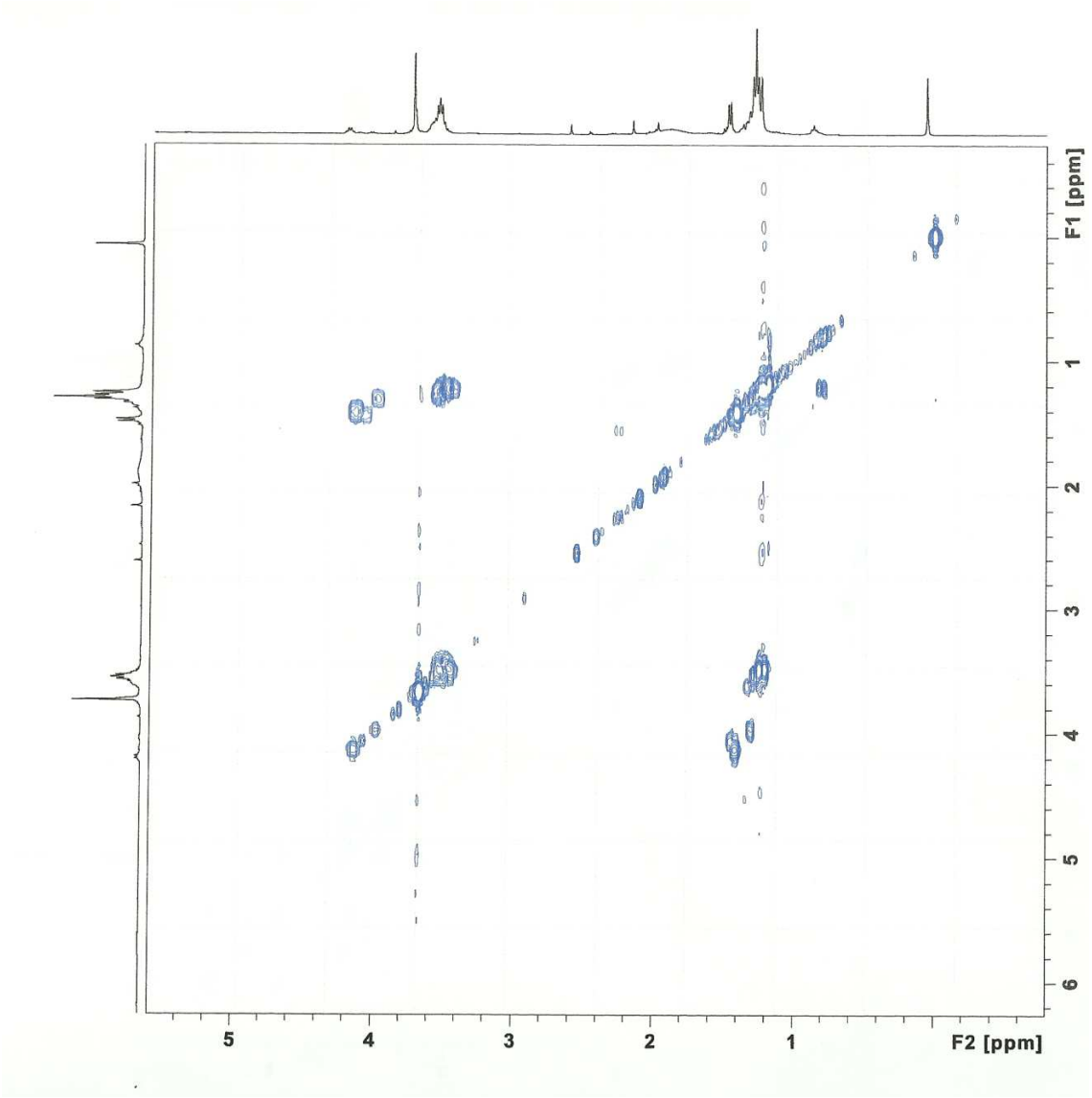


Figure S7. COSY ($^1H/^1H$) NMR spectrum of compound **1** in $CDCl_3$ (amplification 1.0-5.0 ppm).

IV – Titration of compound **1** with the pH

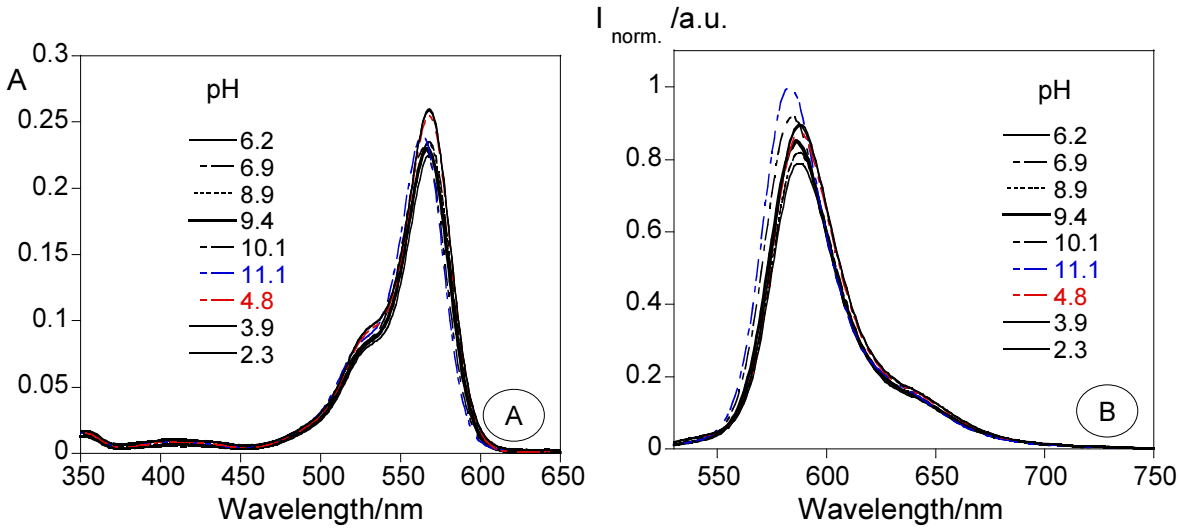


Figure S8 – Absorption and emission titrations of compound **1** in aqueous solution with pH. ([**1**] = 1.16 ×10^{-5} M, $\lambda_{exc.}$ = 535 nm, T = 298K).

V – Theoretical calculations

Table S1: Calculated ^{1}H chemical shieldings (σ) for the amino acid (in ppm), calculated at the B3LYP/6-31G** level (plus LanL2DZ for the Ir^{3+} cation) in implicit acetonitrile, along with the complexation induced chemical shifts (δ) for each group of protons. Since only variations in the chemical shielding are being considered, conversion of chemical shielding to chemical shifts is not required (note, however, that temperature and dynamic effects are completely ignored).

	$\sigma_{\mathbf{1}}$ / ppm	$\sigma_{Ir@\mathbf{1}}$ / ppm	$\sigma_{Ir@\mathbf{1}} - \sigma_{\mathbf{1}}$ / ppm
NH	28.15	25.87	2.28 (0.6[b])
CH_3[(a)]	30.34	29.90	0.44 (0.3[b])
CH	27.07	27.00	-0.07 (-0.3[b])
OCH_3[(a)]	27.08	27.51	-0.43 (-0.4[b])

[a)] average over the three equivalent nuclei;
[b)] experimental values presented for reference;

Table S2: Calculated vertical excitation energies (E_{exc}) for the receptor (**1**) and complex (Ir@**1**) in the gas-phase, calculated at the B3LYP/6-31G** level (plus LanL2DZ for the Ir^{3+} cation), along with the corresponding oscillator strengths ($f_{oscillator}$) and excitation wavelengths (λ_{exc} / nm).

	Ir@1			**1**		
excitation	E_{exc} / *eV*	λ_{exc} / *nm*	$f_{oscillator}$	$E_{exc.}$ / *eV*	λ_{exc} / *nm*	$f_{oscillator}$
1	2.0911	592.91	0.0193	1.9497	635.91	0.0292
2	2.3351	530.96	0.0000	2.6328	470.93	0.0565
3	2.4807	499.79	0.0003	2.8897	429.06	0.6501
4	2.7227	455.37	0.1584	2.9455	420.93	0.0785
5	2.7519	450.53	0.3308	3.0627	404.82	0.0442
6	2.7680	447.92	0.1682	3.3107	374.50	0.0024
7	2.7816	445.73	0.0021	3.6007	344.34	0.0567
8	2.8440	435.95	0.0731	3.6102	343.42	0.0139
9	2.8522	434.70	0.0012	3.8230	324.31	0.0054
10	2.8869	429.46	0.0426	3.8605	321.16	0.0108

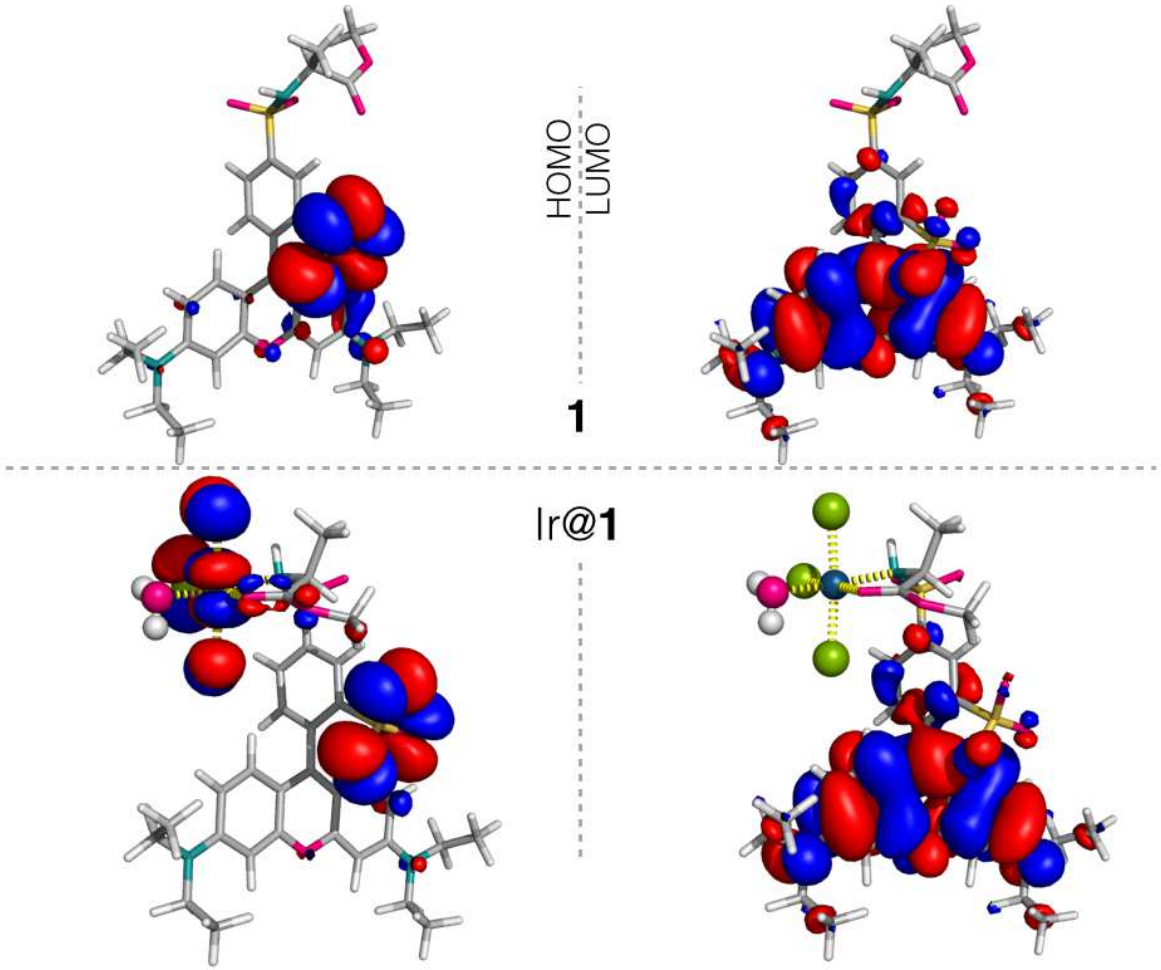


Figure S9. The depiction of the HOMO (left) and LUMO (right) of the free receptor (top) and complex (bottom) drawn at the ± 0.015 isolevel. Three Cl^- counter anions and one water molecule complete the coordination sphere of Ir^{3+}.

References

(1) E. Oliveira, J. L. Capelo, J. C. Lima, C. Lodeiro, *Amino Acids*, 2012, **43**, 1779.