

# Light-up Photoluminescence Sensing of a Nerve Agent Simulant by a Bis-Porphyrin-Salen-UO<sub>2</sub> Complex

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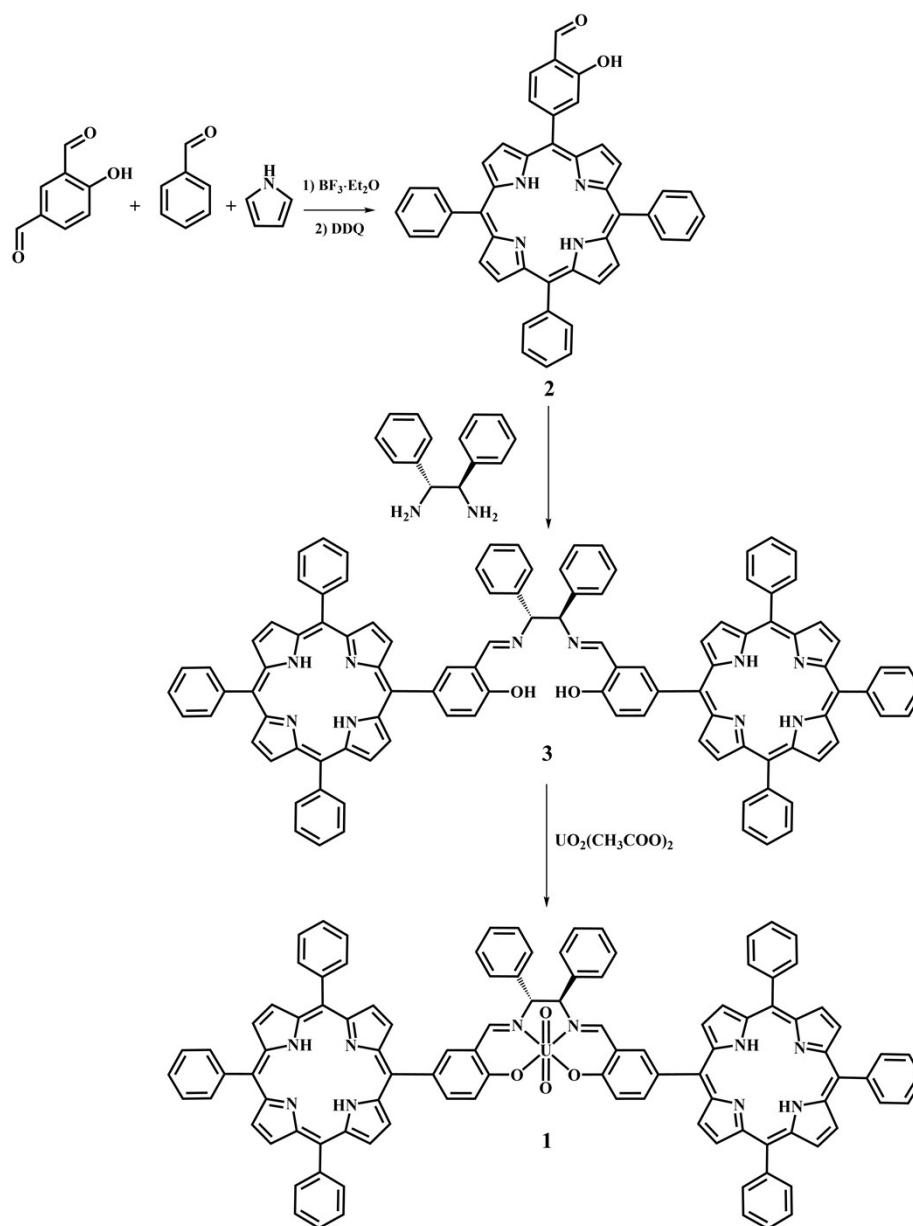
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**General experimental methods.** NMR experiments were carried out at 27 °C on a Varian Unity Inova 500 MHz spectrometer (<sup>1</sup>H NMR at 499.88 MHz, <sup>13</sup>C NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tunable 5 mm Varian inverse detection probe (ID-PFG, Agilent, Santa Clara, CA, USA). The chemical shifts (ppm) were referenced to TMS (<sup>1</sup>H, 0.0 ppm) or CDCl<sub>3</sub> (<sup>13</sup>C, 77.0 ppm). ESI mass spectra were acquired on an ES-MS Thermo-Finnigan spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an ion trap analyzer.

A JASCO V-560 UV-Vis spectrophotometer equipped with a 1 cm path-length cell was used for the UV-Vis measurements. Luminescence measurements were carried out using a Cary Eclipse Fluorescence spectrophotometer with resolution of 0.5 nm, at room temperature. The emission was recorded at 90° with respect to the exciting line beam using 10:10 slit-widths for all measurements. All chemicals were reagent grade and were used without further purification.

**Procedure for fluorescence titrations.** Two mother solutions of complex **1** and **DMMP** ( $1.0 \times 10^{-3}$  M) in dry chloroform were prepared. From these, different solutions with different ratio complex **1**/**DMMP** were prepared as reported below, and emission spectra were recorded at 25 °C ( $\lambda_{\text{ex}}$  422 nm,  $\lambda_{\text{em}}$  625 nm and 725 nm). With this data treatment, the apparent binding affinities of complex **1** with **DMMP** were estimated using HypSpec (version 1.1.33), a software designed to extract equilibrium constants from potentiometric and/or spectrophotometric titration data. HypSpec starts with an assumed complex formation scheme and uses a least-squares approach to derive the spectra of the complexes and the stability constants.  $\chi^2$  test (chi-square) was applied, where the residuals follow a normal distribution (for a distribution approximately normal, the  $\chi^2$  test value is around 12 or less). In all of the cases,  $\chi^2 \leq 10$  were found, as obtained by 3 independent measurements sets.

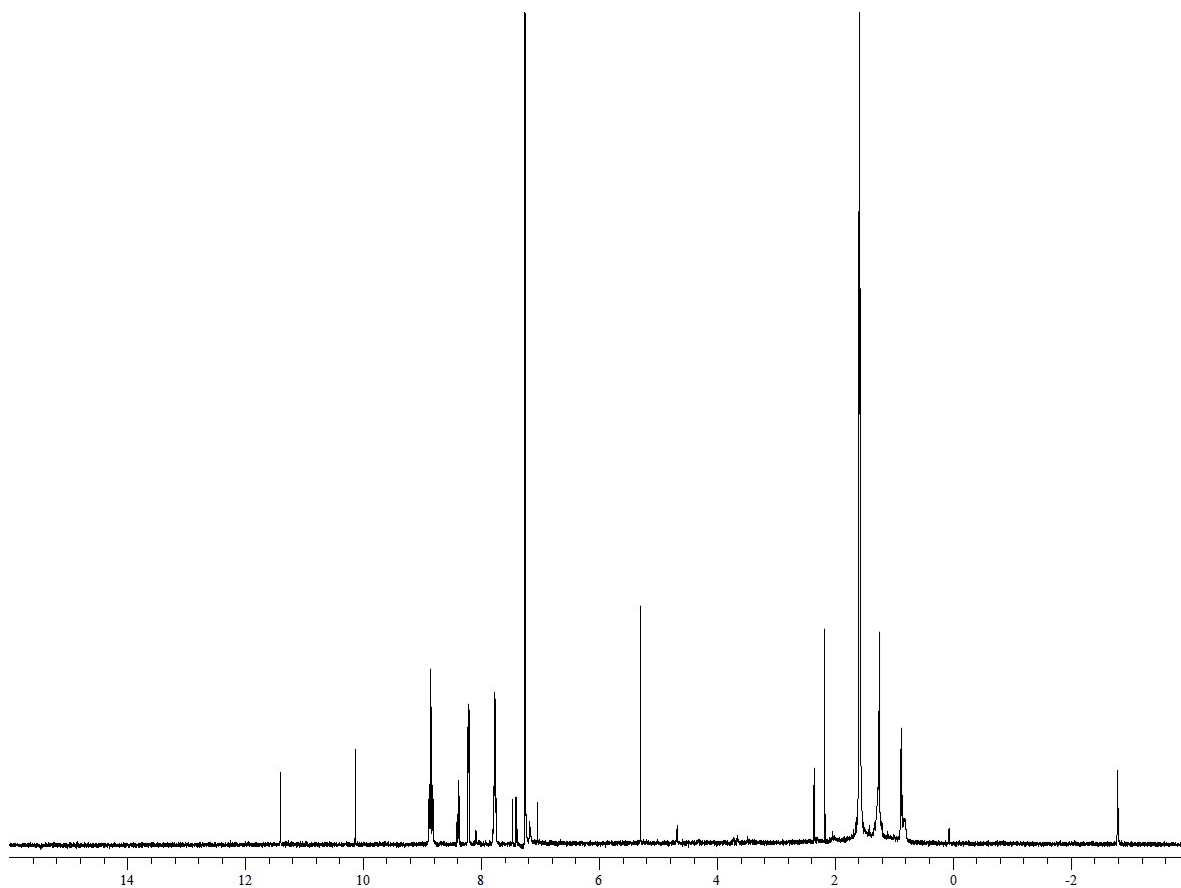
## Synthetic pathway for the synthesis of complex 1



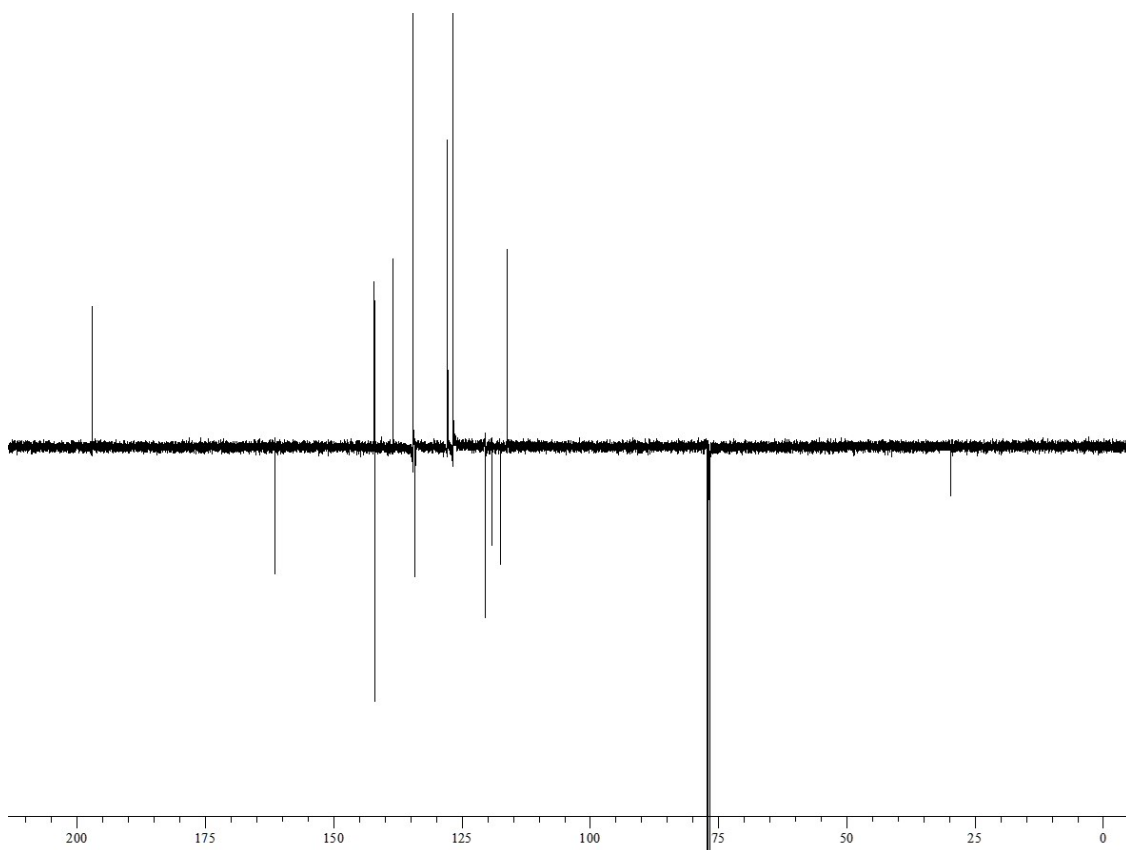
**Scheme 1. Synthesis of complex 1**

**Synthesis of the 2-hydroxy-4-(10,15,20-triphenylporphyrin-5-yl) benzaldehyde 2.** 0.60 g (3,98 mmol) of 4-hydroxyisophthalaldehyde was dissolved with 260 mL of  $\text{CHCl}_3$  in 500 mL round-bottom flask. Then, 1.2 mL of benzaldehyde (11.94 mmol) were added to the solution and stirred under nitrogen atmosphere for 10 minutes, afterward 1,11 mL of distilled pyrrole (15,92 mmol) and 64  $\mu\text{L}$  of  $\text{BF}_3 \cdot \text{OEt}_2$  were added, and the solution was stirred in the dark, at room temperature for 1h. Then, 3.6 g (15,92 mmol) of DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone) were added and the mixture was stirred at room temperature for 24h. The mixture was filtered in order to remove the by-

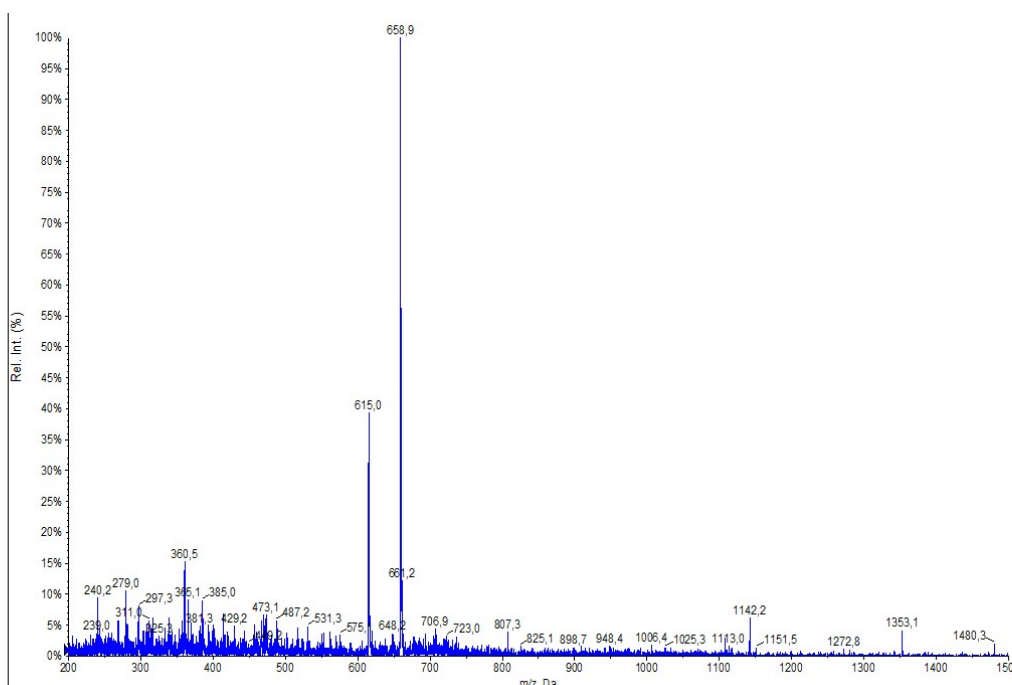
product of DDQ, and the organic solution was concentrated under reduced pressure, obtaining a crude dark product. The organic mixture was purified by column chromatography using *n*-Hexane/ CH<sub>2</sub>Cl<sub>2</sub> 4:1 as eluent mixture, and the desired products **2** was obtained as purple solid (184 mg; 7.0% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, Figure S1): δ= 11.40 (s, 1H); 10.13 (s, 1H); 8.82-8.88 (m, 8H); 8.38-8.40 (m, 2H); 8.20-8.22 (m, 6H); 7.74-7.79 (m, 9H); 7.14 (d, *J*=8.5 Hz, 1H); -2.79 (s, 2H). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>, Figure S2): δ= 116.2, 117.5, 119.2, 120.4 (x2), 120.5 (x2), 126.7 (x3), 127.8 (x3), 134.1, 134.5 (x3), 138.4 (x3), 138.4 (x3), 141.95 (x2), 142.0, 142.05 (x2), 161.4, 197.0. ESI-MS *m/z*= 658.24 [M+H]<sup>+</sup>, (Figure S3).



**Figure S1.** <sup>1</sup>H-NMR of compound **2** in CDCl<sub>3</sub>.

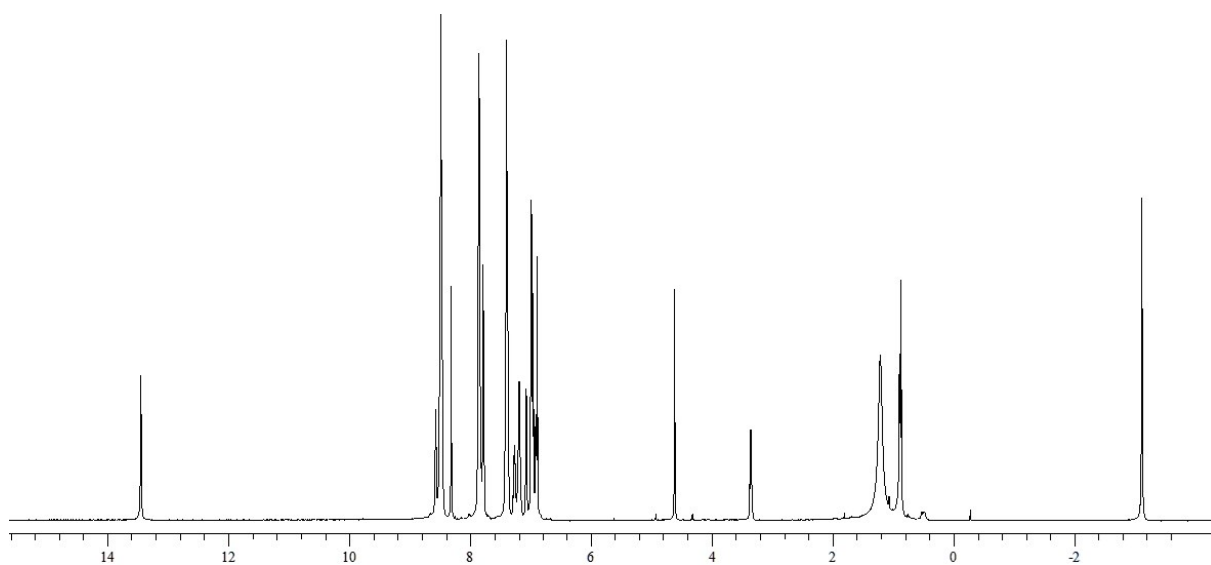


**Figure S2.** APT spectrum of compound **2** in CDCl<sub>3</sub>.



**Figure S3.** ESI-MS of compound **2**.

**Synthesis of the bis-porphyrin-salen ligand 3.** 184 mg of compound **2** were dissolved in 8 mL of CH<sub>2</sub>Cl<sub>2</sub> in a 100 mL round-bottom flask, then 30 mL of methanol were added and the solution was stirred at room temperature for 10 min. Afterwards, 29.44 mg of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine were added and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the crude product was precipitated in ethanol, filtrated and washed with 10 mL of ethanol to afford 156 mg of compound **3** (76% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, Figure S4): δ= 13.45 (s, 2H); 8.45-8.56 (m, 16H); 8.31 (s, 2H); 7.78-7.86 (m, 14H); 7.38-7.40 (m, 10H); 7.24-7.26 (m, 2H); 7.17-7.20 (m, 4H); 7.07 (d, *J*=8.0 Hz, 2H); 6.94-6.99 (m, 10H); 6.88-6.92 (m, 4H); 4.61 (s, 2H); -3.11(s, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, Figure S5): δ= 80.4; 115.6; 117.2; 119.0; 120.1; 120.2; 126.6; 126.7 (x3); 127.9 (x2); 128.1 (x3); 128.5; 132.9; 134.5 (x3); 137.4; 138.5; 139.2; 142.0; 142.1; 160.9; 166.6. ESI-MS *m/z*= 1493.0 [M+H]<sup>+</sup>; ESI-MS *m/z*= 746.2 [M+H]<sup>2+</sup>, (Figure S6).



**Figure S4.** <sup>1</sup>H-NMR of compound **3** in CDCl<sub>3</sub>.

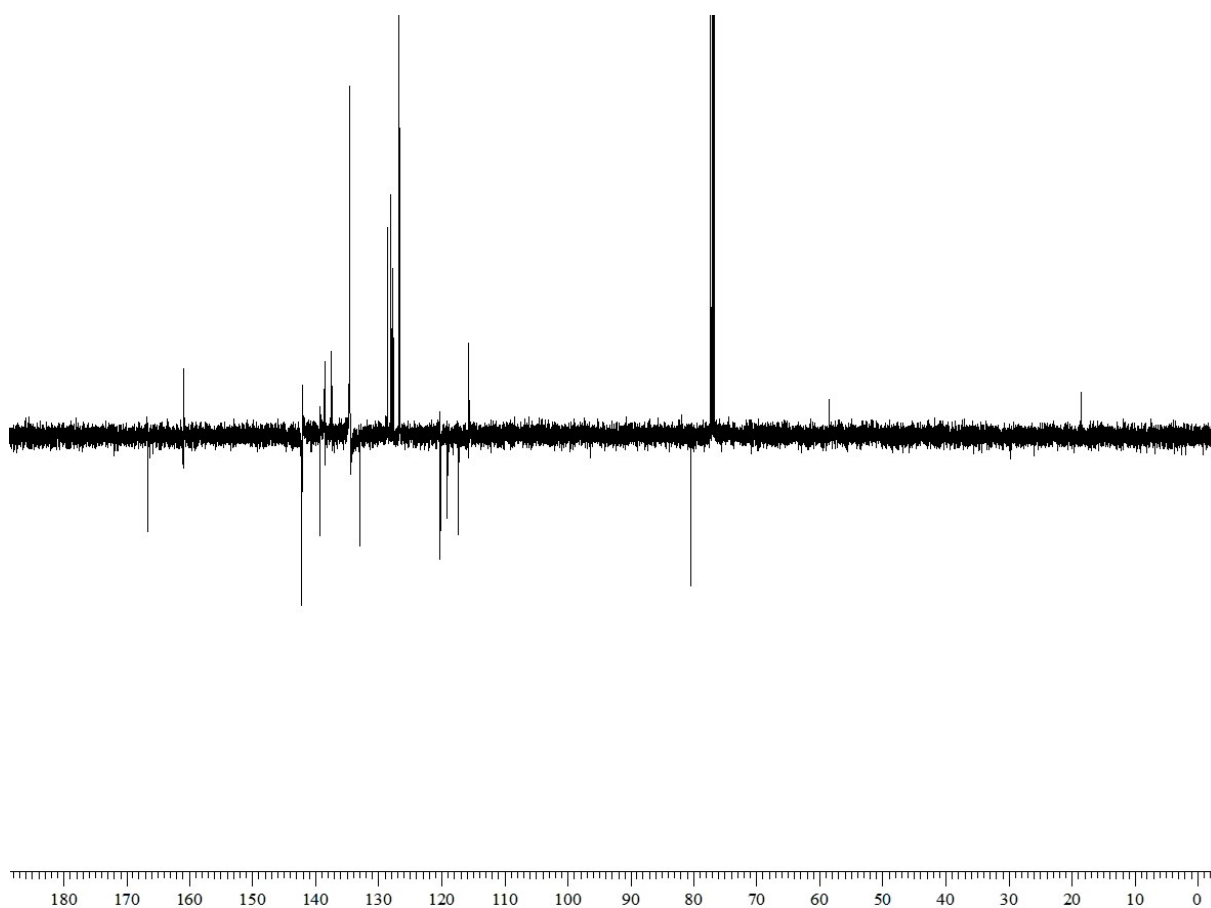


Figure S5. APT spectrum of compound 3 in CDCl<sub>3</sub>.

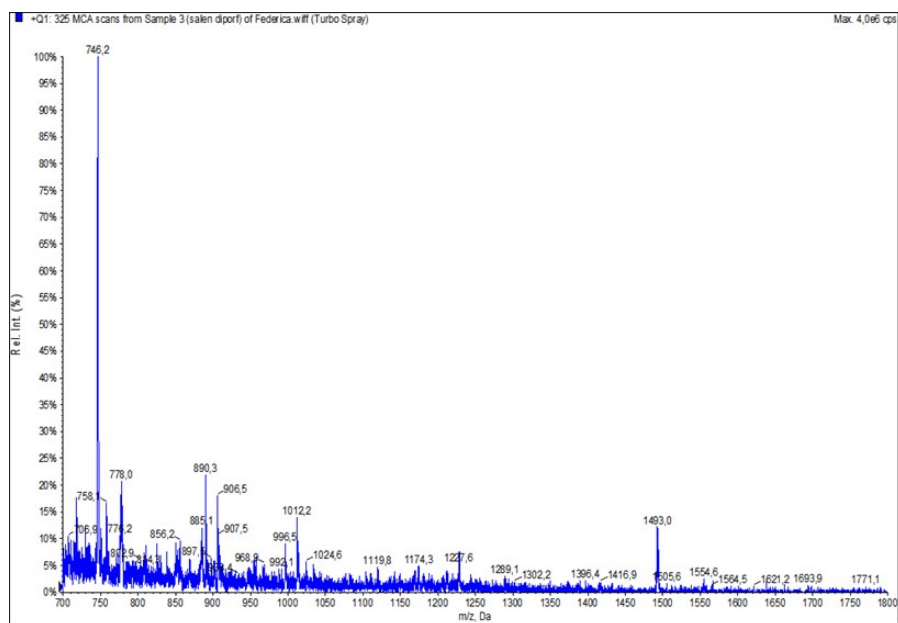
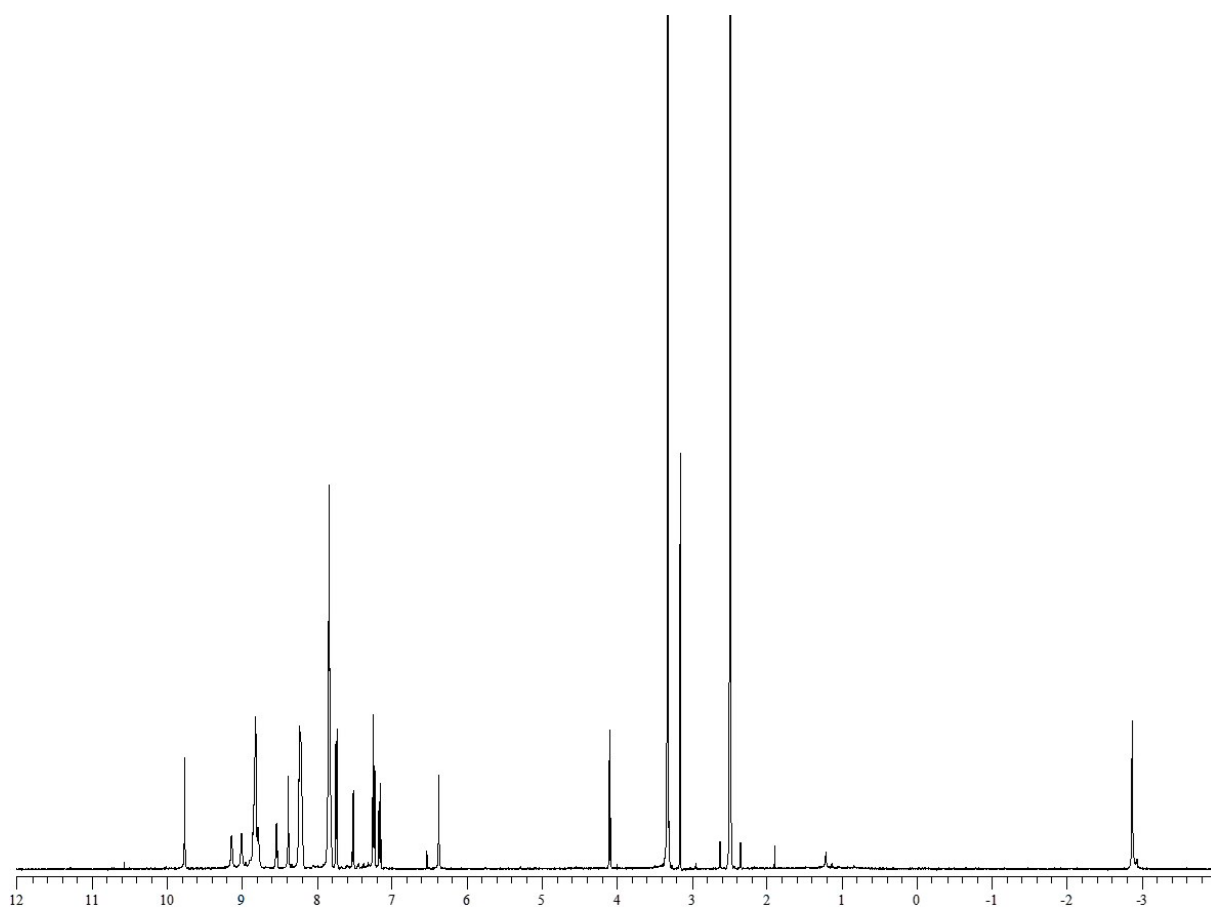


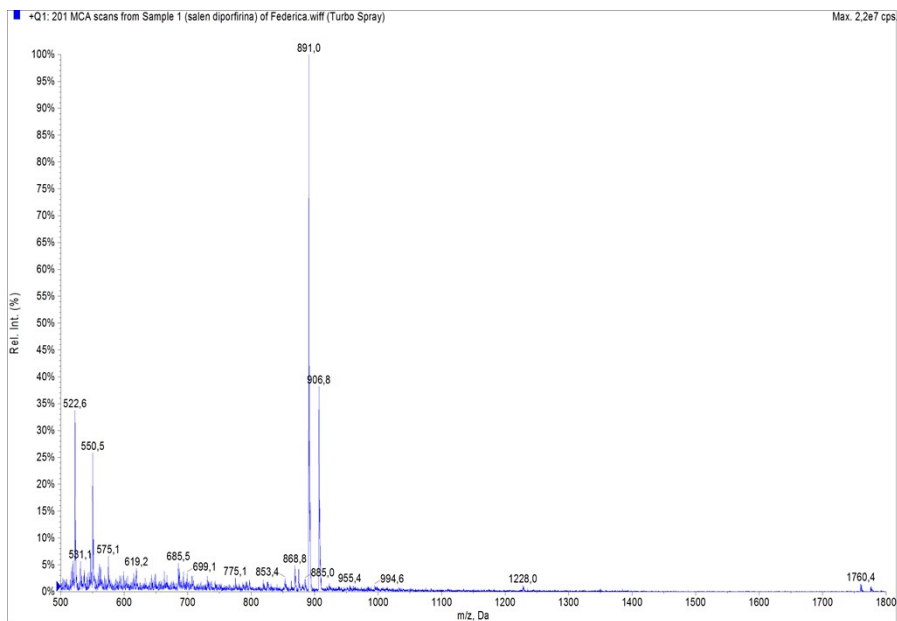
Figure S6. ESI-MS of compound 3.

**Synthesis of the bis-porphyrin-salen-UO<sub>2</sub> complex 1.** In a 25 mL round-bottom flask, 152 mg of compound **3** were dissolved in 10 mL of ethanol, and 43 mg of AcO<sub>2</sub>UO<sub>2</sub>•2H<sub>2</sub>O were added to the solution and stirred at room temperature for 24h. After filtration under reduced pressure, the desired compound was obtained as a brown solid (176 mg, 98% yield). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, Figure S7): δ= 9.81 (s, 2H); 9.17 (bs, 2H); 9.03 (bs, 2H); 8.78- 8.87 (m, 14H); 8.53-8.56 (m, 2H); 8.38-8.42 (m, 2H); 8.21-8.26 (m, 10H); 7.81- 7.88 (m, 18H); 7.75-7.78 (m, 4H); 7.55-7.58 (m, 2H); 7.21-7.25 (m, 4H); 7.16- 7.19 (m, 2H); 6.38 (s, 2H); -2.87 (s, 4H). ESI-MS *m/z*= 1760 [M+H]<sup>+</sup>; ESI-MS *m/z*= 891 [M+Na]<sup>2+</sup>; ESI-MS *m/z*= 907 [M+K]<sup>2+</sup>, (Figure S8).



**Figure S7.** <sup>1</sup>H-NMR of complex **1** in DMSO-*d*<sub>6</sub>.



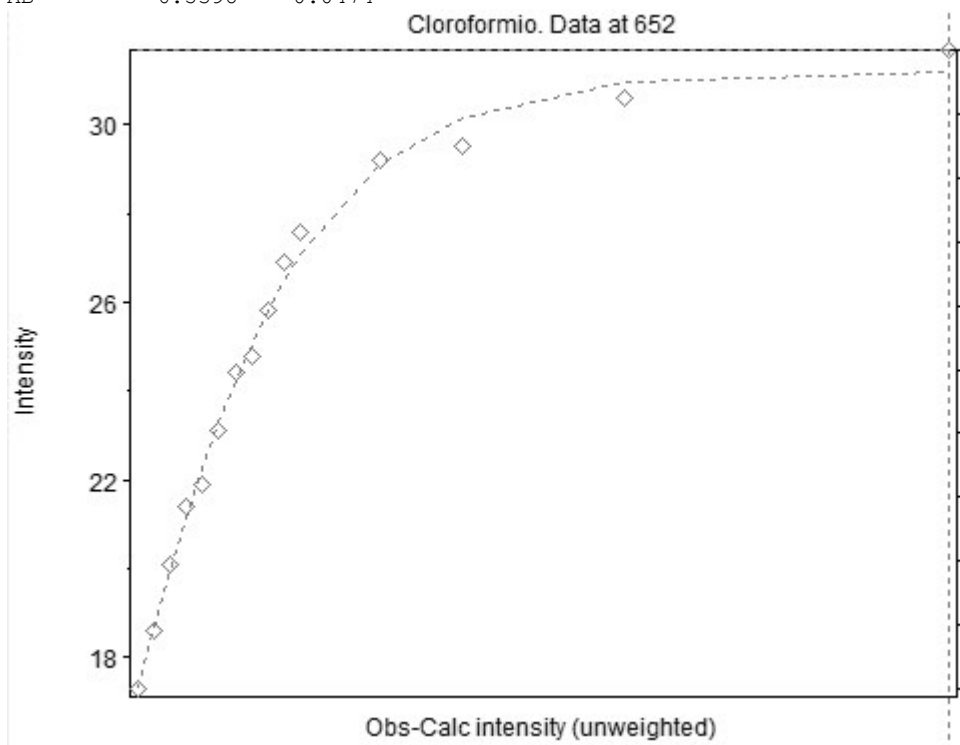


**Figure S8.** ESI-MS of complex 1.

### Fluorescence titration

The refinement was terminated after 1 iterations, sigma = 0,26296

Log beta	value	standard deviation
AB	6.5398	0.0474



**Figure S9.** Determination of binding constant value between complex 1 and DMMP.

### Determination of Stoichiometry:

Complex stoichiometry was investigated by the Job plot method using luminescence measurements. The samples were prepared by mixing equimolecular stock solutions ( $2 \times 10^{-4}$  M) of complex **1** and **DMMP** to cover the whole range of molar fractions keeping constant the total concentration ( $1 \times 10^{-6}$  M). The emission was recorded 625 nm by using  $\lambda_{\text{ex}}$  422 nm, and the changes in emission, compared to uncomplexed complex **1** species ( $\Delta I$ ) were calculated and reported versus the complex **1** mole fraction. These plots show invariably a maximum at 0.5 mol fraction of complex **1** indicating its 1:1 complex formation with the **DMMP**.

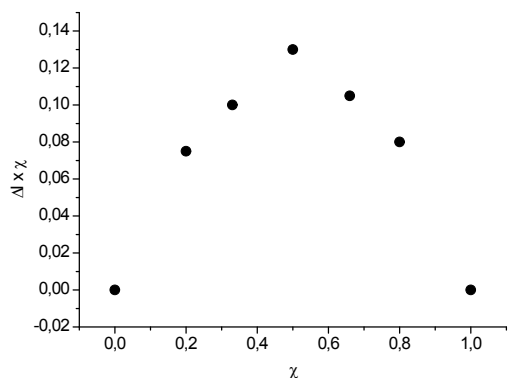


Figure S10. Job's Plot between complex **1** and **DMMP**.

### Selectivity Test

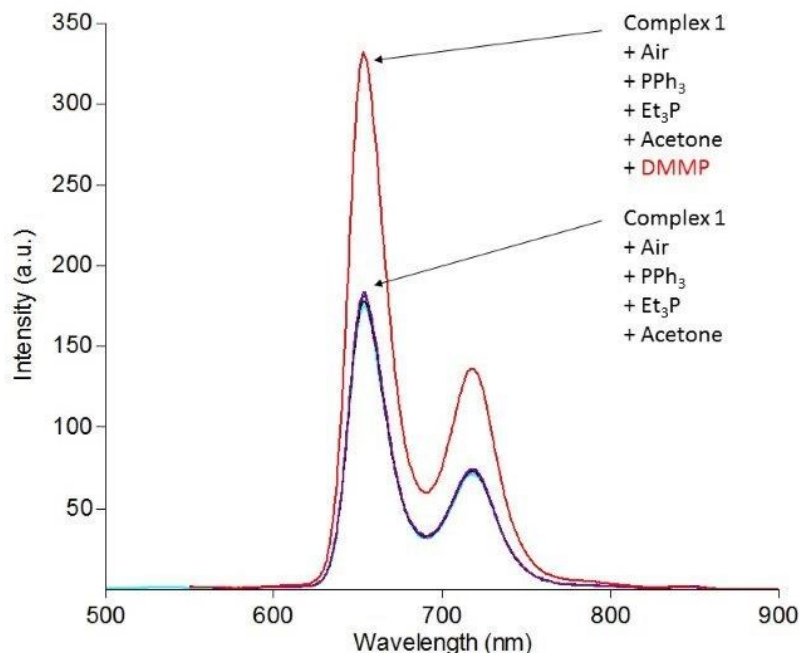
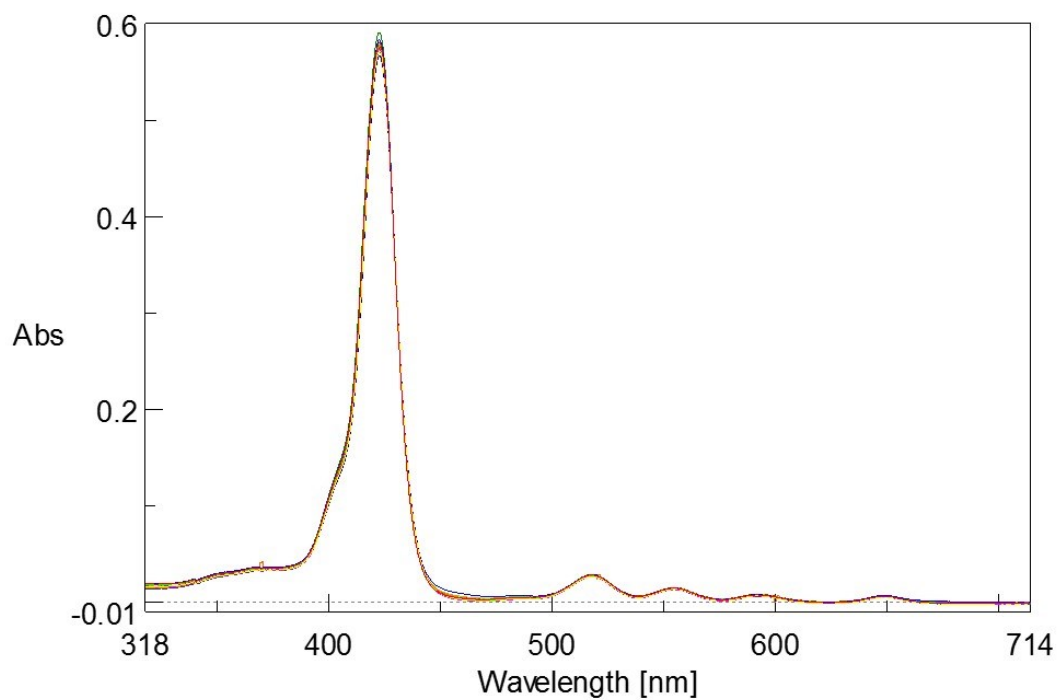
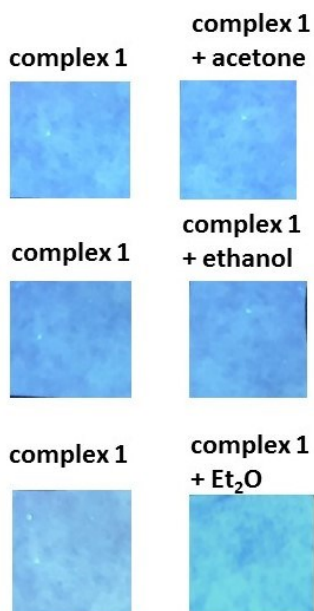


Figure S11. Fluorescence selectivity test. Analytes are successively added up to the final addition of **DMMP**.



**Figure S12.** UV-vis titration of complex **1** ( $1 \mu\text{M}$  in  $\text{CHCl}_3$ ) with increasing amount of DMMP (0-5 eq)



**Figure S13.** Vapour tests of complex **1** ( $10 \mu\text{M}$ ) with acetone ( $100 \mu\text{L}$ ), ethanol ( $100 \mu\text{L}$ ) and  $\text{Et}_2\text{O}$  ( $100 \mu\text{L}$ ), respectively.