Electronic Supplementary Material (ESI) for ChemComm.

SUPRAMOLECULAR RECOGNITION OF CWAs SIMULANT BY METAL-SALEN COMPLEXES: THE FIRST MULTI-TOPIC APPROACH

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General experimental methods. The NMR experiments were carried out at 27° C on a Varian UNITY Inova 500 MHz spectrometer (^{1}H at 499.88 MHz, ^{13}C NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tuneable 5 mm Varian inverse detection probe (ID-PFG). ESI mass spectra were acquired on a API 2000– ABSciex using CH_3CN (positive ion mode). 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. Dry chloroform was prepared by refluxing for 5 h over $CaCl_2$ and further distillation. Dry DMSO was prepared from commercial dry solvent, further dried over activated molecular sieves (3 Å) overnight.

Receptor **Zn-5tBut** was synthesised as reported in a previous paper.[1] 3D minimized structure reported in the manuscript were obtained using HyperChem v8.0.7, MM+ force field.

Procedure for ^{1}H NMR titrations. Two mother solutions of host and guest (7.0×10^{-3} M) in $CDCl_3$ were prepared. From these, different solutions with different ratio host/guest were prepared as reported below, and ^{1}H NMR spectra were recorded at 25 °C.

Procedure for UV-Vis and fluorescence titrations. Two mother solutions of host and guest (1.0×10^{-3} M) in dry solvent were prepared. From these, different solutions with different ratio receptor/guest were prepared as reported below, and UV-Vis or emission spectra were recorded at 25 °C. In the UV-Vis titration using dry $CHCl_3$ of **UO_2-3OH** with DMMP, 302.5 nm and 436.1 nm were monitored to calculate binding constant value. Fluorescence titration with **Zn-5tBut** was carried out using λ_{ex} = 375 nm in dry DMSO, recording at λ_{em} = 474 nm at 25 °C. Fluorescence titration of **Zn-3OH** and DMMP was carried out in dry DMSO, using λ_{ex} = 290 and λ_{em} 340/505 nm, and λ_{ex} = 380 and λ_{em} 430/505 nm, at 25°C. With this data treatment, the apparent binding affinities of receptors with DMMP were estimated using HypSpec (version 1.1.33),[2] 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. χ^2 test (chi-square) was applied, where the residuals follow a normal distribution (for a distribution approximately normal, the χ^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.

Determination of Stoichiometry. Stoichiometry of the complexes were investigated by the Job's plot method, using spectrophotometric measurements. The samples were prepared by mixing equimolecular stock solutions (1.0×10^{-3} M) of the appropriate host and guest to cover the whole range of molar fractions, keeping constant the total concentration (1×10^{-5} M). The changes in absorbance compared to uncomplexed receptor species ($\Delta A \times \chi^{-1}$) were calculated and reported versus the receptor mole fraction (χ). These plots show invariably a maximum at 0.5 mol fraction of receptor, thus suggesting its 1:1 complex formation.

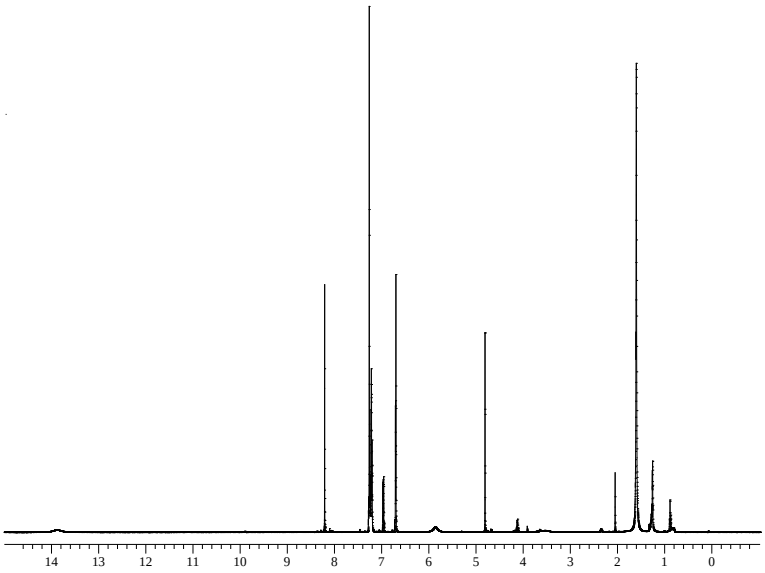
Synthesis of salen ligand 3OH: 2,3-dihydroxybenzaldehyde (0.140 g, 1 mmol) and (*1R,2R*)-1,2-diphenylethane-1,2-diamine (0.113 g, 0.5 mmol) in absolute ethanol (8 mL) were stirred at room temperature for 24h. Then the solvent was removed under reduced pressure leading to the salen ligand as orange crystals (yield 87%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.85 (s. br., 2H), 8.21 (s, 2H), 7.19-7.28 (m, 10H), 6.95-6.97 (m, 2H), 6.69-6.71 (m, 4H), 5.87 (s. br, 2H), 4.81 (s, 2H). ^{13}C NMR (127.5 MHz, CDCl3) δ 166.3, 149.8, 145.0, 138.9, 128.6, 127.9, 127.6, 122.5, 118.6, 117.6, 117.3, 79.0.

ESI-MS: *m/z* 453.2 $[M+H]^+$. Anal. Calcd. for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19. Found: C, 74.28; H, 5.31; N, 6.11.

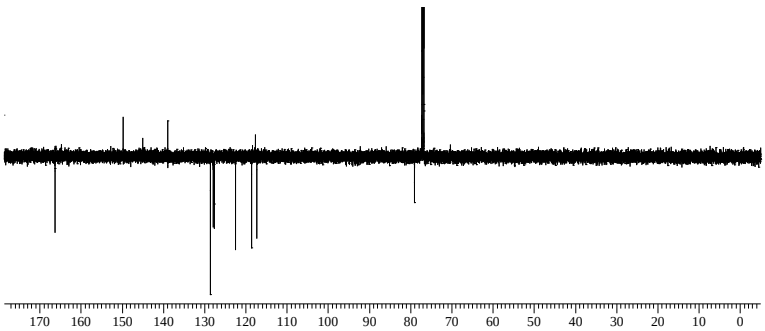
General procedure for the synthesis of metal salen complexes. A solution of the corresponding metal acetate salt (0.2 mmol) in absolute ethanol (8 mL) was added dropwise to a solution of salen ligand 3OH (0.2 mmol) in absolute ethanol (3mL), and the mixture was stirred at reflux under nitrogen for 18h. Then, the precipitate was filtered to yield the corresponding metal salen complex.

UO_2-3OH (yield 90%): ^{1}H NMR (500MHz, DMSO-d_6) δ 9.35 (s, 2H), 8.40 (s, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.11-7.20 (m, 10H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.50 (t, *J* = 8.0 Hz, 2H), 6.30 (s, 2H). ^{13}C NMR (127.5 MHz, DMSO-d_6) δ 158.8, 147.8, 141.4, 128.1, 127.3, 127.1, 124.5, 122.3, 116.2, 79.5. ESI-MS: *m/z* 742.9 $[M+Na]^+$. Anal. Calcd. for $C_{28}H_{22}N_2O_6U$: C, 46.68; H, 3.08; N, 3.89. Found C, 46.62; H, 3.02; N, 3.82.

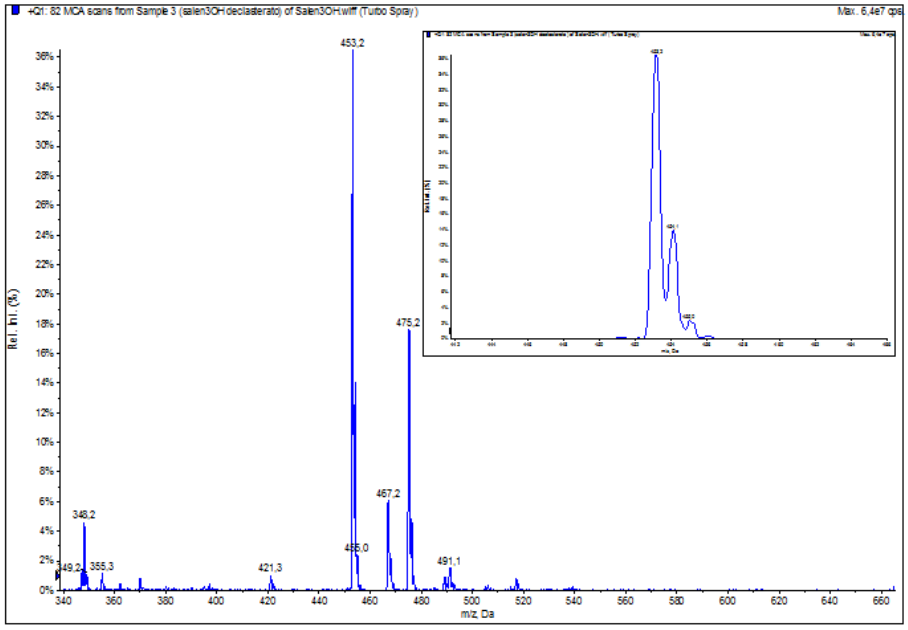
Zn-3OH (yield 74%). ^{1}H NMR (500MHz, DMSO-d_6): δ 8.25 (s, 2H), 7.87 (s, 2H), 7.39-7.41 (m, 4H), 7.32-7.36 (m, 4H), 7.24-7.27 (m, 2H), 6.73 (dd, J_1 =7.5 Hz, J_2 = 1.0 Hz, 2H), 6.53 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 2H), 6.28 (t, *J*=7.5 Hz, 2H), 5.14 (s, 2H). ^{13}C NMR (127.5 MHz, DMSO-d_6) δ 169.6, 159.0, 149.3, 140.9, 128.4, 127.6, 127.4, 123.9, 116.9, 113.2, 112.2, 72.1. ESI-MS: *m/z* 537.0 $[M+Na]^+$.Anal. Calcd. for $C_{28}H_{22}N_2O_4Zn$: C, 65.19; H, 4.30; N, 5.43. Found: C, 65.15; H, 4.25; N, 5.38.



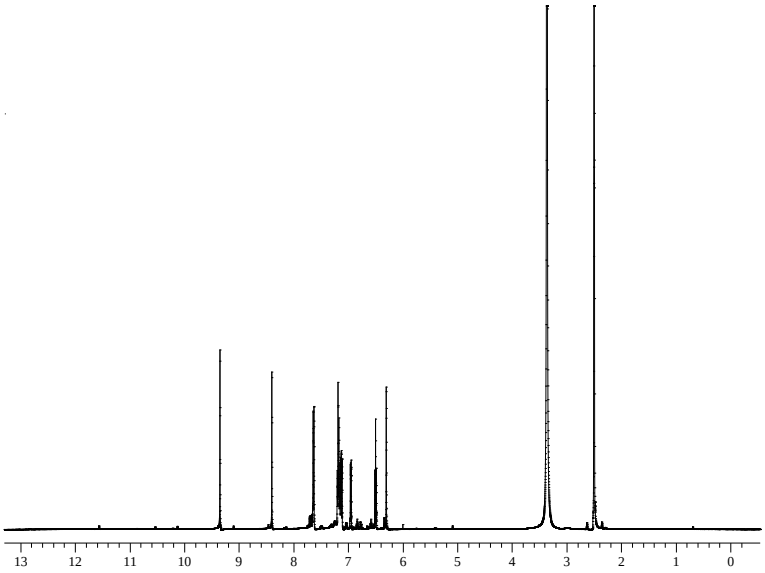
^{1}H NMR spectrum of salen ligand 3OH in $CDCl_3$



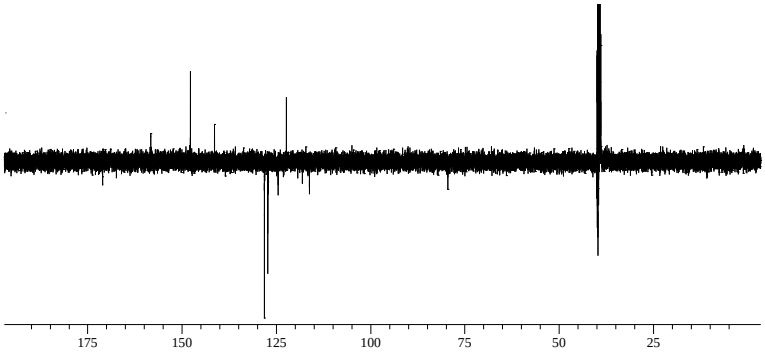
APT spectrum of salen ligand 3OH in $CDCl_3$



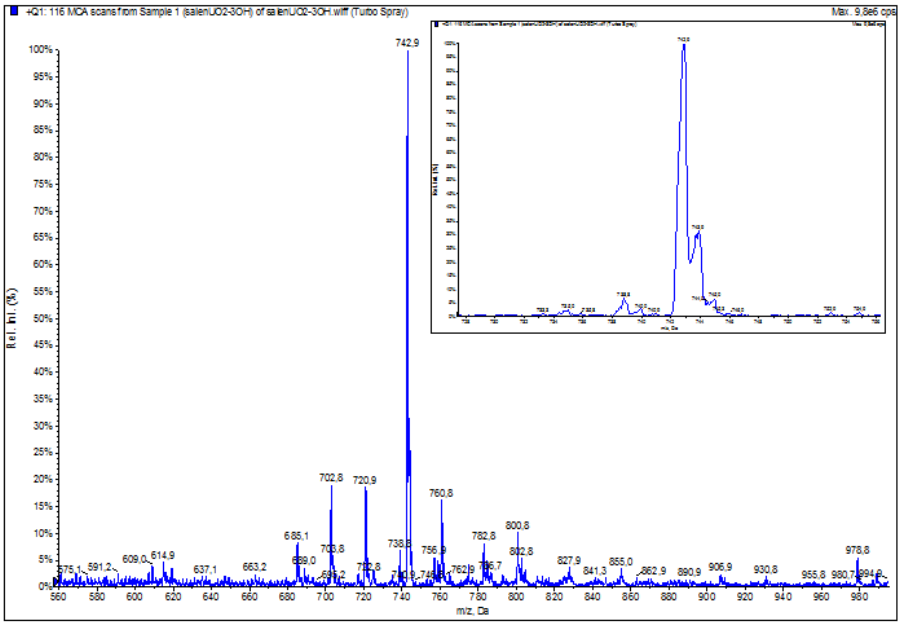
ESI-MS spectrum of salen ligand 3OH. Inset shows the expansion of molecular peak.



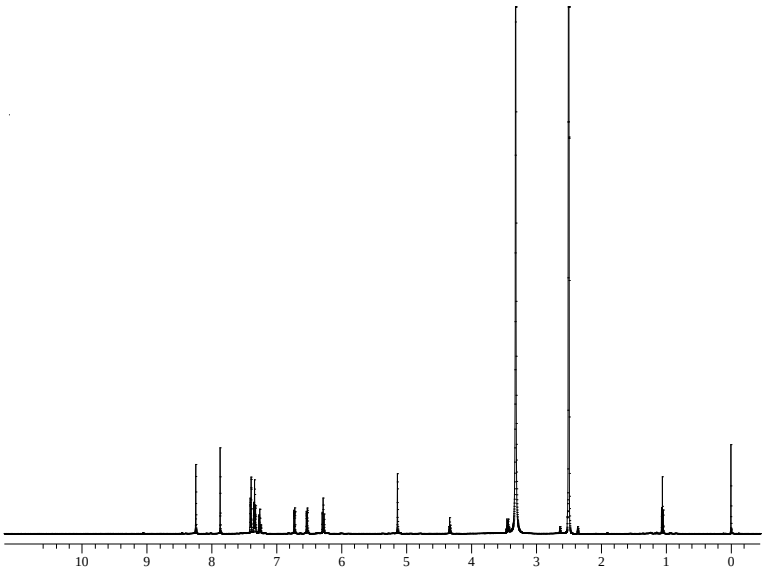
^{1}H NMR spectrum of **UO_2-3OH** in DMSO-d_6



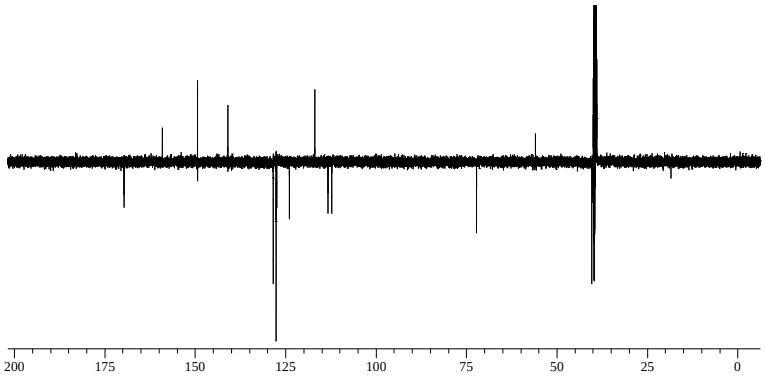
APT spectrum of **UO_2-3OH** in DMSO-d_6.



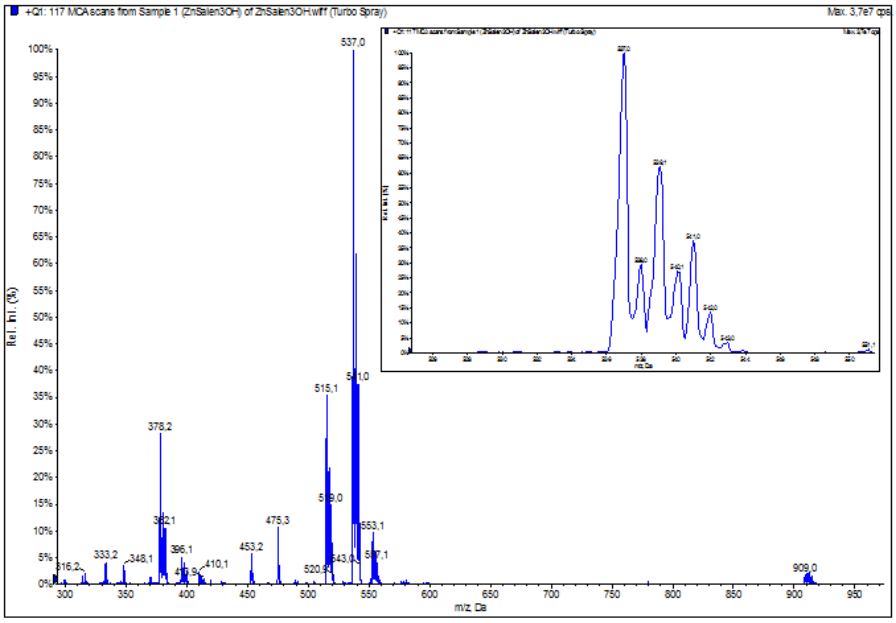
ESI-MS spectrum of **UO_2-3OH**. Inset shows the expansion of molecular peak.



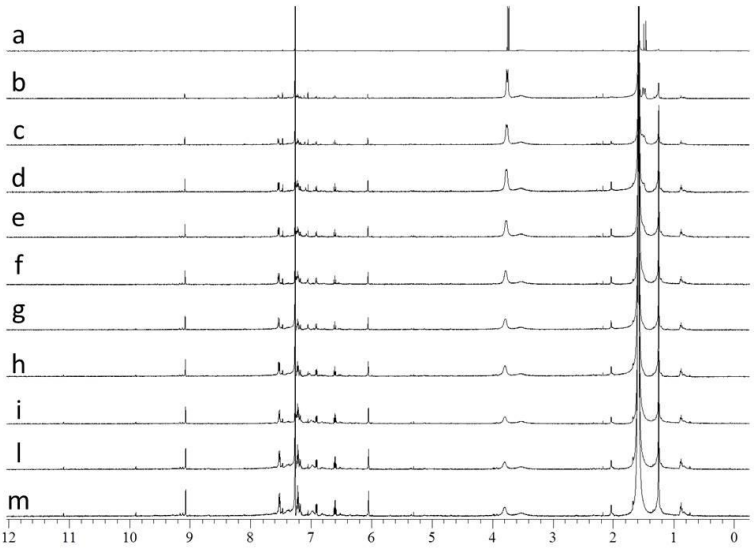
^{1}H NMR spectrum of **Zn-3OH** in DMSO-d_6



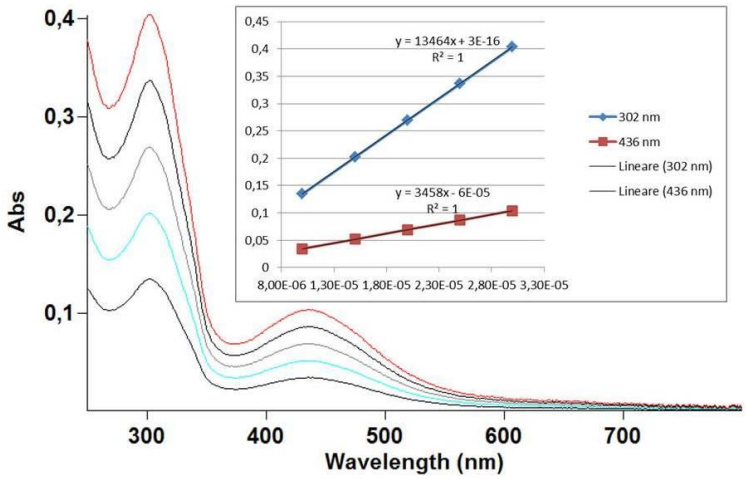
APT spectrum of **Zn-3OH** in DMSO-d_6



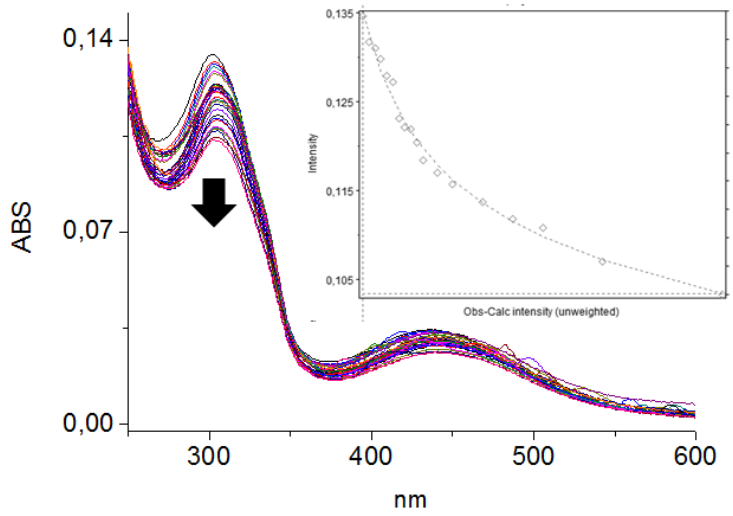
ESI-MS spectrum of **Zn-3OH**. Inset shows the expansion of molecular peak.



^{1}H NMR titration of DMMP with **UO_2-3OH** in $CDCl_3$. The amount of guest was kept constant (1 x 10^{-3} M) and increasing amount of receptor were added: a) GUEST; b) 0.25 eq; c) 0.5 eq; d) 0.75 eq; e) 1.0 eq; f) 1.5 eq; g) 2.0 eq; h) 3.0 eq; i) 5.0 eq; l) 7.0 eq; m) 9.0 eq.



UV-Vis spectra of **UO_2-3OH** in $CHCl_3$ at different concentrations (from 1 x 10^{-5} M to 3.0 x 10^{-5} M), inset shows the plot for the ε determination.



UV-Vis titration between **UO_2-3OH** and DMMP ($CHCl_3$, [**UO_2-3OH**] = 1 x 10^{-5} M, DMMP additions were in the 0-9 equivalent range). Inset shows HypSpec plot

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HypSpec output file

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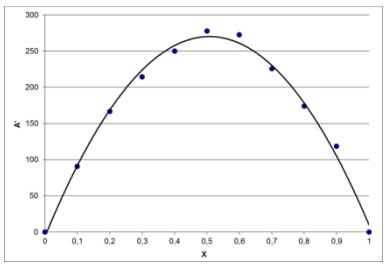
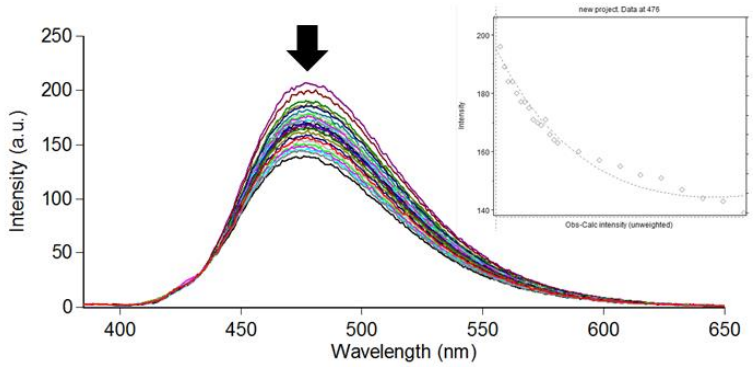


Job's Plot between **UO_2-3OH** and DMMP



Fluorescence titration between **Zn-5tBut** and DMMP (DMSO, [**Zn-5tBut**] = 1 x 10^{-5} M, DMMP additions were in the 0-6 equivalent range). Inset shows HypSpec plot.

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HypSpec output file

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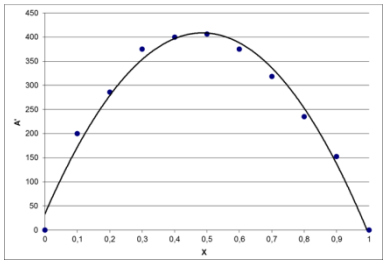
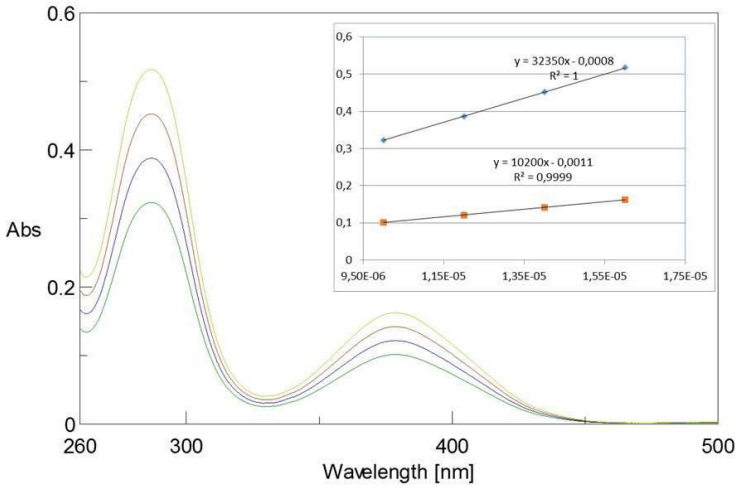
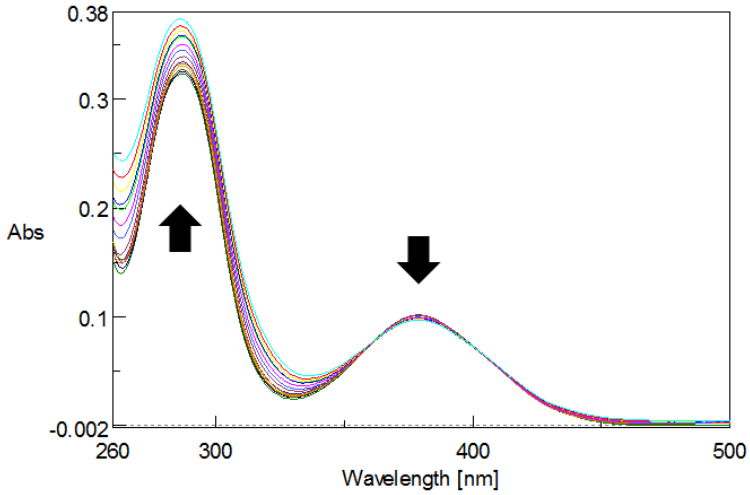


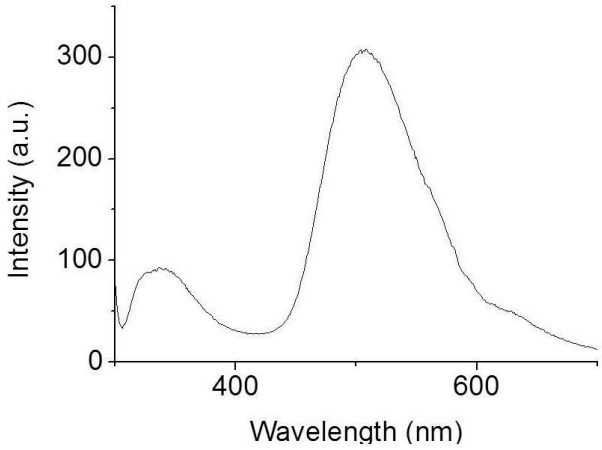
Job's Plot between **Zn-5tBut** and DMMP



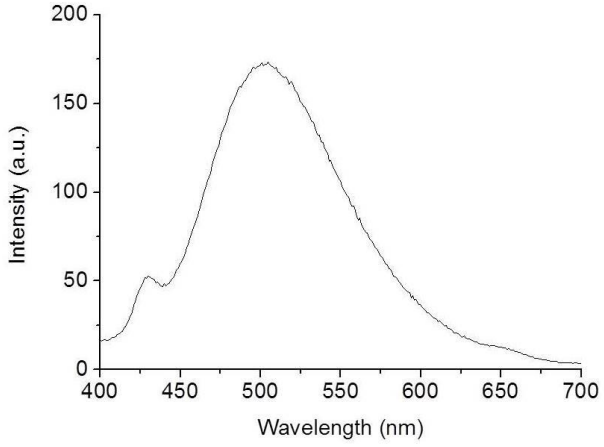
UV-Vis spectra of **Zn-3OH** in DMSO at different concentrations (from 1.0 x 10^{-5} M to 1.6 x 10^{-5} M), inset shows the plot for the ε determination.



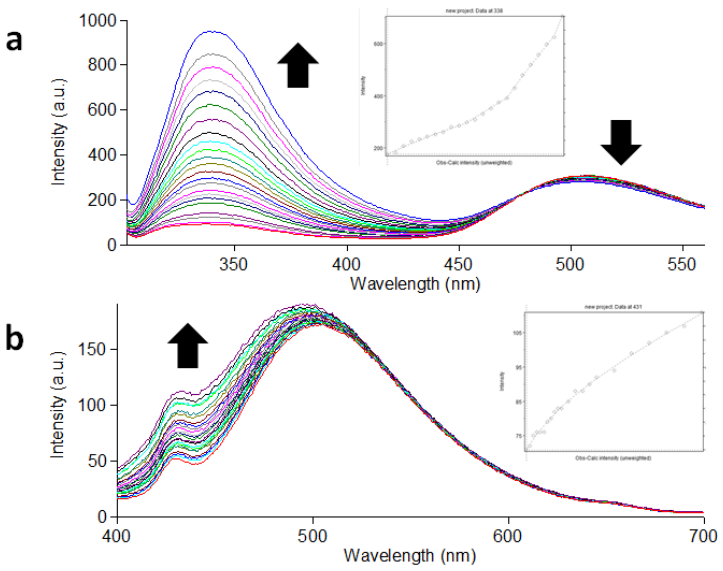
UV-Vis titration between **Zn-3OH** and DMMP (DMSO, [**Zn-3OH**] = 1 x 10^{-5} M, DMMP additions were in the 0-6 equivalent range).



Emission spectrum of **Zn-3OH** in DMSO (1 x 10^{-5} M, λ_{ex} 290 nm)



Emission spectrum of **Zn-3OH** in DMSO (1 x 10^{-5} M, λ_{ex} 380 nm)



Fluorescence titration between **Zn-3OH** and DMMP, a) λ_{ex} 290 nm; b) λ_{ex} 380 nm (DMSO, [**Zn-3OH**] = 1 x 10^{-5} M, DMMP additions were in the 0-6 equivalent range). The insets show HypSpec plots.

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HypSpec output file

Converged in 1 iterations with sigma = 0,93502

                        standard
Log beta    value       deviation
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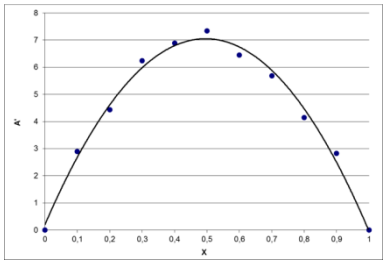
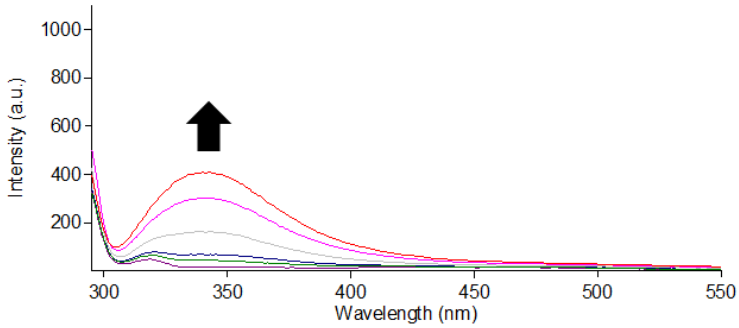
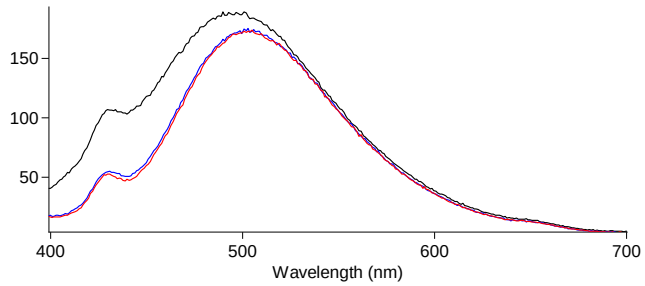


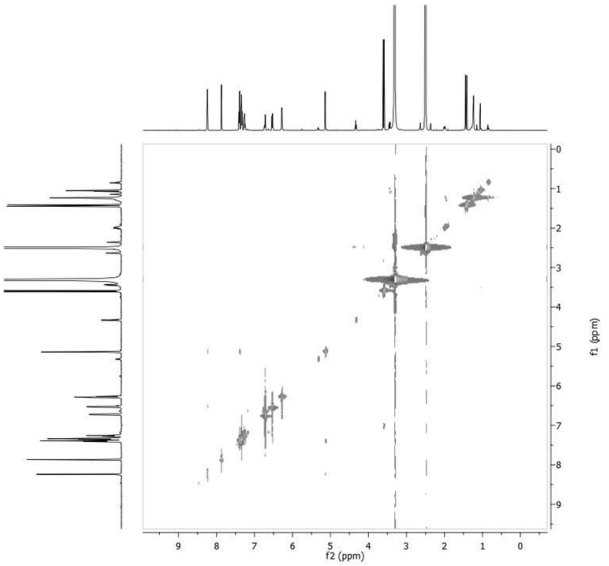
Job's Plot between **Zn-3OH** and DMMP



Emission spectra of DMMP in DMSO (λ_{ex} 290nm, [DMMP] = from 1 x 10^{-6} M to 6 x 10^{-5} M)



Selectivity tests: emission spectra of: **Zn-3OH** (red line, 1 x 10^{-5} M in DMSO), **Zn-3OH** after 10 minutes of air bubbling (blue line), **Zn-3OH** after 10 minutes of air bubbling and 5eq. of DMMP (black line).



TROESY spectrum of **Zn-3OH** (1 x 10^{-3} M, DMSO-d_6, mixing time 500 ms.) with 1 equivalent of DMMP.

[1] R. Puglisi, F. P. Ballistreri, C. M. A. Gangemi, R. M. Toscano, G. A. Tomaselli, A. Pappalardo, G. Trusso Sfrazzetto *New J. Chem.*, **2017**, *41*, 911-915

[2] (a) A. R. Jennings, D. Y. Son *Tetrahedron Lett.*, **2012**, *53*, 2181; (b) A. Pappalardo, F. P. Ballistreri, G. Li Destri, P. G. Mineo, G. A. Tomaselli, R. M. Toscano, G. Trusso Sfrazzetto *Macromolecules*, **2012**, *45*, 7549; (c) A. Pappalardo, M. E. Amato, F. P. Ballistreri, G. A. Tomaselli, R. M. Toscano, G. Trusso Sfrazzetto *J. Org. Chem.*, **2012**, *77*, 7684.