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Nerve Gas Simulant Sensing by an Uranyl-Salen Monolayer Covalently Anchored on Quartz Substrates

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Abstract: We report on an uranyl complex monolayer that easily allows the optical detection of a nerve gas simulant, namely the dimethyl methylphosphonate. Both UV-vis and photoelectronic data confirm that the functional hybrid material coordinates this Lewis basis by means of the P=O group that interacts with the uranium equatorial site available for complexation.

Introduction

Chemical attacks consist in the intentional dispersion of toxic chemicals to harm. Chemical warfare agents (CWA), include a large crop of toxic chemicals already used in the industrialized countries e.g., pesticides, as well as chemicals especially produced to harm people. The modern CWA, such as chlorine, phosgene and vesicant, were introduced with the First World War and since that time, a wide number of chemical compounds were synthesised to act as CWA, with the development of the organophosphorus (OP) of G- and V- series.[1] These compounds inhibit the enzyme acetylcholinesterase (AChE) in the human synapses occupying the active site.[2,3]

Some chemicals can be readily detected, whereas others need the development of safe and real-time detection systems and procedures.

Molecular films for sensing application recently addressed much academic and industrial interest.[4-13] A molecular complementarity between the sensing agent and the target compound assures selective analyte recognition.[14-20]

Nevertheless, the design of effective sensing agents that retain and possibly enhance their molecular recognition properties at the solid-state interface continues to be a major challenge.[21-36]

The development of device-quality monolayer-based sensors requires not only selectivity and sensitivity towards a specific analyte, but also a high degree of stability and a fast non-destructive read-out process.

The risk of chemical attacks with nerve gases has led to the development of selective sensors for the given nerve-agent. The using of CWAs reagents for recognition studies is not open to all researchers for security reasons, thus many studies were conducted by using simulants, less toxic compounds that mimic the properties of CWAs. The choice of the appropriate simulant is crucial to evaluate the detection properties and the sensor efficiency. In this context, recent studies have identified dimethyl methylphosphonate (DMMP, see Supporting Information, Figure S1) as one of the best simulant for G-series nerve agents.[37] DMMP is harmful if inhaled, swallowed or absorbed through the skin and it is used in the synthesis of the Sarin nerve gas (see Supporting Information, Figure S1).[38] Both these compounds show a reactive phosphoryl (P=O) group covalently linked to alkyl-side chains.

Therefore some sensors for CWA involve the formation of a covalent bond between a nucleophilic group of the sensor and the reactive P=O group.[39-44]

Recently a new method consisting in surface-enhanced Raman scattering measurements after the water evaporation and increased concentrating of a DMMP solution was reported.[45] Also IR-ATR spectroscopy has been applied to a study of the interaction of DMMP with amorphous α-SiO_2 grown by plasma oxidation of Si, on Al_2O_3, and on AlO-(OH) surfaces as a function of the relative humidity.[46] Besides a composite nanostructured film comprising of MnO_2 nanofibers modified with ZnO were prepared on a quartz crystal microbalance for nerve gas sensing.[47] Acidic Polymers for Surface Acoustic Wave Sensors and for inverse gas chromatography of DMMP were recently developed.[48-49]

The supramolecular approach, even if it is less used,[50] gives alternative pathways to detect this class of CWAs. Examples for the non-covalent recognition of CWAs simulants include some gels, cyclodextrin and cavitand hosts that grant hydrophobic effects and hydrogen bonds to the guest.[51-64] In the last years, Badjić and co-workers reported on the supramolecular recognition of OP using a molecular basket as hydrophobic host, obtaining an efficient recognition for aromatic OP.[55,57,58,60]

Recently, it has been reported on an important supramolecularly-based recognition of the DMMP using a cavitand anchored onto a porous silicon surface.[65] Another approach used to recognize the P=O group was the formation of coordinative bonds with a Lewis acid center.[66-70] Also an excellent study has been proposed by Atwood and co-workers who used a Salen-aluminum complex as a probe for the Sarin and Soman Lewis base nerve agents in aqueous solution by ESI-MS experiments.[71]

In the light of the supramolecular advantages, here we report on the first example of uranyl Salen complexes (Chart 1) able to recognize the DMMP *via* non-covalent interactions in solution.

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Moreover we anchored this metal complex, especially functionalized with a hydroxymethyl group, onto a silica surface and anticipate that this functional hybrid material easily allows the optical detection of trace levels of DMMP by simple absorption measurements. The advantage of using this uranyl complex to detect DMMP is demonstrated by the host-guest 1:1 supramolecular complex logK binding constant value of 4.35 that corresponds to the highest observed value for these kinds of supramolecular host-DMMP complexes.

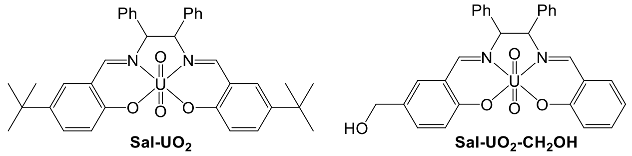


Chart 1. Chemical structures of the uranyl Salen receptors **Sal-UO$_2$** and **Sal-UO$_2$-CH$_2$OH**.

Results and Discussion

The **Sal-UO$_2$** receptor was synthesised and characterized according to the literature.[72] The molecular recognition of DMMP is favored by the pentagonal bipyramidal coordination geometry of the uranyl ion, having the fifth equatorial site available for complexation with monodentate Lewis base ligands (P=O group). In particular, ^{1}H NMR titration of DMMP with **Sal-UO$_2$** (1 mM) shows a progressive downfield shift of resonances of the O-CH$_3$ and P-CH$_3$ methyl groups, relative to the DMMP, thus suggesting its coordination to the uranyl metal center (see Supporting Information, Figure S2). Furthermore, the signals relative to the imine and methine protons of the diphenyl bridge of the receptor undergo a upfield shift with respect to the free receptor, thus confirming the binding event. ^{1}H NMR sensing experiments in water saturated chloroform confirm the DMMP coordination to the uranyl metal centre even in presence of water (Figure S3).

Recognition properties were also evaluated by UV-vis titrations. A 7.01 x 10^{-6} M **Sal-UO$_2$** CHCl$_3$ solution shows three main bands at 268.2, 341.8 and 412.2 nm (Figure 1).

UV-vis spectra obtained upon the successive additions of DMMP, in the 0.1 - 9.0 equivalent range, show a progressive and monotonic intensity increase at 268.2 nm and a concomitant absorbance decrease in the remaining overall region with two isosbestos points at 273.2 and 321.8 nm. This behavior indicates the formation of the host-guest 1:1 supramolecular complex, with a log*K* binding constant value = 4.35 (see Supporting Information, Figure S4-S5).[73] This affinity value is, at the best of our knowledge, the higher reported in the literature for the DMMP recognition.

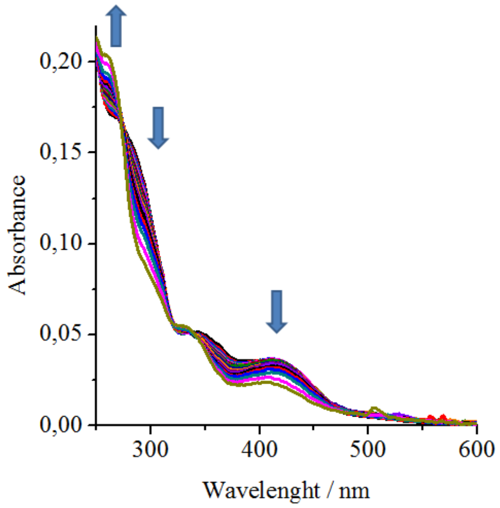


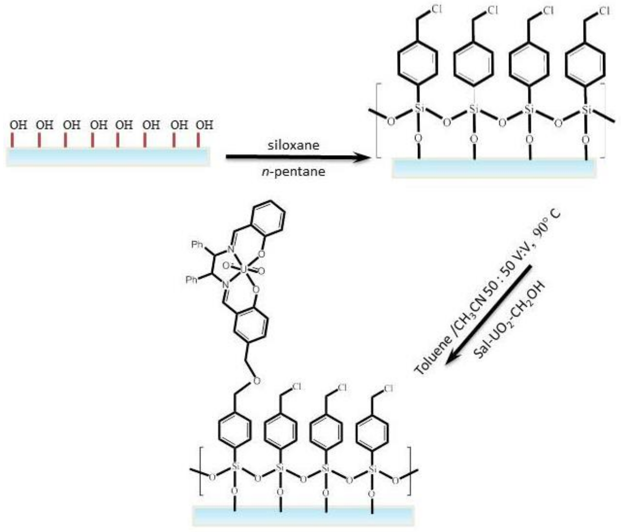
Figure 1. UV-Vis spectra of a 7.01 x 10^{-6} M **Sal-UO$_2$** CHCl$_3$ solution upon progressive addition of DMMP (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.25, 1.50, 1.75, 2.0, 2.5, 3.0, 4.0, 6.0 and 9.0 equivalents).

FTIR measurements on the **Sal-UO$_2$** complex before and after interaction with 1 eq. of DMMP, followed by precipitation with *n*-hexane, are shown in Figure S6. It results evident an overall intensity increase of the IR bands in the 1360-770 cm^{-1} range. In fact the ν_s U=O stretching at 818 cm^{-1} evidently increases in intensity upon DMMP coordination. Moreover there is a strong enhancement on the band centered at 1046 cm^{-1} due to the P=O coordination to the uranium center. Furthermore also the intensity increase of the band at 1204 cm^{-1} indicates the increase in the number of the C-O functionalities due to the DMMP.[74]

Encouraged by these results, the **Sal-UO$_2$** was functionalised to be covalently anchored on silica surfaces (Chart 1, see Experimental and Supporting Information, Figures S7-S17). Then, we cleaned and hydroxylated some SiO$_2$ and Si(100) (see Experimental). The silylation reaction was performed under rigorously inert atmosphere with the trichloro[4-(chloromethyl)phenyl]silane, a bi-functional coupling agent that binds both the substrate and **Sal-UO$_2$-CH$_2$OH**.[75] Then these SiO$_2$ and Si(100) substrates were reacted with a stirred 1.93 x 10^{-4} M toluene / CH$_3$CN 50 : 50 v : v solution of the **Sal-UO$_2$-CH$_2$OH** (90 °C, 70 h) to get the **U_Salen_SAM** monolayer (Scheme 1).

The electronic structure characterization of the **U_Salen_SAM** was carried out by X-ray photoelectron spectroscopy. This technique is ideal as it permits high vertical resolution, gives information on the bonding states of the grafted molecules, and allows estimation of the surface elemental composition, once the relevant atomic sensitivity factors have been taken into account.[76,77]

Figure 2 shows the XP spectrum of the **U_Salen_SAM** in the U 4f - N 1s binding energy region. This spectrum was fitted using five components. The two at 381.0 and 391.9 eV represent the ionization of the U 4f$_{7/2,5/2}$ spin-orbit components (FWHM = 2.9 eV), respectively.



Scheme 1. Synthesis pathway for the **U_Salen_SAM**.

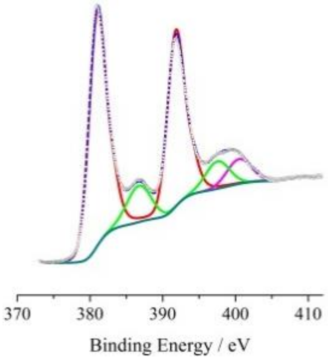


Figure 2. Al-Kα excited XPS of the **U_Salen_SAM** in the U 4f - N 1s binding energy region. Structures due to $K\alpha_{3,4}$ satellites were subtracted from the spectra. The dotted black line refers to the experimental profile, the red line refers to the U 4f components, the green line refer to the U 4f shake-up bands, the magenta line refers to the N 1s component, the dark cyan line refers to the background and the blue line refers to the sum of all components.

These values and the spin-orbit separation of 10.9 eV are consistent with U(VI) states. The band at 400.5 eV accounts for the two nitrogen atoms of the U_Salen molecule. The components at 386.8 and 397.7 eV (5.8 eV from the main peaks) represent the shake-up bands associated to the U 4f states. For a given uranium oxidation state the satellite positions are likely to vary significantly depending upon the uranium chemical environment.[78] These XPS results are the first for uranium Schiff-base complexes.

The XPS atomic concentration analysis gave a N/U atomic ratio exactly of 2 as expected on the basis of the **Sal-UO_2-CH_2OH** formula. Moreover the U/Cl atomic ratio indicates a 41% reaction yield towards the silane coupling layer molecules.

The surface morphology of the **U_Salen_SAM** investigated by AFM (see Supporting Information, Figure S18) shows that the monolayer is homogeneous and its root mean square roughness is 1.9 ± 0.2 nm.

The UV-vis spectrum of a representative **U_Salen_SAM** in the 300-600 nm range is shown in Figure 3. Similarly to the **Sal-UO_2-CH_2OH** solution we clearly observe an evident band at 345.4 nm followed by a shoulder at higher wavelength. The 3.6 nm red shift of this band with respect to that observed in the $CHCl_3$ solution is indicative of a covalent bond of the **Sal-UO_2-CH_2OH** with the surface. After the subtraction of the background due to the higher energy UV component of the **Sal-UO_2-CH_2OH** (268.2 nm in its $CHCl_3$ solution), using the Lambert-Beer law it is possible to calculate the surface coverage that resulted 1.3 x 10^{14} molecules/ cm^2. This value is highly compatible with a molecular monolayer of **Sal-UO_2-CH_2OH** molecules.[79]

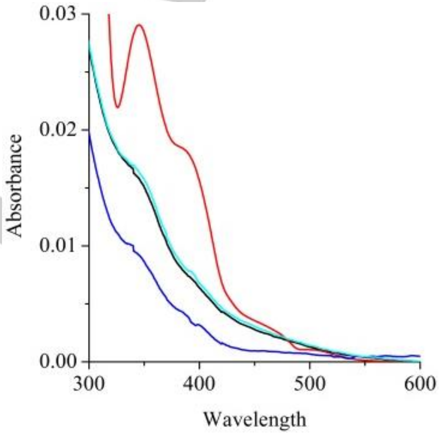


Figure 3. UV-vis spectra of a 3.86 x 10^{-6} M toluene / CH_3CN v : v, 50 : 50 solution of the **Sal-UO_2-CH_2OH** (red line), of the **U_Salen_SAM** (black line), of the **U_Salen_SAM** after immersion in 25 mL of a $CHCl_3$ solution containing 2 μL of DMMP (0.008 % v: v), washing with $CHCl_3$ and drying under nitrogen (blue line), and after heating the as-synthesized **U_Salen_SAM** at 120° C for 24 h (green line).

The linear UO_2^{2+} dioxo ion do form complexes with neutral molecules with coordination numbers that range between 6 and 8.

Therefore to check on the sensing ability of the **U_Salen_SAM** towards DMMP we performed some UV-vis measurements after 10 min immersion of this monolayer in 25 mL of a $CHCl_3$ solution containing 2 μL of DMMP, washing with $CHCl_3$ and drying under nitrogen.

According to that previously observed in the $CHCl_3$ solution we noted a fall-off of the whole spectral area (300-600 nm) consistent with the coordination of the DMMP via the P=O group to the uranyl metal center that, as a consequence, on the surface assumed a grafting geometry suitable to allow the uranium free equatorial site to coordinate the DMMP Lewis base. Therefore the **U_Salen_SAM** allows optical sensing of trace amounts of DMMP and, worthy of note, these experiments have

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been performed in air (real conditions) in which we measured 24000 ppm of water, 400 ppm CO_2, 5 ppm NO, 10 ppm of CO thus inferring a good sensor selectivity.

The detection limit of the **U_Salen_SAM** depends on the optical photometric accuracy of the UV-vis V-650 Jasco spectrophotometer that is ± 0.003 Abs. Therefore, using our present set-up, a 0.001 % v: v DMMP concentration (2 μL of DMMP in 150 mL of $CHCl_3$) represents the optical detection limit (Figure S19).

This behavior was further confirmed by photoelectron measurements. In fact XP spectra of the **U_Salen_SAM** after 10 min immersion in 25 mL of a $CHCl_3$ solution containing 2 μL of DMMP, washing with $CHCl_3$ and drying under nitrogen show a clear P 2p signal at 133.7 eV (Figure 4).

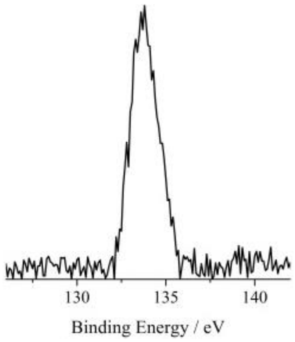

Figure 4. Al-Kα excited XPS of the **U_Salen_SAM**, after immersion 10 min in 25 mL of a $CHCl_3$ solution containing 2 μL of DMMP, washing with $CHCl_3$ and drying under nitrogen, in the P 2p binding energy region. Structures due to $K\alpha_{3,4}$ satellites were subtracted from the spectra.

This value is highly consistent with that expected for a monolayer of DMMP.[80] In fact it has been reported that the P 2p states at 134.5 eV of a DMMP monolayer on Rh(100) are 1.0 eV at lower binding energy with respect to a DMMP multilayer (135.5 eV) on Rh(100), because in the condensed phase of the DMMP there is an extra-atomic relaxation that increases the binding energy.[80] In our case we observe the unique P 2p signal at even lower binding energy 133.7 eV, strongly consistent with the already reported energy value of 133.6 eV for the $(PhO)_3P=O$ similar system.[81] Moreover our value confirms the absence of the above mentioned extra-atomic relaxation and therefore the presence of a mono or sub-monolayer of DMMP on the **U_Salen_SAM**. The XPS atomic concentration analysis totally confirms these findings since the P/U atomic ratio is 0.9. The U 4f states did not show any energy shift upon the DMMP coordination.

The detection limit of the **U_Salen_SAM** was also investigated with XPS and a clear, even though noisy, P 2p spectrum was obtained for a 0.0006 % v: v DMMP concentration (2 μL of DMMP in 300 mL of $CHCl_3$) thus further improving the lower detection limit (Figure S20).

Rinsing 10 min the **U_Salen_SAM** exposed to DMMP with CH_3CN at 70° C caused some reactivation of the UV-vis spectrum thus indicating that the sensor is reversible (Figure 5). Besides, the **U_Salen_SAM** is thermally robust as judged from its UV-vis spectrum that does not change after heating at 120° C for 24 and cooling (Figure 3).

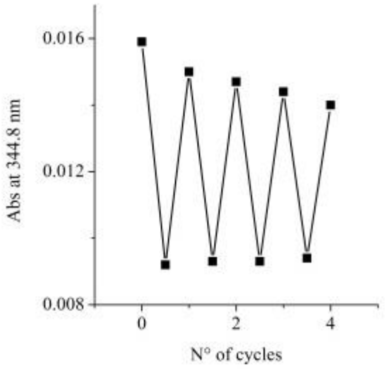

Figure 5. Changes in the absorbance at 344.8 nm of the **U_Salen_SAM** during the cyclic of DMMP detection / reactivation processes.

Each **U_Salen_SAM** contains 5.14 x 10^{-8} g of uranium/cm^2. This quantity is well below any recommended limit for uranium exposure. In fact, the Occupational Safety and Health Administration (OSHA) has set the exposure limit for uranium in the workplace as 0.25 mg/m^3 over an 8-hour workday and the National Institute for Occupational Safety and Health (NIOSH) has set a recommended exposure limit (REL) of 0.2 mg/m^3 over an 8-hour workday and a short-term limit of 0.6 mg/m^3.

Conclusions

Large part of the UO_2^{2+} group chemistry is dominated by its strong propensity to interact with Lewis bases.[82] Some reports present also recently in literature concern the Lewis basic nature of the U=O oxygen atoms in UO_2^{2+} that, in turn, can interact with Lewis acids.[83-85] In this interesting panorama, it was synthesized a monolayer of an uranyl Salen complex that provided to be a good optical sensor of trace amounts of DMMP, thanks to its ability to form an adduct with the O=P group of the dimethyl methylphosphonate Lewis base. This interaction allowed the formation of a supramolecular complex typical of the uranyl moiety. The obtained solid sensor is acceptably reversible thermally and temporally robust and therefore suitable for the detection of organophosphorus compounds.

In fact the lethal dose of DMMP is as following: oral (rat) 8.210 mg/kg, inhalation (rat) 1h 20.13 mg/l. The lethal concentration of sarin in air is 35 mg per cubic meter per minute for a two-minute exposure time. With the **U_Salen_SAM** we can sense much lower DMMP concentrations therefore, we believe that this solid sensor may pave the way for the fabrication of sensor devices for useful organophosphorus compounds.

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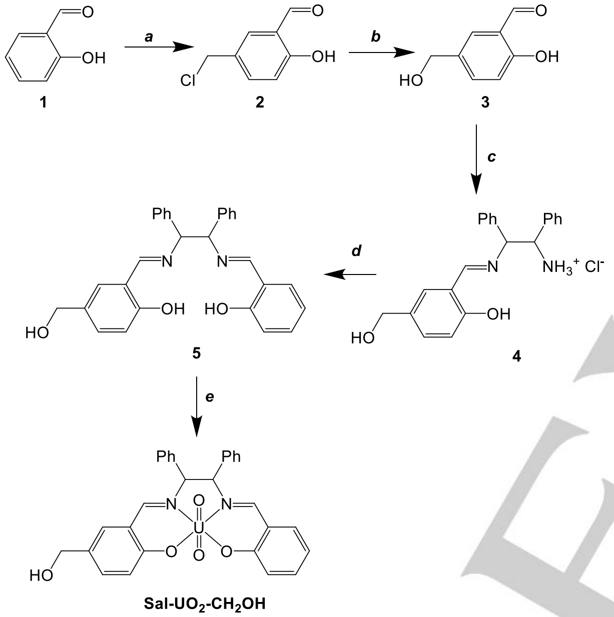
Experimental Section

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 ES-MS Thermo-Finnigan LCQ-DECA using MeOH (positive ion mode). A JASCO V-560 UV-vis spectrophotometer equipped with a 1 cm path-length cell was used for the measurements of Job's plots and for the UV-vis measurements. All chemicals were reagent grade and were used without further purification. The syntheses of the two uranyl Salen complexes have been performed according to the following Scheme 2 and as specified in the following.



Scheme 2. Synthesis of **Sal-UO$_2$-CH$_2$OH**. Reagents and conditions: a) formaldehyde aq. 37%, HCl conc., 70°C, 24 h, 40%; b) CuSO$_4$, H$_2$O/DMSO (1/2), 110 °C, 2 h, 95%; c) diphenylethylendiamine mochlorohydrate,[86-89] EtOH/MeOH (1/1), r.t., 24 h, 50%; d) **1**, Et$_3$N, EtOH, 60°C, 24 h, 47%; e) UO$_2$(AcO)$_2$·2H$_2$O, EtOH, r.t., 24 h, 90%.

Synthesis of 2. The chlorometilation was performed by using a modified synthetic protocol.[86] 3.6 mL (43 mmol) of aqueous formaldehyde and 50 mL of HCl conc. were added to 5.73 g (47 mmol) of the salicylaldehyde. The mixture was stirred at 70°C for 24 h. The precipitate was filtered, washed with water, re-dissolved with diethyl ether and dried over MgSO$_4$. After evaporation of solvent, the compound **2** was crystallized from *n*-hexane affording to white crystals (yield 40%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 11.06 (s, 1H), 9.90 (s, 1H), 7.59 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 4.59 (s, 2H). ESI-MS *m/z* 171.0 [M+H]$^+$. Anal. Calcd. For C8H7ClO2 : C, 56.33; H, 4.14; Cl, 20.78. Found C, 56.27; H, 4.11; Cl, 20.74.

Synthesis of 3. 850 mg (5 mmol) of aldehyde **2** and 795 mg (5 mmol) of CuSO$_4$ were dissolved into 3.5 mL of H$_2$O and 7 mL of DMSO. The mixture was stirred at 110 °C for 2 h, then cooled to room temperature and diluted with water. An extraction with diethyl ether, followed by evaporation of the solvent, leads to compound **3** (yield 95%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.99 (s, 1H), 9.91 (s, 1H), 7.58 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.69 (s, 2H). ESI-MS *m/z* 153.0 [M+H]$^+$. Anal. Calcd. For C8H8O3: C, 63.15; H, 5.30. Found C, 63.07; H, 5.22.

Synthesis of 4. 270 mg (2.16 mmol) of aldehyde **3** and 535 mg (2.16 mmol) of diphenylethylendiamine monochlorohydrate[87-90] were dissolved in 25 mL of a mixture ethanol/methanol (50:50) and stirred at room for 24 h. The reaction was monitored by TLC analysis (*n*-hexane/EtOAc 90:10) and, after total conversion of **3** the solvent was removed under reduced pressure. The resulting yellow oil was washed with diethyl ether and water, obtaining pure mono-immino-amino derivate **4** as solid precipitate, which was filtered and dried (yield 50). ^{1}H NMR (500 MHz, DMSO-*d$_6$*) δ 13.14 (s, 1H), 8.54 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.30-7.40 (m, 4H), 7.14-7.28 (m, 7H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.07 (s, 2H) 4.47 (s, 2H). ^{13}C NMR (125 MHz, DMSO-*d$_6$*) δ 167.5, 141.3, 132.4, 131.2, 129.6, 129.2, 128.4, 119.4, 117.2, 80.5, 80.4, 64.0. ESI-MS *m/z* 347.0 [M]$^+$. Anal. Calcd. For C22H23N2O2 : C, 76.05; H, 6.67; N, 8.06. Found C, 76.01; H, 6.59; N, 8.02.

Synthesis of 5. 250 µL of triethylamine (1.80 mmol) were added to an ethanol solution (20 mL) containing 62.9 mg (0.52 mmol) of salycilaldehyde **1** and 196 mg (0.52 mmol) of aldehyde **4**. The reaction was followed by TLC (*n*-hexane/EtOAc 90:10) to monitor the disappearing of compound **4** and then quenched by evaporation of solvent under vacuum. The compound **5** was isolated by flash chromatography (*n*-hexane/EtOAc 95:5) (yield 47%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 13.17 (s, 2H), 8.29 (s, 2H), 7.24-7.28 (m, 3H), 7.20-7.23 (m, 6H), 7.14-7.19 (m, 4H), 6.89 (m 2H), 6.80 (t, *J* = 7.5 Hz, 2H), 4.78 (s, 2H), 4.51 (s, 2H). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$) δ 166.4, 166.2, 139.5, 132.6, 131.8, 131.7, 130.5, 128., 128.0, 127.6, 118.7, 116.9, 116.7, 80.0, 79.9. ESI-MS *m/z* 451.9 [M+H]$^+$. Anal. Calcd. For C29H26N2O3: C, 77.31; H, 5.82; N, 6.22. Found C, 77.25; H, 5.79; N, 6.17.

Synthesis of Sal-UO$_2$-CH$_2$OH. The absolute ethanol solution of the ligand **5** was stirred for 24 h at room temperature with 1.5 equivalents of Uranyl acetate. When the starting ligand was completely converted (checked by TLC analysis), the solvent was removed under reduced pressure. Then, 5 mL of CH$_2$Cl$_2$ were added to the remaining crude solid to dissolve the UO$_2$ complex. The residual precipitate (unreacted uranyl acetate) was removed and the CH$_2$Cl$_2$ solution was concentrated in vacuo thus giving **Sal-UO$_2$-CH$_2$OH** (yield 90%). ^{1}H NMR (500 MHz, acetone-*d$_6$*) δ 9.35 (s, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.44-7.17 (m, 4H), 7.12-7.22 (m, 6H), 6.93-6.9 (m, 2H), 6.63 (t, *J* = 7.5 Hz, 2H), 6.27 (s, 2H), 4.57 (s, 2H). ^{13}C NMR (125 MHz, acetone-*d$_6$*) δ 171.4, 161.2, 151.3, 141.5, 128.3, 127.8, 127.3, 126.6, 123.6, 117.5, 115.9, 80.8, 56.1. ESI-MS *m/z* 720.6 [M+H]$^+$. Anal. Calcd. For C29H24N2O5U: C, 48.48; H, 3.37; N, 3.90; U, 33.13. Found C, 48.42; H, 3.31; N, 3.86.

Procedure for ^{1}H NMR titrations. Two mother solutions of host (**Sal-UO$_2$**) and guest (DMMP) (7.0 x 10^{-3} M) in CDCl$_3$ were prepared. From these, different solutions with different ratio host/guest were prepared as reported in the Supporting Information, and ^{1}H NMR spectra were recorded.

Procedure for UV-Vis titration. Two mother solutions of host (**Sal-UO$_2$**) and guest (DMMP) (2.00×10^{-4} M) in dry chloroform were prepared. From these, different solutions with different ratio receptor/guest were prepared as reported in the Supporting Information, and UV-Vis spectra were recorded. Binding constants of the complexes were determined following the absorbance variation at 260, 284 and 407 nm, 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. There was also applied the χ^2 test (chi-square), where the residuals should follow a normal distribution. So if the distribution is approximately normal, the value of the χ^2 test should be around 12 or less. In all of the case, $\chi^2 \leq 10$. The final values are obtained by 3 independent measurements sets.

Determination of Stoichiometry. Stoichiometry of the complex was investigated by the Job's plot method using spectrophotometric measurements. The samples were prepared by mixing equimolecular stock solutions (2×10^{-4} M) of host and guest to cover the whole range of molar fractions keeping constant the total concentration (1×10^{-5} M). The changes in absorbance at 284 nm, compared to uncomplexed receptor species ($\Delta A \times \chi^{-1}$) were calculated and reported versus the receptor mole fraction (χ). These plot show invariably a maximum at 0.5 mol fraction of receptor suggesting its 1:1 complex formation.

Monolayer synthesis. Fused silica (quartz) substrates were cleaned by immersion into a "piranha" solution (98% H_2SO_4 : 30% H_2O_2 70 : 30 v/v) at 90 °C for 1 h and then left to cool to room temperature. Substrates were then repeatedly rinsed with double distilled water and kept in a H_2O : 30% H_2O_2 : NH_3 5 : 1 : 1 v/v/v mixture at room temperature for 1 h.[91] A final wash with double distilled water, followed by drying under vacuum was carried out just prior to coupling agent (CA) deposition.

Si(100) substrates, were first cleaned with "piranha" solution for 10 min, rinsed in double distilled water for 5 min, etched in 2.5 % hydrofluoric acid for 150 sec, washed, dried with N_2 (both piranha and hydrofluoric acid solutions need to be handled with caution!), treated for 5 min with ozone using the Ozon-Generator (Fisher 500) system in order to obtain a SiO_2 thin (~10 Å,) layer.[92] Freshly cleaned substrates were transferred in a glove box under a N_2 atmosphere and dipped, at room temperature for 1 h, in a 0.1 : 100 v/v *n*-pentane solution of the trichloro[4-(chloromethyl)phenyl]silane (siloxane) to afford a monolayer of this coupling agent (CA).[93] The siloxane-coated substrates were washed with copious amounts of *n*-pentane, removed from the glovebox and heated up to 135°C for 15 min in an oven to complete the CA grafting. Afterward they were sonicated in *n*-pentane for 10 min to remove any physisorbed CA and then immersed into a stirred 1.93×10^{-4} M toluene/CH_3CN 50 : 50 solution of the **Sal-UO$_2$-CH$_2$OH** and kept at 90 °C for 70 h. The **U_Salen_SAM** monolayer thus formed was cooled to room temperature and sonicated with toluene, CH_3CN and THF to remove any residual unreacted **Sal-UO$_2$-CH$_2$OH** (Scheme 1).

X-ray photoelectron spectra (XPS) were measured at 45°, relative to the surface plane with a PHI 5600 Multi Technique System.[76,77] Spectra were excited with Al-Kα radiation. Structures due to K$\alpha_{3,4}$ satellite radiation were subtracted from the spectra prior to data processing. XPS peak intensities were obtained after Shirley background removal. Experimental uncertainties in binding energies lie within ± 0.4 eV. Deconvolution of a number of these spectra was carried out by fitting the spectral profiles with a series of symmetrical Gaussian envelopes after subtraction of the background. This process involves data refinement, based on the method of the least squares fitting, carried out until there was the highest possible correlation between the experimental spectrum and the theoretical profile. The residual or agreement factor R defined by $R = [\Sigma(F_{obs} - F_{calc})^2 / \Sigma (F_{obs})^2]^{1/2}$ after minimization of the function $\Sigma(F_{obs} - F_{calc})^2$ converged to values of 0.02.

UV-vis measurements on monolayers were carried out on a UV-vis V-650 Jasco spectrophotometer and spectra were recorded with a ± 0.2 nm resolution. Temperature was kept at 25 °C and measurements were repeated using 4 different monolayers.

AFM measurements. The surface morphology studies were carried out by atomic force microscopy (**AFM**) and the images were obtained by an instrument manufactured by the NT-MTD. The noise level before and after each measurement was 0.01 nm. AFM characterizations were performed in a high-amplitude mode (tapping mode) to avoid any possible modification of the grafted layer on the surfaces, caused by the interactions with the tip whose nominal curvature radius is 10 nm.

IR measurements. Infrared transmittance spectra were recorded using a Jasco FT/IR-430 spectrometer in the 4000-400 cm^{-1} scan range, with an instrumental resolution of 4 cm^{-1}. Spectra were collected using KBr/samples mixtures.

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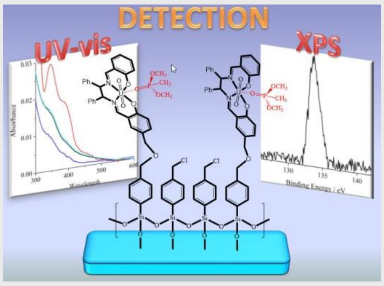
FULL PAPER

We report on the first example of a monolayer of an uranyl Salen complexes that allows the optical detection of DMMP trace levels.



Giuseppe Trusso Sfrazzetto, Salvatrice Millesi, Andrea Pappalardo, Gaetano A. Tomaselli, Francesco P. Ballistreri, Rosa Maria Toscano, Ignazio Fragalà and Antonino Gulino**

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