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Synthesis, structural characterization, electronic spectroscopy, and microfluidic detection of Cu^{+2} and UO_2^{+2} [di-tert-butyl-salphenazine] complexes

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Metal templation by condensation of 2,3-diaminophenazine with 3,5-di-tert-butyl-2-hydroxybenzaldehyde around metal centers [M= Cu(II), and UO_2(VI)] affords a new class of M[di-tert-butyl salphenazine] metal complexes. Reported here is the synthesis, single crystal X-ray structural characterization, electronic spectroscopy, and microfluidic detection of the formation of these M[di-tert-butyl salphenazine] complexes.

The lure of harnessing energy from the actinides is exciting as it provides one means to power generation without contributing to greenhouse gas emissions.[1] Currently, the positive aspects of this are counterbalanced by public perception of highly publicized radioactive material release events.[2] Interest in research regarding the actinide elements has increased in the last decade.[1a, 3] Developing sensors that are able to selectively detect the presence of actinides in the environment is a key goal in rapid, immediate emergency response should release events occur *via* accident or incident.[5] Our interest lies in the development of aromatic organic ligands for selective coordination of actinide ions, and to develop a microfluidic lab-on-a-chip to detect these metal complexes. Here, we have synthesized di-tert-butyl salphenazine [L] and two new metal complexes (Cu[L], UO_2[L]), and we have characterized them in the solid state via single crystal X-ray diffraction (figure 1) and in the liquid phase *via* nuclear magnetic resonance, mass spectroscopy, and with UV and fluorescence spectroscopy. The UO_2^{+2} unit provides a reliable equatorial scaffold for templation of the planar aromatic ligand design, which has only previously been reported with zinc.[6] Also reported is microfluidic sensing *via* a microspectrophotometer on sub-nanoliter droplets.

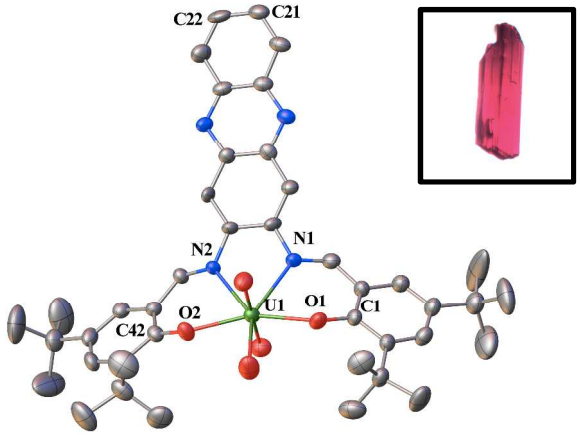


Figure 1 Projection of UO_2[L] complex. Hydrogen atoms have been omitted for clarity. Inset image obtained on a CRAIC 20/20 PV microspectrophotometer shows the crystal after X-ray data collection.

Droplet generating microfluidic devices retain many advantages of standard microfluidics, while allowing the formation of discrete, monodispersed droplets at rates up to 100 kHz.[4, 7] By producing isolated units at high rates, a statistically relevant testing population can be generated in under a minute. A principle tenet of 5*f* chemistry is reduction of waste generation. This reduction, coupled with reduced assay costs and statistically relevant droplet scanning, make pairing the 5*f* analysis and microfluidics ideal.[7-8] An important comparison is copper, which is ten times more abundant in the earth's crust than uranium[9], produced in asymmetric thermal fission [^{235}U and ^{239}Pu][10], and has been found to yield a false positive in systems designed as UO_2^{+2} sensors.[11]

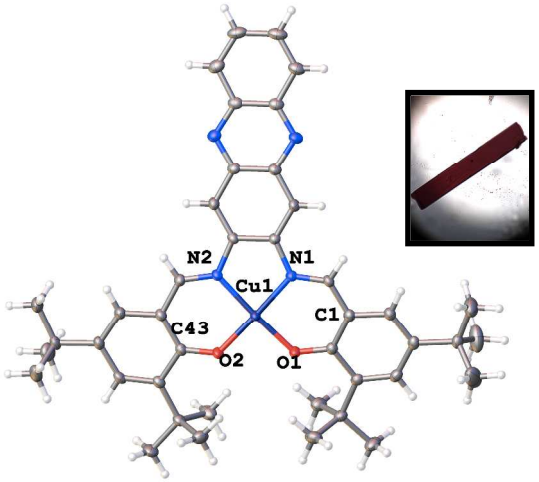


Figure 2 Projection of Cu[L] complex. Inset image obtained on the microspectrophotometer showing the crystal after X-ray data collection.

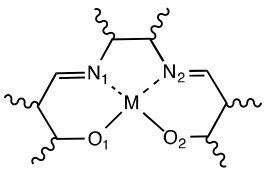
During metal templation, two 3,5-di-tert-butylsalicylaldehyde units and a 2,3-diaminophenazine unit undergo two condensation reactions around the metal center forming a tetradentate coordination pocket. The UO_2[L] complex is shown in figure 1. Bond distances for the binding pocket can be found in table 1. U-N distances are found at 2.560(7) and 2.546(8) Å. U-O_{ligand} distances are found at 2.242(7) and 2.265(7) Å. Also in figure 3 is the mean (M) plane distance, which is defined as the distance the metal center is away from the plane generated by atoms C22-C23-O1-O2. For the UO_2[L] complex this distance is 1.955 Å. The UO_2[L] complex 360° rotation video in the supplemental information provides a pseudo-3d visualization.

The Cu[L] complex is shown in figure 2. Bond distances and angles for the binding pocket are found in table 1. Cu-N distances are found at 1.9304(16) and 1.9477(15) Å. Cu-O_{ligand} distances are found at 1.9091(12) and 1.8906(14) Å. For both the Cu^{+2} and UO_2^{+2} complexes the M-O and M-N bond distances agree with previously reported data.[6, 12] For the Cu[L] complex, the M-plane distance is 0.171 Å. The Cu[L] complex 360° rotation video in the supplemental information provides a pseudo-3d visualization.

As the XRD atomic coordinate data indicates (illustrated numerically in table 1 and graphically in the M[di-tert-butylsal-phenazine] complex movies in the SI), the Cu complex more closely resembles a planar system as compared to the uranyl complex. In the electronic spectra of [L] (figure 3), two major features are observed in the UV-Vis range at 322 and 424 nm; ε

Table 1 Coordination pocket of [L] with bond distances between the coordinating atom and metal.

	Cu[L] Å	UO_2[L] Å
M-N1	1.9304(16)	2.560(7)
M-N2	1.9477(15)	2.546(8)
M-O1	1.9091(12)	2.242(7)
M-O2	1.8906(14)	2.265(7)
N1-N2	2.603(2)	2.711(10)
O2-O1	2.6693(18)	4.422(10)



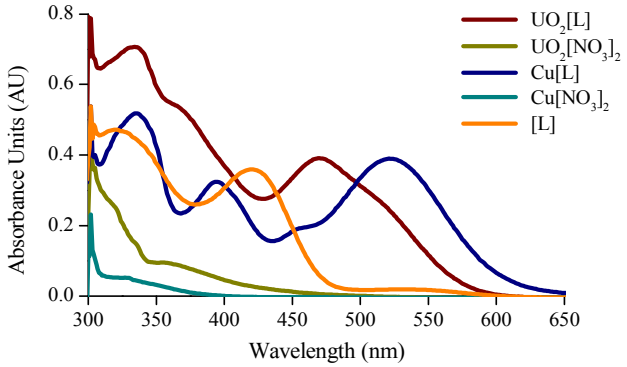


Figure 3 UV-Vis spectrum of the metal starting materials $[Cu(NO_3)_2$, $UO_2(NO_3)_2]$, [L], Cu[L], and UO_2[L] complexes in pyridine at 20 μM.

= 2.4 x 10^4 and 1.8 x 10^4 L mol^{-1} cm^{-1} respectively. The free base [L] was obtained by acid stripping the UO_2[L] complex and used for further electronic spectroscopy characterization. Upon coordination of either metal centre, these two peaks are shifted to higher energy, and two charge transfer bands arise. The middle energy feature (364 nm) in the UO_2[L] complex becomes a shoulder of the higher energy feature (336 nm).The predominant low energy feature in the UO_2[L] complex has a maximum at 472 nm (ε = 1.9 x 10^4), with a shoulder at 520 nm. The Cu[L] complex, however, has a predominate peak at 522 nm (ε = 1.9 x 10^4), with a shoulder at 460 nm. The growth of these low energy peaks is visualized in the metal titration spectra (SI 1).

Thus, metal templation was used to form these two new metal complexes, Cu[L] and UO_2[L], then characterized by X-ray diffraction. The structural data shows that upon ligand binding, the larger UO_2^{+2} unit perturbs the ligand from the expected aromatic planarity as compared to the smaller Cu^{+2} metal ion. The synthesis of the metal-ligand complexes, both the Cu^{+2} and UO_2^{+2}, represents unreported chemistry, and the electronic characterization shows that the aromatic M-L complexes have large molar extinction coefficients. Extending this fact leads to the novel application reported herein, namely the spectral detection of metal-ligand complexes in mere picoliter volumes (4 x 10^2 pL) on a microfluidic chip (figure 4).

Proof of concept for detection of these complexes within microfluidic droplets (pyridine droplets in perfluorocarbon oil) is shown in figure 4. Spectra collected using the microdroplet system match well with spectra from macro-scale measurements (SI2). Reducing sample volume by more than 6 orders of magnitude on this microchopper device[4] with concurrent spectroscopic detection (figure 4C) could have reverberating effects within the field of environmental actinide sensing. By designing simple, easy-to-use devices, sample and waste volumes could be drastically reduced, while opening up the potential for on-site detection. The ability to reliably sense actinide elements at a release event and quickly respond could play a large role in altering the current standards of immediate response in field detection procedures.

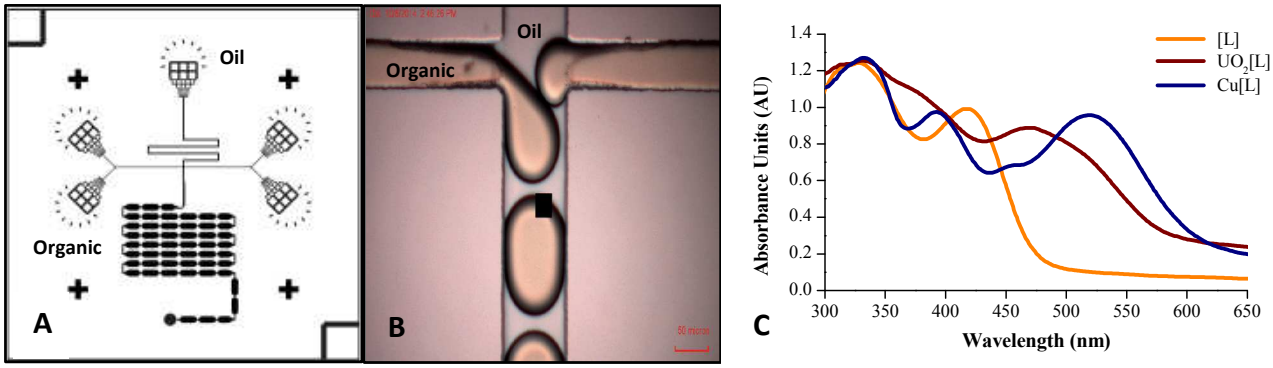


Figure 4 A. Droplet microchopper design. B. Oil and organic phases meet at a T-junction to form organic in oil droplets ($UO_2(NO_3)_2$ and ligand). C. CRAIC spectra of complexes collected on chip with 100μm optical path length[11]

Conclusions

While current sensing methods for actinide elements have high selectivity and low limits of detection, they require large sample and reagent volumes and expensive instrumentation for assays that can take up to several days for the analysis to be completed.[13] Our approach requires less than 5 minutes to collect multiple spectra and determine sample composition in picoliter volumes. This novel combination of droplet microfluidics with spectral detection using synthetic actinide sensors could help establish a foundation for research in microfluidic analysis of radioactive materials.

Notes and references

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† Crystal data for Cu[di-tert-butylsal-phenazine]: Cu[(C42H48N4)2)] M = 704.39, Triclinic, space group P -1, a = 9.9751(2), b = 12.6630(3), c = 14.8623(3), α = 93.610(1)° β = 96.835(1)°, γ = 98.716(1)°, V = 1836.17(7) $Å^3$, T = 180(2) °C, Z= 2, λ = 0.71073 Å, μ = 0.636 mm^{-1}, 7756 measured reflections, 6595 unique reflections, R_{int} = 0.0333, R_1 [I > 2s(I)] = 0.0365, wR2 (all data) = 0.0966, maximum/minimum residual electron density: 0.920 and -0.420 $e^-Å^{-3}$; CCDC 1019624.

Crystal data for UO_2[di-tert-butylsal-phenazine]: $[UO_2(C_{42}H_{50}N_4O_5)(OH_2)]\cdot1.5C_4H_8O$ M = 1037.06, Monoclinic, space group P $2_1/n$, a = 18.0525(18), b = 13.4858(13), c = 20.817(2), β = 97.379(3) °, V = 5025.0(8) $Å^3$, T = 180(2) °C, Z = 4, λ = 0.71073 Å, μ = 3.278 mm^{-1}, 8404 measured reflections, 6341 unique reflections, R_{int} = 0.0550, R_1 [I > 2s(I)] = 0.0717, wR2 (all data) = 0.1427, maximum/minimum residual electron density: 2.544 and -2.230 $e^-Å^{-3}$; CCDC 1019622.

Electronic Supplementary Information (ESI) available: [Synthetic Methods, UV-Vis spectroscopic and titration data, crystallographic details and movies of characterization by microspectrophotometer are included in the ESI]. See DOI: 10.1039/c000000x/

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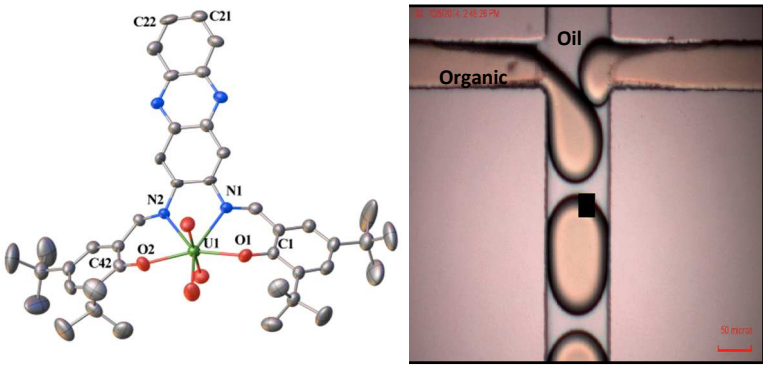
Graphical Abstract



Oil and organic phases meet at a T-junction in droplet microchopper design to droplets. At left, Projection of UO_2[di-tert-butyl salphenazine] complex