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Journal:	*ChemComm*
Manuscript ID	CC-COM-06-2018-005160.R1
Article Type:	Communication

Chemical Communications

COMMUNICATION

Uranyl dication mediated photoswitching of a calix[4]pyrrole-based metal coordination cage

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A set of self-assembled tri- and tetrapodal metal coordination cage structures (cage-1 and cage-2, respectively) constructed from the uranyl dication (UO_2^{2+}) and a dibenzoic acid functionalised *cis*-calix[4]pyrrole (1) are described. The inherent photochemical reactivity of the uranyl dication mediates the transformation of cage-1 to cage-2 via the activation of molecular oxygen.

The actinide elements demonstrate remarkable chemistry that in many instances is not replicated in the case of ostensibly related transition metal or lanthanide species. The ability to support high coordination numbers and stabilise a range of accessible oxidation states often gives rise to unique chemical reactivity.[1-5] Uranium in particular has emerged as a viable tool in the design of chemical transformations showing promise in the activation of CO, CO_2, N_2, alkenes, and alkanes.[1,6,7-9] A number of elegant studies have also explored the inherent photochemical activity of the uranyl dication (UO_2^{2+}), which to date has been exploited for the activation of simple alkanes,[10] water,[11] and molecular oxygen.[12]

Efforts have also been made to incorporate actinide elements into coordination polymers, metal organic frameworks (MOFs), and metal coordination cages (MCCs).[13-16] However, examples of such species remain limited and generally involve polyoxometalate-type cage clusters.[17] Furthermore, actinide-based metallocage systems often fail to recapitulate the broad utility demonstrated in transition metal species, such as robust and quantitative self-assembly, stimuli-responsiveness, and applicability as, e.g., sensors and molecular machines.[18,19] Here we report a new structurally characterized tetrapodal uranyl-derived, calix[4]pyrrole diacid-based cage system (**cage-2**, Fig. 1) that is formed via a photoactivated structural transformation mediated by uranyl and molecular oxygen from an initial tripodal cage system (**cage-1**) whose structure was inferred from analytical data.

In previous studies we found that calix[4]pyrrole (C[4]P) could be exploited as a secondary building unit (SBU) in conjunction with praseodymium(III) to create a metal-macrocycle framework (MMF).[20] The chemically responsive behaviour between Pr(III) and fluoride anion was described, but no photochemical properties were observed. We thus envisaged that marriage of the uranyl cation with a judiciously designed calix[4]pyrrole might furnish new cage frameworks that would respond to uranyl-mediated photochemistry.

To test this possibility, the dibenzoic acid functionalised *cis*-calix[4]pyrrole (**1**) was prepared and, based upon, X-ray crystallographic analysis it was postulated to maintain the appropriate directionality of the carboxylate moieties that would allow for the preparation of MCC systems. Gratifyingly, self-assembly of **cage-2** was observed in the solid state by single crystal X-ray analysis upon the reaction of calix[4]pyrrole **1** with the uranyl dication in the presence of pyridine. Single crystal of the tetrapodal structure **cage-2** was isolated from aforesaid reaction solution that had been concentrated via slow evaporation while it was exposed to ambient light and air. NMR spectroscopy and electrospray ionisation mass spectrometry (ESI-MS) studies revealed that a tripodal **cage-1** was initially formed in solution. The initial construct was observed to undergo a structural reorganization to a dimeric uranyl-peroxo **cage-2**, a process we believe is facilitated by the coordinated uranyl dication.

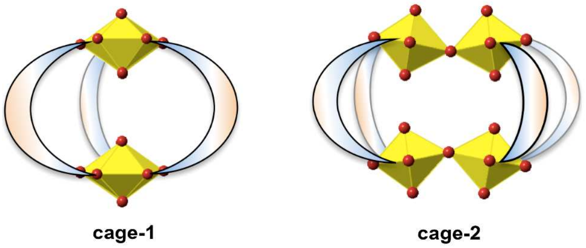

Figure 1. Simplified cartoon representations of the tri- and tetrapodal cages, **cage-1** and **cage-2**, respectively. Yellow polyhedron: uranyl ion, red dot: oxygen, arch shape: compound **1**. The structure of **cage-2** was confirmed by a single crystal X-ray diffraction analysis. That of **cage-1** was inferred from analytical data.

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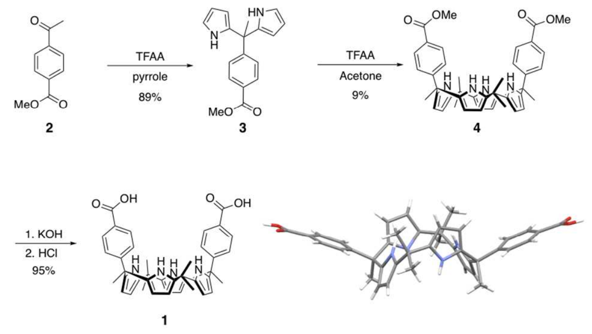
† Electronic Supplementary Information (ESI) available: Synthetic details, experimental procedures, and characterization data. Structural details for **1**, and **cage-2**. CCDC 1850738-1850739. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis and crystal structure of compound **1**.

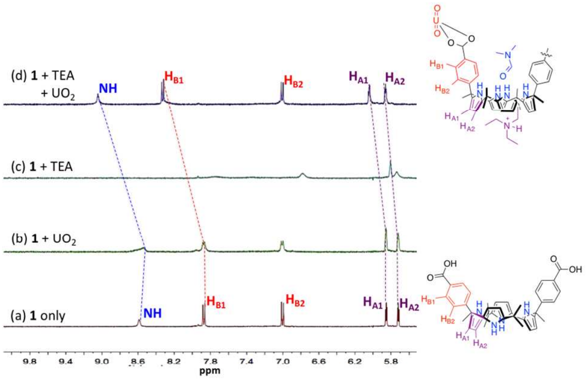


Figure 3. Partial ^{1}H NMR spectra of (a) **1** only (3.75 mM), (b) **1** + 0.66 equiv. of $UO_2(NO_3)_2{\cdot}6H_2O$, (c) **1** + 38.22 equiv. of TEA (triethylamine), and (d) **1** + 0.66 equiv. of $UO_2(NO_3)_2{\cdot}6H_2O$ + 38.22 equiv. of TEA, recorded at room temperature in CD_3CN (1.5% DMF-d_7)

The synthesis of *cis*-calix[4]pyrrole dibenzoic acid (**1**) is shown in Scheme 1. Briefly, methyl 4-acetylbenzoate (**2**) was reacted with pyrrole as the solvent and trifluoroacetic anhydride (TFAA) to give compound **3** in 89% yield. TFAA-catalysed condensation of **3** with acetone (acetone : methanol, 1:1, v/v) gave the *cis* form of the disubstituted *bis*-(methyl benzoate) calix[4]pyrrole (**4**) in 9% yield after silica gel column chromatography. Saponification of the ester produced the desired compound **1** in 95% yield. Slow evaporation of a concentrated acetonitrile solution of **1** yielded single crystals suitable for X-ray diffraction analysis.

Upon exposing compound **1** (7.5 μmol), uranyl nitrate (5.0 μmol) and pyridine (0.6 mmol) in acetonitrile containing 1.5% DMF (2 mL total volume) to ambient light and air, over the course of three weeks, yielded block-shape crystals suitable for single crystal X-ray diffraction analysis.

The resulting structure revealed that four calix[4]pyrrole *bis*-carboxylate ligands (**1**) are bound to two bridged uranyl-peroxo species within a tetrapodal metallo-construct, **cage-2** ($[(UO_2)_2(O_2)_2(\mathbf{1})_4]^{4-}$; Fig 2). The pyrrolic NH protons of each calix[4]pyrrole subunit are hydrogen bonded to a DMF molecule and are found in the respective cone conformations (Fig. S6). The U-O (yl), the U-O (oxo) and the O-O distances were 1.74, 2,30 and 1.47 Å, respectively which are similar to previously reported crystal structures.[12,24-26]

As assembled, **cage-2** is tetra-anionic and requires four counter cations to balance the overall charge. The X-ray crystal structure reveals that a pyridinium cation is incorporated within the "cup" of each calix[4]pyrrole (Fig 2). These pyridinium cations originate, presumably, from protonation of the pyridine base.

Evidence that **1** supports the formation of a uranyl coordination cage in solution came from ^{1}H NMR spectroscopic analyses carried out in CD_3CN containing 1.5% *N,N'*-dimethylformamide-d_7 (DMF-d_7) added to improve the solubility. As shown in Figure 3, when exposed to both uranyl nitrate and triethylamine (or pyridine; Fig. S1), a proton signal corresponding to the *ortho*-position (H_{B1}) on the benzoate unit undergoes a downfield shift ($\Delta\delta_{HB1}$ = 0.44 ppm). This happens rapidly on the laboratory time scale (i.e., by the time mixing is complete and an NMR spectrum can be recorded). In contrast, no substantial chemical shift changes were observed when **1** was exposed separately to either uranyl nitrate or triethylamine (Fig. 3). The change in the chemical shift of the

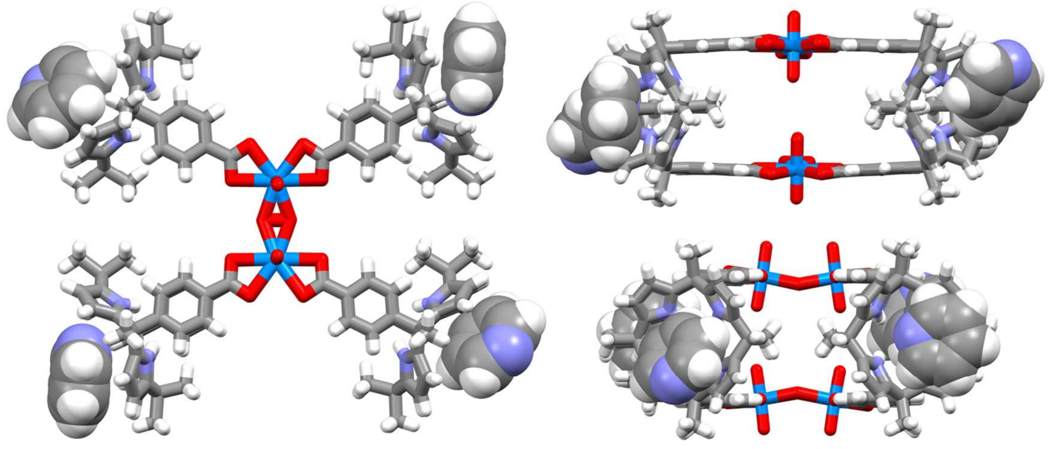


Figure 2. Top view (left) and side views (right) of the single-crystal structure of **cage-2**. Solvent molecules have been omitted for clarity.

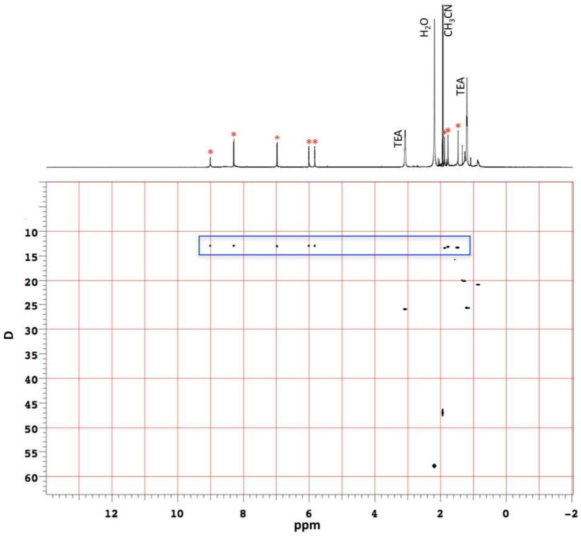


Figure 4. DOSY spectrum of **1** (3.75 mM) + 0.66 equiv. of $UO_2(NO_3)_2{\cdot}6H_2O$ + 38.22 equiv. of TEA, recorded at room temperature in CD_3CN (1.5% DMF-d_7).

H_{B1} signal was ascribed to the proton adjacent to the carboxylate moiety becoming deshielded as a result of uranyl complexation. Downfield shifts for the NH proton and β-pyrrolic proton resonances were also observed. These changes are ascribed to hydrogen bonding between the pyrrolic NHs and the carbonyl group of the DMF-d_7 co-solvent, as well as cation-π interactions between the pyrrole rings and a protonated triethylamine moiety. These changes are taken as evidence that the calix[4]pyrrole unit adopts a cone-like conformation with the benzoate anion substituents oriented in a face-to-face parallel fashion. This stands in contrast to the 1,3-conformation seen for the free calix[4]pyrrole, where the two benzoic acid subunits are oriented in opposite directions from one another (cf. Scheme 1). Indeed, the conformational lability of C[4]P from the 1,3-alternate to the cone conformation in the presence of Lewis basic anions and ammonium and related salts is well documented.[21] The conformational locking seen upon uranyl complexation is expected to impart rigidity to the normally flexible ligand **1** and facilitate the formation of the coordination cage.

DOSY spectral analysis of the uranyl complex solution revealed one set of signals for the complex, which indicates only a single complex species dominates at equilibrium (Fig. 4).

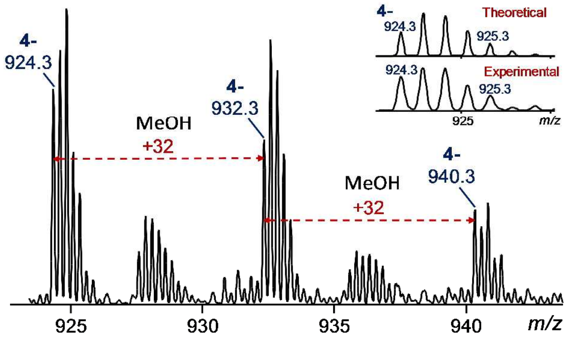


Figure 5. ESI-MS of **cage-2**. MeOH adducts were attributed to the solvent utilized in the ESI measurements.

Initial ESI-MS analysis reveal a species consistent with the proposed tripodal structure (i.e., **cage-1**) with a peak at 2456.36 amu (cf. Fig S5, where three calix[4]pyrroles are bound to two separate uranyl dication via the benzoate ligands, is a major component in solution at initial time points. In light of the aforementioned NMR spectroscopic studies, we suggest that in this structure, the calix[4]pyrrole bis-carboxylate ligands occupy equatorial positions around the uranyl cation and are present in a 3:2 (ligand: uranyl) ratio within a tripodal construct, namely **cage-1** **(**$[(UO_2)_2(\mathbf{1})_3]^{2-}$, Fig. 1). As formed, **cage-1** is expected to bear an overall 2- charge. This charge is presumably balanced by triethylammonium or pyridinium cations formed through protonation of the added bases.

Taking these findings into consideration, we conclude that the reaction of compound **1** and uranyl in the presence of base forms **cage-1**. The dimeric uranyl-peroxo species, **cage-2**, is then thought to arise from **cage-1** through uranyl-mediated photoactivation of molecular oxygen. Similar processes are well documented.[24-29] Moreover, Cahill and co-workers have postulated similar mechanistic explanations in the case of their studies of related transformations; these latter suggestions were based in part on ^{1}H NMR spectral studies.[12,23]

Uranyl-peroxo species have been previously prepared by reacting H_2O_2 with the uranyl cation.[22] An ESI-MS analysis of **cage-1** mixed with H_2O_2 revealed peaks consistent with the formation of **cage-2** (Fig 5). These findings provide support for the notion that the observed transformation of **cage-1** into **cage-2** occurs upon exposure of the starting cage to ambient light in the presence of air; it can also be induced via direct exposure to hydrogen peroxide, although this latter method yields a mixture of products.

As noted above, **cage-1** and **cage-2** are formally anionic. They are thus soluble in methanol allowing high resolution ESI-MS analyses to be carried out. In the case of **cage-1**, a doubly charged negative ion peak at *m/z* = 1227.5 was seen. The isotope pattern agreed well with theoretical modelling and was found to correspond to a chemical composition of $[C_{120}H_{114}N_{12}O_{16}U_2]^{2-}$ as expected for **cage-1**. After mixing **cage-1** with H_2O_2, a quadrupally charged negative ion peak at *m/z* = 924.3 was observed. In this case, the isotope pattern proved consistent with theoretical modelling and was found to correspond to the chemical composition expected for **cage-2**, namely $[C_{160}H_{152}N_{16}O_{28}U_4]^{4-}$. ESI-MS analyses thus provide support for the suggestion that both **cage-1** and **cage-2** may be obtained under solution phase conditions. Note that in the mass spectra of both **cage-1** and **cage-2**, we observed signals at + 32 and +64 amu relative to the dominant peaks. These latter features are attributed to formation of adducts containing one and two methanol molecules, respectively, under conditions of the mass spectrometric ionisation.

In summary, we report a new responsive coordination cage system (**cage-1**) that is readily prepared from a *meso*-substituted *cis*-dibenzoic acid calix[4]pyrrole (**1**) and a uranyl dication source. By harnessing the inherent chemical reactivity of the uranyl dication, this dianionic complex may be converted readily to a larger uranyl-bridged peroxo tetrapodal cage structure (**cage-2**). This conversion can be induced by exposing **cage-1** air and ambient light or via deliberate treatment with hydrogen peroxide. The present study serves to illustrate further the relatively untapped chemical reactivity of the actinide elements and their potential utility in creating stimulus-responsive and structurally modifiable metal coordination cages.

The work in Austin was supported by the Office of Basic Energy Sciences, U.S. Department of Energy (DOE) (grant DE–FG02–01ER15186 to J.L.S.). Support from the Robert A. Welch Foundation (F–0018 to J.L.S.) is also acknowledged. X.L. gratefully acknowledges the support from NSF (CHE-1506722) and the National Institutes of Health (1R01GM128037). J.T.B. would like to thank The University of Texas at Austin Environmental Science Institute for a Scientist in Residence (SciRes) Fellowship.

Conflicts of interest

There are no conflicts to declare.

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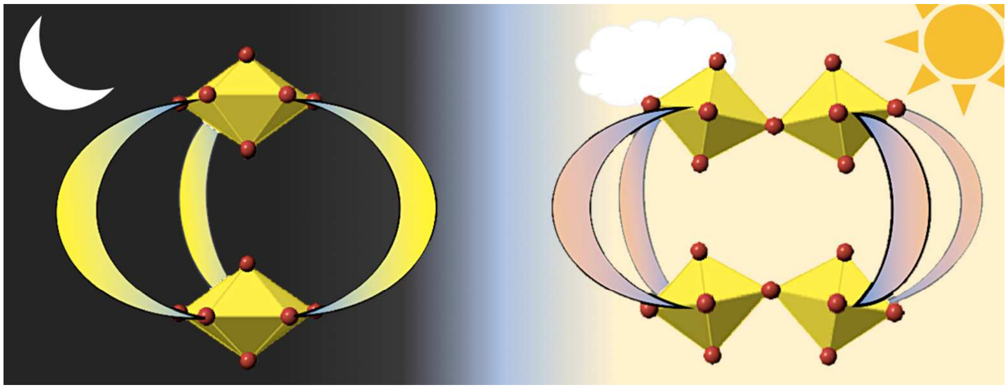

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