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Controlled Photocatalytic Hydrocarbon Oxidation by Uranyl Complexes

Polly L. Arnold,*[a] Jamie M. Purkis,[a] Ryte Rutkauskaite,[a] Daniel Kovacs,[b] Jason B. Love,[a] and Jonathan Austin[c]

Controlled, photocatalytic C–H bond activations are key reactions in the toolkits of the modern synthetic chemist. While it is known that the uranyl(VI) ion, $[U^{VI}O_2]^{2+}$, the environmentally dominant form of uranium, is photoactive, most literature examines its luminescent properties, neglecting its potential synthetic utility for photocatalytic C–H bond cleavage. Here, we synthesise and fully characterise an air-stable and hydrocarbon-soluble uranyl phenanthroline complex, $[U^{VI}O_2(NO_3)_2(Ph_2phen)]$, $\mathbf{U^{Ph2phen}}$, and demonstrate that it can catalytically abstract hydrogen atoms from a variety of organic substrates under visible light irradiation. We show that the commercially available parent complex, uranyl nitrate ($[U^{VI}O_2(NO_3)_2(OH_2)_2]\cdot 4H_2O$; $\mathbf{U^{NO3}}$), is also competent, but from electronic spectroscopy we attribute the higher rates and selectivity of $\mathbf{U^{Ph2phen}}$ to ligand-mediated electronic effects. Ketones are selectively formed over other oxygenated products (alcohols, *etc.*), and the catalytic oxidation of substrates containing a benzylic C–H position is particularly improved for $\mathbf{U^{Ph2phen}}$. We also show uranyl-mediated photocatalytic C–C bond cleavage in a model lignin compound for the first time.

The photo-excited state of the uranyl ion, denoted $[{*}U^{VI}O_2]^{2+}$, is a highly oxidising (*ca.* +2.6 V, *cf.* F_2) and long-lived (~ μs) motif, and is accessible using visible and UV light (*ca.* 300–420 nm).[1] The absorption of 420 nm light causes a weak U(5f)←O(2p) ligand-to-metal charge transfer (LMCT) which is thought to form the highly reactive $5f^1$ uranyl(V) oxyl ion $[O{=}U^V{-}O^\bullet]^+$. This excited state is readily quenched by contact with an organic hydrocarbon, either by hydrogen atom abstraction (HAA) from an aliphatic group to give a functionalised $[O{=}U^V{-}OH]^{2+}$ ion and organic radical,[2] or electron transfer with an unsaturated or aromatic group (*i.e.* toluene[3]) by quenching of the organic radicals with molecular oxygen.[3b,4] Aqueous solutions of uranyl have also been studied in considerable detail for the photocatalytic destruction of organic pollutants.[5] In these cases, uranyl speciation varies substantially with pH or counter-anion (*i.e.* nitrate and carbonate),[6] causing these reactions to be unselective.[7] Recently, however, Sorensen and co-workers reported the first use of photo-excited uranyl in the selective fluorination of cycloalkanes in organic media (Scheme 1).[8] Judicious choice of both organic solvent (CD_3CN or acetone-D_6) and anion (nitrate *vs.* acetate) were crucial, and recent quantum mechanical calculations highlighted the complex interplay of singlet and triplet excited states in the reaction coordinate.[9] Subsequently, Azam and co-workers used a chiral salen¹ ligand to saturate the uranyl equatorial coordination plane, resulting in a photoactive complex that acts as a catalyst for the α-cyanation of anilines (Scheme 1);[10] in this case, commercially available uranyl acetate, $[U^{VI}O_2(OAc)_2(OH_2)_2]$, shows no activity. It has also recently been shown that photoexcited $[U^{VI}O_2(CO_3)_3]^{4-}$ in uranyl tricarbonate, the molecular analogue of the naturally-occurring rutherfordine mineral, can oxidise borohydrides to boric acid under photolysis.[11]

Due to their capability as ligands[12] and ubiquity in photoredox reactions,[13] we reasoned that phenanthroline ligands would be excellent candidates for ligands in new photoactive uranyl complexes; the simplest member of the series, $[U^{VI}O_2(NO_3)_2(phen)]$ (phen = phenanthroline), has been reported previously, but not tested photocatalytically.[14] Here, we report the synthesis and characterisation of a new uranyl phen complex, $[U^{VI}O_2(NO_3)_2(Ph_2phen)]$ ($\mathbf{U^{Ph2phen}}$) (Ph_2phen = 4,7-diphenyl-1,10-phenanthroline), and demonstrate that it is a more effective photocatalyst than uranyl nitrate $[U^{VI}O_2(NO_3)_2(OH_2)_2]\cdot 4H_2O$ ($\mathbf{U^{NO3}}$) for the oxidation of a variety of organic substrates.

The addition of one equivalent of Ph_2phen to $\mathbf{U^{NO3}}$ in acetonitrile solution yields bright yellow, air-stable $\mathbf{U^{Ph2phen}}$ in 94% yield (Scheme 2). Repeating the reaction with $\mathbf{U^{NO3}}$ and phenanthroline (phen) or 2,2′-bipyridine (bipy) yields the known phen adduct which is too insoluble to be useful for catalysis in organic solutions,[i] or simply the protonated adduct $[Hbipy]_2[\{U^{VI}O_2(NO_3)_2\}_2(\mu\text{-}OH)_2]$[15], respectively. The ^1H NMR spectrum of $\mathbf{U^{Ph2phen}}$ (Figure S2) reveals that the H atoms closest to the U^{VI} centre are deshielded by approx. 1.4 ppm and, therefore, that the ligand is likely complexed in CH_3CN. The absence of the H-

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[a] Prof. P. L. Arnold, J. M. Purkis, R. Rutkauskaite, Prof. J. B. Love
EaStCHEM School of Chemistry, Joseph Black Building
University of Edinburgh
Edinburgh, EH9 3FJ (United Kingdom)
E-mail: Polly.Arnold@ed.ac.uk
[b] D. Kovacs
Ångströmslaboratoriet, Uppsala University
Lägerhyddsvägen 1, 752 37 Uppsala (Sweden)
[c] Dr. J. Austin
National Nuclear Laboratory
5th Floor, Chadwick House, Birchwood Park
Warrington WA3 6AE (United Kingdom)

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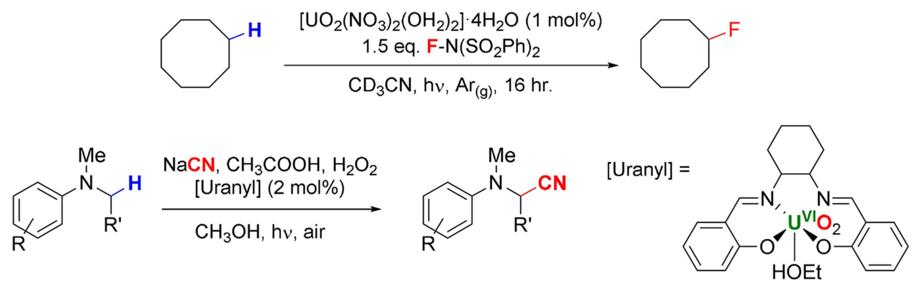
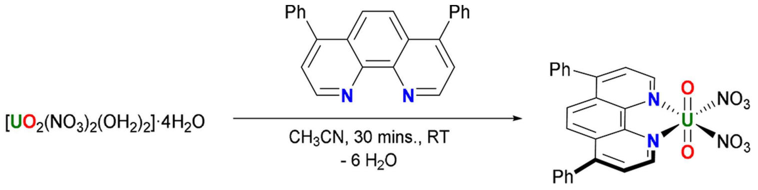
[1] H_2L, salen, is 2,2′-((1E,1′E)-(cyclohexane1,2-diylbis(azanylylidene))bis(methanylylidene))diphenol.



Scheme 1. Photocatalytic fluorination of sp^3 C–H bonds, and α-cyanation of anilines using a uranyl salen complex.



Scheme 2. Synthesis of $\mathbf{U^{Ph2phen}}$ from $\mathbf{U^{No3}}$ and Ph$_2$phen in CH$_3$CN.

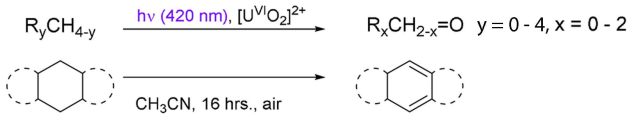
bonding $\nu_{\text{O-H}}$ stretch at *ca.* 3300 cm^{-1} in the infrared spectrum (solid state) suggests the compound is anhydrous (*i.e.* no coordinated water). The asymmetric $\nu_{\text{U=O}}$ stretch at 936 cm^{-1} and diagnostic modes of bidentate[16] nitrato ligands at *ca.* 1280 cm^{-1} for $\mathbf{U^{Ph2phen}}$ are similar to those in the parent [UO$_2$(NO$_3$)$_2$(phen)][14] ($\nu_{\text{U=O}}=942$ cm^{-1}, $\nu_{\text{NO}}=1286$ cm^{-1}) but different from $\mathbf{U^{NO3}}$ ($\nu_{\text{NO}}=1300$, 1330 cm^{-1}), also suggesting complexation (Figures S3 & S4).

The solid-state structure of $\mathbf{U^{Ph2phen}}$ (Figure S13) is also similar to that of the parent [U$^{\text{VI}}$O$_2$(NO$_3$)$_2$(phen)]. The uranium centre possesses a distorted 8-coordinate hexagonal bipyramidal coordination geometry in which the short U=O$_{\text{yl}}$ distances (O$_{\text{yl}}$ = the uranyl oxo group) (1.747(3)–1.756(3) Å) and the essentially linear O=U=O angle (177.0(2)°) are consistent with uranyl(VI) (Table S4).[17]

Pertinently, the presence of the phen ligand in $\mathbf{U^{Ph2phen}}$ increases the peak intensity of the uranyl LMCT band in its electronic absorption spectrum relative to $\mathbf{U^{NO3}}$ (Figures S8 and S9), with ε_{425} increasing from 11 M^{-1}cm^{-1} for $\mathbf{U^{NO3}}$ to *ca.* 65 M^{-1}cm^{-1} in $\mathbf{U^{Ph2phen}}$. UV-energy ligand absorptions for $\mathbf{U^{Ph2phen}}$ are also bathochromically shifted (*i.e.* towards the visible; $\pi\rightarrow\pi^*$, 270→285 nm; $n\rightarrow\pi^*$, 221→225 nm).[18] The emission spectra of $\mathbf{U^{Ph2phen}}$ (Figures S10–12) show a broad featureless band at *ca.* 520 nm, consistent with a reduction in symmetry at the uranium centre, and in contrast to well-resolved fine structure in the analogous emission profile of $\mathbf{U^{NO3}}$.[19] The Stokes shift for $\mathbf{U^{Ph2phen}}$ of 4645 cm^{-1} is larger than that of $\mathbf{U^{NO3}}$, 3820 cm^{-1}, consistent with a greater degree of structural reorganisation in the excited-state for the more complicated ligand. The E$_{0\text{-}0}$ values[2] for the weak U(5f)←O(2p) LMCT band at *ca.* 420 nm for $\mathbf{U^{Ph2phen}}$ (21692 cm^{-1}) and $\mathbf{U^{NO3}}$ (21400 cm^{-1}), are similar, suggesting the energy of this transition is minimally affected by Ph$_2$phen coordination.

The emission spectrum of $\mathbf{U^{Ph2phen}}$ has bands at 288 nm and 365 nm (Figure S12) and also contains a broad, featureless band at *ca.* 520 nm from irradiation at either 288 or 365 nm. These are tentatively assigned as ligand absorptions, and combined with the uranyl absorption at *ca.* 420 nm contribute to the broad emission profile centred at *ca.* 520 nm. While time-dependent density functional theory (TD-DFT) on 5*f* ions with open-shell, 5f^1 excited states are non-trivial,[20] these observations suggest a degree of electronic mixing between metal and ligand that modulates the luminescent properties of $\mathbf{U^{Ph2phen}}$.

Because $\mathbf{U^{Ph2phen}}$ has this readily accessible, ligand-modified excited state, contains no coordinated water, and is soluble in organic solvents (in contrast to the previously reported unsubstituted phen complex),[17] we have studied its capacity to react photolytically with organic substrates in a controlled manner (Scheme 3 and Table 1).



Scheme 3. Conditions employed for substrate oxidation catalysed by $\mathbf{U^{No3}}$ (10 mol%) and $\mathbf{U^{Ph2phen}}$ (5 mol%). R = hydrocarbyl.

It was found that $\mathbf{U^{Ph2phen}}$ gives higher conversions than $\mathbf{U^{NO3}}$ for all substrates tested. For example, using $\mathbf{U^{Ph2phen}}$, the archetypal substrate 9,10-dihydroanthracene (DHA; D(C–H) = 326.4 kJ mol^{-1}, pK_a 30 in DMSO)[21] undergoes catalytic H-atom abstraction to form anthracene in 89% yield (Table 1 entry 1,

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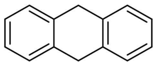
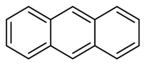
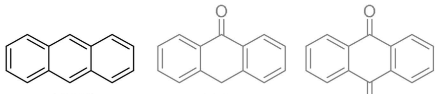
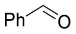
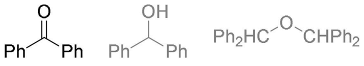
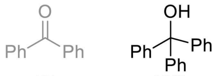
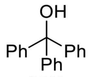
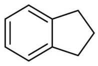
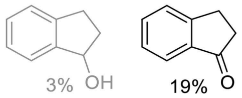
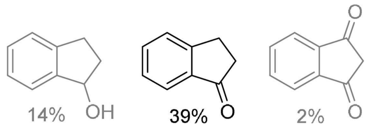
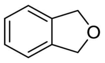
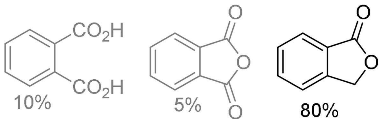
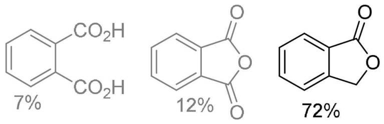
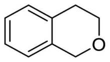
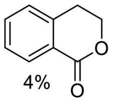
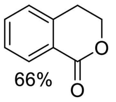
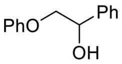
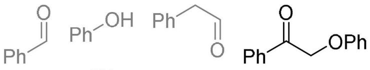
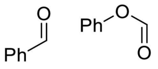
[2] zero-zero transition, E$_{0\text{-}0}$, is the energy difference between ground vibrational state of ground electronic state and ground vibrational state of first electronically-excited state.

Table 1. Comparison of $U^{Ph2phen}$ and U^{No3} as homogeneous photocatalysts for the controlled C–H bond cleavage of a range of substrates.[a]

Entry	Substrate	Overall conversion[a] [%] U^{NO3}	Overall conversion[a] [%] $U^{Ph2phen}$	Major (and minor) measurable product(s) of oxidation (Yield [%]) U^{NO3}	Major (and minor) measurable product(s) of oxidation (Yield [%]) $U^{Ph2phen}$
1	 DHA[d] See Table 2	68[b]	89[b]	 67%[e]	 73%[e] 7% 6%
2	Toluene $PhCH_3$	2[b]	35[c]	 2%	 27% 3%
3	Diphenylmethane Ph_2CH_2	21[c]	33[b]	 12% 4% 5%	 21% 12%
4	Triphenylmethane Ph_3CH	14[b]	37[b]	 4% 10%	 25%
5	 Indane	47[b]	87[b]	 3% 19%	 14% 39% 2%
6	 Phthalan	99[b]	99[c]	 10% 5% 80%	 7% 12% 72%
7	 Isochroman	35[b]	80[c]	 4%	 66%
8	 2P1PE	19[c]	18[c]	 4% 2% 2% 7%	 7% 7%
9	DHA, control	0	0	–	–

[a] U^{NO3} 10 mol% or $U^{Ph2phen}$ 5 mol%, in CH_3CN (5 mL) for 16 hours at 293 K with hν (420 nm); [b] GC-MS; [c] ^1H NMR spectroscopy and GC-MS; [d] DHA is 9,10-dihydroanthracene; [e] inferred (anthracene photo-dimerises under these conditions)

and see below), compared with 68 % conversion using U^{NO3}. The most significant improvement in product conversion is for toluene, with an increase from 2 % to 35 % upon changing from U^{NO3} to $U^{Ph2phen}$ as catalyst (Table 1, entry 2). Conversions of the simple benzylic hydrocarbons Ph_2CH_2 and Ph_3CH are both increased, from 21 % to 33 %, and 14 % to 37 %, respectively (Table 1. entries 3 & 4), and the most favoured products for both catalysts are PhCHO (formed from toluene), Ph_2CO (formed from Ph_2CH_2) or Ph_3COH (formed from Ph_3CH). Conversion of indane and isochroman roughly doubles on changing catalyst from U^{NO3} to $U^{Ph2phen}$, increasing from 47 % to 87 % and 35 % to 80 %, respectively; these compounds are selectively oxidised at the benzylic positions, with the ketones, rather than alcohols, as the favoured products (Table 1, entries 5 & 7). In contrast, conversion of phthalan (entry 6) is quantitative for both catalysts and there is negligible change in product selectivity, forming the lactone in excellent yields (70–80 %). Control reactions (Table 1, entry 9) in the absence of catalyst show no conversion.

We were curious to see if the reaction scope could be extended from catalytic C–H to C–C bond cleavage. Lignin mimics that possess benzylic C–H bonds, such as 2-phenoxy-1-

phenylethanol (2P1PE; Table 1, entry 8), have been reported to undergo C–C bond cleavage rather than C–H bond activation,[22] for example, when treated with $[\mathrm{V^{V}O_2(acac)}]$ (acac = acetylacetonate) under photocatalytic conditions, yielding benzaldehyde and benzoic acid with 54 % conversion in CH_3CN.[23] Similarly, both $\mathbf{U^{NO3}}$ and $\mathbf{U^{Ph2phen}}$ catalyse photolytic C–C bond cleavage, albeit at lower yields (19 % and 18 % by GC-MS, respectively; Table S8, entry 8), suggesting that $^{*}\mathrm{U^{VI}O_2}^{2+}$-mediated reactivity may be viable for lignin decomposition. C–C bond activation with uranyl has been reported previously.[3]

The catalytic oxidation of DHA was studied in more depth to investigate other factors that influence the reactions: the two complexes $\mathbf{U^{NO3}}$ and $\mathbf{U^{Ph2phen}}$ both form anthracene as the oxidation product in low to excellent yields depending on the conditions (Table 2). Using $\mathbf{U^{NO3}}$ at 0.5 mol% loading, the oxidation of DHA is almost complete after 8 h with 86 % conversion (Table 2 and Figure S21), with further irradiation resulting in photodegradation of products. Catalyst loadings of $\mathbf{U^{NO3}}$ between 0.001 and 25 mol% were further tested (Table S2; Figures S15 & S16, S25–S39) and show the reaction is 0th order in catalyst under these photolytic conditions, with conversions of around 35 % at all concentrations (Figure S20; Table S6, entries 1–5, 8–10, 14 & 15); *i.e.* catalyst concentration has no discernible effect on DHA conversion under these conditions. No conversion occurs for samples stored in the dark, and there is no change in DHA conversion in the presence of mercury droplets (5 mol% $\mathbf{U^{NO3}}$), suggesting that the reaction does not proceed heterogeneously (Table S6, entry 13).

Table 2. Comparison of conversions between U^{NO3} and $U^{Ph2phen}$ at different loadings and times.[a]

Entry	Catalyst loading [%]	*T* [h]	DHA conversion [%] U^{NO3}	DHA conversion [%] $U^{Ph2phen}$
1	0.001	3	33	23
2	0.01	3	36	34
3	0.1	3	32	45
4	1	3	37	57
5	0.5	1	16	24
6	0.5	2	28	38
7	0.5	4	48	64
8	0.5	8	86	96

[a] DHA (450 mg), CH_3CN (50 mL), appropriate [cat.], 293 K with hν (420 nm) over time. Analysis by ^{1}H NMR spectroscopy at appropriate time intervals.

For $\mathbf{U^{Ph2phen}}$ increasing catalyst loading from 0.001 %–1 % sees conversion increase from 23 to 57 % within the first 3 hours (Figures S18–S20, S44–S51; Table S7, entries 1–6, 8 (see also entries 1-4 in Table 2)), in marked contrast to conversion employing $\mathbf{U^{NO3}}$. However, at higher loadings of $\mathbf{U^{Ph2phen}}$, precipitation of a yellow solid is commonly observed after several minutes of photolysis in the presence of substrate (no precipitate is observed upon photolysis of a solution of only $\mathbf{U^{Ph2phen}}$ in CH_3CN). This yellow precipitate is characterised as a uranyl- and peroxo-containing oligomer, as ions in the mass spectrum that correspond to $[(\mathrm{U^{VI}O_2})_2(\mu\text{-}\mathrm{O_2})(\mathrm{NO_3})_3]^-$ (758.0274 Da) and $[(\mathrm{U^{VI}O_2})_2(\mu\text{-}\mathrm{O_2})(\mathrm{NO_3})_3(\mathrm{Ph_2phen})]^-$ (1090.1711 Da) are found. Bands in the Raman spectrum at 838 and 849 cm^{-1} (Figure S7) also compare well with the peroxo-bridged complex, $[\{\mathrm{U^{VI}O_2(NO_3)(py)_2}\}_2(\mu\text{-}\mathrm{O_2})]\cdot\mathrm{py}$[24], which has a symmetric μ-O_2 stretch at 860 cm^{-1}. Other reported uranyl-peroxo oligomers have Raman bands between 820 and 870 cm^{-1}.[25] This product could be formed as the result of a photolytically-induced oxygen reduction, something observed very recently in other uranyl complexes derived from photoreactions.[26] Combustion analysis performed on this solid (42.5 % C, 2.7 % H, 6.0 % N) is also consistent with a formulation of $[(\mathrm{U^{VI}O_2})_2(\mu\text{-}\mathrm{O_2})(\mathrm{NO_3})_2(\mathrm{Ph_2phen})_2]$.

DHA consumption plateaus at roughly 6 or 7 hours with $\mathbf{U^{Ph2phen}}$, quicker than $\mathbf{U^{NO3}}$ at 9 hours (Figure S21). The addition of equimolar anthracene at the start of the reaction also causes conversion to drop from 53 to 27 % (Table S6, entry 6; Table S7, entry 7; Figure S24). As both anthracene and $\mathbf{U^{Ph2phen}}$ have absorption bands at *ca.* 360 nm, we suggest there is competitive photon absorption between $\mathbf{U^{Ph2phen}}$ and anthracene (λ_{max} 356 nm) at the tailing edge of the lamp spectral output (Figure. S1), reducing conversion when anthracene is present. This is not observed for $\mathbf{U^{NO3}}$ as there are no absorption bands at *ca.* 360 nm.

Reactions of either catalyst in benzonitrile solvent instead of acetonitrile roughly halve the conversion (Table S6, entry 7; Table S7, entry 8; Figure S23). For example, in a reaction at 0.5 mol% $\mathbf{U^{Ph2phen}}$ loading, switching solvent from CH_3CN to benzonitrile reduces the conversion from 53 to 37 % after 3 hours. This is probably because the benzonitrile solvent can quench the uranyl photoexcited state by forming an exciplex through the aromatic π-systems that decays through non-radiative processes.[3a,27] For $\mathbf{U^{NO3}}$, the role of water was also examined; the addition of 100 eq. of water to the 5 mol% $\mathbf{U^{NO3}}$/DHA/CH_3CN reaction mixture (Table S6, entry 12; Figure S22) increases the initial rate of DHA consumption, which then tails off over time with *ca.* 35 % conversion of DHA observed after 3 h (*i.e.* conversion is initially faster with added water, but after 3 h is equivalent). $\mathbf{U^{Ph2phen}}$ is also hydrolytically stable, and shows no sign of decomplexation in the presence of up to 20 eq. of water in CH_3CN solution (Figure S52). It is possible that the added water for the $\mathbf{U^{NO3}}$ reaction forms stabilising, hydrogen-bonding interactions with oxygen-derived radicals and ions near the outer coordination sphere of the uranyl in the intermediates and thus increases the initial rate of DHA consumption.

Oxygen is necessary in this system for turnover and is likely required to reoxidise the $\mathrm{U^{V}}$ $[\mathrm{UO_2H}]^{2+}$ ion that is first formed from the H atom abstraction, Equation (1).

$$2\ \mathrm{U^{VI}O_2}^{2+} \rightarrow 2\ [\mathrm{U^{V}O_2H}]^{2+} \rightarrow \mathrm{U^{IV}} + \mathrm{U^{VI}O_2}^{2+} \tag{1}$$

A reaction mixture containing 5 mol% $\mathbf{U^{NO3}}$ and DHA was irradiated in the absence of oxygen, upon which a grey-black precipitate (51 mg) is formed (Table S6, entry 11). The uranium-containing (41.8 % U, ICP-MS) precipitate contains no $\mathrm{U^{VI}}$ uranyl but water, nitrate, and organic material are present according to FTIR spectroscopy and combustion analysis (see SI). This precipitate becomes yellow on standing in air for 48 h and a stretch that may be assigned to the asymmetric OUO stretch of the uranyl ion becomes visible in FTIR spectra (Figure S5), suggesting re-oxidation. This compound is probably an aggregate of U^{IV}, nitrate and oxidised substrate which is not regenerated into $[U^{VI}O_2]^{2+}$.

In summary, we have prepared and fully characterised a new uranyl photocatalyst, $\mathbf{U}^{\mathbf{Ph2phen}}$, which shows higher conversions than $\mathbf{U}^{\mathbf{NO3}}$ in the oxidation of selected substrates, attributed to ligand-mediated electronic effects. Substrates with benzylic C–H bonds are most readily oxidised, with toluene, triphenylmethane, indane and isochroman showing the highest improvements in oxidation whencatalysed by $\mathbf{U}^{\mathbf{Ph2phen}}$. We also report preliminary results on the uranyl-mediated photocatalytic C–C bond cleavage in a model lignin compound for the first time. We attribute the higher efficacy of $\mathbf{U}^{\mathbf{Ph2phen}}$ to ligand-tuning of the excited state and work to understand the mechanistic implications of this is underway.

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Conflict of Interest

The authors declare no conflict of interest.

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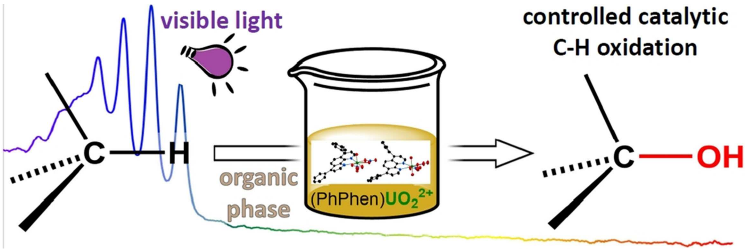

Prof. P. L. Arnold, J. M. Purkis, R. Rutkauskaite, D. Kovacs, Prof. J. B. Love, Dr. J. Austin*

1 – 6

Controlled Photocatalytic Hydrocarbon Oxidation by Uranyl Complexes

HATs off to U An air-stable, organic-soluble uranyl-phenanthroline complex, $[UO_2(NO_3)_2(Ph_2phen)]$, $\mathbf{U}^{\mathbf{Ph2phen}}$ (Ph2phen = 4,7-diphenyl-1,10-phenanthroline) demonstrates catalytic hydrogen atom abstraction from a variety of organic substrates under visible-light irradiation. From photophysical studies we attribute the higher rates and selectivity of $\mathbf{U}^{\mathbf{Ph2phen}}$ compared to the parent uranyl nitrate (also tested here) to ligand-mediated electronic effects. The catalytic oxidation of substrates containing a benzylic C–H position is particularly improved for $\mathbf{U}^{\mathbf{Ph2phen}}$. We also demonstrate uranyl-mediated photocatalytic cleavage in a model lignin compound for the first time.