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Communication

Stabilization of Photocatalytically Active Uranyl Species in a Uranyl−Organic Framework for Heterogeneous Alkane Fluorination Driven by Visible Light

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ABSTRACT: When photoactivated, the uranyl ion is a powerful oxidant capable of abstracting hydrogen atoms from nonactivated C−H bonds. However, the highly reactive singly reduced $[U^{V}O_2]^+$ intermediate is unstable with respect to disproportionation to the uranyl dication and insoluble tetravalent uranium phases, which limits the usage of uranyl ions as robust photocatalysts. Herein, we demonstrate that photoactivated uranyl ions can be stabilized by immobilizing and separating them spatially in a uranyl−organic framework heterogeneous catalyst, NU-1301. The visible-light-photoactivated uranyl ions in NU-1301 exhibited longer-lived U(V) and radicals than those in homogeneous counterparts, as evidenced by X-ray photoelectron spectroscopy and time-dependent electron paramagnetic resonance, leading to higher turnovers and enhanced stability for the fluorination of nonactivated alkanes.

Actinide-based functional materials have been substantially underexplored; however, participation of the unique 5f electrons in bond formation could lead to new materials with unconventional chemical, electronic, and magnetic properties. For instance, uranium has been utilized as an exceptional catalyst for water reduction,[1] photodegradation of organic dyes,[2] oxidative combustion of volatile organic compounds,[3] and activation of small molecules such as N_2,[4,5] CO,[6] CO_2,[7] etc.[8,9]

Photoexcitation of the uranyl ion ($[U^{VI}O_2]^{2+}$), the most prevalent chemical form of uranium in nature, produces a strongly oxidizing excited-state species $[U^{VI}O_2]^{2+*}$ with a standard reduction potential of +2.6 V (vs standard hydrogen electrode).[10] Recently, Sorensen and co-workers have reported the uranyl cation as a visible-light photocatalyst for C−H fluorination (Figure 1).[11] However, at least 1 mol % of the uranyl nitrate catalyst was essential to achieve a high yield; less catalyst would result in a significantly lower yield.[11] It has long been known that the singly reduced uranyl ion $[U^{V}O_2]^+$ is unstable with respect to disproportionation to the uranyl dication and insoluble tetravalent uranium species,[12,13] which would lead to deactivation of the uranyl cation as a photocatalyst. Moreover, when exposed to arenes, the uranyl ion's excited state forms exciplexes that decay unproductively and ultimately quench the uranyl excited state.[14]

Synthetic strategies for the stabilization of pentavalent uranyl species in homogeneous systems have focused on creating steric hindrance around uranyl ions by using bulky ligands to prohibit the formation of dimeric cation−cation complexes. Unfortunately, these complexes are susceptible to disproportionation in the presence of protons.[15,16] While doping and grafting of uranyl ions on solid supports such as TiO_2, alumina, and mesoporous silica are feasible strategies for the immobilization of uranyl species for heterogeneous cataly-

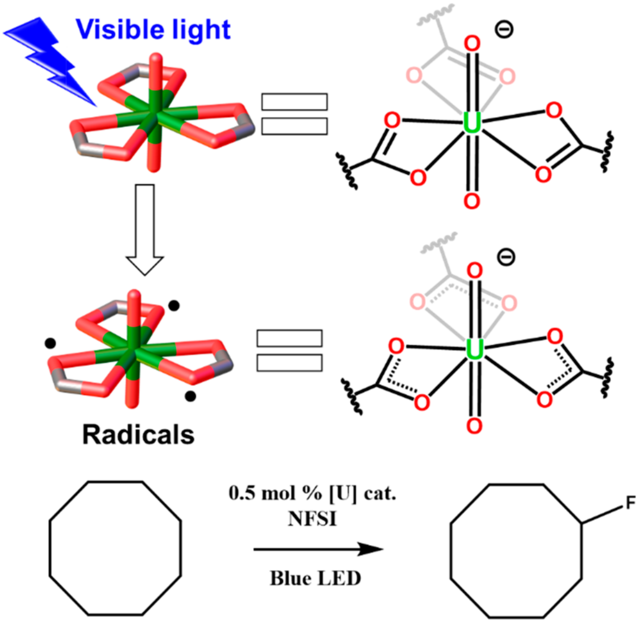

Figure 1. Schematic representation of the photoexcitation of uranyl carboxylate species $[U^{VI}O_2]^{2+}$ to $[U^{VI}O_2]^{2+*}$ under blue light (top). Reaction scheme of the photocatalytic fluorination of cyclooctane (bottom).

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sis,[2,17,18] their development has largely been hindered by the lack of precise structural information.

Metal−organic frameworks (MOFs), a class of highly porous and crystalline materials, have been reported as heterogeneous catalyst supports, with their inorganic nodes and organic linkers serving as metal catalyst anchoring sites.[19−21] The metal-ion nodes have also been studied as catalytically active sites.[22] Recently, a large number of uranyl−organic frameworks (UOFs) have been reported, and the diverse topology, high porosity, and unique physical/chemical properties of UOFs,[23−28] including the detection of small ions,[29] detection of radiation,[30] and nuclear waste removal,[31] have brought great attention to this new family of MOF materials.

To prevent the formation of uranyl cation−cation dimers and subsequent disproportionation reactions, we propose the incorporation of uranyl ions as nodes within MOFs, thus providing a promising heterogeneous catalyst in which the uranyl species will be spatially isolated. We envision that the spatially isolated uranyl ions in UOFs are stable upon photoexcitation and can be used as robust photocatalysts driven by visible light for C−H activation.

Herein, we report visible-light photocatalytic C−H fluorination by a uranyl-based MOF, NU-1301 (Figure 2). The heterogeneous catalyst exhibited enhanced activity and stability compared to the homogeneous catalyst, uranyl nitrate.

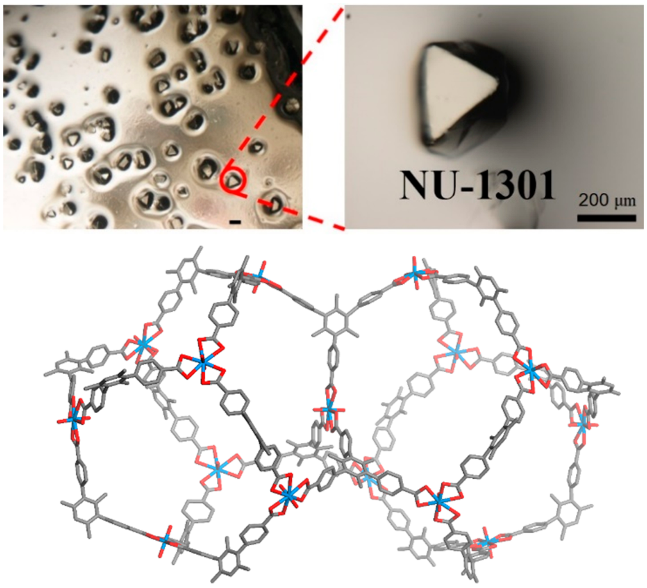

Figure 2. Optical images of the crystals (top) and a fragment of the crystal structure (bottom) of NU-1301.

To test our hypothesis that uranyl species might demonstrate enhanced photocatalytic activity through incorporation into UOFs, NU-1301, a mesoporous MOF with a hierarchical pore system, was synthesized as reported via the solvothermal reaction of uranyl nitrate with 5′-(4-carboxyphenyl)-2′,4′,6′-trimethyl-[1,1′:3′,1′′-terphenyl]-4,4′′-dicarboxylic acid in *N*,*N*-dimethylformamide in the presence of trifluoroacetic acid as an acid modulator[32] and subsequently tested for the visible-light-driven catalytic fluorination of alkanes. The powder X-ray diffraction (PXRD) pattern matched the reported simulated pattern (Figure S1), and N_2 adsorption isotherms confirmed its porosity (Figure S2). The oxidation states of uranium were probed by X-ray photoelectron spectroscopy (XPS). Compared to standard compounds of $U^{VI}O_2(NO_3)_2$ and $U^{IV}Cl_4$, which have U $4f_{7/2}$ binding energies of 382.7 and 381.5 eV, respectively, NU-1301 exhibits a binding energy of 382.3 eV, indicating an intermediate oxidation state between U(VI) and U(IV) (Figure 3a). Electron paramagnetic resonance (EPR) spectroscopic studies were carried out to investigate the photophysical behavior of NU-1301. At room temperature, prior to photoirradiation, NU-1301 shows no EPR signal; however, following photoirradiation, a signal with a slightly rhombic **g** tensor, **g** = [2.0363 2.0172 2.0157], was observed (Figures 3b and S5). The observed EPR signal is consistent with a ligand-based radical generated through charge-transfer reduction by $U^{IV}O_2$.[30,33] After irradiation, the radical EPR signal decayed at a rate of 4×10^{-4} s^{-1} (Figure S6).

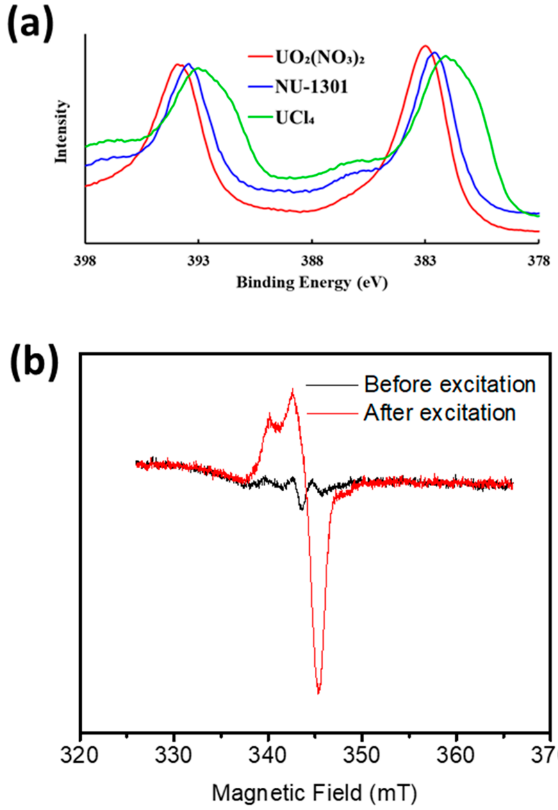

Figure 3. (a) XPS spectra of uranyl nitrate, NU-1301, and UCl_4. (top). (b) Solid-state EPR spectra of NU-1301 before and after photoexcitation.

Photocatalytic $C(sp_3)$−H fluorination reactions in this study were carried out using *N*-fluorobenzenesulfonimide as the fluorination reagent with a blue-light-emitting-diode light source at room temperature.[11] When NU-1301 was employed as a photocatalyst (0.5 mol %), a significant increase in the yield of 1-fluorooctane (99%) was observed compared to the homogeneous catalyst $UO_2(NO_3)_2$ (52%; Figure 4), further supporting a stabilizing effect of carboxylate ligands on uranyl species. Other alkanes such as cyclopentane and *n*-octane were tested as substrates. In all cases, NU-1301 exhibited superior catalytic activity compared to the reported homogeneous catalyst $UO_2(NO_3)_2$ (Table S1).

The incorporation of uranyl species in MOFs also mitigates exciplex decay. Previous reports indicate that the addition of an aromatic compound, i.e., toluene, resulted in quenching of the

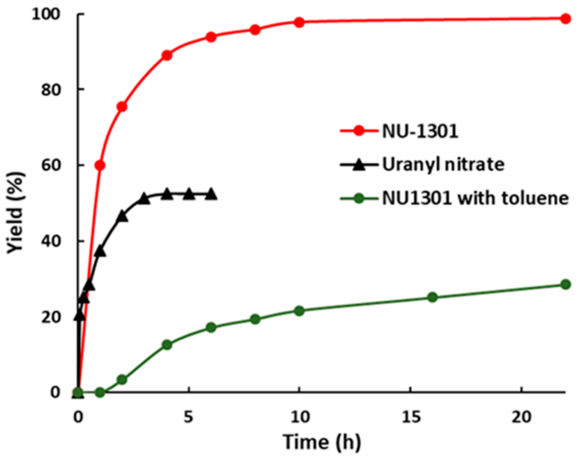

Figure 4. Time-dependent reaction profiles using uranyl nitrate and NU-1301 (in the absence and presence of toluene) as catalysts under blue light.

uranyl excited state in a homogeneous solution, severely decreasing the yield of fluoroalkanes.[11] Compared to homogeneous $UO_2(NO_3)_2$, NU-1301 exhibited an enhanced yield of 1-fluorocyclooctane [25% vs 13% by $UO_2(NO_3)_2$] in the presence of toluene (Figure 4).

Postcatalysis XPS measurements of the materials showed a decrease in the U $4f_{7/2}$ binding energy of uranyl nitrate from 382.7 to 382.1 eV. In comparison, the binding energy of NU-1301 remained almost the same (382.3 and 382.2 eV before and after catalysis, respectively), supporting the stabilization of uranyl in NU-1301 with respect to uranyl nitrate.

In summary, we report the photocatalytic C−H fluorination of unactivated alkanes by the UOF NU-1301. The visible-light-photoactivated uranyl ions in NU-1301 showed longer-lived U(V) and radical species than those in its homogeneous counterparts, as evidenced by XPS and time-dependent EPR. These characteristics ultimately led to faster turnover rates and enhanced stability for the fluorination of a wide scope of $C(sp^3)$−H organic compounds. The current work presents a novel strategy for stabilizing uranyl species and for enhancing their photocatalytic activity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00850.

PXRD, XPS, EPR, and additional data (PDF)

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Notes

The authors declare no competing financial interest.

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