Hydrothermal crystallization of uranyl coordination polymers involving an imidazolium dicarboxylate ligand: effect of pH on the nuclearity of uranyl-centered sub-units.

Nicolas P. Martin,[a] Clément Falaise,[a] Christophe Volkringer,[a,b] Natacha Henry,[a] Pierre Farger,[c] Camille Falk,[c] Emilie Delahaye,[c] Pierre Rabu,[c] Thierry Loiseau.[a,*]

Contribution from
[a]*Unité de Catalyse et Chimie du Solide (UCCS) – UMR CNRS 8181, Université de Lille, ENSCL, Bat C7, BP 90108, 59652 Villeneuve d'Ascq, France.*
[b]*Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 05.*
[c]*IPCMS UMR7504 CNRS-UNISTRA, Département de Chimie des Matériaux Inorganiques, 23, rue du Loess, BP43, Strasbourg cedex 2, France.*

[*] To whom correspondence should be addressed. E-mail: thierry.loiseau@ensc-lille.fr. Phone: (33) 3 20 434 434, Fax: (33) 3 20 43 48 95.

SUPPLEMENTARY INFORMATION

To be submitted to Inorg. Chem.
Version May 20, 2016.
Revised version june 16, 2016.
Revised version july 22, 2016.

Figures

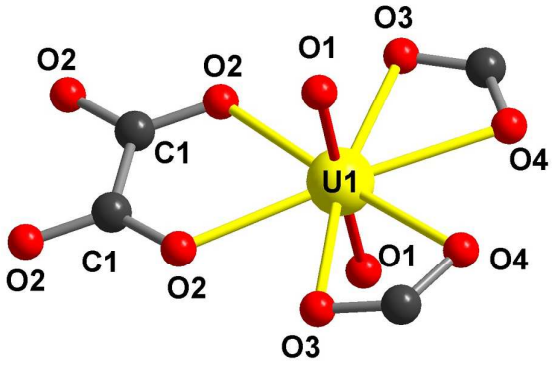

Figure S1a: View of the coordination of uranyl center U1 in $(UO_2)_2(imdc)_2(ox)\cdot 3H_2O$ (**1**).

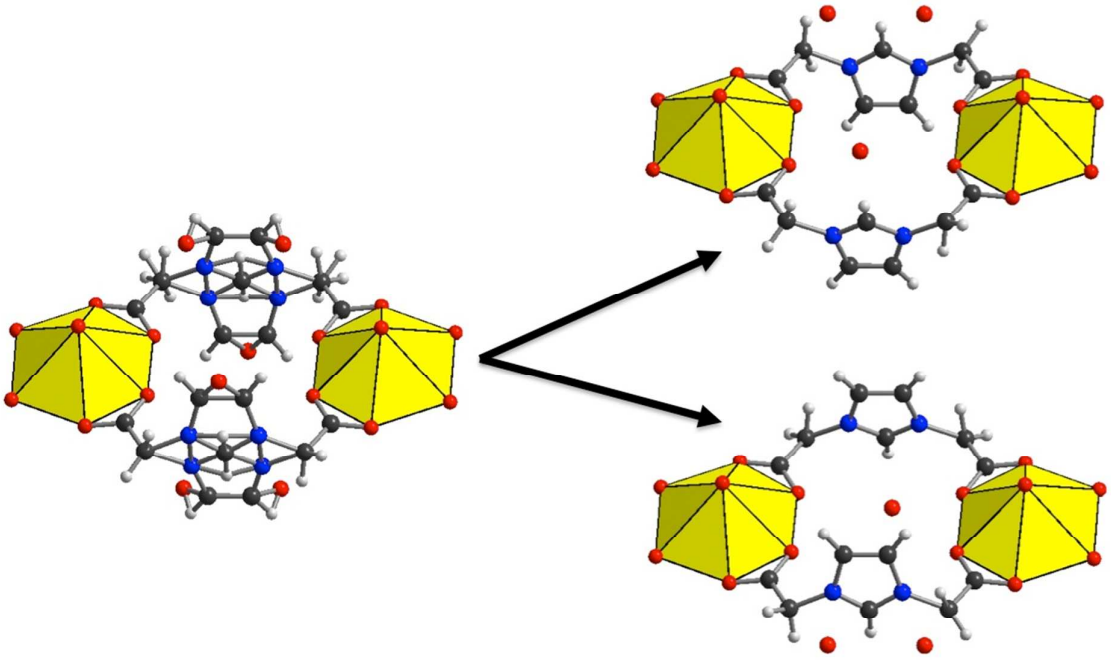

Figure S1b: Detailed view of the disorder of the imidazol ring and water molecules in $(UO_2)_2(imdc)_2(ox)\cdot 3H_2O$ (**1**).

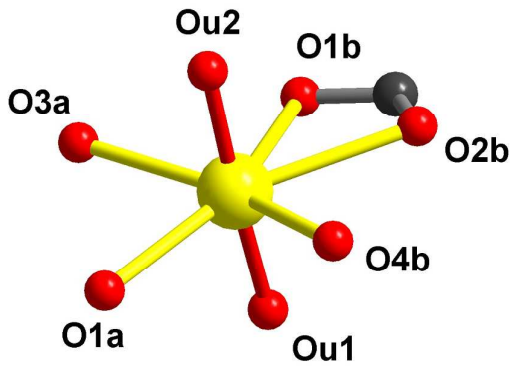

Figure S1c: View of the coordination of uranyl center U1 in $(UO_2)(imdc)_2$ (**2**).

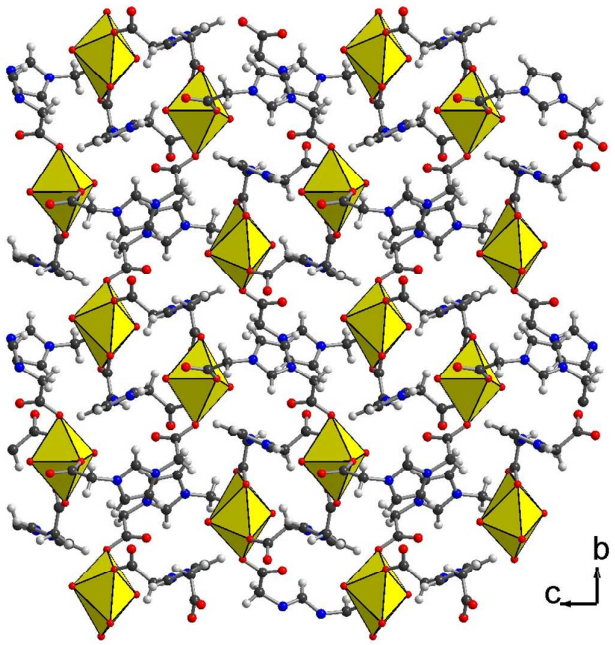

Figure S1d: Representation of a layer in the (*b*,*c*) plane in $(UO_2(imdc)_2)$ (**2**).

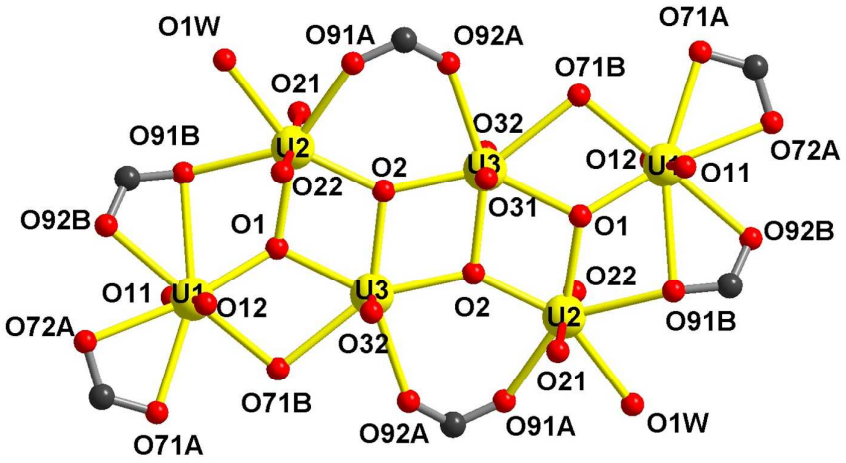

Figure S1e: View of the coordination of uranyl centers U1, U2 & U3 in $(UO_2)_3O_2(H_2O)(imdc)\cdot H_2O$ (**3**).

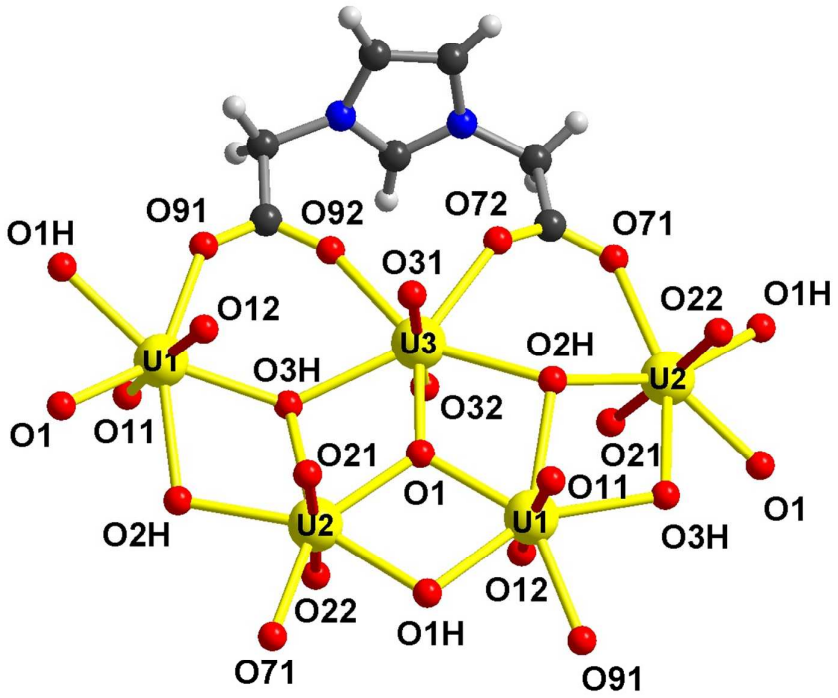

Figure S1f: view of the coordination of uranyl centers U1, U2 & U3 in $(UO_2)_3O(OH)_3(imdc)\cdot 2H_2O$ (**4**).

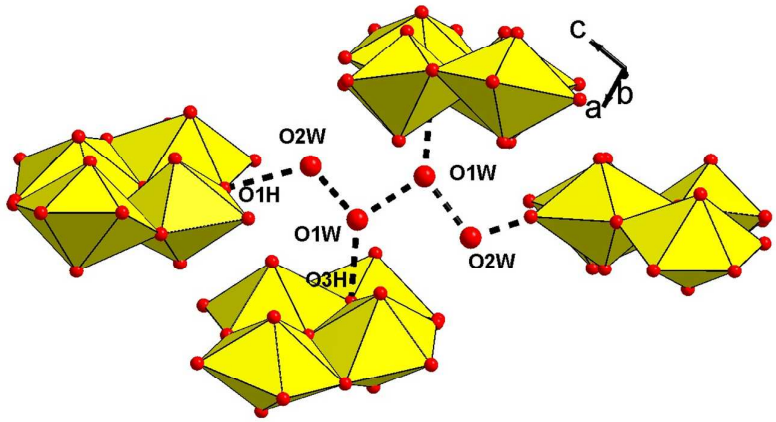

Figure S1g: View of the hydrogen bond scheme in $(UO_2)_3O(OH)_3(imdc)\cdot 2H_2O$ (**4**)

XRD powder patterns

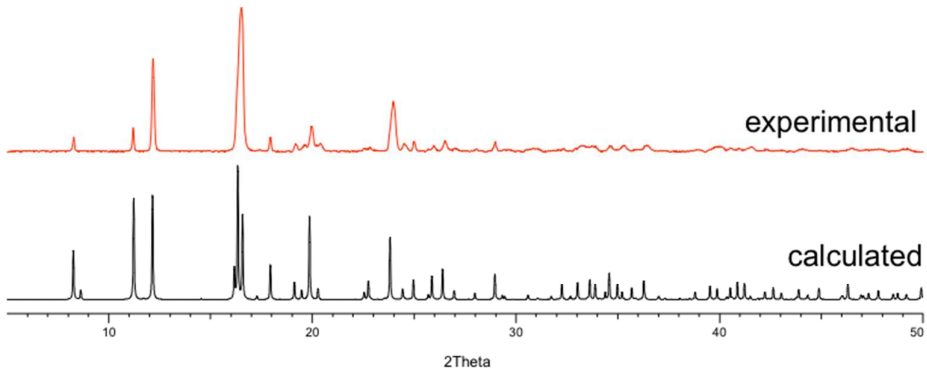

Figure S2a: Comparison between the calculated (black line) and experimental (red line) XRD patterns of $(UO_2)_2(imdc)_2(ox)\cdot 3H_2O$ (**1**) – Copper radiation.

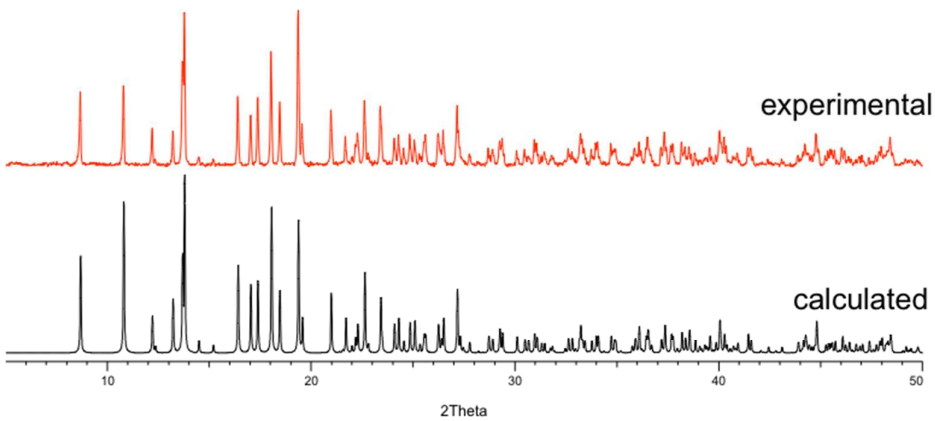

Figure S2b: Comparison between the calculated (black line) and experimental (red line) XRD patterns of $UO_2(imdc)_2$ (**2**)– Copper radiation.

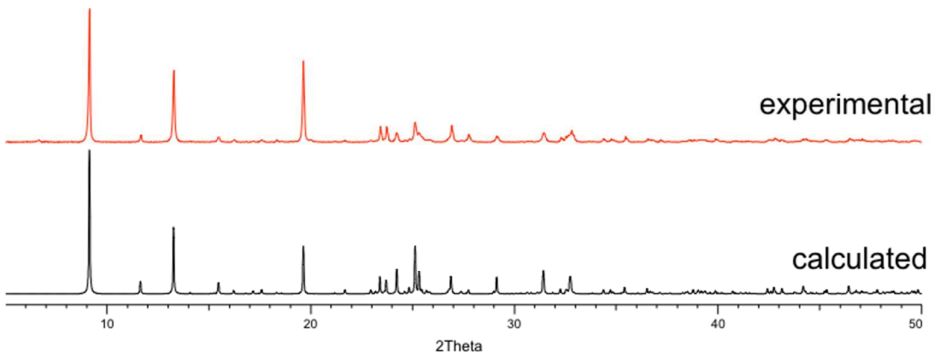

Figure S2c: Comparison between the calculated (black line) and experimental (red line) XRD patterns of $(UO_2)_3O(OH)_3(imdc)\cdot 2H_2O$ (**4**)– Copper radiation.

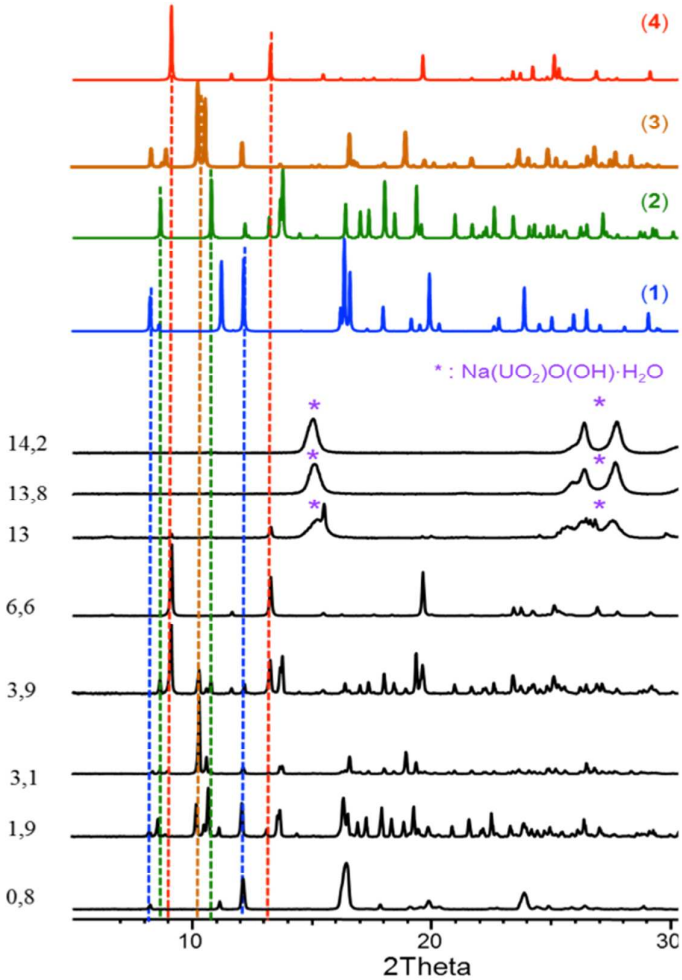

Figure S3: Evolution of the powder XRD patterns of compounds **1**-**4** & $Na(UO_2)O(OH)\cdot H_2O$, as a function of reaction pH.

Thermal anaylsis. The thermogravimetric experiments have been carried out on a thermoanalyzer TGA 92 SETARAM under air atmosphere with a heating rate of 5°C.min^{-1} from room temperature up to 800°C.

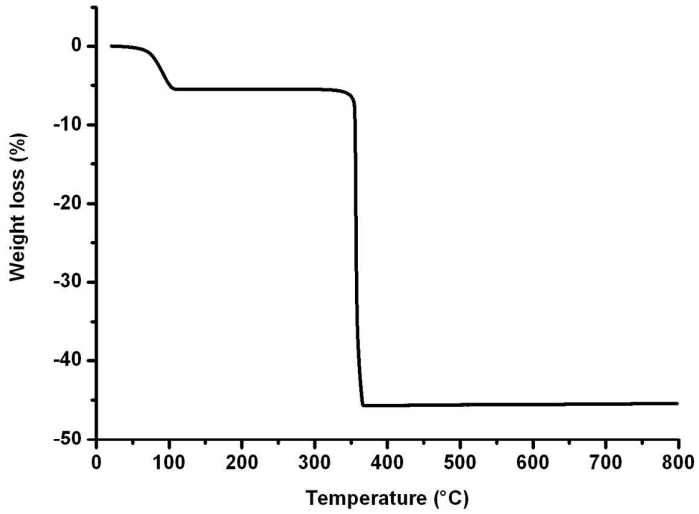

Figure S4a: Thermogravimetric curve of the compound $(UO_2)_2(imdc)_2(ox)\cdot 3H_2O$ (**1**) under air atmosphere (heating rate 5°C.min^{-1}).

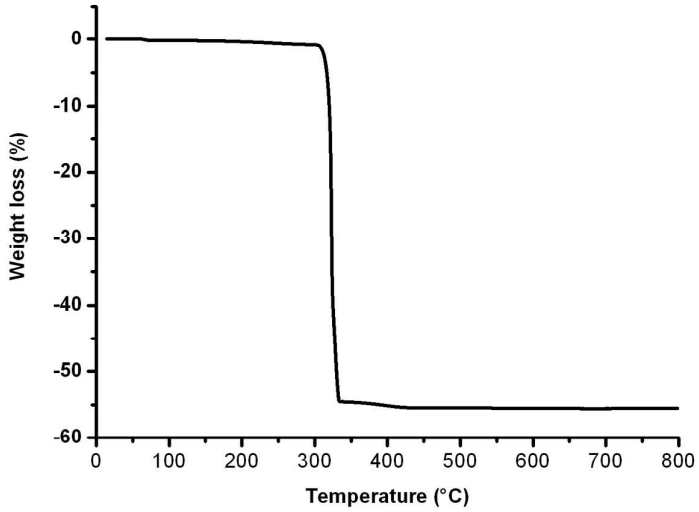

Figure S4b: Thermogravimetric curve of the compound $UO_2(imdc)_2$ (**2**) under air atmosphere (heating rate 5°C.min^{-1}).

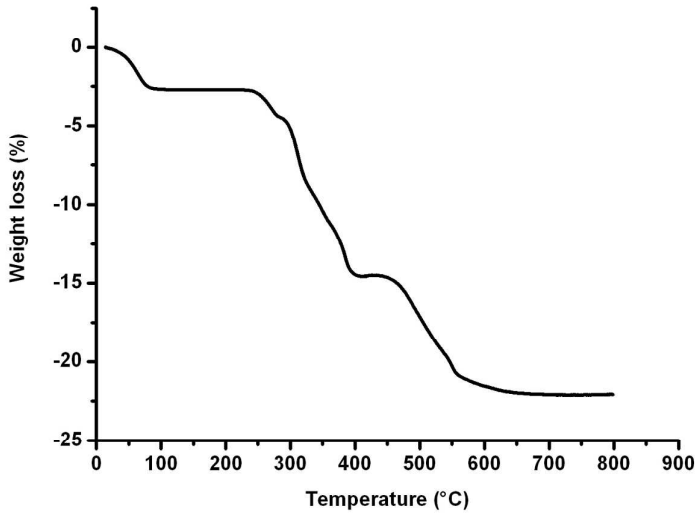

Figure S4c: Thermogravimetric curve of the compound $(UO_2)_3O(OH)_3(imdc)\cdot 2H_2O$ (**4**) under air atmosphere (heating rate 5°C.min^{-1}).

Infrared spectroscopy.

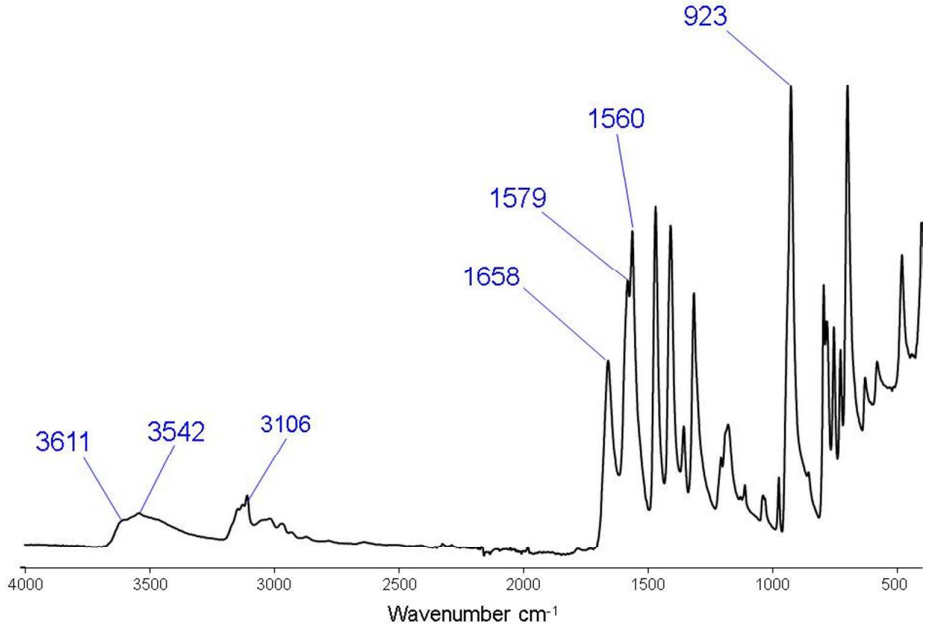

Figure S5a: Infrared spectra of $(UO_2)_2(imdc)_2(ox)\cdot 3H_2O$ (**1**) collected at room temperature.

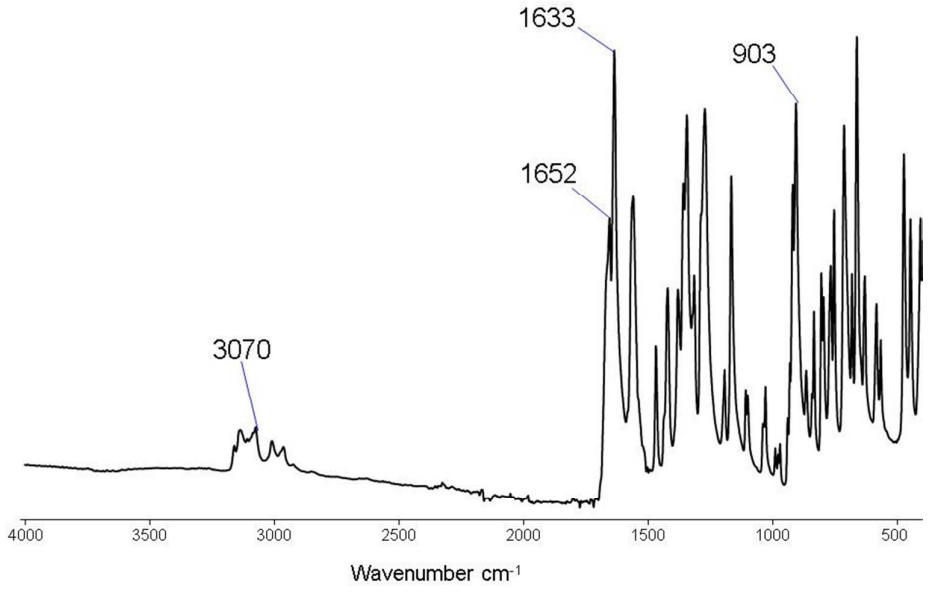

Figure S5b: Infrared spectra of $UO_2(imdc)_2$ (**2**) collected at room temperature.

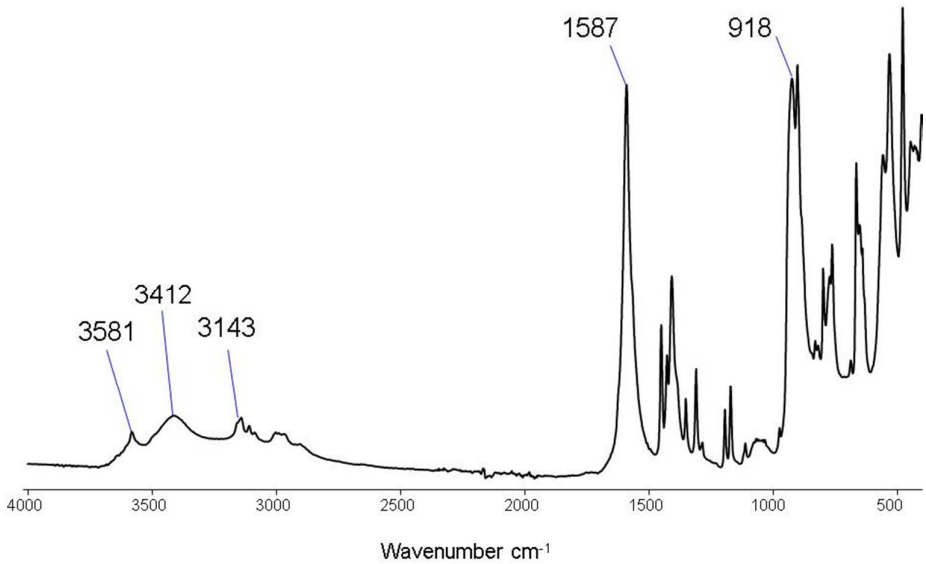

Figure S5c: Infrared spectra of $(UO_2)_3O(OH)_3(imdc)\cdot 2H_2O$ (**4**) collected at room temperature.

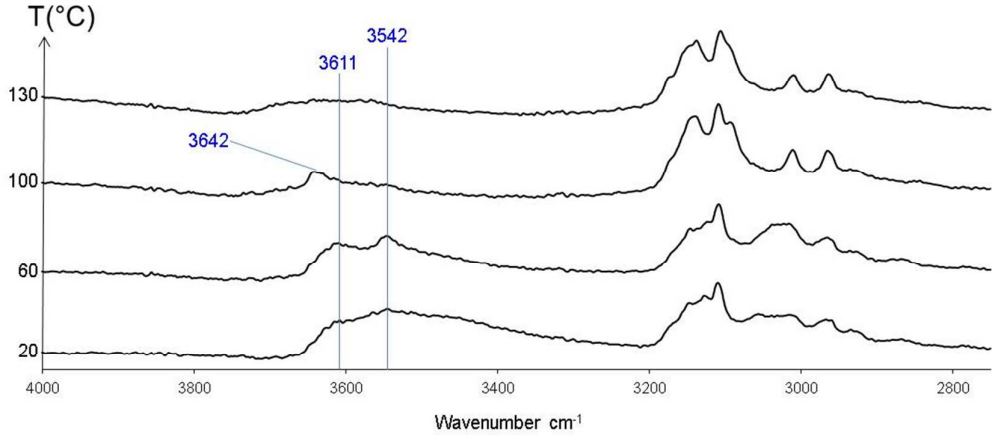

Figure S5d: Evolution of the *in situ* IR spectra of $(UO_2)_2(imdc)_2(ox)\cdot 3H_2O$ (**1**) between 20-130°C in the range 4000-2750 cm^{-1}.

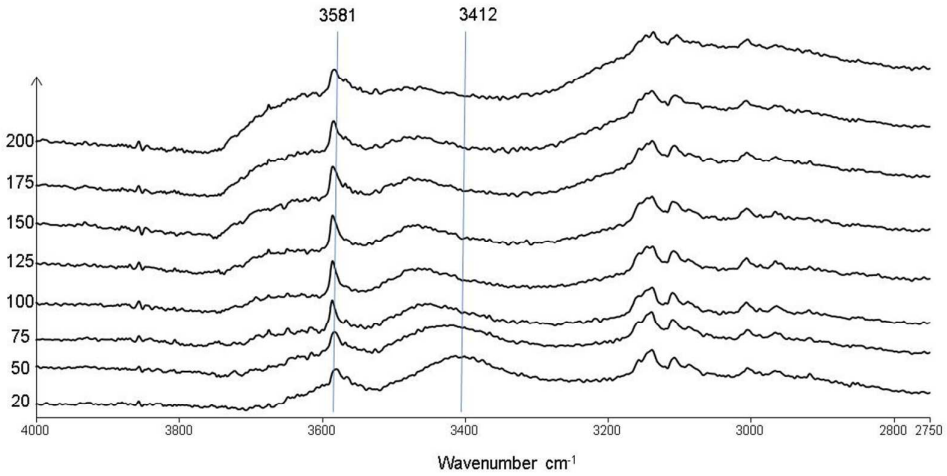

Figure S5e: Evolution of the in situ IR spectra of $(UO_2)_3O(OH)_3(imdc)\cdot 2H_2O$ (**4**) between 20-200°C in the range 4000-2750 cm^{-1}.

Table S2: Comparison of U=O bond distance calculated from the position of $\nu_{asym(U=O)}$ vibration and the crystal structure data.

Phase	$\nu_{asym(U=O)}$	Distance U=O	
		Exp.	Calc.*
1	923	1.73-1.77	1.76
2	903	1.79-1.80	1.78
3	918	1.76-1.78	1.77

*after J.R. Bartlett, R.P. Cooney, J. Mol. Struct. 193 (1989) 295.

Table S3: Positions of the bands (in nm – top – and cm^{-1} – bottom –) in the fluorescence spectra of compounds **1**, **2** & **4**.

Sample					
1	490.5 20408	511 19569	533 18762	558 17921	585 17094
2	494 20243	514.5 19455	537.5 18622	561.5 17825	589 16978
4	/	520 (s) 19231	535(max) 18692	558 (s) 17921	585 (s) 17094

(s) shoulder