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Journal Name

ARTICLE

Inducing selectivity and chirality in group IV metal coordination with high-denticity hydroxypyridinones

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Supporting information

Table S 1. List of stability constants used for data treatment of the metal-competition batch titrations.

Species	Formation constant (log β_{MLH})	Reference
H_{-1}	-13.77	NIST critical database
$[ZrH_{-1}]^{3+}$	1.03	NIST critical database
$[ZrH_{-5}]^{-}$	-14.85	NIST critical database
$[ZrCl]^{3+}$	0.20	NIST critical database
$[HfH_{-1}]^{3+}$	0.83	NIST critical database
$[HfH_{-5}]^{-}$	-16.05	NIST critical database
$[HfCl]^{3+}$	0.34	NIST critical database
$[H343HOPO]^{3-}$	6.64	Abergel et al. 2009 (Inorganic Chemistry)
$[H_2343HOPO]^{2-}$	12.32	Abergel et al. 2009 (Inorganic Chemistry)
$[H_3343HOPO]^{-}$	17.33	Abergel et al. 2009 (Inorganic Chemistry)
$[H_4343HOPO]$	21.2	Abergel et al. 2009 (Inorganic Chemistry)
$[Zr343HOPO]$	43.1	Sturzbecher-Hoehne et al. 2015 (Inorganic Chemistry)

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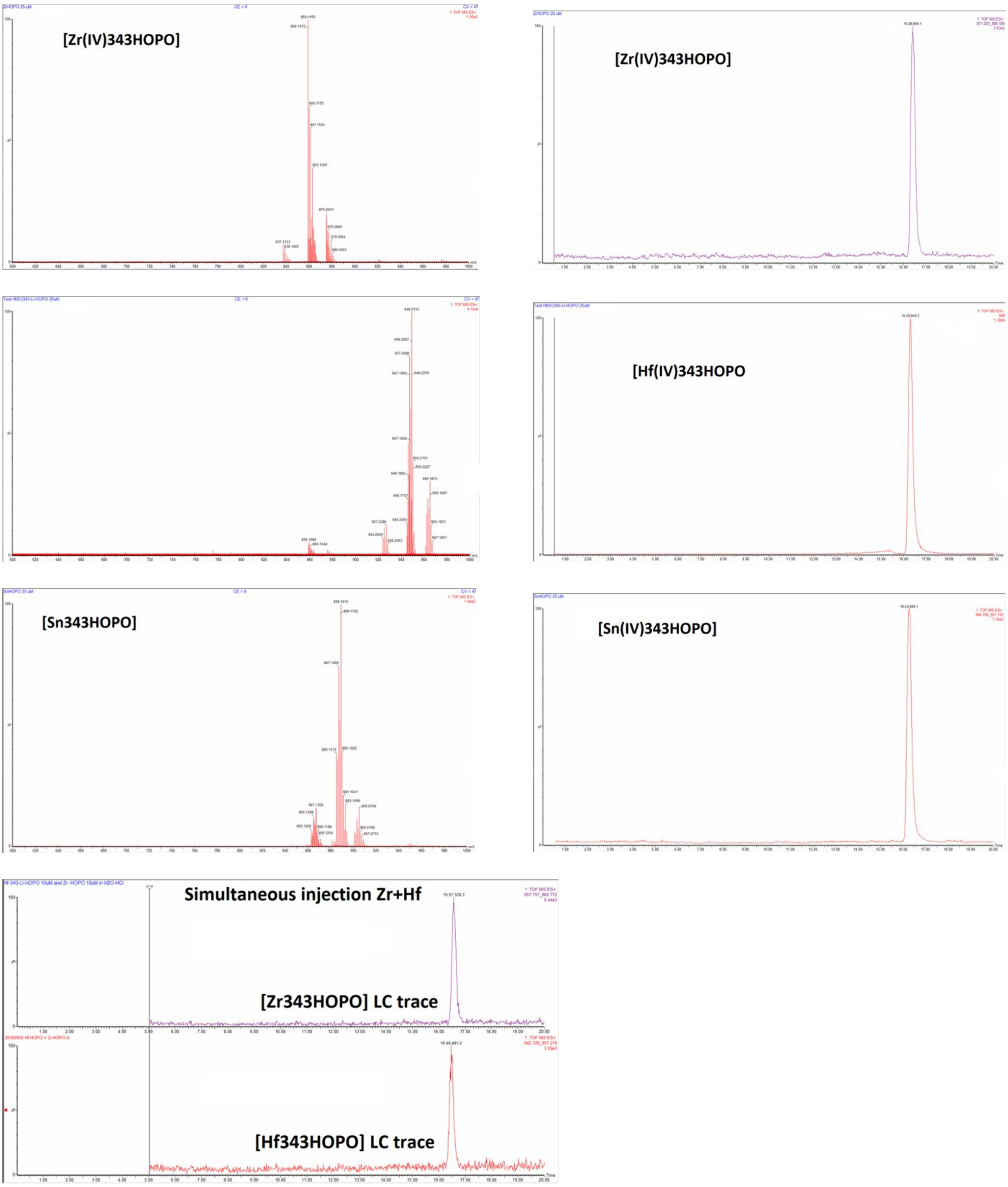

Figure S1. ESI-MS spectra (left) and chromatogram (right) of [Zr^{IV}343HOPO] (top), [Hf^{IV}343HOPO] (middle), and [Sn^{IV}343HOPO] (bottom) samples. Positive mode. [343HOPO] = [M] = 25 µM. Chromatogram of a sample containing simultaneously 10 µM of [Zr343HOPO] and 10 µM of [Hf343HOPO] is also included. These results confirm that the Hf complex exhibits higher polarity compared to its Zr analogue.

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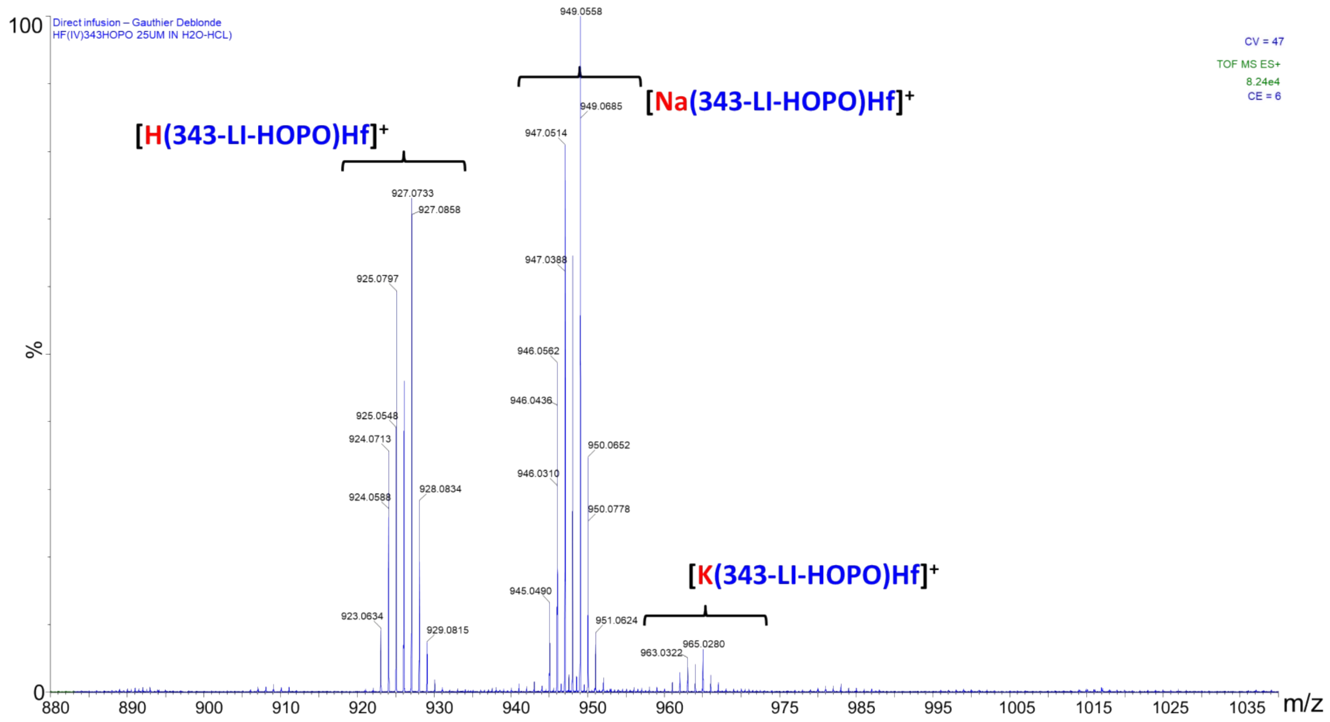

Figure S2. High resolution mass spectrum of an aqueous solution containing 1 equivalent of $HfCl_4$ and 1 equivalent of 343HOPO. [Hf] = [343HOPO] = 25 µM. The isotopic distribution matches that expected for Hf complexes. Media: 0.5% formic acid in water. Electrospray ionization, positive mode.

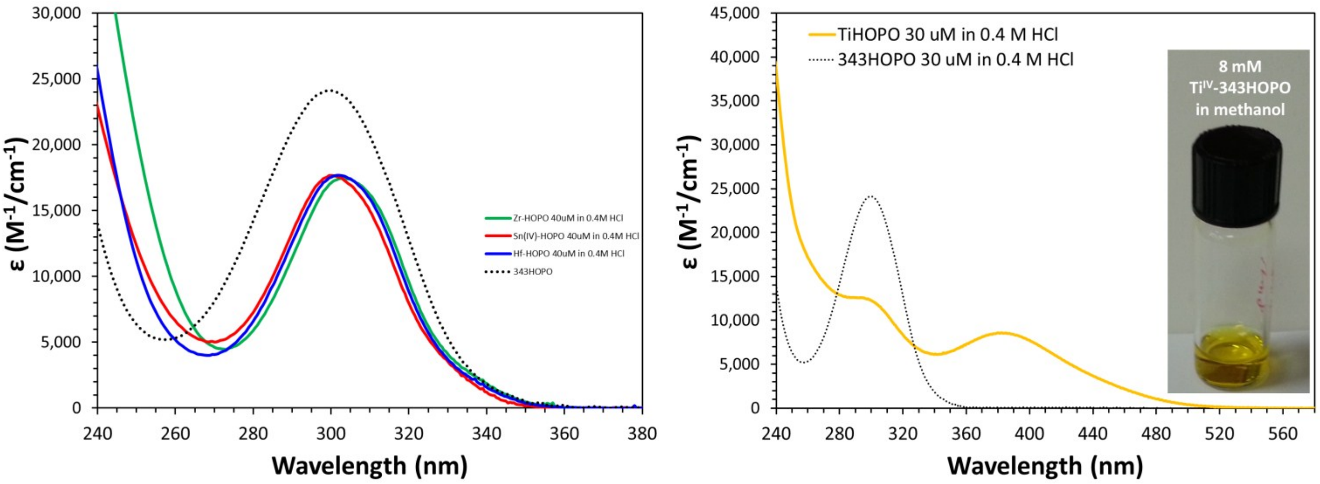

Figure S3. Left: Comparison of the extinction coefficient (ε) of 343HOPO complexes with tetravalent tin (red), zirconium (green), and hafnium (blue). Extinction coefficient of the fee ligand is also given for comparison (dotted line). Matrix: 0.4 M HCl. **Right:** Extinction coefficient of the Ti(IV) complex of 343HOPO. Matrix: 0.4 M HCl. Inset: Picture of a sample containing 8 mM of Ti^{IV}-343HOPO in methanol. The initial 343HOPO and $TiCl_4$ stock solutions are uncolored whereas the metal-ligand species are golden.

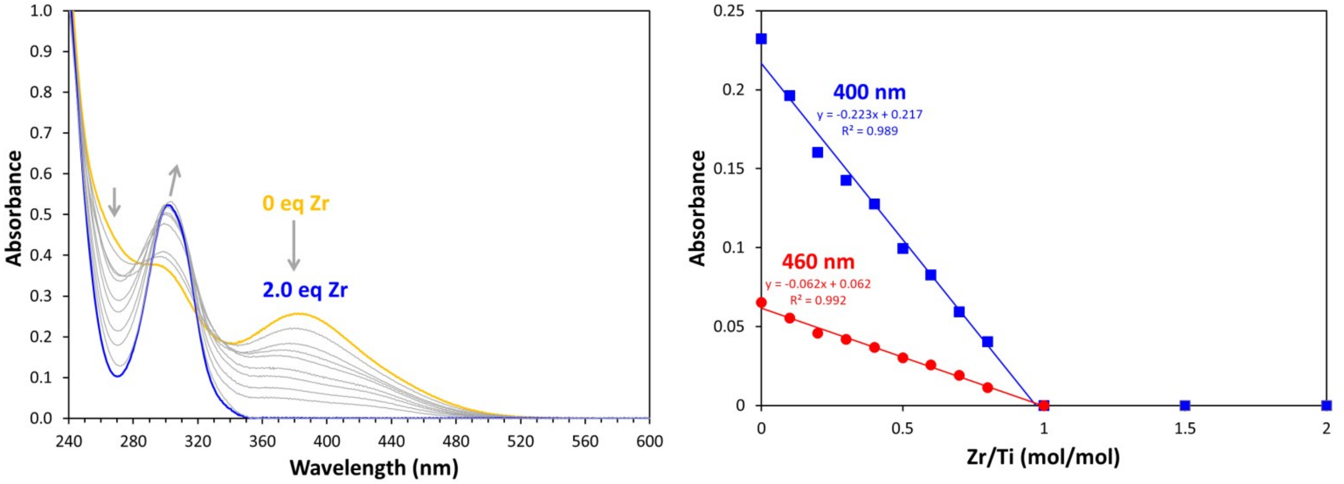

Figure S4. Left: Spectrophotometric batch titration of Ti-HOPO against Zr(IV). The results show that the Ti(IV) complex is much weaker than its Zr(IV) counterpart and that the metal exchange reaction is total. **Right:** Evolution of the absorbance at 400 nm (blue) and 460 nm (red) as a function of the ratio $[Zr]_{total}/[Ti]_{total}$. [343HOPO] = [Ti] = 30 µM. Media: 0.4 M HCl. T = 25°C. Path length = 1 cm.

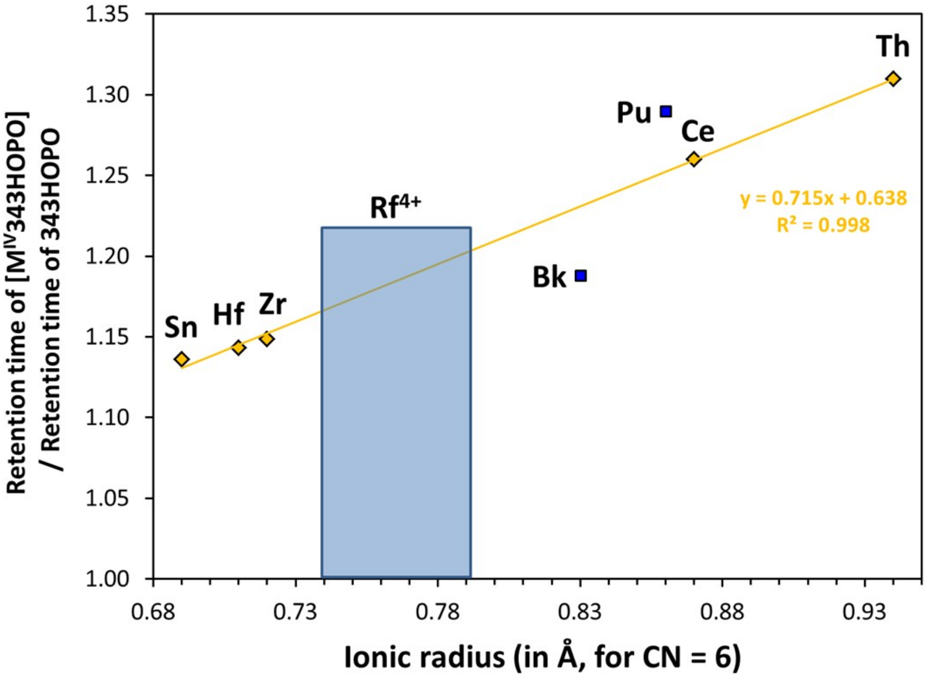

Figure S5. Experimental retention times of the M(IV) complexes of 343HOPO relative to the retention time of the free ligand as a function of the ionic radius of the cations (Coordination number of 6). C18 column. The blue rectangle indicates the predicted zone for the corresponding Rf(IV) complex.

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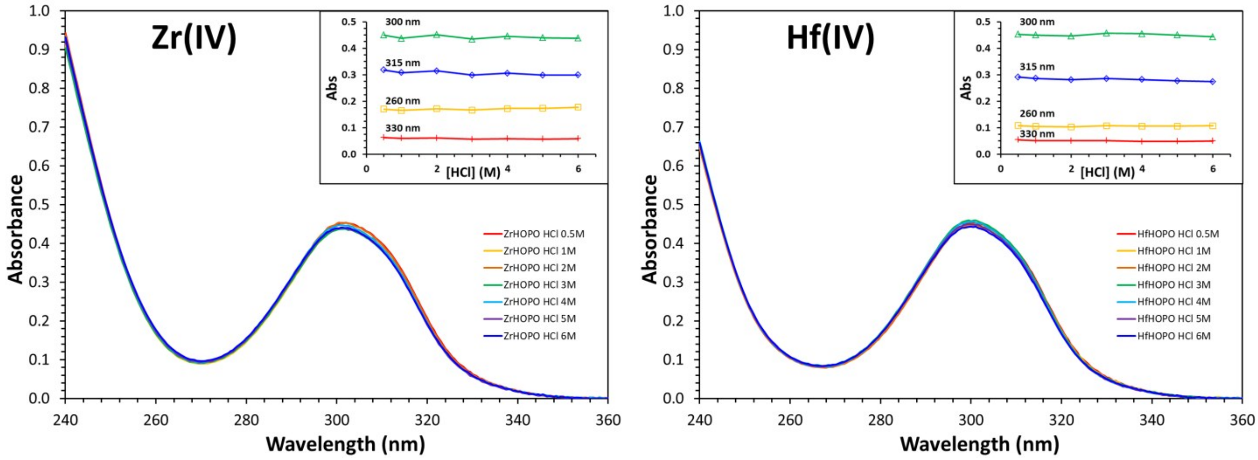

Figure S6. Spectra of Zr-343HOPO and Hf-343HOPO in concentrated HCl solution (0.5 to 6.0 M). UV-vis spectra of concentrated HCl solutions (0.5 to 6 M) containing the Zr^{IV}-343HOPO and Hf^{IV}-343HOPO complexes. [Metal] = [343HOPO]. The results show formation of stable complexes throughout the acidity range tested. Insets: Absorbance at 260 (squares), 300 (triangles), 315 (diamonds) and 330 (crosses), and 400 nm (stars) as a function of the HCl concentration. See Fig. 4 for additional details. Path length = 1 cm.

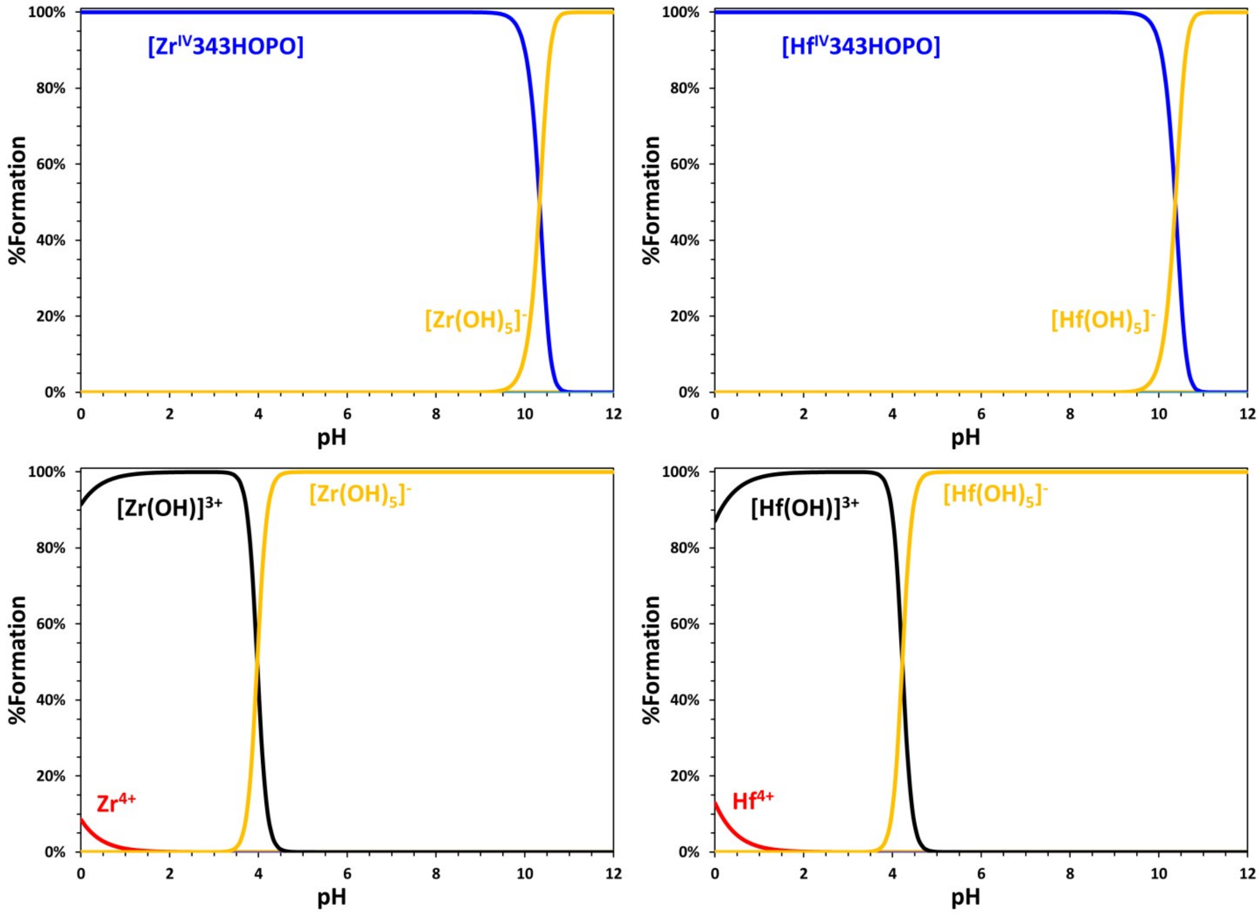

Figure S7. Speciation diagram for Zr(IV) (left) and Hf(IV) (right) in the absence (bottom) or presence (top) of 1 equivalent ([M]= [343HOPO] = 1 µM) of 343HOPO. For homogeneity, both sets of hydroxide species stability constants were taken from the NIST critical database.

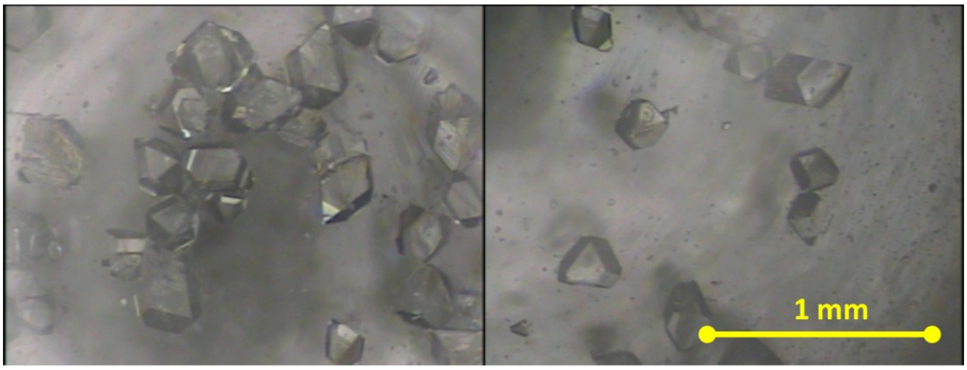

Figure S8. Pictures of crystals of Hf(IV)3,4,3-LI(1,2-HOPO) taken with an optical microscope.

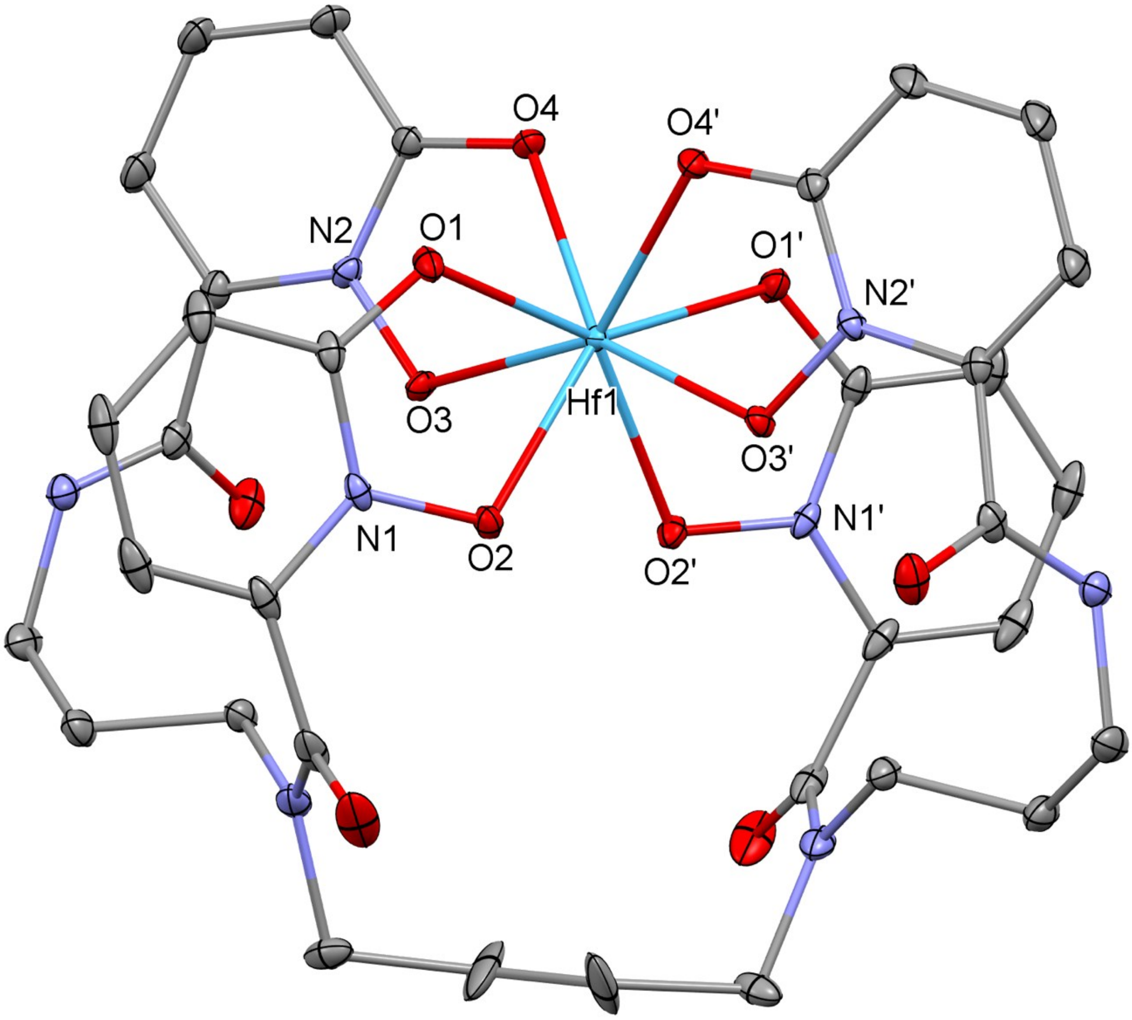

Figure S9. Ellipsoid plot of the Hf(IV)3,4,3-LI(1,2-HOPO) structure.

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