Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Atomic / Molecular Layer Deposition of Cerium (III) Hybrid Thin Films using Rigid Organic Precursors

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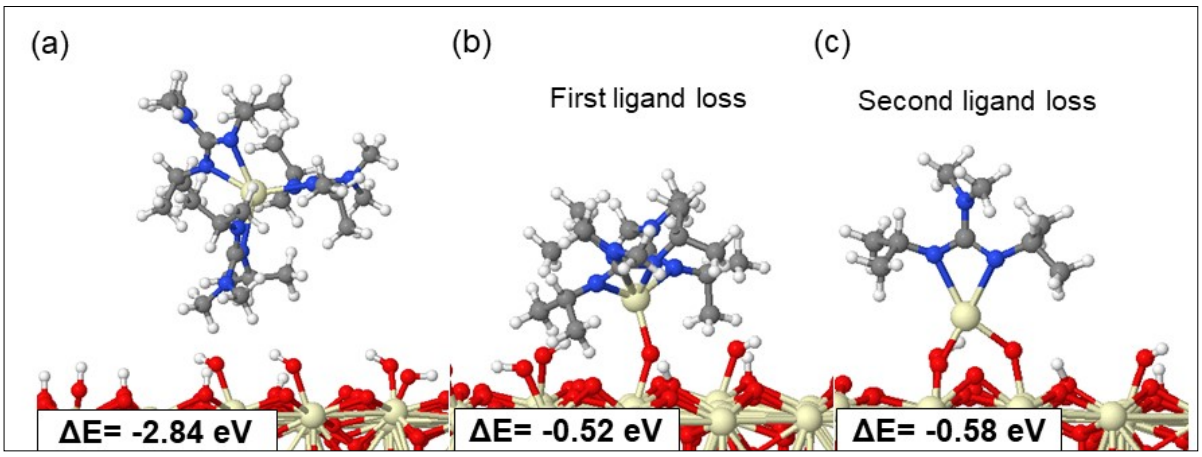

Figure S1 Atomic structure of the hydroxylated CeO_2 surface after (a) adsorption of $[Ce(dpdmg)_3]$, (b) elimination of the first dpdmg ligand and (c) elimination of the second dpdmg ligand.

The computed interaction energy of the $[Ce(dpdmg)_3]$ precursor on the hydroxylated CeO_2 surface is −2.84 eV. The large exothermic interaction energy suggests a favourable interaction of $[Ce(dpdmg)_3]$ with the surface.

The first and second ligand loss reactions of the $[Ce(dpdmg)_3]$ precursor were further investigated. During the first ligand loss reaction, one proton transfers from one OH surface group to the dpdmg ligand and forms a protonated molecule H-dpdmg, that is released as a by-product. The Ce atom of the $[Ce(dpdmg)_3]$ molecule binds to the surface oxygen from which the proton migrates, with a Ce-O distance of 1.93 Å. The calculated change in energy for the first ligand loss reaction is -0.52 eV, giving an overall change of -3.36 eV.

In the second ligand loss reaction, a second proton transfers from a surface OH group to the second dpdmg ligand to form a new H-dpdmg molecule while the Ce atom binds to the surface oxygen with an Ce-O distance of 1.95 Å. The change in energy for the second ligand loss reaction is -0.58 eV, giving an overall energy gain of -4.94 eV. The calculated energies show that the ligand loss reactions of the $[Ce(dpdmg)_3]$ precursor on the hydroxylated surface are favourable.

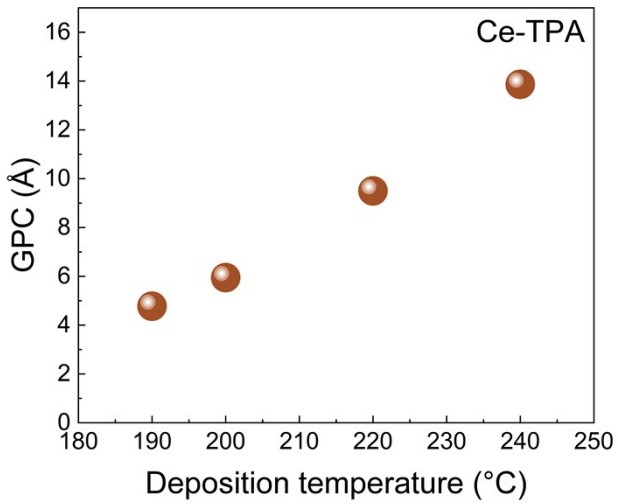

Figure S2 GPC as a function of deposition temperature Ce-TPA hybrid thin films

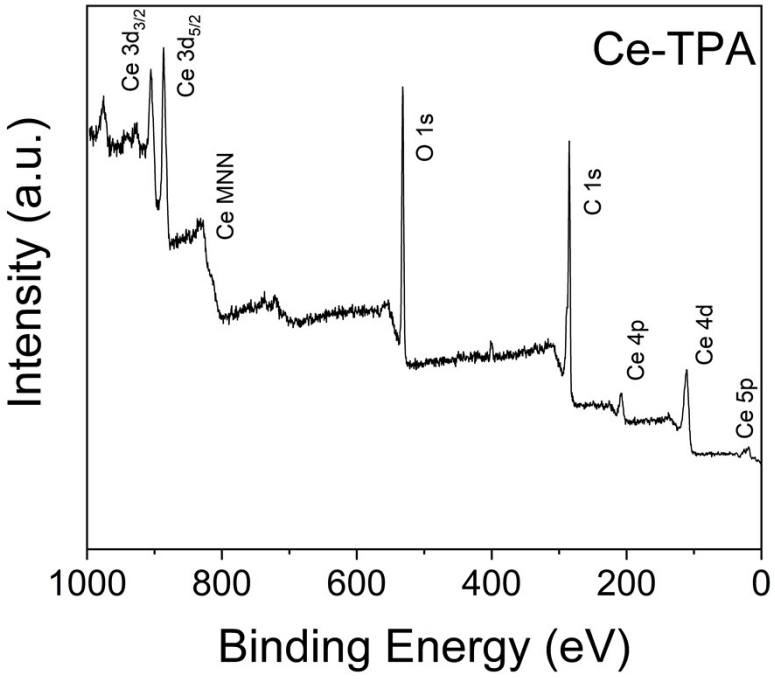

Figure S3 XPS survey spectrum of Ce-TPA hybrid thin films deposited on Si(100) at 200°C

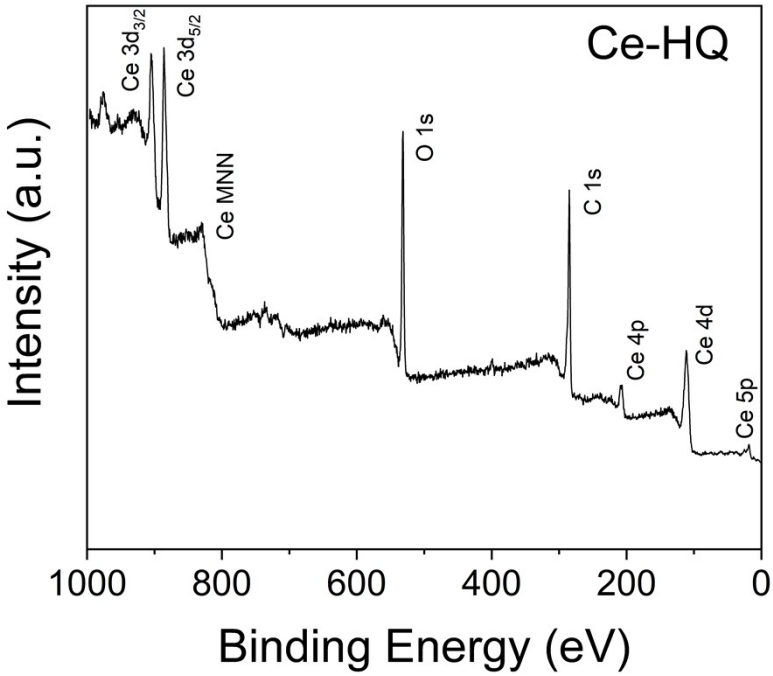

Figure S4 XPS survey spectrum of Ce-HQ hybrid thin films deposited on Si(100) at 200°C

Table S1 Experimental vs calculated composition analysis of the hybrid films.

	Ce (at.%)	Calc. Ce (at.%)	O (at.%)	Calc. O (at.%)	C (at.%)	Calc. C (at.%)
Ce-TPA	6.6	7.7	25.5	23.1	67.9	69.2
Ce-HQ	5.1	5.3	24.4	31.6	70.5	63.2