

Electronic supplementary Information

Preparative and Instrumental details:

[Hf(¹PrNC(O)O¹Pr)₄] (**1**) was synthesized by reacting [Hf(O¹Pr)₄] (2.4 mmol, 1 g) in 30 mL hexane with 0.95 ml (9.6 mmol) isopropylisocyanate in 30 mL of hexane at room temperature. After stirring over night at room temperature, volume of the solution was reduced to 10 mL and kept at room temperature for crystallization. Crystals suitable for single crystal X-ray diffraction studies were obtained after 2 days. Yield: 1.6 g (88 %); mp (uncorrected): 108-111 °C; anal. calcd. for C₂₈H₅₆HfN₄O₈, C: 44.53; H: 7.47; N: 7.42; found: C: 43.92; H: 7.70; N: 7.38%; ¹H NMR: (room temperature, 250 MHz, C₆D₆): 1.53 (24H, d, C(CH₃)₂, ¹J = 6.25 Hz) 1.41 (24H, d, CH(CH₃)₂, ¹J = 6.50 Hz), 4.16 (4H, sep, CH(CH₃)₂, ¹J = 6.50 Hz), 5.18 (4H, sept., CH(CH₃)₂, ¹J = 6.25 Hz). ¹³C NMR: (RT, 62.5 MHz, C₆D₆): 22.69 (CH₃ (N¹Pr)), 23.71 (CH₃ (O¹Pr)), 45.50 (CH (N¹Pr)), 68.66 (CH (O¹Pr)), 165.22 (NCO). EI-mass spectrum (70 eV): 757, <1%, [HfL₄]⁺ (molecular ion); 669, 2%, [HfL₃(N¹Pr)]⁺; 527, <1%, [Hf(HNCOO¹Pr)₃(NCO)]⁺; 500, <1%, [Hf(HNCOO¹Pr)₃N]⁺; 486, 9%, [Hf(HNCOO¹Pr)₃]⁺; 442, 18%, [Hf(HNCOO¹Pr)₂(HNCOOH)]⁺; 401, 100%, [Hf(HNCOO¹Pr)(HNCOOH)₂]⁺; 357, 42%, [Hf(HNCOO)₃]⁺. Compound [Hf(¹PrNC(O)N(Me)Et)₄] (**2**) was synthesized very similar to compound **1** with the yield of 84 %. mp (uncorrected): 79-80 °C. anal. calcd. for C₂₈H₆₀HfN₈O₄, C: 44.76; H: 8.05; N: 14.91; found: C: 43.91; H: 8.33; N: 14.19%. ¹H NMR (room temperature, 250 MHz, C₆D₆): 0.97 (12H, t, CH₃CH₂, ¹J = 7.00 Hz), 1.50 (24H, d, CH(CH₃)₂, ¹J = 6.50 Hz), 2.70 (12H, s, N(CH₃)), 3.18 (8H, qua, CH₂CH₃, ¹J = 7.00 Hz), 4.05 (4H, sep, CH(CH₃)₂, ¹J = 6.50 Hz). ¹³C NMR: (RT, 62.5 MHz, C₆D₆): 13.64 (CH₃(Et)), 24.65 (CH₃(¹Pr)), 35.84 (N(CH₃)), 45.36 (CH(¹Pr)), 46.43 (CH₂(Et)), 167.66 (NCO). EI-mass spectrum (70 eV): 752, <1%, [HfL₄, molecular ion]⁺; 666, <1%, [HfL₃(N(Et)Me)]⁺; 651, <1%, [HfL₃(NEt)]⁺; 609, 100%, [HfL₃]⁺; 524, 74%, [HfL₂(NMeEt)]⁺; 467, 5%, [HfL₂]⁺; 382, 7%, [HfL(NEtMe)]⁺; 324, 3% [HfL]⁺.

Single crystal X-ray diffraction: data collection for both compounds was performed on a Oxford Xcalibur 2 diffractometer, equipped with a cryogenic nitrogen cold stream and using graphite monochromated Mo-K α radiation (0.71073 Å). The structures were solved by direct methods and refined anisotropically with SHELXL-97 program suite. Thermal analysis was carried out using a Seiko TG/DTA 6300S11 in nitrogen atmosphere (300 mL min⁻¹, sample weight ~ 10 mg, ambient pressure, RT-600 °C, heating rate of 5 °C min⁻¹). Film depositions were performed in self-built horizontal cold wall CVD reactor operating at reduced pressure. The deposition conditions employed were: substrate temperature 250-700 °C, vaporization temperature 100 °C, reactor pressure 1.0 mbar, N₂ and O₂ flow of 50 sccm. Films were deposited on p-type silicon (100) wafers. Film thickness was calculated from cross section SEM and RBS analysis. The XRD data were collected using D8-Advance Bruker AXS diffractometer. The samples were measured in Bragg-Brentano geometry. The phase composition was verified by the match search in the International Centre for Diffraction Data (ICDD, PDF-2 Release 2004) database. Film composition was analyzed by employing energy dispersive analysis of X-ray (EDX). The XPS spectrum was recorded on a Perkin Elmer Φ 5600ci spectrometer at a pressure lower than 10⁻⁹ mbar, using a monochromatized AlK α excitation source (1486.6 eV). The spectrometer was calibrated by assigning to the Au 4f_{7/2} line the Binding Energy (BE) of 84.0 eV with respect to the Fermi level. The BE shifts were corrected assigning to the C 1s line of adventitious carbon a value of 284.8 eV. The estimated standard deviation for BEs was \pm 0.2 eV. The atomic compositions were evaluated using sensitivity factors provided by Φ V5.4A software. In order to obtain a more accurate evaluation of atomic percentages, the Hf 4d signal was used in the quantization instead of the more intense Hf 4f photopeak, due to its appreciable BE difference with respect to the O and C peaks. This feature would imply the analysis of photoelectrons with different escape depths, yielding thus to an uncorrected estimation. Ar⁺ sputtering was carried out for 10' at 3.5 kV and 0.5 mA cm⁻² beam current density, with an argon partial pressure of 5 x 10⁻⁸ mbar. The samples were introduced directly into the analysis chamber by a fast entry lock system. Rutherford backscattering (RBS) measurements (to determine the film thickness and composition) were carried out with a 2-MeV He beam of the Dynamitron-Tandem accelerator in Bochum with beam intensities of about 10 nA. A silicon surface barrier detector with an energy resolution of 15 keV was placed at an angle of 170° with respect to the beam axis. The spectra were analyzed with the program *RBS* using the stopping powers of the program *SRIM* [A. Milanov, R. Bhakta, A. Baunemann, H. -W. Becker, R. Thomas, P. Ehrhart, M. Winter and A. Devi, *Inorg. Chem.*, 2006, **45**, 11008].

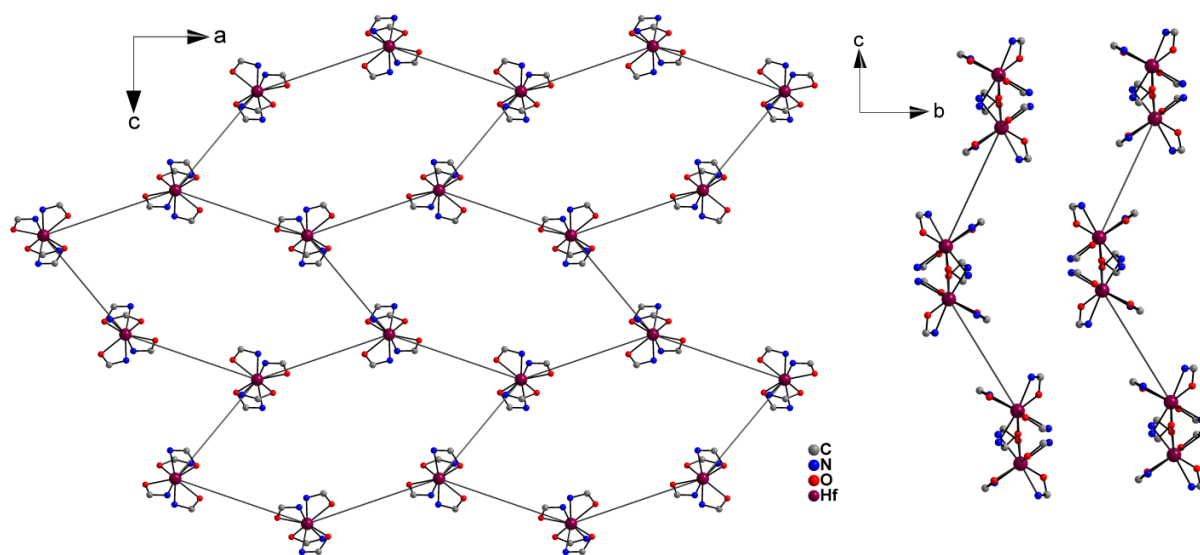


Fig. S1 Packing diagram of [Hf(¹PrNC(O)O¹Pr)₄] (**1**) (substituents on metallocycles are omitted for clarity).

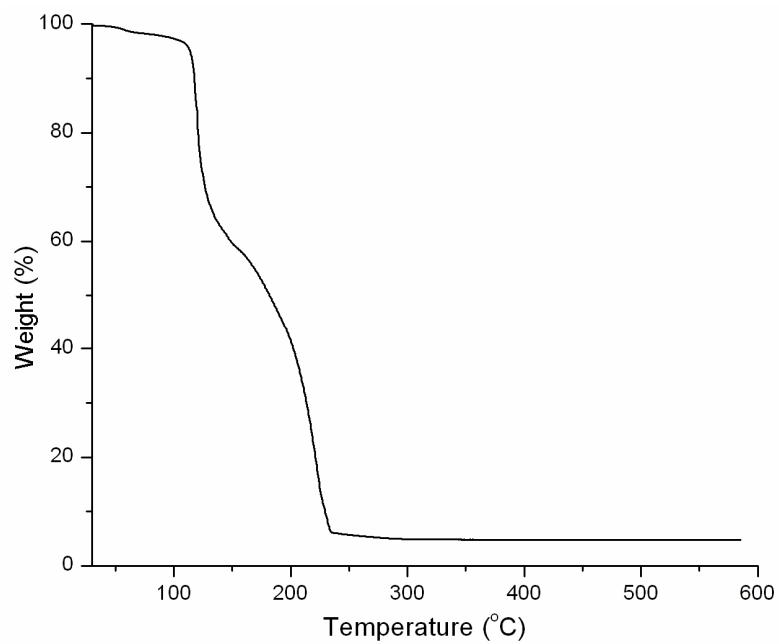


Fig. S2 TG plot of $[\text{Hf}(\text{iPr})\text{NC}(\text{O})\text{O}(\text{iPr})_4]$ (1).

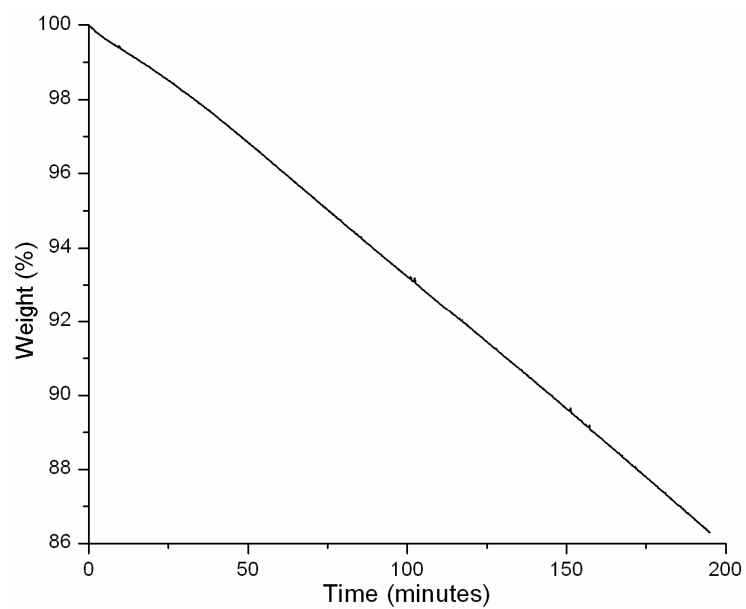


Fig. S3 Isothermal plot of $[\text{Hf}(\text{iPr})\text{NC}(\text{O})\text{O}(\text{iPr})_4]$ (1) at 80 °C.

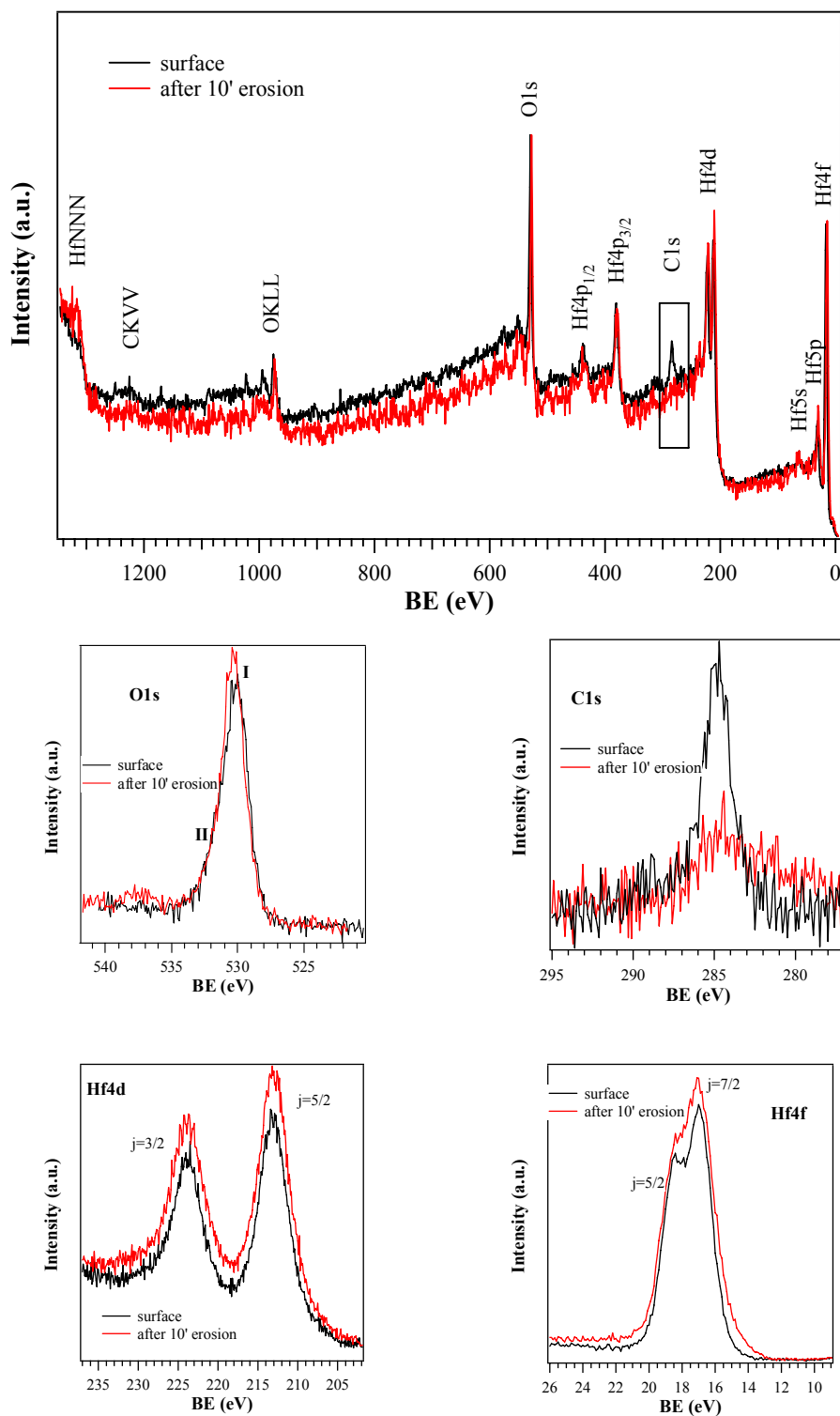


Fig. S4 X-ray photoelectron spectrum (top) and its expansion of film obtained from $[\text{Hf}(\text{}^1\text{PrNC}(\text{O})\text{O}^1\text{Pr})_4]$ (**1**) at 600 °C.

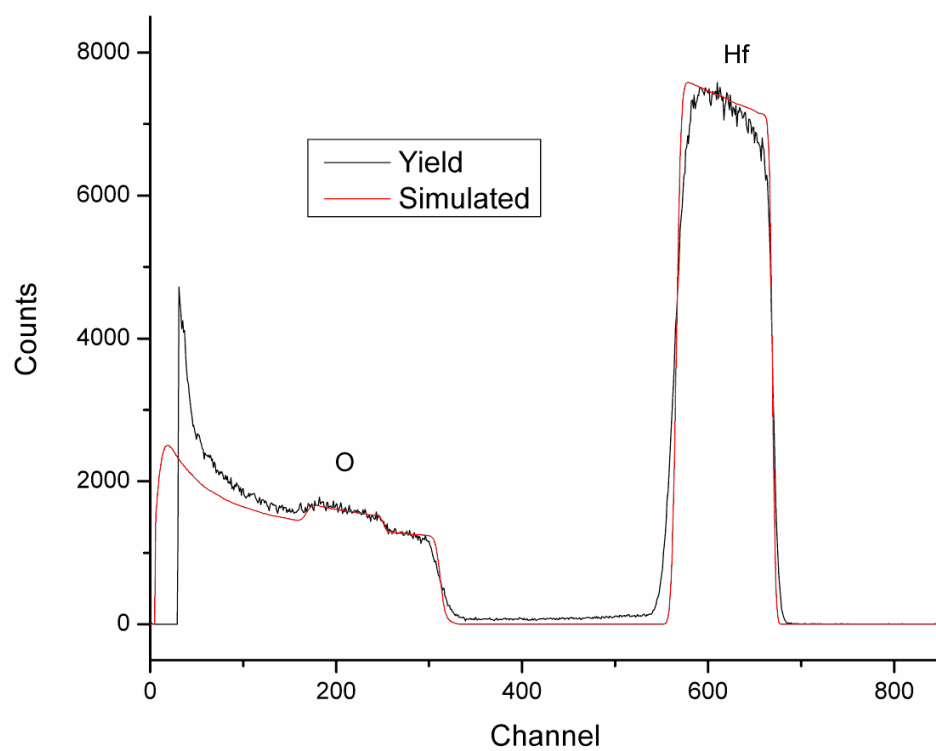


Fig. S5 RBS spectrum of a HfO₂ film grown on Si(100) at 500 °C.