Published in final edited form as:

Eur J Inorg Chem. 2009 June 1; 2009(17): 2459–2466. doi:10.1002/ejic.200900284.

Ternary Porphyrinato Hf(IV) and Zr(IV) - Polyoxometalate Complexes

Alexander Falber^a, Benjamin P. Burton-Pye^a, Ivana Radivojevic^a, Louis Todaro^a, Raihan Saleh^a, Lynn Francesconi^a, and Charles Michael Drain^{a,b,*}

^aDepartment of Chemistry and Biochemistry, Hunter College and Graduate Centre of the City University of New York, 695 park Avenue, New York, NY 10065

^bThe Rockefeller University, 1230 York Avenue, New York, NY 10065

Abstract

We report a facile, high yield synthesis and characterization of discrete, ternary porphyrin-metal-polyoxometalate (Por-M-POM) complexes where a group (IV) transition metal ion is bound both to the porphyrin core and to the lacunary site of a Keggin POM, $PW_{11}O_{39}^{-7}$. The remarkably robust complexes exploit the fact that Hf(IV) and Zr(IV) are 7–8 coordinate and reside outside the plane of the porphyrin macrocycle, thus enabling the simultaneous coordination to meso-tetraphenylporphyrin (TPP) or meso-tetra(4-pyridyl)porphyrin (TPyP) and to the defect site in the Keggin framework. The physical properties of the (TPP)Hf($PW_{11}O_{39}$)[TBA]₅, (TPyP)Hf($PW_{11}O_{39}$)[TBA]₅, and (TPP)Zr($PW_{11}O_{39}$)[TBA]₅ complexes are similar because the metal ions have similar oxidation states, and coordination chemistry.

This architecture couples the photonic properties of the porphyrin to the POM because the metal ion is incorporated into both frameworks. Thus the ternary complexes can serve as a basis for the characterization of Hf(IV) and Zr(IV) porphyrins bound to oxide surfaces via the group (IV) metal ions. The Hf(Por) and Zr(Por) bind strongly to TiO₂ nanoparticles and indium tin oxide (ITO) surfaces, but significantly less binds to crystalline SiO₂ or TiO₂ surfaces. Together, the strong binding of the metalloporphyrins to the POM, nanoparticles, and the ITO surfaces, and paucity of binding to crystalline surfaces, suggests that the 3–4 open coordination sites on the Hf(Por) and Zr(Por) are predominantly bound at surface defect sites.

Keywords

porphyrinoids; polyoxometalate; photochemistry; nanostructures

© WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009

Fax: 212-772-5332, cdrain@hunter.cuny.edu .

Dedicated to Professors Joyce Y. Corey and Lawrence Barton on the occasion of their retirement from the University of Missouri at St. Louis

Supporting information for this article is available on the WWW under <http://www.eurjic.org/> or from the author.

Supporting Information: Further experimental details; UV-visible, IR, and ¹H, COSY, and ³¹P NMR spectra; mass spectrometry; structures with solvent molecules included and crystallographic information files (CIF); and a scheme with hypothesized binding of the Hf and Zr porphyrins to a TiO₂ surface. CCDC- 717412 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Introduction

Polyoxometalates (POMs) and porphyrins (Por) are widely studied as components of functional materials, such as catalysts and photonics, because each possesses enormous potential for structural variation and tuning of their electronic properties. Porphyrins^{1–6} and POMs^{7–12} have been investigated for applications such as photovoltaics and supramolecular materials. There are numerous reports on the adsorption or attachment of porphyrins to a variety of surfaces using exocyclic motifs with a moiety designed to bond to the surface and a linker intervening between the macrocycle and the surface.^{13–20} There are numerous supramolecular constructs of porphyrins and electron acceptor species such as C₆₀.^{21–26} In addition to POMs being good electron acceptors, in many ways the diverse photochemical, and coordination chemistry of porphyrins and POMs are complementary; therefore, robust complexes that photonically couple porphyrins and POMs should have unique properties. There are reports of films and other materials wherein cationic porphyrins and POMs are mixed²⁷ e.g. for catalysis,²⁸ an axially bound POM counterion on Mo(V)Por,²⁹ two metalloporphyrins bridged by a POM bearing two nicotinamide moieties coordinated to the metal centre,³⁰ and other porphyrin – POM structures,^{31–33} but here we describe discrete ternary systems wherein a central metal ion is coordinated to *both* the Por and a *defect* site in the lacunary POM. Previously, Keggin structures have been functionalized with cyclopentadienyl ligands at the lacunary site through Ti(IV), Zr(IV), and/or Hf(IV) metal ions.^{9·34·35} The recent report on the formation of Hf(Por) dimers bridged by oxo ligands such as sulfate, phosphate, and peroxide indicates that multitopic counter ions may serve as tectons to construct arrays of group four metalloporphyrins.³⁶

The three complexes reported herein are made in high yields from previously reported Zr(IV) and Hf(IV) porphyrinates³⁷ and the lacunary POM,¹¹ H₃PW₁₁O₃₉^{4–} (Scheme 1): (TPP)Hf(PW₁₁O₃₉)[TBA]₅, **1**, (TPyP)Hf(PW₁₁O₃₉)[TBA]₅, **2**, and (TPP)Zr(PW₁₁O₃₉)[TBA]₅ **3**. In contrast to the aforementioned systems, this nanoarchitecture enables photonic coupling of the two chelates mediated by the central metal ion. Since the chemistry of Zr(IV) is generally similar to Hf(IV), the significantly greater natural abundance of Zr may make Zr(Por) materials more cost effective if the functional properties are competitive.

Since POMs are often regarded as good models for defect sites in oxide surfaces,¹¹ the crystal structure and physical properties of these ternary complexes suggested to us that one way to self-organize porphyrins onto oxide surfaces such that the photonic properties of the macrocycles are strongly coupled to the semiconductor is to use porphyrins coordinated to oxophilic group IV metals such as Hf, Zr. Indeed, when a variety of oxide particles, such as silica gel,³⁶ ITO or TiO₂, are exposed to a solution containing the (Por)Hf(L)₂ or (Por)Zr(L)₂, where L = acetate or chloride, the spectroscopic signatures are observed to be similar to those of compounds **1–3**. While these group (IV) metalloporphyrins are strongly bound to the nanostructured surfaces, both scanning probe and reflectance data find a paucity of the complexes bound to crystalline TiO₂ and SiO₂ surfaces. Together, these data suggest that the 3–4 open metal ion coordination sites of the Hf(Por)²⁺ and Zr(Por)²⁺ are bound primarily to surface defect sites by displacement of the auxiliary acetate or chloride ligands.

Results and Discussion

Synthesis

Slowly adding a stoichiometric amount of the POM to solutions of the (Por)Hf(OAc)₂ or (Por)Zr(OAc)₂³⁷ affords the Por-M-POM complexes by displacement of the acetate ligands by the lacunary oxygens of the H₃PW₁₁O₃₉[TBA]₄. Since the acidic protons from the POM can cause some demetalation of the porphyrin, the reaction must be buffered by a base such as triethylamine. In addition, the formal charge of the ternary complex is –5 requiring one additional equivalent of [TBA]Br to be added to the mixture to yield the neutral (Por)Hf

(PW₁₁O₃₉)[TBA]₅ or (Por)Zr(PW₁₁O₃₉)[TBA]₅ complexes. The chelating effect of the four oxygens on the POM to the oxophilic Hf(IV) or Zr(IV) centers is strong, such that addition of more than one equivalent of POM can lead to porphyrin demetalation of the Hf complexes; most likely leading to the Hf(PW₁₁O₃₉)³⁻ or the corresponding dimer Hf(PW₁₁O₃₉)₂¹⁰⁻ complexes. Lacunary POMs chelated to lanthanide and group(IV) metal ions have been reported³⁸⁻⁴¹ (see supporting information). The (TPyP)Hf(PW₁₁O₃₉)⁵⁻ complex is somewhat more stable than the (TPP)Hf(PW₁₁O₃₉)⁵⁻ complex possibly due to electronic differences in the macrocycle or buffering effects of pyridyl substituents.

Characterization

The formation of complexes **1** – **3** was monitored by UV-visible absorption spectra of the porphyrinate portion of the complex, *vide infra*. Both the Soret and Q-band regions of the spectra display significant red shifts as the reaction progresses. The Soret bands at 412 nm and 414 nm for the (TPP)Hf(OAc)₂ and (TPyP)Hf(OAc)₂ complexes shift to 425 nm and 426 nm for the ternary complexes, respectively, while the major Q-band near 540 nm shifts to 550 nm and 548 nm. Similarly, the Soret band of (TPP)Zr(OAc)₂ is at 416 nm, while for compound **3** it is at 427 nm. As indicated by the NMR and crystal structure data, the red-shifts arise from three interrelated effects: (a) a structural distortion in the porphyrin macrocycle,⁴² (b) increasing N-Hf bond lengths, and (c) concomitant electronic coupling of the metalloporphyrin to the POM mediated by the group IV metal ion.⁴³ The POM encompasses a large portion of hafnium coordination sphere, drawing the metal centre away from the porphyrin and sterically crowding the macrocycle (*vide infra*). Neither films formed by sequential dipping of these surfaces into solutions of the POM and cationic porphyrins, nor the axial coordinated porphyrin/POM materials exhibit substantial spectral changes relative to the metalloporphyrins.^{27,29}

The ¹H NMR spectra of **1** and **3** (Figure 1, see supporting information for **2**) are highly diagnostic compared to the (Por)M(OAc)₂ starting complexes (M= Hf or Zr). Proton assignments were confirmed by COSY 2D spectra and comparison of data between the three complexes. For the starting (Por)M(OAc)₂ complexes, and for the ternary complexes **1** – **3**, the *ortho* and *meta* ¹H- NMR resonances on each phenyl substituent are not equivalent due to the asymmetry caused by the out-of-plane M(IV) ion binding. For complexes **1** – **3** there is a non-parallel geometry between the porphyrin macrocycle and the mean O₄-plane of the POM lacunary oxygens (see crystallographic analysis), further segregating the phenyl substituents into two types: nearer and further from the POM. Thus the four porphyrin phenyl groups display a total of 10 distinct resonances for **1** and **3**, and eight for **2**. This analysis is also supported by the well-resolved resonances for the pyrrole protons. The distortion of the macrocycle is indicated by the large shift of the *ortho* protons on the opposite side of the porphyrin, e.g. the (TPP)Hf(POM) to ca. 9.25 and 9.55 ppm because they are now tilted inward towards the ring current as found with the (Por)M(OAc)₂ starting materials and lanthanide MPor₂ sandwich complexes.^{44,45} The ¹H NMR spectra of the (TPyP)Hf(PW₁₁O₃₉)[TBA]₅ complex is very similar showing eight distinct aryl resonances and four pyrrolic resonances similar to those found with the TPP ternary complex. ³¹P NMR for all three ternary complexes display a singlet peak between –16.20 and –16.30 ppm, which is comparable to the cyclopentadienyl analogue, (cp)Hf(PW₁₁O₃₉)[TBA]₄, which displays a peak at –12.3 ppm.³⁴

The five TBA counterions are cleanly observed in the NMR for all three complexes, as are small quantities of the TEA buffer. The underlying resonances in the phenyl region can be attributed to other conformations of the complexes and are not consistent with starting materials or decomposition. Variable temperature NMR experiments reveal that there are other accessible conformations of the phenyl groups, in the (Por)Zr(PW₁₁O₃₉)[TBA]₅ complex. The phenyl resonances significantly sharpen at elevated temperatures and become more complex

at lower temperatures (35 °C and 0 °C, respectively). The interconversion and equilibria between conformations in distorted metalloporphyrins have been studied,⁴² but the differences seem to be largely relegated to the aryl moieties in this case. Note that since the 3a, 4a, 3b, 4b resonances (Figure 1) are mostly impacted, it is possible that subtle dynamical differences in the tilt toward the macrocycle or the aryl-porphyrin dihedral angle cause the observed spectra. Likely conformational differences based on the crystal structure are not obvious, but local minima in the rotation of the porphyrin relative to the POM seem unlikely.

Crystallography

The x-ray crystal structure of the (TPyP)Hf(PW₁₁O₃₉)⁵⁻ complex was obtained (Figure 2). Only two TBA units are found for every (TPyP)Hf(PW₁₁O₃₉)⁵⁻ which indicates that the charge balance is accounted for, in part, by protonation and/or highly disordered TBA. There are channels with disordered solvent, but the large number of metal atoms and refinement of data from several crystals yields similar results assures the accuracy of the structure of the ternary complex. Formally, the crystal structure is of (TPyP)Hf(PW₁₁O₃₉)[TBA]₂H⁺₃. This protonation may occur on the pyridyl groups themselves acting as a built in buffer system for the acidic complex, and be another reason for the greater stability of the (TPyP)Hf(PW₁₁O₃₉)⁵⁻ complex.

The entire coordination around the hafnium ion assumes an antiprismatic geometry where the N₄ plane of the porphyrin and the O₄ plane of the lacunary site form the two square faces. There is a 3.1° dihedral angle between the mean N₄ and O₄ planes, thus, the porphyrin is tilted towards the POM on one side giving rise to the distinctive ¹H-NMR spectra. The structure of the Hf(TPyP) portion of ternary complex **2** shows that the porphyrin core adopts a saddle type distortion and the four inner pyrrole N-atoms deviate from the C₂₀-macrocycle towards the Hf ion, which lies above it. The distance of the hafnium from the mean N₄-plane is 1.22 Å which is notably longer than the 1.04 Å deviation measured for the (TPyP)Hf(OAc)₂ complex. The average N-Hf bond length is 2.34 Å compared to 2.26 Å for the acetate derivative,⁴⁶ further illustrating the affect of the POM on the hafnium coordination to the porphyrin core. The structure of the PW₁₁O₃₉⁷⁻ portion of the complex is similar to previously reported structures of zirconium and hafnium Keggin and Wells-Dawson POMs.^{34,41} The monovacant POM binds to the hafnium asymmetrically, deviating from the mean O₄-plane by 1.14 Å. The Hf-O bond varies between 2.20 Å and 2.15 Å, which is nearly identical to the reported Hf(PW₁₁O₃₉)₂¹⁰⁻ dimer complex,⁴¹ indicating that the POM lacunary site binds the hafnium ion similarly. There is no detectable structural perturbation in the POM as a result of the adjoining tetrapyrrole system.

The tertiary structure of the (TPyP)Hf(PW₁₁O₃₉)⁵⁻ crystal is comprised of the complex forming zig-zag chains along the *a*-axis where the top surface of one porphyrin approaches the side of the POM of an adjacent complex (Figure 2). The porphyrin core is in line with the hafnium ion of the neighbouring complex at an angle of approximately 78°. The pattern repeats itself every two units along the chain, over a distance of 9.42 Å. When viewing down the *a*-axis, large channels containing disordered solvent, water, and counterions are observed between the chains of ternary complexes. Unexpectedly, there are no direct inter-porphyrin interactions and the organization of the complex in the crystal is mediated by pyridyl H-bonds to water and solvent.

Hf(TPP) and Zr(TPP) on oxide surfaces

Since the POM is a good model of oxide surfaces¹¹ and the exchange of the acetate ligands on the (Por)M(OAc)₂ complexes for the lacunary site on the POM is facile, the protruding Hf(IV) and Zr(IV) ions may be a good way to attach tetraarylporphyrins to oxide surfaces such as ITO, SiO₂, SnO₂, and TiO₂. Using metal ions that protrude from the macrocycle as mode of

chromophores attachment to oxide surfaces is in contrast to the many organic moieties used to tether porphyrins.^{13–20,47,48} The significant changes in the optical spectra (Figure 3) between the (Por)M(OAc)₂ and the ternary complex indicate good electronic coupling between the porphyrin and the POM.⁴⁹ To evaluate surface binding, drop casting or dipping a glass substrate or glass with an ITO coating, with an rms roughness of < 1 nm, results in robust binding of Zr(TPP)²⁺ and Hf(TPP)²⁺ to the surface. The metalloporphyrin does not wash off with vigorous rinsing with toluene or other solvents, but can be removed with alcohols or organic acids, which further indicates binding via the oxophilic metal ions. UV-visible absorption spectra reveal that more of the Zr(TPP)²⁺ and Hf(TPP)²⁺ complexes bind piranha cleaned glass than ozone cleaned glass, because the former leaves more hydroxyl groups on the surface than the latter,⁵⁰ and note they are similar to the ternary complexes (Figure 3).

Stirring a slurry of ca. 5 nm particles of TiO₂ in a 0.5 mM solution of (TPP)M(OAc)₂, or Hf or Zr metalloporphyrin complexes with other anionic ligands such as Cl[−], in dry toluene for a minimum of 2 h effectively binds the chromophore to this material as well (Figures 4). The rate of binding to the surface is proportional to the lability of the auxiliary anionic ligands (Cl[−] > HPO₄^{2−} > OAc[−]). The metalloporphyrin is not removed from the TiO₂ by washing with toluene and the slurries are readily cast onto glass or ITO for analysis. The charge balance can be accommodated by either deprotonation of hydroxyl groups on the surface or the presence of the anionic ligands in the vicinity. After similar incubation of crystalline SiO₂ and TiO₂ surfaces with the Hf(TPP)²⁺ complex and rinsing, very little metalloporphyrin is observed using AFM and UV-visible reflectance. The (TPP)M(POM) ternary complex, the tight binding of the Hf and Zr TPP complexes to nanopowders of silica and TiO₂, the minimal binding to crystalline SiO₂ surfaces, and the results on glass are all indications that Hf(Por) and Zr(Por) prefer to bind to defect sites and those with a greater surface density of hydroxyl groups (see supporting information for a model).

The diffuse reflectance UV-visible spectra of all surface-bound systems are similar to the ternary complexes in solution, but the red shifts in the Soret bands near 410 nm are somewhat less (Figure 3, supporting information). The smaller red shift likely indicates that the group IV metal ion is not pulled out of the macrocycle to the same extent when bound to the surface compared to the POM. This is expected because the lacunary site of the POM is in an optimal geometry for Hf or Zr binding. The broadened optical spectra are typical of surface bound dyes. While the fluorescence intensity of the (Por)Hf(OAc)₂ and (Por)Zr(OAc)₂ is diminished due to the heavy atom effect, it is further quenched in the ternary complexes and when the Zr(TPP)²⁺ and Hf(TPP)²⁺ are bound to the ITO surfaces. The fluorescence is not similarly quenched when the (Por)M complexes are strongly adsorbed to glass. After similar binding and rinsing of the particles, UV-visible reflectance spectra show that free base and Zn(II) TPP adsorb onto these substrate to a much smaller extent but exhibit much greater fluorescence intensities.⁵¹ The widely studied tetracarboxyphenylporphyrin TCPP also remains on the TiO₂. AFM studies of the compound on the ITO do not reveal large aggregates of the metalloporphyrin and a somewhat decreased rms roughness. Since the Zr(TPP)²⁺ and Hf(TPP)²⁺ complexes robustly bind surfaces, likely at defect sites and we remove unbound materials, the surface coverages are much less than coating of porphyrins such as tetracarboxyphenyl derivatives on ITO or TiO₂ surfaces by chemisorption.^{16,17,20,52} Relative to the surface, the horizontal orientation of the Zr and Hf complexes of TPP also diminishes the maximum potential coverage compared to the vertical orientation of the TCPP.⁵² Thus, the optical cross sections in the visible region for the materials with Hf and Zr porphyrins on TiO₂ and on ITO are smaller compared to the absorbed coatings. These electrochemical and photonic studies are ongoing and will be published elsewhere.

Conclusions

The matching of metal ion size and coordination chemistry to the binding properties of two significantly different ligands, one organic and one inorganic, affords an avenue for the formation of new (Por)M(POM) hybrid materials in high yields. These complexes exploit the light absorbing and photonic properties of porphyrinic systems directly coupled to the complementary photonic and structural properties of POMs via simultaneous multidentate coordination of a single metal ion. The efficiency of charge transport from molecules into semiconductors underpins a variety of hybrid molecular-semiconductor device architectures and other photonic materials. Charge transport efficiency is mediated by appropriate matching of molecular HOMO-LUMO gaps to semiconductor band gaps, the linker, and the proximity of the molecule.^{2,17,18,20-51} Metals that axially bind oxygen, e.g. Ti, and Sn, and Mo may also allow porphyrin attachment to oxide surfaces, but intervening tethers are needed for *meso* tetraarylporphyrins because these metal ions reside near the porphyrin plane and the orthogonal aromatic moieties inhibit direct metal-surface interactions. Therefore, these (Por)M(POM) materials may serve as a new platform to study the fundamental properties porphyrinoids attached to oxide surfaces via group (IV) metals.^{16,53} The properties of the ternary complexes, and by inference those on surfaces, arise because the Hf and Zr ions are coordinated by *both* the lacunary POM and the porphyrin.

Experimental Section

Instrumentation and Reagents. All UV-Visible spectra and diffuse reflectance spectra were taken in 1 cm quartz or glass cuvettes in CH₂Cl₂ on a Carey Bio 3 spectrophotometer unless otherwise indicated. Mass spectrometry was done as a service by the University of Illinois. Urbana-Champaign or on an Agilent 1100 LC/MSD instrument. NMR spectra were run on a 500 MHz Varian Inova and chemical shifts (ppm) are referenced to the proton solvents. A Joel 400 MHz NMR instrument was used for ³¹P spectra. Fluorescence spectra were taken on a Spex Tau-3 fluorometer in 1 cm quartz cuvettes in right angle mode. X-ray data were collected on a Nonius Kappa CCD. Gasses, reagents, and solvents were used as received unless otherwise noted. HfCl₄ and Hf(cp)₂Cl₂ were obtained from Strem Chemicals. Porphyrins were obtained from Aldrich or from Frontier Scientific. All solvents and other reagents were from Aldrich Disposable vials and test tubes were used once. Titanium(IV) oxide (TiO₂), nanopowder, 99.7%, anatase was purchased from Aldrich. ITO coated glass slides were purchased from Aldrich, and the glass cover slips were purchased from Fisher.

The hafnium and zirconium porphyrinate starting materials, (TPP)Hf(OAc)₂ (TPyP)Hf(OAc)₂, (TPP)Zr(OAc)₂ and the corresponding derivatives with two chloride counter ions, were synthesized according to literature methods.^{37,54,55} as was the free base lacunary Keggin polyoxometalate, H₃PW₁₁O₃₉[TBA]₄.⁵⁶ Mass spectrometric, IR, and NMR data of the starting materials are consistent with previous reports, and the spectroscopy of the ternary complexes are consistent with crystal structure data found for (TPP)Hf(PW₁₁O₃₉)[TBA]₅ (supporting information).

meso-tetraphenylporphyrinatohafnium(IV)PW₁₁O₃₉ tetra-butyl ammonium salt (TPP)Hf(PW₁₁O₃₉)[TBA]₅

20 mg of Hf(TPP)(OAc)₂ (910 g/mol, 0.022 mmol) was dissolved in 10 mL of a 1:1 mixture of CH₂Cl₂:CH₃OH in a 18 × 150 mm test tube with a magnetic stir bar at room temperature. 76 mg of H₃PW₁₁O₃₉[TBA]₄ (3650 g/mol, 0.021 mmol) and 5 mg of [TBA]Br was dissolved separately in 5 mL of acetonitrile containing 1% v/v triethylamine. The resulting clear POM solution was added dropwise over the course of 5 minutes to the stirring hafnium porphyrinate solution. The reaction was monitored by UV-Visible spectroscopy, where the presence of the ternary complex is signified by a large red shift in the porphyrin Soret band from 414 nm to

425 nm, over the course of one hour. The solvent was then removed under vacuum and the residue was dissolved in a minimal volume of CH_2Cl_2 , ca. 4 mL. and filtered of a small amount of insoluble salts. The product was precipitated with 25 mL of hexanes and collected on a glass filter. The product was allowed to dry initially in air and then under vacuum without heat to yield 91 mg, 98% yield, of $(\text{TPP})\text{Hf}(\text{PW}_{11}\text{O}_{39})[\text{TBA}]_5$.

$(\text{TPP})\text{Hf}(\text{PW}_{11}\text{O}_{39})[\text{TBA}]_5$

IR (Nujol NaCl) 1100–700 cm^{-1} . 1063(m. br.), 958 (m), 890 (wk), 816 (s., br.) 723 (m) UV-Vis CH_2Cl_2 λ_{max} nm (log ϵ) 403(4.51), 425(5.53), 508 (3.40), 548(4.21). 583 (3.30) ^1H -NMR (ppm) CD_3CN , 30 °C 9.53 (d, 2H- phen-*o*). 9.25 (d, 2H phen-*o*). 8.91(2H pyrrole), 8.71 (d, 2H pyrrole). 8.64 (s, 2H pyrrole), 8.61(4 2H pyrrole), 7.89(t, 2H phen-*m*), 7.82 (t, 2H phen-*m*), 7.75 (t, 2H phen-*p*), 7.69(t, 2H phen-*p*), 7.60(d, 2H phen-*o*), 7.55(t, 2H phen-*m*), 7.49(t, 2H phen-*m*), 7.43(d, 2H phen-*o*), 3.12 (m. 40H N- CH_2 -), 1.61 (m. 40H - CH_2 -), 1.38 (m. 40 - CH_2 -), 0.98 (t. 60H - CH_3). ^{31}P NMR (CD_3CN) -16.29 ppm. Negative ES Mass spectroscopy for $(\text{TPP})\text{Hf}(\text{PW}_{11}\text{O}_{39})^{-2}$ calc. m/z 1726.3 found 1726.4

meso-tetraphenylporphyrinatozirconium(IV) $\text{PW}_{11}\text{O}_{39}$ tetra-butyl ammonium salt $(\text{TPP})\text{Zr}(\text{PW}_{11}\text{O}_{39})[\text{TBA}]_5$

is made using the same methods as the hafnium complex but using $(\text{TPP})\text{Zr}(\text{OAc})_2$ as the starting material; 82 mg 81% yield. **$(\text{TPP})\text{Zr}(\text{PW}_{11}\text{O}_{39})[\text{TBA}]_5$** : IR (KBr disc) 1100–700 cm^{-1} , 1054(m, br.), 954 (s), 890 (wk), 826 (s, br.) 745 (m) UV-Vis CH_2Cl_2 λ_{max} nm (log ϵ) 404 (4.01), 427 (4.84), 509 (3.059), 548 (3.60), 586 (2.77) ^1H -NMR (ppm) CD_3CN , 30 °C; 9.53 (4 2H- phen-*o*), 9.25 (d, 2H phen-*o*). 8.89 (2H pyrrole). 8.66 (d, 2H pyrrole), 8.63 (s. 2H pyrrole), 8.46 (d, 2H pyrrole), 7.90 (t of d, 2H phen-*m*), 7.83 (t of d, 2H phen-*m*), 7.74 (t of t, 2H phen-*p*). 7.69 (t of t, 2H phen-*p*), 7.63 (d of t, 2H phen-*o*). 7.56 (t of d 2H phen-*m*), 7.50 (t of d, 2H phen-*m*), 7.45 (d of t. 2H phen-*o*), 3.16 (m, 40H N- CH_2 -), 1.66 (m, 40H - CH_2 -), 1.41 (m, 40 - CH_2 -), 1.00 (t, 60H - CH_3) ^{31}P NMR (CD_3CN) -16.30 ppm Negative TOF MS for $\text{PW}_{11}\text{O}_{39}\text{ZrC}_{44}\text{H}_{28}\text{N}_4[\text{C}_{16}\text{H}_{36}\text{N}]_2[\text{H}]_2^{2-}$ calc m/z 1933.4776 found 1933.4822 (+2.32 ppm). $\text{PW}_{11}\text{O}_{39}\text{ZrC}_{44}\text{H}_{28}\text{N}_4[\text{C}_{16}\text{H}_{36}\text{N}]_1[\text{H}]_2^{2-}$ calc m/z 1812.81 found 1812.8449 (+20.95 ppm), $\text{PW}_{11}\text{O}_{39}\text{ZrC}_{44}\text{H}_{28}\text{N}_4\text{H}_2^{3-}$ calc m/z 1208.20 found 1208.2313 (+24.28 ppm), $\text{PW}_{11}\text{O}_{39}\text{ZrC}_{44}\text{H}_{28}\text{N}_4\text{H}_2^{3-}$ calc m/z 1127.72 found 1127.8054 (+78.65).

Meso tetra-(4-pyridyl)-porphyrinatohafnium(IV) $\text{PW}_{11}\text{O}_{39}$ tetra-butyl ammonium salt $(\text{TPyP})\text{Hf}(\text{PW}_{11}\text{O}_{39})[\text{TBA}]_5$

20 mg of $(\text{TPyP})\text{Hf}(\text{OAc})_2$ (914 g/mol, 0.022 mmol) was stirred with 75 mg of $\text{H}_3\text{PW}_{11}\text{O}_{39}[\text{TBA}]_4$ and 5 mg of $[\text{TBA}]\text{Br}$ in the same solvents and procedure and described above. The reaction was complete after 20 minutes of stirring. The product was isolated by precipitating the target complex with 15 mL of hexanes from a 5 mL CH_2Cl_2 solution to yield 90 mg; 97% yield of the $(\text{TPyP})\text{Hf}(\text{PW}_{11}\text{O}_{39})[\text{TBA}]_5$.

$(\text{TPyP})\text{Hf}(\text{PW}_{11}\text{O}_{39})[\text{TBA}]_5$

IR (Nujol NaCl) 1100–700 cm^{-1} , 1133 (wk.), 1076 (sh.), 1054 (s.), 949 (s), 880(m), 806 (vs. br.), 749 (sh) Vis CH_2Cl_2 λ_{max} nm (log ϵ) 402 (4.42), 426 (5.41), 505 (3.42), 550 (4.21), 582 (3.44) ^1H -NMR (ppm). CD_3CN , 30 °C 9.50(br. s, 2H py-*o*), 9.18(d, 2H py-*o*), 9.08(d, 2H py-*m*), 9.02(d, 2H py-*m*), 8.94(s, 2H pyrrole), 8.78(br. d, 4H pyrrole and py-*m* overlap), 8.71(br. d., 4H pyrrole and py-*m* overlap), 8.68 (s. 2H pyrrole), 7.64(br.s., 2H py-*o*), 7.47(d, py-*o*). 3.14 (m. 40H N- CH_2 -), 1.64 (m. 40H - CH_2 -), 1.41 (m. 40 - CH_2 -), 0.99 (t. 60H - CH_3) ^{31}P NMR (CD_3CN) -16.25ppm, ESI-MS for $(\text{TPyP})\text{Hf}(\text{PW}_{11}\text{O}_{37})^{-1}$ calc. 3441 neg. ES found 3444.1; for $(\text{TPyP})\text{Hf}(\text{PW}_{11}\text{O}_{38})^{-2}$ calc. m/z 1728.2 neg. ES found 1728.7

Suitable crystals for X-ray diffraction were obtained for the (TPyP)Hf(PW₁₁O₃₉)⁻⁵ complex. 50 mg of the complex was dissolved in 5 mL of a 1:1, CH₃CN:CH₃OH, solution in an 18 × 150 mm test tube with a magnetic stir bar. Diethyl ether was added via pipette while stirring until the solution appeared cloudy. The solution was then placed in a warm water bath to evaporate just enough of the ether to make the solution almost clear of particulates. The solution was capped and placed in a freezer at -10 °C for four days, after which time long, dark purple needles collected on the sides and bottom of the test tube. The structure reveals this material to be (TPyP)Hf(PW₁₁O₃₉)[TBA]₂H⁺₃

Single-Crystal X-ray Diffraction

The intensity data for **I** were measured on an Bruker-Nonius KappaCCD diffractometer (graphite-monochromated Mo *K*α radiation, λ = 0.71073 Å, φ-ω scans) at 100 (2) K. The data were not corrected for absorption. Details of the solution and refinements for this compound are presented below: The crystal of **I**, with approximate dimensions 0.18 × 0.18 × 0.30 mm, were orthorhombic with space group *Pnma*. The final unit-cell constants of **I** were *a* = 19.419 (4), *b* = 27.157(5), *c* = 29.642(6) Å, *V* = 15632(5) Å³, *Z* = 4, ρ = 1.976 g cm⁻³, μ = 8.80 mm⁻¹, formula weight = 4649.55. The structure of **I** was solved with SHELXS-97 and refined by full-matrix least squares on *F*² with SHELXL-97. The hydrogen atoms were included in the structure-factor calculations, but their parameters were not refined. The final discrepancy indices for the 18158 reflections (θ < 27.50°) were *R* = 0.0912 (calculated on *F*) and *R*_w = 0.2076 (calculated on *F*²) with 730 parameters varied. The final difference map peaks < 3.16 e Å⁻³ are near the heavy atoms, hafnium and tungsten.

Binding of Hf(Por) and Zr(Por) to glass, ITO, and TiO₂ surfaces

All glass and ITO substrates were cleaned in an ozone cleaner (20 min) or by a piranha solution (3:1 NH₄OH/H₂O₂ for 30 min) followed by rinsing with copious amounts of water just prior to using. A drop of ca. 4 μM solution of the (TPP)Hf(OAc)₂ or (TPP)Zr(OAc)₂ in dry toluene was placed on the substrate and allowed to dry in air. Alternatively, the substrate was dipped in a ca. 0.4 mM solution for 1 h. After drying, all substrates were washed with toluene to remove any unbound materials. For TiO₂, 0.8 mg of (TPP)Hf(OAc)₂ or (TPP)Zr(OAc)₂ is dissolved in 2 mL of distilled toluene and ca. 30 mg titanium(IV) oxide nanopowder, 99.7% anatase with average size 5 nm (Aldrich) was added to the solution. After sonicating for 5 min, and the slurry was stirred for over night. The slurry was then centrifuged for 5 min to separate the coated particles, which are a pink color due to attachment of Hf(TPP)²⁺ or Zr(TPP)²⁺ on TiO₂. Similar treatment of the TiO₂ particles with Zn(TPP) and TPP in control experiments using, resulted in most of the porphyrin remaining in solution. The solution was decanted, the coated particles were rinsed with toluene 2–3 times to remove unbound materials, and left to dry in air.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the US National Science Foundation [NSF]: CHE-0554703 to CMD, AP Fellows Program DGE-0231800 for support of AF, and IGERT DGE-9972892. CMD acknowledge support from the Israel-United States Binational Science Foundation. Hunter College Chemistry infrastructure is supported by the NSF, the National Institutes of Health, (including RCMI G12-RR-03037), and the City University of New York.

References

1. (a) Cherian S, Wamser CC. *J. Phys. Chem. B* 2000;104:3624–3629. (b) Hao J, Giraudeau A, Ping Z, Ruhlmann L. *Langmuir* 2008;24:1600–1603. [PubMed: 18220432] (c) Hao J, Xia Y, Wang L, Ruhlmann L, Zhu Y, Li Q, Wei Y. *Angew. Chem* 2008;120:2666–2670.
2. Tachibana Y, Haque SA, Mercer IP, Durrant JR, Klug DR. *J. Phys. Chem. B* 2000;104:1198–1205.
3. Drain CM, Bazzan G, Milic T, Vinodu M, Goeltz JC. *Israel J. Chem* 2005;45:255–269.
4. Drain, CM.; Chen, X. *Encyclopedia of Nanoscience & Nanotechnology*. Nalwa, HS., editor. Vol. Vol. 9. New York: American Scientific Press; 2004. p. 593-616.
5. Milic TN, Chi N, Yablon DG, Flynn GW, Batteas JD, Drain CM. *Angew. Chem., Int. Ed* 2002;41:2117–2119.
6. Drain CM, Nifiatis F, Vasenko A, Batteas JD. *Angew. Chem. Int. Ed* 1998;37:2344–2347.
7. Dmitrenko O, Huang W, Polenova TE, Francesconi LC, Wingrave JA, Teplyakov AV. *J. Phys. Chem. B* 2003;107:7747–7752.
8. Toth JE, Anson FC. *J. Am. Chem. Soc* 1989;111:2444–2451.
9. Keana JFW, Ogan MD. *J. Am. Chem. Soc* 1986;108:7951–7957.
10. Keana JFW, Ogan MD, LU Y, Beer M, Varkey J. *J. Am. Chem. Soc* 1986;108:7957–7963.
11. Katsoulis DE. *Chem. Rev* 1998;98:359–388. [PubMed: 11851510]
12. Long DL, Burkholder E, Cronin L. *Chem. Soc. Rev* 2007;36:105–121. [PubMed: 17173149]
13. Drain, CM.; Smeureanu, G.; Batteas, J.; Patel, S. *Dekker Encyclopedia of Nanoscience and Nanotechnology*. Schwartz, JA.; Contescu, CI.; Putyera, K., editors. Vol. Vol. 5. New York: Marcel Dekker, Inc.; 2004. p. 3481-3502.
14. Barlow DE, Scudiero L, Hipps KW. *Langmuir* 2004;20:4413–4421. [PubMed: 15969147]
15. Otsuki J, Kawaguchi S, Yamakawa T, Asakawa M, Miyake K. *Langmuir* 2006;22:5708–5715. [PubMed: 16768498]
16. Nazeeruddin MK, Hunphry-Baker R, Officer DL, Campbell WM, Burrell AK, Graetzel M. *Langmuir* 2004;20:6514–6517. [PubMed: 15248744]
17. Stromberg JR, Marton A, Kee HL, Kirmaier C, Diers JR, Muthiah C, Taniguchi M, Lindsey JS, Bocian DF, Meyer GJ, Holten D. *J. Phys. Chem. C* 2007;111:15464–15478.
18. Chan Y-H, Schuckman AE, Perez LM, Vinodu M, Drain CM, Batteas JD. *J. Phys. Chem. C* 2008;112:6110–6118.
19. Tanaka M, Hayashi S, Eu S, Umeyama T, Matano Y, Imahori H. *Chem. Commun* 2007:2069–2071.
20. Rochford J, Chu D, Hagfeldt A, Galoppini E. *J. Am. Chem. Soc* 2007;129:4655–4665. [PubMed: 17385856]
21. Varotto A, Todaro L, Vinodu M, Koehne J, Liu G-y, Drain CM. *Chem. Comm* 2008:4921–4923. [PubMed: 18931739]
22. Tong, Lok H.; Wietor, J-L.; Clegg, W.; Raithby, Paul R.; Pascu, Sofia I.; Sanders, Jeremy KM. *Chem. Eur. J* 2008;14:3035–3044.
23. Marorri F, Bonifazi D, Gehrig R, Gallani J-L, Diederich F. *Israel J. Chem* 2005;45:303–319.
24. Tashiro K, Aida T. *Chem. Soc. Rev* 2007;36:189–197. [PubMed: 17264922]
25. Hasobe T, Saito K, Kamat PV, Troiani V, Qiu H, Solladie N, Kim KS, Park JK, Kim D, D'Souza F, Fukuzumi S. *J. Mater. Chem* 2007;17:4160–4170.
26. D'Souza F, El-Khouly ME, McCarty AL, Gadde S, Karr PA, Zandler ME, Araki Y, Ito O. *J. Phys. Chem. B* 2005;109:10107–10114. [PubMed: 16852225]
27. Bazzan G, Smith W, Francesconi LC, Drain CM. *Langmuir* 2008;24:3244–3249. [PubMed: 18321141]
28. Santos ICMS, Rebelo SLH, Balula MSS, Martins RRL, Pereira MMMS, Simoes MMQ, Neves MGPMs, Cavaleiro JAS, Cavaleiro AMV. *J. Mol. Catal. A: Chem* 2005;231:35–45.
29. Yokoyama A, Kojima T, Ohkubo K, Fukuzumi S. *Chem. Comm* 2007:3997–3999. [PubMed: 17912394]
30. Allain C, Favette S, Chamoreau L-M, Vaissermann J, Ruhlmann L, Hasenknopf B. *Eur. J. Inorg. Chem* 2008;2008:3433–3441.

31. Hagrman D, Hagrman PJ, Zubieta J. *Angew. Chem. Int. Ed* 1999;38:3165–3168.
32. Tsuda A, Hirahara E, Kim Y-S, Tanaka H, Kawai T, Aida T. *Angew. Chem. Int. Ed* 2004;43:6327–6331.
33. Tsuda A, Hirahara E, Yeong-Sang Kim, Tanaka H, Kawai T, Aida T. *Angew. Chem. Int. Ed* 2004;43:6327–6331.
34. Babcock, LM. *Synthesis and Characterization of Group 4 Organometal Oxide Complexes*. Urbana-Champaign: University of Illinois; 1988.
35. Kim HJ, Jung S, Jeon YM, Whang D, Kim K. *Chem. Comm* 1997:2201–2202.
36. Falber A, Todaro L, Goldberg I, Favilla MV, Drain CM. *Inorg. Chem* 2008;47:454–467. [PubMed: 18088113]
37. Kim HJ, Whang D, Kim K, Do Y. *Inorg. Chem* 1993;32:360–362.
38. Luo Q, Howell RC, Bartis J, Dankova M, William J, Horrocks DeW, Rheingold AL, Francesconi LC. *Inorg. Chem* 2002;41:6112–6117. [PubMed: 12425640]
39. Luo Q-H, Howell RC, Dankova M, Bartis J, Williams CW, William J, Horrocks DeW, Victor J, Young G II, Rheingold AL, Francesconi LC, Antonio MR. *Inorg. Chem* 2001;40:1849–1901.
40. Gaunt AJ, May I, Collison D, Fox OD. *Inorg. Chem* 2003;42:5049–5051. [PubMed: 12924875]
41. Kato CN, Shinohara A, Hayashi K, Nomiya K. *Inorg. Chem* 2006;45:8108–8119. [PubMed: 16999408]
42. Drain CM, Gentemann S, Roberts JA, Nelson NY, Medforth CJ, Jia S, Simpson MC, Smith KM, Fajer J, Shelnutt JA, Holten D. *J. Am. Chem. Soc* 1998;120:3781–3791.
43. Yamase T. *Chem. Rev* 1998;98:307–326. [PubMed: 11851508]
44. Buchler JW, Nawra M. *Inorg. Chem* 1994;33:2830–2837.
45. Davoras EM, Spyroulias CA, Mikros E, Coutsolelos AC. *Inorg. Chem* 1994;33:3440–3434.
46. Huhmann JL, Corey JY, Rath NP, Campana CF. *J. Organomet. Chem* 1996;513:17–26.
47. Rochford J, Galoppini E. *Langmuir* 2008;24:5366–5374. [PubMed: 18410135]
48. Imahori H, Norieda H, Nishimura Y, Yamazaki I, Higuchi K, Kato N, Motohiro T, Yamada H, Tamaki K, Arimura M, Sakata Y. *J. Phys. Chem. B* 2000;104:1253–1260.
49. Lee D-C, Morales GM, Lee Y, Yu L. *Chem. Comm* 2006:101–102.
50. Batteas J, Helt J, Xu C, Weldon M. *ANTEC 2001 Proceedings: Materials* 2001;2:1951–1954.
51. Hagfeldt A, Grätzel M. *Acc. Chem. Res* 2000;33:269–277. [PubMed: 10813871]
52. Campbell WM, Jolley KW, Wagner P, Wagner K, Walsh PJ, Gordon KC, Schmidt-Mende L, Nazeeruddin MK, Wang Q, Grätzel M, Officer DL. *J. Phys. Chem. C* 2007;111:11760–11762.
53. Nazeeruddin MK, Klein C, Liska P, Grätzel M. *Coord. Chem. Rev* 2005;249:1460–1467.
54. The structure of the Hf(TPyP)OAc₂ complex is similar the reported Hf(TPP)OAc₂ complex. Huhmann JL, Rath NP, Corey JY. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun* 1996;52:2486–2488..
55. Ryu S, Whang D, Kim J, Yeo W, Kim K. *J. Chem. Soc., Dalton Trans* 1993:205–209.
56. Radkov E, Beer RH. *Polyhedron* 1995;14:2139–2143.

Figure 1. 500 MHz ¹H NMR of compound **1** (top) and **3** (bottom) in CD₃CN, * indicates a small amount of the starting Hf(TPP)OAc₂ material.

Figure 2.

Two views of the crystal packing of the $(\text{H}_3\text{TPyP})\text{Hf}(\text{PW}_{11}\text{O}_{39})[\text{TBA}]_2$ complex; protons, counter ions and solvent are removed for clarity (see supporting information).

Figure 3.

(A) UV-visible spectra of (TPP)Hf(OAc)₂ in toluene (solid line), reflectance spectrum of a ca. 1 mm film of TiO₂ nanoparticles coated with (TPP)Hf(OAc)₂ (dashed line) and an untreated TiO₂ film (dotted line); (B) UV-visible spectra of (TPP)ZrHf(OAc)₂ in toluene (solid line), reflectance spectrum of a ca. 1 mm film of TiO₂ nanoparticles coated with (TPP)Zr(OAc)₂ (dashed line). The dynamic range of the reflectance-integrating sphere is ca. 1 absorbance unit.

A

B

Figure 4.

(A) Slurries of TiO_2 nanoparticles with left to right: TPP, $(\text{TPP})\text{Zr}(\text{OAc})_2$, $\text{Zn}(\text{TPP})$ and $(\text{TPP})\text{Hf}(\text{OAc})_2$. 30mg of TiO_2 nanoparticles were treated with 2ml of 0.5mM porphyrin solution by mixing slurry overnight, removing the solvent, and rinsing 2–3 times with toluene. (B) Powders on upper row from left : TPP, $\text{Zn}(\text{TPP})$ and $(\text{TPP})\text{Zr}(\text{OAc})_2$; lower row from left : TCPP (THF used as solvent and for rinse) and $(\text{TPP})\text{Hf}(\text{OAc})_2$.

Scheme 1.

Crystal structures of the starting (TPyP)Hf(OAc)₂ and the ternary complex **2**, counter ions left out for clarity. (i) to (TPyP)Hf(OAc)₂ in 1:1: CH₂Cl₂:CH₃OH is added one equivalent of H₃PW₁₁O₃₉[TBA]₄ in CH₃CN with an excess [TBA]Br and 1 % TEA.

Table 1Crystallographic data for (TPyP)Hf(PW₁₁O₃₉)[TBA]₂H₃

Compound 2	(TPyP)HfPW ₁₁ O ₃₉ [TBA] ₂ [CH ₃ CN] ₄ H ₃
Empirical formula	C ₁₁₇ H ₁₇₇ HfN ₁₅ O ₃₉ PW ₁₁
Formula mass	4649.55
System	orthorhombic
Space group	Pnma
unit cell	15632.(5)
<i>a</i> [Å]	19.419(4)
<i>b</i> [Å]	27.157(5)
<i>a</i> [Å]	29.642(6)
β [°]	90
γ [°]	90
Volume [Å ³]	90
<i>Z</i>	4
ρ _{calcd} [Mgcm ⁻³]	1.976
μ(MoKα) mm ⁻¹	8.798
<i>T</i> [°K]	100(2)
<i>F</i> (000)	8788
crystal size (cm)	0.3×0.18×0.18
θ range[°]	1.73 to 27.50
index ranges	−14 ≤ <i>h</i> ≤ 25 −33 ≤ <i>k</i> ≤ 35 −38 ≤ <i>l</i> ≤ 31
data/restraints/parameters	18158/19/730
final R indices [<i>I</i> > 2σ(<i>I</i>)]	
<i>R</i> 1	0.0912
<i>wR</i> 2	0.2076
R indices (all data)	
<i>R</i> 1	0.1752
<i>wR</i> 2	0.1720
largest diff. peak and hole [eÅ ⁻³]	3.158 and −1.669
Selected bond lengths	(Å)
Hf-N	2.328 – 2.358
Hf-O	2.206 – 2.151
W-O _{lacunary}	1.755 – 1.784
W-O _{bridging}	1.847 – 2.087
W=O	1.679 – 1.723
Hf – mean plane of N ₄	1.220
Hf – mean plane of O ₄	1.144