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Ternary phthalocyanato Hf$^{(IV)}$ and Zr$^{(IV)}$ polyoxometalate complexes

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I. Experimental

Reagents and Instrumentation. Mass spectrometry was done as a service by the University of Illinois, using Applied Biosystem Voyager System 4178. A Bruker Avance 500 MHz NMR instrument was used. A Joel 400 MHz NMR instrument was used for ^{31}P NMR spectra. Gasses, reagents, and solvents were used as received. Zirconium tetrachloride, hafnium tetrachloride, 1,2-dicyanobenzene, 1-methylnaphthalene, 1-chloronaphthalene, triethylamine were purchased from Sigma Aldrich. All solvents were from Sigma Aldrich. Disposable vials and test tubes were used once. The free base lacunary Keggin polyoxometalate, $H_3PW_{11}O_{39}[TBA]_4$ was synthesized according to the literature.[1]

Synthesis of Phthalocyanine Hafnium(IV)$PW_{11}O_{39}$ tetra-butylammonium salt, (Pc)Hf($PW_{11}O_{39}$)[TBA]$_5$. 18 mg of (Pc)Hf(OAc)$_2$ [2] (0.022 mmol) was dissolved in 10 mL of a 1:1 mixture of CH_2Cl_2:CH_3OH in a 18 x 150 mm test tube containing a magnetic stir bar at room temperature. 76 mg of the $H_3PW_{11}O_{39}$[TBA]$_4$ POM (0.021 mmol) and 5 mg of [TBA]Br were dissolved separately in 5 mL of acetonitrile containing 1 % v/v triethylamine. The resulting clear POM solution was added drop-wise over the course of 5 minutes to the stirring hafnium phthalocyanine solution, and the reaction was left to run overnight whereupon a small amount of precipitate was observed at the bottom of the test tube. The reaction was monitored by UV-Visible spectroscopy where the presence of the ternary complex is indicated by a small red shift of ~ 2 nm in the Q bands. After the precipitate and supernatant were separated by centrifugation, the solvent from the supernatant was removed under vacuum and the residue was dissolved in a minimal volume of CH_2Cl_2, ~ 4 mL, and a small amount of insoluble salts removed by filtration. The product was precipitated with 25 mL of hexanes and collected on a glass filter. The product was allowed to dry in air to yield of 57 mg, 58% yield, (Pc)Hf($PW_{11}O_{39}$)[TBA]$_5$.

Synthesis of Phthalocyaninato Zirconium(IV)$PW_{11}O_{39}$ tetra-butyl ammonium salt, (Pc)Zr($PW_{11}O_{39}$)[TBA]$_5$. The Zr(IV) ternary complexes was prepared by the same procedure as the Hf(IV) ternary complex except using (Pc)Zr(OAc)$_2$ [2] (16 mg, 0.021 mmol); yield: 50% (Pc)Zr($PW_{11}O_{39}$)[TBA]$_5$;

II. Characterization

Mass spectroscopy. MALDI MS for (Pc)Hf(POM), formula ($C_{36}H_{16}N_8$)Hf($PW_{11}O_{39}$)[$C_{16}H_{36}N$]$_5$ calculated m/z= 4578.27; found m/z= 4579.00. For (Pc)Zr(POM) formula ($C_{36}H_{16}N_8$)Zr($PW_{11}O_{39}$)[$C_{16}H_{36}N$]$_5$ found m/z= 4492.72 while calculated m/z= 4492.1 (Figure S1 and S2 respectively).

^{31}P NMR. ^{31}P NMR for both (Pc)Hf($PW_{11}O_{39}$)[TBA]$_5$ and (Pc)Zr($PW_{11}O_{39}$)[TBA]$_5$ complexes display a singlet at -15.68 ppm and -15.45 ppm, respectively (Figure S10 and S11). Note that for (Pc)Zr($PW_{11}O_{39}$)[TBA]$_5$ a smaller peak at -15.74 ppm is observed that may arise from exchange of TBA cations (consistent with our earlier observations).[3] The phosphorus peaks have similar chemical shifts to those reported in the literature. For example, the cyclopentadienyl analogue, (cp)Hf($PW_{11}O_{39}$)[TBA]$_4$ displays a peak at -12.3 ppm,[4] the porphyrin-free Hf$PW_{11}O_{39}^{-3}$ complex has a peak at -14.67 ppm. Also, TPP and TPyrP hafnium ternary complexes show sharp peaks at -16.20 ppm and -16.25 ppm.[3]

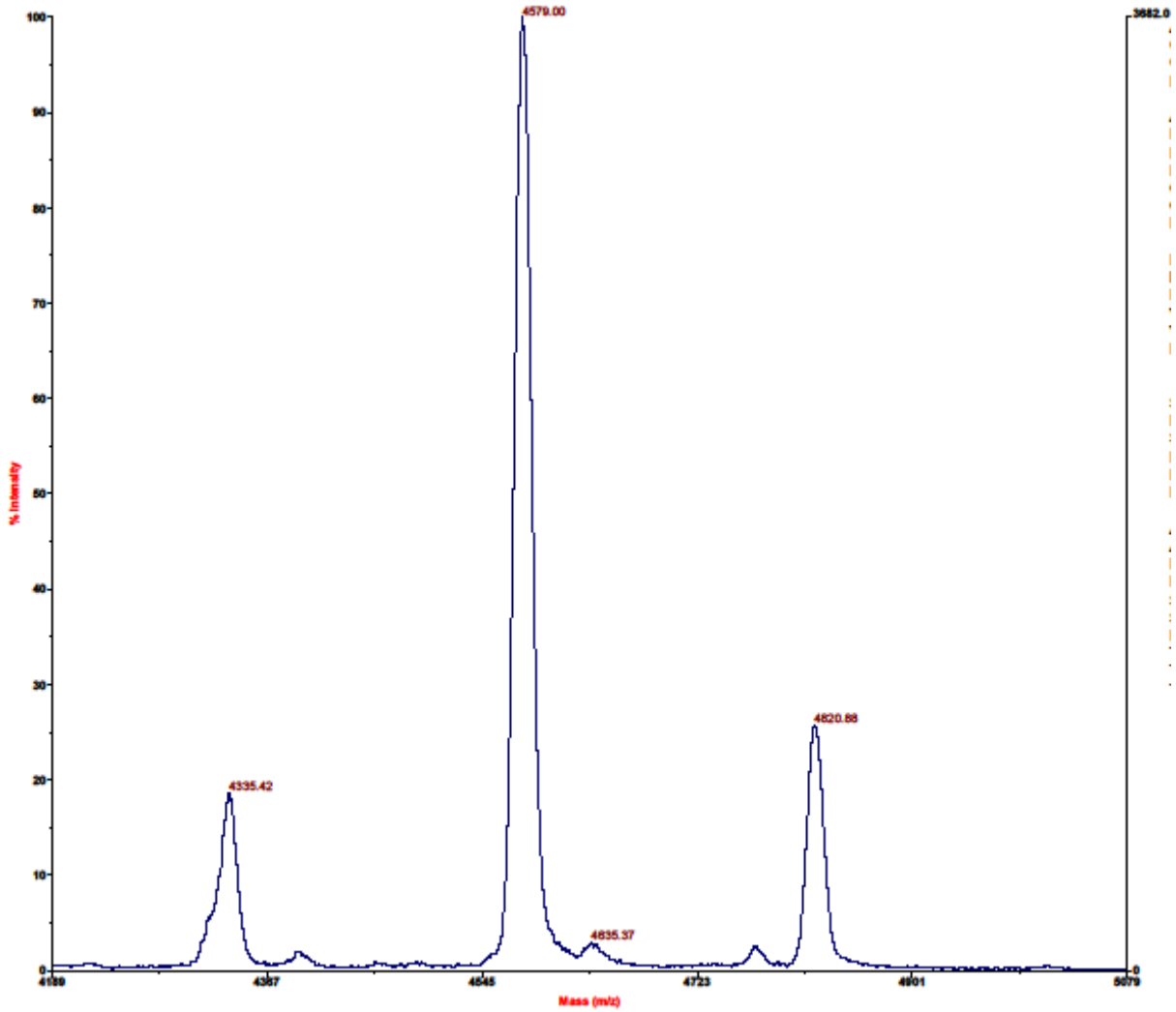

Figure S1. MALDI-MS using 9-nitroanthracene matrix, of (Pc)Hf(POM) m/z= 4578.27 calcd., found 4579.00. The peak at 4820 has an additional TBA and that at 4355 has one less TBA.

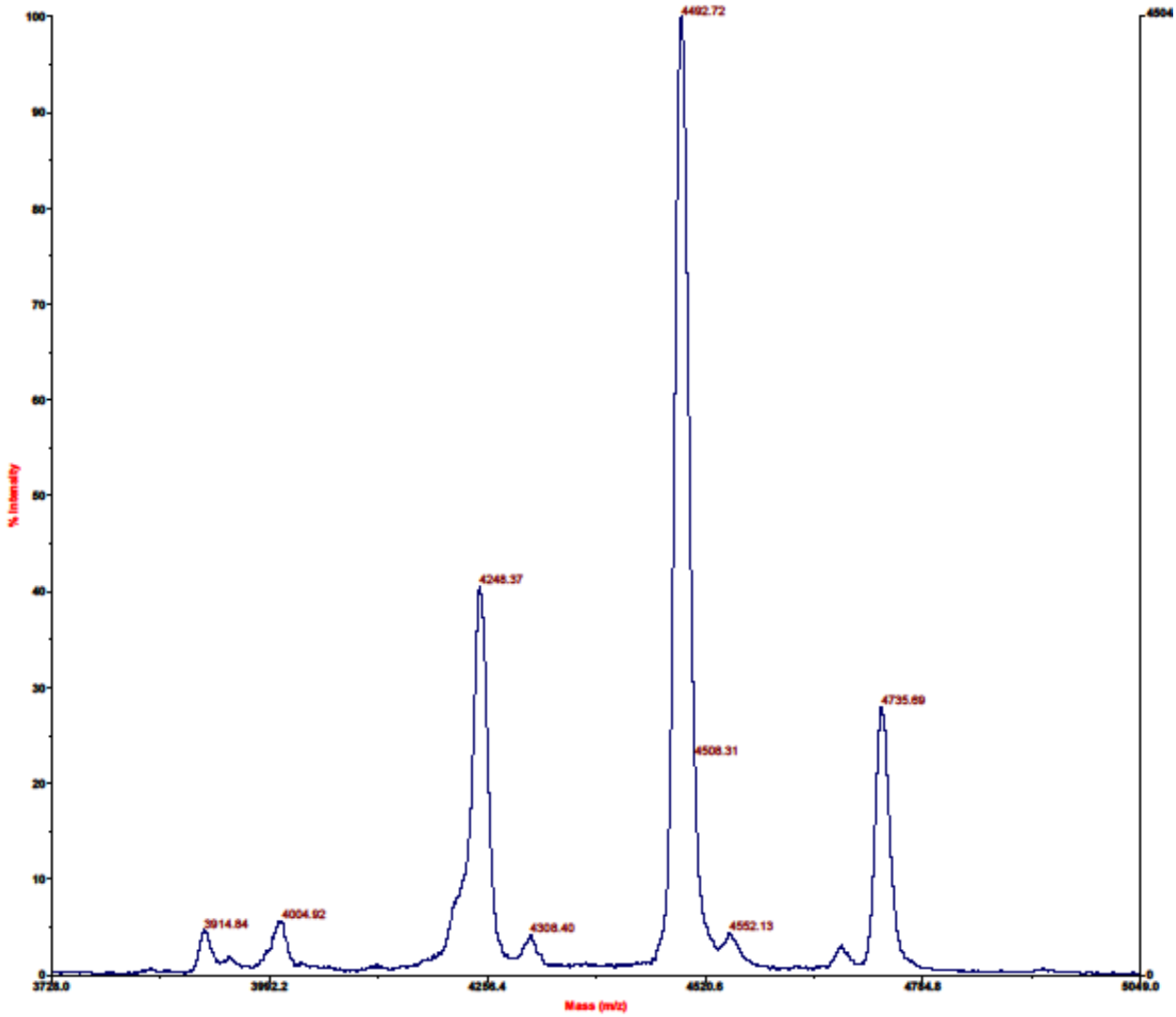

Figure S2. MALDI MS using 9-nitroanthracene matrix, of (Pc)Zr(POM) m/z= 4492.10 calcd., found 4492.72. The peak at 4735 has an additional TBA, and peak at 4248 has one TBA less.

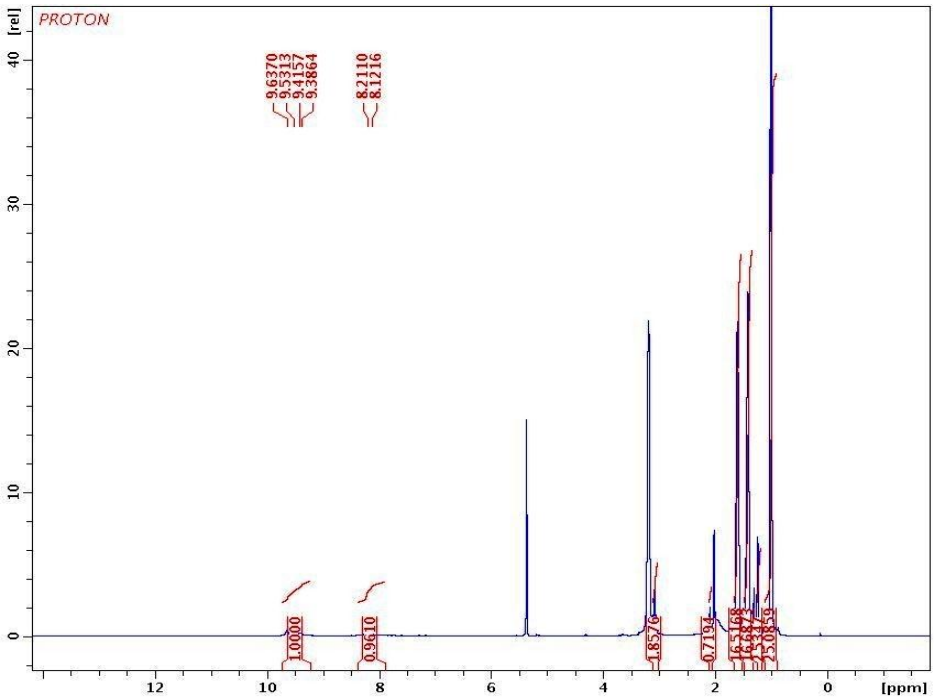

Figure S3. 500 MHz ^{1}H-NMR of (Pc)Hf(POM) in CD_2Cl_2.

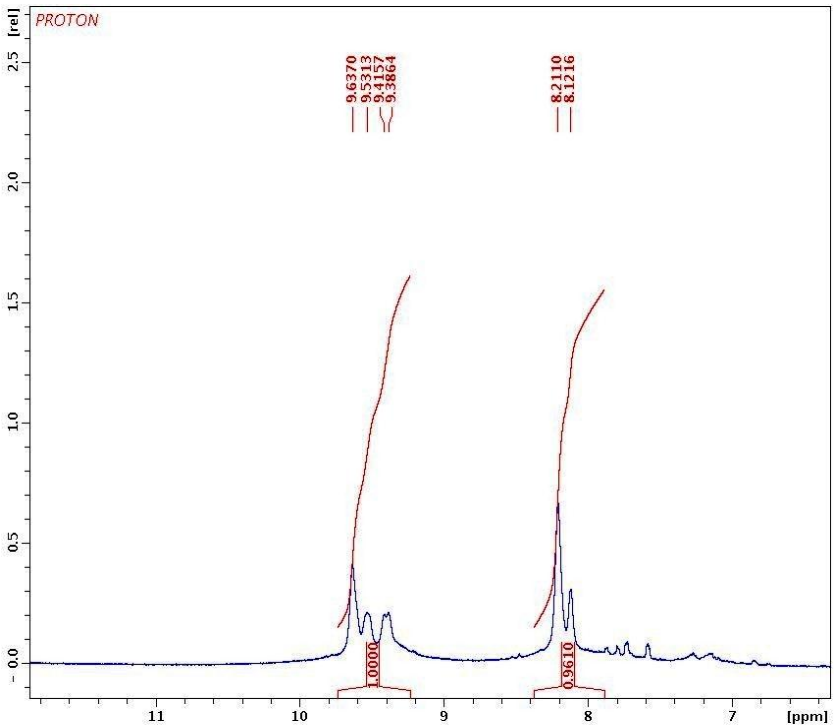

Figure S4. (Pc)Hf(POM) ^{1}H-NMR in CD_2Cl_2, aromatic region.

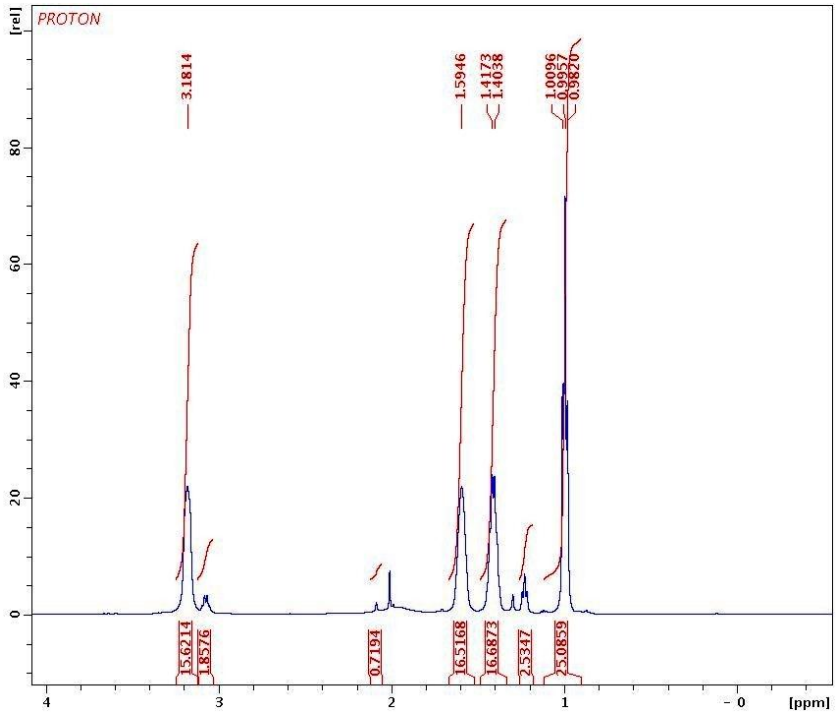

Figure S5. (Pc)Hf(POM) ^{1}H-NMR in CD_2Cl_2, TBA region.

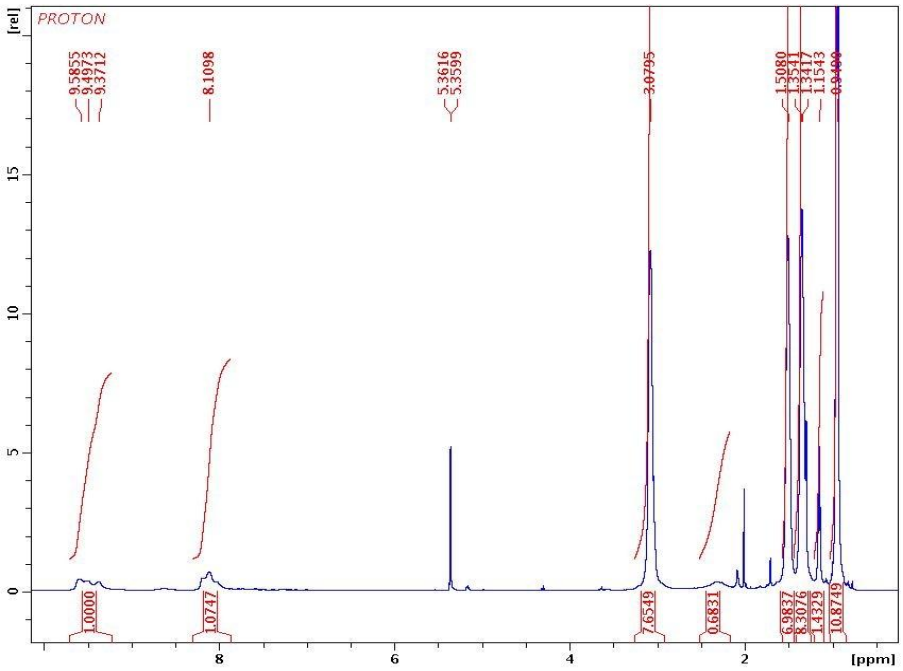

Figure S6. 500 MHz ^{1}H-NMR of (Pc)Zr(POM) in CD_2Cl_2.

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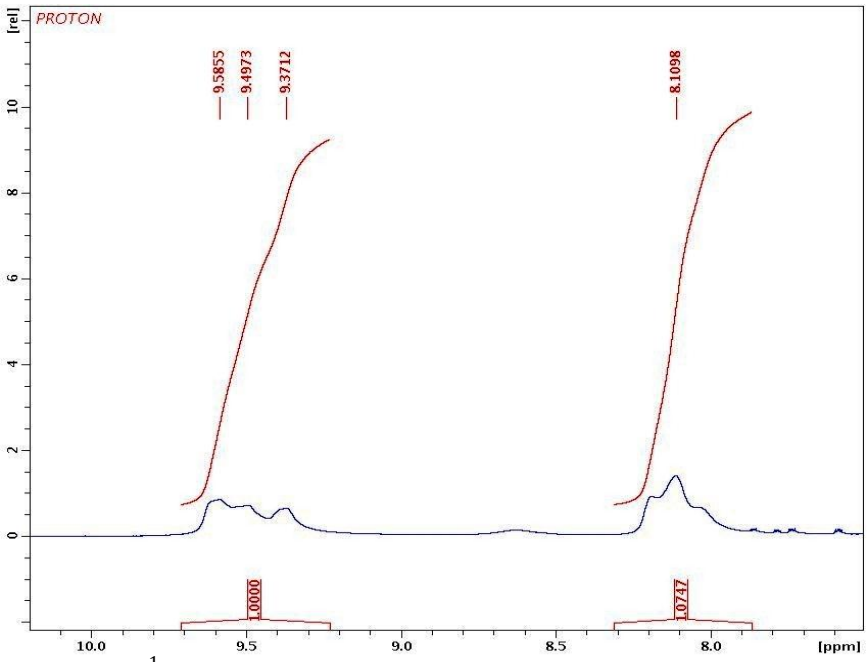


Figure S7. ^{1}H-NMR spectrum of (Pc)Zr(POM) in CD_2Cl_2, aromatic region.

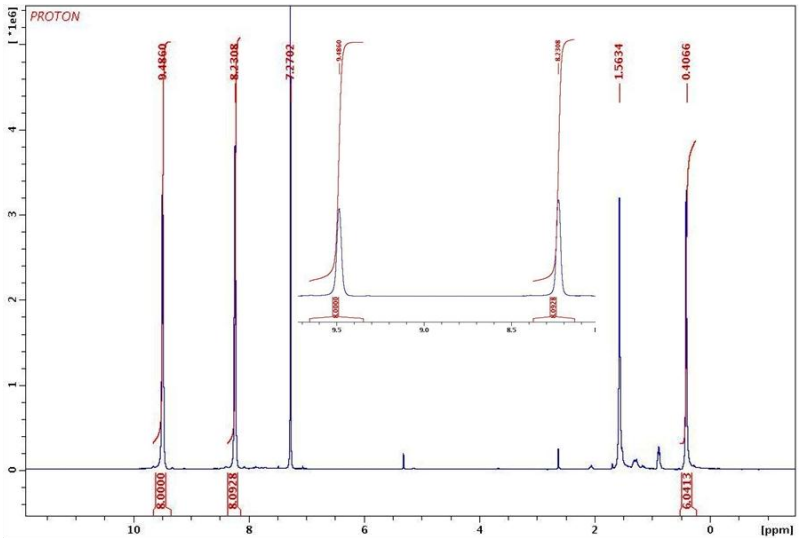


Figure S8 (Pc)Hf(OAc)$_2$ ^{1}H-NMR in $CDCl_3$. 7.27 ppm $CDCl_3$ and 1.56 ppm H_2O. Inset shows the aromatic region.

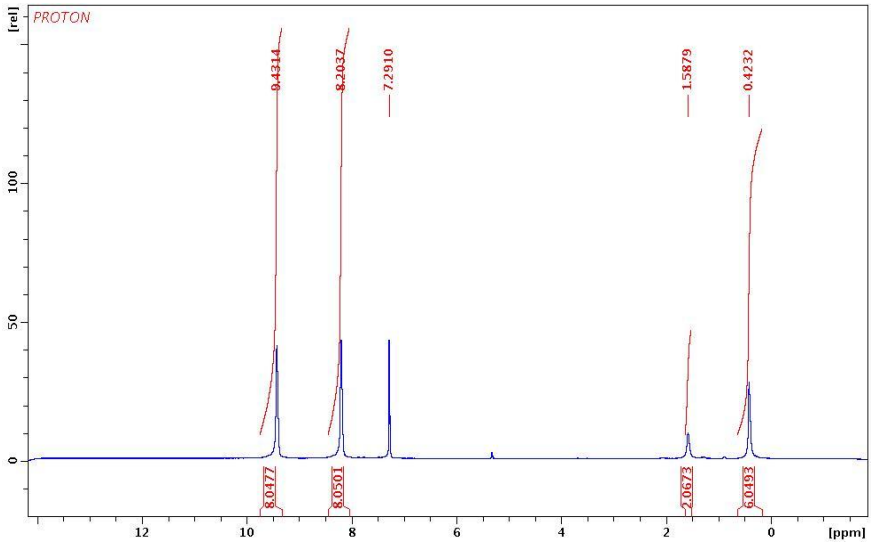


Figure S9 (Pc)Zr(OAc)$_2$ ^{1}H-NMR in $CDCl_3$. 7.29 ppm $CDCl_3$ and 1.58 ppm H_2O.

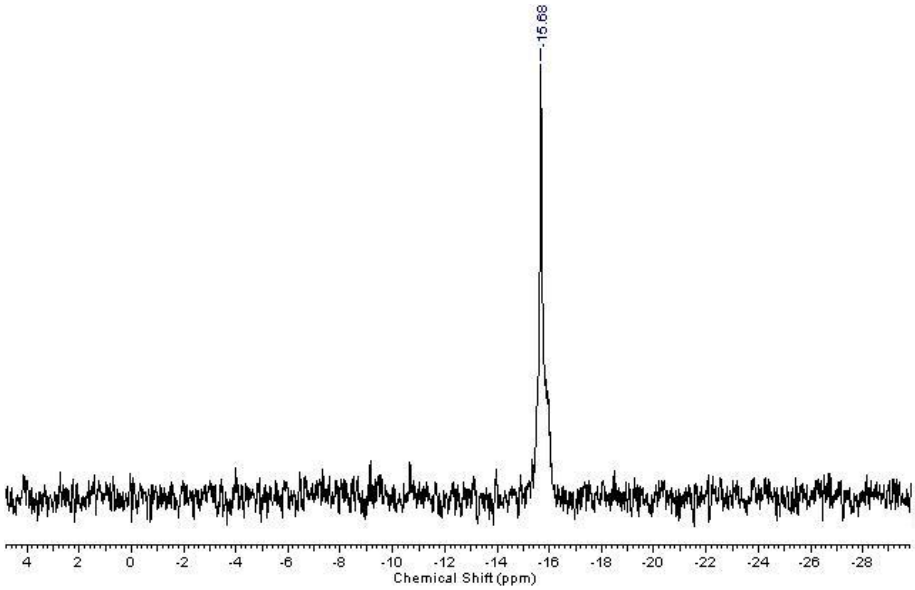


Figure S10. ^{31}P NMR of (Pc)Hf (POM) in CD_2Cl_2.

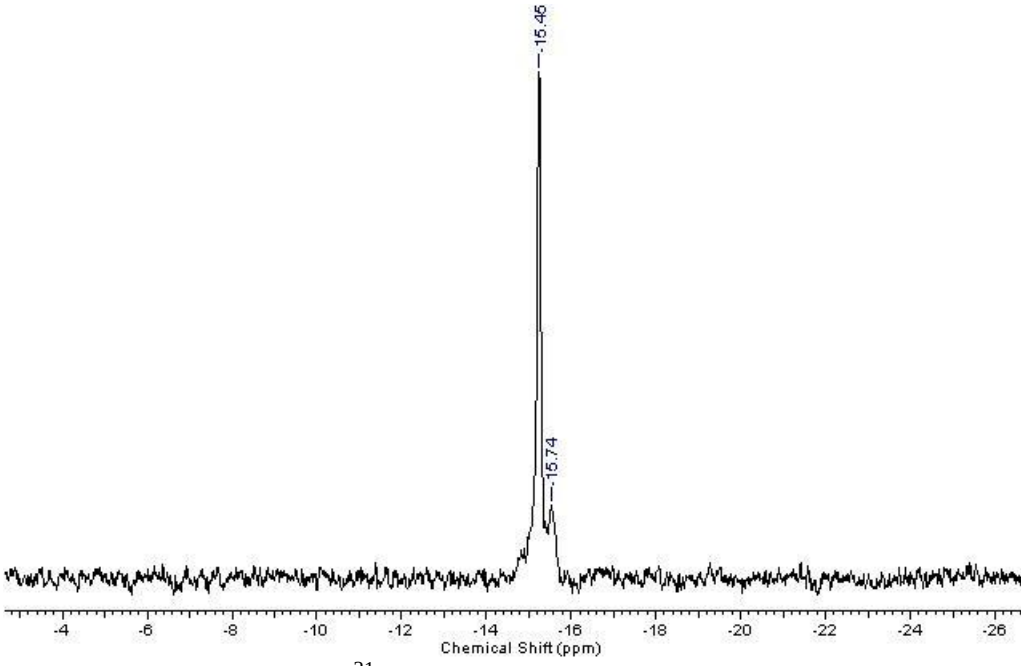


Figure S11. ^{31}P NMR of (Pc)Zr(POM) in CD_2Cl_2.

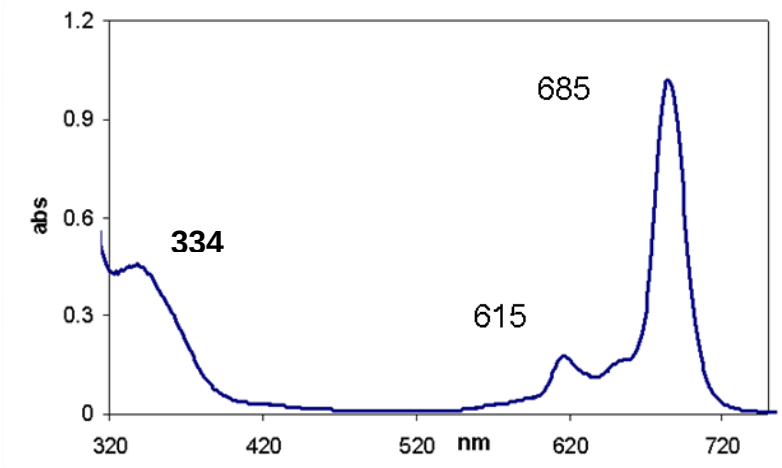


Figure S12. Absorption spectra of (Pc)Hf(POM) in CH_2Cl_2.

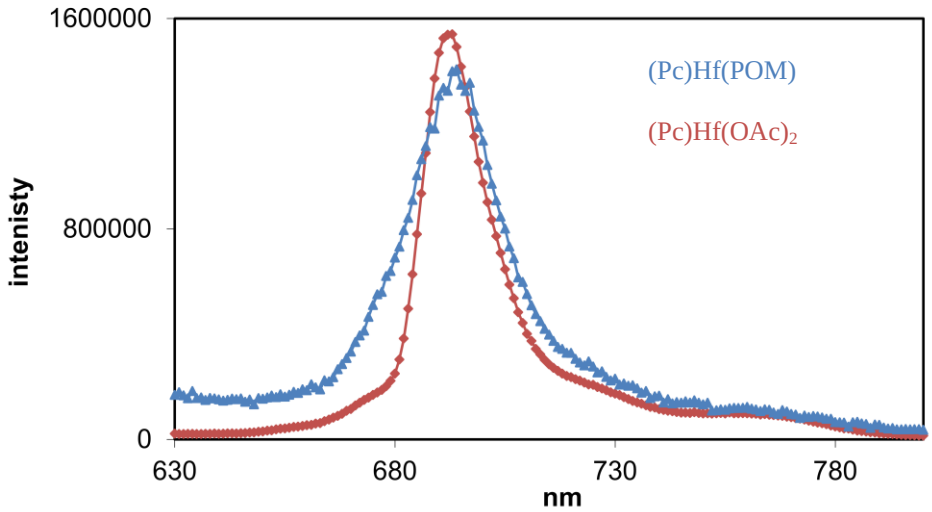


Figure S13. Emission spectra of (Pc)Hf(POM) in CH_2Cl_2 excited in the 616 nm Q band multiplied by 50 (blue line), is compared the emission spectrum of the $(Pc)Hf(OAc)_2$ complex (red line) excited at the same wavelength with the same O.D.

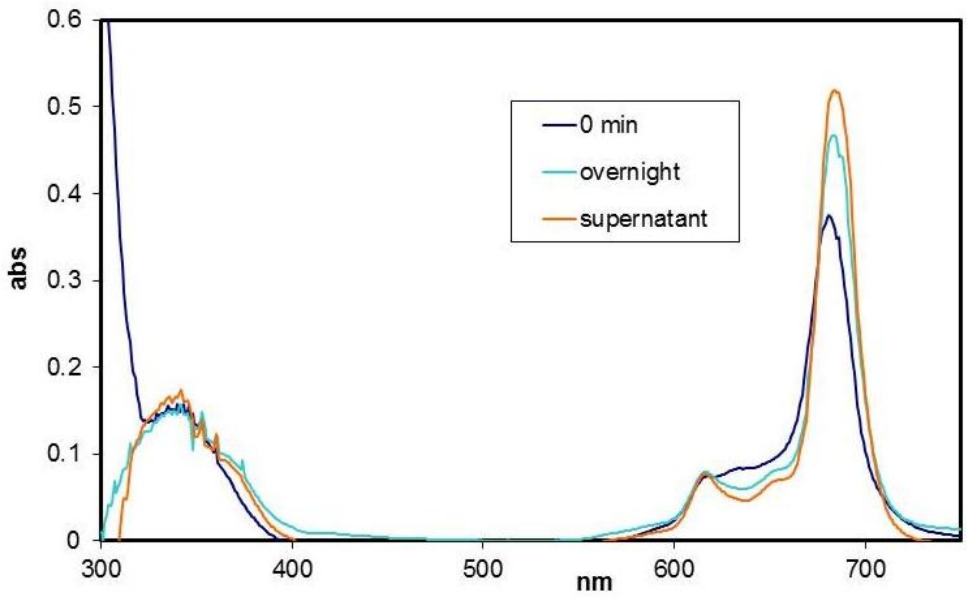


Figure S14. Absorption spectra of (Pc)Hf(POM) in CH_2Cl_2 at the beginning of reaction, after the reaction and after filtration of the supernatant with CH_2Cl_2 and precipitation with hexane. The Q band red shift is around 2 nm. Note that the concentration is not the same.

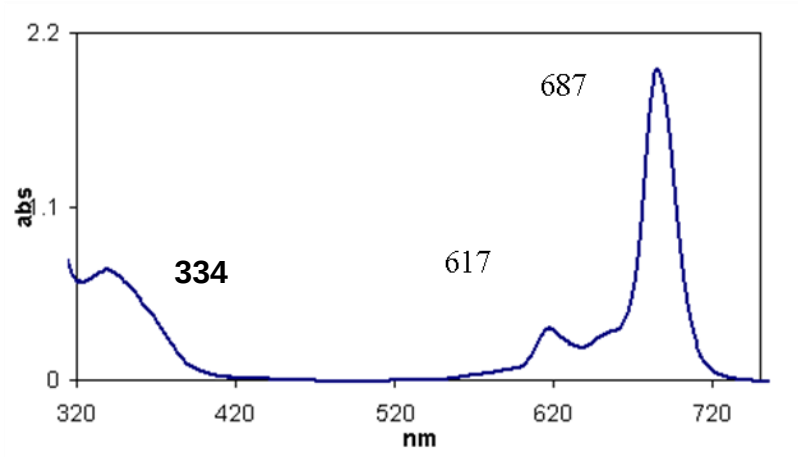


Figure S15. Absorption spectra of (Pc)Zr(POM) in CH_2Cl_2.

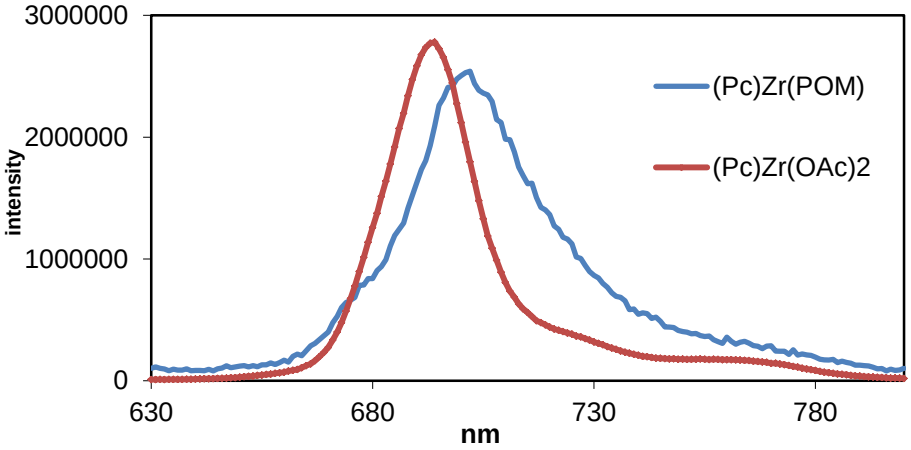
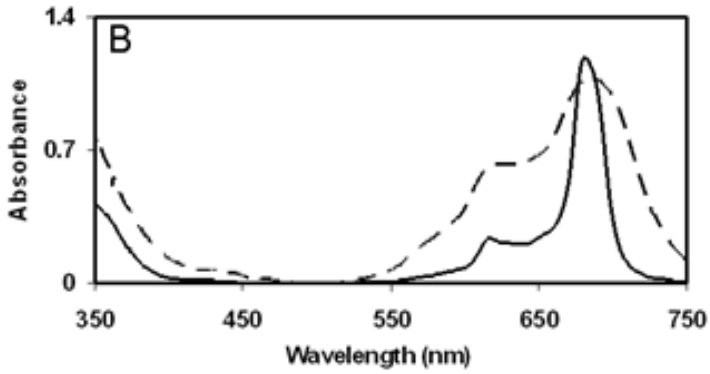


Figure S16. Emission spectra of (Pc)Zr(POM) in CH_2Cl_2 excited at 616 nm Q band multiplied by 40 (blue line), is compared the emission spectrum of the (Pc)Zr$(OAc)_2$ complex (red line) excited at the same wavelength with the same O.D.



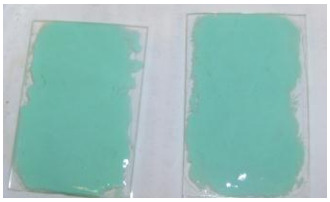


Figure S17. Left: UV-Visible spectra of (Pc)Zr$(OAc)_2$. in toluene (solid line), reflectance spectrum of a ~1 mm film of TiO_2 nanoparticles coated with (Pc)Zr (dashed line). Right: TiO_2 nanoparticles coated with (Pc)Zr and (Pc)Hf.

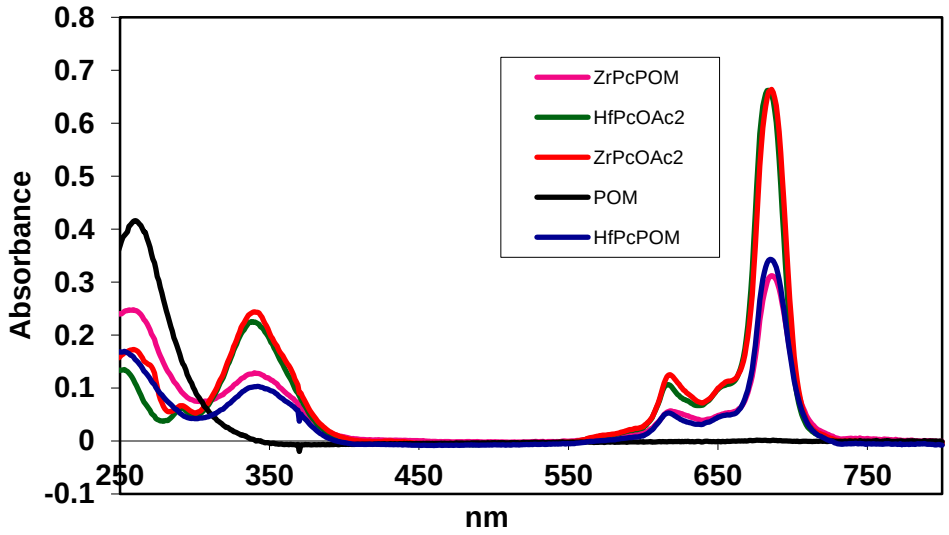


Figure S18. UV-Visible spectra of starting POM (black), starting (Pc)Zr(OAc)$_2$ (red), (Pc)Hf(OAc)$_2$ (green), and ternary complexes (Pc)Zr(POM) (pink) and (Pc)Hf(POM) (blue) .

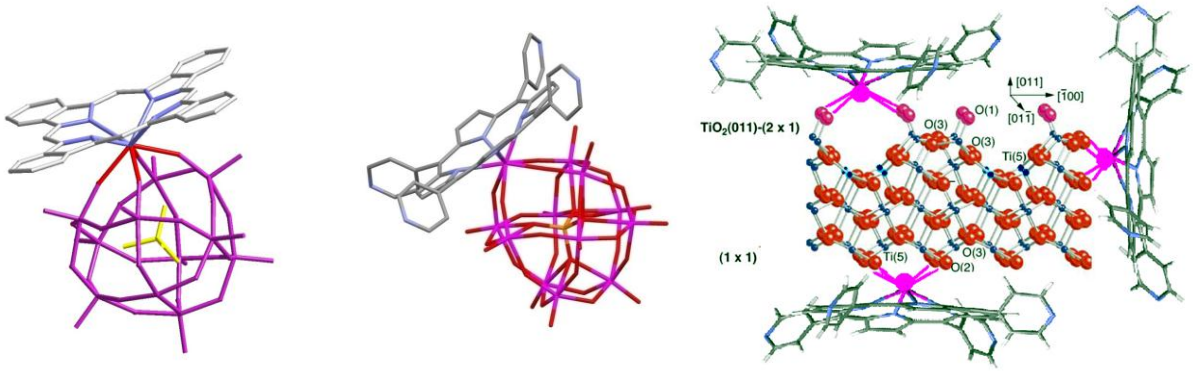


Figure S19. Left: schematic rendering of the (Pc)M(POM) complexes based on, center: the crystal structure of the (tetrapyridylporphyrin)-Hf(IV)-POM complex, and right: schematic of the proposed binding to TiO$_2$ nanoparticles.[2]

Table 1. Lifetimes from time correlated single photon counting (TCSPC) of ternary complex (Pc)-M-($PW_{11}O_{39}$)[TBA]$_5$ and starting material (Pc)M(OAc)$_2$ in CH_2Cl_2

Complexes	λ_B^{max}, nm $S_0 \rightarrow S_2$	λ_Q^{max}, nm $S_0 \rightarrow S_1$		λ_{ex}	λ_F^{max}, nm $S_1 \rightarrow S_0$	Stokes Shift	τ_F, ns
(Pc)Hf(POM)	334	616	685	616	695 730 and 770	10	0.03 (73%); 6 (27%)
(Pc)Zr(POM)	336	618	687	616	700 730 and 770	10	0.9 (63%); 5 (37%)
(Pc)Hf(OAc)$_2$	334	614	684	615	693 730	10	< IRF ; 5 (5%)
(Pc)Zr(OAc)$_2$	336	615	685	615	694 730	10	< IRF; 1.3 (79%)

Laser 670 nm, measuring in the 695 nm strongest emission band (in air). < IRF (<0.2)

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