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**Synthesis, Structural and Physicochemical Characterization of a Ti<sub>6</sub> and a Unique Type of Zr<sub>6</sub> Oxo-Clusters Bearing an Electron-Rich Unsymmetrical {OON} Catecholate/Oxime Ligand and Exhibiting Metalloaromaticity**

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**ABSTRACT**

The chelating catechol/oxime ligand 2,3-dihydroxybenzaldehyde oxime (H<sub>3</sub>dihybo) has been used to synthesize one titanium(IV) and two zirconium(IV) compounds that have been characterized by single-crystal X-ray diffraction, <sup>1</sup>H and <sup>13</sup>C NMR, solid-state UV-vis, and ESI-MS spectroscopies. Reaction of TiCl<sub>4</sub> with H<sub>3</sub>dihybo and KOH in methanol, at ambient temperature, yielded the hexanuclear titanium(IV) compound, K<sub>2</sub>[Ti<sup>IV</sup><sub>6</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ-O)<sub>3</sub>(OCH<sub>3</sub>)<sub>4</sub>(CH<sub>3</sub>OH)<sub>2</sub>(μ-Hdihybo)<sub>6</sub>]-CH<sub>3</sub>OH (**1**), while reaction of ZrCl<sub>4</sub> with H<sub>3</sub>dihybo and either <sup>n</sup>Bu<sub>4</sub>NOH or KOH gave also the hexanuclear zirconium(IV) compounds **2** and **3** respectively. Compounds **1-3** have the same structural motif [M<sup>IV</sup><sub>6</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ-O)<sub>3</sub>] (M = Ti, Zr), which constitutes a unique example with a trigonal prismatic arrangement of the six zirconium atoms, in marked contrast to the octahedral arrangement of the six zirconium atoms in all the Zr<sub>6</sub> clusters reported thus far, and a unique Zr<sub>6</sub> core structure. Multinuclear NMR solution measurements in methanol and water proved that the hexanuclear clusters **1** and **3** retain their integrity. The marriage of the catechol moiety with the oxime group in the ligand H<sub>3</sub>dihybo proved quite efficient in substantially reducing the band-gaps of TiO<sub>2</sub> and ZrO<sub>2</sub> to 1.48 and 2.34 eV for the titanium and zirconium compounds **1** and **3** respectively. The application of **1** and **3** in photocurrent responses was investigated. ESI-MS measurements of the clusters **1** and **3** revealed the existence of the hexanuclear metal-core and also the initial formation of the trinuclear M<sub>3</sub> (M = Ti, Zr) building blocks prior to their self-assembly into the hexanuclear M<sub>6</sub> (M = Ti, Zr) species. Density Functional Theory (DFT) calculations of the NICS<sub>zz</sub> scan curves of these systems revealed that the triangular M<sub>3</sub> (M = Ti or Zr) metallic ring cores exhibit pronounced metalloaromaticity. The latter depends upon the nature of the metallic center with NICS<sub>zz</sub>(1) values equal to -30 and -42 ppm for the Ti (compound **1**) and Zr (compound

2) systems, comparable to the NICS<sub>zz</sub>(1) value of benzene ring being -29.7 ppm calculated at the same level of theory.

## INTRODUCTION

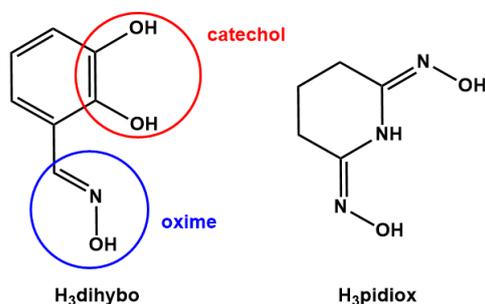
Polyoxo-titanium clusters (PTCs) have drawn unprecedented attention<sup>1</sup> the last years due to their potential applications in photocatalytic hydrogen production,<sup>2</sup> in solar energy conversion,<sup>3</sup> in degradation of environmental pollutants<sup>4</sup> and in the reduction of carbon dioxide.<sup>5</sup>

The precise knowledge of the structures of PTCs, since these oxide clusters are soluble analogues of discrete fragments of solid TiO<sub>2</sub>, originates from the necessity to understand the binding modes of sensitizers to Ti–O surfaces.<sup>6</sup> The large band-gap (3.20 eV) of anatase (TiO<sub>2</sub>) limits its applications in photocatalysis.<sup>7</sup> The employment of organic chelators could allow the manipulation of the band-gap and presumably the subsequent visible light absorption by PTCs.<sup>8</sup>

In a similar manner, the zirconium dioxide has been used in wide range of applications such as the degradation of organic pollutants,<sup>9</sup> as well as in photochemical water splitting,<sup>10</sup> fuel cells<sup>11</sup> and photocatalysis.<sup>12</sup> The band gap of ZrO<sub>2</sub> ranges from 3.25 eV to 5.1 eV depending on its phase and the method of its preparation.<sup>13</sup> Moreover, the field of the zirconium based MOFs has been exploded the last years.<sup>14</sup>

Previous studies demonstrated the strong chelating affinity of catechol towards high oxidation state metals.<sup>15</sup> Additionally, oximes<sup>16</sup> are also strong binders to the group IV transition metals in their highest oxidation state. Thus, it was envisaged that the incorporation of both functional groups within the same chelating system such as in the case of 2,3-dihydroxybenzaldehyde oxime (H<sub>3</sub>dihybo, Scheme 1)<sup>17</sup> could potentially

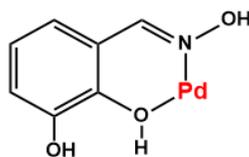
allow us to exploit the structural and electronic effects of both groups and modulate the material's band-gap.



**Scheme 1.** The ligands H<sub>3</sub>dihybo and H<sub>3</sub>pidiox

Research on the band-gap tuning of TOCs, via a dye sensitization method is an important topic and the marriage of the catechol moiety with the oxime group in neighboring positions in the H<sub>3</sub>dihybo (Scheme 1) ligand would lead to the substantial reduction of the TiO<sub>2</sub> and ZrO<sub>2</sub> band-gaps.

Moreover, the presence of the electron-withdrawing -C=N-OH group into the aromatic ring is predicted to significantly lower the catechol protonation constants making them much more effective sequestering ligands at neutral or even acidic pH values. Here we demonstrate for the first time, the effective use of H<sub>3</sub>dihybo ligand for the construction of multinuclear clusters, allowing the modulation of the cluster's band-gap and induction of metalloaromaticity effects. The ligand's chelating ability has been reported only once in the case of a palladium(0) monomeric complex,<sup>17c</sup> [Pd<sup>0</sup>(H<sub>3</sub>dihybo)], where its structure (Scheme 2) has been proposed only on the basis of NMR and IR data.



**Scheme 2.** The proposed structure of the palladium(0) complex,  $[\text{Pd}^0(\text{H}_3\text{dihybo})]$  on the basis of IR and NMR data

Furthermore, the ligand  $\text{H}_3\text{dihybo}$  which also exhibits donor atoms in three neighboring positions of the ring, in a similar fashion to the ligand  $\text{H}_3\text{pidiox}^{16\text{a}}$  (Scheme 1) which gave rise to the formation of a PTC containing two *cyclo*- $\text{Ti}_3$  metallic cores exhibiting metalloaromaticity. Metalloaromaticity is a relatively new concept used to describe the aromaticity of all-metal rings<sup>18</sup> with potential applications in molecular electronics.<sup>19\text{a}}</sup> Additionally, the emergence of metalloaromaticity in metals, metal oxides and mixed metal clusters is of vital importance in explaining the chemical bonding as well as understanding the electronic, and surface properties of the metals, metal oxides and metal alloys.<sup>19\text{b}}</sup> The mixed metal Al-Li, forms a strong and light-weight material which has been used extensively in aerospace engineering.<sup>19\text{c}}</sup> The ongoing research in this field, revealed quite a few examples of compounds bearing all-metal based aromatic rings and characterized as metallo-aromatic. The most popular aromaticity/antiaromaticity criteria are based on structural (ring planarity), energetic (aromatic stabilization energy, ASE), magnetic (paratropicity/diatropicity) and electronic (electron delocalization descriptors) properties. As far as the electronic delocalization descriptors are concerned the aromaticity of organic compounds arises from electron delocalization supported by formation of  $\pi$  MOs ( $\pi$ -type aromaticity), while in all-metal aromatic rings electron delocalization could take place through formation of  $\sigma$ ,  $\pi$ ,  $\delta$  and  $\varphi$  MOs. The aromaticity of three-, four-, five- and six-

membered metal rings have been extensively studied.<sup>18d</sup> For example, it has been reported<sup>18c</sup> that the  $[c-X_3]^-$  ( $X = B, Al, Ga$ ) ‘bare’ metallic rings exhibit double ( $\sigma + \pi$ )-aromaticity. Another example of three member aromatic metallic rings are the ‘ligand stabilized’  $cyclo-M_3(\mu-H)_3$  ( $M = Cu, Ag, Au$ ) systems.<sup>18d</sup> Similar studies have also reported aromaticity for the ‘bare’ four member ring in  $[c-Al_4]^-$  as well for the ‘ligand stabilized’  $[M_4(CO)_{12}]$  ( $M = Fe, Ru, Os$ ) systems.<sup>18f</sup> Similarly, many studies of five and six membered metallic rings were also reported.<sup>18d</sup>

Almost the full range of aromaticity descriptors we employed herein including the structural, magnetic one (particularly the most powerful Nucleus Independent Chemical Shift, NICS descriptor) in an effort to investigate the system’s behaviour.<sup>20</sup> The NICS has widely been applied as a magnetic criterion of the aromaticity of organic rings (e.g. the NICS of the archetype benzene molecule at the ring center, NICS(0) is -9.7 ppm).<sup>21</sup> Notice that comparable or even higher NICS(0) values have been theoretically estimated for all-metal rings.<sup>18d</sup>

In this contribution, we report the successful synthesis of three hexanuclear polyoxometalates of the general formula  $[M^{IV}_6(\mu_3-O)_2(\mu-O)_3(\mu-\eta^1, \eta^2, \eta^1-Hdihydro-O, O', N)_6]$  ( $M = Ti, Zr$ ) by reacting  $MCl_4$  ( $M = Ti, Zr$ ) with  $H_3dihydro$  in the presence of either  $KOH$  or  $nBu_4NOH$  as a base in methanol at room temperature. The three compounds were characterized by single crystal X-ray structure analysis and various physicochemical techniques. Not only, the core structure of the zirconium compounds  $[Zr_6(\mu_3-O)_2(\mu-O)_3]$  but also the trigonal prismatic arrangement of the six zirconium atoms are unique. The  $cyclo-M_3$  ( $M = Ti, Zr$ ) metallic cores exhibit metalloaromaticity. The band-gap investigation of the compounds showed a very low value of 1.48 eV for the titanium (**1**) and 2.34 eV for the zirconium (**3**) compounds.

## EXPERIMENTAL SECTION

### Materials, Syntheses, and Physical Measurements

All chemicals and solvents were purchased from Sigma-Aldrich and Merck, were of reagent grade and used without further purification, except  $\text{TiCl}_4$  which was distilled under high vacuum just prior to use. Merck silica gel 60 F254 TLC plates were used for thin layer chromatography. C, H, and N analyses were conducted by the micro-analytical service of the School of Chemistry, the University of Glasgow. FT-IR transmission spectra of the compounds, in KBr pellets, were acquired using a JASCO-460 model spectrophotometer in the  $4000\text{-}400\text{ cm}^{-1}$  range. The UV-vis diffuse reflectance spectra were recorded at room temperature on an Agilent Cary 60 UV-Vis spectrophotometer.

### Synthesis of the Organic Molecule 2,3-dihydroxybenzaldehyde Oxime ( $\text{H}_3\text{dihybo}$ ).

To a stirred anhydrous ethanol solution (30 mL) containing NaOH (0.694 g, 17.37 mmol) and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (1.207 g, 17.37 mmol) was added in one portion solid 2,3-dihydroxy-benzaldehyde (1.500 g, 10.86 mmol). The reaction mixture was refluxed for 3 h under argon. Then, the solvent was evaporated to dryness under high vacuum to give a crude light brown mixture. Dichloromethane (50 mL) was added to the solid and the solution was refluxed for 10 min under argon. The boiling solution was filtered and cooled first to room temperature ( $\approx 20\text{ }^\circ\text{C}$ ) and then to  $4\text{ }^\circ\text{C}$  for an hour during which period white crystals of the desired product were formed. The crystals were filtered and dried under vacuum to yield 1.33 g of  $\text{H}_3\text{dihybo}$ . Yield: 80%, (based on 2,3-dihydroxy-benzaldehyde). Mp  $113\text{ }^\circ\text{C}$ . High-resolution electrospray ionization mass spectrometry(+) [HR-ESI(+)]-MS: calcd for  $\text{C}_7\text{H}_8\text{NO}_3$  ( $[\text{M} + \text{H}]^+$ ) 154.0504, found 154.0503. Anal. Calcd (%) for  $\text{C}_7\text{H}_7\text{NO}_3$  ( $M_r = 153.137$ ): C, 54.88; H, 4.61; N, 9.15. Found (%): C, 54.90; H, 4.59; N, 9.13.  $R_f = 0.06$  ( $\text{CHCl}_3/\text{C}_6\text{H}_{14}$  4:1).

**Synthesis of  $\text{K}_2[\text{Ti}^{\text{IV}}_6(\mu_3\text{-O})_2(\mu\text{-O})_3(\text{OCH}_3)_4(\text{HOCH}_3)_2(\mu\text{-}\eta^1, \eta^2, \eta^1\text{-Hdihybo-}O, O', N)_6] \cdot \text{CH}_3\text{OH}$  (1).** To a stirred methyl alcohol solution (4 mL) were successively added  $\text{H}_3\text{dihybo}$  (69.8 mg, 0.456 mmol) and  $\text{TiCl}_4$  (0.05 mL, 86.5 mg, 0.456 mmol). The colorless solution of the ligand turned dark red upon addition of  $\text{TiCl}_4$ . Then, addition of solid  $\text{KOH}$  (51.1 mg, 0.912 mmol) in one portion resulted in the formation of a small quantity of precipitate. The solution was kept overnight at  $\approx 4$  °C (to remove most of the formed  $\text{KCl}$ ); the mixture was filtered off and the dark red filtrate was kept at room temperature ( $\approx 20$  °C) for 3-4 days during which period of time 77.0 mg dark red crystals of compound **1** were formed. The crystals were filtered off and dried in ambient atmosphere. (Yield: 65%, based on  $\text{H}_3\text{dihybo}$ ). Elemental anal. calc. for  $(\text{C}_{48}\text{H}_{50}\text{N}_6\text{O}_{29}\text{K}_2\text{Ti}_6 \cdot \text{CH}_3\text{OH}, M_r = 1572.381 \text{ g mol}^{-1})$ : C 37.41, H 3.46, N 5.35; found: C 37.25, H 3.57, N 5.25.

**$[\text{Zr}^{\text{IV}}_6(\mu_3\text{-O})_2(\mu\text{-O})_3(\mu\text{-}\eta^1, \eta^2, \eta^1\text{-Hdihybo-}O, O', N)_6(\text{OH}_2)_6] \text{Cl}_2 \cdot 2\text{Bu}_4\text{NCl} \cdot 2\text{CH}_3\text{OH}$  (2).** To a stirred methyl alcohol solution (2 ml) were successively added 2,3-dihydroxybenzaldehyde oxime (65.7 mg, 0.429 mmol), and  $\text{ZrCl}_4$  (100.0 mg, 0.429 mmol). The colorless solution of the ligand turned orange upon addition of  $\text{ZrCl}_4$ . Then, addition of 2.20 mL tetrabutylammonium hydroxide, 0.39 M in methyl alcohol, (222.0 mg, 0.858 mmol) in one portion, caused the formation of small amount of a white precipitate which was filtered off. The light orange filtrate was kept at room temperature ( $\approx 20$  °C) for 3-4 days during which period yellow crystals of compound **2** were formed. We were unable to prepare analytically pure sample on a preparative scale because compound **2** is very hygroscopic.

**$[\text{Zr}^{\text{IV}}_6(\mu_3\text{-O})_2(\mu\text{-O})_3(\mu\text{-}\eta^1, \eta^2, \eta^1\text{-Hdihybo-}O, O', N)_6(\text{OCH}_3)_2(\text{OH}_2)_4] \cdot 2\text{CH}_3\text{OH}$  (3).** To a stirred methyl alcohol solution (4.0 mL) were successively added 2,3-

dihydroxybenzaldehyde oxime (65.7 mg, 0.429 mmol), ZrCl<sub>4</sub> (100.0 mg, 0.429 mmol) and KOH (48.1 mg, 0.858 mmol). Upon addition of KOH a small amount of a white precipitate was formed. The solution was kept overnight at  $\approx 4$  °C (to remove most of the formed KCl) which was filtered off. The light orange filtrate was kept at room temperature ( $\approx 20$  °C) for 3-4 days during which period, 45 mg yellow crystals of compound **3** were formed. The crystals were filtered off and dried in ambient atmosphere. (Yield 37%, based on H<sub>3</sub>dihybo). Elemental anal. calc. for (C<sub>44</sub>H<sub>44</sub>N<sub>6</sub>O<sub>29</sub>Zr<sub>6</sub>·2CH<sub>3</sub>OH,  $M_r = 1732.28$  g mol<sup>-1</sup>): C 31.89, H 2.96, N 4.85; found: C 31.93, H 3.15, N 4.80.

**X-ray Crystallography.** Suitable single crystal was selected and mounted onto a rubber loop using Fomblin oil. Single-crystal X-ray diffraction data of **1** - **3** were recorded on a Bruker Apex CCD diffractometer ( $\lambda$  (MoK $\alpha$ ) = 0.71073 Å) at 150 K equipped with a graphite monochromator. Structure solution and refinement were carried out with SHELXS-97<sup>22</sup> and SHELXL-97<sup>23</sup> using the WinGX software package.<sup>24</sup> Data collection and reduction were performed using the Apex2 software package. Corrections for incident and diffracted beam absorption effects were applied using empirical absorption corrections.<sup>25</sup> All the atoms and most of the carbon atoms were refined anisotropically. Solvent molecule sites were found and included in the refinement of the structures. Multiple crystallisation efforts allowed us to obtain single crystals and subsequent data collection of compound **3**. However, the poor quality of the single crystal led to structure solution with slightly elevated *R* factor. Final unit cell data and refinement statistics for compounds **1** - **3** are collated in Table S1.

**NMR Analysis.** The solution was transferred into a 5 mm NMR tube. NMR experiments were performed on a Bruker AV500 spectrometer (Bruker Biospin, Rheinstetten, Germany) at 298 K using the Topspin 2.1 suite. All 1D <sup>1</sup>H NMR spectra

were collected using a 30° flip angle, a spectral width of 14 ppm, a relaxation delay of 5 s and an acquisition time of 4.3 s. 64 K data points were collected and the FIDs were treated using a line broadening exponential function of 0.3 Hz. Phase adjustment and baseline correction was carried out using Topspin 2.1 suite. Signal integration was manually performed.

2D  $^1\text{H}$ - $^1\text{H}$  TOCSY,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR experiments were recorded using standard Bruker software.  $T_1$  measurements were obtained by using the inversion recovery method. The 2D  $^1\text{H}$ - $^1\text{H}$  TOCSY experiments were measured using 256 increments of 2 K size (each consisting of 33 scans) covering the full spectrum (10 ppm in both dimensions). The standard grNOESY pulse sequence was used in the 2D  $^1\text{H}$ - $^1\text{H}$  grEXSY-grNOESY measurements. These spectra were acquired using 512 increments of 2 K size (with 60 scans each) covering full spectrum (10 ppm in both dimensions) or partial (3 – 4 ppm) regions of the spectrum. The delay time used in the 2D spectra was 3.0 s, based on the measured  $T_1$  values. Variable mixing times ranging from 0 to 0.1 s were used.  $^1\text{H}$ - $^{13}\text{C}$  grHSQC and  $^1\text{H}$ - $^{13}\text{C}$  grHMBC NMR experiments were measured using 512 increments of 2 K size (each consisting of 40 scans) covering the full spectrum [10 ppm at f2, and 160 ppm (HSQC) and 220 ppm (HMBC) at f1 dimensions]. All NMR samples were prepared by dissolving the crystalline compounds in  $\text{CD}_3\text{OD}$  at room temperature.

**Photocurrent Measurements.** The photocurrent measurement of compounds **1** and **3** was carried out on FTO electrodes by drop casting solutions of the clusters of appropriate concentrations according to the following procedure. Crystals (5 mg) of compounds **1** and **3** were dissolved in 2 mL of methanol. 0.2  $\mu\text{L}$  of the prepared solutions were dropped casted onto a fluorine doped indium–tin oxide (FTO) glass (2.5 x 5 cm). After evaporation under ambient atmosphere, the coated film was used as the

working electrode. Photocurrent measurements were conducted using a CHI 760E electrochemical workstation in a three-electrode system, with an Ag/AgCl electrode as the reference electrode and a Pt wire as the auxiliary electrode. All the tests were performed at the same bias potential of +0.4 V, and an aqueous solution of Na<sub>2</sub>SO<sub>4</sub> (0.1 mol L<sup>-1</sup>) was used as the electrolyte. A 250 W high-pressure xenon lamp was used as a full-wavelength light source, located 10 cm away from the FTO electrode. The on-off irradiation intervals were 10 s.

**ESI Mass Spectrometry.** All MS data was collected using a Q-trap, time-of-flight MS (Maxis Impact MS) instrument supplied by Bruker Daltonics Ltd. The detector was a time-of-flight, microchannel plate detector and all data was processed using the Bruker Daltonics Data Analysis 4.1 software, whilst simulated isotope patterns were investigated using Bruker Isotope Pattern software and Molecular Weight Calculator 6.45. The calibration solution used was Agilent ES tuning mix solution, Recorder No. G2421A, enabling calibration between approximately 100 *m/z* and 3000 *m/z*. This solution was diluted 60:1 with MeCN. Samples were dissolved in MeOH and introduced into the MS via direct injection at 180 μL h<sup>-1</sup>. The ion polarity for all MS scans recorded was negative, at 180 °C, with the voltage of the capillary tip set at 4000 V, end plate offset at -500 V, funnel 1 RF at 300 V<sub>pp</sub> and funnel 2 RF at 400 V<sub>pp</sub>.

**Computational Details.** The NICS<sub>zz</sub> scan curve was calculated using cartesian coordinates obtained from the X-ray structure of the compounds as well for the model compounds employing the GIAO (gauge-including atomic orbitals) DFT method<sup>26,27</sup> as implemented in the Gaussian09 series of programs<sup>28</sup> using the PBE0 functional in combination with the 6-31G(d,p) and the Def2-TZVP basis sets for the non-metal and the Ti and Zr metal atoms respectively. The computational protocol will henceforth be denoted as GIAO/PBE0/Def2-TZVP(M)U6-31G(d,p)(E).

## Results and Discussion

### Synthesis of the Ligand H<sub>3</sub>dihybo and its Ti and Zr Hexanuclear Compounds

The ligand H<sub>3</sub>dihybo was prepared via oximation of 2,3-dihydroxy-benzaldehyde. The synthesis was carried out under argon to avoid the oxidation of the free hydroxylamine and the ligand. The organic molecule H<sub>3</sub>dihybo was synthesized following a modified version of the reported procedure<sup>17</sup> to avoid some unnecessary steps. The completion of the reaction was determined by TLC. The extraction of the crude H<sub>3</sub>dihybo with dichloromethane proved to be an effective purification method.

The hexanuclear Ti<sub>6</sub> cluster **1** was prepared by reacting the ligand H<sub>3</sub>dihybo (1 equiv.) with TiCl<sub>4</sub> (1 equiv., distilled just prior to its use) and KOH (2 equiv.) in methanol. Dark red crystals of **1** were formed after slow evaporation of the methanol (3 d) at ambient temperature ( $\approx 20$  °C). The hexanuclear Zr<sub>6</sub> clusters **2** and **3** were prepared according to the procedure for **1** using ZrCl<sub>4</sub> instead of TiCl<sub>4</sub> and Bu<sub>4</sub>NOH and KOH as bases for the synthesis of **2** and **3** respectively.

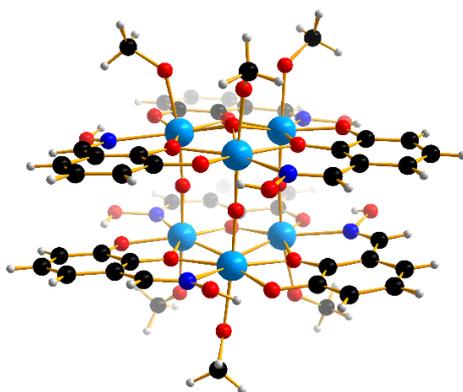
### Crystal structures

Single crystal X-ray diffraction analysis revealed that compounds **1**, **2** and **3** have the same structural motif (Figures 1, 2A, and 3 respectively for **1-3**) and thus, the structure of compound **2** will be reported in detail. The centrosymmetric structure of compound **2** consists of six zirconium atoms, three  $\mu$ -O, two  $\mu_3$ -O, six ( $\mu$ - $\eta^1$ :  $\eta^2$ :  $\eta^1$ -Hdihybo<sup>2-</sup>) ligands (Figure 2B and Scheme 3) and six terminal water molecules. The six zirconium atoms are seven-coordinate, with an NO<sub>6</sub> coordination environment in a pentagonal bipyramidal arrangement. The three edge-sharing zirconium atoms, via a  $\mu_3$ -O and a  $\mu$ -O<sub>phenoxy</sub> atoms (Figure 2B), are linked by one  $\mu_3$ -O atom to generate a Zr<sub>3</sub>( $\mu_3$ -O)

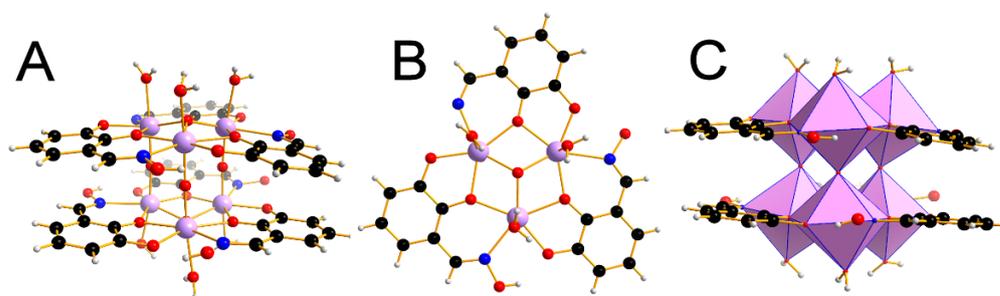
subunit. The two  $Zr_3(\mu_3-O)$  subunits, featuring a pyramidal mode, are connected by three  $-O^{2-}$  atoms via a vertex-sharing mode to form a  $Zr_6O_5$  core structure (Figure 2C). The symmetry related  $\mu_3-O$  atoms in the two  $Zr_3(\mu_3-O)$  subunits are 0.501(3) Å above the plane defined by the  $Zr_3$  structural unit. The Zr - ( $\mu_3-O$ ) bond lengths [2.061(4)-2.072(4) Å, av. 2.067 Å] and the Zr - ( $\mu-O$ ) bond lengths [2.204(4)-2.231(4) Å, av. 2.217 Å] are similar to those reported in the literature.<sup>29,30</sup>

The Zr...Zr distances in the symmetry related structural units  $Zr_3(\mu_3-O)$  [3.471(1)-3.481(1) Å, av. 3.474 Å] are longer than those observed in  $\{[(EtMe_4C_5)Zr^{IV}]_6(\mu_6-O)(\mu_3-O)_8\} \cdot (C_7H_8)^{31}$  [3.1542(9)-3.1709(11) Å, av. 3.1645 Å] but shorter than those in  $\{[(Cp^*Zr^{IV})_6(\mu_4-O)(\mu-O)_4(\mu-OH)_8]2(C_7H_8)\}^{32}$  [3.564(1)-3.608(1) Å, av. 3.586 Å]. The three angles in the symmetry related  $Zr_3$  triangles are almost 60° and thus, it is obvious that the  $Zr_3$  triangles are equilateral in a similar manner to the  $Ti_3$  based triangles observed in **1**. The  $d(Zr^{IV}-O_{cat})_{av.}$  and  $d[Zr^{IV}-(\mu-O_{cat})]_{av.}$  are 2.120(4) and 2.217(4) respectively and are very close to those reported in the literature.<sup>33</sup> The deprotonated catecholate moiety adopts a singly bridging chelate  $\mu-(O, O', O')$  mode.<sup>33</sup> The  $d(Zr^{IV}-N_{ox})_{av.}$  of 2.384(6) Å is much longer in comparison to the reported value of  $\approx 2.20$  Å,<sup>34</sup> but in the latter case the oxime is deprotonated. Compound **2** is the first example of a polyoxo-catecholate zirconium compound to be reported.

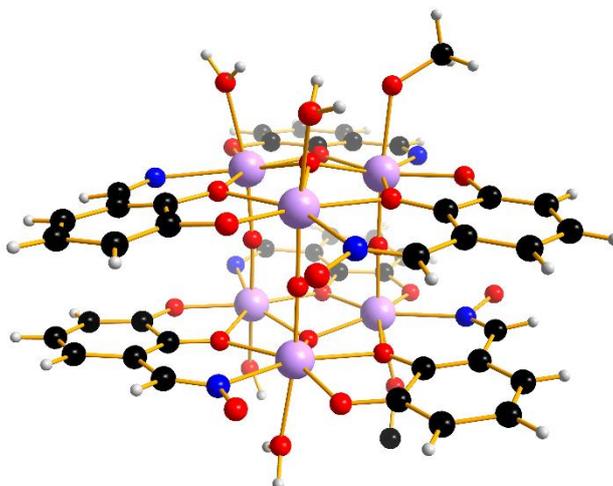
All the  $Zr^{IV}_6$  discrete polyoxo-clusters in the only three different  $Zr_6$  core structures,  $\{[Zr^{IV}_6(\mu_6-O)(\mu_3-O)_8],^{24} [Zr^{IV}_6(\mu_4-O)(\mu-O)_4(\mu-OH)_8]^{32}$  and  $[Zr^{IV}_6(\mu_3-O)_4(\mu_3-OH)_4]^{35}\}$ , reported thus far have the six zirconium atoms in an octahedral arrangement. The octahedral  $Zr_6$  arrangement has also been observed in the  $Zr^{IV}_6$ -MOFs.<sup>14</sup> Thus, the  $Zr_6$  discrete polyoxo-cluster  $[Zr^{IV}_6(\mu_3-O)_2(\mu-O)_3]$  of this study is a unique example with a trigonal prismatic arrangement of the six zirconium atoms and a unique  $Zr_6$  core structure.



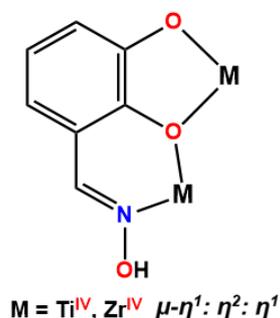
**Figure 1.** Ball-and-stick plot of the anion of **1**.



**Figure 2.** Ball-and-stick plot of the cation of **2** (A). Ball-and-stick plot of the structural unit  $[\text{Zr}_3(\mu_3\text{-O})(\mu\text{-}\eta^1: \eta^2: \eta^1\text{-Hdihydro-}O,O',N)_3(\text{OH}_2)_3]$  (B). The polyhedral/ball-and-stick representation of the cation of **2** (C).



**Figure 3.** Ball-and-stick plot of compound **3**. Solvent molecules have been omitted for clarity.



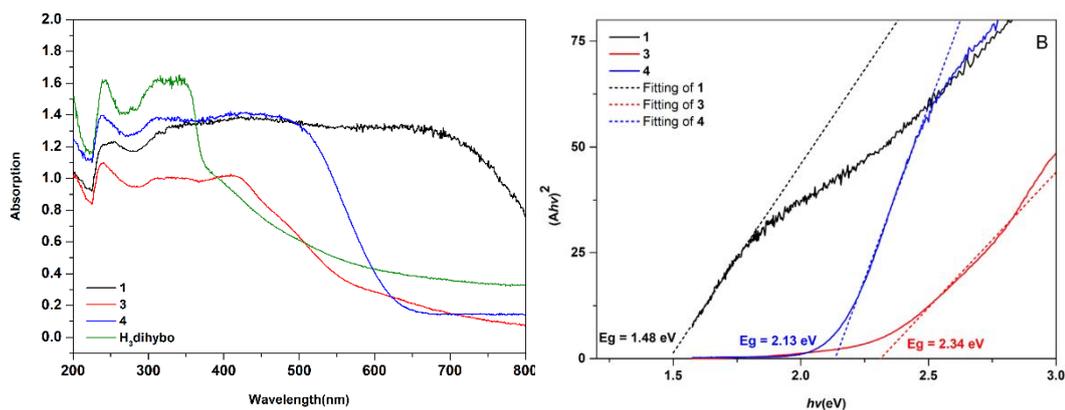
**Scheme 3.** Coordination Mode of the Ligand Hdihybo<sup>2-</sup> in the Compounds **1-3**

In marked contrast to missing polyoxo-catecholate zirconium clusters there are a few examples of polyoxo-catecholate titanium clusters.<sup>1h,3b,36</sup> In these polyoxo-titanium catecholate clusters the main binding modes of the deprotonated catecholate moiety are the singly bridging chelate  $\mu\text{-}(O, O', O')$  and the singly bridging  $\mu\text{-}(O, O')$ .

A comparison of the metrical parameters of the titanium cluster **1** with those of the zirconium cluster **2** reveals the following: In the case of the titanium isostructural cluster **1** the  $\text{Ti}_6$  metallic core appears slightly contracted with the relevant Ti - ( $\mu_3\text{-O}$ ) distances found to be [1.955(3)-1.958(3) Å, av. 1.957 Å] and the Ti - ( $\mu\text{-O}$ ) bond lengths [2.102(3)-2.072(3) Å, av. 2.089 Å]. Additionally, the Ti...Ti distances in the symmetry related structural units  $\text{Ti}_3(\mu_3\text{-O})$  [3.300(1)-3.292(1) Å, av. 3.296 Å] are shorter than those observed in the Zr-analogue [3.471(1)-3.481(1) Å, av. 3.474 Å]. The three angles in the symmetry related  $\text{Ti}_3$  triangles are almost 60° forming  $\text{Ti}_3$  equilateral triangles in a similar manner to the  $\text{Zr}_3$  based triangles observed in **2**. The metrical parameters of the structure of compound **3** (Figure 3) are very similar to those observed in **2**.

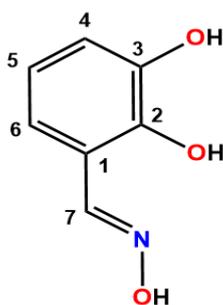
At this point, it is worth noting that the ligands H<sub>3</sub>dihybo and H<sub>3</sub>pidiox<sup>16a</sup> (Scheme 1) which have donor atoms in three neighboring positions of the rings gave the hexanuclear titanium compounds **1** and  $K_6[Ti^{IV}_6(\mu_3-O)_2(\mu_2-O)_3(OCH_3)_6(\mu_2-Hpidiox)_4(\mu_2-pidiox)_2] \cdot 7.5CH_3OH$  (**4**)<sup>16a</sup> respectively with the same core structure  $[Ti_6(\mu_3-O)_2(\mu-O)_3]$ . This observation might demonstrate a new strategy to control the formation of hexanuclear titanium clusters.

**Solid State UV-vis-NIR Spectroscopy.** Figure 4 shows the solid-state UV-vis-NIR spectra of compounds **1**, **3** and **4**<sup>16a</sup> and of the ligand H<sub>3</sub>dihybo. Comparison of the spectra of the titanium compounds **4**<sup>16a</sup> and **1** (this work) reveals a 200 nm expansion of the absorbance band of **1** related to **4** towards the red region of the spectra (Figure 4). The band-gaps for the three compounds found to be 1.48, 2.34 and 2.13 eV respectively and were calculated from the solid state spectra by the Kubelka-Munk method.<sup>37</sup> These low band-gap values for compounds **1** and **3** reveal their potential use as semiconducting photo-catalysts and thus, it is crystal-clear that the marriage of the catechol moiety with the oxime group was quite successful in the modulation of the band-gaps of TiO<sub>2</sub> and ZrO<sub>2</sub>. At this point, it is worth noting that the value of 1.48 eV band-gap in **1** constitutes the lowest value reported thus far for any titanium oxide cluster. The synergistic effect of the oxime group presumably plays a vital role in achieving such a low value for the band-gap in **1**.



**Figure 4.** Solid-state UV-vis-NIR spectra of compounds **1**, **3**, **4** and H<sub>3</sub>dihybo (**A**). Tauc plots of compounds **1**, **3** and **4** (**B**).

**NMR Spectroscopy.** Table 1 displays the <sup>1</sup>H NMR chemical shifts of the ligand H<sub>3</sub>dihybo and of the compounds **1** and **3** in solution (CD<sub>3</sub>OD) and Table 2 displays the <sup>13</sup>C NMR chemical shifts of H<sub>3</sub>dihybo, **1** and **3** in solution as assigned by 2D spectra [(<sup>1</sup>H, <sup>13</sup>C) HSQC / HMBC spectra, see Figures S1 and S2]. The numbering of the carbon atoms of the ligand H<sub>3</sub>dihybo is depicted in Scheme 4.



**Scheme 4.** The numbering of the carbon atoms of the ligand H<sub>3</sub>dihybo

**Table 1.**  $^1\text{H}$  NMR Chemical Shifts for  $\text{H}_3\text{dihybo}$ , **1** and **3** and the Shielding / Deshielding Effect ( $\Delta\delta$ ) upon Complexation.

	<b>H<sub>3</sub>dihybo</b>	<b>1</b> / $\Delta\delta^*$	<b>3</b> / $\Delta\delta^*$
H(7)	8.19	7.85 / (-0.34)	7.86 / (-0.33)
H(4)	6.80	6.78 / (-0.02)	6.83 / (+0.03)
H(5)	6.72	6.86 / (+0.16)	6.74 / (+0.02)
H(6)	6.76	6.43 / (-0.33)	6.32 / (-0.41)

**Table 2.**  $^{13}\text{C}$  NMR Chemical Shifts for  $\text{H}_3\text{dihybo}$ , **1** and **3** and the Shielding / Deshielding effect ( $\Delta\delta$ ) upon Complexation.

	<b>H<sub>3</sub>dihybo</b>	<b>1</b> / $\Delta\delta^*$	<b>3</b> / $\Delta\delta^*$
C(1)	117.6	114.8 / (-2.8)	115.8 / (-1.8)
C(2)	146.5	152.8 / (+6.3)	154.2 / (+8.7)
C(3)	146.4	153.6 / (+8.2)	153.9 / (+7.5)
C(4)	120.4	115.5 / (-4.9)	118.6 / (-1.8)
C(5)	118.8	121.6 / (+2.8)	121.0 / (+2.2)
C(6)	121.7	123.4 / (+1.7)	123.8 / (+2.1)
C(7)	152.3	148.1 / (-4.2)	151.5 (-0.8)

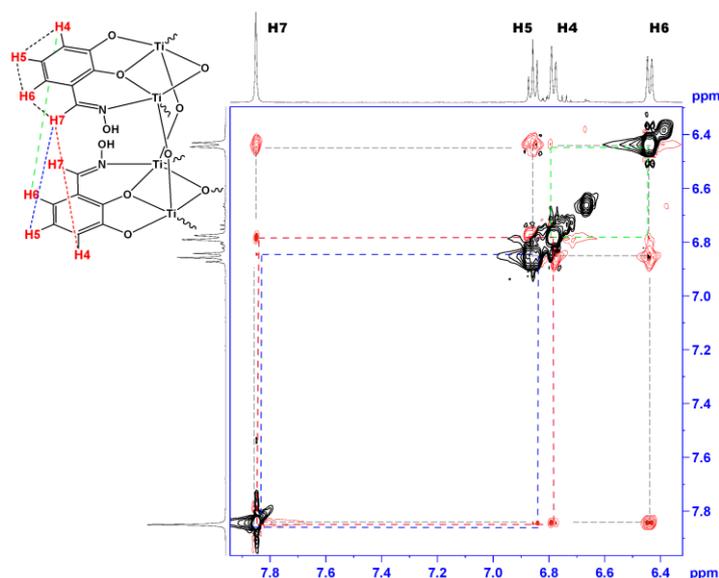
\* $\Delta\delta = \delta_{\text{M-L}} - \delta_{\text{L}}$

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the compounds **1** and **3** in solution gave peaks shifted in comparison to the peaks of the free ligand due to the ligation of  $\text{H}_3\text{dihybo}^{2-}$  to the Ti and Zr metal ions. In particular, C(2) and C(3) show a strong deshielding for both **1** (+6.3 and +8.2 ppm, see Table 2) and **3** (+8.7 and +7.5 ppm, see Table 2) due to the ligation of the deprotonated catecholate oxygen atoms with the metal atoms. The coordination of the metal ions to the oxime nitrogen atom causes shielding of C(7) for both **1** (-4.2 ppm, see Table 2) and **3** (-0.8 ppm, see Table 2). The proton attached to the C(7) carbon atom is also highly deshielded for both complexes ( $\Delta\delta \sim +4.2$  ppm) presumably due to the complexation of the metal atoms with the oxime nitrogen atom and/or the formation of intramolecular hydrogen bond between the oxime proton of one ligand with the catecholate oxygen atom [C(3)-O<sup>-</sup>] of the neighboring  $\text{H}_3\text{dihybo}^{2-}$ .

The differences of the C, H shielding/deshielding values between **1** and **3** might be due to the different through space neighboring anisotropy interactions induced by the applied magnetic field on either the Ti-O and Zr-O bonds or the Ti<sub>3</sub>O and Zr<sub>3</sub>O metalloaromatic cores respectively (see Tables 1 and 2).

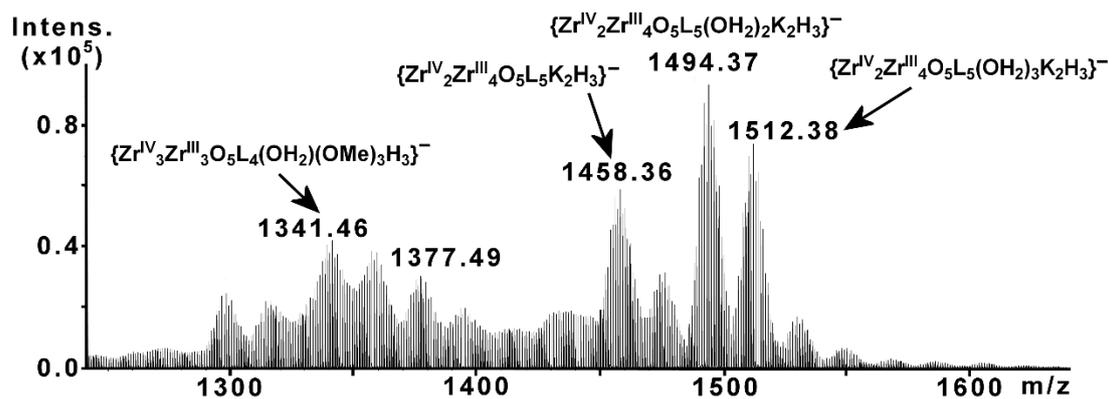
The  $\Delta\delta$  values of H(4) protons in **1** and **3** do not follow the expected trend, that is, either both negative or positive. A reasonable explanation to this, it is that these values are so small, close to zero, in marked contrast to that of all hydrogen and carbon atoms, and even slight differences, such as solvent/bulk properties of molecules around the solute of the proton, minor variance in temperature, etc., alter the 'expected trend'.

The 2D  $\{^1\text{H}\}$  NOESY-EXSY spectra of compounds **1** and **3** in solution gave strong NOESY cross peaks between the neighboring protons of the ligand [H(7)-H(6), H(6)-H(5), H(5)-H(4)] as shown in Figure 5. In addition to the intra-ligand proton interactions the 2D  $\{^1\text{H}\}$  NOESY-EXSY spectra gave weaker NOESY peaks between the protons H(7)-H(4), H(7)-H(5) and H(4)-H(6) (Figure 5). These NOESY peaks were assigned to the interactions between the protons of the ligands belonging to the two  $\text{M}_3(\text{Hdihybo}^{2-})_3$  planes in the complexes as shown for complex **1** in Figure 5. The intensity of the NOESY cross peaks suggests that the distances between the protons 4-7 are  $\text{H}(7)\text{-H}(4) < \text{H}(4)\text{-H}(6) < \text{H}(7)\text{-H}(5)$  which are in agreement with the distances in the crystal structures of **1** and **3**. Thus, the compounds **1** and **3**, in solution, retain their structural integrity. The NMR spectra of **1** and **3** in D<sub>2</sub>O gave similar features to those observed in deuterated methanol and this fact supports that **1** and **3** are hydrolytically stable.



**Figure 5.** 2D  $\{^1\text{H}\}$  NOESY spectrum of the compound **1** and the assignments of the NOESY interactions.

**ESI-MS Spectrometry.** In an effort to characterize further the hexanuclear zirconium(IV) and titanium(IV) clusters in solution we employed high resolution ESI-MS to determine unambiguously the structural integrity and composition of the zirconium and titanium-based species in solution.<sup>38</sup> The ESI-MS studies were performed in methanol. In both cases, the observation of the higher intensity set of distribution envelopes is due to the existence of the hexanuclear moiety, resulting from the combination of protons, counterions and solvent molecules. In the case of the zirconium species (**3**), the region of higher  $m/z$  values is populated by a series of distribution envelopes assigned to -1 charged species and correspond to the intact  $\{\text{Zr}_6\}$  cluster (Figure 6). In this case three of the coordinating axial groups have been removed during the ionization process (e.g.  $\{\text{Zr}^{\text{IV}}_2\text{Zr}^{\text{III}}_4\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_6(\text{OH}_2)_2(\text{OCH}_3)_3\text{K}_3\text{H}_5\}^-$ ), Table 3. In both cases, the observation of different oxidation states for the metal centres and presence of other fragments during the course of the studies is due to the ionization and transfer process and has been observed in numerous occasions.<sup>39,40,41</sup>



**Figure 6.** Negative mode electrospray ionization mass spectrum (ESI-MS) of  $\{\text{Zr}_6\}$  (**3**) cluster in  $\text{CH}_3\text{OH}$ .

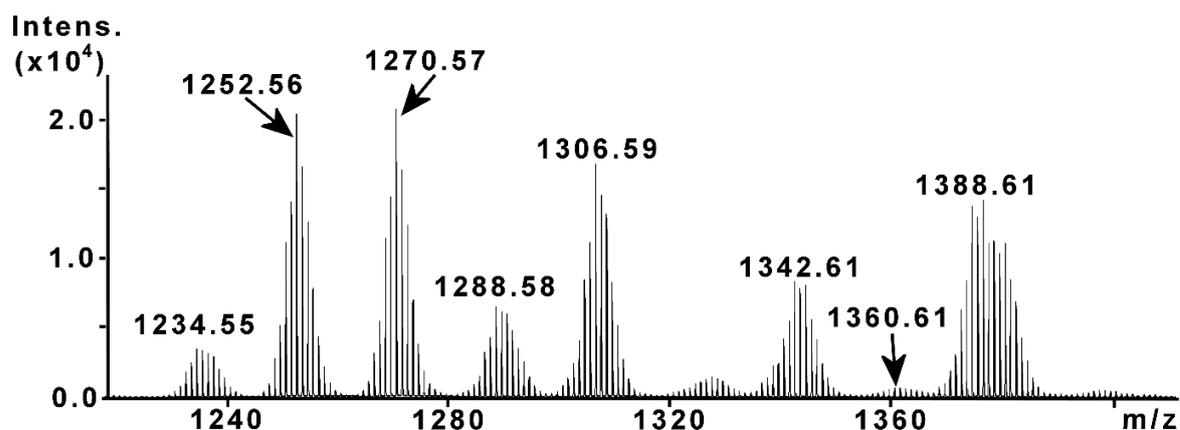
Interestingly, the lower  $m/z$  region (*ca.* 700 – 800) revealed the presence of fundamental trimeric building blocks generated during the ionization process. The distribution envelopes centered at 773.75, 755.75 and 737.74  $m/z$  values have been identified as the intact Zr-oxo centered triangles associated with a different number of counterions and solvent molecules. The identification of the building blocks that appear in the mass spectrometry studies suggests the existence of an underlying sequential mechanism of assembly, where the initial formation of trimeric clusters takes place prior to their subsequently self-assembly into the hexanuclear species that finally crystallize. A similar behavior has been observed in the solution studies conducted for the  $\{\text{Ti}_6\}$  species reported recently.<sup>16a</sup> More specifically, we observed the fully reduced,  $\{\text{Zr}_3^{\text{III}}\text{O}(\text{C}_7\text{NO}_3\text{H}_4)_2(\text{OCH}_3)_3(\text{OH}_2)_5\text{H}\}^-$  (773.75),  $\{\text{Zr}_3^{\text{III}}\text{O}(\text{C}_7\text{NO}_3\text{H}_4)_2(\text{OCH}_3)_3(\text{OH}_2)_4\text{H}\}^-$  (755.75) and  $\{\text{Zr}_3^{\text{III}}\text{O}(\text{C}_7\text{NO}_3\text{H}_4)_2(\text{OCH}_3)_3(\text{OH}_2)_3\text{H}\}^-$  (737.74) Zr-based oxo-centered molecular triangles, respectively.

**Table 3.** Representation of the Experimentally identified and Simulated  $m/z$  Values of Distribution Envelopes of  $\{\text{Zr}_6\}$  Cluster

Exp.	Theor.	Charge	Formula*
1716.36	1716.49	-1	$\{\text{Zr}^{\text{IV}}_2\text{Zr}^{\text{III}}_4\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_6(\text{OCH}_3)(\text{OH}_2)_2\text{K}_3\text{H}_5\}^-$
1512.38	1512.48	-1	$\{\text{Zr}^{\text{IV}}_2\text{Zr}^{\text{III}}_4\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_3\text{K}_2\text{H}_3\}^-$
1494.37	1494.47	-1	$\{\text{Zr}^{\text{IV}}_2\text{Zr}^{\text{III}}_4\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_2\text{K}_2\text{H}_3\}^-$
1476.36	1476.46	-1	$\{\text{Zr}^{\text{IV}}_2\text{Zr}^{\text{III}}_4\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)\text{K}_2\text{H}_3\}^-$
1458.36	1458.45	-1	$\{\text{Zr}^{\text{IV}}_2\text{Zr}^{\text{III}}_4\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5\text{K}_2\text{H}_3\}^-$
1377.49	1377.59	-1	$\{\text{Zr}^{\text{IV}}_3\text{Zr}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_4(\text{OCH}_3)_3(\text{OH}_2)_3\text{H}_3\}^-$
1357.47	1357.56	-1	$\{\text{Zr}^{\text{IV}}_5\text{Zr}^{\text{III}}\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_4(\text{OCH}_3)_3(\text{OH}_2)_2\text{H}\}^-$
1341.46	1341.57	-1	$\{\text{Zr}^{\text{IV}}_3\text{Zr}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_4(\text{OCH}_3)_3(\text{OH}_2)\text{H}_3\}^-$
773.75	773.85	-1	$\{\text{Zr}_3^{\text{III}}\text{O}(\text{C}_7\text{NO}_3\text{H}_4)_2(\text{OCH}_3)_3(\text{OH}_2)_5\text{H}\}^-$
755.75	755.85	-1	$\{\text{Zr}_3^{\text{III}}\text{O}(\text{C}_7\text{NO}_3\text{H}_4)_2(\text{OCH}_3)_3(\text{OH}_2)_4\text{H}\}^-$
737.74	737.84	-1	$\{\text{Zr}_3^{\text{III}}\text{O}(\text{C}_7\text{NO}_3\text{H}_4)_2(\text{OCH}_3)_3(\text{OH}_2)_3\text{H}\}^-$

\* Contamination of compound **3** with small amounts of KCl during the synthesis (which can't be removed even after repeated washing) can be easily detected by the high resolution electrospray ionization Q-TOF instrument with detection limit much lower than the elemental analysis.

In a similar manner, investigation of the titanium adduct in solution under the same experimental conditions revealed a series of distribution envelopes with different amount of solvent molecules associated with the intact hexanuclear cluster of the general formula  $\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_x\}^-$ , where  $x = 0 - 8$  (Figure 7, Table 4). Smaller fragments of the cluster occurring during the studies were observed at lower  $m/z$  values such as  $\{\text{Ti}^{\text{IV}}_4\text{Ti}^{\text{III}}\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_4\text{H}_2\}^-$  (921.75) and  $\{\text{Ti}^{\text{IV}}_4\text{Ti}^{\text{III}}\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_4\text{H}_2(\text{OH}_2)\}^-$  (939.75).  $\{\text{Ti}^{\text{IV}}_4\text{Ti}^{\text{III}}\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_4\text{H}_2(\text{OH}_2)\}^-$  (939.75).

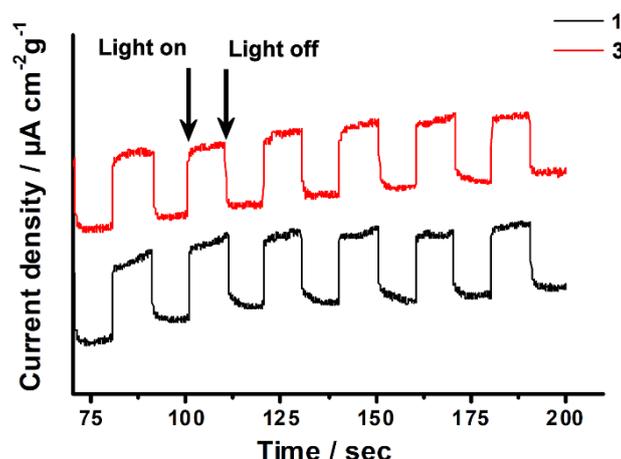


**Figure 7.** Negative mode electrospray ionization mass spectrum (ESI-MS) of  $\{\text{Ti}_6\}$  (**1**) cluster in  $\text{CH}_3\text{OH}$ .

**Table 4.** Representation of the Experimentally Identified and Simulated  $m/z$  Values of Distribution Envelopes of  $\{\text{Ti}_6\}$  Cluster

Exp.	Theor.	Charge	Formula
1234.55	1234.66	-1	$\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5\}^-$
1252.56	1252.66	-1	$\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)\}^-$
1270.57	1270.67	-1	$\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_2\}^-$
1288.58	1288.57	-1	$\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_3\}^-$
1306.59	1306.69	-1	$\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_4\}^-$
1342.61	1342.71	-1	$\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_6\}^-$
1360.61	1360.71	-1	$\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_7\}^-$
1388.61	1388.72	-1	$\{\text{Ti}^{\text{IV}}_3\text{Ti}^{\text{III}}_3\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_5(\text{OH}_2)_8\}^-$
921.75	921.81	-1	$\{\text{Ti}^{\text{IV}}_4\text{Ti}^{\text{III}}\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_4\text{H}_2\}^-$
939.75	939.82	-1	$\{\text{Ti}^{\text{IV}}_4\text{Ti}^{\text{III}}\text{O}_5(\text{C}_7\text{NO}_3\text{H}_4)_4\text{H}_2(\text{OH}_2)\}^-$

**Photocurrent Response.** The charge-separation efficiency of a semiconductor material is one of the important parameters which define its potential for practical applications. The photocurrent response of the two photoelectrodes based on compounds **1** and **3** have been carried out using a three-electrode set up. As shown in Figure 8, clear photocurrent responses were observed for both compounds. Upon illumination, the photocurrents were quickly generated without an obvious intensity decrease and remained constant during the measurement. When the light source was switched off, the photocurrents rapidly decayed, indicative of their good photoelectric response and photophysical stability during the experiment. The two compounds exhibited comparable photocurrent densities per gram of deposited material and found to be approx.  $40 \text{ mA cm}^{-2} \text{ g}^{-1}$ .



**Figure 8.** Photocurrent densities of compounds **1** and **3** (0.1 M  $\text{Na}_2\text{SO}_4$  solution).

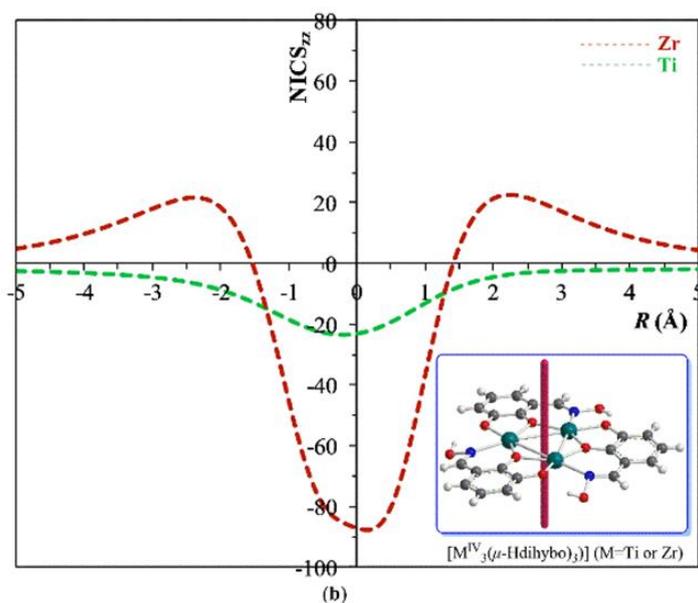
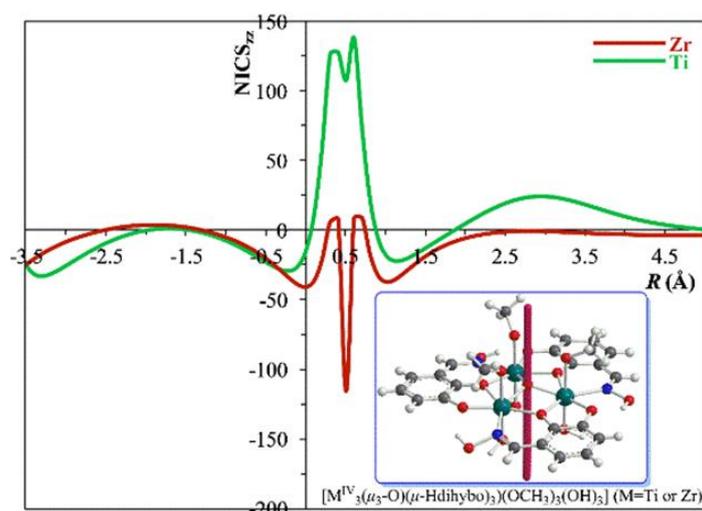
**Theoretical Study.** Having in mind the previously reported<sup>16a</sup> observation of metalloaromaticity phenomenon exhibited by the hexanuclear titanium compound **4** (see page 16) with the ligand (2Z,6Z)-piperidine-2,6-dione dioxime ( $\text{H}_3\text{pidiox}$ ,<sup>16a</sup> Scheme 1) we investigated whether the cyclic trinuclear metallic ring cores  $\text{M}^{\text{IV}}_3$ , ( $\text{M} = \text{Ti}, \text{Zr}$ ) of **1** and **2** exhibit metalloaromaticity<sup>18g</sup> as well employing DFT electronic

structure calculation methods.<sup>16a</sup> The diatropic/paratropic ring current signals are associated with the aromaticity/antiaromaticity of the metallic ring cores. In this context, the Nucleus Independent Chemical Shifts (NICS), by computing the respective NICS<sub>zz</sub> scan curves, could be used very effectively as good indicators of aromaticity/antiaromaticity of cyclic metallic ring cores.<sup>20b,21,42</sup>

Accordingly, we calculated the NICS<sub>zz</sub> scan curve of the *cyclo*-M<sub>3</sub> trinuclear metallic cores (M = Ti or Zr) with the GIAO (gauge-including atomic orbitals) DFT method<sup>26,27</sup> as implemented in the Gaussian09 series of programs<sup>28</sup> employing the PBE0 functional in combination with the 6-31G(d,p) and the Def2-TZVP basis sets for the non-metal and the Ti and Zr metal atoms respectively. The computational protocol will henceforth be denoted as GIAO/PBE0/Def2-TZVP(M)U6-31G(d,p)(E). The NICS<sub>zz</sub> curves were calculated for the model systems [M<sup>IV</sup><sub>3</sub>(μ<sub>3</sub>-O)(μ-Hdihybo)<sub>3</sub>](OCH<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>] (M = Ti, Zr) **1M** and **2M** where the coordination environment of **1** and **2** was truncated by the use of methoxy, and hydroxyl groups in order to reduce the computational cost. In addition, we have calculated the NICS<sub>zz</sub> curves for the simpler model [M<sup>IV</sup><sub>3</sub>(μ-Hdihybo)<sub>3</sub>] (M = Ti, Zr) **3M** and **4M** complexes in order to study the effect of the μ<sub>3</sub>-O ligand on the aromaticity/antiaromaticity of the trimetallic ring cores. The NICS<sub>zz</sub> scan curves were obtained by placing Bq ghost atoms on a line, coinciding with the z-axis, being vertical to the trimetallic ring core and passing through the ring center (Figure 9). The molecular structures of the model compounds used in this study along with the positions of the Bq ghost atoms are depicted in Figure 9.

Figure 9a shows the calculated NICS<sub>zz</sub> scan curves for the model compounds bearing the μ<sub>3</sub>-O ligand, **1M** and **2M** (solid lines green and red lines respectively). The NICS<sub>zz</sub> scan curves for the model compounds without the μ<sub>3</sub>-O ligand, **3M** and **4M** (dashed green and red lines respectively) are depicted in Figure 9b.

Let us first examine the model systems bearing the  $\mu_3$ -O ligand which is capping the  $M_3$  ring. Inspection of Figure 9a (solid green line) reveals that the  $NICS_{zz}$  curve of **1M** exhibits a  $NICS_{zz}(0)$  value equal to -14.5 ppm while the  $NICS_{zz}(1)$  value amounts to -18.4 ppm. Both values indicate that the *cyclo*- $Ti_3$  metallic ring core is aromatic. The  $NICS_{zz}$ -scan curves exhibiting two maxima at a certain distance above and below the molecular plane defined by the three metal atoms and the three  $Hdihybo^{2-}$  ligands are typical for  $(\sigma + \pi)$ -aromatics where the  $\pi$ -diatropic ring current overwhelms the  $\sigma$ -type one.<sup>43</sup>



**Figure 9.** The NICS<sub>zz</sub> scan profiles of **1M** [ $\text{Ti}^{\text{IV}}_3(\mu_3\text{-O})(\mu\text{-Hdihybo})_3(\text{OCH}_3)_3(\text{OH})_3$ ] and **2M** [ $\text{Zr}^{\text{IV}}_3(\mu_3\text{-O})(\mu\text{-Hdihybo})_3(\text{OCH}_3)_3(\text{OH})_3$ ] (**a**) and **3M** [ $\text{Ti}^{\text{IV}}_3(\mu\text{-Hdihybo})_3$ ] and **4M** [ $\text{Zr}^{\text{IV}}_3(\mu\text{-Hdihybo})_3$ ] (**b**) calculated at the PBE0/6-31G(d,p) level (red lines for **1M/3M**, green lines for **2M/4M**).

The NICS<sub>zz</sub> curve of **2M**, depicted in Figure 9a (solid red line), follows the pattern of the respective NICS<sub>zz</sub> curves calculated for the Ti system (Figure 9a solid green line). Along these lines the NICS<sub>zz</sub>(0) value is equal to -40.1 ppm, the NICS<sub>zz</sub>(1) value amounts to -37.3 ppm while the NICS<sub>zz</sub>(-1) value is only -5.2 ppm. For the Zr model system we again observe three aromaticity zones ranging from strongly aromatic to slightly aromatic in a similar manner to its Ti counterpart model system. Noteworthy the aromaticity of these model systems are comparable to that reported for a similar system<sup>16a</sup> bearing *cyclic*-Ti<sub>3</sub> trinuclear ring core with NICS<sub>zz</sub>(1) value of -23.2 ppm. Obviously, the magnitude of aromaticity of the *cyclic*-M<sub>3</sub> trinuclear ring cores depends on the nature of the metal centers as well as of the surrounding ligands.

In order to further delineate the obscuring aromaticity of the metallic ring cores of these systems we have calculated also the NICS<sub>zz</sub> curves for the even more simpler model systems, namely the [M<sup>IV</sup><sub>3</sub>(μ-Hdihydro)<sub>3</sub>] (M = Ti or Zr) **3M** and **4M**. In these systems we have removed both the μ<sub>3</sub>-O capping ligands as well as the methoxy- and hydroxy-ligands, protruding out of the metallic ring core. Figure 9b reveals that indeed the trimetallic ring cores in both **3M** and **4M** are expected to be aromatic with the phenomenon being more pronounced for M = Zr. The NICS<sub>zz</sub>(0), NICS<sub>zz</sub>(1) and NICS<sub>zz</sub>(-1) values are -23.5, -13.0 and -18.6 ppm respectively for **3M** and -87.2, -36.4 and -45.7 ppm for the **4M**. The much higher aromatic character of the Zr metallic ring could be attributed probably to the stronger overlap of the more diffuse 4*d* orbitals of Zr than the 3*d* orbitals of Ti forming the delocalized *d* orbital aromatic system on the respective metallic ring cores.

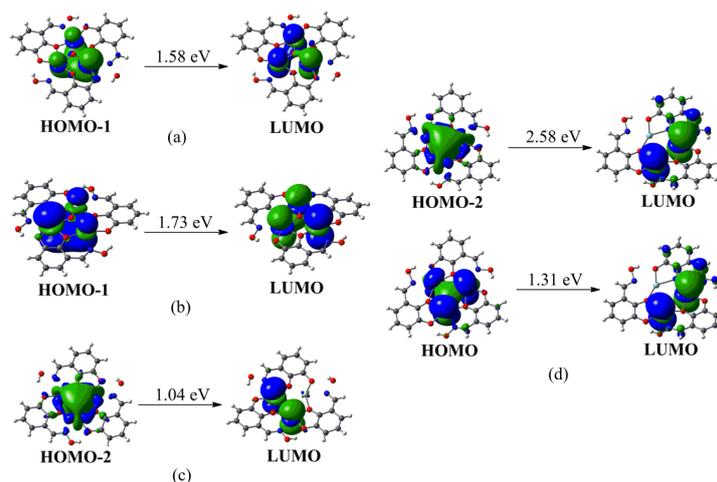
Upon removal of the μ<sub>3</sub>-O ligand and the methoxy- and hydroxy- ligands a dramatic change of the NICS<sub>zz</sub> curves (Figure 9b) of the trimetallic cores of **3M** and **4M** are

observed. More specifically, for **3M** and **4M** the NICS<sub>zz</sub> curves exhibit only one, broad maximum with their shape being indicative of  $\sigma$ -aromaticity.<sup>43</sup>

Figure 10 shows the 3D plots of the Highest Occupied Molecular Orbital (HOMOs) and the Lowest Unoccupied Molecular Orbitals (LUMOs) along with the lowest  $T_{x,y}$ -allowed transitions calculated for **3M** and **4M**. The  $\sigma$ -aromaticity of the metallic ring cores, is further corroborated by examining the shapes of the MOs involved in the  $T_{x,y}$ -allowed transitions that contribute to the diamagnetic ring current (Figure 10). For **3M** the  $T_{x,y}$ -allowed transition arises from a HOMO-2  $\rightarrow$  LUMO transition where the HOMO-2 is a delocalized  $\sigma$  bonding MO, constructed mainly from Ti 3d AOs (Figure 10c). For **4M** there are two  $T_{x,y}$ -allowed transitions i.e., the HOMO-2  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO, where both HOMO-2 and HOMO are  $\sigma$  delocalized bonding MOs, constructed mainly from Zr 4d AOs (Figure 10d).

For the **1M**, there is only one  $T_{x,y}$ -allowed transition inducing a diamagnetic ring current involving HOMO-1 and LUMO (Figure 10a). The former is a  $\pi$ -type bonding MO, while the latter is an antibonding MO, both constructed mainly from the in-phase linear combination of  $d_z^2$  AOs of the three Ti metal centers. The HOMO-1  $\rightarrow$  LUMO transition corresponds to relatively small excitation energy.

The shape of the NICS<sub>zz</sub> curve of **2M** (Figure 9a, solid red line) is only qualitatively like that found for **1M**.



**Figure 10.** 3D plots of the molecular orbitals and significant  $T_{x,y}$ -allowed transitions leading to the diamagnetic ring currents in (a) **1M**, (b) **2M**, (c) **3M** and (d) **4M**.

In contrast to **1M**, the  $\text{NICS}_{zz}(1)$  and  $\text{NICS}_{zz}(-1)$  values of **2M** differ significantly, being -3 and -42 ppm respectively. Obviously, the  $\mu_3\text{-O}$  ligand capping the *cyclo-Zr*<sub>3</sub> ring suppresses significantly the  $\text{NICS}(1)$  value as compared to **1M**. Notice however that the  $\text{NICS}(0)$  value calculated for the **1M** and **2M** amount to -38 and -32 ppm respectively both signifying aromaticity. Both, the  $\text{NICS}_{zz}$ -scan curve shapes and the  $T_{x,y}$ -allowed transition inducing diamagnetic ring current involving HOMO-1 and LUMO (Figure 10b), point to a  $(\sigma + \pi)$ -aromatic system, where the  $\pi$ -diatropic ring current overwhelms the  $\sigma$ -type one. Notice that the Zr system exhibits enhanced aromaticity as compared to its Ti homologue system. From the results discussed so far, it can be concluded that the aromaticity of a metallic ring core depends upon the nature of its metallic center. Moreover, we would like to point out that this is the very first example of a Zr<sub>3</sub> triangle which exhibits metalloaromaticity.

## CONCLUSIONS

In conclusion, a series of hexanuclear titanium(IV) and zirconium(IV) compounds were synthesized by a simple three-component reaction, at room temperature. The three compounds have the same core structure  $[M^{IV}_6(\mu_3-O)_2(\mu-O)_3]$  ( $M = Ti, Zr$ ), which constitutes a unique example with a trigonal prismatic arrangement of the six zirconium(IV) atoms and a unique  $Zr^{IV}_6$  structural motif.

The trend observed in the formation of  $[M^{IV}_6(\mu_3-O)_2(\mu-O)_3]$  ( $M = Ti, Zr$ ) structural motifs with organic molecules having donor atoms in three neighboring positions of the ligand's ring (reference 16a and this work) might reveal a new design principle to control the formation of titanium and zirconium hexanuclear clusters.

Multinuclear solution NMR showed that these hexa-nuclear compounds retain their integrity in both solvents methanol and water and thus, their hydrolytic stability makes them potential building blocks for the preparation of titanium(IV) and zirconium(IV) metal organic frameworks (MOFs).

Nucleus Independent Chemical Shift (NICS) magnetic criterion was used in this study and revealed the aromaticity of the  $M^{IV}_3$  ( $M = Ti, Zr$ ) rings. ESI-MS measurements also support the initial formation of the  $M_3$  structural units prior to their self-assembly into the hexanuclear  $M_6$  species. The metalloaromaticity of the  $M_3$  rings and the ESI-MS measurements suggest that the  $M_3$  rings' formation play an important role in the synthesis of these hexanuclear clusters.

The successful marriage of the catechol moiety with the oxime group in the ligand  $H_3$ dihybo led to the substantial band-gap reduction of the hexanuclear clusters in comparison to  $TiO_2$  and  $ZrO_2$  and induced photocurrent responses in **1** and **3**. The

present study opens up new avenues for the rational design of titanium and zirconium based clusters absorbing in the NIR region of the spectrum for numerous applications.

## **ASSOCIATED CONTENT**

### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: ....

UV-vis-NIR, FT-IR and NMR spectra and final unit cell data

### **Accession Codes**

CCDC for compounds **1** - **3** (CCDC **1**: 2013476, **2**: 2013478 and **3**: 2013477) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

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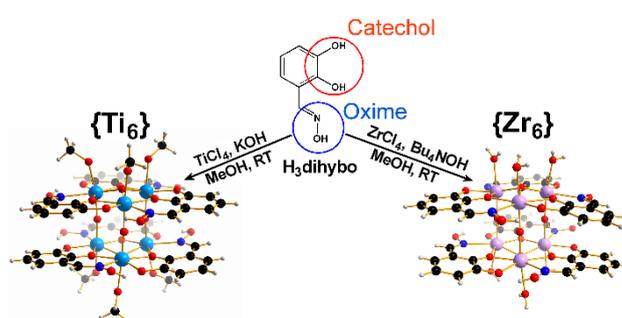
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### Synopsis

Reaction of MCl<sub>4</sub> (M = Ti, Zr) with the catechol/oxime ligand H<sub>3</sub>dihybo gave hexanuclear clusters containing the core structure [M<sup>IV</sup><sub>6</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ-O)<sub>3</sub>] with a trigonal prismatic arrangement of the metal atoms and the M<sub>3</sub> rings exhibiting metalloaromaticity. The marriage of the catechol moiety with the oxime group in H<sub>3</sub>dihybo proved successful in reducing substantially the band-gap of the hexanuclear compounds.