

# Synthesis of Trimeric Organozinc Compounds and their Subsequent Reaction with Oxygen

Joe A. Manzi, Caroline E. Knapp, Ivan P. Parkin, and Claire J. Carmalt<sup>\*[a]</sup>

A conventional solution-based route to a cyclic trimeric organozinc compound  $[\{Zn(Et)(\beta\text{-diketonate})\}_3]$  ( $\beta\text{-diketonate} = \text{OC}(\text{OMe})\text{CHC}(\text{Me})\text{O}$ , **1**) is described, with **1** structurally characterized for the first time. The ligand selection of bidentate  $\beta\text{-diketonates}$  is shown to be key to isolating a cyclic trimer. Additional reaction of  $\beta\text{-diketonates}$  with diethyl zinc were spectroscopically characterized as compounds of the type  $[\{Zn(Et)(\beta\text{-diketonate})\}_n]$  ( $\beta\text{-diketonate} = \text{OC}(\text{Me})\text{CHC}(\text{Me})\text{O}$ , **2**,  $\text{OC}(\text{OtBu})\text{CHC}(\text{Me})\text{O}$ , **3**). Further studies have shown that selective oxidation of these species produces cubanes of the general formula  $[\{Zn(\text{OC}(\text{R})\text{CHC}(\text{Me})\text{O})_2\text{Zn}(\text{Et})\text{OEt}\}_2]$  ( $\text{R} = \text{OMe}$ , **4**;  $\text{Me}$ , **5**;  $\text{OtBu}$ , **6**), allowing a high oxygen content whilst remaining structurally suitable for use as precursors. The successful deposition of thin films of zinc oxide through aerosol-assisted chemical vapor deposition (AACVD), using a novel precursor, is described and fully characterized.

Studies involving zinc alkoxides were first reported by Frankland in 1849<sup>[1]</sup> and the complex chemistry of alkyl zinc reactivity with oxygen has been revealed in the literature over the last century.<sup>[2]</sup> Organozinc compounds find use as catalysts, for example, in ring-opening polymerizations,<sup>[3,4]</sup> as epoxidizing agents for enones,<sup>[5]</sup> and as precursors for nanoparticle synthesis<sup>[6]</sup> and zinc oxide functional thin films (including doping in main-group materials).<sup>[7]</sup>

The widely accepted belief that the oxidation of zinc alkyls is so fast, selectivity is not possible, was first dispelled by the structural characterization of a novel zinc alkylperoxide.<sup>[8]</sup> Since then, the field has undergone a renaissance, owing to re-examination of the oxidation of  $\text{R}_2\text{Zn}$  compounds through the contributions of Lewiński et al. and a handful of other groups.<sup>[9–11]</sup> A study reported by Lewiński et al. in 2003 unequivocally proved that selective oxidation of organozinc compounds is possible, with the synthesis of  $[\text{EtOOZn}(\text{azol})]_2[\text{EtZn}(\text{azol})]_2$ , ( $\text{azol} = \text{deprotonated 1-aziridineethanol}$ , a centrosymmetric cluster including octahedral- and tetrahedral-coordinated zinc environments) bridged by peroxide

groups. Interestingly, this work was the first to 'suggest the presence of a trimer as the predominate species in solution' of the precursor aggregate, namely,  $[\text{EtZn}(\text{azol})]_n$ .<sup>[12]</sup>

It is known that the structure of organozinc compounds can be enormously varied, including multinuclear rings<sup>[11]</sup> or cubanes,<sup>[13]</sup> and DFT studies have even considered cyclic and roof-like structures (Figures 1 a and 1 b).<sup>[14]</sup>

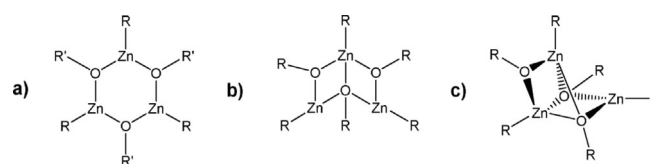


Figure 1. Central  $\text{Zn}_3\text{O}_3$  motifs: a) cyclic, b) roof-like, and c) cluster.

A recent study using a range of flexible donor-functionalized amino alcohols reported a variety of dimeric and tetrameric clusters.<sup>[10,15]</sup> It was proposed through an extensive NMR study that  $[\text{EtZn}(\text{bdmap})]_3$  ( $\text{bdmap}: 1,3\text{-bis}(\text{dimethylamino})\text{-2}(\text{dimethylaminomethyl})\text{-iso-propoxide}$ ), whilst not crystallographically characterized, has a cyclic, not a roof-like, trimeric structure (Figure 1); although, mass spectral data suggested a more complex scenario.

In 2010, the first crystallographically characterized organozinc 'dimeric aggregate' with a  $\text{Zn}_3\text{O}_3$  core cluster (Figure 1 c) was published.<sup>[16]</sup> This was synthesized through a solid-state transformation of  $[\{t\text{BuZn}(\mu\text{-OtBu})(\text{thf})\}_2]$  under mild conditions to give  $[\{t\text{BuZnOtBu}\}_3]$ . This cluster was reported to have two distinct types of organozinc centers: two four-coordinate zinc centers linked by two  $\mu_3$ - and one  $\mu_2$ -oxygen atoms, and one three-coordinate zinc center binding to two  $\mu_2$ -oxygen atoms. It was found to be a metastable product, as solution-based attempts to form the compound resulted solely in the tetramer. Later in 2012, it was shown that by using a more rigid quinoline ligand, thus moving from a  $\text{ZnCO}_3$  coordination environment to  $\text{ZnCNO}_2$ , a trimer could be isolated and was structurally characterized as  $[\text{tBuZn}(\text{q})]_3$  ( $\text{q} = 8\text{-hydroxyquinoline}$ ).<sup>[17]</sup>

Herein, we report the first instance of a conventional solution-based synthetic route to a structurally characterized cyclic trimeric organozinc compound with the coordination environment  $\text{ZnCO}_3$  (Figure 1 a),  $[\{Zn(Et)(\text{OC}(\text{OMe})\text{CHC}(\text{Me})\text{O})\}_3]$  (**1**), in which the use of bidentate  $\beta\text{-diketonate}$  ligands facilitated crystallization. Similar reactions of diethyl zinc with  $\beta\text{-diketonates}$  yielded compounds of the type  $[\{Zn(Et)(\beta\text{-diketonate})\}_n]$ , which were spectroscopically characterized. In addition, selective reaction of these compounds with oxygen yields distorted cubanes of the general formula  $[\{Zn(\beta\text{-diketonate})_2\text{Zn}(\text{Et})\text{OEt}\}_2]$ .

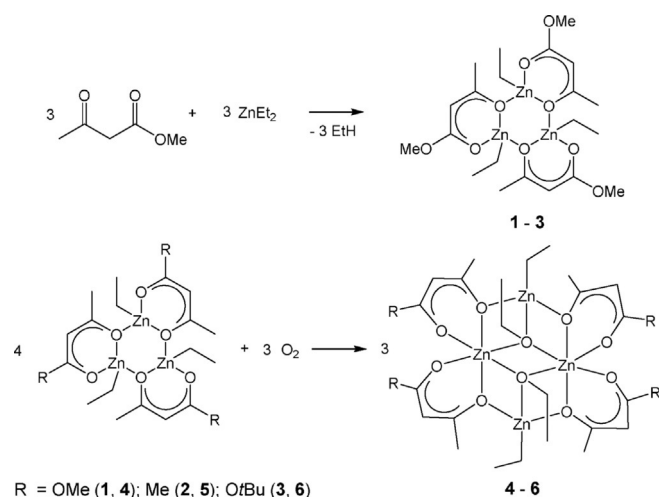
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These compounds exhibit a similar central motif to that reported previously.<sup>[12,17,18]</sup>

The trimeric  $\beta$ -diketonate  $[[\text{Zn}(\text{Et})(\text{OC}(\text{OMe})\text{CHC}(\text{Me})\text{O})_3] (1)$  was isolated and structurally characterized; furthermore, compounds of stoichiometry  $[[\text{Zn}(\text{Et})(\text{OC}(\text{R})\text{CHC}(\text{Me})\text{O})_3]_n$ , where R= Me (**2**) and *Ot*Bu (**3**) (Scheme 1), were confirmed spectroscopically. Compounds **1–3** were isolated from the equimolar reaction of  $\text{Et}_2\text{Zn}$  with the respective carbonyl in high yield (> 90%) and characterized by using spectroscopic techniques. Although **2** and **3** formed crystalline solids, none were of suitable quality for crystallographic analysis.

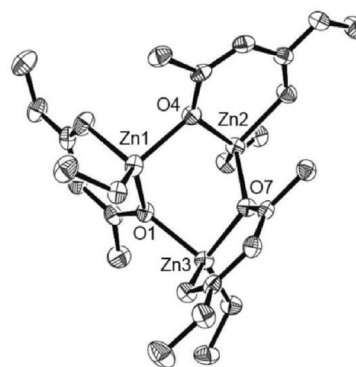


**Scheme 1.** Synthesis of organozinc cyclic trimers **1–3** and selectively oxygenated zinc cluster complexes **4–6**.

Compound **1** crystallizes in the monoclinic space group  $P2_1/n$  with three zinc centers, all exhibiting a distorted tetrahedral coordination (Figure 2). Each four-coordinate zinc atom is linked to two  $\mu_2$ -oxygen atoms and one terminal oxygen atom from the ligand and an ethyl group. The Zn–O bond distances in the  $\text{Zn}_3\text{O}_3$  ring alternate between two types, the shorter Zn–O distance from the ligand [Zn(1)–O(1):2.0489(9) Å, Zn(2)–O(4):2.0247(9) Å, Zn(3)–O(7):2.0367(9) Å] and the longer bridging Zn–O lengths [Zn(1)–O(4):2.0710(10) Å, Zn(2)–O(7):2.0980(9) Å, Zn(3)–O(1):2.0698(10) Å], which is comparable to similar structures found in the literature.<sup>[17]</sup> The distorted nature of the tetrahedral coordination around the Zn centers in **1** results largely from the constraints of the central  $\text{Zn}_3\text{O}_3$  ring and the three outer  $\text{ZnO}_2\text{C}_3$  rings formed from coordination to the bidentate ligands.

For comparison with the previously reported ‘dimeric aggregate’  $[[\text{tBuZnOtBu}]_3]$  (Figure 1c), the closest distance between opposite zinc and oxygen atoms in the ring in **1** is Zn(1)–O(7), 3.042 Å, which is considerably larger than the comparable distance in  $[[\text{tBuZnOtBu}]_3]$  (2.164 Å),<sup>[16]</sup> providing evidence of the cyclic trimeric nature of **1**.

The above data indicate that the use of a rigid bidentate  $\beta$ -diketonate ligand facilitates the isolation of a novel type of cyclic trimeric organozinc complex (**1**) with a coordination en-



**Figure 2.** The molecular structure of **1**. H atoms omitted for clarity, thermal ellipsoids drawn at 50% probability. Selected bond lengths [Å]: Zn(1)–O(1):2.0489(9), Zn(1)–O(4):2.0710(10), Zn(1)–C(6) (ethyl): 1.9676(14).

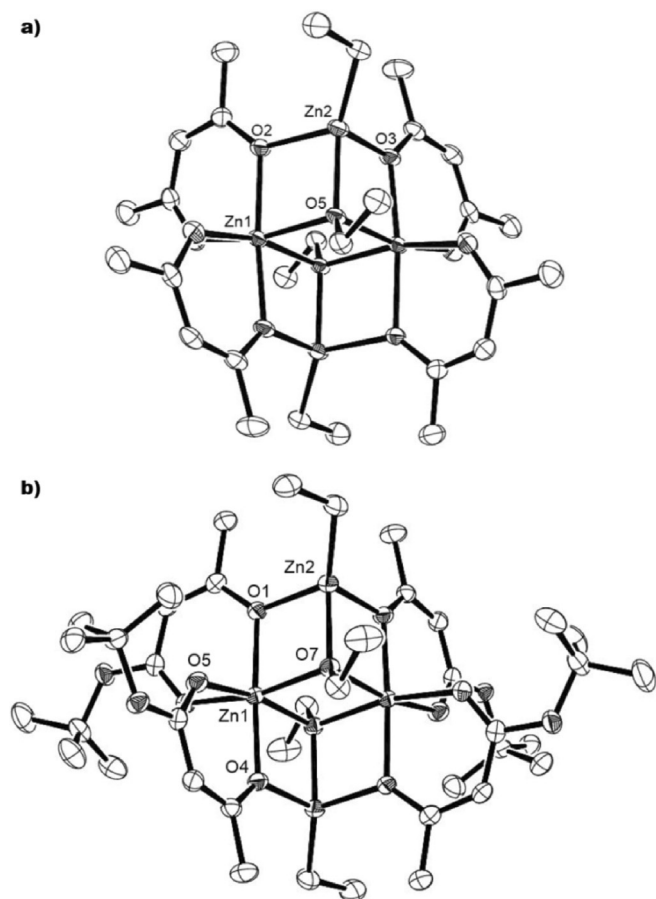
vironment of  $\text{ZnCO}_3$ , as confirmed by crystallographic characterization. The monodentate *t*Bu groups used by Lewiński resulted in a metastable roof-like trimer (or aggregated dimer), whereas the flexible amino alcoholates utilized by Molloy and co-workers yielded oils, not solids, although NMR studies did suggest a cyclic trimeric center.<sup>[10,15,16]</sup>

The rationale behind this ligand choice firstly lies in the successful isolation of a novel structural type, but also in increasing the oxygen loading of the compounds (as zinc precursors can lead to oxygen-deficient thin films).<sup>[19]</sup> Increasing the oxygen content whilst maintaining volatility and suitably high reactivity such that decomposition can occur when required at lower temperature is a challenge in materials chemistry. As such, the following reactions involving the selective oxidation of compounds **1–3** were explored.

$[[\text{Zn}(\text{OC}(\text{R})\text{CHC}(\text{Me})\text{O})_2\text{Zn}(\text{Et})\text{OEt}]_2]$  (R=OMe (**4**), Me (**5**), *Ot*Bu (**6**)) were synthesized through the controlled addition of  $\text{O}_2$  to solutions of **1–3** (Scheme 1), presumably leading to selective insertion of dioxygen into one of the Zn–C bonds of the ethyl group, which, in turn, decomposes to a  $\mu_2$ -OEt group in accordance with previous reports.<sup>[17,18]</sup> Compounds **4–6** were isolated in high yields (> 80%) and characterized by using spectroscopic techniques. Compounds **5** and **6** both crystallized out of concentrated solutions held at  $-18^\circ\text{C}$  as centrosymmetric clusters in the triclinic  $\bar{P}1$  space group with four zinc centers; two of which are unique and two are symmetrically generated about an inversion center (Figure 3). Compound **4** did not form crystals of suitable crystallographic quality; however, spectroscopic analysis confirms **4** is isostructural to **5** and **6** (see the Supporting Information).

The zinc centers in both **5** and **6** also have two different coordination modes: Zn(1) has a distorted octahedral geometry, whereas Zn(2) has a distorted tetrahedral geometry, similar to **1**. Deviations between bond lengths and angles in **5** and **6** are largely attributed to the increased bulk of the *t*Bu group in **6** compared to the Me group in **5**, and are in line with what would be expected.

In **5** and **6**, it can be observed that the octahedral coordination about zinc is distorted; this is likely caused by the steric constraints of the  $\text{ZnO}_2\text{C}_3$  and  $\text{Zn}_2\text{O}_2$  rings, a consequence of



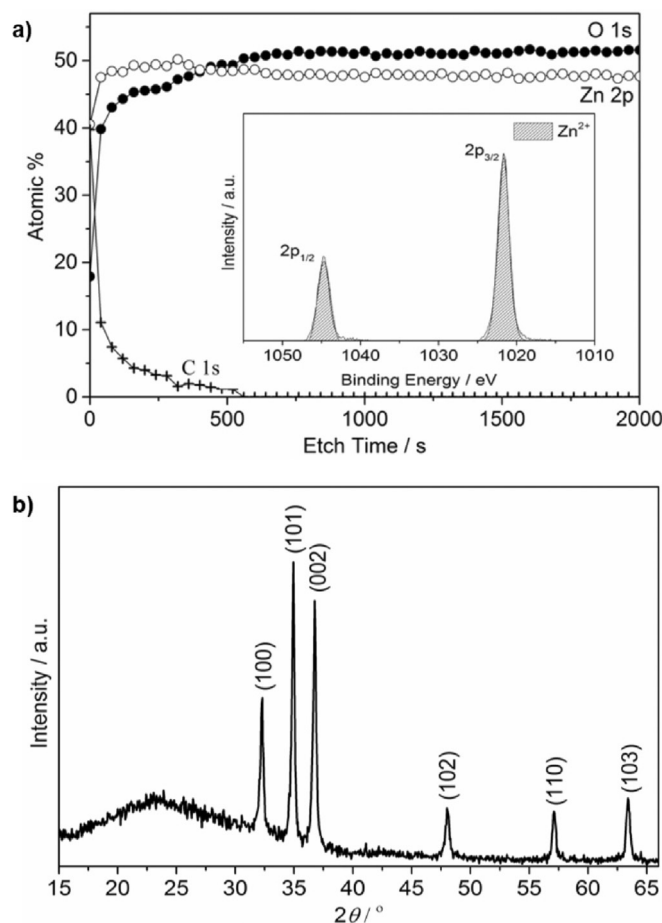
**Figure 3.** a) The molecular structure of **5**. H atoms omitted for clarity, thermal ellipsoids drawn at 50% probability. Selected bond lengths [Å]: Zn(1)–O(1):2.0536(18), Zn(1)–O(5): 2.1217(16), Zn(2)–O(2): 2.0720(17), Zn(2)–O(5):2.0006(15). b) The molecular structure of **6**. H atoms omitted for clarity. Selected bond lengths [Å]: Zn(1)–O(1):2.0821(14), Zn(1)–O(7):2.1293(14), Zn(2)–O(1):2.0642(14), Zn(2)–O(7):2.0253(14). (Symmetry operator for both **5** and **6**:  $i=-x, -y, -z$ ).

the bidentate ligands, just as with the tetrahedral distortion seen here in **1**.

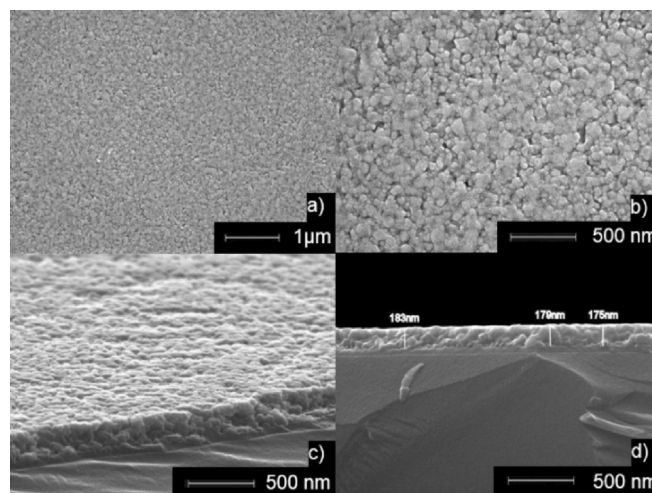
Precursors of this type are of particular interest for technological applications, and as such we have explored the use of **5** as a single-source precursor for the deposition of thin films of zinc oxide through aerosol-assisted chemical vapor deposition (AACVD), details of which are included in the Supporting Information. Compound **5** was successfully employed as an AACVD precursor, resulting in the deposition of zinc oxide thin films by using an optimum substrate deposition temperature of 450 °C and annealing temperature of 600 °C.

In X-ray photoelectron spectroscopy (XPS) of the film, the Zn 2p<sub>1/2</sub> and 2p<sub>3/2</sub> states were fitted by using a Gaussian/Lorentzian product distribution and appear, as expected, at binding energies of 1044.8 and 1021.7 eV, respectively, with an intensity ratio of 1:2 and an energy gap of 23.1 eV<sup>[20]</sup> (Figure 4a, inset). Depth profiling (Figure 4a) revealed a zinc oxide thin film with low carbon contamination (<1 at% C) in the bulk of the film.

Hexagonal wurtzite zinc oxide formation was further confirmed by using XRD (Figure 4b). Scanning electron microsc-

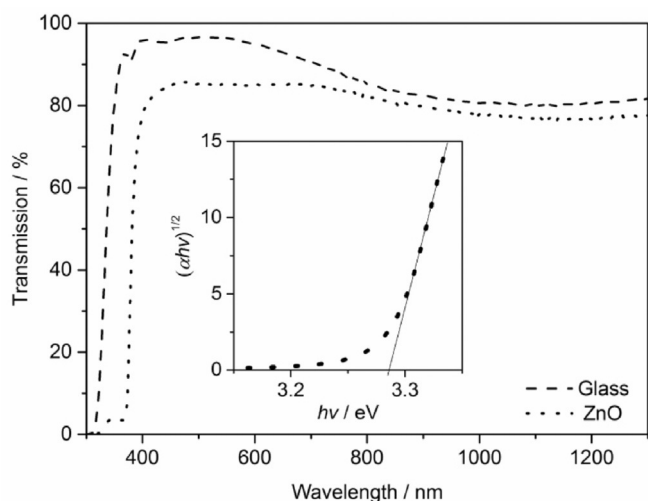


**Figure 4.** a) XPS depth profile, inset: the Zn 2p<sub>1/2</sub> and 2p<sub>3/2</sub> state peaks at 1044.8 and 1021.7 eV binding energy, respectively. b) XRD pattern for hexagonal wurtzite zinc oxide films.



**Figure 5.** SEM images: a, b) plane view at  $\times 20,000$  and  $\times 50,000$  respectively; c, d) cross section at  $\times 50,000$  with an 80° and 90° tilt, respectively.

py (SEM) revealed porous films formed of agglomerated rounded particles with diameters varying from 50 to 200 nm and a thickness of around 180 nm (Figure 5). The films were transparent (84% in the visible-light region) (Figure 6) and had



**Figure 6.** Transmission spectra of the deposited zinc oxide thin film. Inset: Tauc plot for band-gap estimation.

an estimated band gap of 3.29 eV, as determined using the Tauc relation:  $\alpha h\nu = A(h\nu - E_g)^n$ , where  $\alpha$  is the molar extinction coefficient,  $h\nu$  is the energy of a particle of light,  $A$  is a constant,  $E_g$  is the band gap and  $n$  is 0.5 for a direct band gap (Figure 6, inset), consistent with literature values.<sup>[21]</sup>

In summary, we have demonstrated the solution-based synthesis of the first structurally characterized cyclic trimer with a  $Zn_3O_3$  core and  $ZnCO_3$  coordination environment (**1**), and spectroscopically characterized organozinc  $\beta$ -diketonates of the type  $\{[Zn(Et)(\beta\text{-diketonate})]_n\}$  (**2** and **3**). Through selective oxidation, we have subsequently shown the synthesis of  $\{[Zn(OC(R)CHC(Me)O)_2Zn(Et)OEt]_2\}$  (**4–6**). X-ray crystallography of **5** and **6** revealed these complexes to have a face-shared, corner-removed, inversion-related, bis-heterocubane central motif. Of additional importance is that these materials can be used as precursors to thin films of zinc oxide; as exemplified in the successful deposition of hexagonal wurtzite zinc oxide thin films. We believe these results provide a new route, through careful ligand selection, to cyclic organozinc trimers, whose rarity was commented on by Power and co-workers back in 1991.<sup>[22]</sup> Further systematic studies will continue to expand the current collection of organozinc compounds of this type, and a more exhaustive study to optimize the film growth and physical properties of the zinc oxide will be undertaken to provide a platform for the construction of electronic devices.

## Experimental Section

Crystallographic/refinement data for compounds **1**, **5**, and **6** can be found in the Supporting Information.<sup>[23]</sup>

All manipulations were performed under a dry dinitrogen atmosphere by using standard Schlenk techniques. Hexane was stored in an alumina column and dried with anhydrous engineering equipment. Diethylzinc solution (1 M in hexanes) was obtained from Sigma Aldrich and used as supplied. Acetylacetone, methyl acetoacetate, and *tert*-butyl acetoacetate were obtained from Sigma Aldrich, degassed, and stored over activated molecular sieves.

$^1H$  and  $^{13}C$  NMR spectra were obtained on a Bruker Avance III 600 cryo spectrometer and were recorded in  $C_6D_6$ .  $^1H$  and  $^{13}C$  chemical shifts are reported relative to  $SiMe_4$  ( $\delta$  0.00). Mass spectroscopy was performed on a Thermo Finnigan MAT900 XP operating in electron impact and chemical ionization modes. Single-crystal X-ray diffraction datasets were collected on a SuperNova (dual source) Atlas diffractometer by using either monochromated  $Cu K_\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) or monochromated  $Mo K_\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ).

### $\{[Zn(Et)(OC(OMe)CHC(Me)O)]_3\}$ (**1**)

Diethylzinc (9.76 mL, 1 M solution in hexanes, 9.76 mmol) was added to dry hexane (5 mL) at  $-78^\circ C$ . Dry methyl acetoacetate (1.13 g, 9.76 mmol) was added dropwise to the solution and stirred at RT for 48 h. Hexane was fully removed in vacuo, resulting in an off-white solid. Off-white crystals grew from a concentrated solution held at  $-18^\circ C$ . Yield: 1.86 g, 91%;  $^1H$  NMR (600 MHz)  $\delta$  ( $C_6D_6$ ): 0.55 (q, 6H,  $CH_2CH_3$ ,  $J = 8.0$  Hz), 1.47 (t, 9H,  $CH_2CH_3$ ,  $J = 8.00$  Hz), 1.90 (s, 9H,  $CCH_3$ ), 3.27 (s, 9H,  $OCH_3$ ), and 4.95 ppm (s, 3H,  $CCHC$ );  $^{13}C\{^1H\}$  NMR (600 MHz)  $\delta$  ( $C_6D_6$ ): 1.0 ( $CH_2CH_3$ ), 12.5 ( $CH_2CH_3$ ), 27.5 ( $CCH_3$ ), 51.1 ( $OCH_3$ ), 89.3 ( $CCHC$ ), 174.0 ( $COCH_3$ ), and 184.4 ppm ( $CCH_3$ ); anal. calcd. for  $C_{21}H_{36}O_9Zn_3$ : C 40.12, H 5.77; found: C 40.21, H 5.89.

### $\{[Zn(Et)(OC(Me)CHC(Me)O)]_3\}$ (**2**)

Diethylzinc (9.76 mL, 1 M solution in hexanes, 9.76 mmol) was added to dry hexane (5 mL) at  $-78^\circ C$ . Dry acetylacetone (0.98 g, 9.76 mmol) was added dropwise to the solution and stirred at RT for 48 h. Hexane was fully removed in vacuo, resulting in an off-white solid. Yield: 1.71 g, 90%;  $^1H$  NMR (600 MHz)  $\delta$  ( $C_6D_6$ ): 0.57 (q, 6H,  $CH_2CH_3$ ,  $J = 8.2$  Hz), 1.48 (t, 9H,  $CH_2CH_3$ ,  $J = 8.2$  Hz), 1.79 (s, 18H,  $CCH_3$ ), and 5.03 ppm (s, 3H,  $CCHC$ );  $^{13}C\{^1H\}$  NMR (600 MHz)  $\delta$  ( $C_6D_6$ ): 1.0 ( $CH_2CH_3$ ), 12.4 ( $CH_2CH_3$ ), 28.3 ( $CCH_3$ ), 102.0 ( $CCHC$ ), and 193.1 ppm ( $CCH_3$ ); anal. calcd. for  $C_{21}H_{36}O_6Zn_3$ : C 43.44, H 6.25; found: C 43.09, H 6.77.

### $\{[Zn(Et)(OC(OtBu)CHC(Me)O)]_3\}$ (**3**)

Diethylzinc (9.76 mL, 1 M solution in hexanes, 9.76 mmol) was added to dry hexane (5 mL) at  $-78^\circ C$ . Dry *tert*-butyl acetoacetate (1.54 g, 9.76 mmol) was added dropwise to the solution and stirred at RT for 48 h. Hexane was fully removed in vacuo, resulting in an off-white solid. Yield: 2.25 g, 91%;  $^1H$  NMR (600 MHz)  $\delta$  ( $C_6D_6$ ): 0.37 (q, 6H,  $CH_2CH_3$ ,  $J = 8.2$  Hz), 1.31 (s, 27H,  $C(CH_3)_3$ ), 1.33 (t, 9H,  $CH_2CH_3$ ,  $J = 8.2$  Hz), 1.94 (s, 9H,  $CCH_3$ ), and 4.90 ppm (s, 3H,  $CCHC$ );  $^{13}C\{^1H\}$  NMR  $\delta$  (600 MHz) ( $C_6D_6$ ): 3.4 ( $CH_2CH_3$ ), 11.7 ( $CH_2CH_3$ ), 27.6 ( $CCH_3$ ), 28.4 ( $C(CH_3)_3$ ), 80.9 ( $C(CH_3)_3$ ), 91.0 ( $CCHC$ ), 173.8 ( $CO(C(CH_3)_3)$ ), and 183.2 ppm ( $CCH_3$ ); anal. calcd. for  $C_{30}H_{54}O_9Zn_3$ : C 47.73, H 7.21; found: C 46.93; H 6.97.

### $\{[Zn(OC(OMe)CHC(Me)O)_2Zn(Et)OEt]_2\}$ (**4**)

$O_2$  (5 mL) was added to a solution of **1** and stirred for 15 min at  $-78^\circ C$ . The flask was purged with  $N_2$  and stirred at room temperature for 24 h. Off-white crystals formed from a concentrated solution held at  $-18^\circ C$ . Yield: 1.85 g, 87%;  $^1H$  NMR (600 MHz)  $\delta$  ( $C_6D_6$ ): 0.62 (q, 4H,  $J = 8.0$  Hz,  $ZnCH_2CH_3$ ), 1.33 (t, 6H,  $J = 7.0$  Hz,  $OCH_2CH_3$ ), 1.60 (t, 6H,  $J = 8.0$  Hz,  $ZnCH_2CH_3$ ), 1.90 (s, 12H,  $CCH_3$ ), 3.33 (s, 12H,  $OCH_3$ ), 3.87 (q, 4H,  $J = 7.0$  Hz,  $CH_2CH_3$ ), and 4.99 ppm (s, 4H,  $CCHC$ );  $^{13}C\{^1H\}$  NMR (600 MHz)  $\delta$  ( $C_6D_6$ ): 2.2 ( $ZnCH_2CH_3$ ), 12.6 ( $ZnCH_2CH_3$ ), 19.7 ( $OCH_2CH_3$ ), 27.3 ( $CCH_3$ ), 50.6 ( $OCH_3$ ), 61.3

(OCH<sub>2</sub>CH<sub>3</sub>), 87.0 (CCHC), 173.6 (COCH<sub>3</sub>), and 183.3 ppm (CCH<sub>3</sub>); anal. calcd. for C<sub>28</sub>H<sub>48</sub>O<sub>14</sub>Zn<sub>4</sub>: C 38.64, H 5.56; found: C 38.45, H 5.64. MS: *m/z* [M–Zn<sub>2</sub>O<sub>5</sub>C<sub>13</sub>H<sub>27</sub>]<sup>+</sup>: 474.87; [M–Zn<sub>3</sub>O<sub>8</sub>C<sub>18</sub>H<sub>34</sub>]<sup>+</sup>: 294.97.

#### [[Zn(OC(Me)CHC(Me)O)<sub>2</sub>Zn(Et)OEt]<sub>2</sub>] (5)

O<sub>2</sub> (5 mL) was added to a solution of **2** and stirred for 15 min at –78 °C. The flask was purged with N<sub>2</sub> and stirred at room temperature for 24 h. Off-white crystals formed from a concentrated solution held at –18 °C. Yield: 1.66 g, 84%; <sup>1</sup>H NMR (600 MHz) δ (C<sub>6</sub>D<sub>6</sub>): 0.69 (br, 4H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.42 (t, 6H, *J* = 7.0 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 1.61 (br, 6H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.79 (s, 24H, CCH<sub>3</sub>), 3.80 (q, 4H, *J* = 7.0 Hz, OCH<sub>2</sub>CH<sub>3</sub>), and 5.06 ppm (s, 4H, CCHC); <sup>13</sup>C{<sup>1</sup>H} NMR (600 MHz) δ (C<sub>6</sub>D<sub>6</sub>): 2.7 (ZnCH<sub>2</sub>CH<sub>3</sub>), 12.9 (ZnCH<sub>2</sub>CH<sub>3</sub>), 20.1 (OCH<sub>2</sub>CH<sub>3</sub>), 28.1 (CCH<sub>3</sub>), 61.1 (OCH<sub>2</sub>CH<sub>3</sub>), 100.6 (CCHC), and 193.1 ppm (CCH<sub>3</sub>); anal. calcd. for C<sub>28</sub>H<sub>48</sub>O<sub>10</sub>Zn<sub>4</sub>: C 41.71, H 6.00; found: C 42.06, H 5.92. MS: *m/z* [M + C<sub>3</sub>H<sub>3</sub>]<sup>+</sup>: 847.04; [M–C<sub>8</sub>H<sub>20</sub>]<sup>+</sup>: 691.11; [M–Zn<sub>2</sub>O<sub>4</sub>C<sub>13</sub>H<sub>27</sub>]<sup>+</sup>: 426.91; [M–Zn<sub>3</sub>O<sub>6</sub>C<sub>18</sub>H<sub>34</sub>]<sup>+</sup>: 263.00.

#### [[Zn(OC(OtBu)CHC(Me)O)<sub>2</sub>Zn(Et)OEt]<sub>2</sub>] (6)

O<sub>2</sub> (5 mL) was added to a solution of **3** and stirred for 15 min at –78 °C. The flask was purged with N<sub>2</sub> and stirred at room temperature for 24 h. Off-white crystals formed from a concentrated solution held at –18 °C. Yield: 2.09 g, 83%; <sup>1</sup>H NMR (600 MHz) δ (C<sub>6</sub>D<sub>6</sub>): 0.58 (q (br), 4H, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.44 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.51 (t (br), 6H, OCH<sub>2</sub>CH<sub>3</sub>), 1.66 (t, 6H, *J* = 8.1 Hz, ZnCH<sub>2</sub>CH<sub>3</sub>), 1.92 (s, 12H, CCH<sub>3</sub>), 4.02 (q, 4H, *J* = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), and 4.96 ppm (s, 4H, CCHC); <sup>13</sup>C{<sup>1</sup>H} NMR (600 MHz) δ (C<sub>6</sub>D<sub>6</sub>): 1.8 (ZnCH<sub>2</sub>CH<sub>3</sub>), 13.1 (ZnCH<sub>2</sub>CH<sub>3</sub>), 19.8 (OCH<sub>2</sub>CH<sub>3</sub>), 27.4 (CCH<sub>3</sub>), 28.7 (C(CH<sub>3</sub>)<sub>3</sub>), 61.4 (OCH<sub>2</sub>CH<sub>3</sub>), 79.7 (C(CH<sub>3</sub>)<sub>3</sub>), 88.7 (CCHC), 173.4 (COC(CH<sub>3</sub>)<sub>3</sub>), and 182.1 ppm (CCH<sub>3</sub>); anal. calcd. for C<sub>40</sub>H<sub>72</sub>O<sub>14</sub>Zn<sub>4</sub>: C 46.26, H 6.99; found: C 46.43, H 7.27. MS: *m/z* [M–Zn<sub>2</sub>O<sub>5</sub>C<sub>16</sub>H<sub>33</sub>]<sup>+</sup>: 601.05; [M–Zn<sub>3</sub>O<sub>8</sub>C<sub>24</sub>H<sub>46</sub>]<sup>+</sup>: 379.04.

#### Thin-Film Deposition and Analysis

Films were deposited onto float-glass substrates with a 25 nm barrier layer of crystalline SiO<sub>2</sub>. [[Zn(OC(Me)CHC(Me)O)<sub>2</sub>Zn(Et)OEt]<sub>2</sub>] (**5**) (0.7 g, 0.87 mmol) was dissolved in dry toluene (30 mL) under N<sub>2</sub> and stirred for 10 min. Thin films were deposited by using optimal conditions of a N<sub>2</sub> flow rate of 1.2 L min<sup>–1</sup>, a substrate temperature of 450 °C, and annealing in air for 5 h at 600 °C. XRD was performed using a Bruker D8 Discover X-ray diffractometer by using monochromatic Cu K<sub>α1</sub> and Cu K<sub>α2</sub> radiation of wavelengths 1.54056 and 1.54439 Å, respectively, emitted in an intensity ratio of 2:1 with a voltage of 40 kV and a current of 40 mA. SEM was performed by using a Philips XL30 FEG operating in plan and cross-section mode with an electron beam accelerating energy of 30 kV. XPS surface and depth profiling was performed by using a Thermo Scientific K-Alpha XPS system with monochromatic Al K<sub>α</sub> radiation at 1486.6 eV as the X-ray source. Etching was achieved by using an Ar-ion etch beam at 1 KeV with a current of 1.51 μA. CasaXPS software was used to analyze the data with binding energies referenced to an adventitious C 1s peak at 284.8 eV. UV/Vis/NIR transmission spectra were recorded by using a PerkinElmer Lambda 950 spectrometer in the range of 300–1400 nm with an air background.

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