Supporting Information

Dynamic Environment at the Zr$_6$ Oxo Cluster Surface Is Key for the Catalytic Formation of Amide Bonds

Yujie Zhang[1], Ismail Y. Kokculer[1,2], Francisco de Azambuja[1]* and Tatjana N. Parac-Vogt[1]*

[1] Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

[2] Department of Chemistry, Bilkent University, 06800 Ankara, Turkey

*tatjana.vogt@kuleuven.be; francisco.deazambuja@kuleuven.be

Table of contents

General remarks

Unless otherwise mentioned, reactions were performed without any precautions against air and moisture. Amide bond formation reactions were performed in 4mL (1-dram) vials sealed with a PTFE-lined screw cap. Unless otherwise mentioned, reagents were purchased from commercial sources, and used as received.

Hydrogen nuclear magnetic resonance (^{1}H NMR) were recorded on a Bruker Avance 300 (300 MHz) or a Bruker Avance 400 (400 MHz) spectrometer. Carbon nuclear magnetic resonance (^{13}C NMR) were recorded on Bruker Avance 400 (100 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane, and are referenced to resonance of residual solvent peak in the NMR solvent (^{1}H NMR: DMSO: δ = 2.50 ppm; CDCl$_3$: δ = 7.26 ppm; ^{13}C NMR: 39.52 ppm). Fourier-transform infrared spectra (FTIR) were recorded on a Bruker Vertex 70 spectrometer and analysed with the Bruker OPUS software (version 7.5). The solid samples were measured directly, without sample preparation, using the attenuated total reflectance module (Platinum ATR). Powder X-ray diffraction (PXRD) patterns were collected on a Malvern PANalytical Empyrean diffractometer (in transmission mode) over a 1.3 – 45° 2θ range, using a PIXcel3D solid state detector and Cu anode (Cu K$_{\alpha 1}$: 1.5406 Å; Cu K$_{\alpha 2}$: 1.5444 Å).

Synthesis of Zr$_6$

[Zr$_6$O$_4$(OH)$_4$(OMc)$_{12}$] (OMc = methacrylate) (**Zr$_6$**) was prepared as previously reported:[1]

In a Schlenk tube under a nitrogen atmosphere, Zr(O^{n}Pr)$_4$ (1.00 mL of a 70% wt% solution in n-propanol, 3.1 mmol) was mixed with methacrylic acid（1.00 mL, 11.8 mmol). After stirring for a few minutes until homogenization was observed, the mixture was kept still at room temperature until a colorless crystal formed (usually within 5 days). The solid product was collected by vacuum filtration. The compound was washed with 35 mL CH$_2$Cl$_2$, and dried under rotatory evaporator. then dried this compound under high-vacuum for several hours. Yield: 0.60 g, 68% based on Zr. Analysis by ^{1}H NMR spectroscopy was consistent with previous reports, confirming the identity of cluster obtained.[2-3] Despite the washes with CH$_2$Cl$_2$, free methacrylic acid could still be detected by ^{13}C NMR. These molecules are generally assumed to interact with the cluster through H-bonding.[4]
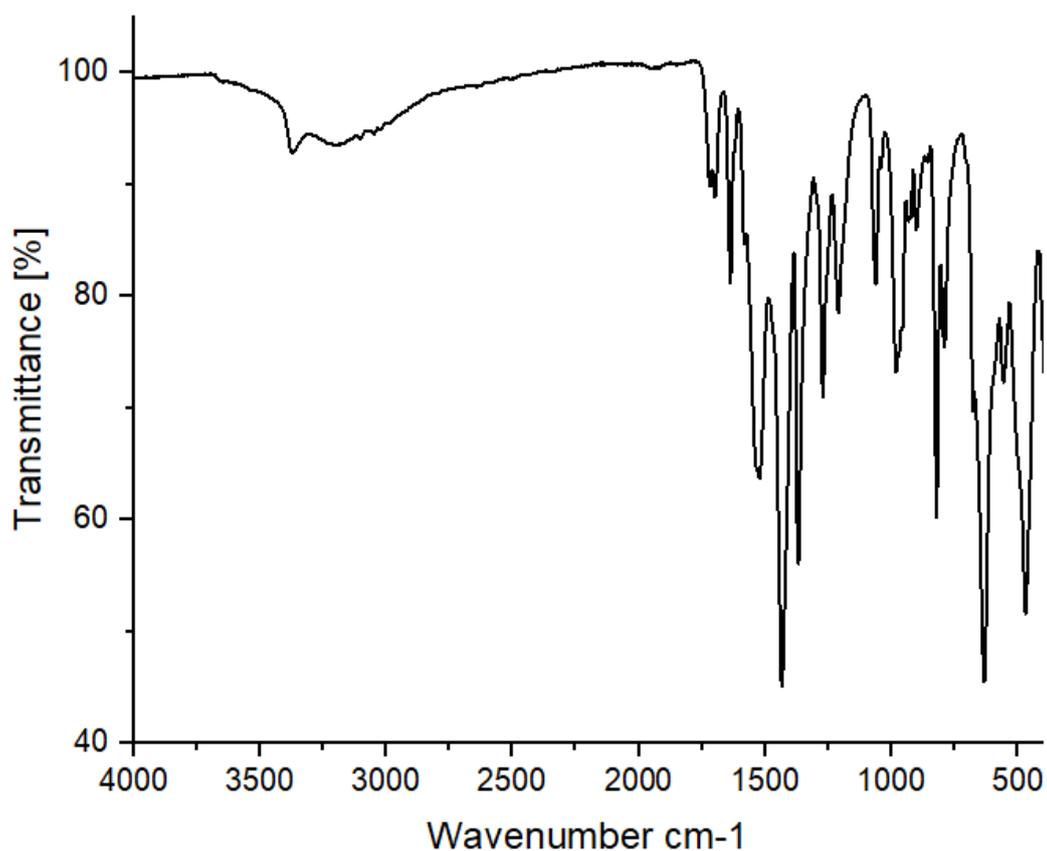
Figure S1. FT-IR (ATR) of $[Zr_6O_4(OH)_4(OMc)_{12}]$ (OMc = methacrylate) (**Zr$_6$**) as synthesized.
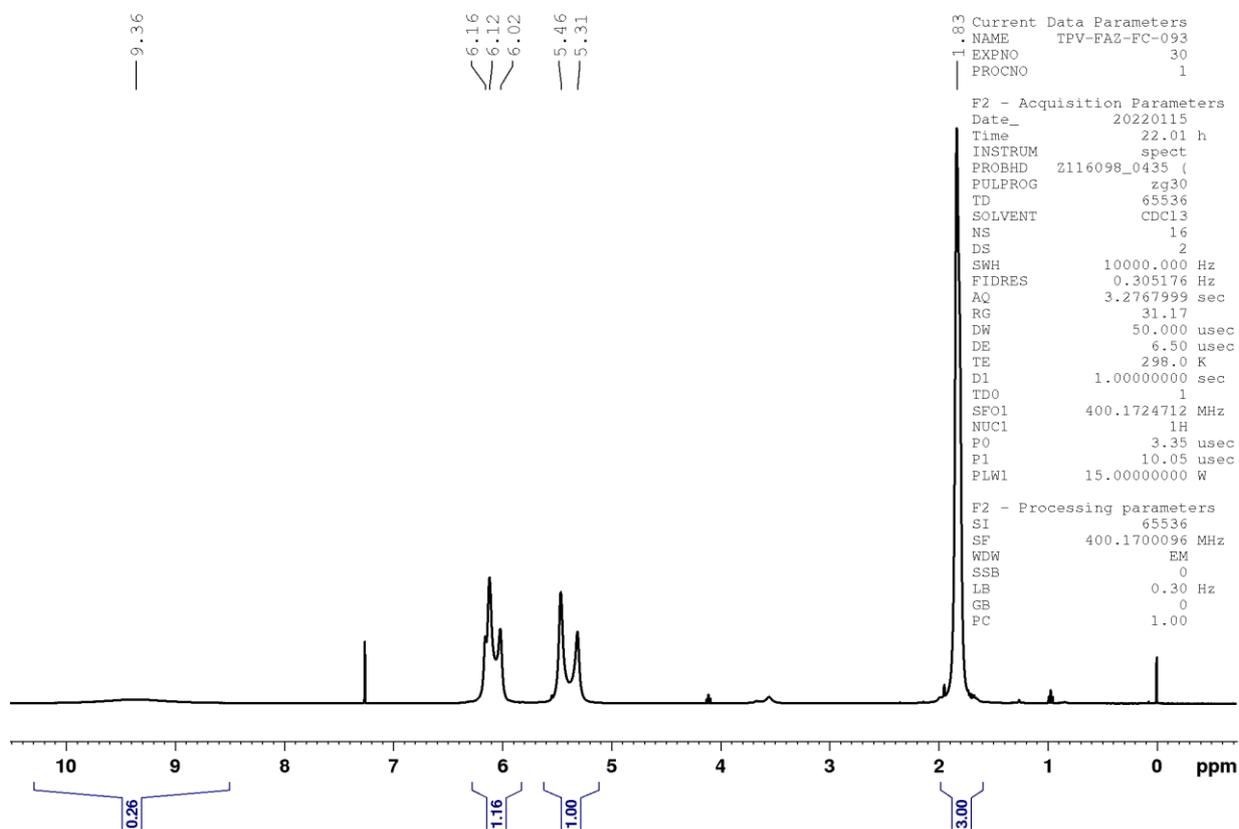
Figure S2. ^1H NMR of $[Zr_6O_4(OH)_4(OMc)_{12}]$ (OMc = methacrylate) (**Zr$_6$**) as synthesized.
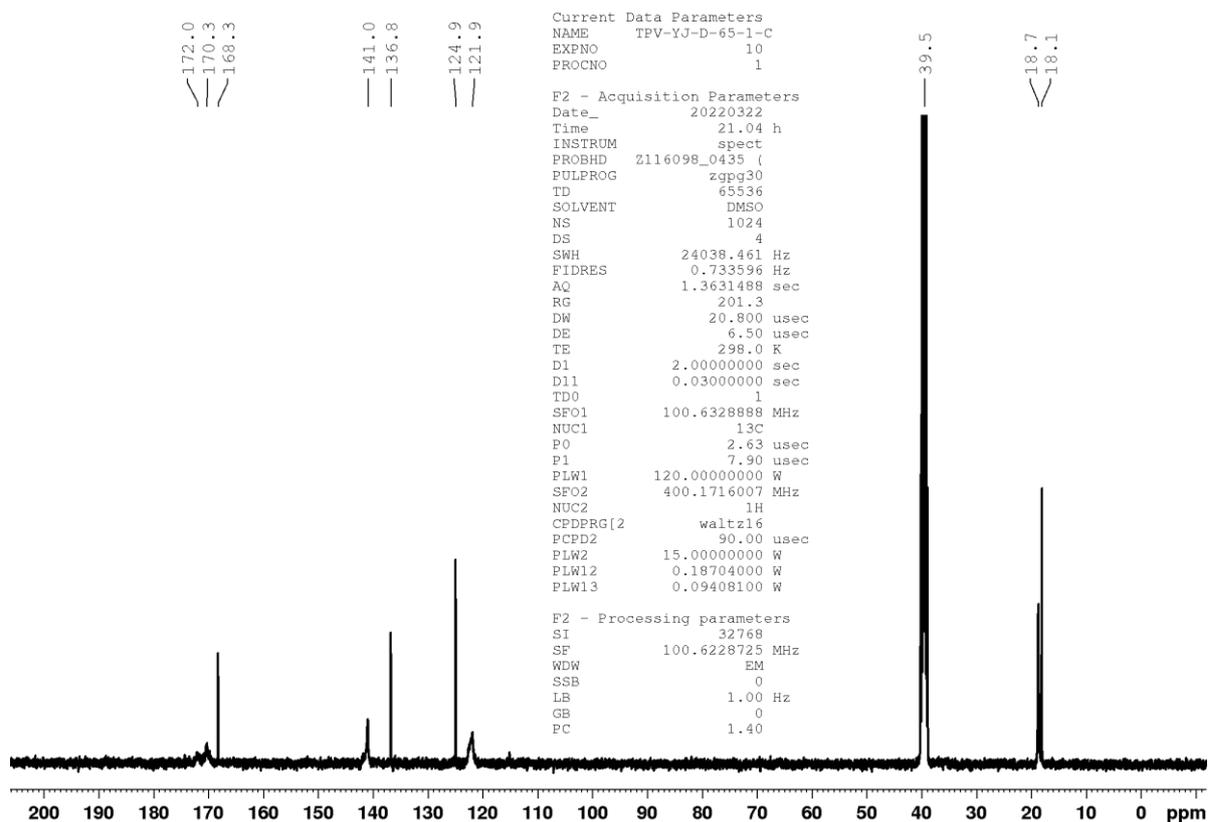
Figure S3. ^{13}C NMR of $[Zr_6O_4(OH)_4(OMc)_{12}]$ (OMc = methacrylate) (**Zr$_6$**) as synthesized.
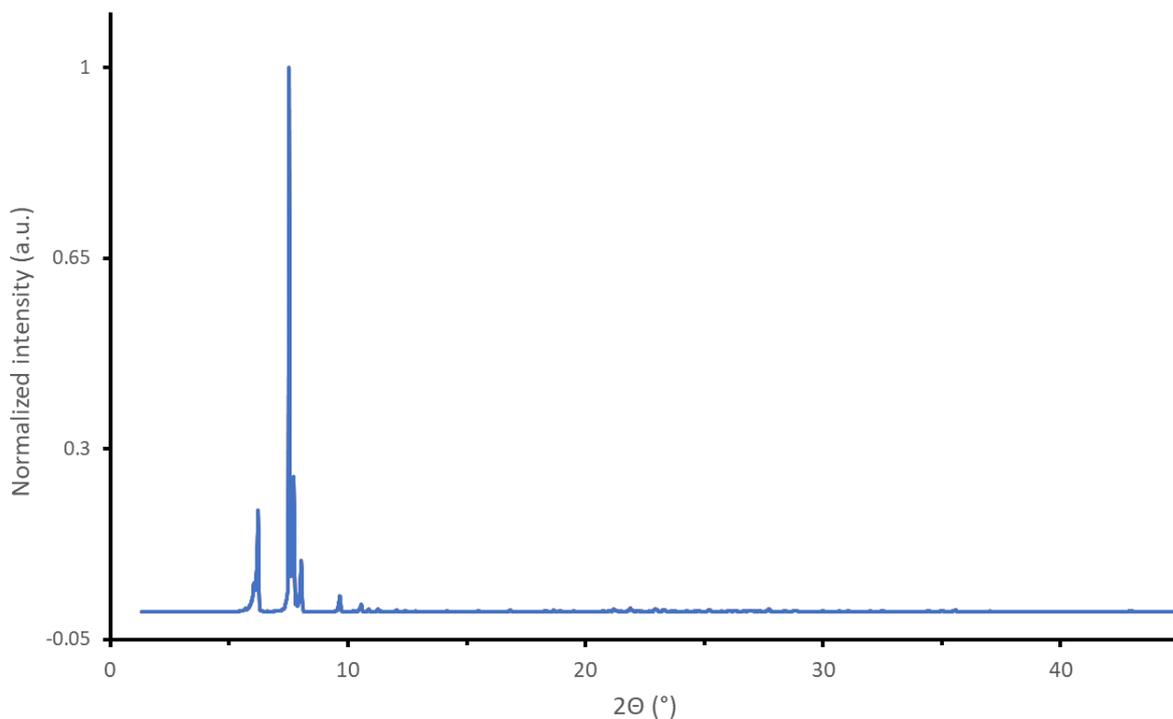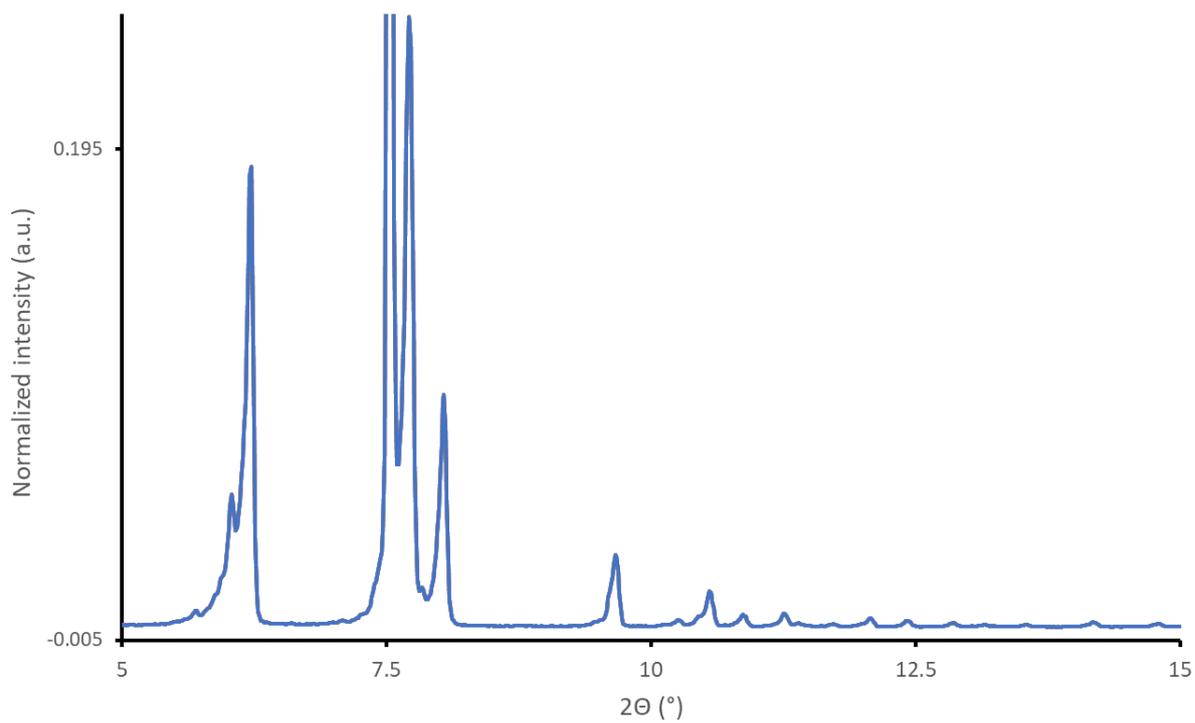
Figure S4. PXRD (λCu = 1.5406 Å) pattern of of [$Zr_6O_4(OH)_4(OMc)_{12}$] (OMc = methacrylate) (**Zr_6**) as synthesized: *Top:* full pattern; *Bottom:* magnification of the 5 – 15° region.

Results and Discussion

Screening of reaction conditions

General Procedure A:

A 4 mL (1 dram) vial was charged with **Zr$_6$** catalyst (0.5 – 50.0 μmol), phenylacetic acid (68.0 – 408.0 mg, 0.50 – 3.0 mmol), benzylamine (128 – 642 mg, 1.2-6.0 mmol), solvent (0.15 – 2.5 mL) and a magnetic stir bar. The reaction mixture was stirred overnight (16 – 24 h) at 50 – 80 °C. After cooling to room temperature, reaction yield was determined ^{1}H NMR. For ^{1}H NMR, the reaction mixture was diluted with CDCl$_3$ (1 mL), 3,5-bistrifluoromethyl-bromobenzene (1.0 equiv.) was added as an internal standard, and the reaction mixture was stirred at room temperature for 10 minutes to ensure thorough mixing. Next, 50 μL of the crude mixture were transferred to a 1.5 mL centrifuge tube and diluted with 450 μL of CDCl$_3$. The final solution was centrifuged. The supernatant (~500 μL) was transferred to an NMR tube, and ^{1}H NMR was recorded. Results are reported based on ^{1}H NMR yields.

NMR experiments

To better understand the **Zr$_6$** ligand exchange dynamics, we evaluated the effect of phenylacetic acid and benzylamine on the ^{1}H NMR spectrum of **Zr$_6$**. DMSO-d$_6$ was used as the solvent to ensure the solubility of the mixture.

Initially, we probed the changes upon addition of increasing amounts phenylacetic acid (**1**).

General Procedure B:

A 2-4 mL vial was charged with 500 µL DMSO-d$_6$, **Zr$_6$** (10.0 µmol, 15.6 mg), and a magnetic stirring bar. The mixture was stirred at 80 °C for around 10 minutes until homogenization has been observed. Then, different amounts of phenylacetic acid were added (see figure below), and the solution was stirred for a few minutes at 80°C until homogenization has been observed. An aliquot of ~450 µL of the solution was transferred to a NMR tube, and analyzed by ^{1}H NMR (300 MHz, room temperature).
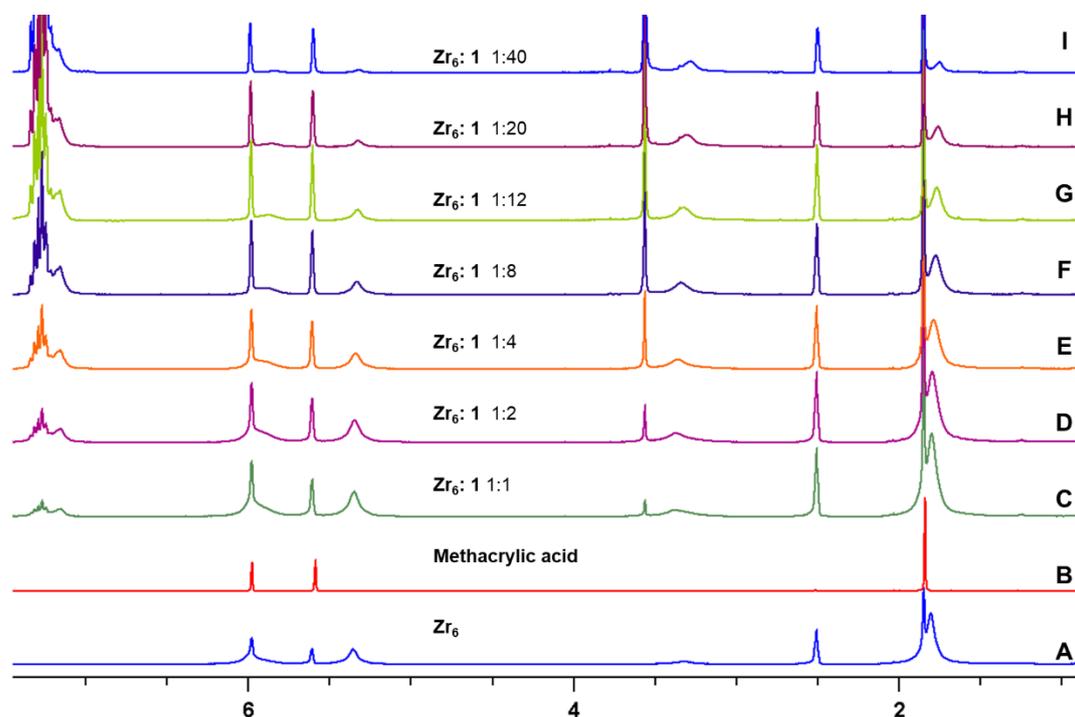
Figure S5. ^{1}H NMR of phenylacetic acid **1** with **Zr$_6$** cluster. (A) **Zr$_6$** with a concentration of 0.02 M, which is equivalent to the amidation reaction using a catalyst loading of 2 mol%. (B) Free methacrylic acid. (C) Solution (A) plus 1 equiv. of **1**. (D) Solution (A) plus 2 equiv. of **1**. (E) Solution (A) plus 4 equiv. of **1**. (F) Solution (A) plus 8 equiv. of **1**. (G) Solution (A) plus 12 equiv. of **1**. (H) Solution (A) plus 20 equiv. of **1**. (I) Solution (A) plus 40 equiv. of **1**.

Upon gradual addition of **1** to the solution of **Zr$_6$** cluster, the initial **Zr$_6$** broad unresolved signals at 5.35 ppm, 5.61 ppm, and 5.98 ppm consistent with the coordination of methacrylate ligand to the Zr oxo core gradually changed to three narrow peaks consistent with free methacrylic acid in solution (Figure S5). This indicates the methacrylate ligands on the surface of **Zr$_6$** cluster were slowly replaced by

phenylacetic acid. As in our previous work, coordination of **1** to **Zr₆** was evidenced by the appearance of a broad singlet at 3.30 ppm, which refers to the benzylic CH_2 group of phenylacetic acid after its coordination to the **Zr₆** cluster. Moreover, addition of methacrylic acid decreasing the intensity of this peak suggested that there is an equilibrium for the coordination between methacrylic acid and phenylacetic acid.[5-6]

Then, we probed the changes upon addition of increasing amounts benzylamine (**2**).

<u>General procedure C:</u>

A 2-4 mL vial was charged with 500 µL DMSO-d_6, **Zr₆** (10.0 µmol, 17.0 mg), and a magnetic stirring bar. The mixture was stirred at 80 °C for around 10 minutes until homogenization has been observed. Then, different amounts of benzylamine were added (see figure below), and the solution was homogenized by gently shaking the NMR tube. An aliquot of ~ 500 µL was transferred to a NMR tube, and analyzed by ¹H NMR (300 MHz, room temperature).

<u>General procedure D:</u>

For the mixtures of benzylamine, and methacrylic acid without **Zr₆** present, the following procedure was used: A 2-4 mL vial was charged with 500 µL DMSO-d_6. In a second vial, methacrylic acid (0.5 mmol, 42 µL), was dissolved in 458 µL of DMSO-d_6. Then, 10 µL (~0.010 mmol) of this solution was added to the first vial. The solution was stirred at 80°C for around 10 minutes until homogenization has been observed. Then, different amounts of benzylamine were added (see figure below), the mixture was stirred at 80°C for a few minutes until homogenization was observed. An aliquot of ~ 500 µL was transferred to a NMR tube, and analyzed by ¹H NMR (300 MHz, room temperature).
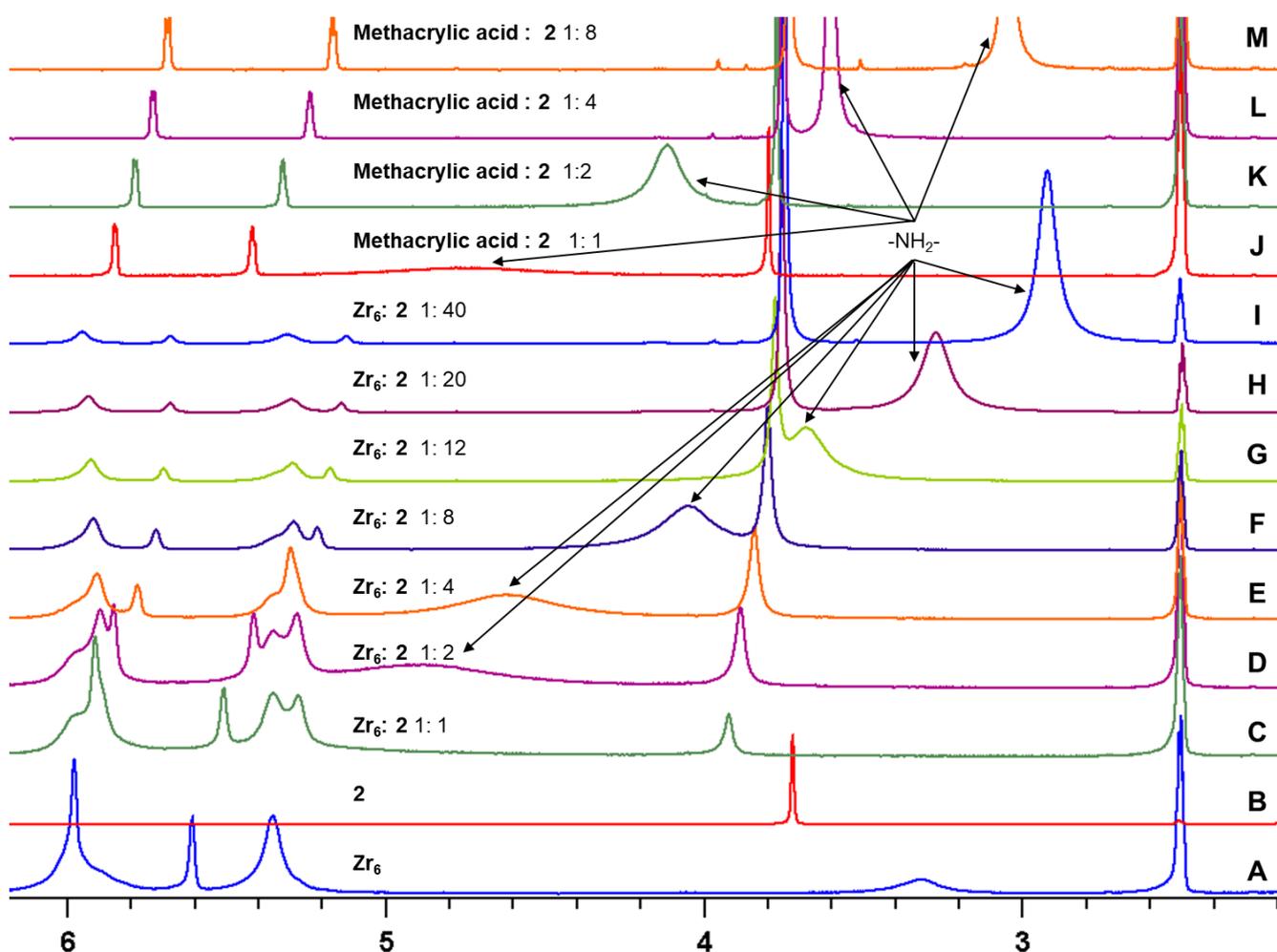
Figure S6. ^{1}H NMR of benzylamine **2** with **Zr$_6$** cluster or methacrylic acid. (A) **Zr$_6$** with a concentration of 0.02 M which is equivalent to the amidation reaction using a catalyst loading of 2 mol%. (B) Benzylamine. (C) Solution A plus 1 equiv. of **2**. (D) Solution A plus 2 equiv. of **2**. (E) Solution A plus 4 equiv. of **2**. (F) Solution A plus 8 equiv. of **2**. (G) Solution A plus 12 equiv. of **2**. (H) Solution A plus 20 equiv. of **2**. (I) Solution A plus 40 equiv. of **2**. (J) A mixture of methacrylic acid/benzylamine = 1:1. (K) A mixture of methacrylic acid/benzylamine = 1:2. (L) A mixture of methacrylic acid/benzylamine = 1:4. (M) A mixture of methacrylic acid/benzylamine = 1:8.

Benzylamine (**2**) coordinates to the Zr centers of **Zr$_6$** cluster, and induce a change in the coordination mode of carboxylate ligands, presumably favoring monodentate and chelating coordination over bridging one. Addition of one equivalent of benzylamine to a solution of **Zr$_6$** initially shifts the non-coordinated methacrylic acid peaks from 5.61 and 5.98 ppm to 5.51 and 5.91 ppm, respectively. These peaks continue shifting up field if more amine is added, which may be caused by the salt formation between benzylamine and methacrylic acid. In addition, these peaks are narrower, and shift faster than the coordinated carboxylate ligands. When amine was mixed with free methacrylic acid with 1:1 ratio, the peaks of the salt could also be found in the system containing **Zr$_6$** and benzylamine with 1:2 ratio. However, the benzylic peak in the later system is broader with a chemical shift range from 3.796 to 3.884 ppm, indicating **2** coordinates to **Zr$_6$**. Addition of more amine partially reverses this shift, bringing the benzylic CH$_2$ resonance closer to the one of free benzylamine, indicating an equilibrium between the coordinated and free amine exists. Apart form the peaks mentioned above, the migration of NH$_2$

peaks were observed over a large range of chemical shift from 1.832 ppm of the free amine to 4.857 ppm (Figure S6). Addition of amine would reverse these shift to upfield, indicating the equilibrium between the free amine and the ones that interact with the cluster.

Besides the single component experiments, we have also probe the solution behavior when both **1** and **2** are present in the solution.

<u>General procedure E:</u>

A 2-4 mL vial was charged with 500 µL DMSO-d_6, **Zr$_6$** (10.0 µmol, 17.0 mg), phenylacetic acid (0.5 mmol, 68 mg), and a magnetic stirring bar. The mixture was stirred at 80 °C for around 10 minutes until homogenization has been observed. Then, different equivalents of benzylamine with respect to phenylacetic acid were added, and the solution was homogenized at 80 °C for 10 min. An aliquot of ~ 500 µL was transferred to a NMR tube, and analyzed by ^{1}H NMR (300 MHz, room temperature).
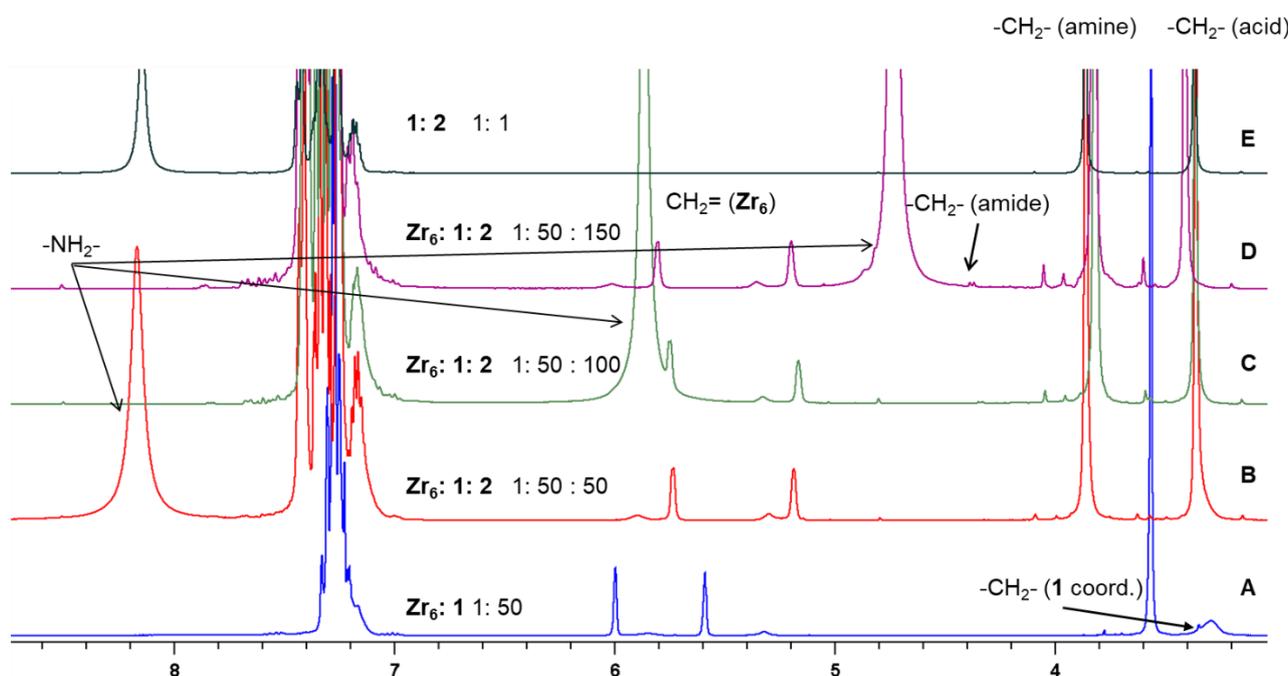
Figure S7. The ^{1}H-NMR signals for phenylacetic acid and benzylamine in a reaction mixture of : (A) Mixture of **Zr$_6$** cluster and 50 equiv. of phenylacetic acid. (B) Solution A plus 50 equiv. of **2**. (C) Solution B plus 50 equiv. of **2**. (D) Solution C plus 50 equiv. of **2**. (E) Mixture of **1** and 1 equiv. of **2**. Analysis performed at room temperature

Addition of one equivalent of benzylamine resulted initially in the formation of an ammonium carboxylate ion pair between **1** and **2**. The broad singlet peak around 3.319 ppm indicating coordination of **1** can still be observed. This peak disappears when more amine is added. Furthermore, the peaks of CH$_2$= group shifted to upfield, similar to Figure S6 when excess amine **2** is added. The NH$_2$ peaks and its migration when excess amine was added can be noticed as well. Notably, formation of product **3** can be observed, demonstrating that the excess amount of amine is beneficial for this reaction.[7-8]

Experimental details of products in Table 2

General Procedure F:

A 4 mL (1 dram) vial was charged with **Zr₆** cluster (3.9 – 15.6 mg, 5.0 – 20 µmol), phenylacetic acid (68.0 mg, 0.500 mmol), benzylamine (161 – 268 mg, 1.50 – 2.50 mmol), solvent (0.15 mL), and a magnetic stir bar. The reaction mixture was stirred for 24 – 48 h at 70 – 80 °C. After cooling to room temperature, reaction yield was determined ^{1}H NMR. For ^{1}H NMR, the reaction mixture was diluted with CDCl₃ (1 mL), 3,5-bistrifluoromethyl-bromobenzene (1 equiv.) was added as an internal standard, and the reaction mixture was stirred at room temperature for 10 minutes to ensure thorough mixing. Next, 50 µL of the crude mixture was transferred to a 1.5 mL centrifuge tube and diluted with 450 µL of CDCl₃. The final solution was centrifuged. The supernatant (~500 µL) was transferred to an NMR tube, and ^{1}H NMR was recorded. Results are reported based on ^{1}H NMR yields.

N-benzyl-2-phenylacetamide (3)
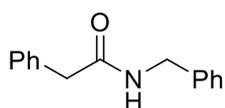
General procedure F was followed using **Zr₆** cluster (5.0 µmol 8.5 mg), phenylacetic acid (68.0 mg, 0.500 mmol), benzylamine (161 mg, 1.50 mmol), and ethanol (0.15 mL). The reaction was stirred at 70 °C for 48 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 85% yield.[9]

N-[(2-chlorophenyl)methyl]-2-phenylacetamide (6)
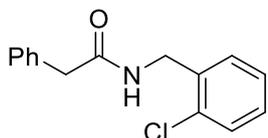
General procedure F was followed using Zr₆ cluster (2.5 µmol 4.3 mg), phenylacetic acid (68.0 mg, 0.500 mmol), 2-chlorobenzylamine (213 mg, 1.50 mmol), and ethanol (0.15 mL). The reaction was stirred at 70 °C for 24 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 60% yield.[8]

N-[(4-chlorophenyl)methyl]-2-phenylacetamide (7)
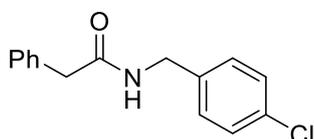
General procedure F was followed using **Zr₆** cluster (2.5 µmol 4.3 mg), phenylacetic acid (68.0 mg, 0.500 mmol), 4-chlorobenzylamine (213 mg, 1.50 mmol) , and ethanol (0.15 mL). The reaction was stirred at 80 °C for 24 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 69% yield.[10]

N-[(2-methoxyphenyl)methyl]-2-phenylacetamide (8)
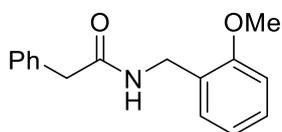
General procedure F was followed using **Zr₆** cluster (10.0 µmol 17.0 mg), phenylacetic acid (68.0 mg, 0.500 mmol), 2-methoxybenzylamine (343 mg, 2.50 mmol) , and ethanol (0.15 mL). The reaction was stirred at 80 °C for 48 h.

Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 89% yield.[11]

tert-Butyl (2-(benzylamino)-2-oxoethyl)carbamate (9)
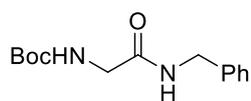
General procedure F was followed using **Zr₆** cluster (2.5 µmol, 4.3 mg), *N*-(*tert*-butoxycarbonyl)glycine (88 mg, 0.500 mmol), benzylamine (161 mg, 1.5 mmol) , and ethanol (0.15 mL). The reaction was stirred at 70 °C for 24 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 82% yield.[12]

N-benzylnicotinamide (10)
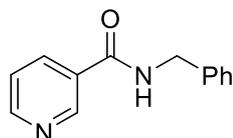
General procedure F was followed using **Zr₆** cluster (10.0 µmol, 17.0 mg), 4-nicotinic acid (62.0 mg, 0.500 mmol), benzylamine (268 mg, 2.50 mmol) , and ethanol (0.15 mL). The reaction was stirred at 80 °C for 26 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 49% yield.[13]

N-benzylthiophene-3-carboxamide (11)
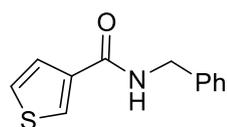
General procedure F was followed using **Zr₆** cluster (10.0 µmol, 17.0 mg), 3-thiophenecarboxylic acid (64.0 mg, 0.500 mmol), benzylamine (268 mg, 2.50 mmol) , and ethanol (0.15 mL). The reaction was stirred at 80 °C for 26 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard showed the product formation in 50% yield.[14]

N-benzylacetamide (12)
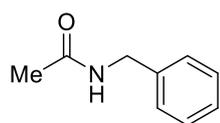
General procedure F was followed using **Zr₆** cluster (10.0 µmol, 17.0 mg), acetic acid (30.0 mg, 0.500 mmol), benzylamine (268 mg, 2.50 mmol) , and ethanol (0.15 mL). The reaction was stirred at 80 °C for 26 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 92% yield.[15]

N-benzylbutyramide (13)
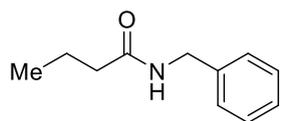
General procedure F was followed using **Zr₆** cluster (10.0 µmol, 17.0 mg), butyric acid (44.0 mg, 0.500 mmol), benzylamine (268 mg, 2.50 mmol) , and ethanol (0.15 mL). The reaction was stirred at 80 °C for 48 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 85% yield.[16]

N-benzylisobutyramide (14)
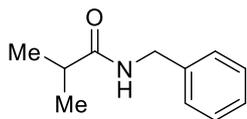
General procedure F was followed using **Zr₆** cluster (10.0 μmol, 17.0 mg), iso butyric acid (44.0 mg, 0.500 mmol), benzylamine (268 mg, 2.50 mmol), and ethanol (0.15 mL). The reaction was stirred at 80 °C for 48 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard, and comparison with previous spectral description, showed the product formation in 68% yield.[17]

N-benzylthiophene-2-carboxamide (15)
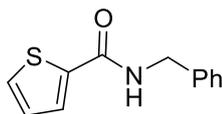
General procedure F was followed using **Zr₆** cluster (10.0 μmol, 17.0 mg), 2-thiophenecarboxylic acid (64.0 mg, 0.500 mmol), benzylamine (168 mg, 2.50 mmol), and ethanol (0.15 mL). The reaction was stirred at 80 °C for 48 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard showed the product formation in 50% yield.[13]

N-benzylfuran-2-carboxamide (16)
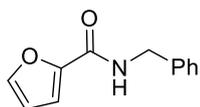
General procedure F was followed **Zr₆** cluster (10.0 μmol, 17.0 mg), 2-furoic acid (56.0 mg, 0.500 mmol), benzylamine (161 mg, 1.5 mmol), and ethanol (0.15 mL). The reaction was stirred at 80 °C for 18 h. Analysis by ^{1}H NMR with 3,5-bistrifluoromethyl-bromobenzene as internal standard showed the product formation in 30% yield.[18]

Control experiments

To probe for the potential complete disassemble of the cluster in 6 mononuclear zirconium complexes, the catalytic reactivity of Zr_6 cluster was compared with 6 equimolar amount of different zirconium salts. Here we choose $ZrCl_4$, $Zr(OH)_4$, ZrO_2 and $ZrOCl_2$ as the representatives.

<u>General Procedure G:</u>

A 4 mL (1 dram) vial was charged with catalyst (0.01 – 0.03 mmol of Zr), phenylacetic acid (68.0 mg, 0.500 mmol), benzylamine (161 mg, 1.5 mmol), ethanol (0.15 mL), and a magnetic stir bar. The reaction mixture was stirred 26 h at 80 °C. After cooling to room temperature, reaction yield was determined by ^{1}H NMR. For ^{1}H NMR, the reaction mixture was diluted with CDCl$_3$ (1 mL), 3,5-bistrifluoromethyl-bromobenzene (1.0 equiv.) was added as an internal standard, and the reaction mixture was stirred at room temperature for 10 minutes to ensure thorough mixing. Next, 50 µL of the crude mixture was transferred to a 1.5 mL centrifuge tube and diluted with 450 µL of CDCl$_3$. The final solution was centrifuged. The supernatant (~500 µL) was transferred to an NMR tube and ^{1}H NMR was recorded. Results are reported based on ^{1}H NMR yields.

Table S1. Catalytic reactivity of different Zr-salts.
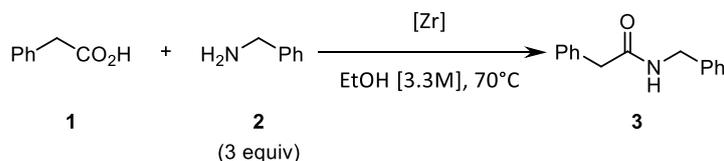
Entry	[Zr]	mol%	Yield of **3** (%)
1	$Zr_6(OMc)_{12}$	1.0	88
2	$ZrOCl_2 \cdot 8H_2O$	6.0	2
3	$Zr(OH)_4$	6.0	-
4	ZrO_2	6.0	1
5	$ZrCl_4$	6.0	3
6	$Zr(OPr)_4$	6.0	80

Reaction conditions: **1** (0.5 mmol), **2** (1.5 mmol), EtOH (0.15 mL), [Zr] (1.0 – 6.0 mol%), 70°C, 22-26 h. ^{1}H NMR yields.

Under same condition, zirconium salts could only provide less than 5% yield of the product, indicating that the mononuclear zirconium complexes were not the catalytic active species and also that Zr_6's catalytic reactivity as a whole in the reaction instead of disassemble into mononuclear zirconium species. The performance of $Zr(OPr)_4$ is attributed to a putative formation of a Zr-oxo cluster in situ, since $Zr(O^nPr)_4$ is a common precursor for the synthesis of ZrOC.[4]

Comparison of Zr–O bond lengths

Table S2. Zr-O bond lengths (Å) for **Zr$_6$** and **Zr$_{12}$** clusters, and Zr-based MOFs UiO-66, MOF-808, and NU-1000.[a]
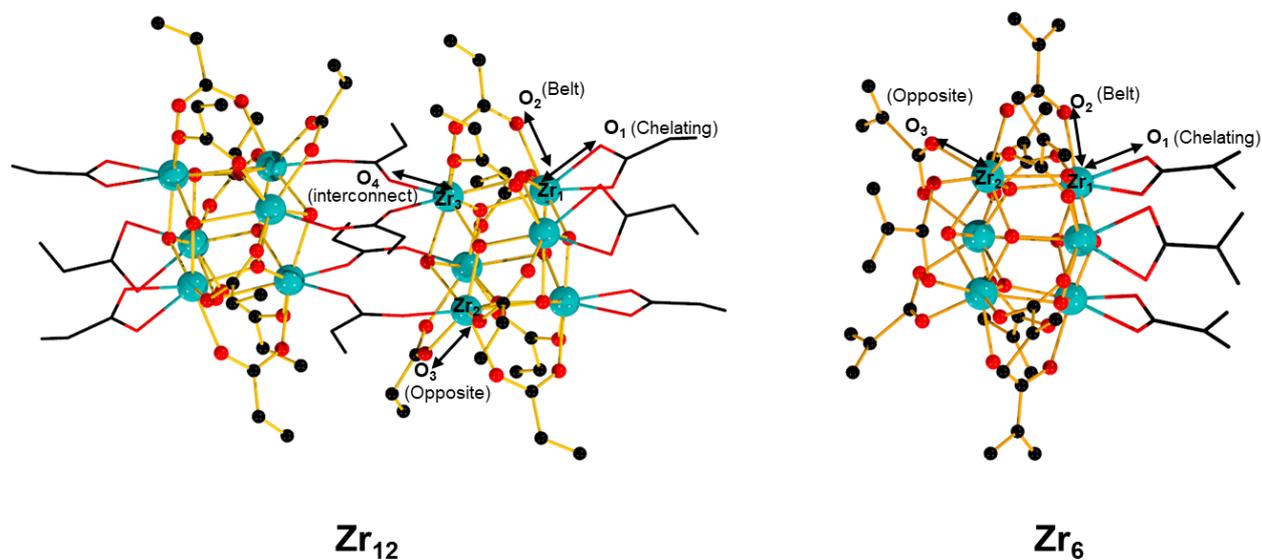
Bond	Zr$_{12}$	Zr$_6$	UiO-66[19]	MOF-808[20]	NU-1000[21]
Zr$_1$-O$_1$ (chelating)	2.2707 – 2.3191	2.3297 – 2.3298			
Zr$_2$-O$_2$ (belt)	2.1916 – 2.2318	2.1293 – 2.1935	2.2667	2.2131	2.1978 – 2.2419
Zr$_2$-O$_3$ (opposite)	2.2134 – 2.2184	2.1004 – 2.1005			
Zr$_3$-O$_4$ (interconn.)	2.1595 – 2.2103				
Zr-O (core)	2.0260 – 2.4087	2.0504 – 2.4109	2.1183	2.0361 – 2.2322	2.1760 – 2.1960
Zr-O (formate)				2.2508	
Zr-O$_{(H2O)}$					2.1893 – 2.1974

[a] Ball and stick representation of **Zr$_6$** and **Zr$_{12}$**. The chelating and the interconnected bridging carboxylate are represented by two-color wires. Color code: Color code: Zr (teal), O (red), C (black). Hydrogen atoms omitted for clarity.

References

1.   Kickelbick, G.; Schubert, U. Oxozirconium Methacrylate Clusters: $Zr_6(OH)_4O_4(OMc)$ and $Zr_4O_2(OMc)_{12}$ (OMc = Methacrylate). *Chem. Ber.* **1997**, *130*, 473-478. https://doi.org/10.1002/cber.19971300406

2.   Kogler, F. R.; Jupa, M.; Puchberger, M.; Schubert, U. Control of the ratio of functional and non-functional ligands in clusters of the type $Zr_6O_4(OH)_4(carboxylate)_{12}$ for their use as building blocks for inorganic–organic hybrid polymers. *J. Mater. Chem.* **2004**, *14*, 3133-3138. http://dx.doi.org/10.1039/B405769D

3.   Epp, K.; Semrau, A. L.; Cokoja, M.; Fischer, R. A. Dual Site Lewis-Acid Metal-Organic Framework Catalysts for CO2 Fixation: Counteracting Effects of Node Connectivity, Defects and Linker Metalation. *ChemCatChem* **2018**, *10*, 3506-3512. https://doi.org/10.1002/cctc.201800336

4.   Zhang, Y.; de Azambuja, F.; Parac-Vogt, T. N. Zirconium oxo clusters as discrete molecular catalysts for the direct amide bond formation. *Catal. Sci. Technol.* **2022**, *12*, 3190-3201. http://dx.doi.org/10.1039/D2CY00421F

5.   Puchberger, M.; Kogler, F. R.; Jupa, M.; Gross, S.; Fric, H.; Kickelbick, G.; Schubert, U. Can the Clusters $Zr_6O_4(OH)_4(OOCR)_{12}$ and $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ Be Converted into Each Other? *Eur. J. Inorg. Chem.* **2006**, *2006*, 3283-3293. https://doi.org/10.1002/ejic.200600348

6.   Kreutzer, J.; Puchberger, M.; Artner, C.; Schubert, U. Retention of the Cluster Core Structure during Ligand Exchange Reactions of Carboxylato-Substituted Metal Oxo Clusters. *Eur. J. Inorg. Chem.* **2015**, *2015*, 2145-2151. https://doi.org/10.1002/ejic.201403209

7.   de Azambuja, F.; Lenie, J.; Parac-Vogt, T. N. Homogeneous Metal Catalysts with Inorganic Ligands: Probing Ligand Effects in Lewis Acid Catalyzed Direct Amide Bond Formation. *ACS Catal.* **2021**, *11*, 271-277. https://doi.org/10.1021/acscatal.0c04189

8.   de Azambuja, F.; Parac-Vogt, T. N. Water-Tolerant and Atom Economical Amide Bond Formation by Metal-Substituted Polyoxometalate Catalysts. *ACS Catal.* **2019**, *9*, 10245-10252. https://doi.org/10.1021/acscatal.9b03415

9.   Lundberg, H.; Tinnis, F.; Adolfsson, H. Direct Amide Coupling of Non-activated Carboxylic Acids and Amines Catalysed by Zirconium(IV) Chloride. *Chem. Eur. J.* **2012**, *18*, 3822-3826. https://doi.org/10.1002/chem.201104055

10.   Lundberg, H.; Adolfsson, H. Hafnium-Catalyzed Direct Amide Formation at Room Temperature. *ACS Catal.* **2015**, *5*, 3271-3277. https://doi.org/10.1021/acscatal.5b00385

11.   Lanigan, R. M.; Starkov, P.; Sheppard, T. D. Direct Synthesis of Amides from Carboxylic Acids and Amines Using $B(OCH_2CF_3)_3$. *J. Org. Chem.* **2013**, *78*, 4512-4523. https://doi.org/10.1021/jo400509n

12.   Sanz Sharley, D. D.; Williams, J. M. J. Acetic Acid as a Catalyst for the N-Acylation of Amines Using Esters as the Acyl Source. *Chem. Commun.* **2017**, *53*, 2020-2023. http://dx.doi.org/10.1039/C6CC09023K

13.   Cui, X.; Zhang, Y.; Shi, F.; Deng, Y. Organic Ligand-Free Alkylation of Amines, Carboxamides, Sulfonamides, and Ketones by Using Alcohols Catalyzed by Heterogeneous Ag/Mo Oxides. *Chem. Eur. J.* **2011**, *17*, 1021-1028. https://onlinelibrary.wiley.com/doi/abs/10.1002/chem.201001915

14.   Ren, W.; Yamane, M. Palladium-Catalyzed Carbamoylation of Aryl Halides by Tungsten Carbonyl Amine Complex. *J. Org. Chem.* **2009**, *74*, 8332-8335. https://doi.org/10.1021/jo901486z

15.   Bi, N.-M.; Ren, M.-G.; Song, Q.-H. Photo-Ritter Reaction of Arylmethyl Bromides in Acetonitrile. *Synth. Commun.* **2010**, *40*, 2617-2623. https://doi.org/10.1080/00397910903297555

16.   Watson, A. J. A.; Maxwell, A. C.; Williams, J. M. J. Borrowing Hydrogen Methodology for Amine Synthesis under Solvent-Free Microwave Conditions. *J. Org. Chem.* **2011**, *76*, 2328-2331. https://doi.org/10.1021/jo102521a

17.   Hardee, D. J.; Kovalchuke, L.; Lambert, T. H. Nucleophilic Acyl Substitution via Aromatic Cation Activation of Carboxylic Acids: Rapid Generation of Acid Chlorides under Mild Conditions. *J. Am. Chem. Soc.* **2010**, *132*, 5002-5003. https://doi.org/10.1021/ja101292a

18.   Chen, C.; Zhang, Y.; Hong, S. H. N-Heterocyclic Carbene Based Ruthenium-Catalyzed Direct Amide Synthesis from Alcohols and Secondary Amines: Involvement of Esters. *J. Org. Chem.* **2011**, *76*, 10005-10010. https://doi.org/10.1021/jo201756z

19.   Valenzano, L.; Civalleri, B.; Chavan, S.; Bordiga, S.; Nilsen, M. H.; Jakobsen, S.; Lillerud, K. P.; Lamberti, C. Disclosing the Complex Structure of UiO-66 Metal Organic Framework: A Synergic Combination of Experiment and Theory. *Chem. Mater.* **2011**, *23*, 1700-1718. https://doi.org/10.1021/cm1022882

20.   Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. Water Adsorption in Porous Metal–Organic Frameworks and Related Materials. *J. Am. Chem. Soc.* **2014**, *136*, 4369-4381. https://doi.org/10.1021/ja500330a

21.   Islamoglu, T.; Otake, K.-i.; Li, P.; Buru, C. T.; Peters, A. W.; Akpinar, I.; Garibay, S. J.; Farha, O. K. Revisiting the structural homogeneity of NU-1000, a Zr-based metal–organic framework. *CrystEngComm* **2018**, *20*, 5913-5918. http://dx.doi.org/10.1039/C8CE00455B