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Thorium Amidates Function as Single-Source Molecular Precursors for Thorium Dioxide

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We report the synthesis of four homoleptic thorium(IV) amidate complexes as single-source molecular precursors for thorium dioxide. Each can be sublimed at atmospheric pressure, with the substituents on the amidate ligands significantly impacting their volatility and thermal stability. These complexes decompose via alkene elimination to give ThO_2 without need for a secondary oxygen source. ThO_2 samples formed from pyrolysis of C-alkyl amidates were found to have higher purity and crystallinity than ThO_2 samples formed from C-aryl amidates.

The chemistry of the early actinides is currently in a resurgence, with tremendous contributions towards new ligand systems[1-5] and advances in actinide materials.[1,6-13] Research in thorium chemistry is often motivated by the global push for energy production, and thorium-fueled reactors are predicted to offer multiple advantages over conventional uranium dioxide-fueled reactors.[14-17] These include significantly lower production of radiotoxic transuranic elements in the thorium fuel cycle[18] and greater earth-abundance of thorium versus uranium.[19] Despite these advantages, some concerns have been expressed about the possibility of component failure in thorium reactors due to poorly-understood chemical behavior under long-term operating conditions.[14,20] Given that solid-state reactions such as corrosion and deposition typically occur at material interfaces, high surface area actinide nanomaterials, such as thin films and nanoparticles, serve as excellent models for studying these processes in bulk systems such as conventional oxide and mixed oxide (MOX) nuclear fuels.[21-27]

Synthesizing well-defined thorium materials from molecular precursors has proven challenging due to the small pool of known thorium precursors and a limited mechanistic understanding of the conversion processes from actinide molecules to materials.[27-29] To address this gap in knowledge, bespoke precursors can be rationally designed with a readily-accessible decomposition pathway, enabling clean formation of the desired materials through careful control of the chemical

behavior of the precursor.[30] In addition to a well-defined decomposition mechanism, ideal precursors for actinide materials should possess adequate thermal stability and volatility, enabling the use of gas-phase methods such as chemical vapor deposition (CVD), atomic layer deposition (ALD), and framework-templated nanoparticle synthesis.[27,30-37] Single-source precursors, which contain all necessary elements for the target material in suitable ratios, are particularly desirable because they avoid the need for reactive secondary gases that can introduce harsh conditions and greater complexity to the decomposition process.[38,39]

As a first step towards satisfying these requirements in thorium precursor design, we turned to amidate ligands, which are formed by deprotonation of organic amides. Due to their significant thermal stability and volatility, metal amidate complexes have been used as molecular precursors for metal oxide film deposition, yielding phase-pure films through a well-defined decomposition pathway.[39-41] While there is some precedent for uranium amidates,[39,42-44] no homoleptic thorium amidates have been reported. Here we describe the synthesis of homoleptic thorium amidate complexes as single-source molecular precursors to ThO_2 and describe the mechanism of their thermal decomposition to ThO_2.

Deprotonation of the amides N-*tert*-butylisobutyramide (H(ITA)), N-*tert*-butyl-(4-*tert*-butyl)benzamide (H(TPTA)), N-(3-pentyl)pivalamide (H(TEPA)), and N-*tert*-butyl-(3,5-bis(trifluoromethyl))benzamide (H(Ar^{F}TA)) with KN(SiMe$_3$)$_2$ in THF yielded the corresponding potassium amidate salts as colorless powders. The homoleptic thorium amidate complexes Th(ITA)$_4$ **(1)**, Th(TEPA)$_4$ **(2)**, Th(Ar^{F}TA)$_4$ **(3)**, and Th(TPTA)$_4$ **(4)** were synthesized via salt metathesis reactions between ThCl$_4$(DME)$_2$ and four equivalents of potassium amidate in THF (Scheme 1) and isolated as colorless, air-sensitive crystals. Single crystal X-ray crystallographic data for **1**, **3**, and **4** revealed these complexes to be 8-coordinate with all four amidate ligands binding in a κ^2-O,N geometry; this ligand coordination mode has also been observed in transition metal[40,41,45] and uranium[39,42,43] complexes (Figure 1). Complexes **1** and **3** adopt
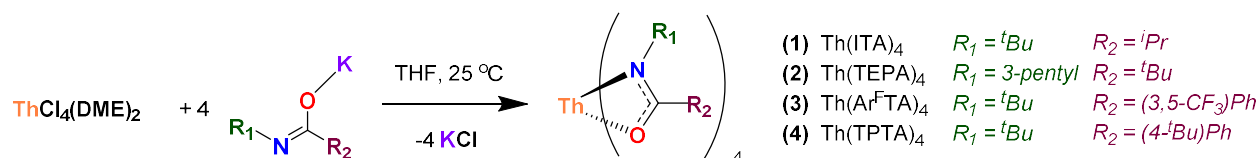
Scheme 1. Synthesis of homoleptic thorium amidate complexes (**1–4**).
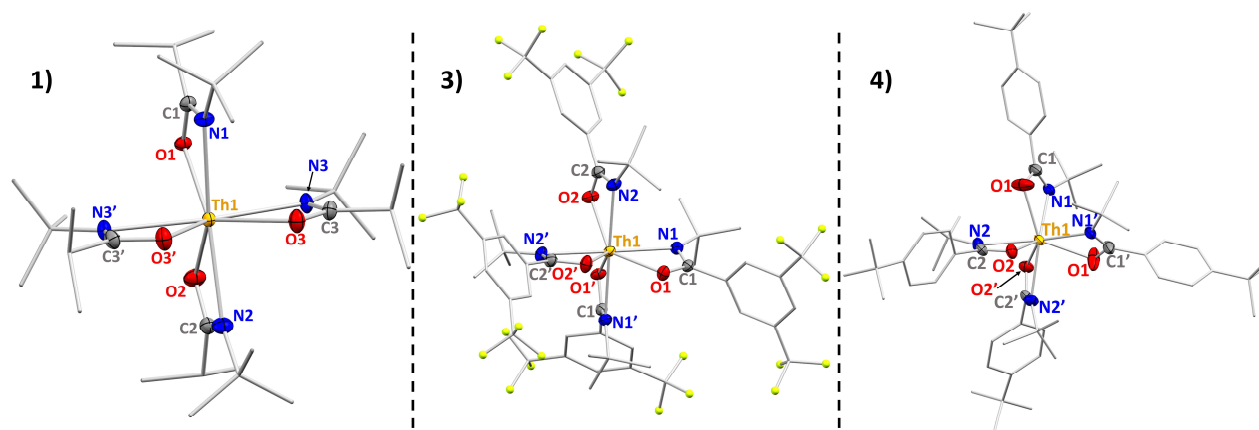

Figure 1. X-ray crystal structures of **1**, **3**, and **4** with 50% probability ellipsoids. Hydrogen atoms are omitted, and amidate substituents are represented as capped sticks for clarity. Bond metrics are listed in Table S2.

similar pseudo-D_{2d} structural geometries, with two sets of amidate ligands related by approximate mirror symmetry, whereas **4** displays a lower-symmetry pseudo-S_4 dodecahedral geometry. The four N atoms in **3** lie in a square plane relative to the Th center, while there is a distortion of the N atoms from this plane in **1** and **4**. Solid-state structures of **1**, **3**, and **4** show Th–O and Th–N bond ranges of 2.331(3)–2.444(2) and 2.522(7)–2.565(2) Å, respectively (Table S2). Within the amidate ligands, the O–C–N angles ranged from 114.9(7)–118.0(9)°, and the C–O and C–N bond lengths ranged from 1.301(3)–1.315(7) and 1.255(9)–1.303(6) Å. These metrical parameters are comparable to reported values for structurally similar uranium amidate complexes.[39,42] Attempts to solve the solid-state structure of **2** were unsuccessful (see ESI).

All four complexes (**1-4**) could be vaporized by heating under atmospheric pressure. Sublimation of the bis(alkyl) amidates **1** and **2** was observed at 261 °C and 190 °C, respectively, with no sign of decomposition. Compound **4** sublimed at 220 °C, although a small amount of amide was also

identified in the sublimate, indicating simultaneous sublimation and gradual decomposition at this temperature. The fluorinated amidate **3** melted at 148 °C and vaporized readily at higher temperatures. Compound **3** was thus the most volatile, despite having the highest molecular weight of the four complexes. This can most likely be attributed to weak intermolecular interactions in **3** as a function of low dispersion forces between fluorinated substituents.

To study the mechanism of decomposition of these precursors to ThO$_2$, solid samples of **1-4** were heated to 300 °C in sealed NMR tubes under nitrogen. This procedure was sufficient to decompose **1**, **3**, and **4**; however, **2** did not decompose in the solid-state at this temperature even after heating for one week. The higher decomposition temperature of **2** is likely due to the increased kinetic barrier of alkene elimination from a secondary alkyl vs. a tertiary alkyl substituent.[46] However, slight decomposition of **2** was observed by heating a d$_{18}$-decalin solution of **2** to 240 °C for 2 weeks. Based on our previous results with related uranium amidate
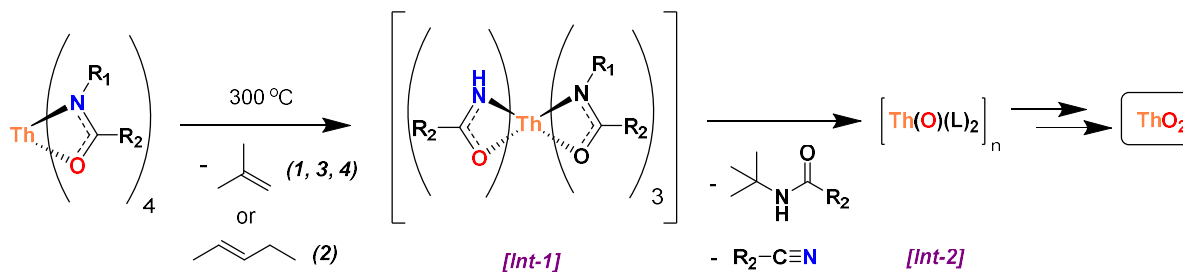
Scheme 2. Proposed decomposition mechanism for complexes **1-4**. Alkene, amide, and nitrile byproducts were observed directly by ^{1}H NMR spectroscopy. Intermediate decomposition products **Int-1** and **Int-2** are postulated.
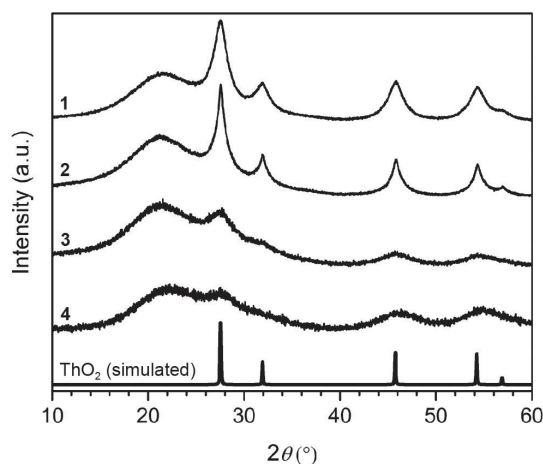
Figure 2. *Powder X-ray diffraction patterns of the products formed by pyrolysis of **1-4** compared with a ThO₂ simulation.*

complexes,[39] we anticipated that **1-4** would decompose through an alkene elimination mechanism (Scheme 2). Indeed, NMR studies of the decomposition products provided strong evidence for this mechanism: clean formation of the expected alkene, amide, and nitrile products were observed for all four species (see ESI).

Preliminary tests of the viability of complexes **1-4** as single-source precursors to ThO_2 were conducted by pyrolyzing the samples in quartz tubes sealed under a nitrogen atmosphere. Analysis using powder X-ray diffraction (PXRD) confirmed that pyrolysis of all four precursors produced ThO_2 (Figure 2). Qualitatively, the presence of sharper diffraction peaks for the ThO_2 products prepared from **1** and **2** relative to **3** and **4** suggested greater crystallinity of the ThO_2 prepared from C-alkyl amidates relative to C-aryl amidates.

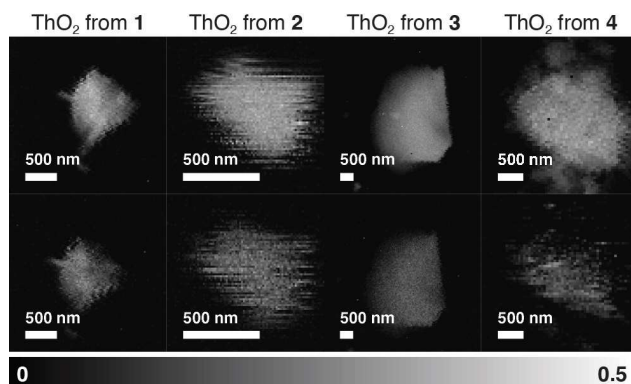To probe chemical purity, oxygen K-edge X-ray absorption spectroscopy was performed with a scanning transmission X-ray

microscope (STXM-XAS). Figure 3 shows a selection of elemental maps obtained from representative particles, demonstrating homogenous distributions of O and Th on the micron scale. Averaged O K-edge XAS data obtained from multiple micron-scale particles are compared with a reference spectrum of pure ThO_2 in Figure 4.[27,47] The overall spectral profiles for the ThO_2 prepared from precursors **1** and **2** agreed well with the ThO_2 reference data, with similar intense features found in all three spectra at low energies (532.4, 535.5, 539.0 eV) and high energies (542.3, 544.7 eV). The O K-edge spectrum obtained for ThO_2 prepared from the C-aryl amidate precursor **3** also exhibited features that were characteristic of ThO_2, however, the weaker relative intensities and disappearance of high-energy features suggested that other oxygen-containing impurities were present in the sample. An even more significant deviation from the ThO_2 reference was observed in the O K-edge XAS for ThO_2 from **4**, which showed signatures of ThO_2 that were barely discernable from other absorptions.

Elemental analysis (EA) of the ThO_2 formed via pyrolysis of the C-aryl amidates **3** and **4** indicated the presence of carbon to be 12.89% and 19.23% in these materials, respectively, while the ThO_2 formed via pyrolysis of the C-alkyl amidates **1** and **2** showed significantly lower carbon contents of 6.43% and 6.56%, respectively. Taken together, the PXRD, O K-edge XAS, and EA data suggest that ThO_2 samples prepared from the C-alkyl amidates **1** and **2** had both higher crystallinity and greater compositional purity than the ThO_2 samples prepared from the C-aryl amidates **3** and **4**.

In conclusion, we have synthesized the first homoleptic thorium amidate complexes and demonstrated their viability as single-source molecular precursors to ThO_2 materials. All complexes displayed sufficient volatility for metal-organic chemical vapor deposition and could be readily sublimed under partial vacuum and atmospheric pressures. Preliminary thermal decomposition studies showed that the complexes can all undergo an alkene elimination mechanism to yield ThO_2
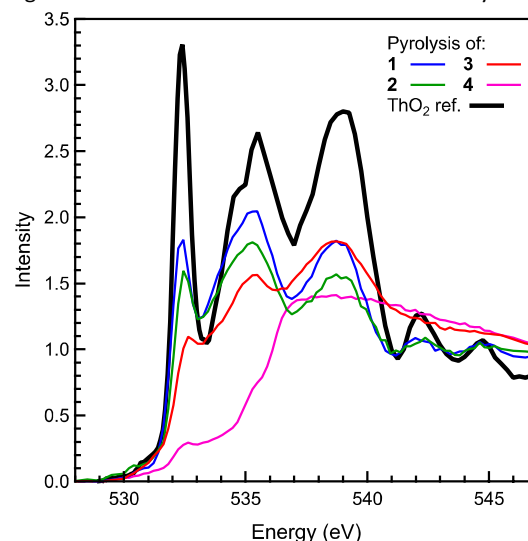

Figure 3. *Representative elemental difference maps of micron-scale ThO_2 particles formed by pyrolysis of **1-4** that were used to obtain X-ray absorption spectra. Lighter regions in the elemental maps correspond to greater concentration of the absorbing atom and were obtained by subtraction of two images: one taken at an energy just below the X-ray absorption edge and another taken at the absorption maximum.*

Figure 4. *Plot comparing the O K-edge XAS for the ThO_2 products obtained by pyrolysis of thorium amidates **1-4** and a ThO_2 reference.*

without the need for an external oxygen source; however, differences in the PXRD and STXM-XAS suggest that ligand substitution can be modified to improve crystallinity and compositional purity. Along these lines, metal-organic chemical vapor decomposition of the most promising C-alkyl amidates **1** and **2** and in-depth characterization of the as-formed ThO_2 materials is the subject of ongoing work.

Acknowledgements

Notes and references

1   J. K. Gibson and W. A. de Jong, *Experimental and Theoretical Approaches to Actinide Chemistry*, Wiley, 1st edn., 2018.
2   M. A. Boreen and J. Arnold, *Multiple Bonding in Actinide Chemistry*, in the *Encyclopedia of Inorganic and Bioinorganic Chemistry*, Wiley, 2018.
3   C. D. Tutson and A. E. V. Gorden, *Coord. Chem. Rev.*, 2017, **333**, 27-43.
4   S. T. Liddle, *Angew. Chem. Int. Ed.*, 2015, **54**, 8604–8641.
5   C. E. Hayes and D. B. Leznoff, *Coord. Chem. Rev.*, 2014, **266-267**, 155-170.
6   J. Leduc, J. I. Pacold, D. K. Shuh, C. L. Dong and S. Mathur, *Z. Anorg. Allg. Chem.*, 2017, **644**, 12–18.
7   C. Falaise, H. A. Neal and M. Nyman, *Inorg. Chem.*, 2017, **56**, 6591–6598.
8   S. N. Kalmykov and M. A. Denecke, *Actinide Nanoparticle Research*, Springer, 1st edn., 2011.
9   D. Hudry, C. Apostolidis, O. Walter, T. Gouder, E. Courtois, C. Kübel and D. Meyer, *Chem. Eur. J.*, 2012, **18**, 8283–8287.
10   C. Schöttle, S. Rudel, R. Popescu, D. Gerthsen, F. Kraus and C. Feldmann, *ACS Omega*, 2017, **2**, 9144–9149.
11   E. L. Bright, S. Rennie, M. Cattelan, N. A. Fox, D. T. Goddard and R. Springell, *Thin Solid Films*, 2018, **661**, 71–77.
12   T. Gouder, L. Havela, L. Black, F. Wastin, J. Rebizant, P. Boulet, D. Bouexière, S. Heathman and M. Idiri, *J. Alloys Compd.*, 2002, **336**, 73–76.
13   K. O. Kvashnina, A. Y. Romanchuk, I. Pidchenko, L. Amidani, E. Gerber, A. Trigub, A. Rossberg, S. Weiss, K. Popa, O. Walter, R. Caciuffo, A. C. Scheinost, S. M. Butorin and S. N. Kalmykov, *Angew. Chem. Int. Ed.*, 2019, **58**, 17558–17562.
14   IAEA, *Thorium fuel cycle- Potential benefits and challenges*, 2005.
15   A. J. Juhasz, R. A. Rarick and R. Rangarajan, *High Efficiency Nuclear Power Plants Using Liquid Fluoride Thorium Reactor Technology*, NASA, 2009.
16   US Atomic Energy Commission, *The Use of Thorium in Nuclear Power Reactors*. US Government Printing Office, 1969.
17   B. M. Elsheikh, *J. Radiat. Res. Appl. Sci.*, 2019, **6**, 63–70.
18   N. Cooper, D. Minakata, M. Begovic and J. Crittenden, *Environ. Sci. Technol.*, 2011, **45**, 6237–6238.
19   K. Maher, J. R. Bargar and G. E. Brown, *Inorg. Chem.*, 2013, **52**, 3510–3532.
20   A. T. Nelson, *Bulletin of the Atomic Scientists,* 2012, **68**, 33–44.
21   A. K. Burrell, T. M. McCleskey, P. Shukla, H. Wang, T. Durakiewicz, D. P. Moore, C. G. Olson, J. J. Joyce and Q. Jia, *Adv. Mater.*, 2007, **19**, 3559–3563.
22   B. L. Scott, J. J. Joyce, T. D. Durakiewicz, R. L. Martin, T. M. McCleskey, E. Bauer, H. Luo and Q. Jia, *Coord. Chem. Rev.*, 2014, **266**–**267**, 137–154.
23   M. M. Strehle, B. J. Heuser, M. S. Elbakhshwan, X. Han, D. J. Gennardo, H. K. Pappas and H. Ju, *Thin Solid Films*, 2012, **520**, 5616–5626.
24   Y. A. Teterin, A. J. Popel, K. I. Maslakov, A. Y. Teterin, K. E. Ivanov, S. N. Kalmykov, R. Springell, T. B. Scott and I. Farnan, *Inorg. Chem.*, 2016, **55**, 8059–8070.
25   K. Liu, R. Bin, H. Xiao, Z. Long, Z. Hong, H. Yang and S. Wu, *Appl. Surf. Sci.*, 2013, **265**, 389–392.
26   N.-T. H. Kim-Ngan, A. G. Balogh, L. Havela and T. Gouder, *Nucl. Instruments Methods Phys. Res. B.* 2010, **268**, 1875–1879.
27   L. M. Moreau, A. Herve, M. D. Straub, D. R. Russo, R. J. Abergel, S. Alayoglu, J. Arnold, A. Braun, G. J. P. Deblonde, Y. Liu, T. D. Lohrey, D. T. Olive, Y. Qiao, J. A. Rees, D. K. Shuh, S. J. Teat, H. Booth and S. G. Minasian, *Chem. Sci.*, 2020, **11**, 4648–4668.
28   Y. Shiokawa, R. Amano, A. Nomura and M. Yagi, *J. Radioanal. Nucl. Chem.*, 1991, **152**, 373–380.
29   L. Amidani, G. B. M. Vaughan, T. V. Plakhova, A. Y. Romanchuk, E. Gerber, R. Svetogorov, S. Weiss, Y. Joly, S. N. Kalmykov and K. O. Kvashnina, *Chem. Eur. J.*, 2021, **27**, 252–263.
30   S. E. Koponen, P. G. Gordon and S. T. Barry, *Polyhedron*, 2016, **108**, 59–66.
31   H. Pierson, *Handbook of Chemical Vapor Deposition (CVD)*, Noyes Publications, 1999.
32   B. Vlaisavljevich, P. Miro, D. Koballa, T. K. Todorova, S. R. Daly, G. S. Girolami, C. J. Cramer, and L. Gagliardi, *J. Phys. Chem. C.,* 2012, **116**, 23194–23200.
33   S. R. Daly, D. Y. Kim, and G. S. Girolami, *Inorg. Chem.*, 2012, **51**, 7050–7065.
34   S. R. Daly, P. M. B. Piccoli, A. J. Schultz, T. K. Todorova, L. Gagliardi, and G. S. Girolami, *Angew. Chem. Int. Ed*., 2010, **49**, 3379–3381.
35   A. Devi, *Coord. Chem. Rev.*, 2013, **257**, 3332–3284.
36   A. P. Milanov, T. B. Thiede, A. Devi, and R. A. Fischer, *J. Am. Chem. Soc.*, 2009, **131**, 17062–17063.
37   L. Appel, J. Leduc, C. L. Webster, J. W. Ziller, W. J. Evans, and S. Mathur, *Angew. Chem. Int. Ed.*, 2015, **54**, 2209–2213.
38   P. Marchand and C. J. Carmalt, *Coord. Chem. Rev.*, 2013, **257**, 3202–3221.
39   M. D. Straub, J. Leduc, M. Frank, A. Raauf, T. D. Lohrey, S. G. Minasian, S. Mathur and J. Arnold, *Angew. Chem. Int. Ed.*, 2019, **58**, 5749–5753.
40   A. L. Catherall, M. S. Hill, A. L. Johnson, G. Kociok-Köhn and M. F. Mahon, *J. Mater. Chem. C*, 2016, **4**, 10731–10739.
41   T. Perera, *Wayne State University Dissertation,* 2012.
42   M. D. Straub, S. Hohloch, S. G. Minasian and J. Arnold, *Dalton Trans.*, 2018, **47**, 1772–1776.
43   W. J. Evans, J. R. Walensky and J. W. Ziller, *Organometallics*, 2010, **29**, 945–950.
44   W. Henderson, A. G. Oliver and C. E. F. Rickard, *Inorganica Chim. Acta*, 2000, **307**, 144–148.
45   C. Li, R. K. Thomson, B. Gillon, B. O. Patrick and L. L. Schafer, *Chem. Commun.*, 2003, **98**, 2462-2463.
46   J. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis,* Vol. 2, University Science Books, 2010.
47   S. M. Butorin, K. O. Kvashnina, J. R. Vegelius, D. Meyer, and D. K. Shuh, *PNAS*, 2016, **113**, 8093–8097.