

## MATERIALS SCIENCE

A fivefold  $\text{UO}_2^{2+}$  node is a path to dodecagonal quasicrystal approximants in coordination polymersVolodymyr Smetana<sup>1\*†</sup>, Steven P. Kelley<sup>2†</sup>, Anja-Verena Mudring<sup>1\*</sup>, Robin D. Rogers<sup>1,3\*</sup>

Aperiodic formations continue to focus interest in areas ranging from advanced scientific theories to practical everyday applications. Starting from diverse and tightly bonded intermetallic compounds, this world showed an important breakthrough toward the so-called soft systems of meso/macroscale: liquid crystals, thin films, polymers, proteins, etc. This work opens a route for making bulk quasicrystals (QC) in an unprecedented but very common area, with molecular ligands. Since these systems are, to a large extent, transparent, they extend the possible areas of QC application to previously unreachable corners, e.g., photonics. We combined efficient bridging ligands with uranyl pentagonal bonding centers and, unexpectedly, brought the unique attributes of f-element coordination chemistry to an interdisciplinary area of aperiodic formations. Taking advantage of the planar coordination of uranyl ions, we were able to direct the structure expansion solely in two directions with a characteristic snub square tiling, a predicted but previously unobtainable dodecagonal approximant.

## INTRODUCTION

Since their discovery in the mid-1980s (1), quasicrystals (QCs) have become broadly recognizable and penetrated into various areas of chemistry, physics, material science, and biology (2) and major areas of the periodic table (3). Since then, some known structures have been revisited (4, 5), pointing toward a larger scale of QC networks that, so far, remain hidden. Besides intermetallics, quasicrystalline ordering has been detected, but only rarely, in chalcogenides (6, 7), mesoscale materials (8), terpolymers (9), liquid crystals (10, 11), colloids (12), thin films (13, 14), proteins (15), or nanoparticle assemblies (16). QC approximants (ACs) represent crystalline materials compositionally and structurally approaching the atomic self-organization present in QCs but with long-range translational order. These systems are primarily important for understanding the atomic distribution in QCs and serve as indicators for the existence of QCs in a previously unexpected area. Within the quasiperiodic structures, any symmetry higher than 10-fold is rare (17). Stable dodecagonal (DD; 12-fold) QCs could be observed in bulk chalcogenides (6, 7). A limited number of thermodynamically metastable DDQCs and DDACs have been discovered in complex metallic alloys (18–20), and a few have been discovered in soft QC systems (9–12).

Here, using the pentagonal planar node offered by the linear  $\text{UO}_2^{2+}$ , we gained evidence with the formation of the metal-organic framework (MOF)  $[\text{Hmim}][(\text{UO}_2)_2(1,2,4\text{-triazolate})_5]\cdot 3\text{mim}$  (mim, methylimidazole) that structures approaching quasiperiodic ordering can also be realized in bulk in systems with strong directional bonding. This structure represents an unprecedented combination of features typical for two different classes exhibiting QC ordering: intermetallics and templated thin films. This discovery suggests that certain molecular linkers with compatible nodes serve as a perfect tool for the formation of irregular tilings and, ultimately, for the designed synthesis of new QCs.

## RESULTS AND DISCUSSION

We isolated  $[\text{Hmim}][(\text{UO}_2)_2(1,2,4\text{-taz})_5]\cdot 3\text{mim}$  from the reaction of  $\text{UO}_2(\text{OAc})_2$  (OAc, acetate) with 1,2,4-triazole and 1-methylimidazole. Its crystal structure (Fig. 1) is characterized by pentagonal bipyramidal uranyl ( $\text{UO}_2^{2+}$ ) centers bridged by five  $[1,2,4\text{-taz}]^-$  anions to five other uranyl ions into nearly planar polymeric anionic layers orthogonal to the *c* axis separated by disordered solvent sheets. A minor fraction of the solvent is protonated to compensate for the overall negative charge of the  $\text{UO}_2^{2+}$  layers. Although uranyl complexes with five equatorial ligands are commonly observed (21), like in  $[\text{UO}_2(\text{NCS})_5]^{3-}$  salts (22), none have ever been reported in which all five ligands are bridging metal centers that would give a pentagonal tiling.

With  $[\text{Hmim}][(\text{UO}_2)_2(1,2,4\text{-taz})_5]\cdot 3\text{mim}$ , we have realized a MOF where the directional fivefold connection capability of  $\text{UO}_2^{2+}$  is used to create an Archimedean (semiregular) tiling of the Euclidian plane, a structural feature common for certain types of QCs and their ACs. The structural arrangement follows a snub square tiling with  $3^2.4.3.4$  coloring (Fig. 1, red and yellow), which can also be regarded as a single-element semiregular dual tiling, Cairo pentagonal tiling. From a mathematical viewpoint, the geometric requirements for such a tiling are circles with five contact (kissing) points. In metallic alloys, where the atoms can be regarded as spheres, the circle requirement can be easily fulfilled, but as there commonly is no directional preference for bonding, the equal distribution of five kissing points is not naturally given. In contrast,  $\text{UO}_2^{2+}$  in this structure offers a pseudospherical symmetry with five directional bonding nodes. Note that the combined four-, five-, and six-node options are also possible mathematically and were observed with different cations in thin films (14). The bonds in  $[\text{Hmim}][(\text{UO}_2)_2(1,2,4\text{-taz})_5]\cdot 3\text{mim}$  are literally visualized through the triazolate ligands. Moreover, they are “colored” because of alternate orientations of the triazolate units evoked by geometric requirements.

Structural features of  $[\text{Hmim}][(\text{UO}_2)_2(1,2,4\text{-taz})_5]\cdot 3\text{mim}$  are shown in Fig. 2. The  $(\text{UO}_2)_2\text{taz}$  building units form rhombi (Fig. 2C), which are checked along the cell face diagonals and mirrored with respect to the central plane forming the main structural pattern (Fig. 2A). Both colored rhombi make an identical angle with the *ab* plane ( $64.2^\circ$ ), while each of them makes a  $29.3^\circ$  angle with the *ac* or the *bc* plane, respectively. Such an orientation of the neighboring triazolate rings leads to the formation of well-shielded, relatively large tetrahedrally shaped cavities (Fig. 2D) surrounding an oblate ellipsoid

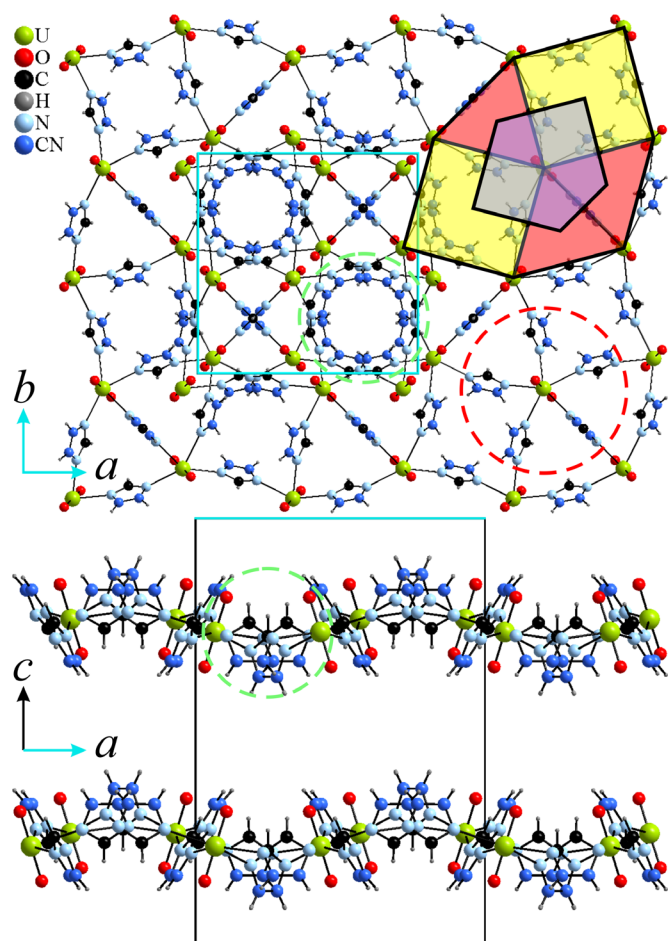
Copyright © 2020 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

<sup>1</sup>Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrhenius väg 16C, Stockholm 10691, Sweden. <sup>2</sup>Department of Chemistry, University of Missouri, 601 S. College Avenue, Columbia, MO 65211, USA. <sup>3</sup>College of Arts and Sciences, The University of Alabama, Tuscaloosa, AL 35487, USA.

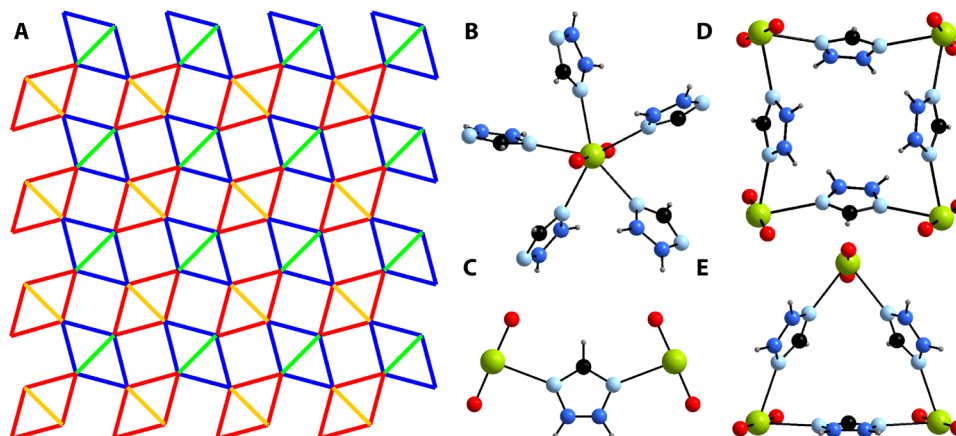
\*Corresponding author. Email: volodymyr.smetana@mmk.su.se (V.S.); anja-verena.mudring@mmk.su.se (A.-V.M.); rdrogers@ua.edu (R.D.R.)

†These authors contributed equally to this work.

of approximately 6 Å by 3 Å in diameter, analogous with the smaller cavities in, e.g., zeolitic imidazolate framework (ZIF-8) (23). The remaining trigonal cavities are meaningfully smaller: ~4.8 Å in diameter. The short rhombi diagonals in both cases are orthogonal to



**Fig. 1. Projections of the crystal structure of [Hmim][(UO<sub>2</sub>)<sub>2</sub>(1,2,4-taz)<sub>5</sub>] 3mim.** Red and green dashed circles outline the coordination sphere of U and the cavities within a layer, respectively. Red and yellow polygons represent the snub square tiling, while the violet one is the only element of the dual Cairo tiling.



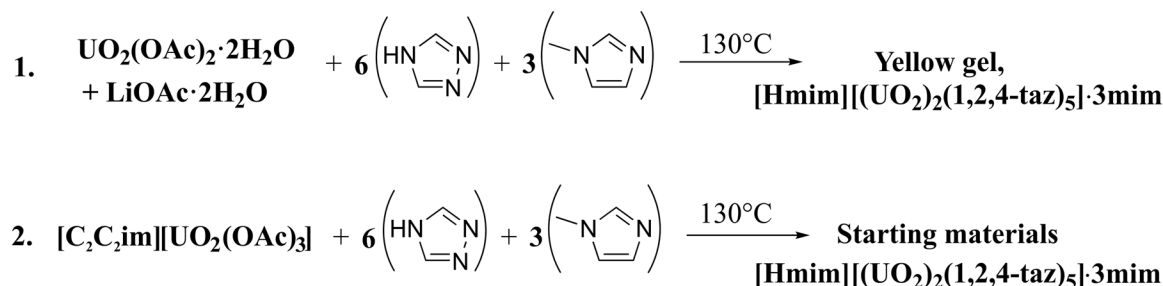
**Fig. 2. Structural features of [Hmim][(UO<sub>2</sub>)<sub>2</sub>(1,2,4-taz)<sub>5</sub>] 3mim.** Schematic representation of the taz coloring (A), coordination of the UO<sub>2</sub><sup>2+</sup> (B) and taz<sup>-</sup> (C), and cavities in the anionic layers (D and E).

the central layer (*ab*) plane and are negligibly shorter, roughly 1%, compared to the rhombi edges.

The dislocation of the U position from the center of the layer of about 0.3 Å together with the corresponding arrangement of the triazolate ligands leads to wave-like motifs similar to those observed in the chalcogenide DDAC system Ta<sub>1.6</sub>Te (6). The lamellar structure of the latter contains multiple stacking sublayers with 3<sup>2</sup>.4.3.4 and (3.6)<sup>2</sup> topologies. Multiple approximant fragments (3<sup>2</sup>.4.3.4, 3<sup>3</sup>.4<sup>2</sup>, and 8/3) have been observed in soft DDQC systems (9), although within one layer. The ideal triangle to square ratio in a DDQC is estimated to be 4/√3 (~2.31), so to achieve an aperiodic arrangement of the same tiles, a second component with sixfold (in plane) coordination (3<sup>6</sup> tiles) must be introduced, i.e., [(UO<sub>2</sub>)<sub>2</sub>(taz)<sub>6/2</sub>]. Essentially, this tiling is not unrealistic, as local structural elements with ∠UUU ≈ 60 are already present. However, introduction of these bonding centers may require all triazolate groups to become identically oriented (orthogonal) with respect to the *ab* plane because of steric repulsion leading to a higher degree of planarization of the lamellae.

In contrast to idealized sphere packing in metallic alloys, structural freedom in coordination compounds is restricted by the directional character of covalent bonds and interactions between the “bonds” themselves. A certain degree of freedom here may come from the rearrangement of the tiles up to maximally random kinetically stabilized schemes including voids, so-called phasons (24), or transformation to a closely related bronze-mean tiling with rectangles instead of squares (25). Similar mechanisms of formation of local quasicrystalline ordering have been recognized for metal-organic coordination networks in the form of thin films on the metallic surfaces (14).

Initially, the discovery of QCs has stimulated renewed interest in complex tilings of multiple (two or more) fragments. These patterns (periodic and aperiodic) have been discovered in, e.g., ancient Islamic architecture (26, 27). Nowadays, the well-developed tiling models are being used in an opposite manner to uncover hidden quasicrystalline formations. In contrast to three-dimensional (3D) QCs (*i*-QCs) ACs that are basically limited to three types with strict sequences of multiply endohedral clusters, 2D ACs reveal a higher degree of freedom and can primarily be detected by the presence of larger geometric fragments with the corresponding rotational symmetry or, in the case of higher order ACs, the combination of simple polygons. In particular, DD systems are characterized by equilateral triangles and squares



**Fig. 3. Reaction schemes leading to the synthesis of [Hmim][(\text{UO}\_2)\_2(1,2,4-taz)\_5]·3mim.**

forming uniform tilings. All soft QCs reported to date have dodecagonal symmetry with a single exclusion for 18-fold symmetry (12). Archimedean-like tilings of the  $3^3.4^2$  type have also been observed on *d*-QC surfaces (28), illustrating a transition between crystalline and quasicrystalline states, and predicted for nonspherical particles (29). Last, temperature-dependent triangle-square tilings have been observed in the layered structures of stable transition metal polymorphic alloys (30) nearby areas of formation of metastable DDQCs, while in the opposite case, the crystallization of quasicrystalline block copolymer melts with approximant structures is also known (4).

This means that the presence of the semiregular tiling is not a lucky accident but rather a strong indicator of the vicinity of a DDQC phase, perhaps at slightly different conditions. The factors controlling the formation and stability of soft QCs differ considerably from those for intermetallic Hume-Rothery mechanisms, and the role of both pentacoordinated uranyl cations and triazolate as a molecular linker cannot be underestimated. Standard electron-counting schemes are hardly applicable even in the DD tantalum tellurides and, apparently, are of no use in coordination compounds since the charge may be balanced by the supporting intermediate network.

The results presented here show that quasicrystalline ordering may occur when charged entities such as complex ions assemble in the process of forming MOFs. The pentagonal planar coordination offered by the azolate ions leads to an extended 2D network creating a paradox for space filling that contains one natural solution, aperiodic tiling. This structure inspires the exploration of directional bonding used to design crystalline frameworks as a guiding principle for uncovering completely new QC and AC systems. The possible pathway for a quasiperiodic structure formation may come through the introduction of random incommensurate nodes or the use of multiple pre-designed organic linkers and is currently being explored.

## MATERIALS AND METHODS

Caution: Standard safeguard procedures should be followed during the handling of uranium-containing materials.

### Reagents

Uranyl acetate dihydrate (Strem Chemicals, Newburyport, MA, USA) and lithium acetate dihydrate (Sigma-Aldrich, St. Louis, MO, USA) were used as received. 1-Methylimidazole (Sigma-Aldrich) was distilled before use under reduced pressure (boiling point, 148° to 150°C).

### Synthesis

We reacted  $\text{UO}_2(\text{OAc})_2$  with 1,2,4-taz and mim and LiOAc at 120° to 130°C. We hypothesized that these conditions would force the protonation of  $[\text{OAc}]^-$  and the evaporation of HOAc, leaving behind metal azolates.

The reaction was conducted as follows: ca. 50 mg of  $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was weighed into a borosilicate glass culture tube. Six molar equivalent 1,2,4-taz, 3 molar equivalent mim, and 1 molar equivalent an  $\text{OAc}^-$  salt (Fig. 3) were then weighed into the container at room temperature. After combining all reagents, the reaction mixture was homogenized by briefly grinding by hand with a glass stirring rod. The reaction mixtures were placed in a temperature-controlled oil bath set to 130°C and heated unsealed under ambient atmosphere. After 24 hours of heating, the reaction was observed to vitrify at elevated temperature. A portion of the hot reaction mixture was removed with a steel spatula and examined under an optical polarizing microscope to reveal thin crystals suspended in a gel. One of these crystals was isolated by hand and determined by single-crystal x-ray diffraction (SCXRD) to be  $[\text{Hmim}][(\text{UO}_2)_2(1,2,4\text{-taz})_5] \cdot 3\text{mim}$ . This compound was also isolated using the same conditions but starting with  $[\text{C}_2\text{C}_2\text{im}][\text{UO}_2(\text{OAc})_3]$  and thus eliminating the need for dehydration with  $\text{LiOAc} \cdot \text{H}_2\text{O}$ .

### Instrumental analysis

Reaction mixtures were examined under a Nikon LABOPHOT-POL (Melville, NY, USA) optical polarizing microscope. Crystals suitable for SCXRD were suspended in Paratone-N oil (Hampton Research, Aliso-Viejo, CA, USA) and mounted on nylon loops or glass fibers. Data were collected on a Bruker diffractometer equipped with a PLATFORM three-circle goniometer and an APEX II charge-coupled device area detector (Bruker AXS, Madison, WI, USA). For structure solution, a hemisphere of unique data was collected with  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71054 \text{ \AA}$ ) using strategies of scans about the  $\omega$  and  $\phi$  axes with 0.5° frame widths. Crystals were cooled to  $-100^\circ\text{C}$  during collection under a cold stream of  $\text{N}_2$  gas using an N-HeliX cryostat (Oxford Cryosystems, Oxford, UK).

### Characterization

Since the “visible” part of the structure is represented by well-separated 2D MOF nanolayers, an important but challenging question would be “What is in between?” In accordance with the excess charge in the anionic layers, the cation number was estimated to be 1 per formula unit or in general 4 per unit cell, and there is at least one evident position in the structure that can accommodate that amount of protonated methylimidazolium ions. A deeper analysis of the observed electron density map (fig. S1) suggested that the charge distribution within the cationic layer could be rather dynamic with little preference around certain positions. A useful hint may also come from a similar 1D uranyl coordination polymer with pyridinium,  $\{[\text{UO}_2\text{py}_5][\text{KI}_2\text{py}_2]\}_n$  (31). Although the bonding schemes are somewhat different, the structure contains N-coordinated  $\text{UO}_2^{2+}$  groups and additional pyridine molecules coordinated to  $\text{K}^+$  in the intermediate layers normal to the polymer axis. The main conclusion

coming from that structure is that the aromatic rings do not tend to coordinate to the  $\text{UO}_2^{2+}$  ions but prefer C-H... $\pi$  interactions with the pyridine molecules coordinated to U. Furthermore, the U-U interlayer distances in both structures are nearly identical, serving as a good criterion to understand the solvent (dis)order observed here. According to void analysis, a solvent-accessible volume of  $1800 \text{ \AA}^3$  per cell with 721 electrons could be located in the interlayer space. Assuming  $18 \text{ \AA}^3$  per nonhydrogen atom, this matches reasonably well with about 16 methylimidazole molecules ( $1728 \text{ \AA}^3$ ,  $704 e^-$ ).

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/6/5/eaay7685/DC1>

Fig. S1. Observed electron density map sections ( $h0l$ ) and ( $hk0$ ).

## REFERENCES AND NOTES

- D. Shechtman, I. Blech, D. Gratias, J. W. Cahn, Metallic phase with long-range orientational order and no translational symmetry. *Phys. Rev. Lett.* **53**, 1951–1953 (1984).
- J.-M. Dubois, Properties- and applications of quasicrystals and complex metallic alloys. *Chem. Soc. Rev.* **41**, 6760–6777 (2012).
- V. Smetana, Q. Lin, D. K. Pratt, A. Kreyssig, M. Ramazanoglu, J. D. Corbett, A. I. Goldman, G. J. Miller, A sodium-containing quasicrystal: Using gold to enhance sodium's covalency in intermetallic compounds. *Angew. Chem. Int. Ed.* **51**, 12699–12702 (2012).
- S. Lee, M. J. Bluemle, F. S. Bates, Discovery of a Frank-Kasper  $\sigma$  phase in sphere-forming block copolymer melts. *Science* **330**, 349–353 (2010).
- W. Steurer, Why are quasicrystals quasiperiodic? *Chem. Soc. Rev.* **41**, 6719–6729 (2012).
- M. Conrad, F. Krumeich, B. Harbrecht, A dodecagonal quasicrystalline chalcogenide. *Angew. Chem. Int. Ed.* **37**, 1383–1386 (1998).
- A. Yamamoto, A five-dimensional model of dodecagonal Ta-Te quasicrystals with fractal occupation domains. *Acta Crystallogr. A* **60**, 142–145 (2004).
- C. Xiao, N. Fujita, K. Miyasaka, Y. Sakamoto, O. Terasaki, Dodecagonal tiling in mesoporous silica. *Nature* **487**, 349–353 (2012).
- K. Hayashida, T. Dotera, A. Takano, Y. Matsushita, Polymeric quasicrystal: Mesoscopic quasicrystalline tiling in ABC star polymers. *Phys. Rev. Lett.* **98**, 195502 (2007).
- X. Zeng, G. Ungar, Y. Liu, V. Percec, A. E. Dulcey, J. K. Hobbs, Supramolecular dendritic liquid quasicrystals. *Nature* **428**, 157–160 (2004).
- J. Dontabhaktuni, M. Ravnik, S. Zumer, Quasicrystalline ordering in thin liquid crystal films. *Crystals* **8**, 275 (2018).
- S. Fischer, A. Exner, K. Zielske, J. Perlich, S. Deloudi, W. Steurer, P. Lindner, S. Förster, Colloidal quasicrystals with 12-fold and 18-fold diffraction symmetry. *Proc. Nat. Acad. Sci. U.S.A.* **108**, 1810–1814 (2011).
- S. Förster, K. Meinel, R. Hammer, M. Trautmann, W. Widdra, Quasicrystalline structure formation in a classical crystalline thin-film system. *Nature* **502**, 215–218 (2013).
- J. I. Urgel, D. Ćija, G. Lyu, R. Zhang, C.-A. Palma, W. Auwärter, N. Lin, J. V. Barth, Quasicrystallinity expressed in two-dimensional coordination networks. *Nat. Chem.* **8**, 657–662 (2016).
- A. Janner, Strongly correlated structure of axial-symmetric proteins. II. Pentagonal, heptagonal, octagonal, nonagonal and ondecagonal symmetries. *Acta Crystallogr. D Biol. Crystallogr.* **61**, 256–268 (2005).
- D. V. Talapin, E. V. Shevchenko, M. I. Bodnarchuk, X. Ye, J. Chen, C. B. Murray, Quasicrystalline order in self-assembled binary nanoparticle superlattices. *Nature* **461**, 964–967 (2009).
- W. Steurer, Twenty years of structure research on quasicrystals. Part I. Pentagonal, octagonal, decagonal and dodecagonal quasicrystals. *Z. Kristallogr. Cryst. Mat.* **219**, 391–446 (2004).
- T. Ishimasa, H. U. Nissen, Y. Fukano, New ordered state between crystalline and amorphous in Ni-Cr particles. *Phys. Rev. Lett.* **55**, 511–513 (1985).
- H. Chen, D. X. Li, K. H. Kuo, New type of two-dimensional quasicrystal with twelffold rotational symmetry. *Phys. Rev. Lett.* **60**, 1645–1648 (1988).
- K. Yoshida, T. Yamada, Y. Taniguchi, Long-period tetragonal lattice formation by solid-state alloying at the interfaces of Bi-Mn double-layer thin films. *Acta Crystallogr. B* **45**, 40–45 (1989).
- A. J. Lussier, R. A. K. Lopez, P. C. Burns, A revised and expanded structure hierarchy of natural and synthetic hexavalent uranium compounds. *Can. Mineral.* **54**, 177–283 (2016).
- S. Nuzzo, B. Twamley, J. A. Platts, R. J. Baker, Pseudohalide tectons within the coordination sphere of the uranyl ion: Experimental and theoretical study of C-H...O, C-H...S, and chalcogenide noncovalent interactions. *Inorg. Chem.* **57**, 3699–3712 (2018).
- K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc. Nat. Acad. Sci. U.S.A.* **103**, 10186–10191 (2006).
- M. de Boissieu, Phonons, phasons and atomic dynamics in quasicrystals. *Chem. Soc. Rev.* **41**, 6778–6786 (2012).
- T. Dotera, S. Bekku, P. Zihlerl, Bronze-mean hexagonal quasicrystal. *Nat. Mater.* **16**, 987–992 (2017).
- R. A. Al Ajlouni, The global long-range order of quasi-periodic patterns in Islamic architecture. *Acta Crystallogr. A* **68**, 235–243 (2012).
- E. Makovicky, N. M. Makovicky, The first find of dodecagonal quasiperiodic tiling in historical Islamic architecture. *J. Appl. Cryst.* **44**, 569–573 (2011).
- J. Mikhael, J. Roth, L. Helden, C. Bechinger, Archimedean-like tiling on decagonal quasicrystalline surfaces. *Nature* **454**, 501–504 (2008).
- A. Haji-Akbari, M. Engel, A. S. Keys, X. Zheng, R. G. Petschek, P. Palffy-Muhoray, S. C. Glotzer, Disordered, quasicrystalline and crystalline phases of densely packed tetrahedra. *Nature* **462**, 773–777 (2009).
- S. Kashimoto, A. Kocjan, Z. Jagličić, S. Jazbec, H. Iga, T. Ishimasa, J. Dolinšek, Magnetic properties of  $\sigma$ - and hexagonal-Mn<sub>76</sub>Si<sub>18</sub>Cr<sub>6</sub> approximant phases of a dodecagonal quasicrystal. *Phys. Rev. B* **84**, 224201 (2011).
- L. Natrajan, F. Burdet, J. Pécaut, M. Mazzanti, Synthesis and structure of a stable pentavalent-uranyl coordination polymer. *J. Am. Chem. Soc.* **128**, 7152–7153 (2006).

### Acknowledgments

**Funding:** This research was supported, in part, through the Göran Gustafsson prize by the Royal Swedish Academy of Science to A.-V.M. and by the Swedish Research Council [Vetenskapsrådet (VR)] through grant number 2016-05405; a Tage Erlander professorship to R.D.R. (VR number grant 2018-00233); and the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Heavy Elements program under award number DE-SC0019220. **Author contributions:** R.D.R. conceived the experiment. V.S. and S.P.K. analyzed and interpreted data. S.P.K. prepared the samples. V.S., S.P.K., A.-V.M., and R.D.R. wrote the manuscript. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Related crystallographic information has been deposited at the Cambridge Structural Database and can be downloaded free of charge from [www.ccdc.cam.ac.uk/](http://www.ccdc.cam.ac.uk/) (accession code: CCDC-1909631). Additional data related to this paper may be requested from the authors.

Submitted 16 July 2019  
Accepted 22 November 2019  
Published 31 January 2020  
10.1126/sciadv.aay7685

**Citation:** V. Smetana, S. P. Kelley, A.-V. Mudring, R. D. Rogers, A fivefold  $\text{UO}_2^{2+}$  node is a path to dodecagonal quasicrystal approximants in coordination polymers. *Sci. Adv.* **6**, eaay7685 (2020).