ORGANIC LETTERS

2012
Vol. 14, No. 6
1460–1463

Polyporous Metal-Coordination Frameworks

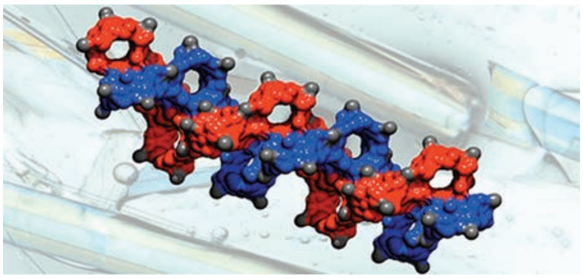
Jeremiah J. Gassensmith,[†] Ronald A. Smaldone,[†] Ross S. Forgan,[†] Christopher E. Wilmer,[†] David B. Cordes,[‡] Youssry Y. Botros,[†,§,∥] Alexandra M. Z. Slawin,[‡] Randall Q. Snurr,[†] and J. Fraser Stoddart*,[†,⊥]

*Center for the Chemistry of Integrated Systems, Department of Chemistry,
Department of Materials Science, Department of Chemical & Biological Engineering,
Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States,
NanoCentury KAIST Institute and Graduate School of EEWS (WCU),
Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong Dong,
Yuseong Gu, Daejeon 305-701, Republic of Korea, University of St. Andrews,
Eastchem School of Chemistry, St. Andrews, Fife KY16 9ST, U.K., Intel Labs,
Building RNB-6-61, 2200 Mission College Boulevard, Santa Clara, California 95054,
United States, and National Center for Nano Technology Research, King Abdulaziz City for
Science and Technology (KACST), P.O. Box 6086, Riyadh 11442, Kingdom of Saudi Arabia*

stoddart@northwestern.edu

Received January 25, 2012

ABSTRACT



Starting from a chiral building block—α-cyclodextrin—and rubidium salts, the crystallization of a complex of chiral helices, which constitute a "green" porous coordination polymer, has been realized. Cyclodextrin molecules coordinated by rubidium ions form porous, infinitely long left-handed helical channels, interdigitated with each other. A theoretical examination of the potential of this new material to act as a medium for chiral separation is presented.

The absolute helicity, which arises from the presence of specific homochiral monomers such as amino acids and nucleic acids in biological polymers, is unmistakably integral[1] to the myriad of functions that pervade the living world. This fundamental link in the relationship between structure and chirality, which is still not well understood, has been the inspiration[2] for several investigations into just how chiral building blocks form helical systems in the solid state as a result of their coordinative[3] bonding. Nevertheless, few studies have been undertaken in which inherently chiral natural products[4] have been employed to

---

[†] Northwestern University.
[‡] University of St. Andrews.
[§] Intel Labs.
[∥] KACST.
[⊥] KAIST.

(1) Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1–76.

(2) (a) Cui, Y.; Ngo, H. L.; Lin, W. *Chem. Commun.* **2003**, 1388–1389. (b) Byrne, P.; Lloyd, G. O.; Anderson, K. M.; Clarke, N.; Steed, J. W. *Chem. Commun.* **2008**, 3720–3722. (c) Juwarker, H.; Jeong, K.-S. *Chem. Soc. Rev.* **2010**, *39*, 3664–3674. (d) Leong, W. L.; Vittal, J. J. *Chem. Rev.* **2010**, *111*, 688–764. (e) Zheng, X.-D.; Lu, T.-B. *CrystEngComm* **2010**, *12*, 324–336. (f) Wang, L.; Song, T.; Huang, L.; Xu, J.; Li, C.; Ji, C.; Shan, L.; Wang, L. *CrystEngComm* **2011**, *13*, 4005–4009.

(3) (a) Wen, H.-R.; Wang, C.-F.; Li, Y.-Z.; Zuo, J.-L.; Song, Y.; You, X.-Z. *Inorg. Chem.* **2006**, *45*, 7032–7034. (b) An, H.; Han, Z.; Xu, T.; Meng, C.; Wang, E. *Inorg. Chem. Commun.* **2008**, *11*, 914–917. (c) Zheng, X.-D.; Hua, Y.-L.; Xiong, R.-G.; Ge, J.-Z.; Lu, T.-B. *Cryst. Growth Des.* **2010**, *11*, 302–310.

(4) (a) Roth, A.; Koth, D.; Gottschaldt, M.; Plass, W. *Cryst. Growth Des.* **2006**, *6*, 2655–2657. (b) Zhang, J.; Bu, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 6115–6118. (c) Banerjee, S.; Adarsh, N. N.; Dastidar, P. *CrystEngComm* **2009**, *11*, 746–749.

10.1021/ol300199a

create functional helical materials, a class of compounds which have been investigated for their potential applications in nonlinear optical materials,[5] molecular recognition, enantiomorphic separations, and asymmetric catalysis.[6]

Although metal-organic frameworks[7] (MOFs), which possess remarkably high porosities, are attractive candidates for creating such materials, until recently, only a handful[8] of MOFs have been derived from natural products. Recently, we reported[9] the structure of a MOF comprised of γ-cyclodextrin (γ-CD) rings coordinated to alkali metal cations, producing highly porous materials from completely nontoxic and naturally occurring materials. While γ-CD is a (chiral) cyclic oligosaccharide composed of eight α-1,4-linked D-glucopyranosyl (α-1,4-D-Glu*p*) residues, the overall topology of the resultant MOF is cubic with extended linear pores along the crystallographic axes.

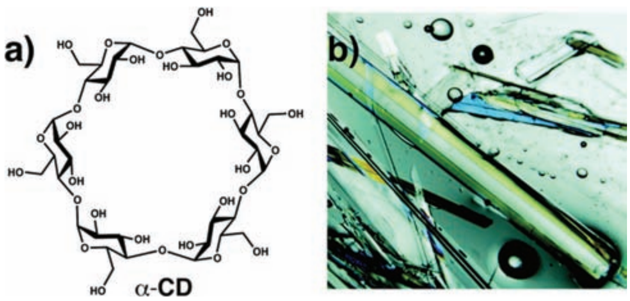


Figure 1. (a) Structural formula of α-cyclodextrin (α-CD), a naturally occurring cyclic oligosaccharide comprised of six α-1,4-D-Glu*p* residues portrayed in their stable $^4C_1$ conformations. (b) The strawlike crystals of CD-MCF obtained under controlled crystallization conditions, formed from the self-assembly of α-CD and Rb^+ ions, contain inner pore diameters in the range of 100 nm to 2 mm.

In our ongoing investigation of materials which are formed by the coordination of cyclic oligosaccharides[10] to alkali metal cations, we have uncovered yet another porous material, this time arising from the crystallization of the six-membered cyclic variant of CD, namely α-cyclodextrin (α-CD, Figure 1a), with RbOH to form elongated hollow needles. Single crystals, colorless and several centimeters in length, were obtained[11] by dissolving 1 equiv of α-CD and 8 equiv of RbOH[12] in H_2O followed by slow vapor diffusion of *i*Pr_2O into the solution. On visualizing selected crystals under an optical microscope, it was immediately evident that they contained long hollow interiors (Figure 1b). Moreover, we were able to observe the displacement of the aqueous solvent contained within the hollow regions of these crystals with Paratone over time (movie in the Supporting Information). Hollow organic crystals, while not very common, are known,[13] and typically occur in crystalline samples of chiral compounds. The hollow nature of the crystal makes this α-CD metal coordination framework (CD-MCF) a unique example of a solid-state material expressing porosity simultaneously on both the nanometer and macroscopic scales.

The crystals were suitable for single-crystal X-ray analysis, and the solid-state structure reveals interdigitated left-handed helical pores (Figure 2b–e) running through the structure created by the ligation of Rb^+ ions to the primary and secondary faces of the α-CD rings.[14] A theoretical analysis of the porosity of the structure exposed significant

---

(5) Meng, X.; Song, Y.; Hou, H.; Fan, Y.; Li, G.; Zhu, Y. *Inorg. Chem.* **2003**, *42*, 1306–1315.

(6) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986. (b) Lee, S. J.; Hu, A.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 12948–12949. (c) Gassensmith, J. J.; Erne, P. M.; Paxton, W. F.; Stoddart, J. F. *Langmuir* **2011**, *50*, 276–279.

(7) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494. (b) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279. (c) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B. T.; Reineke, M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330. (d) Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (e) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238–241. (f) Wong-Foy, A. G.; Lebel, O.; Matzger, A. J. *J. Am. Chem. Soc.* **2007**, *129*, 15740–15741. (g) Ma, S.; Eckert, J.; Forster, P. M.; Yoon, J. W.; Hwang, Y. K.; Chang, J.-S.; Collier, C. D.; Parise, J. B.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 15896–15902. (h) Britt, D.; Furukawa, H.; Wang, B.; Glover, T. G.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 20637–20640. (i) Deng, H.; Doonan, C. J.; Furukawa, H.; Ferreira, R. B.; Towne, J.; Knobler, C. B.; Wang, B.; Yaghi, O. M. *Science* **2010**, *327*, 846–850.

(8) Imaz, I.; Rubio-Martinez, M.; An, J.; Sole-Font, I.; Rosi, N. L.; Maspoch, D. *Chem. Commun.* **2011**, *47*, 7287–7302.

(9) (a) Smaldone, R. A.; Forgan, R. S.; Furukawa, H.; Gassensmith, J. J.; Slawin, A. M. Z.; Yaghi, O. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2010**, *49*, 8630–8634. (b) Gassensmith, J. J.; Furukawa, H.; Smaldone, R. A.; Forgan, R. S.; Yaghi, O. M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 15312–15315. (c) Forgan, R. S.; Smaldone, R. A.; Gassensmith, J. J.; Furukawa, H.; Cordes, D. B.; Li, Q.; Wilmer, C. E.; Botros, Y. Y.; Snurr, R. Q.; Slawin, A. M. Z.; Stoddart, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 406–417.

(10) Gattuso, G.; Nepogodiev, S. A.; Stoddart, J. F. *Chem. Rev.* **1998**, *98*, 1919–1958.

(11) Data were collected at 100 K using a Bruker d8-APEX II CCD diffractometer (Cu Kα radiation, λ = 1.54178 Å). Intensity data were collected using ω and φ scans spanning at least a hemisphere of reciprocal space for all structures (data were integrated using SAINT). Absorption effects were corrected on the basis of multiple equivalent reflections (SADABS). Structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares against *F2* (SHELXL). Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. The crystal data for CD-MCF contained diffuse, disordered solvent molecules which could not be adequately modeled. The bypass procedure in Platon was used to remove the electronic contribution from these solvents. As the exact solvent content is not known, the reported formula reflects only the atoms used in the refinement. Crystal data for CD-MCF: $Rb_5(C_{144}H_{204}O_{122})_2(H_2O)$, Transparent hollow needles, M_r = 4348.44, crystal size 0.69 × 0.44 × 0.43 mm, tetragonal, space group $P4_32_12$, a = 27.165(3) Å, c = 37.905(1) Å, V = 27972.2(3) Å^3, Z = 4, ρ_{calc} = 1.050, T = 100(2) K, $R_1(F^2 > 2\sigma F^2)$ = 9.02, wR_2 = 0.2447. Crystallographic data (excluding structure factors) for the structures reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-844644 (CD-MCF). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ uk (fax: int. code (44) 1223 336−033; email: deposit@ccdc.cam.ac.uk).

(12) In our investigations into the cubic structures formed by γ-CD and alkali metal salts, we found it was possible to prepare a range of isostructural CD-MOFs from salts of Na^+, K^+, Rb^+, and Cs^+. This general trend is not repeated in the synthesis of infinite structures from α-CD. Attempts to prepare extended structures composed of α-CD and Na^+ and K^+ salts by similar protocols failed. In both cases, crystals of an α-CD hydrate, in which the cyclodextrins arrange themselves in perfectly aligned hexagonally close-packed layers, resulted.

(13) Shimizu, T.; Masuda, M.; Minamikawa, H. *Chem. Rev.* **2005**, *105*, 1401–1444.

(14) The Void Analyzer program (Wilmer, C. E.; Snurr, R. Q. *Void Analyzer*, 2011) was used on CD-MCF.

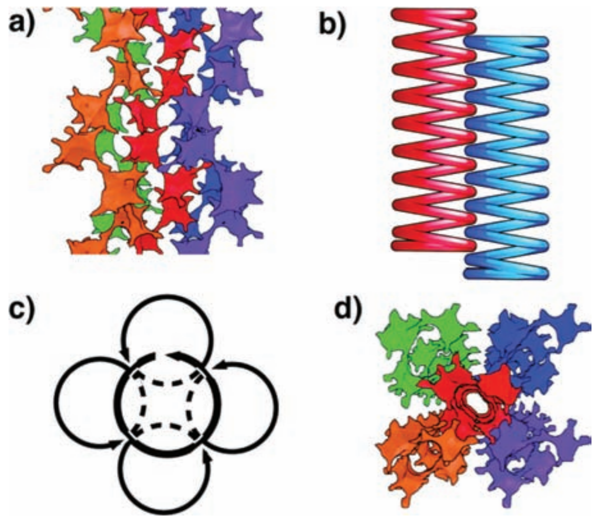


Figure 2. (a) Side-on representation of the pores formed by the left-handed helices of CD-MCF in the solid state wherein larger voids are connected by smaller channels large enough for He, H_2, and N_2 to traverse. The left-handed helices are arranged in (b) an interdigitated fashion wherein one helix of CD-MCF interpenetrates the groove of a neighboring helix. The channels which are formed are punctuated by voids and (c) cluster to form C_4 symmetric arrays which are defined by each pore being interpenetrated partially by four other pores as shown in (d) the pore-filling image wherein each identical pore is colored distinctly to show the connectivities.

voids which should be accessible to small molecules.[15] The analysis used a region defined by four adjacent unit cells (a 2·2·1 configuration, only one unit cell along the axis of the helices), subdivided into a mesh of 0.5 Å resolution. A spherical probe of radius 1.9 Å (approximating to a molecule of N_2) was used to locate the accessible voids. Connected voids were identified by vertex traversal along the triangulated surface mesh, and voids were colored in the following way: complete helices were given a color (either green, red, orange, blue or purple, as deplicted in Figure 2a,d). Adjacent helices are given different colors to distinguish them easily.

Voids which do not form a complete helix (those that were only partially represented in the unit cell) were omitted. From the analysis it is clear that, from the vantage point of a nitrogen molecule, the voids are helical and adjacent, rather than intertwined. Further in silico calculations uncovered potential for the inherent chirality to allow the material to act as a chiral liquid phase chromatographic medium (See ESI). These experimental results which being caried out under HPLC conditions, will be presented in a follow-up communication. Since the crystals do not survive solvent removal in vacuo, simulations of N_2 uptake at 77 K were caried out using grand canonical Monte Carlo (GCMC) simulations[15] which has led to the conclusion that CD-MCF has a BET surface area of 820 $m^2\ g^{-1}$ (see Figure S1, Supporting Information).

The α-CD rings in CD-MCF are coordinated (Figure 3) to Rb^+ cations, with each metal ion binding to α-1,4-D-Glu*p* residues on their primary and secondary faces through the C-2, C-3, C-6, and ring oxygen atoms. Not every α-1,4-D-Glu*p* residue in the α-CD ring is coordinated to a Rb^+ cation. Two different coordination motifs are present (Figure 3a,b) in the extended structure, namely, one in which the α-CD rings interact with Rb^+ ions through four α-1,4-D-Glu*p* residues while the other is coordinated to Rb^+ ions by five of its six α-1,4-D-Glu*p* residues. Moreover, CD-MCF contains three different secondary building units (SBUs), which consist (Figures 3c–e) of 4-, 8-, and 10-coordinate SBUs. The 8- and 10-coordinate SBUs are similar in their arrangements of α-1,4-D-Glu*p* residues; the 10-coordinate SBU includes two oxygen atoms that are not part of any α-CD rings. We speculate that these atoms either correspond to the OH^- counterions that are closely associated with Rb^+ cations, or to residual H_2O molecules that are present as a result of the conditions employed during the synthesis of CD-MCF.

Topological analysis (Figure 4) of the three-dimensional net formed by the CD-MCF showed it to comprise four different nodes. Three of these nodes are four-connected, and based on two of the independent Rb^+ ions and the centroid of one of the independent α-CD rings, while the other node is five-connected and based at the centroid of the other α-CD. The resulting complex topological net, with a

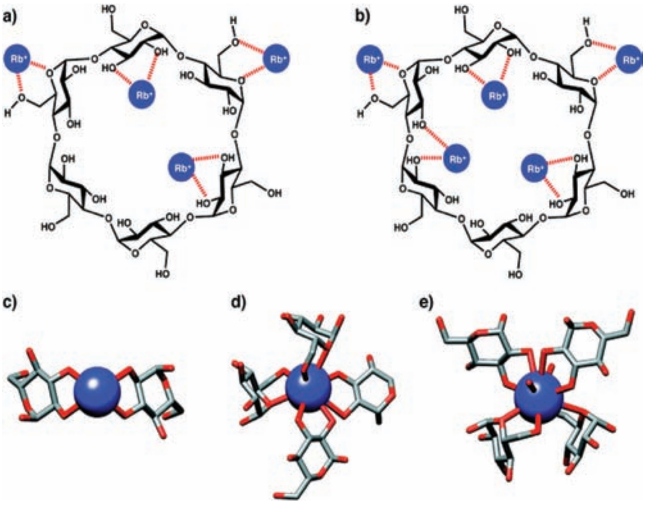


Figure 3. In CD-MCF, (a) one α-CD ring is coordinated to four Rb^+ cations and (b) the other α-CD ring is coordinated to five Rb^+ cations. Note that, in both cases, the Rb^+ cations are coordinated to the primary and secondary faces of adjacent residues in an alternating manner. There are three different Rb^+ cation coordination geometries – (c) a four-coordinate Rb^+ cation to the secondary faces of two α-1,4-D-Glu*p* residues, (d) an eight-coordinate Rb^+ cation to the primary faces of two α-1,4-D-Glu*p* residues, and (e) a 10-coordinate Rb^+ cation with an identical set of coordinating ligands (d) together with two oxygen atoms that could be OH^- anions or H_2O molecules.

---

[15] (a) Walton, K. S.; Snurr, R. Q. *J. Am. Chem. Soc.* **2007**, *129*, 8552–8556. (b) Bae, Y.-S.; Yazaydin, A. O.; Snurr, R. Q. *Langmuir* **2010**, *26*, 5475–5483.

point symbol of $(4^2.5.7^2.8)(4^3.5^3.6.7^3)(4^3.6^2.8)(4^4.5.6)$, has not previously been identified. Suprisingly, as a result of its connectivity, the third independent Rb$^+$ ion does not form a node within the net but instead acts as a link between adjacent five-connected α-CD nodes.

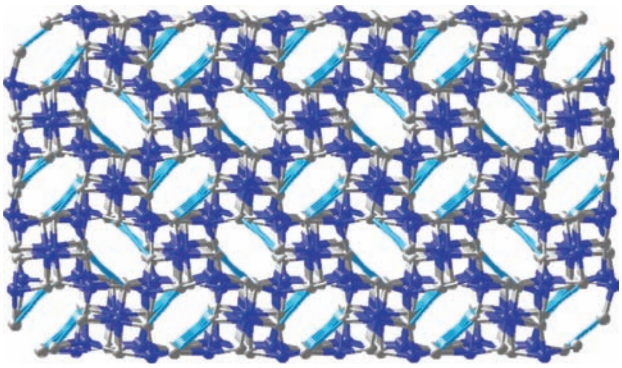


Figure 4. View of the complex topological net formed by the CD-MCF, point (Schläbi) symbol $(4^2.5.7^2.8)(4^3.5^3.6.7^3)$-$(4^3.6^2.8)(4^4.5.6)$, shown down the crystallographic *c*-axis. Nodes based on α-CD are shown as gray spheres, those based on Rb$^+$ ions as dark blue spheres. The Rb$^+$ ions which act as a link between α-CD nodes can be seen as a elongated pale blue bond.

With the development of new porous materials based on the cyclodextrins firmly established as a fruitful area of research, and already providing solutions to problems in areas as diverse as chemical sensing, energy storage and separations, it is not unreasonable to predict that one of the next logical growth areas will be the use of these materials from green and renewable sources in integrated functional systems. This CD-MCF, based on α-CD, and the alkali metal ion Rb$^+$ meet these criteria while also containing chemical sorting domains[16] on both the nanoscopic and macroscopic scales. In common with the CD-MOFs[9] based on γ-CD, we have demonstrated that it is possible to generate remarkably complex solid-state structures spontaneously under extremely simple conditions. While the synthetic protocols have been established for the self-assembly of nanoporous carbohydrates,[9] merely changing the cyclodextrin from γ-CD to α-CD has resulted in the formation of a very different class of extended structures. The CD-MCF structure contains a series of chiral, helical pores, reminiscent[17] of the organizational behavior of other chiral molecules found in nature. Theoretical simulations of its potential capability as a separation material demonstrate (see the Supporting Information) that it is more than just a scientific curiosity. We believe that this new α-CD-based material is noteworthy not only because of its dual-scale porosity and chirality but also because it provides a convincing demonstration of the ease in which solid-state complexity can be generated[18] from readily available starting materials.

Acknowledgment. The research reported in this paper is based upon work supported under the auspices of an international collaboration supported in the US by the National Science Foundation under Grant No. CHE-0924620 and in the UK by the Engineering and Physical Sciences Research Council under Grant No. EP/H003517/1. We also acknowledge support from the DOE Nanofabricated Systems for Clean Energy Storage, Conversion, and Generation, Award No. DE-SC0005462. In addition, we thank Dr. Turki S. Al-Saud and Dr. Mohamed B. Alfageeh at the King Abdullah City for Science and Technology (KACST) in Saudi Arabia for their joint collaborative efforts. Finally, we acknowledge the World Class University (WCU) Program (R-31-2008-000-10055-0) in Korea.

Supporting Information Available. The description of the material characterization and computational methods including BET and surface analysis, as well as supplemental figures and movies is available free of charge via the Internet at http://pubs.acs.org.

---

(16) (a) Li, Q.; Zhang, W. Y.; Miljaníc, O. Š.; Sue, C. H.; Zhao, Y. L.; Liu, L. H.; Knobler, C. B.; Stoddart, J. F.; Yaghi, O. M. *Science* **2009**, *325*, 855–859. (b) Deng, H.; Olson, M. A.; Stoddart, J. F.; Yaghi, O. M. *Nature Chem* **2010**, *2*, 439–443.

(17) Bentley, R. In *Encyclopedia of Molecular Cell Biology and Molecular Medicine*; Wiley- VCH: Weinheim, 2006.

(18) Preparation of CD-MCF is as follows: α-CD (1.30 g, 1 mmol) and RbOH (0.45 g, 8 mmol) were dissolved in H_2O (20 mL). The aqueous solution was filtered, and MeOH (~50 mL) was allowed to vapor diffuse into the solution during the period of a week. Colorless cubic crystals (1.20 g, 66%), suitable for X-ray structure analysis, were isolated, filtered, and washed with MeOH (2 × 30 mL) before being left to dry in air.

The authors declare no competing financial interest.