Angewandte



## Uranium Clusters Hot Paper

How to cite:Angew. Chem. Int. Ed. 2021, 60, 9886–9890International Edition:doi.org/10.1002/anie.202017298German Edition:doi.org/10.1002/ange.202017298

# **Intrinsic Semiconducting Behavior in a Large Mixed-Valent Uranium** (V/VI) Cluster

Mingxing Zhang<sup>+</sup>, Chengyu Liang<sup>+</sup>, Guo-Dong Cheng<sup>+</sup>, Junchang Chen, Yumin Wang, Linwei He, Liwei Cheng, Shicheng Gong, Duo Zhang, Jiong Li, Shu-Xian Hu,\* Juan Diwu, Guozhong Wu, Yaxing Wang,\* Zhifang Chai, and Shuao Wang\*

Abstract: We disclose the intrinsic semiconducting properties of one of the largest mixed-valent uranium clusters,  $[H_3O^+]$ - $[U^{V}(U^{VI}O_{2})_{8}(\mu_{3}-O)_{6}(PhCOO)_{2}(Py(CH_{2}O)_{2})_{4}(DMF)_{4}] \quad (Ph =$ phenyl, Py = pyridyl, DMF = N, N-dimethylformamide) (1). Single-crystal X-ray crystallography demonstrates that  $U^V$ center is stabilized within a tetraoxo core surrounded by eight uranyl(VI) pentagonal bipyramidal centers. The oxidation states of uranium are substantiated by spectroscopic data and magnetic susceptibility measurement. Electronic spectroscopy and theory corroborate that  $U^V$  species serve as electron donors and thus facilitate **1** being a n-type semiconductor. With the largest effective atomic number among all reported radiation-detection semiconductor materials, charge transport properties and photoconductivity were investigated under Xray excitation for 1: a large on-off ratio of 500 and considerable charge mobility lifetime product of  $2.3 \times 10^{-4}$  cm<sup>2</sup>V<sup>-1</sup>, as well as a high detection sensitivity of 23.4  $\mu C G y_{air}^{-1} cm^{-2}$ .

Extending the potential applications of uranium beyond nuclear industry provides useful hint in disposal and recycling of piled depleted uranium.<sup>[1]</sup> The bonding involvement of

[\*] M. Zhang,<sup>[+]</sup> C. Liang,<sup>[+]</sup> J. Chen, Y. Wang, L. He, L. Cheng, S. Gong, Dr. D. Zhang, Prof. J. Diwu, Prof. Y. Wang, Prof. Z. Chai, Prof. S. Wang State Key Laboratory of Radiation Medicine and Protection School for Radiological and interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University Suzhou 215123 (China) E-mail: yxwang@suda.edu.cn shuaowang@suda.edu.cn M. Zhang,<sup>[+]</sup> Prof. G. Wu Shanghai Institute of Applied Physics, Chinese Academy of Sciences Shanghai 201800 (China) M. Zhang,<sup>[+]</sup> University of Chinese Academy of Sciences Beijing 100049 (China) Dr. G.-D. Cheng<sup>[+]</sup> Prof. S.-X. Hu School of Mathematics and Physics University of Science and Technology Beijing Beijing 100083 (China) E-mail: hushuxian@csrc.ac.cn Dr. J. Li Shanghai Synchrotron Radiation Facility Shanghai Advanced Research Institute Chinese Academy of Sciences, Shanghai 201210 (China) [<sup>+</sup>] These authors contributed equally to this work. Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: Ð

https://doi.org/10.1002/anie.202017298.

6d/5f orbitals endows uranium-based materials with many distinct properties not observed in those of transition metals and lanthanides. The common oxidation states of uranium span from III to VI, each with distinct chemical species, physicochemical properties, and related functionalities.<sup>[2]</sup> For instance, U<sup>III</sup> complexes are substantially utilized for catalytic transformation of small molecules owing to their high chemical reactivity.<sup>[3]</sup> The intrinsic luminescence from UVI compounds is fertilized in designing sensors and optical materials.<sup>[4]</sup> Intriguing magnetism have been shown in several U<sup>V</sup> compounds.<sup>[5]</sup> U<sup>IV</sup> compounds often exhibit large electric current outputs and outstanding superconductivity under external stimulation.<sup>[6]</sup> Mixed-valent uranium compounds are unique class where nonidentical metal centers potentially combine disparate physicochemical properties together, and therefore distinct functionalities can be envisioned.

Over the years, several synthetic strategies have been developed to stabilize mixed-valent uranium in solids. Lii et al. demonstrated that U<sup>V/VI</sup> compounds can be prepared by high-temperature and high-pressure supercritical hydrothermal methods.<sup>[7]</sup> U<sup>IV/VI</sup> compounds are readily afforded through in situ partial reduction of UVI under solvothermal methods.<sup>[8]</sup> Oxidation of U<sup>III</sup>/U<sup>IV</sup> organometallic compounds (or reduction of U<sup>VI</sup> organometallic compounds) also leads to the formation of mixed-valent uranium cluster compounds.<sup>[9]</sup> To the best of our knowledge, previous efforts have been devoted to crystal structures, magnetism, and spectroscopy of mixed-valent uranium compounds aiming at understanding their coordination behaviors and electronic structures while their potential applications have been substantially overlooked since their discovery. In this work, for the first time, we disclose the semiconducting nature of a large mixed-valent uranium cluster compound,  $[H_3O^+][U^V(U^{VI}O_2)_8(\mu_3-O)_6 (PhCOO)_2(Py(CH_2O)_2)_4(DMF)_4]$  (Ph = phenyl, Py = pyridyl, DMF = N, N-dimethylformamide) (1). Furthermore, with the combination of a large density of the heaviest naturally abundant element within the molecular structure and its high attenuation coefficient towards high-energy photons, we demonstrated that compound 1 is an ideal semiconducting material for efficient direct conversion of X-ray photons into electrical signals, endowing mixed-valent uranium compounds with a decent functionality with application potentials.

Compound **1** was synthesized by solvothermal method through heating the mixture of  $UO_2(NO_3)_2$ .6H<sub>2</sub>O, macrocyclic oligoboronate, and benzoic acid in mixed solvents of DMF, methanol, and ethanol (Scheme 1, detailed synthetic procedure can be found in Supporting Information, PXRD



Scheme 1. Synthetic route for 1.

data is shown in the Supporting Information, Figure S1). The macrocycle oligoboronate is crucial for the synthesis of 1, which in situ decomposes forming the ligand of  $Py(CH_2O^-)_2$ during the solvothermal reaction. The deep brown block crystals were isolated, where the coloration initially suggests the presence of mixed-valent uranium (Supporting Information, Figure S2). X-ray crystallography analysis shows 1 crystallizes in the monoclinic space group of  $P2_1/c$  (Supporting Information, Table S1), and its structure can be best described as a large rhombus-shaped cluster containing nine uranium centers protected by a series of organic ligands (Figure 1a). Figure 1 b shows that the central U<sup>V</sup> (labeled as U5), located at the intersection of two diagonals, is encompassed by eight uranyl(VI) groups (Figure 1 c). This unique structural arrangement efficiently stabilizes UV, which generally exhibits a large tendency of disproportionation to  $U^{v\bar{i}}$  and  $U^{i\bar{v}}$ . The  $U^{v}$ center is six-coordinated by four  $\mu_3$ -O atoms and two oxygen atoms from DMF molecules, forming a UO<sub>6</sub> tetragonal bipyramid geometry. The bond lengths are typical for tetraoxo core based pentavalent uranium with two relatively longer (2.327(14) Å) U–O bonds in the axial direction and four shorter (2.046(11) and 2.069(10) Å) U-O bonds in the equatorial plane, respectively (Supporting Information, Table S2).<sup>[10]</sup> The calculated bond valence sum of U5 is 5.13



Figure 1. a) Molecular structure of  $1^{(19)}$  b) The polyhedral view of 1. c) A view of the  $U^V U^{VI}_{8}(\mu_3 \text{-} O)_6 O_6$  core.

v.u., further confirming its pentavalent assignment (Supporting Information, Table S3).<sup>[11]</sup> All uranyl(VI) groups display a pentagonal bipyramidal geometry with five coordinated atoms in the equatorial plane. The equatorial atoms for U3 and U4 are two  $\mu_3$ -O atoms as well as two oxygen atoms and one nitrogen atom from a  $Py(CH_2O^-)_2$  ligand. Equatorial atoms for U1 and U2 are  $\mu_3$ -O atoms and oxygen atoms from PhCOO<sup>-</sup> ligand and DMF molecule (Figure 1a). All bond lengths of U=O, U-O, and U-N are listed in the Supporting Information, Table S2, within the range of those found in previous U<sup>VI</sup> and U<sup>V</sup> compounds.<sup>[5a,10,12]</sup> Furthermore, **1** is the third case of  $U^{V/VI}$  oxo cluster and the largest tetraoxo core based U<sup>V/VI</sup> oxo cluster.<sup>[12a,b]</sup> Importantly, the crystallinity of 1 remains intact after being stored in a screw-capped vial for six months, making it sufficiently stable for acting as a functional material. Moreover, 1 is thermally stable up to 261 °C (Supporting Information, Figure S3).

To further study the electronic structure of 1, spectroscopic and magnetic characterizations were performed. Figure 2a illustrates the solid-state UV/Vis absorption spectrum of 1. The pronounced absorption peaks from 300 to 550 nm are typical absorption bands of uranyl, originating from the vibronically coupled transitions from ligand-to-metal charge transfer.<sup>[2]</sup> Two additional peaks centered at 617 nm and 757 nm are ascribed to the characteristic electronic transitions of U<sup>V[9a]</sup> The infrared spectrum of 1 contains the characteristic stretching vibration bands of O=U<sup>VI</sup>=O and O=U<sup>V</sup>=O at 900, 885 and 800 cm<sup>-1</sup> (Supporting Information, Figures S4 and S5). X-ray photoelectron spectroscopy further verifies the existence of U<sup>V</sup>. The U 4f high-resolution core-level energy spectrum is presented in Figure 2b. Two strong and broad peaks appear in the range of 375 to 395 eV, which are the U  $4f_{\scriptscriptstyle 7\!/\!2}$  (381 eV) and U  $4f_{\scriptscriptstyle 5\!/\!2}$  (392 eV) peaks, respectively. The peaks were further fitted with two components with disproportionate satellite peaks, ascribed to  $U^{VI}$  (381.2, 392.1 eV) and U<sup>V</sup> (380.2, 391.2 eV), respectively.<sup>[13]</sup> Furthermore, we investigated the X-ray absorption near edge structure (XANES) spectroscopy at U  $L_3$  edge. Figure 2c shows



Figure 2. a) UV/Vis spectrum of 1. b) XPS spectra of 1. c) U  $L_{III}$ -edge XANES of (UEt<sub>4</sub>)<sub>2</sub>UCl<sub>6</sub>, 1, and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O. d) Temperaturedependent magnetic susceptibility data for 1.

Angew. Chem. Int. Ed. 2021, 60, 9886-9890

normalized XANES spectra for 1 and  $UO_2(NO_3)_2 \cdot 6H_2O$ . The absorption features correspond to electric-dipole-allowed transitions from U  $2p_{3/2}$  core level to unoccupied 6d/7s level, in which the energy of infection point in absorption edge is generally correlated with oxidation state of absorbing atoms.<sup>[14]</sup> From the comparison results, the energy for 1 is 17176.95 eV, lower than that of the hexavalent uranium compound of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (17177.30 eV). Moreover, we collected the variable-temperature magnetic susceptibility for 1, showing a paramagnetic behavior (Figure 2d), in agreement with the structural feature of isolated paramagnetic U<sup>V</sup> surrounded by diamagnetic U<sup>VI</sup>. Fitting of the experimental data using modified Curie–Weiss law ( $\chi = C/$  $(T-\theta) + \chi_{\text{TIP}}$  yields the effective moment  $(\mu_{\text{eff}})$  of 1.76  $\mu_{\text{B}}$ , in agreement with the reported values for U<sup>V</sup> compounds (1.4- $3.0\,\mu_{\rm B}$ ).<sup>[5a,12d,15]</sup>

To understand the semiconducting nature of **1**, density functional theory (DFT) analysis was performed using PBE method implemented in VASP for the electronic structure calculations (computational details are summarized in the Supporting Information). Figure 3a and the Supporting Information, Figure S6 illustrates that band structure of **1** is dominated by U<sup>V1</sup> centers. The calculated band gap is 1.83 eV, close to the experimental value of 1.96 eV. The charge density analysis in Figure 3b clarifies the spatial distribution of electrons in U<sup>V/VI</sup> oxo cluster. Figure 3c illustrates that the valence bands (VB) are mainly contributed by O 2p and U<sup>V1</sup> 5f orbitals, and conduction bands (CB) is formed by U<sup>V1</sup> 5f orbitals. The distinctive feature of **1** is an intermediate band (IB) within the forbidden gap. Further analyzing orbital wavefunction illustrates that IB is mainly from the U<sup>V</sup>, and

electrons localized at  $5f_{x(x2-3y2)}$  orbitals (Figure 3c). Furthermore, the emergence of IB in mixed-valent uranium clusters implies that U<sup>V</sup> species serve as electron donors endowing 1 with n-type semiconducting behavior. The donor level is only 0.01 eV lower than that of CB, beneficial for ionization and conductivity. The electronic transition feature can be inferred from the UV/Vis absorption feature of 1, where two additional electronic transitions emerge under low energy photon excitation. In addition, the calculated energy for allowed f-f transitions from  $U^V$  to  $U^{VI}$  is only 0.26 eV, suggesting feasible charge transport within 1 (Figure 3d and discussion in Supporting Information). The above results clearly confirm that IB in 1 serves as a stepping stone to lower the charge transport barrier, which facilitates the charge carrier mobility.<sup>[16]</sup> The band structure of 1 highlights the functionality of mixed-valent uranium in the charge transport properties of 1.

Figure 4a shows statistical data on the density ( $\rho$ ) and effective atomic numbers ( $Z_{\rm eff}$ ) of the commercial radiation detection materials and recently emerged ones.<sup>[17]</sup> Impressively, **1** shows the largest  $Z_{\rm eff}$  among all reported radiation detection semiconductors, and thus provides intrinsic superiority in absorbing high energy photons. Figure 4b illustrates the role of chemical compositions on the X-ray mass attenuation coefficient (MAC, calculated at 80 keV, data is shown in the Supporting Information, Figure S7 and Table S4). Overall, the combined merit of high X-ray MAC and intrinsic semiconducting behavior endow **1** potential capability for radiation detection.

To evaluate the X-ray detection performance of **1**, we investigated its optoelectronic properties. As shown in Fig-



**Figure 3.** a) Calculated energy gap structure for compound 1. b) 2D charge density analysis on the  $U^{V}U^{V_{1}}_{8}(\mu_{3}-O)_{6}O_{6}$  core of the unit cell. c) Wave function analysis on conduction band minimum (CBM), valence band maximum (VBM), and intermediate band (IB), respectively. The isosurface value is 0.03 eÅ<sup>-3</sup>. d) Representation for f–f transitions of the  $U^{V}U^{V_{1}}_{8}(\mu_{3}-O)_{6}O_{6}$  core within the primitive cell. The energy for  $U^{V}$  5  $f_{x(x2-3y2)}$  orbitals is set to 0 for clarity.

#### 9888 www.angewandte.org

© 2021 Wiley-VCH GmbH



**Figure 4.** a) Comparison of the density and effective atomic numbers ( $Z_{eff}$ ) of the commercial radiation detection materials, recently emerged candidates, and **1**. b) Comparison of the mass attenuation of the commercial radiation detection materials, recently emerged candidates, and **1**. c) *I-V* curves of **1**-based detector under dark conditions and X-ray exposure. d) Photocurrent response of **1**-based detector to the tungsten anode X-ray source. e) X-ray-generated photocurrent versus dose rate. f) Mobility-lifetime product ( $\mu\tau$ ) fitting based on the Hecht equation.

ure S8, an X-ray detector was fabricated by a sandwich structure with an Au/1/Au configuration. Figure 4c shows the I-V characteristics of the detector under dark and X-ray irradiation conditions with the voltage ranging from -10 to +10 V. Under the dark condition, we measured the leakage current of the detector and calculated its resistivity to be about  $2.3 \times 10^{11} \Omega$  cm, close to our previously reported semiconducting metal-organic framework SCU-12<sup>[18]</sup> and the majority of commercial radiation detectors.<sup>[17a]</sup> The photocurrent increases upon X-ray irradiation, indicative of response to X-ray photons and charge carrier generation. Based on above results, we estimated its X-ray detection performance by studying the detection sensitivity. Figure 4d shows the photocurrent response of the detector under X-ray irradiation (on/off) at different bias voltage. Impressively, the on/off ratio reaches 500 at 1 V bias voltage, which suppresses the responsive capacities of SCU-12 and lead-based perovskites,[17c,d,18] indicating the effective charge carriers are generated under the interaction between uranium metals and X-ray photons, resulting in a high sensitivity to X-ray photons. The X-ray detection sensitivity of the detector is 23.04  $\mu C\,Gy^{-1}cm^{-2}$  at 30 V bias voltage as shown in Figure 4 e, on the same level of the SCU-12-based detector and the commercial  $\alpha$ -Se detector.<sup>[17a,b,18]</sup> Besides that, we measured the charge carrier mobility and lifetime product ( $\mu\tau$ ) to assess the charge transport properties of 1. Figure 4 f shows the bias dependence of the photonresponse. The fit of measured data using the Hecht model gives a  $\mu\tau$  product of 2.3×

 $10^{-4} \text{ cm}^2 \text{V}^{-1}$ , which is a considerable value by comparing with reported radiation detection materials<sup>[17a,b,18]</sup> (about range from  $10^{-2}$  to  $10^{-6} \text{ cm}^2 \text{V}^{-1}$  in the Supporting Information, Table S5).

In summary, a distinct mixed-valent uranium oxo cluster has been successfully synthesized and fully characterized. The unique structural arrangement within the cluster substantially stabilizes  $U^{V}$ , providing an opportunity to expand the potential applications of  $U^{V}$ -based materials. The revealed electronic structure and band structure of **1** suggest its intrinsic semiconducting behavior. Since the uranium-based oxo cluster contains a high spatial density of uranium leading to a large effective atomic number and a high MAC, powerful capabilities for direct conversion of X-ray photons into electrical signals is disclosed for this class of compounds.

#### Acknowledgements

We are grateful for funding support from the National Natural Science Foundation of China (21790374, 21825601, 21806118), the Science Challenge Project (TZ2016004), and Defense Industrial Technology Development Program (JCKY2019414D002). The computational work was financially supported by the National Natural Science Foundation of China (21976014 and U1930402). We are grateful for calculation resources provided by Tianhe2-JK, China.

### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** mixed-valent uranium · radiation detection · semiconductors · uranium clusters

- [1] a) A. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* 2008, 455, 341–349; b) S. T. Liddle, *Angew. Chem. Int. Ed.* 2015, 54, 8604–8641; *Angew. Chem.* 2015, 127, 8726–8764.
- [2] I. Grenthe, J. Drodyński, T. Fujino, E. C. Buck, S. F. Wolf, *The Chemistry of the Actinide and Transactinide Elements, Vol. 1*, Springer, Amsterdam, 2006.
- [3] a) M. Falcone, L. Chatelain, R. Scopelliti, I. Zivkovic, M. Mazzanti, *Nature* 2017, *547*, 332–335; b) D. P. Halter, F. W. Heinemann, J. Bachmann, K. Meyer, *Nature* 2016, *530*, 317–321; c) W. Chen, H. M. Yuan, J. Y. Wang, Z. Y. Liu, J. J. Xu, M. Yang, J. S. Chen, *J. Am. Chem. Soc.* 2003, *125*, 9266–9267.
- [4] a) Y. Wang, X. Yin, W. Liu, J. Xie, J. Chen, M. A. Silver, D. Sheng, L. Chen, J. Diwu, N. Liu, Z. Chai, T. E. Albrecht-Schmitt, S. Wang, Angew. Chem. Int. Ed. 2018, 57, 7883-7887; Angew. Chem. 2018, 130, 8009-8013; b) J. Xie, Y. Wang, W. Liu, X. Yin, L. Chen, Y. Zou, J. Diwu, Z. Chai, T. E. Albrecht-Schmitt, G. Liu, S. Wang, Angew. Chem. Int. Ed. 2017, 56, 7500-7504; Angew. Chem. 2017, 129, 7608-7612; c) W. Liu, E. Song, L. Cheng, L. Song, J. Xie, G. Li, Y. Zhang, Y. Wang, Y. Wang, Z. Xia, Z. Chai, S. Wang, Chem. Mater. 2019, 31, 9684-9690.
- [5] a) G. Nocton, P. Horeglad, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2008, 130, 16633-16645; b) L. Chatelain, J. P. Walsh, J. Pecaut, F. Tuna, M. Mazzanti, Angew. Chem. Int. Ed. 2014, 53, 13434-13438; Angew. Chem. 2014, 126, 13652-13656; c) V. Mougel, L. Chatelain, J. Pecaut, R. Caciuffo, E. Colineau, J.-C. Griveau, M. Mazzanti, Nat. Chem. 2012, 4, 1011-1017.
- [6] L. Jiao, S. Howard, S. Ran, Z. Wang, J. O. Rodriguez, M. Sigrist, Z. Wang, N. P. Butch, V. Madhavan, *Nature* **2020**, 579, 523–527.
- [7] a) C. S. Lee, C. H. Lin, S. L. Wang, K. H. Lii, Angew. Chem. Int. Ed. 2010, 49, 4254-4256; Angew. Chem. 2010, 122, 4350-4352;
  b) C. H. Lin, K. H. Lii, Angew. Chem. Int. Ed. 2008, 47, 8711-8713; Angew. Chem. 2008, 120, 8839-8841; c) H.-K. Liu, K.-H. Lii, Inorg. Chem. 2013, 52, 9172-9174.
- [8] a) J. Diwu, T. E. Albrecht-Schmitt, *Inorg. Chem.* 2012, 51, 4432–4434; b) L. Chen, J. Diwu, D. Gui, Y. Wang, Z. Weng, Z. Chai, T. E. Albrecht-Schmitt, S. Wang, *Inorg. Chem.* 2017, 56, 6952–6964.
- [9] a) L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2006, 128, 7152-7153; b) C. T. Palumbo, R. Scopelliti, I. Zivkovic, M. Mazzanti, J. Am. Chem. Soc. 2020, 142, 3149-3157; c) G. Nocton, F. Burdet, J. Pecaut, M. Mazzanti, Angew. Chem. Int. Ed. 2007, 46, 7574-7578; Angew. Chem. 2007, 119, 7718-7722; d) B. Biswas, V. Mougel, J. Pecaut, M. Mazzanti, Angew. Chem. Int. Ed. 2011, 50, 5745-5748; Angew. Chem. 2011, 123, 5863-5866; e) V. Mougel, J. Pecaut, M. Mazzanti, Chem. Commun. 2012, 48, 868-870; f) G. Nocton, J. Pecaut, M.

Mazzanti, Angew. Chem. Int. Ed. 2008, 47, 3040–3042; Angew. Chem. 2008, 120, 3082–3084.

- [10] a) C. S. Chen, S. F. Lee, K. H. Lii, J. Am. Chem. Soc. 2005, 127, 12208-12209; b) J. T. Stritzinger, E. V. Alekseev, M. J. Polinski, J. N. Cross, T. M. Eaton, T. E. Albrecht-Schmitt, Inorg. Chem. 2014, 53, 5294-5299.
- [11] a) N. E. Brese, M. Okeeffe, Acta Crystallogr. Sect. B 1991, 47, 192–197; b) P. C. Burns, R. C. Ewing, F. C. Hawthorne, Can. Mineral. 1997, 35, 1551–1570.
- [12] a) L. Chatelain, S. White, R. Scopelliti, M. Mazzanti, Angew. Chem. Int. Ed. 2016, 55, 14325-14329; Angew. Chem. 2016, 128, 14537-14541; b) V. Mougel, P. Horeglad, G. Nocton, J. Pecaut, M. Mazzanti, Angew. Chem. Int. Ed. 2009, 48, 8477-8480; Angew. Chem. 2009, 121, 8629-8632; c) J. C. Berthet, M. Nierlich, M. Ephritikhine, Angew. Chem. Int. Ed. 2003, 42, 1952-1954; Angew. Chem. 2003, 115, 1996-1998; d) G. Nocton, P. Horeglad, V. Vetere, J. Pecaut, L. Dubois, P. Maldivi, N. M. Edelstein, M. Mazzanti, J. Am. Chem. Soc. 2010, 132, 495-508.
- [13] N. Belai, M. Frisch, E. S. Ilton, B. Ravel, C. L. Cahill, *Inorg. Chem.* 2008, 47, 10135–10140.
- [14] N. H. Anderson, S. O. Odoh, U. J. Williams, A. J. Lewis, G. L. Wagner, J. Lezama Pacheco, S. A. Kozimor, L. Gagliardi, E. J. Schelter, S. C. Bart, J. Am. Chem. Soc. 2015, 137, 4690–4700.
- [15] a) J. Selbin, J. D. Ortego, *Chem. Rev.* **1969**, *69*, 657–671; b) K. A. Pace, V. V. Klepov, G. Morrison, H. C. Zur Loye, *Chem. Commun.* **2018**, *54*, 13794–13797; c) C. R. Graves, J. L. Kiplinger, *Chem. Commun.* **2009**, 3831–3853; d) D. R. Kindra, W. J. Evans, *Chem. Rev.* **2014**, *114*, 8865–8882.
- [16] A. Luque, A. Marti, C. Stanley, *Nat. Photonics* **2012**, *6*, 146–152.
- [17] a) A. Mirzaei, J.-S. Huh, S. S. Kim, H. W. Kim, *Electron. Mater. Lett.* 2018, 14, 261–287; b) B. D. Milbrath, A. J. Peurrung, M. Bliss, W. J. Weber, J. Mater. Res. 2008, 23, 2561–2581; c) H. Wei, Y. Fang, P. Mulligan, W. Chuirazzi, H.-H. Fang, C. Wang, B. R. Ecker, Y. Gao, M. A. Loi, L. Cao, J. Huang, Nat. Photonics 2016, 10, 333–339; d) S. Yakunin, M. Sytnyk, D. Kriegner, S. Shrestha, M. Richter, G. J. Matt, H. Azimi, C. J. Brabec, J. Stangl, M. V. Kovalenko, W. Heiss, Nat. Photonics 2015, 9, 444–449; e) G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Graetzel, S. Mhaisalkar, T. C. Sum, Science 2013, 342, 344–347; f) D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, O. M. Bakr, Science 2015, 347, 519–522.
- [18] Y. Wang, X. Liu, X. Li, F. Zhai, S. Yan, N. Liu, Z. Chai, Y. Xu, X. Ouyang, S. Wang, J. Am. Chem. Soc. 2019, 141, 8030–8034.
- [19] Deposition Number 1882501 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Manuscript received: December 30, 2020 Accepted manuscript online: February 15, 2021 Version of record online: March 18, 2021