

# NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

RSC Publishing

COMMUNICATION

## New Air-Stable Uranium(IV) Complexes with Enhanced Volatility

Cite this: DOI: 10.1039/x0xx00000x

Jennifer Leduc, Rajitha Ravithas, Lisa Rathgeber, and Sanjay Mathur<sup>a</sup>Received 00th January 2012,  
Accepted 00th January 2012

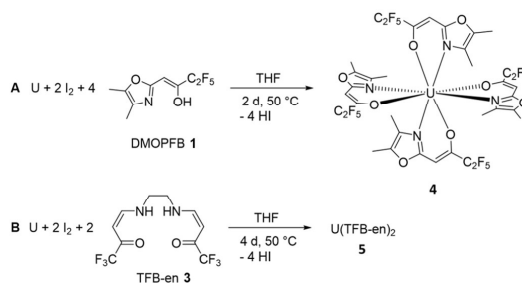
DOI: 10.1039/x0xx00000x

www.rsc.org/

Herein we report the synthesis and characterization of new air-stable uranium(IV) complexes based on three different heteroarylalkenolate ligands namely DMOPFB (**1**) (1-(4,5-dimethyl-oxazol-2-yl)-3,3,4,4,4-pentafluoro-but-1-en-2-ol) with an elongated fluorinated alkyl chain compared to DMOTFP (**2**) (3,3,3-trifluoro-1-(4,5-dimethyloxazol-2-yl)propen-2-ol) and the tetradentate enaminone TFB-en (**3**) (*N,N'*-bis-(4,4,4-trifluorobut-1-en-3-on)-ethylenediamine). These new complexes exhibit sufficiently high volatilities, with respect to previously reported uranium compounds, and are thus promising precursors for chemical vapor deposition (CVD) of uranium oxide materials.

Investigations on uranium complexes has recently attracted substantial attention in fields ranging from subvalent (U(II)) compounds, isotope separation to materials science.<sup>[1-6]</sup> Uranium complexes with fluoride<sup>[7]</sup>, borohydride<sup>[8]</sup>, amide<sup>[9]</sup>, silazane<sup>[9]</sup>, alkoxide<sup>[10,11]</sup> and acetyl acetonate<sup>[12]</sup> ligands are known to be volatile and have been studied especially for isotope separation applications. However, these complexes are mostly not suitable for the gas phase synthesis of uranium oxide materials by chemical vapor deposition (CVD) due to their low vapor pressure<sup>[7]</sup>, uncontrolled thermal decomposition<sup>[8]</sup>, reactivity towards moisture<sup>[9,10]</sup> and visible and UV light sensitivity<sup>[11]</sup> or unsuitability for safe long-term storage<sup>[7,8]</sup>. Recently, we have demonstrated the synthesis of air-stable, volatile uranium(IV) heteroarylalkenolates as well as their gas phase conversion to uranium oxide films.<sup>[5]</sup> However, when applied in a thermal CVD process relatively high precursor temperatures (~150 °C) were required for the heteroarylalkenolates. In our quest for new uranium complexes with enhanced volatility, we report here on two alternative synthetic approaches based on the modification (elongation) of the perfluoroalkyl chain of  $\beta$ -donor alkenolates which is known to enhance the volatility of metal complexes due to electrostatic repulsions between the C<sub>2</sub>F<sub>5</sub>-groups that suppress intermolecular interaction in the solid-state<sup>[13,14]</sup> and reduction of the overall molecular weight using a smaller tetradentate ligand. The heteroarylalkenolate ligand DMOPFB **1** was synthesized using 2,4,5-trimethyloxazole, pentafluoropropionic anhydride and pyridine

as base. The reaction proceeded at room temperature for 12 hours to produce the target ligand that was purified via sublimation (45 °C, 10<sup>-3</sup> mbar) in 52% yield. It was characterized by 1D and 2D NMR spectroscopy. The <sup>1</sup>H NMR spectrum of **1** showed signals corresponding to the enol and enaminone tautomers: the signals at 11.55 and 11.48 ppm could be assigned to the -OH and -NH protons, respectively, whereas the singlet at 5.89 ppm could be attributed to a vinylic proton indicating the existence of the enolic form of **1**. Comparison of the sublimation temperatures with DMOTFP **2** (s.p. 55 °C, 10<sup>-3</sup> mbar)<sup>[15]</sup> showed that **1** was more volatile (s.p. 45 °C, 10<sup>-3</sup> mbar). Tetradentate enaminone ligand **3** was prepared in a straightforward two step synthesis. In the first step, 1-ethoxy-4,4,4-trifluorobut-1-en-3-one (TFAE) was synthesized according to the procedure of *S. Matsuo et al.*<sup>[16,20]</sup> The resulting product was reacted with ethylenediamine<sup>[17]</sup> resulting in TFB-en (*N,N'*-bis-(4,4,4-trifluorobut-1-en-3-on)-ethylenediamine **3**) with an isolated yield of 75%.



Scheme 1. Synthesis of U(DMOPFB)<sub>4</sub> **4** (A) and U(TFB-en)<sub>2</sub> **5** (B).

The reaction of uranium turnings with 2 equiv. of iodine and 4 equiv. of **1** at 50 °C for 2 days resulted in the formation of U(DMOPFB)<sub>4</sub> **4** as a green solid in 50% yield (Scheme 1A).<sup>[5,18]</sup> Compound **4** was characterized by 1D and 2D NMR spectroscopy, elemental analysis and single crystal X-ray diffraction analysis. Compared to the free DMOPFB ligand, the signal of the vinylic proton was strongly

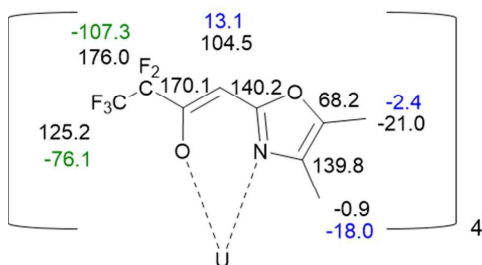
**Comment [S1]:** 1. Please cite the paper of J. Fornalczyk Gregor Fornalczyk, Martin Vallgor, Sanjay Mathur Monomeric Iron Heteroarylalkenolates: Structural Design Concepts and Investigations on Their Application in Chemical Vapor Cryst. Growth Des., 2014, 14 (4), 1811–1816.

**Comment [S2]:**

## COMMUNICATION

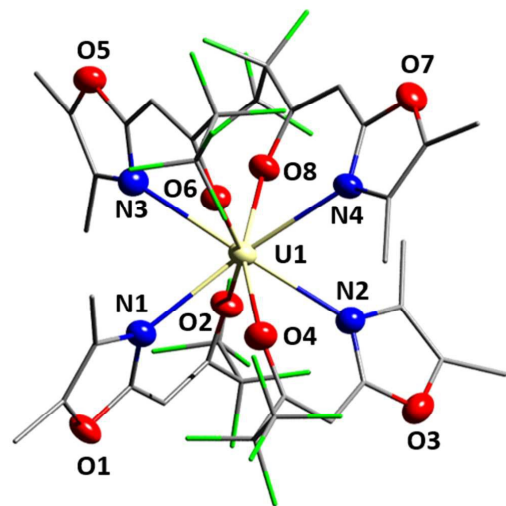
## Journal Name

shifted downfield to 13.1 ppm, and the signals of the methyl groups were shifted upfield to -2.4 and -18.0 ppm, respectively, plausibly due to the paramagnetic character of the complex. The strong upfield signal of -18.0 ppm was assigned to the methyl group oriented toward the uranium center. Since  $^1\text{H}$  NMR data showed only a signal set for the ligand, it can be deduced that the uranium center maintains the symmetric eight coordinate environment such as the square antiprism found in the solid-state structure. In comparison to the  $\text{U}(\text{DMOTFP})_4$  complex **6**,<sup>[5]</sup> the chemical shifts were more pronounced. The fluorine signals appeared at -76.1 ( $-\text{CF}_3$ ) and -107.3 ppm ( $-\text{CF}_2$ ) (Figure 1).



**Figure 1.** Assignment of  $^1\text{H}$  (blue),  $^{13}\text{C}$  (black) and  $^{19}\text{F}$  (green) NMR shifts of  $\text{U}(\text{DMOPFB})_4$  **4** in  $\text{THF-d}_8$  exemplarily shown for one of the four DMOPFB ligands in [ppm].

Time-dependent NMR analysis showed that **4** is slowly oxidized to the diamagnetic species  $\text{UO}_2(\text{DMOPFB})_2(\text{H-DMOPFB})$  **8** in  $\text{THF-d}_8$  probably due to its reaction with water and oxygen inadvertently present in the solvent (further information in SI). Single crystals of  $\text{U}(\text{DMOPFB})_4$  **4** were obtained by recrystallization from a heptane solution.

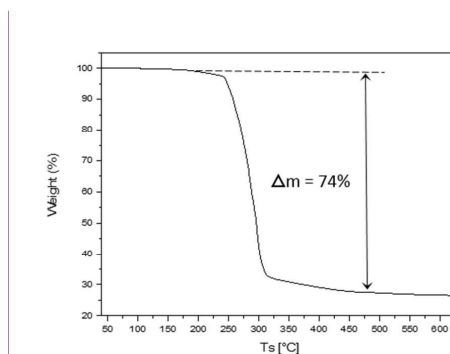


**Figure 2.** Molecular structure of  $\text{U}(\text{DMOPFB})_4$  **4**. Thermal ellipsoids are shown at 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): U1-O2 2.231(5), U1-O4 2.266(5), U1-O6

2.236(5), U1-O8 2.253(5), U1-N1 2.586(6), U1-N2 2.619(7), U1-N3 2.649(6), U1-N4 2.646(6).

Compound **4** crystallized in the orthorhombic space group  $Pbca$ , with eight molecules per unit cell, whereas **6** was reported to crystallize in the monoclinic centrosymmetric space group  $C2/c$  with four molecules per unit cell. The uranium atoms exhibit a distorted square antiprismatic coordination sphere (Figure 2). The two ligands generating one distorted square plane are aligned *trans* to each other. The difference in bond lengths of U–N and U–O is responsible for the distortion of the square antiprismatic coordination sphere resulting in angles deviating from ideal  $90^\circ$  by  $\pm 15^\circ$  for N3-N4-O6-O8 and by  $\pm 10^\circ$  for N1-N2-O2-O4. The mean U–O distances of **4** (ca. 2.25 Å) were similar to those observed in  $\text{U}(\text{DMOTFP})_4$  **6** (2.24 Å).<sup>[5]</sup>

The higher volatility of **4** was confirmed by electron impact mass spectrometry (EI-MS). Due to the technical limit of the mass spectrometer at  $m/z = 1200$ , the  $\text{M}^+$  signal ( $m/z = 1262$ ) could not be detected. Instead, the radical cation derived from the loss of one DMOPFB ligand was found with highest intensity ( $[\text{U}(\text{DMOPFB})_3]^+$ ;  $m/z = 1006$ ). Other signals representing lower masses probably result from the fragmentation of the DMOPFB ligand. This proved the stability of **4** in the gas phase at elevated temperatures.



**Figure 3.** Thermogravimetric analysis of  $\text{U}(\text{DMOPFB})_4$  **4** under nitrogen atmosphere.

Thermogravimetric analysis of **4** performed under nitrogen showed a lower decomposition temperature, when compared with the DMOTFP complex **6**. No mass losses were observed until the onset of decomposition at  $240^\circ\text{C}$  (Figure 3). Decomposition occurs in one step and complete combustion was achieved at  $>290^\circ\text{C}$ . The experimental weight loss (74%) due to the formation of  $\text{UO}_2$  is in good agreement with the theoretical value (79%).

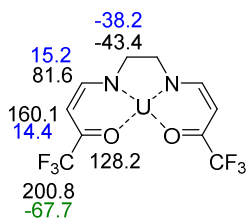
Complex **5** was synthesized following an analogous pathway as described for **4** by reacting uranium turnings with 2 equiv. of iodine and 2 equiv. of TFB-en **3** at  $50^\circ\text{C}$ . The reaction was sluggish and 4 days were needed for full conversion of the educts into product showing a less pronounced tendency of TFB-en towards complexation of uranium.  $\text{U}(\text{TFB-en})_2$  **5** was isolated after sublimation at  $130^\circ\text{C}$  ( $10^{-3}$  mbar) in 20% yield. Compound **5** was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  as well as  $^{19}\text{F}$  NMR spectroscopy (Figure 4) and mass spectrometric analysis.

**Comment [S3]:** We are arguing for NMR data that the coordination sphere is symmetrical.

**Comment [S4]:** Please add the weight loss in % in the text and give the theoretical value in the brackets.

Journal Name

COMMUNICATION



**Figure 4.** Assignment of  $^1\text{H}$  (blue),  $^{13}\text{C}$  (black) and  $^{19}\text{F}$  (green) NMR shifts of  $\text{U}(\text{TfB-en})_2$  **5** in  $\text{THF-d}_8$  exemplarily shown for one ligand in [ppm].

The proton and carbon signals of the ethylene bridge were strongly upfield shifted (-38.2 ppm,  $^1\text{H}$  and -43.4 ppm,  $^{13}\text{C}$ ). The vinylic protons displayed a downfield shift to 15.2 ppm and 14.4 ppm. As observed for **4**, EI-MS showed that **5** also exhibited enhanced volatility compared to our previously published uranium(IV) complexes.<sup>5</sup> The  $\text{M}^+$  signal ( $m/z = 842$ ) with highest intensity was detected at 110 °C. Elemental analysis as well as EI-MS data showed that the compound still contained slight impurities of iodine which was removed by additional washing with heptane and crystallization of **5** from toluene at -30 °C. However, the resulting green/brownish solid was found by  $^1\text{H}$  NMR analysis to be a mixture of **5** and **3**. Further attempts to purify the compound like solvent extraction or recrystallization were unsuccessful and only resulted in decomposition of **5**. Similar to the derivative **4**, **5** decomposed in undried  $\text{THF-d}_8$  to give **TfB-en 3** and a diamagnetic, bright yellow compound with NMR signals, which could be best assigned to  $\text{UO}_2(\text{TfB-en})(\text{THF})$  **9**.<sup>19</sup>

In summary, we could show that the length of the fluorinated alkyl chain in the oxazole-ligand and the decrease in the molecular weight of the complexes by using a tetradentate enaminone ligand represent viable approaches for increasing the volatility of uranium(IV) compounds. Both complexes are stable as solids in air, however only **4** may prove as useful precursor for CVD processes since **5** could not be completely purified due to its instability. Further efforts are currently underway.

## Experimental

### Tetrakis[ $\eta^2$ -*N,O*-1-(4,5-dimethyl-oxazol-2-yl)-3,3,4,4,4-pentafluoro-but-1-en-2-olato] Uranium(IV) (**4**)

Oxide-coated uranium turnings (0.40 g, 1.70 mmol) were stirred for 5 min in 5 ml concentrated nitric acid and rinsed with deionized water and acetone to remove the native oxide. A 100 ml *Schlenk* flask was charged with freshly obtained oxide-free uranium metal turnings, iodine (0.90 g, 3.50 mmol), 1-(4,5-dimethyl-oxazol-2-yl)-3,3,4,4,4-pentafluorobut-1-en-2-ol (DMOPFB) **1** (1.80 g, 7.00 mmol) and 20 ml THF. The reaction mixture was vigorously stirred for 2 d at 50 °C yielding a brown suspension. The reaction mixture was cooled to rt and decanted to collect a mixture of green and black crystals. The mixture was washed with hexane and dried under reduced pressure. The remaining iodine was removed via sublimation at 110 °C under reduced pressure and the product was obtained as a green solid (1.1 g, 50%).

$^1\text{H}$ -NMR (300 MHz, rt,  $\text{THF-d}_8$ ):  $\delta$  [ppm] = 13.1 (s, 4H); -2.4 (s, 12H); -18.0 (s, 12H).

$^{19}\text{F}$ -NMR (282 MHz, rt,  $\text{THF-d}_8$ ):  $\delta$  [ppm] = -76.1 (s, 12F); -107.3 (s, 8F).

$^{13}\text{C}$ -NMR (75 MHz, rt,  $\text{THF-d}_8$ ):  $\delta$  [ppm] = 176.0, 170.1, 140.2, 139.8, 125.2, 104.5, 68.2, -0.9, -21.0.

CHNS (found/calculated) [%]: C (34.09/34.24); N (4.21/4.44); H (2.25/2.24).

EI-MS (20 eV, 115 °C):  $m/z = 1005$  [ $\text{M}^+$ ] (100%), 257 [ $(\text{CF}_2\text{CF}_3)^+$ ] (8%), 138 [ $\text{C}_6\text{H}_7\text{NO}^+$ ] (20%).

### Bis[ $\eta^2$ -*N,O,N,N'*-bis-(4,4,4-trifluorobut-1-en-3-on) ethylenediamine] Uranium(IV) (**5**)

Oxide-coated uranium turnings (0.62 g, 2.61 mmol) were stirred for 5 min in 5 ml concentrated nitric acid and rinsed with deionized water and acetone to remove the native oxide. A 100 ml *Schlenk* flask was charged with freshly obtained oxide-free uranium metal turnings, iodine (1.33 g, 5.22 mmol), *N,N'*-bis-(4,4,4-trifluorobut-1-en-3-on)-ethylenediamine (**TfB-en 3**) (1.59 g, 5.22 mmol) and 25 ml THF. The reaction mixture was vigorously stirred for 4 d at 50 °C yielding a brown suspension. The solvent was directly removed under reduced pressure. The remaining iodine was removed via sublimation at 110 °C under reduced pressure. The crude product was purified via sublimation at 130 °C ( $10^{-3}$  mbar) and the product was received as brownish crystals (0.42 g, 20%).

$^1\text{H}$ -NMR (300 MHz, rt,  $\text{THF-d}_8$ ):  $\delta$  [ppm] = 15.2 (d, 4H); 14.4 (d, 4H); -38.2 (s, 8H).

$^{19}\text{F}$ -NMR (282 MHz, rt,  $\text{THF-d}_8$ ):  $\delta$  [ppm] = -67.7 (s, 12F).

$^{13}\text{C}$ -NMR (100 MHz, rt,  $\text{THF-d}_8$ ):  $\delta$  [ppm] = 200.8, 160.1, 128.2, 81.6, -43.4.

CHNS (found/calculated) [%]: C (27.51/28.52); N (6.36/6.65); H (2.32/1.91).

EI-MS (70 eV, 110 °C):  $m/z = 842$  [ $\text{M}^+$ ] (100%), 152 [ $(\text{C}_5\text{H}_5\text{F}_3\text{NO})^+$ ] (62%), 82 [ $\text{C}_4\text{H}_5\text{NO}^+$ ] (25%).

## Notes and references

<sup>a</sup> Chair of Materials and Inorganic Chemistry

University of Cologne

Greinstr. 6, 50939 Cologne (Germany)

E-mail: sanjay.mathur@uni-koeln.de

<sup>†</sup>We thank the FCI ("Fonds der chemischen Industrie") and the University of Cologne for providing financial assistance. Prof. Dr. Gerd Meyer (Iowa State University, Ames) and Prof. Dr. William J. Evans (University of California, Irvine) are gratefully acknowledged for fruitful discussions.

Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

- R. G. Jones, E. Bindschadler, G. Karmas, F. A. Yoeman, H. Gilman, *J. Am. Chem. Soc.*, 1956, **78**, 4287; M. R. MacDonald, M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 13310.
- H. I. Schlesinger, H. C. Brown, B. Abraham, A. C. Bond, N. Davidson, A. E. Finholt, J. R. Gilbreath, H. Hoekstra, L. Horvitz, E. K. Hyde, J. J. Katz, J. Knight, R. A. Lad, D. L. Mayfield, L. Rapp, D. M. Ritter, A. M. Schwartz, I. Sheft, L. D. Tuck, A. O. Walker, *J. Am. Chem. Soc.*, 1953, **75**, 186.
- D. C. Bradley, R. N. Kapoor, B. C. Smith, *J. Chem. Soc.*, 1963, **204**; D. C. Bradley, R. N. Kapoor, B. C. Smith, *J. Inorg. Nucl. Chem.*, 1962, **24**, 863.
- E. Jacob, *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 142.

## COMMUNICATION

Journal Name

- 5 L. Appel, J. Leduc, C. L. Webster, J. W. Ziller, W. J. Evans, S. Mathur, *Angew. Chem. Int. Ed.*, 2014, **54**, 2209.
- 6 R. G. Gordon, J.-S. Lehn, H. Li, Metal(V) Tetra-Amidinate Compounds and Their Use in Vapor Deposition, US007638645B2, 2009.
- 7 H. S. Booth, W. Krasny-Ergen, R. E. Heath, *J. Am. Chem. Soc.*, 1946, **68**, 1969; F. G. Brickwedde, H. J. Hoge, R. B. Scott, *J. Chem. Phys.*, 1948, **16**, 429.
- 8 H. I. Schlesinger, H. C. Brown, *J. Am. Chem. Soc.*, 1953, **75**, 219-221; M. Ephritikhine, *Chem. Rev.*, 1997, **97**, 2193.
- 9 R. G. Jones, G. Karmas, G. A. Martin Jr., H. Gilman, *J. Am. Chem. Soc.*, 1956, **78**, 4285; J. C. Berthet, M. Ephritikhine, *Coord. Chem. Rev.*, 1998, **83**, 178.
- 10 W. G. Van Der Sluys, A. P. Sattelberger, *Chem. Rev.*, 1990, **90**, 1027; S. Fortier, G. Wu, T. W. Hayton, *Inorg. Chem.*, 2008, **47**, 4752.
- 11 R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin Jr., J. R. Thirtle, F. A. Yeoman, H. Gilman, *J. Am. Chem. Soc.*, 1956, **78**, 6030.
- 12 R. Guillard, A. Dormond, M. Belkalem, J. E. Anderson, Y. H. Liu, K. M. Kadish, *Inorg. Chem.*, 1987, **26**, 1986; A. Vallat, L. Dormond, A. Dormond, *J. Chem. Soc., Dalton Trans.*, 1990, **0**, 921.
- 13 M. F. Richardson, R. E. Sievers, *Inorg. Chem.*, 1971, **10**, 498; K. J. Eisentraut, R. E. Sievers, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1931; R. Sievers, J. Sadlowski, *Science*, 1978, **201**; R. A. O'Ferrall, B. A. Murry, *J. Chem. Soc. Perkin Trans. 2*, 1994.
- 14 L. Brückmann, W. Tyrre, S. Stucky, S. Mathur, *Inorg. Chem.*, 2012, **51**, 536.
- 15 I. Giebelhaus, R. Müller, W. Tyrre, I. Pantenburg, T. Fischer, S. Mathur, *Inorg. Chim. Acta*, 2011, **372**, 340.
- 16 M. Hojo, R. Masuda, Y. Kokuryo, H. Shioda, S. Matsuo, *Chem. Lett.*, 1976, 499.
- 17 Synthesis of the CH<sub>3</sub> analog: E. G. Jäger, B. Kirchhof, E. Schmidt, B. Remde, A. Kipke, R. Müller, *Z. Anorg. Allg. Chem.*, 1982, **485**, 141.
- 18 Based on: M. J. Monreal, R. K. Thomson, T. Cantat, N. E. Travia, B. L. Scott, J. L. Kiplinger, *Organometallics*, 2011, **30**, 2031.
- 19 R. J. Baker, *Chem. Eur. J.*, 2012, **18**, 16258.
- 20 G. Fornalczyk, M. Valldor, S. Mathur, *Cryst. Growth Des.*, 2014, **14**, 1811.