Synthesis and structure of metal-TCPE (metal = Th, Ce) metal-organic frameworks based on 1,2,4,5-tetrakis(4-carboxyphenyl) ethylene

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Two new metal-organic frameworks (MOFs) (Th/ Ce -TCPE) based on 1,2,4,5-tetrakis(4-carboxyphenyl)ethylene were obtained using a straightforward reaction under moderate conditions. Th and Ce formed the central units of this MOF in the mononuclear and in the unusual trinuclear cluster configurations, respectively. The resulting MOFs were analysed by fluorescence spectroscopy to understand their luminescence. The obtained data revealed that benzene’s electron cloud density and torsion angle on the ligand were affected by the acetic acid molecule and Th(IV), which caused Th-TCPE to irradiate stronger blue emission, but Ce-TCPE showed no fluorescence due to the self-quenching. Such a unique luminescence property could be used for fluorescence or radiopharmaceutical sensing.

1. Introduction

Actinides are by-products of spent fuel reprocessing, recycling and separation. Due to the unfilled 5f and 6d electron shells, the physical and chemical properties of actinides are unique [1–3], which attracts scientists worldwide to study compounds of tetravalent actinides including thorium, uranium and plutonium [4,5]. Yet, due to the complexity of their chemistry, the structure, chemical bonding nature and reaction mechanisms of these compounds are still not fully understood [6,7].
Materials based on metal-organic frameworks (MOFs), which are organic–inorganic nanoporous hybrids, have emerged in recent years. They are composed of coordinated metal ions and organic ligands [8,9]. With the synthesis and application of a large number of uranium-based MOFs, thorium-based MOFs has also received extensive attention. For example, O’Hare et al. [10–12] synthesized one-dimensional hexagonal nanotube-like thorium-based MOFs (TOF-1) with 1,3,5-benzotrifluorimide acid as organic ligand. This group also synthesized TOF-2 and TOF-3 with different size cages. Thierry et al. [13] used a bidentate ligand to synthesize Th UiO-66, which was later functionalized by Li et al. [14,15] to synthesize a Th UiO-66-X series of compounds. Islamoglu et al. [16] combined Th with a tridentate ligand and obtained Th-MOF-808, while Li et al. [17] combined Th with a tetraderate ligand to obtain Th-PCN-222. Thorium-based MOFs also exhibit the capability of fluorescent properties. In our previous work, we used H4TCPB to synthesize several fluorescing Th-based MOFs [18]. Fluorescing MOFs based on other tetravalent actinides were also obtained by other groups [19,20].

This paper reports research data obtained as a continuation of those efforts. We used Th(IV) and Ce(IV) nitrates (Ce as a representative tetravalent actinide) and 1,2,4,5-tetrakis(4-carboxyphenyl)ethylene (H4TCPE) ligand to synthesize Th(IV)-based Th-TCPE (compound 1) and Ce(III)-based Ce-TCPE (compound 2) MOFs [21]. Ce(IV) is reduced to Ce(III) in this process, and it is speculated that other tetravalent actinides may also be the case such as Pu(IV). Both compounds were thoroughly characterized. Compound 1 enhanced the luminescence intensity of the ligand, while compound 2 did not exhibit fluorescing properties. Some explanations are given for the mechanism of this phenomenon.

2. Experimental section

Caution! 232Th used in this study is radioactive and toxic. The standard procedure of radioactive material handling should be strictly obeyed during the preparation of the materials below.

2.1. Material and methods

In this work, we used Th(NO3)4·5H2O (99.5%) purchased from Shanghai Aladdin Biochemical Technology Co., Ce(NO3)3·6H2O (99.9%) supplied by Shanghai Macklin Biochemical Co., H4TCPB (98%) from the Jilin Chinese Academy of Sciences-Yanshen Technology Co., and N, N'-Dimethylformamide (DMF, 99.5%) acquired from Shanghai Meirel Chemical Technology Co. We also used glacial acetic (99.5%) and formic (88%) acids as well as ethanol (EtOH, 99.7%) supplied by Sinopharm Chemical Reagent Co. and normal hexane (95%) purchased from Shanghai Honeywell Trading Co.

2.2. Synthesis and structural determination

Compound 1 (Th-TCPE): 11.40 mg of Th(NO3)4·5H2O, 10.17 mg of H4TCPE and 0.40 ml glacial acetic acid were mixed with 1.5 ml of DMF in a 7 ml vial, which was then sealed and heated to 80°C for 48 h. The absinthe-green crystalline powder was filtered to separate it from the mother solution, washed three times with 30 ml of DMF, three times with 30 ml of EtOH and dried at room temperature. The amounts of these reagents were reduced 10 times to synthesize single crystals using the same procedure. The yield was 65.2% recalculated relative to the initial H4TCPB amount. The elemental analysis (EA) confirmed that the formula of the synthesized compounds could be expressed as Th4(TCPE)2(C2H3O2)8(C3H7NO)3(H2O)20. The molecular weight is 2409.36. The theoretical C, H and N weight contents in this compound (equal to 33.89%, 3.73% and 1.53%, respectively) corresponded well to those obtained from the experimental analyses (equal to 34.12%, 3.45% and 1.66%, respectively).

Compound 2 (Ce-TCPE): 10.25 mg of Ce(NO3)3·6H2O, 10.17 mg of H4TCPB, 0.05 ml of glacial acetic acid and 1.5 ml of DMF were sealed in a 7 ml vial and heated at 100°C for 12 h. The resulting powder was filtered, washed three times with 30 ml of DMF, then three times with 30 ml of EtOH and dried at room temperature. The amounts of these reagents were reduced 10 times to synthesize single crystals using the same procedure. The final product yield was 62.2%, calculated relative to the initial H4TCPB amount. The theoretical C, H and N weight contents calculated for the resulting Ce(IV)Ce(III)2(μ-OH)2(TCPE)2(C3H7NO)4(H2O)5 (the molecular weight is 1461.22) compound should be equal to 46.86%, 3.80% and 3.04%, respectively. Corresponding C, H and N contents determined analytically were equal to 46.69%, 3.67% and 2.78%, respectively.
2.3. Characterization

Single-crystal X-ray diffraction (SCXRD) was performed using a Bruker APEX-II CCD diffractometer coupled with a Turbo X-ray source relying on Ga Kα radiation at $\lambda = 1.34139$ Å. The instrument contained a direct-drive rotating anode and a CMOS detector. The crystal temperature was maintained at 173.0 K and 189.99 K during data acquisition. We used Olex2 [22] to solve the structure by an intrinsic phasing method. The data were then refined by ShelXL [23] software using the least square minimization approach. The scattering contribution due to the highly disordered ligand molecules was adjusted by the SQUEEZE simulation package of the PLATON program. All crystallographic data and some bond lengths are given in the electronic supplementary material, tables S1–S3.

Powder X-ray diffraction (PXRD) spectra were collected in the 5–50° range with a 0.02° step using a Bruker D8 Advance instrument equipped with Cu Kα radiation with $\lambda = 1.54178$ Å as an X-ray source. First, we calculated (using SHELXTL-XPOW software) theoretical PXRD patterns using the data from the CIF files. Then, the experimental PXRD data were compared to these patterns to confirm the crystallinity and purity of the obtained compounds (see electronic supplementary material, figure S1).

Infrared spectroscopy (IR) was performed in the 2500–400 cm$^{-1}$ range using a Thermo Scientific Nicolet iS20 instrument coupled with a diamond attenuated total reflectance set-up (see electronic supplementary material, figure S2).

Scanning electron microscopy (SEM) was performed by a Zeiss Merlin Compact LEO 1530 VP instrument. The compound 1 and 2 morphologies were oval and approximately 20 µm in size and columnar and 20–50 µm in size, respectively (see electronic supplementary material, figure S3).

EA was performed by the CHN model of the Elementar Vario EL III instrument.

Thermogravimetric analysis (TGA) was conducted using a Mettler-Toledo instrument under static N$_2$. The samples were heated up to 700°C with a 10°/min rate (figure 4).
Surface area and porosity measurements were performed by recording the N\textsubscript{2} and Ar adsorption/desorption isotherms at 77 K and 87 K by a Micromeritics ASAP 2020 instrument. Before the tests, compounds were soaked in n-hexane for 6 h to exchange DMF and then placed into sealed quartz crucibles, followed by their evacuation to 10\textsuperscript{−2} kPa and consequent heating at 100°C for 6 h (see electronic supplementary material, figure S4).

Fluorescence spectroscopy was recorded by an Edinburgh FLS spectrophotometer. Quantum yield (QY) was obtained using the Hamamatsu QY-plus set-up (figure 6).

X-ray photoelectron spectroscopy (XPS) was recorded by the full spectrum data measurement and analysis of the valence of Ce in compound 2 by a Thermo Fisher Nexsa (see electronic supplementary material, figure S5).

In situ XRD spectra were collected from 25°C to 700°C using a PANalytical Sharp Shadow instrument in the 5–50° range with a 0.02° step (see electronic supplementary material, figure S6).

3. Results and discussion

3.1. Crystal structures

3.1.1. Compound 1

SCXRD revealed that compound 1 crystallizes in the monoclinic space group C2/c and contains nine-coordinated Th simultaneously bridged and chelated by H4TCPE (figure 1a). The whole complex has only one quadrilateral pore, 9.1 × 9.6 Å (diagonally) in size (see packing diagram in figure 1b). Th is coordinated by four carboxyl oxygens of four different ligands and five carboxyl oxygens from four
CH$_3$COO$^-$ molecules (figure 1c). The bond length between Th and carboxylic O is 2.425(12)-2.508(14) Å, while between Th and acetic acid O it is 2.382(11)-2.737(9) Å. Its topology is flu, (4,8)-connected (figure 1d).

3.1.2. Compound 2

It was found that Ce(IV) located on both sides of the trinuclear cluster in compound 2 is reduced to Ce(III) by analysing the XPS data of Ce in compound 2 (see electronic supplementary material, figure S5). SCXRD revealed that compound 2 crystallizes in the monoclinic space group C2/m and contains 10-coordinate Ce (IV) and seven-coordinate Ce(III) units simultaneously bridged and chelated by H$_4$TCPE (figure 2a). The whole complex has only one quadrilateral pore, 8.7 × 8.6 Å (diagonally) in size (see packing diagram in figure 2b). The three Ce atoms form a symmetrical trinuclear cluster Ce(IV)Ce(III)$_2$(µ-OH)$_2$(CO$_2$)$_4$(CO)$_{12}$ with two Ce(IV)-O-Ce(III) bonds (figure 2c). The length of the bond between Ce and O atoms from the carboxyl groups is 2.370(9)-2.839(11), while the Ce(IV)-O-

Figure 3. N$_2$ (a) and Ar (b) adsorption/desorption isotherms and pore size distributions recorded for compound 1 (a) and 2 (b), respectively.

V$_{\text{mic}}$ = 0.163 cm$^3$ g$^{-1}$

V$_{\text{mic}}$ = 0.037 cm$^3$ g$^{-1}$

30Ar uptake ml g$^{-1}$ (STP) N$_2$ uptake ml g$^{-1}$ (STP)

relative pressure (p/p$_0$)

pore width (nm)

V$_{\text{mic}}$ = 0.163 cm$^3$ g$^{-1}$

V$_{\text{mic}}$ = 0.037 cm$^3$ g$^{-1}$

relative pressure (p/p$_0$)

pore width (nm)
Ce(III) bond is equal to $2.514(13)$-$2.624(11)$ Å. The centre of the trinuclear cluster is sixfold node, while the ligand is 12-fold node (figure 2d).

3.2. Specific surface area and porosity

The surface area of compound 1 (equal to 308 m$^2$ g$^{-1}$) was similar to that of Th-TCPB-1, Th-TCPB-2 and Th-TCPB-3 compounds containing the same tetradeutate ligand and possessing surface area in the 200–400 m$^2$ g$^{-1}$ range.$^{18}$ The surface area of compound 2 was equal to 55 m$^2$ g$^{-1}$, which is much smaller than Ce-MOFs, such as Ce-CAU-24 [24]. The pores of compound 2 are so small that the less polar Ar was chosen. The structure was not destroyed by XRD and IR after activation (see electronic supplementary material, figures S1 and S2). We believe that the Ce(IV) trinuclear cluster affected the MOF pores (electronic supplementary material, figure S4). The micropore volumes of compounds 1 and 2 were equal to 0.163 and 0.037 cm$^3$ g$^{-1}$ (figure 3a,b), respectively. These values are consistent with the space occupied by solvent and crystalline water (contents of which were calculated from the TGA data described below performed by the NLDFT method) [25,26]. The pore sizes of compounds 1 and 2 were in the 7–13 Å and 0–5 Å ranges, respectively. Compound 2 has a small specific surface area and a large number of micropores, which results in the difference between its adsorption and desorption isotherms.

3.3. Thermal properties

TGA curves of compounds 1 and 2 showed water and solvent molecule removal below 160 and 170°C, respectively (figure 4), with the corresponding weight losses equal to 10.26% and 8.67%. In situ XRD patterns (electronic supplementary material, figure S6) showed that the characteristic peaks of compounds 1 and 2 disappeared at 400°C and 600°C, respectively. Combined with TGA analysis, structural collapses of compounds 1 and 2 were observed at 343.8°C and 513.3°C. Compound 1 structure could not withstand temperatures as high as the previously synthesized Th-based MOFs [18], potentially because of the acetic acid molecule presence. At the same time, compound 2 demonstrated excellent structural thermal stability, especially relative to other Ce-based MOFs, which was attributed to the presence of the trinuclear Ce cluster [24].
3.4. Luminescence properties

The colours of compounds 1 and 2 under visible light are light blue and white. However, compound 1 emitted intense blue light upon exposure to the UV light (figure 4).

Fluorescence spectra of compounds 1 and H4TCPE showed peaks with maxima at 468 and 434 nm, respectively, when exposed to the 365 nm UV light (figure 5). The QY of compound 1 (equal to 1.15%) was higher than that of the H4TCPE ligand (which was equal to 1.04%). The fluorescence spectrum of compound 1 red-shifted relative to the corresponding spectrum of the H4TCPE ligand (figure 6). Compound 1 is an AIE-type chromophore whose organic ligand provides luminescence. Since Th is bonded to the H4TCPE ligand and four acetic acid molecules, the electron cloud density in the ligand is changed, which translates into this slight red-shift [27]. Thorium still has f-layer electrons after losing the four outermost electrons. Compared with cerium, the outermost electrons of thorium are farther away from the nucleus and require less energy for electronic transition. The fast rotation of the phenyl rings and partial twisting of the C=C bond quench are prevented by Th in the rigid matrix, resulting in enhanced luminescence properties [28–30].

There is enough space in the crystal structure of compound 2 for the free rotation of the benzene ring to cause self-quenching effect, so the luminescence is extinguished. Similar behaviour is observed for Ce-CAU-24 [23].

4. Conclusion

In this work, we synthesized two new MOFs by a simple procedure and under mild conditions. Compound 1, which denoted Th₄(TCPE)₂(CH₃COO)₈, is a mono-nuclear MOF with space group C2/c.
Compound 2, denoted as Ce(IV)Ce(III)₂(u-OH₂)(TCPE)₂, is a trinuclear MOF cluster with space group C2/m. The atoms of Ce(IV) were partially reduced to Ce(III) in the reaction environment. The structure of compound 1 is stable up to 343.8°C. Its surface area and micropore volume are equal to 308 m² g⁻¹ and 0.163 cm³ g⁻¹, respectively. Compound 2 is stable up to 513.3°C and possesses surface area and micropore volume equal to 55 m² g⁻¹ and 0.037 cm³ g⁻¹, respectively. Compound 1 emits stronger pale green luminescence, originating from the ligand. Compound 2 did not exhibit any luminescing properties due to a self-quenching mechanism.

Data accessibility. Electronic supplementary material [31]: PXRD patterns, SEM micrographs, BET and pore size distribution data, XPS as well as CIF files. Accession Codes: CCDC (2 098 332–2 098 333) contains the supplementary crystallographic data for this paper.

Authors’ contributions. L.L.: conceptualization, data curation, formal analysis, investigation, methodology, project administration, visualization, writing—original draft and writing—review and editing; T.Y.: funding acquisition; Z.Q.: conceptualization, data curation, funding acquisition, methodology and project administration; X.W.: methodology; H.H.: methodology and project administration; G.Y.: resources; Y.Q.: formal analysis, funding acquisition and investigation.

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References

1. Taylor RJ, Boug S, Gatz JP, Modolo G. 2015 Development of anion/electrode separation processes for future nuclear fuel cycles in Europe. Nuclear Future 11, 38–43.

2. Moyer BA, Lunetta GJ, Mincher BJ. 2015 Minor anode separation in the reprocessing of spent nuclear fuels: recent advances in the United States. Reprocess. Recycling Spent Nuclear Fuel 12, 289–312. (doi:10.1061/AS878-1-78242-212-9.00011-3)

3. Pastorov KJ, Kemp RS, Jensen MP, Shaffer JC. 2021 Progress in uranium chemistry: driving advances in front-end nuclear fuel cycle forensics. Inorg. Chem. 60, 8347–8367. (doi:10.1021/acs.inorgchem.0c03390)

4. Lv K, Fichter S, Gu M, Marz J, Schmidt M. 2021 An updated status and trends in actinide-metal-organic frameworks (An-MOFs): from synthesis to application. Coord. Chem. Rev. 446, 214011. (doi:10.1016/j.ccr.2021.214011)

5. Andrew G, Budantseva N, Fedoseev A, Moisy P. 2011 Polymeric structure of oxalato-bridged complexes of tetravalent actinides Th, U, Np and Pu. Inorg. Chem. 50, 11 481–11 486. (doi:10.1021/ic103113g)

6. Hoskic I, Frisic T. 2019 Geometric approaches in the design and synthesis of metal-organic frameworks. Phil. Trans. A Math. Phys. Eng. Sci. 377, 20180221. (doi:10.1098/ rsta.2018.0221)

7. Hu Z et al. 2022 Facile synthesis of magnesium-based metal-organic framework with tailored nanostructure for effective volatile organic compounds adsorption. R. Soc. Open Sci. 9, 211544. (doi:10.1098/rsos.211544)

8. Mueller U, Schubert M, Teich F, Puettet H, Schiefer-Amdt K, Pastré J. 2006 Metal–organic frameworks-prospective industrial applications. J. Mater. Chem. 16, 626–636. (doi:10.1039/b511962f)

9. Li J, Wang X, Zhao G, Chen C, Chai Z, Alsasid A, Hayat T, Wang X. 2018 Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. Chem. Soc. Rev. 47, 2322–2356. (doi:10.1039/c7cs00543a)

10. Kim JY, Norquist AJ, O’Hare D. 2003 [(Th4F4)(NC6H4(OH))(H2O)](NO3): an actinide-organic open framework. J. Am. Chem. Soc. 125, 12 688–12 689. (doi:10.1021/ja036832p)

11. OK KM, Sung J, Hu G, Jacobs RJM, O’Hare D. 2008 TOF-2: a large 10 channel thorium organic framework. J. Am. Chem. Soc. 130, 3762–3763. (doi:10.1021/ja073095q)

12. OK KM, O’Hare D. 2008 Synthesis, structure, and characterization of a new thorium-organic framework material, ThF₄[(C₆H₄(OH))(CH₂CO₂)₂](NO₃): Dubban. Trans. 41, 5560–5562. (doi:10.1039/b802629a)

13. Falsace C, Charles JS, Volkinger C, Lesueur T. 2011 Thorium terephthalates coordination polymers synthesized in solvothermal DMF/H₂O system. Inorg. Chem. 50, 2235–2242. (doi:10.1021/ic102725y)

14. Li JZ et al. 2020 Modified synthesis and isoreticular expansion of Th-MOFs with record high pore volume and surface area for iodine adsorption. Chem. Commun. 56, 6715–6718. (doi:10.1039/d0cc02844j)

15. Li JZ et al. 2020 Ultrastable thorium metal-organic frameworks for efficient iodine adsorption. Inorg. Chem. 59, 4423–4442. (doi:10.1021/acs.inorgchem.9b03660)

16. Islamoglu T, Ray D, Li P, Majewski MB, Akpinar I, Zhang X, Cramer CJ, Gagliardi L, Farha OK, Hixon AE. 2020 Advancement of actinide metal-organic framework chemistry via synthesis of Pu-UiO-66. J. Am. Chem. Soc. 142, 9363–9371. (doi:10.1021/acs.jacsat.0c03185)

17. Nelson AO, Bray TH, Stanley FA, Albrecht-Schmitt TE. 2010 Comparisons of Pu(M) and Ce(M) diphosphonates. Inorg. Chem. 49, 3337–3342. (doi:10.1021/ic100184q)

18. Henriksen KE, Jeppesen J, Dam-Johansen K, Li P, Majewski MB, Akpinar I, Zhang X, Cramer CJ, Gagliardi L, Farha OK, Hixon AE. 2020 Development of actinide metal-organic framework chemistry via synthesis of Pu-UiO-66. J. Am. Chem. Soc. 142, 9363–9371. (doi:10.1021/acs.jacsat.0c03185)

19. Puschmann H. 2010 OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. 43, 339–341. (doi:10.1107/S0021889809066236)

20. Akpinar I, Zhang X, Cramer CJ, Gagliardi L, Farha OK, Hixon AE. 2020 Advancement of actinide metal-organic framework chemistry via synthesis of Pu-UiO-66. J. Am. Chem. Soc. 142, 9363–9371. (doi:10.1021/acs.jacsat.0c03185)

21. Nelson AO, Bray TH, Stanley FA, Albrecht-Schmitt TE. 2009 Periodic trends in actinide phosphonates: divergence and convergence between thorium, uranium, neptunium and plutonium systems. Inorg. Chem. 48, 4530–4535. (doi:10.1021/ic900484w)

22. Dokmanovic O, Boursin LI, Gildso RI, Howard J, Puschmann H. 2010 OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. 43, 339–341. (doi:10.1107/S0021889809066236)

24. Slighter GM. 2015 SHELXT - integrated space-group and crystal-structure determination. Acta Crystallogr. A Found Adv. 71, 3–8. (doi:10.1107/ S0001730915005730)

25. Lammet M, Reinou M, Murray CA, Wharmaby MT, Terraschie H, Stock N. 2016 Synthesis and structure of Zr(IV)- and Ce(IV)-based CAU-24 with 1,2,4,5-tetrakis(4-carboxyphenyl)benzene.
25. Lyu J, Zhang X, Li P, Wang X, Buru CT, Bai P, Guo X, Farha OK. 2019 Exploring the role of hexanuclear clusters as Lewis acidic sites in isostructural metal–organic frameworks. Chem. Mater. 31, 4166–4172. (doi:10.1021/acs.chemmater.9b00960)

26. Madden DG et al. 2017 Flue-gas and direct-air capture of CO₂ by porous metal-organic materials. Phil. Trans. A Math. Phys. Eng. Sci. 375, 20160025. (doi:10.1098/rsta.2016.0025)

27. Ren YW, Liang JX, Lu JX, Cai BW, Shi DB, Qi CR, Jiang HF, Chen J, Zheng D. 2011 A novel asymmetric di-Ni(II) system as a highly efficient functional model for phosphodiesterase: synthesis, structures, physicochemical properties and catalytic kinetics. Dalton. Trans. 38, 4369–4376. (doi:10.1039/C0DT01194K)

28. Miller SE, Teplensky MH, Moghadam PZ, Fairen-Jimenez D. 2016 Metal-organic frameworks as biosensors for luminescence-based detection and imaging. Interface Focus 6, 20160027. (doi:10.1098/rsfs.2016.0027)

29. Xie Z, Li X, Li R, Lu S, Zheng W, Tu D, Feng Y, Chen X. 2020 In situ confined growth of ultrasmall perovskite quantum dots in metal-organic frameworks and their quantum confinement effect. Nanoscale 12, 17113–17120. (doi:10.1039/d0nr04741d)

30. Shustova NB, Mccarthy BD, Dinca M. 2011 Turn-on fluorescence in tetraphenylethylene-based metal-organic frameworks: an alternative to aggregation-induced emission. J. Am. Chem. Soc. 133, 20 126–20 129. (doi:10.1021/ja209327q)

31. Li L, Yu T, Qian Z, Wu X, He H, Ye G, Qiao Y. 2022 Synthesis and structure of metal-TCPE (metal=Th, Ce) metal-organic frameworks based on 1,2,4,5-tetakis(4-carboxyphenyl) ethylene. Figshare. (doi:10.6084/m9.figshare.c.6166877)