

## Enclosure 1b. Category 1 Application form 2015 – English version

APPLICATIONS ARE PREFERABLY DRAWN UP IN ENGLISH. AN ENGLISH TRANSLATION HAS TO BE ENCLOSED WITH APPLICATIONS SUBMITTED IN DUTCH.

The application form is available in Dutch on the website <https://vscentrum.be/>.

Title of the application:

Unraveling dehydroxylation pathways on UiO-66 type systems with metadynamics

Name and first name of the applicant:

Hajek Julianna

Institution:

Ghent University

Research group / department:

EA17, Center for Molecular Modeling

Title / position:

PhD fellow

email address:

julianna.hajek@ugent.be

Total computing time that is needed, in node days:

3304

Total disk storage that is applied for (in GiB):

498

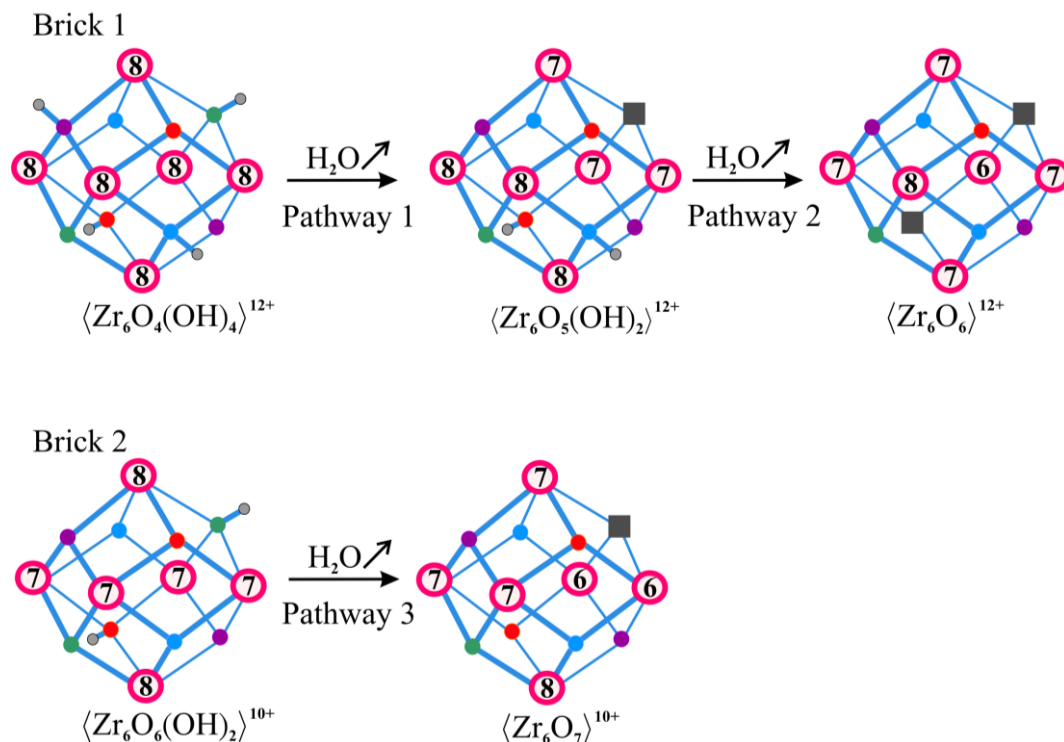
1. Title of the research project (with IWETO or FRIS link if available) within the framework of which computing time is applied for:

Combined experimental and computational study of electronically modulated metal-organic framework (MOF) catalysts, FWO project 3G048612 between COK (Prof. Dirk De Vos) and CMM (Prof. Veronique Van Speybroeck)

Increasing the catalytic activity of metal-organic frameworks by tailor-made modifications (FWO postdoc project Matthias Vandichel)

2. Describe your research project in short. Explicitly mention the scientific questions that you are planning to address and the overall scientific goals of the project. (max. 1 A4 in Arial 12):

In this project, we want to do the next big step based on our two previous TIER1-projects where we computed minimum energy pathways for a variety of dehydroxylation reactions using climbing image Nudged-Elastic Band (cNEB) simulations and we further optimized the local minima and transition states along the obtained minimum energy pathways. Subsequently applying a **dynamical approach** is essential as we want to describe the UiO-66 metal organic framework flexibility during the dehydroxylation process.



**Figure 1:** Zr-brick 1 with formula  $\langle \text{Zr}_6\text{O}_4(\text{OH})_4(\text{RCOO})_{12} \rangle$  is intact with no missing linker, while brick 2  $\langle \text{Zr}_6\text{O}_6(\text{OH})_2(\text{RCOO})_{10} \rangle$  has one missing linker. Dehydroxylation processes can start from brick 1 and from brick 2.

We will perform large-scale ab initio molecular dynamics (AIMD) free energy simulations in two steps. Firstly, molecular dynamics (MD) run will be performed to fully converge framework parameters. Secondly, metadynamics (MTD) simulations will be done to determine a free energy surface of the studied reaction (as an example: Figure 1). MTD technique determines a large fraction of the energy landscape in a configuration space of collective variables. Although this technique is routinely applied for biosystems, application of metadynamics on reactions taking place in the pores of nanoporous materials is not yet done frequently as its use requires a lot of computational power.

Dynamical approach allows as to properly accounting for the temperature effect which is necessary if we want to compute these systems for their activity, meaning that we will have to include the full framework and account for its flexibility. Reaction free energy barriers will be compared with previously obtained free energy barriers using static approach.

3. Provide an abstract (10 lines) for scientific communication on the website in layman's terms. See also item 13 of this application form.

The catalytic activity of metal organic frameworks has not yet been exploited at large scale in industry, but is undoubtedly recognized by the scientific community as having a large potential for valorization. Thermal activation during a post-synthetic process and the dehydroxylation of the inorganic brick has drawn a lot of attention. Structure rearrangement precedes the formation of a released hydroxyl group that then undergoes a protonation with another hydroxyl group to split of water. Advanced computational techniques such as metadynamics are employed to assess the energetics of various possible active sites, to identify likely transition states and intermediates of the reaction as well as to characterize the active sites at high temperature.

4. Financing institution or channel, financing the research project in full or in part (FWO, BOF, IWT, EU, ...): Please attach the confirmation letter as enclosure (see instructions in enclosure 4 "EasyChair proposals submission procedure").

FWO project 3G048612, confirmation letter can be found at the end of the file.

Personal FWO postdoc fellowship of Matthias Vandichel, confirmation letter can be found at the end of the file.

5. Name and email address of the promoter(s) of the research project:

Prof. Dr. ir. Veronique Van Speybroeck

veronique.vanspeybroeck@ugent.be

6. Billing address to which the payment invoice will be sent to:

Veronique Van Speybroeck

Center for Molecular Modeling CMM, Ghent University

Technologiepark 903, 9052 Zwijnaarde, Belgium

7. Persons mandated by the Applicant to compute on the Tier1 within the framework of the present project: Please provide for every person:

- name and first name
- institution
- research group / department
- title / position
- experience of using HPC resources in the past (Tier0/Tier1/Tier2 infrastructure in Belgium and abroad)

Julianna Hajek

Ghent University

EA17, Center for Molecular Modeling

PhD fellow

vsc40880

Experience with TIER1 and TIER2 infrastructure of UGent

Matthias Vandichel

Ghent University

EA17, Center for Molecular Modeling

FWO-postdoc

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Experience with TIER1 and TIER2 infrastructure of UGent

Veronique Van Speybroeck  
Ghent University  
EA17, Center for Molecular Modeling  
Professor  
vsc40021  
Experience with TIER2 infrastructure of UGent

8. Explain why this project needs to run on a Tier1 system, why the machine you have requested is suitable for the project and how the use of the system will enable the science proposed (max. ½ A4 in Arial 12).

The system size (**210 up to 228 atoms**) and time that is required for the calculations to describe the reactions are a strong justification for the need of TIER1. Furthermore, the application of advanced molecular dynamics simulations in the field of heterogeneous catalysis and nanoporous materials is emerging. The Center for Molecular Modeling was one of the first research groups to succeed in applying metadynamics for the prediction of kinetics of zeolite-catalyzed reactions (V. Van Speybroeck et al., First principle chemical kinetics in zeolites: the methanol-to-olefin process as a case study, Chem Soc Rev, 43 (2014) 7326-7357; Doi 10.1039/C4cs00146j). However, to the best of our knowledge no metadynamics simulations have been applied in MOFs.

9. Justify the number of node days requested. This should include information such as: number and nature of computing tasks, software used, and the sequence in which they will be performed.

Indicate for each typical computing task the required resources:

- wall clock time (note that 3 days is the maximal wall clock time for any job; checkpointing should be used for longer run times)
- memory (maximum 64 GiB/node)
- number of nodes
- number of CPU cores
- disk space (estimated volume in GiB and the total number of files); make a clear distinction between usage of Tier2 DATA/HOME partitions and the Tier1 SCRATCH partition
- number of tasks, and an indication of how many such tasks would be submitted concurrently.

This information should take the form of a table (an example is provided as Table 2 in the appendix). Provide additional descriptions of the computing tasks and comments as needed. Resource estimates should be preferably based on the results of actual calculations on Tier1 (via, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, ...). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results and explain how you have calculated/rescaled the wall clock times, number of cores, etc.

(max. 1 A4 Arial 12).

AIMD simulations will be performed with the CP2K software package, using MPI. Two types of AIMD simulations will be done for each system – i.e. combination of material with amount of defects. Our previous TIER1-project concerned 15 water removal trajectories in periodic unit cells. However, within this project we will focus on **9 (system size: 210 up to 228 atoms)** of them:

- **Ideal structure (no terephthalate defect)**  
 $\langle \text{Zr}_6\text{O}_4(\text{OH})_4(\text{OCCCC}_4\text{H}_4\text{CCOO})_6 \rangle_2$   
with **4 water removals**
- **defect structures (1 terephthalate defect)**  
 $\langle \text{Zr}_6\text{O}_4(\text{OH})_4(\text{OCCCC}_4\text{H}_4\text{CCOO})_6 \rangle$   $\langle \text{Zr}_6\text{O}_6(\text{OH})_2(\text{OCCCC}_4\text{H}_4\text{CCOO})_5 \rangle$   
with **3 water removals** and
- $\langle \text{Zr}_6\text{O}_5(\text{OH})_3(\text{OCCCC}_4\text{H}_4\text{CCOO})_{11/2} \rangle$   $\langle \text{Zr}_6\text{O}_5(\text{OH})_3(\text{OCCCC}_4\text{H}_4\text{CCOO})_{11/2} \rangle$   
with **2 water removals**.

The first part of the job consists of **9** equilibration MD runs in the NPT ensemble at high temperature, with duration of 50 ps. This is required to obtain fully converged framework parameters for further simulations. Each of these simulations requires **12 node days**. These estimates were made based on results from our previous TIER1 project.

**On each system** (9), a MTD simulation will be performed. Typical simulation times amount to 100 – 200 ps, depending on the height of the free energy barrier of the studied reaction. Moreover, the complexity of the systems requires the use of two sets of collective variables (CV). In a first instance we have to perform one CV (1D) in order to properly describe a rare event and distinguish between initial, final and intermediate states. After a properly described 1D CV the simulation will be followed by 2D CV, where we describe

all the slow events that are relevant for water removal. To identify the right collective variables **additional 8 MTD** (1D as well as 2D) simulations are required. The simulations will cost **24 or 164 node days** for 1D and 2D CV, respectively. With this information, we can estimate the total node days needed (**Table 1**).

**Table 1:** Estimated core and node days for this project (1 node =16 cores)

Computational task	Node day calculation				# CPU cores per task	Memory usage (GiB) / node per task	OpenMP / MPI / hybrid / vSMP	Storage volume estimate	
	# of such tasks	Wall clock time (days) per task	# Tier1 nodes per task	# node days per task				Tier2 DATA/HOME volume (GiB) + number of files	Tier1 SCRATCH volume (GiB) + number of files
MD	9	6	2	= 108	1728	10	Intranode OpenMP/ Internode MPI	4 GB x 9	4 GB x 9
MTD 1D	17	12	2	= 408	6528	12	Intranode OpenMP/ Internode MPI	6 GB x 17	6 GB x 17
MTD 2D	17	41	4	= 2788	44608	16	Intranode OpenMP/ Internode MPI	6 GB x 60	6 GB x 60
				<b>3304</b>		<b>38 GB</b>		<b>498 GB</b>	<b>498 GB</b>

10. Describe the software required to perform the computing task(s).  
Please clearly provide the following per item in this regard:

- a reference to the software's web page
- the software license system (open source, GPL, etc.)
- if there is no free academic use of the software, state which license makes the installation and the use valid on the Tier1 by the Applicant (+ add a copy of the signed license)
- if need be, which license server will be used (name + IP address)
- whether the software is already available on the Tier1 (see <https://vscentrum.be/nl/Tier1-rekenen>) and, if this is not the case, compilation and installation instructions (possibly with reference to existing Tier2 installation)

Provide the results of scaling tests that were conducted with this software, preferably on Tier1 (using, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, ...). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results.

Provide both a table and scaling plot such as table 1 and plot 1 in the appendix (max. 2 A4 in Arial 12).

The AIMD simulations will be done using the following software packages:

CP2K software package:

<http://www.cp2k.org/>

CP2K is freely available under the GPL license. The software is already available on the TIER1 infrastructure.

In a previous TIER1-project, a scaling MD test of 50 ps and 100 steps on the system under investigation with 228 atoms has been performed.

# nodes	# cores	absolute timing (s)	speedup	# cores x timing
1	16	2211	1.000	35376
2	32	1377	1.605	44064

4	64	993	2.227	63552
8	128	778	2.841	99584

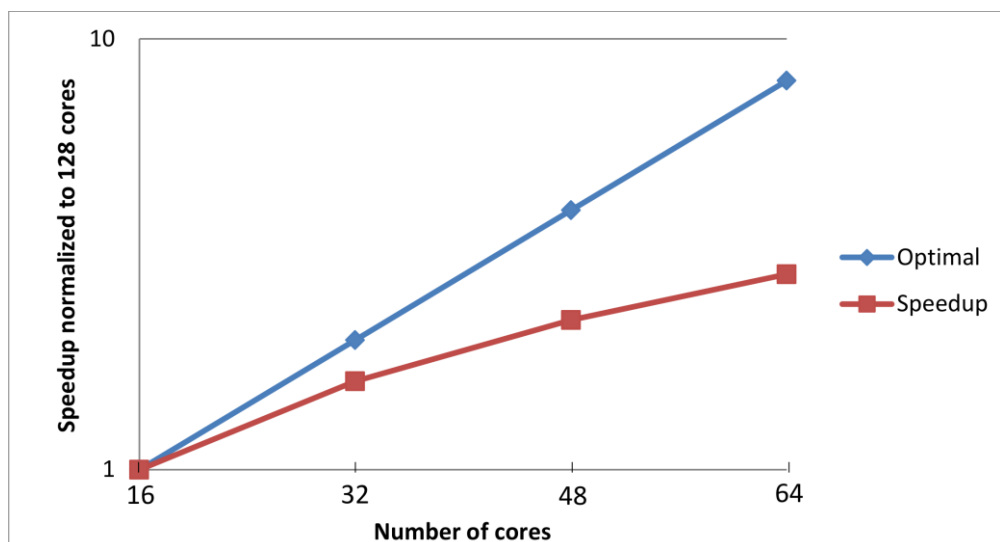


Figure 2: Scaling tests performed on TIER1 for the current system.

Figure 2 shows the current scaling of CP2K on TIER1 for the system of interest. As such, optimal scaling is achieved up to 2 nodes. However, previous scaling test showed a much better performance (cf. Figure 3). The discrepancy between the two scaling test is due to known issues which resulted from a recent systems update. These parallelization problems are not inherent to CP2K. The HPC team is aware of these issues and is currently hard at work trying to resolve them.

We have taken this into account in our workflow, which takes 3 steps which have to be run through in sequence. For the reason stated above, we have decided to run the first 2 steps (MD and MTD 1D) using two nodes per task. By the time these steps are completed, the issues described above should be resolved, and as such our third step (MTD 2D) will be run at 4 nodes per task.

Jobs which exceed the 3 day walltime limit will be run in sequential steps.

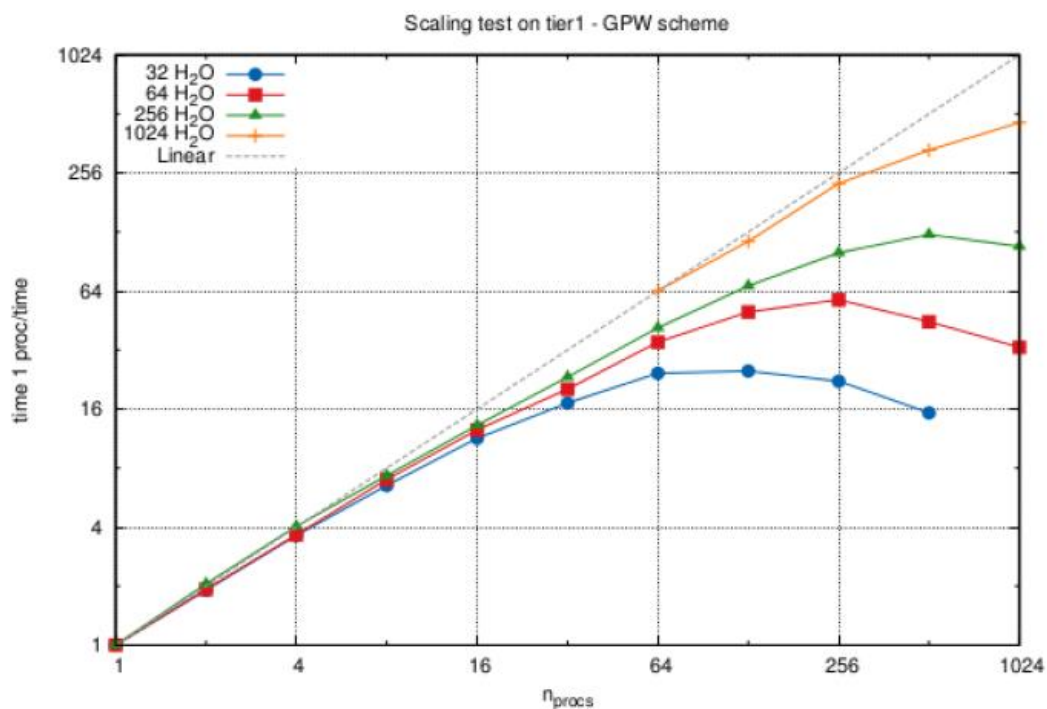


Figure 3: Scaling of the GPW code of CP2K. On the x-axis, the number of cores is plotted in a logarithmic scale. On the y-axis, the total time is given in units of time needed for the one core job

11. Describe how you will manage the resources requested in the period during which the task is to be performed. What usage pattern do you anticipate (similar usage on monthly basis, bursts, ...)?

The calculations are intended to be performed in the timeslot: September 2015 – February 2016 with the same monthly usage.

12. List the granted computing time allocations to the promoter(s) of this research project, on the Flemish Tier1 system, as well as other Tier1 and Tier0 systems. Also, describe the scientific output obtained within the framework of computing time that was granted during the past two years on the Flemish Tier1 or on other Tier1 or Tier0 supercomputers. DOI links are sufficient.

During the previous two Tier1-projects and the pilot usage, several aspects of UiO-66 type MOFs have been investigated:

Structural transformations during dehydroxylation reactions of UiO-66 type metal-organic frameworks; an extension with normal mode analysis Node days: 2726

Structural transformations during dehydroxylation reactions of UiO-66 type metal-organic frameworks Node days: 4720

Modeling aldol condensations in metal-organic frameworks with hybrid functional calculations Node days: 2304

Unraveling reaction pathways on UiO-66 type systems with metadynamics Node days: 4432

Articles:

<http://dx.doi.org/10.1039/C4RA16800C>

<http://dx.doi.org/10.1039/C4CE01672F>

1. Mechanistic studies of aldol condensations in UiO-66 and UiO-66-NH<sub>2</sub> metal organic frameworks  
status: submitted

In this work, hybrid functional calculations on periodic models have been performed (1) to truthfully compare the periodic and cluster calculations; (2) to more accurately describe environmental effects. Due to the size of the systems and the amount of calculations that need to be performed, it is clear that these calculations go beyond what can comfortably be done (within a reasonable timeframe) on a TIER2 cluster. All calculations have finished; the obtained free energy profiles for both periodic and cluster computation compare well, and the stabilization effect the environment is more visible in some reaction steps. The paper will be submitted in October 2014. As not all computational time was granted in the previous Tier1 project, we decided to compute only a part of the intended calculations. {~ 1500 node days used}

2. Unravelling reaction pathways systems with metadynamics  
status: in preparation

In our first TIER1 project, we successfully identified the right collective variables to model the citronellal cyclization within the metadynamics simulations on different UiO-67-X materials (NPT ensemble). We obtained good estimates for the reaction barriers, accounting for both framework and linker flexibility. This type of computations goes beyond the state of the art. We are finalizing the data-mining and writing a research paper and need to perform some NVT simulations to have a more solid benchmark for the obtained results from the NPT simulations. {~ 2000 node days used}

13. Are the applicants of this application bound by a confidentiality agreement? If so, the title and the abstract of this application will not be published on the website of the Hercules Foundation / Flemish Supercomputer Center.

no

Should you have any questions or encounter any difficulties during the electronic submission of an Application, please contact by e-mail:
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## Appendix: Example tables and plots

Table 1

# nodes	# cores	absolute timing (s)	speedup	# cores x timing
16	256	189.6	1.0000	
32	512	99.0	1.9154	
64	1024	55.6	3.4088	
128	2048	30.8	6.1376	

Plot 1

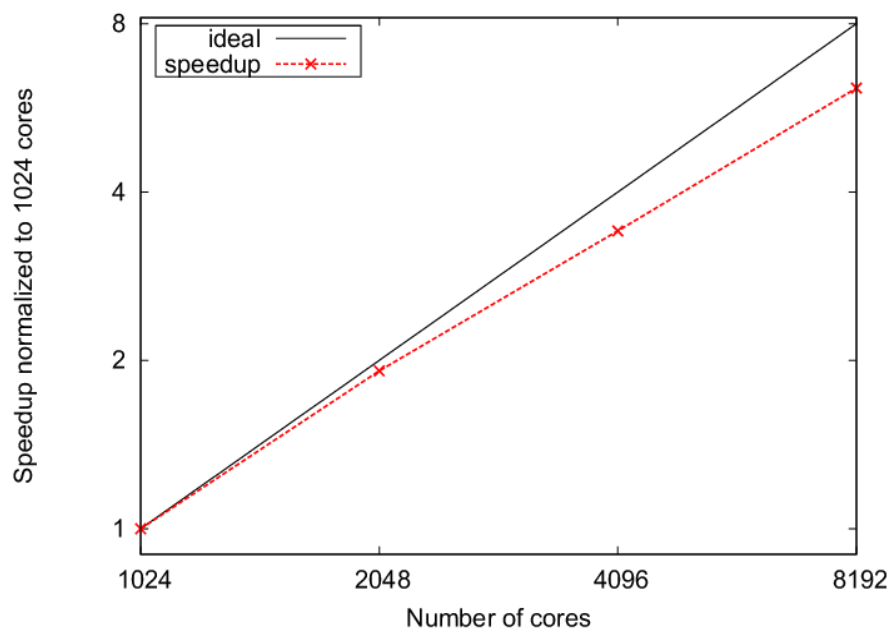


Table 2

	Node day calculation							Storage volume estimate	
Computational task	# of such tasks	Wall clock time (days) per task	# Tier1 nodes per task	# node days per task	# CPU cores per task	Memory usage (GiB) / node per task	OpenMP / MPI / hybrid / vSMP	Tier2 DATA/HOME volume (GiB) + number of files	Tier1 SCRATCH volume (GiB) + number of files
Task1	A	B	C	= A x B x C					
Task2	A	B	C	= A x B x C					



Fonds Wetenschappelijk Onderzoek  
Research Foundation – Flanders

Prof. Dirk De Vos  
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16 november 2011

**Betreft: Toekenning project G.0486.12**

Geachte professor,

De Raad van Bestuur van het FWO heeft uw bovenvermelde aanvraag voor een onderzoeksproject goedgekeurd. De bijgevoegde overeenkomst werd opgesteld volgens het reglement van de Onderzoeksprojecten van het FWO.

Graag wil ik u hierbij feliciteren met de toekenning van het door u aangevraagde onderzoeksproject.

Mag ik u vragen alle exemplaren te ondertekenen, één kopie voor u te bewaren en mij het origineel samen met de overige kopie(ën) per kerende post terug te sturen.

De toegekende toelage is beschikbaar voor zover de financierende overheden hiervoor de nodige middelen vrijmaken. Onderzoek waarvoor medisch ethisch advies noodzakelijk is, kan pas starten als de onthaalinstelling hierover positief advies uitbrengt.

Slechts uitzonderlijk kan, met akkoord van het FWO, de oorspronkelijke bestemming van dit krediet worden gewijzigd.

Tenslotte vraag ik u met aandrang om op uw publicaties steeds te vermelden dat ze tot stand kwamen met de financiële steun van het FWO. Vacatures gekoppeld aan onderzoeksprojecten kunnen bekend worden gemaakt via de FWO-website. U kan het vacaturebericht aan het FWO bezorgen via [communicatie@fwo.be](mailto:communicatie@fwo.be). Aanvullend kan het nuttig zijn om dergelijke berichten ook te publiceren via de Euraxess website van de Europese Commissie: <http://ec.europa.eu/euraxess/>.

./..

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Fonds Wetenschappelijk Onderzoek  
Research Foundation – Flanders

../..

Voor bijkomende inlichtingen kan u steeds terecht bij uw dossierbeheerder. De e-mailadressen zijn voor de Biologische Wetenschappen: [bio@fwo.be](mailto:bio@fwo.be), voor de Cultuurwetenschappen: [cult@fwo.be](mailto:cult@fwo.be), voor de Gedrags- en Maatschappijwetenschappen: [gm@fwo.be](mailto:gm@fwo.be), voor Wetenschap en Technologie: [wt@fwo.be](mailto:wt@fwo.be), voor de Medische Wetenschappen: [med@fwo.be](mailto:med@fwo.be) en voor het Interdisciplinair onderzoek: [interdisciplinair@fwo.be](mailto:interdisciplinair@fwo.be).

Hoogachtend,

dr. ir. Elisabeth Monard  
secretaris-generaal

Bijlagen: 2

Kopie: Prof. Veronique Van Speybroeck

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Research Foundation – Flanders

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26 juni 2013

**Betreft: Toekenning Postdoctoraal Onderzoeker 2013-2016**

Geachte heer,

De Raad van Bestuur heeft u vandaag aangesteld als Postdoctoraal Onderzoeker met ingang van 1 oktober 2013 tot en met 30 september 2016. Het reglement vindt u als bijlage.

Graag wil ik u feliciteren met deze aanstelling als Postdoctoraal Onderzoeker van het FWO.

In het kader van de verdere administratieve opvolging van uw aanstelling zal het FWO u nog vóór 19 juli 2013 een arbeidsovereenkomst bezorgen.

Voor bijkomende inlichtingen kan u steeds terecht bij de dossierbeheerder van uw wetenschapsgebied op bovenvermeld e-mailadres.

Tenslotte vraag ik u met aandrang om op uw publicaties steeds uw titel Postdoctoraal Onderzoeker van het FWO te vermelden.

Ik wens u veel succes toe in uw verdere onderzoekloopbaan.

Hoogachtend,

A handwritten signature in blue ink, appearing to read 'E. Monard', written over a blue ink scribble.

dr.ir. Elisabeth Monard  
secretaris-generaal

Bijlage: 1

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