

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: In situ catalytic studies on Ir(I) and Ir(III) based covalent triazine frameworks	Experiment number: 26-01-1100
Beamline: BM26A	Date of experiment: from: 12/4/2017 to: 16/4/2017	Date of report:
Shifts: 12	Local contact(s): Dipanjan Banerjee	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Karen Leus¹, Pieter Tack², Laszlo Vincze² ¹ Department of Inorganic and Physical Chemistry, Ghent University ² Department of Analytical Chemistry, Ghent University		

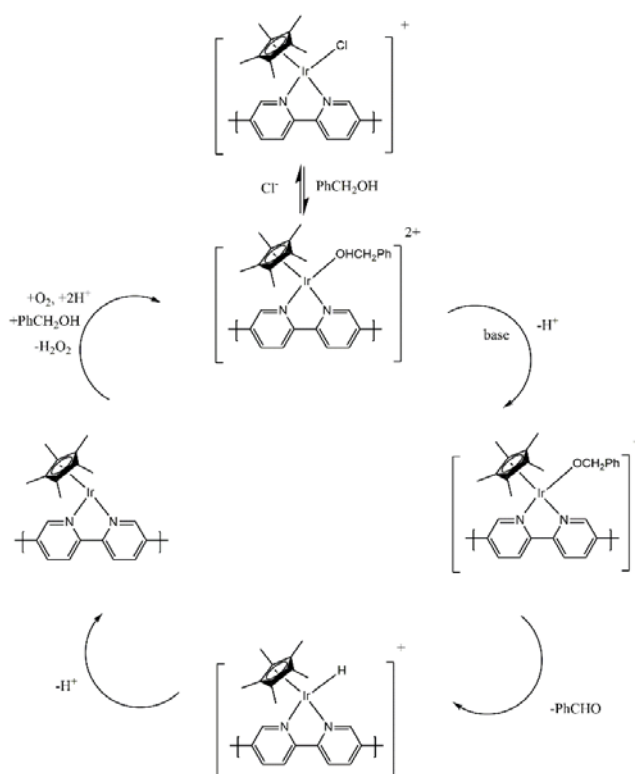
Report:

In our previous work, we presented a new catalytic system for the selective oxidation of benzyl alcohol to benzaldehyde using a heterogeneous iridium-based catalyst. For this purpose, a covalent triazine framework based on bipyridine building blocks (bipy-CTF) offering enhanced porosity, functionality and stability was applied as an ideal catalyst support. EXAFS analysis was performed to determine at which site the Ir complex binds to the bipy-CTF material. Two potential sites can be differentiated: a) complexation with two N atoms of a singular bipyridine moiety and b) complexation with a N atom of the bipyridine functional group and a N of the triazine component. It was found that for the complex before and after catalysis, the Ir^{III}Cp*Cl@bipy-CTF is characterized by an Ir-N bond distances of 2.11 Å (Table 1). This experimentally determined bond distance is in agreement with the theoretically calculated distances of the Ir complexation to the bipyridine moiety (2.131 Å), where the bonding to both a bipyridine and triazine N is sterically hindered. As such, both methods clearly prove that the Ir complex is bound onto the N atoms of the bipyridine sites.

The catalytic mechanism of the heterogeneous Ir^{III}Cp*Cl@bipy-CTF catalyst was examined by employing In Situ XANES. Based on the obtained results and previous reports on homogeneous Ir-based catalysts, a plausible mechanistic pathway for the present aerobic oxidation reaction, involving an Ir^I/Ir^{III} cycle, is depicted in Scheme 1. As the catalytic reaction proceeds, a shift in the local Ir structure was perceived from the Ir^{III}@bipy-CTF state to an Ir^I@bipy-CTF state (Figure 1). This transition in Ir oxidation state can be understood from Scheme 1 as during the in situ studies a limiting amount of benzyl alcohol was present, which is necessary to regenerate the Ir^I compound back to the catalytically active Ir^{III} compound. When all benzyl alcohol is gone from the reaction cell, the Ir complex will be stuck in an Ir^I state. It was observed that this state was immediately regenerated to Ir^{III} after additional addition of benzyl alcohol, which is in line with the cyclical nature of the reaction scheme.

Table 1. EXAFS fit results of the bipy-CTF and Ir^{III}Cp*Cl@bipy-CTF materials before and after catalysis displaying the amount of neighbouring atoms (N), bond distance (R), Debye-Waller factor (DW) and E₀. The amplitude reduction factor S₀² was set to 0.9. DW and N were set as fixed parameters.

		Before	After
N	Ir-N	2	2
	Ir-C	5	5
	Ir-Cl	1	1
R (Å)	Ir-N	2.114	2.1114
	Ir-C	2.2619	2.1249
	Ir-Cl	2.1604	2.0871
DW	Ir-N	4.31E-03	5.27E-03
	Ir-C	4.31E-03	5.27E-03
	Ir-Cl	4.31E-03	5.27E-03
E ₀ (eV)	Ir-N	0.69795	3.3734
	Ir-C	15.674	2.9428
	Ir-Cl	-10.466	6.2874



Scheme 1. Proposed mechanism for Ir^{III}Cp*Cl@bipy-CTF catalyzed the aerobic oxidation of benzyl alcohol.

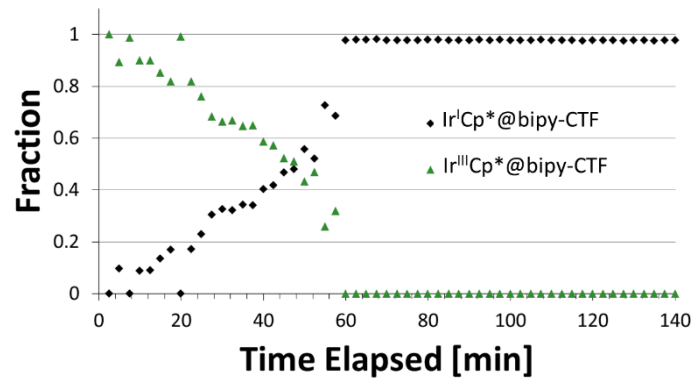


Figure 1. XANES linear combination fit results of the in-situ catalytic run. A clear transition of an Ir^{III} to Ir^I state as a function of reaction time is observed.

