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BL2D-SMC, the supramolecular crystallography beamline at the Pohang Light Source II, Korea

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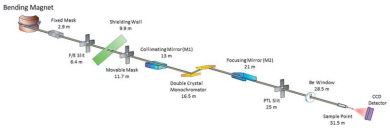
BL2D-SMC at the Pohang Light Source II is a supramolecular crystallography beamline based on a bending magnet. The beamline delivers high-flux tunable X-rays with energies from 8.3 to 20.7 keV and a 100 µm (horizontal) × 85 µm (vertical) full width at half-maximum focal spot. Experiments involving variable temperature, photo-excitation and gas sorption are supported by ancillary equipment and software in the beamline. The design of the beamline, its role and the main components are described.

1. Introduction

X-ray crystallography is a powerful technique for determining atomic arrangement in crystalline solids, whereby X-rays are focused on and diffracted by a sample (Bragg & Bragg, 1913). The method takes advantage of the intra- and inter-atomic spacing of most crystalline solids by exploiting the angström resolution of X-ray wavelengths (10^{-10} m) (Hammond, 2009; Bennett, 2010). In the single-crystal X-ray diffraction technique, the three-dimensional spatial relationships of the diffracted rays are so important in the determination of the diffraction symmetry and resolving intensity data because the single crystals consist of a well ordered arrangement of atoms or molecules that form a crystal lattice compared with powder samples (Chung & Smith, 2000). Thus, single-crystal X-ray diffraction not only determines the atomic positions, and the corresponding bond distances and angles within materials but also the correlation between structural features and physical or chemical properties (Steed & Atwood, 2009; Zhang *et al.*, 2014). The supramolecular crystallography beamline (BL2D-SMC) at the Pohang Light Source II (PLS-II) is a high-flux tunable-wavelength facility for the study of organic or inorganic materials by single-crystal diffraction. The beamline supports various techniques for the structural analysis of crystalline materials and allows the measurement of structural changes caused by the influence of external stimuli, *e.g.* variable temperature, diverse pressure, photo-excitation and gas sorption. The beamline is located at the 2D bending magnet port in the 3 GeV storage ring of the Pohang Light Source II. Two mirrors (one collimating and one focusing) and a double-crystal monochromator (DCM) deliver 6.2 × 10^{11} photons each second to a 100 µm (horizontal) × 85 µm (vertical) full width at half-maximum focal point in the end-station. A water-cooled DCM is designed to select energies between 8.3 keV and 20.7 keV (see Table 1) and the energy or wavelength used in the system can be changed using *BL2D-SMDC* software. The end-station is equipped with a Cryojet 5, photoreactors (laser/UV) and customized gas sorption apparatus.



In 2012, the Pohang Accelerator Laboratory (PAL) upgraded PLS to PLS-II and increased the electron energy in the storage ring from 2.5 GeV to 3.0 GeV (Shin *et al.*, 2013). PLS-II currently operates at 3.0 GeV with a stored current of 400 mA in top-up mode (Hwang *et al.*, 2014). During this upgrade, the two-dimensional supramolecular crystallography (2D-SMC) beamline at PLS-II was constructed for single-crystal X-ray diffraction experiments, and has been opened to domestic and international users since March 2012 (http://pal.postech.ac.kr/paleng/bl/2D/). In this article, we describe the main optical components and equipment in the 2D-SMC beamline.

2. Beamline overview

The 2D-SMC beamline, with a bending magnet for hard X-ray sources, is a highly efficient, high-performance beamline suitable for new crystallographic experiments such as photo-reaction, gas sorption and the investigation of high dimension or large unit-cell crystals. The 2D-SMC beamline includes a front-end, optics hutch, photon transfer line (PTL) and an end-station. The main optical components of the 2D-SMC beamline are two mirrors for vertical collimation and horizontal focusing, and a Si(111) DCM. The optical layout and specification of the 2D-SMC beamline are shown in Fig. 1 and Table 1, respectively.

As shown in Fig. 1, the X-ray beam passes through the fixed mask, front-end slit, movable mask, collimating mirror, DCM, focusing mirror, PTL slit and Be window, and is focused on the sample. In this section, we describe the main optical components: the collimating mirror (M1), the DCM and the focusing mirror (M2).

The first optical component in the beamline is a water-cooled collimating mirror (M1) located in the optics hutch. The mirror was designed by PAL, manufactured from silicon by Thales SESO SAS (France) and coated with a 100 Å Rh layer on top of a 300 Å Pt layer. The synchrotron radiation is collimated by the mirror with a tangential radius (7 km) located 13 m from the X-ray source, and positioned so that incoming X-rays are reflected onto the mirror at an angle of 3 mrad, collimating the beam vertically upward. Cylindrical mirror benders (PAL & Vactron Co. Ltd) provide moments that can change the mirror from flat to concave.

Table 1
Beamline details.

Beamline name	BL2D-SMC
Source type	Bending magnet
Mirrors	Two Si with Rh on Pt-coated stripes: one upward collimating (1000 mm × 95 mm × 55 mm), one downward focusing (1250 mm × 95 mm × 55 mm)
Monochromator	Double-crystal Si(111) water-cooled
Energy range	8.3–20.7 (keV)
Wavelength range	1.5–0.6 (Å)
Beam size	100 (H) × 85 (V) (μm) (uncollimated)
Photon flux	6.2×10^{11} (photons s^{-1}) at 17.7 keV
Goniometer	Crystal Logics Inc. PH6 (horizontal air-bearing)
Cryo capability	Cryojet 5 (Oxford Instruments; temperature range 85–500 K)
Detector type	CCD
Detector model	Quantum 210 (ADSC)
Fluorescence detector	Si-drift detector (Amptek)

The polychromatic beam delivered from M1 is monochromated by a 25 mm fixed beam offset DCM fabricated by KOHZU (Kohzu Precision Co. Ltd, Japan) and is designed to select energies between 8.3 keV and 20.7 keV. The DCM with two Si(111) crystals is positioned 16.5 m from the X-ray source. The first indirectly water-cooled Si(111) crystal (cuboid, 90 mm wide, 90 mm long and 10 mm thick) surface faced upwards, and is placed below the surface of the second crystal. The second Si(111) crystal (cuboid, 90 mm wide, 70 mm long and 10 mm thick) surface faces down and coincides with the center of rotation of the main Bragg axis. Crystal translations, which are necessary to maintain the beam incidence and offset, are controlled by two cams and mechanically linked to the rotation of the main Bragg axis. A change of energy or Bragg angle θ can be performed by actuating one motor. The exit beam is parallel with the incident beam and has a constant offset independent of θ. Both DCM Si(111) crystals are mounted on a copper block by a GaIn eutectic to enhance thermal conductivity. The copper

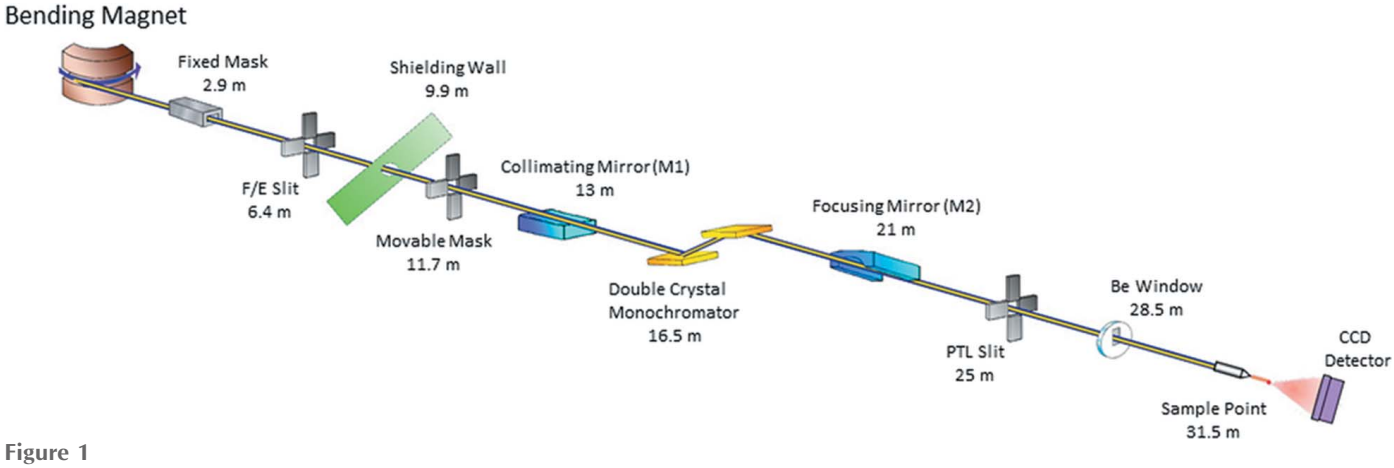


Figure 1
Schematic layout of the supramolecular crystallography beamline (BL2D-SMC). Position of important optical components and equipments from the X-ray source are shown. The units of distances are metres from the X-ray source.

block is nickel plated to prevent interaction between the copper block and the eutectic. Both crystals are clamped to the holder by a phosphor bronze spring plate, which covers the surface 8 mm from the crystal edges.

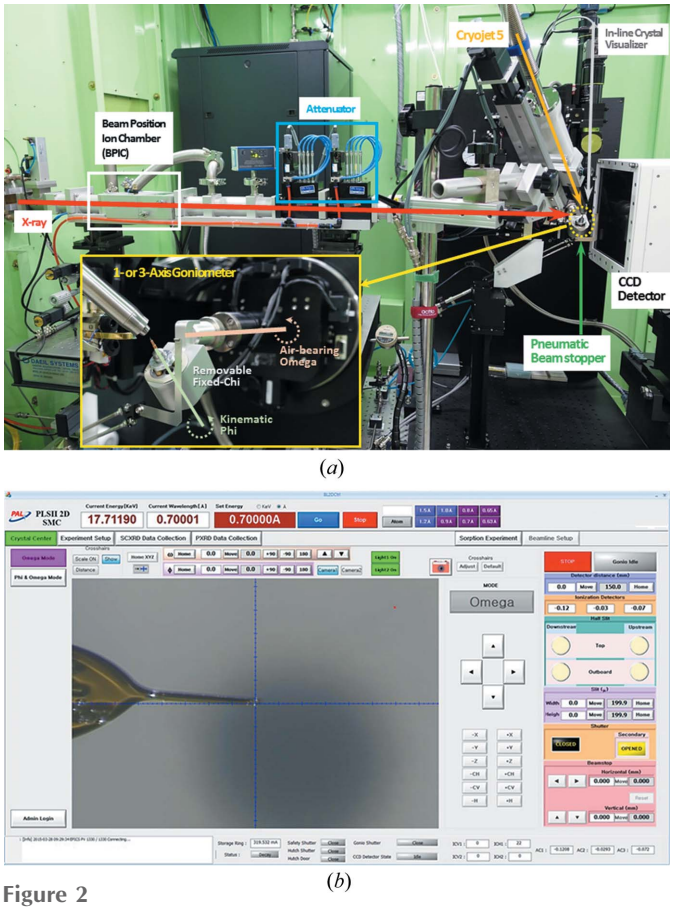
The third optical component of the 2D-SMC beamline is a focusing mirror (M2) located on the PTL. The mirror was designed by PAL and manufactured from silicon by Crystal Scientific Ltd (UK) with the same coating as the collimating mirror M1. The mirror is sagittally bent and located 21 m from the X-ray source to focus the incoming beam. The mirror is positioned to reflect incoming X-ray beams from the mirror at an angle of 3 mrad downward, and the beam is horizontally focused to a 100 µm (horizontal) × 85 µm (vertical) focal spot at the sample (31.5 m from the X-ray source). The focusing mirror M2 is not cooled, and is exposed to a monochromatic beam. The mirror benders were designed by PAL, manufactured by Vactron, and provide equal bending moments to the mirror to adjust focal length.

The monochromatic beam reflected from M2 passes through an evacuated PTL, a Be window, horizontal (FMB Oxford, UK) and vertical (PAL) beam position ion chambers, and is focused on the sample in the end-station (Fig. 2*a*).

The PH-6 goniometer (Crystal Logics Ltd, CA, USA) is a versatile instrument that can be used for either small-molecule or supramolecular experiments. It is designed around an air-bearing ω, with a high-precision three-axis stage and has a sub-micrometre run out at the sample position; it is designed with magic angle fixed χ and kinematic φ axes with built-in sample transition. The compact head is mounted on an IUCr standard thread goniometer, and allows sample-to-detector distances as short as 65 mm (Fig. 2*a*) to be used.

Samples are mounted manually, and the temperature is maintained between 85 and 500 K by a nitrogen stream controlled by a Cryojet 5 (Oxford Instruments, UK) (Fig. 2*a*).

Diffraction data are collected by an ADSC Quantum-210 CCD area detector (ADSC, Poway, CA, USA) allowing sample-to-detector distances between 63 mm and 300 mm (Fig. 2*a*).



(*a*)

(*b*)

Figure 2
(*a*) Photograph of the end-station. Insert: close-up view of the sample position with PH-6 goniometer. (*b*) Interface of the BL2D supramolecular data collection software (*BL2D-SMDC*) with an aligned loop for data collection.

3. Ancillary facilities

The beamline has a sample preparation room for pre-treatment such as evacuation, washing and heating. It includes a glovebox suitable for handling samples in an oxygen-free environment and a high-magnification microscope with a fume hood for sample mounting. *In situ* gas sorption experiments have been conducted on the beamline using customized sorption equipment (from PAL) to explore the positions of gas molecules in highly porous materials such as metal–organic frameworks and porous coordination polymers. A high-power Vibrant 355 LD tunable laser system (300–2100 nm) (OPOTEK Inc. CA, USA), and a 365 nm UV–LED light source (OMRON, Japan) are also installed for the investigation of photoreaction crystallography. The beamline is also equipped with an Si-drift fluorescence detector X-123SDD for single-crystal X-ray fluorescence measurements (Amptek, Inc., Bedford, MA, USA). Other instruments, such as an analytical balance, centrifuge, syringe pump and vibration-free incubator, are also available for crystallography experiments.

4. Beamline software

Data collection from the PH-6 goniometer and ADSC Quantum-210 CCD detector is controlled by custom BL2D supramolecular data collection software (*BL2D-SMDC*) developed by Human Technology, based on the experimental physics and industrial control system *EPICS* (http://www.aps.anl.gov/epics/), and programmed in visual C++ (Microsoft Visual Studio 2010). The software for the PAL 2D-SMC beamline has an interactive GUI and is designed to run on a Windows operating system. The GUI allows the positioning of crystals in the X-ray beam and provides access to the experiment setup, SCXRD data collection, PXRD data collection, sorption experiments and the beamline setup (Fig. 2*b*). *HKL3000sm* (Otwinowski & Minor, 1997) is used for cell refinement and data reduction.

5. Facility access

Users are required to submit beam time proposals to access the 2D-SMC beamline (three terms per year, submissions are

peer-reviewed and scored by the committee) *via* a website (http://pal.postech.ac.kr) before being granted permission by PAL, because the Pohang Light Source II (PLS-II) is operated by Pohang Accelerator Laboratory. Beam proposals are either (*a*) general proposals open to public users or (*b*) urgent request proposals that can be submitted at any time and are intended for important or urgent samples. In general, 70% of beam time is distributed between public users, and the remainder is used for maintenance and upgrades by beamline staff.

6. Highlights

One area of interest is the application of crystalline materials that possess large pore and void spaces to allow sorption/desorption or separation of various gases, *e.g.* CO_2, CH_4, C_2H_2 and H_2, and guest molecules. The structural analysis of these materials requires the synchrotron radiation source over a laboratory-source machine, owing to the weak diffraction, poor data quality and long exposure time caused by the large unit cell, highly disordered solvent and small crystals (<15 µm). Recently, K. B. Yoon's group characterized and reported an interesting and significant microporous new copper silicate ($Na_2CuSi_5O_{12}$) SGU-29 (named after SoGang University-29) using synchrotron single-crystal X-ray diffraction (Datta *et al.*, 2015). The compound displays high stability when exposed to humid flue gases and the atmosphere and also easily adsorbs both H_2O and CO_2 in humid flue gases, but the adsorbing H_2O does not interfere with adsorption of CO_2 (Fig. 3). The self-assembly complex ruthenium(II) metalla[2]-catenane was published by K. Chi's group (Lee *et al.*, 2015). In the complex, two pyrene groups are encapsulated inside the cavity and stabilized *via* π–π interactions between the pyrene ring and the naphthacendione (Fig. 4). In addition, the complex is also rearranged and can be extended into higher-dimensional supramolecular structures by guest template, solvent and concentration.

As previously announced, a number of high-impact scientific results or basically significant study have been published to date using data collected at the 2D-SMC beamline. In addition, many more crystal structures have been collected at the 2D-SMC beamline and more than 40 scientific articles per year have been reported.

7. Discussion and conclusions

The 2D-SMC beamline at PLS-II was designed and constructed for supramolecular crystallography experiments in 2012 and has been operated by domestic and international users in several configurations. The BL2D-SMC uses a tunable high-flux X-ray source to obtain remarkable results, as the bending magnet provides stable and high-energy synchrotron radiation, and the detector collects a large amount of data when compared with laboratory-based X-ray sources.

The *BL2D-SMDC* software has a Windows-based GUI, and various ancillary facilities in the beamline help support high-quality experiments related to gas sorption and photoreaction.

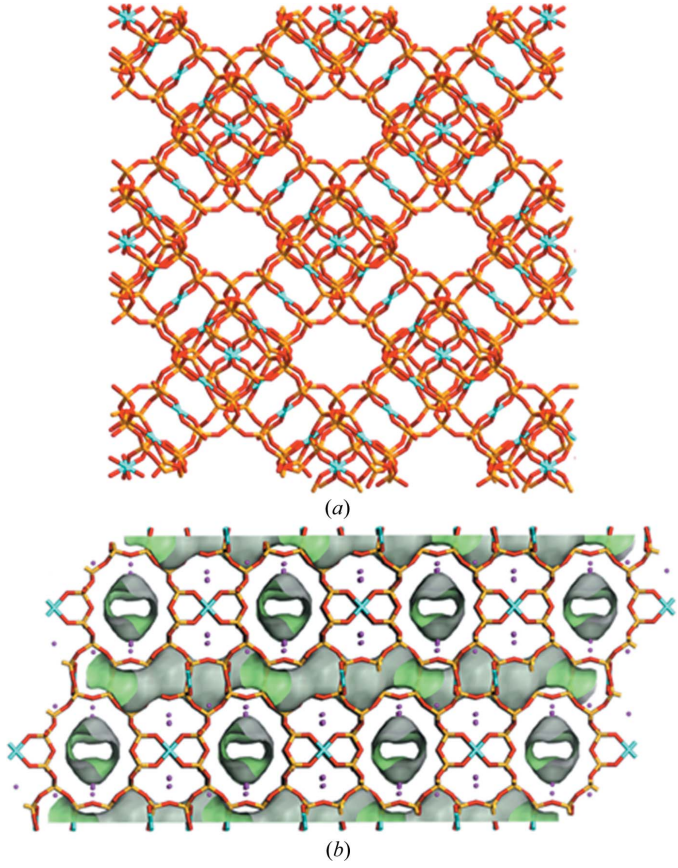


Figure 3
(*a*) X-ray crystal structure view of the microporous copper silicate, SGU-29. (*b*) Positions of Na^+ ions (purple) in the channel (green).

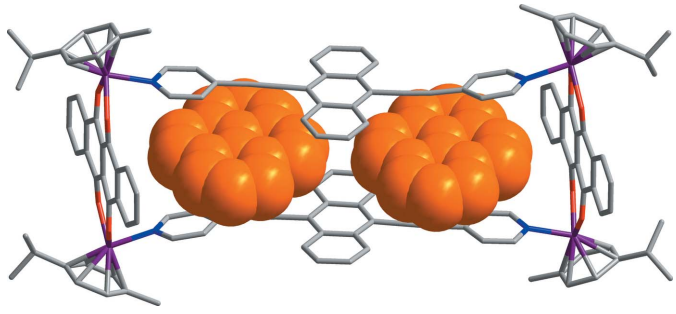


Figure 4
X-ray crystal structure view of the self-assembly Ru^{II} (purple) complex with space-filling models of pyrene rings (orange).

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