XAFS Platform at the BL17B Beamline, Shanghai Synchrotron Radiation Facility Protein Science Center: Extending Structural Characterization from Long-Range Order to Short-Range Order

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Abstract

The BL17B beamline at the National Facility for Protein Science Shanghai (NFPS) is a bending-magnet source beamline located at the Shanghai Synchrotron Radiation Facility (SSRF). Originally designed for diffraction experiments, the beamline supports techniques such as single-crystal diffraction, powder diffraction, and grazing-incidence wide-angle X-ray scattering (GIWAXS), enabling characterization of long-range ordered atomic structures. Its research fields encompass biology, environment, energy, and materials science. However, these fields also have strong demands for characterization of short-range ordered structures. To meet these demands, BL17B has established an advanced X-ray absorption fine structure (XAFS) experimental platform, enabling BL17B to be applicable to various structural systems ranging from crystalline to amorphous, and from long-range ordered to short-range ordered. This XAFS platform has achieved simultaneous acquisition of transmission-mode and fluorescence-mode XAFS data within the energy range of 5-23 keV, covering K-edge XAFS measurements for elements from titanium to ruthenium and L3-edge XAFS measurements for elements from cesium to bismuth. Based on remote sample exchange using a high-capacity sample wheel, the platform has developed functions for automated sample evaluation and automatic data acquisition, significantly improving the level of automation. The highly integrated control system simplifies experimental preparation and data acquisition processes, enhancing experimental efficiency and user experience. Furthermore, the platform can achieve

extremely low detection concentration limits. For low-concentration copper phthalocyanine (CuPc) samples, the detection limit for extended X-ray absorption fine structure (EXAFS) is as low as 0.04 wt%, while the detection limit for X-ray absorption near-edge structure (XANES) is further reduced to 0.01 wt%. These data fully validate the exceptional performance of this XAFS experimental platform in obtaining high-precision XAFS experimental data.

Full Text

Preamble

XAFS Platform at NFPS BL17B at SSRF: Extending Structural Characterization from Long-Range to Short-Range Order

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Abstract

The synchrotron radiation beamline BL17B of the National Facility for Protein Science (NFPS) in Shanghai, situated at the Shanghai Synchrotron Radiation Facility (SSRF), was originally designed for diffraction experiments and accommodates techniques including single-crystal diffraction, powder diffraction, and grazing-incidence wide-angle X-ray scattering (GIWAXS) to enable the characterization of long-range ordered atomic structures. The academic community associated with BL17B engages in research domains encompassing biology, environment, energy, and materials, and a pronounced demand exists for charac-

terizing short-range ordered structures. To address these requirements, BL17B established an advanced X-ray absorption fine structure (XAFS) experimental platform that enables investigation of a wide range of systems, from crystalline to amorphous and from long-range to short-range order. The platform allows simultaneous XAFS data acquisition for both transmission and fluorescence modes within an energy range of 5–23 keV, encompassing the K-edges of titanium to ruthenium and the L3-edges of cesium to bismuth. The platform exemplifies high levels of automation achieved through automated sample assessment and data collection based on large-capacity sample wheels that facilitate remote sample loading. When integrated with a highly integrated control system that simplifies experimental preparation and data collection, the XAFS platform significantly bolsters experimental efficiency and enhances user experience. Notably, the platform boasts an impressively low extended X-ray absorption fine structure (EXAFS) detection limit of 0.04 wt% for dilute copper phthalocyanine (CuPc) samples and an even more remarkable X-ray absorption near-edge structure (XANES) detection threshold of 0.01 wt%. These figures represent a hallmark of the platform' s unwavering commitment to high-fidelity XAFS data acquisition, thereby establishing a new benchmark for structural characterization.

Keywords: XAFS, automated, synchrotron radiation, short-range order

1. Introduction

Beamline BL17B at the Shanghai Synchrotron Radiation Facility (SSRF) is affiliated with the National Facility for Protein Science in Shanghai (NFPS) (https://www.ncpss.org.cn/index.action) and was originally conceived to conduct high-throughput protein crystallography investigations [1-4]. BL17B supports techniques such as single-crystal diffraction [5-6], powder diffraction [7], and grazing-incidence wide-angle X-ray scattering (GIWAXS) [8-10] to enable characterization of long-range ordered atomic structures. Beyond its applications in structural biology [11-13], this beamline supports scientific research across diverse domains, including environmental science [14-15], energy [16-17], and materials [18-20]. In these fields, investigators frequently require understanding of structural order at scales of a few angstroms, namely short-range order. Although traditional crystallographic techniques reveal long-range ordered crystal structures, they may not adequately capture the local amorphous nature of such short-range ordered features. For instance, research on transition metal-containing biological systems necessitates local structural insights into metal sites related to functional diversity [21-22]. In biomedical and ecological environmental research, understanding the local coordination of exogenous metals within biomacromolecules and their transformation processes is essential for revealing interaction mechanisms [23-25]. Similarly, studying the catalytic processes and mechanisms of metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and their derivatives in materials research requires knowledge of active sites along with local atomic coordination and chemical state [26-

27]. Research on perovskite solar cells also benefits from short-range ordered structural characterization to assess the impacts of nanoscale phase impurities on film quality [28].

X-ray absorption fine structure (XAFS) techniques [29-30] can probe local atomic and electronic environments within ranges of approximately 0.5 to 5 Å surrounding element-specific absorbing centers in short-range ordered structures. Moreover, XANES, the near-edge region of XAFS, reveals details regarding oxidation states, electron orbital occupation, and coordination symmetries. In EXAFS, the extended oscillations provide information on atomic distances, coordination numbers, and species of neighboring atoms. The XAFS technique effectively compensates for the limitations of crystallography in characterizing short-range order structures and offers the advantage of being adaptable to various sample forms—that is, XAFS is not limited to crystal structures alone. Beamline BL17B possesses the optical foundation and spatial conditions required to develop an XAFS experimental technique. Thus, we constructed a novel XAFS platform at BL17B to extend our structural characterization capabilities from long- to short-range order. This study provides a valuable reference for similar upgrade projects at synchrotron facilities.

2. Basis for Upgrade

The existing optical configuration of BL17B is primarily designed to accommodate the requirements of single-crystal diffraction experiments. A schematic of the main optical components is shown in Fig. 1 [Figure 1: see original paper]. The SSRF operates at an electron energy of 3.5 GeV with a current of 220 mA in top-up mode. The X-ray photon source is a bending magnet with a magnetic field of 1.27 T, generating a white beam with a critical energy of 10.3 keV. The beam is confined through a 1.5 mrad × 0.1 mrad (H×V) white-beam slit (Slit1) that selects the central cone to alleviate radiation and thermal loads on downstream optics. The beam is subsequently collimated vertically into a quasi-parallel beam to improve energy resolution. The collimating mirror is set at a grazing incidence angle of 2.8 mrad and features two reflection stripes: a Si coating used below 8 keV and a Rh coating used at 8–23 keV. This system suppresses harmonic contamination relative to the fundamental to below 10^{-3}. A fixed-exit Si(111) double-crystal monochromator (DCM) then converts the white beam into a monochromatic beam with an energy resolution of 2$×10^{-4}$ within the 5–23 keV range. Slit2 further refines the beam to decrease its size. Finally, the monochromatic X-rays are focused using a Rh-coated toroidal mirror at a grazing incidence angle of 2.8 mrad. The focal point, located 42 m from the source, serves as the diffractometer sample position with a beam size of 150 μm × 180 μm (H×V) and divergence of 1.5 mrad × 0.2 mrad (H×V), providing a flux of 2×10^{11} photons/s at 12 keV.

Considering the feasibility of incorporating XAFS experiments at BL17B, the current monochromatic beam energy range, energy resolution, and flux meet the requirements for XAFS experiments. However, further suppression of harmonic

content is required. For XAFS, the acceptable level of harmonic contamination relative to the fundamental signal is generally below 10^{-4} [31], as harmonics can lead to amplitude attenuation in XAFS spectra due to the effect of undesirable photons [32-33]. Currently, only energies greater than 10 keV satisfy this criterion. By introducing dedicated harmonic rejection mirrors, the 5–10 keV region can also be rendered compatible. In terms of experimental space, an approximately 2 m segment that is primarily occupied by vacuum pipes exists between the Be window exit and diffractometer in the experimental hutch (highlighted in the red box in the left panel of Fig. 2 [Figure 2: see original paper]). This space can accommodate an XAFS station with the XAFS sample positioned approximately 1 m upstream of the diffraction sample. Adjusting the grazing incidence angle and height of the toroidal mirror focuses the XAFS sample position. By mounting both the XAFS setup and a vacuum tube for the diffraction experiment on a platform that can move perpendicularly to the optical path, rapid switching between XAFS and diffraction modes becomes convenient. The image on the right in Fig. 2 shows the experimental hutch after incorporating the XAFS station according to the proposed scheme.

3. XAFS Experimental Station

We added an XAFS experimental station in the beam path upstream of the diffraction experiment station. As depicted in Fig. 3 [Figure 3: see original paper], the XAFS experimental station consists of two main parts: (1) a standalone harmonic rejection mirror (HRM) installed on the floor, and (2) an XAFS testing platform installed on the existing support stage equipped with a slit, XAFS sample holder, detector, and vacuum tube. A slit is used to shape the incident beam and restrict scattered photons around the central cone. When the vacuum tube is moved in, it switches to diffraction mode, and the I_3 ionization chamber remains in the beam path to monitor the incident beam intensity.

3.1 Harmonic Rejection Mirror (HRM)

The reflectivity of materials for grazing incidence X-rays is nearly 100% below the critical energy but drops sharply above the critical energy [34]. Therefore, a grazing incidence plane mirror can be considered a low-pass filter for X-rays used to suppress higher-order harmonics. Based on this principle, the HRM employs a pair of pre-aligned parallel-plane mirror designs, as shown in Fig. 4 [Figure 4: see original paper]. The plane mirror has 200 mm long Ni and Rh stripes on a Si substrate, and the grazing angle is fixed at 5.8 mrad. The mirrors are placed in parallel with a 100 mm offset and are separated vertically by 0.58 mm. This design further suppresses harmonics at energies above 5 keV to ensure that XAFS amplitude attenuation caused by harmonics is less than 1%. The HRM is positioned 40.2 m downstream of the source and can fully receive the main beam. These settings reflect the fundamental flux with efficiencies of 88% and 65% for the Ni and Rh coatings, respectively. The HRM design ensures suppression of high-order harmonics without excessively affecting the beam size and light flux

downstream. The Ni coating works from 5–8 keV, whereas the Rh coating works from 5.5–11 keV. In the overlapping zone (5.5–8 keV), both coatings are viable, providing ample redundancy; however, the Ni coating offers higher reflectivity, making it the preferred choice. At energies greater than 10 keV, the mirrors are moved out of the beam path. The beam height change between using and not using the mirrors is 1.16 mm, which can be accommodated by lifting the downstream support stage. The HRM box serves as a support base and provides vacuum protection for the mirrors to enable control of the incident angle and coating switching.

The effectiveness of the HRM in XAFS experiments was validated through K-edge XAFS testing on a Ti foil, as shown in Fig. 5 [Figure 5: see original paper]. The total absorption length of the Ti foil at 5 keV is 3.8. Given that harmonic content is higher in lower-energy regions, increased sample thickness exacerbates the amplitude attenuation effect. The spectral shape was severely distorted in the absence of HRM but returned to its normal state upon inclusion of HRM. These results clearly demonstrate the effectiveness of HRM in suppressing harmonics and the necessity of acquiring reliable XAFS data.

3.2 Testing Platform

As shown in Fig. 3, three ionization chambers are arranged along the X-ray path, with the sample wheel and reference sample wheel positioned between them. The I_0 ionization chamber monitors the incident beam intensity, I_1 records the beam intensity transmitted through the sample, and I_3 records the beam intensity transmitted through the reference sample. Because synchrotron X-rays are linearly polarized in the horizontal plane of the synchrotron [35], scattering interference is weakest in the direction perpendicular to the beam path within the horizontal polarization plane. Therefore, fluorescence detector I_2 is placed along the perpendicular direction to collect sample fluorescence. By simultaneously collecting the I_0, I_1, I_2, and I_3 signals, we obtain: (a) the transmission-mode XAFS of the sample using Eq. (1), (b) the fluorescence-mode XAFS of the sample using Eq. (2), and (c) the transmission-mode XAFS of the reference sample using Eq. (3):

Sampled = ln (I_0/I_1); (1)
Sampled I_2/I_0; (2)
Referenced = ln (I_1/I_3), (3)

where represents the absorption coefficient, and d is the sample thickness along the beam path.

The advantage of this setup lies in its ability to simultaneously acquire both transmission and fluorescence spectra from a sample to enhance experimental efficiency. Because a given sample is more suitable for either transmission or fluorescence mode, the decision on which mode to use can be deferred to post-processing stages. Moreover, by concurrently collecting reference sample data, an energy calibration standard is incorporated into the data of each sample to

enable comparison between datasets obtained under varying instrument conditions.

There are two types of fluorescence detectors: a Lytle ionization chamber and an SDD. The Lytle detector has the advantage of handling higher-count-rate signals, and it is simple to operate with low maintenance costs. The SDD detector distinguishes XRF signals from different elements, which is particularly useful for studying multi-element materials. The fluorescence detectors are mounted on a two-level electric stage for rapid switching, as shown in Fig. 6 [Figure 6: see original paper]. Both detectors have an upper stage to adjust the distance between the detector and sample along the perpendicular direction. The detectors and their upper stages share a common lower stage for movement parallel to the beam path. The motor positions for different detectors under operation or standby states are predefined, which allows for one-click rapid switching between the fluorescence detectors.

3.3 Experiment Mode

(i) Transmission mode. I_0, I_1, and I_3 are fixed-length ISIC series standard gas ionization chambers from Tianjin Jingshenfang Company with effective lengths of 30 cm for I_0 and I_1 and 10 cm for I_3. The $He/N_2/Ar$ gas mixture ratios of each ionization chamber are predefined for every absorption edge to maintain absorption ratios of approximately 20% for I_0, 80% for I_1, and 100% for I_3, and are executed through an automatic gas delivery system (as shown in Fig. 7 [Figure 7: see original paper]). This ratio allows transmission data of the sample to approach the optimal signal-to-noise ratio while preserving sufficient transmitted photons for the reference sample to achieve good data quality. Transmission mode is applicable for samples with higher concentrations and generally requires an effective absorption concentration / greater than 10–20%.

(ii) Lytle fluorescence mode. A Lytle ionization chamber [36] with 100% Ar working gas is employed. The Lytle chamber has no energy discrimination capability and cannot distinguish target fluorescence signals from other fluorescent and scattered photon backgrounds through energy identification. However, the Lytle detector employs a combination of a Z-1 filter and Soller slit [37-39] that effectively suppresses background noise while preserving target fluorescence to enhance the signal-to-noise ratio. Because fluorescent and scattered photons have different energies, the Z-1 filter can remove most scattered photons while preserving most fluorescence. The Soller slit, focused on the sample, blocks secondary photons produced by the filter while allowing the majority of sample fluorescence to pass through. The Lytle detector offers a wide acceptance angle for fluorescence signals, reaching up to $10\% \times 4\pi$, and has no saturation current limit, thus enabling detection of high-intensity signals. Fluorescence-mode data are susceptible to self-absorption effects that can lead to XAFS amplitude attenuation. To mitigate self-absorption impact, this experimental mode is generally employed for either low-concentration thick samples, in which the effective absorption concentration is recommended below 10% and the total ab-

sorption thickness d exceeds 3, or high-concentration thin samples, in which the edge-jump Δ d is less than 0.1.

(iii) SDD fluorescence mode. Fluorescence signals are collected using a 3-element Vortex-90EX [40] silicon drift detector (SDD) and processed using an Xspress 3 Mini (X3M) electronics readout system. This detector boasts energy discrimination capability and enables selective extraction of the target fluorescence signal, thereby enhancing the signal-to-noise ratio. However, each probe has a saturation count rate of approximately 2 Mcps, which imposes an upper limit on the signal-to-noise ratio. To increase the proportion of target fluorescence signals within the saturation count range, filters must be incorporated in front of the SDD to attenuate a significant number of scattered photons. This experimental mode primarily serves as a complement to the Lytle fluorescence mode and is typically applied when sample concentrations are lower than the detection limit of the Lytle method or when there is substantial background fluorescence interference. In such cases, the target signal is submerged in background noise, which renders the Lytle detector ineffective, whereas the energy discrimination capability of the SDD is advantageous.

3.4 Sample Loading Condition

The reference sample wheel is equipped with a complete set of reference metal foils [41] from Exafs Materials Company, allowing remote switching of desired samples. There is ample space at the sample position to accommodate remote sample loading with the sample wheel as well as manual sample loading with an in situ sample holder or other sample holder. The sample wheel assumes that all samples are centered at each hole—that is, as long as one hole is aligned, the other holes are also aligned. Thus, the sample wheel is suitable for uniformly prepared large samples and thereby facilitates rapid sample exchange. The sample wheel has 26 holes, each with a diameter of 15 mm and spacing of 25 mm. Samples are attached to the center of the holes for loading. Because Hole #0 is used as a blank, the maximum sample capacity is 25. The wheel is attached to the base using magnets, enabling rapid wheel replacement. The position reset function of the sample wheel eliminates position errors caused by stress during wheel replacement. In particular, when a fixed pointer on the wheel passes the photoelectric sensor at the base, the current position is defined as zero. The sample wheel is generally placed at an angle of 45° relative to the beam path to accommodate simultaneous collection of transmission and fluorescence data.

4. XAFS Control System

The software control system for XAFS experiments was developed using LabVIEW, a system design platform and development environment created by National Instruments (NI), also known as the Laboratory Virtual Instrument Engineering Workbench. LabVIEW offers a user-friendly graphical interface and easily controllable modules that are adaptable to various hardware types. The SDD electronics readout system, along with motion control systems of existing

beamline equipment including monochromators, focusing mirrors, and support stands, were developed based on distributed experimental physics and industrial control systems (EPICS). LabVIEW' s communication mode facilitates seamless data sharing with the EPICS system. Newly incorporated devices such as the HRM, fluorescence detector stage, automatic gas delivery system, sample wheel, ADC, and remote gain controller communicate via Ethernet and connect to the local network through switches, interacting with the XAFS software computer.

4.1 Experiment Preparation

The XAFS software is distinguished by its highly integrated architecture. This software comprehensively manages various equipment configurations involved in XAFS experiments, thereby enhancing efficiency and convenience throughout the experimental process. At the start and end of each XAFS experimental run, the software enables effortless switching between diffraction and XAFS modes. The software can (a) control the focusing mirror to adjust the focus position, (b) sequentially control the HRM coating and height of the support stage for an unobstructed optical path, (c) move the testing platform to switch between the vacuum tube and XAFS devices, and (d) manage the automatic gas filling system, thus filling the I_3 ionization chamber with 100% N_2 during diffraction mode to minimize light attenuation.

Before formal XAFS data acquisition for each element to be measured, the software implements the following preparation workflow: (1) mount the sample using a sample wheel or other sample holder and replace filters for fluorescence detectors; (2) change the gas for ionization chambers through the gas delivery system; (3) optimize the optical configuration, which involves adjusting the HRM working coating, controlling the support stage to compensate for beam height change after HRM, and optimizing monochromator parallelism for maximum photon flux; (4) replace the reference sample via the reference sample wheel and collect its XANES data to calibrate the monochromator energy; and (5) select the appropriate fluorescence detector by controlling the two-level electric stage. Except for the first step, which requires on-site manual operation, all other steps integrate basic subtasks into one-touch control to accomplish the desired task. This highly integrated control system significantly reduces the need for on-site fine-tuning equipment, thus enabling remote experimentation.

4.2 Data Acquisition

The hardware architecture involved in XAFS data collection is shown in Fig. 8 [Figure 8: see original paper]. The monochromatized beam passes through the ionization chambers and samples, with attenuated photons and excited fluorescence detected and fed into the data acquisition system. The initial signal currents from the I_0, I_1, and I_3 ionization chambers as well as the I_2 Lytle detector are in the fA– A range. Being cautious regarding output voltage stability of the high-voltage supply for ionization chambers is crucial, as this could impact background noise. We utilized the HV-3000 model from Tianjin Jingshenfang

Company with an output voltage ripple coefficient of less than 0.001%. Direct long-range transmission and reading of initial signals are susceptible to transmission losses and electromagnetic interference, which introduce significant noise. To improve the signal-to-noise ratio of subsequent electronics, current signals from each ionization chamber are connected to a current-to-voltage amplifier (Femto DLPCA-200), and the amplified voltage signals are then fed to a 4-channel ADC acquisition card (Geekootech FS3326S) and converted to digital signals. The ADC card has 16-bit resolution and a maximum sampling rate of 2 MS/s per channel; however, a 0.5 MS/s rate is used to avoid buffer overflow issues. A 4-channel remote gain controller was developed for the DLPCA-200 amplifier to enable remote control of gain for the four ion chambers. The initial current signal from the I_2 SDD fluorescence detector is converted into a digital signal by a readout system (Quantum Detectors Xspress 3 Mini) and read using an acquisition program.

The XAFS data acquisition system employs a conventional step-by-step scan mode, as shown in Fig. 9 [Figure 9: see original paper]. Here, the monochromator is driven to a specific energy and allowed to stabilize momentarily. Subsequently, the real-time energy readback is recorded. In this step, we do not repeatedly drive the monochromator to fine-tune its readback to the exact energy specification, as this could introduce worse energy errors due to backlash. The strategy of driving the monochromator once and recording the energy readback value effectively improves energy measurement accuracy while conserving time. The ADC and SDD commence data acquisition and transmit data to the XAFS computer. The acquisition software calculates and records the average count rate within the integration time, thereby completing collection of that data point. This process is repeated for the next energy point (cycling) until the spectrum is fully acquired. Collecting a full XAFS spectrum typically requires approximately 20 minutes (integration time of 1 s). Moreover, to prevent signal saturation, which can lead to data distortion, we introduced an innovative auto-gain control function prior to formal data collection. This function performs a preliminary scan of the entire spectrum, identifies the maximum current value for each detector, and automatically adjusts the gain of the corresponding amplifier to ensure that the amplified voltage is as large as possible without saturation. This function provides a linear response and optimal signal-to-noise ratio across various signal intensities, guaranteeing data accuracy and reliability.

The highly integrated XAFS control system enables simple data acquisition and automated measurements based on the sample wheel. A sample evaluation feature was incorporated to enhance automatic measurement efficiency. By collecting data before and after the absorption edge in both the blank (Hole #0) and sample-mounted states, parameters including total absorption thickness, effective absorption concentration, transmission edge jump, and fluorescence edge jump-to-background ratio can be calculated. These parameters assist users in rapidly assessing whether data are worth collecting and optimizing sample preparation. Selected samples are subjected to automated sample exchange and

data acquisition. Notably, automatic measurement is applicable only to samples with the same absorption edge using the Lytle detector because manual filter replacement is required for different elements. Moreover, samples that require SDD detection often involve more complex situations, making them more suitable for individual treatment.

4.3 Data Format

The data adopt the XAFS Data Interchange (XDI) standard format [42] specified by the International X-ray Absorption Society (IXAS). The XDI format aims to share XAFS data across continents, decades, and analysis toolkits, and it is the only accepted data format for the X-ray Absorption Data Library (XASLIB, https://www.xaslib.xrayabsorption.org). As depicted in Fig. 10 [Figure 10: see original paper], our data consist of two parts: a metadata header and data table, separated by "#—-". Our header includes details such as data source, absorbing element, sample evaluation, experimental setup, and user comments, which provide a comprehensive record of the experiment. The data columns correspond to energy; raw data of I_0, I_1, I_2, and I_3; and converted absorption data of transmission, fluorescence, and reference.

5. XAFS Platform Performance

Table 1 . BL17B XAFS Platform Parameters

Parameter	Value
Light source	Bend Magnet
Electron energy	3.5 GeV
Magnetic field intensity	1.27 T
Beam intensity	200 mA
Beamline acceptance angle	1.5 mrad × 0.1 mrad
Energy range	5–23 keV, 7–21 keV (recommended)
Energy resolution (ΔE/E)	2×10^{-4} at 12 keV
Flux at sample	2.2×10^{11} photons/s at 12 keV
Focused spot size	1.5 mm × 0.6 mm (H×V)
Harmonic rejection effect	XAFS amplitude attenuation $< 1\%$

To evaluate the performance of the XAFS experimental platform, we inspected various aspects of its capabilities. Common parameters are summarized in Table 1. The BL17B XAFS platform has an energy range of 5–23 keV, permitting XAFS data collection for elements spanning Ti to the K-edge of Ru and Cs to the L_3-edge of Bi, as shown in Fig. 11 [Figure 11: see original paper]. Notably, Tl, Pm, and actinide elements are not permitted for testing at this platform. This decision was based on concerns regarding chemical toxicity and experimental safety, despite the L-edge energies being within the accessible range of

the monochromator. To measure the XAFS sample spot size, we used X-ray-sensitive exposure paper to record the central beam spot at the sample position. As depicted in Fig. 12 [Figure 12: see original paper], the spot size is approximately 1.5 × 0.6 mm (H × V). By recording current values of the 100% N_2-filled I_0 ionization chamber under various incident beam energies, the corresponding beam flux was calculated using Hephaestus software [43]. As shown in Fig. 13 [Figure 13: see original paper], the flux in the central energy range (7–21 keV) is on the order of 10^{11} photons/s, which is our recommended working energy range. For 5–7 keV, the flux decreases quickly due to absorption by substances along the optical path. At 21–23 keV, the flux declines rapidly with the reflectivity of the Rh-coated collimating and focusing mirrors. Nevertheless, the minimum flux within the XAFS energy range exceeds 10^9 photons/s, enabling high-quality data collection for high-concentration samples. As shown in Fig. 14 [Figure 14: see original paper], high-quality K-edge XAFS data were obtained at the experimental energy limits of Ti and Ru foils. The pre-edge peak of the Ti foil, approximately 2 eV wide, was clearly observed. The amplitude and signal-to-noise ratio of EXAFS typically decrease rapidly with increasing k value at a rate of k^{-2}. However, both EXAFS spectra in Fig. 14 remain smooth up to 15 $Å^{-1}$ without significant noise, demonstrating the platform' s capability to acquire high-quality data within its working energy range.

We further assessed detection limits achievable under different experimental modes to provide guidance for selecting optimal experimental modes for various sample conditions. We prepared copper(II) phthalocyanine (CuPc, $C_{32}H_{16}CuN_8$) samples diluted with LiF at varying Cu concentrations, collected their Cu K-edge XAFS spectra, and determined detection limits based on signal-to-noise ratios of EXAFS and XANES data. As shown in Table 2 , mass fractions of samples range from 3.4 wt% to 0.01 wt%, with corresponding Cu absorption concentration (/) decreasing from 60 to 0.3%. To ensure concentration accuracy, low-concentration samples were further diluted with high-concentration samples. Each sample was meticulously ground to ensure uniform mixing and then compressed into tablets with a diameter of 10 mm. Uniform tablet thickness helps avoid the pinhole effect [44], which can lead to data distortion. The quantity of each sample is controlled to have a total absorption thickness (d) of 2–4, which maximizes signal-to-noise ratio according to the Nordfors criterion [45]. The actual measured total absorption thickness and jump edge in Table 2 align with intended concentrations, demonstrating reliable sample preparation.

Table 2. Different Cu-Concentration CuPc Samples Diluted with LiF

Sample	Mass fraction w /w	Absorption concentration /	Total absorption thickness	Jump edge
3.4 wt%	3.4%	60%	2.5	1.5

Sample	Mass fraction w /w	Absorption concentration /	Total absorption thickness	Jump edge
0.7 wt%	0.7%	12%	2.8	0.33
0.3 wt%	0.3%	5%	3.2	0.15
0.15 wt%	0.15%	2.5%	3.5	0.08
0.07 wt%	0.07%	1.2%	3.8	0.04
0.04 wt%	0.04%	0.7%	4.1	0.025
0.014 wt%	0.014%	0.25%	4.5	0.009
0.01 wt%	0.01%	0.18%	4.7	0.006

Normalized Cu K-edge EXAFS data for diluted CuPc samples are shown in Fig. 15(a) [Figure 15: see original paper]. Higher-concentration data exhibit better signal-to-noise ratios. In transmission mode, the 3.4 wt% sample remained smooth up to 14 $Å^{-1}$. When concentration drops to 0.3 wt%, the data signal-to-noise ratio decreases, but data remain reliable up to 12.5 $Å^{-1}$. Compared with Lytle fluorescence data, transmission data for this sample exhibited less noise but significant distortion beyond 12.5 Å. Hence, 0.3 wt% (10%) represents the EXAFS detection limit for transmission mode. Therefore, transmission mode is recommended for samples with concentrations above 10% to achieve optimal signal-to-noise ratio and maintain jump height greater than 0.2 to minimize data distortion. In Lytle fluorescence mode, noise becomes more noticeable when Cu mass fraction drops to 0.04 wt% (1.5%). However, data remain consistent with real signal trend until 12.5 $Å^{-1}$, which is acceptable. In SDD fluorescence mode, EXAFS data for the 0.04 wt% sample show increased noise compared with corresponding Lytle mode data, yet align better with the actual signal because SDD selectively collects characteristic fluorescent signals, though total intensity is not as high as that of the Lytle detector. Therefore, 0.04 wt% (1.5%) is proposed as the EXAFS detection limit for fluorescence mode.

Figure 15(b) [Figure 15: see original paper] shows Fourier transforms of k^2-weighted Cu K-edge EXAFS spectra of CuPc samples with different Cu concentrations. The Fourier transform k-range is 3–12 $Å^{-1}$. All data exhibit similar peak shapes within the range of 1.3–4 Å, especially at the first shell at 1.53 Å, due to nearest neighboring nitrogen atoms. Peak heights show fluctuations of approximately 10%, which is reasonable due to experimental error. These results indicate that low-concentration data reflect real information and possess good reliability. Moreover, for samples collected under Lytle mode (0.07 and 0.04 wt%), pseudo-peaks appear near 1.1 Å, caused by noise. These results

suggest that data from low-concentration samples near detection limits should be handled with caution. Fitting analyses were conducted on the first shell to quantitatively assess reliability of low-concentration data. The R fitting range is 1.3–2 $Å^{-1}$ for (0.07 wt%, Lytle) and (0.04 wt%, Lytle), and 1–2 $Å^{-1}$ for others. Table 3 shows fitting results, indicating that Cu-N interatomic distance d in the first shell for all samples is approximately 1.94 Å, with coordination number N ranging from 3.8 to 4.1. Exceptions include (0.04 wt%, Lytle), which has a d value of 1.95 Å, and (0.07 wt%, Lytle), which has a slightly lower N value of 3.5. These results further validate that low-concentration data can be reliable; however, when handling low-concentration samples near detection limits, vigilance regarding false peaks and their potential impacts is essential.

Table 3. Structural Parameters Determined by EXAFS Analysis of the First Shell of CuPc Samples with Different Cu Concentrations

Here, N and d represent coordination number and interatomic distance, respectively. The amplitude reduction factor $S_0{}^2$ was fixed at 0.94. All data share the same energy shift (ΔE) and Debye-Waller factor (σ^2) parameters, with ΔE fitted to 6.9$±$0.8 and σ^2 fitted to 0.002$±$0.001. The reliability factor R for this fit was 0.018.

Sample	Shell	N	d (Å)
3.4 wt%, Trans	Cu-N	3.9$±0.3\|1.94±0.01\|\|0.7$wt$±0.3\|1.94±0.01\|\|0.3$wt$±0.4|1.94±0.0	

Normalized Cu K-edge XANES data for diluted CuPc samples are shown in Fig. 16 [Figure 16: see original paper]. The detection limit for XANES was as low as 0.01 wt% (0.3%), approximately one-fifth that for EXAFS. For samples with concentrations exceeding this threshold, noise in XANES data was insignificant; however, potential issues with data distortion must not be overlooked. Such risks can be effectively mitigated by employing appropriate experimental modes. In transmission mode, the jump edge of the 0.15 wt% (5%) sample is only 0.15. Moreover, lower concentrations, along with smaller jump edges, can introduce distortion. Hence, 0.15 wt% (5%) can be regarded as the XANES detection limit for transmission mode, with a recommended jump edge above 0.2. In Lytle fluorescence mode, the self-absorption effect must be considered. XANES data for the 0.15 wt% (5%) sample align with that of the 3.4 wt% sample, indicating no significant self-absorption effect below this concentration. The Lytle mode is capable of detecting concentrations as low as 0.014 wt% (0.5%), with XANES signals remaining consistent with actual signatures. The SDD fluorescence mode further enhanced sensitivity, allowing detection down to 0.01 wt% (0.3%).

In summary, these experiments demonstrate that for EXAFS, the detection limit for transmission mode is 0.3 wt% (10%). Samples with concentrations above this value are recommended for testing in transmission mode while maintaining a jump height of 0.2 or higher. For concentrations below that threshold,

fluorescence mode is more suitable with a detection limit as low as 0.04 wt% (1.5%). For XANES, corresponding detection limits decrease further to 0.15 wt% (5%) and 0.014 wt% (0.5%). Notably, these detection limits were derived under specific ideal conditions: samples were primarily composed of light elements without significant amounts of heavy atoms, which can introduce additional noise and increase actual detection thresholds. Although detection limits may not be directly applicable to all complex samples, they still offer a valuable reference benchmark for assessing XAFS experiment feasibility. These ultralow detection limits reaffirm the outstanding capability of the XAFS platform to acquire high-quality experimental data and render it particularly valuable for characterizing complex systems such as biological, environmental, and material samples containing minute active components.

6. Conclusion

This work presents the successful development of an advanced XAFS platform at NFPS BL17B at SSRF, which alternates with existing diffraction experimental techniques and extends BL17B' s structural characterization capabilities from long-range to short-range order. The key innovations of this new platform are as follows. First, harmonic suppression mirrors effectively reduce higher-order harmonics in the beam to meet stringent purity requirements of XAFS experiments. Second, the platform features a multifunctional testing station constructed with three transmission ionization chambers and two switchable fluorescence detectors to enable simultaneous collection of transmission and fluorescence data as well as synchronous comparison of target and reference samples, thereby enhancing data integrity and transferability. Furthermore, the platform is equipped with an automated high-capacity sample wheel that facilitates remote control of sample loading and includes automatic sample assessment and sampling functions that significantly boost experimental efficiency. Automatic gain control ensures linearity and high signal-to-noise ratio across various signal intensities to guarantee data accuracy and reliability. The platform excels within the energy range of 5–23 keV, covering K-edges of elements from Ti to Ru and L_3-edges of elements from Cs to Bi. In an experiment studying Cu K-edge XAFS of low-concentration CuPc/LiF samples, we achieved an EXAFS detection limit as low as 0.04 wt% and an even lower XANES detection limit of 0.01 wt%. These results unequivocally demonstrate the exceptional performance of this platform in acquiring high-quality XAFS data, suggesting its valuable application in characterizing complex systems, including biological, environmental, and material samples containing minute active components.

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Data Availability Statement: The data supporting this study' s findings are

openly available in Science Data Bank at https://cstr.cn/31253.11.sciencedb.26799 and https://www.doi.org/10.57760/sciencedb.26799.

References

[1] M.H. Jiang, X. Yang, H.J. Xu et al., Shanghai synchrotron radiation facility. Chin. Sci. Bull. 54, 4171–4181 (2009). https://doi.org/10.1007/s11434-009-0689-y
[2] W.Z. Zhang, J.C. Tang, S.S. Wang et al., The protein complex crystallography beamline (BL19U1) at the Shanghai Synchrotron Radiation Facility. Nucl. Sci. Tech. 30, 170 (2019). https://doi.org/10.1007/s41365-019-0683-2
[3] Q.J. Xiao, T.T. Wu, K.W. Bao et al., Upgrade of crystallography beamline BL19U1 at the Shanghai synchrotron radiation facility. J. Appl. Crystallogr. (2024). https://doi.org/10.1107/S1600576724002188
[4] Q.S. Wang, K.H. Zhang, Y. Cui et al., Upgrade of macromolecular crystallography beamline BL17U1 at SSRF. Nucl. Sci. Tech. 29, 68 (2018). https://doi.org/10.1007/s41365-018-0398-9
[5] C. Giacovazzo, H.L. Monaco, G. Artioli et al., Fundamentals of Crystallography. (Oxford University Press, 2011)
[6] K. Li, L. Li, Y.C. Xu, Crystal structure determination of a chimeric FabF by XRD. Nucl. Sci. Tech. 28, 123 (2017). https://doi.org/10.1007/s41365-017-0281-0
[7] V.K. Pecharsky, P.Y. Zavalij, The Powder Diffraction Pattern. 2nd ed. (Springer, Boston, 2009)
[8] J.A. Steele, E. Solano, D. Hardy et al., How to GIWAXS: grazing incidence wide angle X-ray scattering applied to metal halide perovskite thin films. Adv. Energy Mater. 13, 2300760 (2023). https://doi.org/10.1002/aenm.202300760
[9] Z.J. Zhu, L.L. Lu, C.Y. Li et al., GIWAXS experimental methods at the NFPS-BL17B beamline at Shanghai Synchrotron Radiation Facility. J. Synchrotron Radiat. 31, 968–978 (2024). https://doi.org/10.1107/S1600577524004764
[10] M. Luo, S.J. Deng, L. Li et al., XAFS and SRGI-XRD studies of the local structure of tellurium corrosion of Ni–18%Cr alloy. Nucl. Sci. Tech. 30, 153 (2019). https://doi.org/10.1007/s41365-019-0719-7
[11] X.Y. Wang, H.B. Xie, Q. Guo et al., Molecular basis for METTL9-mediated N1-histidine methylation. Cell Discov. 9, 38 (2023). https://doi.org/10.1038/s41421-023-00548-w
[12] W.Y. Hu, B.X. Yang, Q.J. Xiao et al., Characterization of a promiscuous DNA sulfur binding domain and application in site-directed RNA base editing. Nucleic Acids Res. 51, 10782–10794 (2023). https://doi.org/10.1093/nar/gkad743
[13] Y.L. Cao, A. Yisimayi, Y.L. Bai et al., Humoral immune response to circulating SARS-CoV-2 variants elicited by inactivated and RBD-subunit vaccines. Cell Res. 31, 732–741 (2021). https://doi.org/10.1038/s41422-021-00514-9
[14] X.L. Cai, P.F. Wang, Z.J. Li et al., Mobilization and transformation of arsenic from ternary complex OM-Fe(III)-As(V) in the presence of As(V)-reducing bacteria. J. Hazard. Mater. 381, 120975 (2020). https://doi.org/10.1016/j.jhazmat.2019.120975

[15] J.L. Xu, L.K. Koopal, L.C. Fang et al., Proton and copper binding to humic acids analyzed by XAFS spectroscopy and isothermal titration calorimetry. Environ. Sci. Technol. 52, 4099–4107 (2018). https://doi.org/10.1021/acs.est.7b06281
[16] L.M. Kong, Y.Q. Sun, B. Zhao et al., Fabrication of red-emitting perovskite LEDs by stabilizing their octahedral structure. Nature 631, 73–79 (2024). https://doi.org/10.1038/s41586-024-07531-9
[17] P.D. Zhu, D. Wang, Y. Zhang et al., Aqueous synthesis of perovskite precursors for highly efficient perovskite solar cells. Science 383, 524–531 (2024). https://doi.org/10.1126/science.adj7081
[18] Y.M. Liang, S.S. Wang, M. Tang et al., Cascade synthesis of benzotriazulene with three embedded azulene units and large stokes shifts. Angew. Chem. Int. Ed. 62, e202218839 (2023). https://doi.org/10.1002/anie.202218839
[19] T.Q. Ma, E.A. Kapustin, S.X. Yin et al., Single-crystal X-ray diffraction structures of covalent organic frameworks. Science 361, 48–52 (2018). https://doi.org/10.1126/science.aat7679
[20] L. Jiang, X.X. Ye, D.J. Wang et al., Synchrotron radiation-based materials characterization techniques shed light on molten salt reactor alloys. Nucl. Sci. Tech. 31, 6 (2019). https://doi.org/10.1007/s41365-019-0719-7
[21] R. Sarangi, A biological perspective towards a standard for information exchange and reporting in XAS. J. Synchrotron Radiat. 25, 944–952 (2018). https://doi.org/10.1107/s1600577518008779
[22] M.C. Feiters, W. Meyer-Klaucke, X-ray absorption and emission spectroscopy in biology, in Practical Approaches to Biological Inorganic Chemistry, Crichton, R.R.; Louro, R.O., Editors. (Elsevier, Netherlands, 2020). pp. 229-273.
[23] X.-W. Zhang, X.-J. Yan, Z.-R. Zhou et al., Arsenic trioxide controls the fate of the PML-RARα oncoprotein by directly binding. Science (2010). https://doi.org/10.1126/science.1183424
[24] C.C. Qu, P. Cai, K.X. Shi et al., Methods and mechanisms of the interactions between biomacromolecules and heavy metals. Chin. Sci. Bull. 67, 4192–4205 (2022). https://doi.org/10.1360/tb-2022-0636
[25] X.L. Cai, P.F. Wang, Z.J. Li et al., Mobilization and transformation of arsenic from ternary complex OM-Fe(III)-As(V) in the presence of As(V)-reducing bacteria. J. Hazard. Mater. 381, 120975 (2020). https://doi.org/10.1016/j.jhazmat.2019.120975
[26] S. Yang, L.L. Lu, J. Li et al., Boosting hydrogen peroxide production via establishment and reconstruction of single-metal sites in covalent organic frameworks. SusMat 3, 379–389 (2023). https://doi.org/10.1002/sus2.125
[27] K. Sun, Y. Huang, Q.Y. Wang et al., Manipulating the spin state of Co sites in metal-organic frameworks for boosting CO_2 photoreduction. J. Am. Chem. Soc. 146, 3241–3249 (2024). https://doi.org/10.1021/jacs.3c11446
[28] Z.J. Huang, Y. Bai, X.D. Huang et al., Anion-π interactions suppress phase impurities in $FAPbI_3$ solar cells. Nature 623, 531–537 (2023). https://doi.org/10.1038/s41586-023-06637-w
[29] G. Bunker, Introduction to XAFS: A Practical Guide to X-ray Absorption

Fine Structure Spectroscopy. (Cambridge University Press, Cambridge, 2010)
[30] Y. Iwasawa, K. Asakura, M. Tada, XAFS Techniques for Catalysts, Nanomaterials, and Surfaces. (Springer, Switzerland, 2017)
[31] H. Abe, XAFS spectral distortions related to optics issues, in International Tables for Crystallography. (Wiley, 2024). pp. 594-599.
[32] C. Glover, J. McKinlay, M. Clift et al., Status of the X-ray absorption spectroscopy (XAS) beamline at the Australian synchrotron. X-ray Absorption Fine Structure - XAFS13: 13th International Conference, Stanford, California (USA). AIP, (2007). https://doi.org/10.1063/1.2644692
[33] S. Calvin, XAFS for Everyone. (CRC Press, Boca Raton, 2013). pp. 460.
[34] P. Sainctavit, J. Petiau, A. Manceau et al., Two-mirror device for harmonic rejection. Rev. Sci. Instrum. 60, 2027–2029 (1989). https://doi.org/10.1063/1.1140867
[35] J. Als-Nielsen, D. McMorrow, Sources, in Elements of Modern X-ray Physics. (2011). pp. 29-67.
[36] F.W. Lytle, R.B. Greegor, D.R. Sandstrom et al., Measurement of soft X-ray absorption spectra with a fluorescent ion chamber detector. Nucl. Instrum. Meth. Phys. Res. Sect. A Accel. Spectrometers Detect. Assoc. Equip. 226, 542–548 (1984). https://doi.org/10.1016/0168-9002(84)90077-9
[37] B. Bewer, Soller slit design and characteristics. J. Synchrotron Radiat. 19, 185–190 (2012). https://doi.org/10.1107/S0909049511052319
[38] E.A. Stern, S.M. Heald, X-ray filter assembly for fluorescence measurements of X-ray absorption fine structure. Rev. Sci. Instrum. 50, 1579–1582 (1979). https://doi.org/10.1063/1.1135763
[39] Y.Y. Yang, Q. Gao, S.Q. Gu et al., Soller slits automatic focusing method for multi-element fluorescence detector. Nucl. Sci. Tech. 27, 115 (2016). https://doi.org/10.1007/s41365-016-0105-7
[40] L.Y. Feng, J.S. Iwanczyk, B.E. Patt et al., Vortex: a new high performance silicon multicathode detector for XRD and XRF applications. Proc SPIE 5198, 103–110 (2004). https://doi.org/10.1117/12.511849
[41] J. Wong, B. Rupp, Reference X-Ray Spectra of Metal Foils. EXAFS Materials, Inc.: 871 El Cerro Blvd, Danville, CA, USA, (1999).
[42] B. Ravel, M. Newville, XAFS Data Interchange: a single spectrum XAFS data file format. J. Phys. Conf. Ser. 712, 012148 (2016). https://doi.org/10.1088/1742-6596/712/1/012148
[43] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. (2005). https://doi.org/10.1107/s0909049505012719
[44] K.Q. Lu, E.A. Stern, Size effect of powdered sample on EXAFS amplitude. Nucl. Instrum. Meth. Phys. Res. 212, 475–478 (1983). https://doi.org/10.1016/0167-5087(83)90730-5
[45] B. Nordfors, The statistical error in x-ray absorption measurements. Arkiv Fysik 18, 37-47 (1960).

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