

I-1. PROJECT RESEARCHES

Project 5

An Operando Spectroscopic Methodology for Elucidating the Transient Intramolecular Dynamics of Aromatic Polymers under Ionisation

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PROGRAM OVERVIEW:

Aromatic ring polymers demonstrate significant potential for radiation detection without fluorescent dopants; nonetheless, fundamental mechanisms governing such luminescence remain largely unmapped. Observations indicate that exposing these materials to low-intensity charged particles elicits unconventional optical responses that defy explanation via traditional fluorescence frameworks. It is postulated that these signals originate from a transient metamorphosis of the polymer's intrinsic properties during irradiation—a phenomenon that terminates abruptly upon removal of the source. To transcend inherent constraints of "post-irradiation" analysis, an operando methodology has been pioneered. This platform facilitates simultaneous, real-time tracking of interatomic bonding, structural geometry, and electronic configurations. By capturing these "active" molecular states, this enquiry endeavours to pinpoint critical thresholds where optical characteristics transition, thereby unveiling the intricate reorganisation of energy levels occurring during ionisation.

IMPLEMENTATION:

To advance this enquiry, a versatile experimental framework has been engineered to integrate polymer samples with radiation sources within diverse analytical suites. Navigating the stringent spatial limitations of Raman, infrared, and ultraviolet-visible spectrophotometers necessitated a radical reappraisal of source design. Whilst the ultimate objective remains the fabrication of tailored sources via 3D printing, technical hazards during the prototypical phase were mitigated by refining a deposition method based upon 2D printing techniques. By employing functional media upon paper substrates, a significant breakthrough was achieved in the manufacture of prototype emitters. Initial trials focused on Polyethylene Terephthalate to probe its molecular behaviour in situ via operando measurement. These experiments yielded results synchronised with the irradiation cycle: whilst X-ray diffraction confirmed that the underlying atomic framework remained intact, a profound suppression of Rayleigh scattering was witnessed alongside a sharp amplification of Raman signals. Such a distinctive correlation cannot be attributed to internal luminescence alone, suggesting a temporary shift in the electronic landscape. Having amassed a substantial corpus of spectral data, current efforts are occupied with defining the "singular points" of this transition. This knowledge is instrumental in establishing a new paradigm for designing superior radiation-sensitive materials based upon the transient dynamics of polymers under ionisation.

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Elucidation of the Dynamic Structures of Polymers under Ionisation

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INTRODUCTION:

We aim to elucidate the nature of anomalous optical signals observed in synthetic molecules upon exposure to charged particles—signals that are difficult to attribute to internal luminescence, such as fluorescence. It is highly probable that these signals arise from a 'switching phenomenon', whereby exposure to weak charged particles induces a temporal modification of the molecule's intrinsic optical properties. Given that this phenomenon vanishes immediately upon the cessation of irradiation, acquiring detailed observations has historically proven elusive. However, it is increasingly evident that the electronic states within the molecule undergo a dramatic transition between a steady state and an ionised state in response to the initiation and termination of irradiation. By employing operando measurements to track the real-time dynamics of bond strengths, constituent elemental arrangements, and electron distributions under irradiation, this research seeks to establish the fundamental physical mechanism underlying this hitherto unknown switching phenomenon.

IMPLEMENTATION:

Focusing on the enigmatic optical signals exhibited by undoped fluorescent polymers under environmental levels of charged particles, we formulated a working hypothesis: ionising radiation, resonating with the dynamic structure of the base adjacent to the aromatic ring, temporarily delocalises the intramolecular electron distribution. This induces a novel molecular mode that modifies inherent optical properties. To verify this hypothesis, we conducted pilot experiments for the operando measurement of molecular states under ionising radiation, integrating polyethylene terephthalate (PET) samples with a Strontium-90 source within various photometric instruments. These observations yielded critical data approaching the mechanism's core. Specifically, while X-ray diffraction confirmed the static structure remained stable during irradiation, the optical response exhibited profound alterations. We successfully captured mysterious, correlated events unexplained by conventional theories: a substantial attenuation of Rayleigh scattering for visible light, accompanied by a simultaneous, significant increase in Raman scattering intensity. Crucially, these anomalous responses vanished instantly upon removal of the radiation source, with all spectra returning perfectly to their original stable states. The acquisition of these reversible and highly correlated data sets provides robust evidence of the project's progression. Future work will focus on identifying critical points at which the optical system undergoes dramatic transitions relative to dose, while further scrutinising transition processes of bond strengths and electron distributions to fully reveal the mechanisms of ionisation-induced dynamic structural transformation.

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Advancements in the Development of an Operando Ionization Measurement System

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INTRODUCTION:

Undoped fluorescent polymers containing aromatic rings have emerged as a significant focal point in radiation measurement technology. Conventionally, their luminescence behavior has been interpreted through ladder model based on electronic transitions within the molecular structure. However, in the detection of environmental-level charged particles, pulsed fluorescence emissions—distinctly inconsistent with existing theoretical predictions—have been repeatedly observed specifically in the presence of charged particles. To transcend these theoretical frameworks and elucidate this phenomenon as a physical reality, "operando measurement" has become an indispensable methodology, enabling the dynamic tracking of intramolecular electron distribution and bond strength variations associated with the activation and deactivation of radiation.

IMPLEMENTATION:

In this study, we established a robust foundation for operando measurements by developing original sample and radiation-source support stands compatible with a wide array of spectrometers, designed to capture the "live" molecular electronic states within polymers during irradiation. Using this system, we have recently completed a comprehensive spectral analysis under irradiation for a broad range of aromatic polymers, including PET. Following the acquisition of an extensive dataset documenting changes in various spectra in the presence and absence of charged particles, we are now concentrating our efforts on the most critical objective: identifying the "singular points" where optical properties switch. The successful identification of these singular points will reveal, for the first time, the dynamic process of orbital energy reorganization under ionization. These research achievements have served as a novel bridge between science and society through their dissemination to approximately 2,000 high school students. During this initiative, 460 students who deeply internalized the technical essence of the research re-synthesized the information into hand-drawn illustrations in their own sketchbooks. Subsequently, at the Expo 2025 Osaka, Kansai, Japan, these students took the stage with their sketchbooks to enthusiastically introduce our findings to the visitors. This seamless flow of knowledge—from researchers to students and onward to the general public—garnered significant media attention, standing as a testament to the profound social impact of this project.

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Progress in the Development of a Radioactive Source Unit for an Operando Ionization Measurement System

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INTRODUCTION:

In the field of safety management for radiation facilities and nuclear power plants, polymer materials containing aromatic rings have attracted significant attention as functional elements for radiation detection. While their fundamental operational principle is based on the ionizing effects of radiation, the transient, microscale reaction processes occurring at the onset of irradiation remain insufficiently understood. We aim to develop an operando measurement system designed to monitor these microscale physical and chemical transitions within polymer matrices in real-time. A critical technical challenge in realizing this system is the in-house fabrication of radioactive sources with customizable geometries, ensuring compatibility with the highly restricted spatial envelopes of various analytical instruments.

IMPLEMENTATION:

To achieve a precise analysis of intramolecular electronic states under environmental-level low-dose irradiation, it is imperative to simultaneously integrate both the polymer sample and the radiation source within the highly restricted sample chambers of X-ray diffractometers and various spectrometers. Commercially available radioactive sources, which are characterized by standardized dimensions, present significant challenges for such integration across diverse analytical platforms. While our ultimate vision involves the utilization of 3D printing technology for customized source molding, we pivoted toward establishing foundational techniques using a more accessible 2D printing approach to mitigate substantial capital and technical risks during the prototyping phase.

Through this strategic approach, we successfully developed a precision deposition technique using potassium solutions as functional ink on paper substrates, representing a major milestone in the fabrication of prototype beta-particle sources. The cutting-edge insights gained from this project extend far beyond the laboratory. We conducted specialized technical lectures for approximately 2,000 high school students, providing them with a foundational understanding of this innovative measurement technology. Among them, 460 students who demonstrated a profound mastery of the technical essence took a leading role at Expo 2025 Osaka, Kansai, Japan. These students shared and interpreted the research findings for an audience of approximately 10,000 visitors, including both the general public and subject-matter experts. This initiative, bridging the gap between frontier science and society, contributes significantly to the cultivation of the next generation of scientists and the enhancement of public literacy regarding radiation science.

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