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organic materials

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ABSTRACT

This brief report reviews some of the recent findings in the study of synchrotron based X-ray excited optical luminescence (XEOL) from representative organic light emitting device (OLED) and related functional organic materials. The systems of interest include Alq₃, aluminium tris(8-hydroxyquinoline); Ru(bipy)₃²⁺, tris-(2,2-bipyridine) ruthenium(II); Ir(bpy)₃, tris(2-phenyl-bipyridine)iridium; PVK (poly(N-vinylcarbazole)) and [Au₂(dppp)(bipy)]²⁺, a Au(I) polymer containing 1,2-bis(diphenylphosphino)ethane and the 4,40-bipyridyl ligands, as well as TBPe (2,5,8,11-tetra-tert-butylperylene) polyhedral crystals and fluorescein isothiocyanate (FITC) and FITC-labelled proteins. It is shown that tunable and pulsed X-rays from synchrotron light sources enable the detailed tracking of the optical properties of organic functional materials by monitoring the luminescence in both the energy and time domain as the excitation energy is scanned across an element-specific absorption edge. The use of XEOL and X-ray absorption spectroscopy (XAS) in materials analysis is illustrated.

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1. Introduction

The discovery of the light emitting compound Alq₃ (aluminium tris(8-hydroxyquinoline)) as an organic functional material in a device now commonly known as OLED (organic light emitting device) in the last decade of the 20th century led to a revolution in the energy saving lighting and display technology that continues today [1–6]. Of particular interest is the interplay among optical properties, electronic structure, and morphology of OLED materials. A typical OLED comprises a sandwich of an electron transport (ET) layer such as Alq₃ (tris-8-hydroxyquinoline) and a hole transport (HT) layer such as poly(N-vinylcarbazole) (PVK) between two electrodes. The injection of electrons (by applying a negative voltage) into the electron transport layer, usually a material with low-lying lowest unoccupied molecular orbital (LUMO), results in light emission from the electron–hole combination at the ET–HT interface.

In parallel to this development in a different branch of science is the evolution of synchrotron technology and a technique called XEOL (X-ray excited optical luminescence) using tunable synchrotron X-rays. XEOL monitors how a material converts the X-ray energy it absorbs into visible light [7–12]. Tunable X-rays from the synchrotron light source allows for the preferential absorption of X-ray energy by an element in a given site of the system of

interest through the X-ray absorption edges. Thus, it has bearing on understanding the light emitting process in OLED and related applications. While there has been a couple of reviews on XEOL [7,10], discussion specifically devoted to XEOL from OLED and functional organic materials is lacking. This review article fills the gap and highlights representative XEOL studies in both the energy and time domain conducted on organic functional materials.

The objective of this article is to provide a brief yet comprehensive description of the XEOL technique and its application in the study of OLED materials, as to be distinguished from the laboratory techniques such as photoluminescence (PL) and electroluminescence (CL) that are more familiar to the practitioners in the field of OLED [13]. XEOL investigations of representative functional organic materials, such as Alq₃, aluminium tris(8-hydroxyquinoline) [14,15]; Ru(bipy)₃²⁺, trisere-(2,2-bipyridine)ruthenium(II) [16,17]; and Ir(bpy)₃, tris(2-phenyl-bipyridine)iridium [18,19], among others, will be presented to illustrate how XEOL can be used to understand the electronic structure and optical properties of these materials, which also depend on the morphology, dimensionality and crystallinity (impurities and defects) of the materials and the system of interest [20,21]. The results discussed here are necessarily focused in scope and are mainly based on work from the author's laboratory. The implications of the results and the prospects of the interplay between materials properties and the XEOL technique for research of light emitting materials and related phenomena will be discussed.

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2. X-ray absorption spectroscopy (XAS)

The XEOL technique monitors how effectively a functional material converts the X-ray energy it absorbs into optical photons (near UV–visible–IR). This behaviour is intimately related to the composition, morphology, size and crystallinity (defects) of the material as well as the absorption and the de-excitation process [14–21]. While XEOL can be conducted in the laboratory with an X-ray anode of fixed energy and the phenomenon is as old as the discovery of X-rays, XEOL using tunable synchrotron light as an excitation source becomes a very powerful tool when the optical response (light emission from the near UV to IR) of an element in a given functional material following X-ray absorption is tracked across an absorption edge, for example the C, N, O and Al K-edge in Alq₃. Since XEOL induced by X-ray absorption across an edge is element and excitation channel specific and ties to the absorption spectroscopy at a given absorption edge of interest, our discussion begins with X-ray absorption spectroscopy [23–25].

X-ray absorption spectroscopy (XAS) is a general term for X-ray absorption fine structure spectroscopy (XAFS) which deals with the measurement and interpretation of the modulation of the absorption coefficient above an absorption edge when a free atom is placed in a chemical environment. It is also known as core level spectroscopy [25]. Traditionally, XAFS is divided into the “near edge region”, absorption from just below to ~50 eV above the threshold and the “extended region”, absorption from ~50 eV to as much as 1000 eV above the threshold. This division is a matter of convenience since the excited electron in the “near edge region” possesses low kinetic energy favouring multiple scattering pathways and in the “extended region”, high kinetic energy favouring single scattering pathways. The “near edge region” is often referred to as XANES (X-ray absorption near edge structure) or NEXAF (near edge X-ray absorption fine structure) although they are used interchangeably in the literature. In this article we use XAS for short to represent XANES/NEXAFS and it will be the main region of interest. The extended region is called EXAFS (extended X-ray absorption fine structure) which is less applicable for low Z elements and will not be discussed here in detail.

3. Soft X-ray XAS, sampling depth and XEOL

In this discussion, soft X-ray XAS is often used together with XEOL. Soft X-ray in the context of this discussion refers to photons with energy from ~50 eV–5000 eV provided by grating monochromators (up to ~2000 eV) and crystal monochromators using for example InSb(1 1 1) double crystals (~1800 eV–10 keV). Soft X-ray is predominantly used in the XEOL studies of functional organic

materials simply because the core level energy of low Z elements such as C, N and O lies in the soft X-ray region.

Soft X-ray has advantages over hard X-rays in that modern beamline technology can provide photons with extremely high energy resolution: e.g. an undulator based SGM beamline can deliver photons with $E/\Delta E > 10,000$ at the N K-edge (~400 eV) [26]. Also, the inherent core hole lifetime broadening is small. Thus high energy resolution and hence high chemical sensitivity can be obtained. In addition, soft X-rays have shallow penetration depths, thus total absorption condition can often be met. This has very interesting implications for the interpretation of XEOL. Fig. 1 illustrates the penetration depth of soft X-rays across all the edges in Alq₃ and all shallow edges in Ir(pppy)₃ based on atomic calculation [27]. It should be noted that XAS in the soft X-ray energy range can rarely be obtained in the transmission mode which requires a very thin specimen as we can see from Fig. 1, instead, measurements are often made in yields such as total electron yield (TEY), X-ray fluorescence yield (FLY) and photoluminescence yield (PLY), of which TEY is proportional to the absorption while FLY and PLY XAS can suffer from distortion due to self-absorption (thickness effect) and abrupt change of thermalization pathways of electrons across the edge, respectively [22].

Several interesting features from Fig. 1 are noted. First, the penetration depth of soft X-rays is typically small, less than 1 μm up to the O K-edge. Second, C is the dominant element and the penetration depth, hence the sampling depth, changes most abruptly and drastically from below to above the C K-edge, by a factor of 10 from ~μm to ~100 nm. This change will have a noticeable effect on the energy transfer of the absorbed X-ray energy to the optical channel to be discussed below. Finally, high Z element such as Ir has high cross sections for its shallow levels such as Ir N_{7,6} (4f_{7/2,5/2}) below the C K-edge. Competition of photon flux across an edge has some interesting implications for XEOL.

The XEOL process is more complex comparing to the photoluminescence (PL) and electroluminescence (EL) in that XEOL arises from de-excitation through a cascade process following the creation of a core hole. The photoelectrons and Auger electrons thermalize in the solid via inelastic scattering (energy loss), producing shallower holes and secondary electrons, this process continues along a thermalization track until the electrons finally settle down at the bottom of the conduction band (LUMO in molecules) with corresponding holes at the top of the valence band (HOMO in molecules). The thermalization path of electron with a given energy can be tracked with the universal electron escape depth [28]. The electron–hole pair can recombine radiatively via the formation of an exciton in semiconductors and excimers or exciplex in molecules involving more than one molecule in the solid. For example, emitting photon with energy near that of the band gap (HOMO–LUMO

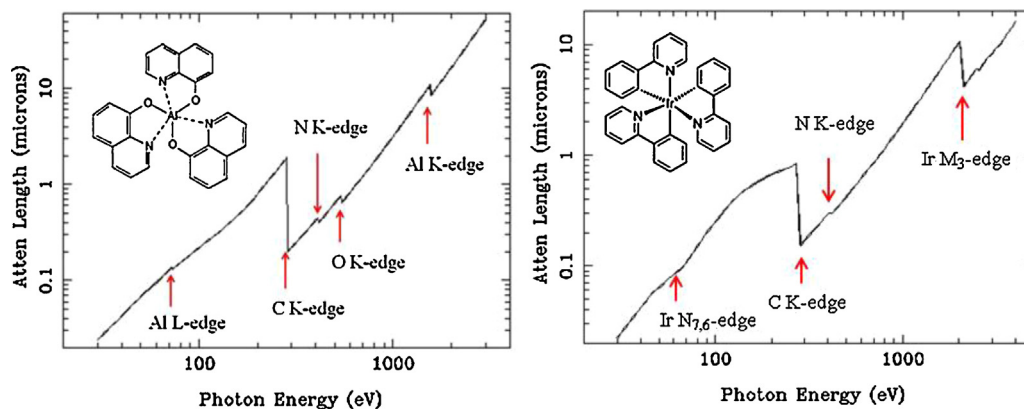


Fig. 1. Attenuation ($1/e$) of X-rays across all absorption edges of elements of interest in Alq₃ (left panel) and shallow edges in Ir(pppy)₃ (right panel).

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