"Soft X-ray excited optical luminescence from functional 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, aluminum 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(dppe)(bipy)]²⁺, a Au(I) polymer containing 1,2-bis(diphenylphosphino)ethane and the 4,4'-bipyridyl ligands, as well as TBPe (2,5,8,11-tetra-tert-butylperylene) polyhedral crystals and fluorescein isothiocyanate (FITC) and FITC-labeled 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.

1. Introduction

The discovery of the light emitting compound Alq₃ (aluminum 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, aluminum tris(8-hydroxyquinoline) [14,15]; Ru(bipy)₃²⁺, tris(2,2'-bipyridine)ruthenium(II) [16,17]; and Ir(bpy)₃, tris(2-phenylbipyridine)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 focussed 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.

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 favoring multiple scattering pathways and in the “extended region”, high kinetic energy favoring 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 any 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 InSb (111) double crystals for example (~ 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 corehole 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. Figure 1 illustrates the penetration depth of soft X-rays across all the edges in Alq_3 and all shallow edges in $\text{Ir}(\text{ppy})_3$ 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]

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

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 $\sim \mu\text{m}$ to $\sim 100 \text{ nm}$. 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 separation) minus the binding energy of the exciton will produce narrow near band gap emission [29]. Energy transfer can also take place in the presence of defects (vacancies and impurities) resulting in optical emissions at longer

wavelengths [10, 11, 21]. Usually, band gap emission is fast and defect emission is slow. The branching ratio (emission intensity of a given band over the intensity of the entire spectrum) is also excitation energy, morphology, size and crystallinity dependent. Fortunately for functional organic materials, the cascade can be tracked more easily since the electrons filling the shallow core hole of low Z elements come directly from the valence band.

The above-mentioned behaviour is illustrated in Figure 2 where a schematic for the excitation and subsequent decay of a core hole associated with XAS is shown on the left [28] and the kinetic energy dependent escape depth of electrons in condensed matter is shown on the right [29]. The escape depth can be used to describe the thermalization path of electrons; that is that the more energetic the electron, the larger the escape depth, and the longer the thermalization path. Since electrons with energy on the order of 10^2 - 10^3 eV are often produced in soft X-ray XAS and the corresponding escape depth is on the order of nm to several tens of nm, respectively, comparable to the size of nanostructure, the thermalization path is truncated in nanostructures; this situation results in incomplete thermalization of the energetic electrons hence a reduction in their contribution to PLY. It has significant bearings on the XEOL behaviour across an absorption edge when the absorption coefficient increases dramatically at the edge hence the sampling depth decreases accordingly as is the redistribution of energy of the electrons when a new Auger channel is turned on, leading to distortion or even inversion in XAS recorded with optical yield.

Figure 2 Left: XAS at and above the edge (vertical arrows), the core hole decays via primarily an Auger process (dotted arrows); the photoelectron and Auger electron thermalize (dashed arrows) producing secondary electrons (e) and holes (h) in their path which settle in the bottom of the CB and the top of the VB, respectively; radiative $e + h$ recombination yields near band gap (*: exciton) and defect emission (downward arrows). Right: the universal curve of the electron escape depth in solid.

4 XEOL from functional organic materials

4.1 XEOL from Alq₃ with core and valence excitation

Figure 3 shows the XEOL (normalized to incoming flux I_0) from Alq₃ with excitation across the C, N and O K-edge and the XAS recorded with total electron yield (TEY), X-ray fluorescence yield (FLY) and photoluminescence yield (PLY) [14]. It is interesting to note that all XEOL spectra exhibit a two-peak pattern which differs from the UV-excited luminescence and electroluminescence which often appear as a broad peak at 530 nm with a short wavelength shoulder [1-4]. The separation of the two optical bands is 0.2 eV, in good accord with the notion of electron-hole recombination suggesting that the HOMO triplets from all three ligands are involved in the luminescence.

XAS recorded in PLY (zero order) shown in Fig. 3 exhibit essentially the same spectral patterns as TEY at all edges. This observation indicates that C, N, and O absorptions transfer the energy effectively to the optical channel. The resonances at C K-edge are associated with transitions from the core (1s) to LUMO and LUMO+1, which contain a significant contribution of the C to the unoccupied molecular orbitals. The complexity of C K-edge XAS arises from the fact that each carbon contributes differently to the unoccupied molecular orbital depending upon where it is on the phenoxide or pyridal ring. These features are enhanced noticeably in the PLY in relation to the intensities of the other C K-edge XAS features compared to TEY. Since the LUMO (π^*) is populated directly by these transitions, and the associated Auger decay populates the HOMO holes, it was proposed that these transitions would produce enhanced luminescence, hence, some degree of site specificity [14].

Figure 3 Left: XEOL from excitation at energies below and above the C, N and O K-edge. Right: XAS recorded with PLY (zero order) TEY and FLY; noticeable enhancement is observed at the C K-edge π^* resonance.

Figure 4 Left: Excitation spectrum (2.3 eV) at the valence region (top) and Al K-edge XAS with TEY, FLY and PLY (bottom). Right: XEOL excited at 5.63 eV, 285.2 eV (C K-edge), 402.5 eV (N K-edge), 540.9 eV (O K-edge) and 1565 eV (Al K-edge) (bottom); the branching ratio of the optical features (top panel) is also shown. The inset compares XEOL from 5.63 and 1565 eV photon excitation with identical area under the curve.

The more interesting comparison can be seen in Fig. 4 where light emission from an Alq_3 film on a Si(100) wafer was tracked when valence electrons and the deepest core electrons in the K shell of Al were excited. Let us consider the PLY, which is analogous to the excitation spectrum in PL with luminescence yield at ~ 2.3 eV. The intense peak at 2.75 eV is attributed to the HOMO–LUMO excitation. The features at 3.6 eV and 4.1 eV are attributed to excitation of HOMO, HOMO minus to LUMO and LUMO plus, etc [14].

The PLY XAS tracks the optical response when the absorption of the incoming flux is abruptly redistributed (e.g. C absorbs a larger fraction of the incoming photon flux above the C K-edge) and nearly all the photons are absorbed below and above the edge for low Z elements. Since Al is nominally 3^+ with no d electrons and it will not directly contribute to XEOL via d-d or metal-ligand electron transfer as is the case in transition metal complexes. When excited below the Al K-edge, the luminescence is induced by the excitation of the lower Z elements, especially carbon via thermalization of the photo and Auger electrons. At photon energies above the Al K-edge, a larger fraction of the photon flux will be absorbed by the Al (see Fig.1). This produces energetic Al KLL Auger electrons and subsequently thermalized secondary electrons and holes in the ligand. Since, the photon has significant penetration depth at the Al K-edge, the Auger electrons will sufficiently thermalize leading to the PLY XAS resembling that of the TEY and FLY. Thus Alq_3 is one example where all excitations contribute nearly equally and effectively to the luminescence channel with perhaps a small enhancement at the C $1-\pi^*$ resonance. A couple of features on the right panel of Fig. 4 are worth noting. First, the intensity ratio of the doublet is

relatively constant for the C, N and O K-edge excitation. Second the relative intensity of the doublet exhibits an opposing trend in that the intensity for both components is about the same with low energy excitation (5 eV) whereas the intensity of the 2.29 eV peak is twice as that of the 2.54 eV peak with high-energy excitation (1565 eV). This is also accompanied by a slight shift. Hence, the difference between valence and Al K-edge excitation (inset) is more dramatic, it may suggest that the presence of the core hole favors the formation of exciplex, excited states involving more than one molecule.

4.2 XEOL from Ru and Ir complexes in both the energy and time domain

The C and N K-edge XAS of $\text{Ru}(\text{bipy})_3(\text{ClO}_4)_2$ in TEY, FLY, and PLY are shown in Figure 5. The inset displays the normalized XEOL across the C K-edge with the most intense yield observed at the first resonance [15, 16].

Figure 5 (a) C K-edge, (b) N K-edge and (c) Ru $L_{3,2}$ -edge XAS of $\text{Ru}(\text{bipy})_3(\text{ClO}_4)_2$. The inset in (a) shows the normalized XEOL at selected photon energies (in eV) below and above the C K-edge; PLY XAS at the N K, Cl K and Ru $L_{3,2}$ edges are also shown.

The two peaks at 285.7 and 286.5 eV at the C K-edge are the $1s-\pi^*$ transitions from non-equivalent carbons on the bipyridine ring. The C atoms not bonded directly to the electronegative N are less tightly bound, in good accord with the results of Alq_3 . From Fig. 5(a), we see that both zero-order and 655 nm PLY are similar as expected. The PLY exhibits two interesting features. First, relative to TEY, the first resonance is more intense than the second. This is attributed to the PLY contribution from the Ru M_4 edge just below the C K-edge. Second, the broad resonance at 289 eV is suppressed in the PLY. This feature is the $1s-\sigma^*$ transition where the electron with

kinetic energy below the universal curve minimum can tunnel out into the continuum, suppressing luminescence. The N K-edge, Fig. 5(b), in PLY is inverted however, indicating that the N 1s to π^* and continuum transition is less effective in transferring the energy it absorbs to the optical channel comparing to the excitation of C at the same photon energy. This is in contrast to the N K-edge PLY observed in Alq₃; this will be discussed further below in connection with ligand metal interaction.

The Ru L_{3,2}-edge XAS of Ru(bipy)₃(ClO₄)₂ monitored with FLY and PLY (similar to TEY, not shown) in Fig. 5 (c) also displays the Cl K-edge from the Cl in the ClO₄⁻ counter ion. It is observed that the PLY also reproduces the edge jump at the Cl K-edge and the Ru L_{3,2}-edge similar to that of the TEY. The more intense edge jump in the FLY for CL K-edge reflects the higher FLY for the Cl K-edge fluorescence since FLY in this case was collected in the total fluorescence yield with a channel plate. The Cl KLL and Ru LMM Auger thermalize sufficiently and the energy transfer to the optical channel effectively reproduces the XAS.

Figure 6 shows the XAS at relevant edges and XEOL from another small molecule OLED compound, Ir(ppy)₃ [18, 19]. It is interesting to note that while there is a dominant emission at 534 nm with longer wavelength shoulders at 580 nm and 630 nm, similar to PL observations, the PLY XAS at the C and N K-edge are both inverted and the Ir M_{3,2} edge PLY is the right side up albeit with a reduced whiteness (WL) intensity relative to the edge jump when compared with the TEY XAS. Inversion in PLY XAS is not uncommon in soft X-ray region, especially when there is an abrupt increase in absorption coefficient at the edge [10, 22]. From Fig. 1, we see that the penetration depth can become very shallow for a sharp increase in absorption coefficient. Thus Auger electrons created in the surface and near surface region will leave the system without undergoing complete thermalization. An increase in absorption coefficient means a decrease in probing depth hence an increase in energetic electrons from the surface and near surface region. The incomplete thermalization of energetic electrons will reduce the quantum yield.

Figure 6. (a) C K-edge, (b) N K-edge and (c) Ir M₃-edge XAS of Ir(ppy)₃. The inset of (a) shows the XEOL at 278 eV. XEOL at the Ir M₃-edge is the inset in (c) where the PLY XAS at the Ir M₃-edge is compared with TEY and FLY.

This effect combines with less effective quantum efficiency above the edge will lead to the inversion of the PLY XAS. This is more likely to occur with nanostructures which possess a much larger surface and near surface area.

We now turn to the dynamics of the XEOL process. Since synchrotron is a pulse source, there is a dark gap between pulses allowing for tracking the optical decay dynamics of the system. For example, the single bunch operation of the Canadian Light Source provides a pulse of ~30 ps width and a dark gap of 570 ns while the Advanced Photon Source provides a ~30 ps pulse with a dark gap of 153 ns during a top-up operation with 24 bunches. Figure 7 shows the schematic of the XEOL measurements in the time domain (left panel) [11]. Using the synchrotron pulse as a stop and the XEOL signal as the start, we can track the lifetime of all light emitted in the optical region in the dark gap using a TAC (Time to Analog Converter) and associated electronics [11]. Time resolved XEOL (TRXEOL) can be used to obtain time-gated luminescence by selecting a time window as shown in the upper right corner of Fig.7 where a red bar and a blue bar represent a fast and a slow window, respectively from the zero order emission. An example of this is illustrated in the bottom left panel where the fast emitting 534 nm is detected in the fast window only while the slower emissions are clearly observed in the slow window [18]. The lifetime of each individual optical channel can also be measured as shown in the bottom right panel.

Figure 7 Top: schematic for the time structure of a synchrotron and time-gated spectroscopy; the decay of the total optical emission can be gated with a fast (red bar) and slow (blue bar) time window. Bottom left: TRXEOL from Ir(bpy)₃ with a fast (0-10 ns) and a slow (10-550 ns) time window using a single bunch at the CLS (570 ns). Bottom right: Decay curve (lifetime) of emission at wavelengths as noted.

XEOL and TRXEOL can also be tracked in the hard X-ray region although the energy transfer is less effective since the de-excitation yields more energetic X-rays, photoelectrons and Auger electrons which will not completely thermalize. Figure 8 (a) shows the TRXEOL from a 1,10 phenanthroline (phen) rthenium complex, Ru(phen)₃²⁺ excited at the Ru K-edge (22140 keV) [17]. It is apparent from Fig. 8 that the fast decay channel from the ligand emission at 324nm is not observable in the un-gated measurement but is clearly revealed when it is time-gated with a fast window. Fig. 8(b) shows the Ru K-edge XAFS of Ru(phen)₃²⁺ monitored with PLY (zero order) which resembles that of the TEY (not shown). Again, TRXEOL can be used to measure the lifetime of each individual optical channel as shown in Figure 8(c) where the fast and slow lifetime decay of the 324nm (ligand alone) and 613nm (metal –ligand) emission is displayed.

Figure 8. (a): TRXEOL from $\text{Ru}(\text{phen})_3^{2+}$ ungated and gated with fast (10 ns) and slow (10 - 150 ns) time windows; data were recorded at APS running in a top-up mode (153 ns). (b): PLY XAS of $\text{Ru}(\text{phen})_3^{2+}$ at the Ru K-edge. (c) Lifetime of the slow 613nm (metal-ligand) and the fast 324nm (ligand only) emission.

4.3 XEOL from poly(N-vinylcarbazole) (PVK)

PVK is a polymer with an alkyl chain and a carbazole group as shown in Fig. 9. It has been used as a HT layer in OLED [30-32]. It contains aliphatic and aromatic carbon linked by a N atom. Delocalization of electrons takes place throughout the carbazole moiety via p bonding. PVK begins to absorb at 350nm in the UV-visible spectrum with well-defined features towards the visible. It is well known that UV excited photoluminescence (PL) of PVK in solution shows a PL maximum at 426 nm and a shoulder at 380 nm. A number of experiments have been conducted to confirm the origin of these two peaks: they are due to the de-excitation of intra-chain excimers with overlapping aryl rings from adjacent units in a sandwich arrangement [33-35]. Similar behavior has been observed in the PL and EL of PVK films [36].

Figures 9(a) and (b) show the XAS of C and N K-edges, respectively, recorded in TEY together those in FLY and PLY [37]. The XEOL of PVK excited with a series of photon energies from 280 eV (just below the C K-edge threshold) to 570 eV, (significantly above the N K edge) is displayed in Fig. 9 (c). The first two peaks at 286.3 and 288.0 eV of the C K-edge XAS are attributed to the C 1s to π^* resonance from the carbon atoms in the carbazole. The more electronegative nitrogen in PVK increases the unoccupied p character at the C site directly bonded to N. We attribute the first resonance to the carbon atoms associated with the rings except for those bonded directly to N and the second resonance to the carbons bonded directly to N. The third peak is attributed to the C 1s to C-H σ^* resonance. The broader peaks at higher

photon energies are due to transitions to quasi-bound states e.g., a C–C σ^* above the vacuum level, sometimes referred to as a multiple scattering state or a shape resonance. The N K-edge XAS in Fig. 9(b) exhibits a less intense peak at the 403.8 eV resonance. This is attributable to the N 1s to the unoccupied molecular orbital containing N p character.

Figure 9. (a) C K-edge and (B) N K-edge XAS of PVK recorded in TEY, PLY and FLY. (c) XEOL from PVK excited with photon energy from below the C K-edge to above the N K-edge.

The XEOL peaks at 410 nm and 380 nm in Fig. 9(c) have been generally recognized as intra-chain excimer emissions [36]. The 550–585 nm spectral features have also been observed previously [36]. These features together with the longer-wavelength emission are attributed to MO-MO type transitions of the carbazole moiety [37]. It is interesting to note that these features become more complex, when the excitation is above the C and N threshold, indicating the involvement of several MO's below the HOMO and LUMO plus.

4.4 XEOL from organo-gold compounds

Another class of organometallic compounds that exhibits interesting properties for OLED, is organo-gold compounds. Gold(I) complexes with oligomeric or polymeric structures are of particular interest since they exhibit strong visible luminescence at room temperature [38,39]. Here we present a gold(I) complex with diphosphine and 4,4-bipyridyl ligands to illustrate the site specificity of XEOL [40, 41].

The system is $[-\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2-\text{AuNC}_5\text{H}_4\text{C}_5\text{H}_4\text{NAu}-]_x^{2x+}[\text{CF}_3\text{CO}_2^-]_{2x}$, where $n = 2$, henceforth denoted $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$ where dppe and bipy represents the 1,2-bis(diphenylphosphino)ethane and the 4,4'-bipyridyl ligand, respectively. This complex is of particular interest among a family of complexes with a varying hydrocarbon chain length (n in the molecular structure above). At issue are the origin of the luminescence and the role of the Au-Au interaction between adjacent chains.

Figure 10. (a) The normalized TEY of $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$, dppe, and bipy ligand at the C K-edge. The vertical lines denote the 1s to π^* transition of primarily bipy and dppe. (b) XEOL at the excitation energy of 285.5 eV; inset: the room temperature UV emission spectrum of $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$ with $h\nu_{\text{ex}} = 300\text{nm}$. (c) C K-edge TEY and PLY (zero order), the arrows show the origin of the π^* resonance showing site specificity.

Fig. 10 (a) and (b) show the C K-edge XAS and XEOL excited at the most intense resonance of $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$ together with those of the individual ligands. For unsaturated organic molecules such as aromatics, the C K-edge typically exhibits two types of main transitions: the

intense and narrow feature at low energy (285–286 eV) represents a C 1s- π^* (bound state) transition, while the broad transition at higher energy (290–292 eV) represents a C 1s- σ^* (quasi-bound state involving carbon–carbon interaction) transition. There are also weak resonances in between associated with C 1s- σ^* transition of the C–H bond. It is apparent from Fig. 10(a) that all XAS exhibit a strong absorption at 285.5 eV, and a weak shoulder at 284.6 eV is seen in the spectra of $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$ and bipy. The XAS of the bipy ligand reveals that there are more than one 1s to π^* transitions and this can be attributed to the existence of three chemically non-equivalent carbons on the bipy ligand while such an effect in dppe is small and unresolved with the experimental energy resolution. The carbon atoms that are directly bonded to the more electronegative nitrogen can be associated with the higher energy transition. It is also apparent that the $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$ XAS is nearly the same as the sum of the XAS of the free ligands. From these results we conclude that the weak π^* shoulder in the C K-edge XAS of the gold(I) complex is mainly from the bipy ligand.

The XEOL in Fig. 10 (b) shows that dppe exhibits two broad bands, at 440 and 550 nm. At first glance it appears that the dppe could be the origin of the luminescence of the complex since the emission appears at the same wavelength region as that of $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$. The bipy ligand shows three broad bands, at 360, 550, and 700 nm with the strongest emission at 360nm showing a significant blue shift compared to the Au complex. It should be noted that bipy is not fluorescent in solution at room temperature. The solid state XEOL of bipy at room temperature is most likely of an excimer origin. It was previously proposed that the strong UV excited emission of this complex in the solid state originates from the ligand-based π – π^* transitions from the bipyridine derivatives since the energy difference between the neighboring bands is similar to the vibrational structure of bipyridine derivatives [41, 42].

Fig. 10(c) displays the C K-edge PLY XAS in which all optical photons from the gold (I) complex are collected (zero order). The PLY exhibits very important features that help track the origin of the luminescence. Close examination of TEY and PLY of $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$ reveals that the first π^* resonance is enhanced in PLY relative to TEY, while the main π^* resonance is significantly suppressed in PLY. Since the first resonance is mainly from the π^* transitions of the bipy ligand, the PLY vs. TEY comparison confirms that the luminescence of this complex is primarily from the bipy ligand. It is also interesting to note that the transition from C 1s to σ^* at

~290 eV shows a broad peak in the PL. This observation is in contrast to the study of $\text{Ru}(\text{bipy})_3^{2+}$ shown in Fig. 5(a) where the σ^* transition was suppressed. This indicates that in this gold(I) complex, both π^* and σ^* of the bipy rings are effectively coupled to the chromophore of the luminescence, probably induced by the Au(I)-Au(I) interaction since bipy emission in the gold complex is red shifted.

4.5 XEOL from TBPe (2,5,8,11-tetra-tert-butylperylene) polyhedral crystals

The recent report of successful synthesis of organic polyhedral crystals of TBPe with tunable shapes from cube, truncated cube, and rhombic dodecahedron via a simple surfactant-assisted process has opened up new opportunities in research and application of novel organic functional materials [43]. More importantly, it was found that changes in morphology were accompanied by changes in optical properties. XAS and XEOL have been used to provide more insight for the electronic and optical behaviour of TBPe polyhedral crystals with varying morphology from cube to truncated cube to rhombic dodecahedron (RD) [44].

Figure 11. SEM images of TBPe (2,5,8,11-tetra-tert-butylperylene) polyhedral crystals: (a) cubes, (b) intermediate, and (c) RDs; (d) the C K-edge XAS of corresponding powder. (e) XEOL from different crystals excited at 270 eV: from top: a, powder; b, cube; c, intermediate and d, dodecahedron. (f) Normalized XEOL of TBPe RD excited at different photon energy: below (270 eV), at (290 eV), and above the C K-edge (310 eV).

Fig. 11 (a)-(c) show the morphology of the TBPe and Fig. 11(d) shows the C K-edge XAS of a powder TBPe specimen where chemical inhomogeneity is clearly revealed with high energy resolution; that is that each chemically different carbon exhibits its own $1s-\pi^*$ transition at a slightly different energy. The XEOL excited at 270 eV are shown in Fig. 11 (e). It can be clearly observed in the inset that all the spectra of micro-crystals are red shifted compared to that of the TBPe powder. This is attributed to a much better defined structure in nano/microcrystals (well defined crystal faces) than that in powder. It is interesting to note that when the TBPe nano/microcrystal changes morphology from cube to RD, the intensity of peak 1 (477 nm) gradually decreases and this is accompanied by an increase in the intensity of peak 3 (535 nm) while the intensity of peak 2 (498 nm) shows no identifiable variation. Figure 11 (f) shows the XEOL of the RD crystal excited with photon energies across the C *K*-edge. All excitations produce a similar spectral pattern but at the C *K*-edge (290 eV) with the highest absorption coefficient, the intensities of peaks in the XEOL decreases. This is equivalent to a dip or inversion in the PLY XAS. It is believed to be related to the energy transfer associated with the TBPe crystal structure; i.e. the incomplete thermalization of Auger and photoelectrons in the crystal lattice and the reduction in sampling depth as observed in Fig. 6 (a).

4.6. XEOL from bio-organic fluorescent label: fluorescein isothiocyanate (FITC) and FITC-labeled proteins

Tracking protein crystal with XEOL is of considerable interest to the protein research community [45]. The molecule fluorescein isothiocyanate (FITC) and proteins labelled with FITC are ideally suited for imaging. Fluorescein-50-isothiocyanate (FITC) is one of the most commonly used fluorescent label in generating fluorescent proteins (antigens), which has been widely used in the immunofluorescence method (IF) [46]. FITC reacts with amino and thiol groups of proteins to yield fluorescein-50-thiocarbamoyl conjugates, N,N-disubstituted thiourea and dithiourethane adducts. The interaction involves the $-N=C=S$ group of the FITC with the thiol and the amino group of the protein [47]. The UV absorption and emission properties of many of the FITC conjugate proteins, such as FITC-Concanavalin A (Con A) lectin and FITC-immunoglobulin G (IgG) are well known [48 -50]. Typically, the FITC solution absorbs intensely around 480 nm and exhibits a emission maximum around 520 nm with excitation

energy of 495 nm, and the fluorescence properties of FITC are not essentially altered by the conjugation to the protein [51].

Fig. 12 shows the schematic of the FITC molecule and the XEOL from FITC, FITC-Con A conjugate, and FITC-IgG conjugate, respectively, excited at selected energies at the C, N and O K-edges [52]. Several interesting features are apparent. First, the XEOL from the FITC label has same spectral pattern with the maximum (~620 nm) red-shifted compared to its PL in solution by UV–Vis excitation, which shows a single peak at 515 nm. Second, FITC-protein conjugates exhibit two emission peaks at ~420 and ~540 nm, regardless of the excitation photon energy although the relative intensity changes somewhat and unlike the well known UV–Vis excited emission of the protein conjugate, which resembles the FITC solution emission (515 nm), the intense luminescence appears at a shorter wavelength (420 nm). Finally, the luminescence of the FITC-protein conjugates is not only blue-shifted but also significantly more intense than that of the FITC label in the solid state, indicating the importance of the conjugation and dilution for the enhancement of the luminescence intensity.

Figure 12 Schematic for FICT molecule and XEOL from FITC, FITC-Con A lectin conjugate, and FITC-goat-anti rabbit IgG conjugate at selected excitation energies at the C, N, and O K-edges.

Figure 13 shows the XAS at the C, N, and O K-edge in TEY and PLY modes. Let us first examine the XAS of the C K-edge. It should be noted that at the energies of interest, the TEY is surface and near-surface sensitive with the probing depth of 1 to 10 nm, while the PLY is bulk sensitive and can be site specific, probing at least an order of magnitude deeper. From Fig. 13, we see that both the TEY and PLY exhibit noticeably different features. The first two peaks around 285–288 eV are C 1s to π^* resonance from the non-equivalent, unsaturated carbon in the FITC (e.g. those in the aromatic ring, Fig. 12) and in the proteins; the peak at 290 eV represents the C 1s to C–H σ^* resonance. The much broader peaks at higher energies are due to the transitions to quasi-bound states of primarily σ character. The two sharp peaks around 298 and 300 eV in the TEY of FITC-Con A are the $L_{3,2}$ -edge from potassium on the surface. The TEY of the FITC shows that there are two peaks at ~285 eV resulting from transitions from C 1s to π^* orbitals of carbon–carbon bonds. Features from 286.5 to 288 eV are transitions to π^* orbital involving C=N, C=S and C=O bonds. The TEY of the conjugates reflect the presence of unsaturated C=C (285 eV), C–H (~289 eV) and saturated C–C (292 eV) bonding in the conjugate. The most interesting feature is found in the PLY XAS of FITC labeled proteins, which exhibit the same profiles as that of FITC. It is interesting to note that the resonance at the lower energy is enhanced in PLY whereas the resonance at slightly higher energy, the C–H σ^* transition at 289 eV for the proteins is inverted. This inversion comes about when the excitation channel is ineffective in transferring the energy to the optical channel (low quantum yield). This situation is reminiscent of the PLY in $[\text{Au}_2(\text{dppe})(\text{bipy})]^{2+}$ shown in Fig. 10 (c) where the aromatic ligand in bipy contributes dominantly to the luminescence. It should be noted that for the protein sample, when the photon is tuned to 289 eV, the C–H σ^* channel is switched on taking away a significant fraction of the incident photon that would have been absorbed by other channels with higher quantum yield. This observation confirms the site selectivity of the XEOL technique, which is that the PLY is associated with excitation of the atoms contributing to the molecular orbitals of FITC responsible for the luminescence.

Figure13. XAS of FITC , Con A lectin-FITC conjugate , and goat-anti rabbit IgG-FITC conjugate at the C, N and O K-edge in TEY and POLY.

The XAS at the N K-edge and O K-edge (Fig. 13) can be examined collectively. The sharp peaks at around 400 and 533 eV, respectively, represent the N and O 1s to π^* resonance. The broader peak at higher energy region is the transition to the quasi-bound states of σ character in both cases. Unlike the C K-edge, the POLY at both the N and O K-edge show completely inverted spectra. This inversion, as noted above, indicates that there is a drastic reduction in luminescence quantum yield when the N and O 1s to π^* transitions are turned on. In other words, the N and O excitation do not couple with the luminescence chromophore as effective as carbon. The inversion in POLY occurs, if N and O absorption is less effective in producing optical photons since all the elements are competing for the same incident photon flux (e.g., just below the N K-edge, most of the incoming photon is absorbed by carbon; in the case of FITC, S also contribute but to a lesser extent). This situation is also observed in the protein conjugates as expected. Similar cases have been presented above for XEOL from Ru and Ir complexes.

Finally, we want to comment on how the luminescence profile of the protein conjugates changes with time. It has been reported that the XEOL spectra of FITC-protein conjugates across the C, N, and O K-edge collected after 1 day in high vacuum chamber exhibited a new emission peak at ~ 290 nm (4.27 eV) as well as other less intense peaks in the low energy region at the expense of a reduction in intensity of the two main peaks shown in Fig.12 for the conjugates [52]. This is

mainly due to the radiation damage to the sample, which is an often-observed effect in the radiation-induced luminescence of proteins [53].

5. Summary and outlook

The element and site specificity of XEOL from functional organic materials when excited across an absorption edge is demonstrated here with a number of representative examples. The maturing and increasing accessibility of synchrotron radiation capabilities will open up new opportunities for research. On the horizon is micro beam and nano beam imaging using XEOL as a detection technique to investigate functional organic material devices among other systems [54-61]. Time-gated spectroscopy, 2D XAS-XEOL spectroscopy and the implementation of an optical streak camera will also enable time-resolved studies and the tracking of the energy and charge transfer processes leading to XEOL more effectively [12, 62].

Acknowledgement

This research at the University of Western Ontario was supported by the Natural Science and Engineering Research Council (NSERC) of Canada, the Canadian Foundation for Innovation (CFI), Canada Research Chairs (TKS) and the Ontario Ministry of Innovation. Results reported herein were obtained at several synchrotrons including the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Centre (SRC), University of Wisconsin Madison; funded by the NSERC Canada and U.S. National Science Foundation (NSF), the Canadian Light Source (funded by, NSERC, NRC, CIHR, CFI and the University of Saskatchewan); the Advanced Photon Source (APS) funded by US Department of Energy. All former group members and collaborators who were involved in the results discussed here are gratefully acknowledged.

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