

Review

Fluorescence and Phosphorescence Spectroscopies and Their Applications in Gem Characterization

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Abstract: Fluorescence and phosphorescence are listed as mineral optical–physical properties in classical gemology textbooks. The trace elements which exist in gems, certain defects in the crystal lattice, and some luminous molecules contribute to luminescence phenomena in gem materials, including fluorescence and phosphorescence. A systematic luminescence study using an excitation–emission matrix (EEM) not only provides detailed information about the emission and excitation peaks, but also indicates the presence of specific trace elements, lattice defects, or luminous substances in gem materials. This provides reliable evidence for the characterization of gems. In this review paper, we briefly summarize luminescence spectroscopy and illustrate its applications in gem materials in our laboratory, including diamonds, fluorite, jadeite jade, hauyne, and amber. Meanwhile, this project is in process and needs more samples from reliable sources to confirm the described data.

Keywords: gemstones; luminescence; fluorescence spectroscopy; application



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1. Introduction

Luminescence is the ability to emit light from any substance. In minerals and organic materials, it has been extensively studied for centuries [1–5]. Based on the nature of the excitation sources, luminescence can be grouped into several categories: photoluminescence (photons from UV-Vis-NIR sources, X-ray, and gamma rays; PL) and cathodoluminescence (electrons; CL), etc. As for the nature of the excited state, luminescence is subdivided to the fluorescence and phosphorescence (or persistent luminescence). The fluorescence results from the excited singlet states with spin-allowed transition, lasting near 10 ns following cessation of the excitation light. While the phosphorescence is emission of light from triplet excited states with spin-forbidden transition, it can last continuous photon emission milliseconds to seconds and even minutes, [2,6]. For example, the rare earth elements, Eu^{2+} and Dy^{3+} , cause the yellow-green color persistent luminescence up to 2000 min in mineral SrAl_2O_4 [7,8]. Luminescence varies in different substances. The most versatile continuous-light Xe lamps or pulsed lasers could excite some materials to emit not only longer-wavelength photons, but also anti-stokes PL at a shorter wavelength, albeit weaker (and of barely any interest in gem testing). Additionally, the tenebrescent minerals, such as sodalite, known for their reversible photochromism, could change color when exposed to sunlight, but have their color restored by heating [9]. This effect can be repeated indefinitely. Owing to the diagnostic reactions to light in substance, PL has become an essential physico-chemical property in mineralogy, gemology, biology, and many other research fields [1,2,10–12], and it especially becomes a useful tool for characterizing trace elements and imperfect crystal lattices or structural defects in minerals [13–15].

Gemmology is the study of all materials that are used as gems. Luminescence analysis is useful in this field [13,16]. Typically, the ultraviolet (UV) lamps with 365 nm (longwave; LW) and 254 nm (shortwave; SW) light are used to excite gemstones' fluorescence and phosphorescence. A rapid-development excitation–emission matrix (EEM) was developed

in a modern laboratory to characterize the emission and excitation peaks. These are closely related to the specific luminescence centers and fluorescence and phosphorescence behavior of the materials [2]. For instance, in benitoite, Ti-doped synthetic sapphire, and spinel, their blue shortwave-excited luminescence is caused by titanate groups (TiO_6) [12]. For natural and synthetic scapolites, $(\text{S}_2)^-$ activators trapped in $[\text{Na}_4]$ square cages produce the yellow-orange luminescence [17]. Phosphorescence spectra and fluorescence EEMs are usually recorded as the measured luminescence intensity versus emission and excitation wavelengths in 2D or 3D plots [1]. Relevant gemstone tests require non- or micro-destruction, visualization, and repeatability, which finally lead to the introduction of a front-surface geometry model for EEM detection of gems [18].

With the EEMs analysis gradually performed in gemology [12,17], the aim of this article is to briefly review the results of our group research on several gems, including HPHT synthetic diamonds, hauyne, fluorite, jadeite jade, and amber. Similarly, with an instrument equipped with the xenon lamp, we mainly reviewed their luminescence spectra, the EEMs patterns, and the currently available applications, such as an understanding of the optical behavior of gem crystals, distinguish natural gems from their synthetic and treated counterparts, and allow traceability of the geographic origins of natural gemstones.

2. Mechanisms and Instruments

2.1. Mechanisms

Ligand field, crystal field, molecular orbital theories, and the role of the defects (intrinsic, extrinsic, and structural defects, as well as defects derived from chemical reactions) are the primary methods used to reveal the luminescence behavior of luminescent materials. Waychunas et al. [1], Gaft et al. [2], and Lakowicz [6] have systematically reviewed these aspects. In the classic Jablonski diagram (Figure 1), absorption is the basis for the emission process, ensuring that the material gains photon energy at higher-energy electronic singlet levels (e.g., S_1 and S_2). Luminescence is the radiation path from an excited electron to its initial singlet state. The emission of light occurs from the first high-energy excited electronic singlet and triplet states (i.e., S_1 and T_1) returning to the lowest-energy ground states (S_0). It formally contains two categories, fluorescence and phosphorescence, according to the nature of the excited state: singlet or triplet, respectively. Thus, the emission energy tends to be lower than the excitation energy. Mirror symmetry between absorption and fluorescence curves has also been investigated for many compounds [3].

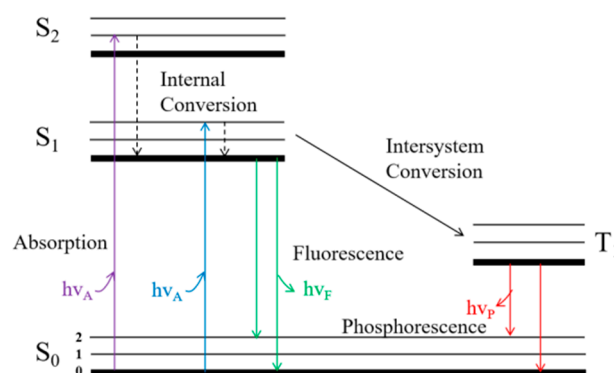


Figure 1. One form of a Jablonski diagram. Vibration levels 0, 1, and 2 show the different energies in the lowest-energy ground states (S_0). Adapted from [6].

Most gems consist of inorganic minerals; particularly, valent ions such as rare earth elements, transition metal elements, and electron-withdrawing elements, which usually occupy specific crystal sites and combine with surrounding ions to form a stable ligand field or some unexpected chemical structural defects. In these situations, abundant electrons keep moving in their orbitals once excited by appropriate energies for their transition to other higher-energy orbitals, and then undergo internal and intersystem conversions and

luminescence to their initial states. These processes are associated with the crystal lattice and certain elements and determine the detailed and distinct “fingerprint” luminescence information for a gemstone [15,19]. Gaft et al. [2] summed up three essential conditions for a mineral to be luminescent: (1) a suitable type of crystal lattice favorable to form emission centers; (2) sufficient content of luminescence center; and (3) a small number of quenchers. They found that, in common, the transition metal ions and REE^{3+} are related to mineral luminescence, such as the Cr^{3+} in corundum showing a $d-d$ electronic transition which contributes to the red fluorescence, and the Ce^{3+} substitution in two different Ca sites in apatite leading the fluorescence at 340 nm, 360 nm, and 430 nm. However, the intrinsic Fe^{3+} , Co^{2+} , and Cu^{2+} , as well as a high concentration of Fe^{3+} , Ti^{4+} , and Ce^{3+} , might restrain the luminescence.

It should be noticed that the xenon lamps have a continuous radiation which are mostly used to induce a steady-state luminescence. However, the laser excitation sources are not only for the PL spectra, but also for calculating the decay time by the time-resolved luminescence spectra, due to the monochromatic radiation, pulsed, or modulated [2,6]. Moreover, fluorescence spectra at low temperatures show clearer details, owing to the weakness of the molecular movement. Zaitsev et al. performed the laser excitation at wavelengths 324.8, 354.8, 457.0, 473, 532, 633 and 830 nm at liquid nitrogen temperature, to discuss the 468 nm luminescence center as being closely related to vacancy clusters in brown CVD diamonds [19].

However, the chemical compositions of organic gems without crystal structures, such as amber, are more complex than those of minerals. Thus, the molecular orbital theory is more suitable for organic luminescent materials. Electronic transitions in organic molecular structures that emit photons usually involve π -bonding molecular orbitals, and thus are generally associated with aromatic structures and molecules with multiple C=C double bonds [1,3].

2.2. Instruments

Fluorescence detection is suitable for gem characterization because of its high sensitivity, rapid analysis, and lack of sample preparation. Hence, luminescence studies of gems have increased dramatically over the past few years, especially for diamonds excited by different laser wavelengths [13–15,19,20]. Classical fluorescence spectroscopy is conducted for liquids with the required measurement geometry for the excitation beam and sample, with the emission beam set to 90° [6]. The emitted light travels through the 1 cm^2 cuvette holding the sample before reaching the detector. The measured emission is the accumulated luminescence along the entire optical path, which is significantly affected by self-absorption and secondary fluorescence [21]. Fortunately, for gem species, these can be substantially removed through front-surface geometry determination [21–23].

Fluorescence properties consist of: (i) an emission spectrum, which records detailed information about the emission under an excitation wavelength; (ii) an excitation spectrum, showing the excitation efficiency of a particular emission wavelength; (iii) a time-resolved fluorescence spectrum, characterizing the emission intensity varying with time; and (iv) luminescence centers, related to the trace elements in minerals or lattice defects in crystals and electronic transitions in organic molecular structures [1]. The main parameters include emission peaks (λ_{em}), excitation peaks (λ_{ex}), lifetime (τ), and quantum yield (Q) [2,24]. Due to the fact that, together, they represent the fluorescence intensity, emission, and excitation wavelengths in a contour or 3D plot, EEM illustrates a complete image of the luminescence pattern of the sample. The advantage of this approach is that it directly provides the λ_{em} and λ_{ex} and decreases the load of detailed processing of statistical and chemometric analysis of raw spectra. Alternatively, the EEM plot can be sliced to provide emission or excitation spectra at a particular excitation or emission wavelength.

Therefore, in our experiments, we used a spectrofluorometer (FP-8500, JASCO, Tokyo, Japan) equipped with a 150 W xenon lamp, double monochromators, and a specially designed accessory (EFA-833). This accessory provides a preferred geometry for gem luminescence

studies: a front-surface mode with an incident angle (between the excitation beam and the normal of the sample surface) of approximately 45° , schematically shown in Figure 2, and a special sample chamber for rough gems and mounted ones without any surface cover. This ensures that no sample pretreatment is required, which makes it a truly nondestructive test. In addition to transparent gems, luminescence from opaque minerals can be detected. At the same time, the sample platform was a special quartz window plate without emissions, which made it suitable for all powder and solid samples, with the only limitation being gems' size, of about 5 cm (length) $\times$ 10 cm (width) $\times$ 5 cm (height). In our laboratory, the collected EEMs were composed of a series of emission spectra (220–750 nm) irradiated at excitation wavelengths of 200–700 nm. Different excitation and emission bandwidths, scan speeds, the sensitivity level of the photomultiplier detector, response time, and the number of accumulations were set according to the specific gem species, for example, in amber and diamonds [18,25].

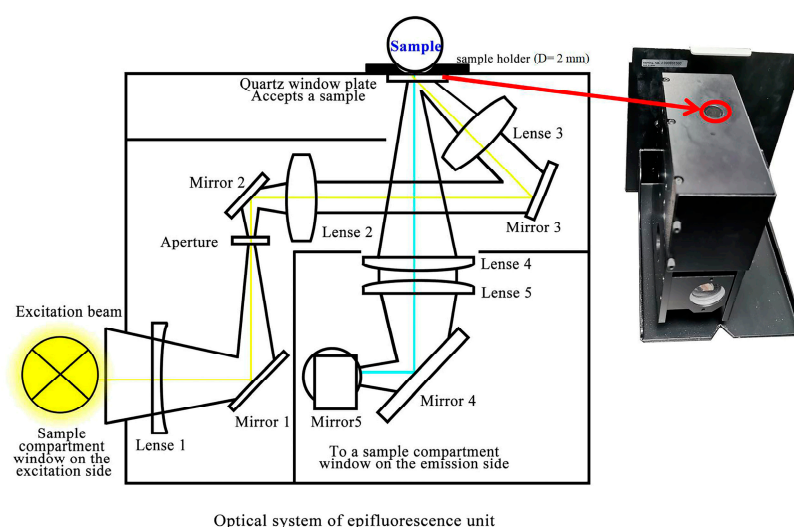


Figure 2. Schematic of the EFA-833 accessory attached in the spectrofluorometer used in this study (redrawn by Z. ZHANG, from the instrument handbook) [18].

In addition to the fluorescence EEM, this machine can record phosphorescence spectra and steady-state time-resolved fluorescence data. The latter provides raw data for calculating the decay time (or lifetime) of phosphorescence. It is suitable for decay times on the order of tens of microseconds. Therefore, the applications of time-resolved fluorescence data analysis are ongoing. We focused on analyzing the phosphorescence spectra and EEMs of fluorescence in various gems.

3. EEM Applications in Gem Characterization

3.1. Investigating the Trace Elements and Lattice Defects in Gem Materials

Until now, we found that the complete EEM fluorescence patterns and phosphorescence spectra and luminescence time-resolved data indeed extend our understanding on optical properties in gem materials, and further our investigation of the trace elements and lattice defects in diamond, fluorite and haüyne.

3.1.1. HPHT Synthetic Diamonds

Owing to the limitations of natural diamond reserves and their increasing industrial demand, millions of synthetic or lab-grown diamonds are produced using chemical vapor deposition (CVD) or high-pressure-high-temperature (HPHT) techniques. Synthetic diamonds share virtually all the chemical, optical, and physical characteristics of their natural counterparts. An ideal diamond only consists of carbon, but at least minute nitrogen-related impurities are unavoidably found in diamonds. These impurities lead to colored diamonds

and cause different defect centers in diamond crystal lattices, contributing to varying luminescence [15,19,20]. For centuries, exploration and explanation of the luminescence phenomenon that occurs in diamonds have attracted the attention of mineralogists and gemologists rather physicists [26].

Luo et al. used a 365 nm UV-LED source to measure 25 pieces of diamonds (including 19 natural ones and 6 treated ones) with an N3 center (due to a vacancy surrounded by three nitrogen atoms on a {111} plane in the diamond lattice), H3 center (from a vacancy trapped at an A aggregate of nitrogen, e.g., (N-V-N)⁰) or H4 center (related to four nitrogen atoms separated by two vacancies), a 480 nm band (because of a 480 nm absorption band), and N-V center (due to a single nitrogen atom adjacent to a vacancy) for their EEM spectra [14,15]. They found that the treated diamonds showed much more (N-V)[−] center related fluorescence, while naturally colored diamonds tended to show a dominant (N-V)⁰ defect emission. As for the HPHT synthetic diamonds, Shao et al. studied a batch of type IIb samples with greenish-blue phosphorescence [25]. The EEM spectrum and emission profile (Figure 3a,b) of these diamonds clearly depicted the main emission extending from 370 to 600 nm, centered around 470 nm, and a shoulder band at 503 nm after exposure to shortwave UV light at 215–240 nm. Simultaneously, the FTIR spectra showed the existence of uncompensated boron, and Electron Paramagnetic Resonance (EPR) signals consistent with neutral isolated nitrogen centers were observed in these synthetic samples. Referring to previous work on the mechanism of the 500 nm phosphorescence band, Shao et al. proposed the donor-acceptor pair (DAP) recombination theory to explain the 470-nm band. In this model (Figure 3c), when the crystals are irradiated with UV light, excited electrons in the valence band are trapped by the ionized positive donor, and the holes remaining in the valence band capture the electrons from the ionized negative acceptor. This results in neutral donor and acceptor recombination associated with phosphorescence release [27]. Uncompensated acceptors can accelerate the recombination process by forming additional holes. Furthermore, based on the DAP theory and radiation energy of 2.64 eV (i.e., 470 nm), the theoretical energy of the bandgap is 5.47 eV, the binding energy of the acceptor is 0.37 eV, and that of the donor is 2.54 eV. In addition to considering lattice relaxation, isolated nitrogen impurities were proposed as the donors in these tested synthetic diamonds, and the phosphorescence at 470 nm and 503 nm could be explained by isolated nitrogen-boron pair recombination. The different distance distributions between the donor-acceptor pairs resulted in these two bands.

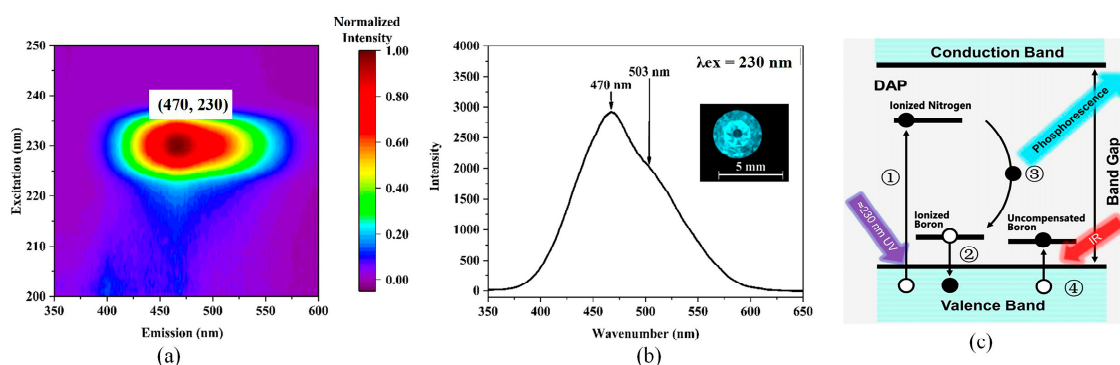


Figure 3. (a) Normalized EEM spectrum for type IIb HPHT synthetic diamond; (b) high-resolved emission curve by 230 nm excitation; (c) concise mechanism model of the 470 nm band in HPHT synthetic diamonds: ① When UV-light irradiated diamond, N_s⁺ trapped an electron from valence band to become N_s⁰; ② Then the hole left in valence band was filled with an electron from B[−] to make B⁰; ③ N_s⁰ and B⁰ recombined with phosphorescence emission. ④ Meanwhile, uncompensated boron provided extra holes in valence band which would accelerate the recombination process between N_s⁰ and B⁰. Adapted from Reference [25].

3.1.2. Fluorite

The Rogerley Mine in Frosterley, County Durham, England, is particularly notable for the production of many well-crystallized specimens of fluorite that exhibit strong daylight fluorescence unique to fluorite from this region [28]. Fluorite is a well-known mineral with a wide range of colors and a CaF_2 lattice. Numerous studies have recorded the luminescence from rare earth elements (REE) content [29–32] and the very common impurity in the CaF_2 crystal structure, such as Mn^{2+} placed in Ca^{2+} sites in the crystal lattice [33]; however, complete EEM fluorescence patterns are still lacking. Therefore, we had focused on the most common fluorite species, a princess-cut green fluorite from Rogerley Mine. It exhibits violet-blue fluorescence under UV irradiation at 365 nm, as shown in the inset of Figure 4.

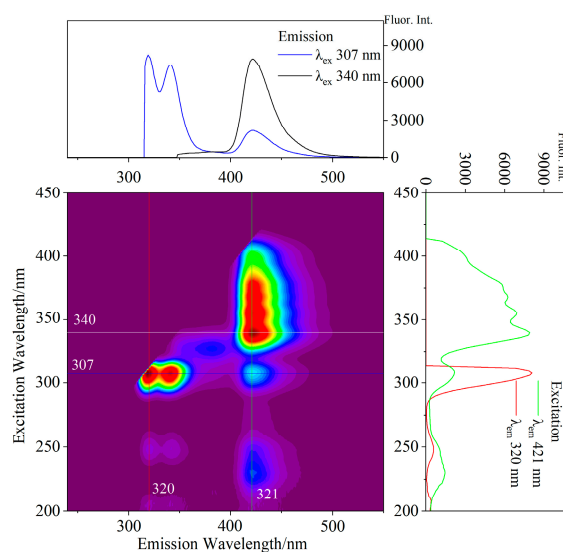


Figure 4. Detailed EEM pattern and emission and excitation curves from green fluorite with violet-blue fluorescence by LW ultraviolet light irradiation.

The EEM spectra and individual profiles (Figure 4) clearly show a mixture of emission centers caused by different ions that substitute for calcium in the crystal lattice. (i) The violet-blue part (with a center at 421 nm) of the emission spectrum could be efficiently excited by radiation at 200–260 nm and 285–415 nm, with the highest peak at 340 nm, which was accompanied by a series of low-energy excitation sub-bands. This emission corresponded to a high concentration of the rare-earth ion Eu^{2+} , and these excitation acromions could be associated with its ground multiplets [29]. (ii) The invisible ultraviolet part of the emission curve exhibited a doublet at 320 and 340 nm when excited by light at 307, 250, and 205 nm. These emission bands originate from f–d electronic transitions of Ce^{3+} [34]. Furthermore, this was supported by the excitation bands at 250 and 205 nm.

Moreover, the green color of the crystal coincided with the interstitial atom samarium, which is a very important coloring ion that substitutes for calcium in the lattice, according to previous results [35,36]. Notably, the diagnostic emissions of Sm^{2+} (708 nm) and Sm^{3+} (596 nm) (Figure 5) did not appear in our results. Nevertheless, the combination of coloration and EEM spectra could demonstrate a very useful role for the rapid characterization and detection of specific impurity elements that occupy the crystal lattice in fluorite minerals, even if chemical element analysis is not performed.

Additionally, a few details of the phosphorescence spectrum of green fluorite have been reported. Upon excitation at 308 nm, this fluorite exhibited visible phosphorescence at 382, 420, 542, 567, and 604 nm and ultraviolet emission at 320 and 340 nm, as shown in Figure 6. The lifetime of all normalized decay scatters was in the order of $604 \text{ nm} \approx 567 \text{ nm} > 542 \text{ nm} > 420 \text{ nm} > 340 \text{ nm} \approx 320 \text{ nm}$, indicating the presence of four potential triplet-state luminescence centers in this crystal. However, the exact assignment of each

long-lifetime emission band requires a combination of other analytical methods, such as EPR spectrometry.

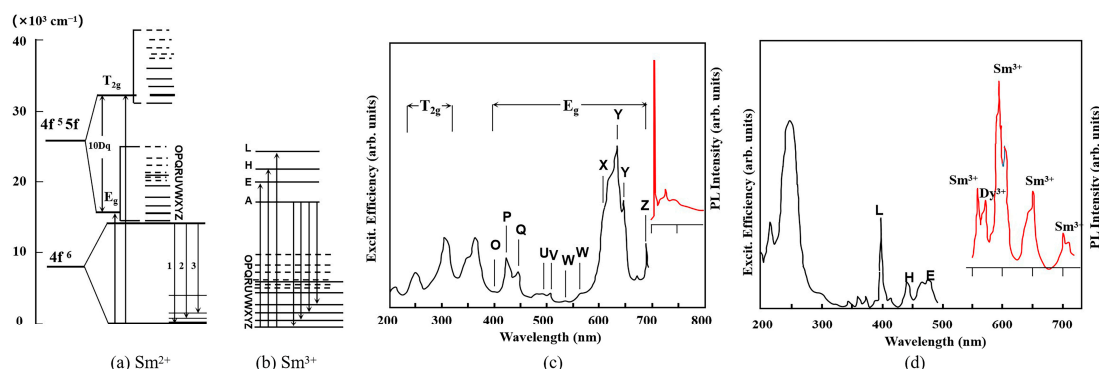


Figure 5. Schematic energy levels of (a) Sm^{2+} and (b) Sm^{3+} in the CaF_2 lattice. Arrows show the excitation and emission (arrows 1, 2, 3) transitions. (c) Excitation spectrum (black, $\lambda_{\text{em}} = 730$ nm), PL spectrum (red, Y-band at $\lambda_{\text{ex}} = 634$ nm) at 10 K. O–Z excitation bands correspond to the transitions in Sm^{2+} (see a). (d) Excitation spectrum (black, $\lambda_{\text{em}} = 596$ nm), PL spectrum (red, $\lambda_{\text{ex}} = 401$ nm) at room temperature. E, H, and L correspond to the Sm^{3+} levels (see (b)). Adapted from Reference [34].

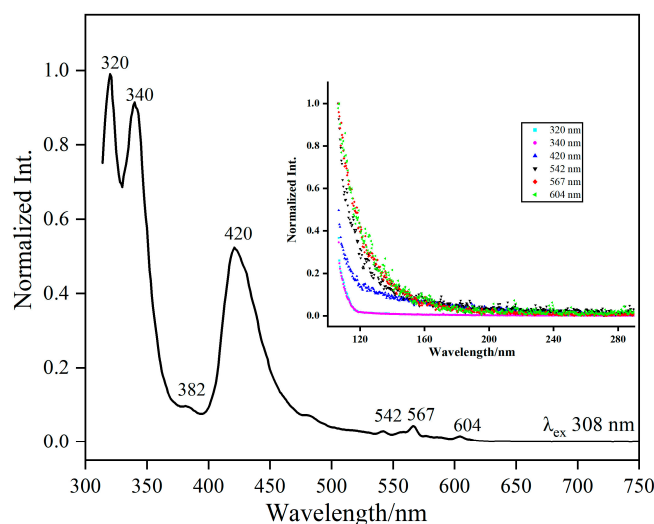


Figure 6. Normalized phosphorescence spectra by excitation at 308 nm (left) and normalized luminescence decay scatters (inset) obtained by monitoring at each phosphorescence peak by irradiation at 308 nm.

3.1.3. Hauyne

Blue hauyne $((\text{Na,Ca})_{4-8}[\text{AlSiO}_4]_6(\text{SO}_4)_{1-2})$ is a rare gem species, and only a few studies have recorded its fluorescence spectra. Lv et al. studied 27 gem-quality hauyne stones from the Eiffel District, Germany [37]. These crystals show pale grayish-blue to dark blue body color but present inert to bright orange fluorescence under 365 nm ultraviolet illumination, while all exhibit inert emission under 254 nm excitation. The absorption, 3D fluorescence, and finer emission spectra were collected using a fluorescence instrument (FP-8500, JASCO, Tokyo, Japan) and a PerkinElmer Lambda 650S UV-Vis spectrometer (Lambda 650S, PerkinElmer, PerkinElmer, MA, USA), as shown in Figures 7 and 8. The results showed two distinct emission regions: the blue region with a center at 425 nm and the yellow region with a peak at 566 nm, which was efficiently excited by 300–500 nm irradiation. This yellow-orange region emission indicates the orange fluorescence of hauyne. It was proposed that the fluorescence peak at 566 nm and its accompanions at 581, 600, 621,

642, and 666 nm were related to the $(S_2)^-$ center. The absorption peak at 400 nm coincided with the most efficient excitation light at 397 nm, which supports this view.

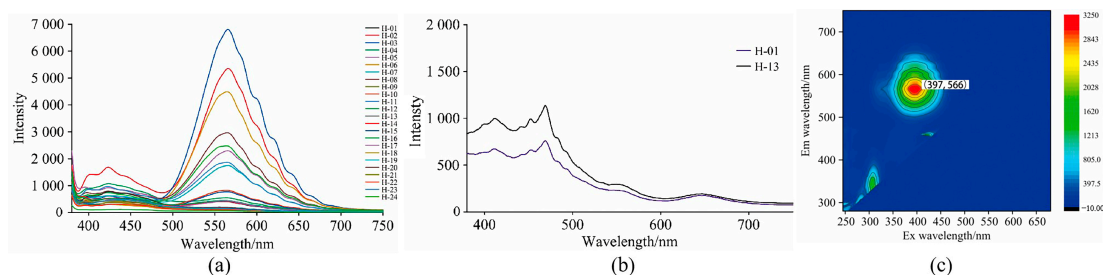


Figure 7. Fluorescence emission spectra of hauyne crystals: (a) $\lambda_{ex} = 365$ nm and (b) $\lambda_{ex} = 254$ nm. (c) 3D fluorescence contour of hauyne (H-03) with strong orange fluorescence. Adapted from Reference [37].

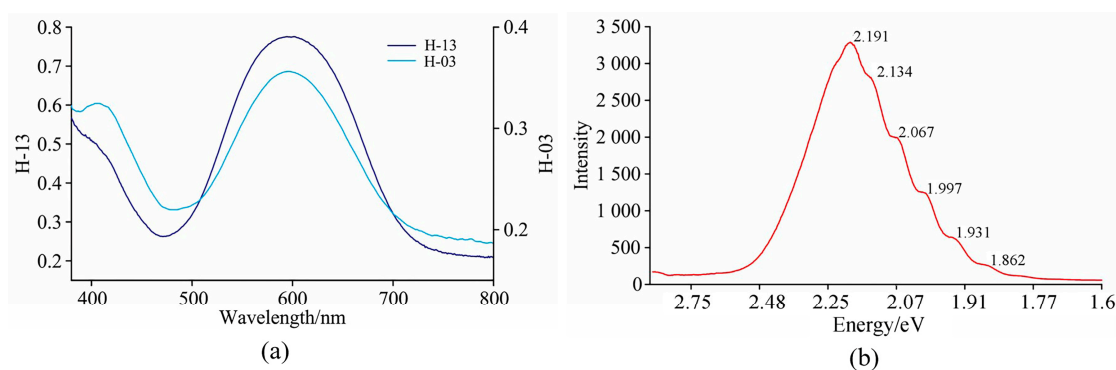


Figure 8. (a) Typical absorption spectra of hauyne. (b) Finer emission spectrum from hauyne (H-03) ($\lambda_{ex} = 397$ nm). Adapted from Reference [37].

In addition, others found that the sodalite and the natural and synthetic scapolites also emit a similar pattern, mentioned in references [17,38–41]. Blemettritt et al. compared the emission spectra of the natural scapolite and the sulfur-doped synthetic scapolite, confirmed that their yellow-orange fluorescence is related to the $(S_2)^-$ in $[Na_4]$ square [17]. Meanwhile, Lv et al. noticed that in the finer emission spectrum from hauyne, the fluorescence peak at 566 nm excited by 397 nm is accompanied by a series of stepped longer wavelength emissions, which have an adjacent energy differential of approximately 0.07 eV [37]. They also thought it caused from the sub-vibration level from S_2^- center excited state, as Gaft et al. proposed in the tugtupite, sodalite, and hackmanite [42].

3.2. Application for Distinguishing Natural and Treated Gems

Discerning how to rapidly and accurately distinguish natural and treated gems is a consistently popular subject in gem characterization. High-price jadeite jade, Oregon sunstone, and some of their treated products can also be recognized by the differences in their EEMs patterns.

3.2.1. Jadeite Jade vs. Impregnated Jadeite Jade

Jadeite jade, a mineral aggregate mainly composed of pyroxene-group minerals ($NaAlSi_2O_6$), is known to exhibit no fluorescence. Artificial treatments to enhance its color and appearance quality can result in visible fluorescence due to extraneous substances during the treatment processes. These processes involve removing intrinsic impurities, such as brownish iron-containing minerals, impregnating them with colorless resin for enhancing stability, or with colored resin for enhancing color. The treated jadeite jades are

named B-Jade (impregnated by colorless resin), C-Jade (dyed), and B+C-Jade (impregnated by colored resin), while the untreated jadeite jade is called A-Jade in the gems market.

Ma et al. found that in addition to micro-inclusions, luster, and absorption spectra, fluorescence plays a useful role in discriminating between A-, B-, C-, and B+C-Jade [43]. The detailed EEM fluorescence patterns blaze a new trail to distinguish natural from treated specimens and determine their exact treatment process. In general, the EEM spectra (Figure 9) showed no emissions from A-jade, but different emission patterns appeared in the treated jadeite jades. B-Jades usually have a strong blue fluorescence with a triplet center at $\lambda_{em} = 417, 441, 464 \text{ nm}/\lambda_{ex} = 340\text{--}410 \text{ nm}$, owing to the impregnated fluorescent aromatic materials and epoxy resin. Similar to B-Jade, C-Jade also radiates a triplet emission but at a longer wavelength of $\lambda_{em} = 418, 444, 470 \text{ nm}/\lambda_{ex} = 340\text{--}410 \text{ nm}$, possibly owing to dyeing with colored organic material.

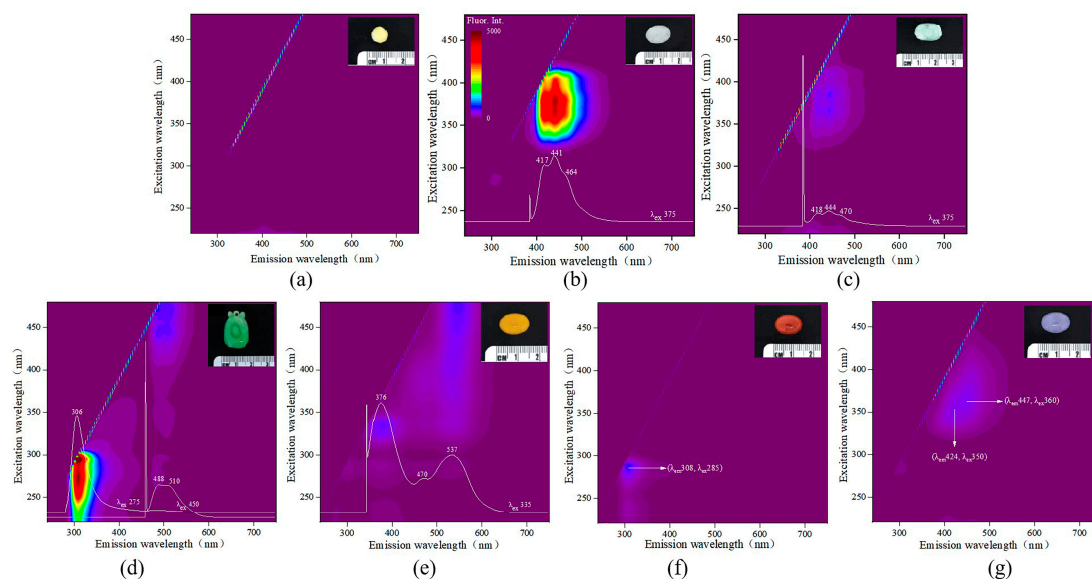


Figure 9. EEM spectra from (a) A-Jade, (b) B-Jade, (c) C-Jade, and (d–g) B+C-Jade. Adapted from Reference [43].

The different staining materials used in B+C-Jade produce a wide range of colors, including green, purple, yellow, and red. The chromium ion chelate in green-colored B+C-Jades results in an ultraviolet emission at $\lambda_{em} = 308 \text{ nm}/\lambda_{ex} = 220\text{--}300 \text{ nm}$. Meanwhile, the chelate of iron ions, a type of fluorescence quenching agent, filled in the yellow B+C-Jades and led to the weaker emissions at $\lambda_{em} = 377 \text{ nm}/\lambda_{ex} = 335 \text{ nm}$ and $\lambda_{em} = 537 \text{ nm}/\lambda_{ex} = 335\text{--}480 \text{ nm}$. The high concentration of iron results in the red-colored B+C-Jade and further weakens their radiation at $\lambda_{em} = 308 \text{ nm}/\lambda_{ex} = 285 \text{ nm}$. However, the purple B+C-Jade has a whitish blue fluorescence at $\lambda_{em} = 380\text{--}500 \text{ nm}/\lambda_{ex} = 340\text{--}410 \text{ nm}$ due to its Mn-bearing extraneous polymers. These EEM fluorescence spectra provide evident features for the identification of natural versus treated jadeite jades as well as different enhancement processes.

3.2.2. Oregon Sunstone vs. Copper-Diffused Plagioclase Crystals

Natural red and greenish sunstone were obtained from Oregon, USA. Zhou et al. [44–46] found that copper-diffused plagioclase crystals exhibited red, light red, and blue-green colors under different conditions. Cu diffusion in both red and light red sunstones results in orange fluorescence when illuminated by ultraviolet light at 320 nm, while the Cu-Li diffusion-treated blue-green plagioclase crystal only exhibits weak fluorescence similar to natural sunstone [45,46]. Compared with natural Oregon sunstone, which only has a weak emission at $\sim 395 \text{ nm}$, the Cu-diffused sunstone with orange fluorescence has a stronger emission band at $\sim 394 \text{ nm}$ and an additional emission band at $\sim 555 \text{ nm}$ (Figure 10). Through

a series of copper-related diffusion experiments, Zhou et al. found that the Cu^+-Cu^+ dimer, rather than the Cu^{2+} ions, diffused into the sunstone crystal lattice responsible for the ~ 555 nm emission [44,47]. The weak emission peak at ~ 395 nm also indicates that it was caused by Cu^+ [46]. Therefore, the additional band at ~ 555 nm is an indicative feature for distinguishing red copper-diffused sunstones from natural sunstones.

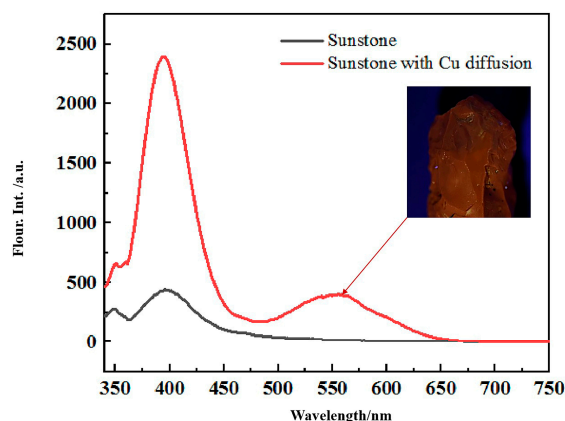


Figure 10. Fluorescence spectra of sunstone and Cu-diffused sunstone ($\lambda_{\text{ex}} = 320$ nm). (Data from Zhou et al. [44–46]).

3.3. Tracing the Specific Geographic Producing Areas of Amber

Amber belongs to matured fossilized resin generated from resin-producing plants (including Conifer and Fabaceae families) millions of years ago that underwent rapid solidification. These solidified plants then accumulated and underwent extremely long diagenesis in the primary sediment region, or in secondary deposits by river transportation. It has been documented that amber is widely distributed across all continents of the world, except Antarctica, but commercial gem-quality amber is found in the Baltic Sea region, Dominican Republic, Myanmar, Mexico, and Fushun in China [48–50].

Fluorescence has been observed in amber for decades [51–54], and LWUV light irradiation usually excites Baltic amber to a greenish-yellow glow; Dominican and Mexican amber exhibits blue emission; and Burmese and Fushun amber exhibits violet-blue fluorescence. After long-term exposure to this condition, some Mexican, Burmese, and Fushun amber can even exhibit a noticeable yellowish phosphorescence. By introducing a front-surface fluorescence detection instrument, we first measured the 3D fluorescence of amber from the aforementioned geographic locations; details are provided in references [12,55]. For ordinary golden and brown amber species, Baltic amber has a stable broad irradiation center at $\lambda_{\text{em}} = 435$ nm/ $\lambda_{\text{ex}} = 350$ nm. The emissions of Mexican and Dominican amber resembled those of the Baltic amber but were stronger. Fushun and Burmese amber both exhibited ultraviolet radiation at $\lambda_{\text{em}} = 334, 347$ nm/ $\lambda_{\text{ex}} = 240, 295$ nm [55]. Meanwhile, Jiang et al. [56] and Shi et al. [57] found that EEM fluorescence patterns can not only help to identify whether the amber came from Myanmar, but also further distinguish seven kinds of special Burmese amber from some other ordinary species. What is more, when illuminated by a strong LWUV light for one minute, the order of phosphorescence intensity and lifetime of the amber was as follows: Myanmar > Fushun > Dominican Republic $\approx$ Mexico > Baltic Sea (Figure 11) [58]. This is the first time the phosphorescence in amber from Fushun, Dominican Republic, Mexico, and Baltic Sea regions has been noticed and measured. Additionally, FTIR provides another significant feature to distinguish Baltic amber from other locations' amber, because it shows a “Baltic shoulder”, that is, an absorption mode within 1260 cm^{-1} – 1150 cm^{-1} [58]. These properties of amber provide reliable information regarding the traceability of amber deposit locations.

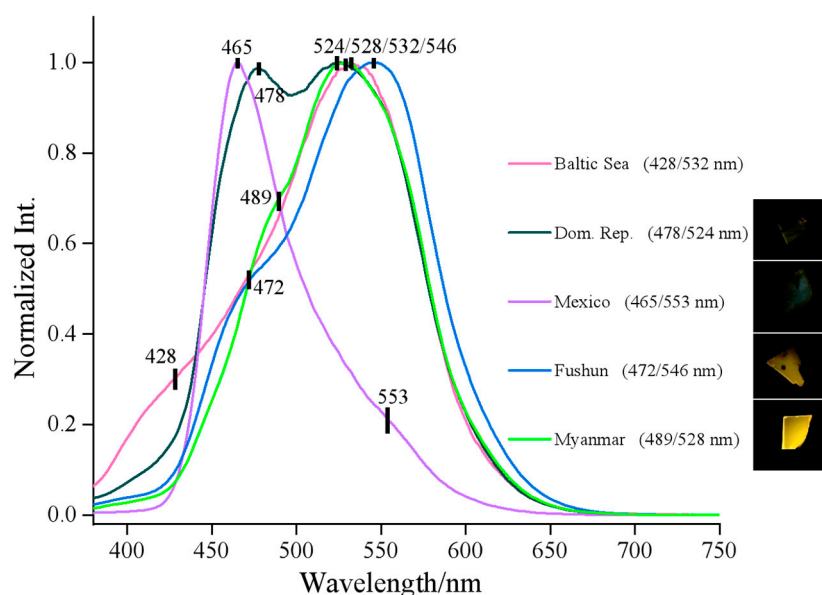


Figure 11. Normalized phosphorescence spectra of golden amber from five locations. The lifetime of the phosphorescence of Baltic amber is too short to capture its irradiation by camera; the inset presents phosphorescence images of amber from four locations. Adapted from Reference [58].

The rarest blue amber with extraordinarily visible fluorescence was mainly sourced from the Dominican Republic; however, its Mexican and Burmese counterparts were forced to imitate Dominican blue amber. Through a combination of EEM and UV-Vis spectra, we constructed a flowchart to rapidly discriminate blue amber from these three geographic origins according to their diagnostic triplet emission peaks at $\lambda_{em} = 445, 474, 508 \text{ nm}$ / $\lambda_{ex} = 415, 440 \text{ nm}$ and the invisible ultraviolet part of fluorescence at $\lambda_{em} = 334, 347 \text{ nm}$ / $\lambda_{ex} = 240, 295 \text{ nm}$, as well as the 412 nm and 442 nm absorption bands (Figure 12). Recently, Li et al. [59] noticed that Indonesian fossil resins show an extremely similar appearance and EEM patterns to Dominican blue amber. However, the 1384 cm^{-1} , 1377 cm^{-1} and 1367 cm^{-1} in FTIR spectra from Indonesian fossil resin indicate its Dipterocarpaceae plant origin. Therefore, it is dissimilar to Dominican blue amber from the Fabaceae plant. Thus, the luminescence properties could at times trace the specific geographic producing areas of amber, but other methods are also needed.

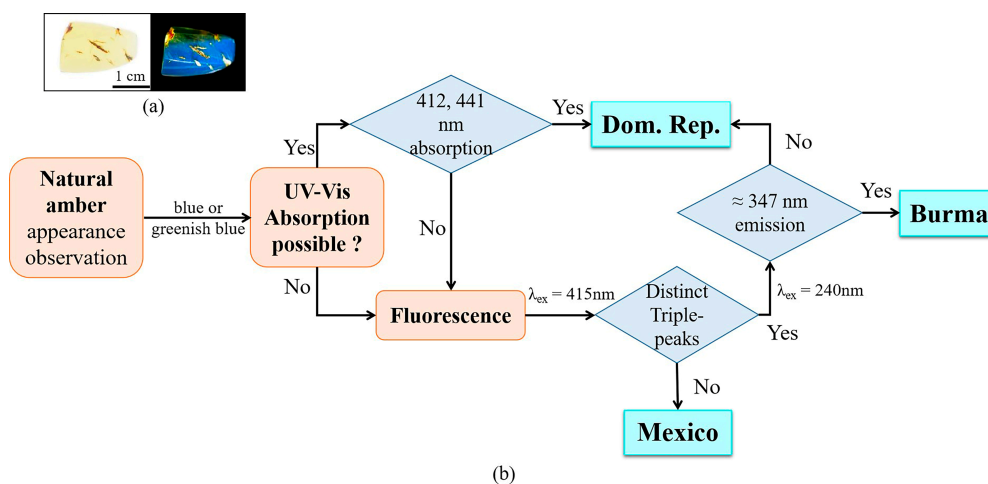


Figure 12. (a) Dominican blue amber. (b) A preliminary flowchart for blue amber to assist in determining its geographic origin, adapted from Reference [18].

3.4. Assisted Analysis on the Potential Luminous Molecules in Fossil Resins

Amber contains complex chemical components that can be used to extract and purify a single substance in a single step. The luminous matter in amber is difficult to obtain. Yellow-colored Dominican blue amber glows with intense blue fluorescence when illuminated by sunlight. We extracted the fluorescent components using ethanol (Figure 13a) and then performed EEM, gas chromatography–mass spectrometry (GC–MS), and FTIR analyses [58]. In the GCMS analysis, the retention times of the concentrated solutions of amber and perylene appeared in 14.786–15.393 min with a 252 m/z base peak. The FTIR spectra of the enriched solution from amber also showed characteristic peaks of the perylene-ethanol solution at 817 and 771 cm^{-1} , as well as at 3076, 1600, and 1580 cm^{-1} related to aromatic molecular structures with multiple C=C double bonds. The EEM results from the extracted solution are shown in Figure 13b), with typical emissions at 448, 473, and 505 nm. When the unknown fluorescent agent was enriched in this solution by blowing dry nitrogen, the EEM pattern underwent significant changes, as shown in Figure 13c. We prepared a saturated pure perylene-ethanol solution (Figure 13d), and its EEM pattern (Figure 13e) was substantially different from that of the amber-extracted solution. Nevertheless, when diluting the perylene-ethanol solution by adding pure ethanol to factors of 2.5 and 16, the EEM patterns changed dramatically, as shown in Figure 13f,g, and were very similar to those of the enriched and original extracted solutions. Therefore, we propose that perylene and its derivatives probably led to the three typical emission peaks in Dominican blue amber. However, we have not purified the fluorescent components directly, which will be the main subject of future research.

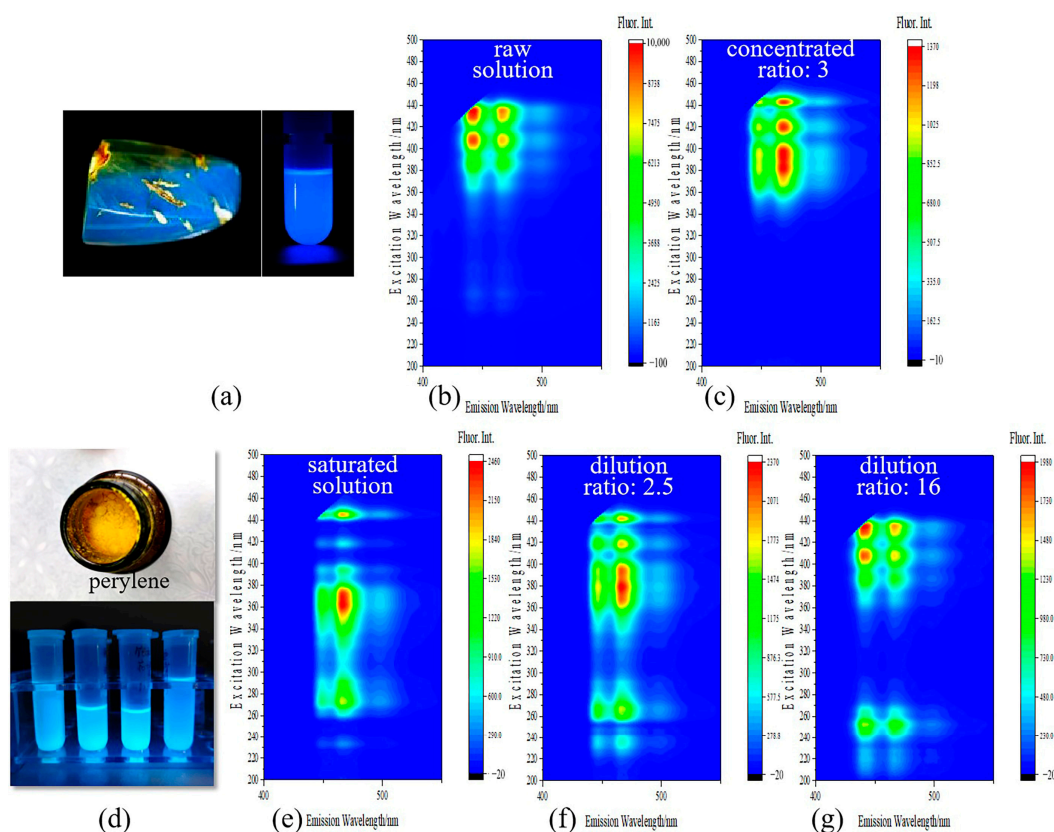


Figure 13. EEM spectra of solid samples and their solutions, adapted from Reference [58]. (a) the Dominican blue amber and its ethanol solution; (b) EEM from the solution in (a); (c) EEM of the concentrated solution from (a); (d) perylene and its ethanol solutions with different concentrations; (e) EEM of the saturated perylene- ethanol solution; (f) EEM from the diluted perylene- ethanol solution; (g) EEM from the perylene- ethanol solution with a dilution ratio 16.

4. Summary

With the rapid development of relevant fluorescence spectroscopy and gemological science, luminescence from gem materials has been extensively studied. Gemology is closely connected to scientific research and commercial markets. The luminescence properties of some gem materials, combined with new-tech fluorescence spectroscopy and widely used theories, act as a window for understanding the exact trace element ions or lattice defects in certain gem crystals or potential fluorescent aromatic molecules in organic materials. In addition, they provide an abundance of useful information to distinguish natural from treated jadeite jades, indicate the specific enhancement process in treated jadeite jades, and discern blue ambers of different geographic origins. Hence, we look forward to fluorescence spectroscopy being applied to other gem materials, offering more details on photoluminescence properties (EEMs, phosphorescence spectra, lifetime, and quantum yield), and applying them more extensively in mineralogical and gemological characterization, identification, and traceability processes. This is a project in process, and our research group are collecting more samples from reliable sources to confirm the data described above.

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