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A practical guide to measuring and reporting photophysical data

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Research on photoluminescent compounds is common in inorganic chemistry journals like *Dalton Transactions*, and as applications related to luminescent devices, energy conversion, and photoredox catalysis gain and hold prominence, reporting on the photophysical properties of inorganic compounds will become increasingly prevalent. The accessibility, ease-of-use, and throughput of many modern instruments make it simple for most researchers to acquire data, although recognizing common issues and properly reporting the data can involve a significant learning curve. In this tutorial review, we introduce a systematic guideline on how to properly measure, analyze, and report key photophysical data, including UV-vis absorption and photoluminescence (PL) spectra, PL quantum yield (Φ_{PL}), and PL lifetime (τ). In addition to detailed protocols, we outline common pitfalls to avoid, tips to improve data quality, and suggestions to ensure data is correctly and accurately reported when submitting for publication. We intend this tutorial to serve as a useful resource for new and experienced researchers aiming to produce reliable and high-quality photophysical data.

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Key learning points

1. Thorough analysis of the properties of a photoluminescent compound typically includes the following measurements: UV-vis absorption spectrum, photoluminescence spectrum, photoluminescence quantum yield, and photoluminescence lifetime.
2. There are several sample types that can be used for these measurements, and guidelines for their preparation vary depending on the characteristics of the compound being studied and the types of experiments being conducted.
3. Modern instrumentation makes it simple for researchers to collect photophysical data, but a working knowledge of the experimental parameters and potential sources of error covered in this Tutorial is critical for accurate and reproducible data collection.
4. This Tutorial also covers the basics of properly analyzing and reporting photophysical data, important to ensure that published data is presented in a way that gives other researchers the tools to properly evaluate and contextualize the compound's properties.
5. Common pitfalls that lead to inaccuracies in the collection and interpretation of photophysical data include sample impurities, exceeding detector limits, overinterpretation of photoluminescence intensity, improper fitting of time-resolved data, and assuming an unreasonably high level of precision when reporting data and comparing metrical parameters.

Introduction

Photoluminescence (PL) is the process in which a photoactive compound absorbs photons, promoting the compound to an excited state, which subsequently returns to the ground state while emitting light. Depending on the nature of the excited state of the molecule, photoluminescence is generally classified into two main types: phosphorescence and fluorescence. These photophysical processes are commonly illustrated using a Jablonski diagram (Fig. 1), which considers the case of a closed-shell molecule with a singlet ground state (S_0). Almost all luminescent organic and organotransition metal compounds have closed-shell ground states, although there are many examples of 3d coordination compounds and f-element complexes that luminesce with open-shell electronic structures. Initially, the luminescent compound in its S_0 ground state absorbs a photon to excite into a singlet excited state ($S_{n>0}$); rapid internal conversion to the lowest singlet excited state (S_1) follows. In fluorescence, emission involves a spin-allowed transition from the singlet excited state to the singlet ground state ($S_1 \rightarrow S_0$). In some molecules, particularly those with strong spin–orbit coupling (SOC), the triplet excited-state manifold can be populated through intersystem crossing (ISC) from S_1, leading to the population of the lowest triplet excited state (T_1). Phosphorescence then occurs *via* a spin-forbidden radiative transition from the triplet excited state (T_1) to the singlet ground state (S_0).

Photoluminescent compounds can be applied in various areas, including photocatalysts,[1–5] organic light-emitting

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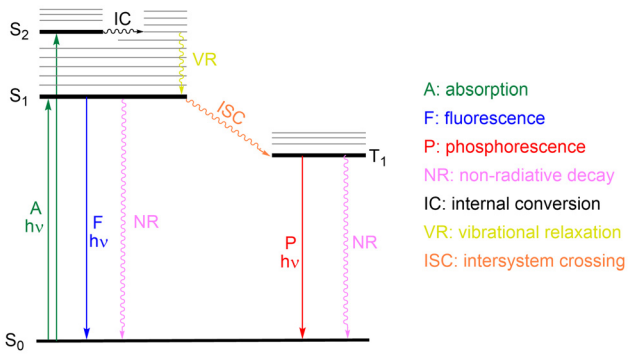
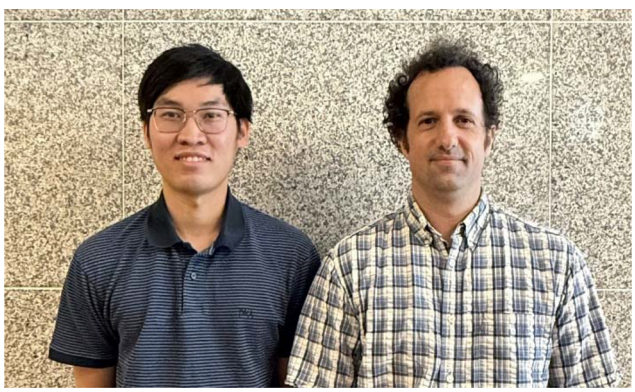


Fig. 1 Representative Jablonski diagram.

diodes (OLEDs),[6–11] sensors,[12–15] biological imaging,[16–18] and photodynamic therapy.[19–23] In some applications (*e.g.*, OLEDs and sensors), photoluminescence is the property of interest, and comprehensive reporting of the photophysical properties can indicate the suitability of the compound for those applications. In other cases, *e.g.*, photocatalysis and photodynamic therapy, photoluminescence measurements are often used to characterize the nature, energetics, and kinetics of excited-state processes that are critical for these applications, even though the PL itself is not directly involved in the final application. As inorganic compounds are widely featured in the above-mentioned applications of photoluminescent compounds, reports that include photoluminescence and other photophysical properties are common in *Dalton Transactions* and other inorganic chemistry journals.

Several measurements can be performed to understand the behavior of photoluminescent compounds, but five key metrics are particularly significant in selecting photoluminescent compounds for specific applications and understanding their properties: UV-vis absorption, emission spectra, excitation spectra, PL quantum yield (Φ_{PL}), and PL lifetime (τ).[24] UV-vis absorption spectroscopy is a popular and powerful technique commonly used to characterize chemical compounds. By measuring how much light compounds absorb across the ultraviolet and visible regions, UV-vis absorption measurement can provide information about transitions from occupied molecular orbitals to unoccupied molecular orbitals. UV-vis absorption spectra are most often recorded as a function of wavelength, and with concentration-dependent measurements the molar absorption coefficient (ε) can be determined at each wavelength. In inorganic complexes, the UV-vis absorption spectrum, often in concert with electrochemical measurements and/or DFT calculations, is useful for assigning the types of electronic transitions and excited states that occur, which can include ligand-centered (LC), metal-centered (MC), metal-to-ligand charge-transfer (MLCT), and ligand-to-metal charge-transfer (LMCT).[25,26] Meanwhile, the molar absorption coefficient (ε) is important for evaluating a compound's light-harvesting efficiency.

Photoluminescence spectroscopy is used to analyze the emitted light of luminescent compounds after excitation by incident photons. Using typical instrumentation, three key measurements can be obtained: the photoluminescence emission and excitation spectra, both recorded as intensity *vs.* wavelength plots, and Φ_{PL}. Requiring more sophisticated instrumentation, time-resolved PL allows measurement of τ, which represents the average time that the luminescent compound stays in the excited state before decaying to the ground state. Specifically, if the excited state decays *via* first-order kinetics, the PL lifetime is defined as the time required for a defined concentration of excited states to decrease to $1/e$ of its initial value. PL emission and excitation spectra can reveal or clarify aspects of the excited-state properties of luminescent compounds, such as the energy gap between the excited and ground states. The assignment of the luminescence mechanism (*e.g.*, fluorescence or phosphorescence) can be clarified by a combination of PL spectral features and the PL lifetime. Φ_{PL} indicates the ratio of emitted photons to absorbed photons and can be thought of as an efficiency measurement for the photoluminescence process. Φ_{PL} is a critical factor for



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LED and OLED applications where high quantum yield is essential for efficient device performance. Finally, τ is an important parameter for a variety of applications mentioned above, and time-resolved PL measurements are also powerful for extracting kinetic parameters of excited-state processes, whether those are inherent PL decay processes or reactions that occur from the excited state. Φ_{PL} and τ are often measured together, and *via* eqn (1) and (2) below, the radiative rate constants (k_r) and non-radiative rate constant (k_{nr}) can be obtained under the assumption that no unimolecular photoreaction involving the excited state occurs. These two values will provide deeper insight into the excited-state decay dynamics, which is necessary for understanding and designing efficient luminescent compounds.

$$\Phi_{PL} = \frac{k_r}{k_r + k_{nr}} \quad (1)$$

$$\tau = \frac{1}{k_r + k_{nr}} \quad (2)$$

While photophysical measurements are essential for obtaining insight into the behavior of photoactive compounds and are becoming more accessible to researchers, there is a significant amount of background knowledge needed to ensure consistent experimental design and to generate reproducible data. In addition, we think it is critical for all authors who report photophysical data to be mindful of data reporting conventions and present their data in a way that promotes clarity and accuracy, allowing the data to be properly contextualized by readers and compared to other studies. In this tutorial review, we aim to provide practical guidance for measuring and reporting photophysical data. We focus on the five key measurements described above – UV-vis absorption, emission spectra, excitation spectra, PL quantum yield, and PL lifetime – due to their prevalence and utility. This tutorial review provides the fundamental concepts behind each technique and guidance on sample preparation, experimental parameters, and how to correctly interpret and report data. Additionally, we also include pointers and common pitfalls throughout the article to help researchers recognize and avoid potential errors that sometimes occur in reported data. For readers who are seeking a deeper understanding of these techniques, we encourage consultation of published textbooks on photoluminescence.[24,26–32]

Sample preparation

While there are no universal rules for sample preparation when making photophysical measurements, considerations related to the compound's properties, the instrumentation being used, and the type(s) of measurements being made lead to some general guidelines. The aim of this section is to provide readers with a general overview of the role of each component in a typical sample and describe how to prepare a sample for photophysical measurements. While there are many types of samples used in photophysical measurements, this tutorial review will focus on three common categories: solution samples, solid samples, and film samples.

Sample purity

To make any reliable measurement, it is necessary to ensure that there are minimal impurities in the sample. Minor impurities can be particularly problematic in photoluminescence measurements, and in some cases can quench (reduce the intensity of) the PL features. One impurity that commonly interferes with photophysical measurements on inorganic or organometallic compounds is oxygen, which quenches the triplet excited state of phosphorescent compounds.[14,15] The presence of oxygen in samples is acceptable for UV-vis absorption or fluorescence measurements of oxygen-stable compounds. When oxygen-sensitive compounds or phosphorescence are involved, the use of a deoxygenated solvent and preparation in an inert atmosphere is necessary. Samples in such cases are commonly prepared in a glovebox, and degassing *via* freeze–pump–thaw or sparging with inert gas can be employed if the sample is initially prepared under ambient conditions. Moreover, given the sensitivity of many modern fluorimeters, a very minor photoluminescent impurity with a high quantum yield could produce a spurious signal that either interferes with the desired photoluminescence or in some cases is misinterpreted as arising from the sample of interest. Residual organic or organometallic precursors used to prepare the compound of interest can interfere in this way. Since many photoluminescent molecular compounds contain aromatic ligands or functional groups, special attention should be paid to aromatic impurities that show up during characterization of the sample (*e.g.*, by NMR), as these can often have significant luminescence.

Solution samples

In photoluminescence measurements, solution samples are most common, in which the active compound is dissolved in an appropriate solvent and the solution is contained in a cuvette for analysis.

Solvent. There are several characteristics that need to be considered during solvent selection. Depending on the type of measurement, solvent requirements can vary. Here we have listed some typical considerations for common photophysical measurements: (i) The solvent completely dissolves the active compounds at the required concentration for measurement (typically μM if standard 1 cm cuvettes are being used). (ii) The compound needs to be stable in the selected solvent. (iii) The solvent should be transparent in the relevant spectral range. To determine the transparency of the solvent, the solvent's UV cutoff (Table 1) is useful information, as below the cutoff wavelength, the solvent absorption becomes significant. Many solvents also absorb in the near-infrared (NIR) region *via* vibrational overtone transitions, which must be considered for long-wavelength measurements beyond *ca.* 1000 nm. Such measurements are less common but can be important for

Table 1 UV cutoff and refractive indices of common solvents[35]

Solvent	UV cutoff/nm	Refractive index (n) at 20 °C
Acetone	330	1.359
Acetonitrile	190	1.344
Chlorobenzene	287	1.525
Chloroform	245	1.446
Dimethylformamide	268	1.430
Dimethyl sulfoxide	265	1.478
Ethyl acetate	256	1.372
Hexane	200	1.375
Methanol	205	1.328
Dichloromethane	233	1.424
Pentane	200	1.357
2-propanol	205	1.377
Tetrahydrofuran	212	1.407
Toluene	284	1.497
Water	<190	1.333

certain classes of luminescent compounds (particularly lanthanides).[33,34]

Cuvette. There are different types of cuvettes used to contain solution samples, which vary in terms of the constituent material they are made from and their physical dimensions. The three most common cuvette materials are plastic (typically polystyrene and polymethylmethacrylate), borosilicate glass, and quartz. Due to the instability of plastic to organic solvents and the narrow wavelength range (~340–800 nm for polystyrene cuvettes), plastic cuvettes are mainly used for aqueous biological applications, where measurement is in the visible light region. Compared to the plastic cuvette, borosilicate glass provides higher chemical resistance and a wider wavelength range (~334–2500 nm). However, due to the strong absorption of UV light, borosilicate glass cuvettes are limited to use in the visible light and NIR range. The most versatile material for a cuvette used in photophysical measurement is quartz, which has transparency from the UV to the NIR region (~190–2700 nm) and high chemical resistance.

The most common shape of a cuvette used in photophysical measurement is rectangular. In UV-vis absorption measurements, cuvettes are required to have at least two transparent faces on opposite sides to allow the excitation light from the light source to pass through the sample to the detector. Conversely, to reduce signal from the light source, photoluminescence measurements use cuvettes with four transparent sides in which excitation light enters one face of the cuvette while emission is collected at a 90° angle to the excitation light. The selection of cuvette path length is largely influenced by sample concentration. Although 10 mm is the standard path length, samples with high concentrations may benefit from using a shorter path length of 1 mm to 5 mm to reduce absorption. Conversely, for trace analysis, path lengths greater than 10 mm can enhance sensitivity. In addition to the various cuvette materials and sizes, there are multiple types of enclosures available. In oxygen-insensitive photophysical measurements such as UV-vis absorption and fluorescence, an open-top cuvette with no lid or Teflon cap is acceptable. However, when using highly volatile solvents or when the experiment requires accurate concentration, it is better to use cuvettes that can be tightly sealed, *e.g.*, with Teflon stoppers. Cuvettes with air-tight screw caps are required for oxygen-sensitive samples or oxygen-sensitive techniques such as phosphorescence measurements. Solid screw caps can be used if the sample can be prepared under inert atmosphere inside a glovebox. Screw caps with septum tops are more versatile and are particularly useful when a series of measurements requires different concentrations, in which a stock solution of the component being varied can be sequentially added to the cuvette *via* syringe. Additionally, the deoxygenation process can be conducted on cuvettes with a septum-topped screw cap by sparging with inert gas, although the solution concentration can be changed during this process due to solvent evaporation. In addition to standard cuvette designs, several specialized cuvettes are available for specific applications. For instance, micro cuvettes (V < 1 mL) can be used for precious samples with limited quantities available. Flow-through cuvettes enable continuous sample flow and are commonly used in kinetic studies, in automated systems, or when the sample of interest is prone to photodegradation. Beyond commercially available options, cuvettes can be customized for particular applications. An example commonly used in photoluminescence measurements is shown in Fig. 2, in which a cuvette is combined with a high-vacuum valve and glass bulb. This design allows sample to be degassed *via* freeze–pump–thaw cycles or for a gas-phase substrate to be introduced for quenching or reactivity studies.

To preserve the longevity of cuvettes and accuracy of measurement, care must be taken to properly clean and main-

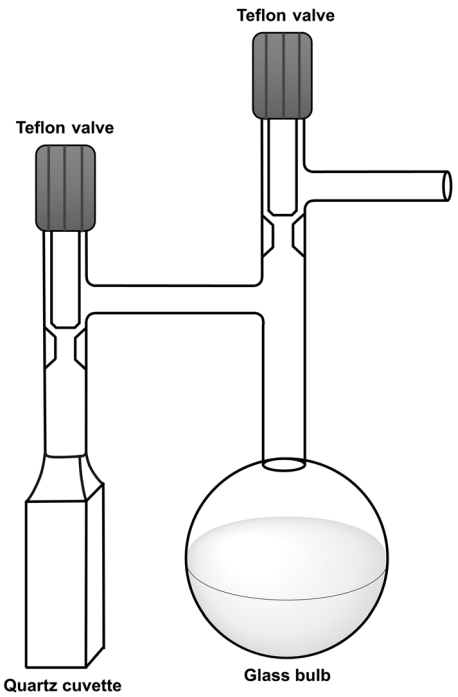

Fig. 2 Custom high-vacuum cuvette for air-sensitive photophysical measurements.

tain them. Before measurement, it is necessary to ensure the cuvette windows are free of fingerprints, dust, or any other impurities, as they would absorb or scatter light and affect the measurement. It is normally advised to promptly remove the sample from the cuvettes after use and rinse with an appropriate solvent to prevent the sample or decomposition products from depositing and sticking to the cuvette walls. For deeper cleaning, quartz and glass cuvettes can be immersed in a dilute nitric acid (10%) solution overnight, or even stronger acid if necessary, followed by rinsing with deionized water and acetone/ethanol. Ultrasonic baths should not be used to clean cuvettes, because there is a high chance of breakage when the resonant frequency of the cuvette's material is similar to that of the ultrasonic waves. Since high temperatures can disrupt the binding materials that hold cuvette walls together and alter their size due to thermal expansion, it is recommended to dry the cuvettes under ambient conditions or use very mild heating. Alternatively, vacuum drying can be used to facilitate the drying process if needed. Finally, cuvettes should be stored in an appropriate fabric or foam-lined container to prevent scratches on the windows. Scratches can increase light scattering as it passes through the cuvette and alter measured intensities.

Solid samples

Photophysical measurements are commonly performed on solid-state samples, usually prepared from powders or polycrystalline materials. Generally, the measurement of such samples requires the use of an appropriate solid sample holder, one example of which is shown in Fig. 3. This holder typically consists of three main components: rotatable stage, sample base, and sample cover. The sample base is usually made of plastic or metal with a flat base to house the solid material. The cover, made from borosilicate glass or quartz, secures the sample in place while allowing both excitation and emission light to pass through. Since solid samples have high optical density and promote significant light scattering, emitted light is commonly collected from the front face of the sample, rather than being allowed to pass through, as is the case for solution measurements. This setup often requires precise angular adjustment of the rotatable stage to find the optimal alignment between the excitation light, sample, and detector to achieve maximum signal with minimal scattering from the excitation source. In most cases, angles of 30° or 45° between the excitation light and the sample front-face provide good results. Unfortunately, a limitation of this method of measuring solid samples is that it is difficult to accommodate oxygen-sensitive samples or measurements, as it does not provide a sealed environment. To exclude oxygen, an inert gas flow into the instrument's sample chamber is typically required. Alternatively, quartz tubes with high-vacuum valves can be used to prepare and isolate solid samples from air. In this approach, either a solid is loaded into the tube in an inert-atmosphere glovebox, or a solution of the sample is loaded into the tube, and the solvent is removed under vacuum to produce a solid residue. Another simple method involves sandwiching the sample between two transparent slides. Preparation in an inert atmosphere is typically required for this method, and applying grease to the slide edges is essential to prevent permeation of air into the sample.

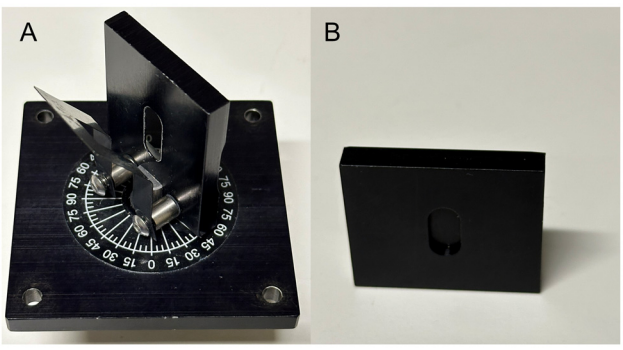

Fig. 3 Example of a solid sample holder. (A) Rotatable sample stage. (B) Sample base.

Film samples

Transparent films are commonly employed in photophysical measurements, either as neat films composed solely of the compound or more commonly as composite films where the compound is dispersed within a transparent polymer matrix and deposited onto a solid, transparent substrate, with quartz again being the most common substrate material. To prepare a composite film, first the compound and the polymer matrix material are dissolved together, necessitating a solvent that can effectively dissolve both components. A mixture of solvents can be used in necessary cases, where the sample will be dissolved in a different solvent before being added to the polymer solution. Because the film must be fully dried before measurement, highly volatile solvents are typically recommended. If a high-boiling-point solvent is necessary, the sample can be dried under vacuum to facilitate the process. In terms of polymer selection, the polymer matrix should have high transparency, good solubility in common solvents, and chemical inertness. Poly(methyl methacrylate) (PMMA) and polystyrene (PS) are two of the most commonly used polymers for this purpose.

Film deposition onto substrates can be carried out in different ways, with drop-casting and spin-coating widely used. In drop casting, a volume of solution is repeatedly pipetted onto the substrate and left to dry to form a thin film as the solvent evaporates. While film thickness is not precisely controlled in this method, it is still suitable for routine photoluminescence measurements where consistency in film thickness is not critical. In contrast, spin coating is a more efficient method and allows for better control of film thickness through adjustable spin speed and solution volume. For large-scale or uniform coatings, other techniques such as dip-coating, blade coating, or slot-die coating can be used. After deposition, films should be allowed to dry completely under ambient conditions. For oxygen-sensitive compounds or when measure-

ments must be performed in the absence of oxygen, all sample preparation steps, including dissolution, coating, drying, and storage, should be done in an inert atmosphere (*e.g.*, inside a nitrogen-filled glovebox). If the proper facilities are not available, the preparation can be done under ambient conditions. Then, the sample should be stored under vacuum overnight, followed by the reabsorption of inert gas to obtain the oxygen-free sample. While the polymer matrix may provide short-term protection against oxygen during measurement, additional encapsulation layers may be necessary for highly sensitive materials. For photophysical measurements, the film sample is placed on a rotatable stage (Fig. 3A), and angular adjustment of the sample stage is needed to optimize the alignment of the excitation light, sample, and detector to maximize signal collection.

UV-vis absorption measurements

UV-vis spectrophotometry is a versatile technique that has been used for a variety of applications in different fields. This technique is used to determine which wavelengths of light are absorbed by the sample, during which the compound of interest is promoted from the ground state to higher-lying excited states. Most commonly the range of wavelengths evaluated spans the ultraviolet to visible regions (200–900 nm), but some spectrophotometers can also probe transitions in the near-infrared (NIR) region (800–3200 nm). In these regions, electronic transitions are normally being observed, and because of the spin-selection rule the most intense features in UV-vis experiments on closed-shell molecules involve transitions to singlet excited states. In an absorption spectroscopy measurement, light with intensity I_0 passes through the sample, and the intensity of the light (I) transmitted through the sample is measured. Using the values of I_0 and I, the absorbance (A) or transmittance (T) can be calculated *via* eqn (3) below.

$$A = -\log(T) = -\log\left(\frac{I}{I_0}\right) \quad (3)$$

While absorbance (A) and transmittance (T) both quantify the proportion of light absorbed or transmitted, respectively, at a specific wavelength, absorbance is more commonly used in UV-vis experiments as it is linearly proportional to the sample concentration and cuvette's path length (see below).

Instrumentation

The four main components in UV-vis spectrophotometers are the light source, monochromator, sample holder, and a detector (Fig. 4). Initially, the light source generates broad-spectrum light. Then, the light goes through a monochromator to narrow down to a selected wavelength. Light at the specified wavelength passes through the sample and its intensity is registered by the detector. Among different light sources, deuterium arc lamps, tungsten-halogen lamps, and xenon arc lamps are the most common. Specifically, the deuterium arc lamp provides good intensity in the UV range with medium

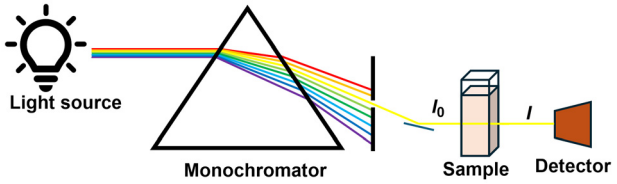

Fig. 4 Simplified diagram of UV-vis spectrophotometer.

intensity in the visible range. In contrast, the tungsten-halogen lamp has good intensity in the visible to NIR range, with weaker intensity in the UV region. Due to the properties of these two light sources, a combination of deuterium arc and tungsten-halogen is commonly used to provide broad light from the UV to the NIR region. Xenon arc lamps provide light with good intensity from the UV to the NIR regions, making them popular choices for instruments with a single source. The monochromator, usually comprised of a diffraction grating, disperses the white light from the source and separates it into its constituent wavelengths. Through the rotation of the monochromator relative to the exit slit, a specific wavelength can be selected. Usually, a single monochromator is used in spectrophotometers, although some high-performance models have dual monochromators for even more precise wavelength selection. Depending on the wavelength range of the instrument, there are different detector options available. A photomultiplier tube (PMT) is good for detecting UV-visible light with a range from 200 to 900 nm, sufficient for most experiments. A PMT has the advantage of being very sensitive to low photon counts and is typically used in concert with a monochromator to detect one wavelength at a time, which results in comparatively slow measurement. A silicon diode array is a better choice than a PMT when a wider range of detection is needed (170 nm to 1000 nm). An advantage of diode array or CCD detectors over PMTs is that they can detect all wavelengths of the dispersed light simultaneously, drastically shortening collection times and especially useful for kinetics or spectroelectrochemistry experiments that require rapid measurement. However, compared to PMTs, silicon photodiode arrays suffer from lower sensitivity, while CCDs are limited by higher cost. For detection in the NIR region, semiconductor detectors such as InGaAs or PbS can be used.

Experimental considerations

Solutions samples are most common in UV-vis absorption spectroscopy, although neat solid and film samples can be accommodated, often with additional sample holders and accessories that allow the instrument to operate in reflectance mode. To start the measurement, a blank sample with pure solvent is used to determine the intensity I_0 at each wavelength. Then, the sample is measured to obtain the attenuated intensity I at each wavelength. While it is generally fine to measure the I_0 and I at different times, fluctuations in light source intensity can sometimes cause baseline drift, so it is recommended to allow the lamp to warm up and stabilize for

at least 30 minutes before measurement and to record the blank and the sample consecutively. Alternatively, a double-beam UV-vis spectrophotometer where the source light passes through a beam splitter and the blank and sample are measured simultaneously can be used to overcome this problem, although allowing the lamp to warm up is also important when using a double-beam UV-vis spectrophotometer.

Data analysis and proper reporting

Typical data analysis of UV-vis measurements follows the Lambert–Beer Law, which gives the relationship of absorbance (A), molar absorption coefficient (ε), concentration (c), and path length (l), is shown in eqn (4) below.

$$A = \varepsilon c l \quad (4)$$

The standard units for c are molarity (mol L^{-1}) and for l are cm, such that ε is reported in units of L mol^{-1} cm^{-1}. In some literature sources ε is referred to as molar absorptivity or extinction coefficient. However, according to IUPAC, the use of these terms in place of "molar absorption coefficient" is discouraged.[36] UV-vis spectra are commonly presented in two ways: absorbance (A) *vs.* wavelength (λ) or molar absorption coefficient (ε) *vs.* (λ). We recommend the latter, as ε is a useful parameter for other researchers who may want to use the compound of interest in their own work, and it allows "apples-to-apples" comparisons with other light-absorbing compounds. If absorbance is used as the y-axis quantity, the concentration of the sample should be clearly stated. The molar absorption coefficient (ε) at a certain wavelength is best obtained by measuring absorption spectra across a range of concentrations and determining the slope of the best-fit line from a plot of absorbance (A) *versus* concentration (c), where the slope equals εl. When the molar absorption coefficient at a specific wavelength (ε_λ) is known, the A *vs.* λ spectrum at any concentration can be first normalized by dividing all absorbance values by the absorbance (A_λ) at that wavelength. Then, the y values of the resulting normalized spectrum are rescaled by multiplying by ε_λ, converting the UV-vis absorption spectrum to units of molar absorption coefficient.

Although the Lambert–Beer Law works well as a framework to analyze UV-vis absorption data in most cases, it is important to be aware of potential deviations that can occur. One of the most common reasons is aggregation, which can occur in certain compounds as the concentration is increased, introducing new absorption features attributed to the aggregated state (s). High sample concentrations can also change the refractive index of the solution and possibly impact the measured absorbance of the sample. While there is no specific concentration required for UV-vis absorption, samples with a concentration below 10 mM usually follow the Lambert–Beer Law.[37,38] One other factor to be aware of is that because measuring A requires detection and quantification of transmitted light, there is a practical limit to the range of absorbance values that can be accurately measured, which is instrument-specific. In very dilute samples I and I_0 are similar, such that reproducible determination of A can be challenging. In the opposite extreme, if the sample is too concentrated the ratio I/I_0 becomes vanishingly small, *i.e.*, the fraction of light absorbed approaches 100%, and the spectrum will start to appear noisy with unreliable absorbance values. According to eqn (3), 90% of photons are absorbed when $A = 1$, whereas $A = 2$ means that 99% of the light is absorbed, further increasing to 99.9% at $A = 3$ and 99.99% at $A = 4$. While the range of absorbance values that can be reliably measured varies depending on the instrument characteristics, the most reliable absorption data usually has A in the range of ~0.1–2.

A common error in UV-vis absorption data reported in the literature is the inclusion of "a.u" when absorbance is plotted on the ordinate axis, which authors presumably intend to mean either "arbitrary units" or "absorption units", but neither is correct since absorbance is a unitless quantity. Another common error is incorrect usage of "absorption" and "absorbance"; the latter describes the process and the experiment (*i.e.*, absorption of light, absorption spectroscopy), whereas "absorbance" is the measured quantity as defined in eqn (3). The term "absorbance spectrum" is incorrect, and it is likewise incorrect to refer to the measured quantity as the "absorption" of the sample.

Photoluminescence spectroscopy

Photoluminescence spectroscopy is a common research technique used to investigate the photophysical properties of luminescent compounds. In this technique, the compound is excited by absorbing a photon, and then the relaxation of the compound to the ground state results in the emission of light. The instruments used to measure photoluminescence, most often called (spectro)fluorimeters or (spectro)fluorometers, are used to control the excitation light and measure the emitted light, which provides useful information about the electronic and optical properties of luminescent compounds. With typical commercial instrumentation, photoluminescence spectra, excitation spectra, and quantum yields can all be measured.

Instrumentation

Similar to UV-vis spectrophotometers, there are also four main components in spectrofluorometers: the light source, monochromators, sample holder, and detector. While the function of these components is the same, the setup of the instrument is different (Fig. 5). In spectrofluorometers, the light from the lamp is narrowed to a selected wavelength *via* the excitation monochromator, which then passes through the sample. After absorption, which generates an excited state, any emitted light produced as the compound relaxes back to the ground state is split into its constituent wavelengths *via* the emission monochromator and directed to the detector. To reduce the amount of excitation light that reaches the detector, the emitted light is collected at a 90° angle relative to the excitation source. In

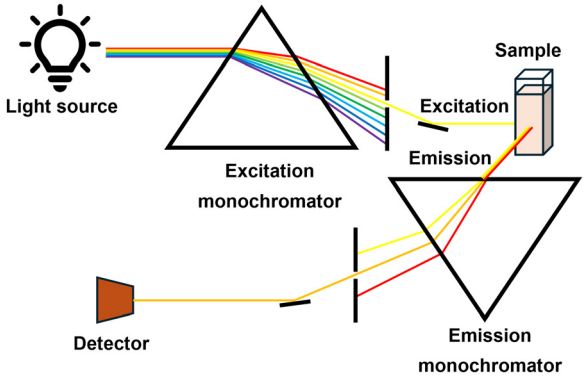

Fig. 5 Simplified diagram of a typical spectrofluorometer.

photoluminescence spectra, the excitation wavelength is fixed, and the detector measures the intensity of the emitted light over a specific wavelength range. Conversely, an excitation measurement only measures the intensity of the emitted light at a single wavelength while varying the wavelength of the excitation light. Additionally, spectrofluorometers can be used to measure the photoluminescence quantum yield, as described later.

Instrument parameters

By using different sample holders, fluorimeters can measure samples in solution, solid, and film types, described in the section above on sample preparation. Before recording the photoluminescence or excitation spectrum, it is important to understand and appropriately adjust several key instrument parameters.

Excitation wavelength. The excitation wavelength is fixed at a single wavelength to record the emission spectrum, or it can be set up as a range of wavelengths to measure the excitation spectrum. In general, the choice of excitation wavelength(s) needs to be in the working range of the light source and monochromator and must be a wavelength or range of wavelengths absorbed by the sample. In the emission spectrum, the excitation wavelength is often chosen as the maximum absorption wavelength of the sample, but it need not be. In the excitation spectrum, the range of excitation light should terminate at least 10 nm below the selected wavelength of emission, to avoid detection of the excitation light (due to Rayleigh scattering).

Emission wavelength. In an emission experiment, this is selected as a range of wavelengths that are measured by the detector. In an excitation experiment, the emission wavelength is held constant. In terms of wavelength selection, the emission wavelength needs to be in the detection range of the specific detector and the calibration range of the monochromator, which are instrument specific. To reduce interference from scattered excitation light, the start of the emission range should have a good separation from the excitation wavelength; we recommend at least 10 nm. Another factor that needs to be considered when choosing the emission range is second-order diffraction of light that passes through the monochromator. This effect can create a false emission signal at the 2λ peak of any emitted light. Second-order peaks from scattered excitation light are also commonly observed. For example, if the excitation wavelength is 310 nm, a false emission peak may appear at 620 nm due to the second-order diffraction of the excitation light. To prevent this, the use of an appropriate long-pass filter and/or avoiding scanning into the second-order diffraction peak is recommended.

Long-pass filters. The long-pass filter is an optical filter that blocks the light with wavelengths that are shorter than the cutoff wavelength specified for the filter (the cutoff wavelength is typically defined as the wavelength at which T = 50%). In photoluminescence spectroscopy, a long-pass filter is commonly placed in front of the detector, between the cuvette and the emission monochromator and typically in a dedicated filter holder in the sample chamber, to prevent the scattered excitation light from reaching the detector. To ensure efficient blocking of the excitation light, the cutoff wavelength of the filter should be at least 20 nm higher than the excitation wavelength. Moreover, the cutoff wavelength of the filter also needs to be at least 10 nm lower than the wavelength at which the first emission signal appears. Since there are different physical shapes and dimensions of long-pass filters on the market, the compatibility of long-pass filters and the instrument also needs to be considered.

Slit widths. In a spectrofluorometer, the slit width is used to control the amount of light exiting the monochromator before reaching the sample or detector. There are two slits in a typical photoluminescence spectrofluorometer that can be adjusted, termed the entrance (or excitation) slit and exit (or emission) slit. While the entrance slit controls the amount of light that passes through the sample, the exit slit controls the amount of emission light that reaches the detector. In most instrument control software, the entrance slit is specified in the excitation settings, while the exit slit is part of the emission settings. The typical unit of slit width is nm, which corresponds to a bandwidth of light passed. The values of the slit widths are varied based on the properties of the sample and the measurements. A narrow slit-width provides higher wavelength resolution in the spectra, but it reduces the light intensity and can cause low signal-to-noise ratio. Conversely, increasing the slit width can enhance the detected intensity and improve the signal-to-noise ratio. However, peak broadening and reduced resolution can be a problem if the PL bands are particularly sharp, and a more serious issue is exceeding the linear range of the detector, often referred to as "detector saturation", which leads to inaccuracies in measured intensity. A slit width between 1–5 nm is commonly used for typical experiments, offering a good balance between resolution and signal intensity.

Scan speed and integration time. The scan speed refers to how quickly the instrument scans through the wavelengths, typically measured in nm min^{-1}. Another replated parameter is integration time (s nm^{-1}), which is the length of time the detector integrates the signal at each wavelength. Although a decrease in scan speed or increase in integration time leads to

improved signal-to-noise ratio, the cost is a longer collection time, which could lead to degradation of particularly sensitive samples. In spectrofluorometer instruments, a typical scan speed is 1 nm every 0.1 s (*i.e.*, 600 nm min^{-1}). Adjustments can be made according to the sample's properties, and slower scan speeds and/or longer integration times can be beneficial for weakly emitting samples or for measurements conducted at low temperatures where noise is more common.

Experimental considerations

While it is quite simple with modern instruments to set up and record an emission spectrum, it is important to be able to recognize situations where the recorded data may be inaccurate or unreliable. The first common reason is the presence of impurities. Given the sensitivity of modern instrumentation, even trace amounts of luminescent impurities can produce detectable signals, that either present as additional features or can be easily misinterpreted as originating from the compound of interest. As discussed later, a comparison between excitation and absorption spectra can be helpful to rule out emission from spurious impurities. Detector saturation, another common issue in PL measurements, can present as oddly shaped bands, often "plateau–shaped", or can be recognized when the observed intensity approaches the upper limit of the detector (as specified in the instrument manual). To avoid detector saturation, narrowing the slit widths or placing neutral-density filters in front of the detector are common solutions. Finally, in some samples, distortion of the PL spectrum can be caused by the inner-filter effect, which can be a primary inner-filter effect or secondary inner-filter effect. The primary inner-filter effect occurs when the sample is too concentrated and strongly absorbing, which attenuates excitation intensity and decreases penetration depth, such that the sample is not uniformly excited. While this will not necessarily distort the spectrum, it does make the observed intensity inaccurate, which can cause problems in quantum yield measurements or other situations where it is important to quantify intensity. The secondary inner-filter effect commonly happens when there is an overlap between the absorption and emission spectra, most often in fluorescent samples, resulting in reabsorption of the emitted light by the sample and distortion of the emission spectrum. Both inner-filter effects can be minimized by diluting the sample, and the primary inner-filter effect can be obviated by choosing an excitation wavelength where the absorbance is lower.

Low-temperature photoluminescence spectra

Some samples require the measurement of photoluminescence spectra at low temperatures. Cooling the sample can drastically reduce the nonradiative decay rate constant (k_r), allowing significant PL to be observed from samples that are non-emissive or weakly emissive at room temperature. Moreover, it is often possible to clearly resolve vibronic transitions at low temperature, which can provide valuable information about the emissive excited state. Finally, comparisons of spectra recorded at room temperature and low temperature can yield important insights about the nature of the emissive excited state and any thermally activated processes that occur. To carry out a low-temperature measurement, a special sample holder is necessary to control the temperature of the sample. The most sophisticated way to adjust the temperature of the sample is with a cryostat, which electronically controls the temperature using a coolant like liquid nitrogen or liquid helium. A more economical sample holder is a quartz dewar (Fig. 6), which does not give precise temperature control but allows the sample to be cooled to a discrete temperature using a coolant, most often liquid nitrogen (T = 77 K). The dewar can be a customized EPR dewar placed in the instrument's beam path, or a specialty sample holder provided by the instrument manufacturer, as shown in Fig. 6. The sample is placed in the quartz dewar filled with liquid nitrogen or another coolant of choice. Since quartz cuvettes cannot withstand such low temperatures without breaking, the sample is usually contained in a quartz ampule or EPR tube. For a solution sample, it is important to choose an appropriate solvent or solvent mixture that forms a transparent glass when frozen.[39,40] Some common solvents with this property are toluene, 2-methyltetrahydrofuran, ethanol, and isopropanol. If the product is not soluble in any of these solvents, a small amount of a different solvent can be used to dissolve the sample before adding an aliquot to the above solvents.

Data analysis and proper reporting

A typical PL spectrum is reported as observed intensity (y-axis) *vs.* wavelength (x-axis). The observed intensity is dependent on several factors related to the sample, the instrument hardware, and instrument settings,[24,27] so it is important not to overinterpret the values when comparing data. Relatedly, it is often common to normalize PL intensity before plotting multiple spectra together, since differences in observed intensity are often not meaningful. When reporting PL data, it is also recommended to specify the excitation wavelength and the details

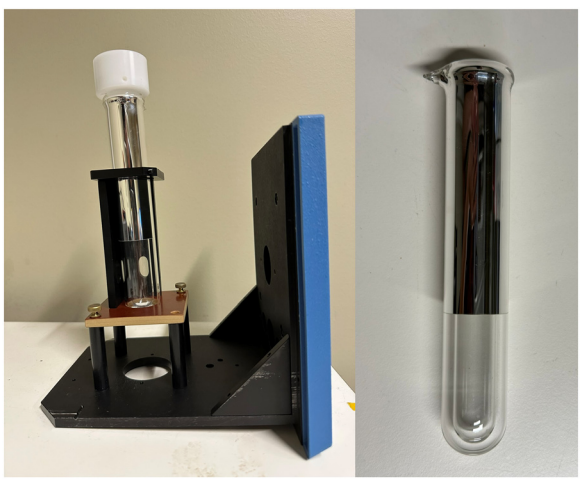

Fig. 6 Example of a sample compartment and quartz dewar for low-temperature photoluminescence measurements.

of the sample matrix (solvent for solution sample, polymer for film sample, and sample concentration) to ensure data reproducibility.

An excitation spectrum shows the intensity of emission at a specific wavelength (which should be specified when reporting the data), plotted as a function of the excitation wavelength. Excitation spectra are less commonly collected or reported compared to PL spectra, but they can provide valuable information. An excitation spectrum can be used as a purity check for the sample. In optically dilute samples ($A < 0.1$ at all wavelengths), the luminescence intensity and absorbance are nearly in a linear relationship. Thus, if the material follows Kasha's rule, the UV-vis absorption spectrum should be identical to the excitation spectrum. There are a few potential causes when the excitation and absorption spectra deviate: (i) Most likely, the sample is not pure and one or more luminescent impurities are partly or entirely responsible for the observed luminescence. This can be especially problematic in samples that have weak emission, where even a very minor impurity (<1%) can dwarf the signal from the compound of interest. (ii) The sample does not follow Kasha's rule. While uncommon in molecules, there are some situations where localized emissive excited states can only be accessed *via* excitation at specific wavelengths. Solid-state samples are typically not optically dilute and include localized states with poor interconversion between them, making differences between excitation and absorption spectra more likely. Excitation spectra can also help clarify the assignment of the emissive state(s) and determine the optimal excitation wavelength.

Photoluminescence quantum yield

Photoluminescence quantum yield (Φ_{PL}, or sometimes PLQY) is a crucial metric for photoluminescent compounds, representing the efficiency of converting absorbed photons to emitted photons. Fundamentally, Φ_{PL} is the ratio of the number of emitted photons to the number of absorbed photons. The typical range of Φ_{PL} is from 0 to 1 (or 0% to 100%), although in certain cases a lower maximum is possible, for example in triplet–triplet upconversion or two-photon absorption processes, where two low-energy photons are required to generate one emitted high-energy photon, making the maximum $\Phi_{PL} = 0.5$. Since Φ_{PL} is not instrument-dependent, it is the most useful metric to compare the luminescence intensity or efficiency of different compounds, and thus we recommend that it always be included in any report that presents one or more new luminescent compounds. Absolute and relative methods to measure Φ_{PL}, described below, are most often used. These measurements can be made on the same spectrofluorometers used to record PL spectra.

Relative quantum yield

The relative method is the most common way to measure the quantum yield of a solution sample. The basis of this method is eqn (5) below, which involves emission intensity (I_{PL}), an instrument-specific parameter (k), intensity of the excitation light (I_0), quantum yield (Φ_{PL}), and absorbance (A) at the excitation wavelength.

$$I_{PL} = kI_0\Phi_{PL}(1\text{–}10^{-A}) \quad (5)$$

If the term kI_0 remains unchanged by using the same instrument and experiment settings, and if the sample is optically dilute ($A < 0.1$), the quantum yield will be directly proportional to the ratio of the emission intensity to absorbance. Based on this idea, the quantum yield of the sample can be determined by comparing the absorbance and emission intensity of both the sample and a well-characterized standard at low concentrations. When performing a relative quantum yield measurement, there are several considerations.

Standard selection. In principle, the standard can be any material with a known quantum yield. However, to ensure the accuracy and reproducibility of the data, several critical factors should be considered. (i) The standard should be the well-known compound with a widely accepted quantum yield. If the quantum yield of the standard is misreported, quantum yields determined with that standard will be inaccurate. As an example, the quantum yield of *fac*-Ir(ppy)$_3$ (ppy = 2-phenylpyridine) was originally misreported as 0.40,[41] and was subsequently revised to 0.97, resulting in many reported quantum yields that used it as a standard to be incorrect.[42] (ii) To minimize errors from fluctuations in excitation intensity and variable detector sensitivity at different wavelengths, it is recommended to use a standard with emission and absorption spectra that closely overlap with those of the sample. In many modern instruments there are built-in corrections for these factors, making this consideration less critical. (iii) The standard should be of high purity and stable during measurement to avoid the effects of impurities on the data. There are some reliable sources to find appropriate standards, such as the PhotochemCAD database[43] and IUPAC reports.[44] Some standards commonly used in relative quantum yield measurements are quinine sulfate in sulfuric acid (Φ_{PL} = 0.546), Rhodamine B in ethanol (Φ_{PL} = 0.70), Rhodamine 6G in ethanol (Φ_{PL} = 0.94), and tetraphenylporphyrin in toluene (Φ_{PL} = 0.11).

Sample preparation. As mentioned above, to ensure the accuracy of the measurement, the absorbance of the sample at the excitation wavelength and at longer wavelengths should be ≤0.1. Additionally, to minimize error, the use of the same cuvette for the sample and standard is recommended. While the use of the same solvent for sample and standard in applicable cases is encouraged, different solvents can be used as the quantum yield formula also includes a correction for solvent refractive index (n, see below). It is possible to measure a relative quantum yield using a single sample of the standard and a single sample of the compound of interest, although it is also common to perform the measurements over a range of concentrations for increased accuracy. From our own experiences, trace oxygen is a common source of error when measuring quantum yields of phosphorescent compounds, particu-

larly if a stock solution is injected into a septum-topped screw-cap cuvette to prepare the desired concentrations, and sometimes it is necessary to do all sample preparation inside of a glovebox to avoid this issue.

Sample measurement. There are two measurements involved in a relative quantum yield experiment: absorbance at the excitation wavelength and the photoluminescence spectrum. These measurements are performed identically on both the standard and the sample of interest. It is critical to ensure that the experimental settings (especially slit widths, integration time, and detector settings) for the studied compound and the standard are identical when measuring the relative quantum yield. Excitation wavelengths and emission ranges can be altered between the two if necessary, although a good practice is to excite at isosbestic points of the sample and standard absorption spectra, which helps maintain uniform light absorption during the measurements. When choosing the excitation wavelength and emission range, it is important that the emission spectrum is fully collected and that the second-order diffraction of the excitation light is avoided.

Quantum yield calculation. If a single sample is measured for both the standard and the compound of interest, the relative quantum yield of the compound (Φ_x) can be calculated *via* eqn (6) below, where x refers to the compound of interest and st indicates the standard used for comparison. Φ_{st} is the known quantum yield of the standard compound, I in this case is the integrated emission intensity, which can be obtained *via* integration of the PL spectrum using software like OriginLab or MATLAB. A is the absorbance at the excitation wavelength and the "n" is the solvent refractive index (Table 1).

$$\Phi_x = \Phi_{st}\frac{I_x}{I_{st}}\frac{A_{st}}{A_x}\frac{{n_x}^2}{{n_{st}}^2} \quad (6)$$

When multiple sets of spectra are collected at different concentrations for the compound of interest and standard, the calculation involves the slope of the best-fit line obtained by plotting the integrated emission intensity (I) *versus* the absorbance (A). One benefit of measuring at different concentrations is that we can check that the absorbance and the integrated emission intensity are linearly related, which is a key assumption of a relative quantum yield measurement. Deviations from linearity could indicate sample degradation, oxygen contamination, or aggregation. When linearity is not met, corrections to emission spectra are necessary to ensure accurate quantum yield calculations.[40,45] With these slopes determined, we can use eqn (7), a variation of eqn (6), to determine the quantum yield.

$$\Phi_x = \Phi_{st}\frac{\text{slope}_x}{\text{slope}_{st}}\frac{{n_x}^2}{{n_{st}}^2} \quad (7)$$

Absolute quantum yield

Absolute PL quantum yields can also be measured, in which the instrument setup allows for accurate counting of the number of absorbed and emitted photons by using an integrating sphere. The quantum yield will be equal to the number of emitted photons divided by the number of absorbed photons.

Experiment setup. The measurement of the absolute quantum yield commonly requires an integrating sphere attachment and compatible sample holder (Fig. 7), usually sold as accessories to a commercial spectrofluorometer. An integrating sphere is a hollow spherical compartment that is coated on the inside with a totally reflective polymer material. There are two apertures on the integrating sphere, one in the beam path to allow the excitation light to enter, and the other at a 90° angle to direct light into the detector. The sample will be placed in the center of the integrating sphere, and all the light from the source that is not absorbed and all the emitted light from the sample will reflect to the exit aperture and reach the detector. An integrating sphere collects all light from the sample, which differs from the typical collection method with a standard sample holder, where only part of the emitted light is collected and detected. Absolute quantum yield measurements with an integrating sphere can be recorded on any sample type, offering an advantage over the relative method described above that is only amenable to solution samples in cuvettes. In addition, the samples need not be optically dilute when recording an absolute quantum yield.

Sample measurement. An absolute quantum yield measurement involves collecting emission spectra to determine the number of emitted photons and measuring attenuation of Rayleigh-scattered excitation light by the sample to determine the number of absorbed photons. To start the experiment, the scattered excitation light and emission spectrum of a blank sample are measured. If the sample is a solution, the blank sample is the cuvette with pure solvent. For a film sample, the blank sample is the substrate coated with only polymer material. The scattered excitation from the blank sample provides information about the intensity of the light source, and the emission spectrum of the blank sample gives the background luminescence that the sample may have. Then, the experiment is repeated with the samples using identical set-

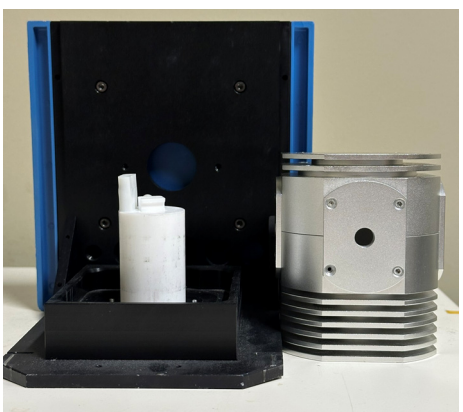

Fig. 7 Example of an integrating sphere and sample holder for absolute quantum yield measurements.

tings. Since the exit light contains photons from the excitation source and sample emission, it is important to choose an excitation wavelength not in the emission range of the sample. Additionally, the use of the appropriate long-pass filters during the emission measurement is necessary to reduce the noise and second-order diffraction from the excitation light.

Quantum yield calculation. After the measurement, it is common to use the instrument software to calculate the quantum yield of the sample. The software uses the instrument-specific correction file, the excitation intensity of the blank and sample, the emission spectra of the blank and sample, the excitation wavelength range, and the emission wavelength range as inputs. The integrated emission intensity of the blank is subtracted from the sample's integrated emission to determine the number of emitted photons, and the difference between the integrated Rayleigh scattering of the blank and sample determines the number of absorbed photons (Fig. 8). Then, the quantum yield can be calculated by dividing these two quantities. Commonly, the software reports the quantum yield to a high level of precision. However, based on the typical reproducibility of absolute quantum yields, it is normally best to report the value with 2 significant figures. A common pitfall with absolute quantum yield measurements is treating the experiment as a "black box" and blindly trusting the number the software returns. However, to ensure that the data are reliable, it is important to verify that the observed emission in the quantum yield experiment is clearly above that of the blank and occurs within the expected wavelength range. In addition, it is important that the sample concentration and excitation wavelength are chosen to ensure appreciable absorption by the sample, such that the Rayleigh intensity of the sample and the blank will be substantially different. If there is very little absorption by the sample, calculation of the number of absorbed photons is prone to error, and the emission signal will likely be weak and unreliable as well.

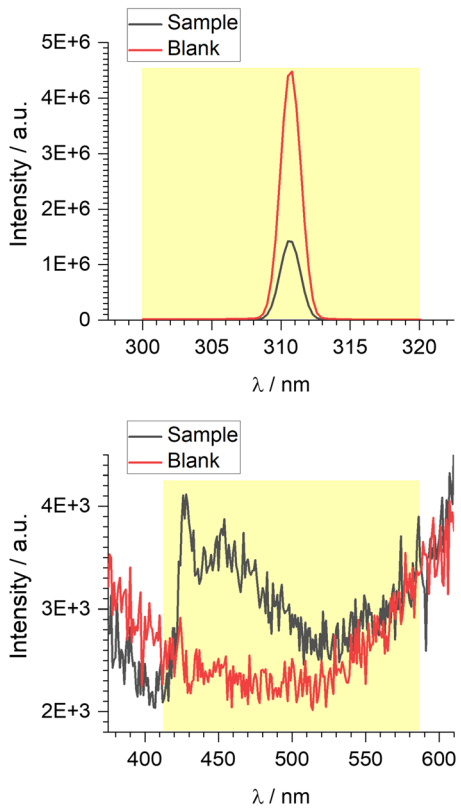

Fig. 8 Example of Rayleigh scattering (top) and emission (bottom) spectra recorded during an absolute quantum yield measurement. Data for the blank is shown in red, and for the sample in black. The yellow box denotes a suitable range over which to integrate the data when calculating the quantum yield.

Photoluminescence lifetime

One of the important parameters to report in studies on new luminescent compounds is the photoluminescence lifetime. Generally, the lifetime is the average time that the luminescent molecules stay in the excited state before returning to the ground state. For ideal materials that follow first-order excited-state decay kinetics, the lifetime is mathematically defined as the time needed for a defined concentration of excited states of the chemical species to decrease to $1/e$ of its initial value. To measure PL lifetime, time-resolved photoluminescence experiments are carried out, which measure the decay of the photoluminescence signal following a fast excitation pulse. The most popular method to measure time-resolved luminescence lifetime is time-correlated single-photon counting (TCSPC). This method is based on the principle that the luminescence intensity at a given time is directly proportional to the probability of detecting a single photon at that moment. The excitation pulse occurs at $t = 0$ and the time at which the first emitted photon is recorded is measured over many repetitions, giving a histogram that represents the time-resolved decay of the PL intensity. In ideal systems, the relationship between the lifetime and the luminescence intensity is shown in eqn (8), where I is the emission intensity, I_0 is the intensity at $t = 0$, t is time after excitation, and the time constant τ is the excited-state lifetime.

$$I = I_0 e^{-t/\tau} \tag{8}$$

Considering that TCSPC is the most common method due to its high sensitivity and large coverage range, this section is mainly focused on the TCSPC method.

Instrumentation

While there are variations in TCSPC instrument setups, a simplified, typical configuration is diagrammed in Fig. 9. To start the measurement, a pulsed light source excites the sample, and at the same time, the timing electronics start the timer. After a short time, the compound begins to return to ground state and emits a photon. When the first emitted photon is detected by the detector, it will send the signal to the timing device to stop the timer, record the time, and finish the measurement. After many measurements (often thousands),

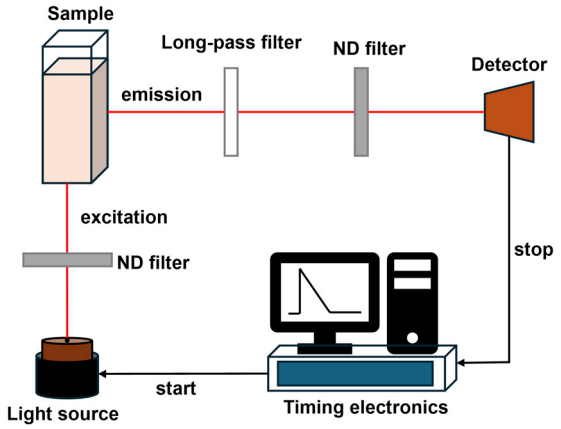

Fig. 9 Simplified diagram of a photoluminescence lifetime system.

the cumulated data provides the photon count *vs.* time histogram, which is analyzed to determine the excited-state lifetime. TCSPC can either be performed in a stand-alone instrument containing all the components shown in Fig. 9, or in some cases the necessary components are installed as accessories onto a steady-state spectrofluorometer. Not shown in Fig. 9, some TCSPC setups have monochromators to select individual wavelengths for detection, although many instruments do not include one since monochromators reduce light intensity and increase collection time, and in typical luminescent compounds the measured lifetime would be the same across the entire range of emitted light. As a result, optical filters are sometimes used to coarsely select wavelength ranges for TCSPC measurements.

Light source. Since the TCSPC method assumes that the time the sample is excited (t = 0) is the same as the time the light source generates light, it is necessary that the light source can generate high-intensity light during a very short time to rapidly excite the sample. These pulsed sources generally produce a fixed wavelength, although wavelength-tunable light sources are also available in some instruments. The common sources used in TCSPC instruments are laser diodes and LEDs. While laser diodes such as Ti:Sapphire and Nd:YAG produce intense pulses with very short time resolution (femtoseconds to picoseconds), their high cost limits their accessibility. On the other hand, LEDs are much more cost effective, and they can be used in experiments with resolution as short as picoseconds. However, LEDs typically have lower light intensity than lasers, which may pose challenges with weakly emissive samples or require longer collection times. The light source's repetition rate, which is the number of pulses per unit time, also relates to the data acquisition time.

Detectors. TCSPC uses similar detector types as steady-state measurements, such as a microchannel plate (MCP), photomultiplier tube (PMT), or charge-coupled device (CCD). It is important to combine a suitable light source and detector to obtain high-quality data. For example, the use of femtosecond lasers requires a fast response detector (like MCP), while a slower-responding detector is suitable for picosecond light sources.

Neutral density filter (ND filter). A neutral density filter is an optical filter that reduces the intensity of the light uniformly over all wavelengths. TCSPC relies on timing the first photon that is generated after the excitation pulse. Inaccuracies can occur when the emitted light is too intense, which can result in multiple photons being detected following excitation, known as the "pile-up" effect, discussed later in this section. By using a neutral density filter, the intensity of the light can be controlled to meet the instrument standard.

Experimental measurement

Sample preparation guidelines are identical to those described above for steady-state measurements, so they are not repeated here. Ideally, the measured lifetime is independent of sample concentration, but using as dilute of samples as possible is recommended to reduce self-absorption and guard against the possibility of aggregation or triplet–triplet self-quenching, which could influence the measured lifetime. Sample holders for time-resolved instruments are the same as those used in a spectrofluorometer for cuvettes or solid samples (Fig. 3). It is helpful to collect UV-vis absorption and PL spectra before beginning the lifetime measurement, to determine the suitable light source for excitation and the long-pass filter for emission. Long-pass filters are not strictly necessary in a lifetime measurement, although in samples with multiple emission bands they can be useful for coarse wavelength selection when the instrument lacks a monochromator. In some instrument models, different pulsed light sources are used for shorter (~ns to low μs) and longer (>μs) timescales, so the selection of light source may also depend on the decay timescale of the compound. While it is not strictly required to know the lifetime of the sample before measurement, it is helpful to have an approximate idea of the lifetime to save time in choosing the correct light source and time range for measurement.

Once the sample is placed in the appropriate position and a suitable light source and long-pass filter are selected, the TCSPC measurement can be conducted following the steps below:

1. The timescale for the measurement is selected. In general, the time range is recommended to be *ca.* 10× longer than the expected lifetime. For a compound with an unknown lifetime, it will require some "trial and error" before obtaining a suitable time range for measurement. The suitable time range should be long enough to observe the PL decay all the way to baseline, but short enough to ensure that the baseline signal does not occupy a large portion of the collected time range. Additionally, along with the selection of the time range, some instruments allow the repetition rate to be manually altered. However, it is typical for the repetition rate to be automatically adjusted to align with the relevant time range.

2. Neutral density filters are selected. During a lifetime measurement, it is usually necessary to use neutral density filters to reduce the intensity of the emission light, placed in

front of the detector or the light source. Neutral density filters are needed to mitigate the "pile-up" effect. If a second photon reaches the detector during the specified collection timescale, it will be counted, which results in artificially high intensity at early time points. The count rate, normally displayed in the instrument software, specifies what percentage of excitation pulses result in an emitted photon being counted. To minimize pile-up, it is important to adjust the count rate to <5% of the repetition rate by using neutral density filters or adjusting the emission slits if available.

3. Once the instrument settings are chosen, the measurement can begin. In general, the experiment is run until a set number of counts is reached at the maximum intensity; generally, a maximum of 1000 to 10 000 counts will produce high-quality data. The amount of time needed to reach the pre-set maximum depends on how strongly luminescent the sample is, so for weakly-emitting compounds a lower setpoint closer to 1000 is often used.

While the above steps are normally required for common instruments, additional steps may need to be taken depending on the sample type and the instrument's capabilities. For example:

1. The sample position may need to be adjusted. Some instruments allow the sample to be rotated to maximize the signal-to-noise ratio and minimize detection of the excitation light. Such adjustments are important for solid or film samples, where the scattered excitation light can strongly affect the data collection.

2. If the TCSPC is interfaced with a cryostat or other temperature-control sample holder, the temperature of the sample can be adjusted and should be at a stable value before measurement. PL lifetimes are temperature-dependent and the quantitative response of the lifetime to the temperature can give valuable information in certain applications.

Instrument response function (IRF). The TCSPC method determines the lifetime based on measuring the time between the sample excitation and the first photon reaching the detector. However, there is a built-in early-time lag during which the light source generates the excitation pulse and the detector records the signal. The IRF is the total response time of the light source and detector. Since IRF is often very short, in our experience it is not necessary to measure it for a sample with a lifetime approaching or exceeding the microsecond scale. However, it is important to measure the IRF for samples having nanosecond-scale lifetimes or shorter. The IRF can be measured by using a blank sample or a sample with scattering particles.

Data fitting

Once the measurement is done, it is necessary to fit the data to extract the lifetime. Although the raw data can be analyzed using data analysis software like Origin or MATLAB, it is common that instrument software will offer a data-fitting function. In an ideal case with a single emitter luminescing from a single excited state, the lifetime raw data should fit the exponential decay function given in eqn (8). As mentioned above, the intensity of emission is proportional to the number of counted photons at each time point.

The first step in data analysis is data selection. It is important to select enough data to achieve a high-accuracy lifetime. Commonly, the data should be fit from the point where the decay starts until the signal reaches the *x*-axis or merges with the background noise (Fig. 10). For a sample with a short lifetime (nanosecond scale), the fit should begin after the decay of instrument response function (IRF), although some versions of instrument software allow the IRF to be subtracted out during the fit, in which case the entire decay can be reliably used for fitting (Fig. 10, bottom trace). A common malpractice in reported PL lifetimes is fitting an inappropriate data range. Fitting too small of a range can result in a lifetime that is inaccurate and leaves out valuable data from the fit. Fitting too large of a range, *e.g.*, including too much baseline signal in the fit, is not usually problematic in samples with well-behaved exponential decays, but also is not necessary since no useful information is obtained by fitting the baseline noise. For a reliable fit, we recommend selecting a data range that is 5× the PL lifetime. According to the exponential decay equation, $5 \times \tau$ means that 99.32% of the signal has decayed, so fitting data in this range of windows will ensure that most of the PL decay is accounted for in the fit.

Once the analysis range has been selected, the next step is fitting the data to the appropriate exponential decay. Typically, if the sample has a single emissive pathway, the monoexpo-

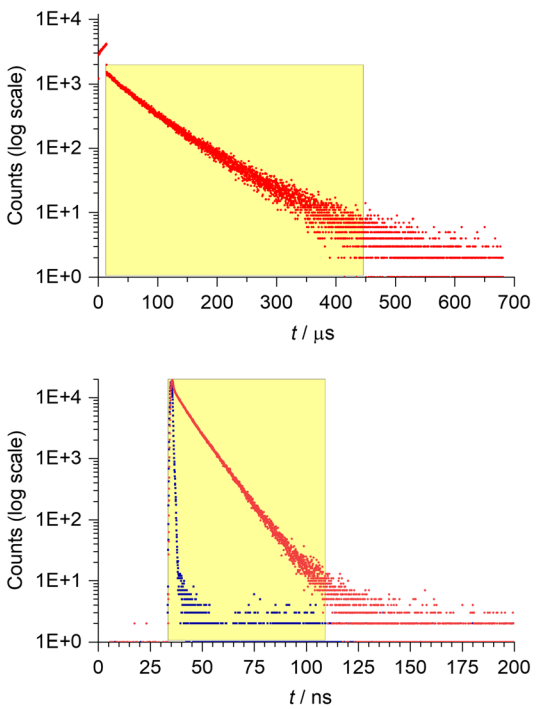

Fig. 10 Examples of PL decay data recorded *via* TCSPC: blue data points represent the IRF and red data points represent the sample. Top: 63 μs phosphorescence lifetime. Bottom: 9.9 ns fluorescence lifetime. The yellow boxes indicate appropriate fitting ranges for the raw data.

nential model should be selected. In the case that the sample has more than one decay pathway, a multiexponential model will be used. For most luminescent molecules in solution, a monoexponential or biexponential decay fit is appropriate. Conversely, solid-state materials or nanomaterials with heterogeneity or defects, such as perovskites, quantum dots, and semiconductors, rarely follow a monoexponential decay equation. After selecting the data and the appropriate exponential decay, the fitting parameters are optimized by the software to give a best-fit curve for the selected data range. The two main criteria used to determine whether a fit is satisfactory are the chi-squared test (χ^2) and the distribution of weighted residuals. A discussion of the χ^2 test is beyond the scope of this article, but most instrument software will return χ^2 as one of the fitting parameters and will specify recommendations for a "good" fit. Ideally, the χ^2 should be as close as possible to 1. If the fit is satisfactory, the weighted residuals should be randomly distributed around 0 and should not display any periodic behavior. If the quality of the fit is not satisfactory, using a higher-order exponential equation can improve the outcome. However, from the standpoint of reporting and interpreting results, there needs to be a reasonable physical explanation for the higher-order fit, *e.g.*, multiple emissive states, different relaxation pathways, or environmental heterogeneity.

Proper reporting

It is straightforward to report the lifetime for a sample that exhibits monoexponential PL decay, where the reported lifetime is simply the time constant of the exponential decay. On the other hand, it is more complex to report the lifetime of a sample that has more than one exponential decay, which will have multiple time constants and weighting parameters (pre-exponential terms) to consider. For full transparency, we recommend specifying in a publication when a higher-order exponential fitting function was used, and in some cases, it is appropriate to report the fitting parameters in full. If the purpose is to just report a lifetime, there are two values that need to be considered when the decay is multiexponential. The first is the proportion of the total decay attributed to each component, and the second is the average lifetime. To understand how to properly evaluate and report these terms, an example is presented below.

Example. After finishing collecting the data for the sample, the researcher used the instrument software to fit the data to eqn (9), where I is photon counts, τ_i represents the time constants of the components, and α_i represents the pre-exponential terms.

$$I(t) = \sum_{i=1}^{n} \alpha_i e^{t/\tau_i} \tag{9}$$

The researcher found that a satisfactory χ^2 value and residuals were obtained with a biexponential decay. The fitting parameters were τ_1 = 22 μs, τ_2 = 59 μs, α_1 = 665, and α_2 = 415. First, the fractional intensity or relative amplitude (f) of each component can be calculated following eqn (10) below.

$$f_i = \frac{\alpha_i \tau_i}{\sum_{i=1}^{n} \alpha_i \tau_i}$$
$$f_1 = \frac{\alpha_1 \tau_1}{\alpha_1 \tau_1 + \alpha_2 \tau_2} = 0.37; f_2 = \frac{\alpha_2 \tau_2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} = 0.63 \tag{10}$$

These values indicate that 37% of the decay comes from the first component and 63% of the decay comes from the second component.

Then, the average lifetime of the sample can be calculated *via* the intensity-weighted method, using eqn (11) below.

$$\tau_{\text{avg}} = \frac{\sum_{i=1}^{n} \alpha_i {\tau_i}^2}{\sum_{i=1}^{n} \alpha_i \tau_i} = \sum_{i=1}^{n} f_i \tau_i$$
$$\tau_{\text{avg}} = \frac{\alpha_1 {\tau_1}^2 + \alpha_2 {\tau_2}^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} = 45\ \mu\text{s} \tag{11}$$

The average lifetime is also sometimes calculated *via* the amplitude-weighted method, given by eqn (12) below.

$$\tau_{\text{avg}} = \frac{\sum_{i=1}^{n} \alpha_i \tau_i}{\sum_{i=1}^{n} \alpha_i} \tag{12}$$

The intensity-weighted average lifetime (eqn (11)) is used for samples with multiple emissive species, which is generally applicable when reporting the average lifetime of new luminescent compounds. On the other hand, the amplitude-weighted average lifetime (eqn (12)) is most appropriate when measuring changes in excited-state decay kinetics (*e.g.*, Stern–Volmer quenching or energy transfer processes).[27,46] In situations where biexponential decay occurs, the average lifetime is normally reported, but including the individual lifetimes and the fractional intensity of each component is recommended. In the same vein as absolute quantum yields, the instrument software will often display fitting parameters with an arbitrarily high level of precision, but the typical reproducibility of lifetime measurements does not justify such precise reporting, so we recommend reporting the lifetime with two significant figures, unless multiple replicates and rigorous statistical analysis indicate that a different level of precision is appropriate.

Summary and conclusions

Photophysical data, including UV-vis absorption spectra, photoluminescence (PL) spectra, PL quantum yields, and PL lifetimes, are crucial for understanding the behavior of luminescent compounds. With the rapid progress in photoluminescence-related research and its increasing importance in the field of inorganic chemistry, accurate and reproducible measurement and interpretation of these photophysical data are critical. In this tutorial review, we aim to provide research-

ers with clear, concise guidelines for collecting and reporting photophysical data, along with strategies to avoid common pitfalls. While the appropriate data to report in a paper depends on the message that is being conveyed, below we summarize a final, concise set of recommendations to follow when publishing a report that includes photophysical data recorded on new compounds:

1. *UV-vis absorption data*: it is best to plot the data with ε as the vertical axis and the temperature and solvent used for the experiment should be clearly specified.

2. *Photoluminescence and excitation spectra*: for PL spectra, the nature of the sample (solution, film, or neat solid), the temperature of data collection, and the excitation wavelength should be specified in figures and/or tables. For solution and film samples, the solvent or support medium should be stated, and the concentration of the sample is also a useful parameter to include. We also strongly encourage the inclusion of excitation spectra, normalized and overlaid with the UV-vis absorption spectra.

3. *Photoluminescence quantum yields*: we recommend always including Φ_{PL} values when reporting any new luminescent compound. Comparisons of raw emission intensity are often meaningless and do not properly contextualize the results. Detailed experimental procedures for the quantum yield measurements should be included, and it is usually best to perform two or more self-consistent trials and report the average value.

4. *Photoluminescence lifetime*: we recognize that instrumentation for time-resolved PL measurement is not as widely accessible as steady-state spectrofluorometers, but lifetimes should be included when possible. Similar to quantum yield measurements, multiple replicates to ensure accuracy and reproducibility should be carried out. Experimental details related to the instrument used, excitation wavelength, and temperature should be clearly stated in the text.

We hope this tutorial contributes to improving data quality, enhancing reproducibility, and supporting further progress in the field.

Author contributions

Vinh Q. Dang: conceptualization, visualization, writing – original draft, writing – review & editing. Thomas S. Teets: conceptualization, funding acquisition, project administration, supervision, visualization, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included, and no new data were generated or analysed as part of this review.

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