Luminescence: a fascinating phenomenon that engages learners

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Abstract There are several 'cool' mechanisms that result in materials luminescing or emitting light. Artificial luminescence has often been created by mimicking nature and there are many examples of applications in society. It is very likely that most of your students will have observed luminescence in one form or another, such as glow sticks, high-visibility jackets, sea creatures that glow in the darkness of the deep sea, fireflies and highlighter pens. This article explores the nature of luminescence and introduces some interesting natural and synthetic examples. It also reports on some innovative applications of luminescence in food science and medicine, and introduces a range of activities to engage and challenge your students. Luminescence, a term first used by Eilhardt Wiedemann in 1888, is a phenomenon that can be integrated into chemistry, physics and biology studies, and it offers a wow factor for students.

Observations of luminescence in nature have been recorded as far back as 1500 BC in early Chinese literature (Goldberg and Weiner, 1989) when describing fireflies and glow worms. Notable names associated with the study of luminescence in the 17th and 18th centuries include Francis Bacon, Robert Boyle, Isaac Newton, Humphry Davy and Galileo. It was at this time that Boyle discovered that bioluminescence required air. Later it was shown by Spallanzani in 1797 that the prerequisite for this bioluminescence was oxygen (Roda, 2011; Goldberg and Weiner, 1989). In 1603, Vincenzo Cascariolo discovered that heating the mineral barite ($BaSO_4$) with carbon produced a solid (BaS) that glowed after it had been exposed to light. Later investigations found that the luminescence was catalysed by trace amounts of bismuth and manganese in the barium sulfide.

Research into luminescence mushroomed during the 20th century. Not only were new luminescent materials discovered, such as luminal, but individual chemicals involved in bioluminescence were beginning to be characterised (Roda, 2011). During the late 1940s and early 1950s, McElroy and Hastings investigated bacterial luminescence and found that ATP and FMH were essential for luminescence (McElroy, 1947; McElroy *et al.*, 1953).

Types of luminosity

Table 1 shows some of the more common ways in which light can be produced from materials.

This article will focus predominantly on fluorescence, phosphorescence and bioluminescence. For each process, a simple explanation will be provided with some natural examples and applications.

Table 1 Common types of luminosity

Type	Energy source	Cause
Fluorescence	Light, e.g., UV	Emission of light when an electron transitions from an excited state to ground state. The transition is from a excited singlet state to a singlet ground state and is 'allowed'.
Phosphorescence	Light, e.g., UV	Emission of light when an electron transitions from an excited state to a ground state. The transition is from a triplet excited state to a singlet ground state and is said to be 'forbidden'.
Chemiluminescence	Energy transfer during a chemical reaction	Electrons are excited through chemical reactions. They transition to ground state as before.
Bioluminescence	Chemical reactions that are of biological origin	This is the same as chemiluminescence but is a product of biochemical reactions.
Electroluminescence	Electrical energy	Emission of light follows the introduction of electrical current.
Sonoluminescence	Sound energy	Emission of light follows the introduction of sound.
Triboluminescence or Piezo luminescence	Pressure (force)	Light is produced through surface charges created by frictional forces when crystals are crushed or rubbed. The energy is mechanical.

What is luminosity?

Luminosity is defined as the production of light from the transition of electrons from an excited electronic state to a ground state. The process is the same for fluorescence, phosphorescence, chemiluminescence or bioluminescence, although the mechanisms may be slightly different.

Students studying at key stage 4 (ages 14–16) will be aware of the basic electronic shell structure in atoms and may have been introduced to transitions of electrons between these shells when investigating flame tests or learning about transition metals. At key stage 5 (ages 16–18) students will be aware of quantised electronic levels and orbitals and of electronic transitions between excited and ground states. An explanation for luminescence can be built upon this knowledge with the depth dependent on your students' prior knowledge and understanding.

What's the difference between fluorescence and phosphorescence?

Both processes are examples of photoluminescence and rely on a material's ability to absorb light of a particular energy, then emit light of a lower energy (some energy is absorbed by molecular collisions, vibrations and rotations).

The key observable difference between these phenomena is the delay between absorbing and emitting the light energy (photons). The delay for fluorescence is extremely small (10^{-9} to 10^{-6} seconds), so emission of light appears to need a continuous source of energy and it appears instantaneous. This means that fluorescence is only seen when shining a light source on the material. The process that defines phosphorescence takes significantly longer (10^{-3} seconds to several hours), so it appears that the material can continue to 'glow' after the light source (energy) is removed.

Scientific explanation

To understand what fluorescence and phosphorescence are, some understanding of the electronic and vibrational structures of atoms is required.

We know from the Pauli exclusion principle that electrons in an atom can't have the same four quantum numbers (n, l, m_l and m_s – the quantum numbers that describe an atom, Table 2) because they must exist in different quantum states, and that a maximum of two electrons can occupy each shell (orbital). This requires electrons occupying the same orbital to have opposite spins, that is, their m_s values must be different.

We know that electron pairs are energetically more stable when they have opposite spins and are said to be in a singlet state (+½ and −½). However, the electrons can have the same spins (+½ and +½ or −½ and −½), which is far less likely because this configuration has a significantly higher energy. This is referred to as the triplet state.

Table 2 The quantum numbers that describe an atom

Quantum number	Symbol	Purpose
Principle	n	Describes the energy levels in an atom
Angular momentum	l	Defines the type of orbital or sub-shells (s, p, d, f) – shapes are linked to probabilities of finding an electron in 3-D space of a particular energy
Magnetic	m_l	Identifies the sub-orbital and orientation (e.g. px, py, pz)
Spin	m_s	Defines the spin angular momentum as +½ or −½

There are several quantum mechanical 'rules' that govern transitions between electronic energy levels. One is that a transition of an electron is far more likely if the transition retains the spin of the electron; that is, it is far more likely for an electron in a ground state to transition to an excited state and retain its +½ spin. It is far less likely for an electron to transition if there is a change in spin; that is, an electron with +½ spin transitions to a excited state with −½ spin or an excited electron with a −½ spin transitions to a ground state with +½ spin.

So, although both processes occur, the transition that retains the spin occurs more rapidly (10^{-9} to 10^{-6} sec). This is fluorescence. The slower process, where the spin in the excited state is opposite to the ground state, takes far longer because it is far less probable (10^{-3} to several hours). It is referred to as a 'forbidden' transition. This is phosphorescence. These processes are illustrated in Figure 1.

So how do we understand spin?

The spin of an electron can be understood as a type of angular momentum. All electrons possess this intrinsic property. Singlet states have electrons in opposite spin orientations, so are diamagnetic – they do not possess a resultant magnetic field. When a magnetic field is applied to a diamagnetic electronic system the electrons are unaffected. However, when electrons are orientated in the same direction (or only one electron exists in an orbital), the system is said to be paramagnetic. A magnetic field will interact with the electrons as they now possess their own intrinsic magnetic field. The spin state for the electrons in an orbital can be obtained using the expression $2S+1$, where S is the value of the total spin angular momentum. For example, if electrons in an orbital have opposite spin values (+½ and −½) the total spin angular momentum is 0 and $2S+1=1$ (singlet state). If the electrons have the same spin orientation the total spin angular momentum is 1. The value of $2S+1=3$ $(2\times1+1$ triplet state).

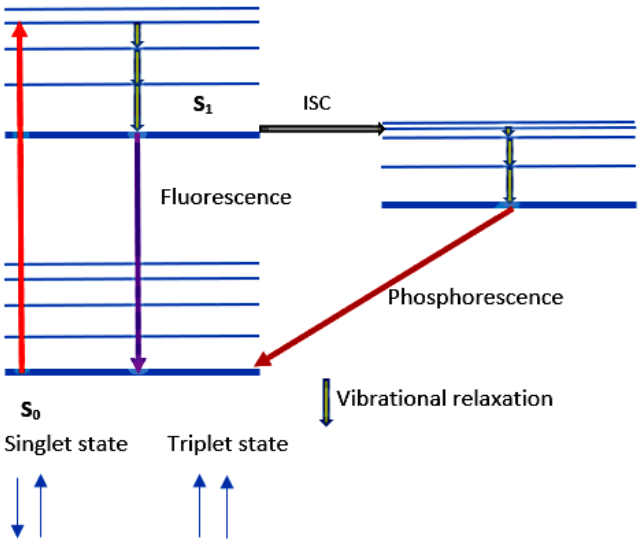

Figure 1 The difference between fluorescence and phosphorescence transitioning; ISC = internal spin conversion; S_0 = ground state and S_1 = first excited state

For each electronic energy state there are several associated vibrational states. An excited electron will often exist in an excited vibrational state. This additional energy is transferred to the heat energy store through intermolecular collisions (similar molecules, gas molecules in air or solvent molecules in solution). These transitions are non-radiant (Figure 1).

It is far more likely for an electron to be excited from a singlet ground state to a singlet excited state. However, the electron may very rarely undergo internal spin conversion (ISC) where it ends up in a triplet excited state. The 'allowed' fluorescent transition is much more likely so faster than the 'forbidden' phosphorescent transition.

Chemiluminescence and bioluminescence

The basic chemical processes involved in bioluminescence are very similar to chemiluminescence. Chemical reactions provide energy that transitions an electron into an excited state and the energy is emitted as light on returning to the ground state. Glow pens are a familiar example of chemiluminescence. Bioluminescence refers to light produced in chemical reactions that are biological; that is, produced by living organisms. This article will focus now on the fascinating world of bioluminescence.

Haddock, Moline and Case (2010) identified around 10 000 species that naturally luminesce and suggested that the evolution of luminescence has provided organisms with survival advantages. For example, luminescence is used for deterring predators, luring prey, attracting a mate or for camouflage (Fleiss and Sarkisyan, 2019).

Four main bioluminescent groups have been identified. These are insects, bacteria, fungi and marine organisms, which constitute the largest group and include copepods and shrimp. In each group there are examples of various colours being produced, from blues to yellows and reds, but each group has unique biochemical reactions that produce the light. In general, each organism requires a substrate molecule that can absorb energy to become excited. This molecule is generically called a luciferin. The reaction also requires a catalyst, which is generically called luciferase. This luciferin–luciferase pair is unique to each species. In some systems the chemical reactions also require additional chemicals such as oxygen, calcium or magnesium ions, or more complex molecules such as ATP and NAHD (Syed and Anderson, 2021).

Insects

Each bioluminescent insect has its own unique luciferase catalyst, yet they all share the same D-luciferin substrate (Kaskova, Tsarkova and Yampolsky, 2016; Fleiss and Sarkisyan, 2019). Research has shown that for fireflies the chemical process that produces luminescence also requires the cofactor ATP in the presence of Mg^{2+} ions to initiate the reaction and molecular O_2 to oxidise the substrate. It has been suggested that the molecule that is converted into a high-energy intermediate contains a strained cyclic peroxide group (Lee, 2017). The process ultimately results in the substrate forming an excited molecule that then emits light energy when it drops back to its ground state. Insects can produce a range of colours, typically yellow, orange and red. The high sensitivity of D-luciferin to ATP has led to this process being used to measure ATP concentrations in the study of cancer metabolism and for monitoring bacterial contamination in foods. A simplified reaction scheme is shown in Figure 2.

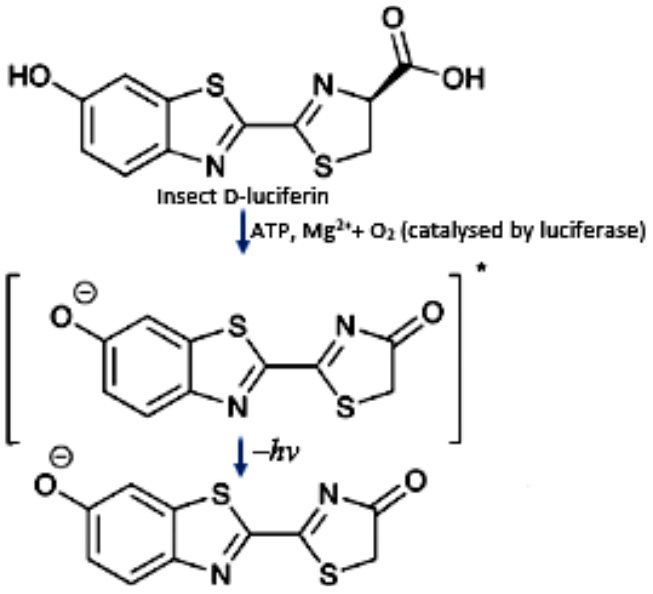

Figure 2 Simplified biochemical process for insect D-luciferin (adapted from Syed and Anderson, 2021); the process produces an excited molecule that produces light (*hν*) on return to its ground state

Marine

The largest group of organisms that exhibit bioluminescence are marine animals. Most organisms use the luciferin coelenterazine, a complex polypeptide, and, as with insects, each organism often uses a unique luciferase catalyst (Kaskova *et al.*, 2016, Bandaranayake, 2006). Often, the photochemical reaction only requires molecular O_2 to occur. The most common colour produced is blue. It is interesting to note that many organisms that display bioluminescence obtain the coelenterazine from their food rather than synthesising it themselves (Haddock, Rivers and Robinson, 2001). A simplified reaction scheme is shown in Figure 3.

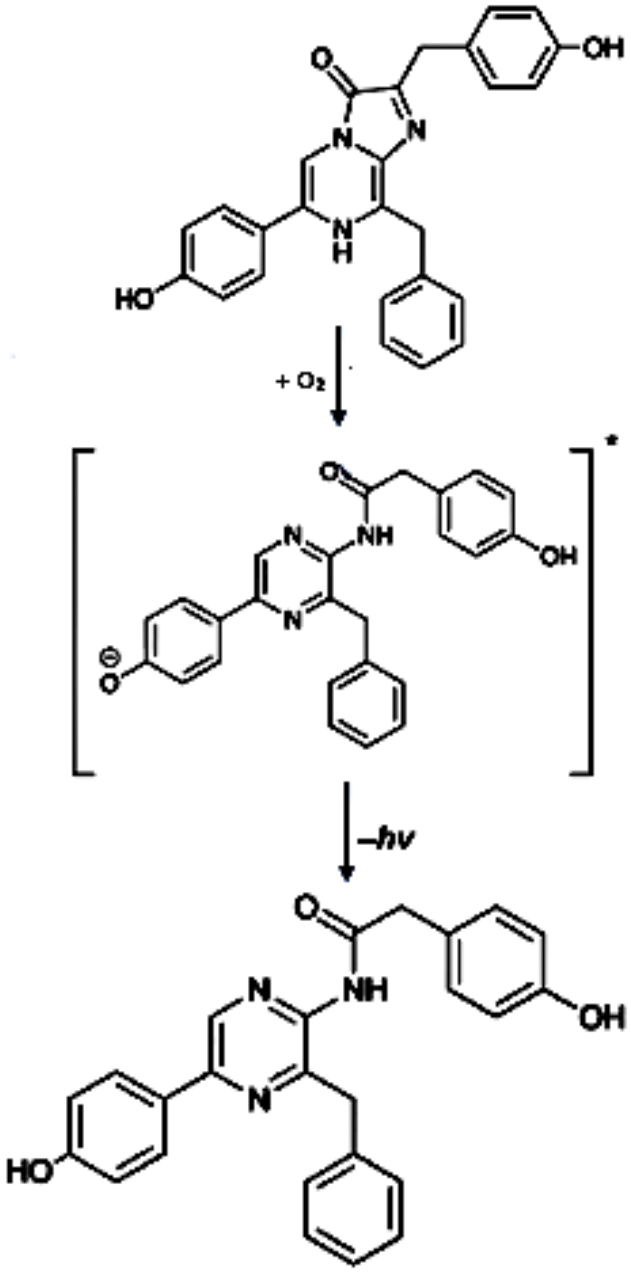

Figure 3 Simplified biochemical process for marine luciferin coelenterazine in coelenterates (adapted from Syed and Anderson, 2021)

Bacteria

The chemical process that produces light in bacteria has been studied in some depth and the mechanism is relatively well understood (Syed and Anderson, 2021; Kaskova *et al.*, 2016). The process requires a long-chain aldehyde as the luciferin, along with flavin mononucleotide (FMN), NADH (reducing agent) and molecular O_2 (Figure 4). The luciferase (the catalyst/enzyme) molecules are complex polypeptide chains. Both the luciferase and the enzymes that support the production of luciferin molecules are encoded in the lux operon (encodes the genes so they can form the protein molecules). Originally, bacterial luciferase was encoded by a single lux gene, but this evolved into a two-gene system, which now encodes for current luciferases.

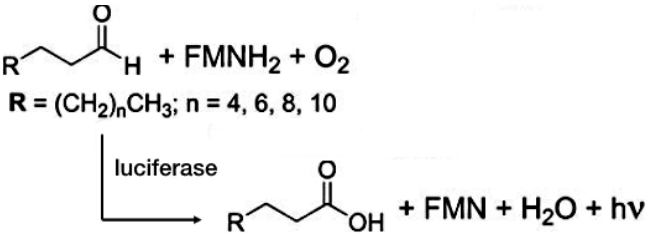

Figure 4 Bacterial luciferin-long-chained aldehyde (Adapted from Brodl, Winkler and Macheroux, 2018)

Most typically, blue light is emitted by luminescent bacteria. The applications of bacterial bioluminescence are wide ranging, for example, in the use of identifying pathogenic bacteria and viruses.

What is the purpose of bioluminescence?

Figures 5 shows some fascinating images of bioluminescence in action. Animals that use bioluminescence do so for a number of reasons. These could be to attract a mate, advertise their territory to others, camouflage themselves from potential predators or attract their prey!

Figure 5 Clockwise from top left, bioluminescent fish, jelly fish, fireflies and scorpion

Applications for fluorescence and phosphorescence

Hygiene control

Luminescence adapted from firefly chemistry is used in a range of hygiene-monitoring environments, such as in hospitals to check for bacterial contamination on surfaces, in food-processing industries, and to measure environmental bio-pollution (Syed and Anderson, 2021). The process relies on the high sensitivity of luciferins on ATP, an essential component of living cells.

Medicine

Bioimaging is used extensively to measure the absorption and metabolism of drugs in the body. The most recent luminescent molecules have been created on a nanometre scale so that they can be used for *in vivo* studies. In the past, excitation of the chemicals occurred while in the body with the use of X-rays and UV sources. This often led to undesirable side effects resulting from cell and tissue damage and death (Tan *et al.*, 2019). However, the creation of nano-sized particles with persistent luminescence, lasting several hours, and that can be excited outside the body, has led to much safer practice. The most recent research into medical delivery systems for medication and to monitor cell function has employed hydrogels. These aqueous-based structures encapsulate chemicals, so offer even greater protection against cell damage from treatments such as chemotherapy and from luminescent molecules (Yang *et al.*, 2021; Wang *et al.*, 2017).

Road safety

Many signs and safety clothing, whether for working on roads, cycling or in industrial environments that are potentially hazardous, make good use of luminescent materials (Figure 5).

Figure 5 High-visibility jacket

Examples and activities

Health and safety

It is extremely important that a low-energy and child-safe UVA source is used. For guidance, please refer to CLEAPSS GL 127 (11/2021).

Fluorescent minerals

Several minerals glow in the dark if radiated with a child-safe UV light source. Many are very easy to obtain, such as calcite, ruby, hackmanite, fluorite and willemite.

This activity is very engaging and complements learning about electron shells and excitation mechanisms. Figure 6 shows minerals illuminated by visible light and UV. For each mineral, the chemical formula is given and

Figure 6 Minerals illuminated by visible light and UV

the trace ions responsible for the fluorescence are shown in blue.

Common household chemicals

There are many household materials that fluoresce when radiated with UV light. These include glow pens, highlighter markers, high-visibility clothing, olive oil, soluble vitamin C, tonic water, and phosphorescent paint on clock and watch hands. Figure 7 shows a selection of materials before and during UV radiation. This activity is similar to the previous one and can be used to support students' understanding of the excitation of electrons from ground state to excited state and what happens when they return to ground state. This can be useful when explaining why we get different colours with certain metals in flame tests.

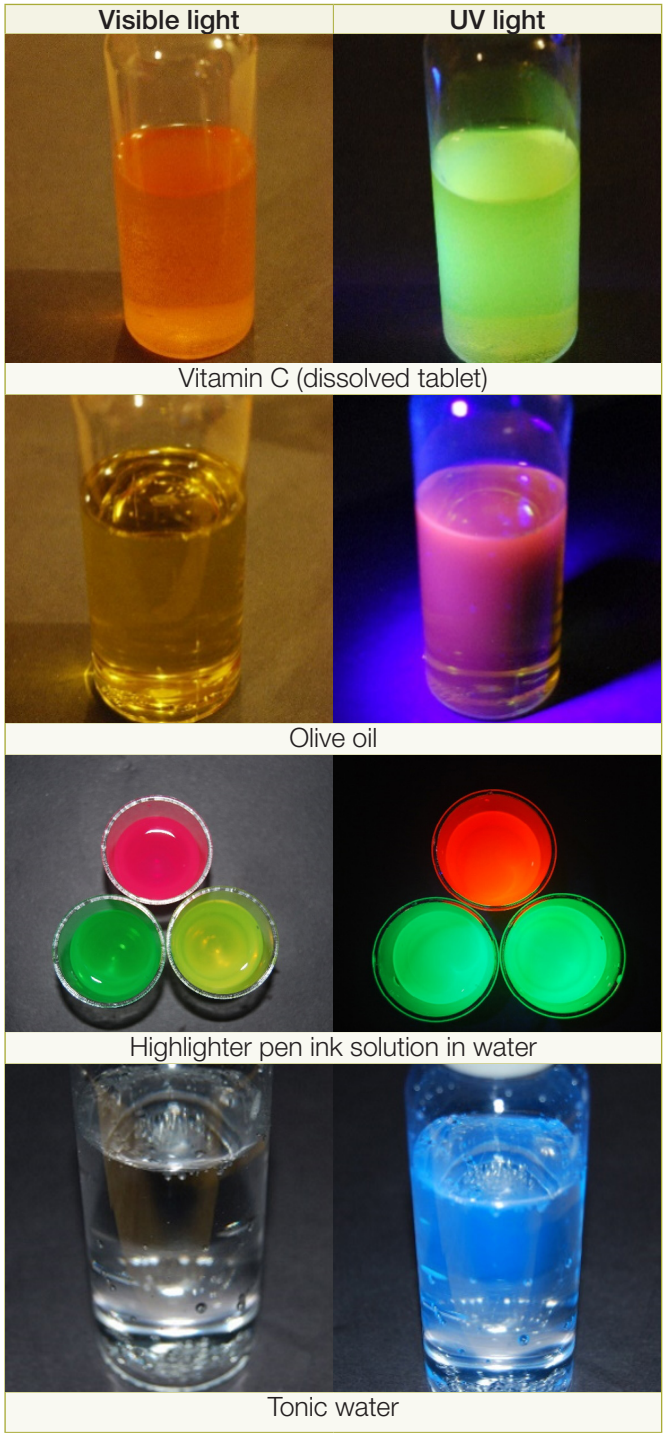

Figure 7 Some household materials luminescing

Rates of reaction with glow sticks

Understanding rates of reaction is an important scientific concept that students will become familiar with. There are several tried-and-tested practical investigations that help students to conceptualise rates of reaction. However, as a novel experiment, students might like to measure how the rates of luminescence change over time at different temperatures. The following method provides a qualitative view of rates of reaction.

Method

To provide greater significance to this experiment you may like to use a range of coloured glow sticks.

1 Place a glow stick (or one of each colour) at the same time in a fridge, in a freezer and in a place at room temperature.
2 At 20-minute intervals (or whatever is convenient) look at the glow sticks and describe what you see. What happens to the amount of light emitted? Is there any difference between the light being emitted by the same glow sticks at different temperatures?
3 Can you explain your results?

Figure 8 shows that at the start of the experiment, the glow sticks kept at 20°C emitted more light than those at 4°C. However, after 12 hours the opposite was seen. This observation can be explained by the greater rate of reaction at the higher temperature.

The investigation can be developed so that students record observations in more detail. Table 3 shows a potential way to record and compare photographic results at room temperature, 4°C and –19°C over a period of 4 hours.

Possible questions for students to consider:

- Which glow stick (at which temperature) will glow brightest and why?
- Which glow stick will last longest and why?
- Will the order of brightness of the glow sticks change over time and why?

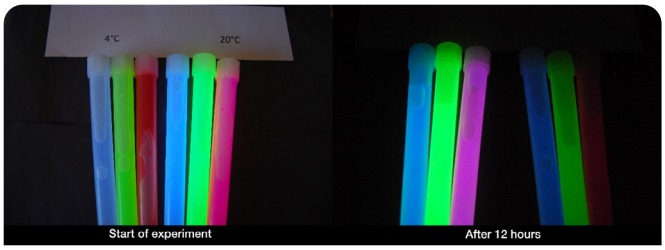

Figure 8 Coloured glow sticks kept at 4°C and 20°C over a period of 12 hours

Table 3 Recording photographic evidence

Time	Temperature / °C		
	Room temp	4°C (fridge)	–19°C (freezer)
20 mins	*Photo 1*	*Photo 1*	*Photo 1*
1 hour	*Photo 2*	*Photo 2*	*Photo 2*
2 hours	*Photo 3*	*Photo 3*	*Photo 3*
3 hours	*Photo 4*	*Photo 4*	*Photo 4*
4 hours	*Photo 5*	*Photo 5*	*Photo 5*

Encourage students to explain their observations using collision theory models and relate their ideas to rates of reaction.

Using datalogging

The activity can be further developed by using data-logging. Place a glow stick in a box (shoe box or similar) and make a hole in the side of the box, just large enough for a light sensor to be inserted. Record the light levels emitted by the glow stick over 24 hours. Data can be converted directly into graphical form. Students might want to compare the rate of decay of light intensity for different-coloured glow sticks.

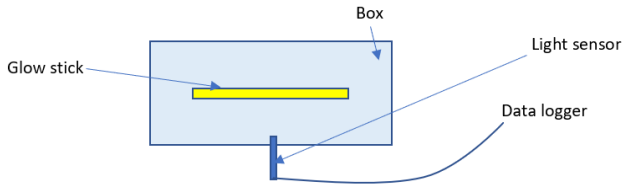

Figure 9 Using a datalogger to measure rate of reaction

A potential research project

Investigating the aurora borealis

This investigation can be given to students of any age. The phenomenon is well documented and at different conceptual levels. Students can be guided by these questions:

1 What does the aurora borealis look like and where can it be found?
2 What causes the aurora borealis?
3 What implications does this have for the safety of life on Earth?

Depending on the age, ability and interest of the student, answers will be differentiated by outcome.

The science behind the aurora borealis

The aurora borealis is a phenomenon that is predominantly observed at the Earth's poles. It is caused by the entrapment of high-energy electrons and positive ions (cations) from the Sun's 'solar wind' by the Earth's magnetic field. The charged particles oscillate between the poles in a helical path and, as they do, they collide with molecules in the atmosphere, such as oxygen and nitrogen. The oscillation between the poles is caused by the interaction between the magnetic fields produced by the charged particle motion and the Earth's magnetic field.

The collisions transfer energy between the charged particles and the atmospheric molecules. This raises the molecules into an excited electronic state. On returning to the ground state the molecules emit visible light (green, red and blue depending on the molecule).

Conclusion

Students are invariably fascinated by luminescence in all its forms and through exploring the types of luminescence they can build upon their knowledge of atomic structure and energy transfers, and see how it has already been applied by nature. Activities can be easily differentiated to support any age group and ability to create a truly engaging inclusive experience for all.

References

Bandaranayake, W. M. (2006) The nature and role of pigments of marine invertebrates. *Natural Product Reports*, **23**, 223–255.

Brodl, E., Winkler, A. and Macheroux, P. (2018) Molecular mechanisms of bacterial bioluminescence. *Computational and Structural Biotechnology Journal*, **16**, 551–564.

Fleiss, A. and Sarkisyan, K. (2019) A brief review of bioluminescent systems. *Current genetics*, **65**, 877–882.

Goldberg, M. C. and Weiner, E. R. (1989) The Science of Luminescence. *ACS Symposium Series*, **383**, 1–22.

Haddock, S. H. D., Rivers, T. and Robinson, B. H. (2001) Can coelenterates make coelenterazine? Dietary requirement for luciferin in cnidarian luminescence. *Proceedings of the National Academy of Sciences USA*, **98**(20), 11148–11151.

Haddock, S. H. D., Moline, M. A. and Case, J. F. (2010) Bioluminescence in the sea. *Annual Review Marine Science*, **2**, 443–493.

Kaskova, Z., Tsarkova, A. S. and Yampolsky, I. (2016) 101 lights: luciferins, luciferases, their mechanisms of action and applications in chemical analysis, biology and medicine. *Chemical Society Review*, **45**, 5048–5077.

Lee, J. (2017) Perspectives on bioluminescence mechanisms. *Photochemistry and Photobiology*, **93**, 389–404.

McElroy, W. D. (1947) The energy source for bioluminescence in an isolated system. *Proceedings of the National Academy of Sciences USA*, **33**, 342–345.

McElroy, W. D., Hastings, J. W., Coulombre, J. and Sonnenfeld, V. (1953) The mechanism of action of pyrophosphate in firefly luminescence. *Archives of Biochemistry and Biophysics*, **46**, 399–416.

Roda, A. (2011) A history of bioluminescence and chemiluminescence from ancient to the present. In *Chemiluminescence and Bioluminescence: Past, Present and Future*, ed. Roda, A. Royal Society of Chemistry.

Syed, A. J. and Anderson, J. C. (2021) Applications of bioluminescence in biotechnology and beyond. *Chemical Society Reviews*, **50**, 5668.

Tan, H., Wang, T., Shao, Y., Yu, C. and Hu, L. (2019) Crucial breakthrough of functional persistent luminescence materials for biomedical and information technological applications. *Frontiers in Chemistry*, **7**, 387.

Wang, J., Ma, Q., Wang, Y., Shen, H. and Yuan, Q. (2017) Recent progress in biomedical applications of persistent luminescence nanoparticles. *Nanoscale*, **9**, 6204–6218.

Yang, Y., Zhang, Y., Xie, Sheng., Tang, Y., Zeng, Z. and Tang, B. Z. (2021) Hydrogel-derived luminescent scaffolds for biomedical applications. *Materials Chemistry Frontiers*, **5**, 3524–3548.

Useful websites

Basic difference between phosphorescence and fluorescence:
https://www.youtube.com/watch?v=OzPCzFu472Y
Understanding electron spin and electron configurations:
https://www.youtube.com/watch?v=EM2J0BWXyxM
More challenging ideas around luminescence:
https://www.youtube.com/watch?v=l_26zzP8Eik
https://www.youtube.com/watch?v=CcssdJf0pKQ

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