

# Exploring Triboluminescence and Paramagnetism: A Rapid Mn Complex Synthesis for High School and Undergraduate Chemistry Laboratories

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**ABSTRACT:** Triboluminescence is a fascinating phenomenon that can engage students' interest in chemistry. However, safe, cost-effective, and accessible laboratory experiments featuring highly triboluminescent substances are limited. To bridge this gap, we present a simple, rapid, semimicro test tube preparation of the visually engaging manganese complex  $[\text{MnBr}_2(\text{Ph}_3\text{PO})_2]$ , conducted by high school students. During the laboratory session, students practice various laboratory skills, including handling semimicro quantities of substances, ascertaining the melting point, and recrystallizing the synthesized complex. They also investigate the complex's triboluminescent, fluorescent, and magnetic properties through straightforward and illustrative experiments. Furthermore, this laboratory activity has been successfully implemented in an undergraduate chemistry didactics course for chemistry educators. The experiment's simplicity, combined with the safety of starting materials and use of nontoxic solvents, makes it an optimal choice for a variety of educational environments, such as high school and university laboratory sessions, science clubs, and public science outreach activities.

**KEYWORDS:** *Coordination Compounds, Ligand Field Theory, Equilibrium, Fluorescence Spectroscopy, Luminescence, Triboluminescence, Undergraduate Research*



## INTRODUCTION

Chemical reactions and processes that emit cold light are one of topics in science education and communication that can reliably arouse interest in chemistry in broad audiences almost regardless of age or prior knowledge.<sup>1</sup> The series of phenomena, known collectively as luminescence, can be sorted into numerous categories based on their origin and the mechanism behind their light generation. The classification briefly outlined in Table 1 is traditional, and it might not encapsulate all aspects of the current understanding in every instance. However, it provides a helpful foundation for readers to quickly familiarize themselves with the subject matter.

Apart from traditionally popular and widely known photoluminescent and chemiluminescent experiments, mechanoluminescence, the emission of light that is produced when mechanical stress is applied to crystals, is the least known and the one that is most surrounded by mystery.

Triboluminescence (TL) has gained attention in recent years with the development of highly triboluminescent (HTL) substances that can be seen even by the naked eye under daylight conditions.<sup>2</sup> Francis Bacon was the first to report a faint blue TL of crushed or cut sugar loaves as early as 1605,

but it is highly likely that sugar merchants had noticed the phenomenon several centuries before.<sup>3</sup> Despite the fact that TL is probably one of the longest known luminescence phenomena, it has been marginalized as a curiosity aside the main interest of the chemical community, lacking practical use cases.<sup>4</sup> It was only in the second half of the last century that sufficiently sensitive instruments with photomultiplier tubes allowed TL to be studied in more depth and, along with its development, stimulated interest in the synthesis of new HTL compounds and their possible industrial applications.<sup>2,5,6</sup> As evidenced by the steep growth of new TL-focused publications over the last two decades, it is apparent that TL is now undergoing its well-deserved renaissance.<sup>2</sup>

Unfortunately, when it comes to conducting laboratory experiments on HTL substances in a safe and cost-effective

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Table 1. Overview and Description of Different Types of Luminescence Together with Their Typical Examples

Category	Type	Mechanism Description	Example
Photoluminescence	Fluorescence	Absorption and immediate re-emission of photons, no change in spin multiplicity	Optical brighteners, fluorescent lamps, leak detection
	Phosphorescence	Absorption and delayed re-emission of photons, change in spin multiplicity	Glow-in-the-dark toys, safety signs
Pyroluminescence		Light emission from atoms/compounds excited by high temperature (e.g., vaporized salts in a flame)	Flame test, combustion of boron-rich compounds
		Biochemical reaction in a living organism	Fireflies, dinoflagellates (glowing tides), glowing mushrooms, etc.
Chemiluminescence	Chemiluminescence	Emission of light as a result of a chemical reaction	Glow sticks, forensic blood detection (luminol), detection of NO <sub>x</sub>
	Lyoluminescence	Emission of light from free radicals produced by dissolution of previously irradiated solids	Radiation damage studies and research
Thermoluminescence		Re-emission of absorbed energy from radiation dose when a substance is heated. The energy is stored as localized defects in the crystal lattice.	Dosimetry for radiation exposure, archeological dating. Used with minerals or ceramics.
	Candoluminescence	Radiation of some materials at elevated temperatures that differs from the expected blackbody radiation, e.g., due to free radical recombination catalysis	Welsbach gas combustion mantle, material analysis
Mechanoluminescence	Triboluminescence	Emission of light when materials are scratched, crushed, pressed, or rubbed	Crushing of sugar candies, uranyl nitrate, or metal complexes; pulling Scotch tape
	Fractoluminescence	Emission of light caused by stress resulting in the formation of fractures	Specific subcategory of triboluminescence
Piezoluminescence		Emission of light from the action of pressure	Mechanical stress on pure alkali halide crystals, zinc sulfide phosphors, or quartz crystals. The term elasticoluminescence is also used.
	Sonoluminescence	Result of imploding bubbles in a liquid when excited by sound or rapid pressure changes	Seen in lab conditions when a liquid is subjected to intense sound waves. Also observable in certain marine animals, such as pistol shrimp during prey attack.
Crystalloluminescence		Light produced during crystallization	Rapid crystallization of sodium–potassium sulfate, Sr(BrO <sub>3</sub> ) <sub>2</sub> , or Ba(BrO <sub>3</sub> ) <sub>2</sub> from an aqueous solution, melt crystallization of carbazole derivatives.
	Cryoluminescence	Emission of light when an object is cooled or luminescence observable only at low temperatures	ZnS phosphors, wulfenite
Electroluminescence		Emission resulting from an electric current passed through a substance	Light-emitting capacitors, LEDs
	Ionizing radiation	Emission resulting from a luminescent material being struck by electrons	CRT TV screens, electron microscopy
Radioluminescence		Light emission initiated by ionizing radiation	Glow-in-the-dark paints or tubes for wristwatch faces and gun sights

Table 2. Learning Objectives for Specific Parts of the Designed Experiment

Part of Experiment	Students Will Be Able to
1. Preparation of the complex	<ul style="list-style-type: none"> <li>Execute the laboratory experiment to prepare a triboluminescent complex.</li> <li>Operate the vacuum filtration apparatus, work with organic solvents, and use a hot water bath on a semimicro scale.</li> <li>Apply their skills for the synthesis of a complex with an organic ligand in a nonaqueous environment.</li> <li>Interpret how the Le Chatelier principle can be used in chemical synthesis to favor the formation of a complex.</li> </ul>
2. Calculation of theoretical and percent yield	<ul style="list-style-type: none"> <li>Calculate the theoretical and percent yield of a chemical reaction with their previously acquired knowledge about stoichiometric calculations.</li> <li>Evaluate the percent yield based on their laboratory experience.</li> </ul>
3. Characterization of the product by melting point	<ul style="list-style-type: none"> <li>Use the melting point apparatus to determine the melting point of their product.</li> <li>Relate the measured melting point to the purity of their product and judge the quality of the product.</li> </ul>
4. Observation of the triboluminescent and fluorescent properties of the product	<ul style="list-style-type: none"> <li>Explain the phenomenon of fluorescence and relate it to the electronic structure of molecules.</li> <li>Describe and observe the phenomenon of triboluminescence.</li> <li>Compare the phenomena of fluorescence and triboluminescence.</li> <li>Formulate possible technical applications of the prepared compounds.</li> </ul>
5. Observation of magnetic properties of the reactants and the product	<ul style="list-style-type: none"> <li>Classify paramagnetic and diamagnetic compounds based on their electronic structure and differentiate between them.</li> <li>Formulate how molar and mass magnetic susceptibility are related to the magnetic behavior of compounds.</li> </ul>
6. Recrystallization of the product	<ul style="list-style-type: none"> <li>Execute the recrystallization of the product.</li> <li>Judge the effect of recrystallization on the size and quality of crystals and the triboluminescence intensity of the product.</li> </ul>

manner, there are limited options available to teachers. Many of the compounds that exhibit bright luminescence pose health and safety risks, such as uranyl salts,<sup>7,8</sup> are restricted by drug legislation, such as anthranilic acid derivatives,<sup>9,10</sup> or are relatively expensive or difficult to obtain, such as trivalent lanthanide complexes,<sup>11,12</sup> doped zinc sulfide, or modern rare-earth-doped ceramics.<sup>13</sup> In addition to the relatively well-known Wint-O-Green Life Savers candies containing methyl salicylate (also known as “oil of wintergreen”) as an enhancer of sucrose triboluminescence,<sup>14</sup> only a few recently published HTL complexes are suitable for educational purposes.<sup>15,16</sup>

The company CF Plus Chemicals, specifically its division Chemistry and Light, commercializes the school didactic kits “Chemistry and Light” that offer chemicals and experiments associated with luminescence and photochemistry, including the bright-red triboluminescent europium complexes and materials for their multidecagram-scale preparation. Thus, we decided to adapt a published synthesis<sup>17</sup> of the visually attractive complex  $[\text{MnBr}_2(\text{Ph}_3\text{PO})_2]$  showing HTL and simplify it so that it can be easily performed on a semimicro preparative scale in a test tube in a short period of time. Our proposed preparation is based on safe and stable compounds, manganese(II) bromide tetrahydrate and triphenylphosphine oxide. This simplified synthesis protocol takes advantage of the rapid evaporation of ethanolic solutions due to vacuum vapor stripping above the warm solution surface.

Our proposed preparation can be completed in one laboratory session (90 minutes) of a high school course, with students being able to prepare 0.2 g of the complex in a short time (within 30 minutes). As a follow-up activity, students can investigate the properties of the complex, including its melting point, solubility, bright-green TL, and fluorescence as well as its magnetic properties (dia/paramagnetism) using a strong neodymium magnet. An extended variant includes an extra laboratory session dealing with crystallization of the product.

## COURSE DESCRIPTION AND LEARNING OBJECTIVES

This experiment was carried out as part of the Organic Chemistry laboratory exercise in the second year (of four) at the Secondary School of Technical Education in Chemistry with two groups of 12 students (age 16 to 17) and was conducted in its extended variant in two laboratory sessions (2 × 90 minutes).

The laboratory experiment is designed to build on students’ knowledge of basic lab techniques from previous courses and general chemistry knowledge and to introduce them to new techniques and concepts related to chemical synthesis and compound characterization and also to let them observe macroscopic properties of a complex based on its electronic structure.

The activities covered in the experiment described below are based on the previously acquired knowledge about electronic structure of molecules and ions, coordination chemistry, chemical equilibrium (especially the Le Chatelier principle), and stoichiometric calculations. The experiment is divided into six parts, each with its own learning objectives, as listed in Table 2.

An abbreviated variant of this experiment was successfully executed in a single 90-minute session with a group of 10 undergraduate chemistry education students at UCT Prague. This version included only the activities from parts 4 and 5. This version primarily included activities from parts 4 and 5, with supplemental educational tasks like group discussions, role-playing student–teacher scenarios, mutual feedback sessions, identification of challenges in subject matter explanation, curriculum analysis, and determination of appropriate educational contexts related to the activity.

Student worksheets for both the [high school/undergraduate version](#) and the [chemistry education student version](#) of the experiment are provided in the Supporting Information.

The inherent versatility of this designed experiment allows for its easy integration into various course levels, ranging from introductory chemistry classes at high schools to advanced

university courses. High schools could utilize it as a simple yet motivating laboratory technique experiment due to the visually striking fluorescence and triboluminescence phenomena. With the inclusion of melting point measurement and interpretation along with the demonstration and discussion of fluorescent, triboluminescent, and magnetic properties, it serves well as an advanced placement experiment in high schools. The experiment can be carried out in an inquiry-based manner when exploring the magnetic properties. Meanwhile, university-level courses could benefit from a complete version of the experiment.

## EXPERIMENTAL SECTION

### Complex Preparation

The apparatus for the preparation of the complex was assembled, as shown in Figure 1 (a video is available in the

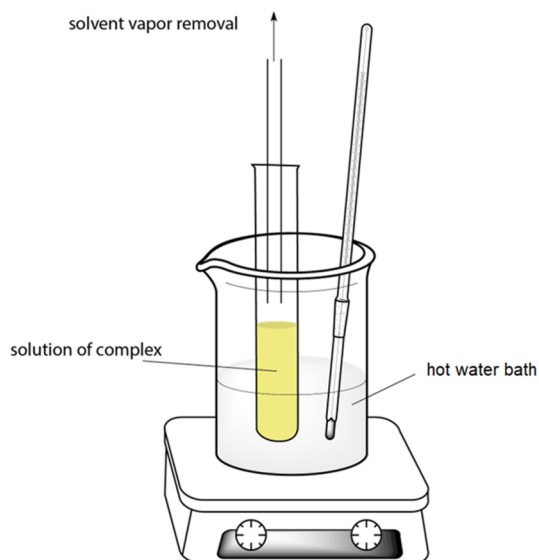


Figure 1. Apparatus for preparation of the complex

Supporting Information). An ethanolic solution of manganese(II) bromide tetrahydrate (0.2 M solution in 96% EtOH, 2 mL, 0.4 mmol, 1 equiv) was added to a test tube, followed by an ethanolic solution of triphenylphosphine oxide (0.4 M solution in 96% EtOH, 2 mL, 0.8 mmol, 2 equiv). The resulting mixture was stirred thoroughly with a glass rod. A stiff HDPE plastic tube, previously inserted into a soft silicon suction tube, was connected to a source of vacuum. The free end of the HDPE tube was inserted perpendicularly into the center of the test tube, approximately 1 cm above the level of

the reaction mixture, and fixed with a clamp. A beaker was filled with boiling water from the kettle to act as a heat source for the evaporation, and the emerging ethanolic vapors in the test tube were removed by vacuum. During evaporation, the position of the vacuum tube was gradually adjusted to maintain its original distance from the surface. After the first evaporation to dryness (3–5 min), the crude complex deposited on the walls of the test tube was mixed with a new portion of solvent (4–6 mL, 96% EtOH), and a new evaporation cycle was repeated to shift the reaction equilibrium to the products by removing the residues of water.

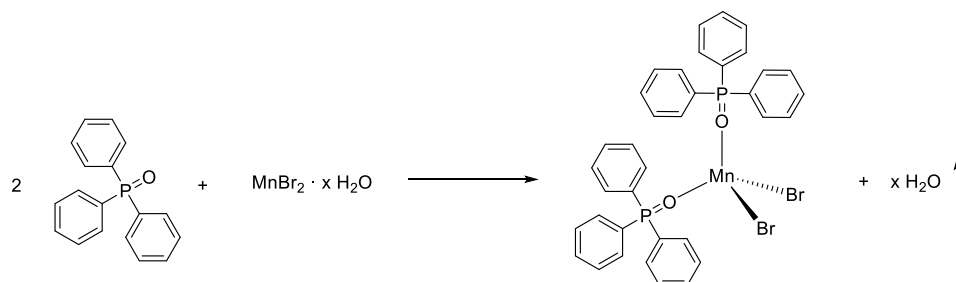
To purify the crude yellowish complex, precooled acetone (2 mL, 0–5 °C) was added to the cold tube, and the deposits on the walls were gently scraped and triturated with a glass rod toward the bottom of the tube. Using a glass Pasteur pipet, the supernatant was carefully removed and discarded. The tube was returned to the hot bath, and the residual acetone was removed by vacuum (2–4 min) to obtain a dry crystalline yellow-green powder of manganese bis(triphenylphosphine oxide) dibromide (Scheme 1).

The average student yield was 244 mg (77% of the theoretical yield). *Elemental analysis*: C, 55.9%; H, 3.7%; P, 7.7%; Br, 21.0%; Mn, 7.2% (calculated values for  $[\text{MnBr}_2(\text{Ph}_3\text{PO})_2]$ : C, 56.06%; H, 3.92%; P, 8.03%; Br, 20.72%; Mn, 7.12%). *Melting point (DSC)*: 242.6 °C (in accordance with the published value of 243 °C).<sup>17</sup> According to a published crystallographic analysis, the title complex is a molecular compound with a four-coordinate manganese(II) center in a tetrahedral environment composed of two O-bound triphenylphosphine oxide groups and two bromide ions. The compound crystallizes in the triclinic crystal system in the space group  $P\bar{1}$ .<sup>18</sup> The FT-IR spectrum together with details on the instrumental analysis and detailed methodological notes on the preparation are available in the Supporting Information.

### Making Larger Crystals by Solution Evaporation or Recrystallization

The ethanolic solution can be evaporated to dryness at room temperature in a crystallization dish or Petri dish in a well-ventilated area. Alternatively, to obtain larger, well-developed crystals, the powdered residue can be dissolved in hot refluxing ethanol (5.0 g/100 mL, 96% EtOH), allowed to freely crystallize (preferably in a refrigerator), and then filtered and air-dried. Note that recoveries using this alternative method tend to be lower, ranging from 10 to 40%, and it is strongly recommended to perform this operation with larger batches of product.

### Scheme 1. Synthesis of the Complex $[\text{MnBr}_2(\text{Ph}_3\text{PO})_2]$





## HAZARDS

All included organic solvents are flammable; therefore, all sources of open flame must be avoided. Alcoholic solutions of manganese(II) bromide tetrahydrate (CAS 10031-20-6) and triphenylphosphine oxide (CAS 791-28-6) are irritating in contact with the skin and mucous membranes. In the case of contamination, immediately remove the contaminated clothing and wash the affected skin thoroughly with soap. The process of heating organic solvents with boiling water without simultaneous vapor extraction poses a potential risk of overheating. To mitigate this, it is advisable to employ a controlled bath of 80–90 °C, adhering strictly to procedural instructions, thus ensuring a minimized risk of reaction mixture overheating. If the ethanolic solution enters the eye, immediately rinse it with a stream of water and seek medical attention. References to material safety data sheets are included in the [Supporting Information](#). Certain risks are associated with working with UV light (254 and 365 nm) emitted from a laboratory UV lamp. This includes potential skin and eye damage, particularly to the cornea. As such, it is essential to wear certified UV-filter-equipped safety glasses. Observing the complex's fluorescence should be conducted behind a glass barrier, thereby reducing direct UV exposure for enhanced safety.

## RESULTS AND DISCUSSION

### Complex Preparation

All students in the high school laboratory exercise successfully prepared the desired complex in relatively good yields (32 to 96% of the theoretical yield; the average yield was 77%). Lower yields were mostly caused by handling losses, particularly from accidentally drawing the reaction mixture into the suction tube or, to a lesser degree, from pipetting the suspension during the acetone wash. Almost all of the students correctly calculated the theoretical yield. Based on the laboratory experience and the feedback data, the synthesis of the complex was straightforward for the students. However, for the first time, they encountered and learned the technique of the preparation of crystals via solvent evaporation.

The melting point of the product was determined during the lesson using a standard digital melting point apparatus, and almost all of the students achieved a melting point between 239 and 244 °C. This is in line with the previously established reference value (243 °C),<sup>17</sup> indicating a relatively high quality of the prepared product.

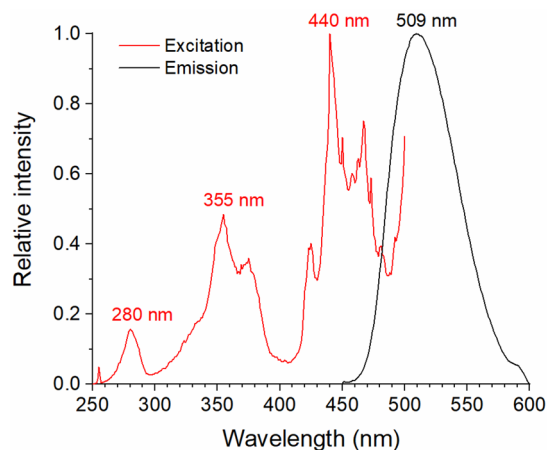
### Observation of the Triboluminescent and Fluorescent Properties

The triboluminescence phenomenon, resulting from mechanical stress applied to the crystal, is often attributed to the separation of charges during the fracture process. Unfortunately, the underlying mechanism of the process is still unclear. While past research suggested that this was exclusive to noncentrosymmetric or piezoelectric crystals,<sup>18</sup> recent findings report triboluminescence in centrosymmetric materials, challenging the initial assumption.<sup>19</sup> When the charges reunite, an electron transition in the manganese atom is supposed to occur ( ${}^4T_1 \rightarrow {}^6A_1$ ), which is responsible for the green glow.<sup>20</sup>

The majority of high school students were able to perform a TL test, as they had a sufficient amount of the product. The title complex exhibited a strong TL that was clearly visible immediately after preparation by rubbing the walls of the tube

with a glass rod. However, the most intense luminescence was obtained when the crystals were crushed between two flat glass surfaces of Petri dishes placed inside each other. Under full daylight conditions, well-formed crystals of the complex under study notably exhibit triboluminescence discernible to the naked eye. However, the spectacle significantly intensifies when ambient light is diminished, thus enhancing the students' observational experience. When dealing with unrecrystallized or finely powdered samples, the use of dimmed lighting is advisable, given the size-dependent nature of the effect.

Students from both groups were asked to verify whether the observed fluorescence was consistent with the excitation and emission fluorescence spectra of the solid complex, which had been measured earlier for the purpose of this exercise ([Figure 2](#)). Using a laboratory UV lamp with the option to switch the

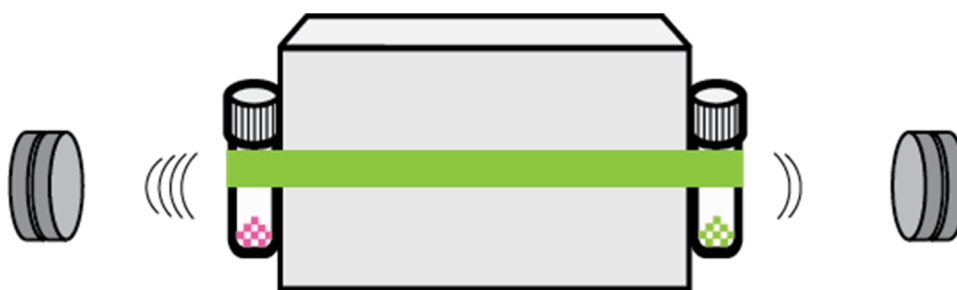


**Figure 2.** Excitation (red) and emission (black) fluorescence spectra of solid  $[\text{MnBr}_2(\text{Ph}_3\text{PO})_2]$  complex. Local maxima are marked with wavelength labels. The fluorescence excitation–emission matrix is shown in [Figure S2](#).

wavelength between 254 and 365 nm, almost all students observed strong green fluorescence for both wavelengths. In some cases, students from both groups subjectively evaluated the emission as slightly more intense when using the 254 nm source compared to the 365 nm source. However, due to the unknown light output of the used sources, it was not possible to utilize this observation for precise quantification. It is also noteworthy that the fluorescence of the complex completely disappeared upon dissolution in protic solvents (methanol or ethanol) or even in weakly coordinating solvents (e.g., dichloromethane), suggesting that its fluorescence is exclusively tied to its solid form.

A particularly interesting situation arose when some of the high school students did not observe any fluorescence under any UV light with the product covered with a Petri dish. This occurred due to the absorption of UV light by borosilicate glass. Students were not advised about this phenomenon in advance, which led to fruitful discussion of the absorption behavior of borosilicate glass. This learning effect was therefore purposefully incorporated as one of the subtasks in a laboratory exercise for the student teachers.

Finally, an interesting visual effect, a short, strong green flash of light, was obtained by rapidly cooling the crystals in liquid nitrogen. A likely explanation for this phenomenon appears to be induced stress of the crystal lattice caused by thermal shock leading to light emission (a [video](#) is available in the Supporting



**Figure 3.** Styrofoam boat experiment comparing the magnetic properties of  $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$  and the title complex.

Information). This effect was a surprising discovery and added an extra dimension to students' understanding of the complex's properties.

Overall, the observations of triboluminescence and fluorescence properties provide valuable insight into the complex's behavior in different states and under different conditions. These observations are a testament to the students' skills in performing the necessary tests and to the quality of the experimental setup. Additionally, the unique visual effect during the experiment adds an element of excitement and discovery to the learning experience.

### Observation of the Magnetic Properties

The predominant spin state of the  $\text{Mn}^{\text{II}}$  complexes aligns with a high-spin  $d^5$  configuration, marked by the stability of a half-filled d-electron shell. Manganese complexes that adopt a low-spin state are far less common, typically isolated only with strong-field ligands, as exemplified by cyanide in the complex  $[\text{Mn}(\text{CN})_6]^{4-}$ .<sup>21</sup>

Given the nature of triphenylphosphine oxide, water, and bromide, which are all considered weak- to medium-field ligands within the spectrochemical series, the high-spin states of both the tetrahedral  $[\text{MnBr}_2(\text{Ph}_3\text{PO})_2]$  and octahedral  $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$  complexes are expected. The inherent strong paramagnetism in these compounds can be attributed to the presence of five unpaired electrons.

The associated high magnetic susceptibility of  $\text{Mn}^{\text{II}}$  ( $d^5$ ) in manganese(II) bromide and the synthesized complex allowed their paramagnetic properties to be observed using neodymium magnets, which are readily available in a school laboratory (see Figure 3 and the video of the experiment in the Supporting Information). Although the molar magnetic susceptibility of the synthesized complex ( $15.045 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ )<sup>17</sup> does not differ from those of similar  $\text{Mn}^{\text{II}}$  complexes without ferromagnetic interactions,<sup>22</sup> the mass magnetic susceptibility is inversely proportional to the molar mass. This can be demonstrated by the reduction of the strength of interaction with the magnetic field when the synthesized complex is compared with manganese(II) bromide tetrahydrate, which has almost 3 times lower molar mass. Even though the possibility of measuring magnetic susceptibilities directly in the school laboratory is beyond the scope of this article, several procedures using equipment available for educational purposes have been published.<sup>23</sup>

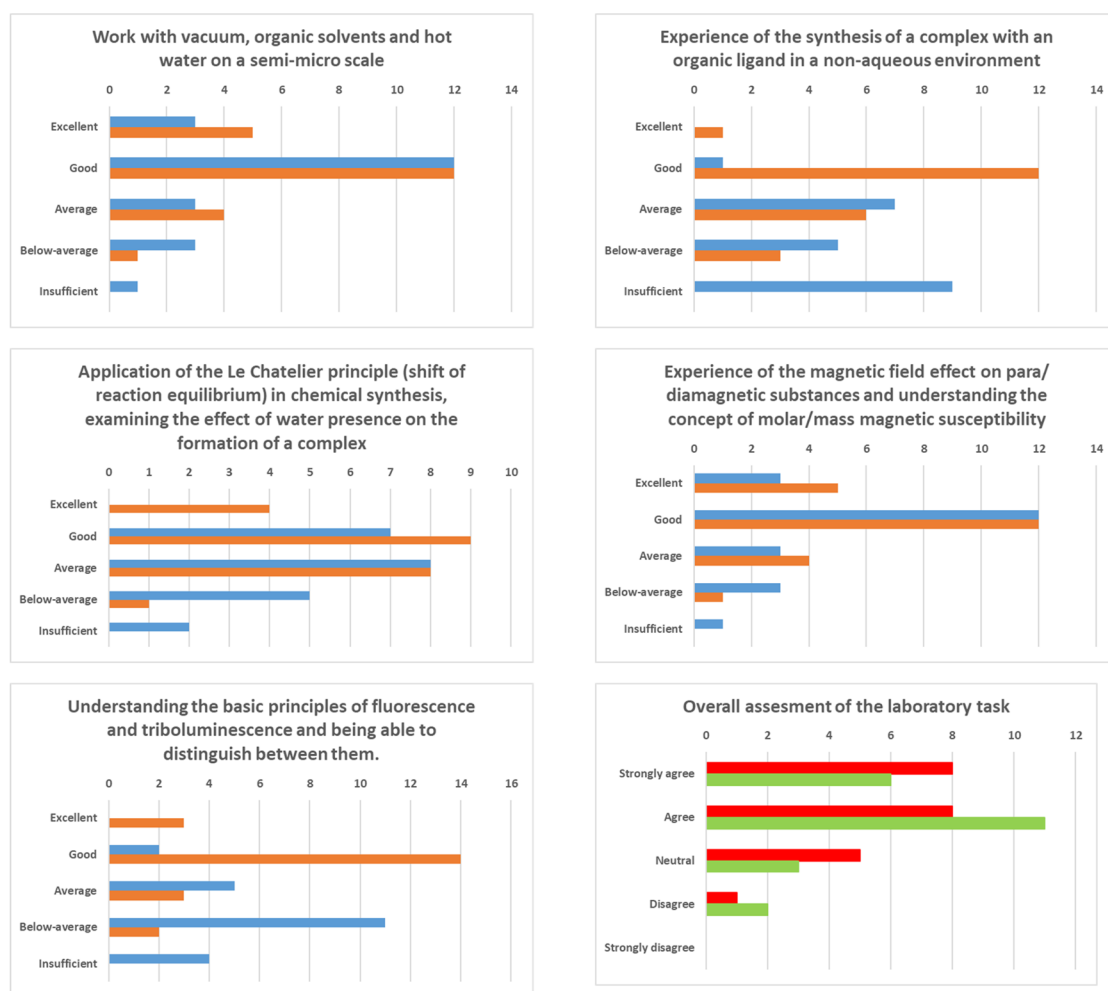
To observe the magnetic properties, students were instructed to suspend three samples in glass vials by using a 50 cm thread attached to the neck of each vial. The first vial contained manganese(II) bromide tetrahydrate; the second vial contained the synthesized complex; and the third vial contained triphenylphosphine oxide (a diamagnetic compound) for comparison purposes. Once the vials were

suspended, the students waited until the vials stopped swinging. Then they brought a neodymium magnet to approximately 1 cm distance from the vials. When the magnet was brought close to the vial containing manganese(II) bromide tetrahydrate, there was a rapid pulling of the vial toward the magnet, which caused an audible clinking of the glass against the magnet. However, for the synthesized complex, there was only a slight movement of the vial toward the magnet, and it was necessary to bring the magnet much closer to attract the vial. In contrast, the magnet did not elicit any observable magnetic response from the vial containing triphenylphosphine oxide, even when applied directly to the vial wall. This indicates that triphenylphosphine oxide is diamagnetic and is not attracted to the magnet.

Differences in the magnetic behavior of manganese(II) bromide tetrahydrate and the synthesized complex were demonstrated further using a polystyrene boat experiment on the surface of water. The experiment involved attaching two vials of an equal weight of manganese(II) bromide tetrahydrate and the synthesized complex to opposite sides of a Styrofoam boat, which was then immersed in a bowl of water (Figure 3; see the video in the Supporting Information). Two students were then tasked with trying to pull the boat to their respective sides without directly touching it using two identical neodymium magnets.

It was observed that the vial containing manganese(II) bromide tetrahydrate showed a significantly higher magnetic response compared with the vial containing the synthesized complex. This difference was evident to all observers after a moment of effort by the two students. The strength of the magnets used affected the magnitude of the observed magnetic response. These two experiments were particularly popular among the students from both groups, as it allowed them to observe and understand the practical applications of paramagnetism and diamagnetism, in addition to applying their theoretical knowledge of electron configuration. The evaluation showed that most high school students were able to understand the concepts of paramagnetism and diamagnetism at the end of the exercise, even though they did not know these concepts before the laboratory exercise. Student teachers made extensive use of the references to this practical demonstration in their later assignments to explain the theoretical foundations of these phenomena and valued it as an illustrative resource that they could use in their future teaching practice.

Almost all students from both groups were also able to connect the observed drop in the mass magnetic susceptibility of the synthesized complex compared to manganese(II) bromide tetrahydrate to the mass fraction of manganese ions present in both compounds.



**Figure 4.** Student survey results on learning gains related to the designed experiment. Blue bars represent prelab self-assessment, orange bars represent reflection after experiment, green bars represent identification with the statement “I got engaged to the work and enjoyed the laboratory task”, and red bars represent identification with the statement “The laboratory task was professionally beneficial for me”.

### Regrowing Crystals and Recrystallization

The final part of the laboratory exercise for high school students involved recrystallization of the synthesized complex, which provided the students with an opportunity to practice an important technique commonly used in chemical synthesis. The recrystallization process involved dissolving the product in a minimum amount of refluxing ethanol followed by either rapid cooling of the ethanolic solution or free evaporation of the solvent.

The rapid cooling method proved to be challenging for many students who were not accustomed to working with semimicro amounts of products. The yield of the product obtained using this method was poor, with only 10 to 40% of the product recovered, and more than half of the students lost their product during the recrystallization process (due to excessive use of solvent).

On the contrary, the free solvent evaporation method yielded well-formed crystals in high yields (ranging from 76 to 100% recovery). The product of this crystal regrowth exhibited equally strong triboluminescent properties, which were clearly observable.

### Assessment Outcomes

In the final evaluation and feedback phase, high school students were asked to self-assess their progress on key

learning outcomes associated with this laboratory exercise, which included:

- Working with vacuum, organic solvents, and hot water on a semimicro scale.
- Synthesizing a complex with an organic ligand in a nonaqueous environment.
- Applying the Le Chatelier principle (shift of reaction equilibrium) in chemical synthesis and understanding the influence of water on complex formation.
- Experiencing the effect of a magnetic field on paramagnetic and diamagnetic substances and understanding the concept of molar/mass magnetic susceptibility.
- Understanding the fundamental principles of fluorescence and triboluminescence and their distinctions.

Feedback from the students revealed that the majority experienced significant advancement in their understanding and hands-on experience related to the key learning outcomes. Detailed insight into the students' self-assessment of the key learning outcomes before and after the laboratory experience is shown in Figure 4. The areas with the most noticeable progress were understanding the magnetic properties of substances and the concepts of fluorescence and triboluminescence. The students also found the observation and analysis of the fluorescence, triboluminescence, and magnetic behavior of the

complex most intriguing and exciting, adding substantial value and interdisciplinary relevance to the laboratory project. The simplicity of the experimental protocol, leading to quick product formation, was widely appreciated.

However, during the recrystallization of the complex via cooling, some students faced challenges with low product recoveries. To overcome this issue, students are encouraged to strictly adhere to the suggested solvent volumes, work on a larger scale, or consider pooling resources by combining their individual batches.

## CONCLUSIONS

The laboratory experiment presented in this study showcases a rapid, safe, and cost-effective method for preparing a triboluminescent and photoluminescent Mn(II) complex. It allows students to synthesize visually appealing material while exploring several key principles in chemistry. The use of vacuum techniques and work with organic solvents on a semimicro scale helps to enhance students' laboratory skills. Moreover, the observation of the complex's triboluminescence and fluorescence properties aids in understanding the underlying principles of these phenomena. The experiment further exposes students to the magnetic properties of the compound, fostering a deeper comprehension of the magnetism of complex compounds. The simplicity and accessibility of the procedure also make it an ideal choice for laboratory exercises in high schools, colleges, science clubs, and science museums.

## ASSOCIATED CONTENT

### Data Availability Statement

The present experiment including the necessary chemicals is contained in the Standard and Professional version of the commercial school didactic kit Chemistry and Light (<https://www.chemistryandlight.eu/>).

### Supporting Information

The Supporting Information is available at <https://pubs.acs.org/doi/10.1021/acs.jchemed.3c00372>.

Methodological notes of instructors on the complex preparation; material information and references to material safety data sheets; photo documentation from the courses of laboratory practice (PDF)

Details on the instrumental analysis and 3D fluorescence spectra (PDF)

Lab protocols and worksheets with solution for high school students and chemistry education students (PDF)

Laboratory introduction and schedule for student teachers; worksheet with solutions (PDF)

Video describing the preparation and testing of the complex (MP4)

Video describing the triboluminescence upon cooling of the complex with liquid nitrogen (MP4)

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<https://pubs.acs.org/10.1021/acs.jchemed.3c00372>

## Notes

The authors declare the following competing financial interest(s): V.M. is the main creator of the commercial school didactic kit Chemistry and Light that uses highly visually appealing luminescence and photochemistry experiments (fluorescence, safe peroxyoxalate chemiluminescence, phosphorescence, cyanotypes, photosynthesis, preparation of triboluminescent complexes, etc.) to explain generally taught chemical principles in a hands-on, interactive, and attractive fashion.

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