# Synthesis of a Photoluminescent and Triboluminescent Copper(I) Compound: An Experiment for an Advanced Inorganic Chemistry Laboratory

Fabio Marchetti,*,[†] Corrado Di Nicola,[‡] Riccardo Pettinari,[‡] Ivan Timokhin,[†] and Claudio Pettinari[‡]

[†]School of Science and Technology and [‡]School of Pharmacy, Chemistry Division, Via S. Agostino 1, University of Camerino, 62032 Camerino, Italy

S *Supporting Information*

ABSTRACT: A simple synthesis is proposed from inexpensive reactants of a copper(I) derivative that exhibits strong photoluminescence and, in the crystalline form, exhibits strong triboluminescence. This laboratory provides an opportunity for introducing students to the phenomenon of triboluminescence.
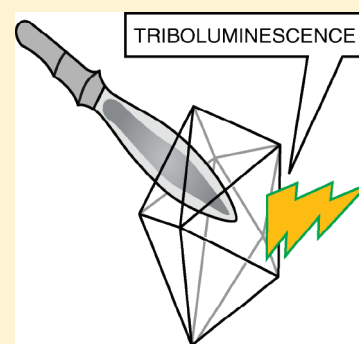
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Photochemistry, the branch of chemistry for which luminescence is significant, is a recent area of rapid growth.[1,2] Luminescence is a fascinating phenomenon to observe for both laymen and scientists, and yet this field of science has been, and still is, neglected in chemical training. Didactical approaches to theory and experiments devoted to introduce students to light emission from substances under an applied stress (i.e., an incident light of greater frequency, an electrical current, or a chemical transformation) have appeared in this educational *Journal*,[3–6] but very few have been dedicated to triboluminescence,[7–10] a particular kind of luminescence induced by mechanical stress.

Triboluminescence is the emission of light induced by a mechanical deformation (grinding, crushing, or fracturing) of certain crystalline compounds. The exact mechanism of triboluminescence is under investigation, but theories propose that the breaking of the structure causes charge separation that releases energy upon recombination.[11–16] This energy is picked up by nearby atoms and released as light according to their ionization or fluorescence spectra. Triboluminescence is fascinating, and students are always delighted by this kind of phenomenon.

From a historical point of view, triboluminescence has been known for over 300 years[17] and its name, coined by Wiedemann,[18] comes from the Greek "triben", to rub. It has remained a curiosity without an obvious application until very recently when Sage postulated that this effect could be used to detect flaws in composite materials.[19,20] Some well-known examples of triboluminescent substances are sugar,[17] phthalic

anhydride,[21] acenaphthene,[21] *cis*-octene,[22] and uranyl nitrate hexahydrate.[23] In recent years, several complexes of the lanthanide elements exhibiting brilliant triboluminescent properties have received attention because these complexes can be used for optical sensors, being sensitive to impact, tension, or pressure.[24,25]

There is considerable evidence that triboluminescence is an electrical phenomenon, with charge separation the primary event.[26] The recombination of charges separated during fracture results in triboluminescence. So triboluminescent activity is usually assumed to be a consequence of crystal asymmetry, that is, only piezoelectric (noncentrosymmetric) crystals may be triboluminescent because only such crystals can develop opposite charges on the opposing faces of a developing crack. Many of the brightest triboluminescent compounds are also piezoelectric and photoluminescent.[16] However, when the photon is emitted in photoluminescence, the crystals are not shattered. The process can be repeated and repeated, whereas, in triboluminescence, the material is fractured. Thus triboluminescence in these ionic compounds can be explained by a fracturing of the crystal causing electrical charges to be formed along the new surfaces, from which an electrical discharge occurs in the crack line. Nitrogen from the air present in this discharge emits UV light, which is absorbed into the crystal and then re-emitted as visible light.

For centrosymmetric crystals triboluminescence cannot happen as the surfaces will be the same on both sides of the

crack line.[27−29] In these cases it is postulated that traces of impurities play an important role in the effect.[27] Recent studies on nonionic centrosymmetrical europium compounds containing thenoyltrifluoroacetonate ligands seem, however, to prove that disorder of a thienyl ring and the CF_3 groups may be responsible for their triboluminescent activities.[24,25] A particular case of triboluminescence is provided by dinuclear gold(I) trifluoroacetate compounds containing bis(diphenylphosphino) methane and uracilate (or methyluracilate) ligands. They form helical crystals with weak Au−Au intermolecular contacts. Under gentle crushing with a spatula, the samples eliminate trifluoroacetic acid, thus becoming more linear and enforcing the Au−Au contacts, which are the reason for the bright blue photoluminescence emitted.[30]

A new example of a photoluminescent and triboluminescent inorganic compound containing copper(I) and triphenylphosphine was recently published.[31] This complex can easily be prepared from inexpensive reactants and provides a good opportunity to introduce students to the rather unclear phenomenon of triboluminescence. Other examples of oligonuclear copper(I) compounds containing alkynyl and arenethiolato ligands have been reported in the literature,[32,33] exhibiting triboluminescence in the crystalline form, but their preparation is not feasible for students, as the use of organolithium reactants is required.

The synthesis, characterization (^{1}H, ^{31}P and ^{13}C NMR, IR, TGA), and investigation of the luminescence of the copper(I) complex is an experiment for upper-level chemistry majors in an advanced inorganic chemistry laboratory.[34] It has been carried out by groups of 10 students, working in pairs, and it takes two days.

■ EXPERIMENTAL PROCEDURE AND RESULTS

Day 1: Synthesis of [Cu(NCS)(py)$_2$(PPh$_3$)]

The synthetic procedure for the synthesis of the photo- and triboluminescent derivative is reported in Scheme 1. A pyridine

Scheme 1. Reaction To Synthesize [Cu(NCS)(py)$_2$(PPh$_3$)]
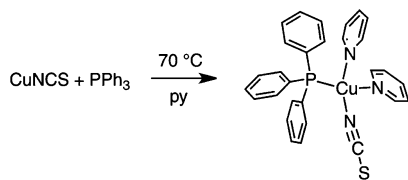
solution (5 mL) containing CuNCS (0.121 g, 1.00 mmol) and PPh$_3$ (0.262 g, 1.00 mmol) is stirred by warming to about 70 °C for 3 h, after which slow cooling and evaporation to half the volume of the initial solution affords in high yields (within the range 80−90%) pale-yellow crystals. It is possible to obtain very big and colorless crystals of the compound by very slow cooling of an 80 °C saturated pyridine solution. The compound is air- and moisture-stable and soluble in chlorinated solvents, acetonitrile and DMSO.

Day 2: Compound Characterization and Analysis of Luminescence

The IR spectrum of the compound shows an absorption at 1594 cm^{-1} due to pyridine and two characteristic strong absorptions at 2065 and 748 cm^{-1} of NCS (Figure 1), in accordance with a nitrogen-bonded thiocyanate group.[35]
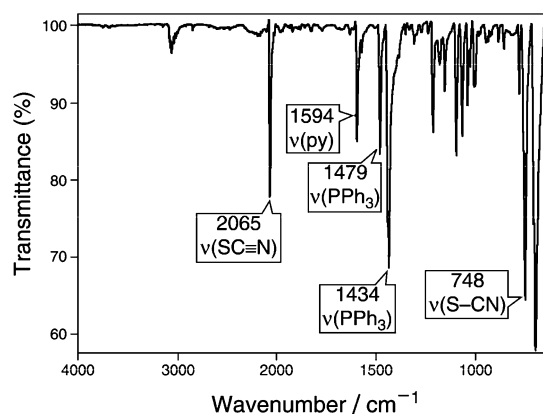
Figure 1. IR spectrum of [Cu(NCS)(py)$_2$(PPh$_3$)].

Additionally, bands at 1479 and 1434 cm^{-1} are caused by phosphine ligand vibrations.[36]

The compound exhibits strong photoluminescence when excited with a UV lamp emitting a 365 nm beam (Figure 2).
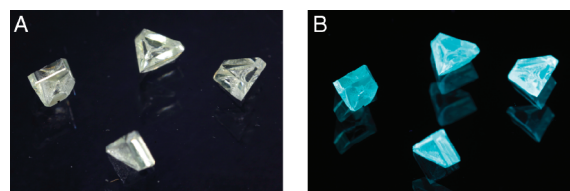
Figure 2. Crystals of [Cu(NCS)(py)$_2$(PPh$_3$)] (A) under daylight and (B) in the dark under UV lamp emitting a 365 nm beam, which excites the photoluminescence of the compound.

Triboluminescence can be visualized by grinding crystals of the compound with mortars such as glass or agate, in a darkened lecture room; however, it exhibits very intense blue−green triboluminescence also in daylight (see the movie in the Supporting Information). The triboluminescence is emitted in the form of light blue−green flashes, the intensity of which is directly related to the mechanical energy exerted on the crystals. As the crystals are ground to an increasingly fine powder, the intensity decreases until it disappears.

■ HAZARDS

Pyridine is a possible reproductive toxin, it easily dissolves in water and harms both animals and plants in aquatic systems, and it is harmful if inhaled, swallowed, or absorbed through the skin. Triphenylphosphine irritates the skin, eyes, and respiratory tract and is harmful if swallowed or inhaled. Copper(I) thiocyanate is extremmely hazardous in case of ingestion and inhalation, and it irritates the skin, eyes, and respiratory tract. The experiments should be performed in a fume hood. Care should be taken to avoid contact during the preparation of the solution.

■ DISCUSSION

The crystal analysis has been published,[31] and the instructor can give this information to the students. It is a molecular compound with the four-coordinate copper(I) center in a tetrahedral environment composed of an N-bonded thiocyanate group, two pyridine molecules, and the triphenylphosphine, as shown in Figure 3. The compound crystallizes in the space group P2(1), monoclinic, and the only crystallo-
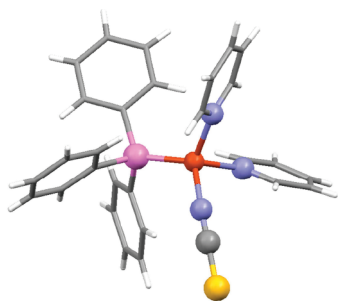
Figure 3. Molecular structure of $[Cu(NCS)(py)_2(PPh_3)]$ (color codes: Cu, orange; P, violet; N, blue; S, yellow; and C, gray).

graphically imposed symmetry is a translational screw axis. The lack of a center of symmetry is demonstrated by the packing of the molecules along the *a* axis (Figure 4).
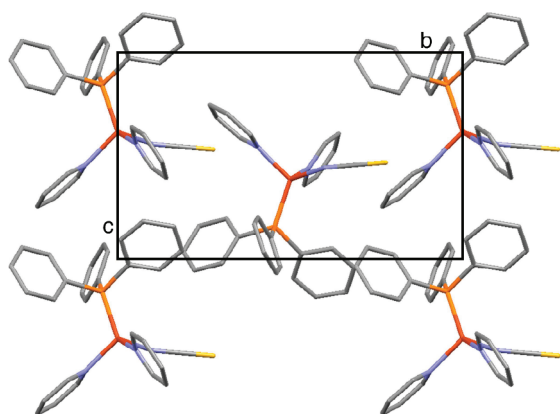

Figure 4. Crystal packing of $[Cu(NCS)(py)_2(PPh_3)]$ along the *a* axis.

The basic mechanism of the triboluminescence of this compound is not yet clear, but evidence of the same color emission in both the photoluminescence and triboluminescence phenomena supports a hypothesis based on the breaking of Cu−NCS bonds under grinding, in such a manner that a sufficient number of bonding electrons (or negative NCS⁻ ions) remain on the surface of the resulting fracture. At the same time, the opposite, positively charged, surface forms, based on cationic $\{Cu(py)_2(PPh_3)\}^+$ fragments. After that, electrical discharges take place. Such electrical discharges are responsible for the detected light emission. Similar to many other known triboluminescent derivatives, the noncentrosymmetry of the molecules in the crystalline material seems to play an important role.

CONCLUSION

A simple synthetic procedure is presented for a copper(I) derivative that exhibits strong triboluminescence either in the dark or in daylight. The preparation can be easily reproduced by students in an advanced inorganic chemistry laboratory where synthesis, recrystallization, and IR characterization procedures of metal coordination compounds are involved, to show the mechanochromic behavior of metal compounds. Student response to the photoluminescence and, mainly, the triboluminescence is always of great astonishment, and instructors can use it to increase student interest in chemistry.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed student handout; instructor notes with background, procedures, experimental setup, and ¹H, ³¹P and ¹³C NMR spectra, IR spectrum, TGA plot; movies of triboluminescent effect by crystals of derivative $[Cu(NCS)(py)_2(PPh_3)]$ in the dark and daylight. This material is available via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: fabio.marchetti@unicam.it.

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