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Blue Emitting Compounds

Fine-Tuning: Advances in Chlorine-Free Blue-Light-Generating Pyrotechnics

Johann Glück,[a][‡] Thomas M. Klapötke,*[a] and Teresa Küblböck[a][‡]

Abstract: One of the most challenging tasks in the field of light-producing pyrotechnics is the generation of saturated blue light with high spectral purity. Only copper salts in combination with chlorine seem to be high-performing blue light emitters. However, in modern pyrotechnics the application of chlorine should be avoided. Different strategies are presented to further fine-tune literature-known chlorine-free blue-light-emitting pyrotechnical compositions. The copper iodate as well as the copper bromate systems have been studied by using small amounts of nitrogen-rich compounds like 1,2,4-triazole, 5-amino-1*H*-tetrazole or 3-nitro-1*H*-1,2,4-triazole. To overcome sensitivity issues, a two-component epoxy binder system was introduced. The application of both copper(I) iodide and copper(I) bromide in the same pyrotechnical formulation were considered as blue-light-emitting species. Further, a quite new approach by using copper(I) nitrogen-rich coordination compounds was investigated to give a blue flame color. All relevant formulations were characterized with respect to their dominant wavelength and spectral purity as well as impact and friction sensitivity.

Introduction

Pyrotechnical disseminated blue light is supposed to be the most challenging color of all.[1] This assumption is not only supported by the limited number of publications, but also by the quite recent steps forward regarding higher spectral purity (SP) and optimized dominant wavelength (DW).[2] Traditionally, a combination of copper salts and chlorine sources were applied to give the desired blue color.[3] Usually, ammonium perchlorate or potassium perchlorate fulfil both the role of an oxidizing agent and as chlorine source.[1,4] In the case of proper flame tuning, the combustion temperature is sufficient to produce the blue light emitter copper(I) chloride. As a result, blue emission in the visible spectrum ranging from 435–480 nm and 428–452 nm with additional peaks between 476–488 nm is observed.[2c] If the temperature exceeds a certain level, the molecular emitter decomposes to give copper(II) oxide and copper(I) hydroxide.[5] CuO can sometimes be spotted as red tip on the top of flame, whereas CuOH emits in the green region and therefore, weakens the overall color quality.[3,6] The formation of the blue light emitter copper(I) chloride is limited by a maximum reaction temperature; for example, Conkling and Shidlovsky supposed 1500 K.[7] Several other temperatures were discussed in the literature, but according to Sturman they should be wrong.[7] Thermodynamic modelling applying the NASA Chemical Equilibria with Applications (NASA-CEA) computer code confirmed Shimizu's hypothesis that it should be possible to obtain blue compositions of high purity and saturated blue color with copper(I) chloride up to 2500 K.[8] Further increased temperatures should lead to dissociation of copper(I) chloride.

For a long time, it was believed that copper(I) chloride is the only suitable emitter in the blue region. In 2014, Klapötke et al. reported on chlorine-free pyrotechnical mixtures with copper(I) iodide as blue light emitter.[2c] The best working formulation consisted of copper iodate, 5-amino-1*H*-tetrazole (5-AT), magnesium, copper(I) iodide, and an epoxy binder system (Epon 828/Epikure 3140). To this date, these compositions achieved the highest recorded spectral purity (65 %) and dominant wavelength (473 nm).[2c] In 2015, Juknelevicius et al. outlined another possible blue-light emitter – copper(I) bromide – which was found to achieve SP ≤38 % and DW = 479 nm.[2b] From a toxicity point of view, especially the formulations based on copper(I) iodide are more advantageous, since the postulated formation of highly carcinogenic polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and analogous brominated compounds like polybrominated biphenyls (PBBs) can be avoided.[9] In 2004, the U.S. Department of Health and Human Services summarized earlier publications and indicated that PBBs might accumulate in the environment and were found to cause cancer in selected animal studies.[9c] Potentially formed polyiodinated biphenyls (PIBs) are not believed to be associated with health hazards as they are applied as contrast agents for radiological purposes in medicine, but there are insufficient information given in the literature.[10] Next to halogenated compounds and perchlorates, soluble copper salts tend to show aqueous toxicity and therefore, are considered as part of the problem to create environmentally friendly blue light-generat-

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[‡] Shared co-first author.

[a] *Department of Chemistry Ludwig-Maximilian University,*
Energetic Materials Research,
Butenandtstraße 9 (Haus D), 81377 Munich, Germany
E-mail: tmk@cup.uni-muenchen.de
https://www.hedm.cup.uni-muenchen.de/index.html

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ing pyrotechnical formulations.[11] In 2019, the author's considered indium as a possible blue light emitter; however, the resulting flame color was dominated by sodium and potassium impurities.[12] Due to the lack of suitable alternatives, the application of copper salts has to be accepted by the military in illumination signals and by the civilian sectors for firework displays or indoor pyrotechnics.[3,13]

The main task of this presented study was to develop a new pyrotechnic composition that surpasses the performance of known formulations and yields a deep blue color with a DW of 465 ± 20 nm and SP of ≥65 %. For this reason, the author's defined additional requirements for the improvement of newly developed pyrotechnics: The smoke formation should be significantly reduced compared to black powder and only little-produced ash is tolerated. Further, the avoidance of chlorates, perchlorates or other chlorine sources is mandatory. All applied compounds should be commercially feasible, which means sufficient availability to moderate prices. As a consequence, multistep syntheses were not considered for the ongoing investigation. Since all mixtures should be safe in handling, storing and preparing, the sensitivity as well as toxicity should be considered. Regarding the toxicity requirements, compounds with known major toxicity issues were ruled out. Also high amounts of metals and metal salts should be avoided. The safety aspect mainly included the sensitivities towards mechanical stimuli such as impact (IS) and friction (FS). Only formulations which guarantee safe handling are likely to be produced on a larger scale.

Different strategies were applied to achieve the above-mentioned goals, which can be summarized as followed:

- Improvement of the $Cu(IO_3)_2$ system
- Improvement of the $Cu(BrO_3)_2$ system
- Copper(I) nitrogen-rich coordination compounds

Results and Discussion

Improvement of the $Cu(IO_3)_2$ System

The $Cu(IO_3)_2$ system by Klapötke et al. was chosen as starting point for further investigations. More accurate, the idea was to tune the flame conditions by applying small amounts of nitrogen-rich compounds to increase the spectral purity. The produced nitrogen gas would not only be beneficial to reduced smoke volume, and thus increased spectral purity, but also consumes heat to tailor the flame temperature. This literature-known and proven concept was successfully applied earlier in numerous publications and seemed to be very promising at first.[14]

However, initial experiments applying $Cu(IO_3)_2$, hexamine, CuBr and nitrogen-rich compounds such as 1,2,4-triazole (Tr), 5-AT, and 3-nitro-1*H*-1,2,4-triazole (3-NT) only produced brown smoke (see Supporting Information: Table S1, Figure 1). The hint of a small blue flame was only detected at the very beginning of ignition stage and disappeared quickly.

Various other formulations applying guanidine nitrate, copper or urea suffered from stability issues and were not considered for further investigations. As a consequence, the focus shifted to the $Cu(BrO_3)_2$ system, which was supposed to show bigger potential for improvement regarding the spectral purity and dominant wavelength.

Figure 1. Burning and smoke generation of formulation **I7**.

Improvement of the $Cu(BrO_3)_2$ System

The introduced $Cu(BrO_3)_2$ system by Juknelevicius et al. achieved lower spectral purities (SP ≤38 %)[2b] compared to Klapötke's $Cu(IO_3)_2$ system as well as the literature-known publication by Shimizu applying undesired potassium perchlorate, copper, poly(vinyl chloride) (PVC) and starch (Table 1).[2c] Shimizu's formulation shows comparatively high impact sensitivity (8 J), but is less sensitive towards friction.

Table 1. Blue reference formulation **S** by Shimizu (in wt.-%) and its resulting properties.[2c]

	$KClO_4$	Cu	PVC	Starch	DW /nm	SP /%	IS /J	FS /N
S	70	10	20	5	475	61	8	324

To overcome the disadvantage of low spectral purity, the previously pursued strategy applied for the $Cu(IO_3)_2$ case was also applied for an analogous $Cu(BrO_3)_2$ system. In this context, the initial formulations consisted of $Cu(BrO_3)_2$, hexamine and CuBr only. In the next step, the effect of nitrogen-rich compounds such as Tr, 5-AT and 3-NT was investigated. The amount of introduced nitrogen-rich additive was either 5 wt.-% or 10 wt.-% (Table 2).

All developed formulations showed dominant wavelengths in the desired range of 465 ± 20 nm. The three starting formulations **Br1**–**Br3** already exceeded the best formulation by Juknelevicius et al. without incorporating any nitrogen-rich compound.[2b] The addition of Tr, 5-AT and 3-NT further increased the spectral purity up to 50–54 %. Only formulation **Br5** suffered from a reduced spectral purity compared to the formulations **Br1**–**Br3**. It is noteworthy that, upon burning of formulation **Br9**, no residue was left at all (Figure 2).

Unfortunately, the sensitivities towards mechanical stimuli increased to a non-tolerable level (Table 2). According to the *Bundesanstalt für Materialforschung* (BAM), the friction sensitivity of formulations **Br1**–**Br3** was characterized as very sensitive and changed for the worse with addition of nitrogen-rich additives.[15] It was discovered that a higher amount of additive resulted in higher sensitivity and safety risk. Whereas formula-

Table 2. $Cu(BrO_3)_2$-based formulations **Br1**–**Br9** (in wt.-%) and their resulting properties.

No.	$Cu(BrO_3)_2$	Hexamine	CuBr	Tr	5-AT	3-NT	DW /nm	SP /%	IS /J	FS /N
Br1	70	10	20	–	–	–	465	44	2	30
Br2	70	15	15	–	–	–	468	40	7	36
Br3	65	15	20	–	–	–	466	46	8	40
Br4	65	10	20	5	–	–	468	52	10	20
Br5	65	10	20	–	5	–	464	39	8	20
Br6	65	10	20	–	–	5	467	54	5	24
Br7	60	10	20	10	–	–	468	53	3	16
Br8	60	10	20	–	10	–	468	50	1	16
Br9	60	10	20	–	–	10	470	53	1	18

Figure 2. Burning of formulation **Br9**.

tions **Br2**–**Br6** were classified as sensitive towards impact, formulation **Br1** and **Br7**–**Br9** had to be classified as very sensitive. Upon preparation of these formulations, several accidently decompositions such as fast deflagration and sometimes crackling sounds occurred.

Since the best performance was obtained for formulations containing nitrogen-rich additives, further fine-tuning was undertaken to achieve even higher spectral purities and optimized burning behavior. Small changes in the ratio of oxidizing agent and hexamine in combination with a fixed amount of nitrogen-rich additives resulted in blue light emission within the required dominant wavelength range (see Supporting Information: Table S3). Bigger variations were observed for the spectral purities differing in between 30–50 %. In contrast to former mixtures, the formation of unwanted CuO as red tip was observed in most cases. Only formulations **Br12**, **Br15** and **Br18** did not exhibit red flame impurities and were characterized according to their energetic properties. The sensitivities were classified as very sensitive towards friction and impact (Table 3, see Supporting Information: Table S3).

Formulations **Br19**–**Br30** were prepared to investigate the effect of slightly increased amounts of CuBr (max. 25 wt.-%), while keeping the oxidizer level constant (see Supporting Information: Table S4). **Br19**, **Br20**, **Br22**–**Br25**, and **Br30** also showed a red tip and therefore, were excluded from further investigations. Only **Br21** was further characterized and classified as sensitive towards impact and friction (Table 3). During the grinding step, formulations **Br26** to **Br29** accidently decomposed with a big flame and crackling sound. It was assumed that these formulations were even more sensitive than previous compositions.

Even though the spectral purities of these formulations increased up to 54 % and also fulfilled the requirement for dominant wavelength, the resulting sensitivities were considered as a serious problem. One literature-known strategy to reduce the sensitivity of pyrotechnical formulations is the addition of non-energetic binder materials such as carbohydrates, oils or epoxy resins.[16] These binder materials usually do not only increase the mechanical stability of the pressed pellet, but also coat the particles, which further should reduce the sensitivity by minimizing the emerging shearing forces.[16b] However, the burning behavior as well as optical properties can also be influenced by binder systems. The binder itself can act as fuel providing more heat to the combustion process and thus, alter the resulting combustion temperature. **Br31**–**Br42** were prepared to study the effect of an epoxy binder system (Epon 813/Versamid 140, 4:1) on the occurring properties (see Supporting Information: Table S5).

The spectral purity of **Br31**, **Br32**, **Br35**, **Br36** and **Br40** dropped to 39–43 % and therefore, these formulations were excluded from further investigations. The same compositions with additional 5–8 wt.-% binder did not reveal the intended effect of reduced sensitivity (Table 3). Quite contrary to the expecta-

Table 3. Selected $Cu(BrO_3)_2$ based formulations (in wt.-%) and their resulting properties.[a]

No.	$Cu(BrO_3)_2$	Hexamine	CuBr	Tr	5-AT	3-NT	Binder	DW /nm	SP /%	IS /J	FS /N
Br12	60	15	20	–	–	5	–	463	50	3	24
Br15	55	15	20	–	–	10	–	467	50	2	32
Br18	60	20	15	–	–	5	–	464	48	2	18
Br21	60	10	20	–	–	10	–	468	54	3	42
Br33	65	10	20	–	5	–	5	469	50	4	14
Br34	65	10	20	–	5	–	8	470	49	5	18
Br37	60	10	20	10	–	–	5	468	53	2	48
Br38	60	10	20	10	–	–	8	469	47	1	36
Br41	60	10	20	–	–	10	5	470	48	2	36
Br42	60	10	20	–	–	10	8	465	44	3	30

[a] Binder = Epon 813/Versamid 140 (4:1); weight percentage in total = 100 wt.-% + 5–8 wt.-% binder = 105–108 wt.-% per formulation.

Table 4. Formulation **BrI1** with a minimum amount of copper and its resulting properties.[a]

No.	$KBrO_3$	Hex	Cu	CuI	NH_4Br	Binder	DW /nm	SP /%	IS /J	FS /N
BrI1	65	10	5	5	10	5	461	47	1	42

[a] Binder = Epon 813/Versamid 140 (4:1); weight percentage in total = 100 wt.-% + 5–8 wt.-% binder = 105–108 wt.-% per formulation; Hex = Hexamine.

tions, the sensitivities of formulations **Br37** and **Br38** surprisingly increased with higher binder content. This phenomenon might be explained by the altered stoichiometry resulting in higher reactivity. A comparison of the pair **Br33** and **Br34** indicated only a slight loss in sensitivity, which might be negligible due to measurement errors. For **Br41** and **Br42**, an increase of friction sensitivity was accompanied by a small decrease in the sensitivity towards impact. It is obvious that in this case there is no connection between the binder content and the formulation's resulting sensitivity performance.

It has to be stated that especially the grinding process of all solid materials turned out to provide the highest risk for accidental decomposition. Other methods for safe sample preparation have to be considered in the future. Grinding and coating every single component separately before wet-mixing the ingredients might be an option for further investigations. However, the sensitivities in a dry state of these so-prepared formulations are questionable.

Finally, compositions applying a minimum content of metal or metals salts were developed to meet the above-introduced requirements for modern pyrotechnics. **BrI1** provides a blue formulation applying minimum amounts of copper or copper salts by using potassium bromate ($KBrO_3$) as an oxidizing agent (Table 4).

The halogen source of choice was ammonium bromide NH_4Br as well as CuI. In combination with elemental copper, the blue light was generated by a mixture of two emitters – copper(I) bromide and copper(I) iodide. Unfortunately, the impact sensitivity was found to be one of the most hazardous ones; therefore, a spontaneous decomposition during the manufacturing process is very likely. As a result, these kinds of pyrotechnical mixtures were excluded from further investigation, since they prevent safe sample preparation, storing as well as handling.

Copper(I) Nitrogen-Rich Coordination Compounds

The performance of pyrotechnical formulations is influenced by a lot of factors, e.g. environmental factors, sample preparation or material shape.[3,8b] Small deviations in the production step, chemicals from another supplier or even different batches of the same supplier can cause big effects on the resulting performance and require a batch-to-batch reformulation.

To overcome the inconsistencies arising from mixing of several powders, the idea was to reduce the number of ingredients by combining the colorant, oxidizer and fuel in just one molecule.[17] Analogue to the tetrakis(acetonitrile) copper(I) perchlorate complex published by Csöregh et al. in 1974, the first step was to synthesize the tetrakis(acetonitrile) copper(I) periodate complex (Scheme 1). In a second step, the corresponding tetrakis(acetonitrile) copper(I) periodate complex with various nitrogen-rich compounds as stabilizing ligands should be obtained via metathesis reaction.[18]

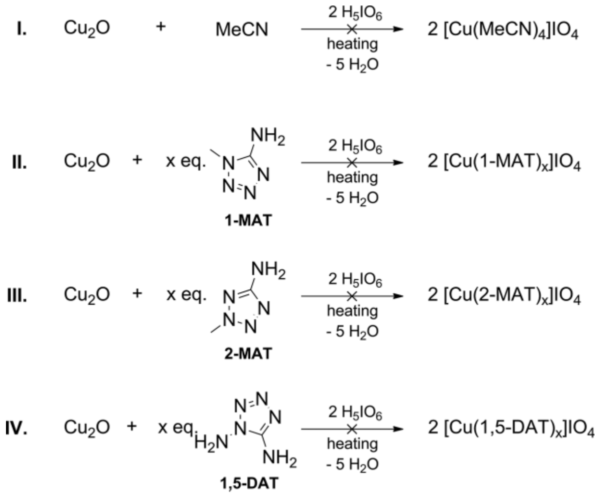
$$Cu_2O + 2\,H_5IO_6 + MeCN \dashrightarrow 2\,[Cu(MeCN)_4]IO_4 + 5\,H_2O$$

$$[Cu(MeCN)_4]IO_4 + x\text{ N-rich ligands} \dashrightarrow [Cu(\text{N-rich ligands})_x]IO_4 + MeCN$$

Scheme 1. Planned synthetic route to $[Cu(MeCN)_4]IO_4$; with N-rich ligand = 5-amino-1-methyl-1*H*-tetrazole (1-MAT); 5-amino-2-methyl-2*H*-tetrazole (2-MAT); 1,5-diaminoterazol (1,5-DAT).

A mixture of periodic acid and acetonitrile was provided. Subsequently, Cu_2O was added and heated until a clear solution was observed. This so-prepared solution was allowed to stand in air for crystallization. Unfortunately, all solutions turned blue and the intended complex could not be observed in the elemental analysis.

The blue color already indicated the formation of copper(II) salts. In an attempt to overcome the occurring oxidation process, the nitrogen-rich ligands were first dissolved in periodic acid resulting in the same color shift (Scheme 2).



Scheme 2. Attempts at preparing copper(I) complexes.

The tetrakis(acetonitrile) copper(I) periodate could not be isolated. Furthermore, 1,5-DAT instantly decomposed upon addition to the periodic acid solution, which was indicated by an instant gas formation. For the ligands 1-MAT and 2-MAT, a mixture of green and blue solid material was obtained after crystallization. The solution applying 1-MAT showed small colorless crystals in the glass vessel. X-ray analysis proved the formation of the corresponding 1-MAT periodate salt instead of the intended product. It was concluded that the formation of $[Cu(\text{N-rich ligands})_x]IO_4$ complexes is not possible by applying the literature-stated procedure for analogous perchlorate complexes. Due to the blue colored solution, the copper(I) ions were oxidized to copper(II) during the reaction. The oxidizing properties of periodic acid already decomposed one N-rich ligand upon addition, which further reduces the number of possible compounds for future investigations.

Domyati et al. reported on copper(I) complexes with pincer *N*-heterocyclic carbene (NHC) ligands starting from the reaction of $[Cu(MeCN)_4]PF_6$ or $[Cu(MeCN)_4]SbF_6$ and an in situ generated NHC at room temperature in the absence of air and moisture.[19] Consequently, other tetrakis(acetonitrile) copper(I) complexes with varying anions are known, which might serve as starting materials for simple metathesis reaction to obtain $[Cu(MeCN)_4]IO_4$. Some of them are already commercially available, e.g. $[Cu(MeCN)_4]^+$ Y with Y = SbF_6^-, BF_4^-, ClO_4^-, PF_6^-. Acetonitrile (MeCN) is a weakly coordinated ligand, which can be substituted by stronger coordinating ligands such as triphenylphosphine (PPh_3) as well as bidentate ligands like diphenylphosphinomethane (dppm) or 1,10-phenanthroline (phen).[20] Most of the reported copper(I) complexes are also moisture- or air-sensitive; therefore, they cannot be considered in any pyrotechnical formulation.[21]

Further attempts to synthesize the $[Cu(MeCN)_4]IO_4$ complexes starting from the commercially available compound $[Cu(MeCN)_4]BF_4$ via metathesis reactions failed (Scheme 3). In this study, it was not possible to successfully introduce copper(I) complexes in blue-light-emitting pyrotechnical formulations. Finally, it was concluded that copper(I) complexes need further research as well as improvement to meet the stability and sensitivity requirements for the application in modern pyrotechnical systems.

$$\textbf{V.}\quad [Cu(MeCN)_4]BF_4 + H_5IO_6\,(aq.) \xrightarrow[\substack{50\,^{\circ}C \\ -\,2\,H_2O}]{\substack{MeCN \\ \times}} 2\,[Cu(MeCN)_4]IO_4 + H^+ + BF_4^-$$

$$\textbf{VI.}\quad [Cu(MeCN)_4]BF_4 + NaIO_4 \xrightarrow[\substack{50\,^{\circ}C \\ -\,2\,H_2O}]{\substack{MeCN \\ \times}} 2\,[Cu(MeCN)_4]IO_4 + NaBF_4$$

Scheme 3. Failed metathesis reactions applying $[Cu(MeCN)_4]BF_4$.

Conclusions

In the presented work, three different strategies are discussed to further fine-tune the performance of literature-known blue-light-emitting pyrotechnical compositions. The author's defined several requirements for these modern mixtures. The most important one is that the formulation should provide a deep blue color with a dominant wavelength of 465 ± 20 nm and spectral purity of ≥65 %.

The first approach was the improvement of the most-promising $Cu(IO_3)_2$ system, however, it was not possible to generate a blue flame and most of the mixtures suffer from stability issues. As a result, the focus shifted to the fine-tuning of the $Cu(BrO_3)_2$ system. The author's summarized the optical performance and the corresponding impact and friction sensitivity of discussed formulations together with Shimizu's blue reference and Juknelevicius' $KBrO_3$ system in an overview (Figure 3).[2b,3]

The literature-known $KBrO_3$-based formulation reached only a spectral purity of ≤38 %. The flame conditions were tailored with nitrogen-rich compounds – 1,2,4-triazole, 5-amino-1*H*-tetrazole and 3-nitro-1*H*-1,2,4-triazole – to reduce smoke generation, increase spectral purity and control temperature. With this strategy spectral purities up to 54 % could be observed. Unfortunately, these mixtures suffer from impact and friction sensitivity (IS: 1–5 J, FS: 14–48 N), whereby a safe manufacturing process cannot be guaranteed. Also the addition of a two-component binder system was not able to reduce the sensitivity against mechanical manipulation. However, the authors proved that it is possible to reach the optical performance of Shimizu's perchlorate-based blue reference formulation (SP: 61 %, DW: 475 nm, IS: 8 J, FS: 324 N) with the fine-tuning of bromate-based mixtures. The application of both blue-light-emitters copper(I) bromide and copper(I) iodide was excluded from further investigation, because of sensitivity issues.

The last concept to improve the performance of blue-light-emitting pyrotechnics was the addition of copper(I) nitrogen-

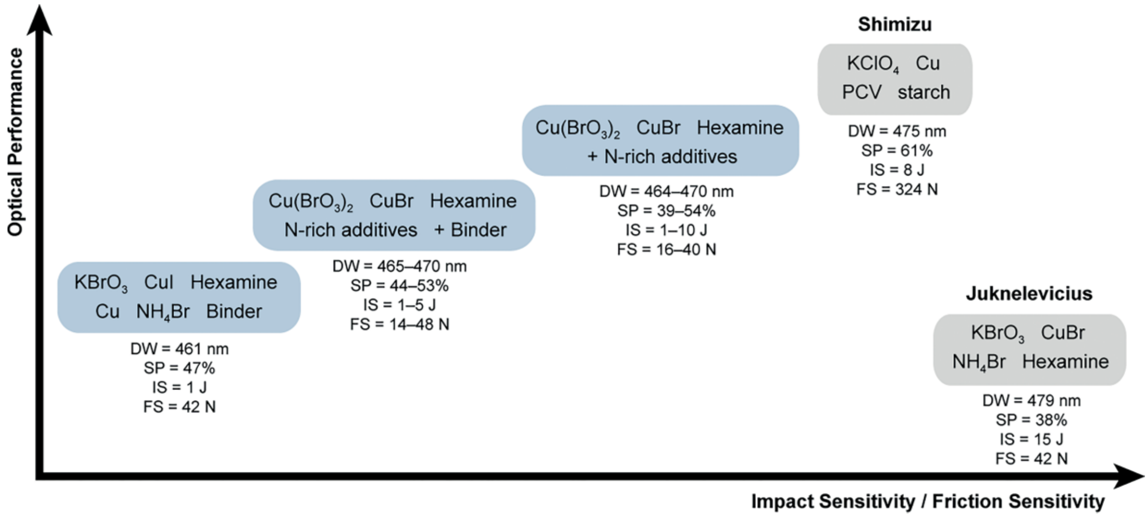


Figure 3. Optical performance (DW and SP) and sensitivities (IS and FS) of $Cu(BrO_3)_2$-based formulations in comparison with Shimizu's blue reference and Juknelevicius' $KBrO_3$ system.[2b,3]

rich coordination compounds served as colorant, fuel and gas generator in one molecule. Due to stability and sensitivity issues, it was not possible to introduce copper(I) complexes to pyrotechnical mixtures.

Experimental Section

CAUTION! The described pyrotechnical mixtures might explode during preparing, handling or manipulating! They are potential explosives, which are sensitive to environmental stimuli such as impact, friction, heat, and electrostatic discharge. Please handle these materials with care! Precautionary measures are mandatory and protective equipment like safety glasses, face shields, leather coats, Kevlar® gloves, and ear protectors is highly recommended.

Chemicals. The following materials were used as provided without further purification: 5-amino-1*H*-tetrazole (98 %), abcr Chemicals; 1,2,3-triazole (99.5 %), Acros Organics; 3-nitro-1*H*-1,2,4-triazole (97 %), Sigma-Aldrich; Hexamethylenetetramine (99.5 %), abcr Chemicals; copper (–40+100 mesh, 99.5 %), Alfa Aesar; ammonium bromide (99 %), Sigma-Aldrich; copper bromide (99 %), Sigma-Adrich; copper iodide (98 %), Sigma-Aldrich; copper iodate (95 %), Alfa Aesar; potassium bromate (99 %), Sigma-Aldrich; Epon 813, Hexion; Versamid 140, BASF. All other compounds were synthesized according to literature procedures or provided at the laboratory stock.

Sample Preparation. All pyrotechnic samples were prepared in 1.0 g scale using the same procedure in order to ensure the reproducibility. Therefore, the different ingredients were weighed into a sample glass according to their respective weight percentages as given in the formulations. Each sample was transferred into a porcelain mortar and carefully ground to a homogeneous powder. After grinding, the binder solutions were added followed by a curing step. The so-prepared compositions were ground again and then, pressed into a cylindrical shape with the aid of a tooling die using a hydraulic press with a dead load of 2.0 t for 3.0 s.

Optical Measurements. Optical emissive properties were characterized using both an OceanOptics HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector (range 190–1100 nm) and included software from OceanOptics. Spectra were recorded with a detector-sample distance of 1.0 m and an acquisition time of 1 ms per scan. The dominant wavelength (DW) and spectral purity (SP) were measured based on the 1931 CIE method using illuminant C as the white reference point. Five samples were measured for each formulation and all given values are averaged based on the full burn of the mixture. The controlled burn was filmed with a digital video camera recorder (SONY, DCR-HC37E).

Synthesis of copper(I) complexes

Route (I): A mixture of periodic acid (2 M, 5 mL) and acetonitrile (15 mL) was prepared. Subsequently, Cu_2O (71.6 mg, 0.05 mmol) was added and heated (50 °C) until a clear solution was observed. After crystallization on air, the solution turned blue. A blue-greenish precipitate was obtained after removal of the solvent. EA ($C_8H_{12}N_4O_4CuI$, 418.66 g mol^{-1}) calcd. C 22.95, H 2.89, N 13.38 %; found C 0.00, H 0.00, N 0.00 %.

Route (II)–(IV): The nitrogen-rich ligands (200 mg, 4 equiv.) were dissolved in a mixture of periodic acid (2 M, 5 mL) and acetonitrile (15 mL). After addition of Cu_2O (1 equiv.), the solution was heated (50 °C) until all solid material was dissolved. The solution was allowed to stand on air for crystallization. A blue-greenish precipitate was obtained after removal of the solvent. EA ($C_8H_{20}N_{20}O_4CuI$, 650.83 g mol^{-1}) calcd. C 14.76, H 3.01, N 43.04 %; found C 7.14, H 2.03, N 20.33 %.

Route (V)–(VI): $[Cu(MeCN)_4]BF_4$ (200 mg, 0.62 mmol) was dissolved in an excess of acetonitrile (15 mL) and heated (50 °C) until a clear solution was observed. Upon addition of one droplet of H_5IO_6 (2 M), a green precipitate occurred immediately. EA ($C_8H_{12}N_4O_4CuI$, 418.66 g mol^{-1}) calcd. C 22.95, H 2.89, N 13.38 %; found C 0.00, H 0.85, N 0.00 %. Applying $NaIO_4$ (133 mg, 0.62 mmol) instead resulted in the same product. The formation of a green precipitate was observed approximately 2 min after the addition of $NaIO_4$. EA ($C_8H_{12}N_4O_4CuI$, 418.66 g mol^{-1}) calcd. C 22.95, H 2.89, N 13.38 %; found C 0.00, H 0.00, N 0.00 %.

Sensitivity Data. The impact and friction sensitivities were determined using a BAM Drophammer and a BAM Friction Tester. The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+). Impact: insensitive >40 J, less sensitive >35 J, sensitive >4 J, very sensitive <4 J; friction: insensitive >360 N, less sensitive = 360 N, sensitive 360 N > x > 80 N, very sensitive <80 N, extreme sensitive <10 N. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive <0.1 J, insensitive >0.1 J. The thermal stability was carried out using an OZM Research DTA 552 Ex Differential Thermal Analyzer with a heating rate of 5 °C min^{-1} [15].

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Keywords: Blue emission · Copper · Photophysics · Pyrotechnics

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